

Sodium hydroxide–catalyzed dehydrocoupling of alcohols with hydrosilanes

Anton A. Toutov,¹ Kerry N. Betz,¹ Michael C. Haibach, Andrew M. Romine,¹
& Robert H. Grubbs^{1*}

rhg@caltech.edu

¹ Division of Chemistry and Chemical Engineering, California Institute of Technology
Pasadena, California 91125, United States

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General information.

Unless otherwise stated, reactions were performed in oven-dried brand-new Fisherbrand scintillation vials flushed with argon or in flame-dried Schlenk flasks under argon connected on a Schlenk line using dry, degassed solvents and brand-new stirring bars. Solvents were dried by passage through an activated alumina column under argon.¹ Reaction progress was monitored by thin-layer chromatography (TLC), GC-MS, or GC-FID analyses. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, phosphomolybdic acid, or KMnO₄ staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ¹H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer in CDCl₃, THF-*d*₈, or Benzene-*d*₆ and are reported relative to residual solvent peak at δ 7.26 ppm, δ 3.58 ppm, or δ 7.16 ppm respectively. ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (126 MHz) in CDCl₃, THF-*d*₈, or Benzene-*d*₆ and are reported relative to residual solvent peak at δ 77.16 ppm, δ 67.21 ppm, or δ 128.06 ppm respectively. Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ¹³C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained on a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm⁻¹). GC-FID analyses were obtained on an Agilent 6890N gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High resolution mass spectra (HRMS) were acquired from the California Institute of Technology Mass Spectrometry Facility.

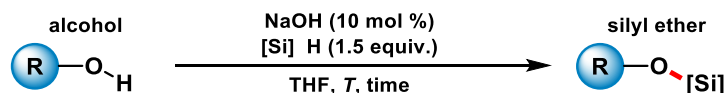
Silanes were purchased from Aldrich and distilled before use. NaOH was purchased from Aldrich (semiconductor grade, pellets, 99.99% trace metals basis) and was pulverized

¹ Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

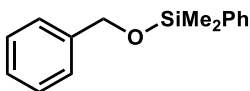
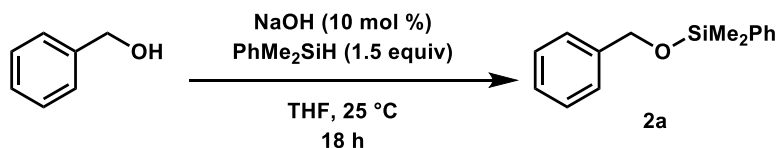
(mortar and pestle) and heated (150 °C) under vacuum prior to use. Powdered and vacuum-dried (as above) ACS grade $\geq 97\%$ NaOH from Aldrich gives identical results. Alcohol and phenol substrates were purchased from Aldrich, TCI, or Acros.

Part I. General observations.

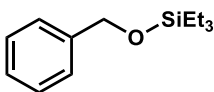
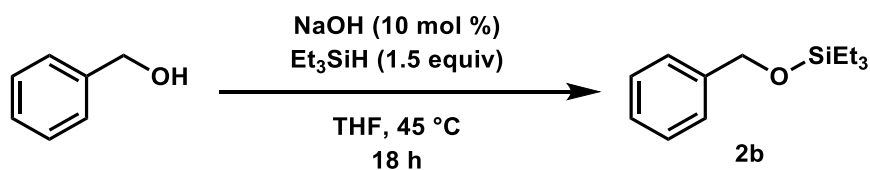
THF and DME proved to be suitable solvents. The addition of DMF to reaction mixtures enabled the silylation in challenging cases; several substrates failed to silylate without the addition of DMF. See characterization data (Part II) for a comprehensive view of all substrates that required addition of DMF. No product was observed in the absence of catalyst.

Part II. Experimental and analytics.**1. General procedure for cross-dehydrogenative O–H silylation and characterization data.**

To a hot, oven-dried 2 dram scintillation vial equipped with a magnetic stirring bar, NaOH (0.05 mmol, 10 mol %) was added and the vial was purged with argon until cool. Alcohol (0.5 mmol, 1 equiv) was then added under a steady stream of argon, followed by solvent (0.5 mL) and silane (0.75 mmol, 1.5 equiv). The vial was then sealed and the mixture was stirred at the indicated temperature for the indicated time. After the reaction was complete, the reaction mixture was diluted with diethyl ether (2 mL), filtered through a short pad of silica gel, and concentrated under reduced pressure. Volatiles were removed under high vacuum and the resultant material was purified by silica gel flash chromatography if necessary to give the desired O–Si product. Note that since this silylation protocol produces stoichiometric H₂, the reaction – especially when performed on a reasonable scale as in the case of **11** (page 24) – should be conducted in a well vented system and under conditions that are appropriately suitable and safe. Reactions were carried out behind protective shielding when performed in closed vials. In cases where this was not possible, the reactions were carried out in septum-capped vials connected via a needle to an argon manifold and a bubbler if necessary.



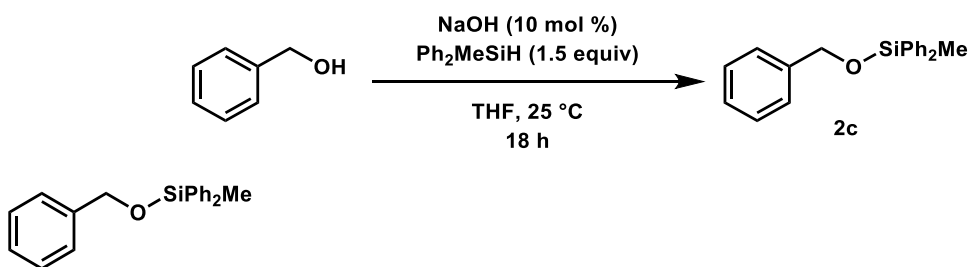
(Benzyloxy)dimethyl(phenyl)silane 2a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 $^\circ$ C for 18 h. The desired product **2a** (113.9 mg, 94% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.53 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.70 – 7.66 (m, 2H), 7.48 – 7.42 (m, 3H), 7.40 – 7.35 (m, 4H), 7.30 (dddd, J = 6.7, 6.2, 3.1, 1.7 Hz, 1H), 4.77 (s, 2H), 0.49 (s, 6H). This compound has been previously characterized.²



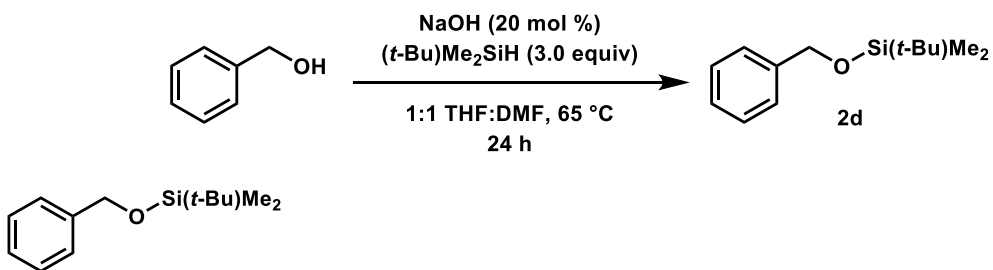
(Benzyloxy)triethylsilane 2b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), Et₃SiH (87 mg, 120 μ L, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 $^\circ$ C for 18 h. The desired product **2b** (101.2 mg, 91% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.27 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 4.75 (s, 2H), 1.00 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 7.9 Hz, 6H). This compound has been previously characterized.³

² Mitsudome, T.; Yamamoto, Y.; Noujima, A.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Eur. J.* **2013**, *19*, 14398–14402.

³ Abri, A.; Assadi, M.G.; Pourreza, S. *J. Chin. Chem. Soc.* **2012**, *59*, 1449–1454.



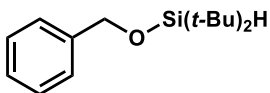
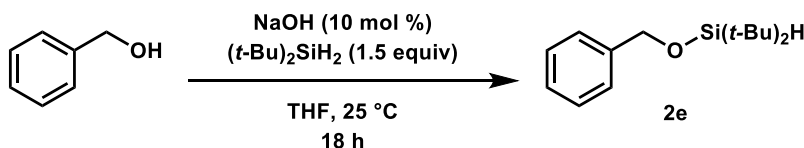
(Benzyloxy)(methyl)diphenylsilane 2c: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), Ph₂MeSiH (149 mg, 150 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **2c** (129.4 mg, 85% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.50$ (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.62 (m, 4H), 7.44 – 7.37 (m, 6H), 7.36 – 7.32 (m, 4H), 7.29 – 7.26 (m, 1H), 4.82 (d, J = 0.9 Hz, 2H), 0.68 (s, 3H). This compound has been previously characterized.⁴



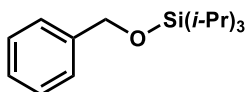
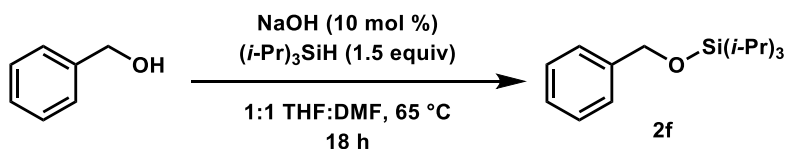
(Benzyloxy)(tert-butyl)dimethylsilane 2d: The general procedure was followed. The reaction was performed with NaOH (4.0 mg, 0.1 mmol, 20 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), (t-Bu)Me₂SiH (87 mg, 124 μL, 1.5 mmol, 3.0 equiv), 0.25 mL dimethylformamide (DMF) and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product **2d** (66.2 mg, 60% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.42$ (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, J = 4.6 Hz, 4H), 7.28 – 7.24 (m, 1H), 4.78 (d, J = 0.6 Hz, 2H), 0.98 (s, 9H), 0.14 (s, 6H). This compound has been previously characterized.⁵

⁴ Igarashi, M.; Matsumoto, T.; Sato, K.; Ando, W.; Shimada, S. *Chem. Lett.* **2014**, *43*, 429–431.

⁵ Yamamoto, K.; Takemae, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2111–2113.



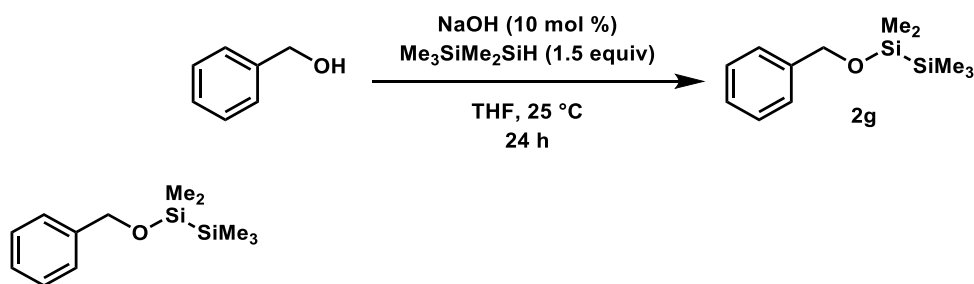
(Benzyloxy)di-*tert*-butylsilane 2e: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), (*t*-Bu)₂SiH₂ (108 mg, 148 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **2e** (120.2 mg, 96% yield) was obtained as a colorless oil after removal of volatiles under high vacuum (45 mtorr) for 2 hours. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.34 (m, 4H), 7.29 – 7.25 (m, 1H), 4.88 (d, *J* = 0.7 Hz, 2H), 4.12 (s, 1H), 1.05 (s, 18H). This compound has been previously characterized.⁶



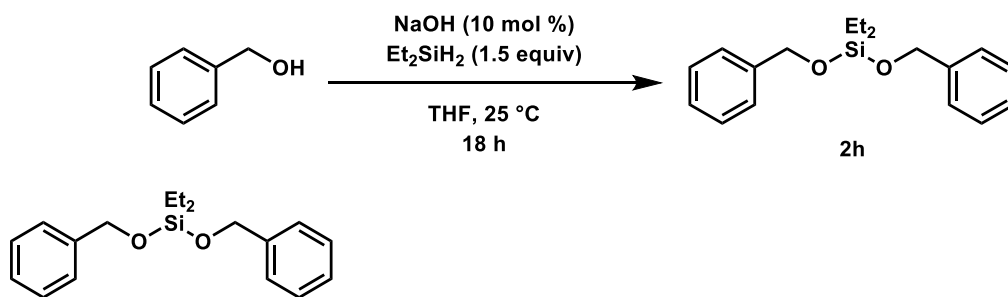
(Benzyloxy)triisopropylsilane 2f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), (*i*-Pr)₃SiH (119 mg, 154 μL, 0.75 mmol, 1.5 equiv), 0.25 mL dimethylformamide (DMF), and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product **2f** (112.4 mg, 85% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). *R_f* = 0.52 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 4.87 (d, *J* = 1.5 Hz, 2H), 1.26 – 1.17 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 18H). This compound has been previously characterized.⁷

⁶ Curran, D. P.; Xu, J.; Lazzarini, E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 24, 3049–3060.

⁷ Khalafi-Nezhad, A.; Fareghi Alamdari, R.; Zekri, N. *Tetrahedron* **2000**, 56, 7503–7506.

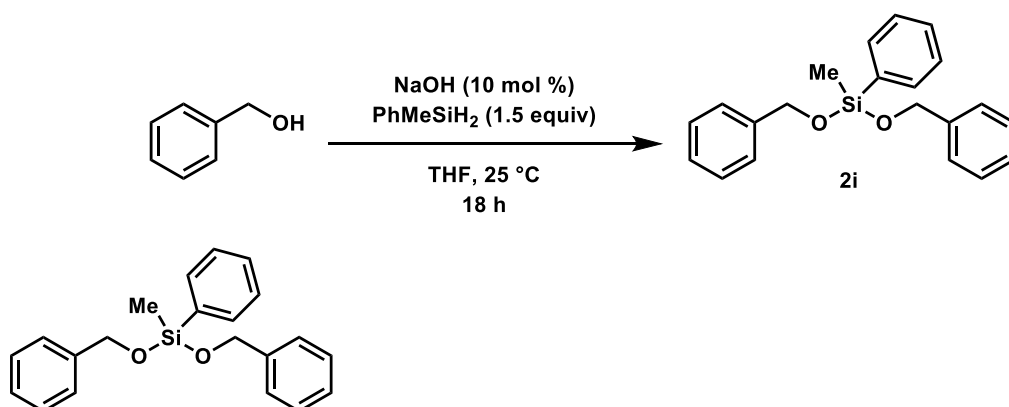


1-(Benzyloxy)-1,1,2,2,2-pentamethyldisilane 2g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (54 mg, 0.5 mmol, 1.0 equiv), $\text{Me}_5\text{Si}_2\text{H}$ (99 mg, 137 μL , 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 $^\circ\text{C}$ for 24 h. Concentration of the reaction mixture and purification of the resulting residue via Kugelrohr distillation (120 mTorr, 60 $^\circ\text{C}$) gave 79.9 mg (67% yield) of **2g** as a colorless oil. ^1H NMR (500 MHz, THF- d_8) δ 7.31 – 7.24 (m, 4H), 7.21 – 7.15 (m, 1H), 4.68 (q, $J = 0.7$ Hz, 2H), 0.23 (s, 6H), 0.10 (s, 9H); ^{13}C NMR (126 MHz, THF- d_8) δ 142.61, 128.96, 127.71, 127.01, 66.02, -0.52, -1.79. IR (Neat Film NaCl) 3363, 3088, 3065, 3030, 2952, 2893, 1595, 1495, 1453, 1376, 1259, 1246, 1207, 1091, 1067, 1026, 835, 803, 766, 729, 695, 655, 617 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{12}\text{H}_{23}\text{OSi}_2$ [M+H]: 239.1288, found 239.1295.

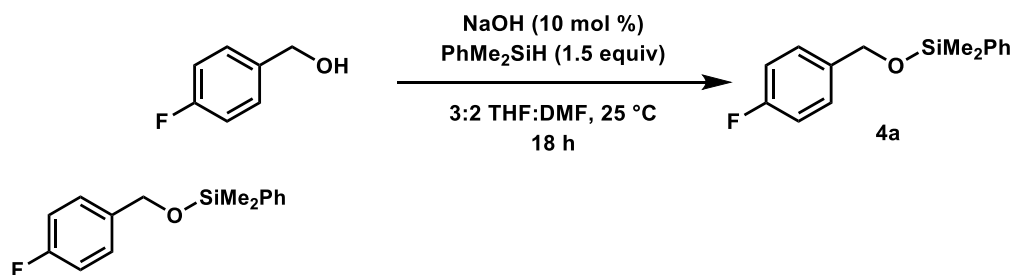


Bis(benzyloxy)diethylsilane 2h: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (108 mg, 1.0 mmol, 1.0 equiv), Et_2SiH_2 (49 mg, 71 μL , 0.55 mmol, 0.55 equiv), and 1.0 mL of tetrahydrofuran (THF) at 25 $^\circ\text{C}$ for 18 h. The desired product **2h** (120.8 mg, 80% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.43$ (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 4.4$ Hz, 8H), 7.31 – 7.26

(m, 2H), 4.82 (s, 4H), 1.05 (t, $J = 7.9$ Hz, 6H), 0.76 (q, $J = 8.0$ Hz, 4H). This compound has been previously characterized.⁸



Bis(benzyloxy)(methyl)(phenyl)silane 2i: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), benzyl alcohol (108 mg, 1.0 mmol, 1.0 equiv), MePhSiH₂ (67 mg, 76 μ L, 0.55 mmol, 0.55 equiv), and 1.0 mL of tetrahydrofuran (THF) at 25 $^\circ$ C for 18 h. The desired product **2i** (158.8 mg, 95% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.44$ (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.76 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.49 – 7.43 (m, 3H), 7.39 – 7.37 (m, 8H), 7.33 – 7.28 (m, 2H), 4.91 – 4.82 (m, 4H), 0.50 (s, 3H). This compound has been previously characterized.⁹

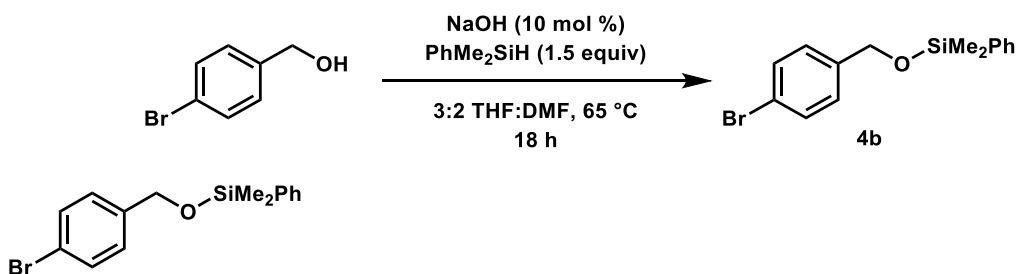


((4-Fluorobenzyl)oxy)dimethyl(phenyl)silane 4a: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-fluorobenzyl alcohol (63 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv),

⁸ Chatterjee, B.; Gunanathan, C. *Chem. Commun.* **2014**, 50, 888–890.

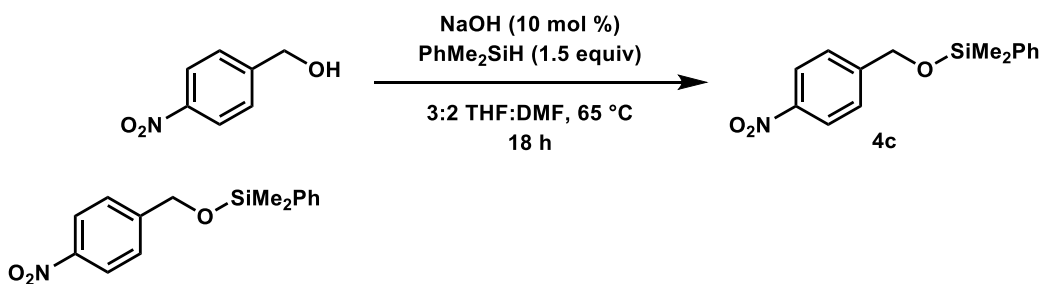
⁹ Kita, Y.; Yasuda, H.; Sugiyama, Y.; Fukata, F.; Haruta, J.; Yasumitsu, T. *Tetrahedron Lett.* **1983**, 24, 1273–1276.

0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **4a** (146.0 mg, 79% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.48$ (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.65 – 7.59 (m, 2H), 7.46 – 7.37 (m, 3H), 7.31 – 7.25 (m, 2H), 7.06 – 6.97 (m, 2H), 4.67 (q, $J = 0.8$ Hz, 2H), 0.45 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.14 (d, $J = 244.4$ Hz), 137.50, 136.53 (d, $J = 2.9$ Hz), 133.64, 129.90, 128.37 (d, $J = 8.3$ Hz), 128.06, 115.19 (d, $J = 21.1$ Hz), 64.48, -1.60. IR (Neat Film NaCl) 3440, 3070, 3050, 3022, 2958, 2866, 1605, 1509, 1463, 1427, 1417, 1375, 1294, 1253, 1221, 1155, 1117, 1082, 1014, 826, 789, 741, 700, 645 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{15}\text{H}_{16}\text{OSiF}$ [(M+H)- H_2]: 259.0955, found 259.0951.

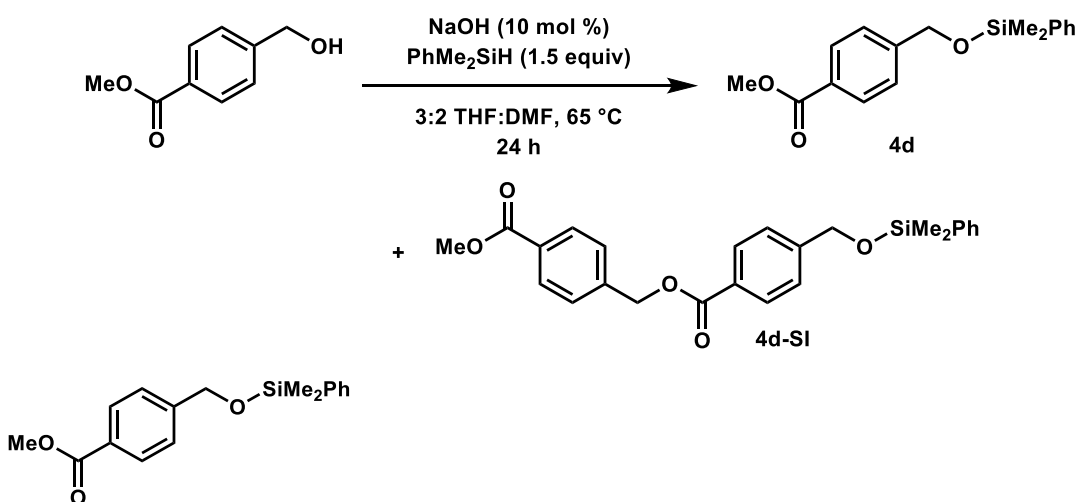


((4-Bromobenzyl)oxy)dimethyl(phenyl)silane 4b: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-bromobenzyl alcohol (94 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL , 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product **4b** (146.2 mg, 91% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.48$ (5% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.61 (dd, $J = 7.7, 1.8$ Hz, 2H), 7.47 – 7.34 (m, 5H), 7.19 (dt, $J = 8.7, 0.7$ Hz, 2H), 4.66 (d, $J = 0.8$ Hz, 2H), 0.44 (s, 6H). This compound has been previously characterized.¹⁰

¹⁰ Kennedy-Smith, J. J.; Nolin, K. A.; Gunterman, H. P.; Toste, D. F. *J. Am. Chem. Soc.* **2003**, *125*, 4056–4057.

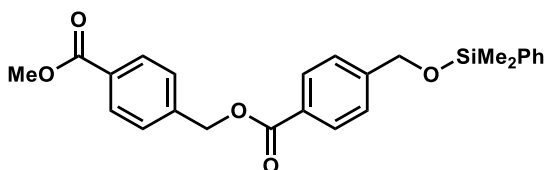


Dimethyl((4-nitrobenzyl)oxy)(phenyl)silane 4c: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-nitrobenzyl alcohol (77 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 $^\circ$ C for 18 h. The desired product **4c** (102.2 mg, 71% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.38$ (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 8.21 – 8.15 (m, 2H), 7.60 (dd, $J = 7.8, 1.7$ Hz, 2H), 7.47 (dt, $J = 8.8, 0.8$ Hz, 2H), 7.44 – 7.38 (m, 3H), 4.79 (t, $J = 0.8$ Hz, 2H), 0.47 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 148.51, 147.18, 136.92, 133.59, 130.13, 128.18, 126.77, 123.68, 64.03, -1.73. IR (Neat Film NaCl) 3423, 2958, 1641, 1608, 1519, 1527, 1253, 1117, 1094, 856, 830, 786, 735, 700 cm^{-1} ; HRMS (EI⁺) calc'd for C₁₅H₁₈SiO₃N [M+H]: 288.1056, found 288.1058.



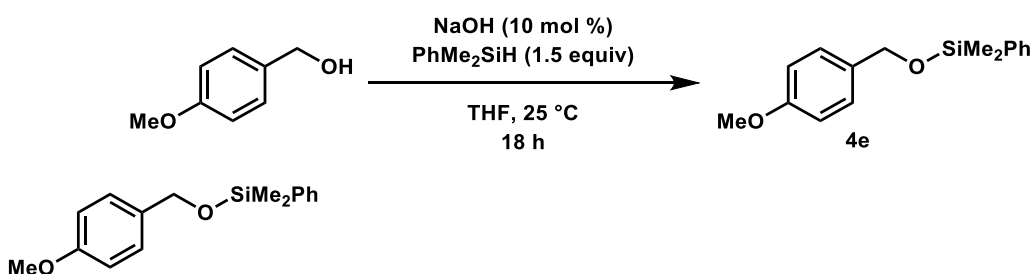
Methyl 4-(((dimethyl(phenyl)silyl)oxy)methyl)benzoate 4d: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), methyl 4-(hydroxymethyl)benzoate (83 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L,

0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product **4d** (100.6 mg, 67% yield) was obtained as a colorless oil by silica gel flash chromatography (gradient 15% EtOAc to 30% EtOAc in hexanes). $R_f = 0.62$ (15% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.3$ Hz, 2H), 7.63 – 7.60 (m, 2H), 7.45 – 7.36 (m, 5H), 4.76 (d, $J = 0.8$ Hz, 2H), 3.92 (s, 3H), 0.46 (s, 6H). This compound has been previously characterized.¹¹



4-((Methoxycarbonyl)benzyl 4-(((dimethyl(phenyl)silyl)oxy)methyl)benzoate 4d-SI:

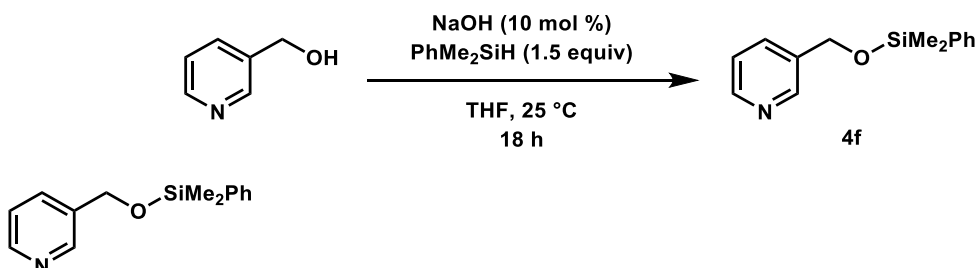
Also isolated from the column was **4d-SI** (36.9 mg, 34% silylation yield / 17% yield based on methyl 4-(hydroxymethyl)benzoate stoichiometry) as a colorless solid. $R_f = 0.43$ (15% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 – 8.03 (m, 4H), 7.62 – 7.58 (m, 2H), 7.51 (dt, $J = 8.6, 0.7$ Hz, 2H), 7.43 – 7.37 (m, 5H), 5.42 (s, 2H), 4.76 (d, $J = 0.8$ Hz, 2H), 3.93 (s, 3H), 0.44 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.88, 166.31, 146.62, 141.30, 137.26, 133.61, 130.02, 129.97, 129.90, 128.63, 128.09, 127.72, 126.27, 65.94, 64.53, 52.32, -1.64.



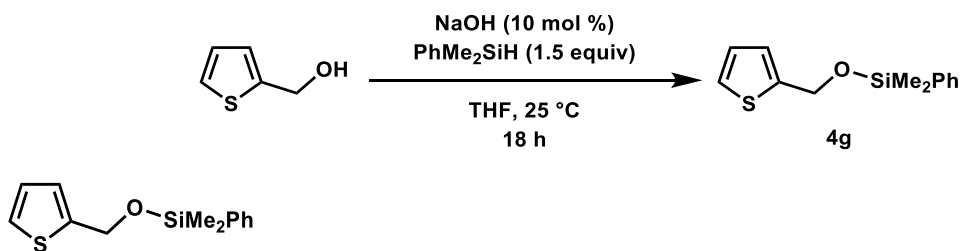
((4-Methoxybenzyl)oxy)dimethyl(phenyl)silane 4e: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-methoxybenzyl alcohol (69 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL , 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **4e** (117.9 mg, 87% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.29$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500

¹¹ Fernandez, A. C.; Fernandez, R.; Romao, C. C.; Royo, B. *Chem. Commun.* **2005**, 2, 213–214.

MHz, CDCl₃) δ 7.62 (dd, $J = 7.5, 2.0$ Hz, 2H), 7.44 – 7.37 (m, 3H), 7.25 – 7.20 (m, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 4.64 (d, $J = 0.6$ Hz, 2H), 3.81 (s, 3H), 0.42 (s, 6H). This compound has been previously characterized.¹²



3-(((Dimethyl(phenyl)silyl)oxy)methyl)pyridinesilane 4f: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), pyridin-3-ylmethanol (55 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **4f** (118.1 mg, 97% yield) was obtained as a colorless oil by removal of volatiles at 80 °C at 60mTorr. ¹H NMR (500 MHz, CDCl₃) δ 8.52 (dt, $J = 2.3, 0.8$ Hz, 1H), 8.49 (dd, $J = 4.8, 1.6$ Hz, 1H), 7.65 (dtd, $J = 7.8, 1.7, 0.9$ Hz, 1H), 7.61 – 7.57 (m, 2H), 7.43 – 7.37 (m, 3H), 7.26 (ddd, $J = 7.9, 4.8, 0.9$ Hz, 1H), 4.70 (dt, $J = 0.6$ Hz, 2H), 0.44 (s, 6H). This compound has been previously characterized.¹³

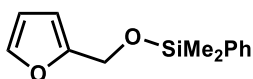
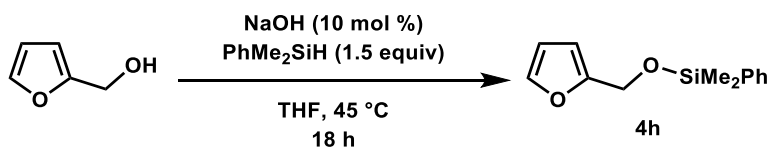


Dimethyl(phenyl)(thiophen-2-ylmethoxy)silane 4g: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), thiophen-2-ylmethanol (57 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **4g** (119.2 mg, 96% yield) was obtained as a colorless oil by removal of volatiles

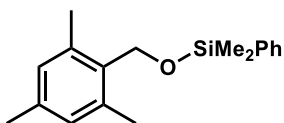
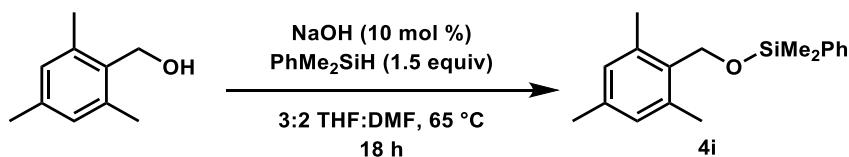
¹² Bideau, F. L.; Coradin, T.; Henique, J.; Samuel, E. *Chem. Commun.* **2001**, 15, 1408–1409.

