APPENDIX THREE

X-ray Crystallography Reports Relevant to Chapter Two: Studies Directed Toward the Total Synthesis of Saudin and the Development of a Tandem Stille-Oxa-Electrocyclization Reaction

A3.1 Crystal Structure Analysis of 66a

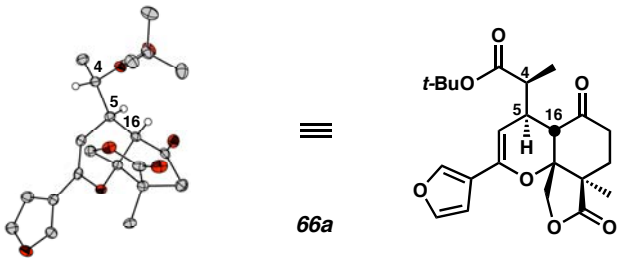


Figure A3.1.1 Ketone **66a** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 175515.

Table A3.1.1 Crystal data and structure refinement for **66a** (CCDC 175515).

Empirical formula	$C_{23}H_{28}O_7$
Formula weight	416.45
Crystallization Solvent	Ether
Crystal Habit	Irregular fragment
Crystal size	Not measured
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 12296 reflections used in lattice determination	2.22 to 28.17°
Unit cell dimensions	a = 8.2333(6) Å b = 25.9013(19) Å β= 95.7760(10)° c = 9.8295(7) Å
Volume	2085.5(3) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.326 Mg/m^3
F(000)	888
Data collection program	Bruker SMART v5.054
θ range for data collection	1.57 to 28.23°
Completeness to θ = 28.23°	95.1 %
Index ranges	$-10 \le h \le 10$, $-32 \le k \le 34$, $-12 \le l \le 12$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.22
Reflections collected	30345
Independent reflections	4886 [R_{int}= 0.0543]
Absorption coefficient	0.098 mm^{-1}
Absorption correction	None

Table A3.1.1 **(cont.)**

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4886 / 0 / 383
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.845
Final R indices [$I>2\sigma(I)$, 3765 reflections]	R1 = 0.0418, *w*R2 = 0.0643
R indices (all data)	R1 = 0.0574, *w*R2 = 0.0657
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.404 and -0.295 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table A3.1.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **66a** (CCDC 175515). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	8639(1)	3834(1)	4601(1)	29(1)
O(2)	8194(1)	4245(1)	2608(1)	22(1)
O(3)	11695(1)	2720(1)	142(1)	21(1)
O(4)	7428(1)	3279(1)	66(1)	16(1)
O(5)	3617(1)	3010(1)	-2777(1)	24(1)
O(6)	13803(1)	4143(1)	617(1)	26(1)
O(7)	11834(1)	4617(1)	1480(1)	19(1)
C(1)	8369(2)	3813(1)	3377(1)	20(1)
C(2)	8169(2)	3333(1)	2491(1)	17(1)
C(3)	6399(2)	3144(1)	2504(1)	20(1)
C(4)	9385(2)	2914(1)	3023(1)	21(1)
C(5)	9899(2)	2586(1)	1863(1)	20(1)
C(6)	10710(2)	2902(1)	842(1)	16(1)
C(7)	10239(2)	3476(1)	740(1)	15(1)
C(8)	8477(1)	3547(1)	1078(1)	15(1)
C(9)	7933(2)	4112(1)	1170(1)	18(1)
C(10)	7624(2)	3422(1)	-1270(1)	15(1)
C(11)	6141(2)	3297(1)	-2143(1)	16(1)
C(12)	5839(2)	3328(1)	-3601(1)	22(1)
C(13)	4324(2)	3153(1)	-3926(1)	25(1)
C(14)	4762(2)	3105(1)	-1705(1)	19(1)
C(15)	9002(2)	3622(1)	-1634(1)	16(1)
C(16)	10525(2)	3693(1)	-674(1)	15(1)
C(17)	11219(2)	4255(1)	-723(1)	17(1)
C(18)	12034(2)	4328(1)	-2041(1)	22(1)
C(19)	12456(2)	4333(1)	509(1)	18(1)
C(20)	12799(2)	4717(1)	2823(1)	22(1)
C(21)	14328(2)	5015(1)	2589(2)	33(1)
C(22)	11655(2)	5045(1)	3566(2)	27(1)
C(23)	13149(2)	4212(1)	3576(2)	30(1)

Table A3.1.3 Bond lengths [Å] and angles [°] for **66a** (CCDC 175515).

O(1)-C(1)	1.2027(14)
O(2)-C(1)	1.3503(15)
O(2)-C(9)	1.4497(14)
O(3)-C(6)	1.2103(14)
O(4)-C(10)	1.3887(13)
O(4)-C(8)	1.4295(14)
O(5)-C(14)	1.3640(14)
O(5)-C(13)	1.3722(15)
O(6)-C(19)	1.2084(14)
O(7)-C(19)	1.3457(14)
O(7)-C(20)	1.4939(14)
C(1)-C(2)	1.5174(17)
C(2)-C(4)	1.5313(18)
C(2)-C(3)	1.5387(17)
C(2)-C(8)	1.5399(16)
C(3)-H(3A)	0.985(12)
C(3)-H(3B)	0.995(13)
C(3)-H(3C)	1.001(13)
C(4)-C(5)	1.5171(18)
C(4)-H(4A)	0.996(13)
C(4)-H(4B)	0.981(12)
C(5)-C(6)	1.5033(17)
C(5)-H(5A)	0.959(13)
C(5)-H(5B)	0.979(13)
C(6)-C(7)	1.5372(17)
C(7)-C(8)	1.5312(16)
C(7)-C(16)	1.5394(16)
C(7)-H(7)	0.954(12)
C(8)-C(9)	1.5374(17)
C(9)-H(9A)	0.992(12)
C(9)-H(9B)	0.978(12)
C(10)-C(15)	1.3289(16)
C(10)-C(11)	1.4572(16)
C(11)-C(14)	1.3491(17)
C(11)-C(12)	1.4314(17)
C(12)-C(13)	1.3354(18)
C(12)-H(12)	0.956(13)
C(13)-H(13)	0.971(13)
C(14)-H(14)	0.958(12)
C(15)-C(16)	1.5030(17)
C(15)-H(15)	0.926(11)
C(16)-C(17)	1.5649(16)
C(16)-H(16)	1.004(11)
C(17)-C(19)	1.5158(17)
C(17)-C(18)	1.5292(17)
C(17)-H(17)	1.001(12)
C(18)-H(18A)	0.999(13)
C(18)-H(18B)	0.956(13)
C(18)-H(18C)	1.004(13)
C(20)-C(22)	1.5102(19)
C(20)-C(21)	1.5142(19)

C(20)-C(23)	1.5169(19)
C(21)-H(21A)	1.015(15)
C(21)-H(21B)	0.987(15)
C(21)-H(21C)	0.973(16)
C(22)-H(22A)	0.996(15)
C(22)-H(22B)	0.953(14)
C(22)-H(22C)	0.990(15)
C(23)-H(23A)	0.988(14)
C(23)-H(23B)	1.033(15)
C(23)-H(23C)	0.977(15)

