Supplementary Material

A New Synthesis and Stereocontrolled Functionalization of Substituted Silacyclopent-3-enes

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Allyldiphenyl-(3-tributylstannylpropanylsilane) (12). To a mixture of diallyldiphenylsilane **9** (2.02 g, 7.6 mmol) in dry THF (24 mL) was added dropwise at 0°C, a 2.5 M solution of *n*-BuLi in hexane (3.35 mL, 8.4 mmol). The resulting orange solution was stirred at 0°C for 1 h, then cooled to -78°C. Tributyltin chloride (2.07 mL, 7.6 mmol) was added dropwise and the reaction mixture was stirred at this temperature for 1 h. An aqueous solution of NH₄Cl was then added carefully and the organic layer was decanted. The aqueous layer was extracted with ether, dried over MgSO₄ and the solvents were evaporated under reduced pressure to afford **12** as a pale yellow oil (4.02 g, 95%), which was used in the next step without further purification. - *R*_f = 0.90 (Petroleum ether-EtOAc 9:1). IR (neat) ν_{max} 3068, 2956, 1630, 1590, 1428, 1245, 1110 cm⁻¹; ¹H NMR (250 MHz, CDCl₃): δ 7.59 (m, 4H), 7.40 (m, 6H), 6.35 (dt, *J* = 18.3, 8.2 Hz, 1H), 5.89 (m, 1H), 5.72 (m, 1H), 4.95 (m, 2H), 2.21 (dd, *J* = 7.9, 1.2 Hz, 2H), 2.08 (d, *J* = 8.2 Hz, 2H), 1.57 (m, 6H), 1.39 (m, 10H), 1.02- 0.85 (m, 11H); ¹³C NMR (63 MHz, CDCl₃): δ 152.9, 136.1, 135.4, 135.4, 134.6, 129.2, 127.7, 116.6, 114.3, 29.3, 27.5, 21.9, 21.0, 13.8, 9.5; MS (LSIMS, Na) *m/z* (%): 497 [M-Bu•]⁺ (45), 439 (8), 383 (17), 311 (18), 291 (100), 289 (76), 235 (73). HRMS calcd for C₂₆H₃₇SiSn [M+Na]⁺ 497.168654, found 497.168367. Anal. Calcd for C₃₀H₄₆SiSn: C, 65.10; H, 8.38. Found: C, 65.28; H, 8.61.

(*E*)-Bis-(3-bromopropenyl)diphenylsilane (13). To a stirred solution of diallyldiphenylsilane **9** (1.06 g, 4.0 mmol) in dry CCl₄ (12 mL) was added freshly recrystallized N-bromosuccinimide (1.42 g, 8.0 mmol) and a catalytic amount of benzoyl peroxide. The mixture was refluxed under nitrogen for 12 h. After completion of the reaction, succinimide was filtered off and washed with CCl₄. The filtrates were combined together and solvents evaporated *in vacuo*. The crude product

was purified by chromatography through silica gel (Petroleum ether-EtOAc 97:3) to give **13** as a colourless oil (998 mg, 72%). - $R_f = 0.63$ (Petroleum ether-EtOAc 9:1). IR (neat): $\nu_{\max}$ 2956, 1736, 1607, 1249, 1201, 1112 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.56-7.44 (m, 10H), 6.31 (br s, 4H), 4.07 (br s, 4H); ^{13}C NMR (63 MHz, CDCl_3): δ 146.6, 136.3, 136.2, 135.9, 135.6, 133.4, 130.6, 130.3, 129.4, 128.5, 34.6. MS (EI) m/z (%): 343, 263, 221, 199, 145, 105 (100).

Acetic acid (1R*,2S*)-2-(allyldiphenylsilyl)-1-propyl-but-3-enyl ester (15b). Following the general acetylation protocol described for **8a**, **8c** (724 mg, 2.15 mmol) gave, after chromatography through silica gel (Petroleum ether-EtOAc 95:5), the acetate **15b** as a thick oil (648 mg, 79%). $R_f = 0.57$ (petroleum ether-EtOAc 9:1). IR (CHCl_3): $\nu_{\max}$ 1723, 1628, 1589, 1487, 1428, 1373, 1244 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.55 (m, 5H), 7.4 (m, 5H), 5.84 (m, 2H), 5.22 (td, $J = 7, 3$ Hz, 1H), 5.0 (m, 4H), 2.57 (dd, $J = 11, 3$ Hz, 1H), 2.2 (m, 2H), 1.58 (s, 3H), 1.5 (m, 2H), 1.3 (m, 2H), 0.82 (t, $J = 7$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 170.0, 135.6, 135.5, 134.1, 133.6, 129.5, 129.4, 127.7, 127.7, 115.1, 73.0, 36.3, 36.2, 20.8, 20.2, 18.6, 13.8; MS (EI) m/z (%) : 241 (100), 223, 199, 183, 145, 105, 77.

Acetic acid (E)-(1R*)-1-[(1S*)-1-(allyldiphenylsilyl)-allyl]-but-2-enyl ester (15c). Following the general acetylation protocol described for **8a**, **8f** (403 mg, 1.2 mmol) gave, after chromatography through silica gel (Petroleum ether-EtOAc 95:5), the acetate **15c** as a thick oil (369 mg, 81%). - $R_f = 0.65$ (Petroleum ether-EtOAc 9:1). IR (CHCl_3): $\nu_{\max}$ 1731, 1628, 1588, 1487, 1428, 1371, 1243 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.6 (m, 4H), 7.4 (m, 6H), 5.99-5.48 (m, 4H), 5.44-4.29 (m,

1H), 5.11-4.84 (m, 4H), 2.61 (dd, $J = 10, 5$ Hz, 1H), 2.17 (d, $J = 8$ Hz, 2H), 1.71 (s, 3H), 1.56 (dd, $J = 7, 2$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 170.0, 135.6, 135.6, 134.5, 133.54, 133.46, 129.7, 129.5, 129.4, 127.7, 116.7, 115.1, 74.5, 38.3, 21.0, 20.45, 17.6; M.S (EI) m/z (%): 241 (100), 223, 199, 183, 145, 107, 94, 79. Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2\text{Si}$: C, 76.59; H, 7.44. Found: C, 76.56; H, 7.59.

Acetic acid (2S*,3R*)-(1,1-Diphenyl-2-vinyl-1,2,3,6-tetrahydro-silan-3-yl) ester (17). β -Hydroxysilane **15c** (300 mg, 0.79 mmol) was subjected to the standard ring-closing metathesis conditions described above, to afford after purification by column chromatography through silica gel (Petroleum ether-EtOAc 95:5), **17** as a black gum (163 mg, 61%). - IR (CHCl_3): ν_{max} 1728, 1630, 1589, 1487, 1428, 1371, 1248, 1216 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.6 (m, 4H), 7.4 (m, 6H), 6.1 (m, 1H), 5.64 (m, 3H), 4.96 (s, 1H), 4.9 (d, $J = 7$ Hz, 1H), 2.7 (t, $J = 10$ Hz, 1H), 2.3 (s, 3H), 1.8 (dd, $J = 5, 2$ Hz, 2H); ^{13}C NMR (63 MHz, CDCl_3): δ 135.6, 135.5, 135.0, 133.6, 132.0, 130.7, 130.1, 129.9, 128.1, 128.0, 127.3, 115.2, 73.5, 36.7, 21.2, 11.2; MS (EI) m/z (%): 334 $[\text{M}]^+$ 288, 274, 241, 222, 199 (100), 144, 105, 91, 77; HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2\text{Si}$ 334.136503, found 334.136597.

