PROGRESS TOWARD THE ENANTIOSELECTIVE TOTAL SYNTHESIS OF INELEGANOLIDE AND THE POLYCYCLIC NORCEMBRANOID DITERPENES AND CONSTRUCTION OF THE INELEGANOLOIDS

VOLUME II

Thesis by

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CHAPTER 5

Lewis Acid Mediated (3+2) Cycloadditions of Donor–Acceptor Cyclopropanes with Heterocumulenes†

5.1 Introduction

Donor–acceptor cyclopropanes are a useful class of building blocks for organic synthesis.[1] Indeed, (3 + 2) cycloadditions of donor–acceptor cyclopropanes have proven to be a powerful strategy for the direct synthesis of five-membered carbo- and heterocycles, and such methodologies have been applied toward natural product syntheses.[2] Given our own interest in this field,[2e] we sought to examine heterocumulenes as potential dipolarophiles in stereoselective (3 + 2) cycloadditions to enable access to five-membered heterocycles. At the outset of this project, isocyanates[3a,b] and isothiocyanates[3c,d] had previously been shown to be reactive with alkoxy-substituted donor–acceptor cyclopropanes in only low to moderate yields, and stereocontrol of these

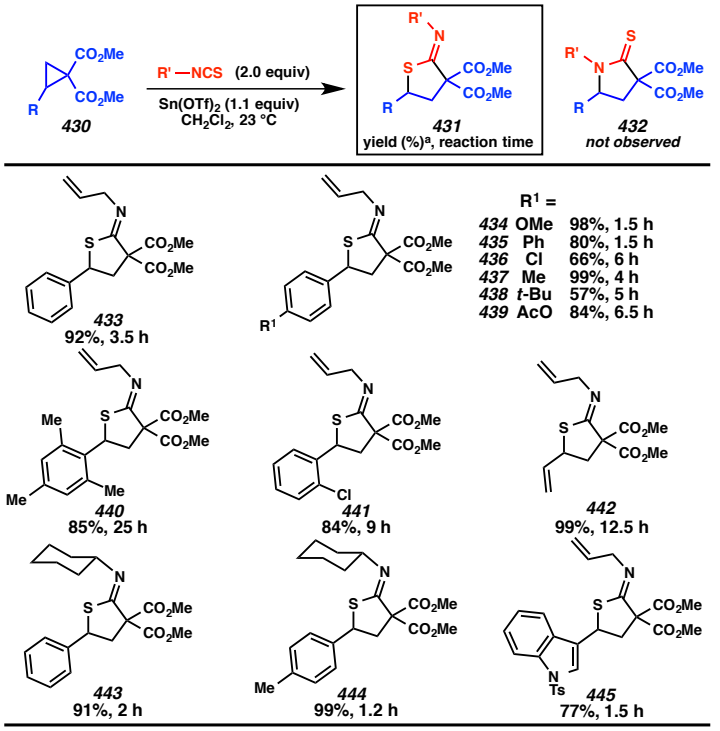
† This work was performed in collaboration with Nicholas R. O'Connor and Dr. Alexander F. G. Goldberg, a graduate student in and an alumnus of the Stoltz group, respectively. Additionally, this work has been published and adapted with permission from Goldberg, A. F. G.; O'Connor, N. R.; Craig, R. A., II; Stoltz, B. M. *Org. Lett.* **2012**, *14*, 5314–5317.

reactions has relied on existing stereocenters remote from the site of reactivity. Based on the work of Johnson, Kerr, and others, we envisioned that the use of aryl substituents as the donor component would allow for an enantiospecific process by means of nucleophilic attack at the chiral benzylic center.[4,5] The products formed could serve as useful building blocks toward optically active natural products and pharmaceutically relevant heterocyclic compounds.

5.2 Initial Reaction Development Using Allyl and Alkyl Isothiocyanates

We began by examining the reactivity of allyl isothiocyanate with aryl-substituted cyclopropanes (**430**). We found that a stoichiometric amount of tin(II) triflate enabled full conversion of the starting materials to thioimidates (**431**, Scheme 5.2.1). Notably, the chemoselectivity of this reaction is complementary with respect to the previous studies in which alkoxy-substituted donor–acceptor cyclopropanes are converted to thioamides.[3,6]

Scheme 5.2.1. Substrate Scope of Isothiocyanate (3 + 2) Cycloaddition



Conditions: cyclopropane **430** (0.4 mmol), isothiocyanate (0.8 mmol), $Sn(OTf)_2$ (0.44 mmol), CH_2Cl_2 (1.3 mL). [a] Isolated yields.

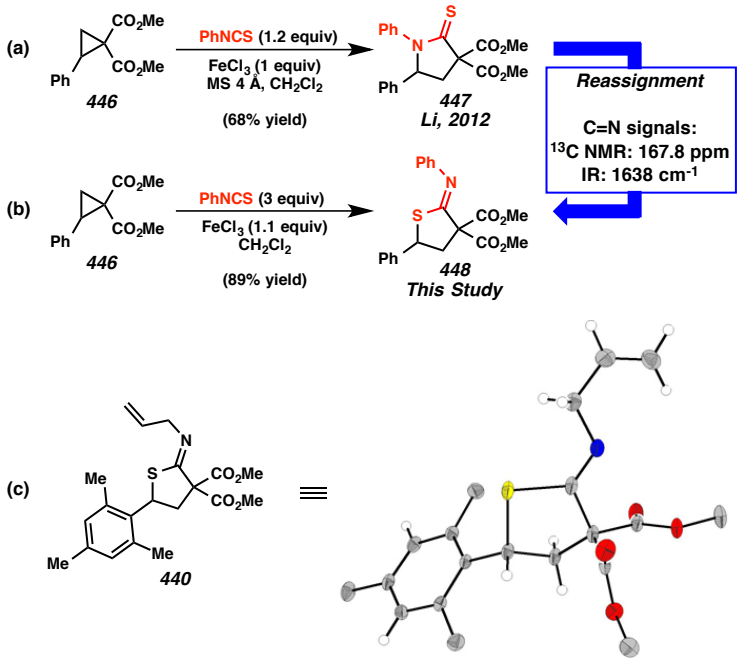
We found that a variety of substituted aryl groups were tolerated in this reaction. Thioimidates with electron-rich aryl substituents (**434**, **435**, **445**) were obtained with the shortest reaction times. Reactions leading to products with *ortho* or electron-withdrawing arene substituents (**436**, **440**, **441**) were the slowest. Cyclopropanes were not limited to those with aryl substituents; a vinyl group could also be used as an electron-donating substituent, offering 5-vinylthioimidate **442** in quantitative yield. In addition, cyclohexyl isothiocyanate was also compatible under these conditions, providing thioimidates **443** and **444** in 91% and 99% yield, respectively.

5.3 Unambiguous Structural Assignment of Heterocyclic Products

Under tin(II) triflate mediated conditions, we found aryl isothiocyanates to be poorly reactive; however, concurrent with our studies, Li and co-workers disclosed an iron(III) chloride mediated (3 + 2) cycloaddition of aryl isothiocyanates with donor–acceptor cyclopropanes to form thiolactams (e.g., **447**) rather than thioimidates (e.g., **448**, Scheme 5.3.1).[7] We suspected that the products reported by Li may have been misassigned and decided to investigate this further. Upon comparison of the ^{13}C NMR spectra of our products (e.g., **433**–**445**) to those reported by Li, we found similar shifts in the carbonyl range for both sets of spectra. In both cases, three signals are typically observed near 160 ppm: two correspond to the ester functionalities, and the third is consistent with a thioimidate; by contrast, a thioamide C=S ^{13}C NMR signal is expected at approximately 200 ppm.[8] Furthermore, our IR spectra consistently exhibited C=N stretches near 1650 cm^{-1}, and C=S signals were not observed.[9] Although no IR spectra were included in Li's report, we reacted cyclopropane **446** with phenyl isothiocyanate under similar conditions to those reported by Li and obtained a compound with NMR

spectra matching those reported (Scheme 5.3.1.B). The product IR spectrum contained a C=N stretch at 1638 cm^{-1}, and no C=S peak was observed. Finally, we found that the 5-mesityl substituted thioimidate (**440**, Scheme 5.2.1) was crystalline, and its structure was confirmed by single crystal X-ray diffraction (Scheme 5.3.1.C).[10a] Combined, the IR, ^{13}C NMR, and X-ray crystallography data support our assignment of both the Li group's and our products as thioimidates and not thioamides.

Scheme 5.3.1. Structural Reassignment of Li's Aryl Isothiocyanate (3 + 2) Products

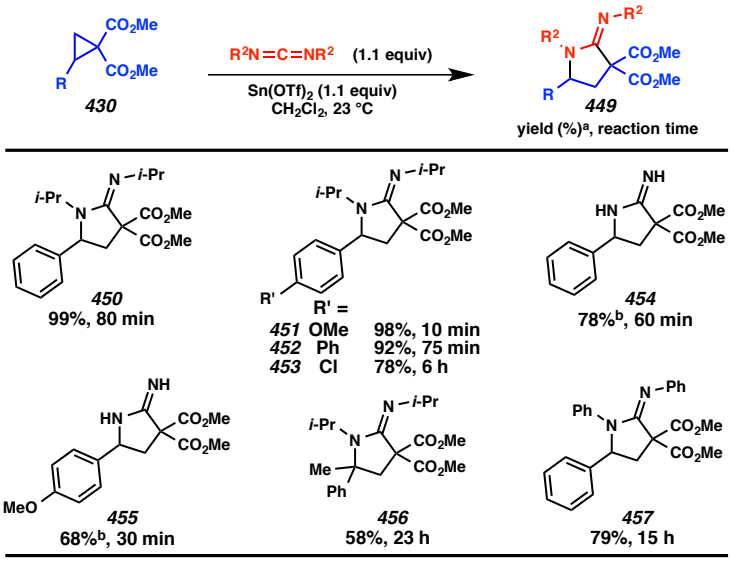


5.4 Carbodiimides as Competent Cycloaddition Partners

We then turned our attention to carbodiimide dipolarophiles and observed that, under tin(II) triflate mediated reaction conditions, the use of diisopropylcarbodiimide resulted in complete conversion of cyclopropane **430** to amidine **450** in only 80 min and required only 1.1 equivalent of the dipolarophile.[10b] Electron-rich 5-(4-methoxyphenyl)-amidine **451** was formed almost quantitatively in less than 10 min (Scheme 5.4.1). Primary amidines (**454** and **455**) could also be accessed using bis(trimethylsilyl)-

carbodiimide. Notably, (3 + 2) reactions were possible with cyclopropanes that are unreactive with isothiocyanates. For instance, a sterically congested 5,5-disubstituted amidine **456** could be generated in 58% yield. In addition, while aryl isothiocyanates were poorly reactive in the presence of tin(II) triflate, use of diphenylcarbodiimide resulted in the formation of the corresponding amidine (**457**) in 79% yield. Overall, the shorter reaction times indicate that carbodiimides are considerably more reactive dipolarophiles than comparable isothiocyanates in these reactions.

Scheme 5.4.1. Substrate Scope of Carbodiimide (3 + 2) Cycloaddition



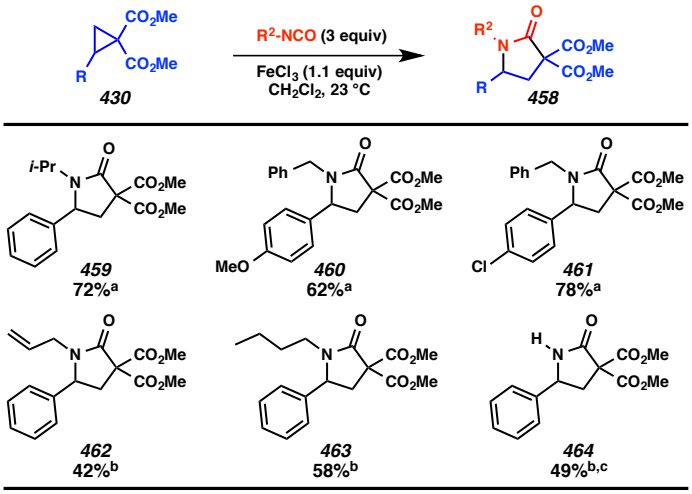
Conditions: cyclopropane **430** (0.4 mmol), carbodiimide (0.44 mmol), $Sn(OTf)_2$ (0.44 mmol), CH_2Cl_2 (1.3 mL). [a] Isolated yields. [b] Bis(trimethylsilyl)carbodiimide was used.

5.5 Use of Isocyanates Under Modified Conditions

We also examined isocyanates in (3 + 2) cycloadditions; however, they suffered from poor reactivity under tin-mediated reaction conditions. Microwave heating resulted in shorter reaction times but an array of side products. Fortunately, we were able to obtain lactams in moderate yields using iron(III) chloride (Scheme 5.5.1).[11] A variety of *N*-alkyl substituted lactams could be prepared, including isopropyl (**459**), benzyl (**460** and

461), allyl (**462**), and *n*-butyl (**463**). In addition, a secondary lactam (**464**) could be synthesized using trimethylsilylisocyanate as a dipolarophile. In general, these isocyanate reactions were considerably lower yielding than those with carbodiimides and isothiocyanates; nevertheless, they provide a meaningful entry into the important lactam series.

Scheme 5.5.1. Substrate Scope of Isocyanate (3 + 2) Cycloaddition



[a] Conditions: cyclopropane **430** (0.4 mmol), $FeCl_3$ (glovebox, 0.44 mmol), isocyanate (1.2 mmol), CH_2Cl_2 (1.3 mL). [b] Conditions: cyclopropane **430** (0.4 mmol), $FeCl_3$ (benchtop, 0.44 mmol), isocyanate (1.2 mmol), MS 4 Å (50 mg), CH_2Cl_2 (1.3 mL). [c] Trimethylsilylisocyanate was used.

5.6 Enantiospecific (3 + 2) Cycloaddition

Finally, we sought to establish whether stereochemical information from the starting material is transferred to the product under the reaction conditions. We prepared enantioenriched cyclopropane **(*S*)-446** according to literature methods and subjected it to our standard reaction conditions (Scheme 5.6.1).[12] Although treatment of this substrate with an isocyanate in the presence of iron(III) chloride resulted in complete racemization of the benzylic stereocenter (Scheme 5.6.1.A),[13] we observed a transfer of chirality in the case of tin(II) triflate mediated (3 + 2) cycloadditions (Schemes 5.6.1.B and 5.6.1.C). Notably substrates that required longer reaction times resulted in increased erosion of

optical activity.[14] We were able to confirm the absolute stereochemistry of the HBr salt of **(*R*)-450** by single crystal X-ray diffraction, which revealed an inversion of configuration at the benzylic stereocenter through the course of the reaction (Figure 5.6.1).

Scheme 5.6.1. Investigations into the Stereochemical Outcome of the (3 + 2) Cycloaddition

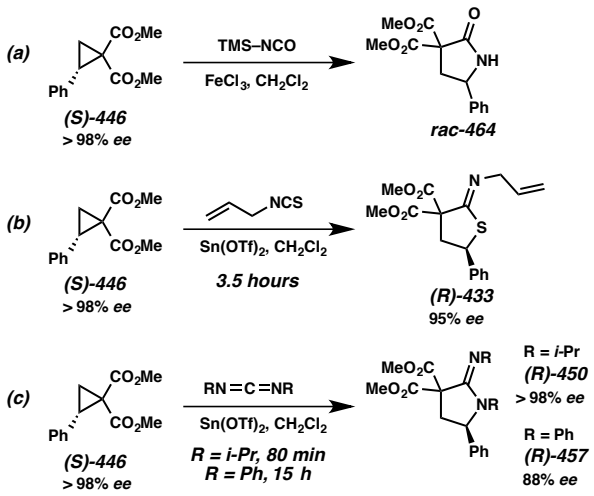
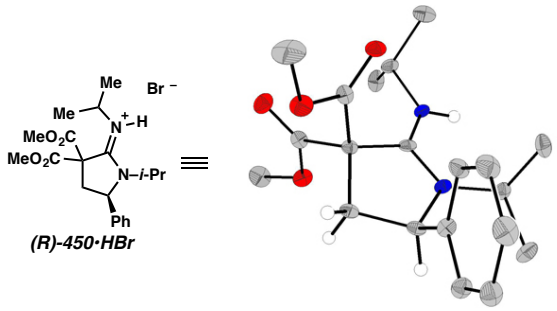


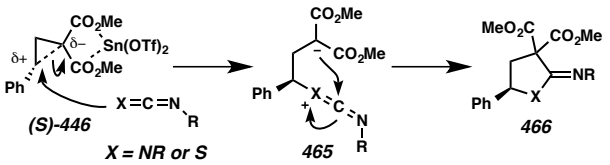
Figure 5.6.1. Determination of Absolute Configuration[15]



We propose that the mechanism of the isothiocyanate and carbodiimide reactions with tin(II) triflate involves a stereospecific intimate-ion pair mechanism analogous to that invoked by Johnson and co-workers for (3 + 2) cycloadditions of aldehydes and donor–acceptor cyclopropanes developed in their laboratories (Scheme 5.6.2).[4c,d,16] Our observations including stereochemical inversion at the benzylic position, along with the

greater reactivity of electron-rich dipolarophiles and of cyclopropanes with electron-rich aromatic substituents, are all consistent with this mechanistic hypothesis.

Scheme 5.6.2. Proposed Mechanism for (3 + 2) Cycloaddition



5.7 Conclusion

We have disclosed an effective method for formation of pyrrolidinones, thioimidates, and amidines from donor–acceptor cyclopropanes. Our data suggest that, with comparable substituents, carbodiimides are generally more reactive than isothiocyanates, which are in turn more reactive than isocyanates. We have also disclosed a new mode of reactivity for isothiocyanates with donor–acceptor cyclopropanes. Furthermore, while iron(III) chloride caused racemization of the cyclopropane and formed racemic cycloadducts, tin(II) triflate mediated (3 + 2) reactions with isothiocyanates and carbodiimides were shown to proceed through an enantiospecific pathway, with inversion of configuration. Efforts to develop conditions catalytic in Lewis acid, as well as conditions for the enantioselective reactions of isocyanates with donor–acceptor cyclopropanes, are currently underway. Applications of these methods for a range of purposes are also being investigated.

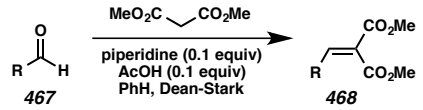
5.8 Experimental Methods and Analytical Data

5.8.1 Materials and Methods

Unless stated otherwise, reactions were performed in flame-dried or oven-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).[17] Diazodimethylmalonate was prepared according to the method of Davies and coworkers.[18] Commercially obtained reagents were used as received with the exception of tin(II) triflate and iron(III) chloride, which were stored in a nitrogen-filled glovebox. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 (at 400 MHz and 100 MHz, respectively) or on a Varian Mercury 500 (at 500 MHz and 126 MHz, respectively) and are reported relative to $CHCl_3$ (δ 7.26 & 77.16 ppm, respectively) or tetramethylsilane (0.00 ppm). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = complex multiplet, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode; HRMS were also acquired using a JEOL JMS-600H with fast atom bombardment (FAB). Optical rotations were recorded on a JASCO P-2000

Polarimeter. Enantiomeric excesses were determined by chiral HPLC (Agilent 1100 Series) or chiral SFC (Thar).

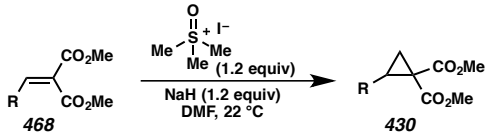
5.8.2 General Experimental Procedures



467 *468*

General Procedure A. *Knoevenagel condensation*.

A round-bottom flask was charged with the appropriate aldehyde (**467**, 14.4 mmol), followed by benzene (85 mL), dimethyl malonate (15.8 mmol), piperidine (1.44 mmol), and acetic acid (1.44 mmol). The flask was equipped with a Dean-Stark trap and condenser and the solution heated to reflux. Upon completion (as determined by TLC analysis), evaporation of the solvent gave the crude product, which was purified by silica gel column chromatography

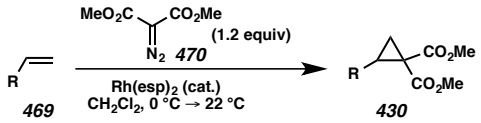


468 *430*

General Procedure B. *Corey-Chaykovsky cyclopropanation*.

Sodium hydride (2.56 mmol, 60% dispersion in mineral oil) was suspended in anhydrous DMF (4 mL) in a flame-dried round-bottom flask under nitrogen. Trimethylsulfoxonium iodide (2.56 mmol) was added, and the solution stirred at ambient temperature for 1 hour. A solution of the appropriate benzylidene malonate (**468**, 2.13 mmol) in anhydrous DMF (2 mL) was added, and the reaction mixture allowed to stir at

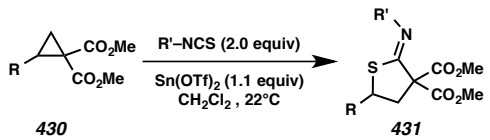
room temperature. Upon completion (as determined by TLC analysis), the solution was poured onto a mixture of ice and aqueous 2 M HCl (10 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed once with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo* to give the crude product, which was purified by silica gel column chromatography.



General Procedure C. *Styrene cyclopropanation.*

$Rh(esp)_2$ (0.3 mg) was added to a flame-dried round-bottom flask, which was then evacuated and backfilled with nitrogen three times. The appropriate styrene (**469**, 5.0 mmol) and anhydrous dichloromethane (5 mL) were then added and the solution was stirred under nitrogen and cooled in an ice bath. A solution of diazodimethylmalonate (**470**, 6.0 mmol) in anhydrous dichloromethane (5 mL) was added dropwise over 20 minutes. The reaction solution was then allowed to warm to ambient temperature. Upon completion (as determined by TLC analysis), the crude product was adsorbed onto silica gel and purified by column chromatography. When traces of the rhodium catalyst remained after chromatography (as determined by a blue discoloration), the product was dissolved in anhydrous benzene (1.5 mL) in a flame-dried round-bottom flask. A solution of tetrakis(hydroxymethyl)phosphonium hydroxide (10 mL, 1 M in isopropanol) was added,[19] and the mixture was stirred at 60 °C for 12 hours. The solution was then cooled to room temperature, diluted with diethyl ether (20 mL), washed once with water

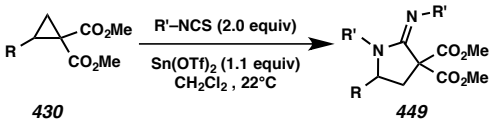
and once with brine, dried over magnesium sulfate, filtered and concentrated to give the purified product.



430 *431*

General Procedure D. *Isothiocyanate (3 + 2) reaction with D-A cyclopropanes*.

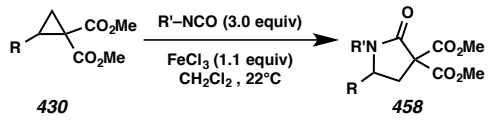
To an oven-dried 1 dram vial equipped with a magnetic stir bar was added tin(II) trifluoromethanesulfonate (0.44 mmol) in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon® septum, removed from the glovebox and placed under a nitrogen atmosphere. To a separate, oven-dried 1 dram vial were added the appropriate cyclopropane (**430**, 0.4 mmol) and isothiocyanate (0.8 mmol). The vial was sealed with a screw cap fitted with a Teflon® septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (1 mL + 0.33 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature under nitrogen. Upon consumption of the cyclopropane (as determined by TLC analysis), the reaction solution was diluted with dichloromethane (3 mL) and methanol (1 mL), adsorbed onto Celite, and purified by silica gel column chromatography. The products of this reaction were often found to be unstable during prolonged storage (~1 week) at ambient temperature; the decomposition products have not been identified.



430 *449*

General Procedure E. *Carbodiimide (3 + 2) reaction with D-A cyclopropanes*.

To an oven-dried 1 dram vial equipped with a magnetic stir bar was added tin(II) trifluoromethanesulfonate (0.44 mmol) in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon® septum, removed from the glovebox and placed under a nitrogen atmosphere. To a separate, oven-dried 1 dram vial were added the appropriate cyclopropane (**430**, 0.4 mmol) and carbodiimide (0.44 mmol). The vial was sealed with a screw cap fitted with a Teflon® septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (1 mL + 0.33 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature under nitrogen. Upon consumption of the cyclopropane (as determined by TLC analysis), the reaction solution was diluted with dichloromethane (3 mL) and methanol (1 mL), adsorbed onto Celite, and purified by silica gel column chromatography. The product obtained after column chromatography is an amidinium salt, which is dissolved in DCM, and washed with aqueous sodium hydroxide (0.1 M) and brine, then dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield the free amidine base.



430 *458*

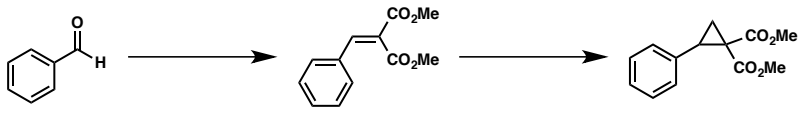
General Procedure F. *Isocyanate (3 + 2) reaction with D-A cyclopropanes, Method A*.

To a flame-dried 10 mL flask equipped with a magnetic stir bar was added iron(III) chloride (0.44 mmol) in an inert atmosphere glovebox. The flask was sealed with a

Teflon septum, removed from were glovebox and placed under a nitrogen atmosphere. To an oven-dried 1 dram vial were added the appropriate cyclopropane (**430**, 0.4 mmol) and isocyanate (1.2 mmol). The vial was sealed with a screw cap fitted with a Teflon septum, and this mixture was transferred to the reaction flask as a solution in anhydrous dichloromethane (1 mL + 0.33 mL rinse). The solution was then allowed to stir at ambient temperature under nitrogen. Upon consumption of the cyclopropane (as determined by TLC analysis), the reaction solution was diluted with dichloromethane, adsorbed onto Celite, and purified by silica gel column chromatography.

General Procedure G. *Isocyanate (3 + 2) reaction with D-A cyclopropanes, Method B*. To an oven-dried 1 dram vial equipped with a magnetic stir bar was added iron (III) chloride (0.44 mmol) and oven-dried 4Å molecular sieves (50 mg). The vial was sealed with a screw cap fitted with a rubber septum, and was placed under a nitrogen atmosphere. To a second oven-dried 1 dram vial was added the appropriate cyclopropane (0.4 mmol) and isocyanate (1.2 mmol). The vial was sealed with a screw cap fitted with a Teflon septum and this mixture was transferred to the first vial as a solution in anhydrous dichloromethane (1 mL + 0.33 mL rinse). The mixture was then allowed to stir at ambient temperature under nitrogen. Upon consumption of the cyclopropane (as determined by TLC analysis), the reaction mixture was partitioned between dichloromethane and saturated aqueous sodium bicarbonate. The layers were separated and the aqueous phase was washed twice with dichloromethane. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography.

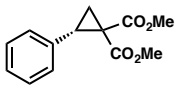
5.8.3 Cyclopropane Characterization Data



470 *471* *446*

dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (446):

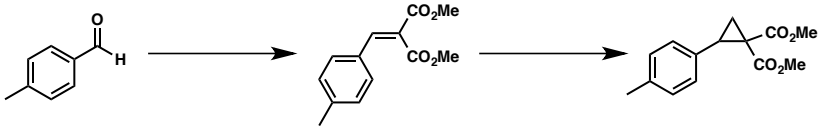
Benzylidene dimethylmalonate **471** was prepared according to General Method A: 99% yield. R_f = 0.60 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[20] Cyclopropane **446** was prepared according to General Method B: 66% yield. R_f = 0.60 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[21]



(S)-446

(*S*)-dimethyl 2-phenylcyclopropane-1,1-dicarboxylate ((*S*)-446):

Cyclopropane **(*S*)-446** was prepared according to literature methods.[22] $[\alpha]_D^{25.0}$ –133.17° (*c* 0.99, $CHCl_3$, >98% *ee*).

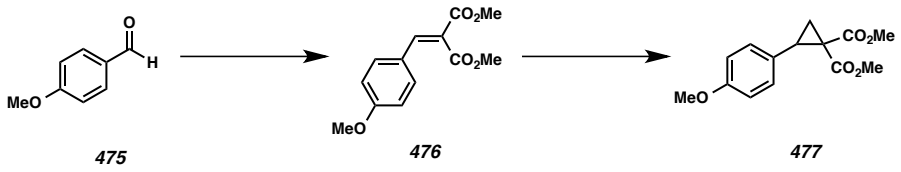


472 *473* *474*

dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (474):

Benzylidene dimethylmalonate **473** was prepared according to General Method A: 30% yield. R_f = 0.19 (3:1 Heaxanes:EtOAc eluent). Characterization data matches those reported in the literature.[23] Cyclopropane **474** was prepared according to General Method

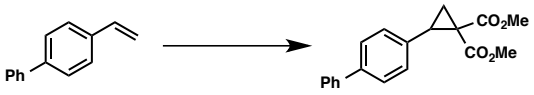
B: 77% yield. R_f = 0.60 (3:1 Hexanes:EtOAc). Characterization data matches those reported in the literature.[24]



475 *476* *477*

dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (477):

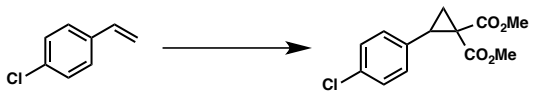
Benzylidene dimethylmalonate **476** was prepared according to General Method A: 92% yield. R_f = 0.27 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[25] Cyclopropane **477** was prepared according to General Method B: 95% yield. R_f = 0.40 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[26]



478 *479*

dimethyl 2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate (479):

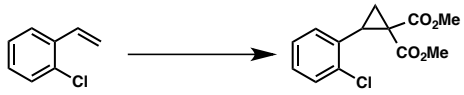
Cyclopropane **479** was prepared according to General Method C: 99% yield. R_f = 0.48 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[27]



480 *481*

dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (481):

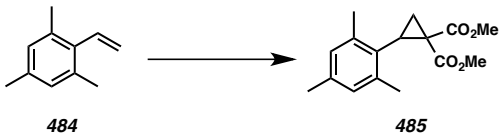
Cyclopropane **481** was prepared according to General Method C: 99% yield. R_f = 0.53 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[25]



482 *483*

dimethyl 2-(2-chlorophenyl)cyclopropane-1,1-dicarboxylate (483):

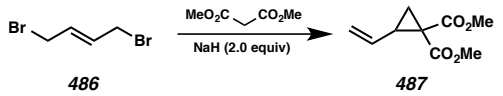
Cyclopropane **483** was prepared according to General Method C: 60% yield. R_f = 0.50 (3:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 1H), 7.22–7.15 (m, 2H), 7.11–7.07 (m, 1H), 3.81 (s, 3H), 3.36 (s, 4H), 2.26 (dd, *J* = 8.3, 5.2 Hz, 1H), 1.79 (dd, *J* = 9.1, 5.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 167.1, 136.6, 132.8, 129.3, 129.0, 128.9, 126.5, 53.0, 52.4, 36.5, 31.3, 19.0; IR (Neat Film, NaCl) 3001, 2953, 1732, 1483, 1435, 1377, 1331, 1288, 1219, 1131, 1055, 894, 785, 754 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{13}H_{14}{}^{35}ClO_4$ $[M+H]^+$: 269.0575, found 269.0573.



484 *485*

dimethyl 2-mesitylcyclopropane-1,1-dicarboxylate (485):

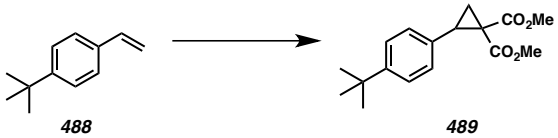
Cyclopropane **485** was prepared according to General Method C: 71% yield. R_f = 0.40 (3:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 2H), 3.83 (s, 3H), 3.34 (s, 3H), 3.10–3.02 (app t, *J* = 9.3 Hz, 1H), 2.42–2.36 (dd, *J* = 8.9, 4.9 Hz, 1H), 2.32 (s, 6H), 2.22 (s, 3H), 1.97–1.89 (dd, *J* = 9.6, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 168.0, 136.6, 129.2, 128.5, 52.9, 52.2, 35.3, 32.0, 24.0, 21.0; IR (Neat Film, NaCl) 2953, 2921, 1728, 1612, 1437, 1372, 1328, 1287, 1224, 1196, 1128, 1096, 1032, 1015, 992, 894, 852, 782, 718 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found 277.1420.



486 *487*

dimethyl 2-vinylcyclopropane-1,1-dicarboxylate (487):

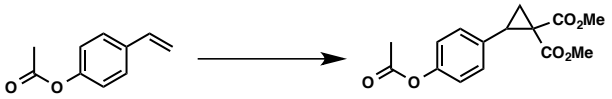
Cyclopropane **487** was prepared according to the method of Johnson and coworkers.[28]



488 *489*

dimethyl 2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate (489):

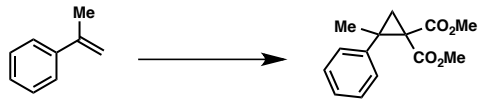
Cyclopropane **489** was prepared according to General Method C: 89% yield. R_f = 0.50 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[29]



490 ***491***

dimethyl 2-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (491):

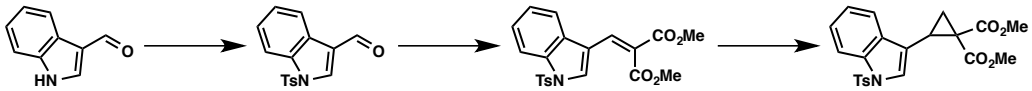
Cyclopropane **491** was prepared according to General Method C: 67% yield. R_f = 0.30 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[4c]



492 ***493***

dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate (493):

Cyclopropane **493** was prepared according to General Method C: 41% yield. R_f = 0.53 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[30]



494 ***495*** ***496*** ***497***

dimethyl 2-(1-tosyl-1*H*-indol-3-yl)cyclopropane-1,1-dicarboxylate (497):

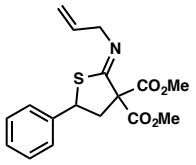
N-Tosylindole-3-carboxaldehyde (**495**) was prepared according to literature methods from indole-3-carbodaldehyde (**494**).[31]

Benzylidene dimethylmalonate **496** was prepared according to General Method A: 75% yield. R_f = 0.20 (3:1 Hexanes:EtOAc eluent). Characterization data matches those reported in the literature.[32]

Cyclopropane **497** was prepared according to General Method B: 95% yield. R_f = 0.30 (3:1 Hexanes:EtOAc eluent).[32]

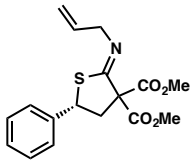
5.8.4 Thioimidate Characterization Data

Unless stated otherwise, all thioimidates were prepared according to General Method D



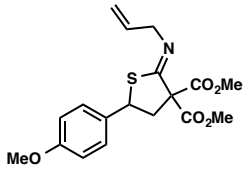
433

(*Z*)-dimethyl 2-(allylimino)-5-phenyldihydrothiophene-3,3(2*H*)-dicarboxylate (433): 92% yield. R_f = 0.45 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.39–7.34 (m, 2H), 7.33–7.29 (m, 1H), 5.99 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.13 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.73 (dd, *J* = 11.7, 4.9 Hz, 1H), 4.00 (dtd, *J* = 5.5, 1.8, 0.7 Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.12 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.90 (dd, *J* = 13.0, 11.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 168.1, 166.0, 138.2, 134.0, 129.0, 128.5, 127.8, 116.0, 71.0, 59.8, 53.8, 53.6, 50.9, 44.3; IR (Neat Film, NaCl) 3010, 2952, 1738, 1652, 1495, 1435, 1269, 1227, 1169, 1098, 1064, 977, 921, 862, 842, 799, 765 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{20}NO_4S$ $[M+H]^+$: 334.1108, found 334.1113.



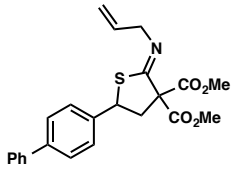
(R)-433

(*R*,*Z*)-dimethyl 2-(allylimino)-5-phenyldihydrothiophene-3,3(2H)-dicarboxylate ((*R*)-433): Characterization data is same as above; $[\alpha]_D^{25.0}$ +8.8° (*c* 0.445, $CHCl_3$, 95% *ee*).



434

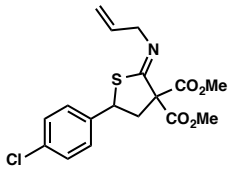
dimethyl 1-allyl-5-(4-methoxyphenyl)-2-thioxopyrrolidine-3,3-dicarboxylate (434): 98% yield. R_f = 0.49 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 6.90–6.85 (m, 2H), 6.03–5.92 (m, 1H), 5.24 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.12 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.71 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.99 (dt, *J* = 5.2, 1.8 Hz, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.07 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.87 (dd, *J* = 13.0, 11.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 168.1, 166.5, 159.7, 134.0, 130.0, 129.0, 116.0, 114.3, 71.1, 59.7, 55.5, 53.8, 53.6, 50.6, 44.5; IR (Neat Film, NaCl) 3003, 2953, 2837, 1736, 1638, 1610, 1513, 1435, 1305, 1250, 1175, 1098, 1070, 1032, 922, 831, 792 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{22}NO_5S$ $[M+H]^+$: 364.1213, found 364.1193.



435

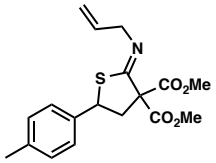
(*Z*)-dimethyl 5-([1,1'-biphenyl]-4-yl)-2-(allylimino)dihydrothiophene-3,3(2*H*)-dicarboxylate (435): 80% yield. R_f = 0.53 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.56 (m, 4H), 7.53–7.49 (m, 2H), 7.48–7.42 (m, 2H), 7.39–7.33 (m, 1H), 6.00 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.27 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.14 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.79 (dd, *J* = 11.7, 4.9 Hz, 1H), 4.02 (dt, *J* = 5.2, 1.8 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.16 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.94 (dd, *J* = 13.0, 11.7 Hz, 1H);; ^{13}C

NMR (126 MHz, $CDCl_3$) δ 168.3, 168.0, 166.2, 141.4, 140.4, 137.0, 133.8, 128.9, 128.2, 127.6, 127.1, 116.0, 71.0, 59.6, 53.7, 53.5, 50.6, 44.2; IR (Neat Film, NaCl) 3029, 2952, 1736, 1651, 1639, 1487, 1435, 1412, 1279, 1263, 1226, 1168, 1099, 1070, 1008, 977, 920, 836, 799, 767, 738 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{24}NO_4S$ $[M+H]^+$: 410.1421, found 410.1408.



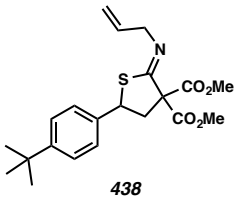
436

(*Z*)-dimethyl 2-(allylimino)-5-(4-chlorophenyl)dihydrothiophene-3,3(2*H*)-dicarboxylate (436): 66% yield. R_f = 0.49 (7:3 Hexanes:EtOAc eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.19 (m, 4H), 5.97 (ddt, *J* = 17.1, 10.4, 5.1 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.9 Hz, 1H), 5.12 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.69 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.98 (dt, *J* = 5.1, 1.8 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.09 (dd, *J* = 13.0, 5.0 Hz, 1H), 2.82 (dd, *J* = 13.0, 11.6 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.8, 165.3, 136.7, 134.2, 133.8, 129.0, 129.0, 115.9, 70.8, 59.7, 53.7, 53.4, 50.0, 44.1; IR (Neat Film, NaCl) 2953, 1733, 1652, 1637, 1491, 1434, 1266, 1221, 1167, 1090, 1068, 1011 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{19}{}^{35}ClNO_4S$ $[M+H]^+$: 368.0718, found 368.0729.



437

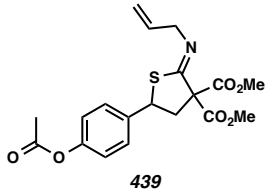
(Z)-dimethyl 2-(allylimino)-5-(p-tolyl)dihydrothiophene-3,3(2H)-dicarboxylate (437): 99% yield. R_f = 0.47 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.19–7.15 (m, 2H), 5.98 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.14 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.72 (dd, *J* = 11.8, 4.8 Hz, 1H), 4.01 (dt, *J* = 5.2, 1.8 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.10 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.88 (dd, *J* = 13.0, 11.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ168.2, 168.0, 138.5, 134.9, 133.7, 129.7, 127.7, 116.3, 71.1, 59.5, 53.9, 53.7, 51.1, 44.5, 21.3; IR (Neat Film, NaCl) 3011, 2952, 1737, 1652, 1639, 1515, 1435, 1278, 1269, 1257, 1228, 1169, 1071, 1018, 978, 921, 864, 848, 818, 790 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{22}NO_4S$ $[M+H]^+$: 348.1264, found 348.1254.



438

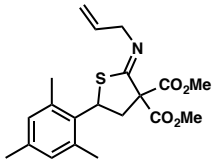
(*Z*)-dimethyl 2-(allylimino)-5-(4-(*tert*-butyl)phenyl)dihydrothiophene-3,3(2*H*)-dicarboxylate (438): 41% yield. R_f = 0.30 (3:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.32 (m, 4H), 5.98 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.13 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.71 (dd, *J* = 11.8, 4.9 Hz, 1H), 3.99 (dt, *J* = 5.1, 1.7 Hz, 2H), 3.88 (s, 3H), 3.81 (s, 3H), 3.07 (dd, J = 13.0, 4.9 Hz, 1H), 2.90 (dd, J = 13.0, 11.8 Hz, 1H) 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.2,

166.3, 151.6, 135.1, 134.1, 127.5, 125.9, 116.0, 71.1, 59.8, 53.8, 53.6, 50.7, 44.3, 34.8, 31.4; IR (Neat Film, NaCl) 2955, 2904, 2868, 1737, 1652, 1639, 1509, 1435, 1363, 1280, 1267, 1227, 1168, 1111, 1070, 1016, 978, 920, 828 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{28}NO_4S$ $[M+H]^+$: 390.1734, found 390.1726.



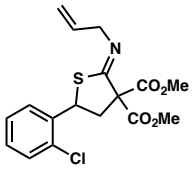
439

(*Z*)-dimethyl 5-(4-acetoxyphenyl)-2-(allylimino)dihydrothiophene-3,3(2*H*)-dicarboxylate (439): 84% yield. R_f = 0.20 (3:1 Hexanes:EtOAc eluent); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.41 (m, 2H), 7.12–7.05 (m, 2H), 5.97 (ddt, *J* = 17.2, 10.3, 5.2 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.13 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.72 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.99 (ddd, *J* = 7.0, 1.7, 1.0 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.11 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.85 (dd, *J* = 13.1, 11.6 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 168.4, 168.0, 165.8, 150.6, 135.8, 134.0, 129.0, 122.2, 116.0, 71.0, 59.8, 53.8, 53.6, 50.3, 44.5, 21.3; IR (Neat Film, NaCl) 2953, 1736, 1649, 1639, 1507, 1436, 1370, 1280, 1257, 1194, 1167, 1099, 1016, 911, 851 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{22}NO_6S$ $[M+H]^+$: 392.1162, found 392.1159.



440

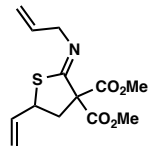
(*Z*)-dimethyl 2-(allylimino)-5-mesityldihydrothiophene-3,3(2*H*)-dicarboxylate (440): 85% yield. White, translucent crystals were obtained by slow diffusion of 1% benzene in heptane into a solution of thioimidate **440** in EtOAc, M.P.: 89–91 °C; R_f = 0.52 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87–6.84 (m, 2H), 5.99 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.32 (dd, *J* = 12.5, 5.3 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.13 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.02 (dtd, *J* = 5.2, 1.8, 0.8 Hz, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 3.24 (dd, *J* = 13.3, 12.5 Hz, 1H), 2.93 (dd, *J* = 13.3, 5.3 Hz, 1H), 2.46 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 168.3, 166.8, 137.9, 134.0, 130.9, 129.2, 116.0, 71.1, 59.8, 53.8, 53.6, 46.2, 40.0, 21.3, 20.9; IR (Neat Film, NaCl) 3010, 2952, 2918, 1737, 1649, 1638, 1611, 1435, 1267, 1230, 1203, 1167, 1097, 1073, 1015, 976, 921, 954, 822, 799, 774, 739 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{26}NO_4S$ $[M+H]^+$: 376.1577, found 376.1563.



441

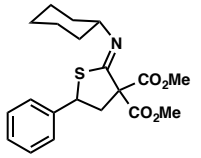
(*Z*)-dimethyl 2-(allylimino)-5-(2-chlorophenyl)dihydrothiophene-3,3(2*H*)-dicarboxylate (441): 84% yield. R_f = 0.48 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.38 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.31 (td, *J* = 7.6, 1.4 Hz, 1H), 7.23 (td, *J* = 7.6, 1.7, 1H), 5.98 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H),

5.30–5.22 (m, 2H), 5.14 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.03 (td, *J* = 4.4, 2.0 Hz, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 3.19 (dd, *J* = 13.0, 5.1 Hz, 1H), 2.84 (dd, *J* = 13.0, 11.0 Hz, 1H);; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 168.0, 165.7, 135.8, 134.0, 133.9, 130.0, 129.5, 128.5, 127.5, 116.1, 70.6, 59.7, 53.8, 53.6, 47.0, 42.6; IR (Neat Film, NaCl) 3011, 2953, 1737, 1651, 1639, 1435, 1279, 1256, 1228, 1171, 1130, 1100, 1069, 1051, 1038, 977, 921, 760 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{19}{}^{35}ClNO_4S$ $[M+H]^+$: 368.0718, found 368.0700.



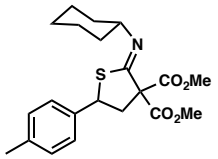
442

(*Z*)-dimethyl 2-(allylimino)-5-vinyldihydrothiophene-3,3(2*H*)-dicarboxylate (442): 99% yield. R_f = 0.45 (7:3 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.80 (ddd, *J* = 16.9, 10.0, 8.4 Hz, 1H), 5.33 (dq, *J* = 16.9, 0.8 Hz, 1H), 5.23 (ddd, *J* = 17.3, 1.8, 0.6 Hz, 1H), 5.19 (d, *J* = 10.1. 1H), 5.13 (ddd, *J* = 10.4, 1.7, 0.7 Hz, 1H), 4.22 (m, 1H), 3.98 (dd, *J* = 5.2, 2.0 Hz, 2H), 3.84 (s, 3H), 3.81 (d, *J* = 0.6 Hz, 3H), 2.97 (ddd, *J* = 13.1, 5.1, 0.8 Hz, 1H), 2.61 (dd, *J* = 13.1, 10.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 168.0, 135.7, 133.6, 118.9, 116.3, 70.5, 59.4, 53.8, 53.7, 50.3, 42.2; IR (Neat Film, NaCl) 2952, 1735, 1649, 1638, 1434, 1328, 1272, 1254, 1169, 1139, 1097, 1068, 987, 923, 859, 787, 728 cm^{-1}; HRMS (Low Voltage MM: ESI-APCI) *m/z* calc'd for $C_{13}H_{18}NO_4S$ $[M+H]^+$: 284.0951, found 284.0962.



443

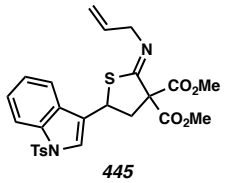
(*Z*)-dimethyl 2-(cyclohexylimino)-5-phenyldihydrothiophene-3,3(2*H*)-dicarboxylate (443): 91% yield. R_f = 0.40 (3:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.42 (m, 2H), 7.36 (ddd, *J* = 8.2, 7.1, 0.9 Hz, 2H), 7.30 (m, 1H), 4.69 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.08 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.98 (tt, *J* = 10.1, 3.6 Hz, 1H), 2.85 (dd, *J* = 13.0, 11.7 Hz, 1H), 1.85–1.72 (m, 4H), 1.65–1.57 (m, 1H), 1.57–1.44 (m, 2H), 1.37–1.20 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 168.3, 161.5, 138.6, 128.9, 128.4, 127.8, 70.8, 67.1, 53.7, 53.4, 50.6, 44.0, 32.8, 31.7, 25.8, 24.7, 24.6; IR (Neat Film, NaCl) 2930, 2854, 1738, 1651, 1435, 1168, 1067, 973, 912, 764 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{20}H_{26}NO_4S$ $[M+H]^+$: 376.1577, found 356.1589.



444

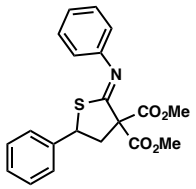
(*Z*)-dimethyl 2-(cyclohexylimino)-5-(*p*-tolyl)dihydrothiophene-3,3(2*H*)-dicarboxylate (444): 99% yield. R_f = 0.63 (2:1 Hexanes: EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.18–7.14 (m, 2H), 4.67 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.05 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.98 (tt, *J* = 10.1, 3.6 Hz, 1H), 2.83 (dd, *J* = 13.0, 11.8 Hz, 1H), 2.35 (s, 3H), 1.83–1.72 (m, 4H), 1.65–1.57 (m, 1H), 1.56–1.44 (m, 2H), 1.38–1.21 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 168.3, 161.5, 138.2, 135.5, 129.6, 127.6, 70.9, 67.0, 53.6, 53.4, 50.4, 44.0, 32.8, 31.7, 25.8, 24.7, 24.5, 21.2; IR (Neat

Film, NaCl) 2929, 2853, 1735, 1648, 1434, 1255, 1167, 1071, 973, 818 cm^{-1}; HRMS (APCI) *m/z* calc'd for $C_{21}H_{28}NO_4S$ $[M+H]^+$: 390.1734, found 390.1738.



445

(*Z*)-dimethyl 2-(allylimino)-5-(1-tosyl-1*H*-indol-3-yl)dihydrothiophene-3,3(2*H*)-dicarboxylate (445): 77% yield. R_f = 0.80 (1:1 Hexanes:EtOAc eluent); ^1H NMR (500 MHz, $CDCl_3$) δ 168.1, 167.9, 166.2, 145.4, 135.5, 135.1, 133.6, 130.2, 128.9, 127.1, 125.5, 123.9, 123.5, 119.9, 116.3, 114.0, 77.4, 70.5, 59.7, 53.9, 53.7, 42.7, 41.7, 21.7; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.9, 166.2, 145.4, 135.5, 135.1, 133.6, 130.2, 128.9, 127.1, 125.5, 123.9, 123.5, 119.9, 116.3, 114.0, 77.4, 70.5, 59.7, 53.9, 53.7, 42.7, 41.7, 21.7; IR (Neat Film, NaCl) 2953, 1738, 1639, 1447, 1372, 1275, 1175, 1126, 1095, 974, 912, 733 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{26}H_{27}N_2O_6S_2$ $[M+H]^+$: 527.1305, found 527.1298.



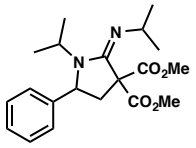
448

(*Z*)-dimethyl 5-phenyl-2-(phenylimino)dihydrothiophene-3,3(2*H*)-dicarboxylate (448): Prepared using General Method F, using phenylisothiocyanate. 89% yield. R_f = 0.60 (3:1 Hexanes:EtOAc eluent); ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.37 (m, 2H), 7.36–7.31 (m, 4H), 7.30–7.27 (m, 1H), 7.16–7.11 (m, 1H), 7.05–7.01 (m, 2H), 4.76 (dd, *J*

= 11.7, 4.9 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H), 3.19 (dd, *J* = 13.1, 4.9 Hz, 1H), 2.99 (dd, *J* = 13.1, 11.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 167.9, 167.8, 151.0, 137.8, 129.1, 129.0, 128.5, 127.8, 125.3, 120.2, 71.4, 54.0, 53.8, 51.2, 43.9; IR (Neat Film, NaCl) 3030, 2952, 1735, 1638, 1593, 1486, 1434, 1268, 1224, 1170, 1063, 973, 763 cm^{-1}; HRMS (ESI) *m/z* calc'd for $C_{20}H_{20}NO_4S$ $[M+H]^+$: 370.1108, found 370.1098.

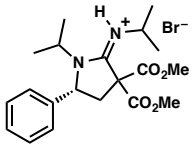
5.8.5 Amidine Characterization Data

All amidines were synthesized according to General Method E.



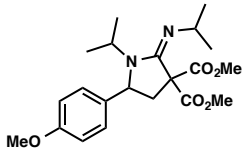
450

(*E*)-dimethyl 1-isopropyl-2-(isopropylimino)-5-phenylpyrrolidine-3,3-dicarboxylate (450): 98% yield. R_f = 0.39 (9:1 CH_2Cl_2:MeOH eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 5H), 4.52 (t, *J* = 7.1 Hz, 1H), 3.99 (p, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.50 (hept, *J* = 6.0 Hz, 1H), 2.95 (dd, *J* = 12.8, 7.0 Hz, 1H), 2.33 (dd, *J* = 12.8, 7.2 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.05 (d, *J* = 5.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.2, 151.3, 143.8, 128.5, 127.8, 127.0, 60.5, 59.8, 53.1, 52.9, 51.4, 47.3, 43.4, 24.7, 24.3, 19.6, 19.2; IR (Neat Film, NaCl) 2963, 1731, 1659, 1436, 1261, 1212, 1063, 969 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{29}N_2O_4$ $[M+H]^+$: 361.2122, found 361.2018.



(R)-450·HBr

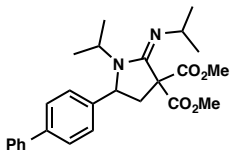
(*R*,*E*)-dimethyl 1-isopropyl-2-(isopropylimino)-5-phenylpyrrolidine-3,3-dicarboxylate ((*R*)-450•HBr): Acetyl bromide (22 mL, 0.3 mmol) was dissolved in dichloromethane (3 mL) in a 10 mL round bottom flask. Methanol (41 mL, 1 mmol) was added to the solution and this mixture was transferred into a second flask containing a solution of amidine **(*R*)-450** (72 mg, 0.2 mmol). The mixture was concentrated in vacuo and crystallized by vapor diffusion of diethyl ether into dichloromethane to produce fine colorless needles suitable for X-ray crystallography. $[\alpha]_D^{25.0}$ +8.8° (*c* 0.445, $CHCl_3$, >98% *ee*).



451

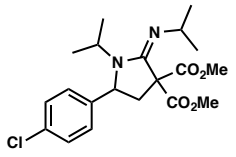
(*E*)-dimethyl 1-isopropyl-2-(isopropylimino)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (451): 98% yield. R_f = 0.42 (9:1 CH_2Cl_2:MeOH eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 6.89 – 6.79 (m, 2H), 4.50 (br t, *J* = 6.9 Hz, 1H), 4.07 – 3.95 (br m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.49 (p, *J* = 6.0 Hz, 1H), 2.93 (br dd, *J* = 12.8, 6.9 Hz, 1H), 2.30 (br dd, *J* = 12.9, 7.3 Hz, 1H), 1.14 (br d, *J* = 6.9 Hz, 4H), 1.11 (d, *J* = 4.3 Hz, 2H), 1.05 (d, *J* = 6.0 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ169.5, 169.0, 159.3, 151.6, 135.2, 128.2, 113.9, 60.7, 59.6, 55.3, 53.2, 53.0, 51.4, 47.4, 43.4, 24.5, 24.1, 19.7, 19.2.; IR (Neat Film, NaCl) 2963,

2928, 1736, 1654, 1612, 1513, 1249, 1214, 1172, 1081 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{31}N_2O_5$ $[M+H]^+$: 391.2227, found 391.2208.



452

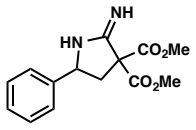
(*E*)-dimethyl 5-([1,1'-biphenyl]-4-yl)-1-isopropyl-2-(isopropylimino)pyrrolidine-3,3-dicarboxylate (452): 92% yield. R_f = 0.42 (9:1 CH_2Cl_2:MeOH eluent); ^1H NMR (500 MHz, $CDCl_3$) δ 7.63–7.53 (m, 4H), 7.47–7.38 (m, 4H), 7.37–7.32 (m, 1H), 4.59 (t, *J* = 7.1 Hz, 1H), 4.04 (hept, *J* = 6.9 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.53 (hept, *J* = 5.9 Hz, 1H), 3.00 (dd, *J* = 12.8, 7.0 Hz, 1H), 2.37 (dd, *J* = 12.8, 7.3 Hz, 1H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.08 (d, *J* = 5.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H);; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 169.2, 151.4, 142.9, 140.8, 140.7, 128.9, 127.5, 127.4, 127.2, 127.1, 60.6, 59.6, 53.2, 53.0, 51.5, 47.4, 43.4, 24.7, 24.4, 19.8, 19.2; IR (Neat Film, NaCl) 2964, 1733, 1658, 1486, 1435, 1375, 1358, 1264, 1216, 1165, 1126, 1076, 1008, 973, 841, 767, 733 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{26}H_{33}N_2O_4$ $[M+H]^+$: 437.2435, found 437.2411.



453

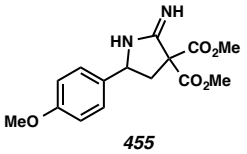
(*E*)-dimethyl 5-(4-chlorophenyl)-1-isopropyl-2-(isopropylimino)pyrrolidine-3,3-dicarboxylate (453): 78% yield. R_f = 0.40 (9:1 CH_2Cl_2:MeOH eluent); ^1H NMR (500

MHz, $CDCl_3$) δ 7.30–7.23 (m, 4H), 4.50 (t, *J* = 7.1 Hz, 1H), 4.00 (hept, *J* = 6.9 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.48 (hept, *J* = 5.9 Hz, 1H), 2.95 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.27 (dd, *J* = 12.9, 7.1 Hz, 1H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.0 Hz, 3H), 1.04 (d, *J* = 5.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 169.1, 151.2, 142.6, 133.4, 128.7, 128.3, 60.4, 59.1, 53.2, 53.0, 51.5, 47.3, 43.3, 24.7, 24.3, 19.9, 19.1; IR (Neat Film, NaCl) 2965, 1733, 1658, 1489, 1435, 1376, 1359, 1269, 1214, 1165, 1126, 1088, 1014, 974, 831 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{28}{}^{35}ClN_2O_4$ $[M+H]^+$: 395.1732, found 395.1755.



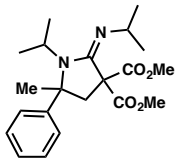
454

dimethyl 2-imino-5-phenylpyrrolidine-3,3-dicarboxylate (454): 78% yield. R_f = 0.45 (9:1 CH_2Cl_2:MeOH eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.34–7.27 (m, 3H), 7.25–7.21 (m, 2H), 4.99 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.10 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.37 (dd, *J* = 13.6, 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 168.3, 160.2, 144.2, 128.6, 127.1, 126.4, 68.4, 67.4, 53.6, 53.4, 42.8; IR (Neat Film, NaCl) 3449, 3028, 1729, 1665, 1600, 1435, 1386, 1354, 1279, 1243, 1201, 1154, 1114, 1075, 765 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{17}N_2O_4$ $[M+H]^+$: 277.1188, found 277.1176.



455

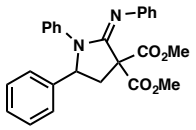
dimethyl 2-imino-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (455): 68% yield. R_f = 0.47 (9:1 CH_2Cl_2:MeOH eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.16 (m, 2H), 6.84 (dd, *J* = 6.8, 1.9 Hz, 2H), 4.97–4.88 (m, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.06 (dd, *J* = 13.6, 6.9 Hz, 1H) 2.34 (dd, *J* = 13.6, 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 168.3, 160.1, 158.7, 136.3, 127.5, 113.9, 113.9, 67.8, 67.4, 55.4, 53.6, 53.4, 42.9; IR (Neat Film, NaCl) 3464, 3374, 3102, 2955, 2838, 1738, 1662, 1612, 1514, 1439, 1351, 1247, 1213, 1175, 1105, 1077, 1034, 831, 733 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}N_2O_5$ $[M+H]^+$: 307.1294, found 307.1287.



456

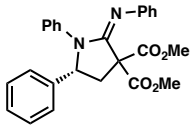
(*E*)-dimethyl 1-isopropyl-2-(isopropylimino)-5-methyl-5-phenylpyrrolidine-3,3-dicarboxylate (456): 58% yield. R_f =0.35 (10:1 $CHCl_3$:MeOH eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.38–7.33 (m, 2H), 7.29–7.24 (m, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 3.44 (dt, *J* = 11.8, 5.9 Hz, 1H), 3.09 ? 2.99 (hept, *J* = 6.7 Hz, 1H), 2.83–2.72 (m, 2H), 1.61 (s, 3H), 1.35 (dd, *J* = 17.2, 6.7 Hz, 6H), 1.10 (dd, *J* = 18.8, 5.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.2, 148.5, 146.8, 128.3, 127.2, 126.7, 64.8, 60.3, 53.2, 53.1, 51.4, 50.5, 47.1, 24.9, 24.8, 24.5, 19.9, 19.1; IR (Neat Film, NaCl) 2963,

1731, 1654, 1375, 1251, 1217, 1090 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{31}N_2O_4$ $[M+H]^+$: 375.2278, found 375.2297.



457

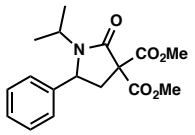
(*E*)-dimethyl 1,5-diphenyl-2-(phenylimino)pyrrolidine-3,3-dicarboxylate (457): 79% yield. R_f =0.32 (10:1 CH_2Cl_2:MeOH eluent); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.34 – 7.16 (m, 8H), 7.10 (dt, *J* = 15.2, 7.6 Hz, 5H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 2H), 5.28 (t, *J* = 7.0 Hz, 1H), 3.66 (s, 3H) 3.45 (s, 3H), 3.17 (dd, *J* = 13.0, 7.2 Hz, 1H), 3.05 (s, 1H), 2.71 (dd, *J* = 13.0, 6.9 Hz, 1H);^{13}C NMR (101 MHz, DMSO-d_6, 100 °C) δ 168.5, 168.2, 152.0, 148.4, 148.3, 140.9, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.2, 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 127.2, 126.6, 125.9, 124.6, 122.0, 121.9, 120.9, 64.1, 63.1, 62.7, 55.3, 54.5, 54.3, 53.4, 52.6, 52.4, 51.9, 43.0; IR (Neat Film, NaCl) 3062, 3027, 2948, 1730, 1661, 1592, 1493, 1372, 1263, 1051 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{26}H_{25}N_2O_4$ $[M+H]^+$: 429.1809, found 429.1825.



(R)-457

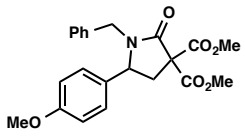
(*R*,*E*)-dimethyl 1,5-diphenyl-2-(phenylimino)pyrrolidine-3,3-dicarboxylate ((*R*)-457): Characterization data same as above; $[\alpha]_D^{25.0}$ +36.7° (*c* 0.805, $CHCl_3$, 88% *ee*).

5.8.6 Lactam Characterization Data



459

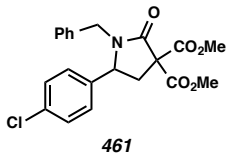
dimethyl 1-isopropyl-2-oxo-5-phenylpyrrolidine-3,3-dicarboxylate (459): Prepared according to General Method F. 72% yield. R_f = 0.46 (1:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.26 (m, 5H), 4.64 (t, *J* = 7.3 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80–3.71 (m, 1H), 3.02 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.59 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 168.1, 167.2, 141.0, 129.0, 128.6, 127.2, 63.4, 59.7, 53.7, 53.5, 47.1, 38.4, 19.8, 19.7; IR (Neat Film, NaCl) 2954, 1735, 1703, 1495, 1457, 1434, 1367, 1342, 1259, 1218, 1130, 1090, 1065, 998, 966, 919, 894, 774 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}NO_5$ $[M+H]^+$: 320.1492, found 320.1490.



460

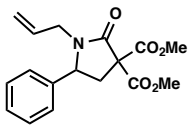
dimethyl 1-butyl-2-oxo-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (460): Prepared according to General Method F. 62% yield. R_f = 0.39 (1:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 3H), 7.08–7.02 (m, 4H), 6.94–6.87 (m, 2H), 5.11 (d, *J* = 14.5 Hz, 1H), 4.31 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.46 (d, *J* = 14.6 Hz, 1H), 2.94 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.65 (dd, *J* = 13.8, 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ168.1, 167.9, 167.1, 160.0, 135.5, 130.4,

128.8, 128.7, 128.6, 127.9, 114.6, 63.4, 58.3, 55.5, 53.7, 53.6, 45.2, 38.1; IR (Neat Film, NaCl) 2953, 1735, 1705, 1513, 1434, 1281, 1247 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{24}NO_6$ $[M+H]^+$: 398.1598, found 398.1581.



461

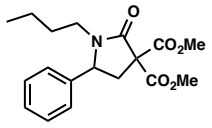
dimethyl 1-butyl-2-oxo-5-(4-chlorophenyl)pyrrolidine-3,3-dicarboxylate (461): Prepared according to General Method F. 78% yield. R_f = 0.41 (1:1 Hexanes:EtOAc eluent); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.29–7.24 (m, 3H), 7.10–7.05 (m, 2H), 7.04–7.00 (m, 2H), 5.13 (d, *J* = 14.6 Hz, 1H), 4.33 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.46 (d, *J* = 14.6 Hz, 1H), 2.97 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.60 (dd, *J* = 13.9, 7.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 167.7, 167.2, 137.3, 135.1, 134.7, 129.5, 128.8, 128.7, 128.6, 128.0, 63.2, 58.1, 53.8, 53.7, 45.3, 37.9; IR (Neat Film, NaCl) 2953, 1736, 1708, 1435, 1242, 1204, 1090 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{21}H_{21}{}^{35}ClNO_5$ $[M+H]^+$: 402.1103, found 402.1084.



462

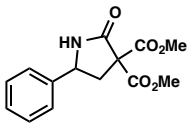
dimethyl 1-allyl-2-oxo-5-phenylpyrrolidine-3,3-dicarboxylate (462): Prepared according to General Method G. 42% yield. R_f = 0.52 (1:1 Hexanes:EtOAc eluent);^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.29 (m, 3H), 7.24–7.18 (m, 2H), 5.71–5.52 (m, 1H), 5.12 (ddt, *J* = 10.1, 1.3, 0.7 Hz, 1H), 4.99–4.91 (m, 1H), 4.64 (t, *J* = 7.5 Hz, 1H), 4.40 (m,

1H), 3.90–3.84 (m, 3H), 3.82 (d, *J* = 0.9 Hz, 3H), 3.15–3.02 (m, 2H), 2.62 (dd, *J* = 13.8, 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.9, 166.8, 138.9, 131.0, 129.2, 128.8, 127.3, 118.9, 63.1, 59.1, 53.8, 53.6, 44.1, 38.0; IR (Neat Film, NaCl) 2953, 1735, 1707, 1433, 1245, 1214, 1070 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{20}NO_5$ $[M+H]^+$: 318.1341, found 318.1356.



463

dimethyl 1-butyl-2-oxo-5-phenylpyrrolidine-3,3-dicarboxylate (463): Prepared according to General Method G. 58% yield. R_f = 0.10 (4:1 Hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.31 (m, 3H), 7.25–7.20 (m, 2H), 4.63 (t, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.70 (dt, *J* = 13.7, 7.9 Hz, 1H), 3.06 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.57–2.53 (m, 2H), 1.43–1.30 (m, 2H), 1.29–1.10 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 168.0, 166.9, 139.1, 129.2, 128.7, 127.1, 63.2, 59.5, 53.7, 53.6, 41.1, 38.3, 28.6, 19.8, 13.7; IR (Neat Film, NaCl) 2957, 2873, 1732, 1708, 1495, 1456, 1435, 1370, 1278, 1242, 1202, 1108, 1090, 1070, 893, 771 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{24}NO_5$ $[M+H]^+$: 334.1654, found 334.1646.



464

dimethyl 2-oxo-5-phenylpyrrolidine-3,3-dicarboxylate (464): Prepared according to General Method G. 49% yield. R_f = 0.48 (1:1 Hexanes:EtOAc eluent); ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.40–7.33 (m, 2H), 7.33–7.28 (m, 3H), 6.93–6.69 (bs, 1H), 4.75 (t, *J* = 7.4 Hz, 1H), 3.85 (d, *J* = 1.6 Hz, 3H), 3.77 (dd, *J* = 2.1, 0.9 Hz, 3H), 3.18 (ddt, *J* = 13.6, 7.2, 0.8 Hz, 1H), 2.63 (ddd, *J* = 13.5, 7.8, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 167.5, 167.4, 140.3, 129.0, 128.4, 126.0, 63.2, 55.4, 53.7, 53.6, 40.4; IR (Neat Film, NaCl) 3251, 2955, 1729, 1435, 1250, 1208, 1060 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{16}NO_5$ $[M+H]^+$: 278.1028, found 278.1042.

5.9 Notes and References

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2. Examples include: (a) Karadeolian, A.; Kerr, M. A. *Angew. Chem., Int. Ed*. **2010**, *49*, 1133–1135. (b) Campbell, M. J.; Johnson, J. S. *J. Am. Chem. Soc*. **2009**, *131*, 10370–10371. (c) Zhang, H.; Curran, D. P. *J. Am. Chem. Soc*. **2011**, *133*, 10376–10378. (d) Morales, C. L.; Pagenkopf, B. L. *Org. Lett*. **2008**, *10*, 157–159. (e) Goldberg, A. F. G.; Stoltz, B. M. *Org. Lett*. **2011**, *13*, 4474–4476.

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4. Stereoselective (3 + 2) reactions of donor–acceptor cyclopropanes with aldimines: (a) Parsons, A. T.; Smith, A. G.; Neel, A. J.; Johnson, J. S. *J. Am. Chem. Soc*. **2010**, *132*, 9688–9692. Aldehydes: (b) Parsons, A. T.; Johnson, J. S. *J. Am. Chem. Soc*. **2009**, *131*, 3122–3123. (c) Pohlhaus, P. D.; Sanders, S. D.; Parsons, A. T.; Li, W.; Johnson, J. S. *J. Am. Chem. Soc*. **2008**, *130*, 8642–8650. (d)

Pohlhaus, P. D.; Johnson, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 16014–16015. Vinylcyclopropanes with azlactones: (e) Trost, B. M.; Morris, P. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 6167–6170. Alkynes: (f) Lin, M.; Kang, G.-Y.; Guo, Y.-A.; Yu, Z.-X. *J. Am. Chem. Soc.* **2012**, *134*, 398–405.

5. Additional examples of stereoselective cycloadditions of donor–acceptor cyclopropanes can be found in the review articles in reference 1.

6. Chemoselectivity comparable to that observed in our studies has been shown in a palladium-catalyzed (3 + 2) cycloaddition of isothiocyanates with aziridines, see: Baeg, J.-O.; Bensimon, C.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4700–4701.

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8. Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds*, 4th ed.; Springer-Verlag: Berlin, 2009.

9. A thioamide C=S IR stretch is expected as a strong band near 1140–1190 cm^{-1}.[8]

10. (a) The assignment of *Z*-stereochemistry for thioimidate **440** was established via single-crystal X-ray diffraction, and other thioimidates in Scheme 5.2.1 were assigned by analogy. (b) The assignment of *E*-stereochemistry for amidine **450** is based on the crystal structure of its HBr salt (vide infra), and other amidines in Scheme 5.4.1 were assigned by analogy.

11. Two methods were used to set up reactions with dry iron(III) chloride: (a) iron(III) chloride stored in a nitrogen-filled glovebox was dispensed into a flame-dried flask or (b) iron(III) chloride stored on a benchtop was dispensed into an oven-dried vial, and used in conjunction with 4 Å molecular sieves. Although (b)

is more operationally convenient, method (a) appears to result in shorter reaction times and higher yields.

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13. Treatment of cyclopropane **(*R*)-446** with iron(III) chloride, in the absence of a dipolarophile, results in racemization of the material.

14. Prolonged exposure of cyclopropane **(*R*)-446** to $Sn(OTf)_2$ results in racemization. See reference 4c.

15. Methyl and phenyl hydrogen atoms and the bromide counterion are omitted for clarity.

16. Related mechanistic investigations were originally performed on cyclopropane nitrone cycloadditions: (a) Karadeolian, A.; Kerr, M. A. *J. Org. Chem.* **2007**, *72*, 10251–10253. (b) Sapeta, K.; Kerr, M. A. *J. Org. Chem.* **2007**, *72*, 8597–8599. (c) Wanapun, D.; Van Gorp, K. A.; Mosey, N. J.; Kerr, M. A.; Woo, T. K. *Can. J. Chem.* **2005**, *83*, 1752–1767.

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APPENDIX 12

Spectra Relevant to Chapter 5:

Lewis Acid Mediated (3+2) Cycloadditions of

Donor–Acceptor Cyclopropanes with Heterocumulenes

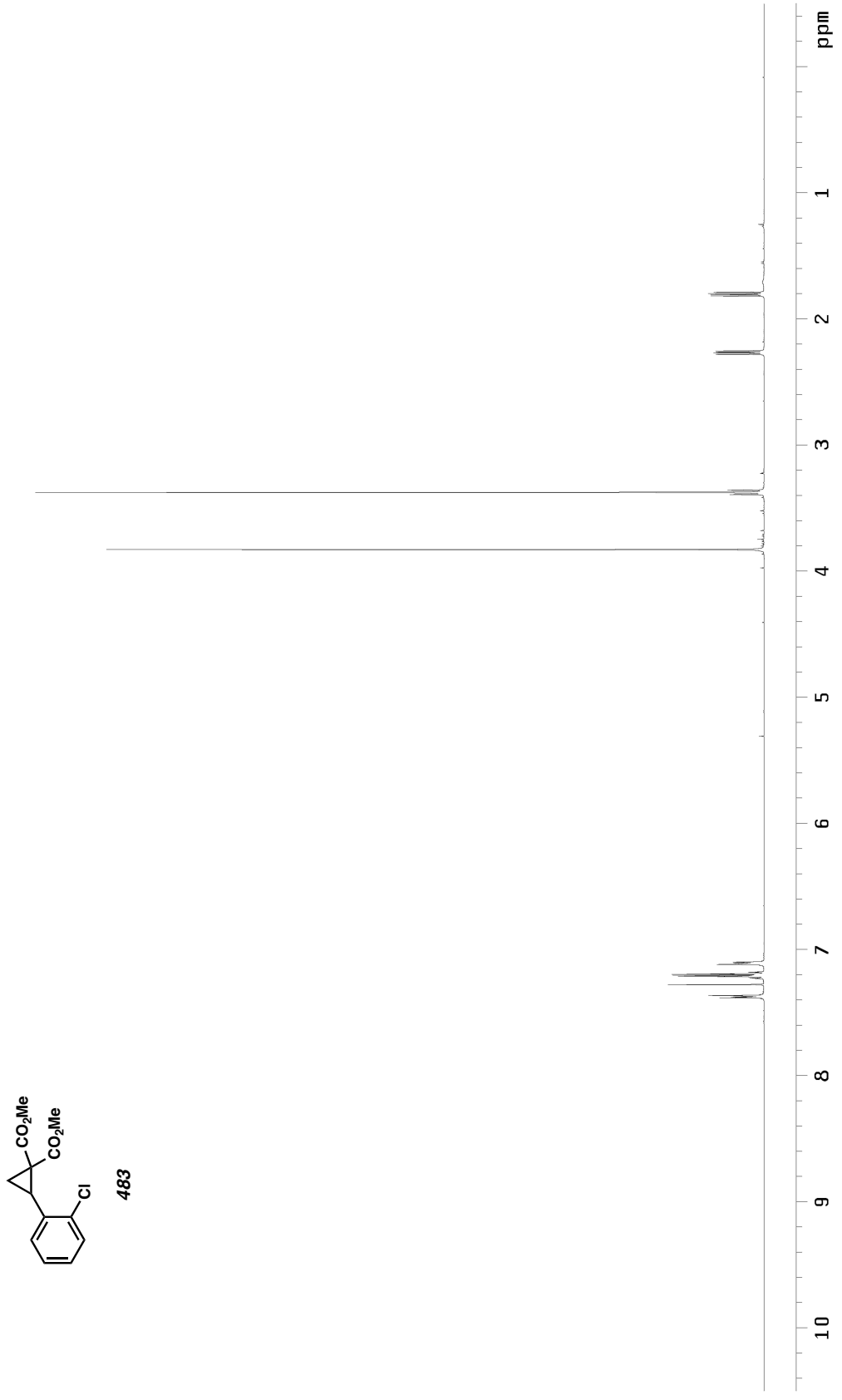


Figure A12.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **483**.

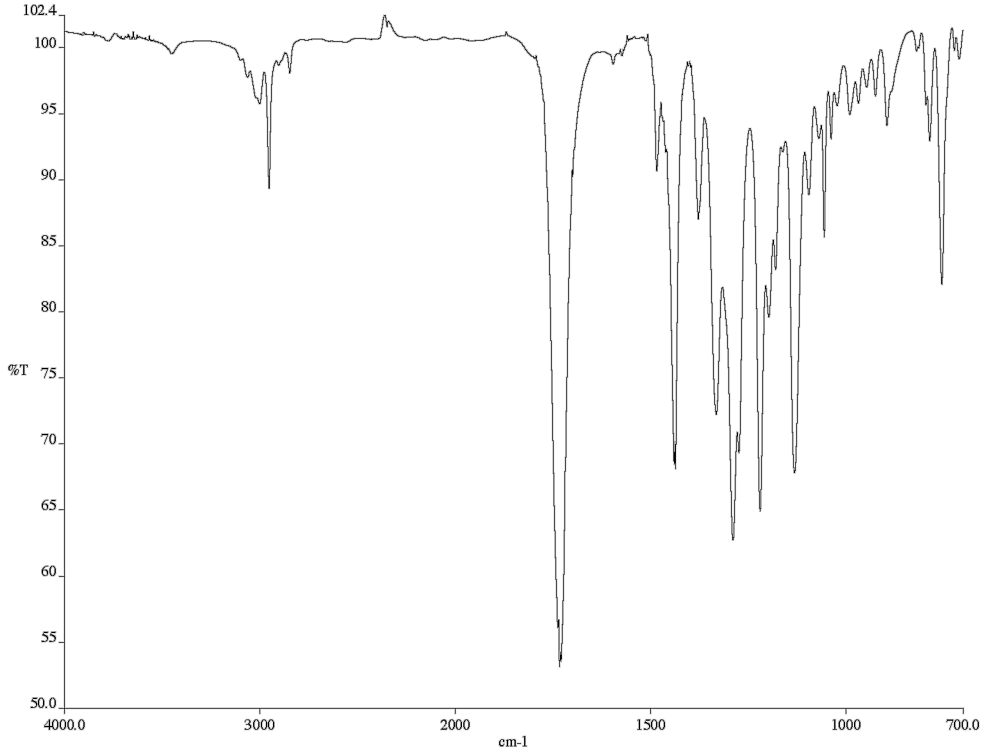


Figure A12.2. Infrared spectrum (thin film/NaCl) of compound **483**.

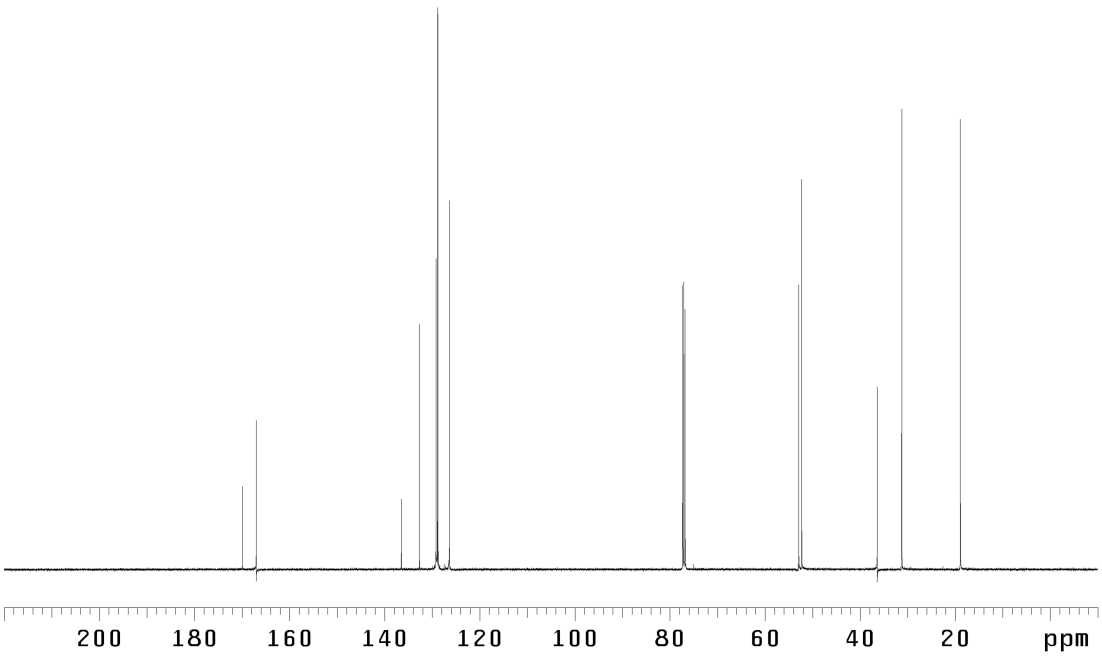


Figure A12.3. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **483**.

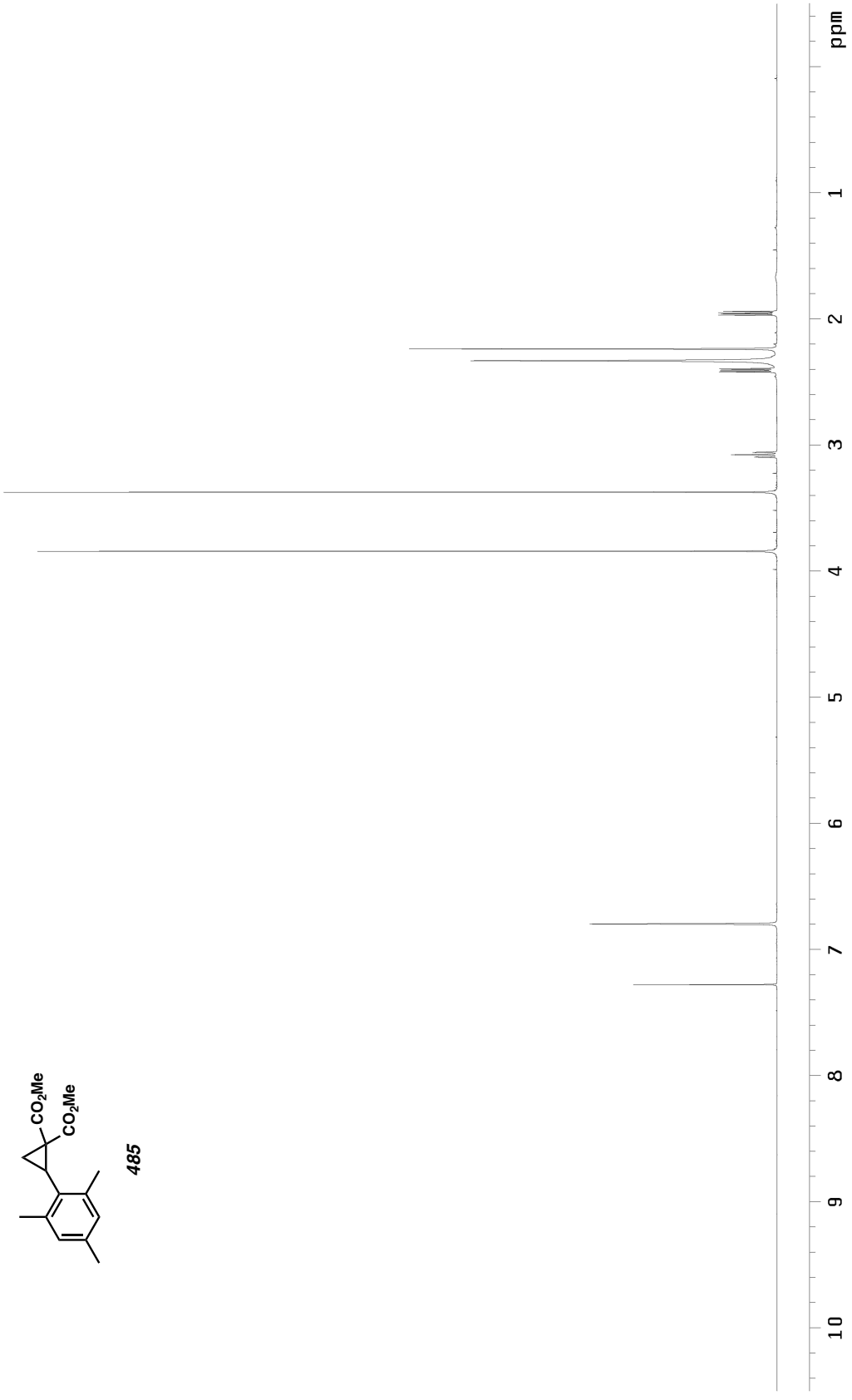


Figure A12.4. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **485**.

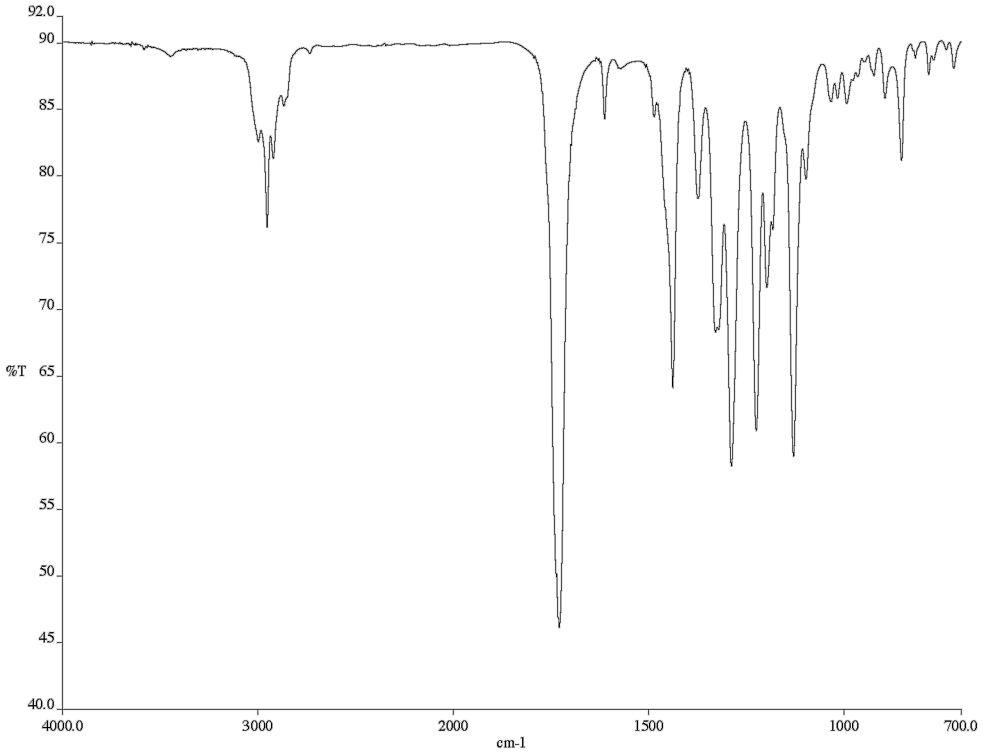


Figure A12.5. Infrared spectrum (thin film/NaCl) of compound **485**.

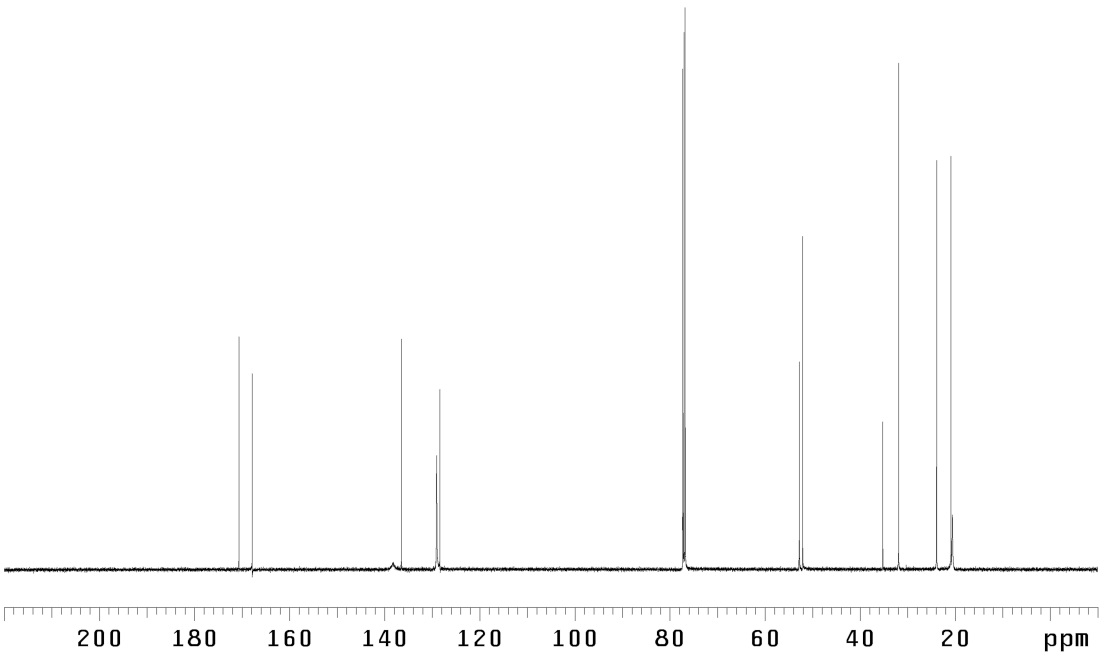


Figure A12.6. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **485**.

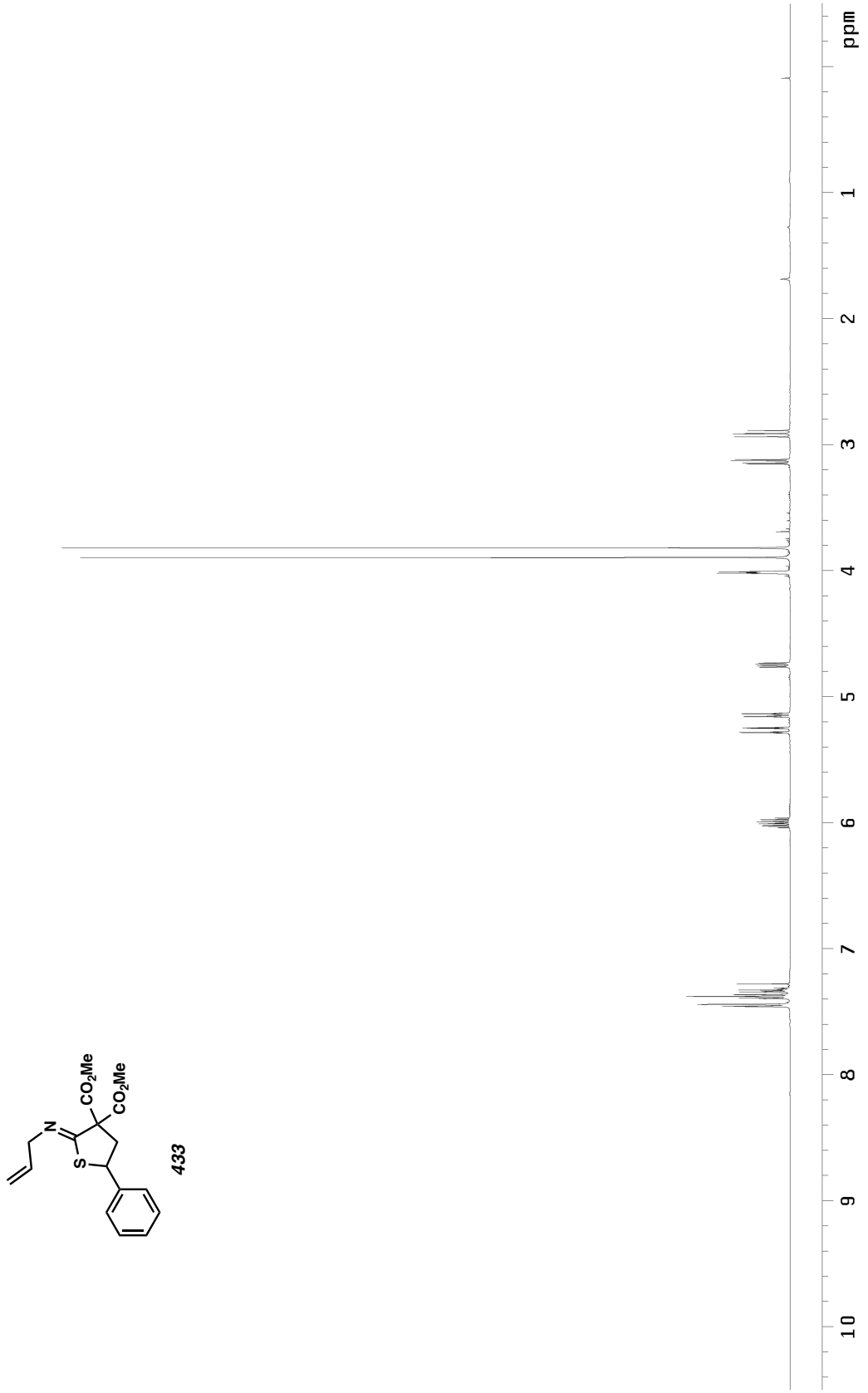


Figure A12.7. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **433**.

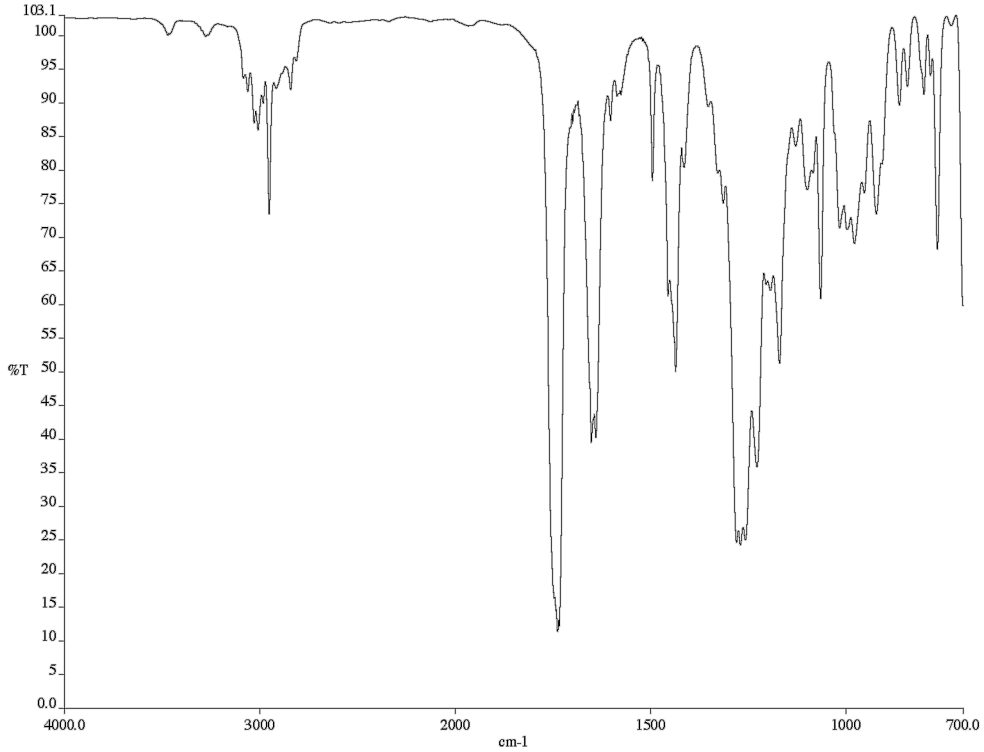


Figure A12.8. Infrared spectrum (thin film/NaCl) of compound **433**.

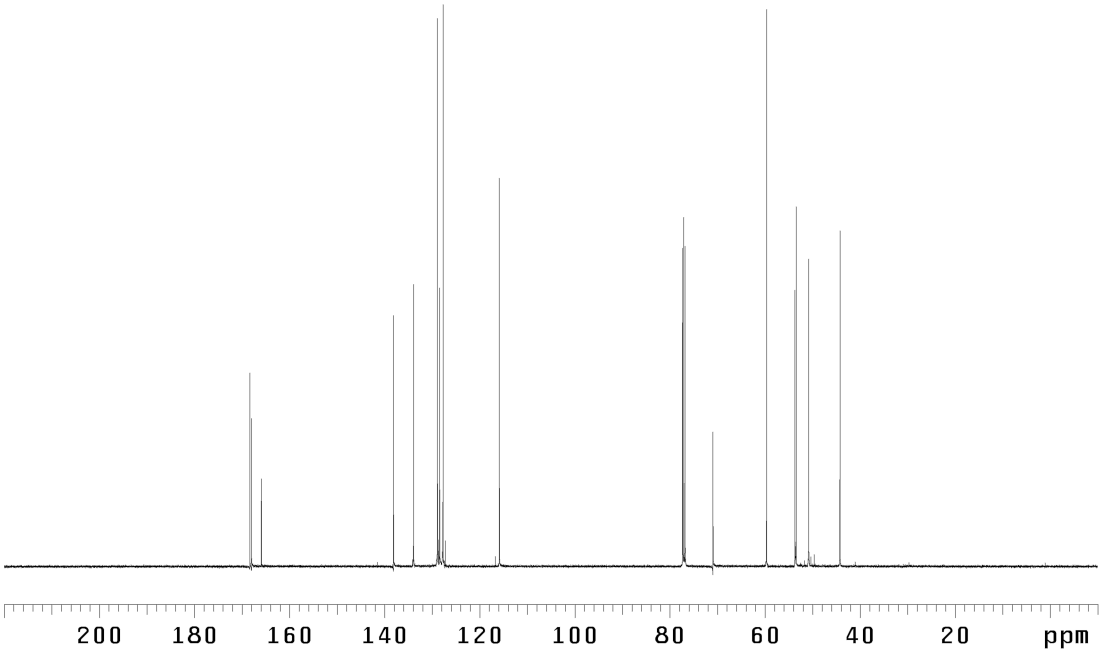


Figure A12.9. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **433**.

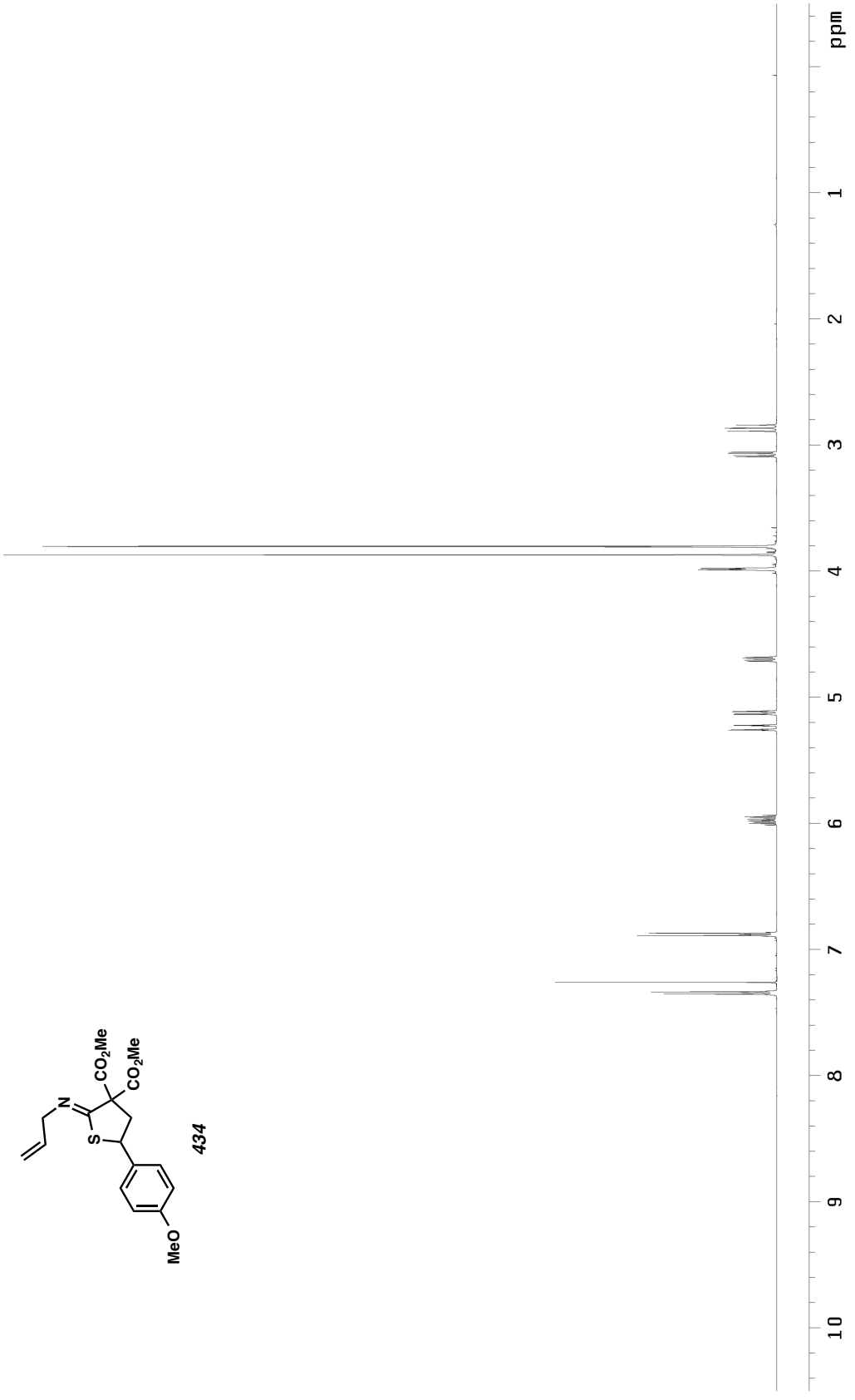


Figure A12.10. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **434**.

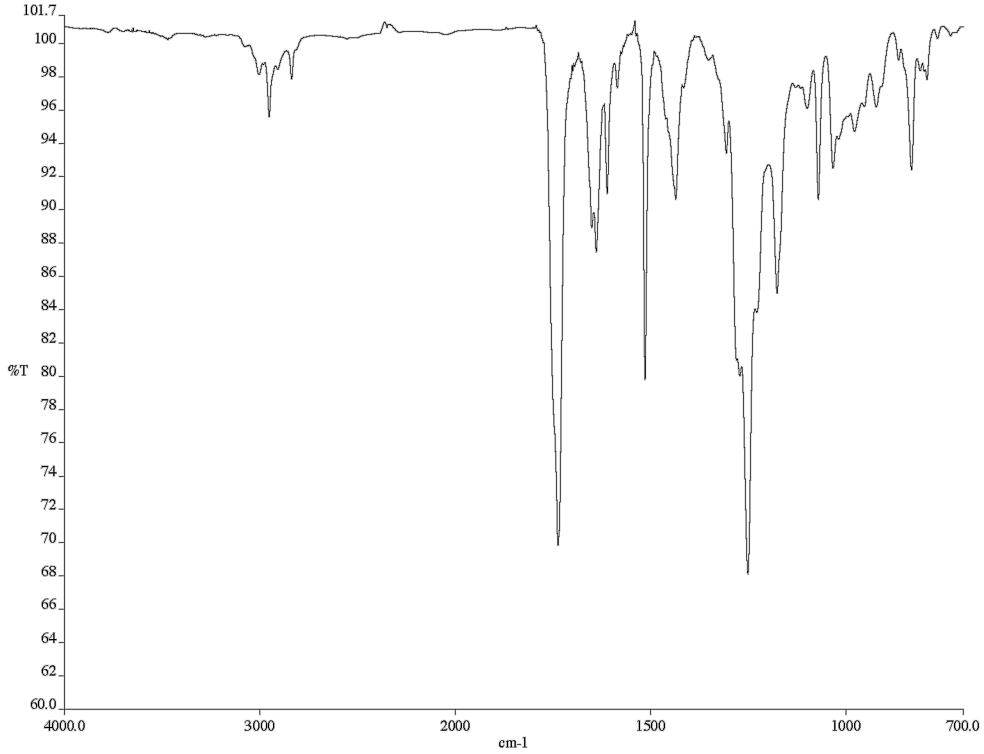


Figure A12.11. Infrared spectrum (thin film/NaCl) of compound **434**.

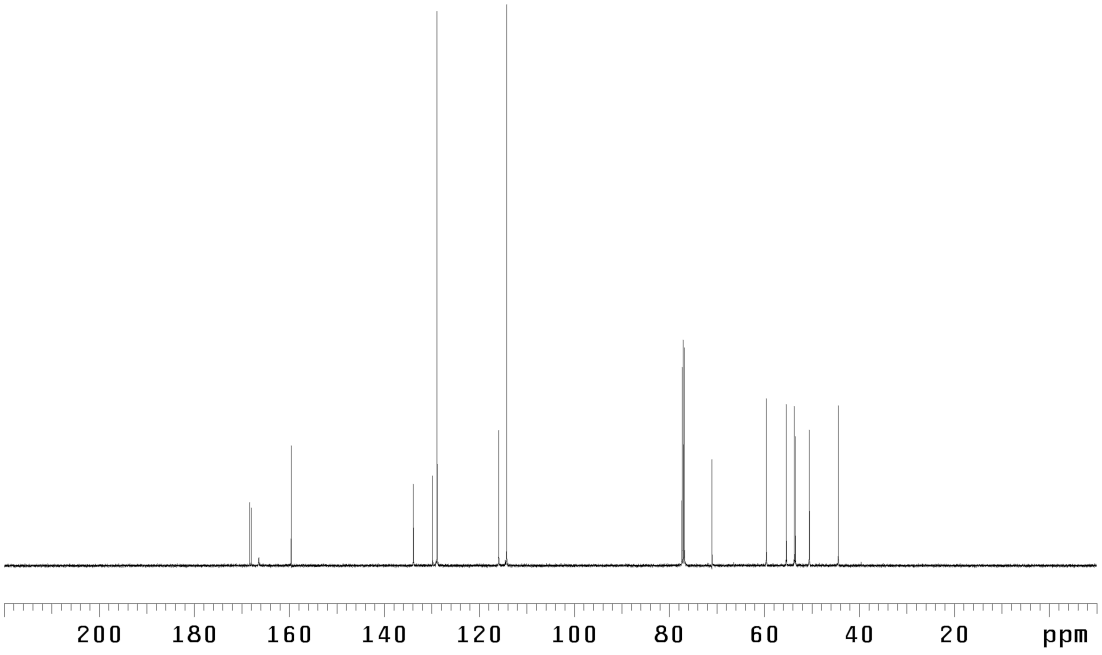


Figure A12.12. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **434**.

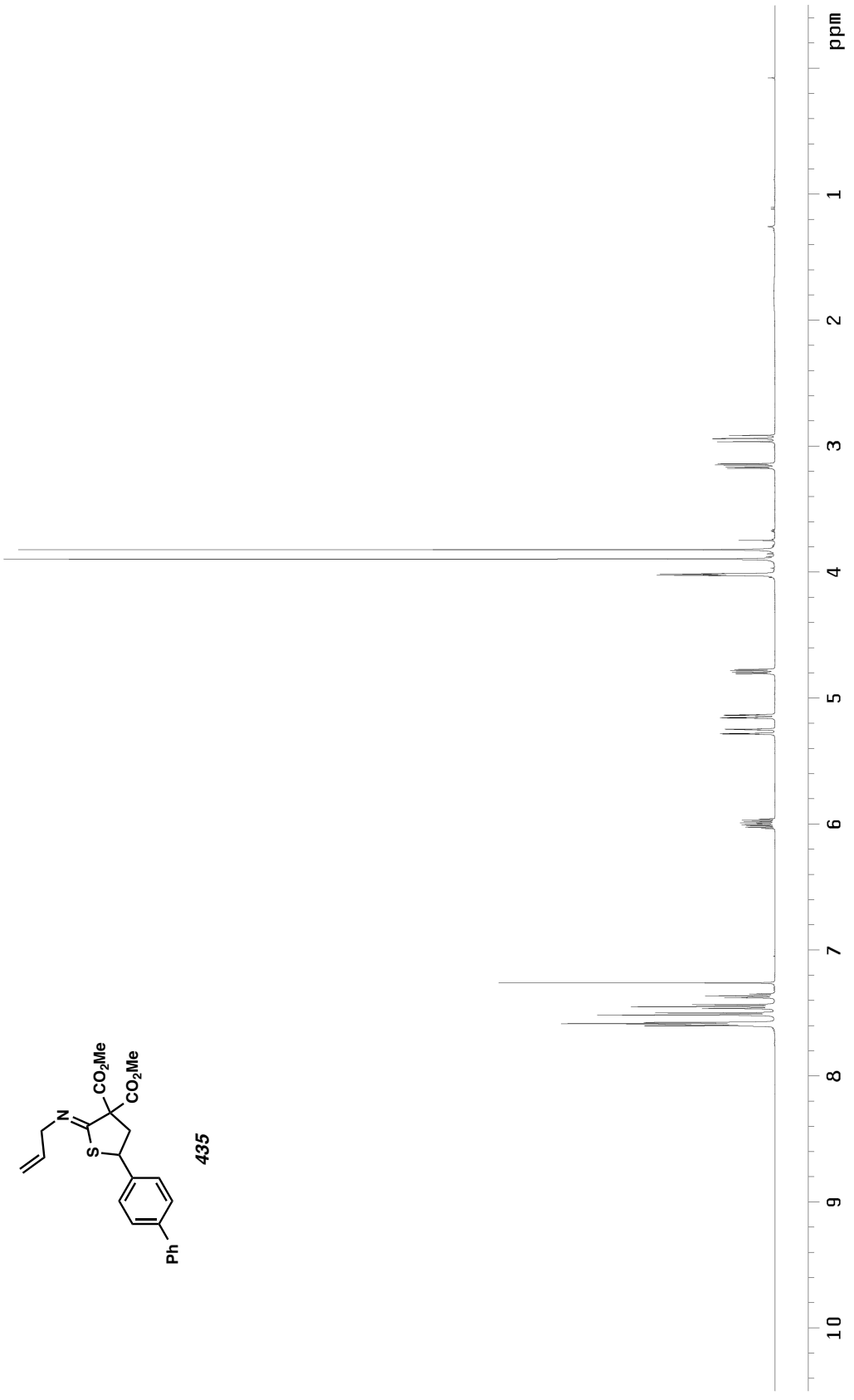


Figure A12.13. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **435**.

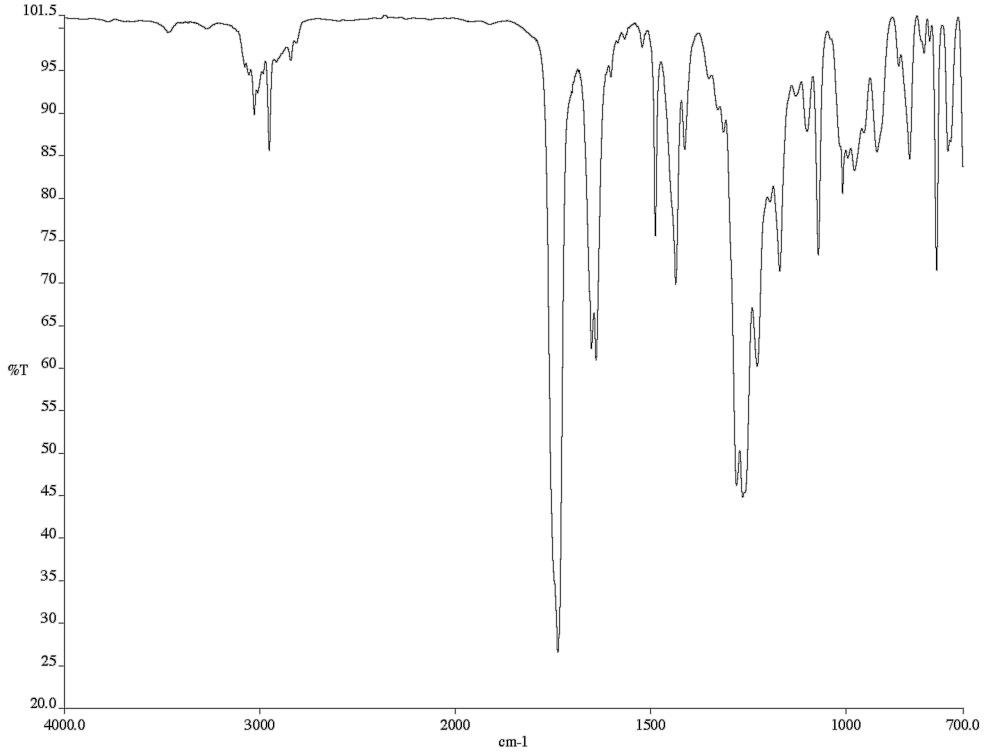


Figure A12.14. Infrared spectrum (thin film/NaCl) of compound **435**.

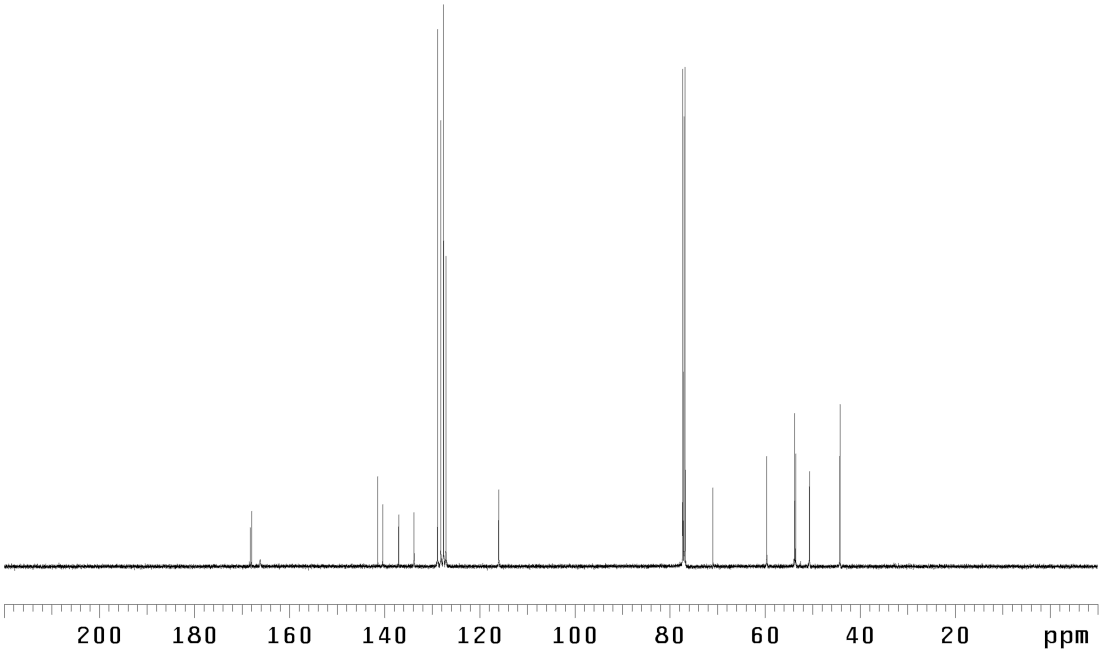


Figure A12.15. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **435**.

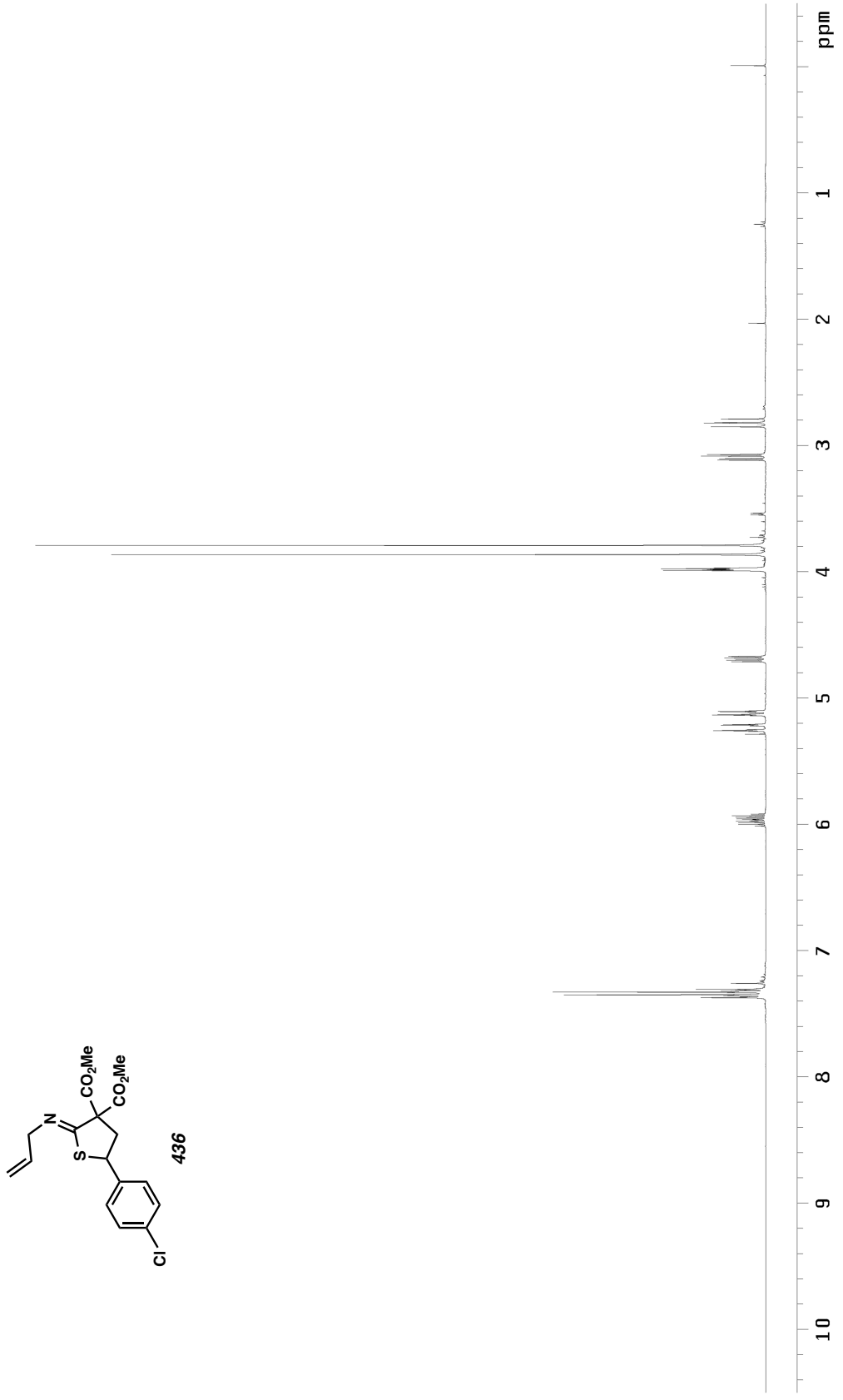


Figure A12.16. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **436**.

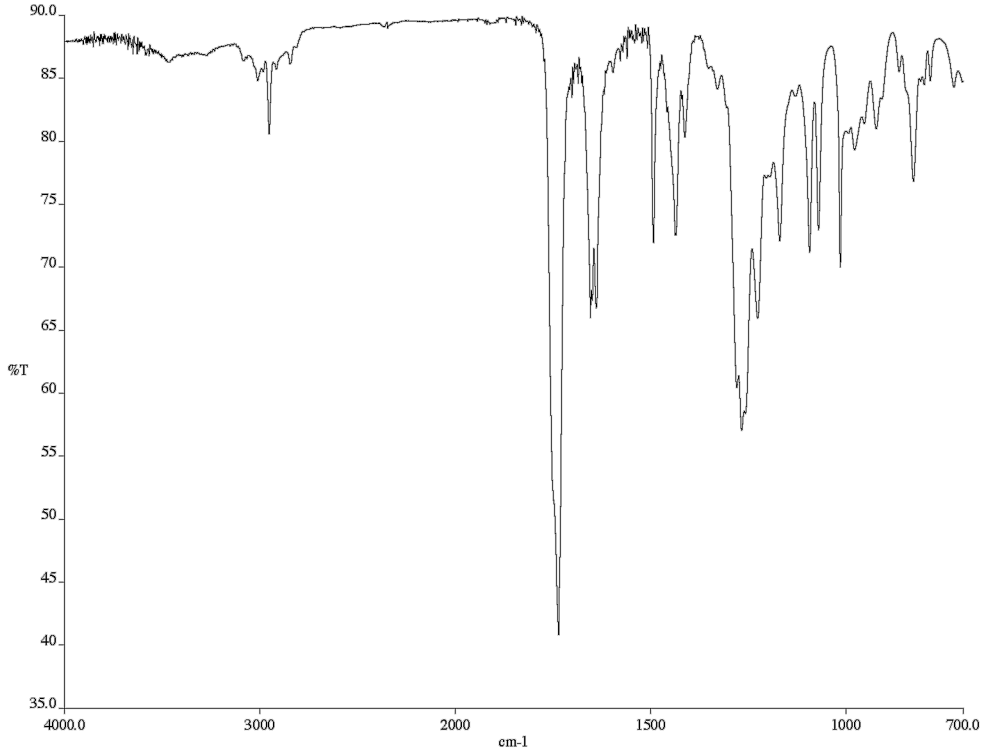


Figure A12.17. Infrared spectrum (thin film/NaCl) of compound **436**.

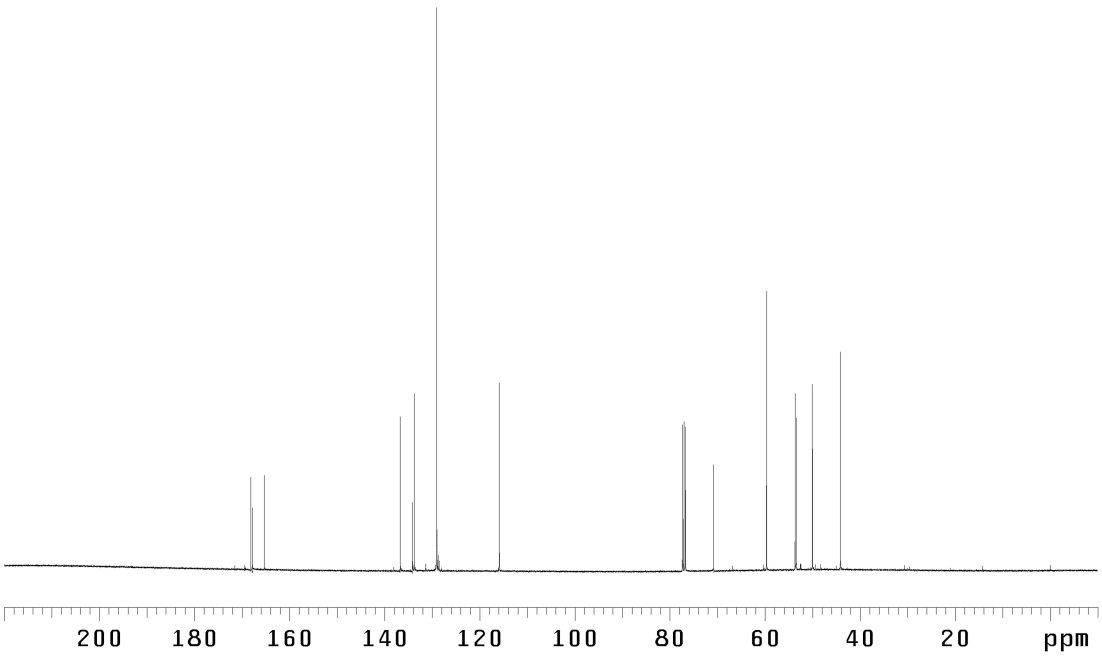


Figure A12.18. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **436**.

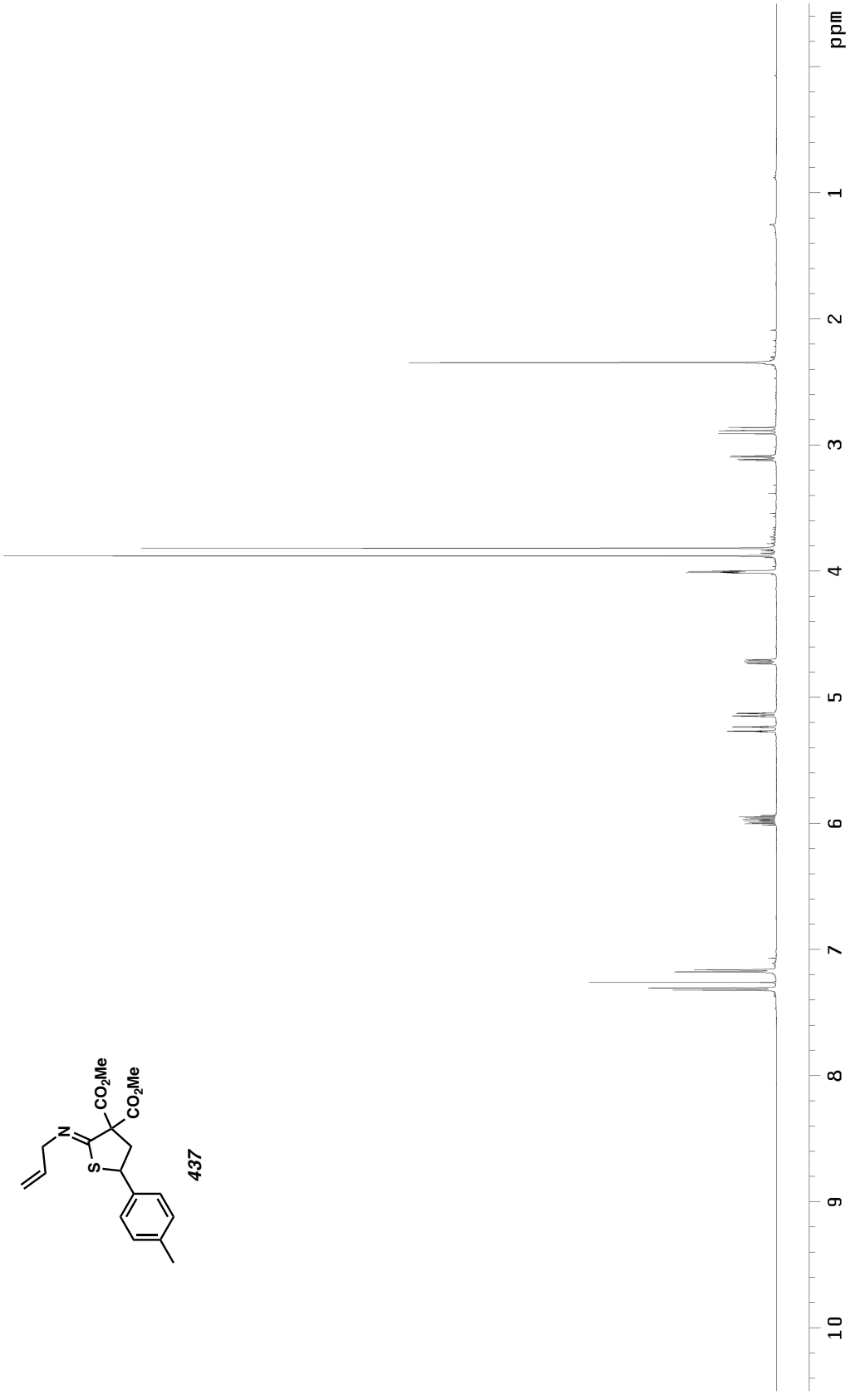


Figure A12.19. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **437**.

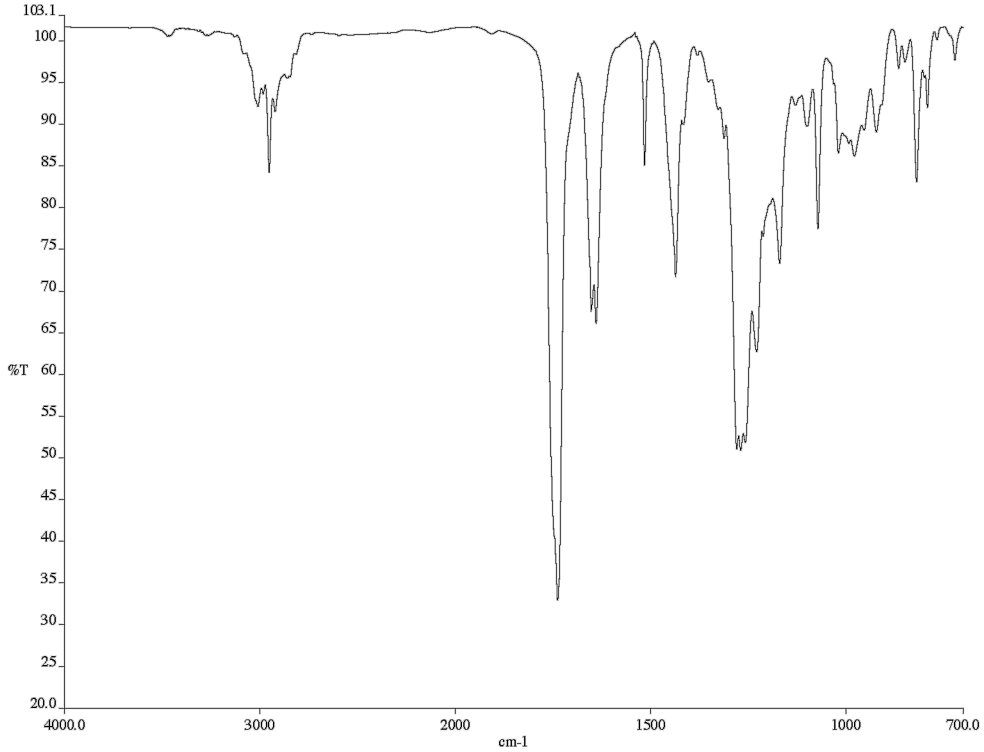


Figure A12.20. Infrared spectrum (thin film/NaCl) of compound **437**.

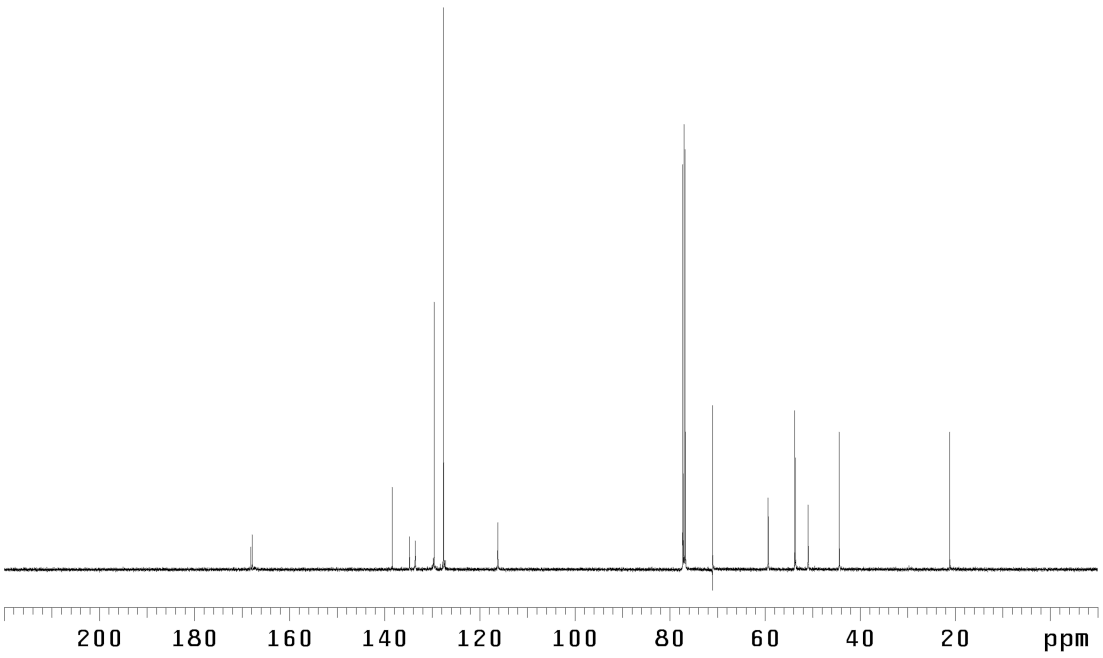


Figure A12.21. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **437**.

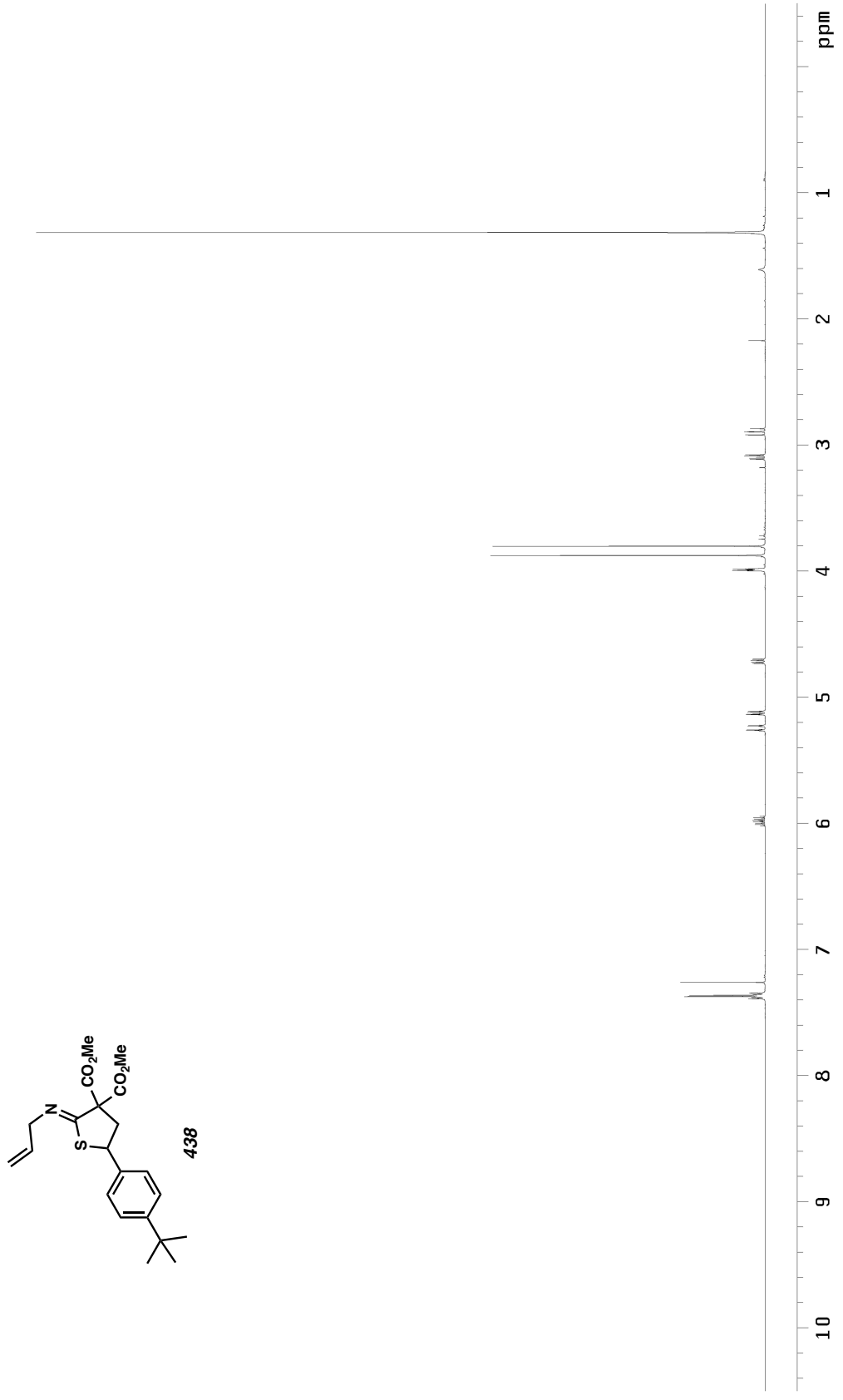


Figure A12.22. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **438**.

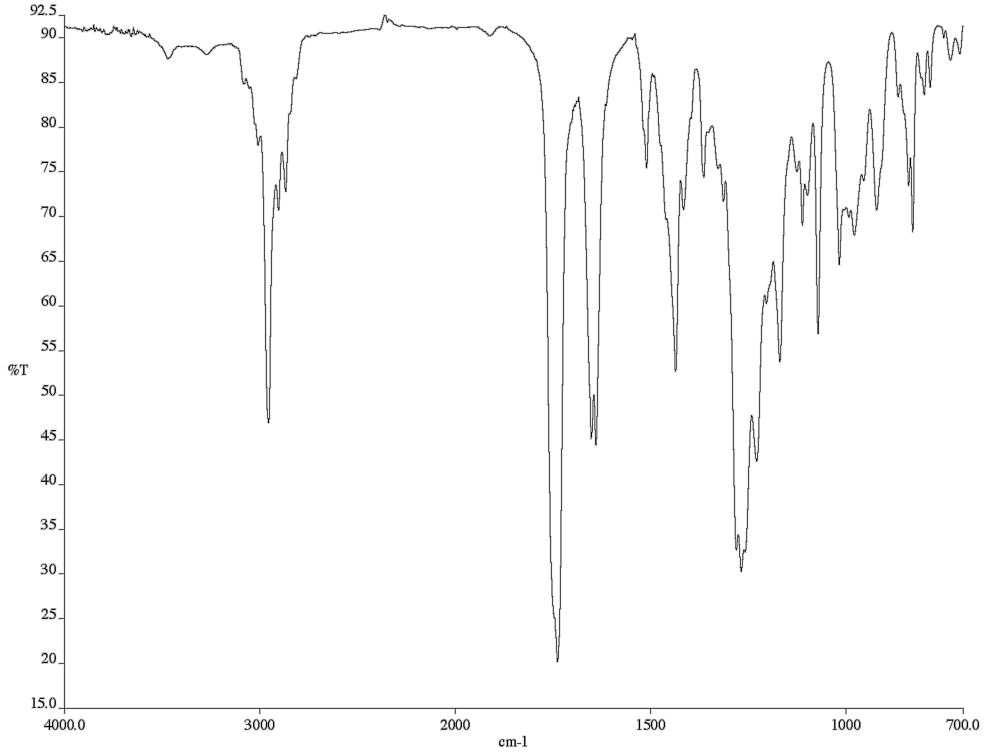


Figure A12.23. Infrared spectrum (thin film/NaCl) of compound **438**.

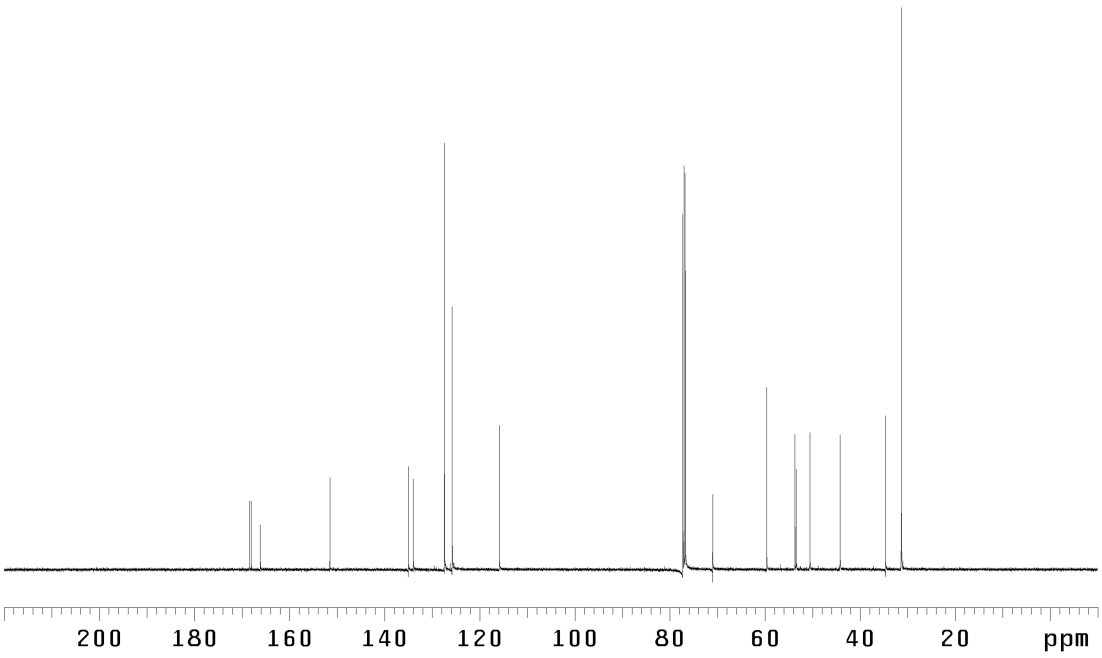


Figure A12.24. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **438**.

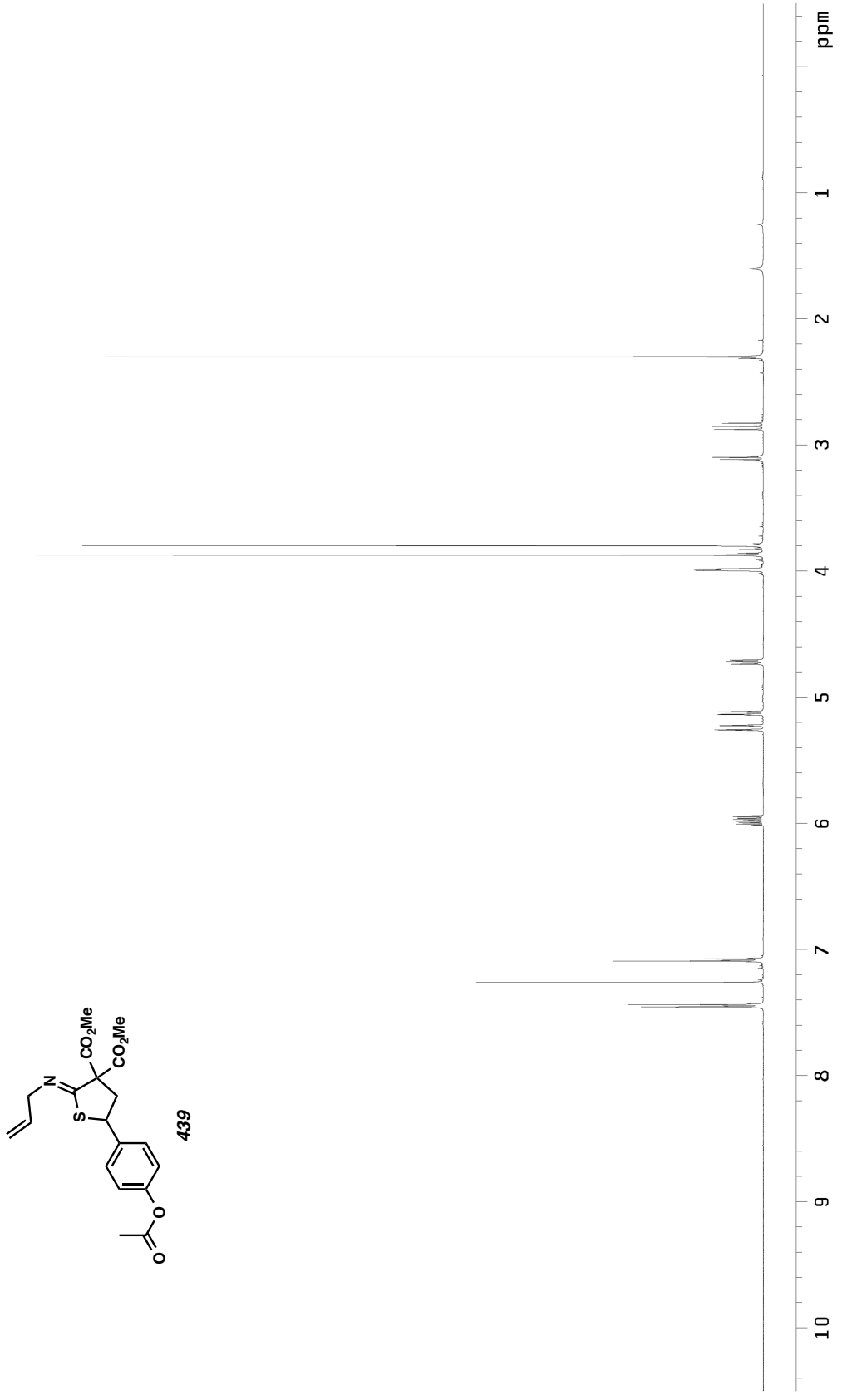


Figure A12.25. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **439**.

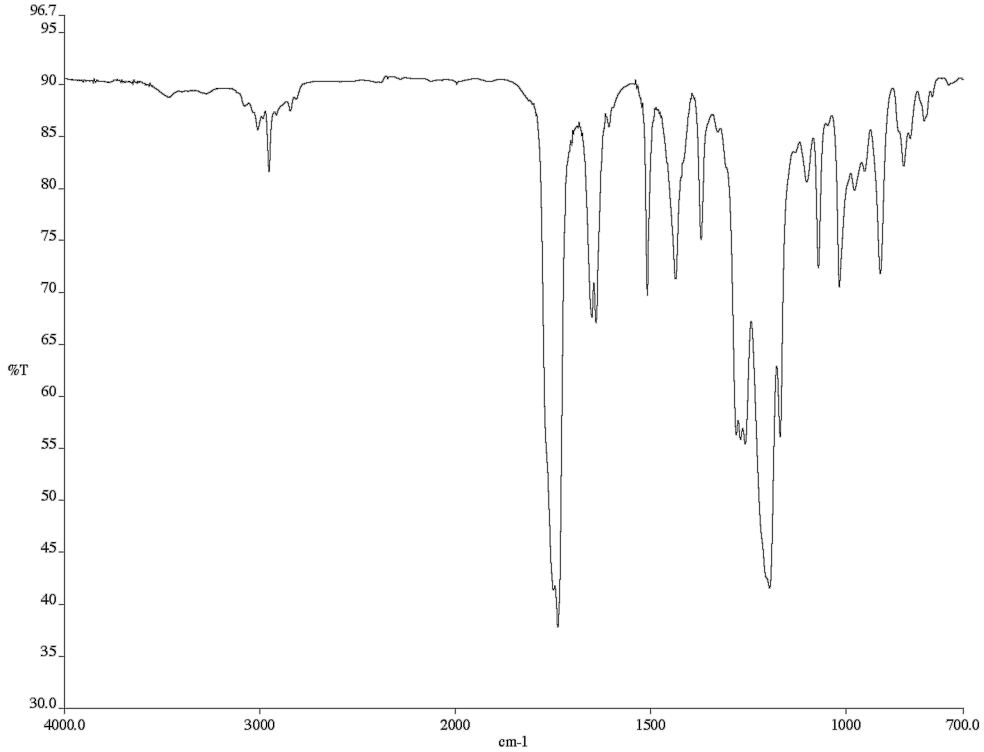


Figure A12.26. Infrared spectrum (thin film/NaCl) of compound **439**.

