CHAPTER 6

Multifunctional Monomers and Materials for Advanced Lithographic Applications via Olefin Metathesis

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Abstract Well-defined ruthenium olefin metathesis catalysts display the high reactivity and functional group tolerance required for the synthesis of new monomers and materials for deep ultraviolet lithography. Ring-opening metathesis polymerization of hexafluorocarbinol-functionalized tetracyclododecene monomers affords polymers which, after hydrogenation, are highly transparent at 193 nm, provided the acidic alcohol is protected prior to polymerization. However, these same ROMP polymers continue to exhibit inherently high absorbance (~3.0 μm^{-1}) at 157 nm despite our best efforts. Ruthenium-catalyzed cross-metathesis can serve as a mild and convenient route to the production of hexafluorocarbinol-functionalized products which would ordinarily be synthesized via alkylations of highly toxic hexafluoroacetone. The presence of the acidic fluoroalcohol leads to uncharacteristically low E/Z ratios in certain instances. Further investigation into the origin of this low stereoselectivity resulted in the discovery that additives such as acetic acid can be effective in eliminating problematic olefin migration side-reactions. An example of the benefits of the cross-metathesis approach is the 2-step synthesis of norbornene monomers with both ester and hexafluorocarbinol functionalities. Gas-phase ultraviolet spectroscopy reveals that these difunctional norbornane structures have extraordinarily high transparency at 157 nm. The intramolecularly hydrogen-bound functionalities of these structures are expected to impart modified dissolution properties (including reduced swelling behavior) to advanced resist materials for deep ultraviolet lithography.

Introduction

The development of selectively fluorinated monomers and materials for deep ultraviolet lithographic applications has been widely explored due to the high transparency of fluorinated materials at 157 nm.[1] A wide variety of fluorinated backbone structures have been explored,

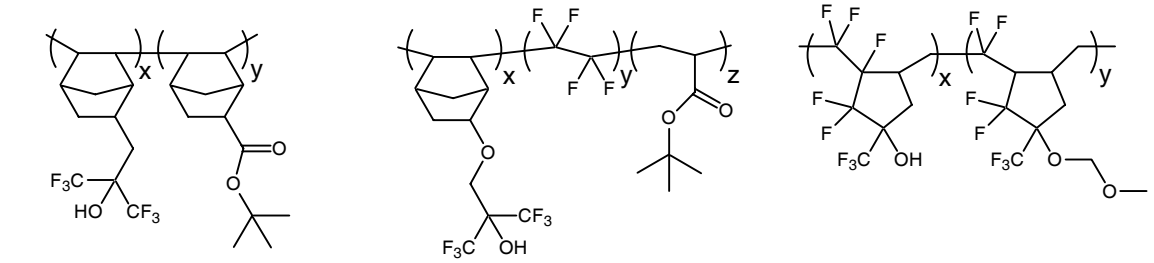


Figure 6.1. Fluoropolymers for use as photoresists at 157 nm

including metal-catalyzed norbornene and tricyclononene addition polymers,[2] free-radical copolymers of fluorinated acrylates and methacrylates,[3] free-radical copolymers of tetrafluoroethylene with functionalized olefins,[4] and free-radical cycloaliphatic polymers,[5] some of which are shown in Figure 6.1. The key development, however, was the discovery of the remarkable transparency[1,6] and dissolution properties[7] imparted by the use of highly fluorinated alcohols, particularly hexafluorocarbinols. The pKa of heavily fluorinated alcohols is comparable to phenols due to the strong inductive stabilization of their conjugate bases.[8] Unlike carboxylic acid ester-based materials, hexafluorocarbinol-functionalized resists offer the unique combination of extremely high transparency with ideal dissolution behavior (and a notable lack of swelling[7] in the developing solution which has been a particular problem with ester-functionalized norbornene-type addition polymers).

Free-radical polymerization processes have dominated resist development efforts due to their advantages of low cost, synthetic ease, and, most importantly, the lack of residual metallic contaminants which are difficult to remove and may detrimentally affect subsequent device performance/lifetime. However, the unique problems associated with developing materials with high transparency at 157 nm while maintaining good mechanical properties has caused many research labs to examine fluorinated norbornene monomers. While a tremendous variety of norbornene and norbornene-like monomers are readily accessible via cycloaddition processes

with functionalized olefins,[9] norbornene-type monomers do not homopolymerize efficiently via radical processes[10] and must be copolymerized with electron-deficient olefins such as tetrafluoroethylene.[4] Norbornene-type monomers are, however, readily polymerized via a number of metal-catalyzed pathways including addition (coordination) polymerization and ring-opening metathesis polymerization.[9] A particular challenge of employing metal catalysis to synthesize resist materials for 157 nm is the large number of polar and relatively acidic functionalities which must be tolerated by the metal catalysts. This requirement of high functional group tolerance rules out the use of oxophilic early transition metal catalysts and favors the use of late-transition metal catalysts. Specifically, neutral nickel[11] and cationic palladium[12] catalysts have been widely used for the synthesis of norbornene addition polymers and ruthenium catalysts[13] have been employed for the synthesis of ring-opening metathesis polymers.

The high activity and functional group tolerance of ruthenium-based olefin metathesis catalysts such as **6.1** and **6.2** (Figure 6.2) makes them particularly attractive in the synthesis of the highly functionalized monomers and polymers useful for lithographic applications.[13] While removal of metallic contaminants from polymeric materials to the parts per billion level required by the semiconductor industry is extraordinarily difficult, removal of metallic species from low molecular weight monomeric species capable of being purified by distillation or sublimation is

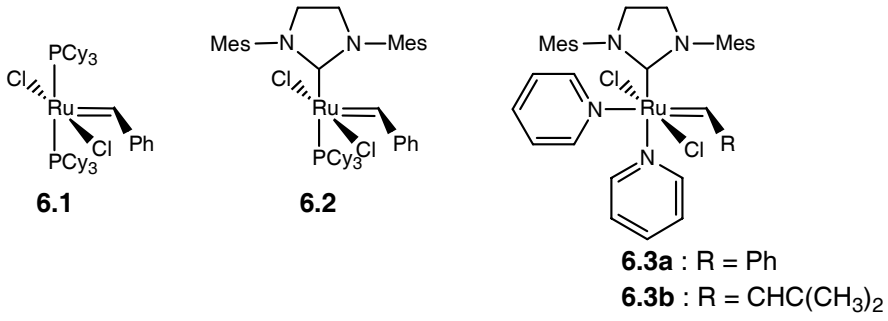


Figure 6.2. Ruthenium olefin metathesis catalysts

trivial. Therefore, application of transition metal catalysis towards monomer synthesis rather than polymer synthesis may be a more practical way to take advantage of the unique chemical transformations performed by these catalysts. In this work, various applications of ruthenium-catalyzed olefin metathesis are explored in the construction of multiply functionalized monomers and low molecular weight materials for use in deep ultraviolet lithography, with a particular focus on hexafluorocarbinol-functionalized compounds.

Results and Discussion

ROMP of Hexafluorocarbinol-containing Monomers Ring-opening metathesis polymerization (ROMP) of norbornene-type monomers had been explored during the development of 193 nm resists.[14] ROMP of 8-functionalized tetracyclo[4.4.$0^{1,6}$.$1^{2,5}$.$1^{7,10}$]dodec-3-ene (TCD) monomers using various metathesis catalysts yielded photoresist materials of only moderate utility. High loadings of free carboxylic acid-containing monomer were required for the resulting materials to have glass transition temperatures above 120 °C. These polymers exhibited undesirable swelling behavior and were not fully phase compatible with a large number of standard photoacid generators. TCD monomer **6.4a** is a byproduct of the Diels-Alder reaction used to produce the most widely used hexafluorocarbinol-functionalized norbornene. In spite of the failure of previous ROMP polymers as resist materials, the ability to turn this waste stream into a potentially high value-added material via olefin metathesis is particularly attractive.

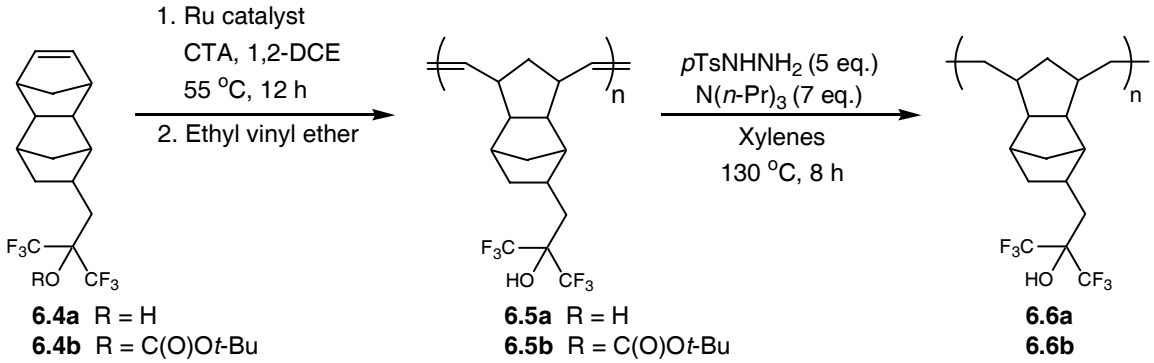


Figure 6.3. ROMP of hexafluorocarbinol-functionalized TCD monomers

ROMP of **6.4a** with catalyst **6.2a** in the presence of chain transfer agent afforded excellent yields of a brownish polymer (Figure 6.3). Standard chain transfer protocols called for the use of a symmetric internal olefinic chain transfer agent (CTA) such as 1,4-diacetoxy-*cis*-2-butene or *trans*-3- hexene and high reaction temperatures (55 °C, 16-24 h).[15] However, the secondary metathesis reactions which efficiently redistribute the chain lengths to the statistically determined value (DP = [M]/[CTA]) in the polymerization of norbornene are not as facile with the more hindered backbone olefins in the TCD ROMP polymer. As a result, molecular weights were consistently much higher than expected. With these bulkier TCD monomers, molecular weights were only able to be controlled kinetically through the use of either catalyst control (using a rapidly initiating catalyst such as **6.3a/b**) or the use of a terminal olefin chain transfer agent such as allyl acetate.[16] Unfortunately, the glass transition temperatures of polymer **6.5a** is only moderate (~115 °C) and falls further to ~ 85 °C after hydrogenation.[16] The large amount of color remaining in these polymers after reaction is equally problematic. The transparency of the hydrogenated polymer **6.6a** as measured by variable angle scanning ellipsometry (VASE) is fairly high as shown in Figure 6.4. A large number of copolymers of **6.4a** with various functionalized norbornene monomers were synthesized; however, all had unacceptable absorbance at (~ 3.5 μm^{-1}).[16] ROMP polymers consistently show higher, unacceptable absorbance at 157 nm relative to radical and metal-catalyzed addition polymers made from the same. The relative contributions of residual catalyst, hydrogenation by-products, polymer end groups, and the actual saturated ring-opened TCD structure to this higher absorbance are unknown. As a result, a conscientious effort to produce an ultra-clean "ideal" sample was attempted.

One difficulty in obtaining clean polymer is the inability to cleanly precipitate polymer **6.5a** into common solvents due to its amphiphilic nature. The acidic alcohols confer solubility in polar solvents such as methanol while the lipophilic backbone prevents the polymer from precipitating cleanly out of hexanes or pentanes. While the polymer is insoluble in aqueous

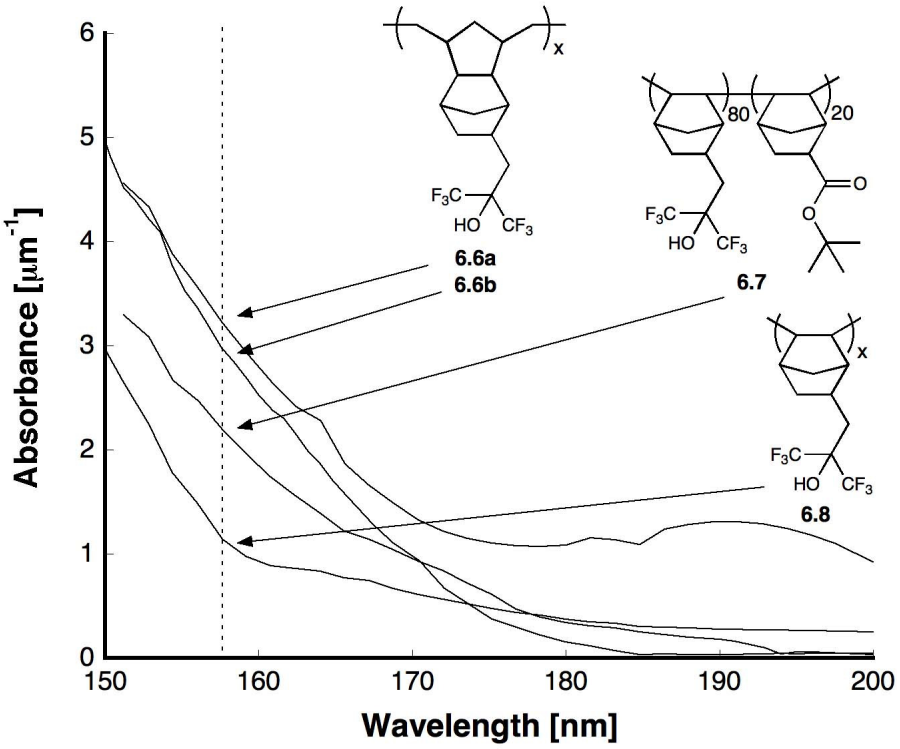


Figure 6.4. VASE spectra of metal-catalyzed polymers with hexafluorocarbinols

solutions, the monomer and catalyst by-products are also insoluble and the resulting polymer is particularly difficult to dry completely. A number of various techniques stated in the literature[17,18] for efficient removal of ruthenium metathesis catalyst by-products were attempted in order to clean up the brown polymer obtained after precipitation. The acidity of the fluorinated alcohols caused the polymer to stick excessively to a silica gel plug, resulting in large losses of material. The bound polymer could only be eluted with pure dichloromethane or ethyl acetate with little reduction in coloration. Attempts were made to exchange a water soluble phosphine ligand onto the residual catalyst to enable aqueous extraction according to the procedure of Maynard *et al*.[18] After extended exchange periods with excess of the water soluble phosphine, no color was observed to migrate to the aqueous extraction layer. Performing the ligand exchange directly after polymerization under inert conditions was also ineffective. Dialysis in methanol using regenerated cellulose dialysis tubes (500 molecular weight cutoff) was effective at

