Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Rhodium-Catalysed Intramolecular *trans*-Bis-Silylation of Alkynes to Synthesise 3-Silyl-1-benzosiloles

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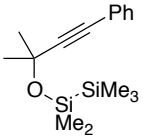
Supporting Information

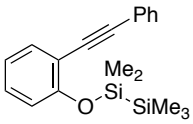
General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel C-200 (75–150 μm). Preparative thin-layer chromatography was performed on silica gel 60 PF_{254} (Merck). Proton chemical shifts were referenced to the residual solvent signals ($CDCl_3$ at 7.26 and C_6D_6 at 7.15 ppm). Carbon chemical shifts were referenced to the central solvent signals ($CDCl_3$ at 77.0 ppm and C_6D_6 at 128 ppm).

Materials. Rhodium complexes, $[RhCl(nbd)]_2$[1] and $RhCl(PPh_3)_3$,[2] [2-(2-bromophenyl)-ethynyl]trimethylsilane,[3] chlorodimethyl{2-[2-(4-methylphenyl)ethynyl]phenyl}silane,[4] and (*Z*)-(4-bromo-3-propylhept-3-en-1-yn-1-yl)benzene[5] were prepared by the literature methods. Disilanyl ethers were prepared by silylation of the corresponding alkynols with 1-chloro-1,1,2,2,2-pentamethyldisilane. 1-Chloro-2-isobutyl-1,1,2,2-tetramethyldisilane was prepared by electrophilic chlorination of 1-isobutyl-1,1,2,2-tetramethyl-2-phenyldisilane with HCl. All other commercially available chemical resources were used as received without further purification.

(1) E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.
(2) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A*, 1966, 1711.
(3) Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796.
(4) (a) T. Matsuda, S. Kadowaki, T. Goya and M. Murakami, *Org. Lett.*, 2007, **9**, 133; (b) T. Matsuda, S. Kadowaki, Y. Yamaguchi and M. Murakami, *Chem. Commun.*, 2008, 2744.
(5) Y. Li, X. Liu, H. Jiang and Z. Feng, *Angew. Chem., Int. Ed.*, 2010, **49**, 3338.

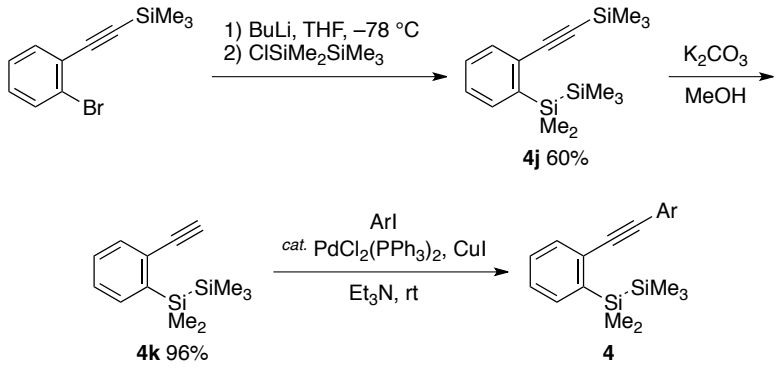


1,1,1,2,2-Pentamethyl-2-[(2-methyl-4-phenylbut-3-yn-2-yl)oxy]disilane (1a). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.09 (s, 9H), 0.33 (s, 6H), 1.56 (s, 6H), 7.28–7.33 (m, 3H), 7.38–7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –2.0, 1.5, 33.2, 67.1, 83.0, 94.9, 123.1, 128.1, 128.2, 131.5; HRMS (ESI) *m/z* calcd for $C_{16}H_{26}ONaSi_2$ $[M + Na]^+$: 313.1414; found: 313.1417.



1,1,1,2,2-Pentamethyl-2-[2-(phenylethynyl)phenoxy]disilane (1b). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.08 (s, 9H), 0.44 (s, 6H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.18–7.23 (m, 1H), 7.30–7.37 (m, 3H), 7.45–7.48 (m, 1H), 7.51–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ –2.3, 0.4, 86.8, 92.9, 116.0, 119.8, 121.3, 123.8, 128.0, 128.3, 129.4, 131.5, 133.3, 157.1; HRMS (EI) *m/z* calcd for $C_{19}H_{24}OSi_2$ $[M]^+$: 324.1366; found: 324.1365.

General Procedure for Preparation of [2-(Arylethynyl)phenyl]disilanes 4



To a solution of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene (3.87 g, 15.3 mmol) in THF (130 mL) was added dropwise *n*-BuLi (1.5 M in hexane, 15.3 mL, 23.0 mmol) at –78 °C. After stirring at –78 °C for 30 min., 1-chloro-1,1,2,2,2-pentamethyldisilane (3.59 g, 21.5 mmol) was added dropwise to the mixture. The reaction mixture was stirred at –78 °C for 1 h, and then allowed to warm to room temperature. The reaction was quenched with saturated NH_4Cl aqueous solution (80 mL). The layers were separated and the aqueous layer was extracted with hexane (9×10 mL). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was subjected to column chromatography on

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silica gel (hexane) to give 1,1,1,2,2-pentamethyl-2-{2-[2-(trimethylsilyl)ethynyl]phenyl}-disilane (**4j**, 2.78 g, 60%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 9H), 0.25 (s, 9H), 0.44 (s, 6H), 7.21–7.30 (m, 2H), 7.37–7.42 (m, 1H), 7.44–7.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.2, –1.4, –0.1, 96.9, 107.3, 127.6, 128.1, 128.6, 133.5, 134.1, 142.1; HRMS (EI) *m/z* calcd for $C_{16}H_{28}Si_3$ $[M]^+$ 304.1499, found 304.1496.

A mixture of **4j** (2.78 g, 9.12 mmol), K_2CO_3 (1.89 g, 13.7 mmol), and MeOH (46 mL) was stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure, and hexane (15 mL) and water (30 mL) were added to the residue. The layers were separated and the aqueous layer was extracted with hexane (4×15 mL). The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated to give 1-(2-ethynylphenyl)-1,1,2,2,2-pentamethyldisilane (**4k**, 2.04 g, 96%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 9H), 0.43 (s, 6H), 3.20 (s, 1H), 7.25–7.32 (m, 2H), 7.41–7.44 (m, 1H), 7.49–7.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.2, –1.3, 80.4, 85.7, 127.5, 127.9, 128.2, 133.2, 134.1, 142.9; HRMS (EI) *m/z* calcd for $C_{13}H_{20}Si_2$ $[M]^+$ 232.1104, found 232.1103.

To a mixture of $PdCl_2(PPh_3)_2$ (106.6 mg, 0.152 mmol), CuI (47.6 mg, 0.250 mmol), and **4k** (1.18 g, 5.06 mmol) in Et_3N (25 mL) was added 4-iodotoluene (1.18 g, 5.40 mmol) at room temperature. After stirring overnight at room temperature, the volatile materials were removed in vacuo. The residue was filtered through a pad of Celite® (hexane), and the filtrate was concentrated. The crude product was purified by column chromatography on silica gel (hexane) to afford 1,1,1,2,2-pentamethyl-2-{2-[2-(4-methylphenyl)ethynyl]phenyl}disilane (**4a**, 1.01 g, 62%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.49 (s, 6H), 2.38 (s, 3H), 7.17 (d, J = 7.8 Hz, 2H), 7.24–7.34 (m, 2H), 7.39–7.47 (m, 3H), 7.51–7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –1.5, 21.5, 91.0, 92.1, 120.5, 127.2, 128.2, 128.9, 129.1, 131.2, 132.7, 134.2, 138.3, 141.9; HRMS (EI) *m/z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1572.

Other derivatives **4b**–**h** were obtained in the following yields.

4 (Ar)	yield
4b (Ph)	67%
4c (3,5-$Me_2C_6H_3$)	70%
4d (2-MeC_6H_4)	68%
4e (4-$MeOC_6H_4$)	68%

4 (Ar)	yield
4f (3-AcC_6H_4)	50%
4g (4-$O_2NC_6H_4$)	68%
4h (5-methyl-2-thienyl)	69%

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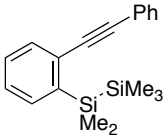
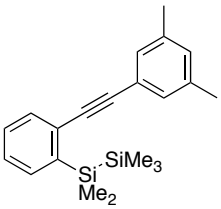
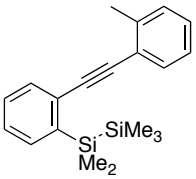


1,1,1,2,2-Pentamethyl-2-[2-(2-phenylethynyl)phenyl]disilane (4b). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.50 (s, 6H), 7.27–7.40 (m, 5H), 7.44–7.48 (m, 1H), 7.50–7.58 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –1.6, 91.7, 91.9, 123.5, 127.4, 128.2, 128.3, 128.4, 128.7, 131.3, 132.8, 134.2, 142.0; HRMS (EI) *m/z* calcd for $C_{19}H_{24}Si_2$ $[M]^+$ 308.1417, found 308.1416.



1-{2-[2-(3,5-Dimethylphenyl)ethynyl]phenyl}-1,1,2,2,2-pentamethyldisilane (4c). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 9H), 0.50 (s, 6H), 2.32 (s, 6H), 6.98 (s, 1H), 7.15 (s, 2H), 7.25–7.35 (m, 2H), 7.42–7.49 (m, 1H), 7.50–7.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –1.5, 21.2, 91.0, 92.3, 123.2, 127.2, 128.2, 128.9, 129.0, 130.1, 132.8, 134.2, 137.9, 141.9; HRMS (EI) *m/z* calcd for $C_{21}H_{28}Si_2$ $[M]^+$ 336.1730, found 336.1730.



1,1,1,2,2-Pentamethyl-2-{2-[2-(2-methylphenyl)ethynyl]phenyl}disilane (4d). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.49 (s, 6H), 2.52 (s, 3H), 7.16–7.21 (m, 1H), 7.22–7.35 (m, 4H), 7.44–7.50 (m, 2H), 7.54–7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.0, –1.6, 20.8, 91.0, 95.5, 123.3, 125.6, 127.3, 128.2, 128.3, 129.0, 129.5, 131.5, 133.0, 134.2, 140.2, 141.7; HRMS (EI) *m/z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1571.

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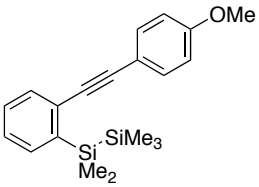
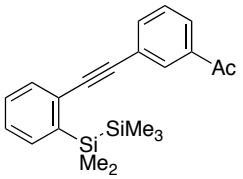
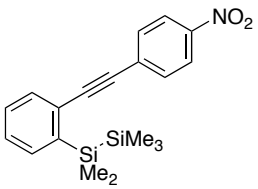


1-{2-[2-(4-Methoxyphenyl)ethynyl]phenyl}-1,1,2,2,2-pentamethyldisilane (4e). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.49 (s, 6H), 3.84 (s, 3H), 6.86–6.92 (m, 2H), 7.26–7.31 (m, 2H), 7.42–7.48 (m, 3H), 7.50–7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –1.5, 55.3, 90.4, 92.0, 114.0, 115.7, 127.1, 128.2, 129.1, 132.6, 132.7, 134.2, 141.7, 159.5; HRMS (EI) *m/z* calcd for $C_{20}H_{26}OSi_2$ $[M]^+$ 338.1522, found 338.1523.



1-{2-[2-(3-Acetylphenyl)ethynyl]phenyl}-1,1,2,2,2-pentamethyldisilane (4f). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.08 (s, 9H), 0.50 (s, 6H), 2.63 (s, 3H), 7.28–7.36 (m, 2H), 7.45–7.50 (m, 2H), 7.55–7.59 (m, 1H), 7.70 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.93 (dt, *J* = 8.0, 1.5 Hz, 1H), 8.10 (t, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –1.6, 26.6, 90.8, 92.7, 124.1, 127.7, 128.1, 128.3, 128.8, 131.3, 132.9, 134.3, 135.4, 137.2, 142.1, 197.3; HRMS (EI) *m/z* calcd for $C_{21}H_{26}OSi_2$ $[M]^+$ 350.1522, found 350.1520.



1,1,1,2,2-Pentamethyl-2-{2-[2-(4-nitrophenyl)ethynyl]phenyl}disilane (4g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.06 (s, 9H), 0.50 (s, 6H), 7.32–7.38 (m, 2H), 7.47–7.52 (m, 1H), 7.56–7.60 (m, 1H), 7.63–7.68 (m, 2H), 8.22–8.27 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz), δ –3.1, –1.6, 89.9, 97.1, 123.7, 127.4, 128.4, 130.4, 131.9, 133.2, 134.4, 142.6, 146.9; HRMS (EI) *m/z* calcd for $C_{19}H_{23}NO_2Si_2$ $[M]^+$ 353.1267, found 353.1265.

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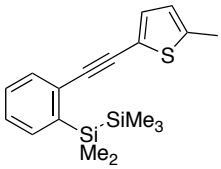
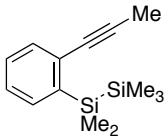
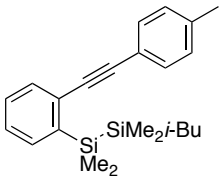


1,1,1,2,2-Pentamethyl-2-{2-[2-(5-methyl-2-thienyl)ethynyl]phenyl}disilane (4h). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9H), 0.49 (s, 6H), 2.50 (s, 3H), 6.68 (d, *J* = 3.0 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 7.25–7.36 (m, 2H), 7.43–7.49 (m, 1H), 7.49–7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.2, –1.6, 15.4, 85.9, 94.6, 121.2, 125.4, 127.3, 128.2, 128.6, 131.7, 132.4, 134.2, 141.96, 142.01; HRMS (EI) *m/z* calcd for $C_{18}H_{24}SSi_2$ $[M]^+$ 328.1137, found 328.1135.



1,1,1,2,2-Pentamethyl-2-[2-(prop-1-yn-1-yl)phenyl]disilane (4i). The title compound was prepared by lithiation of **4k** with *n*-BuLi, followed by treatment with iodomethane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.41 (s, 6H), 2.06 (s, 3H), 7.20–7.26 (m, 2H), 7.35–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.3, –1.5, 4.7, 82.0, 88.7, 126.7, 128.2, 129.6, 132.2, 134.0, 141.8; HRMS (EI) *m/z* calcd for $C_{14}H_{22}Si_2$ $[M]^+$ 246.1260, found 246.1263.



2-Isobutyl-1,1,2,2-tetramethyl-1-{2-[2-(4-methylphenyl)ethynyl]phenyl}disilane (4l). The title compound was prepared analogously to the synthesis of **4a**, using 1-chloro-2-isobutyl-1,1,2,2-tetramethyldisilane in place of 1-chloro-1,1,2,2,2-pentamethyldisilane. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.09 (s, 6H), 0.50 (s, 6H), 0.62 (d, *J* = 6.9 Hz, 2H), 0.82 (d, *J* = 6.3 Hz, 6H), 1.69 (septet, *J* = 6.6 Hz, 1H), 2.38 (s, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.26–7.32 (m, 2H), 7.40–7.47 (m, 3H), 7.52–7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –2.8, –2.4, 21.5, 25.47, 25.54, 26.3, 91.1, 92.1, 120.5, 127.2, 128.2, 128.9, 129.1, 131.2, 132.8, 134.2, 138.3, 142.1; HRMS (EI) *m/z* calcd for $C_{23}H_{32}Si_2$ $[M]^+$ 364.2043, found 364.2042.

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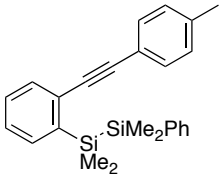
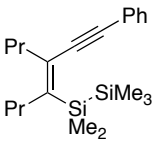
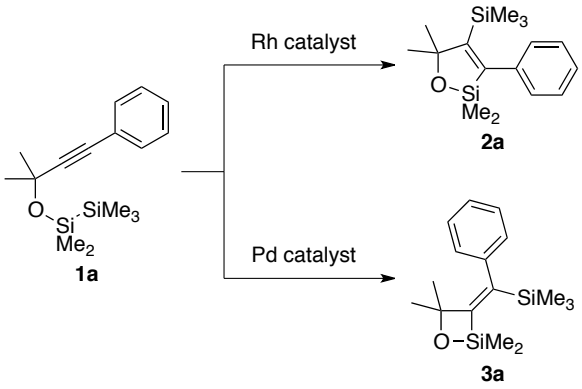


1,1,2,2-Tetramethyl-1-{2-[2-(4-methylphenyl)ethynyl]phenyl}-2-phenyldisilane (4m). The title compound was prepared from the reaction of chlorodimethyl{2-[2-(4-methylphenyl)ethynyl]phenyl}silane and [dimethyl(phenyl)silyl]lithium in THF. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.36 (s, 6H), 0.46 (s, 6H), 2.39 (s, 3H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.20–7.42 (m, 10H), 7.51–7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –3.1, –2.9, 21.5, 91.1, 92.3, 120.4, 127.2, 127.6, 128.2, 128.4, 129.0, 129.1, 131.2, 132.8, 133.8, 134.4, 138.3, 139.4, 141.2; HRMS (EI) *m*/*z* calcd for $C_{25}H_{28}Si_2$ $[M]^+$ 384.1730, found 384.1732.



(*Z*)-1,1,1,2,2-Pentamethyl-2-[5-(2-phenylethynyl)oct-4-en-4-yl]disilane (4n). The title compound was prepared by lithiation of (*Z*)-(4-bromo-3-propylhept-3-en-1-yn-1-yl)benzene with *n*-BuLi, followed by treatment with 1-chloro-1,1,2,2,2-pentamethyldisilane. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.32 (s, 6H), 0.90–1.00 (m, 6H), 1.20–1.39 (m, 2H), 1.57–1.70 (m, 2H), 2.12–2.22 (m, 2H), 2.24–2.34 (m, 2H), 7.20–7.35 (m, 3H), 7.35–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –2.5, –1.2, 13.9, 14.4, 22.1, 23.7, 34.5, 35.2, 92.1, 93.2, 124.2, 127.6, 128.3, 131.1, 132.6, 149.0; HRMS (EI) *m*/*z* calcd for $C_{21}H_{34}Si_2$ $[M]^+$ 342.2199, found 342.2195.

Rhodium- and Palladium-Catalysed Intramolecular Bis-Silylation of Disilanyl Ethers



2,2,5,5-Tetramethyl-3-phenyl-4-(trimethylsilyl)-2,5-dihydro-1,2-oxasilole (2a)[6] To a solution of $[RhCl(nbd)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) in toluene (1.0 mL) was added **1a** (57.6 mg, 0.198 mmol), and the mixture was stirred at 110 °C for 6 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (10:1). The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane:AcOEt = 50:1) to give **2a** (11.4 mg, 20%) as a pale yellow solid: mp 62–65 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ –0.08 (s, 9H), 0.20 (s, 6H), 1.47 (s, 6H), 6.95–7.00 (m, 2H), 7.15–7.22 (m, 1H), 7.24–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.2, 1.9, 30.7, 89.4, 125.5, 126.8, 127.9, 141.5, 155.1, 165.0; HRMS (EI) *m/z* calcd for $C_{16}H_{26}OSi_2$ $[M]^+$ 290.1522, found 290.1521.

(*Z*)-2,2,4,4-Tetramethyl-3-(phenyl(trimethylsilyl)methylene)-1,2-oxasiletane (3a). To a mixture of $Pd(OAc)_2$ (0.9 mg, 4.0 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (9.6 mg, 68.9 μmol) were added toluene (2.0 mL) and **1a** (58.1 mg, 0.200 mmol), and the mixture was stirred at 80 °C for 2.5 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (50:1). The filtrate was concentrated under reduced pressure to give **3a** (48.7 mg, 84%) as a pale yellow solid: mp 96–99 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.02 (s, 9H), 0.50 (s, 6H), 1.36 (s, 6H), 6.85–6.93 (m, 2H), 6.94–7.05 (m, 1H), 7.06–7.19 (m, 2H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ –0.9, 3.9, 30.9, 89.4, 125.9, 127.9, 128.0, 142.8, 152.0, 166.1; HRMS (EI) *m/z* calcd for $C_{16}H_{26}OSi_2$ $[M]^+$ 290.1522, found 290.1523.

(6) [61800-32-6]: M. Ishikawa, H. Sugisawa, T. Fuchikami, M. Kumada, T. Yamabe, H. Kawakami, K. Fukui, Y. Ueki and H. Shizuka, *J. Am. Chem. Soc.*, 1982, **104**, 2872.

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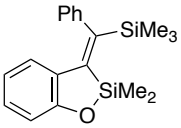
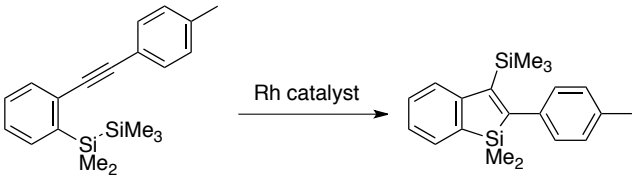


(*Z*)-2,2-Dimethyl-3-(phenyl(trimethylsilyl)methylene)-2,3-dihydrobenzo[*d*][1,2]oxasilole (3b). To a solution of $[RhCl(CO)_2]_2$ (1.9 mg, 4.9 μmol, 5 mol % Rh) in toluene (1.0 mL) was added **1b** (64.8 mg, 0.200 mmol), and the mixture was stirred at 110 °C for 6 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt (20:1). The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane:AcOEt = 20:1) to give **3b** (40.7 mg, 63%) as a pale yellow solid. The title compound was analogously obtained in 97% yield by the reaction catalysed by $Pd(OAc)_2$–1,1,3,3-tetramethylbutyl isocyanide in toluene at 80 °C. mp 73–76 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9H), 0.61 (s, 6H), 6.07 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.33–6.40 (m, 1H), 6.80 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.95–7.02 (m, 3H), 7.24–7.30 (m, 1H), 7.34–7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.4, 1.3, 115.3, 119.5, 125.8, 126.5, 127.1, 129.0, 129.3, 130.5, 144.9, 145.9, 157.5, 160.4; HRMS (EI) *m*/*z* calcd for $C_{19}H_{24}OSi_2$ $[M]^+$ 324.1366, found 324.1368.

General Procedure for Rhodium-Catalysed Intramolecular *trans*-Bis-Silylation of 4



4a **5a**

1,1-Dimethyl-2-(4-methylphenyl)-3-(trimethylsilyl)-1*H*-1-benzosilole (5a). To a solution of $[RhCl(CO)_2]_2$ (1.9 mg, 4.9 μmol, 5 mol % Rh) in toluene (1.0 mL) was added **4a** (64.8 mg, 0.201 mmol), and the mixture was stirred at 110 °C for 7 h. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane. The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to preparative thin-layer chromatography (hexane) to give **5a** (42.6 mg, 66%) as a white solid: mp 86–94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.29 (s, 6H), 2.39 (s, 3H), 6.92–6.97 (m, 2H), 7.10–7.16 (m, 2H), 7.18–7.24 (m, 1H), 7.37 (dt, *J* = 1.3, 7.6 Hz, 1H), 7.54–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.5, 1.5, 21.2, 125.56, 125.63, 126.7, 128.6, 129.6, 131.8, 135.2, 138.6, 140.4, 152.9, 155.3, 163.5; HRMS (EI) *m*/*z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1571.

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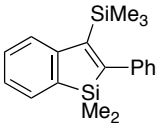
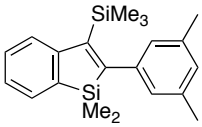
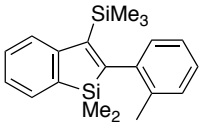


1,1-Dimethyl-2-phenyl-3-(trimethylsilyl)-1*H*-1-benzosilole[7] **(5b).** According to the general procedure, **5b** (34.4 mg, 55%) was obtained as a white solid from **4b** (62.2 mg, 0.202 mmol) using $[RhCl(CO)_2]_2$ (1.9 mg, 4.9 μmol, 5 mol % Rh) in toluene at 110 °C for 13.5 h. mp 80–83.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 9H), 0.29 (s, 6H), 7.03–7.08 (m, 2H), 7.19–7.27 (m, 2H), 7.28–7.35 (m, 2H), 7.38 (dt, *J* = 1.5, 7.7 Hz, 1H), 7.55–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.5, 1.4, 125.63, 125.68, 125.73, 126.8, 127.9, 129.6, 131.8, 138.6, 143.5, 152.8, 155.4, 163.4.



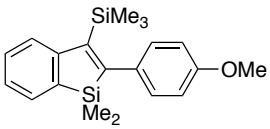
2-(3,5-Dimethylphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1*H*-1-benzosilole (5c). According to the general procedure, **5c** (43.4 mg, 64%) was obtained as a white solid from **4c** (67.6 mg, 0.201 mmol) using $[RhCl(CO)_2]_2$ (3.9 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 8 h. mp 79–86 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.31 (s, 6H), 2.34 (s, 6H), 6.67 (s, 2H), 6.88 (s, 1H), 7.18–7.25 (m, 1H), 7.37 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.54–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.4, 1.5, 21.4, 124.6, 125.5, 125.6, 127.4, 129.5, 131.8, 137.1, 138.7, 143.3, 152.9, 155.1, 163.6; HRMS (EI) *m/z* calcd for $C_{21}H_{28}Si_2$ $[M]^+$ 336.1730, found 336.1731.



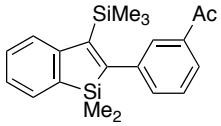
1,1-Dimethyl-2-(2-methylphenyl)-3-(trimethylsilyl)-1*H*-1-benzosilole (5d). According to the general procedure, **5d** (25.0 mg, 38%) was obtained as a white solid from **4d** (65.6 mg, 0.203 mmol) using $RhCl(PPh_3)_3$ (9.3 mg, 10 μmol, 5 mol % Rh) in toluene at 110 °C for 26 h. mp 95–97 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 9H), 0.27 (s, 3H), 0.28 (s, 3H), 2.19 (s, 3H), 6.84–6.90 (m, 1H), 7.10–7.19 (m, 3H), 7.19–7.26 (m, 1H), 7.39 (dt, *J* = 1.5, 7.6 Hz, 1H),

(7) [1160757-51-6]: M. Tobisu, M. Onoe, M. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 7506.

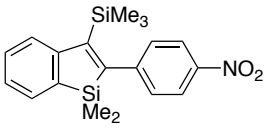
7.56–7.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.5, –3.8, 0.5, 20.3, 125.2, 125.4, 125.65, 125.71, 126.9, 129.62, 129.65, 131.8, 134.0, 138.7, 142.6, 152.4, 155.4, 162.5; HRMS (EI) *m/z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1568.



2-(4-Methoxyphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1*H*-1-benzosilole (5e). According to the general procedure, **5e** (42.8 mg, 63%) was obtained as a pale yellow solid from **4e** (67.9 mg, 0.201 mmol) using $RhCl(PPh_3)_3$ (9.3 mg, 10 μmol, 5 mol % Rh) in xylene at 130 °C for 3.5 h. mp 86–94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9H), 0.28 (s, 6H), 3.84 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.52–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.4, 1.5, 55.2, 113.4, 125.55, 125.61, 127.9, 129.5, 131.8, 135.8, 138.6, 153.0, 155.5, 158.0, 163.1; HRMS (EI) *m/z* calcd for $C_{20}H_{26}OSi_2$ $[M]^+$ 338.1522, found 338.1524.

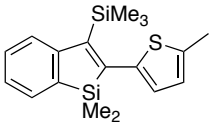


2-(3-Acetylphenyl)-1,1-dimethyl-3-(trimethylsilyl)-1*H*-1-benzosilole (5f). According to the general procedure, **5f** (39.0 mg, 56%) was obtained as a white solid from **4f** (69.3 mg, 0.198 mmol) using $RhCl(PPh_3)_3$ (9.3 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 6.5 h. mp 116–120 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 9H), 0.29 (s, 6H), 2.62 (s, 3H), 7.19–7.29 (m, 2H), 7.34–7.45 (m, 2H), 7.54–7.60 (m, 2H), 7.63–7.67 (m, 1H), 7.80–7.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.5, 1.5, 26.7, 125.78, 125.85, 126.0, 126.5, 128.3, 129.7, 131.5, 131.9, 136.8, 138.3, 144.1, 152.4, 156.7, 161.9, 198.2; HRMS (EI) *m/z* calcd for $C_{21}H_{26}OSi_2$ $[M]^+$ 350.1522, found 350.1522.

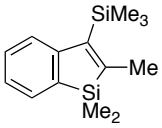


1,1-Dimethyl-2-(4-nitrophenyl)-3-(trimethylsilyl)-1*H*-1-benzosilole (5g). According to the general procedure, **5g** (38.6 mg, 55%) was obtained as a yellow solid from **4g** (70.5 mg,

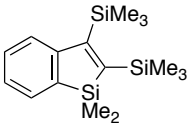
0.199 mmol) using $[RhCl(CO)_2]_2$ (3.9 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 7 h. mp 188–196 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 9H), 0.28 (s, 6H), 7.15–7.22 (m, 2H), 7.22–7.30 (m, 1H), 7.35–7.43 (m, 1H), 7.54–7.62 (m, 2H), 8.15–8.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.6, 1.5, 123.4, 126.0, 126.4, 127.5, 129.9, 132.0, 138.1, 146.0, 151.7, 152.0, 157.4, 160.8; HRMS (EI) *m/z* calcd for $C_{19}H_{23}NO_2Si_2$ $[M]^+$ 353.1267, found 353.1271.



1,1-Dimethyl-2-(5-methyl-2-thienyl)-3-(trimethylsilyl)-1*H*-1-benzosilole (5h). According to the general procedure, **5h** (29.7 mg, 46%) was obtained as a yellow solid from **4h** (64.9 mg, 0.197 mmol) using $RhCl(PPh_3)_3$ (18.5 mg, 20 μmol, 10 mol % Rh) in toluene at 110 °C for 5 h. mp 87–102 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 9H), 0.31 (s, 6H), 2.48 (s, 3H), 6.45 (d, *J* = 3.3 Hz, 1H), 6.60–6.64 (m, 1H), 7.15–7.22 (m, 1H), 7.30–7.37 (m, 1H), 7.48–7.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.5, 1.5, 15.4, 123.7, 125.2, 125.8, 125.9, 129.5, 131.8, 138.6, 138.9, 142.5, 152.7, 155.7, 158.4; HRMS (EI) *m/z* calcd for $C_{18}H_{24}SSi_2$ $[M]^+$ 328.1137, found 328.1137.



1,1,2-Trimethyl-3-(trimethylsilyl)-1*H*-1-benzosilole[8] **(5i).** According to the general procedure, **5i** (19.0 mg, 37%) was obtained as a colourless oil from **4i** (51.1 mg, 0.207 mmol) using $[RhCl(nbd)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) in xylene at 130 °C for 3 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.25 (s, 6H), 0.38 (s, 9H), 2.14 (s, 3H), 7.08–7.15 (m, 1H), 7.25–7.32 (m, 1H), 7.43–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.7, 2.2, 17.2, 124.5, 124.9, 129.5, 131.6, 138.1, 152.6, 153.7, 158.5.



(8) [1160757-50-5]: M. Tobisu, M. Onoe, M. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 7506.

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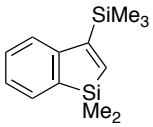
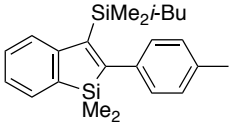
1,1-Dimethyl-2,3-bis(trimethylsilyl)-1*H*-1-benzosilole[9] (5j). According to the general procedure, **5j** (31 mg, 52%) was obtained as a yellow oil from **4j** (59.8 mg, 0.196 mmol) using $[RhCl(nbd)]_2$ (4.6 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 31.5 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.29 (s, 9H), 0.33 (s, 6H), 0.41 (s, 9H), 7.16–7.23 (m, 1H), 7.28–7.35 (m, 1H), 7.51–7.56 (m, 1H), 7.57–7.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –2.2, 2.96, 3.01, 125.6, 126.1, 129.0, 131.1, 140.5, 153.9, 162.4, 173.2; HRMS (EI) *m/z* calcd for $C_{16}H_{28}Si_3$ $[M]^+$ 304.1499, found 304.1503.



1,1-Dimethyl-3-(trimethylsilyl)-1*H*-1-benzosilole (5k). According to the general procedure, **5k** (7.5 mg, 16%) was obtained as a yellow oil from **4k** (47.8 mg, 0.206 mmol) using $[RhCl(nbd)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) in toluene at 110 °C for 5.5 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.296 (s, 6H), 0.299 (s, 9H), 6.74 (s, 1H), 7.17–7.24 (m, 1H), 7.33 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.40–7.45 (m, 1H), 7.53–7.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.1, –0.6, 124.9, 126.2, 129.5, 131.7, 139.6, 145.6, 151.7, 165.5; HRMS (EI) *m/z* calcd for $C_{13}H_{20}Si_2$ $[M]^+$ 232.1104, found 232.1103.



3-(Isobutyldimethylsilyl)-1,1-dimethyl-2-(4-methylphenyl)-1*H*-1-benzosilole (5l). According to the general procedure, **5l** (43.1 mg, 60%) was obtained as a colourless oil from **4l** (72.3 mg, 0.198 mmol) using $[RhCl(CO)_2]_2$ (3.9 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 24 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ –0.06 (s, 6H), 0.26 (s, 6H), 0.79 (d, *J* = 6.6 Hz, 2H), 0.88 (d, *J* = 6.3 Hz, 6H), 1.74 (septet, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 6.93 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.16–7.23 (m, 1H), 7.36 (dt, *J* = 1.3, 7.7 Hz, 1H), 7.52–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.6, 0.6, 21.2, 25.1, 26.2, 28.2, 125.6, 126.7, 128.6, 129.5, 131.7, 135.1, 138.6, 140.4, 153.1, 155.2, 163.6; HRMS (EI) *m/z* calcd for $C_{23}H_{32}Si_2$ $[M]^+$ 364.2043, found 364.2044.

(9) [92014-22-7]: D. Seyferth, S. C. Vick, M. L. Shannon, *Organometallics*, 1984, **3**, 1897.

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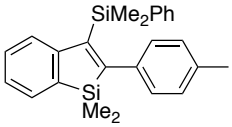
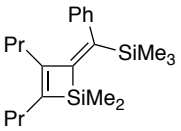


3-[Dimethyl(phenyl)silyl]-1,1-dimethyl-2-(4-methylphenyl)-1*H*-1-benzosilole (5m). According to the general procedure, **5m** (33.6 mg, 43%) was obtained as a white solid from **4m** (78.1 mg, 0.203 mmol) using $[RhCl(CO)_2]_2$ (3.9 mg, 10 μmol, 10 mol % Rh) in toluene at 110 °C for 24 h. mp 104–109 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.14 (s, 6H), 0.32 (s, 6H), 2.35 (s, 3H), 6.96 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 7.11–7.19 (m, 2H), 7.22–7.35 (m, 4H), 7.49–7.58 (m, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.4, 0.4, 21.2, 125.6, 126.4, 126.6, 127.8, 128.6, 128.7, 129.5, 131.6, 133.8, 135.4, 138.3, 140.1, 140.3, 152.6, 152.8, 166.0; HRMS (EI) m/z calcd for $C_{25}H_{28}Si_2$ $[M]^+$ 384.1730, found 384.1732.



(*Z*)-1,1-Dimethyl-2-[phenyl(trimethylsilyl)methylene]-3,4-dipropyl-1,2-dihydrosilete (6n). According to the general procedure, **6n** (58.3 mg, 86%) was obtained as a pale yellow oil from **4n** (67.8 mg, 0.198 mmol) using $[RhCl(CO)_2]_2$ (1.9 mg, 4.9 μmol, 5 mol % Rh) in toluene at 110 °C for 4.5 h. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 9H), 0.41 (t, J = 7.4 Hz, 3H), 0.42 (s, 6H), 0.91 (t, J = 7.2 Hz, 3H), 0.90–1.03 (m, 2H), 1.36–1.49 (m, 4H), 2.17 (t, J = 7.5 Hz, 2H), 6.97–7.03 (m, 2H), 7.09–7.16 (m, 1H), 7.18–7.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.5, 0.4, 14.0, 14.5, 21.8, 23.1, 30.3, 31.0, 124.8, 127.2, 128.2, 139.7, 145.4, 156.4, 161.9, 165.1; HRMS (EI) m/z calcd for $C_{21}H_{34}Si_2$ $[M]^+$ 342.2199, found 342.2196.

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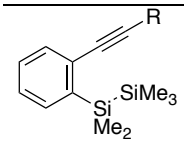
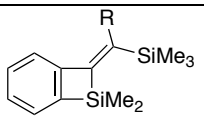
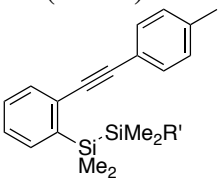
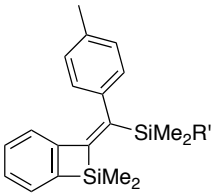
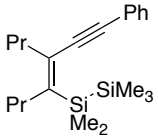
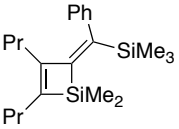
Appendix: Palladium-Catalysed Intramolecular *cis*-Bis-Silylation of 4

General Procedure: To a mixture of $Pd(OAc)_2$ (2 mol %) and 1,1,3,3-tetramethylbutyl isocyanide (30–40 mol %) were added toluene (or xylene) and **4** (0.200 mmol), and the mixture was heated. The reaction mixture was passed through a plug of Florisil® followed by elution with hexane–AcOEt. The filtrate was concentrated under reduced pressure, and the resulting residue was subjected to column chromatography on silica gel to give **6**.

4	conditions	**6**	yield
			
4a (R = 4-MeC_6H_4)	toluene, 80 °C, 2 h	**6a**	83%
4b (R = Ph)	toluene, 80 °C, 2 h	**6b**	82%
4c (R = 3,5-$Me_2C_6H_3$)	toluene, 80 °C, 2.5 h	**6c**	72%
4d (R = 2-MeC_6H_4)	toluene, 80 °C, 2.5 h	**6d**	79%
4e (R = 4-$MeOC_6H_4$)	toluene, 100 °C, 2.5 h	**6e**	88%
4f (R = 3-AcC_6H_4)	xylene, 130 °C, 2.5 h	**6f**	93%
4g (R = 4-$O_2NC_6H_4$)	toluene, 110 °C, 2 h	**6g**	48%
4i (R = Me)	toluene, 80 °C, 2.5 h	**6i**	70%
4j (R = $SiMe_3$)	toluene, 110 °C, 22.5 h	**6j**	14%
4k (R = H)	toluene, 80 °C, 2 h	**6k**	80%[a]
			
4l (R' = *i*-Bu)	toluene, 80 °C, 2.5 h	**6l**	88%
4m (R' = Ph)	toluene, 80 °C, 2.5 h	**6m**	89%
 **4n**	toluene, 80 °C, 3 h	 **6n**	91%

[a] Obtained as a 9:1 mixture of stereoisomers.

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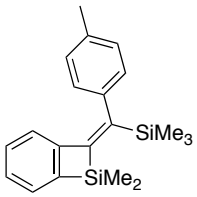
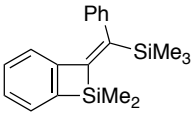
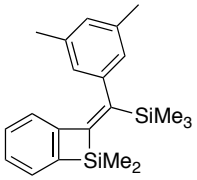


(*Z*)-7,7-Dimethyl-8-[(4-methylphenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6a). white solid; mp 96–103 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H), 0.60 (s, 6H), 2.40 (s, 3H), 5.97 (d, *J* = 7.8 Hz, 1H), 6.90–6.95 (m, 2H), 6.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.07 (dt, *J* = 0.7, 7.1 Hz, 1H), 7.14–7.20 (m, 2H), 7.44 (dt, *J* = 7.0, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.8, 0.3, 21.2, 122.6, 126.6, 127.5, 129.5, 130.0, 130.5, 134.8, 142.3, 149.6, 150.4, 154.0, 155.7; HRMS (EI) *m/z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1574.



(*Z*)-7,7-Dimethyl-8-[phenyl(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6b). white solid; mp 80–83.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9H), 0.61 (s, 6H), 5.90 (d, *J* = 7.8 Hz, 1H), 6.92–6.99 (m, 1H), 7.02–7.10 (m, 3H), 7.23–7.30 (m, 1H), 7.33–7.40 (m, 2H), 7.41–7.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.8, 0.3, 122.6, 125.5, 126.8, 127.6, 128.7, 130.0, 130.6, 145.5, 149.7, 150.2, 154.1, 155.6; HRMS (EI) *m/z* calcd for $C_{19}H_{24}Si_2$ $[M]^+$ 308.1417, found 308.1416.



(*Z*)-8-[(3,5-Dimethylphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6c). pale yellow solid; mp 80–84 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9H), 0.64 (s, 6H), 2.34 (s, 6H), 6.02 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.68–6.71 (m, 2H), 6.90–6.94 (m, 1H), 7.01 (dt, *J* = 1.3, 7.7 Hz, 1H), 7.10 (dt, *J* = 1.0, 7.3 Hz, 1H), 7.44–7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.7, 0.3, 21.4, 122.7, 124.3, 127.0, 127.5, 130.0, 130.5, 138.0, 145.3, 149.6, 150.8, 153.6, 155.7; HRMS (EI) *m/z* calcd for $C_{21}H_{28}Si_2$ $[M]^+$ 336.1730, found 336.1732.

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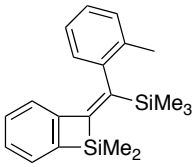
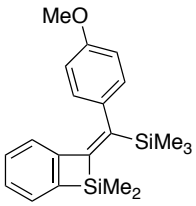
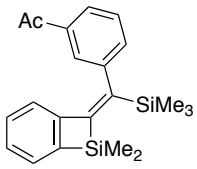


(*Z*)-7,7-Dimethyl-8-[(2-methylphenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6d). pale yellow solid; mp 52–54 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9H), 0.62 (s, 3H), 0.63 (s, 3H), 2.13 (s, 3H), 5.85 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.89–7.00 (m, 2H), 7.08 (dt, *J* = 0.9, 7.2 Hz, 1H), 7.16–7.25 (m, 3H), 7.45 (dt, *J* = 7.2, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.6, 0.2, 0.6, 19.6, 121.9, 125.7, 126.2, 126.5, 127.6, 130.1, 130.39, 130.45, 134.1, 144.5, 149.0, 149.5, 154.4, 155.9; HRMS (EI) *m/z* calcd for $C_{20}H_{26}Si_2$ $[M]^+$ 322.1573, found 322.1572.



(*Z*)-8-[(4-Methoxyphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6e). yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9H), 0.60 (s, 6H), 3.86 (s, 3H), 6.01 (dt, *J* = 7.8, 0.9 Hz, 1H), 6.89–7.01 (m, 5H), 7.07 (dt, *J* = 0.6, 6.9 Hz, 1H), 7.44 (dt, *J* = 6.9, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.8, 0.3, 55.2, 114.1, 122.6, 127.5, 127.8, 130.0, 130.6, 137.7, 149.6, 149.9, 154.6, 155.7, 157.6; HRMS (EI) *m/z* calcd for $C_{20}H_{26}OSi_2$ $[M]^+$ 338.1522, found 338.1524.



(*Z*)-8-[(3-Acetylphenyl)(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6f). white solid; 109–112 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9H), 0.62 (s, 6H), 2.61 (s, 3H), 5.82–5.86 (m, 1H), 6.93 (dt, *J* = 1.4, 7.7 Hz, 1H), 7.08 (dt, *J* = 0.8, 7.4 Hz, 1H), 7.28 (t, *J* = 1.5 Hz, 1H), 7.45 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 1.5 Hz, 1H), 7.86–7.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.8, 0.3, 26.8, 122.4, 125.6, 127.0, 127.9, 129.1, 130.1, 130.7, 132.0, 137.6, 146.0, 148.7, 149.9, 155.1, 198.4; HRMS (EI) *m/z* calcd for $C_{21}H_{26}OSi_2$ $[M]^+$ 350.1522, found 350.1523.

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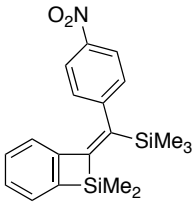
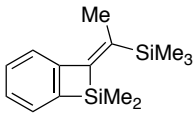
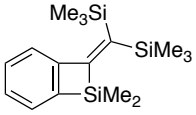


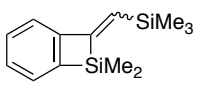
(*Z*)-7,7-Dimethyl-8-[(4-nitrophenyl)(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6g). yellow solid; 142–145 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.13 (s, 9H), 0.63 (s, 6H), 5.86–5.91 (m, 1H), 6.99 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.12 (dt, *J* = 0.8, 7.4 Hz, 1H), 7.20–7.27 (m, 2H), 7.48 (dt, *J* = 7.2, 1.1 Hz, 1H), 8.23–8.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –0.8, 0.3, 122.4, 124.3, 127.9, 128.2, 130.3, 131.0, 146.1, 147.7, 150.1, 153.8, 154.6, 155.5; HRMS (EI) *m/z* calcd for $C_{19}H_{23}NO_2Si_2$ $[M]^+$ 353.1267, found 353.1267.



(*Z*)-7,7-Dimethyl-8-[(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6i). yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 0.53 (s, 6H), 2.15 (s, 3H), 7.15–7.22 (m, 1H), 7.33–7.40 (m, 1H), 7.47–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –1.0, 0.2, 19.7, 127.7, 126.8, 130.2, 130.7, 144.4, 149.6, 152.8, 156.5; HRMS (EI) *m/z* calcd for $C_{14}H_{22}Si_2$ $[M]^+$ 246.1260, found 246.1259.



8-[Bis(trimethylsilyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6j). colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 9H), 0.30 (s, 9H), 0.54 (s, 6H), 7.15–7.22 (m, 1H), 7.29–7.36 (m, 1H), 7.40–7.44 (m, 1H), 7.51–7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 1.0, 1.9, 2.0, 123.7, 127.5, 129.4, 130.2, 150.1, 151.9, 156.9, 174.0; HRMS (EI) *m/z* calcd for $C_{16}H_{28}Si_3$ $[M]^+$ 304.1499, found 304.1498.



(*Z*)-and (*E*)-7,7-Dimethyl-8-[(trimethylsilyl)methylene]-7-silabicyclo[4.2.0]octa-1,3,5-triene (6k). colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ **major** 0.294 (s, 6H), 0.297 (s, 9H),

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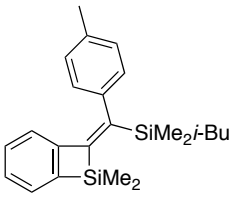
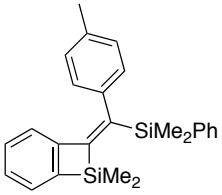
6.74 (s, 1H), 7.17–7.23 (m, 1H), 7.30–7.36 (m, 1H), 7.40–7.45 (m, 1H), 7.53–7.57 (m, 1H) **minor** 0.14 (s, 9H), 0.54 (s, 6H), 6.72 (s, 1H), 7.17–7.51 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –4.0, 0.6, 125.0, 126.2, 129.5, 131.7, 139.6, 145.6, 151.7, 165.5; HRMS (EI) *m/z* calcd for $C_{13}H_{20}Si_2$ $[M]^+$ 232.1104, found 232.1105.



(*Z*)-8-[(Isobutyldimethylsilyl)(4-methylphenyl)methylene]-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1,3,5-triene (6l). pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 6H), 0.59 (d, *J* = 6.9 Hz, 2H), 0.61 (s, 6H), 0.93 (d, *J* = 6.3 Hz, 6H), 1.78 (septet, *J* = 6.7 Hz, 1H), 2.40 (s, 3H), 5.92 (d, *J* = 8.1 Hz, 1H), 6.89–6.94 (m, 2H), 6.97 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.06 (dt, *J* = 0.9, 7.2 Hz, 1H), 7.13–7.20 (m, 2H), 7.39–7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –1.5, 0.5, 21.2, 24.9, 25.7, 26.4, 122.6, 127.4, 129.4, 129.9, 130.5, 134.8, 143.8, 142.4, 149.6, 150.4, 154.3, 155.8; HRMS (EI) *m/z* calcd for $C_{23}H_{32}Si_2$ $[M]^+$ 364.2043, found 364.2045.