C(1)-O(2)-C(9)	110.26(9)
C(10)-O(4)-C(8)	114.18(9)
C(14)-O(5)-C(13)	105.68(10)
C(19)-O(7)-C(20)	121.01(9)
O(1)-C(1)-O(2)	121.41(11)
O(1)-C(1)-C(2)	127.58(12)
O(2)-C(1)-C(2)	111.01(10)
C(1)-C(2)-C(4)	110.80(11)
C(1)-C(2)-C(3)	107.69(10)
C(4)-C(2)-C(3)	111.03(11)
C(1)-C(2)-C(8)	101.83(10)
C(4)-C(2)-C(8)	113.66(10)
C(3)-C(2)-C(8)	111.35(10)
C(2)-C(3)-H(3A)	110.4(7)
C(2)-C(3)-H(3B)	111.8(7)
H(3A)-C(3)-H(3B)	109.0(10)
C(2)-C(3)-H(3C)	111.1(7)
H(3A)-C(3)-H(3C)	106.1(10)
H(3B)-C(3)-H(3C)	108.2(10)
C(5)-C(4)-C(2)	111.27(11)
C(5)-C(4)-H(4A)	108.8(7)
C(2)-C(4)-H(4A)	109.3(7)
C(5)-C(4)-H(4B)	109.8(7)
C(2)-C(4)-H(4B)	108.9(7)
H(4A)-C(4)-H(4B)	108.7(10)
C(6)-C(5)-C(4)	111.88(11)
C(6)-C(5)-H(5A)	109.2(8)
C(4)-C(5)-H(5A)	110.9(8)
C(6)-C(5)-H(5B)	106.3(7)
C(4)-C(5)-H(5B)	109.4(7)
H(5A)-C(5)-H(5B)	109.1(11)
O(3)-C(6)-C(5)	122.32(12)
O(3)-C(6)-C(7)	121.28(11)
C(5)-C(6)-C(7)	116.39(10)
C(8)-C(7)-C(6)	109.85(10)
C(8)-C(7)-C(16)	112.76(10)
C(6)-C(7)-C(16)	110.59(10)
C(8)-C(7)-H(7)	108.3(7)
C(6)-C(7)-H(7)	103.6(7)
C(16)-C(7)-H(7)	111.3(7)
O(4)-C(8)-C(7)	108.07(9)
O(4)-C(8)-C(9)	110.07(10)
C(7)-C(8)-C(9)	114.49(10)

O(4)-C(8)-C(2)	108.12(9)
C(7)-C(8)-C(2)	113.49(10)
C(9)-C(8)-C(2)	102.37(9)
O(2)-C(9)-C(8)	105.54(10)
O(2)-C(9)-H(9A)	105.0(7)
C(8)-C(9)-H(9A)	115.9(7)
O(2)-C(9)-H(9B)	108.0(6)
C(8)-C(9)-H(9B)	110.3(7)
H(9A)-C(9)-H(9B)	111.4(9)
C(15)-C(10)-O(4)	122.84(11)
C(15)-C(10)-C(11)	128.00(11)
O(4)-C(10)-C(11)	109.11(10)
C(14)-C(11)-C(12)	105.87(11)
C(14)-C(11)-C(10)	125.18(11)
C(12)-C(11)-C(10)	128.91(11)
C(13)-C(12)-C(11)	106.55(12)
C(13)-C(12)-H(12)	128.2(8)
C(11)-C(12)-H(12)	125.3(8)
C(12)-C(13)-O(5)	110.94(12)
C(12)-C(13)-H(13)	134.9(8)
O(5)-C(13)-H(13)	114.1(8)
C(11)-C(14)-O(5)	110.96(11)
C(11)-C(14)-H(14)	134.4(8)
O(5)-C(14)-H(14)	114.6(7)
C(10)-C(15)-C(16)	124.02(11)
C(10)-C(15)-H(15)	116.5(7)
C(16)-C(15)-H(15)	119.3(7)
C(15)-C(16)-C(7)	109.17(10)
C(15)-C(16)-C(17)	112.24(10)
C(7)-C(16)-C(17)	117.18(10)
C(15)-C(16)-H(16)	108.1(6)
C(7)-C(16)-H(16)	106.5(6)
C(17)-C(16)-H(16)	103.0(6)
C(19)-C(17)-C(18)	110.08(11)
C(19)-C(17)-C(16)	108.54(10)
C(18)-C(17)-C(16)	109.53(10)
C(19)-C(17)-H(17)	107.9(6)
C(18)-C(17)-H(17)	110.9(6)
C(16)-C(17)-H(17)	109.9(7)
C(17)-C(18)-H(18A)	110.3(7)
C(17)-C(18)-H(18B)	111.1(7)
H(18A)-C(18)-H(18B)	108.5(10)
C(17)-C(18)-H(18C)	111.2(7)
H(18A)-C(18)-H(18C)	106.8(10)
H(18B)-C(18)-H(18C)	108.7(10)
O(6)-C(19)-O(7)	124.86(12)
O(6)-C(19)-C(17)	123.54(11)
O(7)-C(19)-C(17)	111.53(10)
O(7)-C(20)-C(22)	102.87(10)
O(7)-C(20)-C(21)	109.31(11)
C(22)-C(20)-C(21)	110.83(12)
O(7)-C(20)-C(23)	109.84(10)
C(22)-C(20)-C(23)	110.28(12)
C(21)-C(20)-C(23)	113.22(13)

C(20)-C(21)-H(21A)	108.3(8)
C(20)-C(21)-H(21B)	108.3(8)
H(21A)-C(21)-H(21B)	105.0(12)
C(20)-C(21)-H(21C)	112.3(9)
H(21A)-C(21)-H(21C)	113.3(12)
H(21B)-C(21)-H(21C)	109.4(12)
C(20)-C(22)-H(22A)	108.9(8)
C(20)-C(22)-H(22B)	110.6(8)
H(22A)-C(22)-H(22B)	107.8(11)
C(20)-C(22)-H(22C)	110.4(8)
H(22A)-C(22)-H(22C)	108.7(11)
H(22B)-C(22)-H(22C)	110.4(11)
C(20)-C(23)-H(23A)	107.6(8)
C(20)-C(23)-H(23B)	109.3(8)
H(23A)-C(23)-H(23B)	109.6(11)
C(20)-C(23)-H(23C)	111.1(9)
H(23A)-C(23)-H(23C)	109.6(11)
H(23B)-C(23)-H(23C)	109.6(12)

