APPENDIX 4

X-ray Crystallography Reports

Relevant to Chapter 3

A4.1 CRYSTAL STRUCTURE ANALYSIS FOR COMPOUND 100f

Ketoester **100f** (>99% ee) was recrystallized from *i*-PrOH/hexanes (liquid/liquid diffusion) to provide suitable crystals for X-ray analysis, mp = 98-99 °C. *NOTE: Crystallographic data have been deposited in the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 939243.*

Figure A4.1.1. *ORTEP drawing of* ***100f****.*

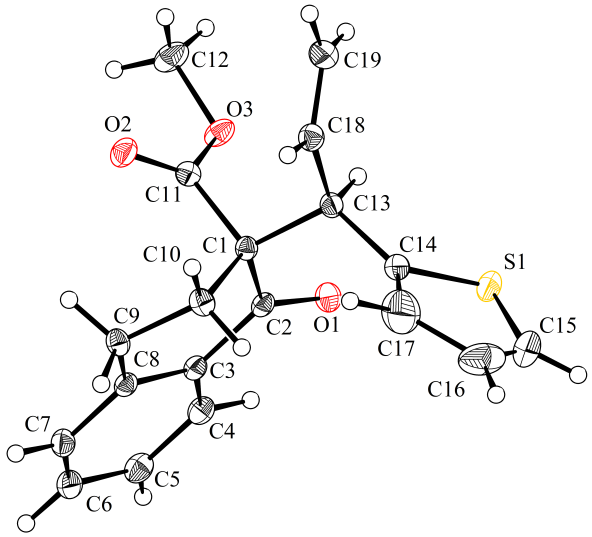

Table A4.1*. Crystal Data and Structure Analysis Details for allylation ketoester* ***100f****.*

Empirical formula	C19 H18 O3 S
Formula weight	326.39
Crystallization solvent	*i*-PrOH/hexanes
Crystal shape	block
Crystal color	colourless
Crystal size	0.13 x 0.23 x 0.29 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Wavelength	0.71073 Å MoK	
Data collection temperature	100 K	
Theta range for 9849 reflections used		
in lattice determination	2.30 to 30.92°	
Unit cell dimensions	a = 8.4853(3) Å	a= 90°

	b = 10.8613(4) Å	b= 90°
	c = 17.6979(6) Å	g = 90°
Volume	1631.06(10) $Å^3$	
Z	4	
Crystal system	orthorhombic	
Space group	P 21 21 21 (# 19)	
Density (calculated)	1.329 g/cm^3	
F(000)	688	
Theta range for data collection	2.2 to 36.7°	
Completeness to theta = 25.000°	99.9%	
Index ranges	-14 £ h £ 14, -18 £ k £ 18, -29 £ l £ 29	
Data collection scan type	and scans	
Reflections collected	49310	
Independent reflections	7841 [R_{int}= 0.0476]	
Reflections > 2s(I)	6228	
Average s(I)/(net I)	0.0436	
Absorption coefficient	0.21 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9025	

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	?
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7841 / 0 / 303
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.55
Final R indices [I>2s(I), 6228 reflections]	R1 = 0.0483, wR2 = 0.0806
R indices (all data)	R1 = 0.0694, wR2 = 0.0846
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.01(3)
Extinction coefficient	n/a

Largest diff. peak and hole 0.37 and -0.24 e·Å^{-3}

_refine_ls_abs_structure_details;
Flack x determined using 2400 quotients [(I+)-(I-)]/[(I+)+(I-)];
(Parsons and Flack (2004), Acta Cryst. A60, s61).
_refine_ls_abs_structure_Flack 0.01(3)
_refine_ls_abs_structure_Hooft 0.02(3)