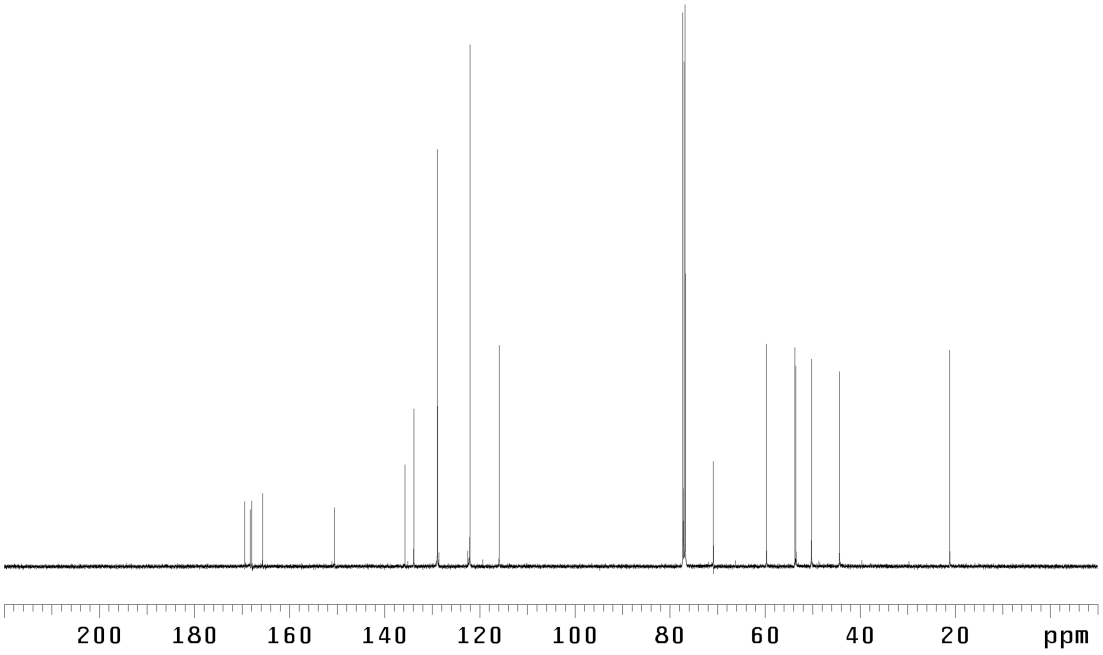


Figure A12.27. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **439**.

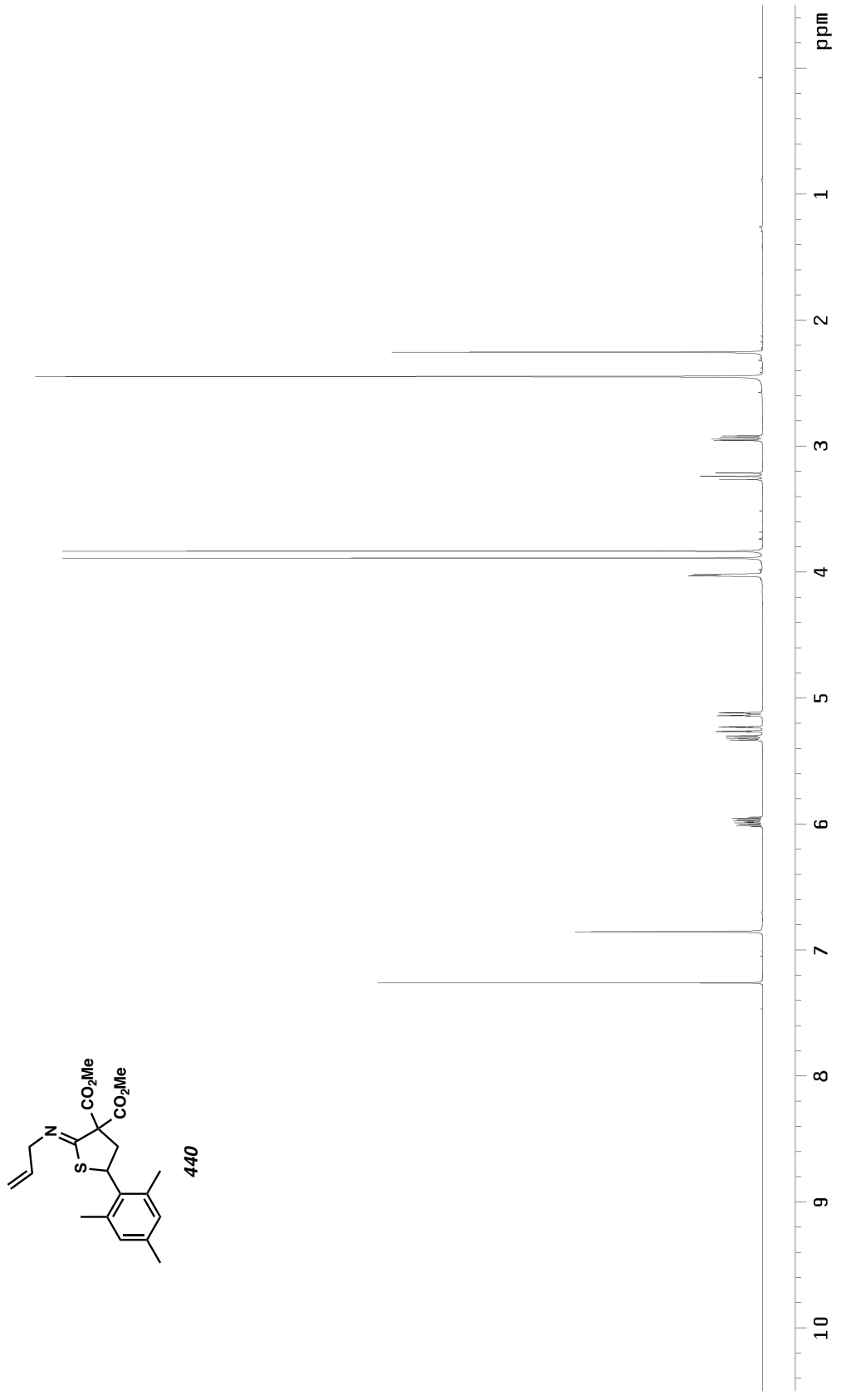


Figure A12.28. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **440**.

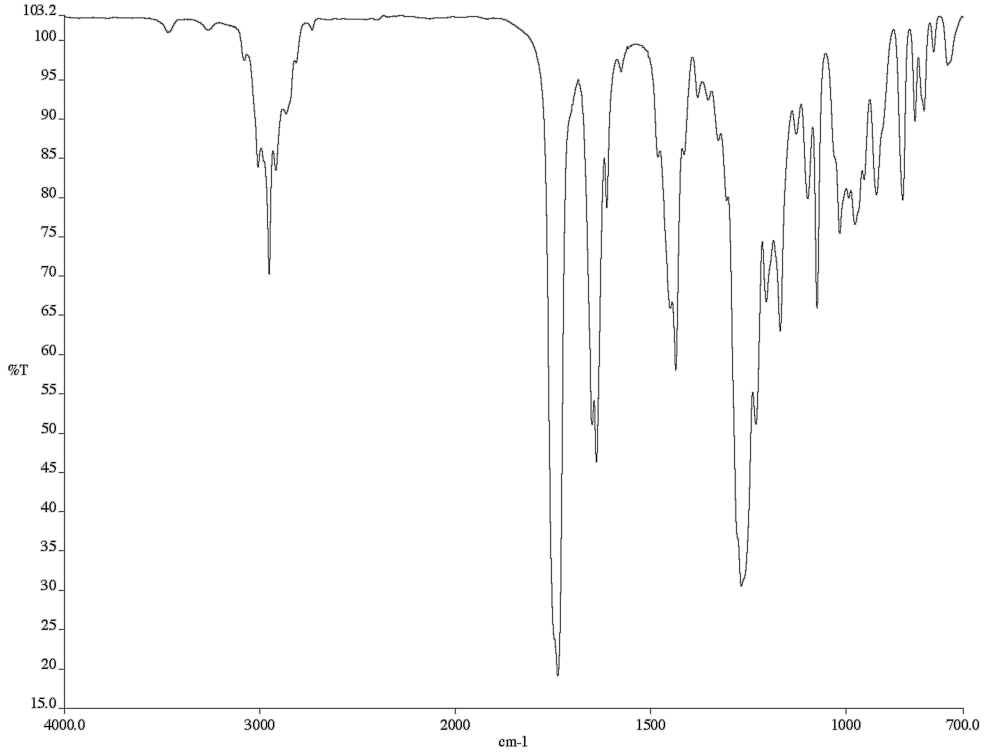


Figure A12.29. Infrared spectrum (thin film/NaCl) of compound **440**.

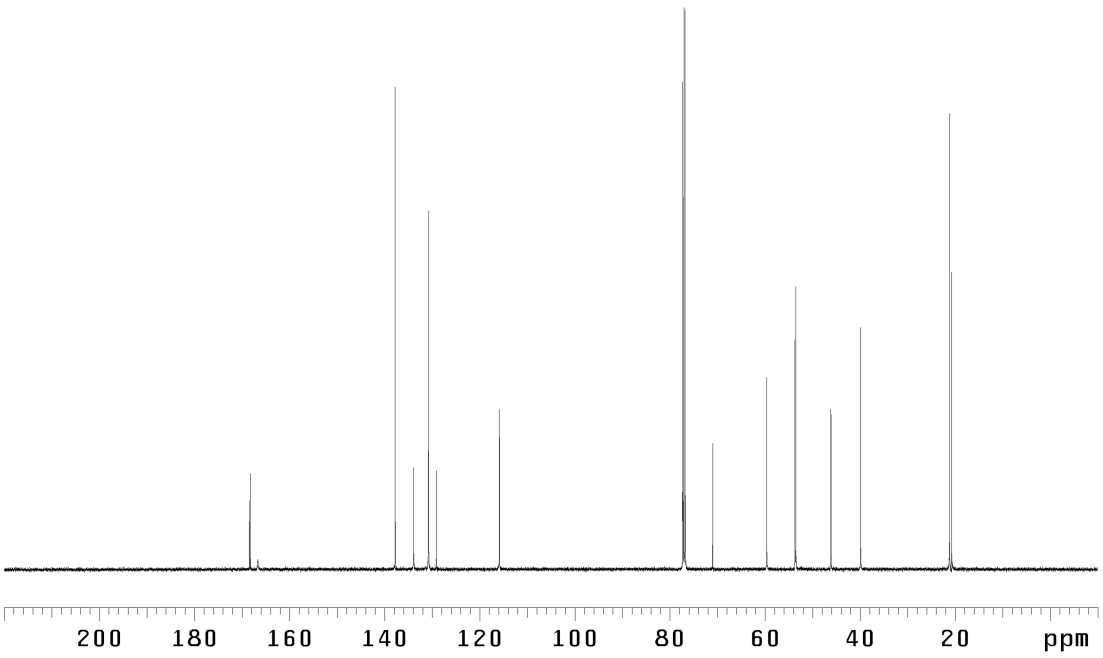


Figure A12.30. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **440**.

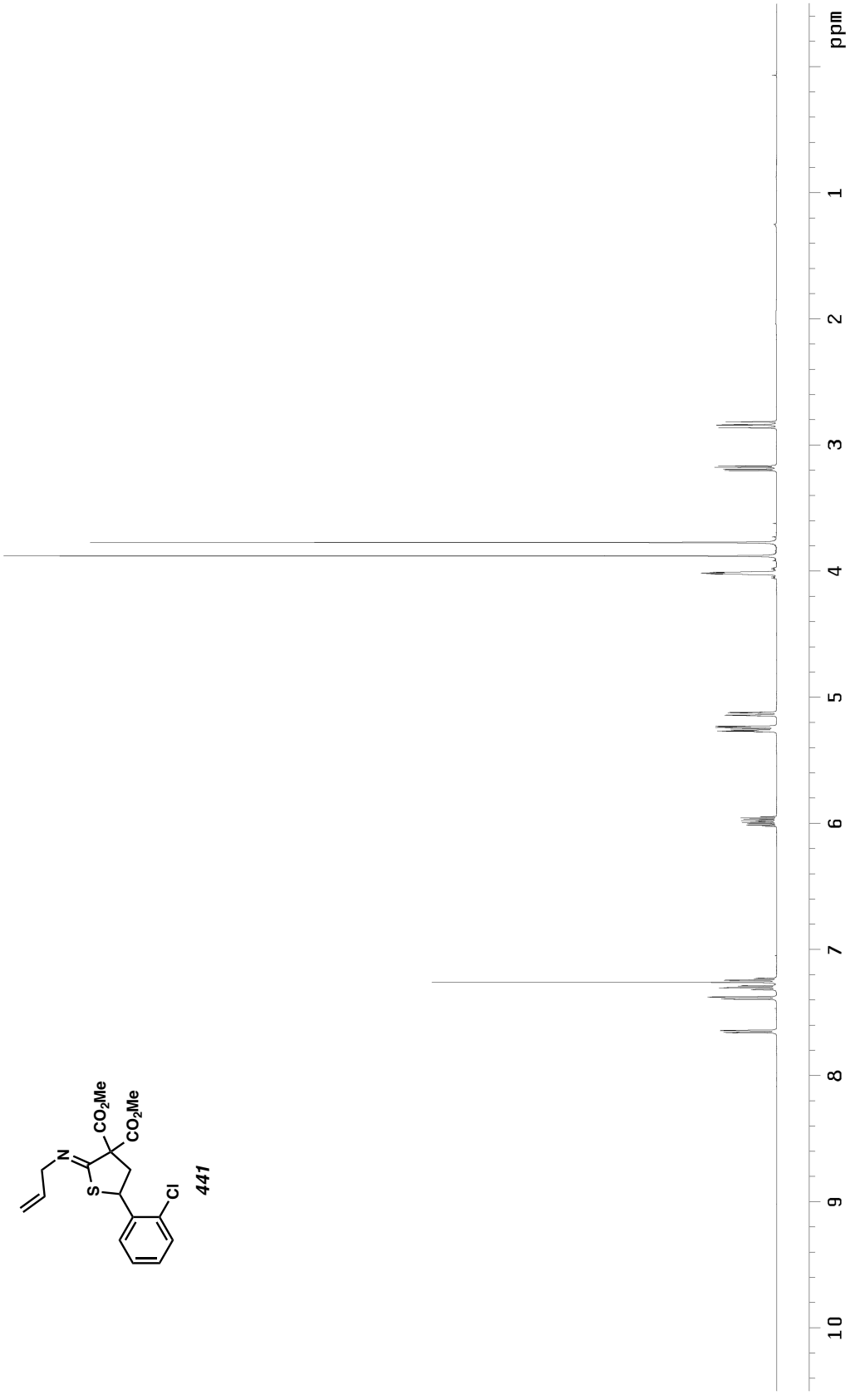


Figure A12.31. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **441**.

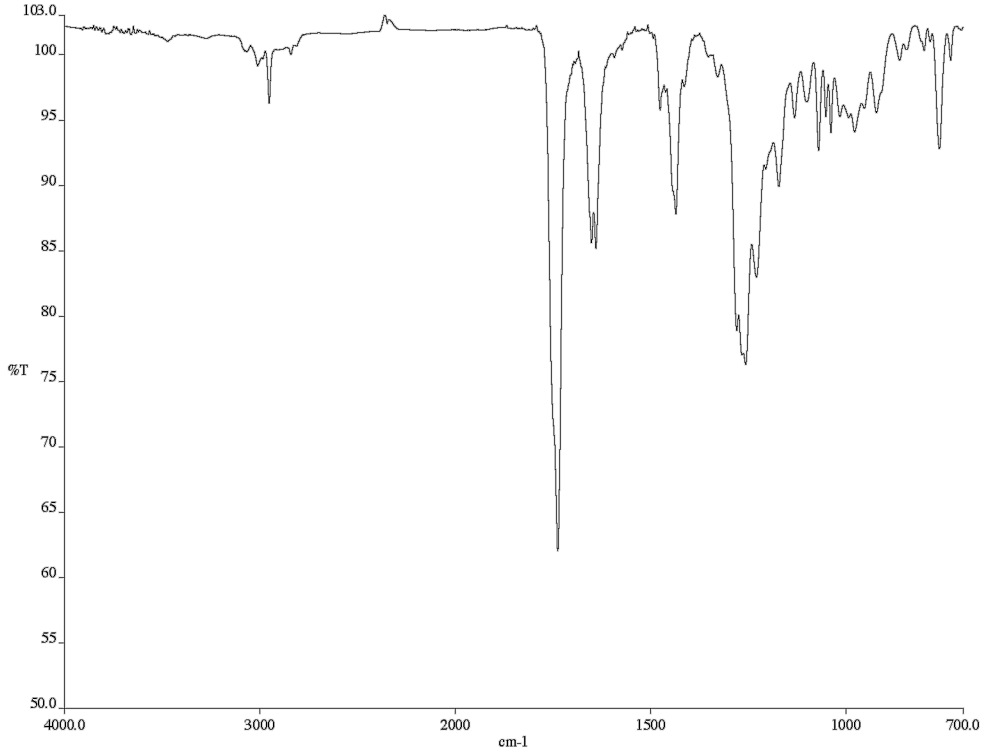


Figure A12.32. Infrared spectrum (thin film/NaCl) of compound **441**.

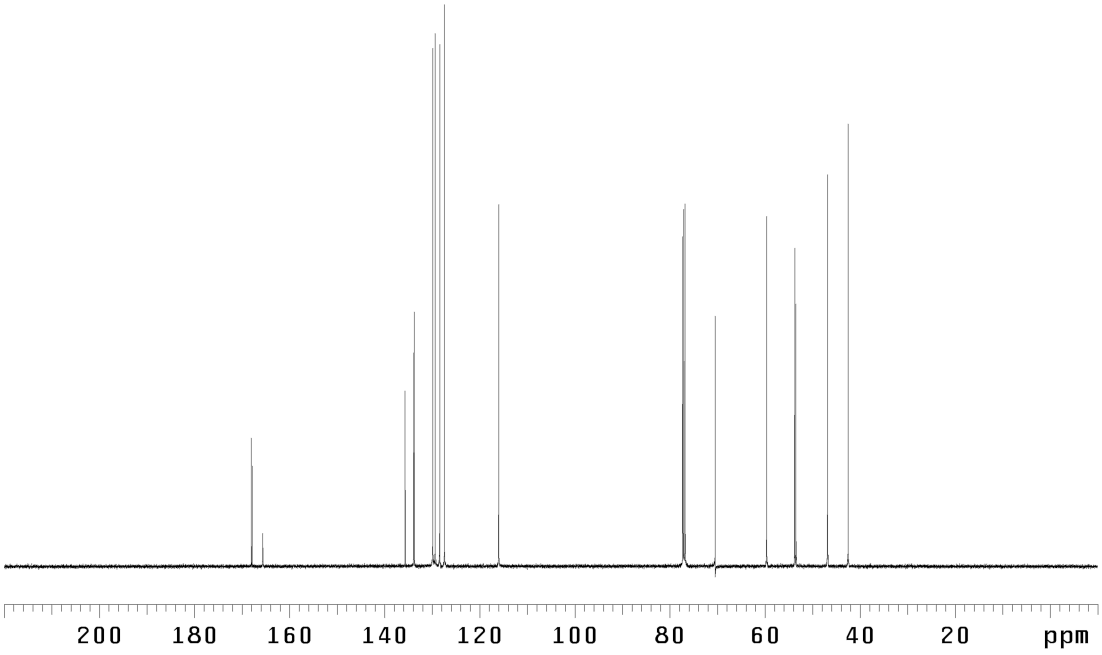


Figure A12.33. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **441**.

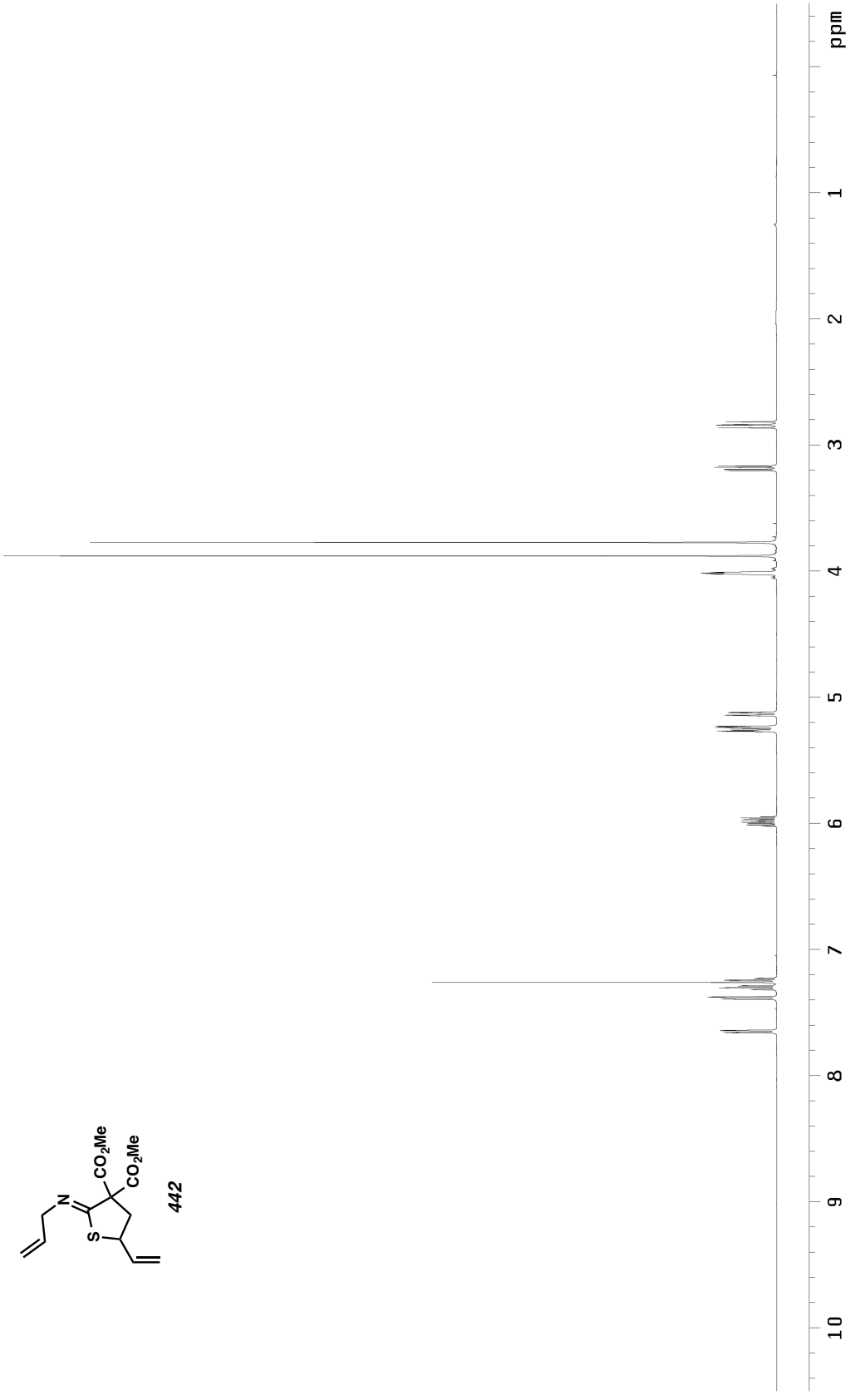


Figure A12.34. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **442**.

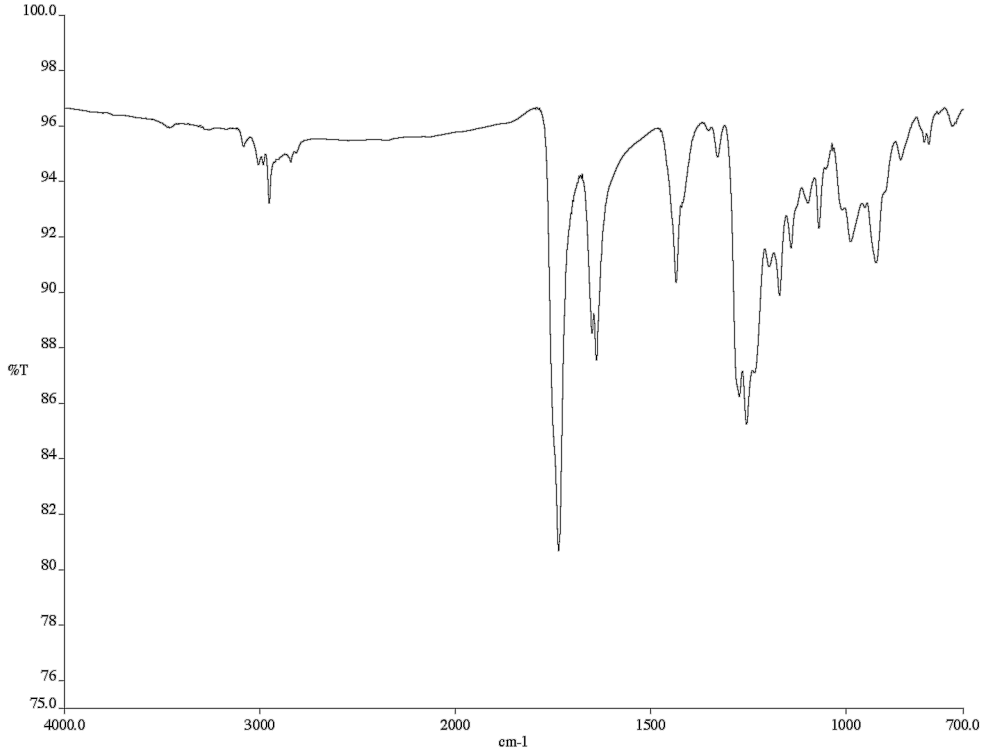


Figure A12.35. Infrared spectrum (thin film/NaCl) of compound **442**.

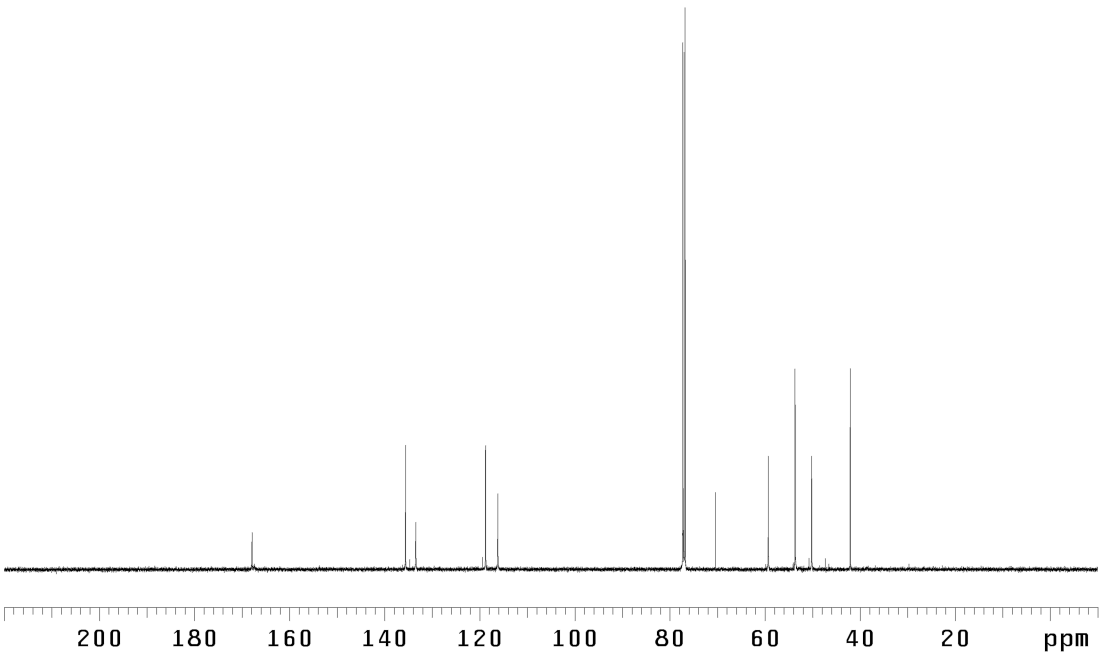


Figure A12.36. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **442**.

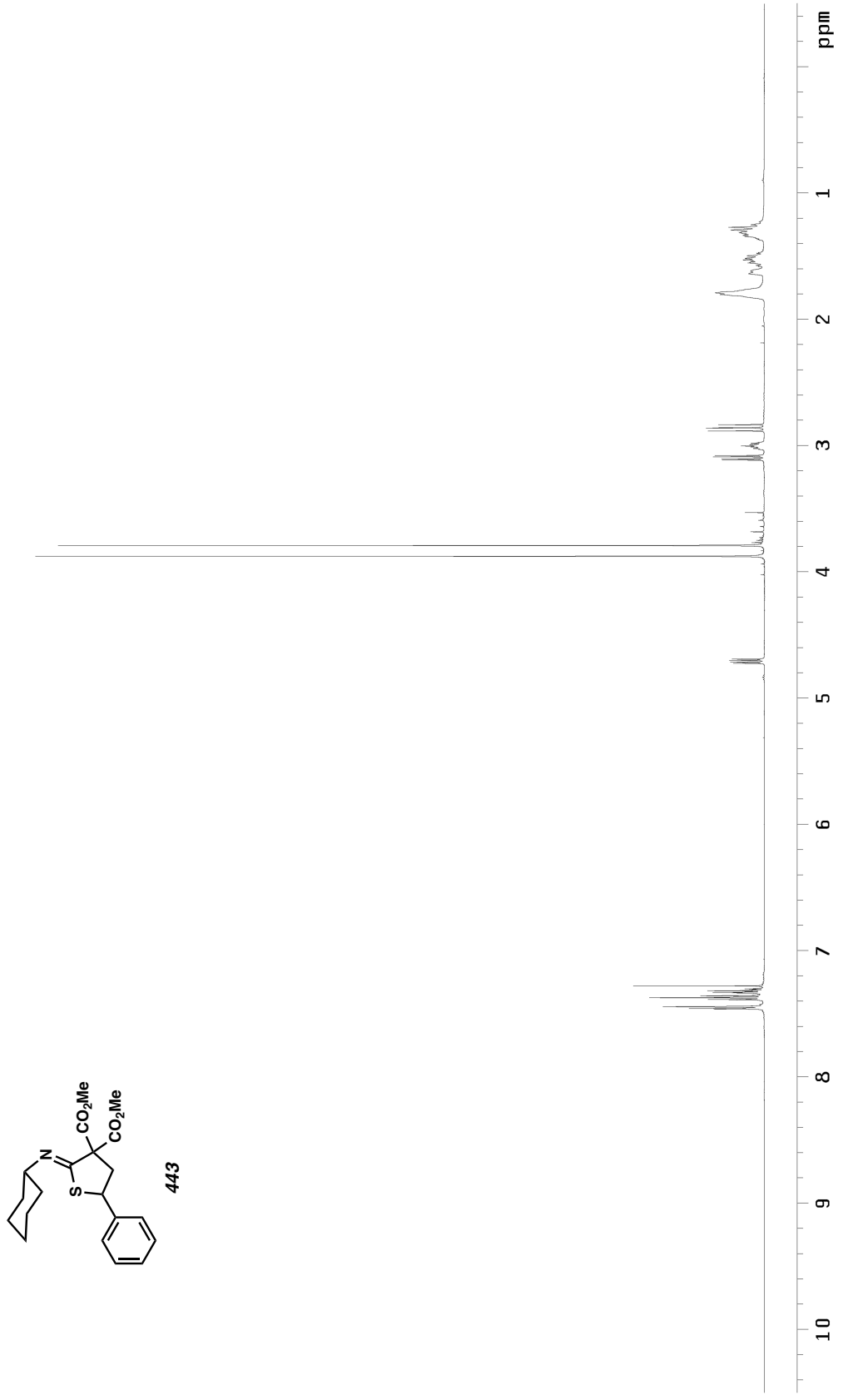


Figure A12.37. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **443**.

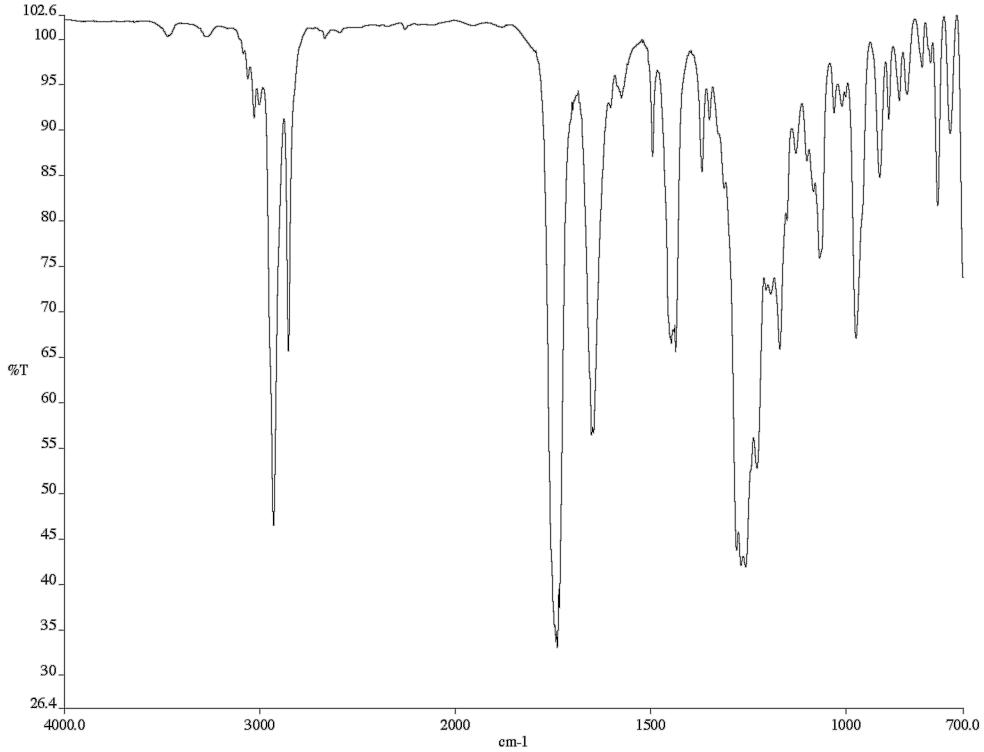


Figure A12.38. Infrared spectrum (thin film/NaCl) of compound **443**.

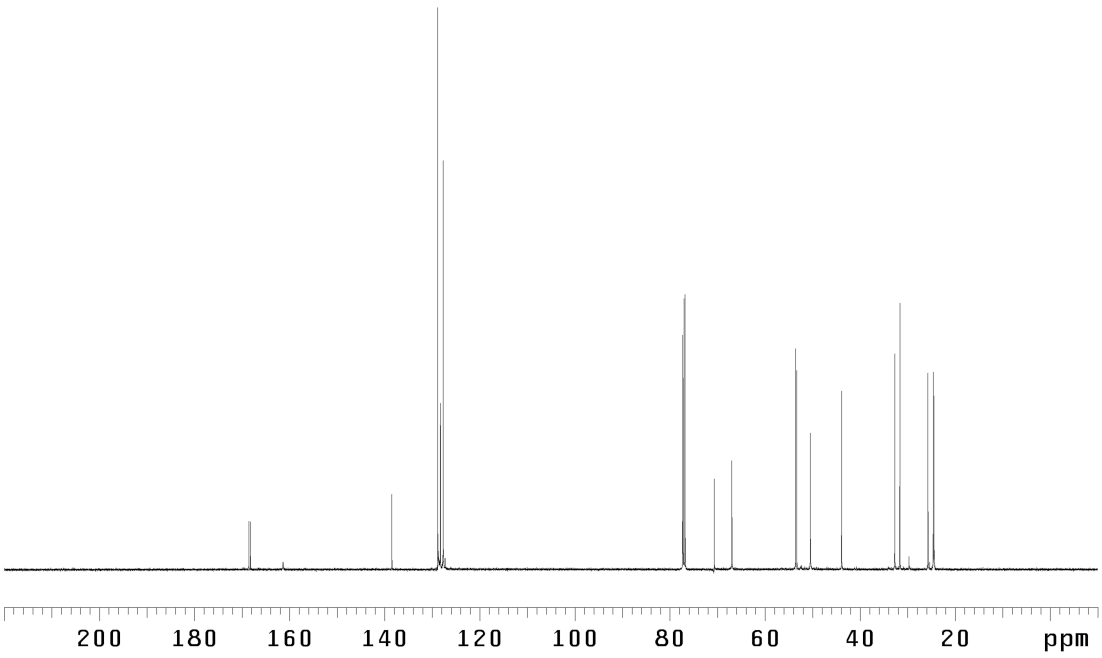


Figure A12.39. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **443**.

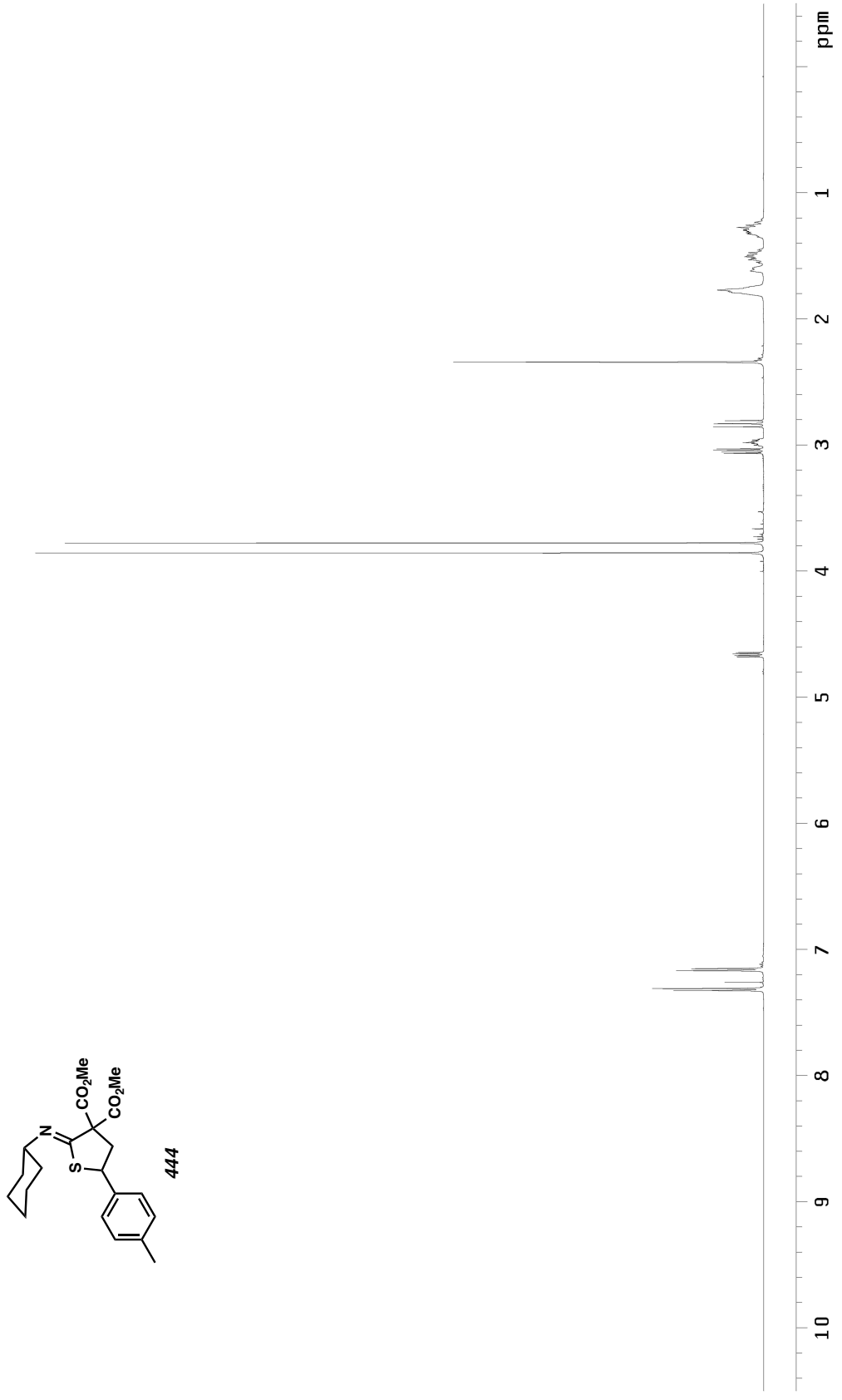


Figure A12.40. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **444**.

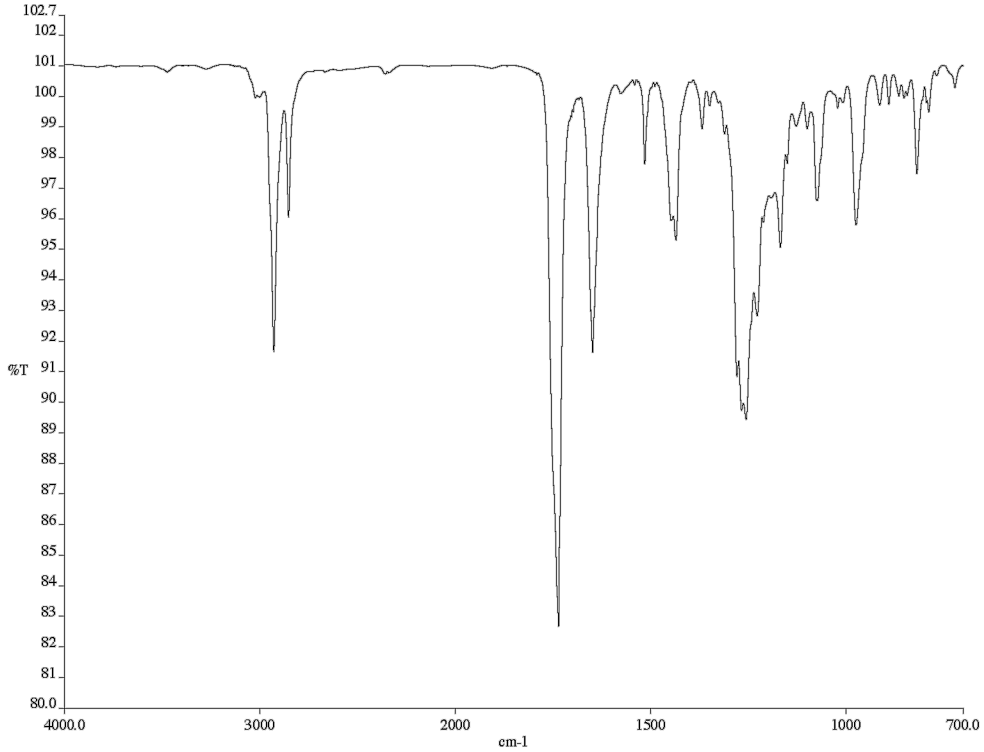


Figure A12.41. Infrared spectrum (thin film/NaCl) of compound **444**.

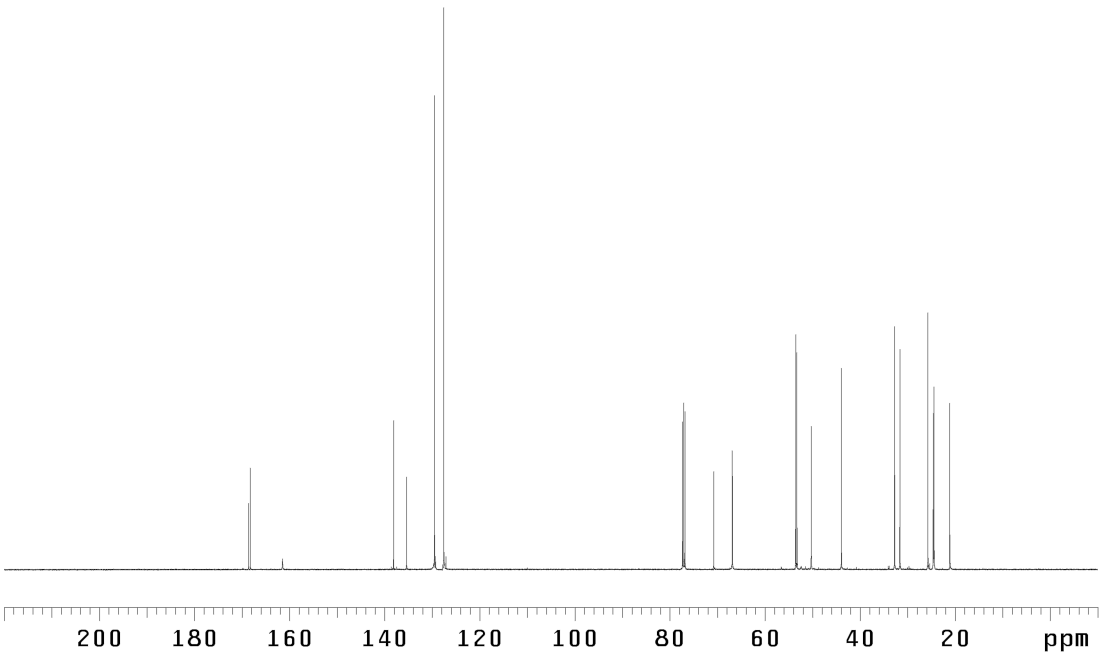


Figure A12.42. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **444**.

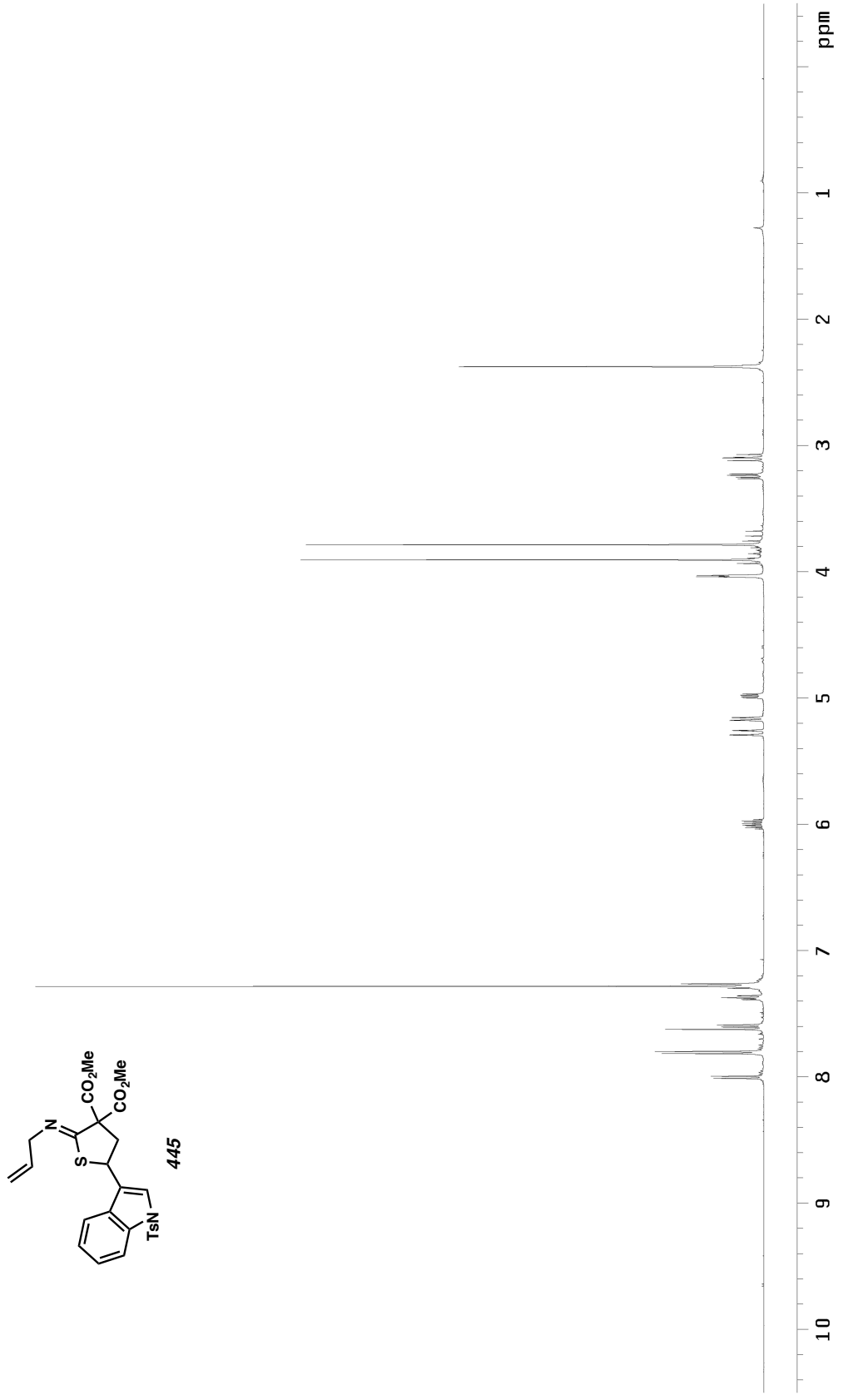


Figure A12.43. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **445**.

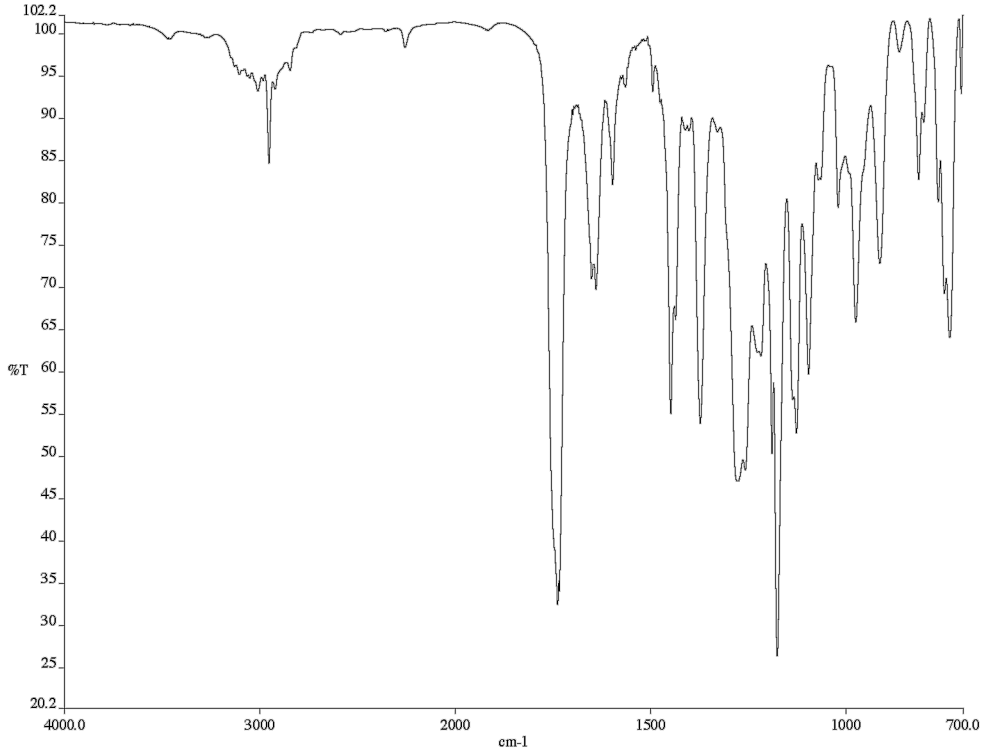


Figure A12.44. Infrared spectrum (thin film/NaCl) of compound **445**.

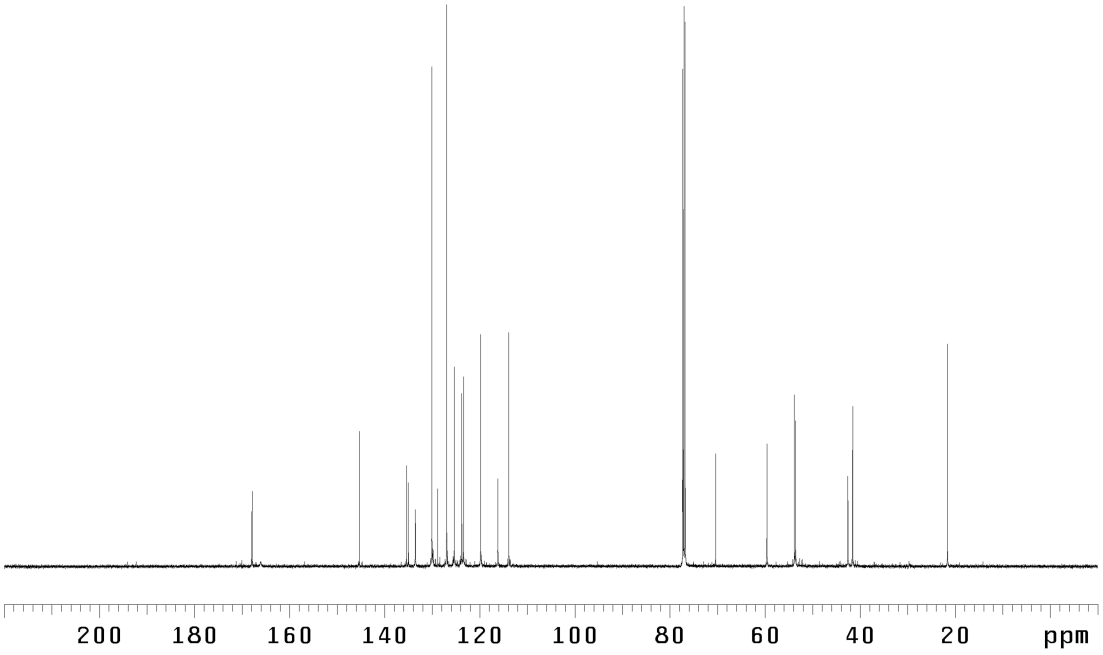


Figure A12.45. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **445**.

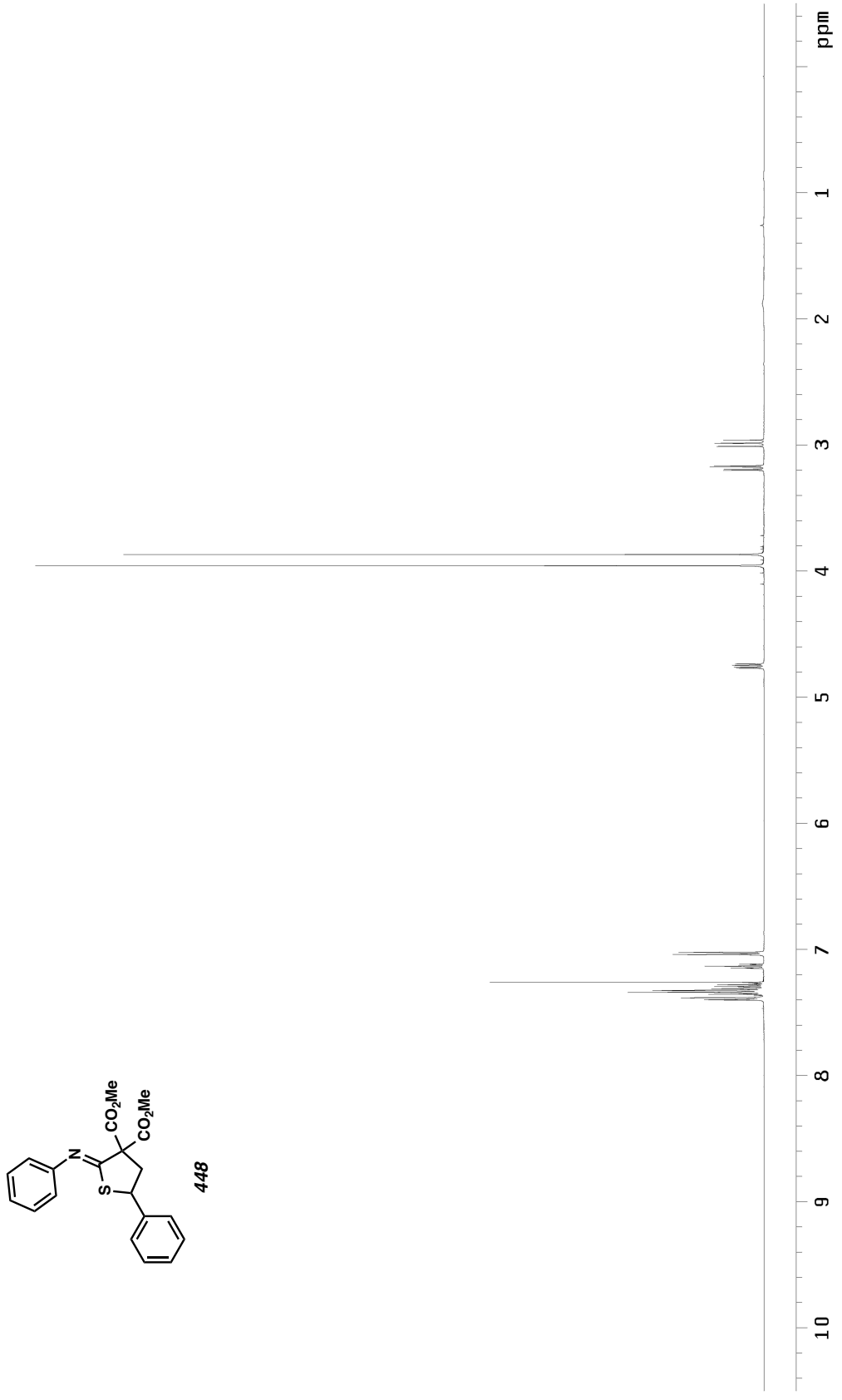


Figure A12.46. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **448**.

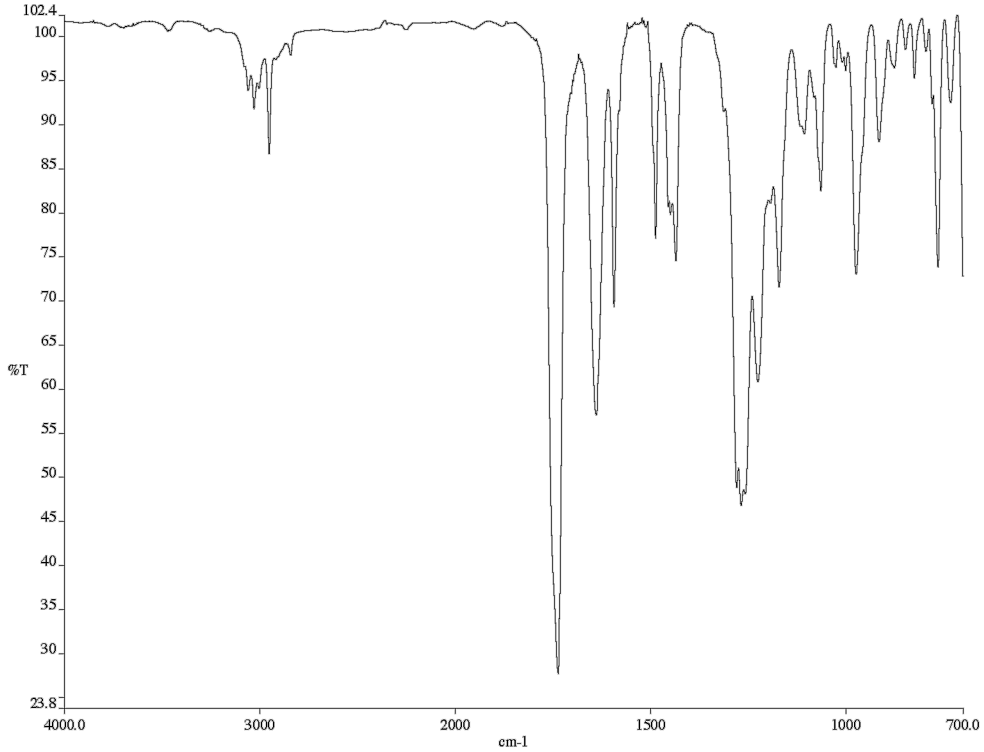


Figure A12.47. Infrared spectrum (thin film/NaCl) of compound **448**.

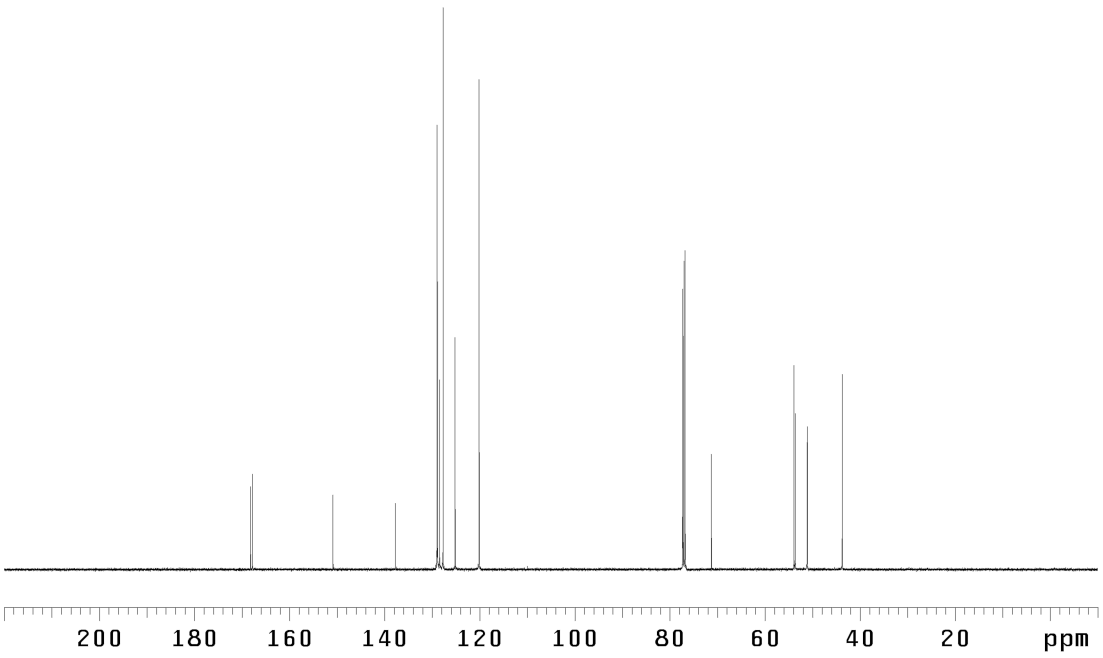


Figure A12.48. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **448**.

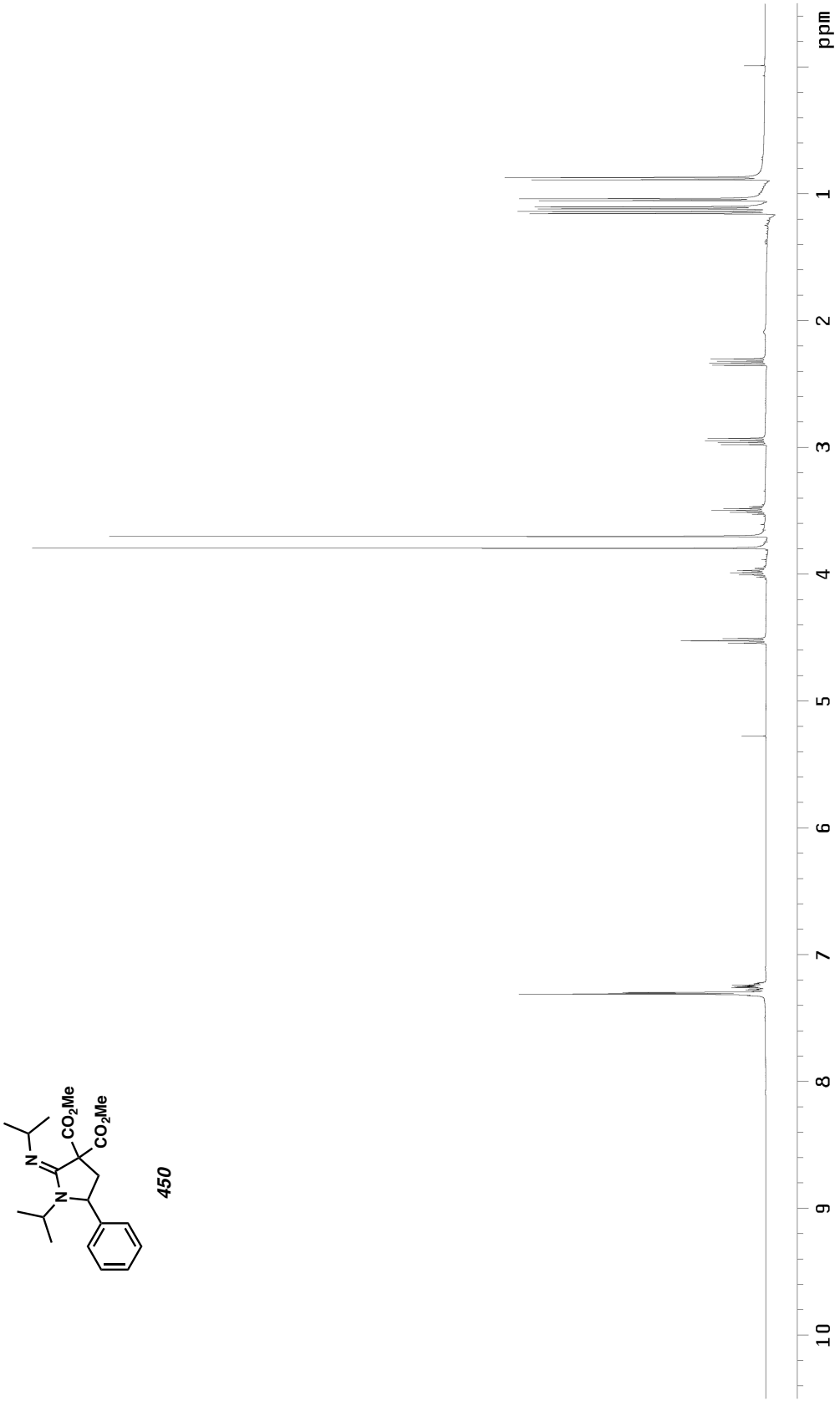


Figure A12.49. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **450**.

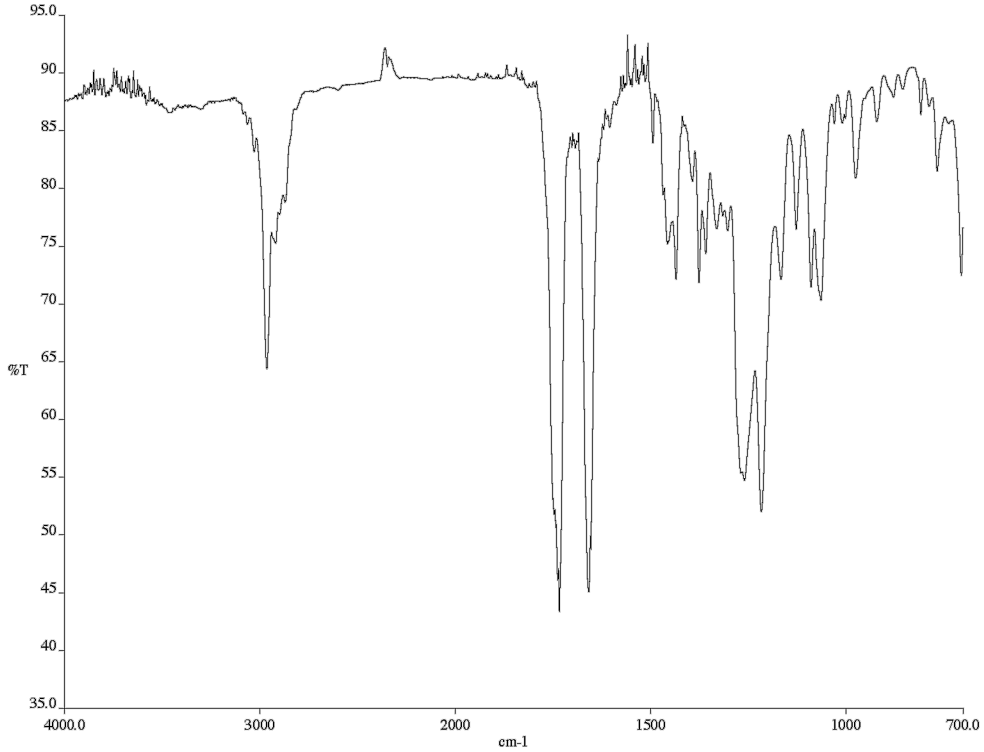


Figure A12.50. Infrared spectrum (thin film/NaCl) of compound **450**.

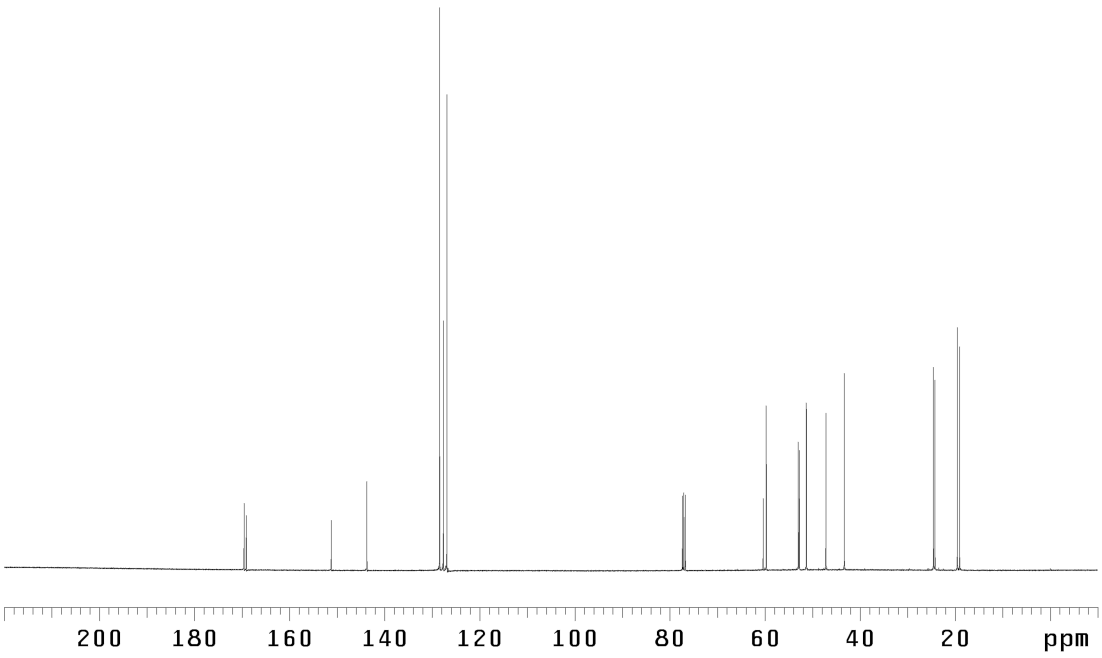
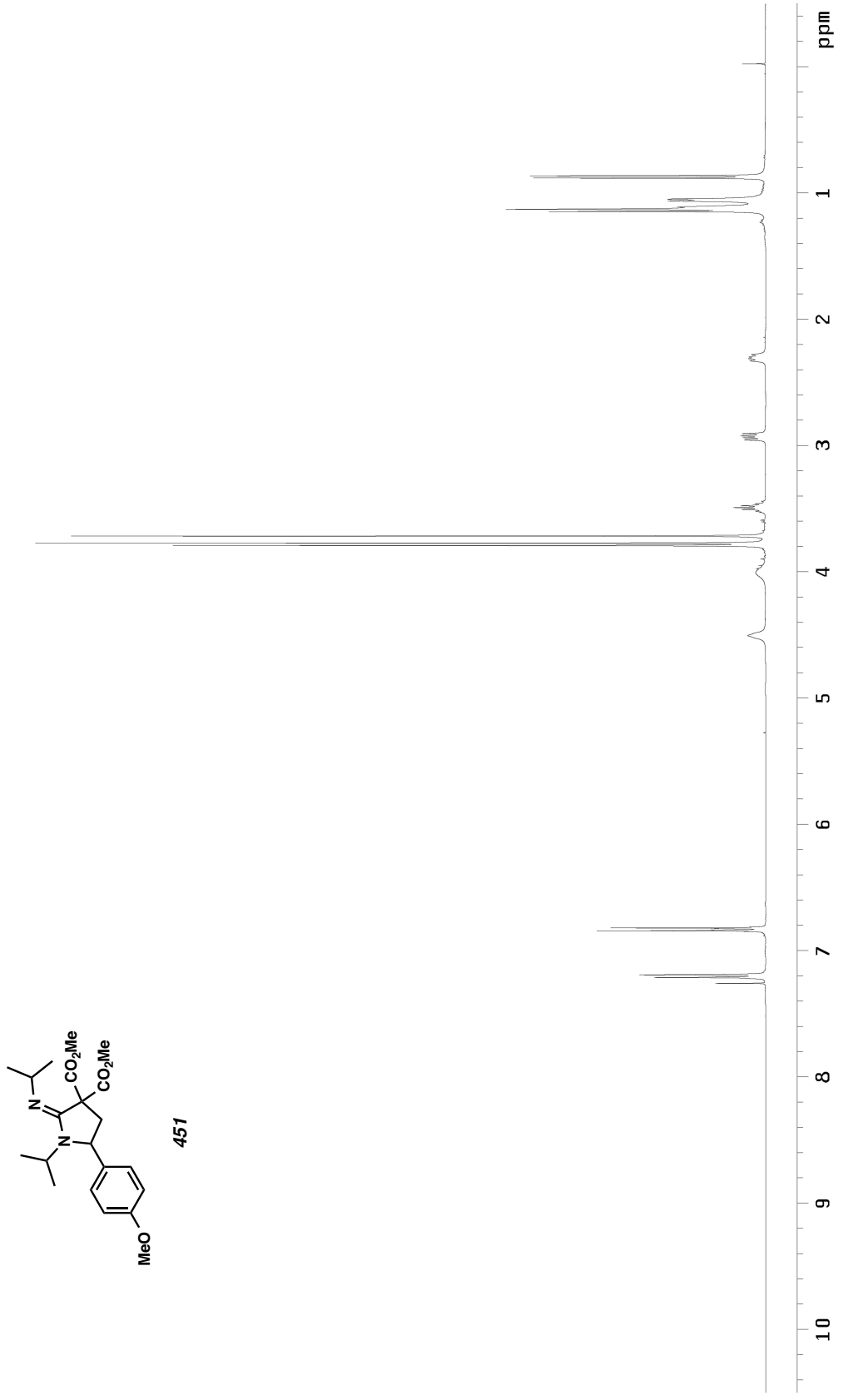


Figure A12.51. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **450**.



451

Figure A12.52. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **451**.

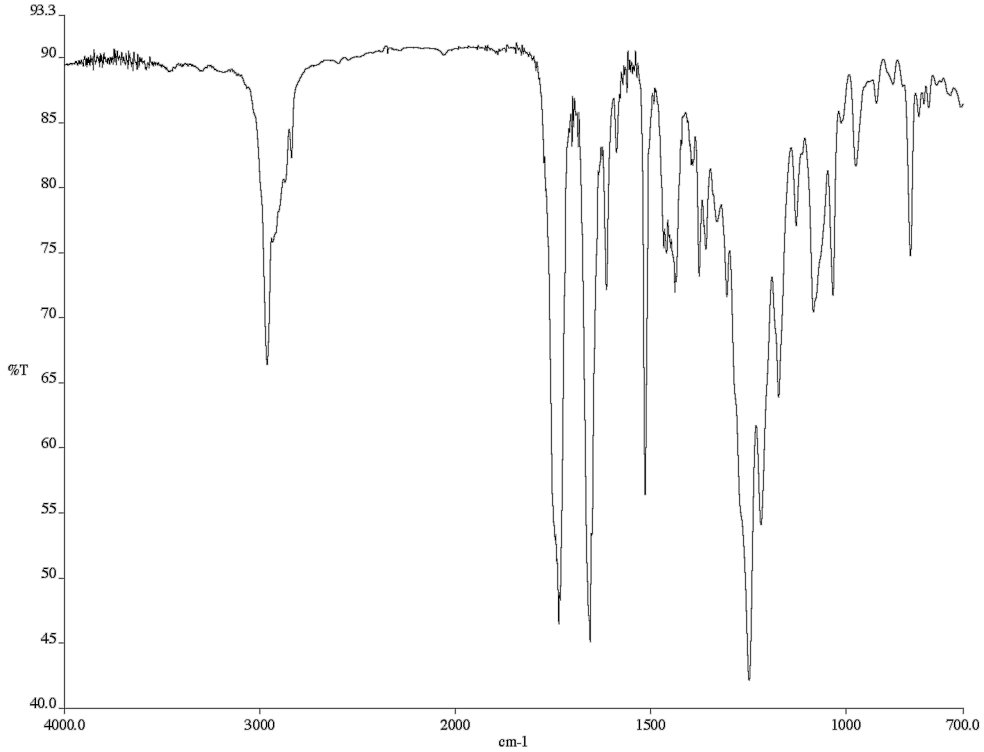


Figure A12.53. Infrared spectrum (thin film/NaCl) of compound **451**.

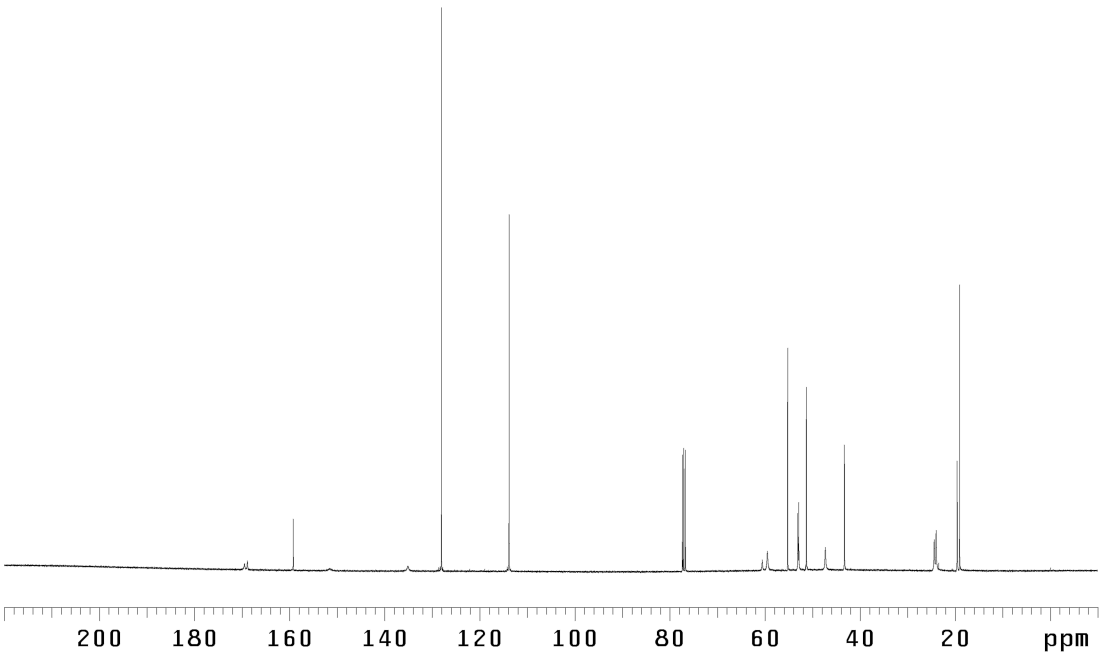


Figure A12.54. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **451**.

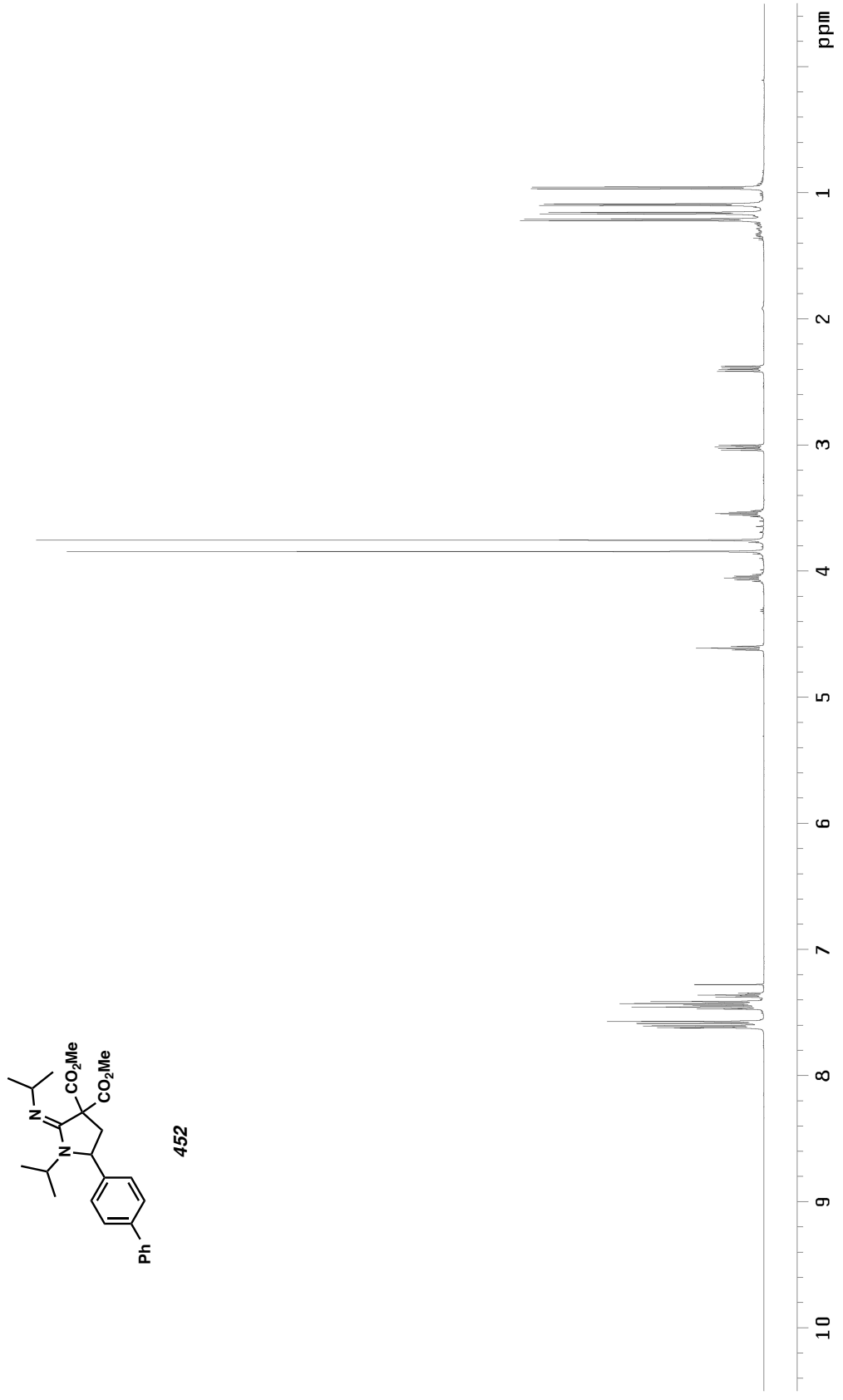


Figure A12.55. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **452**.

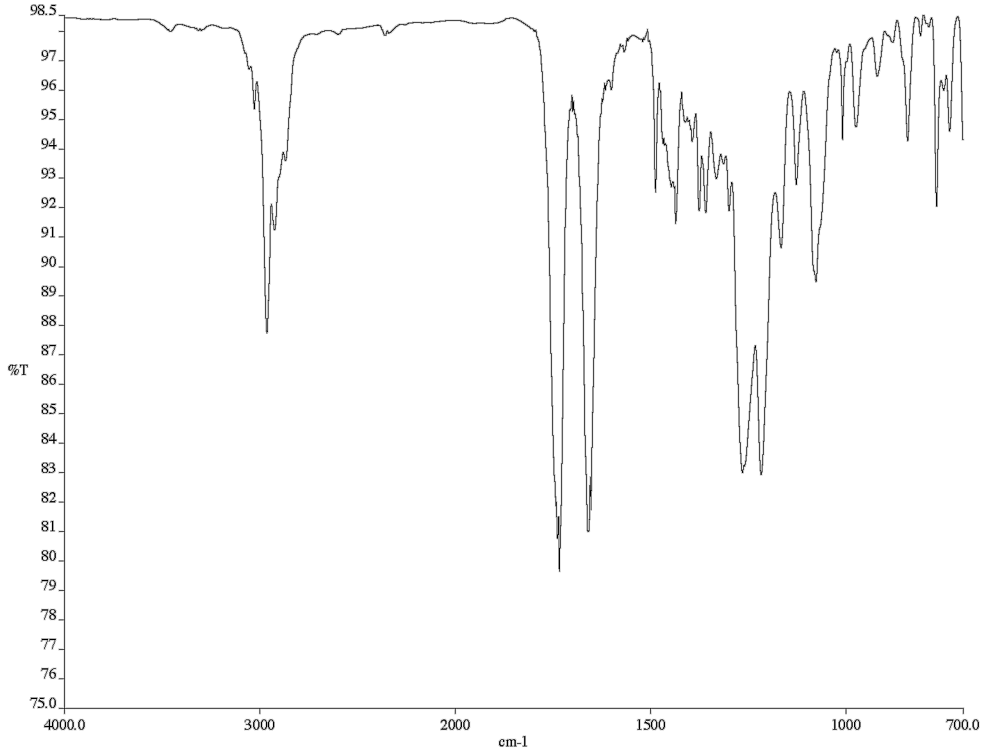


Figure A12.56. Infrared spectrum (thin film/NaCl) of compound **452**.

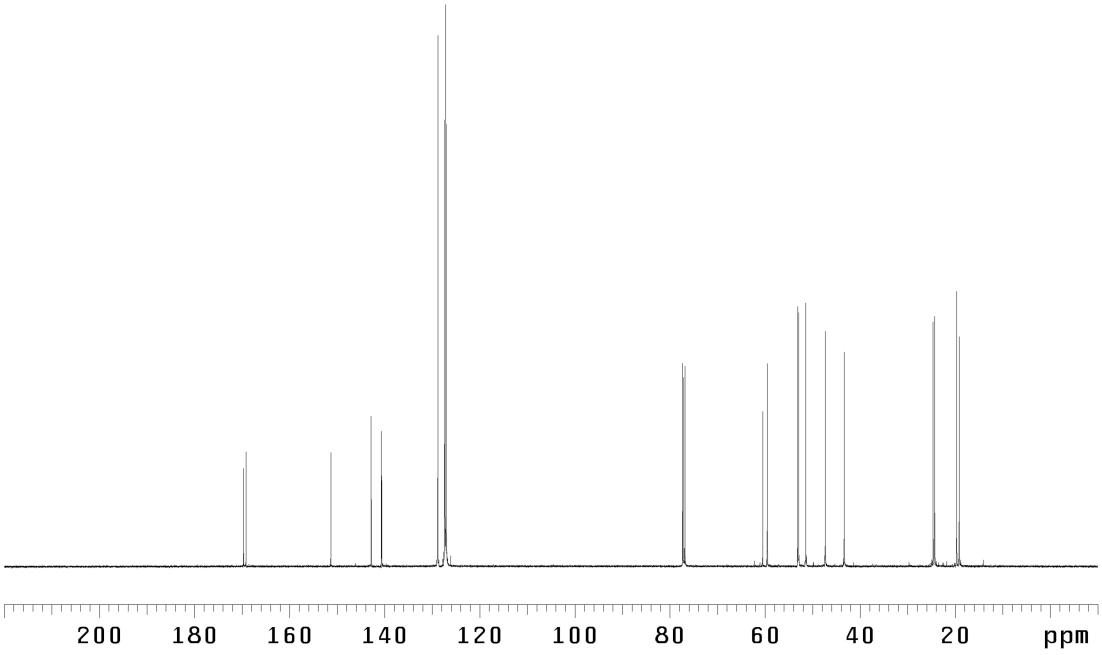


Figure A12.57. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **452**.

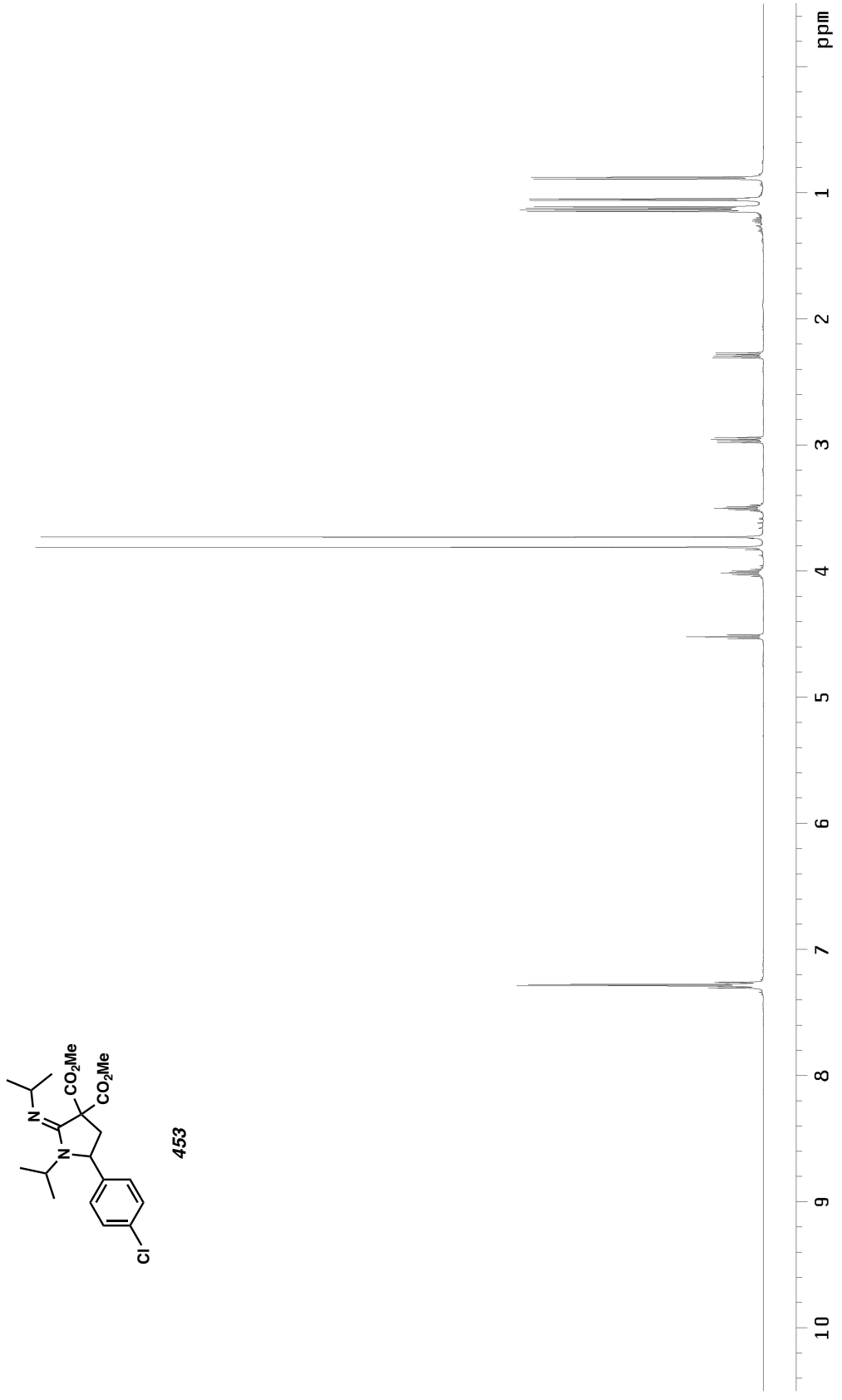


Figure A12.58. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **453**.

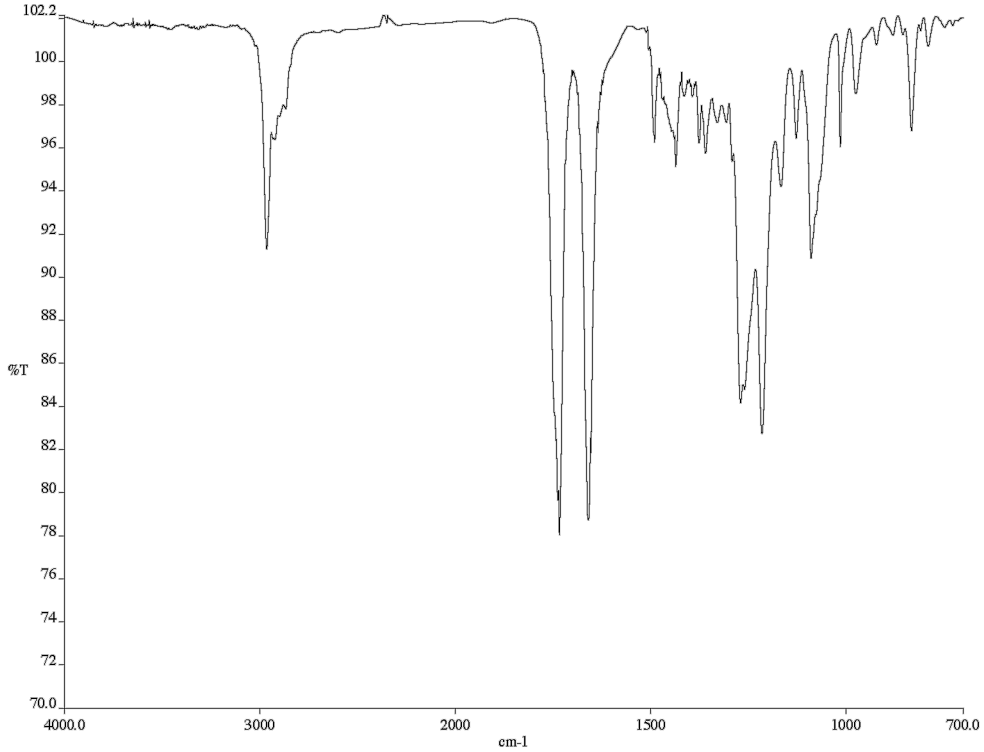


Figure A12.59. Infrared spectrum (thin film/NaCl) of compound **453**.

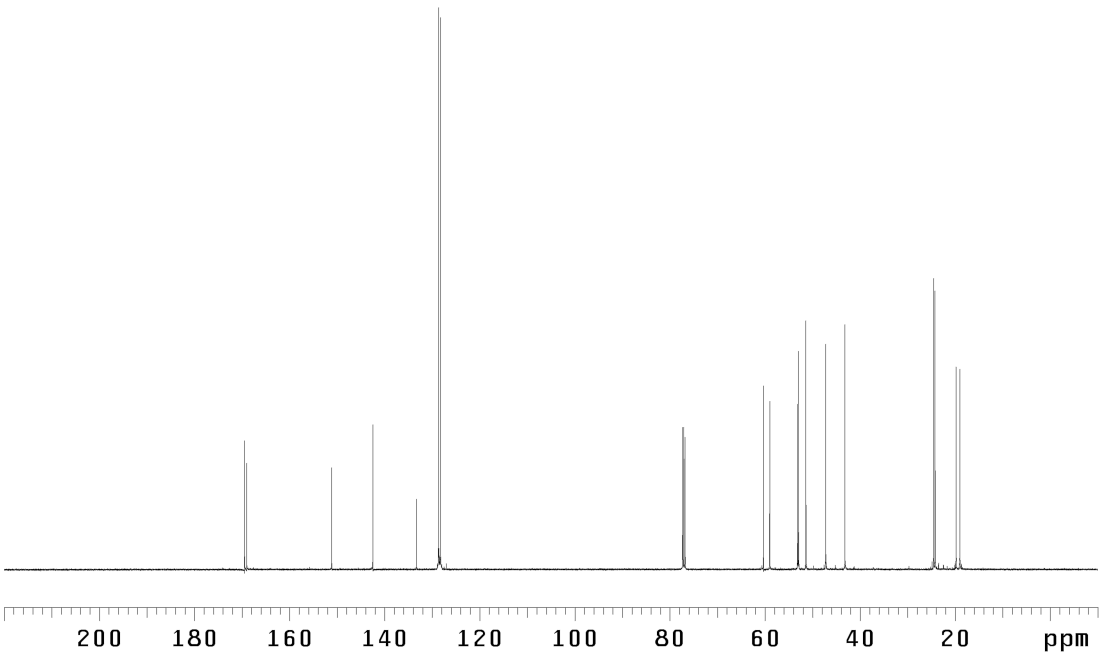


Figure A12.60. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **453**.

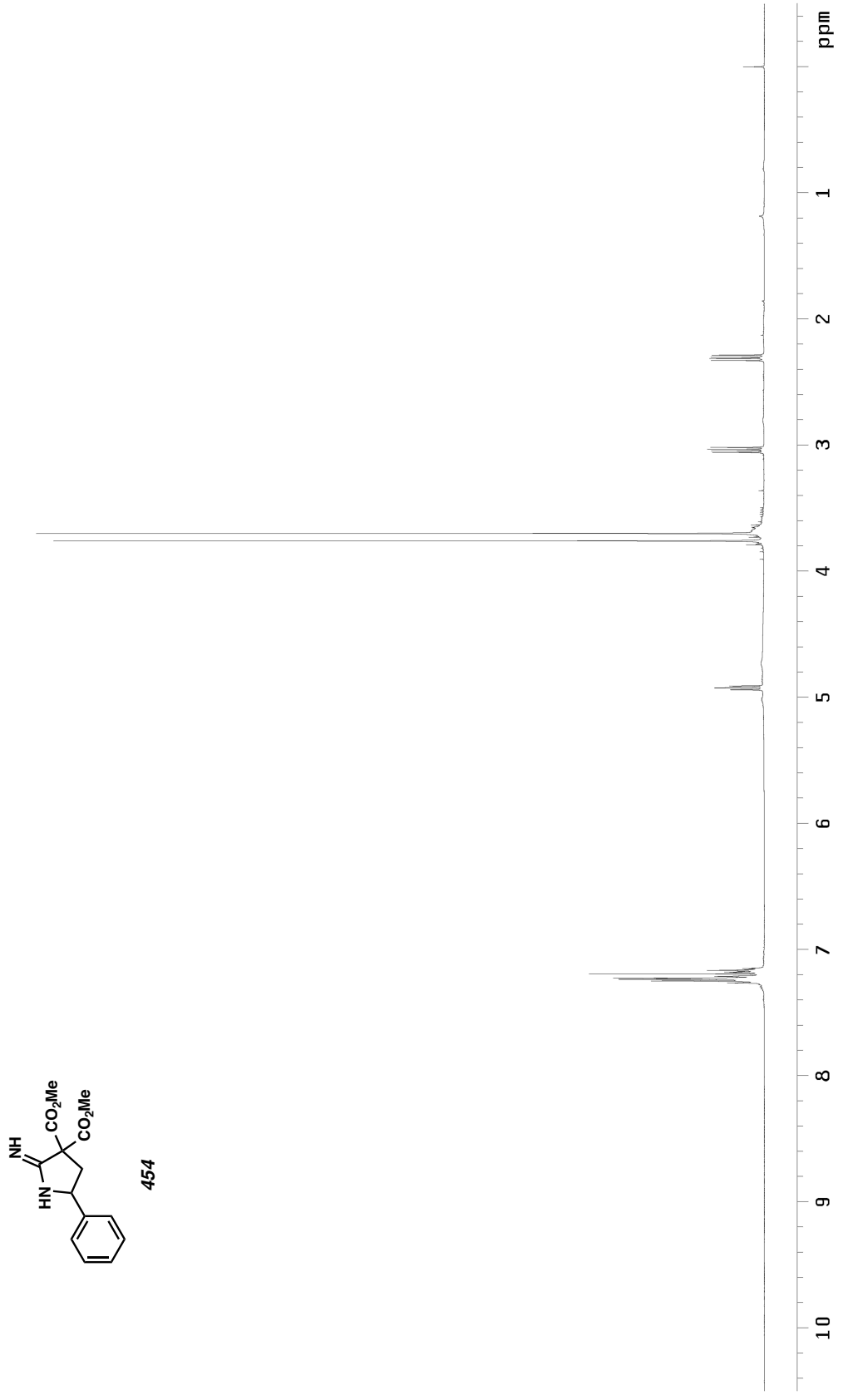


Figure A12.61. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **454**.

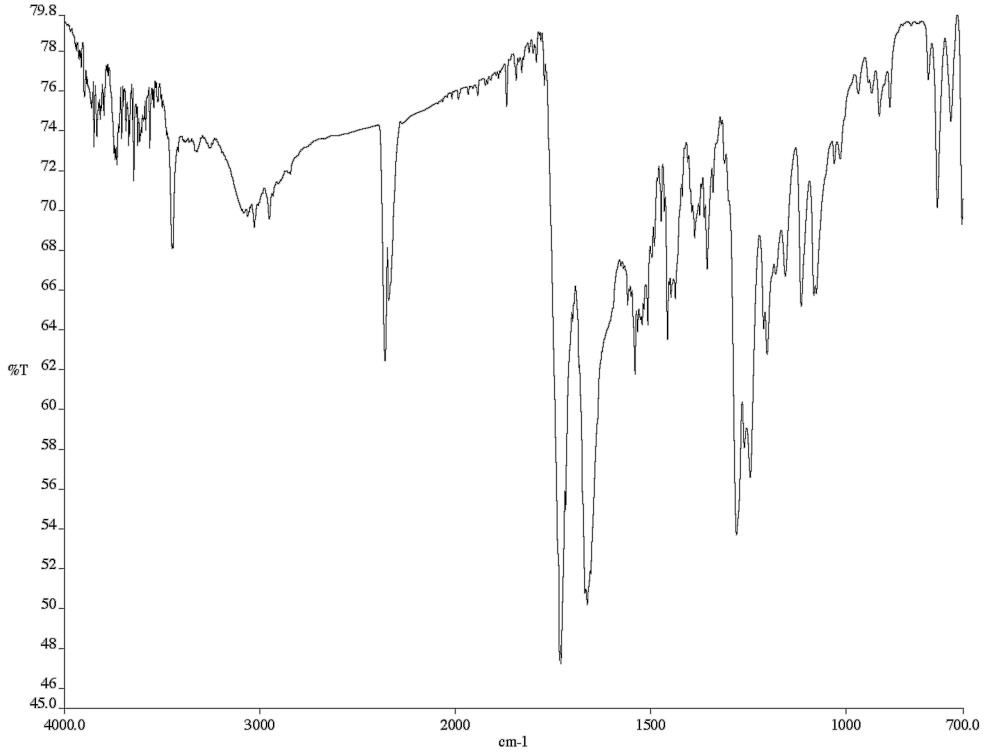


Figure A12.62. Infrared spectrum (thin film/NaCl) of compound **454**.

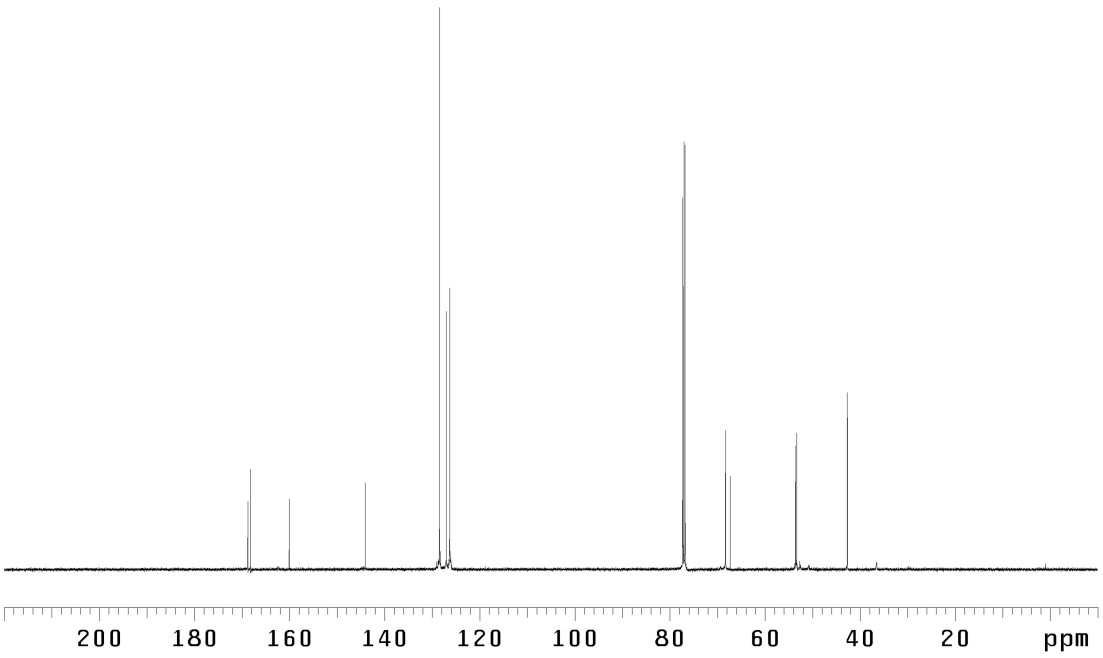


Figure A12.63. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **454**.

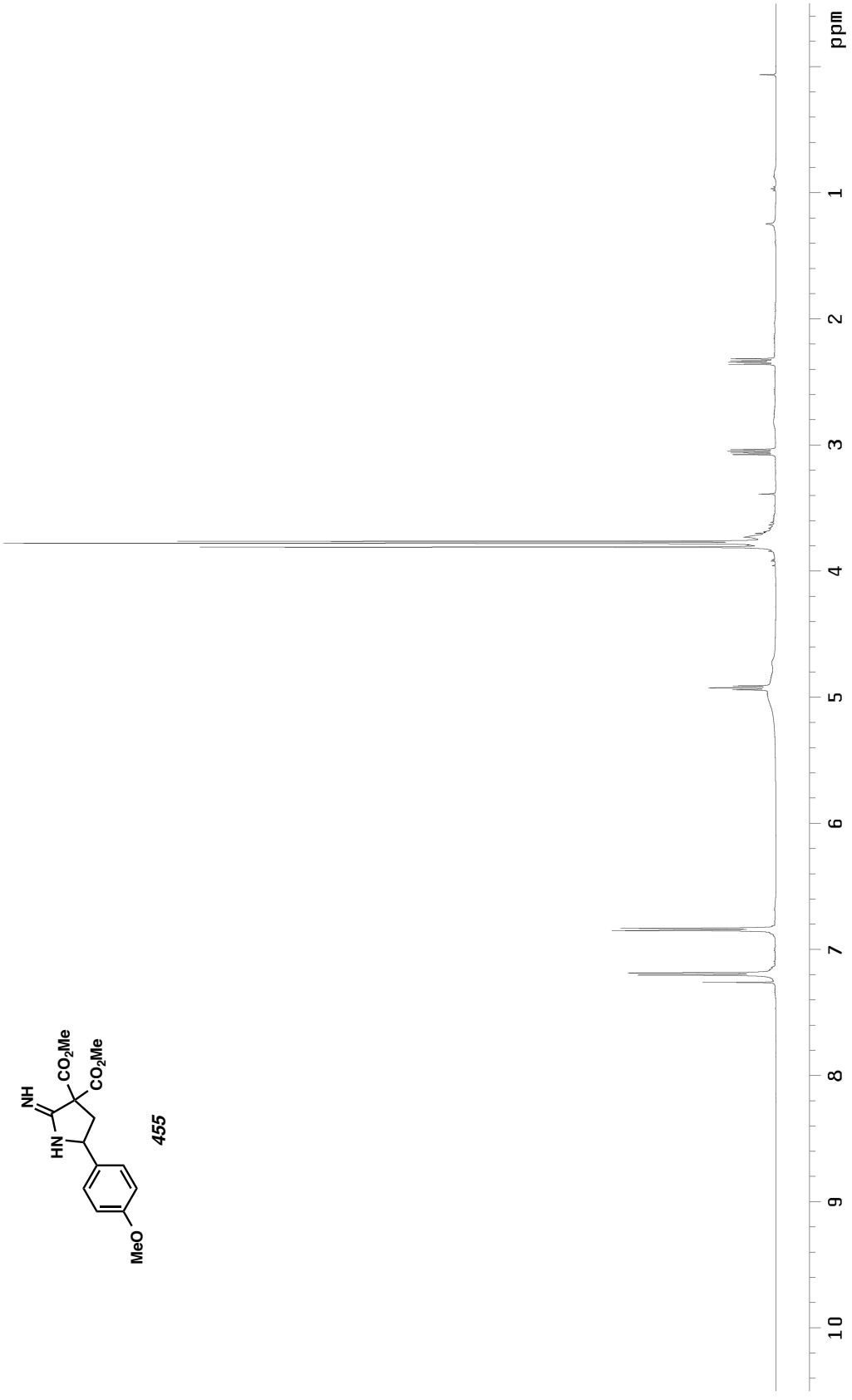


Figure A12.64. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **455**.

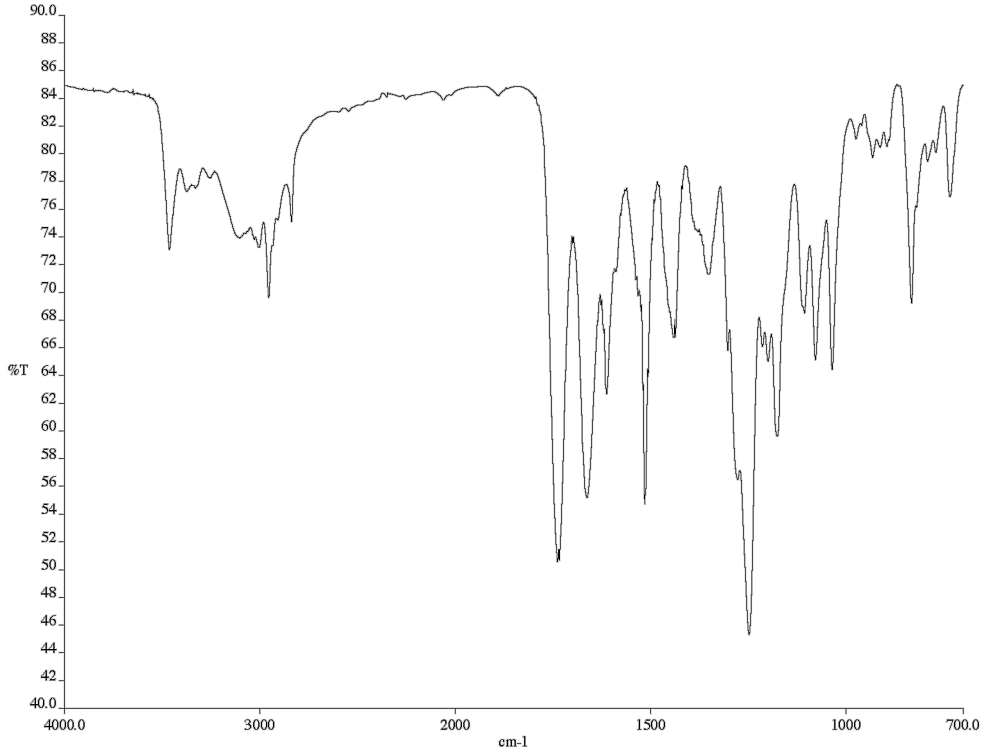


Figure A12.65. Infrared spectrum (thin film/NaCl) of compound **455**.

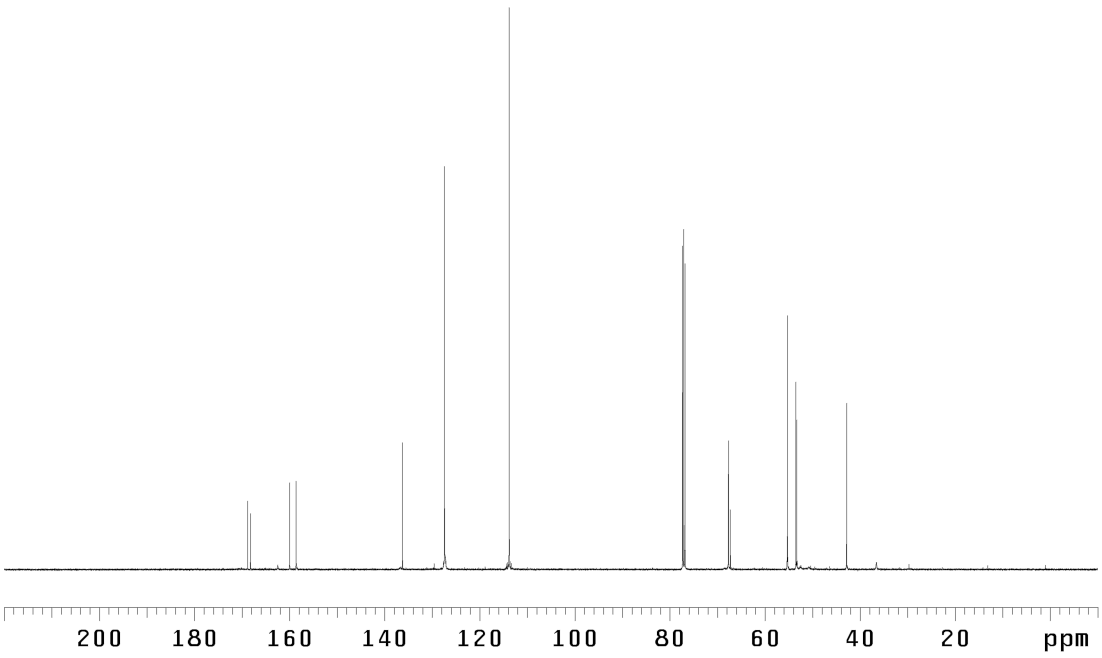


Figure A12.66. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **455**.

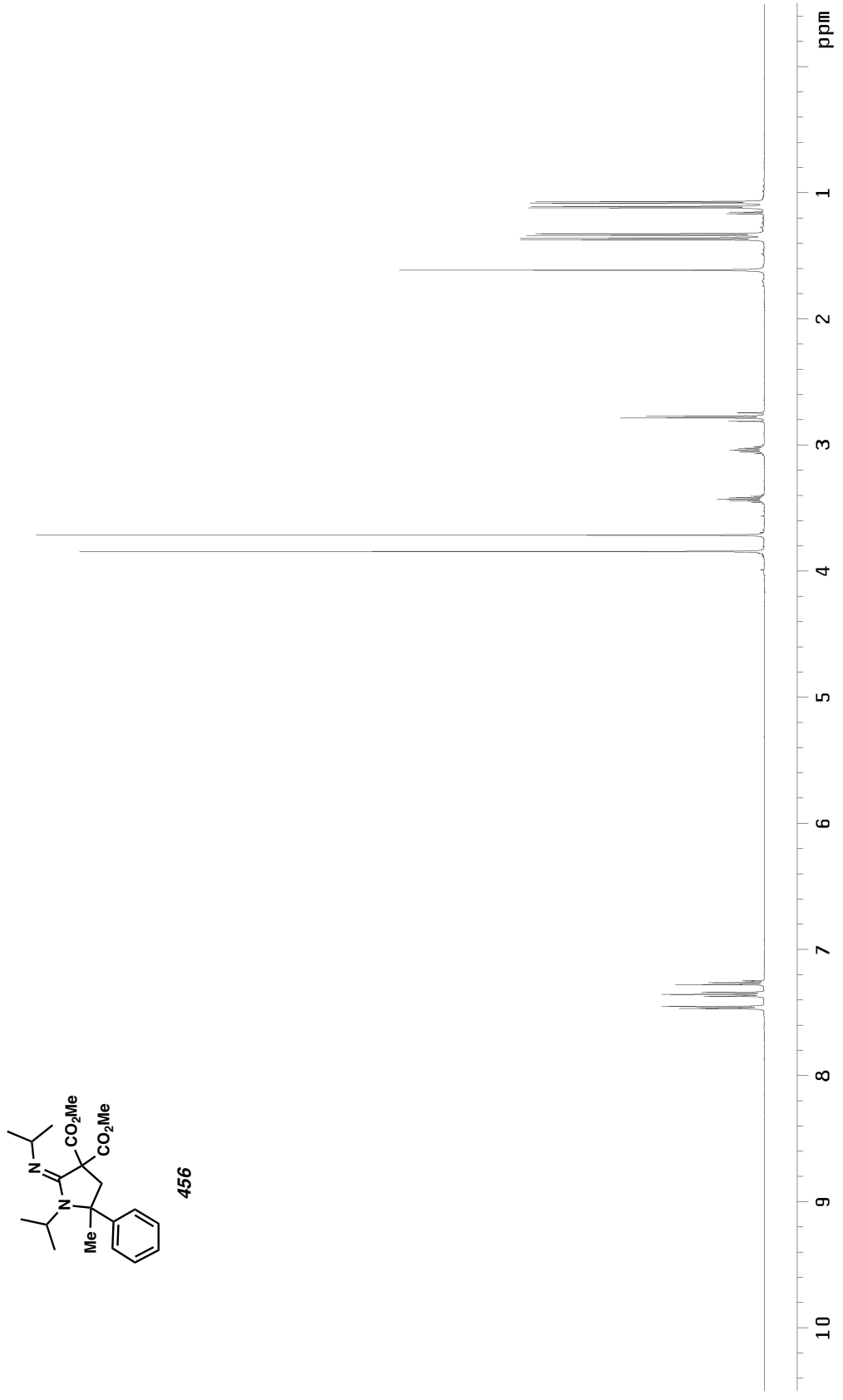


Figure A12.67. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **456**.

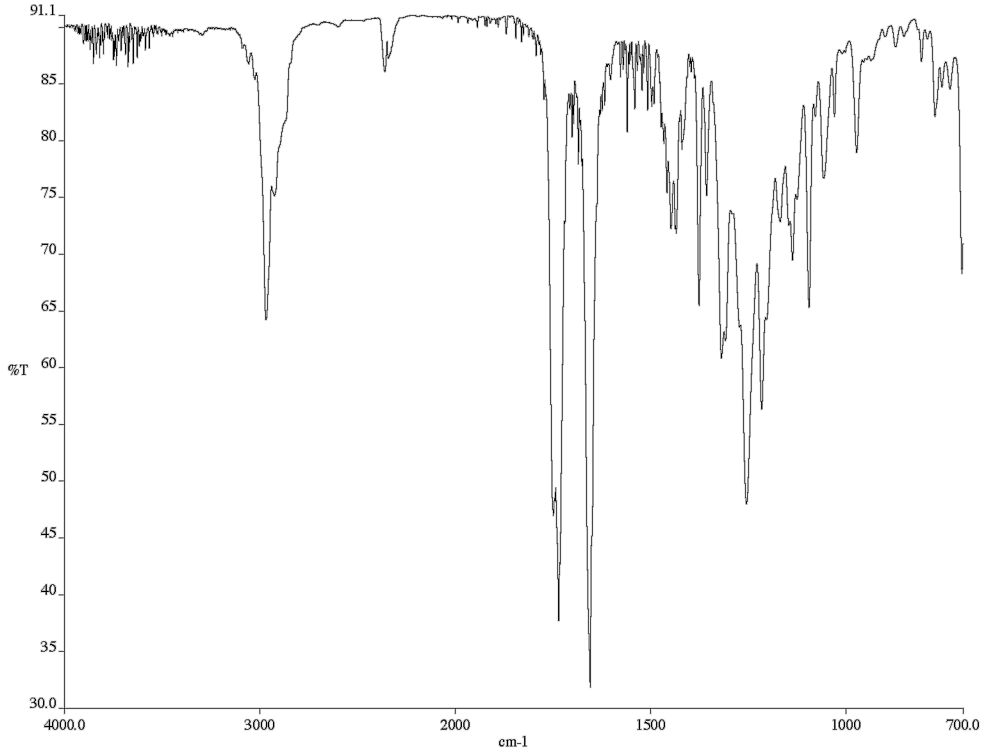


Figure A12.68. Infrared spectrum (thin film/NaCl) of compound **456**.

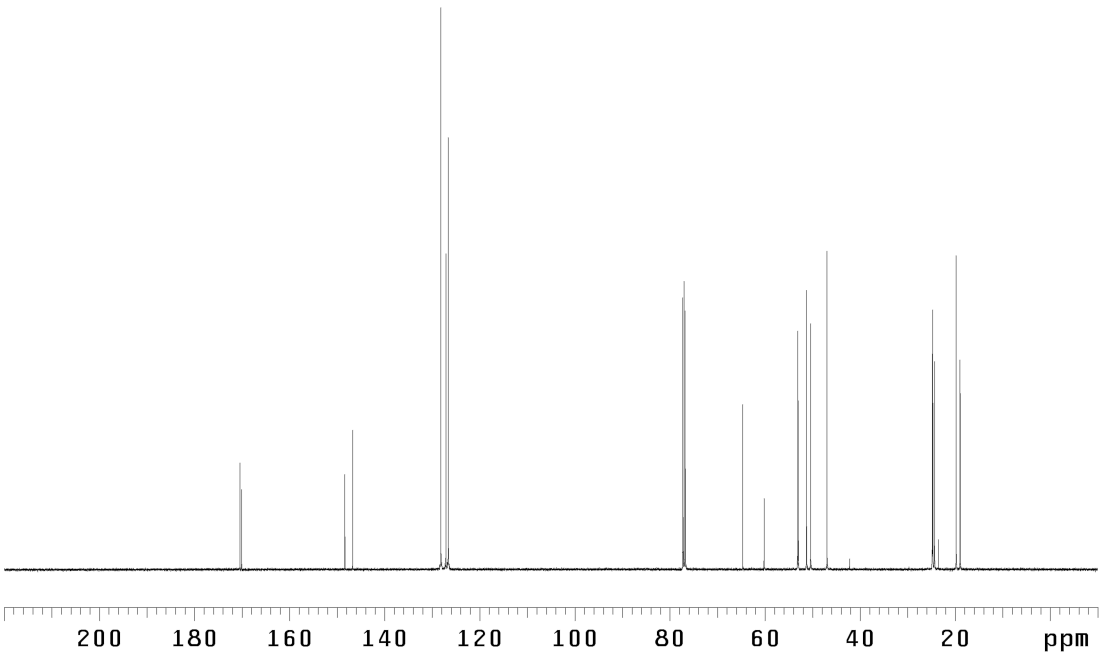


Figure A12.69. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **456**.

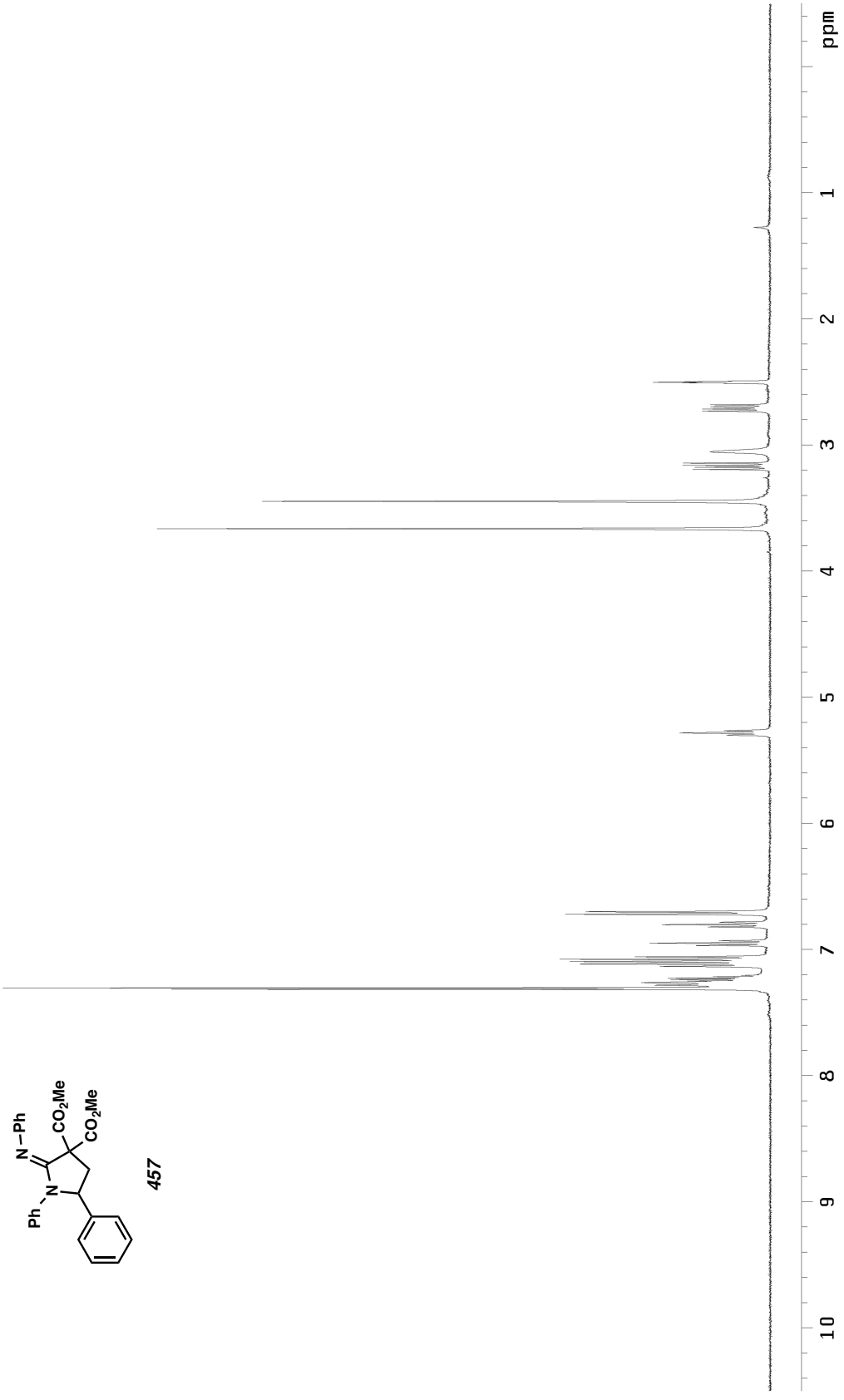


Figure A12.70. ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) of compound **457**.

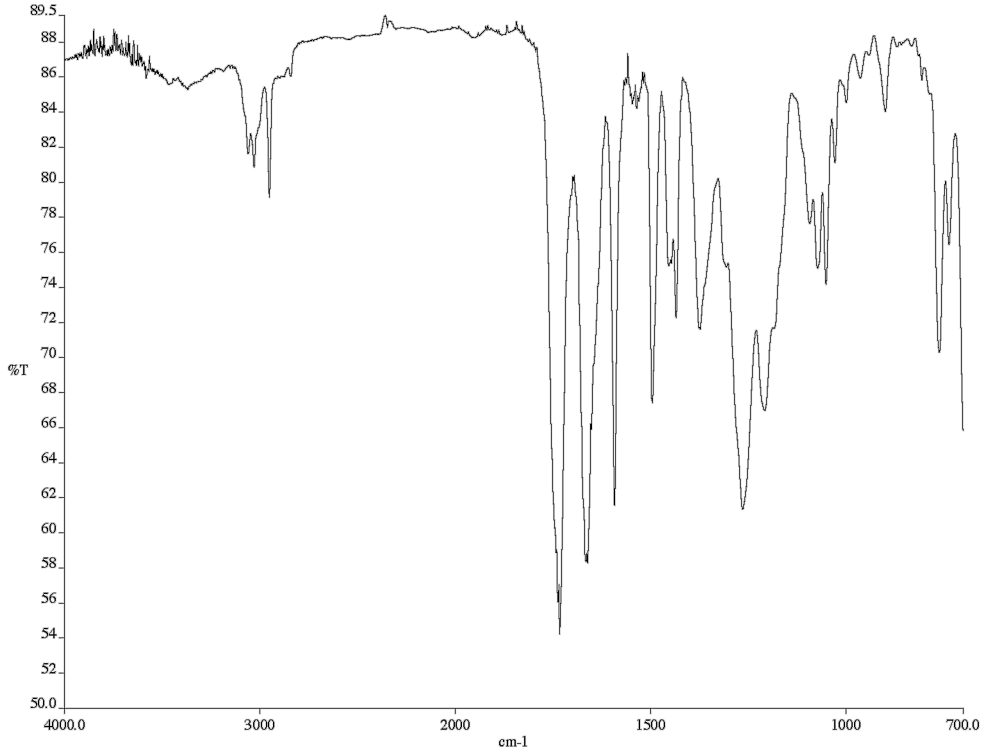


Figure A12.71. Infrared spectrum (thin film/NaCl) of compound **457**.

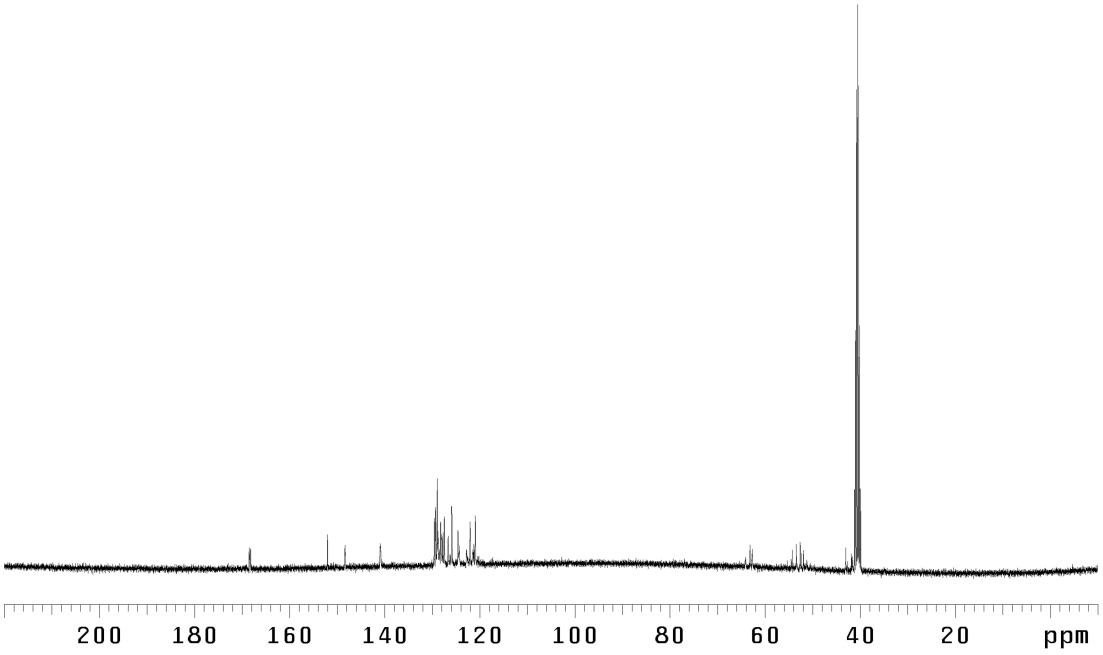


Figure A12.72. ^{13}C NMR (101 MHz, DMSO-d_6, 100 °C) of compound **457**.

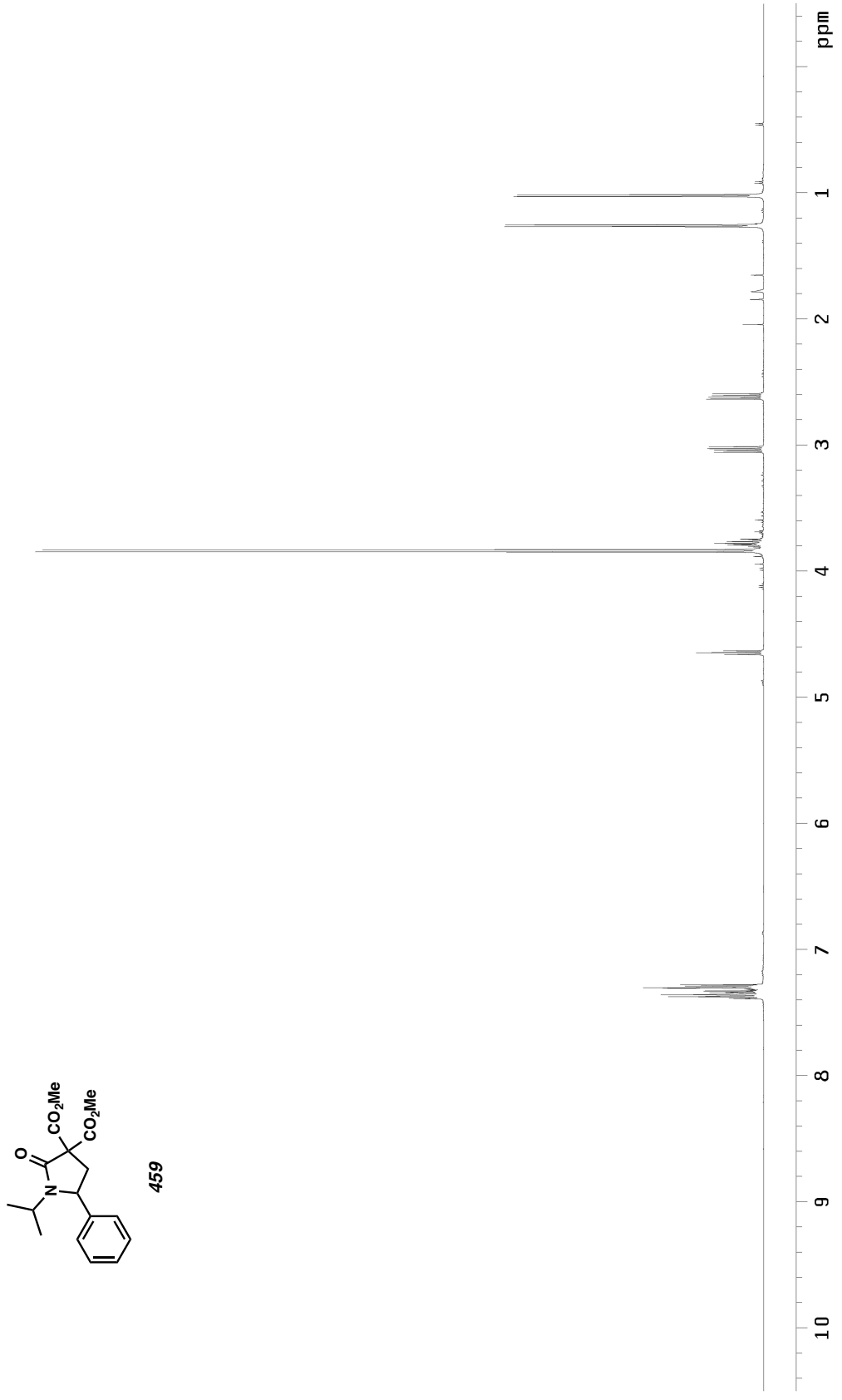


Figure A12.73. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **459**.

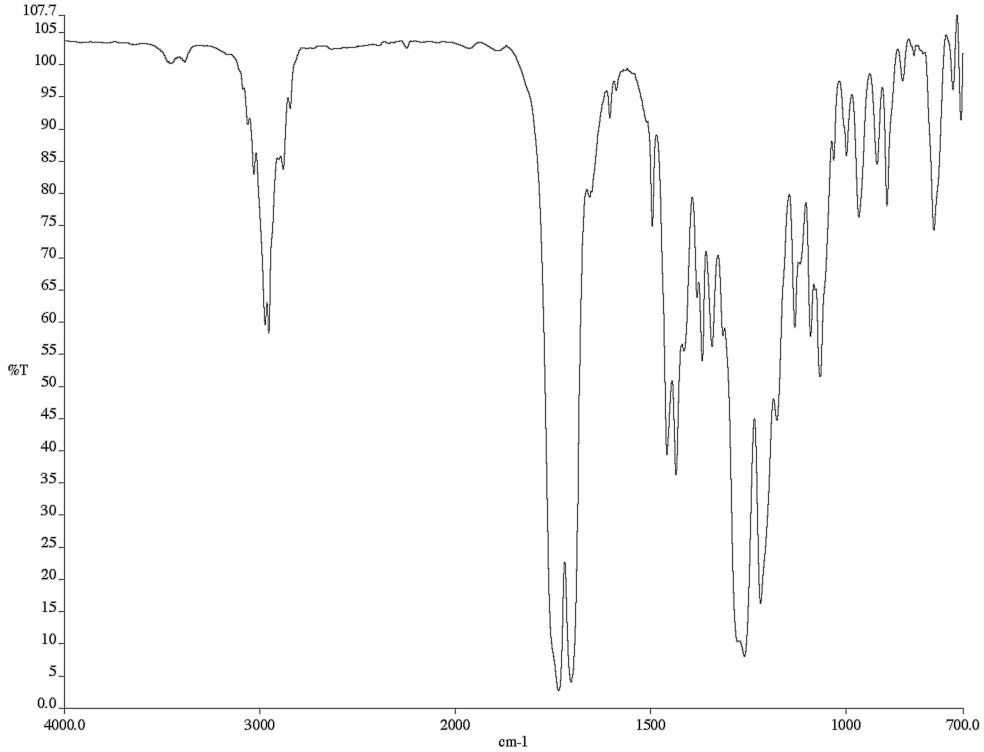


Figure A12.74. Infrared spectrum (thin film/NaCl) of compound **459**.

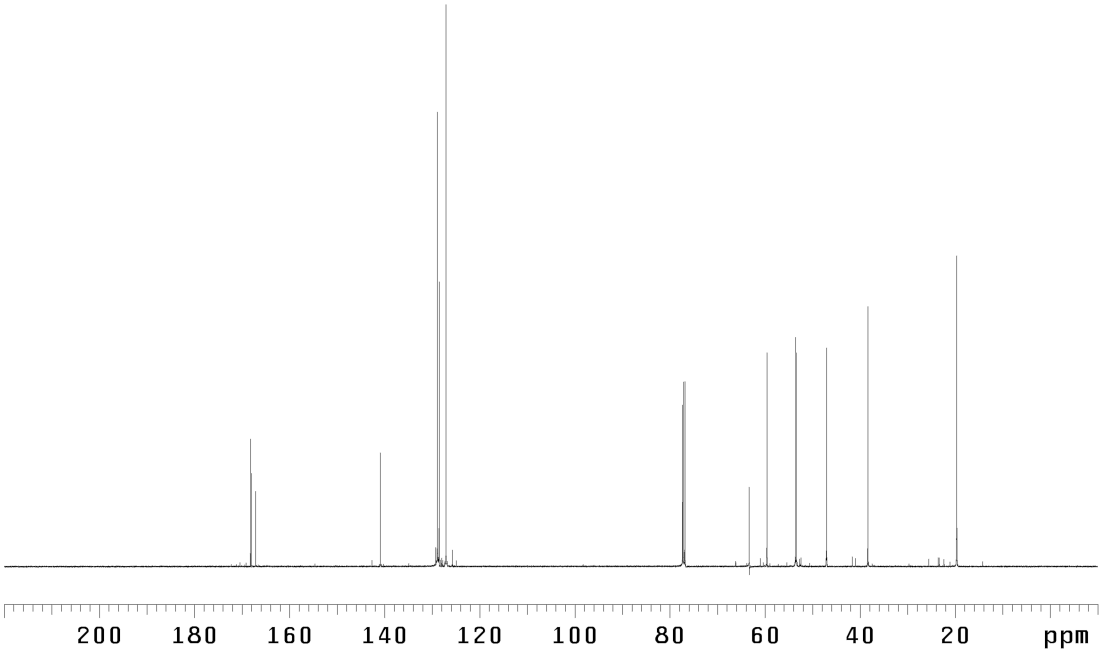


Figure A12.75. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **459**.

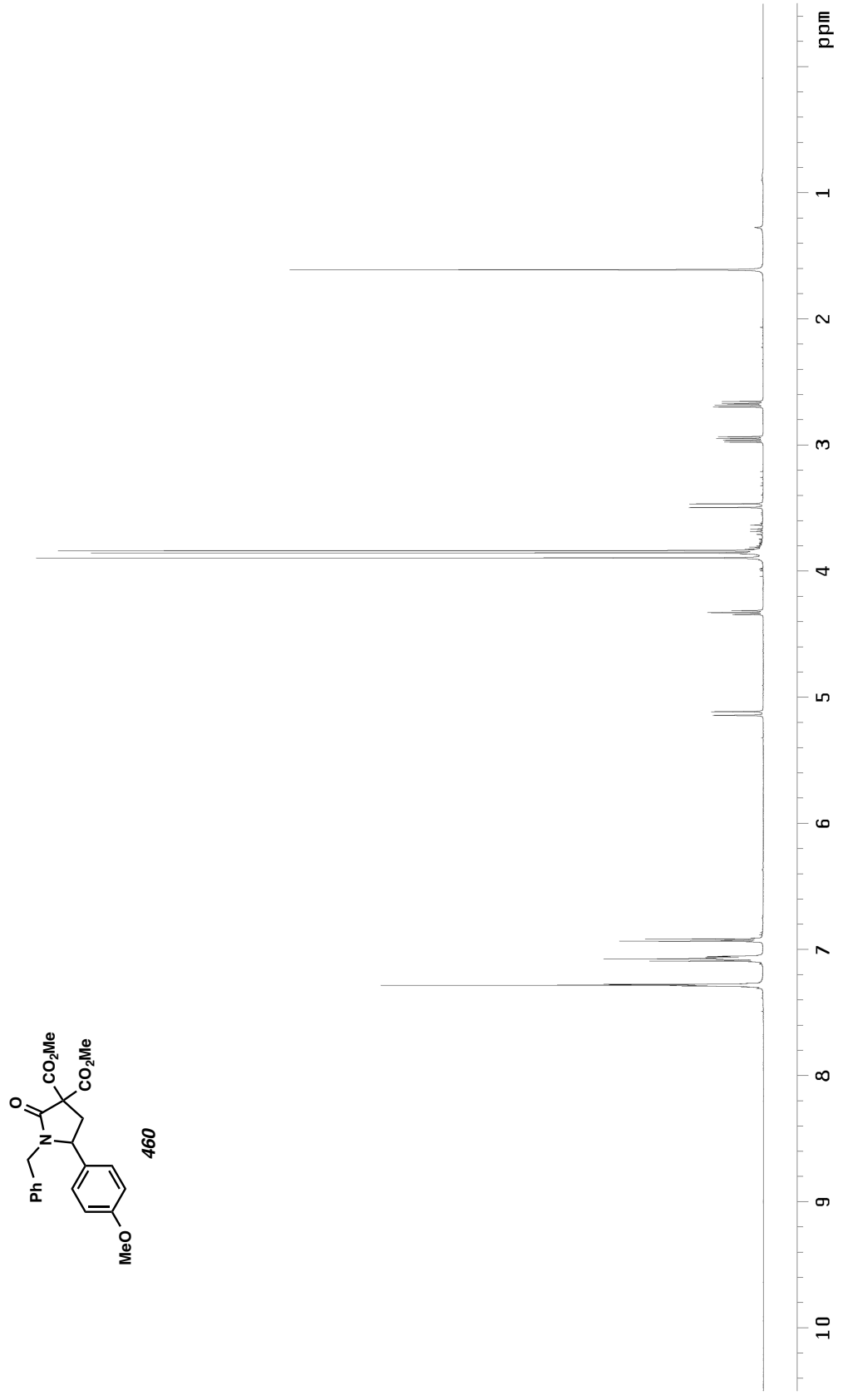


Figure A12.76. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **460**.

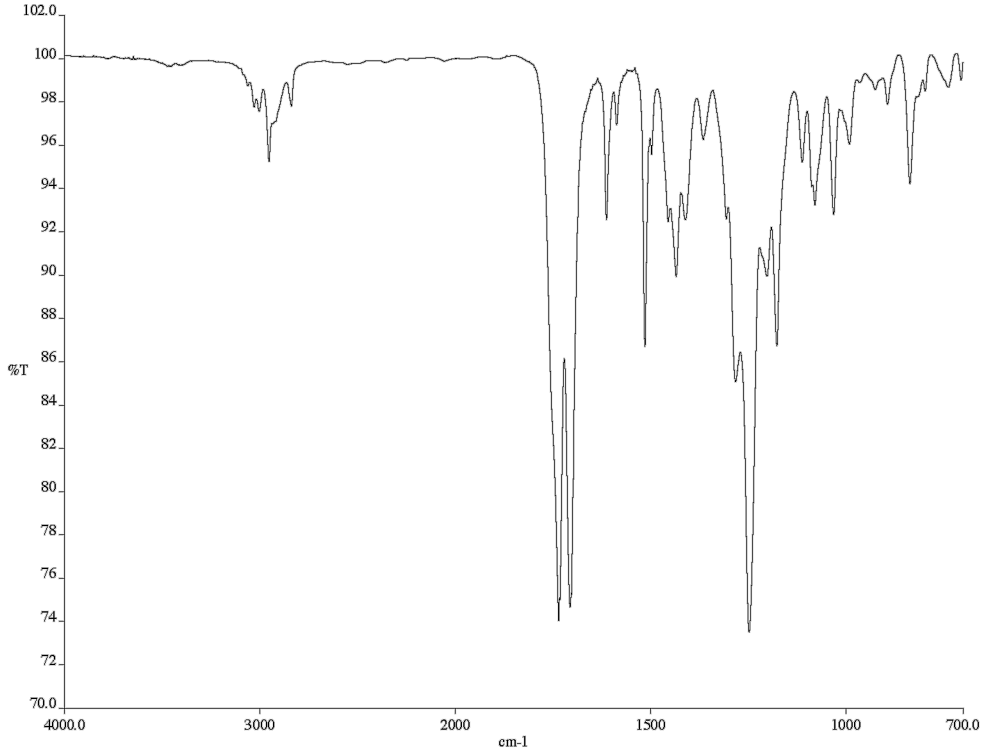


Figure A12.77. Infrared spectrum (thin film/NaCl) of compound **460**.