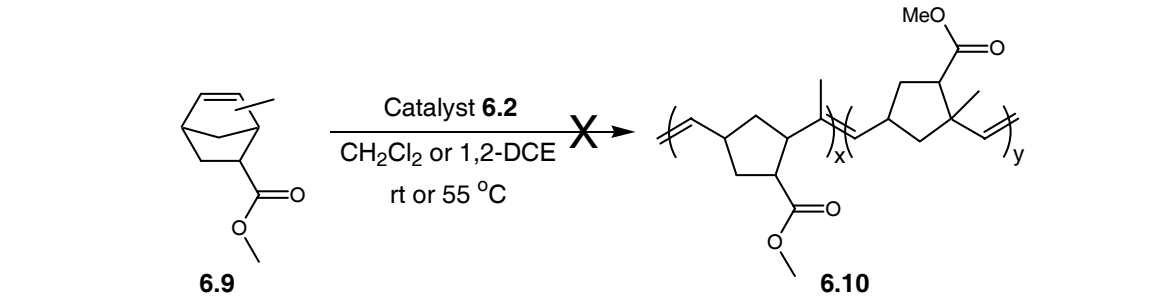
removing residual monomer; however, little reduction in coloration was observed. Extended heating in the presence of a hydrogen atmosphere or hydrochloric acid solution was similarly ineffective and only served to exacerbate the problem. Clearly, either the catalyst or a catalyst decomposition product must be interacting with the acidic hexafluorocarbinols (perhaps forming polymer-bound metal alkoxides) given the colorless ROMP polymers typically obtained using monomers like 4,4-bis(trifluoromethyl)-3-oxa-tricyclo[4.2.1.$0^{2,5}$]non-7-ene and catalyst **6.3a**.[19]

In order to observe the effect of the acidic hexafluorocarbinol, the alcohol of **6.4a** was protected with a *t*-butoxy carbonyl protecting group. The protected monomer **6.4b** was polymerized with the dimethylvinyl carbene catalyst **6.3b**. Fortunately, the *t*-Boc protected polymer **6.5b** precipitated cleanly from methanol, affording a nearly colorless polymer. Hydrogenation of **6.5b** resulted in the colorless saturated polymer **6.6b**, whose VASE spectrum is shown in Figure 6.4. While the transparency at 193 nm is greatly enhanced (1.28 μm^{-1} to 0.04 μm^{-1}), the improvement at 157 nm is less significant (3.23 μm^{-1} to 2.98 μm^{-1}). Several important conclusions can be made from these results. First, in agreement with theoretical calculations, the ring-opened TCD structure is considerably more absorbing than the norbornene addition structure.[20] Second, while the overall performance of the catalyst is unaffected by the presence of the hexafluorocarbinols, the presence of such acidic species results in entrapment of catalyst or catalyst decomposition products and highly colored polymers. Finally, ROMP-based polymers such as **6.6b** with their extremely high transparency at 193 nm are potentially attractive for use with 193 nm or 193 nm immersion lithography.

Other Approaches Toward High T_g Metathesis-based Structures One of the characteristic problems with ROMP materials is their moderate to low glass transition temperatures (T_g).[21] These are the result of the flexible ethylene linkage formed during hydrogenation of these materials. Traditionally, the solution has been to use higher cyclopentadiene analogs (such as TCD monomers); however, the increase in T_g is roughly independent of the nature of the

additional cyclic structure.[22] In addition, expansion of the hydrocarbon backbone has the additional effect of reducing the solubility of the resulting structure in aqueous developing solutions. Previously, we showed that rigidifying the cyclopentane backbone structure with a bridging unit was sufficient to dramatically increase the resultant ROMP polymer's T_g.[19] However, a more direct approach would be to increase the barriers to rotation around the ethylene bridge via the incorporation of a methyl group on the bridgehead carbon or the olefinic carbon.

The methyl-functionalized norbornene carboxylic acid methyl ester **6.9** was readily synthesized via the Diels-Alder reaction of methyl cyclopentadiene and methyl acrylate. Attempts at ROMP of **6.9** using catalyst **6.2** resulted in no isolable polymer. The use of higher temperatures or the faster initiating catalyst **6.3a** was also unsuccessful. Purification of the monomer via fractional distillation or column chromatography also proved to be ineffective. Monitoring of the reaction by NMR shows initiation of the catalyst and formation of very small amounts of ring-opened material, but no substantial consumption of monomer. This was



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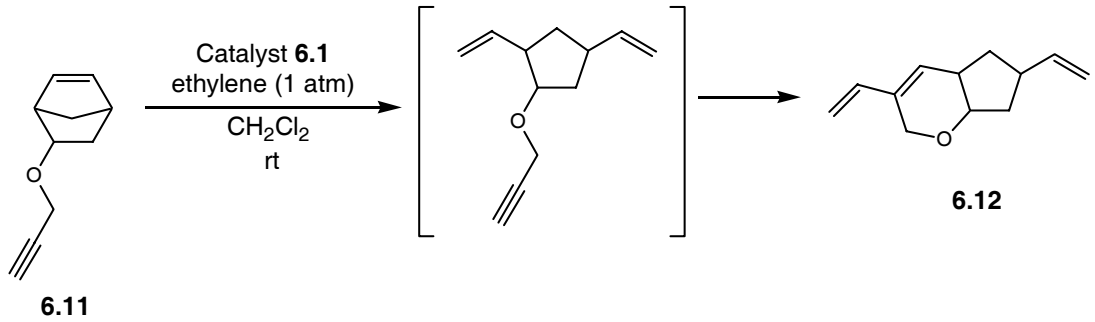


Figure 6.5. Other approaches toward high T_g metathesis structures

unexpected since the ROMP of 1-methyl norbornene with catalyst **6.1** has been reported in the literature.[23] Also, Morgan *et al.* observed the successful ring-opening cross-metathesis of the exo isomer of the dimethyl ester of 1-methyl nadic anhydride, while the endo isomers and the trisubstituted olefin isomers were unreactive but did not decompose the catalyst.[24] Additional work is needed to further elucidate this behavior.

Acyclic diene metathesis (ADMET)[25] polymerization is a potentially useful polymerization methodology since it simplifies the chemical design considerations. Instead of carefully placing steric bulk on an existing norbornene framework, an ADMET approach simply calls for the presence of two terminal olefins on an arbitrary functionalized structure. Given the ability of enyne cascade metathesis reactions to produce polycyclic structures,[26] we imagined the synthesis of an asymmetric polycyclic structure starting from the propargyl ether-functionalized norbornene **6.11**. For use as a lithographic material, polar functional groups could be placed at the 3-position. Following the procedure of North *et al.*,[27] ring-opening metathesis of **6.11** with catalyst **6.1** in the presence of ethylene followed by in-situ ring-closing enyne metathesis upon removal of the ethylene afforded the polycyclic triene **6.12**. Unfortunately, no polymer formation was observed when **6.12** was subjected to ADMET conditions with catalyst **6.**2. Primarily, metathetical dimerization at the terminal olefin was observed while the less reactive terminal dienes were left unreacted. While second generation metathesis catalysts such as **6.2** have been shown to perform cross-metathesis on terminal dienes, the additional sterics imparted by the polycyclic structures are sufficient to prevent the efficient cross-coupling metathesis reactions required for high conversions and significant molecular weight development. Other groups have attempted to design polycyclic structures with pendant allyl ethers suitable for polymerization via ADMET.[28] The lack of polymer formation in these reactions was likely due to the in-situ isomerization of the allyl ether to a crotyl ether capable of reacting with and deactivating the catalyst.[29] These longer tethers would also likely have a more detrimental impact on the T_g than

the polycyclic core would have a positive impact. As a result, ADMET currently seems to be an ineffective approach to produce high T_g materials.

Cross-Metathesis in Resist Material Development The use of olefin cross-metathesis (CM) in the synthesis of monomers suitable for polymerization by conventional means appeared to be a practical way to employ metathesis without concern for glass transition temperatures or the difficult removal of residual metal contamination from hard-to-purify polymeric materials. A number of carboxylic acid ester-functionalized norbornene addition polymers such as **6.7** exhibit substantial swelling problems in aqueous developer solutions.[2b,7] Polyfunctional dissolution inhibitors[30] such as those shown in Figure 6.6 are required to alleviate this swelling behavior. Characteristic of these dissolution inhibitors is the presence of multiple protected hexafluorocarbinol groups. These functionalities are typically synthesized via alkylation of the extremely toxic hexafluoroacetone. With the recent commercial availability of a variety of olefin-functionalized hexafluorocarbinols (such as **6.13** and **6.14**), olefin cross-metathesis could potentially serve as a convenient synthetic methodology for the introduction of hexafluorocarbinols.

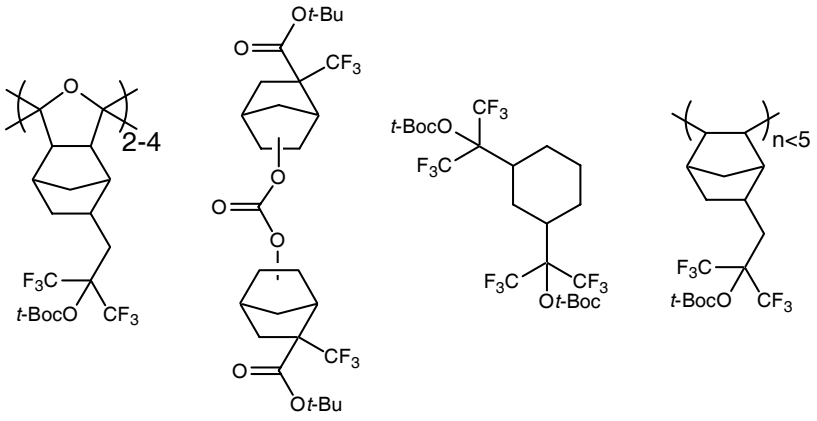


Figure 6.6. Dissolution inhibitors for use at 157 nm

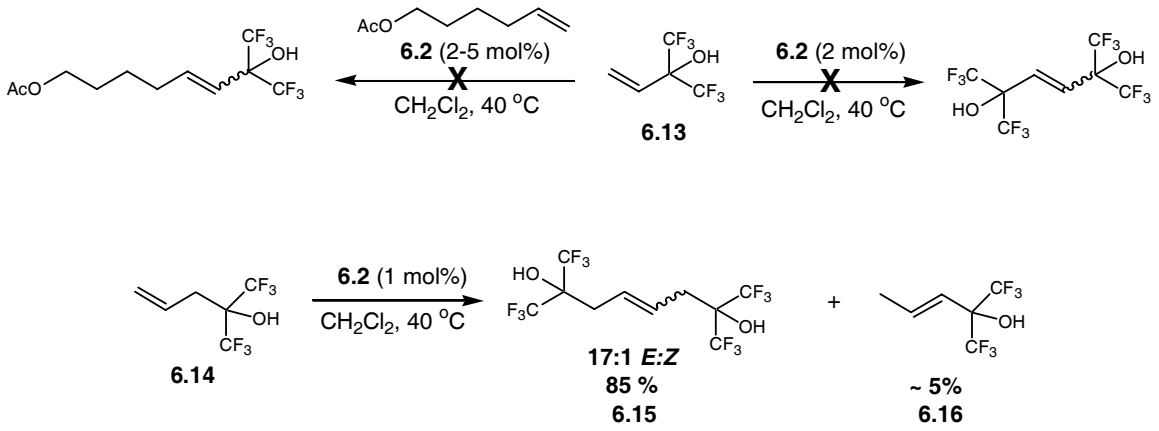


Figure 6.7. Cross-metathesis of hexafluorocarbinol-functionalized olefins

Cross-Metathesis of Hexafluorocarbinol-Functionalized Olefins The allylic hexafluorocarbinol **6.13** does not undergo cross-metathesis with either 5-hexenyl acetate or self-metathesis (Figure 6.7). This is perhaps not surprising given the additional detrimental effects of the increased steric hindrance and reduced electron density on the olefin due to the fluorine substituents in **6.13** to the already low reactivity of the non-fluorinated 1,1-dimethyl-prop-2-ene-1-ol.[31] However, the homoallylic alcohol **6.14**, in which the steric and electronic influences of the trifluoromethyl groups are further removed from the olefin, displays high cross-metathesis activity. High yields of self-metathesis product **6.15** can be obtained with good trans selectivity. The remaining hexafluorocarbinol species were isolated as the starting material and the isomerization product *E*-1,1,1-trifluoro-2-trifluoromethyl-pent-3-ene-2-ol (**6.16**), which is inert to olefin metathesis.

