

Supporting Information

Tandem Carbon–Carbon Bond Constructions via Catalyzed Cyanation/Brook Rearrangement/Acylation Reactions of Acylsilanes

Xin Linghu, David A. Nicewicz, and Jeffrey S. Johnson*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

jsj@unc.edu

Experimental Section

Materials and Methods: General. Infrared (IR) spectra were obtained using a Nicolet 560-E.S.P. infrared spectrometer. Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on the following instruments: Bruker model Avance 400 (^1H NMR at 400 MHz and ^{13}C NMR at 100 MHz) and Varian Gemini 300 (^1H NMR at 300 MHz and ^{13}C at 75 MHz) spectrometers with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.23 ppm and ^{13}C NMR: CDCl_3 at 77.0 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet), coupling constants (Hz), and integration. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA. Analytical thin layer chromatography (TLC) was performed on Whatman 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light and aqueous ceric ammonium nitrate molybdate solution followed by heating. Purification of the reaction products was carried out by flash chromatography using Sorbent Technologies silica gel 60 (32–63 μm). All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Yield refers to isolated yield of analytically pure material. Yields are reported for a specific experiment and as a result may differ slightly from those found in the tables, which are averages of at least two experiments. Diethyl ether, tetrahydrofuran, and toluene were dried by passage through a column of neutral alumina under nitrogen prior to use.¹⁷ Dithianes were prepared from the corresponding aldehydes using Graham's procedure.¹⁸ Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. 18-crown-6 was recrystallized from acetonitrile. Potassium cyanide was dried at 180 °C under vacuum. **CAUTION:** Potassium cyanide is toxic and releases HCN upon exposure to acid. While we have encountered no problems in the chemistry described herein, we regularly employ an HCN detector (BW Technologies, Ltd.) in manipulations involving cyanide reagents as a precautionary measure. Reactions should be conducted in a well-ventilated fume hood.

General Procedure (A) for the preparation of silyldithianes.^{19,20} To a dry 100 mL round-bottom flask with a magnetic stir bar was added 7.5 mmol of dithiane. THF (35 mL) was

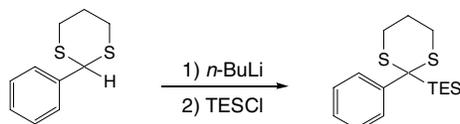
(17) Alaimo, P.J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, *78*, 64.

(18) Graham, A. E. *Synth. Comm.* **1999**, *29*, 697-703.

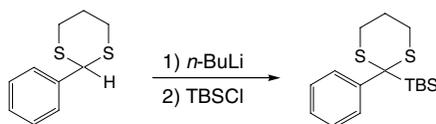
(19) Corey, E. J.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1077-1078.

(20) Page, P. C. B.; Graham, A. E.; Park, B. K. *Tetrahedron* **1992**, *48*, 7265-7274.

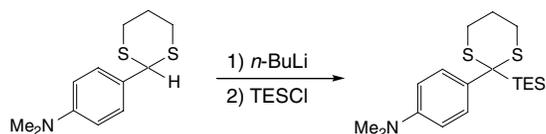
added *via* syringe. The resulting solution was kept under N₂ at -78 °C for 30 min, then *n*-butyllithium (2.5 M in hexanes, 8.3 mmol, 1.1 equiv) was added dropwise to the solution *via* syringe. The reaction was stirred at -78 °C for 2 h and 8.3 mmol triethylsilyl chloride (1.1 equiv) was added dropwise *via* syringe at the same temperature. After 30 min, the reaction was warmed to 25 °C for 30 min and then quenched with 40 mL of saturated aqueous NH₄Cl. The aqueous layer was extracted with three 30 mL portions of Et₂O. The organic extracts were combined, dried (MgSO₄), filtered, and the solvent was removed with a rotary evaporator. The crude product was purified by flash chromatography, eluting with the indicated solvent system to afford the pure silyldithiane.



2-Phenyl-2-triethylsilyl-1,3-dithiane. The title compound was prepared according to General Procedure A using 1.47 g (7.5 mmol) of dithiane, 3.30 mL of *n*-BuLi (2.5 M in hexanes, 8.3 mmol), and 1.4 mL (8.3 mmol) of TESCl to yield 2.33 g (100%) of the silyl dithiane as a clear oil after flash chromatography with 80:1 Hexanes/EtOAc. Analytical data for title compound: **IR** (thin film, cm⁻¹) 3076, 3056, 3025, 3010, 2952, 2904, 2830, 1954, 1910, 1816, 1774, 1591, 1477, 1458, 1421, 1272, 1240, 1033, 1010, 928, 799; **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 8.4 Hz, 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 2.77 (ddd, *J* = 14.4 Hz, 14.4 Hz, 12.8 Hz, 2H), 2.37 (ddd, *J* = 14.0 Hz, 4.0 Hz, 4.0 Hz, 2H), 2.03 (dtt, *J* = 14.0 Hz, 13.6 Hz, 2.4 Hz, 1H), 1.87 (dtt, *J* = 14.0 Hz, 4.0 Hz, 4.0 Hz, 1H), 0.917 (t, *J* = 8.4 Hz, 9H), 0.70 (q, *J* = 8.4 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 140.9, 129.7, 128.3, 125.1, 48.3, 25.3, 25.3, 7.8, 1.8; TLC (70:1 hexanes/EtOAc) R_f 0.42. **Anal.** Calcd for C₁₆H₂₆S₂Si: C, 61.87; H, 8.44. Found: C, 61.67; H, 8.40.

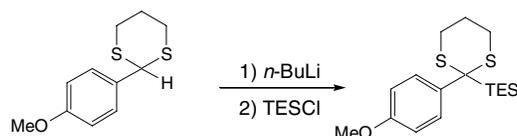


2-Phenyl-2-*tert*-butyl dimethylsilyl-1,3-dithiane. The title compound was prepared according to General Procedure A using 2.50 g (12.7 mmol) of dithiane, 5.60 mL of a 2.5 M *n*-BuLi in hexanes (14.0 mmol), and 2.11 mL (14.0 mmol) of TBSCl to yield 3.60 g (91%) of the silyl dithiane as a clear oil after flash chromatography (1:99 EtOAc/petroleum ether) Analytical data for title compound: **IR** (thin film, cm⁻¹) 3057, 2928, 2901, 2856, 1592, 1471, 1441, 1423, 1364, 1257; **¹H NMR** (400 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.37-7.33 (m, 2H), 7.18-7.14 (m, 1H), 2.76 (ddd, *J* = 13.2 Hz, 13.2 Hz, 1.8 Hz, 2H), 2.37 (ddd, *J* = 14.4 Hz, 14.4 Hz, 3.2 Hz, 2H), 1.99 (dtt, *J* = 13.2 Hz, 12.8 Hz, 2.8 Hz, 1H), 1.86 (dtt, *J* = 13.6 Hz, 4.0 Hz, 4.0 Hz, 1H), 0.79 (s, 9H), 0.13 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 141.0, 130.4, 128.5, 125.6, 48.9, 28.0, 25.5, 25.4, 20.0; TLC (95:5 petroleum ether/EtOAc) R_f 0.62. Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.

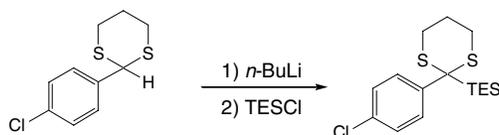


2-(4-*N,N*-Dimethylphenyl)-2-*tert*-butyldimethylsilyl-1,3-dithiane. The title compound

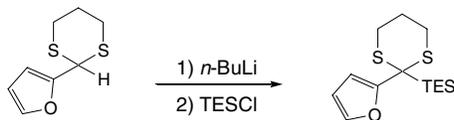
was prepared according to General Procedure A using 1.50 g (6.3 mmol) of dithiane, 2.80 mL of *n*-BuLi (2.5 M in hexanes, 6.9 mmol), and 1.2 mL (6.9 mmol) of TESCl to yield 1.60 g (72%) of the silyl dithiane as a yellow solid after flash chromatography (5:95 EtOAc/petroleum ether) Analytical data for title compound: **IR** (CHCl₃, cm⁻¹) 3031, 2954, 2909, 2878, 2401, 1608, 1510, 1423, 1232, 1207, 1011; **¹H NMR** (300 MHz, CDCl₃) δ 7.70 (d, *J* = 6.6 Hz, 2H), 6.71 (d, *J* = 6.6 Hz, 2H), 2.98 (s, 6H), 2.78 (ddd, *J* = 10.5 Hz, 10.5 Hz, 1.8 Hz, 2H), 2.33 (ddd, *J* = 10.5 Hz, 2.4 Hz, 1.8 Hz, 2H), 1.96 (dt, *J* = 10.5 Hz, 9.6 Hz, 2.4 Hz, 1H), 1.83 (dt, *J* = 10.5 Hz, 10.5 Hz, 2.4 Hz), 0.90 (t, *J* = 5.7 Hz, 9H), 0.66 (q, *J* = 5.7 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 148.5, 130.9, 128.4, 112.8, 48.2, 41.0, 25.9, 8.3, 2.5; TLC (95:5 petroleum ether/EtOAc) R_f 0.46. **Anal.** Calcd for C₁₈H₃₁NS₂Si: C, 61.13; H, 8.84; N, 3.96. Found: C, 61.04; H, 8.85; N, 3.91.