Table A3.1.4 Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **66a** (CCDC 175515). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	359(6)	331(6)	178(5)	-64(4)	65(4)	-105(5)
O(2)	270(5)	198(5)	213(5)	-44(4)	69(4)	-27(4)
O(3)	213(5)	210(5)	222(5)	7(4)	44(4)	44(4)
O(4)	162(5)	186(5)	133(4)	-1(4)	13(4)	-35(4)
O(5)	191(5)	320(6)	211(5)	-10(4)	-1(4)	-60(4)
O(6)	162(5)	292(6)	312(5)	-56(4)	5(4)	25(4)
O(7)	165(5)	185(5)	225(5)	-37(4)	2(4)	0(4)
C(1)	167(7)	234(7)	217(7)	-31(6)	71(6)	-49(6)
C(2)	178(7)	182(7)	148(6)	-10(5)	29(5)	-20(5)
C(3)	214(8)	207(8)	191(7)	3(6)	62(6)	-33(6)
C(4)	219(8)	246(8)	165(7)	41(6)	25(6)	-11(6)
C(5)	198(7)	178(7)	235(7)	46(6)	15(6)	35(6)
C(6)	131(7)	183(7)	167(6)	-12(5)	-33(5)	-6(5)
C(7)	136(7)	160(7)	139(6)	-14(5)	-4(5)	-19(5)
C(8)	146(7)	152(7)	151(6)	-13(5)	9(5)	-12(5)
C(9)	169(7)	182(7)	193(7)	-10(6)	40(6)	4(6)
C(10)	196(7)	116(6)	135(6)	3(5)	20(5)	32(5)
C(11)	175(7)	132(6)	165(6)	-12(5)	20(5)	8(5)
C(12)	225(8)	242(8)	188(7)	5(6)	28(6)	-33(6)
C(13)	269(8)	295(8)	175(7)	11(6)	-19(6)	-46(6)
C(14)	179(7)	217(7)	174(7)	-26(6)	3(6)	-9(5)
C(15)	186(7)	153(7)	129(6)	4(5)	28(5)	11(5)
C(16)	149(7)	142(7)	166(6)	-2(5)	36(5)	0(5)
C(17)	148(7)	141(7)	229(7)	12(5)	38(6)	0(5)
C(18)	202(8)	199(8)	254(8)	30(6)	61(6)	-14(6)
C(19)	164(7)	133(7)	258(7)	10(5)	50(6)	-34(5)
C(20)	187(7)	212(7)	234(7)	-53(6)	-43(6)	-7(6)
C(21)	260(9)	359(10)	372(10)	-110(8)	20(7)	-86(8)
C(22)	255(9)	265(9)	282(9)	-66(7)	-2(7)	5(7)
C(23)	361(10)	263(9)	261(8)	-40(7)	-58(7)	58(7)

Table A3.1.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **66a** (CCDC 175515).

	x	y	z	U_{iso}
H(3A)	6160(14)	3071(5)	3447(13)	19(3)
H(3B)	5599(15)	3402(5)	2092(12)	23(4)
H(3C)	6220(15)	2812(5)	1989(13)	26(4)
H(4A)	10372(16)	3080(5)	3503(12)	26(4)
H(4B)	8875(14)	2696(5)	3677(12)	17(3)
H(5A)	10626(16)	2316(5)	2205(13)	26(4)
H(5B)	8931(16)	2431(5)	1363(12)	21(3)
H(7)	10949(15)	3634(5)	1448(12)	18(3)
H(9A)	8579(15)	4368(5)	702(12)	19(3)
H(9B)	6765(15)	4144(4)	879(11)	11(3)
H(12)	6599(16)	3449(5)	-4201(13)	26(4)
H(13)	3621(16)	3110(5)	-4773(13)	29(4)
H(14)	4421(15)	3026(5)	-825(12)	22(4)
H(15)	9019(14)	3702(4)	-2550(12)	12(3)
H(16)	11412(14)	3478(4)	-1018(11)	12(3)
H(17)	10319(14)	4511(4)	-665(11)	14(3)
H(18A)	12311(15)	4700(5)	-2164(12)	26(4)
H(18B)	13014(16)	4130(5)	-2023(12)	25(4)
H(18C)	11283(16)	4225(5)	-2864(13)	27(4)
H(21A)	13993(17)	5336(6)	2039(14)	37(4)
H(21B)	14823(17)	5145(5)	3480(15)	39(4)
H(21C)	15119(19)	4804(6)	2172(15)	47(5)
H(22A)	12173(17)	5117(5)	4507(15)	39(4)
H(22B)	10658(17)	4866(5)	3648(13)	28(4)
H(22C)	11439(17)	5378(6)	3083(13)	37(4)
H(23A)	13729(16)	4295(5)	4480(14)	32(4)
H(23B)	12061(19)	4029(6)	3706(14)	43(4)
H(23C)	13828(18)	3986(6)	3074(15)	44(5)

A3.2 Crystal Structure Analysis of 71c

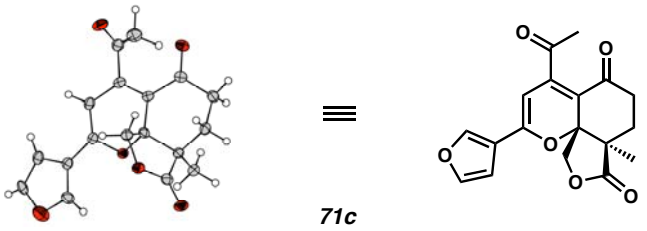


Figure A3.2.1 Polycycle **71c** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 201414.

Table A3.2.1 Crystal data and structure refinement for **71c** (CCDC 201414).

Empirical formula	$C_{18}H_{16}O_6$
Formula weight	328.31
Crystallization Solvent	Hexanes/ethylacetate
Crystal Habit	Fragment
Crystal size	0.28 x 0.22 x 0.15 mm^3
Crystal color	Yellow

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 7975 reflections used in lattice determination	2.26 to 28.15°
Unit cell dimensions	a = 12.3799(11) Å b = 7.2521(7) Å β= 101.892(2)° c = 17.2138(15) Å
Volume	1512.3(2) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.442 Mg/m^3
F(000)	688
Data collection program	Bruker SMART v5.054
θ range for data collection	1.86 to 28.22°
Completeness to θ = 28.22°	94.4 %
Index ranges	$-15 \le h \le 16$, $-9 \le k \le 9$, $-22 \le l \le 21$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	21320
Independent reflections	3525 [R_{int}= 0.0530]
Absorption coefficient	0.109 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9838 and 0.9701