Cursory examination of olefins **6.14** and **6.15** show them to be potential analogues of two commonly used ROMP chain transfer agents: allyl acetate and 1,4-diacetoxy-*cis*-2-butene.[15] While ROMP of TCD monomer **6.4a** afforded a polymer potentially useful at 193 nm, use of olefins **6.14** or **6.15** in the ring-opening cross metathesis (ROCM) of **6.4a** would result in polyfunctional monomeric or oligomeric structures reminiscent of the dissolution inhibitors shown in Figure 6.6. Initial experiments showed that the internal olefin of **6.15** is insufficiently

reactive to compete with ROMP, leading to high molecular weight material. Conversely, the terminal olefin **6.14**, when used in super-stoichiometric amounts, affords good yields of oligomeric ROCM products and dimer **6.15,** which can be separated by column chromatography and recovered.

Development of Difunctional Monomers The homoallylic alcohol **6.14** is primarily used in a Diels-Alder reaction with cyclopentadiene to produce a hexafluorocarbinol-functionalized norbornene.[2e] While 1,2-disubstituted olefins are typically less reactive in Diels-Alder processes, if olefin **6.15** could undergo cycloaddition, perhaps at higher temperatures or pressures, it would constitute a facile route to monomers with multiple hexafluorocarbinol groups. Since dissolution inhibitors presumably act by sequestering ionizable functionalities with intermolecular hydrogen bonds,[30] incorporation of a hydrogen bond acceptor or donor on the same monomer as the solubility switch could allow for an *intra*molecular dissolution inhibition effect, leading to a reduction of swelling behavior and modification of dissolution behavior. A few model polymers are shown in Figure 6.8. Since **6.14** is a good CM substrate, olefin cross-metathesis is an ideal route to the difunctional olefins necessary to synthesize the respective norbornene monomers. As a result of this strategy, both functionalities in the commercial resist **6.7** could be incorporated into a single monomer.

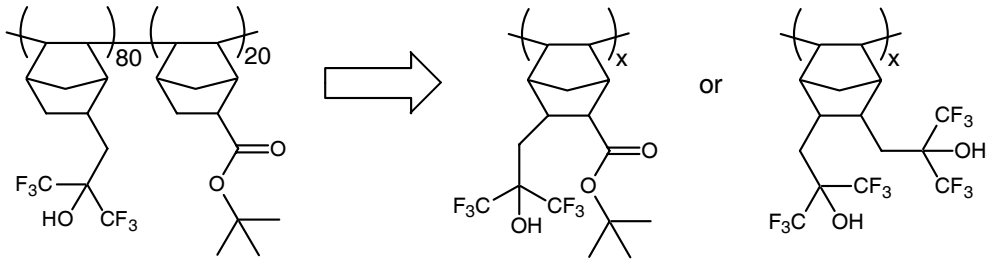


Figure 6.8. Polymers from multifunctional monomers

The Diels-Alder reaction of diol **6.15** with cyclopentadiene was attempted as shown in Figure 6.9. Only very low yields of the di(hexafluorocarbinol)norbornene **6.17** was isolated. The product was contaminated with small amounts of higher cyclopentadiene adducts. Since the internal olefin of **6.15** does not have the steric problems which cause the allylic alcohol **6.13** to be unreactive towards cycloaddition with cyclopentadiene, increasing the dienophilicity of the olefin with an ester-substituent should be sufficient to achieve useful cycloaddition yields. Fortunately, the cross-metathesis of α,β-unsaturated carbonyl compounds such as acrylates with terminal olefins can be performed with high product and stereoselectivity using second-generation catalysts such as **6.2**.[32]

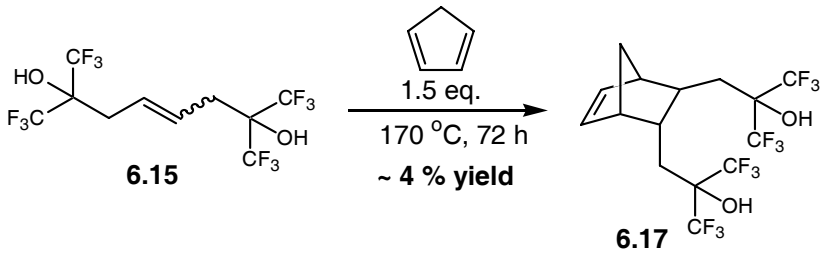


Figure 6.9. Diels-Alder synthesis of difunctional monomer

Cross-metathesis of the homoallylic alcohol **6.15** with methyl acrylate afforded the hexafluorocarbinol-substituted unsaturated ester **6.18** in good yield (Figure 6.10). While cross-metathesis of α,β-unsaturated carbonyl compounds with α-olefins using catalyst **6.2** typically results in product distributions with high trans content (E/Z > 20:1),[31,32] cross-metathesis with **6.14** resulted in an uncharacteristically low E/Z ratio of 2.5:1. Cross-metathesis with *t*-butyl acrylate resulted higher yields of **6.18b** but similar E/Z ratios. Interestingly, the ^{1}H NMR resonance for the alcohol proton was strikingly different between the two isomers, with the Z-isomer being far downfield relative to the E-isomer. The two isomers were readily separable by column chromatography. While these two phenomena would seem to indicate the presence of

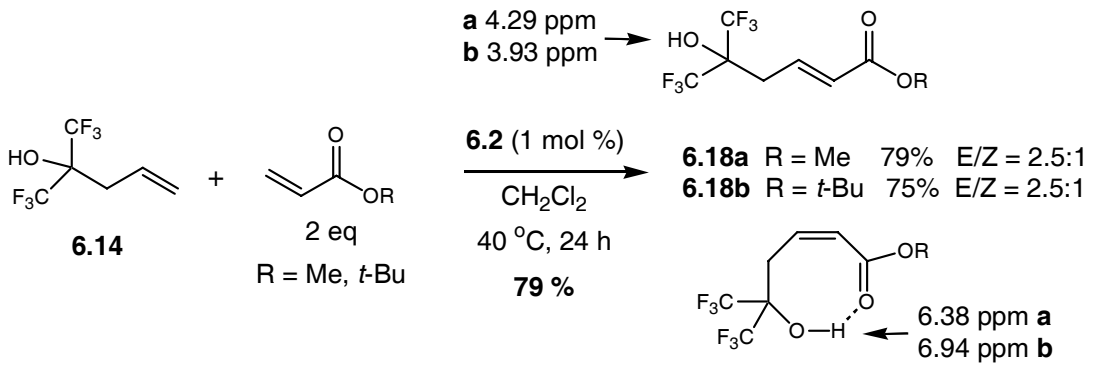


Figure 6.10. Synthesis of substituted crotonates via cross-metathesis

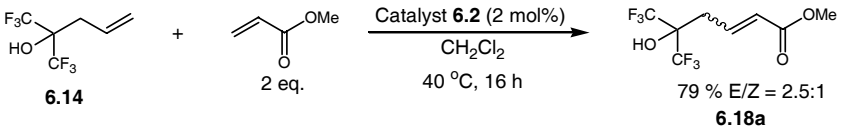
strong intramolecular hydrogen bonding in the Z-isomer, whether this is the root cause of the low E/Z ratio is unclear.

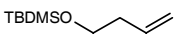
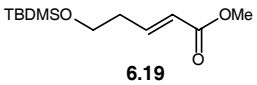
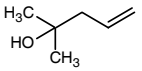
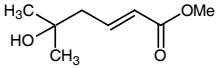
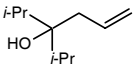
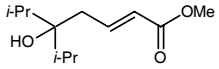
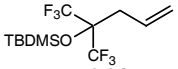
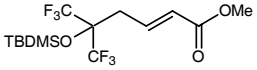
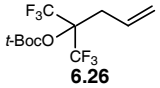
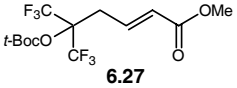
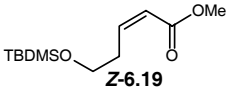
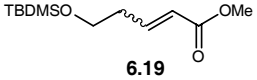
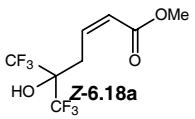
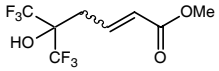
Investigations into Low E/Z Ratios In order to investigate the origin of the low E/Z ratios observed in cross-metathesis of **6.14** with acrylates, a number of fluorinated and non-fluorinated analogues of **6.14** were synthesized and subjected to cross-metathesis conditions with methyl acrylate using **6.2** (Table 6.1). While unprotected 3-pentenyl alcohol underwent facile isomerization to aldehyde products and resulted in poor CM yields, the *t*-butyldimethylsilyl-protected alcohol afforded the 5-(*t*-butyldimethylsilanyloxy)-pent-2-enoic acid methyl ester **6.19** with high E selectivity (Entry 1, Table 6.1). Similarly, CM with the non-fluorinated analogue of **6.14**, 2-methyl-pent-4-en-2-ol **6.20**, afforded the methyl-substituted product **6.21** with high E selectivity. Since isopropyl groups are more isosteric with trifluoromethyl groups,[33] the bis(isopropyl)-functionalized alcohol **6.22** was synthesized and found to again produce cross-product with high E content. Since equally bulky alcohols afford only trans product, steric hindrance by the trifluoromethyl groups in **6.18a** is not preventing secondary metathesis from isomerizing any cis isomers to the more stable trans isomer.

In order to examine the effect of the acidic alcohol, two protected versions of **6.14** were synthesized. Again, the protected alcohols afforded only trans products, although the yield with the *t*-butoxycarbonyl-protected alcohol was extremely low and no self-metathesis dimer of **6.26**

was observed by NMR. These results indicate the presence of the acidic hexafluorocarbinol is responsible for the low stereoselectivity of the reaction. However, it is not known what the dominant interaction is: intermolecular hydrogen bonding between the alcohol and the incoming acrylate during olefin binding and metallacycle formation, interaction between the dissociated basic phosphine and the acidic alcohol, or intramolecular interaction with the catalyst during metathesis.

Table 6.1. Investigation into the E/Z selectivity of cross-metathesis with **6.14**



Entry	Substrate	Equiv. MA	Time (h)	Product	Yield (%)	E/Z
1		2	20	 **6.19**	80*	20:1
2	 **6.20**	2	18	 **6.21**	81	> 20:1
3	 **6.22**	2	16	 **6.23**	49	> 17:1
4	 **6.24**	2	16	 **6.25**	46	> 12:1
5	 **6.26**	2	16	 **6.27**	26	> 20:1
6	 ***Z*-6.19**	1	20	 **6.19**		12:1
7	 ***Z*-6.18a**	1	16	 **6.18a**		1.6:1

Yields determined by NMR. *Isolated yield.

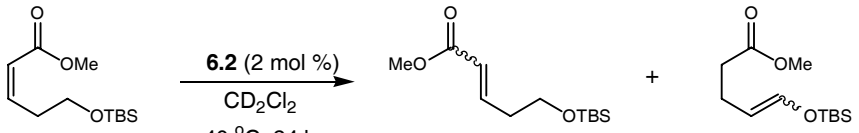
Although *E*-crotonates are thermodynamically more stable than *Z*-crotonates, it is not known whether the high trans selectivity in cross-metathesis with acrylates is a result of kinetic or thermodynamic preference. In order to test the ability of *cis*-α,β-unsaturated esters to undergo secondary metathesis-based isomerization to the trans isomer, ***Z*-6.19** was synthesized directly from the unsaturated lactone, 5,6-dihydro-pyran-2-one.[34] Reaction of ***Z*-6.19** directly with catalyst **6.2** resulted predominantly in the 2-bond migration of the double bond to form the more electron-rich silyl enol ether **6.28** (E:Z ~ 1.1). Addition of one equivalent of methyl acrylate relative to substrate reduced this isomerization to negligible levels. The E/Z of the resulting product was 12:1, indicating that the olefins of the α,β-unsaturated carbonyl compounds are able to undergo secondary metathesis albeit with more difficulty than regular aliphatic internal olefins. Resubjection of ***Z*-6.18a** (isolated from a 2.5:1 E/Z mixture by column chromatography) afforded **6.18a** with an E/Z ratio of ~1.6:1, consistent with the results from ***Z*-6.28**. These results support the E/Z ratios obtained in these CM reactions being the thermodynamic distributions with a strong intramolecular hydrogen bond in **6.18** responsible for the lower than expected E/Z ratio.

Prevention of Ruthenium-Catalyzed Olefin Isomerization The isomerization/migration of olefins during olefin metathesis is a side-reaction which lowers reaction yields and results in complex product mixtures which are often difficult to separate.[35] While the exact mechanism(s)[35,36] (metal-based hydride, π-allyl, or other pathways) responsible for this isomerization are unknown, recent results indicate that ruthenium hydride species formed by decomposition of the ruthenium metathesis catalysts can catalyze the migration of olefins under metathesis conditions.[37,38] Currently, to avoid olefin migration during the metathesis reaction, the reactions must be stopped as soon as high conversion is reached as further reaction leads only to product degradation via olefin isomerization.[39] This is a particular problem in the cross-metathesis of products such as insect pheromones where the product olefin will not be hydrogenated and the location of the olefin is critical for activity. The high efficiency of the 2-

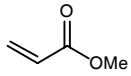
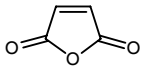
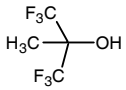
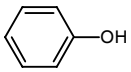
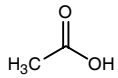
bond isomerization of ***Z*-6.19** to the silyl enol ether **6.28** coupled with the extremely diagnostic signals associated with the starting *Z*-vinyl ester and the product *E*-vinyl ester and vinyl ether olefinic protons make this an excellent system for studying the isomerization process. This system is a good mimic of a metathesis reaction which has already reached full conversion while not being complicated by the presence of ruthenium methylidenes. Of particular interest was the reduction of olefin migration observed when an additional equivalent of methyl acrylate was added to the reaction mixture. This provided evidence that simple additives may be sufficient to prevent olefin isomerization in certain systems by either modifying the ruthenium decomposition process or by scavenging ruthenium hydrides before they can initiate isomerization.

