Intermolecular Silacarbonyl Ylide Cycloadditions: A Direct Pathway to Oxasilacyclopentenes

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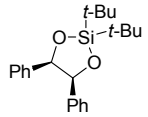
Supporting Information

Contents:

Experimental Section

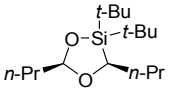
General. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature using Bruker DRX 400, DRX 500, or DRX 600 spectrometers, as indicated. The data are reported as follows: chemical shift in ppm from an internal tetramethylsilane standard on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Due to difficulties with purification for certain products, only characteristic peaks are listed in tabulated ^{1}H NMR spectroscopic data. High resolution mass spectra was acquired on a VG analytical 7070E or Fisions Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM reagents silica gel (SiO_2) 60 (230-400). Silacyclopropanes were stored and manipulated in an Innovative Technologies nitrogen dry box. All reactions were performed under an atmosphere of nitrogen or argon in glassware that had been flame-dried under a stream of nitrogen or under vacuum. Solvents were distilled or filtered through alumina before use. Sodium hydride and potassium hydride were used dry and weighed out in a nitrogen dry box. Cyclohexene silacyclopropane was constructed by known methods.[1,2]

I. Silacarbonyl Cycloadditions



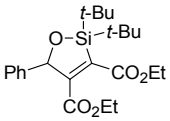
7

Dioxasilacyclopentane 7. To a solution of benzaldehyde (0.212 g, 2.00 mmol) in 6.7 mL of toluene was added silacyclopropane **6** (0.224 g, 1.00 mmol). AgOTf (0.003 g, 0.01 mmol) was then added. The brown solution was maintained at ambient temperature for 15 min, at which point the mixture was concentrated *in vacuo*. The resultant yellow oil as purified by flash chromatography (98:2 hexanes:EtOAc) to afford **7** (0.255 g, 72%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.30 (m, 10H), 4.80 (s, 2H), 1.26 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 128.3, 128.1, 126.8, 84.6, 27.4, 21.6; IR (thin film) 2934, 2859, 1474, 1209, 1024, 853 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{22}H_{30}O_2SiNa$ $(M + Na)^+$ 355.2093, found 355.2101. Anal. Calcd for $C_{22}H_{30}O_2Si$: C, 74.53; H, 8.53. Found: C, 74.08; H, 8.55.



9

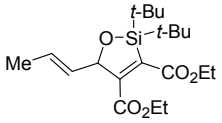
Dioxasilacyclopentane acetal 9. To a solution of *n*-butyraldehyde (0.144 g, 2.00 mmol) in 6.7 mL of toluene was added silacyclopropane **6** (0.224 g, 1.00 mmol). $CuBr_2$ (0.011 g, 0.05 mmol) was then added. The brown solution was maintained at ambient temperature for 12 h, at which point the mixture was concentrated *in vacuo*. The resultant yellow oil as purified by flash chromatography (98:2 hexanes:EtOAc) to afford **9** (0.253 g, 89%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (t, J = 4.0, 1H), 3.52–3.55 (m, 1H), 1.94–2.09 (m, 1H), 1.70–1.76 (m, 1H), 1.59–1.67 (m, 3H), 1.45–1.51 (m, 2H), 1.35–1.41 (m, 1H), 1.08 (s, 9H), 1.07 (s, 9H), 0.93–0.99 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.7, 70.0, 38.6, 33.4, 28.3, 27.9, 22.1, 20.6, 20.5, 17.8, 14.1; IR (thin film) 2935, 2860, 1473, 1365, 1009, 825 cm^{-1}; HRMS (APCI) *m* / *z* calcd for $C_{16}H_{35}O_2Si$ $(M + H)^+$ 287.2406, found 287.2401. Anal. Calcd for $C_{16}H_{34}O_2Si$: C, 67.07; H, 11.96. Found: C, 66.88; H, 11.92.



11

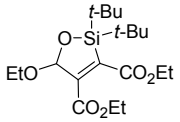
Representative procedure for the synthesis of oxasilacyclopentenes (oxasilacyclopentene 11). To a solution of benzaldehyde (0.109 g, 1.00 mmol) and diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol) in 6.7 mL of toluene was added silacyclopropane **6** (0.247 g, 1.10 mmol). AgOTf (0.003 g, 0.01 mmol) was then added. The brown solution was maintained at ambient temperature for 15 min, at which point the mixture was concentrated *in vacuo*. The resultant yellow oil as purified by flash chromatography

(95:5 hexanes:EtOAc) to afford **11** (0.356 g, 85%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.38 (m, 5H), 5.92 (s, 1H), 4.28–4.31 (m, 2H), 4.03–4.07 (m, 2H), 1.34 (t, *J* = 7.2, 3H), 1.15 (s, 9H), 1.11 (s, 9H), 1.03 (t, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 164.0, 154.9, 139.6, 139.4, 128.5, 128.4, 127.8, 84.8, 61.1, 61.0, 27.7, 27.2, 22.6, 21.0, 14.3, 13.8; IR (thin film) 3032, 2860, 1721, 1240, 1053, 825 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{23}H_{34}O_5SiNa$ $(M + Na)^+$ 441.2073, found 441.2077. Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 65.99; H, 8.19. Found: C, 65.73; H, 8.29.