(2S*,4S*)-2-(2-hydroxypropyl)-1,1-diphenyl-silolane-3,4-diol (20a). Following the general protocol reported above for **7c**, silacyclopentene **10b** (69.1 mg, 0.23 mmol) afforded after 16 h the corresponding triol **20a** as an inseparable 74:26 mixture of two diastereomers (65.5 mg, 85%). **20a** (Major). $R_f = 0.33$ (Petroleum ether-EtOAc 4:6). IR (CHCl_3): ν_{max} 3354, 2965, 1589, 1486, 1428,

1375, 1261, 1112 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.67 (m, 4H), 7.41 (m, 6H), 4.46 (m, 1H), 3.88 (dd, $J = 10.5, 3.0$ Hz, 1H), 3.75 (m, 1H), 1.78 (m, 1H), 1.72 (m, 2H), 1.39 (m, 1H), 1.37 (m, 1H), 1.08 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): 135.9, 135.1, 134.8, 134.4, 134.2, 134.0, 130.0, 128.2, 127.8, 81.9, 74.1, 70.5, 39.0, 28.8, 24.4, 17.3; MS (LSIMS, Na) m/z (%): 351 $[\text{M}+\text{Na}]^+$ (100), 319 (61), 293 (46), 259 (60), 233 (30), 225 (29), 215 (27). HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 351.139243, found 351.139130. - **20a** (Minor). $R_f = 0.22$ (Petroleum ether-EtOAc 4:6); ^1H NMR (250 MHz, CDCl_3): δ 7.67 (m, 4H), 7.41 (m, 6H), 4.36 (m, 1H), 4.05 (dd, $J = 10.5, 3.0$ Hz, 1H), 3.81 (m, 1H), 1.81 (m, 1H), 1.64 (m, 2H), 1.50 (m, 2H), 1.02 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 76.8, 75.1, 69.6, 40.8, 29.4, 23.7, 18.1.

(2S*,4R*)-2-(2-hydroxy-propyl)-1,1-diphenyl-silolane-3,4-diol (20b). Following the general protocol reported above for **7c**, silacyclopentene **10e** (242 mg, 0.82 mmol) afforded after 4 h the corresponding triol **20b** as an inseparable 75:25 mixture of two diastereomers (269 mg, 100%). **20b** (Major). $R_f = 0.45$ (Petroleum ether-EtOAc 4:6). - IR (CHCl_3): ν_{max} 3384, 2969, 1428, 1378, 1331, 1113 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.62 (m, 4H), 7.39 (m, 6H), 4.49 (m, 1H), 4.04 (m, 1H), 3.91 (dd, $J = 10.3, 3.2$ Hz, 1H), 2.00 (m, 1H), 1.63 (m, 2H), 1.45 (m, 2H), 1.19 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 135.8, 135.3, 134.8, 134.7, 134.3, 133.9, 129.5, 129.4, 128.0, 127.92, 127.87, 81.3, 74.1, 66.8, 37.7, 23.6, 22.2, 17.1; MS (LSIMS, Na) m/z (%): 351 $[\text{M}+\text{Na}]^+$, 297, 258, 199 $[(\text{Ph})_2\text{SiOH}]^+$ (100). HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 351.139243, found 351.139593. - **20b** (Minor). $R_f = 0.32$ (Petroleum ether-EtOAc 4:6). ^1H NMR (250 MHz, CDCl_3): δ 7.62 (m, 4H), 7.39 (m, 6H), 4.35 (m, 1H), 4.08 (m, 1H), 3.93 (dd, $J = 10.3, 3.2$ Hz, 1H), 1.91 (m,

1H), 1.73 (m, 2H), 1.36 (m, 2H), 1.17 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 76.5, 75.1, 67.1, 34.7, 26.7, 23.1, 17.9.

(2S*,4S*)-1-(3,3-diphenyl-6-oxa-3-silabicyclo[3.1.0]-hex-2-yl)propan-2-ol (23a). Following the general epoxidation procedure described for **7c**, silacyclopentene **10b** (123 mg, 0.42 mmol) afforded after stirring for 15 h, **23a** as an inseparable 60:40 mixture of two diastereomers (101 mg, 78%). **23a** (Major): IR (CHCl_3): ν_{max} 3388, 2926, 1715, 1428, 1378, 1258, 1115 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.71-7.45 (m, 10H), 3.73 (m, 1H), 3.66 (m, 1H), 3.56 (m, 1H), 2.23 (m, 1H), 1.85 (m, 2H), 1.54 (m, 2H), 1.07 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 137.1, 136.3, 135.0, 134.6, 134.4, 133.5, 129.7, 129.6, 129.4, 129.2, 128.2, 128.1, 127.8, 127.6, 68.4, 62.3, 57.4, 37.4, 27.9, 24.1, 16.3; MS (LSIMS, Na) m/z (%): 333 $[\text{M}+\text{Na}]^+$ (29), 293 $[\text{M}-\text{OH}\cdot]^+$ (48), 265 $[\text{293}-\text{CHCH}_3\cdot]^+$ (39), 251 $[\text{265}-\text{CH}_2\cdot]^+$ (30), 239 (39), 225 (76), 223 $[\text{Si}(\text{CH}_2-\text{CH}=\text{CH}_2)\text{Ph}_2]^+$ (100), 215 (54), 207 (86). HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 333.128678, found 333.128232. - **23a** (Minor). ^1H NMR (250 MHz, CDCl_3): δ 7.71-7.45 (m, 10H), 4.42 (m, 1H), 4.25 (m, 1H), 4.10 (m, 1H), 2.27 (m, 1H), 1.94 (m, 2H), 1.46 (m, 2H), 1.21 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 91.3, 79.6, 77.0, 36.8, 26.2, 25.3, 16.8.

(2S*,4R*)-1-(3,3-diphenyl-6-oxa-3-sila-bicyclo[3.1.0]-hex-2-yl)propan-2-ol (23b). Following the general epoxidation procedure described for **7c**, silacyclopentene **10e** (64.6 mg, 0.22 mmol) afforded after stirring for 12 h, **23b** as an inseparable 65:35 mixture of two diastereomers (67 mg, 98%). **23b** (Major). $R_f = 0.51$ (Petroleum ether-EtOAc 6:4). - IR (CHCl_3): ν_{max} 3411, 3071, 2970,

1428, 1259, 908, 734 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3): δ 7.49 (m, 10H), 3.95 (m, 1H), 3.66 (br s, 1H), 3.59 (br s, 1H), 2.18 (m, 1H), 1.82 (m, 2H), 1.49 (m, 2H), 1.15 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 136.3, 135.3, 135.0, 134.7, 134.4, 133.7, 130.2, 129.8, 129.7, 129.5, 128.20, 128.16, 128.07, 127.8, 67.5, 61.2, 57.5, 37.3, 25.9, 24.2, 16.0. MS (LSIMS, Na) m/z (%): 333 $[\text{M}+\text{Na}]^+$ (71), 311 $[\text{M}+\text{H}]^+$ (29), 293 $[\text{M}-\text{OH}\cdot]^+$ (39), 265 $[\text{293}-\text{CHCH}_3\cdot]^+$ (48), 251 $[\text{265}-\text{CH}_2\cdot]^+$ (49), 239 (58), 225 (100), 215 (80), 207 (66). HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 333.128678, found 333.126854. **23b** (Minor). $R_f = 0.46$ (Petroleum ether-EtOAc 6:4). ^1H NMR (250 MHz, CDCl_3): δ 7.49 (m, 10H), 4.63 (m, 1H), 4.48 (m, 1H), 4.07 (q, $J = 6.1$ Hz, 1H), 2.29 (m, 1H), 1.64 (m, 2H), 1.42 (m, 2H), 1.12 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (63 MHz, CDCl_3): δ 75.4, 61.7, 58.0, 35.4, 26.3, 24.7, 16.2.