The effect of a number of simple additives on the amount of olefin migration of ***Z*-6.19** is shown in Table 6.2. In place of the metathesis active methyl acylate, maleic anhydride was utilized and found to result only in catalyst deactivation. Nolan *et al.* observed that the amount of olefin isomerization is strongly solvent dependent and the addition of small amounts of tricyclohexylphosphine oxide eliminated the formation of isomerized products.[36b] Since less isomerization was observed in slightly acidic solvents such as 1,2-dichloroethane, we decided to examine the effects of acidic additives on the isomerization process. Previously, our group has shown that one of the decomposition pathways leading to hydride formation involves attack by the phosphine. The use of acidic additives was hoped to buffer the reaction and scavenge either the phosphine prior to hydride formation or react directly with any metal hydride directly. Alcohols with pK_as $\geq$ 9 had little effect; however, the more acidic acetic acid afforded excellent yields of ***E*-6.19** without any observable olefin migration. The higher efficiency of cis to trans isomerization using acetic acid in place of methyl acrylate is due to the rate acceleration due to phosphine scavenging and lower stability (i.e. higher decomposition rate) of ruthenium enoic carbenes formed by reaction with methyl acrylate. Morgan *et al.* have employed a large number of acidic and metallic phosphine scavengers and showed that acids with pK_as ~4-5 lead to optimal rate acceleration without decreasing catalyst lifetimes.[24,40] Our results indicate that simple

Table 6.2. Effect of additives on olefin migration



***Z*-6.19** [0.4 M] **6.19** **6.28**

Additive	^{1}H NMR Product Distribution	
None	19 % E/Z = 20:1	81% E/Z ~ 1:2
	Quant. E/Z = 12:1	0 %
	> 95 % E/Z ~ 1:10	0 %
CF_3CH_2OH	11% E/Z > 20:1	89 % E/Z ~ 1:2
	19 % E/Z > 20:1	81 % E/Z ~ 1:2
	17 % E/Z > 20:1	83 % E/Z ~ 1:2
	> 95 % E/Z > 20:1	0 %

carboxylic acids such as acetic and benzoic acids would be an ideal reaction additive for certain cross-metathesis reactions with **6.2** to eliminate olefin migration and afford shorter reaction times.

Unfortunately, in a few other cross-metathesis reaction systems, the presence of acetic acid was insufficient to shut down the olefin migration. Whether this failure is due to the additional presence ruthenium methylidene (and its decomposition by-products)[38] or the presence of an alternative isomerization pathway is unknown. However, our results have shown that simple additives can be highly effective at shutting down olefin migration processes, and screening of more effective inhibitors is ongoing.[41]

Synthesis of Difunctional Monomers The Diels-Alder reaction of ***E*-6.18** with cyclopentadiene afforded the difunctional monomer **6.29** in good yield, although the methyl ester

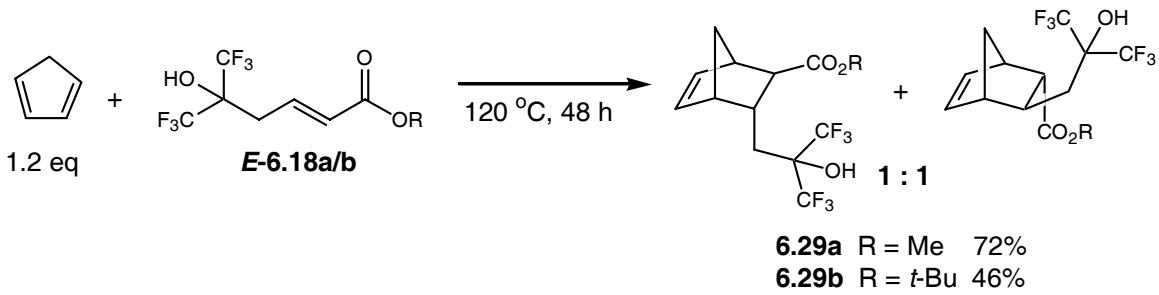


Figure 6.11. Diels-Alder synthesis of difunctional monomers

resulted in higher yields than the *t*-butyl ester. The more facile cycloaddition resulted in the formation of only a small amount (< 5%) of higher cyclopentadiene adducts. Consistent with the Diels-Alder reactions of *trans*-methyl crotonate,[42] no exo/endo selectivity was observed with ***E*-6.18**. ^{1}H NMR spectroscopy of **6.29** showed the presence of two distinct downfield hydroxyl resonances, indicating that the hydroxyl groups are participating in intramolecular hydrogen bonding interactions with the nearby ester groups in the chlorinated NMR solvent.

The *t*-butyl ester serves as an excellent solubility switch with which to observe the deprotection reaction, although virtually any acid-labile ester protecting group could be installed via cross-metathesis with the appropriately protected acrylic acid. Removal of the *t*-butyl protecting group was achieved via heating in the presence of *p*-toluene sulfonic acid to afford the carboxylic acids **6.30** (Figure 6.12). No lactonization was observed by NMR. The *anti*-configuration of the two functionalities and the low nucleophilicity of the tertiary hexafluorocarbinols effectively prevents any undesirable lactonization.

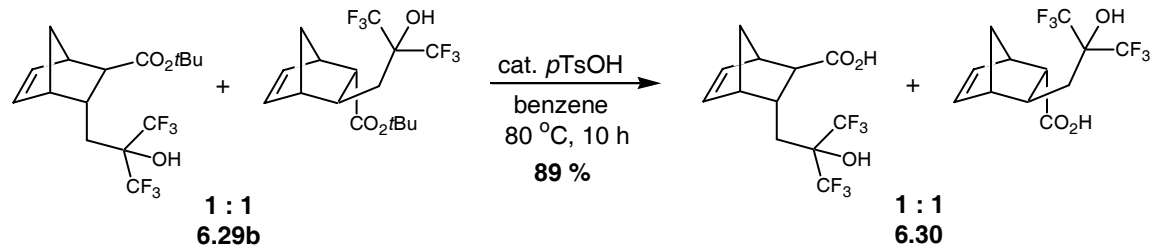


Figure 6.12. Acid-catalyzed deprotection of difunctional monomers

Given the high transparency of the norbornane hexafluorocarbinol **6.31** (1.15 μm^{-1}) relative to the norbornane methyl ester **6.32** (6.02 μm^{-1}), it was unclear just how transparent monomer **6.29** would be since it contains both heavily absorbing and highly transparent groups. Hydrogenation of **6.29a** and **6.29b** over Pd/C afforded clean production of the saturated compounds **6.33a** and **6.33b**, respectively. Their vacuum ultraviolet spectra are shown in Figure 6.13. The saturated difunctional monomers exhibit remarkable transparency at 157 nm. In fact, their absorbance is virtually identical to the mono-hexafluorocarbinol functionalized norbornane **6.31**.

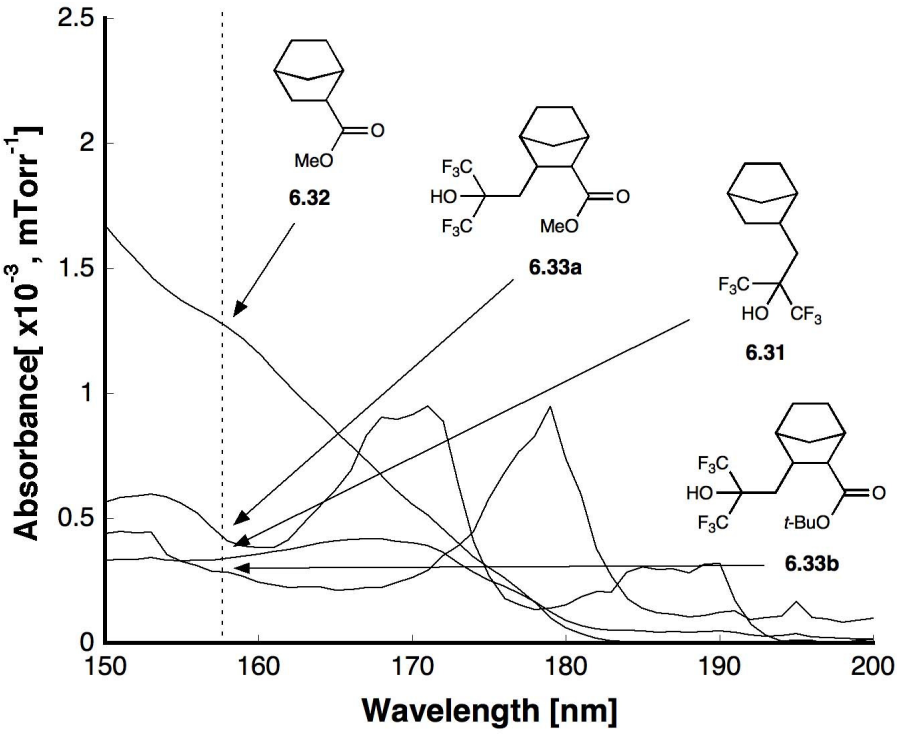


Figure 6.13. Vacuum UV spectra of difunctional norbornanes

While one must not be overzealous in drawing conclusions from this preliminary data, it seems clear that a significant red-shifting of the ester absorption band has occurred, similar to the results obtained via the incorporation of a trifluoromethyl group alpha to the ester group. The most likely explanation for this phenomenon is the intramolecular hydrogen-bonding of the polar

alcohol to the ester group. The magnitude of the red-shifting parallels the downfield shifting of the hexafluorocarbinol proton resonances in the ^{1}H NMR spectra upon proceeding from the methyl ester (δ = 6.17 and 5.42 ppm) to the *t*-butyl ester (δ = 6.77 and 5.96 ppm). For comparison, the hexafluorocarbinol proton appears at 2.78 ppm for the non-ester functionalized norbornene. It may be that the more bulky *t*-butyl ester is favoring a conformation more amenable to hydrogen bonding, thereby influencing the strength of the hydrogen bonding and the transparency. Because the low volatility of these difunctional monomers results in less than ideal gas phase spectra, syntheses of polymeric samples for VASE are being pursued to confirm these exciting results.

The syn versions of **6.29** would be potentially useful for negative tone resists if the lactonization were reasonably facile, or if the equilibrium lay on the side of the ring-opened product, the lactone versions could undergo acid-catalyzed hydrolysis to afford a mass-persistent solubility switch.[43] A ring-closing metathesis route toward the synthesis of the bis(trifluoromethyl)dihydropyranone **6.35** is shown in Figure 6.14. Esterification of the sodium

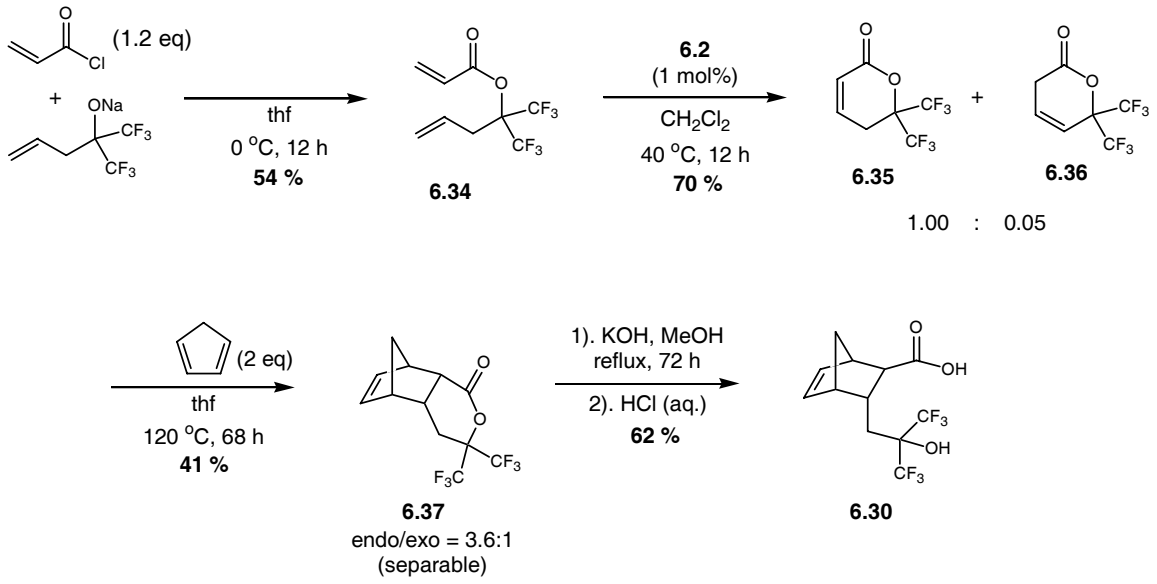


Figure 6.14. Synthesis of lactone-functionalized monomers

salt of **6.14** with acryoyl chloride afforded diene **6.34** in moderate yield. Ring-closing metathesis of **6.34** resulted in good yields of the bis(trifluoromethyl)dihydropyranone **6.35**; however, a small amount of the olefin migration product **6.36** was observed. Hydrolysis of lactone **6.35** with potassium hydroxide and protection of the methyl ester afforded **6.18a** in 47% yield, but only a 1:3 E/Z ratio. Given the loss of product due to isomerization, the unsaturated lactone **6.35** was reacted directly with cyclopentadiene to afford the norbornenyl lactone **6.37**. Although only moderate yields were achieved, it is likely that Lewis acid catalysis would be effective in boosting product yields and endo selectivity.[44] ***Endo*-6.37** was isolated cleanly by column chromatography with no contamination by ***exo*-6.37** or higher cyclopentadiene adducts. Base-catalyzed hydrolysis of ***endo*-6.37** resulted in the production of a single isomer of **6.30** in which the ester has been epimerized to the exo-configuration. Spectroscopic comparison to the isomeric mixture of **6.30** (Figure 6.12) confirmed the identity of the product.