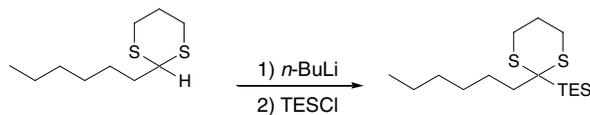
2-(4-Methoxyphenyl)-2-triethylsilyl-1,3-dithiane. The title compound was prepared according to General Procedure A using 1.69 g (7.5 mmol) of dithiane, 3.3 mL of *n*-BuLi (2.5 M in hexanes, 8.3 mmol), and 1.4 mL (8.3 mmol) of TESCl to yield 2.55 g (100%) of the silyl dithiane as a clear oil after flash chromatography with 55:1 Hexanes/EtOAc. Analytical data for title compound: **IR** (thin film, cm⁻¹) 3065, 3032, 2950, 2905, 1603, 1501, 1288, 1247, 1180, 1037, 1010, 839, 717; **¹H NMR** (400 MHz, CDCl₃) δ 7.82 (dd, *J* = 9.2 Hz, 2.4 Hz, 2H), 6.89 (dd, *J* = 9.2 Hz, 3.2 Hz, 2H) 3.82 (s, 3H), 2.77 (ddd, *J* = 14 Hz, 14 Hz, 2.8 Hz, 2H), 2.36 (ddd, *J* = 14 Hz, 3.2 Hz, 3.2 Hz, 2H), 2.01 (dt, *J* = 14 Hz, 14 Hz, 3.2 Hz, 1H), 1.86 (dt, *J* = 14.0 Hz, 3.2 Hz, 3.2 Hz, 1H), 0.92 (t, *J* = 7.6 Hz, 9H), 0.68 (q, *J* = 7.6 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 157.2, 132.6, 130.8, 113.5, 55.1, 47.6, 25.3, 25.0, 7.8, 1.7; TLC (55:1 Hexanes/EtOAc) R_f 0.3. **Anal.** Calcd for C₁₇H₂₈OS₂Si: C, 59.94; H, 8.29. Found: C, 60.14; H, 8.32.



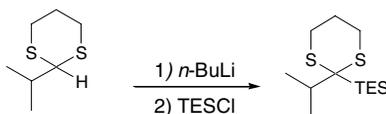
2-(4-Chlorophenyl)-2-triethylsilyl-1,3-dithiane. The title compound was prepared according to General Procedure A using 1.73 g (7.5 mmol) of dithiane, 3.30 mL of *n*-BuLi (2.5 M in hexanes, 8.3 mmol), and 1.4 mL (8.3 mmol) of TESCl to yield 2.54 g (98%) of the silyl dithiane as a clear oil after flash chromatography with 80:1 Hexanes/EtOAc. Analytical data for title compound: **IR** (thin film, cm⁻¹) 3059, 2951, 2905, 2876, 1481, 1094, 1011, 917, 840, 711; **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H), 7.32 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H), 2.73 (ddd, *J* = 14.0 Hz, 14.0 Hz, 2.4 Hz, 2H), 2.38 (ddd, *J* = 14.0 Hz, 4.0 Hz, 4.0 Hz, 2H), 2.02 (dt, *J* = 14.0 Hz, 13.6 Hz, 2.4 Hz, 1H), 1.89 (dt, *J* = 13.6 Hz, 4.0 Hz, 2.4 Hz, 1H), 0.927 (t, *J* = 8.0 Hz, 9H), 0.69 (q, *J* = 8 Hz, 6H); **¹³C NMR** (100MHz, CDCl₃) δ 139.9, 131.1, 131.1, 128.4, 47.8, 25.1, 25.1, 7.8, 1.70; TLC (80:1 Hexanes/EtOAc) R_f 0.30. **Anal.** Calcd for C₁₆H₂₅ClS₂Si: C, 55.70; H, 7.30. Found: C, 55.86; H, 7.37.



2-(2-Furyl)-2-triethylsilyl-1,3-dithiane. The title compound was prepared according to General Procedure A using 0.88 g (4.7 mmol) of dithiane, 2.1 mL of *n*-BuLi (2.5 M in hexanes, 5.2 mmol), and 0.88 mL (5.2 mmol) of TESCl to yield 1.42 g (100%) of the silyl dithiane as a clear oil after flash chromatography with 35:1 Hexanes/EtOAc. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3112, 2951, 2876, 1492, 1412, 1011, 937, 812, 729; **^1H NMR** (400 MHz, CDCl_3) δ 7.42 (dd, $J = 2.0$ Hz, 0.4 Hz, 1H), 6.43 (dd, $J = 2.8$ Hz, 0.4 Hz, 1H), 6.37 (dd, $J = 3.2$ Hz, 2.0 Hz, 1H), 2.93 (ddd, $J = 13.6$ Hz, 3.2 Hz, 3.2 Hz, 2H), 2.44 (ddd, $J = 13.6$ Hz, 3.2 Hz, 3.2 Hz, 2H), 2.02-1.90 (m, 2H), 0.95 (t, $J = 8.0$ Hz, 9H), 0.75 (q, $J = 8.0$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 154.7 141.6, 110.9, 109.7, 41.5, 25.8, 25.3, 7.6, 2.0; TLC (35:1 Hexanes/EtOAc) R_f 0.27. **Anal.** Calcd for $\text{C}_{14}\text{H}_{24}\text{OS}_2\text{Si}$: C, 55.95; H, 8.05. Found: C, 56.12; H, 8.12.

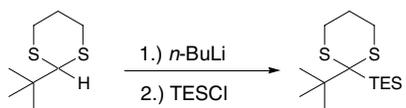


2-Hexyl-2-triethylsilyl-1,3-dithiane. To a dry 100 mL round-bottom flask with a magnetic stir bar was added 1.02 g (5.0 mmol) of the dithiane. THF (18 mL) was added *via* syringe. The resulting solution was kept under N_2 at -30 °C for 30 min, then 2.2 mL of *n*-butyllithium (2.5 M in hexanes, 5.5 mmol, 1.1equiv) was added dropwise to the solution via syringe. The reaction was stirred at -30 °C for 3 h, then cooled to -78 °C. Triethylsilyl chloride (0.93 mL, 5.5 mmol, 1.1 equiv) was added dropwise via syringe. After 30 min, the reaction was warmed to 25 °C for 30 min, and quenched with 40 mL of saturated aqueous NH_4Cl . The aqueous layer was extracted with three 30 mL portions of Et_2O and dried over MgSO_4 . The organic extracts were combined and the solvent was removed with a rotary evaporator. The crude product was purified by flash chromatography with 35:1 Hexanes/EtOAc to afford 1.54 g (97%) of a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 2954, 2931, 2875, 1458, 1236, 1010, 727; **^1H NMR** (400 MHz, CDCl_3) δ 3.06 (ddd, $J = 14.1$ Hz, 12.3 Hz, 2.7 Hz, 2H), 2.22 (ddd, $J = 14.1$ Hz, 3.9 Hz, 3.9 Hz, 2H), 2.20-2.25 (m, 2H), 2.1-1.8 (m, 2H), 1.55-1.42 (m, 2H), 1.30-1.24 (m, 6H), 1.06 (t, $J = 7.8$ Hz, 9H), 0.95-0.85 (m, 3H), 0.79 (q, $J = 7.8$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 39.9, 37.6, 31.8, 29.9, 28.0, 25.3, 23.4, 22.7, 14.1, 8.2, 2.9; TLC (35:1 Hexanes/EtOAc) R_f 0.3. **Anal.** Calcd for $\text{C}_{16}\text{H}_{34}\text{S}_2\text{Si}$: C, 60.31; H, 10.75. Found: C, 60.42; H, 10.93.



