

Supporting Information

Synthesis of Silafluorenes by Iridium-Catalyzed [2+2+2] Cycloaddition of Silicon-Bridged Diyne with Alkynes

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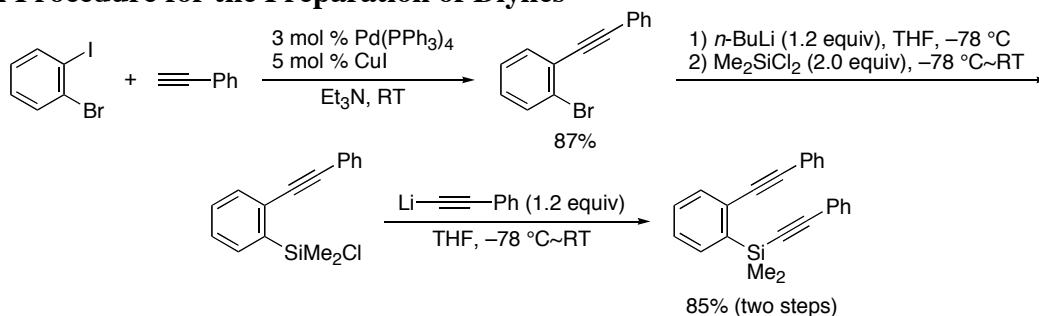
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General. All manipulations were carried out in a nitrogen-filled gloved box and with standard Schlenk techniques under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). NMR spectra were recorded on a Varian Gemini 2000 (¹H at 300.77 MHz and ¹³C NMR at 75.46 MHz), a JEOL JNM-ECA600 (¹³C at 150.92 MHz), or a JEOL JNM-A400 (²⁹Si at 79.30 Hz). Proton chemical shifts were referenced to residual solvent signals in CDCl₃ (δ 7.26) and C₆D₆ (δ 7.16). Carbon chemical shifts were referenced to the deuterated solvent signals in CDCl₃ (δ 77.00) and C₆D₆ (δ 128.00). Silicon Chemical shifts were referenced to Me₄Si (δ 0.00). High resolution mass spectra were recorded on a JEOL JMS-SX102A. UV–vis spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-777. Thermal data were obtained using an SII EXSTAR6000 DSC6220 at a heating rate 10°C/min.

Materials. 1-Bromo-2-iodo-4,5-dimethoxybenzene,¹ 3-bromo-2-iodopyridine,² 1,4-dibromo-2,5-diiodobenzene,³ [IrCl(cod)]₂⁴ were prepared according to the literature procedures. Dibutyl ether was distilled from CaH₂ prior to use. All other commercially available chemical resources were used as received without further purification.

Typical Procedure for the Preparation of Diynes



To a solution of PdCl₂(PPh₃)₂ (316 mg, 0.45 mmol, 3.0 mol %) and 2-bromoiodobenzene (4.24 g, 15 mmol) in triethylamine (100 mL) were added CuI (95 mg, 0.50 mmol, 5.0 mol %) and ethynylbenzene (1.53 g, 15 mmol), and the mixture was stirred at room temperature for 18 h. The precipitate was filtrated, and volatile materials were removed under reduced pressure. The residue was taken up in ether, washed with water, dried over MgSO₄, and concentrated. The crude product was further purified by column chromatography on silica gel (hexane) to give 1-bromo-2-(phenylethynyl)benzene (3.35 g, 87%).

To a solution of 1-bromo-2-(phenylethynyl)benzene (3.35 g, 13.0 mmol) in THF (22.0 mL) was added dropwise *n*-butyllithium (1.54 M hexane solution; 10 mL) at -78 °C over 30 min. After stirring for 1 h at -78 °C, dichlorodimethylsilane (3.33 g, 26.0 mmol) in THF (22 mL) was added to the mixture at -78 °C. After being stirred at room temperature for 20 h, the reaction was quenched by a hexane, and the precipitate was filtrated off. The filtrate was evaporated to give crude chlorodimethyl[2-(phenylethynyl)phenyl]silane, which was used for next step without further purification.

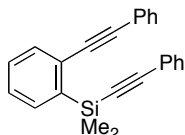
(1) Castanet, A.-S.; Colobert, F.; Broutin, P.-E. *Tetrahedron Lett.* **2002**, 43, 5047.

(2) Cottet, F.; Marull, M.; Lefebvre, O.; Schlosser, M. *Eur. J. Org. Chem.* **2003**, 1559.

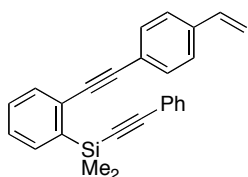
(3) Chanteau, S. H.; Tour, J. M. *J. Org. Chem.* **2003**, 68, 8750.

(4) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, 12, 407.

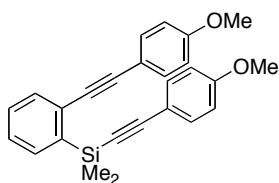
To a solution of ethynylbenzene (1.59 g, 15.6 mmol) in THF (12 mL) at $-78\text{ }^{\circ}\text{C}$ was added dropwise *n*-butyllithium (1.54 M hexane solution; 12 mL) over 30 min. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, chlorodimethyl[2-(phenylethynyl)phenyl]silane (3.75 g, 13.0 mmol) in THF (9 mL) was added to the mixture at $-78\text{ }^{\circ}\text{C}$. After being stirred at room temperature for 19 h, the reaction was quenched by water, extracted with ether, dried over MgSO_4 , and concentrated. The residue was purified by column chromatography on silica gel (hexane) to give dimethyl(phenylethynyl)[2-(phenylethynyl)phenyl]silane (**1a**, 3.72 g, 85% in two steps).



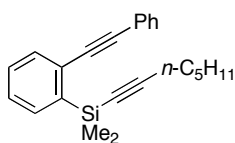
Dimethyl(phenylethynyl)[2-(phenylethynyl)phenyl]silane (1a). ^1H NMR (CDCl_3) δ 0.66 (s, 6H), 7.27-7.40 (m, 9H), 7.46-7.49 (m, 2H), 7.55-7.60 (m, 2H), 7.88-7.91 (m, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.7, 90.6, 92.3, 92.7, 107.0, 123.0, 123.3, 127.6, 128.1, 128.3, 128.4, 128.6, 129.4, 131.2, 131.3, 132.0, 132.2, 135.0, 138.9; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{20}\text{Si}$ (M^+) 336.1334, found 336.1335. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Si}$: C, 85.66; H, 5.99. Found: C, 85.41; H, 5.99.



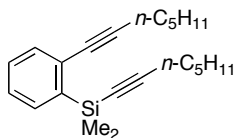
Dimethyl(phenylethynyl){2-[(4-vinylphenyl)ethynyl]phenyl}silane (1b). ^1H NMR (CDCl_3) δ 0.66 (s, 6H), 5.30 (d, $J = 10.8$ Hz, 1H), 5.78 (d, $J = 17.4$ Hz, 1H), 6.72 (dd, $J = 17.4, 10.8$ Hz, 1H), 7.28-7.33 (m, 3H), 7.36-7.42 (m, 4H), 7.46-7.59 (m, 5H), 7.88-7.91 (m, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.7, 91.3, 92.3, 92.8, 107.0, 114.8, 122.6, 123.0, 126.2, 127.6, 128.1, 128.3, 128.6, 129.4, 131.5, 132.0, 132.2, 135.0, 136.2, 137.5, 138.9; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{22}\text{Si}$ (M^+) 362.1491, found 362.1492.



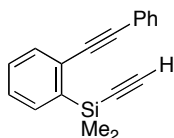
[(4-Methoxyphenyl)ethynyl]{2-[(4-methoxyphenyl)ethynyl]phenyl}dimethylsilane (1c). ^1H NMR (CDCl_3) δ 0.64 (s, 6H), 3.81 (s, 3H), 3.83 (s, 3H), 6.81 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.3$ Hz, 2H), 7.22-7.44 (m, 4H), 7.47-7.56 (m, 3H), 7.86-7.89 (m, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.7, 55.27, 55.31, 89.4, 90.8, 92.7, 107.1, 113.8, 114.1, 115.2, 115.5, 127.2, 128.7, 129.3, 132.0, 132.7, 133.5, 135.0, 138.9, 159.6, 159.8; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 396.1546, found 396.1547.



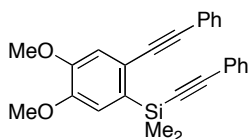
Hept-1-ynyldimethyl[2-(phenylethynyl)phenyl]silane (1d). ^1H NMR (CDCl_3) δ 0.56 (s, 6H), 0.88 (t, $J = 7.1$ Hz, 3H), 1.26-1.43 (m, 4H), 1.49-1.59 (m, 2H), 2.27 (t, $J = 7.2$ Hz, 2H), 7.31-7.40 (m, 5H), 7.54-7.57 (m, 3H), 7.84-7.87 (m, 1H); ^{13}C NMR (C_6D_6 , 75.46 MHz) δ -0.1, 14.1, 20.3, 22.5, 28.6, 31.3, 83.0, 91.6, 93.2, 110.3, 124.0, 127.8, 128.4, 128.7, 128.9, 129.6, 131.6, 132.7, 135.6, 140.1; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{Si}$ (M^+) 330.1804, found 330.1803.



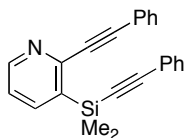
Hept-1-ynyl[2-(hept-1-ynyl)phenyl]dimethylsilane (1e). ^1H NMR (CDCl_3) δ 0.49 (s, 6H), 0.91 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H), 1.31-1.46 (m, 8H), 1.56-1.65 (m, 4H), 2.30 (t, $J = 7.5$ Hz, 2H), 2.42 (t, $J = 7.5$ Hz, 2H), 7.23-7.32 (m, 2H), 7.38-7.41 (m, 1H), 7.81-7.84 (m, 1H); ^{13}C NMR (CDCl_3 , 150.92 MHz) δ -0.6, 13.96, 13.98, 19.5, 20.0, 22.18, 22.24, 28.2, 28.4, 31.1, 31.3, 81.7, 82.6, 93.8, 109.8, 126.7, 129.0, 129.1, 132.1, 135.1, 139.0; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{32}\text{Si}$ (M^+) 324.2273, found 324.2269.



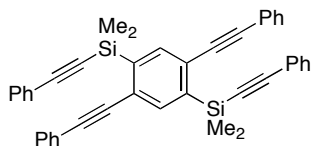
Ethynyldimethyl[2-(phenylethynyl)phenyl]silane (1f). ^1H NMR (CDCl_3) δ 0.61 (s, 6H), 2.58 (s, 1H), 7.33-7.43 (m, 5H), 7.54-7.58 (m, 3H), 7.83-7.86 (m, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.9, 88.3, 90.4, 92.7, 95.2, 123.2, 127.6, 128.2, 128.35, 128.40, 129.6, 131.3, 132.3, 134.9, 138.0; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{16}\text{Si}$ (M^+) 260.1021, found 260.1023.



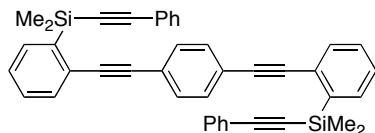
[4,5-Dimethoxy-2-(phenylethynyl)phenyl]dimethyl(phenylethynyl)silane (1g). ^1H NMR (CDCl_3) δ 0.65 (s, 6H), 3.93 (s, 3H), 3.95 (s, 3H), 7.11 (s, 1H), 7.29-7.35 (m, 6H), 7.45-7.49 (m, 3H), 7.53-7.56 (m, 2H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.6, 55.7, 55.8, 90.6, 91.2, 92.5, 107.1, 115.2, 117.5, 121.0, 122.9, 123.4, 128.0, 128.2, 128.3, 128.6, 131.0, 131.2, 131.8, 148.6, 149.6; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 396.1546, found 396.1545.



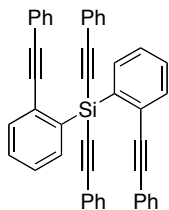
Dimethyl(phenylethynyl)[2-(phenylethynyl)pyridin-3-yl]silane (1h). ^1H NMR (CDCl_3) δ 0.69 (s, 6H), 7.25-7.38 (m, 7H), 7.46-7.50 (m, 2H), 7.62-7.65 (m, 2H), 8.20 (dd, $J = 7.8, 2.1$ Hz, 1H), 8.63 (dd, $J = 4.8, 2.1$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -1.3, 90.0, 90.9, 91.6, 107.8, 122.1, 122.4, 128.1, 128.2, 128.3, 128.7, 128.9, 131.6, 131.8, 134.3, 142.8, 147.3, 150.4; HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{20}\text{NSi}$ ($\text{M}^+ + \text{H}$) 338.1365, found 338.1365.



[2,5-Bis(phenylethynyl)-1,4-phenylene]bis[dimethyl(phenylethynyl)silane] (4). ^1H NMR (CDCl_3) δ 0.67 (s, 12H), 7.27-7.36 (m, 12H), 7.46-7.49 (m, 4H), 7.56-7.60 (m, 4H), 8.04 (s, 2H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.9, 90.9, 91.8, 94.6, 100.0, 107.3, 123.0, 123.3, 127.3, 128.2, 128.4, 128.6, 131.4, 132.0, 138.5, 140.1; HRMS (FAB) calcd for $\text{C}_{42}\text{H}_{34}\text{Si}_2$ (M^+) 594.2199, found 594.2202.



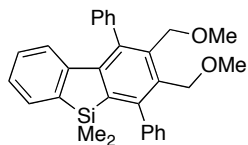
1,4-Bis({2-[dimethyl(phenylethynyl)silyl]phenyl}ethynyl)benzene (6). ^1H NMR (CDCl_3) δ 0.68 (s, 12H), 7.27-7.33 (m, 6H), 7.36-7.42 (m, 4H), 7.46-7.50 (m, 4H), 7.55 (s, 4H), 7.59-7.62 (m, 2H), 7.88-7.91 (m, 2H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -0.7, 92.2, 92.4, 92.5, 107.1, 122.9, 123.2, 127.8, 128.1, 128.2, 128.6, 129.4, 131.3, 132.0, 132.3, 135.0, 139.0; HRMS (FAB) calcd for $\text{C}_{42}\text{H}_{34}\text{Si}_2$ (M^+) 594.2199, found 594.2200.



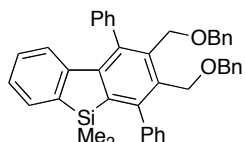
Bis(phenylethynyl)bis[2-(phenylethynyl)phenyl]silane (8). ^1H NMR (CDCl_3) δ 7.17-7.42 (m, 24H), 7.59 (d, $J = 7.2$ Hz, 2H), 8.08 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ 88.1, 90.3, 94.3, 108.2, 122.7, 123.3, 127.4, 127.9, 128.0, 128.8, 129.0, 130.0, 131.6, 132.1, 132.2, 134.3, 136.8 [one aromatic carbon missing due to overlapping]; HRMS (FAB) calcd for $\text{C}_{44}\text{H}_{28}\text{Si}$ (M^+) 584.1960, found 584.1961.

General Procedure for Iridium(I)-Catalyzed [2+2+2] Cycloaddition of Diynes with Monoynes

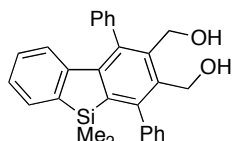
To a solution of $[\text{IrCl}(\text{cod})]_2$ (5.0 mg, 7.5 μmol , 2.5 mol %) and triphenylphosphine (7.9 mg, 0.030 mmol, 10 mol%) in dry dibutyl ether (0.6 mL) was added a solution of **1a** (101.0 mg, 0.30 mmol) and **2a** (68.5 mg, 0.60 mmol) in dry dibutyl ether (3.0 mL). After being stirred under argon atmosphere for 24 h at 110 $^\circ\text{C}$, the volatile material was removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:AcOEt = 10:1) to give 2,3-bis(methoxymethyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (**3aa**, 116.8 mg, 86%).



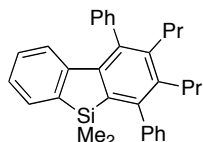
2,3-Bis(methoxymethyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (3aa). ^1H NMR (CDCl_3) δ 0.04 (s, 6H), 3.20 (s, 3H), 3.25 (s, 3H), 4.27 (s, 2H), 4.33 (s, 2H), 6.34 (d, $J = 8.1$ Hz, 1H), 6.91-6.97 (m, 1H), 7.10 (dt, $J = 7.2, 0.9$ Hz, 1H), 7.39-7.55 (m, 11H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.4, 58.5, 68.7, 69.1, 126.0, 126.4, 127.2, 127.3, 127.4, 128.5, 129.2, 129.8, 129.9, 131.9, 133.3, 138.4, 139.3, 140.8, 141.1, 141.4, 141.7, 145.3, 147.9, 148.7; ^{29}Si NMR (CDCl_3) δ -1.13; HRMS (EI) calcd for $\text{C}_{30}\text{H}_{30}\text{O}_2\text{Si}$ (M^+) 450.2015, found 450.2013.



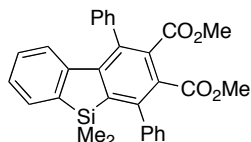
2,3-Bis(benzyloxymethyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (3ab). ^1H NMR (CDCl_3) δ -0.01 (s, 6H), 4.12 (s, 2H), 4.18 (s, 2H), 4.24 (s, 2H), 4.29 (s, 2H), 6.29 (d, $J = 7.8$ Hz, 1H), 6.88 (t, $J = 7.8$ Hz, 1H), 7.05 (t, $J = 7.2$ Hz, 1H), 7.17-7.30 (m, 11H), 7.36-7.47 (m, 10H); ^{13}C NMR (CDCl_3 , 150.92 Hz) δ -2.5, 66.5, 66.8, 73.1, 73.2, 126.1, 126.4, 127.3, 127.4, 127.5, 127.59, 127.62, 128.25, 128.26, 128.27, 128.29, 128.6, 129.2, 129.9, 130.0, 132.0, 133.6, 138.06, 138.11, 138.6, 139.4, 140.9, 141.2, 141.5, 141.7, 145.4, 148.0, 148.8; HRMS (EI) calcd for $\text{C}_{42}\text{H}_{38}\text{O}_2\text{Si}$ (M^+) 602.2641, found 602.2642.



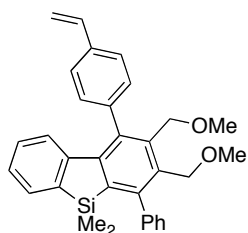
2,3-Bis(hydroxymethyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (3ac). ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 2.20-2.45 (bs, 2H), 4.56 (s, 2H), 4.62 (s, 2H), 6.28 (d, $J = 8.4$ Hz, 1H), 6.92 (dt, $J = 8.7, 1.5$ Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 7.35-7.39 (m, 4H), 7.43-7.57 (m, 7H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.5, 60.1, 60.5, 126.0, 126.6, 127.5, 127.6, 127.9, 129.2, 129.3, 129.5, 129.7, 132.0, 136.0, 138.6, 140.8, 141.0, 141.4, 141.6, 145.1, 147.7, 148.0 [one aromatic carbon signal was missing due to overlapping]; HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 422.1702, found 422.1702.



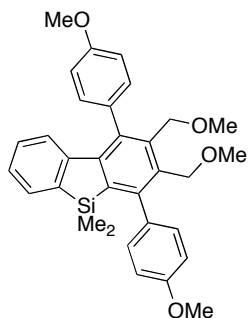
9,9-Dimethyl-1,4-diphenyl-2,3-dipropyl-9-silafluorene (3ad). ^1H NMR (C_6D_6) δ 0.09 (s, 6H), 0.74 (t, $J = 7.5$ Hz, 3H), 0.80 (t, $J = 7.5$ Hz, 3H), 1.54-1.68 (m, 4H), 2.57-2.70 (m, 4H), 6.61-6.64 (m, 1H), 6.93-7.02 (m, 3H), 7.13-7.35 (m, 8H), 7.42-7.45 (m, 1H); ^{13}C NMR (C_6D_6 , 75.46 MHz) δ -1.95, 15.2 [overlapping], 25.3, 25.6, 33.2, 33.4, 126.3, 126.7, 127.3, 127.5, 128.0, 129.3, 129.9, 130.3, 130.4, 132.6, 138.0, 138.4, 139.1, 141.6, 142.8, 143.1, 143.7, 143.8, 148.4, 149.3; HRMS (EI) calcd for $\text{C}_{32}\text{H}_{34}\text{Si}$ (M^+) 446.2430, found 446.2434.



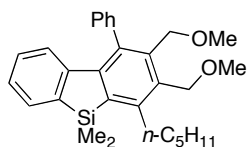
2,3-Bis(methoxycarbonyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (3ae). ^1H NMR (CDCl_3) δ 0.07 (s, 6H), 3.46 (s, 3H), 3.49 (s, 3H), 6.49 (d, $J = 8.1$ Hz, 1H), 6.96 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.15 (dt, $J = 7.5, 0.9$ Hz, 1H), 7.31-7.55 (m, 11H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.4, 52.0, 52.1, 126.6, 127.5, 127.7, 128.0, 128.6, 129.1, 129.4, 129.5, 132.3, 135.1, 137.1, 138.9, 140.9, 141.7, 143.6, 145.9, 146.6, 147.3, 168.2, 168.6; HRMS (FAB) calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4\text{Si}$ (M^+) 478.1600, found 478.1604.



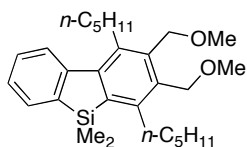
2,3-Bis(methoxymethyl)-9,9-dimethyl-1-phenyl-4-(4-vinylphenyl)-9-silafluorene (3ba). ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 3.21 (s, 3H), 3.24 (s, 3H), 4.25 (s, 2H), 4.31 (s, 2H), 5.37 (dd, $J = 10.8, 0.6$ Hz, 1H), 5.91 (dd, $J = 17.4, 0.6$ Hz, 1H), 6.47 (d, $J = 8.1$ Hz, 1H), 6.88 (dd, $J = 17.4, 10.8$ Hz, 1H), 6.96 (t, $J = 8.1$ Hz, 1H), 7.10 (dt, $J = 7.2, 0.6$ Hz, 1H), 7.36-7.49 (m, 8H), 7.58 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.4, 58.48, 58.53, 68.7, 69.1, 113.8, 126.1, 126.4, 126.5, 127.2, 127.5, 129.3, 129.9, 130.0, 132.0, 133.4, 136.4, 136.7, 138.5, 139.0, 140.5, 141.2, 141.4, 141.7, 145.3, 147.9, 148.8; HRMS (EI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_2\text{Si}$ (M^+) 476.2172, found 476.2169.



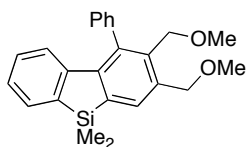
2,3-Bis(methoxymethyl)-1,4-bis(4-methoxyphenyl)-9,9-dimethyl-9-silafluorene (3ca). ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 3.20 (s, 3H), 3.24 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 4.23 (s, 2H), 4.28 (s, 2H), 6.41 (d, $J = 8.1$ Hz, 1H), 6.93-7.11 (m, 6H), 7.24-7.30 (m, 4H), 7.46 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (C_6D_6 , 150.92 MHz) δ -2.1, 54.70, 54.71, 58.28, 58.34, 69.3, 69.7, 113.1, 114.4, 126.8, 126.9, 129.9, 131.4, 131.6, 132.6, 133.7, 134.8, 135.2, 139.7, 140.4, 141.5, 141.8, 146.3, 149.0, 149.1, 159.4, 159.5; HRMS (EI) calcd for $\text{C}_{32}\text{H}_{34}\text{O}_4\text{Si}$ (M^+) 510.2226, found 510.2228.



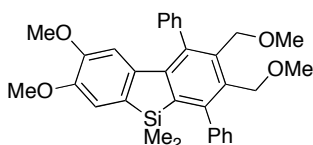
2,3-Bis(methoxymethyl)-9,9-dimethyl-1-pentyl-4-phenyl-9-silafluorene (3da). ^1H NMR (CDCl_3) δ 0.46 (s, 6H), 0.97 (t, $J = 7.2$ Hz, 3H), 1.42-1.55 (m, 4H), 1.61-1.72 (m, 2H), 2.82-2.88 (m, 2H), 3.14 (s, 3H), 3.51 (s, 3H), 4.13 (s, 2H), 4.58 (s, 2H), 6.23 (d, $J = 8.1$ Hz, 1H), 6.89 (dt, $J = 7.8, 1.5$ Hz, 1H), 7.09 (t, $J = 7.1$ Hz, 1H), 7.28-7.31 (m, 2H), 7.43-7.47 (m, 3H), 7.51-7.54 (m, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.3, 14.1, 22.6, 32.7 [overlapping], 36.3, 58.3, 58.9, 68.4, 68.7, 125.9, 126.3, 127.1, 128.5, 129.3, 129.8, 131.8, 133.4, 138.2, 139.0, 140.4, 140.8, 141.1, 146.0, 147.5, 148.3; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{36}\text{O}_2\text{Si}$ (M^+) 444.2485, found 444.2491.



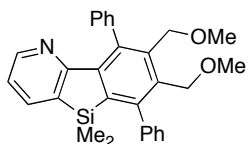
2,3-Bis(methoxymethyl)-9,9-dimethyl-1,4-dipentyl-9-silafluorene (3ea). ^1H NMR (CDCl_3) δ 0.42 (s, 6H), 0.94 (t, $J = 7.2$ Hz, 3H), 0.98 (t, $J = 7.2$ Hz, 3H), 1.34-1.61 (m, 10H), 1.72-1.84 (m, 2H), 2.75-2.80 (m, 2H), 3.05-3.10 (m, 2H), 3.50 (s, 3H), 3.51 (s, 3H), 4.52 (s, 2H), 4.59 (s, 2H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 8.3$ Hz, 1H), 7.63 (d, $J = 6.0$ Hz, 1H), 7.92 (d, $J = 8.1$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.3, 14.1, 14.2, 22.5, 22.6, 30.0, 30.3, 32.3, 32.7, 32.8, 36.5, 58.7, 58.8, 68.4, 68.7, 125.6, 126.3, 129.9, 132.2, 133.9, 137.8, 139.4, 141.1, 141.5, 145.5, 146.9, 149.0; HRMS (EI) calcd for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{Si}$ (M^+) 438.2954, found 438.2955. Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{Si}$: C, 76.66; H, 9.65. Found: C, 76.39; H, 9.52.