Although these monomers are quite promising, it would be nice to find a route to these monomers which does not involve the relatively expensive ruthenium metathesis catalyst **6.2**. The oxidation of activated allylic carbons (such as in 3,6-dihydro-2H-pyran) to unsaturated lactones by pyridinium chlorochromate has been reported in the literature.[45] The bis-trifluoromethylated version of this dihydropyran is readily obtained via the Diels-Alder reaction of hexafluoroacetone with 1,3-butadiene.[46] With the synthesis of large quantities of **6.38** possible, screening of several oxidation catalysts was performed. Oxidation with pyridinium chlorochromate in a sealed tube afforded a moderate yield of the desired unsaturated lactone **6.35**. Unfortunately, this process was quite lengthy and required several additions of PCC and long reaction times at elevated temperatures.[45] Prolonged reaction at higher temperatures lead to two deleterious side reactions: the retro-Diels-Alder reaction of **6.38** and the 1,3-allylic rearrangement of the initial chromate adduct to form the dihydropyranone **6.39**.

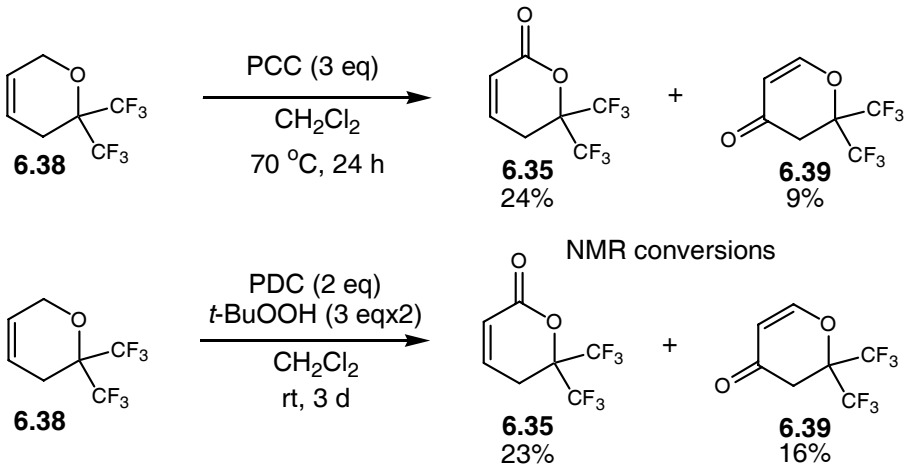


Figure 6.15. Alternative syntheses of fluorinated unsaturated lactones

Screening of several reaction conditions was unable to improve product yields. An alternative oxidant, selenium dioxide, was unreactive towards allylic oxidation of this substrate. However, the oxidation of 3,4-dihydro-2H-pyran with pyridinium dichromate/*t*-butyl hydroperoxide has been reported to produce the identical unsaturated lactone structures.[47] Subjection of **6.38** to these oxidation conditions afforded similar results to the PCC oxidations, albeit with slightly higher yields of the non-desired product **6.39**. Unfortunately, it seems the detrimental electron-withdrawing effects of the trifluoromethyl groups prevent the allylic position from being sufficiently activated towards oxidation. The resulting slow oxidation process allows for isomerization of the initial chromate oxidized species leading to a mixture of products.

Conclusions

Well-defined ruthenium olefin metathesis catalysts display the high reactivity and functional group tolerance required for the synthesis of new monomers and materials for deep ultraviolet lithography. Ring-opening metathesis polymerization of hexafluorocarbinol-functionalized tetracyclododecene monomers affords polymers which, after hydrogenation, are highly transparent at 193 nm, provided the acidic alcohol is protected prior to polymerization.

However, these same ROMP polymers continue to exhibit inherently high absorbance (~3.0 μm^{-1}) at 157 nm despite our best efforts. Alternative metathesis-based approaches to the synthesis of high T_g structures via ROMP of methyl-substituted norbornenes and ADMET of polycyclic structures were unsuccessful.

Ruthenium-catalyzed cross-metathesis can efficiently introduce hexafluorocarbinol groups onto a variety of olefin-containing substrates using readily available hexafluorocarbinol-functionalized olefins. The cross-metathesis approach serves as a mild and convenient route to products which would ordinarily be synthesized via alkylation of highly toxic hexafluoroacetone. Cross-metathesis of homoallylic hexafluorocarbinols with acrylates affords cross-products which exhibit uncharacteristically low E/Z ratios. The presence of the acidic alcohol is the key to the production of higher amounts of cis olefin in this system. *Cis*-α,β-unsaturated carbonyl compounds are subject to secondary metathesis-based isomerization to their trans isomers; however, olefin migration to form more electron-rich olefins was observed in certain instances. The addition of acetic acid to the reaction solution resulted in higher catalyst reactivity while eliminating olefin migration. Work is continuing in this area to further understand the nature of olefin migration and find more effective additives which can eliminate this migration in a general manner. An example of the benefits of the cross-metathesis approach to introduction of hexafluorocarbinol groups is the 2-step synthesis of norbornene monomers with both ester and hexafluorocarbinol functionalities. Gas-phase ultraviolet spectroscopy reveals that these difunctional norbornane structures have extraordinarily high transparency at 157 nm. Alternatively, ring-closing metathesis can be employed to synthesize unsaturated, trifluoromethylated lactones suitable for production of the same class of difunctional norbornenes. Work is continuing towards the polymerization of these structures in order to confirm their high transparency and examine their dissolution properties.

Experimental

Materials: All air sensitive manipulations and polymerizations were carried out in an N_2-filled drybox or using standard Schlenk techniques. All solvents were rigorously degassed in 18 L reservoirs and passed through two sequential purification columns consisting of activated alumina.[48] All starting materials were procured from Aldrich except 1,1,1-trifluoro-2-(trifluoromethyl)-pent-4-ene-2-ol (Oakwood), hexafluoroacetone (Oakwood), or unless otherwise mentioned. Compounds **6.4a**, **6.13**, **6.32**, and **6.31** and polymer **6.8** were generously donated or synthesized by the Willson Lab at the University of Texas, Austin. Photoresist **6.7** was generously donated by Ralph Dammel of AZ-Clariant. The norbornenyl propargyl ether **6.11** and the bicyclic triene **6.12** were synthesized by Dr. Emmanuelle Despagnet-Ayoub. Ruthenium olefin metathesis catalysts **6.1** and **6.2** were obtained from Materia, Inc. Catalysts **6.3a** and **6.3b** were synthesized according to the literature.[49] All liquid reagents used for vacuum UV measurements were distilled from appropriate drying agents, thoroughly degassed by freeze, pump, thaw cycles and sealed in glass ampoules under vacuum.

Methods: Nuclear magnetic resonance (NMR) spectra were obtained using a Varian *Mercury 300* spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz). Shifts for NMR spectra are reported in ppm relative to TMS (for ^{19}F, internal C_6F_6 (~ 0.5 %) at -162.2 ppm) or to the chemical shift of the residual proteo solvent. Molecular weights (M_n) and polydispersity indices (PDI) were measured from THF solutions by size exclusion chromatography (SEC) using a GPC apparatus equipped with two PLgel 5 μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multi-angle laser light scattering (MALLS) detector and an Optilab DSP digital refractometer (both from Wyatt Technology). All molecular weight values are given relative to polystyrene standards. When no calibration standards were used, *dn/dc* values were obtained for each injection by assuming 100% mass elution from the columns. All reported molecular weights are relative to polystyrene standards. Differential scanning calorimetry (DSC) measurements was performed on either a Perkin Elmer *Series-7* or *Pyris* thermal analysis system.

Vacuum UV Spectroscopy: Gas phase VUV measurements were made on an Acton *CAMS-507* spectrophotometer fitted with a custom-made gas cell attachment. The details of the cell design and implementation have been described previously.[1c] All liquid compounds for vacuum UV measurements were distilled from appropriate drying agents, thoroughly degassed by freeze, pump, thaw cycles and sealed in glass ampoules under vacuum.

Synthesis: **8-(1,1,1,3,3,3-Hexafluoro-2-t-butyldimethylsilanyloxy-propyl)-tetracyclo[4.4.0^{1,6}.1^{2,5}.1^{7,10}]dodec-3-ene (6.4b).** To a flame-dried 100 mL 2-neck flask was added sodium hydride (153 mg, 6.35 mmol, 1.1 eq.). 70 mL of dry degassed tetrahydrofuran was added via cannula. To the stirring suspension was added hexafluorocarbinol **6.4a** (2.0 g, 5.78 mmol, 1.0 eq.) slowly via syringe. After the evolution of gas had ceased (~ 5 minutes) the solution was stirred for 40 minutes at room temperature. A solution of di-*t*-butyl dicarbonate (1.39 g, 6.35 mmol, 1.1 eq.) in 5 mL of tetrahydrofuran was transferred to the reaction flask. The reaction immediately turned cloudy and was allowed to stir overnight. The reaction was then diluted with water and extracted into 250 mL of ether. The organic layer was washed with water until the washings were neutral. The organic layer was then washed with brine and dried over sodium sulfate. The ether was removed *in vacuo* to afford 1.88 g (73 %) of **6.4b** as a colorless liquid. R_f = 0.64 (20:1 hexane:ethyl acetate). Data tabulated for major isomer only: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.05-5.95 (m, 2H), 2.85 (m, 2H), 2.3-2.2 (m, 2H), 2.03 (unresolved m, 2H), 1.52 (s, 9H), 1.4-1.2 (m, 4H), 0.64 (d, *J* = 10.5 Hz, 1H), 0.59 (dm, *J* = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 149.23, 136.19, 135.94, 84.80, 53.22, 49.27, 47.22, 46.87, 43.59, 41.34, 340.69, 9.48, 35.67, 35.20, 31.46, 29.57, 27.73. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -71.9 - -72.3 (m, 6F).

General Ring-Opening Metathesis Polymerization Procedure: To a 20 mL vial with Teflon stirbar and teflon-coated septa cap was added the ruthenium catalyst. The vial was purged with argon and degassed, anhydrous dichloromethane or 1,2-dichloroethane was injected. Upon

dissolution of the catalyst, a solution of monomer was injected and allowed to stir at room temperature. The reaction was quenched by the addition of more than 50 equivalents (relative to catalyst) of ethyl vinyl ether and allowed to stir at room temperature for 1 hour. The solvent was removed *in vacuo* and the crude polymer dissolved in a minimal amount of ethyl acetate. The polymer was precipitated into methanol, centrifuged, and rinsed with methanol. After 2-3 precipitation cycles, the colorless polymer was dried under vacuum (10 mTorr) to afford a white polymeric solid.

Polymer 6.5a. 6.4b (3.0 g, 8.84 mmol, 1 eq.) was polymerized using catalyst **6.3a** (4.0 mg, 0.0047 mmol, [M]/[C] = 1875) using the general procedure detailed above with *trans*-3-hexene (24.7 mg, 0.29 mmol, [M]/[CTA] = 30:1) as a chain transfer agent. After 12 hours, the reaction was quenched accordingly and the ruthenium was attempted to be removed via exchange with a water-soluble phosphine (See reference 18). However, the polymer could only be filtered through a plug of silica using methanol, resulting in the loss of significant amounts of material and little reduction in coloration. Yield: 1.70 g (57%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.04 (s, 0.5 H), 5.50 (m, 2H), 3.6-2.6 (m, 5H), 2.6-0.5 (m, 10H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.0 - -79.8 (m, 6F). DSC: T_g = ~115 °C. SEC (GPC): M_n = 147.8 kDa. PDI = 2.1.

Polymer 6.5b. 6.4b (1.88g, 4.21 mmol, 1 eq.) was polymerized using catalyst **6.3b** (29.7 mg, 0.042 mmol, 0.01 eq.) using the general procedure detailed above without the use of a chain transfer agent. After 12 hours, the reaction was quenched accordingly and the solution concentrated, taken up in a minimal quantity of ethyl acetate and precipitated into methanol. The polymer was dried under high vacuum overnight to afford 1.59 g (85 %) of polymer **6.5b.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.6-5.4 (br s, 2H), 3.2-0.8 (15 H), 1.53 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.55 (s, 3F), -72.76 (s, 3F). SEC (GPC): M_n = 36.3 kDa. PDI = 1.18. DSC: T_g = 83 °C.

General Hydrogenation Procedure for Ring-Opening Metathesis Polymers: In a flame-dried, 100 mL 2-neck round bottom flask equipped with a Teflon stirbar and reflux condenser, *p*-tosylhydrazide (5 eq. per olefin eq.) was added. ROMP polymer dissolved in 25 mL xylenes was added, followed by tri-*n*-propylamine (7 eq. per olefin eq.). The mixture was degassed via 3 freeze-pump-thaw cycles. The reaction was heated to 130 °C under argon at which point gas evolution began. After 4 hours, a second portion of *p*-tosylhydrazide was added and the reaction was allowed to stir for 6 hours. Upon completion, the reaction was cooled to room temperature, taken up in ethyl acetate, washed with 0.1 N HCl solution, $NaHCO_3$ solution, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated. Repeated precipitation into methanol, centrifugation, and washing with methanol produced colorless polymer which was dried overnight to produce a white polymeric solid.