2-iso-Propyl-2-triethylsilyl-1,3-dithiane. To a dry 100 mL round-bottom flask with a magnetic stir bar was added 1.00 g (6.17 mmol) of the dithiane. THF (35 mL) was added *via*

syringe. The resulting solution was kept under N₂ at -30 °C for 30 min, then 2.7 mL of *n*-butyllithium (2.5 M in hexanes, 6.8 mmol, 1.1 equiv) was added dropwise to the solution *via* syringe. The reaction was stirred at -30 °C for 3 h, then cooled to -78 °C. Triethylsilyl chloride (1.15 mL, 6.8 mmol, 1.1 equiv) was added dropwise *via* syringe. After 30 min, the reaction was warmed to 25 °C for 30 min, and quenched with 40 mL of saturated aqueous NH₄Cl. The aqueous layer was extracted with three 30 mL portions of Et₂O. Organic extracts were combined and the solvent was removed with a rotary evaporator. The crude product was purified by flash chromatography with 35:1 Hexanes/EtOAc to afford 1.63 g of a clear oil in 96% yield. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2952, 2909, 2876, 1457, 1415, 1008, 724; **¹H NMR** (400 MHz, CDCl₃) δ 2.99 (ddd, *J* = 14.1 Hz, 12.6 Hz, 3.0 Hz, 2H), 2.68 (tt, *J* = 6.9 Hz, 1H), 2.41 (ddd, *J* = 14.0 Hz, 3.6 Hz, 3.6 Hz, 2H), 2.1-1.8 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.06 (t, *J* = 7.2 Hz, 9H), 0.83 (dq, *J* = 7.2 Hz, 1.8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 45.6, 36.1, 24.7, 24.3, 21.2, 8.4, 4.6; TLC (25:1 Hexanes/EtOAc) R_f 0.48. Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.

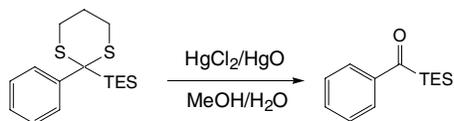


2-tert-Butyl-2-triethylsilyl-1,3-dithiane. To a dry 100 mL round-bottom flask with a magnetic stir bar was added 869 mg (4.94 mmol) of the dithiane. THF (22 mL) was added *via* syringe. The resulting solution was kept under N₂ at -30 °C for 30 min, then 2.1 mL of *n*-butyllithium (2.5 M in hexanes, 5.4 mmol, 1.1equiv) was added dropwise to the solution *via* syringe. The reaction was stirred at -30 °C for 8 h, then cooled to -78 °C. Triethylsilyl chloride (0.92 mL, 5.4 mmol, 1.1 equiv) was added dropwise *via* syringe. After 30 min, the reaction was warmed to 25 °C for 30 min, and quenched with 40 mL of saturated aqueous NH₄Cl. The aqueous layer was extracted with three 30 mL portions of Et₂O. The organic extracts were combined and the solvent was removed with a rotary evaporator. The crude product was purified by flash chromatography with 35:1 Hexanes/EtOAc to afford 1.26 g of a clear oil in 88% yield. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2954, 2876, 2733, 1631, 1463, 1422, 1387, 1360, 1272, 1097, 1005; **¹H NMR** (400 MHz, CDCl₃) δ 2.81 (ddd, *J* = 13.6 Hz, 12.8 Hz, 4.0 Hz, 2H), 2.47 (ddd, *J* = 13.2 Hz, 4.0 Hz, 4.0 Hz, 2H), 2.04 (dt, *J* = 13.2 Hz, 4.0 Hz, 4.0 Hz, 1H), 1.77 (dt, *J* = 13.2 Hz, 12.8 Hz, 4.0 Hz, 1H), 1.19 (s, 9H), 1.02 (t, *J* = 7.6 Hz, 9H), 0.88 (q, *J* = 7.6 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 47.5, 46.1, 29.8, 27.6, 23.4, 9.1, 6.9; TLC (95:5 Hexanes/EtOAc) R_f 0.67. Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.

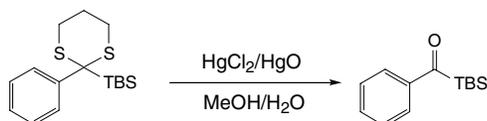
General procedure (B) for the preparation of acylsilanes.²¹ A 250 mL round-bottom flask with a magnetic stir bar was charged with 5 mmol of silyldithiane, 10 mmol mercuric chloride, 10 mmol of mercuric oxide, and 30 mL of a methanol/water solution (9:1). The reaction mixture was refluxed for 4-5 h. After cooling to 25 °C, the solids were removed by filtration. The filtrate was extracted three times with pentane. The organic extracts were combined, dried (MgSO₄), and the solvent was evaporated to afford oily material that was purified

(21) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 979-982.

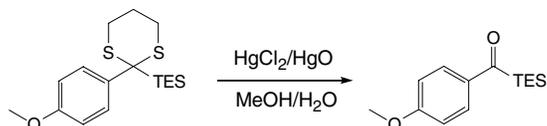
by flash chromatography using the indicated eluent.



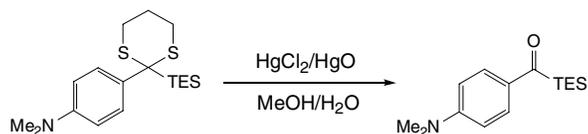
Phenyl triethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 2.33 g (7.5 mmol) of the silyl dithiane, 5.15 g (19 mmol) of mercuric chloride, and 4.10 g (19 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 25:1 petroleum ether/ether to afford 1.59 g (96%) of the product as a clear yellow oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3062, 2955, 2876, 1613, 1277, 1209, 769; **^1H NMR** (400 MHz, CDCl_3) δ 7.85-7.76 (m, 2H), 7.58-7.42 (m, 3H), 1.05-0.85 (m, 15H); **^{13}C NMR** (100 MHz, CDCl_3) δ 236.1, 142.4, 132.6, 128.6, 127.1, 7.4, 3.6; TLC (25:1 petroleum ether/ether) R_f 0.32. **Anal.** Calcd for $\text{C}_{13}\text{H}_{20}\text{OSi}$: C, 70.85; H, 9.15. Found: C, 70.72; H, 9.13.



Phenyl *tert*-butyldimethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 3.6 g (11.6 mmol) of the silyl dithiane, 7.87 g (29 mmol) of mercuric chloride, and 6.28 g (29 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 99:1 petroleum ether/acetone to afford 2.1 g (82%) of the product as a clear yellow oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3062, 2955, 2876, 1613, 1277, 1209, 769; **^1H NMR** (400 MHz, CDCl_3) δ 7.80-7.74 (m, 2H), 7.52-7.49 (m, 3H), 0.94 (s, 9H), 0.36 (s, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 236.1, 142.4, 132.6, 128.6, 127.1, 7.4, -5.5; TLC (96:4 petroleum ether/acetone) R_f 0.43.

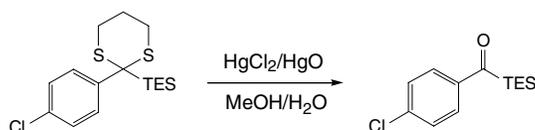


4-Methoxyphenyl triethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 1.56 g (4.59 mmol) of the silyl dithiane, 2.57 g (9.5 mmol) of mercuric chloride, and 2.06 g (9.5 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 15:1 petroleum ether/ether to afford 2.14 g (90%) of a clear yellow oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3007, 2954, 2911, 1584, 1570, 1261, 1217, 1163, 1032, 837, 738; **^1H NMR** (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.7$ Hz, 1.8 Hz, 2H), 6.95 (dd, $J = 8.7$ Hz, 2.1 Hz, 2H), 3.86 (s, 3H), 1.03-0.84 (m, 15H); **^{13}C NMR** (100 MHz, CDCl_3) δ 233.0, 163.1, 136.3, 129.5, 113.7, 55.4, 7.5, 3.8; TLC (20:1 petroleum ether/ether) R_f 0.16; **Anal.** Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}$: C, 67.15; H, 8.86. Found: C, 67.42; H, 9.03.