Figure S1. ^1H NMR of **7a**

Figure S2. ^{13}C NMR of **7a**

Figure S3. ^1H NMR of **7c**

Figure S4. ^{13}C NMR of **7c**

Figure S5. ^1H NMR of **7d**

Figure S6. ^{13}C NMR of **7d**

Figure S7. ^1H NMR of **8a**

Figure S8. ^{13}C NMR of **8a**

Figure S9. ^1H NMR of **8b**

Figure S10. ^{13}C NMR of **8b**

Figure S11. ^1H NMR of **8c**

Figure S12. ^{13}C NMR of **8c**

Figure S13. ^1H NMR of **8d**

Figure S14. ^{13}C NMR of **8d**

Figure S15. ^1H NMR of **8e**

Figure S16. ^{13}C NMR of **8e**

Figure S17. ¹H NMR of 10b

Figure S18. ^{13}C NMR of 10b

Figure S19. ¹H NMR of 10e

Figure S20. ^{13}C NMR of 10e

Figure S22. ^{13}C NMR of 11a

Figure S23. ^1H NMR of **11b**

Figure S24. ^{13}C NMR of **11b**

Figure S25. ^1H NMR of **11c**

Figure S26. ^{13}C NMR of 11c

Figure S27. ^1H NMR of **12** (crude)

Figure S28. ^{13}C NMR of **12** (crude)

13

Figure S29. ^1H NMR of **13** (crude)

Figure S30. ^{13}C NMR of **13** (crude)

Figure S31. ^1H NMR of **14a**

Figure S32. ^{13}C NMR of 14a

Figure S33. ¹H NMR of **14b**

Figure S34. ^{13}C NMR of **14b**

Figure S35. ¹H NMR of **14c**

Figure S36. ^{13}C NMR of **14c**

15a

Figure S37. ¹H NMR of 15a

Figure S38. ^{13}C NMR of **15a**

Figure S39. ¹H NMR of **15b**

Figure S40. ^{13}C NMR of **15b**

Figure S41. ^1H NMR of 16

16

Figure S42. ^{13}C NMR of **16**

Figure S43. ^1H NMR of **19b**

Figure S44. ^{13}C NMR of **19b**

Figure S45. ^1H NMR of **20a** (crude)

Figure S46. ^{13}C NMR of **20a** (crude)

Figure S48. ^{13}C NMR of 21a

Figure S49. ^1H NMR of 22c

Figure S50. ^{13}C NMR of 22c

Figure S51. X-ray crystal structure of **10b**

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  'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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Bond distances (Angstroms)

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Si1 C1	1.875(2)
Si1 C20	1.8783(18)
Si1 C4	1.8990(18)
O6 C6	1.425(3)
C1 C2	1.501(3)
C2 C3	1.305(3)
C3 C4	1.508(3)
C4 C5	1.5368(19)
C5 C6	1.519(2)
C6 C7	1.512(2)
C20 C21	1.381(3)
C20 C25	1.396(3)
C21 C22	1.384(3)
C22 C23	1.357(3)
C23 C24	1.364(3)
C24 C25	1.373(3)
C30 C31	1.388(2)
C30 C35	1.390(3)
C31 C32	1.385(3)
C32 C33	1.350(4)
C33 C34	1.351(3)
C34 C35	1.373(3)
Si1A C20A	1.866(2)
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C1A C2A	1.460(3)
C2A C3A	1.318(3)
C3A C4A	1.492(3)
C4A C5A	1.515(3)
C5A C6A	1.497(3)
C6A C7A	1.476(3)
C20A C21A	1.376(3)
C20A C25A	1.393(3)
C21A C22A	1.377(3)
C22A C23A	1.347(4)
C23A C24A	1.354(4)
C24A C25A	1.363(4)
C30A C35A	1.372(3)
C30A C31A	1.403(3)
C31A C32A	1.377(3)
C32A C33A	1.373(4)
C33A C34A	1.376(3)
C34A C35A	1.382(3)

loop_
geom_angle_atom_site_label_1
geom_angle_atom_site_label_2
geom_angle_atom_site_label_3

geom_angle
 geom_angle_site_symmetry_1
 geom_angle_site_symmetry_3
 geom_angle_publ_flag

Bond angles (degrees)

C30 Si1 C1	112.72(9)
C30 Si1 C20	109.41(8)
C1 Si1 C20	112.58(10)
C30 Si1 C4	112.40(8)
C1 Si1 C4	96.65(9)
C20 Si1 C4	112.67(7)
C2 C1 Si1	102.20(15)
C3 C2 C1	119.6(2)
C2 C3 C4	120.87(19)
C3 C4 C5	112.45(14)
C3 C4 Si1	100.66(12)
C5 C4 Si1	115.78(12)
C6 C5 C4	114.94(14)
O6 C6 C7	109.14(17)
O6 C6 C5	111.76(16)
C7 C6 C5	112.40(17)
C21 C20 C25	116.79(17)
C21 C20 Si1	121.78(14)
C25 C20 Si1	121.42(16)
C20 C21 C22	121.1(2)
C23 C22 C21	120.6(2)
C22 C23 C24	119.8(2)
C23 C24 C25	120.1(2)
C24 C25 C20	121.6(2)
C31 C30 C35	115.88(17)
C31 C30 Si1	122.58(16)
C35 C30 Si1	121.54(12)
C32 C31 C30	121.3(2)
C33 C32 C31	120.6(2)
C32 C33 C34	119.7(2)
C33 C34 C35	20.5(3)
C34 C35 C30	121.97(18)
C20A Si1A C30A	110.11(10)
C20A Si1A C1A	111.25(12)
C30A Si1A C1A	113.57(11)
C20A Si1A C4A	113.33(9)
C30A Si1A C4A	112.15(10)
C1A Si1A C4A	95.85(9)
C2A C1A Si1A	103.11(17)
C3A C2A C1A	119.0(3)
C2A C3A C4A	121.6(2)
C3A C4A C5A	114.98(19)
C3A C4A Si1A	100.39(14)
C5A C4A Si1A	118.38(14)
C6A C5A C4A	117.39(18)
O6A C6A C7A	111.65(16)

O6A C6A C5A	109.52(18)
C7A C6A C5A	117.93(19)
C21A C20A C25A	117.0(2)
C21A C20A Si1A	123.72(17)
C25A C20A Si1A	119.24(17)
C20A C21A C22A	121.2(2)
C23A C22A C21A	120.3(3)
C22A C23A C24A	119.9(3)
C23A C24A C25A	120.8(3)
C24A C25A C20A	120.8(2)
C35A C30A C31A	116.7(2)
C35A C30A Si1A	121.78(14)
C31A C30A Si1A	121.55(18)
C32A C31A C30A	121.5(2)
C33A C32A C31A	120.1(2)
C32A C33A C34A	119.5(2)
C33A C34A C35A	119.8(3)
C30A C35A C34A	122.4(2)
diffraction_measured_fraction_theta_max	0.901
diffraction_reflns_theta_full	25.87
diffraction_measured_fraction_theta_full	0.901
refine_diff_density_max	0.202
refine_diff_density_min	-0.184
refine_diff_density_rms	0.029