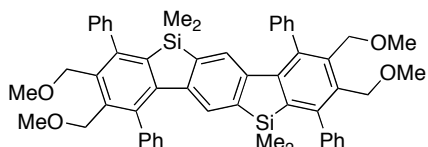
2,3-Bis(methoxymethyl)-9,9-dimethyl-4-phenyl-9-silafluorene (3fa). ^1H NMR (CDCl_3) δ 0.43 (s, 6H), 3.14 (s, 3H), 3.52 (s, 3H), 4.15 (s, 2H), 4.66 (s, 2H), 6.25 (d, $J = 8.1$ Hz, 1H), 6.92 (t, $J = 7.8$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.30-7.32 (m, 2H), 7.47-7.49 (m, 3H), 7.56 (d, $J = 6.9$ Hz, 1H), 7.75 (s, 1H); ^{13}C NMR (C_6D_6 , 75.46 MHz) δ -3.2, 58.0, 58.4, 68.8, 72.8, 126.4, 126.9, 127.6, 129.0, 130.1, 130.3, 132.4, 132.9, 137.2, 137.8, 140.1, 140.8, 141.7, 145.4, 149.3 [one aromatic carbon signal was missing due to overlapping]; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 374.1702, found 374.1695.



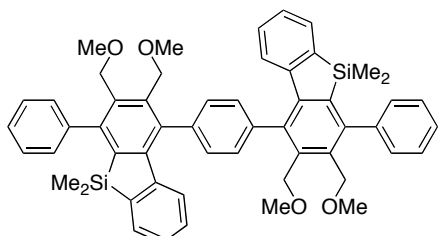
6,7-Dimethoxy-2,3-bis(methoxymethyl)-9,9-dimethyl-1,4-diphenyl-9-silafluorene (3ga). ^1H NMR (CDCl_3) δ 0.01 (s, 6H), 3.16 (s, 3H), 3.22 (s, 3H), 3.25 (s, 3H), 3.85 (s, 3H), 4.22 (s, 2H), 4.29 (s, 2H), 6.22 (s, 1H), 6.92 (s, 1H), 7.36-7.47 (m, 8H), 7.51-7.57 (m, 2H); ^{13}C NMR (CDCl_3 , 150.92 MHz) δ -2.3, 54.8, 55.7, 58.38, 58.45, 68.7, 69.1, 110.2, 113.6, 127.2, 127.3, 127.4, 128.6, 129.9, 130.4, 132.5, 132.9, 138.1, 138.4, 141.02, 141.04, 141.5, 141.8, 145.0, 147.8, 148.6, 149.4; HRMS (EI) calcd for $\text{C}_{32}\text{H}_{34}\text{O}_4\text{Si}$ (M^+) 510.2226, found 510.2226.



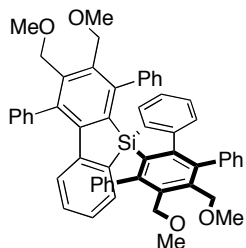
7,8-Bis(methoxymethyl)-5,5-dimethyl-6,9-diphenyl-5-silaindeno[3,2-b]pyridine (3ha). ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 3.18 (s, 3H), 3.23 (s, 3H), 4.26 (s, 2H), 4.33 (s, 2H), 6.86 (dd, $J = 6.9, 4.8$ Hz, 1H), 7.27-7.31 (m, 2H), 7.37-7.47 (m, 8H), 7.68 (dd, $J = 6.9, 1.8$ Hz, 1H), 8.06 (dd, $J = 5.1, 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.9, 58.5 [overlapping], 68.5, 69.1, 120.8, 125.9, 127.1, 127.3, 127.6, 129.5, 129.9, 134.0, 134.9, 139.2, 139.3, 140.3, 141.19, 141.22, 141.6, 144.8, 148.6, 149.7, 165.6; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{30}\text{NO}_2\text{Si}$ ($\text{M}+\text{H}$) 452.2046, found 452.2047.



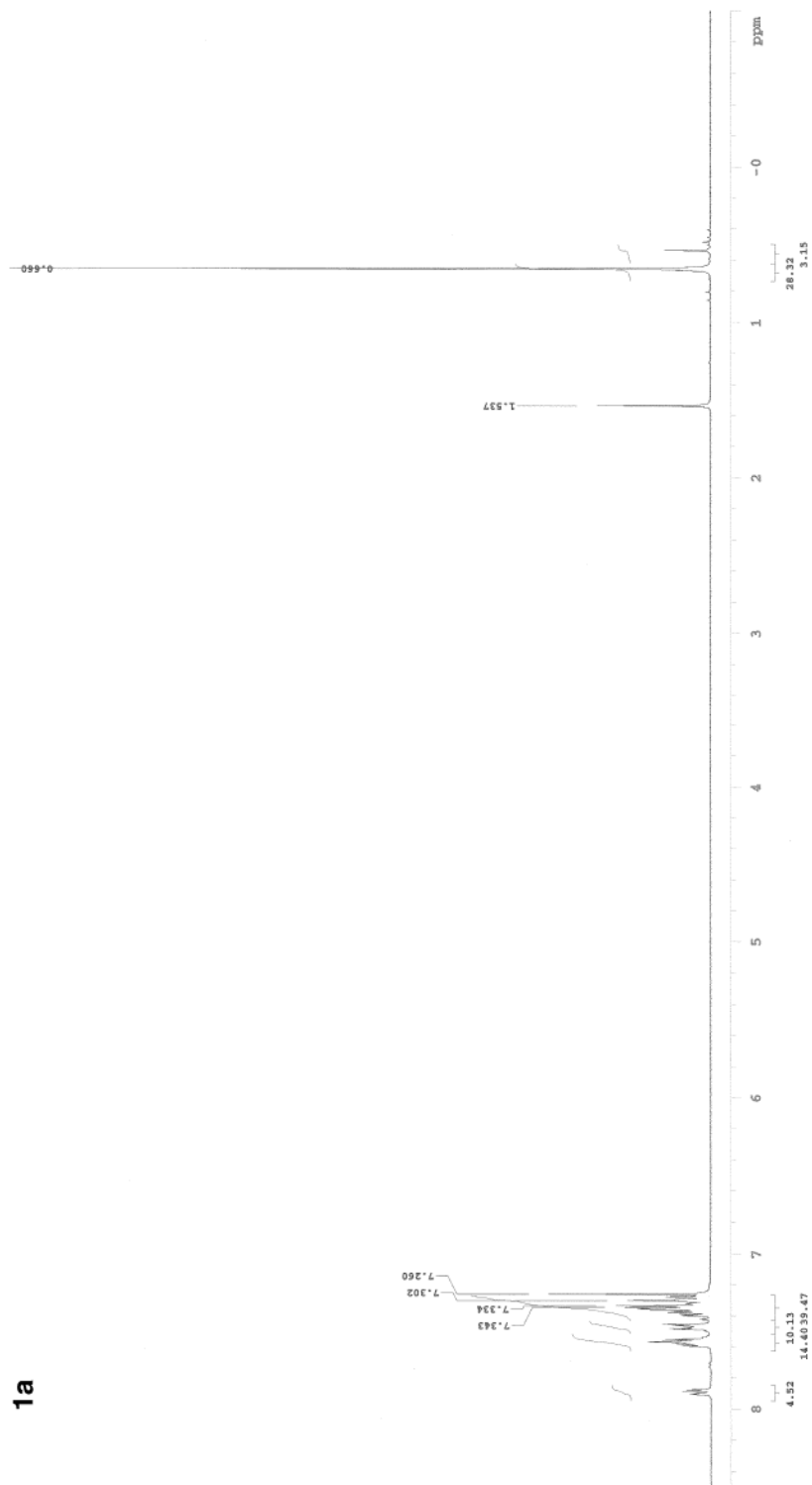
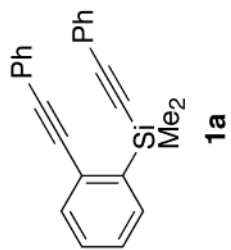
2,3,8,9-Tetrakis(methoxymethyl)-6,6,12,12-tetramethyl-1,4,7,10-tetraphenyl-6,12-disilaindeno[1,2-b]fluorene (5). ^1H NMR (CDCl_3 , 400 MHz) δ -0.26 (s, 12H), 3.16 (s, 6H), 3.21 (s, 6H), 4.26 (s, 4H), 4.27 (s, 4H), 6.10 (s, 2H), 7.28-7.33 (m, 8H), 7.37-7.44 (m, 12H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -3.0, 58.48, 58.51, 68.7, 69.1, 127.0, 127.1, 127.4, 128.5, 129.2, 129.8, 129.9, 132.9, 137.9, 139.3, 141.1, 141.6, 141.8, 142.6, 145.3, 145.6, 148.7; HRMS (FAB) calcd for $\text{C}_{54}\text{H}_{54}\text{O}_4\text{Si}_2$ (M^+) 822.3561, found 822.3566.

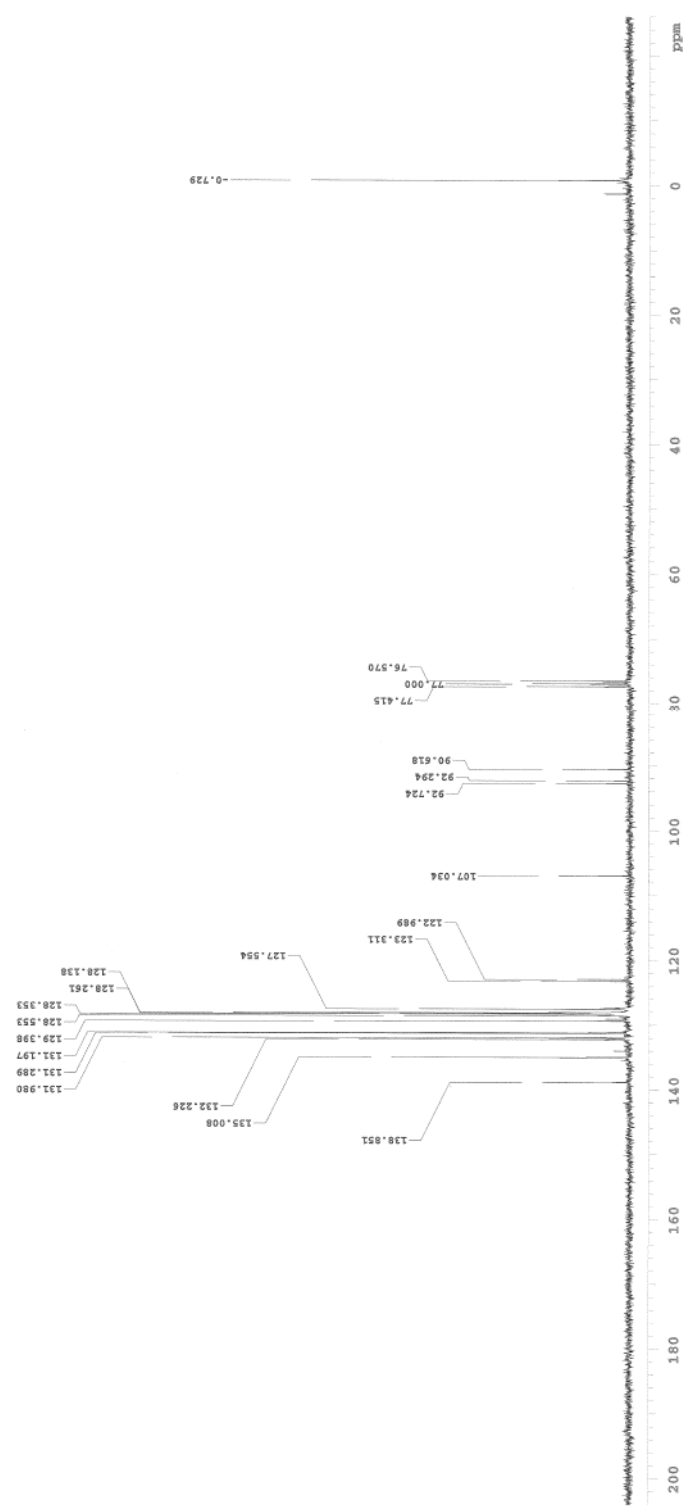
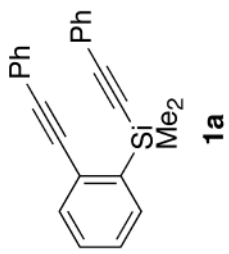


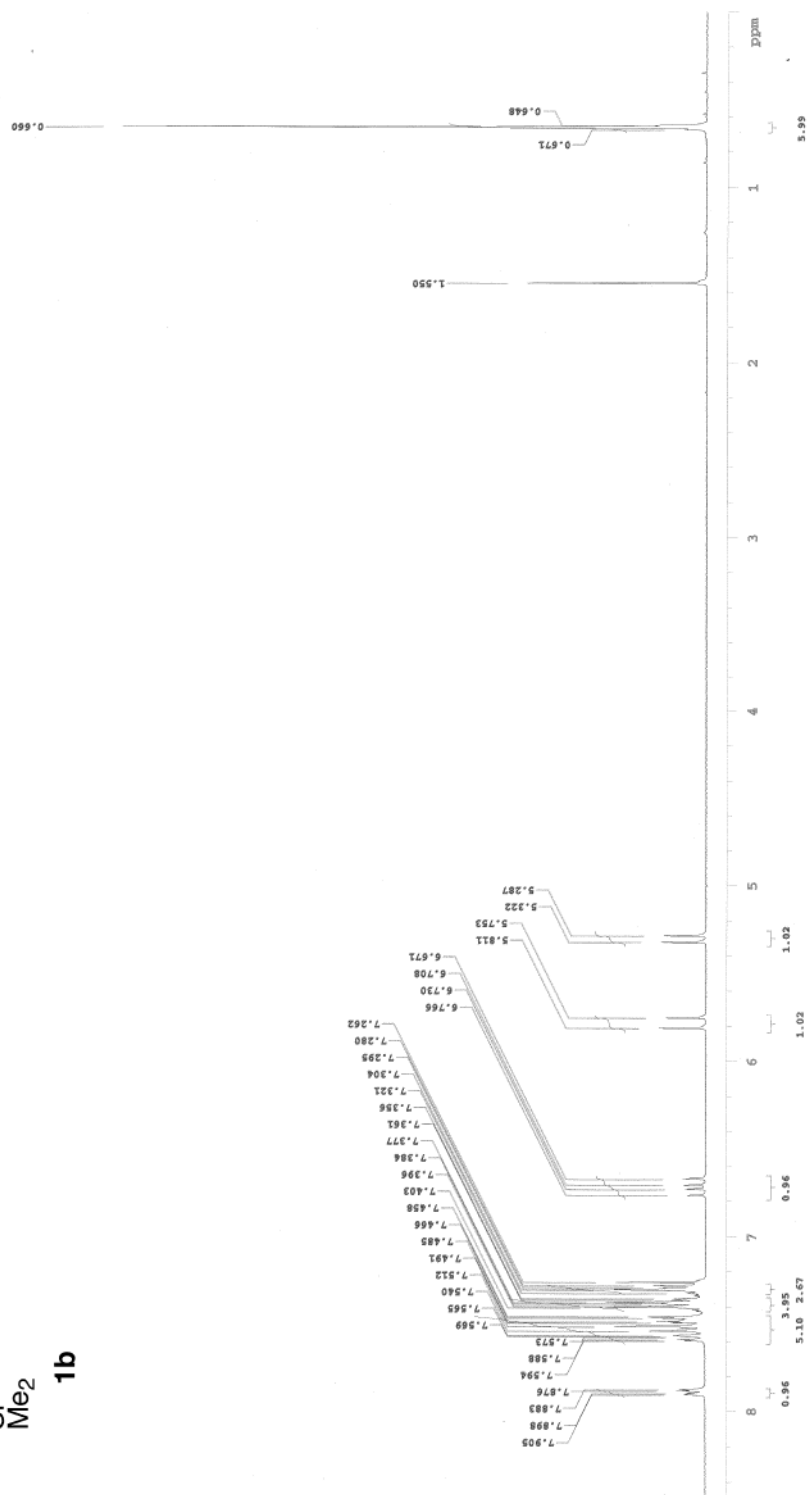
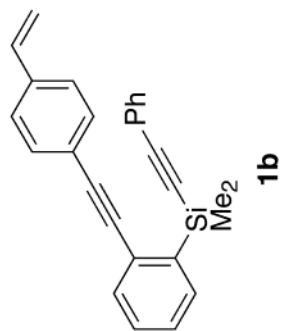
1,4-Bis[2,3-bis(methoxymethyl)-9,9-dimethyl-1-phenyl-9-silafluoren-4-yl]benzene (7). ^1H NMR (CDCl_3 , an approximately 3:1 mixture of rotational isomers) δ 0.03 (s, 6H, major), 0.04 (s, 12H, minor), 3.24 (s, 6H, minor), 3.25 (s, 6H, minor), 3.27 (s, 6H, major), 3.36 (s, 6H, major), 4.25 (s, 4H, minor), 4.31 (s, 4H, minor), 4.36 (s, 4H, major), 4.52 (s, 4H, major), 6.71 (d, $J = 7.9$ Hz, 2H), 7.01 (t, $J = 7.7$ Hz, 2H), 7.13 (t, $J = 7.1$ Hz, 2H), 7.36-7.52 (m, 12H), 7.56 (s, 4H); ^{13}C NMR (CDCl_3 , 75.46 MHz) δ -2.4, 58.58, 58.64, 68.9, 69.2, 126.3, 126.6, 127.3, 127.6, 128.9, 130.0, 130.4, 132.2, 133.6, 138.6, 139.1, 140.1, 141.4, 141.7, 141.8, 145.3, 148.1, 148.9; HRMS (FAB) calcd for $\text{C}_{54}\text{H}_{54}\text{O}_4\text{Si}_2$ (M^+) 822.3561, found 822.3561.

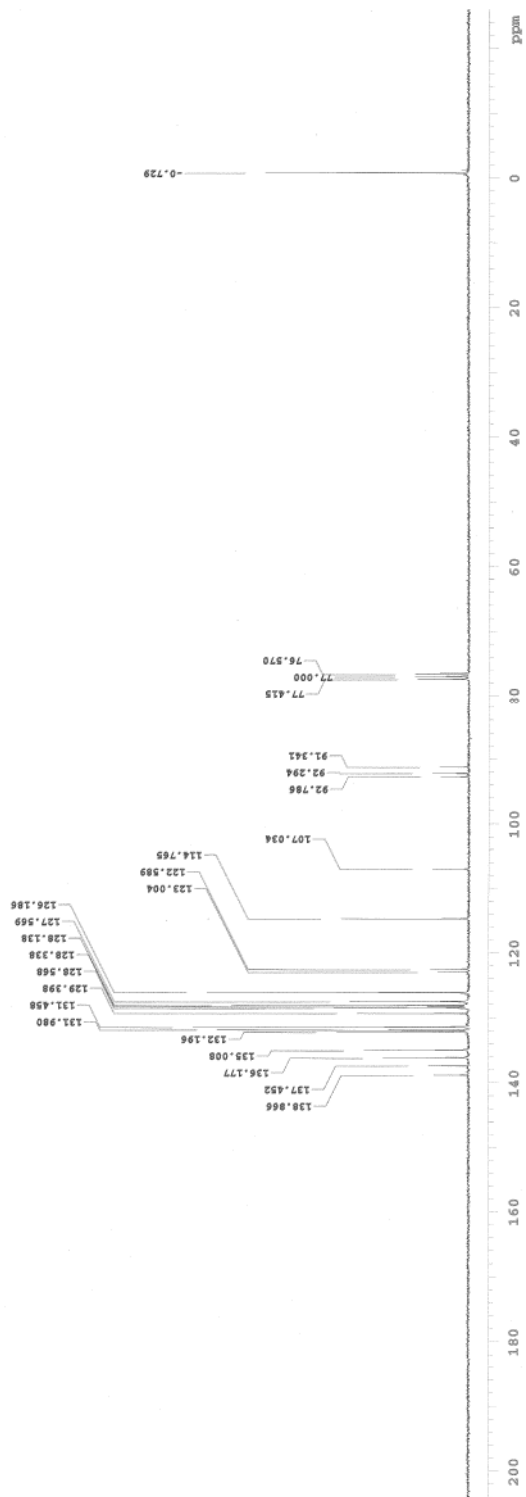
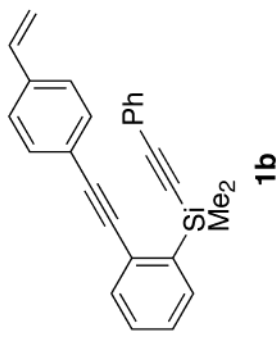


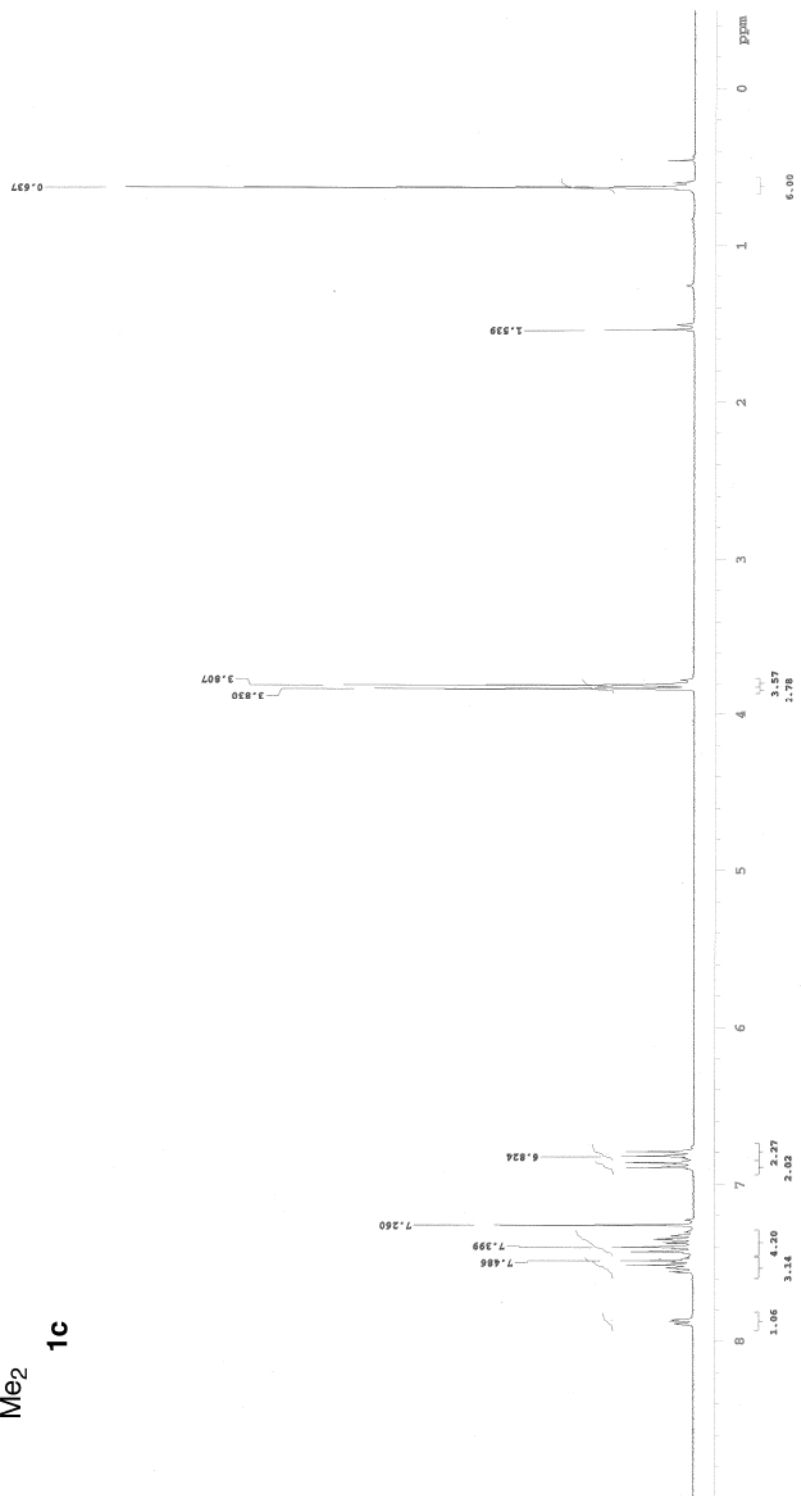
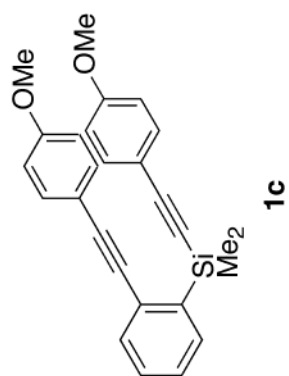
1,1',4,4'-Tetraphenyl-2,2',3,3'-tetrakis(methoxymethyl)-9,9'-spirobi(9-silafluorene) (9). ^1H NMR (CDCl_3) δ 3.15 (s, 6H), 3.16 (s, 6H), 4.21 (s, 8H), 6.06 (d, $J = 8.1$ Hz, 2H), 6.55-6.63 (m, 4H), 6.83 (dt, $J = 7.8, 1.5$ Hz, 2H), 6.90-7.04 (m, 8H), 7.13 (d, $J = 6.9$ Hz, 2H), 7.33-7.39 (m, 4H), 7.49-7.62 (m, 6H); ^{13}C NMR (CDCl_3 , 150.92 MHz at 45 °C) δ 58.0, 58.2, 68.7, 69.0, 126.1, 126.3, 126.4, 126.60, 126.62, 127.3, 128.4, 128.5, 128.6, 129.59, 129.64, 129.8, 130.0, 133.0, 133.8, 135.7, 135.8, 139.0, 139.4, 140.4, 140.9, 146.8, 149.1, 149.8; HRMS (FAB) calcd for $\text{C}_{56}\text{H}_{48}\text{O}_4\text{Si}$ (M^+) 812.3322, found 812.3322.