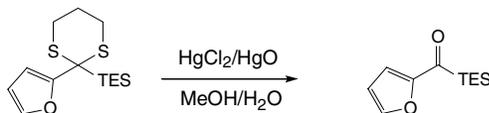


4-*N,N*-Dimethylphenyl triethylsilyl ketone. The title compound was prepared according

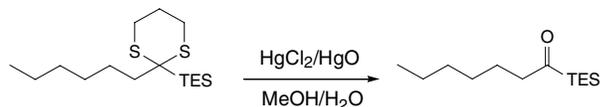
to General Procedure **B**, using 1.40 g (3.96 mmol) of the silyl dithiane, 2.69 g (9.9 mmol) of mercuric chloride, and 2.14 g (9.9 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 95:5 petroleum ether/EtOAc to afford 620 mg (54%) of the product as a yellow solid. Analytical data for title compound: **IR** (CHCl_3 , cm^{-1}) 2955, 2911, 2876, 1611, 1569, 1540, 1534, 1370, 1315, 1239, 1230; **^1H NMR** (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.0$ Hz, 2H), 6.64 (d, $J = 8.0$ Hz, 2H), 3.01 (s, 6H), 0.96 (t, $J = 6.8$ Hz, 9H), 0.85 (q, $J = 6.8$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 232.1, 153.4, 132.4, 129.9, 110.9, 40.3, 7.8, 4.2; TLC (95:5 petroleum ether/EtOAc) R_f 0.21. **Anal.** Calcd for $\text{C}_{15}\text{H}_{25}\text{NOSi}$: C, 68.38; H, 9.56; N, 5.32. Found: C, 68.39; H, 9.31; N, 5.51.



4-Chlorophenyl triethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 1.26 g (3.66 mmol) of the silyl dithiane, 2.00 g (7.4 mmol) of mercuric chloride, and 1.60 g (7.4 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 37:1 petroleum ether/ether to afford 690 mg (74%) of a clear yellow oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3062, 2956, 2876, 1615, 1583, 1568, 1203, 1012, 834, 740; **^1H NMR** (400 MHz, CDCl_3) δ 7.74 (dd, $J = 8.7$ Hz, 1.8 Hz, 2H), 7.44 (dd, $J = 8.7$ Hz, 1.5 Hz, 2H), 1.03-0.84 (m, 15H); **^{13}C NMR** (100 MHz, CDCl_3) δ 234.6, 140.5, 139.0, 129.0, 128.5, 7.7, 3.6; TLC (37:1 petroleum ether/ether) R_f 0.2; **Anal.** Calcd for $\text{C}_{13}\text{H}_{19}\text{ClOSi}$: C, 61.27; H, 7.52. Found: C, 61.33; H, 7.61.

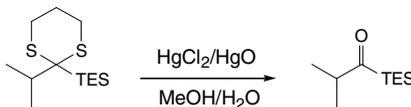


2-Furyl triethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 1.93 g (6.43 mmol) of the silyl dithiane, 3.50 g (13 mmol) of mercuric chloride, and 2.80 g (13 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 12:1 hexanes/EtOAc to afford 635 mg (47%) of a clear yellow oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3145, 3124, 2955, 2876, 1591, 1555, 1454, 1381, 1239, 1010, 739; **^1H NMR** (400 MHz, CDCl_3) δ 7.57 (d, $J = 1.6$ Hz, 1H), 7.05 (d, $J = 3.6$ Hz, 1H), 6.52 (dd, $J = 3.6$ Hz, 1.6 Hz, 1H), 0.84-1.03 (m, 15H); **^{13}C NMR** (100 MHz, CDCl_3) δ 221.5, 158.7, 145.8, 114.5, 112.0, 7.3, 2.4; TLC (15:1 hexanes/EtOAc) R_f 0.2; **Anal.** Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{Si}$: C, 62.8; H, 8.63. Found: C, 63.13; H, 8.74.

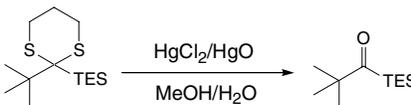


Hexyl triethylsilyl ketone. The title compound was prepared according to General Procedure **B**, using 1.46 g (4.6 mmol) of the silyl dithiane, 2.55 g (9.4 mmol) of mercuric chloride, and 2.00 g (9.4 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 25:1 hexanes/EtOAc to afford 818 mg (78%) of a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 2955, 2935, 2875, 1641, 1466, 1458, 1018, 735, 721; **^1H**

NMR (400 MHz, CDCl₃) δ 2.54 (t, J = 7.6 Hz, 2H), 1.45-1.55 (m, 2H), 1.18-1.32 (m, 6H), 0.96 (t, J = 8.0 Hz, 9H), 0.86 (t, J = 6.8 Hz, 3H). 0.72 (q, J = 8.0 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 248.5, 50.2, 31.7, 29.0, 22.5, 21.8, 14.0, 7.3, 2.1; TLC (25:1 hexanes/EtOAc) R_f 0.25; **Anal.** Calcd for C₁₃H₂₈OSi: C, 68.35; H, 12.35. Found: C, 68.41; H, 12.47.

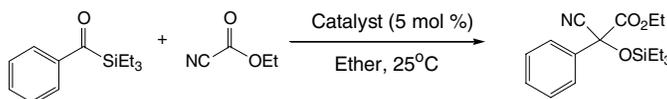


iso-Propyl triethylsilyl ketone. The title compound was prepared according to General Procedure B, using 1.51 g (5.48 mmol) of the silyl dithiane, 2.97 g (11 mmol) of mercuric chloride, and 2.38 g (11 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 25:1 hexanes/EtOAc to afford 744 mg (73%) of a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2958, 2877, 1637, 1465, 1019, 739, 726; **¹H NMR** (400 MHz, CDCl₃) δ 2.88 (sep, J = 6.8 Hz, 1H), 0.97 (d, J = 6.8 Hz, 6H), 0.96 (t, J = 6.8 Hz, 9H), 0.75 (q, J = 6.8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 250.7, 45.6, 16.2, 7.3, 2.6; TLC (20:1 hexanes/EtOAc) R_f 0.36; **Anal.** Calcd for C₁₀H₂₂OSi: C, 64.45; H, 11.90. Found: C, 64.67; H, 11.62.



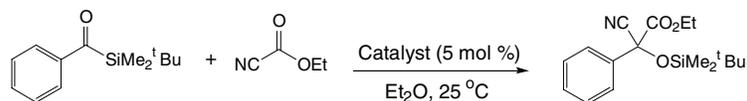
tert-Butyl triethylsilyl ketone. The title compound was prepared according to General Procedure B, using 1.25 g (4.3 mmol) of the silyl dithiane, 2.33 g (8.6 mmol) of mercuric chloride, and 1.86 g (8.6 mmol) of mercuric oxide. The crude product was purified by flash chromatography with 25:1 hexanes/EtOAc to afford 781 mg (91%) of a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2960, 2877, 1630, 1475, 1415, 1362, 1240, 1008, 940; **¹H NMR** (400 MHz, CDCl₃) δ 1.05 (s, 9H), 0.95 (t, J = 7.6 Hz, 9H), 0.79 (q, J = 7.6 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 250.1, 48.8, 24.7, 7.7, 4.0; TLC (20:1 hexanes/EtOAc) R_f 0.40; **Anal.** Calcd for C₁₁H₂₄OSi: C, 65.93; H, 12.07. Found: C, 66.30; H, 11.86.

General procedure (C) for the reaction of acylsilanes with cyanofornates. A dry round-bottom flask with a magnetic stir bar was charged with 0.3 mmol of acylsilane, a spatula tip of KCN, the indicated amounts of 18-crown-6 and the indicated solvent. To the resulting mixture, the cyanofornate (1.2 equiv) was added *via* syringe. The reaction was stirred at the indicated temperature under N₂ until the starting material was consumed (TLC analysis). The solvent was removed *in vacuo* and the reaction mixture was purified by flash chromatography, eluting with the indicated solvent system to afford the pure α -cyanosiloxy ester.