Crystallographic Data 18a

Figure S52. X-ray crystal structure of 18a


```

audit_creation_method          SHELXL-97
chemical_formula_moiety        'C20 H26 O3 Si'
chemical_formula_weight        342.50
atom_type_symbol
atom_type_description
atom_type_scatter_dispersion_real
atom_type_scatter_dispersion_imag
atom_type_scatter_source      'C'   'C'   0.0033   0.0016
International Tables Vol C Tables 4.2.6.8 and 6.1.1.4 'H'   'H'   0.0000
0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'O'   'O'   .0106
0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'Si'  'Si'
0.0817 0.0704
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

symmetry_cell_setting          triclinic
symmetry_space_group_name_H-M  'P -1'

loop_ symmetry_equiv_pos_as_xyz 'x, y, z' '-x, -y, -z'

cell_length_a                  10.0927(7)
cell_length_b                  13.6087(9)
cell_length_c                  15.3571(10)
cell_angle_alpha               103.9090(10)
cell_angle_beta                99.2830(10)
cell_angle_gamma               105.4380(10)

cell_volume                    1915.5(2)
cell_formula_units_Z           4
cell_measurement_temperature    293(2)
cell_measurement_reflns_used    6075
cell_measurement_theta_min      2.2505
cell_measurement_theta_max      30.027

exptl_crystal_description      prism
exptl_crystal_colour           colourless
exptl_crystal_size_max         0.6
exptl_crystal_size_mid        0.34
exptl_crystal_size_min        0.2
exptl_crystal_density_meas     ?
exptl_crystal_density_diffn    1.188
exptl_crystal_density_method   'not measured'
exptl_crystal_F_000            736
exptl_absorpt_coefficient_mu    0.137
exptl_absorpt_correction_type   'none'
exptl_absorpt_correction_T_min ?
exptl_absorpt_correction_T_max ?
exptl_absorpt_process_details  ?

exptl_special_details
The crystal habitus consists of the {100}, {001}, {\=102} and 03\=1)
pinacoids.