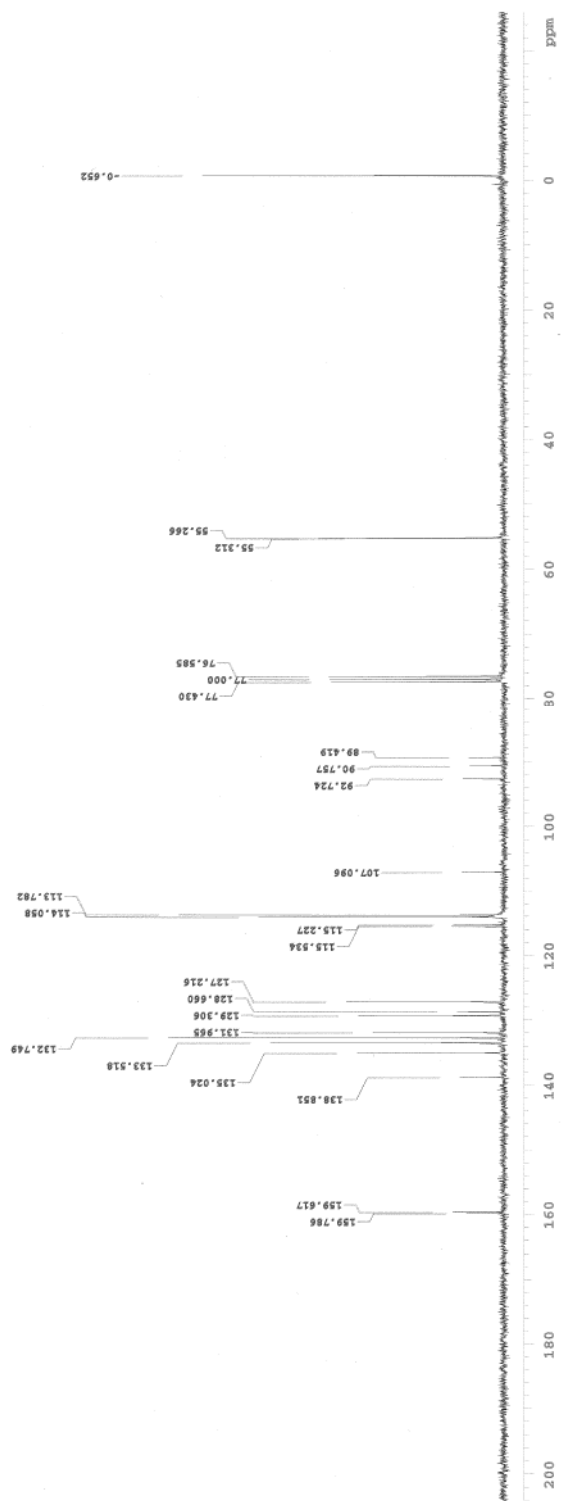
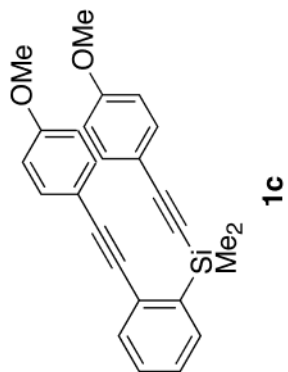


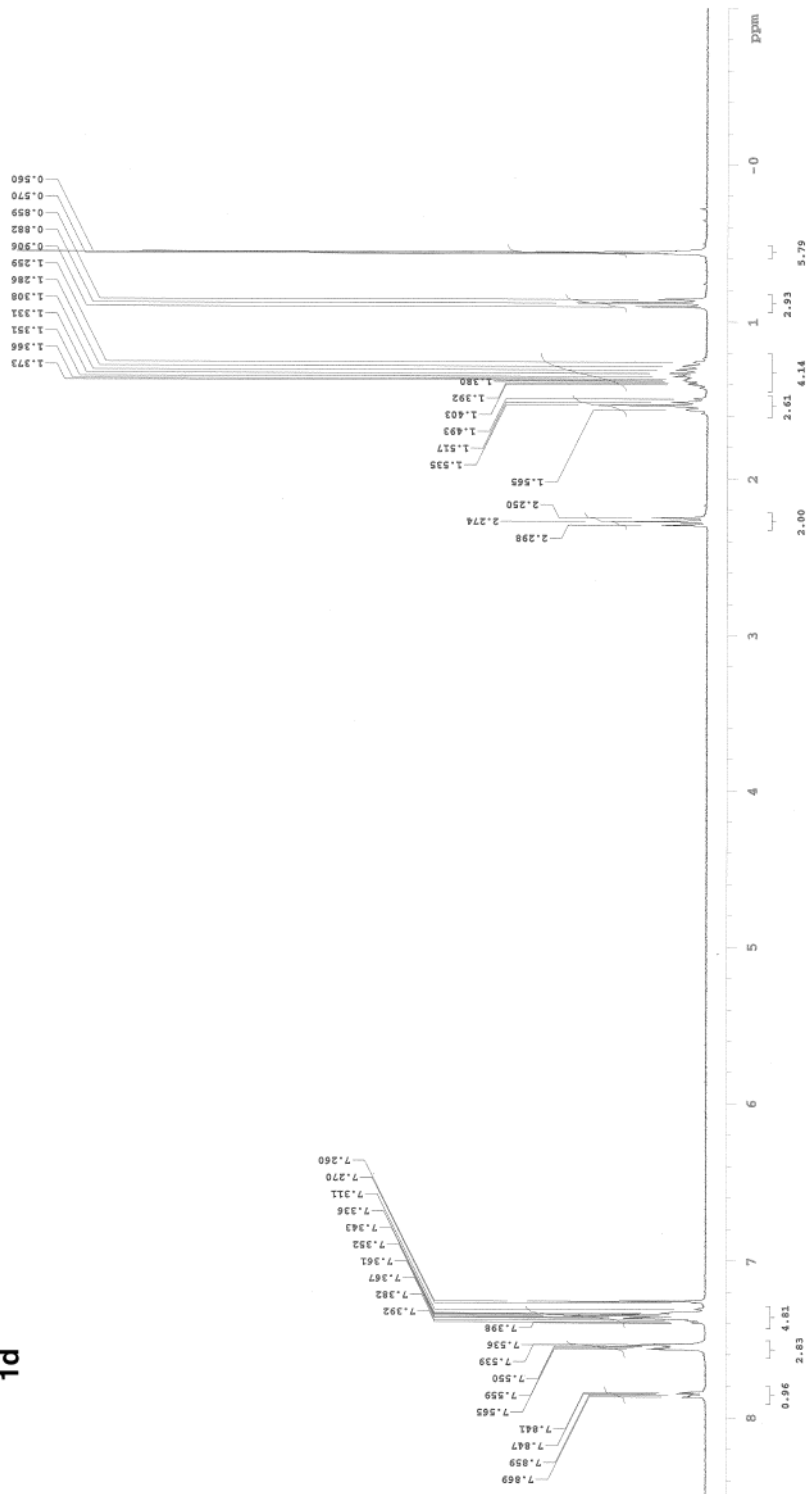
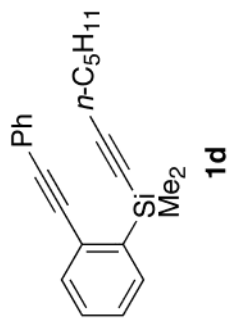


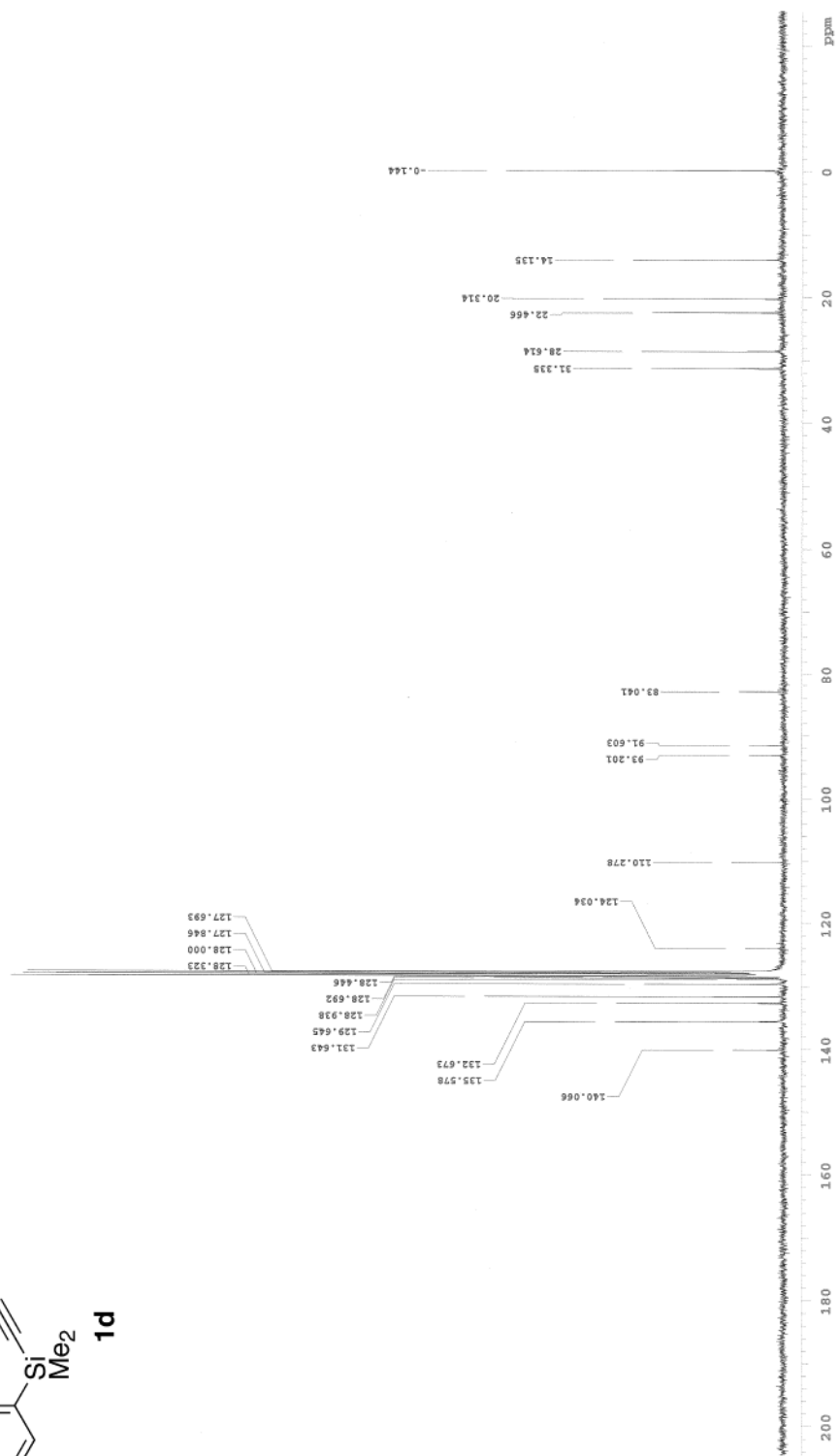
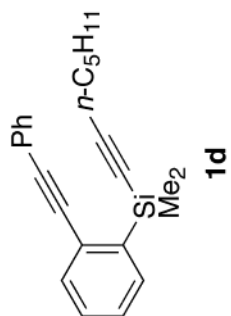


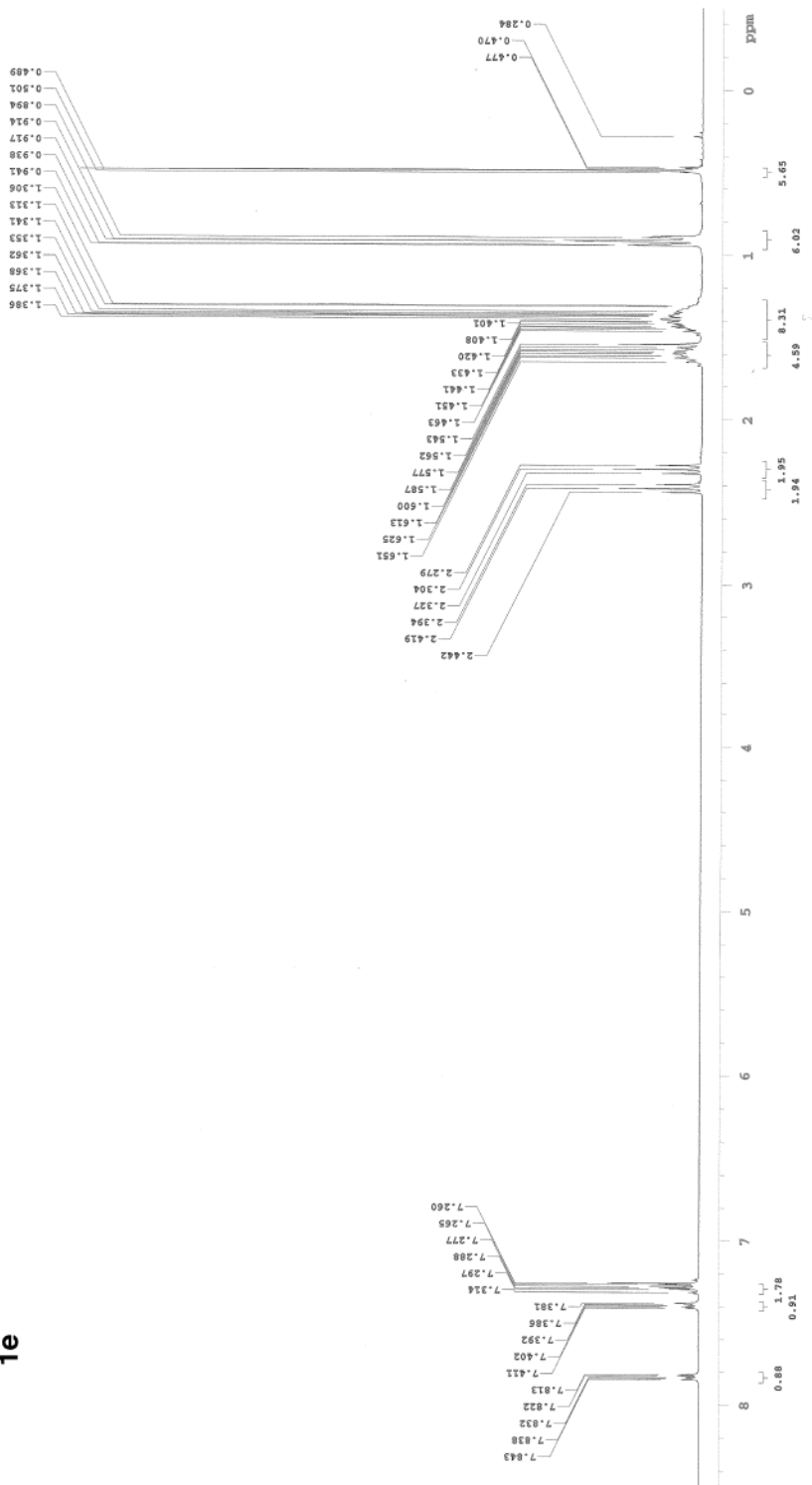
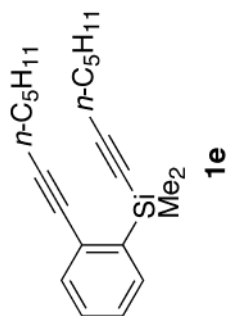


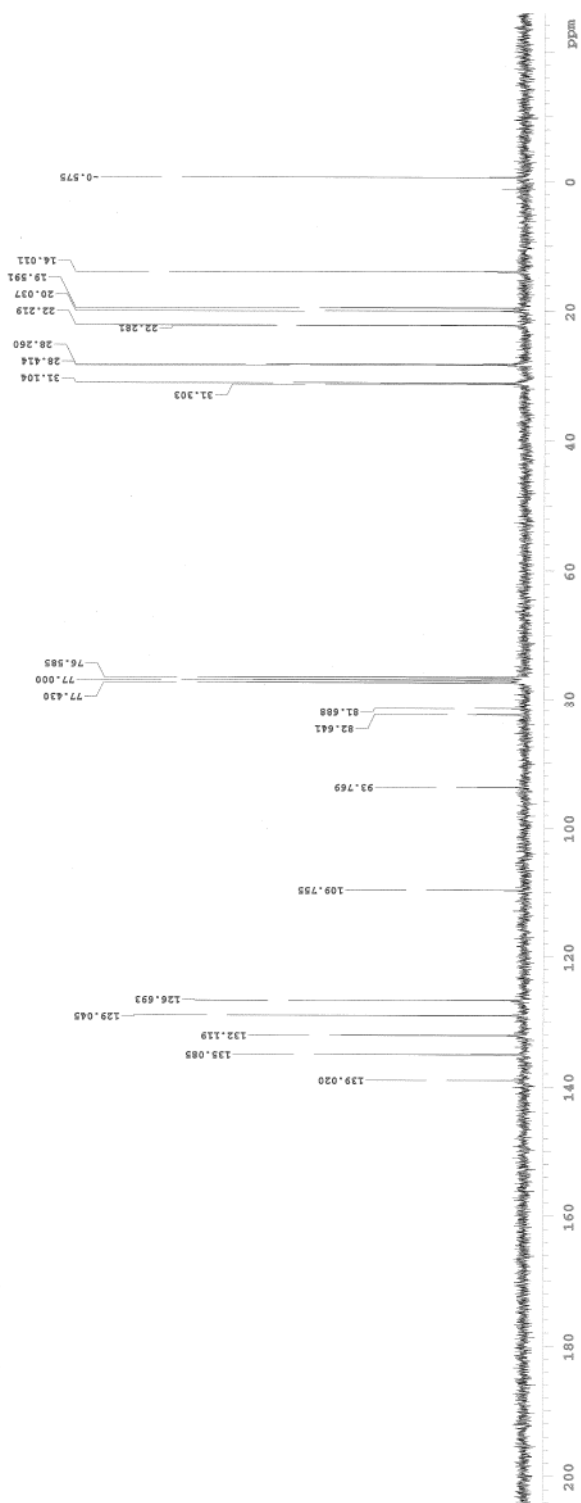
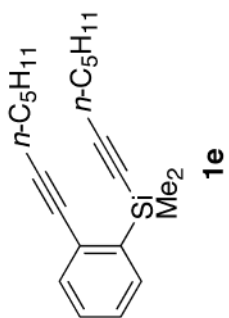


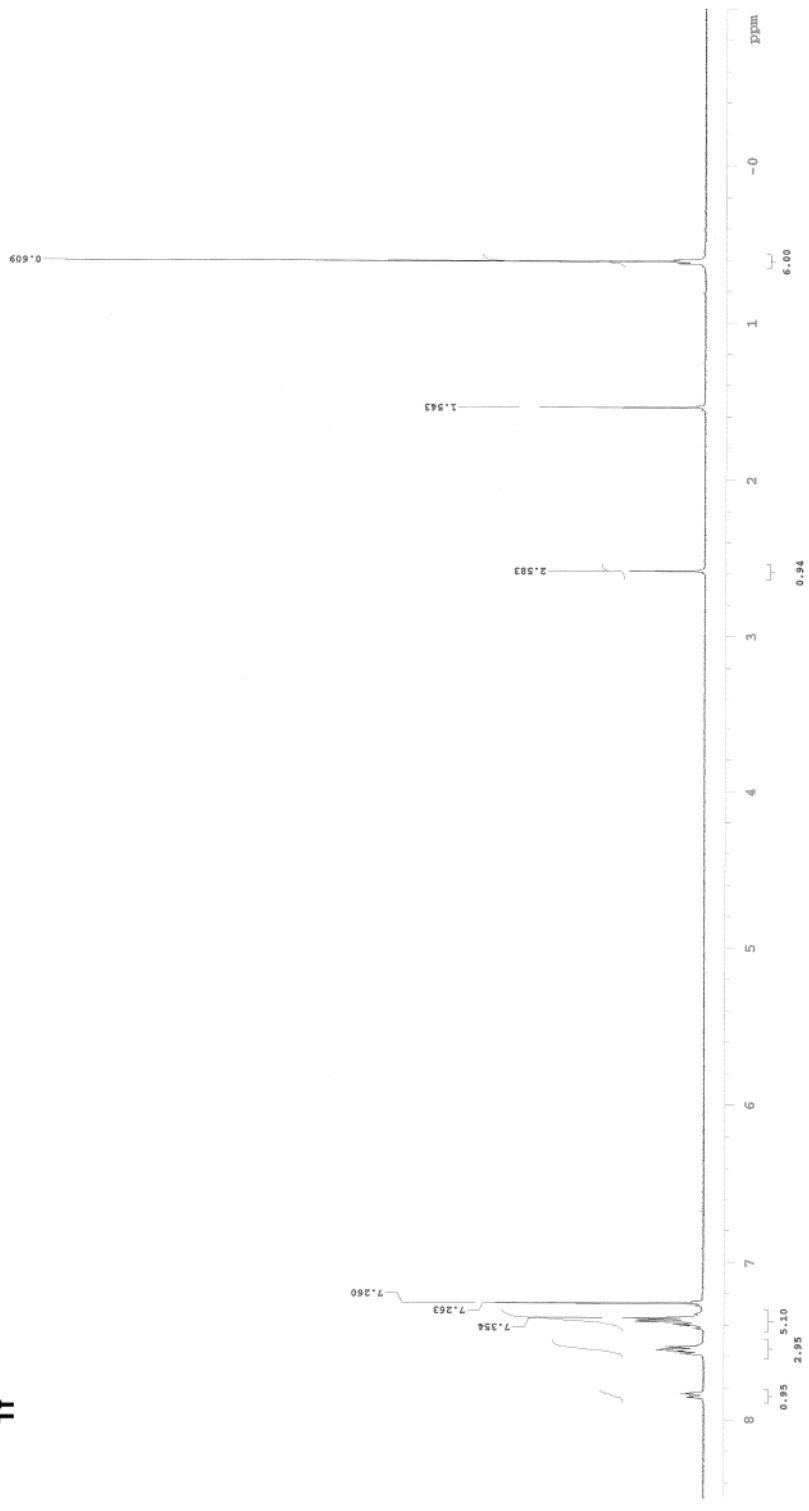
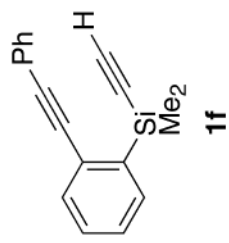


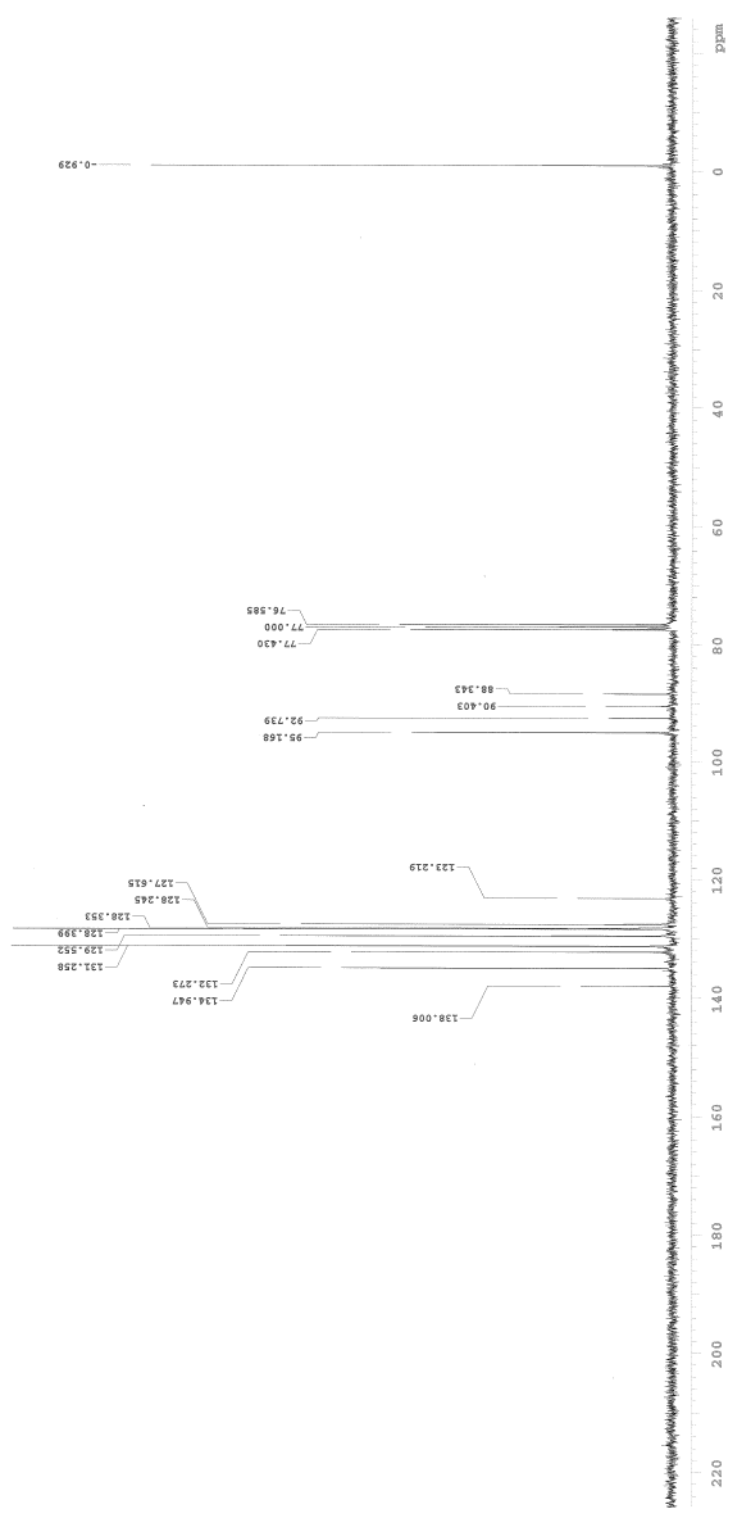
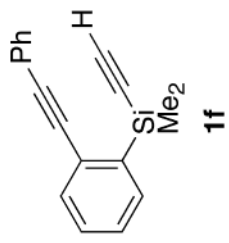