¹³ Goldberg, Y.; Rubina, K.; Shymanska, M.; Lukevics, E. *Synth. Commun.* **1990**, 20, 2439–2446.

at 80 °C at 60mTorr. ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.58 (m, 2H), 7.44 – 7.37 (m, 3H), 7.28 (dd, J = 4.4, 1.9 Hz, 1H), 7.00 (d, J = 4.4 Hz, 2H), 4.76 (d, J = 0.8 Hz, 2H), 0.41 (s, 6H). This compound has been previously characterized.¹⁴



(Furan-2-ylmethoxy)dimethyl(phenyl)silane 4h: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), furfuryl alcohol (49 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 18 h. The desired product **4h** (101.1 mg, 87% yield) was obtained as a colorless oil by removal of volatiles at 80 °C at 60mTorr. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (ddd, J = 7.5, 2.4, 1.3 Hz, 2H), 7.46 – 7.33 (m, 4H), 6.32 (dt, J = 3.4, 1.8 Hz, 1H), 6.21 (t, J = 2.5 Hz, 1H), 4.62 (d, J = 2.0 Hz, 2H), 0.43 (d, J = 1.9 Hz, 6H). This compound has been previously characterized.¹⁵

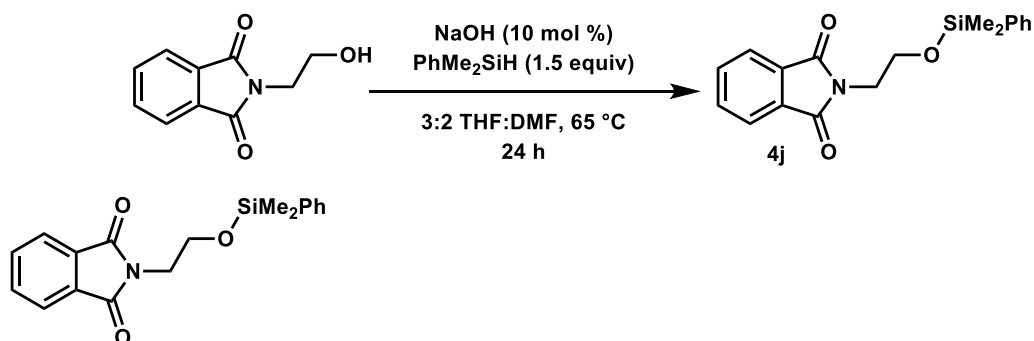


Dimethyl(phenyl)((2,4,6-trimethylbenzyl)oxy)silane 4i: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), mesitylmethanol (75 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. Concentration of the reaction mixture and purification of the resulting residue

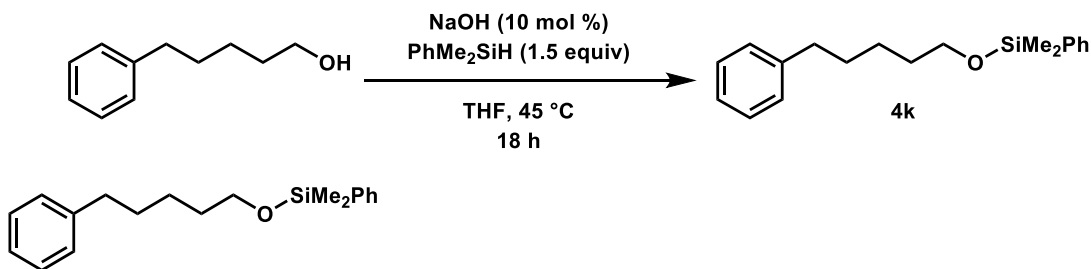
¹⁴ Goldberg, Y.; Abele, E.; Shymanska, M.; Lukevics, E. *J. Organomet. Chem.* **1991**, *410*, 127–133.

¹⁵ Goldberg, Y.; Abele, E.; Shymanska, M.; Lukevics, E. *J. Organomet. Chem.* **1991**, *410*, 127–133.

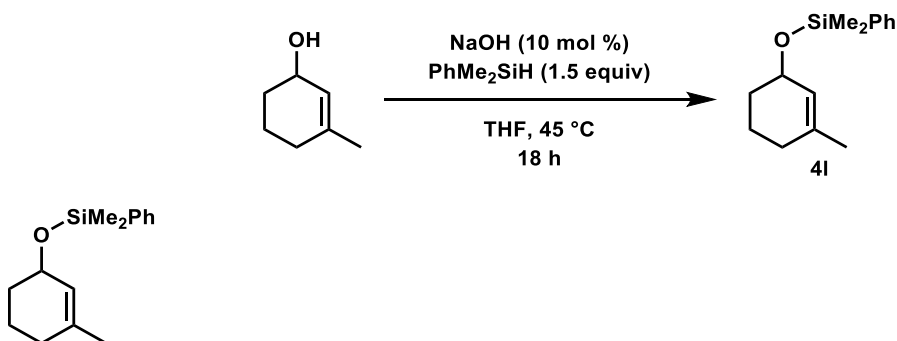
via Kugelrohr distillation (100 mTorr, 210 °C) gave 118.7 mg (84% yield) of **4i** as a colorless oil. (Note: the purified material obtained by Kugelrohr distillation was accompanied by ca. 5% unidentified by-products; however, further purification by chromatography was precluded by the instability of **4i** on SiO₂ as well as its decomposition under prolonged heating). ¹H NMR (500 MHz, THF-*d*₈) δ 7.59 – 7.55 (m, 2H), 7.36 – 7.30 (m, 3H), 6.79 – 6.73 (m, 2H), 4.66 (s, 2H), 2.24 (t, J = 0.6 Hz, 6H), 2.20 (s, 3H), 0.35 (s, 6H); ¹³C NMR (126 MHz, THF-*d*₈) δ 139.02, 137.93, 137.61, 134.72, 134.46, 130.42, 129.65, 128.68, 59.98, 21.23, 19.79, -1.48. IR (Neat Film NaCl) 3421, 3069, 3048, 3008, 2957, 2918, 1614, 1583, 1427, 1373, 1253, 1147, 1118, 1046, 848, 829, 784, 740, 699, 644 cm⁻¹; HRMS (EI+) calc'd for C₁₆H₁₆FSi [(M+H)-H₂]: 283.1518, found 283.1526.



2-(2-((Dimethyl(phenyl)silyl)oxy)ethyl)isoindoline-1,3-dione **4j:** The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 2-(2-hydroxyethyl)isoindoline-1,3-dione (96 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product **4j** (101.6 mg, 62% yield) was obtained as a colorless oil by silica gel flash chromatography (20% EtOAc in hexanes). *R_f* = 0.45 (20% EtOAc in hexanes); ¹H NMR (500 MHz, Benzene-*d*₆) δ 7.52 – 7.50 (m, 1H), 7.50 (dd, J = 2.4, 0.6 Hz, 1H), 7.43 (dd, J = 5.4, 3.0 Hz, 2H), 7.16 – 7.15 (m, 1H), 7.15 – 7.14 (m, 1H), 7.14 (d, J = 2.3 Hz, 1H), 6.87 (ddd, J = 5.5, 3.0, 0.5 Hz, 2H), 3.74 – 3.67 (m, 2H), 3.68 – 3.62 (m, 2H), 0.26 (s, 6H); ¹³C NMR (126 MHz, Benzene-*d*₆) δ 167.96, 137.77, 133.81, 133.39, 132.66, 129.84, 128.13, 122.95, 60.16, 40.23, -1.81. IR (Neat Film NaCl) 2956, 1773, 1713, 1615, 1467, 1427, 1392, 1362, 1319, 1252, 1189, 1116, 1022, 929, 859, 829, 788, 718, 700 cm⁻¹; HRMS (EI+) calc'd for C₁₈H₂₀O₃SiN [M+H]: 326.1213, found 326.1223.

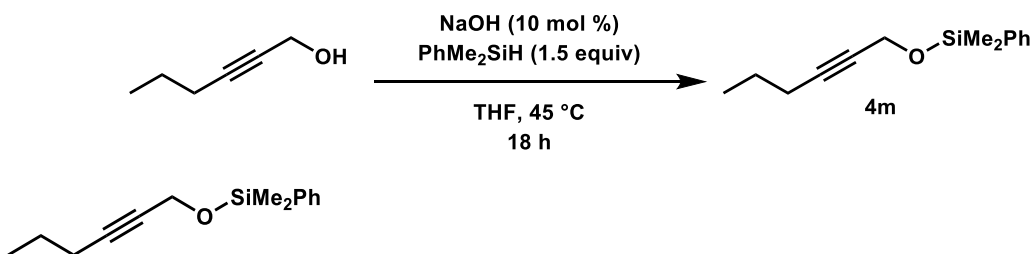


Dimethyl(phenyl)((5-phenylpentyl)oxy)silane 4k: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 5-phenylpentan-1-ol (82 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 $^\circ$ C for 18 h. The desired product **4k** (146.3 mg, 98% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). R_f = 0.46 (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl₃) δ 7.63 (ddq, J = 6.2, 1.9, 0.9 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.32 (tt, J = 7.5, 0.9 Hz, 2H), 7.22 (ddt, J = 9.9, 7.3, 1.3 Hz, 3H), 3.65 (td, J = 6.7, 1.1 Hz, 2H), 2.67 – 2.63 (m, 2H), 1.74 – 1.58 (m, 4H), 1.47 – 1.38 (m, 2H), 0.44 (t, J = 1.0 Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl₃) δ 142.79, 138.10, 133.58, 129.66, 128.51, 128.34, 127.93, 125.71, 63.15, 36.04, 32.57, 31.41, 25.59, -1.65. IR (Neat Film NaCl) 3385, 3067, 3025, 2933, 2857, 1603, 1495, 1452, 1427, 1341, 1254, 1119, 1055, 831, 791, 726, 698 cm^{-1} ; HRMS (EI+) calc'd for C₁₉H₂₇OSi [M+H]: 299.1831, found 299.1840.

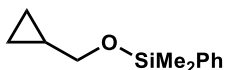
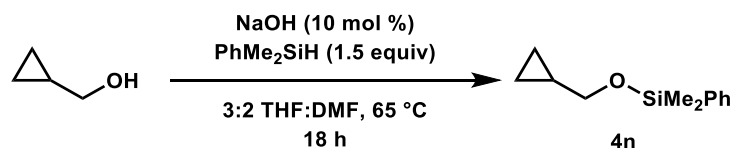


Dimethyl((3-methylcyclohex-2-en-1-yl)oxy)(phenyl)silane 4l: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 3-methylcyclohex-2-en-1-ol (56 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75

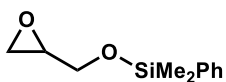
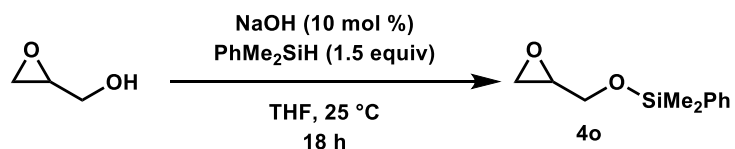
mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 45 °C for 48 h. The desired product **4l** (113.4 mg, 92% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.43$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64 – 7.56 (m, 2H), 7.38 (dd, $J = 5.0, 1.9$ Hz, 3H), 5.34 (dd, $J = 3.1, 1.6$ Hz, 1H), 4.20 (dt, $J = 5.0, 1.6$ Hz, 1H), 1.99 – 1.69 (m, 4H), 1.64 (tt, $J = 1.6, 0.9$ Hz, 3H), 1.55 – 1.42 (m, 2H), 0.40 (d, $J = 1.1$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.64, 137.78, 133.69, 129.59, 127.89, 125.14, 67.41, 32.13, 30.08, 23.80, 19.83, -0.80, -0.91. IR (Neat Film NaCl) 3423, 3069, 2935, 2862, 1645, 1427, 1251, 1116, 1074, 1024, 992, 894, 880, 828, 786, 738, 700 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{15}\text{H}_{21}\text{OSi}$ [(M+H)- H_2]: 245.1362, found 245.1368.



(Hex-2-yn-1-yloxy)dimethyl(phenyl)silane 4m: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), hex-2-yn-1-ol (49 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL , 0.75 mmol, 1.5 equiv), and 0.5 mL of 1 tetrahydrofuran (THF) at 45 °C for 18 h. The desired product **4m** (99.9 mg, 86% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.43$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 – 7.59 (m, 2H), 7.42 – 7.36 (m, 3H), 4.27 (t, $J = 2.2$ Hz, 2H), 2.16 (tt, $J = 7.1, 2.2$ Hz, 2H), 1.51 (h, $J = 7.3$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H), 0.45 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 137.36, 133.71, 129.84, 127.97, 85.99, 78.37, 51.93, 22.11, 20.92, 13.66, -1.46. *Note: this product decomposes slowly in CDCl_3 .* IR (Neat Film NaCl) 3420, 2956, 1646, 1254, 1118, 1067, 1026, 830, 789, 726, 698 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{14}\text{H}_{19}\text{OSi}$ [M+H]: 231.1205, found 231.1207.

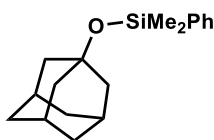
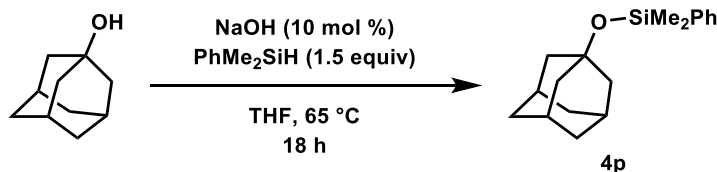


(Cyclopropylmethoxy)dimethyl(phenyl)silane 4n: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), cyclopropanemethanol (36 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. Concentration of the reaction mixture and purification of the resulting residue via Kugelrohr distillation (120 mTorr, 65 °C) gave 65.4 mg (63% yield) of **4n** as a colorless oil. *Note: product is volatile under high vacuum.* (Note: the purified material obtained by Kugelrohr distillation was accompanied by ca. 5% unidentified by-products; however, further purification by chromatography was precluded by the instability of **4n** on SiO₂). ¹H NMR (500 MHz, Benzene-*d*₆) δ 7.63 – 7.58 (m, 2H), 7.27 – 7.19 (m, 3H), 3.40 (d, J = 6.4 Hz, 2H), 0.95 (ttt, J = 8.0, 6.4, 4.9 Hz, 1H), 0.34 (s, 6H), 0.32 – 0.28 (m, 2H), 0.12 – 0.05 (m, 2H); ¹³C NMR (126 MHz, Benzene-*d*₆) δ 138.63, 133.92, 129.80, 128.15, 67.54, 13.68, 3.23, -1.38. IR (Neat Film NaCl) 3070, 3006, 2958, 2862, 1470, 1427, 1403, 1251, 1177, 1116, 1073, 851, 826, 785, 740, 699 cm⁻¹; HRMS (EI+) calc'd for C₁₂H₁₈OSi [M+•]: 206.1127, found 206.1148.

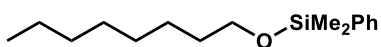
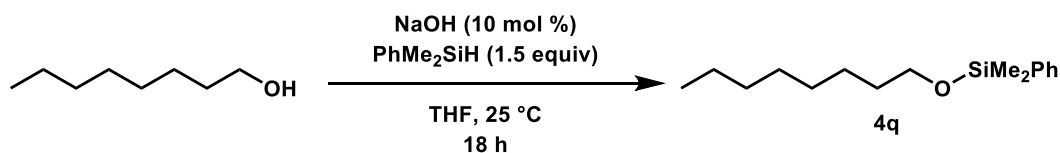


Dimethyl(oxiran-2-ylmethoxy)(phenyl)silane 4o: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), glycidol (37 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μL, 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 °C for 18 h. The desired product **4o** (74.8 mg, 72% yield) was obtained as a colorless oil by silica gel flash chromatography (10% EtOAc in hexanes). R_f

= 0.60 (10% EtOAc in hexanes); ^1H NMR (500 MHz, Benzene- d_6) δ 7.63 – 7.53 (m, 2H), 7.22 (dd, J = 5.5, 1.8 Hz, 3H), 3.58 (dd, J = 11.9, 2.9 Hz, 1H), 3.33 (dd, J = 11.9, 5.3 Hz, 1H), 2.78 (ddt, J = 5.4, 3.9, 2.7 Hz, 1H), 2.24 (dd, J = 5.3, 4.0 Hz, 1H), 2.16 (dd, J = 5.3, 2.6 Hz, 1H), 0.33 (s, 6H). This compound has been previously characterized.¹⁶



(((3s,5s,7s)-Adamantan-1-yl)oxy)dimethyl(phenyl)silane 4p: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 1-adamantol (76 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL , 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 65 $^\circ\text{C}$ for 18 h. The desired product **4p** (66.2 mg, 60% yield) was obtained as a colorless oil by removal of volatiles at 80 $^\circ\text{C}$ at 60mTorr. ^1H NMR (500 MHz, CDCl_3) δ 7.68 – 7.62 (m, 2H), 7.40 – 7.38 (m, 3H), 2.13 – 2.08 (m, 3H), 1.80 (dt, J = 3.3, 0.8 Hz, 6H), 1.64 – 1.55 (m, 6H), 0.43 (s, 6H). This compound has been previously characterized.¹⁷

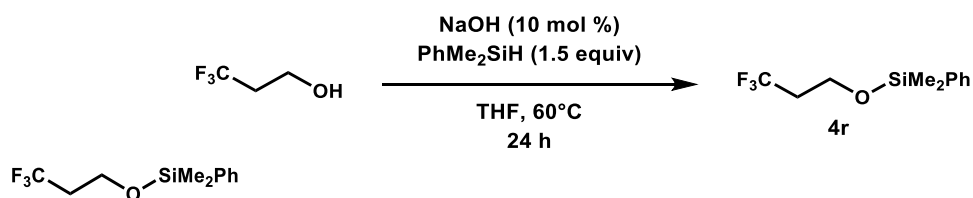


Dimethyl(octyloxy)(phenyl)silane 4q: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 1-octanol (65 mg, 0.5 mmol, 1.0 equiv), PhMe_2SiH (102 mg, 115 μL , 0.75 mmol, 1.5 equiv), and 0.5 mL of tetrahydrofuran (THF) at 25 $^\circ\text{C}$ for 18 h. The desired product **4q** (111.1 mg, 84% yield)

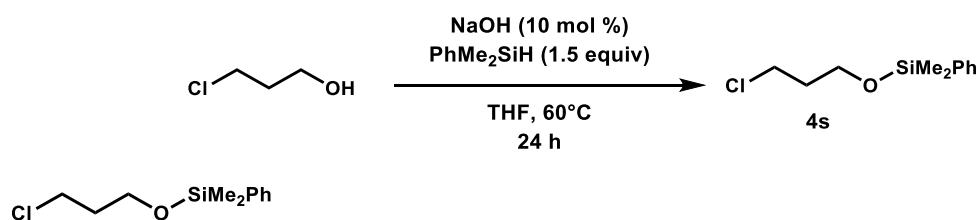
¹⁶ Bideau, F. L.; Coradin, T.; Henique, J.; Samuel, E. *Chem. Commun.* **2001**, 15, 1408–1409.

¹⁷ Park, J.-W.; Jun, C.-H. *Org. Lett.* **2007**, 9, 4073–4076.

was obtained as a colorless oil by silica gel flash chromatography (100% hexanes). $R_f = 0.49$ (100% hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64 – 7.58 (m, 2H), 7.41 (dd, $J = 5.0, 1.9$ Hz, 3H), 3.62 (t, $J = 6.7$ Hz, 2H), 1.60 – 1.51 (m, 2H), 1.32 – 1.24 (m, 10H), 0.97 – 0.85 (m, 3H), 0.41 (s, 6H). This compound has been previously characterized.¹⁸



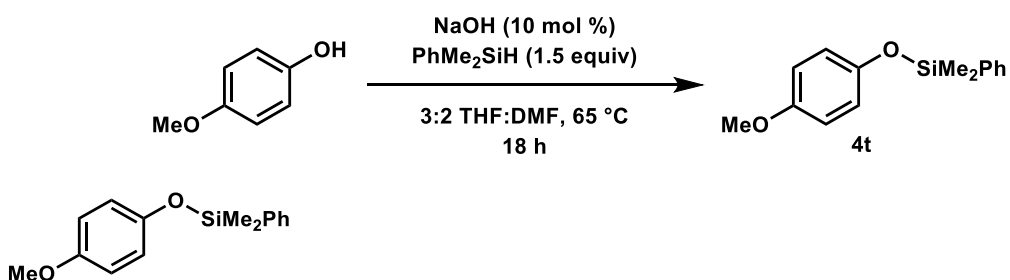
Dimethyl(phenyl)(3,3,3-trifluoropropoxy)silane 4r: The general procedure was followed. The reaction was performed with 3,3,3-trifluoropropanol (114 mg, 1.00 mmol, 1.0 equiv), Me_2PhSiH (204 mg, 230 μL , 1.5 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was heated to 60°C for 24 hours, then concentrated in vacuo and purified by silica gel column chromatography (5% EtOAc in hexanes) to afford **4r** (220 mg, 89% yield) as a colorless oil. $R_f = 0.48$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.76 – 7.55 (m, 2H), 7.55 – 7.41 (m, 3H), 3.91 (t, $J = 6.7$ Hz, 2H), 2.43 (qt, $J = 10.7, 6.7$ Hz, 2H), 0.49 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 137.18, 133.54, 130.00, 128.11, 56.34 (q, $J = 3.9$ Hz), 36.96 (q, $J = 27.4$ Hz), -1.96; $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -64.60 (t, $J = 10.7$ Hz). IR (Neat Film NaCl) 3051, 3070, 3022, 3012, 2959, 3002, 2892, 1591, 1410, 1382, 1347, 1255, 1152, 1137, 1119, 1094, 1050, 1025, 1006, 917, 830, 728, 699 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Si}$ [$\text{M}+\bullet$]: 248.0844, found 248.0836.



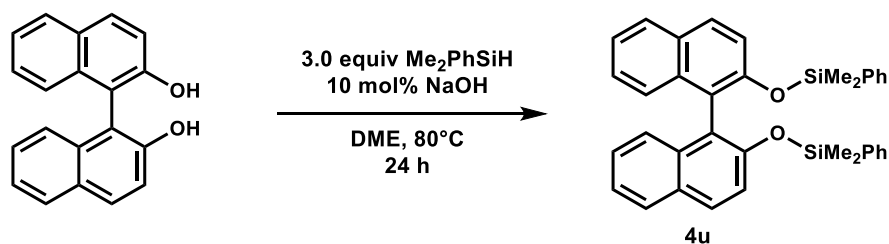
(3-chloropropoxy)dimethyl(phenyl)silane 4s: The general procedure was followed. The reaction was performed with 3-chloropropanol (94 mg, 1.00 mmol, 1.0 equiv), Me_2PhSiH

¹⁸ Itagaki, S.; Sunaba, H.; Kamata, K.; Yamaguchi, K.; Mizuno, N. *Chem. Lett.* **2013**, *42*, 980–982.

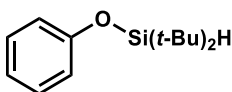
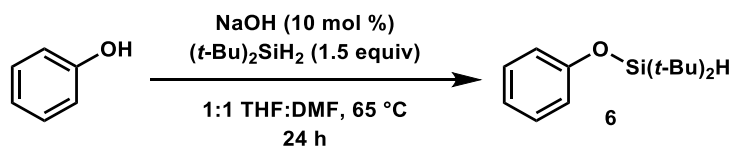
(204 mg, 230 μ L, 1.5 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was heated to 60°C for 24 hours, then concentrated in vacuo and purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford **4s** (178 mg, 78% yield) as a colorless oil. $R_f = 0.43$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80 – 7.60 (m, 2H), 7.57 – 7.38 (m, 3H), 3.84 (t, $J = 5.8$ Hz, 2H), 3.73 (q, $J = 6.5$ Hz, 2H), 3.58 (q, $J = 7.0$ Hz, 1H), 2.17 – 1.96 (m, 2H), 1.31 (t, $J = 7.0$ Hz, 1H), 0.50 (d, $J = 4.3$ Hz, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 137.61, 133.47, 129.75, 127.96, 59.44, 41.71, 35.21, -1.87. Note the high volatility of the product, which prevents quantitative solvent removal by high vacuum (i.e., that some residual solvent signals remain). IR (Neat Film NaCl) 3069, 3050, 3011, 2958, 2874, 2361, 2343, 1427, 1253, 1118, 1097, 1068, 830, 788, 699 cm^{-1} ; HRMS (FAB+) calc'd for $\text{C}_{11}\text{H}_{17}\text{ClOSi}$ [$\text{M}+\text{H}$]: 229.0816, found 229.0797.



(4-Methoxyphenoxy)dimethyl(phenyl)silane 4t: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), 4-methoxyphenol (62 mg, 0.5 mmol, 1.0 equiv), PhMe₂SiH (102 mg, 115 μ L, 0.75 mmol, 1.5 equiv), 0.2 mL dimethylformamide (DMF) and 0.3 mL of tetrahydrofuran (THF) at 65 °C for 18 h. The desired product **4t** (106.0 mg, 82% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). $R_f = 0.45$ (5% EtOAc in hexanes); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.63 (dd, $J = 7.8, 1.7$ Hz, 2H), 7.45 – 7.36 (m, 3H), 6.74 (s, 4H), 3.74 (s, 3H), 0.50 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.32, 148.85, 137.40, 133.61, 130.00, 128.06, 120.73, 114.57, 55.70, -1.11. IR (Neat Film NaCl) 3420, 2958, 2833, 1638, 1505, 1465, 1441, 1427, 1253, 1233, 1118, 1037, 911, 831, 787, 729, 700 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Si}$ [$\text{M}+\bullet$]: 258.1076, found 258.1083.

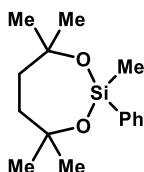
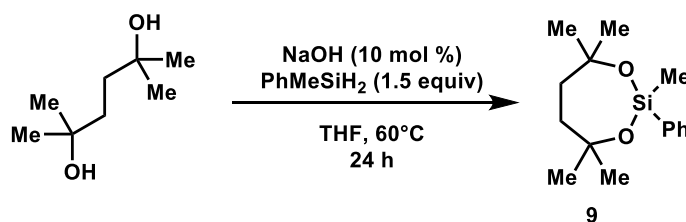


2,2'-bis((dimethyl(phenyl)silyloxy)-1,1'-binaphthalene 4u: The general procedure was followed. The reaction was performed with 2,2'-binaphthol (286 mg, 1.00 mmol, 1.0 equiv), Me₂PhSiH (408 mg, 460 μL, 3.0 mmol, 3.0 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and DME (1.0 mL). The reaction was heated to 80°C for 24 hours, then concentrated in vacuo and purified by silica gel column chromatography (5% EtOAc in hexanes) to afford **4u** (393 mg, 71% yield) as a colorless oil. *R_f* = 0.41 (5% EtOAc in hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.87 (m, 4H), 7.43 – 7.28 (m, 8H), 7.28 – 7.21 (m, 10H), 0.27 (s, 6H), 0.18 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 151.11, 137.66, 134.54, 133.31, 129.52, 128.99, 127.72, 126.22, 126.03, 123.71, 122.48, 121.14, -0.63, -0.95. Note that some small impurity signals are present, which could not be removed with further purification. IR (Neat Film NaCl) 3067, 3052, 2958, 2921, 1955, 1889, 1620, 1591, 1503, 1473, 1459, 1355, 1338, 1264, 1249, 1120, 1004, 995, 842, 832, 745, 699 cm⁻¹; HRMS (FAB⁺) calc'd for C₃₆H₃₄O₂Si₂ [M⁺•]: 554.2090, found 554.2097.

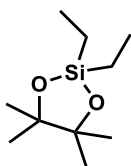
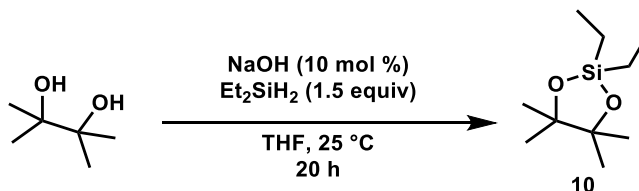


Di-tert-butyl(phenoxy)silane 6: The general procedure was followed. The reaction was performed with NaOH (2.0 mg, 0.05 mmol, 10 mol %), phenol (47 mg, 0.5 mmol, 1.0 equiv), (t-Bu)₂SiH₂ (108 mg, 148 μL, 0.75 mmol, 1.5 equiv), 0.25 mL dimethylformamide (DMF) and 0.25 mL of tetrahydrofuran (THF) at 65 °C for 24 h. The desired product **6** (106.5 mg, 90% yield) was obtained as a colorless oil by silica gel flash chromatography (5% EtOAc in hexanes). *R_f* = 0.77 (5% EtOAc in hexanes); ¹H NMR (500 MHz, CDCl₃) δ

7.26 – 7.21 (m, 3H), 6.95 – 6.93 (m, 2H), 4.44 (s, 1H), 1.07 (s, 18H). This compound has been previously characterized.¹⁹

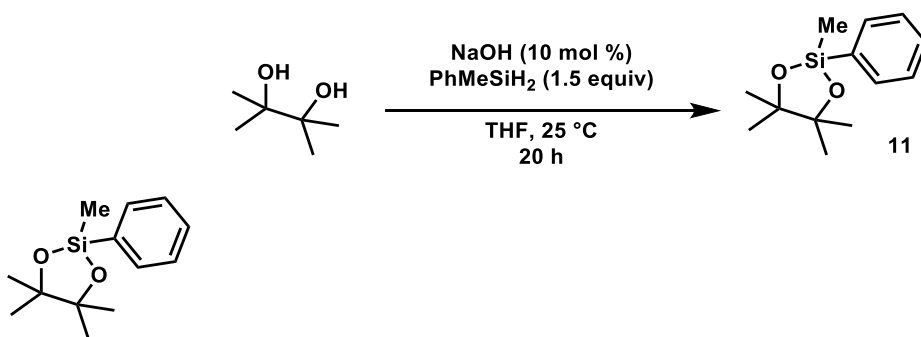


2,4,4,7,7-pentamethyl-2-phenyl-1,3,2-dioxasilepane 9: The general procedure was followed. The reaction was performed with 2,5-dimethyl-2,5-hexanediol (146 mg, 1.00 mmol, 1.0 equiv), MePhSiH₂ (183 mg, 205 μL , 1.50 mmol, 1.5 equiv), NaOH (4.0 mg, 0.10 mmol, 10 mol%) and THF (1.0 mL). The reaction was stirred at 60°C for 24 h, then concentrated in vacuo to afford the product **9** (235 mg, 89% yield) as a clear oil. ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.70 (m, 2H), 7.46 – 7.40 (m, 3H), 1.94 – 1.86 (m, 4H), 1.42 (s, 6H), 1.31 (s, 6H), 0.42 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.65, 133.75, 129.33, 127.58, 74.92, 68.02, 38.06, 25.70, 0.78. IR (Neat Film NaCl) 3069, 3050, 3025, 2973, 2933, 2131, 1591, 1429, 1258, 1143, 1122, 1038, 1028, 1011, 998, 782, 724, 699 cm⁻¹; HRMS (EI⁺) calc'd for C₁₅H₁₈O₂Si [M⁺]: 264.1546, found 264.1536. This product is quite unstable hydrolytically.



¹⁹ Huang, C.; Chattopadhyay, B.; Gevorgyan, V. *J. Am. Chem. Soc.* **2011**, *133* (32), 12406–12409.

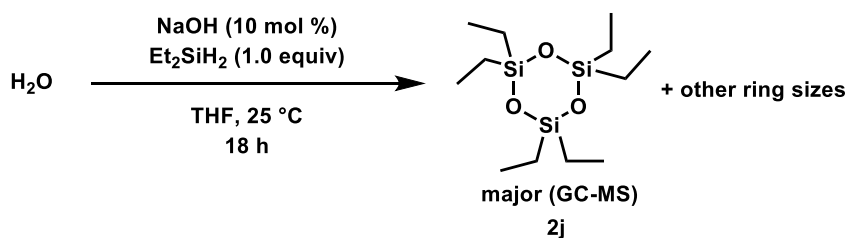
2,2-diethyl-4,4,5,5-tetramethyl-1,3,2-dioxasilolane 10: The general procedure was followed. The reaction was performed with pinacol (118 mg, 1.0 mmol, 1.0 equiv), Et_2SiH_2 (132 mg, 194 μL , 1.5 mmol, 1.5 equiv), and 1.0 mL of tetrahydrofuran (THF), then NaOH (40.0 mg, 1.0 mmol, 10 mol %) was added and the mixture was stirred at 25 °C for 20 h. GC analyses showed full and clean conversion to product; however, concentration of the reaction mixture and attempts at purification of the resulting residue via Kugelrohr distillation or column chromatography on silica gel or silica gel treated with NEt_3 resulted in decomposition and the formation of siloxanes and recovery of pinacol.



