

Supplementary Information

Facile Synthesis of Tribenzosilepins from Terphenyls and Dihydrosilanes by Electrophilic Double Silylation

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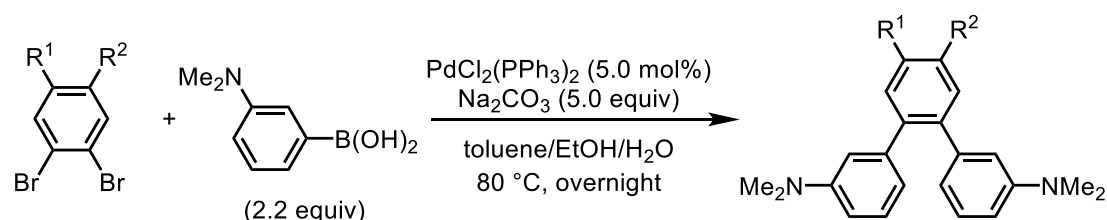
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1. General

All reactions were performed under an inert atmosphere using standard Schlenk techniques or in glovebox. All reagents were purchased from commercial sources and used without further purification unless otherwise specified. Silica gel column chromatography was carried using Silica gel 60 (Kanto Chemical, particle size: 40–50 μm or 63–210 μm). NMR spectra were recorded on JEOL JNM-ECA600 (600 MHz for ^1H NMR, 150 MHz for ^{13}C NMR), JEOL ECZ-400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR), JEOL JNM-LA400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR) spectrometers. Proton and carbon chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.00 (^1H NMR, ^{13}C NMR)) or the residual solvent (CHCl_3 (δ 7.26 for ^1H NMR or δ 77.16 for ^{13}C NMR), CH_2Cl_2 (δ 5.32 for ^1H NMR or δ 53.84 for ^{13}C NMR), DMSO (δ 2.49 for ^1H NMR or δ 39.6 for ^{13}C NMR)) used as an internal reference. HRMS were measured on a JEOL JMS-700 spectrometer. UV/vis absorption and photoluminescence (PL) spectra were measured with a V650 spectrophotometer (JASCO), and C9920-02 (Hamamatsu Photonics).

3-Bromo-*N,N*-dimethylaniline,¹ (3-(dimethylamino)phenyl)boronic acid,² 9,9-dihydro-9-silafluorenes,³ 1,2-dibromo-4,5-diiodobenzene,⁴ Turbo Grignard reagents,⁵ and 1-(hexyloxy)-3-iodobenzene,⁶ 3,4-dibromoaniline,⁷ 3,4-dibromo-*N,N*-dimethylaniline¹ were prepared according to the literature procedures.

2. Synthesis and Characterization of Substrates

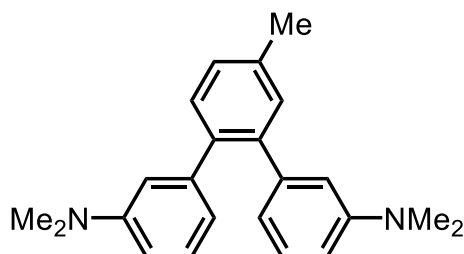


*N*³,*N*³,*N*^{3''},*N*^{3''}-Tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (**1a**)

Compound **1a** was synthesized by Suzuki-Miyaura coupling reaction.⁸ A mixture of (3-(dimethylamino)phenyl)boronic acid (0.550 g, 8.80 mmol, 2.2 equiv), 1,2-dibromobenzene (0.940 g, 4.00 mmol, 1.0 equiv), Na_2CO_3 (2.10 g, 20.0 mmol, 5.0 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.140 mg, 0.200 mmol, 5.0 mol%) in a mixture of toluene (30 mL), water (4.0 mL) and ethanol (8.0 mL) was heated to 80 °C under nitrogen atmosphere. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 \times 50 mL). The combined organic phases were dried over MgSO_4 and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 15:1) on silica gel

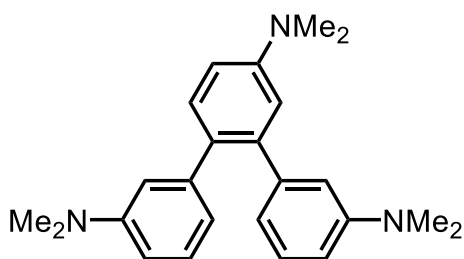
to give **1a** (0.970 g, 76%) as colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.47 (dd, $J = 5.5, 3.7$ Hz, 2H), 7.38–7.41 (m, 2H), 7.11 (dd, $J = 8.0, 8.0$ Hz, 2H), 6.58–6.61 (m, 4H), 6.53 (s, 2H), 2.76 (s, 12H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 150.4, 142.5, 141.5, 130.5, 128.6, 127.3, 118.7, 115.4, 111.3, 40.9; HRMS(EI⁺) Calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2$ ($[\text{M}]^+$) 316.1934, Found 316.1939.