```

```

diffraction_ambient_temperature      293(2)
diffraction_radiation_wavelength     0.71073
diffraction_radiation_type           MoK\alpha
diffraction_radiation_source          'fine-focus sealed tube'
diffraction_radiation_monochromator   graphite
diffraction_measurement_device_type    'Bruker SMART'
diffraction_measurement_method        '\w scans'
diffraction_detector_area_resolution ?
diffraction_standards_number          0
diffraction_standards_interval_count  ?
diffraction_standards_interval_time   ?
diffraction_standards_decay_percent  ?
diffraction_reflections_number        11940
diffraction_reflections_average_R_equivalents 0.0479
diffraction_reflections_average_sigmaI/netI 0.0432
diffraction_reflections_limit_h_min   -13
diffraction_reflections_limit_h_max   12
diffraction_reflections_limit_k_min   -16
diffraction_reflections_limit_k_max   19
diffraction_reflections_limit_l_min   -21
diffraction_reflections_limit_l_max   16
diffraction_reflections_theta_min     2.27
diffraction_reflections_theta_max     30.62
reflections_number_total              9110
reflections_number_gt                 6796
reflections_threshold_expression       >2sigma(I)

computing_data_collection              'Bruker SMART'
computing_cell_refinement              'Bruker SMART'
computing_data_reduction               'Bruker SMART'
computing_structure_solution           'SIR97 (Altomare, 1997)'
computing_structure_refinement         'SHELXL-97 (Sheldrick, 1997)'
computing_molecular_graphics           'Bruker SHELXTL'
computing_publication_material         'Bruker SHELXTL'

refinement_ls_structure_factor_coef    Fsqd
refinement_ls_matrix_type              full
refinement_ls_weighting_scheme          calc
refinement_ls_weighting_details         sigma
atom_sites_solution_primary             direct
atom_sites_solution_secondary           difmap
atom_sites_solution_hydrogens           geom
refinement_ls_hydrogen_treatment        mixed
refinement_ls_extinction_method         SHELXL
refinement_ls_extinction_coef           0.0092(5)
refinement_ls_extinction_expression     'Fc^*=kFc[1+0.001xFc^2^/l^3^/sin(2\q)]^-1/4^'
refinement_ls_number_reflections        9110
refinement_ls_number_parameters         458
refinement_ls_number_restraints         0
refinement_ls_R_factor_all              0.0613
refinement_ls_R_factor_gt               0.0444
refinement_ls_wR_factor_ref             0.0860
refinement_ls_wR_factor_gt              0.0843

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refine_ls_goodness_of_fit_ref	2.293
refine_ls_restrained_S_all	2.293
refine_ls_shift/su_max	0.001
refine_ls_shift/su_mean	0.000

Bond distances (Angstroms)

Si1 C30	1.8760(16)
Si1 C20	1.8779(19)
Si1 C1	1.8954(17)
Si1 C4	1.8998(15)
O2 C2	1.429(2)
O2 H2O	0.74(3)
O3 C3	1.432(2)
O3 H3O	0.752(17)
O5 C5	1.4367(18)
O5 H5O	0.795(17)
C1 C2	1.525(3)
C1 H1A	0.9700
C1 H1B	0.9700
C2 C3	1.526(2)
C2 H2	0.9800
C3 C4	1.538(2)
C3 H3	0.9800
C4 C5	1.5299(19)
C4 H4	0.9800
C5 C6	1.539(2)
C5 H5	0.9800
C6 C7	1.515(3)
C6 C8	1.520(3)
C6 H6	0.9800
C7 H7A	0.9600
C7 H7B	0.9600
C7 H7C	0.9600
C8 H8A	0.9600
C8 H8B	0.9600
C8 H8C	0.9600
C20 C21	1.391(2)
C20 C25	1.395(2)
C21 C22	1.387(3)
C21 H21	0.9300
C22 C23	1.362(3)
C22 H22	0.9300
C23 C24	1.382(3)
C23 H23	0.9300
C24 C25	1.377(3)
C24 H24	0.9300
C25 H25	0.9300
C30 C31	1.381(3)
C30 C35	1.398(2)
C31 C32	1.391(2)
C31 H31	0.9300

C32 C33	1.375(3)
C32 H32	0.9300
C33 C34	1.355(3)
C33 H33	0.9300
C34 C35	1.392(2)
C34 H34	0.9300
C35 H35	0.9300
Si1A C20A	1.8714(17)
Si1A C30A	1.8762(19)
Si1A C1A	1.8889(18)
Si1A C4A	1.8997(17)
O2A C2A	1.424(2)
O2A H2AO	0.83(2)
O3A C3A	1.420(2)
O3A H3AO	0.75(2)
O5A C5A	1.4509(19)
O5A H5AO	0.817(19)
C1A C2A	1.521(3)
C1A H1AA	0.9700
C1A H1AB	0.9700
C2A C3A	1.521(2)
C2A H2A	0.9800
C3A C4A	1.539(2)
C3A H3A	0.9800
C4A C5A	1.530(2)
C4A H4A	0.9800
C5A C6A	1.524(2)
C5A H5A	0.9800
C6A C7A	1.518(3)
C6A C8A	1.530(2)
C6A H6A	0.9800
C7A H7AA	0.9600
C7A H7AB	0.9600
C7A H7AC	0.9600
C8A H8AA	0.9600
C8A H8AB	0.9600
C8A H8AC	0.9600
C20A C21A	1.381(2)
C20A C25A	1.390(2)
C21A C22A	1.389(2)
C21A H21A	0.9300
C22A C23A	1.374(3)
C22A H22A	0.9300
C23A C24A	1.363(3)
C23A H23A	0.9300
C24A C25A	1.382(3)
C24A H24A	0.9300
C25A H25A	0.9300
C30A C31A	1.386(3)
C30A C35A	1.391(3)
C31A C32A	1.380(3)
C31A H31A	0.9300
C32A C33A	1.363(4)
C32A H32A	0.9300

C33A C34A 1.365(3)
 C33A H33A 0.9300
 C34A C35A 1.374(3)
 C34A H34A 0.9300
 C35A H35A 0.9300

loop_
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 geom_angle_atom_site_label_2
 geom_angle_atom_site_label_3
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 geom_angle_site_symmetry_1
 geom_angle_site_symmetry_3
 geom_angle_publ_flag

Bond angles (degrees)

C30 Si1 C20 108.05(8)
 C30 Si1 C1 114.06(8)
 C20 Si1 C1 113.88(8)
 C30 Si1 C4 115.69(8)
 C20 Si1 C4 109.61(7)
 C1 Si1 C4 95.25(7)
 C2 O2 H2O 112.5(19)
 C3 O3 H3O 105.6(17)
 C5 O5 H5O 109.0(14)
 C2 C1 Si1 103.05(11)
 C2 C1 H1A 111.2
 Si1 C1 H1A 111.2
 C2 C1 H1B 111.2
 Si1 C1 H1B 111.2
 H1A C1 H1B 109.1
 O2 C2 C1 107.38(15)
 O2 C2 C3 110.86(14)
 C1 C2 C3 106.63(15)
 O2 C2 H2 110.6
 C1 C2 H2 110.6
 C3 C2 H2 110.6
 O3 C3 C2 109.29(14)
 O3 C3 C4 112.59(13)
 C2 C3 C4 109.88(12)
 O3 C3 H3 108.3
 C2 C3 H3 108.3
 C4 C3 H3 108.3
 C5 C4 C3 111.79(12)
 C5 C4 Si1 115.44(11)
 C3 C4 Si1 102.37(10)
 C5 C4 H4 109.0
 C3 C4 H4 109.0
 Si1 C4 H4 109.0
 O5 C5 C4 108.61(12)
 O5 C5 C6 110.36(13)

C4 C5 C6	113.07(12)
O5 C5 H5	108.2
C4 C5 H5	108.2
C6 C5 H5	108.2
C7 C6 C8	111.09(15)
C7 C6 C5	112.09(15)
C8 C6 C5	110.75(15)
C7 C6 H6	107.6
C8 C6 H6	107.6
C5 C6 H6	107.6
C6 C7 H7A	109.5
C6 C7 H7B	109.5
H7A C7 H7B	109.5
C6 C7 H7C	109.5
H7A C7 H7C	109.5
H7B C7 H7C	109.5
C6 C8 H8A	109.5
C6 C8 H8B	109.5
H8A C8 H8B	109.5
C6 C8 H8C	109.5
H8A C8 H8C	109.5
H8B C8 H8C	109.5
C21 C20 C25	116.17(18)
C21 C20 Si1	122.00(15)
C25 C20 Si1	121.30(14)
C22 C21 C20	121.9(2)
C22 C21 H21	119.1
C20 C21 H21	119.1
C23 C22 C21	120.5(2)
C23 C22 H22	119.8
C21 C22 H22	119.8
C22 C23 C24	119.2(2)
C22 C23 H23	120.4
C24 C23 H23	120.4
C25 C24 C23	120.3(2)
C25 C24 H24	119.9
C23 C24 H24	119.9
C24 C25 C20	122.00(19)
C24 C25 H25	119.0
C20 C25 H25	119.0
C31 C30 C35	117.22(16)
C31 C30 Si1	124.03(13)
C35 C30 Si1	118.75(15)
C30 C31 C32	121.87(19)
C30 C31 H31	119.1
C32 C31 H31	119.1
C33 C32 C31	119.4(2)
C33 C32 H32	120.3
C31 C32 H32	120.3
C34 C33 C32	120.22(19)
C34 C33 H33	119.9
C32 C33 H33	119.9
C33 C34 C35	120.57(19)
C33 C34 H34	119.7

C35 C34 H34	119.7
C34 C35 C30	120.7(2)
C34 C35 H35	119.6
C30 C35 H35	119.6
C20A Si1A C30A	108.61(8)
C20A Si1A C1A	112.10(8)
C30A Si1A C1A	113.53(9)
C20A Si1A C4A	115.97(8)
C30A Si1A C4A	111.04(7)
C1A Si1A C4A	95.24(8)
C2A O2A H2AO	110.4(15)
C3A O3A H3AO	109(2)
C5A O5A H5AO	102.3(16)
C2A C1A Si1A	104.07(12)
C2A C1A H1AA	110.9
Si1A C1A H1AA	110.9
C2A C1A H1AB	110.9
Si1A C1A H1AB	110.9
H1AA C1A H1AB	109.0
O2A C2A C1A	107.90(15)
O2A C2A C3A	109.26(16)
C1A C2A C3A	107.85(15)
O2A C2A H2A	110.6
C1A C2A H2A	110.6
C3A C2A H2A	110.6
O3A C3A C2A	108.70(15)
O3A C3A C4A	113.27(16)
C2A C3A C4A	109.40(13)
O3A C3A H3A	108.5
C2A C3A H3A	108.5
C4A C3A H3A	108.5
C5A C4A C3A	112.19(12)
C5A C4A Si1A	118.08(11)
C3A C4A Si1A	102.23(11)
C5A C4A H4A	108.0
C3A C4A H4A	108.0
Si1A C4A H4A	108.0
O5A C5A C6A	109.07(14)
O5A C5A C4A	108.63(13)
C6A C5A C4A	115.03(13)
O5A C5A H5A	108.0
C6A C5A H5A	108.0
C4A C5A H5A	108.0
C7A C6A C5A	113.12(16)
C7A C6A C8A	110.73(17)
C5A C6A C8A	110.45(16)
C7A C6A H6A	107.4
C5A C6A H6A	107.4
C8A C6A H6A	107.4
C6A C7A H7AA	109.5
C6A C7A H7AB	109.5
H7AA C7A H7AB	109.5
C6A C7A H7AC	109.5
H7AA C7A H7AC	109.5

H7AB C7A H7AC	109.5
C6A C8A H8AA	109.5
C6A C8A H8AB	109.5
H8AA C8A H8AB	109.5
C6A C8A H8AC	109.5
H8AA C8A H8AC	109.5
H8AB C8A H8AC	109.5
C21A C20A C25A	116.60(16)
C21A C20A Si1A	123.15(14)
C25A C20A Si1A	120.19(15)
C20A C21A C22A	121.81(19)
C20A C21A H21A	119.1
C22A C21A H21A	119.1
C23A C22A C21A	119.8(2)
C23A C22A H22A	120.1
C21A C22A H22A	120.1
C24A C23A C22A	119.68(19)
C24A C23A H23A	120.2
C22A C23A H23A	120.2
C23A C24A C25A	120.1(2)
C23A C24A H24A	119.9
C25A C24A H24A	119.9
C24A C25A C20A	122.0(2)
C24A C25A H25A	119.0
C20A C25A H25A	119.0
C31A C30A C35A	115.61(19)
C31A C30A Si1A	122.19(15)
C35A C30A Si1A	121.96(15)
C32A C31A C30A	122.5(2)
C32A C31A H31A	118.7
C30A C31A H31A	118.7
C33A C32A C31A	120.2(2)
C33A C32A H32A	119.9
C31A C32A H32A	119.9
C32A C33A C34A	118.8(2)
C32A C33A H33A	120.6
C34A C33A H33A	120.6
C33A C34A C35A	121.0(2)
C33A C34A H34A	119.5
C35A C34A H34A	119.5
C34A C35A C30A	121.8(2)
C34A C35A H35A	119.1
C30A C35A H35A	119.1
diffn_measured_fraction_theta_max	0.770
diffn_reflns_theta_full	30.62
diffn_measured_fraction_theta_full	0.770
refine_diff_density_max	0.359
refine_diff_density_min	-0.240
refine_diff_density_rms	0.041

Crystallographic data 21a

Figure S53. X-ray crystal structure of 21a