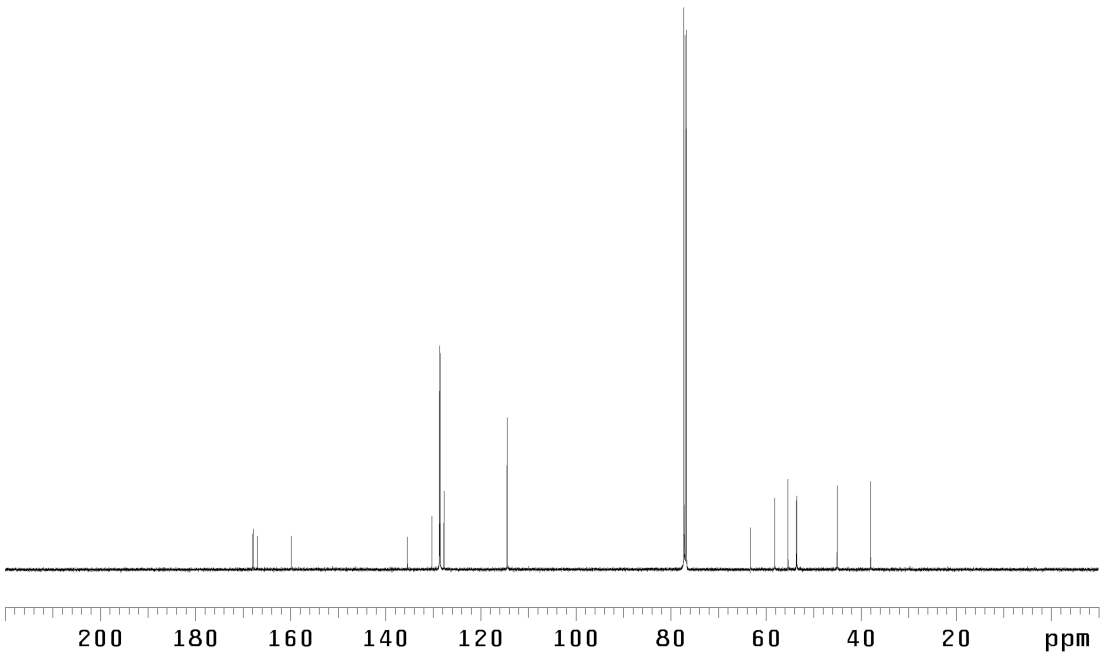


Figure A12.78. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **460**.

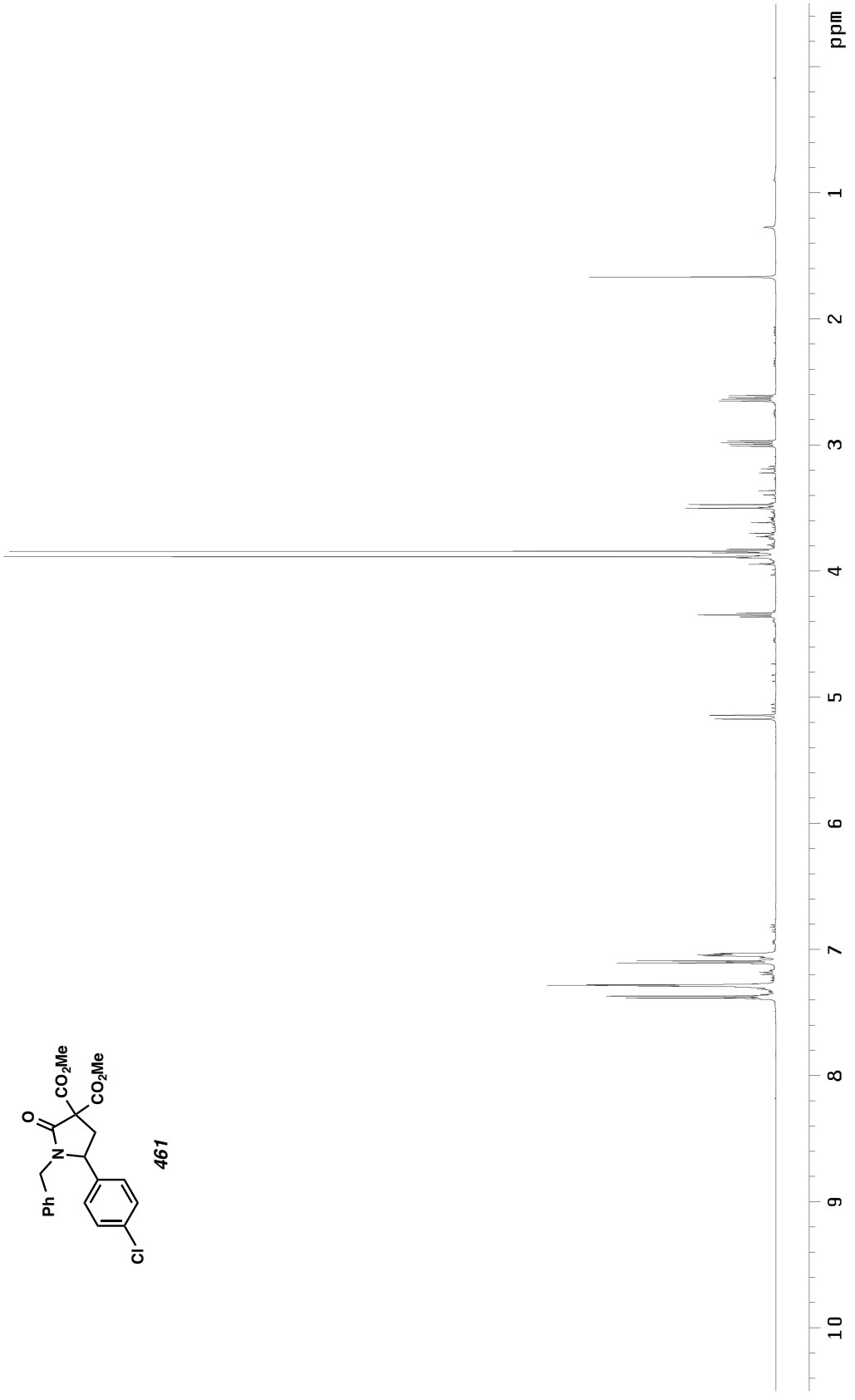


Figure A12.79. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **461**.

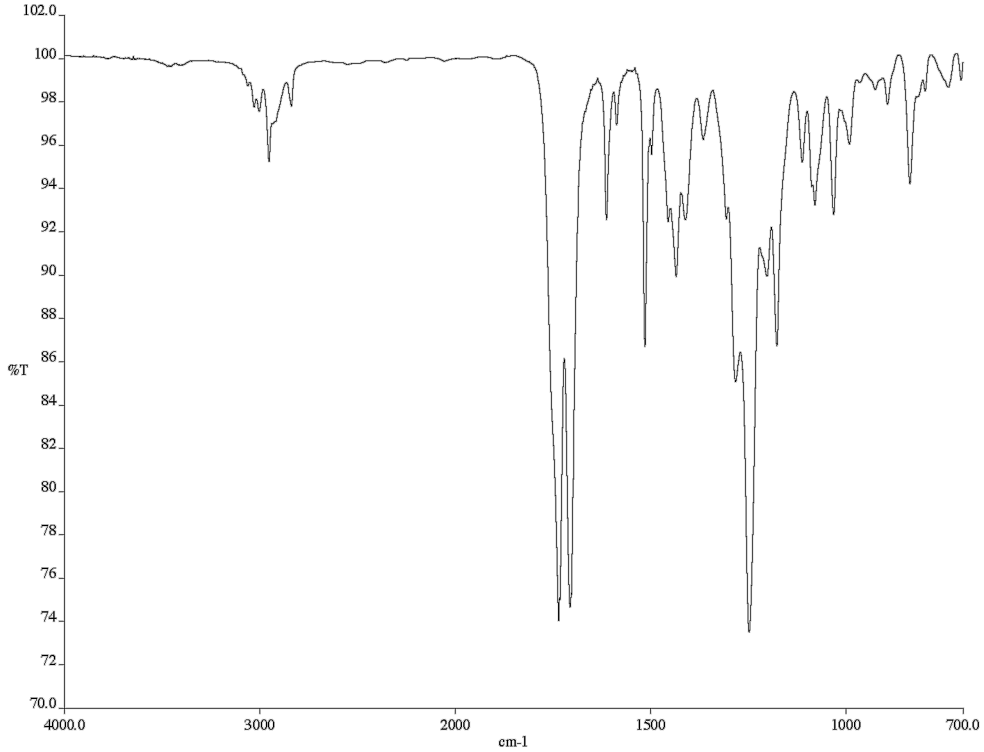


Figure A12.80. Infrared spectrum (thin film/NaCl) of compound **461**.

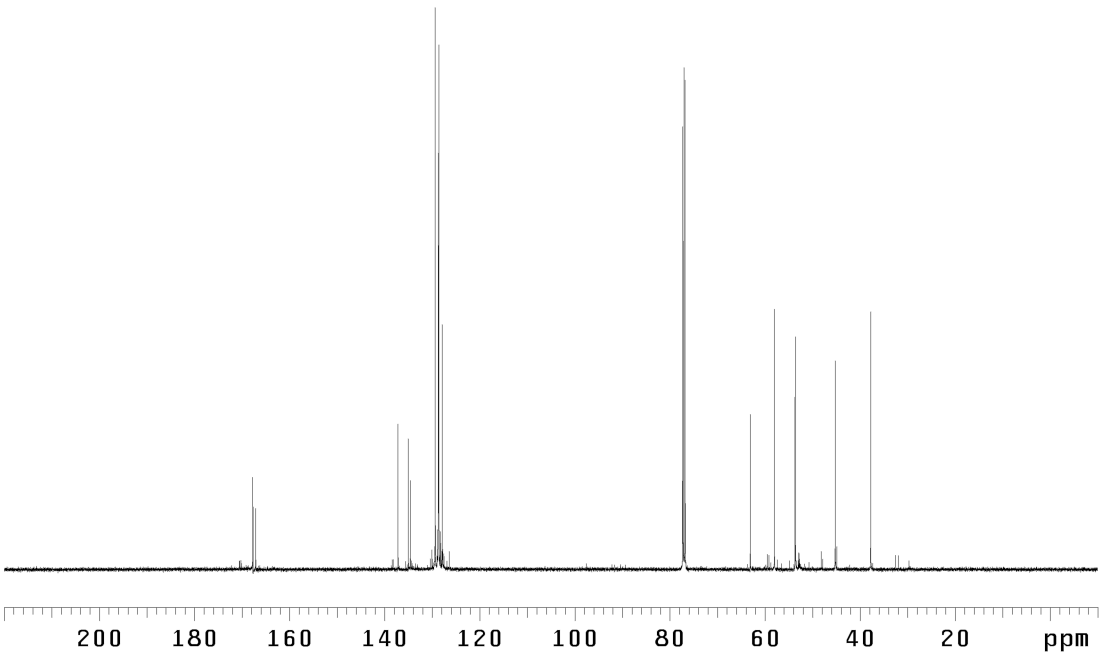


Figure A12.81. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **461**.

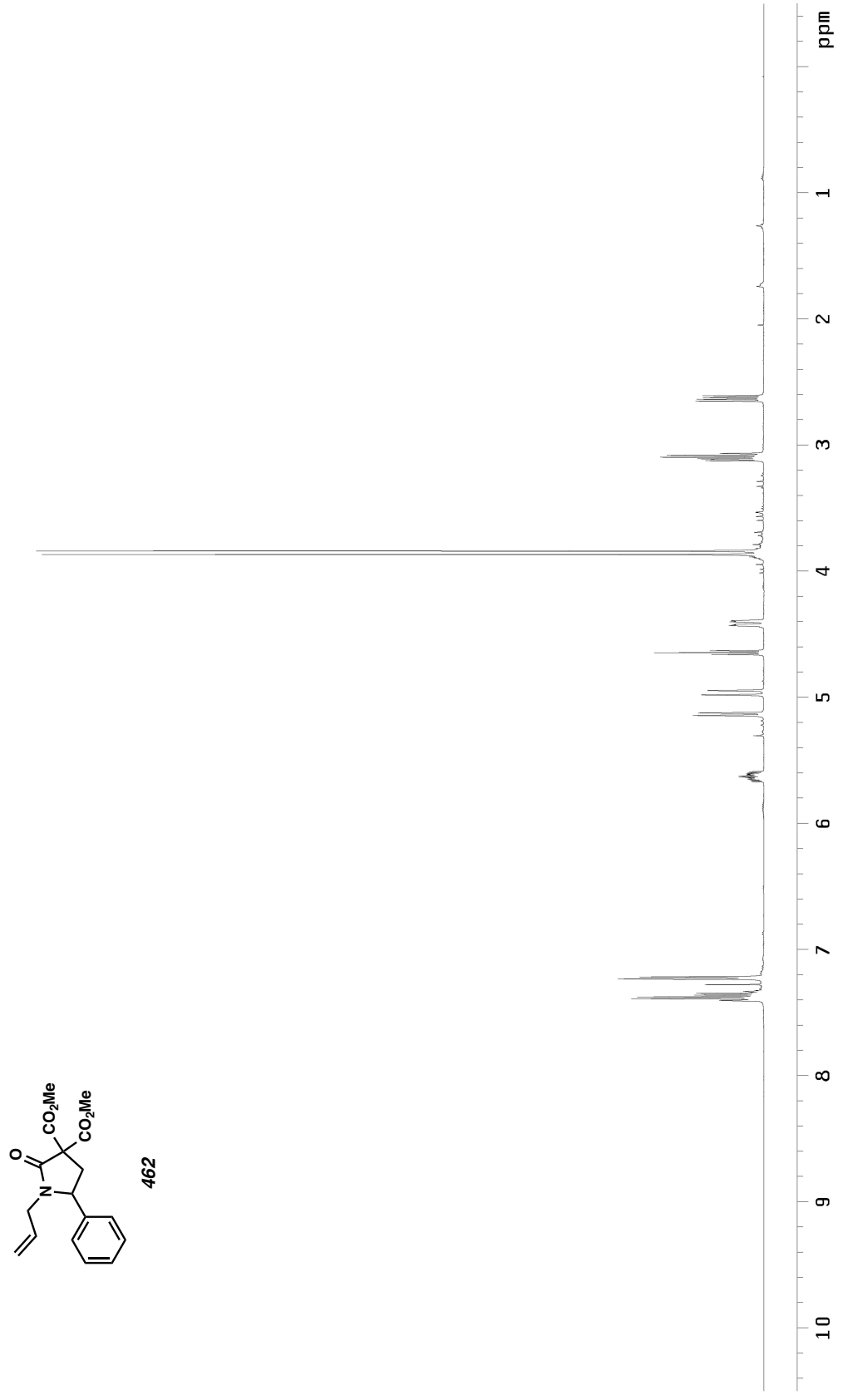


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Figure A12.82. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **462**.

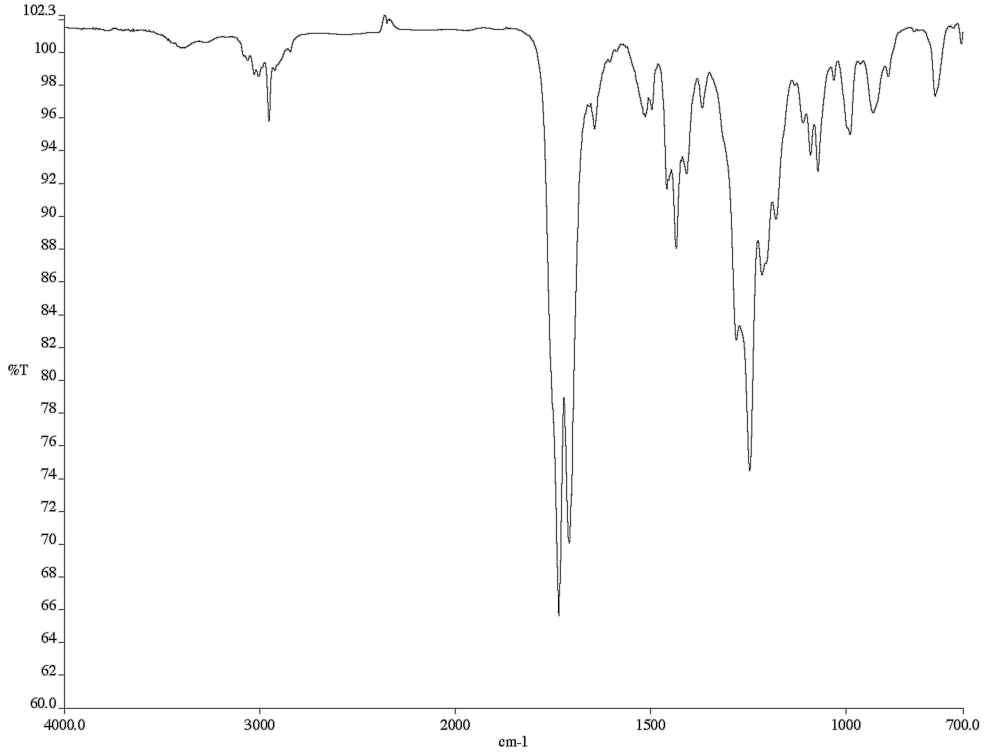


Figure A12.83. Infrared spectrum (thin film/NaCl) of compound **462**.

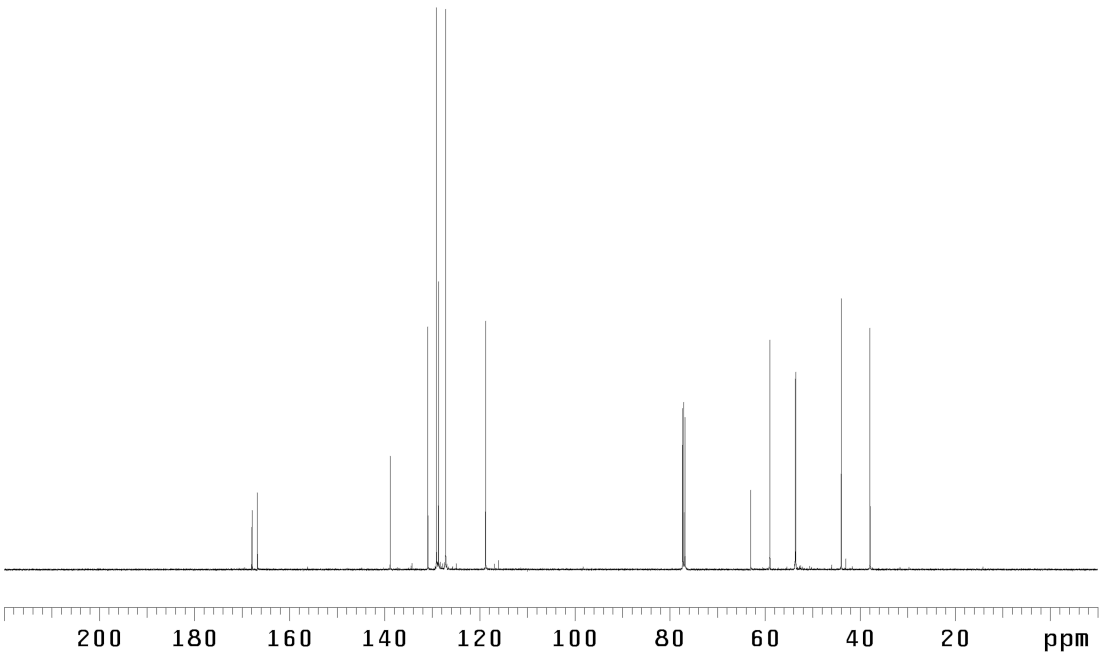


Figure A12.84. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **462**.

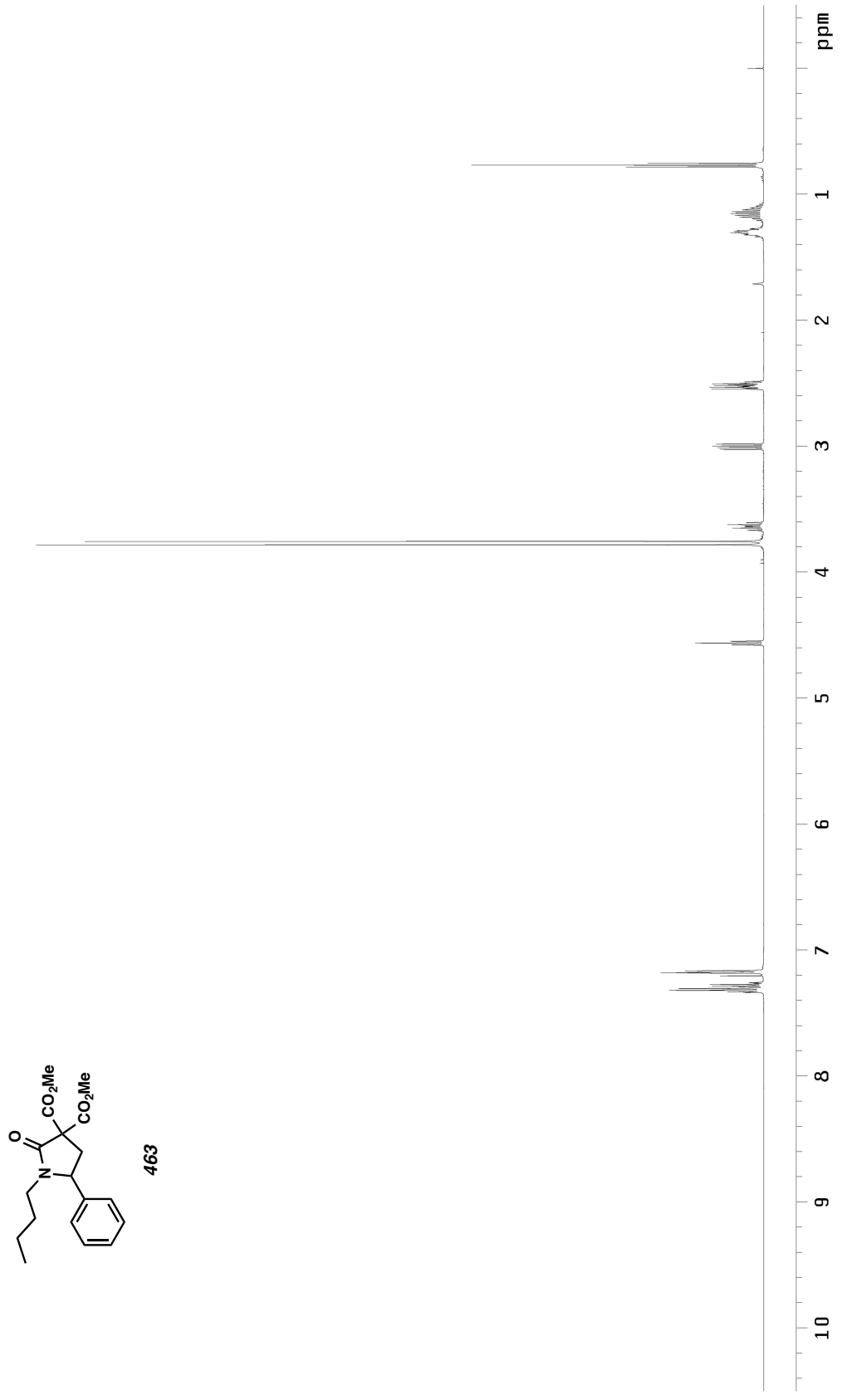


Figure A12.85. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **463**.

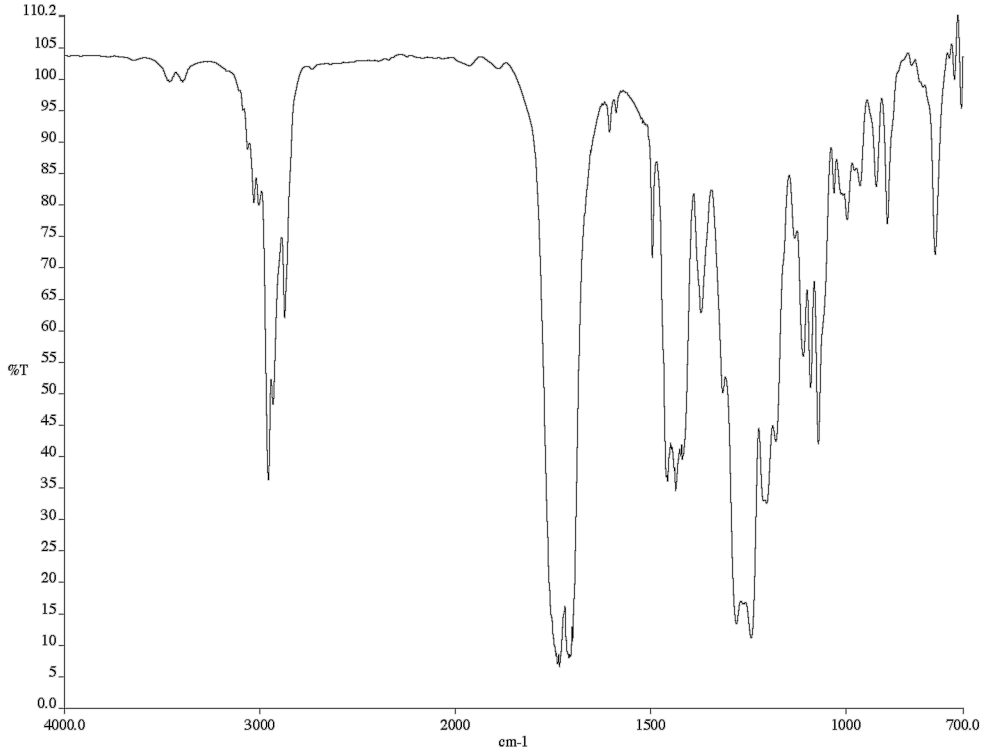


Figure A12.86. Infrared spectrum (thin film/NaCl) of compound **463**.

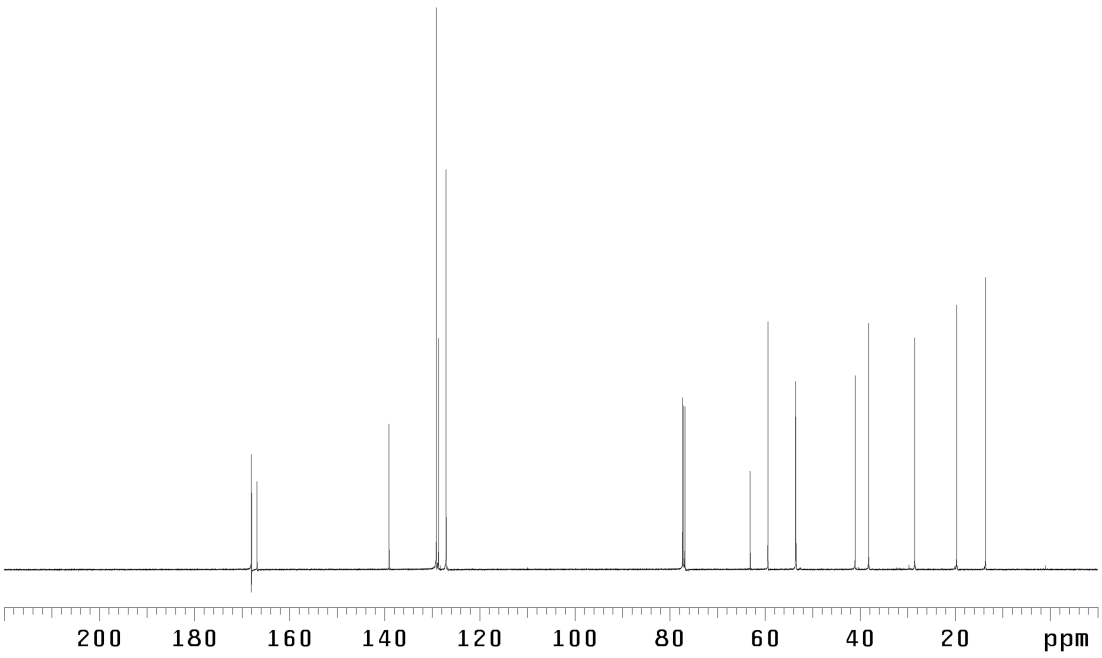


Figure A12.87. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **463**.

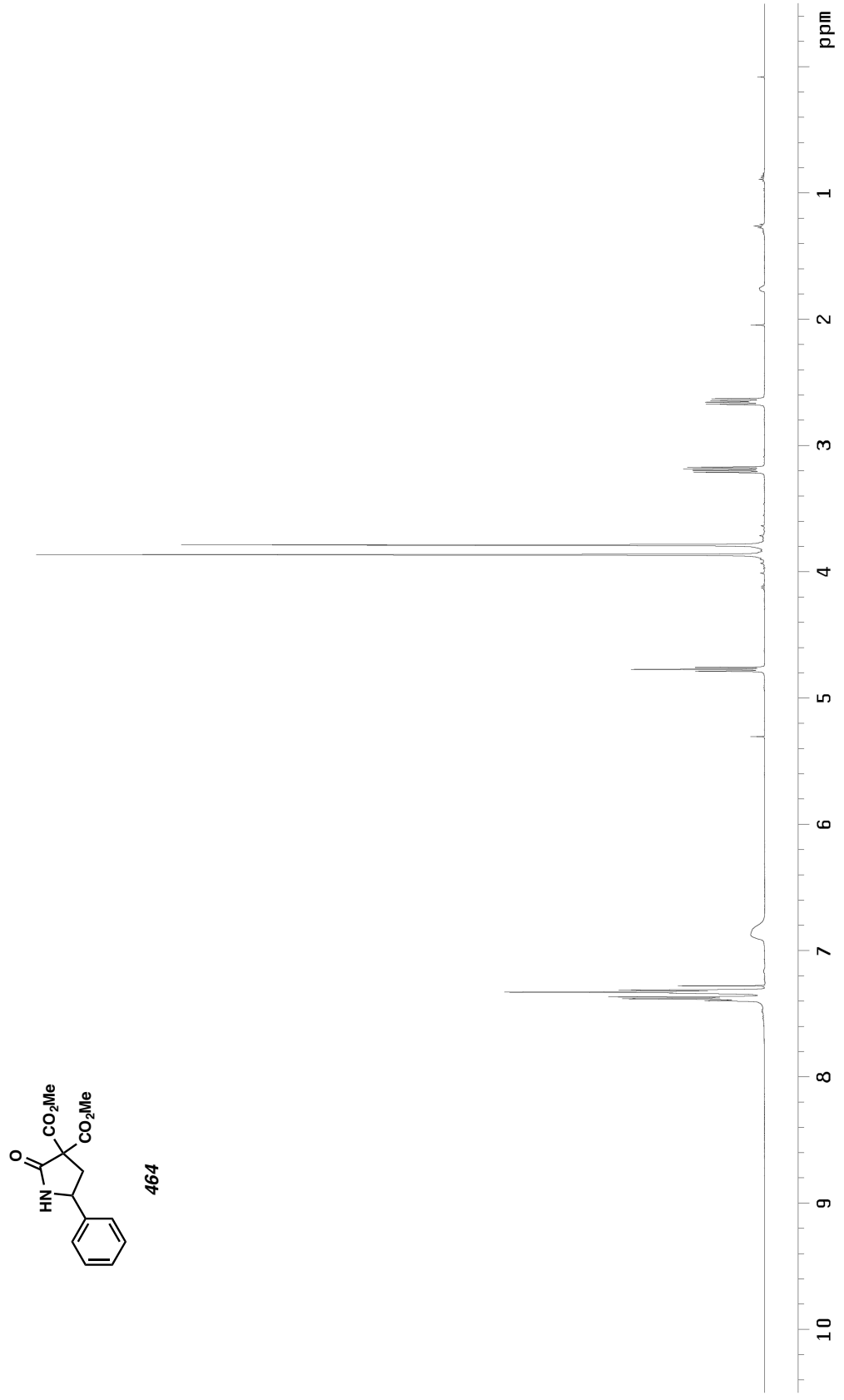


Figure A12.88. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **464**.

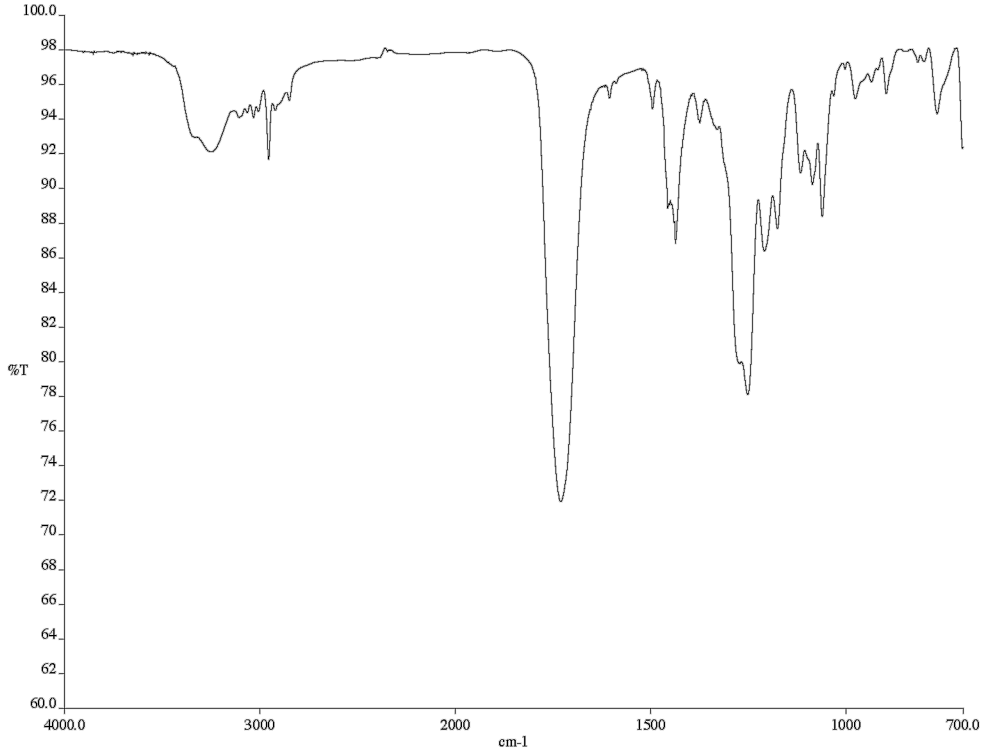


Figure A12.89. Infrared spectrum (thin film/NaCl) of compound **464**.

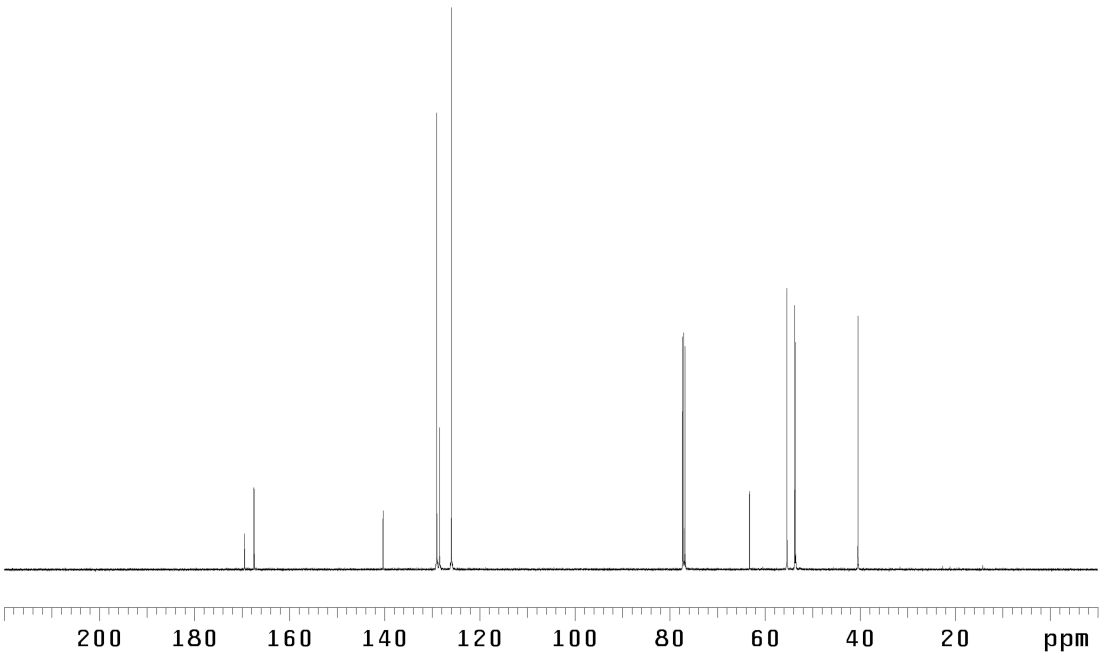


Figure A12.90. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **464**.

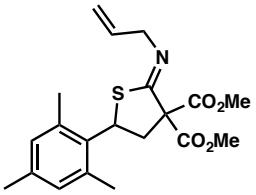
APPENDIX 13

X-Ray Crystallography Reports Relevant to Chapter 5:

Lewis Acid Mediated (3+2) Cycloadditions of

Donor–Acceptor Cyclopropanes with Heterocumulenes

A13.1 X-Ray Crystal Structure Analysis of Thioimidate 440



440

Contents

Figure A13.1.1. X-Ray Crystal Structure of Thioimidate ***440***

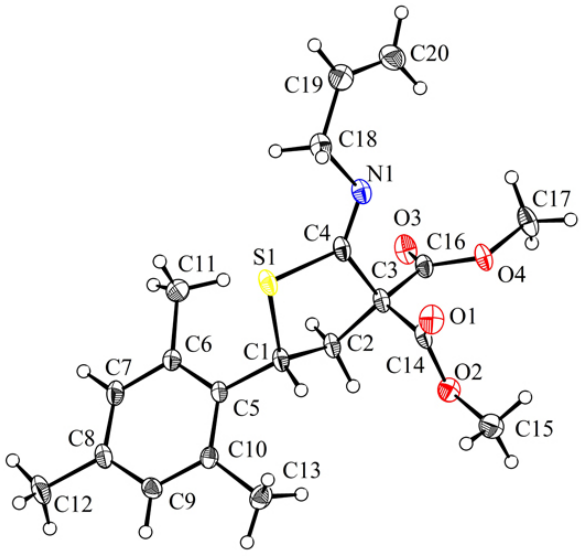


*Table A13.1.1. Crystal Data and Structure Refinement for Thioimidate **440**.*

Caltech Identification Number	rac13
CCDC Deposition Number	911991
Empirical formula	C20 H25 N O4 S
Formula weight	375.47
Crystallization solvent	Benzene/Heptane/Ethyl Acetate
Crystal color	colourless
Crystal size	0.08 x 0.19 x 0.46 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 ≈ MO K	
Data collection temperature	100.15 K	
Theta range for 5787 reflections used in lattice determination	2.521 to 31.600°	
Unit cell dimensions	a = 14.5982(10) ≈ b = 16.1620(12) ≈ c = 8.2014(6) ≈	α= 90° β= 92.145(4)° γ = 90°
Volume	1933.7(2) $\approx^3$	
Z	4	
Crystal system	monoclinic	
Space group	P 1 21/c 1 (# 14)	
Density (calculated)	1.290 g/cm^3	
F(000)	800	
Theta range for data collection	1.4 to 37.4∞	
Completeness to theta = 25.00°	100.0%	
Index ranges	–24 ≤ h ≤ 24, 0 ≤ k ≤ 27, 0 ≤ l ≤ 13	
Data collection scan type	narrow and scans	
Reflections collected	15085	
Independent reflections	15085 [R_{int}= 0.0000]	
Reflections > 2s(I)	10418	
Average s(I)/(net I)	0.0676	
Absorption coefficient	0.19 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9848 and 0.9170	

Table A13.1.1. (cont'd)

Reflections monitored for decay	0
Decay of standards	0%
Structure Solution and Refinement	
Primary solution method	direct
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15085 / 0 / 241
Treatment of hydrogen atoms	constr
Goodness-of-fit on F^2	1.06
Final R indices [I>2s(I), 10418 reflections]	R1 = 0.0592, wR2 = 0.1221
R indices (all data)	R1 = 0.1034, wR2 = 0.1431
Type of weighting scheme used	calc
Weighting scheme used	calc w=1/[^2^(Fo^2^)+(0.0645P)^2^+0.3700P] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.49 and -0.37 e$\sum\approx^{-3}$
Programs Used	
Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2 2012.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXS-97 (Sheldrick, 1990)
Structure refinement	SHELXL-97 (Sheldrick, 1997)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table A13.1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Thioimidate ***440****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
S(1)	7001(1)	6892(1)	2895(1)	22(1)
O(1)	8360(1)	6282(1)	6404(1)	27(1)
O(2)	7480(1)	5212(1)	7100(1)	22(1)
O(3)	7866(1)	4219(1)	2706(1)	26(1)
O(4)	8857(1)	4560(1)	4768(1)	22(1)
N(1)	8660(1)	6157(1)	2476(1)	20(1)
C(1)	6183(1)	6259(1)	4018(2)	18(1)
C(2)	6567(1)	5375(1)	4014(2)	18(1)
C(3)	7607(1)	5456(1)	4275(2)	17(1)
C(4)	7894(1)	6152(1)	3131(2)	18(1)
C(5)	5192(1)	6358(1)	3430(1)	15(1)
C(6)	4890(1)	6274(1)	1789(1)	18(1)
C(7)	3969(1)	6418(1)	1363(2)	20(1)
C(8)	3336(1)	6643(1)	2493(2)	20(1)
C(9)	3634(1)	6687(1)	4121(2)	19(1)
C(10)	4541(1)	6543(1)	4608(1)	17(1)
C(11)	5514(1)	6056(1)	420(2)	26(1)
C(12)	2354(1)	6831(1)	1995(2)	29(1)
C(13)	4795(1)	6554(1)	6414(1)	24(1)
C(14)	7874(1)	5710(1)	6034(2)	18(1)
C(15)	7719(1)	5383(1)	8800(2)	26(1)
C(16)	8111(1)	4667(1)	3805(2)	18(1)
C(17)	9433(1)	3862(1)	4390(2)	29(1)
C(18)	8876(1)	6851(1)	1424(2)	23(1)
C(19)	9690(1)	6694(1)	428(2)	27(1)
C(20)	10218(1)	6036(1)	521(2)	31(1)

*Table A13.1.3. Bond lengths [Å] and angles [°] for Thioimidate **440**.*

S(1)-C(1)	1.8457(13)
S(1)-C(4)	1.7750(12)
O(1)-C(14)	1.1975(14)
O(2)-C(14)	1.3343(15)
O(2)-C(15)	1.4511(15)
O(3)-C(16)	1.1997(14)
O(4)-C(16)	1.3320(15)
O(4)-C(17)	1.4486(16)
N(1)-C(4)	1.2587(17)
N(1)-C(18)	1.4571(16)
C(1)-H(1)	1.0000
C(1)-C(2)	1.5343(16)
C(1)-C(5)	1.5167(17)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(3)	1.5308(17)
C(3)-C(4)	1.5333(17)
C(3)-C(14)	1.5361(17)
C(3)-C(16)	1.5297(16)
C(5)-C(6)	1.4066(16)
C(5)-C(10)	1.4121(18)
C(6)-C(7)	1.3959(18)
C(6)-C(11)	1.5136(19)
C(7)-H(7)	0.9500
C(7)-C(8)	1.3812(19)
C(8)-C(9)	1.3904(17)
C(8)-C(12)	1.5075(18)
C(9)-H(9)	0.9500
C(9)-C(10)	1.3892(17)
C(10)-C(13)	1.5126(16)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

Table A13.1.3. (cont'd)

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(18)-C(19)	1.489(2)
C(19)-H(19)	0.9500
C(19)-C(20)	1.313(2)
C(20)-H(20A)	0.9500
C(20)-H(20B)	0.9500

C(4)-S(1)-C(1)	93.31(6)
C(14)-O(2)-C(15)	114.91(10)
C(16)-O(4)-C(17)	116.24(10)
C(4)-N(1)-C(18)	118.20(11)
S(1)-C(1)-H(1)	106.7
C(2)-C(1)-S(1)	105.80(9)
C(2)-C(1)-H(1)	106.7
C(5)-C(1)-S(1)	114.20(8)
C(5)-C(1)-H(1)	106.7
C(5)-C(1)-C(2)	116.22(10)
C(1)-C(2)-H(2A)	110.5
C(1)-C(2)-H(2B)	110.5
H(2A)-C(2)-H(2B)	108.7
C(3)-C(2)-C(1)	106.28(9)

Table A13.1.3. (cont'd)

C(3)-C(2)-H(2A)	110.5
C(3)-C(2)-H(2B)	110.5
C(2)-C(3)-C(4)	105.66(9)
C(2)-C(3)-C(14)	111.69(10)
C(4)-C(3)-C(14)	108.25(9)
C(16)-C(3)-C(2)	112.20(10)
C(16)-C(3)-C(4)	108.18(10)
C(16)-C(3)-C(14)	110.60(9)
N(1)-C(4)-S(1)	127.60(9)
N(1)-C(4)-C(3)	122.25(10)
C(3)-C(4)-S(1)	110.15(9)
C(6)-C(5)-C(1)	123.69(11)
C(6)-C(5)-C(10)	118.76(11)
C(10)-C(5)-C(1)	117.55(10)
C(5)-C(6)-C(11)	123.86(11)
C(7)-C(6)-C(5)	119.14(11)
C(7)-C(6)-C(11)	116.99(11)
C(6)-C(7)-H(7)	118.7
C(8)-C(7)-C(6)	122.59(11)
C(8)-C(7)-H(7)	118.7
C(7)-C(8)-C(9)	117.69(11)
C(7)-C(8)-C(12)	121.68(12)
C(9)-C(8)-C(12)	120.63(12)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-C(8)	121.88(11)
C(10)-C(9)-H(9)	119.1
C(5)-C(10)-C(13)	121.74(11)
C(9)-C(10)-C(5)	119.79(11)
C(9)-C(10)-C(13)	118.41(11)
C(6)-C(11)-H(11A)	109.5
C(6)-C(11)-H(11B)	109.5
C(6)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5

Table A13.1.3. (cont'd)

H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(1)-C(14)-O(2)	124.42(11)
O(1)-C(14)-C(3)	124.85(12)
O(2)-C(14)-C(3)	110.72(10)
O(2)-C(15)-H(15A)	109.5
O(2)-C(15)-H(15B)	109.5
O(2)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(3)-C(16)-O(4)	125.53(11)
O(3)-C(16)-C(3)	124.03(11)
O(4)-C(16)-C(3)	110.43(10)
O(4)-C(17)-H(17A)	109.5
O(4)-C(17)-H(17B)	109.5
O(4)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(1)-C(18)-H(18A)	109.0
N(1)-C(18)-H(18B)	109.0
N(1)-C(18)-C(19)	112.84(11)

Table A13.1.3. (cont'd)

H(18A)-C(18)-H(18B)	107.8
C(19)-C(18)-H(18A)	109.0
C(19)-C(18)-H(18B)	109.0
C(18)-C(19)-H(19)	117.1
C(20)-C(19)-C(18)	125.79(13)
C(20)-C(19)-H(19)	117.1
C(19)-C(20)-H(20A)	120.0
C(19)-C(20)-H(20B)	120.0
H(20A)-C(20)-H(20B)	120.0

Symmetry transformations used to generate equivalent atoms:

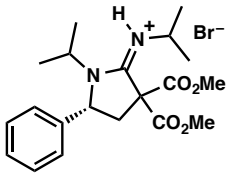
*Table A13.1.4. Anisotropic displacement parameters ($Å^2x10^3$) for Thioimidate **440**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	146(1)	147(1)	372(2)	67(1)	-20(1)	19(1)
O(1)	275(6)	192(4)	326(5)	-16(4)	-66(4)	-65(4)
O(2)	204(5)	218(4)	232(4)	-6(3)	-28(3)	-45(3)
O(3)	261(5)	201(4)	313(5)	-57(4)	-71(4)	32(4)
O(4)	175(5)	176(4)	300(5)	-10(3)	-55(3)	60(3)
N(1)	170(5)	157(4)	275(5)	8(4)	-34(4)	-1(4)
C(1)	140(6)	152(5)	228(5)	21(4)	-52(4)	-1(4)
C(2)	142(6)	134(5)	259(6)	23(4)	-55(4)	-3(4)
C(3)	136(6)	125(5)	245(5)	10(4)	-47(4)	5(4)
C(4)	160(6)	127(5)	256(6)	6(4)	-50(5)	11(4)
C(5)	138(5)	139(5)	181(5)	20(4)	-28(4)	4(4)
C(6)	174(6)	184(5)	173(5)	13(4)	-19(4)	7(4)
C(7)	185(6)	211(6)	210(5)	35(4)	-70(5)	-12(5)
C(8)	145(6)	157(5)	286(6)	54(4)	-41(5)	-6(4)
C(9)	177(6)	168(5)	237(5)	19(4)	25(5)	20(4)
C(10)	192(6)	127(5)	180(5)	16(4)	-14(4)	13(4)
C(11)	258(7)	331(7)	186(5)	-2(5)	10(5)	35(6)
C(12)	152(6)	289(7)	436(8)	87(6)	-65(6)	12(5)
C(13)	311(8)	249(6)	171(5)	-12(5)	-13(5)	31(5)
C(14)	130(6)	132(5)	272(6)	0(4)	-39(4)	27(4)
C(15)	236(7)	302(7)	241(6)	-38(5)	-11(5)	-12(5)
C(16)	158(6)	137(5)	248(6)	31(4)	-22(5)	14(4)
C(17)	232(7)	237(7)	401(8)	-37(6)	-48(6)	116(5)
C(18)	207(7)	182(5)	301(6)	22(5)	-30(5)	-21(5)
C(19)	219(7)	292(7)	309(7)	32(5)	-34(5)	-87(5)
C(20)	211(7)	391(8)	323(7)	-5(6)	2(6)	-20(6)

*Table A13.1.5. Hydrogen coordinates ($x10^3$) and isotropic displacement parameters ($Å^2x10^3$) for Thioimidate **440**.*

	x	y	z	U_{iso}
H(1)	622	645	518	21
H(2A)	631	504	490	22
H(2B)	641	510	296	22
H(7)	377	636	25	24
H(9)	320	682	492	23
H(11A)	516	576	-44	39
H(11B)	601	570	84	39
H(11C)	578	656	-2	39
H(12A)	227	677	81	44
H(12B)	221	740	230	44
H(12C)	195	645	255	44
H(13A)	424	663	704	37
H(13B)	522	701	665	37
H(13C)	509	603	672	37
H(15A)	839	538	896	39
H(15B)	745	496	949	39
H(15C)	748	593	910	39
H(17A)	907	335	441	44
H(17B)	994	382	520	44
H(17C)	968	394	330	44
H(18A)	899	735	211	28
H(18B)	834	697	68	28
H(19)	984	711	-34	33
H(20A)	1009	561	128	37
H(20B)	1072	599	-17	37

A13.2 X-Ray Crystal Structure Analysis of Amidine (*R*)-450•HBr



(R)-450·HBr

Contents

Figure A13.2.1. X-Ray Crystal Structure of Amidine ***(R)-450•HBr***

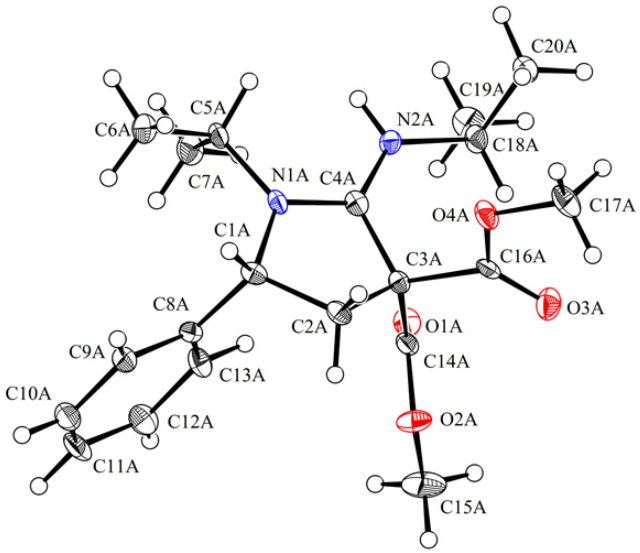


Table A13.2.1. Crystal Data and Structure Refinement for Amidine ***(R)-450•HBr***.

Caltech Identification Number	afg04
CCDC Deposition Number	911990
Empirical formula	C20 H31 Br N2 O5
Formula weight	459.38
Crystallization solvent	diethyl ether / dichloromethane
Crystal shape	prism
Crystal color	colourless
Crystal size	0.17 x 0.18 x 0.47 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 ≈ MO K	
Data collection temperature	100.15 K	
Theta range for 9397 reflections used in lattice determination	2.620 to 31.334∞	
Unit cell dimensions	a = 8.0748(6) ≈ b = 15.1323(12) ≈ c = 29.190(2) ≈	α= 98.815(5)∞ β= 92.189(5)∞ γ = 105.250(4)∞
Volume	3388.9(5) ≈^{3}	
Z	6	
Crystal system	triclinic	
Space group	P 1 (# 1)	
Density (calculated)	1.351 g/cm^3	
F(000)	1440	
Theta range for data collection	1.7 to 35.3∞	
Completeness to theta = 25.00∞	99.7%	
Index ranges	–12 ≤ h ≤ 12, –24 ≤ k ≤ 24, –46 ≤ l ≤ 45	
Data collection scan type	narrow and scans	
Reflections collected	161414	
Independent reflections	54469 [R_{int}= 0.0430]	
Reflections > 2σ(I)	44420	
Average σ(I)/(net I)	0.0781	
Absorption coefficient	1.85 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	

Table A13.2.1. (cont'd)

Max. and min. transmission	1.0000 and 0.8047
Reflections monitored for decay	0
Decay of standards	0%

Structure Solution and Refinement

Primary solution method	direct
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	54469 / 21 / 1585
Treatment of hydrogen atoms	mixed
Goodness-of-fit on F^2	1.65
Final R indices [I>2σ(I), 44420 reflections]	R1 = 0.0568, wR2 = 0.1138
R indices (all data)	R1 = 0.0743, wR2 = 0.1159
Type of weighting scheme used	calc
Weighting scheme used	calc w=1/[^2^(Fo^2^)+(0.0000P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	0.029(3)
Largest diff. peak and hole	3.05 and -1.34 e∑≈$^{-3}$

Programs Used

Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2_2011.2-3 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXS-97 (Sheldrick, 1990)
Structure refinement	
Graphics	

*Table A13.2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Amidine **(R)-450•HBr**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
O(1A)	5205(3)	3297(1)	8553(1)	18(1)
O(2A)	8042(3)	3464(1)	8523(1)	23(1)
O(3A)	7013(3)	1830(2)	9013(1)	23(1)
O(4A)	6394(3)	573(1)	8452(1)	19(1)
N(1A)	4511(3)	1542(2)	7520(1)	13(1)
N(2A)	2967(3)	1288(2)	8164(1)	14(1)
C(1A)	6285(4)	1836(2)	7379(1)	14(1)
C(2A)	7391(4)	1877(2)	7827(1)	14(1)
C(3A)	6203(4)	1976(2)	8227(1)	12(1)
C(4A)	4428(4)	1573(2)	7975(1)	14(1)
C(5A)	2951(4)	1256(2)	7188(1)	16(1)
C(6A)	3358(5)	925(2)	6694(1)	24(1)
C(7A)	2076(4)	2039(2)	7207(1)	23(1)
C(8A)	6672(4)	2728(2)	7175(1)	15(1)
C(9A)	7542(4)	2761(2)	6775(1)	18(1)
C(10A)	8003(4)	3575(2)	6590(1)	21(1)
C(11A)	7600(4)	4364(2)	6807(1)	23(1)
C(12A)	6731(4)	4340(2)	7206(1)	22(1)
C(13A)	6259(4)	3527(2)	7390(1)	18(1)
C(14A)	6408(4)	2992(2)	8455(1)	14(1)
C(15A)	8393(5)	4430(2)	8746(1)	34(1)
C(16A)	6583(4)	1461(2)	8621(1)	14(1)
C(17A)	6827(5)	27(2)	8784(1)	25(1)
C(18A)	2705(4)	1332(2)	8666(1)	18(1)
C(19A)	1333(5)	1853(2)	8773(1)	26(1)
C(20A)	2143(4)	350(2)	8781(1)	23(1)
O(1B)	2761(3)	3136(1)	5141(1)	17(1)
O(2B)	5580(3)	3478(1)	5045(1)	21(1)
O(3B)	5020(3)	2039(1)	5691(1)	20(1)

Table A13.2.2. (cont'd)

O(4B)	4388(3)	642(1)	5224(1)	15(1)
N(1B)	2497(3)	1144(2)	4168(1)	13(1)
N(2B)	861(3)	1029(2)	4810(1)	13(1)
C(1B)	4227(4)	1579(2)	4036(1)	12(1)
C(2B)	5323(4)	1771(2)	4507(1)	14(1)
C(3B)	4061(4)	1890(2)	4879(1)	11(1)
C(4B)	2345(4)	1315(2)	4624(1)	10(1)
C(5B)	1134(4)	495(2)	3828(1)	16(1)
C(6B)	1108(6)	-489(2)	3872(1)	34(1)
C(7B)	1377(5)	664(2)	3331(1)	25(1)
C(8B)	4279(4)	2426(2)	3819(1)	16(1)
C(9B)	5329(4)	2597(2)	3455(1)	20(1)
C(10B)	5427(5)	3384(2)	3252(1)	27(1)
C(11B)	4507(5)	4012(2)	3411(1)	27(1)
C(12B)	3444(5)	3838(2)	3769(1)	29(1)
C(13B)	3321(4)	3048(2)	3970(1)	21(1)
C(14B)	4016(4)	2910(2)	5039(1)	14(1)
C(15B)	5731(5)	4454(2)	5218(1)	35(1)
C(16B)	4545(4)	1538(2)	5321(1)	11(1)
C(17B)	4834(4)	217(2)	5610(1)	19(1)
C(18B)	562(4)	1128(2)	5308(1)	16(1)
C(19B)	-769(4)	1662(2)	5395(1)	24(1)
C(20B)	24(5)	159(2)	5438(1)	23(1)
O(1C)	7414(3)	3248(1)	1843(1)	18(1)
O(2C)	10170(3)	3462(1)	1676(1)	20(1)
O(3C)	9486(3)	1908(1)	2270(1)	18(1)
O(4C)	8375(3)	559(1)	1779(1)	17(1)
N(1C)	6577(3)	1420(2)	803(1)	12(1)
N(2C)	5107(3)	1248(2)	1469(1)	14(1)
C(1C)	8322(4)	1713(2)	645(1)	14(1)
C(2C)	9463(4)	1764(2)	1090(1)	14(1)
C(3C)	8351(4)	1926(2)	1498(1)	12(1)
C(4C)	6541(4)	1503(2)	1260(1)	12(1)
C(5C)	4995(4)	1095(2)	474(1)	16(1)

Table A13.2.2. (cont'd)

C(6C)	5401(5)	735(2)	-8(1)	25(1)
C(7C)	4090(4)	1873(2)	480(1)	23(1)
C(8C)	8674(4)	2610(2)	448(1)	14(1)
C(9C)	9607(4)	2662(2)	57(1)	17(1)
C(10C)	10051(4)	3492(2)	-124(1)	22(1)
C(11C)	9592(4)	4260(2)	85(1)	21(1)
C(12C)	8658(4)	4211(2)	475(1)	19(1)
C(13C)	8190(4)	3389(2)	650(1)	17(1)
C(14C)	8566(4)	2959(2)	1696(1)	15(1)
C(15C)	10528(5)	4459(2)	1838(1)	28(1)
C(16C)	8817(4)	1481(2)	1902(1)	13(1)
C(17C)	8809(5)	56(2)	2138(1)	24(1)
C(18C)	4905(4)	1339(2)	1975(1)	15(1)
C(19C)	3653(5)	1915(2)	2094(1)	24(1)
C(20C)	4316(4)	374(2)	2103(1)	20(1)
O(1D)	1240(3)	5108(1)	6240(1)	20(1)
O(2D)	3700(3)	4743(1)	6402(1)	20(1)
O(3D)	4660(3)	6149(1)	5724(1)	18(1)
O(4D)	5282(3)	7583(1)	6158(1)	16(1)
N(1D)	3160(3)	7177(2)	7194(1)	15(1)
N(2D)	1547(3)	7222(2)	6524(1)	14(1)
C(1D)	4426(4)	6735(2)	7354(1)	16(1)
C(2D)	5261(4)	6488(2)	6909(1)	15(1)
C(3D)	3823(4)	6343(2)	6516(1)	13(1)
C(4D)	2718(4)	6949(2)	6737(1)	12(1)
C(5D)	2529(5)	7876(2)	7495(1)	21(1)
C(6D)	3492(7)	8846(2)	7419(1)	44(1)
C(7D)	2737(6)	7782(3)	8001(1)	40(1)
C(8D)	3631(4)	5924(2)	7600(1)	16(1)
C(9D)	4577(4)	5780(2)	7978(1)	19(1)
C(10D)	3931(5)	5037(2)	8204(1)	24(1)
C(11D)	2319(5)	4419(2)	8048(1)	24(1)
C(12D)	1365(4)	4564(2)	7676(1)	24(1)
C(13D)	2023(4)	5321(2)	7453(1)	19(1)

Table A13.2.2. (cont'd)

C(14D)	2742(4)	5328(2)	6366(1)	14(1)
C(15D)	2805(5)	3759(2)	6283(1)	26(1)
C(16D)	4603(4)	6663(2)	6069(1)	18(1)
C(17D)	6055(4)	7985(2)	5766(1)	20(1)
C(18D)	1059(4)	7056(2)	6019(1)	16(1)
C(19D)	-850(4)	6519(2)	5928(1)	22(1)
C(20D)	1460(5)	7990(2)	5849(1)	23(1)
O(1E)	8189(3)	5002(1)	2884(1)	17(1)
O(2E)	10789(3)	4812(1)	3084(1)	20(1)
O(3E)	11510(3)	6349(1)	2459(1)	19(1)
O(4E)	11784(3)	7706(1)	2936(1)	16(1)
N(1E)	9306(3)	6863(2)	3901(1)	14(1)
N(2E)	7912(3)	7004(2)	3214(1)	13(1)
C(1E)	10840(4)	6612(2)	4078(1)	15(1)
C(2E)	11850(4)	6544(2)	3643(1)	16(1)
C(3E)	10485(4)	6346(2)	3224(1)	13(1)
C(4E)	9125(4)	6767(2)	3441(1)	12(1)
C(5E)	8093(4)	7202(2)	4207(1)	17(1)
C(6E)	8924(5)	7597(2)	4695(1)	24(1)
C(7E)	6434(4)	6429(2)	4205(1)	25(1)
C(8E)	10401(4)	5743(2)	4298(1)	14(1)
C(9E)	11448(4)	5716(2)	4684(1)	18(1)
C(10E)	11196(5)	4923(2)	4890(1)	24(1)
C(11E)	9887(4)	4130(2)	4696(1)	25(1)
C(12E)	8829(4)	4150(2)	4313(1)	22(1)
C(13E)	9087(4)	4951(2)	4113(1)	20(1)
C(14E)	9677(4)	5308(2)	3044(1)	13(1)
C(15E)	10098(5)	3806(2)	2945(1)	28(1)
C(16E)	11305(4)	6788(2)	2820(1)	13(1)
C(17E)	12685(5)	8211(2)	2588(1)	22(1)
C(18E)	7528(4)	6881(2)	2704(1)	14(1)
C(19E)	5668(4)	6298(2)	2585(1)	19(1)
C(20E)	7882(4)	7829(2)	2556(1)	20(1)
O(1F)	3235(3)	5134(1)	-412(1)	19(1)

Table A13.2.2. (cont'd)

O(2F)	5671(3)	4755(1)	-225(1)	18(1)
O(3F)	6672(3)	6143(1)	-899(1)	18(1)
O(4F)	7152(3)	7587(1)	-500(1)	16(1)
N(1F)	5150(3)	7135(2)	573(1)	13(1)
N(2F)	3519(3)	7236(2)	-81(1)	12(1)
C(1F)	6479(4)	6698(2)	719(1)	14(1)
C(2F)	7291(4)	6503(2)	261(1)	14(1)
C(3F)	5819(4)	6356(2)	-119(1)	12(1)
C(4F)	4727(4)	6948(2)	117(1)	12(1)
C(5F)	4508(5)	7803(2)	905(1)	21(1)
C(6F)	5459(6)	8792(2)	852(1)	36(1)
C(7F)	4692(5)	7654(2)	1401(1)	27(1)
C(8F)	5722(4)	5850(2)	939(1)	16(1)
C(9F)	6733(5)	5676(2)	1296(1)	21(1)
C(10F)	6146(5)	4885(2)	1498(1)	26(1)
C(11F)	4527(5)	4264(2)	1334(1)	32(1)
C(12F)	3517(5)	4448(2)	988(1)	30(1)
C(13F)	4112(4)	5250(2)	793(1)	22(1)
C(14F)	4735(4)	5344(2)	-269(1)	14(1)
C(15F)	4757(5)	3776(2)	-342(1)	23(1)
C(16F)	6572(4)	6673(2)	-552(1)	11(1)
C(17F)	7860(4)	7967(2)	-903(1)	20(1)
C(18F)	3033(4)	7127(2)	-582(1)	15(1)
C(19F)	1129(4)	6619(2)	-683(1)	21(1)
C(20F)	3407(5)	8094(2)	-714(1)	23(1)
Br(1A)	8079(1)	123(1)	6649(1)	21(1)
Br(1B)	6474(1)	134(1)	3290(1)	18(1)
Br(1C)	137(1)	-30(1)	-14(1)	21(1)
Br(1D)	8418(1)	8234(1)	7949(1)	23(1)
Br(1E)	4521(1)	8396(1)	4618(1)	20(1)
Br(1F)	358(1)	8210(1)	1391(1)	21(1)
O(5A)	9657(3)	349(1)	7734(1)	19(1)
O(5B)	7574(3)	112(2)	4381(1)	21(1)
O(5C)	1767(3)	255(2)	1077(1)	20(1)

Table A13.2.2. (cont'd)

O(5D)	9265(3)	8257(2)	6859(1)	25(1)
O(5E)	5655(3)	8046(1)	3544(1)	18(1)
O(5F)	1187(3)	8178(2)	296(1)	24(1)

Table A13.2.3. Bond lengths [Å] and angles [°] for Amidine ***(R)-450•HBr****.*

O(1A)-C(14A)	1.207(4)
O(2A)-C(14A)	1.316(4)
O(2A)-C(15A)	1.456(3)
O(3A)-C(16A)	1.189(3)
O(4A)-C(16A)	1.326(3)
O(4A)-C(17A)	1.454(4)
N(1A)-C(1A)	1.479(4)
N(1A)-C(4A)	1.327(3)
N(1A)-C(5A)	1.483(4)
N(2A)-H(2A)	0.8800
N(2A)-C(4A)	1.319(4)
N(2A)-C(18A)	1.482(4)
C(1A)-H(1A)	1.0000
C(1A)-C(2A)	1.539(4)
C(1A)-C(8A)	1.521(4)
C(2A)-H(2AA)	0.9900
C(2A)-H(2AB)	0.9900
C(2A)-C(3A)	1.555(4)
C(3A)-C(4A)	1.513(4)
C(3A)-C(14A)	1.541(4)
C(3A)-C(16A)	1.548(4)
C(5A)-H(5A)	1.0000
C(5A)-C(6A)	1.531(4)
C(5A)-C(7A)	1.527(4)
C(6A)-H(6AA)	0.9800
C(6A)-H(6AB)	0.9800
C(6A)-H(6AC)	0.9800
C(7A)-H(7AA)	0.9800
C(7A)-H(7AB)	0.9800
C(7A)-H(7AC)	0.9800
C(8A)-C(9A)	1.386(4)
C(8A)-C(13A)	1.401(4)
C(9A)-H(9A)	0.9500

Table A13.2.3. (cont'd)

C(9A)-C(10A)	1.388(4)
C(10A)-H(10A)	0.9500
C(10A)-C(11A)	1.386(5)
C(11A)-H(11A)	0.9500
C(11A)-C(12A)	1.382(4)
C(12A)-H(12A)	0.9500
C(12A)-C(13A)	1.385(4)
C(13A)-H(13A)	0.9500
C(15A)-H(15G)	0.9800
C(15A)-H(15H)	0.9800
C(15A)-H(15I)	0.9800
C(17A)-H(17G)	0.9800
C(17A)-H(17H)	0.9800
C(17A)-H(17I)	0.9800
C(18A)-H(18A)	1.0000
C(18A)-C(19A)	1.535(5)
C(18A)-C(20A)	1.529(4)
C(19A)-H(19G)	0.9800
C(19A)-H(19H)	0.9800
C(19A)-H(19I)	0.9800
C(20A)-H(20G)	0.9800
C(20A)-H(20H)	0.9800
C(20A)-H(20I)	0.9800
O(1B)-C(14B)	1.186(4)
O(2B)-C(14B)	1.325(3)
O(2B)-C(15B)	1.456(4)
O(3B)-C(16B)	1.204(3)
O(4B)-C(16B)	1.314(3)
O(4B)-C(17B)	1.458(3)
N(1B)-C(1B)	1.473(4)
N(1B)-C(4B)	1.332(3)
N(1B)-C(5B)	1.485(3)
N(2B)-H(2B)	0.8800
N(2B)-C(4B)	1.330(4)

Table A13.2.3. (cont'd)

N(2B)-C(18B)	1.473(3)
C(1B)-H(1B)	1.0000
C(1B)-C(2B)	1.552(4)
C(1B)-C(8B)	1.505(4)
C(2B)-H(2BA)	0.9900
C(2B)-H(2BB)	0.9900
C(2B)-C(3B)	1.540(4)
C(3B)-C(4B)	1.524(4)
C(3B)-C(14B)	1.552(4)
C(3B)-C(16B)	1.544(4)
C(5B)-H(5B)	1.0000
C(5B)-C(6B)	1.509(5)
C(5B)-C(7B)	1.523(4)
C(6B)-H(6BA)	0.9800
C(6B)-H(6BB)	0.9800
C(6B)-H(6BC)	0.9800
C(7B)-H(7BA)	0.9800
C(7B)-H(7BB)	0.9800
C(7B)-H(7BC)	0.9800
C(8B)-C(9B)	1.398(4)
C(8B)-C(13B)	1.401(4)
C(9B)-H(9B)	0.9500
C(9B)-C(10B)	1.395(4)
C(10B)-H(10B)	0.9500
C(10B)-C(11B)	1.391(5)
C(11B)-H(11B)	0.9500
C(11B)-C(12B)	1.391(5)
C(12B)-H(12B)	0.9500
C(12B)-C(13B)	1.393(4)
C(13B)-H(13B)	0.9500
C(15B)-H(15D)	0.9800
C(15B)-H(15E)	0.9800
C(15B)-H(15F)	0.9800
C(17B)-H(17D)	0.9800

Table A13.2.3. (cont'd)

C(17B)-H(17E)	0.9800
C(17B)-H(17F)	0.9800
C(18B)-H(18B)	1.0000
C(18B)-C(19B)	1.513(5)
C(18B)-C(20B)	1.527(4)
C(19B)-H(19D)	0.9800
C(19B)-H(19E)	0.9800
C(19B)-H(19F)	0.9800
C(20B)-H(20D)	0.9800
C(20B)-H(20E)	0.9800
C(20B)-H(20F)	0.9800
O(1C)-C(14C)	1.194(4)
O(2C)-C(14C)	1.327(4)
O(2C)-C(15C)	1.457(3)
O(3C)-C(16C)	1.192(3)
O(4C)-C(16C)	1.334(3)
O(4C)-C(17C)	1.470(4)
N(1C)-C(1C)	1.476(4)
N(1C)-C(4C)	1.322(3)
N(1C)-C(5C)	1.492(4)
N(2C)-H(2C)	0.8800
N(2C)-C(4C)	1.324(4)
N(2C)-C(18C)	1.481(3)
C(1C)-H(1C)	1.0000
C(1C)-C(2C)	1.544(4)
C(1C)-C(8C)	1.517(4)
C(2C)-H(2CA)	0.9900
C(2C)-H(2CB)	0.9900
C(2C)-C(3C)	1.546(4)
C(3C)-C(4C)	1.524(4)
C(3C)-C(14C)	1.544(4)
C(3C)-C(16C)	1.525(4)
C(5C)-H(5C)	1.0000
C(5C)-C(6C)	1.510(4)

Table A13.2.3. (cont'd)

C(5C)-C(7C)	1.539(4)
C(6C)-H(6CA)	0.9800
C(6C)-H(6CB)	0.9800
C(6C)-H(6CC)	0.9800
C(7C)-H(7CA)	0.9800
C(7C)-H(7CB)	0.9800
C(7C)-H(7CC)	0.9800
C(8C)-C(9C)	1.392(4)
C(8C)-C(13C)	1.391(4)
C(9C)-H(9C)	0.9500
C(9C)-C(10C)	1.403(4)
C(10C)-H(10C)	0.9500
C(10C)-C(11C)	1.373(5)
C(11C)-H(11C)	0.9500
C(11C)-C(12C)	1.390(4)
C(12C)-H(12C)	0.9500
C(12C)-C(13C)	1.383(4)
C(13C)-H(13C)	0.9500
C(15C)-H(15A)	0.9800
C(15C)-H(15B)	0.9800
C(15C)-H(15C)	0.9800
C(17C)-H(17A)	0.9800
C(17C)-H(17B)	0.9800
C(17C)-H(17C)	0.9800
C(18C)-H(18C)	1.0000
C(18C)-C(19C)	1.516(5)
C(18C)-C(20C)	1.522(4)
C(19C)-H(19A)	0.9800
C(19C)-H(19B)	0.9800
C(19C)-H(19C)	0.9800
C(20C)-H(20A)	0.9800
C(20C)-H(20B)	0.9800
C(20C)-H(20C)	0.9800
O(1D)-C(14D)	1.197(4)

Table A13.2.3. (cont'd)

O(2D)-C(14D)	1.333(4)
O(2D)-C(15D)	1.454(3)
O(3D)-C(16D)	1.184(4)
O(4D)-C(16D)	1.335(3)
O(4D)-C(17D)	1.462(3)
N(1D)-C(1D)	1.460(4)
N(1D)-C(4D)	1.335(3)
N(1D)-C(5D)	1.478(4)
N(2D)-H(2D)	0.8800
N(2D)-C(4D)	1.300(4)
N(2D)-C(18D)	1.477(4)
C(1D)-H(1D)	1.0000
C(1D)-C(2D)	1.529(4)
C(1D)-C(8D)	1.525(4)
C(2D)-H(2DA)	0.9900
C(2D)-H(2DB)	0.9900
C(2D)-C(3D)	1.549(4)
C(3D)-C(4D)	1.531(4)
C(3D)-C(14D)	1.541(4)
C(3D)-C(16D)	1.559(4)
C(5D)-H(5D)	1.0000
C(5D)-C(6D)	1.523(5)
C(5D)-C(7D)	1.514(4)
C(6D)-H(6DA)	0.9800
C(6D)-H(6DB)	0.9800
C(6D)-H(6DC)	0.9800
C(7D)-H(7DA)	0.9800
C(7D)-H(7DB)	0.9800
C(7D)-H(7DC)	0.9800
C(8D)-C(9D)	1.394(4)
C(8D)-C(13D)	1.384(4)
C(9D)-H(9D)	0.9500
C(9D)-C(10D)	1.385(4)
C(10D)-H(10D)	0.9500

Table A13.2.3. (cont'd)

C(10D)-C(11D)	1.400(5)
C(11D)-H(11D)	0.9500
C(11D)-C(12D)	1.384(5)
C(12D)-H(12D)	0.9500
C(12D)-C(13D)	1.397(4)
C(13D)-H(13D)	0.9500
C(15D)-H(15P)	0.9800
C(15D)-H(15Q)	0.9800
C(15D)-H(15R)	0.9800
C(17D)-H(17P)	0.9800
C(17D)-H(17Q)	0.9800
C(17D)-H(17R)	0.9800
C(18D)-H(18D)	1.0000
C(18D)-C(19D)	1.533(4)
C(18D)-C(20D)	1.527(4)
C(19D)-H(19P)	0.9800
C(19D)-H(19Q)	0.9800
C(19D)-H(19R)	0.9800
C(20D)-H(20P)	0.9800
C(20D)-H(20Q)	0.9800
C(20D)-H(20R)	0.9800
O(1E)-C(14E)	1.215(4)
O(2E)-C(14E)	1.325(4)
O(2E)-C(15E)	1.462(3)
O(3E)-C(16E)	1.200(3)
O(4E)-C(16E)	1.325(3)
O(4E)-C(17E)	1.465(3)
N(1E)-C(1E)	1.485(4)
N(1E)-C(4E)	1.327(3)
N(1E)-C(5E)	1.486(4)
N(2E)-H(2E)	0.8800
N(2E)-C(4E)	1.317(4)
N(2E)-C(18E)	1.481(4)
C(1E)-H(1E)	1.0000

Table A13.2.3. (cont'd)

C(1E)-C(2E)	1.541(4)
C(1E)-C(8E)	1.515(4)
C(2E)-H(2EA)	0.9900
C(2E)-H(2EB)	0.9900
C(2E)-C(3E)	1.553(4)
C(3E)-C(4E)	1.520(4)
C(3E)-C(14E)	1.533(4)
C(3E)-C(16E)	1.532(4)
C(5E)-H(5E)	1.0000
C(5E)-C(6E)	1.514(4)
C(5E)-C(7E)	1.528(4)
C(6E)-H(6EA)	0.9800
C(6E)-H(6EB)	0.9800
C(6E)-H(6EC)	0.9800
C(7E)-H(7EA)	0.9800
C(7E)-H(7EB)	0.9800
C(7E)-H(7EC)	0.9800
C(8E)-C(9E)	1.394(4)
C(8E)-C(13E)	1.394(4)
C(9E)-H(9E)	0.9500
C(9E)-C(10E)	1.396(4)
C(10E)-H(10E)	0.9500
C(10E)-C(11E)	1.398(5)
C(11E)-H(11E)	0.9500
C(11E)-C(12E)	1.390(5)
C(12E)-H(12E)	0.9500
C(12E)-C(13E)	1.396(4)
C(13E)-H(13E)	0.9500
C(15E)-H(15M)	0.9800
C(15E)-H(15N)	0.9800
C(15E)-H(15O)	0.9800
C(17E)-H(17M)	0.9800
C(17E)-H(17N)	0.9800
C(17E)-H(17O)	0.9800

Table A13.2.3. (cont'd)

C(18E)-H(18E)	1.0000
C(18E)-C(19E)	1.525(4)
C(18E)-C(20E)	1.520(4)
C(19E)-H(19M)	0.9800
C(19E)-H(19N)	0.9800
C(19E)-H(19O)	0.9800
C(20E)-H(20M)	0.9800
C(20E)-H(20N)	0.9800
C(20E)-H(20O)	0.9800
O(1F)-C(14F)	1.209(4)
O(2F)-C(14F)	1.328(4)
O(2F)-C(15F)	1.451(3)
O(3F)-C(16F)	1.212(3)
O(4F)-C(16F)	1.321(3)
O(4F)-C(17F)	1.459(3)
N(1F)-C(1F)	1.481(4)
N(1F)-C(4F)	1.329(3)
N(1F)-C(5F)	1.497(4)
N(2F)-H(2F)	0.8800
N(2F)-C(4F)	1.316(4)
N(2F)-C(18F)	1.473(3)
C(1F)-H(1F)	1.0000
C(1F)-C(2F)	1.533(4)
C(1F)-C(8F)	1.517(4)
C(2F)-H(2FA)	0.9900
C(2F)-H(2FB)	0.9900
C(2F)-C(3F)	1.542(4)
C(3F)-C(4F)	1.526(4)
C(3F)-C(14F)	1.537(4)
C(3F)-C(16F)	1.513(4)
C(5F)-H(5F)	1.0000
C(5F)-C(6F)	1.526(5)
C(5F)-C(7F)	1.506(4)
C(6F)-H(6FA)	0.9800

Table A13.2.3. (cont'd)

C(6F)-H(6FB)	0.9800
C(6F)-H(6FC)	0.9800
C(7F)-H(7FA)	0.9800
C(7F)-H(7FB)	0.9800
C(7F)-H(7FC)	0.9800
C(8F)-C(9F)	1.398(4)
C(8F)-C(13F)	1.383(4)
C(9F)-H(9F)	0.9500
C(9F)-C(10F)	1.394(4)
C(10F)-H(10F)	0.9500
C(10F)-C(11F)	1.410(5)
C(11F)-H(11F)	0.9500
C(11F)-C(12F)	1.381(6)
C(12F)-H(12F)	0.9500
C(12F)-C(13F)	1.397(4)
C(13F)-H(13F)	0.9500
C(15F)-H(15J)	0.9800
C(15F)-H(15K)	0.9800
C(15F)-H(15L)	0.9800
C(17F)-H(17J)	0.9800
C(17F)-H(17K)	0.9800
C(17F)-H(17L)	0.9800
C(18F)-H(18F)	1.0000
C(18F)-C(19F)	1.521(4)
C(18F)-C(20F)	1.527(4)
C(19F)-H(19J)	0.9800
C(19F)-H(19K)	0.9800
C(19F)-H(19L)	0.9800
C(20F)-H(20J)	0.9800
C(20F)-H(20K)	0.9800
C(20F)-H(20L)	0.9800
O(5A)-H(5AA)	0.846(17)
O(5A)-H(5AB)	0.830(17)
O(5B)-H(5BA)	0.863(17)

Table A13.2.3. (cont'd)

O(5B)-H(5BB)	0.845(17)
O(5C)-H(5CA)	0.882(17)
O(5C)-H(5CB)	0.850(17)
O(5D)-H(5DA)	0.874(18)
O(5D)-H(5DB)	0.895(17)
O(5E)-H(5EA)	0.857(17)
O(5E)-H(5EB)	0.891(17)
O(5F)-H(5FA)	0.866(19)
O(5F)-H(5FB)	0.896(18)

C(14A)-O(2A)-C(15A)	115.9(3)
C(16A)-O(4A)-C(17A)	115.2(2)
C(1A)-N(1A)-C(5A)	123.7(2)
C(4A)-N(1A)-C(1A)	113.8(2)
C(4A)-N(1A)-C(5A)	122.5(2)
C(4A)-N(2A)-H(2A)	116.3
C(4A)-N(2A)-C(18A)	127.4(3)
C(18A)-N(2A)-H(2A)	116.3
N(1A)-C(1A)-H(1A)	108.2
N(1A)-C(1A)-C(2A)	102.6(2)
N(1A)-C(1A)-C(8A)	113.9(2)
C(2A)-C(1A)-H(1A)	108.2
C(8A)-C(1A)-H(1A)	108.2
C(8A)-C(1A)-C(2A)	115.3(2)
C(1A)-C(2A)-H(2AA)	110.7
C(1A)-C(2A)-H(2AB)	110.7
C(1A)-C(2A)-C(3A)	105.2(2)
H(2AA)-C(2A)-H(2AB)	108.8
C(3A)-C(2A)-H(2AA)	110.7
C(3A)-C(2A)-H(2AB)	110.7
C(4A)-C(3A)-C(2A)	101.9(2)
C(4A)-C(3A)-C(14A)	109.6(2)
C(4A)-C(3A)-C(16A)	114.3(2)
C(14A)-C(3A)-C(2A)	113.6(2)

Table A13.2.3. (cont'd)

C(14A)-C(3A)-C(16A)	106.5(2)
C(16A)-C(3A)-C(2A)	111.1(2)
N(1A)-C(4A)-C(3A)	110.6(2)
N(2A)-C(4A)-N(1A)	122.7(3)
N(2A)-C(4A)-C(3A)	126.8(2)
N(1A)-C(5A)-H(5A)	107.5
N(1A)-C(5A)-C(6A)	111.8(3)
N(1A)-C(5A)-C(7A)	110.5(2)
C(6A)-C(5A)-H(5A)	107.5
C(7A)-C(5A)-H(5A)	107.5
C(7A)-C(5A)-C(6A)	111.9(3)
C(5A)-C(6A)-H(6AA)	109.5
C(5A)-C(6A)-H(6AB)	109.5
C(5A)-C(6A)-H(6AC)	109.5
H(6AA)-C(6A)-H(6AB)	109.5
H(6AA)-C(6A)-H(6AC)	109.5
H(6AB)-C(6A)-H(6AC)	109.5
C(5A)-C(7A)-H(7AA)	109.5
C(5A)-C(7A)-H(7AB)	109.5
C(5A)-C(7A)-H(7AC)	109.5
H(7AA)-C(7A)-H(7AB)	109.5
H(7AA)-C(7A)-H(7AC)	109.5
H(7AB)-C(7A)-H(7AC)	109.5
C(9A)-C(8A)-C(1A)	118.4(3)
C(9A)-C(8A)-C(13A)	119.2(3)
C(13A)-C(8A)-C(1A)	122.3(3)
C(8A)-C(9A)-H(9A)	119.8
C(8A)-C(9A)-C(10A)	120.4(3)
C(10A)-C(9A)-H(9A)	119.8
C(9A)-C(10A)-H(10A)	120.0
C(11A)-C(10A)-C(9A)	120.0(3)
C(11A)-C(10A)-H(10A)	120.0
C(10A)-C(11A)-H(11A)	119.9
C(12A)-C(11A)-C(10A)	120.1(3)

Table A13.2.3. (cont'd)

C(12A)-C(11A)-H(11A)	119.9
C(11A)-C(12A)-H(12A)	119.9
C(11A)-C(12A)-C(13A)	120.1(3)
C(13A)-C(12A)-H(12A)	119.9
C(8A)-C(13A)-H(13A)	119.9
C(12A)-C(13A)-C(8A)	120.1(3)
C(12A)-C(13A)-H(13A)	119.9
O(1A)-C(14A)-O(2A)	125.7(3)
O(1A)-C(14A)-C(3A)	123.3(3)
O(2A)-C(14A)-C(3A)	111.1(2)
O(2A)-C(15A)-H(15G)	109.5
O(2A)-C(15A)-H(15H)	109.5
O(2A)-C(15A)-H(15I)	109.5
H(15G)-C(15A)-H(15H)	109.5
H(15G)-C(15A)-H(15I)	109.5
H(15H)-C(15A)-H(15I)	109.5
O(3A)-C(16A)-O(4A)	126.2(3)
O(3A)-C(16A)-C(3A)	123.8(2)
O(4A)-C(16A)-C(3A)	110.0(2)
O(4A)-C(17A)-H(17G)	109.5
O(4A)-C(17A)-H(17H)	109.5
O(4A)-C(17A)-H(17I)	109.5
H(17G)-C(17A)-H(17H)	109.5
H(17G)-C(17A)-H(17I)	109.5
H(17H)-C(17A)-H(17I)	109.5
N(2A)-C(18A)-H(18A)	109.3
N(2A)-C(18A)-C(19A)	107.7(3)
N(2A)-C(18A)-C(20A)	109.9(2)
C(19A)-C(18A)-H(18A)	109.3
C(20A)-C(18A)-H(18A)	109.3
C(20A)-C(18A)-C(19A)	111.3(3)
C(18A)-C(19A)-H(19G)	109.5
C(18A)-C(19A)-H(19H)	109.5
C(18A)-C(19A)-H(19I)	109.5

Table A13.2.3. (cont'd)

H(19G)-C(19A)-H(19H)	109.5
H(19G)-C(19A)-H(19I)	109.5
H(19H)-C(19A)-H(19I)	109.5
C(18A)-C(20A)-H(20G)	109.5
C(18A)-C(20A)-H(20H)	109.5
C(18A)-C(20A)-H(20I)	109.5
H(20G)-C(20A)-H(20H)	109.5
H(20G)-C(20A)-H(20I)	109.5
H(20H)-C(20A)-H(20I)	109.5
C(14B)-O(2B)-C(15B)	115.1(3)
C(16B)-O(4B)-C(17B)	115.6(2)
C(1B)-N(1B)-C(5B)	122.4(2)
C(4B)-N(1B)-C(1B)	113.4(2)
C(4B)-N(1B)-C(5B)	123.9(2)
C(4B)-N(2B)-H(2B)	116.3
C(4B)-N(2B)-C(18B)	127.4(2)
C(18B)-N(2B)-H(2B)	116.3
N(1B)-C(1B)-H(1B)	109.3
N(1B)-C(1B)-C(2B)	101.5(2)
N(1B)-C(1B)-C(8B)	112.3(2)
C(2B)-C(1B)-H(1B)	109.3
C(8B)-C(1B)-H(1B)	109.3
C(8B)-C(1B)-C(2B)	114.9(2)
C(1B)-C(2B)-H(2BA)	110.8
C(1B)-C(2B)-H(2BB)	110.8
H(2BA)-C(2B)-H(2BB)	108.9
C(3B)-C(2B)-C(1B)	104.9(2)
C(3B)-C(2B)-H(2BA)	110.8
C(3B)-C(2B)-H(2BB)	110.8
C(2B)-C(3B)-C(14B)	114.4(2)
C(2B)-C(3B)-C(16B)	110.6(2)
C(4B)-C(3B)-C(2B)	101.5(2)
C(4B)-C(3B)-C(14B)	110.4(2)
C(4B)-C(3B)-C(16B)	113.9(2)

Table A13.2.3. (cont'd)

C(16B)-C(3B)-C(14B)	106.2(2)
N(1B)-C(4B)-C(3B)	110.4(2)
N(2B)-C(4B)-N(1B)	122.7(2)
N(2B)-C(4B)-C(3B)	126.9(2)
N(1B)-C(5B)-H(5B)	108.1
N(1B)-C(5B)-C(6B)	108.7(3)
N(1B)-C(5B)-C(7B)	112.4(2)
C(6B)-C(5B)-H(5B)	108.1
C(6B)-C(5B)-C(7B)	111.1(3)
C(7B)-C(5B)-H(5B)	108.1
C(5B)-C(6B)-H(6BA)	109.5
C(5B)-C(6B)-H(6BB)	109.5
C(5B)-C(6B)-H(6BC)	109.5
H(6BA)-C(6B)-H(6BB)	109.5
H(6BA)-C(6B)-H(6BC)	109.5
H(6BB)-C(6B)-H(6BC)	109.5
C(5B)-C(7B)-H(7BA)	109.5
C(5B)-C(7B)-H(7BB)	109.5
C(5B)-C(7B)-H(7BC)	109.5
H(7BA)-C(7B)-H(7BB)	109.5
H(7BA)-C(7B)-H(7BC)	109.5
H(7BB)-C(7B)-H(7BC)	109.5
C(9B)-C(8B)-C(1B)	118.6(3)
C(9B)-C(8B)-C(13B)	118.9(3)
C(13B)-C(8B)-C(1B)	122.4(3)
C(8B)-C(9B)-H(9B)	120.0
C(10B)-C(9B)-C(8B)	120.0(3)
C(10B)-C(9B)-H(9B)	120.0
C(9B)-C(10B)-H(10B)	119.6
C(11B)-C(10B)-C(9B)	120.8(3)
C(11B)-C(10B)-H(10B)	119.6
C(10B)-C(11B)-H(11B)	120.3
C(10B)-C(11B)-C(12B)	119.3(3)
C(12B)-C(11B)-H(11B)	120.3

Table A13.2.3. (cont'd)

C(11B)-C(12B)-H(12B)	119.9
C(11B)-C(12B)-C(13B)	120.2(3)
C(13B)-C(12B)-H(12B)	119.9
C(8B)-C(13B)-H(13B)	119.7
C(12B)-C(13B)-C(8B)	120.6(3)
C(12B)-C(13B)-H(13B)	119.7
O(1B)-C(14B)-O(2B)	125.7(3)
O(1B)-C(14B)-C(3B)	124.5(2)
O(2B)-C(14B)-C(3B)	109.8(2)
O(2B)-C(15B)-H(15D)	109.5
O(2B)-C(15B)-H(15E)	109.5
O(2B)-C(15B)-H(15F)	109.5
H(15D)-C(15B)-H(15E)	109.5
H(15D)-C(15B)-H(15F)	109.5
H(15E)-C(15B)-H(15F)	109.5
O(3B)-C(16B)-O(4B)	127.1(3)
O(3B)-C(16B)-C(3B)	123.2(2)
O(4B)-C(16B)-C(3B)	109.7(2)
O(4B)-C(17B)-H(17D)	109.5
O(4B)-C(17B)-H(17E)	109.5
O(4B)-C(17B)-H(17F)	109.5
H(17D)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17F)	109.5
H(17E)-C(17B)-H(17F)	109.5
N(2B)-C(18B)-H(18B)	108.8
N(2B)-C(18B)-C(19B)	108.8(3)
N(2B)-C(18B)-C(20B)	108.3(2)
C(19B)-C(18B)-H(18B)	108.8
C(19B)-C(18B)-C(20B)	113.3(3)
C(20B)-C(18B)-H(18B)	108.8
C(18B)-C(19B)-H(19D)	109.5
C(18B)-C(19B)-H(19E)	109.5
C(18B)-C(19B)-H(19F)	109.5
H(19D)-C(19B)-H(19E)	109.5

Table A13.2.3. (cont'd)

H(19D)-C(19B)-H(19F)	109.5
H(19E)-C(19B)-H(19F)	109.5
C(18B)-C(20B)-H(20D)	109.5
C(18B)-C(20B)-H(20E)	109.5
C(18B)-C(20B)-H(20F)	109.5
H(20D)-C(20B)-H(20E)	109.5
H(20D)-C(20B)-H(20F)	109.5
H(20E)-C(20B)-H(20F)	109.5
C(14C)-O(2C)-C(15C)	116.4(2)
C(16C)-O(4C)-C(17C)	114.6(2)
C(1C)-N(1C)-C(5C)	122.5(2)
C(4C)-N(1C)-C(1C)	114.1(2)
C(4C)-N(1C)-C(5C)	123.3(2)
C(4C)-N(2C)-H(2C)	116.0
C(4C)-N(2C)-C(18C)	128.0(2)
C(18C)-N(2C)-H(2C)	116.0
N(1C)-C(1C)-H(1C)	108.9
N(1C)-C(1C)-C(2C)	101.6(2)
N(1C)-C(1C)-C(8C)	113.8(2)
C(2C)-C(1C)-H(1C)	108.9
C(8C)-C(1C)-H(1C)	108.9
C(8C)-C(1C)-C(2C)	114.5(2)
C(1C)-C(2C)-H(2CA)	110.6
C(1C)-C(2C)-H(2CB)	110.6
C(1C)-C(2C)-C(3C)	105.5(2)
H(2CA)-C(2C)-H(2CB)	108.8
C(3C)-C(2C)-H(2CA)	110.6
C(3C)-C(2C)-H(2CB)	110.6
C(4C)-C(3C)-C(2C)	101.2(2)
C(4C)-C(3C)-C(14C)	109.0(2)
C(4C)-C(3C)-C(16C)	115.9(2)
C(14C)-C(3C)-C(2C)	114.2(2)
C(16C)-C(3C)-C(2C)	110.4(2)
C(16C)-C(3C)-C(14C)	106.4(2)

Table A13.2.3. (cont'd)

N(1C)-C(4C)-N(2C)	123.3(3)
N(1C)-C(4C)-C(3C)	110.4(2)
N(2C)-C(4C)-C(3C)	126.3(2)
N(1C)-C(5C)-H(5C)	107.5
N(1C)-C(5C)-C(6C)	111.3(3)
N(1C)-C(5C)-C(7C)	110.1(2)
C(6C)-C(5C)-H(5C)	107.5
C(6C)-C(5C)-C(7C)	112.6(3)
C(7C)-C(5C)-H(5C)	107.5
C(5C)-C(6C)-H(6CA)	109.5
C(5C)-C(6C)-H(6CB)	109.5
C(5C)-C(6C)-H(6CC)	109.5
H(6CA)-C(6C)-H(6CB)	109.5
H(6CA)-C(6C)-H(6CC)	109.5
H(6CB)-C(6C)-H(6CC)	109.5
C(5C)-C(7C)-H(7CA)	109.5
C(5C)-C(7C)-H(7CB)	109.5
C(5C)-C(7C)-H(7CC)	109.5
H(7CA)-C(7C)-H(7CB)	109.5
H(7CA)-C(7C)-H(7CC)	109.5
H(7CB)-C(7C)-H(7CC)	109.5
C(9C)-C(8C)-C(1C)	117.5(2)
C(13C)-C(8C)-C(1C)	123.6(2)
C(13C)-C(8C)-C(9C)	118.8(3)
C(8C)-C(9C)-H(9C)	120.0
C(8C)-C(9C)-C(10C)	119.9(3)
C(10C)-C(9C)-H(9C)	120.0
C(9C)-C(10C)-H(10C)	119.8
C(11C)-C(10C)-C(9C)	120.4(3)
C(11C)-C(10C)-H(10C)	119.8
C(10C)-C(11C)-H(11C)	120.0
C(10C)-C(11C)-C(12C)	119.9(3)
C(12C)-C(11C)-H(11C)	120.0
C(11C)-C(12C)-H(12C)	120.1

Table A13.2.3. (cont'd)

C(13C)-C(12C)-C(11C)	119.8(3)
C(13C)-C(12C)-H(12C)	120.1
C(8C)-C(13C)-H(13C)	119.4
C(12C)-C(13C)-C(8C)	121.1(3)
C(12C)-C(13C)-H(13C)	119.4
O(1C)-C(14C)-O(2C)	125.9(3)
O(1C)-C(14C)-C(3C)	123.2(3)
O(2C)-C(14C)-C(3C)	110.9(2)
O(2C)-C(15C)-H(15A)	109.5
O(2C)-C(15C)-H(15B)	109.5
O(2C)-C(15C)-H(15C)	109.5
H(15A)-C(15C)-H(15B)	109.5
H(15A)-C(15C)-H(15C)	109.5
H(15B)-C(15C)-H(15C)	109.5
O(3C)-C(16C)-O(4C)	126.0(3)
O(3C)-C(16C)-C(3C)	124.1(2)
O(4C)-C(16C)-C(3C)	109.9(2)
O(4C)-C(17C)-H(17A)	109.5
O(4C)-C(17C)-H(17B)	109.5
O(4C)-C(17C)-H(17C)	109.5
H(17A)-C(17C)-H(17B)	109.5
H(17A)-C(17C)-H(17C)	109.5
H(17B)-C(17C)-H(17C)	109.5
N(2C)-C(18C)-H(18C)	108.7
N(2C)-C(18C)-C(19C)	109.0(2)
N(2C)-C(18C)-C(20C)	109.0(2)
C(19C)-C(18C)-H(18C)	108.7
C(19C)-C(18C)-C(20C)	112.7(3)
C(20C)-C(18C)-H(18C)	108.7
C(18C)-C(19C)-H(19A)	109.5
C(18C)-C(19C)-H(19B)	109.5
C(18C)-C(19C)-H(19C)	109.5
H(19A)-C(19C)-H(19B)	109.5
H(19A)-C(19C)-H(19C)	109.5

Table A13.2.3. (cont'd)

H(19B)-C(19C)-H(19C)	109.5
C(18C)-C(20C)-H(20A)	109.5
C(18C)-C(20C)-H(20B)	109.5
C(18C)-C(20C)-H(20C)	109.5
H(20A)-C(20C)-H(20B)	109.5
H(20A)-C(20C)-H(20C)	109.5
H(20B)-C(20C)-H(20C)	109.5
C(14D)-O(2D)-C(15D)	115.9(3)
C(16D)-O(4D)-C(17D)	114.6(2)
C(1D)-N(1D)-C(5D)	123.8(2)
C(4D)-N(1D)-C(1D)	113.7(2)
C(4D)-N(1D)-C(5D)	122.3(2)
C(4D)-N(2D)-H(2D)	116.2
C(4D)-N(2D)-C(18D)	127.6(3)
C(18D)-N(2D)-H(2D)	116.2
N(1D)-C(1D)-H(1D)	108.5
N(1D)-C(1D)-C(2D)	102.4(2)
N(1D)-C(1D)-C(8D)	112.9(2)
C(2D)-C(1D)-H(1D)	108.5
C(8D)-C(1D)-H(1D)	108.5
C(8D)-C(1D)-C(2D)	115.6(2)
C(1D)-C(2D)-H(2DA)	110.9
C(1D)-C(2D)-H(2DB)	110.9
C(1D)-C(2D)-C(3D)	104.1(2)
H(2DA)-C(2D)-H(2DB)	109.0
C(3D)-C(2D)-H(2DA)	110.9
C(3D)-C(2D)-H(2DB)	110.9
C(2D)-C(3D)-C(16D)	110.7(2)
C(4D)-C(3D)-C(2D)	102.1(2)
C(4D)-C(3D)-C(14D)	111.0(2)
C(4D)-C(3D)-C(16D)	112.7(2)
C(14D)-C(3D)-C(2D)	114.5(2)
C(14D)-C(3D)-C(16D)	106.1(2)
N(1D)-C(4D)-C(3D)	109.1(2)

Table A13.2.3. (cont'd)

N(2D)-C(4D)-N(1D)	124.0(3)
N(2D)-C(4D)-C(3D)	126.9(2)
N(1D)-C(5D)-H(5D)	108.5
N(1D)-C(5D)-C(6D)	109.5(3)
N(1D)-C(5D)-C(7D)	111.0(3)
C(6D)-C(5D)-H(5D)	108.5
C(7D)-C(5D)-H(5D)	108.5
C(7D)-C(5D)-C(6D)	110.9(3)
C(5D)-C(6D)-H(6DA)	109.5
C(5D)-C(6D)-H(6DB)	109.5
C(5D)-C(6D)-H(6DC)	109.5
H(6DA)-C(6D)-H(6DB)	109.5
H(6DA)-C(6D)-H(6DC)	109.5
H(6DB)-C(6D)-H(6DC)	109.5
C(5D)-C(7D)-H(7DA)	109.5
C(5D)-C(7D)-H(7DB)	109.5
C(5D)-C(7D)-H(7DC)	109.5
H(7DA)-C(7D)-H(7DB)	109.5
H(7DA)-C(7D)-H(7DC)	109.5
H(7DB)-C(7D)-H(7DC)	109.5
C(9D)-C(8D)-C(1D)	118.6(3)
C(13D)-C(8D)-C(1D)	121.9(3)
C(13D)-C(8D)-C(9D)	119.5(3)
C(8D)-C(9D)-H(9D)	119.7
C(10D)-C(9D)-C(8D)	120.7(3)
C(10D)-C(9D)-H(9D)	119.7
C(9D)-C(10D)-H(10D)	120.3
C(9D)-C(10D)-C(11D)	119.5(3)
C(11D)-C(10D)-H(10D)	120.3
C(10D)-C(11D)-H(11D)	119.9
C(12D)-C(11D)-C(10D)	120.1(3)
C(12D)-C(11D)-H(11D)	119.9
C(11D)-C(12D)-H(12D)	120.1
C(11D)-C(12D)-C(13D)	119.9(3)

Table A13.2.3. (cont'd)

C(13D)-C(12D)-H(12D)	120.1
C(8D)-C(13D)-C(12D)	120.3(3)
C(8D)-C(13D)-H(13D)	119.9
C(12D)-C(13D)-H(13D)	119.9
O(1D)-C(14D)-O(2D)	125.5(3)
O(1D)-C(14D)-C(3D)	123.7(3)
O(2D)-C(14D)-C(3D)	110.8(2)
O(2D)-C(15D)-H(15P)	109.5
O(2D)-C(15D)-H(15Q)	109.5
O(2D)-C(15D)-H(15R)	109.5
H(15P)-C(15D)-H(15Q)	109.5
H(15P)-C(15D)-H(15R)	109.5
H(15Q)-C(15D)-H(15R)	109.5
O(3D)-C(16D)-O(4D)	127.4(3)
O(3D)-C(16D)-C(3D)	124.0(3)
O(4D)-C(16D)-C(3D)	108.5(2)
O(4D)-C(17D)-H(17P)	109.5
O(4D)-C(17D)-H(17Q)	109.5
O(4D)-C(17D)-H(17R)	109.5
H(17P)-C(17D)-H(17Q)	109.5
H(17P)-C(17D)-H(17R)	109.5
H(17Q)-C(17D)-H(17R)	109.5
N(2D)-C(18D)-H(18D)	108.8
N(2D)-C(18D)-C(19D)	108.8(2)
N(2D)-C(18D)-C(20D)	108.8(2)
C(19D)-C(18D)-H(18D)	108.8
C(20D)-C(18D)-H(18D)	108.8
C(20D)-C(18D)-C(19D)	112.7(3)
C(18D)-C(19D)-H(19P)	109.5
C(18D)-C(19D)-H(19Q)	109.5
C(18D)-C(19D)-H(19R)	109.5
H(19P)-C(19D)-H(19Q)	109.5
H(19P)-C(19D)-H(19R)	109.5
H(19Q)-C(19D)-H(19R)	109.5

Table A13.2.3. (cont'd)

C(18D)-C(20D)-H(20P)	109.5
C(18D)-C(20D)-H(20Q)	109.5
C(18D)-C(20D)-H(20R)	109.5
H(20P)-C(20D)-H(20Q)	109.5
H(20P)-C(20D)-H(20R)	109.5
H(20Q)-C(20D)-H(20R)	109.5
C(14E)-O(2E)-C(15E)	115.7(2)
C(16E)-O(4E)-C(17E)	115.6(2)
C(1E)-N(1E)-C(5E)	123.7(2)
C(4E)-N(1E)-C(1E)	113.6(2)
C(4E)-N(1E)-C(5E)	122.7(3)
C(4E)-N(2E)-H(2E)	116.0
C(4E)-N(2E)-C(18E)	128.1(3)
C(18E)-N(2E)-H(2E)	116.0
N(1E)-C(1E)-H(1E)	108.6
N(1E)-C(1E)-C(2E)	102.3(2)
N(1E)-C(1E)-C(8E)	113.7(2)
C(2E)-C(1E)-H(1E)	108.6
C(8E)-C(1E)-H(1E)	108.6
C(8E)-C(1E)-C(2E)	114.8(2)
C(1E)-C(2E)-H(2EA)	110.7
C(1E)-C(2E)-H(2EB)	110.7
C(1E)-C(2E)-C(3E)	105.2(2)
H(2EA)-C(2E)-H(2EB)	108.8
C(3E)-C(2E)-H(2EA)	110.7
C(3E)-C(2E)-H(2EB)	110.7
C(4E)-C(3E)-C(2E)	101.4(2)
C(4E)-C(3E)-C(14E)	109.2(2)
C(4E)-C(3E)-C(16E)	114.9(2)
C(14E)-C(3E)-C(2E)	113.6(2)
C(16E)-C(3E)-C(2E)	109.9(2)
C(16E)-C(3E)-C(14E)	107.9(2)
N(1E)-C(4E)-C(3E)	110.5(2)
N(2E)-C(4E)-N(1E)	123.4(3)

Table A13.2.3. (cont'd)

N(2E)-C(4E)-C(3E)	126.1(2)
N(1E)-C(5E)-H(5E)	107.7
N(1E)-C(5E)-C(6E)	111.4(3)
N(1E)-C(5E)-C(7E)	110.5(2)
C(6E)-C(5E)-H(5E)	107.7
C(6E)-C(5E)-C(7E)	111.8(3)
C(7E)-C(5E)-H(5E)	107.7
C(5E)-C(6E)-H(6EA)	109.5
C(5E)-C(6E)-H(6EB)	109.5
C(5E)-C(6E)-H(6EC)	109.5
H(6EA)-C(6E)-H(6EB)	109.5
H(6EA)-C(6E)-H(6EC)	109.5
H(6EB)-C(6E)-H(6EC)	109.5
C(5E)-C(7E)-H(7EA)	109.5
C(5E)-C(7E)-H(7EB)	109.5
C(5E)-C(7E)-H(7EC)	109.5
H(7EA)-C(7E)-H(7EB)	109.5
H(7EA)-C(7E)-H(7EC)	109.5
H(7EB)-C(7E)-H(7EC)	109.5
C(9E)-C(8E)-C(1E)	117.9(2)
C(13E)-C(8E)-C(1E)	123.2(3)
C(13E)-C(8E)-C(9E)	118.8(3)
C(8E)-C(9E)-H(9E)	119.2
C(8E)-C(9E)-C(10E)	121.6(3)
C(10E)-C(9E)-H(9E)	119.2
C(9E)-C(10E)-H(10E)	120.6
C(9E)-C(10E)-C(11E)	118.8(3)
C(11E)-C(10E)-H(10E)	120.6
C(10E)-C(11E)-H(11E)	120.0
C(12E)-C(11E)-C(10E)	120.0(3)
C(12E)-C(11E)-H(11E)	120.0
C(11E)-C(12E)-H(12E)	119.8
C(11E)-C(12E)-C(13E)	120.5(3)
C(13E)-C(12E)-H(12E)	119.8

Table A13.2.3. (cont'd)

C(8E)-C(13E)-C(12E)	120.2(3)
C(8E)-C(13E)-H(13E)	119.9
C(12E)-C(13E)-H(13E)	119.9
O(1E)-C(14E)-O(2E)	125.6(2)
O(1E)-C(14E)-C(3E)	122.3(3)
O(2E)-C(14E)-C(3E)	112.1(2)
O(2E)-C(15E)-H(15M)	109.5
O(2E)-C(15E)-H(15N)	109.5
O(2E)-C(15E)-H(15O)	109.5
H(15M)-C(15E)-H(15N)	109.5
H(15M)-C(15E)-H(15O)	109.5
H(15N)-C(15E)-H(15O)	109.5
O(3E)-C(16E)-O(4E)	126.0(3)
O(3E)-C(16E)-C(3E)	123.6(2)
O(4E)-C(16E)-C(3E)	110.3(2)
O(4E)-C(17E)-H(17M)	109.5
O(4E)-C(17E)-H(17N)	109.5
O(4E)-C(17E)-H(17O)	109.5
H(17M)-C(17E)-H(17N)	109.5
H(17M)-C(17E)-H(17O)	109.5
H(17N)-C(17E)-H(17O)	109.5
N(2E)-C(18E)-H(18E)	108.7
N(2E)-C(18E)-C(19E)	108.1(2)
N(2E)-C(18E)-C(20E)	109.4(2)
C(19E)-C(18E)-H(18E)	108.7
C(20E)-C(18E)-H(18E)	108.7
C(20E)-C(18E)-C(19E)	113.2(3)
C(18E)-C(19E)-H(19M)	109.5
C(18E)-C(19E)-H(19N)	109.5
C(18E)-C(19E)-H(19O)	109.5
H(19M)-C(19E)-H(19N)	109.5
H(19M)-C(19E)-H(19O)	109.5
H(19N)-C(19E)-H(19O)	109.5
C(18E)-C(20E)-H(20M)	109.5

Table A13.2.3. (cont'd)

C(18E)-C(20E)-H(20N)	109.5
C(18E)-C(20E)-H(20O)	109.5
H(20M)-C(20E)-H(20N)	109.5
H(20M)-C(20E)-H(20O)	109.5
H(20N)-C(20E)-H(20O)	109.5
C(14F)-O(2F)-C(15F)	115.7(2)
C(16F)-O(4F)-C(17F)	116.4(2)
C(1F)-N(1F)-C(5F)	122.3(2)
C(4F)-N(1F)-C(1F)	113.4(2)
C(4F)-N(1F)-C(5F)	123.9(2)
C(4F)-N(2F)-H(2F)	116.3
C(4F)-N(2F)-C(18F)	127.5(2)
C(18F)-N(2F)-H(2F)	116.3
N(1F)-C(1F)-H(1F)	109.2
N(1F)-C(1F)-C(2F)	101.6(2)
N(1F)-C(1F)-C(8F)	112.3(2)
C(2F)-C(1F)-H(1F)	109.2
C(8F)-C(1F)-H(1F)	109.2
C(8F)-C(1F)-C(2F)	115.1(2)
C(1F)-C(2F)-H(2FA)	110.9
C(1F)-C(2F)-H(2FB)	110.9
C(1F)-C(2F)-C(3F)	104.4(2)
H(2FA)-C(2F)-H(2FB)	108.9
C(3F)-C(2F)-H(2FA)	110.9
C(3F)-C(2F)-H(2FB)	110.9
C(4F)-C(3F)-C(2F)	101.8(2)
C(4F)-C(3F)-C(14F)	110.5(2)
C(14F)-C(3F)-C(2F)	115.0(2)
C(16F)-C(3F)-C(2F)	109.2(2)
C(16F)-C(3F)-C(4F)	114.2(2)
C(16F)-C(3F)-C(14F)	106.4(2)
N(1F)-C(4F)-C(3F)	109.5(2)
N(2F)-C(4F)-N(1F)	123.0(3)
N(2F)-C(4F)-C(3F)	127.5(2)

Table A13.2.3. (cont'd)

N(1F)-C(5F)-H(5F)	108.0
N(1F)-C(5F)-C(6F)	108.8(3)
N(1F)-C(5F)-C(7F)	112.4(3)
C(6F)-C(5F)-H(5F)	108.0
C(7F)-C(5F)-H(5F)	108.0
C(7F)-C(5F)-C(6F)	111.4(3)
C(5F)-C(6F)-H(6FA)	109.5
C(5F)-C(6F)-H(6FB)	109.5
C(5F)-C(6F)-H(6FC)	109.5
H(6FA)-C(6F)-H(6FB)	109.5
H(6FA)-C(6F)-H(6FC)	109.5
H(6FB)-C(6F)-H(6FC)	109.5
C(5F)-C(7F)-H(7FA)	109.5
C(5F)-C(7F)-H(7FB)	109.5
C(5F)-C(7F)-H(7FC)	109.5
H(7FA)-C(7F)-H(7FB)	109.5
H(7FA)-C(7F)-H(7FC)	109.5
H(7FB)-C(7F)-H(7FC)	109.5
C(9F)-C(8F)-C(1F)	117.4(3)
C(13F)-C(8F)-C(1F)	122.6(3)
C(13F)-C(8F)-C(9F)	120.0(3)
C(8F)-C(9F)-H(9F)	119.9
C(10F)-C(9F)-C(8F)	120.3(3)
C(10F)-C(9F)-H(9F)	119.9
C(9F)-C(10F)-H(10F)	120.5
C(9F)-C(10F)-C(11F)	119.0(3)
C(11F)-C(10F)-H(10F)	120.5
C(10F)-C(11F)-H(11F)	119.7
C(12F)-C(11F)-C(10F)	120.6(3)
C(12F)-C(11F)-H(11F)	119.7
C(11F)-C(12F)-H(12F)	120.1
C(11F)-C(12F)-C(13F)	119.8(3)
C(13F)-C(12F)-H(12F)	120.1
C(8F)-C(13F)-C(12F)	120.3(3)

Table A13.2.3. (cont'd)

C(8F)-C(13F)-H(13F)	119.8
C(12F)-C(13F)-H(13F)	119.8
O(1F)-C(14F)-O(2F)	125.8(2)
O(1F)-C(14F)-C(3F)	123.1(3)
O(2F)-C(14F)-C(3F)	111.1(2)
O(2F)-C(15F)-H(15J)	109.5
O(2F)-C(15F)-H(15K)	109.5
O(2F)-C(15F)-H(15L)	109.5
H(15J)-C(15F)-H(15K)	109.5
H(15J)-C(15F)-H(15L)	109.5
H(15K)-C(15F)-H(15L)	109.5
O(3F)-C(16F)-O(4F)	124.5(2)
O(3F)-C(16F)-C(3F)	123.4(2)
O(4F)-C(16F)-C(3F)	112.0(2)
O(4F)-C(17F)-H(17J)	109.5
O(4F)-C(17F)-H(17K)	109.5
O(4F)-C(17F)-H(17L)	109.5
H(17J)-C(17F)-H(17K)	109.5
H(17J)-C(17F)-H(17L)	109.5
H(17K)-C(17F)-H(17L)	109.5
N(2F)-C(18F)-H(18F)	109.5
N(2F)-C(18F)-C(19F)	109.5(2)
N(2F)-C(18F)-C(20F)	108.1(2)
C(19F)-C(18F)-H(18F)	109.5
C(19F)-C(18F)-C(20F)	110.7(3)
C(20F)-C(18F)-H(18F)	109.5
C(18F)-C(19F)-H(19J)	109.5
C(18F)-C(19F)-H(19K)	109.5
C(18F)-C(19F)-H(19L)	109.5
H(19J)-C(19F)-H(19K)	109.5
H(19J)-C(19F)-H(19L)	109.5
H(19K)-C(19F)-H(19L)	109.5
C(18F)-C(20F)-H(20J)	109.5
C(18F)-C(20F)-H(20K)	109.5

Table A13.2.3. (cont'd)

C(18F)-C(20F)-H(20L)	109.5
H(20J)-C(20F)-H(20K)	109.5
H(20J)-C(20F)-H(20L)	109.5
H(20K)-C(20F)-H(20L)	109.5
H(5AA)-O(5A)-H(5AB)	117(3)
H(5BA)-O(5B)-H(5BB)	113(3)
H(5CA)-O(5C)-H(5CB)	109(2)
H(5DA)-O(5D)-H(5DB)	105(2)
H(5EA)-O(5E)-H(5EB)	107(2)
H(5FA)-O(5F)-H(5FB)	107(4)

Symmetry transformations used to generate equivalent atoms:

Table A13.2.4. Anisotropic displacement parameters ($Å^2x10^3$) for Amidine ***(R)-450•HBr****. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	246(12)	132(9)	182(10)	11(8)	35(9)	80(8)
O(2A)	202(12)	132(9)	284(12)	-45(8)	-6(10)	-9(8)
O(3A)	331(14)	195(10)	173(11)	39(8)	-26(9)	90(9)
O(4A)	285(12)	137(9)	176(10)	71(8)	42(9)	65(8)
N(1A)	177(13)	123(10)	105(10)	40(8)	46(9)	41(9)
N(2A)	155(12)	152(11)	102(10)	1(8)	21(9)	42(9)
C(1A)	149(14)	90(11)	175(13)	15(9)	50(11)	44(10)
C(2A)	140(14)	140(12)	166(13)	42(10)	68(11)	49(10)
C(3A)	147(14)	99(11)	127(12)	30(9)	28(10)	48(9)
C(4A)	192(15)	94(11)	134(12)	6(9)	48(11)	67(10)
C(5A)	163(15)	194(13)	128(13)	75(10)	35(11)	34(11)
C(6A)	268(18)	294(16)	135(14)	33(12)	30(13)	16(14)
C(7A)	220(17)	257(16)	255(16)	115(13)	-14(13)	95(13)
C(8A)	149(14)	127(12)	145(13)	25(10)	14(11)	4(10)
C(9A)	168(15)	212(14)	163(13)	51(11)	30(11)	29(11)
C(10A)	199(16)	235(15)	212(15)	95(12)	31(12)	45(12)
C(11A)	228(17)	202(14)	290(17)	162(12)	62(14)	43(12)
C(12A)	259(17)	168(13)	260(16)	73(11)	35(13)	94(12)
C(13A)	190(16)	203(13)	187(14)	96(11)	63(12)	100(11)
C(14A)	140(14)	141(12)	161(13)	67(10)	21(11)	28(10)
C(15A)	360(20)	110(13)	450(20)	-96(14)	49(18)	-22(13)
C(16A)	117(14)	129(12)	180(13)	69(10)	40(11)	3(10)
C(17A)	302(19)	203(14)	296(17)	153(13)	75(14)	93(13)
C(18A)	193(16)	232(14)	115(13)	25(11)	59(11)	65(12)
C(19A)	259(18)	254(16)	277(17)	30(13)	97(14)	104(14)
C(20A)	185(16)	288(16)	213(16)	120(12)	7(13)	4(13)
O(1B)	177(11)	139(9)	201(11)	-4(8)	21(9)	82(8)
O(2B)	154(11)	78(8)	366(13)	-25(8)	34(10)	-8(7)
O(3B)	257(12)	180(10)	138(10)	-21(8)	-66(9)	43(9)
O(4B)	246(12)	108(8)	107(9)	31(7)	-2(8)	55(8)
N(1B)	116(12)	124(10)	121(10)	30(8)	7(9)	-3(8)

Table A13.2.4. (cont'd)

N(2B)	113(12)	158(11)	100(10)	4(8)	13(9)	1(9)
C(1B)	119(13)	108(11)	130(12)	20(9)	38(10)	4(9)
C(2B)	114(13)	121(11)	168(13)	28(10)	7(11)	21(10)
C(3B)	104(13)	107(11)	104(11)	5(9)	-30(10)	13(9)
C(4B)	115(13)	72(10)	113(12)	21(9)	9(10)	35(9)
C(5B)	144(14)	199(13)	96(12)	-27(10)	6(10)	-10(11)
C(6B)	490(20)	151(14)	245(17)	-70(12)	-74(17)	-43(15)
C(7B)	207(17)	349(18)	140(14)	29(12)	38(12)	-12(14)
C(8B)	162(15)	128(12)	167(13)	19(10)	-22(11)	-9(10)
C(9B)	205(16)	190(14)	179(14)	59(11)	19(12)	-31(12)
C(10B)	277(19)	219(15)	241(16)	117(12)	7(14)	-80(13)
C(11B)	350(20)	161(14)	267(17)	92(12)	-67(15)	-32(13)
C(12B)	400(20)	211(15)	274(18)	68(13)	-41(15)	112(14)
C(13B)	270(18)	165(13)	208(15)	52(11)	16(13)	69(12)
C(14B)	155(14)	87(11)	158(13)	29(9)	11(11)	16(10)
C(15B)	340(20)	73(13)	550(20)	-81(14)	87(18)	-24(13)
C(16B)	122(13)	81(11)	116(12)	1(9)	15(10)	-4(9)
C(17B)	277(17)	193(13)	122(13)	67(10)	20(12)	100(12)
C(18B)	198(16)	172(13)	74(12)	-18(10)	23(11)	7(11)
C(19B)	122(15)	279(16)	282(17)	-48(13)	56(13)	44(12)
C(20B)	232(17)	285(16)	180(15)	103(12)	63(13)	32(13)
O(1C)	224(12)	106(9)	222(11)	35(8)	32(9)	54(8)
O(2C)	191(12)	114(9)	264(11)	14(8)	58(9)	-16(8)
O(3C)	211(12)	148(9)	152(10)	8(7)	-45(8)	31(8)
O(4C)	276(12)	117(9)	126(9)	37(7)	7(8)	61(8)
N(1C)	160(12)	110(10)	107(10)	28(8)	49(9)	39(9)
N(2C)	150(12)	162(11)	83(10)	17(8)	14(9)	30(9)
C(1C)	205(15)	133(12)	116(12)	57(10)	76(11)	71(11)
C(2C)	175(15)	139(12)	130(12)	40(9)	53(11)	63(10)
C(3C)	117(13)	100(11)	131(12)	9(9)	13(10)	27(9)
C(4C)	156(14)	80(11)	120(12)	33(9)	20(10)	37(10)
C(5C)	183(15)	176(13)	95(12)	27(10)	4(11)	27(11)
C(6C)	291(19)	258(16)	136(14)	-22(12)	0(13)	3(13)
C(7C)	197(17)	208(14)	280(17)	79(12)	-25(13)	51(12)

Table A13.2.4. (cont'd)

C(8C)	176(15)	122(12)	119(12)	32(9)	19(11)	39(10)
C(9C)	222(16)	183(13)	124(13)	54(10)	83(11)	51(11)
C(10C)	269(18)	221(14)	201(15)	137(12)	107(13)	49(13)
C(11C)	280(18)	154(13)	213(15)	108(11)	56(13)	43(12)
C(12C)	275(17)	124(12)	199(14)	51(10)	31(12)	73(11)
C(13C)	246(17)	155(13)	161(13)	49(10)	98(12)	102(11)
C(14C)	205(15)	111(12)	96(12)	29(9)	1(11)	-5(10)
C(15C)	320(20)	139(13)	348(19)	12(12)	154(16)	-19(13)
C(16C)	98(14)	131(12)	192(14)	64(10)	31(11)	54(10)
C(17C)	350(20)	200(14)	228(15)	150(12)	56(14)	115(13)
C(18C)	160(15)	214(13)	83(12)	53(10)	0(10)	29(11)
C(19C)	311(19)	283(16)	89(13)	-87(11)	12(12)	92(14)
C(20C)	206(16)	223(15)	157(14)	76(11)	13(12)	10(12)
O(1D)	206(12)	167(10)	223(11)	30(8)	2(9)	26(8)
O(2D)	223(12)	110(9)	280(12)	53(8)	49(9)	69(8)
O(3D)	225(12)	131(9)	181(10)	15(8)	12(9)	35(8)
O(4D)	216(11)	87(8)	170(10)	36(7)	16(8)	4(8)
N(1D)	224(14)	153(11)	80(10)	19(8)	-16(9)	79(9)
N(2D)	181(13)	132(10)	105(10)	19(8)	5(9)	63(9)
C(1D)	184(15)	166(13)	128(13)	35(10)	-17(11)	64(11)
C(2D)	134(14)	177(13)	175(13)	64(10)	-15(11)	77(11)
C(3D)	118(13)	113(11)	148(13)	17(9)	2(10)	22(10)
C(4D)	167(14)	70(10)	127(12)	23(9)	-21(10)	26(10)
C(5D)	310(18)	229(14)	132(13)	-30(11)	-18(12)	167(13)
C(6D)	750(30)	164(15)	360(20)	-54(14)	0(20)	124(18)
C(7D)	780(30)	490(20)	120(15)	39(14)	63(17)	510(20)
C(8D)	174(15)	148(12)	171(13)	43(10)	-12(11)	77(11)
C(9D)	209(16)	158(13)	192(14)	28(11)	-26(12)	59(11)
C(10D)	312(19)	235(15)	202(15)	74(12)	-17(14)	108(13)
C(11D)	308(19)	221(15)	211(15)	116(12)	57(14)	76(13)
C(12D)	223(17)	249(15)	206(15)	93(12)	-12(13)	-12(13)
C(13D)	159(15)	240(14)	152(14)	86(11)	-33(11)	2(12)
C(14D)	174(15)	132(12)	115(12)	57(9)	36(11)	20(10)
C(15D)	330(20)	115(13)	308(18)	33(12)	31(15)	43(12)

Table A13.2.4. (cont'd)

C(16D)	137(15)	141(13)	296(17)	48(12)	79(13)	57(11)
C(17D)	227(17)	170(13)	199(15)	86(11)	30(12)	31(12)
C(18D)	166(15)	187(13)	120(13)	29(10)	-25(11)	64(11)
C(19D)	229(17)	246(15)	180(15)	49(12)	-67(13)	67(13)
C(20D)	274(18)	202(14)	207(15)	74(12)	-23(13)	51(12)
O(1E)	127(11)	105(9)	242(11)	17(8)	-31(9)	-22(7)
O(2E)	186(11)	130(9)	271(12)	11(8)	-32(9)	54(8)
O(3E)	205(12)	141(9)	192(10)	5(8)	50(9)	13(8)
O(4E)	206(11)	121(9)	142(9)	41(7)	-18(8)	-3(8)
N(1E)	182(13)	111(10)	108(11)	17(8)	-20(9)	32(9)
N(2E)	147(12)	147(11)	117(11)	22(8)	4(9)	62(9)
C(1E)	146(14)	134(12)	139(13)	24(10)	-37(11)	-6(10)
C(2E)	113(14)	146(12)	192(14)	63(10)	-21(11)	-20(10)
C(3E)	118(13)	97(11)	149(12)	26(9)	-8(10)	-6(9)
C(4E)	113(13)	91(11)	131(12)	15(9)	-13(10)	-22(9)
C(5E)	233(16)	159(13)	131(13)	39(10)	28(11)	78(11)
C(6E)	330(20)	286(16)	104(13)	37(11)	-32(13)	89(14)
C(7E)	231(18)	286(17)	260(17)	79(13)	89(14)	70(13)
C(8E)	150(14)	136(12)	139(12)	34(10)	-17(10)	33(10)
C(9E)	159(15)	203(13)	176(14)	60(11)	-20(11)	35(11)
C(10E)	284(19)	223(15)	235(16)	93(12)	-43(13)	83(13)
C(11E)	278(18)	203(14)	275(17)	115(12)	-25(14)	54(13)
C(12E)	209(17)	175(13)	258(16)	114(12)	-28(13)	-8(12)
C(13E)	185(16)	198(14)	208(15)	85(11)	-32(12)	43(12)
C(14E)	168(14)	113(11)	108(12)	32(9)	3(10)	30(10)
C(15E)	330(20)	83(12)	420(20)	14(12)	-59(16)	79(12)
C(16E)	115(13)	116(11)	167(13)	44(10)	15(11)	15(10)
C(17E)	259(18)	179(14)	194(15)	105(11)	14(13)	-8(12)
C(18E)	173(15)	177(13)	87(12)	35(10)	-15(10)	75(11)
C(19E)	150(15)	196(14)	222(15)	-15(11)	-45(12)	65(11)
C(20E)	226(17)	224(14)	194(15)	100(12)	23(12)	93(12)
O(1F)	190(12)	151(10)	243(11)	61(8)	13(9)	47(8)
O(2F)	231(12)	101(9)	213(11)	20(8)	15(9)	35(8)
O(3F)	243(12)	163(9)	150(10)	-4(8)	55(9)	67(8)

Table A13.2.4. (cont'd)

O(4F)	257(12)	107(8)	99(9)	34(7)	29(8)	12(8)
N(1F)	168(13)	136(10)	110(10)	33(8)	-17(9)	80(9)
N(2F)	141(12)	133(10)	98(10)	20(8)	-12(9)	52(9)
C(1F)	147(14)	163(12)	135(12)	46(10)	1(11)	71(10)
C(2F)	167(14)	134(12)	121(12)	35(9)	7(11)	39(10)
C(3F)	126(13)	91(11)	132(12)	27(9)	-2(10)	16(9)
C(4F)	140(14)	81(11)	132(12)	26(9)	10(10)	17(9)
C(5F)	326(18)	192(14)	160(14)	0(11)	9(13)	160(13)
C(6F)	630(30)	219(16)	240(17)	2(13)	13(18)	172(17)
C(7F)	380(20)	330(17)	125(14)	-28(12)	-34(14)	192(15)
C(8F)	225(16)	146(12)	131(13)	35(10)	39(11)	85(11)
C(9F)	310(18)	229(15)	174(14)	68(11)	42(13)	174(13)
C(10F)	430(20)	278(16)	180(15)	111(12)	94(14)	237(15)
C(11F)	550(30)	199(15)	261(17)	104(13)	208(17)	145(15)
C(12F)	430(20)	203(15)	258(17)	91(13)	153(16)	59(15)
C(13F)	246(18)	229(15)	183(15)	69(12)	45(13)	60(13)
C(14F)	157(14)	123(12)	128(12)	21(9)	13(11)	24(10)
C(15F)	350(20)	72(11)	238(15)	8(10)	62(14)	23(12)
C(16F)	132(14)	155(12)	50(11)	17(9)	-21(10)	62(10)
C(17F)	238(17)	216(14)	155(14)	107(11)	27(12)	22(12)
C(18F)	177(15)	168(12)	99(12)	22(10)	-28(11)	61(11)
C(19F)	215(17)	139(13)	200(15)	-5(11)	-47(13)	-39(11)
C(20F)	351(19)	240(15)	129(13)	76(11)	-9(13)	130(13)
Br(1A)	265(2)	205(1)	172(1)	6(1)	-6(1)	118(1)
Br(1B)	212(2)	209(1)	143(1)	38(1)	18(1)	89(1)
Br(1C)	286(2)	173(1)	186(2)	-11(1)	-24(1)	92(1)
Br(1D)	242(2)	223(2)	175(2)	45(1)	22(1)	-12(1)
Br(1E)	225(2)	166(1)	142(1)	0(1)	31(1)	-40(1)
Br(1F)	212(2)	228(2)	157(1)	45(1)	-2(1)	10(1)
O(5A)	202(12)	160(10)	207(11)	8(8)	11(9)	47(8)
O(5B)	155(11)	210(10)	200(11)	29(8)	-5(9)	-74(9)
O(5C)	189(12)	159(10)	246(12)	43(8)	21(9)	55(9)
O(5D)	342(15)	272(12)	219(12)	50(9)	23(10)	202(11)
O(5E)	200(12)	176(10)	162(10)	29(8)	54(9)	63(8)

Table A13.2.4. (cont'd)

O(5F)	253(13)	291(12)	214(12)	35(9)	37(10)	159(10)

Table A13.2.5. Hydrogen coordinates (x10^3) and isotropic displacement parameters (Å^{2}x10^3) for Amidine ***(R)-450•HBr***.

	x	y	z	U_{iso}
H(2A)	204	104	797	17
H(1A)	646	133	714	16
H(2AA)	842	242	787	17
H(2AB)	776	130	782	17
H(5A)	213	72	729	19
H(6AA)	404	146	657	37
H(6AB)	228	64	650	37
H(6AC)	402	47	670	37
H(7AA)	186	224	753	35
H(7AB)	98	182	702	35
H(7AC)	282	256	709	35
H(9A)	782	222	663	22
H(10A)	859	359	632	25
H(11A)	792	492	668	27
H(12A)	646	488	735	26
H(13A)	565	351	766	21
H(15G)	784	477	855	51
H(15H)	964	472	878	51
H(15I)	794	446	905	51
H(17G)	691	-57	862	37
H(17H)	593	-8	900	37
H(17I)	793	36	896	37
H(18A)	381	168	885	21
H(19G)	173	248	870	38
H(19H)	114	190	910	38
H(19I)	25	151	859	38
H(20G)	99	3	863	35
H(20H)	211	38	912	35
H(20I)	296	1	867	35
H(2B)	-4	75	461	16
H(1B)	460	112	381	15

Table A13.2.5. (cont'd)

H(2BA)	580	124	454	16
H(2BB)	628	234	453	16
H(5B)	0	59	391	20
H(6BA)	226	-58	383	50
H(6BB)	27	-92	363	50
H(6BC)	78	-61	418	50
H(7BA)	134	130	331	37
H(7BB)	45	22	312	37
H(7BC)	249	58	324	37
H(9B)	598	218	334	25
H(10B)	613	349	300	32
H(11B)	460	456	328	33
H(12B)	280	426	388	35
H(13B)	258	293	421	25
H(15D)	494	467	503	53
H(15E)	692	482	520	53
H(15F)	543	453	554	53
H(17D)	488	-42	549	28
H(17E)	396	20	584	28
H(17F)	596	58	576	28
H(18B)	166	149	549	19
H(19D)	-33	229	532	36
H(19E)	-101	171	572	36
H(19F)	-183	134	520	36
H(20D)	-108	-19	527	35
H(20E)	-10	21	577	35
H(20F)	90	-16	536	35
H(2C)	416	99	128	16
H(1C)	849	121	40	17
H(2CA)	1052	228	112	17
H(2CB)	979	118	109	17
H(5C)	419	57	59	19
H(6CA)	606	125	-15	37
H(6CB)	432	43	-20	37

Table A13.2.5. (cont'd)

H(6CC)	608	29	1	37
H(7CA)	386	208	80	34
H(7CB)	300	164	28	34
H(7CC)	483	240	36	34
H(9C)	994	214	-9	21
H(10C)	1067	352	-39	26
H(11C)	991	482	-4	25
H(12C)	834	474	62	23
H(13C)	753	336	91	21
H(15A)	1026	476	158	42
H(15B)	1175	471	195	42
H(15C)	982	457	209	42
H(17A)	855	-61	201	36
H(17B)	813	14	240	36
H(17C)	1004	30	224	36
H(18C)	605	167	215	18
H(19A)	412	254	202	36
H(19B)	349	197	243	36
H(19C)	254	161	192	36
H(20A)	317	5	195	30
H(20B)	427	43	244	30
H(20C)	513	2	200	30
H(2D)	98	754	670	16
H(1D)	531	721	758	19
H(2DA)	563	591	691	18
H(2DB)	628	700	687	18
H(5D)	128	777	740	26
H(6DA)	471	898	753	65
H(6DB)	300	931	760	65
H(6DC)	339	888	709	65
H(7DA)	236	712	803	60
H(7DB)	204	812	818	60
H(7DC)	395	804	812	60
H(9D)	568	620	808	22

Table A13.2.5. (cont'd)

H(10D)	458	495	846	29
H(11D)	188	390	820	28
H(12D)	26	415	757	28
H(13D)	136	542	720	23
H(15P)	229	362	596	38
H(15Q)	190	360	649	38
H(15R)	363	339	631	38
H(17P)	515	793	552	30
H(17Q)	688	765	564	30
H(17R)	665	864	587	30
H(18D)	176	667	586	19
H(19P)	-101	589	600	33
H(19Q)	-123	649	560	33
H(19R)	-153	684	613	33
H(20P)	67	834	598	34
H(20Q)	132	788	551	34
H(20R)	265	834	596	34
H(2E)	725	727	339	16
H(1E)	1153	714	432	18
H(2EA)	1241	603	363	19
H(2EB)	1274	713	364	19
H(5E)	778	772	408	20
H(6EA)	909	709	485	36
H(6EB)	818	791	487	36
H(6EC)	1004	804	468	36
H(7EA)	600	615	388	38
H(7EB)	557	669	436	38
H(7EC)	667	595	437	38
H(9E)	1236	625	481	22
H(10E)	1190	492	516	29
H(11E)	972	358	483	30
H(12E)	792	362	419	26
H(13E)	836	496	385	23
H(15M)	935	367	266	42

Table A13.2.5. (cont'd)

H(15N)	943	355	319	42
H(15O)	1105	352	290	42
H(17M)	1192	808	230	32
H(17N)	1372	801	252	32
H(17O)	1302	888	271	32
H(18E)	830	654	255	17
H(19M)	557	566	263	29
H(19N)	533	629	226	29
H(19O)	491	656	279	29
H(20M)	708	816	269	30
H(20N)	772	775	222	30
H(20O)	907	819	266	30
H(2F)	294	753	11	15
H(1F)	736	716	95	17
H(2FA)	771	594	25	17
H(2FB)	827	704	23	17
H(5F)	326	770	82	25
H(6FA)	669	891	94	54
H(6FB)	499	923	105	54
H(6FC)	530	887	53	54
H(7FA)	413	700	142	40
H(7FB)	415	806	160	40
H(7FC)	592	780	150	40
H(9F)	782	610	140	26
H(10F)	683	477	174	31
H(11F)	413	372	146	38
H(12F)	242	403	88	35
H(13F)	341	538	56	26
H(15J)	426	364	-66	34
H(15K)	383	363	-14	34
H(15L)	556	340	-30	34
H(17J)	696	780	-116	30
H(17K)	882	771	-100	30
H(17L)	828	864	-82	30

Table A13.2.5. (cont'd)

H(18F)	373	676	-76	18
H(19J)	93	599	-62	31
H(19K)	78	660	-101	31
H(19L)	45	695	-49	31
H(20J)	267	844	-55	34
H(20K)	318	804	-105	34
H(20L)	462	843	-62	34
H(5AA)	998(5)	-14(2)	771(1)	29
H(5AB)	915(5)	48(2)	797(1)	29
H(5BA)	681(4)	-35(2)	445(1)	32
H(5BB)	758(5)	62(1)	454(1)	32
H(5CA)	145(5)	-29(1)	117(1)	29
H(5CB)	114(4)	59(2)	119(1)	29
H(5DA)	897(5)	875(2)	681(1)	38
H(5DB)	901(5)	820(2)	715(1)	38
H(5EA)	601(5)	860(2)	349(1)	26
H(5EB)	528(5)	808(2)	383(1)	26
H(5FA)	230(2)	832(3)	35(1)	35
H(5FB)	75(5)	820(3)	57(1)	35

CHAPTER 6

Stereoselective Lewis Acid Mediated (3 + 2) Cycloadditions of N-H- and N-Sulfonylaziridines with Heterocumulenes†

6.1 Introduction

Aziridines are versatile intermediates and reaction partners for the preparation of a structurally diverse assortment of nitrogen-containing architectures.[1] These heterocycles are characterized by a unique reactivity profile, in part due to the large strain energy (27 kcal mol^{-1}) contained within their three-membered ring structure,[2] rendering them susceptible to nucleophilic ring opening,[3] carbonylation,[4] and ring expansion.[5] Previous work has shown the utility of 2-arylaziridines in transition metal-mediated and -catalyzed (3 + 2) cycloadditions with heterocumulenes for the formation of imidazolines,[6a–e] oxazolidines,[6d–e] iminoazolidinones,[6f–i] iminothiazolidines,[6i–k] and iminoimidazolidines.[6f,l] Iminothiazolidines and iminoimidazolidines have enjoyed broad application as effective

† This work was performed in collaboration with Nicholas R. O'Connor and Dr. Alexander F. G. Goldberg, a graduate student in and an alumnus of the Stoltz group, respectively. Additionally, this work has been published and adapted with permission from Craig, R. A., II; O'Connor, N. R.; Goldberg, A. F. G.; Stoltz, B. M. *Chem. Eur. J.* **2014**, *20*, 4806–4813.

organic catalysts in asymmetric transformations including Strecker reactions,[7a] *O*- and *N*-acylations,[7b–c] and Michael additions,[7d] and as highly active pharmacophores for the treatment of a wide range of medical conditions including obesity, diabetes, cancer, and arthritis.[8]

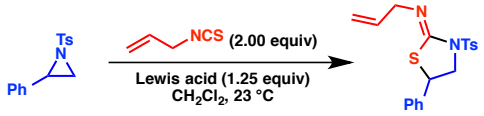
The critical limitation of the majority of the existing (3 + 2) cycloaddition manifolds is the requirement that aziridine starting materials bear either alkyl or aryl *N*-substitution. The harsh conditions necessary for the removal of such robust groups severely limits the potential for derivatization and, thus, the utility of the products. Despite this, the use of *N*-sulfonyl-protected aziridines in (3 + 2) cycloadditions has been explored minimally.[6a–e,k] Prior to our studies, the work of Nadir and co-workers stood as the only previous study of (3 + 2) cycloadditions of *N*-sulfonyl-2-arylaziridines with heterocumulenes.[6k,9] Their reaction system has a narrow scope and is only able to accommodate aryl isocyanates and aryl isothiocyanates, resulting in similarly limited product derivatization options. This transformation depends on the use of an alkali metal iodide as a noninnocent reaction partner; Nadir and co-workers explicitly demonstrate the formation of the ring-opened iodide intermediate prior to product formation.

Additionally, only a single example is known for the synthesis of enantioenriched iminothiazolidines by a stereoselective (3 + 2) cycloaddition[6i] despite readily available enantioenriched aziridine starting materials.[1,2,6h] This method, however, has an extremely narrow substrate scope, requiring the use of *N*-alkyl- or *N*-arylaziridines and aryl heterocumulenes. There are no examples of this transformation with *N*-sulfonyl-protected aziridines or more synthetically versatile heterocumulenes.

6.2 Initial Reaction Development

From this foundation, we sought to develop the first stereoselective Lewis acid mediated (3 + 2) cycloaddition reaction of *N*-sulfonyl-2-substituted aziridines and alkyl heterocumulenes. The Lewis acid mediated conditions would likely enable the use of a broad variety of heterocumulenes and consequently furnish readily derivatizable, highly enantioenriched heterocyclic building blocks.

Table 6.2.1. Optimization of Reaction Conditions



498 ***499***

Entry	*Lewis acid*	*t (h)*	*Yield (%)*[a]
1	$Sn(OTf)_2$	1.0	0
2	$Zn(OTf)_2$	60.0	79
3	$ZnCl_2$	6.0	95
4	ZnI_2	3.0	95
5	$ZnBr_2$	1.3	99
6	$LiBr_2$[b]	72.0[c]	7
7	$ZnBr_2$[d]	72.0[c]	4

Conditions: aziridine **498** (0.40 mmol), isothiocyanate (0.80 mmol), Lewis acid (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] 1.00 mmol of LiBr. [c] Starting material was not fully consumed. [d] 0.12 mmol of $ZnBr_2$ with 0.40 mmol of tetra(*n*-buty)lammonium bromide additive

Initial reaction development focused on the cycloaddition of *N*-tosyl-2-phenylaziridine (**498**) with allyl isothiocyanate (Table 6.2.1). In contrast to our previous work on (3 + 2) cycloadditions of donor–acceptor cyclopropanes with heterocumulenes,[10] tin(II) triflate was found to be an ineffective Lewis acid mediator for the desired transformation (Table 6.2.1, entry 1). Alternatively, zinc(II) salts proved competent for the formation of iminothiazolidine **499**. While zinc(II) triflate furnished the product in good yield, the reaction times were greatly reduced when zinc(II) halides were employed (entries 2–5). Lithium bromide mediated reaction conditions resulted in low conversion (entry 6). Attempts to develop a catalytic system with zinc(II) bromide proved unsuccessful, even in the presence of an additional bromide ion (entry 7). Ultimately, the

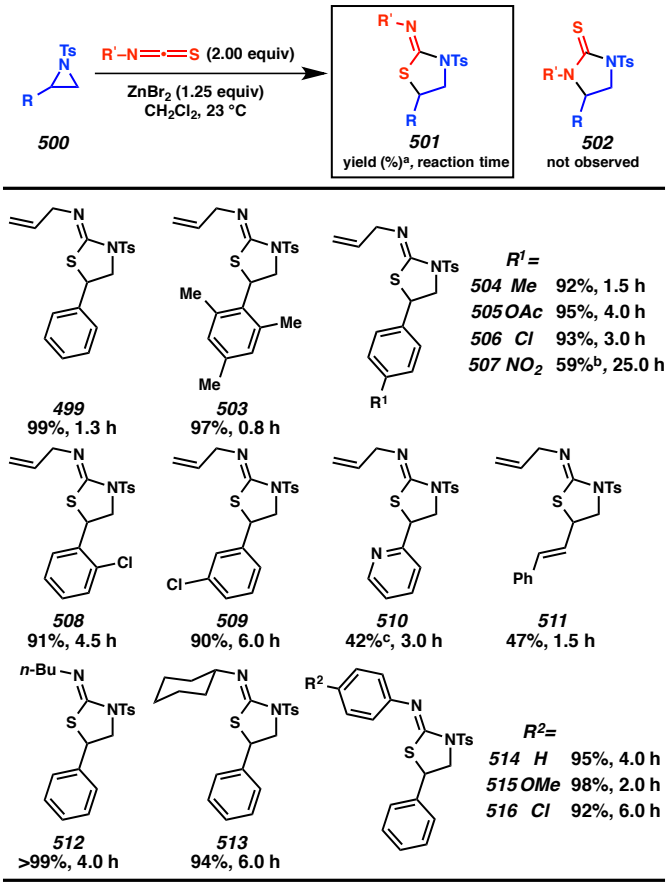
use of 1.25 equivalents of zinc(II) bromide and 2.00 equivalents of allyl isothiocyanate in dichloromethane at ambient temperature proved optimal (entry 5).[11]

6.3 Exploration of 2-Aziridine and Heterocumulene Substitution

With optimal conditions identified, we examined the substrate scope of the reaction. We found that a variety of *N*-tosyl-2-aryl-substituted aziridines participated effectively in the zinc(II) bromide mediated (3 + 2) cycloaddition with allyl isothiocyanate to yield the corresponding iminothiazolidine products with complete chemo- and regioselectivity (Scheme 6.3.1).[12,13] Altering the *C*-aryl substitution from phenyl to mesityl allowed for the formation of the corresponding heterocycle (**503**) in a shorter reaction time despite the increased steric bulk.[14] Similarly, (*p*-tolyl)thiazolidine **504** was successfully furnished with a slightly decreased yield. Acetoxy substitution was compatible with the reaction conditions as well, generating **505** in excellent yield. Compared to the *p*-chlorophenyl- or *o*-chlorophenylthiazolidines (**506** and **508**, respectively), the more electronically deactivated *m*-chlorophenylthiazolidine **509** was produced more slowly, albeit without any significant reduction in yield.[15] The highly electron-deficient *p*-nitrophenyl-thiazolidine **507** was formed in modest yield, with a significant portion of starting material lost to nucleophilic ring opening of the aziridine by the bromide counterion.[16] Substrates bearing coordinating *C*-aryl substituents served to slow the rate of reaction (e.g. **505** and **507**) or require additional $ZnBr_2$ to drive the reaction to completion (**510**). Styrenyl thiazolidine **511** could also be synthesized in approximately the same reaction time as phenyl product **499**. Additionally, primary and secondary alkyl isothiocyanates were found to be highly compatible under the reaction conditions as were

electron-neutral, -rich, and -deficient aryl isothiocyanates, all furnishing the desired iminothiazolidines in excellent yields (**512**–**516**, respectively).