(*Z*)-8-{[Dimethyl(phenyl)silyl](4-methylphenyl)methylene}-7,7-dimethyl-7-silabicyclo[4.2.0]octa-1(6),2,4-triene (6m). colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.326 (s, 6H), 0.334 (s, 6H), 2.38 (s, 3H), 6.01 (d, *J* = 7.8 Hz, 1H), 6.86–6.91 (m, 2H), 6.93–7.00 (m, 1H), 7.03–7.09 (m, 1H), 7.10–7.15 (m, 2H), 7.32–7.43 (m, 4H), 7.55–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ –1.9, 0.1, 21.2, 122.7, 126.9, 127.65, 127.74, 129.1, 129.4, 129.9, 130.5, 134.7, 135.0, 138.5, 142.1, 148.1, 150.2, 155.6, 156.4; HRMS (EI) *m/z* calcd for $C_{25}H_{28}Si_2$ $[M]^+$ 384.1730, found 384.1729.

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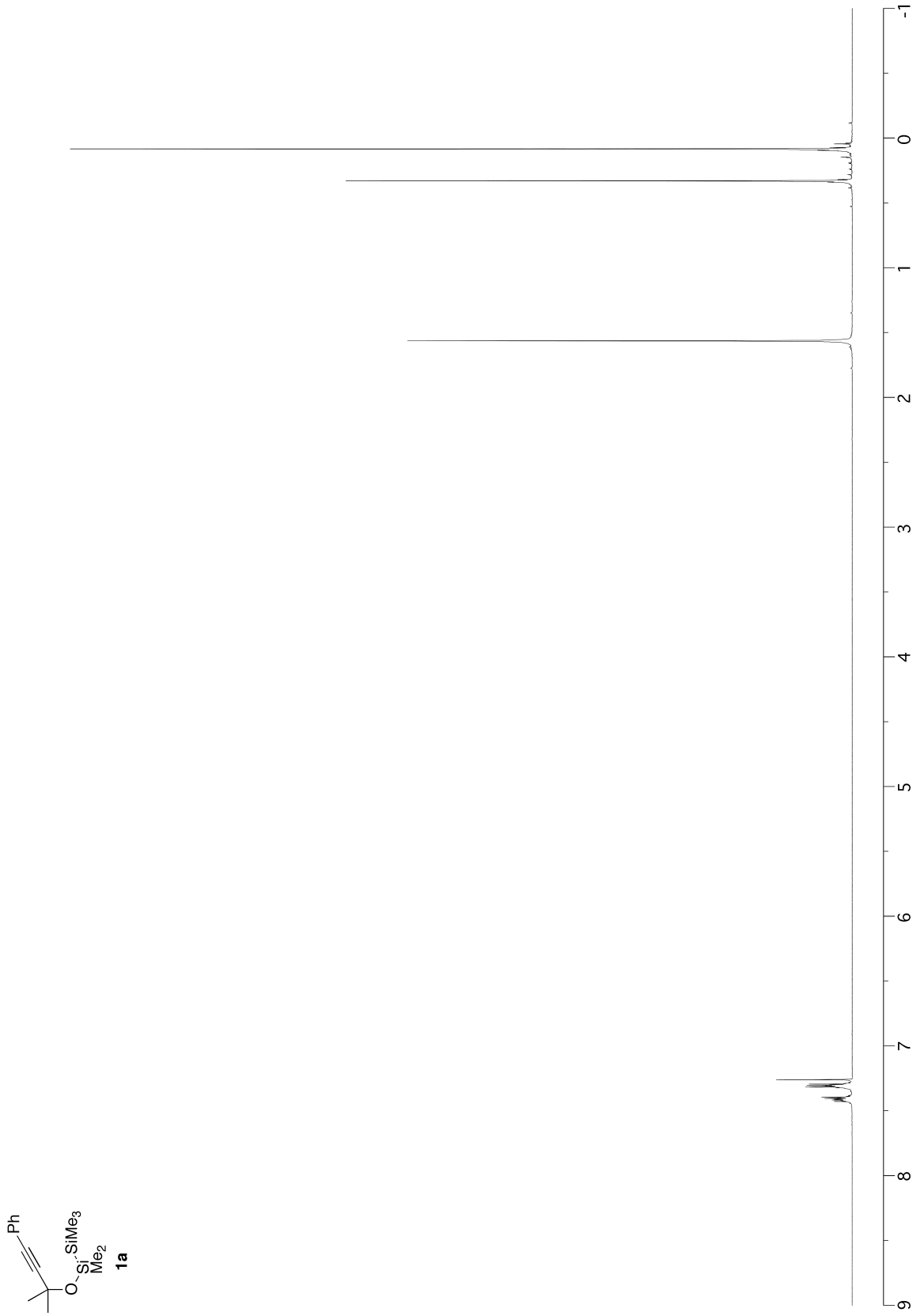

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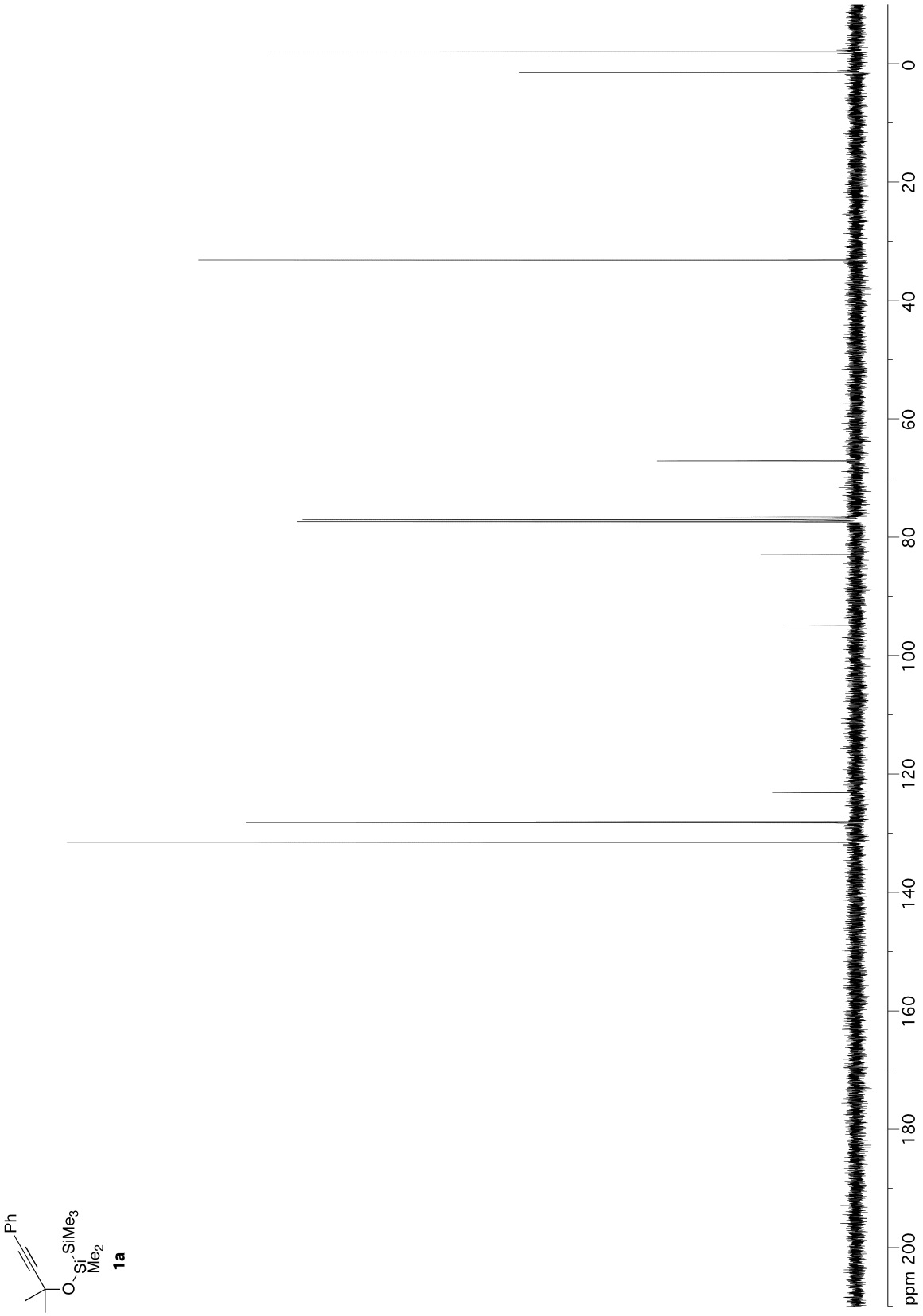

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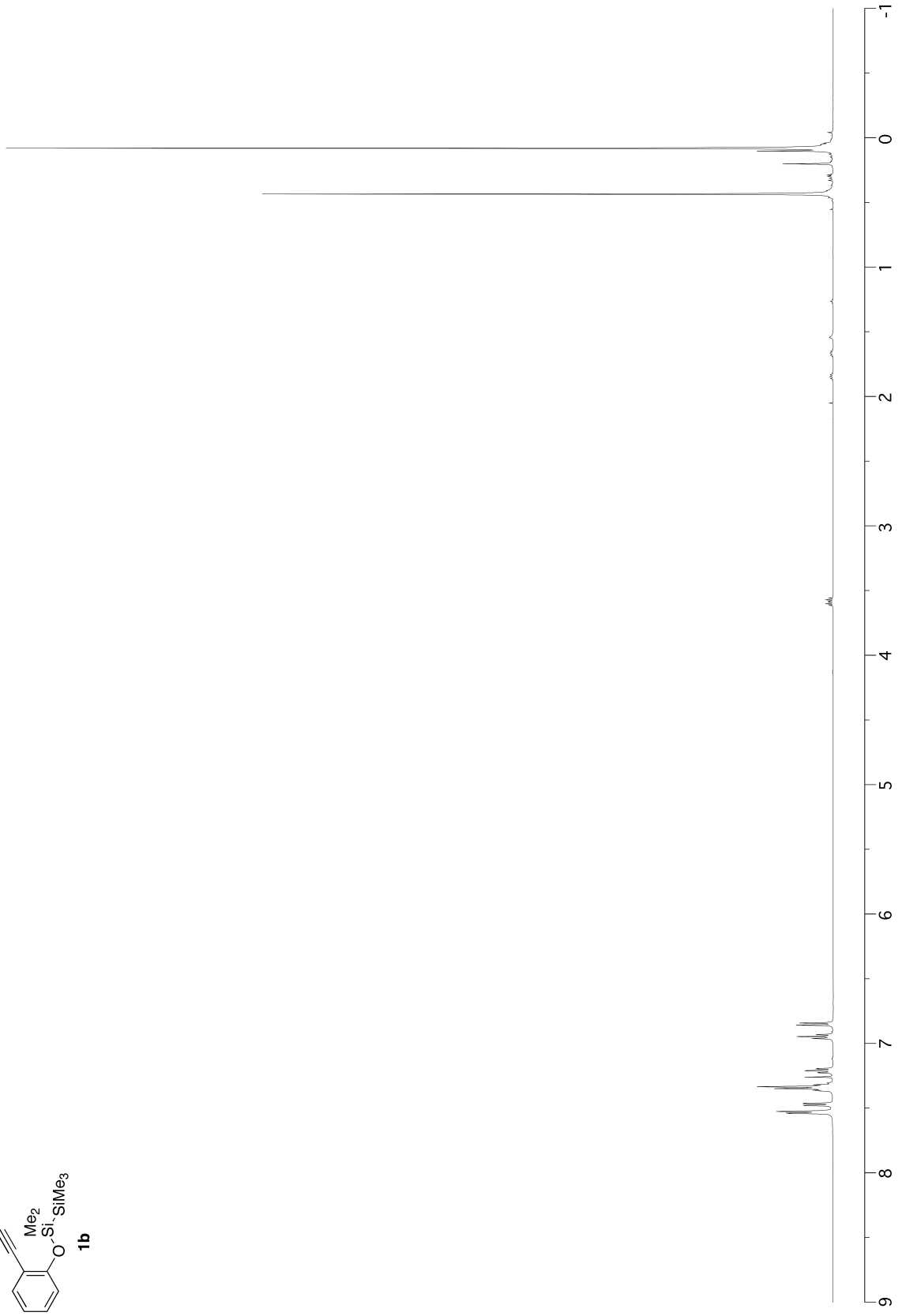

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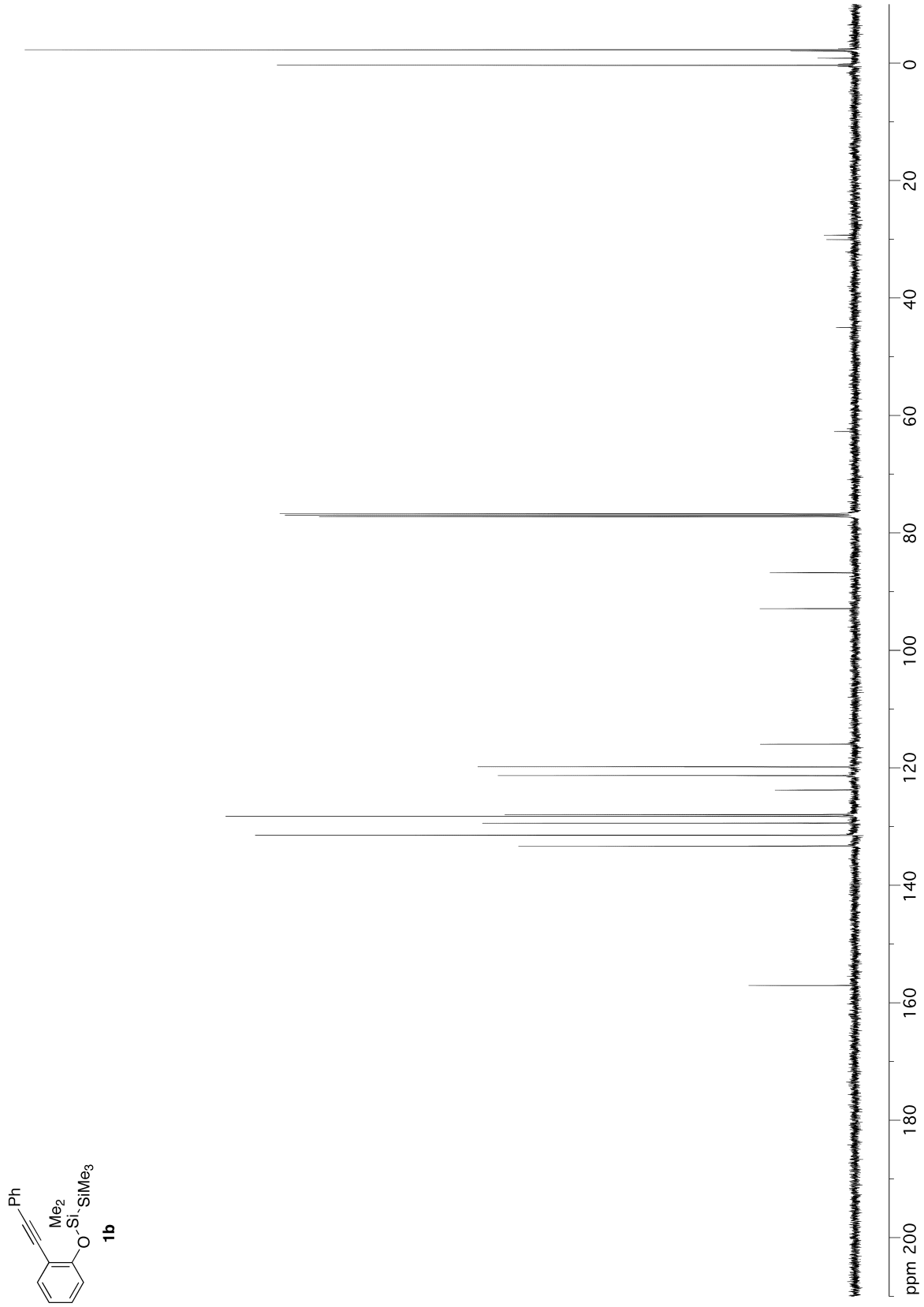

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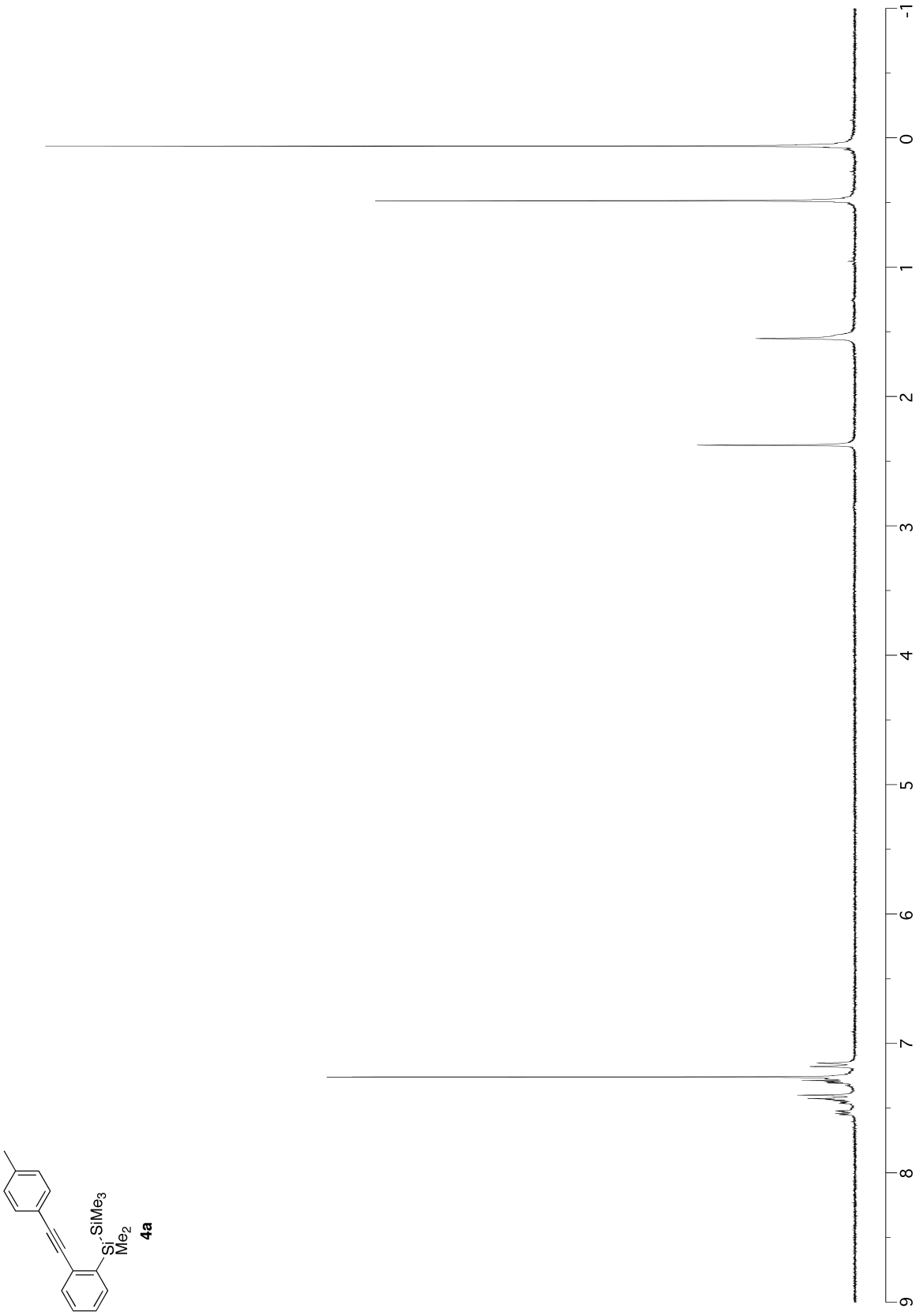

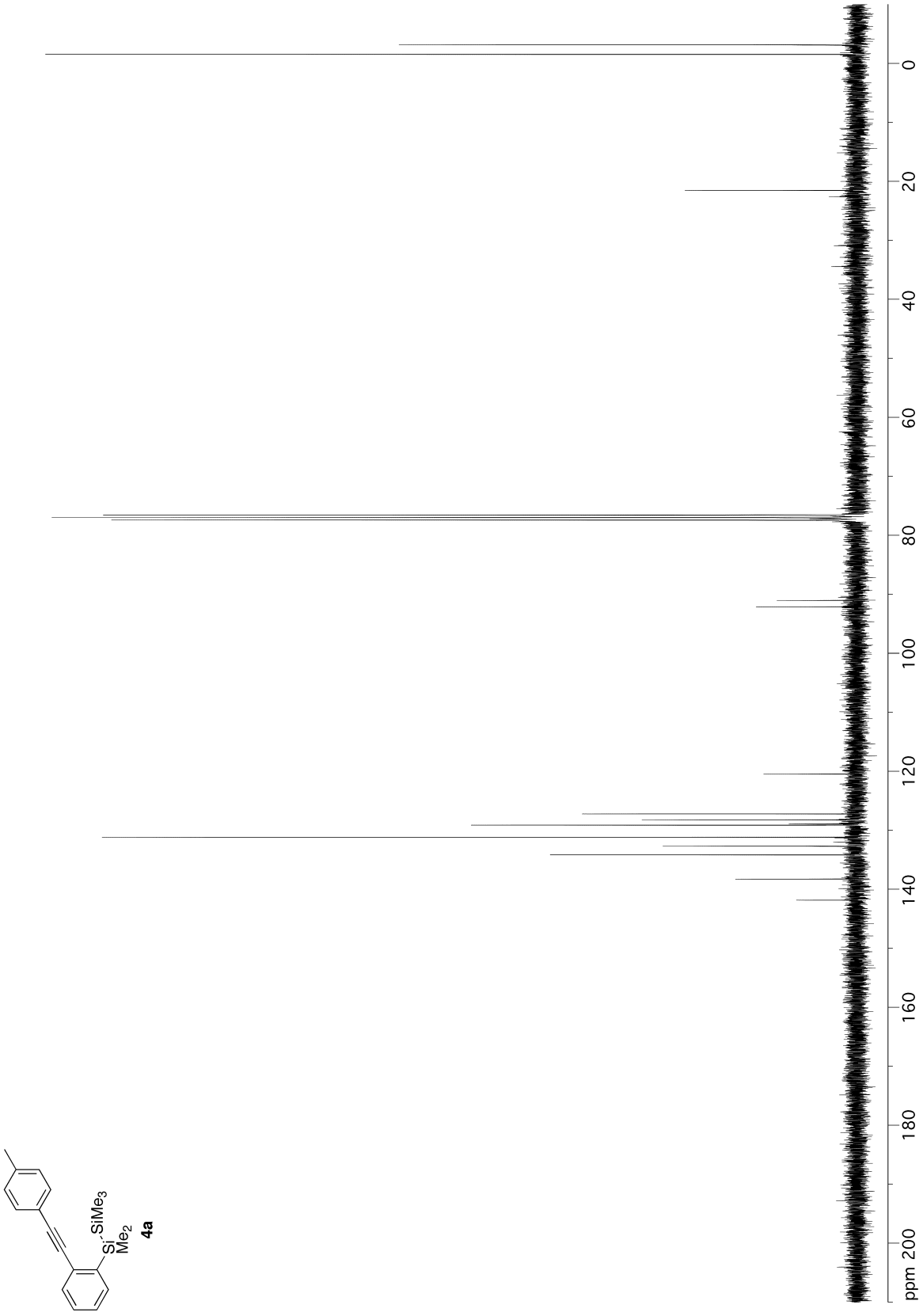
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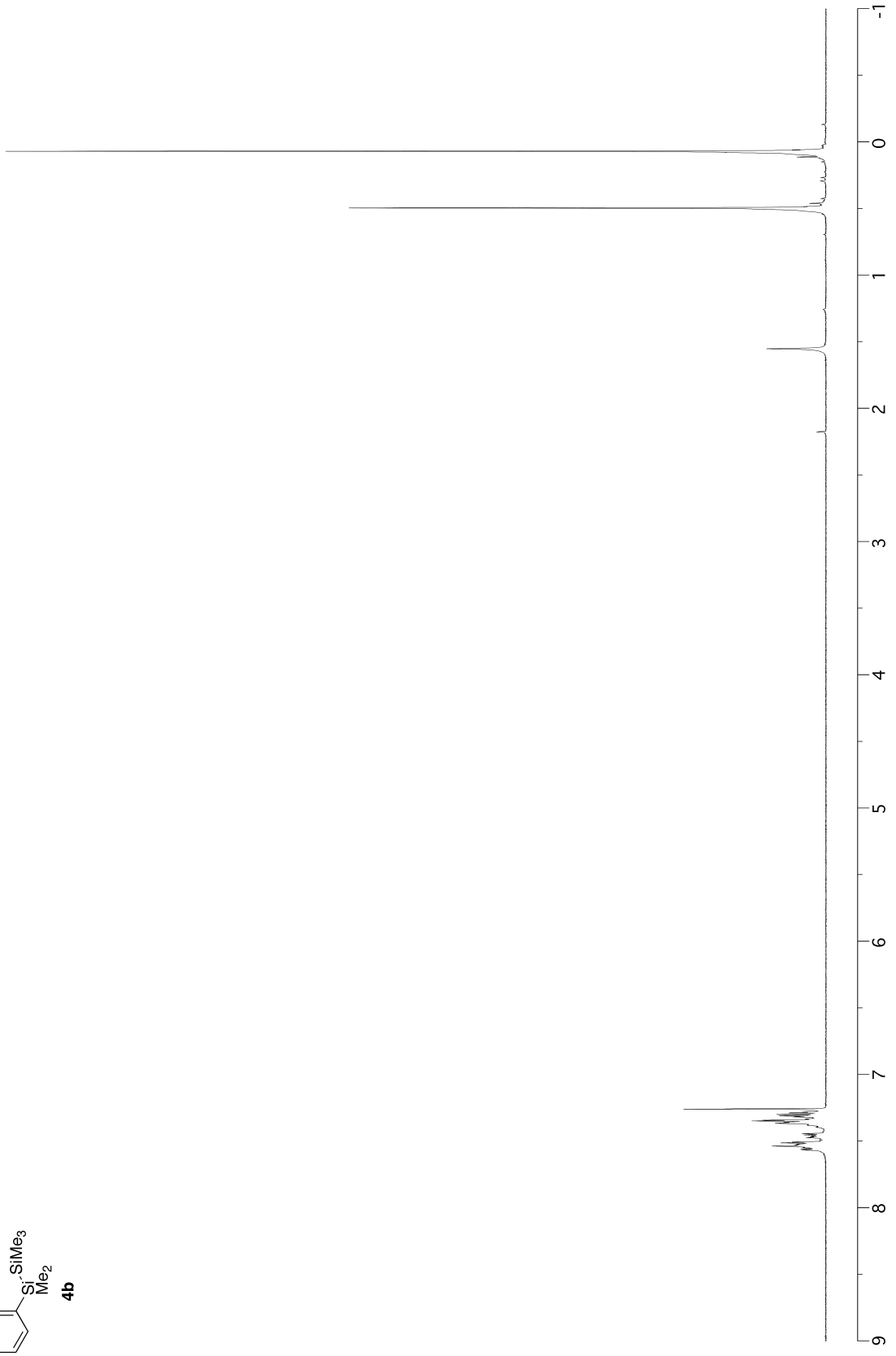

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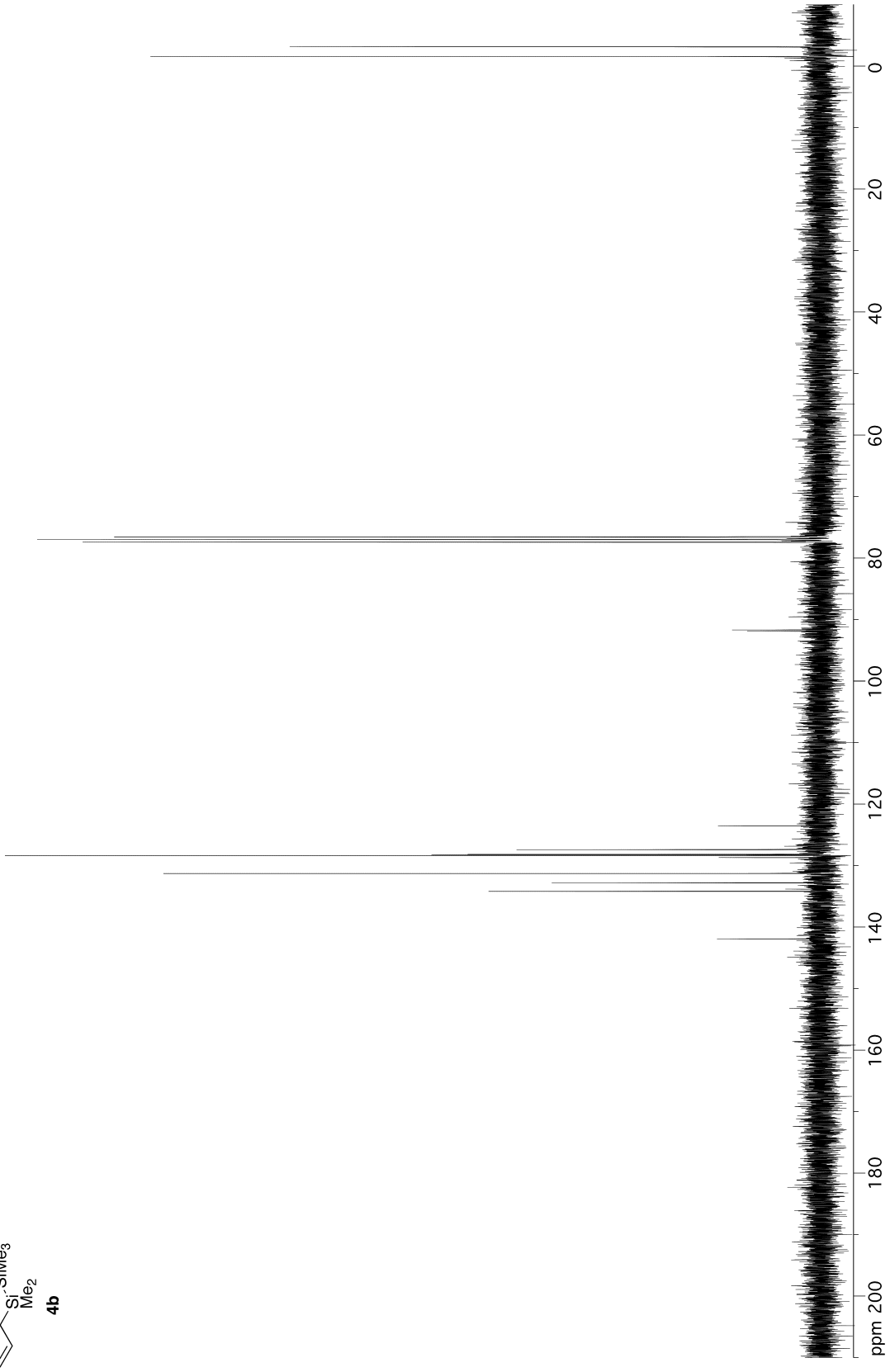

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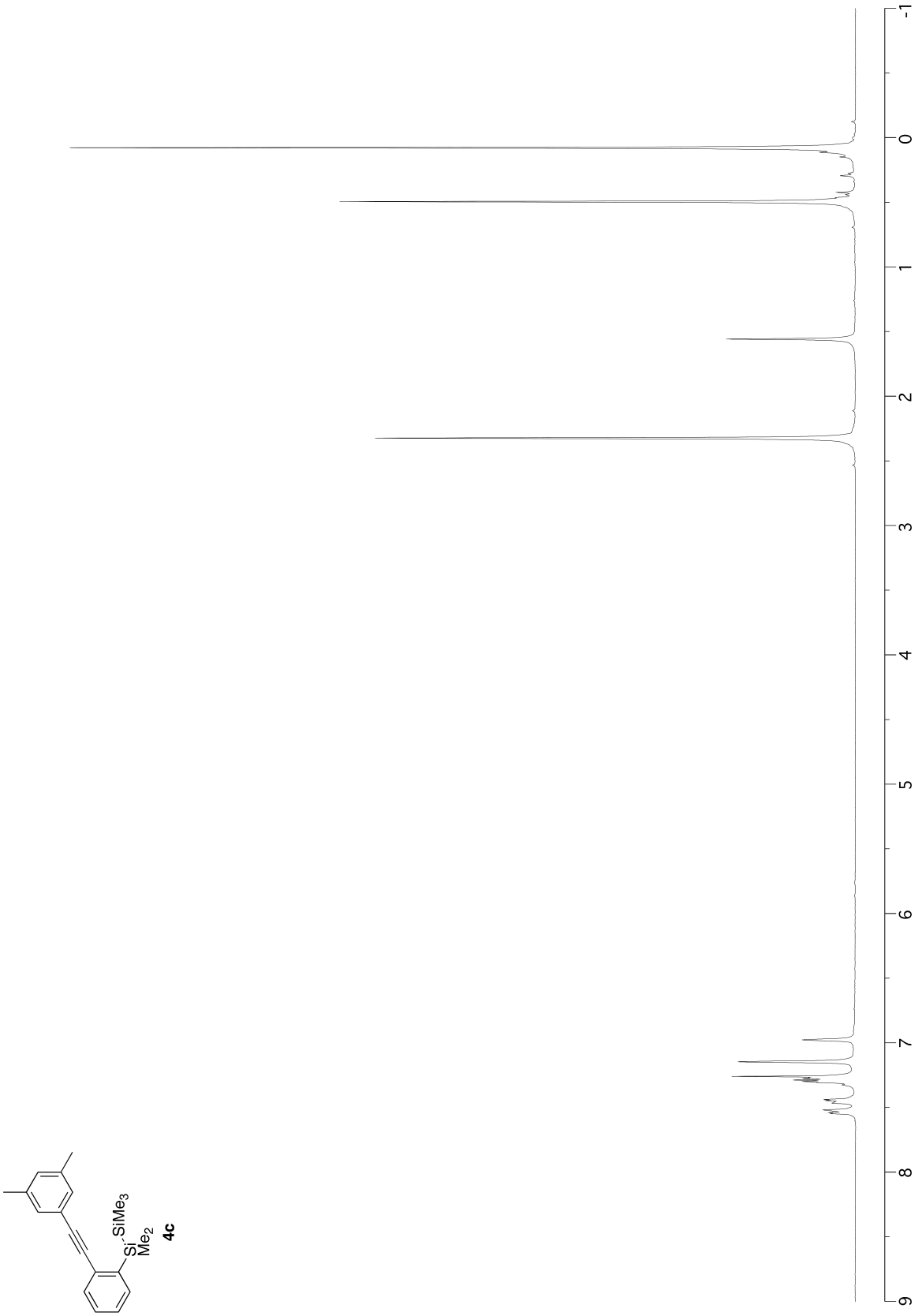

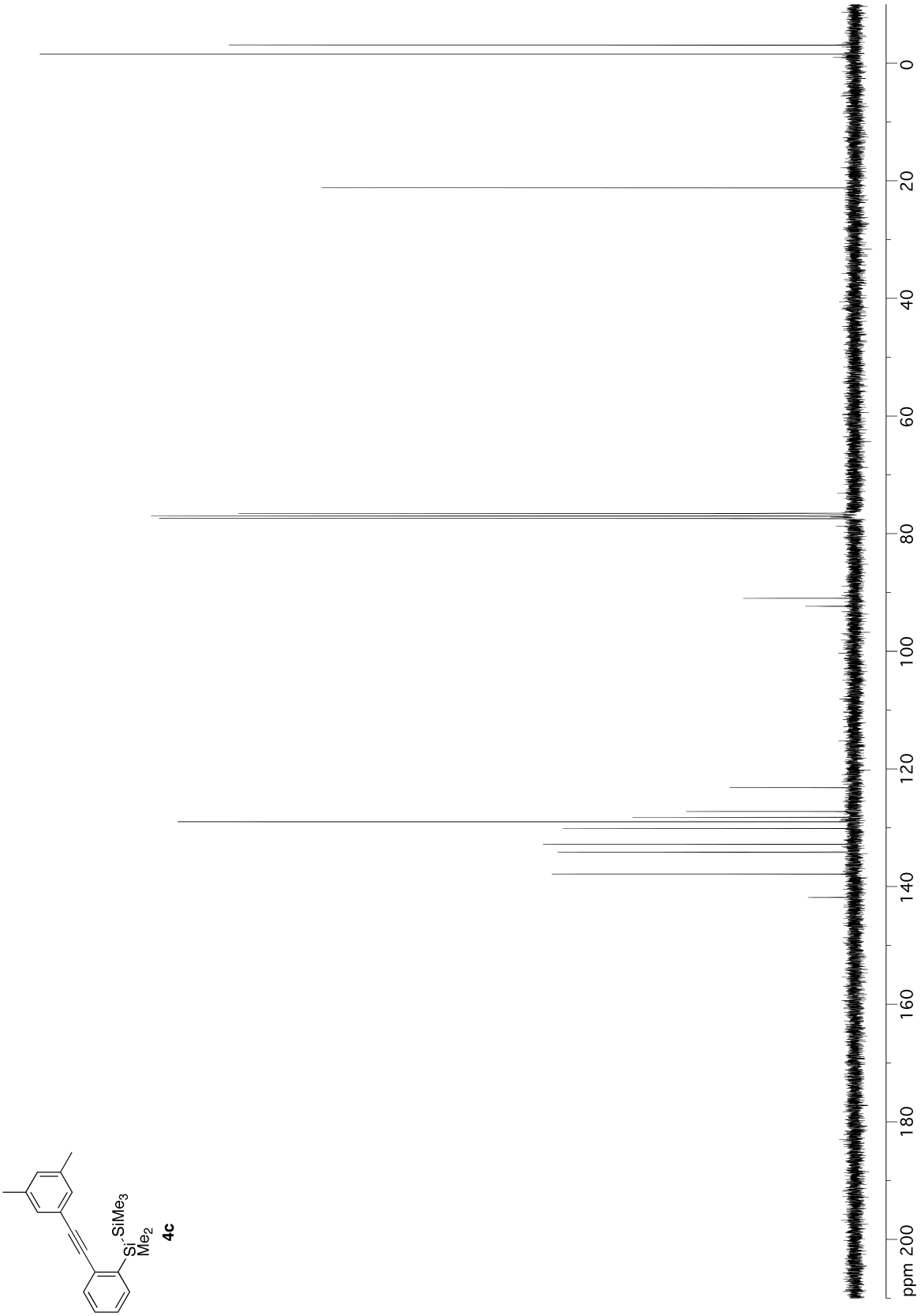
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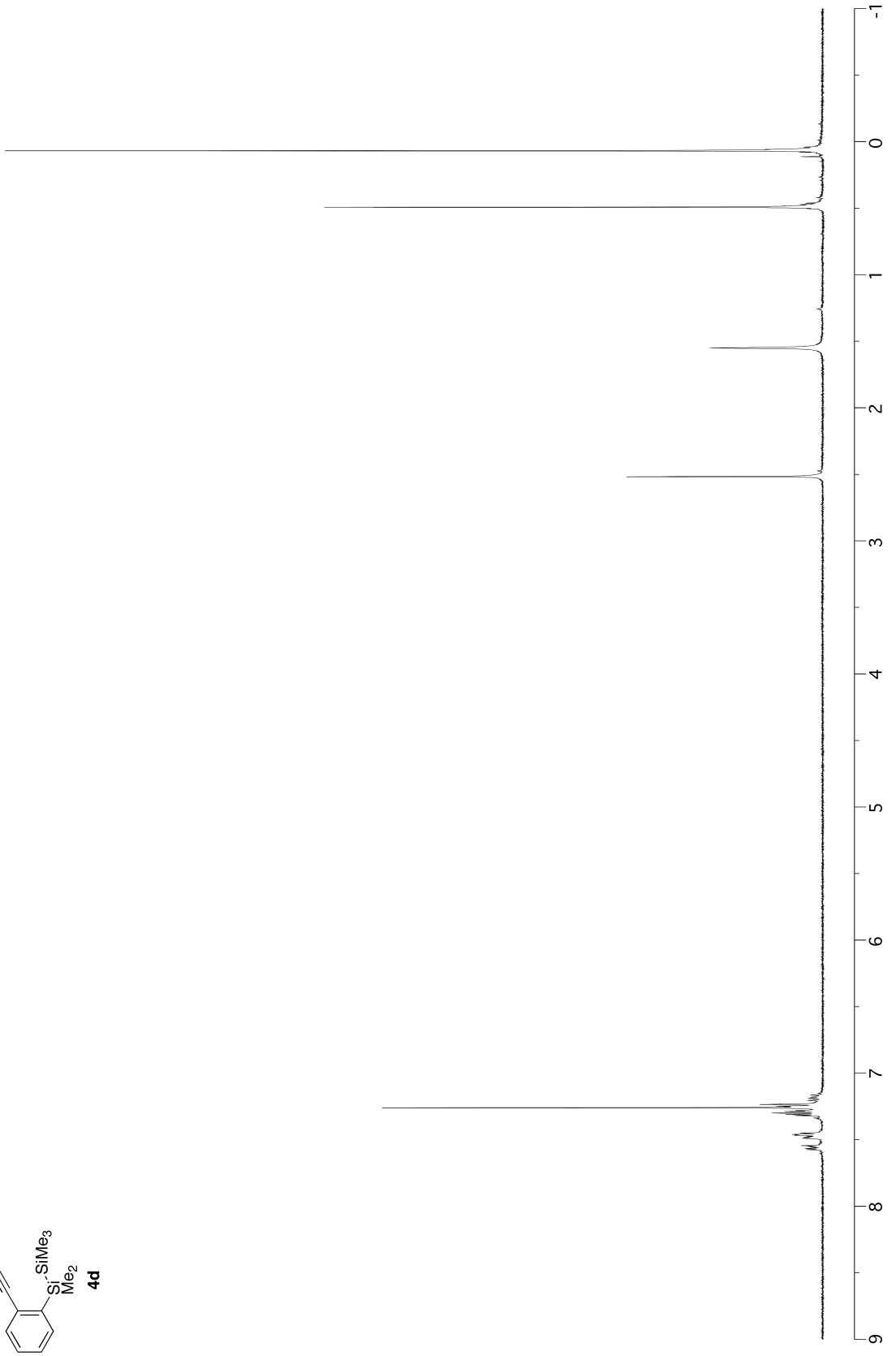

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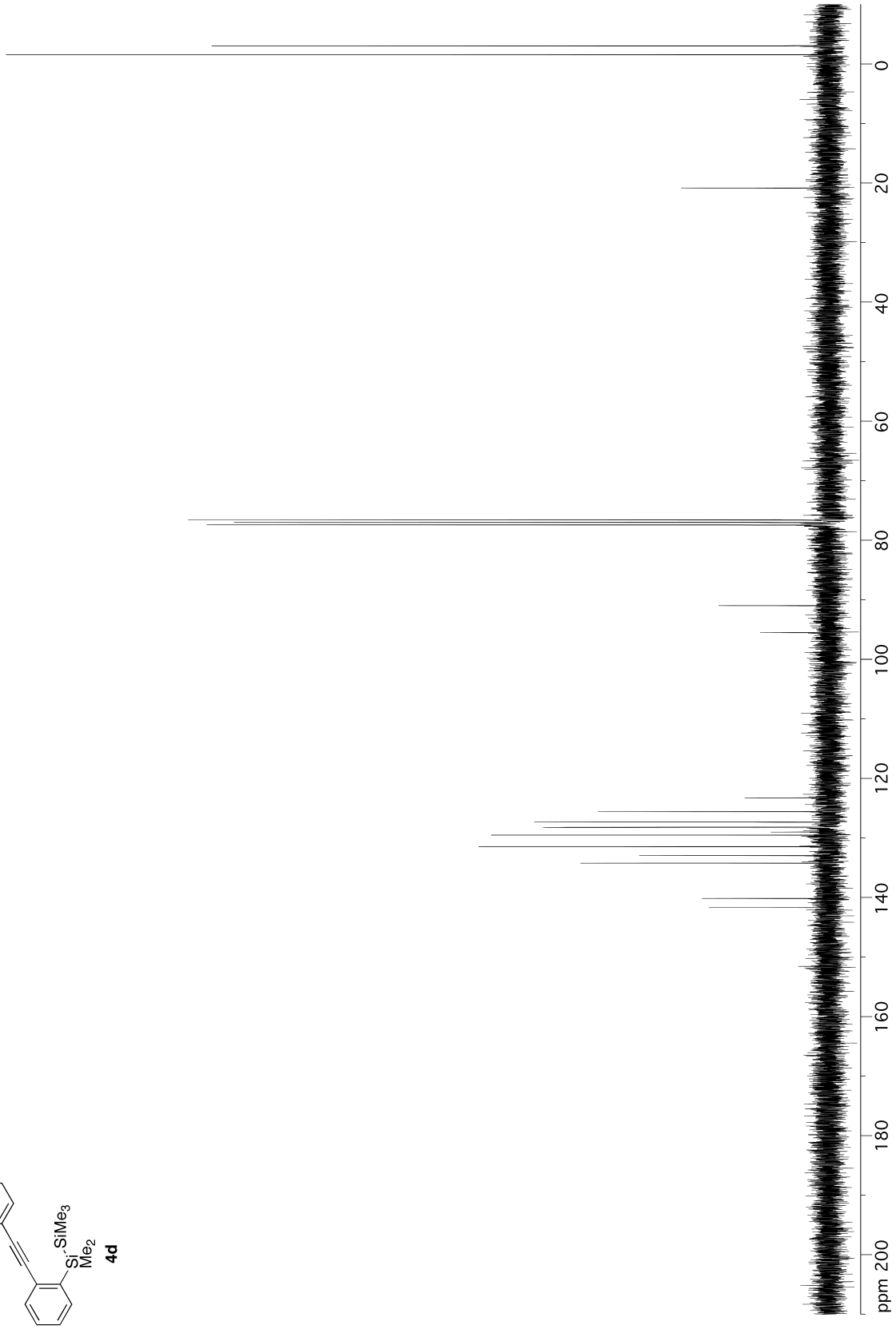

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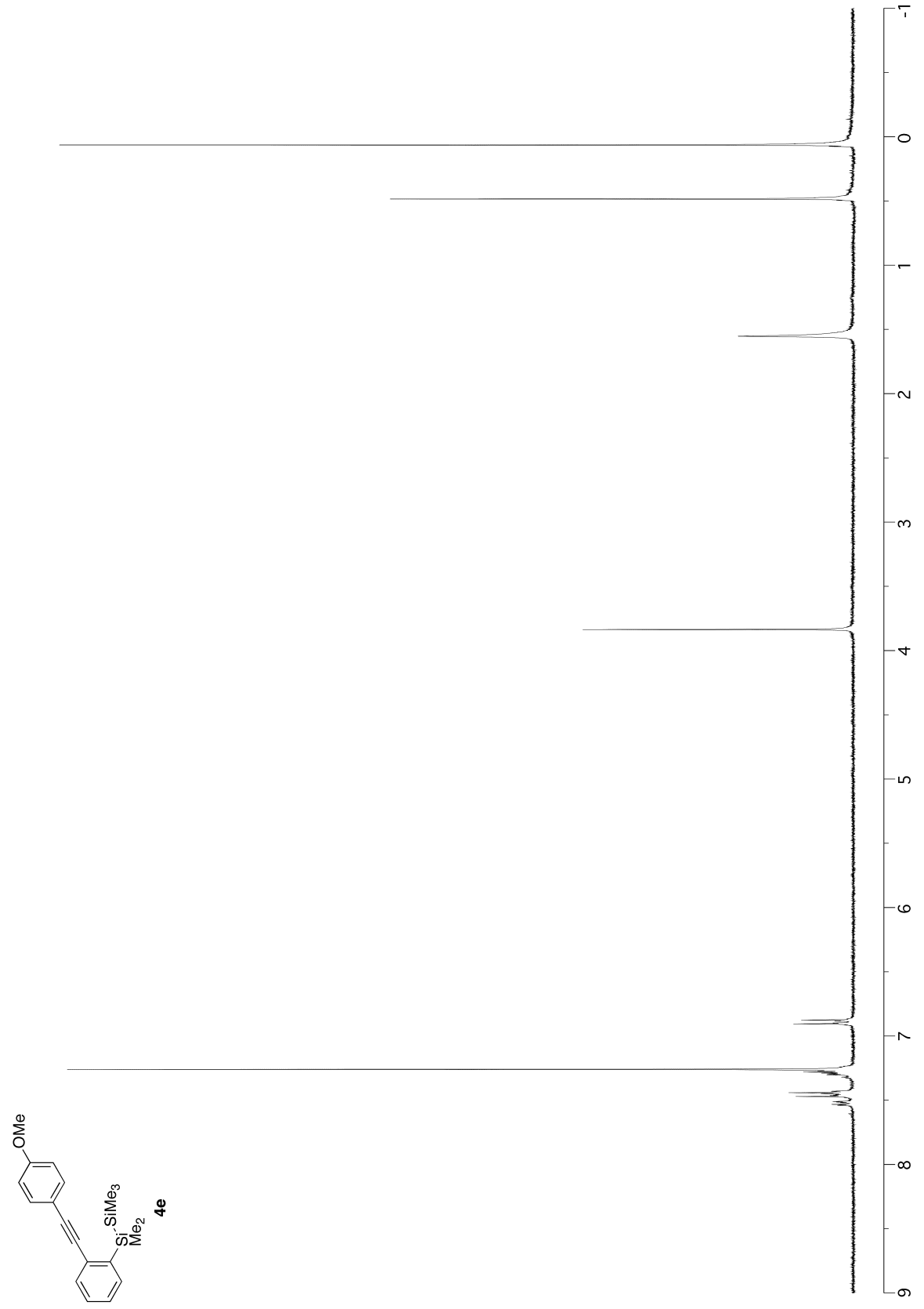