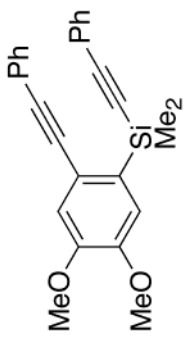




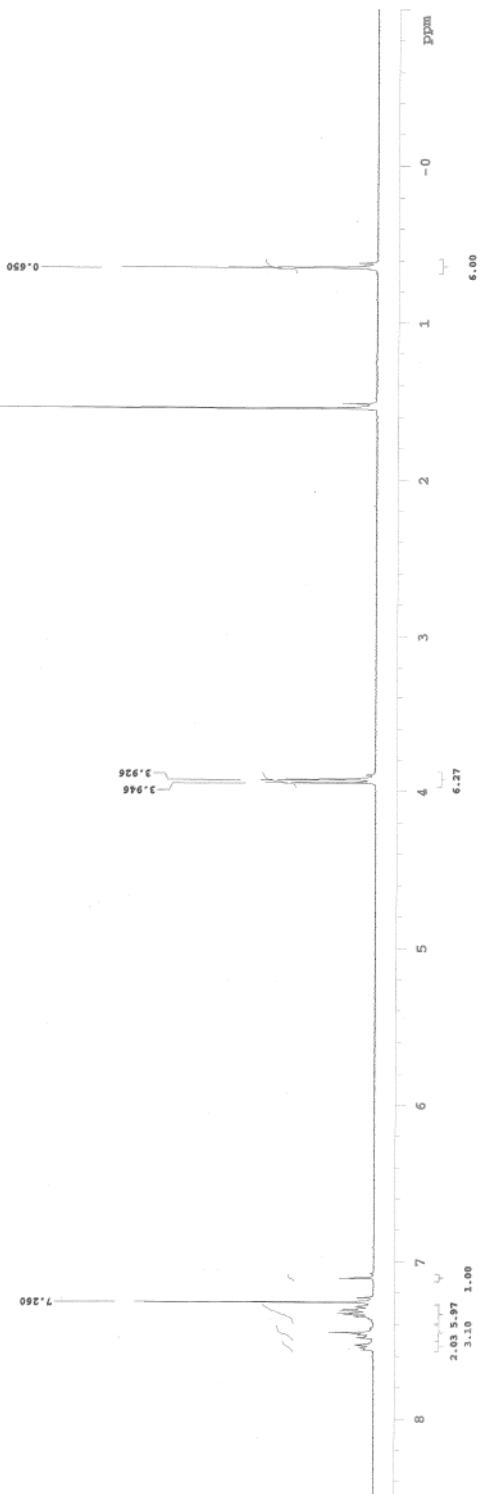


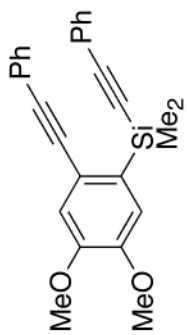




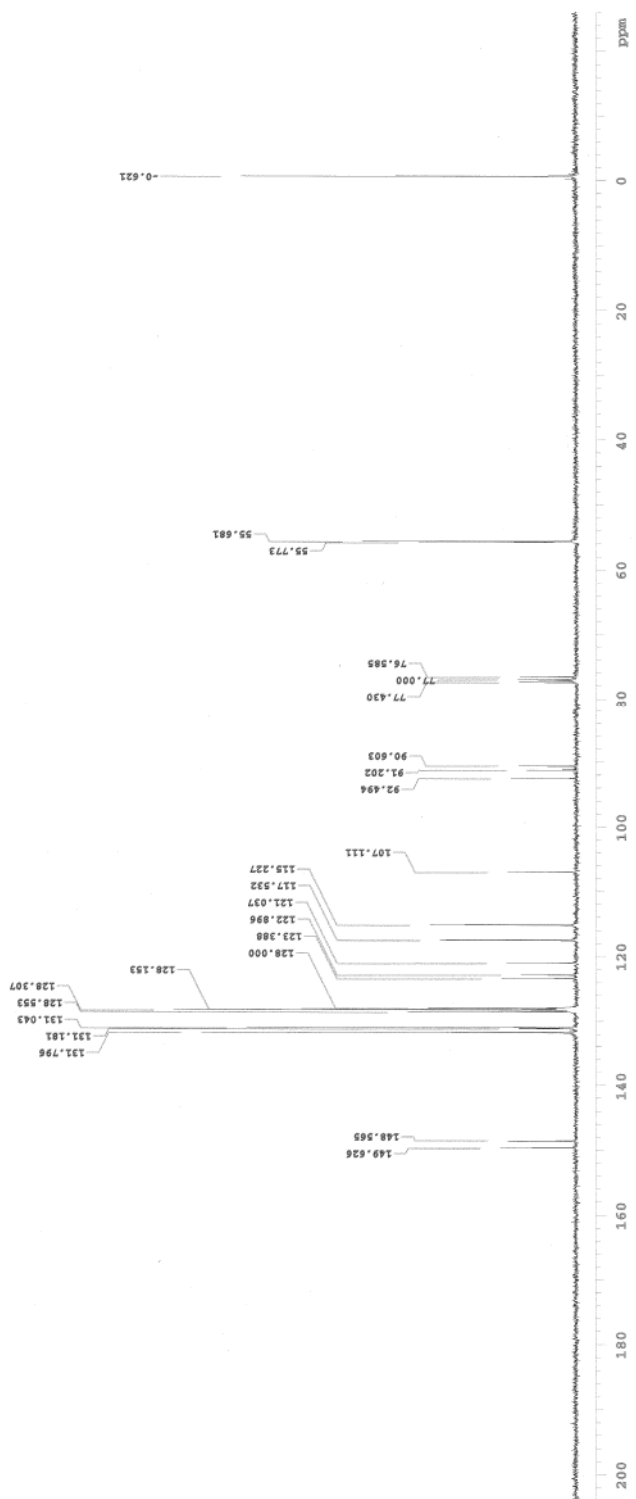


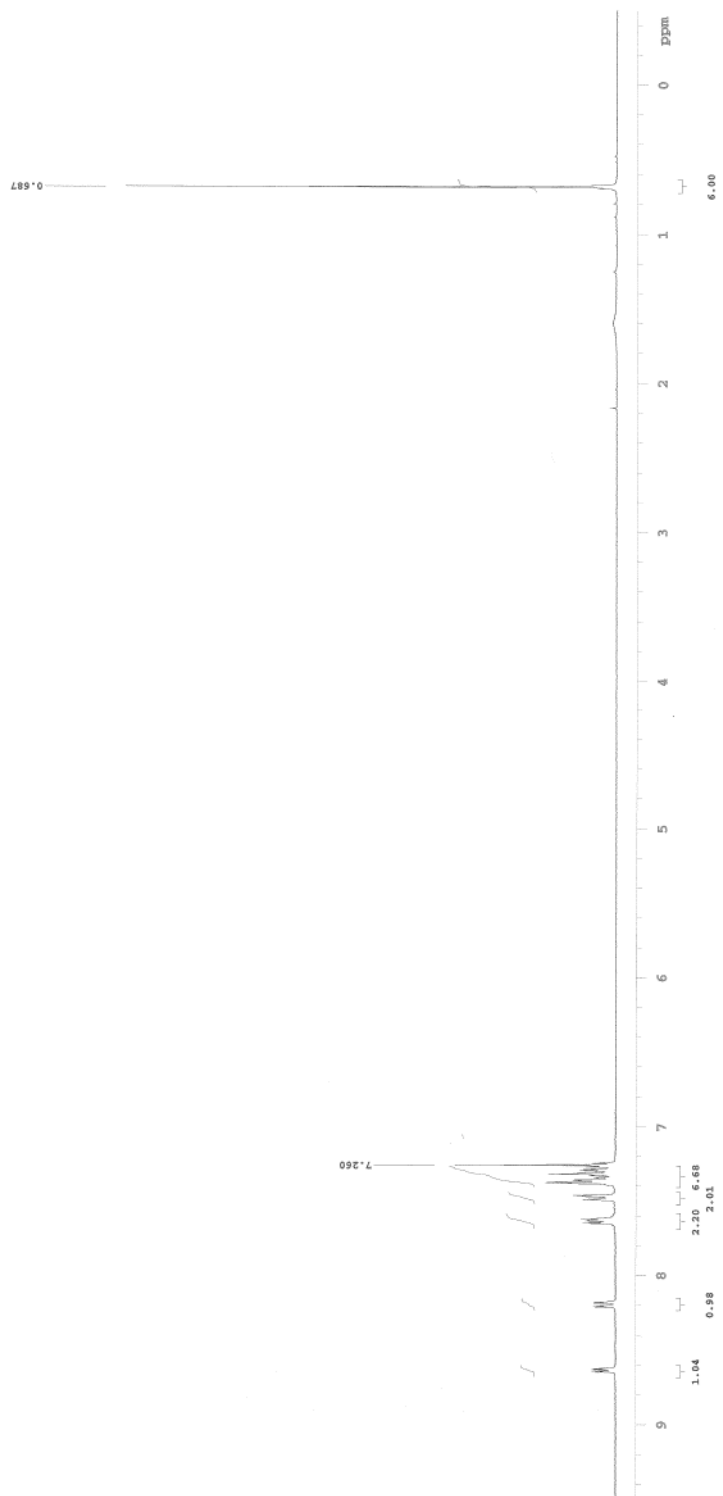
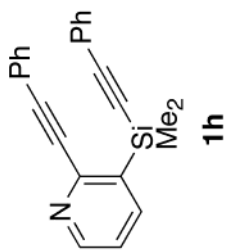
19

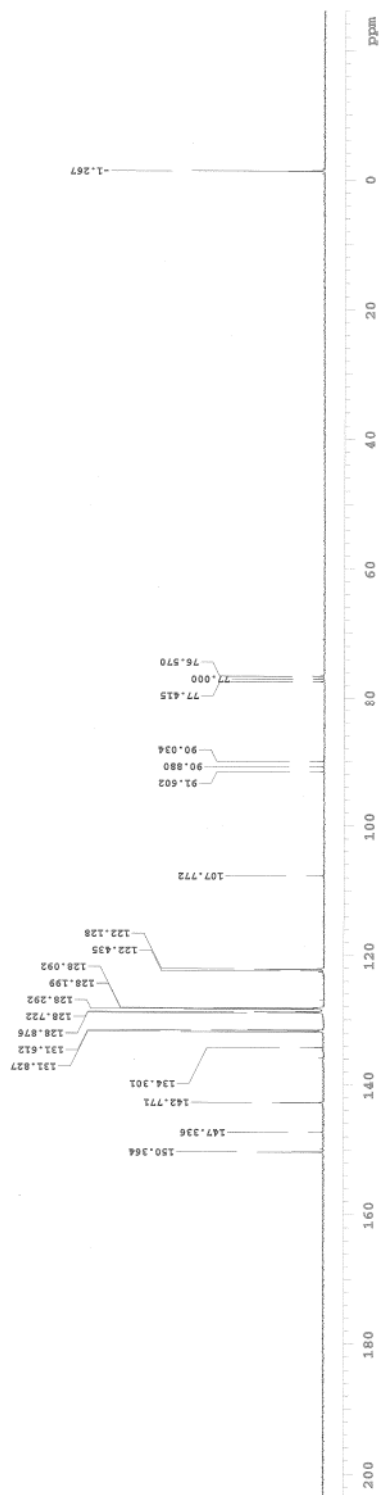
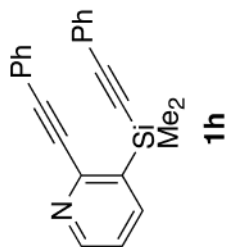


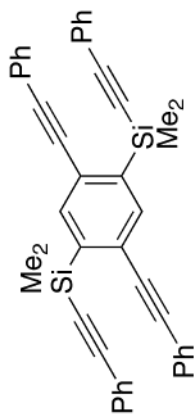


1g

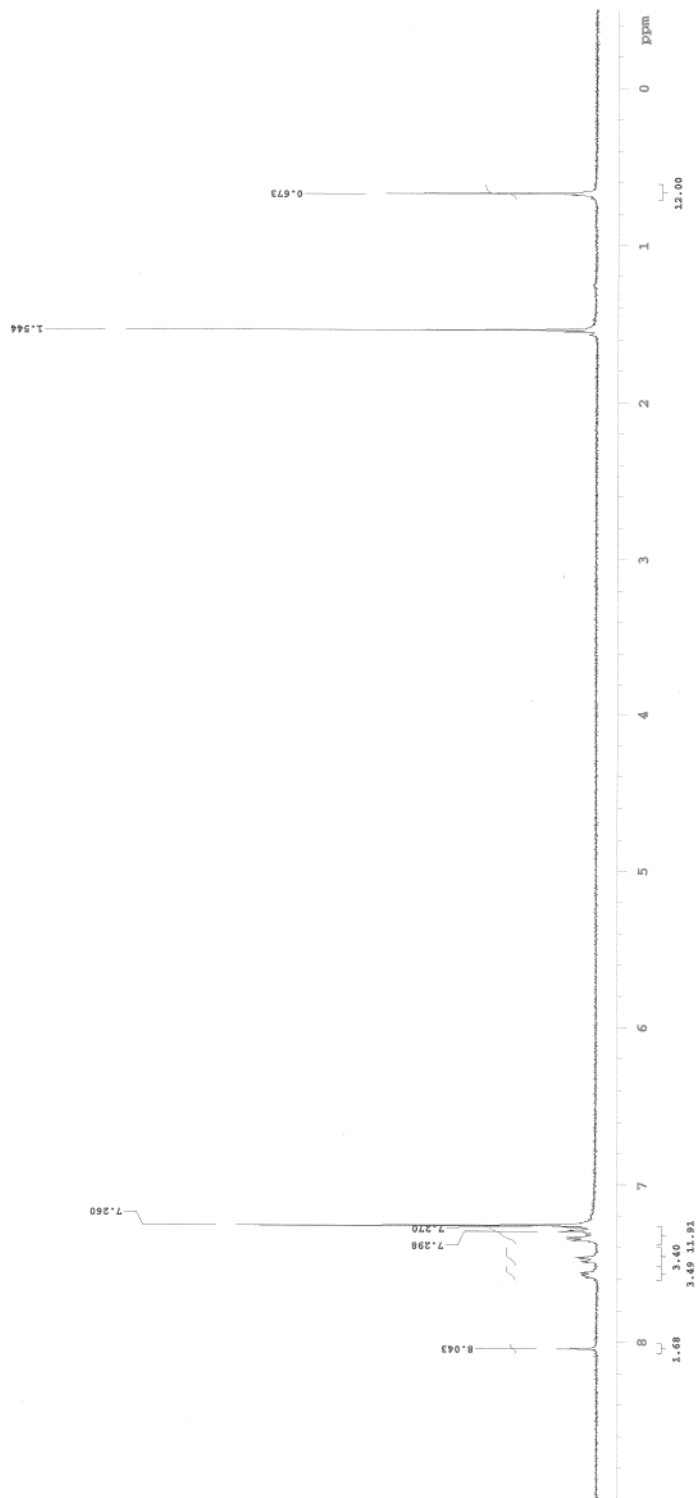


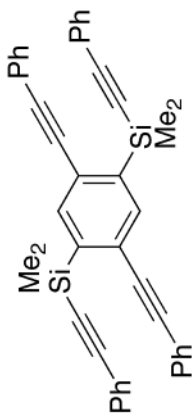




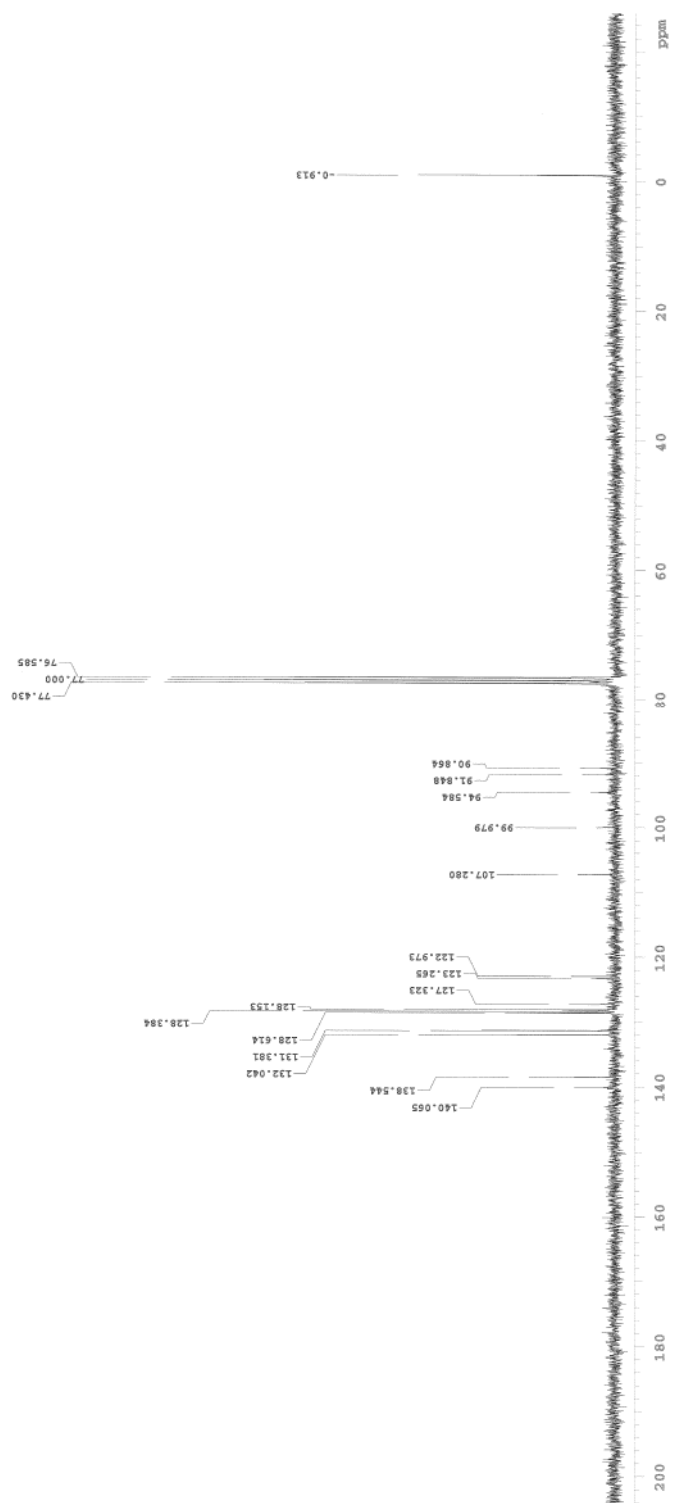


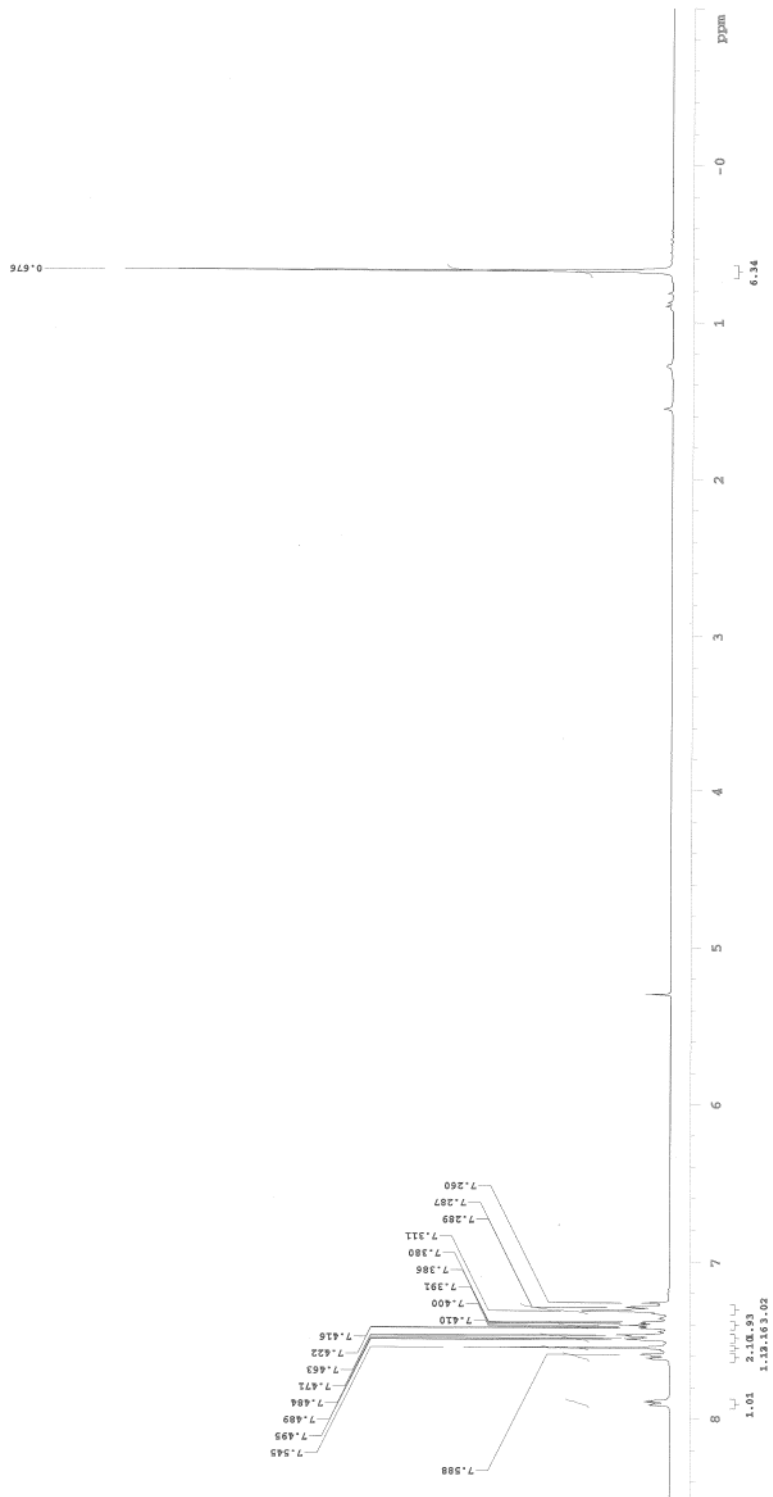
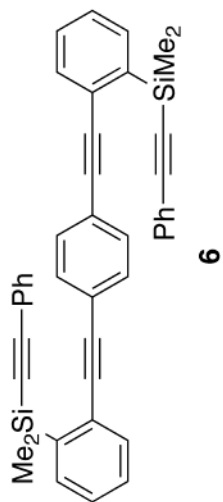
4

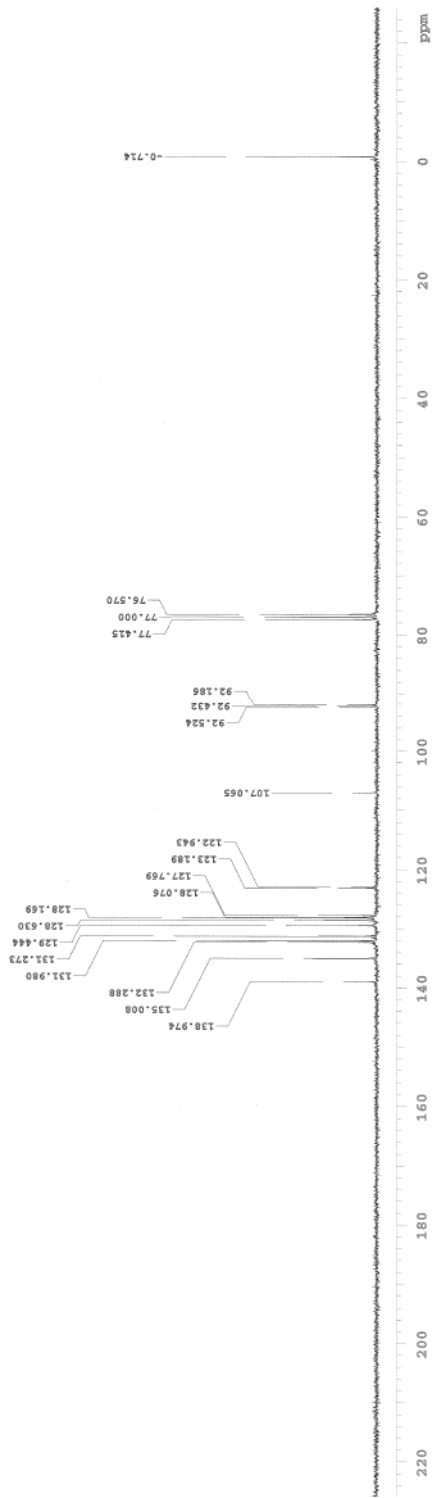
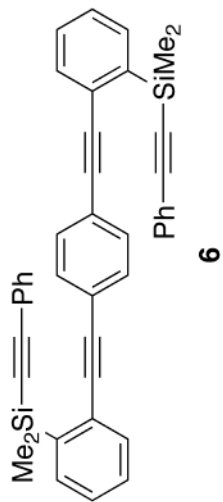