***N*³,*N*³,*N*^{3''},*N*^{3''},4'-Pentamethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (1b)**



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (0.730 g, 4.40 mmol, 2.2 equiv), 1,2-dibromo-4-methylbenzene (0.500 g, 2.00 mmol, 1.0 equiv), Na_2CO_3 (1.10 g, 10.0 mmol, 5.0 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (120 mg, 0.100 mmol, 5.0 mol%) in a mixture of toluene (20 mL), water (3.0 mL) and ethanol (6.0 mL) was heated to 80 °C under nitrogen atmosphere. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phases were dried over MgSO_4 and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 20:1) on silica gel to give **1b** (0.48 g, 68%) as colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.37 (d, $J = 7.8$ Hz, 1H), 7.29 (s, 1H), 7.21 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.07–7.12 (m, 2H), 6.57–6.60 (m, 4H), 6.51–6.53 (m, 2H), 2.76 (s, 6H), 2.75 (s, 6H), 2.43 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 150.39, 150.37, 142.6, 142.4, 141.3, 138.7, 137.0, 131.2, 130.4, 128.5, 128.0, 118.8, 118.7, 115.5, 115.4, 111.3, 111.1, 40.9, 21.3; HRMS(EI⁺) Calcd for $\text{C}_{23}\text{H}_{26}\text{N}_2$ ($[\text{M}]^+$) 330.2091, Found 330.2097.

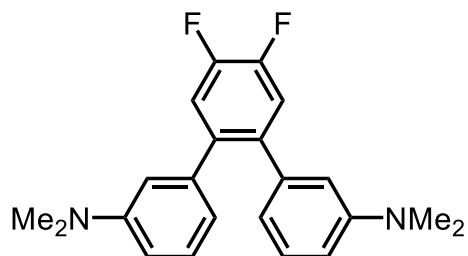
***N*³,*N*³,*N*^{3'},*N*^{3'},*N*^{4'},*N*^{4'}-hexamethyl-[1,1':2',1''-terphenyl]-3,3',4'-triamine (1c)**



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (0.623 g, 3.75 mmol, 2.5 equiv), 3,4-dibromo-*N,N*-dimethylaniline (0.426 g, 1.5 mmol, 1.0 equiv), Na_2CO_3 (0.812 g, 7.5 mmol, 5.0 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (57.8 mg, 0.075 mmol, 5.0 mol%) in a mixture of toluene (14 mL), degassed water (2.0 mL) and ethanol (2.0 mL) was heated to 80 °C under nitrogen. After the completion of the reaction monitored by TLC (12 h), the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 10:1) on silica gel to give **1c** (471 mg,

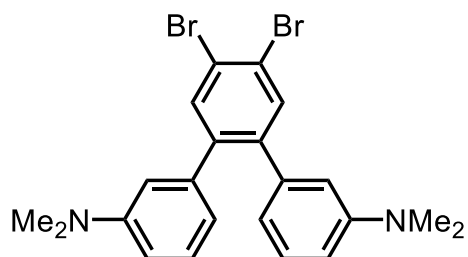
87%) as yellowish solid. ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, $J = 8.7$ Hz, 1H), 7.09–7.17 (m, 2H), 6.86 (d, $J = 2.3$ Hz, 1H), 6.83 (dd, $J = 8.5, 3.0$ Hz, 1H), 6.60–6.70 (m, 5H), 6.53–6.54 (m, 1H), 3.03 (s, 6H), 2.79 (s, 6H), 2.76 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 130.0, 128.6, 128.5, 119.2, 118.9, 115.9, 115.6, 114.7, 111.7, 111.4, 110.9, 41.11, 41.00, 40.85; HRMS(EI $^+$) Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3$ ($[\text{M}]^+$) 359.2356, Found 359.2361.

4',5'-difluoro- $N^3,N^3,N^{3'}$, $N^{3''}$ -tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (1d)



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (0.500 g, 3.00 mmol, 3.0 equiv), 1,2-dibromo-4,5-difluorobenzene (0.278 g, 1.00 mmol, 1.0 equiv), Na_2CO_3 (0.546 g, 5.20 mmol, 5.0 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (37.0 mg, 0.050 mmol, 5.0 mol%) in a mixture of toluene (10 mL), degassed water (1.5 mL) and ethanol (1.5 mL) was heated to 80 °C under nitrogen. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 \times 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 20:1) on silica gel to give **1d** (198 mg, 56%) as colorless oil. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.25–7.30 (m, 2H), 7.10 (dd, $J = 7.6, 8.4$ Hz, 2H), 6.64 (dd, $J = 8.2, 2.3$ Hz, 2H), 6.54 (d, $J = 7.3$ Hz, 2H), 6.48–6.49 (m, 2H), 2.78 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 150.6, 149.4 (dd, $J = 248.5, 14.4$ Hz), 141.0, 138.6 (dd, $J = 7.3, 5.6$ Hz), 129.0, 119.2 (dd, $J = 15.8, 10.1$ Hz), 118.6, 115.2, 111.9, 40.9; HRMS(EI $^+$) Calcd for $\text{C}_{22}\text{H}_{22}\text{F}_2\text{N}_2$ ($[\text{M}]^+$) 352.1746, Found 352.1752.