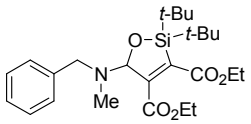
13a

Oxasilacyclopentene 13a. The representative procedure for the synthesis of oxasilacyclopentenes was followed using crotonaldehyde (0.035 g, 0.50 mmol), diethyl acetylenedicarboxylate (0.085 g, 0.50 mmol), silacyclopropane **6** (0.123 g, 0.55 mmol), AgOTf (0.002 g, 0.01 mmol), and 6.7 mL of toluene for 15 min. Purification by flash chromatography (95:5 hexanes:EtOAc) afforded **13a** (0.157 g, 82%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.90 (m, 1H), 5.42–5.47 (m, 1H), 5.32–5.34 (m, 1H), 4.21–4.28 (m, 4H), 1.72 (d, *J* = 6.6, 3H), 1.26–1.33 (m, 6H), 1.12 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 164.1, 155.0, 137.4, 130.1, 128.9, 83.7, 61.2, 60.9, 27.5, 27.1, 22.0, 20.7, 17.7, 14.2, 14.1; IR (thin film) 2936, 2862, 1732, 1257, 1038, 824 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{20}H_{34}O_5SiNa$ $(M + Na)^+$ 405.2073, found 405.2076.



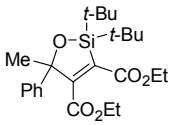
13b

Oxasilacyclopentene 13b. The representative procedure for the synthesis of oxasilacyclopentenes was followed using ethyl formate (0.074 g, 1.00 mmol), diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol), silacyclopropane **6** (0.247 g, 1.10 mmol), AgOTf (0.003 g, 0.01 mmol), and 6.7 mL of toluene for 15 min. Purification by flash chromatography (95:5 hexanes:EtOAc) afforded **13b** (0.248 g, 64%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (s, 1H), 4.18–4.32 (m, 4H), 3.87–3.95 (m, 1H), 3.65–3.73 (m, 1H), 1.28–1.33 (m, 6H), 1.24 (t, *J* = 7.0, 3H), 1.13 (s, 9H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 162.9, 148.8, 143.1, 103.0, 64.7, 61.2, 61.0, 27.4, 27.1, 21.0, 20.7, 15.3, 14.2, 14.0; IR (thin film) 2935, 2861, 1720, 1241, 1029, 825 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{19}H_{34}O_6SiNa$ $(M + Na)^+$ 409.2022, found 409.2020. Anal. Calcd for $C_{19}H_{34}O_6Si$: C, 59.04; H, 8.87. Found: C, 59.20; H, 8.88.



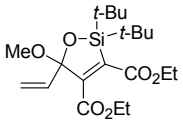
13c

Oxasilacyclopentene 13c. The representative procedure for the synthesis of oxasilacyclopentenes was followed using *N*-methyl-*N*-(benzyl)-formamide (0.111 g, 0.75 mmol), diethyl acetylenedicarboxylate (0.085 g, 0.50 mmol), silacyclopropane **6** (0.168 g, 0.75 mmol), AgOTf (0.003 g, 0.01 mmol), and 6.7 mL of toluene for 12 h at 50 °C. Purification by flash chromatography (95:5 hexanes:EtOAc) afforded **13c** (0.157 g, 68%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.30 (m, 5H), 5.63 (s, 1H), 4.19–4.24 (m, 2H), 4.25–4.33 (m, 2H), 3.85 (d, *J* = 13.6, 1H), 3.75 (d, *J* = 13.5, 1H), 2.31 (s, 3H), 1.27–1.32 (m, 6H), 1.18 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 166.0, 159.8, 139.2, 136.6, 128.6, 128.2, 127.0, 97.0, 61.3, 61.0, 57.5, 36.7, 27.7, 27.2, 22.4, 21.5, 14.2, 14.1; IR (thin film) 2924, 2709, 1730, 1470, 1062, 821 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{25}H_{39}NO_5SiNa$ $(M + Na)^+$ 484.2495, found 484.2505. Anal. Calcd for $C_{25}H_{39}NO_5Si$: C, 65.04; H, 8.51. Found: C, 65.16; H, 8.72.



13d

Oxasilacyclopentene 13d. The representative procedure for the synthesis of oxasilacyclopentenes was followed using acetophenone (0.129 g, 1.00 mmol), diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol), silacyclopropane **6** (0.247 g, 1.10 mmol), AgOTf (0.003 g, 0.01 mmol), and 6.7 mL of toluene for 3 h. Purification by flash chromatography (95:5 hexanes:EtOAc) afforded **13d** (0.333 g, 77%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.49 (m, 5H), 4.23–4.32 (m, 4H), 2.62 (s, 3H), 1.32 (t, *J* = 7.1, 3H), 1.27 (t, *J* = 7.1, 3H), 1.12 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 165.7, 159.4, 144.7, 138.4, 127.9, 127.3, 125.9, 88.2, 61.5, 60.9, 30.7, 28.0, 27.7, 21.3, 21.0, 14.3, 13.9; IR (thin film) 2969, 2860, 1720, 1240, 1037, 824 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{24}H_{36}O_5SiNa$ $(M + Na)^+$ 455.2230, found 455.2220. Anal. Calcd for $C_{24}H_{36}O_5Si$: C, 66.63; H, 8.39. Found: C, 66.61; H, 8.50.