Table A3.2.1 **(cont.)**

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3525 / 0 / 281
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.948
Final R indices [$I>2\sigma(I)$, 2658 reflections]	R1 = 0.0425, *w*R2 = 0.0689
R indices (all data)	R1 = 0.0606, *w*R2 = 0.0710
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.376 and -0.393 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table A3.2.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **71c** (CCDC 201414). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	7557(1)	-202(1)	-1544(1)	32(1)
O(2)	9763(1)	1794(1)	-583(1)	23(1)
O(3)	9007(1)	2746(1)	3057(1)	27(1)
O(4)	8289(1)	483(1)	2230(1)	22(1)
O(5)	7079(1)	2940(1)	971(1)	18(1)
O(6)	3873(1)	3651(2)	1211(1)	39(1)
C(1)	6423(1)	1692(2)	-309(1)	20(1)
C(2)	7531(1)	1661(2)	-435(1)	18(1)
C(3)	8392(1)	1951(2)	179(1)	17(1)
C(4)	9524(1)	2132(2)	62(1)	18(1)
C(5)	10385(1)	2853(2)	743(1)	22(1)
C(6)	10145(1)	2438(2)	1559(1)	21(1)
C(7)	8975(1)	3043(2)	1635(1)	17(1)
C(8)	8765(1)	2161(2)	2391(1)	21(1)
C(9)	8083(1)	134(2)	1380(1)	20(1)
C(10)	8135(1)	2030(2)	997(1)	17(1)
C(11)	6232(1)	2420(2)	372(1)	18(1)
C(12)	5164(1)	2845(2)	541(1)	18(1)
C(13)	4133(1)	2958(2)	1(1)	22(1)
C(14)	3386(1)	3403(2)	410(1)	23(1)
C(15)	4958(1)	3270(2)	1271(1)	25(1)
C(16)	7661(1)	1354(2)	-1282(1)	22(1)
C(17)	7785(2)	2990(2)	-1776(1)	29(1)
C(18)	8853(1)	5134(2)	1645(1)	22(1)

Table A3.2.3 Bond lengths [Å] and angles [°] for **71c** (CCDC 201414).

O(1)-C(16)	1.2118(16)
O(2)-C(4)	1.2302(15)
O(3)-C(8)	1.2008(15)
O(4)-C(8)	1.3562(17)
O(4)-C(9)	1.4550(16)
O(5)-C(11)	1.3639(15)
O(5)-C(10)	1.4564(16)
O(6)-C(15)	1.3551(18)
O(6)-C(14)	1.3979(19)
C(1)-C(11)	1.3495(19)
C(1)-C(2)	1.433(2)
C(1)-H(1)	0.947(14)
C(2)-C(3)	1.3548(18)
C(2)-C(16)	1.5151(19)
C(3)-C(4)	1.4630(19)
C(3)-C(10)	1.5061(18)
C(4)-C(5)	1.507(2)
C(5)-C(6)	1.5238(19)
C(5)-H(5A)	1.013(14)
C(5)-H(5B)	0.982(15)
C(6)-C(7)	1.5453(19)
C(6)-H(6A)	0.963(14)
C(6)-H(6B)	1.007(14)
C(7)-C(8)	1.5191(19)
C(7)-C(10)	1.5352(18)
C(7)-C(18)	1.524(2)
C(9)-C(10)	1.5325(19)
C(9)-H(9A)	0.956(15)
C(9)-H(9B)	1.028(14)
C(11)-C(12)	1.4439(19)
C(12)-C(15)	1.367(2)
C(12)-C(13)	1.4186(19)
C(13)-C(14)	1.313(2)
C(13)-H(13)	0.963(14)
C(14)-H(14)	0.706(15)
C(15)-H(15)	0.951(15)
C(16)-C(17)	1.487(2)
C(17)-H(17A)	0.951(18)
C(17)-H(17B)	1.000(17)
C(17)-H(17C)	0.990(17)
C(18)-H(18A)	1.024(15)
C(18)-H(18B)	0.972(15)
C(18)-H(18C)	0.986(15)
C(8)-O(4)-C(9)	109.86(10)
C(11)-O(5)-C(10)	116.28(10)
C(15)-O(6)-C(14)	105.53(12)
C(11)-C(1)-C(2)	118.85(14)
C(11)-C(1)-H(1)	118.0(8)
C(2)-C(1)-H(1)	122.5(8)

C(3)-C(2)-C(1)	120.16(13)
C(3)-C(2)-C(16)	123.44(13)
C(1)-C(2)-C(16)	116.37(12)
C(2)-C(3)-C(4)	121.86(12)
C(2)-C(3)-C(10)	116.87(12)
C(4)-C(3)-C(10)	121.25(12)
O(2)-C(4)-C(3)	121.49(13)
O(2)-C(4)-C(5)	120.57(13)
C(3)-C(4)-C(5)	117.86(12)
C(4)-C(5)-C(6)	114.14(12)
C(4)-C(5)-H(5A)	105.8(8)
C(6)-C(5)-H(5A)	110.0(8)
C(4)-C(5)-H(5B)	108.1(8)
C(6)-C(5)-H(5B)	109.9(8)
H(5A)-C(5)-H(5B)	108.6(11)
C(5)-C(6)-C(7)	112.68(12)
C(5)-C(6)-H(6A)	109.4(8)
C(7)-C(6)-H(6A)	108.0(8)
C(5)-C(6)-H(6B)	107.4(8)
C(7)-C(6)-H(6B)	110.9(8)
H(6A)-C(6)-H(6B)	108.5(11)
C(8)-C(7)-C(10)	101.65(11)
C(8)-C(7)-C(18)	111.96(12)
C(10)-C(7)-C(18)	115.50(12)
C(8)-C(7)-C(6)	106.35(11)
C(10)-C(7)-C(6)	108.23(11)
C(18)-C(7)-C(6)	112.29(12)
O(3)-C(8)-O(4)	121.56(13)
O(3)-C(8)-C(7)	128.07(13)
O(4)-C(8)-C(7)	110.30(11)
O(4)-C(9)-C(10)	105.25(11)
O(4)-C(9)-H(9A)	107.7(9)
C(10)-C(9)-H(9A)	111.4(9)
O(4)-C(9)-H(9B)	111.4(8)
C(10)-C(9)-H(9B)	110.5(8)
H(9A)-C(9)-H(9B)	110.5(11)
O(5)-C(10)-C(3)	110.50(10)
O(5)-C(10)-C(7)	106.03(10)
C(3)-C(10)-C(7)	116.40(11)
O(5)-C(10)-C(9)	107.60(11)
C(3)-C(10)-C(9)	113.81(11)
C(7)-C(10)-C(9)	101.72(11)
C(1)-C(11)-O(5)	121.35(13)
C(1)-C(11)-C(12)	126.13(13)
O(5)-C(11)-C(12)	112.43(11)
C(15)-C(12)-C(13)	106.02(13)
C(15)-C(12)-C(11)	125.81(13)
C(13)-C(12)-C(11)	128.15(13)
C(14)-C(13)-C(12)	107.52(14)
C(14)-C(13)-H(13)	124.6(9)
C(12)-C(13)-H(13)	127.9(9)
C(13)-C(14)-O(6)	110.62(15)
C(13)-C(14)-H(14)	136.8(13)
O(6)-C(14)-H(14)	112.3(13)