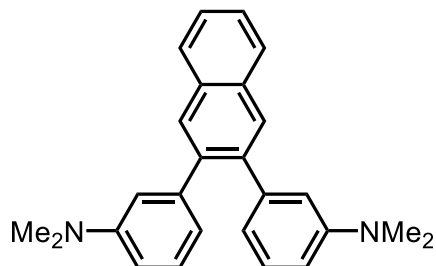
4',5'-Dibromo- $N^3,N^3,N^{3'}$, $N^{3''}$ -tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (1e)



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (0.18 g, 1.1 mmol, 2.2 equiv), 1,2-dibromo-4,5-diodobenzene (0.240 g, 0.50 mmol, 1.0 equiv), Na_2CO_3 (0.270 g, 2.5 mmol, 5.0 equiv) and $\text{PdCl}_2(\text{PPh}_3)_2$ (18.0 mg, 0.0250 mmol, 5.0 mol%) in a mixture of toluene (10 mL), degassed water (2.0 mL) and ethanol (4.0 mL) was heated to 50 °C under nitrogen. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 \times 20 mL). The combined organic phases were dried over MgSO_4 and concentrated under reduced pressure. The crude product was then purified further by column

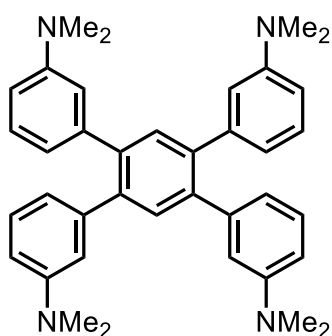
chromatography (eluent: hexane/ethyl acetate = 20:1) on silica gel to give **1e** (203 mg, 85%) as colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 2H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.59 (d, *J* = 7.7 Hz, 4H), 6.45 (s, 2H), 2.77 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 142.1, 140.2, 135.1, 128.9, 123.3, 118.5, 114.8, 112.0, 40.9; HRMS(EI⁺) Calcd for C₂₂H₂₂Br₂N₂ ([M]⁺) 472.0145, Found 472.0149.

3,3'-(Naphthalene-2,3-diyl)bis(*N,N*-dimethylaniline) (**1f**)



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (0.550 g, 3.30 mmol, 2.2 equiv), naphthalene-2,3-diyl bis(trifluoromethanesulfonate) (0.640 g, 1.50 mmol, 1.0 equiv), Na₂CO₃ (0.800 g, 7.50 mmol, 5.0 equiv) and PdCl₂(PPh₃)₂ (53.0 mg, 0.0750 mmol, 5.0 mol%) in a mixture of toluene (15 mL), water (2.0 mL) and ethanol (4.0 mL) was heated to 80 °C under nitrogen. After completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 15:1) on silica gel to give **1f** (0.59 g, quant) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 2H), 7.88 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.49 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.14 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.60–6.64 (m, 4H), 2.78 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 142.4, 140.1, 132.7, 129.1, 128.6, 127.8, 126.2, 118.8, 115.5, 111.4, 40.9; HRMS(EI⁺) Calcd for C₂₆H₂₆N₂ ([M]⁺) 366.2091, Found 366.2094.

4',5'-Bis(3-(dimethylamino)phenyl)-*N*³,*N*³,*N*^{3''},*N*^{3''}-tetramethyl-[1,1':2',1''-terphenyl]-3,3''-diamine (**4**)



The same method as **1a**. A mixture of (3-(dimethylamino)phenyl)boronic acid (1.50 g, 9.00 mmol, 4.5 equiv), 1,2,4,5-tetrabromobenzene (0.790 g, 2.00 mmol, 1.0 equiv), Na₂CO₃ (2.10 g, 20.0 mmol, 10 equiv) and PdCl₂(PPh₃)₂ (0.14 g, 0.2 mmol, 10 mol%) in a mixture of toluene (25 mL), water (3.0 mL) and ethanol (6.0 mL) was heated to 80 °C under nitrogen. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phases were dried over MgSO₄ and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: dichloromethane/hexane = 5:1) on silica gel to give **4** (0.43 g, 39%) as a pale yellow powder. ¹H NMR (400 MHz, CDCl₃): δ 7.64 (s, 2H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 4H), 6.60–6.66 (m, 12H), 2.78 (s, 24H); ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 142.1, 140.3,

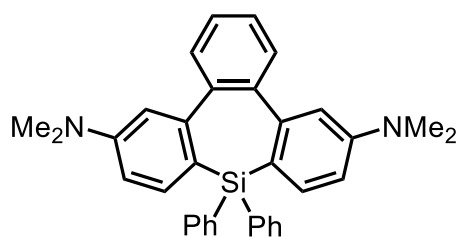
132.5, 128.6, 118.8, 115.2, 111.2, 40.9; HRMS(EI⁺) Calcd for C₃₈H₄₂N₄ ([M]⁺) 554.3404, Found 554.3409.

3. General Procedure for Synthesis of Silepin Derivatives by a

Borane Catalyst⁹

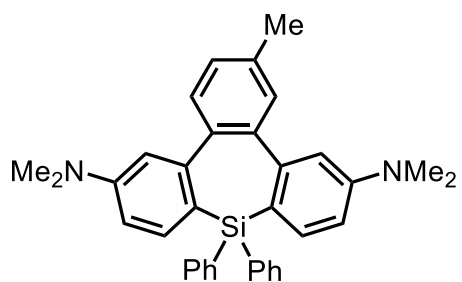
To a test tube with a screw cap equipped with a magnetic stir bar was charged biphenyl **1a** (63.0 mg, 0.200 mmol, 1.0 equiv) and tris(pentafluorophenyl)borane (B(C₆F₅)₃, 3.10 mg, 0.00600 mmol, 3.0 mol%). The test tube was evacuated and filled with nitrogen. Chlorobenzene (0.40 mL) was added via syringe. Diphenylsilane **2a** (55.3 μL, 0.30 mmol, 1.5 equiv) and 2,6-lutidine (1.70 μL, 0.0150 mmol, 7.5 mol%) were then added to the mixture. The test tube was closed with a cap. The reaction mixture was stirred at 100 °C (oil bath) for 24 h. After the completion of the reaction, the mixture was cooled to room temperature. The desired silepin **3a** was obtained by column chromatography (eluent: hexane/ethyl acetate = 20:1) on silica gel in 80% isolated yield.