Programs Used

Cell refinement	SAINT V8.27B (Bruker-AXS, 2007)
Data collection	Bruker SMART v5.054 (Bruker-AXS, 2007)
Data reduction	SAINT V8.27B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table A4.2. *Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for* ***100f***. *U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
S(1)	9499(4)	3027(2)	9424(2)	26(1)
S(1A)	7396(4)	1194(2)	8920(1)	26(1)
O(1)	10909(1)	3864(1)	7769(1)	20(1)
O(2)	6712(1)	3819(1)	6298(1)	22(1)
O(3)	8198(1)	5196(1)	6915(1)	20(1)
C(1)	8415(2)	3108(1)	7316(1)	14(1)
C(2)	10216(2)	3266(1)	7292(1)	14(1)
C(3)	11064(2)	2667(1)	6651(1)	14(1)
C(4)	12665(2)	2961(1)	6537(1)	18(1)
C(5)	13491(2)	2453(2)	5941(1)	21(1)
C(6)	12737(2)	1641(2)	5451(1)	21(1)

C(7)	11165(2)	1346(1)	5556(1)	18(1)
C(8)	10300(2)	1842(1)	6161(1)	14(1)
C(9)	8605(2)	1477(1)	6273(1)	16(1)
C(10)	7999(2)	1793(1)	7062(1)	17(1)
C(11)	7676(2)	4054(1)	6775(1)	15(1)
C(12)	7433(2)	6145(2)	6468(1)	27(1)
C(13)	7740(2)	3432(1)	8120(1)	16(1)
C(14)	8255(2)	2565(1)	8741(1)	19(1)
C(15)	9443(3)	1759(2)	9876(1)	44(1)
C(16)	8455(3)	892(2)	9630(1)	42(1)
C(17)	7757(14)	1354(11)	8921(7)	51(4)
C(17A)	9366(19)	2793(11)	9301(7)	45(3)
C(18)	5962(2)	3506(2)	8090(1)	18(1)
C(19)	5128(2)	4517(2)	8192(1)	25(1)

Table A4.3. *Bond lengths [Å] and angles [°] for* ***100f***.

S(1)-C(14)	1.681(3)
S(1)-C(15)	1.594(4)
S(1A)-C(14)	1.688(3)
S(1A)-C(16)	1.579(3)
O(1)-C(2)	1.2177(17)
O(2)-C(11)	1.2030(18)
O(3)-C(11)	1.3403(17)
O(3)-C(12)	1.452(2)
C(1)-C(2)	1.538(2)
C(1)-C(10)	1.539(2)
C(1)-C(11)	1.539(2)
C(1)-C(13)	1.5733(19)
C(2)-C(3)	1.492(2)
C(3)-C(4)	1.409(2)
C(3)-C(8)	1.406(2)
C(4)-H(4)	0.967(17)
C(4)-C(5)	1.380(2)
C(5)-H(5)	0.950(19)

C(5)-C(6)	1.394(2)
C(6)-H(6)	0.958(18)
C(6)-C(7)	1.385(2)
C(7)-H(7)	0.963(16)
C(7)-C(8)	1.405(2)
C(8)-C(9)	1.505(2)
C(9)-H(9A)	0.942(17)
C(9)-H(9B)	1.013(17)
C(9)-C(10)	1.527(2)
C(10)-H(10A)	0.977(17)
C(10)-H(10B)	0.966(18)
C(12)-H(12A)	0.96(2)
C(12)-H(12B)	1.03(2)
C(12)-H(12C)	1.02(2)
C(13)-H(13)	0.996(18)
C(13)-C(14)	1.511(2)
C(13)-C(18)	1.511(2)
C(14)-C(17)	1.418(11)
C(14)-C(17A)	1.391(12)
C(15)-H(15)	0.90(3)
C(15)-C(16)	1.334(3)
C(15)-C(17A)	1.517(15)
C(16)-H(16)	0.98(3)
C(16)-C(17)	1.476(12)
C(17)-H(17)	1.04(4)
C(17A)-H(17A)	0.97(5)
C(18)-H(18)	0.950(18)
C(18)-C(19)	1.319(2)
C(19)-H(19A)	0.97(2)
C(19)-H(19B)	1.01(2)

C(15)-S(1)-C(14)	94.87(18)
C(16)-S(1A)-C(14)	95.02(18)
C(11)-O(3)-C(12)	114.07(12)
C(2)-C(1)-C(10)	108.86(12)
C(2)-C(1)-C(11)	108.20(11)
C(2)-C(1)-C(13)	111.27(11)