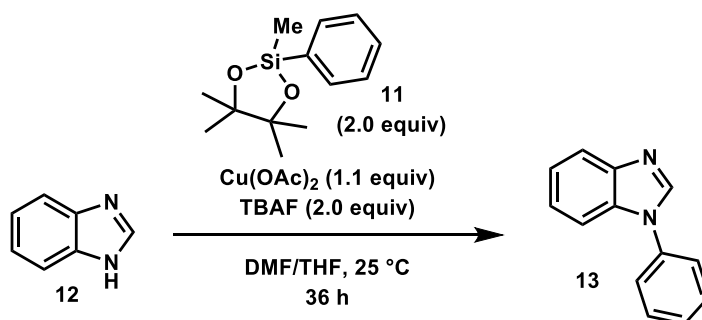
2,4,4,5,5-Pentamethyl-2-phenyl-1,3,2-dioxasilolane 11: A modified general procedure was followed to account for greater volumes of hydrogen evolution since this reaction is performed on a larger scale. The reaction is performed in a flame-dried 50 mL round bottom Schlenk flask equipped with a magnetic stirring bar that is allowed to cool to room temperature and which is connected to an argon manifold by means of a hose attached to the side arm of the flask. The side arm contains a lightly greased glass stopcock valve. The tap is opened subjecting the flask to a positive pressure of argon. The flask is charged with pinacol (1.18 g, 10.0 mmol, 1.0 equiv), MePhSiH_2 (1.22 g, 1.37 mL, 10.0 mmol, 1.0 equiv), and 10.0 mL of tetrahydrofuran (THF) (liquids are added through a rubber septum via a syringe). Next, the rubber septum is briefly removed while the flask is under a constant argon stream, and NaOH (40.0 mg, 1.0 mmol, 10 mol %) was added [*Note: vigorous evolution of hydrogen occurs upon addition of NaOH*]. Once vigorous hydrogen evolution is visibly completed, the rubber septum is replaced and a bubbler is installed by means of a needle through the flask's septum connected to the bubbler by Tygon tubing, enabling the hydrogen to be safely vented as the reaction progresses. The mixture was stirred at 25 °C for 20 h. Concentration of the reaction mixture and purification of the resulting residue

via Kugelrohr distillation (150 mTorr, 120 °C) gave 2.19 g (93% yield) of **11** as a colorless oil. *Note: product is volatile under high vacuum.* ^1H NMR (500 MHz, Benzene- d_6) δ 7.77 – 7.71 (m, 2H), 7.20 – 7.17 (m, 3H), 1.22 (s, 6H), 1.16 (s, 6H), 0.43 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 136.58, 134.03, 130.42, 128.21, 81.80, 26.03, -0.35. IR (Neat Film NaCl) 3441, 3071, 2980, 1643, 1464, 1428, 1366, 1260, 1161, 1121, 1026, 793, 736, 699 cm^{-1} ; HRMS (EI+) calc'd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$ [$\text{M}+\bullet$]: 236.1233, found 236.1237.

2. Synthesis of 2,2,4,4,6,6-Hexaethyl-1,3,5,2,4,6-trioxatrisilinane 2j.

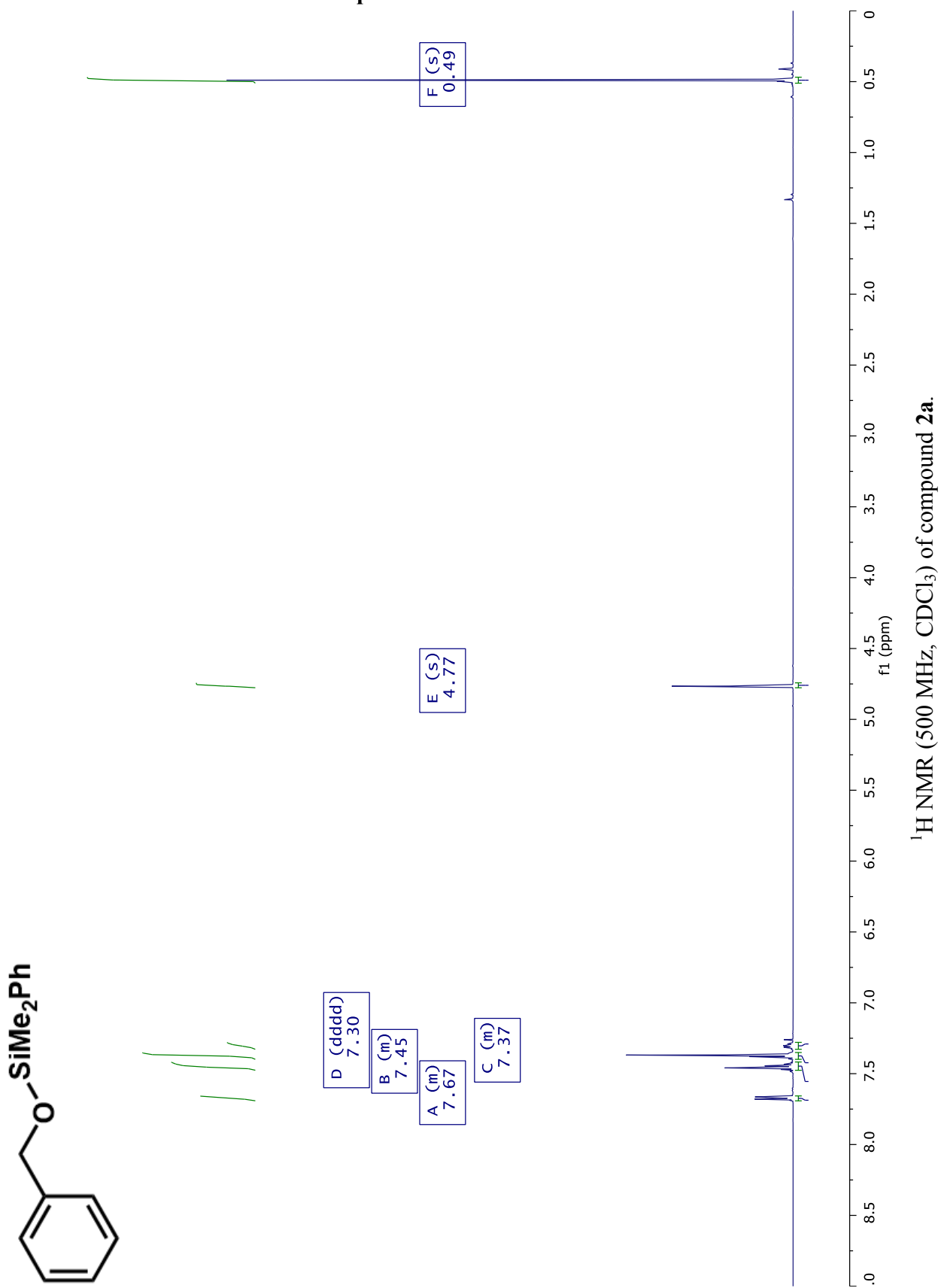


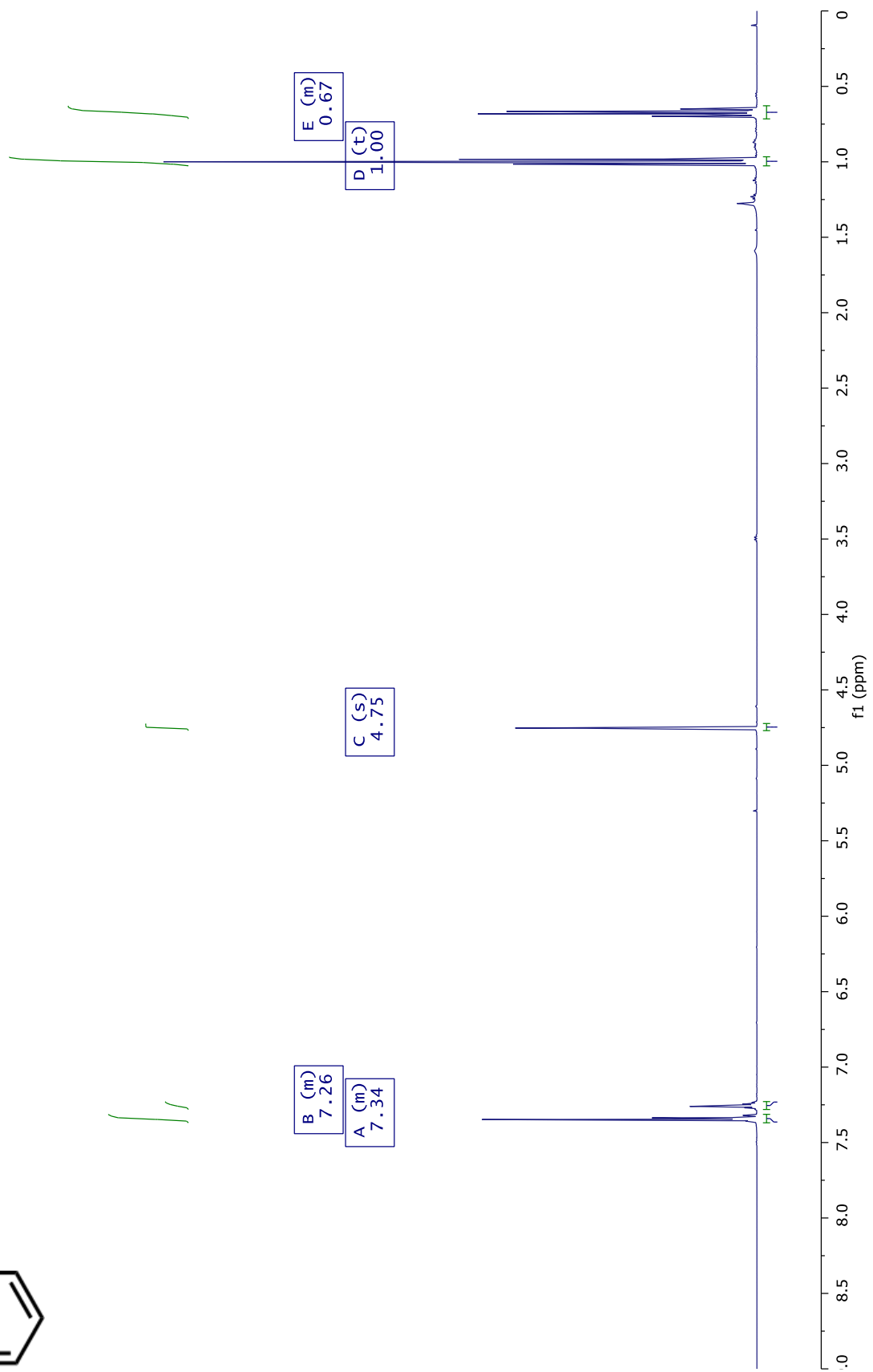
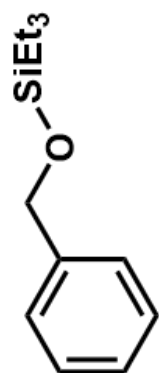
2,2,4,4,6,6-Hexaethyl-1,3,5,2,4,6-trioxatrisilinane 2j: To a solution of diethylsilane (0.5 mL, 3.85 mmol, 1.0 equiv) in THF (2.0 mL) was added NaOH (15.4 mg, 0.39 mmol, 10 mol %) and H_2O (1.0 mL, 55 mmol, 15 equiv). The vial was then sealed and the mixture was stirred at 25 °C for 24 h. The reaction mixture was diluted with 2 mL Et_2O and analyzed by GC-MS, in which 2,2,4,4,6,6-hexaethyl-1,3,5,2,4,6-trioxatrisilinane was the major product observed (mass = 306.2). Several other larger ring sizes were observed in smaller amounts.

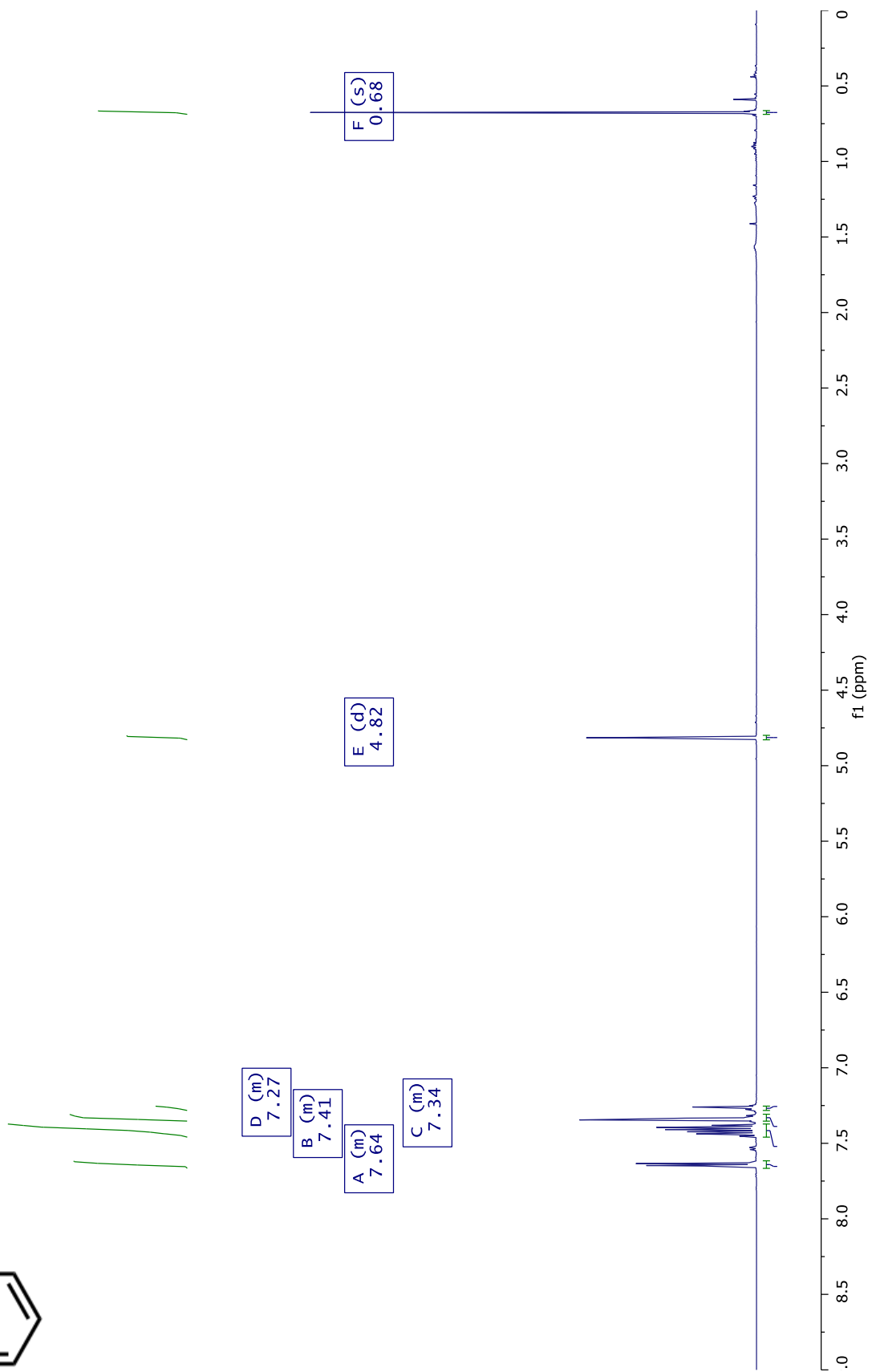
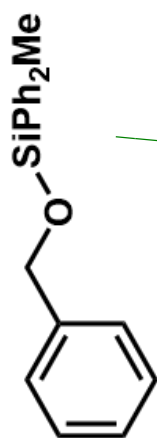
3. Procedure for cross-coupling using 2,4,4,5,5-Pentamethyl-2-phenyl-1,3,2-dioxasilolane **11.**

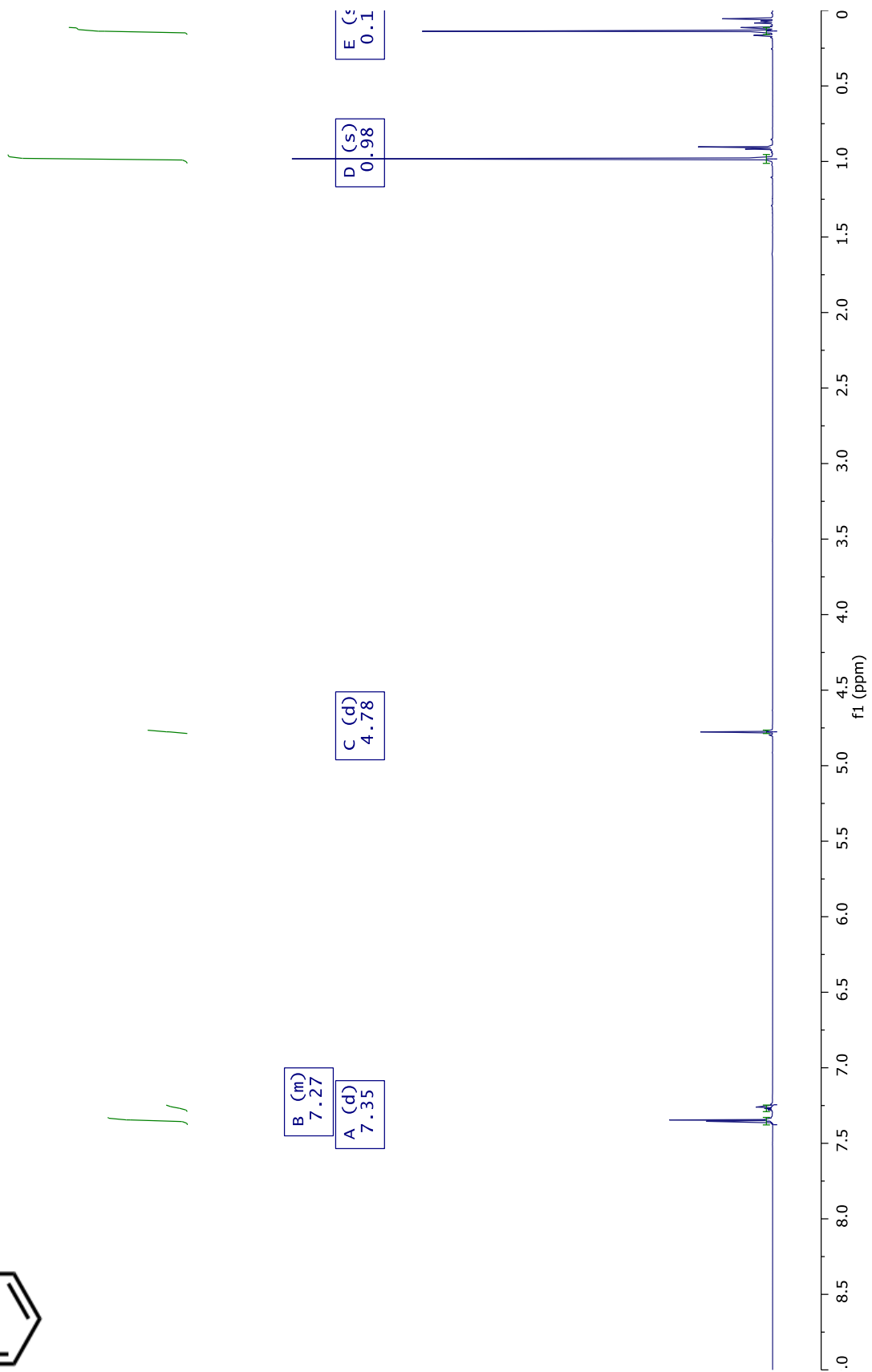
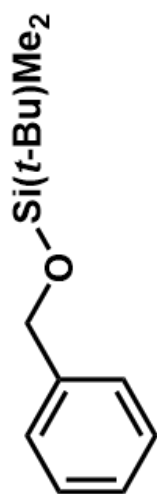
1-phenyl-1H-benzo[d]imidazole **13:** To a mixture of the $\text{PhSi}^{\text{Me}}(\text{pin})$ reagent **11** (freshly prepared, 71.0 mg, 0.3 mmol, 2.0 equiv), benzimidazole **12** (17.6 mg, 0.15 mmol, 1.0 equiv) and $\text{Cu}(\text{OAc})_2$ (30.0 mg, 0.165 mmol, 1.1 equiv) in DMF (1.5 mL) is added TBAF (0.3 mL, 1.0M solution in THF) dropwise at 25 °C. The mixture is allowed to stir for 36 h at 25° C, after which NaHCO_3 saturated solution (2.0 mL) is carefully added and then the mixture is partitioned between EtOAc and hexanes (5.0 mL each). The aqueous layer is extracted with a 1:1 EtOAc:hexanes mixture (2x15 mL) then the combined organic layers are washed with H_2O (2x10 mL) and brine (1x10 mL), then dried over MgSO_4 . The mixture is then filtered, the solvent is removed, and the resulting residue is purified via silica gel flash chromatography (gradient 20% EtOAc in hexanes to 70% EtOAc in hexanes) to yield **13** as a colorless solid (21.2 mg, 71% yield). $R_f = 0.25$ (20% EtOAc in hexanes). This compound has been previously characterized.²⁰

²⁰ Cheng, C., Hartwig, J.F., *Science* **2014**, 343, 853–857.

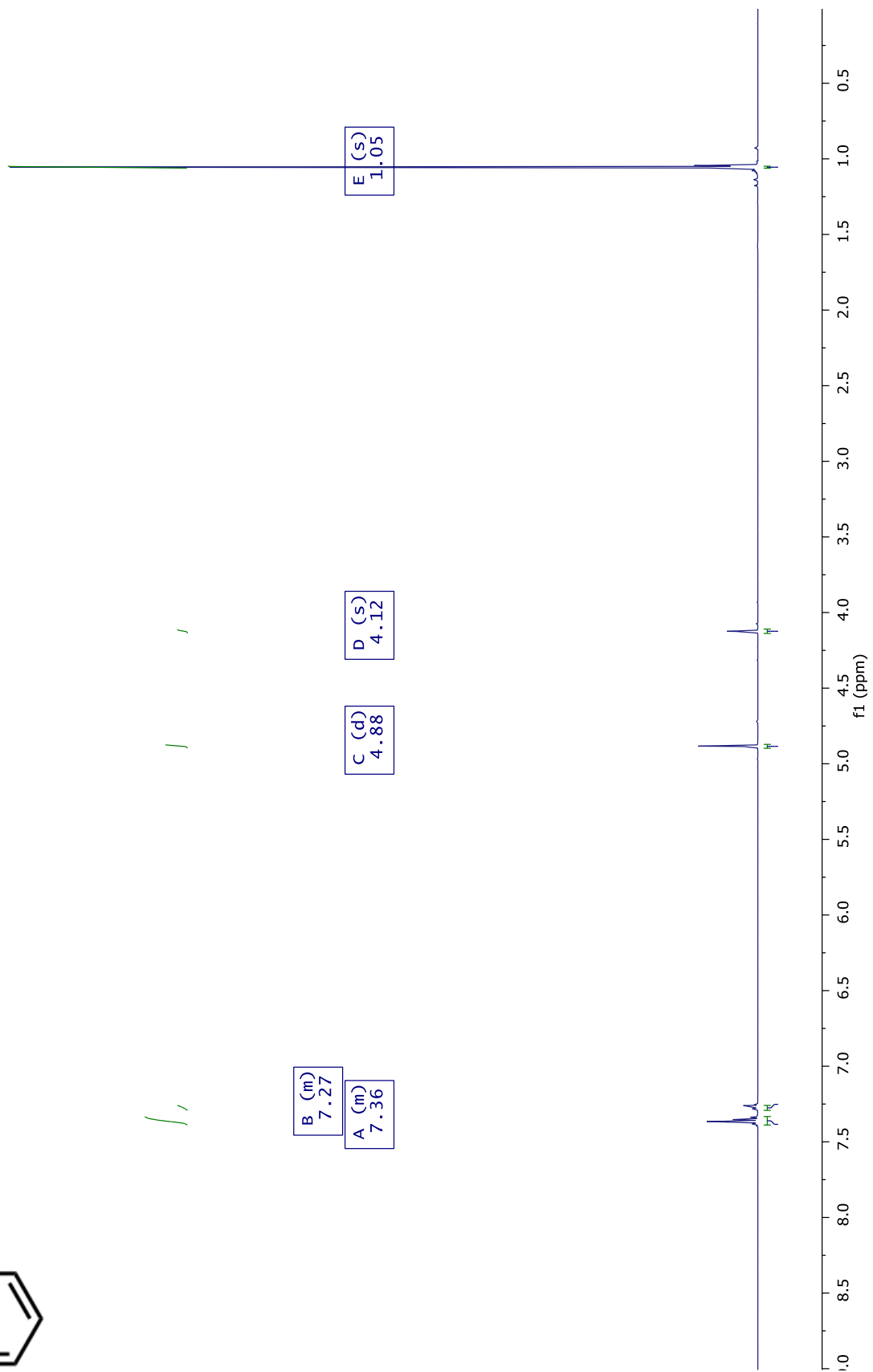
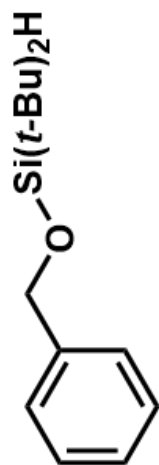
Part III. ^1H NMR and ^{13}C NMR spectra.

¹H NMR (500 MHz, CDCl₃) of compound **2b**.

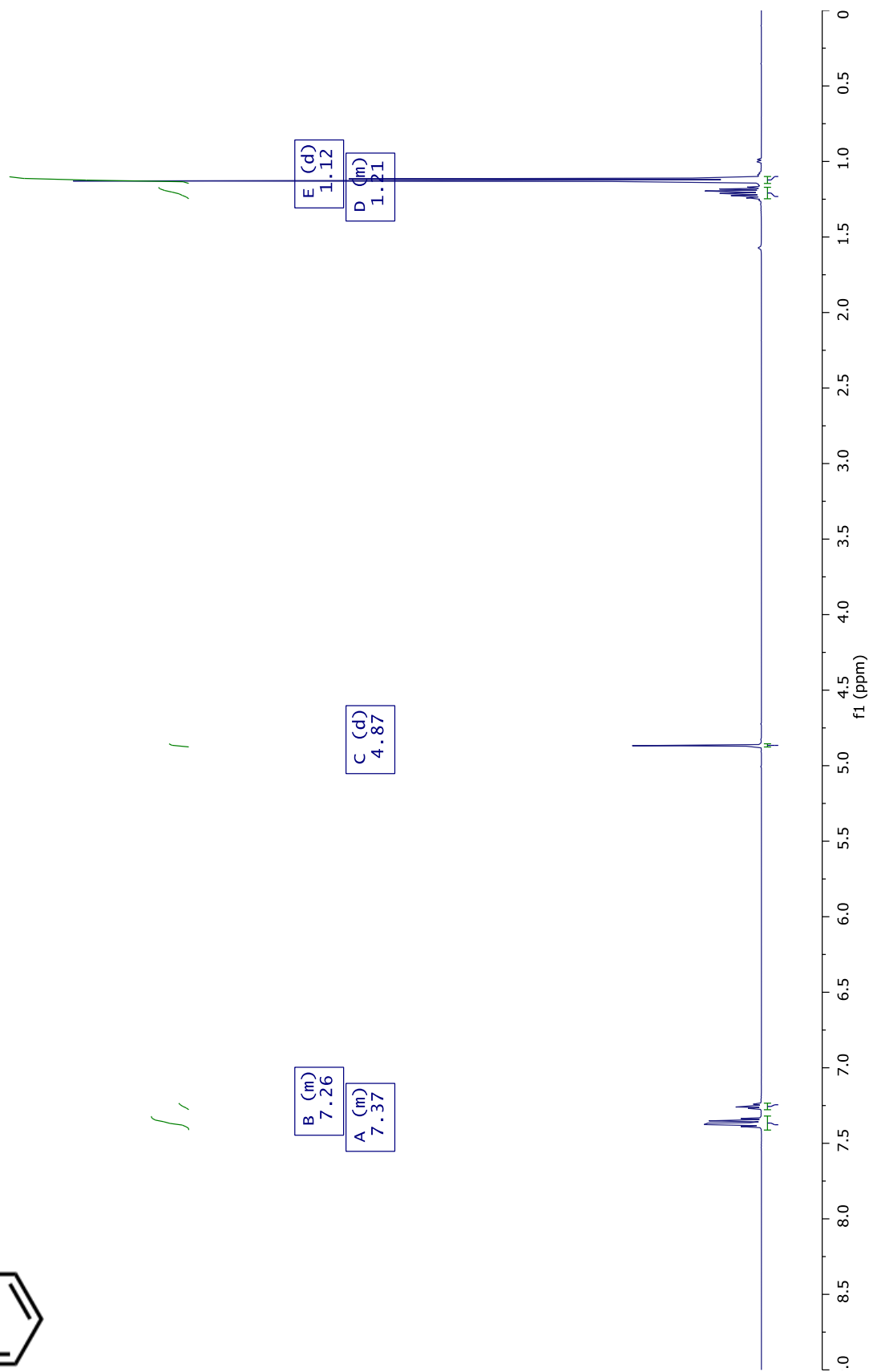
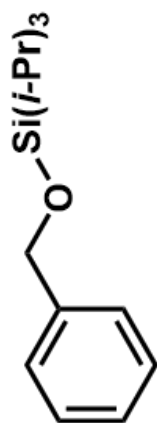
¹H NMR (500 MHz, CDCl₃) of compound **2c**.

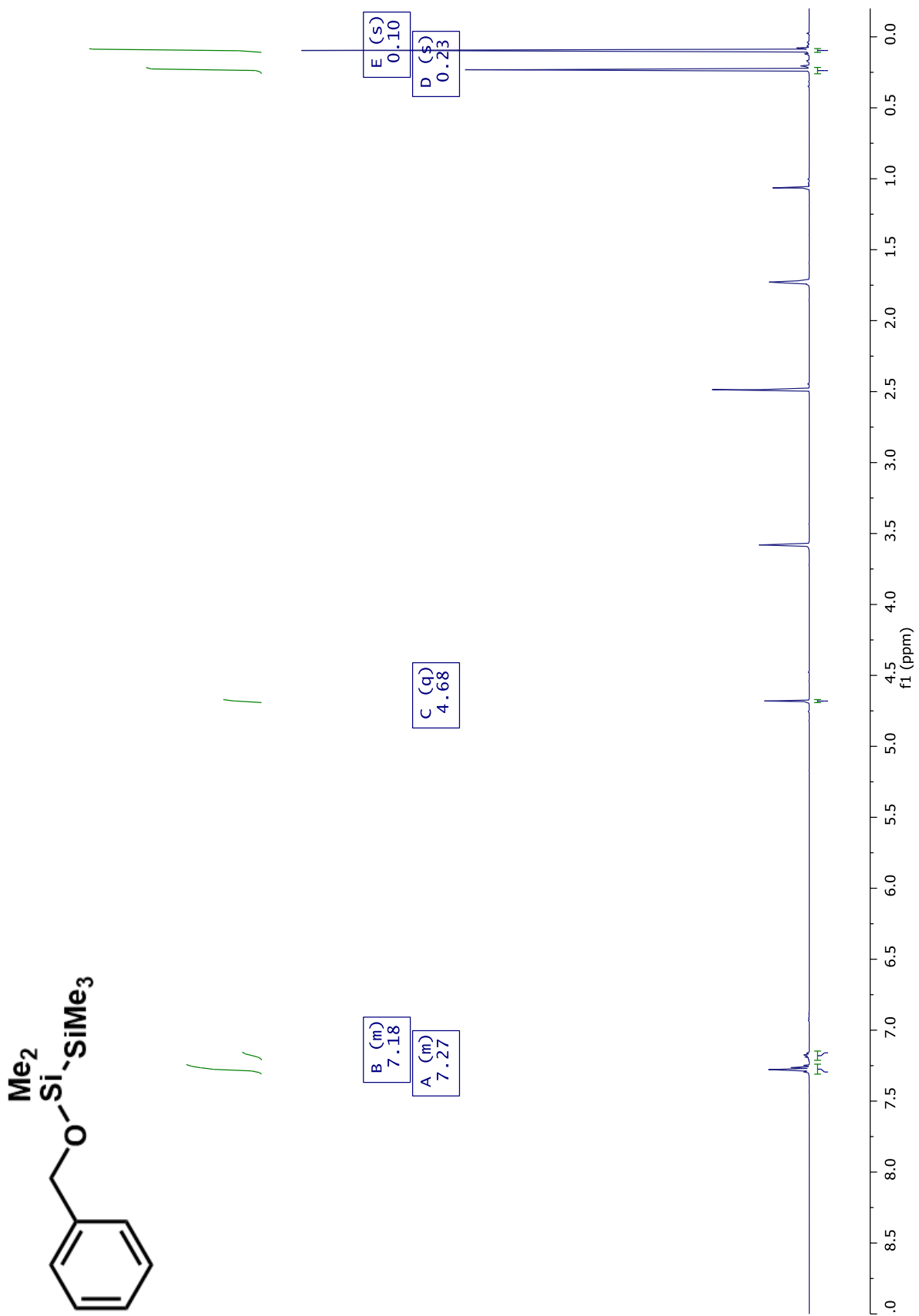


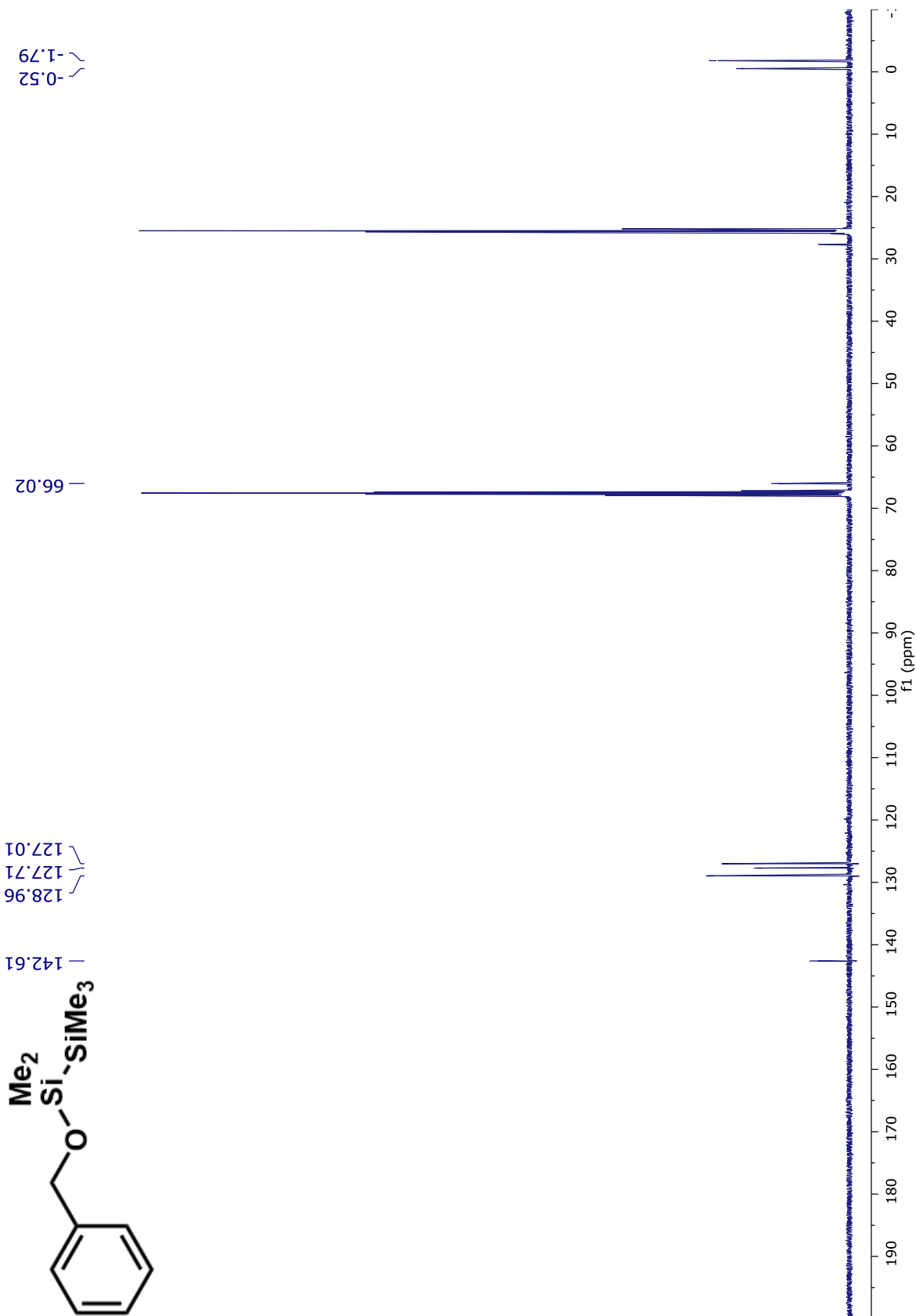
¹H NMR (500 MHz, CDCl₃) of compound **2d**.