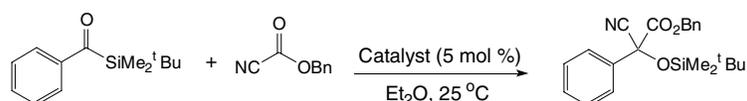


Ethyl 2-cyano-2-phenyl-2-triethylsiloxy acetate (Table 2, entry 1). The title compound was prepared according to General Procedure C using 102 mg (0.46 mmol) of acylsilane, 51 μ L (0.51 mmol) of ethyl cyanofornate, 6.6 mg (0.02 mmol) of 18-crown-6, and 10 mL of Et₂O. After 3-4 h at 25 °C, The crude product was purified by flash chromatography with 22:1 hexanes/EtOAc to afford 123 mg (84%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 3067, 2959, 2878, 2242, 1764, 1746, 1451, 1240, 1193, 1153,

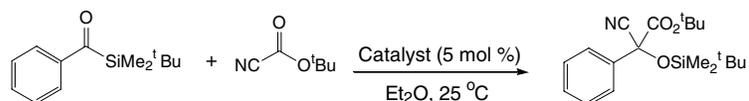
1013, 734, 695; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72-7.62 (m, 2H), 7.46-7.36 (m, 3H), 4.26-4.13 (ABX, $J_{\text{AB}} = 10.8$ Hz, $J_{\text{AX}} = 6.8$ Hz, 2H), 1.24 (t, $J = 6.8$ Hz, 3H), 0.99 (t, $J = 7.6$ Hz, 9H), 0.76 (q, $J = 7.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.1, 136.8, 129.6, 128.7, 125.4, 118.2, 74.8, 63.4, 13.8, 6.6, 5.2; TLC (20:1 hexanes/EtOAc) R_f 0.33; **Anal.** Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{Si}$: C, 63.91; H, 7.89; N, 4.38. Found: C, 64.09; H, 7.98; N, 4.41.



Ethyl 2-tert-butyl(dimethylsilyloxy)-2-cyano-2-phenyl acetate (Table 3, entry 1). The title compound was prepared according to General Procedure C using 30 mg (0.14 mmol) of acylsilane, 15 μL (0.15 mmol) of ethylcyanoformate, 2.0 mg (0.007 mmol) of 18-crown-6, and 5 mL of Et_2O . After 1-2 h at 25 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 41.4 mg (96%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3070, 2958, 2897, 2859, 2257, 1764, 1599, 1472, 1255, 1150, 844, 784, 734; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65-7.63 (m, 2H), 7.41-7.36 (m, 3H), 4.23-4.14 (ABX, $J_{\text{AB}} = 10.4$ Hz, $J_{\text{AX}} = 7.2$ Hz, 2H), 1.22 (t, $J = 7.2$ Hz, 3H), 0.97 (s, 9H), 0.26 (s, 3H), 0.16 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.4, 137.0, 129.9, 129.0, 125.7, 118.4, 75.4, 63.7, 25.9, 18.7, 14.0, -3.9, -4.1; TLC (95:5 hexanes/EtOAc) R_f 0.36; **Anal.** Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3\text{Si}$: C, 63.91; H, 7.89; N, 4.38. Found: C, 63.72; H, 7.95; N, 4.36.



Benzyl 2-tert-butyl(dimethylsilyloxy)-2-cyano-2-phenyl acetate (Table 3, entry 2). The title compound was prepared according to General Procedure C using 30 mg (0.14 mmol) of acylsilane, 24 mg (0.15 mmol) of benzylcyanoformate,²² 2.0 mg (0.007 mmol) of 18-crown-6, and 5 mL of Et_2O . After 1-2 h at 25 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 46.4 mg (88%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3067, 3036, 2957, 2930, 2858, 2241, 1767, 1588, 1472, 1258, 1148; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67-7.61 (m, 2H), 7.40-7.34 (m, 3H), 7.31-7.25 (m, 3H), 7.20-7.16 (m, 2H), 5.18 (s, 2H), 0.94 (s, 9H), 0.22 (s, 3H), 0.14 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.1, 136.9, 134.6, 129.9, 129.0, 128.9, 128.8, 128.3, 125.8, 118.2, 75.8, 69.0, 25.8, 25.8, 18.6, -3.9, -4.2; TLC (95:5 hexanes/EtOAc) R_f 0.35; Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.

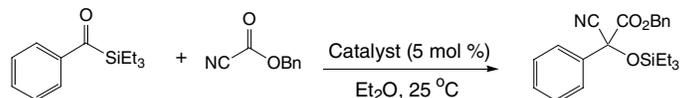


tert-Butyl 2-tert-butyl(dimethylsilyloxy)-2-cyano-2-phenyl acetate (Table 3, entry 3). The title compound was prepared according to General Procedure C using 30 mg (0.14 mmol) of acylsilane, 19 mg (0.15 mmol) of tert-butylcyanoformate,²³ 2.0 mg (0.007 mmol) of 18-crown-6, and 5 mL of Et_2O . After 1-2 h at 25 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 44.7 mg (91%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3072, 2958, 2931, 2859, 2245, 1760, 1600, 1473, 1371,

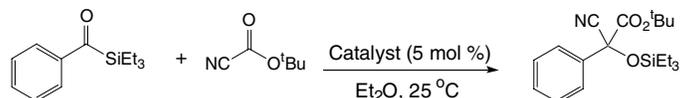
(22) Childs, M. E.; Weber, W. P. J. *Org. Chem.* **1976**, *41*, 3486-3587.

(23) Carpino, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 2725-2727.

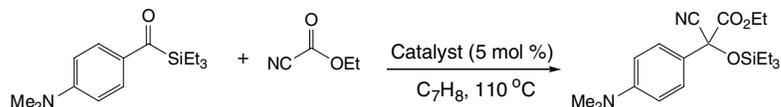
1256, 1147, 838; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66-7.59 (m, 2H), 7.39-7.31 (m, 3H), 1.39 (s, 9H), 0.99 (s, 9H), 0.29 (s, 3H), 0.18 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.0, 137.4, 129.6, 128.8, 125.6, 118.7, 84.9, 75.3, 27.7, 25.9, 18.7, -3.7, -4.1; TLC (95:5 hexanes/EtOAc) R_f 0.36; **Anal.** Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_3\text{Si}$: C, 65.67; H, 8.41; N, 4.03. Found: C, 65.51; H, 8.42; N, 4.02.



Benzyl 2-cyano-2-phenyl-2-triethylsiloxy acetate (Table 3, entry 5). The title compound was prepared according to General Procedure C using 30 mg (0.14 mmol) of acylsilane, 24 mg (0.15 mmol) of benzylcyanoformate, 2.0 mg (0.007 mmol) of 18-crown-6, and 5 mL of Et_2O . After 1-2 h at 25 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 44.4 mg (84%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3067, 3035, 2958, 2878, 2245, 1766, 1588, 1451, 1241, 1152, 1003, 835; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63-7.61 (m, 2H), 7.38-7.35 (m, 3H), 7.29-7.26 (m, 3H), 7.19-7.17 (m, 2H), 5.17 (s, 2H), 0.93 (t, $J = 7.6$ Hz, 9H), 0.70 (q, $J = 7.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.1, 134.5, 129.9, 128.9, 128.8, 128.7, 128.2, 125.7, 118.3, 75.1, 68.9, 6.8, 5.4; TLC (95:5 hexanes/EtOAc) R_f 0.35; **Anal.** Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{Si}$: C, 69.25; H, 7.13; N, 3.67. Found: C, 69.37; H, 7.28; N, 3.60.

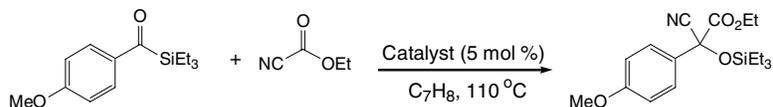


tert-Butyl 2-cyano-2-phenyl-2-triethylsiloxy acetate (Table 3, entry 6). The title compound was prepared according to General Procedure C using 30 mg (0.14 mmol) of acylsilane, 19 mg (0.15 mmol) of *tert*-butylcyanoformate, 2.0 mg (0.007 mmol) of 18-crown-6, and 5 mL of Et_2O . After 1-2 h at 25 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 36.5 mg (74%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3066, 2959, 2879, 2242, 1761, 1599, 1451, 1371, 1256, 1148, 1011, 733; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.70-7.62 (m, 2H), 7.42-7.37 (m, 3H), 1.41 (s, 9H), 1.01 (t, $J = 7.2$ Hz, 9H), 0.75 (q, $J = 7.2$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.0, 137.4, 129.6, 128.8, 125.5, 118.8, 84.9, 75.3, 27.7, 6.9, 5.5; TLC (95:5 hexanes/EtOAc) R_f 0.28; Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.