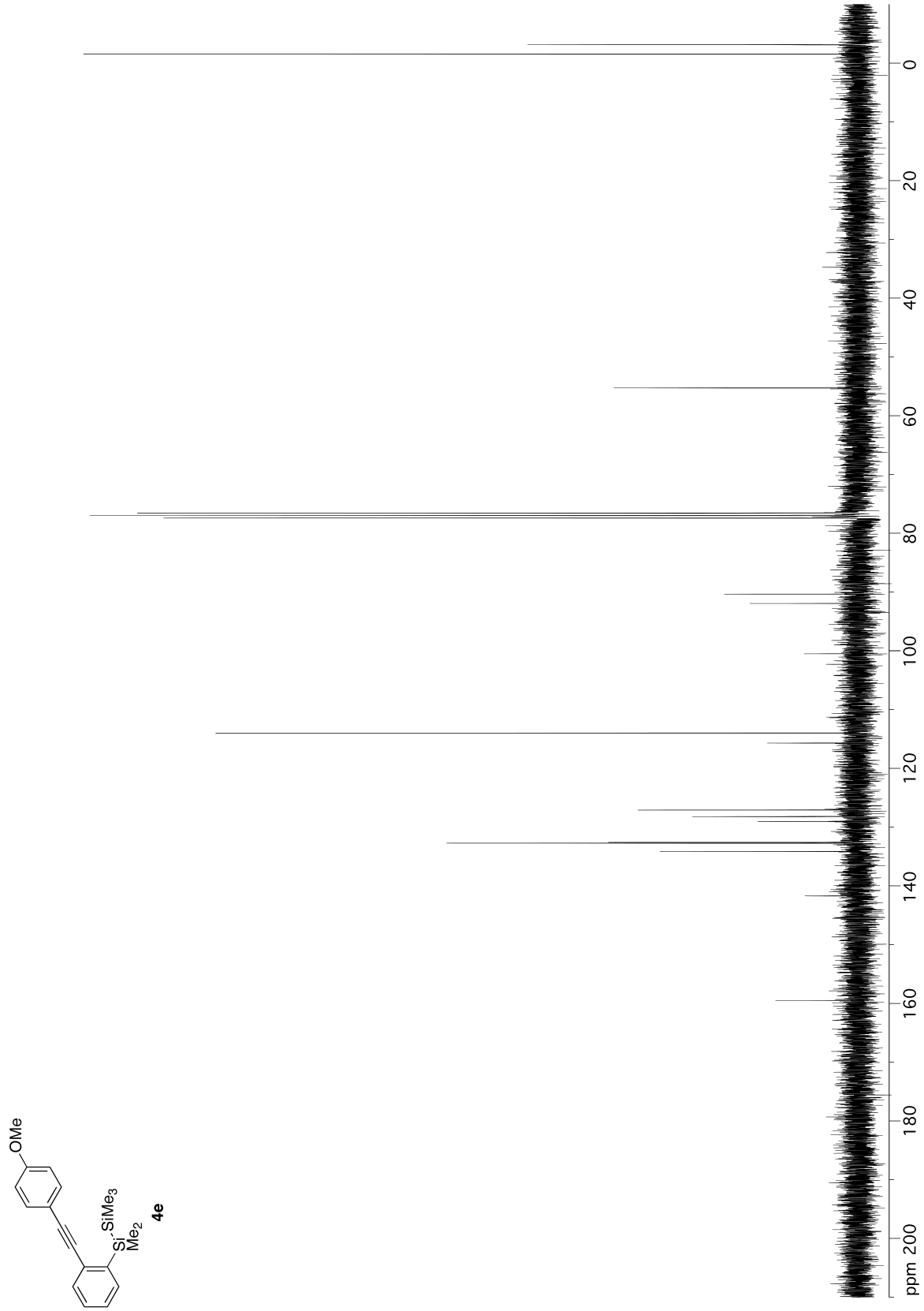
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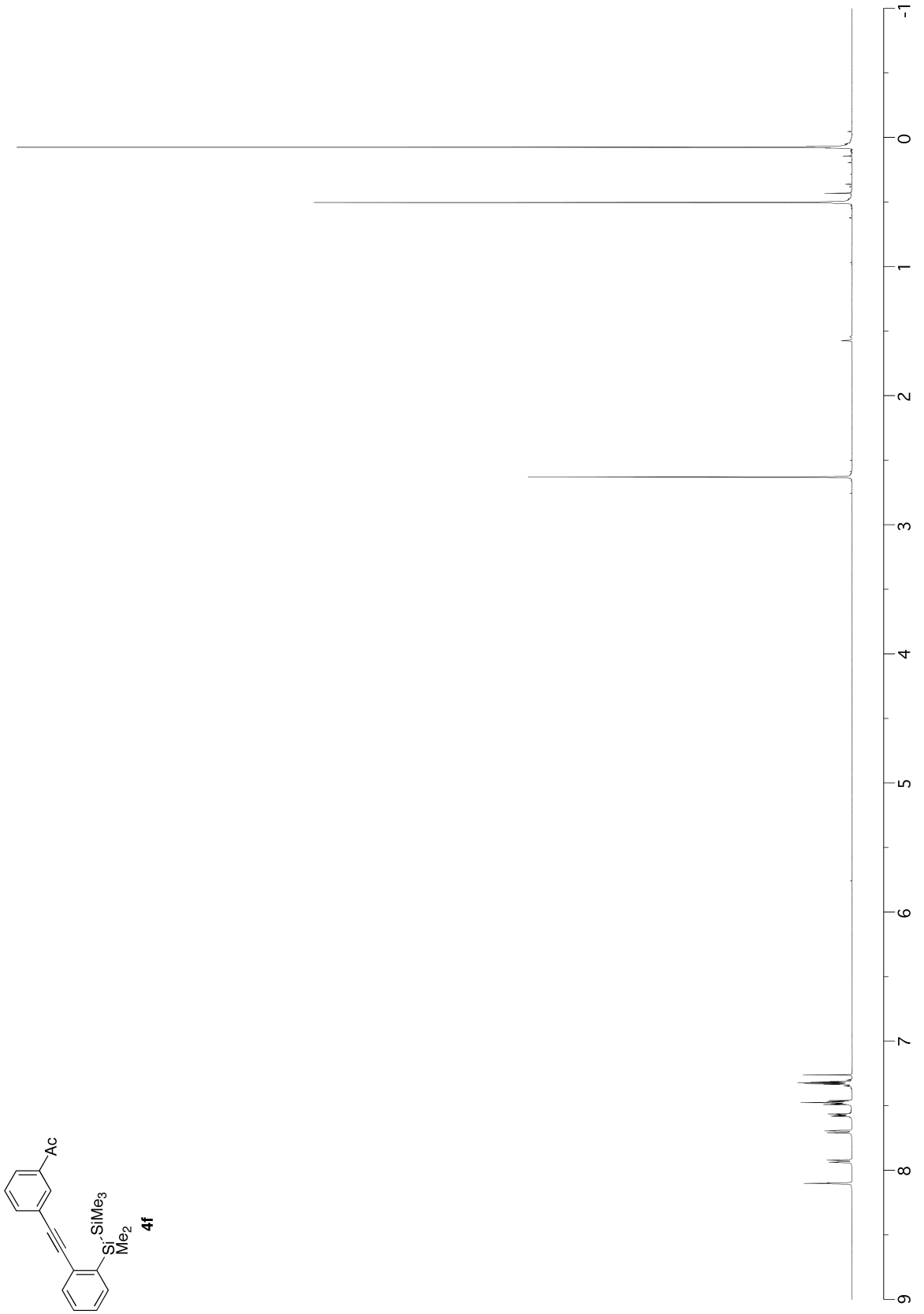
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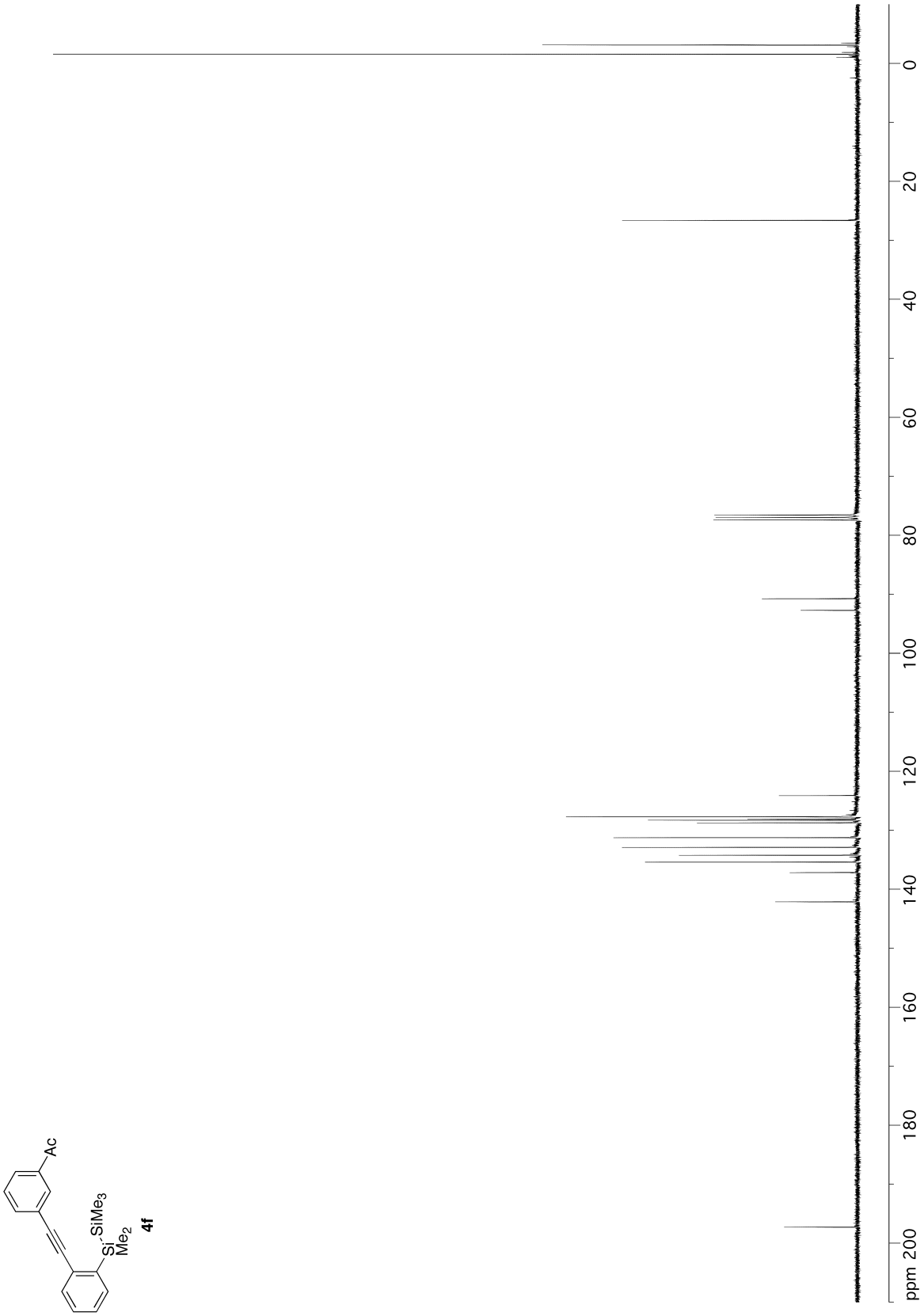

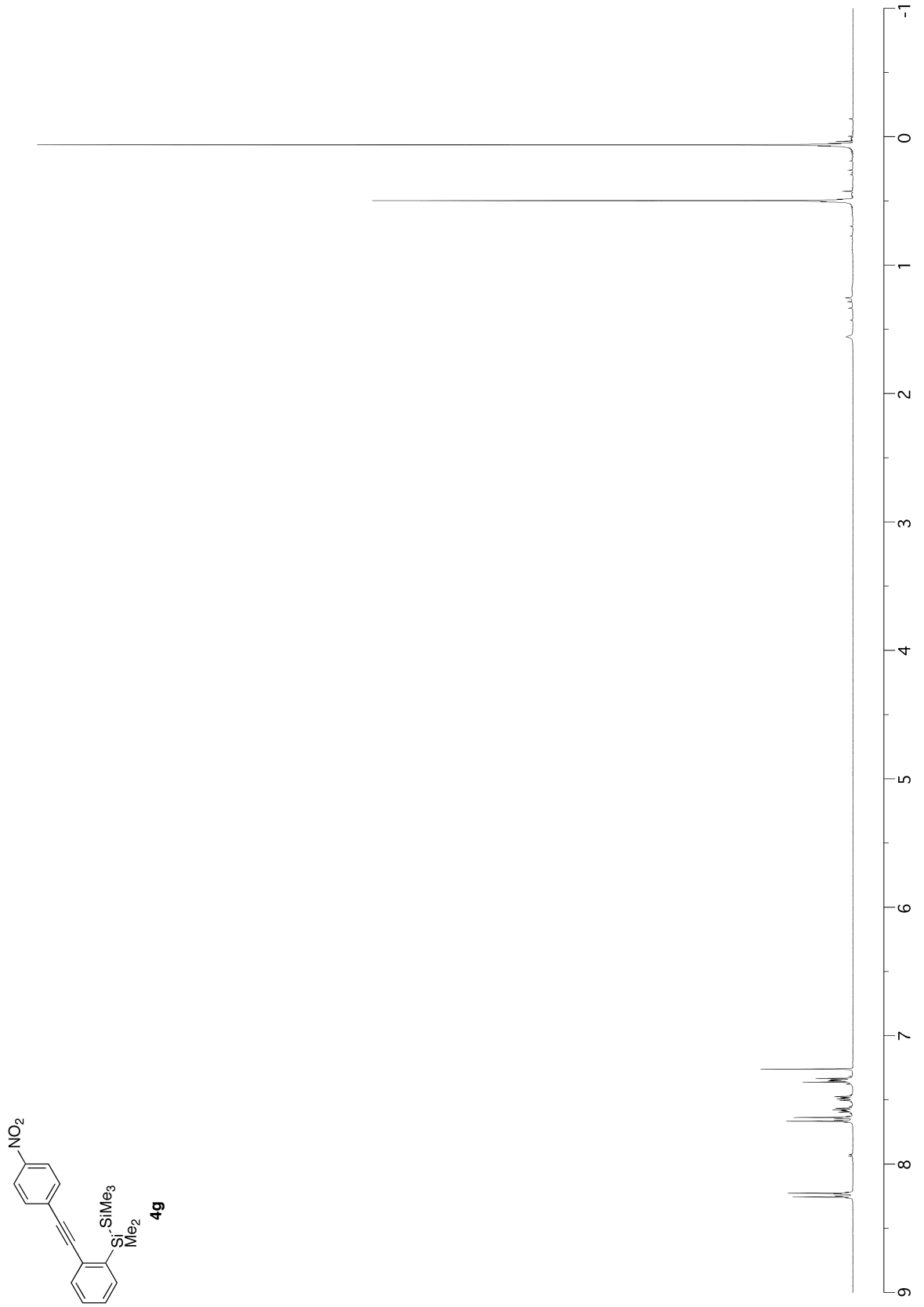
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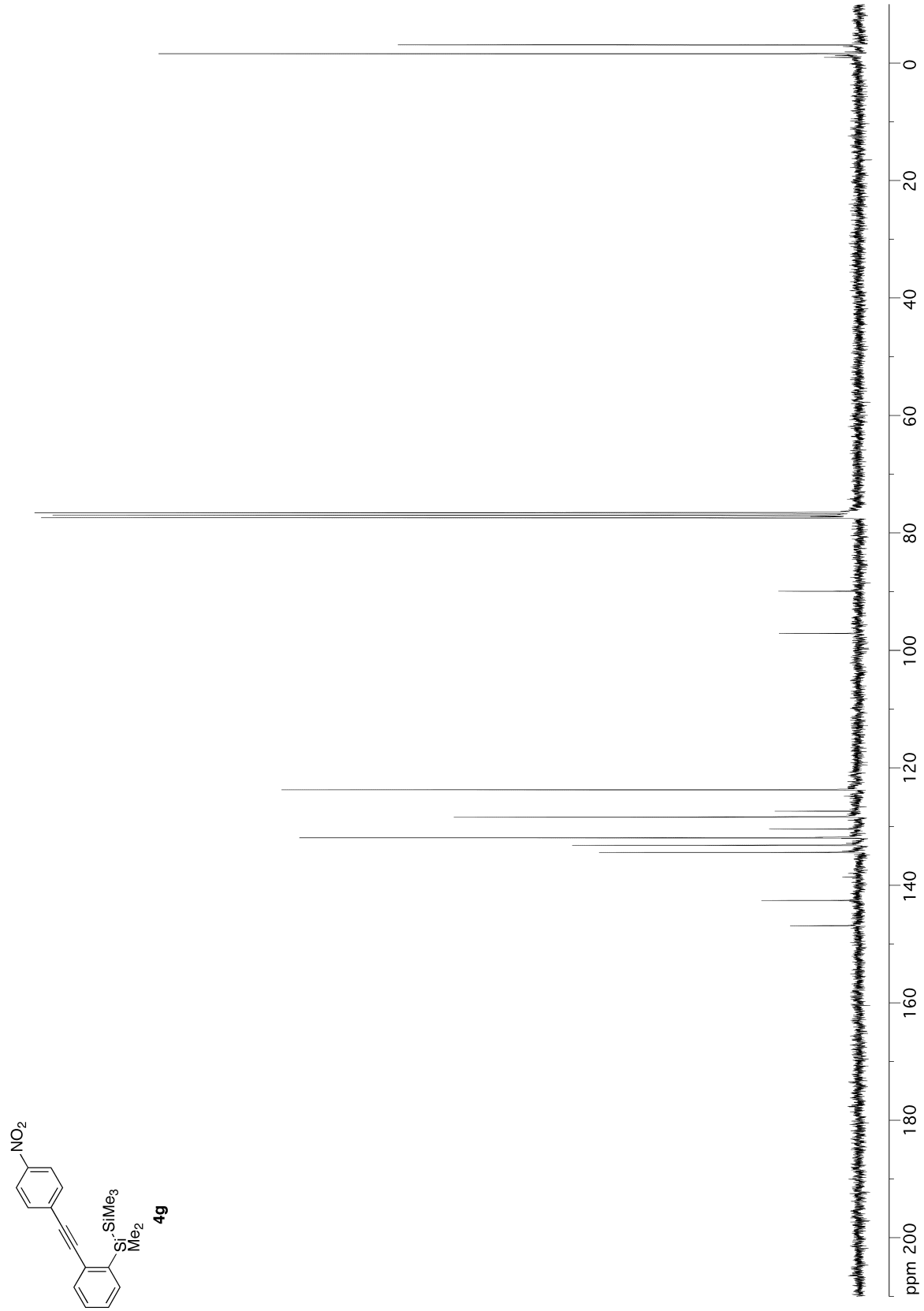

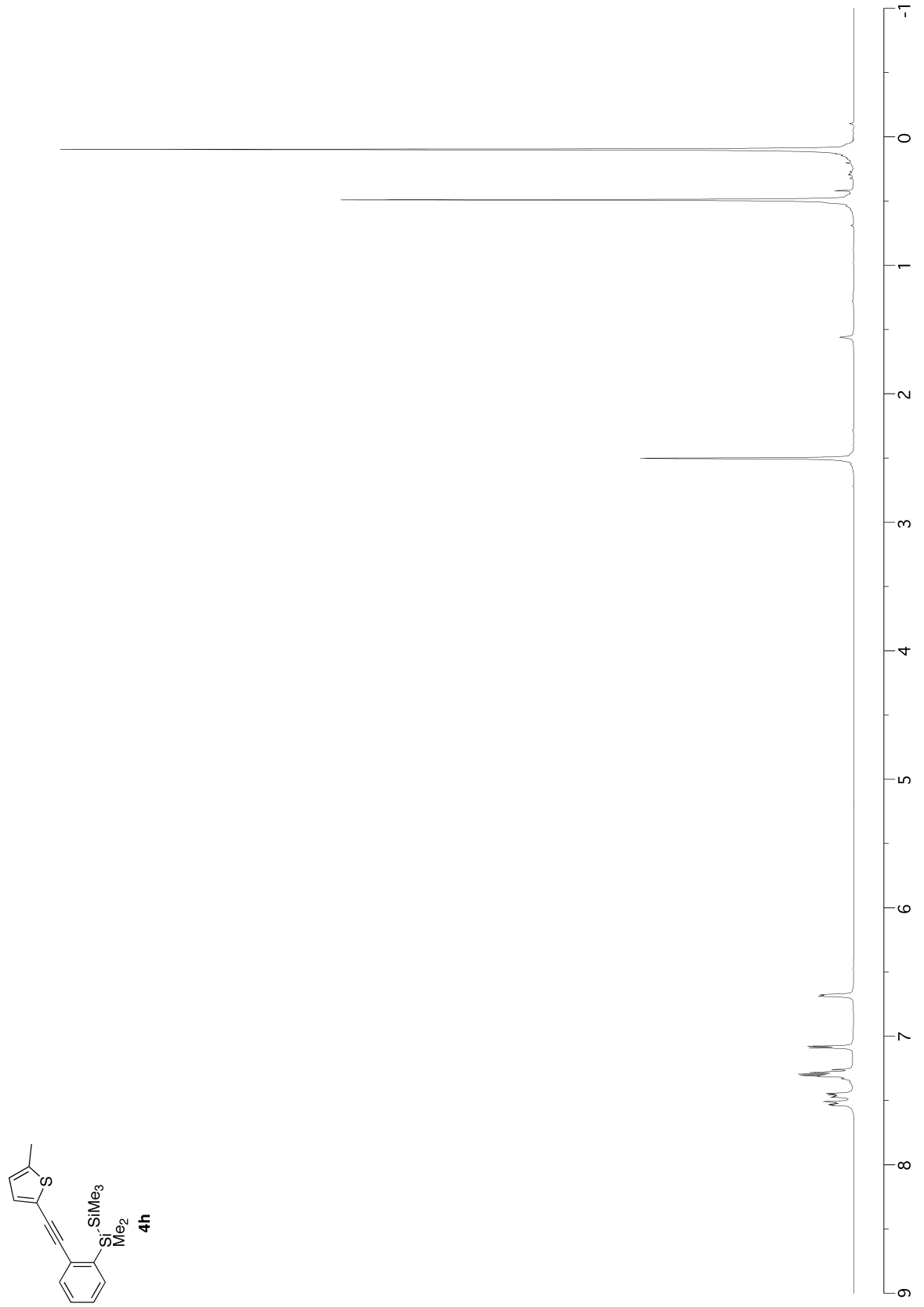
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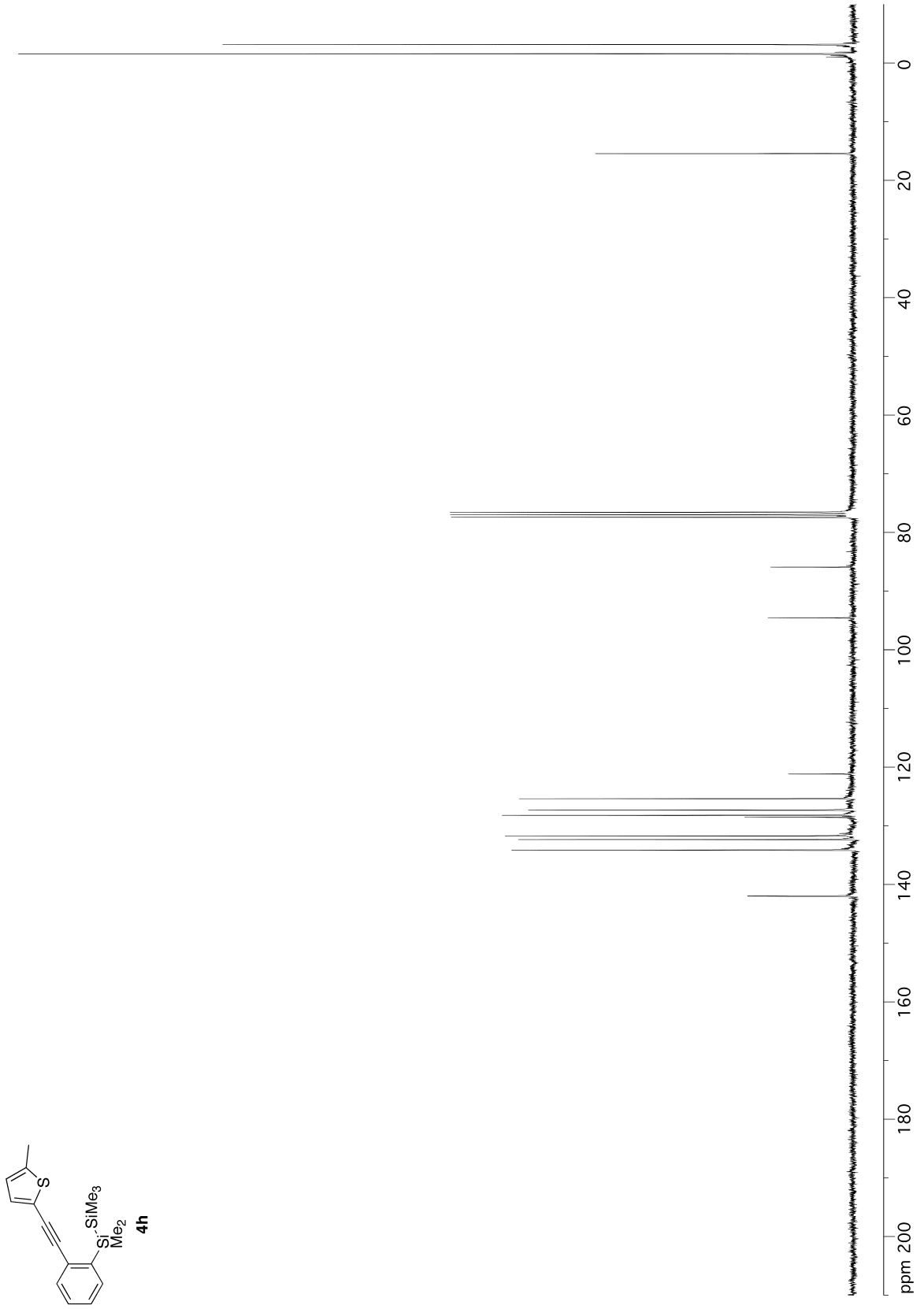
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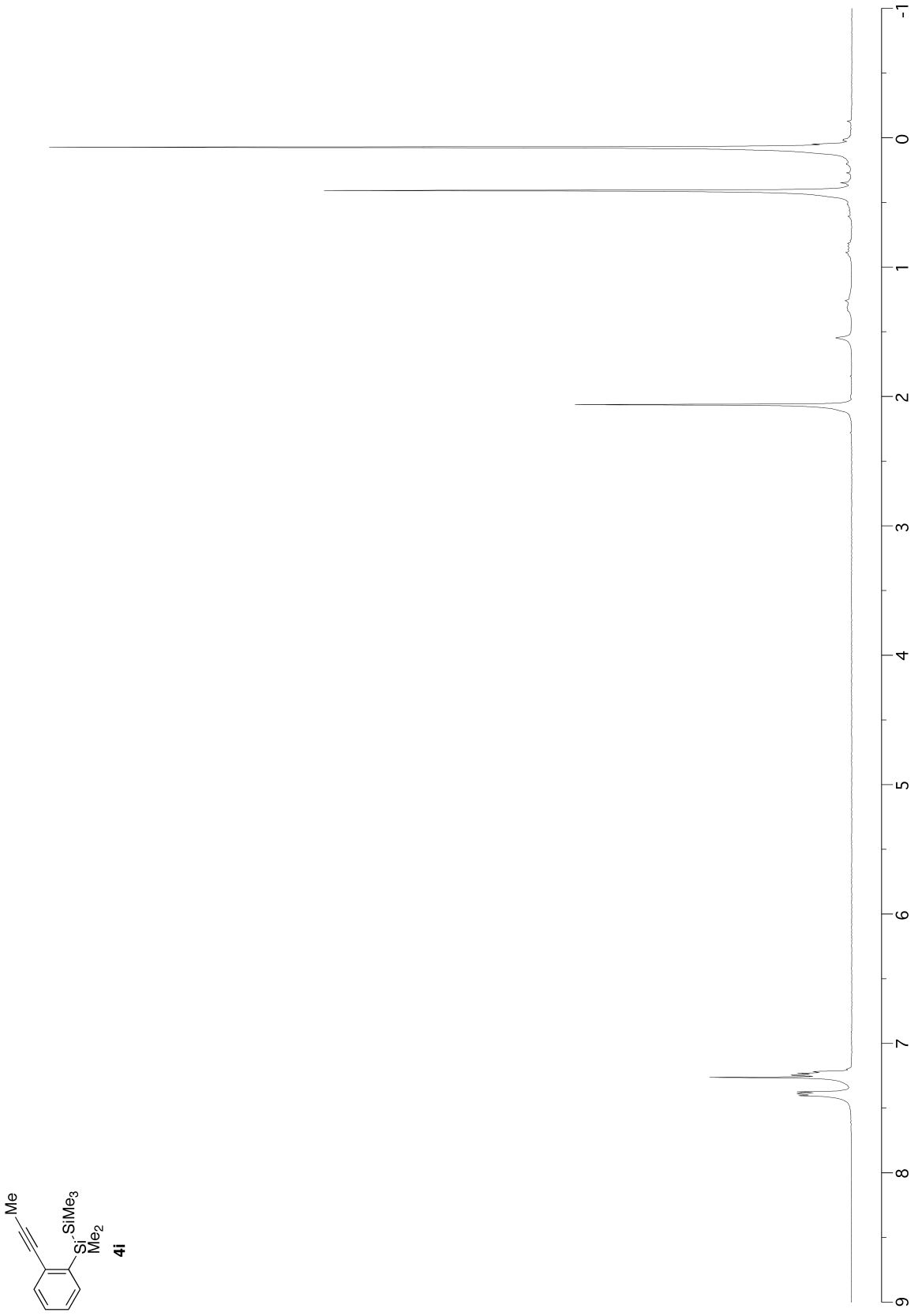

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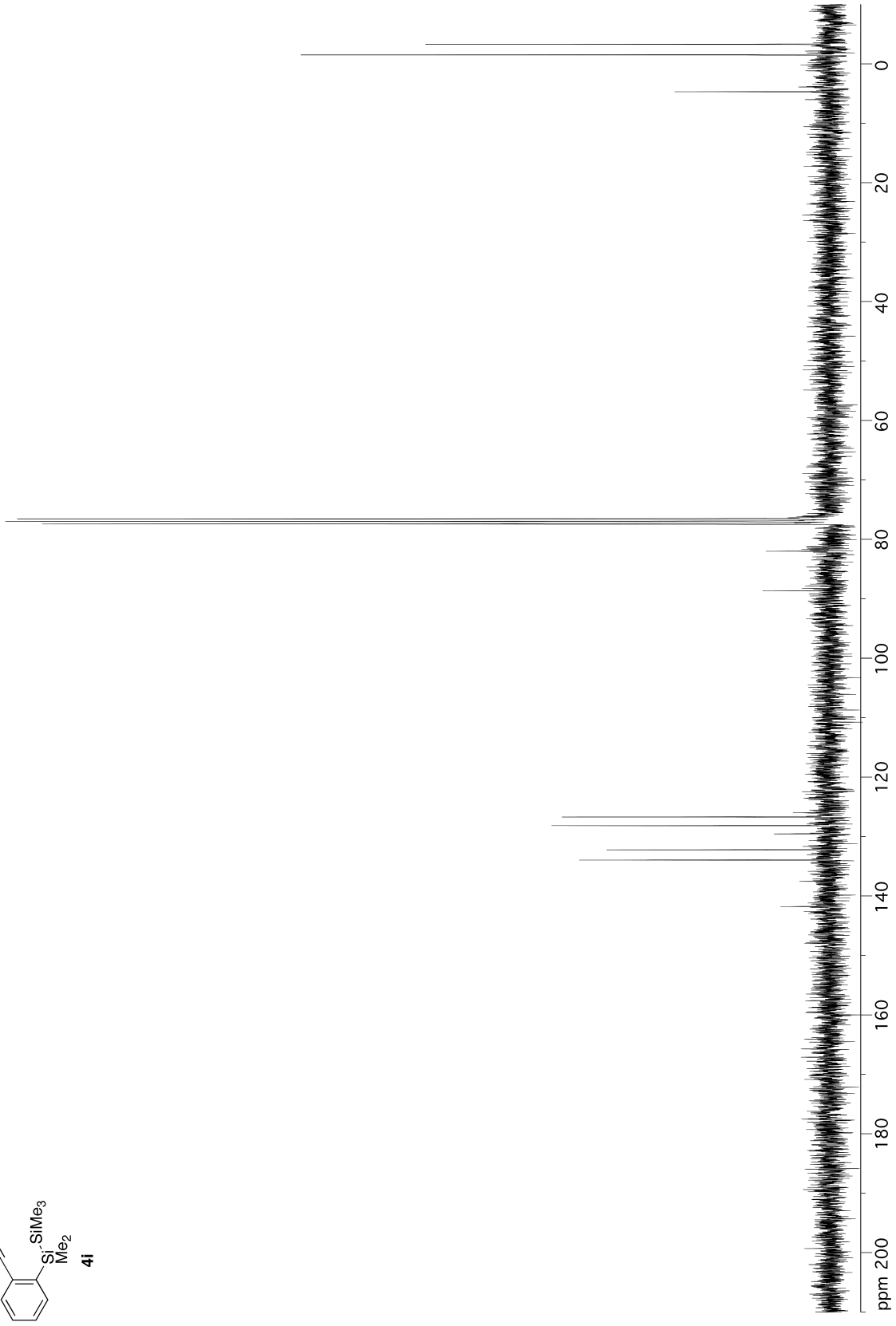

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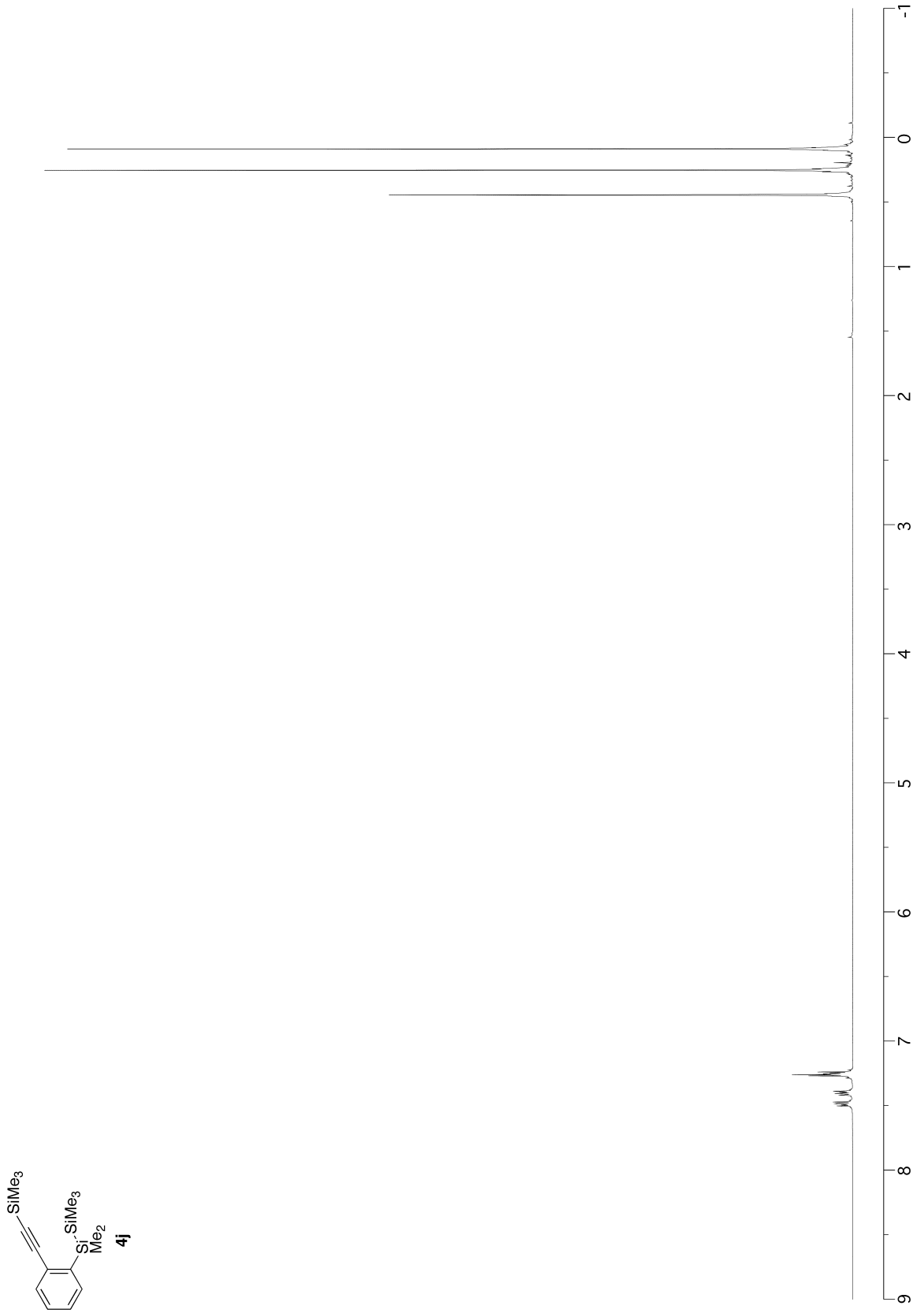

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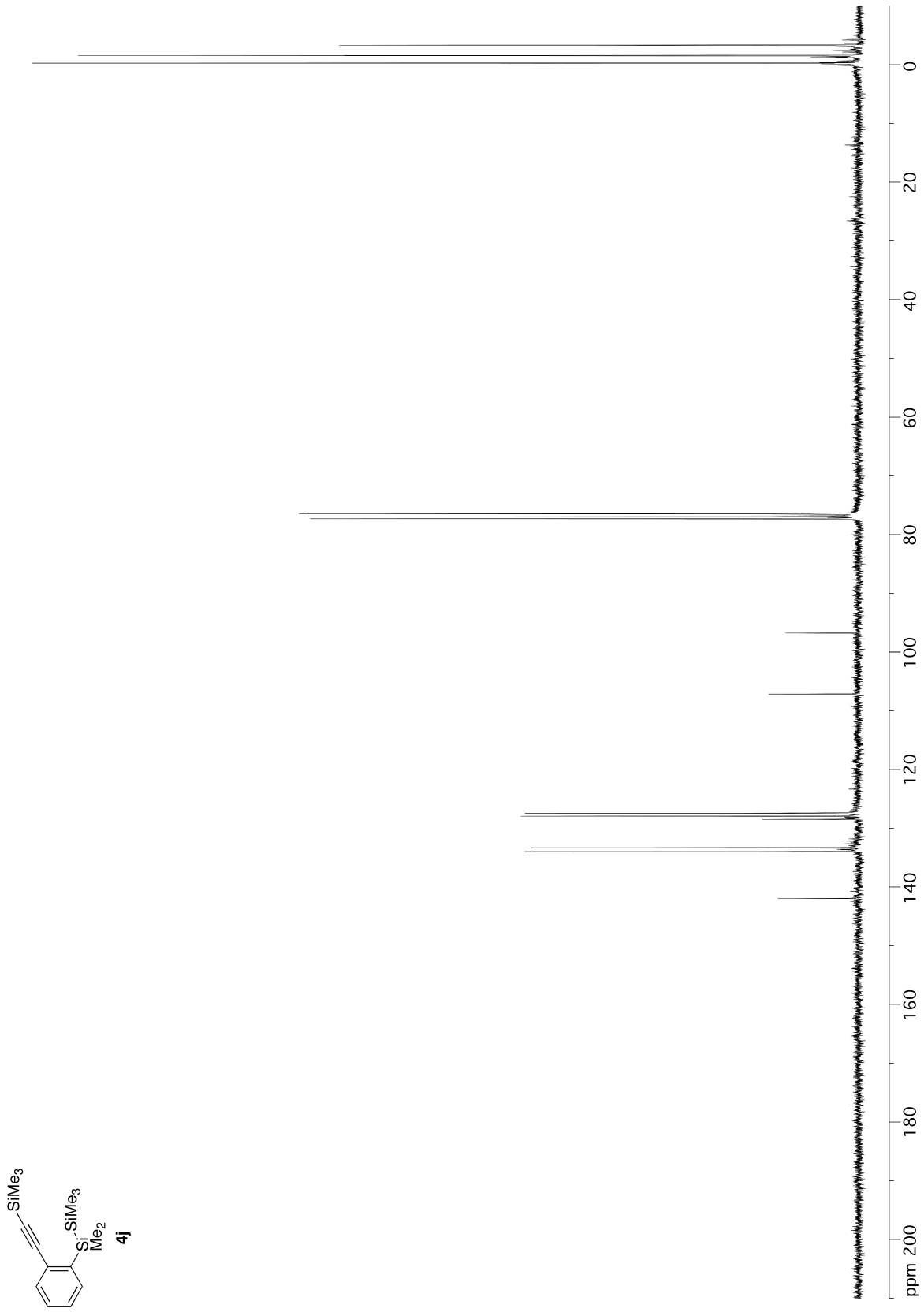

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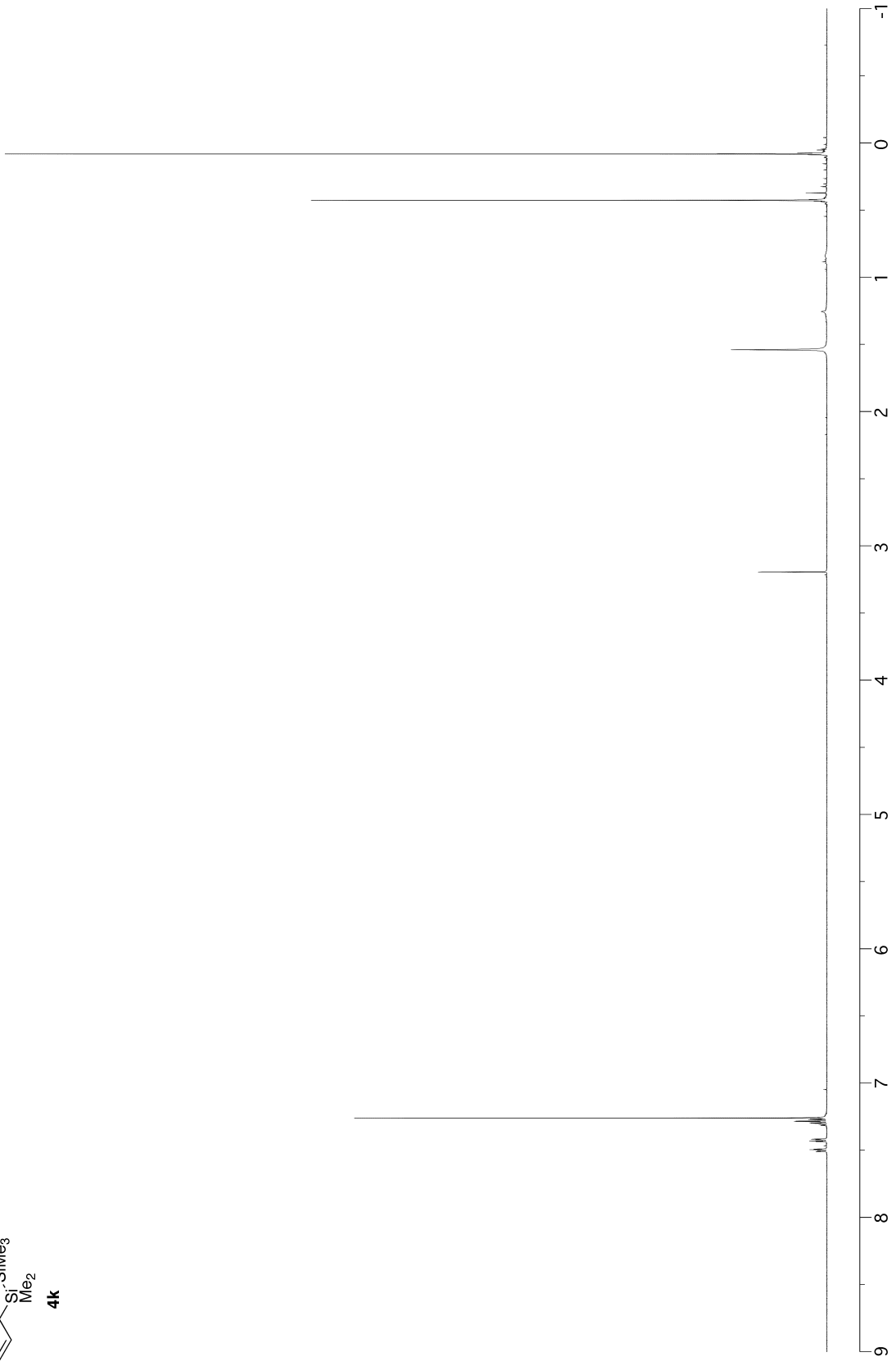