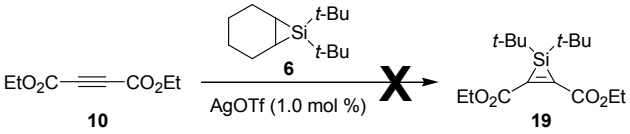


13e

Oxasilacyclopentene 13e. The representative procedure for the synthesis of oxasilacyclopentenes was followed using methyl acrylate (0.344 g, 4.00 mmol), diethyl acetylenedicarboxylate (0.170 g, 1.00 mmol), silacyclopropane **6** (0.897 g, 4.00 mmol), AgOTf (0.003 g, 0.01 mmol), and 6.7 mL of toluene for 15 min. Purification by flash chromatography (95:5 hexanes:EtOAc) afforded **13e** (0.295 g, 74%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15–6.22 (m, 1H), 5.66–5.71 (m, 1H), 5.43–5.46 (m,

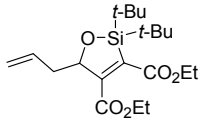
1H), 4.21–4.28 (m, 4H), 3.28 (s, 3H), 1.28–1.32 (m, 6H), 1.14 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 163.7, 153.3, 139.8, 134.5, 119.4, 106.5, 61.5, 61.0, 49.7, 27.7, 27.6, 21.1, 21.0, 14.2, 14.0; IR (thin film) 2936, 2861, 1732, 1243, 1059, 824 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{20}H_{34}O_6SiNa$ $(M + Na)^+$ 421.2022, found 421.2019. Anal. Calcd for $C_{20}H_{34}O_6Si$: C, 60.27; H, 8.60. Found: C, 60.36; H, 8.76.

II. Silacyclopropene Control Experiment



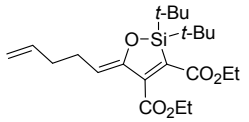
Silacyclopropene control experiment. To a J. Young tube was added diethyl acetylenedicarboxylate (0.017 g, 0.10 mmol), silacyclopropane **6** (0.022 g, 0.10 mmol), AgOTf (0.038 mL of a 0.026 M solution in benzene, 1.0 μmol), and 0.7 mL of benzene-d_6. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy at ambient temperature. After 15 min, all starting material had disappeared and two new peaks had formed. Neither peaks were located in the silacyclopropene range[3] (δ −71.7 to −65.3 ppm): ^{29}Si NMR (99.3 MHz, C_6D_6) δ 18.0, 4.8.

III. Oxasilacyclopentene functionalization



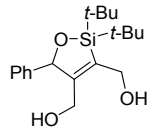
21

Oxasilacyclopentene 21. To a −78 °C solution of oxasilacyclopentene **13b** (0.210 g, 0.54 mmol) and $SnBr_4$ (0.475 g, 1.09 mmol) in 4.0 mL of CH_2Cl_2 was added allyltrimethylsilane (0.35 mL, 2.17 mmol). The reaction mixture was warmed to ambient temperature and maintained for 48 h. The solution was diluted with 15 mL of $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with 15 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (95:5 hexanes:EtOAc) to afford **21** (0.132 g, 64%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.99 (m, 1H), 5.08–5.14 (m, 2H), 4.95–4.98 (m, 1H), 4.20–4.29 (m, 4H), 2.56–2.58 (m, 1H), 2.27–2.30 (m, 1H), 1.29–1.32 (m, 6H), 1.10 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 164.4, 155.5, 138.4, 134.7, 117.4, 82.2, 61.4, 60.9, 40.3, 27.6, 27.1, 22.1, 20.7, 14.2, 14.0; IR (thin film) 2935, 2860, 1719, 1239, 1054, 824 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{20}H_{34}O_5SiNa$ $(M + Na)^+$ 405.2073, found 405.2072. Anal. Calcd for $C_{20}H_{34}O_5Si$: C, 62.79; H, 8.96. Found: C, 62.77; H, 8.99.



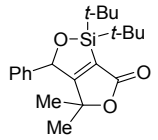
22

Oxasilacyclopentene 22. To a −78 °C solution of oxasilacyclopentene **13e** (0.100 g, 0.25 mmol) and $SnBr_4$ (0.219 g, 0.50 mmol) in 2.0 mL of CH_2Cl_2 was added allyltrimethylsilane (0.16 mL, 1.00 mmol). The reaction mixture was warmed to ambient temperature and maintained for 12 h. The solution was diluted with 10 mL of $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with 10 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (95:5 hexanes:EtOAc) to afford **22** (0.051 g, 50%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83–5.85 (m, 1H), 4.99–5.06 (m, 3H), 4.20–4.36 (m, 4H), 2.35–2.39 (m, 2H), 2.18–2.19 (m, 2H), 1.28–1.37 (m, 6H), 1.08 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 166.0, 155.0, 153.3, 138.3, 129.4, 114.9, 113.1, 61.7, 60.9, 33.2, 27.9, 27.8, 27.2, 25.3, 21.3, 14.2, 14.1; IR (thin film) 2935, 2861, 1738, 1239, 1090, 824 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{22}H_{37}O_5Si$ $(M + H)^+$ 409.2410, found 409.2404.