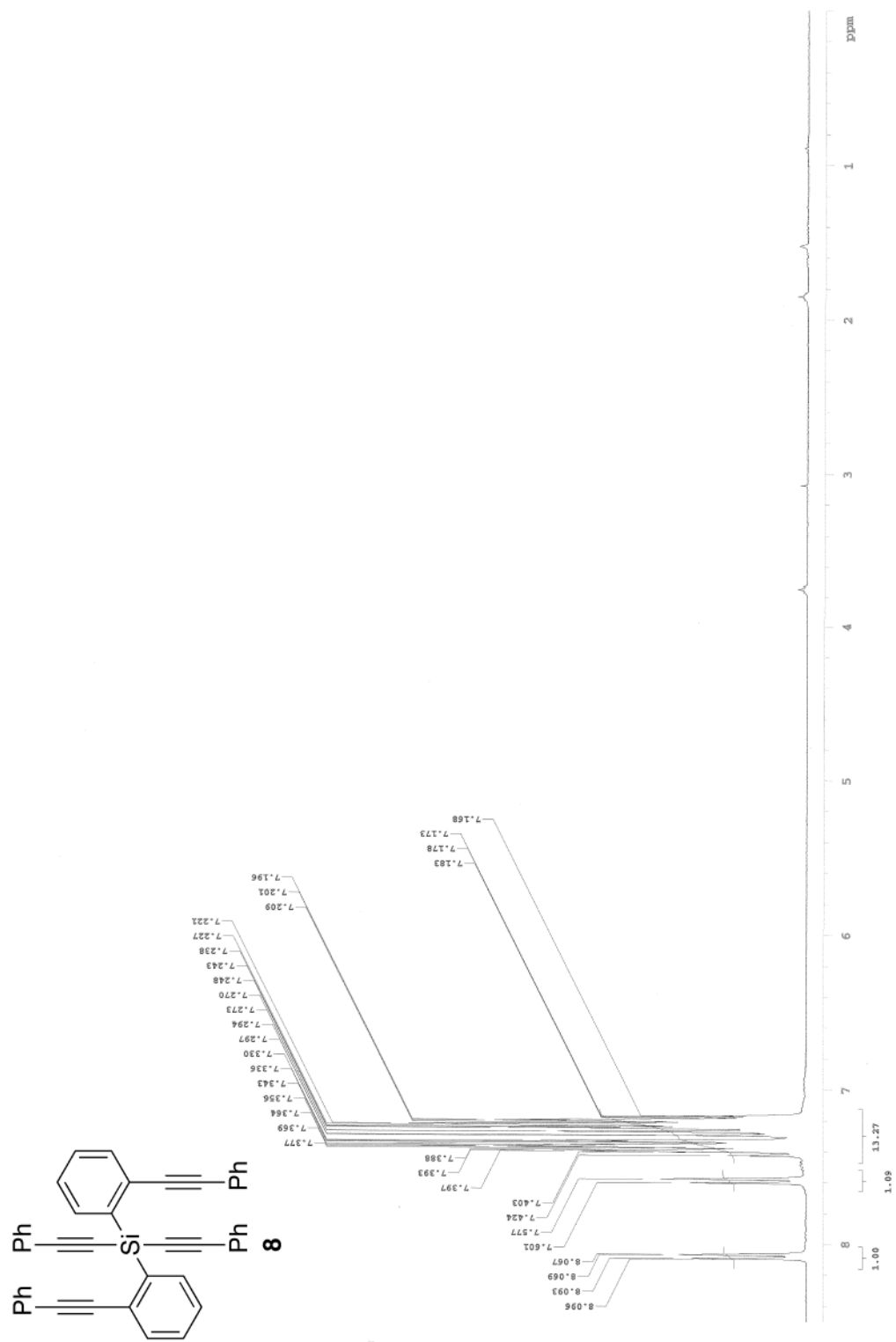


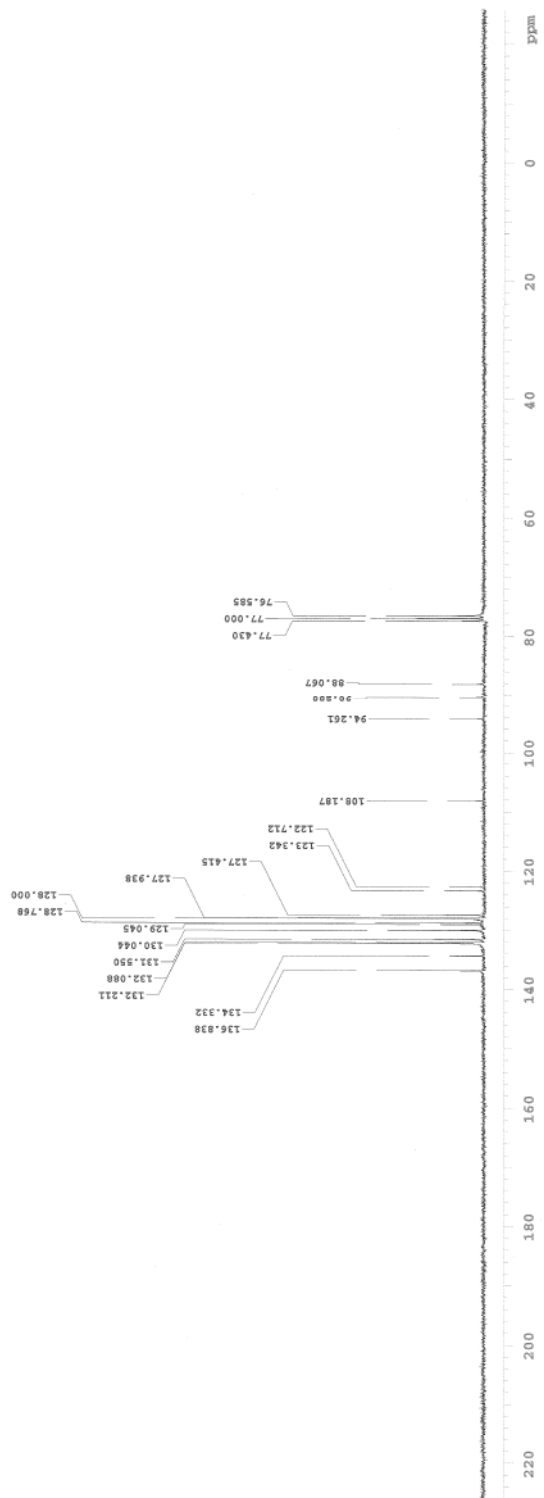
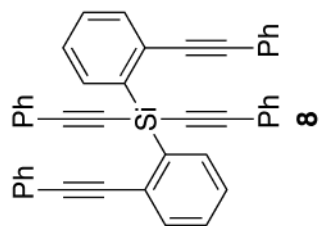
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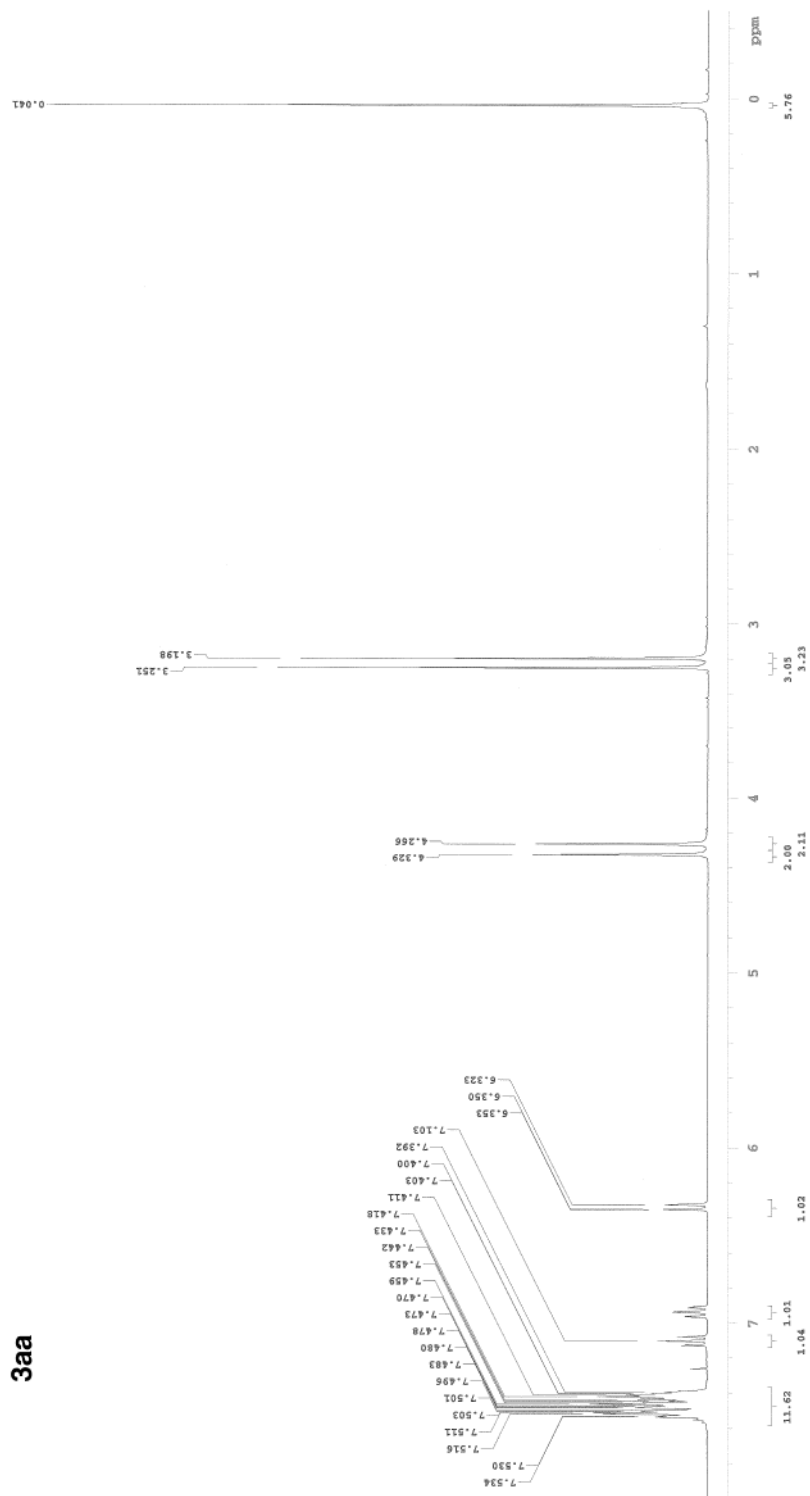
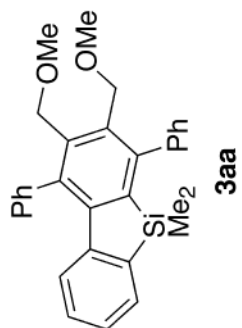


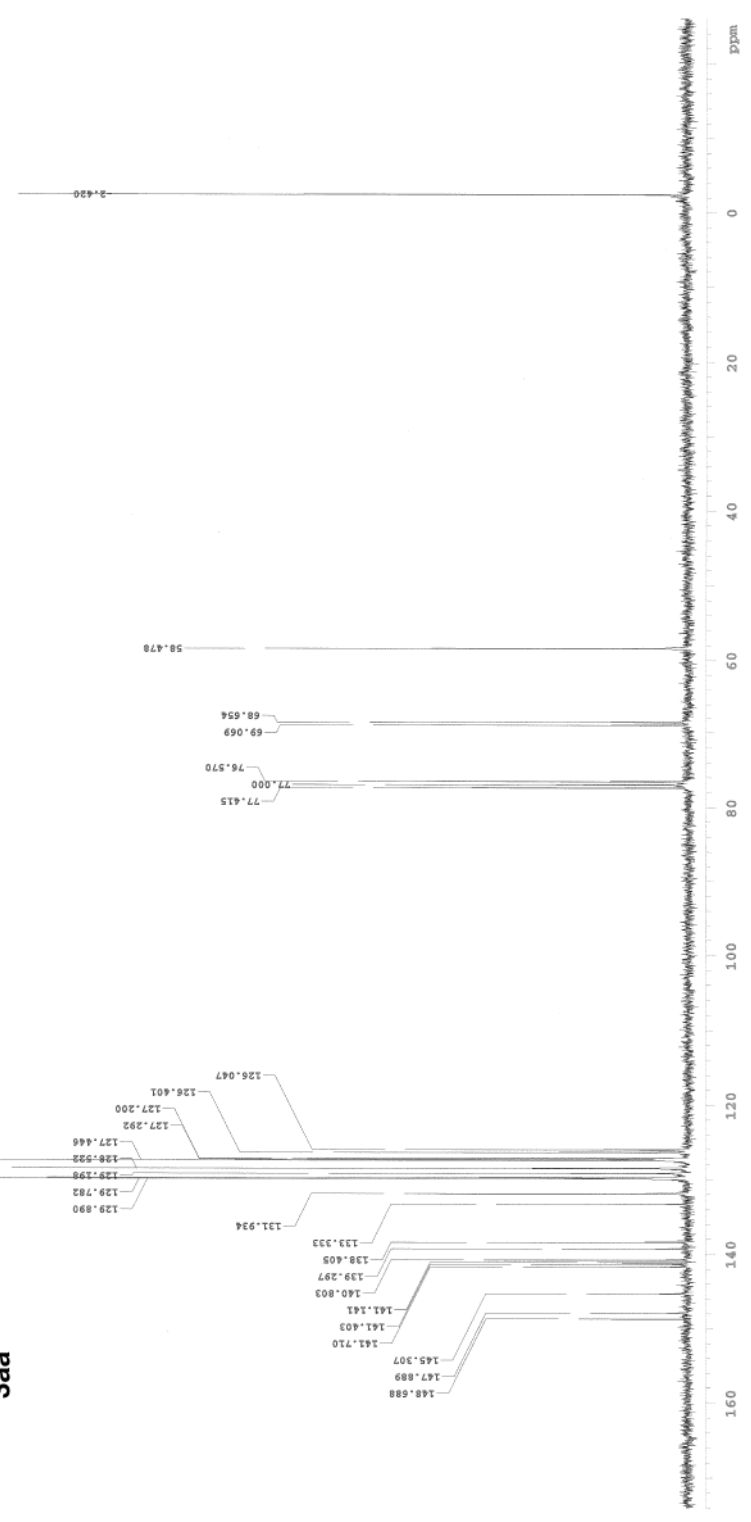
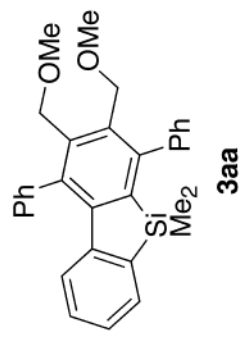


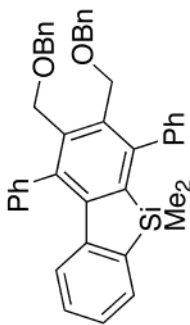




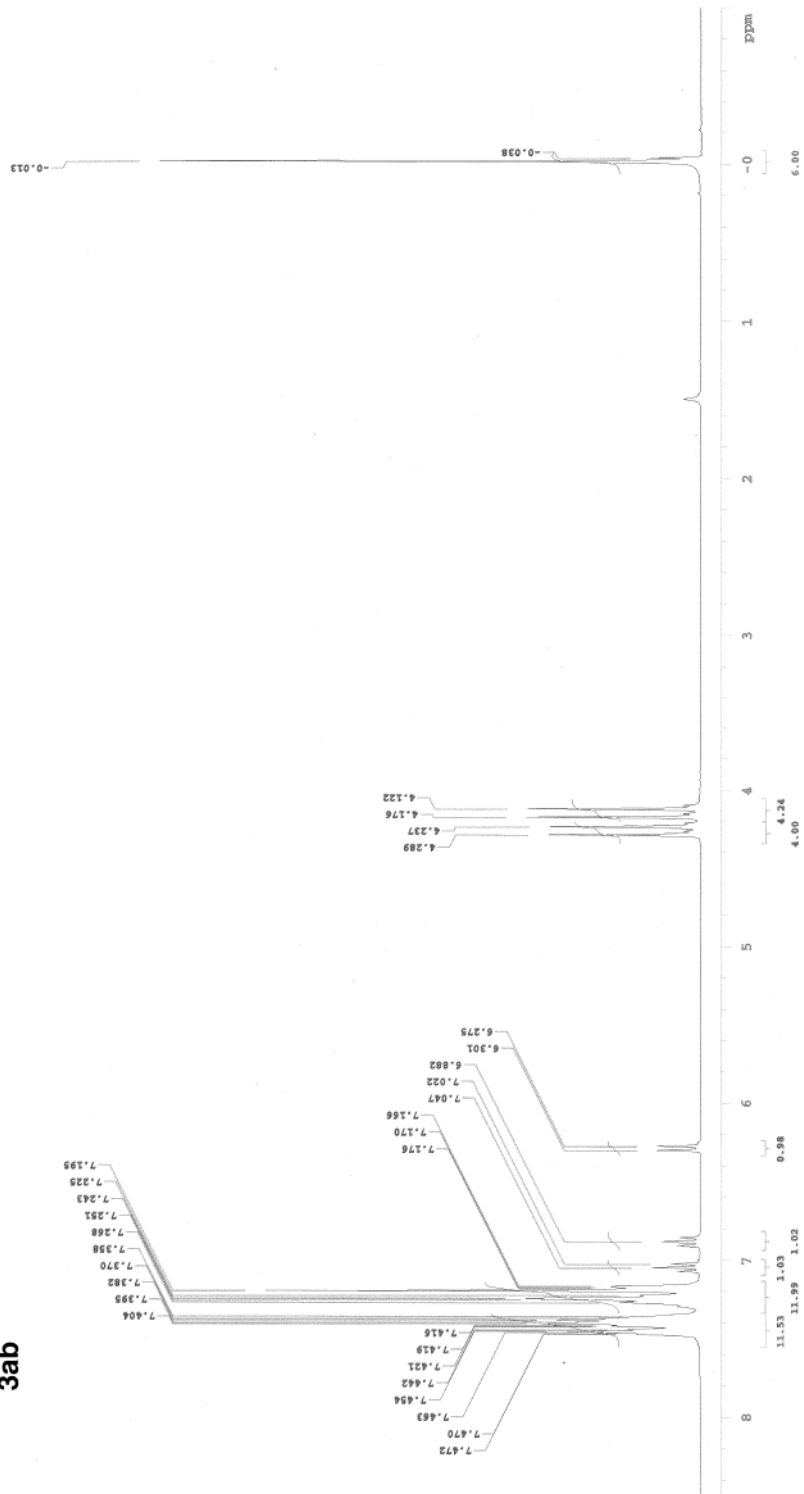


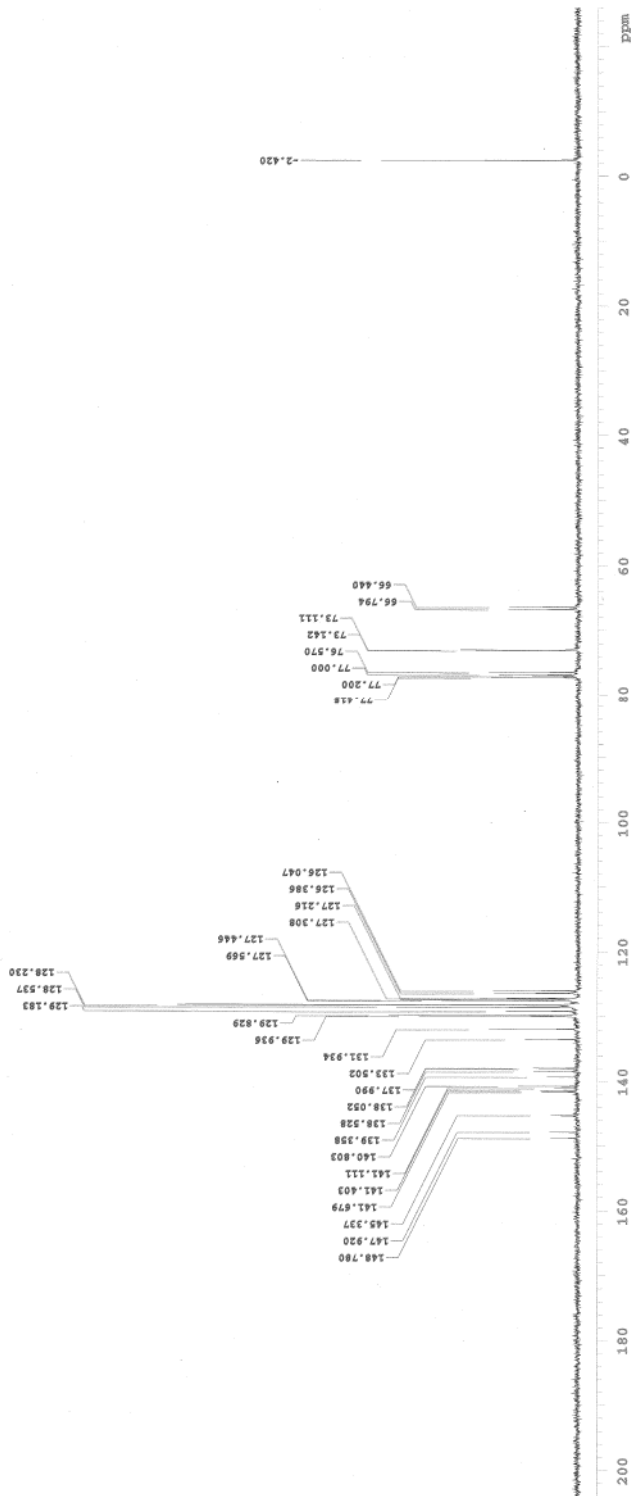
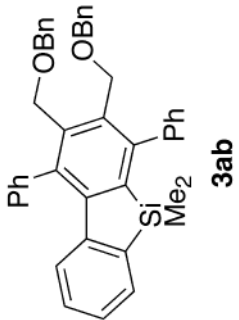


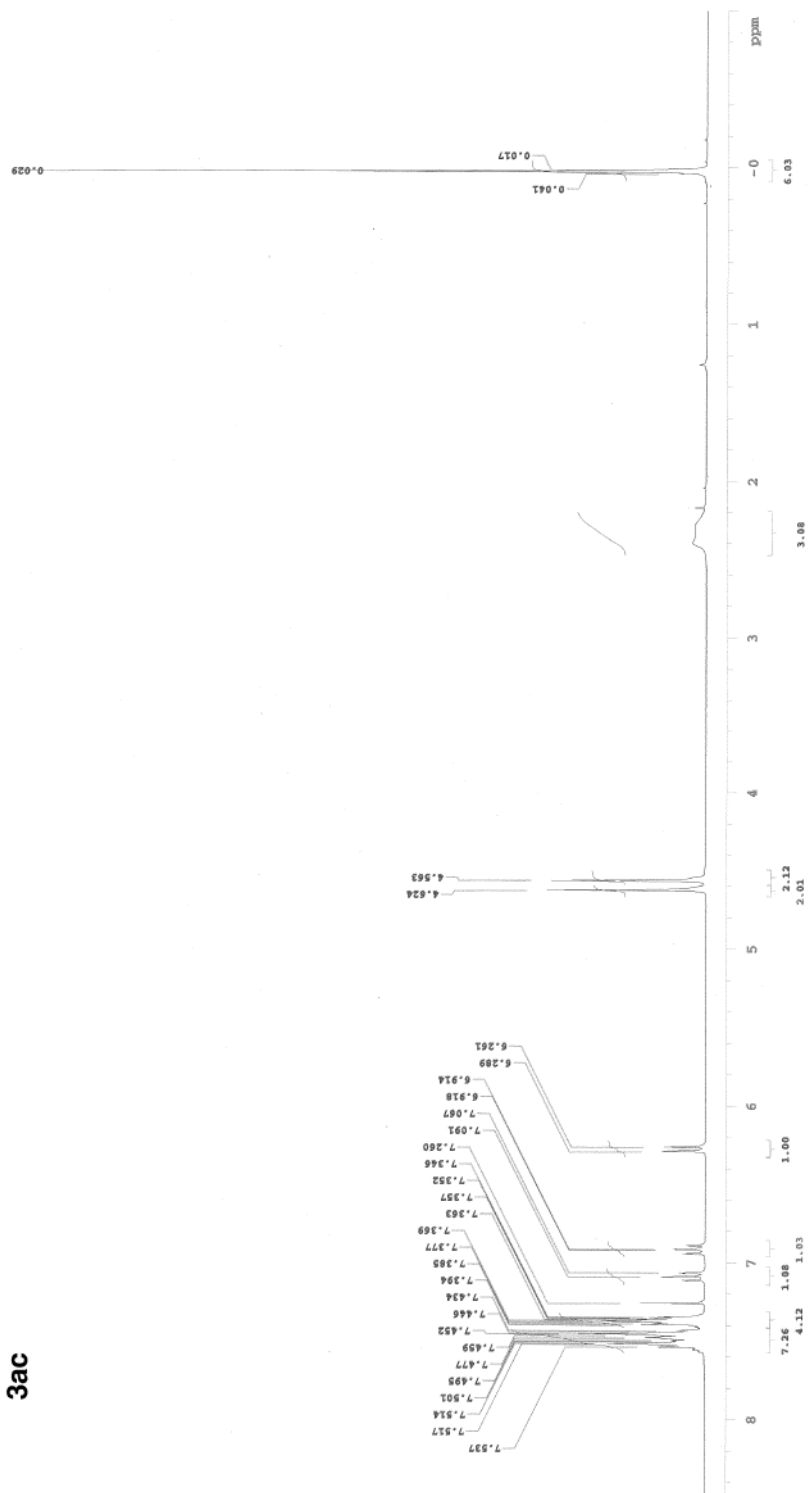
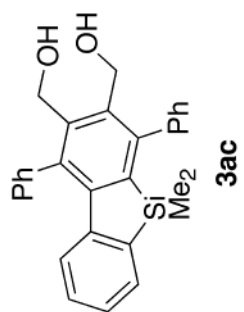


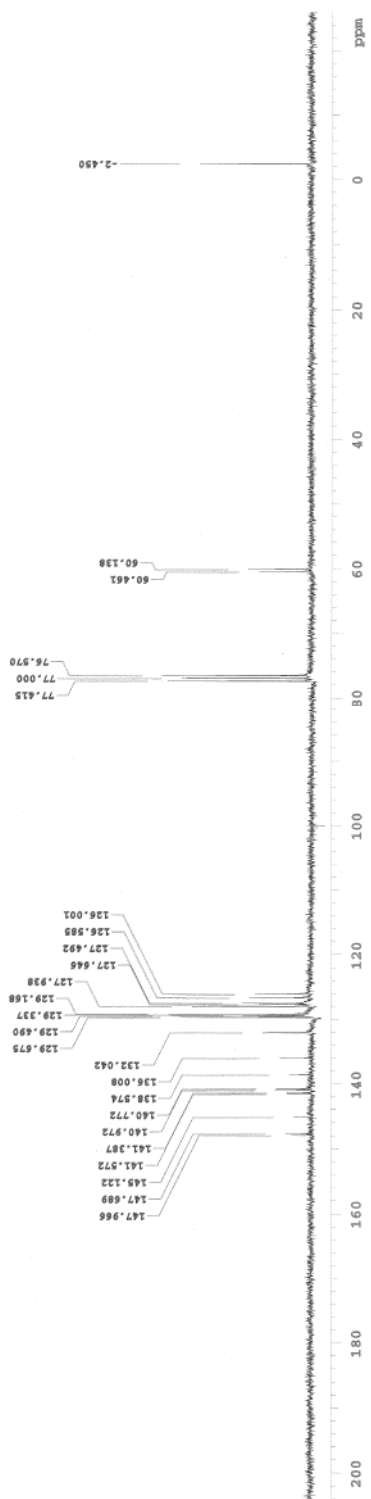
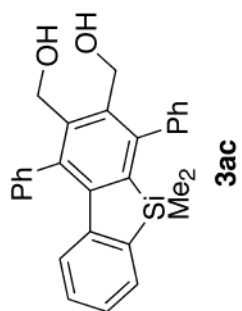