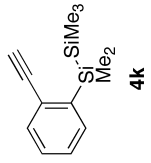

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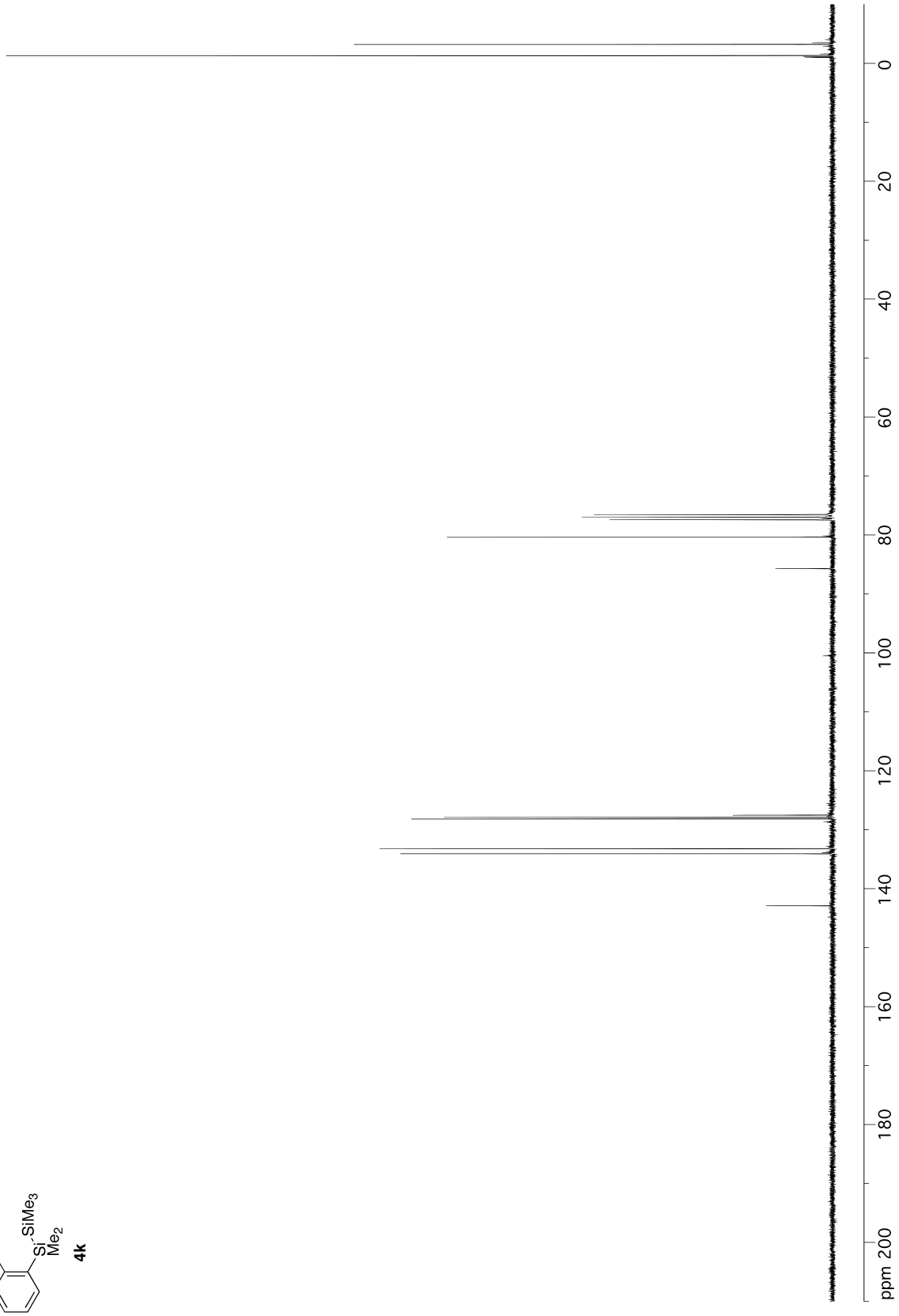

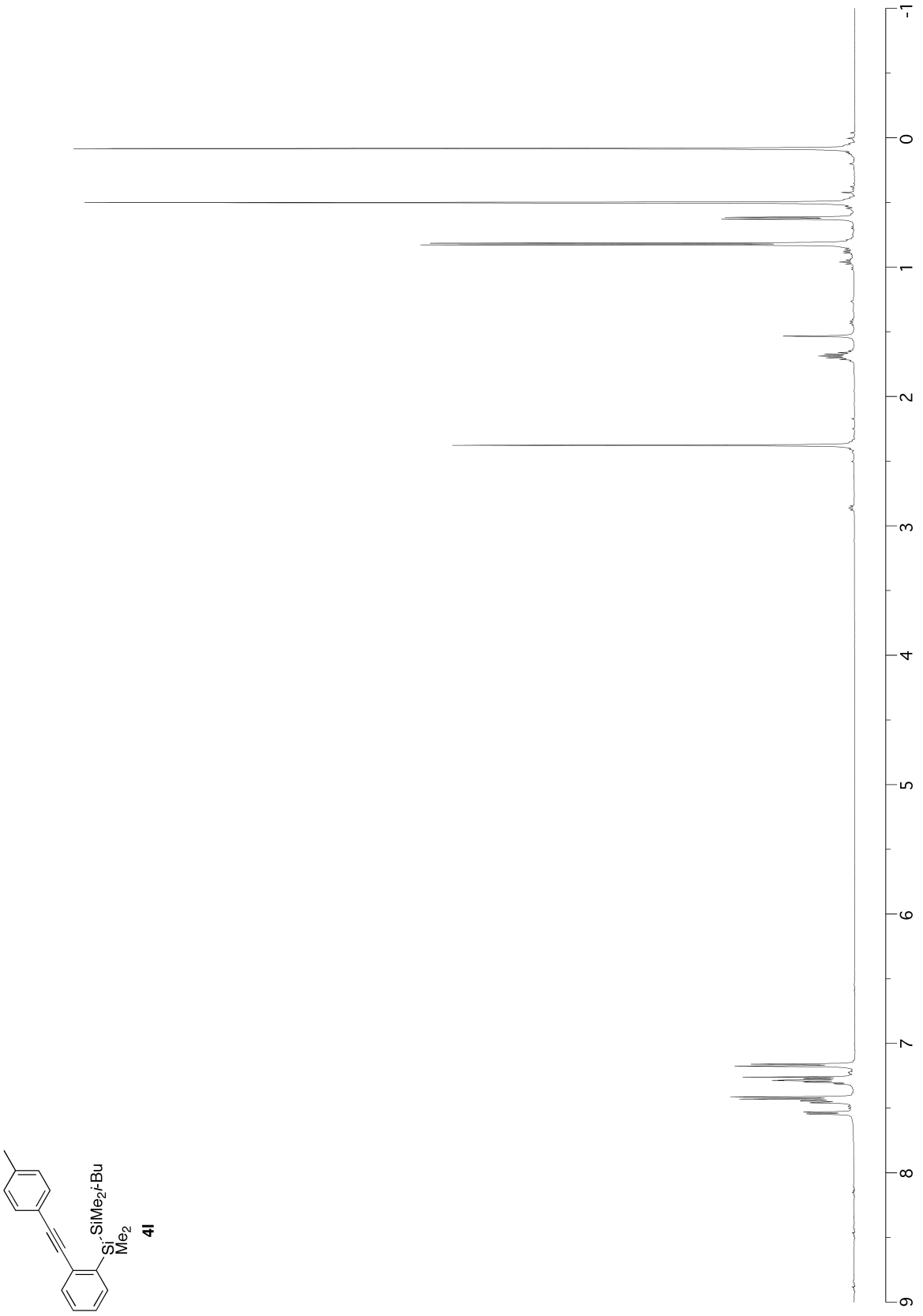
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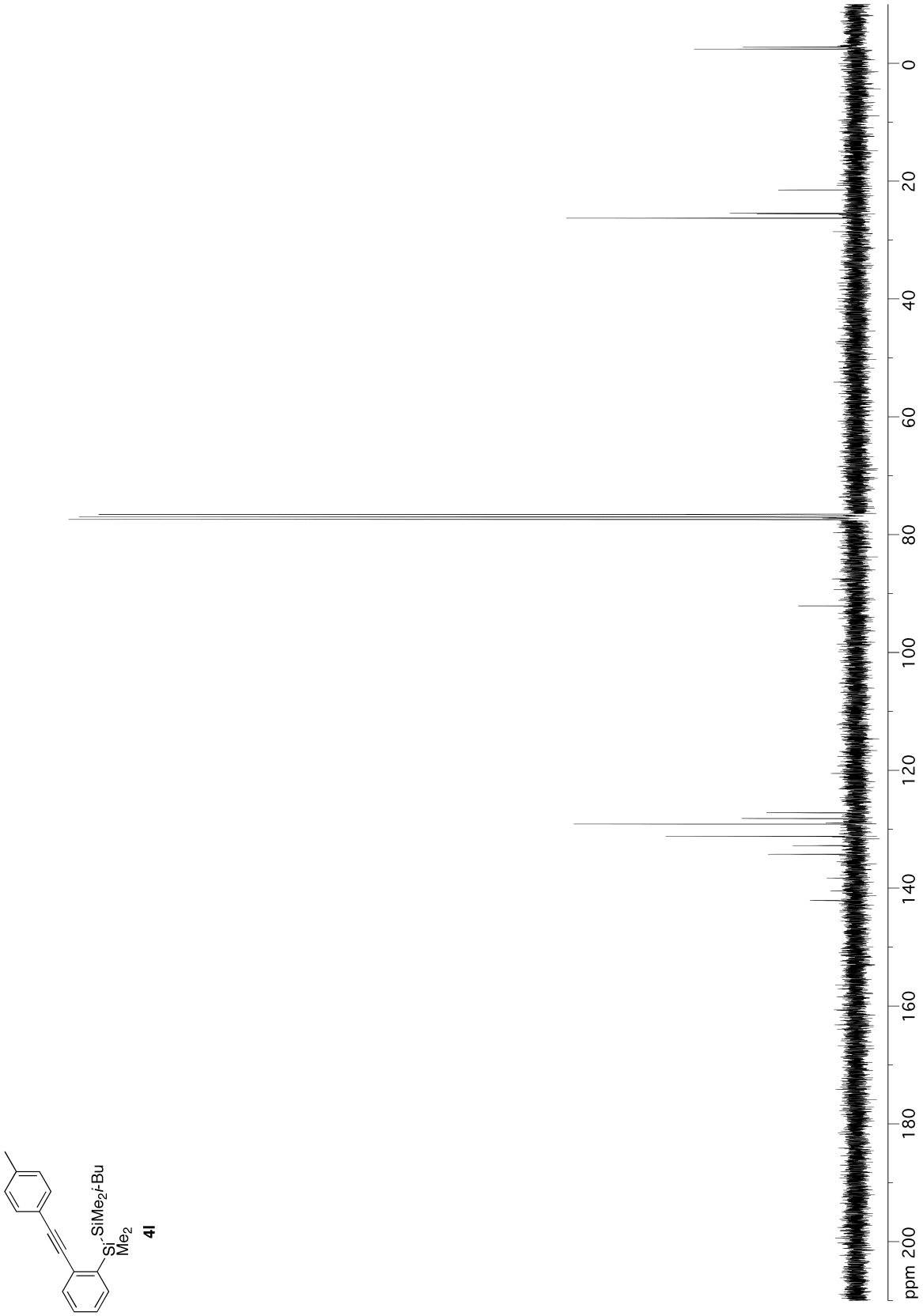

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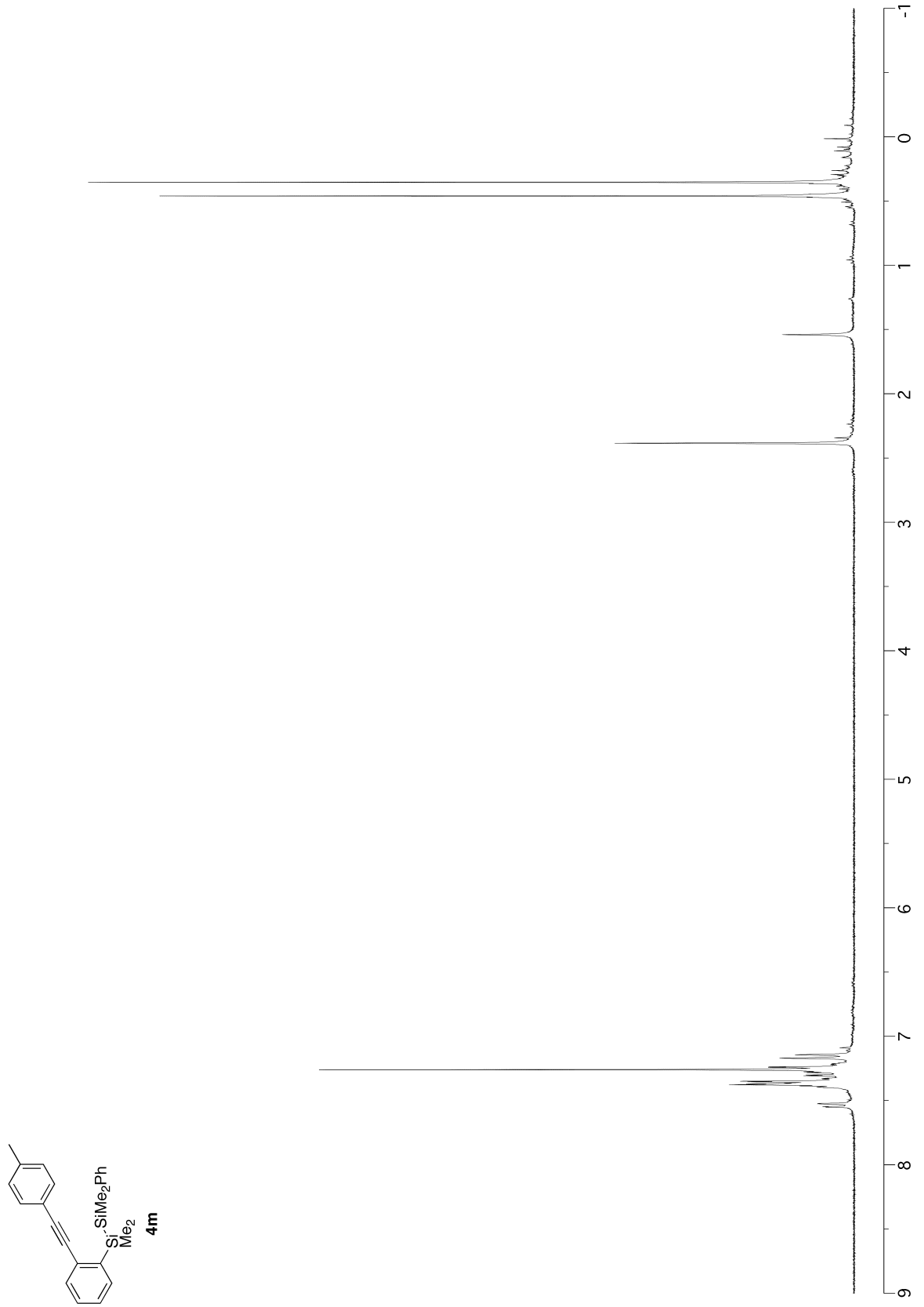

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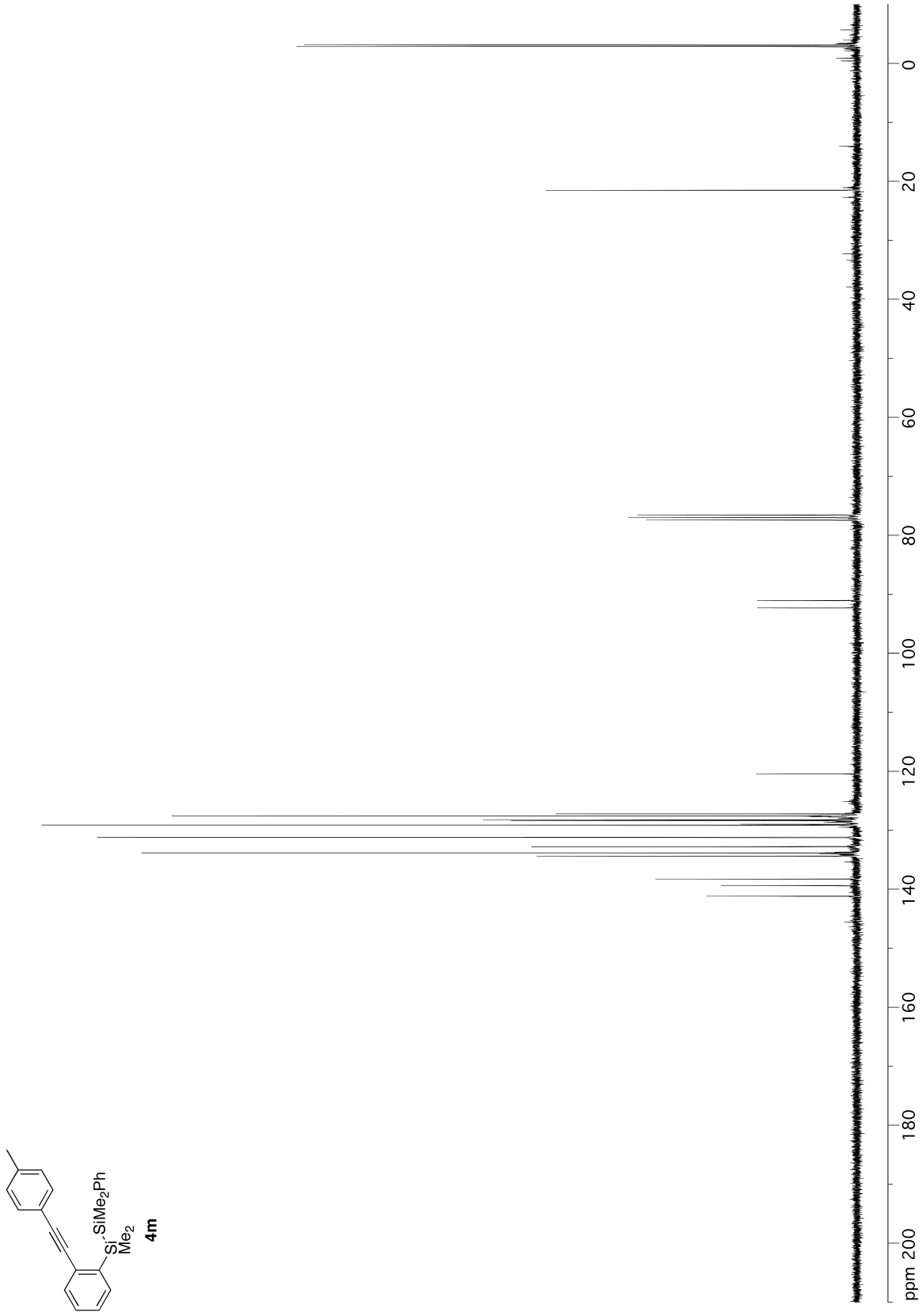

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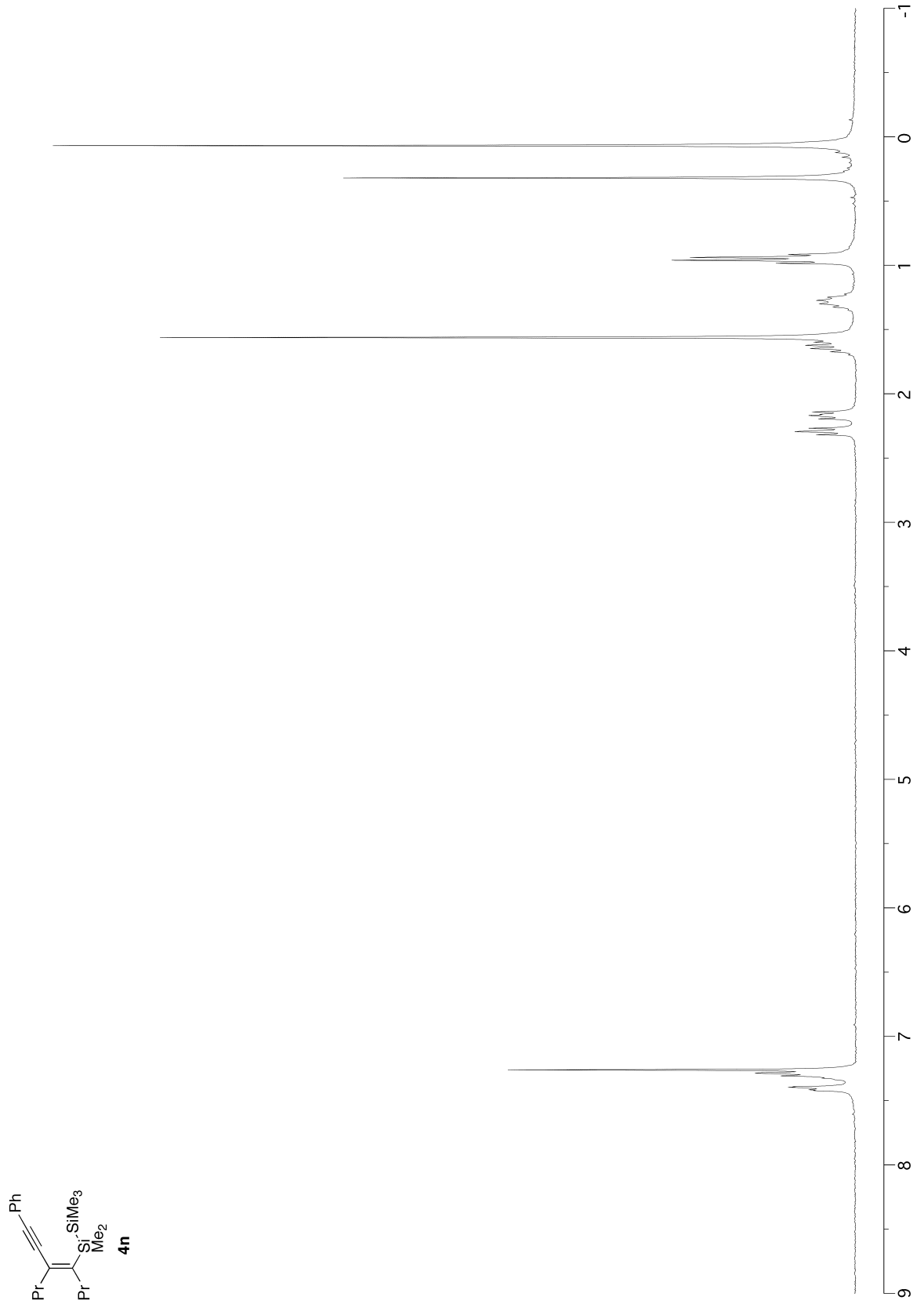

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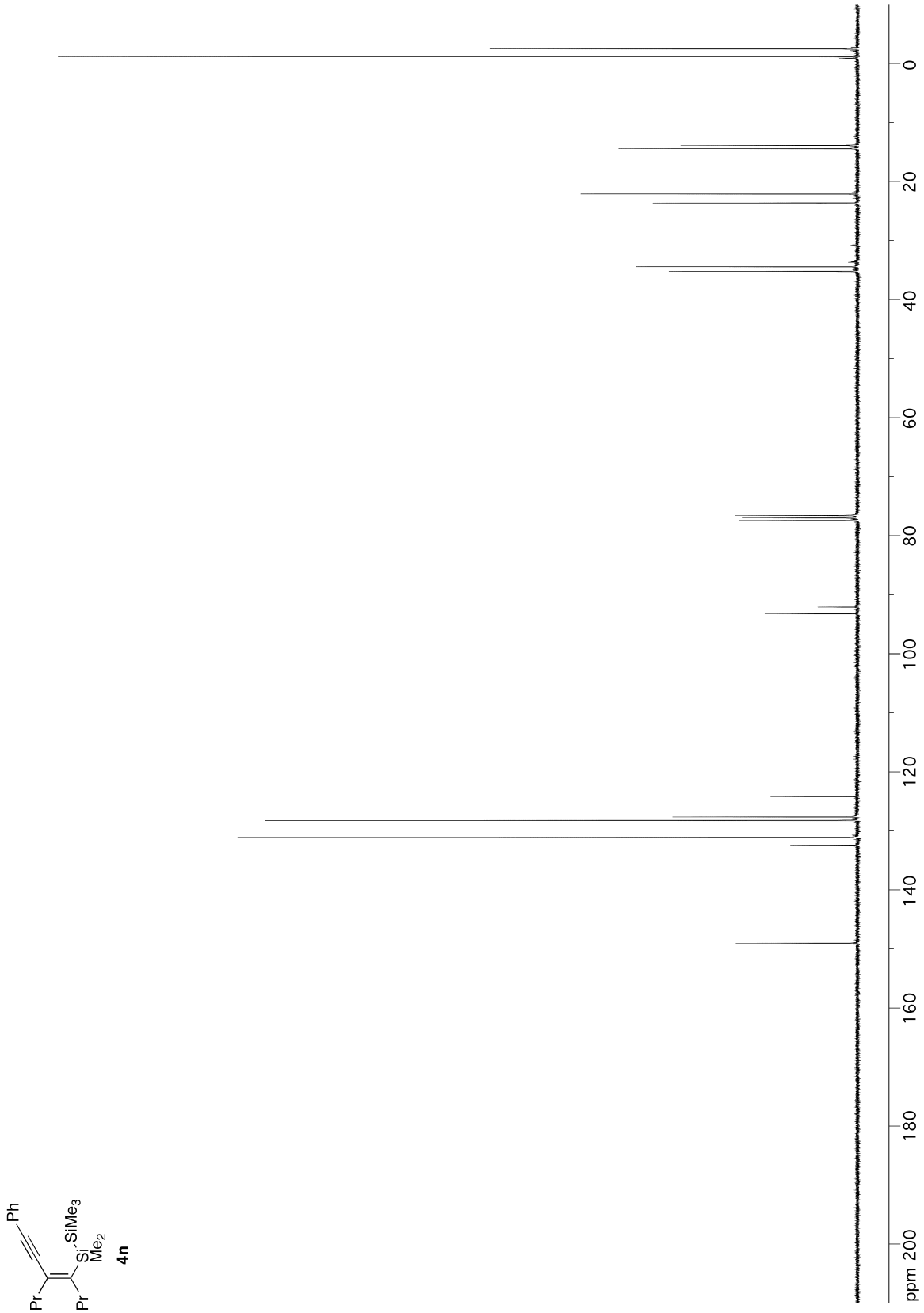

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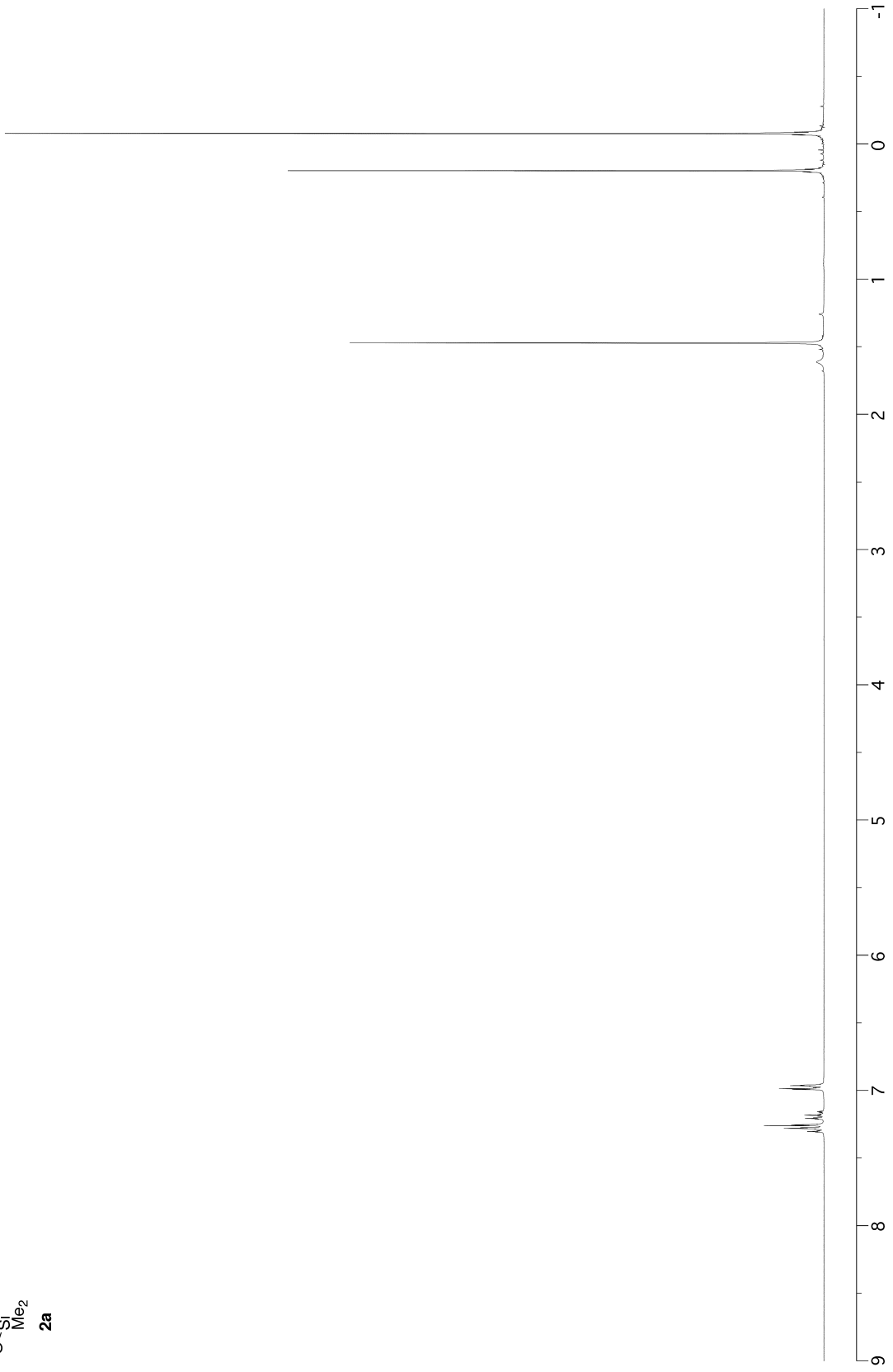

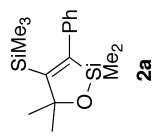

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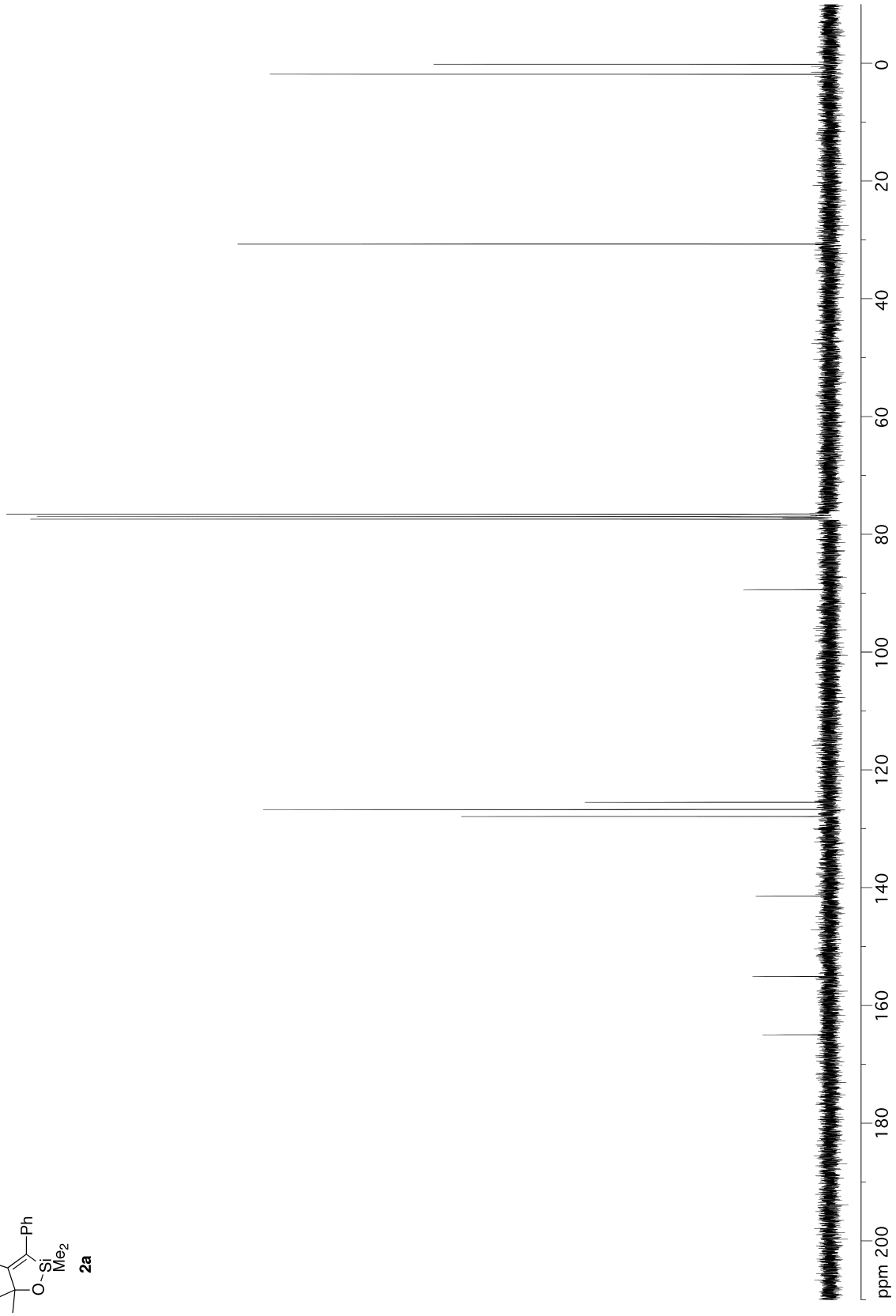

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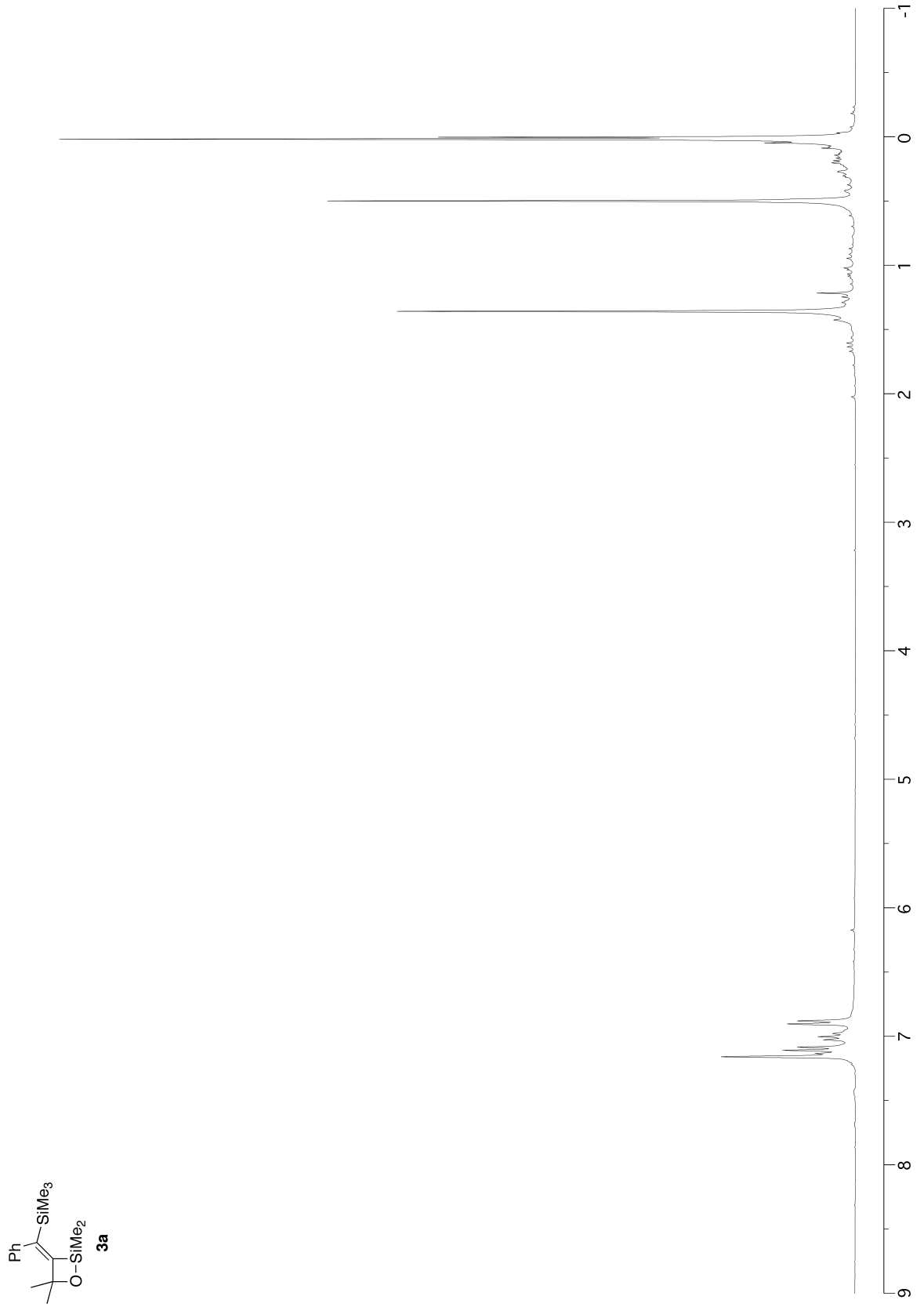

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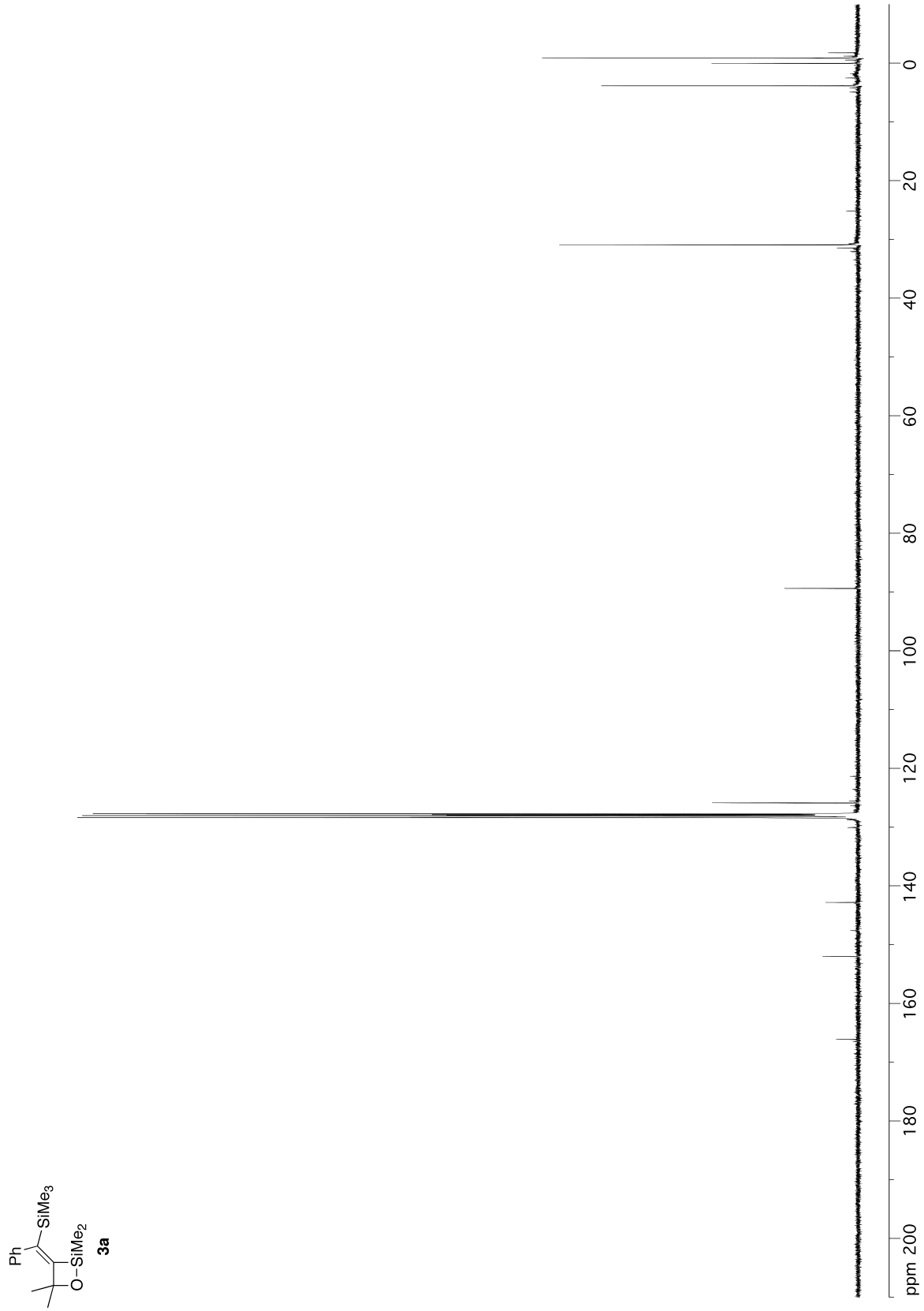

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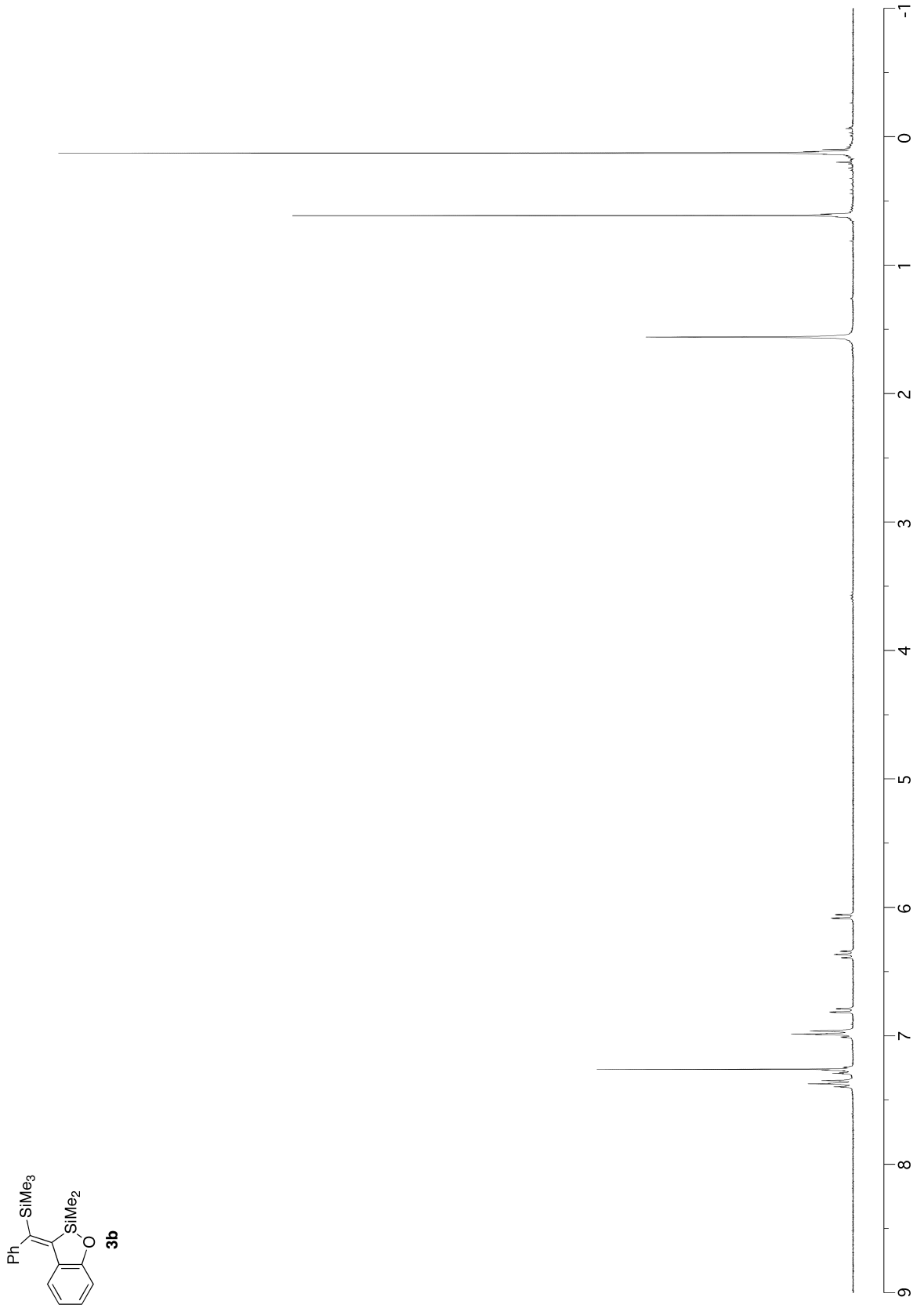

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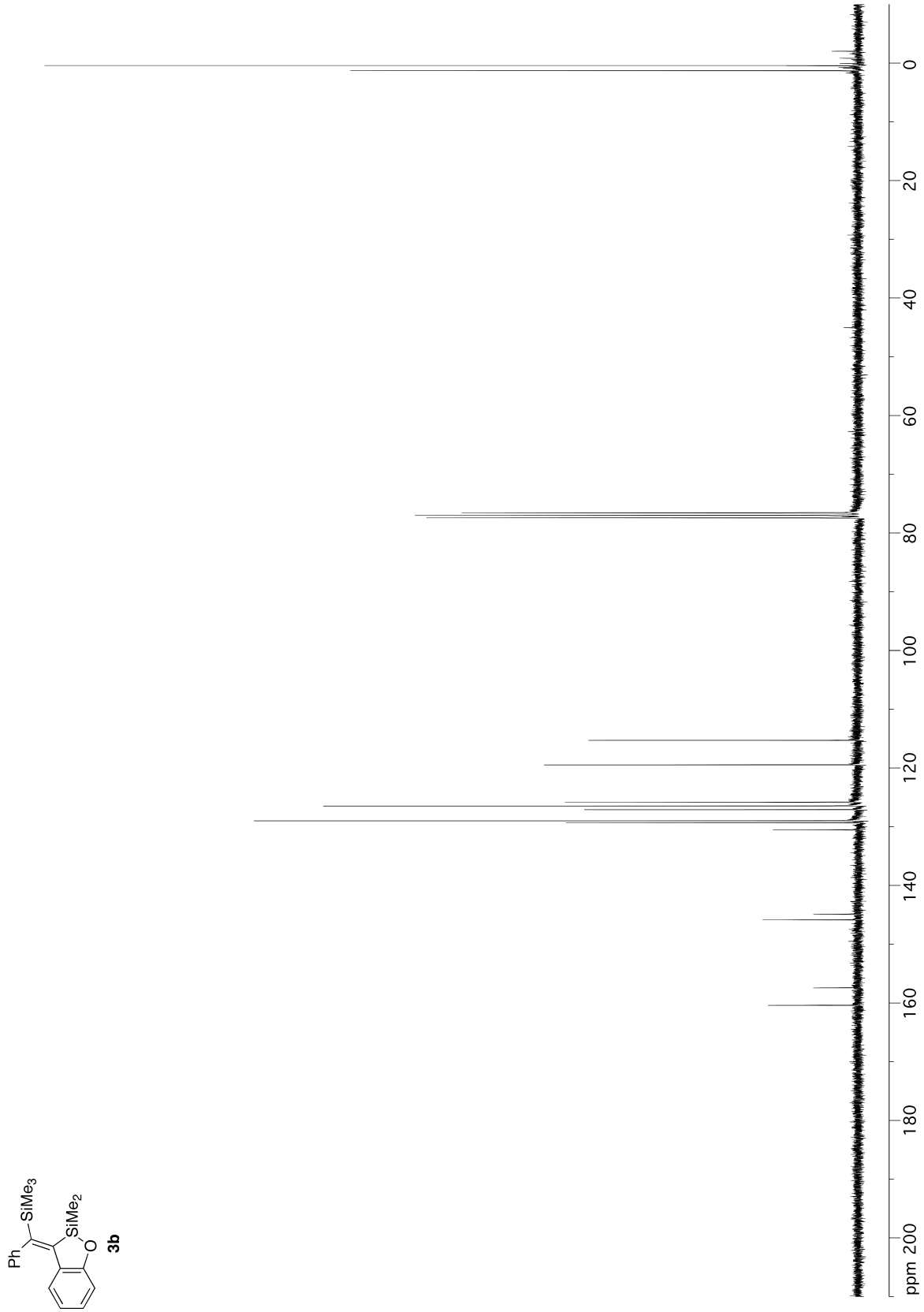