*N*⁶,*N*⁶,*N*¹²,*N*¹²-Tetramethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepin-6,12-diamine (**3a**)



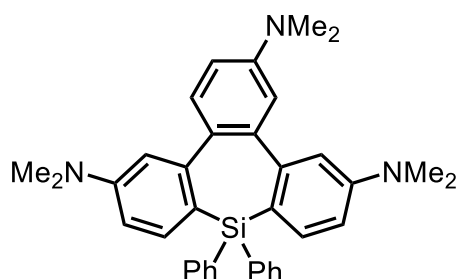
3a was obtained as a white solid (80 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.41–7.49 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.17–7.22 (m, 4H), 7.06–7.11 (m, 3H), 6.99 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.82 (d, *J* = 2.3 Hz, 2H), 6.62 (dd, *J* = 8.2, 2.3 Hz, 2H), 2.96 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 148.7, 142.0, 137.9, 135.3, 134.8, 134.2, 133.0, 131.9, 129.6, 128.5, 127.8, 126.9, 126.7, 125.3, 114.9, 110.2, 40.4; HRMS(EI⁺) Calcd for C₃₄H₃₂N₂Si ([M]⁺) 496.2330, Found 496.2333.

*N*⁶,*N*⁶,*N*¹²,*N*¹²-2-Pentamethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepin-6,12-diamine (**3b**)



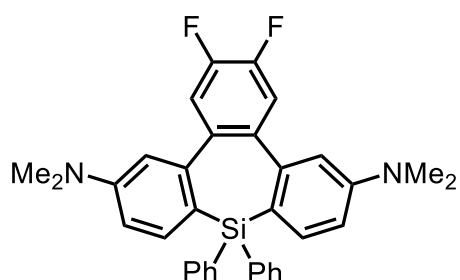
3b was obtained as a white solid (87 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.40–7.48 (m, 3H), 7.25–7.27 (m, 2H), 7.17 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.07–7.12 (m, 2H), 6.97–7.03 (m, 3H), 6.88 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.81 (dd, *J* = 9.4, 2.5 Hz, 2H), 6.59–6.63 (m, 2H), 2.96 (s, 6H), 2.94 (s, 6H), 2.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.59, 151.56, 148.8, 148.7, 141.8, 139.2, 137.9, 136.2, 135.4, 134.8, 134.7, 134.3, 133.1, 132.4, 131.9, 129.6, 128.4, 127.8, 127.4, 126.8, 125.3, 125.2, 119.6, 114.8, 110.2, 110.1, 40.5, 40.4, 21.0; HRMS(EI⁺) Calcd for C₃₅H₃₄N₂Si ([M]⁺) 510.2486, Found 510.2490.

***N*²,*N*²,*N*⁶,*N*⁶,*N*¹²,*N*¹²-Hexamethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepin-2,6,12-triamine (3c)**



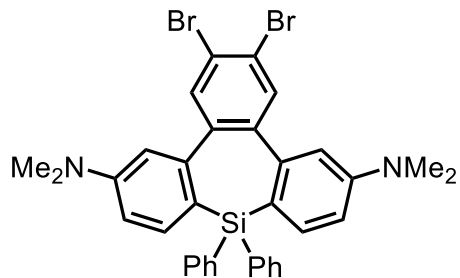
3c was obtained as a white solid (51 mg, 38%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.50–7.53 (m, 2H), 7.46–7.49 (m, 1H), 7.41–7.45 (m, 2H), 7.21 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.17–7.19 (m, 2H), 7.12–7.16 (m, 1H), 7.02–7.06 (m, 3H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.76 (s, 1H), 6.64 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.56–6.61 (m, 3H), 2.96 (s, 6H), 2.95 (s, 6H), 2.85 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 151.5, 149.4, 149.2, 148.9, 142.5, 137.9, 135.4, 134.7, 134.6, 134.5, 133.3, 132.8, 129.5, 128.4, 127.8, 126.8, 125.3, 125.2, 116.4, 114.9, 114.7, 112.4, 110.2, 109.7, 41.2, 40.5(2C) (one carbon is missing); HRMS(EI⁺) Calcd for C₃₆H₃₇N₃Si ([M]⁺) 539.2752, Found 539.2757.

2,3-Difluoro-*N*⁶,*N*⁶,*N*¹²,*N*¹²-tetramethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepine-6,12-diamine (3d)



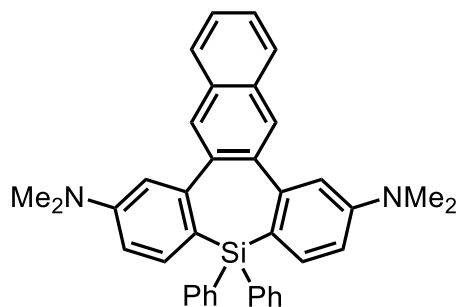
3d was obtained as a white solid (31 mg, 24%). ¹H NMR (600 MHz, CDCl₃): δ 7.55–7.57 (m, 2H), 7.48–7.52 (m, 1H), 7.44–7.46 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.18–7.21 (m, 3H), 7.01–7.09 (m, 4H), 6.74 (br, 2H), 6.65 (br, 2H), 2.97 (s, 12H); ¹³C NMR (150 MHz, CDCl₃): δ 151.5, 148.3 (dd, *J* = 250.0, 14.4 Hz), 146.7, 139.0, 137.8, 135.3, 135.0, 133.8, 132.4, 129.8, 129.0, 127.9, 127.1, 125.11, 120.13 (dd, *J* = 9.4, 7.9 Hz), 114.5 (d, *J* = 7.8 Hz), 110.6 (d, *J* = 5.6 Hz), 40.4; HRMS(EI⁺) Calcd for C₃₄H₃₀F₂N₂Si ([M]⁺) 532.2141, Found 532.2144.