Scheme 6.3.1. Substrate Scope of Isothiocyanate (3 + 2) Cycloadditions

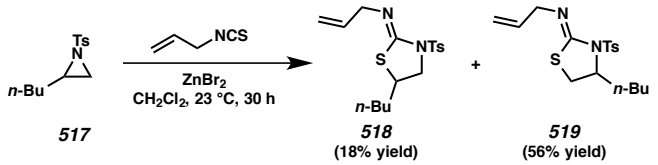


Conditions: aziridine **500** (0.40 mmol), isothiocyanate (0.80 mmol), $ZnBr_2$ (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] The product of nucleophilic ring opening of the starting material by a bromide ion was isolated in 35 % yield. [c] 0.90 mmol of $ZnBr_2$ were used.

In contrast to the *C*-aryl-substituted aziridines, *C*-alkyl-substituted aziridine **517** reacted with allyl isothiocyanate under the reaction conditions to furnish two isomeric (3 + 2) adducts (Scheme 6.3.2). Formation of 5-alkyl-substituted iminothiazolidine **518** was accomplished in only 18% yield, whereas 4-alkyl-substituted product **519** was furnished in 56% yield. While *C*-alkyl-substituted aziridines are suitable reaction partners in the (3 + 2) cycloaddition and the heterocyclic products are formed with

complete chemoselectivity, they are not formed with the regiofidelity exhibited by aziridines substituted at carbon with aryl groups or other conjugated systems.

*Scheme 6.3.2. (3 + 2) Cycloaddition with 2-Alkylaziridine **517***

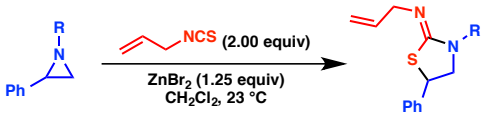


517 ***518*** (18% yield) ***519*** (56% yield)

6.4 Effect of Aziridine *N*-Substitution

As an extension of the substrate scope, we investigated the effect of *N*-substitution on the aziridine (Table 6.4.1). Aziridines protected with *N*-sulfonyl groups provided the desired iminothiazolidines (**499**, **522**–**524**) in excellent yields, generally showing reaction times that were slightly shorter for electron-deficient sulfonyl groups (Table 6.4.1, entry 2) and slightly longer for more electron-rich sulfonyl groups (entries 3–4) in comparison to the *N*-tosyl-substituted substrate (entry 1).

Table 6.4.1. N-Substitution Scope of Isothiocyanate (3 + 2) Cycloaddition



520 ***521***

Entry	*R*	*Product*	*t (h)*	*Yield (%)*[a]
1	tosyl	*499*	1.3	99
2	*p*-NO_2-C_6H_4-SO_2	*522*	1.2	94
3	mesyl	*523*	1.8	91
4	*p*-OMe-C_6H_4-SO_2	*524*	2.0	90
5	H	*525*	0.5	75
6	*n*-$C_{10}H_{21}$	*526*	96.0[b]	0
7	pivaloyl	*527*	96.0[b]	0
8	benzoyl	*528*	96.0[b]	0

Conditions: aziridine **520** (0.40 mmol), isothiocyanate (0.80 mmol), $ZnBr_2$ (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] Starting material was not fully consumed.

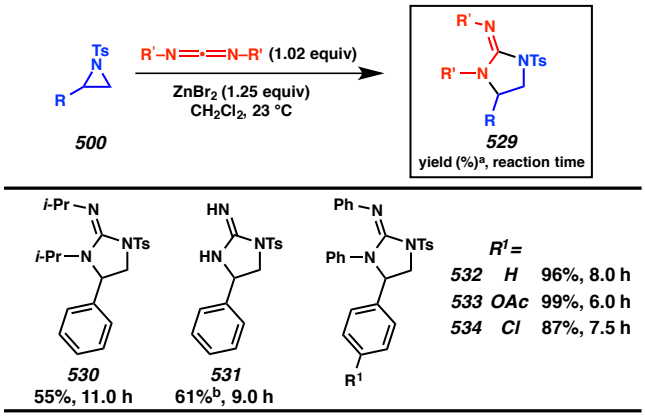
Interestingly, unprotected 2-phenylaziridine showed an improved reaction time yet a partially decreased yield of the heterocyclic product **525**, whereas *N*-(*n*-decyl)-

substituted aziridine was unreactive under the reaction conditions (entries 5–6). *N*-Acyl aziridines also failed to furnish any of the desired heterocycles **527** and **528** (entries 7–8).

6.5 Extension of Heterocumulene Scope

Subsequently, we turned our attention to broadening the scope of competent heterocumulenes and found that while isocyanates gave only trace yields of the (3 + 2) cycloaddition adducts,[17] carbodiimides were compatible with the conditions, furnishing iminoimidazolidines (Scheme 6.5.1).[18] Our unique zinc-mediated conditions enabled the (3 + 2) cycloadditions of *N*-sulfonylaziridines with dialkyl- and disilylcarbodiimides, unlike any previously published systems,[6,9] furnishing diisopropyliminoimidazolidine **530** and secondary imidazolidine **531**. In accordance with our observations in the isothiocyanate (3 + 2) cycloadditions, a variety of 2-arylaziridines were suitable reaction partners with diphenylcarbodiimide (**532**–**534**).

Scheme 6.5.1. Substrate Scope of Carbodiimide (3 + 2) Cycloaddition



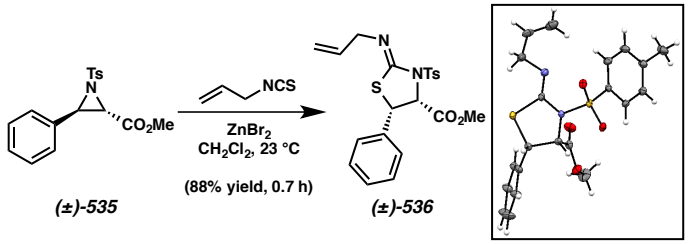
Conditions: aziridine **498** (0.40 mmol), carbodiimide (0.41 mmol), $ZnBr_2$ (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] Bis(trimethylsilyl)carbodiimide was used.

6.6 Cycloaddition of Disubstituted *N*-Sulfonylaziridines

During our investigation of the substrate scope of the (3 + 2) cycloaddition of *N*-sulfonylaziridines with isothiocyanates, we discovered that *trans*-2,3-disubstituted

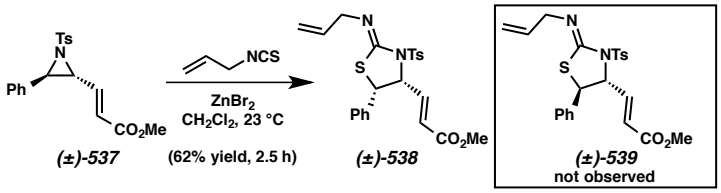
aziridine **535** was an acceptable reaction partner, furnishing *cis*-thiazolidine **536** in high yield in the shortest reaction time observed for any *N*-tosyl-substituted substrate (Scheme 6.6.1). Iminothiazolidine **536** was formed as a single diastereomer, and the relative stereochemistry was confirmed by single-crystal X-ray diffraction. The *cis* configuration of product **536** led to the hypothesis that the mechanism of the reaction involves inversion at the benzylic position of the aziridine starting material.[19]

*Scheme 6.6.1. Diastereoselective (3 + 2) Cycloaddition with Aziridine **535***



To confirm that the chemo-, regio-, and diastereoselective formation of *cis*-thiazolidine **536** was not substrate dependent, we exposed *trans*-2,3-disubstituted acroylaziridine **537** to identical reaction conditions and were pleased to find that *cis*-acroylthiazolidine **538** was similarly formed as the sole product and as a single diastereomer (Scheme 6.6.2).

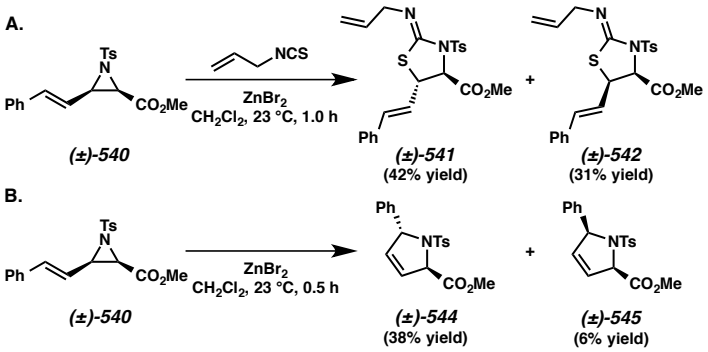
*Scheme 6.6.2. Diastereoselective (3 + 2) Cycloaddition with Aziridine **537***



Contrastingly, the (3 + 2) cycloaddition of allyl isothiocyanate with *cis*-2,3-disubstituted aziridine **540** resulted in the nondiastereoselective formation of both *trans*-thiazolidine **541** and the *cis* isomer **542** (Scheme 6.6.3.A). Interestingly, exposure of *cis*-aziridine **540** to the reaction conditions in the absence of heterocumulene resulted in the

rapid formation of pyrrolines **544** and **545** (Scheme 6.6.3.B).[20] Finally, we found that geminally disubstituted *N*-tosyl-2-methyl-2-phenylaziridine failed to provide any (3 + 2) cycloaddition product.[21]

*Scheme 6.6.3. (3 + 2) Cycloaddition with Aziridine **540***

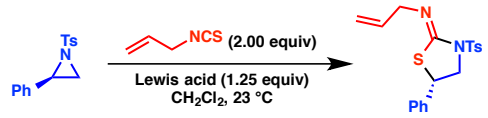


6.7 Development of a Stereoselective (3 + 2) Cycloaddition

The formation of *cis*-thiazolidines **538** and **541** with excellent chemo-, regio-, and diastereoselectivity intimated the potential to develop a stereoselective reaction manifold. Initial development focused on the (3 + 2) cycloaddition of (*R*)-*N*-tosyl-2-phenylaziridine (**(*R*)-498**) with allyl isothiocyanate (Table 6.7.1).[22] The optimized zinc(II) bromide mediated reaction conditions furnished **(*S*)-499** in excellent yield and with 42% enantiomeric excess (*ee*) (Table 6.7.1, entry 1). Other zinc(II) halide salts furnished the desired product in similar yield with increased *ee* when zinc(II) chloride was employed (entries 2–3). Zinc(II) triflate provided no improvement in the *ee* of **(*S*)-499** (entry 4). Lithium bromide mediated and catalytic zinc(II) bromide conditions both exhibited incomplete conversion of **(*R*)-498** (entries 5–6). Interestingly, while the lithium bromide conditions furnished the opposite enantiomer **(*R*)-498**, the catalytic zinc(II) bromide conditions produced **(*S*)-499** with an improved 69 % *ee*. Inspired by this result, we were pleased to find that increasing the equivalents of isothiocyanate in the presence of

stoichiometric zinc(II) bromide could provide a similar boost in *ee* while maintaining full conversion of the starting material (entry 7). Ultimately, the use of 1.25 equivalents of zinc(II) chloride and 10.0 equivalents of allyl isothiocyanate in dichloromethane at ambient temperature proved optimal, furnishing **(*S*)-499** in 99 % yield and with 94 % *ee* (entry 8).

Table 6.7.1. Optimization of Stereoselective Reaction Conditions



***(R)*-498**
99% *ee*

***(S)*-499**

Entry	*Lewis acid*	*t (h)*	*Yield (%)*[a]	*ee (%)*[b]
1	$ZnBr_2$	1.3	99	42
2	ZnI_2	3.0	95	32
3	$ZnCl_2$	6.0	95	63
4	$Zn(OTf)_2$	60.0	79	31
5	LiBr	96[c]	10	–76
6	$ZnBr_2$[d]	72[c]	67	69
7	$ZnBr_2$[e]	1.3	98	65
8	$ZnCl_2$[f]	2.0	99	94

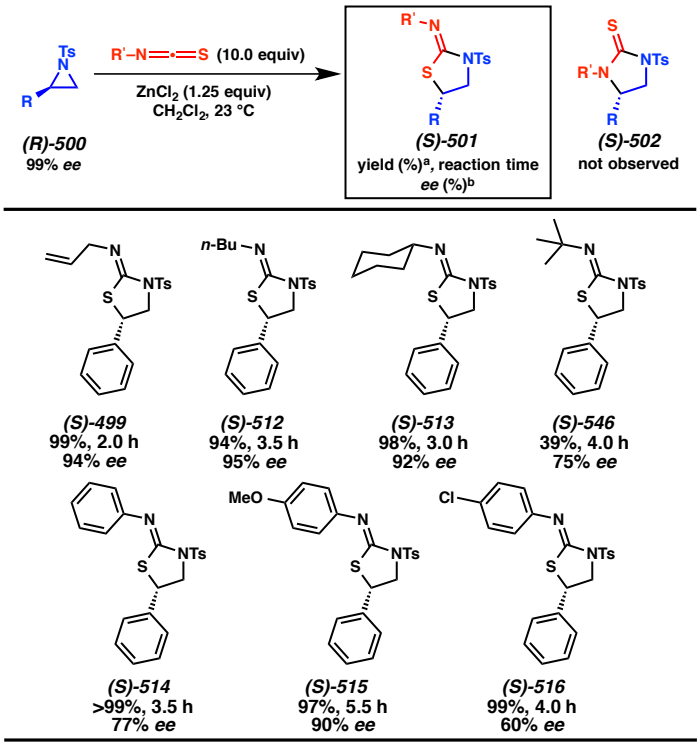
Conditions: aziridine **(*R*)-498** (0.40 mmol, 99% *ee*), isothiocyanate (0.80 mmol), Lewis acid (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] Determined by analytical chiral SFC. [c] Starting material was not fully consumed. [d] 0.12 mmol of $ZnBr_2$. [e] 6.00 equiv allyl isothiocyanate. [f] 10.0 equiv allyl isothiocyanate.

6.8 Isothiocyanate Substitution in Stereoselective (3 + 2) Cycloaddition

With optimal conditions identified, we examined the scope of heterocumulene substitution in the reaction.[23] We found that, along with allyl isothiocyanate, primary and secondary alkyl isothiocyanates were all highly compatible under the reaction conditions, furnishing desired enantioenriched iminothiazolidines **(*S*)-49**, **(*S*)-512**, and **(*S*)-513** in uniformly excellent yields and *ee* (Scheme 6.8.1).[13] The use of a tertiary isothiocyanate, however, extended the reaction time and provided thiazolidine **(*S*)-546** in decreased yield and *ee*. Additionally, aryl isothiocyanates were competent cycloaddition reaction partners under the zinc(II) chloride mediated conditions, providing thiazolidine products **(*S*)-514**, **(*S*)-515**, and **(*S*)-516** in excellent yields. While phenyliminothiazolidine **(*S*)-514**

was isolated with good *ee*, the use of a more electron-rich isothiocyanate resulted in the formation of a thiazolidine product ((***S*)-515**) with an excellent 90% *ee*, whereas the use of a more electron-deficient isothiocyanate provided a product with a significantly lower *ee* ((***S*)-516**).

Scheme 6.8.1. Substrate Scope of Stereoselective Isothiocyanate (3 + 2) Cycloaddition



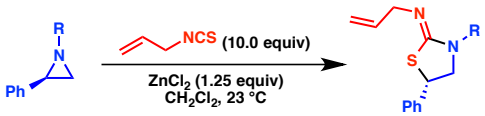
Conditions: aziridine **(*R*)-500** (0.40 mmol, 99% *ee*), isothiocyanate (4.00 mmol), $ZnCl_2$ (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] Determined by analytical chiral SFC.

6.9 Effect of Aziridine *N*-Substitution on Transfer of Chiral Information

We subsequently investigated the effect of *N*-substitution on the aziridine in the stereoselective (3 + 2) cycloaddition. Aziridines with *N*-sulfonyl substitutions were extremely well tolerated under the reaction conditions, furnishing the desired thiazolidines ((***S*)-499**, (***S*)-522**–(***S*)-524**) in excellent yield with uniformly high *ee*'s, exhibiting reaction times that increased slightly moving from more electron-deficient (Table 6.9.1, entry 2) to more electron-rich (entry 4) sulfonyl groups. While unprotected

2-phenylaziridine showed an improved reaction time, unfortunately both the yield and *ee* of thiazolidine **(*S*)-525** were reduced (entry 5).

Table 6.9.1. N-Substitution Scope of Stereoselective Isothiocyanate (3 + 2) Cycloaddition



(R)-520 **99% *ee***

(S)-521

Entry	*R*	*Product*	*t (h)*	*Yield (%)*[b]	*ee (%)*[c]
1	tosyl	*(S)-499*	2.0	99	94
2	*p*-NO_2-C_6H_4-SO_2	*(S)-522*	1.8	>99	95
3	mesyl	*(S)-523*	4.0	95	90
4	*p*-OMe-C_6H_4-SO_2	*(S)-524*	5.0	94	91
5	H	*(S)-525*	0.5	31	34

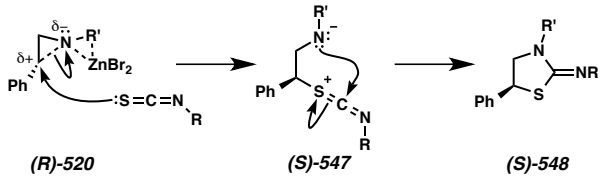
Conditions: aziridine **(*R*)-520** (0.40 mmol, 99% *ee*), isothiocyanate (4.00 mmol), $ZnCl_2$ (0.50 mmol), CH_2Cl_2 (0.80 mL). [a] Isolated yield. [b] Determined by analytical chiral SFC.

6.10 Proposed Mechanism of Stereoselective (3 + 2) Cycloaddition

We hypothesize that the mechanism of the (3 + 2) cycloadditions presented herein proceeds through a stereoselective intimate-ion-pair mechanism similar to that invoked in our previous work[10] and by Johnson[24] and Kerr[25] in related work on the cycloadditions of donor–acceptor cyclopropanes (Scheme 6.10.1). Our observations including lack of reactivity in the absence of Lewis acid,[11,26] inversion at the benzylic position, greater reactivity of aziridines with electron-rich aryl substituents, and shorter reaction times of *N*-substituted aziridines with more electron-withdrawing groups are all consistent with this mechanistic hypothesis. The formation of **(*R*)-499** under lithium bromide mediated conditions strongly suggests we have developed a Lewis acid mediated process in contrast to the related alkali metal halide mediated system reported by Nadir and co-workers,[6k,9] who observe overall stereoretention as a result of a double inversion pathway, which proceeds through an iodinated intermediate, and the palladium(II)-catalyzed reaction conditions of Alper and co-workers[6i] who also observe the stereoretentive product as the major enantiomer. This hypothesis also accounts for the observed

nondiastereoselective formation of thiazolidines **541** and **542** and pyrrolines **544** and **545**, considering the fully separated ion-pair intermediate that likely results from destabilization of the polarized C–N bond by the steric interaction between the *cis* substituents on aziridine **540** (see Scheme 6.6.3).

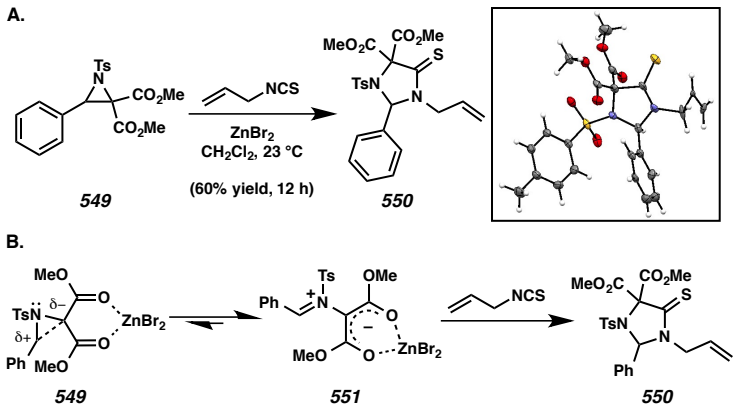
Scheme 6.10.1. Proposed General Reaction Mechanism for Stereoselective (3 + 2) Cycloaddition



6.11 Cycloaddition of a Diester Aziridine

Noting the apparent mechanistic similarities with our previous work,[10] we synthesized diester aziridine **549** to assess the potential for selective activation of the C–C or C–N bond under either our tin(II)- or zinc(II)-mediated conditions, respectively.[27] Unfortunately, $Sn(OTf)_2$ failed to provide any cycloaddition product.[28] Alternatively, use of $ZnBr_2$ provided thiolactam **550** as the sole (3 + 2) adduct (Scheme 6.11.1.A).

*Scheme 6.11.1. (3 + 2) Cycloaddition with Diester Aziridine **549***



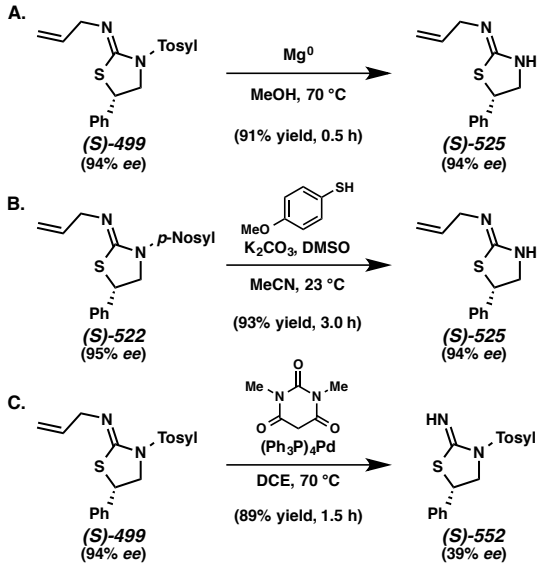
This is the only thiolactam (3 + 2) cycloaddition product observed during our studies.[13] The ability of the malonate group to stabilize the negative charge and the

nitrogen to further stabilize the benzylic positive charge allows for the formation of zwitterion **551**, likely resulting in the observed divergent reactivity (Scheme 6.11.1.B).[29]

6.12 Deprotection of *N*-Sulfonyl Heterocycles

Having explored a range of substrates, heterocumulenes, and *N*-protecting groups, we next sought to assess the potential to derivatize our heterocyclic products. As expected, the *N*-sulfonyl protecting group removal was trivial. Secondary iminothiazolidine **(*S*)-525** could be accessed rapidly in an excellent 91% yield without any loss of enantiomeric excess through detosylation of thiazolidine **(*S*)-499** (Scheme 6.12.1.A)[30] or through the desulfonylation of *p*-nosyl-protected thiazolidine **(*S*)-522** with slightly increased yield (Scheme 6.12.1.B), furnishing thiazolidine **(*S*)-525** in 87% yield and with 94% *ee* over two steps from (*R*)-*N*-(*p*-nitrobenzenesulfonyl)-2-phenylaziridine.[31]

Scheme 6.12.1. Desulfonylation and Deallylation of Iminothiazolidine Products



Alternatively, cleavage of the allyl imine C–N bond of heterocycle **(*S*)-499** in the presence of palladium(0) enabled access to secondary iminothiazolidine **(*S*)-552** with some loss of enantiomeric excess (Scheme 6.12.1.C). While the cleavage of *N*-allyl

bonds has been shown in the literature for functional groups including amines[32] and amides,[33] this is the first known example of the cleavage of an imino *N*-allyl bond.

Iminothiazolidines **(*S*)-525** and **(*S*)-552** are extremely versatile heterocycles. Derivatization and synthetic manipulations of the imine, allyl group, and secondary nitrogen could be envisioned to provide rapid access to highly enantioenriched oxothiazolidines, thiazoles, and a variety of polycyclic scaffolds.[34] Critically, access to the enantioenriched secondary thiazolidine and imidazolidine products enabled by our (3 + 2) cycloaddition allows for their use as asymmetric organic catalysts, as the free secondary nitrogen functions as a necessary hydrogen bond donor for the majority of these applications.[7a–d]

6.13 Conclusion

We have disclosed the first stereoselective Lewis acid mediated (3 + 2) cycloaddition of *N*-H- and *N*-sulfonylaziridines with alkyl heterocumulenes. These zinc(II)-mediated conditions offer broad tolerance of alkyl, silyl, and aryl heterocumulenes, as well as aziridine substitution, enabling the formation of iminoimidazolidines and enantioenriched iminothiazolidines in overall excellent yields from enantioenriched aziridines, which are easily accessible from their amino acid precursors. Combined with the exhibited ability to simply and orthogonally remove the sulfonyl and allyl protecting groups, this reaction system enables the installation of a broad number of functional group handles for further derivatization of these biologically and catalytically important heterocyclic scaffolds.

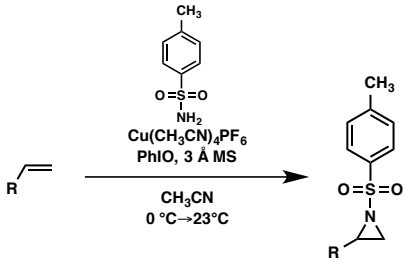
6.14 Experimental Methods and Analytical Data

6.14.1 Materials and Methods

Unless stated otherwise, reactions were performed at ambient temperature (23 °C) in flame-dried or oven-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).[35] Commercially obtained reagents were used as received with the exception of tetra(*n*-butyl)ammonium bromide (TBAB), zinc(II) chloride, zinc(II) bromide, zinc(II) iodide, zinc(II) triflate, tin(II) triflate, lithium bromide, tetrakis(acetonitrile)copper(I) hexafluorophosphate, and tetrakis(triphenylphosphine)palladium(0), which were stored in a nitrogen-filled glovebox. Et_3N and pyridine were distilled from calcium hydride immediately prior to use. Methanol was distilled from magnesium methoxide immediately prior to use. Iodosobenzene[36] and diphenylcarbodiimide[37]were prepared by known methods. Reactions requiring external heat were modulated to the specified temperatures using an IKAmag temperature controller. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-LCMS. TLC was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 500 spectrometer (500 MHz and 126 MHz, respectively) and are reported in terms of chemical shift relative to residual $CHCl_3$ (δ 7.26 and δ 77.16 ppm, respectively), $D_3CS(O)CHD_2$ (δ 2.50 and δ 39.52 ppm, respectively), or $CHDCl_2$ (δ 5.32 and δ 53.84 ppm, respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ

ppm) (multiplicity, coupling constant (Hz), integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = complex multiplet, bs = broad singlet. Infrared (IR) spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer with fast atom bombardment (FAB+) ionization mode or were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in atmospheric pressure chemical ionization (APCI+), electrospray ionization (ESI+), or mixed (MultiMode: ESI-APCI) ionization mode. Optical rotations were measured on a JASCO P-2000 polarimeter using a 100 mm path length cell at 589 nm. Analytical supercritical fluid chromatography (SFC) was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H or AS-H) or Chiralcel (OB-H or OD-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd.

6.14.2 General Experimental Procedures

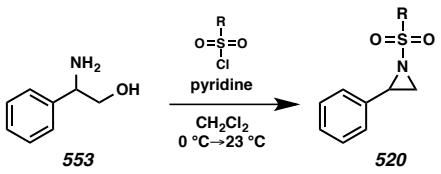


469 *500*

General Procedure A. *Direct aziridination of olefins.*[38]

To a flame-dried round-bottom flask with a stir bar were added *p*-toluenesulfonamide (5.60 mmol, 1.40 equiv), tetrakis(acetonitrile)copper(I)

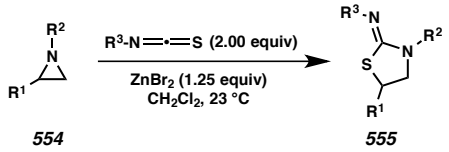
hexafluorophosphate (0.40 mmol, 0.10 equiv), the appropriate olefin (**469**, 4.00 mmol, 1.00 equiv), activated 3 Å molecular sieves (2.40 g, 600 mg/mmol olefin), and acetonitrile (10 mL). The stirred suspension was cooled to 0 °C (ice/H_2O bath) at which time iodosobenzene (5.60 mmol, 1.40 equiv) was added as a solid in one portion. The bath was immediately removed and the reaction mixture was allowed to warm to ambient temperature. Upon consumption of starting material (determined by TLC or LCMS analysis, ca. 12–48 h), the mixture was filtered through Celite, washing with acetonitrile (50 mL) and ethyl acetate (50 mL). The filtrate was concentrated in vacuo to give the crude product, which was purified by silica gel column chromatography (EtOAc in hexanes eluent).



General Procedure B. *Ring closure of amino alcohols.*[39]

A flame-dried round-bottom flask with a stir bar was charged with 2-phenylglycinol (**553**, 0.73 mmol, 1.00 equiv), which was then suspended in CH_2Cl_2 (500 μL) and pyridine (250 μL). The stirred suspension was cooled to 0 °C (ice/H_2O bath) at which time the appropriate sulfonyl chloride (2.19 mmol, 3.00 equiv) was added in one portion. The bath was immediately removed and the reaction mixture was allowed to warm to ambient temperature. Upon completion (determined by TLC or LCMS analysis, ca. 1–5 h), the mixture was diluted with CH_2Cl_2 (12 mL), and washed with aqueous 2 N HCl (3 x 4 mL). The combined acidic aqueous layers were extracted with CH_2Cl_2 (1 x 4 mL). The organic layers were combined and carefully washed with aqueous 2 N KOH (6 x 8

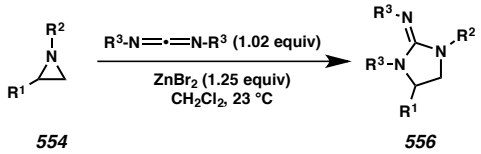
mL). The combined basic aqueous layers were then extracted with CH_2Cl_2 (1 x 12 mL) and the combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography (EtOAc in hexanes eluent).



554 *555*

General Procedure C. *Isothiocyanate (3 + 2) cycloaddition with 2-subsituted aziridines.*

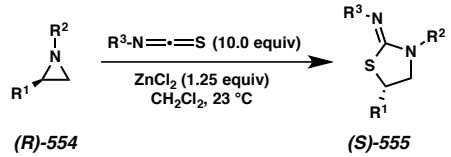
To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (113 mg, 0.50 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox, and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added the appropriate aziridine (**554**, 0.40 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum and anhydrous CH_2Cl_2 (0.60 mL) and isothiocyanate (0.80 mmol, 2.00 equiv) were added. The mixture was transferred to the first vial with a rinse of anhydrous CH_2Cl_2 (0.20 mL). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Upon consumption of the aziridine (determined by TLC or LCMS analysis), the reaction solution was diluted with CH_2Cl_2 (3 mL) and CH_3OH (1 mL), adsorbed onto Celite, and purified by silica gel column chromatography (acetone in hexanes eluent).



554 *556*

General Procedure D. *Carbodiimide (3 + 2) cycloaddition with 2-subsituted aziridines.*

To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (113 mg, 0.50 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox, and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added the appropriate aziridine (**554**, 0.40 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum and anhydrous CH_2Cl_2 (0.60 mL) and carbodiimide (0.41 mmol, 1.02 equiv) were added. The mixture was transferred to the first vial with a rinse of anhydrous CH_2Cl_2 (0.20 mL). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Upon consumption of the aziridine (determined by TLC or LCMS analysis), the reaction solution was diluted with CH_2Cl_2 (3 mL) and CH_3OH (1 mL), adsorbed onto Celite, and purified by silica gel column chromatography (acetone in hexanes or CH_3OH in CH_2Cl_2 eluent).



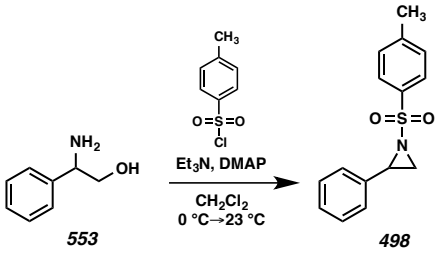
(R)-554 *(S)-555*

General Procedure E. *Stereoselective Isothiocyanate (3 + 2) cycloaddition with 2-subsituted aziridines.*

To an oven-dried 1-dram vial equipped with a magnetic stir bar was added powdered zinc(II) chloride (68 mg, 0.50 mmol, 1.25 equiv) in an inert atmosphere

glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox, and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added the appropriate aziridine (**(*R*)-554**, 0.40 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum and anhydrous CH_2Cl_2 (0.60 mL) and isothiocyanate (4.00 mmol, 10.0 equiv) were added. The mixture was transferred to the first vial with a rinse of anhydrous CH_2Cl_2 (0.20 mL). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Upon consumption of the aziridine (determined by TLC or LCMS analysis), the reaction solution was diluted with CH_2Cl_2 (3 mL) and CH_3OH (1 mL), adsorbed onto Celite, and purified by silica gel column chromatography (acetone in hexanes).

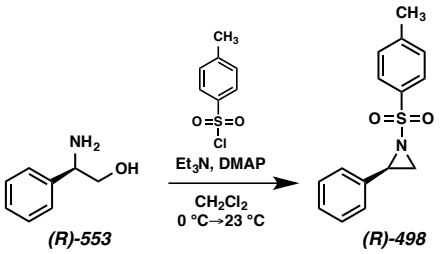
6.14.3 Aziridine Synthesis and Characterization Data



553 *498*

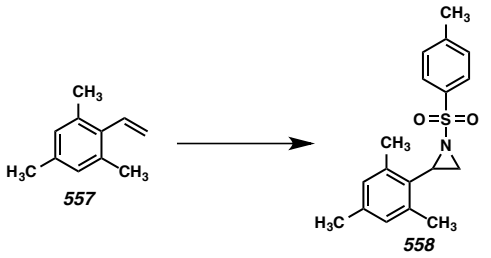
***N*-tosyl-2-phenylaziridine (498)**:

Aziridine **498** was prepared according to General Procedure B from 2-phenylglycinol (**553**): 85% yield; R_f = 0.25 (1:4 Acetone:Hexanes eluent); characterization data match those reported in the literature.[40]



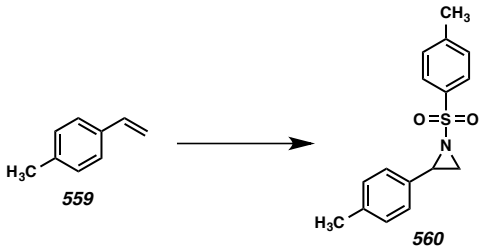
(*R*)-*N*-tosyl-2-phenylaziridine ((*R*)-498):

Aziridine **(*R*)-498** was prepared according to a procedure modified from literature methods.[41] A flame-dried round-bottom flask with a stir bar was charged with (*R*)-(–)-2-phenylglycinol (**(*R*)-553**, 5.00 g, 36.4 mmol, 1.00 equiv), *p*-toluenesulfonyl chloride (17.4 g, 91.1 mmol, 2.50 equiv), and 4-(dimethylamino)pyridine (DMAP, 445 mg, 3.64 mmol, 0.10 equiv). The solids were suspended in dichloromethane under nitrogen, and the flask was cooled in an ice-water bath. Triethylamine (Et_3N, 15.2 mL, 109 mmol, 3.00 equiv) was added dropwise, and the reaction mixture became clear and colorless. The flask was allowed to warm to room temperature and stir under nitrogen. Upon completion (as determined by LCMS analysis, ca. 8 h), the reaction was quenched by addition of saturated aqueous NH_4Cl (80 mL). The organic layer was removed and the aqueous layer extracted with dichloromethane (3 x 60 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. The crude solid was purified by silica gel column chromatography (10% EtOAc in hexanes eluent) to give aziridine **(*R*)-498** (6.34 g, 64% yield) as a fluffy white solid: characterization data are the same as above; $[\alpha]_D^{25.0}$ –108.6° (*c* 0.950, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OB-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.5 minutes, minor retention time: 10.2 minutes, >99% ee).



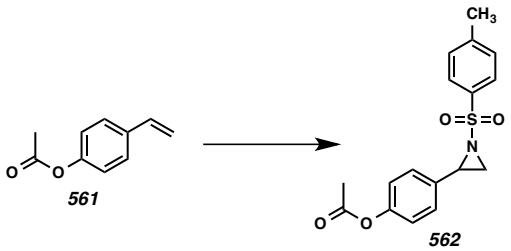
***N*-tosyl-2-mesitylaziridine (558)**:

Aziridine **558** was prepared according to General Procedure A: 40% yield; R_f = 0.29 (1:9 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[42]



***N*-tosyl-2-(*p*-tolyl)aziridine (560)**:

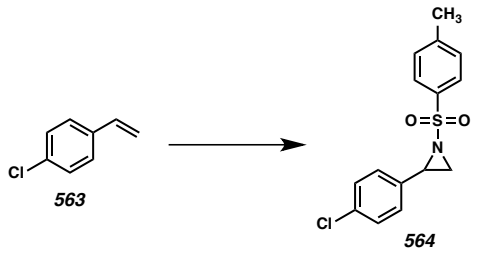
Aziridine **560** was prepared according to General Procedure A: 75% yield; R_f = 0.34 (1:4 Acetone:Hexanes eluent); characterization data match those reported in the literature.[42]



***N*-tosyl-2-(*p*-acetoxyphenyl)aziridine (562)**:

Aziridine **562** was prepared according to General Procedure A: 76% yield; R_f = 0.32 (3:7 EtOAc:Hexanes eluent); characterization data for ^{1}H NMR, ^{13}C NMR, and IR spectra

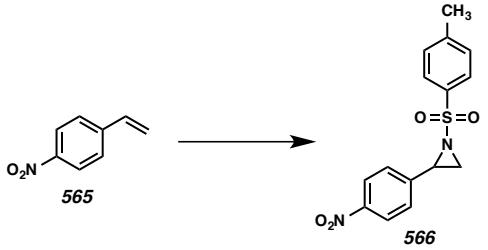
match those reported in the literature;[42a] HRMS (ESI+) *m/z* calc'd for $C_{17}H_{18}NO_4S$ $[M+H]^+$: 332.0951, found 332.0958.



563 ***564***

***N*-tosyl-2-(*p*-chlorophenyl)aziridine (564)**:

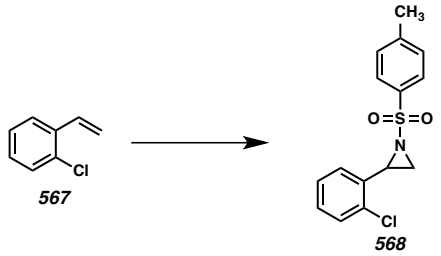
Aziridine **564** was prepared according to General Procedure A: 82% yield; R_f = 0.30 (3:17 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[42]



565 ***566***

***N*-tosyl-2-(*p*-nitrophenyl)aziridine (566)**:

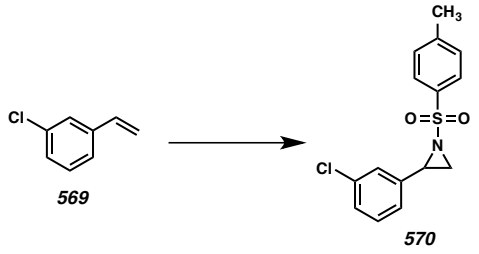
Aziridine **566** was prepared according to General Procedure A: 31% yield; R_f = 0.27 (1:4 Acetone:Hexanes eluent); characterization data match those reported in the literature.[42b]



567 ***568***

***N*-tosyl-2-(*o*-chlorophenyl)aziridine (568)**:[43]

Aziridine **568** was prepared according to General Procedure A: 90% yield; R_f = 0.45 (1:3 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93–7.87 (m, 2H), 7.37–7.34 (m, 2H), 7.34–7.31 (m, 1H), 7.23–7.14 (m, 3H), 4.04 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.03 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.29 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 145.0, 134.8, 133.9, 133.2, 129.9, 129.4, 129.3, 128.2, 127.6, 127.1, 39.1, 35.8, 21.8; IR (Neat Film, NaCl) 3065, 1596, 1444, 1328, 1163, 1093, 913, 815, 759, 732 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{15}{}^{35}ClNO_2S$ $[M+H]^+$: 308.0512, found 308.0520.

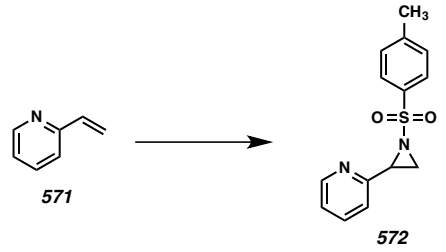


569 ***570***

***N*-tosyl-2-(*m*-chlorophenyl)aziridine (570)**:[43]

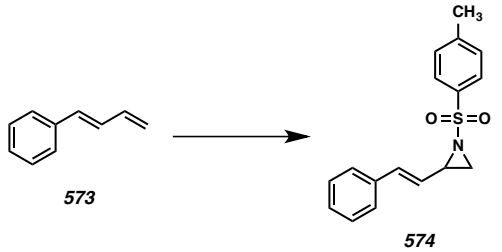
Aziridine **570** was prepared according to General Procedure A: 97% yield; R_f = 0.46 (1:3 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89–7.84 (m, 2H), 7.37–7.32 (m, 2H), 7.26–7.17 (m, 3H), 7.12 (dtd, *J* = 7.1, 1.5, 0.5 Hz, 1H), 3.73 (dd, *J* = 7.1, 4.4 Hz, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 2.35 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 145.0, 137.4, 134.9, 134.7, 130.0, 129.9, 128.6, 128.1, 126.7, 125.0, 40.2,

36.3, 21.8; IR (Neat Film, NaCl) 3062, 1597, 1451, 1326, 1161, 1092, 919, 786, 723 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{15}{}^{35}ClNO_2S$ $[M+H]^+$: 308.0512, found 308.0515.



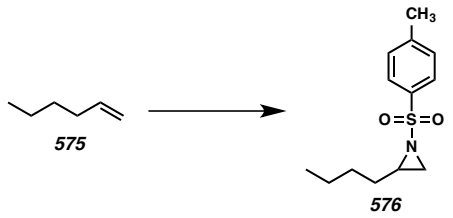
***N*-tosyl-2-(*o*-pyridyl)aziridine (572)**:[44]

Aziridine **572** was prepared according to General Procedure A: 68% yield; R_f = 0.34 (1:1 EtOAc:Hexanes eluent); ^1H NMR ($CDCl_3$, 500 MHz) δ 8.52 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.89–7.83 (m, 2H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34–7.30 (m, 2H), 7.26 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.19 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 3.90 (dd, *J* = 7.2, 4.4 Hz, 1H), 2.97 (d, *J* = 7.2 Hz, 1H), 2.65 (d, *J* = 4.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 154.4, 149.7, 144.9, 136.9, 134.6, 129.9, 128.2, 123.4, 121.9, 41.4, 35.1, 21.8; IR (Neat Film, NaCl) 3064, 1594, 1477, 1437, 1326, 1204, 1161, 1092, 915, 804, 715 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{14}H_{15}N_2O_2S$ $[M+H]^+$: 275.0849, found 275.0835.



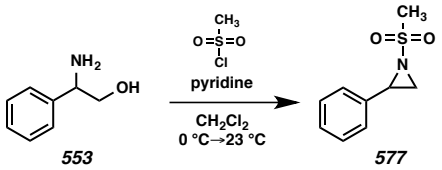
***N*-tosyl-2-((*E*)-styryl)aziridine (574)**:

Aziridine **574** was prepared according to General Procedure A: 11% yield; R_f = 0.18 (1:9 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90–7.82 (m, 2H), 7.36–7.23 (m, 7H), 6.73 (d, *J* = 15.9 Hz, 1H), 5.84 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.46 (dddd, *J* = 7.8, 7.1, 4.5, 0.7 Hz, 1H), 2.87 (d, *J* = 7.1 Hz, 1H), 2.44 (s, 3H), 2.32 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.8, 135.9, 135.2, 129.9, 128.8, 128.4, 128.0, 126.6, 126.6, 124.2, 41.4, 34.8, 21.8; IR (Neat Film, NaCl) 3287, 3028, 2924, 1597, 1494, 1450, 1323, 1160, 1090, 964, 939, 884, 815, 753, 714 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{18}NO_2S$ $[M+H]^+$:300.1053, found 300.1057.



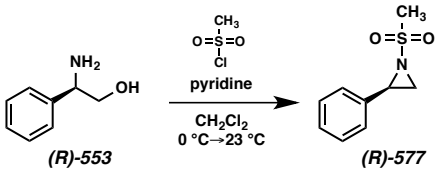
***N*-tosyl-2-(*n*-butyl)aziridine (576)**:

Aziridine **576** was prepared according to General Procedure A: 32% yield; R_f = 0.44 (1:3 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[42b]



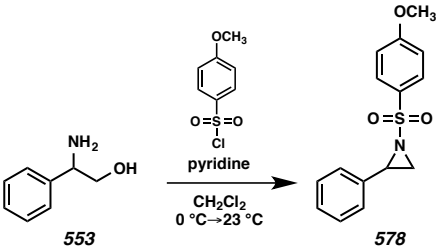
***N*-mesyl-2-phenylaziridine (577)**:

Aziridine **577** was prepared according to General Procedure B from 2-phenylglycinol (**553**); 88% yield; R_f = 0.29 (3:7 Acetone:Hexanes eluent); characterization data match those reported in the literature.[45]



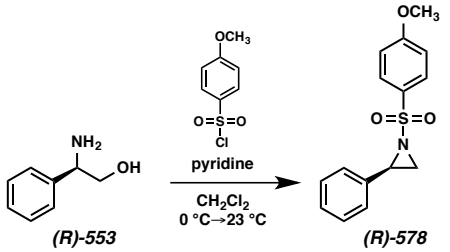
(*R*)-*N*-mesyl-2-phenylaziridine ((*R*)-577):

Aziridine **(*R*)-577** was prepared according to General Procedure B from (*R*)-(–)-2-phenylglycinol (**(*R*)-553**): characterization data are the same as above; $[\alpha]_D^{25.0}$ –194.5° (*c* 0.500, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 3.0 minutes, minor retention time: 3.3 minutes, 99% ee).



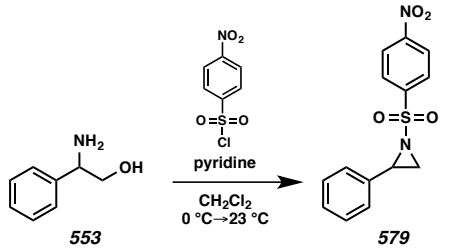
***N*-(*p*-methoxybenzenesulfonyl)-2-phenylaziridine (578)**:

Aziridine **578** was prepared according to General Procedure B from 2-phenylglycinol (**553**): 81% yield; R_f = 0.39 (3:7 Acetone:Hexanes eluent); characterization data match those reported in the literature.[40]



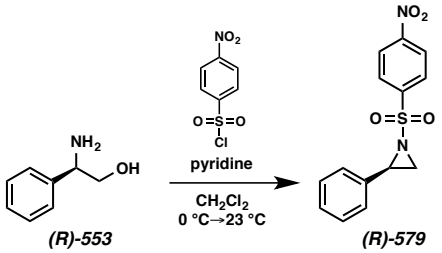
(*R*)-*N*-(*p*-methoxybenzenesulfonyl)-2-phenylaziridine ((*R*)-578):

Aziridine **(*R*)-578** was prepared according to General Procedure B from (*R*)-(–)-2-phenylglycinol (**(*R*)-553**): characterization data are the same as above; $[\alpha]_D^{25.0}$ –78.0° (*c* 0.850, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 10.0 minutes, minor retention time: 11.3 minutes, >99% ee).



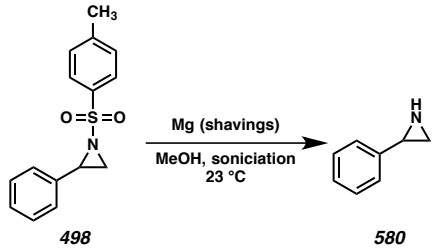
***N*-(*p*-nitrobenzenesulfonyl)-2-phenylaziridine (579)**:

Aziridine **579** was prepared according to General Procedure B from 2-phenylglycinol (**553**): 76% yield; R_f = 0.24 (1:4 Acetone:Hexanes eluent); characterization data match those reported in the literature.[40]



(*R*)-*N*-(*p*-nitrobenzenesulfonyl)-2-phenylaziridine ((*R*)-579):

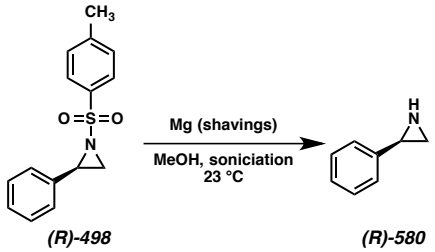
Aziridine **(*R*)-579** was prepared according to General Procedure B from (*R*)-(–)-2-phenylglycinol (**(*R*)-553**): characterization data are the same as above; $[\alpha]_D^{25.0}$ –58.4° (*c* 0.600, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OD-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 8.9 minutes, minor retention time: 9.8 minutes, >99% ee).



2-phenylaziridine (580):

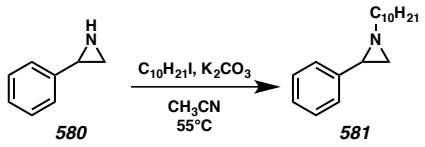
Aziridine **580** was prepared according to literature methods from *N*-tosyl-2-phenylaziridine (**498**).[30] To a suspension of magnesium metal shavings (474 mg, 19.5 mmol, 5.33 equiv) in CH_3OH (37 mL) was added a solution of aziridine **498** (1.00 g, 3.66 mmol, 1.00 equiv) in CH_3OH (24 mL) quickly dropwise. The reaction mixture was then sonicated at ambient temperature until consumption of the starting material was complete (determined by TLC analysis, ca. 30 min). The resulting white suspension was poured over brine (200 mL) and extracted with CH_2Cl_2 (4 x 150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to generate a white

solid. The crude residue was purified by column chromatography (85% EtOAc and 3% Et_3N in hexanes→3%Et_3N in EtOAc eluent) to afford aziridine **580** (342 mg, 78% yield) as a clear, colorless oil: R_f = 0.42 (EtOAc eluent); characterization data match those reported in the literature.[30]



(*R*)-2-phenylaziridine ((*R*)-580):

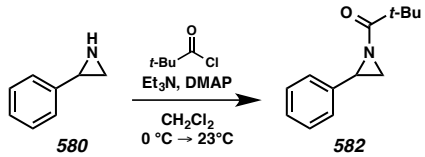
Aziridine **(*R*)-580** was prepared according to literature methods from (*R*)-*N*-tosyl-2-phenylaziridine (**(*R*)-498**) as described above: characterization data are the same as above; $[\alpha]_D^{25.0}$ –59.4° (*c* 0.750, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OD-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.8 minutes, minor retention time: 4.4 minutes, >99% ee).



***N*-(*n*-decyl)-2-phenylaziridine (581)**:

Aziridine **581** was prepared according to a procedure modified from literature methods.[5c] To an oven-dried vial with a stir bar were added aziridine **580** (113 mg, 0.95 mmol, 1.20 equiv) and acetonitrile (1.2 mL). Potassium carbonate (130 mg, 0.95 mmol, 1.20 equiv)

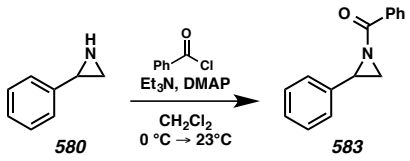
and decyl iodide (170 μL, 0.79 mmol, 1.00 equiv) were then added, and the vial was sealed and heated to 55 °C. Upon consumption of starting material (determined by LCMS analysis, ca. 17 h), the reaction mixture was allowed to cool to room temperature, concentrated in vacuo, and the residue partitioned between diethyl ether and brine. The organic layer was separated and concentrated in vacuo to afford a gold oil. The crude residue was purified by column chromatography (5% EtOAc in hexanes eluent) to furnish alkylated aziridine **581** (138 mg, 67% yield) as a clear, colorless oil: R_f = 0.33 (1:19 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33–7.18 (m, 5H), 2.52–2.44 (m, 1H), 2.36–2.26 (m, 2H), 1.89 (dd, *J* = 3.4, 0.7 Hz, 1H), 1.65 (dd, *J* = 6.5, 0.7 Hz, 1H), 1.64–1.56 (m, 2H), 1.41–1.18 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.7, 128.4, 126.9, 126.3, 62.1, 41.4, 37.9, 32.1, 30.0, 29.8, 29.7, 29.7, 29.5, 27.6, 22.8, 14.3; IR (Neat Film, NaCl) 3036, 2925, 2853, 1606, 1495, 1467, 1377, 1207, 1084, 746 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{18}H_{30}N$ $[M+H]^+$: 260.2373, found 260.2378.



***N*-pivoyl-2-phenylaziridine (582)**:

To a stirred solution of 2-phenylaziridine (**580**, 568 mg, 4.77 mmol, 1.00 equiv) in CH_2Cl_2 (12 mL) were added triethylamine (Et_3N, 0.39 mL, 5.25 mmol, 1.10 equiv) and trimethylacetyl chloride (1.17 mL, 9.54 mmol, 2.00 equiv) dropwise. The reaction mixture was cooled to 0 °C (ice/H_2O bath) at which time 4-(dimethylamino)pyridine (DMAP, 59 mg, 0.49 mmol, 0.10 equiv) was added as a solid in one portion. The bath

was immediately removed and the reaction mixture was allowed to warm to ambient temperature. Upon consumption of starting material (determined by TLC analysis, ca. 1 h), the reaction mixture was concentrated in vacuo to afford a gold oil. The crude residue was purified by column chromatography (20% EtOAc in hexanes eluent) to afford aziridine **582** (204 mg, 21% yield) as a clear, colorless oil: R_f = 0.31 (1:4 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38–7.33 (m, 2H), 7.32–7.28 (m, 1H), 7.27–7.24 (m, 2H), 5.44 (dd, *J* = 10.3, 7.8 Hz, 1H), 4.24 (dd, *J* = 14.2, 10.3 Hz, 1H), 3.74 (dd, *J* = 14.2, 7.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.2, 141.8, 128.8, 128.1, 125.6, 80.7, 63.0, 33.4, 27.9; IR (Neat Film, NaCl) 2971, 2873, 1661, 1480, 1455, 1265, 1132, 988, 954, 759 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{13}H_{18}NO$ $[M+H]^+$: 204.1388, found 204.1385.

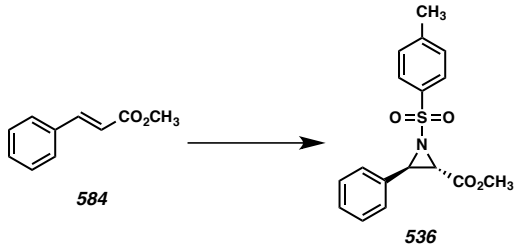


580 *583*

_N_-benzoyl-2-phenylaziridine (583):

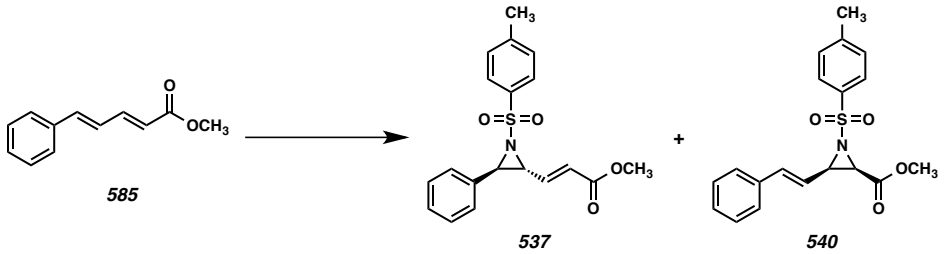
To a stirred solution of 2-phenylaziridine (**580**, 119 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) were added triethylamine (Et_3N, 0.16 mL, 1.10 mmol, 1.10 equiv) and benzoyl chloride (0.23 mL, 2.00 mmol, 2.00 equiv) dropwise. The reaction mixture was cooled to 0 °C (ice/H_2O bath) at which time 4-(dimethylamino)pyridine (12 mg, 0.10 mmol, 0.10 equiv) was added as a solid in one portion. The bath was immediately removed and the reaction mixture was allowed to warm to ambient temperature. Upon consumption of starting material (determined by TLC analysis, ca. 1 h), the reaction mixture was concentrated in vacuo to afford a gold oil. The crude residue was purified by

column chromatography (10% EtOAc with 1% Et_3N in hexanes eluent) to afford aziridine **583** (222 mg, 99% yield) as a white amorphous solid: R_f = 0.40 (1:9 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[46]



***trans*-methyl *N*-tosyl-3-phenylaziridine-2-carboxylate (536)**:

Aziridine **536** was prepared according to General Procedure A: 52% yield; R_f = 0.29 (3:7 Acetone:Hexanes eluent); characterization data match those reported in the literature.[42]



***trans*-*N*-tosyl-2-((*E*)-2-(methoxycarbonyl)ethenyl)-3-phenylaziridine (537) and *cis*-methyl *N*-tosyl-3-((*E*)-styryl)aziridine-2-carboxylate (540)**:

Aziridines **537** and **540** were prepared according to General Procedure A:

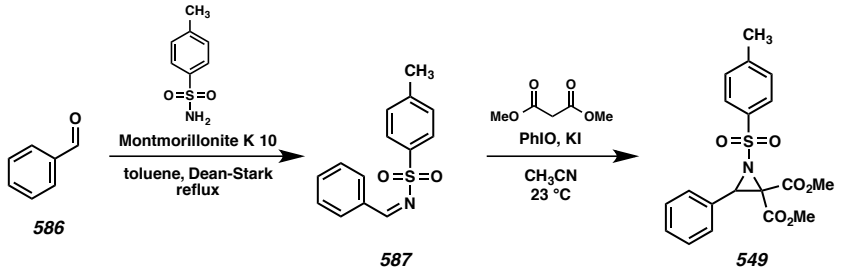
***trans*-*N*-tosyl-2-((*E*)-2-(methoxycarbonyl)ethenyl)-3-phenylaziridine (537)**:

20% yield; R_f = 0.42 (3:7 EtOAc:Hexanes eluent); characterization data for ^1H and ^{13}C NMR spectra match those reported in the literature;[47] IR (Neat Film, NaCl) 3032, 2952, 2256, 1722, 1651, 1597, 1495, 1435, 1407, 1329, 1268, 1162, 1089, 1034, 980, 900, 865,

815, 766, 733 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{19}H_{20}NO_4S$ $[M+H]^+$: 358.1108, found 358.1108.

***cis*-methyl *N*-tosyl-3-((*E*)-styryl)aziridine-2-carboxylate (540)**:

30% yield; R_f = 0.45 (3:7 EtOAc:Hexanes eluent); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.90–7.83 (m, 2H), 7.37–7.24 (m, 7H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.74 (s, 3H), 3.72 (ddd, *J* = 8.5, 7.4, 0.6 Hz, 1H), 3.62 (d, *J* = 7.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 166.0, 145.3, 137.8, 135.7, 134.3, 130.1, 128.8, 128.7, 128.2, 126.8, 119.8, 52.9, 46.0, 42.0, 21.9; IR (Neat Film, NaCl) 3029, 2955, 2256, 1747, 1597, 1445, 1329, 1207, 1161, 1090, 1035, 969, 915, 802, 761, 734 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{20}NO_4S$ $[M+H]^+$: 358.1108, found 358.1110.

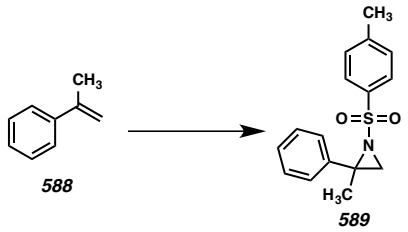


dimethyl *N*-tosyl-3-phenylaziridine-2,2-dicarboxylate (549):

Aziridine **549** was prepared according to literature methods from benzaldehyde over two steps. Procedure for the condensation of *p*-toluenesulfonamide onto benzaldehyde (**586**) was followed from the literature.[48] A stirred suspension of benzaldehyde (**586**, 1.02 mL, 10.0 mmol, 1.00 equiv), *p*-toluenesulfonamide (1.71 g, 10.0 mmol, 1.00 equiv), and montmorillonite K 10 (900 mg) in toluene (50 mL) was heated to reflux under a Dean-Stark apparatus. After 2.5 h, the consumption of starting material was complete (as

determined by TLC analysis) and the reaction mixture was allowed to cool and filtered through Celite rinsing with toluene eluent (30 mL). The filtrate was concentrated in vacuo and the crude solids were purified by silica gel column chromatography (40% Et_2O in hexanes eluent), ensuring the product was eluted quickly,[49] to furnish imine **587** (2.13 g, 82% yield) as a white solid: R_f = 0.32 (2:3 Et_2O:Hexanes eluent); characterization data matches those reported in the literature.[50]

Procedure for the oxidative cycloaddition of dimethyl malonate with imine **587** was followed from the literature.[51] To a stirred solution of imine **587** (648 mg, 2.50 mmol, 1.00 equiv) and dimethyl malonate (0.32 mL, 2.75 mmol, 1.10 equiv) in acetonitrile (5 mL) were added iodosobenzene (1.10 g, 5.00 mmol, 2.00 equiv) and potassium iodide (85 mg, 0.50 mmol, 0.20 equiv) as solids, each in a single portion. After 10 minutes, the consumption of starting material was complete (as determined by TLC analysis) and the reaction mixture was diluted with dichloromethane (20 mL), dry loaded onto Celite (2.5 g), and purified by silica gel column chromatography (25% EtOAc in hexanes eluent) to afford aziridine **549** (658 mg, 68% yield) as a viscous clear, colorless oil; R_f = 0.17 (1:4 EtOAc:Hexanes eluent); characterization data for ^1H and ^{13}C NMR and HRMS spectra match those reported in the literature;[52] IR (Neat Film, NaCl) 3281, 2956, 1749, 1435, 1344, 1234, 1165, 1092, 816.



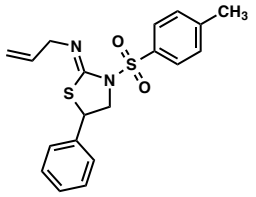
_N_-tosyl-2-methyl-2-phenylaziridine (589):

Aziridine **589** was prepared according to General Procedure A: 32% yield; R_f = 0.44 (1:3 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[42]

6.14.4 Iminothiazolidine Synthesis and Characterization Data

Iminothiazolidine Synthesis and Characterization Data

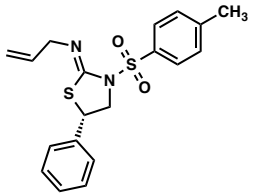
Unless otherwise stated, all iminothiazolidines were prepared according to General Procedure C and were isolated as amorphous white solids.



499

(*Z*)-5-phenyl-3-tosyl-2-(allylimino)thiazolidine (499):

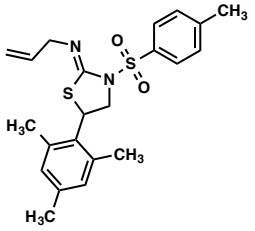
99% yield; R_f = 0.28 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94–7.89 (m, 2H), 7.40–7.32 (m, 5H), 7.32–7.28 (m, 2H), 5.84 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.12–4.98 (m, 2H), 4.80 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.50 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.94 (dd, *J* = 10.3, 8.5 Hz, 1H), 3.86 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.77 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.2, 144.6, 136.8, 135.0, 134.9, 129.2, 129.1, 129.0, 128.8, 127.6, 115.3, 58.0, 56.6, 47.1, 21.8; IR (Neat Film, NaCl) 2923, 1653, 1596, 1355, 1168, 1108, 810, 764 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{19}H_{21}N_2O_2S_2$ $[M+H]^+$: 373.1039, found 373.1049.



(S)-499

(*S*,*Z*)-5-phenyl-3-tosyl-2-(allylimino)thiazolidine ((*S*)-499):

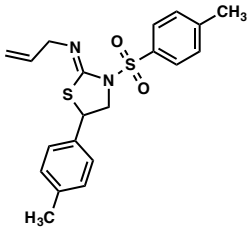
Thiazolidine **(*S*)-499** was prepared according to General Procedure E: 99% yield; R_f = 0.28 (1:4 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D^{25.0}$ –13.1° (*c* 1.600, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AD-H, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 5.4 minutes, minor retention time: 3.8 minutes, 94% ee).



503

(*Z*)-5-mesityl-3-tosyl-2-(allylimino)thiazolidine (503):

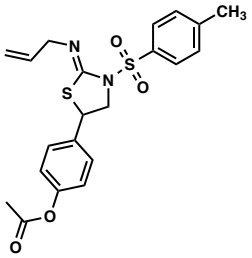
97% yield; R_f = 0.23 (1:4 Et_2O:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99–7.91 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 2H), 5.83 (ddt, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.43 (dd, *J* = 11.0, 7.6 Hz, 1H), 5.11–4.97 (m, 2H), 4.41 (dd, *J* = 10.4, 7.6 Hz, 1H), 4.14 (t, *J* = 10.7 Hz, 1H), 3.85 (ddt, *J* = 16.0, 5.1, 1.8 Hz, 1H), 3.73 (ddt, *J* = 16.0, 5.2, 1.7 Hz, 1H), 2.45 (s, 3H), 2.40 (s, 6H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.9, 144.6, 138.4, 138.0, 135.4, 135.2, 131.0, 129.3, 129.1, 127.3, 115.2, 58.0, 52.3, 42.4, 21.8, 21.6, 20.9; IR (Neat Film, NaCl) 2920, 1656, 1637, 1450, 1357, 1170, 1106, 1090, 858, 789 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{22}H_{27}N_2O_2S_2$ $[M+H]^+$: 415.1508, found 415.1519.



504

(*Z*)-5-(*p*-tolyl)-3-tosyl-2-(allylimino)thiazolidine (504):

92% yield; R_f = 0.38 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95–7.89 (m, 2H), 7.32–7.28 (m, 2H), 7.28–7.24 (m, 2H), 7.19–7.13 (m, 2H), 5.84 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.06 (dq, *J* = 17.2, 1.9 Hz, 1H), 5.02 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.77 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.48 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.91 (dd, *J* = 10.3, 8.7 Hz, 1H), 3.85 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.76 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.4, 144.6, 138.7, 135.1, 135.0, 133.7, 129.8, 129.2, 129.1, 127.5, 115.2, 58.0, 56.6, 47.0, 21.8, 21.2; IR (Neat Film, NaCl) 3007, 2922, 1657, 1639, 1597, 1514, 1358, 1170, 1110, 915, 814, 774, 732 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{20}H_{23}N_2O_2S_2$ $[M+H]^+$: 387.1195, found 387.1202.

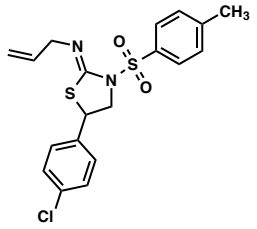


505

(*Z*)-5-(*p*-acetoxyphenyl)-3-tosyl-2-(allylimino)thiazolidine (505):

95% yield; R_f = 0.37 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93–7.87 (m, 2H), 7.42–7.34 (m, 2H), 7.32–7.27 (m, 2H), 7.10–7.04 (m, 2H), 5.83 (ddt, *J* =

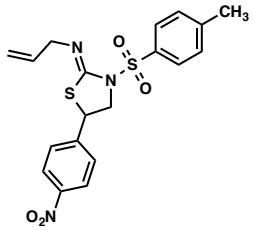
17.1, 10.3, 5.1 Hz, 1H), 5.12–4.97 (m, 2H), 4.78 (dd, *J* = 8.3, 6.3 Hz, 1H), 4.47 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.91 (dd, *J* = 10.3, 8.3 Hz, 1H), 3.84 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.76 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.4, 151.0, 150.8, 144.7, 135.0, 134.9, 134.5, 129.2, 129.1, 128.8, 122.3, 115.3, 58.0, 56.6, 46.5, 21.8, 21.2; IR (Neat Film, NaCl) 2922, 1760, 1657, 1505, 1360, 1202, 1169, 1107, 912, 811 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{21}H_{23}N_2O_4S_2$ $[M+H]^+$: 431.1094, found 431.1113.



506

(*Z*)-5-(*p*-chlorophenyl)-3-tosyl-2-(allylimino)thiazolidine (506):

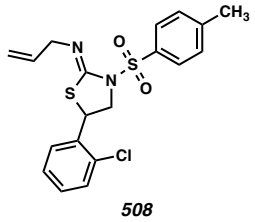
93% yield; R_f = 0.29 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92–7.87 (m, 2H), 7.32–7.27 (m, 6H), 5.83 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.10–4.99 (m, 2H), 4.75 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.45 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.93 (dd, *J* = 10.3, 7.8 Hz, 1H), 3.84 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.77 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.7, 144.7, 135.7, 135.0, 134.9, 134.7, 129.3, 129.2, 129.1, 129.0, 115.4, 58.1, 56.4, 46.4, 21.8; IR (Neat Film, NaCl) 2924, 1651, 1597, 1493, 1354, 1168, 1090, 1014, 917, 809, 731 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{19}H_{20}{}^{35}ClN_2O_2S_2$ $[M+H]^+$: 407.0649, found 407.0665.



507

(*Z*)-5-(*p*-nitrophenyl)-3-tosyl-2-(allylimino)thiazolidine (507):

59% yield; R_f = 0.20 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.25–8.19 (m, 2H), 7.93–7.87 (m, 2H), 7.59–7.53 (m, 2H), 7.34–7.28 (m, 2H), 5.84 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.12–5.01 (m, 2H), 4.84 (t, *J* = 6.5 Hz, 1H), 4.47 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.06 (dd, *J* = 10.5, 6.7 Hz, 1H), 3.88–3.77 (m, 2H), 2.45 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 149.8, 148.1, 145.0, 134.8, 134.7, 129.4, 129.1, 128.6, 124.4, 115.6, 58.3, 55.9, 46.0, 21.8; IR (Neat Film, NaCl) 1656, 1597, 1521, 1347, 1169, 1107, 857, 813 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{20}N_3O_4S_2$ $[M+H]^+$: 418.0890, found 418.0907.

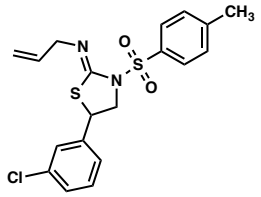


508

(*Z*)-5-(*o*-chlorophenyl)-3-tosyl-2-(allylimino)thiazolidine (508):

91% yield; R_f = 0.35 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92–7.87 (m, 2H), 7.60–7.56 (m, 1H), 7.43–7.38 (m, 1H), 7.31–7.26 (m, 4H), 5.83 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.19 (dd, *J* = 6.3, 5.2 Hz, 1H), 5.09–5.00 (m, 2H), 4.39 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.20 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.85 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.79 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.8,

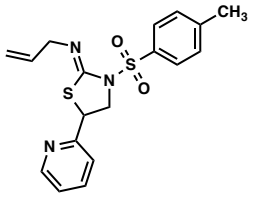
144.7, 135.6, 135.0, 134.9, 133.6, 130.0, 129.7, 129.3, 129.1, 128.1, 127.7, 115.3, 58.1, 54.9, 42.8, 21.8; IR (Neat Film, NaCl) 3067, 2881, 1657, 1597, 1470, 1444, 1361, 1284, 1171, 1109, 919, 811, 750 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{19}H_{20}{}^{35}ClN_2O_2S_2$ $[M+H]^+$: 407.0649, found 407.0665.



509

(*Z*)-5-(*m*-chlorophenyl)-3-tosyl-2-(allylimino)thiazolidine (509):

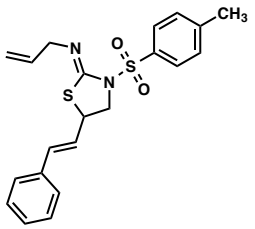
90% yield; R_f = 0.35 (1:4 Acetone:Hexanes eluent); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.92–7.86 (m, 2H), 7.37–7.34 (m, 1H), 7.33–7.25 (m, 5H), 5.83 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.09–5.00 (m, 2H), 4.74 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.48 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.94 (dd, *J* = 10.4, 7.8 Hz, 1H), 3.85 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.77 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.6, 144.8, 139.3, 135.0, 134.9, 134.8, 130.5, 129.3, 129.1, 129.0, 127.8, 125.9, 115.4, 58.1, 56.4, 46.4, 21.8; IR (Neat Film, NaCl) 2923, 1656, 1596, 1479, 1360, 1169, 1110, 917, 812 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{20}{}^{35}ClN_2O_2S_2$ $[M+H]^+$: 407.0649, found 407.0669.



510

(*Z*)-5-(*o*-pyridyl)-3-tosyl-2-(allylimino)thiazolidine (510):

General Procedure C followed using 2.25 equivalents of zinc(II) bromide: 42% yield; R_f = 0.28 (1:1 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.58 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.86–7.79 (m, 2H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.26–7.21 (m, 3H), 5.98–5.93 (m, 1H), 5.85 (ddt, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.10 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.03 (dq, *J* = 10.3, 1.7 Hz, 1H), 3.88 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 3.77 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.69 (dd, *J* = 11.0, 7.2 Hz, 1H), 3.53 (dd, *J* = 11.0, 1.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.5, 152.2, 149.6, 144.6, 137.0, 136.1, 135.1, 129.2, 129.1, 123.1, 121.1, 115.3, 64.5, 58.4, 34.6, 21.8; IR (Neat Film, NaCl) 2921, 1655, 1638, 1590, 1352, 1169, 1110, 1088, 792 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{18}H_{20}N_3O_2S_2$ $[M+H]^+$: 374.0991, found 374.1006.

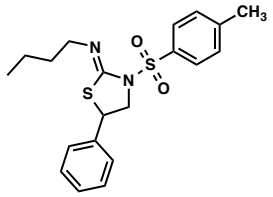


511

(*Z*)-5-((*E*)-styryl)-3-tosyl-2-(allylimino)thiazolidine (511):

47% yield; R_f = 0.34 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94–7.90 (m, 2H), 7.38–7.26 (m, 7H), 6.64 (dd, *J* = 15.6, 0.8 Hz, 1H), 6.13 (dd, *J* = 15.6, 8.9 Hz, 1H), 5.82 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.09–4.97 (m, 2H), 4.42 (dddd, *J* = 8.9,

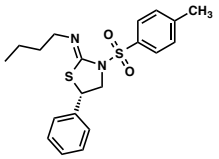
7.4, 6.0, 0.8 Hz, 1H), 4.34 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.87 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.82 (ddt, *J* = 15.8, 5.1, 1.8 Hz, 1H), 3.75 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.2, 144.7, 135.6, 135.0, 134.9, 134.4, 129.3, 129.1, 128.9, 128.6, 126.8, 124.6, 115.3, 58.1, 54.9, 46.2, 21.8; IR (Neat Film, NaCl) 2925, 2254, 1645, 1452, 1353, 1259, 1168, 1090, 1019, 915, 811, 753 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{21}H_{23}N_2O_2S_2$ $[M+H]^+$: 399.1195, found 399.1201.



512

(*Z*)-5-phenyl-3-tosyl-2-((*n*-butyl)imino)thiazolidine (512):

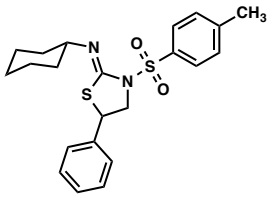
>99% yield; R_f = 0.36 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92–7.87 (m, 2H), 7.40–7.32 (m, 5H), 7.31–7.27 (m, 2H), 4.78 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.48 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.91 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.20 (dt, *J* = 12.6, 6.7 Hz, 1H), 3.08 (dt, *J* = 12.7, 6.8 Hz, 1H), 2.44 (s, 3H), 1.50 (dddd, *J* = 13.5, 8.7, 6.7, 2.2 Hz, 2H), 1.23–1.13 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 149.4, 144.5, 137.1, 135.1, 129.1, 129.1, 129.1, 128.8, 127.7, 56.4, 56.1, 47.0, 32.9, 21.8, 20.5, 14.0; IR (Neat Film, NaCl) 2955, 2928, 2870, 1658, 1455, 1357, 1170, 1096, 811, 765 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{25}N_2O_2S_2$ $[M+H]^+$: 389.1352, found 389.1368.



(S)-512

(*S*,*Z*)-5-phenyl-3-tosyl-2-(*n*-butylimino)thiazolidine ((*S*)-512):

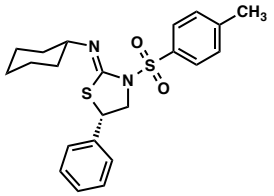
Thiazolidine **(*S*)-512** was prepared according to General Procedure E: 94% yield; R_f = 0.36 (1:4 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D^{25.0}$ –6.45° (*c* 2.800, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AD-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 4.7 minutes, minor retention time: 3.6 minutes, 95% ee).



513

(*Z*)-5-phenyl-3-tosyl-2-(cyclohexylimino)thiazolidine (513):

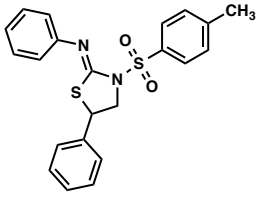
94% yield; R_f = 0.41 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95–7.89 (m, 2H), 7.41–7.31 (m, 5H), 7.31–7.27 (m, 2H), 4.76 (dd, *J* = 8.5, 6.3 Hz, 1H), 4.46 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.87 (dd, *J* = 10.2, 8.5 Hz, 1H), 2.77 (tt, *J* = 9.5, 3.9 Hz, 1H), 2.44 (s, 3H), 1.79–1.62 (m, 3H), 1.58 (dddd, *J* = 12.8, 5.9, 3.6, 1.7 Hz, 2H), 1.40 (ddtd, *J* = 22.7, 16.6, 9.5, 4.6 Hz, 2H), 1.33–1.18 (m, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 147.2, 144.4, 137.2, 135.0, 129.3, 129.1, 129.0, 128.7, 127.6, 65.5, 56.1, 47.0, 33.6, 33.4, 25.8, 24.5, 24.5, 21.8; IR (Neat Film, NaCl) 2928, 2853, 1652, 1450, 1362, 1171, 1100, 812, 760 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{22}H_{27}N_2O_2S_2$ $[M+H]^+$: 415.1508, found 415.1493.



(S)-513

(*S*,*Z*)-5-phenyl-3-tosyl-2-(cyclohexylimino)thiazolidine ((*S*)-513):

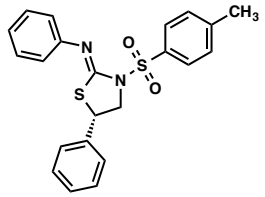
Thiazolidine **(*S*)-513** was prepared according to General Procedure E: 98% yield; R_f = 0.41 (1:4 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D^{25.0}$ 0.72° (*c* 4.200, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 5.1 minutes, minor retention time: 4.0 minutes, 92% ee).



514

(*Z*)-5-phenyl-3-tosyl-2-(phenylimino)thiazolidine (514):

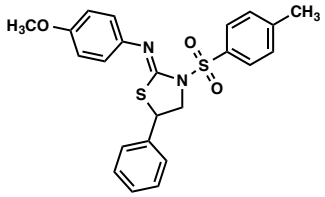
95% yield; R_f = 0.23 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.96 (m, 2H), 7.41–7.29 (m, 7H), 7.30–7.22 (m, 2H), 7.12–7.03 (m, 1H), 6.83–6.75 (m, 2H), 4.80 (dd, *J* = 8.5, 6.4 Hz, 1H), 4.60 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.06 (dd, *J* = 10.4, 8.5 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.3, 150.1, 145.0, 136.6, 134.7, 129.3, 129.2, 129.1, 129.0, 128.9, 127.6, 124.4, 120.9, 56.9, 47.1, 21.9; IR (Neat Film, NaCl) 3030, 1640, 1591, 1487, 1360, 1171, 1135, 1100, 763 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{22}H_{21}N_2O_2S_2$ $[M+H]^+$: 409.1039, found 409.1051.



(S)-514

(*S*,*Z*)-5-phenyl-3-tosyl-2-(phenylimino)thiazolidine ((*S*)-514):

Thiazolidine **(*S*)-514** was prepared according to General Procedure E: >99% yield; R_f = 0.23 (1:4 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D^{25.0}$ 49.9° (*c* 3.400, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.3 minutes, minor retention time: 5.7 minutes, 77% ee).

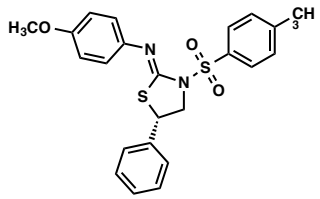


515

(*Z*)-5-phenyl-3-tosyl-2-((*p*-methoxyphenyl)imino)thiazolidine (515):

98% yield; R_f = 0.31 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.94 (m, 2H), 7.39–7.28 (m, 7H), 6.85–6.79 (m, 2H), 6.79–6.73 (m, 2H), 4.79 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.59 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.05 (dd, *J* = 10.4, 8.5 Hz, 1H), 3.76 (s, 3H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 156.6, 151.9, 144.9, 143.4, 136.7, 134.8, 129.3, 129.2, 129.1, 128.8, 127.6, 121.9, 114.2, 56.7, 55.5, 47.0, 21.8; IR (Neat Film, NaCl) 2949, 1640, 1505, 1455, 1360, 1290, 1242, 1168, 1101, 1033, 910, 832, 811,

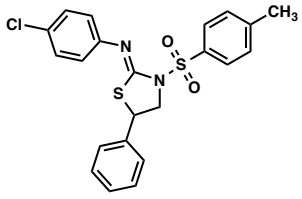
768, 733 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{23}H_{23}N_2O_3S_2$ $[M+H]^+$: 439.1145, found 439.1161.



(S)-515

(*S*,*Z*)-5-phenyl-3-tosyl-2-(*p*-methoxyphenylimino)thiazolidine ((*S*)-515):

Thiazolidine **(*S*)-515** was prepared according to General Procedure E: 97% yield; R_f = 0.31 (3:7 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D^{25.0}$ 61.6° (*c* 2.800, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 9.1 minutes, minor retention time: 6.9 minutes, 90% ee).

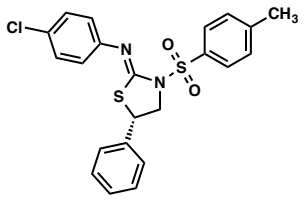


516

(*Z*)-5-phenyl-3-tosyl-2-((*p*-chlorophenyl)imino)thiazolidine (516):

92% yield; R_f = 0.29 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01–7.93 (m, 2H), 7.39–7.30 (m, 7H), 7.25–7.18 (m, 2H), 6.76–6.70 (m, 2H), 4.81 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.60 (dd, *J* = 10.4, 6.5 Hz, 1H), 4.07 (dd, *J* = 10.4, 8.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 153.0, 148.5, 145.2, 136.4, 134.6, 129.7, 129.4, 129.2, 129.2, 129.1, 129.0, 127.6, 122.3, 56.9, 47.2, 21.9; IR (Neat Film, NaCl) 2924,

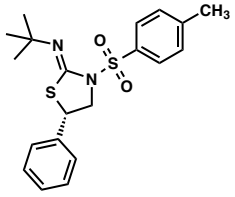
1634, 1588, 1486, 1360, 1172, 1139, 1088, 833, 812 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{22}H_{20}{}^{35}ClN_2O_2S_2$ $[M+H]^+$: 443.0649, found 443.0664.



(S)-516

(*S*,*Z*)-5-phenyl-3-tosyl-2-(*p*-chlorophenylimino)thiazolidine ((*S*)-516):

Thiazolidine **(*S*)-516** was prepared according to General Procedure E: 99% yield; R_f = 0.29 (1:4 Acetone:Hexanes eluent); characterization data match those above; $[\alpha]_D{}^{25.0}$ 44.7° (*c* 4.950, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.7 minutes, minor retention time: 6.1 minutes, 60% ee).

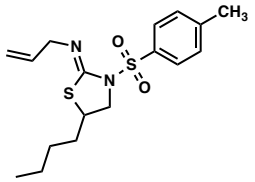


(S)-546

(*S*,*Z*)-5-phenyl-3-tosyl-2-(*t*-butylimino)thiazolidine ((*S*)-546):

39% yield; R_f = 0.38 (1:4 Acetone:Hexanes eluent); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.88–7.83 (m, 2H), 7.42–7.31 (m, 5H), 7.30–7.26 (m, 2H), 4.79 (dd, *J* = 8.4, 6.2 Hz, 1H), 4.47 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.88 (dd, *J* = 10.3, 8.4 Hz, 1H), 2.44 (s, 3H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 144.2, 142.9, 137.3, 135.7, 129.4, 129.1, 128.8, 128.7, 127.7, 55.0, 54.7, 48.3, 28.9, 21.8; IR (Neat Film, NaCl) 2971, 1653, 1600,

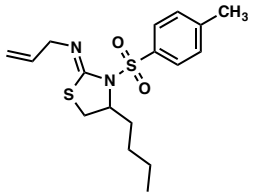
1496, 1454, 1360, 1167, 1092, 810, 771, 701 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{20}H_{25}N_2O_2S_2$ $[M+H]^+$: 389.1352, found 389.1362; $[\alpha]_D^{25.0}$ 3.33° (*c* 1.900, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak IC-3 column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 6.2 minutes, minor retention time: 7.0 minutes, 75% ee).



518

(*Z*)-5-(*n*-butyl)-3-tosyl-2-(allylimino)thiazolidine (518):[53]

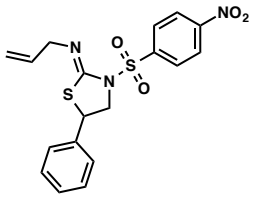
18% yield; R_f = 0.44 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.94–7.86 (m, 2H), 7.30–7.26 (m, 2H), 5.80 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.04–4.96 (m, 2H), 4.21 (dd, *J* = 10.0, 5.9 Hz, 1H), 3.81–3.73 (m, 2H), 3.70 (dd, *J* = 10.0, 7.1 Hz, 1H), 3.59 (ddt, *J* = 8.4, 7.0, 6.0 Hz, 1H), 2.42 (s, 3H), 1.82–1.70 (m, 1H), 1.71–1.60 (m, 1H), 1.42–1.27 (m, 4H), 0.90 (td, *J* = 7.4, 3.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.6, 144.5, 135.2, 130.0, 129.2, 129.0, 115.1, 58.0, 55.0, 44.0, 33.9, 30.1, 22.5, 21.8, 14.0; IR (Neat Film, NaCl) 2957, 2928, 2871, 1652, 1598, 1456, 1357, 1170, 1106, 918, 812 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{17}H_{25}N_2O_2S_2$ $[M+H]^+$: 353.1352, found 353.1364.



519

(*Z*)-4-(*n*-butyl)-3-tosyl-2-(allylimino)thiazolidine (519):[53]

56% yield; R_f = 0.44 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95–7.85 (m, 2H), 7.29–7.24 (m, 2H), 5.80 (ddt, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.03 (dq, *J* = 17.2, 1.9 Hz, 1H), 4.99 (dq, *J* = 10.3, 1.8 Hz, 1H), 4.82–4.74 (m, 1H), 3.81 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 3.70 (ddt, *J* = 15.9, 5.1, 1.8 Hz, 1H), 3.33 (dd, *J* = 11.0, 6.8 Hz, 1H), 2.94 (dd, *J* = 11.1, 0.8 Hz, 1H), 2.41 (s, 3H), 1.88–1.73 (m, 2H), 1.47–1.27 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.8, 144.2, 136.8, 135.1, 129.2, 128.9, 115.1, 61.2, 58.2, 33.1, 32.3, 28.7, 22.5, 21.7, 14.1; IR (Neat Film, NaCl) 2957, 2928, 2860, 1651, 1598, 1455, 1351, 1164, 1117, 1088, 918, 813 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{17}H_{25}N_2O_2S_2$ $[M+H]^+$: 353.1352, found 353.1358.

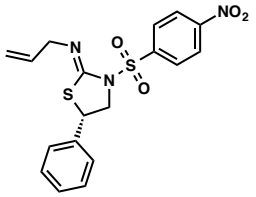


522

(*Z*)-5-phenyl-3-(*p*-nitrobenzenesulfonyl)-2-(allylimino)thiazolidine (522):

94% yield; R_f = 0.28 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37–8.28 (m, 2H), 8.26–8.16 (m, 2H), 7.42–7.31 (m, 5H), 5.82 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.11–5.03 (m, 2H), 4.86 (dd, *J* = 8.3, 6.3 Hz, 1H), 4.54 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.98 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.83 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H), 3.75 (ddt, *J* = 15.8,

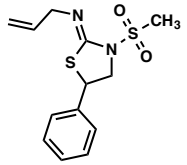
5.3, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 151.1, 150.6, 143.6, 136.3, 134.6, 130.4, 129.2, 129.1, 127.6, 123.7, 115.7, 57.9, 56.5, 47.5; IR (Neat Film, NaCl) 3106, 1656, 1530, 1349, 1314, 1175, 1109, 854, 740 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{18}H_{18}N_3O_4S_2$ $[M+H]^+$: 404.0733, found 404.0742.



(S)-522

(*S*,*Z*)-5-phenyl-3-(*p*-nitrobenzenesulfonyl)-2-(allylimino)thiazolidine ((*S*)-522):

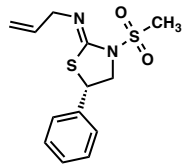
Thiazolidine **(*S*)-522** was prepared according to General Procedure E and was isolated as a white crystalline solid: 95% yield; R_f = 0.28 (1:4 Acetone:Hexanes eluent); characterization data match those above; colorless, translucent X-ray quality crystals were obtained by slow diffusion of 1% benzene in heptane into a solution of iminothiazolidine **(*S*)-522** in ethyl acetate, mp: 70–72 °C; $[\alpha]_D^{25.0}$ 1.7° (*c* 2.250, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OD-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 6.6 minutes, minor retention time: 5.5 minutes, 95% ee).



523

(*Z*)-5-phenyl-3-mesyl-2-(allylimino)thiazolidine (523):

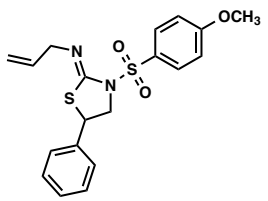
Thiazolidine **523** was isolated as a clear, colorless oil: 91% yield; R_f = 0.40 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46–7.31 (m, 5H), 5.97 (ddt, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.27 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.13 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.84 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.41 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.99–3.90 (m, 3H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 153.0, 136.6, 134.9, 129.2, 129.0, 127.7, 115.8, 58.1, 55.6, 47.6, 40.5; IR (Neat Film, NaCl) 3011, 1656, 1651, 1346, 1163, 1113, 964, 764 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{13}H_{17}N_2O_2S_2$ $[M+H]^+$: 297.0726, found 297.0739.



(S)-523

(*S*,*Z*)-5-phenyl-3-mesyl-2-(allylimino)thiazolidine ((*S*)-523):

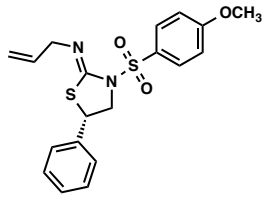
Thiazolidine **(*S*)-523** was prepared according to General Procedure E and was isolated as a clear, colorless oil: 95% yield; R_f = 0.40 (3:7 Acetone:Hexanes eluent); characterization data match those reported above; $[\alpha]_D^{25.0}$ –55.5° (*c* 2.200, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AD-H column, 7% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 12.6 minutes, minor retention time: 11.3 minutes, 90% ee).



524

(*Z*)-5-phenyl-3-(*p*-methoxybenzenesulfonyl)-2-(allylimino)thiazolidine (524):

90% yield; R_f = 0.40 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01–7.93 (m, 2H), 7.42–7.29 (m, 5H), 6.98–6.93 (m, 2H), 5.85 (ddt, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.08 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.03 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.79 (dd, *J* = 8.4, 6.3 Hz, 1H), 4.49 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.92 (dd, *J* = 10.3, 8.4 Hz, 1H), 3.88 (s, 3H), 3.88–3.83 (m, 1H), 3.77 (ddt, *J* = 15.9, 5.2, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 163.8, 151.3, 136.9, 135.1, 131.4, 129.5, 129.2, 128.8, 127.7, 115.3, 113.8, 58.1, 56.6, 55.8, 47.1; IR (Neat Film, NaCl) 2927, 1655, 1595, 1497, 1356, 1262, 1162, 1110, 1090, 1025, 833, 810 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{19}H_{21}N_2O_3S_2$ $[M+H]^+$: 389.0988, found 389.1004.

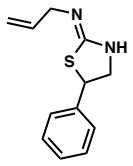


(S)-524

(*S*,*Z*)-5-phenyl-3-(*p*-methoxybenzenesulfonyl)-2-(allylimino)thiazolidine ((*S*)-524):

Thiazolidine **(*S*)-524** was prepared according to General Procedure E: 94% yield; R_f = 0.40 (3:7 Acetone:Hexanes eluent); characterization data match those reported above; $[\alpha]_D^{25.0}$ –6.6° (*c* 2.000, $CHCl_3$); enantiomeric excess was determined by analytical SFC

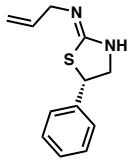
(Chiralpak AD-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 4.4 minutes, minor retention time: 6.6 minutes, 91% ee).



525

(*Z*)-5-phenyl-2-(allylimino)thiazolidine (525):

75% yield; R_f = 0.19 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.36 (m, 2H), 7.35–7.30 (m, 2H), 7.29–7.26 (m, 1H), 5.94 (ddt, *J* = 17.2, 10.2, 5.5 Hz, 1H), 5.27 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.18 (dq, *J* = 10.3, 1.4 Hz, 1H), 5.02 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.34 (dd, *J* = 13.4, 7.8 Hz, 1H), 4.10 (dd, *J* = 13.4, 6.3 Hz, 1H), 3.97 (dt, *J* = 5.5, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 160.7, 141.3, 134.5, 128.9, 127.9, 127.4, 116.6, 68.4, 56.7, 47.3; IR (Neat Film, NaCl) 2924, 2853, 1612, 1454, 1260, 1023, 802, 758 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{12}H_{15}N_2S$ $[M+H]^+$: 219.0950, found 219.0950.

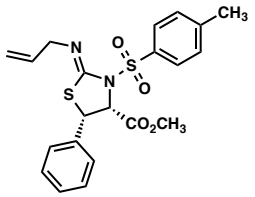


(S)-525

(*S*,*Z*)-5-phenyl-2-(allylimino)thiazolidine ((*S*)-525):

Thiazolidine **(*S*)-525** was prepared according to General Procedure E: 31% yield; R_f = 0.19 (3:7 Acetone:Hexanes eluent); characterization data match those reported above; $[\alpha]_D^{25.0}$ 26.4° (*c* 0.200, $CHCl_3$); enantiomeric excess was determined by analytical SFC

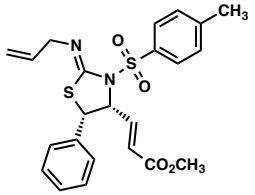
(Chiralcel OB-H column, 10% methanol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 3.9 minutes, minor retention time: 8.4 minutes, 34% ee).



536

***cis*-methyl (*Z*)-5-phenyl-3-tosyl-2-(allylimino)thiazolidine-4-carboxylate (536)**:

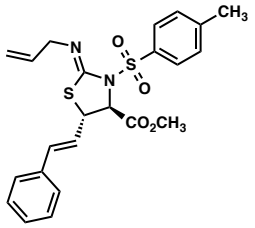
Thiazolidine **536** was isolated as a white crystalline solid and colorless, translucent X-ray quality crystals were obtained by slow diffusion of 1% benzene in heptane into a solution of iminothiazolidine **536** in ethyl acetate, mp: 107–109 °C: 88% yield; R_f = 0.32 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96–7.90 (m, 2H), 7.38–7.31 (m, 5H), 7.30–7.25 (m, 2H), 5.86 (ddt, *J* = 17.1, 10.3, 4.9 Hz, 1H), 5.33 (d, *J* = 8.0 Hz, 1H), 5.26 (d, *J* = 8.0 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.9 Hz, 1H), 5.03 (dq, *J* = 10.4, 1.8 Hz, 1H), 3.91 (ddt, *J* = 16.1, 4.9, 1.8 Hz, 1H), 3.83 (ddt, *J* = 16.1, 4.8, 1.9 Hz, 1H), 3.25 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 168.0, 150.2, 144.7, 135.4, 134.8, 132.9, 129.7, 129.3, 128.9, 128.8, 128.4, 115.1, 65.7, 57.9, 52.1, 49.8, 21.8; IR (Neat Film, NaCl) 2952, 2253, 1748, 1660, 1595, 1444, 1353, 1166, 1107, 915, 811 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{21}H_{23}N_2O_4S_2$ $[M+H]^+$: 431.1094, found 431.1114.



538

***cis*-(*Z*)-4-((*E*)-2-(methoxycarbonyl)ethenyl)-5-phenyl-3-tosyl-2-(allylimino)thiazolidine (538)**:

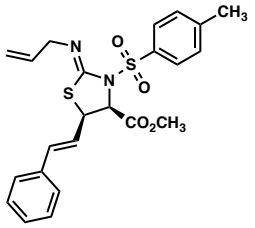
62% yield; R_f = 0.43 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93–7.87 (m, 2H), 7.36–7.27 (m, 5H), 7.26–7.23 (m, 2H), 6.60 (dd, *J* = 15.6, 7.4 Hz, 1H), 5.88 (ddt, *J* = 17.1, 10.2, 5.0 Hz, 1H), 5.80 (dd, *J* = 15.7, 1.1 Hz, 1H), 5.42 (ddd, *J* = 7.5, 6.5, 1.1 Hz, 1H), 5.22 (d, *J* = 6.5 Hz, 1H), 5.11 (dq, *J* = 17.1, 1.9 Hz, 1H), 5.06 (dq, *J* = 10.3, 1.7 Hz, 1H), 3.90 (ddt, *J* = 16.0, 4.9, 1.8 Hz, 1H), 3.84 (ddt, *J* = 16.0, 5.1, 1.8 Hz, 1H), 3.66 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.6, 149.6, 144.7, 140.3, 135.9, 134.9, 132.2, 129.6, 129.2, 129.1, 129.0, 128.7, 125.8, 115.4, 65.3, 58.1, 52.8, 51.9, 21.8; IR (Neat Film, NaCl) 2951, 1726, 1659, 1436, 1360, 1276, 1168, 1109, 917, 812 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{23}H_{25}N_2O_4S_2$ $[M+H]^+$: 457.1250, found 457.1268.



541

***trans*-methyl (*Z*)-5-((*E*)-styryl)-3-tosyl-2-(allylimino)thiazolidine-4-carboxylate (541)**:[54]

42% yield; R_f = 0.39 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98–7.93 (m, 2H), 7.34 (m, 4H), 7.32–7.27 (m, 1H), 7.25–7.20 (m, 2H), 6.62 (dd, *J* = 15.7, 0.9 Hz, 1H), 6.22 (dd, *J* = 15.6, 8.5 Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.1, 4.9 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 5.07–4.99 (m, 2H), 4.57 (ddd, *J* = 8.5, 1.8, 1.0 Hz, 1H), 3.82 (ddd, *J* = 5.1, 3.5, 1.8 Hz, 2H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.4, 149.2, 144.6, 135.7, 135.5, 134.8, 133.2, 129.7, 128.9, 128.8, 128.6, 126.9, 125.9, 115.2, 66.9, 58.0, 53.4, 48.3, 21.8; IR (Neat Film, NaCl) 2954, 1756, 1661, 1597, 1495, 1435, 1354, 1167, 1113, 1089, 916, 813, 781, 754 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{23}H_{25}N_2O_4S_2$ $[M+H]^+$: 457.1250, found 457.1252.



542

***cis*-methyl (*Z*)-5-((*E*)-styryl)-3-tosyl-2-(allylimino)thiazolidine-4-carboxylate (542)**:[54]

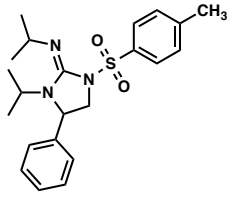
31% yield; R_f = 0.39 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97–7.92 (m, 2H), 7.36–7.27 (m, 7H), 6.66 (dd, *J* = 15.6, 0.9 Hz, 1H), 6.00 (dd, *J* = 15.5, 9.1

Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.3, 4.9 Hz, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 5.09–4.98 (m, 2H), 4.80 (ddd, *J* = 9.1, 7.6, 0.9 Hz, 1H), 3.85 (ddt, *J* = 16.1, 4.9, 1.9 Hz, 1H), 3.80 (ddt, *J* = 16.1, 4.8, 1.9 Hz, 1H), 3.68 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 168.2, 150.2, 144.7, 135.7, 135.5, 135.5, 134.8, 129.7, 129.0, 128.9, 128.8, 126.9, 121.2, 115.2, 64.5, 58.0, 52.6, 48.3, 21.8; IR (Neat Film, NaCl) 2952, 1750, 1661, 1597, 1495, 1450, 1354, 1206, 1169, 1121, 1089, 966, 916, 841, 813, 751 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{23}H_{25}N_2O_4S_2$ $[M+H]^+$: 457.1250, found 457.1253.

6.14.5 Iminoimidazolidine Synthesis and Characterization Data

Iminoimidazolidine Synthesis and Characterization Data

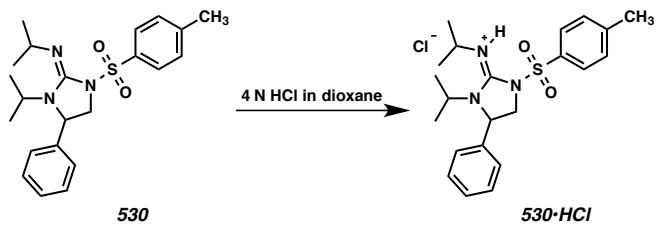
Unless otherwise stated, all iminothiazolidines were prepared according to General Procedure D and were isolated as amorphous white solids.



530

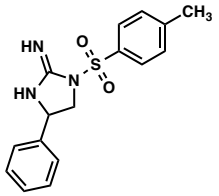
(*E*)-3-isopropyl-4-phenyl-1-tosyl-2-(isopropylimino)imidazolidine (530):

Product was initially prepared according to General Procedure D, isolating the product as a salt after column chromatography (2%→5% CH_3OH in CH_2Cl_2eluent). The resulting white foam was dissolved in 20 mL CH_2Cl_2 and washed with aqueous 0.1 N NaOH (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to give imidazolidine **530** (88 mg, 55% yield) as a colorless oil.



530 ***530•HCl***

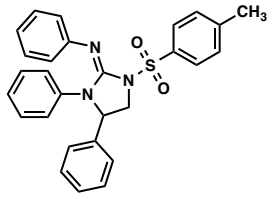
For the purpose of characterization, to a portion of iminoimidazolidine **530** (ca. 0.20 mmol) as a neat oil was added 4 N HCl in dioxane (3 mL) immediately followed by Et_2O (40 mL) causing a white precipitate to form. The supernatant was decanted and the residual white solid was washed with Et_2O (3 x 10 mL) and dried in vacuo furnishing iminoimidazolidinium hydrochloride **530•HCl** as a white solid: R_f = 0.39 (1:9 CH_3OH:CH_2Cl_2 eluent); ^1H NMR ($CDCl_3$, 500 MHz) δ 10.95 (bs, 1H), 7.69–7.59 (m, 2H), 7.30–7.24 (m, 3H), 7.18 (dd, *J* = 8.2, 6.9 Hz, 2H), 6.96–6.85 (m, 2H), 5.52–5.32 (m, 1H), 4.82–4.75 (m, 1H), 4.48–4.26 (m, 2H), 4.03 (dd, *J* = 12.0, 3.0 Hz, 1H), 2.46 (s, 3H), 1.70 (d, *J* = 6.4 Hz, 3H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.28–1.21 (m, 3H), 0.95 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 154.7, 146.9, 137.9, 133.7, 130.8, 129.3, 128.8, 127.7, 125.9, 57.0, 56.1, 54.0, 51.3, 24.3, 22.2, 21.9, 21.3, 20.8; IR (Neat Film, NaCl) 2972, 1636, 1457, 1435, 1367, 1260, 1172, 1088, 1036, 907, 814, 729 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{22}H_{30}N_3O_2S$ $[M–Cl]^+$: 400.2053, found 400.2067.



531

4-phenyl-1-tosyl-2-iminoimidazolidine (531):

Prepared according to General Procedure D followed by purification by column chromatography using deactivated silica gel (1% Me_2NEt and 1% MeOH in CH_2Cl_2 eluent): 61% yield; R_f = 0.41 (1:9 CH_3OH:CH_2Cl_2 eluent); ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.86–7.79 (m, 2H), 7.46 (dd, *J* = 8.4, 0.9 Hz, 2H), 7.21–7.16 (m, 3H), 6.92 (dd, *J* = 6.7, 2.9 Hz, 2H), 4.77 (dd, *J* = 9.2, 6.5 Hz, 1H), 4.14 (t, *J* = 9.6 Hz, 1H), 3.35 (bs, 2H), 3.26 (dd, *J* = 9.9, 6.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (DMSO-d_6, 126 MHz) δ 151.2, 145.0, 143.6, 132.9, 130.1, 128.2, 127.5, 126.9, 125.9, 61.4, 55.2, 21.1; IR (Neat Film, NaCl) 3445, 2920, 1683, 1397, 1350, 1161, 1091, 1002 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{16}H_{18}N_3O_2S$ $[M+H]^+$: 316.1114, found 316.1126.

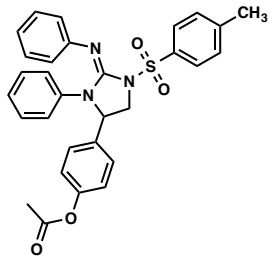


532

(*E*)-3,4-diphenyl-1-tosyl-2-(phenylimino)imidazolidine (532):

96% yield; R_f = 0.22 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.96 (m, 2H), 7.37–7.28 (m, 5H), 7.24–7.15 (m, 2H), 6.82–6.73 (m, 5H), 6.60–6.48 (m, 3H), 6.42–6.34 (m, 2H), 4.77 (dd, *J* = 8.2, 5.7 Hz, 1H), 4.45 (dd, *J* = 9.9, 8.2 Hz, 1H),

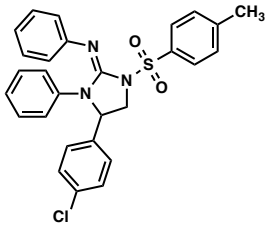
3.94 (dd, J = 9.9, 5.8 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.6, 144.6, 143.4, 139.9, 139.8, 135.0, 129.4, 129.3, 129.2, 128.8, 128.3, 127.8, 126.9, 125.8, 125.6, 121.9, 121.4, 64.9, 52.5, 21.9; IR (Neat Film, NaCl) 3027, 2924, 1667, 1593, 1488, 1354, 1166, 1089, 813, 759 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{28}H_{26}N_3O_2S$ $[M+H]^+$: 468.1740, found 468.1755.



533

(*E*)-4-(*p*-acetoxyphenyl)-3-phenyl-1-tosyl-2-(phenylimino)imidazolidine (533):

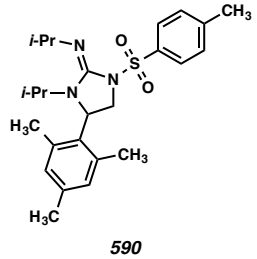
99% yield; R_f = 0.28 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.96 (m, 2H), 7.37–7.29 (m, 2H), 7.22–7.18 (m, 2H), 7.08–7.02 (m, 2H), 6.82–6.75 (m, 5H), 6.61–6.55 (m, 1H), 6.55–6.52 (m, 2H), 6.41–6.36 (m, 2H), 4.80 (dd, J = 8.1, 5.7 Hz, 1H), 4.44 (dd, J = 9.9, 8.1 Hz, 1H), 3.92 (dd, J = 9.9, 5.7 Hz, 1H), 2.48 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 169.4, 150.9, 146.1, 144.8, 143.5, 139.6, 137.2, 134.7, 129.4, 129.3, 128.4, 128.0, 127.9, 126.0, 125.7, 122.5, 122.0, 121.6, 64.4, 52.4, 21.9, 21.3; IR (Neat Film, NaCl) 3057, 2928, 1760, 1670, 1591, 1495, 1367, 1211, 1167, 1113, 1090, 1017, 911, 813, 763, 734 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{30}H_{28}N_3O_4S$ $[M+H]^+$: 526.1795, found 526.1800.



534

(*E*)-4-(*p*-chlorophenyl)-3-phenyl-1-tosyl-2-(phenylimino)imidazolidine (534):

87% yield; R_f = 0.19 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.03–7.95 (m, 2H), 7.35–7.31 (m, 2H), 7.30–7.27 (m, 2H), 7.16–7.12 (m, 2H), 6.83–6.75 (m, 5H), 6.61–6.56 (m, 1H), 6.53 (dd, *J* = 6.8, 2.9 Hz, 2H), 6.42–6.35 (m, 2H), 4.79 (dd, *J* = 8.1, 5.6 Hz, 1H), 4.44 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.90 (dd, *J* = 9.9, 5.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 146.0, 144.8, 143.4, 139.4, 138.2, 134.7, 134.6, 129.4, 129.4, 129.2, 128.4, 128.3, 127.9, 126.1, 125.7, 122.0, 121.7, 64.3, 52.3, 21.9; IR (Neat Film, NaCl) 3062, 1668, 1591, 1492, 1360, 1213, 1167, 1090, 1014, 910, 813, 761, 734 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{28}H_{25}{}^{35}ClN_3O_2S$ $[M+H]^+$: 502.1351, found 502.1355.

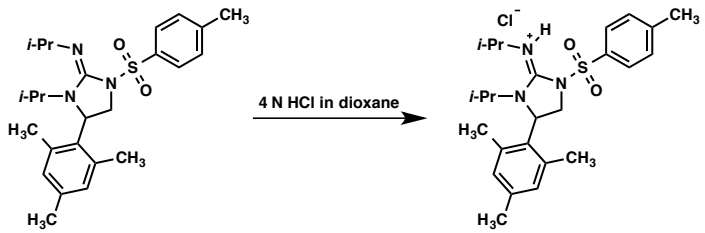


590

(*E*)-3-isopropyl-4-mesityl-1-tosyl-2-(isopropylimino)imidazolidine (590):

Product was initially prepared according to General Procedure D, isolating the product as the H($ZnBr_3$•CH_3OH) salt after column chromatography (2%→5% CH_3OH in CH_2Cl_2 eluent). A portion of this resulting white foam was crystallized, forming colorless,

translucent X-ray quality crystals after slow evaporation from a solution of **590** in CH_3OH, mp: 118–120 °C.

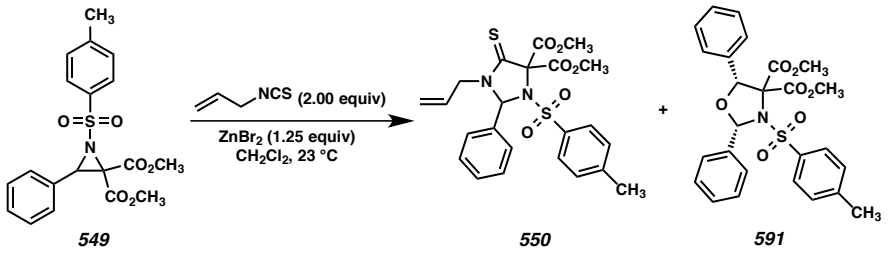


590 ***590•HCl***

The remaining portion of the white foam was dissolved in 20 mL CH_2Cl_2 and washed with aqueous 0.1 N NaOH (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to give iminoimidazolidine **590** as a colorless oil.

To neat **590** was then added 4 N HCl in dioxane (3 mL) immediately followed by Et_2O (40 mL). The organics were then concentrated in vacuo to furnish iminoimidazolidinium hydrochloride **590•HCl** as a white foam: R_f = 0.41 (1:9 MeOH:CH_2Cl_2 eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.98 (bs, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 2H), 6.83 (s, 1H), 6.79 (s, 1H), 5.16 (bs, 1H), 4.56 (bs, 2H), 4.28 (bs, 1H), 3.92–3.81 (m, 1H), 2.52 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 2.03 (s, 3H), 1.72 (d, *J* = 6.0 Hz, 3H), 1.54 (d, *J* = 6.0 Hz, 3H), 0.94–0.80 (m, 6H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 155.1, 147.5, 139.7, 136.7, 136.2, 133.4, 132.6, 131.1, 130.5, 128.2, 127.8, 56.0, 54.9, 51.9, 50.9, 24.7, 22.0, 21.8, 20.9, 20.5, 20.5, 20.4, 19.7; IR (Neat Film, NaCl) 2925, 1640, 1441, 1366, 1276, 1171, 1089, 815 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{25}H_{36}N_3O_2S$ $[M–Cl]^+$: 442.2523, found 442.2514.

6.14.6 Preparation of Thioxoimidazolidine 550

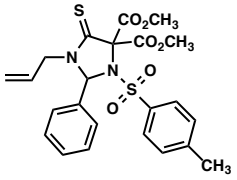


549 *550* *591*

*Imidazolidine **550** was prepared from diester aziridine **549** according to two procedures:*

Initially, imidazolidine **550** was prepared according to General Procedure C. The reaction mixture was an intensely neon orange-red color throughout the duration of the reaction (ca. 11 h). Upon purification of the reaction mixture by silica gel column chromatography (20% acetone in hexanes eluent), imidazolidine **550** (70 mg, 36% yield) and *cis*-oxazolidine **591** (48 mg, 24% yield) were both isolated as white crystalline solids.

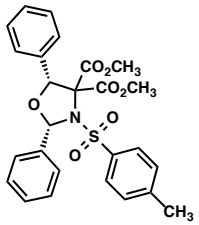
Suspecting the formation of *cis*-oxazolidine **591** was a result of partial hydrolysis of the ion-paired intermediate during the course of the reaction, imidazolidine **550** was subsequently prepared according to General Procedure C in the anhydrous environment of an inert atmosphere glovebox. The reaction mixture was an intensely neon orange-red color throughout the duration of the reaction (ca. 12 h) under these conditions as well. Upon purification of the reaction mixture by silica gel column chromatography (20% acetone in hexanes eluent), imidazolidine **550** (116 mg, 60% yield) was isolated in the absence of an isolable portion of *cis*-oxazolidine **591**.



550

dimethyl 3-allyl-2-phenyl-4-thioxo-1-tosyl-imidazolidine-5,5-dicarboxylate (550):

Colorless, translucent X-ray quality crystals of imidazolidine **550** were obtained by slow diffusion of 1% benzene in heptane into a solution of imidazolidine **550** in ethyl acetate, mp: 147–150 °C: R_f = 0.41 (3:7 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.15 (m, 5H), 7.05–6.95 (m, 2H), 6.94–6.86 (m, 2H), 6.39 (s, 1H), 5.63 (dddd, *J* = 17.4, 10.3, 7.3, 4.3 Hz, 1H), 5.24 (ddt, *J* = 10.3, 1.8, 1.0 Hz, 1H), 5.10 (ddt, *J* = 17.2, 2.1, 1.2 Hz, 1H), 4.87–4.70 (m, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.25 (ddt, *J* = 15.4, 7.4, 1.1 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 186.5, 164.9, 164.3, 143.9, 136.7, 133.3, 130.6, 129.5, 129.0, 128.8, 128.3, 127.8, 120.1, 82.4, 82.3, 54.1, 53.9, 47.6, 21.6; IR (Neat Film, NaCl) 2952, 1794, 1771, 1489, 1354, 1257, 1162, 1090, 1061, 913, 850, 810, 777, 731 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{23}H_{25}N_2O_6S_2$ $[M+H]^+$: 489.1149, found 489.1164.



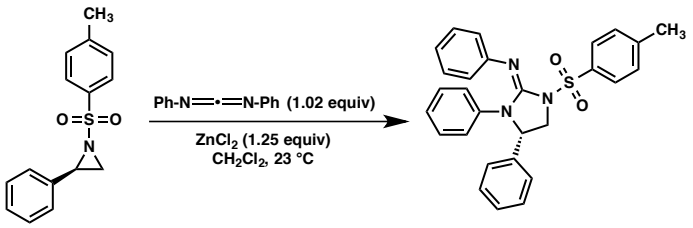
591

***cis*-dimethyl 2,5-diphenyl-3-tosyloxazolidine-4,4-dicarboxylate (591)**:

Colorless, translucent X-ray quality crystals of *cis*-oxazolidine **591** were obtained by slow evaporation of a solution of *cis*-oxazolidine **591** in ethyl acetate, mp: 145–147 °C:

R_f = 0.50 (3:7 Acetone:Hexanes eluent); characterization data match those reported in the literature.[55]

6.14.7 Stereoselective (3 + 2) Cycloaddition with Diphenylcarbodiimide

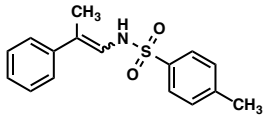


(R)-498 *(S)-532* 10% ee

(*S*,*E*)-3,4-diphenyl-1-tosyl-2-(phenylimino)imidazolidine ((*S*)-532):[56]

Imidazolidine **(*S*)-532** was prepared according to General Procedure E using diphenylcarbodiimide (79 mg, 0.41 mmol, 1.02 equiv) in place of isothiocyanate:[57] 96% yield; R_f = 0.22 (1:4 Acetone:Hexanes eluent); characterization data match those reported above; $[\alpha]_D^{25.0}$ 46.6° (*c* 0.550, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AS-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 9.6 minutes, minor retention time: 7.0 minutes, 10% ee).

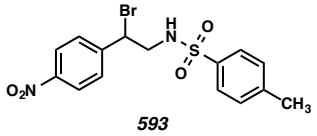
6.14.8 (3 + 2) Cycloaddition Byproduct Characterization Data



592

4-methyl-*N*-(2-phenylprop-1-en-1-yl)benzenesulfonamide (592):

Sulfonamide **592** was prepared by General Procedure C from aziridine **589**: 65% combined yield as a 2:1 *Z*:*E* ratio of products as an amorphous white solid; R_f = 0.15 (1:4 Acetone:Hexanes eluent); ^{1}H and ^{13}C NMR spectra match those reported in the literature;[58] IR (Neat Film, NaCl) 3357, 3260, 1721, 1683, 1598, 1448, 1337, 1301, 1269, 1161, 1096, 904, 817, 761 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{16}H_{18}NO_2S$ $[M+H]^+$: 288.1053, found 288.1044.



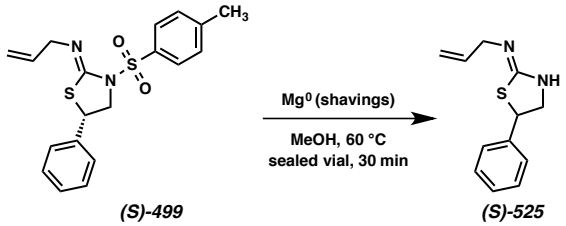
593

1-bromo-1-(4-nitrophenyl)-2-(p-toluenesulfonamido)ethane (593):[59]

Bromide **593** was isolated as a byproduct of the reaction of aziridine **566** under the reaction conditions specified in General Procedure C: 35% yield as an amorphous white solid; R_f = 0.15 (1:4 Acetone:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24–8.14 (m, 2H), 7.75–7.67 (m, 2H), 7.53–7.46 (m, 2H), 7.35–7.29 (m, 2H), 5.02 (t, *J* = 7.1 Hz, 1H), 4.83 (dd, *J* = 7.4, 5.9 Hz, 1H), 3.64–3.50 (m, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 148.1, 145.3, 144.3, 136.8, 130.1, 129.0, 127.1, 124.3, 50.5, 50.1, 21.7; IR (Neat Film, NaCl) 3278, 1598, 1522, 1423, 1346, 1157, 1092, 855, 814 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{14}{}^{81}BrN_2O_4S$ $[(M–H_2)+H]^+$: 398.9837, found 398.9834.

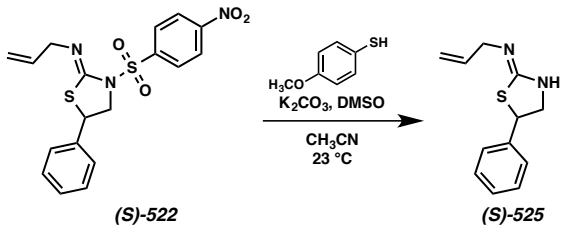
6.14.9 Deprotection of Iminothiazolidines (S)-499 and (S)-522

6.14.9.1 Desulfonylation of Tosylthiazolidine (S)-499



Procedure for the desulfonylation of thiazolidine **(*S*)-499** was adapted from the literature.[30] Iminothiazolidine **(*S*)-499** (50 mg, 0.13 mmol, 1.00 equiv) was suspended in freshly distilled CH_3OH (2.2 mL) in an oven-dried vial with a stir bar and heated to 70 °C until a homogeneous solution was formed. Magnesium turnings (49 mg, 2.01 mmol, 15 equiv) were then added and the vial was sealed. The reaction mixture was stirred at 70 °C. Upon consumption of starting material (determined by LCMS analysis, ca. 30 min), the reaction mixture was allowed to cool to room temperature and filtered through Celite, washing with CH_2Cl_2 (20 mL) and CH_3OH (20 mL). The filtrate was adsorbed onto Celite and purified by silica gel column chromatography (30% acetone and 1% Et_3N in hexanes) to give iminothiazolidine **(*S*)-525** (26 mg, 91% yield) as a white amorphous solid; characterization data match those reported above; $[\alpha]_D^{25.0}$ –61.2° (*c* 0.23, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OB-H column, 10% methanol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 3.9 minutes, minor retention time: 8.4 minutes, 94% ee).

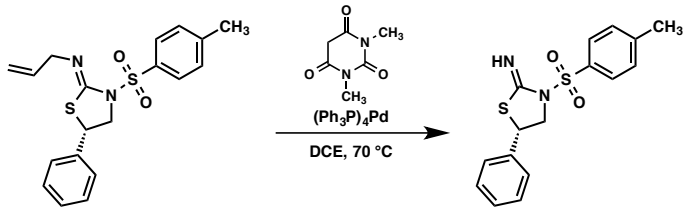
6.14.9.2 Desulfonylation of (p-Nosyl)thiazolidine (S)-522



(S)-522 *(S)-525*

Procedure for the desulfonylation of thiazolidine **(*S*)-522** was adapted from the literature.[31a] To a solution of iminothiazolidine **(*S*)-522** (120 mg, 0.30 mmol, 1.00 equiv, 95% ee) and *p*-methoxythiophenol (110 μL, 0.89 mmol, 3.00 equiv) in acetonitrile (1.96 mL) was added DMSO (40 μL), followed by potassium carbonate (164 mg, 1.18 mmol, 4.00 equiv). The vial was loosely capped and the heterogeneous mixture was stirred at room temperature until the reaction was complete (determined by TLC analysis, ca. 3 h). The reaction mixture was concentrated and the residue partitioned between ethyl acetate and water. The organic layer was separated, washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by silica gel column chromatography (30% acetone and 1% Et_3N in hexanes eluent) to give iminothiazolidine **(*S*)-525** (60 mg, 93% yield) as a white amorphous solid; characterization data match those reported above; $[\alpha]_D^{25.0}$ –61.2° (*c* 0.23, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralcel OB-H column, 10% methanol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 3.9 minutes, minor retention time: 8.4 minutes, 94% ee).

6.14.9.3 Deallylation of Tosylthiazolidine (S)-499

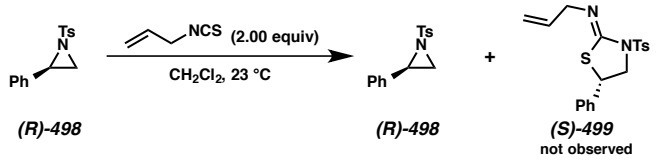


(S)-499 *(S)-552*

Procedure for the deallylation of thiazolidine **(*S*)-499** was adapted from the literature.[60] To a solution of iminothiazolidine **(*S*)-499** (25 mg, 0.067 mmol, 1.00 equiv) in dichloroethane (750 μL) in an oven dried vial with a stir bar were added tetrakis(triphenylphosphine)palladium(0) (39 mg, 0.034 mmol, 0.50 equiv) and 1,3-dimethylbarbituric acid (157 mg, 1.01 mmol, 15.0 equiv). The vial was sealed and stirred at 70 °C until the reaction was complete (determined by LCMS analysis, ca. 1.5 h). The reaction mixture was diluted with CH_2Cl_2, adsorbed onto Celite, and purified by silica gel column chromatography (10% acetone and 1% Et_3N in hexanes) to give iminothiazolidine **(*S*)-552** (20 mg, 89% yield) as a white amorphous solid; R_f = 0.30 (3:7 Acetone:Hexanes eluent); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.83–7.78 (m, 2H), 7.38–7.34 (m, 2H), 7.34–7.31 (m, 5H), 4.77 (t, *J* = 7.0 Hz, 1H), 4.46 (dd, *J* = 10.5, 6.4 Hz, 1H), 4.01 (dd, *J* = 10.5, 7.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (CD_2Cl_2, 126 MHz) δ 160.3, 145.9, 137.3, 130.4, 129.8, 129.4, 129.0, 128.1, 127.8, 58.8, 21.8; IR (Neat Film, NaCl) 3311, 3031, 2922, 1622, 1597, 1494, 1454, 1358, 1168, 1089, 1054, 814 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{16}H_{17}N_2O_2S_2$ $[M+H]^+$: 333.0726, found 333.0736; $[\alpha]_D^{25.0}$ – 10.0° (*c* 0.1, $CHCl_3$); enantiomeric excess was determined by analytical SFC (Chiralpak AD-H column, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.3 minutes, minor retention time: 8.4 minutes, 39% ee).

6.14.10 Control Reaction Experimental Procedures[61]

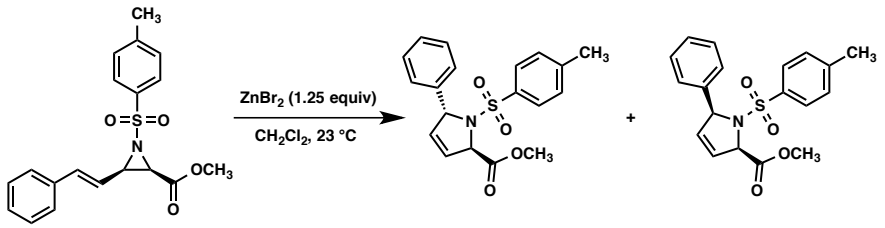
6.14.10.1 Lewis Acid Control



(R)-498 *(R)-498* *(S)-499* not observed

To an oven-dried 1-dram vial equipped with a magnetic stir bar were added (*R*)-*N*-tosyl-2-phenylaziridine (**(*R*)-498**, 109 mg, 0.40 mmol, 1.00 equiv, >99% ee) and allyl isothiocyanate (79 μL, 0.80 mmol, 2.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, placed under an inert atmosphere, and dissolved in anhydrous dichloromethane (0.80 mL). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Over the course of 96 hours, no formation of thiazolidine **(*S*)-499** was observed. At 96 hours, the enantiomeric excess of the remaining aziridine **(*R*)-498** was determined by analytical SFC (Chiralcel OB-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.5 minutes, minor retention time: 10.2 minutes, >99% ee).

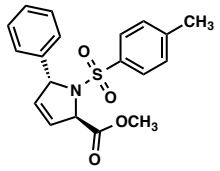
6.14.10.2 Isomerization of Disubstituted Aziridine 540



540 *544* *545*

To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (25 mg, 0.113 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon

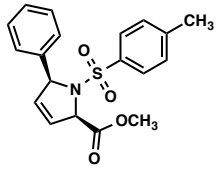
septum, removed from the glovebox and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added *cis*-aziridine **540** (32 mg, 0.090 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.15 mL + 0.05 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Upon consumption of starting material (determined by LCMS, ca. 30 min), the reaction mixture directly purified by silica gel column chromatography (20% acetone in hexanes eluent) to furnish *trans*-pyrroline **544** (12 mg, 38% yield) and *cis*-pyrroline **545** (2 mg, 6% yield) as white amorphous solids.



544

methyl *trans*-5-phenyl-1-tosyl-3-pyrroline-2-carboxylate (544):

R_f = 0.38 (3:7 EtOAc:Hexanes eluent); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21–7.16 (m, 1H), 7.12–7.05 (m, 4H), 7.00–6.96 (m, 2H), 6.95–6.90 (m, 2H), 5.87 (dt, *J* = 6.2, 1.6 Hz, 1H), 5.84 (dt, *J* = 6.2, 1.8 Hz, 1H), 5.76 (dt, *J* = 6.2, 1.6 Hz, 1H), 5.18 (dt, *J* = 5.7, 1.7 Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 171.2, 142.6, 137.9, 136.9, 134.7, 129.0, 128.9, 128.4, 128.3, 126.8, 124.0, 70.5, 69.3, 53.0, 21.5; IR (Neat Film, NaCl) 2953, 1747, 1598, 1456, 1343, 1262, 1200, 1158, 1100, 1018, 813, 763 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{19}H_{20}NO_4S$ $[M+H]^+$: 358.1108, found 358.1106.

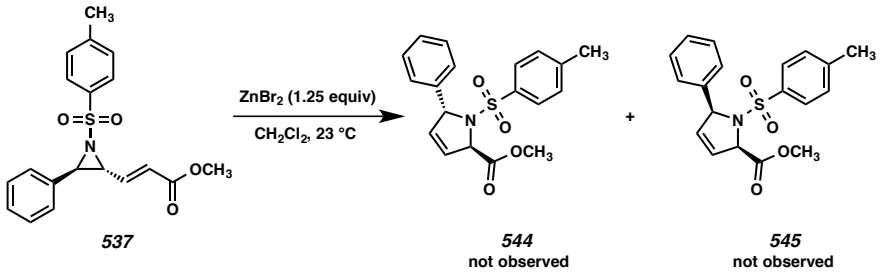


545

methyl *cis*-5-phenyl-1-tosyl-3-pyrroline-2-carboxylate (545):

R_f = 0.47 (3:7 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[62]

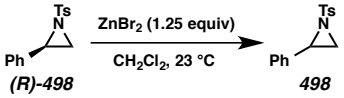
6.14.10.3 Isomerization of Disubstituted Aziridine 537



537 ***544*** not observed ***545*** not observed

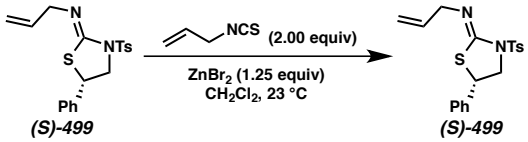
To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (17 mg, 0.074 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added *trans*-aziridine **537** (21 mg, 0.059 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.15 mL + 0.05 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. The slow decomposition of aziridine **537** was complete after 96 h (determined by LCMS) and was characterized by the formation of no major products including neither *trans*-pyrroline **544** nor *cis*-pyrroline **545**.[63]

6.14.10.4 Racemization of Aziridine Starting Material (R)-498



To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (113 mg, 0.50 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial was added *N*-tosyl-2-phenylaziridine (**(*R*)-498**, 109 mg, 0.40 mmol, 1.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.60 mL + 0.20 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Racemization of the aziridine was complete after 10 minutes as determined by analytical SFC (Chiralcel OB-H column, 10% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 7.5 minutes, minor retention time: 10.2 minutes).

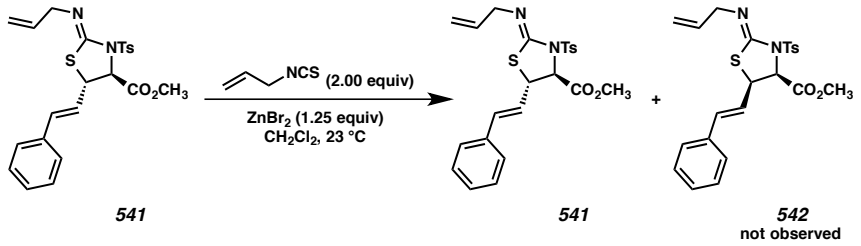
6.14.10.5 Racemization of Product (S)-499



To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (31 mg, 0.14 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox and placed under an inert atmosphere. To a separate,

oven-dried 1-dram vial were added the iminothiazolidine **(*S*)-499** (40 mg, 0.11 mmol, 1.00 equiv, 94% ee) and allyl isothiocyanate (22 μL, 0.22 mmol, 2.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.15 mL + 0.10 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. After 96 hours, the enantiomeric excess of thiazolidine **(*S*)-499** was determined by analytical SFC (Chiralpak AD-H, 30% isopropyl alcohol in CO_2, 2.5 mL/min, λ = 254 nm, major retention time: 5.4 minutes, minor retention time: 3.8 minutes, 94% ee).

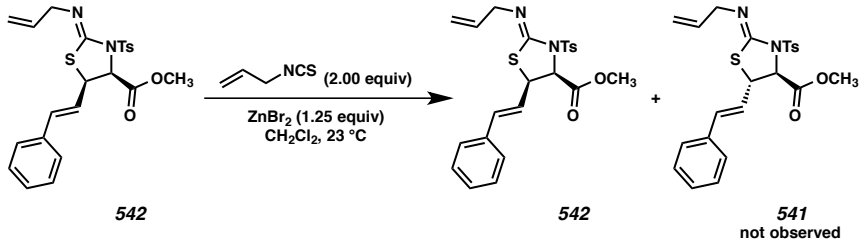
6.14.10.6 Isomerization of trans-Disubstituted Thiazolidine Product 541



To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (10 mg, 0.044 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial were added the *trans*-iminothiazolidine **541** (16 mg, 0.035 mmol, 1.00 equiv) and allyl isothiocyanate (7 μL, 0.070 mmol, 2.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.10 mL + 0.05 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Over the

course of 96 hours, no decomposition of *trans*-iminothiazolidine **541** or isomerization of *trans*-iminothiazolidine **541** to *cis*-iminothiazolidine **542** was observed (determined by LCMS).

6.14.10.7 Isomerization of cis-Disubstituted Thiazolidine Product 542



To an oven-dried 1-dram vial equipped with a magnetic stir bar was added zinc(II) bromide (10 mg, 0.044 mmol, 1.25 equiv), freshly powdered with a mortar and pestle, in an inert atmosphere glovebox. The vial was sealed with a screw cap fitted with a Teflon septum, removed from the glovebox and placed under an inert atmosphere. To a separate, oven-dried 1-dram vial were added the *cis*-iminothiazolidine **542** (16 mg, 0.035 mmol, 1.00 equiv) and allyl isothiocyanate (7 μL, 0.070 mmol, 2.00 equiv). The vial was sealed with a screw cap fitted with a Teflon septum, and the mixture was transferred to the first vial as a solution in anhydrous dichloromethane (0.10 mL + 0.05 mL rinse). The heterogeneous reaction mixture was then allowed to stir at ambient temperature. Over the course of 96 hours, no decomposition of *cis*-iminothiazolidine **542** or isomerization of *cis*-iminothiazolidine **542** to *trans*-iminothiazolidine **541** was observed (determined by LCMS).

6.15 Notes and References

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11. No reaction was observed in the absence of Lewis acid. For full details, see Section 6.14.10.1.

12. The *Z*-imino stereochemistry of the iminothiazolidine products was assigned by analogy to the structure of thiazolidine **536**, which was unambiguously established by single-crystal X-ray diffraction. For full details, see the appendix 15.

13. Thiourea product **502** was not observed in any case during this study. Similarly, the analogous thiolactam product was not observed during our previous studies of (3 + 2) cycloadditions of donor–acceptor cyclopropanes with heterocumulenes, see reference 10.

14. This observation is in stark contrast to our previous studies of (3 + 2) cycloadditions of donor–acceptor cyclopropanes with heterocumulenes, in which increased steric bulk on the ring caused a large increase in reaction time, see reference 10.

15. (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem*. *Rev*. **1991**, *91*, 165–195. (b) Hammett, L. P. *J*. *Am*. *Chem*. *Soc*. **1937**, *59*, 96–103.

16. This was the only substrate found to be susceptible to nucleophilic ring opening by the zinc(II) counterion during our studies. For full details, see Section 6.14.8.

17. A variety of isocyanates were tested under zinc(II) bromide mediated conditions, including trimethylsilyl, phenyl, and allyl isocyanates.

18. The assignment of the *E*-imino-stereochemistry of the iminoimidazolidine products was assigned by analogy to a structure related to imidazolidine **530**, which was unambiguously established by single-crystal X-ray diffraction of the corresponding imidazolidinium ion. For full details, see Appendix 15.

19. Inversion at the benzylic position was observed in our previous studies of stereoselective (3 + 2) cycloadditions of donor–acceptor cyclopropanes with heterocumulenes, see reference 10.

20. Alternatively, *trans*-aziridine **537** did not undergo this transformation under the same conditions, although both styryl- and acroylaziridines are known to isomerize to pyrrolines, see: (a) Brichacek, M.; Villalobos, M. N.; Plichta, A.; Njardarson, J. T. *Org. Lett.* **2011**, *13*, 1110–1113. (b) Li, A.-H.; Dai, L.-X.; Hou, X.-L. *J. Chem. Soc. Perkin Trans. 1* **1996**, 2725–2729. (c) Atkinson, R. S.; Rees, C. W. *J. Chem. Soc. Chem. Commun. (London)* **1967**, 1232.

21. *N*-Tosyl-2-methyl-2-phenylaziridine proved susceptible to isomerization under the reaction conditions, furnishing no (3 + 2) adduct, but rather a mixture of *E* and *Z* enamine isomers. For full details, see Section 6.14.8.

22. Absolute stereochemistry of the iminothiazolidine products was assigned by analogy to the structure of thiazolidine **(*S*)-522**, which was unambiguously established by single-crystal X-ray diffraction. For full details, see appendix 15.

23. As with the zinc(II) bromide mediated conditions, isocyanates were not suitable cycloaddition partners under our stereospecific reaction conditions.

Diphenylcarbodiimide was compatible with the zinc(II) chloride mediated conditions, furnishing the iminoimidazolidine product in excellent yield, but with comparatively reduced *ee*. For full details, see Section 6.14.7.

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26. In the absence of heterocumulene, aziridine **(*R*)-498** was completely racemized in 10 minutes. Concurrently, no reduction in *ee* of **(*S*)-499** was observed upon reexposure to the reaction conditions. For full details, see Section 6.14.10.5.

27. The selective C–C bond cleavage of *N*-tosyl-3-arylaziridine-2,2-dicarboxylates has been explored previously in the literature, see: (a) Li, L.; Zhang, J. *Org. Lett.* **2011**, *13*, 5940–5943. (b) Jiang, Z.; Wang, J.; Lu, P.; Wang, Y. *Tetrahedron* **2011**, *67*, 9609–9617. (c) Pohlhaus, P. D.; Bowman, R. K.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 2294–2295.

28. Conditions: aziridine **549** (0.40 mmol), allyl isothiocyanate (0.80 mmol), $Sn(OTf)_2$ (0.44 mmol), CH_2Cl_2 (1.3 mL). See reference 10 and general procedure D in Section 5.8.2.

29. The same mode of reactivity has been previously observed in (3 + 2) cycloadditions with the *N*-alkylated and *N*-arylated derivatives of aziridine **549**

under thermolysis conditions with isothiocyanates, see: Benhaoua, H.; Texier, F. *Tetrahedron* **1978**, *34*, 1153–1161.

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38. Procedure adapted from the literature and typically run on 3.0–4.0 mmol scale; see reference 36.

39. Procedure adapted from the literature and typically run on 1.0–4.0 mmol scale, see: Farràs, J.; Ginesta, X.; Sutton, P. W.; Taltavull, J.; Egeler, F.; Romea, P.; Urpí, F.; Vilarrasa, J. *Tetrahedron* **2001**, *57*, 7665–7674.

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52. The IR spectrum for aziridine **549** is not reported in the literature. For ^{1}H and ^{13}C NMR and HRMS spectra, see: Fan, R.; Ye, Y. *Adv. Synth. Catal.* **2008**, *350*, 1526–1530.

53. For the purpose of characterization, thiazolidines **518** and **519** were purified using an Agilent 1200 series preparative HPLC (Agilent Prep-SIL column (5 mm, 30 x 250 mm), 6% EtOAc in hexane, 50.00 mL/min, l = 254 nm, compound **518**: 12.036 min, compound **519**: 11.372 min).

54. For the purpose of characterization, *trans*-thiazolidine **541** and *cis*-thiazolidine **542** were purified using an Agilent 1200 series preparative HPLC (Agilent Prep-SIL column (5 mm, 30 x 250 mm), 15% EtOAc in hexane, 50.00 mL/min, l = 254 nm, *trans*-thiazolidine **541**: 12.218 min, *cis*-thiazolidine **542**: 8.845 min).

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56. The absolute stereochemistry of iminoimidazolidine **(*S*)-532** was assigned by analogy to the absolute stereochemistry of thiazolidine **(*S*)-530** that was unambiguously established by single crystal X-ray diffraction.

57. The use of additional equivalents of carbodiimide greatly increased the reaction time.

58. Lee, K. Y.; Lee, C. G.; Kim, J. N. *Tetrahedron Lett*. **2003**, *44*, 1231–1234.

59. Compound **593** is known in the literature, but characterized as a mixture with 2-bromo-1-(4-nitrophenyl)-1-(*p*-toluenesulfonamido)ethane, see: Hayakawa, J.; Kuzuhara, M.; Minakata, S. *Org*. *Biomol*. *Chem*. **2010**, *8*, 1424–1430.

60. For examples of palladium-catalyzed deallylation of amines, see reference 32. For examples of palladium-catalyzed deallylation of amides, see reference 33.

61. Zinc(II) bromide was used as the Lewis acid for the control experiments as it was the most effective zinc(II) salt at preforming the (3 + 2) cycloaddition of aziridines with heterocumulenes.

62. Jones, A. D.; Redfern, A. L.; Knight, D. W.; Morgan, I. R.; Williams, A. C. *Tetrahedron* **2006**, *62*, 9247–9257.

63. Although the pyrroline products of the vinylaziridine-pyrroline rearrangement were not observed, aziridine **537** is known to readily undergo this transformation, see reference 20.

APPENDIX 14

Spectra Relevant to Chapter 6:

Stereoselective Lewis Acid Mediated (3 + 2) Cycloadditions of

N-*H- and* N-*Sulfonylaziridines with Heterocumulenes*

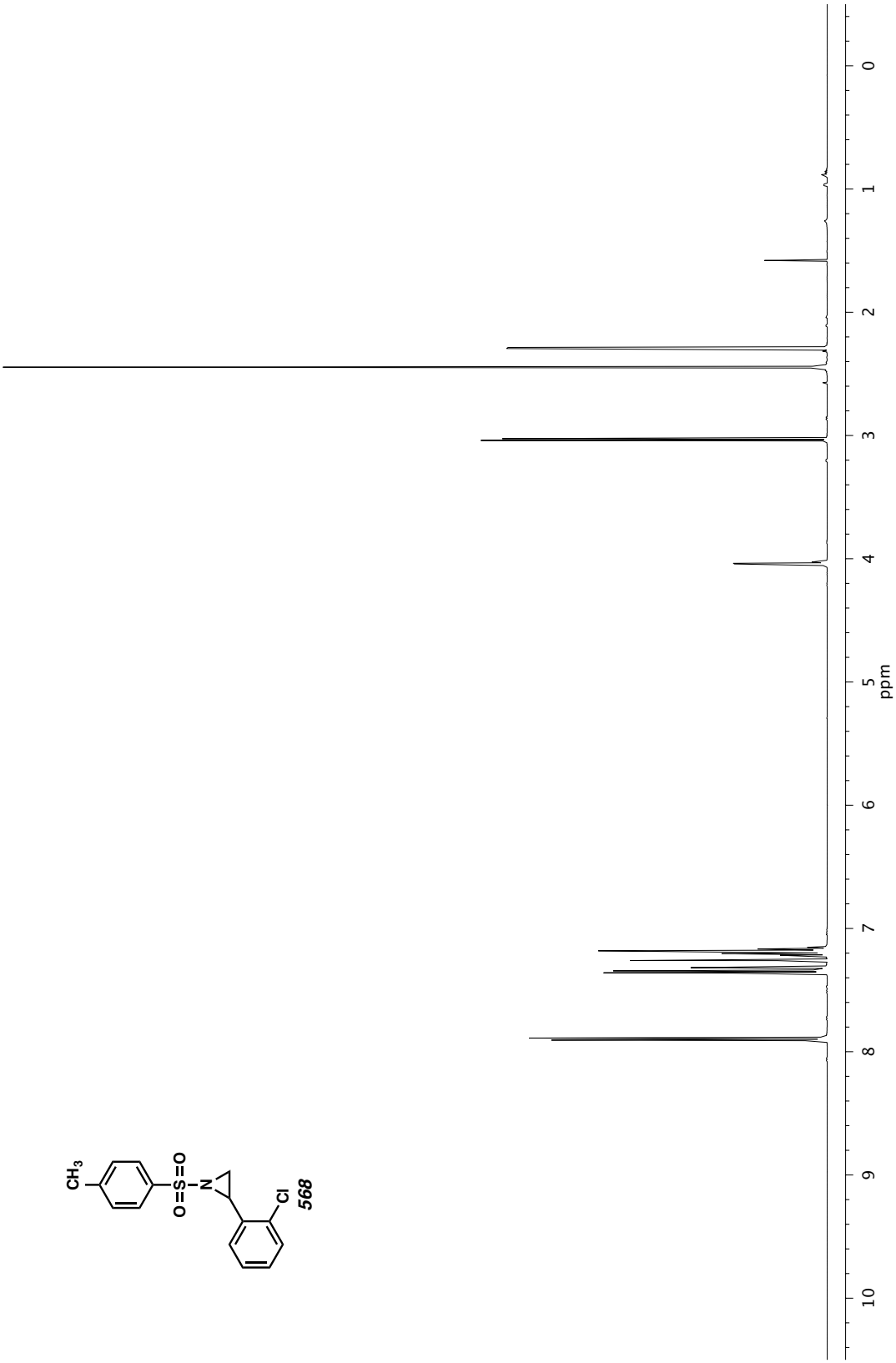


Figure A14.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **568**.