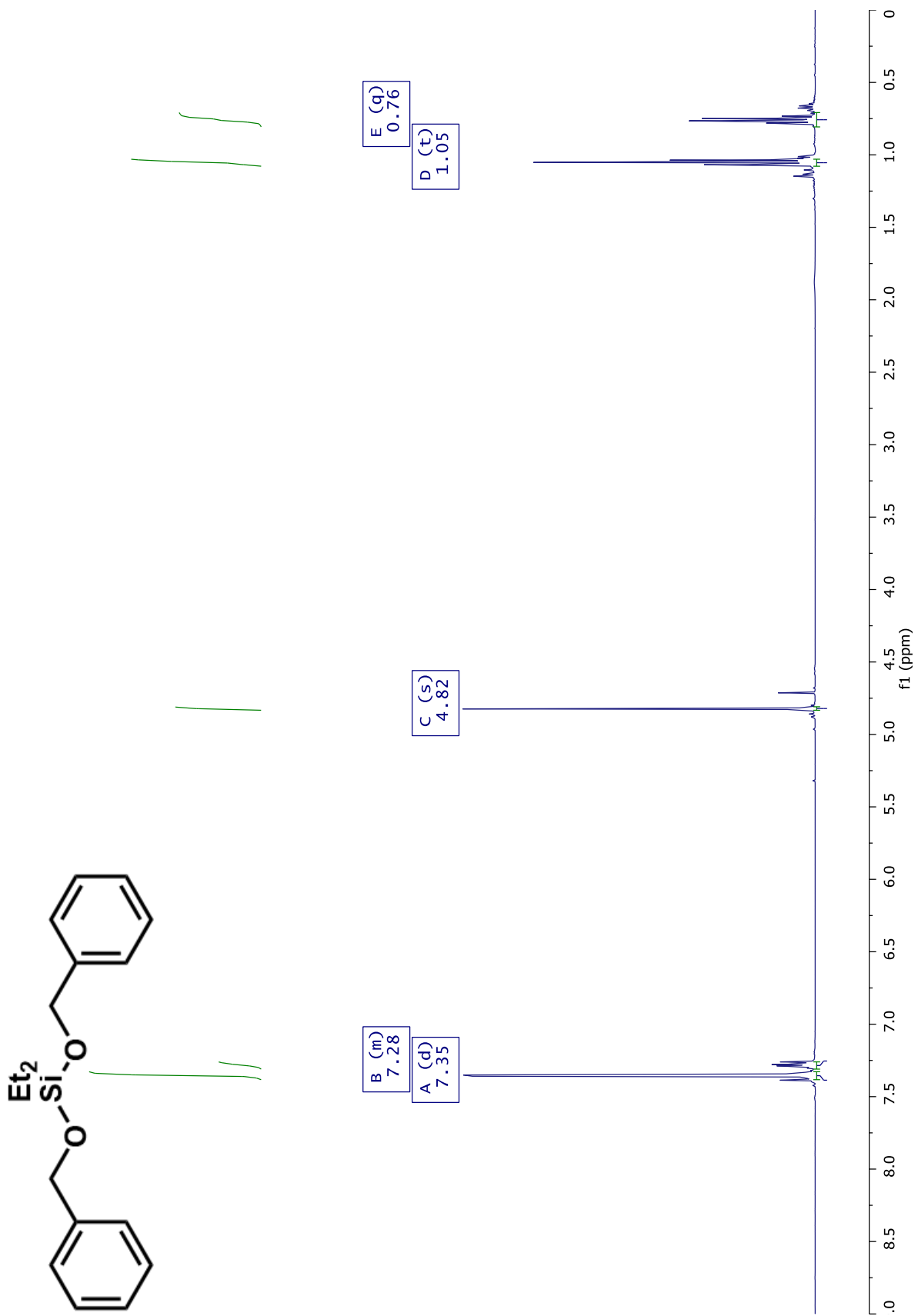


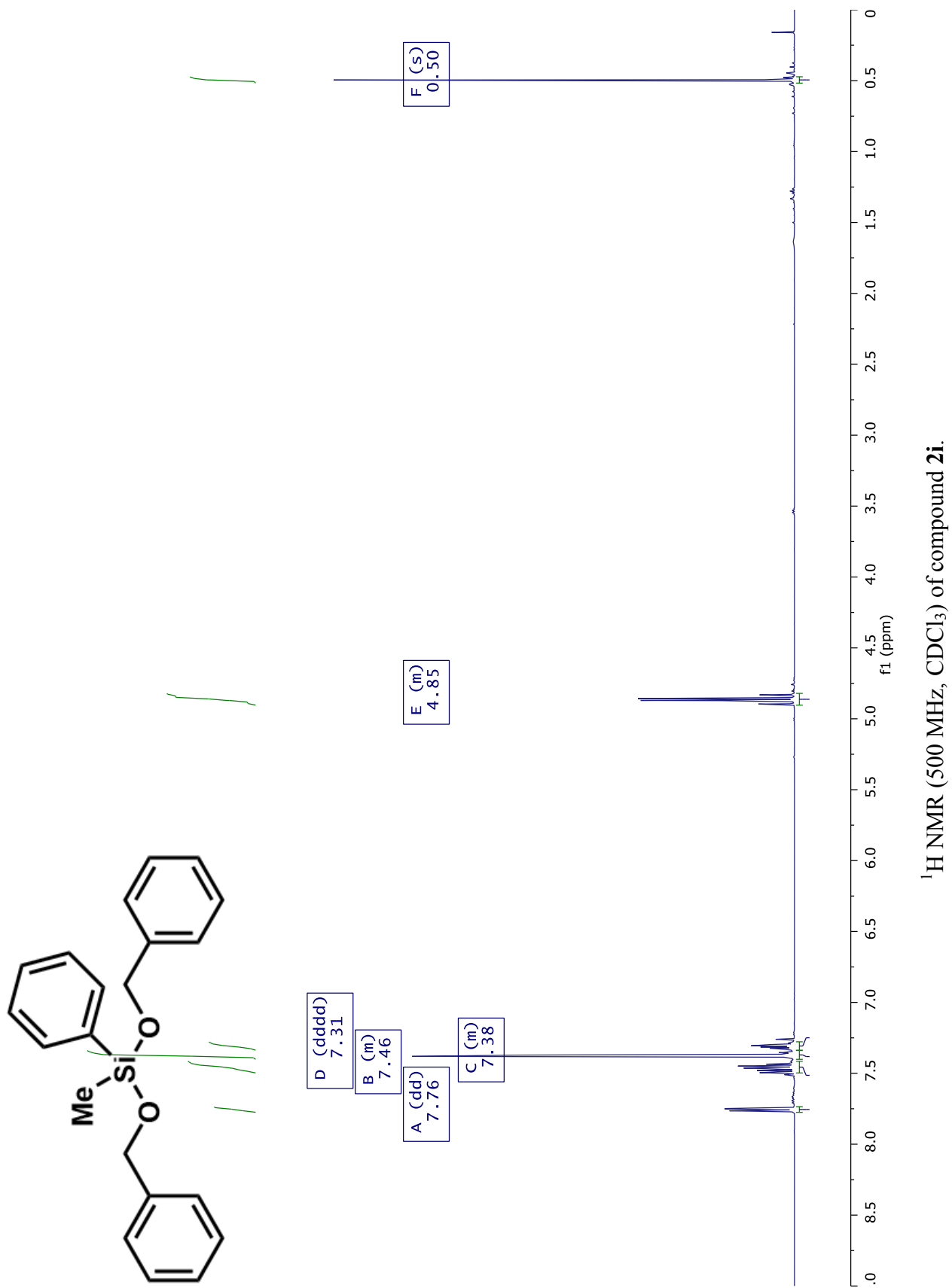
¹H NMR (500 MHz, CDCl₃) of compound **2e**.

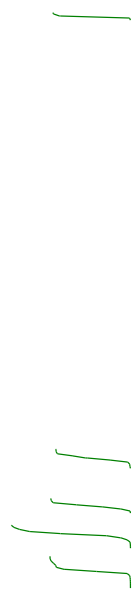
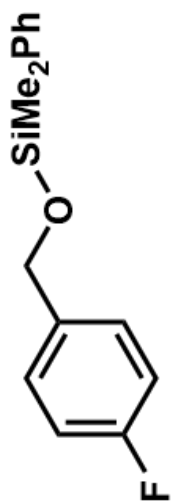
¹H NMR (500 MHz, CDCl₃) of compound 2f.

¹H NMR (500 MHz, THF-*d*₈) of compound **2g**.



¹H NMR (500 MHz, CDCl₃) of compound **2h**.

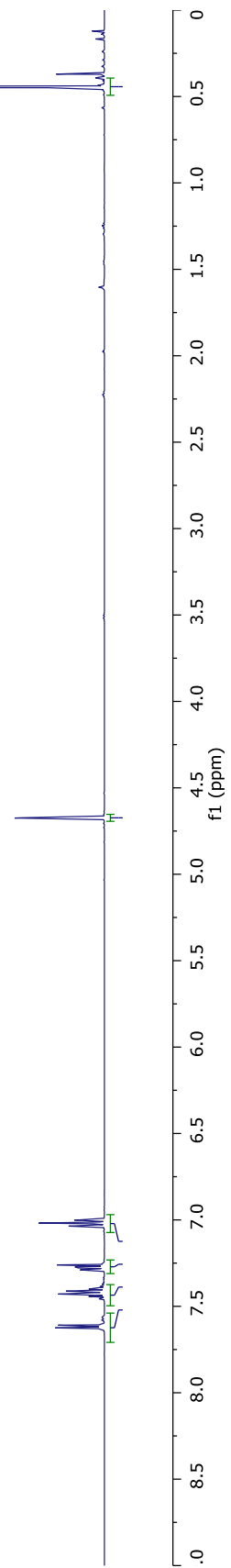




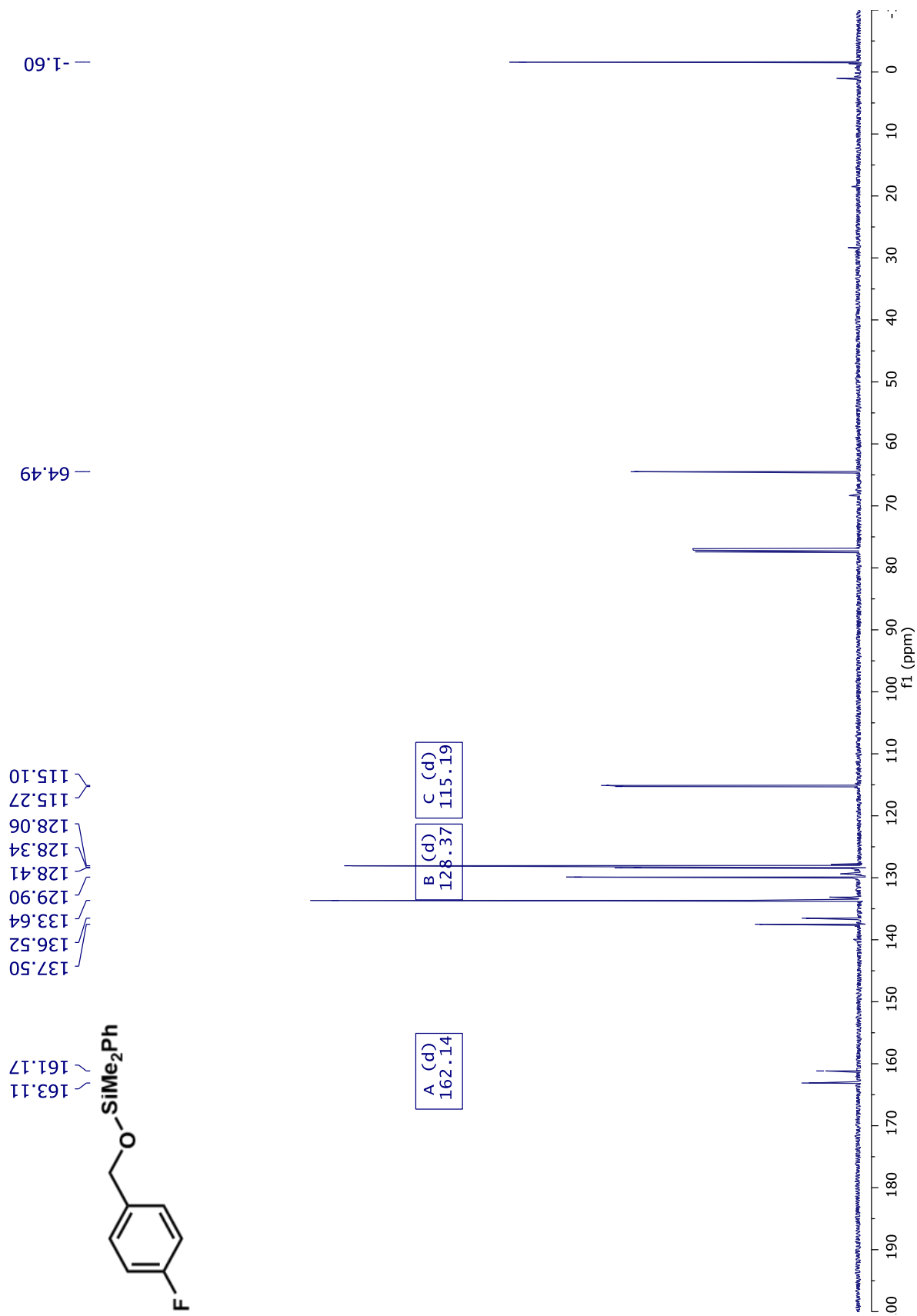
B (m)	7.42
A (m)	7.62
D (m)	7.02
C (m)	7.28

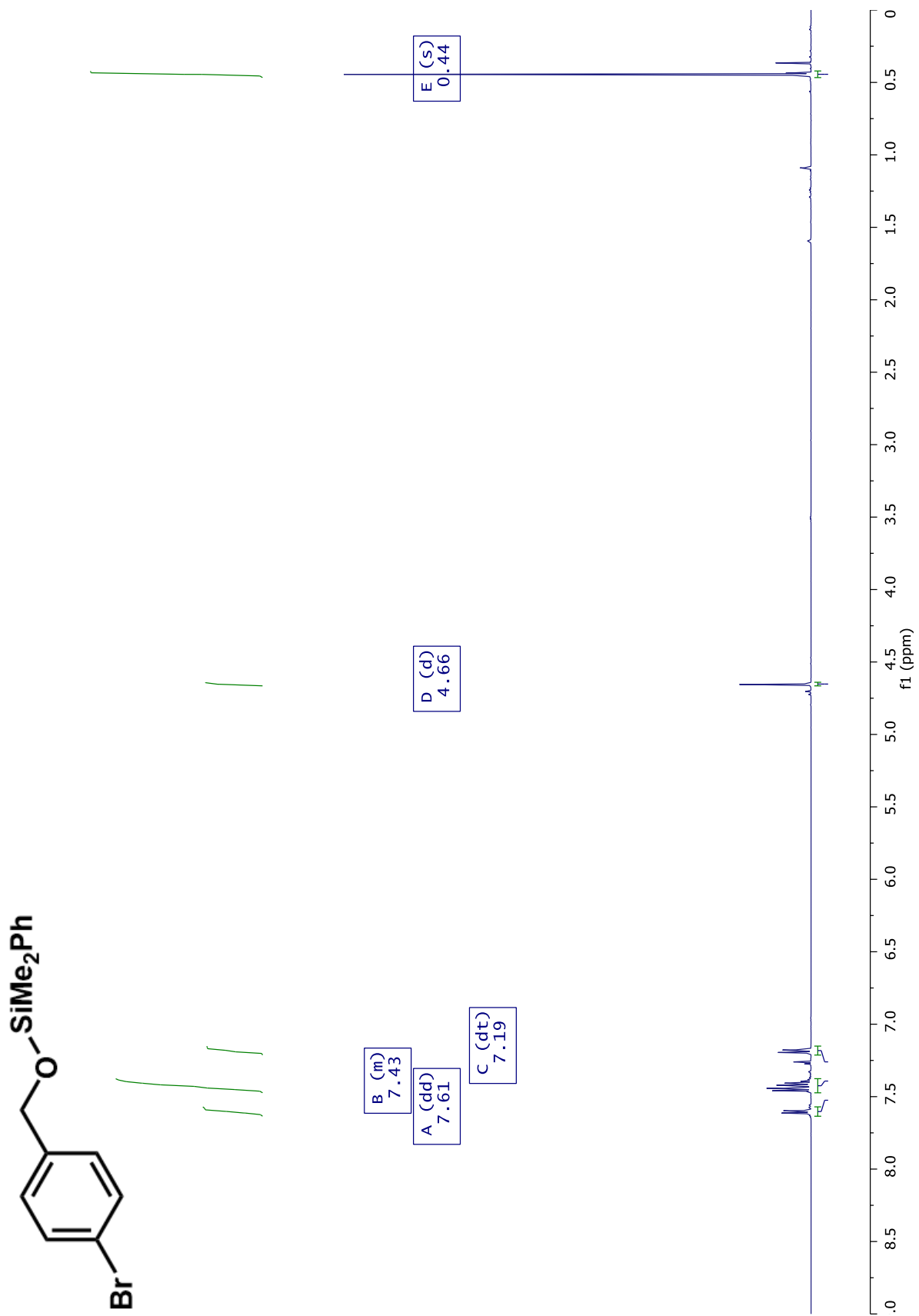
E (q)	4.67
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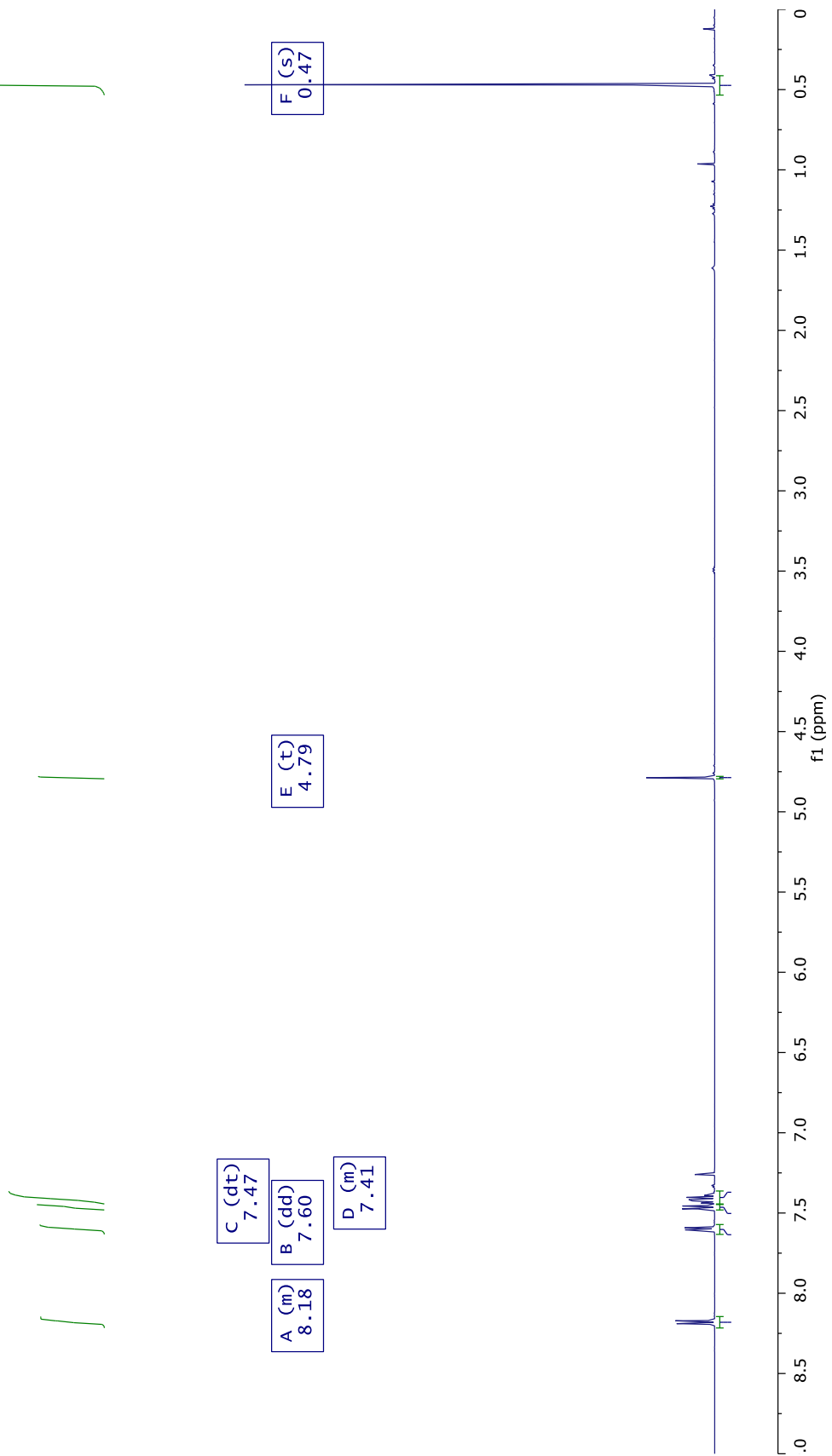
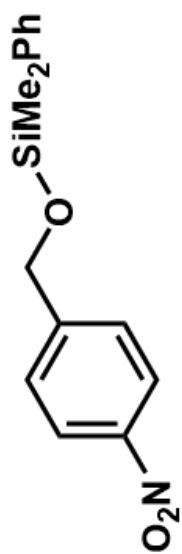
F (s)	0.45
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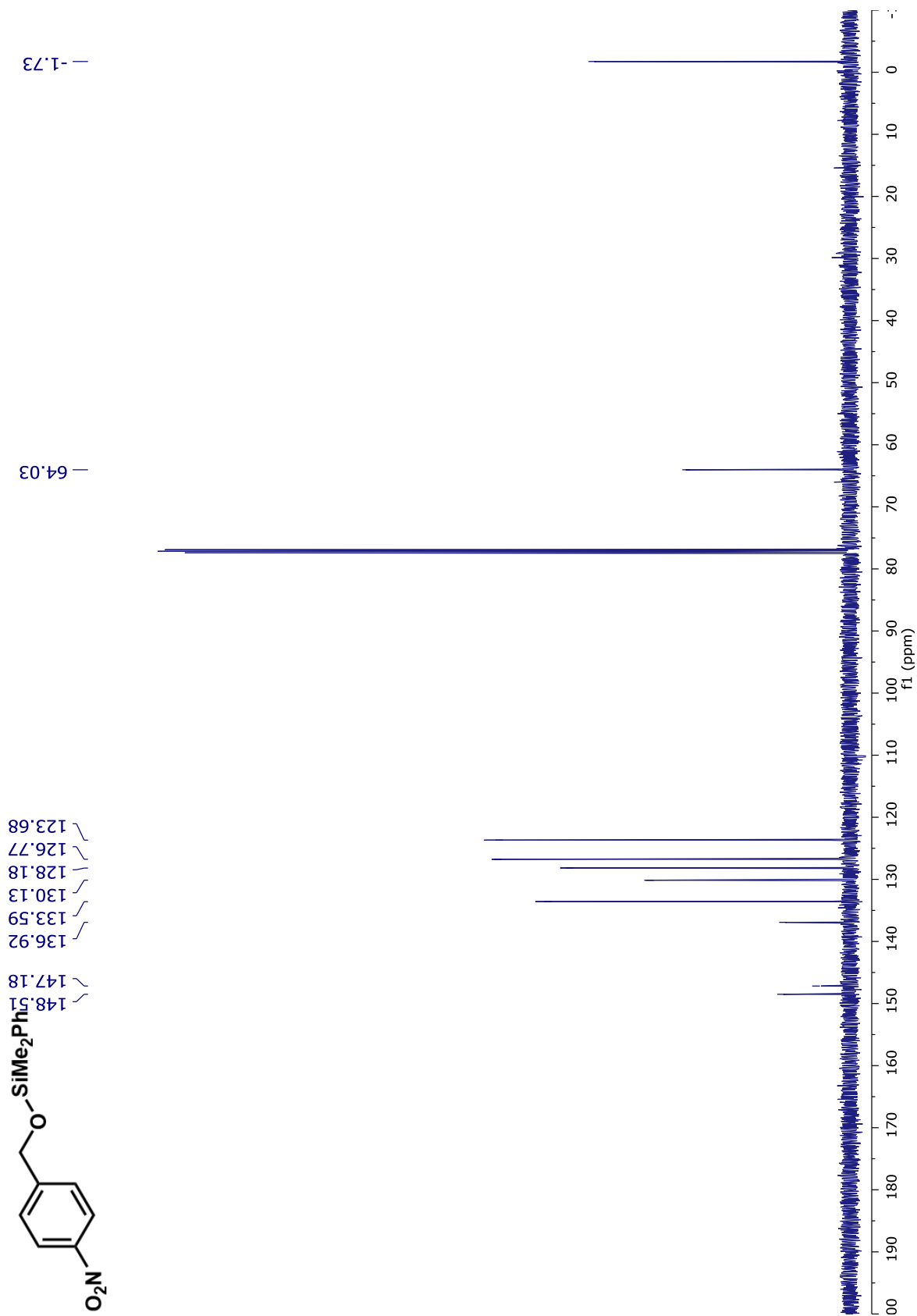


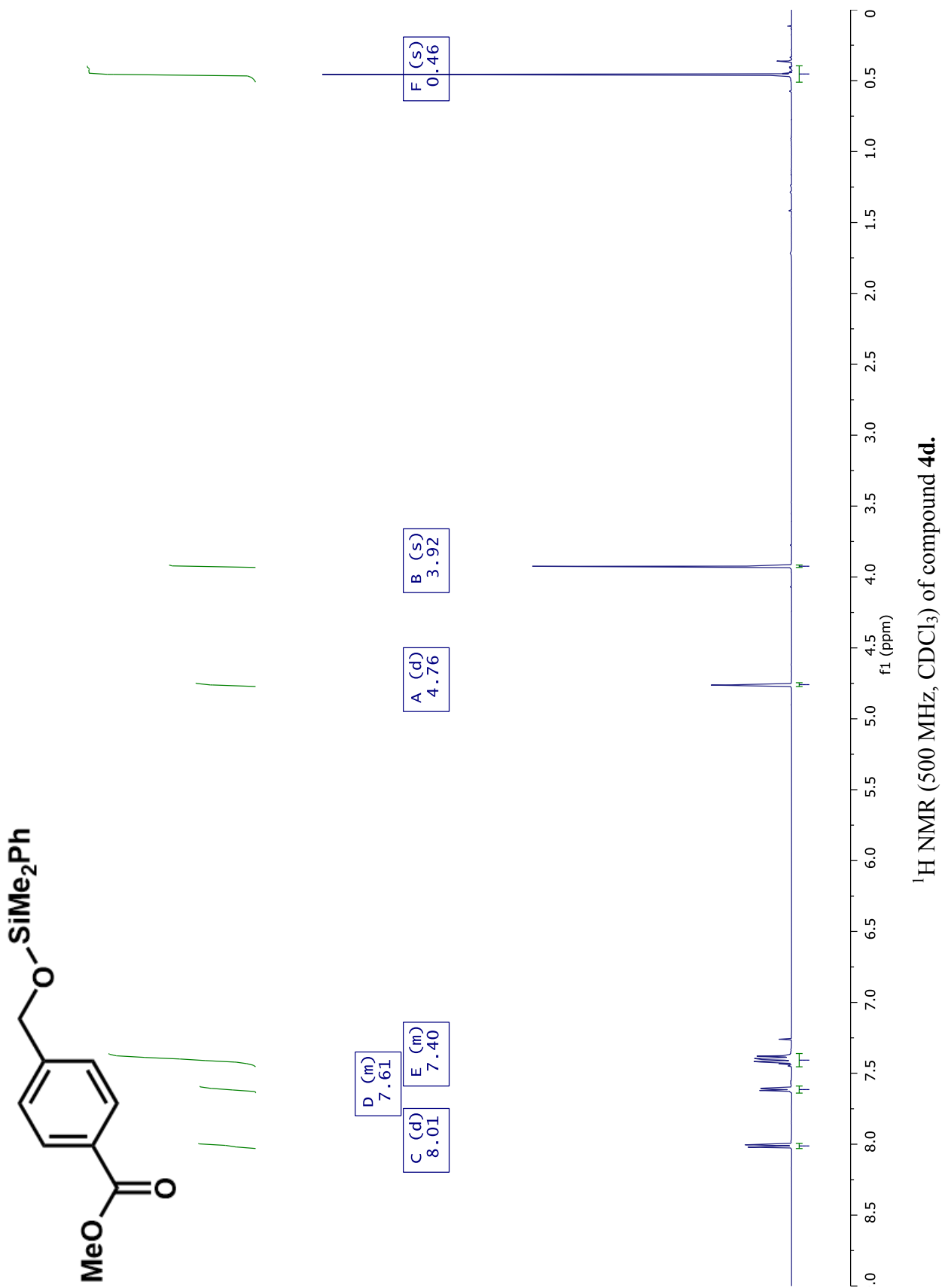
^1H NMR (500 MHz, CDCl_3) of compound **4a**.