2,3-Dibromo-*N*⁶,*N*⁶,*N*¹²,*N*¹²-tetramethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepine-6,12-diamine (3e)



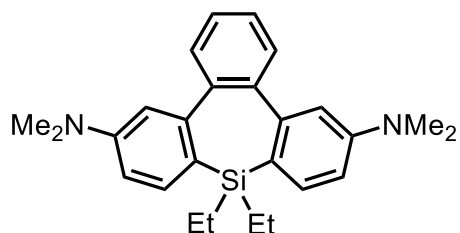
3e was obtained as a white solid (56 mg, 43%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.48–7.54 (m, 2H), 7.42–7.46 (m, 2H), 7.41 (s, 2H), 7.26–7.28 (m, 2H), 7.15–7.20 (m, 2H), 7.06 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.72 (d, *J* = 2.3 Hz, 2H), 6.63 (dd, *J* = 8.5, 2.5 Hz, 2H), 2.96 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 146.2, 142.7, 137.8, 136.2, 135.4, 134.9, 133.6, 132.1, 129.9, 129.0, 128.0, 127.0, 125.4, 122.3, 114.2, 110.8, 40.4. HRMS(EI⁺) Calcd for C₃₄H₃₀Br₂N₂Si ([M]⁺) 652.0540, Found 652.0547.

***N*⁷,*N*⁷,*N*¹³,*N*¹³-Tetramethyl-10,10-diphenyl-10*H*-dibenzo[*b,f*]naphtho-[2,3-*d*]silepin-7,13-diamine (3f)**



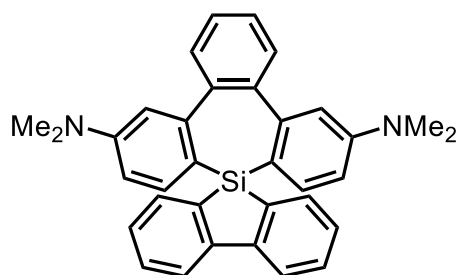
3f was obtained as a white solid (49 mg, 45%).
¹H NMR (400 MHz, CDCl₃) δ 7.67–7.70 (m, 4H), 7.57 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.42–7.49 (m, 3H), 7.37 (q, *J* = 3.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.16 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.94 (d, *J* = 2.3 Hz, 2H), 6.77–6.84 (m, 3H), 6.64 (dd, *J* = 8.2, 2.7 Hz, 2H), 2.98 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 151.7, 148.9, 140.9, 137.9, 135.3, 134.9, 133.9, 132.9, 132.0, 130.7, 129.6, 128.4, 127.8, 127.4, 126.6, 125.8, 125.3, 115.3, 110.1, 40.5; HRMS(EI⁺) Calcd for C₃₈H₃₄N₂Si ([M]⁺) 546.2486, Found 546.2492.

9,9-Diethyl-*N*⁶,*N*⁶,*N*¹²,*N*¹²-tetramethyl-9*H*-tribenzo[*b,d,f*]silepin-6,12-diamine (3g)



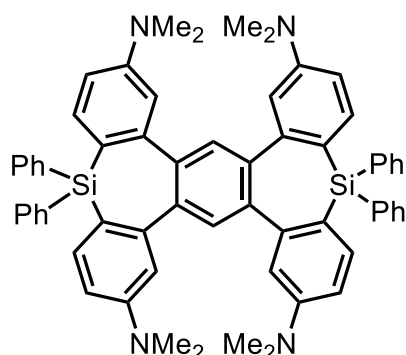
3g was obtained as a white solid (47 mg, 59%).
¹H NMR (400 MHz, CDCl₃): δ 7.44–7.48 (m, 2H), 7.38–7.41 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 2.3 Hz, 2H), 6.64 (dd, *J* = 8.2, 2.7 Hz, 2H), 2.93 (s, 12H), 1.28 (m, 5H), 0.59 (t, *J* = 8.0 Hz, 3H), 0.14 (q, *J* = 7.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.2, 147.7, 142.4, 132.4, 131.7, 127.5, 127.0, 114.9, 110.6, 40.5, 8.1, 7.8, 2.5, 1.0; HRMS(EI⁺) Calcd for C₂₆H₃₂N₂Si ([M]⁺) 400.2330, Found 400.2334.