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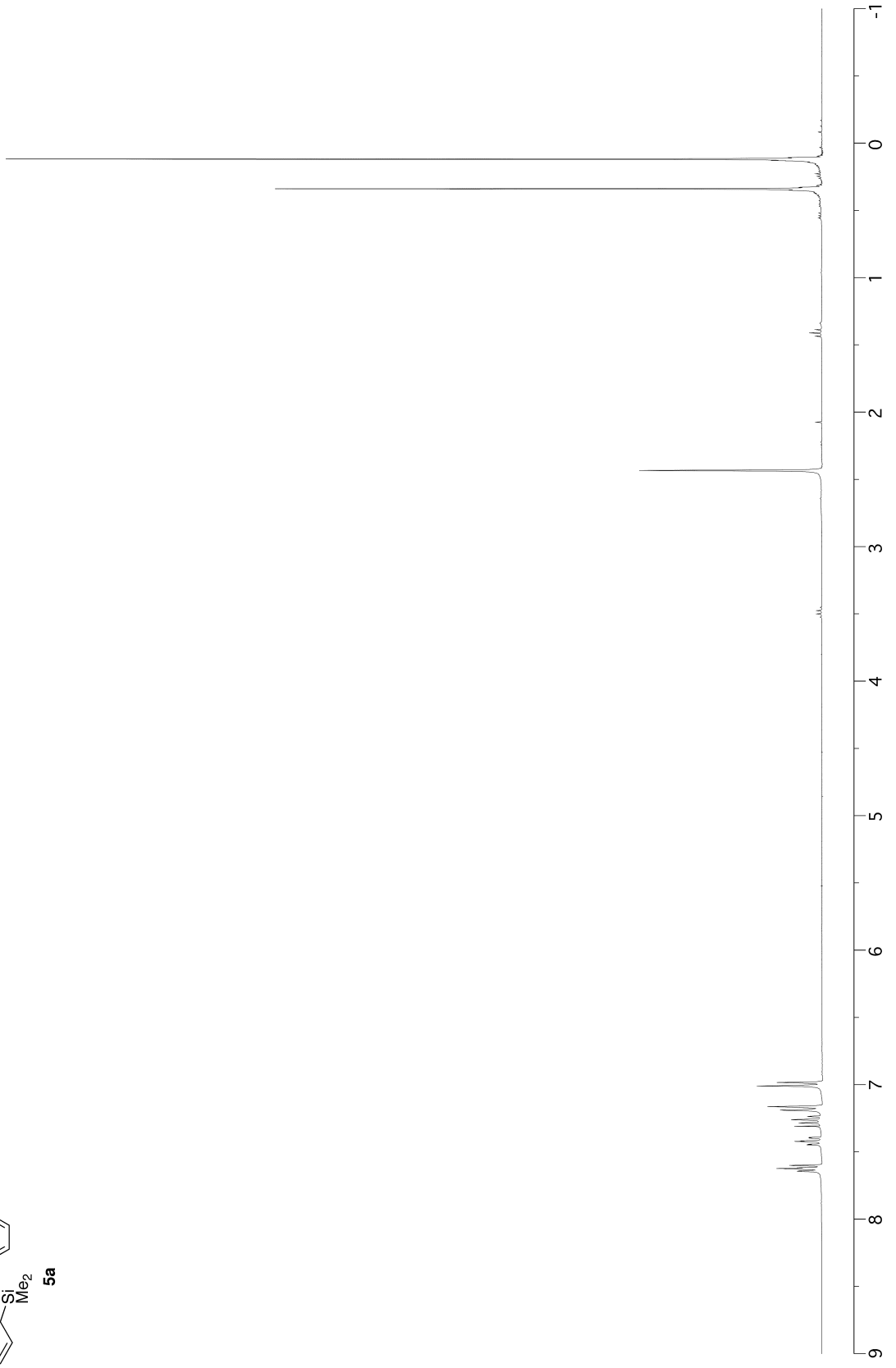

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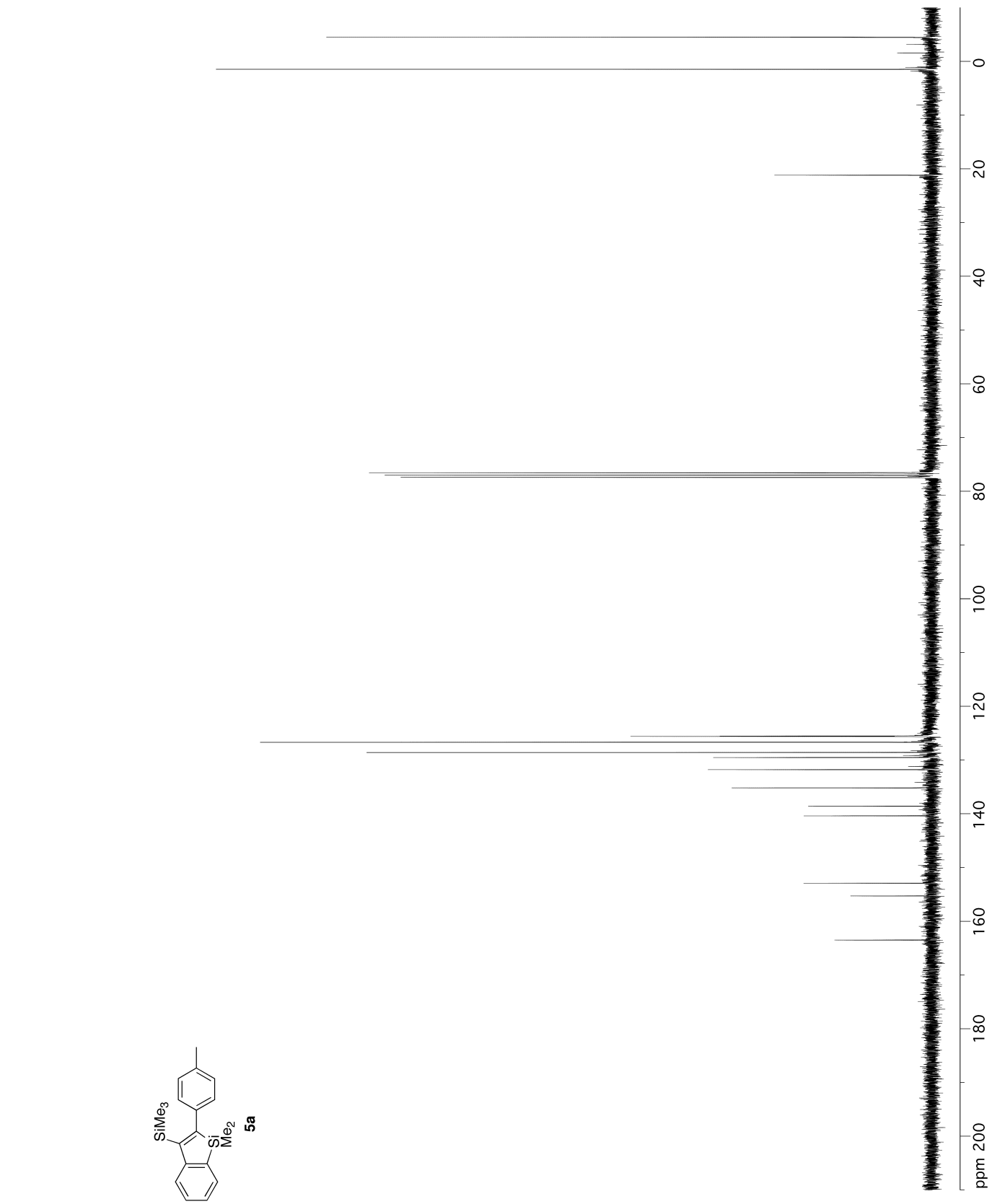

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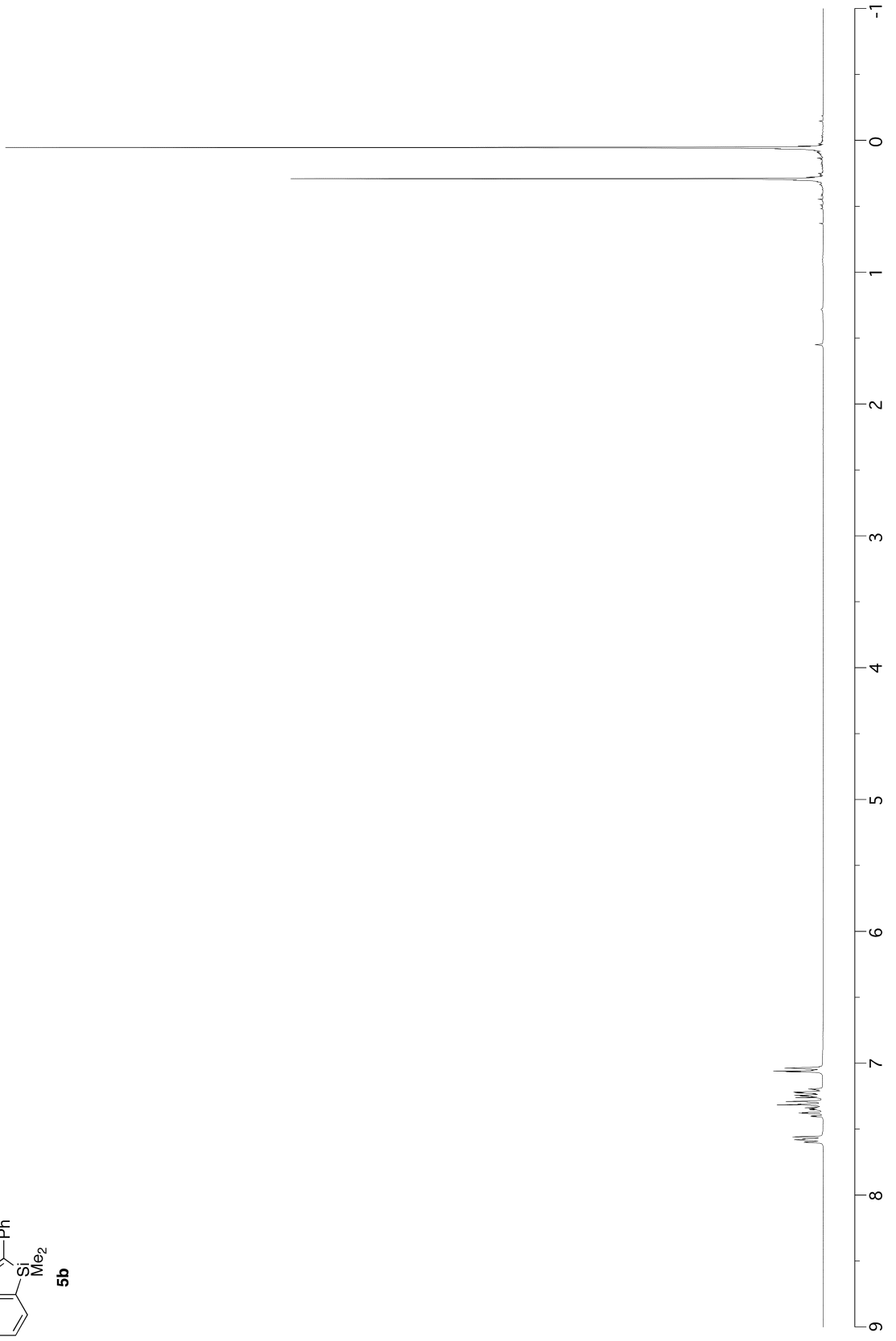

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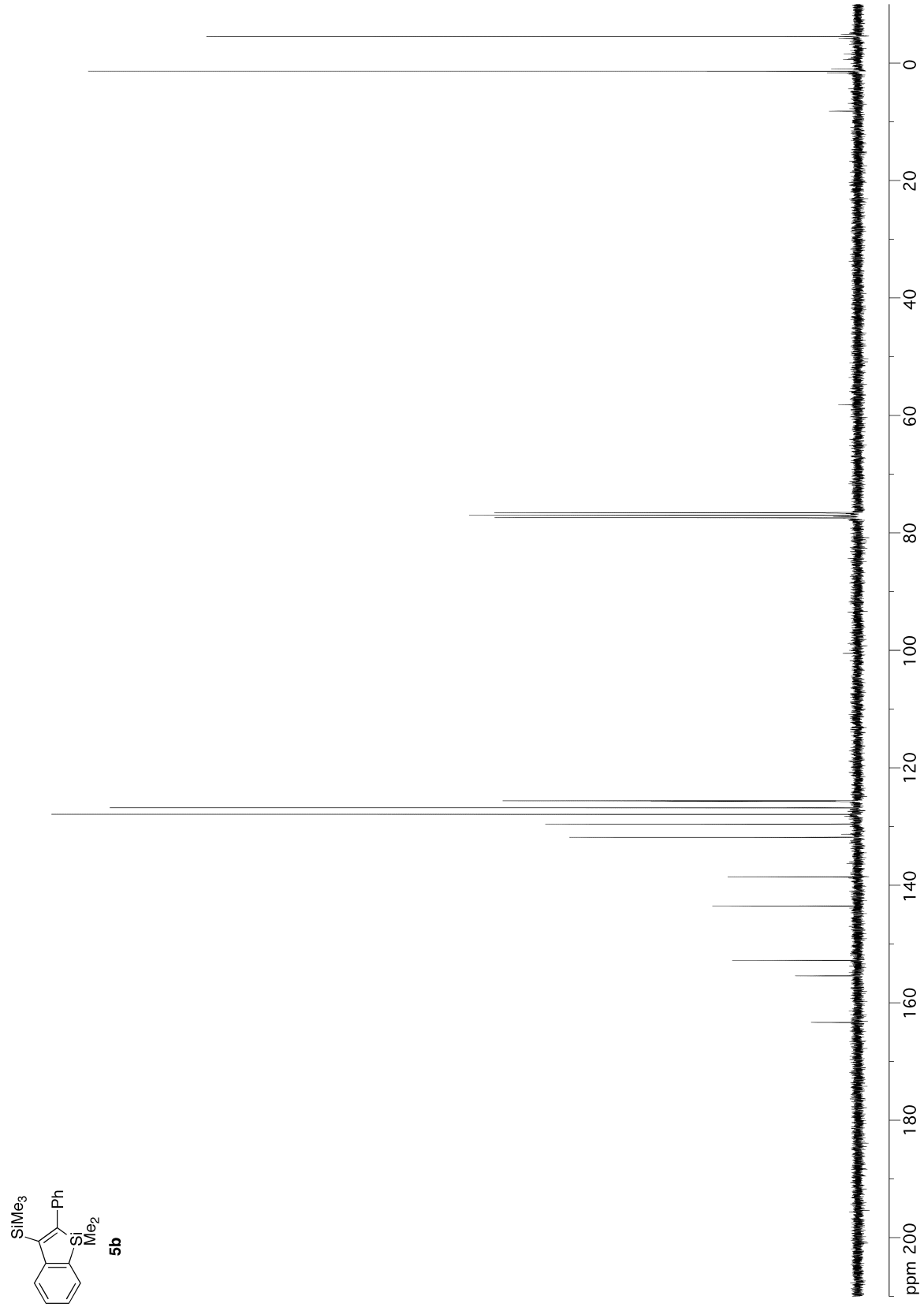

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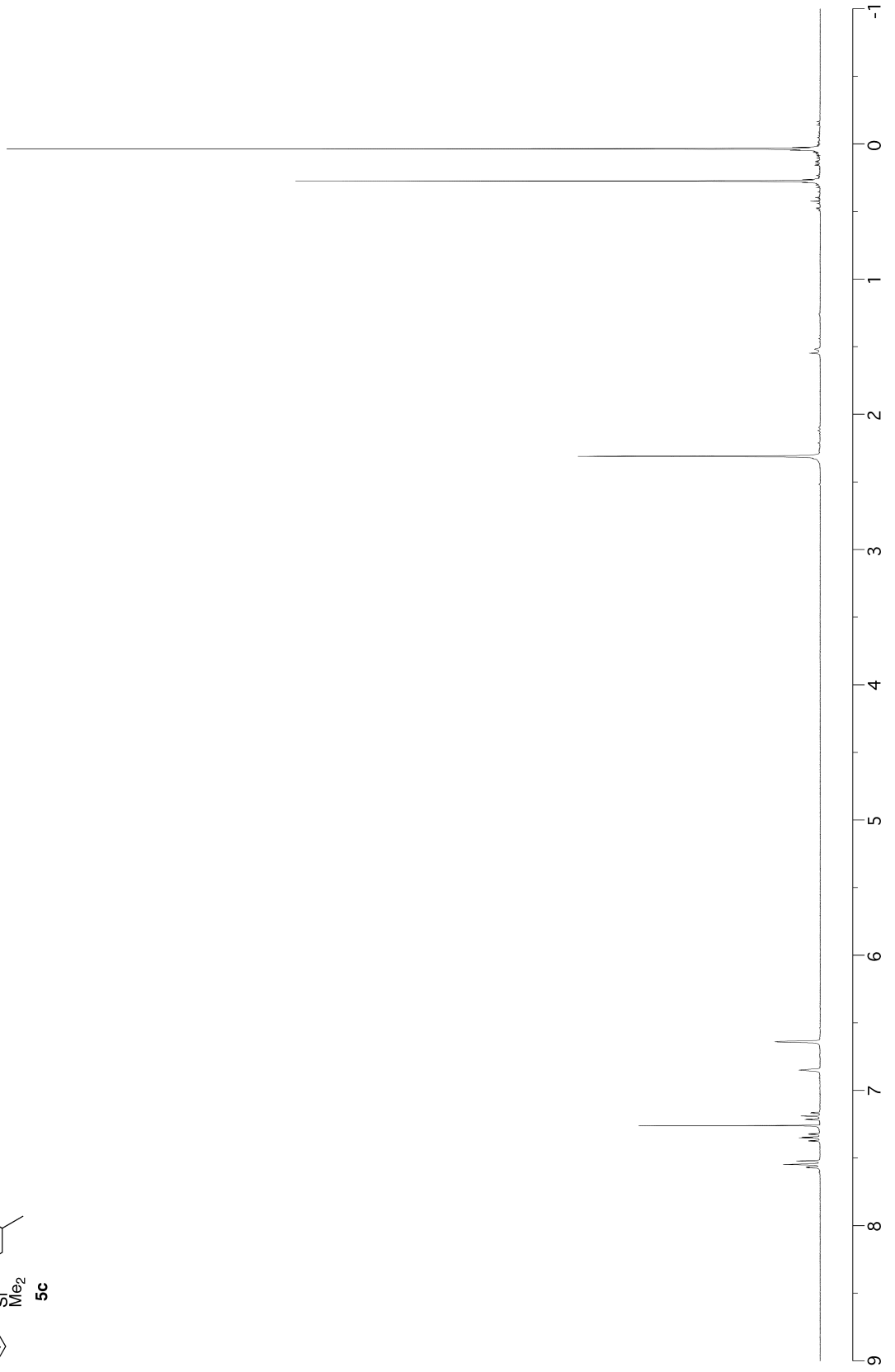

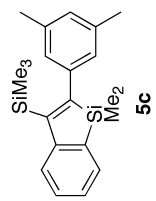

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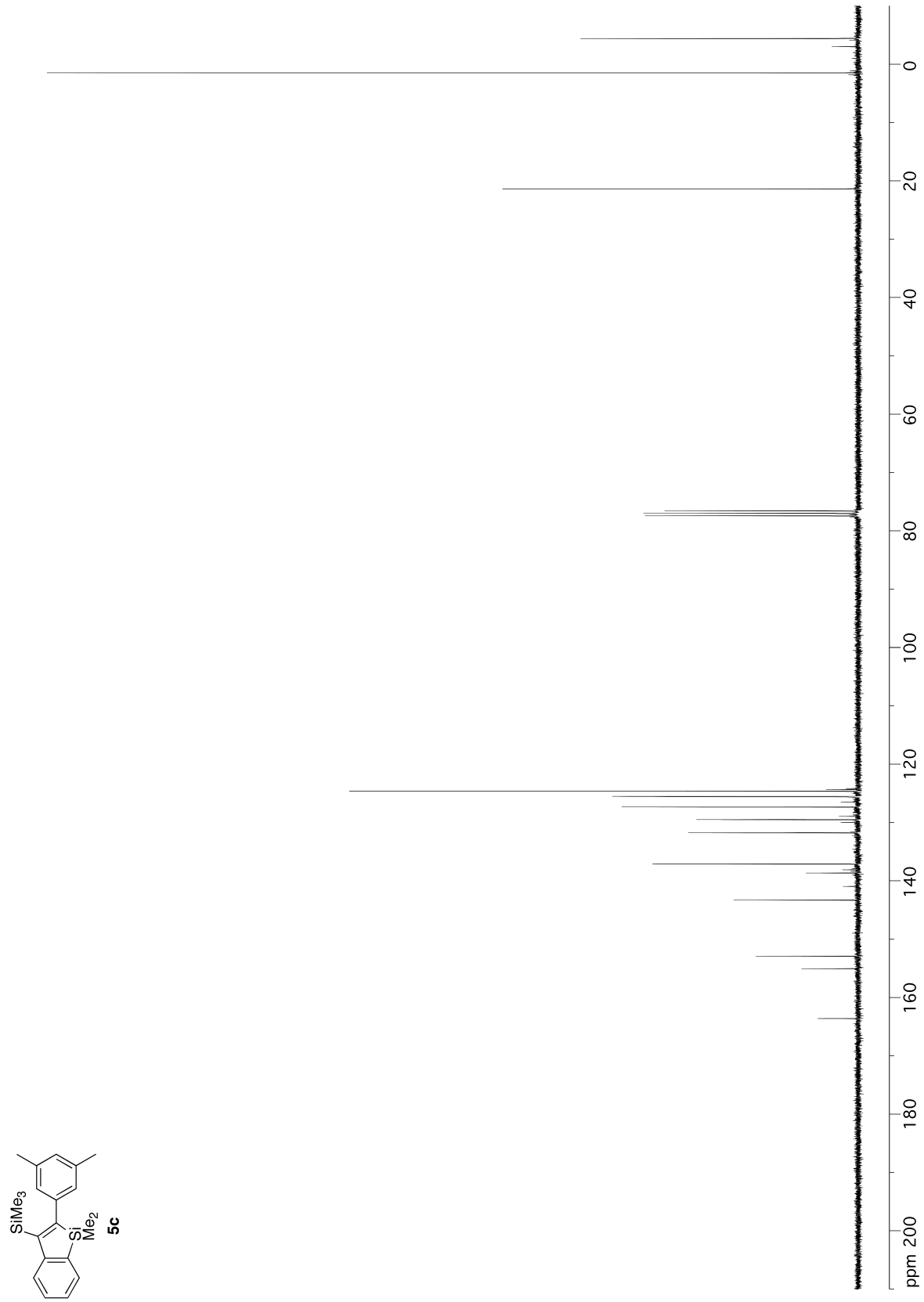

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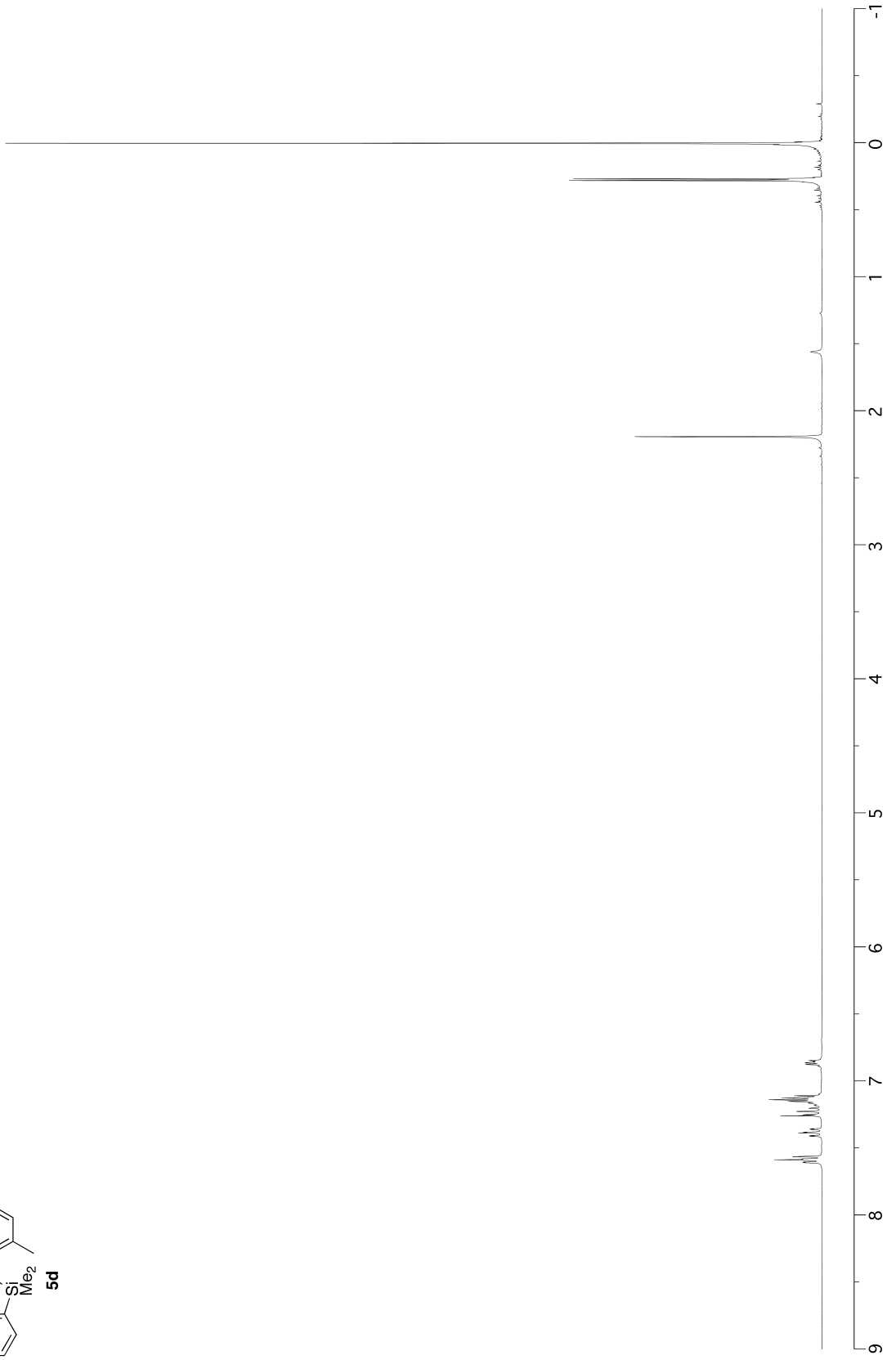

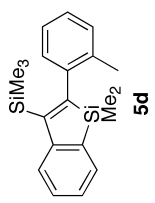

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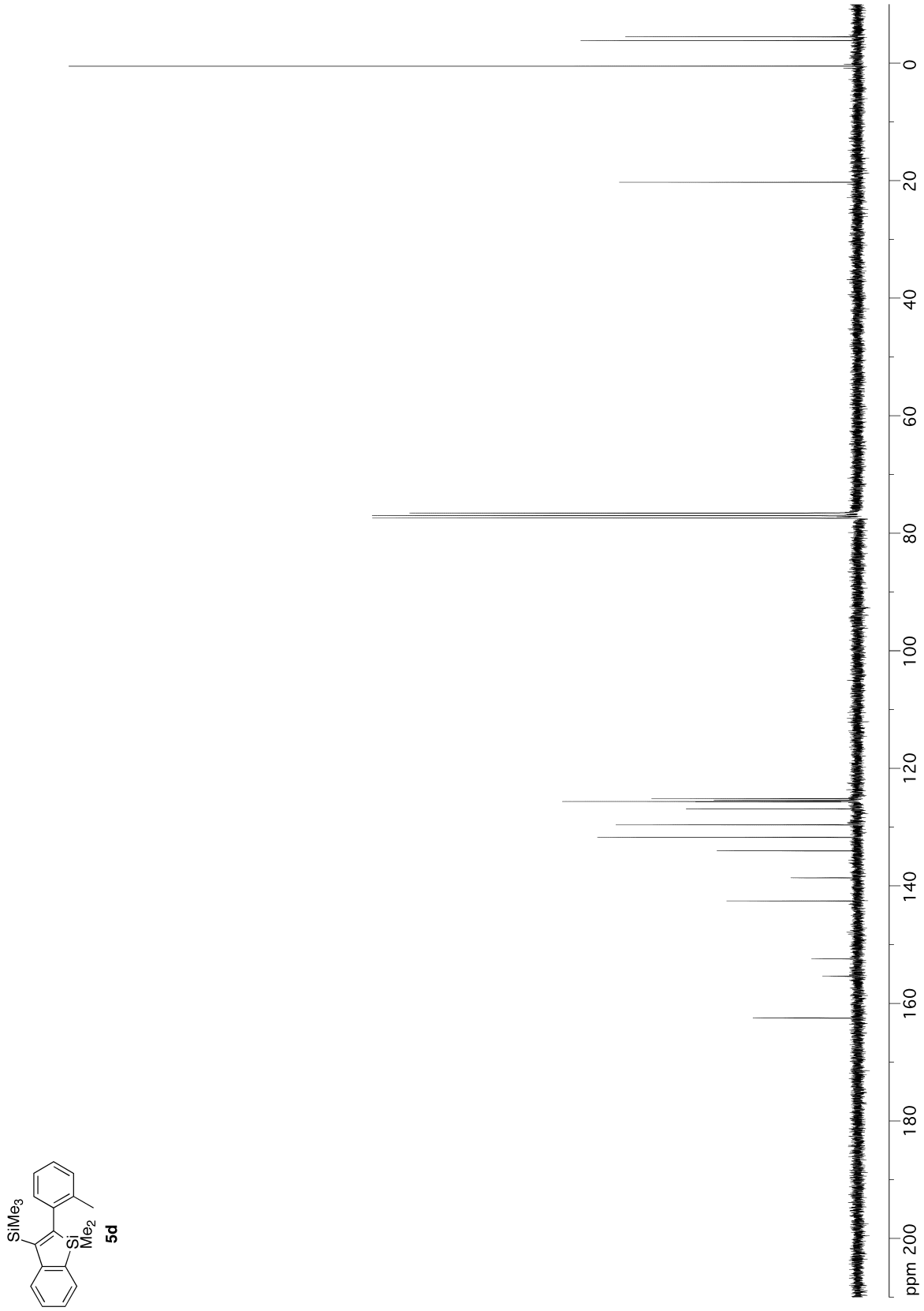

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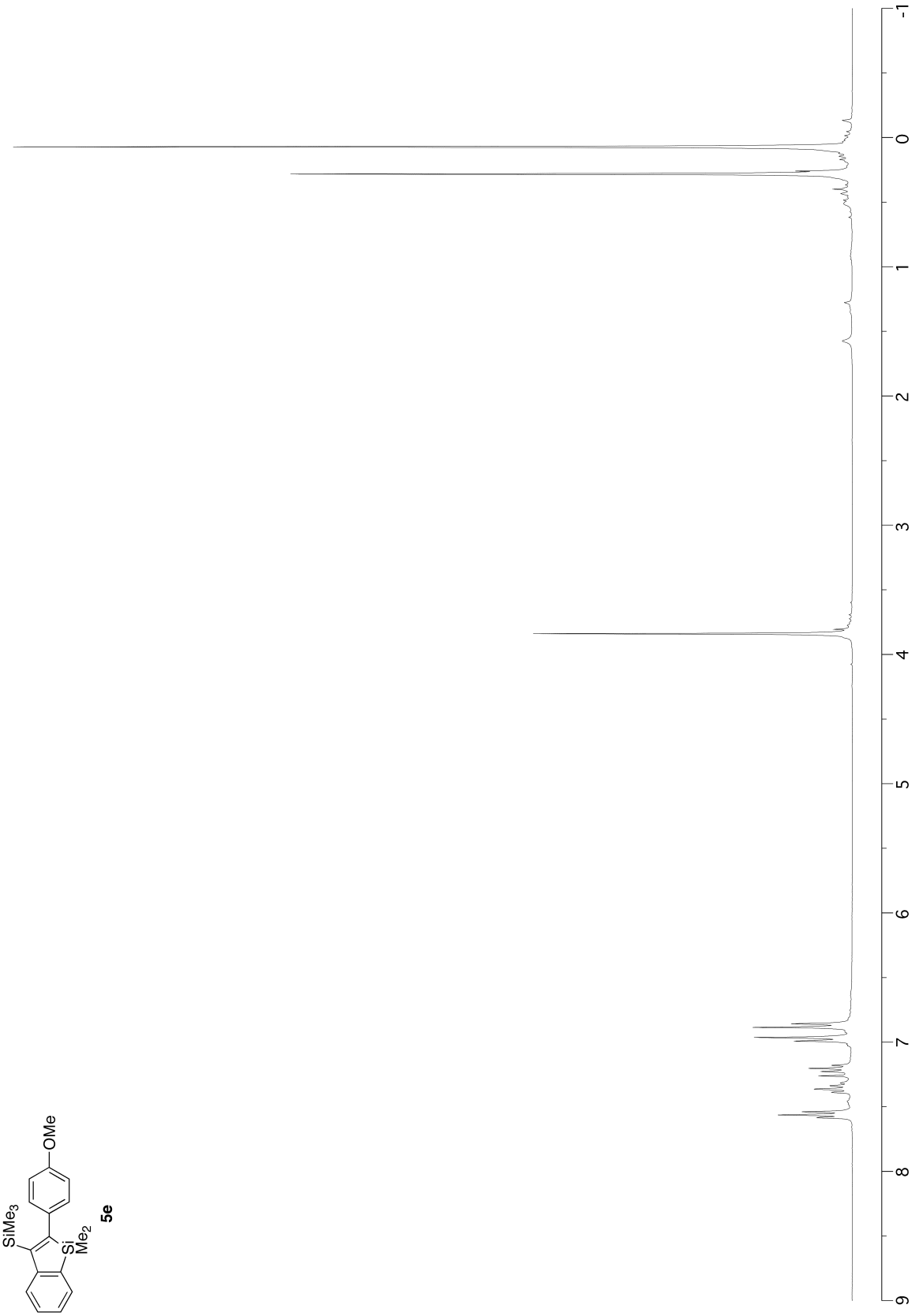

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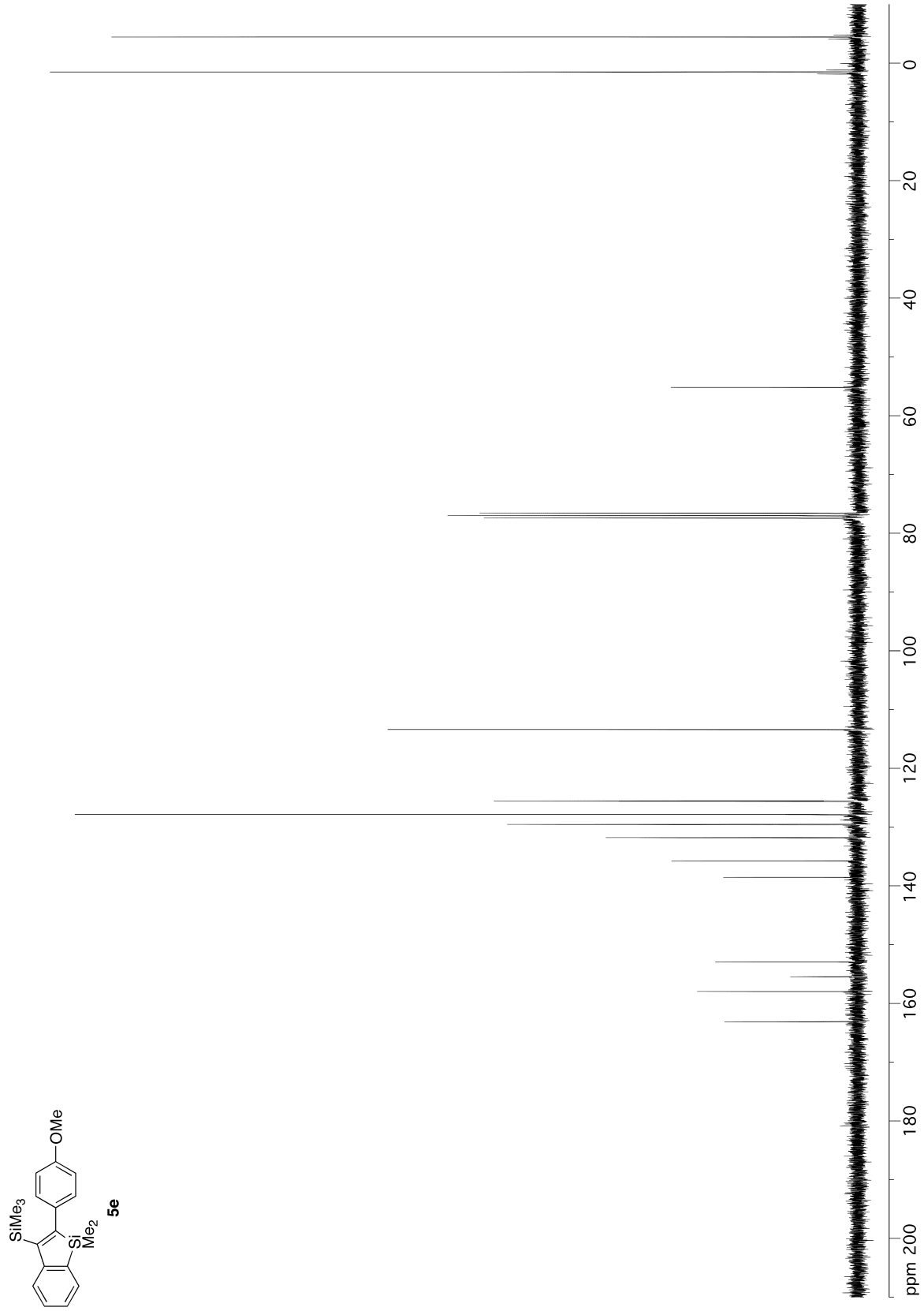

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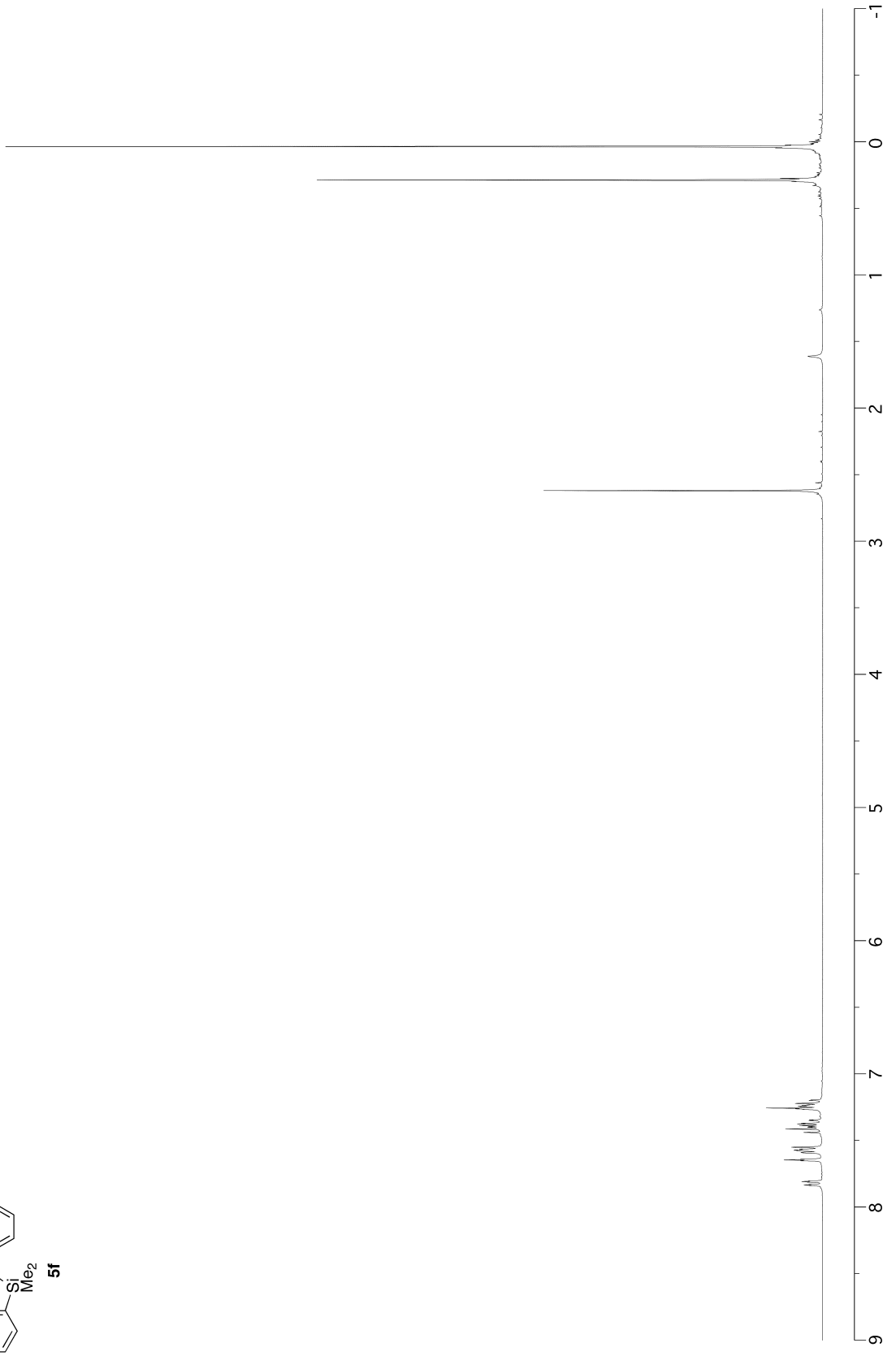

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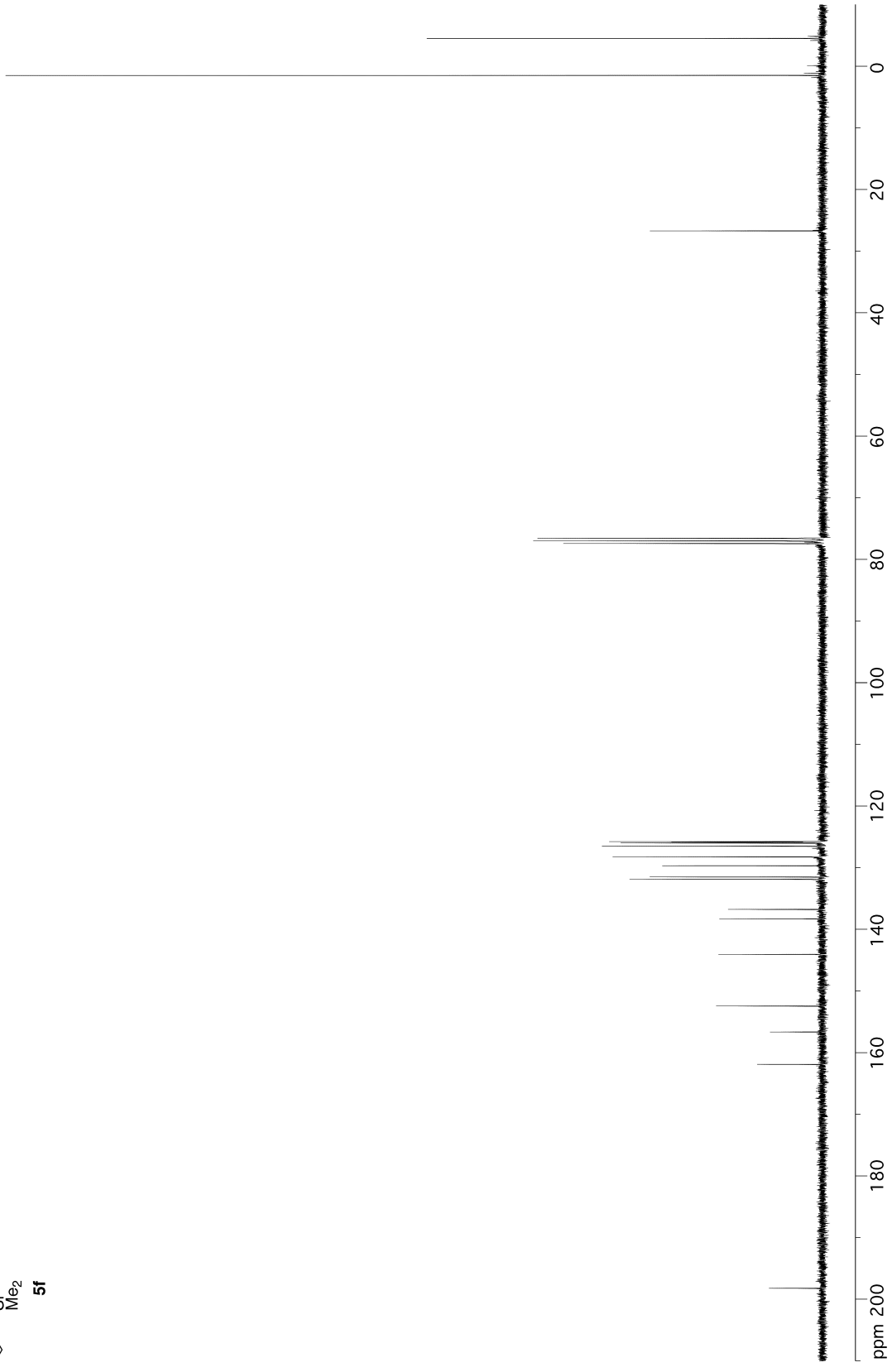

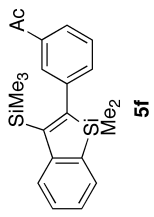

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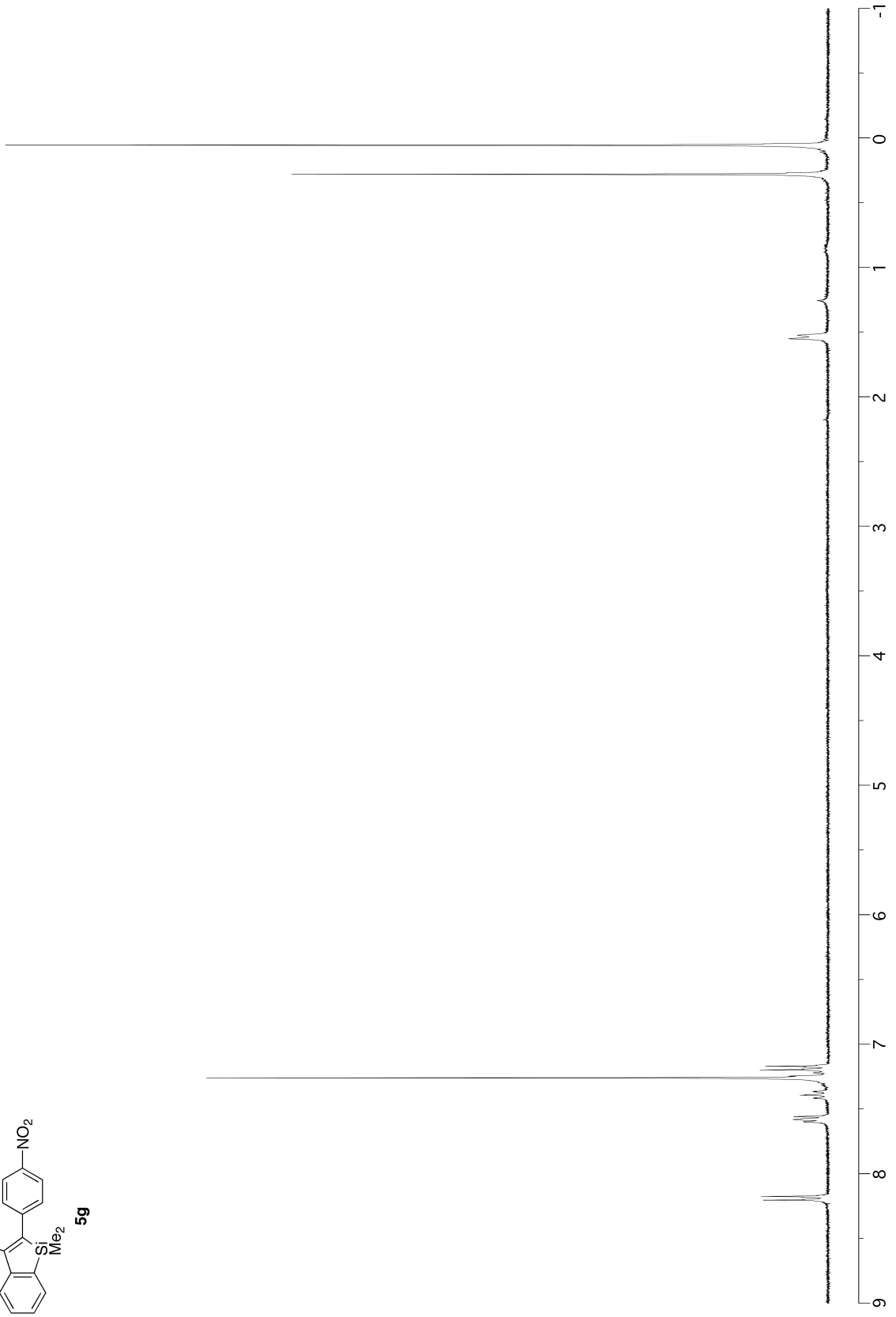