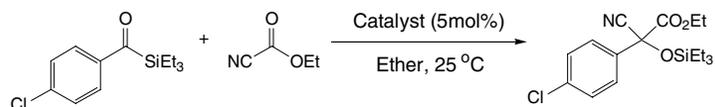


Ethyl 2-cyano-2-(4-*N,N*-dimethylphenyl)-2-triethylsiloxy acetate (Table 2, entry 5). The title compound was prepared according to General Procedure C using 30 mg (0.11 mmol) of acylsilane, 12 μL (0.13 mmol) of ethylcyanoformate, 1.5 mg (0.006 mmol) of 18-crown-6, and 5 mL of toluene. After 12 h at 110 °C, the crude product was purified by flash chromatography with 9:1 hexanes/EtOAc to afford 43.5 mg (100%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 2957, 2878, 2810, 2238, 1761, 1742, 1612, 1523, 1446, 1362, 1237, 1168, 1127, 1051, 1018; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 9.0$ Hz, 2H), 4.29-4.16 (ABX, $J_{AB} = 10.8$ Hz, $J_{AX} = 7.2$ Hz, 2H), 2.99 (s, 6H), 1.26 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 8.1$ Hz, 9H), 0.76 (q, $J = 8.1$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz,

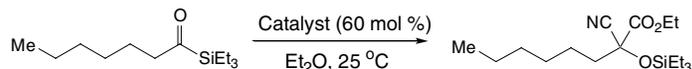
CDCl₃) δ 167.7, 151.3, 126.7, 118.8, 112.0, 75.0, 63.3, 40.5, 14.0, 7.0, 5.5; TLC (2:3 hexanes/MeOCMe₃) R_f 0.46; Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.



Ethyl 2-cyano-2-(4-methoxyphenyl)-2-triethylsiloxy acetate (Table 2, entry 4). The title compound was prepared according to General Procedure C using 30 mg (0.12 mmol) of acylsilane, 13 μ L (0.13 mmol) of ethylcyanoformate, 1.6 mg (0.006 mmol) of 18-crown-6, and 5 mL of toluene. After 12 h at 110 °C, the crude product was purified by flash chromatography with 95:5 hexanes/EtOAc to afford 40.0 mg (95%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2959, 2913, 2879, 2840, 2242, 1763, 1744, 1609, 1584, 1511, 1464, 1444, 1306, 1255, 1176, 1152, 1115, 1018; **¹H NMR** (400 MHz, CDCl₃) δ 7.60-7.57 (d, *J* = 9.0 Hz, 2H), 6.93-6.91 (d, *J* = 9.0 Hz, 2H), 4.32-4.12 (m, 2H), 3.83 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.78 (q, *J* = 7.8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 167.2, 160.5, 128.8, 126.8, 118.3, 114.0, 74.5, 63.3, 55.3, 13.8, 6.6, 5.5; TLC (95:5 hexanes/EtOAc) R_f 0.23; **Anal.** Calcd for C₁₈H₂₇NO₄Si: C, 61.86; H, 7.79; N, 4.01. Found: C, 62.15; H, 8.01; N, 4.00.

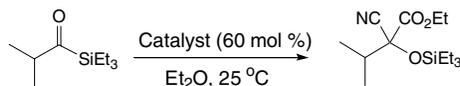


Ethyl 2-(4-chlorophenyl)-2-cyano-2-triethylsiloxy acetate (Table 2, entry 2). The title compound was prepared according to General Procedure C using 52 mg (0.25 mmol) of acylsilane, 25 μ L (0.25 mmol) of ethylcyanoformate, 3 mg (0.01 mmol) of 18-crown-6, and 5 mL of Et₂O. The reaction took 30 min to go to completion at 25 °C. The crude product was purified by flash chromatography with 30:1 hexanes/EtOAc to afford 65 mg (74%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 3153, 3125, 2959, 2879, 2244, 1771, 1751, 1463, 1232, 1158, 1141, 1018, 747; **¹H NMR** (400 MHz, CDCl₃) δ 7.61 (m, *J* = 8.7 Hz, 2.1 Hz, 2H), 7.39 (m, *J* = 8.7 Hz, 2.1 Hz, 2H), 4.23 (ABX, *J*_{AB} = 10.8 Hz, *J*_{AX} = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 8.1 Hz, 9H), 0.77 (q, *J* = 8.1 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.7, 135.8, 135.4, 128.9, 126.9, 117.9, 74.3, 63.6, 13.8, 6.6, 5.2; TLC (30:1 hexanes/EtOAc) R_f 0.2; **Anal.** Calcd for C₁₇H₂₄ClNO₃Si: C, 57.69; H, 6.84; N, 3.96. Found: C, 57.93; H, 6.95; N, 4.01.

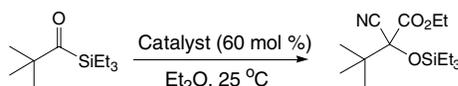


Ethyl 2-cyano-2-triethylsiloxy octanoate (Table 2, entry 6). To a dry 25 mL round bottom flask with a magnetic stir bar was added the acylsilane (100 mg, 0.44 mmol) and 18 mL of Et₂O. To a dry 50 mL round bottom flask was added a spatula tip of KCN, 69.5 mg (0.26 mmol) of 18-crown-6, 173 μ L (1.75 mmol) of ethylcyanoformate, and 4 mL of Et₂O. The acylsilane solution was added slowly *via* cannula to the flask containing the cyanoformate over the course of 1.5 h with vigorous stirring. The solvent was then removed *in vacuo* and the crude product was purified by flash chromatography (96:4 petroleum ether/MeOCMe₃) to yield 105 mg (73%) of the product as a colorless oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2959, 2936,

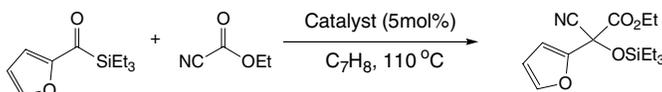
2878, 2242, 1763, 1458, 1415, 1380, 1248, 1167, 1018; **¹H NMR** (400 MHz, CDCl₃) δ 4.35-4.24 (ABX, $J_{AB} = 10.8$ Hz, $J_{AX} = 7.2$ Hz, 2H), 1.96 (ddd, $J = 6.8$ Hz, 6.8 Hz, 2.0 Hz, 2H), 1.50-1.44 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.22-1.36 (m, 6H), 0.98 (t, $J = 8.0$ Hz, 9H), 0.88 (t, $J = 6.8$ Hz, 3H), 0.80-0.65 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.1, 118.5, 73.4, 63.0, 40.8, 31.4, 29.7, 28.7, 23.5, 22.5, 14.0, 13.9, 6.6, 5.2; TLC (9:1 hexanes/MeOCMe₃) R_f 0.54; **Anal.** Calcd for C₁₇H₃₃NO₃Si: C, 62.34; H, 10.16; N, 4.28. Found: C, 62.50; H, 10.16; N, 4.26.



Ethyl 2-cyano-3-methyl-2-(triethylsilyloxy) butanoate (Table 2, entry 7). To a dry 10 mL round bottom flask with a magnetic stir bar was added the acylsilane (30 mg, 0.16 mmol) and 8 mL of Et₂O. To a dry 25 mL round bottom flask was added a spatula tip of KCN, 25.3 mg (0.096 mmol) of 18-crown-6, 63 μL (0.64 mmol) of ethylcyanofornate, and 2 mL of Et₂O. The acylsilane mixture was added slowly *via* cannula to the flask containing the cyanofornate over the course of 1.5 h with vigorous stirring. The solvent was then removed in vacuo and the crude product was purified by flash chromatography (98.5:2.5 petroleum ether/EtOAc) to yield 26.4 mg (58%) of the product as a colorless oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2961, 2879, 2238, 1763, 1467, 1251, 1168, 1137, 1082, 1019; **¹H NMR** (400 MHz, CDCl₃) δ 4.34-4.27 (ABX, $J_{AX} = 7.2$ Hz, $J_{AB} = 0.6$ Hz, 2H), 2.28 (sep, $J = 6.9$ Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.08 (d, $J = 6.9$ Hz, 3H), 1.02 (d, $J = 6.9$ Hz, 3H), 0.99 (t, $J = 8.1$ Hz, 9H), 0.78-0.68 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.2, 118.2, 77.7, 63.1, 38.4, 17.2, 16.4, 14.3, 6.9, 5.4; TLC (95:5 hexanes/MeOCMe₃) R_f 0.37; Attempts to obtain acceptable combustion analysis were not successful. See Appendix for proton and carbon spectra.