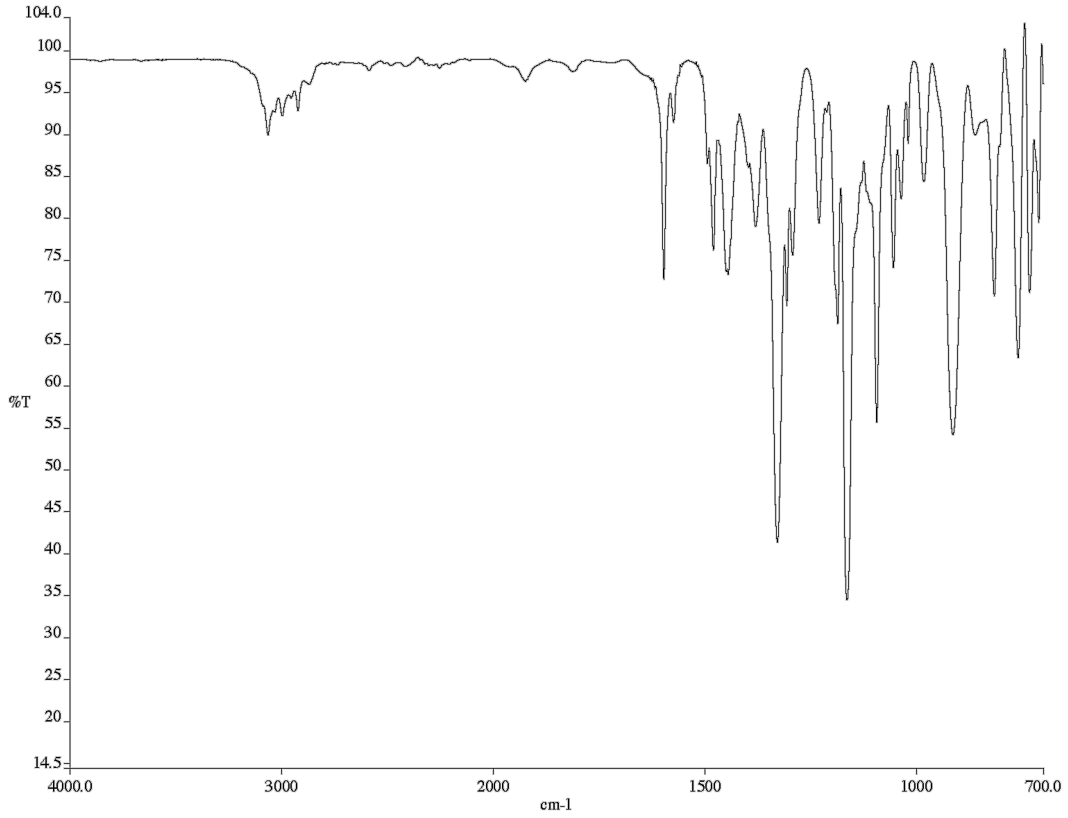


Figure A14.2. Infrared spectrum (thin film/NaCl) of compound **568**.

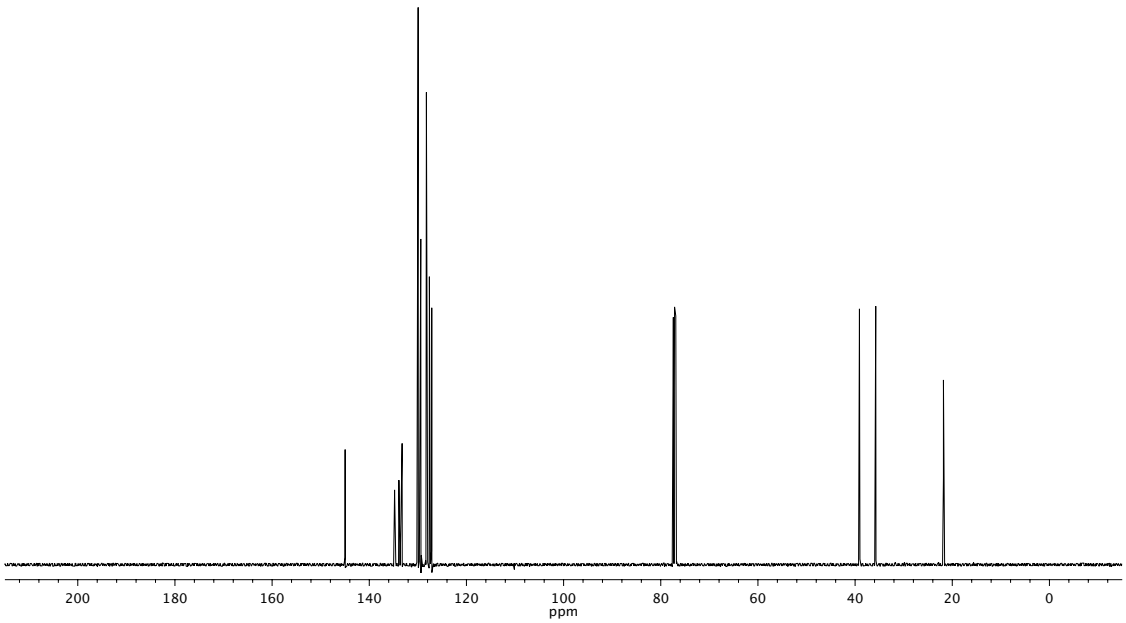
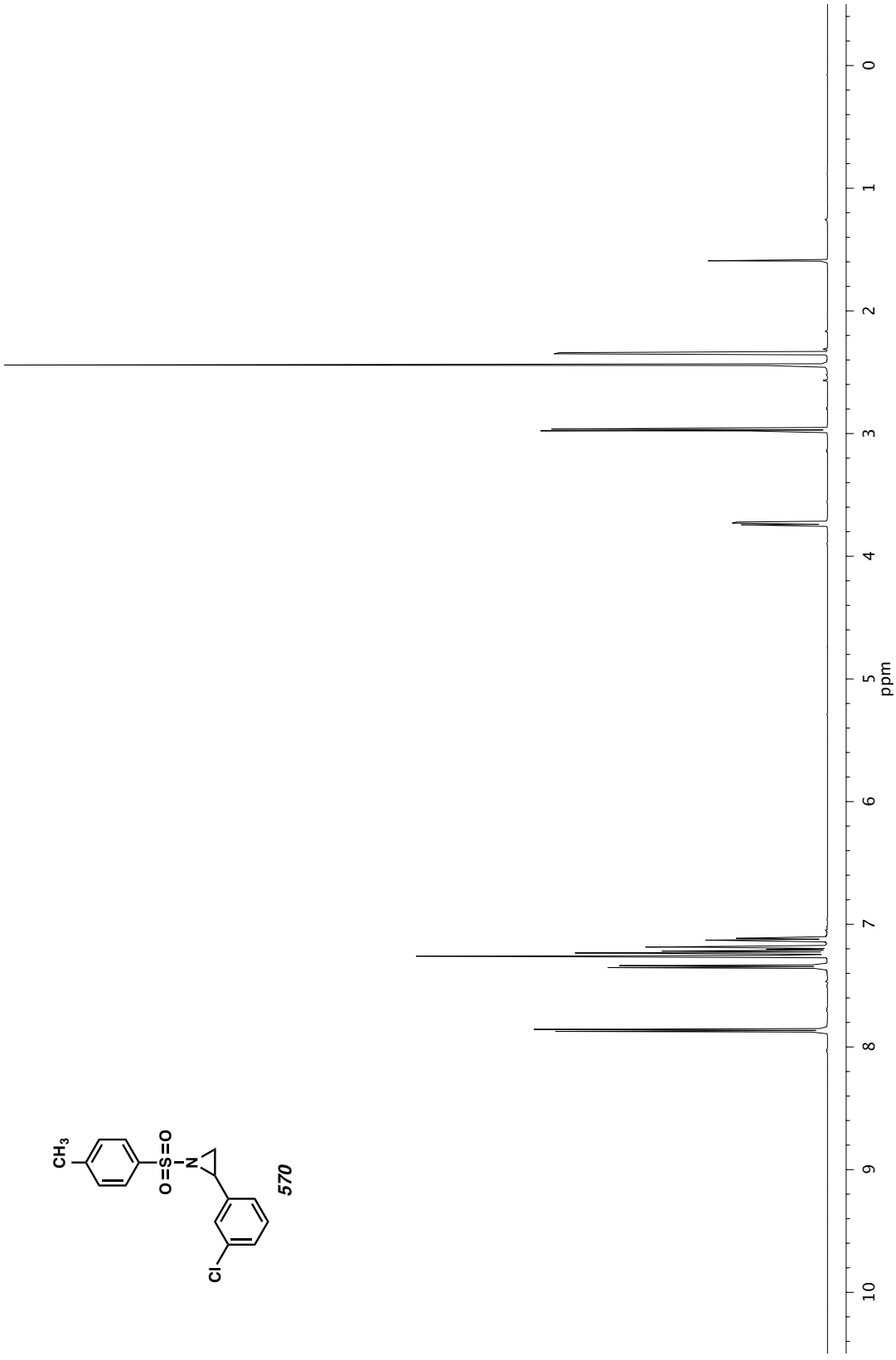


Figure A14.3. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **568**.



570

Figure A14.4. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **570**.

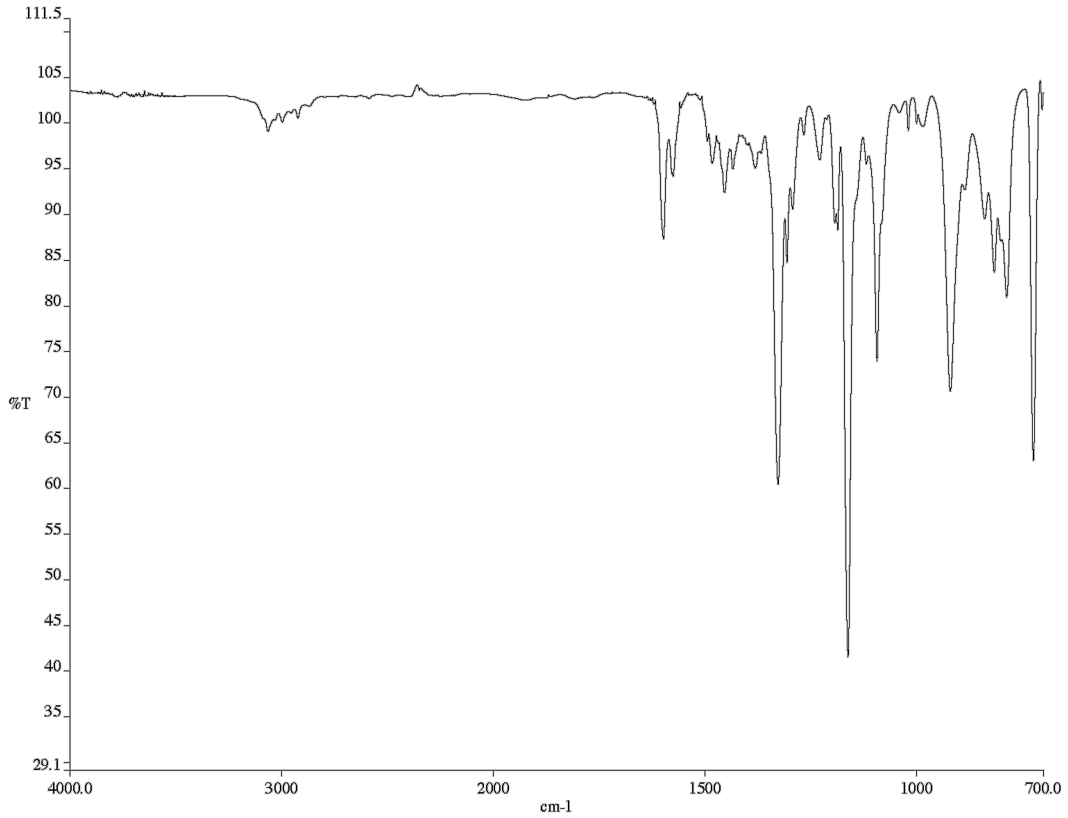


Figure A14.5. Infrared spectrum (thin film/NaCl) of compound **570**.

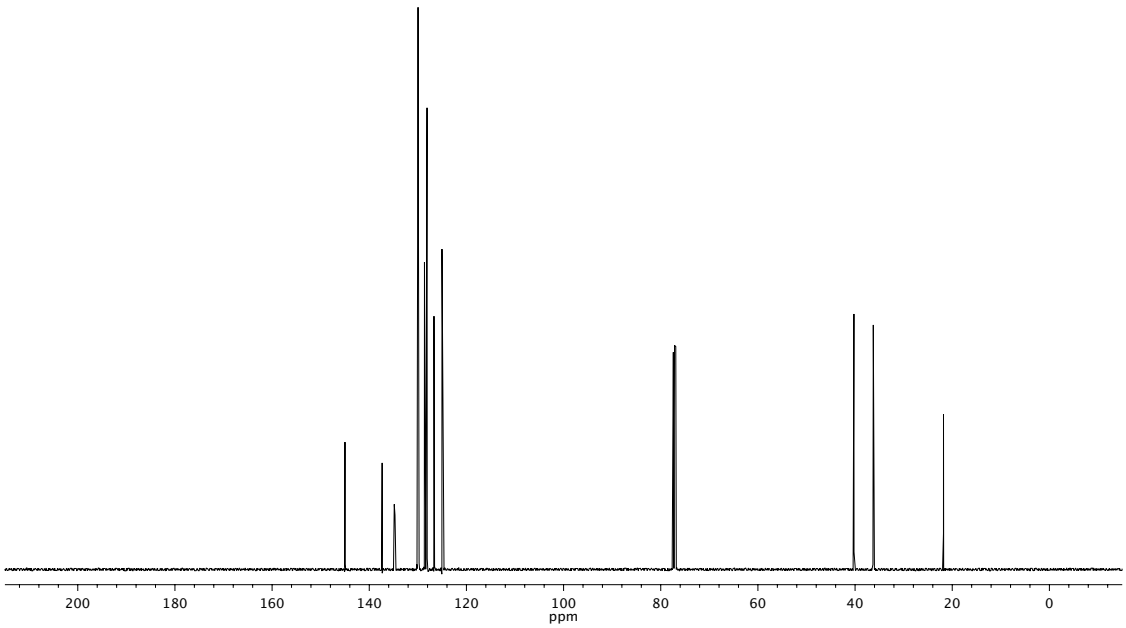


Figure A14.6. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **570**.

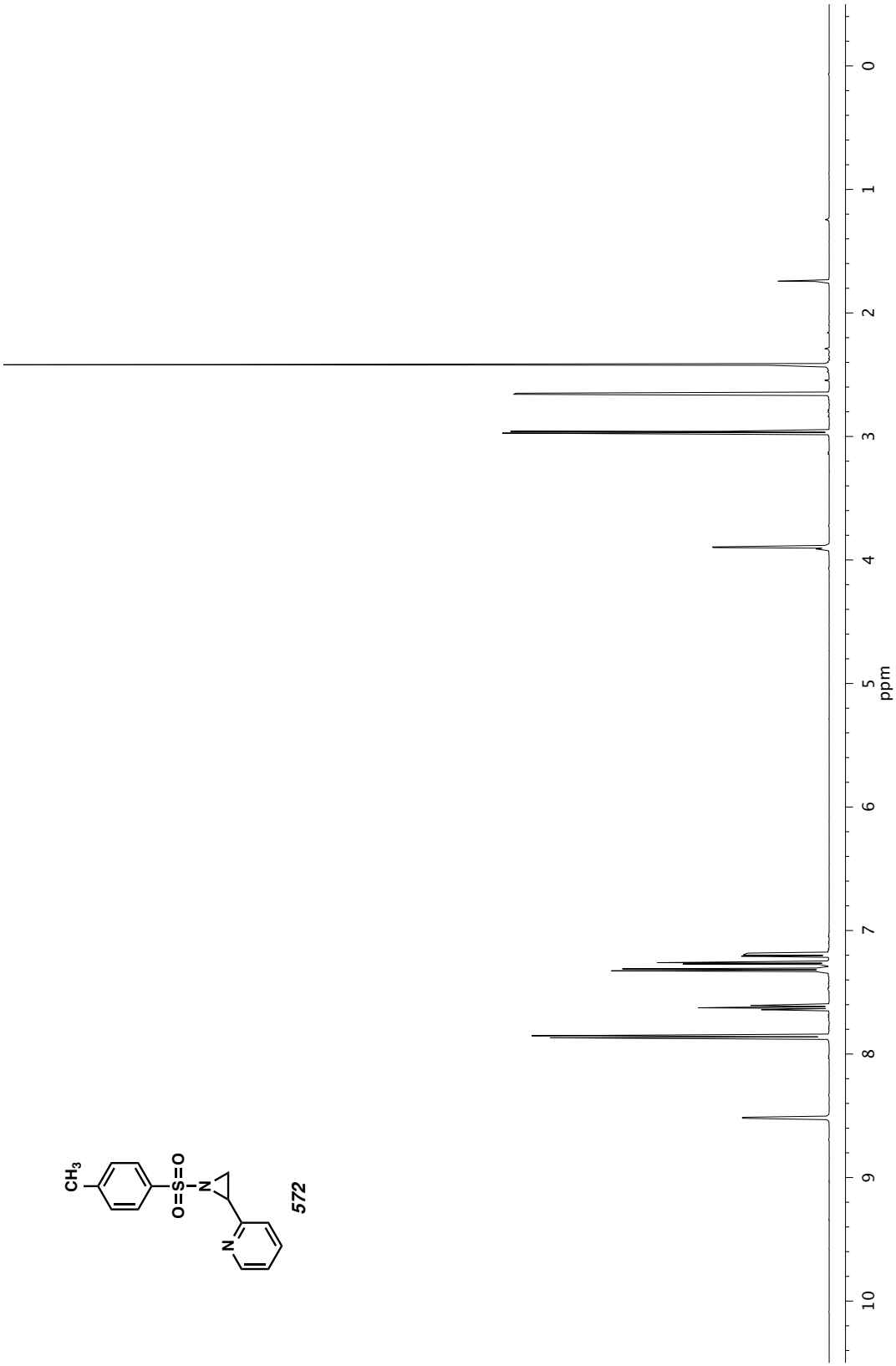


Figure A14.7. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **572**.

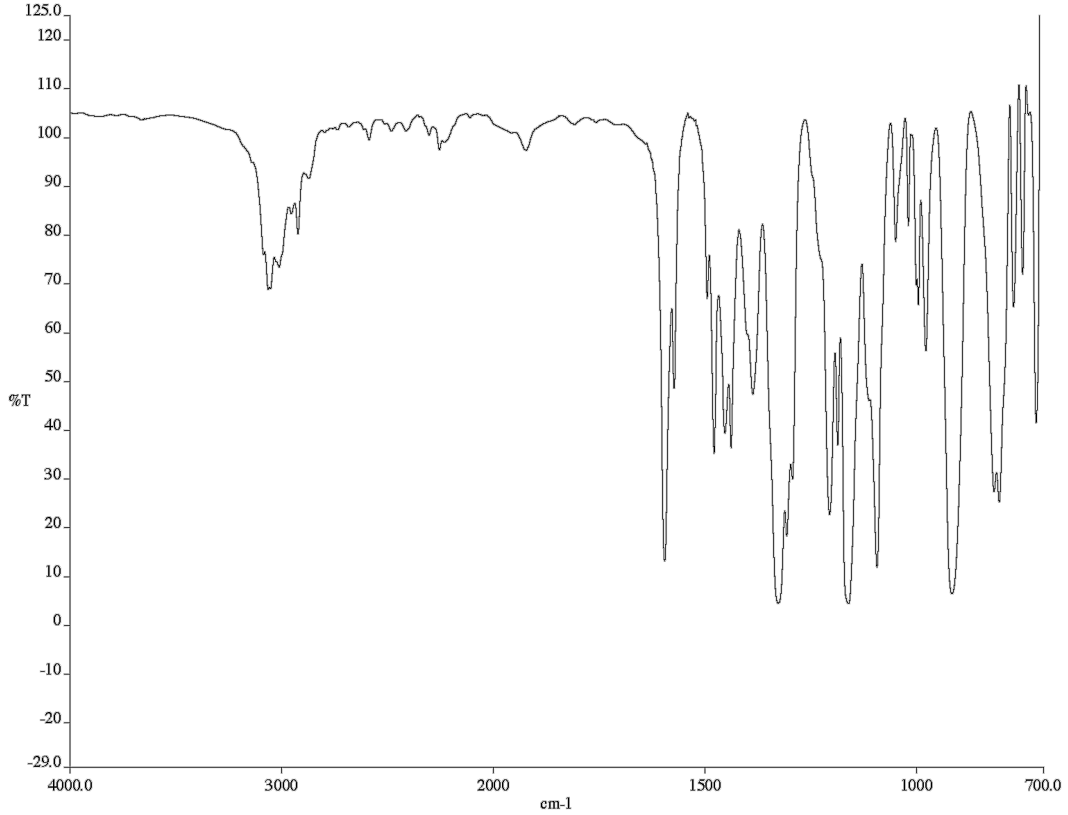


Figure A14.8. Infrared spectrum (thin film/NaCl) of compound **572**.

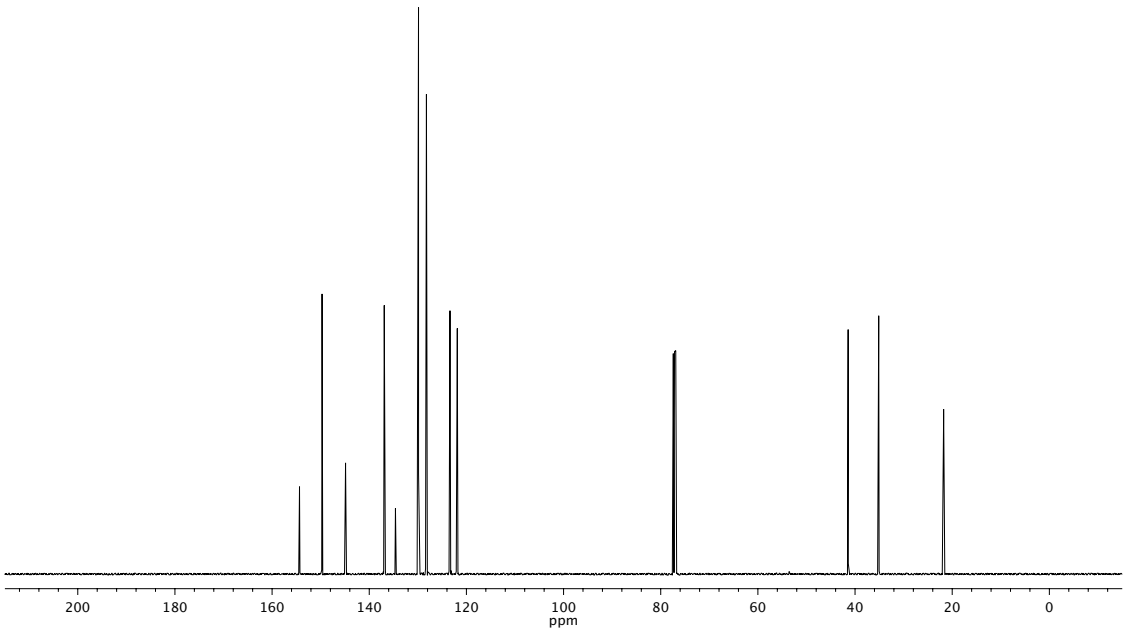


Figure A14.9. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **572**.

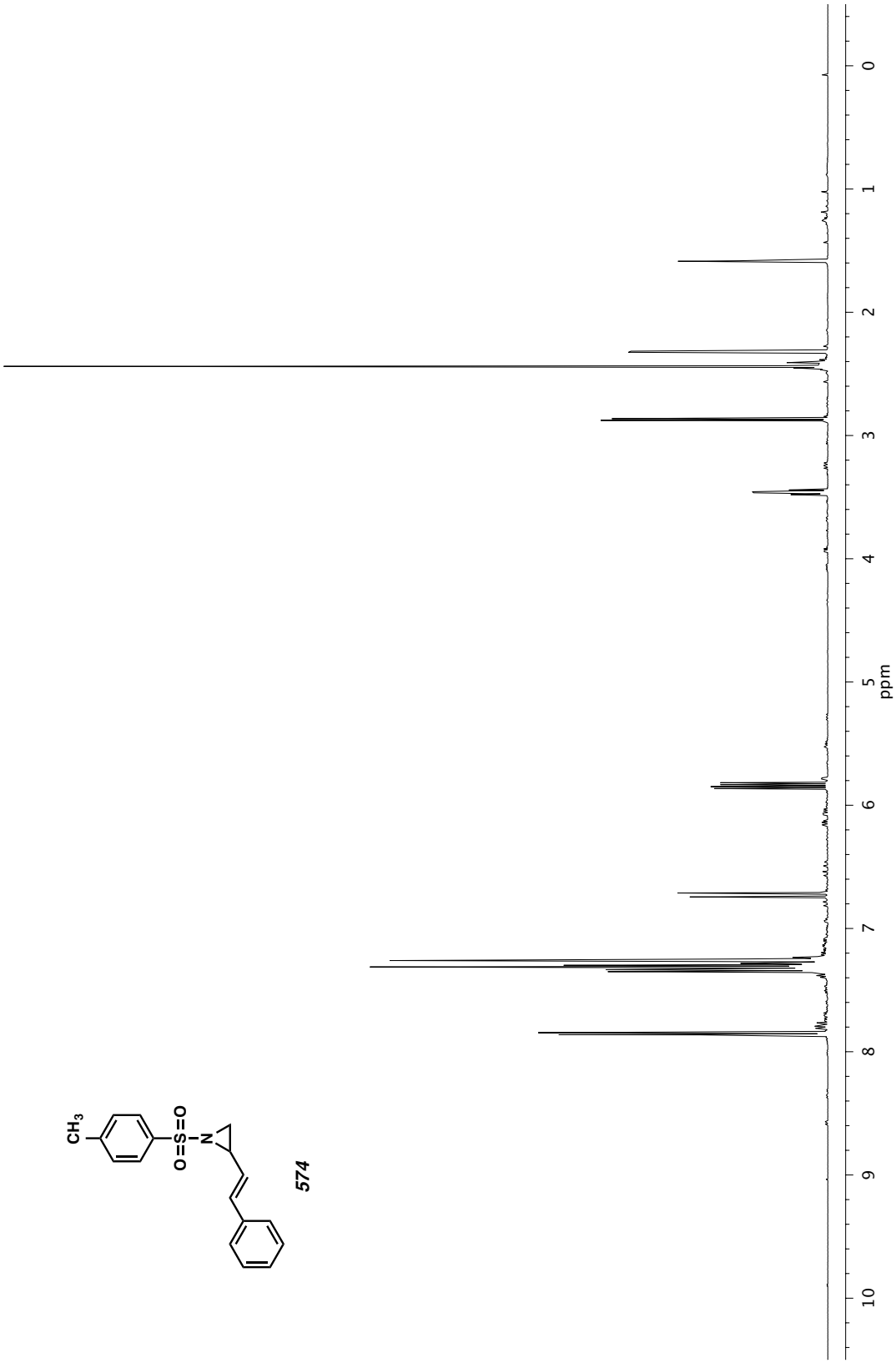


Figure A14.10. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **574**.

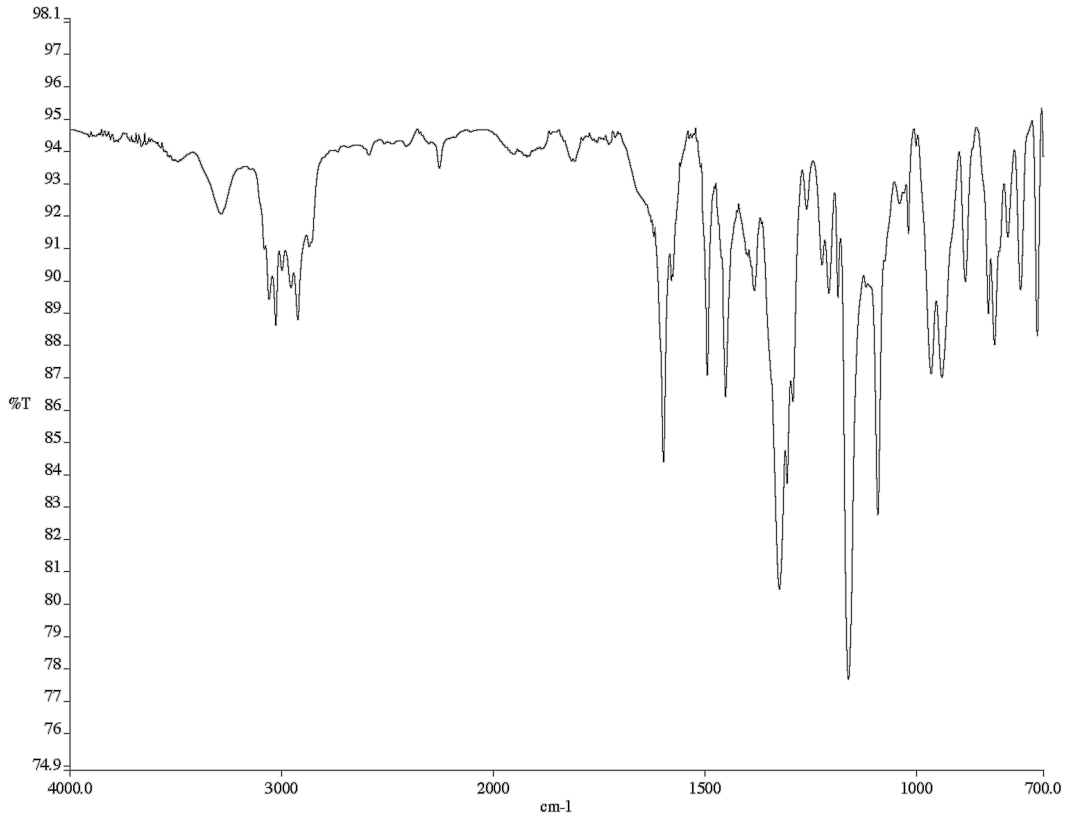


Figure A14.11. Infrared spectrum (thin film/NaCl) of compound **574**.

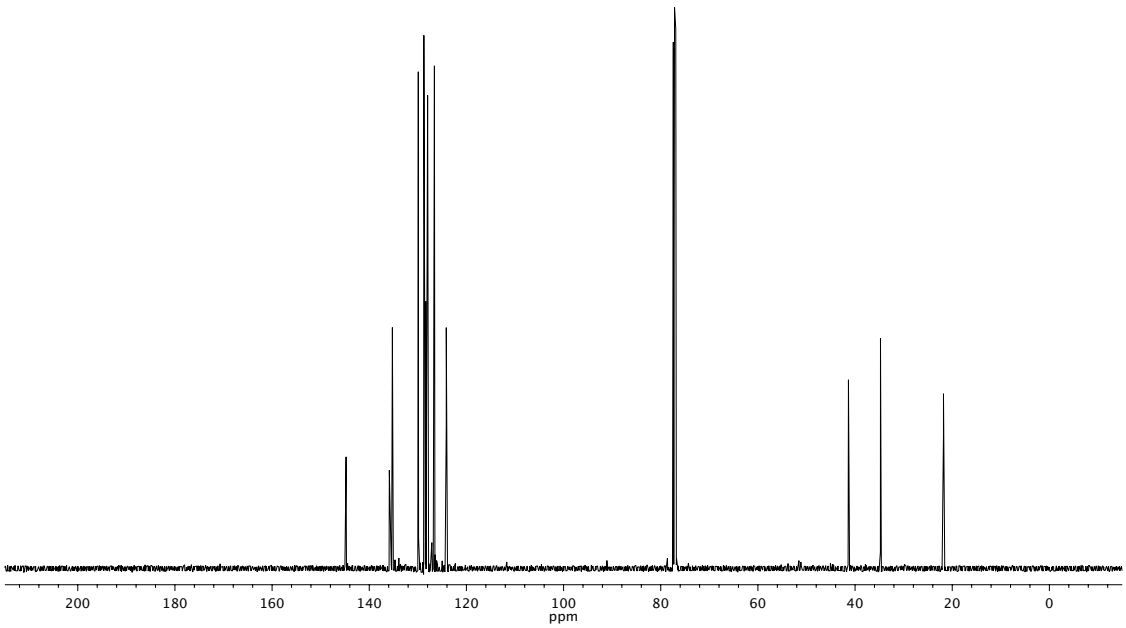


Figure A14.12. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **574**.

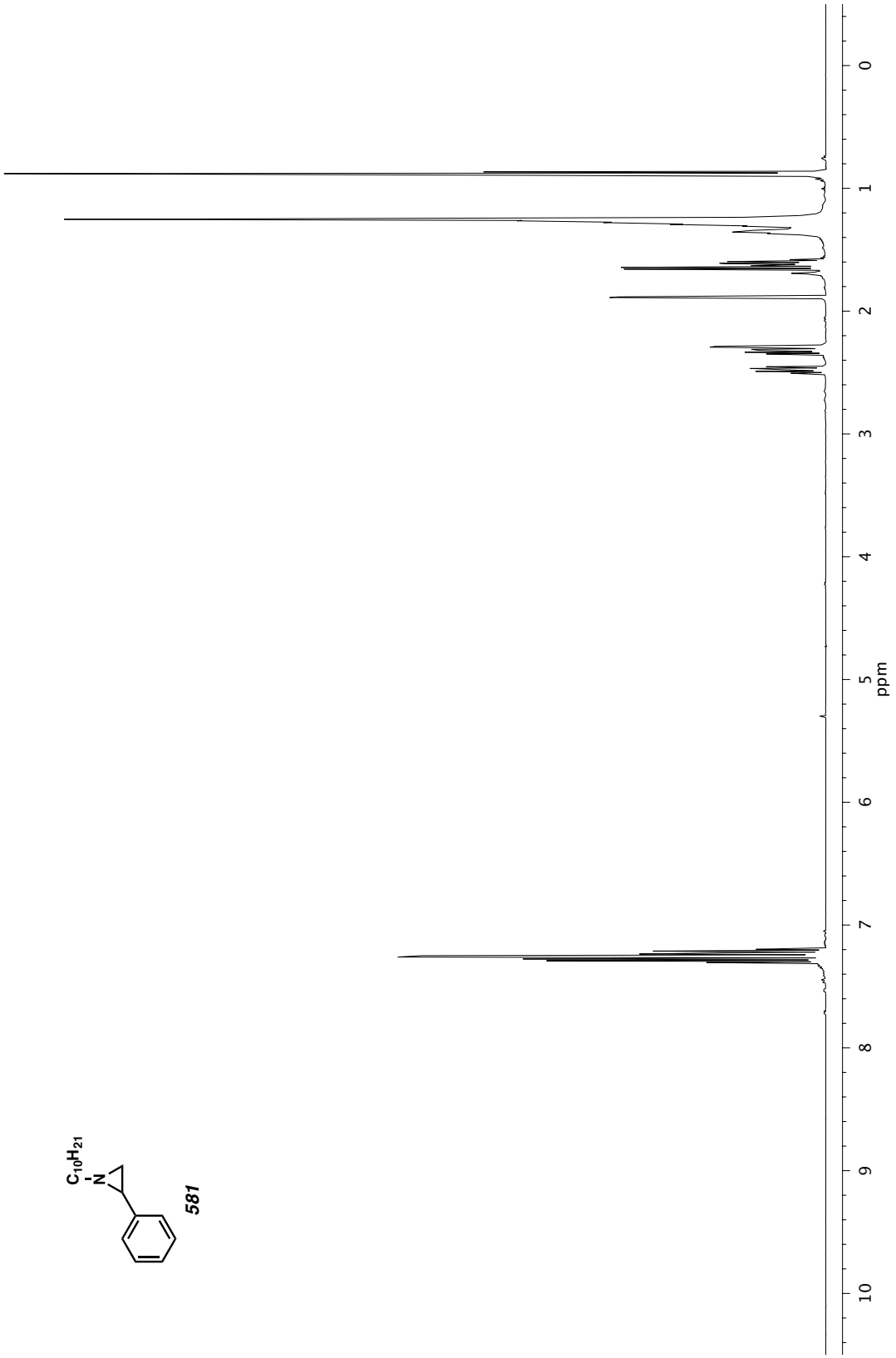


Figure A14.13. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **581**.

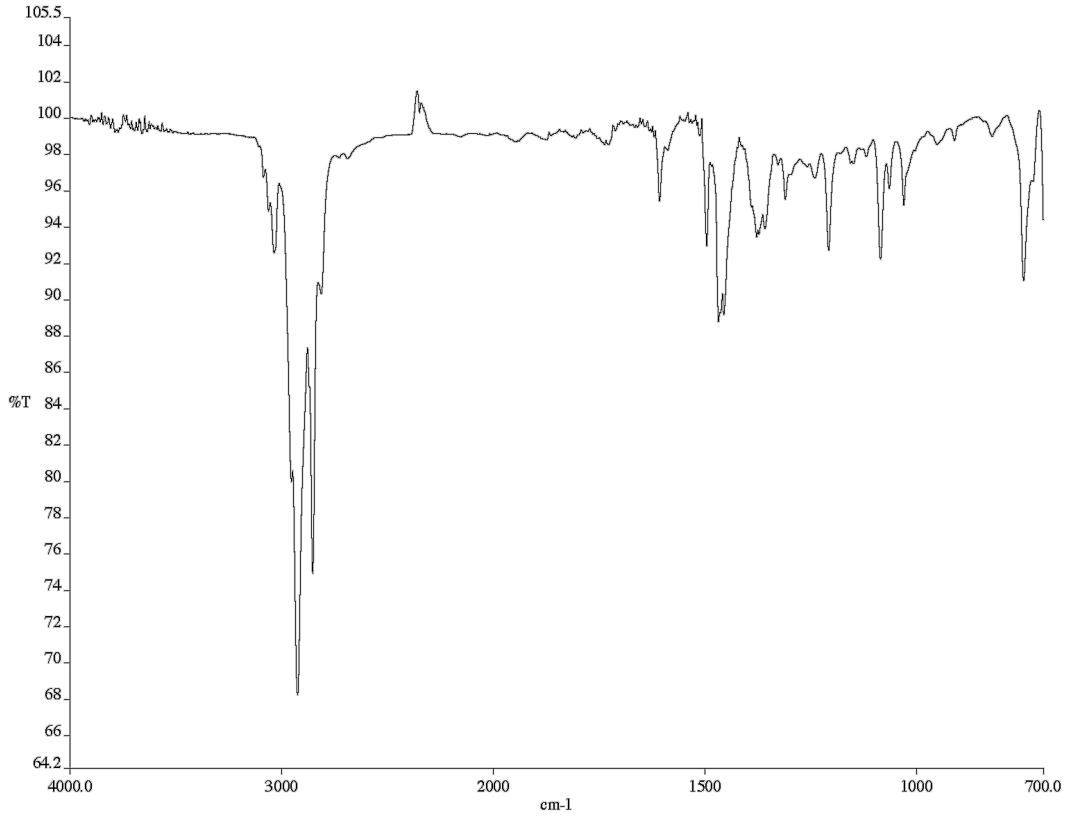


Figure A14.14. Infrared spectrum (thin film/NaCl) of compound **581**.

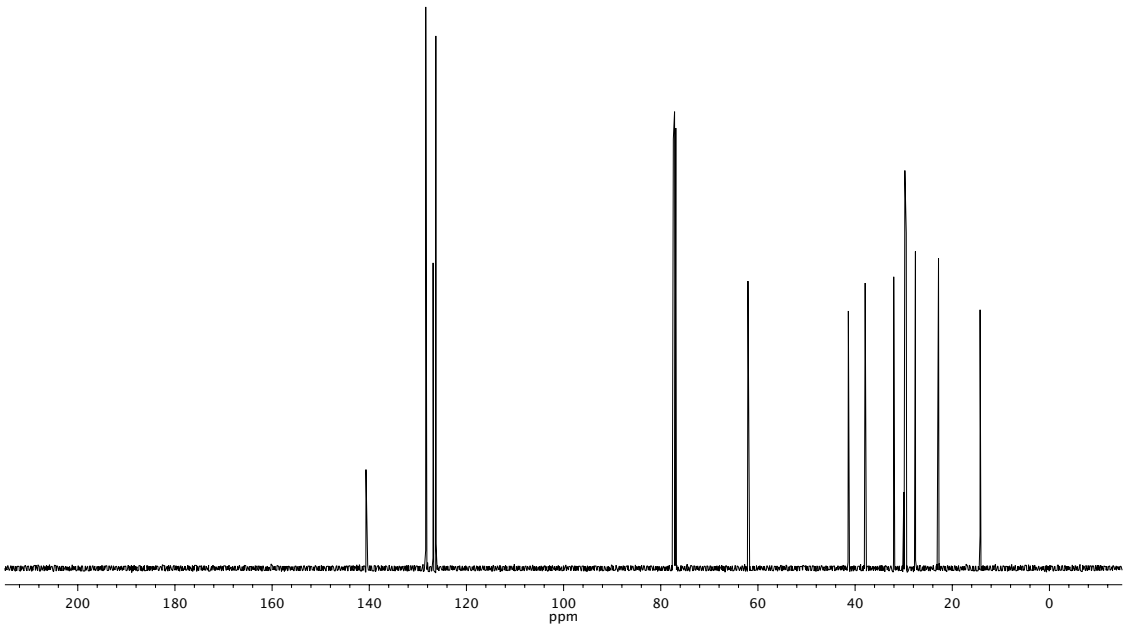


Figure A14.15. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **581**.

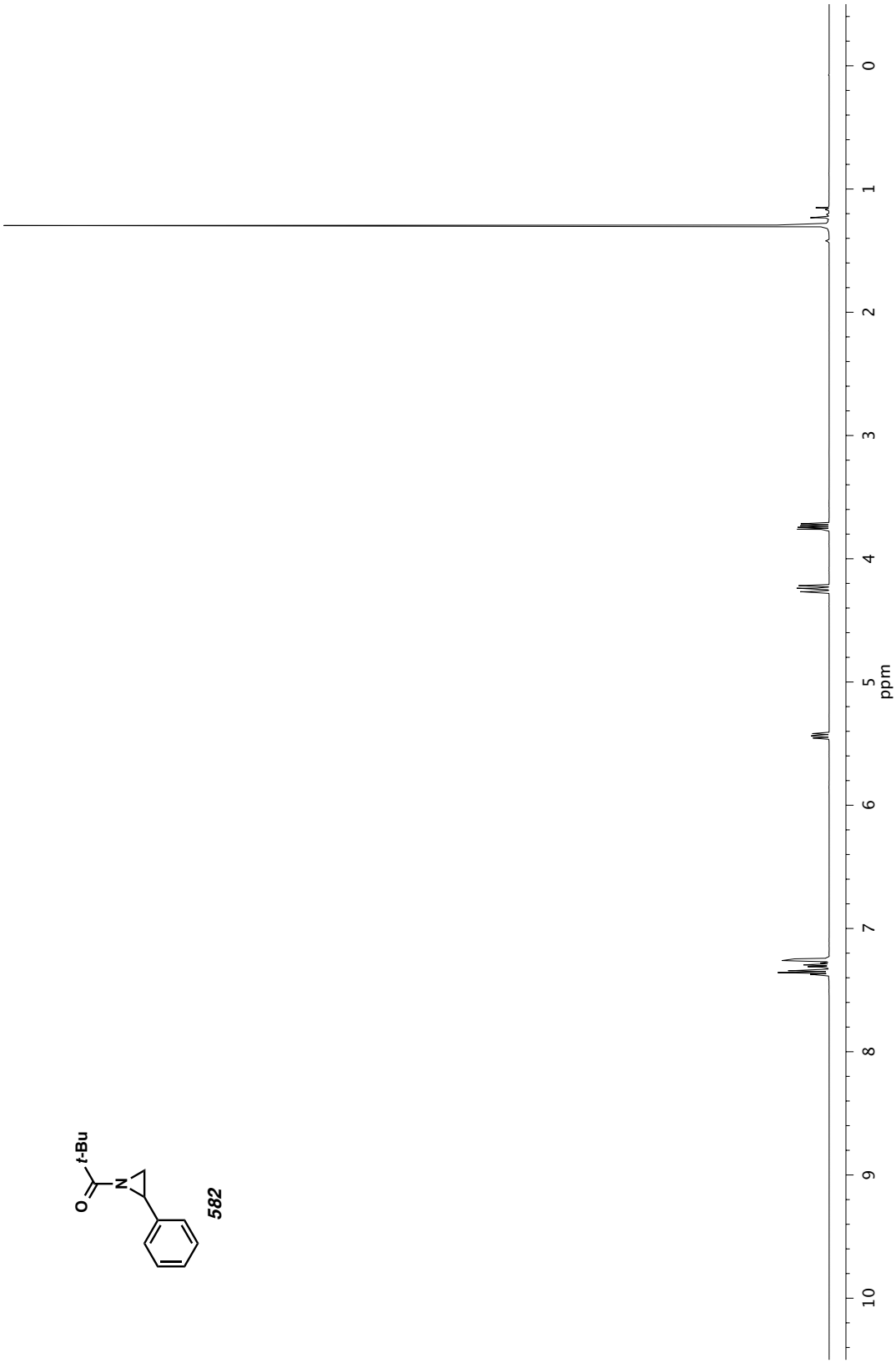


Figure A14.16. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **582**.

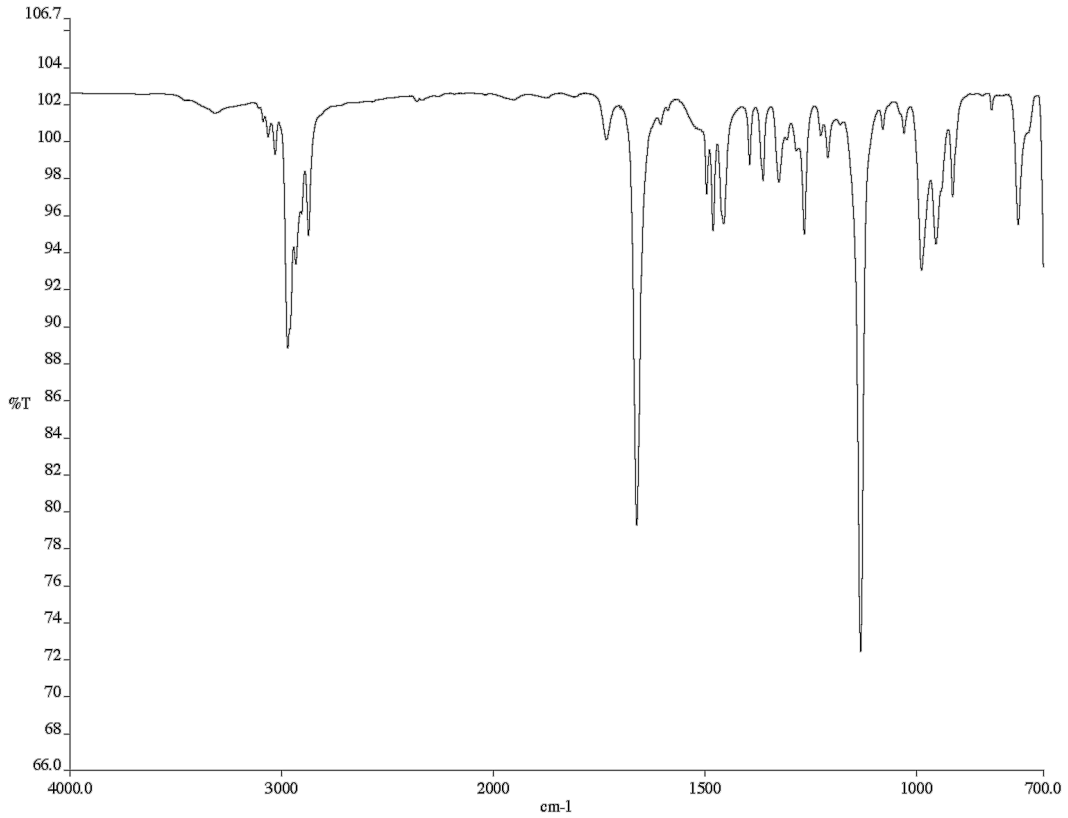


Figure A14.17. Infrared spectrum (thin film/NaCl) of compound **582**.

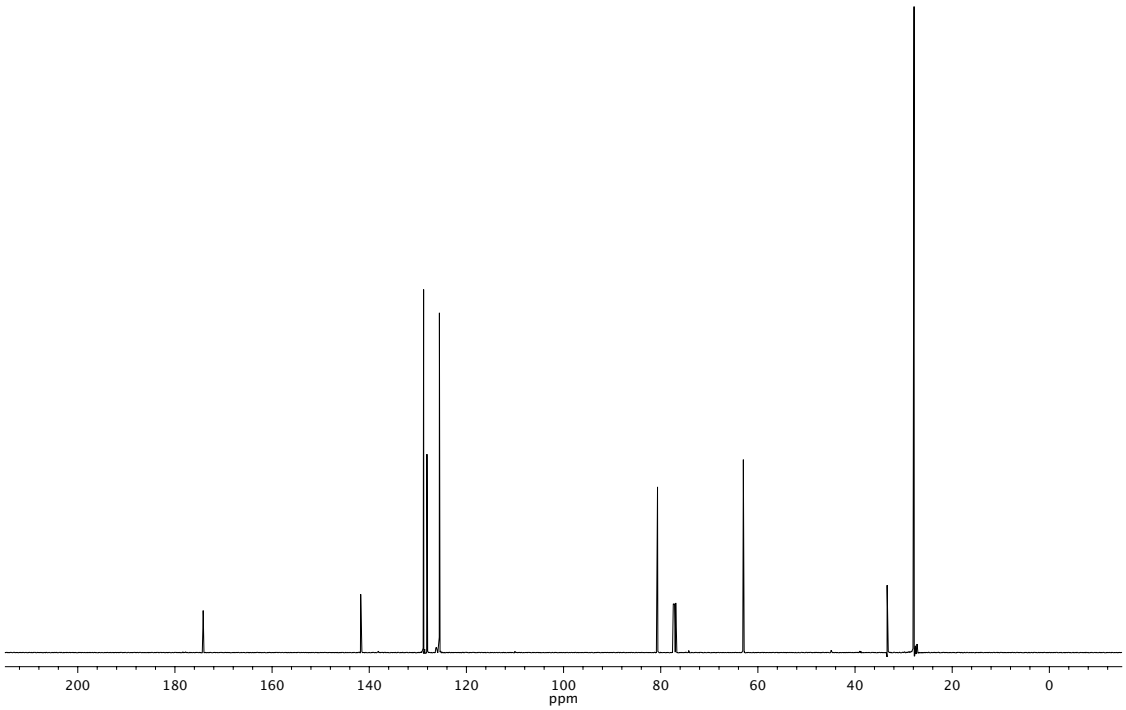


Figure A14.18. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **582**.

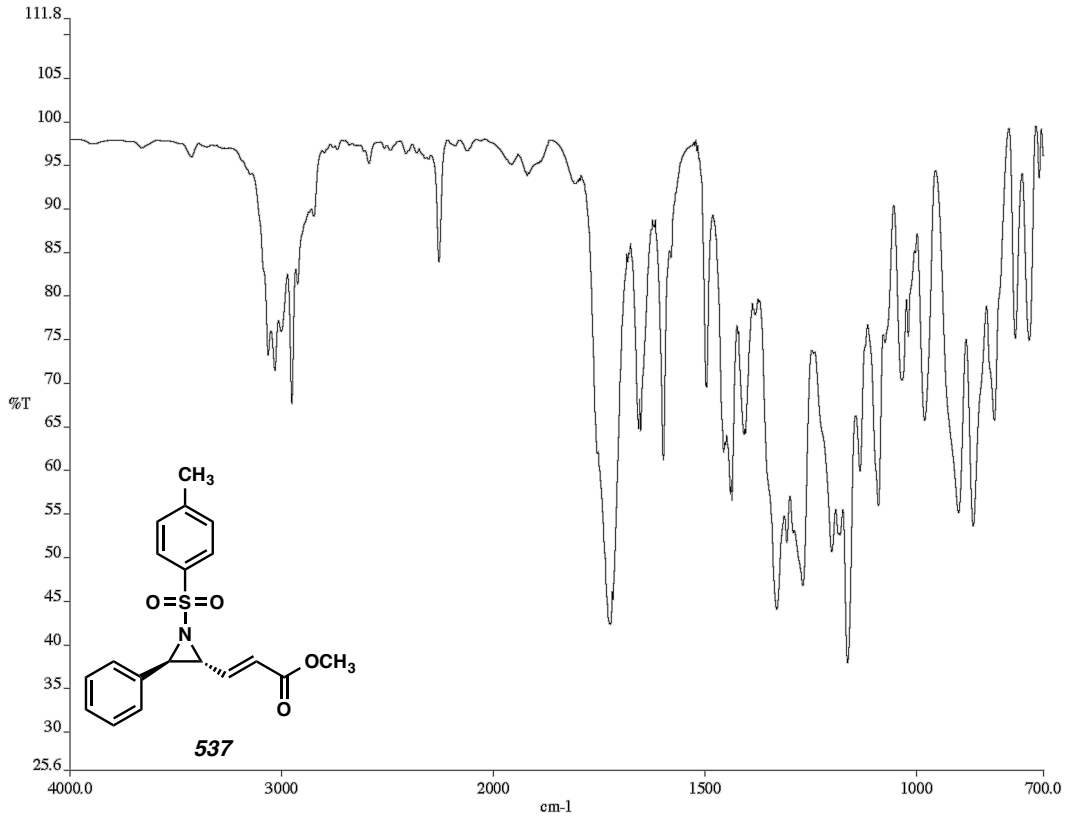
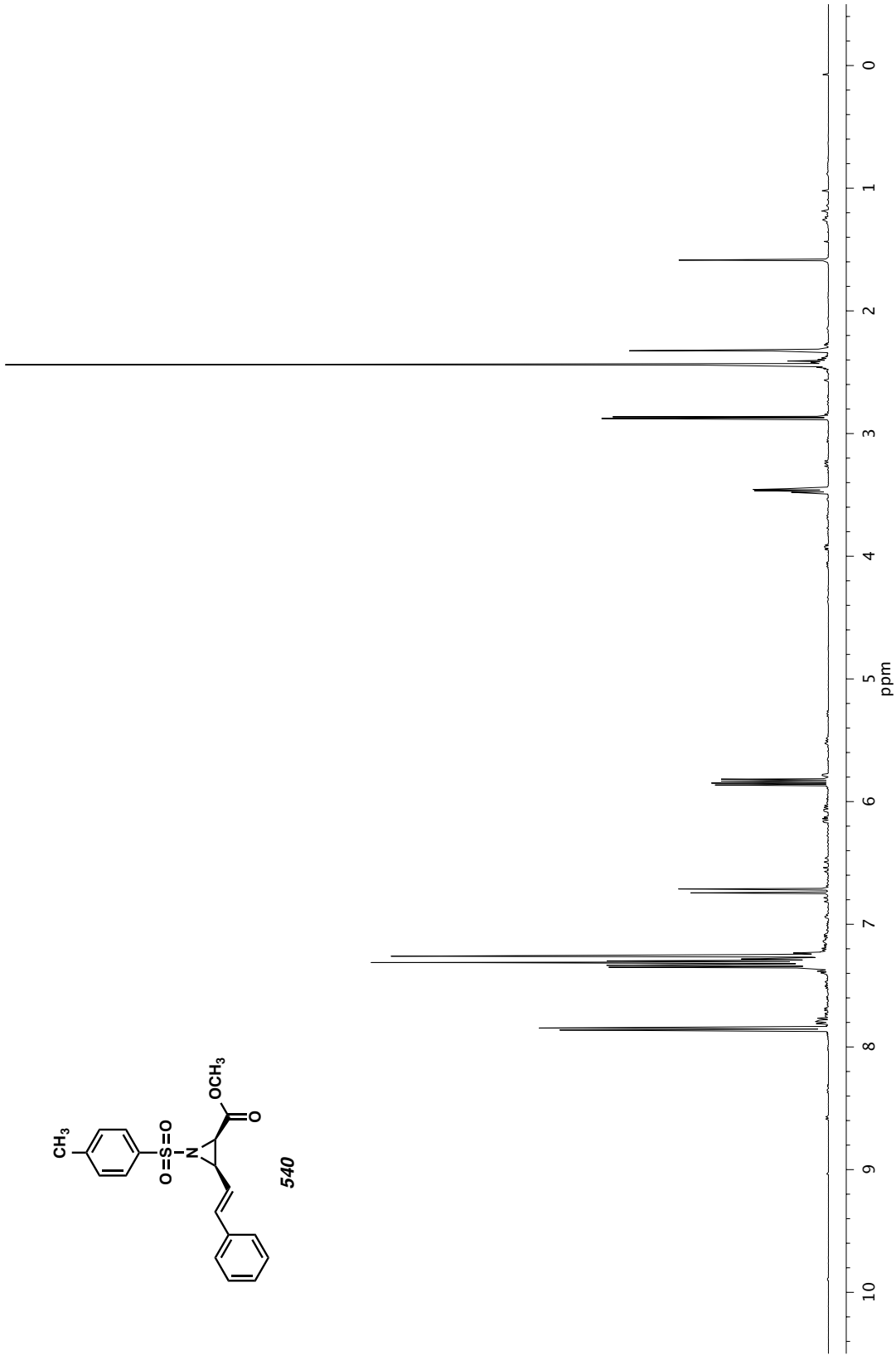


Figure A14.19. Infrared spectrum (thin film/NaCl) of compound **537**.



540

Figure A14.20. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **540**.

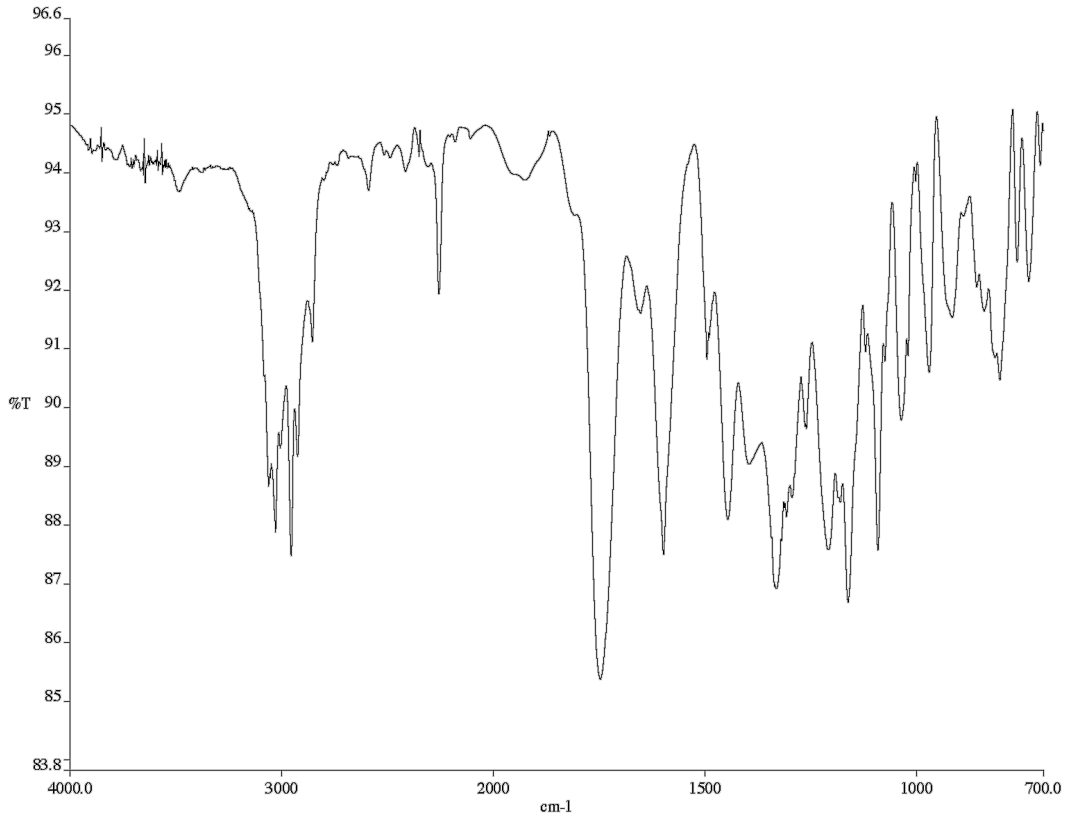


Figure A14.21. Infrared spectrum (thin film/NaCl) of compound **540**.

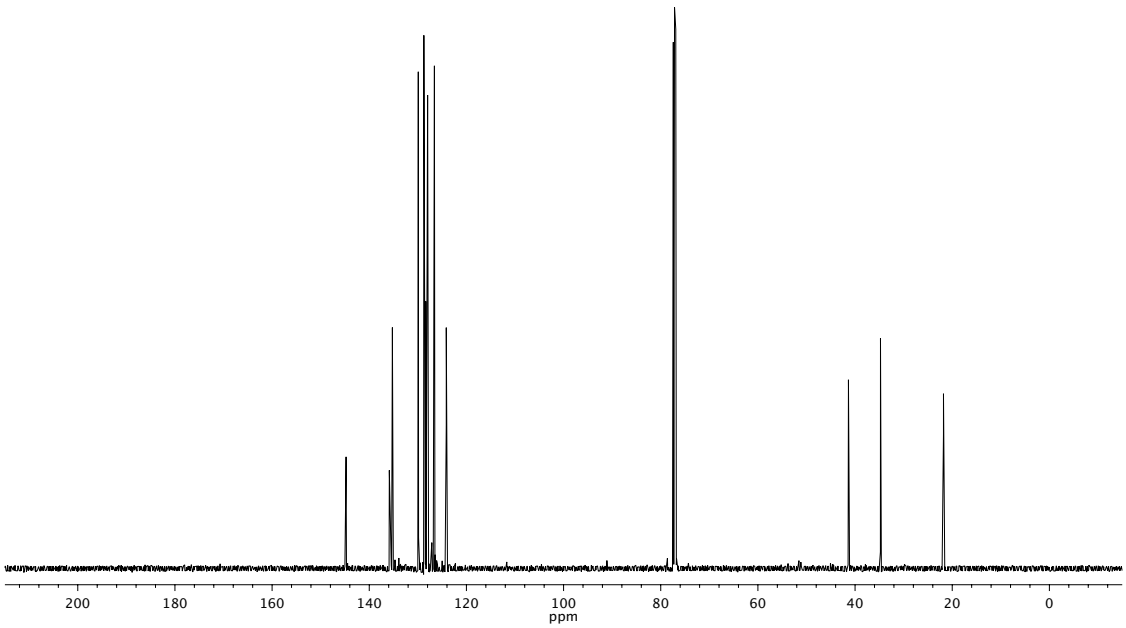


Figure A14.22. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **540**.

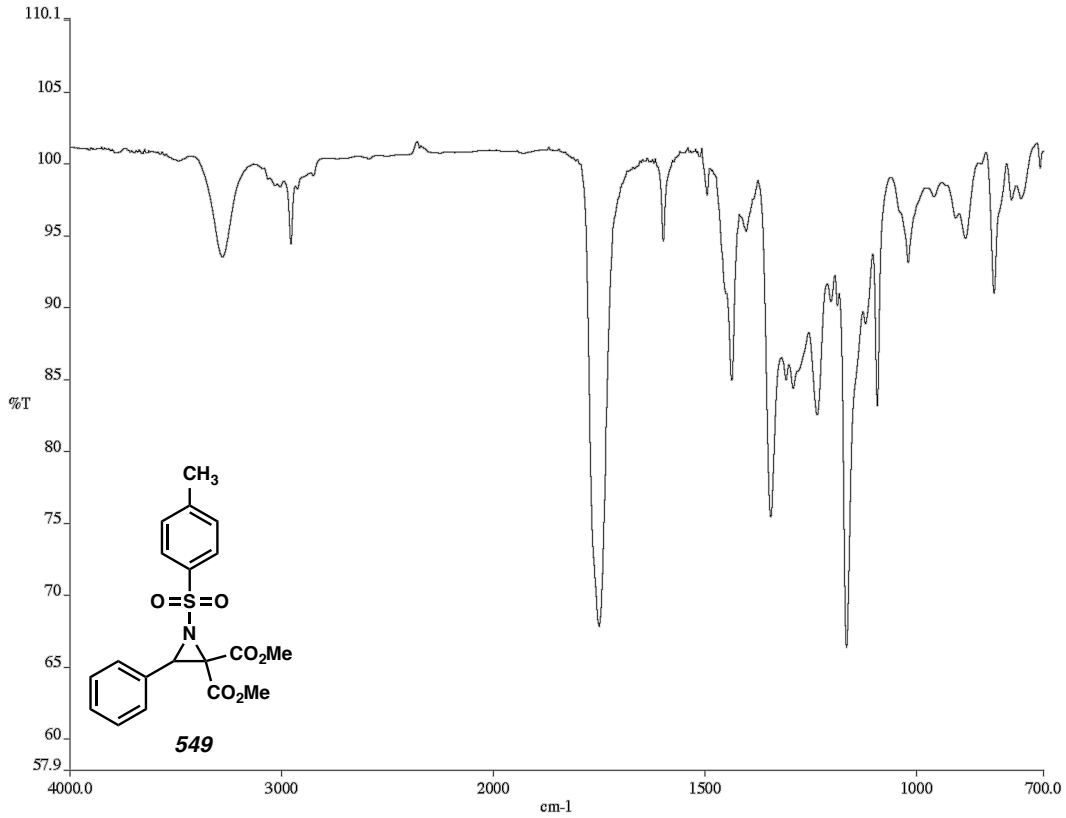


Figure A14.23. Infrared spectrum (thin film/NaCl) of compound **549**.

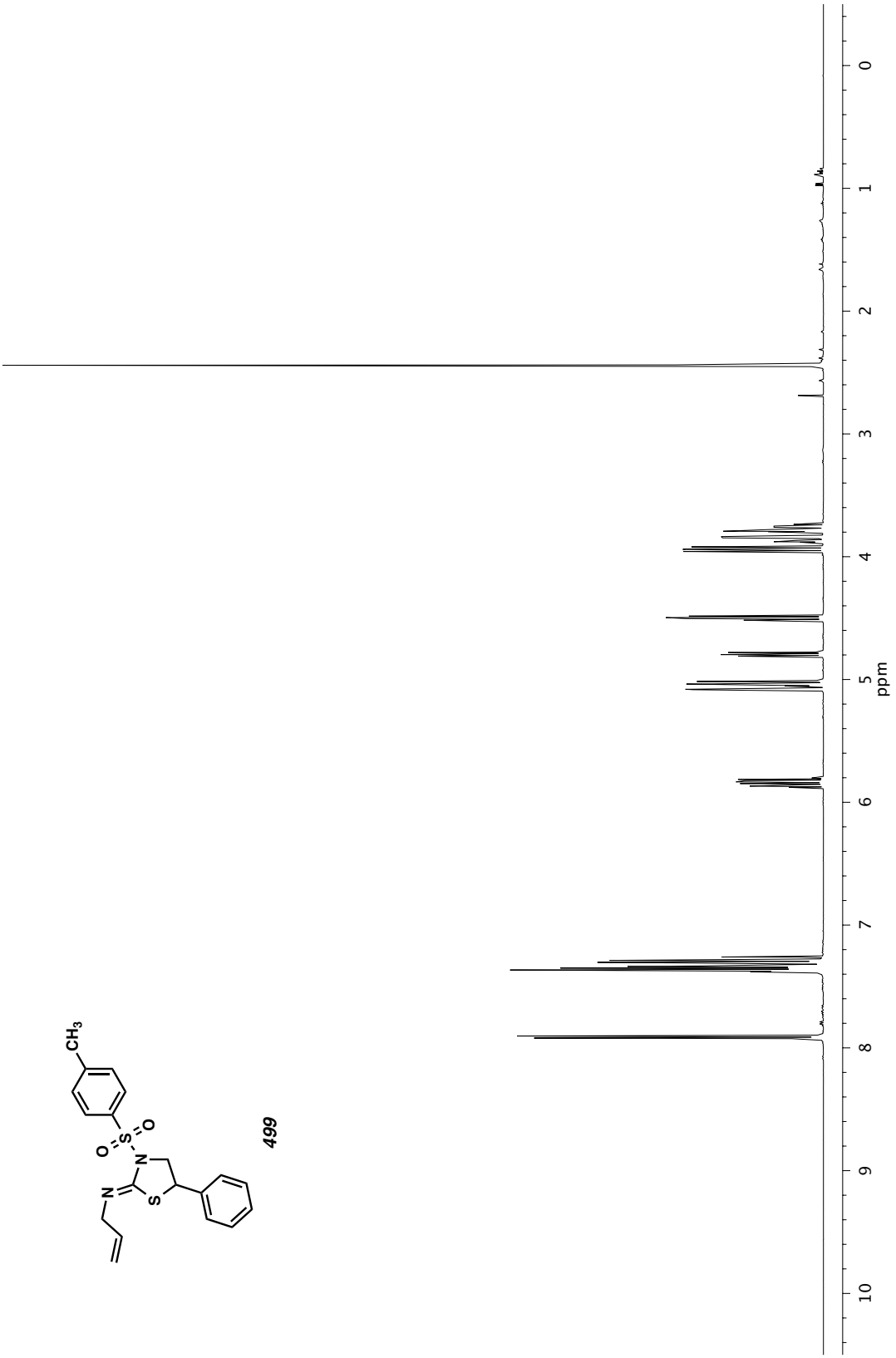


Figure A14.24. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **499**.

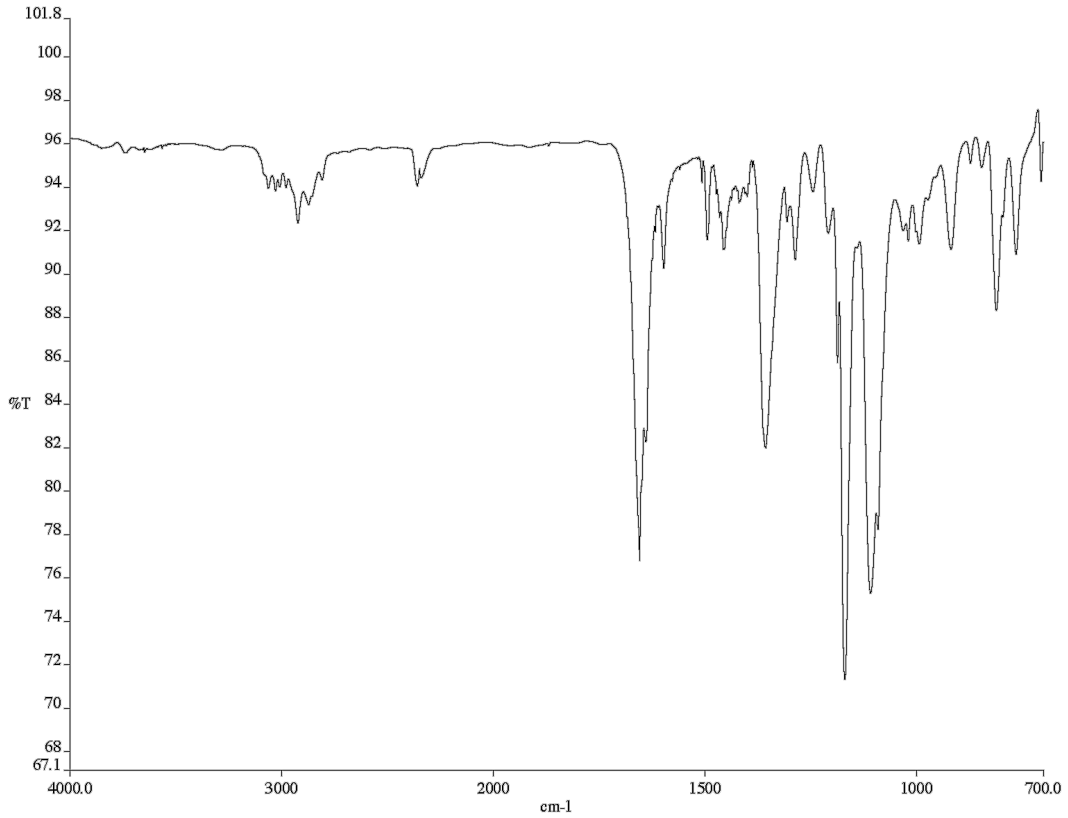


Figure A14.25. Infrared spectrum (thin film/NaCl) of compound **499**.

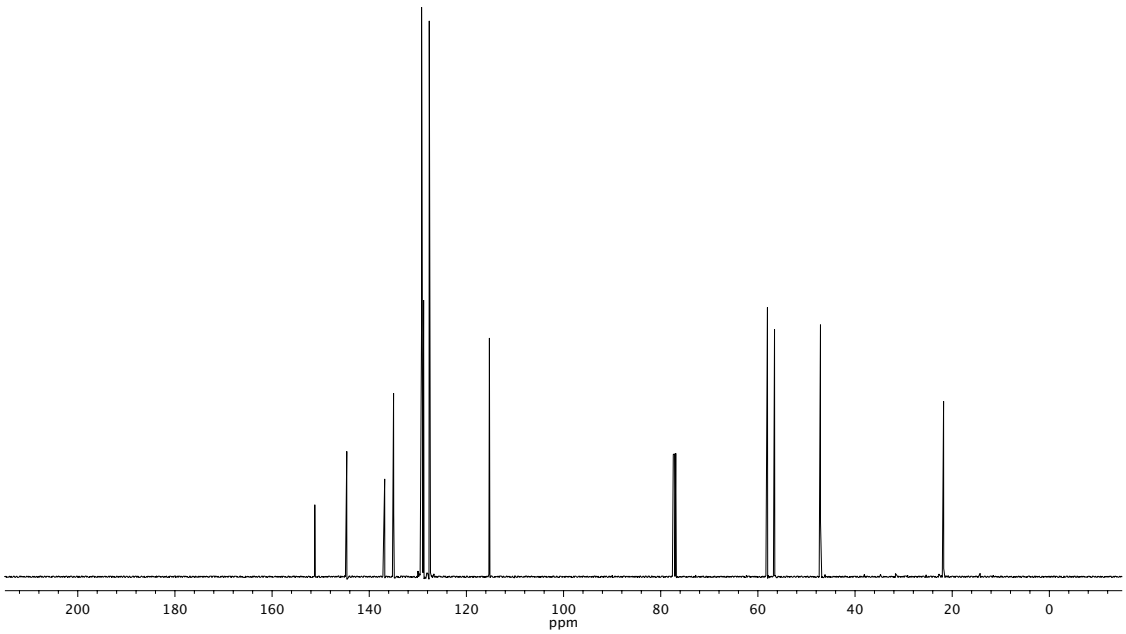


Figure A14.26. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **499**.

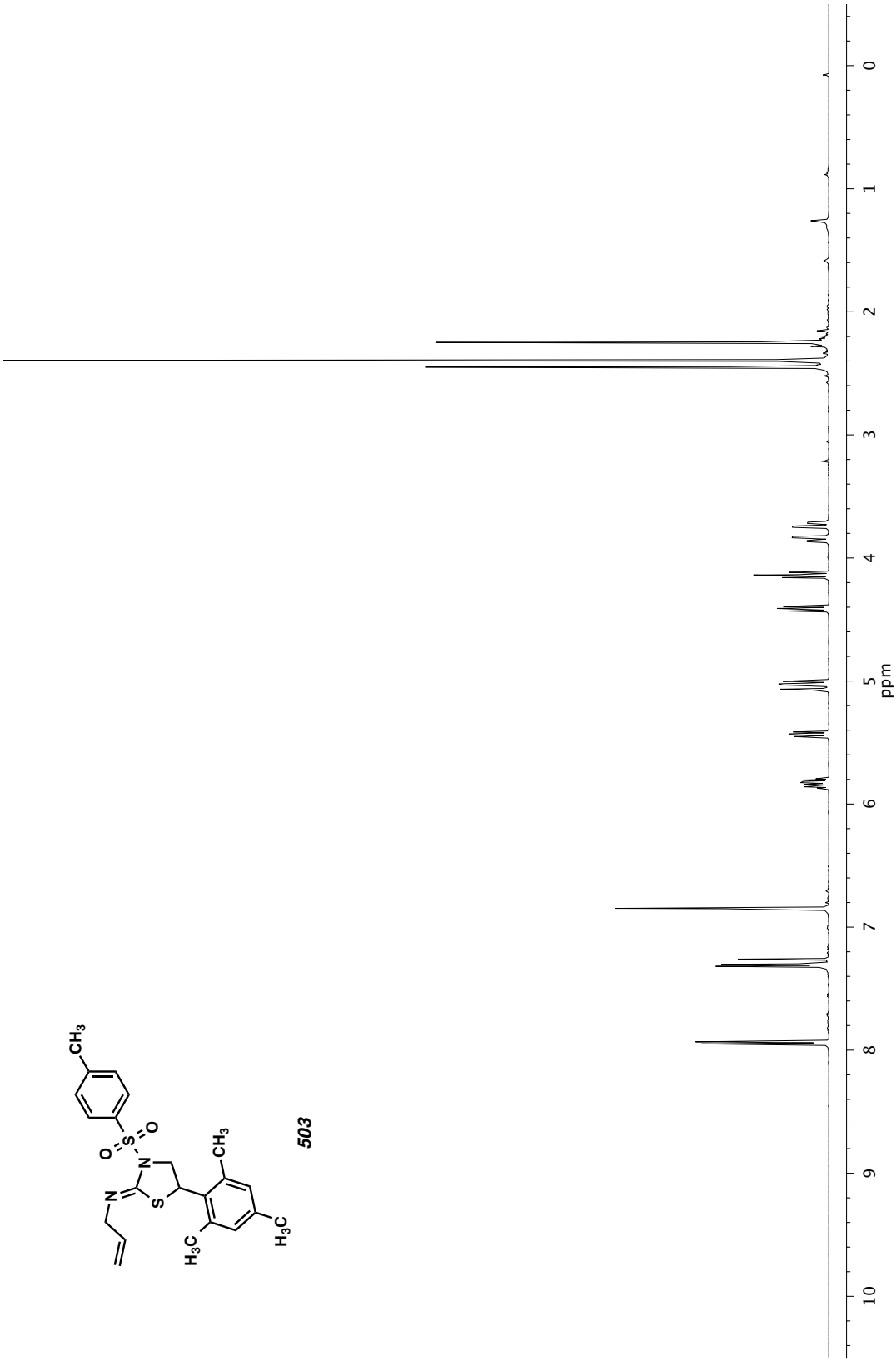


Figure A14.27. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **503**.

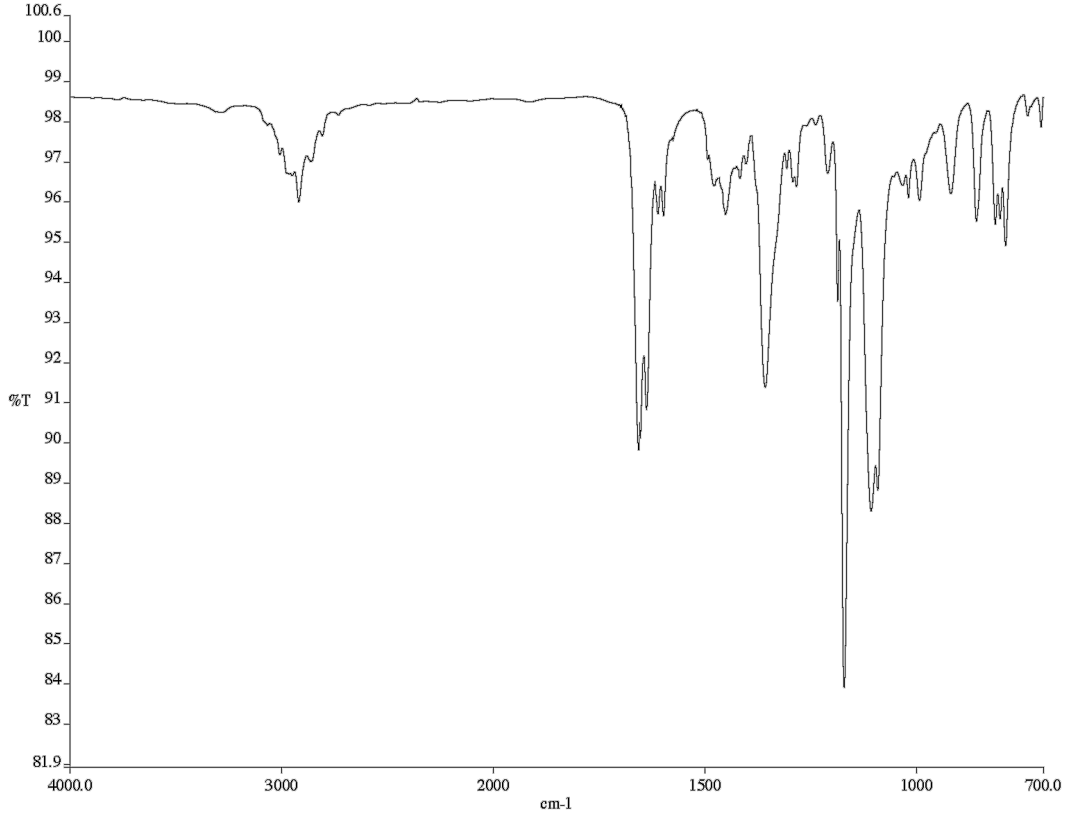


Figure A14.28. Infrared spectrum (thin film/NaCl) of compound **503**.

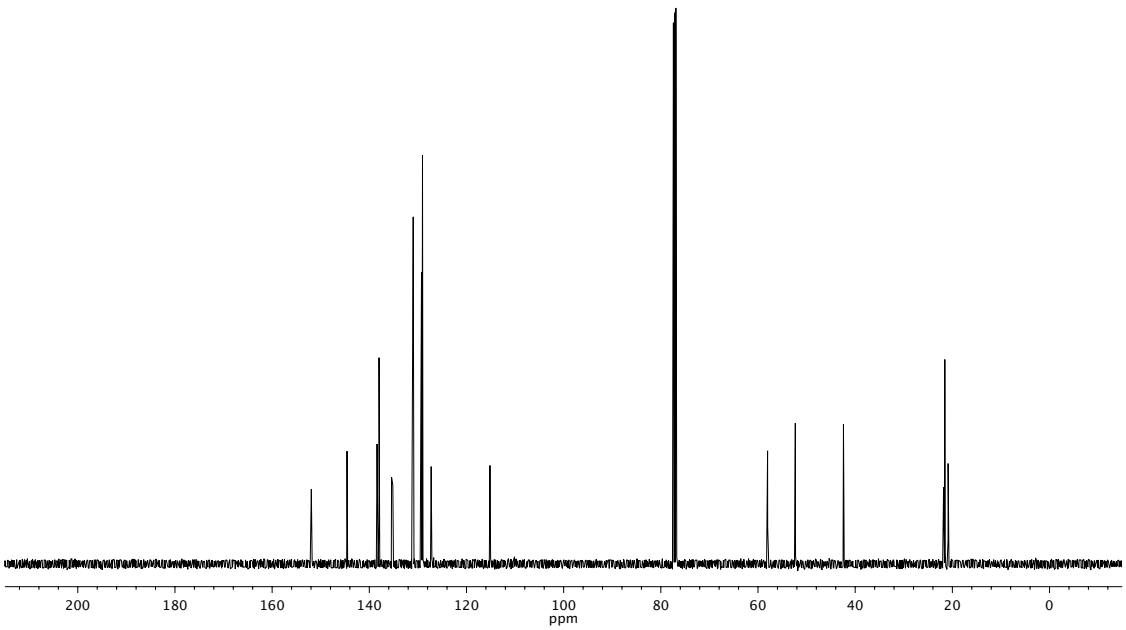


Figure A14.29. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **503**.

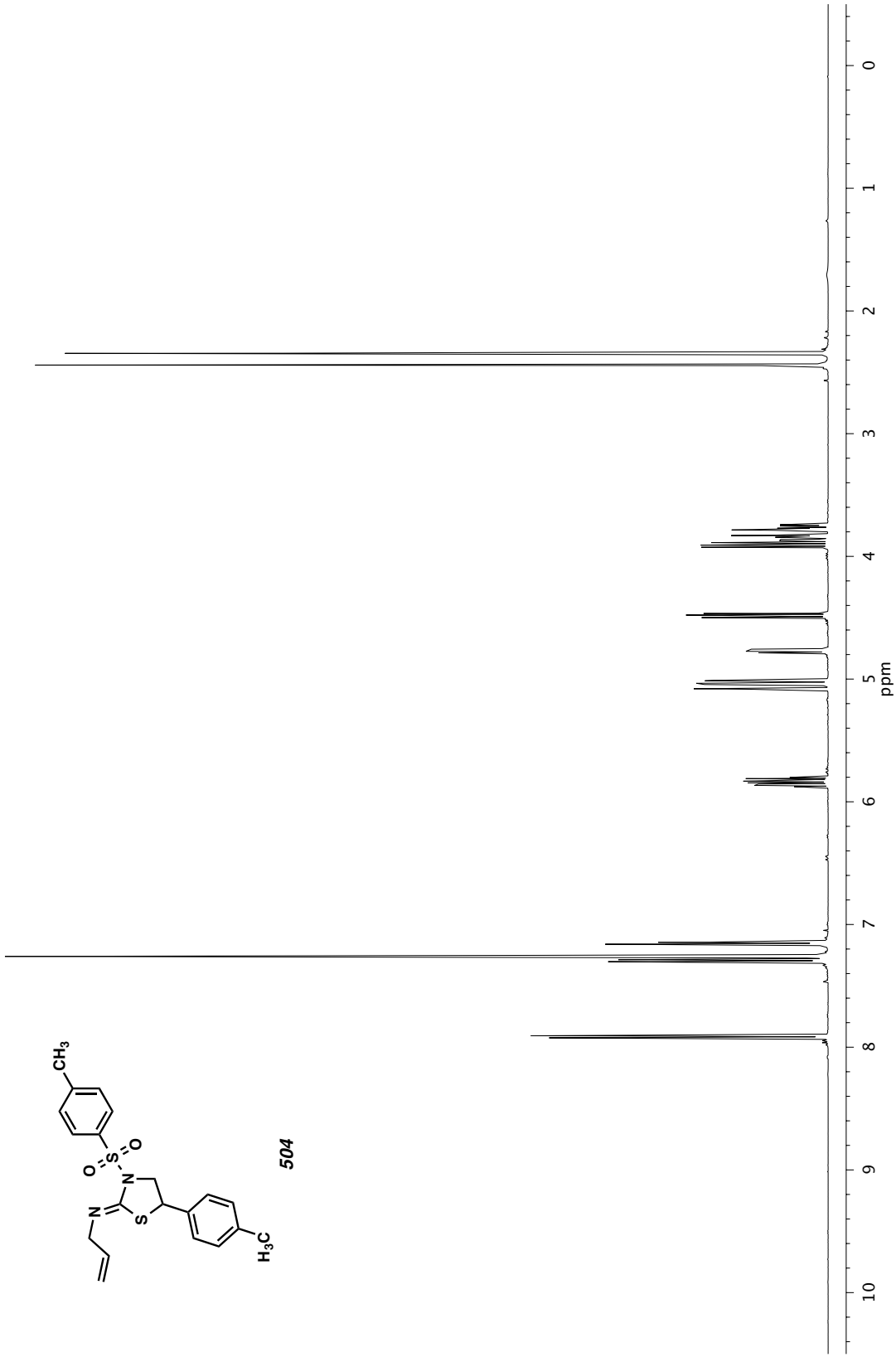


Figure A14.30. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **504**.

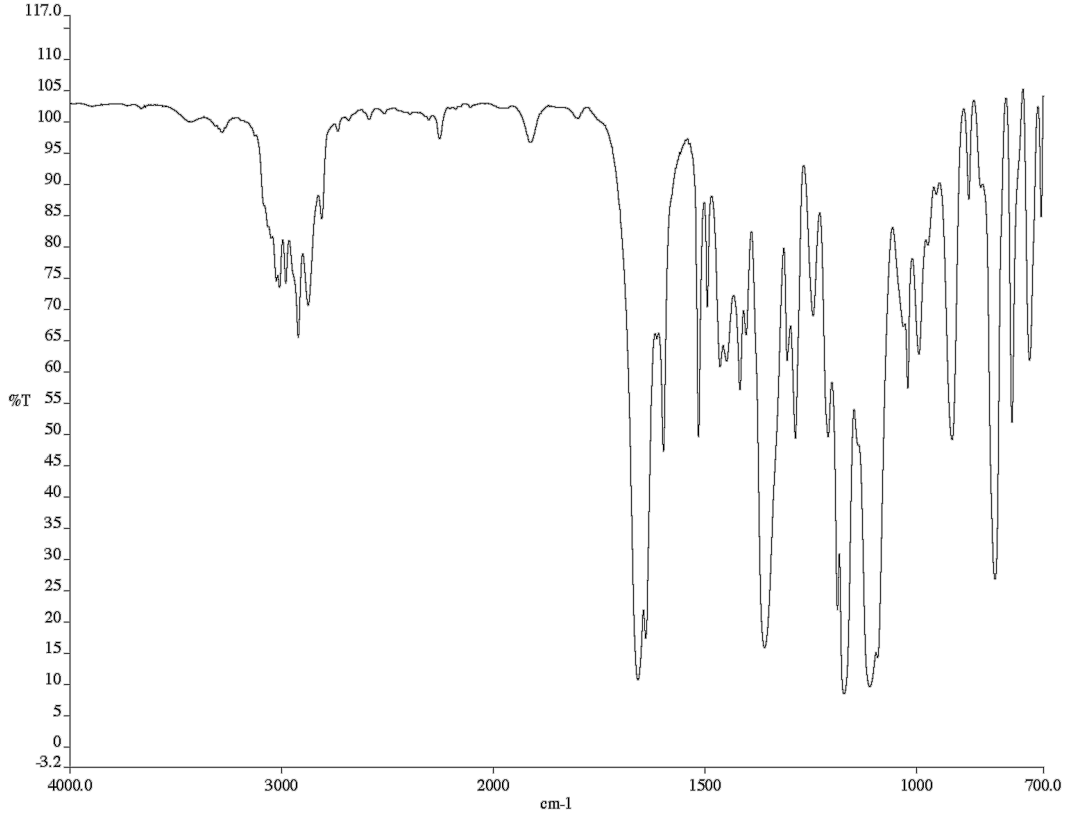


Figure A14.31. Infrared spectrum (thin film/NaCl) of compound **504**.

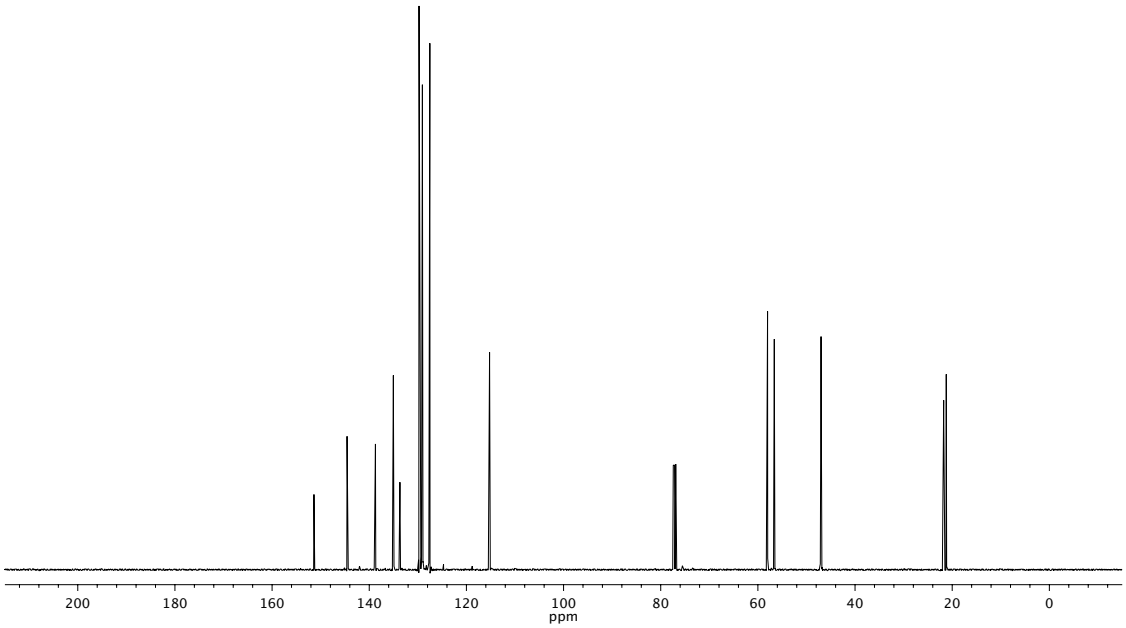


Figure A14.32. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **504**.

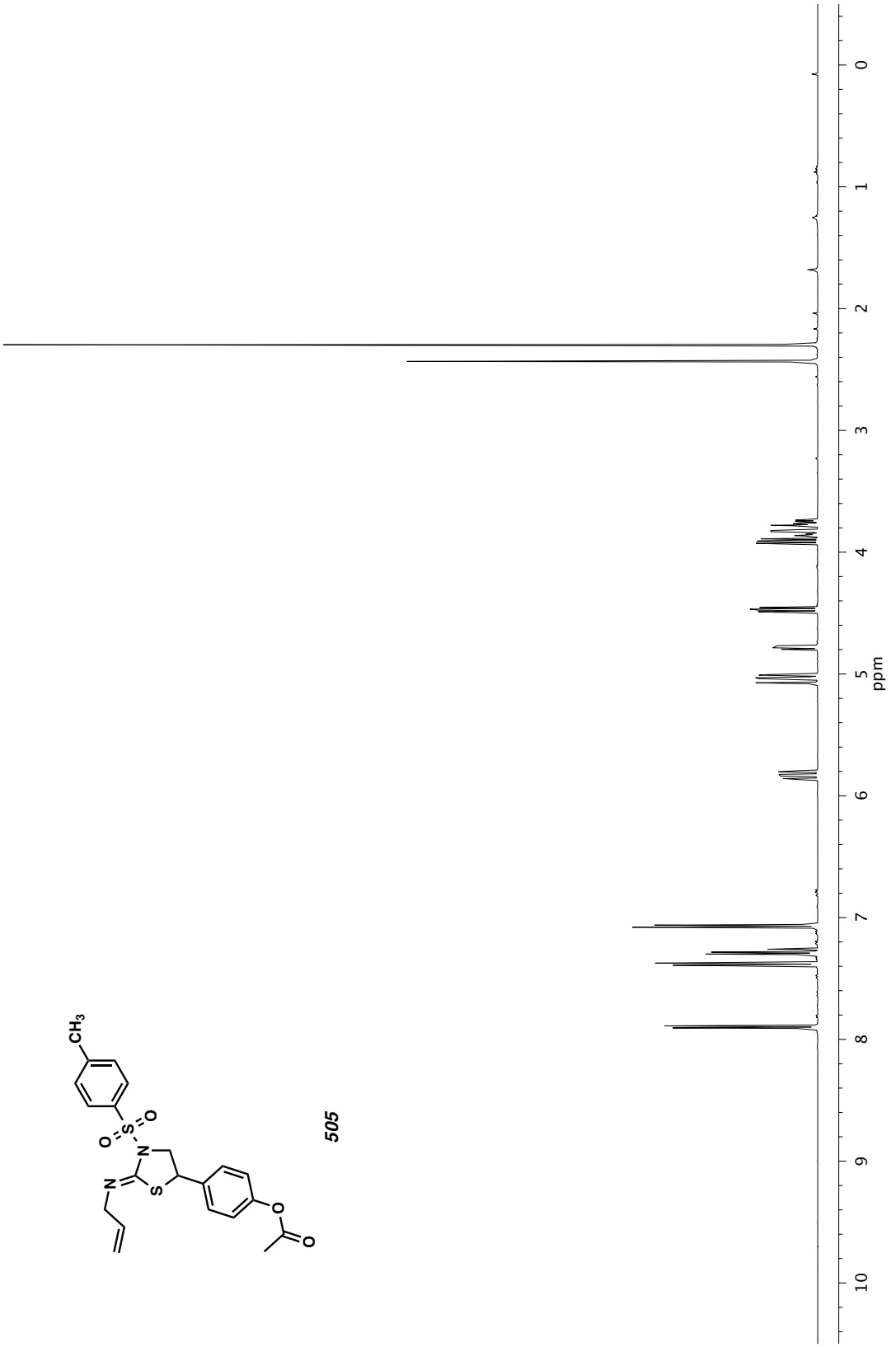


Figure A14.33. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **505**.

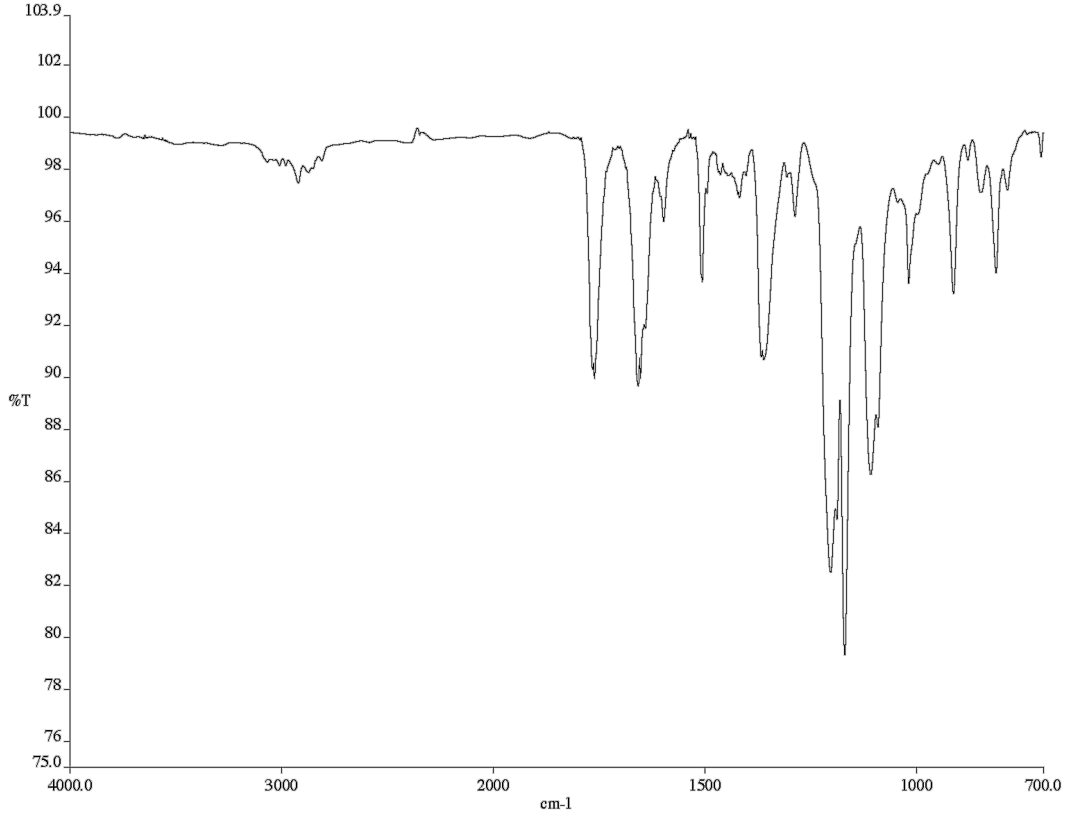


Figure A14.34. Infrared spectrum (thin film/NaCl) of compound **505**.

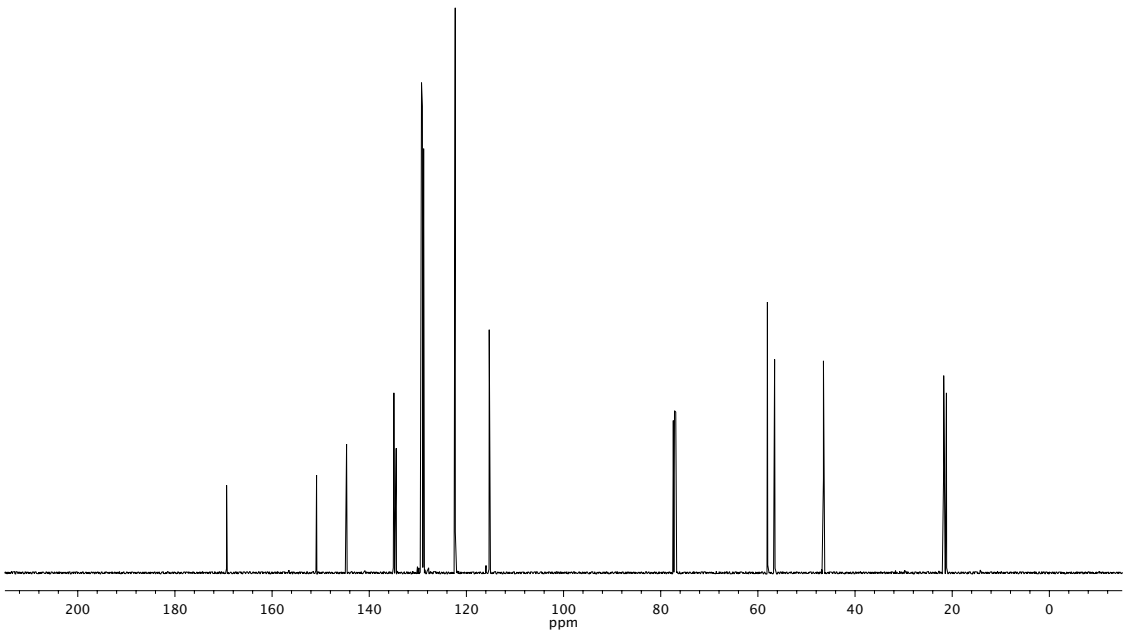


Figure A14.35. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **505**.

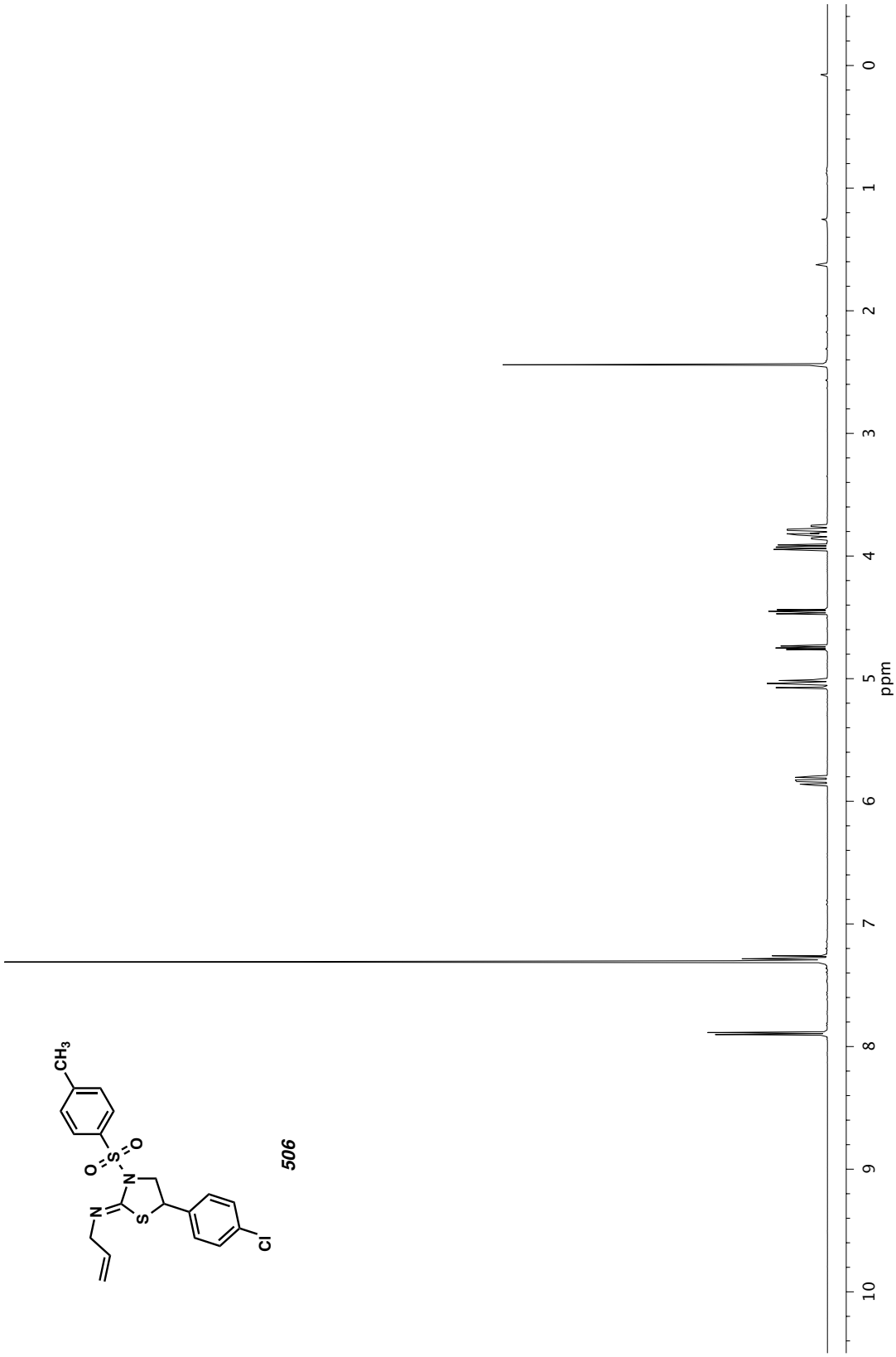


Figure A14.36. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **506**.

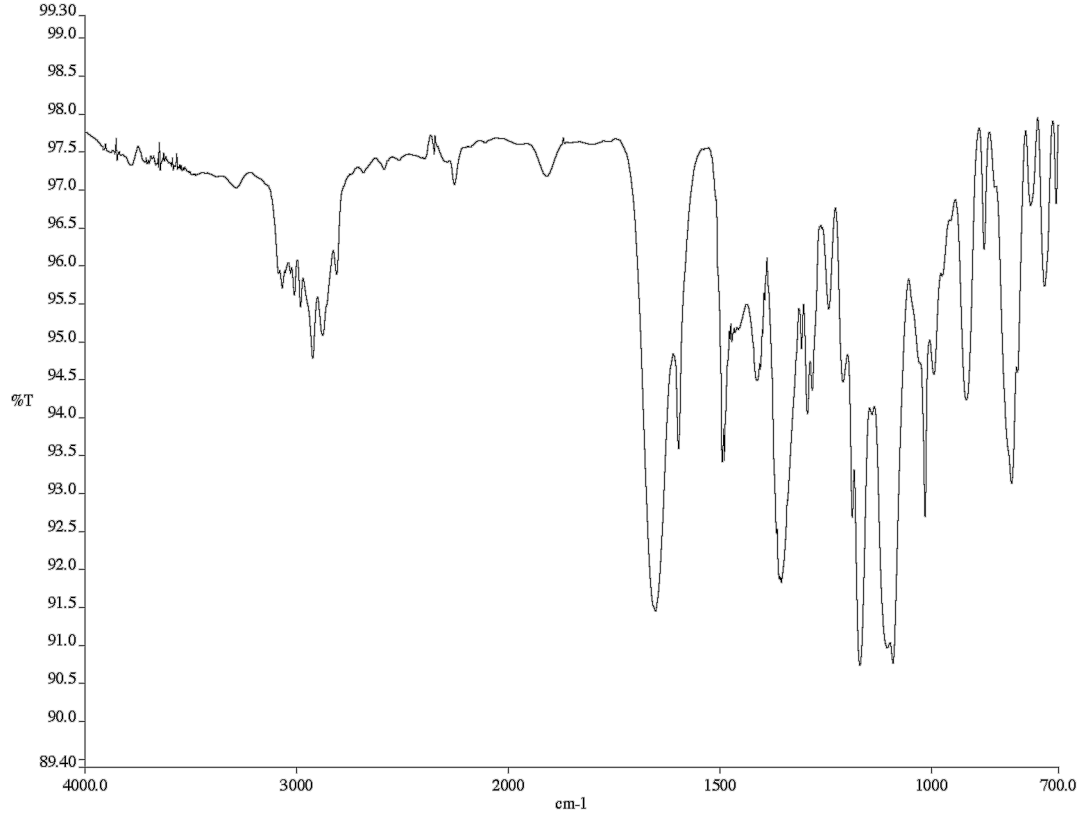


Figure A14.37. Infrared spectrum (thin film/NaCl) of compound **506**.

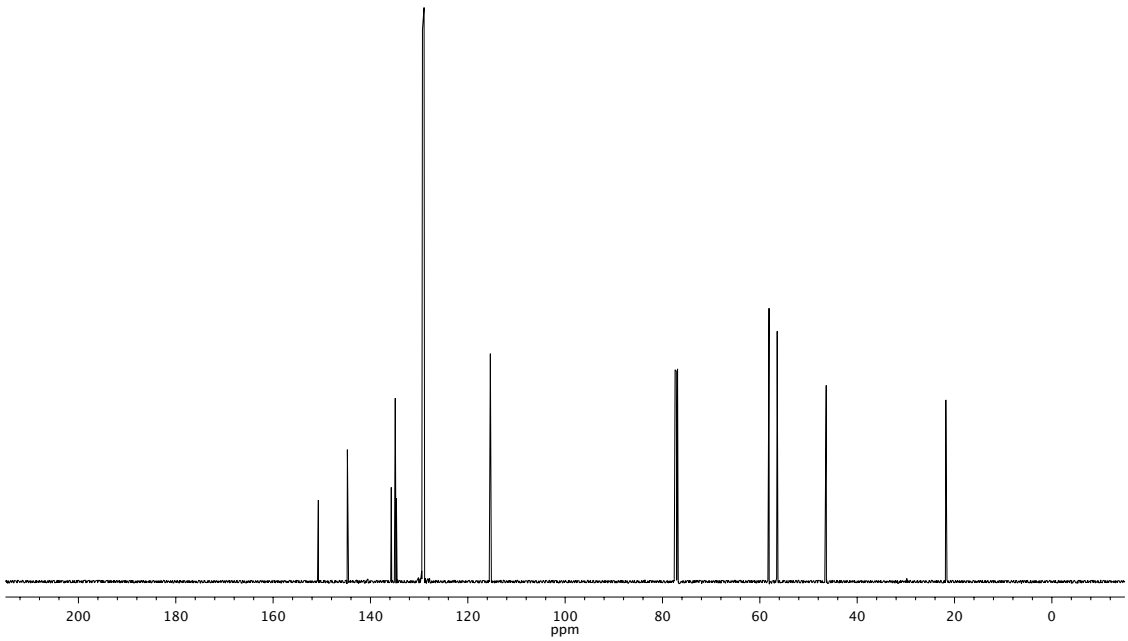


Figure A14.38. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **506**.

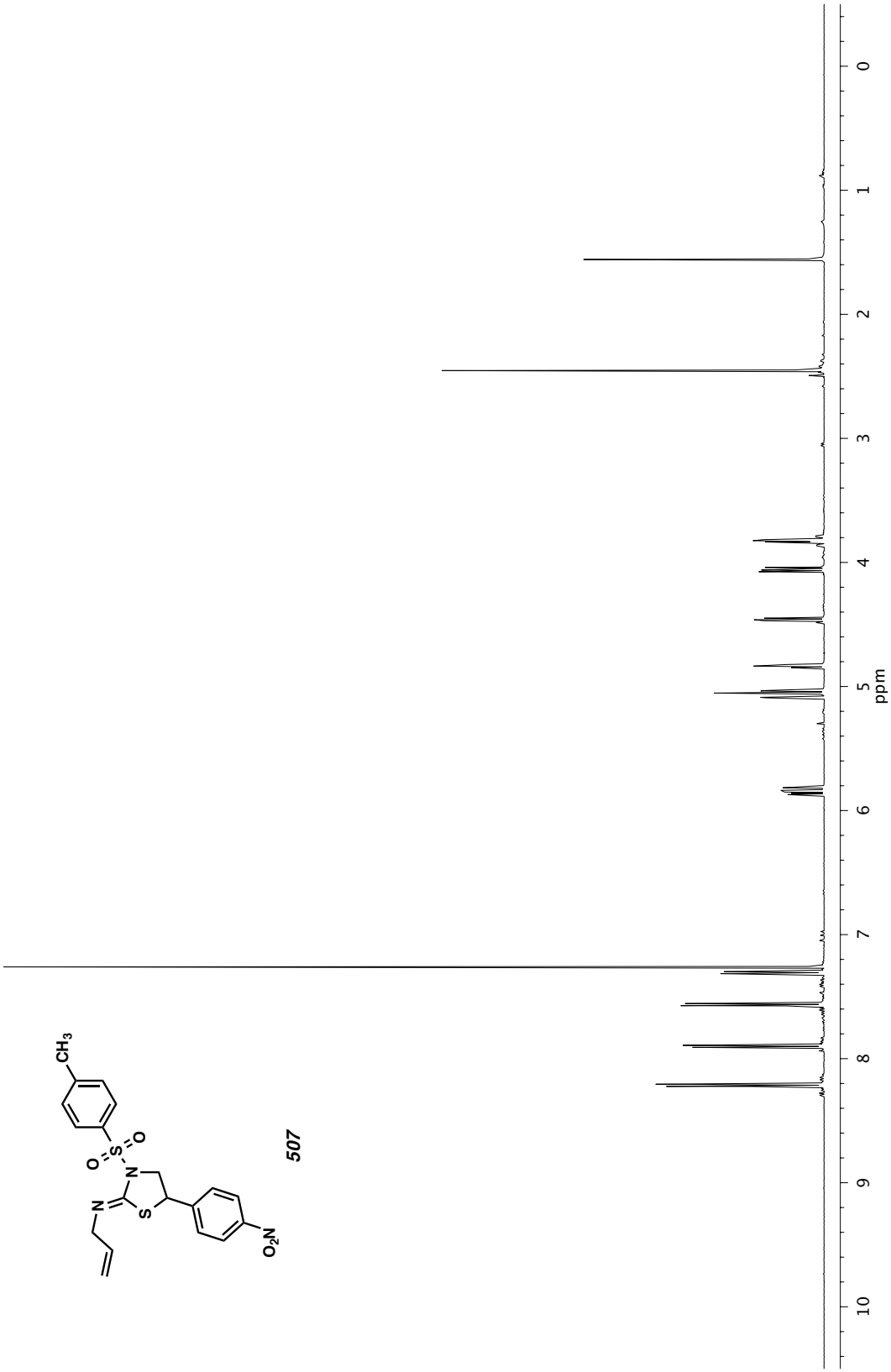


Figure A14.39. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **507**.

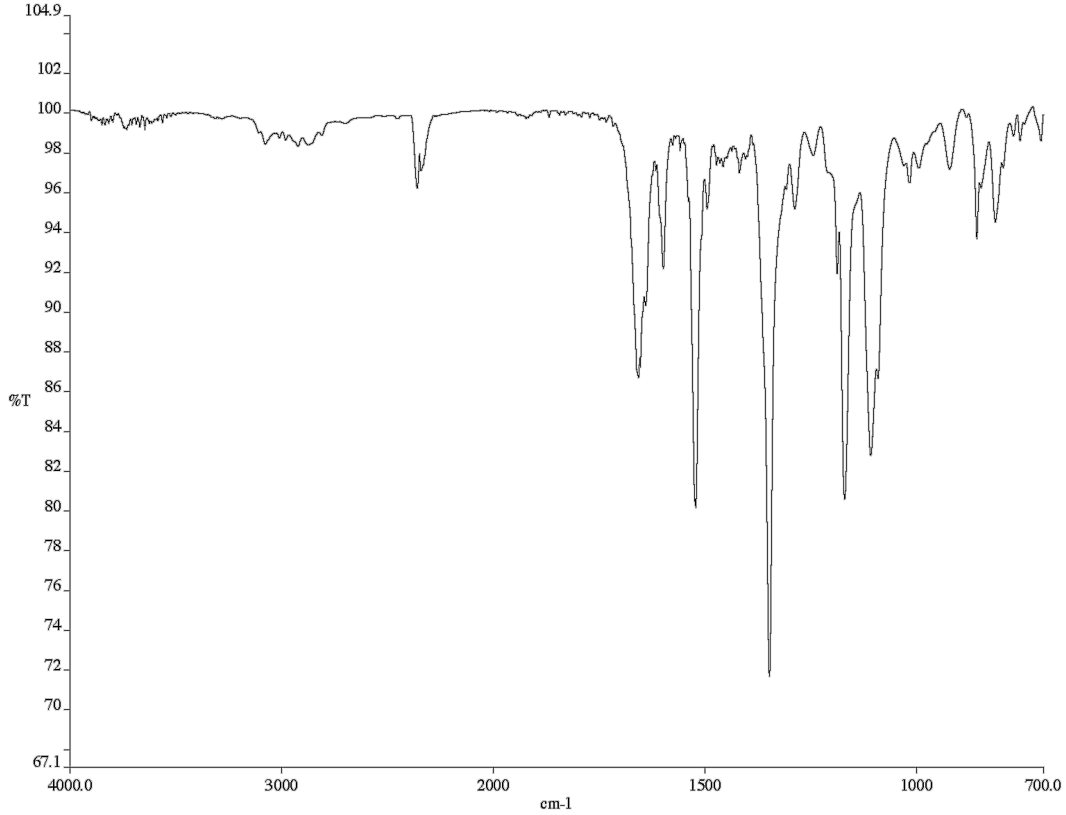


Figure A14.40. Infrared spectrum (thin film/NaCl) of compound **507**.

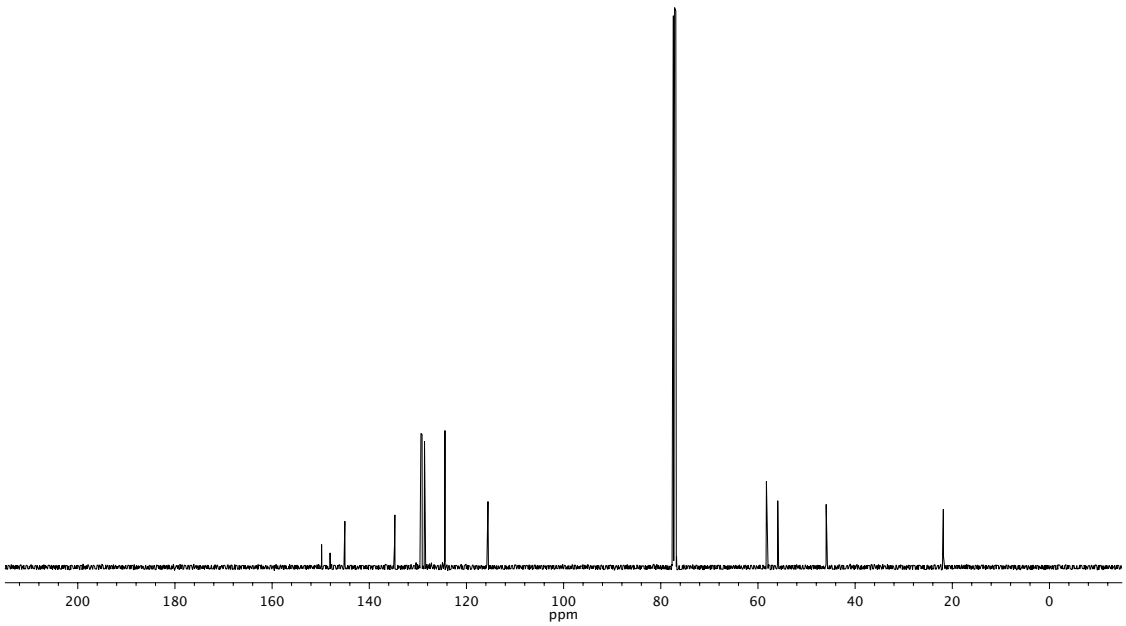


Figure A14.41. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **507**.

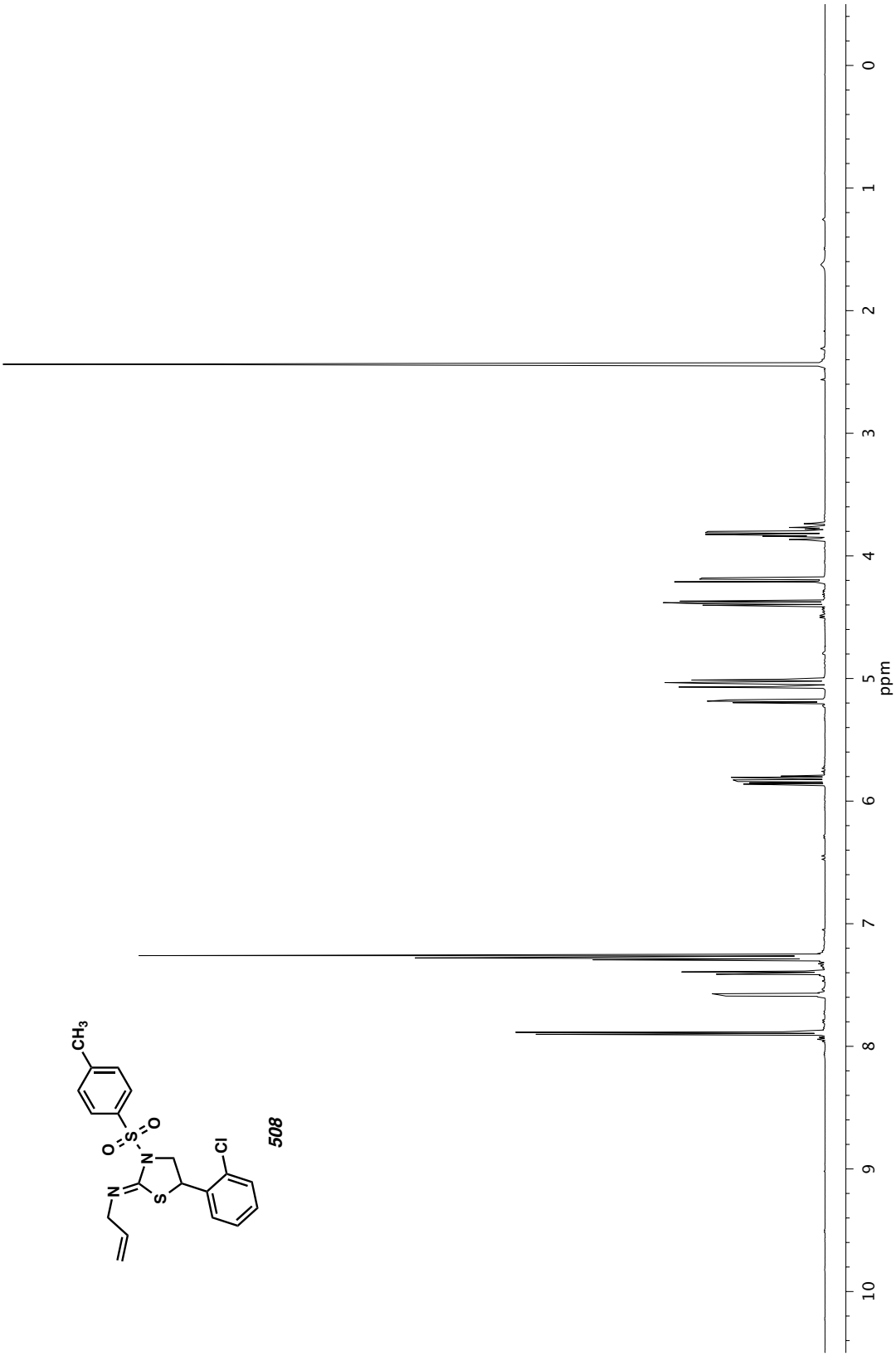


Figure A14.42. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **508**.

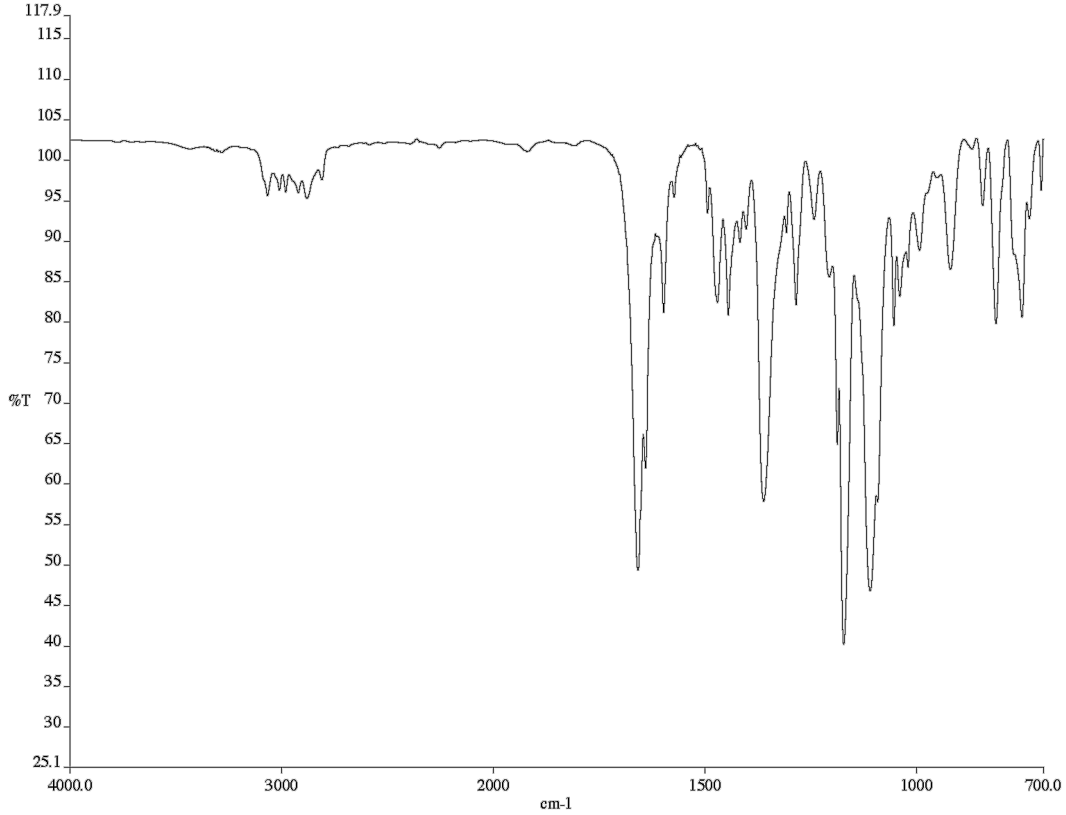


Figure A14.43. Infrared spectrum (thin film/NaCl) of compound **508**.

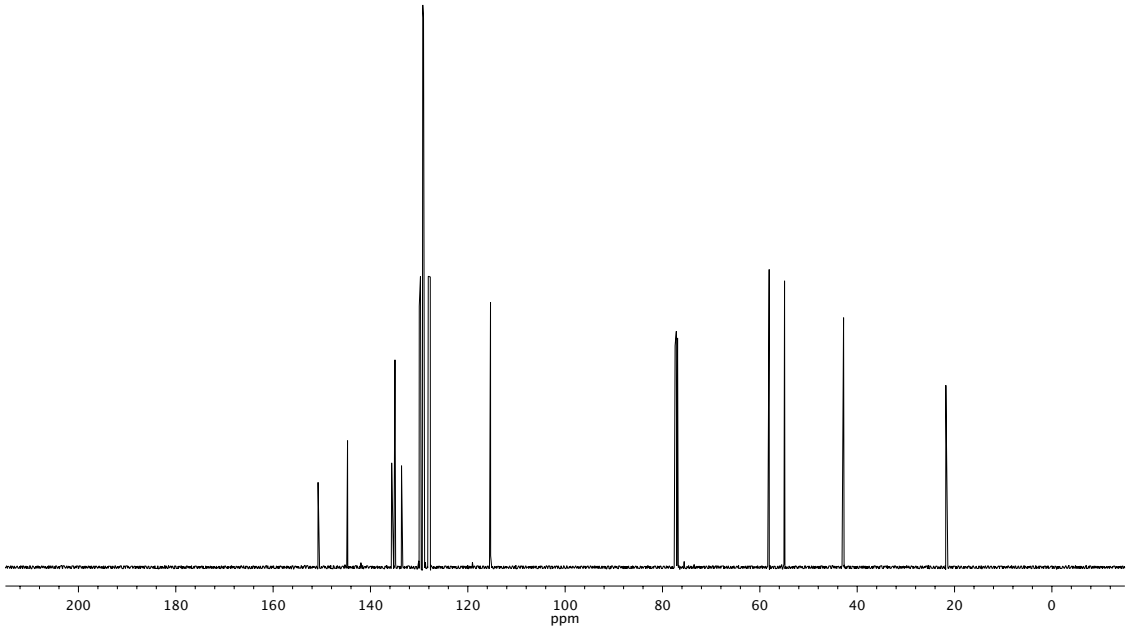


Figure A14.44. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **508**.

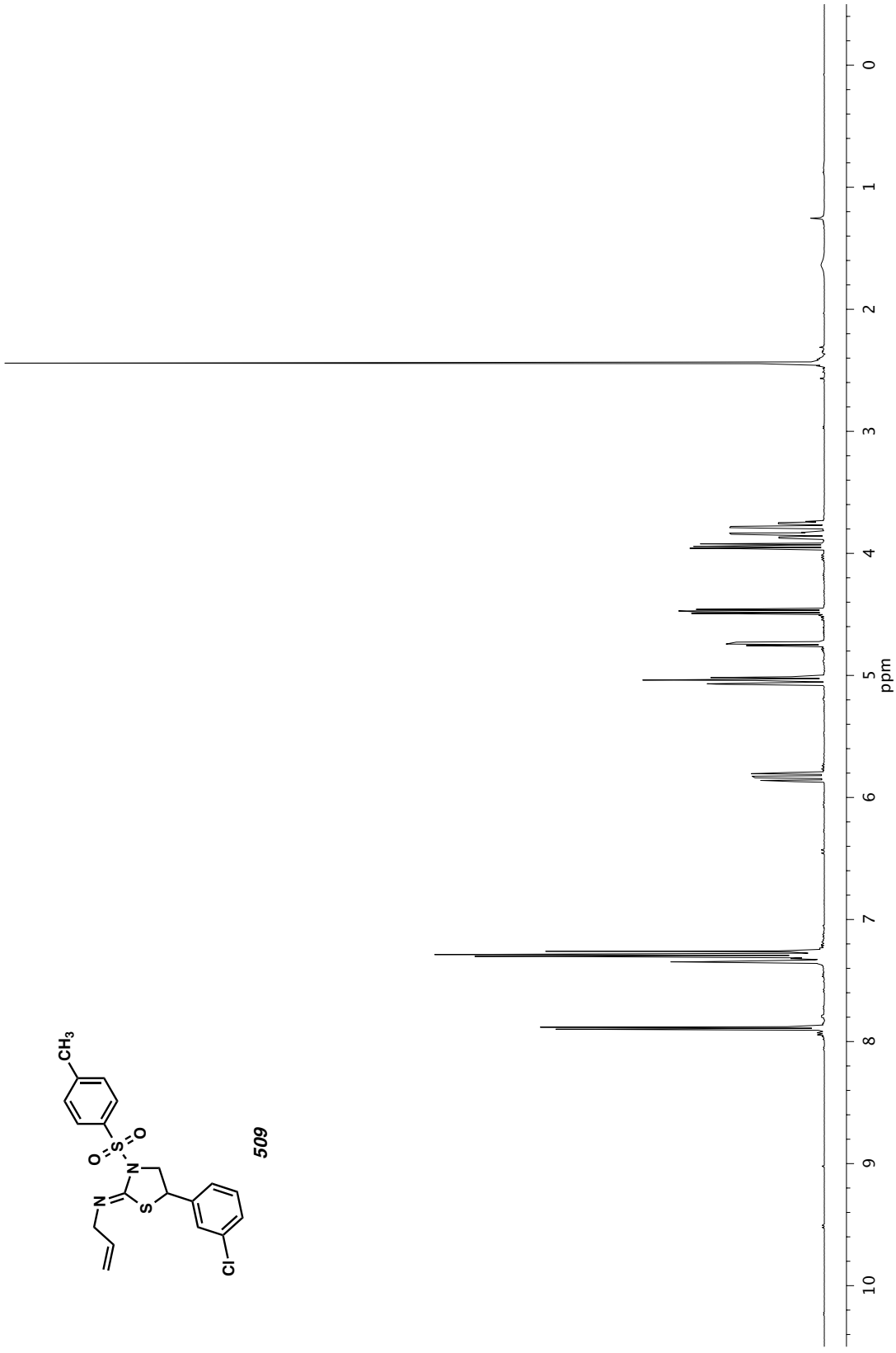


Figure A14.45. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **509**.

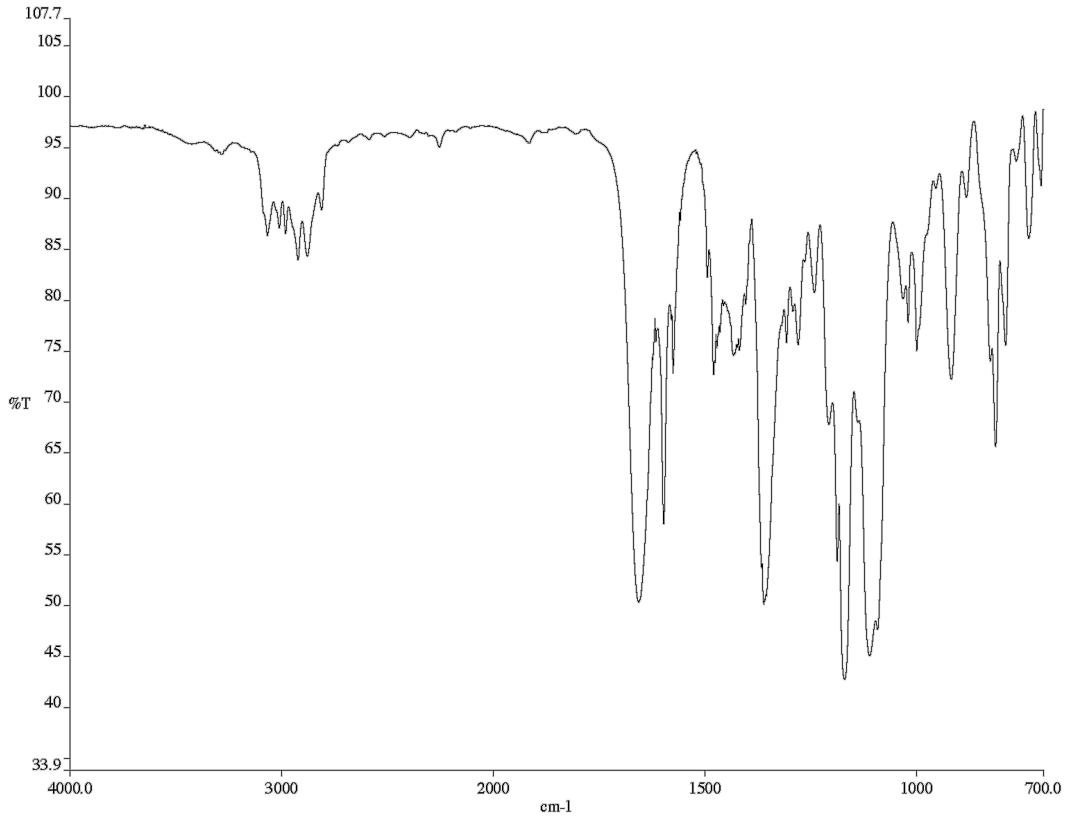


Figure A14.46. Infrared spectrum (thin film/NaCl) of compound **509**.

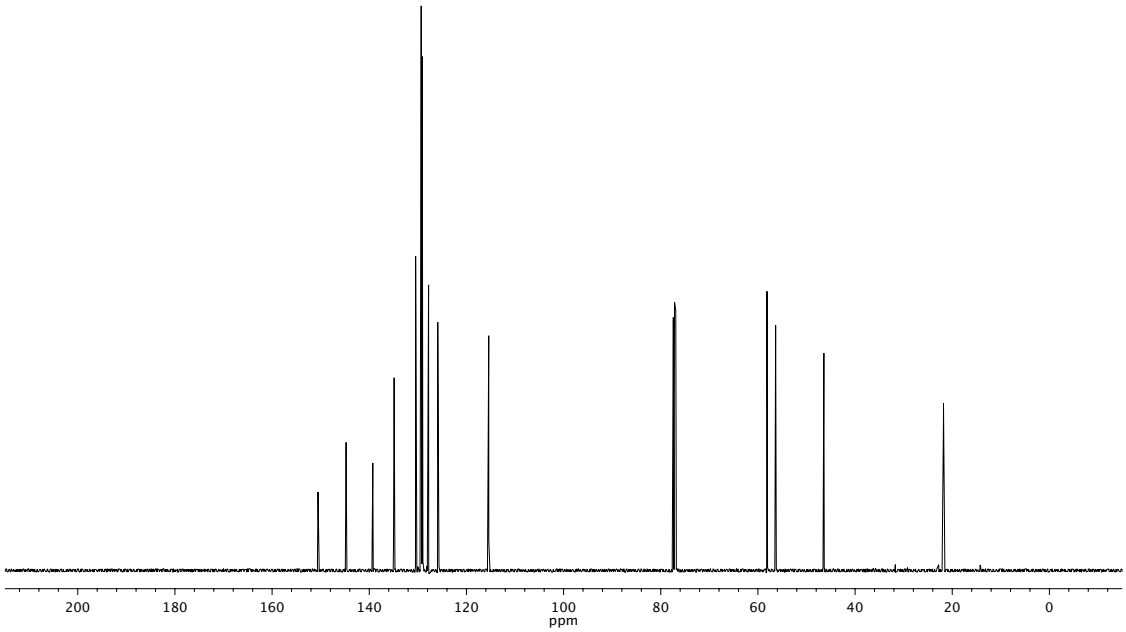


Figure A14.47. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **509**.

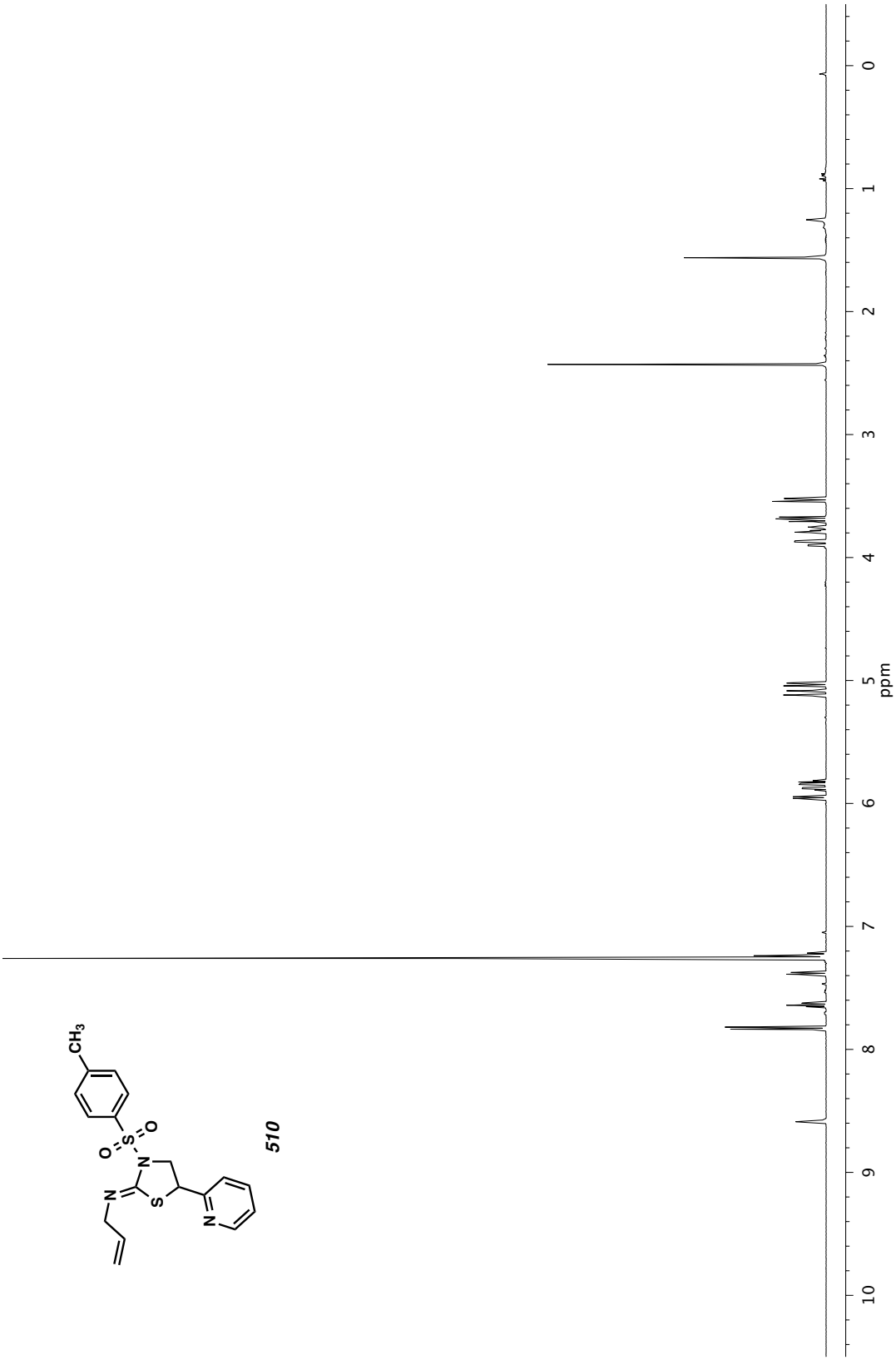


Figure A14.48. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **510**.

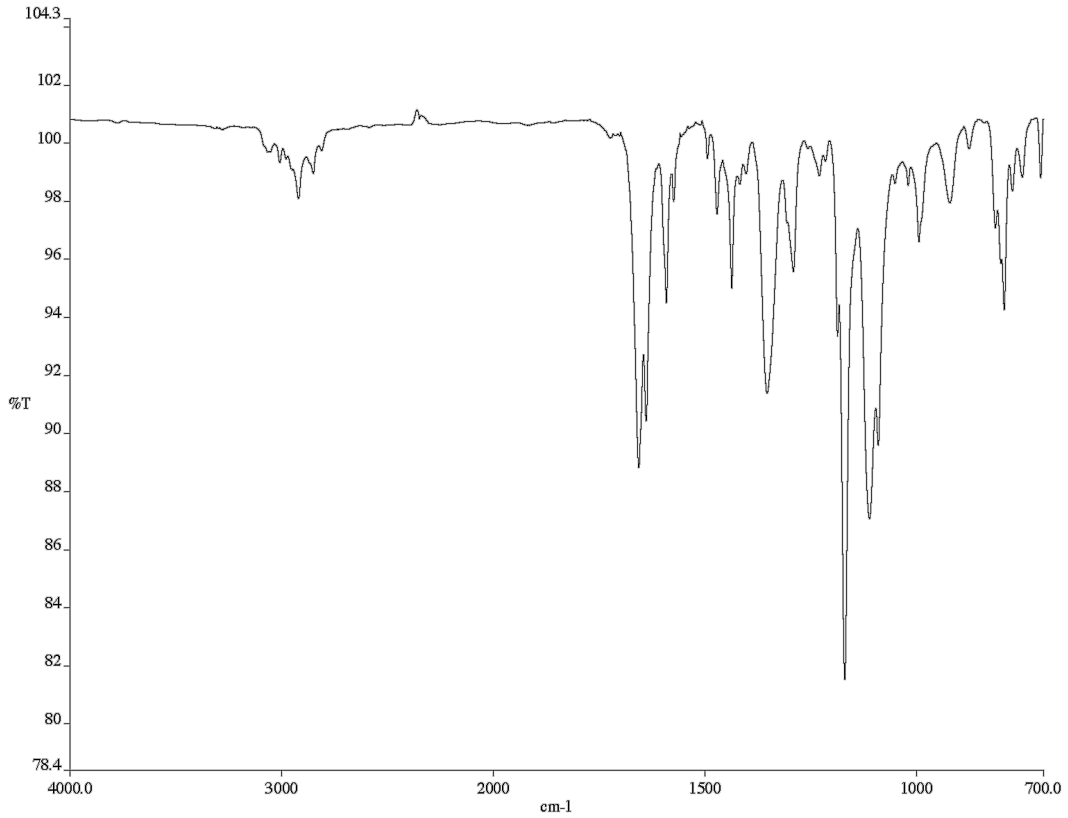


Figure A14.49. Infrared spectrum (thin film/NaCl) of compound **510**.

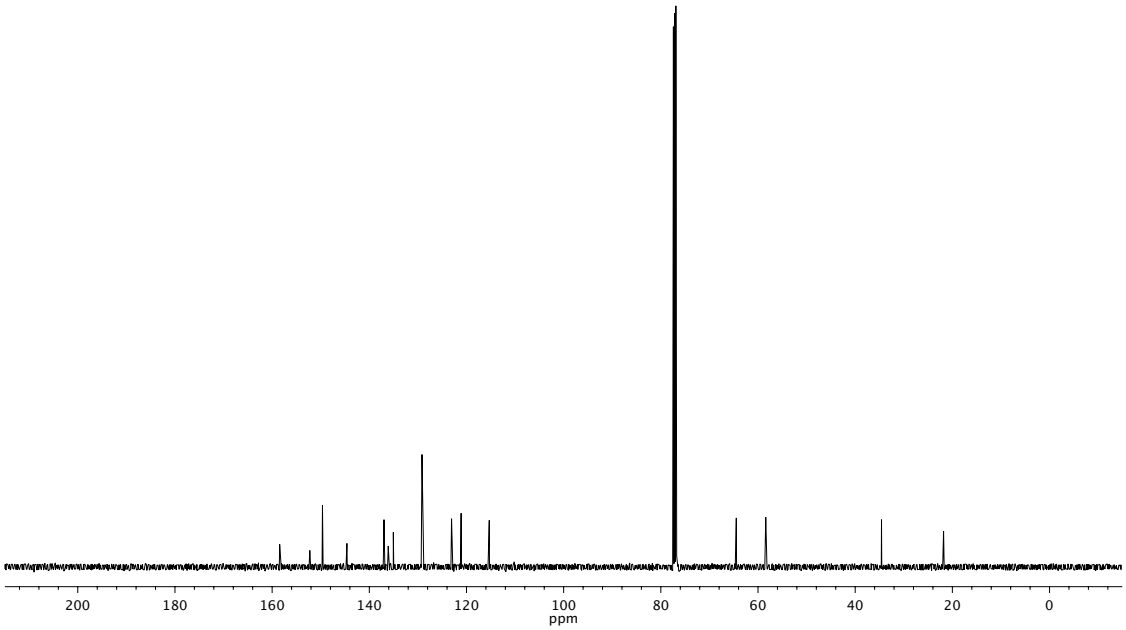


Figure A14.50. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **510**.