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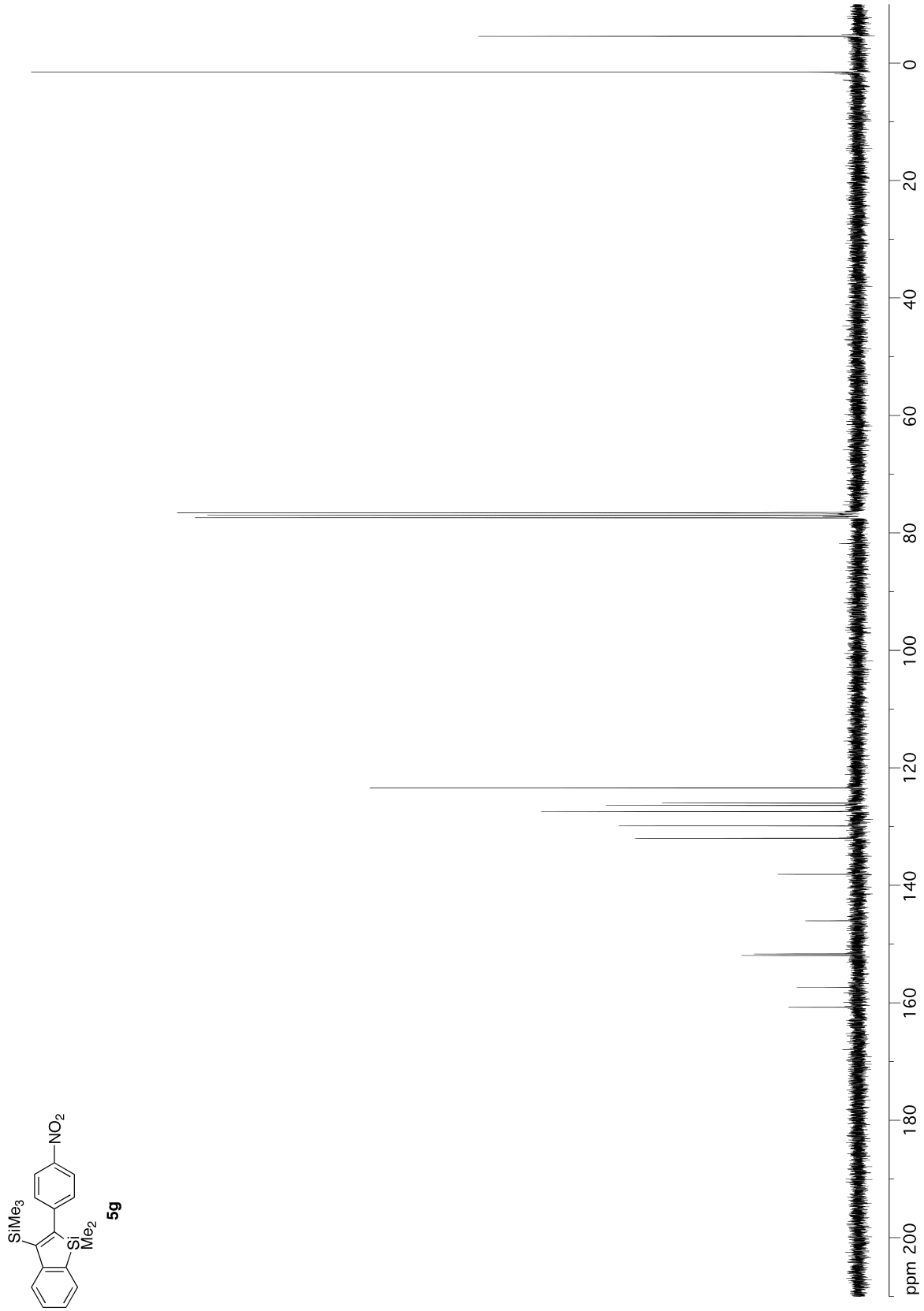

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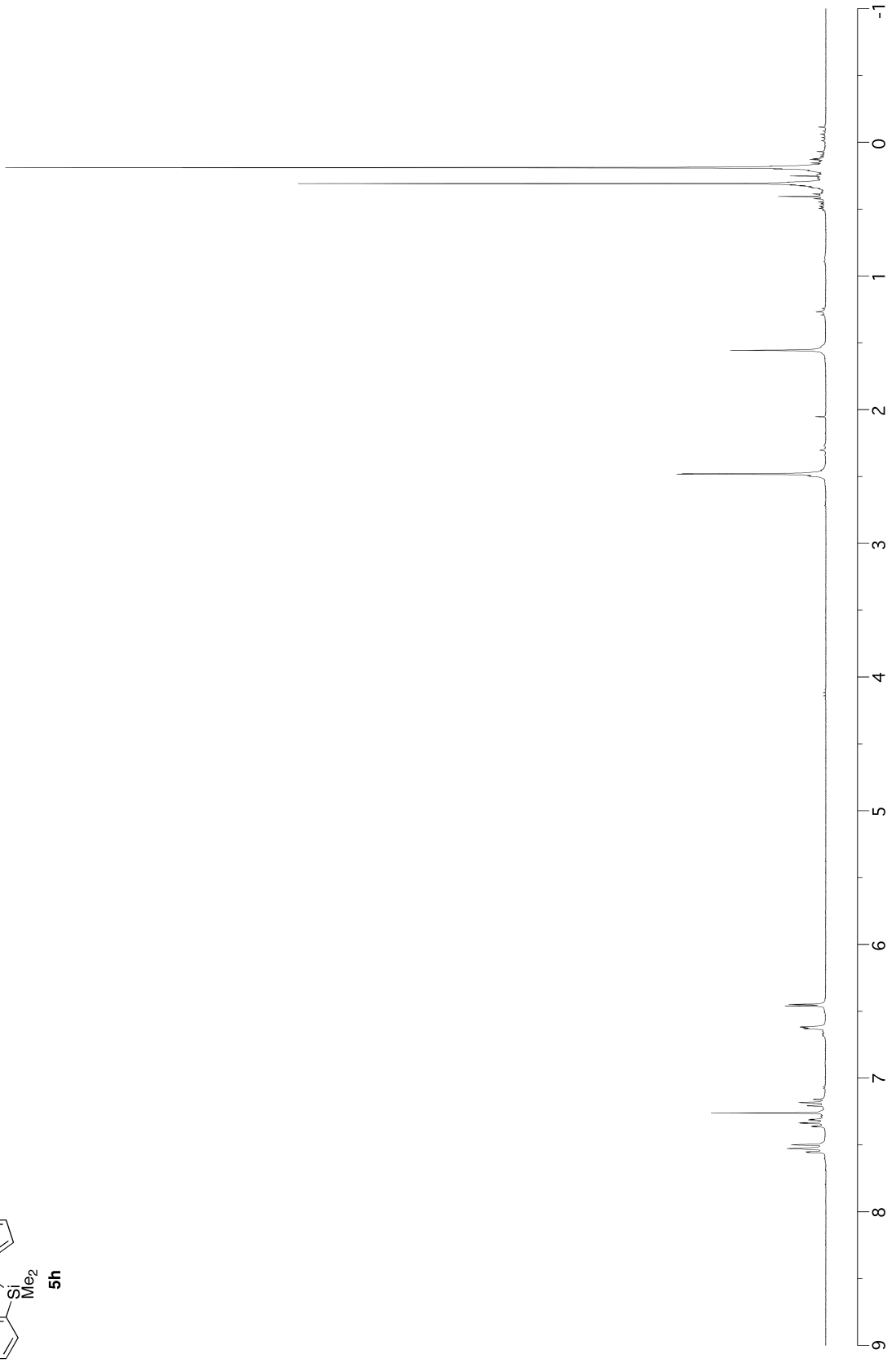

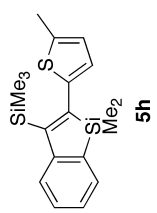

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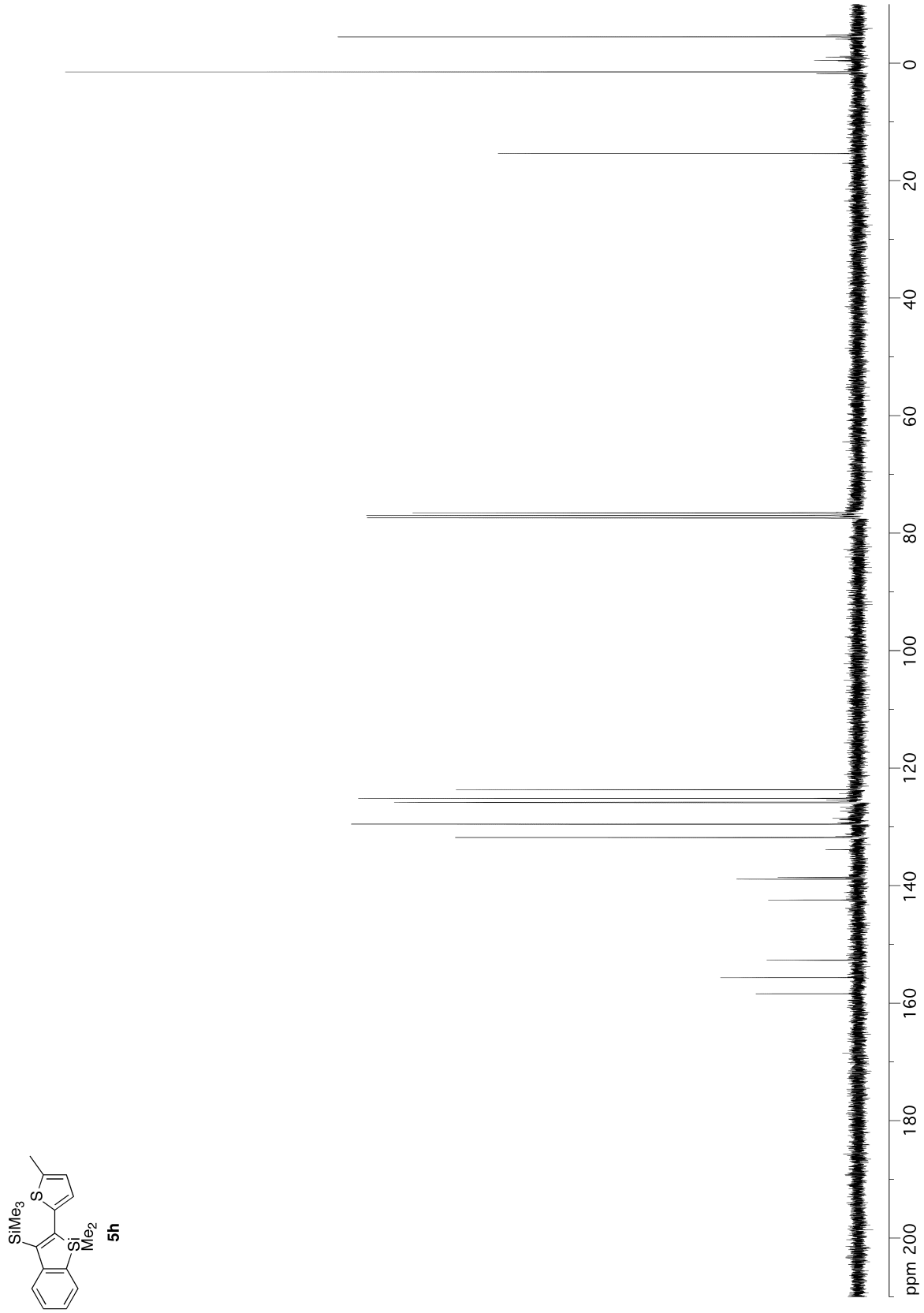

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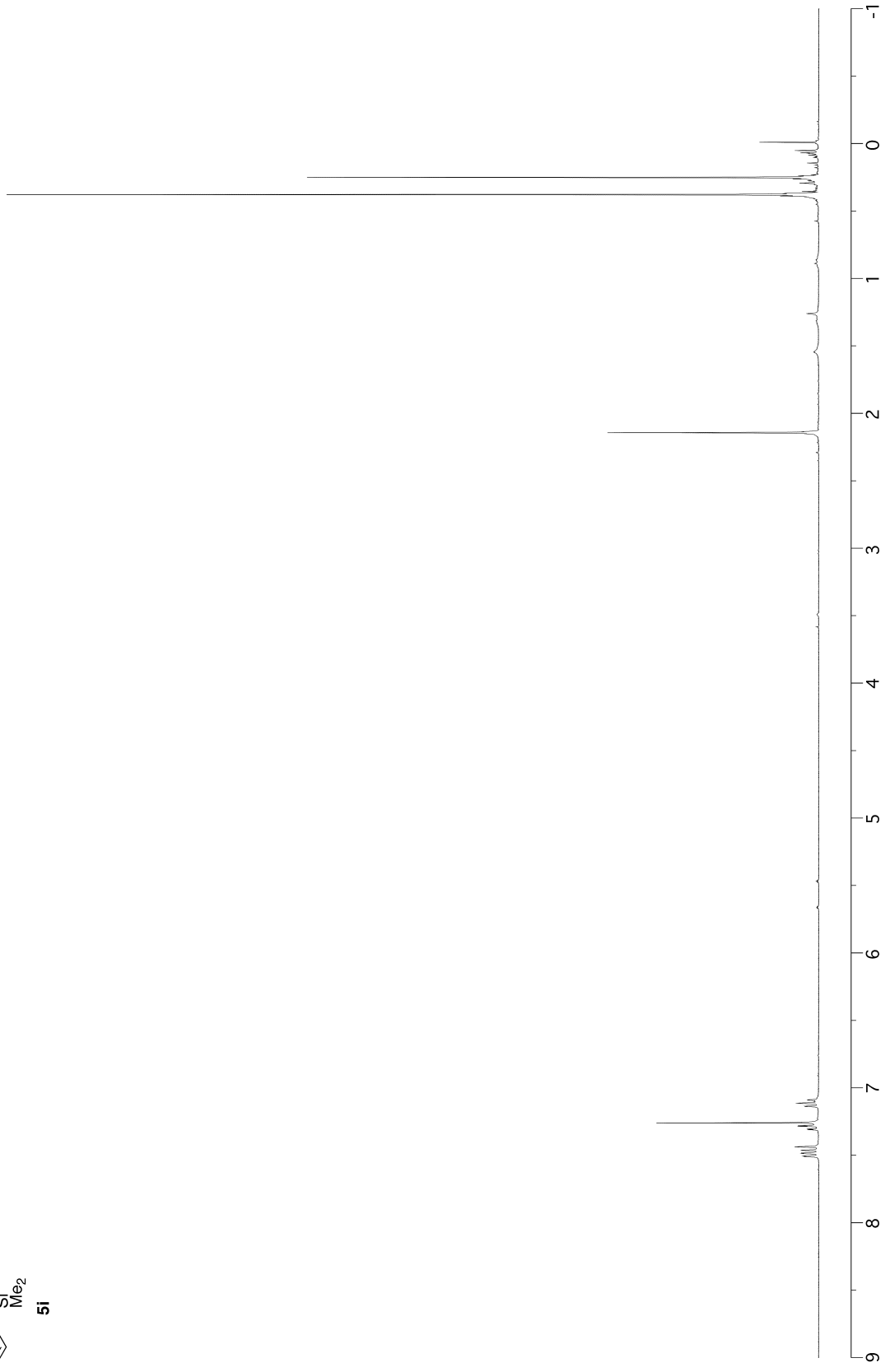

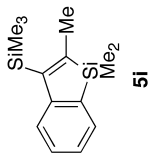

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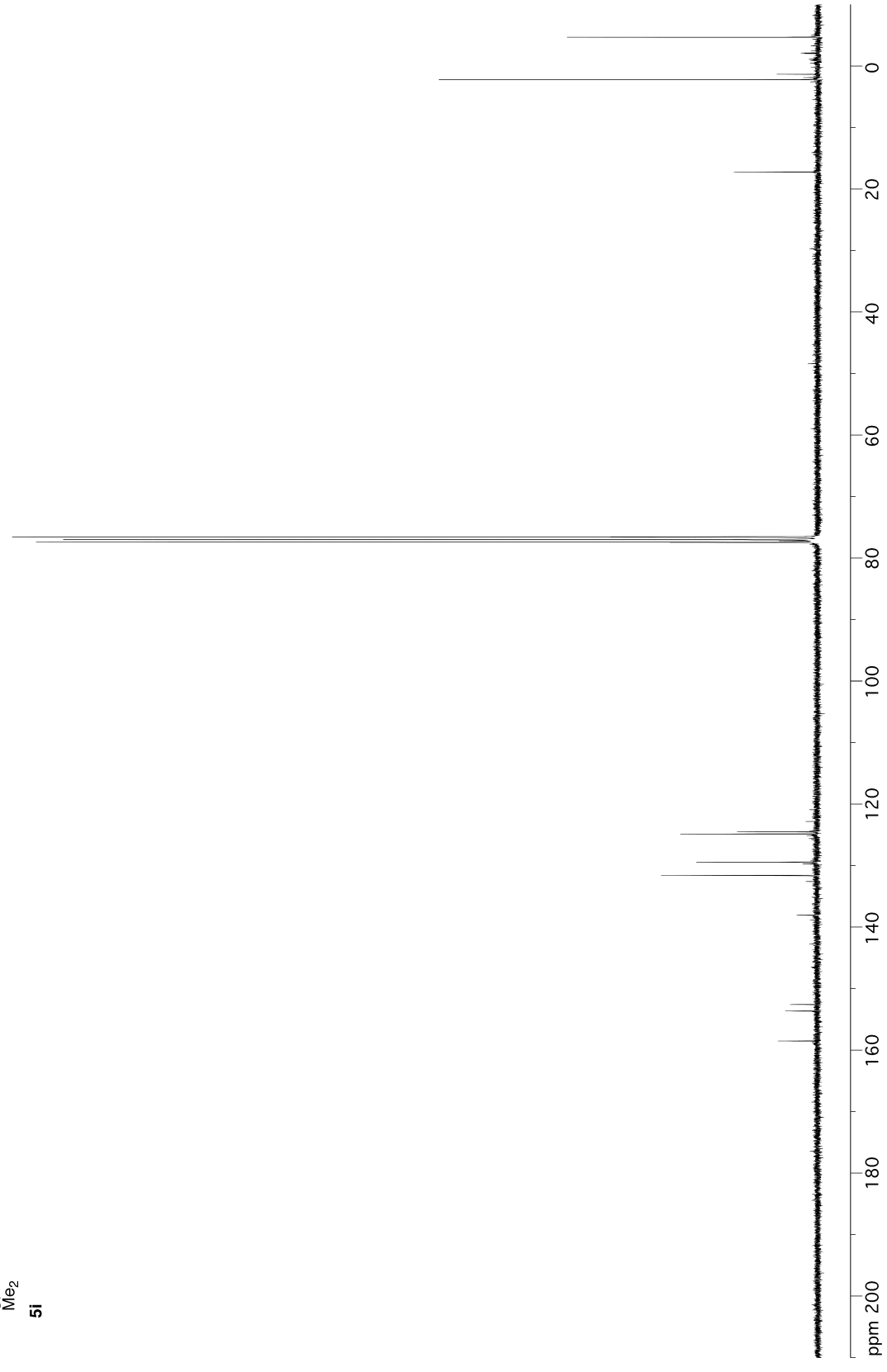

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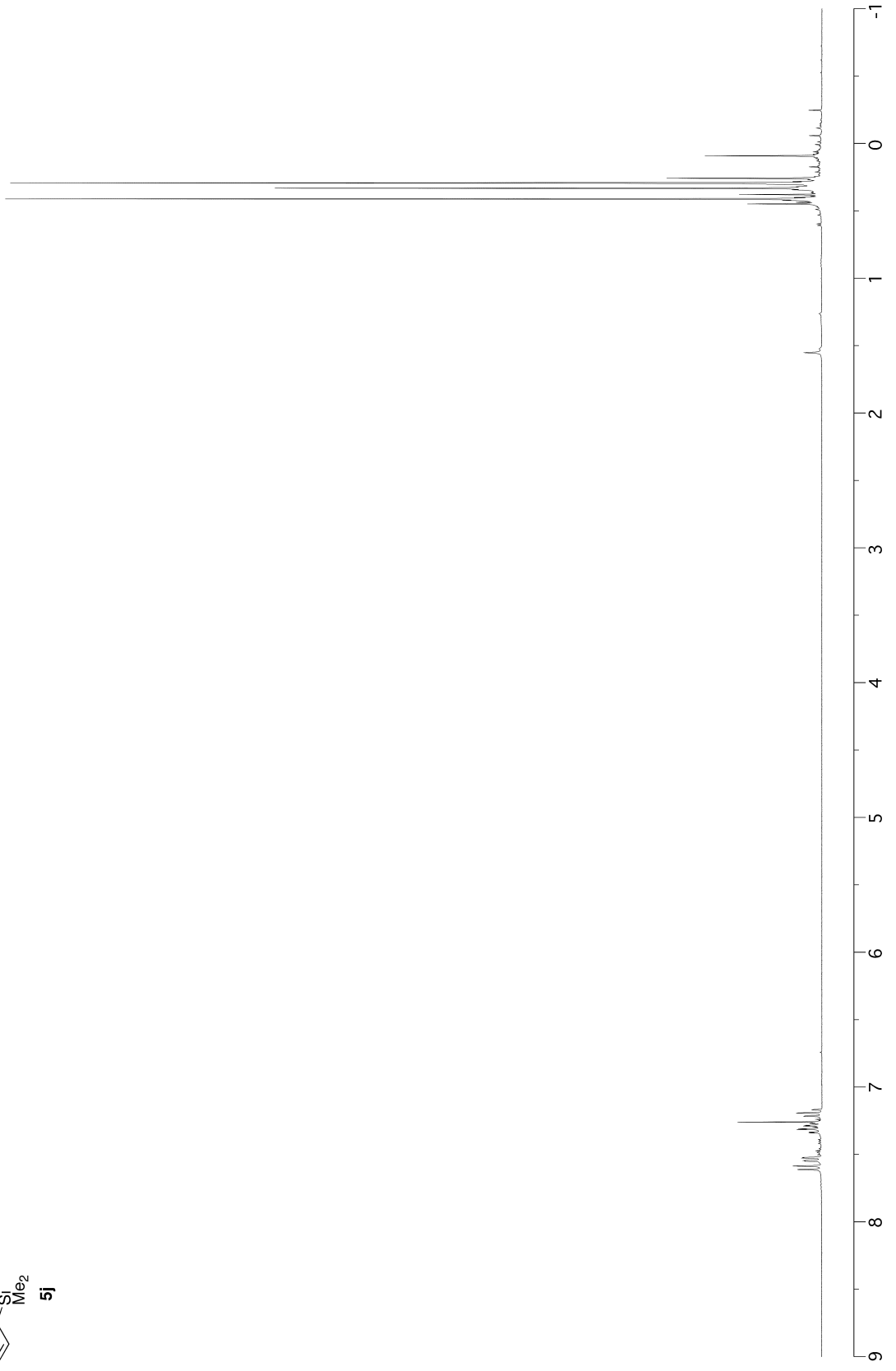

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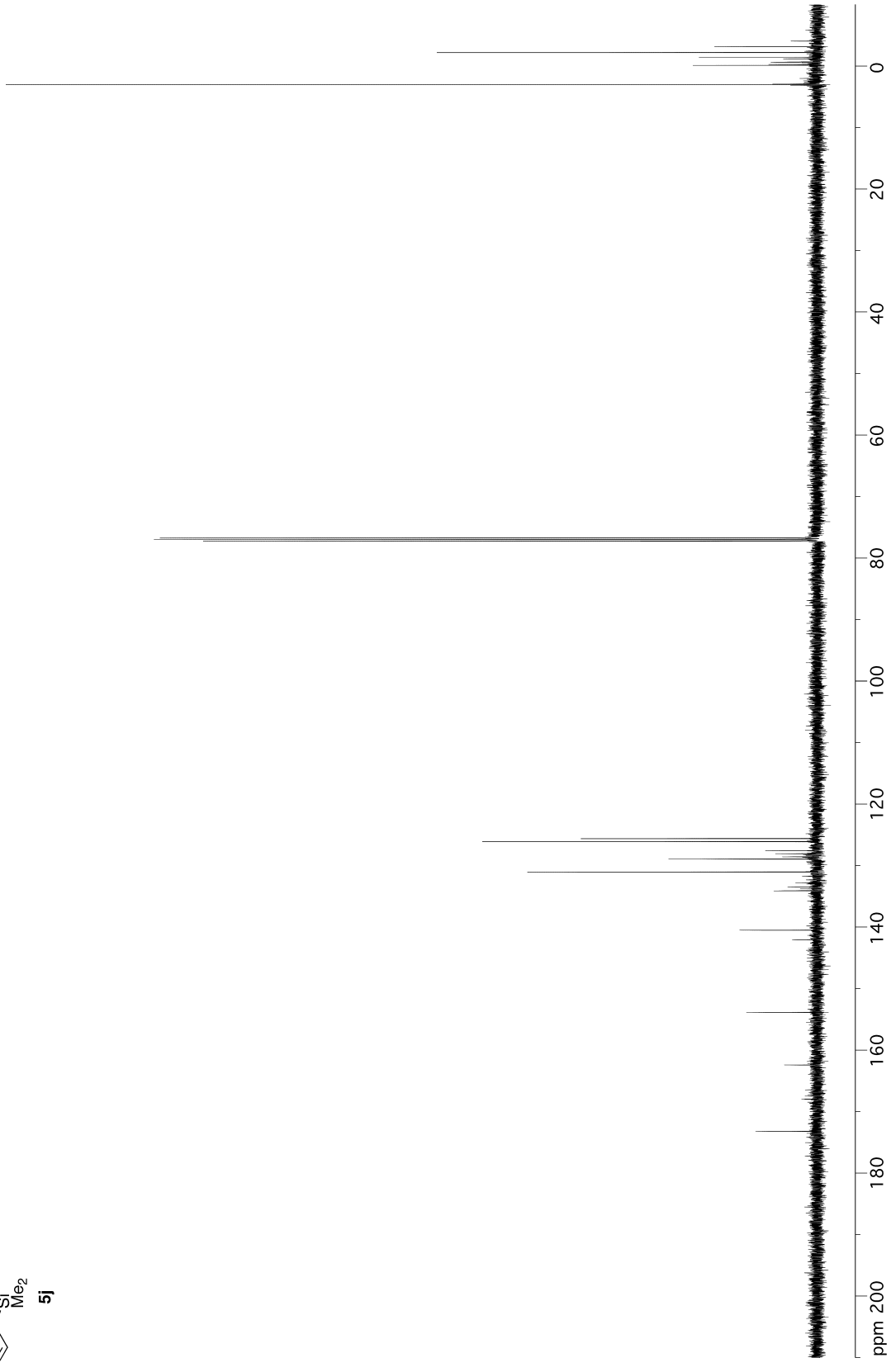

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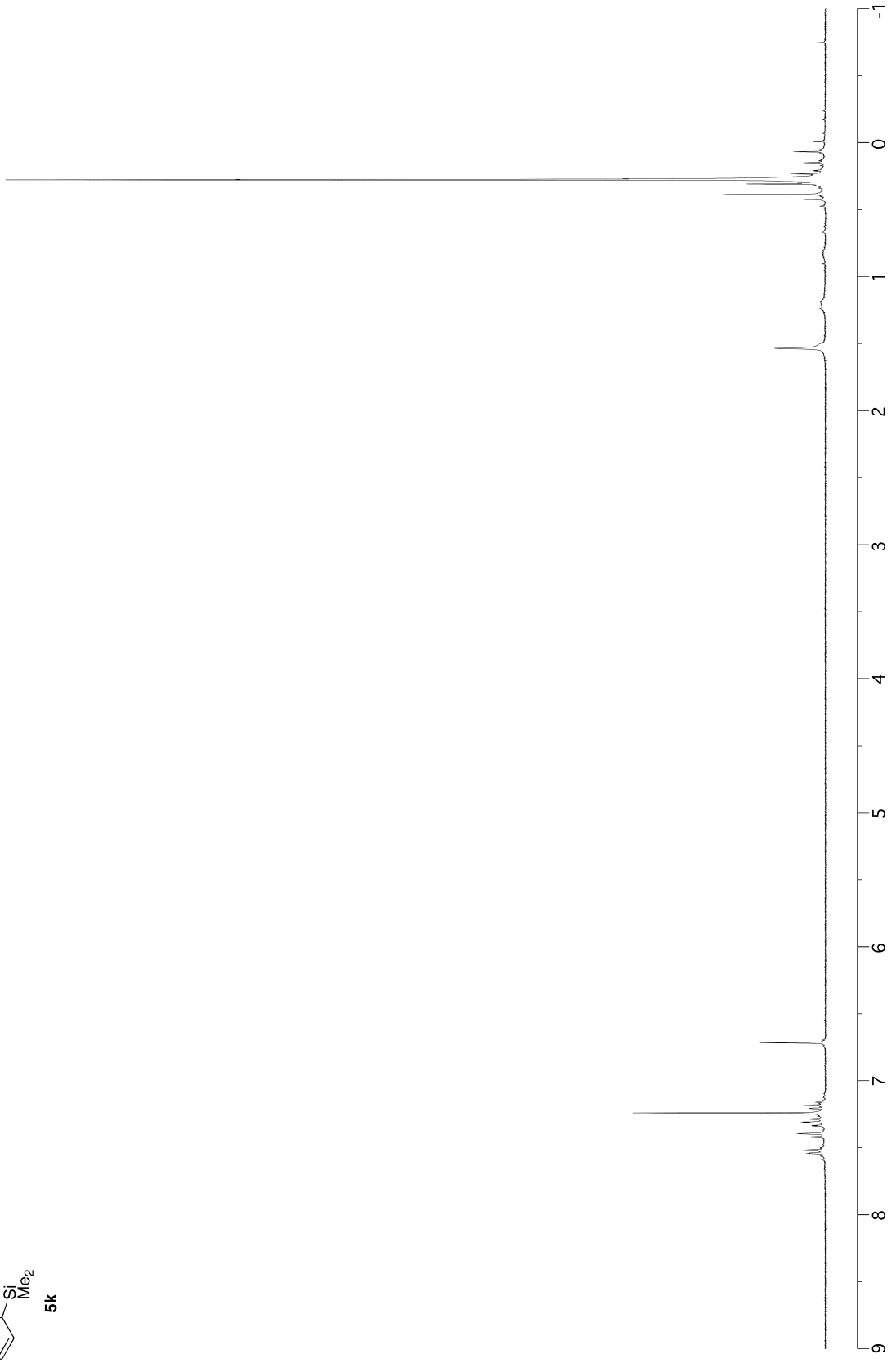

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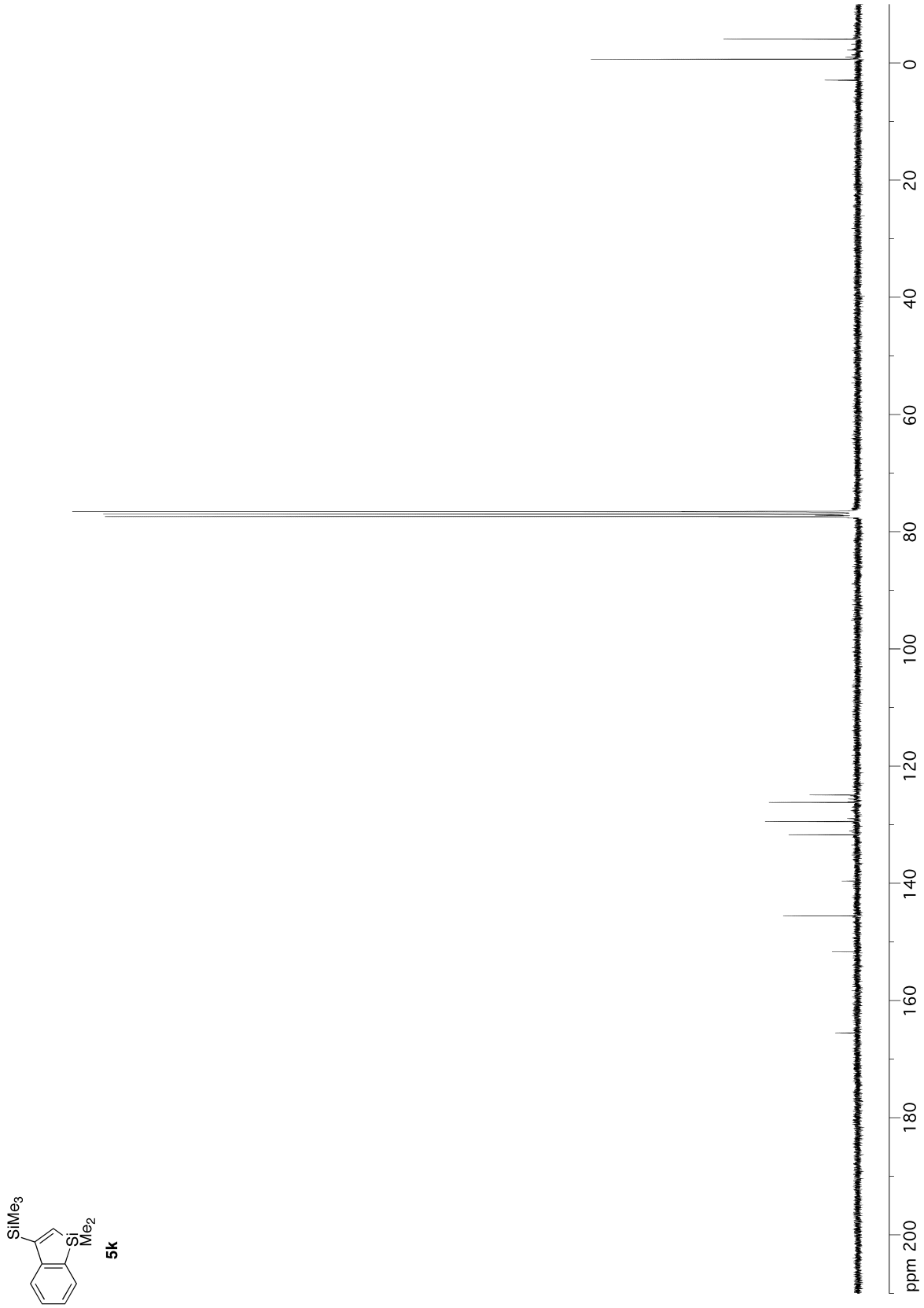

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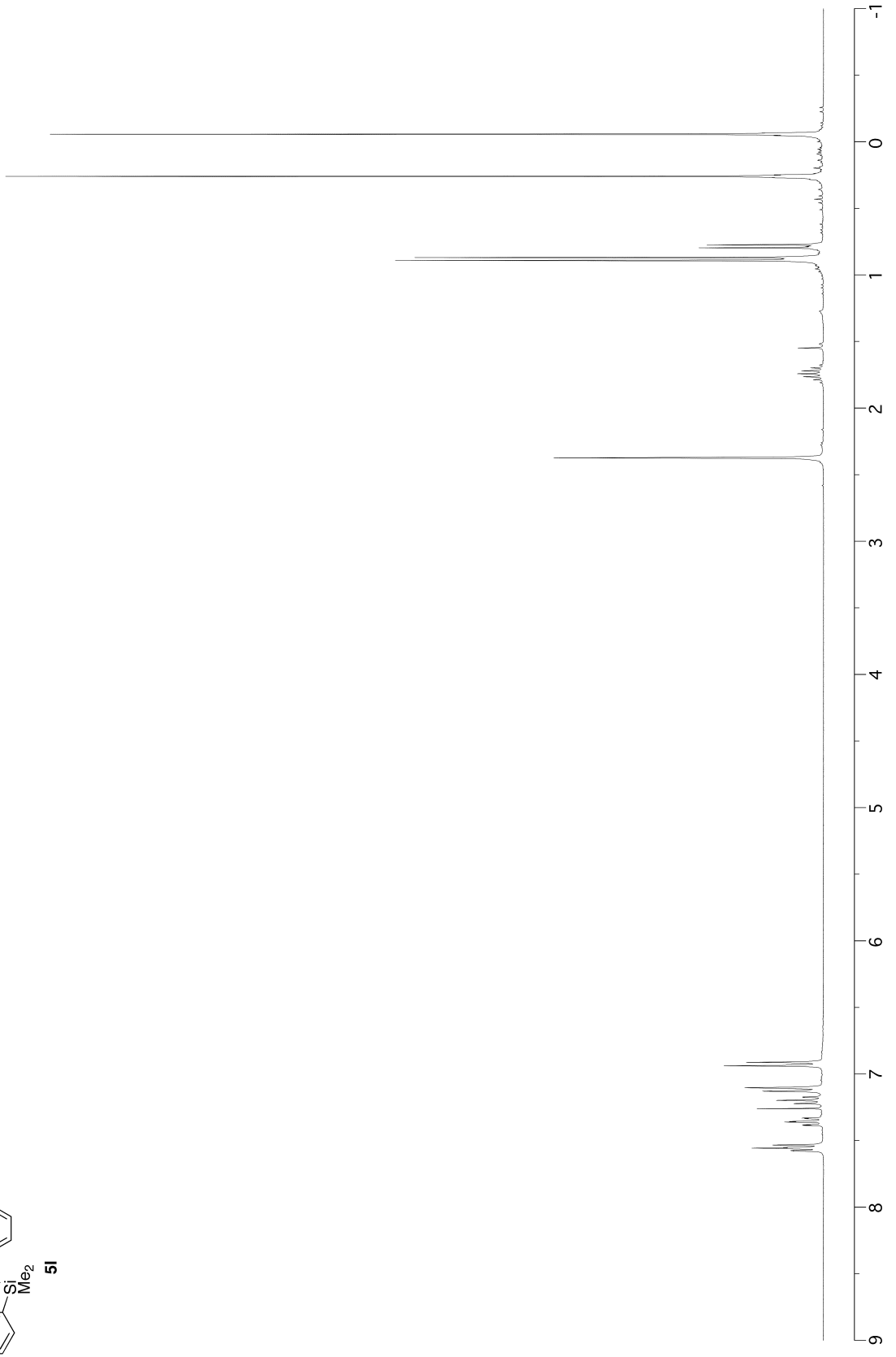

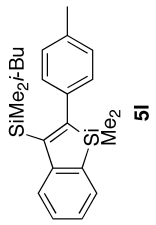

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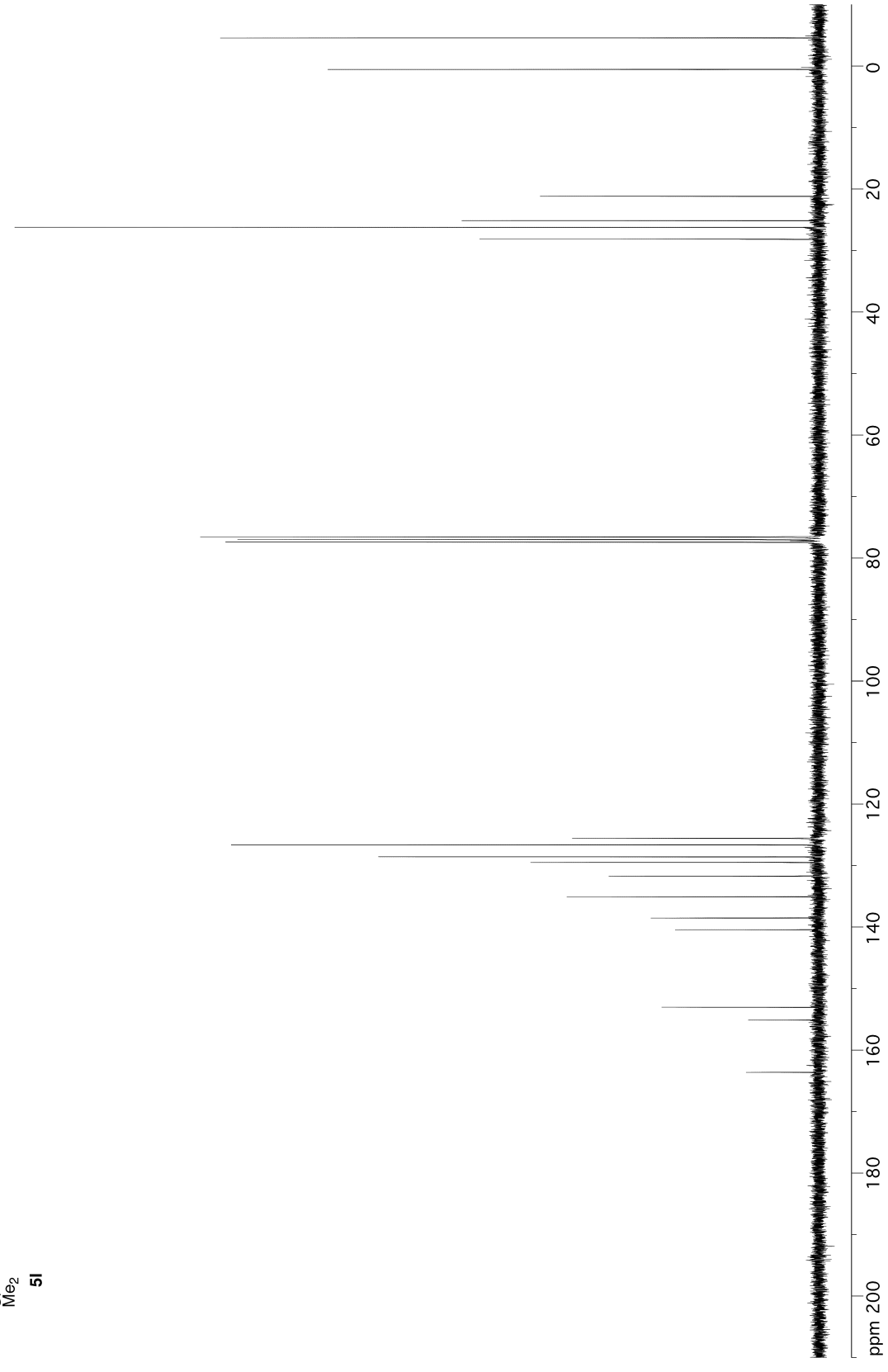

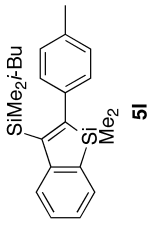

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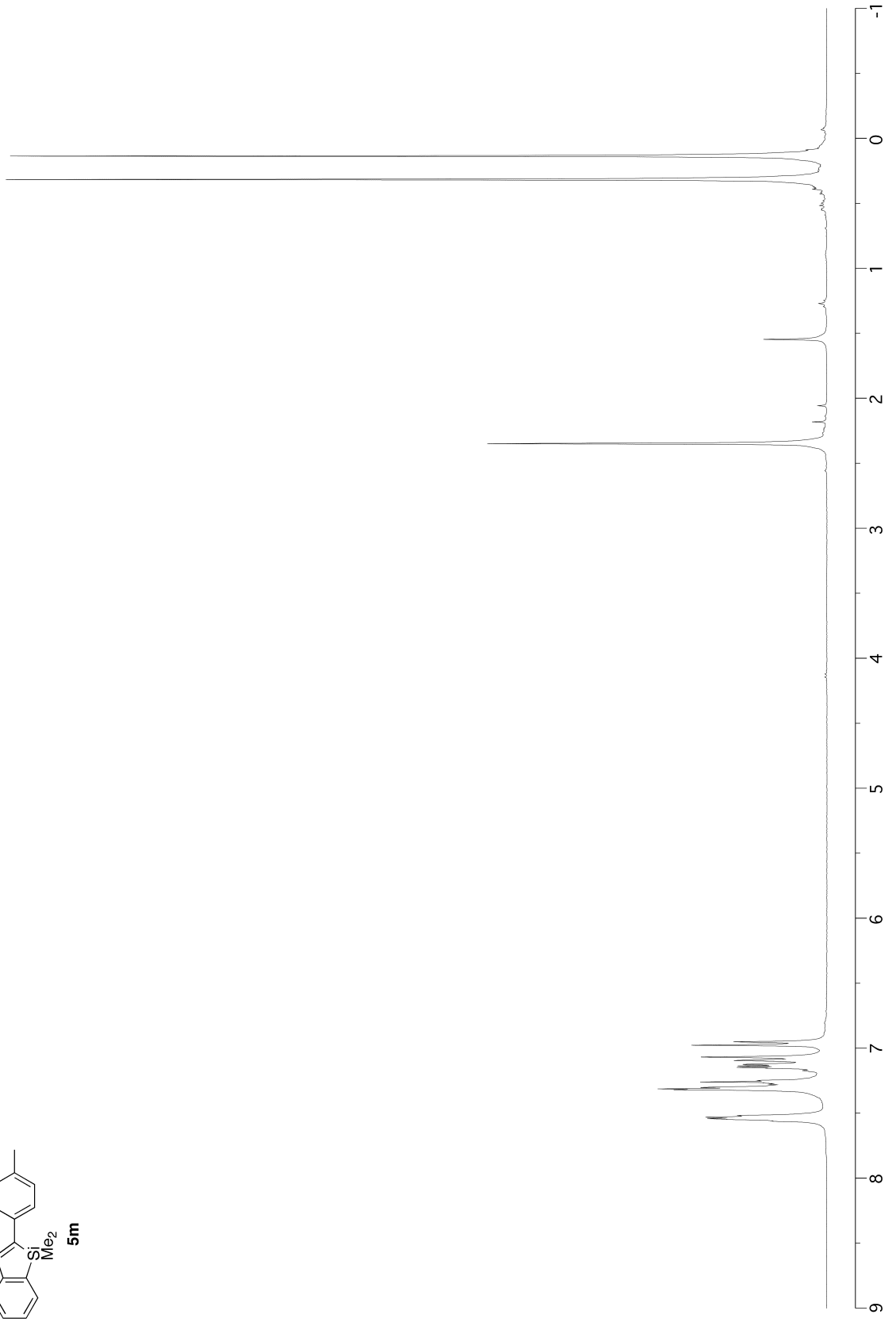