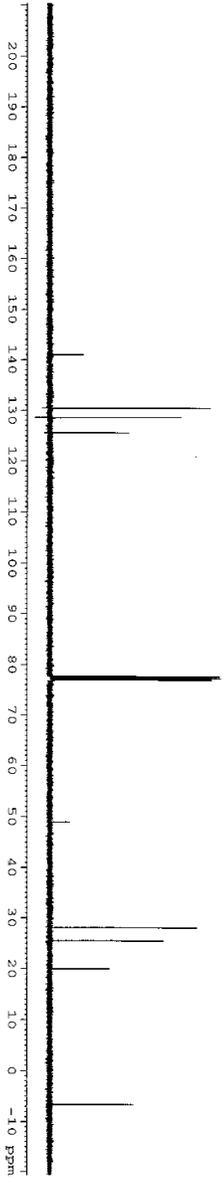
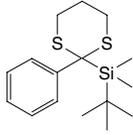
Ethyl 2-cyano-3,3-dimethyl-2-(triethylsilyloxy) butanoate (Table 2, entry 8). The title compound was prepared according to General Procedure C using 50 mg (0.25 mmol) of acylsilane, 99 μL (1.0 mmol) of ethylcyanofornate, 39.6 mg (0.15 mmol) of 18-crown-6, and 8 mL of Et₂O. After 3-4 h at 25 °C, the crude product was purified by flash chromatography with 98.5:2.5 hexanes/EtOAc to afford 38.1 mg (51%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm⁻¹) 2962, 2879, 2238, 1758, 1743, 1466, 1400, 1367, 1262, 1210, 1149, 1074, 1018; **¹H NMR** (400 MHz, CDCl₃) δ 4.23-4.38 (ABX, $J_{AB} = 10.8$, $J_{AX} = 7.2$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H), 1.10 (s, 9H), 0.99 (t, 9H), 0.63-0.83 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 167.5, 118.5, 80.5, 62.8, 40.8, 25.1, 14.3, 6.9, 5.3; TLC (95:5 hexanes/EtOAc) R_f 0.37; **Anal.** Calcd for C₁₅H₂₉NO₃Si: C, 60.16; H, 9.76; N, 4.68. Found: C, 59.94; H, 9.74; N, 4.26.



Ethyl 2-cyano-2-(2-furyl)-2-(triethylsilyloxy) acetate (Table 2, entry 9). The title compound was prepared according to General Procedure C using 47 mg (0.22 mmol) of acylsilane, 25 μL (0.25 mmol) of ethylcyanofornate, 3.5 mg (0.011 mmol) of 18-crown-6, and 5 mL of C₇H₈. After 4-5 h at 110 °C, the crude product was purified by flash chromatography with 15:1

hexanes/EtOAc to afford 49.6 mg (73%) of the product as a clear oil. Analytical data for title compound: **IR** (thin film, cm^{-1}) 3149, 3127, 2959, 2879, 2244, 1772, 1751, 1460, 1233, 1159, 1142, 1014, 747; **^1H NMR** (400 MHz, CDCl_3) δ 7.45 (d, $J = 1.8$ Hz, 1H), 6.63 (d, $J = 3.3$, 1H), 6.42 (dd, $J = 3.6$ Hz, 1.8 Hz, 1H), 4.32 (ABX, $J_{\text{AB}} = 10.8$ Hz, $J_{\text{AX}} = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.8$ Hz, 9H), 0.64 (q, $J = 7.8$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 164.8, 147.9, 144.0, 116.4, 111.0, 110.4, 70.0, 63.7, 13.8, 6.5, 4.9; TLC (15:1 hexanes/EtOAc) R_f 0.25; **Anal.** Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4\text{Si}$: C, 58.22; H, 7.49; N, 4.53. Found: C, 58.52; H, 7.58; N, 4.51.

Appendix



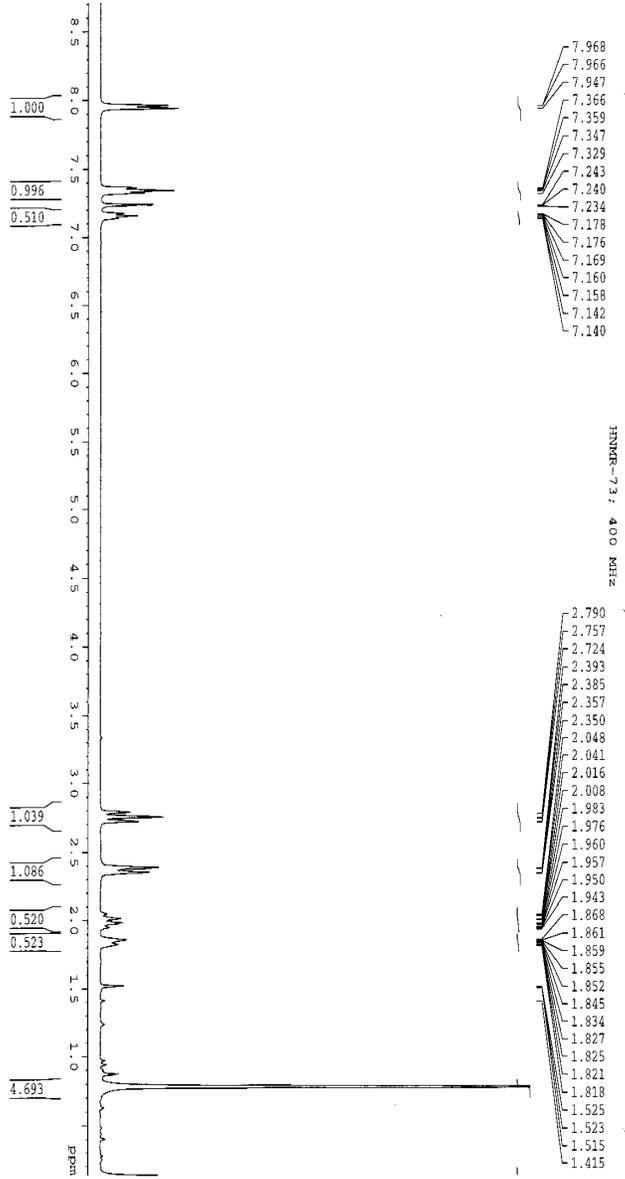
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28.007
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19.966