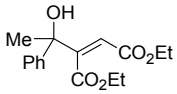
23

Diol 23. To a −78 °C solution of oxasilacyclopentene **11** (0.267 g, 0.64 mmol) in 5.0 mL of CH_2Cl_2 was added DIBAL–H (2.56 mL of a 1.00 M solution in hexanes, 2.56 mmol). The reaction mixture was warmed to ambient temperature and maintained for 12 h. The solution was diluted with 10 mL of H_2O and 10 mL NH_4Cl. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with 10 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (50:50 hexanes:EtOAc) to afford **23** (0.159 g, 74%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.35 (m, 5H), 5.56 (s, 1H), 4.58–4.59 (m, 2H), 4.11 (d, J = 13.2, 1H), 3.92 (d, J = 13.0, 1H), 2.48–2.66 (m, 2H), 1.12 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 141.1, 137.5, 128.7, 128.4, 128.1, 86.4, 60.3, 59.1, 28.3, 27.6, 22.3, 20.5; IR (thin film) 3326 (br), 2954, 2870, 1266, 1047, 823 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{19}H_{30}O_3SiNa$ $(M + Na)^+$ 357.1862, found 357.1862. Anal. Calcd for $C_{19}H_{30}O_3Si$: C, 68.22; H, 9.04. Found: C, 67.96; H, 9.17.



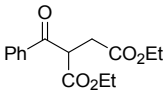
24

Lactone 24. To a solution of oxasilacyclopentene **11** (0.268 g, 0.64 mmol) in 4.3 mL of THF was added MeMgBr (1.37 mL of a 1.40 M solution in THF, 1.92 mmol). The colorless solution was maintained at ambient temperature for 3 h, at which point the mixture was diluted with 10 mL of NH_4Cl. The layers were separated, and the aqueous layer was extracted with hexanes (3 x 10 mL). The combined organic layers were washed with 10 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (95:5 hexanes:EtOAc) to afford **24** (0.161 g, 70%) as a white solid: mp 109 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.40 (m, 5H), 5.75 (s, 1H), 1.50 (s, 3H), 1.22 (s, 9H), 1.12 (s, 9H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 170.1, 138.2, 130.5, 129.3, 129.0, 127.6, 86.0, 81.3, 27.9, 27.1, 26.0, 25.6, 22.4, 20.3; IR (thin film) 2933, 2859, 1755, 1270, 1018, 823 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{21}H_{30}O_3SiNa$ $(M + Na)^+$ 381.1862, found 381.1866. Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.08; H, 8.43.



25

Alcohol 25. To a solution of tetrabutylammonium fluoride (0.60 mL of a 1.0 M solution in THF, 0.60 mmol) and $Pd(dba)_2$ (0.018 g, 0.03 mmol) in 3.0 mL of THF was added a solution of oxasilacyclopentene **11** (0.125 g, 0.30 mmol) in 1.0 mL of THF. The solution was maintained at ambient temperature for 12 h, at which point the mixture was diluted with 15 mL of H_2O and 15 mL of MTBE. The layers were separated, and the aqueous layer was extracted with MTBE (3 x 15 mL). The combined organic layers were washed with H_2O (5 x 15 mL) followed by 15 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (60:40 hexanes:EtOAc) to afford **25** (0.059 g, 67%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.47 (m, 2H), 7.36–7.38 (m, 2H), 7.27–7.31 (m, 1H), 6.13 (s, 1H), 4.10–4.22 (m, 4H), 3.17 (br s, 1H), 1.80 (s, 3H), 1.29 (t, *J* = 7.2, 3H), 1.10 (t, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 165.1, 135.3, 143.8, 128.4, 127.8, 125.6, 120.2, 75.6, 61.6, 61.1, 28.3, 14.1, 13.7. ^1H and ^{13}C NMR spectroscopic data matched those previously reported.[4]

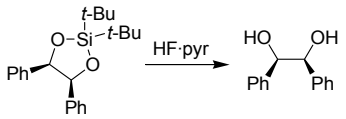


27

Ketone 27. To a solution of tetrabutylammonium fluoride (0.48 mL of a 1.0 M solution in THF, 0.48 mmol) and $Pd(dba)_2$ (0.014 g, 0.02 mmol) in 2.0 mL of THF was added a solution of oxasilacyclopentene **11** (0.100 g, 0.24 mmol) in 1.0 mL of THF. The solution was maintained at ambient temperature for 12 h, at which point the mixture was diluted with 10 mL of H_2O and 10 mL of

MTBE. The layers were separated, and the aqueous layer was extracted with MTBE (3 x 10 mL). The combined organic layers were washed with H_2O (5 x 10 mL) followed by 10 mL of saturated aqueous NaCl, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resultant yellow oil was purified by flash chromatography (78:20:2 hexanes:CH_2Cl_2:NEt_3) to afford **27** (0.037 g, 58%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.06 (m, 2H), 7.59–7.61 (m, 1H), 7.48–7.52 (m, 2H), 4.87 (dd, *J* = 7.7, 6.7, 1H), 4.11–4.18 (m, 4H), 2.99–3.13 (m, 2H), 1.24 (t, *J* = 7.1, 3H), 1.16 (t, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 171.3, 168.8, 136.0, 133.7, 128.9, 128.8, 61.9, 61.1, 49.7, 33.3, 14.1, 14.0. ^{1}H and ^{13}C NMR spectroscopic data matched those previously reported.[5]

IV. Stereochemical Proofs of Dioxasilacyclopentanes

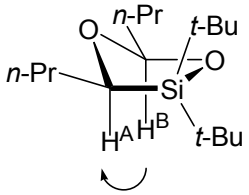


7 **S1**

Diol S1. The stereochemistry of dioxasilacyclopentane **7** was determined by hydrolysis to afford known diol **S1**. The stereochemistry of **S1** was determined by ^{1}H NMR spectroscopic analysis and comparison to literature values.[6,7]

Dioxasilacyclopentane 5. The stereochemistry of dioxasilacyclopentane **9** was determined using DPFGSE-nuclear Overhauser effect (nOe) enhancements.