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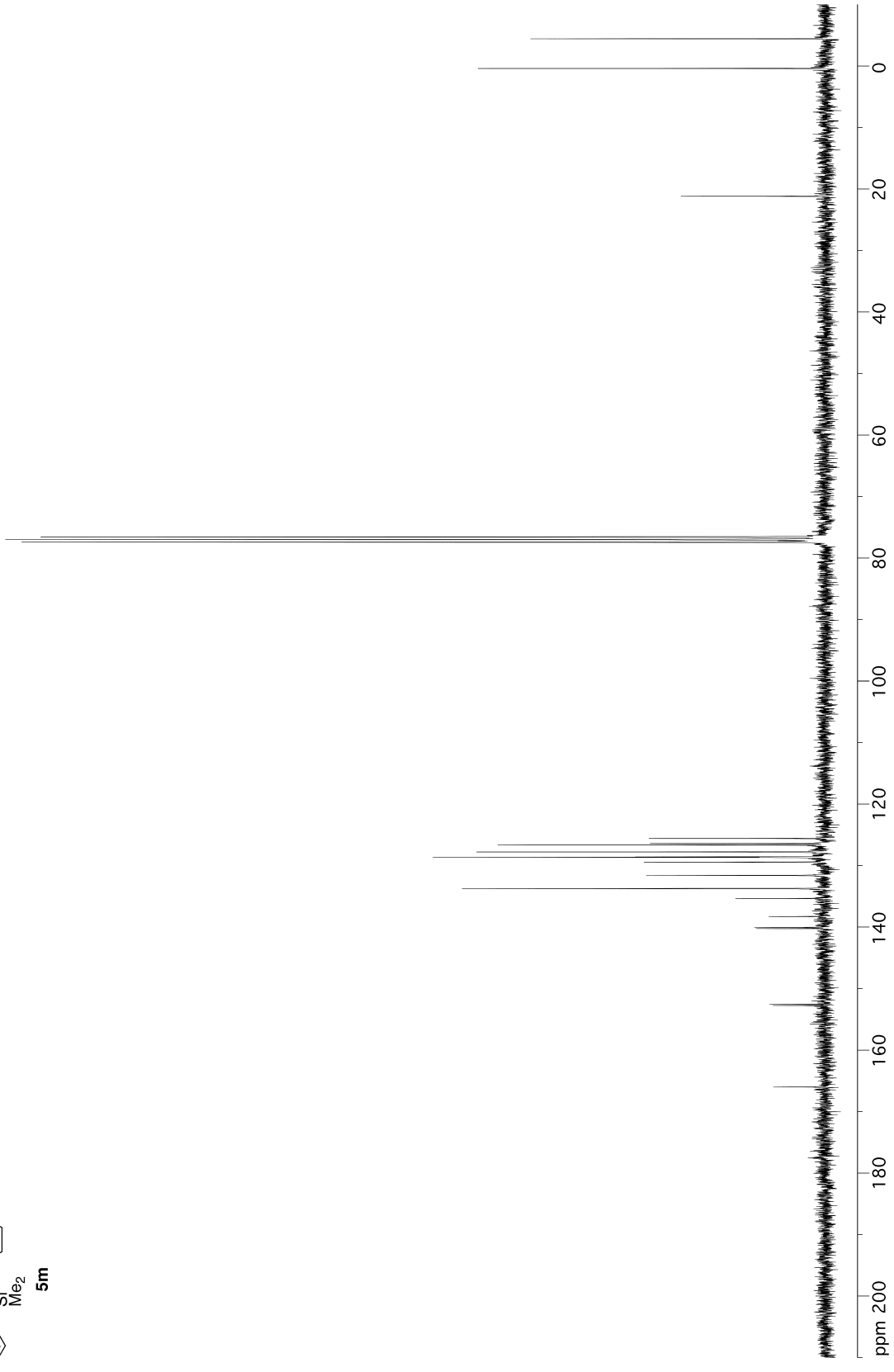

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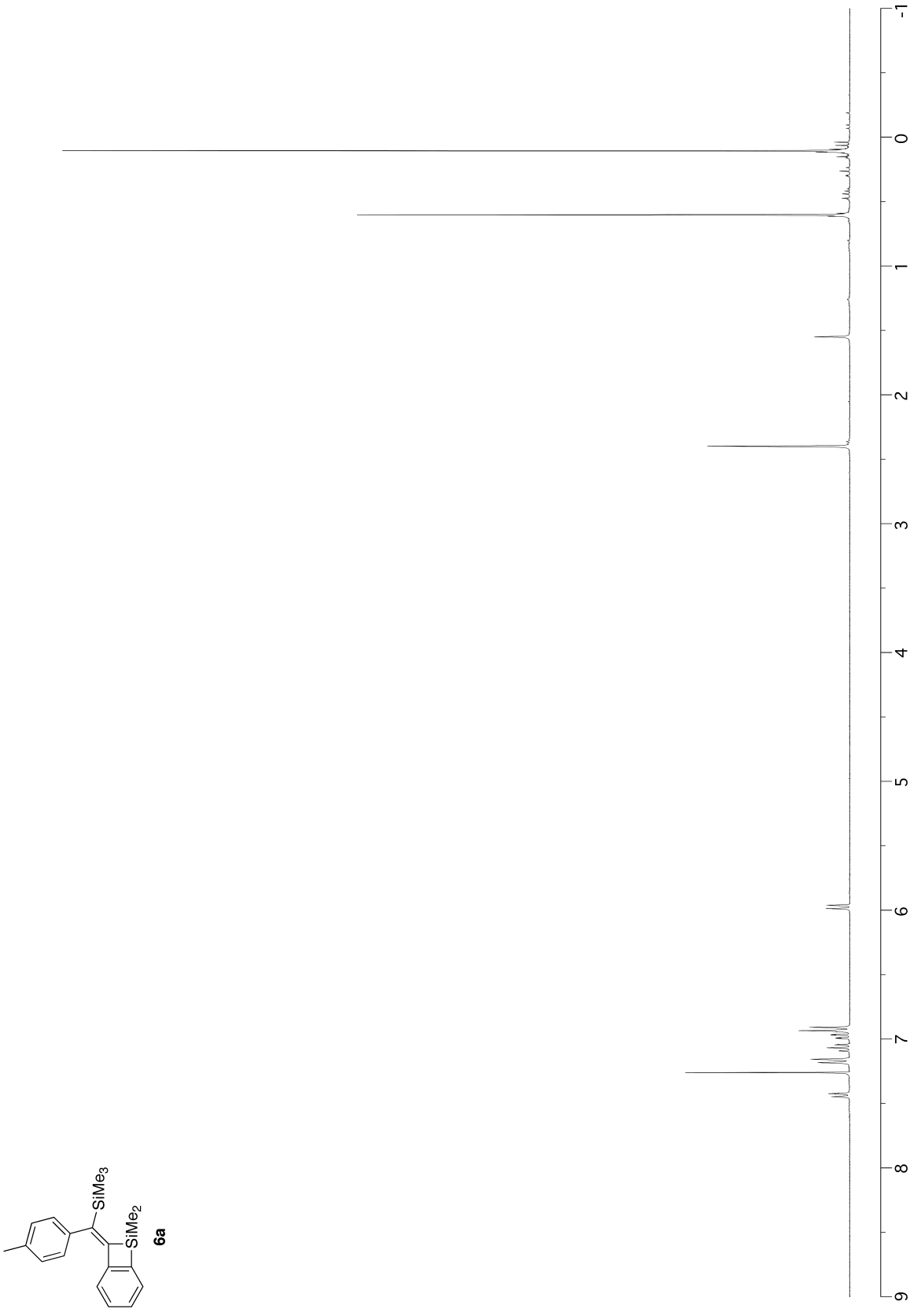

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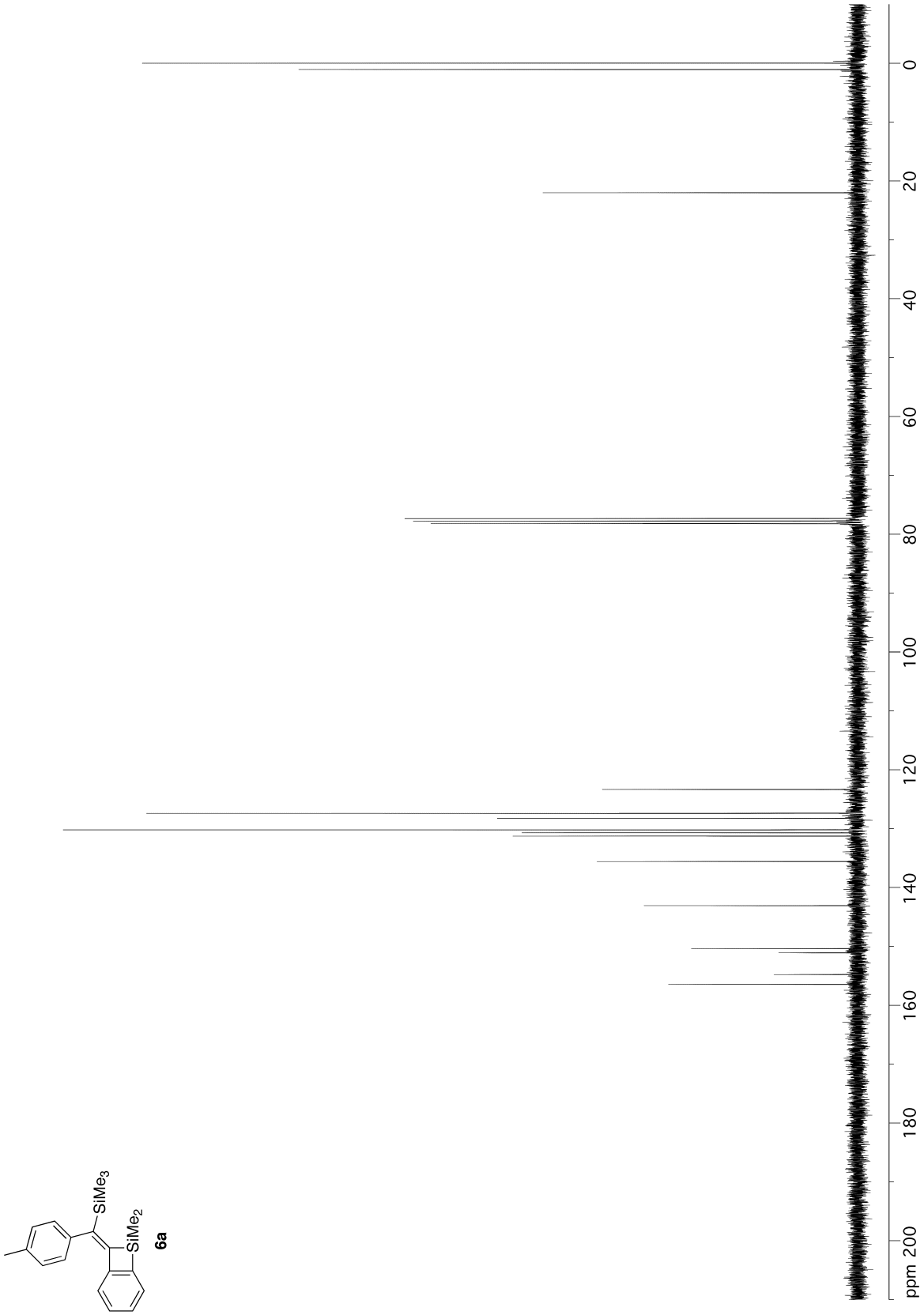

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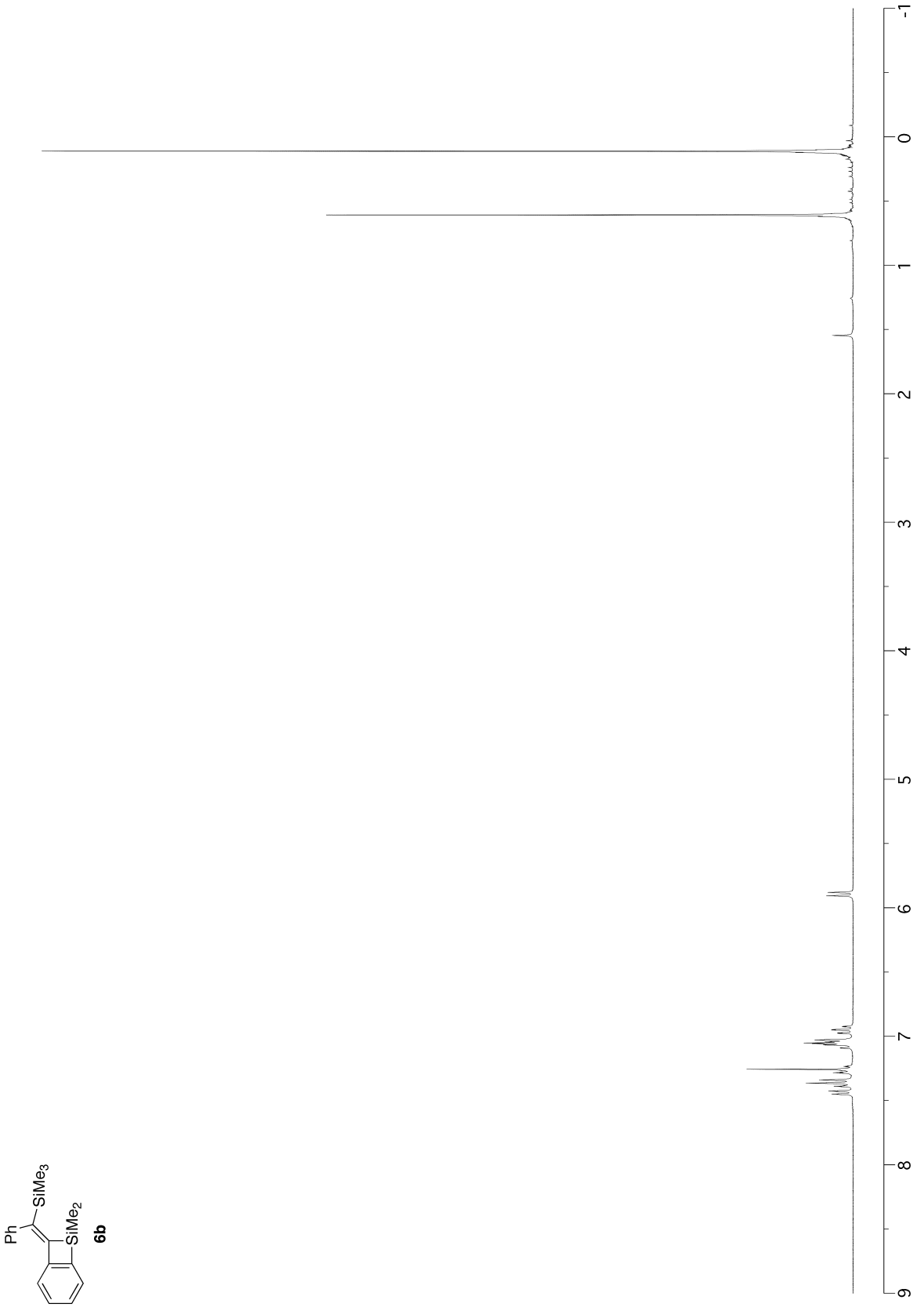

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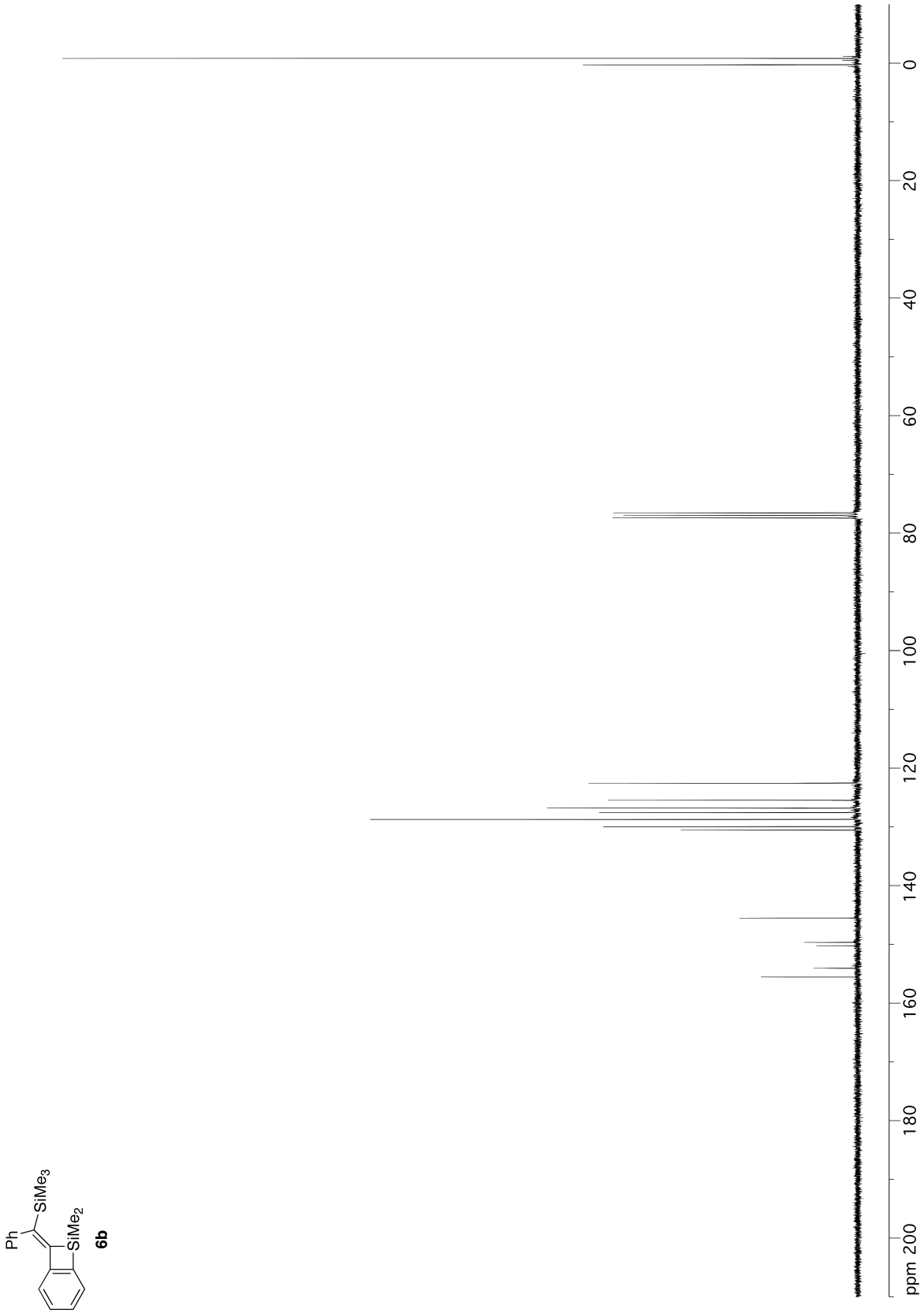

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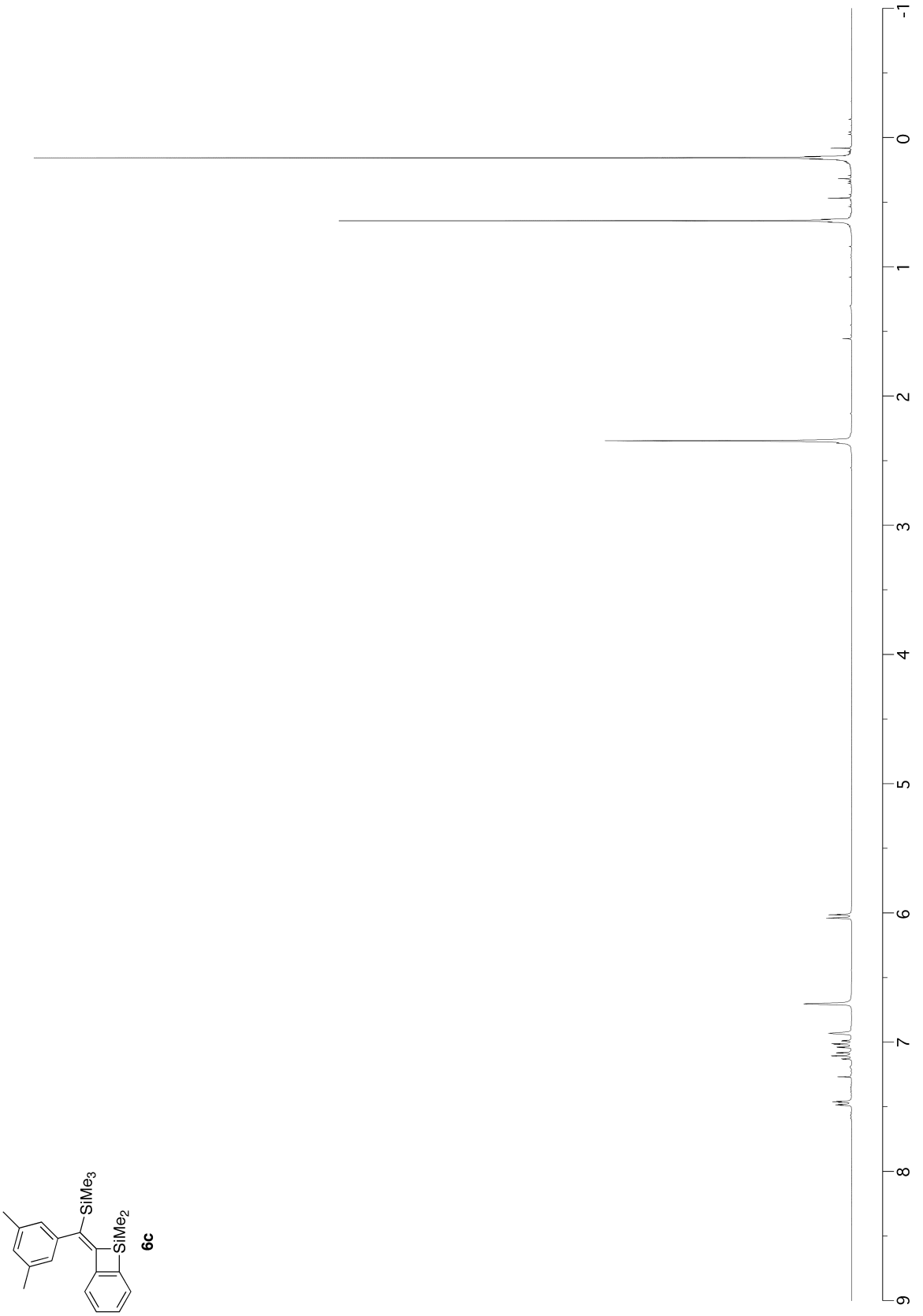

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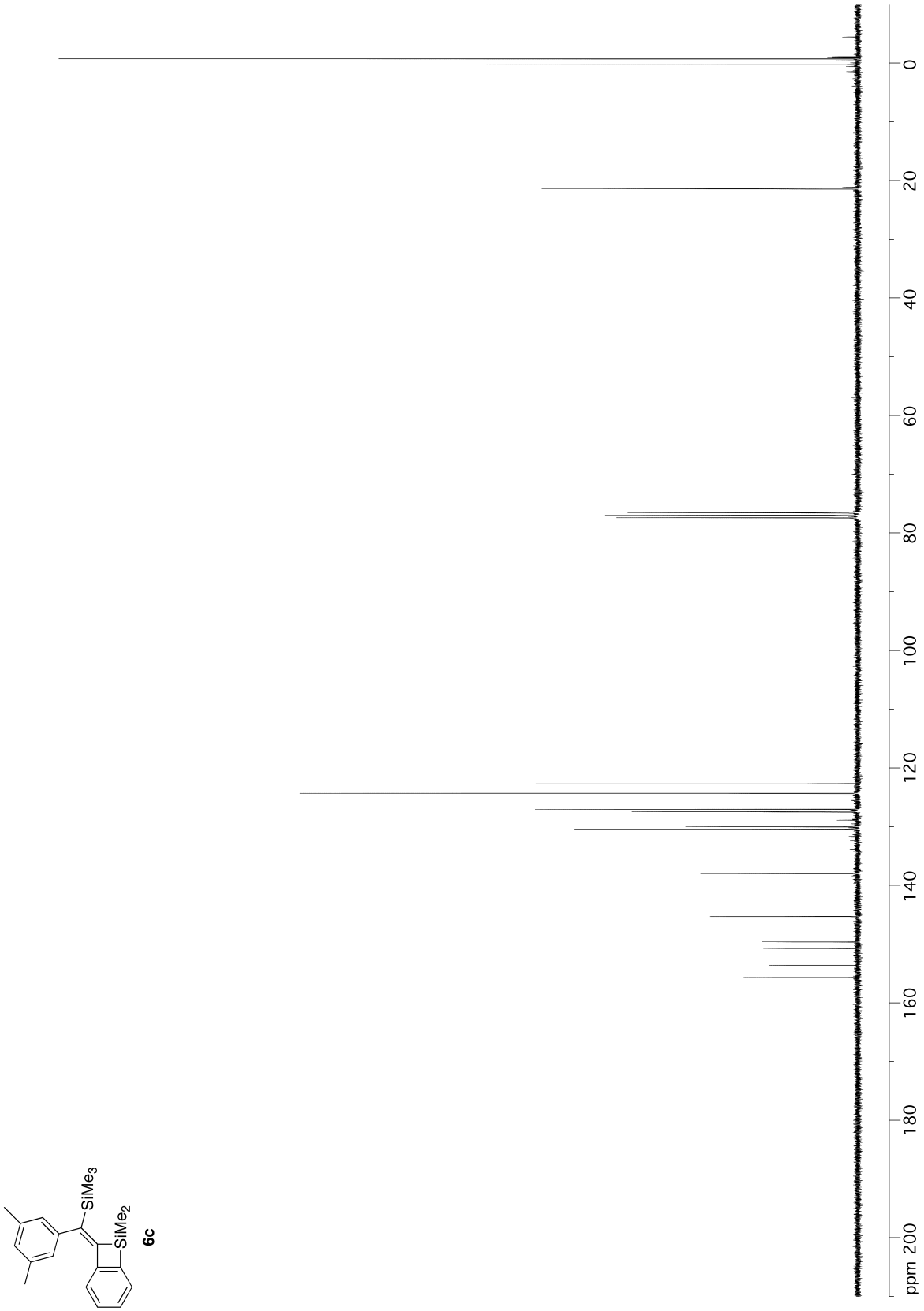

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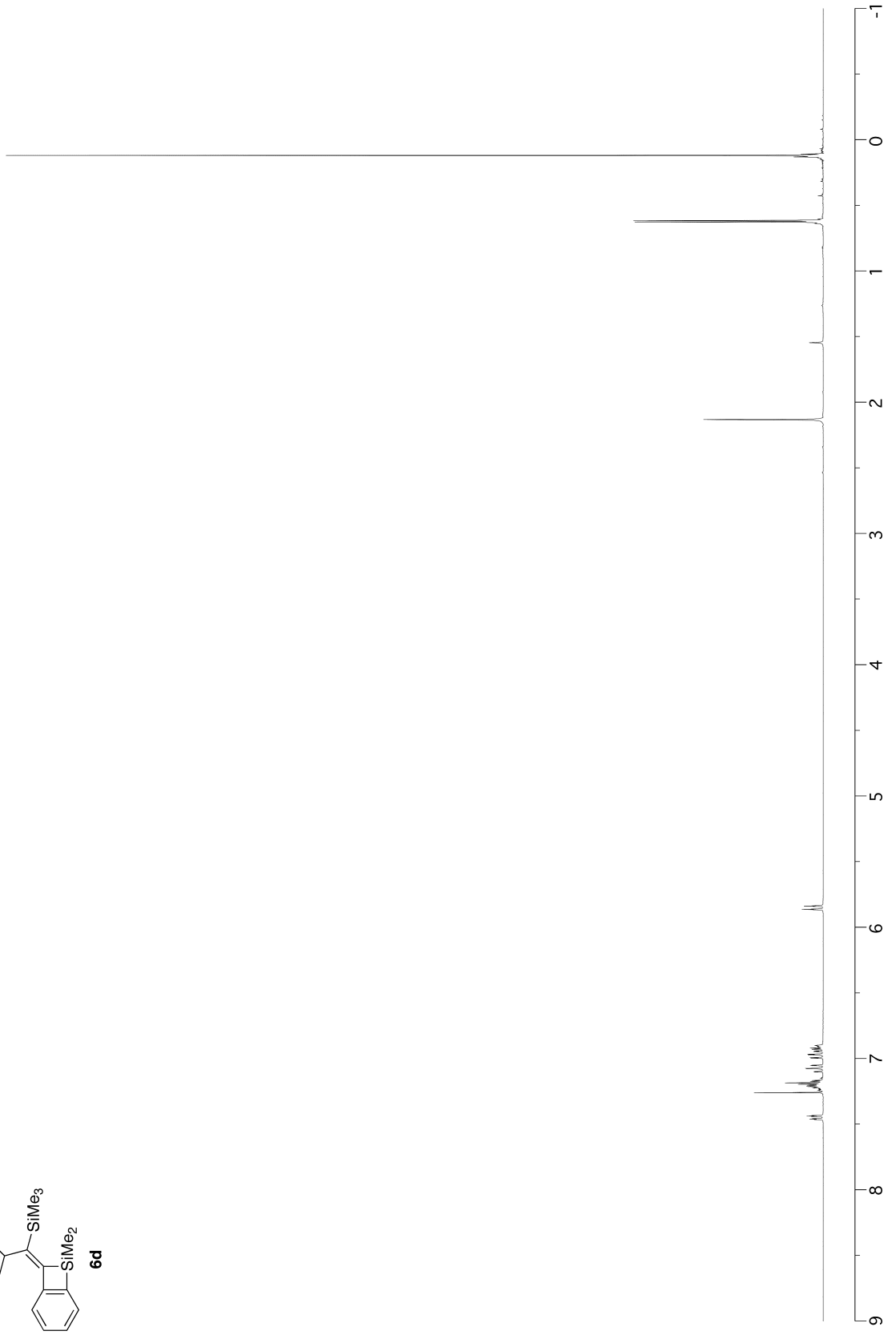

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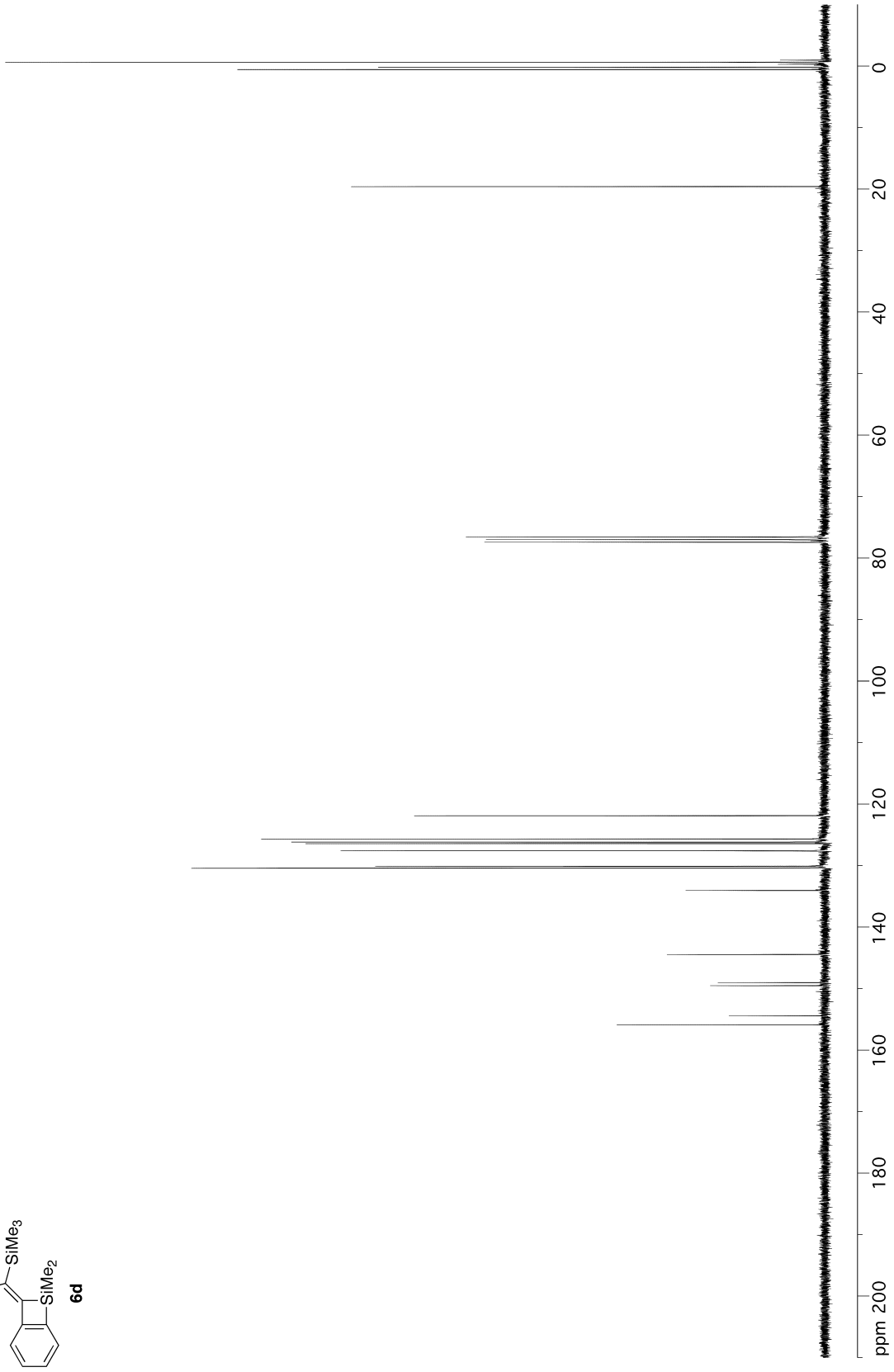

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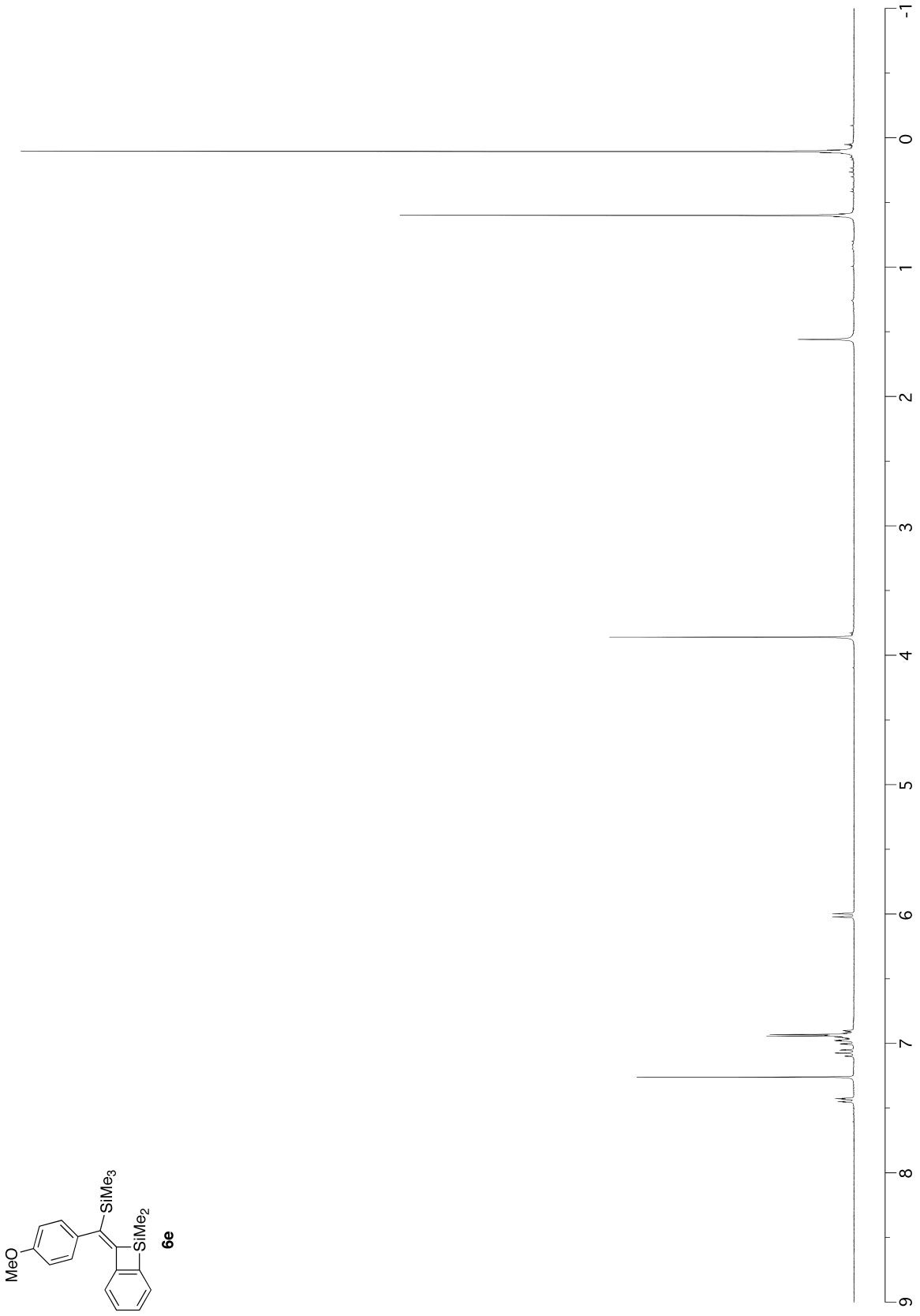

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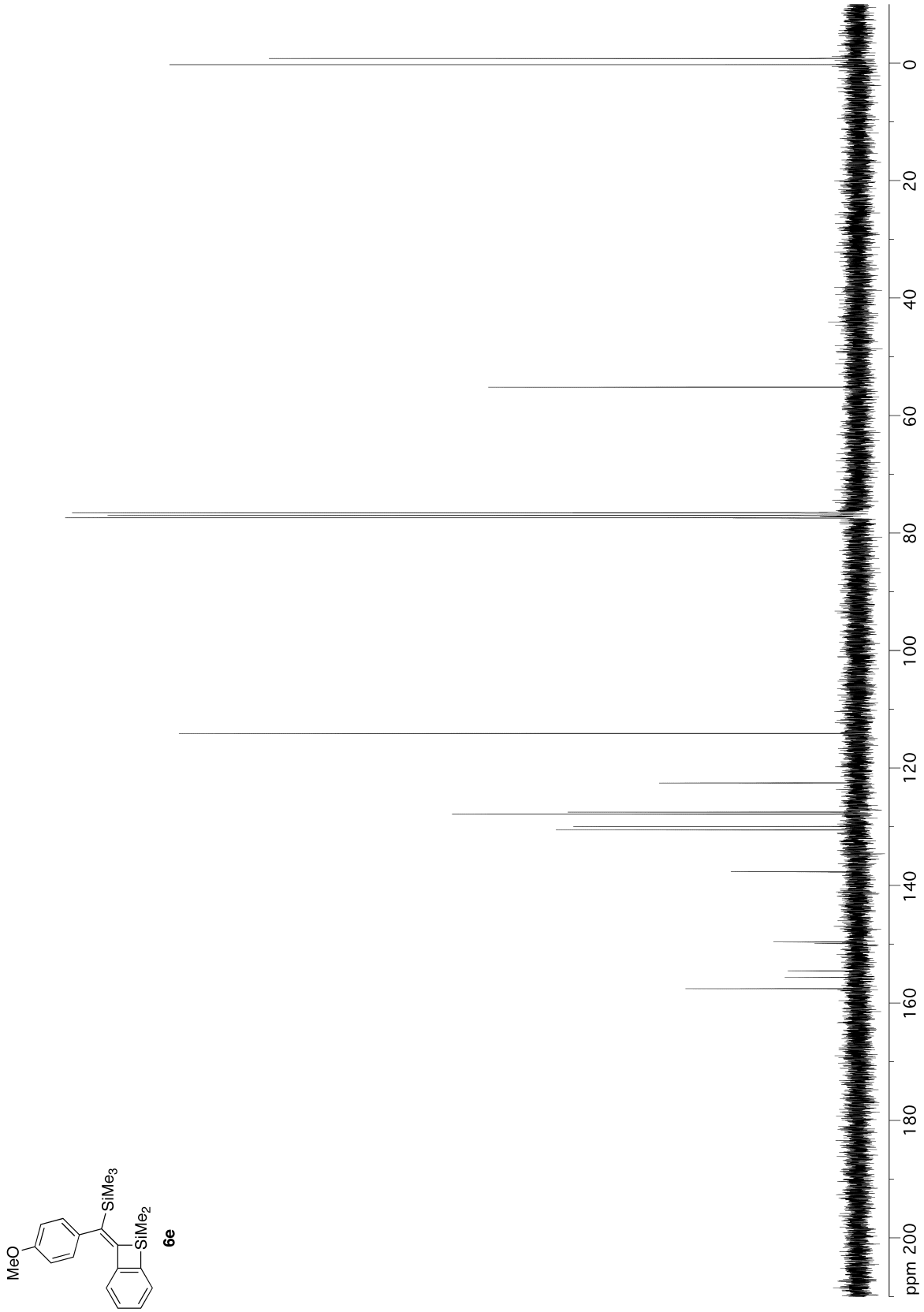

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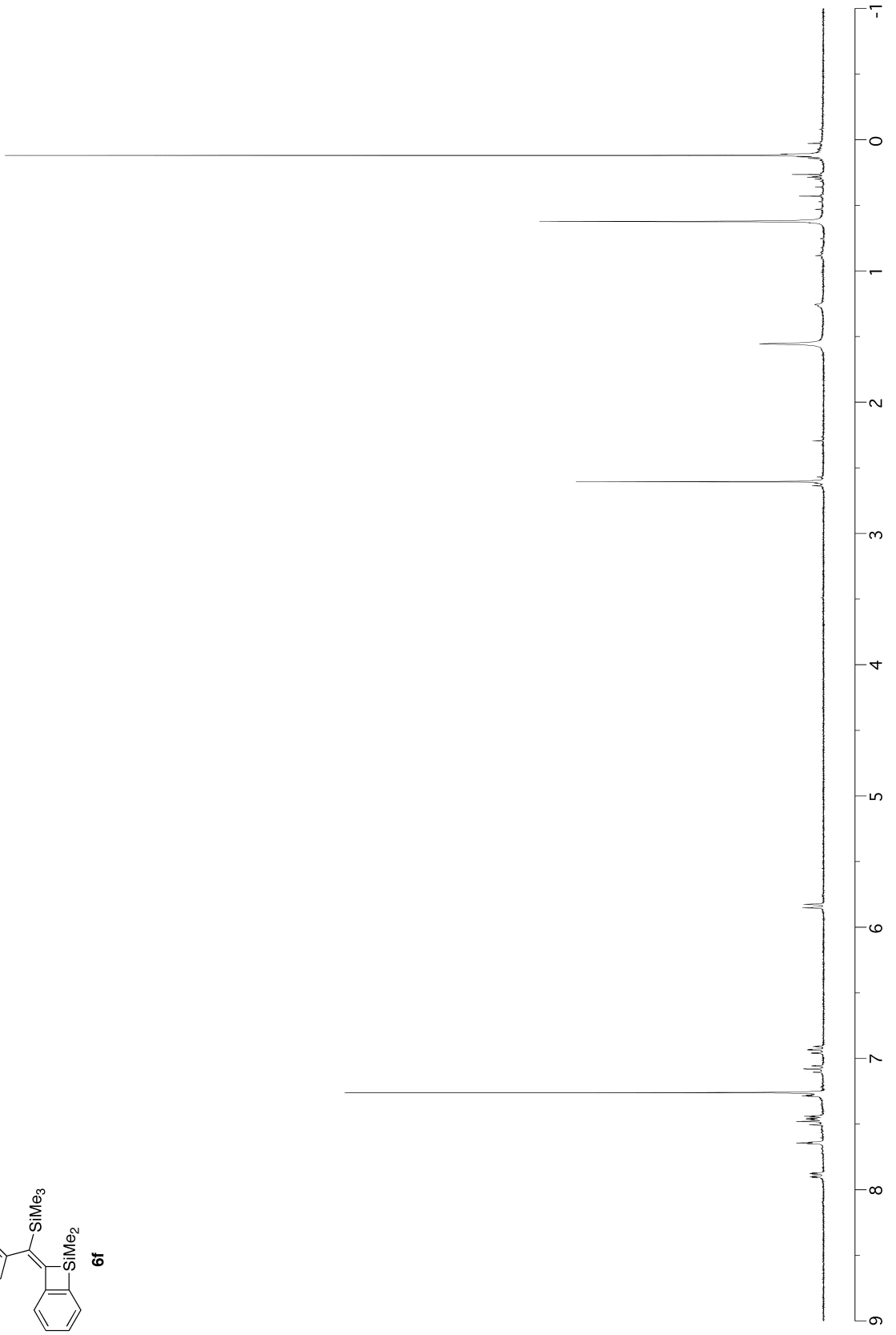

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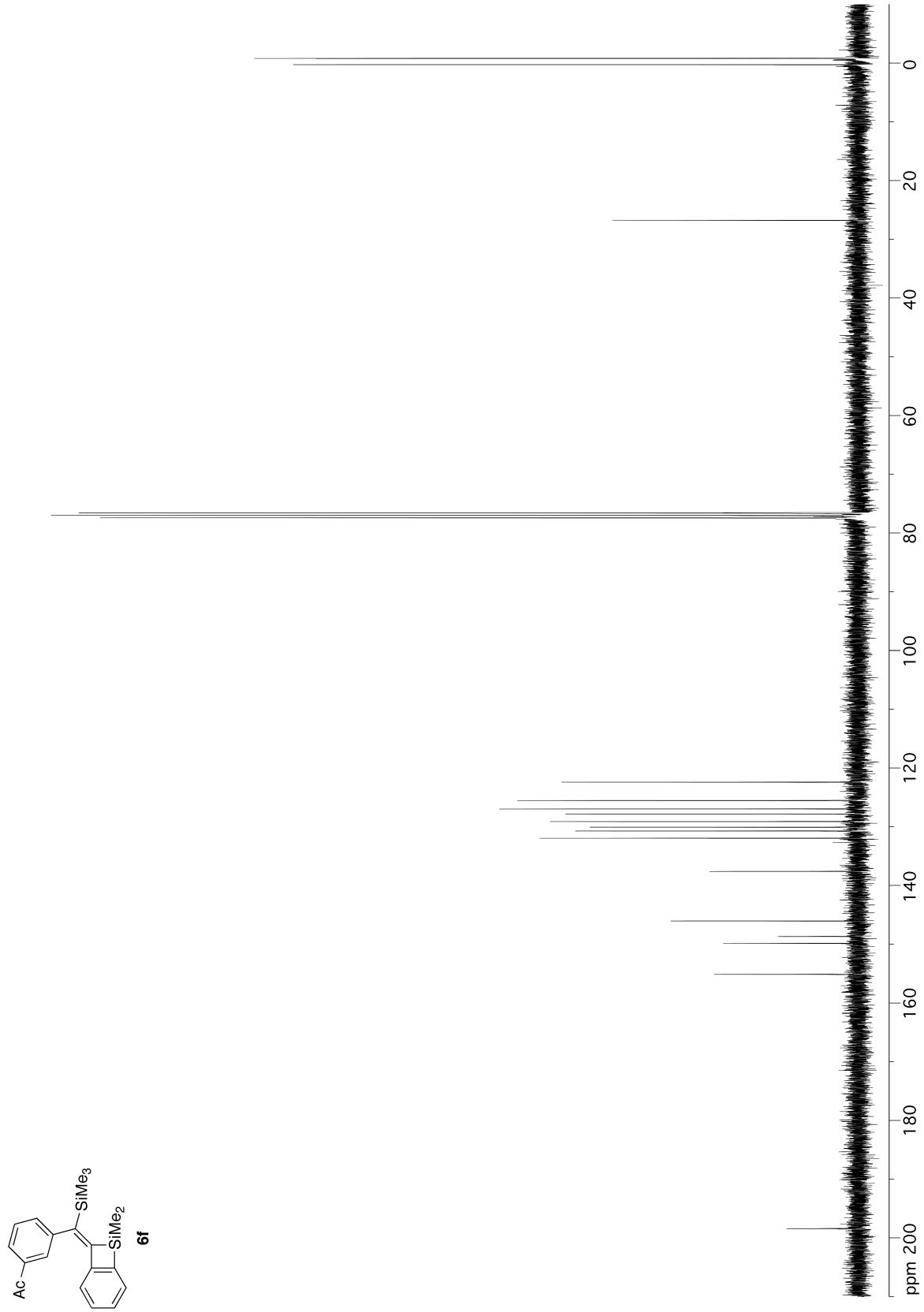