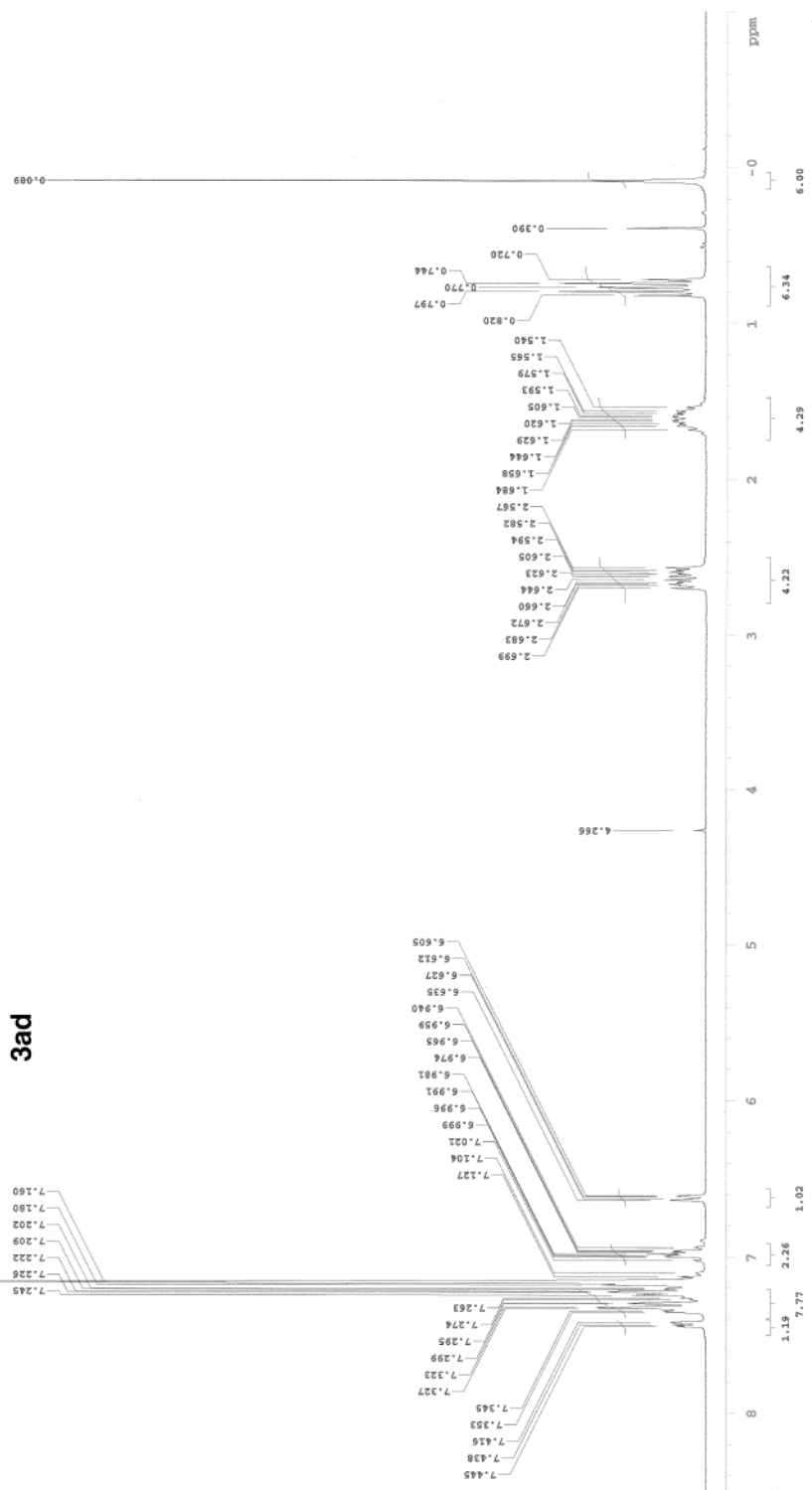
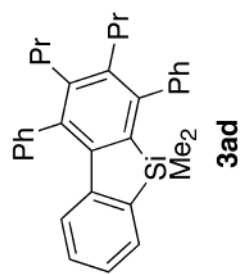
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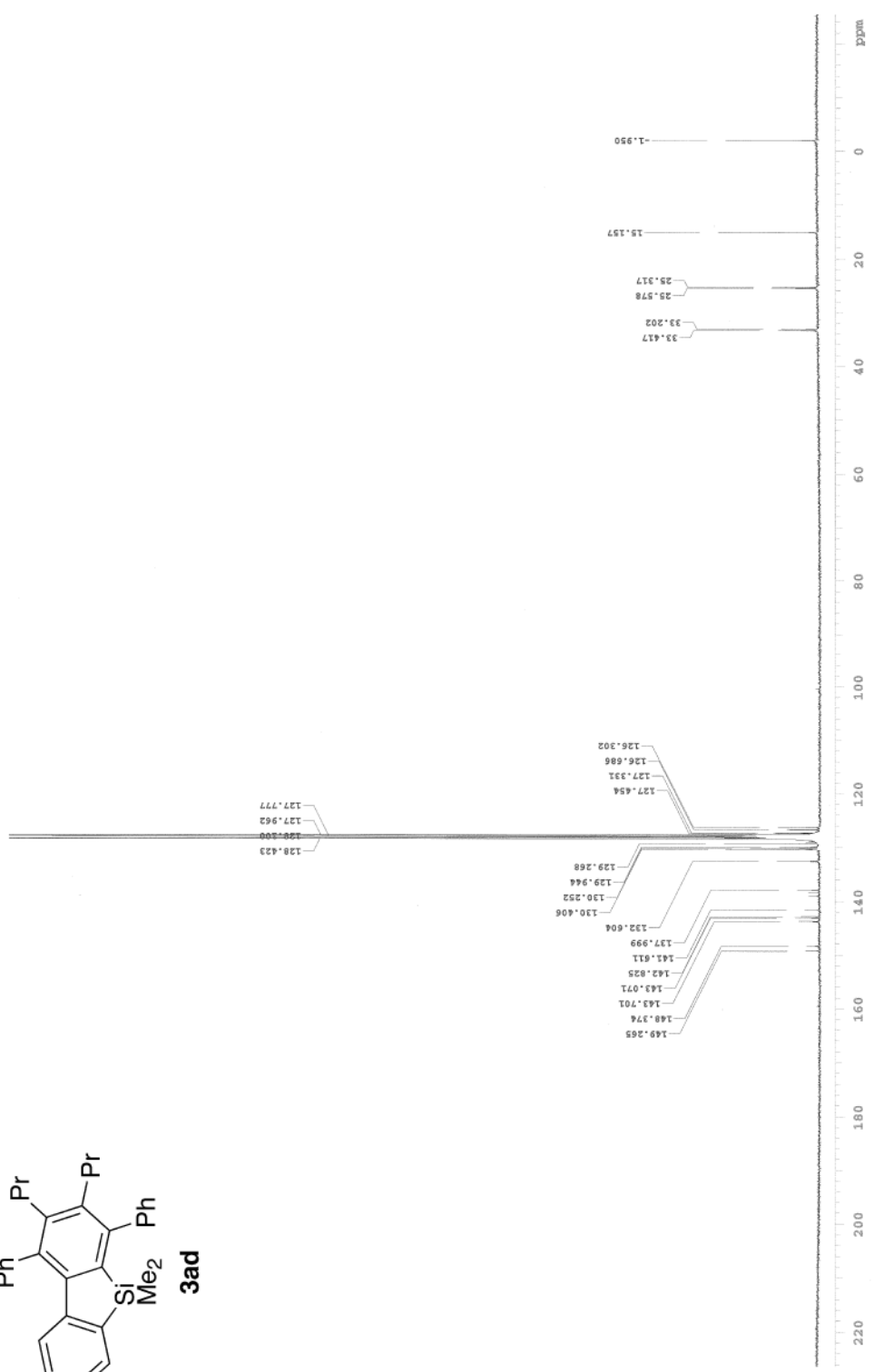
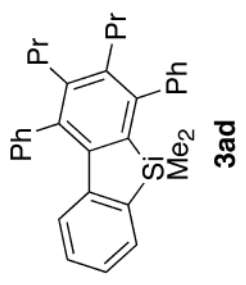


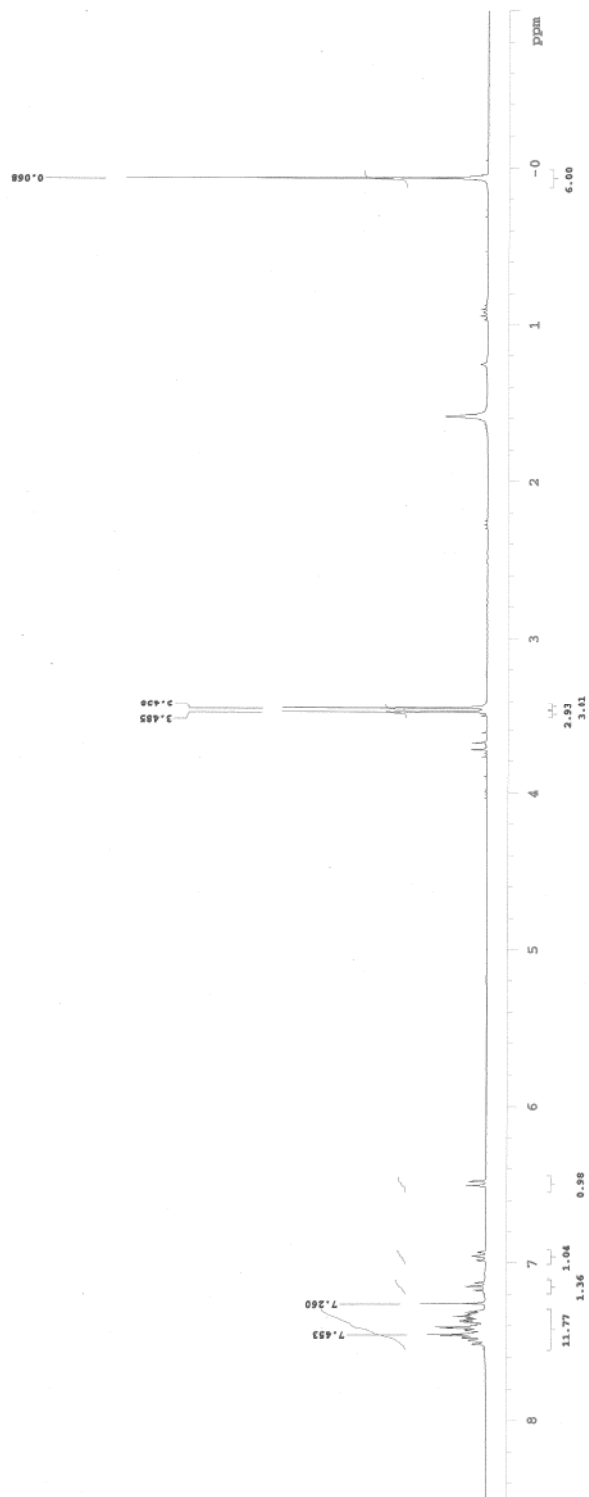
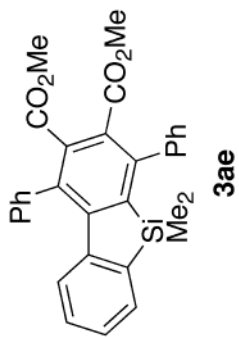


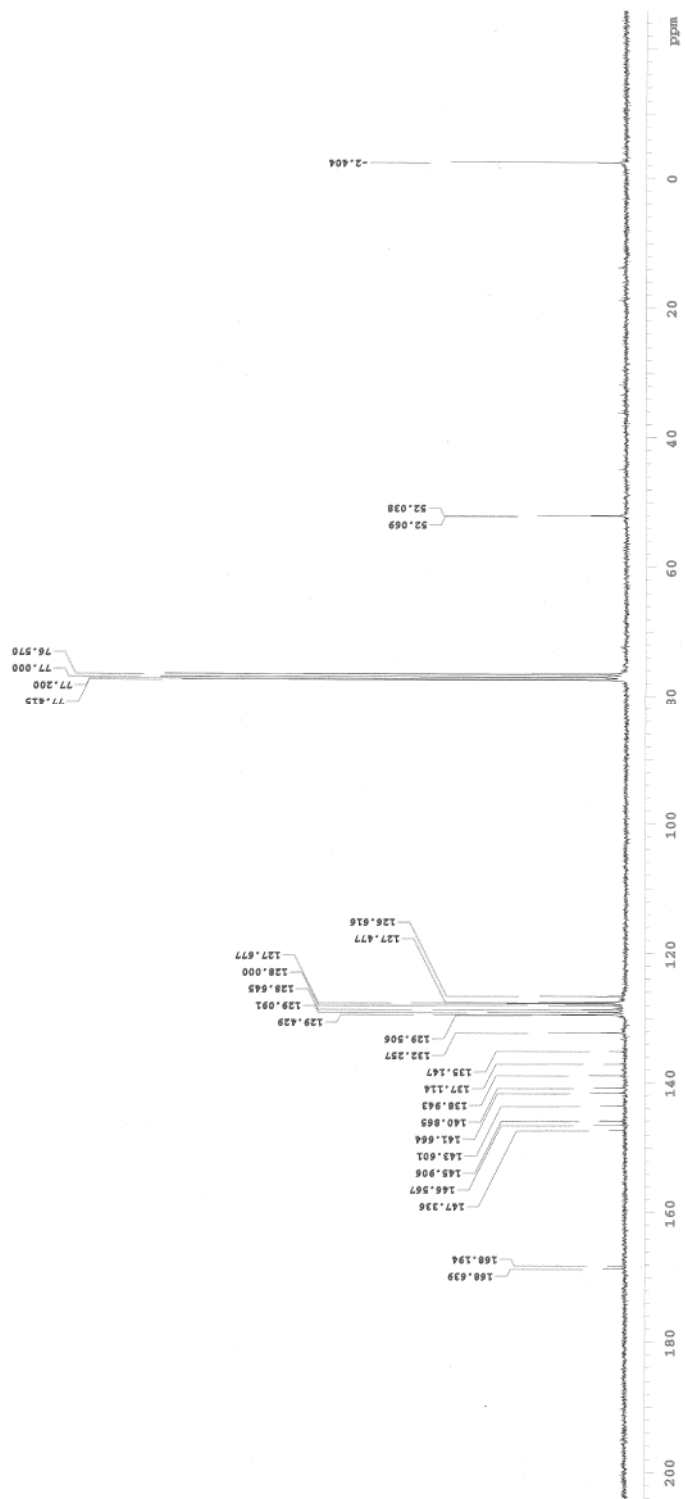
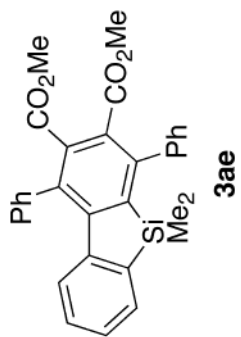


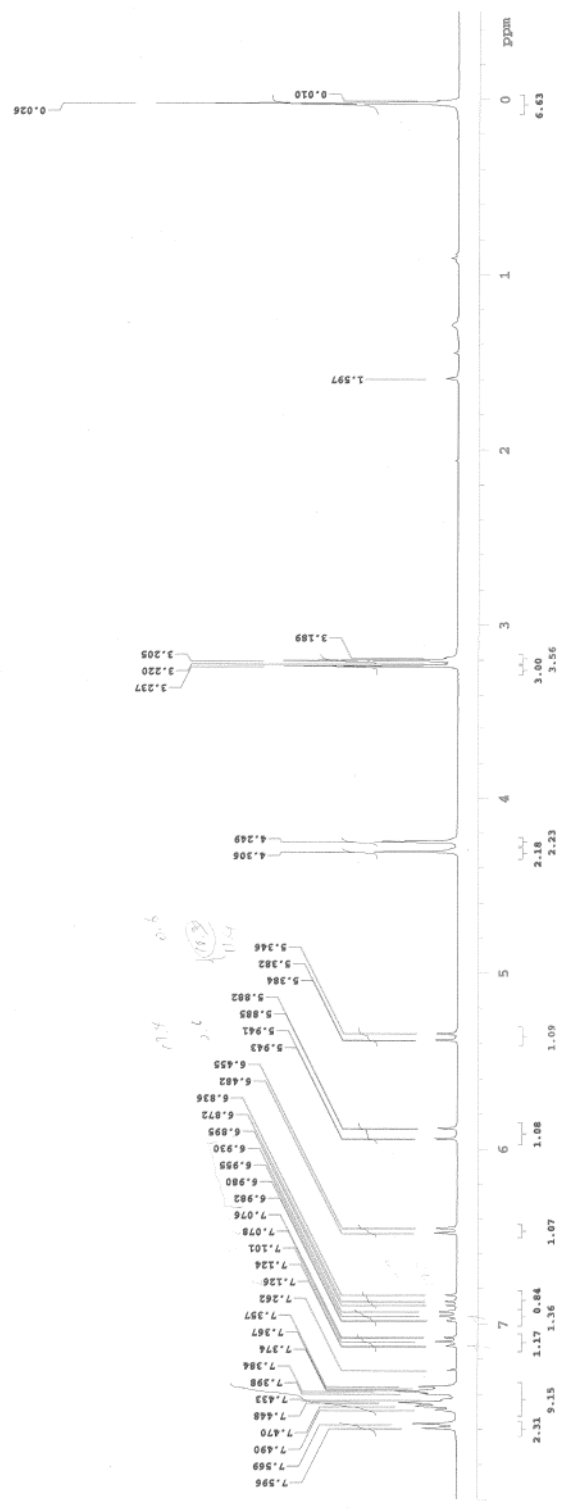
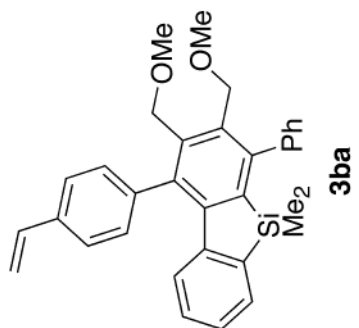


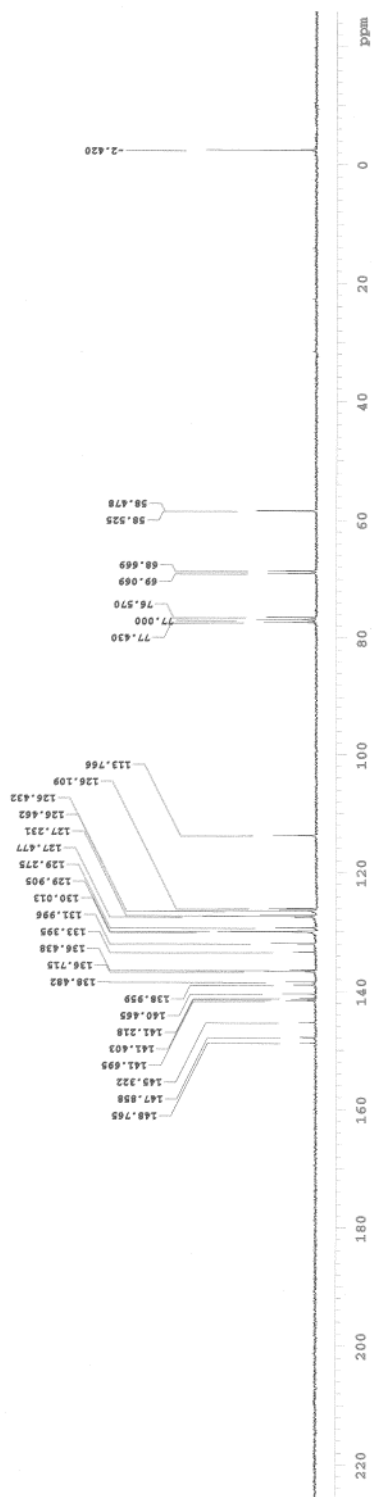
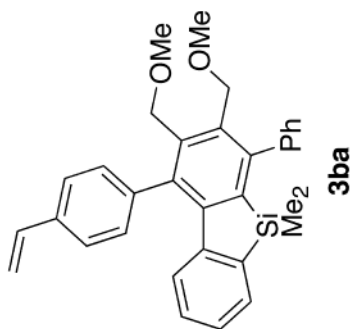