Figure S1. Relevant DPFGSE-nOe data (mixing time 0.5 s):



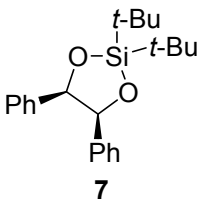
S2

H^A irradiated: H^B (1.7%)
H^B irradiated: H^A (1.6%)

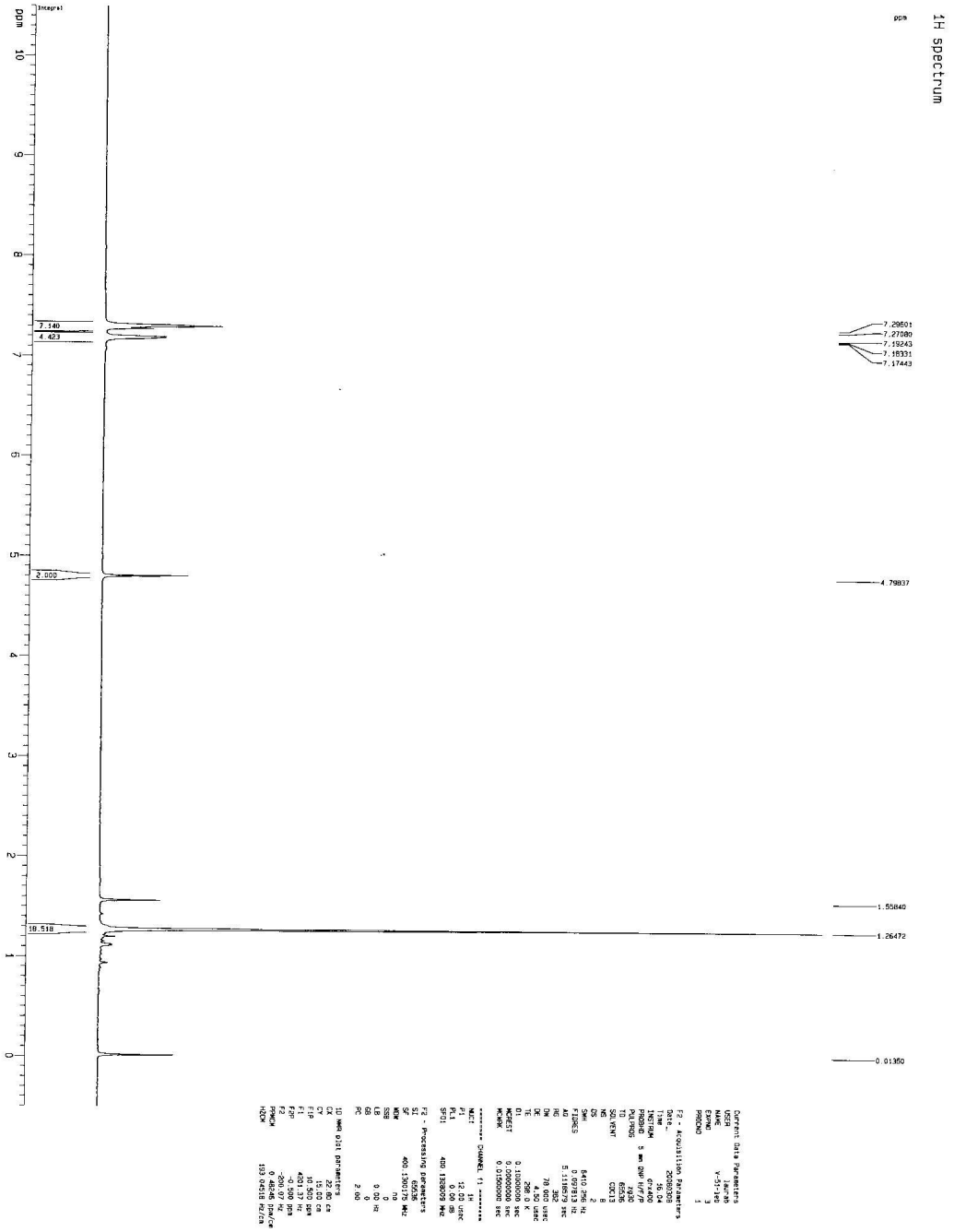
V. References

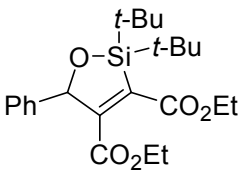
(1) Driver, T. G.; Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6524–6525.
(2) Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095–2096.
(3) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824–4827.
(4) Harrowven, D. C.; Poon, H. S. *Tetrahedron* **1996**, *52*, 1389–1398.
(5) Mattson, A. E.; Bharadwaj, A. R.; Scheidt, K. J. *J. Am. Chem. Soc.* **2004**, *126*, 2314–2315.
(6) Corey, E. J.; Hopkins, P. B. *Tetrahedron. Lett.* **1982**, *23*, 4871–4874.
(7) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76–81.