C(10)-C(1)-C(13)	112.89(12)
C(11)-C(1)-C(10)	110.12(12)
C(11)-C(1)-C(13)	105.36(11)
O(1)-C(2)-C(1)	121.30(13)
O(1)-C(2)-C(3)	121.79(13)
C(3)-C(2)-C(1)	116.91(12)
C(4)-C(3)-C(2)	118.41(13)
C(8)-C(3)-C(2)	121.60(13)
C(8)-C(3)-C(4)	119.98(13)
C(3)-C(4)-H(4)	118.7(10)
C(5)-C(4)-C(3)	120.59(14)
C(5)-C(4)-H(4)	120.7(10)
C(4)-C(5)-H(5)	120.4(11)
C(4)-C(5)-C(6)	119.70(15)
C(6)-C(5)-H(5)	119.9(11)
C(5)-C(6)-H(6)	119.0(11)
C(7)-C(6)-C(5)	120.27(15)
C(7)-C(6)-H(6)	120.7(11)
C(6)-C(7)-H(7)	121.4(10)
C(6)-C(7)-C(8)	121.19(15)
C(8)-C(7)-H(7)	117.4(10)
C(3)-C(8)-C(9)	121.84(13)
C(7)-C(8)-C(3)	118.25(13)
C(7)-C(8)-C(9)	119.90(13)
C(8)-C(9)-H(9A)	108.3(10)
C(8)-C(9)-H(9B)	109.8(10)
C(8)-C(9)-C(10)	112.49(12)
H(9A)-C(9)-H(9B)	104.7(14)
C(10)-C(9)-H(9A)	108.8(10)
C(10)-C(9)-H(9B)	112.4(9)
C(1)-C(10)-H(10A)	107.6(10)
C(1)-C(10)-H(10B)	109.6(10)
C(9)-C(10)-C(1)	113.53(12)
C(9)-C(10)-H(10A)	109.2(10)
C(9)-C(10)-H(10B)	109.8(10)
H(10A)-C(10)-H(10B)	106.8(14)
O(2)-C(11)-O(3)	123.43(13)

O(2)-C(11)-C(1)	124.93(13)
O(3)-C(11)-C(1)	111.60(12)
O(3)-C(12)-H(12A)	113.2(14)
O(3)-C(12)-H(12B)	106.2(11)
O(3)-C(12)-H(12C)	110.2(11)
H(12A)-C(12)-H(12B)	109.9(18)
H(12A)-C(12)-H(12C)	106.8(18)
H(12B)-C(12)-H(12C)	110.5(16)
C(1)-C(13)-H(13)	106.6(10)
C(14)-C(13)-C(1)	114.33(12)
C(14)-C(13)-H(13)	107.1(10)
C(18)-C(13)-C(1)	110.12(12)
C(18)-C(13)-H(13)	108.2(10)
C(18)-C(13)-C(14)	110.28(13)
C(13)-C(14)-S(1)	121.21(15)
C(13)-C(14)-S(1A)	124.16(14)
C(17)-C(14)-S(1)	107.6(5)
C(17)-C(14)-C(13)	131.0(5)
C(17A)-C(14)-S(1A)	108.4(6)
C(17A)-C(14)-C(13)	127.1(6)
S(1)-C(15)-H(15)	120.9(19)
C(16)-C(15)-S(1)	117.68(19)
C(16)-C(15)-H(15)	121.4(19)
C(16)-C(15)-C(17A)	106.1(5)
C(17A)-C(15)-H(15)	132(2)
S(1A)-C(16)-H(16)	113.9(17)
C(15)-C(16)-S(1A)	118.07(19)
C(15)-C(16)-H(16)	128.0(17)
C(15)-C(16)-C(17)	106.8(5)
C(17)-C(16)-H(16)	125.0(17)
C(14)-C(17)-C(16)	112.8(8)
C(14)-C(17)-H(17)	116(2)
C(16)-C(17)-H(17)	131(2)
C(14)-C(17A)-C(15)	112.1(9)
C(14)-C(17A)-H(17A)	124(3)
C(15)-C(17A)-H(17A)	124(3)
C(13)-C(18)-H(18)	118.4(11)