***N*⁶,*N*⁶,*N*¹²,*N*¹²-Tetramethylspiro[dibenzo[*b,d*]silole-5,9'-tribenzo[*b,d,f*]silepin]-6',12'-diamine (3h)**



3h was obtained as a white solid (92 mg, 93%).
¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 6.9 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.55–7.64 (m, 5H), 7.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.18–7.22 (m, 1H), 6.88 (d, *J* = 2.1 Hz, 2H), 6.80 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.56 (dd, *J* = 8.5, 2.5 Hz, 2H), 5.64 (d, *J* = 6.9 Hz, 1H), 2.93 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 151.9, 150.1, 148.0, 147.6, 142.3, 137.2, 135.6, 133.5, 133.3, 133.2, 133.0, 131.0, 130.0, 127.7, 127.6, 127.3, 125.0, 121.5, 120.6, 114.8, 110.7, 40.5. HRMS(EI⁺) Calcd for C₃₄H₃₀N₂Si ([M]⁺) 494.2173, Found 494.2173.

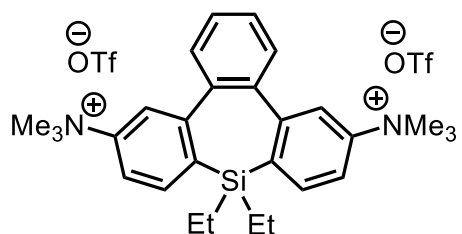
(*N*⁶,*N*⁶,*N*¹²,*N*¹²-Tetramethyl-9,9-diphenyl-9*H*-6,12-diamine) tribenzo[*b,d,f*]silepin (5**)**



5 was obtained as a white solid (78 mg, 85%, 0.10 mmol scale). ¹H NMR (400 MHz, CDCl₃): δ 7.62 (dd, *J* = 7.8, 1.4 Hz, 4H), 7.44–7.50 (m, 6H), 7.27–7.30 (m, 8H), 6.99–7.05 (m, 6H), 6.84 (s, 2H), 6.59 (dd, *J* = 8.2, 2.7 Hz, 4H), 6.44 (d, *J* = 2.3 Hz, 4H), 2.94 (s, 24H); ¹³C NMR (100 MHz, CDCl₃): δ 151.4, 148.4, 140.0, 137.8, 135.7, 134.8, 134.3, 134.1, 132.7, 129.7, 128.5, 127.9, 126.4, 125.4, 114.6, 110.0, 40.4; HRMS(FAB⁺) Calcd for C₆₂H₅₈N₄Si ([M+H]⁺)

915.4273, Found 915.4277.

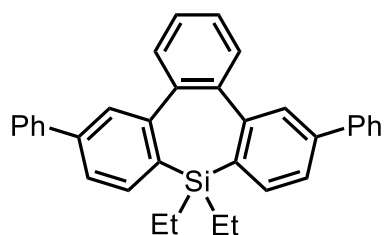
9,9-Diethyl-*N*⁶,*N*⁶,*N*⁶,*N*¹²,*N*¹²,*N*¹²-hexamethyl-9*H*-tribenzo[*b,d,f*]silepin-6,12-diaminium triflate (6**)**



The compound **6** was prepared according to the procedure in the previous literature.¹⁰ In a dry two neck round bottom flask equipped with a magnetic stir bar was charged the compound **3g** (200.3 mg, 0.50 mmol, 1.0 equiv) and CH₂Cl₂ (5.0 mL). To the resultant stirring solution was added dropwise MeOTf (206 mg, 1.25 mmol, 2.5

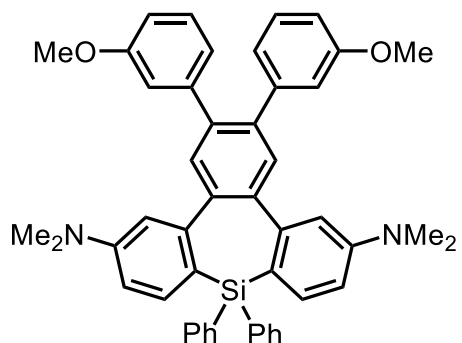
equiv) at room temperature. The solution was stirred at room temperature for 2 h. The reaction mixture was concentrated to remove CH₂Cl₂ and the residue was treated with Et₂O (20 mL). The resultant solid was filtered, washed with Et₂O and hexane, and then dried under vacuum to give silepin **6** as a white solid (333 mg, 91%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.88–7.92 (m, 4H), 7.60–7.69 (m, 6H), 3.59 (s, 18H), 1.45 (q, *J* = 7.8 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H), 0.52 (t, *J* = 8.0 Hz, 3H), 0.14 (q, *J* = 7.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 148.6, 147.2, 141.3, 139.2, 133.4, 132.4, 128.8, 121.9, 120.8 (q, *J* = 321 Hz), 118.6, 56.4, 7.6, 7.1, 0.44, -0.07; HRMS(FAB⁺) Calcd for C₂₉H₃₈F₃N₂O₃SSi⁺ ([M-OTf⁻]⁺) 579.2319, Found 579.2326.