O(6)-C(15)-C(12)	110.27(14)
O(6)-C(15)-H(15)	117.5(9)
C(12)-C(15)-H(15)	132.2(9)
O(1)-C(16)-C(2)	118.03(13)
O(1)-C(16)-C(17)	123.07(14)
C(2)-C(16)-C(17)	118.53(13)
C(16)-C(17)-H(17A)	108.8(10)
C(16)-C(17)-H(17B)	111.6(9)
H(17A)-C(17)-H(17B)	108.0(14)
C(16)-C(17)-H(17C)	112.2(9)
H(17A)-C(17)-H(17C)	107.1(13)
H(17B)-C(17)-H(17C)	108.9(13)
C(7)-C(18)-H(18A)	109.3(8)
C(7)-C(18)-H(18B)	111.6(8)
H(18A)-C(18)-H(18B)	110.3(12)
C(7)-C(18)-H(18C)	108.4(8)
H(18A)-C(18)-H(18C)	109.7(12)
H(18B)-C(18)-H(18C)	107.5(12)

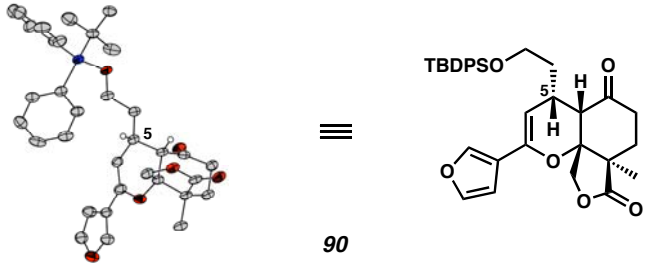
Table A3.2.4 Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **71c** (CCDC 201414). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	418(7)	297(6)	249(6)	-92(5)	72(5)	-20(5)
O(2)	260(6)	276(6)	180(6)	23(4)	93(5)	30(5)
O(3)	301(6)	360(6)	136(6)	-24(5)	30(5)	22(5)
O(4)	269(6)	256(6)	146(5)	28(4)	46(4)	-23(5)
O(5)	162(5)	229(5)	155(5)	-18(4)	26(4)	11(4)
O(6)	329(7)	498(8)	371(7)	25(6)	133(6)	42(6)
C(1)	194(8)	211(8)	173(8)	14(6)	1(7)	-24(6)
C(2)	248(8)	126(7)	164(8)	9(6)	48(6)	5(6)
C(3)	213(8)	148(7)	151(7)	7(6)	39(6)	16(6)
C(4)	236(8)	154(7)	168(8)	44(6)	59(6)	28(6)
C(5)	194(9)	256(9)	220(8)	8(7)	61(7)	-4(7)
C(6)	186(8)	250(9)	167(8)	1(6)	13(7)	-14(7)
C(7)	167(8)	212(8)	135(7)	-3(6)	22(6)	0(6)
C(8)	167(8)	257(8)	195(8)	10(6)	34(6)	40(6)
C(9)	216(9)	234(8)	152(8)	7(6)	42(7)	-15(7)
C(10)	154(7)	188(7)	165(7)	7(6)	45(6)	26(6)
C(11)	197(8)	162(7)	161(7)	31(6)	19(6)	-21(6)
C(12)	206(8)	160(7)	184(8)	13(6)	40(6)	-20(6)
C(13)	241(9)	205(8)	216(9)	33(6)	25(7)	-47(7)
C(14)	113(9)	313(9)	256(9)	79(7)	35(7)	21(7)
C(15)	195(9)	326(9)	236(9)	5(7)	47(7)	30(7)
C(16)	189(8)	270(9)	177(8)	-14(6)	15(6)	19(7)
C(17)	360(11)	336(10)	175(9)	44(7)	42(8)	8(9)
C(18)	228(9)	234(8)	207(9)	-31(7)	36(7)	-18(7)

Table A3.2.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **71c** (CCDC 201414).

	x	y	z	U_{iso}
H(1)	5805(11)	1389(18)	-713(8)	19(4)
H(5A)	10412(11)	4230(20)	661(8)	28(4)
H(5B)	11101(12)	2324(19)	701(8)	25(4)
H(6A)	10670(12)	3082(19)	1959(8)	23(4)
H(6B)	10250(11)	1070(20)	1653(8)	19(4)
H(9A)	7364(13)	-399(19)	1229(8)	28(4)
H(9B)	8668(12)	-733(19)	1235(8)	22(4)
H(13)	3987(12)	2801(19)	-567(9)	28(4)
H(14)	2817(13)	3610(20)	328(9)	27(5)
H(15)	5430(12)	3399(19)	1778(9)	27(4)
H(17A)	7096(15)	3620(20)	-1906(10)	47(5)
H(17B)	8001(13)	2630(20)	-2283(10)	44(5)
H(17C)	8333(13)	3880(20)	-1492(9)	38(5)
H(18A)	8984(11)	5666(19)	1121(9)	26(4)
H(18B)	8131(13)	5499(19)	1731(8)	25(4)
H(18C)	9410(12)	5627(19)	2091(9)	27(4)

A3.3 Crystal Structure Analysis of 90



90

Figure A3.3.1 Ketone **90** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 197200.

Table A3.3.1 Crystal data and structure refinement for **90** (CCDC 197200).

Empirical formula	$C_{34}H_{38}O_6Si$
Formula weight	570.73
Crystallization Solvent	Benzene
Crystal Habit	Fragment
Crystal size	0.30 x 0.26 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 12272 reflections used in lattice determination	2.41 to 27.51°
Unit cell dimensions	a = 10.3188(7) Å b = 10.5705(8) Å β= 92.9410(10)° c = 27.269(2) Å
Volume	2970.5(4) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.276 Mg/m^3
F(000)	1216
Data collection program	Bruker SMART v5.054
θ range for data collection	1.50 to 28.26°
Completeness to θ = 28.26°	93.9 %
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 13$, $-35 \le l \le 35$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	49441
Independent reflections	6912 [R_{int}= 0.0683]
Absorption coefficient	0.124 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9709 and 0.9638