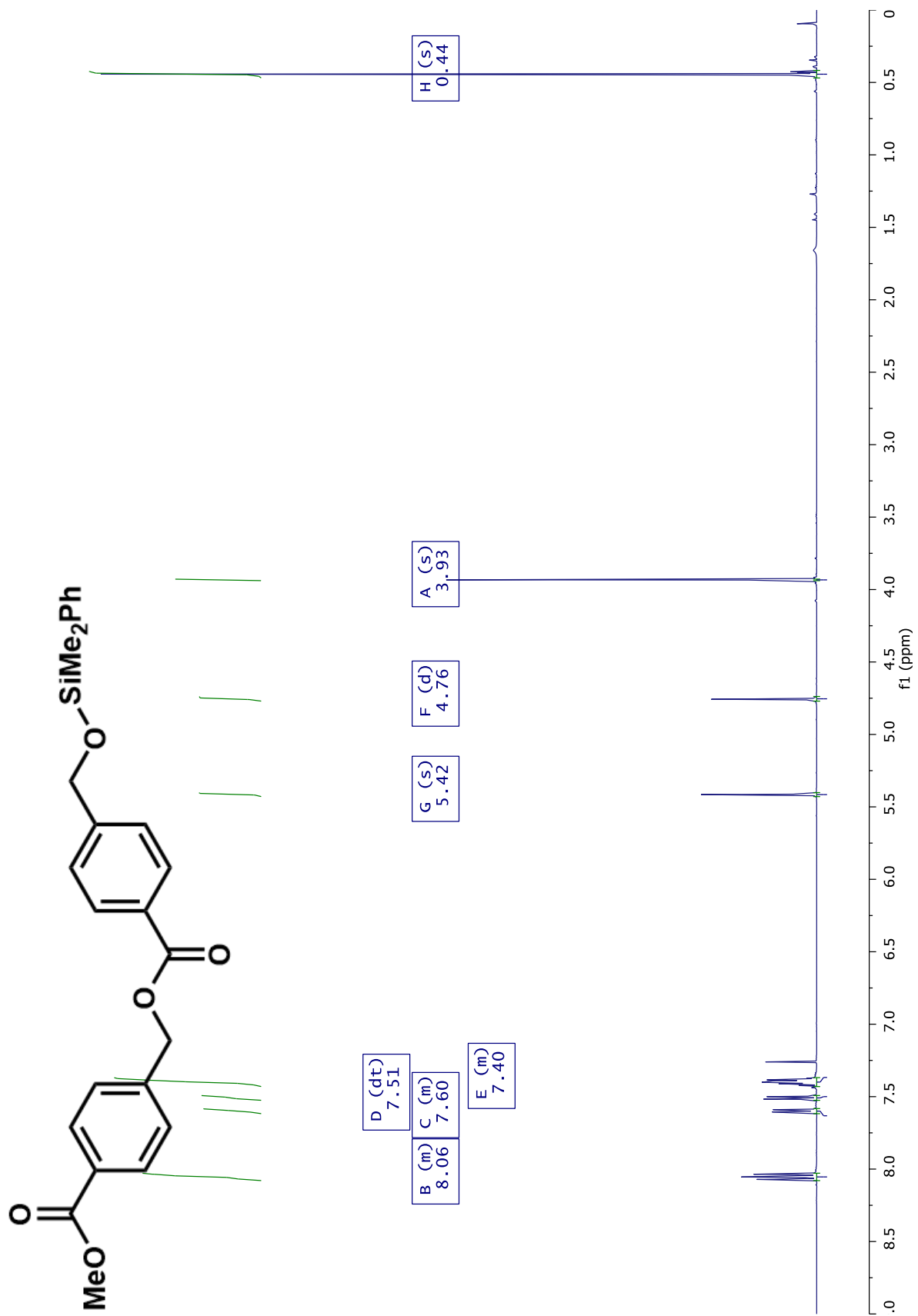


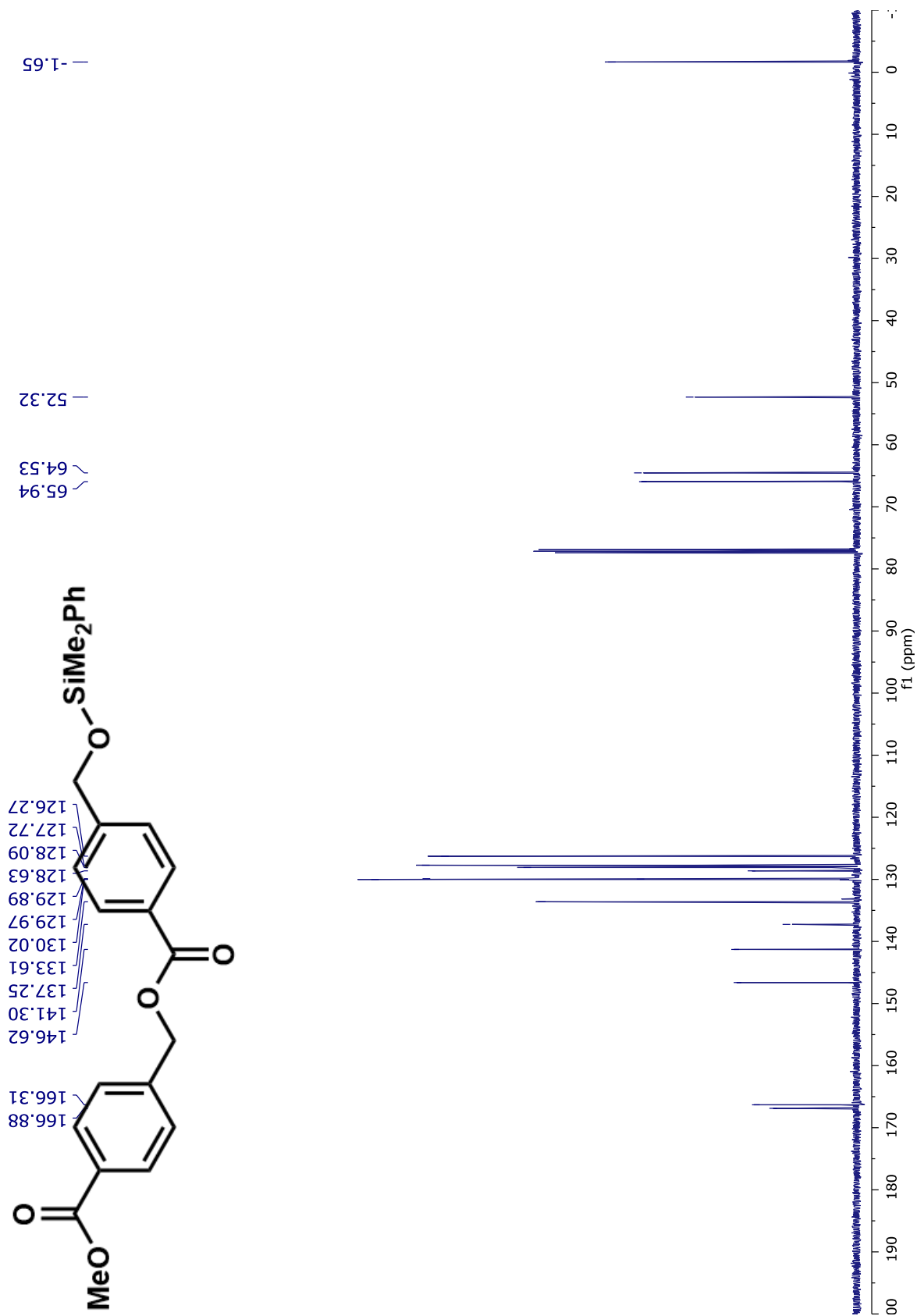
¹H NMR (500 MHz, CDCl₃) of compound **4b**.

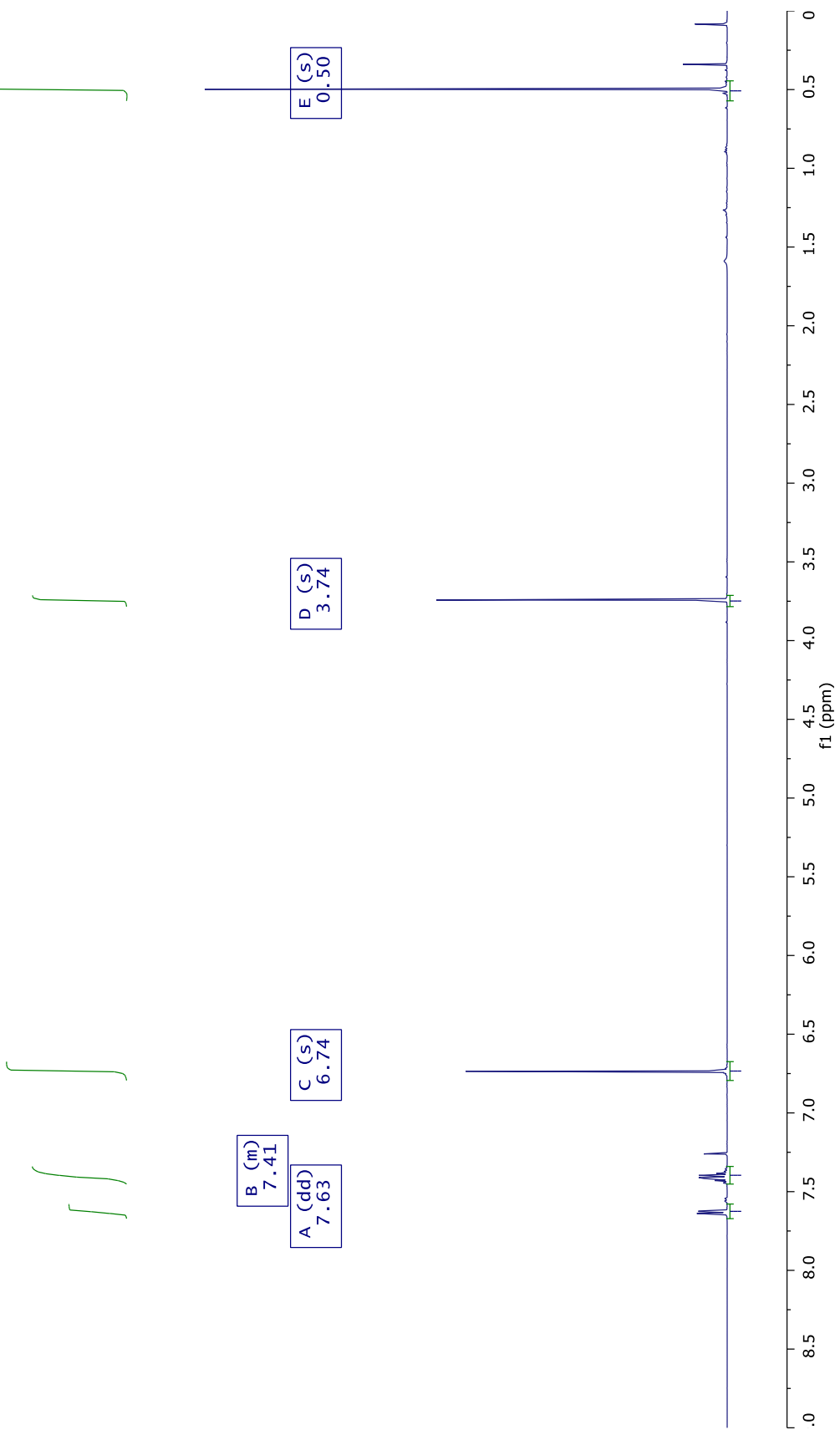
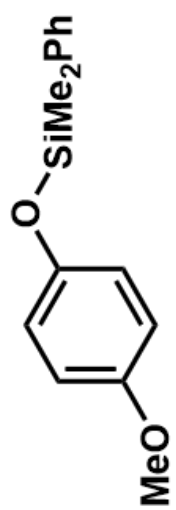
 ^1H NMR (500 MHz, CDCl_3) of compound **4c**.



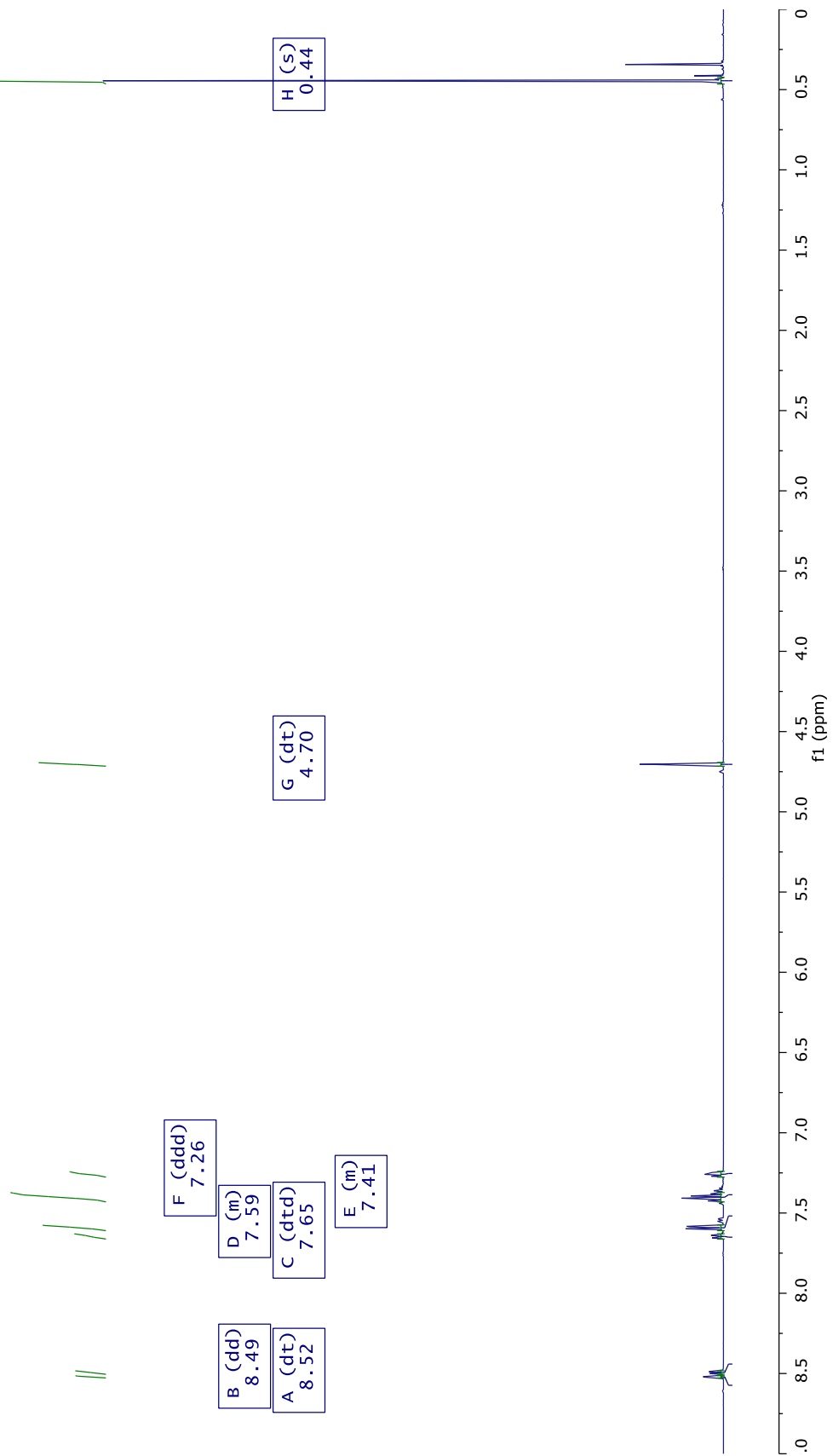
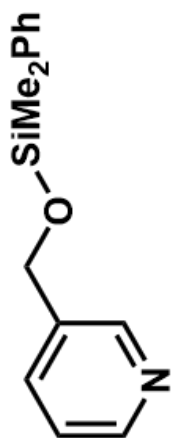


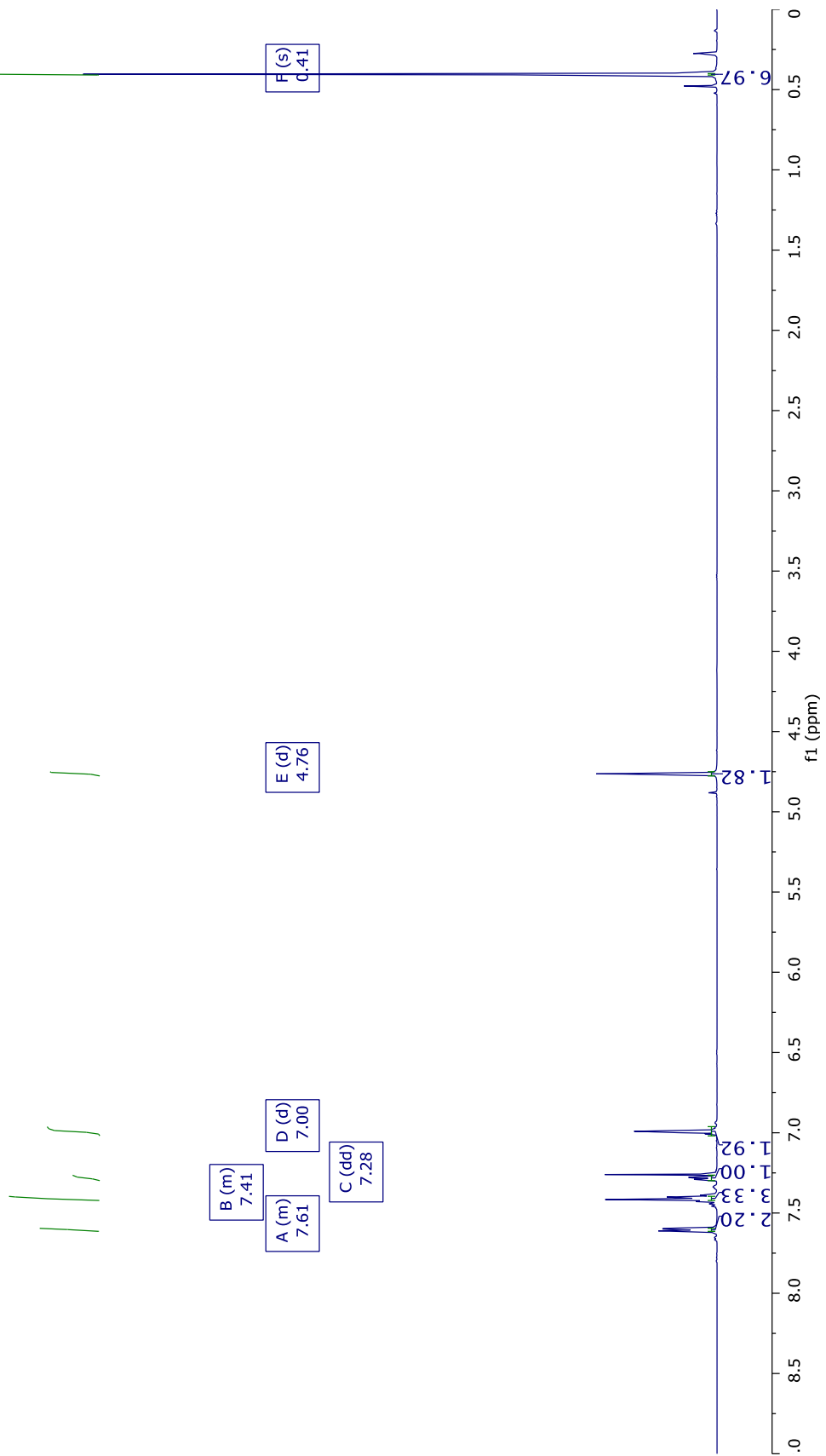
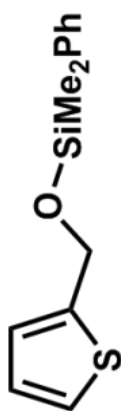


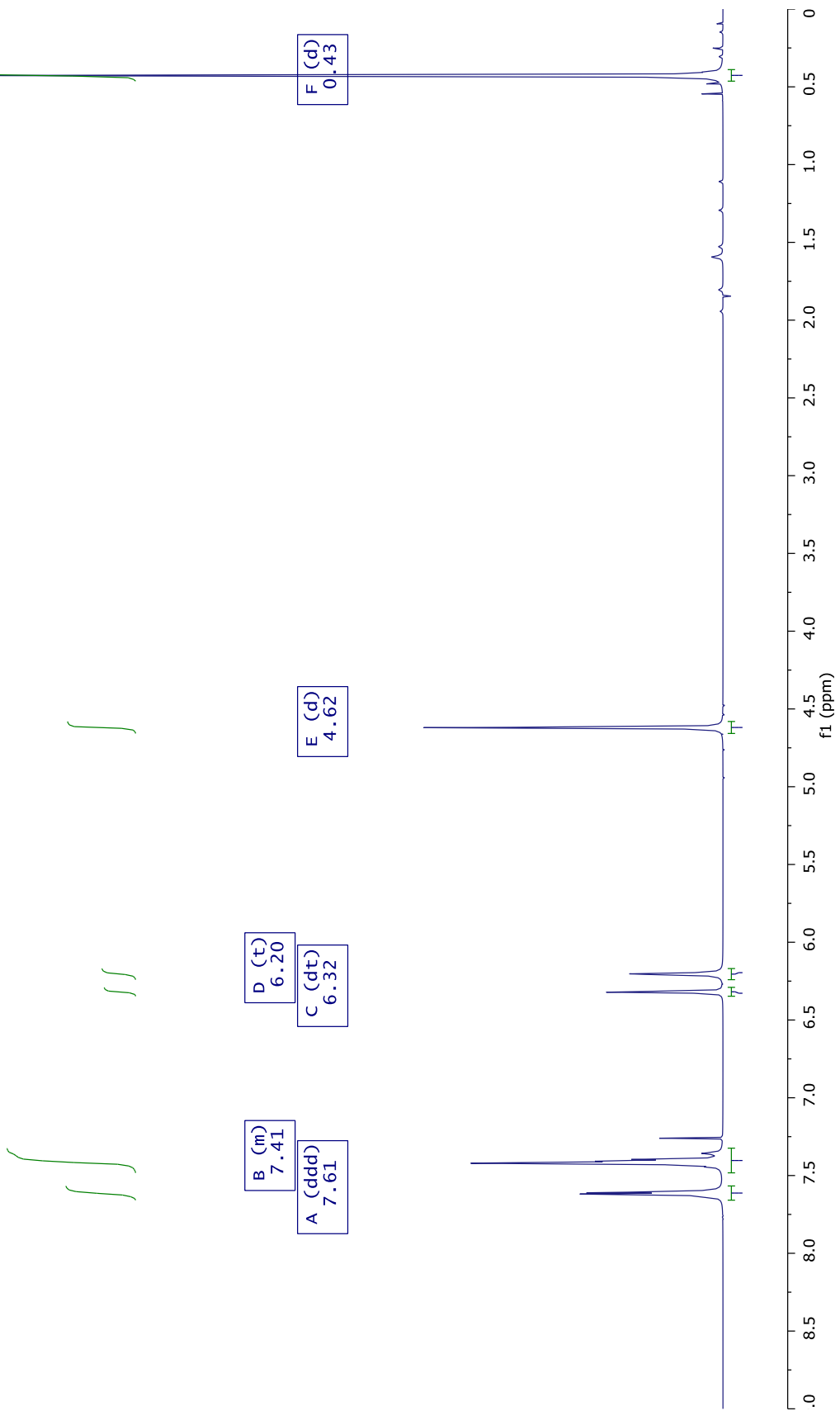
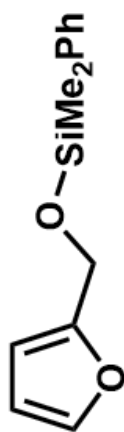
 ^{13}C NMR (126 MHz, CDCl_3) of compound **4d-SI**.



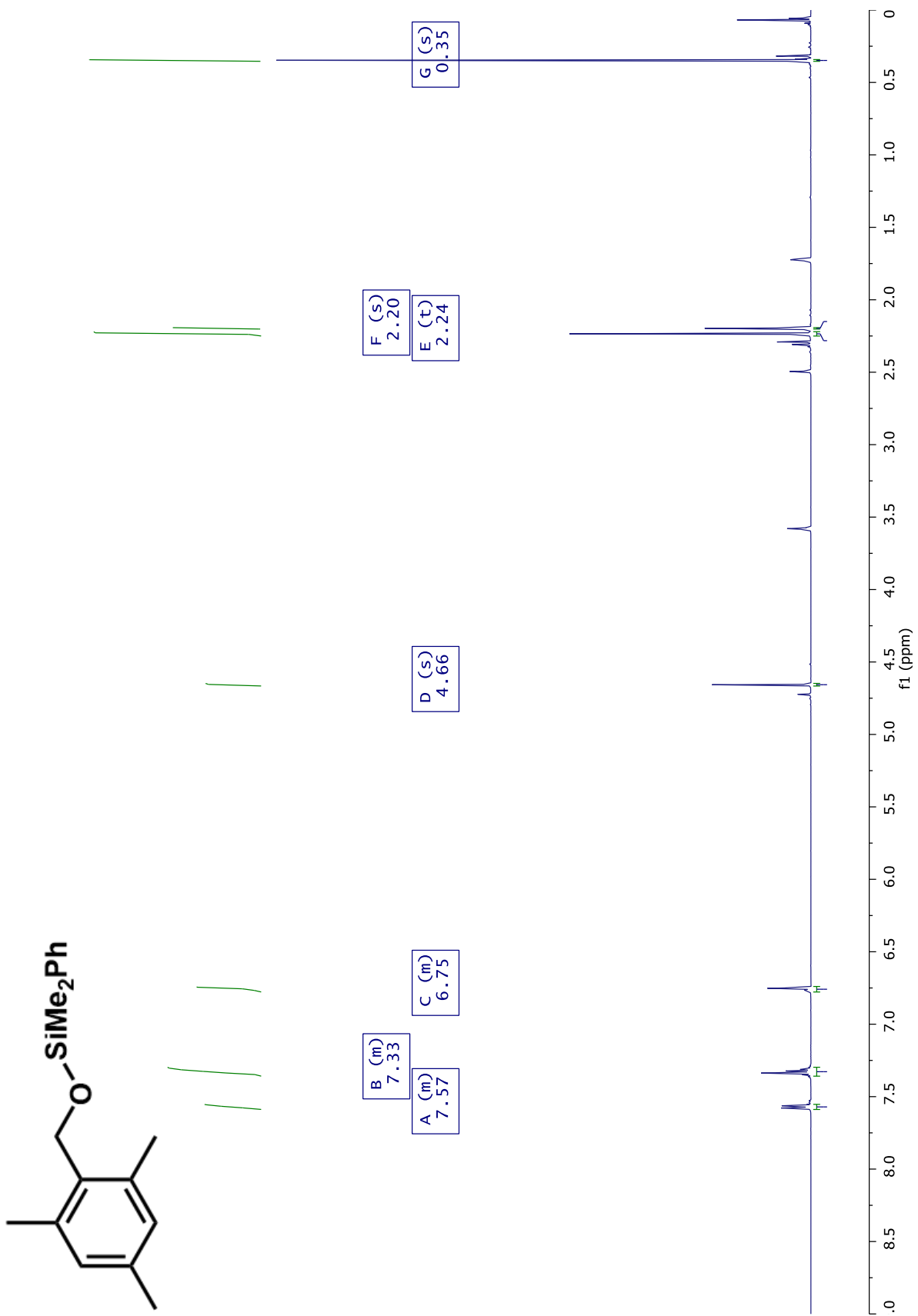
¹H NMR (500 MHz, CDCl₃) of compound **4e**.

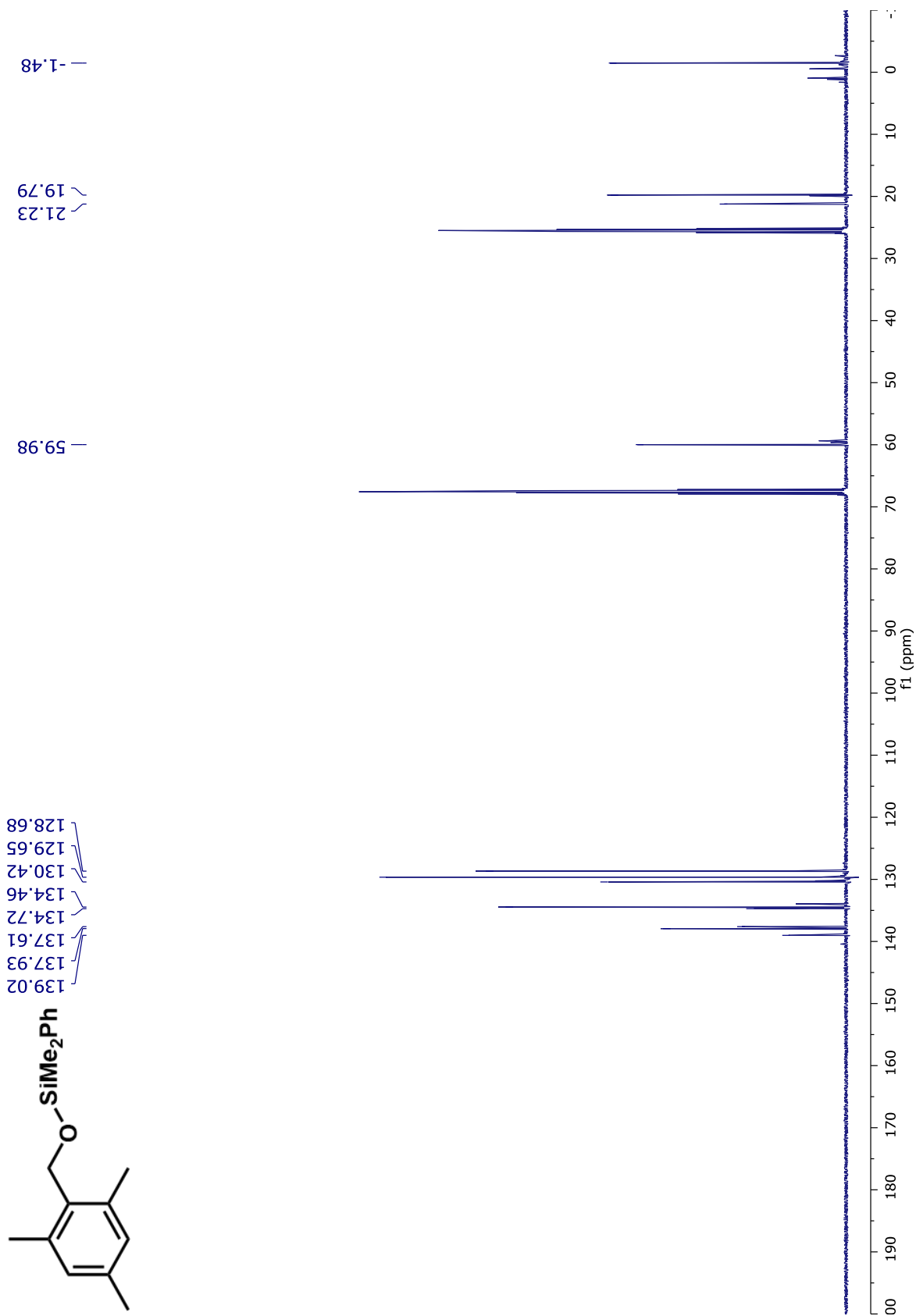
¹H NMR (500 MHz, CDCl₃) of compound 4f.

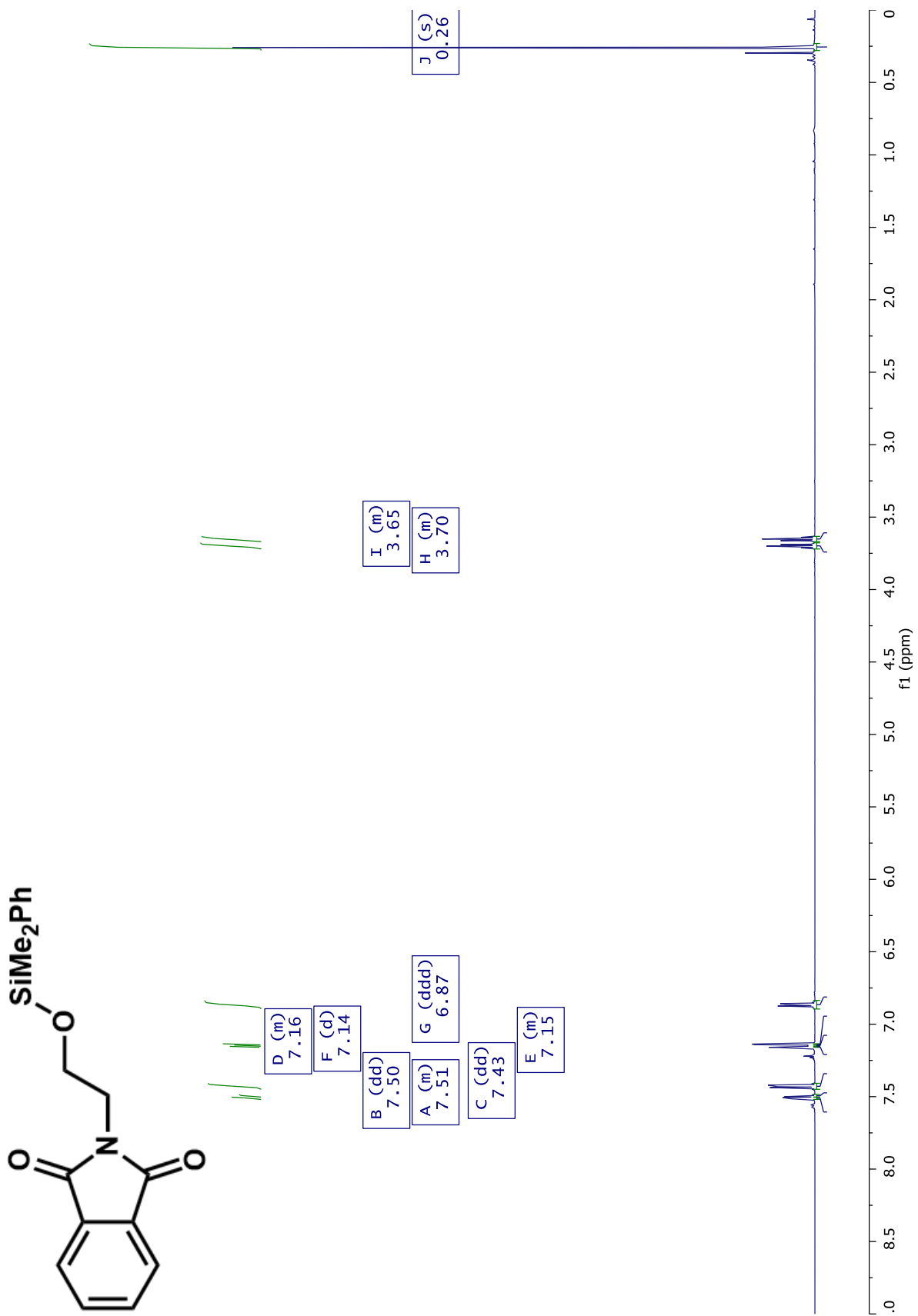
¹H NMR (500 MHz, CDCl₃) of compound 4g.