Polymer 6.6a. Polymer **6.5a** was hydrogenated using the general procedure detailed above by Brian Osborn (Wilson Group, University of Texas, Austin). DSC: T_g = 85 °C. SEC (GPC): M_n = 147.8 kDa. PDI = 2.01. $\alpha_{10}^{157nm} = 3.23\ \mu m^{-1}$. $\alpha_{10}^{193nm} = 1.28\ \mu m^{-1}$. $\alpha_{10}^{248nm} = 0.19\ \mu m^{-1}$.

Polymer 6.6b. Polymer **6.5b** (1.1g, 2.46 mmol, 1 eq.) was hydrogenated using the general procedure detailed above without the use of a chain transfer agent. After the standard workup, the polymer was evacuated to dryness, taken up in acetone and precipitated into hexanes. Upon stripping of the solvent, the polymer emerges as a white colorless polymer. The resultant polymer was submitted to dialysis conditions using a 500 molecular weight cut-off dialysis tube (Spectra/Por DispoDialyzer) in methanol for 24 hours, changing the solvent bath every 6 hours. The resulting methanol solution was evacuated to dryness and the polymer washed with hexanes. The polymer was transferred to a vial containing hexanes using acetone and then evacuated to dryness. The colorless tacky polymer was dried under high vacuum overnight to afford 0.59 g (53 %) of polymer **6.6b.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.1-2.8 (m), 2.4-0.6 (m). ^{19}F NMR

($CDCl_3$, 282 MHz, ppm): δ -76.2 - -78.6 (m, 6F). DSC: T_g = 83 °C. SEC (GPC): M_n = 46.1 kDa. PDI = 1.22. α_{10}^{157nm} = 2.98 μm^{-1}. α_{10}^{193nm} = 0.04 μm^{-1}. α_{10}^{248nm} = 0.02 μm^{-1}.

1/6-Methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid methyl ester (6.9). To a flame-dried, nitrogen cooled, 500 mL round bottom flask with dropping funnel and reflux condenser were added: 4-*t*-butyl catechol (0.20g, 1.3 mmol, 0.003 eq.) and methyl acrylate (35 mL, 387 mmol, 1 eq.). The addition funnel was charged with freshly cracked methyl cyclopentadiene (33 mL). The reaction was heated to 50 °C and the methyl cyclopentadiene added dropwise over 15 minutes. The reaction temperature was raised to 80 °C and heated for 2.5 hours. The reaction mixture was distilled under reduced pressure (water aspirator) with the main fraction being collected at 130 °C. 7.4 g of the distilled product was purified by column chromatography (95:5 hexane/ethyl acetate) to afford 7.12 g of **6.9** as a colorless liquid. R_f = 0.38 (95:5 hexane/ethyl acetate). 7 isomers observed by gc/ms. GC/MS: *m/z* = 166. Composition (in order of increased retention time). 0.6%:11.4%:21.8%:6.2%:29.2%:19.2%:11.7% Spectra agree with those of Mellor *et al*. *JCS Perkin Trans. II* **1974**, 26-31.

1,1,1,8,8,8-Hexafluoro-2,7-bis-trifluoromethyl-oct-4-ene-2,7-diol (6.15). Hexafluorocarbinol **6.14** (3.0 g, 14.4 mmol, 1 eq.) was added to a flame-dried 50 mL 2-neck, round bottom flask with a reflux condenser containing catalyst **6.2** (122 mg, 0.144 mmol, 0.01 eq.) in 30 mL of dry, degassed CH_2Cl_2. The reaction was heated at 40 °C with a slow nitrogen sparge for 24 hours. The reaction was concentrated and purified via silica gel column chromatography (90:10 hexane:ethyl acetate to 1:1 hexane:ethyl acetate) to afford 2.36 g (85%) of **6.15** as a water white liquid. R_f = 0.10 (90:10 hexane/ethyl acetate). E/Z = 17:1. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.75 (t, 2H), 4.29 (br s, 2H), 2.76 (d, *J* = 5.1 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 128.15, 123.10 (q, *J* = 288 Hz), 75.52 (m), 33.63. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.97 (s, *E*), -77.15 (s, *Z*). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{10}H_8F_{12}O_2$, 388.0332; found, 388.0341.

***E*-1,1,1-Trifluoro-2-trifluoromethyl-pent-3-en-2-ol (6.16).** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.3-6.4(m, 1H), 5.60 (d, *J* = 15.9 Hz, 1H), 1.86 (dd, *J* = 1.5, 7.2 Hz, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -78.10 (s).

1,1,1,3,3,3-Hexafluoro-2-[3-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]hept-5-en-2-ylmethyl]-propan-2-ol (6.17). To a 20 mL thick-walled Schlenk tube were added freshly cracked cyclopentadiene (0.31 g, 4.69 mmol, 1.4 eq.). **6.15** (1.3 g, 3.35 mmol, 1 eq.), α,α,α-trifluorotoluene (2 mL), and hydroquinone (10 mg). The reaction mixture was degassed by 3 freeze-pump-thaw cycles and the vessel sealed under argon. The reaction was heated at 130 °C for 72 hours and cooled to room temperature. The reaction mixture was separated via silica gel column chromatography (80:20 hexane:ethyl acetate) to afford **6.17** (~ 4%) (R_f = 0.63, 70:30 hexane:ethyl acetate) with the recovery of 1.19 g (36%) of **6.15**. The product **6.17** coeluted with ~ 0.25 eq. of **6.15** and 0.60 eq. of the tetracyclododecene biscarbinol. **6.17.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.27 (dd, *J* = 2.7, 5.7 Hz, 1H), 6.08 (dd, *J* = 3.0, 5.7 Hz, 1H), 2.87 (s, 1H), 2.75 (s, 1H), 2.66 (s, 1H), 2.5-1.0 (7H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.82 (q, 3F), -76.31 (s, 3F), -78.28 (q, 3F), -78.44 (s, 3F). GC/MS: *m/z* = 453 [M-H], 435 [$M–H_2O$], 66 [cyclopentadiene].

6,6,6-Trifluoro-5-hydroxy-5-trifluoromethyl-hex-2-enoic acid methyl ester (6.18a). Hexafluorocarbinol **6.14** (2.0g, 9.6 mmol, 1 eq.) and methyl acrylate (1.73 mL, 19.2 mmol, 2 eq.) were added to a flame-dried 50 mL 2-neck, round bottom flask with a reflux condenser containing catalyst **6.2** (163mg, 0.192 mmol, 0.02 eq.) in 15 mL of dry, degassed CH_2Cl_2. The reaction was heated at 40 °C with a slow nitrogen sparge for 20 hours. The reaction was concentrated and purified via silica gel column chromatography (20:1 hexane:ethyl acetate to 85:15 hexane:ethyl acetate). Two fractions were collected: Fraction A (R_f = 0.29): 0.57 g (22%) of ***Z*-6.18a**. Fraction B (R_f = 0.19): 1.75 g of a 1:0.12 mix of ***E*-6.18a**:**6.15**.

***E*-6.18a.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.02 (dd, *J* = 7.8, 15.3 Hz, 1H), 6.01 (dd, *J* = 1.2, 15.9 Hz, 1H), 4.29 (br s, 1H), 3.76 (s, 3H), 2.86 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.73, 139.05, 125.96, 52.29, 33.34. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.01 (s).

***Z*-6.18a.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.38 (s, 2H), 6.35 (m, 1H), 6.22 (d, *J* = 11.4 Hz, 1H), 3.82 (s, 3H), 3.11 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 169.36, 139.39, 125.69, 53.01, 29.41. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.27 (s). HRMS-[EI+] (m/z): [M•]+ calc'd for $C_8H_8F_6O_3$, 266.0378; found, 266.0376.

6,6,6-Trifluoro-5-hydroxy-5-trifluoromethyl-hex-2-enoic acid *t*-butyl ester (6.18b).

Hexafluorocarbinol **6.14** (2.0g, 9.6 mmol, 1 eq.) and *t*-butyl acrylate (1.70 mL, 11.5 mmol, 1.2 eq.) were added to a flame-dried 50 mL 2-neck, round bottom flask with a reflux condenser containing catalyst **6.2** (81.6 mg, 0.096 mmol, 0.01 eq.) in 10 mL of dry, degassed CH_2Cl_2. The reaction was heated at 40 °C with a slow nitrogen sparge for 30 hours. The reaction was concentrated and purified via silica gel column chromatography (20:1 pentane:ether ramping to 85:15 pentane ether). Crude NMR indicated E/Z = 3.1:1 and 80% conversion. When the reaction was performed with 2 eq. of *t*-butyl acrylate the E/Z ratio was 2.5:1 at 75% conversion. Two fractions were collected: Fraction A (R_f = 0.42): 0.47 g (11%) of ***Z*-6.18b:6.15** (1:0.07). Fraction B (R_f = 0.2, 0.15): 1.75 g (64%) of ***E*-6.18b**.

***E*-6.18b.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.94 (dt, *J* = 7.5, 15.0 Hz, 1H), 5.94 (dt, *J* = 1.5, 14.1 Hz, 1H), 3.93 (s, 1H), 2.82 (d, *J* = 7.2 Hz, 2H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.03, 137.97, 127.83, 81.83, 33.00, 28.21. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.73 (s). HRMS-[FAB+] (m/z): [M•]+ calc'd for $C_{11}H_{15}F_6O_3$, 309.0925; found, 309.0925.

***Z*-6.18b.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.94 (s, 1H), 6.21 (m, 1H), 6.14 (d, *J* = 11.4 Hz, 1H), 3.05 (d, *J* = 7.8 Hz, 2H), 1.51 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.24 (s).

General Procedure for E/Z Selectivity Studies: In a nitrogen filled drybox, catalyst **6.2** (5.2 mg, 0.0061 mmol, 0.02 eq.) was added to a screw-cap NMR tube along with 1 mL dry CD_2Cl_2. On

the benchtop, the unsaturated carbinol was added (0.31 mmol, 1 eq.) via syringe followed by methyl acrylate (55 μL, 0.61 mmol, 2 eq.). The NMR tube was heated on an oil bath at 40 °C for 16 hours. The product distribution was determined by NMR analysis of the olefin and allylic proton resonances.

5-(*t*-Butyldimethylsilanyloxy)-pent-2-enoic acid methyl ester (6.19). After 16 hours of reaction, silica gel chromatography afforded 80% isolated yield of **6.19** (E/Z > 20:1). Also isolated 10% yield 5-(t-butyldimethylsilanyloxy)-pent-4-enoic acid methyl ester (**6.28**) (E/Z = 1.00:1.03).

***E*-6.19.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.97 (dt, *J* = 7.2, 15.6 Hz, 1H), 5.88 (dt, *J* = 1.5, 15.6 Hz, 1H), 3.73 (s, 3H), 3.72 (t, *J* = 6.6 Hz, 2 H), 2.42(ddt, *J* = 1.5, 6.3 Hz, 7.2 Hz, 2H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 167.13, 146.43, 122.71, 61.74, 51.62, 35.94, 26.09, 18.50, -5.13. HRMS-[GC-EI+] (m/z): [M-H]+ calc'd for $C_{12}H_{23}O_3Si$, 243.1417; found, 243.1407.

6.28. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.29 (dm, *J* = 12.0 Hz, 1H, *E*), 6.20(dt, *J* = 5.7 Hz, 1H, *Z*), 4.97 (dt, *J* = 7.5,12.0 Hz, 1H, *E*), 4.46(dt, *J* = 6.0, 6.0 Hz, 1H, *Z*), 3.67 (s, 3H, *E*), 3.66 (s, 3H, *Z*), 2.45-2.35 (m, 2H, *E*), 2.3-2.2 (m, 2H, *Z*), 0.93 (s, 9H, *E*), 0.91 (s, 9H, *Z*), 0.12 (s, 12H, *E/Z*). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 174.16, 173.77, 141.61, 139.84, 109.51, 108.31, 51.67, 35.35, 34.35, 25.89, 25.83, 23.29, 19.62, 18.54, 18.48, -5.47, -5.59. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{12}H_{24}O_3Si$, 244.1495; found, 244.1482.

2-Methyl-pent-4-en-2-ol (6.20). To a flame-dried 3 neck flask with stirbar was added 35 mL of 1M allyl magnesium bromide solution (in diethyl ether) (35 mmol, 1.2 eq.). The solution was cooled to 0 °C and dry acetone (2.13 mL, 1.68g) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature and stir for 7 hours. The reaction was then cooled to 0 °C and quenched with saturated ammonium chloride solution. The aqueous layer was extracted 3 times with ether. The organic layers were combined and washed with sodium

bicarbonate solution and brine. After drying over sodium sulfate, the solution was concentrated and purified directly by silica gel chromatography (3:2 pentane:ether) to afford 0.97g (26%) of **6.20** as a colorless liquid. R_f = 0.43 (70:30 ethyl acetate /hexane). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 5.88 (ddt, J = 7.2, 9.9, 17.1 Hz, 1H), 5.2-5.1 (m, 2H), 2.27 (d, *J* = 7.5 Hz, 2 H), 1.52 (s, 1H), 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 134.42, 118.86, 70.52, 48.38, 29.27. HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_6H_{12}O$, 100.0888; found, 100.0896.