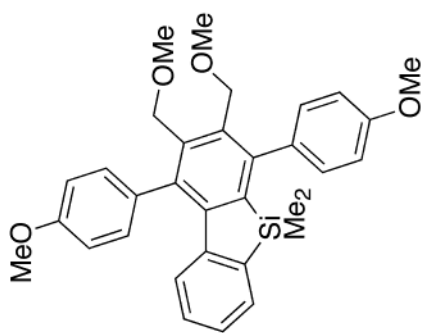




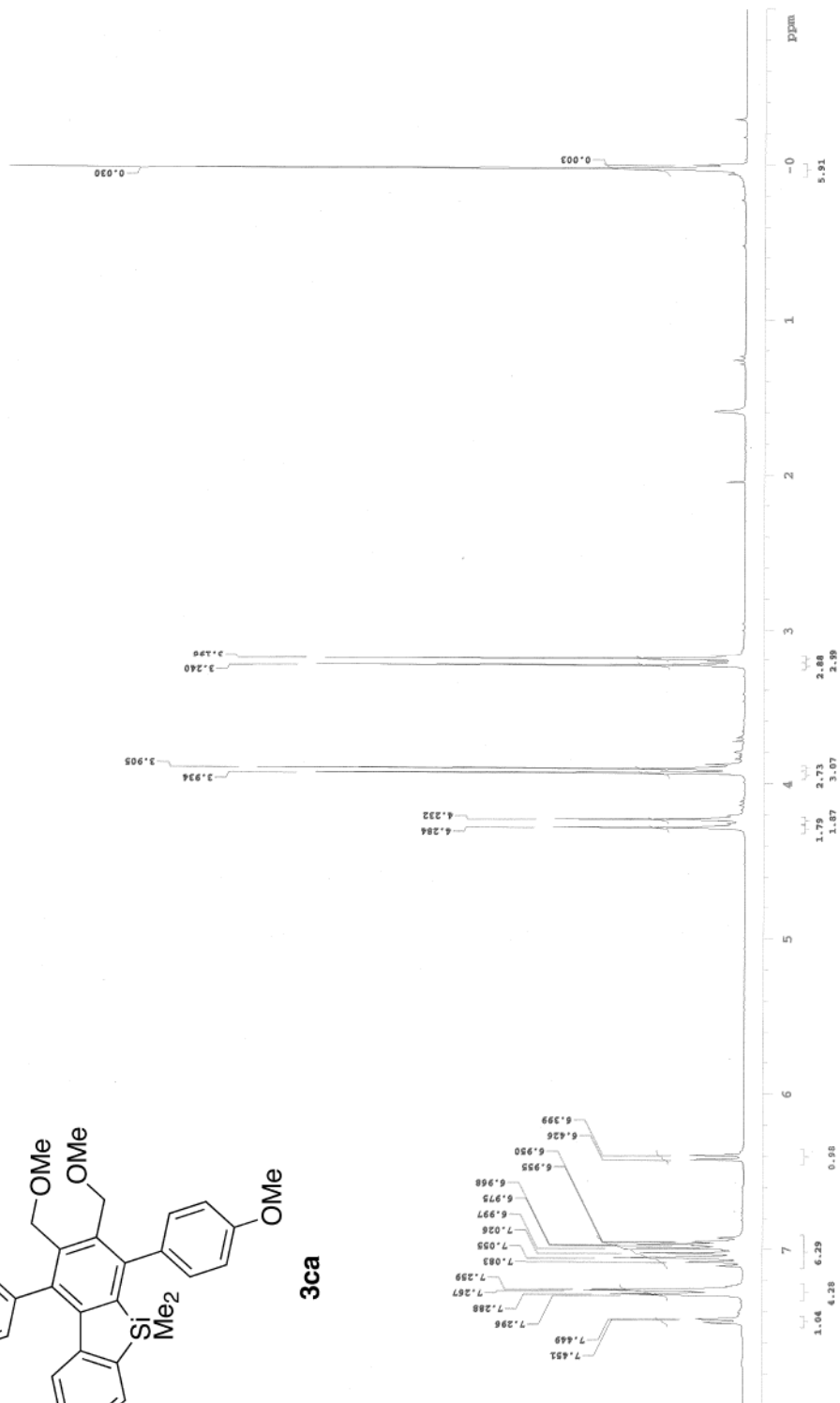


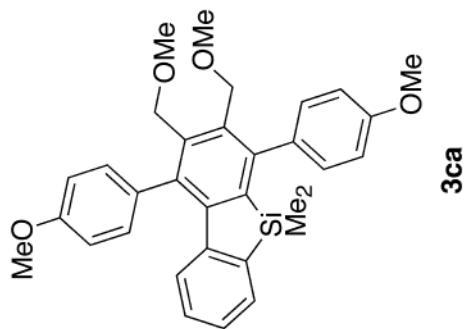




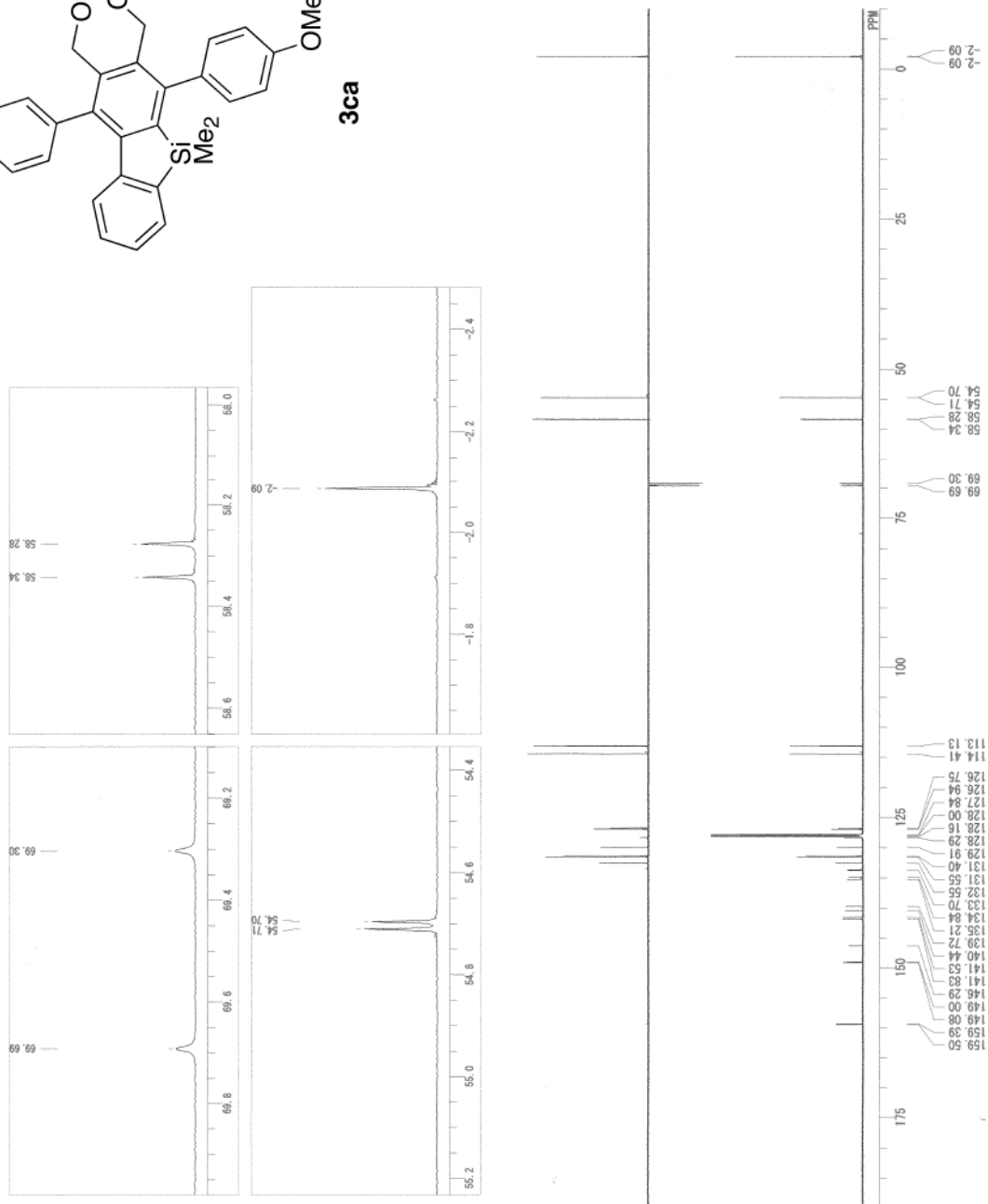


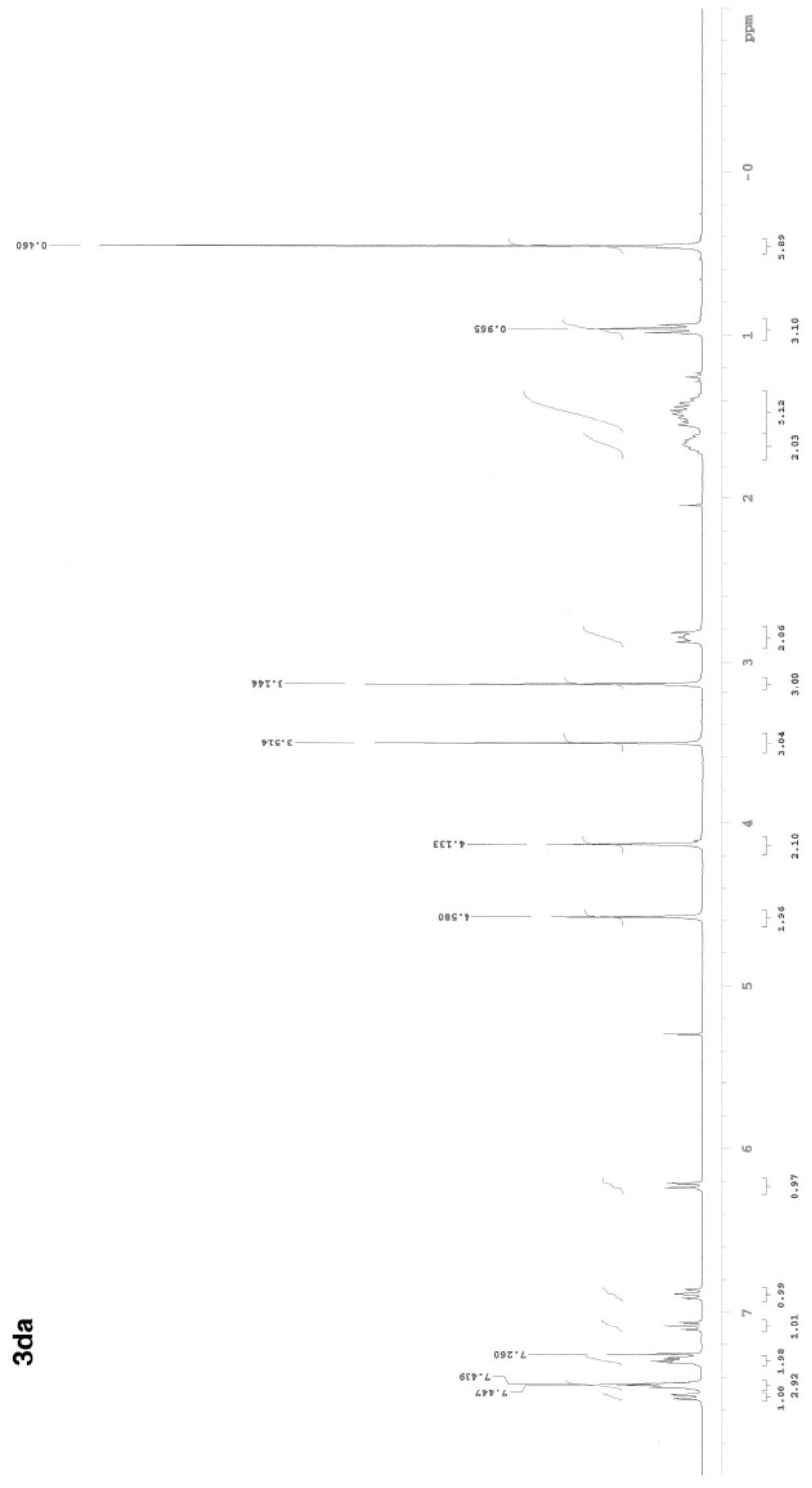
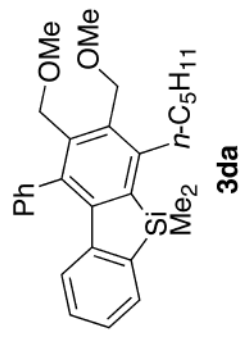
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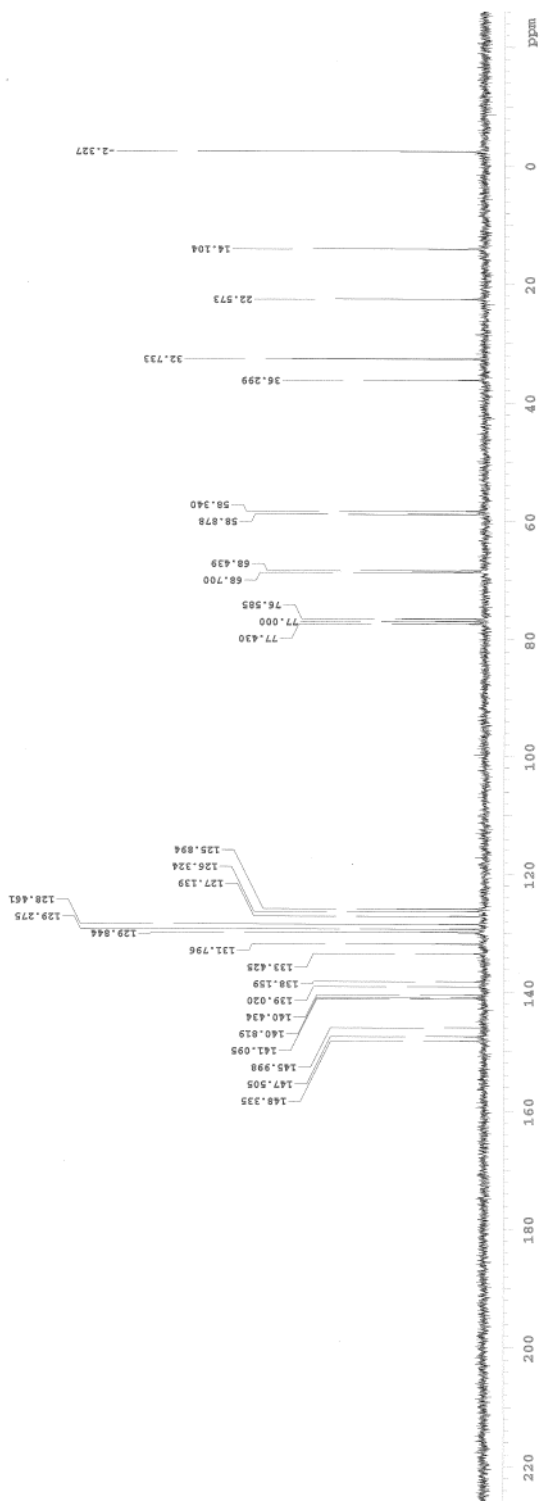
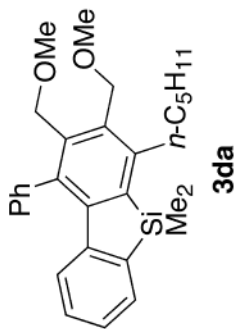


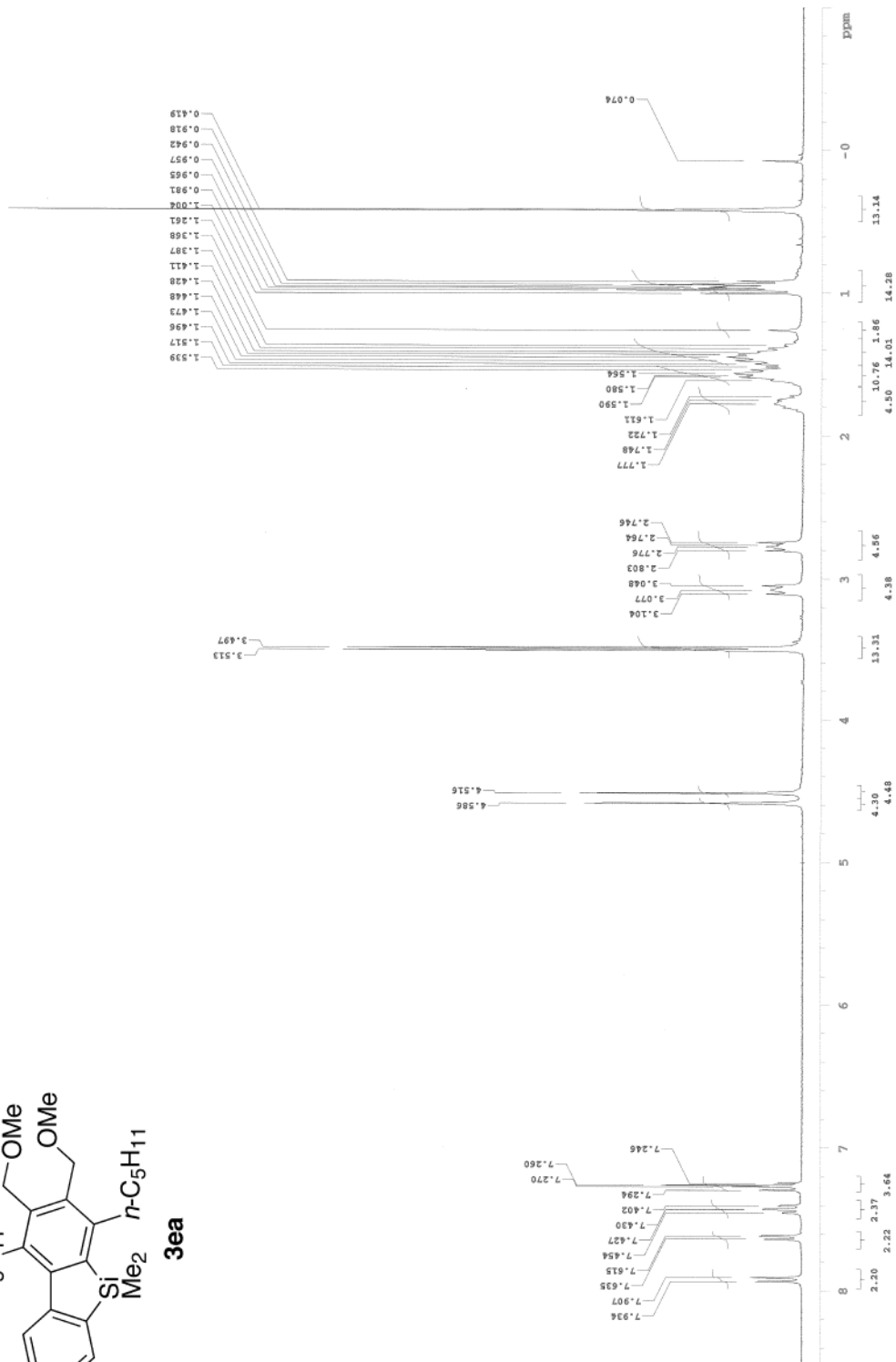
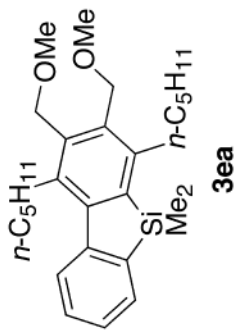


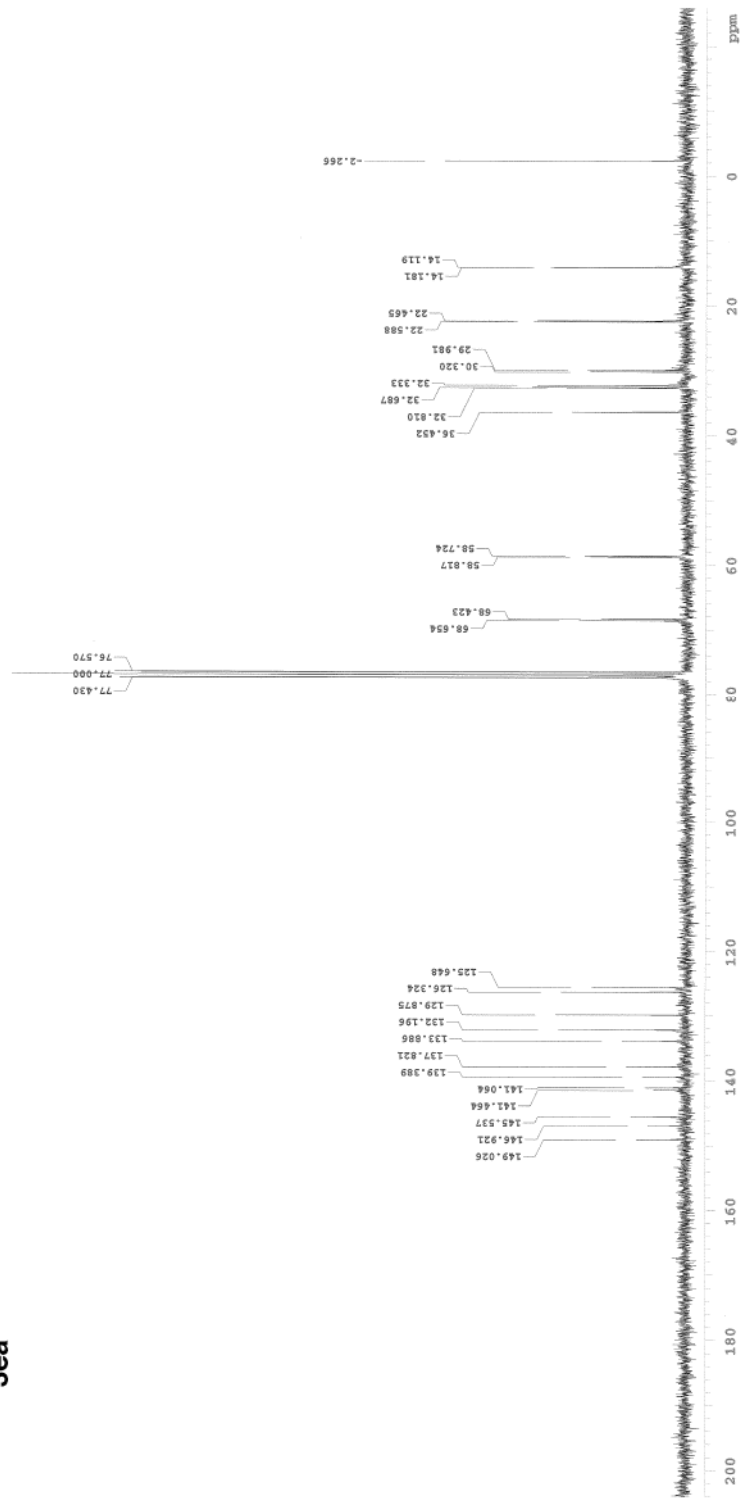
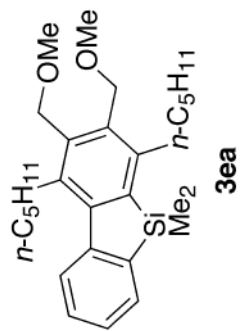
COUNT 21-06-2006 15:18:36
 DANUM single_pulse_dec
 EXPNO Difference NUC(Nuclear
 OBNUC 13C
 OBFRQ 150.92 MHz
 OBFTN 11.74 Hz
 SFO 114.96 Hz
 FREQW 33332.86 Hz
 ACQTM 1.5726 sec
 PD 2.0000 sec
 SCANS 1000
 DUMMY 4
 PWT 3.73 usec
 FWH 45.00 usec
 FWHZ 43.00 usec
 P1 80.0000 msec
 P13 20.0000 msec
 IRNUC 1H
 IRFREQ 600.17 MHz
 IRFST 5.00 MHz
 IRXFL 4.30 Hz
 CTEMP 26.4 C
 SLVMT CS06
 EXREF 128.00 ppm
 RGAIN 60
 RESOL 0.32 Hz
 PRGME THS
 measurement no
 by FWJTA

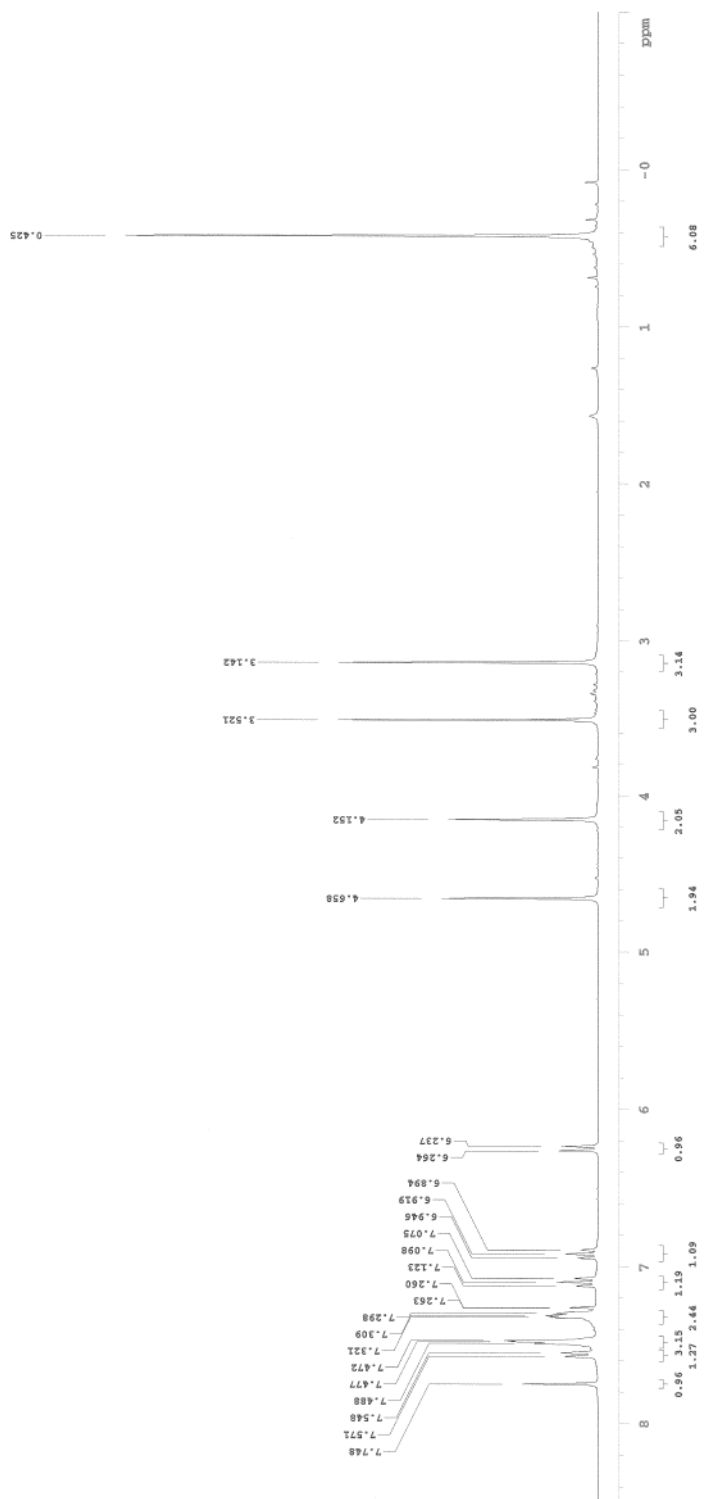
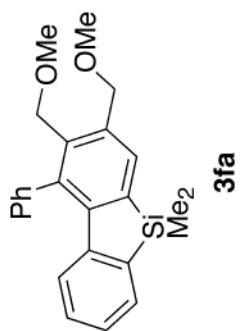


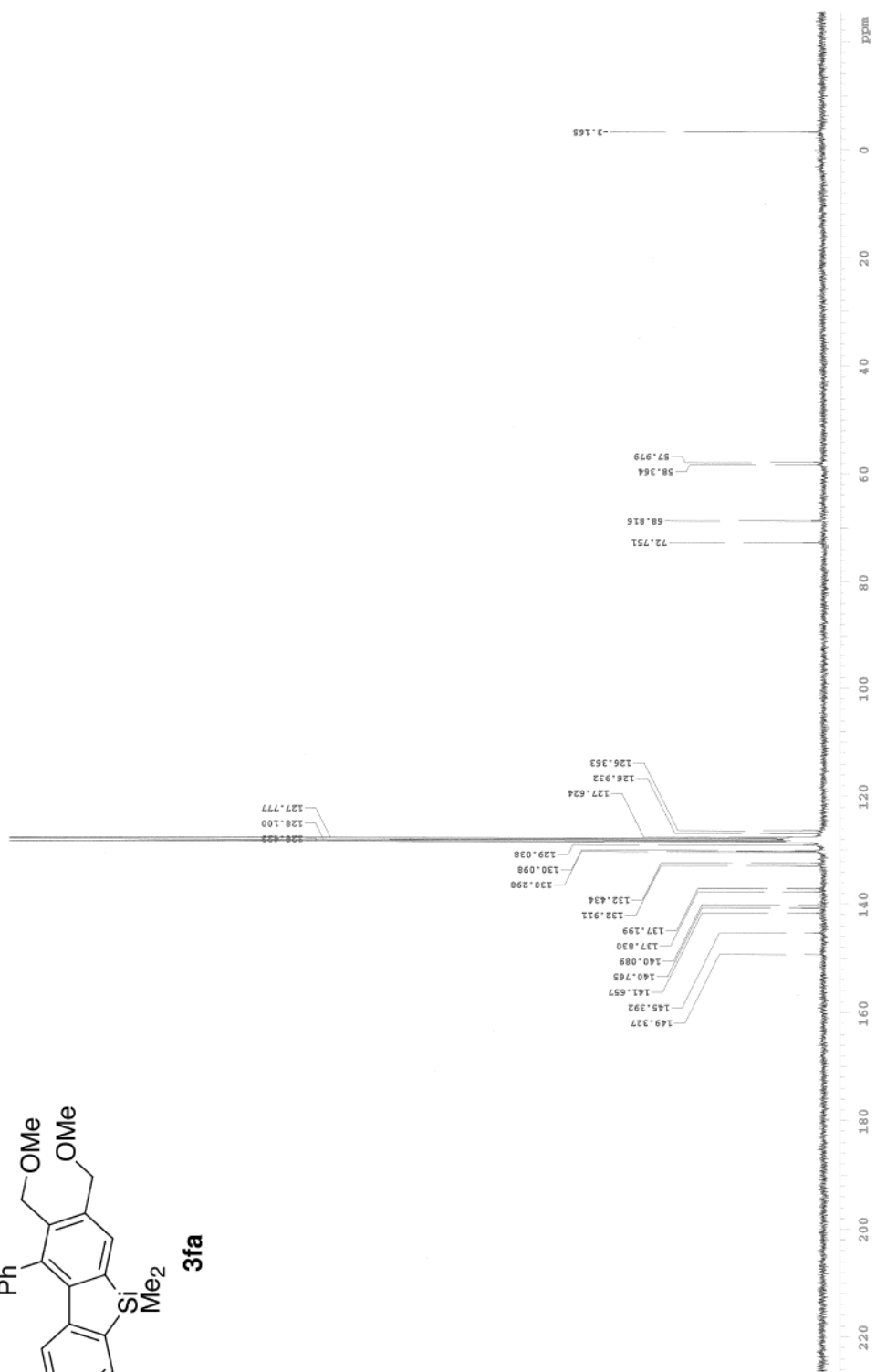
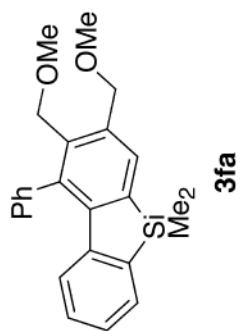