VI. Selected Spectra



7

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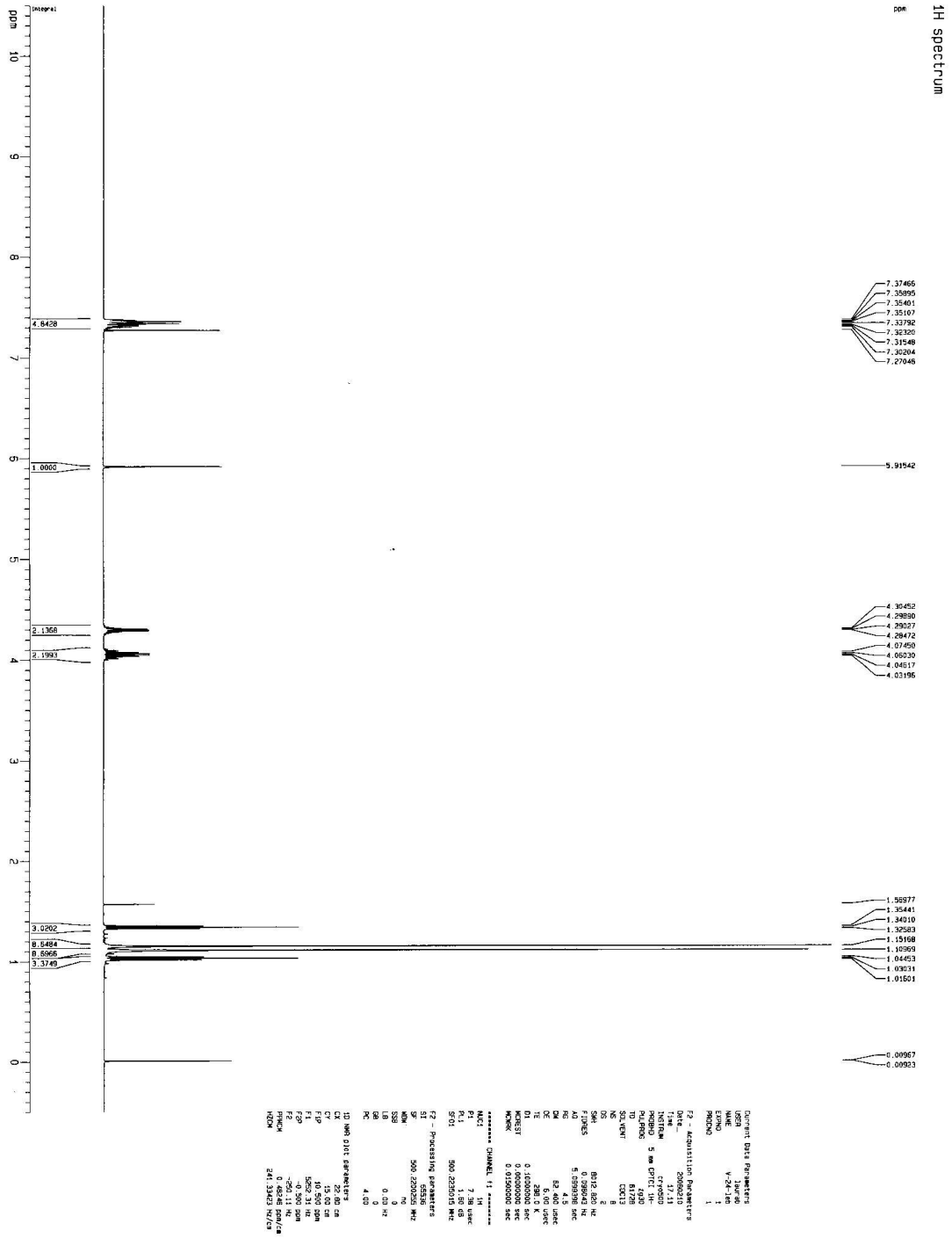
O–Si–t-Bu
Ph
CO2Et
CO2Et