5-Hydroxy-5-methyl-hex-2-enoic acid methyl ester (6.21). The product distribution after 16 hrs: 1.00 **6.21** (> 20:1 E/Z), 1.14 methyl acrylate, 0.72 **6.20**, 0.17 homodimer of **6.20**. *E*-isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 7.01 (dt, *J* = 7.8, 15.6 Hz, 1H), 5.88 (dt, *J* = 1.5, 15.6 Hz, 1H), 3.71 (s, 3H), 2.37(dd, *J* = 1.5, 7.8 Hz, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 167.10, 145.74, 124.29, 70.94, 51.83, 46.89, 30.12, 29.76. HRMS-[GC-CI] (m/z): [M+H]+ calc'd for $C_8H_{15}O_3$, 159.1021; found, 159.1021.

3-Isopropyl-2-methyl-hex-5-en-3-ol (6.22). Compound **6.22** was prepared via the procedure of Masuyama *et al.*[50] The product was purified by silica gel chromatography (3:2 pentane:ether) to afford 4.77 g of a mixture of 1:0.33 **6.22**:diisopropyl ketone corresponding to 56 % yield. No further purification attempts were made. R_f = 0.21 (20:1 Hexane /ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.88 (m, 1H), 5.2-5.0 (m, 2H), 2.32 (dm, *J* = 7.5 Hz, 2H), 1.93 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 135.32, 117.88, 76.98, 38.51, 34.40, 17.76, 17.52. HRMS-[GC-EI+] (m/z): [M-H]+ calc'd for $C_{10}H_{19}O$, 155.1436; found, 155.1435.

5-Hydroxy-5-isopropyl-6-methyl-hept-2-enoic acid methyl ester (6.23). The product distribution after 16 hrs: 1.33 **6.23** (17:1 E/Z), 1.75 methyl acrylate, 0.72 **6.22**, 0.32 homodimer of **6.22**. *E*-isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 7.03 (dt, *J* = 7.8, 15.6 Hz, 1H), 5.85 (dm, *J* = 15.6 Hz, 1H), 3.70 (s, 3H), 2.44(dd, *J* = 1.8, 7.8 Hz, 2H), 1.39 (s, 1H), 0.95 (t, *J* = Hz, 12H).

Z-isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 2.90-2.85 (dd, 1H). Homodimer: ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 2.26 (m, 4H), 1.32 (s, 2H).

1,1,1-Trifluoro-2-(*t*-butyldimethylsilanyloxy-2-trifluoromethyl-pent-4-ene (6.24). To a flame-dried 50 mL 2-neck flask was added sodium hydride (0.38 g, 15.8 mmol, 1.1 eq.). 30 mL of dry degassed tetrahydrofuran was added via cannula. To the stirring suspension was added hexafluorocarbinol **6.14** (3.0 g, 14.4 mmol, 1.0 eq.) slowly via syringe. The solution was heated at 40 °C for 1 hour. The solution was cooled to 0 °C prior to a solution of t-butyldimethylsilyl chloride (2.39g, 15.8 mmol, 1.1 eq.) in 5 mL of tetrahydrofuran was added. The reaction was subsequently heated at 40 °C overnight. The solution was concentrated and purified directly by silica gel chromatography (50:1 pentane:ether) to afford 4.16 g (90%) of **6.24** as a colorless liquid. R_f = 0.91 (20:1 hexane ether). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.95-5.75 (m, 1H), 5.25-5.15 (m, 2H), 2.70 (d, *J* = 7.2 Hz, 2H), 0.91 (s, 9H), 0.19 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 129.32, 123.18 (q, J = 289 Hz), 120.36, 37.23, 25.61, 18.87, -3.28. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.55 (s).

5-(*t*-Butyldimethylsilanyloxy)-6,6,6-trifluoro-5-trifluoromethyl-hex-2-enoic acid methyl ester (6.25). Product distribution after 16 hours: 1.33 **6.25** (> 12:1 E/Z), 0.85 methyl acrylate, 1.00 **6.24**, < 0.15 homodimer of **6.24**. *E*-isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.97 (m, 1H), 5.96 (dt, *J* = 1.5, 15.6 Hz, 1H), 3.78 (s, 3H), 2.82(d, *J* = 7.5 Hz, 2H), 0.92 (s, 9H), 0.20 (s, 6H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.07 (s).

1,1,1-Trifluoro-2-*t*-butoxycarbonyloxy-2-trifluoromethyl-pent-4-ene (6.26). To a flame-dried 25 mL 2-neck flask was added sodium hydride (57 mg, 2.11 mmol, 1.1 eq.). 15 mL of dry degassed tetrahydrofuran was added via cannula. To the stirring suspension was added hexafluorocarbinol **6.14** (0.40 g, 1.92 mmol, 1.0 eq.) slowly via syringe. After the evolution of gas had ceased (~ 5 minutes) the solution turned clear. A solution of di-t-butyl dicarbonate (0.46 g, 2.11 mmol, 1.1 eq.) in 2 mL of tetrahydrofuran was transferred to the reaction flask. The

reaction immediately turned cloudy and was allowed to stir overnight. The reaction was then diluted with water and extracted into 200 mL of ether. The organic layer was washed with water until the washings were neutral. The organic layer was then washed with brine and dried over sodium sulfate. The solution was concentrated and purified directly by silica gel chromatography (20:1 pentane:ether) to afford 0.41g (70%) of **6.26** as a colorless liquid. R_f = 0.66 (20:1 hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.9-5.7 (m, 1H), 5.35-5.35 (m, 2H), 3.22 (d, *J* = 7.2 Hz, 2 H), 1.51 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 127.87, 122.05 (q, J = 267.4 Hz), 122.03, 84.93, 31.60, 27.68. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.54 (s). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_{11}H_{14}F_6O_3$, 308.0847; found, 308.0845.

5-*t*-Butoxycarbonyloxy-6,6,6-trifluoro-5-trifluoromethyl-hex-2-enoic acid methyl ester (6.27). Product distribution after 16 hours: 0.35 **6.27** (> 20:1 E/Z), 1.25 methyl acrylate, 1.00 **6.26**. *E*-isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 6.9-6.75 (m, 1H), 6.04 (dm, *J* =15.3 Hz, 1H), 3.73 (s, 3H), 2.44(d, *J* = 7.8 Hz, 2H), 1.50 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.86 (s).

***Z*-5-(*t*-Butyldimethylsilanyloxy)-pent-2-enoic acid methyl ester (*Z*-6.19).** ***Z*-6.19** in 44% yield from 5,6-dihydro-2H-pyran-2-one according to the procedure of Herold *et al*.[51] ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.36 (dt, *J* = 7.2, 11.7 Hz, 1H), 5.85 (dt, *J* =1.5, 11.7 Hz, 1H), 3.71 (s, 3H), 2.88 (ddt, *J* = 1.5, 6.0, 6.0 Hz, 2H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.97, 147.60, 120.59, 62.24, 51.23, 32.79, 26.10, 18.50, -5.53.

Isomerization of *Z*-6.19. After 16 hours of isomerization in the presence of 1 equivalent of methyl acrylate, NMR analysis indicated an E/Z ratio of 12:1.

Isomerization of *Z*-6.18a. After 16 hours of isomerization in the presence of 1 equivalent of methyl acrylate, NMR analysis indicated an E/Z ratio of 1.6:1.

General Procedure for Olefin Isomerization Studies: In a nitrogen filled drybox, catalyst **6.2** (3.4 mg, 0.004 mmol, 0.02 eq.) was added to a screw-cap vial with a teflon stirbar along with 1

mL dry CD_2Cl_2. On the benchtop, the additive (1 eq.) was added via syringe followed by substrate ***E*-6.19** (50 μL, 0.20 mmol, 1 eq.). The vial was heated on an oil bath at 40 °C for 16 hours. The product distribution was determined by NMR analysis of the olefin and allylic proton resonances.

Methyl 3-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ester (6.29a). To a 10 mL thick-walled Schlenk tube were added ***E*-6.18a** (1.5 g, 5.6 mmol, 1.0 eq.), and MEHQ (10 mg) followed by freshly cracked cyclopentadiene (450 mg, 6.8 mmol, 1.2 eq.). The reaction mixture was degassed via 3 freeze-pump thaw cycles and the vessel sealed under argon. The reaction was stirred at room temperature for 2 days after which no reaction had taken place. The mixture was degassed again and heated at 80 °C for 48 hours, after which time the reaction was purified by silica gel column chromatography (10:1 hexane:ethyl acetate) to afford 1.12 g (72%) of **6.29a** as a 1.02:1.00 mixture of isomers (R_f = 0.38, 85:15 hexane:ethyl acetate) with ~5% tetracyclododecene compounds.

6.29a (1.02:1.00 mixture of isomers)**:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.28 (m, 1H), 6.20 (s, 1H), 6.13 (m, 1H), 5.80 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.24 (s, 1H), 3.19 (s, 1H), 2.91 (s, 1H), 2.77 (t, *J* = 3.9 Hz, 1H), 2.66 (m, 1H), 2.56 (m, 1H), 2.35 (m, 1H), 2.30 (m, 1H), 2.15 (m, 1H), 2.11 (m, 1H), 2.07 (m, 1H), 1.98 (m, 1H), 1.7-1.6 (m, 2H), 1.6-1.45 (m, 3H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.23(q, 3F, major), -76.58 (q, 3F, minor), -78.70 (q, 3F, major), -78.91 (q, 3F, minor). GC-MS: 91.8% **6.29a**, *m/z* = 332, and 5.2% tetracyclodecenes, *m/z* = 398.

***t*-Butyl 3-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ester (6.29b).** To a 10 mL thick-walled Schlenk tube was added ***E*-6.18b** (1.5 g, 4.87 mmol, 1 eq.), MEHQ (10 mg), and 5 mL benzene followed by freshly cracked cyclopentadiene (386 mg, 5.84 mmol, 1.2 eq.). The reaction mixture was degassed via 3 freeze-pump thaw cycles and the vessel sealed under argon. The reaction was heated at 80 °C for 16 hours, after which time 26 % conversion had been reached. The addition of 1.2 equivalents of

additional cyclopentadiene and heating at 115 °C for 12 hours afforded 53% conversion, at which time the reaction was purified by silica gel column chromatography (10:1 hexane:ethyl acetate) to afford 0.86 g (47%) of **6.29b** as a 1.04:1.00 mixture of isomers (R_f = 0.56, 85:15 hexane:ethyl acetate) and recovery of 0.47 g (31 %) of **6.18b** (R_f = 0.35, 85:15 hexane:ethyl acetate).

6.29b (1.04:1.00 mixture of isomers)**:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.73 (s, 1H), 6.47 (s, 1H), 6.27 (m, 2H), 6.14 (m, 2H), 3.18 (s, 1H), 3.14 (s, 1H), 2.87 (s, 1H), 2.72 (t, *J* = 9.9 Hz, 1 H), 2.47 (dm. *J* = 6.0 Hz, 1 H), 2.34 (s, 1H), 2.29 (s, 1H), 2.18 (s, 1H), 2.13 (s, 1H), 2.07(dm, *J* = 14.7 Hz, 1H), 1.99 (dd, *J* = 4.5 Hz, 1H), 1.93(dm, *J* = 8.7 Hz, 1H), 1.75-1.5 (m, 6H), 1.49 (s, 9H). 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 177.11, 176.80, 138.01, 137.58, 135.37, 134.88, 123.91 (q, *J* = 288 Hz), 123.31 (q, *J* = 288 Hz), 83.26, 83.12, 54.67, 52.74, 50.13, 48.14, 46.17, 46.03, 45.36, 39.29, 38.18, 36.87, 35.27, 28.13, 18.07. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.81(q, *J* = 9.9 Hz, 3F, minor), -76.53 (q, *J* = 10.5 Hz, 3F, major), -78.94 (q, *J* = 9.9 Hz, 3F), -79.05 (q, *J* = 9.9 Hz, 3F). HRMS-[FAB+] (m/z): [M+H]+ calc'd for $C_{16}H_{21}F_6O_3$, 375.1395; found, 375.1391.

3-(3,3,3-Trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (6.30). *t*-Butyl ester **6.29b** (108 mg, 0.288 mmol, 1 eq.) and *p*-toluenesulfonic acid monohydrate (8.5 mg, 0.045 mmol, 0.15 eq.) were added to a 10 mL 2 neck flask with 2 mL of benzene. The reaction was heated at 80 °C for 10 hours. Silica gel column chromatography (10:1 CH_2Cl_2: MeOH) afforded 85 mg (89%) of **6.30**. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.8-6.3 (br s, 2 H, OH), 6.25 (m, 2H), 6.12 (m, 2H), 3.17 (m, 1H), 3.08 (m, 1H), 2.87 (m, 1H), 2.17 (t, *J* = 3.3 Hz, 1H), 2.65 (m, 1H), 2.54 (m, 1H), 2.45 (s, 1H), 2.29 (d, *J* = 14.1 Hz, 1H), 2.12 (d, *J* = 15.6 Hz, 1H), 2.09 (d, *J* = 15.9 Hz, 1H), 1.96 (m, 2H), 1.67 (d, *J* = 10.5 Hz, 1H), 1.62 (d, *J* = 10.5 Hz, 1H), 1.49 (d, *J* = 10.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 184.18, 183.28, 138.14, 137.63, 135.15, 14.86, 123.73 (q, *J* = 288 Hz), 123.27 (q, *J* = 287 Hz), 54.09, 52.47, 50.05, 47.92, 47.82, 46.66, 46.37, 45.53, 38.91, 37.83, 36.57, 34.87., 135.37, 134.88, 123.91 123.31 (q, *J* = 288

Hz), 83.26, 83.12, 54.67, 52.74, 50.13, 48.14, 46.17, 46.03, 45.36, 39.29, 38.18, 36.87, 35.27, 28.13, 18.07. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -76.61 (m, 3F), -76.77 (q, 3F), -78.65 (m, 3F), -78.88 (q, 3F). HRMS-[DIP-EI+] (m/z): [M•]+ calc'd for $C_{12}H_{12}F_6O_3$, 318.0691; found, 318.0695.