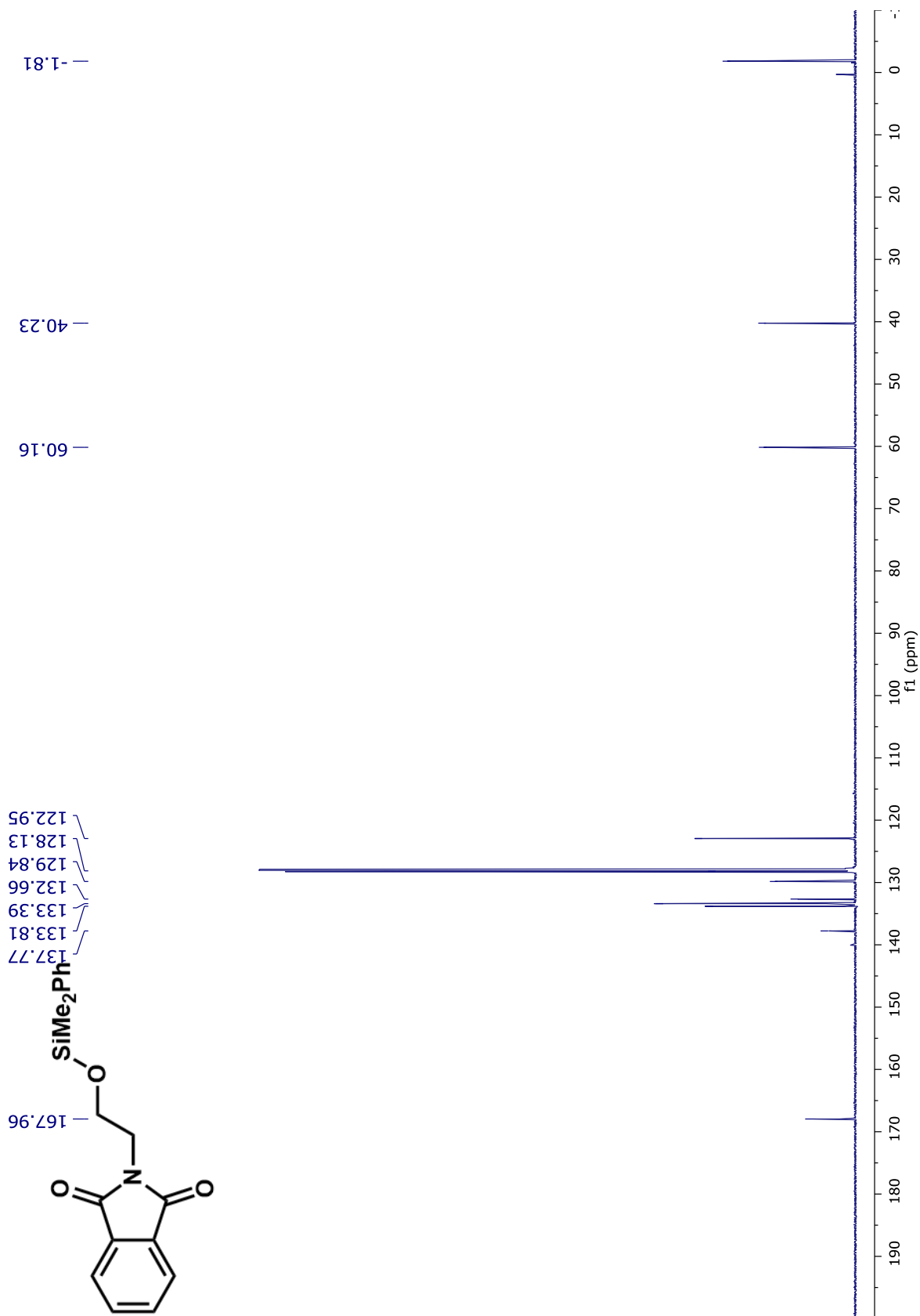


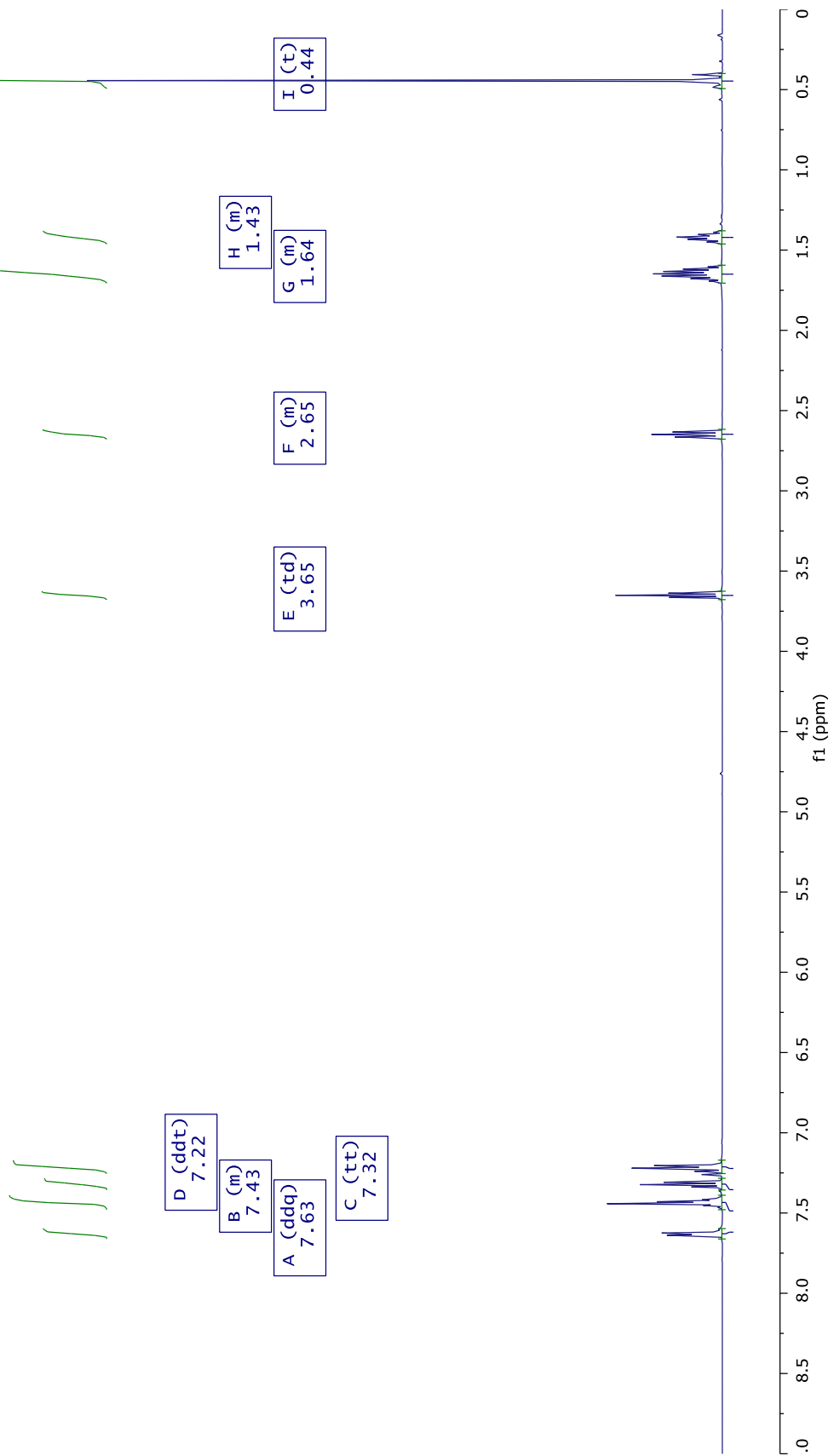
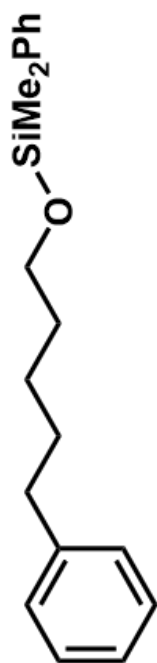
¹H NMR (500 MHz, CDCl₃) of compound **4h**.

¹H NMR (500 MHz, THF-*d*₈) of compound **4i**.

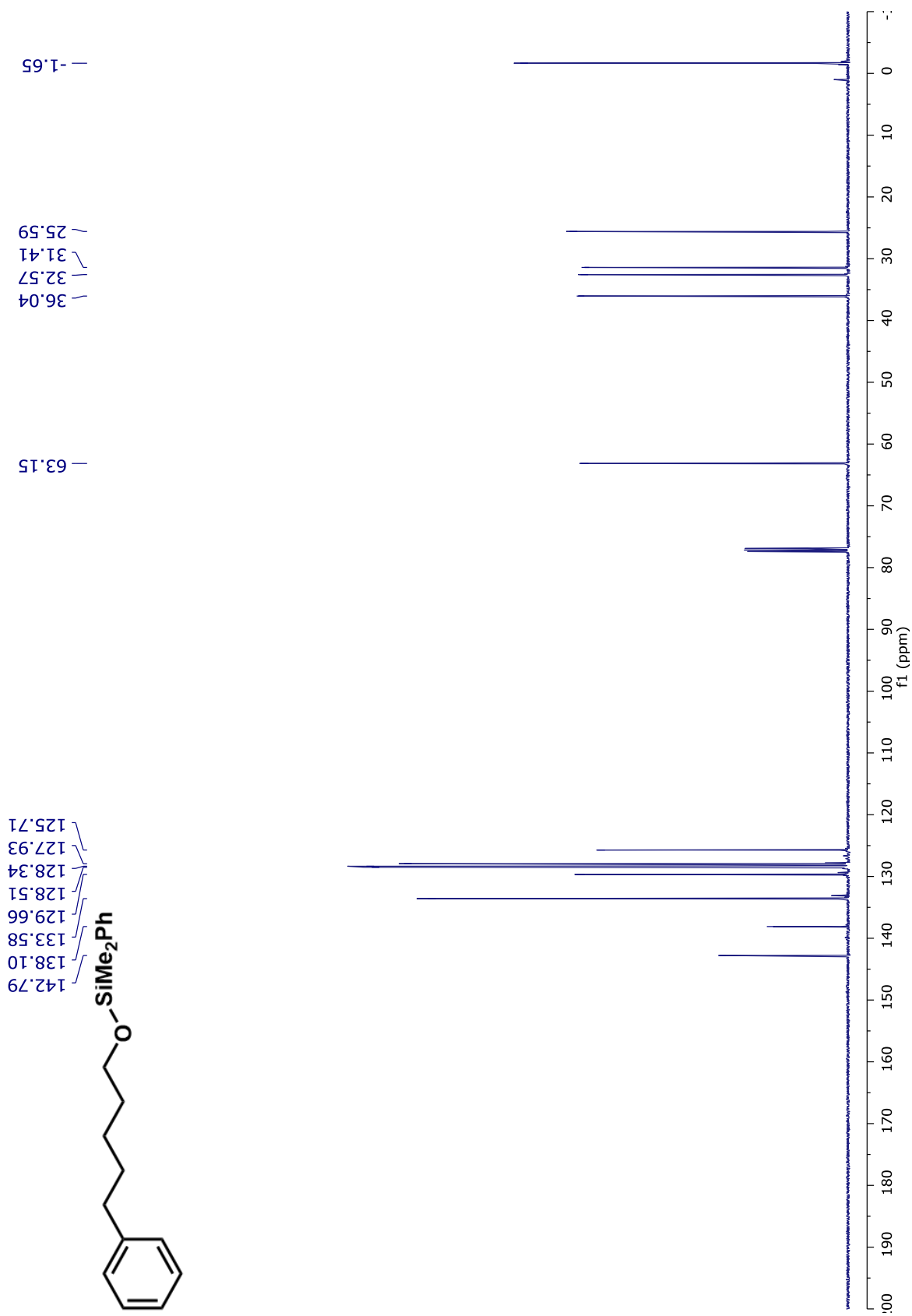
¹³C NMR (126 MHz, THF-*d*₈) of compound **4i**.

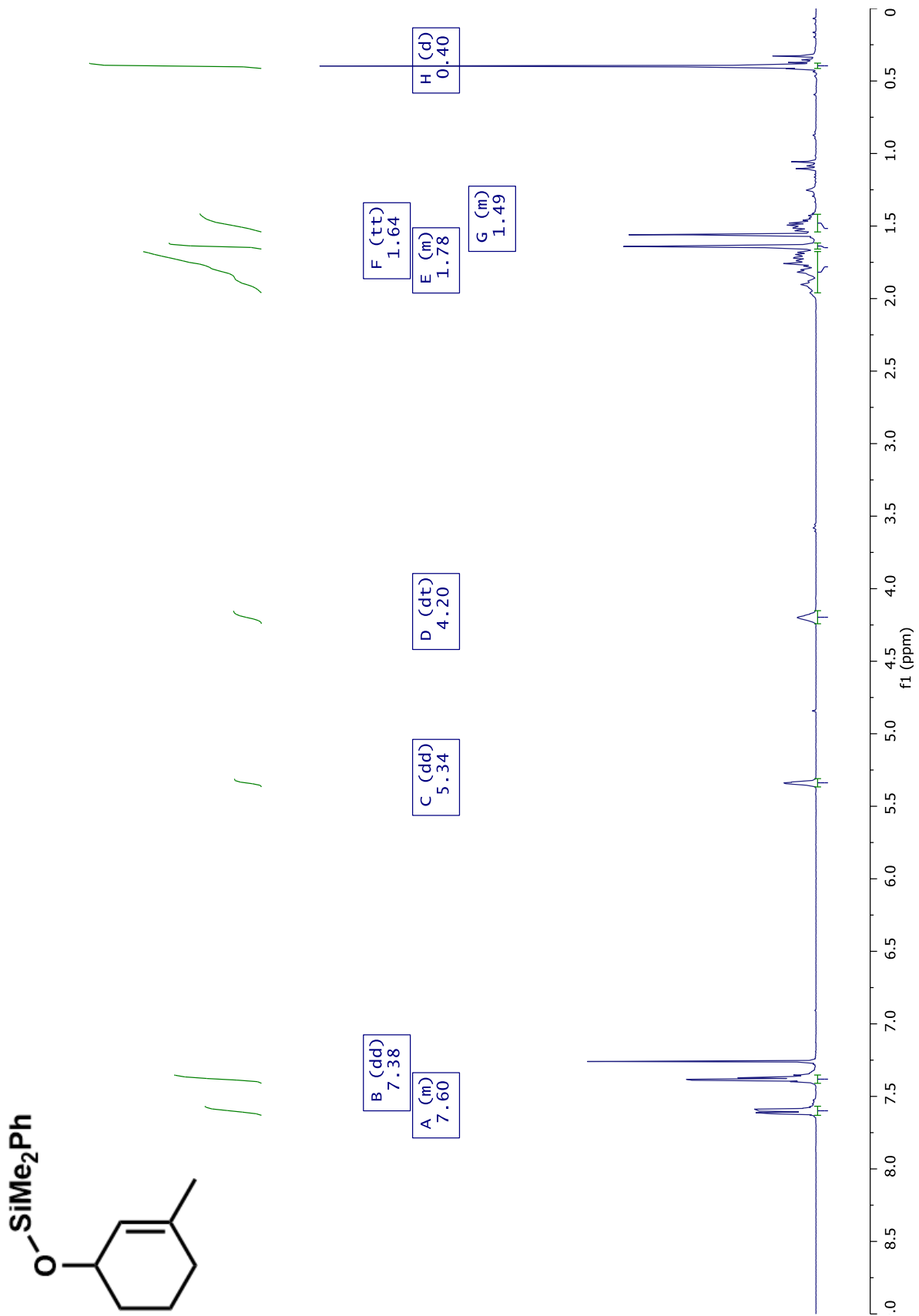
 ^1H NMR (500 MHz, Benzene- d_6) of compound **4j**.

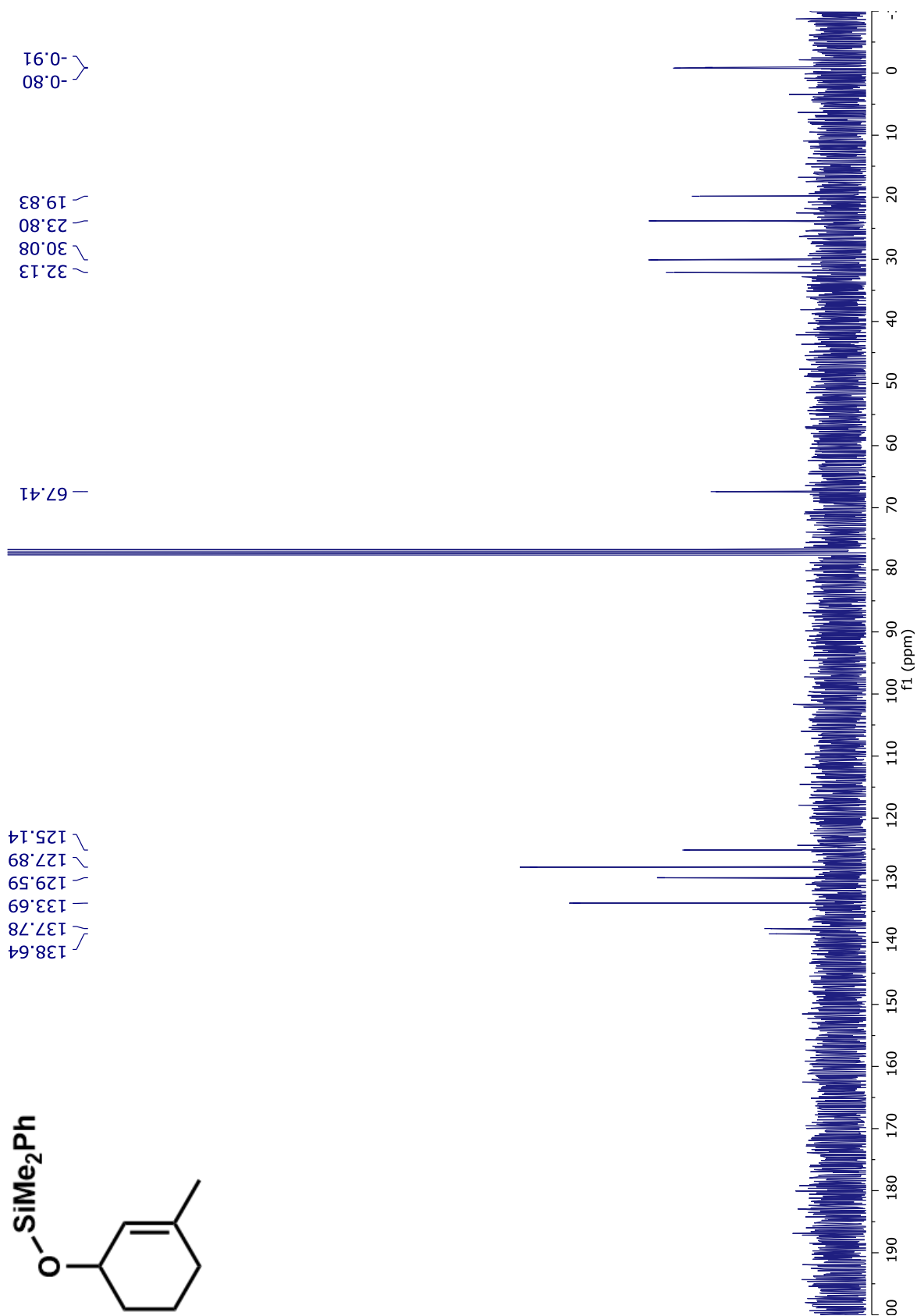


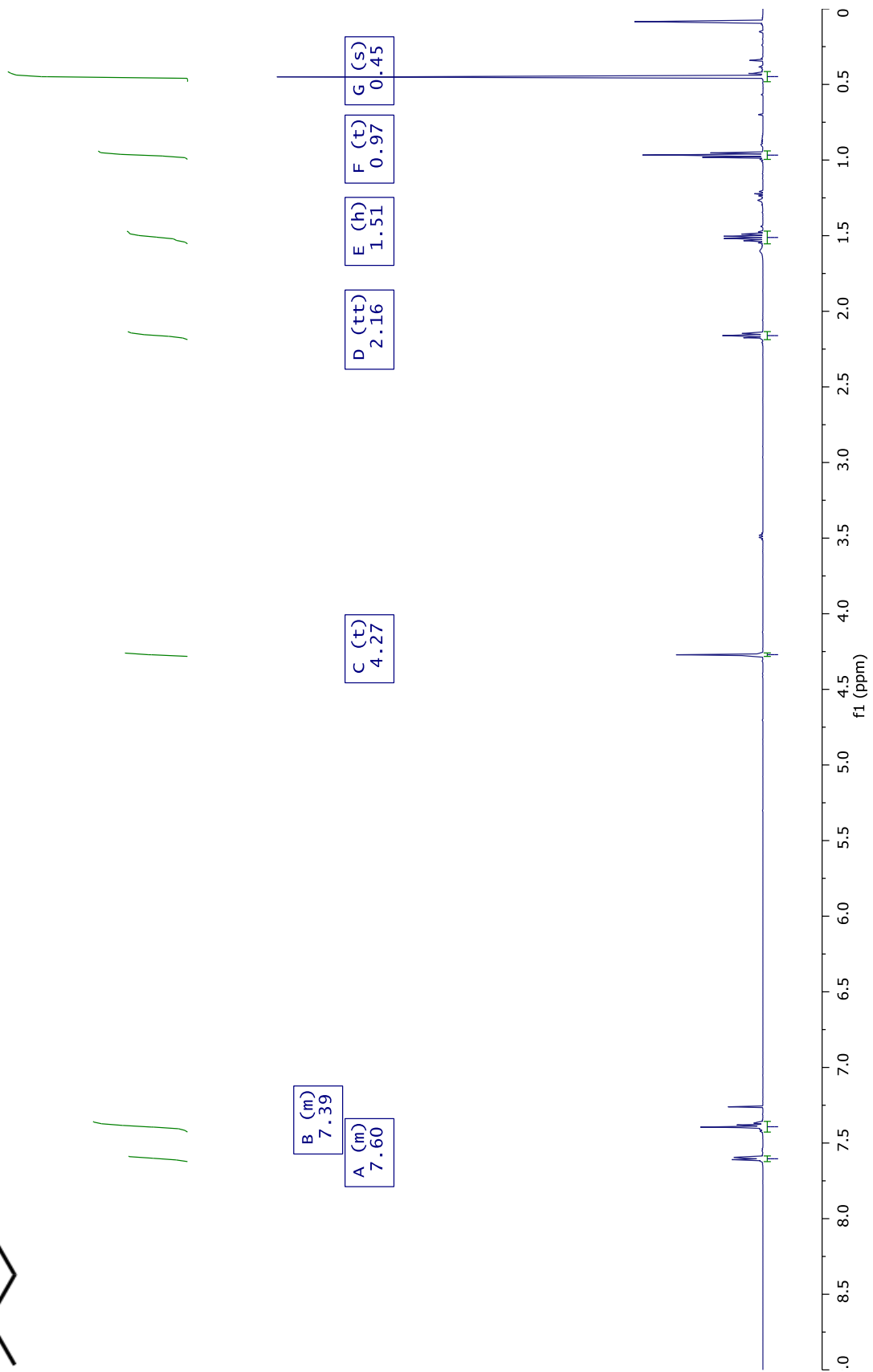


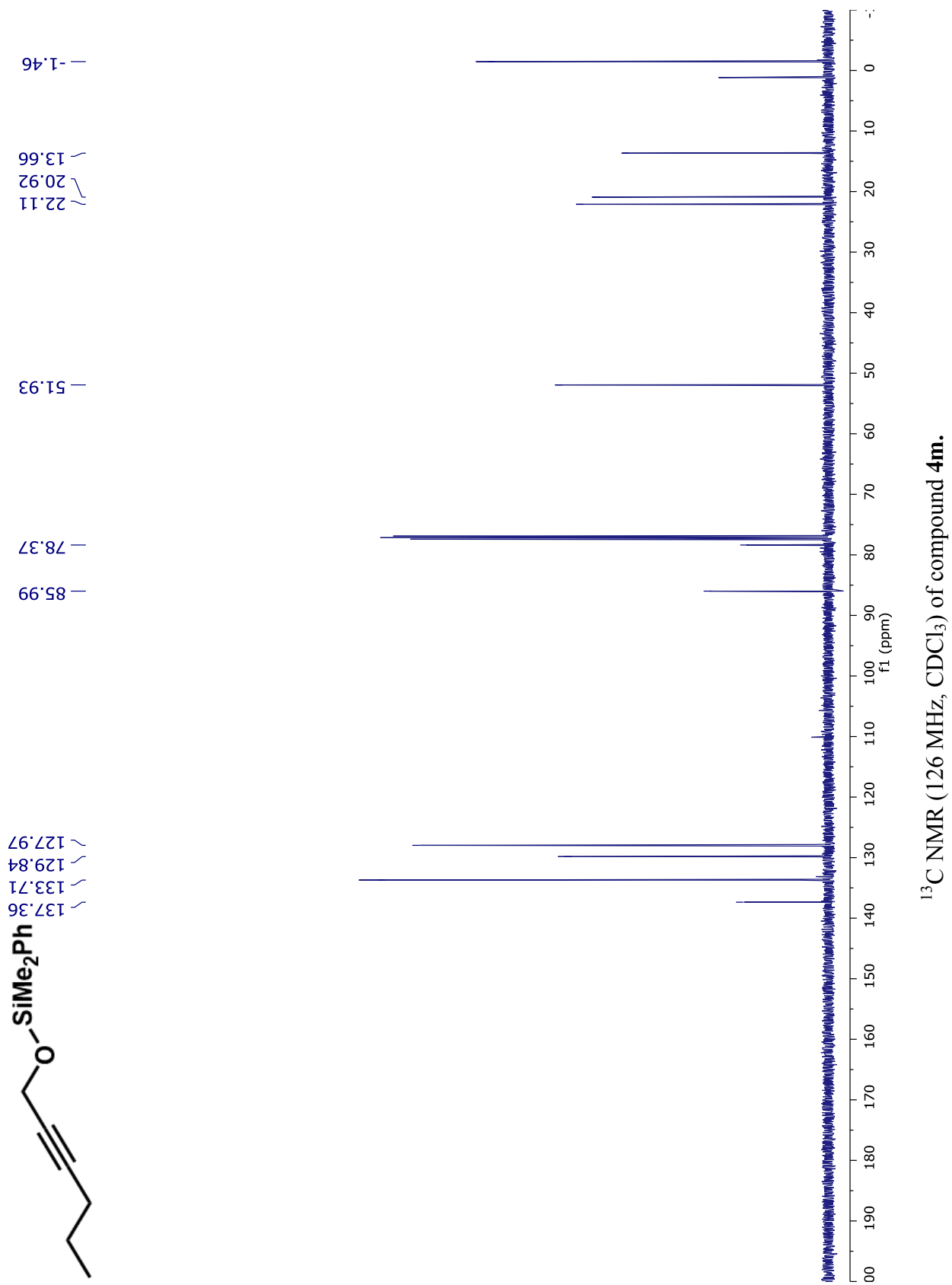
¹H NMR (500 MHz, CDCl₃) of compound **4k**.