9,9-Diethyl-6,12-diphenyl-9H-tribenzo[*b,d,f*]silepin (7)



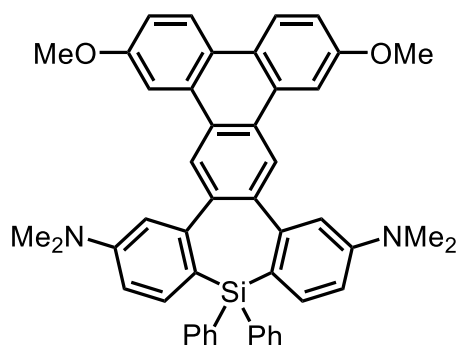
To a dry 20 mL Schlenk flask equipped with a magnetic stir bar was added the compound **6** (0.150 g, 0.20 mmol, 1.0 equiv) and PdCl₂(PPh₃)₂ (2.80 mg, 0.00400 mmol, 2.0 mol%). The flask was sealed with a rubber septum, evacuated/filled with nitrogen. THF (2.0 mL) was added via syringe, and the resultant slurry was stirred for 5 min at room temperature. Then phenylmagnesium bromide (0.5 M solution in THF, 0.88 mL, 0.440 mmol, 2.2 equiv) was added dropwise. After 1 h, the reaction mixture was quenched with water (1 mL) and 1N HCl (5 mL), and then extracted with Et₂O. The organic extract was dried over MgSO₄, filtered, and concentrated. The crude product was purified by chromatography on silica gel (eluent: hexane/ethyl acetate = 100:0 to 20:1) to give the compound **7** as white powder (82 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 1.8 Hz, 2H), 7.57–7.60 (m, 6H), 7.49–7.53 (m, 4H), 7.40–7.48 (m, 6H), 7.31–7.35 (m, 2H), 1.37–1.46 (m, 5H), 0.65 (t, *J* = 7.8 Hz, 3H), 0.27 (q, *J* = 7.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 147.1, 142.2, 141.5, 141.1, 139.1, 132.2, 131.9, 129.2, 128.9, 127.5, 127.3, 125.2, 8.1, 7.6, 1.6, 1.0 (one carbon is missing); HRMS(EI⁺) Calcd for C₃₄H₃₀Si ([M]⁺) 466.2112, Found 466.2118.

2,3-Bis(3-methoxyphenyl)-*N*⁶,*N*⁶,*N*¹²,*N*¹²-tetramethyl-9,9-diphenyl-9H-tribenzo[*b,d,f*]silepin-6,12-diamine (8)



Compound **8** was synthesized by Suzuki-Miyaura coupling reaction. A mixture of **3e** (156.0 mg, 0.24 mmol, 1.0 equiv), (3-methoxyphenyl)boronic acid (110 mg, 0.72 mmol, 3.0 equiv), Na₂CO₃ (127 mg, 1.2 mmol, 5.0 equiv) and Pd(PPh₃)₄ (14.0 mg, 0.012 mmol, 5.0 mol%) in a mixture of toluene (3 mL), water (0.75 mL) and ethanol (0.75 mL) was heated to 80 °C under nitrogen. After the completion of the reaction monitored by TLC, the mixture was cooled to room temperature, then diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 10:1) on silica gel to give **8** (142 mg, 84%) as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.62–7.64 (m, 2H), 7.45–7.53 (m, 3H), 7.34 (d, *J* = 6.9 Hz, 2H), 7.08–7.22 (m, 8H), 7.03 (dd, *J* = 7.2, 7.2 Hz, 2H), 6.90 (s, 1H), 6.60–6.74 (m, 6H), 6.48–6.51 (m, 2H), 3.63 (s, 6H), 2.96 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 151.7, 148.0, 142.7, 141.4, 138.4, 137.8, 135.6, 134.5, 133.8, 132.5, 129.7, 128.8, 128.3, 127.9, 126.8, 125.74, 125.65, 122.3, 115.2, 114.4, 112.5, 110.4, 55.2, 40.4; HRMS(EI⁺) Calcd for C₄₈H₄₄N₂O₂Si ([M]⁺) 708.3167, Found 708.3171.

3,17-Dimethoxy-*N*⁷,*N*⁷,*N*¹³,*N*¹³-tetramethyl-10,10-diphenyl-10*H*-dibenzo[*b,f*]triphenylene[2,3-*d*]silepin-7,13-diamine (9)



Compound **9** was synthesized according to the reported procedure.¹² Silepin **8** (142 mg, 0.2 mmol, 1.0 equiv) was dissolved in dry dichloromethane (6.0 mL) and cooled to 0 °C in an ice/water bath under a nitrogen atmosphere. A solution of iron(III) chloride (250 mg, 1.54 mmol, 8.0 equiv) in nitromethane (1.0 mL) was added dropwise to the above solution at 0 °C and the mixture was stirred for 3 h at room temperature.

To the resulting mixture was added methanol (10 mL) followed by water (10 mL) and dichloromethane (20 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ and evaporated to produce a brown oil. The purification of the crude product by column chromatography using hexanes as eluent afforded **9** (122.8 mg, 88%) as white solid. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.44 (d, *J* = 8.7 Hz, 2H), 8.38 (s, 2H), 7.95 (d, *J* = 2.7 Hz, 2H), 7.44–7.57 (m, 5H), 7.32–7.35 (m, 3H), 7.19–7.26 (m, 4H), 7.02 (s, 1H), 6.74–6.84 (m, 5H), 3.98 (s, 6H), 3.02 (s, 12H); ¹³C NMR (100 MHz, CD₂Cl₂): δ 158.7, 152.0, 148.8, 141.6, 138.1, 135.5, 135.1, 134.1, 132.8, 130.12, 130.06, 128.9, 128.6, 128.2, 127.1, 126.8, 124.7, 124.2, 116.2, 115.6, 110.7, 106.2, 55.9, 40.7 (one carbon is missing); HRMS(EI⁺) Calcd for C₄₈H₄₂N₂O₂Si ([M]⁺) 706.3011, Found 706.3018.