3-(3,3,3-Trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]heptane-2-carboxylic acid methyl ester (6.33a). To a 100 mL round bottom flask was added **6.29a** (0.50 g, 1.50 mmol, 1 eq.) and Pd/C (10 wt % Pd, ~60 mg), and 15 mL ethyl acetate. The reaction mixture was degassed via 3 freeze-pump thaw cycles and the placed under a balloon of hydrogen. The reaction was stirred for 16 hours, at which time the catalyst was filtered off with a 0.45 μm^{-1} PTFE syringe filter. Removal of the solvent *in vacuo* afforded **6.33a** (95 %) as a colorless liquid (contains ~6 % tetracyclododecane compounds).

6.33a (1.07:1.00 mixture of isomers)**:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.17 (s, 1H), 5.42 (s, 1H), 3.76 (s, 6H), 2.69 (m, 1H), 2.64 (m, 1H), 2.53 (s, 1H), 2.5-1.8 (11H), 1.8-1.3 (15H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 178.55, 177.42, 66.06, 57.06, 55.23, 53.00, 52.68, 44.74, 42.64, 40.53, 40.29, 38.70, 38.56, 37.47, 37.31, 33.52, 30.11, 29.09, 24.26, 22.06, 15.46. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.73(q, 3F, minor), -76.61 (q, 3F, major), -78.34 (q, 3F, minor), -78.43 (q, 3F, major). GC/MS: 91.6% **6.33a**, *m/z* = 334 (Ratio: 1.07:1), 6.0% Tetracyclododecanes, *m/z* = 400 (ratio 1.29:1).

3-(3,3,3-Trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]heptane-2-carboxylic acid *t*-butyl ester (6.33b). To a 100 mL round bottom flask was added **6.29b** (0.83 g, 2.22 mmol, 1 eq.) and Pd/C (10 wt % Pd, ~150 mg), and 15 mL dry benzene. The reaction mixture was degassed via 3 freeze-pump thaw cycles and placed under a balloon of hydrogen. The reaction was stirred for 6 hours, at which time the catalyst was filtered off with a 0.45 μm^{-1} PTFE syringe filter. Removal of the solvent *in vacuo* afforded **6.33b** (95 %) as a colorless liquid.

6.33b (1.05:1.00 mixture of isomers)**:** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.77 (s, 1H), 5.96 (s, 1H), 2.7-2.55 (m, 2H), 2.46 (m, 1H), 2.4-2.15 (m, 4H), 2.15-2.05 (m, 2H), 2.05-1.85 (m, 3H), 1.75-1.20 (12H), 1.48 (s, 9H). 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 177.63, 176.63, 123.79 (q, *J* = 288 Hz), 123.54 (q, *J* = 288 Hz), 83.06, 82.68, 58.14, 55.19, 45.07, 42.72, 40.61, 40.49, 38.69, 38.50, 38.36, 37.46, 37.40, 33.76, 30.29, 28.80, 28.20, 28.05, 23.98, 22.12. . ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -75.41(q, 3F, minor), -76.67 (q, 3F, major), -78.39 (q, 3F, major), -78.52 (q, 3F, minor). HRMS-[FAB+] (m/z): [M+H]+ calc'd for $C_{16}H_{23}F_6O_3$, 377.1551; found, 377.1566.

Acrylic acid 1,1-bis-trifluoromethyl-but-3-enyl ester (6.34). To a flame-dried 25 mL 2-neck flask was added sodium hydride (253 mg, 10.6 mmol, 1.1 eq.). 15 mL of dry degassed tetrahydrofuran was added via cannula. The solution was cooled to 0 °C. To the stirring suspension was added hexafluorocarbinol **6.14** (2.0 g, 9.60 mmol, 1.0 eq.) slowly via syringe. After bubbling ceased, the reaction was warmed for 20 minutes at 40 °C. The reaction was cooled to 0 °C and *N,N*-dimethylaminopyridine (0.12 g, 0.96 mmol, 0.1 eq.) was added. Acryloyl chloride was slowly injected via syringe. The reaction was allowed to stir for 6 hours. The solution was concentrated and purified directly by silica gel chromatography (20:1 pentane:ether) to afford 1.36 g (54%) of **6.34** as a colorless liquid. R_f = 0.49 (20:1 hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.50 (dd, *J* = 1.2, 17.1 Hz, 1H), 6.14 (dd, *J* = 10.5, 17.1 Hz, 1H), 5.99 (dd, *J* = 1.2, 10.5 Hz, 1H), 5.75-5.65 (m, 1H), 5.35-5.2 (m, 2H), 3.28(d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.05, 133.89, 127.80, 127.29, 122.01, 31.83. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.68 (s). HRMS-[GC-EI+] (m/z): [M•]+ calc'd for $C_9H_8F_6O_2$, 262.0464; found, 262.0429.

6,6-Bis-trifluoromethyl-5,6-dihydro-pyran-2-one (6.35). To a flame-dried 300 mL airless flask with reflux condenser was added catalyst **6.2** (39 mg, 0.046 mmol, 0.01 eq.). 100 mL of dry degassed dichloromethane was added via cannula followed by **6.34** (0.95 g, 3.62 mmol, 1 eq.).

The reaction was heated on an oil bath at 40 °C for 24 hours under nitrogen. The solution was concentrated and purified directly by silica gel chromatography (3:1 pentane:ether) to afford 0.40 g (47 %) of **6.35** as a colorless liquid. The product coeluted with ~5 % of 6,6-bis-trifluoromethyl-3,6-dihydro-pyran-2-one **(6.36)**. R_f = 0.23 (80:20 hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.84 (dd, *J* = 1.2, 10.2 Hz, 1H), 6.15 (dd, *J* = 2.1, 10.5 Hz, 1H), 2.95 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 156.93, 140.56, 121.87 (q, J = 287 Hz), 119.53, 22.57. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -78.06 (s). HRMS-[CI+] (m/z): [M•]+ calc'd for $C_7H_4F_6O_2$, 234.0115; found, 234.0107.

6,6-Bis-trifluoromethyl-3,6-dihydro-pyran-2-one (6.36) ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.5-6.4 (dt, 1H), 6.07-6.0 (dt, 1H), 3.35-3.30 (dd, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.34 (s).

5,5-Bis-trifluoromethyl-4-oxa-tricyclo[6.2.1.02,7]undec-9-en-3-one (6.37). Freshly cracked cyclopentadiene (0.67 mL, 8.4 mmol, 2 eq.) and **6.35** (0.97g, 4.2 mmol, 1 eq.) were added to a 10 mL thick walled Schlenk tube. The system was degassed via 3 freeze-pump-thaw cycles and sealed under argon. The tube was heated to 120 °C for 68 hours. The reaction products were purified by silica gel column chromatography (15:1 pentane:ether) to afford 0.40 g (32%) of ***endo*-6.37** and 0.13 g (9%) of ***exo*-6.37**. endo/exo = 3.6:1. Total yield: 41 %.

***endo*-6.37.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.36 (dd, *J* = 3.0, 5.7 Hz, 1H), 6.19 (dd, *J* = 3.0, 5.7 Hz, 1H), 3.42 (m, 1H), 3.11 (ddd, *J* = 1.2, 3.9, 10.2 Hz, 1H), 3.03 (s, 1H), 2.79 (m, 1H), 1.66 (dt, *J* = 1.8, 9.0 Hz, 1H), 1.66 (dt, *J* = 1.8, 10.5 Hz, 1H), 1.44 (dt, *J* = 1.5, 7.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 169.29, 138.42, 135.25, 122.23 (q, *J* = 288 Hz), 121.47 (q, *J* = 288 Hz), 81.72 (m), 48.28, 46.45, 45.99, 42.92, 34.53, 26.54. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.81 (q, 3F), -77.96 (q, 3F). HRMS-[CI+] (m/z): [M•]+ calc'd for $C_{12}H_{10}F_6O_2$, 300.0585; found, 300.0581.

***exo*-6.37.** ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.3-6.2 (m, 2H), 3.47 (m, 1H), 2.77 (s, 1H), 2.67 (dd, *J* = 7.2, 15.0 Hz, 1H), 2.43 (d, *J* = 9 Hz, 1H), 2.3-2.0 (m, 1H), 1.72-1.67 (m, 1H), 1.51 (d, *J* = 9.6 Hz, 1H), 1.34 (d, *J* = 9.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 169.40, 136.90, 136.44, 122.29 (q, *J* = 288 Hz), 121.52 (q, *J* = 284 Hz), 81.03 (m), 47.24, 46.38, 44.14, 42.72, 33.32, 27.89. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -72.67 (m, 3F), -77.97 (m, 3F).

Base-catalyzed hydrolysis of *endo*-6.37. ***Endo*-6.37** (0.20 g, 0.68 mmol, 1 eq.), potassium hydroxide (228 mg, 4.1 mmol, 6 eq.) and 5 mL methanol were added to a 2-necked flask with reflux condenser. The mixture was refluxed for 72 hours. The mixture was concentrated to dryness and taken up in water/ether. The mixture was acidified with 1M HCl solution. The product was extracted 3 times into ether. The organic layer was washed with brine until the washings were neutral. The solvent was removed *in vacuo* and the slightly yellowish solid washed with hexanes to produce 0.133 g (62%) of 3-*endo*-(3,3,3-Trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-bicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid (***endo*,*exo*-6.30**) as a snow white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.33 (dd, J = 3.0, 5.7 Hz, 1H), 6.18 (dd, *J* = 3.0, 5.7 Hz, 1H), 4.8 (br s, 0.5H), 3.20 (s, 1H), 2.97 (s, 1H), 2.66 (m, 1H), 2.10 (dd, *J* = 3.6 Hz, 1H), 2.07 (d, *J* = 6.3 Hz, 1H), 1.72 (ddd, *J* = 1.5, 6.6, 15.3 Hz, 1H), 1.58 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 183.07, 137.54, 135.19, 51.70, 47.91, 46.75, 39.11, 34.73. ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -73.28 (q, *J* = 10.0 Hz), -78.43 (q, *J* = 9.9 Hz). HRMS-[CI+] (m/z): [M•]+ calc'd for $C_{12}H_{12}F_6O_3$, 318.0691; found, 318.1689.

2,2-Bis-trifluoromethyl-3,6-dihydro-2H-pyran (6.38). To a 100 mL oven-dried Fischer-Porter bottle was added 25 mg 4-*t*-butyl catechol. The pressure bottle was sealed and 1,3-butadiene was condensed in at -78 °C. The bottle was cooled with liquid nitrogen while the hexafluoroacetone tank was attached. 2 pump backfill cycles were used to remove any air that had entered the system. Hexafluoroacetone was condensed into the bottle at -78 °C, forming two distinct layers. The bottle was sealed and the temperature slowly warmed to room temperature. Gradually, the

system formed one phase and the pressure rose to 80 psi. The vessel was heated at 55 °C overnight. The excess gases were vented in the hood through a saturated potassium hydroxide solution. The product was purified by Kugelrohr distillation at room temperature. R_f = 0.53 (20:1 hexane:ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.0-5.9 (m, 2H), 4.38 (m 2H), 2.51 (m, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.49 (s). HRMS-[CI+] (m/z): [M•]+ calc'd for $C_7H_6F_6O$, 220.0323; found, 220.0313.

Allylic Oxidation of 6.38. Compound **6.38** was oxidized with pyridinium chlorochromate according to the procedure of Bonini *et al.*[45] Aliquots were extracted for analysis by NMR. After 6 hours at 70 °C, NMR analysis revealed the reaction to contain: 68% **6.38**, 24% **6.35**, and 9% 24% 2,2-Bis-trifluoromethyl-2,3-dihydro-pyran-4-one **(6.39**). Adding more oxidant and increasing the temperature gradually increased the conversion to ~35% **6.35** (with about 3% of the isomeric **6.36**); however, heating above 100 °C resulted in the production of many degradation products. Structural assignments were confirmed by comparing spectra with independently synthesized **6.35** (see above) and column chromatography of the reaction mixture to afford samples for NMR analysis. The addition of 1 equivalent of pyridine per equivalent PCC seemed to accelerate the formation of by-products.

Similarly, oxidation with pyridinium dichromate/*t*-butyl hydroperoxide according to the procedure of Chandrasekaran *et al.*[47] was unable to increase the yields of the desired product.

2,2-Bis-trifluoromethyl-2,3-dihydro-pyran-4-one (6.39). Silica gel column chromatography (4:1 pentane: ether) on the reaction mixture from the PCC oxidation of **6.38** afforded a mixture of two side products: **6.39** and an overoxidized product in a 2:1 ratio, respectively. R_f = 0.36 (85:15 hexane/ethyl acetate).

(6.39). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.31 (d, J = 6.3 Hz, 1H), 5.62 (d, J = 6.6 Hz, 1H), 3.07 (s, 2H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -77.41 (s). GC/MS: m/z = 234.

Overoxidized product: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.49 (d, J = 5.4 Hz, 1H), 6.65 (d, J = 6.0 Hz, 1H). ^{19}F NMR ($CDCl_3$, 282 MHz, ppm): δ -74.53 (s). GC/MS: m/z = 248.

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