Table A3.3.1 **(cont.)**

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	6912 / 0 / 522
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.686
Final R indices [$I>2\sigma(I)$, 4526 reflections]	R1 = 0.0491, *w*R2 = 0.0689
R indices (all data)	R1 = 0.0835, *w*R2 = 0.0712
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.534 and -0.364 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table A3.3.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **90** (CCDC 197200). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Si(1)	2828(1)	9991(1)	2058(1)	24(1)
O(1)	4132(1)	6866(1)	133(1)	33(1)
O(2)	51(1)	4263(1)	-799(1)	36(1)
O(3)	-763(1)	6000(1)	-466(1)	30(1)
O(4)	1492(1)	8495(1)	-683(1)	31(1)
O(5)	2833(1)	11714(1)	-1323(1)	39(1)
O(6)	2483(1)	8760(1)	1706(1)	26(1)
C(1)	1069(2)	7330(2)	-477(1)	24(1)
C(2)	1800(2)	7014(2)	17(1)	23(1)
C(3)	3127(2)	6442(2)	-55(1)	26(1)
C(4)	3089(2)	5294(2)	-380(1)	29(1)
C(5)	2507(2)	5661(2)	-886(1)	28(1)
C(6)	1184(2)	6286(2)	-870(1)	25(1)
C(7)	146(2)	5373(2)	-720(1)	29(1)
C(8)	-396(2)	7321(2)	-413(1)	30(1)
C(9)	756(2)	6771(2)	-1385(1)	31(1)
C(10)	1766(2)	8152(2)	364(1)	25(1)
C(11)	2258(2)	9287(2)	100(1)	30(1)
C(12)	2051(2)	9419(2)	-384(1)	30(1)
C(13)	2508(2)	10459(2)	-680(1)	27(1)
C(14)	3375(2)	11462(2)	-530(1)	37(1)
C(15)	3529(2)	12177(2)	-922(1)	36(1)
C(16)	2225(2)	10654(2)	-1160(1)	33(1)
C(17)	2423(2)	7959(2)	873(1)	26(1)
C(18)	1803(2)	8820(2)	1236(1)	27(1)
C(19)	1354(2)	10465(2)	2386(1)	25(1)
C(20)	187(2)	9866(2)	2284(1)	36(1)
C(21)	-939(2)	10165(2)	2533(1)	42(1)
C(22)	-853(2)	11039(2)	2901(1)	44(1)
C(23)	306(2)	11618(2)	3031(1)	47(1)
C(24)	1383(2)	11359(2)	2769(1)	41(1)
C(25)	3332(2)	11291(2)	1640(1)	25(1)
C(26)	4203(2)	11045(2)	1272(1)	30(1)
C(27)	4499(2)	11948(2)	929(1)	35(1)
C(28)	3931(2)	13125(2)	942(1)	39(1)
C(29)	3075(2)	13413(2)	1300(1)	35(1)
C(30)	2782(2)	12501(2)	1645(1)	29(1)
C(31)	4151(2)	9415(2)	2501(1)	28(1)
C(32)	3668(2)	8237(2)	2761(1)	32(1)
C(33)	5347(2)	9070(3)	2216(1)	43(1)
C(34)	4556(3)	10399(2)	2891(1)	46(1)

Table A3.3.3 Bond lengths [Å] and angles [°] for **90** (CCDC 197200).

Si(1)-O(6)	1.6437(12)
Si(1)-C(19)	1.8717(18)
Si(1)-C(25)	1.8745(18)
Si(1)-C(31)	1.8779(18)
O(1)-C(3)	1.2182(19)
O(2)-C(7)	1.197(2)
O(3)-C(7)	1.365(2)
O(3)-C(8)	1.452(2)
O(4)-C(12)	1.3799(19)
O(4)-C(1)	1.4312(19)
O(5)-C(15)	1.368(2)
O(5)-C(16)	1.371(2)
O(6)-C(18)	1.432(2)
C(1)-C(8)	1.531(2)
C(1)-C(2)	1.544(2)
C(1)-C(6)	1.547(2)
C(2)-C(3)	1.519(2)
C(2)-C(10)	1.533(2)
C(2)-H(2)	0.977(14)
C(3)-C(4)	1.502(2)
C(4)-C(5)	1.526(2)
C(4)-H(4A)	0.969(16)
C(4)-H(4B)	0.967(16)
C(5)-C(6)	1.519(2)
C(5)-H(5A)	0.937(16)
C(5)-H(5B)	0.971(16)
C(6)-C(7)	1.513(2)
C(6)-C(9)	1.540(2)
C(8)-H(8A)	0.987(16)
C(8)-H(8B)	1.003(17)
C(9)-H(9A)	1.004(17)
C(9)-H(9B)	0.988(18)
C(9)-H(9C)	0.999(18)
C(10)-C(11)	1.501(2)
C(10)-C(17)	1.526(2)
C(10)-H(10)	0.995(15)
C(11)-C(12)	1.333(2)
C(11)-H(11)	0.946(15)
C(12)-C(13)	1.456(2)
C(13)-C(16)	1.341(2)
C(13)-C(14)	1.433(2)
C(14)-C(15)	1.326(3)
C(14)-H(14)	0.949(17)
C(15)-H(15)	0.923(18)
C(16)-H(16)	0.969(17)
C(17)-C(18)	1.511(2)
C(17)-H(17A)	0.962(16)
C(17)-H(17B)	0.931(16)
C(18)-H(18A)	1.025(14)
C(18)-H(18B)	0.965(15)
C(19)-C(20)	1.376(2)

C(19)-C(24)	1.407(2)
C(20)-C(21)	1.412(3)
C(20)-H(20)	0.955(17)
C(21)-C(22)	1.363(3)
C(21)-H(21)	0.900(18)
C(22)-C(23)	1.374(3)
C(22)-H(22)	0.92(2)
C(23)-C(24)	1.380(3)
C(23)-H(23)	1.08(2)
C(24)-H(24)	1.02(2)
C(25)-C(30)	1.399(2)
C(25)-C(26)	1.407(2)
C(26)-C(27)	1.381(3)
C(26)-H(26)	0.992(16)
C(27)-C(28)	1.376(3)
C(27)-H(27)	0.975(17)
C(28)-C(29)	1.385(3)
C(28)-H(28)	0.915(16)
C(29)-C(30)	1.389(3)
C(29)-H(29)	0.923(14)
C(30)-H(30)	0.949(15)
C(31)-C(32)	1.529(3)
C(31)-C(34)	1.530(3)
C(31)-C(33)	1.535(3)
C(32)-H(32A)	0.965(19)
C(32)-H(32B)	0.962(17)
C(32)-H(32C)	0.989(17)
C(33)-H(33A)	0.99(2)
C(33)-H(33B)	0.98(2)
C(33)-H(33C)	1.05(2)
C(34)-H(34A)	0.962(19)
C(34)-H(34B)	0.981(19)
C(34)-H(34C)	1.06(2)

O(6)-Si(1)-C(19)	109.50(7)
O(6)-Si(1)-C(25)	106.52(7)
C(19)-Si(1)-C(25)	110.59(8)
O(6)-Si(1)-C(31)	104.27(7)
C(19)-Si(1)-C(31)	111.17(8)
C(25)-Si(1)-C(31)	114.41(8)
C(7)-O(3)-C(8)	109.54(14)
C(12)-O(4)-C(1)	120.28(13)
C(15)-O(5)-C(16)	105.20(15)
C(18)-O(6)-Si(1)	124.65(11)
O(4)-C(1)-C(8)	111.89(15)
O(4)-C(1)-C(2)	112.50(14)
C(8)-C(1)-C(2)	109.92(14)
O(4)-C(1)-C(6)	107.80(13)
C(8)-C(1)-C(6)	100.70(14)
C(2)-C(1)-C(6)	113.46(14)
C(3)-C(2)-C(10)	116.14(15)
C(3)-C(2)-C(1)	112.18(14)
C(10)-C(2)-C(1)	110.10(14)
C(3)-C(2)-H(2)	106.4(8)