11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2.1993
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7.33792
7.32320
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7.30204
7.27048
5.91542
4.30452
4.29890
4.29027
4.28472
4.07458
4.06030
4.04617
4.03196
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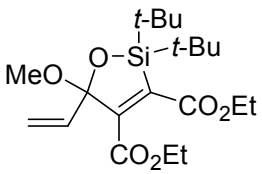
0.00923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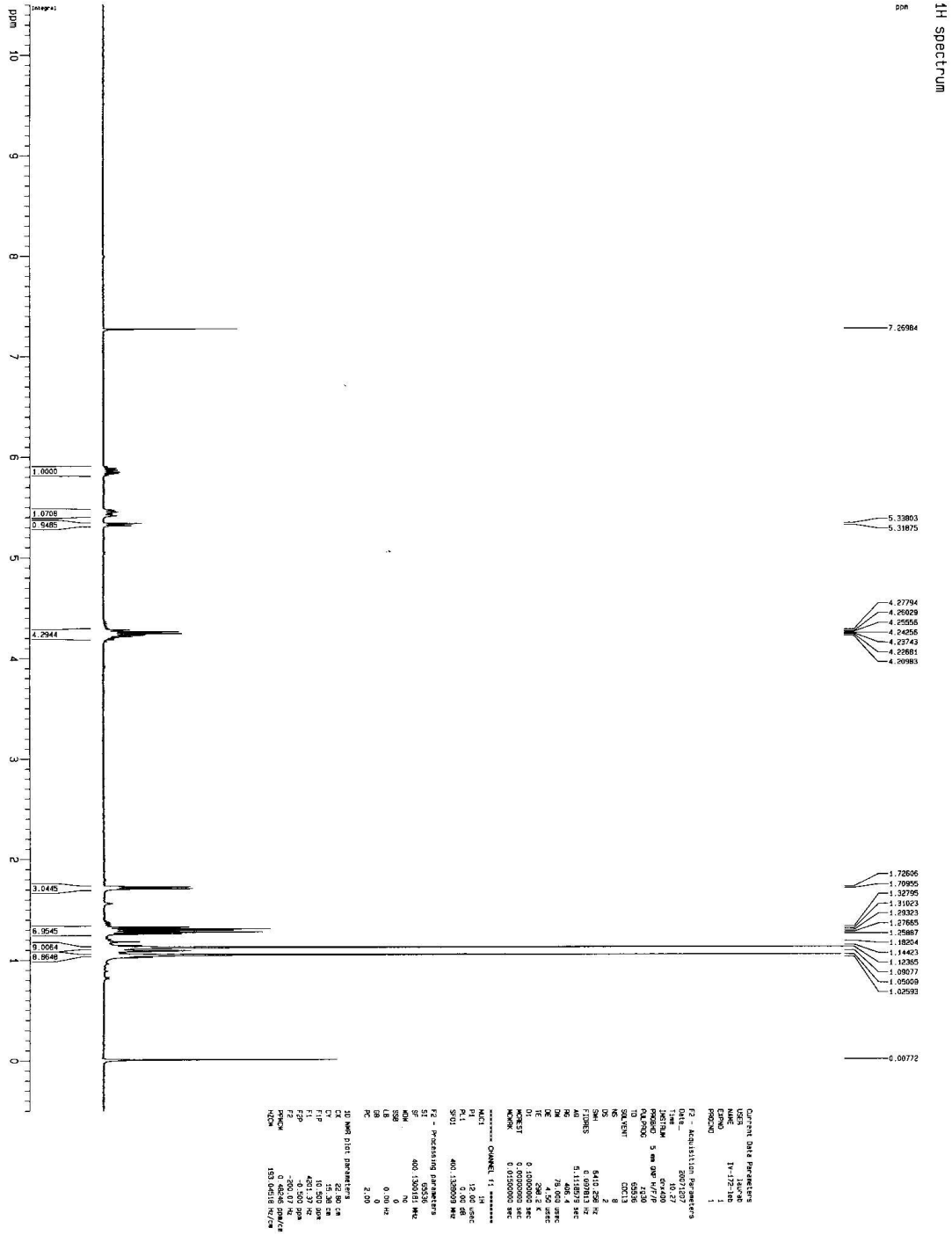
O–Si–t-Bu
MeO
CO2Et
CO2Et