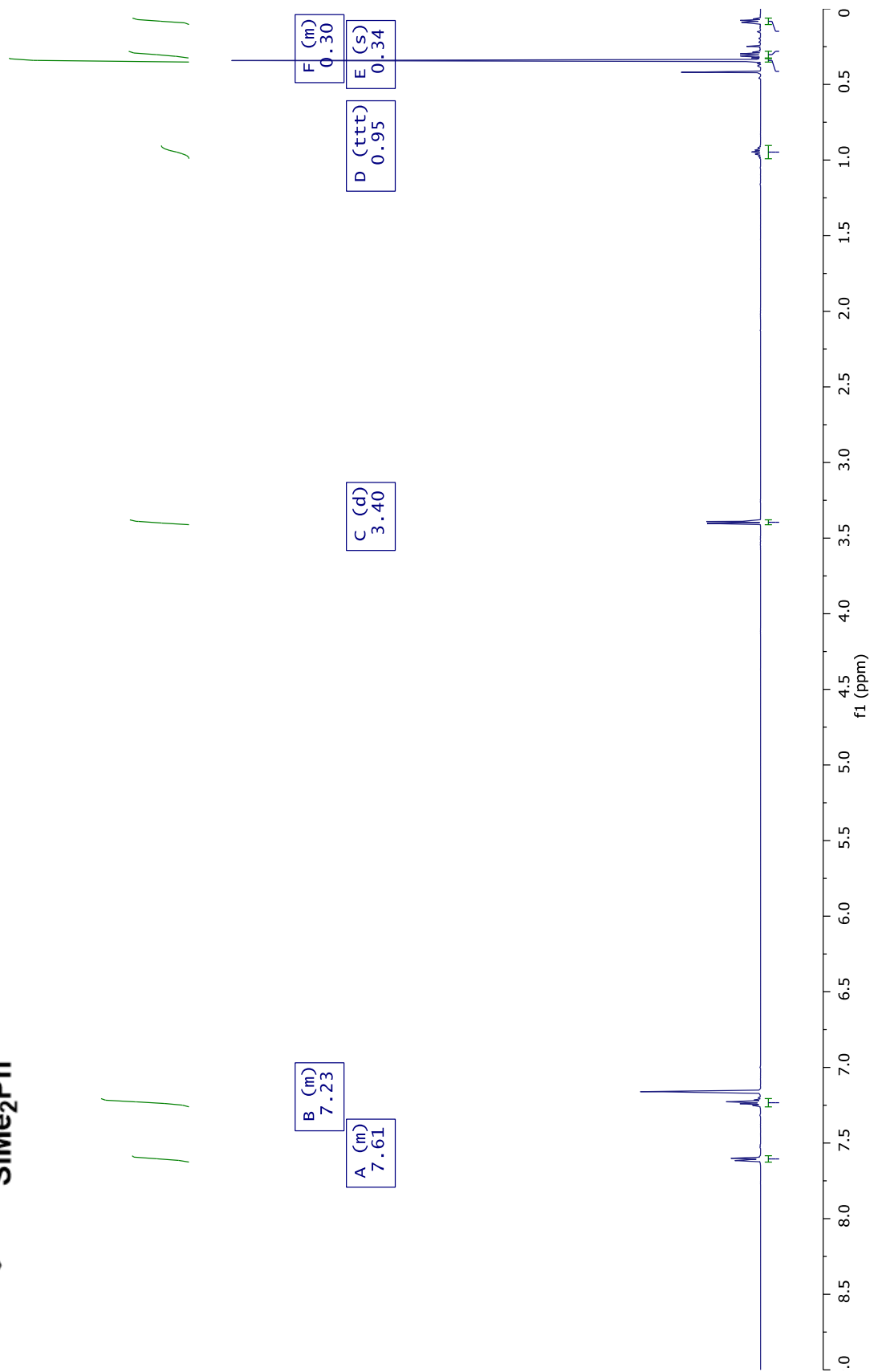
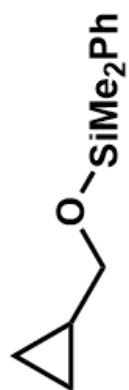


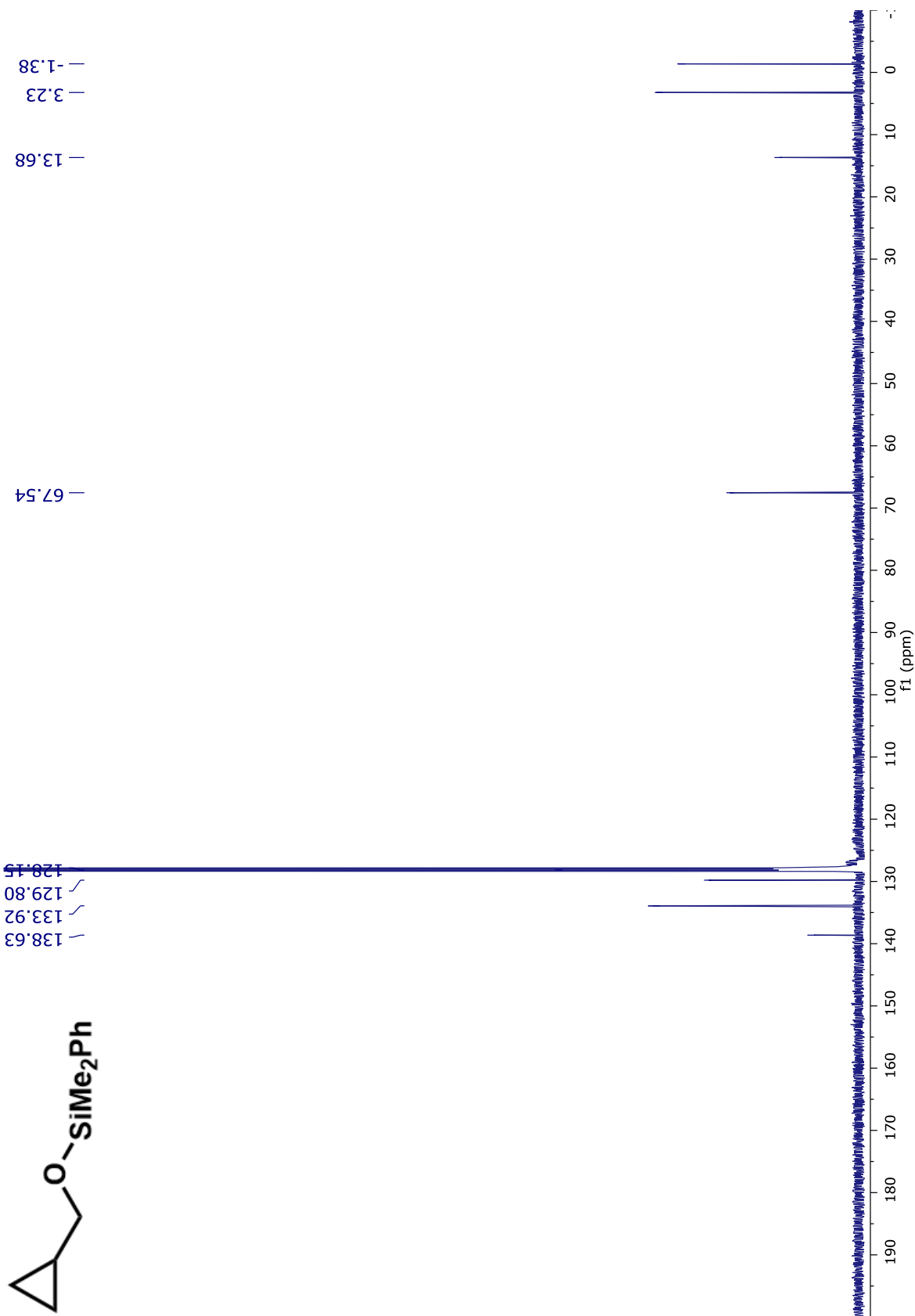


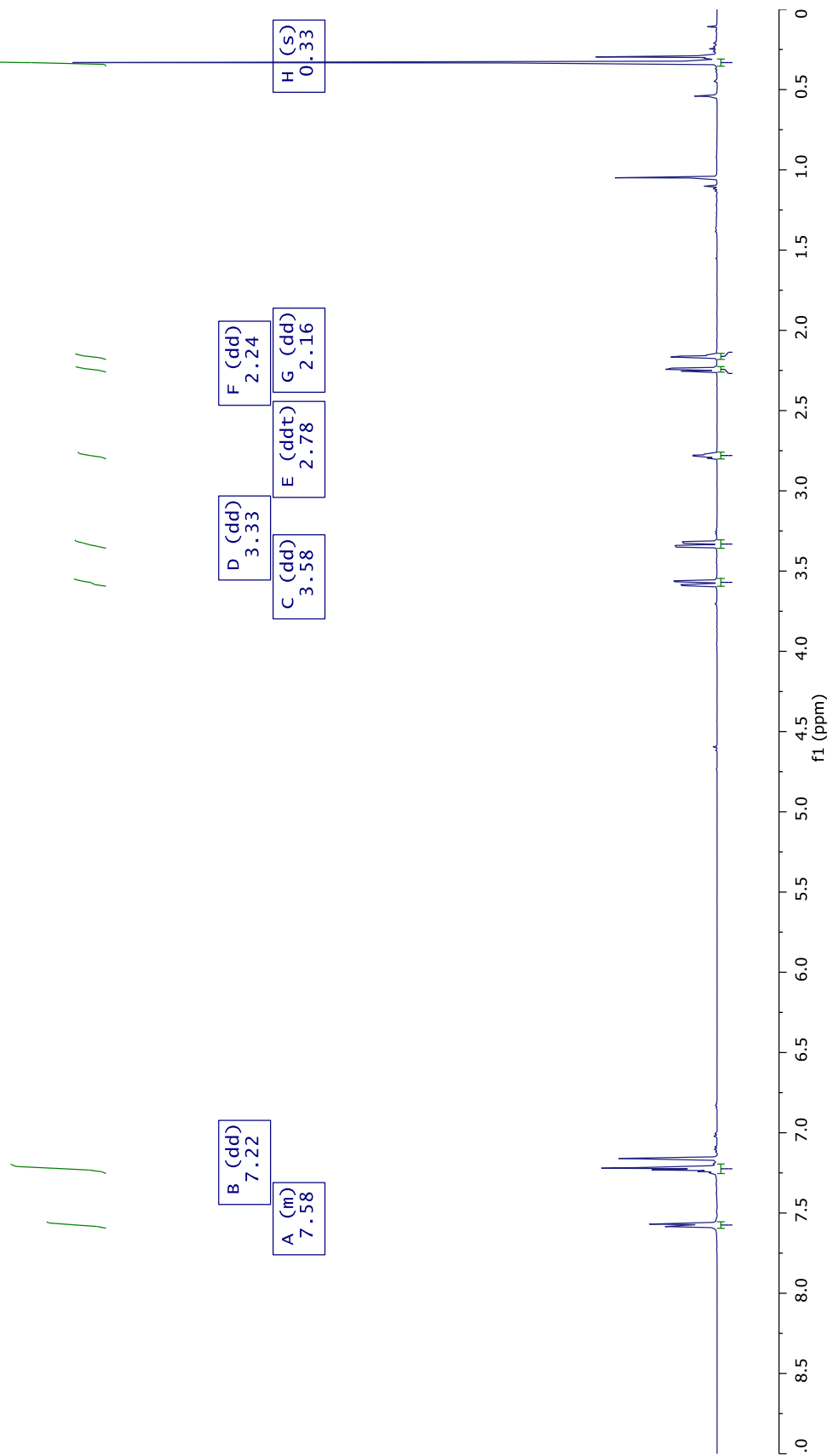
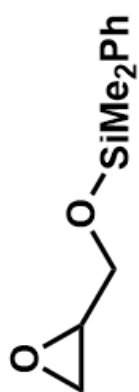




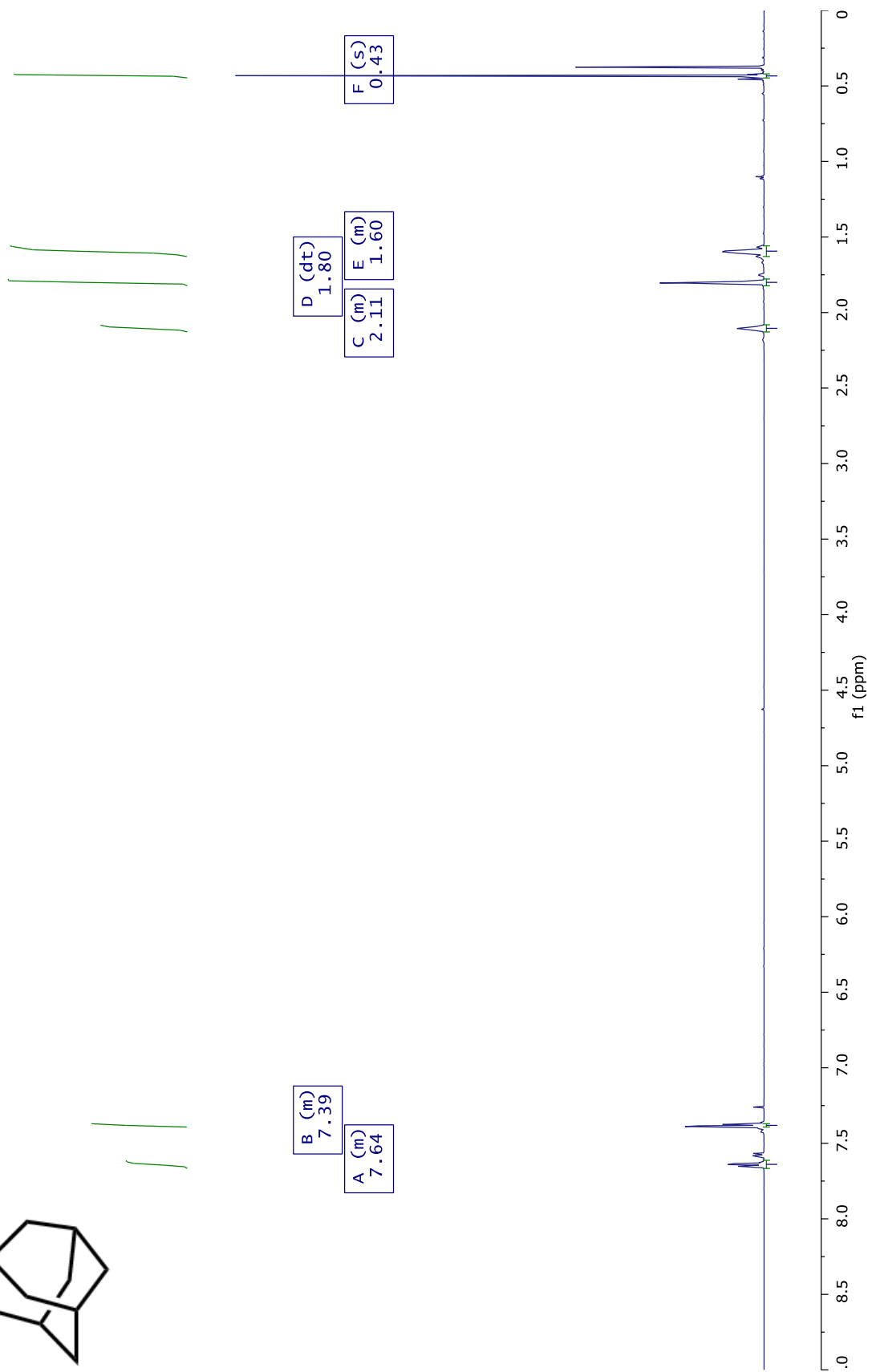
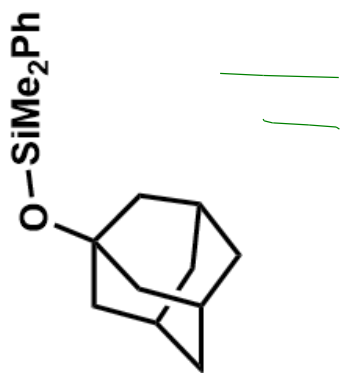


¹H NMR (500 MHz, Benzene-*d*₆) of compound **4n**.

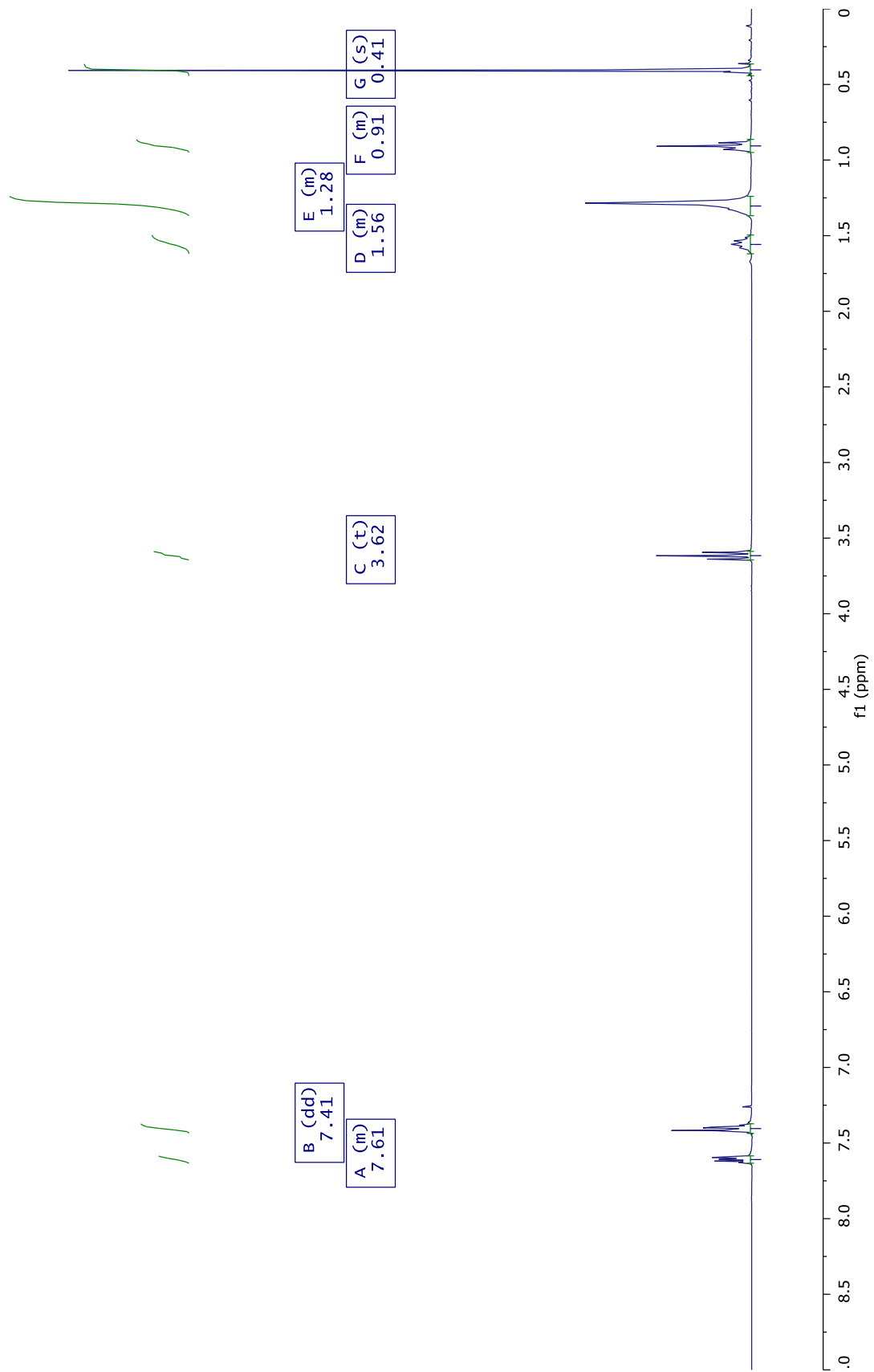


¹H NMR (500 MHz, Benzene-*d*₆) of compound **40**.

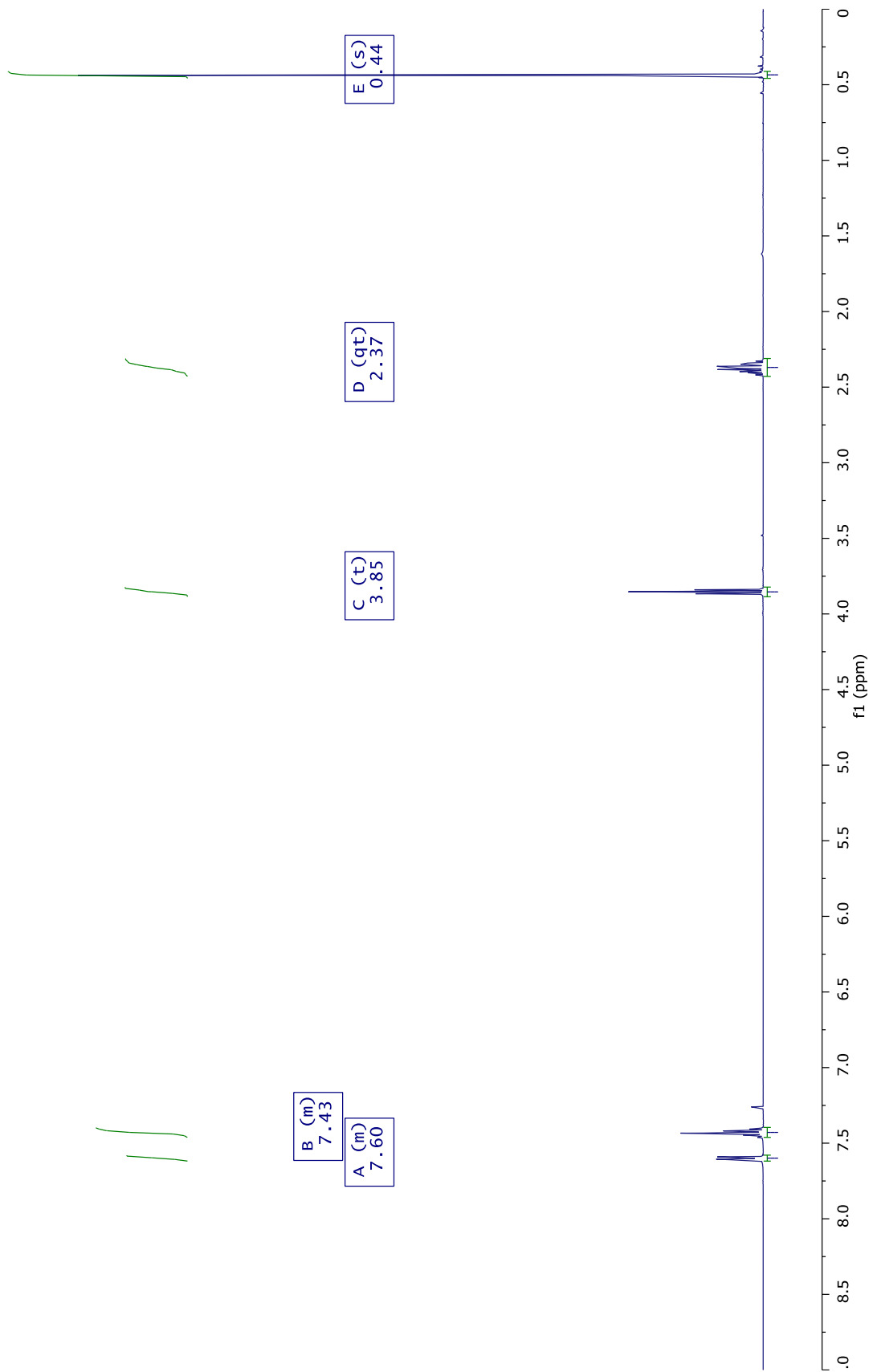
O-SiMe₂Ph



¹H NMR (500 MHz, CDCl₃) of compound **4p**.



¹H NMR (500 MHz, CDCl₃) of compound 4q.



¹H NMR (500 MHz, CDCl₃) of compound **4r**.

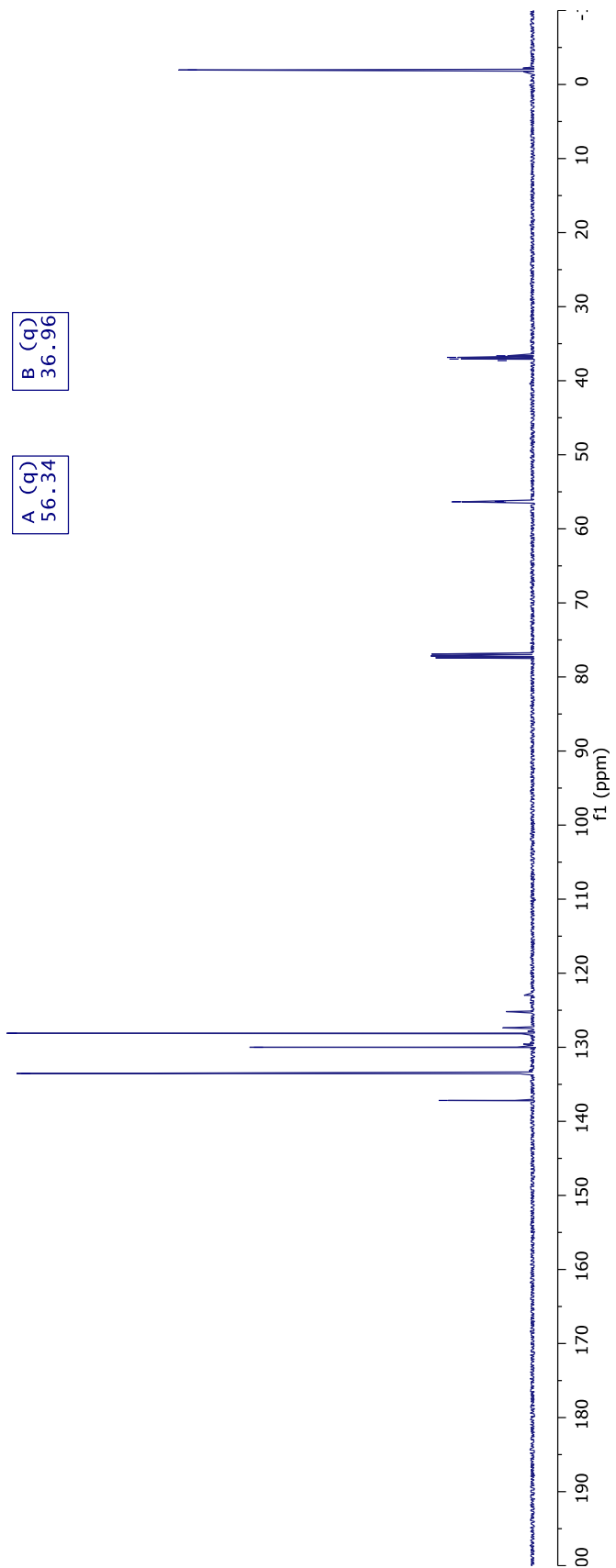


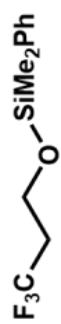
137.18
133.54
130.00
128.11

56.39
56.36
56.33
56.30

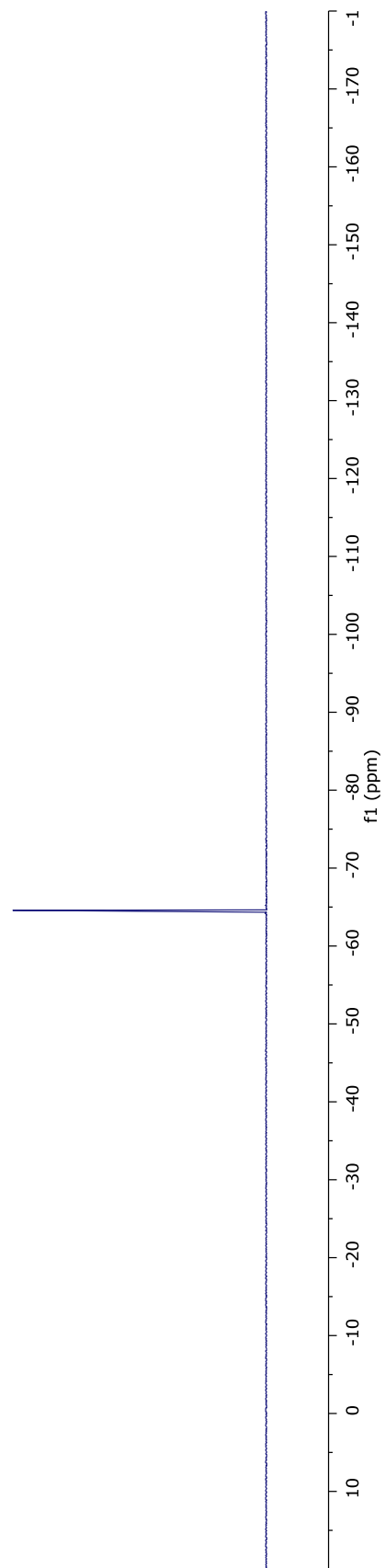
37.29
37.07
36.85
36.63

-1.96

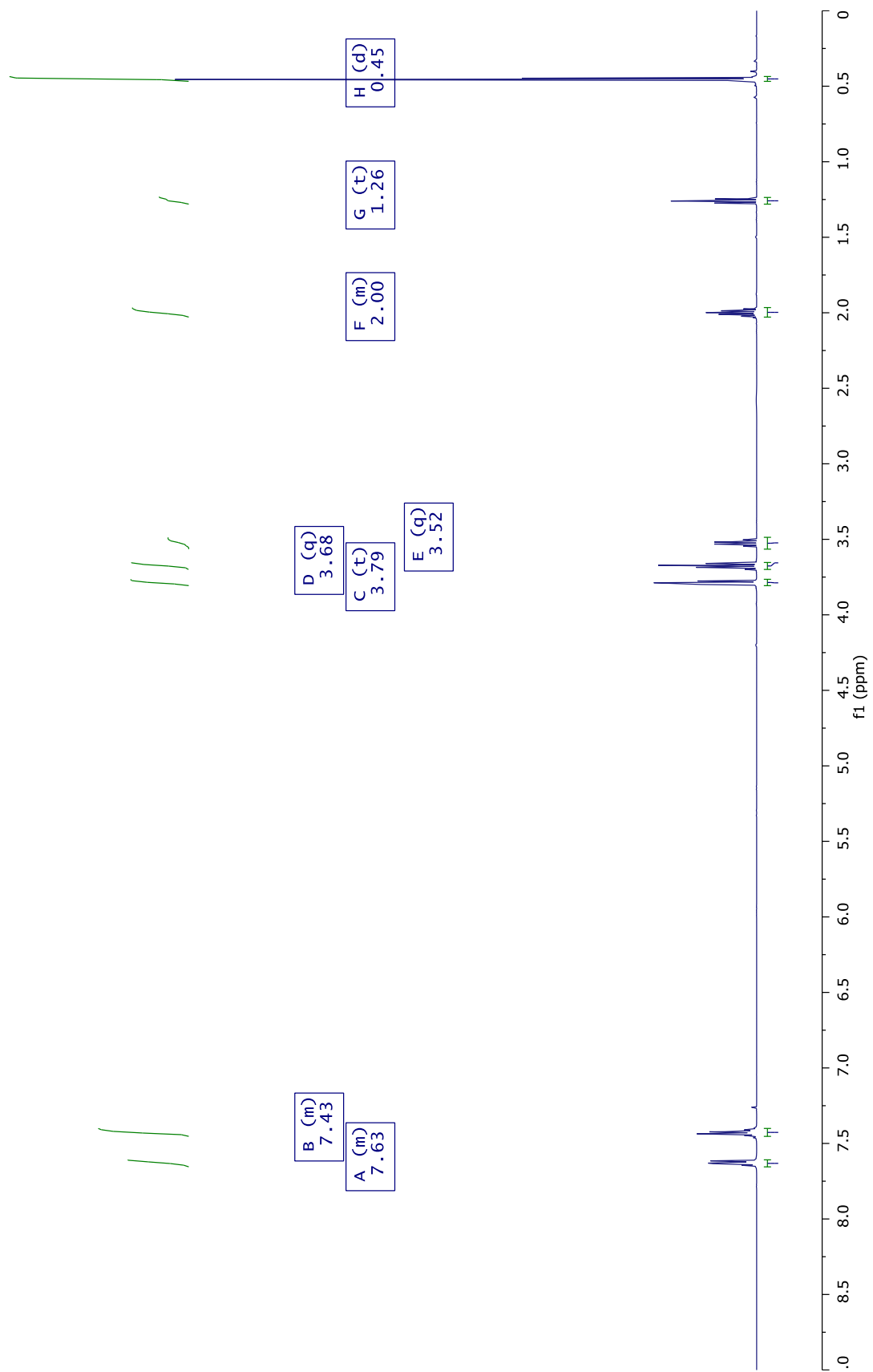


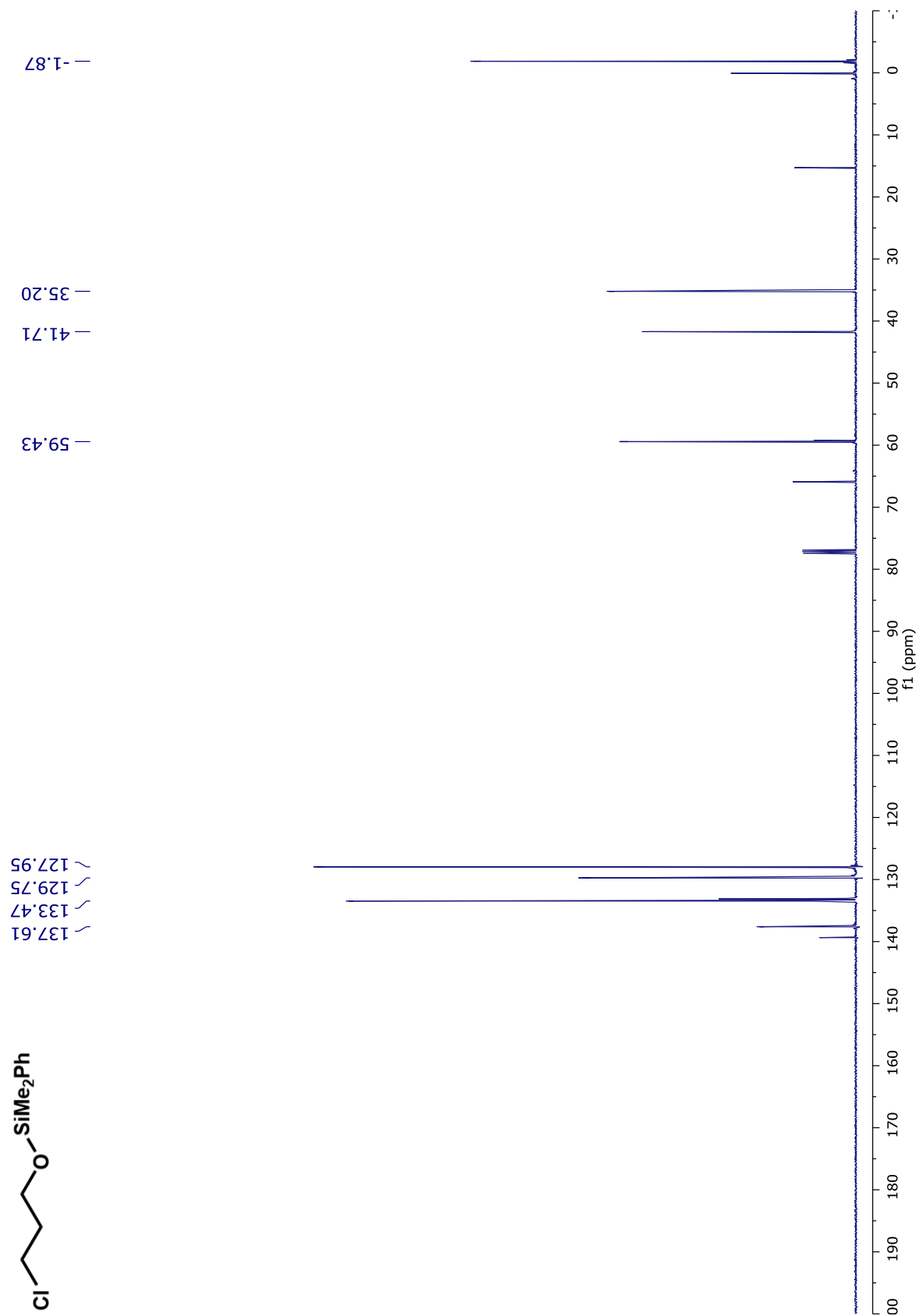


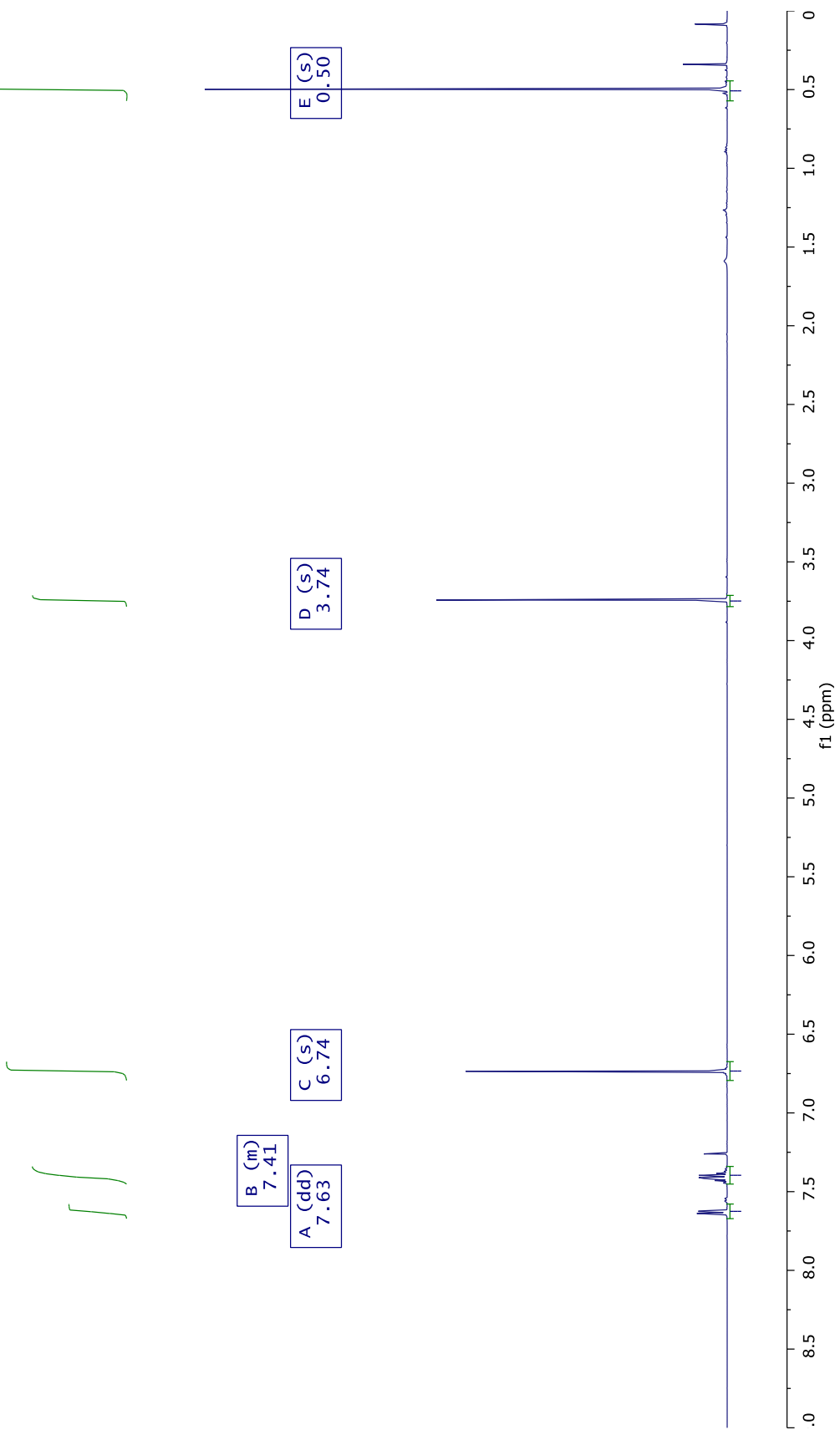
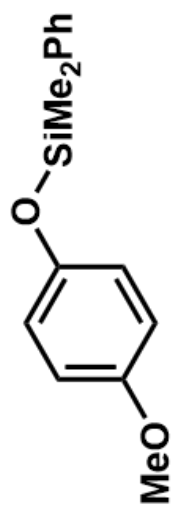
A (t)
-64.58