C(10)-C(2)-H(2)	108.5(8)
C(1)-C(2)-H(2)	102.5(9)
O(1)-C(3)-C(4)	122.83(17)
O(1)-C(3)-C(2)	123.55(16)
C(4)-C(3)-C(2)	113.61(16)
C(3)-C(4)-C(5)	109.00(16)
C(3)-C(4)-H(4A)	109.7(9)
C(5)-C(4)-H(4A)	108.5(10)
C(3)-C(4)-H(4B)	109.3(9)
C(5)-C(4)-H(4B)	113.0(9)
H(4A)-C(4)-H(4B)	107.3(13)
C(6)-C(5)-C(4)	113.43(15)
C(6)-C(5)-H(5A)	110.5(10)
C(4)-C(5)-H(5A)	106.7(10)
C(6)-C(5)-H(5B)	108.6(10)
C(4)-C(5)-H(5B)	110.0(10)
H(5A)-C(5)-H(5B)	107.5(13)
C(7)-C(6)-C(5)	112.31(16)
C(7)-C(6)-C(9)	106.55(15)
C(5)-C(6)-C(9)	109.58(15)
C(7)-C(6)-C(1)	100.75(13)
C(5)-C(6)-C(1)	115.55(15)
C(9)-C(6)-C(1)	111.52(15)
O(2)-C(7)-O(3)	121.04(17)
O(2)-C(7)-C(6)	128.96(17)
O(3)-C(7)-C(6)	110.00(15)
O(3)-C(8)-C(1)	104.39(15)
O(3)-C(8)-H(8A)	105.9(9)
C(1)-C(8)-H(8A)	111.7(9)
O(3)-C(8)-H(8B)	111.9(9)
C(1)-C(8)-H(8B)	110.7(9)
H(8A)-C(8)-H(8B)	111.9(13)
C(6)-C(9)-H(9A)	108.0(9)
C(6)-C(9)-H(9B)	110.6(10)
H(9A)-C(9)-H(9B)	110.3(13)
C(6)-C(9)-H(9C)	114.1(10)
H(9A)-C(9)-H(9C)	106.2(14)
H(9B)-C(9)-H(9C)	107.5(14)
C(11)-C(10)-C(17)	113.45(16)
C(11)-C(10)-C(2)	108.15(15)
C(17)-C(10)-C(2)	115.73(15)
C(11)-C(10)-H(10)	106.1(9)
C(17)-C(10)-H(10)	107.1(9)
C(2)-C(10)-H(10)	105.6(9)
C(12)-C(11)-C(10)	121.20(18)
C(12)-C(11)-H(11)	118.3(9)
C(10)-C(11)-H(11)	120.3(9)
C(11)-C(12)-O(4)	123.46(17)
C(11)-C(12)-C(13)	126.02(17)
O(4)-C(12)-C(13)	110.13(14)
C(16)-C(13)-C(14)	105.43(17)
C(16)-C(13)-C(12)	126.59(17)
C(14)-C(13)-C(12)	127.95(17)
C(15)-C(14)-C(13)	106.89(19)

C(15)-C(14)-H(14)	125.6(10)
C(13)-C(14)-H(14)	127.5(10)
C(14)-C(15)-O(5)	111.17(19)
C(14)-C(15)-H(15)	132.6(12)
O(5)-C(15)-H(15)	116.1(12)
C(13)-C(16)-O(5)	111.29(18)
C(13)-C(16)-H(16)	130.8(10)
O(5)-C(16)-H(16)	117.9(10)
C(18)-C(17)-C(10)	109.36(16)
C(18)-C(17)-H(17A)	106.5(9)
C(10)-C(17)-H(17A)	111.1(9)
C(18)-C(17)-H(17B)	111.4(10)
C(10)-C(17)-H(17B)	109.2(10)
H(17A)-C(17)-H(17B)	109.3(13)
O(6)-C(18)-C(17)	110.81(15)
O(6)-C(18)-H(18A)	109.6(8)
C(17)-C(18)-H(18A)	110.0(8)
O(6)-C(18)-H(18B)	108.3(9)
C(17)-C(18)-H(18B)	109.0(9)
H(18A)-C(18)-H(18B)	109.1(12)
C(20)-C(19)-C(24)	116.33(18)
C(20)-C(19)-Si(1)	120.30(14)
C(24)-C(19)-Si(1)	123.19(15)
C(19)-C(20)-C(21)	122.3(2)
C(19)-C(20)-H(20)	119.8(11)
C(21)-C(20)-H(20)	117.7(11)
C(22)-C(21)-C(20)	118.8(2)
C(22)-C(21)-H(21)	123.7(12)
C(20)-C(21)-H(21)	117.5(12)
C(21)-C(22)-C(23)	121.0(2)
C(21)-C(22)-H(22)	118.6(13)
C(23)-C(22)-H(22)	120.1(13)
C(22)-C(23)-C(24)	119.4(2)
C(22)-C(23)-H(23)	123.7(12)
C(24)-C(23)-H(23)	116.9(12)
C(23)-C(24)-C(19)	122.1(2)
C(23)-C(24)-H(24)	118.0(12)
C(19)-C(24)-H(24)	119.9(12)
C(30)-C(25)-C(26)	116.67(17)
C(30)-C(25)-Si(1)	122.66(14)
C(26)-C(25)-Si(1)	120.39(14)
C(27)-C(26)-C(25)	121.8(2)
C(27)-C(26)-H(26)	117.0(10)
C(25)-C(26)-H(26)	121.2(10)
C(28)-C(27)-C(26)	119.9(2)
C(28)-C(27)-H(27)	120.8(10)
C(26)-C(27)-H(27)	119.3(10)
C(27)-C(28)-C(29)	120.3(2)
C(27)-C(28)-H(28)	121.7(11)
C(29)-C(28)-H(28)	118.1(11)
C(28)-C(29)-C(30)	119.6(2)
C(28)-C(29)-H(29)	122.0(10)
C(30)-C(29)-H(29)	118.3(10)
C(29)-C(30)-C(25)	121.74(19)

C(29)-C(30)-H(30)	118.1(9)
C(25)-C(30)-H(30)	120.1(9)
C(32)-C(31)-C(34)	108.36(17)
C(32)-C(31)-C(33)	109.37(17)
C(34)-C(31)-C(33)	108.35(19)
C(32)-C(31)-Si(1)	108.58(13)
C(34)-C(31)-Si(1)	112.96(14)
C(33)-C(31)-Si(1)	109.17(13)
C(31)-C(32)-H(32A)	111.1(10)
C(31)-C(32)-H(32B)	109.1(10)
H(32A)-C(32)-H(32B)	110.5(14)
C(31)-C(32)-H(32C)	110.1(10)
H(32A)-C(32)-H(32C)	107.6(14)
H(32B)-C(32)-H(32C)	108.3(14)
C(31)-C(33)-H(33A)	110.3(11)
C(31)-C(33)-H(33B)	111.8(12)
H(33A)-C(33)-H(33B)	106.9(16)
C(31)-C(33)-H(33C)	108.3(11)
H(33A)-C(33)-H(33C)	110.2(15)
H(33B)-C(33)-H(33C)	109.4(16)
C(31)-C(34)-H(34A)	114.2(12)
C(31)-C(34)-H(34B)	110.1(11)
H(34A)-C(34)-H(34B)	101.4(16)
C(31)-C(34)-H(34C)	109.4(11)
H(34A)-C(34)-H(34C)	112.9(16)
H(34B)-C(34)-H(34C)	108.4(16)