```

audit_creation_method          SHELXL-97
chemical_name_systematic
chemical_formula_moiety        'C26 H40 N2 O5 Os Si, (H2 O)'
chemical_formula_sum            'C26 H42 N2 O6 Os Si'
chemical_formula_weight        696.91

loop_
atom_type_symbol
atom_type_description
atom_type_scatter_dispersion_real
atom_type_scatter_dispersion_imag
atom_type_scatter_source
'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'H' 'H' 0.0000
0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'N' 'N' 0.0061
0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'O' 'O' 0.0106
0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'Os' 'Os' -
1.2165 7.6030
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'Si' 'Si' 0.0817
0.0704
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

symmetry_cell_setting          monoclinic
symmetry_space_group_name_H-M  'P 21/n'

loop_
symmetry_equiv_pos_as_xyz
'x, y, z'
'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x-1/2, -y-1/2, z-1/2'

cell_length_a                  13.446(3)
cell_length_b                  9.983(2)
cell_length_c                  21.619(4)
cell_angle_alpha               90.00
cell_angle_beta                91.76(3)
cell_angle_gamma               90.00
cell_volume                    2900.6(10)
cell_formula_units_Z           4
cell_measurement_temperature    293(2)
cell_measurement_reflns_used    5700
cell_measurement_theta_min      4.05
cell_measurement_theta_max      23.9

exptl_crystal_description      platelet
exptl_crystal_colour           dark brown-grey
exptl_crystal_size_max         0.79
exptl_crystal_size_mid         0.59
exptl_crystal_size_min         0.24
exptl_crystal_density_meas     ?

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exptl_crystal_density_diffn      1.596
exptl_crystal_density_method    'not measured'
exptl_crystal_F_000             1400
exptl_absorpt_coefficient_mu     4.478
exptl_absorpt_correction_type    'integration'
exptl_absorpt_correction_T_min   0.0890
exptl_absorpt_correction_T_max   0.3804
exptl_absorpt_process_details    ?

```

exptl_special_details

The crystal habitus consisted of the partial {0 $\bar{1}$ =1} prism, the {10 $\bar{1}$ } pinacoid and the (101), ($\bar{1}$ =11 $\bar{2}$), ($\bar{1}$ =12 $\bar{2}$), (54 $\bar{3}$) and ($\bar{1}$ =3 $\bar{1}$ =6) pedions. The (10 $\bar{1}$) is the platelet faces.

```

diffn_ambient_temperature        293(2)
diffn_radiation_wavelength       0.71073
diffn_radiation_type             MoK $\alpha$ 
diffn_radiation_source           'fine-focus sealed tube'
diffn_radiation_monochromator     graphite
diffn_measurement_device_type     'Stoe IPDS'
diffn_measurement_method         '\f scans'
diffn_detector_area_resol_mean   6.67
diffn_standards_number           0
diffn_standards_interval_count   ?
diffn_standards_interval_time    ?
diffn_standards_decay_%          ?
diffn_reflns_number              17403
diffn_reflns_av_R_equivalents    0.0622
diffn_reflns_av_sigmaI/netI      0.0384
diffn_reflns_limit_h_min         -15
diffn_reflns_limit_h_max         15
diffn_reflns_limit_k_min         -11
diffn_reflns_limit_k_max         11
diffn_reflns_limit_l_min         -24
diffn_reflns_limit_l_max         24
diffn_reflns_theta_min           1.88
diffn_reflns_theta_max           24.03
reflns_number_total              4433
reflns_number_gt                 4203
reflns_threshold_expression       >2sigma(I)

computing_data_collection         'Stoe IPDS'
computing_cell_refinement         'Stoe IPDS'
computing_data_reduction          'Stoe IPDS & Stoe XRed 1.22'
computing_structure_solution      'SHELXS-97 (Sheldrick, 1990)'
computing_structure_refinement    'SHELXL-97 (Sheldrick, 1997)'
computing_molecular_graphics      'Bruker SHELXTL'
computing_publication_material    'SHELXL-97 (Sheldrick, 1997)'

refine_ls_structure_factor_coef   Fsqd

```

refine_ls_matrix_type	full
refine_ls_weighting_scheme	sigma
atom_sites_solution_primary	direct
atom_sites_solution_secondary	difmap
atom_sites_solution_hydrogens	geom
refine_ls_hydrogen_treatment	mixed
refine_ls_extinction_method	none
refine_ls_extinction_coef	?
refine_ls_number_reflns	4433
refine_ls_number_parameters	338
refine_ls_number_restraints	3
refine_ls_R_factor_all	0.0319
refine_ls_R_factor_gt	0.0304
refine_ls_wR_factor_ref	0.0612
refine_ls_wR_factor_gt	0.0610
refine_ls_goodness_of_fit_ref	2.862
refine_ls_restrained_S_all	2.861
refine_ls_shift/su_max	0.309
refine_ls_shift/su_mean	0.005

```

loop_
geom_bond_atom_site_label_1
geom_bond_atom_site_label_2
geom_bond_distance
geom_bond_site_symmetry_2
geom_bond_publ_flag

```

Bond distances (Angstroms)

Os1 O1	1.734(4)
Os1 O4	1.736(4)
Os1 O3	1.954(3)
Os1 O2	1.978(3)
Os1 N6	2.219(4)
Os1 N5	2.240(4)
Si1 C1	1.871(5)
Si1 C4	1.885(5)
Si1 C30	1.887(4)
Si1 C20	1.900(5)
O2 C2	1.406(5)
O3 C3	1.432(5)
O5 C5	1.413(7)
N5 C52	1.448(8)
N5 C56	1.480(9)
N5 C51	1.524(10)
N6 C62	1.439(6)
N6 C61	1.478(7)
N6 C65	1.548(7)
C56 C65	1.392(11)
C1 C2	1.543(6)
C2 C3	1.524(7)
C3 C4	1.547(6)
C4 C5	1.537(7)

C5 C6	1.508(8)
C6 C7	1.451(11)
C6 C8	1.528(9)
C20 C25	1.375(7)
C20 C21	1.419(7)
C21 C22	1.344(7)
C22 C23	1.395(8)
C23 C24	1.358(9)
C24 C25	1.400(7)
C30 C35	1.385(7)
C30 C31	1.395(7)
C31 C32	1.391(7)
C32 C33	1.376(8)
C33 C34	1.404(9)
C34 C35	1.353(7)