C(19)-C(18)-C(13)	125.07(16)
C(19)-C(18)-H(18)	116.5(11)
C(18)-C(19)-H(19A)	121.1(14)
C(18)-C(19)-H(19B)	119.8(11)
H(19A)-C(19)-H(19B)	119.1(17)

Symmetry transformations used to generate equivalent atoms:

Table A4.4. *Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **100f**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	360(9)	243(10)	173(5)	5(6)	-83(5)	58(8)
S(1A)	335(10)	229(6)	231(7)	93(6)	-46(6)	-2(6)
O(1)	198(5)	189(5)	197(5)	-39(4)	-40(4)	-28(4)
O(2)	242(6)	202(5)	213(5)	-7(4)	-87(5)	5(4)
O(3)	220(6)	136(5)	253(6)	36(4)	-82(5)	-16(4)
C(1)	145(6)	132(6)	130(6)	-2(5)	-6(5)	-11(5)
C(2)	168(7)	127(6)	140(6)	26(5)	-27(5)	-4(5)
C(3)	151(6)	139(6)	138(6)	19(5)	-17(5)	-6(5)
C(4)	166(7)	188(7)	188(7)	24(5)	-23(6)	-20(6)
C(5)	160(7)	267(8)	204(7)	46(6)	-2(6)	-6(6)
C(6)	232(8)	258(8)	146(7)	24(6)	23(6)	39(6)
C(7)	223(8)	188(7)	143(6)	4(5)	-6(6)	3(6)
C(8)	168(7)	131(6)	136(6)	23(5)	-18(5)	4(5)
C(9)	185(7)	142(6)	153(6)	-24(5)	-2(5)	-32(5)
C(10)	191(7)	139(7)	170(7)	-10(5)	10(5)	-36(5)
C(11)	149(7)	150(6)	157(6)	4(5)	14(5)	-6(5)
C(12)	330(10)	151(7)	333(9)	58(7)	-107(8)	5(7)
C(13)	197(7)	140(6)	136(6)	-6(5)	-7(5)	4(5)
C(14)	215(7)	198(7)	152(7)	4(5)	7(6)	34(6)
C(15)	537(14)	571(14)	214(9)	-26(9)	-113(9)	224(12)
C(16)	451(13)	329(11)	469(12)	186(9)	150(10)	127(10)
C(17)	480(60)	540(60)	500(50)	-210(40)	-180(40)	20(40)

C(17A)	510(50)	330(50)	510(70)	90(40)	70(50)	-90(40)
C(18)	185(7)	194(7)	163(7)	6(6)	6(6)	-3(6)
C(19)	262(9)	251(9)	244(8)	-56(7)	-34(7)	49(7)

Table A4.5. *Hydrogen coordinates (x 10^3) and isotropic displacement parameters (Å^{2}x 10^3) for* ***100f***.

	x	y	z	U_{iso}
H(4)	1318(2)	350(2)	689(1)	11(4)
H(5)	1457(2)	265(2)	587(1)	23(5)
H(6)	1331(2)	131(2)	503(1)	18(4)
H(7)	1063(2)	79(1)	522(1)	12(4)
H(9A)	852(2)	62(2)	620(1)	14(4)
H(9B)	793(2)	185(2)	586(1)	14(4)
H(10A)	846(2)	122(2)	743(1)	14(4)
H(10B)	687(2)	168(2)	708(1)	17(4)
H(12A)	766(3)	608(2)	594(1)	44(6)
H(12B)	784(2)	697(2)	667(1)	32(5)
H(12C)	624(3)	608(2)	652(1)	32(5)
H(13)	815(2)	426(2)	825(1)	17(4)
H(15)	1003(3)	165(3)	1030(2)	72(8)
H(16)	827(3)	7(3)	985(2)	80(9)
H(17)	689(4)	98(3)	857(2)	10(8)
H(17A)	1003(5)	352(4)	932(2)	9(11)
H(18)	539(2)	277(2)	799(1)	20(4)
H(19A)	564(3)	531(2)	828(1)	40(6)
H(19B)	394(2)	448(2)	818(1)	27(5)

Table A4.6. *Hydrogen bonds for* ***100f*** *[Å and °].*

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12)-H(12B)...O(1)#1	1.03(2)	2.52(2)	3.539(2)	173.4(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z+3/2