Table A3.3.4 Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **90** (CCDC 197200). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	236(3)	306(3)	166(3)	-13(2)	11(2)	-33(2)
O(1)	279(8)	449(8)	263(8)	-59(6)	-6(6)	-61(7)
O(2)	462(9)	375(8)	249(8)	-81(6)	78(6)	-163(7)
O(3)	278(8)	389(8)	241(7)	-41(6)	36(6)	-103(6)
O(4)	406(8)	307(7)	199(7)	8(6)	-43(6)	-130(6)
O(5)	466(9)	398(8)	313(8)	87(7)	15(7)	-48(7)
O(6)	314(7)	328(7)	136(7)	-24(6)	-3(5)	-36(6)
C(1)	249(11)	294(11)	171(10)	0(8)	-3(8)	-59(8)
C(2)	263(11)	290(11)	143(10)	-8(8)	21(8)	-93(9)
C(3)	327(12)	296(11)	168(10)	43(8)	-2(9)	-74(9)
C(4)	290(12)	317(13)	254(11)	-35(9)	22(9)	-43(10)
C(5)	297(12)	362(13)	196(11)	-53(10)	37(9)	-76(10)
C(6)	267(11)	324(11)	155(10)	-23(8)	17(8)	-84(9)
C(7)	299(11)	427(13)	130(10)	-40(9)	5(8)	-86(10)
C(8)	320(12)	370(13)	221(12)	-45(10)	8(10)	-59(10)
C(9)	296(13)	437(14)	184(11)	-29(10)	6(9)	-89(11)
C(10)	267(11)	301(11)	179(10)	-21(8)	12(9)	-37(9)
C(11)	403(13)	262(11)	231(11)	-42(9)	22(9)	-61(10)
C(12)	386(12)	306(11)	206(11)	-40(9)	-5(9)	-104(9)
C(13)	329(11)	294(11)	193(10)	-2(9)	8(8)	-33(9)
C(14)	455(14)	371(13)	265(13)	13(10)	-52(10)	-114(11)
C(15)	435(14)	307(13)	327(13)	-1(10)	13(11)	-94(11)
C(16)	354(12)	367(12)	259(12)	31(10)	-21(9)	-80(10)
C(17)	295(13)	296(12)	192(11)	-2(9)	25(9)	-73(10)
C(18)	251(12)	390(13)	180(11)	-5(9)	7(9)	-67(10)
C(19)	284(11)	270(11)	203(10)	32(8)	1(8)	-4(9)
C(20)	316(12)	501(14)	260(11)	-37(11)	3(9)	34(11)
C(21)	295(13)	665(17)	305(12)	67(12)	-30(10)	-48(12)
C(22)	441(15)	509(15)	394(14)	53(12)	146(12)	154(12)
C(23)	598(17)	377(14)	435(15)	-2(11)	166(13)	43(12)
C(24)	500(15)	386(13)	349(13)	-22(10)	151(11)	-36(11)
C(25)	217(10)	338(11)	198(10)	-23(9)	-39(8)	-71(9)
C(26)	292(12)	377(13)	223(11)	4(10)	-15(9)	-86(10)
C(27)	326(13)	487(15)	228(12)	12(10)	-4(10)	-134(11)
C(28)	364(13)	502(15)	277(13)	158(11)	-101(10)	-176(12)
C(29)	326(13)	340(14)	357(13)	47(11)	-133(10)	-30(11)
C(30)	221(11)	419(13)	227(11)	25(10)	-58(9)	-44(10)
C(31)	258(11)	364(11)	204(10)	16(9)	-11(8)	-53(9)
C(32)	265(13)	426(14)	253(12)	65(11)	-11(10)	3(10)
C(33)	232(12)	674(18)	388(15)	199(14)	10(11)	5(12)
C(34)	533(17)	465(16)	369(15)	26(12)	-159(13)	-115(13)

Table A3.3.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **90** (CCDC 197200).

	x	y	z	U_{iso}
H(2)	1269(14)	6339(13)	147(5)	15(4)
H(4A)	2545(15)	4651(15)	-243(6)	27(5)
H(4B)	3953(16)	4944(15)	-391(6)	29(5)
H(5A)	3101(15)	6208(14)	-1025(6)	24(5)
H(5B)	2426(15)	4918(15)	-1094(6)	32(5)
H(8A)	-608(15)	7565(14)	-77(6)	24(5)
H(8B)	-856(16)	7867(15)	-668(6)	31(5)
H(9A)	748(15)	6032(15)	-1617(6)	34(5)
H(9B)	1355(17)	7431(16)	-1493(6)	38(5)
H(9C)	-140(18)	7133(15)	-1409(6)	39(6)
H(10)	831(16)	8316(14)	412(6)	25(5)
H(11)	2661(14)	9960(14)	278(5)	24(5)
H(14)	3790(16)	11587(15)	-215(7)	35(5)
H(15)	4040(18)	12875(17)	-976(7)	45(6)
H(16)	1708(16)	10161(15)	-1397(6)	37(5)
H(17A)	2301(14)	7109(15)	987(6)	23(5)
H(17B)	3307(16)	8122(14)	859(6)	22(5)
H(18A)	1800(13)	9734(14)	1110(5)	15(4)
H(18B)	919(16)	8551(14)	1273(5)	23(5)
H(20)	141(16)	9170(16)	2061(6)	37(6)
H(21)	-1667(18)	9728(17)	2450(7)	47(6)
H(22)	-1570(19)	11186(17)	3078(7)	56(7)
H(23)	440(20)	12270(20)	3335(8)	84(8)
H(24)	2220(20)	11840(20)	2859(8)	79(8)
H(26)	4631(15)	10209(16)	1246(6)	35(5)
H(27)	5122(16)	11746(15)	684(6)	36(5)
H(28)	4105(16)	13738(15)	718(6)	29(5)
H(29)	2716(14)	14207(14)	1328(5)	16(5)
H(30)	2168(15)	12708(13)	1879(6)	15(4)
H(32A)	4317(18)	7919(15)	2996(7)	40(6)
H(32B)	3437(16)	7601(16)	2520(7)	35(6)
H(32C)	2888(17)	8444(15)	2941(6)	33(5)
H(33A)	6017(19)	8670(17)	2438(7)	51(6)
H(33B)	5747(19)	9821(19)	2075(7)	61(7)
H(33C)	5054(19)	8444(18)	1932(8)	63(7)
H(34A)	3867(19)	10662(18)	3092(7)	48(7)
H(34B)	4779(18)	11198(18)	2733(7)	51(6)
H(34C)	5390(20)	10069(18)	3099(8)	75(7)