```

loop_
geom_angle_atom_site_label_1
geom_angle_atom_site_label_2
geom_angle_atom_site_label_3
geom_angle
geom_angle_site_symmetry_1
geom_angle_site_symmetry_3
geom_angle_publ_flag

```

Bond angles (degrees)

O1 Os1 O4	163.03(15)
O1 Os1 O3	96.86(16)
O4 Os1 O3	96.64(15)
O1 Os1 O2	97.23(16)
O4 Os1 O2	94.29(14)
O3 Os1 O2	84.36(13)
O1 Os1 N6	84.25(16)
O4 Os1 N6	84.44(15)
O3 Os1 N6	94.69(14)
O2 Os1 N6	178.32(14)
O1 Os1 N5	84.1(2)
O4 Os1 N5	82.07(19)
O3 Os1 N5	177.57(15)
O2 Os1 N5	97.78(17)
N6 Os1 N5	83.14(18)
C1 Si1 C4	95.9(2)
C1 Si1 C30	112.4(2)
C4 Si1 C30	111.2(2)
C1 Si1 C20	113.5(2)
C4 Si1 C20	114.5(2)
C30 Si1 C20	108.9(2)
C2 O2 Os1	110.7(2)
C3 O3 Os1	110.0(3)
C52 N5 C56	111.9(7)
C52 N5 C51	108.2(6)

C56 N5 C51	108.1(7)
C52 N5 Os1	114.7(4)
C56 N5 Os1	103.1(4)
C51 N5 Os1	110.6(4)
C62 N6 C61	109.1(5)
C62 N6 C65	111.3(5)
C61 N6 C65	108.0(5)
C62 N6 Os1	112.4(3)
C61 N6 Os1	111.7(3)
C65 N6 Os1	104.1(3)
C65 C56 N5	117.1(7)
C56 C65 N6	114.5(5)
C2 C1 Si1	106.2(3)
O2 C2 C3	109.3(3)
O2 C2 C1	112.0(4)
C3 C2 C1	108.6(3)
O3 C3 C2	107.2(4)
O3 C3 C4	109.6(4)
C2 C3 C4	110.9(4)
C5 C4 C3	112.6(4)
C5 C4 Si1	116.2(3)
C3 C4 Si1	102.2(3)
O5 C5 C6	107.5(6)
O5 C5 C4	111.9(4)
C6 C5 C4	112.5(4)
C7 C6 C5	117.6(7)
C7 C6 C8	111.0(7)
C5 C6 C8	110.1(6)
C25 C20 C21	119.0(5)
C25 C20 Si1	119.6(4)
C21 C20 Si1	121.3(4)
C22 C21 C20	120.8(6)
C21 C22 C23	119.9(6)
C24 C23 C22	120.3(5)
C23 C24 C25	120.6(6)
C20 C25 C24	119.4(6)
C35 C30 C31	116.6(4)
C35 C30 Si1	121.5(4)
C31 C30 Si1	121.6(4)
C32 C31 C30	121.4(5)
C33 C32 C31	119.6(5)
C32 C33 C34	119.9(5)
C35 C34 C33	118.7(5)
C34 C35 C30	123.7(5)
diffn_measured_fraction_theta_max	0.969
diffn_reflns_theta_full	24.03
diffn_measured_fraction_theta_full	0.969
refine_diff_density_max	0.771
refine_diff_density_min	-0.911
refine_diff_density_rms	0.081

Crystallographic Data 22c

Figure S54. X-ray crystal structure of 22c

```

audit_creation_method      SHELXL-97
chemical_formula_moiety    'C25 H26 O2 Si'
chemical_formula_weight    386.55

atom_type_symbol
atom_type_description
atom_type_scatter_dispersion_real
atom_type_scatter_dispersion_imag
atom_type_scatter_source
'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'H' 'H'
0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'O' 'O' 0.0106
0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 'Si' 'Si'
0.0817 0.0704

```

'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

symmetry_cell_setting	monoclinic
symmetry_space_group_name_H-M	'C 2/m'
symmetry_equiv_pos_as_xyz	'x, y, z' '-x, y, -z+1/2' 'x+1/2, y+1/2, z' '-x+1/2, y+1/2, -z+1/2' '-x, -y, -z' 'x, -y, z-1/2' '-x+1/2, -y+1/2, -z' 'x+1/2, -y+1/2, z-1/2'
cell_length_a	26.856(5)
cell_length_b	20.058(4)
cell_length_c	16.646(3)
cell_angle_alpha	90.00
cell_angle_beta	91.11(3)
cell_angle_gamma	90.00
cell_volume	8965(3)
cell_formula_units_Z	16
cell_measurement_temperature	293(2)
cell_measurement_reflns_used	?
cell_measurement_theta_min	?
cell_measurement_theta_max	?
exptl_crystal_description	?
exptl_crystal_colour	'colourless'
exptl_crystal_size_max	?
exptl_crystal_size_mid	?
exptl_crystal_size_min	?
exptl_crystal_density_meas	?
exptl_crystal_density_diffn	1.146
exptl_crystal_density_method	'not measured'
exptl_crystal_F_000	3296
exptl_absorpt_coefficient_mu	0.121
exptl_absorpt_correction_type	'none'
exptl_absorpt_correction_T_min	?
exptl_absorpt_correction_T_max	?
exptl_absorpt_process_details	?
exptl_special_details	
diffn_ambient_temperature	293(2)
diffn_radiation_wavelength	0.71073
diffn_radiation_type	MoK\alpha
diffn_radiation_source	'fine-focus sealed tube'
diffn_radiation_monochromator	graphite
diffn_measurement_device_type	'Kuma CCD'
diffn_measurement_method	'\w scans'
diffn_detector_area_resol_mean	?
diffn_standards_number	0
diffn_standards_interval_count	?
diffn_standards_interval_time	?
diffn_standards_decay_%	?
diffn_reflns_number	37706
diffn_reflns_av_R_equivalents	0.0287


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diffn_reflns_av_sigmaI/netI      0.0314
diffn_reflns_limit_h_min         -38
diffn_reflns_limit_h_max         24
diffn_reflns_limit_k_min         -28
diffn_reflns_limit_k_max         27
diffn_reflns_limit_l_min         -23
diffn_reflns_limit_l_max         21
diffn_reflns_theta_min           3.38
diffn_reflns_theta_max           31.00
reflns_number_total               12968
reflns_number_gt                  7934
reflns_threshold_expression       >2sigma(I)

computing_data_collection         'Kuma Crysalis'
computing_cell_refinement         'Kuma Crysalis'
computing_data_reduction         'Kuma Crysalis'
computing_structure_solution      'SHELXS-97 (Sheldrick, 1990)'
computing_structure_refinement    'SHELXL-97 (Sheldrick, 1997)'
computing_molecular_graphics      'Bruker SHELXTL'
computing_publication_material    'SHELXL-97 (Sheldrick, 1997)'

refine_ls_structure_factor_coef    Fsqd
refine_ls_matrix_type              full
refine_ls_weighting_scheme         sigma
atom_sites_solution_primary        direct
atom_sites_solution_secondary      difmap
atom_sites_solution_hydrogens      geom
refine_ls_hydrogen_treatment       mixed
refine_ls_extinction_method         SHELXL
refine_ls_extinction_coef           0.00090(2)
refine_ls_extinction_expression     'Fc**kFc[1+0.001xFc^2^l^3^/sin(2\q)]^-1/4^'
refine_ls_number_reflns            12968
refine_ls_number_parameters         512
refine_ls_number_restraints         0
refine_ls_R_factor_all              0.0975
refine_ls_R_factor_gt               0.0582
refine_ls_wR_factor_ref             0.0730
refine_ls_wR_factor_gt              0.0715
refine_ls_goodness_of_fit_ref       2.846
refine_ls_restrained_S_all          2.846
refine_ls_shift/su_max              0.005
refine_ls_shift/su_mean             0.000

geom_bond_atom_site_label_1
geom_bond_atom_site_label_2
geom_bond_distance
geom_bond_site_symmetry_2
geom_bond_publ_flag