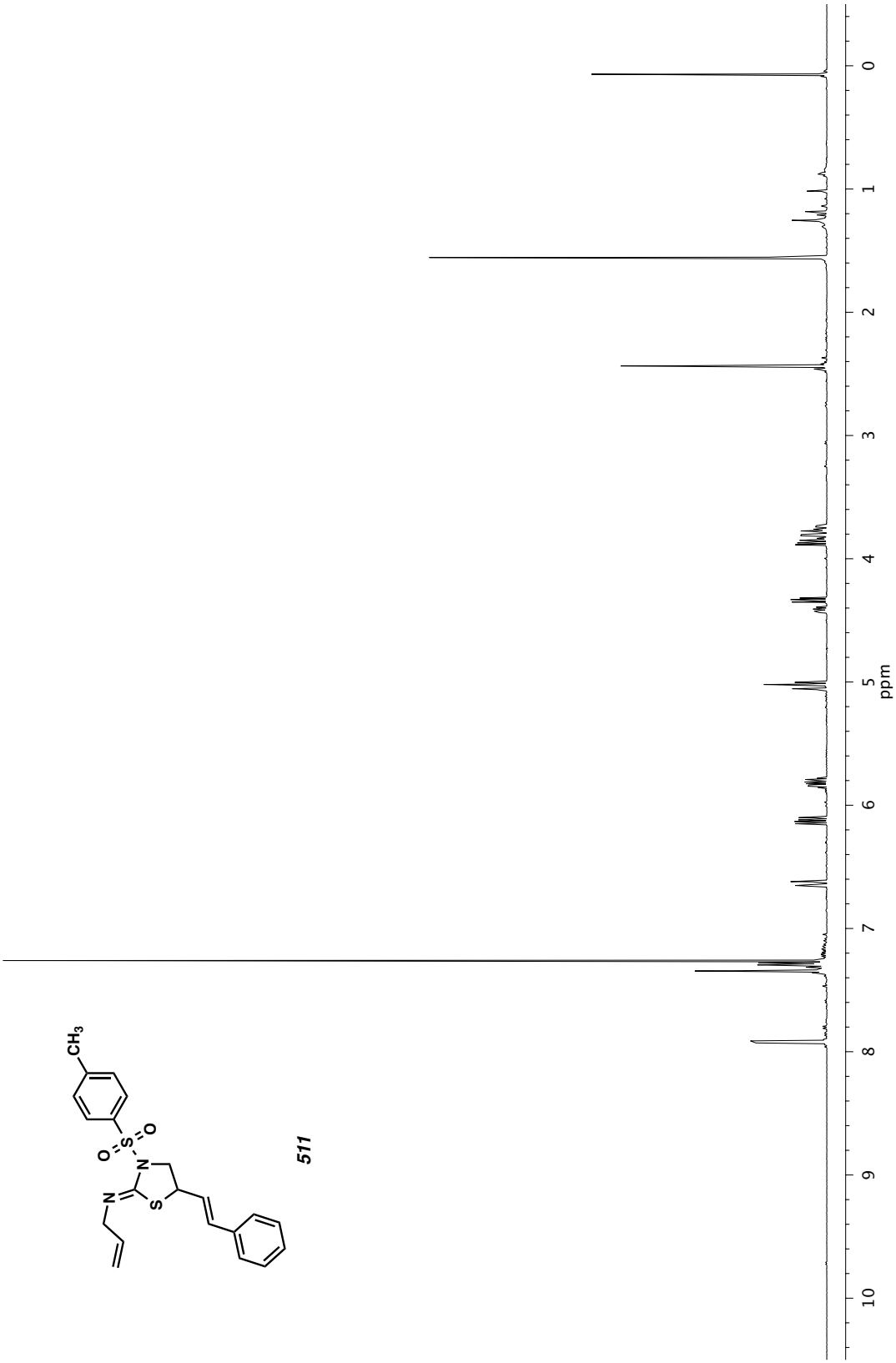


Figure A14.51. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **511**.

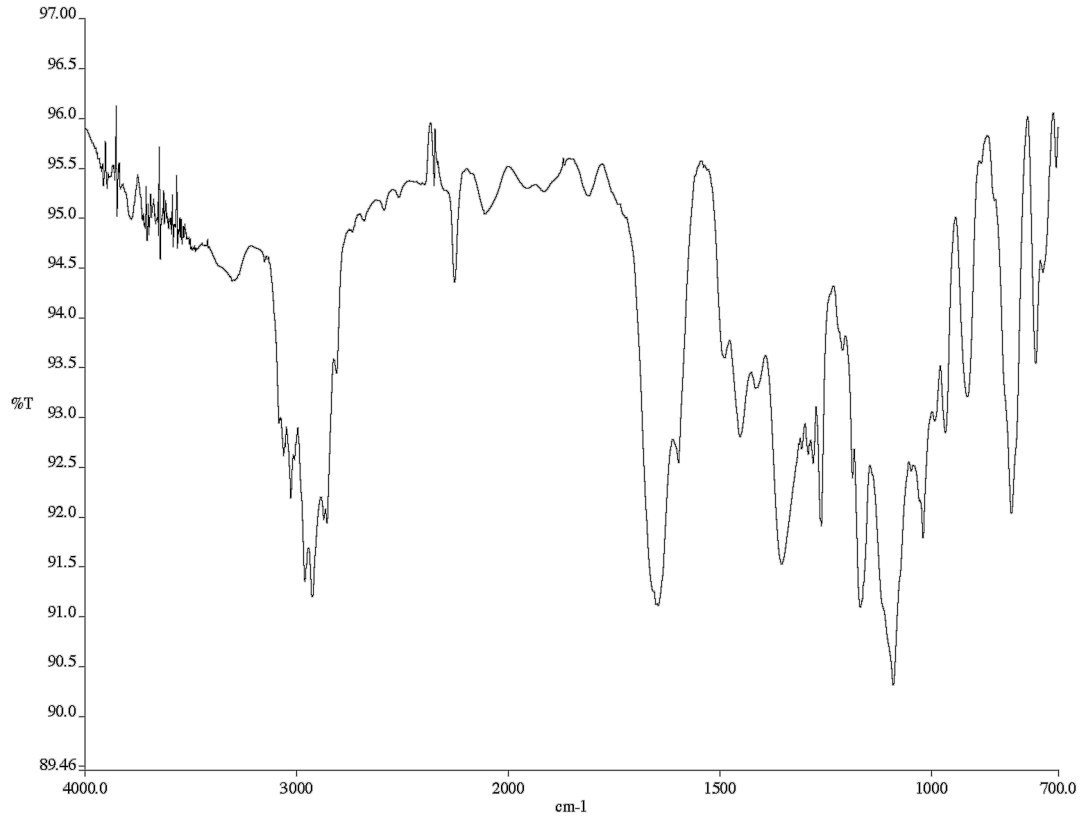


Figure A14.52. Infrared spectrum (thin film/NaCl) of compound **511**.

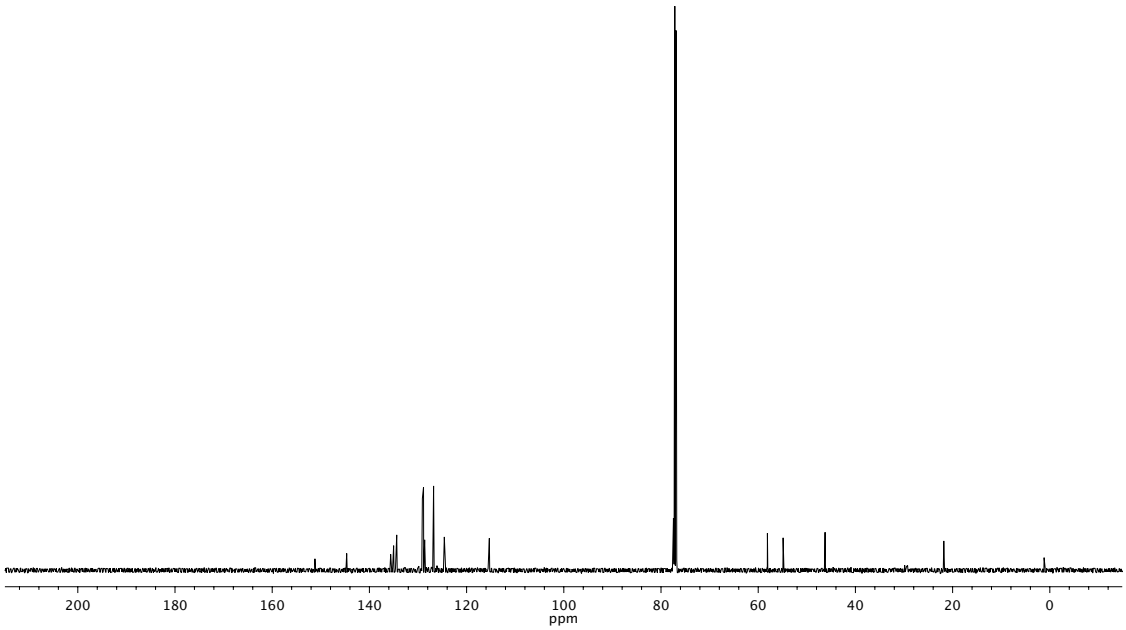


Figure A14.53. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **511**.

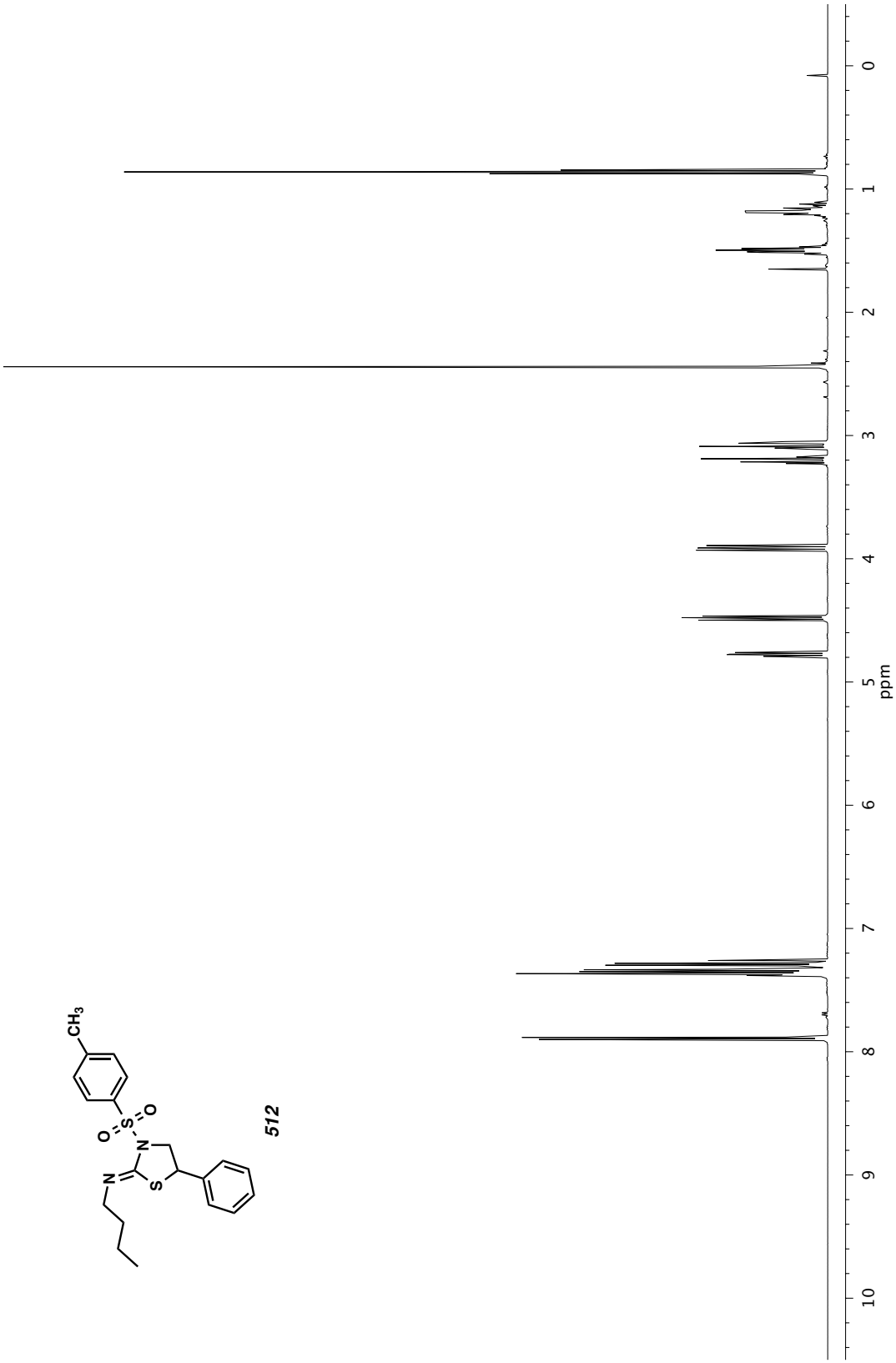


Figure A14.54. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **512**.

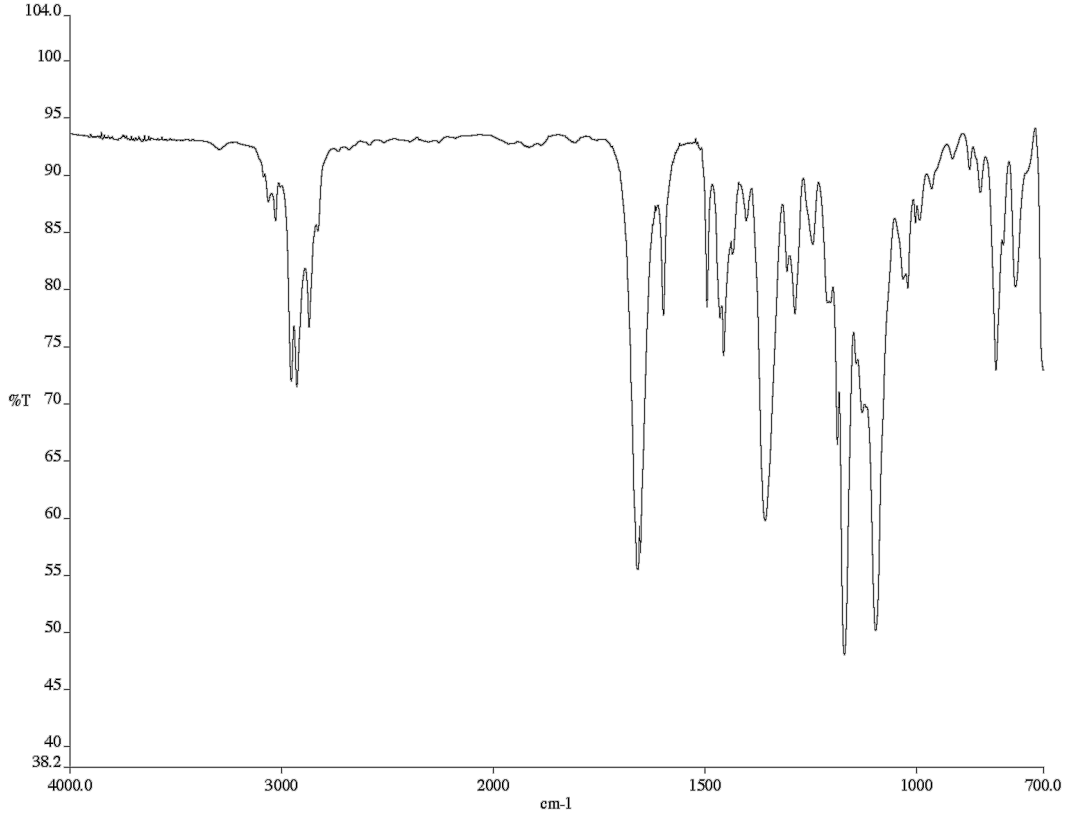


Figure A14.55. Infrared spectrum (thin film/NaCl) of compound **512**.

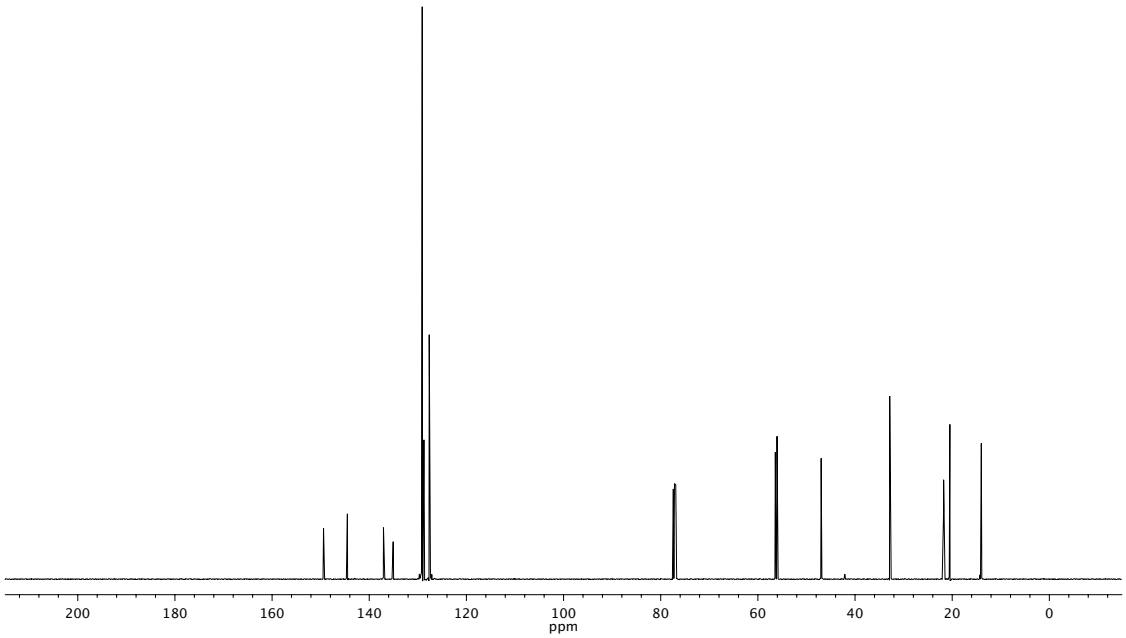


Figure A14.56. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **512**.

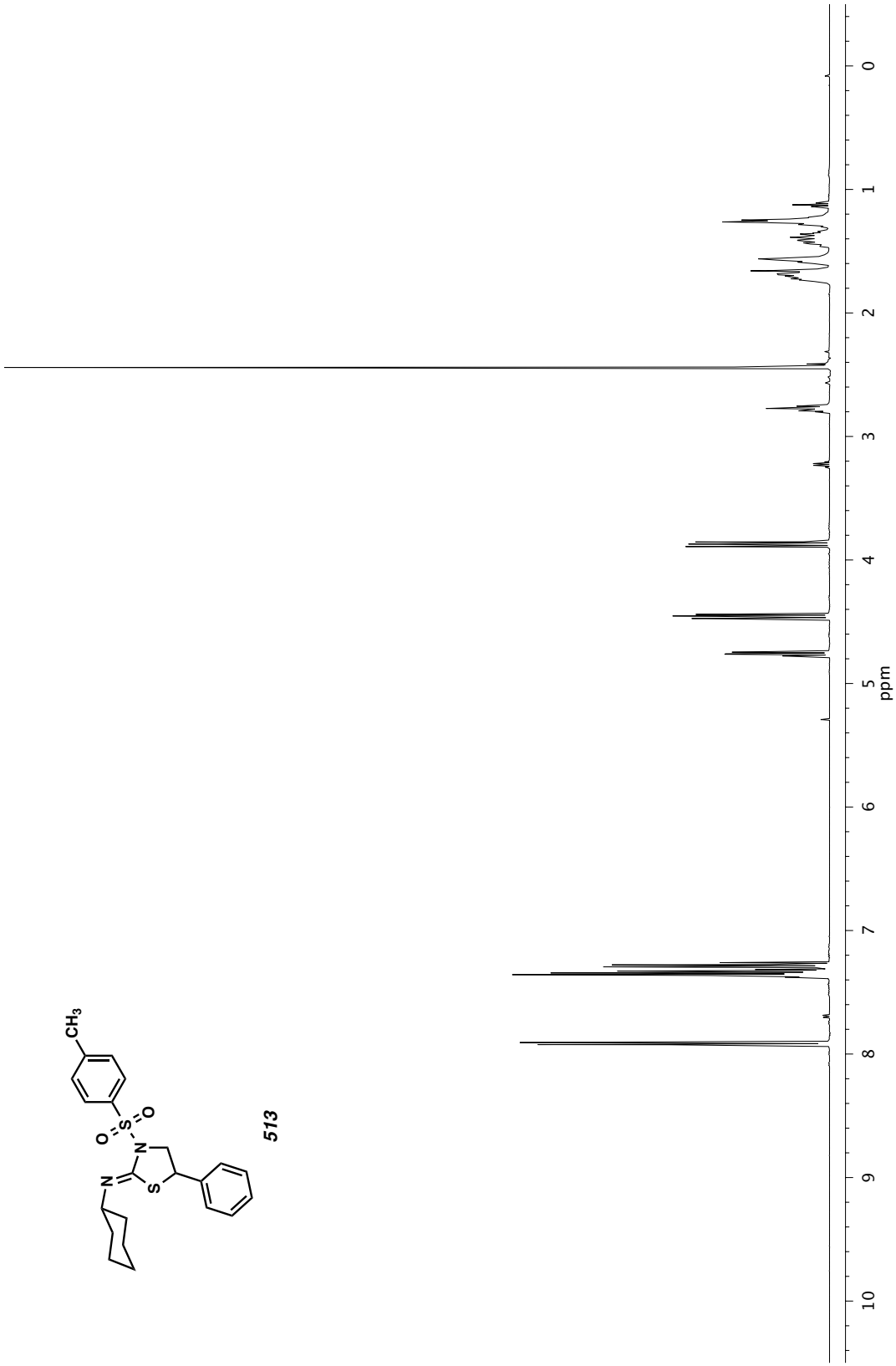


Figure A14.57. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **513**.

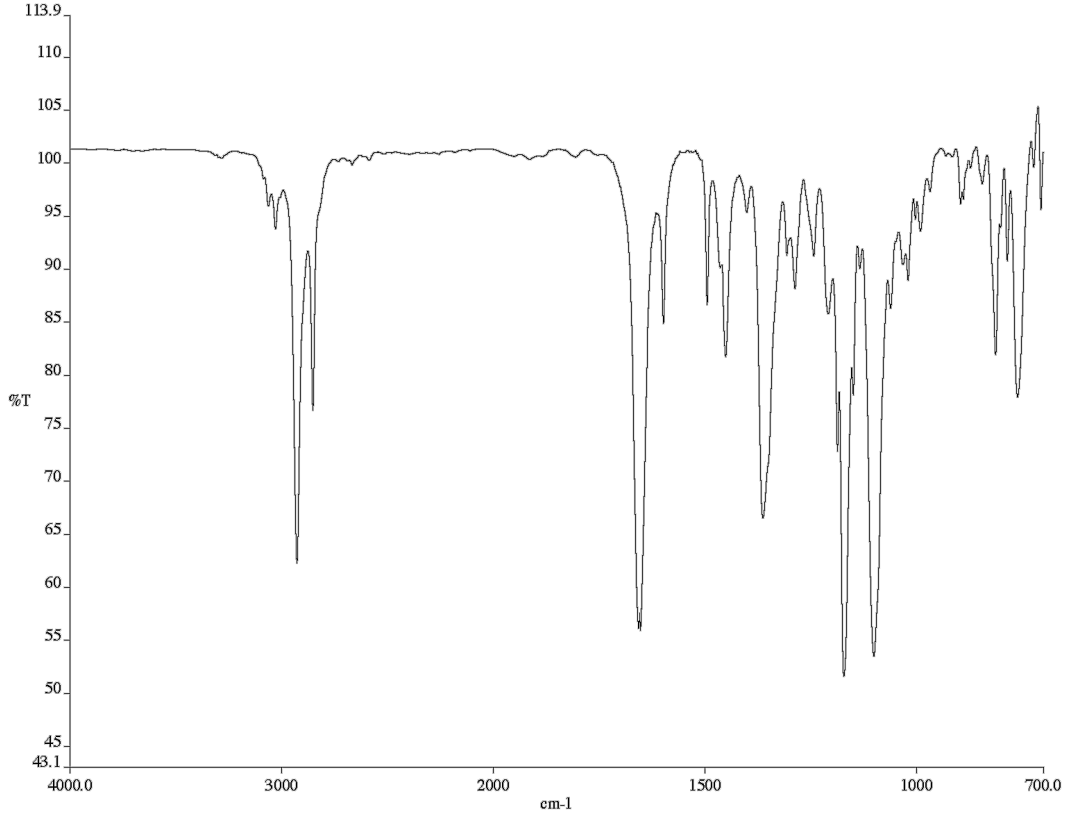


Figure A14.58. Infrared spectrum (thin film/NaCl) of compound **513**.

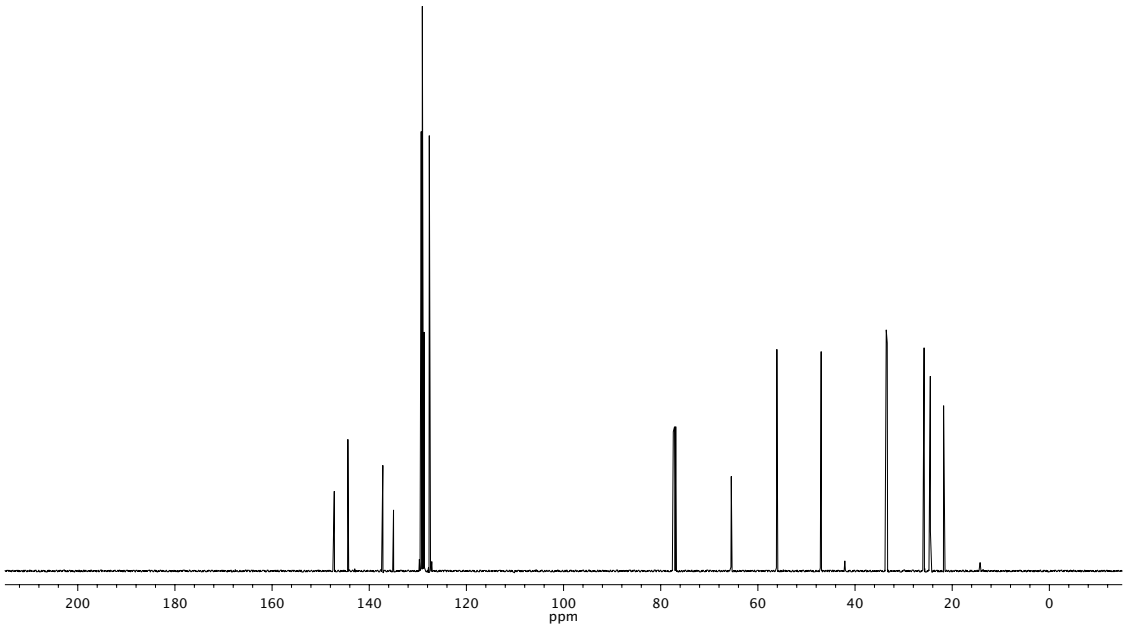


Figure A14.59. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **513**.

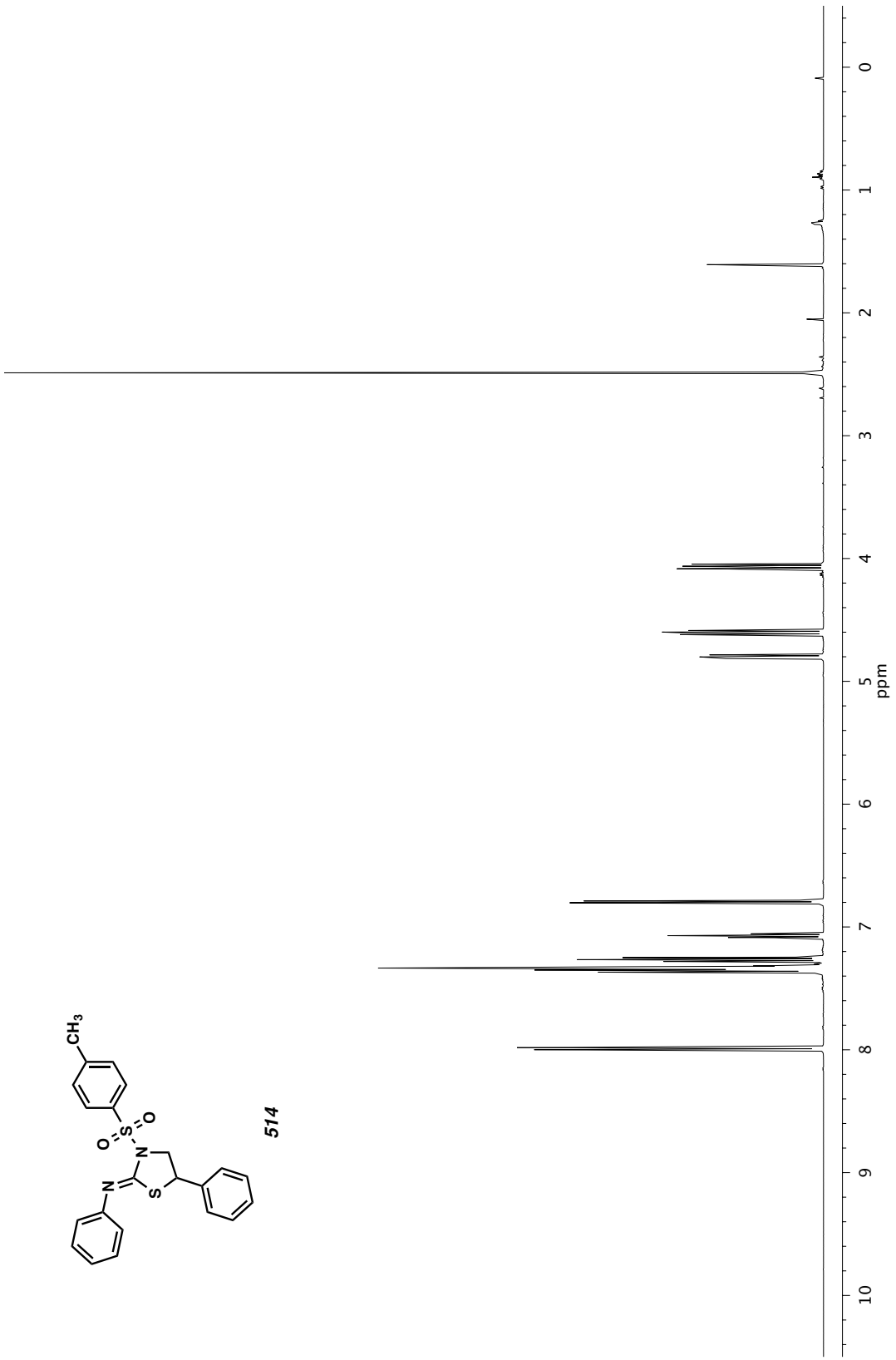


Figure A14.60. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **514**.

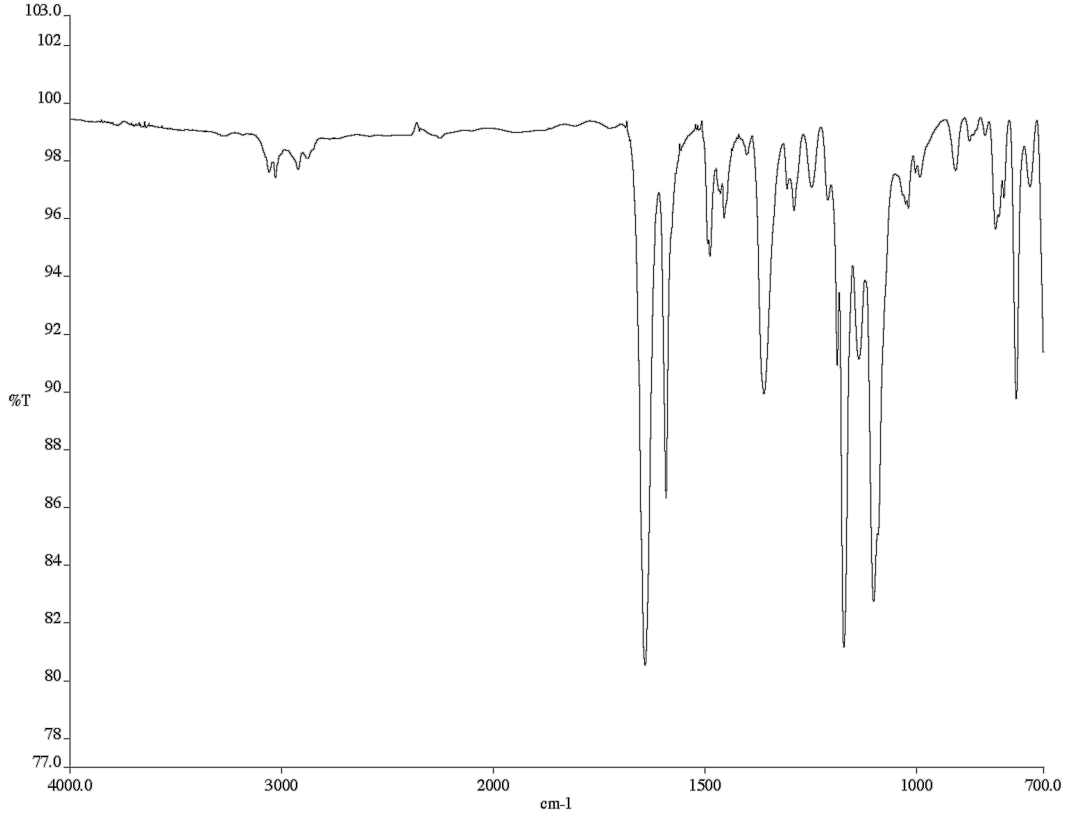


Figure A14.61. Infrared spectrum (thin film/NaCl) of compound **514**.

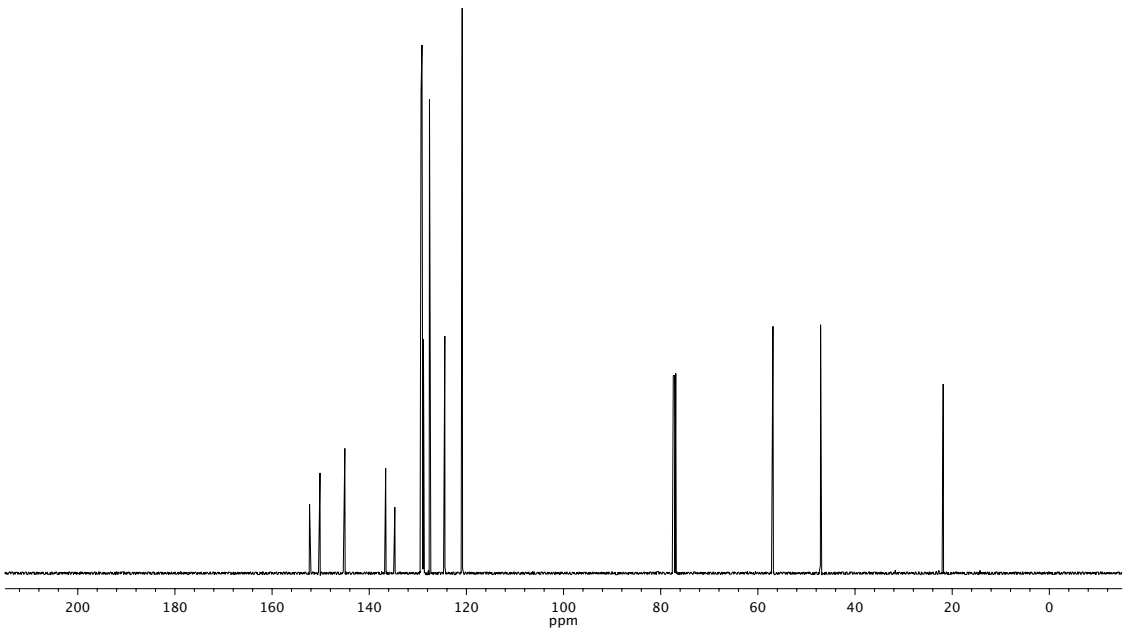


Figure A14.62. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **514**.

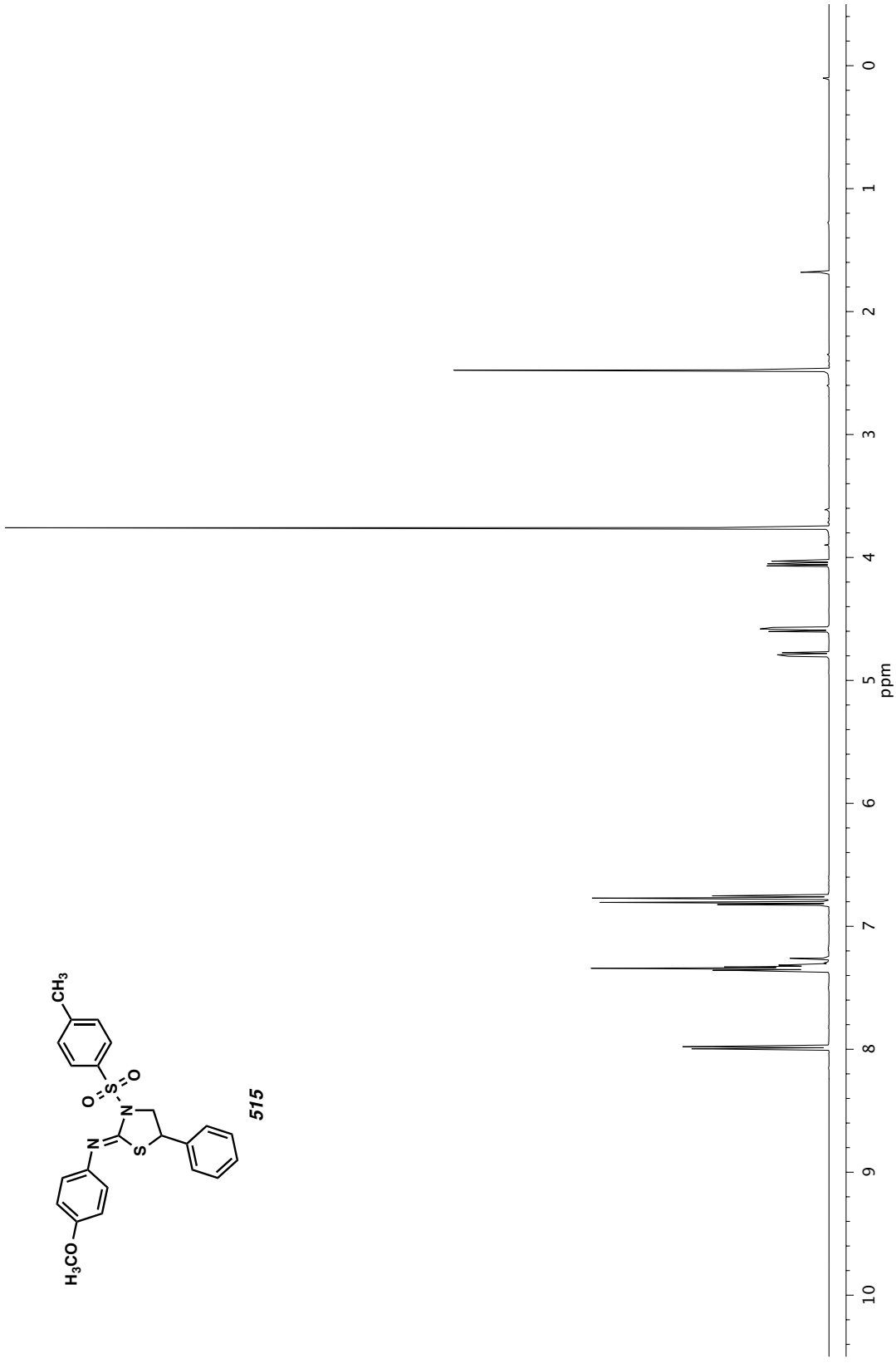


Figure A14.63. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **515**.

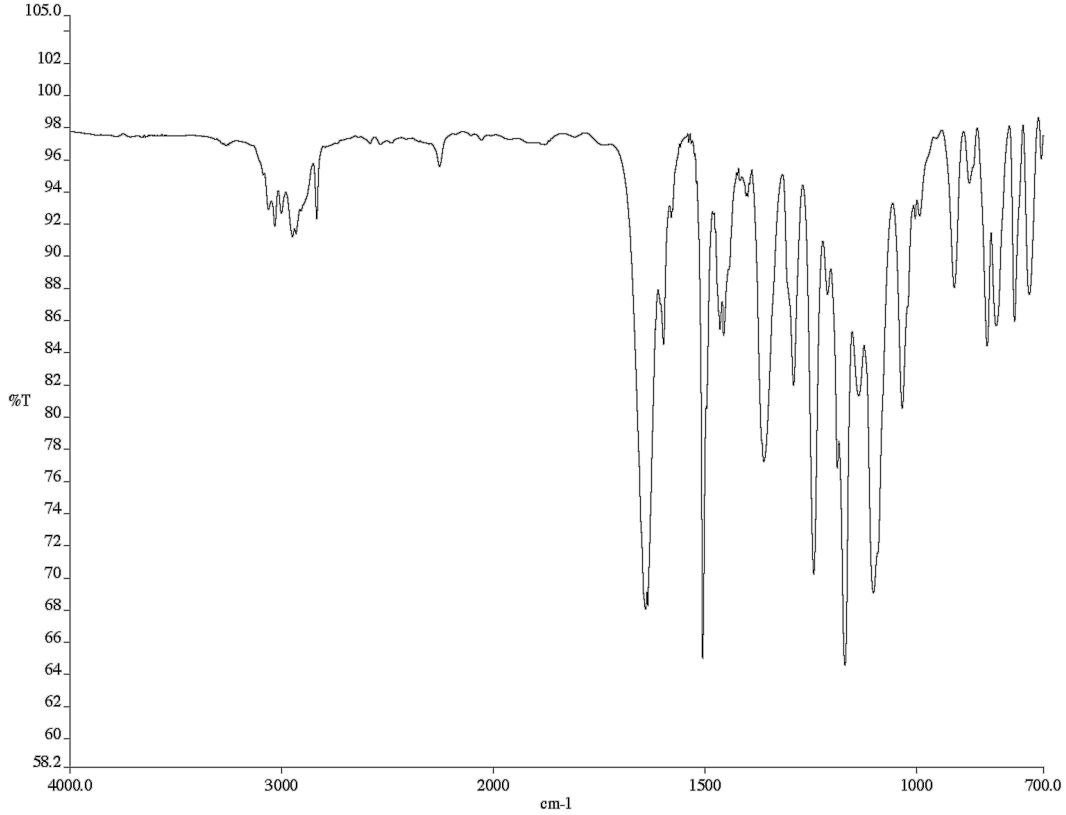


Figure A14.64. Infrared spectrum (thin film/NaCl) of compound **515**.

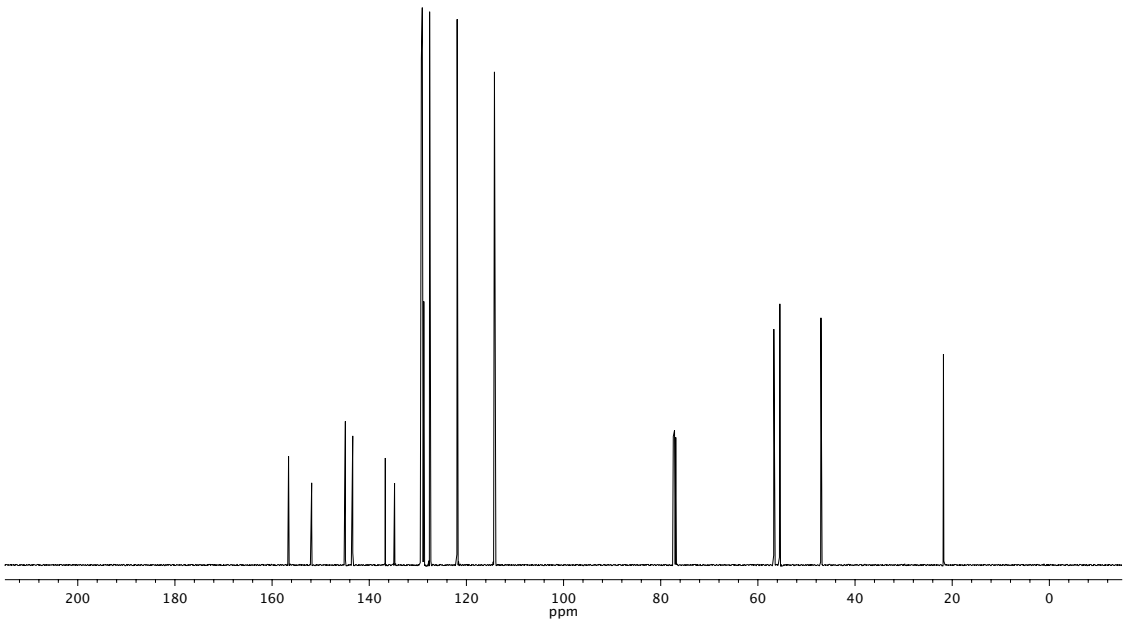


Figure A14.65. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **515**.

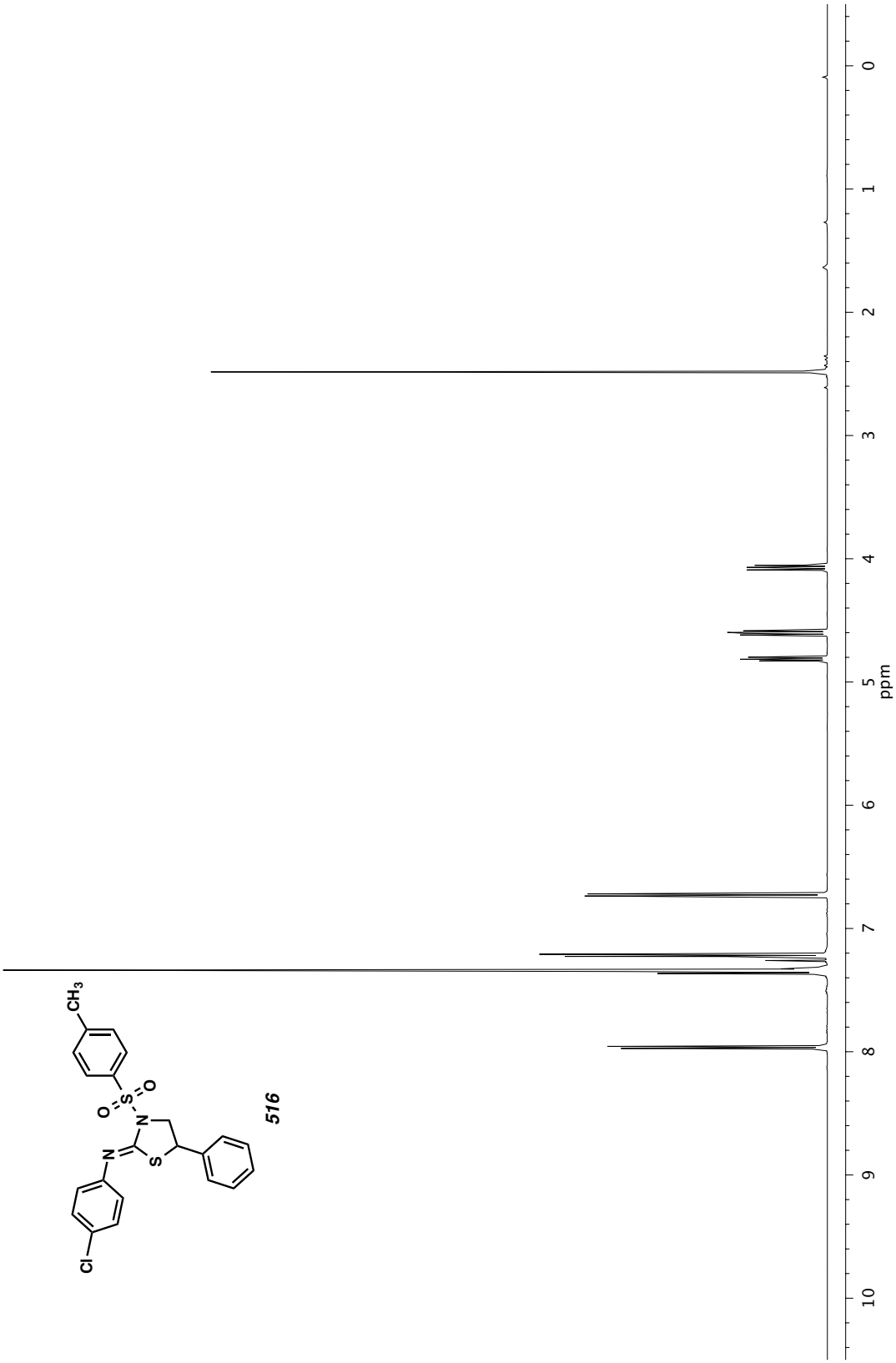


Figure A14.66. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **516**.

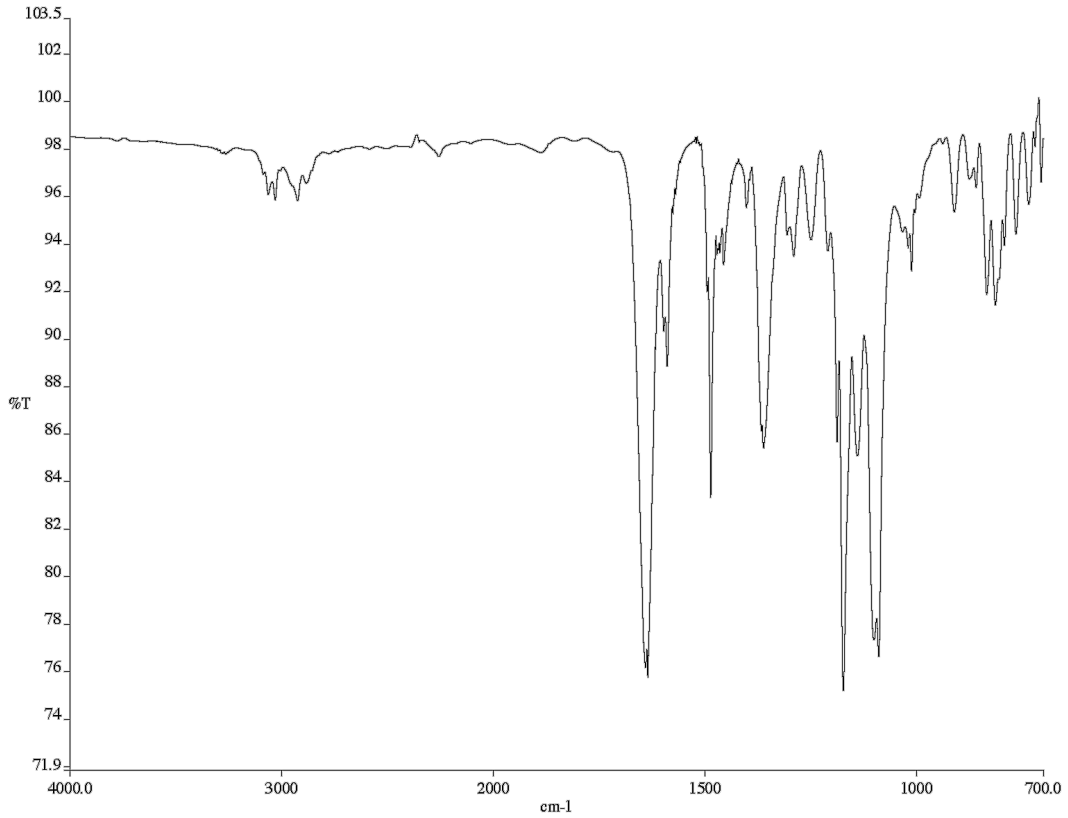


Figure A14.67. Infrared spectrum (thin film/NaCl) of compound **516**.

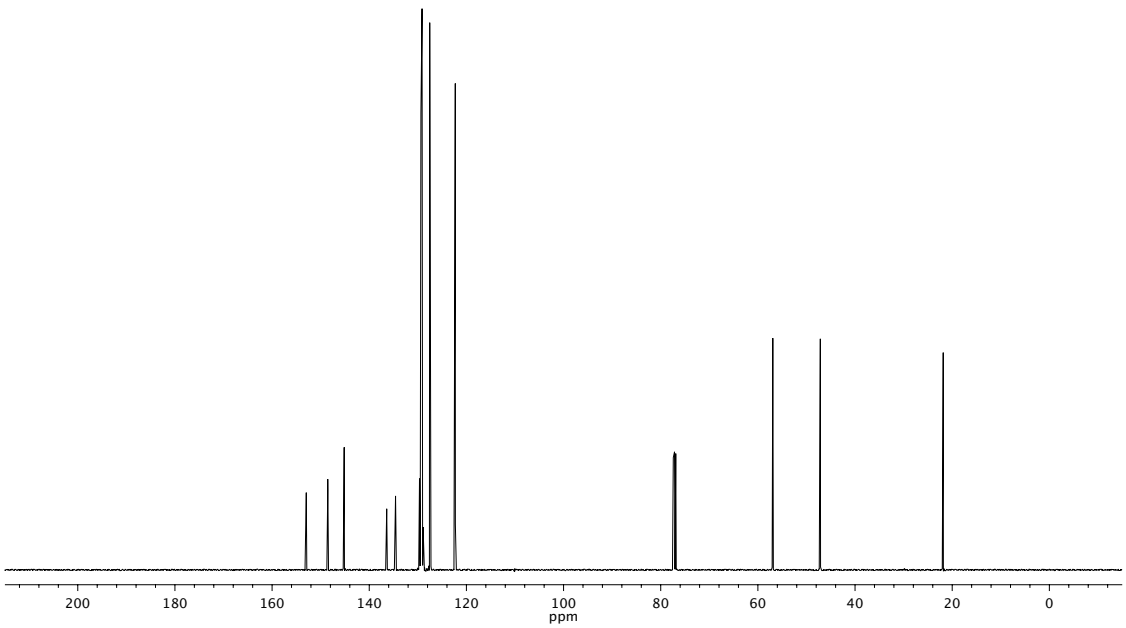


Figure A14.68. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **516**.

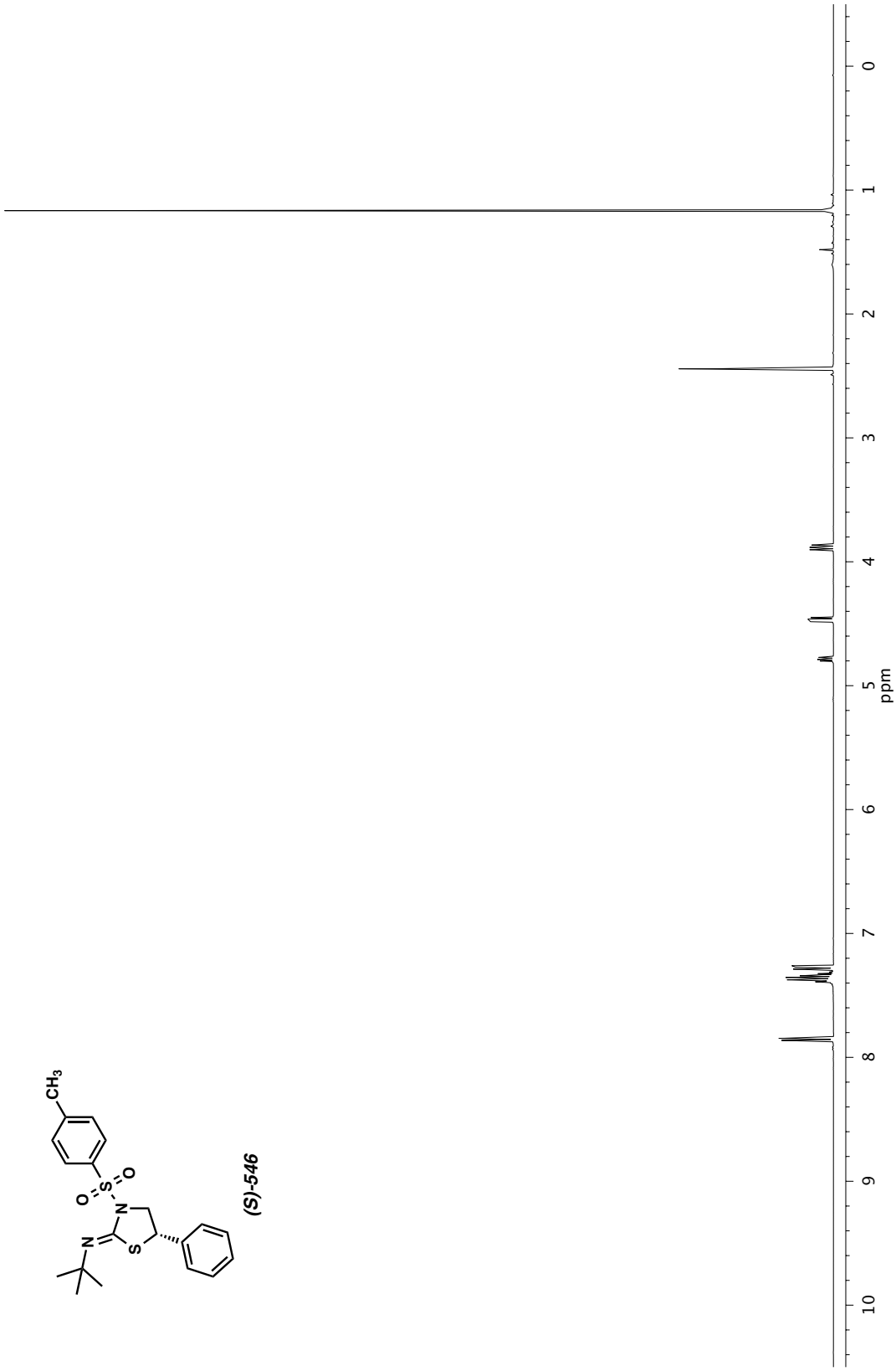


Figure A14.69. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **(*S*)-546**.

(S)-546

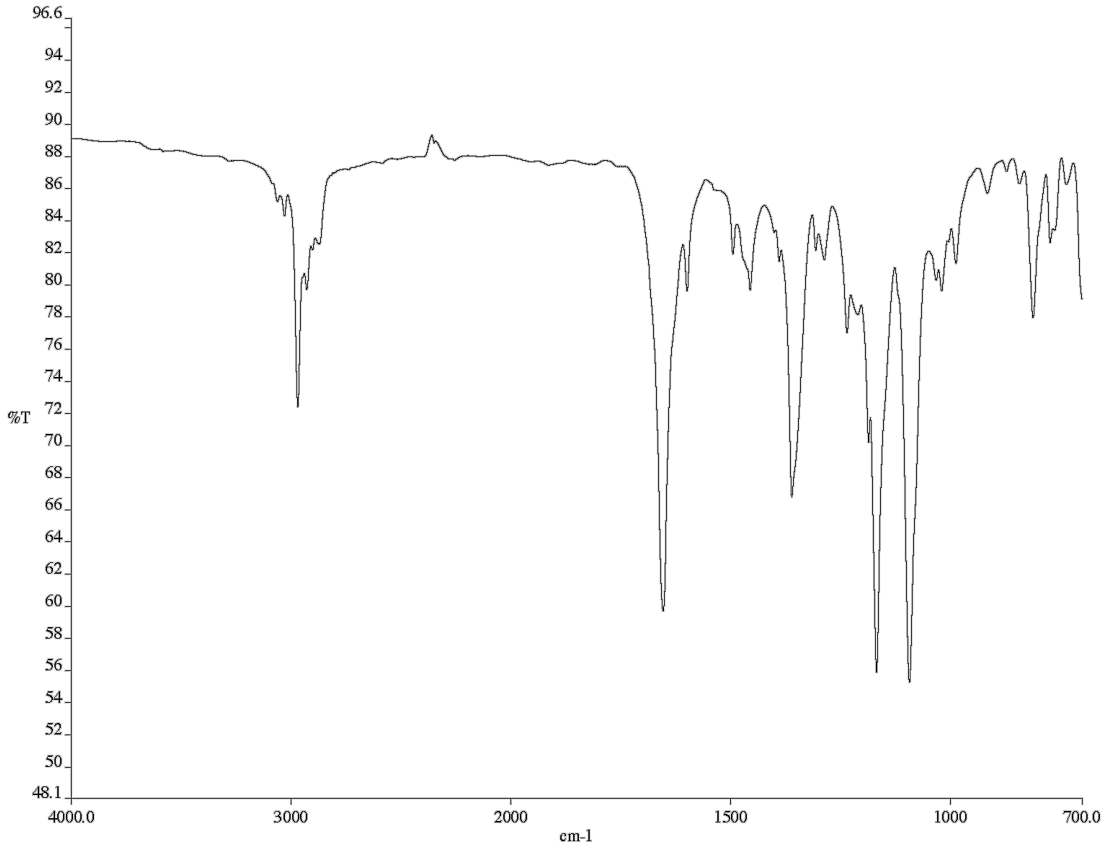


Figure A14.70. Infrared spectrum (Thin Film, NaCl) of compound **(*S*)-546**.

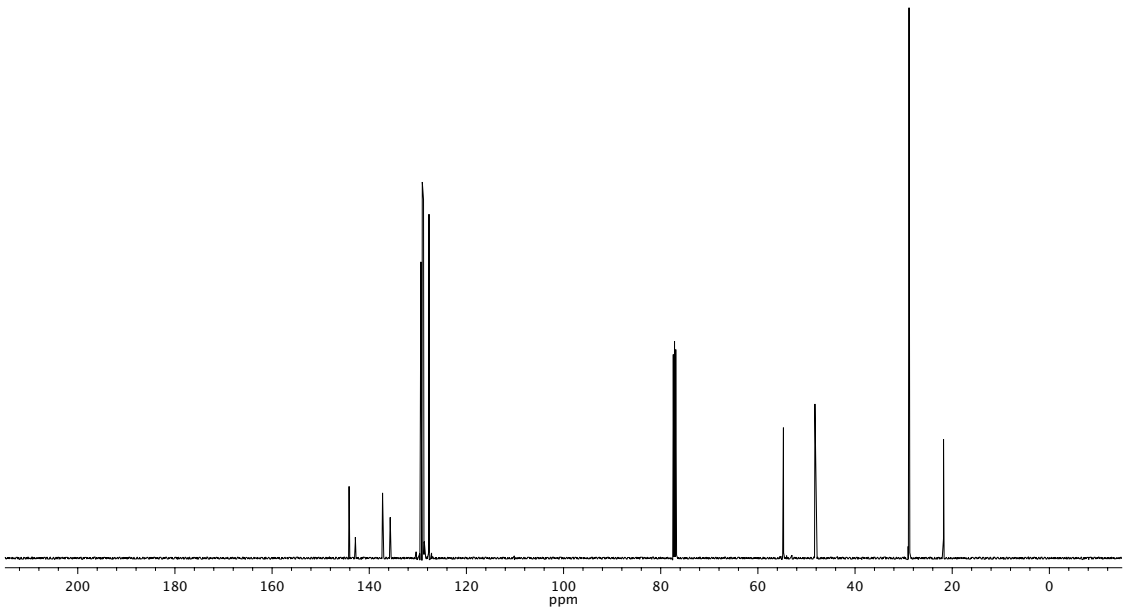


Figure A14.71. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **(*S*)-546**.

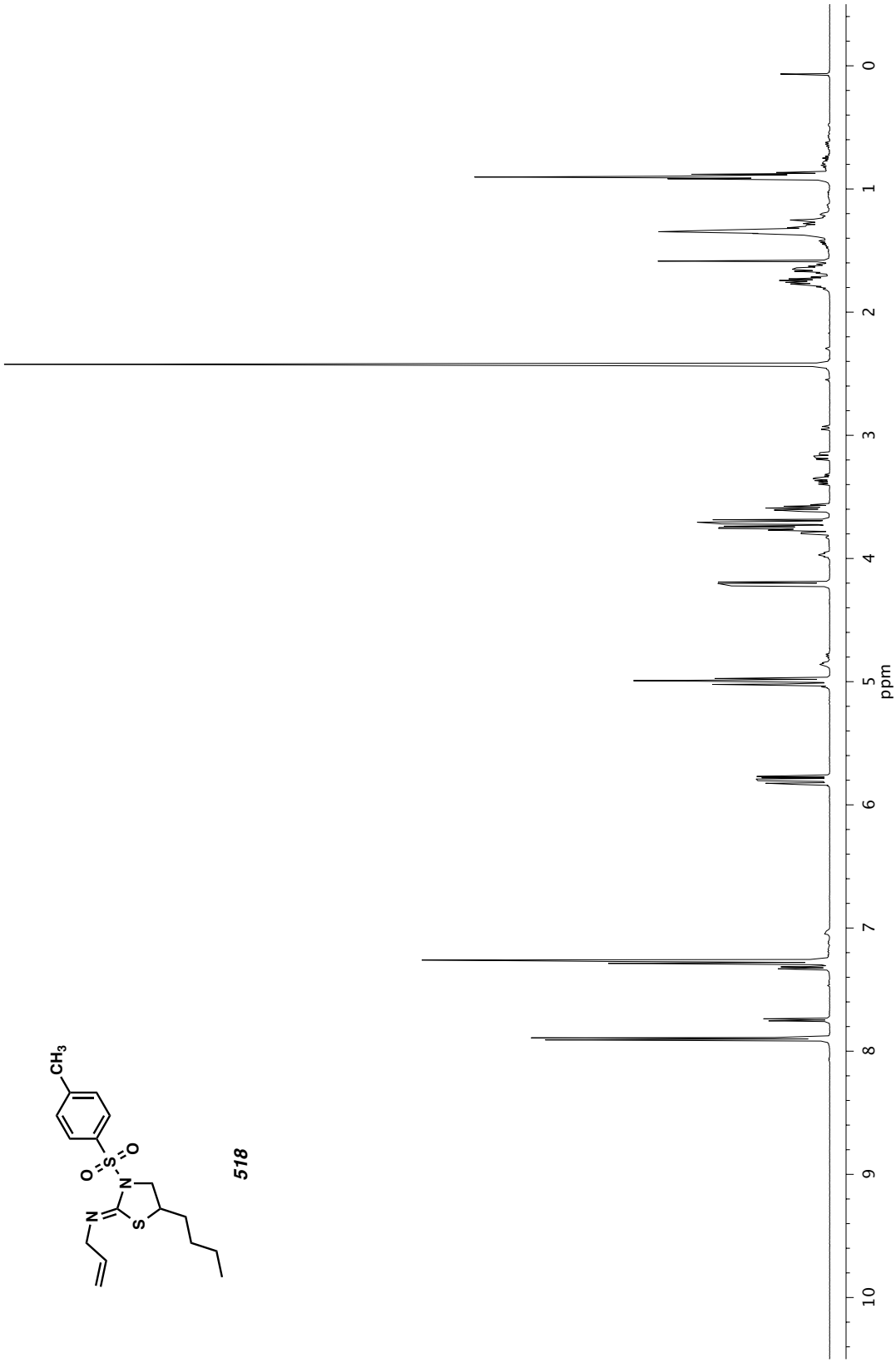


Figure A14.72. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **518**.

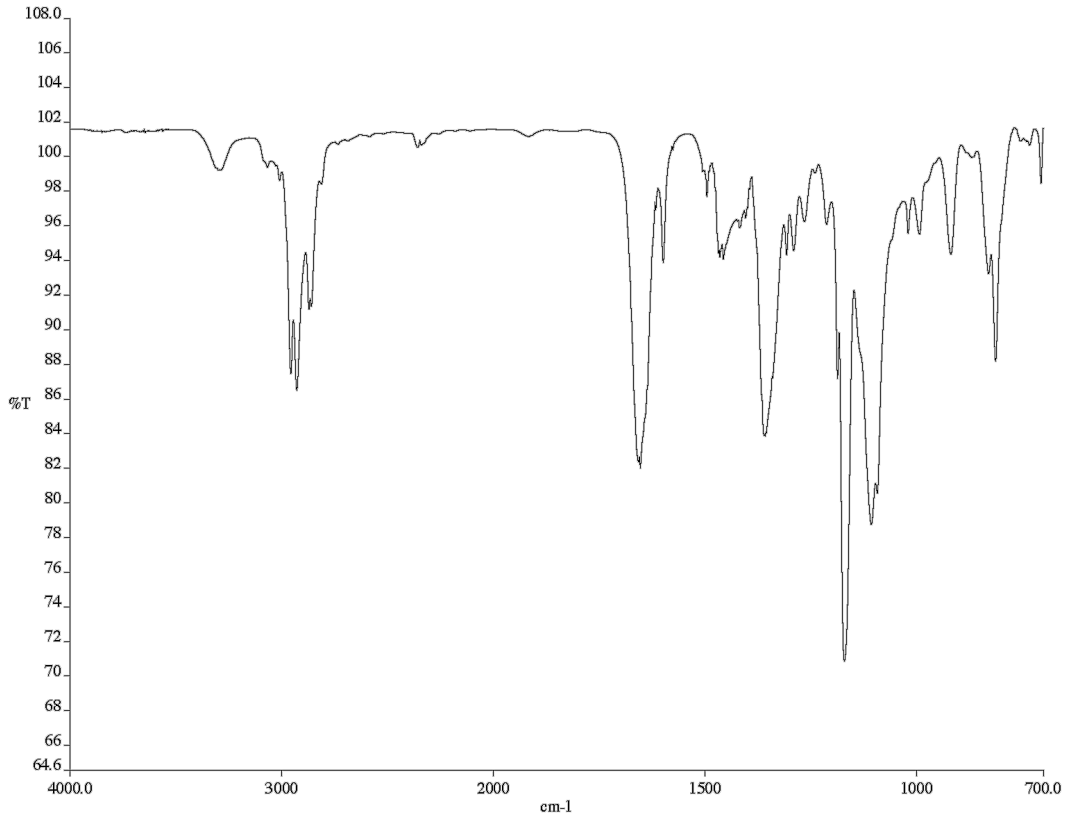


Figure A14.73. Infrared spectrum (thin film/NaCl) of compound **518**.

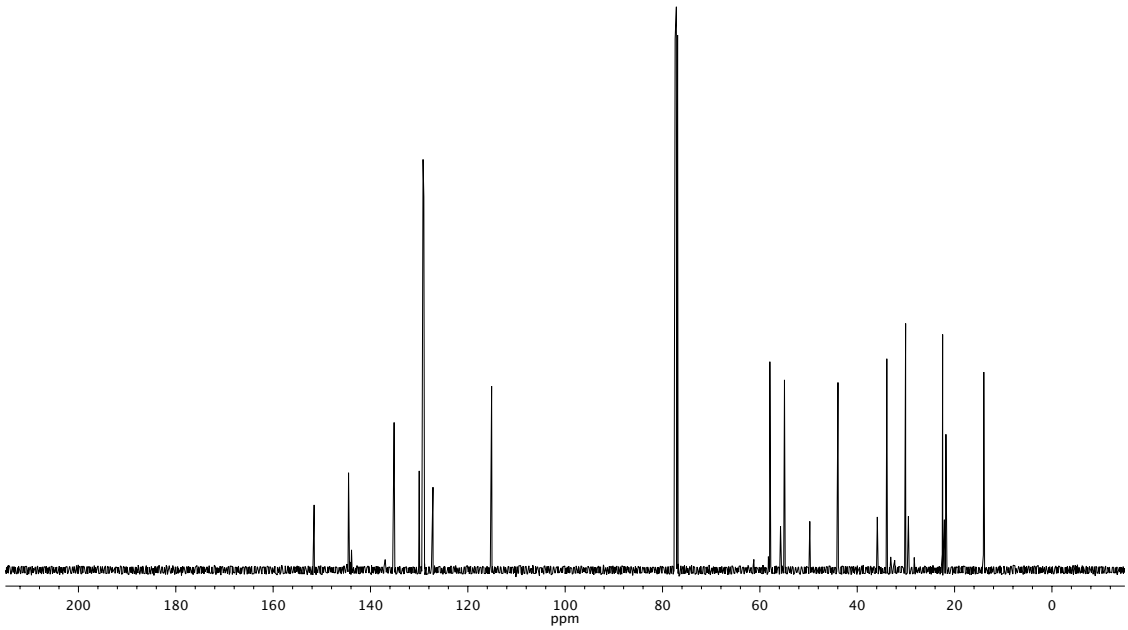


Figure A14.74. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **518**.

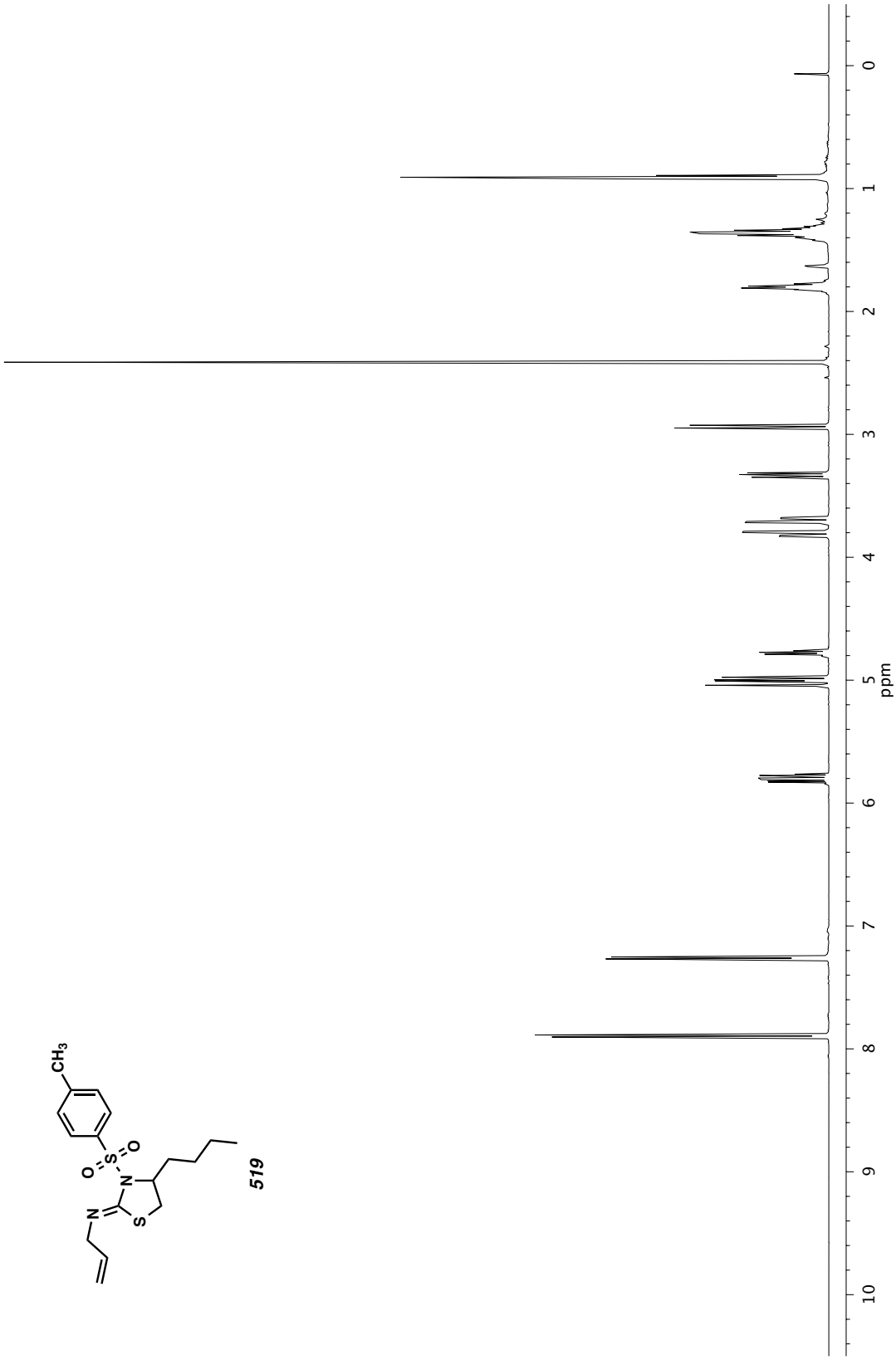


Figure A14.75. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **519**.

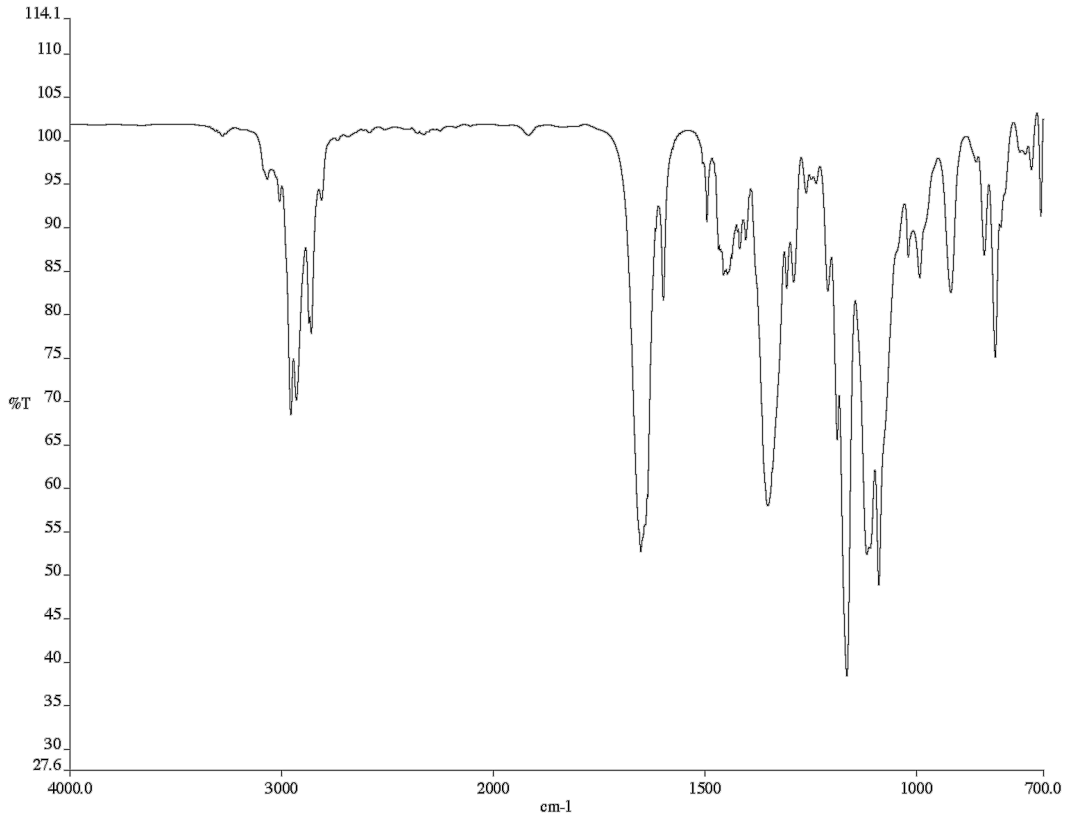


Figure A14.76. Infrared spectrum (thin film/NaCl) of compound **519**.

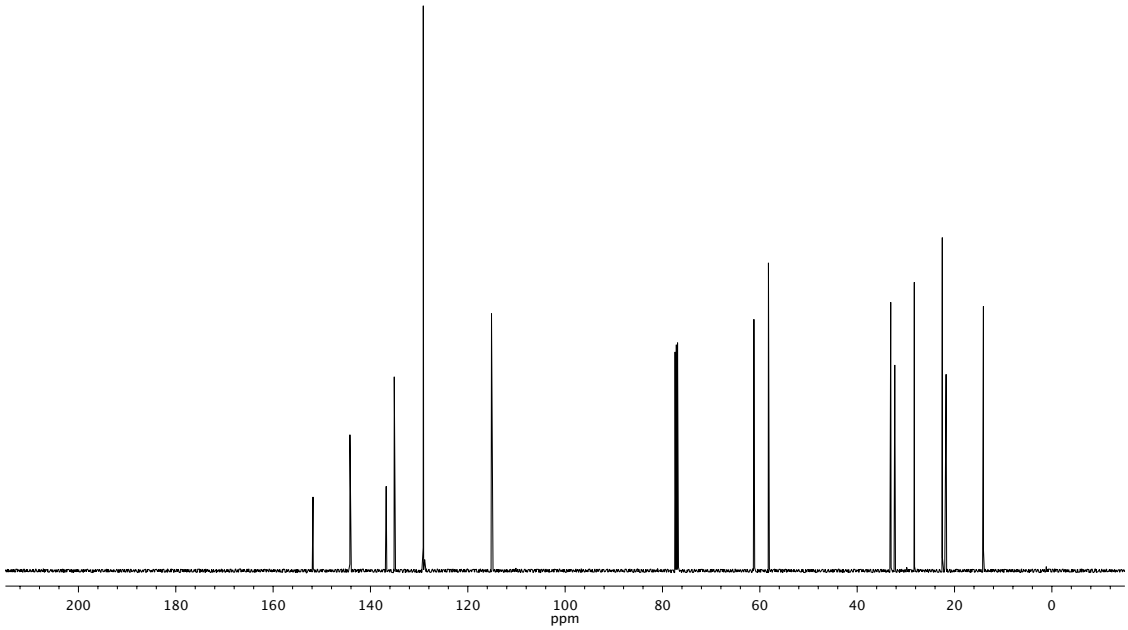


Figure A14.77. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **519**.

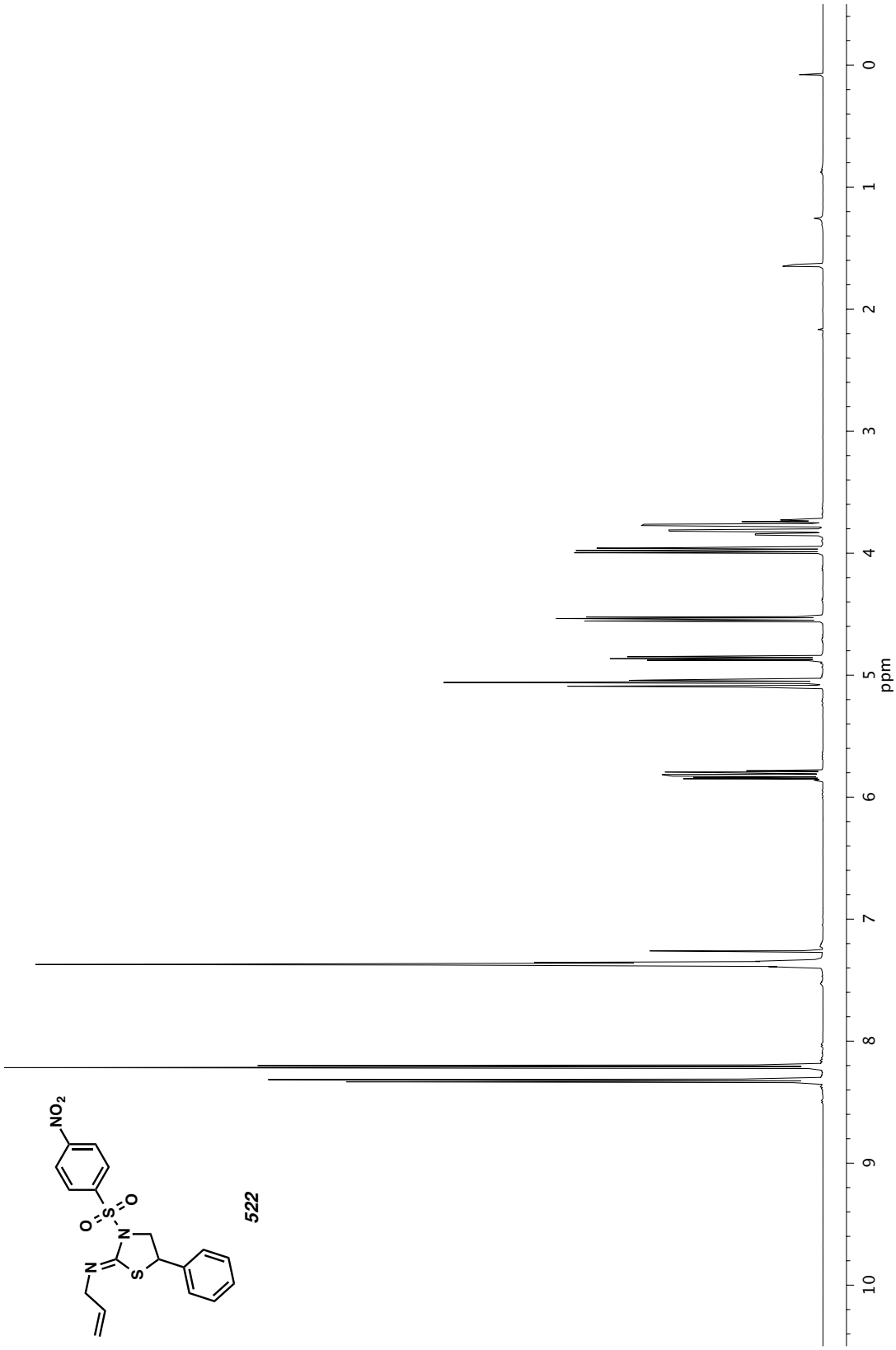


Figure A14.78. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **522**.

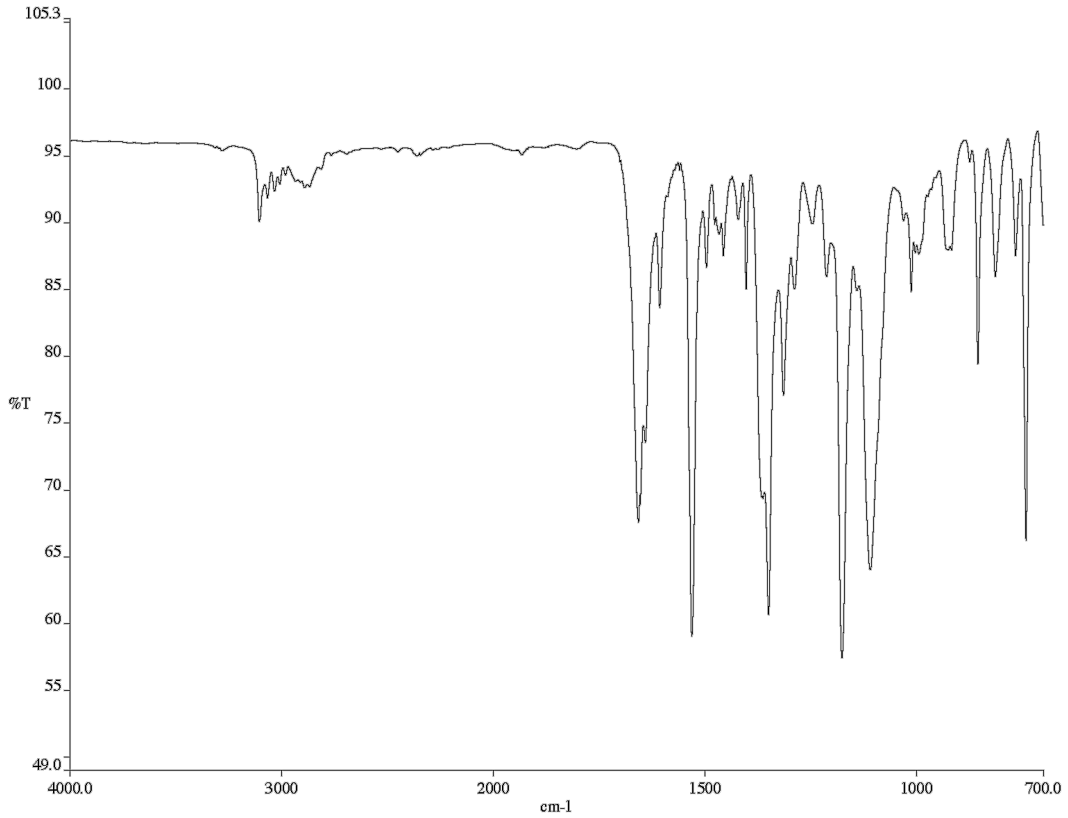


Figure A14.79. Infrared spectrum (thin film/NaCl) of compound **522**.

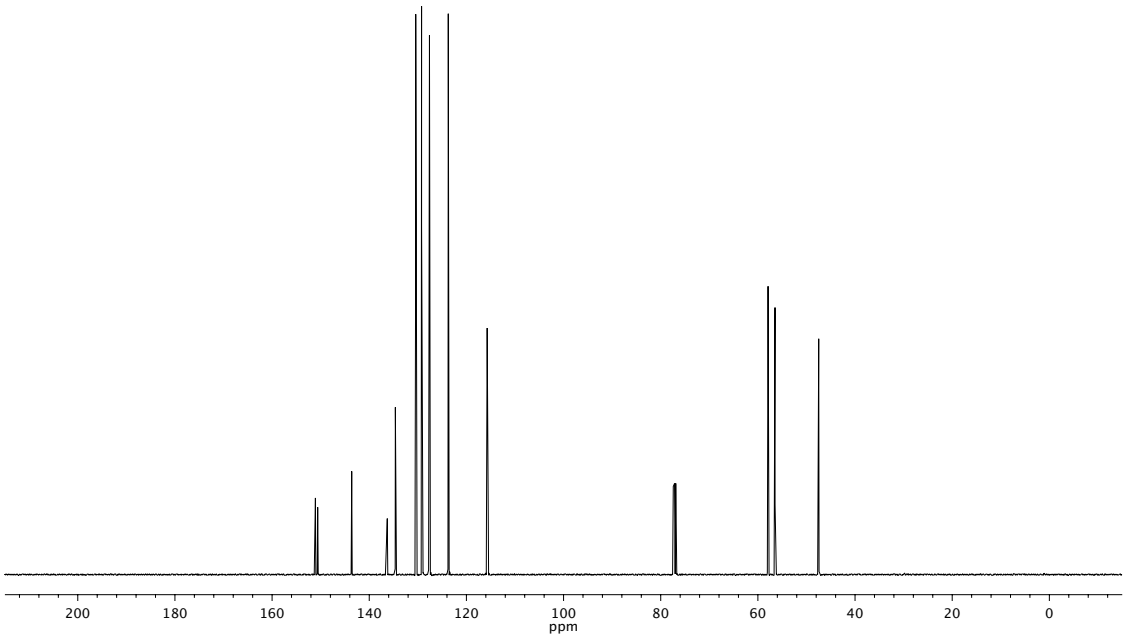


Figure A14.80. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **522**.

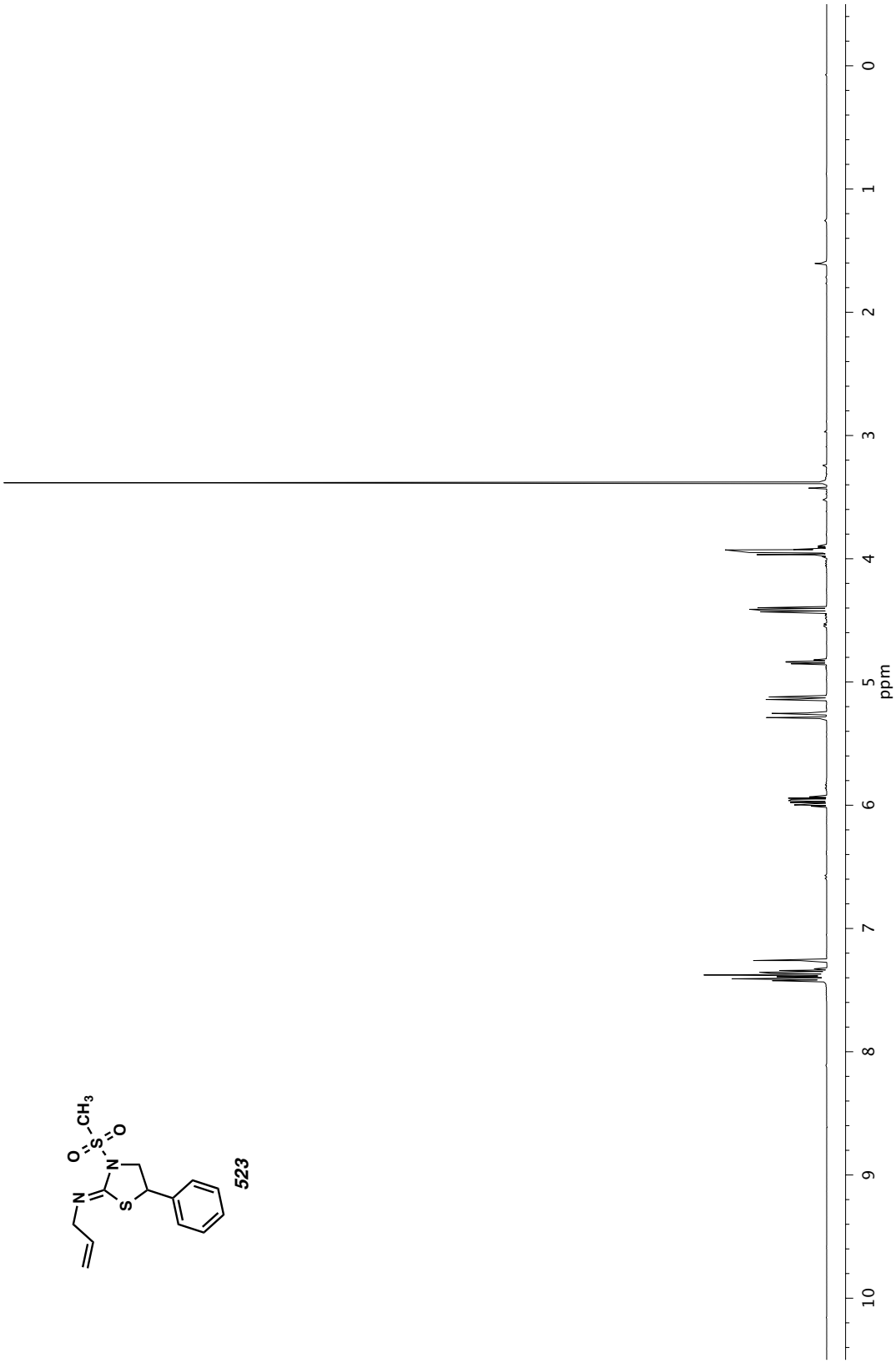


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Figure A14.81. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **523**.

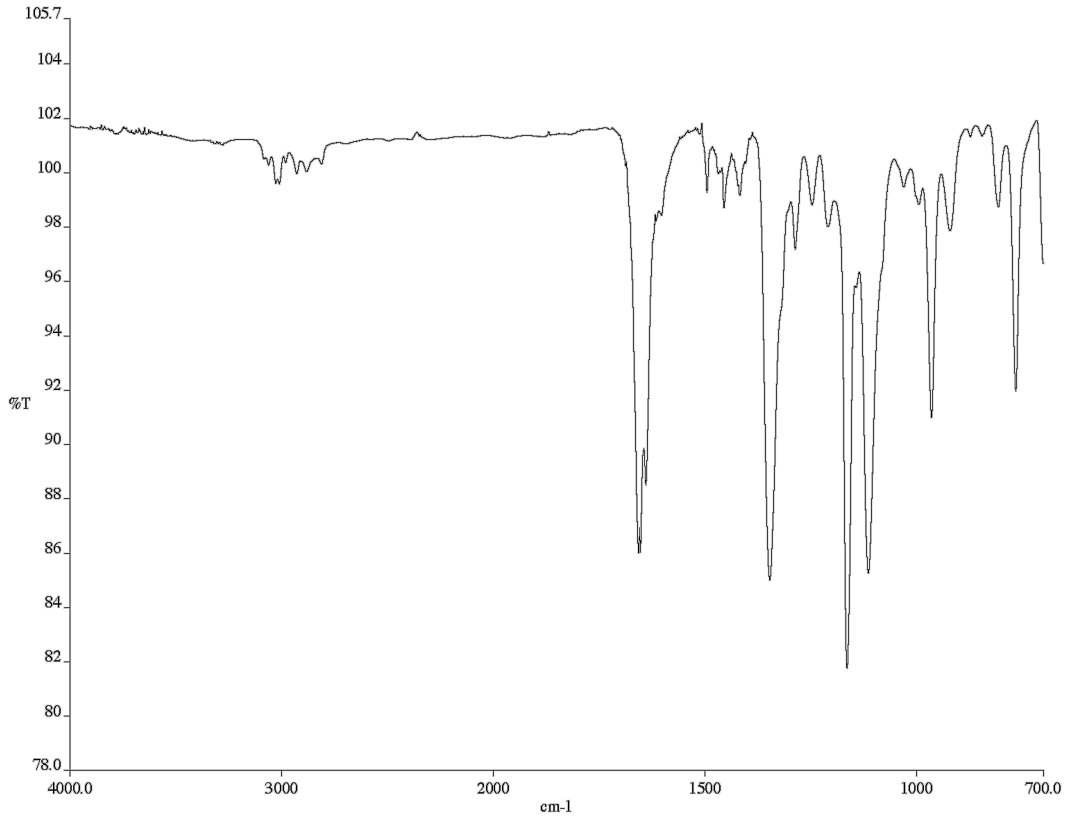


Figure A14.82. Infrared spectrum (thin film/NaCl) of compound **523**.

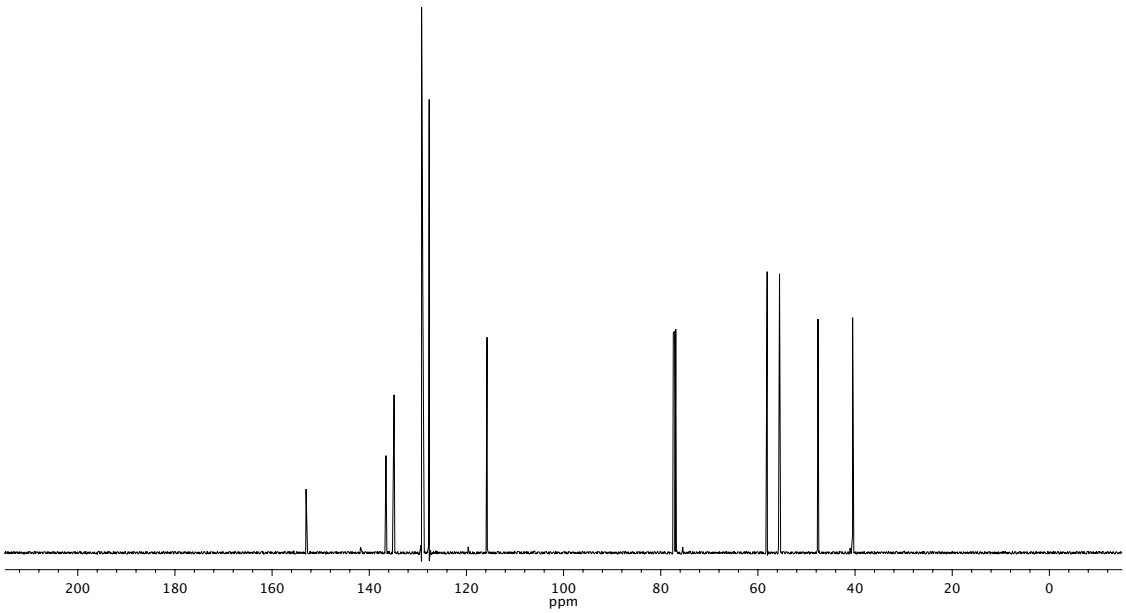


Figure A14.83. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **523**.

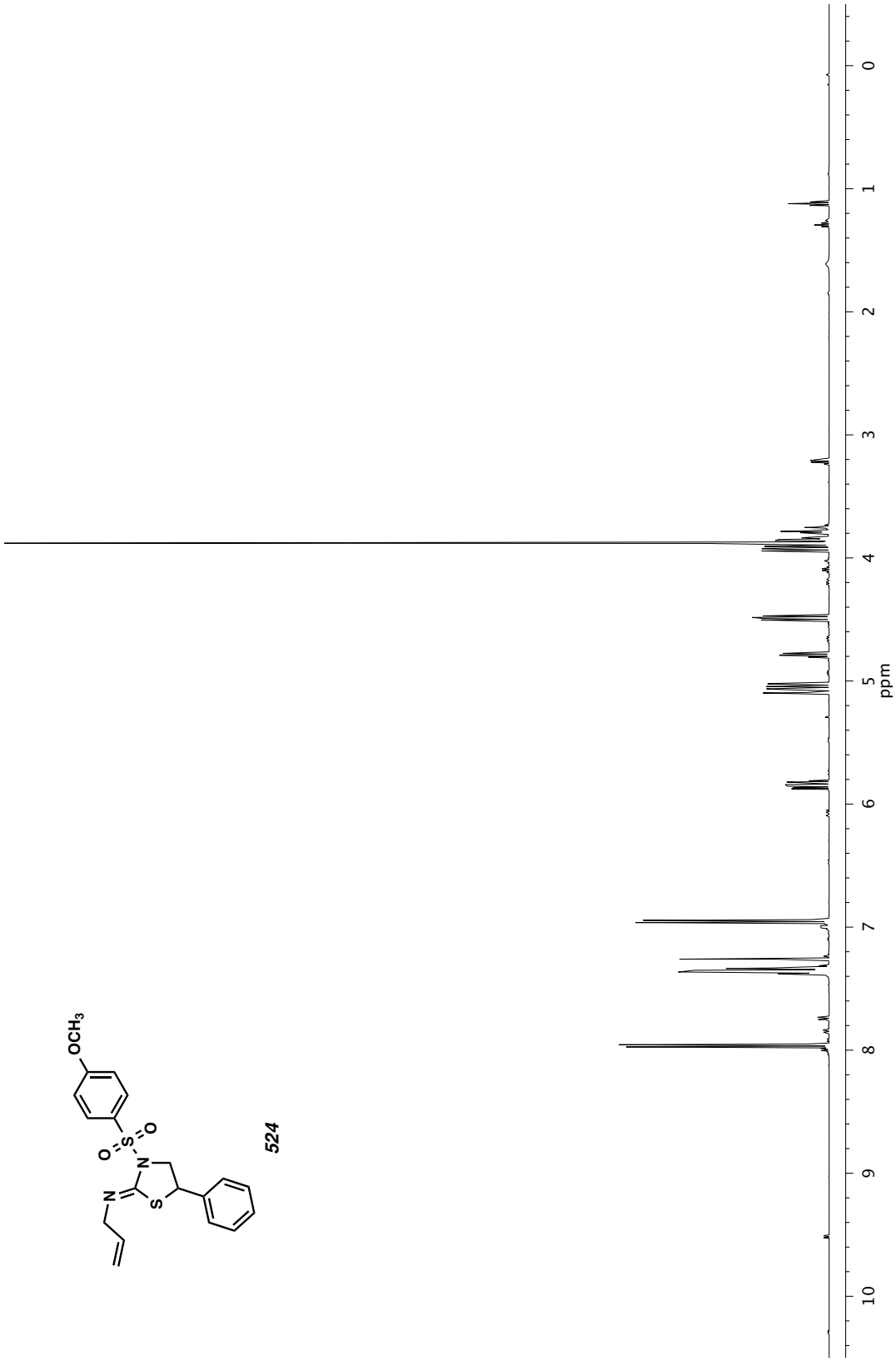


Figure A14.84. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **524**.

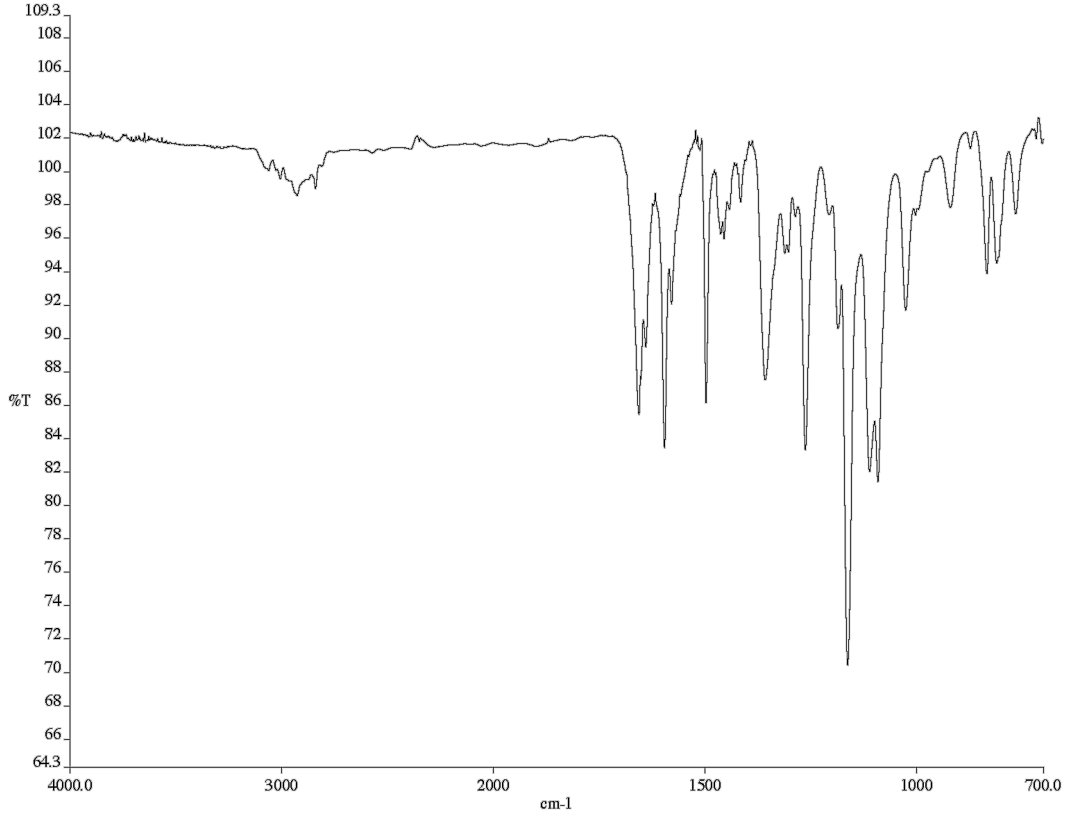


Figure A14.85. Infrared spectrum (thin film/NaCl) of compound **524**.

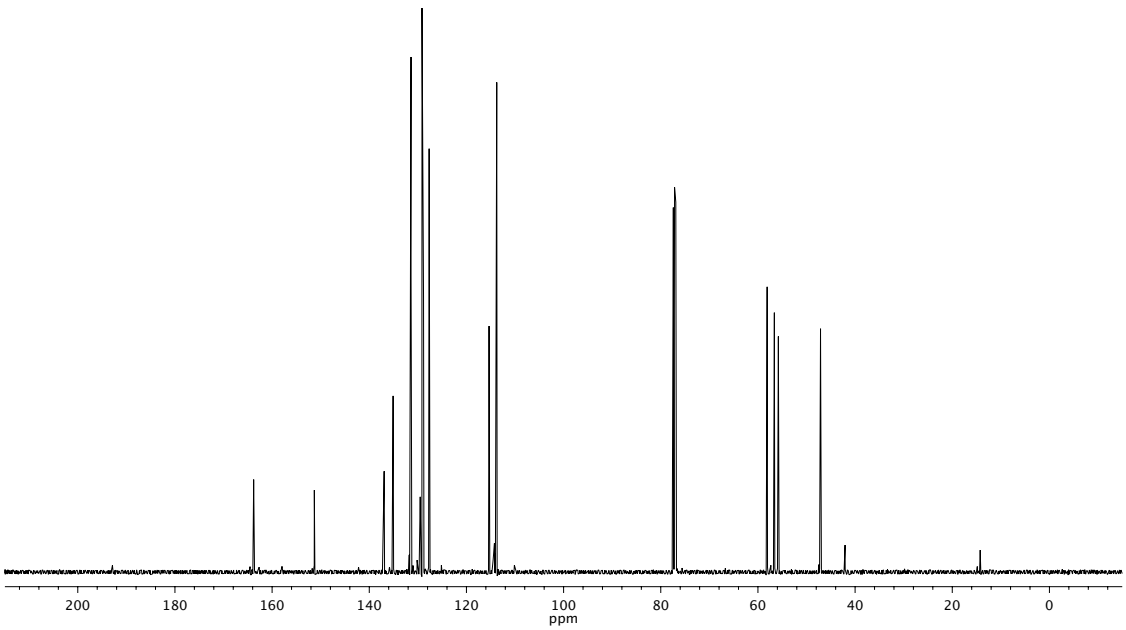


Figure A14.86. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **524**.

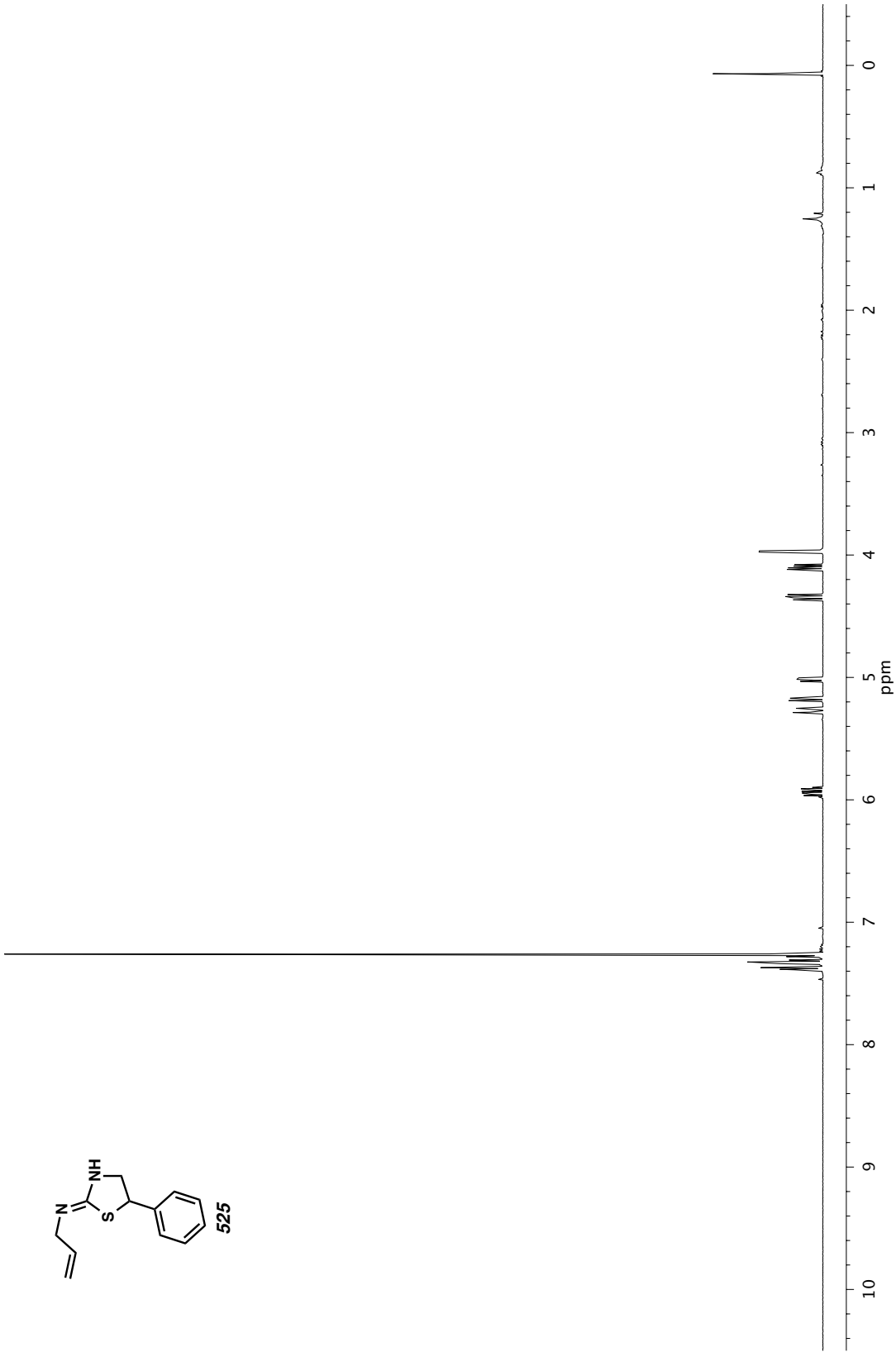


Figure A14.87. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **525**.

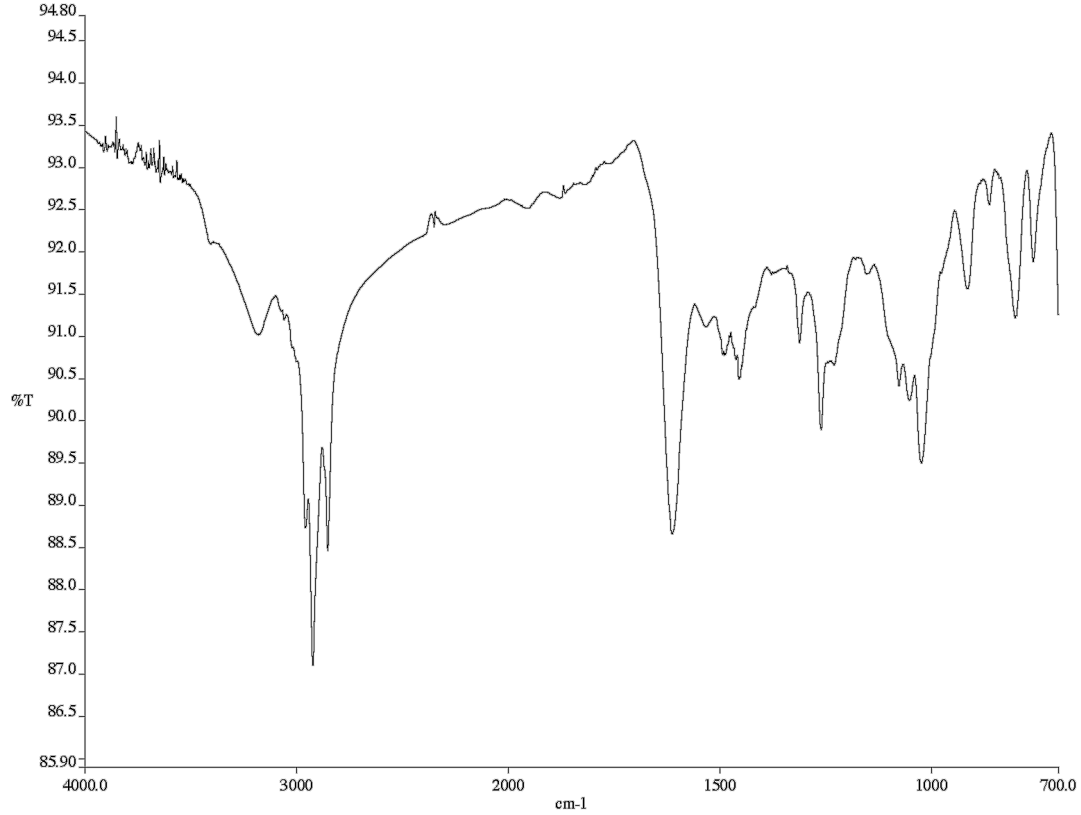


Figure A14.88. Infrared spectrum (thin film/NaCl) of compound **525**.

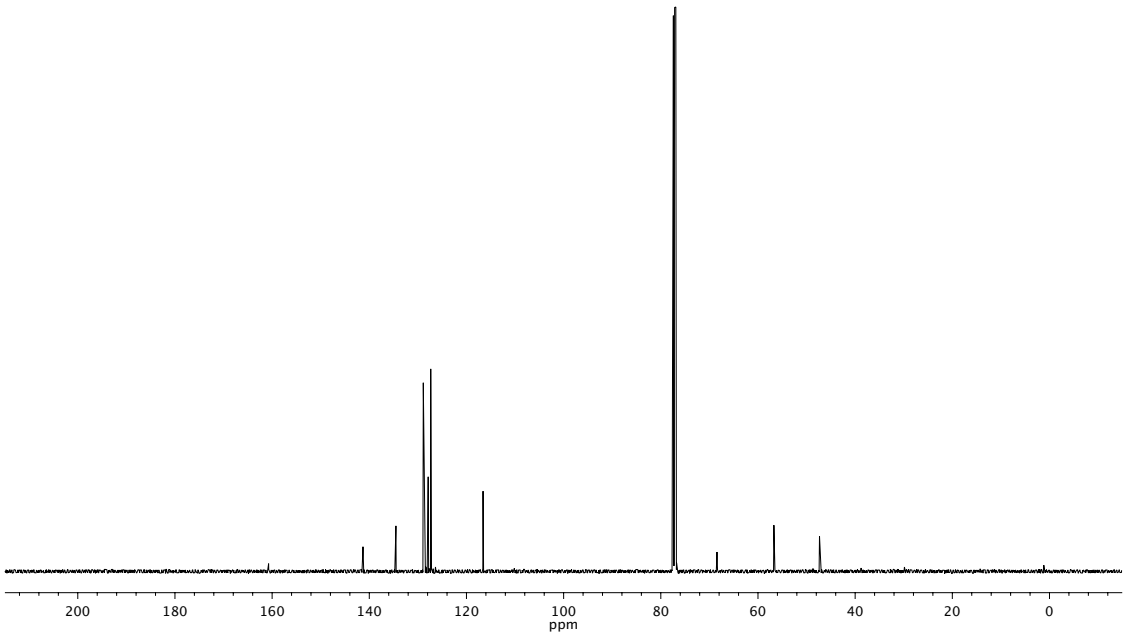


Figure A14.89. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **525**.

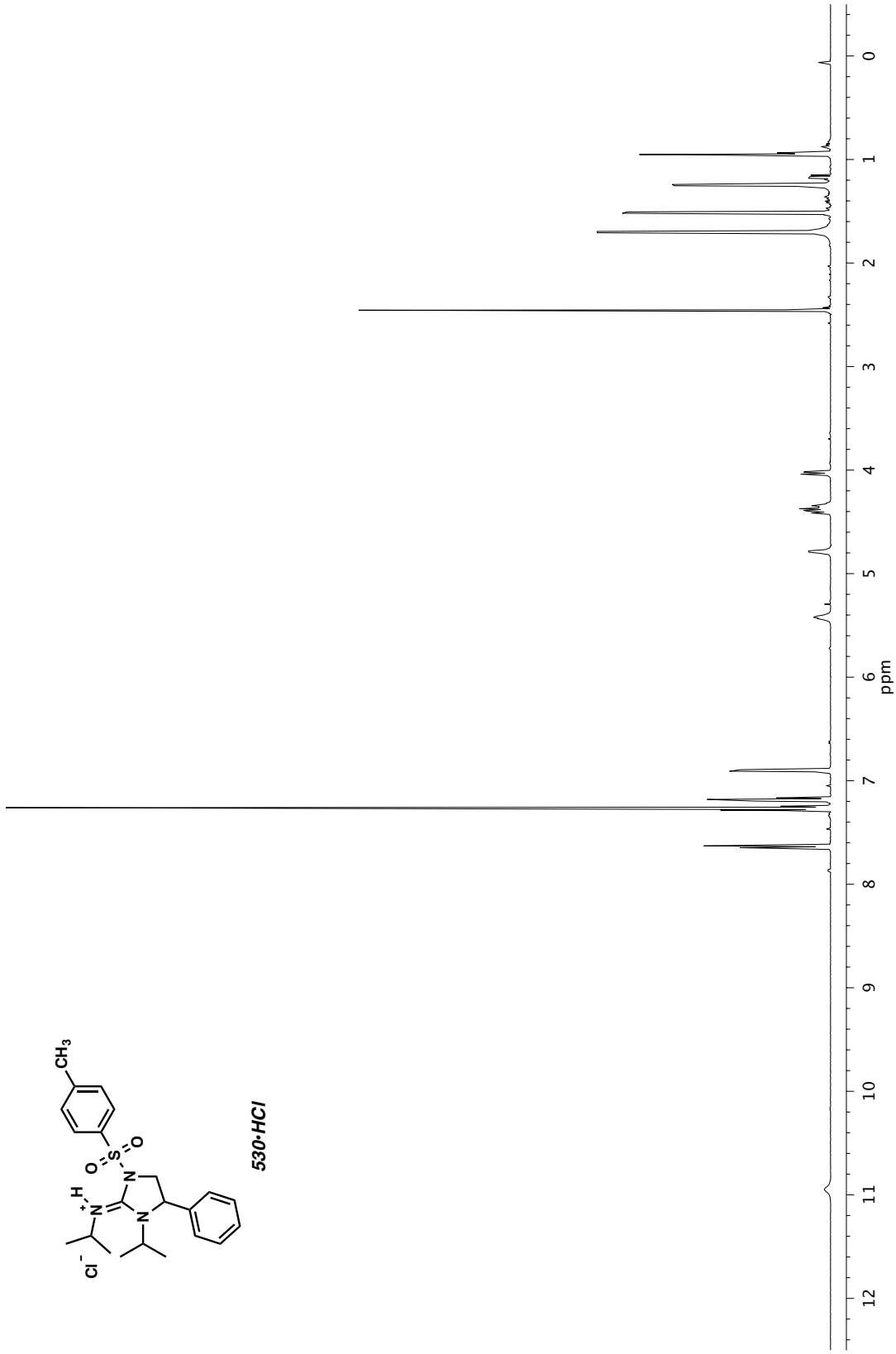


Figure A14.90. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **530•HCl**.

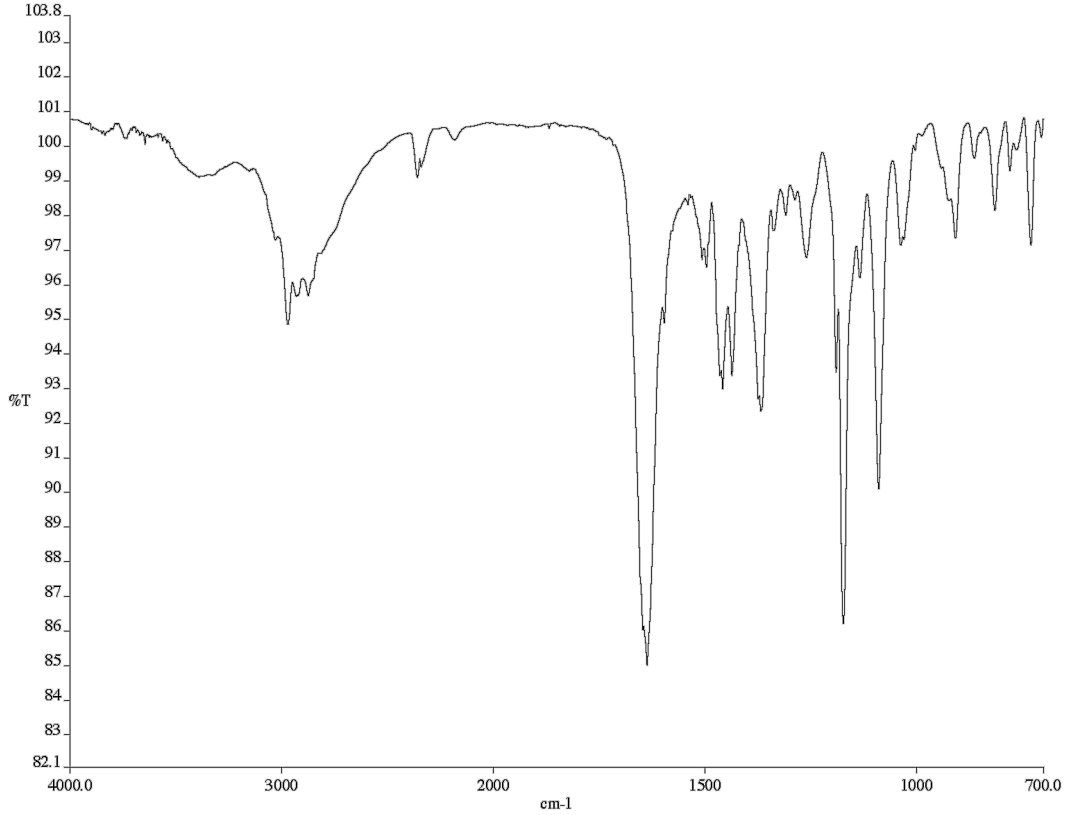


Figure A14.91. Infrared spectrum (Thin Film, NaCl) of compound **530•HCl**.

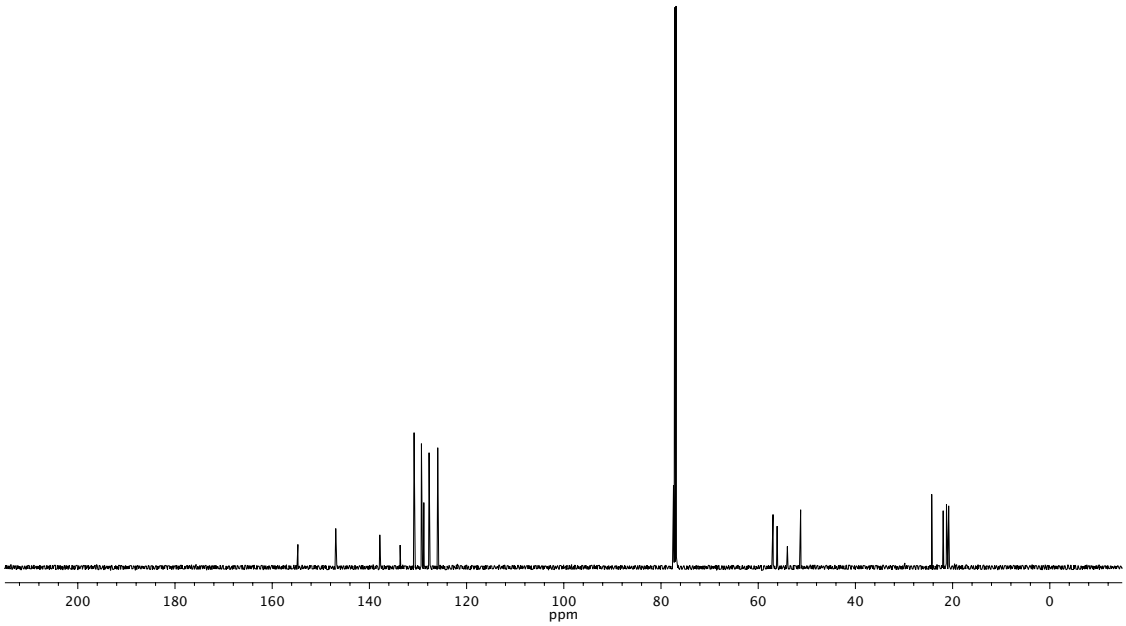


Figure A14.92. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **530•HCl**.

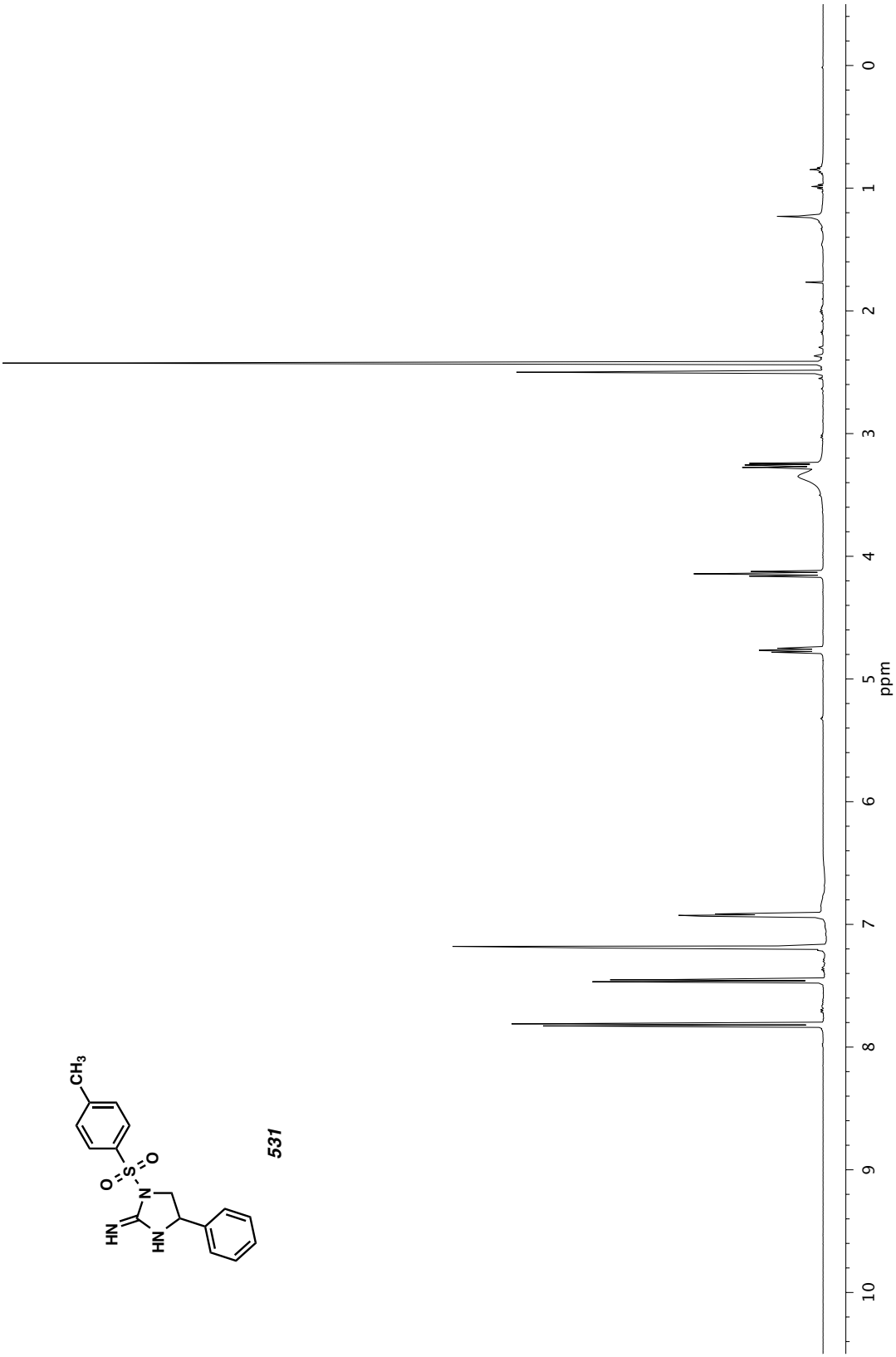


Figure A14.93. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **531**.

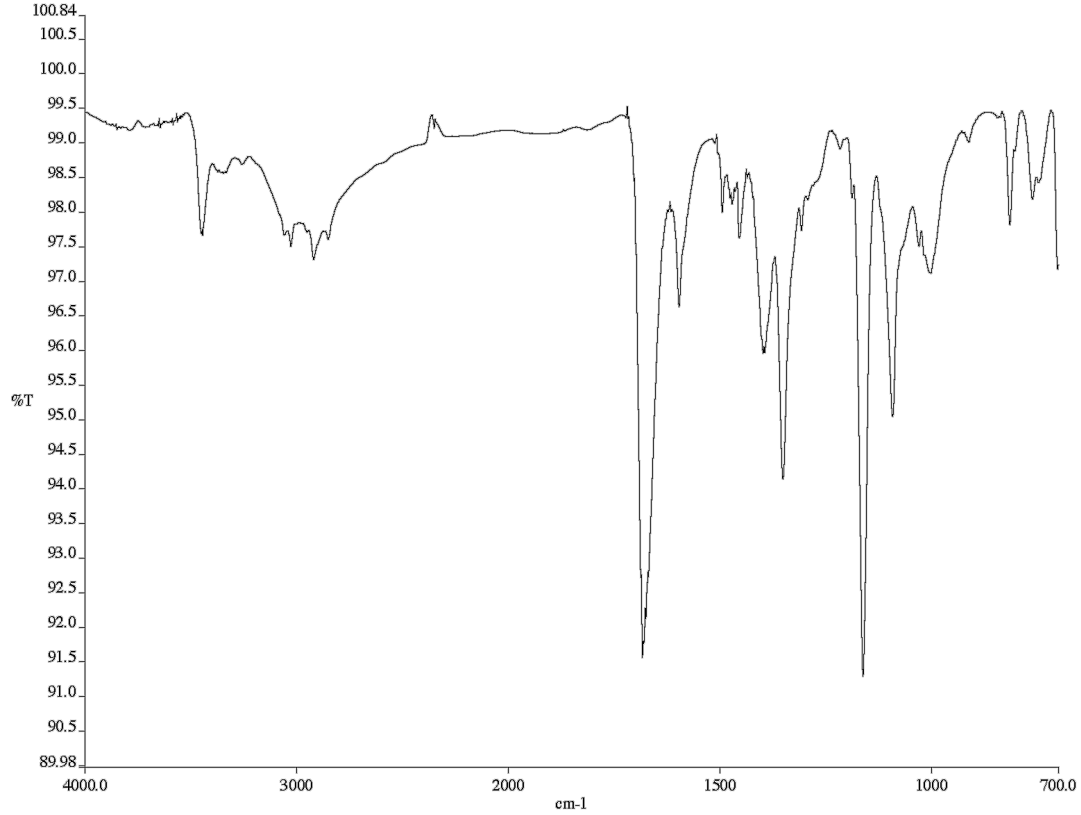


Figure A14.94. Infrared spectrum (thin film/NaCl) of compound **531**.

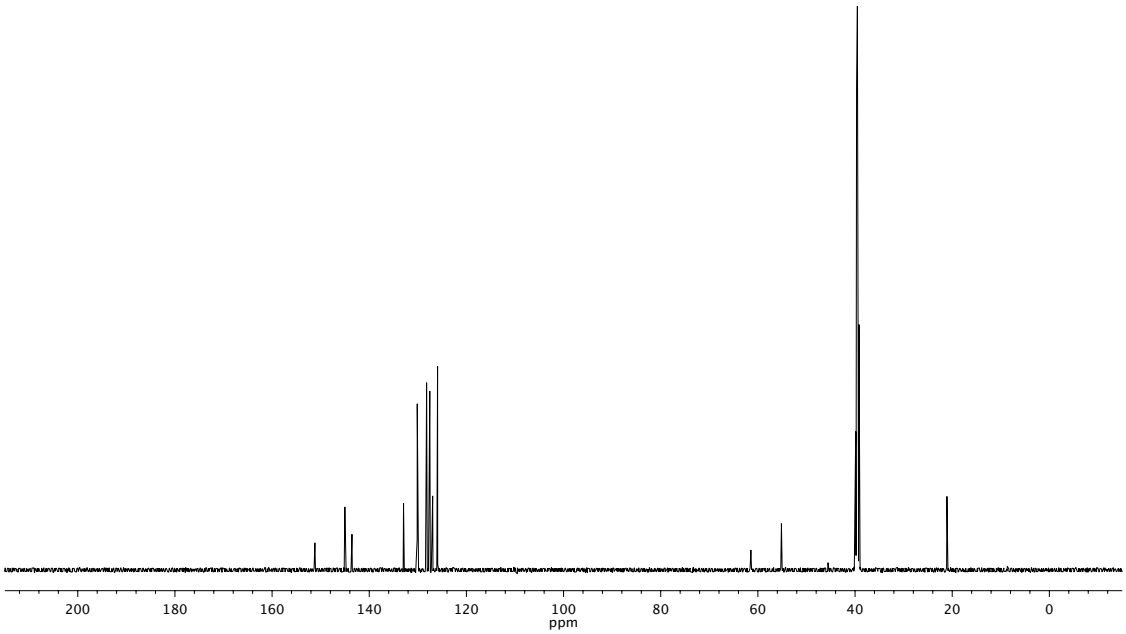


Figure A14.95. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **531**.

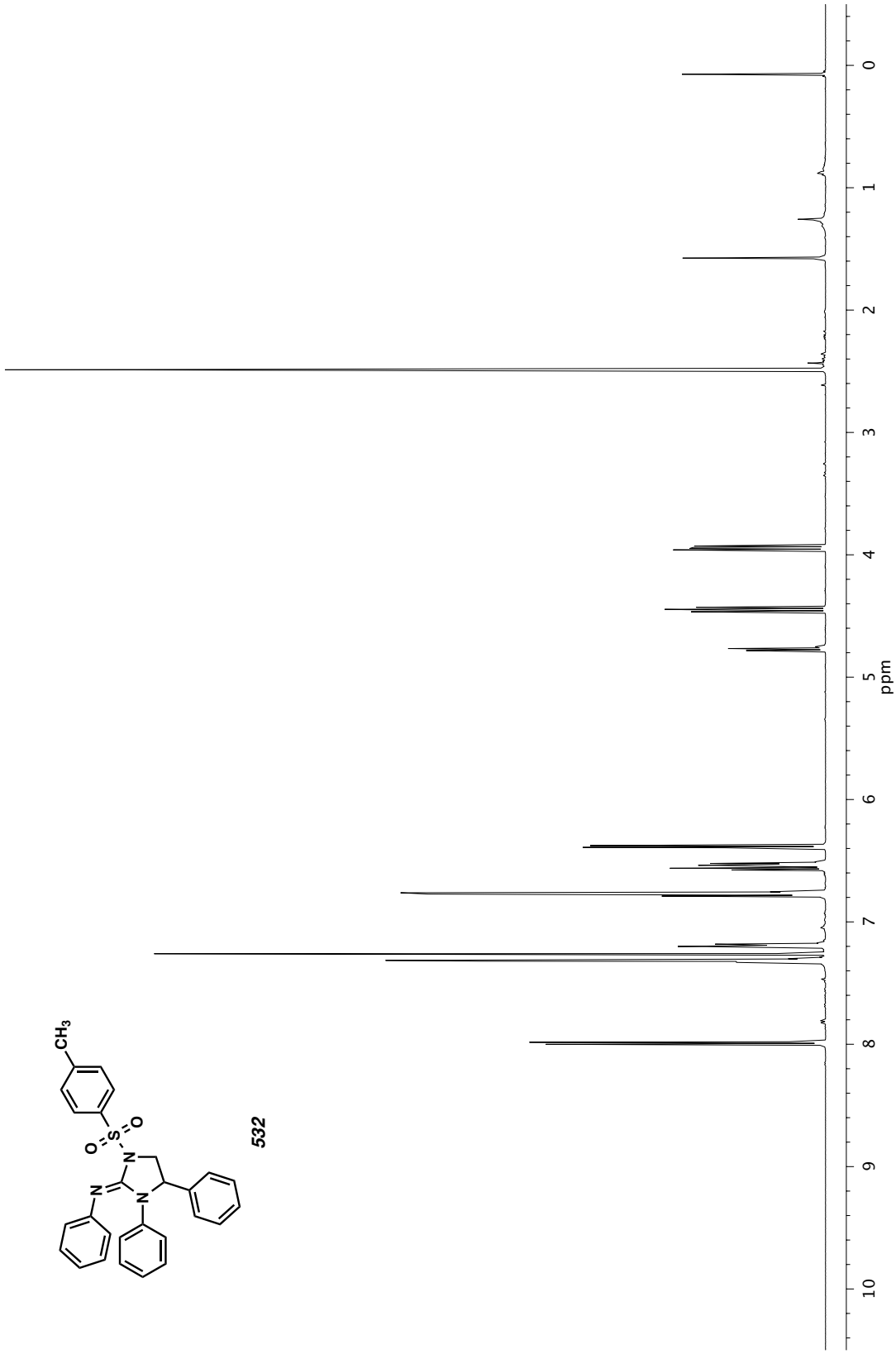


Figure A14.96. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **532**.

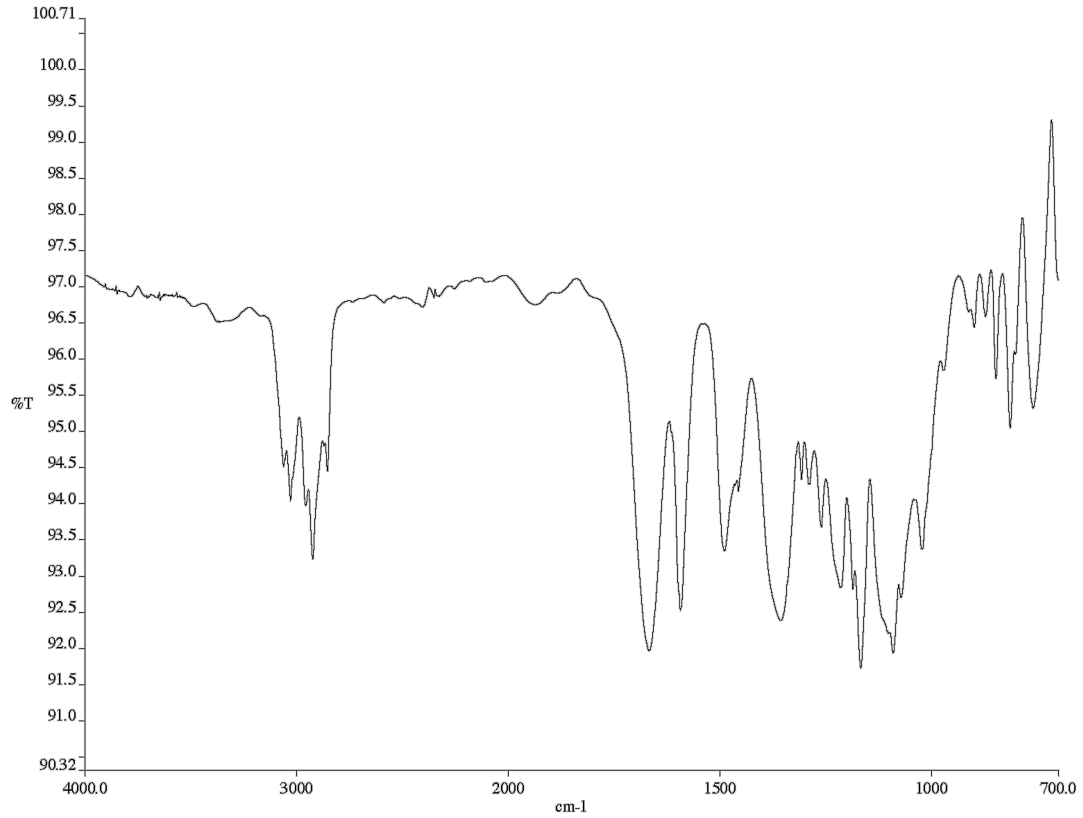


Figure A14.97. Infrared spectrum (thin film/NaCl) of compound **532**.

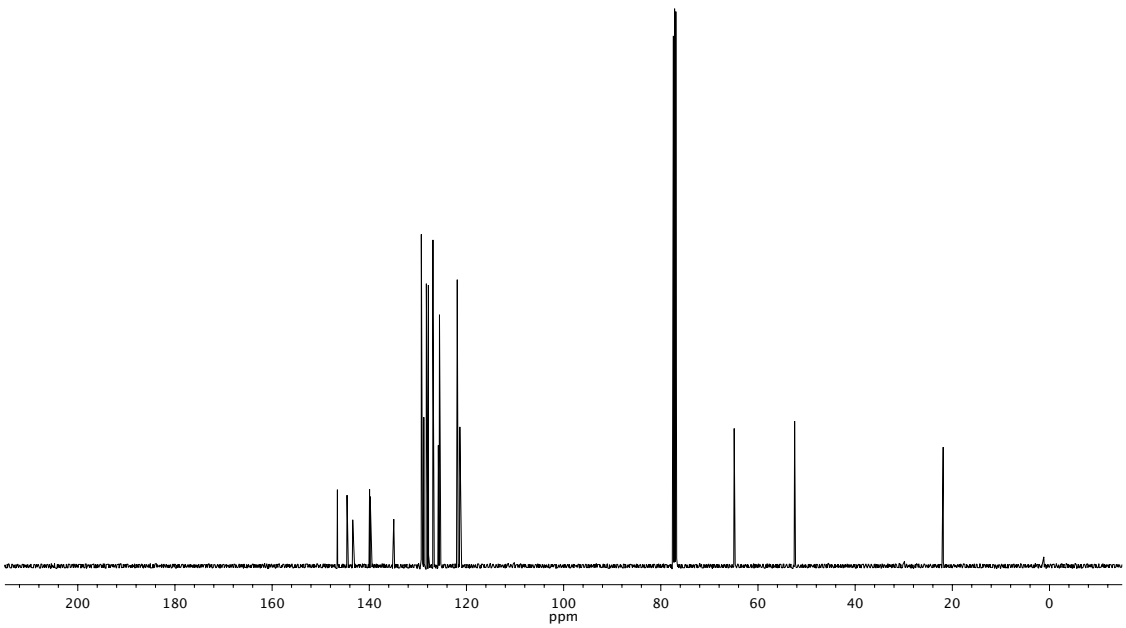
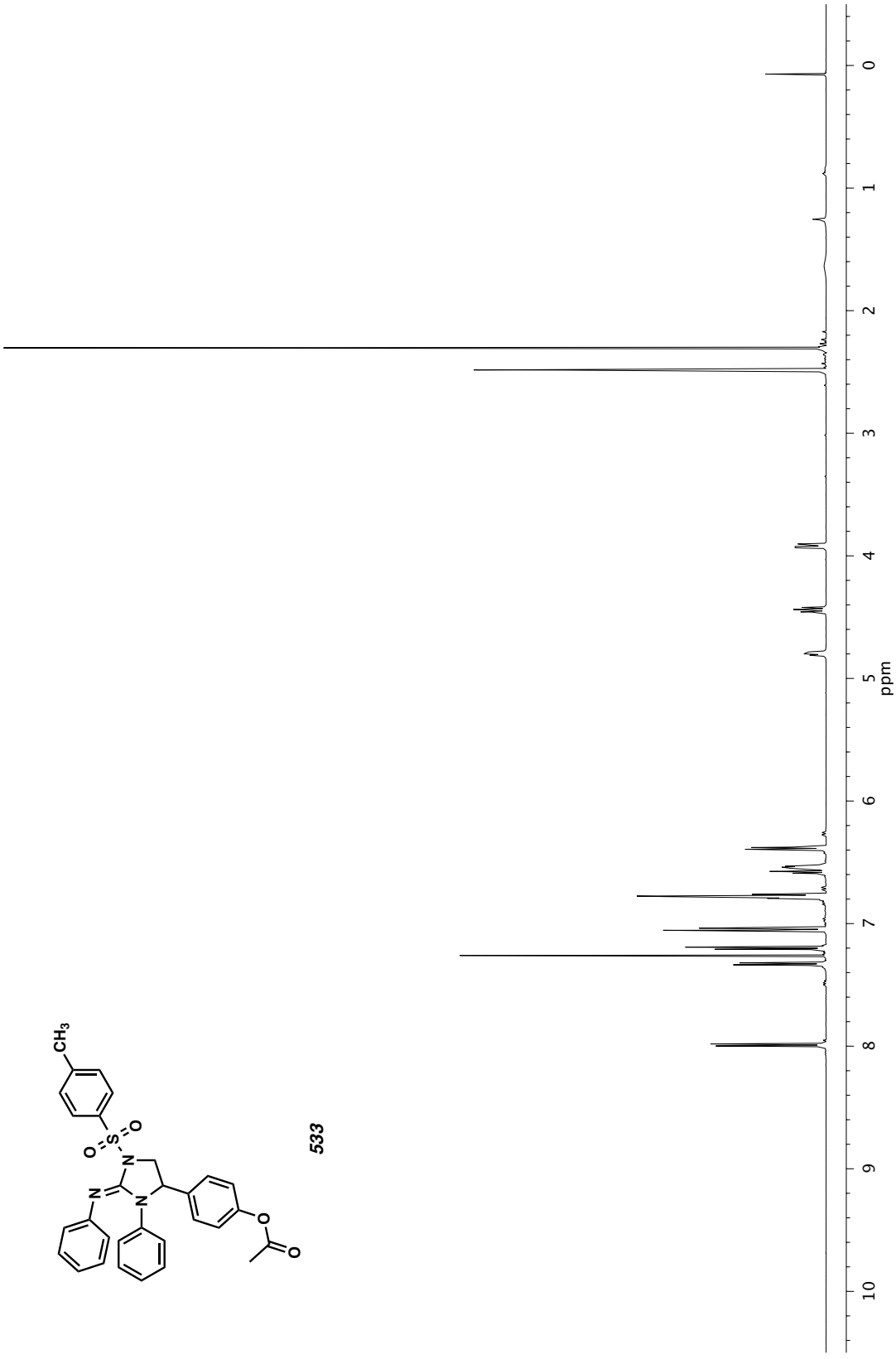


Figure A14.98. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **532**.