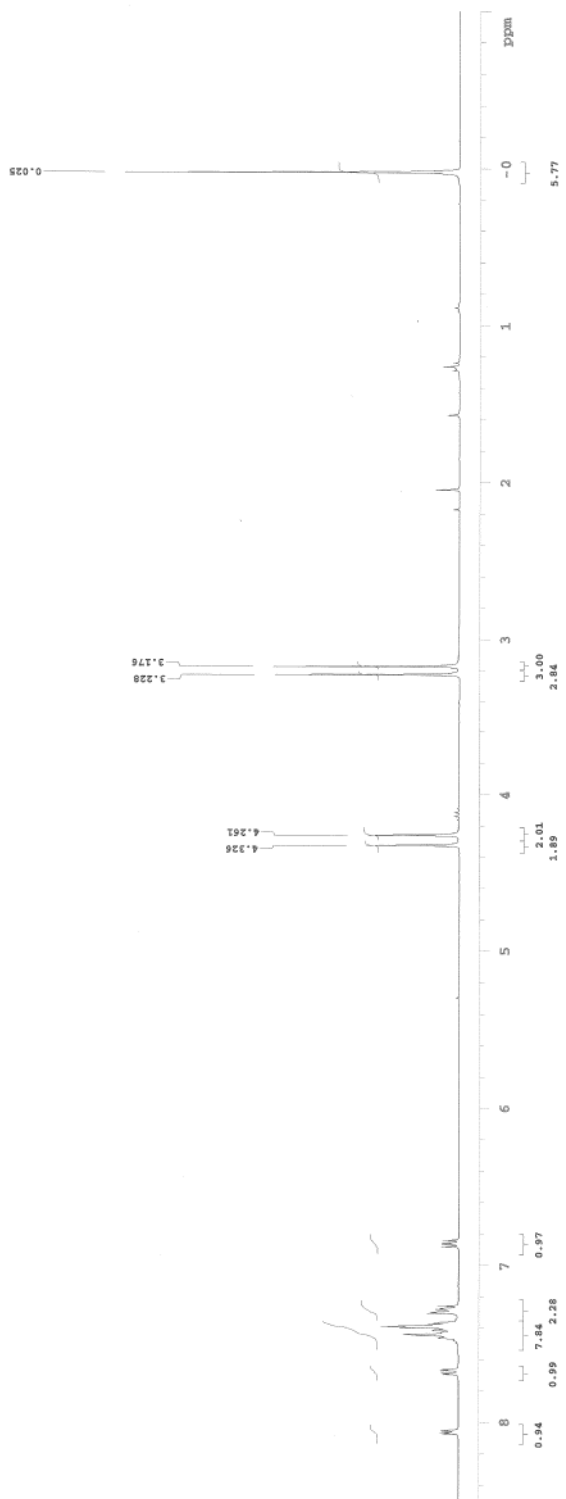
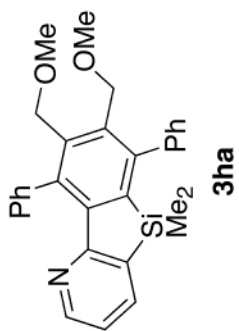


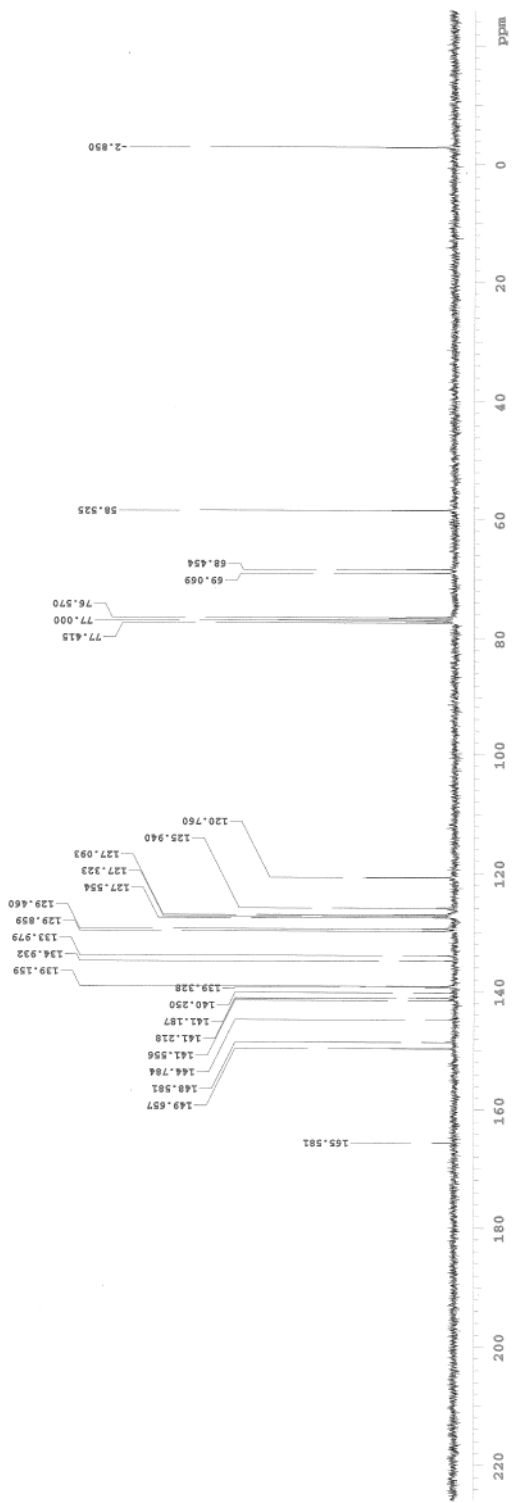
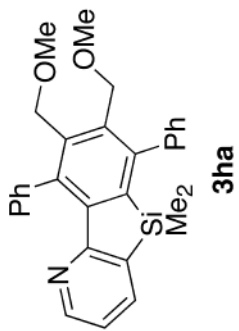


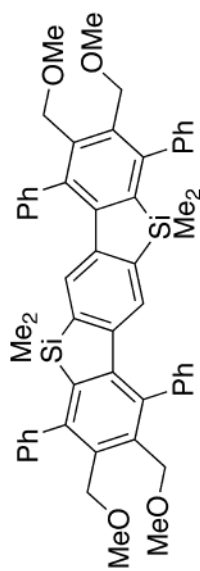




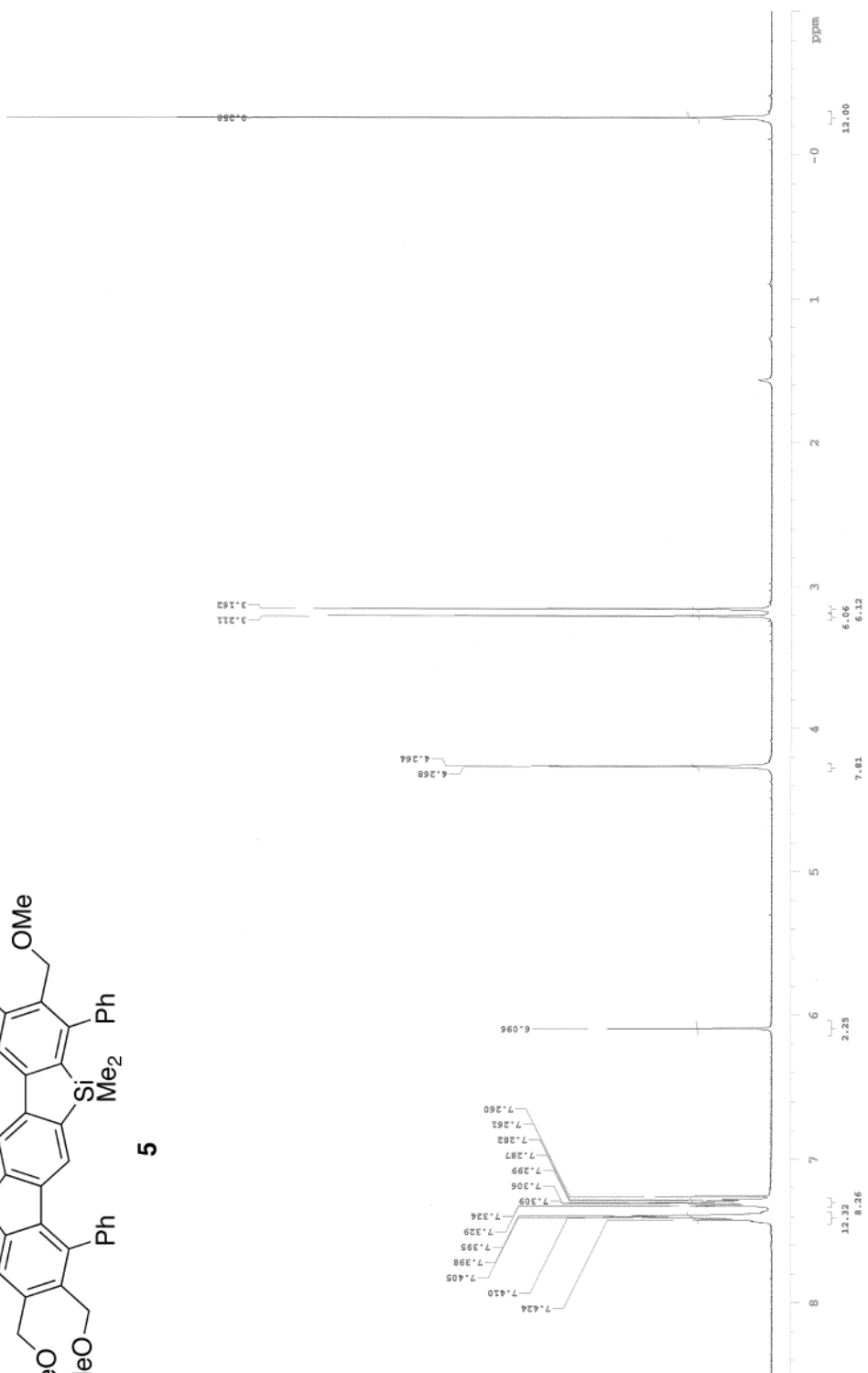


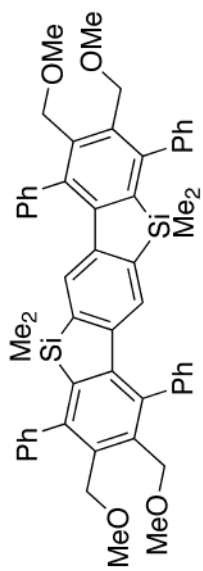




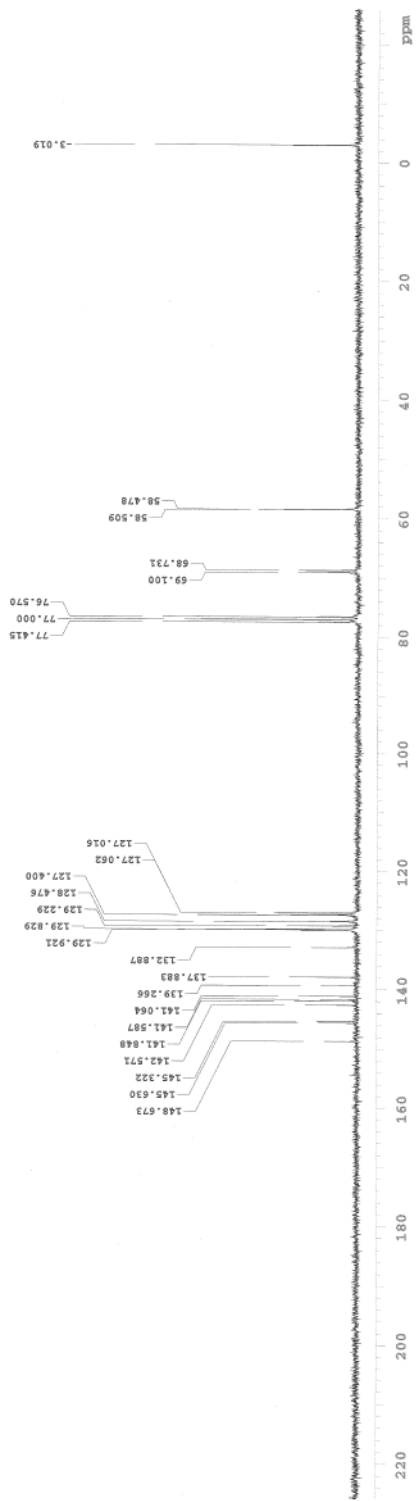


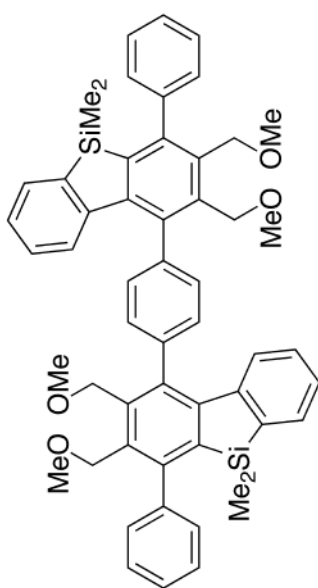
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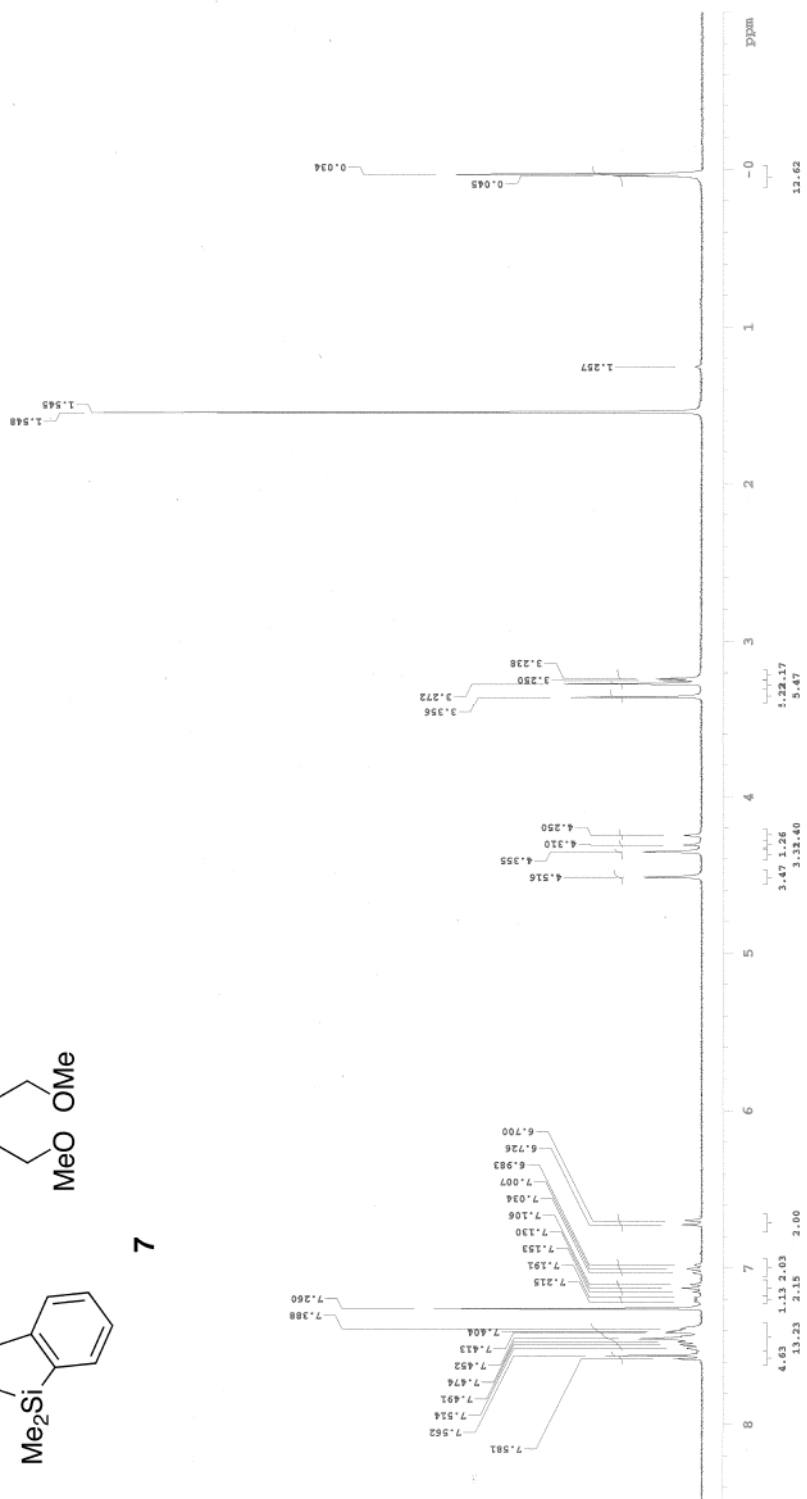


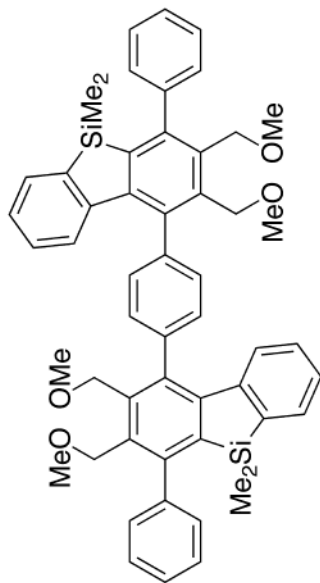
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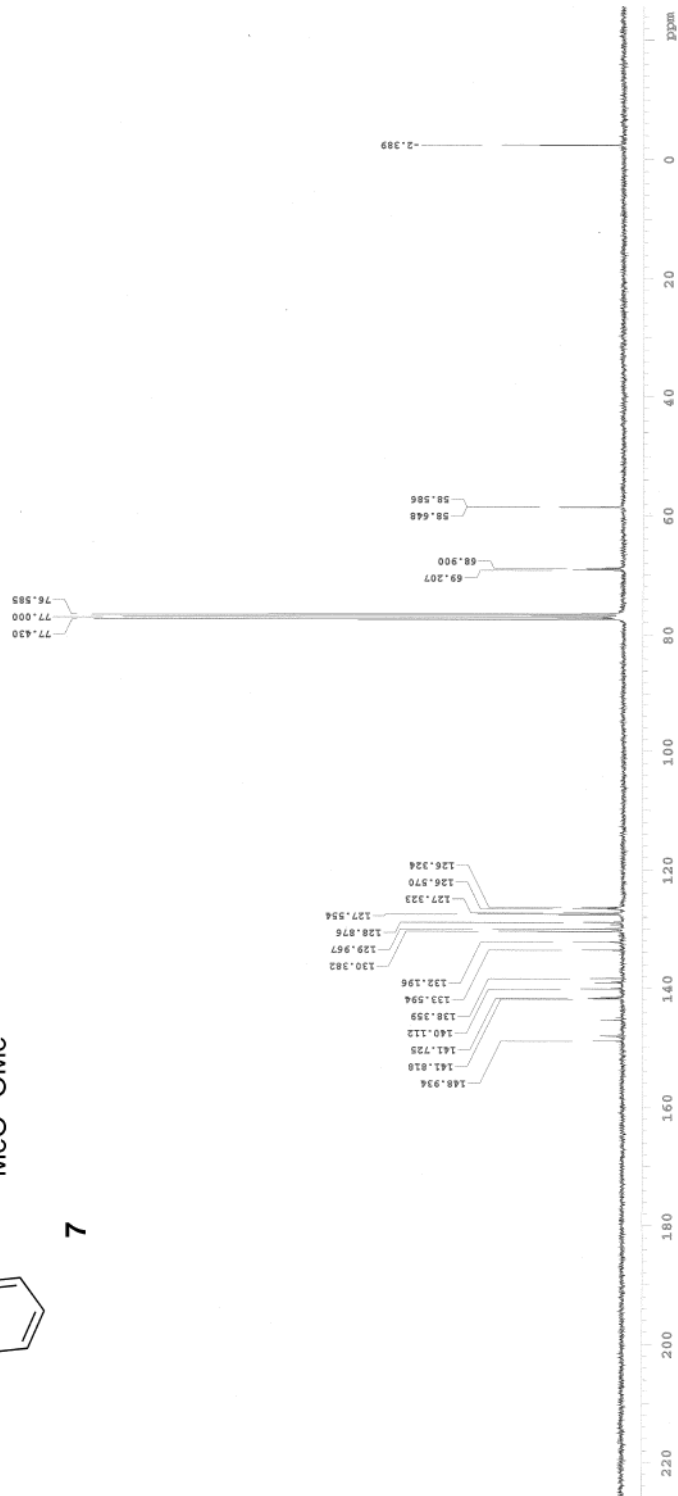


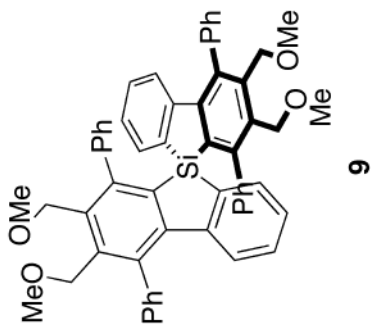
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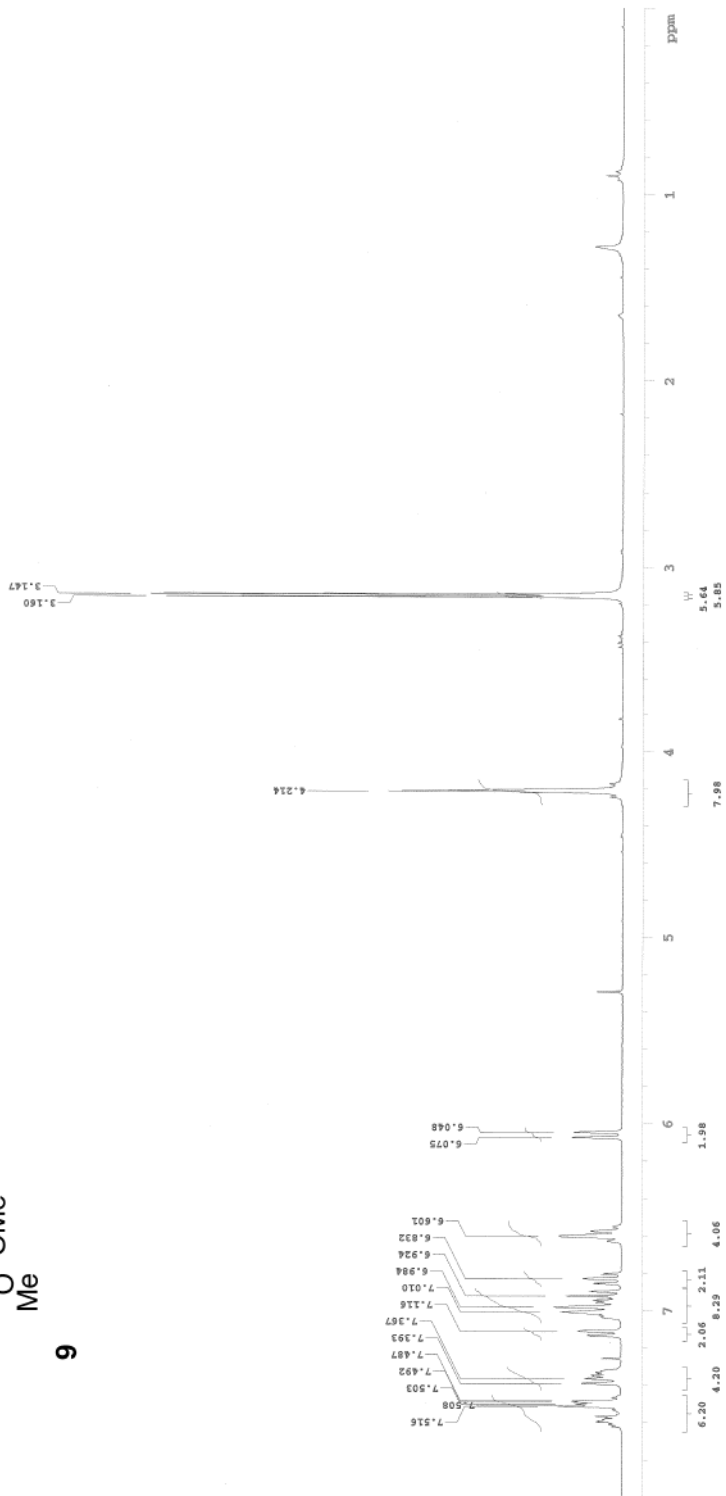


7





9



COMPT 27-03-2006 08:52:56
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 EXPO single_pulse
 GRNUC 130
 OBFRQ 150.92 MHz
 OBFIN 52428
 POINT 33332.82 Hz
 FREQ0 0.7864 sec
 ACQIN 1.000 sec
 SCANS 2.1000
 DUMMY 4
 PWT 3.73 usec
 PW2 26.00 usec
 PW3 13.00 usec
 P1 80.0000 msec
 P11 20.0000 msec
 IRNUC NONE
 IRNUC 1H
 IRFRQ 600.17 MHz
 IRSET 5.30 KHz
 IRATH 511
 STW 45.0 c
 SREF CDCL3
 EXREF 77.00 ppm
 RGAIN 0.64 Hz
 RESOL 0.64 Hz
 CTEMP 45.0 c
 PROBE THIS
 measurement no
 by FLUTTA