13e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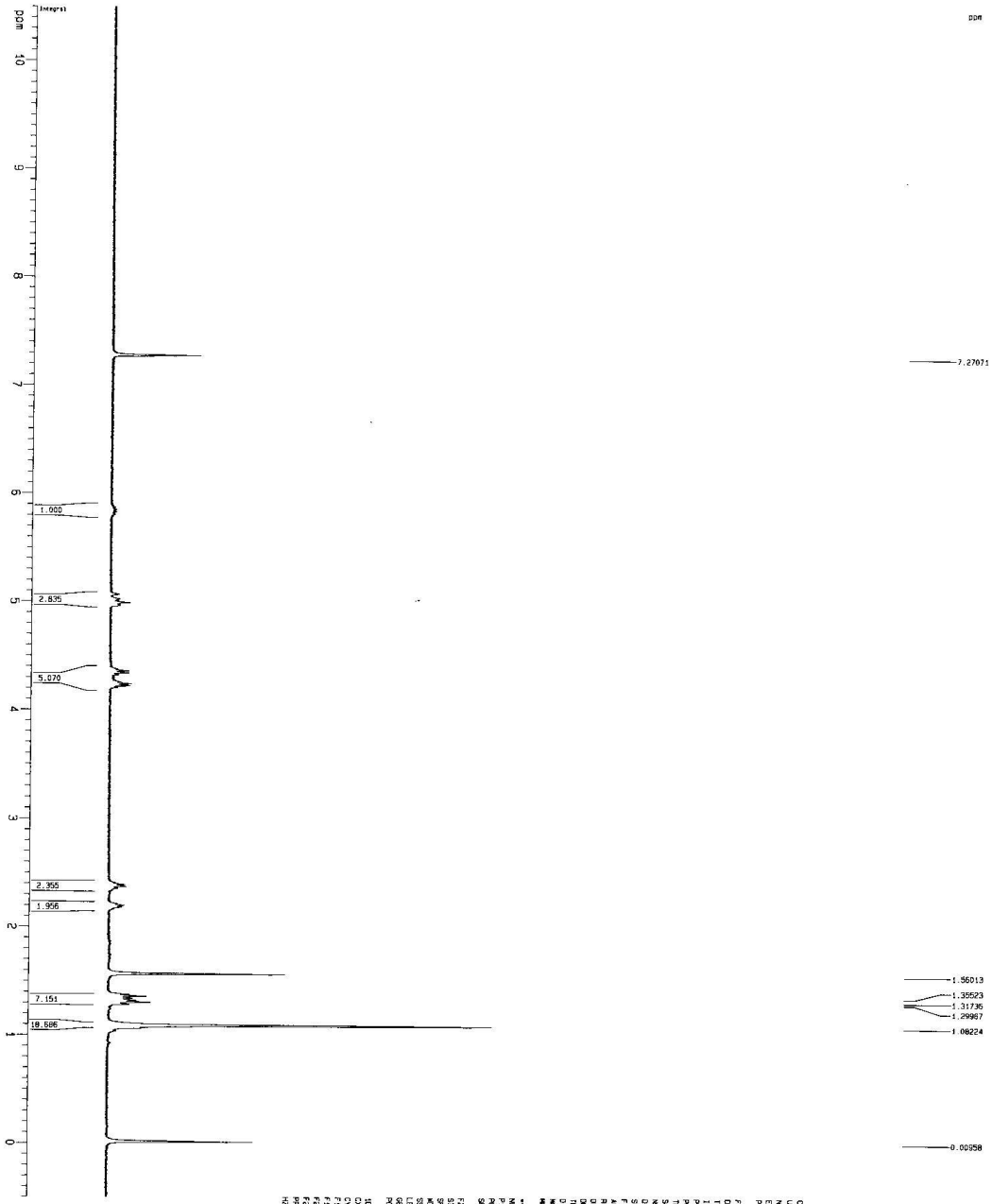
1.05009
1.02593
0.00772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5.070
2.355
1.956
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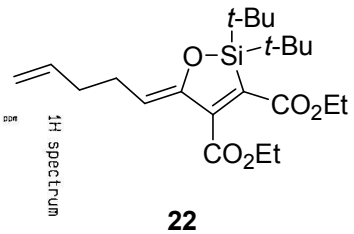
18.686
7.27071
1.56013
1.35523
1.31736
1.29967
1.08224
0.00958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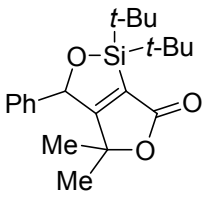
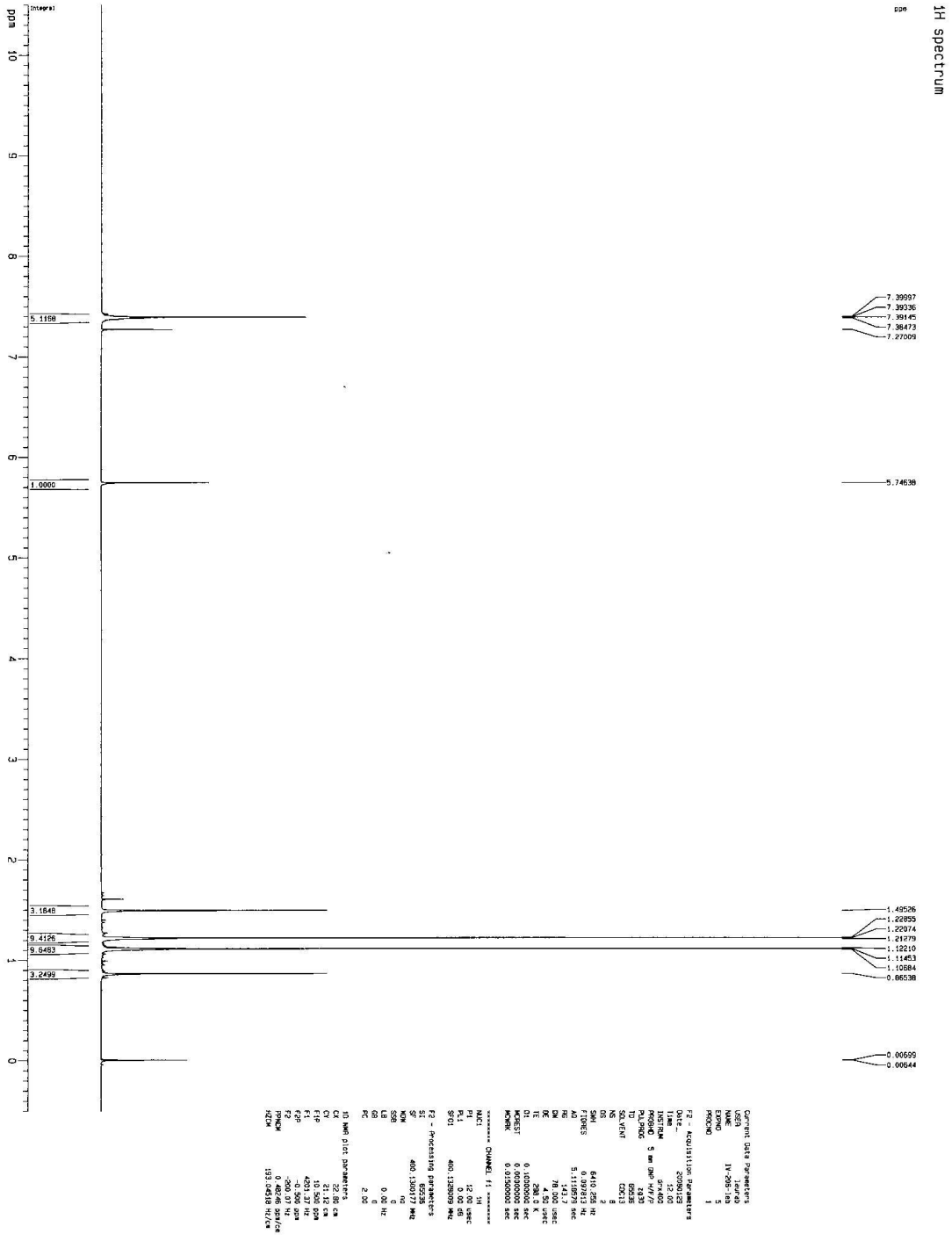
t-Bu
O–Si
CO2Et
CO2Et
1H spectrum

22


t-Bu
O–Si–t-Bu
Ph
O
Me
O
Me

24


1H spectrum
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Integral
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7.27009
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1.49526
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1.12210
1.11453
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