533

Figure A14.99. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **533**.

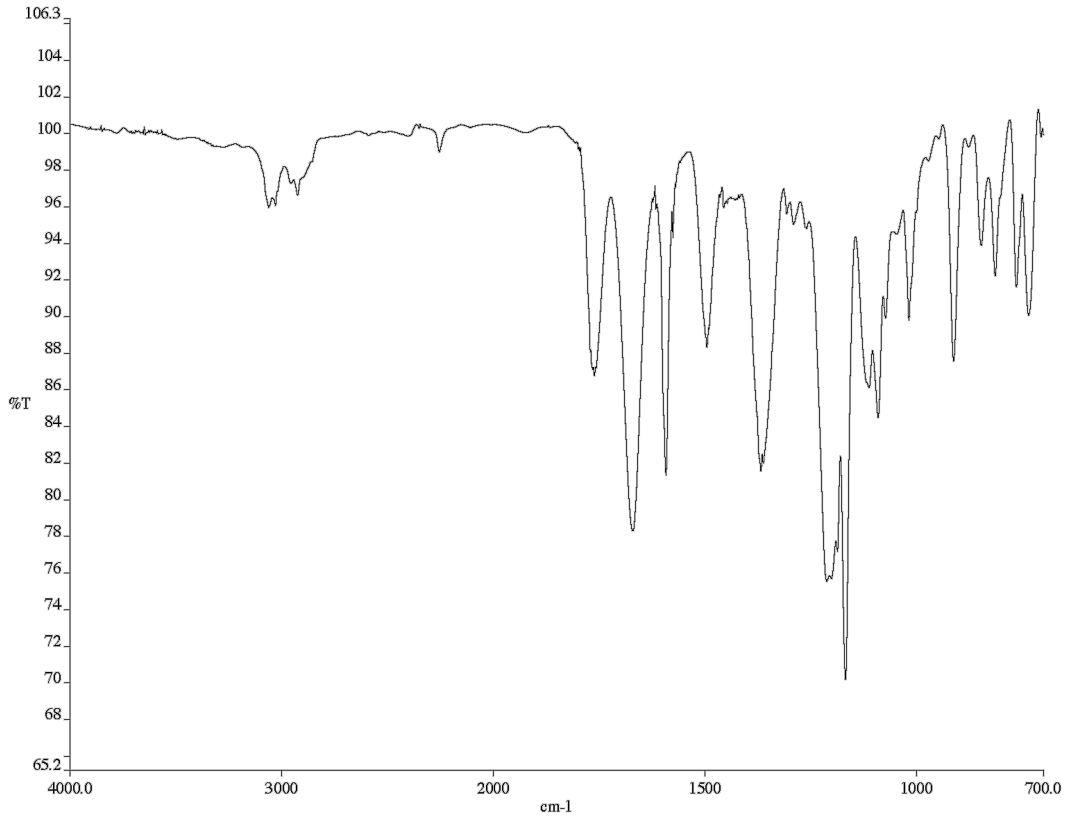


Figure A14.100. Infrared spectrum (thin film/NaCl) of compound **533**.

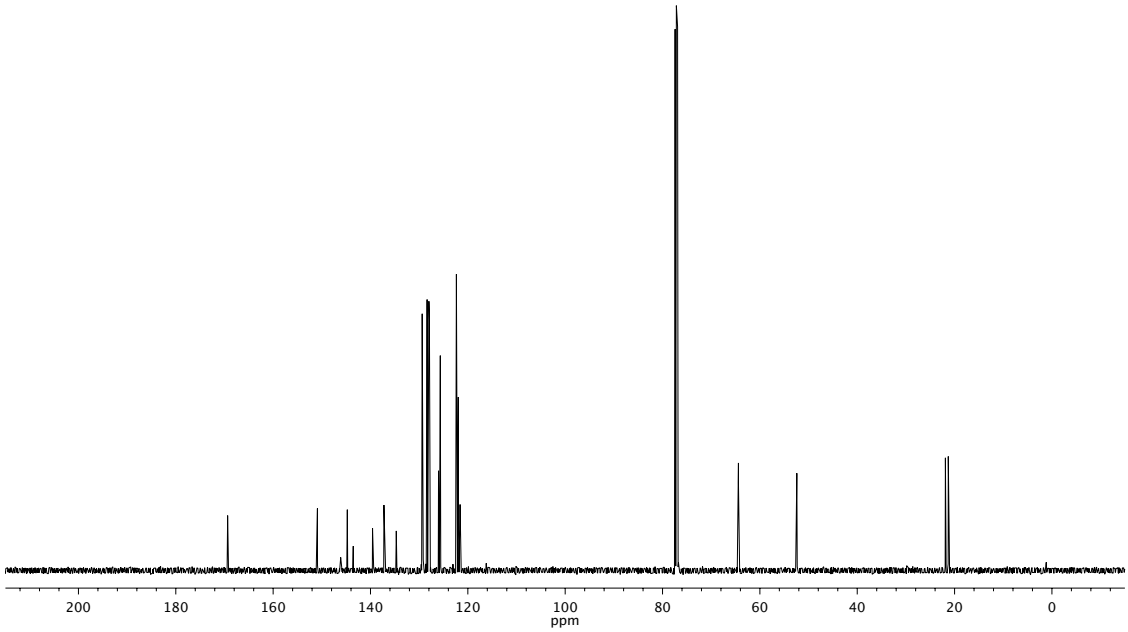


Figure A14.101. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **533**.

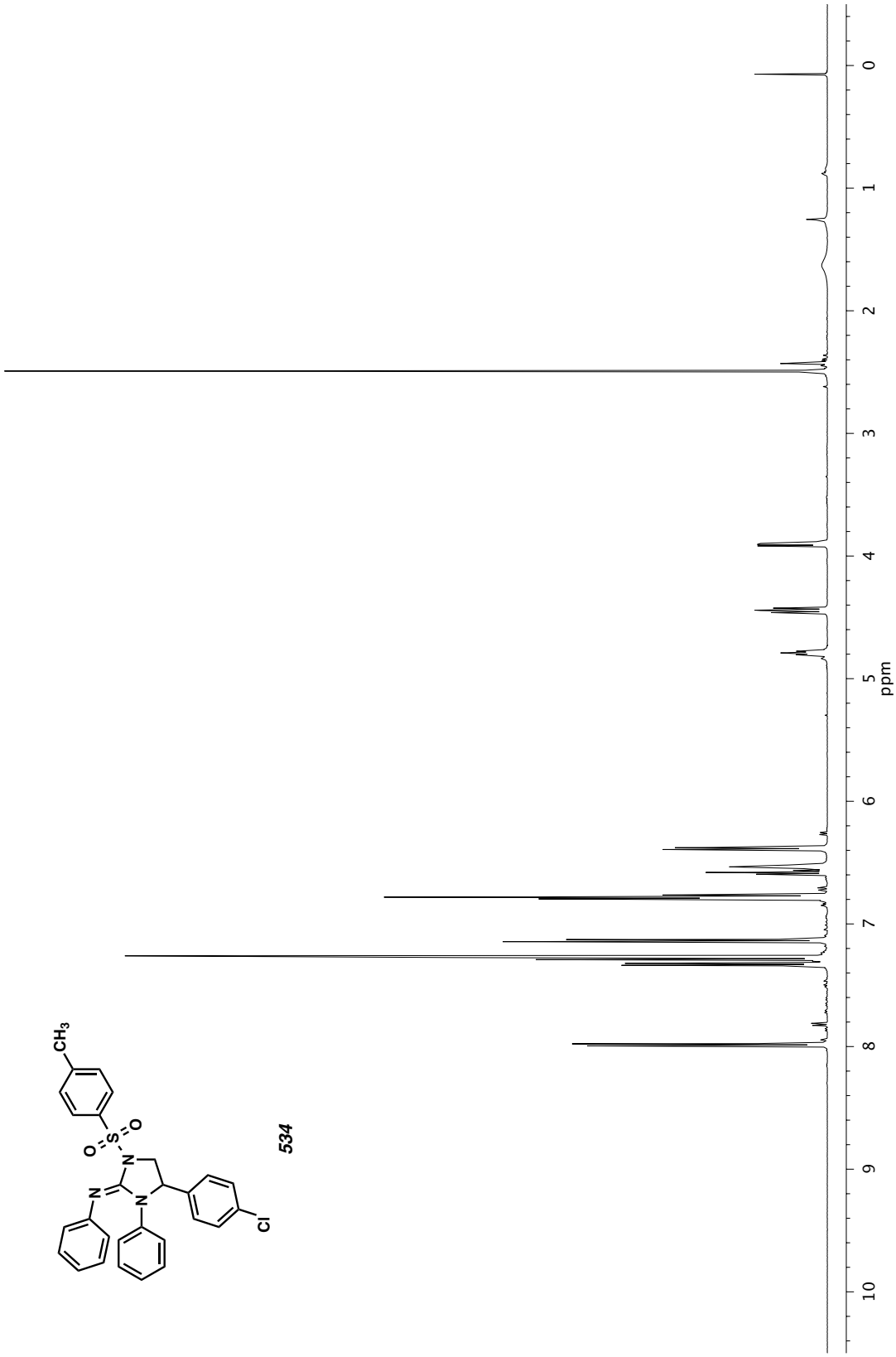


Figure A14.102. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **534**.

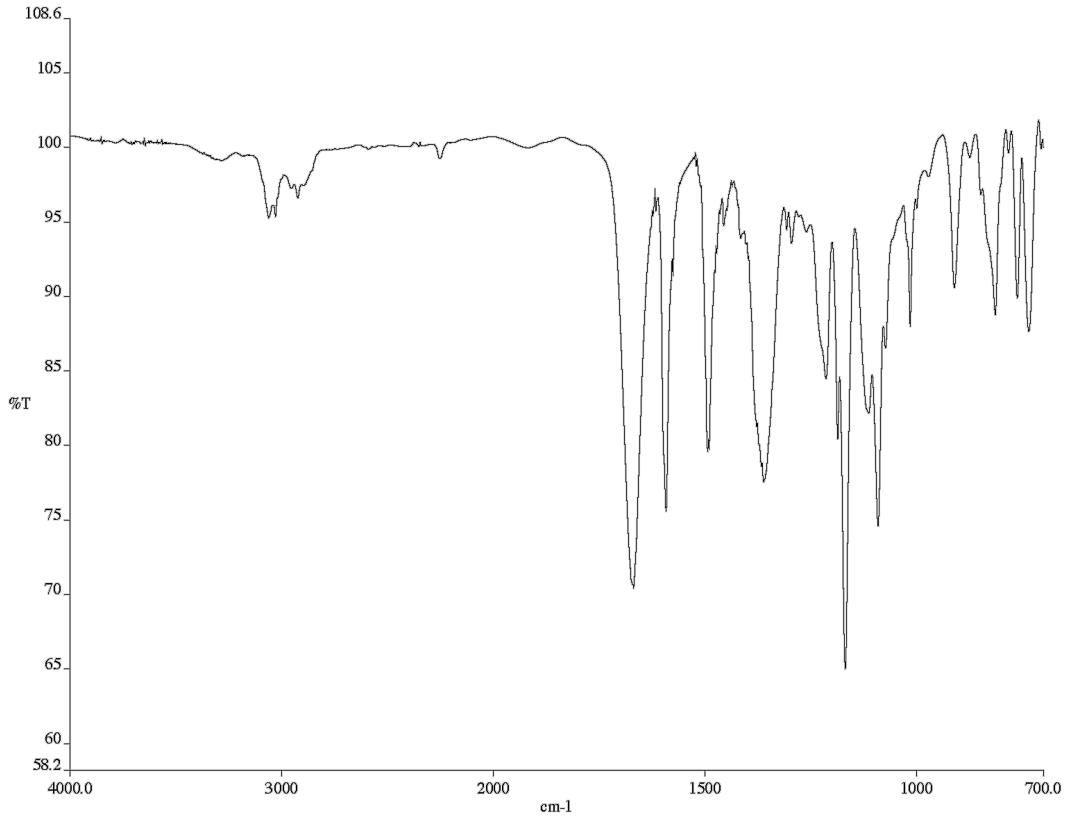


Figure A14.103. Infrared spectrum (thin film/NaCl) of compound **534**.

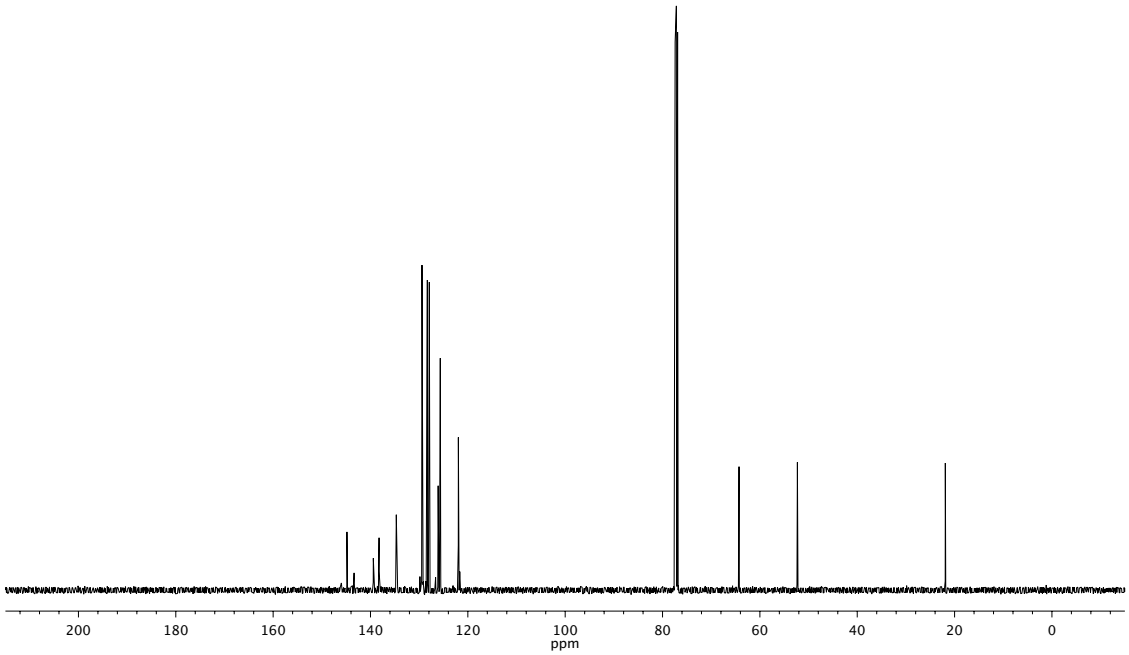


Figure A14.104. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **534**.

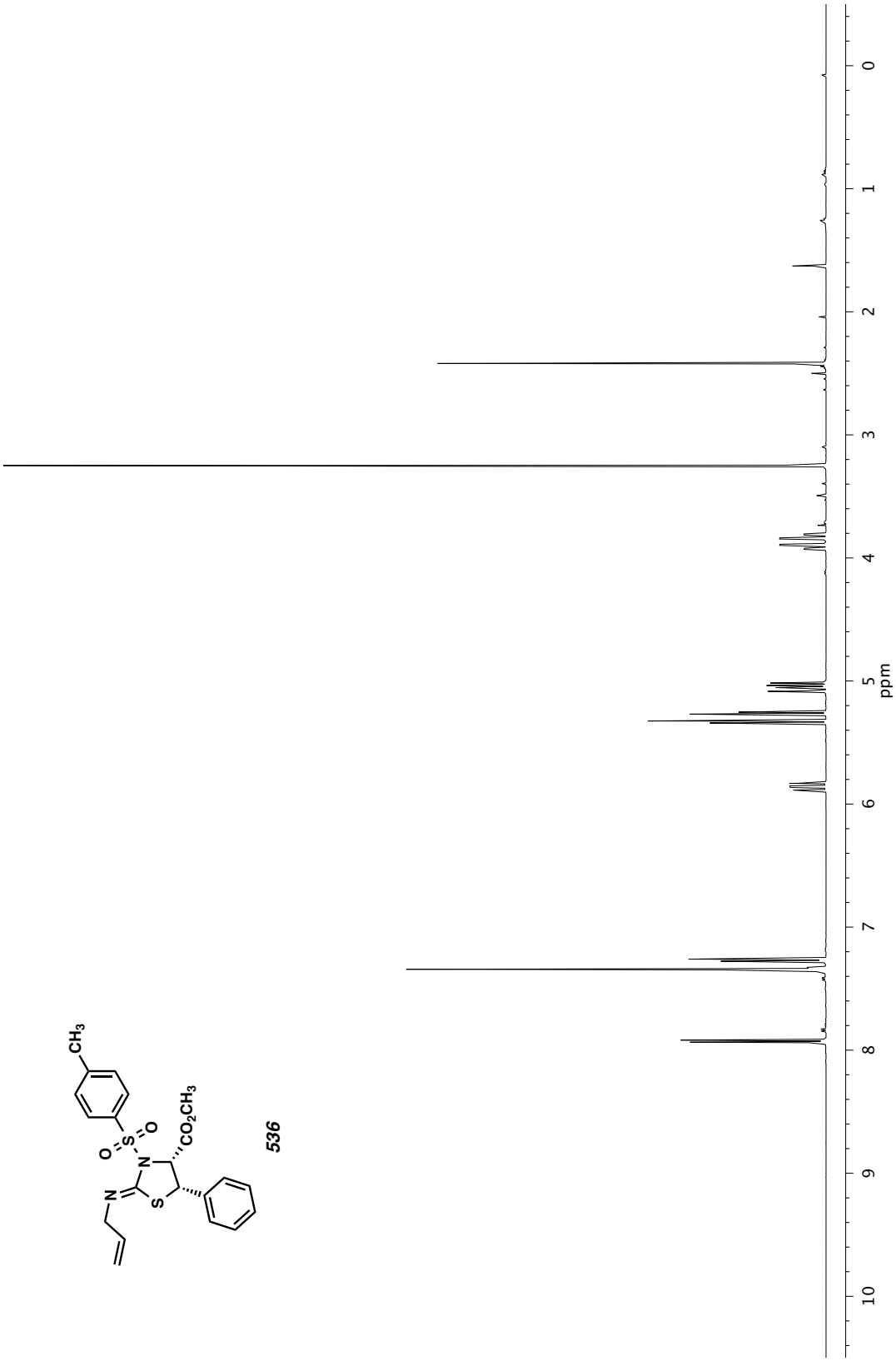


Figure A14.105. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **536**.

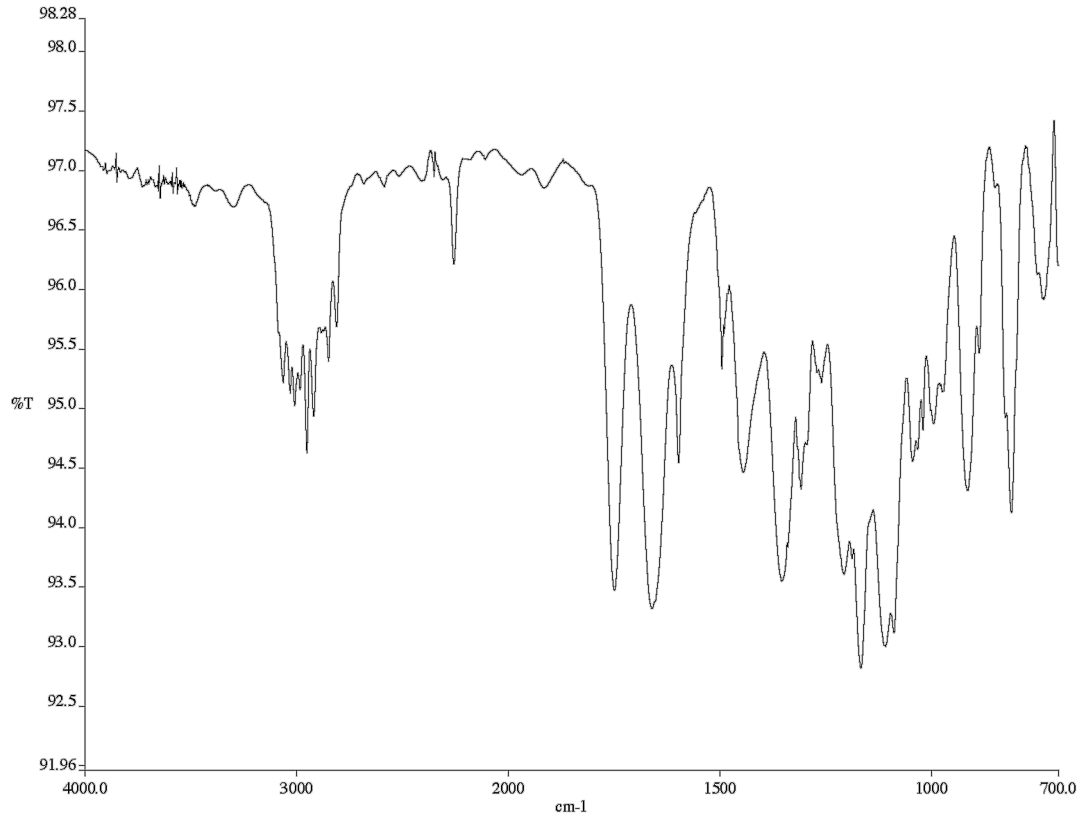


Figure A14.106. Infrared spectrum (thin film/NaCl) of compound **536**.

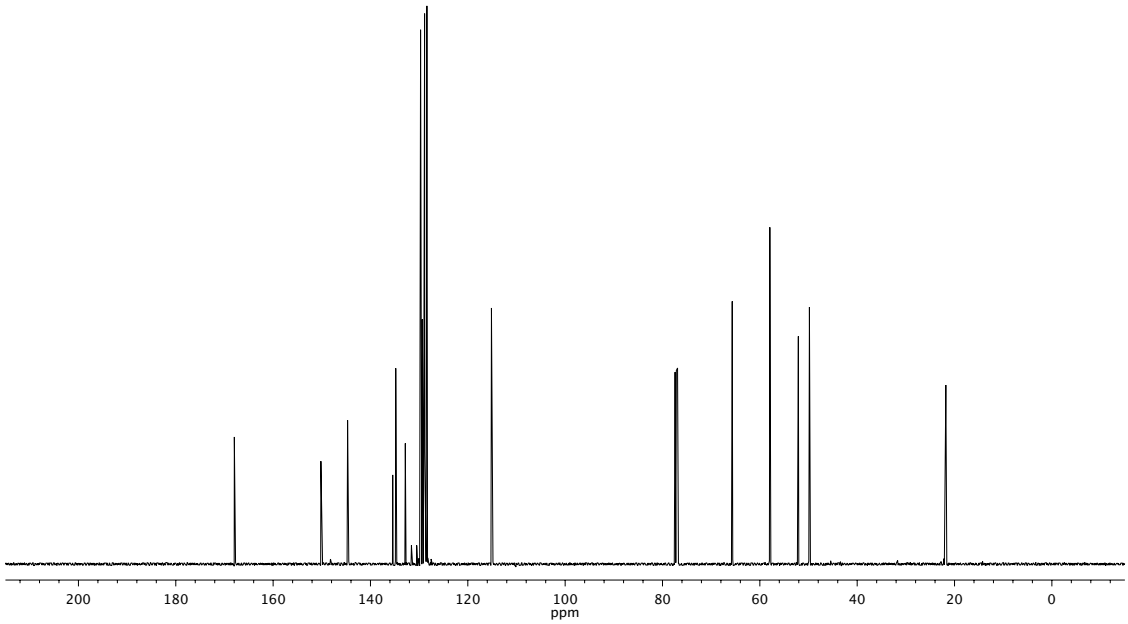


Figure A14.107. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **536**.

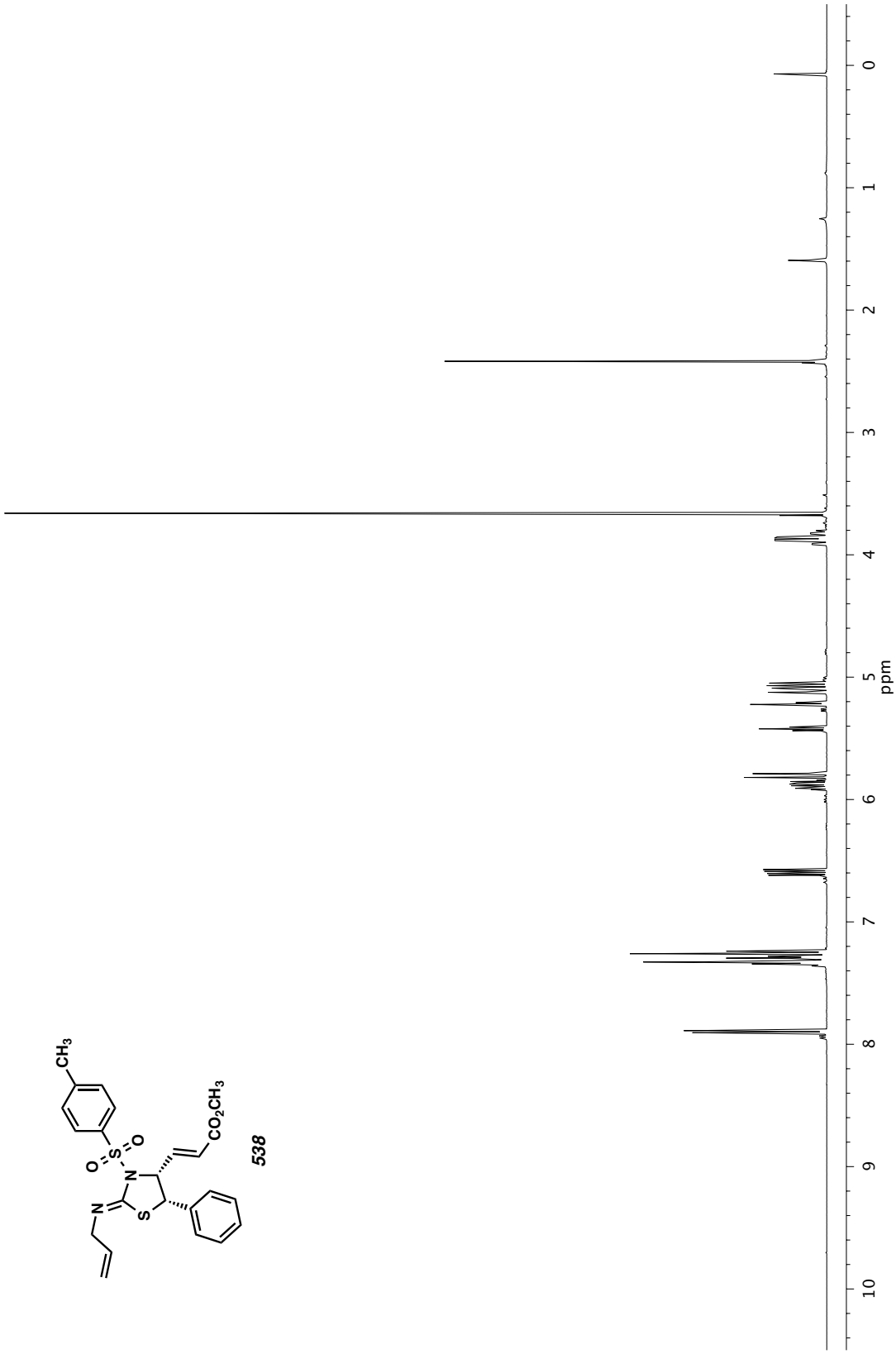


Figure A14.108. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **538**.

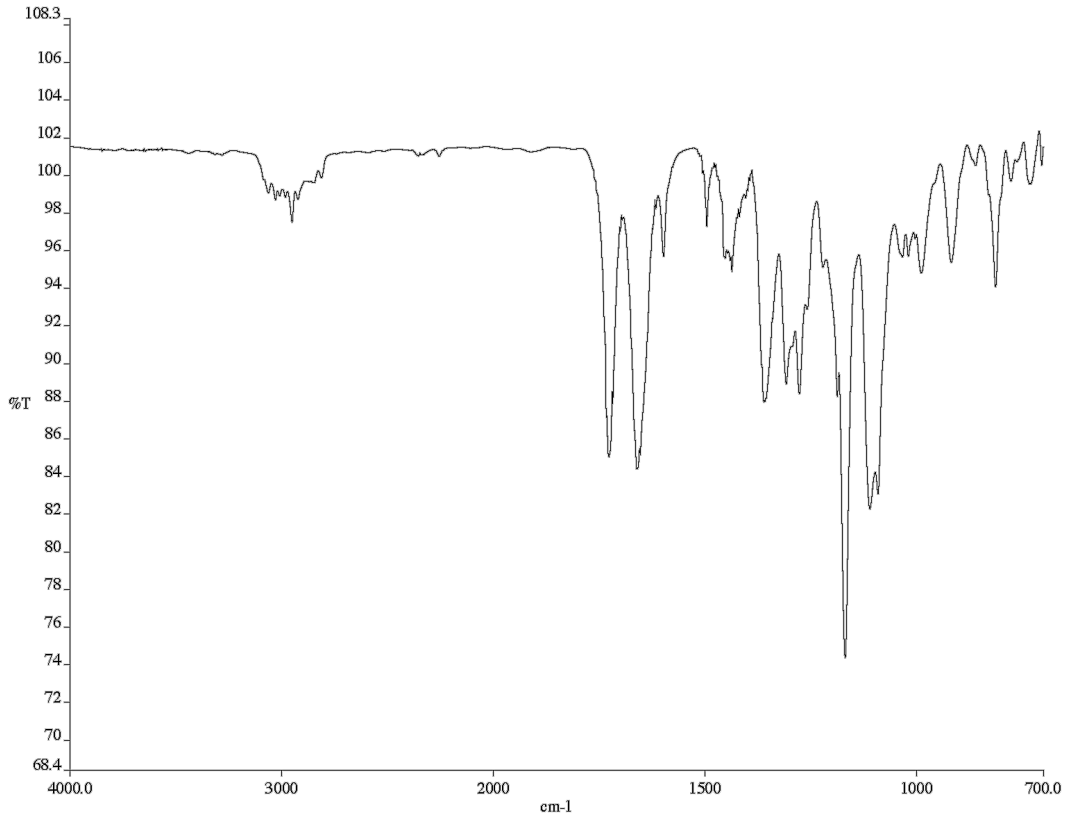


Figure A14.109. Infrared spectrum (thin film/NaCl) of compound **538**.

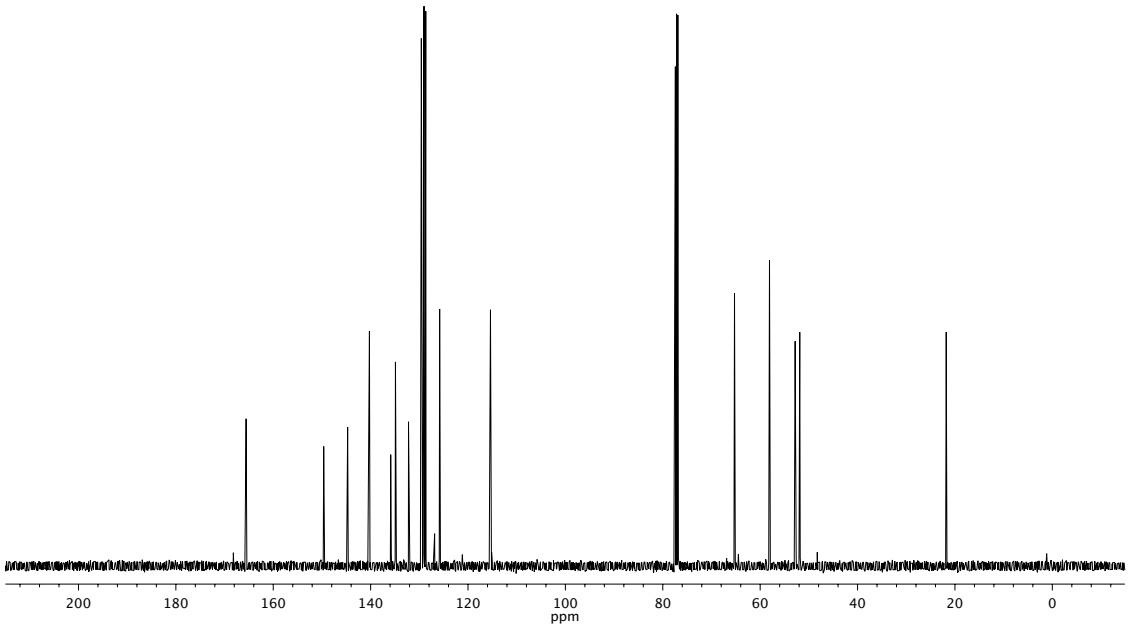


Figure A14.110. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **538**.

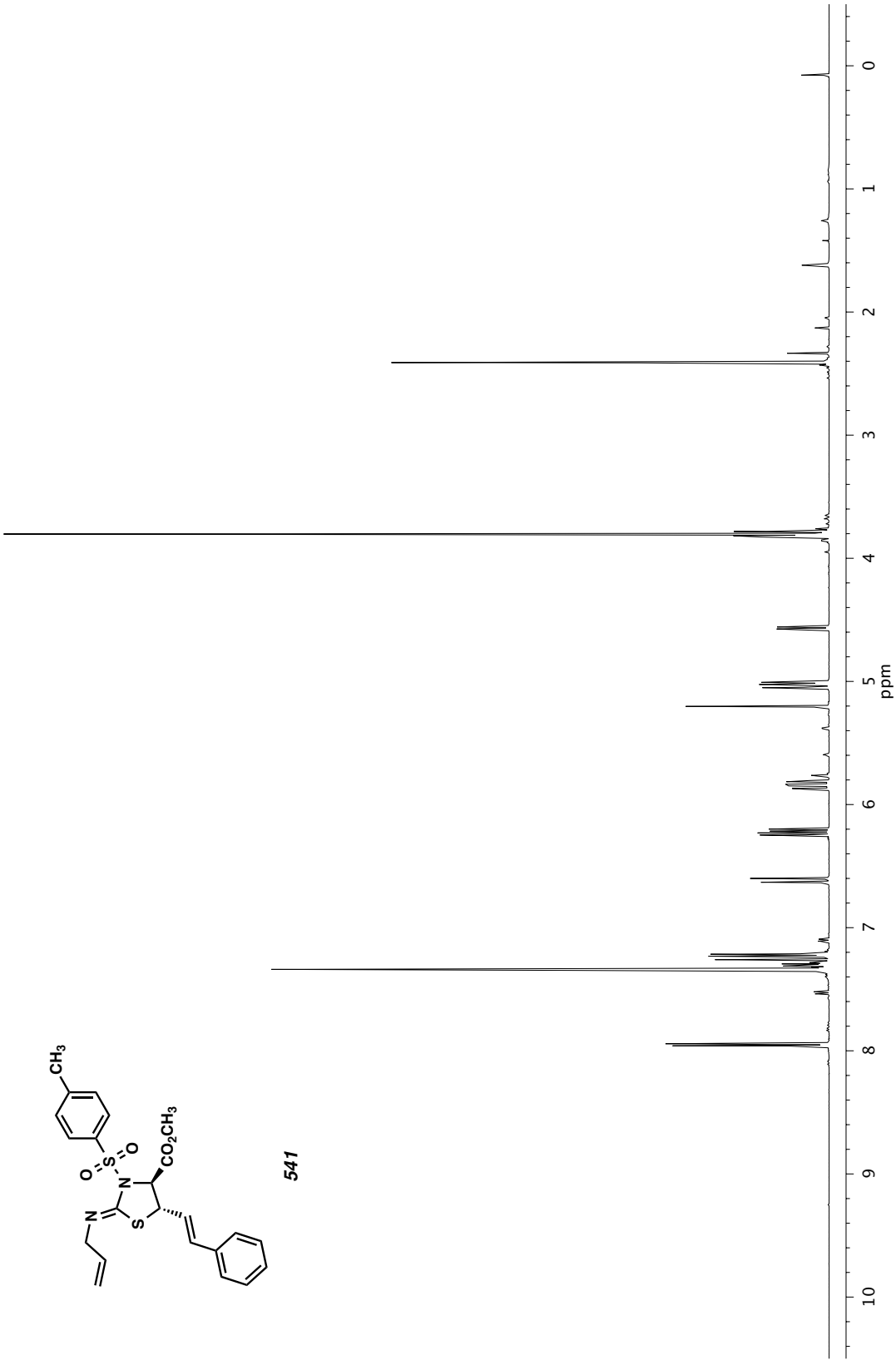


Figure A14.111. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **541**.

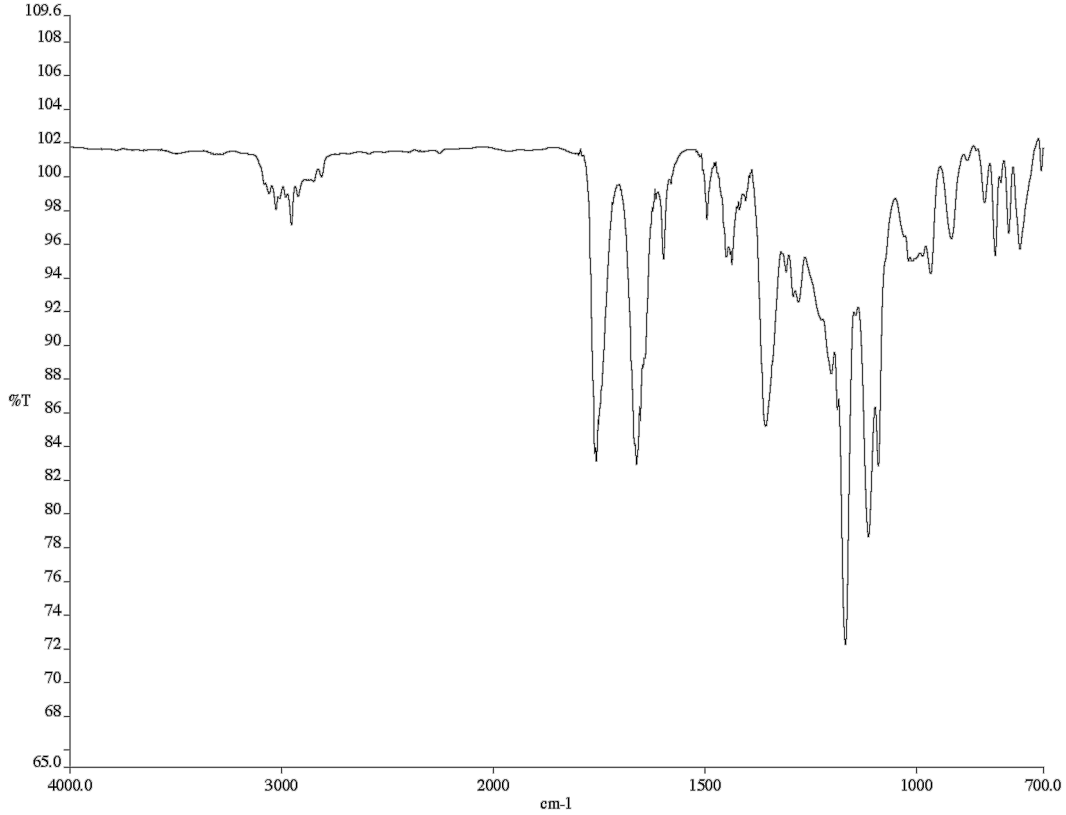


Figure A14.112. Infrared spectrum (thin film/NaCl) of compound **541**.

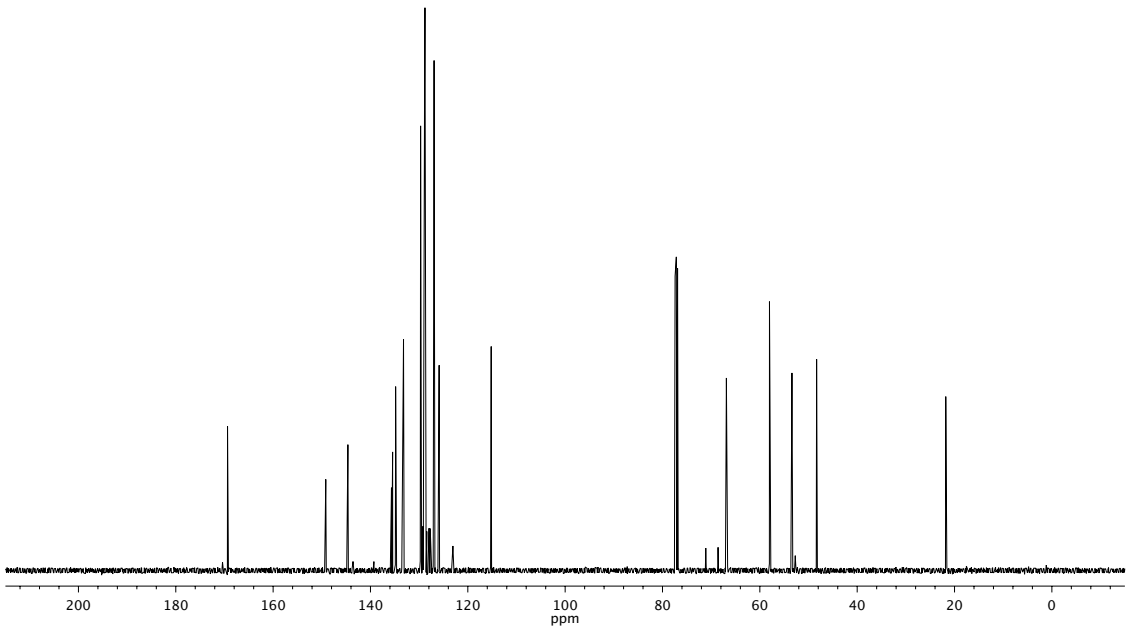


Figure A14.113. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **541**.

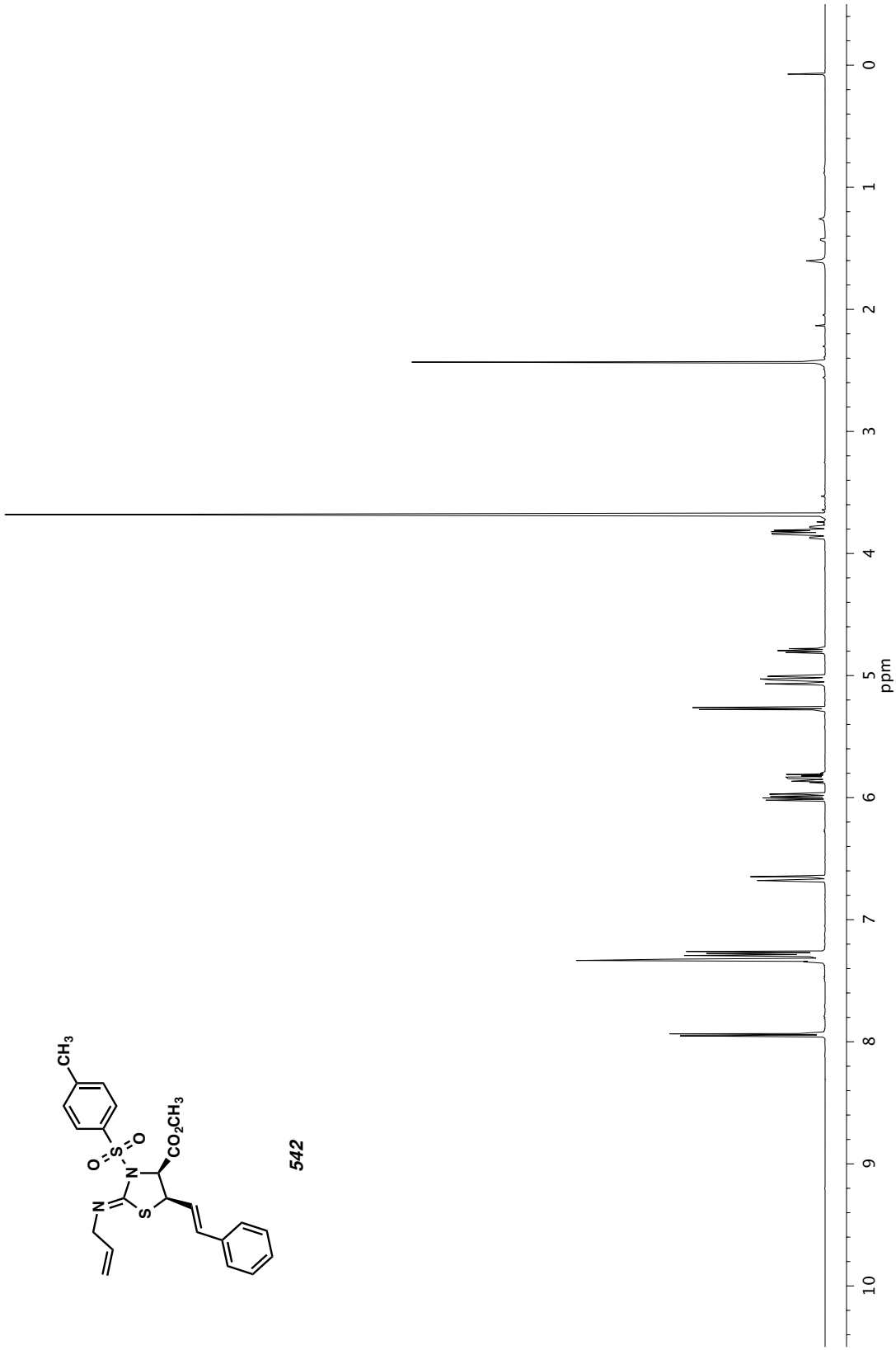


Figure A14.114. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **542**.

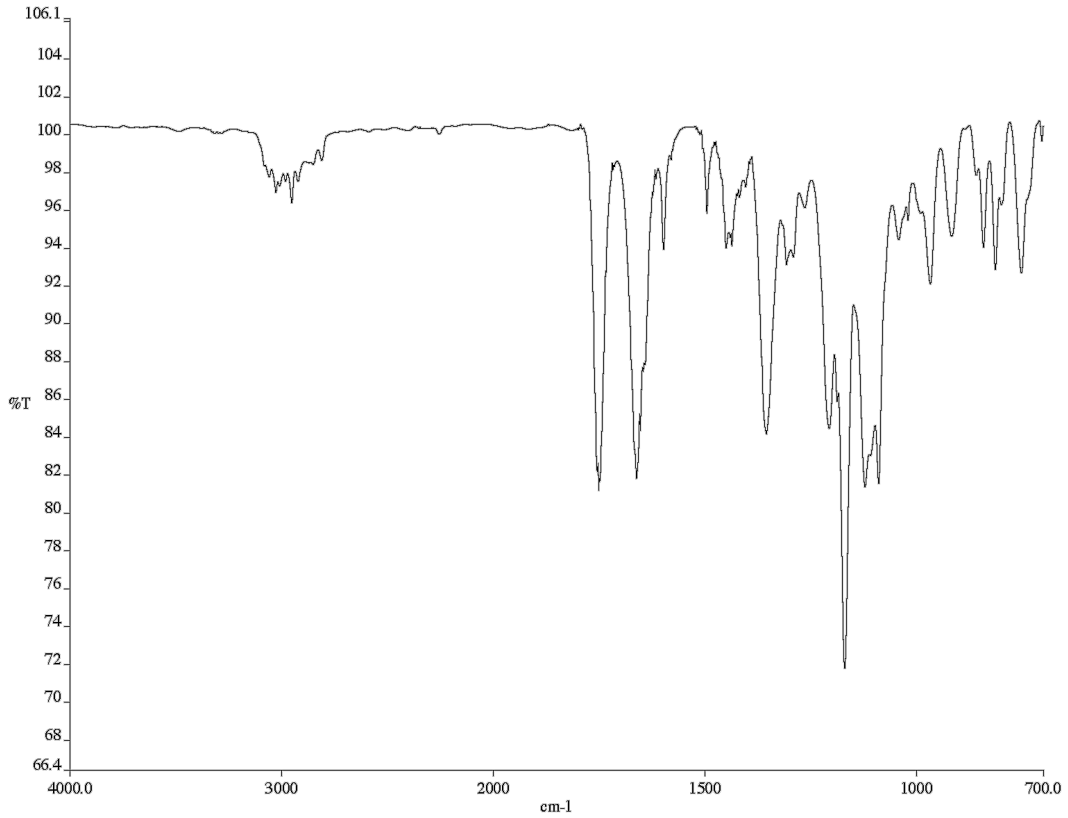


Figure A14.115. Infrared spectrum (thin film/NaCl) of compound **542**.

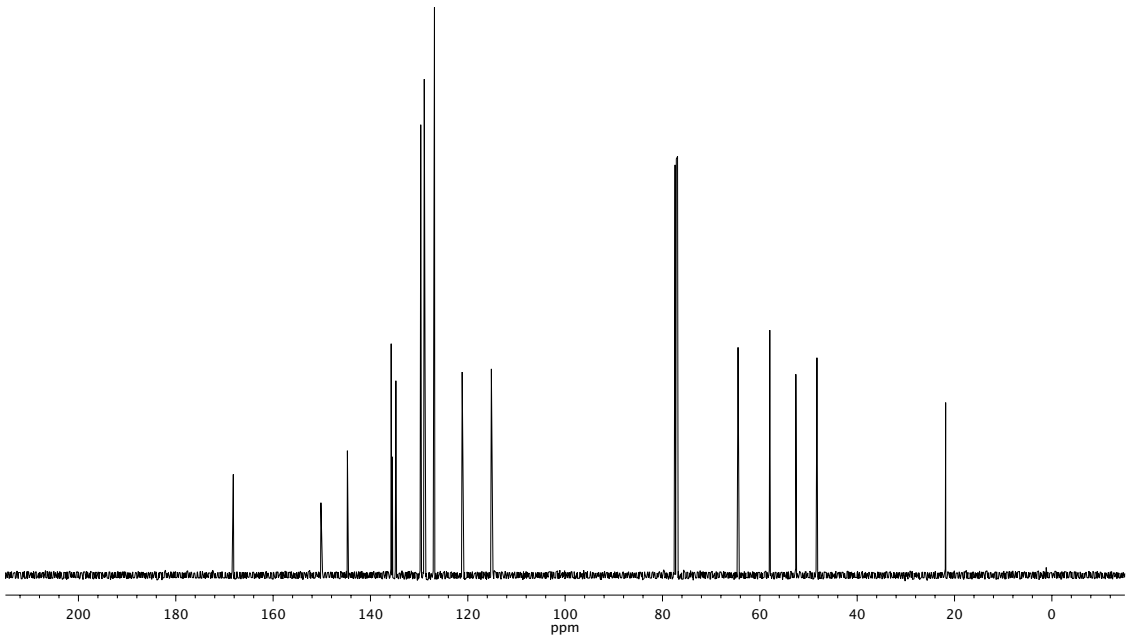


Figure A14.116. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **542**.

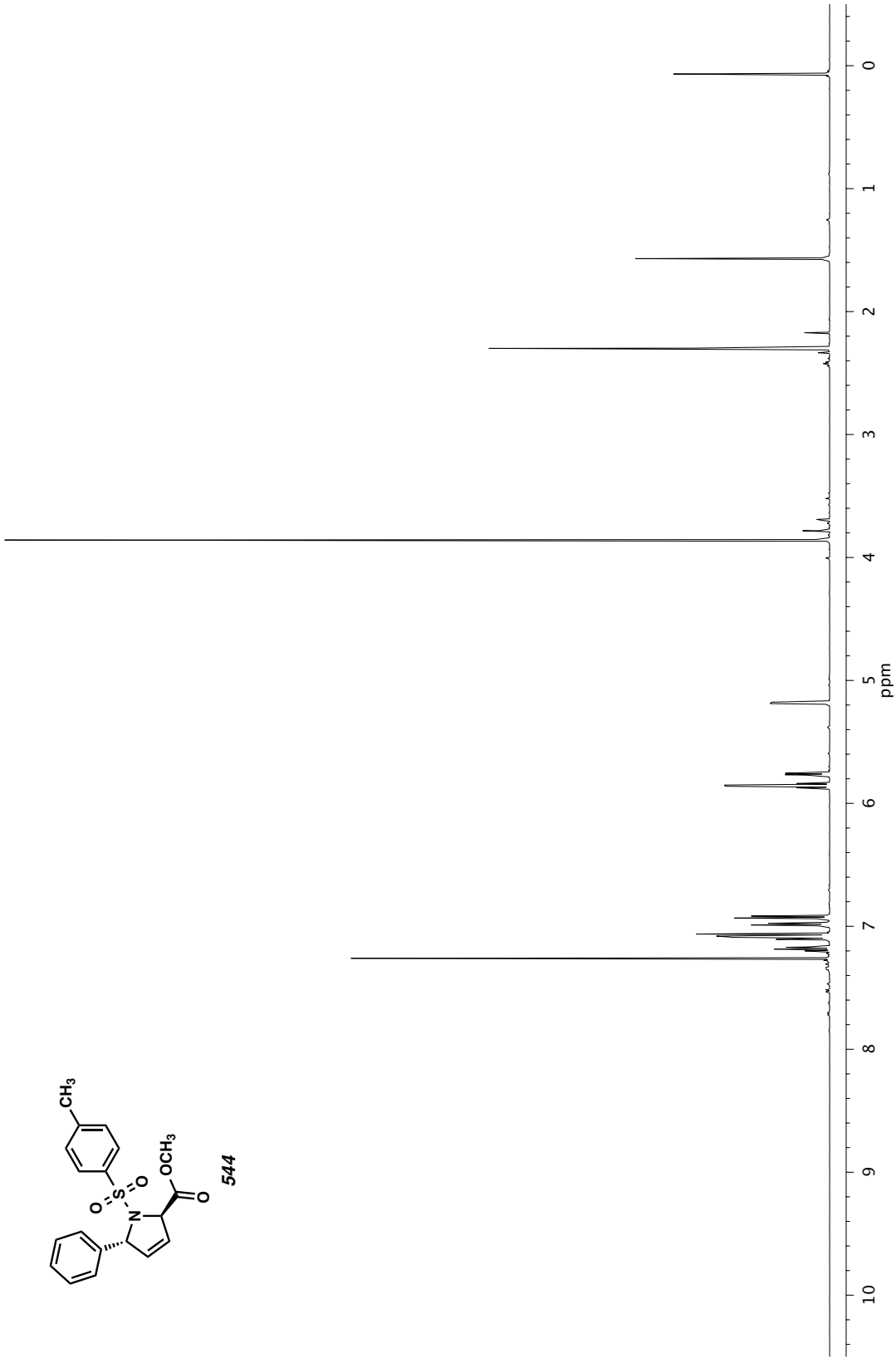


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Figure A14.117. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **544**.

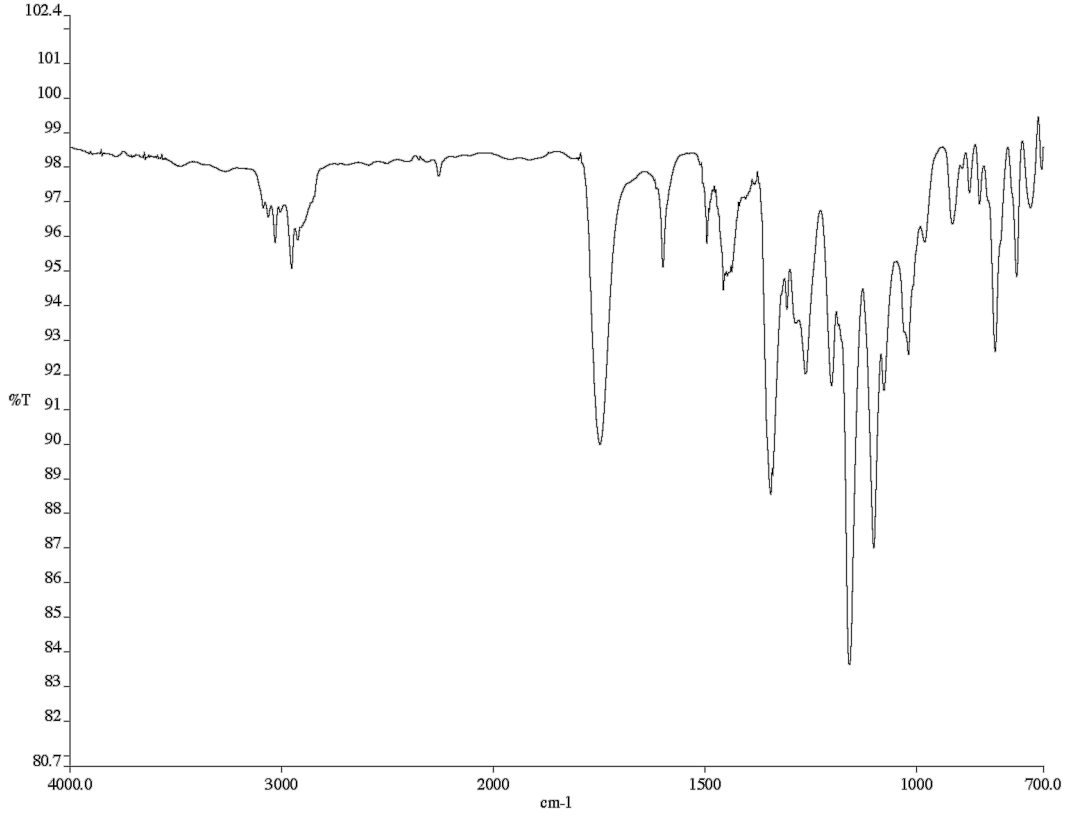


Figure A14.118. Infrared spectrum (thin film/NaCl) of compound **544**.

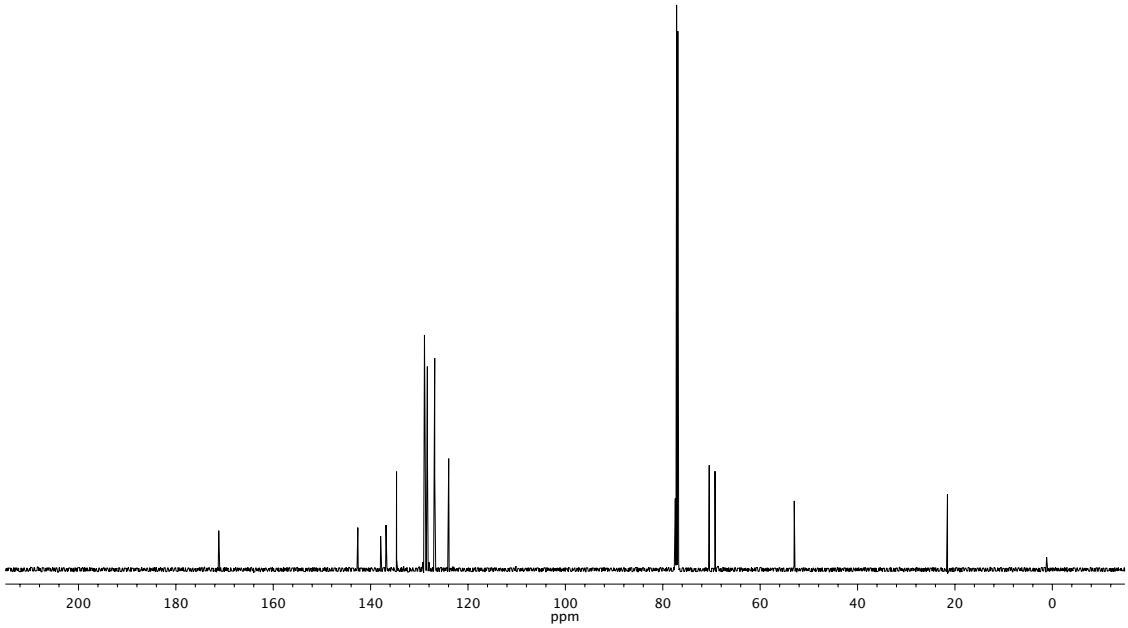


Figure A14.119. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **544**.

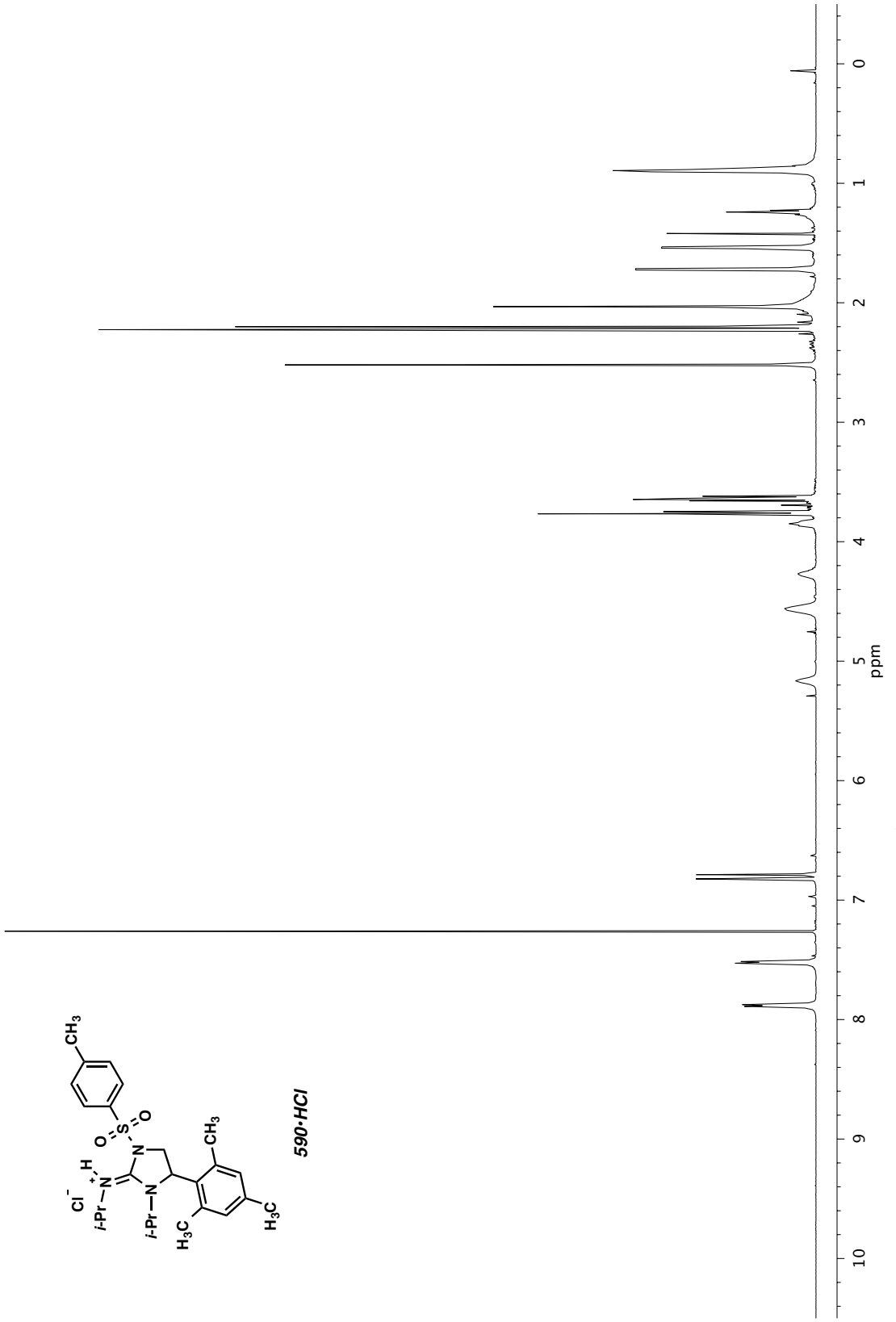


Figure A14.120. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **590 • HCl**.

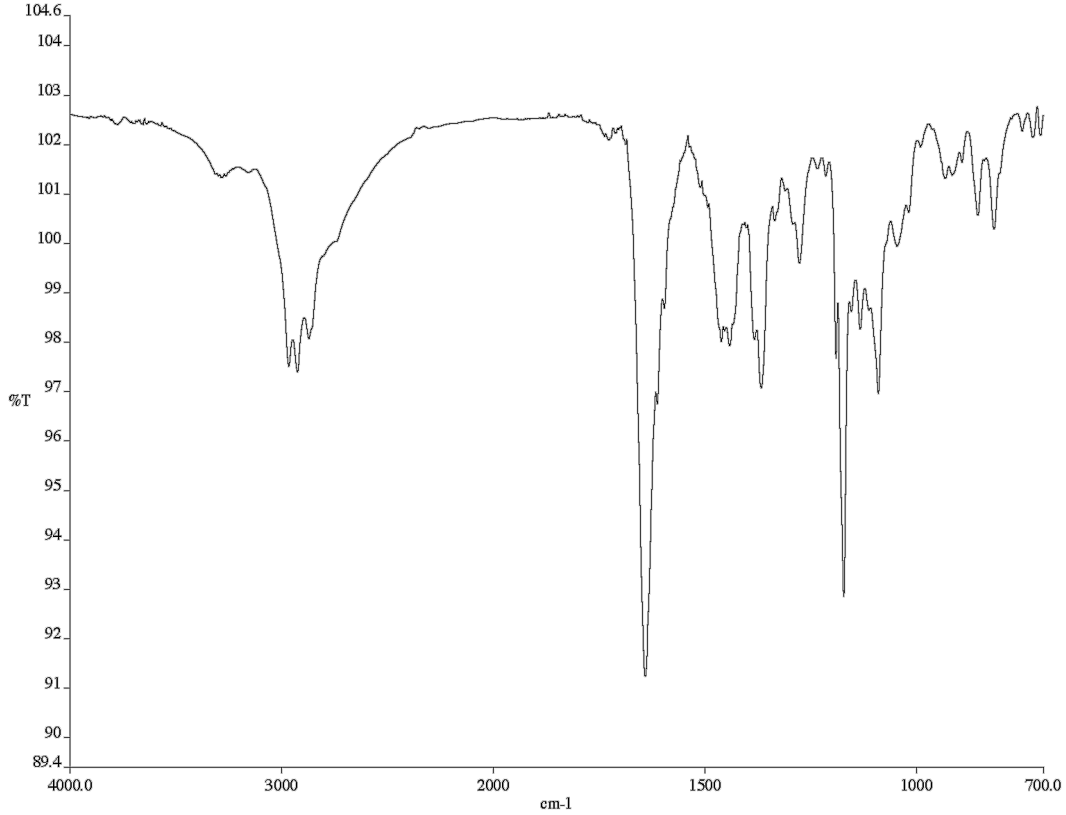


Figure A14.121. Infrared spectrum (Thin Film, NaCl) of compound **590•HCl**.

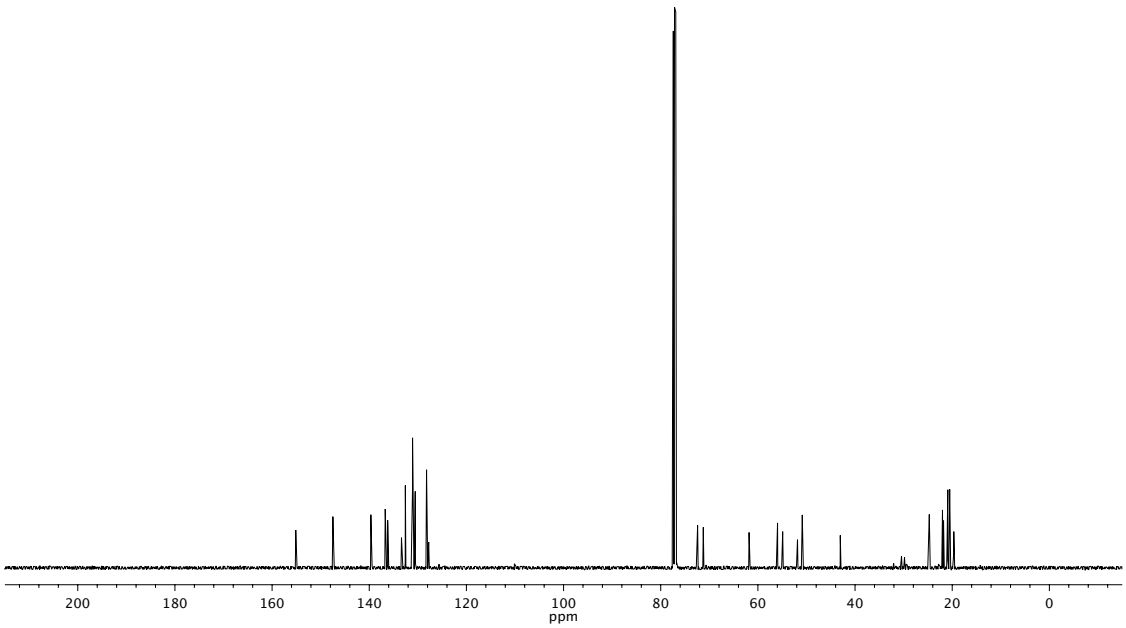


Figure A14.122. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **590•HCl**.

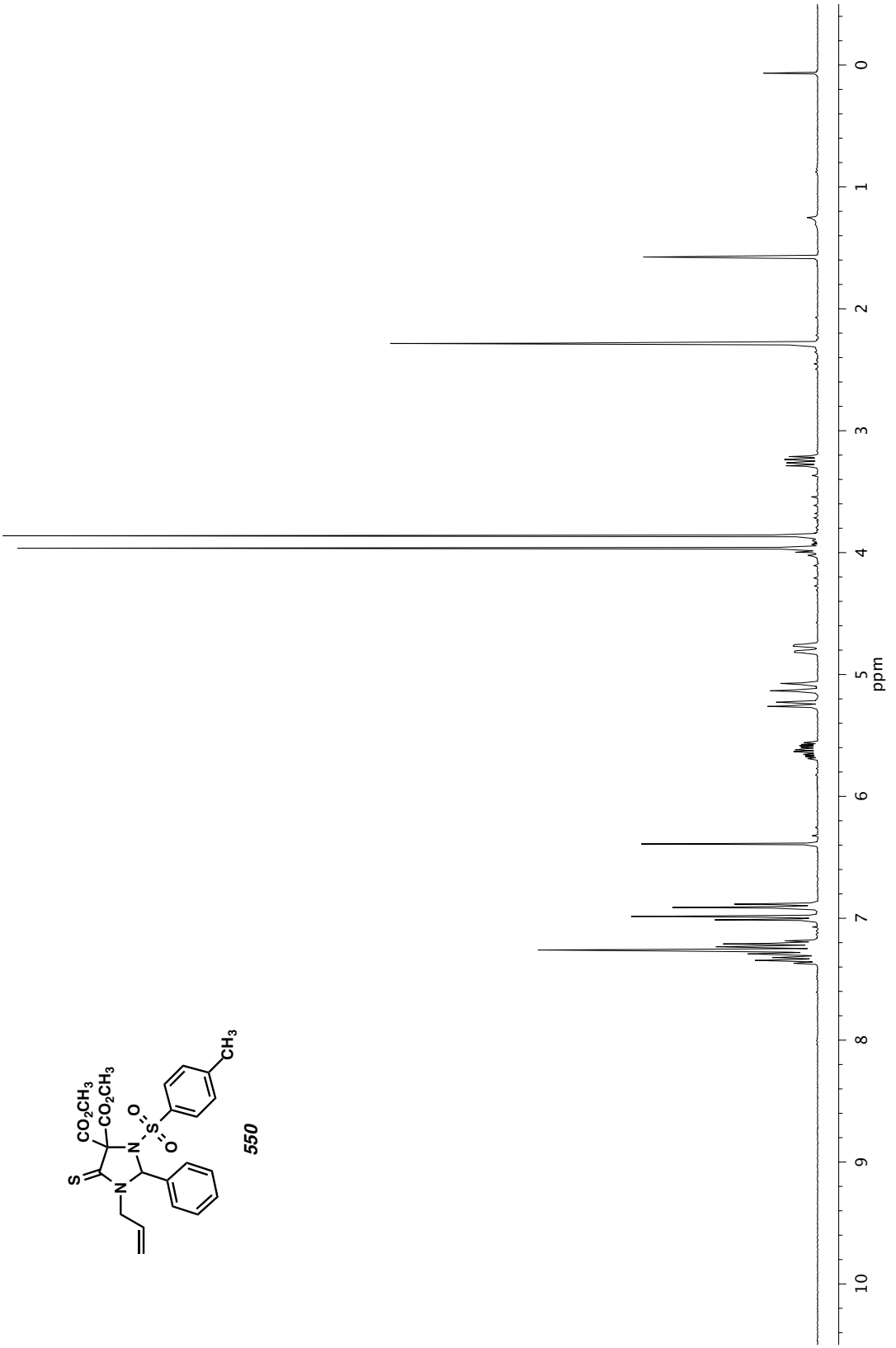


Figure A14.123. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **550**.

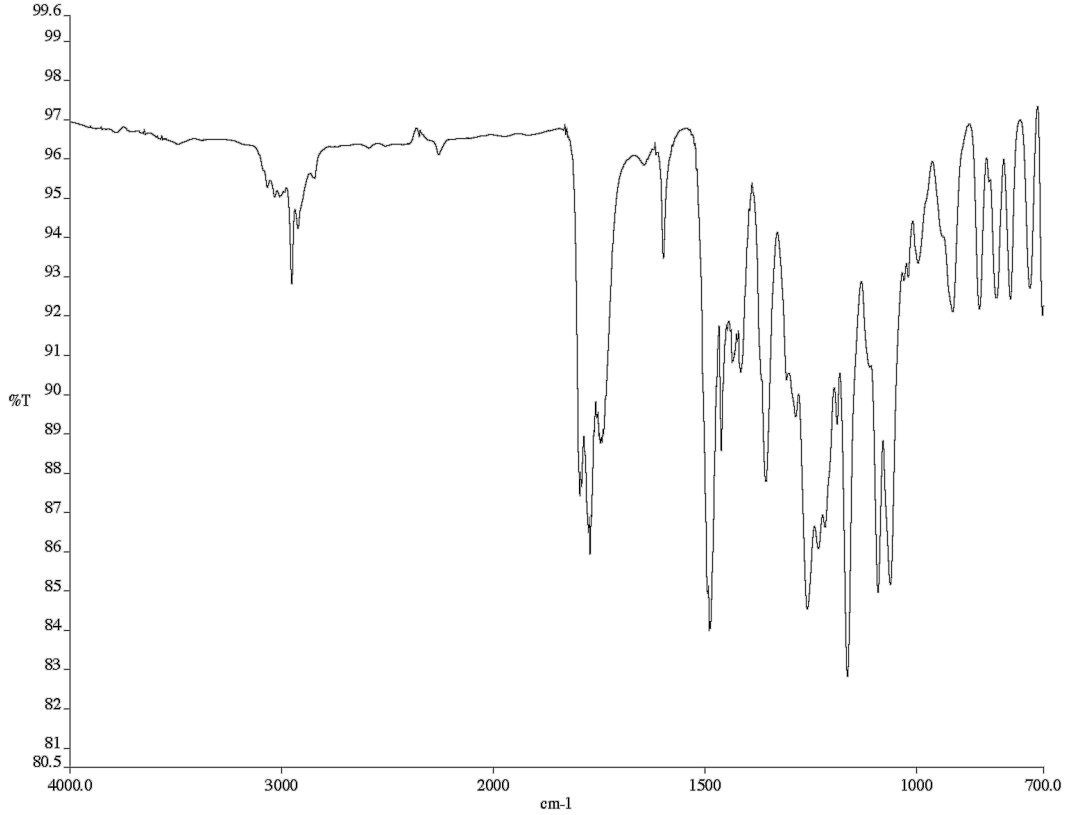


Figure A14.124. Infrared spectrum (thin film/NaCl) of compound **550**.

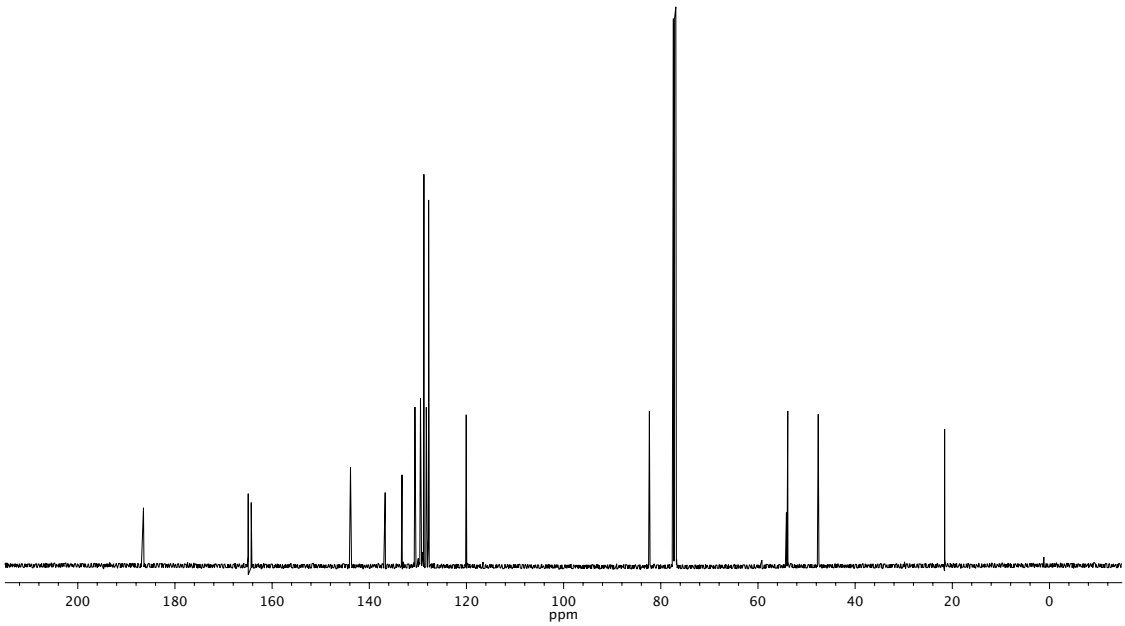


Figure A14.125. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **550**.

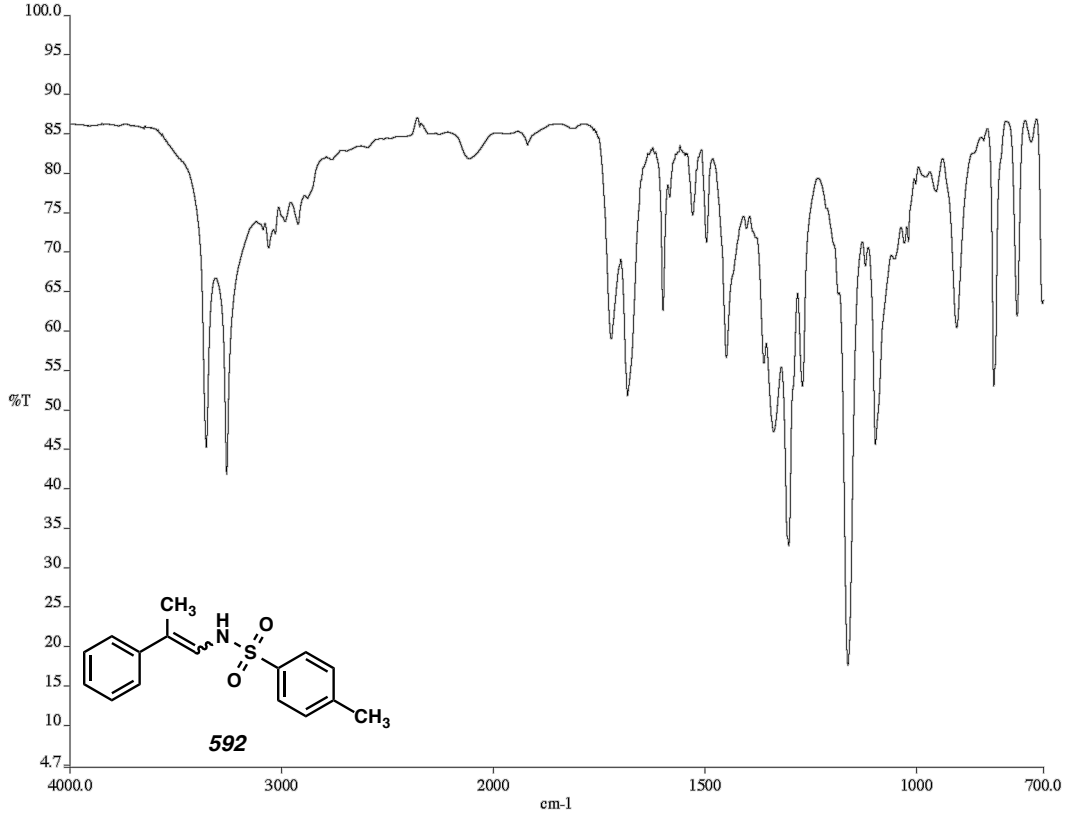


Figure A14.126. Infrared spectrum (thin film/NaCl) of compound **592**.

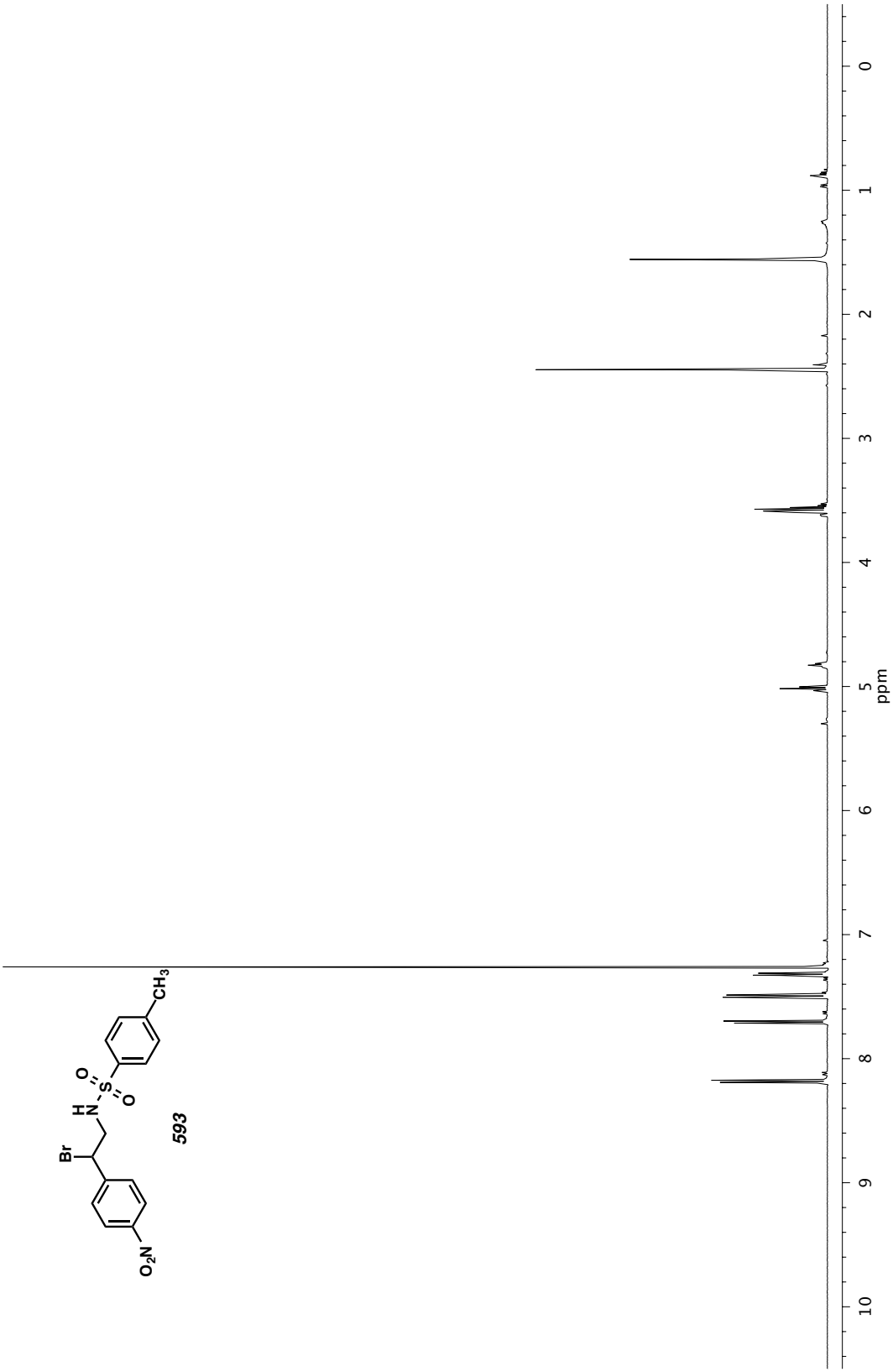


Figure A14.127. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **593**.

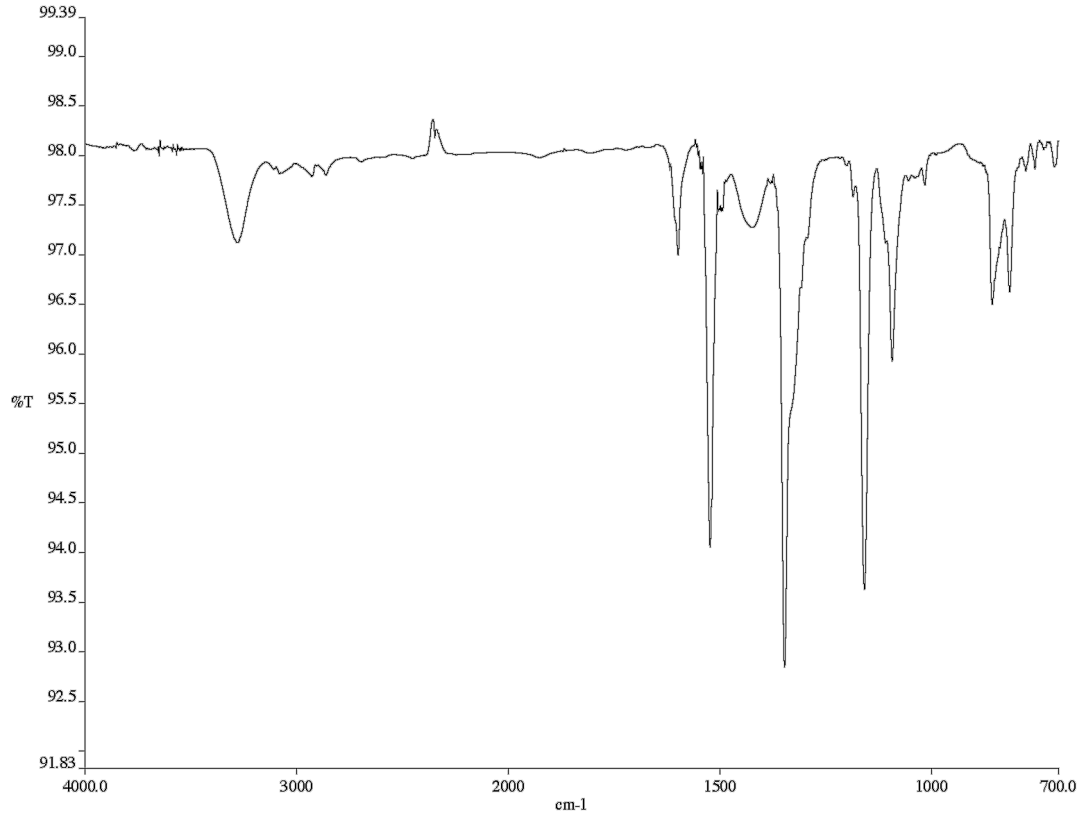


Figure A14.128. Infrared spectrum (thin film/NaCl) of compound **593**.

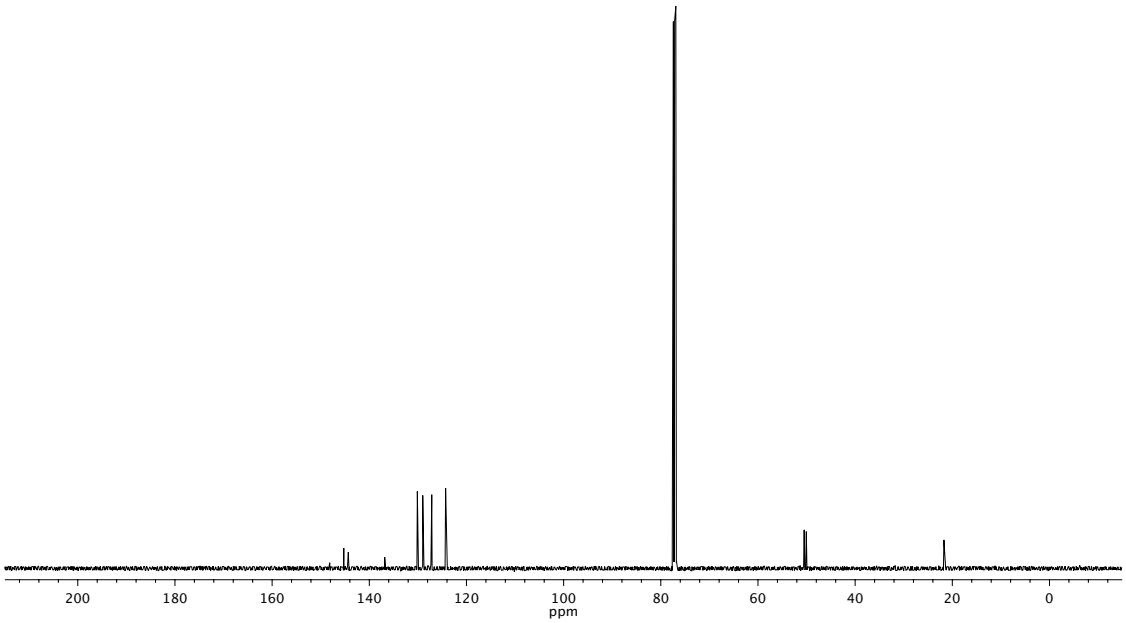


Figure A14.129. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **593**.

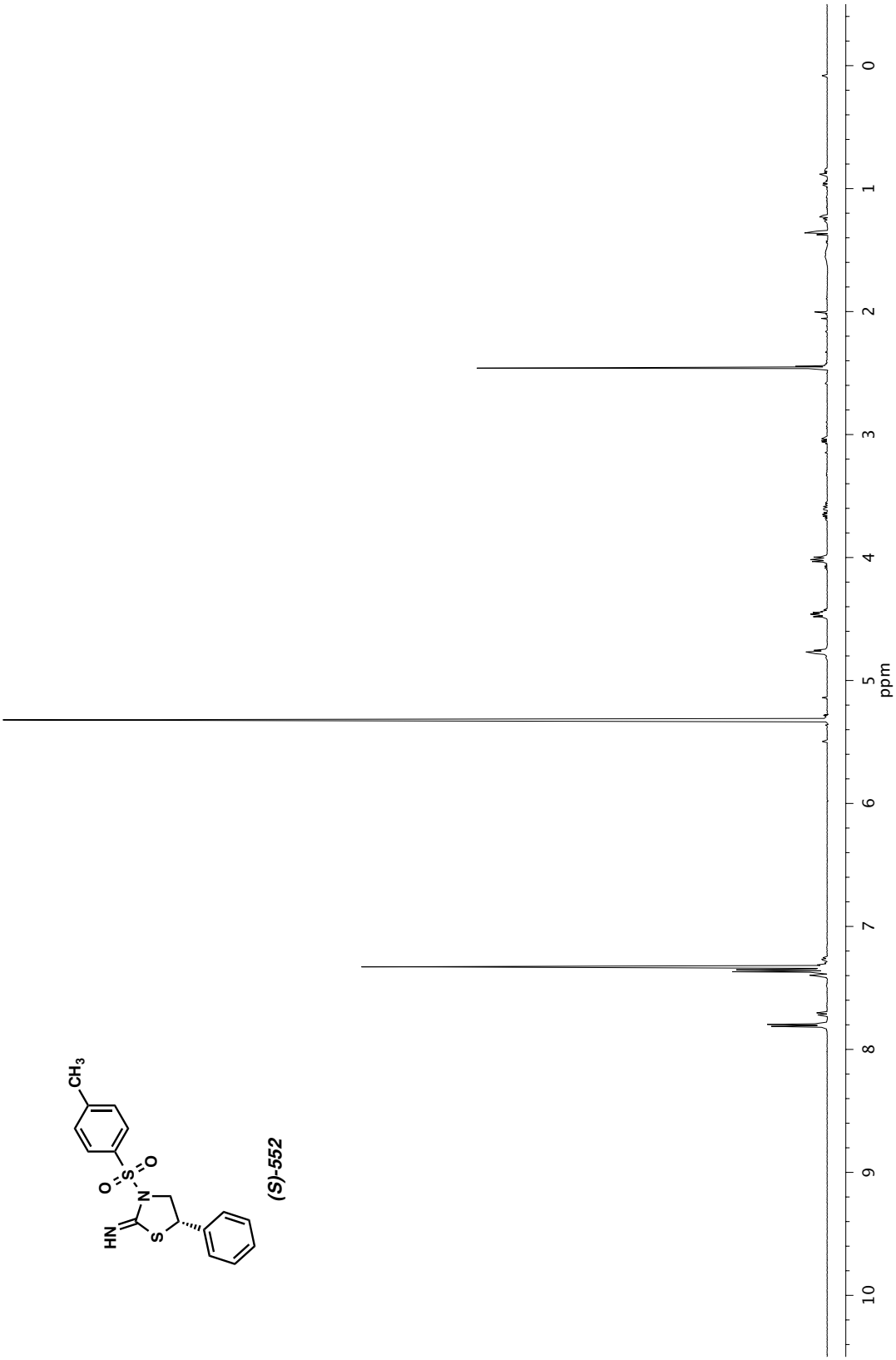


Figure A14.130. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **(*S*)-552**.

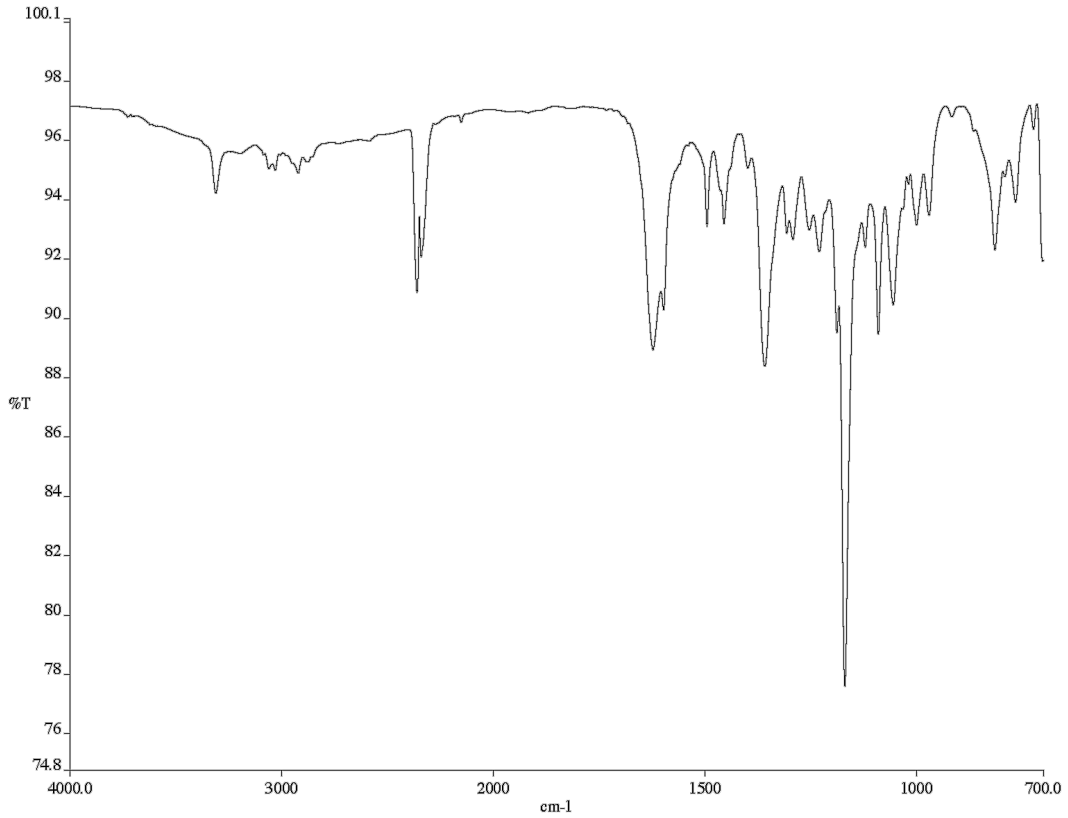


Figure A14.131. Infrared spectrum (Thin Film, NaCl) of compound **(*S*)-552**.

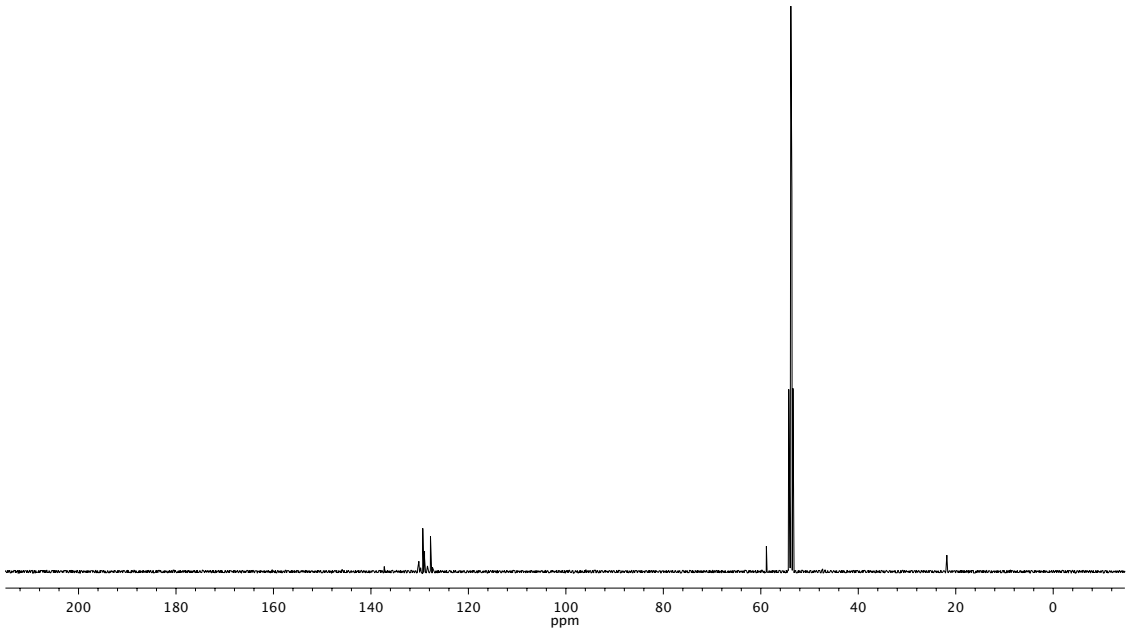


Figure A.14.132. ^{13}C NMR (126 MHz, $CDCl_3$) of compound **(*S*)-552**.

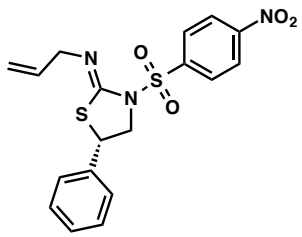
APPENDIX 15

X-Ray Crystallography Reports Relevant to Chapter 6:

Stereoselective Lewis Acid Mediated (3 + 2) Cycloadditions of

N-*H- and* N-*Sulfonylaziridines with Heterocumulenes*

A15.1 X-Ray Crystal Structure Analysis of Thiazolidine (*S*)-522



(S)-522

Contents

Figure A15.1.1. X-Ray Crystal Structure of Thiazolidine ***(S)-522***

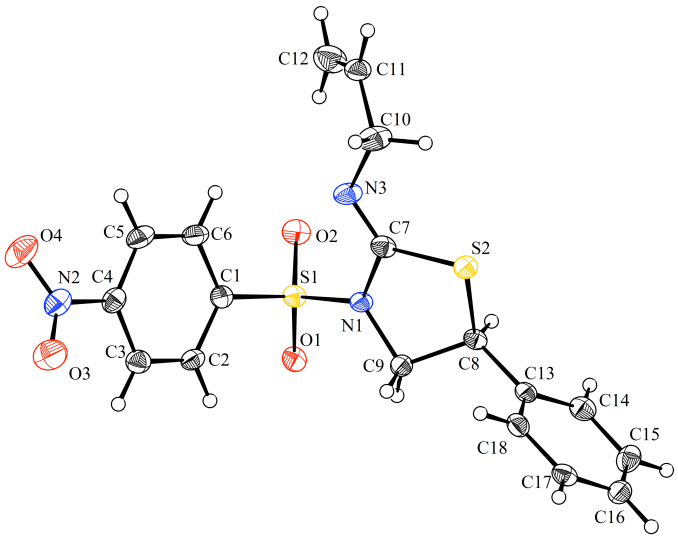


Table A15.1.1. Experimental Details for X-Ray Structure Determination of Thiazolidine ***(S)- 522***

Low-temperature diffraction data (and scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo *K* radiation (= 0.71073 Å) for the structure of thiazolidine **(*S*)-522**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 refinement using established techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Table A15.1.2. Crystal Data and Structure Refinement for Thiazolidine ***(S)-522***

Caltech Identification code	a13024
CCDC Deposition Number	973929
Empirical formula	C18 H17 N3 O4 S2
Formula weight	433.95
Crystallization solvent	Ethyl Acetate/Heptane/Benzene
Crystal shape	blade
Crystal color	colourless
Crystal size	0.04 x 0.11 x 0.40 mm
Preliminary photograph(s)	rotation
Type of diffractometer	Bruker APEX-II CCD
Wavelength	0.71073 Å MoK

Table A15.1.2. (cont'd)

Data collection temperature	100 K	
Theta range for 9894 reflections used in lattice determination	2.34 to 26.36°	
Unit cell dimensions	a = 29.071(2) Å b = 6.0386(5) Å c = 23.0477(19) Å	α= 90° β= 94.233(3)° γ = 90°
Volume	4034.9(6) $Å^3$	
Z	8	
Crystal system	monoclinic	
Space group	C 1 2 1 (# 5)	
Density (calculated)	1.429 g/cm^3	
F(000)	1802	
Theta range for data collection	1.6 to 33.0°	
Completeness to theta = 25.000°	99.9%	
Index ranges	$-42 \le h \le 44, -8 \le k \le 9, -35 \le l \le 35$	
Reflections collected	71248	
Independent reflections	12862 [R_{int}= 0.0785]	
Reflections > 2s(I)	8839	
Average s(I)/(net I)	0.0814	
Absorption coefficient	0.30 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8747	
Primary solution method	dual	
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12862 / 57 / 594	
Treatment of hydrogen atoms	constr	
Goodness-of-fit on F^2	1.01	
Final R indices [I>2s(I), 8839 reflections]	R1 = 0.0523, wR2 = 0.1051	
R indices (all data)	R1 = 0.0985, wR2 = 0.1215	
Type of weighting scheme used	calc	
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0559P)^2^+1.2322P] where P=(Fo^2^+2Fc^2^)/3	
Max shift/error	0.001	

Table AX.XX. (cont'd)

Average shift/error	0.000
Absolute structure parameter	0.08(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.63 and -0.45 e·Å^{-3}

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)
Data collection	APEX2 2013.6-2 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table A15.1.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Thiazolidine ***(S)-522****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
S(1)	8262(1)	-810(2)	7758(1)	19(1)
S(2)	7657(1)	76(2)	9340(1)	21(1)
O(1)	8012(1)	158(4)	7260(1)	22(1)
O(2)	8329(1)	-3134(4)	7794(1)	25(1)
O(3)	10067(1)	5822(5)	8110(1)	40(1)
O(4)	10425(1)	2713(5)	8234(1)	44(1)
N(1)	7986(1)	23(5)	8320(1)	20(1)
N(2)	10073(1)	3806(6)	8126(1)	28(1)
N(3)	8456(1)	-1870(5)	9026(1)	26(1)
C(1)	8809(1)	482(6)	7843(1)	20(1)
C(2)	8859(1)	2557(6)	7599(1)	20(1)
C(3)	9278(1)	3659(6)	7690(1)	24(1)
C(4)	9634(1)	2609(6)	8012(1)	23(1)
C(5)	9595(1)	498(6)	8237(1)	26(1)
C(6)	9177(1)	-574(6)	8158(1)	24(1)

Table A15.1.3. (cont'd)

C(7)	8098(1)	-772(6)	8892(1)	21(1)
C(8)	7276(1)	855(5)	8701(1)	18(1)
C(9)	7616(1)	1693(6)	8273(1)	20(1)
C(10)	8540(1)	-2675(7)	9616(1)	35(1)
C(11)	8739(1)	-4949(7)	9632(1)	26(1)
C(12)	8780(1)	-6214(7)	9179(2)	38(1)
C(13)	6914(1)	2514(6)	8844(1)	19(1)
C(14)	6448(1)	1979(6)	8723(1)	24(1)
C(15)	6108(1)	3500(6)	8831(1)	27(1)
C(16)	6225(1)	5531(6)	9070(1)	26(1)
C(17)	6686(1)	6055(6)	9207(1)	22(1)
C(18)	7027(1)	4541(5)	9093(1)	22(1)
S(1A)	1850(1)	2774(2)	7236(1)	24(1)
S(2A)	2370(2)	1779(14)	5621(2)	32(1)
S(2AA)	2253(3)	897(17)	5560(2)	29(1)
O(1A)	2091(1)	1685(4)	7716(1)	27(1)
O(2A)	1813(1)	5115(5)	7229(1)	31(1)
O(3A)	-335(1)	-199(6)	6712(2)	52(1)
O(4A)	-13(1)	-3389(5)	6842(1)	46(1)
N(1A)	2107(1)	1906(5)	6660(1)	25(1)
N(2A)	0(1)	-1372(6)	6830(1)	33(1)
N(3A)	1711(1)	4307(6)	5995(1)	32(1)
C(1A)	1291(1)	1635(6)	7142(1)	22(1)
C(2A)	1220(1)	-452(6)	7371(1)	26(1)
C(3A)	792(1)	-1444(6)	7274(2)	28(1)
C(4A)	450(1)	-287(7)	6954(2)	28(1)
C(5A)	509(1)	1817(7)	6744(2)	31(1)
C(6A)	940(1)	2785(7)	6830(1)	28(1)
C(7A)	1997(1)	2800(7)	6099(1)	25(1)
C(8A)	2550(1)	-700(8)	6107(2)	39(1)
C(9A)	2328(4)	-430(20)	6676(4)	32(2)
C(9AA)	2448(5)	360(20)	6736(6)	18(3)
C(10A)	1625(1)	5058(8)	5392(1)	38(1)
C(11A)	1359(2)	7136(9)	5353(2)	55(1)

Table A15.1.3. (cont'd)

C(12A)	1227(2)	8304(9)	5780(2)	66(2)
C(13A)	3068(1)	-809(7)	6117(1)	23(1)
C(14A)	3272(1)	-2798(6)	5960(1)	28(1)
C(15A)	3756(1)	-2909(9)	5974(2)	43(1)
C(16A)	4014(1)	-1147(10)	6144(2)	51(1)
C(17A)	3809(2)	801(9)	6298(2)	55(1)
C(18A)	3343(2)	954(7)	6286(2)	39(1)
C(19)	50(20)	8890(100)	4820(20)	234(16)
C(20)	-10(17)	6960(100)	5284(17)	235(14)
C(21)	-90(18)	5080(100)	4796(17)	219(12)
C(22)	168(14)	3320(90)	5179(15)	209(12)
C(23)	33(10)	1280(80)	4797(11)	170(10)
C(24)	9986(11)	1970(170)	10141(12)	340(30)
C(25)	10106(12)	3650(130)	9638(15)	360(30)
C(26)	10000	5830(130)	10000	360(30)
C(27)	9890(13)	7930(120)	9647(18)	370(30)
C(28)	9970(16)	9370(170)	10187(16)	340(30)

Table A15.1.4. Bond lengths [Å] and angles [°] for Thiazolidine ***(S)-522****.*

S(1)-O(1)	1.437(2)
S(1)-O(2)	1.418(3)
S(1)-N(1)	1.653(3)
S(1)-C(1)	1.767(3)
S(2)-C(7)	1.780(3)
S(2)-C(8)	1.839(3)
O(3)-N(2)	1.218(4)
O(4)-N(2)	1.228(4)
N(1)-C(7)	1.416(4)
N(1)-C(9)	1.473(4)
N(2)-C(4)	1.472(4)
N(3)-C(7)	1.253(4)
N(3)-C(10)	1.447(4)
C(1)-C(2)	1.386(5)
C(1)-C(6)	1.401(4)
C(2)-H(2)	0.9500
C(2)-C(3)	1.389(5)
C(3)-H(3)	0.9500
C(3)-C(4)	1.382(4)
C(4)-C(5)	1.384(5)
C(5)-H(5)	0.9500
C(5)-C(6)	1.378(5)
C(6)-H(6)	0.9500
C(8)-H(8)	1.0000
C(8)-C(9)	1.533(4)
C(8)-C(13)	1.508(4)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10C)	0.9900
C(10)-H(10D)	0.9900
C(10)-C(11)	1.490(5)
C(11)-H(11)	0.9500
C(11)-C(12)	1.306(5)
C(12)-H(12C)	0.9500

Table A15.1.4. (cont'd)

C(12)-H(12D)	0.9500
C(13)-C(14)	1.399(4)
C(13)-C(18)	1.383(5)
C(14)-H(14)	0.9500
C(14)-C(15)	1.384(5)
C(15)-H(15)	0.9500
C(15)-C(16)	1.376(5)
C(16)-H(16)	0.9500
C(16)-C(17)	1.390(5)
C(17)-H(17)	0.9500
C(17)-C(18)	1.389(5)
C(18)-H(18)	0.9500
S(1A)-O(1A)	1.426(2)
S(1A)-O(2A)	1.418(3)
S(1A)-N(1A)	1.656(3)
S(1A)-C(1A)	1.763(3)
S(2A)-C(7A)	1.718(4)
S(2A)-C(8A)	1.919(6)
S(2AA)-C(7A)	1.886(7)
S(2AA)-C(8A)	1.763(6)
O(3A)-N(2A)	1.218(4)
O(4A)-N(2A)	1.219(4)
N(1A)-C(7A)	1.415(4)
N(1A)-C(9A)	1.548(12)
N(1A)-C(9AA)	1.364(14)
N(2A)-C(4A)	1.472(5)
N(3A)-C(7A)	1.243(5)
N(3A)-C(10A)	1.465(4)
C(1A)-C(2A)	1.388(5)
C(1A)-C(6A)	1.389(5)
C(2A)-H(2A)	0.9500
C(2A)-C(3A)	1.384(5)
C(3A)-H(3A)	0.9500
C(3A)-C(4A)	1.384(5)

Table A15.1.4. (cont'd)

C(4A)-C(5A)	1.375(6)
C(5A)-H(5A)	0.9500
C(5A)-C(6A)	1.383(5)
C(6A)-H(6A)	0.9500
C(8A)-H(8A)	1.0000
C(8A)-H(8AA)	1.0000
C(8A)-C(9A)	1.512(10)
C(8A)-C(9AA)	1.630(13)
C(8A)-C(13A)	1.506(5)
C(9A)-H(9AA)	0.9900
C(9A)-H(9AB)	0.9900
C(9AA)-H(9AC)	0.9900
C(9AA)-H(9AD)	0.9900
C(10A)-H(10A)	0.9900
C(10A)-H(10B)	0.9900
C(10A)-C(11A)	1.473(6)
C(11A)-H(11A)	0.9500
C(11A)-C(12A)	1.293(6)
C(12A)-H(12A)	0.9500
C(12A)-H(12B)	0.9500
C(13A)-C(14A)	1.399(5)
C(13A)-C(18A)	1.370(5)
C(14A)-H(14A)	0.9500
C(14A)-C(15A)	1.409(5)
C(15A)-H(15A)	0.9500
C(15A)-C(16A)	1.343(7)
C(16A)-H(16A)	0.9500
C(16A)-C(17A)	1.378(7)
C(17A)-H(17A)	0.9500
C(17A)-C(18A)	1.358(7)
C(18A)-H(18A)	0.9500
C(19)-C(19)#1	0.90(10)
C(19)-C(20)	1.60(2)
C(19)-C(20)#1	1.20(4)

Table A15.1.4. (cont'd)

C(19)-C(23)#2	1.45(4)
C(19)-C(23)#3	1.72(4)
C(20)-C(19)#1	1.20(4)
C(20)-C(20)#1	1.31(8)
C(20)-C(21)#1	1.19(4)
C(20)-C(21)	1.60(2)
C(21)-C(20)#1	1.19(4)
C(21)-C(21)#1	1.04(7)
C(21)-C(22)#1	1.09(4)
C(21)-C(22)	1.54(2)
C(22)-C(21)#1	1.09(4)
C(22)-C(22)#1	1.23(7)
C(22)-C(23)#1	1.37(4)
C(22)-C(23)	1.55(2)
C(23)-C(19)#4	1.72(4)
C(23)-C(19)#5	1.45(4)
C(23)-C(22)#1	1.37(4)
C(23)-C(23)#1	0.97(4)
C(24)-C(24)#6	0.66(5)
C(24)-C(25)	1.60(2)
C(24)-C(25)#6	1.18(5)
C(24)-C(28)#5	1.57(7)
C(24)-C(28)#7	1.75(6)
C(25)-C(24)#6	1.18(5)
C(25)-C(25)#6	1.82(7)
C(25)-C(26)	1.60(2)
C(26)-C(25)#6	1.60(2)
C(26)-C(27)#6	1.53(2)
C(26)-C(27)	1.53(2)
C(27)-C(27)#6	1.70(8)
C(27)-C(28)	1.52(2)
C(27)-C(28)#6	1.02(6)
C(28)-C(24)#8	1.75(6)
C(28)-C(24)#2	1.57(7)

Table A15.1.4. (cont'd)

C(28)-C(27)#6	1.02(6)
C(28)-C(28)#6	0.89(9)
O(1)-S(1)-N(1)	104.85(13)
O(1)-S(1)-C(1)	107.87(15)
O(2)-S(1)-O(1)	120.48(15)
O(2)-S(1)-N(1)	109.13(15)
O(2)-S(1)-C(1)	108.25(15)
N(1)-S(1)-C(1)	105.26(14)
C(7)-S(2)-C(8)	91.39(14)
C(7)-N(1)-S(1)	122.3(2)
C(7)-N(1)-C(9)	114.6(2)
C(9)-N(1)-S(1)	123.0(2)
O(3)-N(2)-O(4)	123.6(3)
O(3)-N(2)-C(4)	118.4(3)
O(4)-N(2)-C(4)	118.0(3)
C(7)-N(3)-C(10)	119.3(3)
C(2)-C(1)-S(1)	118.3(2)
C(2)-C(1)-C(6)	121.5(3)
C(6)-C(1)-S(1)	120.2(3)
C(1)-C(2)-H(2)	120.4
C(1)-C(2)-C(3)	119.3(3)
C(3)-C(2)-H(2)	120.4
C(2)-C(3)-H(3)	120.8
C(4)-C(3)-C(2)	118.3(3)
C(4)-C(3)-H(3)	120.8
C(3)-C(4)-N(2)	118.4(3)
C(3)-C(4)-C(5)	123.0(3)
C(5)-C(4)-N(2)	118.6(3)
C(4)-C(5)-H(5)	120.7
C(6)-C(5)-C(4)	118.6(3)
C(6)-C(5)-H(5)	120.7
C(1)-C(6)-H(6)	120.4
C(5)-C(6)-C(1)	119.2(3)
C(5)-C(6)-H(6)	120.4

Table A15.1.4. (cont'd)

N(1)-C(7)-S(2)	108.5(2)
N(3)-C(7)-S(2)	129.0(2)
N(3)-C(7)-N(1)	122.5(3)
S(2)-C(8)-H(8)	108.9
C(9)-C(8)-S(2)	102.8(2)
C(9)-C(8)-H(8)	108.9
C(13)-C(8)-S(2)	112.5(2)
C(13)-C(8)-H(8)	108.9
C(13)-C(8)-C(9)	114.6(3)
N(1)-C(9)-C(8)	103.2(2)
N(1)-C(9)-H(9A)	111.1
N(1)-C(9)-H(9B)	111.1
C(8)-C(9)-H(9A)	111.1
C(8)-C(9)-H(9B)	111.1
H(9A)-C(9)-H(9B)	109.1
N(3)-C(10)-H(10C)	109.3
N(3)-C(10)-H(10D)	109.3
N(3)-C(10)-C(11)	111.8(3)
H(10C)-C(10)-H(10D)	107.9
C(11)-C(10)-H(10C)	109.3
C(11)-C(10)-H(10D)	109.3
C(10)-C(11)-H(11)	117.4
C(12)-C(11)-C(10)	125.3(3)
C(12)-C(11)-H(11)	117.4
C(11)-C(12)-H(12C)	120.0
C(11)-C(12)-H(12D)	120.0
H(12C)-C(12)-H(12D)	120.0
C(14)-C(13)-C(8)	119.0(3)
C(18)-C(13)-C(8)	122.0(3)
C(18)-C(13)-C(14)	119.0(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-C(13)	120.2(3)
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-H(15)	119.8

Table A15.1.4. (cont'd)

C(16)-C(15)-C(14)	120.4(3)
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-H(16)	120.1
C(15)-C(16)-C(17)	119.8(3)
C(17)-C(16)-H(16)	120.1
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-C(16)	119.9(3)
C(18)-C(17)-H(17)	120.1
C(13)-C(18)-C(17)	120.6(3)
C(13)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.7
O(1A)-S(1A)-N(1A)	104.59(15)
O(1A)-S(1A)-C(1A)	108.09(16)
O(2A)-S(1A)-O(1A)	120.09(16)
O(2A)-S(1A)-N(1A)	110.18(16)
O(2A)-S(1A)-C(1A)	108.57(17)
N(1A)-S(1A)-C(1A)	104.15(15)
C(7A)-S(2A)-C(8A)	93.6(2)
C(8A)-S(2AA)-C(7A)	93.3(2)
C(7A)-N(1A)-S(1A)	121.7(3)
C(7A)-N(1A)-C(9A)	115.8(5)
C(9A)-N(1A)-S(1A)	118.7(4)
C(9AA)-N(1A)-S(1A)	118.7(6)
C(9AA)-N(1A)-C(7A)	119.5(6)
O(3A)-N(2A)-O(4A)	124.1(4)
O(3A)-N(2A)-C(4A)	118.0(3)
O(4A)-N(2A)-C(4A)	117.9(3)
C(7A)-N(3A)-C(10A)	118.3(3)
C(2A)-C(1A)-S(1A)	118.0(3)
C(2A)-C(1A)-C(6A)	121.7(3)
C(6A)-C(1A)-S(1A)	120.3(3)
C(1A)-C(2A)-H(2A)	120.4
C(3A)-C(2A)-C(1A)	119.2(3)
C(3A)-C(2A)-H(2A)	120.4

Table A15.1.4. (cont'd)

C(2A)-C(3A)-H(3A)	121.0
C(2A)-C(3A)-C(4A)	118.0(3)
C(4A)-C(3A)-H(3A)	121.0
C(3A)-C(4A)-N(2A)	118.2(3)
C(5A)-C(4A)-N(2A)	118.4(3)
C(5A)-C(4A)-C(3A)	123.4(3)
C(4A)-C(5A)-H(5A)	120.8
C(4A)-C(5A)-C(6A)	118.4(4)
C(6A)-C(5A)-H(5A)	120.8
C(1A)-C(6A)-H(6A)	120.4
C(5A)-C(6A)-C(1A)	119.1(4)
C(5A)-C(6A)-H(6A)	120.4
N(1A)-C(7A)-S(2A)	109.7(3)
N(1A)-C(7A)-S(2AA)	107.2(3)
N(3A)-C(7A)-S(2A)	125.7(3)
N(3A)-C(7A)-S(2AA)	127.5(3)
N(3A)-C(7A)-N(1A)	124.0(3)
S(2A)-C(8A)-H(8A)	108.0
S(2AA)-C(8A)-H(8AA)	108.6
C(9A)-C(8A)-S(2A)	107.8(5)
C(9A)-C(8A)-H(8A)	108.0
C(9AA)-C(8A)-S(2AA)	108.1(6)
C(9AA)-C(8A)-H(8AA)	108.6
C(13A)-C(8A)-S(2A)	105.7(3)
C(13A)-C(8A)-S(2AA)	118.1(4)
C(13A)-C(8A)-H(8A)	108.0
C(13A)-C(8A)-H(8AA)	108.6
C(13A)-C(8A)-C(9A)	118.8(5)
C(13A)-C(8A)-C(9AA)	104.6(6)
N(1A)-C(9A)-H(9AA)	110.5
N(1A)-C(9A)-H(9AB)	110.5
C(8A)-C(9A)-N(1A)	106.3(7)
C(8A)-C(9A)-H(9AA)	110.5
C(8A)-C(9A)-H(9AB)	110.5

Table A15.1.4. (cont'd)

H(9AA)-C(9A)-H(9AB)	108.7
N(1A)-C(9AA)-C(8A)	109.4(9)
N(1A)-C(9AA)-H(9AC)	109.8
N(1A)-C(9AA)-H(9AD)	109.8
C(8A)-C(9AA)-H(9AC)	109.8
C(8A)-C(9AA)-H(9AD)	109.8
H(9AC)-C(9AA)-H(9AD)	108.2
N(3A)-C(10A)-H(10A)	109.2
N(3A)-C(10A)-H(10B)	109.2
N(3A)-C(10A)-C(11A)	112.0(3)
H(10A)-C(10A)-H(10B)	107.9
C(11A)-C(10A)-H(10A)	109.2
C(11A)-C(10A)-H(10B)	109.2
C(10A)-C(11A)-H(11A)	116.5
C(12A)-C(11A)-C(10A)	127.0(4)
C(12A)-C(11A)-H(11A)	116.5
C(11A)-C(12A)-H(12A)	120.0
C(11A)-C(12A)-H(12B)	120.0
H(12A)-C(12A)-H(12B)	120.0
C(14A)-C(13A)-C(8A)	118.4(4)
C(18A)-C(13A)-C(8A)	122.1(4)
C(18A)-C(13A)-C(14A)	119.5(3)
C(13A)-C(14A)-H(14A)	120.8
C(13A)-C(14A)-C(15A)	118.4(4)
C(15A)-C(14A)-H(14A)	120.8
C(14A)-C(15A)-H(15A)	119.8
C(16A)-C(15A)-C(14A)	120.4(4)
C(16A)-C(15A)-H(15A)	119.8
C(15A)-C(16A)-H(16A)	119.7
C(15A)-C(16A)-C(17A)	120.5(4)
C(17A)-C(16A)-H(16A)	119.7
C(16A)-C(17A)-H(17A)	119.9
C(18A)-C(17A)-C(16A)	120.2(4)
C(18A)-C(17A)-H(17A)	119.9

Table A15.1.4. (cont'd)

C(13A)-C(18A)-H(18A)	119.6
C(17A)-C(18A)-C(13A)	120.9(4)
C(17A)-C(18A)-H(18A)	119.6
C(19)#1-C(19)-C(20)#1	98(4)
C(19)#1-C(19)-C(20)	48(2)
C(19)#1-C(19)-C(23)#2	91(2)
C(19)#1-C(19)-C(23)#3	57.4(16)
C(20)#1-C(19)-C(20)	54(4)
C(20)#1-C(19)-C(23)#2	164(6)
C(20)-C(19)-C(23)#3	104(3)
C(20)#1-C(19)-C(23)#3	155(5)
C(23)#2-C(19)-C(20)	139(4)
C(23)#2-C(19)-C(23)#3	34.3(18)
C(19)#1-C(20)-C(19)	34(4)
C(19)#1-C(20)-C(20)#1	79(4)
C(19)-C(20)-C(21)	94(3)
C(19)#1-C(20)-C(21)	123(4)
C(20)#1-C(20)-C(19)	47.3(19)
C(20)#1-C(20)-C(21)	46.9(19)
C(21)#1-C(20)-C(19)	124(4)
C(21)#1-C(20)-C(19)#1	157(7)
C(21)#1-C(20)-C(20)#1	79(3)
C(21)#1-C(20)-C(21)	41(3)
C(20)#1-C(21)-C(20)	54(4)
C(20)#1-C(21)-C(22)	129(4)
C(21)#1-C(21)-C(20)#1	92(4)
C(21)#1-C(21)-C(20)	48(2)
C(21)#1-C(21)-C(22)	44.9(19)
C(21)#1-C(21)-C(22)#1	93(3)
C(22)#1-C(21)-C(20)#1	174(6)
C(22)#1-C(21)-C(20)	132(4)
C(22)-C(21)-C(20)	93(2)
C(22)#1-C(21)-C(22)	53(4)
C(21)#1-C(22)-C(21)	42(4)

Table A15.1.4. (cont'd)

C(21)#1-C(22)-C(22)#1	83(3)
C(21)#1-C(22)-C(23)#1	142(5)
C(21)#1-C(22)-C(23)	139(4)
C(21)-C(22)-C(23)	97(2)
C(22)#1-C(22)-C(21)	44.5(17)
C(22)#1-C(22)-C(23)#1	73(2)
C(22)#1-C(22)-C(23)	57.5(18)
C(23)#1-C(22)-C(21)	117(3)
C(23)#1-C(22)-C(23)	38.1(19)
C(19)#5-C(23)-C(19)#4	31(3)
C(19)#5-C(23)-C(22)	140(4)
C(22)-C(23)-C(19)#4	115(2)
C(22)#1-C(23)-C(19)#5	156(4)
C(22)#1-C(23)-C(19)#4	131(3)
C(22)#1-C(23)-C(22)	50(3)
C(23)#1-C(23)-C(19)#5	88(2)
C(23)#1-C(23)-C(19)#4	57.4(15)
C(23)#1-C(23)-C(22)	61(2)
C(23)#1-C(23)-C(22)#1	81.2(19)
C(24)#6-C(24)-C(25)#6	118(3)
C(24)#6-C(24)-C(25)	40(2)
C(24)#6-C(24)-C(28)#5	94(2)
C(24)#6-C(24)-C(28)#7	63.7(17)
C(25)#6-C(24)-C(25)	80(5)
C(25)#6-C(24)-C(28)#5	146(3)
C(25)-C(24)-C(28)#7	103(3)
C(25)#6-C(24)-C(28)#7	171(4)
C(28)#5-C(24)-C(25)	134(4)
C(28)#5-C(24)-C(28)#7	31(4)
C(24)#6-C(25)-C(24)	21.4(19)
C(24)-C(25)-C(25)#6	40(2)
C(24)#6-C(25)-C(25)#6	60(2)
C(24)#6-C(25)-C(26)	115(4)
C(26)-C(25)-C(24)	95(4)

Table A15.1.4. (cont'd)

C(26)-C(25)-C(25)#6	55.3(15)
C(25)-C(26)-C(25)#6	69(3)
C(27)-C(26)-C(25)	116.5(19)
C(27)#6-C(26)-C(25)	157(2)
C(27)-C(26)-C(25)#6	157(2)
C(27)#6-C(26)-C(25)#6	116.5(19)
C(27)#6-C(26)-C(27)	68(3)
C(26)-C(27)-C(27)#6	56.2(17)
C(28)#6-C(27)-C(26)	116(5)
C(28)-C(27)-C(26)	91(4)
C(28)#6-C(27)-C(27)#6	62(3)
C(28)-C(27)-C(27)#6	36(3)
C(28)#6-C(27)-C(28)	35(5)
C(24)#2-C(28)-C(24)#8	22.2(18)
C(27)#6-C(28)-C(24)#2	149(4)
C(27)-C(28)-C(24)#8	100(3)
C(27)-C(28)-C(24)#2	121(4)
C(27)#6-C(28)-C(24)#8	152(6)
C(27)#6-C(28)-C(27)	82(6)
C(28)#6-C(28)-C(24)#8	63.7(17)
C(28)#6-C(28)-C(24)#2	86(2)
C(28)#6-C(28)-C(27)	40(3)
C(28)#6-C(28)-C(27)#6	105(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1 #2 x,y+1,z #3 -x,y+1,-z+1 #4 -x,y-1,-z+1
#5 x,y-1,z #6 -x+2,y,-z+2 #7 -x+2,y-1,-z+2
#8 -x+2,y+1,-z+2

Table A15.1.5. Anisotropic displacement parameters ($Å^2x10^3$) for Thiazolidine ***(S)-522****. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	238(4)	213(4)	119(3)	-6(3)	17(3)	23(3)
S(2)	242(4)	282(4)	118(3)	15(3)	13(3)	50(3)
O(1)	256(11)	298(13)	112(9)	4(10)	11(8)	11(10)
O(2)	328(13)	232(13)	197(11)	-32(10)	9(10)	17(11)
O(3)	336(15)	298(16)	559(18)	-20(14)	-52(13)	-32(12)
O(4)	236(13)	475(18)	579(18)	-18(16)	-69(12)	67(14)
N(1)	236(13)	233(14)	117(11)	37(11)	22(9)	60(12)
N(2)	242(15)	320(20)	285(15)	-33(13)	-11(11)	40(13)
N(3)	339(16)	298(17)	139(12)	30(12)	2(11)	116(13)
C(1)	232(15)	216(19)	140(13)	-14(12)	31(11)	28(12)
C(2)	219(15)	213(18)	167(14)	-4(13)	9(11)	63(13)
C(3)	260(17)	233(19)	213(15)	9(13)	21(12)	27(13)
C(4)	212(15)	260(18)	214(15)	-36(14)	13(12)	33(14)
C(5)	243(17)	290(20)	239(17)	4(14)	-41(13)	88(14)
C(6)	283(17)	234(19)	210(15)	33(14)	14(12)	84(14)
C(7)	289(16)	198(16)	150(14)	2(14)	25(11)	21(14)
C(8)	230(15)	171(15)	133(13)	3(11)	4(11)	-2(12)
C(9)	206(15)	249(17)	130(13)	22(13)	14(11)	39(13)
C(10)	480(20)	430(30)	142(15)	30(15)	1(14)	196(19)
C(11)	307(17)	262(18)	198(15)	49(15)	29(13)	72(16)
C(12)	500(20)	260(20)	390(20)	26(18)	74(18)	21(18)
C(13)	229(15)	231(18)	113(13)	50(12)	28(11)	30(13)
C(14)	271(17)	259(18)	170(14)	19(13)	-21(12)	-16(14)
C(15)	195(16)	380(20)	218(16)	4(15)	-18(12)	29(14)
C(16)	247(17)	330(20)	194(15)	60(14)	44(12)	81(14)
C(17)	317(18)	165(16)	177(14)	3(13)	50(12)	8(13)
C(18)	233(16)	236(19)	186(14)	32(12)	36(12)	-16(13)
S(1A)	327(4)	267(5)	126(3)	-18(3)	-5(3)	-33(4)
S(2A)	324(16)	500(30)	143(9)	71(12)	55(9)	189(17)
S(2AA)	313(19)	400(30)	162(12)	-68(14)	22(11)	50(20)
O(1A)	313(13)	344(15)	152(11)	14(10)	-14(9)	-53(11)

Table A15.1.5. (cont'd)

O(2A)	425(14)	302(14)	193(11)	-37(11)	-40(10)	-56(12)
O(3A)	272(15)	510(20)	770(20)	-73(18)	-53(14)	63(14)
O(4A)	383(17)	385(19)	600(20)	13(16)	-35(14)	-55(14)
N(1A)	313(15)	304(16)	129(12)	11(12)	29(11)	-16(13)
N(2A)	288(17)	370(20)	343(17)	-34(14)	13(13)	-2(14)
N(3A)	427(18)	369(18)	152(13)	16(13)	-6(12)	57(15)
C(1A)	277(17)	226(18)	150(14)	-37(13)	39(12)	-15(14)
C(2A)	272(17)	330(20)	198(15)	25(14)	51(12)	18(14)
C(3A)	309(19)	280(20)	244(17)	29(14)	56(14)	0(14)
C(4A)	242(17)	340(20)	281(18)	-55(16)	41(13)	6(14)
C(5A)	303(19)	320(20)	300(19)	-35(17)	-45(15)	49(16)
C(6A)	366(19)	245(19)	239(16)	-45(16)	-8(14)	13(16)
C(7A)	248(16)	370(20)	113(13)	-1(15)	-10(11)	-51(16)
C(8A)	350(20)	620(30)	197(16)	42(18)	76(14)	120(20)
C(9A)	360(50)	390(70)	200(30)	20(40)	80(30)	150(40)
C(9AA)	260(60)	170(70)	110(40)	-40(40)	40(40)	60(40)
C(10A)	510(20)	520(30)	105(14)	-12(17)	-3(14)	130(20)
C(11A)	770(30)	660(30)	204(19)	90(20)	-10(20)	330(30)
C(12A)	1110(40)	550(30)	330(20)	60(20)	70(30)	370(30)
C(13A)	273(16)	291(18)	128(13)	27(14)	11(11)	69(15)
C(14A)	420(20)	270(20)	139(14)	41(13)	6(13)	-3(15)
C(15A)	370(20)	680(30)	245(18)	180(20)	48(16)	220(20)
C(16A)	290(20)	890(40)	360(20)	340(30)	-41(16)	-50(20)
C(17A)	610(30)	580(30)	420(20)	310(20)	-230(20)	-280(30)
C(18A)	650(30)	260(20)	240(18)	41(16)	-118(18)	-90(20)
C(19)	1400(200)	2800(400)	2700(300)	0(200)	-600(200)	-300(200)
C(20)	1970(190)	2600(400)	2500(200)	-50(180)	200(200)	-100(200)
C(21)	2200(200)	2200(300)	2200(200)	-100(160)	430(180)	70(190)
C(22)	2300(200)	2200(300)	1810(190)	320(160)	500(160)	300(180)
C(23)	1900(200)	2000(300)	1310(170)	170(140)	850(160)	450(190)
C(24)	950(140)	8800(900)	600(160)	500(200)	610(130)	400(300)
C(25)	1010(160)	8800(900)	1100(200)	300(200)	-70(140)	200(200)
C(26)	320(70)	8700(900)	1600(200)	0	-210(100)	0
C(27)	1240(180)	8500(900)	1300(200)	100(200)	60(160)	-400(200)

Table A15.1.5. (cont'd)

C(28)	1070(170)	8300(900)	860(190)	-100(300)	-550(170)	-700(300)

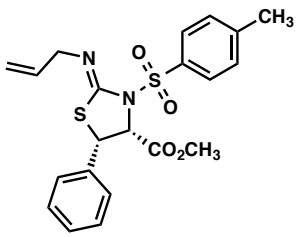
Table A15.1.6. Hydrogen coordinates (x10^3) and isotropic displacement parameters (Å^{2}x10^3) for Thiazolidine ***(S)-522****.*

	x	y	z	U_{iso}
H(2)	861	322	737	24
H(3)	932	510	754	28
H(5)	985	-20	844	31
H(6)	914	-201	831	29
H(8)	712	-51	854	21
H(9A)	747	176	787	23
H(9B)	774	318	839	23
H(10C)	825	-268	981	42
H(10D)	876	-166	984	42
H(11)	885	-552	1000	31
H(12C)	868	-570	880	46
H(12D)	891	-765	923	46
H(14)	636	57	857	28
H(15)	579	314	874	32
H(16)	599	657	914	31
H(17)	677	744	938	26
H(18)	734	490	919	26
H(2A)	146	-119	759	32
H(3A)	74	-288	742	33
H(5A)	26	259	654	37
H(6A)	100	422	668	34
H(8A)	242	-207	591	46
H(8AA)	243	-224	609	46
H(9AA)	256	-55	701	38
H(9AB)	209	-158	672	38
H(9AC)	235	-83	700	21
H(9AD)	273	105	692	21
H(10A)	145	390	516	46
H(10B)	192	528	522	46
H(11A)	128	768	497	66
H(12A)	130	784	617	79

Table A15.1.6. (cont'd)

H(12B)	106	963	570	79
H(14A)	309	-405	585	33
H(15A)	390	-424	586	52
H(16A)	434	-124	616	62
H(17A)	400	204	641	66
H(18A)	320	230	640	47

A15.2 X-Ray Crystal Structure Analysis of Thiazolidine 536



536

Contents

Figure A15.2.1. X-Ray Crystal Structure of Thiazolidine ***536***

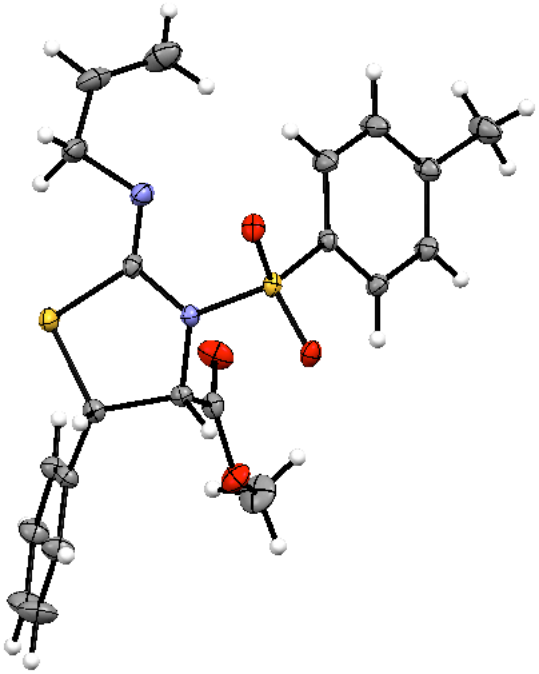


*Table A15.2.1. Experimental Details for X-Ray Structure Determination of Thiazolidine **536**.*

Low-temperature diffraction data (and scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo *K* radiation (=0.71073 Å) for the structure of thiazolidine **536**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 refinement using established techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Thiazolidine **536** crystallizes in the triclinic space group *P*-1 with one molecule in the asymmetric unit along with 0.389(2) molecules of benzene and 0.111(2) molecules of ethyl acetate. The partially occupied benzene and ethyl acetate molecules are located at mutually exclusive positions near a crystallographic inversion center and are disordered accordingly. This leads to non-integer values for the atoms in the empirical formula. The carbon atoms in the benzene were restrained to be flat. The 1,2- and 1,3- distances for the ethyl acetate were restrained to be similar to the distances in the ester moiety of the main molecule.