```

Bond distances (Angstroms)

Si1 C30	1.8728(15)
Si1 C1	1.8832(15)
Si1 C20	1.8854(15)
Si1 C4	1.9055(14)
O5 C5	1.4388(19)
O23 C2	1.4512(16)
O23 C3	1.4564(16)
C1 C2	1.5003(19)
C2 C3	1.471(2)
C3 C4	1.5182(17)
C4 C5	1.5394(17)
C5 C6	1.5345(18)
C6 C7	1.5188(19)
C6 C13	1.5451(18)
C7 C12	1.387(2)
C7 C8	1.390(2)
C8 C9	1.390(2)
C9 C10	1.366(3)
C10 C11	1.364(3)
C11 C12	1.385(2)
C20 C25	1.382(2)
C20 C21	1.3845(19)
C21 C22	1.391(2)
C22 C23	1.363(2)
C23 C24	1.352(2)
C24 C25	1.394(2)
C30 C31	1.3786(19)
C30 C35	1.393(2)
C31 C32	1.387(2)
C32 C33	1.359(2)
C33 C34	1.378(2)
C34 C35	1.3960(19)
Si1A C30A	1.8633(18)
Si1A C20A	1.8768(18)
Si1A C1A	1.8842(17)
Si1A C4A	1.9019(14)
O5A C5A	1.4497(18)
O23A C3A	1.4465(19)
O23A C2A	1.449(2)
C1A C2A	1.499(2)
C2A C3A	1.459(2)
C3A C4A	1.5152(18)
C4A C5A	1.5296(18)
C5A C6A	1.5467(17)
C6A C7A	1.5155(19)
C6A C13A	1.5354(18)
C7A C12A	1.3839(19)
C7A C8A	1.388(2)
C8A C9A	1.381(2)
C9A C10A	1.370(3)
C10A C11A	1.364(3)

C11A	C12A	1.390(2)
C20A	C21A	1.384(2)
C20A	C25A	1.396(2)
C21A	C22A	1.395(3)
C22A	C23A	1.383(3)
C23A	C24A	1.352(3)
C24A	C25A	1.385(3)
C30A	C35A	1.349(2)
C30A	C31A	1.366(2)
C31A	C32A	1.392(3)
C32A	C33A	1.346(4)
C33A	C34A	1.325(3)
C34A	C35A	1.411(2)

Bond angles (degrees)

```

geom_angle_atom_site_label_1
geom_angle_atom_site_label_2
geom_angle_atom_site_label_3
geom_angle
geom_angle_site_symmetry_1
geom_angle_site_symmetry_3
geom_angle_publ_flag
C30 Si1 C1      111.59(7)
C30 Si1 C20     109.35(7)
C1 Si1 C20      111.32(7)
C30 Si1 C4      114.04(6)
C1 Si1 C4       96.63(7)
C20 Si1 C4      113.44(6)
C2 O23 C3       60.79(9)
C2 C1 Si1      105.05(10)
O23 C2 C3       59.78(9)
O23 C2 C1      114.22(12)
C3 C2 C1       116.44(13)
O23 C3 C2       59.43(9)
O23 C3 C4      114.39(11)
C2 C3 C4       117.03(13)
C3 C4 C5       111.18(11)
C3 C4 Si1      103.53(10)
C5 C4 Si1      117.49(9)
O5 C5 C6       108.83(12)
O5 C5 C4       112.03(11)
C6 C5 C4       114.36(11)
C7 C6 C5       110.01(11)
C7 C6 C13      113.62(13)
C5 C6 C13      112.41(11)
C12 C7 C8      117.13(15)
C12 C7 C6      123.58(16)
C8 C7 C6       119.29(15)
C7 C8 C9       121.08(18)
C10 C9 C8      120.3(2)
C11 C10 C9     119.8(2)

```

C10 C11 C12	120.3(2)
C11 C12 C7	121.46(19)
C25 C20 C21	116.01(15)
C25 C20 Si1	122.88(12)
C21 C20 Si1	121.08(12)
C20 C21 C22	121.79(17)
C23 C22 C21	120.30(18)
C24 C23 C22	119.61(18)
C23 C24 C25	120.05(18)
C20 C25 C24	122.24(17)
C31 C30 C35	117.18(14)
C31 C30 Si1	122.42(12)
C35 C30 Si1	120.37(12)
C30 C31 C32	121.62(16)
C33 C32 C31	120.32(19)
C32 C33 C34	120.15(18)
C33 C34 C35	119.24(18)
C30 C35 C34	121.48(16)
C30A Si1A C20A	107.24(9)
C30A Si1A C1A	112.16(8)
C20A Si1A C1A	113.79(9)
C30A Si1A C4A	115.01(8)
C20A Si1A C4A	112.30(7)
C1A Si1A C4A	96.28(7)
C3A O23A C2A	60.53(11)
C2A C1A Si1A	104.17(11)
O23A C2A C3A	59.67(11)
O23A C2A C1A	114.79(17)
C3A C2A C1A	116.93(15)
O23A C3A C2A	59.80(11)
O23A C3A C4A	113.77(13)
C2A C3A C4A	116.73(14)
C3A C4A C5A	111.00(11)
C3A C4A Si1A	103.33(10)
C5A C4A Si1A	116.39(10)
O5A C5A C4A	111.39(12)
O5A C5A C6A	107.10(11)
C4A C5A C6A	115.09(11)
C7A C6A C13A	113.83(13)
C7A C6A C5A	109.15(11)
C13A C6A C5A	112.70(12)
C12A C7A C8A	116.93(16)
C12A C7A C6A	122.92(15)
C8A C7A C6A	120.01(14)
C9A C8A C7A	122.28(18)
C10A C9A C8A	119.6(2)
C11A C10A C9A	119.5(2)
C10A C11A C12A	120.96(19)
C7A C12A C11A	120.75(18)
C21A C20A C25A	116.24(18)
C21A C20A Si1A	122.38(16)
C25A C20A Si1A	121.35(15)
C20A C21A C22A	122.0(2)
C23A C22A C21A	119.7(2)

C24A	C23A	C22A	119.3(3)
C23A	C24A	C25A	121.0(2)
C24A	C25A	C20A	121.7(2)
C35A	C30A	C31A	115.25(19)
C35A	C30A	Si1A	125.45(15)
C31A	C30A	Si1A	119.27(18)
C30A	C31A	C32A	121.8(2)
C33A	C32A	C31A	121.3(3)
C34A	C33A	C32A	118.5(3)
C33A	C34A	C35A	120.0(3)
C30A	C35A	C34A	123.1(2)

diffraction_measured_fraction_theta_max	0.907
diffraction_reflns_theta_full	31.00
diffraction_measured_fraction_theta_full	0.907
refine_diff_density_max	0.310
refine_diff_density_min	-0.235
refine_diff_density_rms	0.036