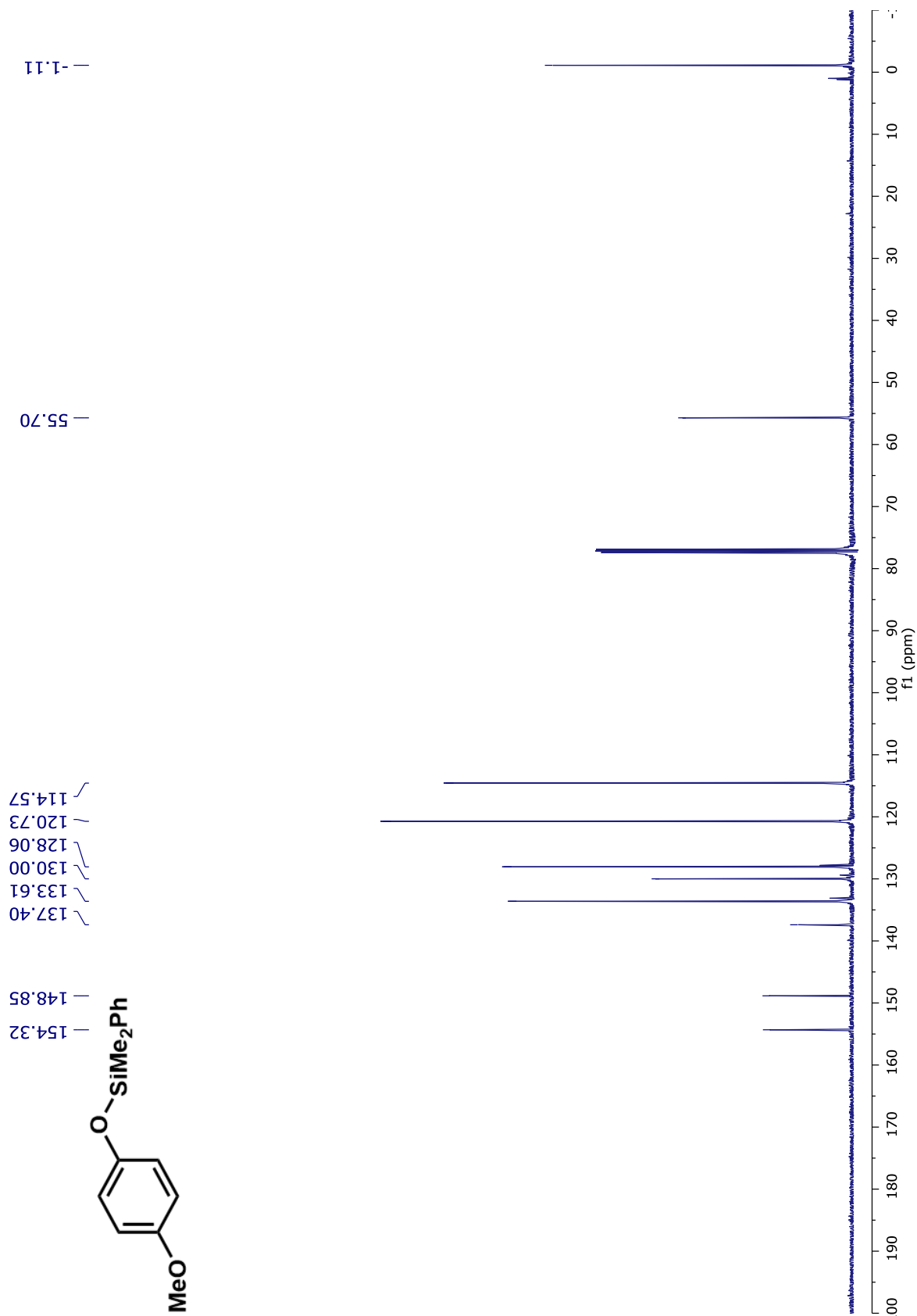
^{19}F NMR (282 MHz, CDCl_3) of compound **4r**.

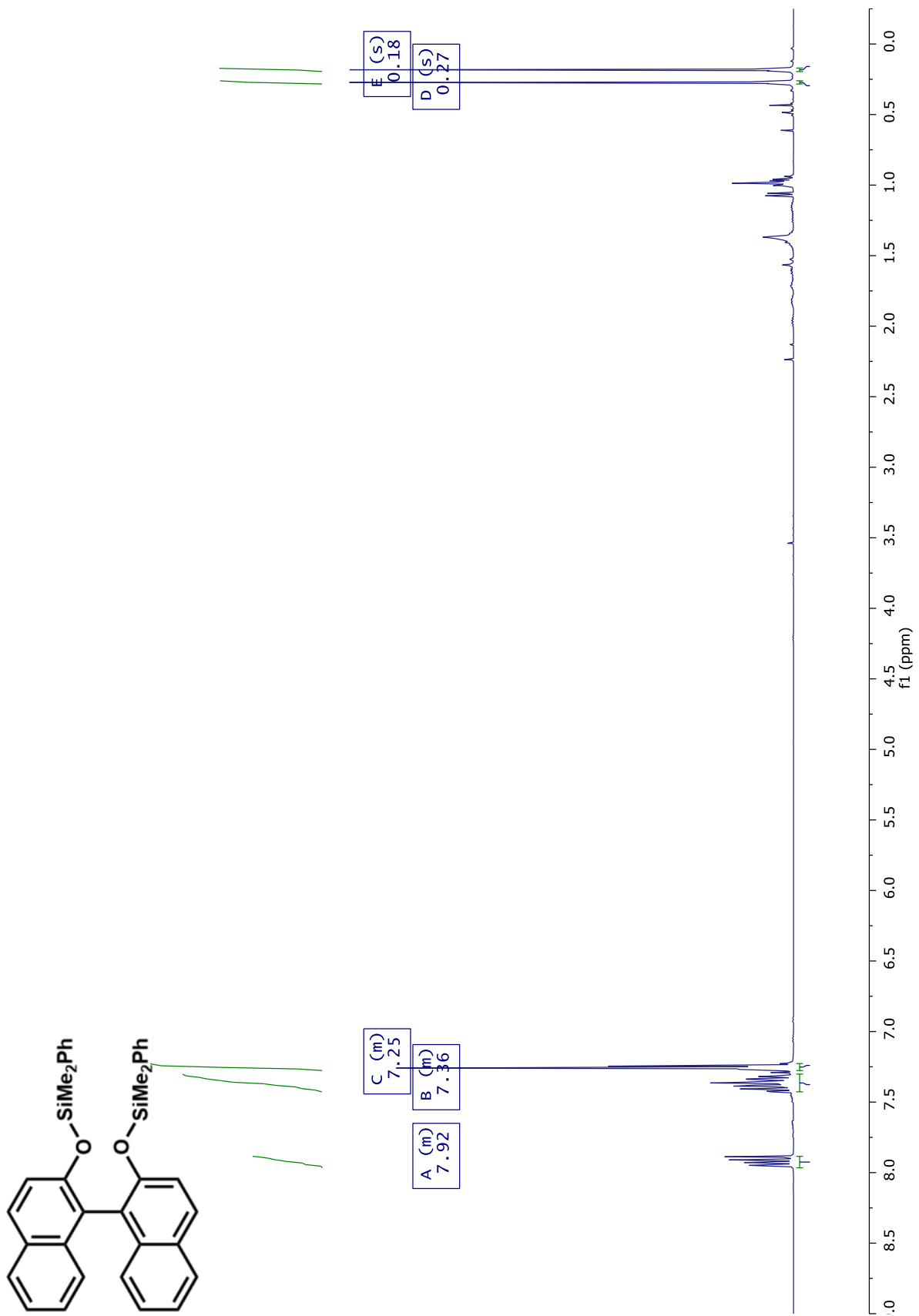


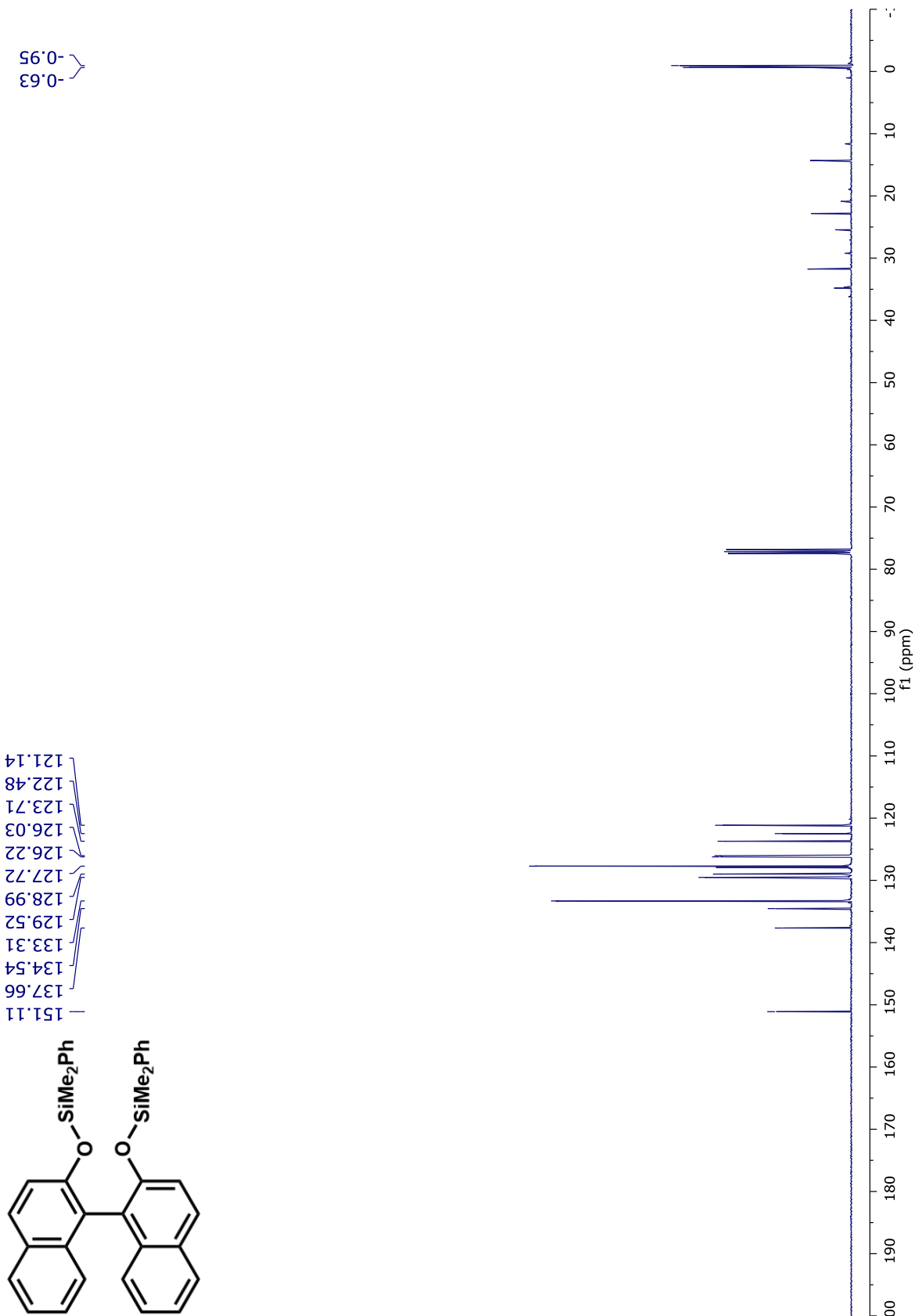


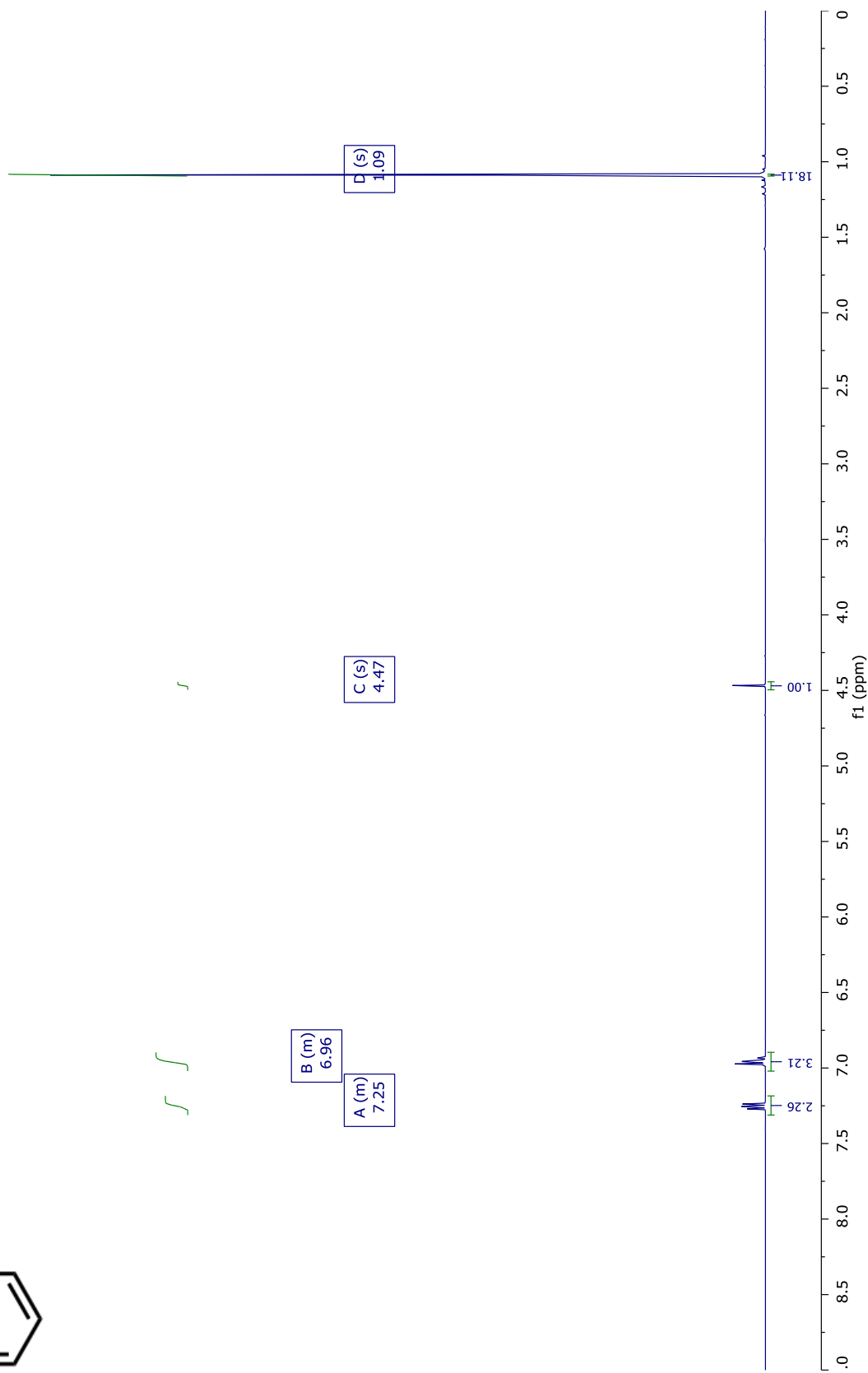
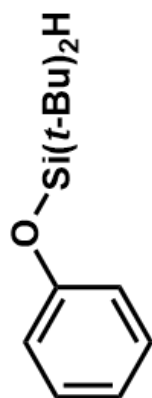


¹H NMR (500 MHz, CDCl₃) of compound **4t**.

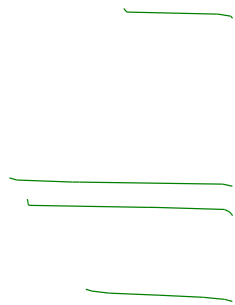
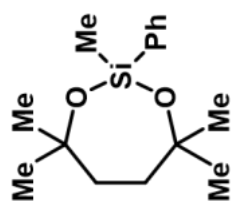








¹H NMR (500 MHz, CDCl₃) of compound **6**.



B (m)
7.73

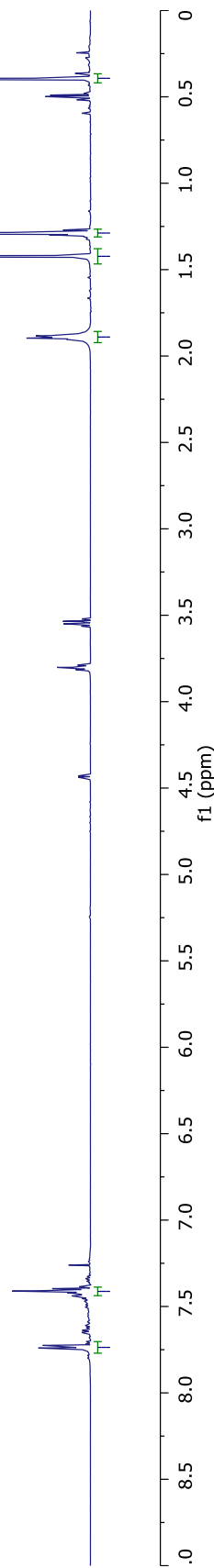
A (m)
7.41

E (s)
1.29

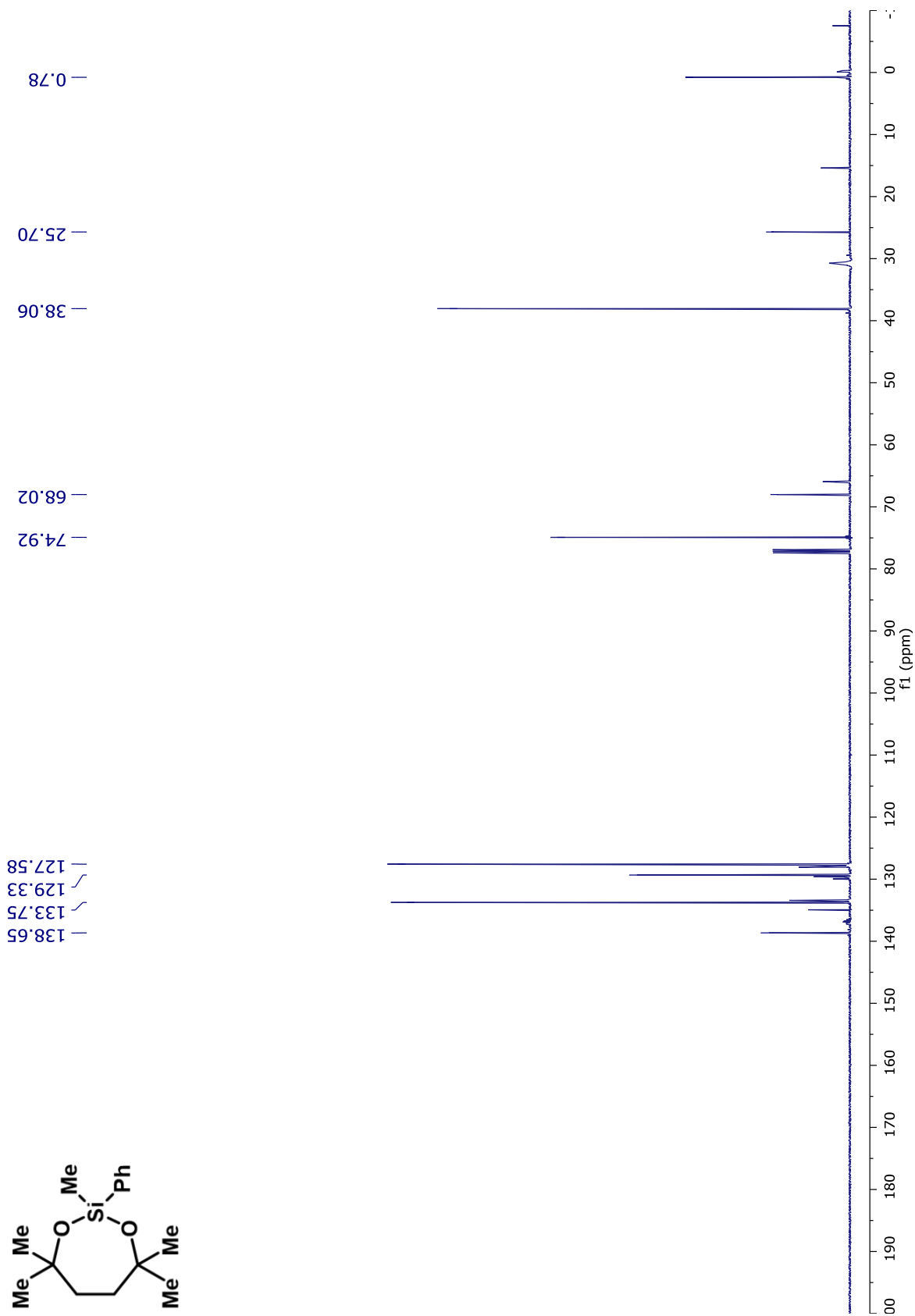
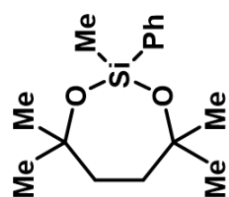
D (s)
1.42

C (m)
1.89

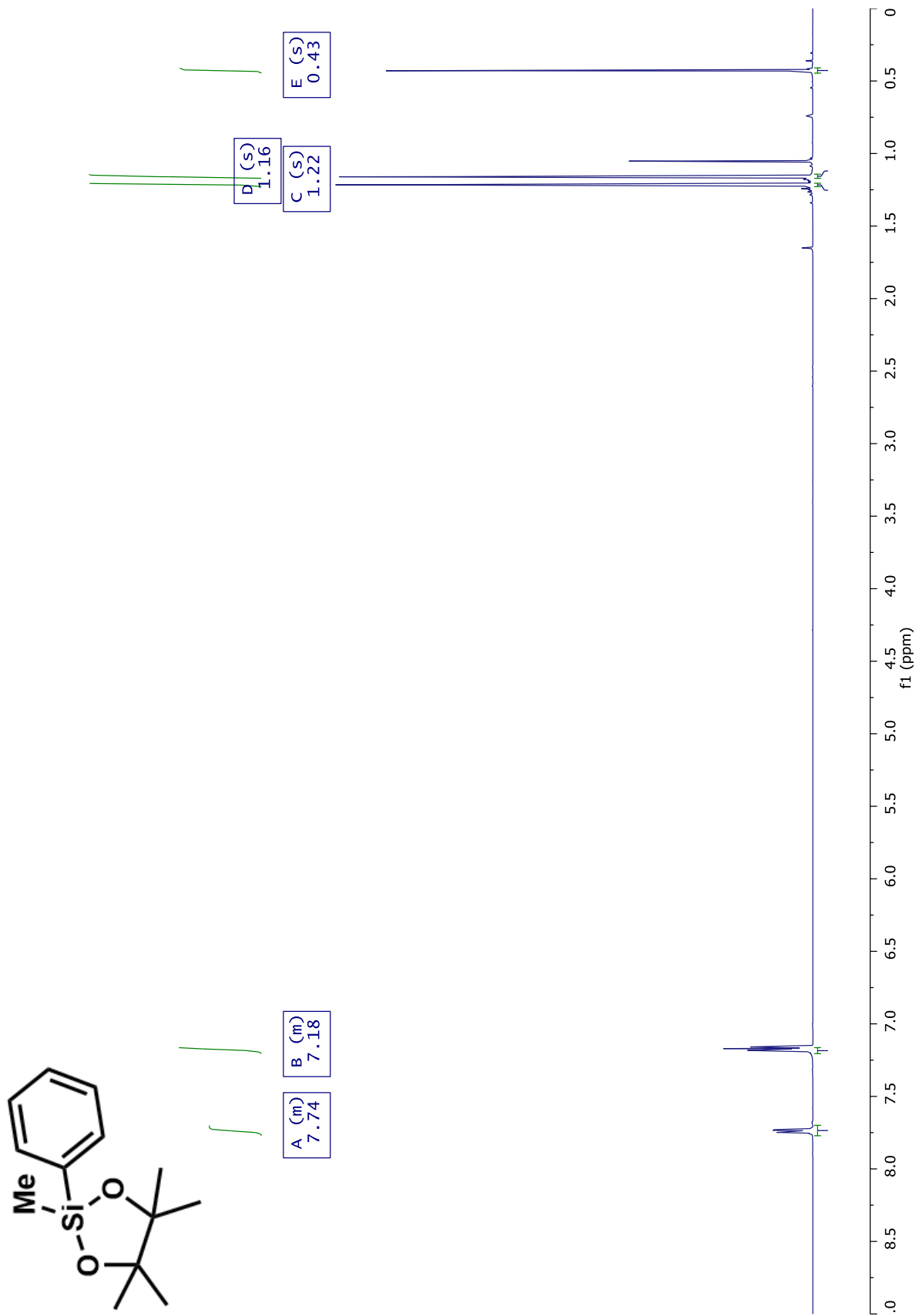
F (s)
0.39

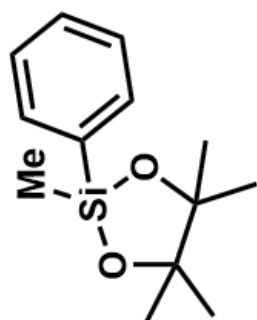


¹H NMR (500 MHz, CDCl₃) of compound **9**.



^{13}C NMR (126 MHz, CDCl_3) of compound **9**.

 ^1H NMR (500 MHz, Benzene- d_6) of compound **11**.

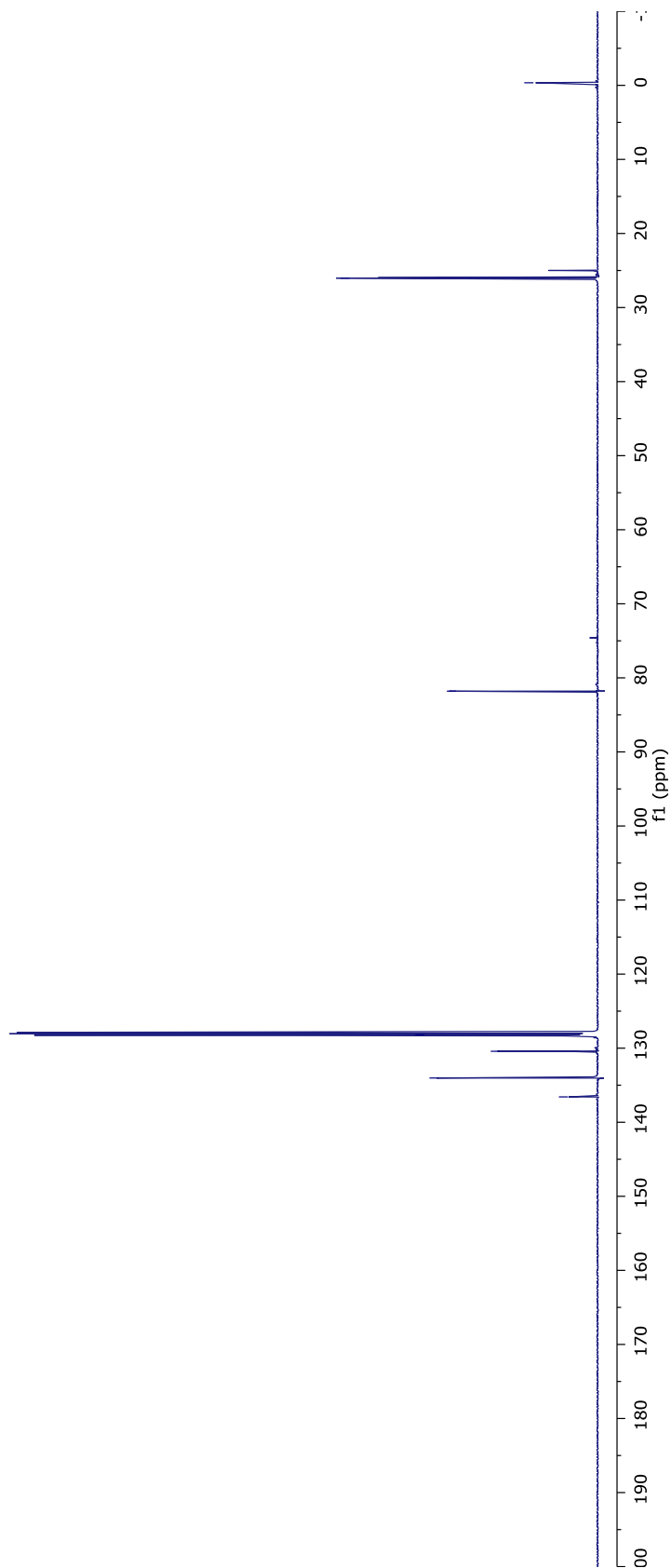


136.58
134.03
130.42
128.21

81.80

26.03

-0.35



^{13}C NMR (126 MHz, Benzene- d_6) of compound **11**.