*Table A15.2.2. Crystal Data and Structure Refinement for Thiazolidine **536**.*

Caltech Identification code	rac15	
CCDC Deposition Number	956878	
Empirical formula	C23.78 H25.22 N2 O4.22 S2	
Formula weight	470.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0719(4) Å	α= 108.416(4)°.
	b = 10.9911(6) Å	β= 102.525(3)°.
	c = 14.6381(8) Å	γ = 100.436(2)°.
Volume	1158.33(11) $Å^3$	
Z	2	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	0.264 mm^{-1}	
F(000)	495	
Crystal size	0.450 x 0.400 x 0.050 mm^3	
Theta range for data collection	2.028 to 30.611°.	
Index ranges	$-11 \le h \le 11, -15 \le k \le 15, -20 \le l \le 20$	
Reflections collected	73111	
Independent reflections	7117 [R(int) = 0.0401]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6920	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7117 / 241 / 375	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0852	
R indices (all data)	R1 = 0.0411, wR2 = 0.0910	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.519 and -0.298 $e \cdot Å^{-3}$	

Table A15.2.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Thiazolidine ***536****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	6720(1)	912(1)	6958(1)	19(1)
O(2)	7685(1)	-166(1)	5483(1)	18(1)
S(1)	7769(1)	1012(1)	6298(1)	14(1)
C(1)	9977(1)	1738(1)	7028(1)	15(1)
C(2)	10368(2)	2473(1)	8051(1)	22(1)
C(3)	12116(2)	2931(1)	8639(1)	25(1)
C(4)	13466(2)	2658(1)	8223(1)	21(1)
C(5)	13041(1)	1962(1)	7189(1)	20(1)
C(6)	11303(1)	1495(1)	6586(1)	18(1)
C(7)	15338(2)	3066(2)	8883(1)	30(1)
N(1)	7101(1)	1999(1)	5728(1)	14(1)
C(8)	6907(1)	3260(1)	6257(1)	16(1)
N(2)	7432(1)	3818(1)	7202(1)	20(1)
C(11)	6995(2)	5071(1)	7627(1)	27(1)
C(12)	8307(2)	6001(1)	8604(1)	30(1)
C(13)	9751(2)	5797(2)	9062(1)	37(1)
S(2)	5817(1)	3868(1)	5380(1)	19(1)
C(9)	5708(1)	2434(1)	4293(1)	15(1)
C(14)	5921(1)	2800(1)	3405(1)	17(1)
C(15)	4955(2)	1907(1)	2438(1)	25(1)
C(16)	5200(2)	2182(2)	1604(1)	33(1)
C(17)	6411(2)	3338(2)	1730(1)	31(1)
C(18)	7365(2)	4231(1)	2688(1)	24(1)
C(19)	7112(2)	3970(1)	3524(1)	18(1)
C(10)	7117(1)	1788(1)	4692(1)	14(1)
C(20)	8939(1)	2443(1)	4674(1)	17(1)
O(3)	9954(1)	3388(1)	5361(1)	27(1)
O(4)	9225(1)	1840(1)	3801(1)	25(1)
C(21)	10843(2)	2499(2)	3681(1)	39(1)
C(1S)	11128(19)	-483(17)	9748(10)	51(2)

Table A15.2.3. (cont'd)

C(2S)	10130(17)	77(11)	9173(10)	49(2)
C(3S)	8871(17)	592(13)	9507(10)	53(3)
C(4S)	8570(20)	585(17)	10386(11)	58(2)
C(5S)	9491(17)	-5(13)	10916(10)	53(2)
C(6S)	10810(18)	-484(13)	10638(9)	48(2)
C(1T)	11250(60)	-420(70)	9690(20)	54(4)
C(2T)	10990(40)	-780(20)	8564(14)	69(5)
O(1T)	12404(19)	-714(14)	10186(10)	63(3)
O(2T)	9820(20)	-163(16)	9947(14)	51(3)
C(3T)	10080(30)	210(30)	11027(16)	56(4)
C(4T)	8270(30)	370(20)	11135(15)	62(5)

*Table A15.2.4. Bond lengths [Å] and angles [°] for Thiazolidine **536**.*

O(1)-S(1)	1.4310(8)
O(2)-S(1)	1.4361(8)
S(1)-N(1)	1.6597(9)
S(1)-C(1)	1.7533(11)
C(1)-C(6)	1.3894(14)
C(1)-C(2)	1.3904(15)
C(2)-C(3)	1.3888(17)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3931(16)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3938(16)
C(4)-C(7)	1.5053(16)
C(5)-C(6)	1.3880(15)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
N(1)-C(8)	1.4129(13)
N(1)-C(10)	1.4640(13)
C(8)-N(2)	1.2593(14)
C(8)-S(2)	1.7704(11)
N(2)-C(11)	1.4617(15)
C(11)-C(12)	1.4965(19)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.307(2)
C(12)-H(12)	0.9500
C(13)-H(13A)	0.9500
C(13)-H(13B)	0.9500
S(2)-C(9)	1.8239(11)
C(9)-C(14)	1.5114(14)
C(9)-C(10)	1.5510(14)

Table A15.2.4. (cont'd)

C(9)-H(9)	1.0000
C(14)-C(15)	1.3929(15)
C(14)-C(19)	1.3949(15)
C(15)-C(16)	1.3908(18)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(2)
C(16)-H(16)	0.9500
C(17)-C(18)	1.3827(18)
C(17)-H(17)	0.9500
C(18)-C(19)	1.3898(15)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(10)-C(20)	1.5249(14)
C(10)-H(10)	1.0000
C(20)-O(3)	1.1980(14)
C(20)-O(4)	1.3313(14)
O(4)-C(21)	1.4494(16)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(1S)-C(6S)	1.381(9)
C(1S)-C(2S)	1.396(10)
C(1S)-H(1S)	0.9500
C(2S)-C(3S)	1.358(9)
C(2S)-H(2S)	0.9500
C(3S)-C(4S)	1.363(10)
C(3S)-H(3S)	0.9500
C(4S)-C(5S)	1.348(11)
C(4S)-H(4S)	0.9500
C(5S)-C(6S)	1.354(9)
C(5S)-H(5S)	0.9500
C(6S)-H(6S)	0.9500
C(1T)-O(1T)	1.202(18)
C(1T)-O(2T)	1.340(18)

Table A15.2.4. (cont'd)

C(1T)-C(2T)	1.529(17)
C(2T)-H(2T1)	0.9800
C(2T)-H(2T2)	0.9800
C(2T)-H(2T3)	0.9800
O(2T)-C(3T)	1.458(18)
C(3T)-C(4T)	1.539(18)
C(3T)-H(3T1)	0.9900
C(3T)-H(3T2)	0.9900
C(4T)-H(4T1)	0.9800
C(4T)-H(4T2)	0.9800
C(4T)-H(4T3)	0.9800

O(1)-S(1)-O(2)	119.28(5)
O(1)-S(1)-N(1)	107.46(5)
O(2)-S(1)-N(1)	103.82(5)
O(1)-S(1)-C(1)	108.38(5)
O(2)-S(1)-C(1)	108.19(5)
N(1)-S(1)-C(1)	109.37(5)
C(6)-C(1)-C(2)	121.16(10)
C(6)-C(1)-S(1)	119.28(8)
C(2)-C(1)-S(1)	119.42(8)
C(3)-C(2)-C(1)	118.85(10)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(2)-C(3)-C(4)	121.14(11)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	118.72(10)
C(3)-C(4)-C(7)	120.57(11)
C(5)-C(4)-C(7)	120.68(11)
C(6)-C(5)-C(4)	121.06(10)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	118.98(10)

Table A15.2.4. (cont'd)

C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(8)-N(1)-C(10)	114.00(8)
C(8)-N(1)-S(1)	122.79(7)
C(10)-N(1)-S(1)	121.40(7)
N(2)-C(8)-N(1)	123.68(10)
N(2)-C(8)-S(2)	127.37(8)
N(1)-C(8)-S(2)	108.95(7)
C(8)-N(2)-C(11)	116.34(10)
N(2)-C(11)-C(12)	113.38(11)
N(2)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11A)	108.9
N(2)-C(11)-H(11B)	108.9
C(12)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
C(13)-C(12)-C(11)	126.39(12)
C(13)-C(12)-H(12)	116.8
C(11)-C(12)-H(12)	116.8
C(12)-C(13)-H(13A)	120.0
C(12)-C(13)-H(13B)	120.0
H(13A)-C(13)-H(13B)	120.0
C(8)-S(2)-C(9)	93.46(5)
C(14)-C(9)-C(10)	114.60(9)
C(14)-C(9)-S(2)	112.74(7)
C(10)-C(9)-S(2)	105.20(7)
C(14)-C(9)-H(9)	108.0
C(10)-C(9)-H(9)	108.0
S(2)-C(9)-H(9)	108.0

Table A15.2.4. (cont'd)

C(15)-C(14)-C(19)	119.35(10)
C(15)-C(14)-C(9)	118.64(10)
C(19)-C(14)-C(9)	121.95(9)
C(16)-C(15)-C(14)	119.89(11)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(17)-C(16)-C(15)	120.38(12)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(18)-C(17)-C(16)	119.95(12)
C(18)-C(17)-H(17)	120.0
C(16)-C(17)-H(17)	120.0
C(17)-C(18)-C(19)	119.94(11)
C(17)-C(18)-H(18)	120.0
C(19)-C(18)-H(18)	120.0
C(18)-C(19)-C(14)	120.48(10)
C(18)-C(19)-H(19)	119.8
C(14)-C(19)-H(19)	119.8
N(1)-C(10)-C(20)	110.41(8)
N(1)-C(10)-C(9)	104.82(8)
C(20)-C(10)-C(9)	111.54(8)
N(1)-C(10)-H(10)	110.0
C(20)-C(10)-H(10)	110.0
C(9)-C(10)-H(10)	110.0
O(3)-C(20)-O(4)	125.32(10)
O(3)-C(20)-C(10)	123.43(10)
O(4)-C(20)-C(10)	111.24(9)
C(20)-O(4)-C(21)	114.48(11)
O(4)-C(21)-H(21A)	109.5
O(4)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Table A15.2.4. (cont'd)

C(6S)-C(1S)-C(2S)	119.1(7)
C(6S)-C(1S)-H(1S)	120.5
C(2S)-C(1S)-H(1S)	120.5
C(3S)-C(2S)-C(1S)	118.6(7)
C(3S)-C(2S)-H(2S)	120.7
C(1S)-C(2S)-H(2S)	120.7
C(2S)-C(3S)-C(4S)	121.8(8)
C(2S)-C(3S)-H(3S)	119.1
C(4S)-C(3S)-H(3S)	119.1
C(5S)-C(4S)-C(3S)	119.2(8)
C(5S)-C(4S)-H(4S)	120.4
C(3S)-C(4S)-H(4S)	120.4
C(4S)-C(5S)-C(6S)	121.2(8)
C(4S)-C(5S)-H(5S)	119.4
C(6S)-C(5S)-H(5S)	119.4
C(5S)-C(6S)-C(1S)	120.0(8)
C(5S)-C(6S)-H(6S)	120.0
C(1S)-C(6S)-H(6S)	120.0
O(1T)-C(1T)-O(2T)	125(2)
O(1T)-C(1T)-C(2T)	120(2)
O(2T)-C(1T)-C(2T)	111.4(18)
C(1T)-C(2T)-H(2T1)	109.5
C(1T)-C(2T)-H(2T2)	109.5
H(2T1)-C(2T)-H(2T2)	109.5
C(1T)-C(2T)-H(2T3)	109.5
H(2T1)-C(2T)-H(2T3)	109.5
H(2T2)-C(2T)-H(2T3)	109.5
C(1T)-O(2T)-C(3T)	111.6(19)
O(2T)-C(3T)-C(4T)	102.8(17)
O(2T)-C(3T)-H(3T1)	111.2
C(4T)-C(3T)-H(3T1)	111.2
O(2T)-C(3T)-H(3T2)	111.2
C(4T)-C(3T)-H(3T2)	111.2
H(3T1)-C(3T)-H(3T2)	109.1

Table A15.2.4. (cont'd)

C(3T)-C(4T)-H(4T1)	109.5
C(3T)-C(4T)-H(4T2)	109.5
H(4T1)-C(4T)-H(4T2)	109.5
C(3T)-C(4T)-H(4T3)	109.5
H(4T1)-C(4T)-H(4T3)	109.5
H(4T2)-C(4T)-H(4T3)	109.5

Symmetry transformations used to generate equivalent atoms:

*Table A15.2.5. Anisotropic displacement parameters ($Å^2x10^3$) for Thiazolidine **536**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	17(1)	20(1)	26(1)	14(1)	11(1)	6(1)
O(2)	19(1)	13(1)	23(1)	5(1)	6(1)	5(1)
S(1)	13(1)	13(1)	18(1)	8(1)	6(1)	4(1)
C(1)	13(1)	17(1)	16(1)	7(1)	5(1)	5(1)
C(2)	19(1)	32(1)	18(1)	8(1)	9(1)	9(1)
C(3)	21(1)	38(1)	15(1)	6(1)	6(1)	7(1)
C(4)	16(1)	27(1)	18(1)	9(1)	4(1)	4(1)
C(5)	15(1)	25(1)	20(1)	6(1)	7(1)	6(1)
C(6)	16(1)	19(1)	16(1)	4(1)	6(1)	6(1)
C(7)	17(1)	46(1)	22(1)	10(1)	2(1)	4(1)
N(1)	16(1)	12(1)	15(1)	6(1)	5(1)	5(1)
C(8)	18(1)	14(1)	19(1)	9(1)	8(1)	6(1)
N(2)	27(1)	17(1)	18(1)	7(1)	9(1)	9(1)
C(11)	44(1)	21(1)	21(1)	6(1)	12(1)	17(1)
C(12)	44(1)	21(1)	24(1)	3(1)	17(1)	8(1)
C(13)	32(1)	32(1)	33(1)	-3(1)	11(1)	2(1)
S(2)	27(1)	18(1)	19(1)	10(1)	9(1)	12(1)
C(9)	14(1)	15(1)	17(1)	7(1)	4(1)	2(1)
C(14)	16(1)	18(1)	16(1)	7(1)	4(1)	4(1)
C(15)	25(1)	23(1)	19(1)	5(1)	3(1)	-2(1)
C(16)	38(1)	35(1)	16(1)	4(1)	4(1)	-2(1)
C(17)	36(1)	37(1)	19(1)	12(1)	10(1)	5(1)
C(18)	26(1)	25(1)	22(1)	12(1)	8(1)	3(1)
C(19)	20(1)	17(1)	17(1)	7(1)	5(1)	2(1)
C(10)	13(1)	13(1)	15(1)	4(1)	4(1)	2(1)
C(20)	14(1)	19(1)	21(1)	10(1)	6(1)	4(1)
O(3)	20(1)	28(1)	24(1)	9(1)	2(1)	-7(1)
O(4)	22(1)	28(1)	29(1)	9(1)	16(1)	8(1)
C(21)	27(1)	51(1)	51(1)	23(1)	27(1)	11(1)
C(1S)	55(4)	24(4)	77(4)	14(3)	33(3)	12(3)
C(2S)	84(6)	18(3)	38(3)	9(3)	18(3)	0(3)

Table A15.2.5. (cont'd)

C(3S)	54(5)	22(3)	53(4)	0(3)	-16(3)	5(3)
C(4S)	52(5)	21(3)	87(5)	-2(3)	30(3)	6(3)
C(5S)	64(5)	35(4)	38(3)	-4(2)	16(3)	-13(3)
C(6S)	45(4)	38(5)	50(4)	25(4)	-5(3)	-5(3)
C(1T)	64(7)	30(9)	58(6)	10(8)	14(6)	3(7)
C(2T)	104(15)	48(10)	60(7)	23(9)	25(8)	30(10)
O(1T)	62(7)	50(7)	56(7)	6(6)	3(6)	9(6)
O(2T)	66(6)	25(6)	52(4)	13(4)	7(4)	8(5)
C(3T)	63(8)	33(9)	53(5)	5(7)	12(6)	-6(8)
C(4T)	58(9)	49(10)	41(8)	-12(8)	-6(6)	0(8)

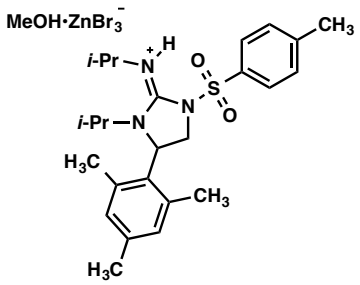
*Table A15.2.6. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for Thiazolidine **536**.*

	x	y	z	U(eq)
H(2)	9455	2659	8342	27
H(3)	12396	3439	9338	30
H(5)	13956	1805	6891	24
H(6)	11024	1016	5883	21
H(7A)	15481	2462	9246	46
H(7B)	15613	3979	9367	46
H(7C)	16140	3022	8464	46
H(11A)	5821	4873	7734	33
H(11B)	6918	5519	7136	33
H(12)	8068	6820	8923	36
H(13A)	10049	4993	8773	44
H(13B)	10502	6453	9683	44
H(9)	4525	1788	4083	18
H(15)	4130	1113	2348	30
H(16)	4535	1575	946	40
H(17)	6585	3514	1157	37
H(18)	8191	5023	2775	29
H(19)	7755	4592	4182	22
H(10)	6777	813	4282	17
H(21A)	11839	2619	4251	59
H(21B)	10772	3370	3658	59
H(21C)	11013	1953	3053	59
H(1S)	12012	-858	9531	61
H(2S)	10329	97	8561	59
H(3S)	8179	967	9116	63
H(4S)	7723	992	10623	69
H(5S)	9209	-86	11495	64
H(6S)	11517	-821	11054	57
H(2T1)	12065	-360	8455	103
H(2T2)	10010	-464	8284	103

Table A15.2.6. (cont'd)

H(2T3)	10709	-1751	8229	103
H(3T1)	11018	1056	11413	67
H(3T2)	10402	-495	11258	67
H(4T1)	7342	-330	10569	93
H(4T2)	8170	1244	11135	93
H(4T3)	8157	295	11769	93

A15.3 X-Ray Crystal Structure Analysis of Imidazolidinium 590•($ZnBr_3$•MeOH)



590·(ZnBr$_3$·MeOH)

Contents

Figure A15.3.1. X-Ray Crystal Structure of Imidazolidinium ***590•(ZnBr$_3$•MeOH)***

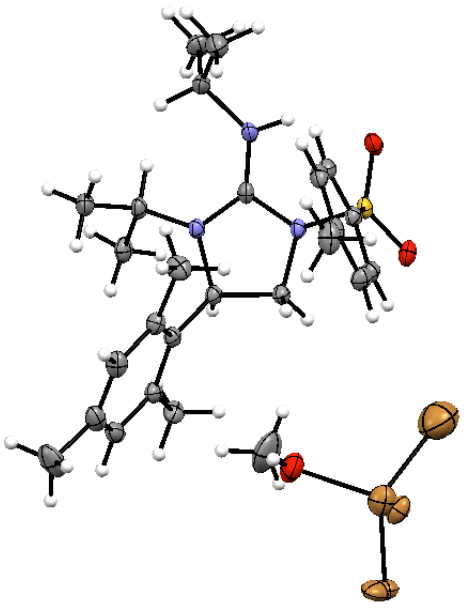


Table A15.3.1. Experimental Details for X-Ray Structure Determination of Imidazolidinium ***590•(ZnBr$_3$•MeOH)***.

Low-temperature diffraction data (and scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo *K* radiation (= 0.71073 Å) for the structure of imidazolidinium **590•(ZnBr$_3$•MeOH)**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl and hydroxide groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Imidazolidinium **590•(ZnBr$_3$•MeOH)** crystallizes in the triclinic space group *P*-1 with one molecule in the asymmetric unit along with one molecule of methanol. The coordinates for the hydrogen atoms on N3 and O3were taken from the difference Fourier synthesis and refined semi-freely with the help of a distance restraint, 0.91(2) and 0.83(2) Å respectively. An additional restraint was required for the hydrogen atom bound to O3 and the atoms Zn1, O3, C31 and H3O were restrained to be flat. All three bromine atoms were disordered over two positions. The solvent methanol had vey elongated ellipsoids and was disordered over two positions. The methanol is not very stable and the C-O distance was restrained to 1.43(2) Å. Additionally, the anisotropic displacement parameters for the two atoms in the second component of the disorder were constrained

to be equivalent. Even with the disorder the methanol has elongated ellipsoids, however, refinement of additional components was not successful.

Table A15.3.2. Crystal Data and Structure Refinement for Imidazolidinium ***590•(ZnBr$_3$•MeOH)***.

Caltech Identification code	rac14	
CCDC Deposition Number	956877	
Empirical formula	C27 H44 Br3 N3 O4 S Zn	
Formula weight	811.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.5054(14) Å	α= 103.177(3)°.
	b = 12.5274(17) Å	β= 109.093(2)°.
	c = 14.785(2) Å	γ = 102.841(3)°.
Volume	1694.7(4) Å^3	
Z	2	
Density (calculated)	1.591 Mg/m^3	
Absorption coefficient	4.357 mm^{-1}	
F(000)	820	
Crystal size	0.580 x 0.380 x 0.270 mm^3	
Theta range for data collection	1.764 to 30.560°.	
Index ranges	$-15 \le h \le 15, -17 \le k \le 17, -21 \le l \le 21$	
Reflections collected	100294	
Independent reflections	10353 [R(int) = 0.0346]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.1292 and 0.0684	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10353 / 82 / 412	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0793	

Table A15.3.2. (cont'd)

R indices (all data)	R1 = 0.0418, wR2 = 0.0842
Extinction coefficient	n/a
Largest diff. peak and hole	0.878 and -0.917 e·Å^{-3}

Table A15.3.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Imidazolidinium ***590•(ZnBr$_3$•MeOH)****. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	4177(2)	6547(2)	5223(1)	24(1)
O(2)	4429(2)	8386(1)	4821(1)	24(1)
S(1)	4213(1)	7168(1)	4530(1)	18(1)
C(1)	2695(2)	6459(2)	3406(2)	18(1)
C(2)	2284(2)	7039(2)	2722(2)	21(1)
C(3)	1068(2)	6464(2)	1841(2)	24(1)
C(4)	270(2)	5323(2)	1631(2)	24(1)
C(7)	-1077(2)	4724(3)	691(2)	33(1)
C(5)	717(2)	4751(2)	2324(2)	24(1)
C(6)	1922(2)	5310(2)	3212(2)	22(1)
N(1)	5573(2)	6976(2)	4235(1)	18(1)
C(8)	6315(2)	7626(2)	3813(2)	18(1)
N(3)	6281(2)	8679(2)	3862(2)	22(1)
C(11)	6662(2)	9434(2)	3284(2)	22(1)
C(12)	5359(3)	9741(2)	2755(2)	31(1)
C(13)	7911(3)	10511(2)	4005(2)	31(1)
N(2)	7008(2)	7029(2)	3402(1)	18(1)
C(14)	8269(2)	7560(2)	3202(2)	20(1)
C(15)	7914(2)	7273(2)	2070(2)	25(1)
C(16)	9538(2)	7195(2)	3714(2)	24(1)
C(9)	6792(2)	5874(2)	3547(2)	17(1)
C(21)	6427(2)	4851(2)	2623(2)	18(1)
C(22)	7171(2)	4051(2)	2748(2)	20(1)
C(27)	8267(2)	4165(2)	3761(2)	25(1)
C(23)	6873(2)	3098(2)	1914(2)	25(1)
C(24)	5860(2)	2920(2)	967(2)	28(1)
C(28)	5587(3)	1911(3)	62(2)	44(1)
C(25)	5097(2)	3697(2)	865(2)	26(1)

Table A15.3.3. (cont'd)

C(26)	5343(2)	4650(2)	1680(2)	21(1)
C(29)	4402(2)	5400(2)	1501(2)	28(1)
C(10)	5663(2)	5793(2)	4001(2)	19(1)
Zn(1)	727(1)	1039(1)	2621(1)	25(1)
O(3)	1824(2)	1549(2)	1805(2)	42(1)
C(31)	3303(4)	2206(4)	2288(4)	69(1)
Br(1)	-1687(2)	97(1)	1446(2)	31(1)
Br(2)	1081(1)	2756(1)	3849(1)	16(1)
Br(3)	1841(2)	-171(2)	3374(2)	30(1)
Br(1A)	-1582(4)	220(5)	1241(6)	39(1)
Br(2A)	1081(4)	2743(3)	3828(3)	83(3)
Br(3A)	1793(7)	-231(6)	3212(7)	47(1)
O(1S)	10478(14)	1719(7)	9938(6)	64(2)
C(1S)	8692(15)	1307(5)	9413(8)	65(3)
O(1T)	11160(20)	2063(15)	10107(8)	46(3)
C(1T)	9360(20)	1417(16)	9601(11)	46(3)

Table A15.3.4. Bond lengths [Å] and angles [°] for Imidazolidinium ***590•(ZnBr$_3$•MeOH)***.

O(1)-S(1)	1.4260(16)
O(2)-S(1)	1.4310(17)
S(1)-N(1)	1.6740(17)
S(1)-C(1)	1.748(2)
C(1)-C(2)	1.387(3)
C(1)-C(6)	1.398(3)
C(2)-C(3)	1.387(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.392(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.397(3)
C(4)-C(7)	1.504(3)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(5)-C(6)	1.384(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
N(1)-C(8)	1.389(2)
N(1)-C(10)	1.475(3)
C(8)-N(3)	1.314(3)
C(8)-N(2)	1.334(2)
N(3)-C(11)	1.485(3)
N(3)-H(3N)	0.868(17)
C(11)-C(12)	1.518(3)
C(11)-C(13)	1.524(3)
C(11)-H(11)	1.0000
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800

Table A15.3.4. (cont'd)

N(2)-C(9)	1.490(3)
N(2)-C(14)	1.497(2)
C(14)-C(15)	1.525(3)
C(14)-C(16)	1.526(3)
C(14)-H(14)	1.0000
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(9)-C(21)	1.515(3)
C(9)-C(10)	1.538(3)
C(9)-H(9)	1.0000
C(21)-C(26)	1.407(3)
C(21)-C(22)	1.409(3)
C(22)-C(23)	1.397(3)
C(22)-C(27)	1.514(3)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(23)-C(24)	1.386(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.396(3)
C(24)-C(28)	1.512(3)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(25)-C(26)	1.395(3)
C(25)-H(25)	0.9500
C(26)-C(29)	1.512(3)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800

Table A15.3.4. (cont'd)

C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
Zn(1)-O(3)	2.030(2)
Zn(1)-Br(3A)	2.310(6)
Zn(1)-Br(2A)	2.314(4)
Zn(1)-Br(2)	2.3423(6)
Zn(1)-Br(3)	2.369(2)
Zn(1)-Br(1)	2.3860(13)
Zn(1)-Br(1A)	2.408(4)
O(3)-C(31)	1.428(4)
O(3)-H(3O)	0.816(18)
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
O(1S)-C(1S)	1.680(8)
O(1S)-H(1S)	0.8400
C(1S)-H(1S1)	0.9800
C(1S)-H(1S2)	0.9800
C(1S)-H(1S3)	0.9800
O(1T)-C(1T)	1.704(14)
O(1T)-H(1T)	0.8400
C(1T)-H(1T1)	0.9800
C(1T)-H(1T2)	0.9800
C(1T)-H(1T3)	0.9800

O(1)-S(1)-O(2)	121.07(10)
O(1)-S(1)-N(1)	103.94(9)
O(2)-S(1)-N(1)	106.90(9)
O(1)-S(1)-C(1)	108.90(10)
O(2)-S(1)-C(1)	109.46(10)
N(1)-S(1)-C(1)	105.36(9)
C(2)-C(1)-C(6)	121.2(2)
C(2)-C(1)-S(1)	119.77(16)
C(6)-C(1)-S(1)	119.03(16)

Table A15.3.4. (cont'd)

C(3)-C(2)-C(1)	118.8(2)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(2)-C(3)-C(4)	121.3(2)
C(2)-C(3)-H(3)	119.3
C(4)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	118.9(2)
C(3)-C(4)-C(7)	120.8(2)
C(5)-C(4)-C(7)	120.3(2)
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(5)-C(4)	120.9(2)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	119.0(2)
C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
C(8)-N(1)-C(10)	110.49(16)
C(8)-N(1)-S(1)	127.75(15)
C(10)-N(1)-S(1)	117.14(13)
N(3)-C(8)-N(2)	129.07(18)
N(3)-C(8)-N(1)	120.52(18)
N(2)-C(8)-N(1)	110.40(18)
C(8)-N(3)-C(11)	131.07(17)
C(8)-N(3)-H(3N)	112.5(19)
C(11)-N(3)-H(3N)	116.4(19)
N(3)-C(11)-C(12)	108.11(18)
N(3)-C(11)-C(13)	109.48(19)
C(12)-C(11)-C(13)	111.6(2)
N(3)-C(11)-H(11)	109.2

Table A15.3.4. (cont'd)

C(12)-C(11)-H(11)	109.2
C(13)-C(11)-H(11)	109.2
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(8)-N(2)-C(9)	111.32(16)
C(8)-N(2)-C(14)	124.62(17)
C(9)-N(2)-C(14)	119.92(15)
N(2)-C(14)-C(15)	111.62(17)
N(2)-C(14)-C(16)	111.36(17)
C(15)-C(14)-C(16)	110.66(17)
N(2)-C(14)-H(14)	107.7
C(15)-C(14)-H(14)	107.7
C(16)-C(14)-H(14)	107.7
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5

Table A15.3.4. (cont'd)

H(16B)-C(16)-H(16C)	109.5
N(2)-C(9)-C(21)	116.28(16)
N(2)-C(9)-C(10)	103.46(15)
C(21)-C(9)-C(10)	114.31(16)
N(2)-C(9)-H(9)	107.4
C(21)-C(9)-H(9)	107.4
C(10)-C(9)-H(9)	107.4
C(26)-C(21)-C(22)	119.84(19)
C(26)-C(21)-C(9)	122.58(18)
C(22)-C(21)-C(9)	117.50(18)
C(23)-C(22)-C(21)	119.3(2)
C(23)-C(22)-C(27)	118.13(19)
C(21)-C(22)-C(27)	122.50(19)
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(24)-C(23)-C(22)	121.5(2)
C(24)-C(23)-H(23)	119.3
C(22)-C(23)-H(23)	119.3
C(23)-C(24)-C(25)	118.4(2)
C(23)-C(24)-C(28)	121.0(2)
C(25)-C(24)-C(28)	120.6(2)
C(24)-C(28)-H(28A)	109.5
C(24)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(24)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(25)-C(24)	122.0(2)
C(26)-C(25)-H(25)	119.0
C(24)-C(25)-H(25)	119.0

Table A15.3.4. (cont'd)

C(25)-C(26)-C(21)	118.7(2)
C(25)-C(26)-C(29)	117.7(2)
C(21)-C(26)-C(29)	123.54(19)
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
N(1)-C(10)-C(9)	103.18(15)
N(1)-C(10)-H(10A)	111.1
C(9)-C(10)-H(10A)	111.1
N(1)-C(10)-H(10B)	111.1
C(9)-C(10)-H(10B)	111.1
H(10A)-C(10)-H(10B)	109.1
O(3)-Zn(1)-Br(3A)	102.1(2)
O(3)-Zn(1)-Br(2A)	104.27(11)
Br(3A)-Zn(1)-Br(2A)	116.2(3)
O(3)-Zn(1)-Br(2)	104.66(6)
O(3)-Zn(1)-Br(3)	105.41(9)
Br(2)-Zn(1)-Br(3)	110.95(5)
O(3)-Zn(1)-Br(1)	106.04(9)
Br(2)-Zn(1)-Br(1)	113.94(4)
Br(3)-Zn(1)-Br(1)	114.79(6)
O(3)-Zn(1)-Br(1A)	96.5(3)
Br(3A)-Zn(1)-Br(1A)	117.44(17)
Br(2A)-Zn(1)-Br(1A)	115.77(13)
C(31)-O(3)-Zn(1)	120.9(2)
C(31)-O(3)-H(3O)	120(3)
Zn(1)-O(3)-H(3O)	118(3)
O(3)-C(31)-H(31A)	109.5
O(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
O(3)-C(31)-H(31C)	109.5

Table A15.3.4. (cont'd)

H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(1S)-O(1S)-H(1S)	109.5
O(1S)-C(1S)-H(1S1)	109.5
O(1S)-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	109.5
O(1S)-C(1S)-H(1S3)	109.5
H(1S1)-C(1S)-H(1S3)	109.5
H(1S2)-C(1S)-H(1S3)	109.5
C(1T)-O(1T)-H(1T)	109.5
O(1T)-C(1T)-H(1T1)	109.5
O(1T)-C(1T)-H(1T2)	109.5
H(1T1)-C(1T)-H(1T2)	109.5
O(1T)-C(1T)-H(1T3)	109.5
H(1T1)-C(1T)-H(1T3)	109.5
H(1T2)-C(1T)-H(1T3)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A15.3.5. Anisotropic displacement parameters ($Å^2x10^3$) for Imidazolidinium ***590•($ZnBr_3$•MeOH)***. *The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	34(1)	21(1)	12(1)	12(1)	9(1)
O(2)	23(1)	23(1)	27(1)	3(1)	15(1)	6(1)
S(1)	16(1)	22(1)	19(1)	6(1)	11(1)	6(1)
C(1)	15(1)	22(1)	21(1)	8(1)	10(1)	7(1)
C(2)	21(1)	23(1)	26(1)	9(1)	13(1)	10(1)
C(3)	24(1)	33(1)	23(1)	12(1)	13(1)	15(1)
C(4)	17(1)	35(1)	21(1)	7(1)	10(1)	10(1)
C(7)	20(1)	49(2)	23(1)	8(1)	7(1)	7(1)
C(5)	18(1)	26(1)	28(1)	8(1)	10(1)	3(1)
C(6)	18(1)	24(1)	25(1)	10(1)	10(1)	6(1)
N(1)	15(1)	20(1)	20(1)	7(1)	11(1)	6(1)
C(8)	15(1)	21(1)	15(1)	3(1)	7(1)	3(1)
N(3)	26(1)	18(1)	26(1)	5(1)	19(1)	6(1)
C(11)	26(1)	19(1)	26(1)	6(1)	17(1)	6(1)
C(12)	35(1)	34(1)	34(1)	14(1)	19(1)	16(1)
C(13)	32(1)	21(1)	36(1)	6(1)	18(1)	1(1)
N(2)	15(1)	18(1)	20(1)	5(1)	10(1)	4(1)
C(14)	17(1)	22(1)	23(1)	6(1)	12(1)	4(1)
C(15)	28(1)	26(1)	25(1)	8(1)	17(1)	9(1)
C(16)	17(1)	30(1)	28(1)	9(1)	13(1)	5(1)
C(9)	14(1)	19(1)	20(1)	7(1)	8(1)	5(1)
C(21)	14(1)	19(1)	20(1)	6(1)	8(1)	4(1)
C(22)	16(1)	22(1)	25(1)	9(1)	12(1)	7(1)
C(27)	22(1)	34(1)	29(1)	16(1)	12(1)	15(1)
C(23)	24(1)	20(1)	36(1)	8(1)	18(1)	7(1)
C(24)	23(1)	24(1)	31(1)	0(1)	14(1)	1(1)
C(28)	38(1)	36(1)	42(2)	-11(1)	16(1)	4(1)
C(25)	19(1)	29(1)	22(1)	3(1)	7(1)	1(1)

Table A15.3.5. (cont'd)

C(26)	16(1)	23(1)	22(1)	7(1)	6(1)	4(1)
C(29)	21(1)	34(1)	26(1)	10(1)	4(1)	12(1)
C(10)	18(1)	22(1)	23(1)	9(1)	11(1)	8(1)
Zn(1)	24(1)	22(1)	29(1)	9(1)	12(1)	7(1)
O(3)	50(1)	47(1)	36(1)	19(1)	25(1)	11(1)
C(31)	53(2)	75(3)	85(3)	35(2)	44(2)	0(2)
Br(1)	27(1)	37(1)	25(1)	12(1)	7(1)	2(1)
Br(2)	18(1)	14(1)	17(1)	3(1)	8(1)	4(1)
Br(3)	31(1)	24(1)	36(1)	14(1)	12(1)	11(1)
Br(1A)	28(1)	42(1)	36(2)	9(1)	8(1)	4(1)
Br(2A)	85(3)	84(3)	96(4)	48(3)	40(2)	32(2)
Br(3A)	42(2)	36(1)	85(3)	32(2)	35(2)	27(1)
O(1S)	112(6)	44(3)	47(3)	14(3)	51(4)	17(4)
C(1S)	118(6)	31(2)	69(5)	15(3)	71(5)	16(4)
O(1T)	74(8)	40(5)	25(3)	15(3)	18(4)	14(5)
C(1T)	74(8)	40(5)	25(3)	15(3)	18(4)	14(5)

Table A15.3.6. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for Imidazolidinium ***590•(ZnBr$_3$•MeOH)***.

	x	y	z	U(eq)
H(2)	2826	7815	2855	25
H(3)	773	6857	1372	29
H(7A)	-1896	4599	880	49
H(7B)	-1048	3976	329	49
H(7C)	-1164	5207	252	49
H(5)	187	3969	2183	29
H(6)	2219	4918	3681	26
H(3N)	5930(30)	8950(20)	4288(19)	26
H(11)	6941	9000	2765	27
H(12A)	4592	9033	2276	47
H(12B)	5597	10263	2389	47
H(12C)	5047	10125	3259	47
H(13A)	7661	10915	4539	46
H(13B)	8132	11027	3630	46
H(13C)	8744	10285	4311	46
H(14)	8547	8420	3501	24
H(15A)	7648	6434	1758	37
H(15B)	8747	7664	1967	37
H(15C)	7118	7537	1759	37
H(16A)	9696	7321	4426	36
H(16B)	10389	7658	3672	36
H(16C)	9345	6373	3372	36
H(9)	7696	5909	4079	20
H(27A)	8580	3481	3698	38
H(27B)	7844	4227	4264	38
H(27C)	9085	4860	3978	38
H(23)	7376	2560	1999	30
H(28A)	6006	2192	-376	66
H(28B)	4559	1533	-317	66
H(28C)	6019	1353	294	66

Table A15.3.6. (cont'd)

H(25)	4387	3573	222	31
H(29A)	3713	5092	795	41
H(29B)	4989	6193	1641	41
H(29C)	3893	5402	1951	41
H(10A)	4736	5221	3507	23
H(10B)	5966	5574	4621	23
H(3O)	1370(40)	1460(30)	1211(15)	62
H(31A)	3421	3011	2631	103
H(31B)	3714	2180	1779	103
H(31C)	3791	1876	2786	103
H(1S)	10767	1332	9552	96
H(1S1)	8373	1939	9684	98
H(1S2)	8297	623	9573	98
H(1S3)	8364	1119	8677	98
H(1T)	11346	2769	10163	70
H(1T1)	8935	1883	9964	70
H(1T2)	9141	641	9663	70
H(1T3)	8973	1354	8884	70

Table A15.3.7. Hydrogen bonds for Imidazolidinium ***590•(ZnBr$_3$•MeOH)*** *[Å and °].*

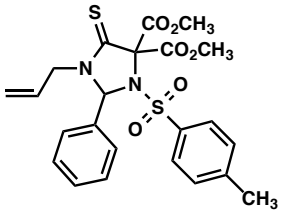
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...Br(3)#1	0.95	2.97	3.584(3)	123.6
C(2)-H(2)...Br(3A)#1	0.95	2.90	3.519(6)	123.9
C(6)-H(6)...Br(2)	0.95	2.81	3.545(2)	135.1
N(3)-H(3N)...O(2)	0.868(17)	2.05(2)	2.767(2)	140(3)
C(16)-H(16A)...Br(2)#2	0.98	2.93	3.855(2)	156.7
C(16)-H(16B)...Br(3)#3	0.98	3.01	3.872(3)	147.4
C(16)-H(16B)...Br(3A)#3	0.98	3.06	3.925(7)	147.6
C(9)-H(9)...Br(2)#2	1.00	2.82	3.523(2)	127.7
C(10)-H(10B)...Br(2)#2	0.99	3.08	3.550(2)	110.5
O(3)-H(3O)...O(1S)#4	0.816(18)	1.95(2)	2.741(7)	164(3)
O(3)-H(3O)...O(1T)#4	0.816(18)	1.92(3)	2.645(11)	148(4)
O(1S)-H(1S)...Br(1)#5	0.84	2.61	3.440(6)	170.0
C(1S)-H(1S2)...Br(1)#6	0.98	2.99	3.753(8)	136.0
C(1S)-H(1S3)...Br(3)#5	0.98	2.91	3.845(8)	159.8
C(1T)-H(1T3)...Br(3A)#5	0.98	2.85	3.749(18)	153.3

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x+1,-y+1,-z+1 #3 x+1,y+1,z

#4 x-1,y,z-1 #5 -x+1,-y,-z+1 #6 x+1,y,z+1

A15.4 X-Ray Crystal Structure Analysis of Imidazolidine 550



550

Contents

*Figure A15.4.1. X-Ray Crystal Structure of Imidazolidine **550***

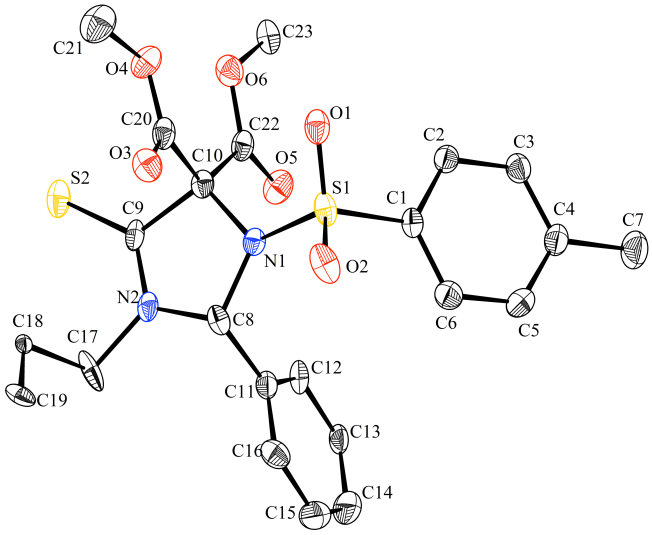


*Table A15.4.1. Experimental Details for X-Ray Structure Determination of Imidazolidine **550**.*

Low-temperature diffraction data (and scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo *K* radiation (= 0.71073 Å) for the structure of imidazolidine **550**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 using established refinement techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups).

Imidazolidine **550** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit. A majority of the molecule was disordered over two positions. All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances. All atoms were refined with the help of similarity as well as rigid bond restraints for anisotropic displacement parameters.

*Table A15.4.2. Crystal Data and Structure Refinement for Imidazolidine **550**.*

Caltech Identification code	rac16	
CCDC Deposition Number	973927	
Empirical formula	C23 H24 N2 O6 S2	
Formula weight	488.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 7.5481(4) Å	α= 90°.
	b = 21.3568(13) Å	β= 90°.
	c = 28.1256(18) Å	γ = 90°.
Volume	4533.9(5) $Å^3$	
Z	8	
Density (calculated)	1.431 Mg/m^3	
Absorption coefficient	0.278 mm^{-1}	
F(000)	2048	
Crystal size	0.400 x 0.250 x 0.150 mm^3	
Theta range for data collection	1.907 to 30.677°.	
Index ranges	$-10 \le h \le 10, -30 \le k \le 30, -39 \le l \le 40$	
Reflections collected	98231	
Independent reflections	7007 [R(int) = 0.0490]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6817	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7007 / 1023 / 507	
Goodness-of-fit on F^2	1.116	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1269	
R indices (all data)	R1 = 0.0597, wR2 = 0.1324	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.662 and -0.538 $e \cdot Å^{-3}$	

*Table A15.4.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Imidazolidine **550**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
O(1)	5335(2)	1620(1)	1380(1)	26(1)
O(2)	4409(2)	2342(1)	726(1)	31(1)
S(1)	4127(1)	2069(1)	1184(1)	21(1)
C(1)	3945(2)	2681(1)	1599(1)	20(1)
C(2)	4527(2)	2582(1)	2061(1)	22(1)
C(3)	4518(2)	3079(1)	2378(1)	24(1)
C(4)	3935(2)	3668(1)	2242(1)	26(1)
C(5)	3339(3)	3752(1)	1780(1)	32(1)
C(6)	3336(3)	3263(1)	1455(1)	28(1)
C(7)	3924(3)	4209(1)	2587(1)	37(1)
N(1)	2138(13)	1760(4)	1128(4)	18(1)
C(8)	877(12)	1912(3)	744(3)	21(1)
C(11)	-60(19)	2527(4)	804(4)	21(1)
C(12)	-830(30)	2682(7)	1243(5)	21(2)
C(13)	-1790(30)	3228(7)	1286(4)	21(2)
C(14)	-1950(20)	3623(6)	896(4)	33(2)
C(15)	-1186(18)	3468(5)	464(4)	32(2)
C(16)	-231(16)	2926(4)	418(4)	26(1)
N(2)	-368(12)	1385(3)	805(3)	20(1)
C(17)	-1909(11)	1330(3)	484(2)	29(2)
C(18)	-1271(4)	782(1)	140(1)	11(1)
C(19)	-1060(4)	1020(2)	-290(1)	20(1)
C(9)	88(11)	951(4)	1108(4)	21(1)
S(2)	-891(4)	277(1)	1228(1)	28(1)
C(10)	1879(10)	1142(3)	1327(2)	18(1)
C(20)	3219(6)	664(2)	1106(2)	23(1)
O(3)	3612(9)	724(3)	689(2)	27(1)
O(4)	3688(6)	201(2)	1380(2)	26(1)
C(21)	4655(6)	-280(2)	1124(2)	39(1)
C(22)	1640(20)	1198(6)	1871(3)	21(1)

Table A15.4.3. (cont'd)

O(5)	720(20)	1617(8)	2024(6)	28(2)
O(6)	2335(18)	750(5)	2130(2)	27(1)
C(23)	2074(14)	822(5)	2643(3)	26(1)
N(1A)	2257(12)	1661(4)	1182(4)	17(1)
C(8A)	967(11)	1778(3)	803(3)	16(1)
C(11A)	53(16)	2403(4)	818(4)	17(1)
C(12A)	-880(30)	2594(7)	1223(5)	22(2)
C(13A)	-1780(30)	3161(7)	1216(4)	28(2)
C(14A)	-1815(18)	3529(5)	811(4)	31(2)
C(15A)	-907(16)	3334(4)	410(4)	31(1)
C(16A)	12(14)	2775(4)	415(4)	23(1)
N(2A)	-258(11)	1253(3)	881(3)	17(1)
C(17A)	-1788(11)	1187(3)	566(2)	23(1)
C(18A)	-1586(8)	1051(4)	20(2)	64(2)
C(19A)	-321(12)	812(4)	-170(3)	92(3)
C(9A)	244(10)	839(3)	1203(3)	17(1)
S(2A)	-720(4)	172(1)	1345(1)	22(1)
C(10A)	1983(9)	1075(3)	1432(2)	18(1)
C(20A)	3358(5)	561(2)	1297(2)	19(1)
O(3A)	4024(5)	193(2)	1558(2)	29(1)
O(4A)	3553(8)	579(2)	823(2)	25(1)
C(21A)	4614(4)	87(2)	615(2)	33(1)
C(22A)	1630(20)	1207(6)	1960(2)	20(1)
O(5A)	920(20)	1681(7)	2086(5)	33(2)
O(6A)	2257(17)	779(5)	2248(2)	28(1)
C(23A)	1896(15)	893(5)	2748(3)	36(2)

*Table A15.4.4. Bond lengths [Å] and angles [°] for Imidazolidine **550**.*

O(1)-S(1)	1.4335(14)
O(2)-S(1)	1.4295(14)
S(1)-N(1)	1.648(9)
S(1)-N(1A)	1.659(8)
S(1)-C(1)	1.7562(16)
C(1)-C(6)	1.387(2)
C(1)-C(2)	1.387(2)
C(2)-C(3)	1.387(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.388(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.387(3)
C(4)-C(7)	1.508(2)
C(5)-C(6)	1.386(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
N(1)-C(10)	1.446(8)
N(1)-C(8)	1.476(8)
C(8)-N(2)	1.476(8)
C(8)-C(11)	1.500(8)
C(8)-H(8)	1.0000
C(11)-C(16)	1.385(8)
C(11)-C(12)	1.407(9)
C(12)-C(13)	1.378(9)
C(12)-H(12)	0.9500
C(13)-C(14)	1.387(9)
C(13)-H(13)	0.9500
C(14)-C(15)	1.383(8)
C(14)-H(14)	0.9500
C(15)-C(16)	1.371(7)

Table A15.4.4. (cont'd)

C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
N(2)-C(9)	1.307(6)
N(2)-C(17)	1.477(7)
C(17)-C(18)	1.593(5)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.323(4)
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9500
C(19)-H(19B)	0.9500
C(9)-C(10)	1.542(8)
C(9)-S(2)	1.653(6)
C(10)-C(22)	1.544(8)
C(10)-C(20)	1.567(7)
C(20)-O(3)	1.215(6)
C(20)-O(4)	1.301(6)
O(4)-C(21)	1.451(6)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-O(5)	1.209(9)
C(22)-O(6)	1.312(9)
O(6)-C(23)	1.464(7)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(1A)-C(10A)	1.450(7)
N(1A)-C(8A)	1.466(7)
C(8A)-N(2A)	1.469(7)
C(8A)-C(11A)	1.503(7)
C(8A)-H(8A)	1.0000
C(11A)-C(16A)	1.383(7)
C(11A)-C(12A)	1.400(9)

Table A15.4.4. (cont'd)

C(12A)-C(13A)	1.387(9)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.384(9)
C(13A)-H(13A)	0.9500
C(14A)-C(15A)	1.384(8)
C(14A)-H(14A)	0.9500
C(15A)-C(16A)	1.381(6)
C(15A)-H(15A)	0.9500
C(16A)-H(16A)	0.9500
N(2A)-C(9A)	1.320(5)
N(2A)-C(17A)	1.463(7)
C(17A)-C(18A)	1.569(6)
C(17A)-H(17C)	0.9900
C(17A)-H(17D)	0.9900
C(18A)-C(19A)	1.207(7)
C(18A)-H(18A)	0.9500
C(19A)-H(19C)	0.9500
C(19A)-H(19D)	0.9500
C(9A)-C(10A)	1.546(7)
C(9A)-S(2A)	1.649(6)
C(10A)-C(22A)	1.535(7)
C(10A)-C(20A)	1.557(7)
C(20A)-O(3A)	1.187(5)
C(20A)-O(4A)	1.342(5)
O(4A)-C(21A)	1.444(6)
C(21A)-H(21D)	0.9800
C(21A)-H(21E)	0.9800
C(21A)-H(21F)	0.9800
C(22A)-O(5A)	1.199(9)
C(22A)-O(6A)	1.310(8)
O(6A)-C(23A)	1.452(7)
C(23A)-H(23D)	0.9800
C(23A)-H(23E)	0.9800
C(23A)-H(23F)	0.9800

Table A15.4.4. (cont'd)

O(2)-S(1)-O(1)	121.63(8)
O(2)-S(1)-N(1)	102.3(4)
O(1)-S(1)-N(1)	110.4(3)
O(2)-S(1)-N(1A)	109.8(3)
O(1)-S(1)-N(1A)	101.0(2)
O(2)-S(1)-C(1)	107.88(8)
O(1)-S(1)-C(1)	106.97(8)
N(1)-S(1)-C(1)	106.8(4)
N(1A)-S(1)-C(1)	109.0(4)
C(6)-C(1)-C(2)	120.95(15)
C(6)-C(1)-S(1)	119.99(13)
C(2)-C(1)-S(1)	118.93(12)
C(3)-C(2)-C(1)	119.01(15)
C(3)-C(2)-H(2)	120.5
C(1)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	121.20(16)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	118.54(16)
C(5)-C(4)-C(7)	120.23(17)
C(3)-C(4)-C(7)	121.22(17)
C(6)-C(5)-C(4)	121.41(16)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	118.88(16)
C(5)-C(6)-H(6)	120.6
C(1)-C(6)-H(6)	120.6
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(10)-N(1)-C(8)	113.4(6)

Table A15.4.4. (cont'd)

C(10)-N(1)-S(1)	116.9(6)
C(8)-N(1)-S(1)	124.7(6)
N(2)-C(8)-N(1)	99.1(5)
N(2)-C(8)-C(11)	110.7(7)
N(1)-C(8)-C(11)	114.5(8)
N(2)-C(8)-H(8)	110.7
N(1)-C(8)-H(8)	110.7
C(11)-C(8)-H(8)	110.7
C(16)-C(11)-C(12)	120.3(7)
C(16)-C(11)-C(8)	119.6(8)
C(12)-C(11)-C(8)	120.0(8)
C(13)-C(12)-C(11)	119.6(9)
C(13)-C(12)-H(12)	120.2
C(11)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	119.3(9)
C(12)-C(13)-H(13)	120.3
C(14)-C(13)-H(13)	120.3
C(15)-C(14)-C(13)	120.9(8)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	120.2(7)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	119.6(7)
C(15)-C(16)-H(16)	120.2
C(11)-C(16)-H(16)	120.2
C(9)-N(2)-C(8)	116.7(5)
C(9)-N(2)-C(17)	123.3(6)
C(8)-N(2)-C(17)	119.5(6)
N(2)-C(17)-C(18)	101.0(6)
N(2)-C(17)-H(17A)	111.6
C(18)-C(17)-H(17A)	111.6
N(2)-C(17)-H(17B)	111.6
C(18)-C(17)-H(17B)	111.6

Table A15.4.4. (cont'd)

H(17A)-C(17)-H(17B)	109.4
C(19)-C(18)-C(17)	108.0(4)
C(19)-C(18)-H(18)	126.0
C(17)-C(18)-H(18)	126.0
C(18)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19B)	120.0
H(19A)-C(19)-H(19B)	120.0
N(2)-C(9)-C(10)	107.7(5)
N(2)-C(9)-S(2)	129.3(5)
C(10)-C(9)-S(2)	122.8(5)
N(1)-C(10)-C(9)	101.9(5)
N(1)-C(10)-C(22)	109.1(7)
C(9)-C(10)-C(22)	108.3(8)
N(1)-C(10)-C(20)	110.8(6)
C(9)-C(10)-C(20)	103.6(6)
C(22)-C(10)-C(20)	121.3(6)
O(3)-C(20)-O(4)	125.8(4)
O(3)-C(20)-C(10)	118.1(5)
O(4)-C(20)-C(10)	115.8(5)
C(20)-O(4)-C(21)	112.4(4)
O(4)-C(21)-H(21A)	109.5
O(4)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(5)-C(22)-O(6)	124.8(10)
O(5)-C(22)-C(10)	118.5(10)
O(6)-C(22)-C(10)	116.5(7)
C(22)-O(6)-C(23)	114.6(7)
O(6)-C(23)-H(23A)	109.5
O(6)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(6)-C(23)-H(23C)	109.5

Table A15.4.4. (cont'd)

H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(10A)-N(1A)-C(8A)	113.8(5)
C(10A)-N(1A)-S(1)	125.0(5)
C(8A)-N(1A)-S(1)	118.5(6)
N(1A)-C(8A)-N(2A)	100.3(5)
N(1A)-C(8A)-C(11A)	115.8(6)
N(2A)-C(8A)-C(11A)	112.6(6)
N(1A)-C(8A)-H(8A)	109.2
N(2A)-C(8A)-H(8A)	109.2
C(11A)-C(8A)-H(8A)	109.2
C(16A)-C(11A)-C(12A)	119.2(7)
C(16A)-C(11A)-C(8A)	119.8(6)
C(12A)-C(11A)-C(8A)	120.8(7)
C(13A)-C(12A)-C(11A)	119.4(9)
C(13A)-C(12A)-H(12A)	120.3
C(11A)-C(12A)-H(12A)	120.3
C(14A)-C(13A)-C(12A)	121.0(8)
C(14A)-C(13A)-H(13A)	119.5
C(12A)-C(13A)-H(13A)	119.5
C(15A)-C(14A)-C(13A)	119.3(7)
C(15A)-C(14A)-H(14A)	120.4
C(13A)-C(14A)-H(14A)	120.4
C(16A)-C(15A)-C(14A)	120.1(7)
C(16A)-C(15A)-H(15A)	119.9
C(14A)-C(15A)-H(15A)	119.9
C(15A)-C(16A)-C(11A)	121.0(6)
C(15A)-C(16A)-H(16A)	119.5
C(11A)-C(16A)-H(16A)	119.5
C(9A)-N(2A)-C(17A)	125.3(5)
C(9A)-N(2A)-C(8A)	115.6(5)
C(17A)-N(2A)-C(8A)	118.6(5)
N(2A)-C(17A)-C(18A)	122.3(7)
N(2A)-C(17A)-H(17C)	106.8

Table A15.4.4. (cont'd)

C(18A)-C(17A)-H(17C)	106.8
N(2A)-C(17A)-H(17D)	106.8
C(18A)-C(17A)-H(17D)	106.8
H(17C)-C(17A)-H(17D)	106.6
C(19A)-C(18A)-C(17A)	126.1(8)
C(19A)-C(18A)-H(18A)	117.0
C(17A)-C(18A)-H(18A)	117.0
C(18A)-C(19A)-H(19C)	120.0
C(18A)-C(19A)-H(19D)	120.0
H(19C)-C(19A)-H(19D)	120.0
N(2A)-C(9A)-C(10A)	108.1(4)
N(2A)-C(9A)-S(2A)	128.1(5)
C(10A)-C(9A)-S(2A)	123.7(4)
N(1A)-C(10A)-C(22A)	109.4(7)
N(1A)-C(10A)-C(9A)	101.6(4)
C(22A)-C(10A)-C(9A)	108.5(7)
N(1A)-C(10A)-C(20A)	113.3(6)
C(22A)-C(10A)-C(20A)	118.7(5)
C(9A)-C(10A)-C(20A)	103.7(5)
O(3A)-C(20A)-O(4A)	125.9(4)
O(3A)-C(20A)-C(10A)	126.7(4)
O(4A)-C(20A)-C(10A)	107.2(4)
C(20A)-O(4A)-C(21A)	116.2(4)
O(4A)-C(21A)-H(21D)	109.5
O(4A)-C(21A)-H(21E)	109.5
H(21D)-C(21A)-H(21E)	109.5
O(4A)-C(21A)-H(21F)	109.5
H(21D)-C(21A)-H(21F)	109.5
H(21E)-C(21A)-H(21F)	109.5
O(5A)-C(22A)-O(6A)	124.5(10)
O(5A)-C(22A)-C(10A)	121.2(9)
O(6A)-C(22A)-C(10A)	114.1(6)
C(22A)-O(6A)-C(23A)	114.6(7)
O(6A)-C(23A)-H(23D)	109.5

Table A15.4.4. (cont'd)

O(6A)-C(23A)-H(23E)	109.5
H(23D)-C(23A)-H(23E)	109.5
O(6A)-C(23A)-H(23F)	109.5
H(23D)-C(23A)-H(23F)	109.5
H(23E)-C(23A)-H(23F)	109.5

Symmetry transformations used to generate equivalent atoms:

*Table A15.4.5. Anisotropic displacement parameters ($Å^2x10^3$) for Imidazolidine **550**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(1)	26(1)	34(1)	-10(1)	3(1)	-3(1)
O(2)	26(1)	47(1)	19(1)	-7(1)	6(1)	-12(1)
S(1)	16(1)	27(1)	21(1)	-8(1)	5(1)	-7(1)
C(1)	20(1)	20(1)	19(1)	-4(1)	2(1)	-5(1)
C(2)	25(1)	19(1)	22(1)	0(1)	-1(1)	-3(1)
C(3)	28(1)	24(1)	21(1)	-4(1)	-2(1)	-2(1)
C(4)	26(1)	20(1)	31(1)	-6(1)	0(1)	-2(1)
C(5)	41(1)	19(1)	34(1)	1(1)	-7(1)	2(1)
C(6)	36(1)	26(1)	22(1)	1(1)	-6(1)	-2(1)
C(7)	41(1)	28(1)	41(1)	-14(1)	-2(1)	0(1)
N(1)	15(2)	17(2)	22(3)	-3(2)	3(2)	-2(2)
C(8)	18(2)	25(3)	19(2)	-4(2)	-1(2)	-6(2)
C(11)	17(2)	19(3)	26(2)	-7(2)	-2(2)	0(2)
C(12)	24(3)	20(4)	19(2)	-7(2)	3(2)	-10(3)
C(13)	23(2)	18(3)	23(3)	-10(2)	-3(3)	-1(2)
C(14)	43(3)	24(4)	32(4)	-8(3)	-3(3)	4(3)
C(15)	38(4)	28(4)	31(3)	-1(3)	-7(2)	6(2)
C(16)	27(3)	32(4)	18(2)	-2(3)	-2(2)	1(3)
N(2)	17(2)	17(3)	26(3)	-11(2)	2(2)	2(2)
C(17)	16(2)	51(4)	21(2)	-22(3)	0(2)	-7(2)
C(18)	8(1)	11(1)	15(1)	-4(1)	-2(1)	2(1)
C(19)	14(1)	32(2)	14(2)	-5(1)	-3(1)	10(1)
C(9)	14(2)	15(3)	33(4)	-10(2)	2(2)	-2(2)
S(2)	24(1)	24(1)	35(1)	-9(1)	6(1)	-9(1)
C(10)	16(2)	19(2)	20(2)	-7(2)	4(2)	1(1)
C(20)	14(2)	21(2)	35(3)	-8(2)	2(2)	-3(1)
O(3)	26(2)	32(3)	24(2)	-9(2)	4(2)	3(2)
O(4)	27(2)	21(2)	31(2)	-2(2)	10(2)	3(1)
C(21)	34(2)	33(2)	51(3)	-5(2)	9(2)	5(2)
C(22)	18(2)	18(2)	26(3)	-3(2)	4(3)	-6(2)

Table A15.4.5. (cont'd)

O(5)	36(3)	25(3)	24(4)	-7(2)	8(3)	3(3)
O(6)	31(2)	29(2)	21(3)	-7(2)	0(3)	1(1)
C(23)	25(2)	27(2)	27(3)	-7(2)	-1(2)	-7(2)
N(1A)	14(2)	16(2)	21(2)	-2(2)	-3(1)	-3(2)
C(8A)	17(2)	15(2)	16(2)	-3(2)	3(1)	0(2)
C(11A)	17(2)	15(2)	18(2)	-2(2)	-2(1)	-5(2)
C(12A)	19(3)	17(3)	29(3)	-6(2)	1(2)	-2(3)
C(13A)	25(2)	26(3)	32(4)	-14(3)	2(3)	-4(2)
C(14A)	31(3)	21(3)	42(4)	-10(2)	-9(3)	2(2)
C(15A)	33(4)	28(4)	31(3)	2(3)	-4(2)	6(2)
C(16A)	22(3)	20(3)	26(2)	-1(2)	-6(2)	1(2)
N(2A)	15(2)	11(2)	26(2)	-4(2)	-2(1)	-1(2)
C(17A)	18(2)	27(2)	24(2)	-6(2)	-3(2)	0(1)
C(18A)	55(3)	89(5)	50(3)	-38(3)	-13(3)	3(3)
C(19A)	107(6)	83(5)	87(6)	-44(4)	53(5)	-25(4)
C(9A)	16(2)	15(2)	21(3)	-4(1)	3(1)	1(2)
S(2A)	22(1)	18(1)	26(1)	0(1)	-1(1)	-7(1)
C(10A)	14(2)	14(2)	24(2)	1(2)	-1(2)	-4(1)
C(20A)	16(1)	16(2)	26(2)	0(2)	-1(2)	-3(1)
O(3A)	27(2)	22(1)	40(2)	1(2)	-8(2)	3(1)
O(4A)	24(1)	25(2)	27(2)	-11(2)	2(2)	2(1)
C(21A)	16(1)	24(2)	59(2)	-27(2)	6(1)	0(1)
C(22A)	18(2)	21(2)	21(2)	-2(2)	2(2)	-7(2)
O(5A)	50(5)	23(3)	26(4)	-4(2)	6(3)	5(3)
O(6A)	33(2)	32(2)	20(3)	-3(2)	-8(3)	6(1)
C(23A)	37(3)	53(4)	19(3)	-3(3)	-6(2)	7(2)

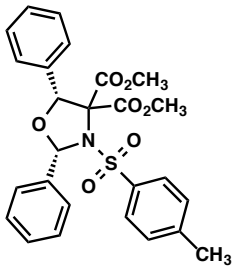
Table A15.4.6. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for Imidazolidine ***550****.*

	x	y	z	U(eq)
H(2)	4925	2180	2158	26
H(3)	4920	3014	2694	29
H(5)	2924	4152	1683	38
H(6)	2923	3327	1140	34
H(7A)	2760	4236	2740	55
H(7B)	4166	4599	2416	55
H(7C)	4838	4142	2829	55
H(8)	1472	1890	427	25
H(12)	-697	2412	1509	26
H(13)	-2345	3334	1579	26
H(14)	-2581	4005	926	39
H(15)	-1326	3739	199	39
H(16)	310	2823	123	31
H(17A)	-2122	1724	307	35
H(17B)	-2996	1213	660	35
H(18)	-1076	358	229	14
H(19A)	-1288	1452	-345	24
H(19B)	-680	760	-544	24
H(21A)	5017	-609	1346	59
H(21B)	5708	-95	976	59
H(21C)	3893	-459	877	59
H(23A)	2690	483	2810	40
H(23B)	805	803	2715	40
H(23C)	2550	1226	2746	40
H(8A)	1560	1725	487	19
H(12A)	-896	2339	1499	26
H(13A)	-2382	3298	1494	33
H(14A)	-2456	3912	809	38
H(15A)	-915	3585	132	37
H(16A)	624	2643	137	27

Table A15.4.6. (cont'd)

H(17C)	-2485	1578	595	27
H(17D)	-2531	848	699	27
H(18A)	-2549	1167	-179	77
H(19C)	673	689	15	111
H(19D)	-320	748	-504	111
H(21D)	4647	139	269	50
H(21E)	4094	-321	693	50
H(21F)	5821	109	742	50
H(23D)	2360	545	2938	54
H(23E)	614	927	2797	54
H(23F)	2470	1283	2847	54

A15.5 X-Ray Crystal Structure Analysis of Oxazolidine 591



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Contents

*Figure A15.5.1. X-Ray Crystal Structure of Oxazolidine **591***

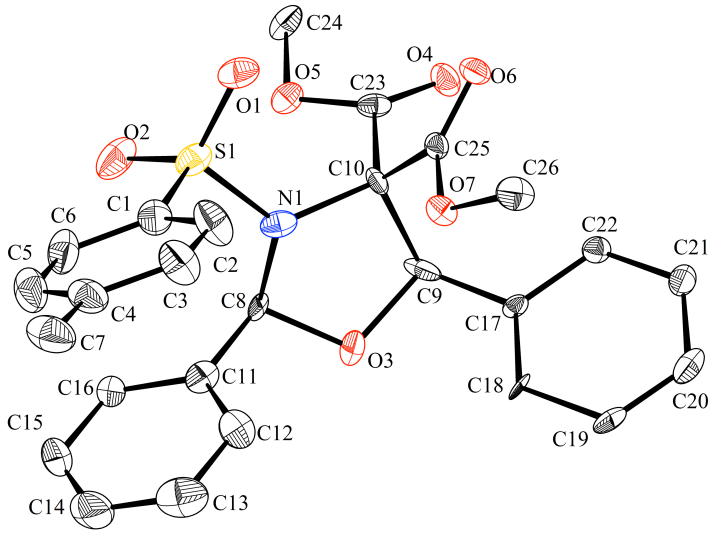


Table A15.5.1. Experimental Details for X-Ray Structure Determination of Oxazolidine ***591***

Low-temperature diffraction data (and scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo *K* radiation (= 0.71073 Å) for the structure of oxazolidine **591**. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2013 refinement using established techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

*Table A15.5.2. Crystal Data and Structure Refinement for Oxazolidine **591**.*

Empirical formula	C26 H25 N O7 S	
CCDC Deposition Number	973928	
Formula weight	495.53	
Crystallization solvent	Ethyl Acetate	
Crystal shape	block	
Crystal color	colourless	
Crystal size	0.34 x 0.39 x 0.41 mm	
Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker APEX-II CCD	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9033 reflections used in lattice determination	2.40 to 34.83°	
Unit cell dimensions	a = 26.2830(13) Å b = 10.5471(5) Å c = 8.4772(4) Å	α= 90° β= 90° γ = 90°
Volume	2350.0(2) $Å^3$	
Z	4	
Crystal system	orthorhombic	
Space group	P c a 21 (# 29)	
Density (calculated)	1.401 g/cm^3	
F(000)	1040	
Theta range for data collection	1.9 to 35.2°	
Completeness to theta = 25.000°	99.8%	
Index ranges	$-42 \le h \le 41, -16 \le k \le 16, -13 \le l \le 13$	
Reflections collected	85187	
Independent reflections	10087 [R_{int}= 0.0399]	
Reflections > 2s(I)	9439	
Average s(I)/(net I)	0.0240	
Absorption coefficient	0.19 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9213	
Primary solution method	dual	
Hydrogen placement	geom	
Refinement method	Full-matrix least-squares on F^2	

Table A15.5.2. (cont'd)

Data / restraints / parameters	10087 / 13 / 538
Treatment of hydrogen atoms	constr
Goodness-of-fit on F^2	1.19
Final R indices [I>2s(I), 9439 reflections]	R1 = 0.0430, wR2 = 0.1033
R indices (all data)	R1 = 0.0470, wR2 = 0.1048
Type of weighting scheme used	calc
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	0.044(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.33 and -0.36 e·$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)
Data collection	APEX2 2013.6-2 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

*Table A15.5.3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Oxazolidine **591**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
S(1)	8926(1)	6201(1)	5357(1)	24(1)
O(1)	8757(1)	5962(1)	6946(2)	28(1)
O(2)	8828(1)	5297(2)	4131(2)	35(1)
N(1)	8669(1)	7567(1)	4885(2)	21(1)
C(1)	9589(1)	6443(2)	5403(3)	26(1)
C(2)	9800(1)	7205(3)	6560(3)	36(1)
C(3)	10325(1)	7313(3)	6651(3)	38(1)
C(4)	10644(1)	6666(2)	5619(2)	32(1)
C(5)	10424(1)	5912(2)	4466(3)	37(1)
C(6)	9899(1)	5798(2)	4339(3)	32(1)
C(7)	11214(1)	6743(3)	5801(3)	41(1)
O(3)	8454(4)	9290(10)	3416(13)	31(2)
O(4)	7331(1)	7845(3)	6401(4)	23(1)
O(5)	7789(6)	6381(13)	5033(14)	20(1)
O(6)	8103(1)	8362(3)	8651(3)	20(1)
O(7)	8770(1)	9307(3)	7484(3)	18(1)
C(8)	8655(4)	7986(7)	3269(11)	13(2)
C(9)	8056(7)	9322(18)	4700(20)	22(3)
C(10)	8209(5)	8173(18)	5850(20)	16(2)
C(11)	9116(4)	8065(15)	2442(16)	21(2)
C(12)	9471(3)	8980(7)	2868(7)	26(1)
C(13)	9938(2)	9060(6)	2102(10)	40(1)
C(14)	10053(3)	8198(8)	966(11)	44(2)
C(15)	9701(3)	7272(7)	552(10)	44(2)
C(16)	9233(3)	7206(6)	1270(9)	29(1)
C(17)	8091(3)	10654(7)	5427(12)	13(1)
C(18)	8430(3)	11443(5)	4959(11)	16(1)
C(19)	8464(3)	12722(6)	5697(9)	24(1)
C(20)	8107(2)	13055(4)	6806(6)	25(1)

Table A15.5.3. (cont'd)

C(21)	7731(2)	12188(4)	7246(5)	19(1)
C(22)	7720(2)	10989(4)	6570(5)	16(1)
C(23)	7715(2)	7381(7)	5901(9)	17(1)
C(24)	7324(6)	5619(14)	5180(20)	23(2)
C(25)	8350(2)	8604(3)	7505(4)	14(1)
C(26)	8860(2)	10020(4)	8925(4)	26(1)
O(3A)	8459(2)	9216(8)	3393(7)	13(1)
O(4A)	7556(1)	7446(3)	7202(4)	30(1)
O(5A)	7767(6)	6217(12)	5341(14)	22(1)
O(6A)	8992(1)	9186(3)	7025(4)	23(1)
O(7A)	8266(1)	8980(3)	8372(3)	22(1)
C(8A)	8668(6)	8051(11)	3175(15)	37(3)
C(9A)	8106(5)	9189(15)	4546(18)	13(2)
C(10A)	8303(5)	8102(13)	5730(17)	11(1)
C(11A)	9229(3)	8166(12)	2597(11)	17(1)
C(12A)	9556(2)	8999(5)	3331(6)	19(1)
C(13A)	10052(2)	9131(4)	2790(6)	26(1)
C(14A)	10225(2)	8406(6)	1527(6)	31(1)
C(15A)	9903(3)	7558(7)	790(6)	30(1)
C(16A)	9402(2)	7438(6)	1290(7)	25(1)
C(17A)	8008(3)	10427(7)	5241(10)	15(1)
C(18A)	8397(5)	11464(10)	5114(14)	45(3)
C(19A)	8298(3)	12553(7)	5784(10)	38(2)
C(20A)	7868(3)	12772(5)	6675(6)	39(1)
C(21A)	7503(2)	11837(5)	6819(5)	36(1)
C(22A)	7578(2)	10668(4)	6104(5)	26(1)
C(23A)	7845(2)	7284(7)	6149(8)	16(1)
C(24A)	7299(7)	5528(16)	5250(30)	41(4)
C(25A)	8564(2)	8793(3)	7139(4)	14(1)
C(26A)	8481(2)	9837(5)	9541(4)	31(1)

*Table A15.5.4. Bond lengths [Å] and angles [°] for Oxazolidine **591**.*

S(1)-O(1)	1.4406(16)
S(1)-O(2)	1.4334(17)
S(1)-N(1)	1.6401(16)
S(1)-C(1)	1.762(2)
N(1)-C(8)	1.440(10)
N(1)-C(10)	1.592(12)
N(1)-C(8A)	1.537(13)
N(1)-C(10A)	1.326(11)
C(1)-C(2)	1.384(3)
C(1)-C(6)	1.393(3)
C(2)-H(2)	0.9500
C(2)-C(3)	1.386(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.390(3)
C(4)-C(5)	1.386(4)
C(4)-C(7)	1.510(3)
C(5)-H(5)	0.9500
C(5)-C(6)	1.389(4)
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
O(3)-C(8)	1.478(14)
O(3)-C(9)	1.51(2)
O(4)-C(23)	1.198(8)
O(5)-C(23)	1.301(19)
O(5)-C(24)	1.47(2)
O(6)-C(25)	1.196(5)
O(7)-C(25)	1.330(5)
O(7)-C(26)	1.454(5)
C(8)-H(8)	1.0000
C(8)-C(11)	1.403(16)
C(9)-H(9)	1.0000

Table A15.5.4. (cont'd)

C(9)-C(10)	1.60(3)
C(9)-C(17)	1.54(2)
C(10)-C(23)	1.546(18)
C(10)-C(25)	1.52(2)
C(11)-C(12)	1.389(12)
C(11)-C(16)	1.379(16)
C(12)-H(12)	0.9500
C(12)-C(13)	1.393(10)
C(13)-H(13)	0.9500
C(13)-C(14)	1.359(12)
C(14)-H(14)	0.9500
C(14)-C(15)	1.389(11)
C(15)-H(15)	0.9500
C(15)-C(16)	1.374(9)
C(16)-H(16)	0.9500
C(17)-C(18)	1.283(10)
C(17)-C(22)	1.418(11)
C(18)-H(18)	0.9500
C(18)-C(19)	1.490(9)
C(19)-H(19)	0.9500
C(19)-C(20)	1.374(9)
C(20)-H(20)	0.9500
C(20)-C(21)	1.396(6)
C(21)-H(21)	0.9500
C(21)-C(22)	1.389(6)
C(22)-H(22)	0.9500
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
O(3A)-C(8A)	1.358(15)
O(3A)-C(9A)	1.348(18)

Table A15.5.4. (cont'd)

O(4A)-C(23A)	1.185(8)
O(5A)-C(23A)	1.334(17)
O(5A)-C(24A)	1.43(2)
O(6A)-C(25A)	1.203(5)
O(7A)-C(25A)	1.320(4)
O(7A)-C(26A)	1.455(5)
C(8A)-H(8A)	1.0000
C(8A)-C(11A)	1.558(17)
C(9A)-H(9A)	1.0000
C(9A)-C(10A)	1.61(2)
C(9A)-C(17A)	1.456(19)
C(10A)-C(23A)	1.523(15)
C(10A)-C(25A)	1.558(16)
C(11A)-C(12A)	1.378(11)
C(11A)-C(16A)	1.423(12)
C(12A)-H(12A)	0.9500
C(12A)-C(13A)	1.391(7)
C(13A)-H(13A)	0.9500
C(13A)-C(14A)	1.393(7)
C(14A)-H(14A)	0.9500
C(14A)-C(15A)	1.380(8)
C(15A)-H(15A)	0.9500
C(15A)-C(16A)	1.390(8)
C(16A)-H(16A)	0.9500
C(17A)-C(18A)	1.500(13)
C(17A)-C(22A)	1.371(11)
C(18A)-H(18A)	0.9500
C(18A)-C(19A)	1.307(14)
C(19A)-H(19A)	0.9500
C(19A)-C(20A)	1.379(11)
C(20A)-H(20A)	0.9500
C(20A)-C(21A)	1.381(9)
C(21A)-H(21A)	0.9500
C(21A)-C(22A)	1.388(6)

Table A15.5.4. (cont'd)

C(22A)-H(22A)	0.9500
C(24A)-H(24D)	0.9800
C(24A)-H(24E)	0.9800
C(24A)-H(24F)	0.9800
C(26A)-H(26D)	0.9800
C(26A)-H(26E)	0.9800
C(26A)-H(26F)	0.9800

O(1)-S(1)-N(1)	104.74(9)
O(1)-S(1)-C(1)	108.06(10)
O(2)-S(1)-O(1)	120.43(10)
O(2)-S(1)-N(1)	109.52(9)
O(2)-S(1)-C(1)	106.81(11)
N(1)-S(1)-C(1)	106.53(8)
C(8)-N(1)-S(1)	120.8(3)
C(8)-N(1)-C(10)	110.1(8)
C(10)-N(1)-S(1)	122.7(7)
C(10A)-N(1)-C(8A)	111.5(8)
C(2)-C(1)-S(1)	119.77(16)
C(2)-C(1)-C(6)	120.5(2)
C(6)-C(1)-S(1)	119.58(17)
C(1)-C(2)-H(2)	120.4
C(1)-C(2)-C(3)	119.1(2)
C(3)-C(2)-H(2)	120.4
C(2)-C(3)-H(3)	119.2
C(2)-C(3)-C(4)	121.6(2)
C(4)-C(3)-H(3)	119.2
C(3)-C(4)-C(7)	120.5(2)
C(5)-C(4)-C(3)	118.4(2)
C(5)-C(4)-C(7)	121.1(2)
C(4)-C(5)-H(5)	119.4
C(4)-C(5)-C(6)	121.2(2)
C(6)-C(5)-H(5)	119.4
C(1)-C(6)-H(6)	120.4

Table A15.5.4. (cont'd)

C(5)-C(6)-C(1)	119.2(2)
C(5)-C(6)-H(6)	120.4
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(8)-O(3)-C(9)	109.2(11)
C(23)-O(5)-C(24)	105.8(12)
C(25)-O(7)-C(26)	114.3(3)
N(1)-C(8)-O(3)	102.4(6)
N(1)-C(8)-H(8)	109.6
O(3)-C(8)-H(8)	109.6
C(11)-C(8)-N(1)	118.1(8)
C(11)-C(8)-O(3)	107.2(10)
C(11)-C(8)-H(8)	109.6
O(3)-C(9)-H(9)	110.4
O(3)-C(9)-C(10)	104.1(13)
O(3)-C(9)-C(17)	105.5(12)
C(10)-C(9)-H(9)	110.4
C(17)-C(9)-H(9)	110.4
C(17)-C(9)-C(10)	115.7(13)
N(1)-C(10)-C(9)	100.7(11)
C(23)-C(10)-N(1)	115.9(12)
C(23)-C(10)-C(9)	102.4(12)
C(25)-C(10)-N(1)	114.0(11)
C(25)-C(10)-C(9)	113.2(13)
C(25)-C(10)-C(23)	109.7(10)
C(12)-C(11)-C(8)	119.4(11)
C(16)-C(11)-C(8)	120.9(9)
C(16)-C(11)-C(12)	119.6(10)
C(11)-C(12)-H(12)	119.5
C(11)-C(12)-C(13)	120.9(8)

Table A15.5.4. (cont'd)

C(13)-C(12)-H(12)	119.5
C(12)-C(13)-H(13)	120.5
C(14)-C(13)-C(12)	119.0(6)
C(14)-C(13)-H(13)	120.5
C(13)-C(14)-H(14)	119.9
C(13)-C(14)-C(15)	120.1(6)
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-C(14)	121.3(7)
C(16)-C(15)-H(15)	119.4
C(11)-C(16)-H(16)	120.5
C(15)-C(16)-C(11)	119.0(7)
C(15)-C(16)-H(16)	120.5
C(18)-C(17)-C(9)	120.7(11)
C(18)-C(17)-C(22)	121.8(7)
C(22)-C(17)-C(9)	117.4(9)
C(17)-C(18)-H(18)	120.0
C(17)-C(18)-C(19)	119.9(9)
C(19)-C(18)-H(18)	120.0
C(18)-C(19)-H(19)	120.7
C(20)-C(19)-C(18)	118.6(5)
C(20)-C(19)-H(19)	120.7
C(19)-C(20)-H(20)	120.1
C(19)-C(20)-C(21)	119.9(4)
C(21)-C(20)-H(20)	120.1
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-C(20)	120.1(4)
C(22)-C(21)-H(21)	120.0
C(17)-C(22)-H(22)	120.2
C(21)-C(22)-C(17)	119.7(4)
C(21)-C(22)-H(22)	120.2
O(4)-C(23)-O(5)	131.1(9)
O(4)-C(23)-C(10)	119.8(8)
O(5)-C(23)-C(10)	107.1(10)

Table A15.5.4. (cont'd)

O(5)-C(24)-H(24A)	109.5
O(5)-C(24)-H(24B)	109.5
O(5)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(6)-C(25)-O(7)	125.5(3)
O(6)-C(25)-C(10)	123.6(7)
O(7)-C(25)-C(10)	110.8(7)
O(7)-C(26)-H(26A)	109.5
O(7)-C(26)-H(26B)	109.5
O(7)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(9A)-O(3A)-C(8A)	111.0(10)
C(23A)-O(5A)-C(24A)	125.9(13)
C(25A)-O(7A)-C(26A)	113.7(3)
N(1)-C(8A)-H(8A)	112.3
N(1)-C(8A)-C(11A)	108.6(9)
O(3A)-C(8A)-N(1)	100.0(8)
O(3A)-C(8A)-H(8A)	112.3
O(3A)-C(8A)-C(11A)	110.8(10)
C(11A)-C(8A)-H(8A)	112.3
O(3A)-C(9A)-H(9A)	107.5
O(3A)-C(9A)-C(10A)	104.2(11)
O(3A)-C(9A)-C(17A)	113.3(11)
C(10A)-C(9A)-H(9A)	107.5
C(17A)-C(9A)-H(9A)	107.5
C(17A)-C(9A)-C(10A)	116.3(11)
N(1)-C(10A)-C(9A)	101.5(10)
N(1)-C(10A)-C(23A)	117.3(10)
N(1)-C(10A)-C(25A)	107.1(9)
C(23A)-C(10A)-C(9A)	107.1(9)

Table A15.5.4. (cont'd)

C(23A)-C(10A)-C(25A)	115.7(9)
C(25A)-C(10A)-C(9A)	106.7(9)
C(12A)-C(11A)-C(8A)	119.8(9)
C(12A)-C(11A)-C(16A)	119.7(7)
C(16A)-C(11A)-C(8A)	120.4(8)
C(11A)-C(12A)-H(12A)	120.0
C(11A)-C(12A)-C(13A)	120.0(6)
C(13A)-C(12A)-H(12A)	120.0
C(12A)-C(13A)-H(13A)	119.8
C(12A)-C(13A)-C(14A)	120.3(5)
C(14A)-C(13A)-H(13A)	119.8
C(13A)-C(14A)-H(14A)	119.9
C(15A)-C(14A)-C(13A)	120.2(5)
C(15A)-C(14A)-H(14A)	119.9
C(14A)-C(15A)-H(15A)	119.9
C(14A)-C(15A)-C(16A)	120.2(5)
C(16A)-C(15A)-H(15A)	119.9
C(11A)-C(16A)-H(16A)	120.3
C(15A)-C(16A)-C(11A)	119.5(6)
C(15A)-C(16A)-H(16A)	120.3
C(9A)-C(17A)-C(18A)	120.4(10)
C(22A)-C(17A)-C(9A)	121.8(8)
C(22A)-C(17A)-C(18A)	117.7(8)
C(17A)-C(18A)-H(18A)	120.8
C(19A)-C(18A)-C(17A)	118.3(11)
C(19A)-C(18A)-H(18A)	120.8
C(18A)-C(19A)-H(19A)	118.4
C(18A)-C(19A)-C(20A)	123.2(8)
C(20A)-C(19A)-H(19A)	118.4
C(19A)-C(20A)-H(20A)	120.0
C(19A)-C(20A)-C(21A)	119.9(5)
C(21A)-C(20A)-H(20A)	120.0
C(20A)-C(21A)-H(21A)	120.1
C(20A)-C(21A)-C(22A)	119.8(5)

Table A15.5.4. (cont'd)

C(22A)-C(21A)-H(21A)	120.1
C(17A)-C(22A)-C(21A)	121.0(5)
C(17A)-C(22A)-H(22A)	119.5
C(21A)-C(22A)-H(22A)	119.5
O(4A)-C(23A)-O(5A)	114.2(8)
O(4A)-C(23A)-C(10A)	126.9(8)
O(5A)-C(23A)-C(10A)	118.7(9)
O(5A)-C(24A)-H(24D)	109.5
O(5A)-C(24A)-H(24E)	109.5
O(5A)-C(24A)-H(24F)	109.5
H(24D)-C(24A)-H(24E)	109.5
H(24D)-C(24A)-H(24F)	109.5
H(24E)-C(24A)-H(24F)	109.5
O(6A)-C(25A)-O(7A)	124.5(3)
O(6A)-C(25A)-C(10A)	120.7(5)
O(7A)-C(25A)-C(10A)	114.6(5)
O(7A)-C(26A)-H(26D)	109.5
O(7A)-C(26A)-H(26E)	109.5
O(7A)-C(26A)-H(26F)	109.5
H(26D)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26F)	109.5
H(26E)-C(26A)-H(26F)	109.5

Symmetry transformations used to generate equivalent atoms:

*Table A15.5.5. Anisotropic displacement parameters ($Å^2x10^3$) for Oxazolidine **591**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	307(2)	186(2)	231(2)	33(2)	-63(2)	-10(2)
O(1)	299(7)	260(6)	277(7)	110(5)	-33(6)	3(5)
O(2)	504(10)	189(6)	359(8)	-28(6)	-108(7)	-39(6)
N(1)	222(7)	202(6)	190(6)	63(5)	-40(5)	-31(5)
C(1)	303(8)	267(8)	212(7)	15(7)	-14(8)	46(6)
C(2)	286(10)	507(13)	276(10)	-125(9)	36(8)	-28(9)
C(3)	307(11)	485(13)	337(11)	-73(10)	37(9)	-18(10)
C(4)	296(9)	390(10)	257(10)	110(8)	35(7)	86(8)
C(5)	410(12)	399(12)	294(10)	26(9)	30(9)	217(10)
C(6)	417(11)	278(9)	275(9)	-42(7)	-51(8)	135(9)
C(7)	304(10)	553(15)	381(12)	187(11)	61(9)	93(10)
O(3)	460(40)	160(30)	310(40)	0(20)	120(30)	110(30)
O(4)	174(12)	241(13)	269(14)	-59(11)	87(10)	-40(10)
O(5)	190(17)	160(30)	240(40)	-20(20)	-30(20)	-50(20)
O(6)	217(12)	216(13)	152(11)	5(9)	47(9)	-27(10)
O(7)	153(13)	231(13)	161(11)	-15(10)	-1(10)	-22(11)
C(8)	230(30)	62(19)	100(30)	-50(18)	-40(20)	-7(18)
C(9)	150(30)	330(60)	170(40)	120(40)	70(20)	30(30)
C(10)	160(50)	180(30)	140(20)	-39(17)	70(30)	0(30)
C(11)	240(40)	190(20)	200(30)	0(20)	-60(20)	-20(30)
C(12)	250(30)	340(20)	200(30)	-40(20)	-40(20)	-1(19)
C(13)	240(20)	470(30)	510(40)	130(30)	-50(20)	-60(20)
C(14)	290(30)	460(40)	590(50)	160(40)	210(30)	110(30)
C(15)	500(40)	320(30)	490(40)	40(30)	300(40)	140(30)
C(16)	410(40)	180(20)	280(20)	-15(17)	140(30)	0(20)
C(17)	90(30)	90(20)	200(30)	15(18)	7(19)	-23(16)
C(18)	220(20)	15(15)	230(30)	-4(13)	16(19)	2(14)
C(19)	320(30)	90(20)	330(20)	38(15)	50(20)	-60(18)
C(20)	340(20)	119(15)	290(20)	-3(14)	-48(18)	14(15)
C(21)	245(17)	156(15)	180(16)	-8(13)	-10(14)	27(13)

Table A15.5.5. (cont'd)

C(22)	171(16)	153(15)	149(15)	-6(11)	-8(12)	-31(12)
C(23)	190(30)	180(20)	140(20)	25(15)	-25(17)	-80(20)
C(24)	220(30)	130(20)	350(50)	10(30)	-40(30)	-10(30)
C(25)	133(15)	148(13)	145(15)	4(11)	12(12)	34(12)
C(26)	303(19)	281(18)	184(16)	-36(13)	-26(13)	-96(15)
O(3A)	140(20)	190(30)	70(20)	66(16)	-31(17)	-61(18)
O(4A)	256(14)	344(14)	299(15)	-66(12)	118(12)	-107(12)
O(5A)	260(20)	140(30)	270(40)	0(20)	-50(30)	-14(18)
O(6A)	177(13)	288(13)	215(12)	-71(10)	12(10)	-61(10)
O(7A)	191(11)	331(15)	125(10)	-33(10)	4(9)	-16(10)
C(8A)	500(60)	380(50)	210(30)	200(30)	-110(30)	-90(30)
C(9A)	70(30)	190(20)	120(30)	32(17)	-20(30)	-40(30)
C(10A)	150(40)	90(20)	90(30)	0(17)	30(20)	-30(20)
C(11A)	220(40)	210(30)	90(20)	-4(17)	10(20)	20(30)
C(12A)	210(20)	216(16)	150(20)	-35(17)	29(16)	-32(15)
C(13A)	225(18)	255(18)	290(20)	37(15)	101(16)	-5(14)
C(14A)	260(20)	390(20)	290(20)	84(19)	134(17)	40(20)
C(15A)	320(30)	390(30)	182(17)	24(19)	100(20)	120(20)
C(16A)	310(30)	270(30)	175(16)	2(16)	17(19)	21(19)
C(17A)	140(30)	140(30)	170(20)	58(19)	-45(16)	-15(17)
C(18A)	500(50)	630(60)	210(30)	0(30)	10(30)	250(40)
C(19A)	540(50)	150(20)	440(30)	31(19)	-160(30)	-80(30)
C(20A)	660(40)	220(20)	290(20)	-85(19)	-130(30)	210(20)
C(21A)	550(30)	320(20)	207(17)	30(16)	42(19)	250(20)
C(22A)	310(20)	248(18)	212(18)	64(14)	66(15)	117(16)
C(23A)	160(30)	163(16)	140(20)	-14(14)	-3(16)	-17(18)
C(24A)	420(50)	300(50)	510(80)	-30(50)	-110(50)	-210(30)
C(25A)	146(15)	150(13)	116(12)	12(10)	-2(12)	17(12)
C(26A)	312(18)	480(20)	150(14)	-139(15)	-44(13)	16(17)

*Table A15.5.6. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for Oxazolidine **591**.*

	x	y	z	U_{iso}
H(2)	959	765	728	43
H(3)	1047	784	744	45
H(5)	1064	546	375	44
H(6)	975	529	354	39
H(7A)	1131	760	612	62
H(7B)	1138	654	479	62
H(7C)	1133	614	661	62
H(8)	841	745	266	16
H(9)	771	918	425	26
H(12)	939	956	369	31
H(13)	1017	971	237	48
H(14)	1037	823	45	53
H(15)	979	667	-24	52
H(16)	899	658	96	35
H(18)	866	1121	414	19
H(19)	873	1330	541	29
H(20)	811	1387	727	30
H(21)	748	1242	801	23
H(22)	747	1040	687	19
H(24A)	737	481	462	35
H(24B)	704	608	471	35
H(24C)	725	545	629	35
H(26A)	909	1074	870	38
H(26B)	902	947	971	38
H(26C)	854	1034	933	38
H(8A)	846	751	246	44
H(9A)	778	889	407	15
H(12A)	944	948	421	23
H(13A)	1028	972	329	31
H(14A)	1057	850	117	38

Table A15.5.6. (cont'd)

H(15A)	1003	706	-6	36
H(16A)	918	687	76	30
H(18A)	871	1133	456	54
H(19A)	853	1323	565	45
H(20A)	782	1356	719	47
H(21A)	720	1199	740	43
H(22A)	733	1003	622	31
H(24D)	706	597	455	62
H(24E)	715	547	631	62
H(24F)	736	467	485	62
H(26D)	851	1069	909	47
H(26E)	882	954	985	47
H(26F)	826	986	1047	47

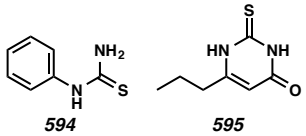
APPENDIX 16

Synthesis of Functionalized Thiouracils as G Protein-Coupled Receptor Agonists

A16.1 Introduction

G protein-coupled receptors (GPCRs) are a large family of transmembrane proteins integral to mammalian life.[1] The abnormal expression or functioning of GPCRs can lead to cardiac, inflammatory, and central nervous system disease as well as cancer among many other ailments.[2] Recently, the GPCRs responsible for the sensation of bitter taste have been discovered in the mammalian gastrointestinal (GI) tract and have been shown to up-regulate insulin levels when activated.[1,3] Intrigued by the interesting activity of the bitter taste GPCRs in the GI tract, the Goddard group at Caltech performed a computational binding study, assessing the binding affinity of thiocarbamide **594** and thiouracil **595** at the known binding site within the GPCR bitter taste receptor TAS2R38 (Figure A16.1.1).[1b] Previously, both thiocarbamide **594** and *n*-propylthiouracil **595** had empirically been determined to be bitter taste receptor agonists.[4]

Figure A16.1.1. Computationally-Validated Bitter Taste GPCR Agonists

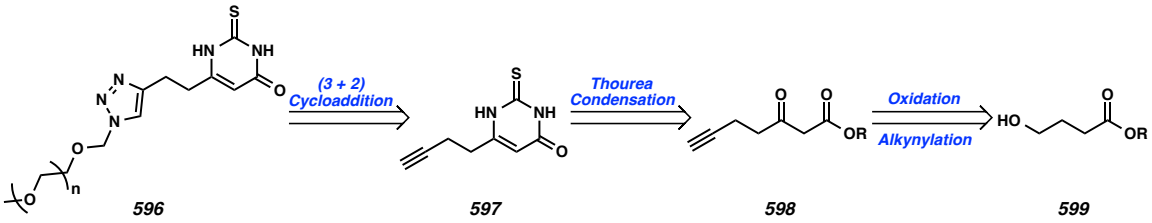


594 ***595***

A16.2 Retrosynthetic Analysis

We hypothesized that the functionalization of a thiouracil with a polymeric (ca. 20 kDa) polyethylene glycol (PEG) chain (**596**) could serve as a potential therapeutic for diabetic patients (Scheme A16.2.1). After ingestion, the GI tract could not absorb the PEGylated thiouracil. Rather, PEGylated thiourcail **596** would remain on the inner surface of the GI tract, interacting with the bitter taste GPCRs, causing persistent activation, up-regulation of insulin, and thus normalization of blood glucose levels.

Scheme A16.2.1. Retrosynthetic Analaysis of PEGylated Thiouracil



596 ***597*** ***598*** ***599***

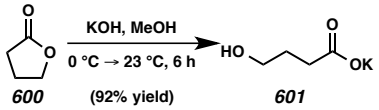
Retrosynthetically, we envisioned accessing PEGylated thiouracil **596** through a azide/alkyne (3 + 2) dipolar cycloaddition between alkyne **597** and a 20 kDa PEG azide. Heterocycle **597** would be formed after the condensation of thiourea onto β-ketoester **598**. Alkyne **598** would in turn be synthesized from γ-hydroxybutyrate **599** by sequential oxidation and alkynylation.

A16.3 Synthesis of a Functionalized Thiouracil

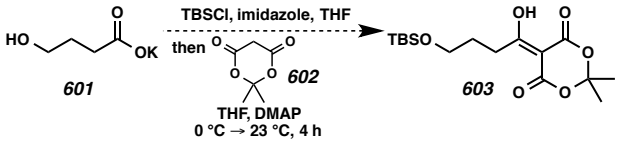
Our synthetic explorations began with the development of an efficient and concise route toward β-ketoester **598** beginning with butyrolactone (**600**) as the feedstock

(Scheme A16.3.1). Saponification of lactone **600** with KOH in dry MeOH provided potassium salt in 92% yield.[5] We subsequently explored the potential to convert metal carboxylate **601** into the corresponding β-ketoester by formation of the silyl ether and the condensation onto Meldrum's acid (**602**, Scheme A16.3.2).[6,7] Unfortunately, the formation of the TBS ester of carboxylate **601** provided any trace of enol **603**.

*Scheme A16.3.1. Saponification of Lactone **600***

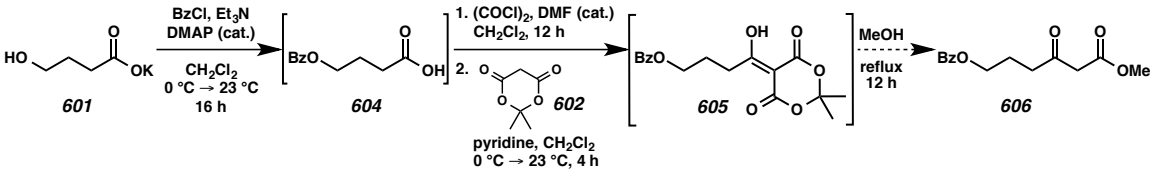


*Scheme A16.3.2. Attempted Condensation of Carboxylate Salt **601** onto Meldrum's Acid (**602**)*



Alternatively, we set about advancing toward the β-ketoester of carboxylate **601** in a step-wise fashion, beginning with the benzoylation of the primary alcohol (Scheme A16.3.3). The crude acid **604** was advanced by acid chloride formation and subsequent condensation with Meldrum's acid (**602**). Crude diester **605** was immediately subjected to methanolysis conditions, however, the formation of β-ketoester **606** was not observed.

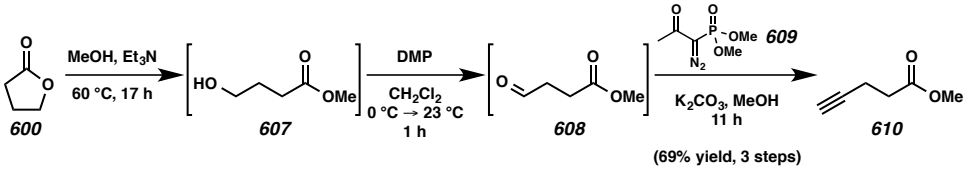
*Scheme A16.3.3. β-Ketoester Formation from Carboxylate Salt **601***



Without any success generating γ-hydroxy-β-ketoesters, we targeted modifying our synthetic procedure by installing the alkyne moiety prior to dicarbonyl formation. Butyrolacone (**600**) was alternatively opened by methanolysis to provide ester **607**

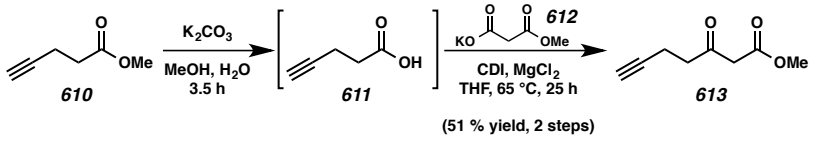
(Scheme A16.3.4).[8] Oxidation of crude primary alcohol **607** to intermediate aldehyde **608** followed by homologation with the Ohira–Bestmann reagent (**609**)[9] provided methyl 4-pentynoate (**610**) in 69% yield over three steps.

*Scheme A16.3.4. Synthetic Access to Alkyne **610***



Methyl ester **610** was then saponified under standard conditions to provide intermediate acid **611** (Scheme A16.3.5). Crude acid **611** was transformed to β-ketoester **613** using CDI and malonate salt **612**.[10] Applying a carefully choreographed experimental procedure for the transformation of acid **611**, we could isolate β-ketoester **613** in 51% yield over two steps.[11]

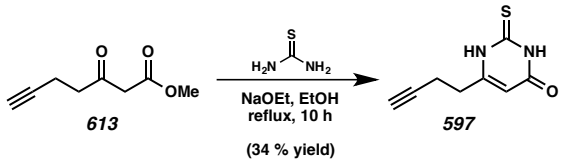
*Scheme A16.3.5. Construction of β-Ketoester **613***



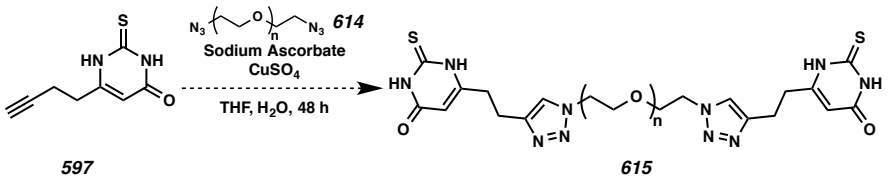
Formation of the corresponding thiouracil **597** from β-ketoester **613** proceeded smoothly under standard condensation conditions employing freshly formed NaOEt in 34% yield (Scheme A16.3.6).[12] With alkyne **597** in hand, we next needed to develop conditions for the desired (3 + 2) cycloaddition with 20 kDa PEG azide **614** (Scheme A16.3.7). Using bisazide **614**, the most readily available PEG azide polymer, we would need to be mindful of mono- and difunctionalization of each PEG chain. Although we hypothesized that both the mono- and difunctionalized PEG chains would have similar

biological activity profiles and pharmacokinetics (PK), we would need to gather biological activity and PK data on each functionalized PEG separately.

Scheme A16.3.6. Thiouracil Formation



*Scheme A16.3.7. Attempted PEGylation of Thiouracil **597** by Click Reaction*



Initially, to avoid complex mixture of variably functionalized polymers, we sought to exhaustively functionalize bisazide **614** using standard azide/alkyne (3 + 2) dipolar cycloaddition conditions with a 3-fold excess of alkyne **597**.[13] Unfortunately, no trace of bisthiouracil PEG **615** was ever detected.[14] Reaction conditions in which $CuSO_4$ was substituted for $CuBr_2$ also failed to provide any trace of product **615**. We suspect the commercially available azide, which possessed *no trace* of the characteristic azide IR stretch frequency, was the troublesome component in the click reaction.

Although the production of the 20 kDa PEGylated thiouracil compounds (e.g. **615**) was never completed, the potential of these compounds as drug candidates remains exceptional. Using thiouracil drug candidates modeled on the PTU scaffold to up-regulate the natural production of insulin in vivo to correct blood glucose levels would represent a new paradigm in the treatment of mammalian diabetes. This could conceivably lead to the more effective, painless treatment of diabetes in million of humans across the globe and progress state of the art medicine toward a cure for diabetes.

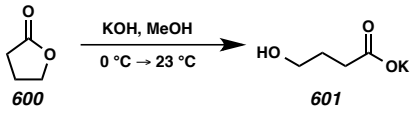
A16.4 Experimental Methods and Analytical Data

A16.4.1 Materials and Methods

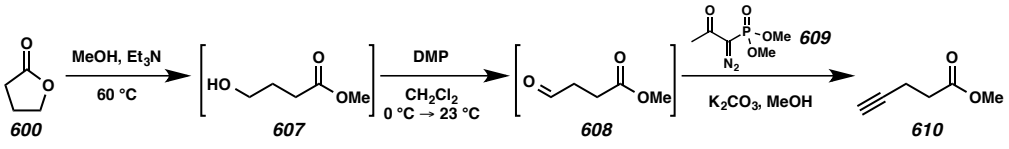
Unless stated otherwise, reactions were performed at ambient temperature (23 °C) in flame-dried glassware under an argon atmosphere using dry, deoxygentated solvents (distilled or passed over a column of activated alumina)[15] using a Teflon®-coated magnetic stirring bar. Commercially available reagents were used as received unless otherwise noted. Et_3N was distilled from calcium hydride immediately prior to use. MeOH was distilled from magnesium methoxide immediately prior to use. Purified H_2O was obtained using a Barnstead NANOpure Infinity UV/UF system. 4 Å molecular sieves were oven-dried at 120 °C for a minimum of 24 h and cooled in a desiccator to ambient temperature immediately prior to use. Ohira–Bestmann reagent[16] was prepared by known methods. Reactions requiring external heat were modulated to the specified temperatures using an IKAmag temperature controller. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (250 nm) and visualized by UV fluorescence quenching, potassium permanganate, or *p*-anisaldehyde staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40-63 nm) was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on Bruker AV III HD spectrometer equipped with a Prodigy liquid nitrogen temperature cryoprobe (400 MHz and 101 MHz, respectively) and are reported in terms of chemical shift relative to residual protio-methanol (in CD_3OD, δ 4.87, 3.31 and δ 49.00, respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Infrared (IR) spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). High

resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) ionization mode. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path length cell at 589 nm.

A16.4.2 Experimental Procedures



Carboxylate 601:[17] To a homogenous solution of KOH (1.24 g, 22.1 mmol, 1.00 equiv) in MeOH (11 mL) at 0 °C (ice/H_2O bath) was added lactone **600** (2.00 g, 23.2 mmol, 1.05 equiv) as a solution in MeOH (5.2 mL) quickly dropwise over 2 minutes. After 5 minutes, the homogeneous, colorless reaction mixture was removed from the cooling bath and allowed to warm to ambient temperature (ca. 23 °C). After an additional 6 h, the reaction mixture was concentrated in vacuo. The crude pale yellow solid was triturated with Et_2O (3 x 40 mL) and then dried in vacuo to provide carboxylate **601** (2.90 g, 92% yield) as an amorphous white solid: characterization data match those reported in the literature.[5]



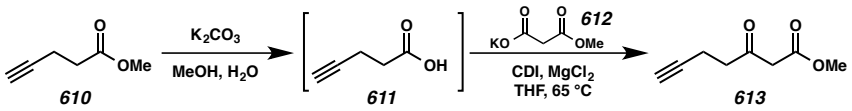
Alkyne 610:[18] To a solution of lactone **600** (0.76 mL, 10.0 mmol, 1.00 equiv) in MeOH (50 mL) was added Et_3N (8.40 mL, 60.0 mmol, 6.00 equiv) quickly dropwise. The reaction mixture was then introduced to a preheated 60 °C bath. After 17 h, the reaction

mixture was removed from the heating bath and allowed to cool to ambient temperature (ca. 23 °C). The reaction was then concentrated in vacuo and the resultant pale yellow oil was carried on to the next transformation without further purification.

To a stirred solution of crude methyl ester **607** (11.8 g, 10.0 mmol, 1.00 equiv) in CH_2Cl_2 (100 mL) at 0 °C (ice/H_2O bath) was added DMP (5.09 g, 12.0 mmol, 1.20 equiv) as a solid in a single portion. After 30 minutes, the reaction was removed from the cooling bath and allowed to warm to ambient temperature (ca. 23 °C). After an additional 30 minutes, the consumption of starting material was complete as determined by TLC (1:1 EtOAc:Hexanes eluent). The reaction was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (50 mL) with vigorous stirring. After 15 minutes, the biphasic reaction mixture was poured onto saturated aqueous $NaHCO_3$ (75 mL). The organics were separated and the aqueous was extracted with CH_2Cl_2 (3 x 75 mL). The combined organics were washed with H_2O (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The resultant crude yellow oil (**608**) was carried on to the next transformation without further purification.

To a stirred solution of aldehyde **608** (11.6 g, 10.0 mmol, 1.00 equiv) in MeOH (140 mL) was added K_2CO_3 (2.76 g, 20.0 mmol, 2.00 equiv) as a solid in a single portion. After 5 minutes, to the homogenous solution was added phosphonate **609** (2.31 g, 12.0 mmol, 1.20 equiv) slowly dropwise neat as a bright yellow oil. After 11 h, the consumption of starting material was complete as determined by TLC (3:7 EtOAc:Hexanes eluent). The reaction mixture was then diluted with Et_2O (250 mL) and washed with saturated aqueous $NaHCO_3$ (100 mL). The aqueous was then extracted with Et_2O (1 x 100 mL). The combined organics were dried over Na_2SO_4, filtered and

concentrated in vacuo to provide alkyne **610** (765 mg, 69% from lactone **600**) as a clear, colorless oil: characterization data match those reported in the literature.[19]



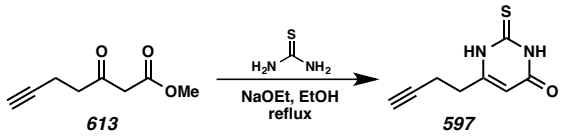
β-Ketoester 613:[20] To a solution of ester **610** (765 mg, 6.88 mmol, 1.00 equiv) in a mixture of MeOH (23 mL) and H_2O (23 mL) was added K_2CO_3 (3.81 g, 27.5 mmol, 4.00 equiv) as a solid in a single portion. After 3.5 h, the consumption of starting material was complete as determined by TLC (3:7 EtOAc:Hexanes eluent). The reaction mixture was then cooled to 0 °C (ice/H_2O bath) at which time the pH was adjusted to between 1 and 2 by the careful addition of aqueous 1 N HCl (CAUTION: Vigorous gas evolution!). The reaction mixture was then extracted with Et_2O (4 x 75 mL). The combined organics were washed with aqueous 1 N HCl (2 x 50 mL) and then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude gold oil was carried on to the next transformation without further purification.

To the reaction flask was charged magnesium chloride (560 mg, 5.88 mmol, 1.00 equiv) and potassium monomethyl malonate (**612**, 1.19 g, 7.64 mmol, 1.30 equiv). A reflux condenser was attached and the flask was subsequently evacuated and back-filled with argon (3 x 5 minutes cycles). To the solids was added THF (9.0 mL) with stirring and the white suspension was introduced to a preheated 65 °C for 3 h.

After the above reaction had proceeded for 2 h, to a solution of a portion of crude acid **611** (570 mg, 5.88 mmol, 1.00 equiv) in THF (6.0 mL) in a separate reaction vessel was added carbonyl diimidazole (CDI, 1.15 g, 7.06 mmol, 1.20 equiv) in three portions,

allowing for effervescence to subside between additions (CAUTION: Vigorous gas evolution!). The reaction mixture was stirred at ambient temperature (ca. 23 °C) for 30 minutes, until bubbling ceased, and then heated to 40 °C for an additional 30 minutes.

Simultaneously, upon completion of the 3 h stir of the magnesium malonate suspension at 65 °C, the reaction mixture was cooled to 30 °C. Subsequently, the acyl-imidazole solution was added dropwise with vigorous stirring. The resulting fine white suspension was stirred at 30 °C for 22 h. The reaction mixture was then cooled to 0 °C (ice/H_2O bath). The reaction was quenched by the addition of aqueous 1 N HCl (25 mL). The resultant biphasic mixture was further diluted with aqueous 1 N HCl (125 mL). The aqueous was then extracted with Et_2O (4 x 80 mL). The combined organics were washed with H_2O (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL) and then dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude tan oil was purified by silica gel column chromatography (50% EtOAc in hexanes eluent) to furnish β-ketoester **613** (457 mg, 51% yield) as a clear, colorless oil: R_f = 0.18 (1:1 EtOAc:Hexanes eluent); characterization data match those reported in the literature.[10]



613 *597*

Thiouracil 597:[21] To a stirred solution of EtOH (1.7 mL) was added sodium metal (23 mg, 1.00 mmol, 3.00 equiv). After 20 minutes, the exothermic reaction was complete as determined by complete dissolution of the solid metal and the reaction mixture had returned to ambient temperature (ca. 23 °C). A solution of β-ketoester **613** (50 mg, 0.33 mmol, 1.00 equiv) in EtOH (1.0 mL) was then added slowly dropwise. The flask

containing the resultant colorless, homogeneous reaction mixture was sealed and introduced to a preheated 80 °C bath. After 10 h, the consumption of starting material was complete as determined by TLC (3:1 EtOAc:Hexanes eluent). The reaction vessel was then removed from the heating bath and allowed to cool to ambient temperature (ca. 23 °C). The crude reaction mixture was concentrated in vacuo and the resultant yellow solids were dissolved in H_2O (20 mL). The pH of the homogenous aquesous mixture was then adjusted to between 2 and 3 by the addition of aqueous 1 N HCl, causing a precipitate to form. The heterogeneous aqueous solution was extracted with Et_2O (4 x 30 mL) and then EtOAc (3 x 30 mL). The combined organics were then dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude tan solid was then adsorbed onto Celite (1.0 g) and purified by silica gel column chromatography (100% EtOAc eluent) to afford thiouracil **597** (1.11 g, 95% yield) as an amorphous white solid: R_f = 0.33 (EtOAc eluent); ^{1}H NMR (CD_3OD, 400 MHz) δ 5.81 (s, 1H), 2.64 (dd, *J* = 8.3, 6.3 Hz, 2H), 2.60–2.52 (m, 2H), 2.40 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (CD_3OD, 101 MHz) δ 178.0, 164.1, 156.9, 104.2, 82.2, 71.6, 32.1, 17.5; IR (Neat Film, NaCl) 3278, 3085, 2923, 2312, 1653, 1550, 1468, 1433, 1313, 1242, 1189, 1158, 842 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_8H_9ON_2S$ $[M+H]^+$: 181.0436, found 181.0428.

A.16.5 Notes and References

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11. For full experimental details, see the Section A16.4.2.

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17. The procedure for the formation of carboxylate **601** was adapted from the literature, see reference 5.

18. The procedure for the methanolysis of lactone **600** was adapted from the literature, see reference 8.

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20. The procedure for the construction of β-ketoester **613** was adapted from the literature, see reference 10.

21. The procedure for the construction of thiouracil **597** was adapted from the literature, see reference 12.

APPENDIX 17

Spectra Relevant to Appendix 16:

Synthesis of Functionalized Thiouracils

as G Protein-Coupled Receptor Agonists

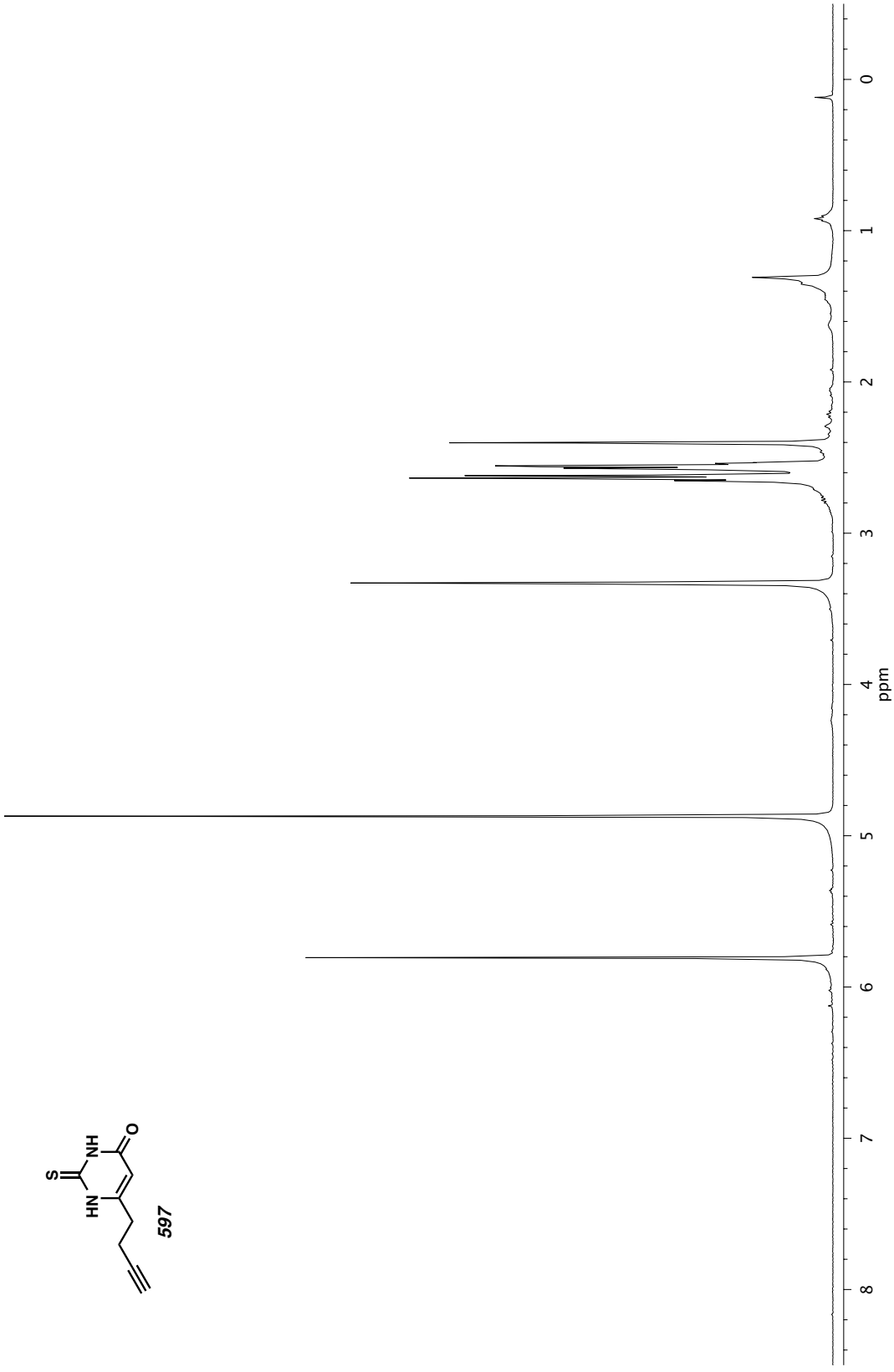

Figure A17.1. ^{1}H NMR (400 MHz, CD_3OD) of compound **597**.

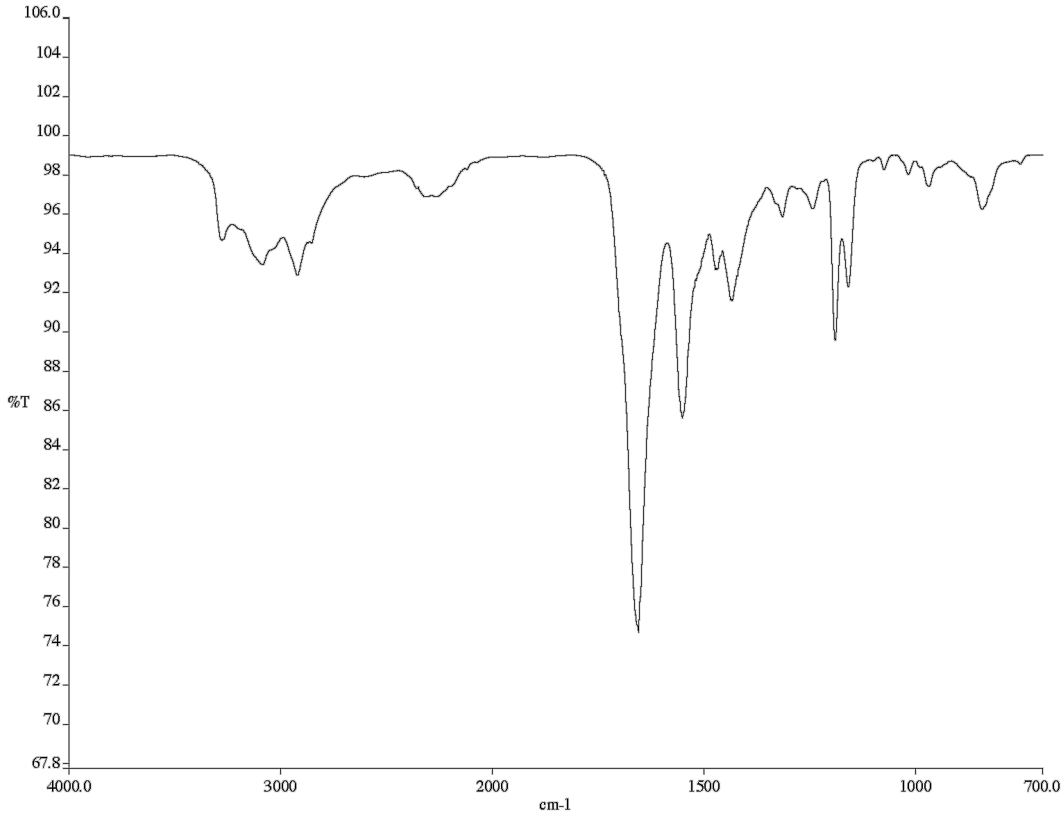

Figure A17.2. Infrared spectrum (Thin Film, NaCl) of compound **597**.

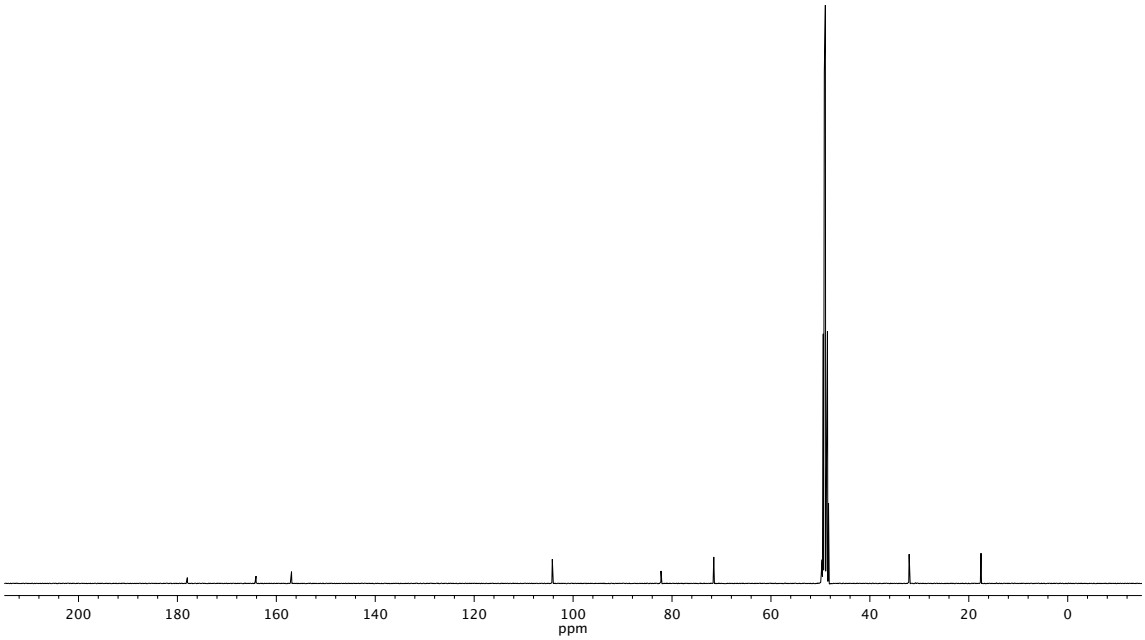

Figure A17.3. ^{13}C NMR (101 MHz, CD_3OD) of compound **597**.

APPENDIX 18

Notebook Cross-Reference for New Compounds

A18.1 Contents

The following notebook cross-reference has been included to facilitate access to the original spectroscopic data obtained for the compounds presented within this thesis. The information is organized by chapter and sequentially by compound number, noting the instrument on which the primary NMR data was collected. All ^{1}H NMR, ^{13}C NMR, and any two-dimensional NMR data available as well as ^{19}F NMF and ^{31}P NMR, if applicable, are electronically stored on the NMR laboratory server (mangia.caltech.edu, most typically under the username 'rcraig') and on the Stoltz group server. All IR spectra were taken on the Stoltz group IR and an electronic copy of each spectrum as a postscript file can be found on the Stoltz group server. A hard copy of each spectrum has been provided with this text, as well. All laboratory notebooks are stored in the Stoltz group archive. The initials used to catalog primary data correspond to the following current Stoltz group members or alumni: RAC – Rob Craig, RCS – Russell Smith, AG – Alex Goldberg, NRO – Nick O'Connor, JLR – Jenny Roizen, ACJ – Amanda Jones, MS – Masaki Seto.

A18.2 Notebook Cross-Reference Tables

Table A18.2.1. Notebook Cross-Reference For Compounds in Chapter 2

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
250	JLR-XIV-241a4 (Hg3)	JLR-XIV-241a5 (Hg3)	JLR-XIV-241a	JLR-XIV-241
257	RAC-III-145-col1a (Indy)	RAC-III-145-col1a (Indy)	RAC-III-145-col-I-A-CH	RAC-II-171
258	RCS-II-177col1a-CH (Indy)	RCS-II-177col1a-CH (Indy)	RAC-I-283col1ach	RAC-I-283
260	RAC-III-245-col-I-A-CH-3 (Hg3)	RAC-III-245-col-I-A-CH (Indy)	RAC-III-245-col-I-A-CH	RAC-II-281
262	RAC-II-95-col-I-A-CH (Indy)	RAC-II-95-col-I-A-CH (Indy)	RAC-II-95-col-I-A-CH	RAC-II-95
271	RAC-III-93-filt-2-CH (Indy)	RAC-III-93-filt-2-CH (Indy)	RAC-I-261-CR-CH	RAC-I-185
272	RAC-II-123-CR-CH (Indy)	RAC-II-123-CR-CH (Indy)	RAC-II-123-CR-CH	RAC-II-123
273	RCS-II-165col1a-CH (Indy)	RCS-II-165col1a-CH (Indy)	RAC-III-139-col-I-A-CH	RAC-III-139
253	MS-II-291 (Hg3)	MS-II-291 (Hg3)	RAC-IX-123-kugel	RAC-IX-123
275	RAC-II-91-col-I-A-CH (Indy)	RAC-II-91-col-I-A-CH (Indy)	RAC-II-91-col-I-A-CH	RAC-II-87 / RAC-III-57
276	RAC-IV-161-col-I-A-CH (Indy) ^{19}F: RAC-IV-161-col-I-A (Hg3)	RAC-IV-161-col-I-A-CH (Indy)	RAC-IV-161-col-I-A-CH	RAC-IV-161
277	RAC-IV-167-col-I-A-CH (Indy) ^{19}F: RAC-IV-167-col-I-A (Hg3)	RAC-IV-167-col-I-A-CH (Indy)	RAC-IV-167-col-I-A-CH	RAC-IV-167
279	RAC-IV-179-col-I-A-CH (Indy) ^{19}F: RAC-IV-179-col-I-A-CH (Hg3) ^{31}P: RAC-IV-179-col-I-A-CH (Hg3)	RAC-IV-179-col-I-A-CH (Indy)	RAC-IV-179-col-I-A-CH	RAC-IV-179

Table A18.2.2. Notebook Cross-Reference For Compounds in Appendix 3

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
287	RAC-I-41-filtrate2 (Hg3)	–	–	RCS-I-295
288	RAC-I-55-Vaced_Product (Hg3)	–	–	RCS-I-297
289	RAC-I-71-col-I-A (Hg3)	–	–	RAC-I-69 / RAC-I-71
290	RAC-I-55-col-I-A (Hg3)	–	–	RAC-I-77
291	RAC-I-81-col-II-A (Hg3)	–	–	RAC-I-81
296	RCS-I-163col1a (Hg3)	–	–	RCS-I-151
297	RCS-I-163col1b (Hg3)	–	–	RCS-I-151
298	RCS-I-205col1a (Hg3)	–	–	RCS-I-287
299	RCS-I-205col1b (Hg3)	–	–	RCS-I-287
302	RCS-II-83col1a (Hg3)	–	–	RCS-II-83
303	RCS-II-83col1b (Hg3)	–	–	RCS-II-83
305	RCS-I-165col1a (Hg3)	–	–	RCS-I-165
306	RCS-I-141col1a (Hg3)	–	–	RCS-I-141
310	RCS-I-161-cr (Hg3)	–	–	RCS-I-161
312	RCS-II-81col1a (Hg3)	–	–	RAC-I-164

Table A18.2.3. Notebook Cross-Reference For Compounds in Chapter 3

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
354	RAC-II-103-col-I-A (Indy)	RAC-II-103-col-I-A (Indy)	RAC-II-103-col-I-A-CH	RAC-II-39 / RAC-II-41
***ent*-322**	JLR-XIII-69b (Hg2)	JLR-XIII-69b (Hg2)	JLR-XIII-69b	RAC-IV-85
323	RAC-II-93-col-I-A-CH (Indy)	RAC-II-93-col-I-A-CH (Indy)	RAC-II-93-col-I-A-CH	RAC-II-109 / RAC-II-93
***ent*-320**	RAC-III-125-CH-PROTON-FINAL (FID)	RAC-III-125-CH-CARBON (Indy)	RAC-III-125-CH	RAC-III-107 / RAC-II-143 / RAC-II-279
324	RAC-IV-93-col-II-B (Indy)	RAC-IV-93-col-II-C-D-CH (Indy)	RAC-II-73-CH	RAC-III-157
325	RAC-III-157-col-III-Et2O (FID)	RAC-III-157-col-III-Et2O (Daytona)	RAC-III-157-col-I-B-CH	RAC-III-157
328	RAC-III-163-col-I-A-CH (FID)	RAC-III-163-col-I-A-CH (Daytona)	RAC-III-163-col-I-A-CH	RAC-XII-145
329	RAC-IX-253-PLUG (FID)	RAC-IX-253-PLUG (Daytona)	RAC-IX-253-PLUG	RAC-IX-253-
331	RAC-XIII-105-col-I-B (Flo)	RAC-XIII-105-col-I-B (Flo)	RAC-XIII-105-col-I-B	RAC-XIII-109
336	RAC-II-213-col-I-A-CH (Indy)	RAC-II-213-col-I-A-CH (Indy)	RAC-II-213-col-I-A-CH	RAC-II-151 / RAC-II-211 / RAC-II-213
337A	RAC-II-221-col-I-A-CH (Indy)	RAC-II-221-col-I-A-CH (Indy)	RAC-II-221-col-I-A-CH	RAC-II-173 / RAC-II-175
337B	RAC-II-221-col-I-B-CH (Indy)	RAC-II-221-col-I-B-CH (Indy)	RAC-II-221-col-I-B-CH	RAC-II-173 / RAC-II-175
338	RAC-II-233-CR-CH (Flo)	RAC-II-233-CR-CH (Flo)	RAC-II-233-CR-CH	RAC-II-177
***ent*-335**	RAC-XIII-93-col-I-B-CH (Flo)	RAC-XIII-93-col-I-B-CH (Flo)	RAC-XIII-93-col-I-B-CH	RAC-XIII-93
340	RAC-XIII-97-col-I-B-CH (Flo)	RAC-XIII-97-col-I-B-CH (Flo)	RAC-XIII-97-col-I-B-CH	RAC-II-183 / RAC-II-199
341	RAC-II-203-col-I-B-detail (FID)	RAC-II-203-col-I-B-carbon (Daytona)	RAC-II-203-col-I-B	RAC-II-203
344	RAC-XIII-105-col-I-C (Flo)	RAC-XIII-105-col-I-C-CH (Flo)	RAC-XIII-105-col-I-D-CH	RAC-XIII-105

345	RAC-IV-193-col-I-C-CH (Indy)	RAC-IV-193-col-I-C-CH (indy)	RAC-IV-193-col-I-C-CH	RAC-XIII-105
346	RAC-III-165-col-I-A-CH (FID)	RAC-III-165-col-I-A-CH (Daytona)	RAC-III-165-col-I-A-CH	RAC-III-203
347	RAC-III-173-col-I-A-CH (Indy)	RAC-III-173-col-I-A-CH (Indy)	RAC-III-173-col-I-A-CH	RAC-IV-109
349/350	RAC-IV-113-col-I-B-CH (Daytona)	RAC-IV-113-col-I-B-CH (Daytona)	RAC-IV-113-col-I-B-CH.2	RAC-IV-195
***ent*-313**	RAC-III-179-col-I-B (FID)	RAC-III-183-col-I-B-CH (Daytona)	RAC-III-183-col-I-B-CH	RAC-IV-115
351	RAC-IV-119-col-I-A-CH (Daytona)	RAC-IV-119-col-I-A-CH (Daytona)	RAC-IV-119-col-I-A-CH	RAC-IV-115
352	RAC-IV-115-col-I-B-CH (Daytona)	RAC-IV-115-col-I-B-CH (Daytona)	RAC-IV-115-col-I-B-CH	RAC-IV-115

Table A18.2.4. Notebook Cross-Reference For Compounds in Chapter 4

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
372	RAC-XI-131-col-I-B-CH (Daytona)	RAC-XI-131-col-I-B-CH (Daytona)	RAC-XI-131-col-I-B-CH	RAC-XI-157 / RAC-XI-159
371	RAC-X-275-col-I-B-CH (FID)	RAC-X-275-col-I-B-CH (Daytona)	RAC-X-275-col-I-B-CH	RAC-XI-177
374	RAC-XI-31-col-I-B-CH (FID)	RAC-XI-31-col-I-B-CH (Daytona)	RAC-XI-31-col-I-B-CH	RAC-XI-31
373	RAC-XI-203-col-I-C-CH (Daytona)	RAC-XI-203-col-I-C-CH (Daytona)	RAC-XI-203-col-I-C-CH	RAC-XI-169 / RAC-XI-183
375	RAC-XI-101-col-I-B-CH (FID)	RAC-XI-101-col-I-B-CH (Daytona)	RAC-XI-101-col-I-B-CH	RAC-XI-169 / RAC-XI-183
376	RAC-XI-229-col-I-A (Flo)	RAC-XI-229-col-I-A (Flo)	RAC-XI-229-col-I-A	RAC-XI-215 / RAC-XI-229
377	RAC-XI-235-col-I-A (Flo)	RAC-XI-235-col-I-A (Flo)	RAC-XI-235-col-I-A	RAC-XI-235
378	RAC-XI-277-col-II-A-CH (Flo)	RAC-XI-277-col-II-A-CH (Flo)	RAC-XI-277-col-II-A-CH	RAC-XI-277

383	RAC-X-239-col-I-A (FID)	RAC-X-239-col-I-A (Daytona)	RAC-X-239-col-I-A	RAC-X-239
384	RAC-X-249-col-I-B-CH (FID)	RAC-X-249-col-I-B-CH (Daytona)	RAC-X-249-col-I-B-CH	RAC-X-249
385	RAC-X-259-col-I-B-CH (FID)	RAC-X-259-col-I-B-CH (Daytona)	RAC-X-259-col-I-B-CH	RAC-X-259
389	RAC-XI-273-col-I-D-CH (Flo)	RAC-XI-273-col-I-D-CH (Flo)	RAC-XI-273-col-I-D-CH	RAC-XII-151
390	RAC-XI-273-col-I-B-CH (Flo)	RAC-XI-273-col-I-B-CH (Flo)	RAC-XI-273-col-I-B-CH	RAC-XII-151
391	RAC-XII-155-col-I-A-CH (Flo)	RAC-XII-155-col-I-A-CH (Flo)	RAC-XII-161-col-I-B-CH	RAC-XII-161
393	RAC-XI-281-col-II-A (Flo)	RAC-XI-281-col-II-A (Flo)	RAC-XI-281-col-II-A-CH	RAC-XI-281
396	RAC-XI-279-col-II-A (Flo)	RAC-XI-279-col-II-A (Flo)	RAC-XI-279-col-II-A-CH	RAC-XI-279
394	RAC-XIII-123-col-I-A (Flo)	RAC-XIII-123-col-I-A (Flo)	RAC-XIII-123-col-I-A-CH	RAC-XIII-123
397	RAC-XI-287-col-I-A (Flo)	RAC-XI-287-col-I-A (Flo)	RAC-XII-123-col-I-A-CH	RAC-XII-123
399	RAC-XIII-131-col-I-B-CH (Flo)	RAC-XIII-131-col-I-B-CH (Flo)	RAC-XIII-131-col-I-B-CH	RAC-XIII-131
401	RAC-XII-63-col-I-A (Flo)	RAC-XII-63-col-I-A (Flo)	RAC-XII-63-col-I-A	RAC-XII-63
403	RAC-XII-263-col-I-A-CH (Flo)	RAC-XII-263-col-I-A-CH (Flo)	RAC-XII-263-col-I-A-CH	RAC-XIII-65
404	RAC-XII-269-col-I-A (Flo)	RAC-XII-269-col-I-A (Flo)	RAC-XII-269-col-I-A-CH	RAC-XII-269
405	RAC-XIII-57-col-I-A (Flo)	RAC-XIII-57-col-I-A (Flo)	RAC-XIII-57-col-I-A-CH	RAC-XIII-57
406	RAC-XII-281-col-I-A (Flo)	RAC-XII-281-col-I-A (Flo)	RAC-XII-281-col-I-A-CH	RAC-XIII-67
407	RAC-XIII-31-col-I-A (Flo)	RAC-XIII-31-col-I-A (Flo)	RAC-XIII-31-col-I-A-CH	RAC-XIII-61

408	RAC-XIII-63-col-I-C-CH (Flo)	RAC-XIII-63-col-I-C-CH (Flo)	RAC-XIII-63-col-I-C-CH	RAC-XIII-63
412	RAC-IX-95-HPLC-A-1H (FID)	RAC-IX-95-HPLC-A (Daytona)	RAC-IX-95-HPLC-A-CH	RAC-IX-109 / RAC-IX-111
413	RAC-IX-111-HPLC-B-NON-CH-CDCl3 (Flo)	RAC-IX-111-HPLC-B-NON-CH-CDCl3 (Flo)	RAC-IX-95-HPLC-B-CH	RAC-IX-109 / RAC-IX-111
415	RAC-XII-171-col-I-A (Flo)	RAC-XII-171-col-I-A (Flo)	RAC-XII-171-col-I-A-CH	RAC-XII-171
416	RAC-XII-169-col-I-A (Flo)	RAC-XII-169-col-I-A (Flo)	RAC-XII-169-col-I-A-CH	RAC-XII-181
420	RAC-XII-237-col-I-A (Flo)	RAC-XII-237-col-I-A (Flo)	RAC-XII-237-col-I-A-CH	RAC-XII-233/ RAC-XII-235
422	RAC-XII-177-col-I-A-CH (Flo)	RAC-XII-177-col-I-A-CH (Flo)	RAC-XII-177-col-I-A-CH	RAC-XII-227/ RAC-XII-229
423	RAC-XIII-43-col-I-C-CH (Flo)	RAC-XIII-43-col-I-C-CH (Flo)	RAC-XIII-43-col-I-C-CH	RAC-XIII-43

Table A18.2.5. Notebook Cross-Reference For Compounds in Chapter 5

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
433	RAC-VI-59-col-I-A-CH (Indy)	RAC-VI-59-col-I-A-CH (Indy)	RAC-VI-59-col-I-A-CH	RAC-VI-59
434	RAC-VI-39-col-3-CH (Indy)	RAC-VI-39-col-3-CH (Indy)	RAC-VI-39-col-3-CH	RAC-VI-39
435	RAC-VI-35-col-3-CH (Indy)	RAC-VI-35-col-3-CH (Indy)	RAC-VI-35-col-3-CH	RAC-VI-35
436	AG-XI-73 (Siena)	AG-XI-73 (Siena)	AG-XI-73	AG-XI-73
437	RAC-VI-31-col-I-C-CH (Indy)	RAC-VI-31-col-I-C-CH (Indy)	RAC-VI-31-col-I-C-CH	RAC-VI-31
438	NRO-I-219-CH (Indy)	NRO-I-219-CH (Indy)	NRO-I-219-CH	NRO-I-219
439	NRO-I-217-CH (Indy)	NRO-I-217-CH (Indy)	NRO-I-217-CH	NRO-I-217
440	RAC-VI-37-col-3-CH (Indy)	RAC-VI-37-col-3-CH (Indy)	RAC-VI-37-col-3-CH	RAC-VI-37

441	RAC-VI-41-col-3-CH (Indy)	RAC-VI-41-col-3-CH (Indy)	RAC-VI-41-col-3-CH	RAC-VI-41
442	RAC-VI-33-col-I-B-CH (Indy)	RAC-VI-33-col-I-B-CH (Indy)	RAC-VI-33-col-I-B-CH	RAC-VI-33
443	NRO-II-57-CH (Indy)	NRO-II-57-CH (Indy)	NRO-II-57-CH	NRO-II-57
444	RAC-VI-77-col-I-B-CH (Indy)	RAC-VI-77-col-I-B-CH (Indy)	RAC-VI-77-col-I-B-CH	RAC-VI-77
445	NRO-II-75-CH (Indy)	NRO-II-75-CH (Indy)	NRO-II-75-CH	NRO-II-75
448	NRO-II-63-CH (Indy)	NRO-II-63-CH (Indy)	NRO-II-63-CH	NRO-II-63
450	AG-XI-81 (Siena)	AG-XI-81 (Siena)	AG-XI-81	AG-XI-81
451	AG-XI-91 (Siena)	AG-XI-91 (Siena)	AG-XI-91	AG-XI-91
452	RAC-VI-53-col-I-A-CH (Indy)	RAC-VI-53-col-I-A-CH (Indy)	RAC-VI-53-col-I-A-CH	RAC-VI-53
453	RAC-VI-55-col-I-A-CH (Indy)	RAC-VI-55-col-I-A-CH (Indy)	RAC-VI-55-col-I-A-CH	RAC-VI-55
454	RAC-VI-43-col-I-A-trit-CH (Indy)	RAC-VI-43-col-I-A-trit-CH (Indy)	RAC-VI-43-col-I-A-trit	RAC-VI-43
455	RAC-VI-45-col-I-A-trit-CH (Indy)	RAC-VI-45-col-I-A-trit-CH (Indy)	RAC-VI-45-col-I-A-trit	RAC-VI-45
456	AG-XI-115a (Indy)	AG-XI-115a (Indy)	AG-XI-115a	AG-XI-115a
457	AG-XI-113 (Siena)	AG-XI-113 (Siena)	AG-XI-113	AG-XI-113
459	AG-XI-125-B-CH (Indy)	AG-XI-125-B-CH (Indy)	AG-XI-125-B-CH	AG-XI-125
460	AG-XI-109-C-CH (Indy)	AG-XI-109-C-CH (Indy)	AG-XI-109-C-CH	AG-XI-179
461	AG-XI-109-A-CH (Indy)	AG-XI-109-A-CH (Indy)	AG-XI-109-A-CH	AG-XI-179
462	AG-XI-143char (Indy)	AG-XI-143char (Indy)	AG-XI-143char	AG-XI-143
463	AG-XI-145a-CH (Indy)	AG-XI-145a-CH (Indy)	AG-XI-145a-CH	AG-XI-145a
464	AG-XI-141char (Indy)	AG-XI-141char (Indy)	AG-XI-141char	AG-XI-141
483	NRO-I-203-CH (Indy)	NRO-I-203-CH (Indy)	NRO-I-203-CH	NRO-I-203
485	NRO-I-205-CH (Indy)	NRO-I-205-CH (Indy)	NRO-I-205-CH	NRO-I-205

Table A18.2.6. Notebook Cross-Reference For Compounds in Chapter 6

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
499	RAC-VI-199-col-I-B-CH (Indy)	RAC-VI-199-col-I-B-CH (Indy)	RAC-VI-199-col-I-B-CH	RAC-VI-199
503	RAC-VI-203-col-I-B-CH (Indy)	RAC-VI-203-col-I-B-CH (Indy)	RAC-VI-203-col-I-B-CH	RAC-VI-203
504	NRO-III-209a-CH (Indy)	NRO-III-209a-CH (Indy)	NRO-III-209a-CH	RAC-VIII-33
505	RAC-VI-235-col-I-B-CH (Indy)	RAC-VI-235-col-I-B-CH (Indy)	RAC-VI-235-col-I-B-CH	RAC-VI-235
506	RAC-VI-233-col-I-B-CH (Indy)	RAC-VI-233-col-I-B-CH (Indy)	RAC-VI-233-col-I-B-CH	RAC-VI-233
507	NRO-III-279a-CH (Indy)	NRO-III-279a-CH (Indy)	NRO-III-279a-CH	NRO-III-279
508	NRO-III-205a-CH (Indy)	NRO-III-205a-CH (Indy)	NRO-III-205a-CH	NRO-III-205
509	NRO-III-203-c2a-CH (Indy)	NRO-III-203-c2a-CH (Indy)	NRO-III-203-c2a-CH	NRO-III-203
510	NRO-III-207-CH (Indy)	NRO-III-207-CH (Indy)	NRO-III-207-CH	NRO-III-207
511	RAC-VIII-113-col-I-B-CH (Indy)	RAC-VIII-113-col-I-B-CH (Indy)	RAC-VIII-113-col-I-B-CH	RAC-VIII-113
512	NRO-III-277a-CH (Indy)	NRO-III-277a-CH (Indy)	NRO-III-277a-CH	NRO-III-277
513	RAC-VI-257-col-I-B-CH (Indy)	RAC-VI-257-col-I-B-CH (Indy)	RAC-VI-257-col-I-B-CH	RAC-VI-257
514	RAC-VI-237-col-I-B-CH (Indy)	RAC-VI-237-col-I-B-CH (Indy)	RAC-VI-237-col-I-B-CH	RAC-VI-237
515	RAC-VI-279-col-I-B-CH (Indy)	RAC-VI-279-col-I-B-CH (Indy)	RAC-VI-279-col-I-B-CH	RAC-VI-279
516	RAC-VIII-99-col-I-B-CH (Indy)	RAC-VIII-99-col-I-B-CH (Indy)	RAC-VIII-99-col-I-B-CH	RAC-VIII-99
546	RAC-VIII-147/149-col-I-B-CH (Indy)	RAC-VIII-147/149-col-I-B-CH (Indy)	RAC-VIII-147/149-col-I-B-CH	RAC-VIII-149
518	RAC-VIII-111-prepHPLC-B (Indy)	RAC-VIII-111-prepHPLC-B	RAC-VIII-111-prepHPLC-B	RAC-VIII-111
519	RAC-VIII-111-prepHPLC-A (Indy)	RAC-VIII-111-prepHPLC-A (Indy)	RAC-VIII-111-prepHPLC-A	RAC-VIII-111

522	RAC-VIII-41-col-I-B-CH (Indy)	RAC-VIII-41-col-I-B-CH (Indy)	RAC-VIII-41-col-I-B-CH	RAC-VIII-41
523	RAC-VI-261-col-I-B-CH (Indy)	RAC-VI-261-col-I-B-CH (Indy)	RAC-VI-261-col-I-B-CH	RAC-VI-261
524	RAC-VI-259-col-I-B-CH (Indy)	RAC-VI-259-col-I-B-CH (Indy)	RAC-VI-259-col-I-B-CH	RAC-VI-259
525	RAC-VIII-37-col-I-B-CH (Indy)	RAC-VIII-37-col-I-B-CH (Indy)	RAC-VIII-37-col-I-B-CH	RAC-VIII-37
530•HCl	NRO-III-273-CH (Indy)	NRO-III-273-CH (Indy)	NRO-III-273-CH	NRO-III-273
531	RAC-VI-147-col-I-B-CH (Indy)	RAC-VI-147-col-I-B-CH (Indy)	RAC-VI-147-col-I-B-CH	RAC-VI-147
532	RAC-VI-277-col-I-B-CH (Indy)	RAC-VI-277-col-I-B-CH (Indy)	RAC-VI-277-col-I-B-CH	RAC-VIII-35
533	RAC-VIII-91-col-I-B-CH (Indy)	RAC-VIII-91-col-I-B-CH (Indy)	RAC-VIII-91-col-I-B-CH	RAC-VIII-91
534	RAC-VIII-93-col-I-B-CH (Indy)	RAC-VIII-93-col-I-B-CH (Indy)	RAC-VIII-93-col-I-B-CH	RAC-VIII-93
536	RAC-VI-241-col-I-B-CH (Indy)	RAC-VI-241-col-I-B-CH (Indy)	RAC-VI-241-col-I-B-CH	RAC-VI-241
537	RAC-VIII-109-col-I-G-CH (Indy)	RAC-VIII-109-col-I-G-CH (Indy)	RAC-VIII-109-col-I-G-CH	RAC-VIII-109
538	RAC-VIII-121-col-I-B-CH (Indy)	RAC-VIII-121-col-I-B-CH (Indy)	RAC-VIII-121-col-I-B-CH	RAC-VIII-121
540	RAC-VIII-109-col-I-C-CH (Indy)	RAC-VIII-109-col-I-C-CH (Indy)	RAC-VIII-109-col-I-C-CH	RAC-VIII-109
541	RAC-VIII-123-prepHPLC-B (Indy)	RAC-VIII-123-prepHPLC-B (Indy)	RAC-VIII-123-prepHPLC-B	RAC-VIII-123
542	RAC-VIII-123-prepHPLC-A (Indy)	RAC-VIII-123-prepHPLC-A (Indy)	RAC-VIII-123-prepHPLC-A	RAC-VIII-123
544	RAC-VIII-141-col-I-B-CH (Indy)	RAC-VIII-141-col-I-B-CH (Indy)	RAC-VIII-141-col-I-B-CH	RAC-VIII-141
549	-	-	RAC-VI-231-col-I-A	RAC-VI-231
550	RAC-VI-263-col-I-D-CH (Indy)	RAC-VI-263-col-I-D-CH (Indy)	RAC-VI-263-col-I-D-CH	RAC-VI-263

552	NRO-IV-199-CH (Indy)	NRO-IV-199-CH (Indy)	NRO-IV-199-CH	NRO-IV-199
568	NRO-III-169a-CH (Indy)	NRO-III-169a-CH (Indy)	NRO-III-169a-CH	NRO-III-169
570	NRO-III-171-CH (Indy)	NRO-III-171-CH (Indy)	NRO-III-171-CH	NRO-III-171
572	NRO-II-223-CH (Indy)	NRO-II-223-CH (Indy)	NRO-II-223-CH	NRO-II-223
574	RAC-VIII-107-col-I-B-CH (Indy)	RAC-VIII-107-col-I-B-CH (Indy)	RAC-VIII-107-col-I-B-CH	RAC-VIII-107
581	NRO-IV-33a-CH (Indy)	NRO-IV-33a-CH (Indy)	NRO-IV-33a-CH	NRO-IV-33a
582	RAC-VI-87-col-II-A-CH (Indy)	RAC-VI-87-col-II-A-CH (Indy)	RAC-VI-87-col-II-A-CH	RAC-VI-87
590•HCl	RAC-VI-191-HCL_salt_CH (Indy)	RAC-VI-191-HCL_salt_CH (Indy)	RAC-VI-191-HCL_salt_CH	RAC-VI-191
593	NRO-III-279 (Indy)	NRO-III-279 (Indy)	NRO-III-279	NRO-III-279

Table A18.2.7. Notebook Cross-Reference For Compounds in Appendix 16

Compound	^{1}H NMR (instrument)	^{13}C NMR (instrument)	IR	Yield and Procedure
597	RAC-VII-79-col-I-A (Flo)	RAC-VII-79-col-I-A (Flo)	RAC-VII-79-col-I-A	RAC-VII-79

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About the Author

Robert Allen Craig II was born in Wilmington, Delaware on June 22nd, 1988. He is the only child of Robert Allen Craig and Ross Ann Craig. Rob spent his formative years in the West Chester, Pennsylvania. As a child, Rob was fascinated by engineering, building complex structures from Legos, K'nex, blocks, paper towel rolls, cups, and anything he could find. From Prekindergarten through 12th grade, Rob attended Westtown School, a small, private, Quaker boarding school in the West Chester area. As a student there, Rob was active in sports year-round, playing soccer, basketball, and golf. His love for science was sparked during his time at Westtown, beginning with T. Bob in 7th grade science and developing into a love for chemistry with T. Kurt Wicks in 10th grade.

In the fall of 2006, Rob matriculated at Davidson College in Davidson, North Carolina. He immediately fell in love with organic chemistry, taking nearly all of the available organic chemistry classes within his first two years. Rob was also drawn to the liberal arts style of education, taking a number of math courses as well as fascinating classes such as "Religion and Racism" and "Tibetan Religion" en route to a minor in religion. At Davidson, Rob also spent four years on the Crew Team and as a member of the Sigma Phi Epsilon Fraternity. During the fall semester of 2008, Rob studied abroad at the University of St. Andrews in Scotland, U.K., where he continued taking classes and spent time playing golf and rowing for the St. Andrews Crew Team. In the summer of 2009, Rob interned at Abbott Labs in the analytical chemistry department developing a method for the systematic pairing of antioxidants with active pharmaceutical ingredients.

In the fall of 2010, Rob moved to Pasadena, California, where he began his doctoral studies with Professor Brian M. Stoltz at the California Institute of Technology. His doctoral research has focused on the pursuit of the asymmetric total synthesis of ineleganolide and the related polycyclic furanobutenolide norcembranoid natural products. This training in synthetic chemistry will serve as an exceptional foundation for his postdoctoral studies with Professor Justin Du Bois at Stanford University, beginning in the fall of 2015, which will use veratridine and its derivatives to better understand the conformation and mechanical properties and inner-channel conformation of voltage-gated sodium ion channels.