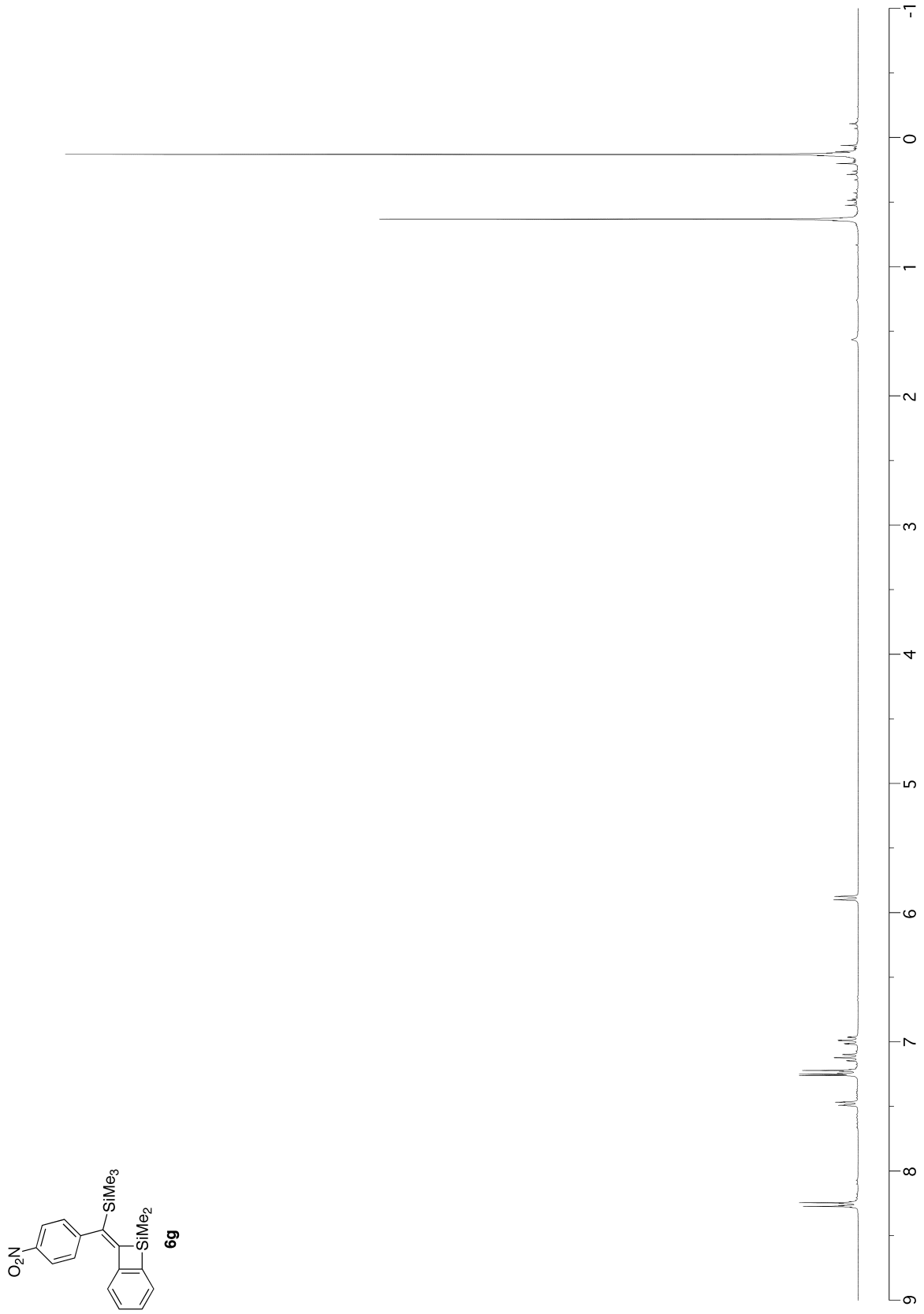
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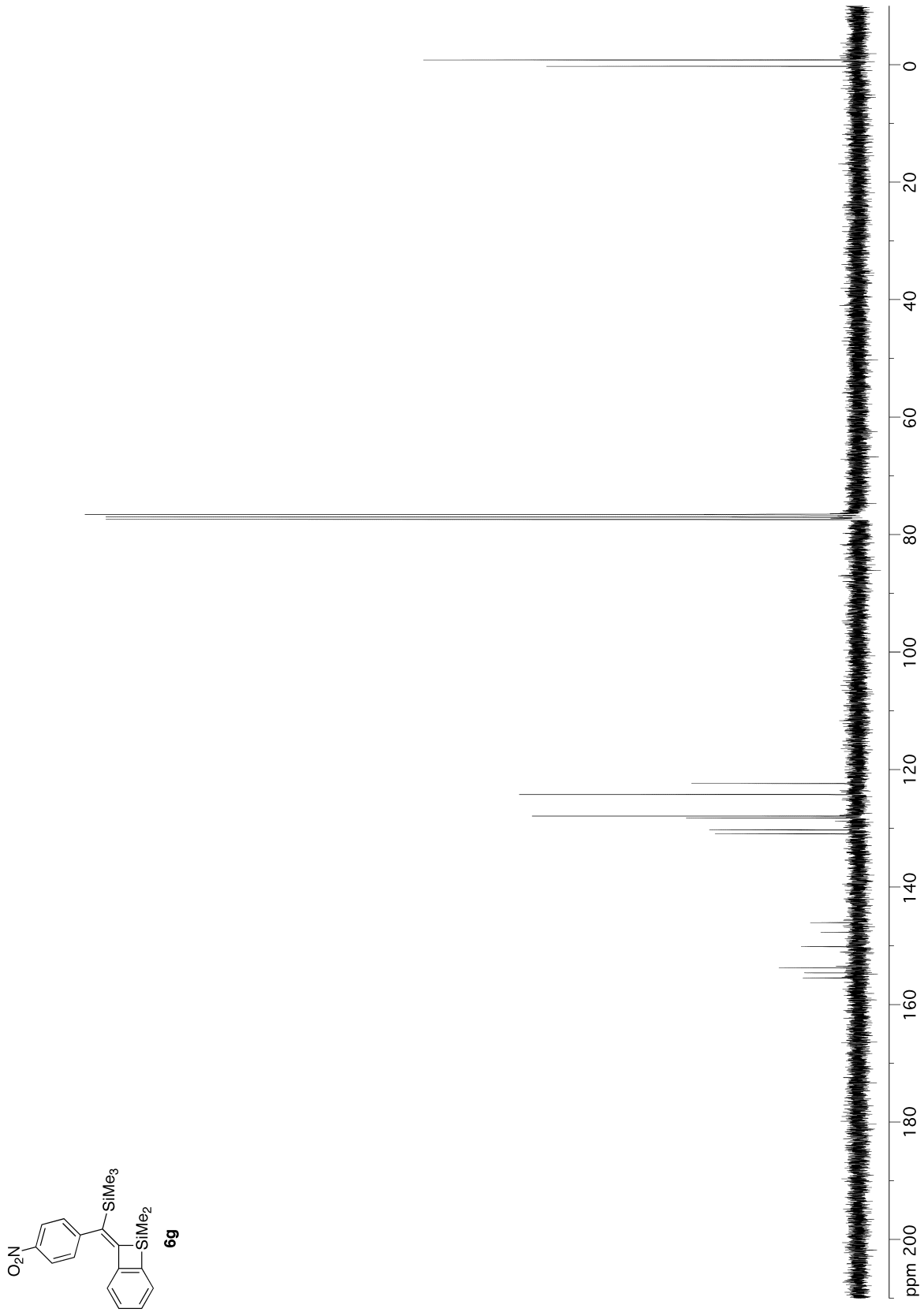

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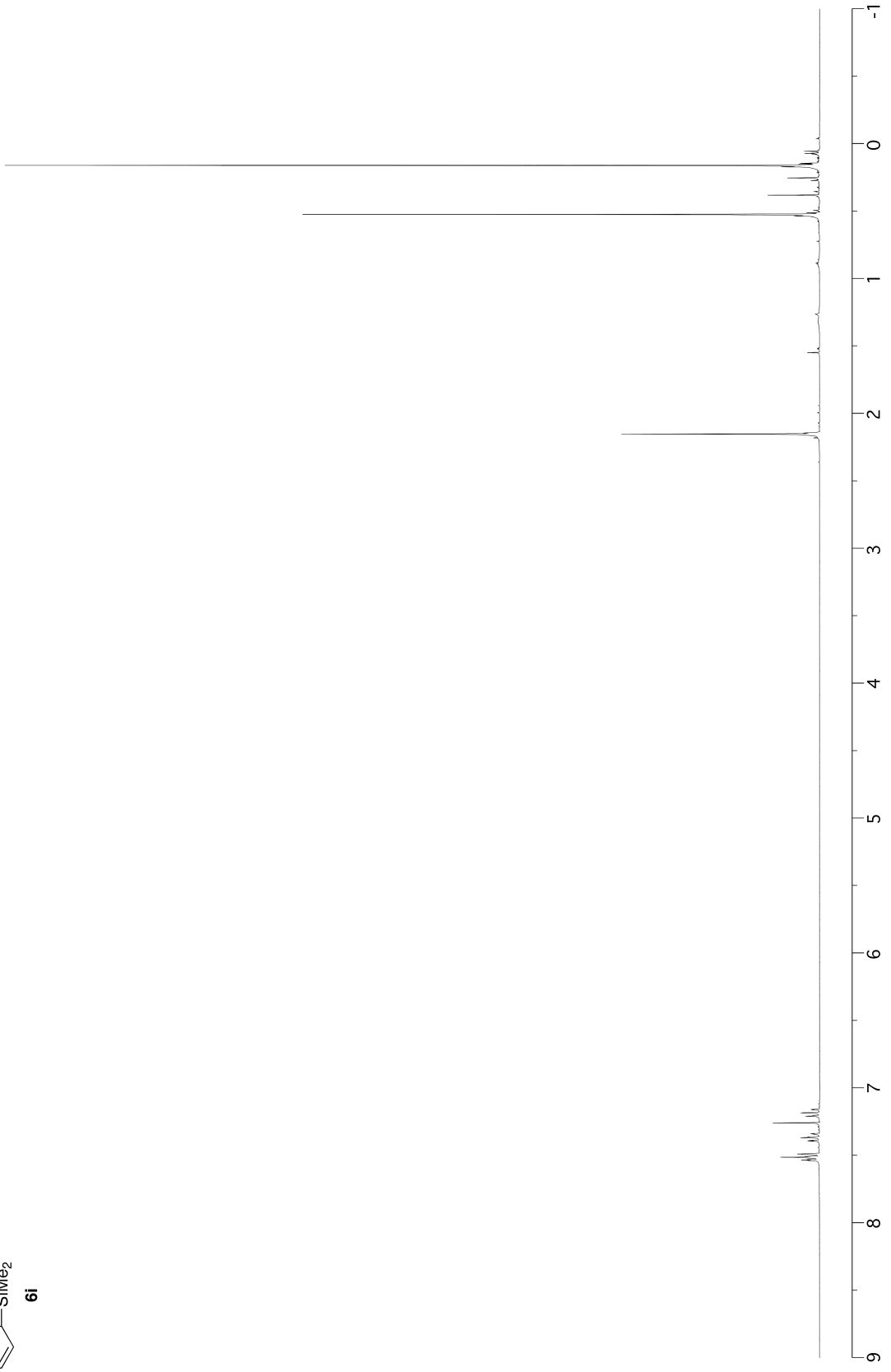

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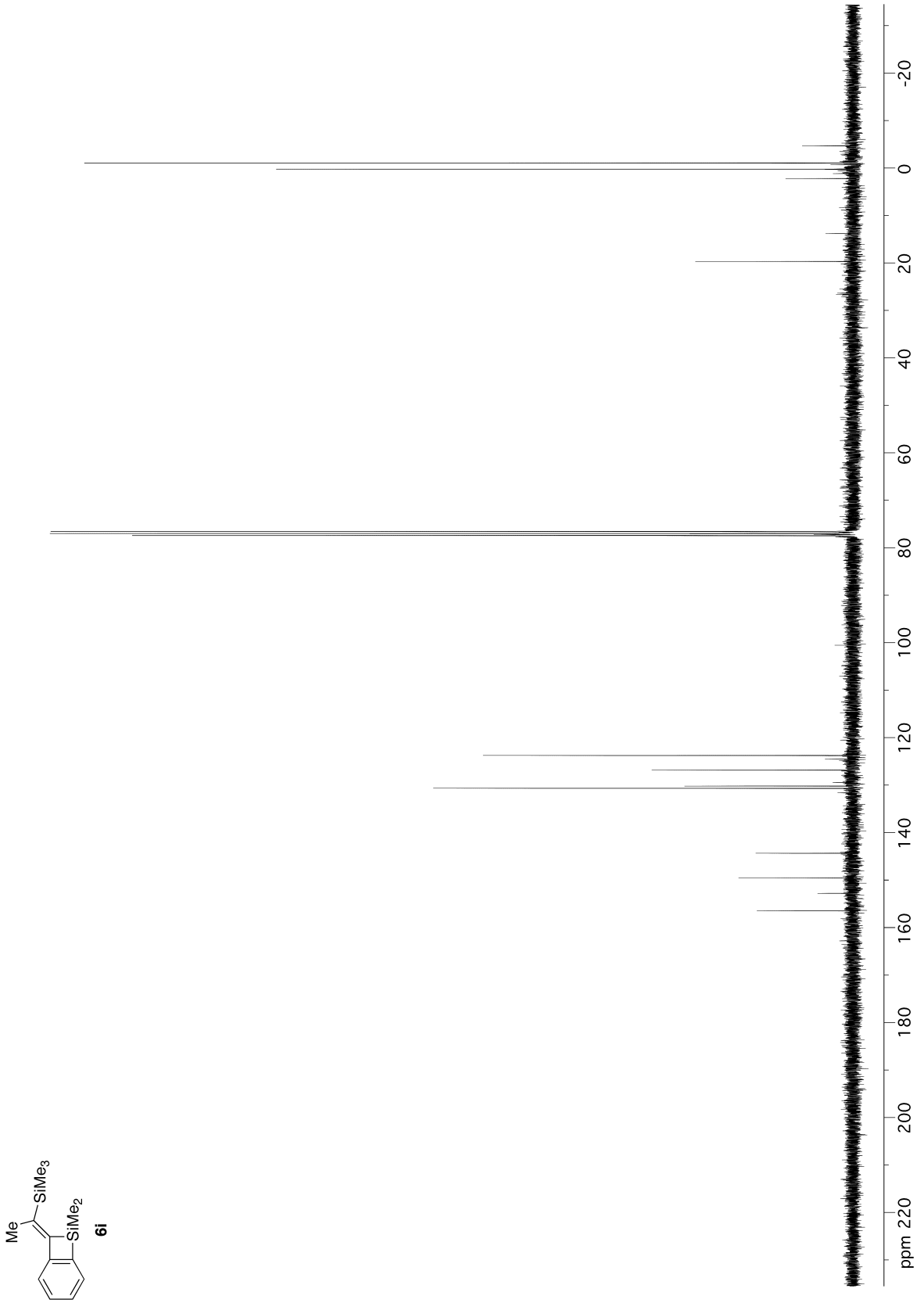

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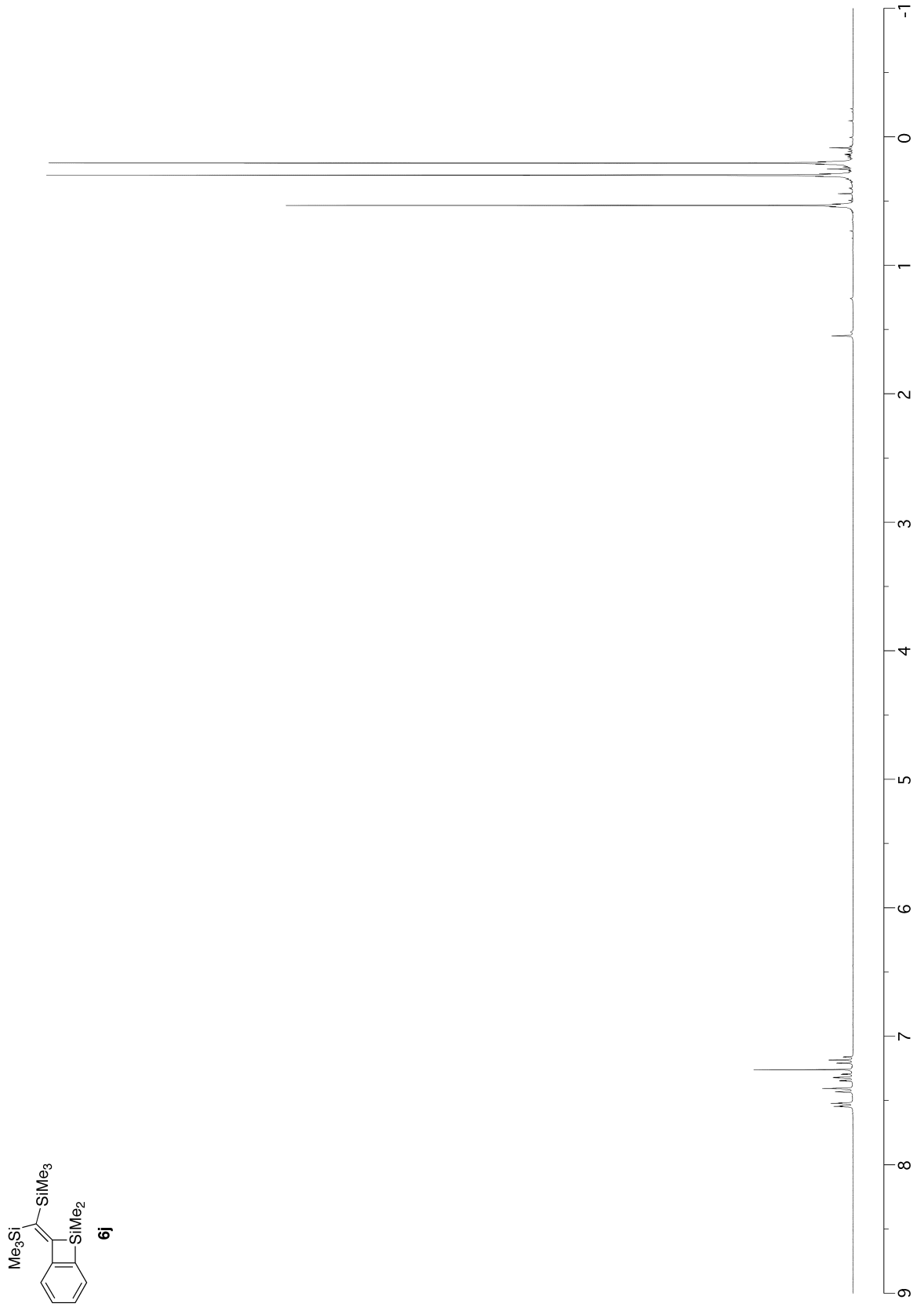

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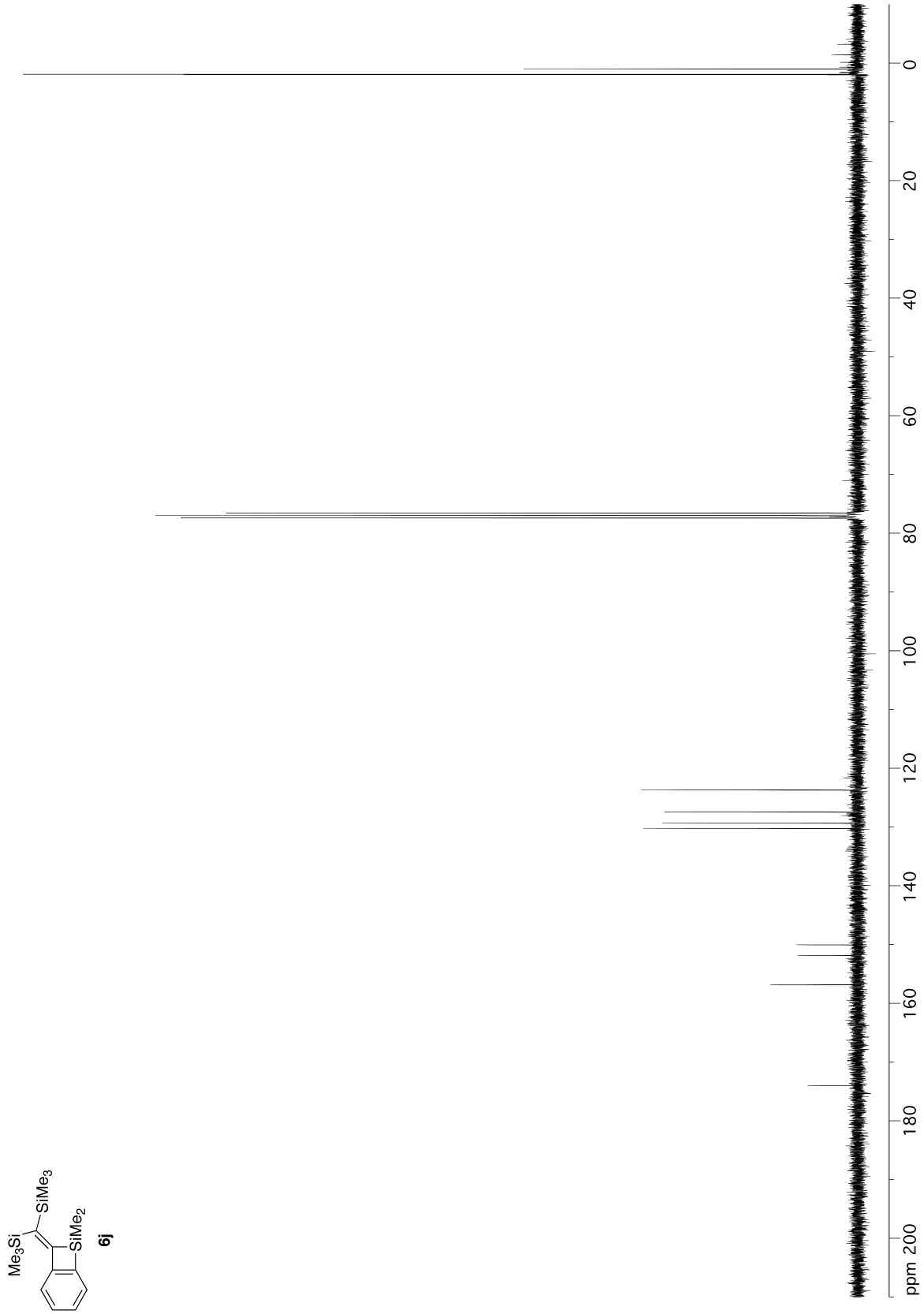

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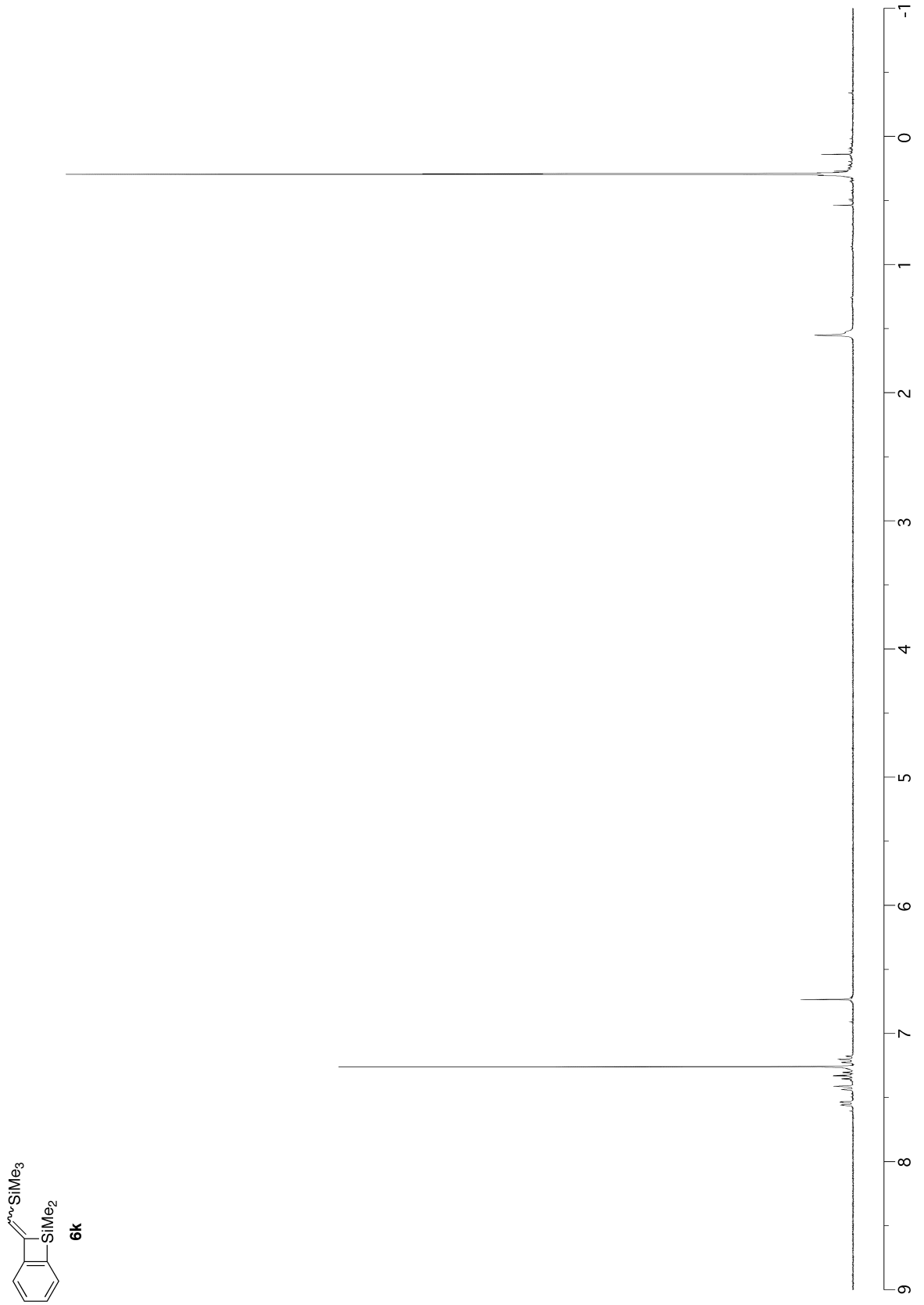

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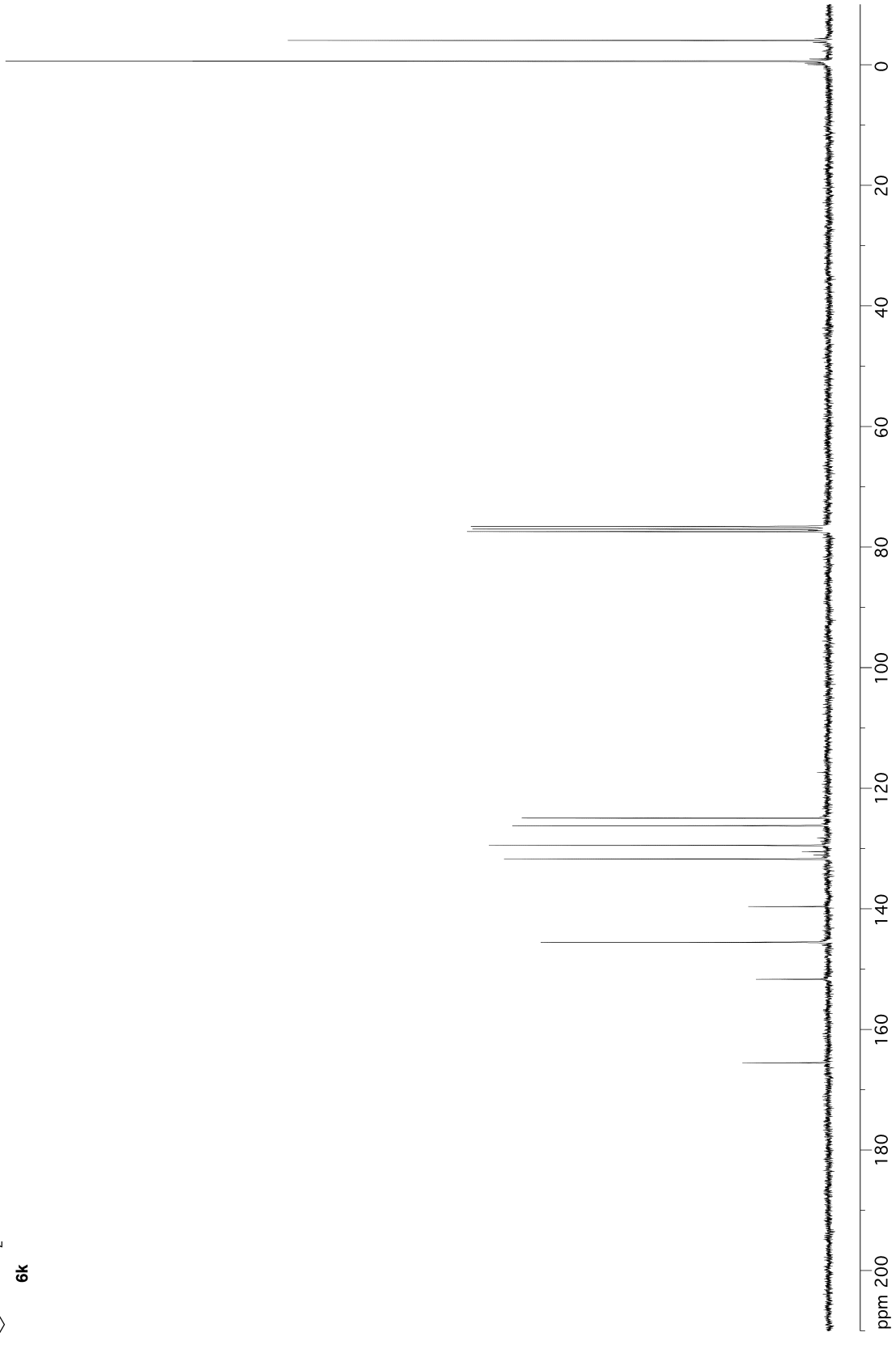

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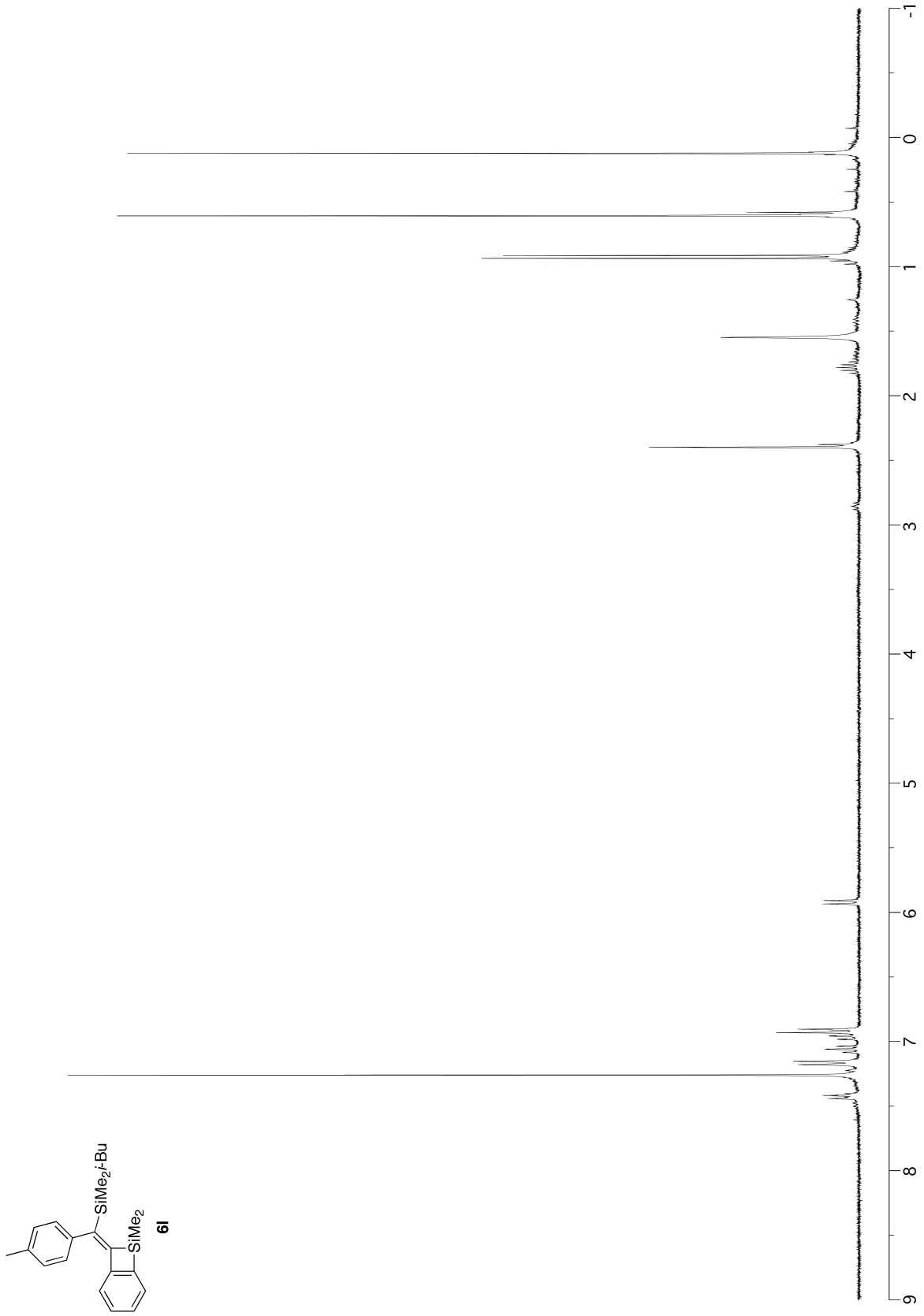

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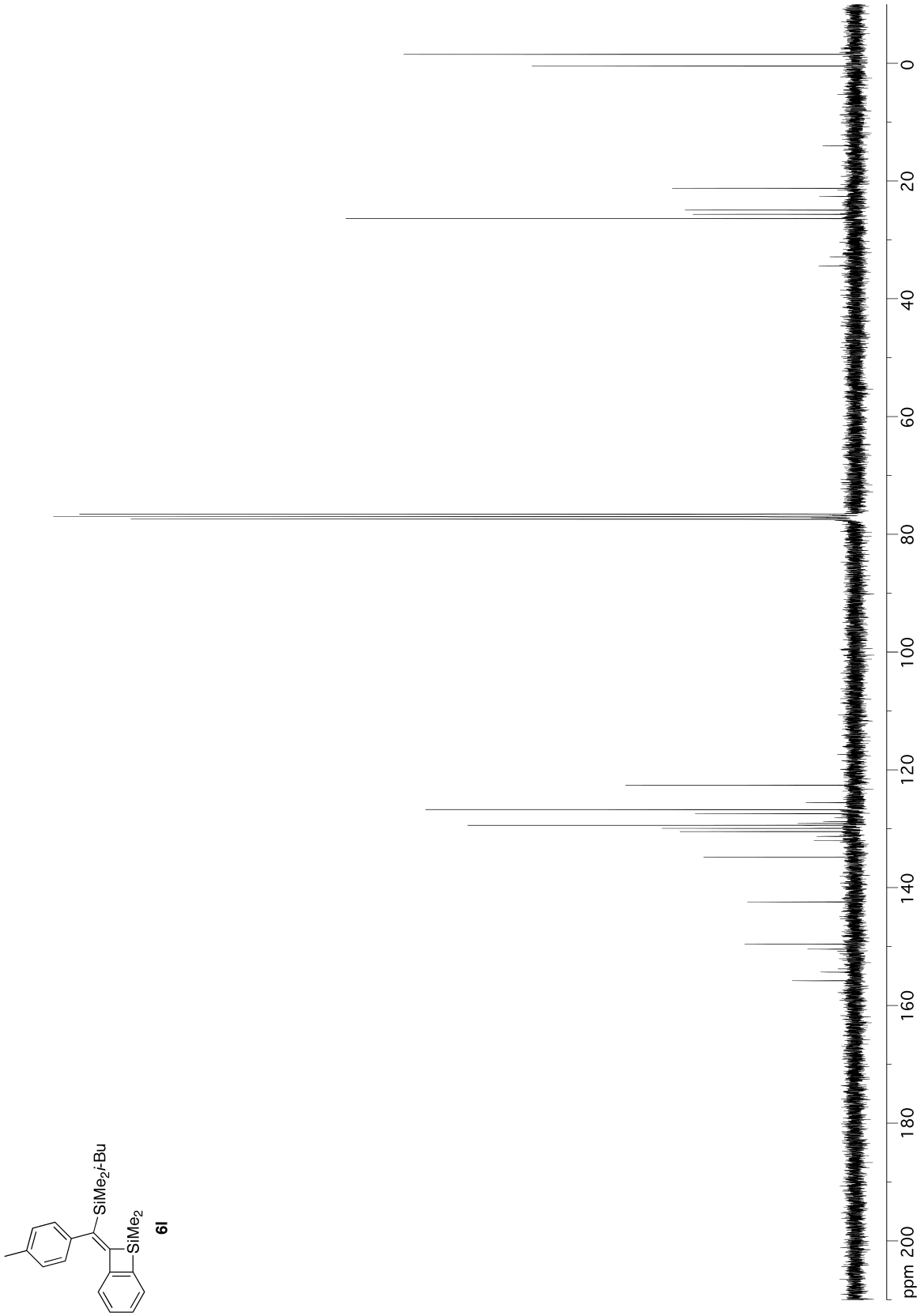

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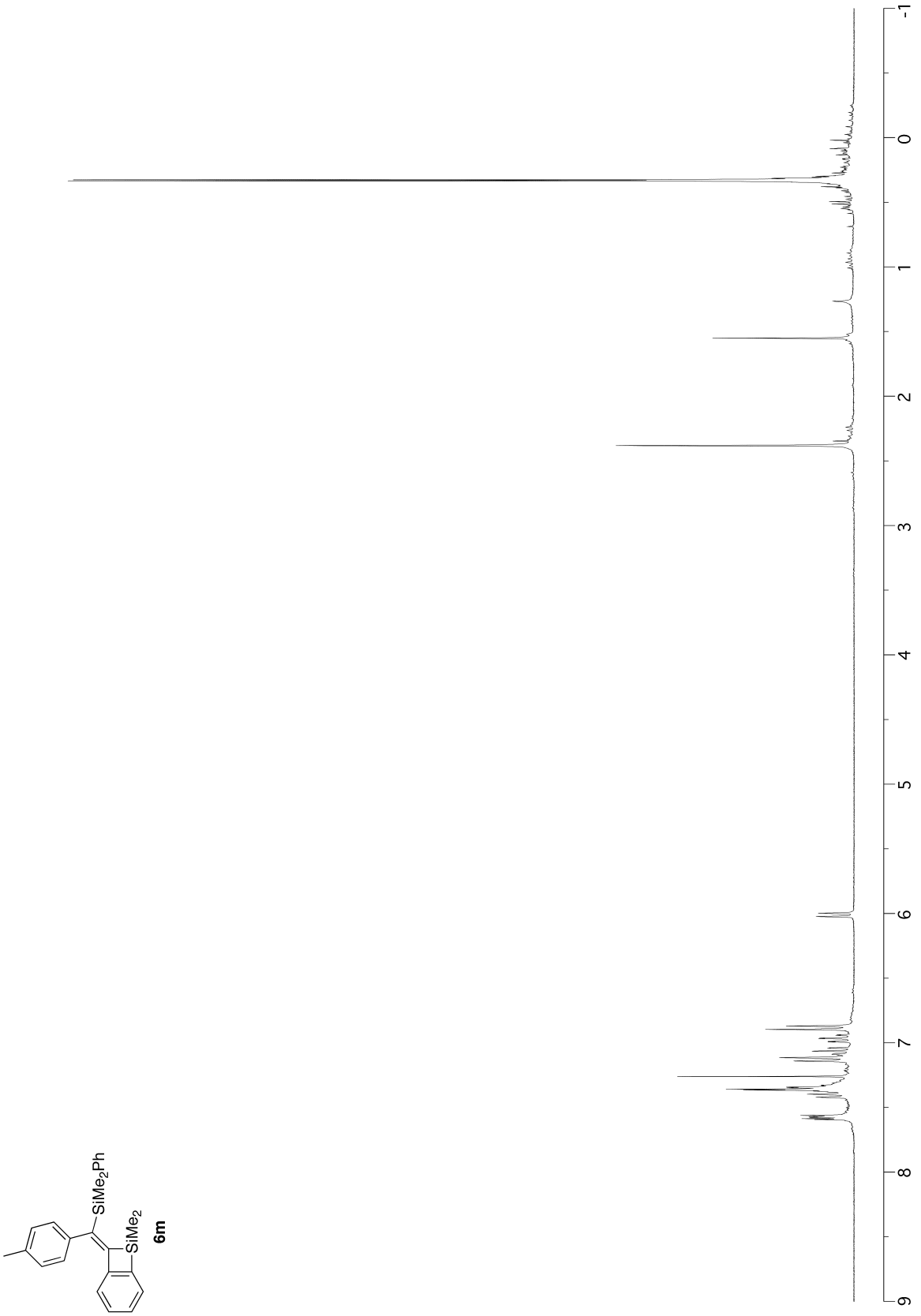

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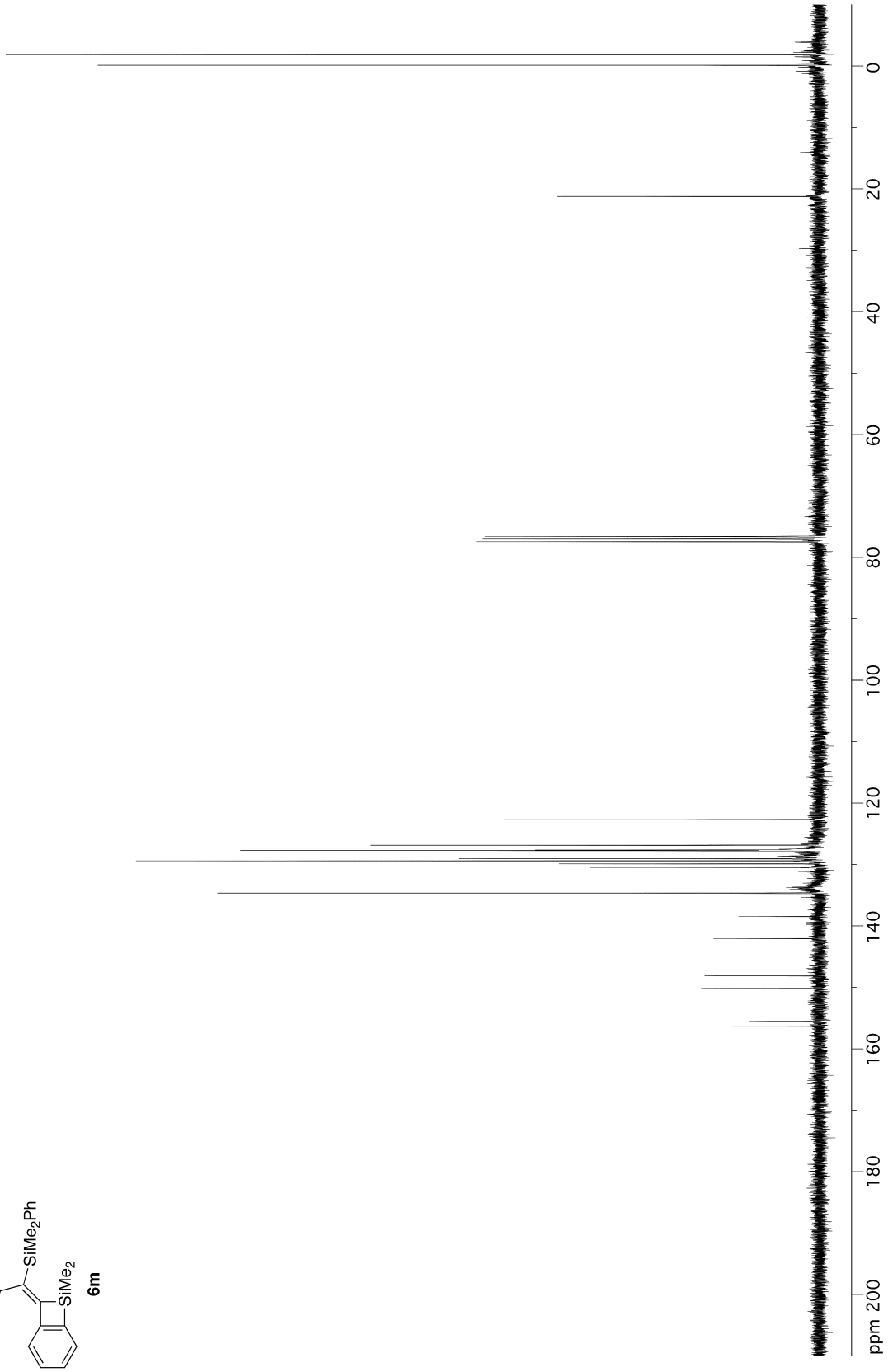

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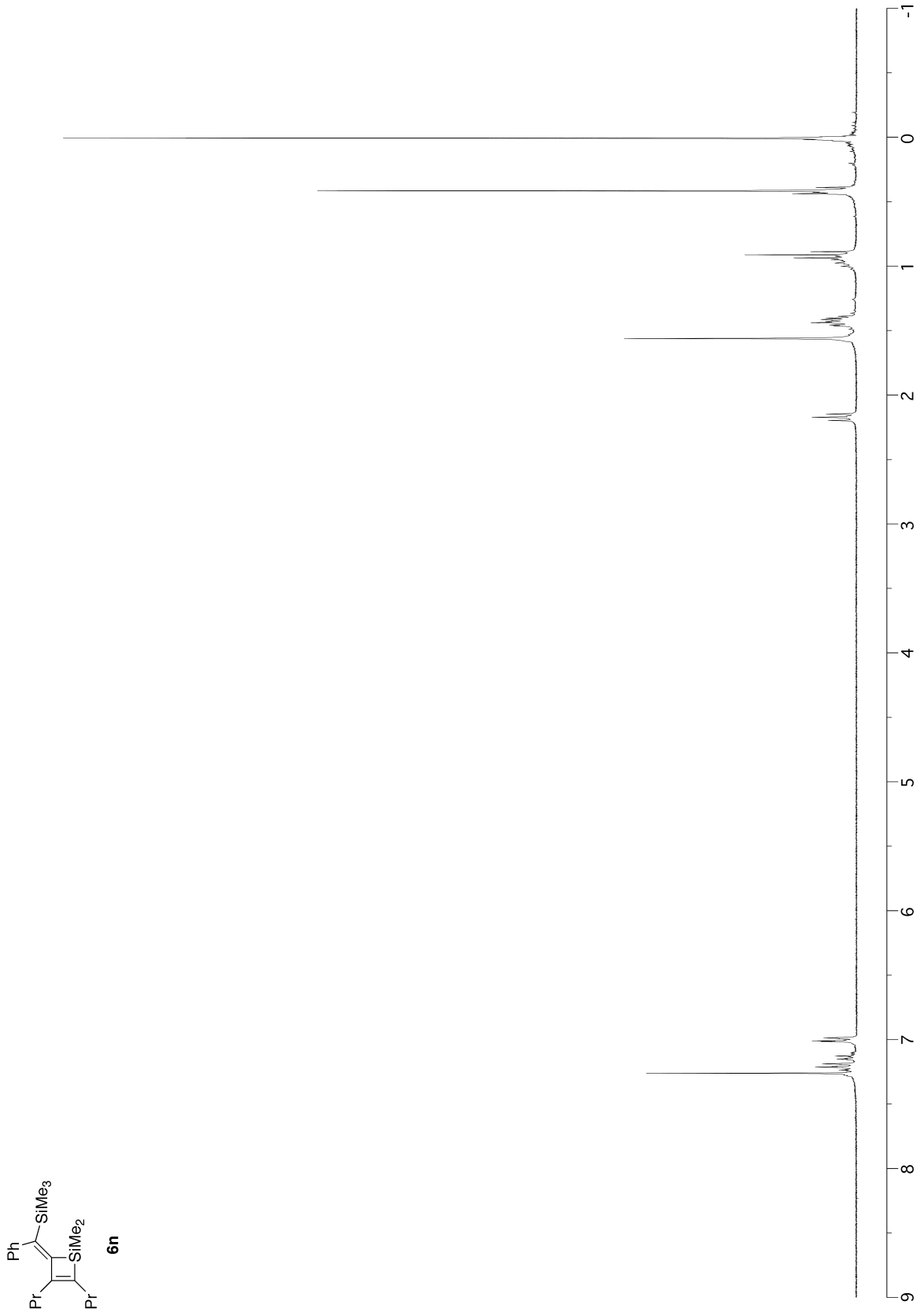

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