CL3NMR-73; 100 MHz



7.968
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7.947
7.366
7.359
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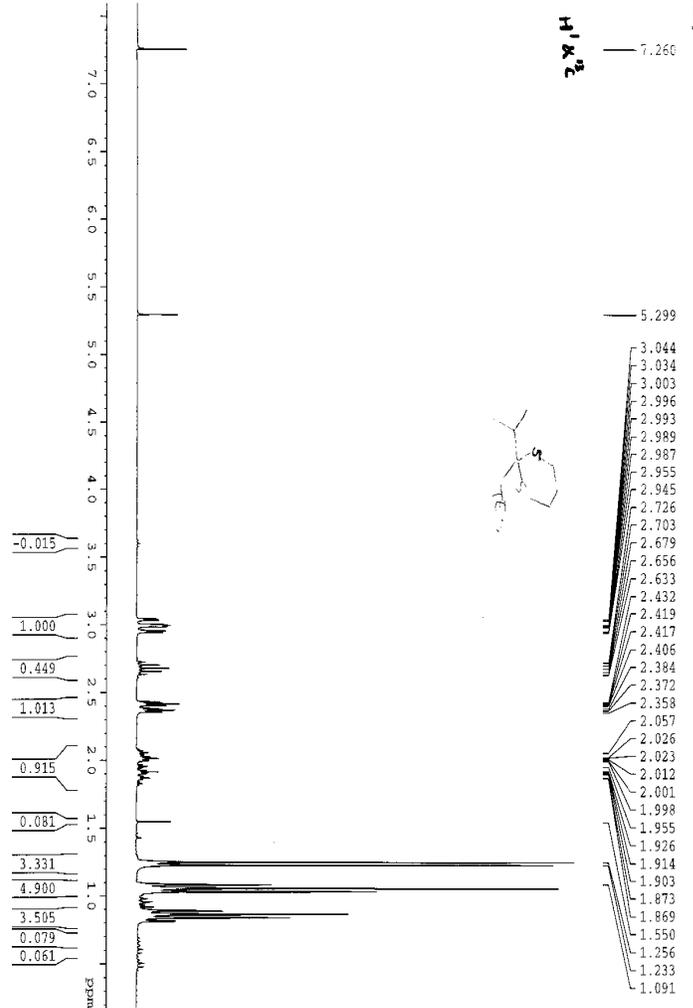
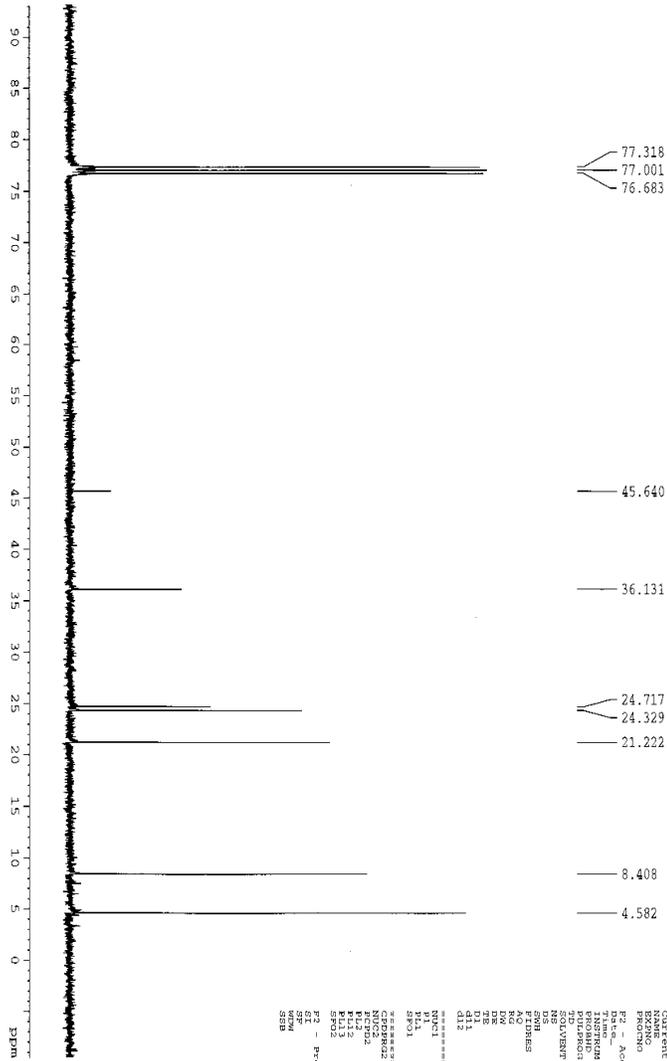
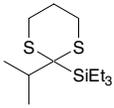
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1.983
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1.957
1.950
1.943
1.868
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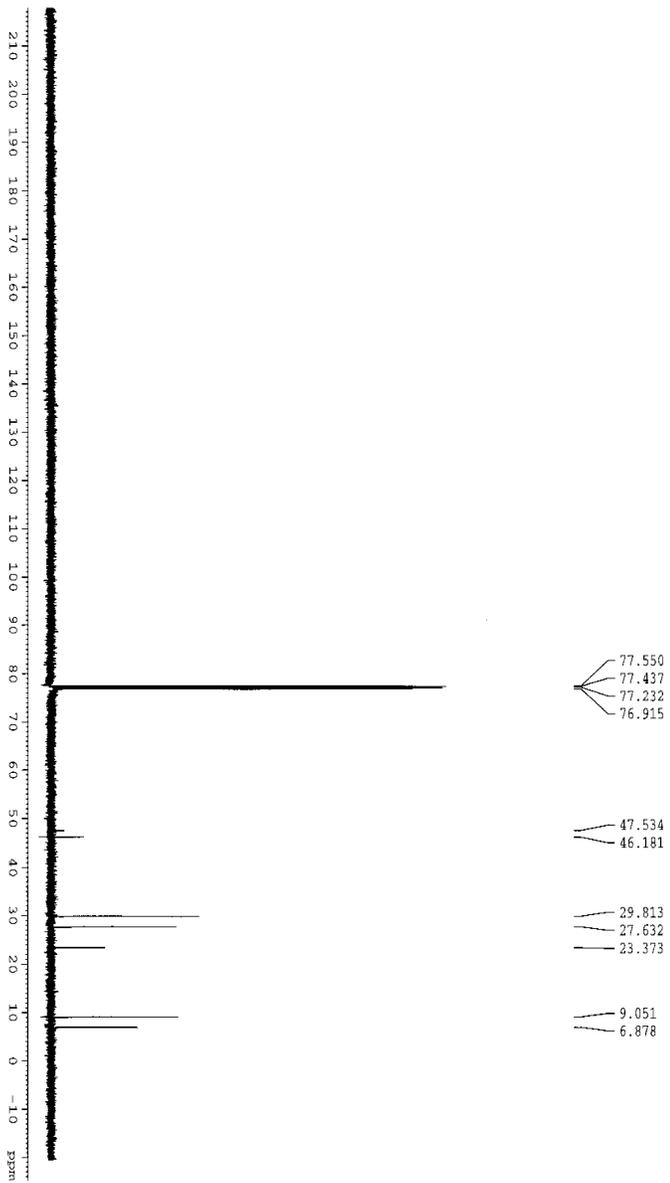
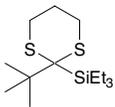
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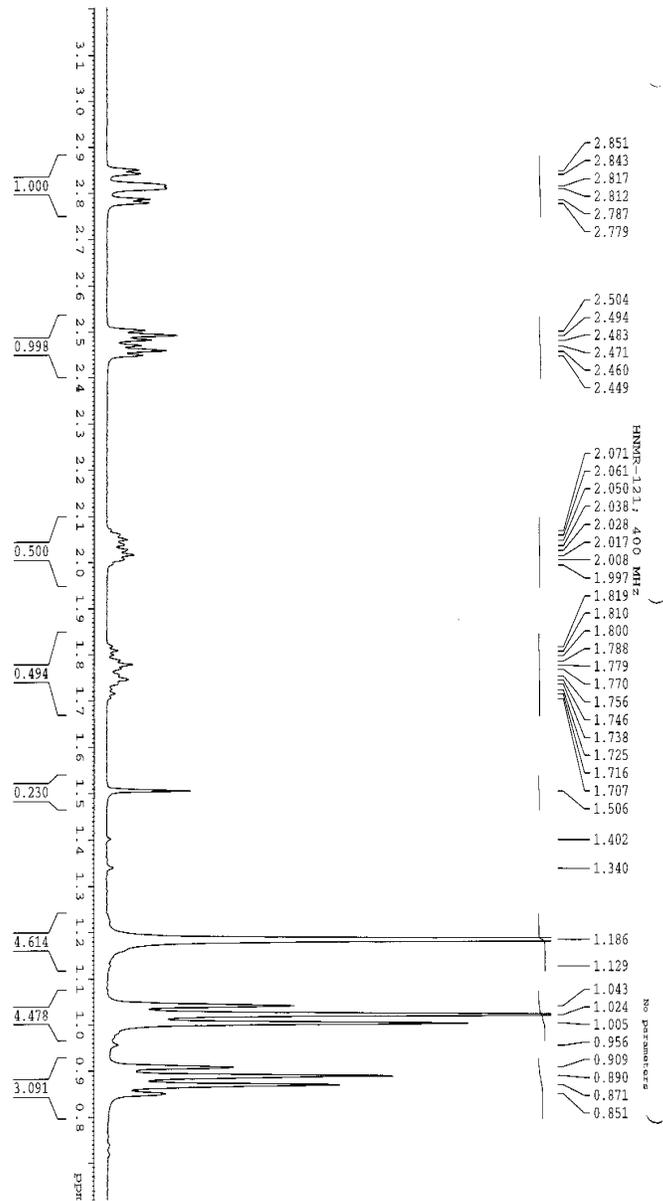


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13C NMR-121; 100 MHz



1H NMR-121; 400 MHz

NO DISTORTION