4. Variable Temperature ^1H NMR of **3g**

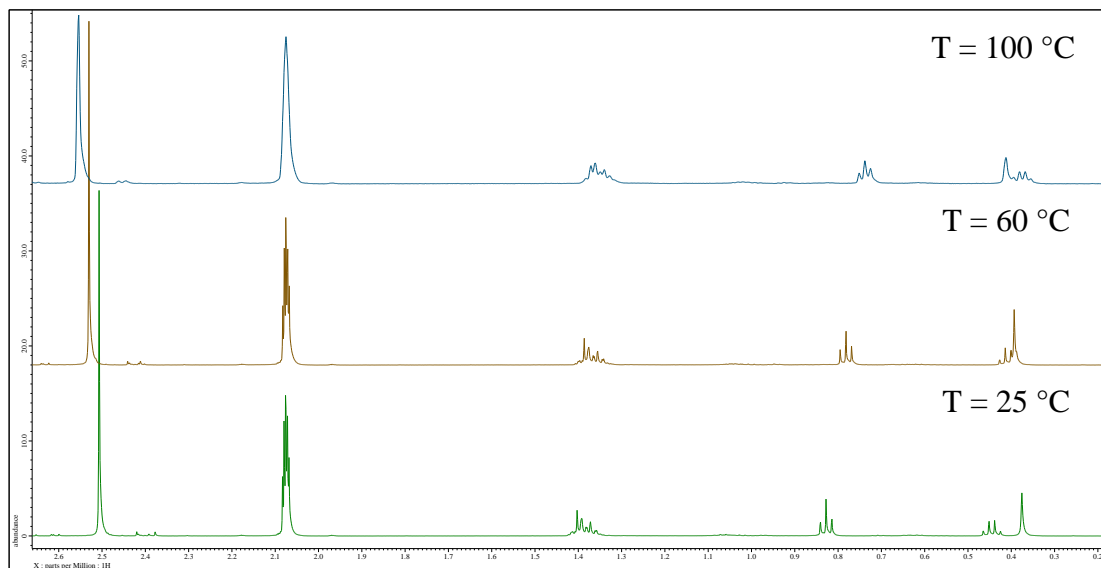
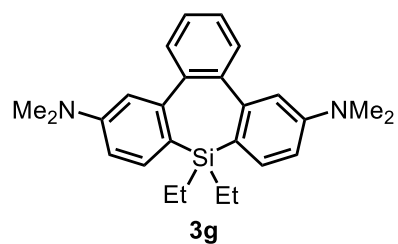


Figure S1. Variable Temperature ^1H NMR of **3g** in $\text{toluene-}d_8$.

The two ethyl groups of **3g** appeared independently in the ^1H NMR spectra at 25, 60, and 100 °C in $\text{toluene-}d_8$, even though the shift of peaks was observed.



5. Optical Properties of 3a, 3f, 5, 9

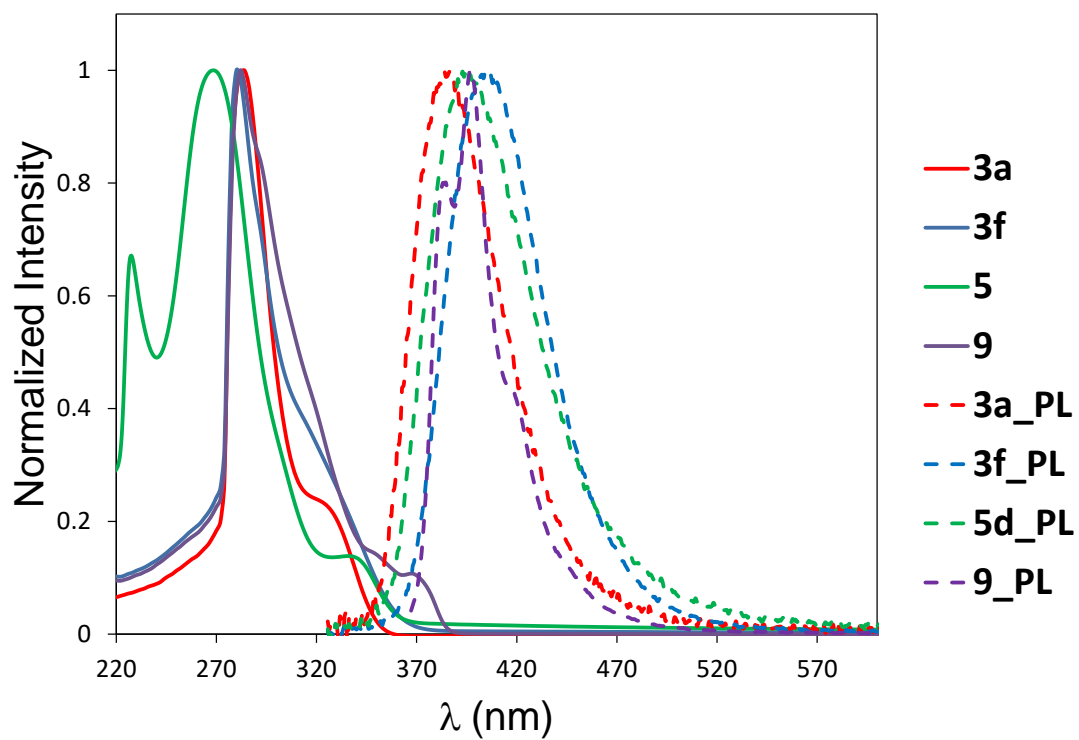
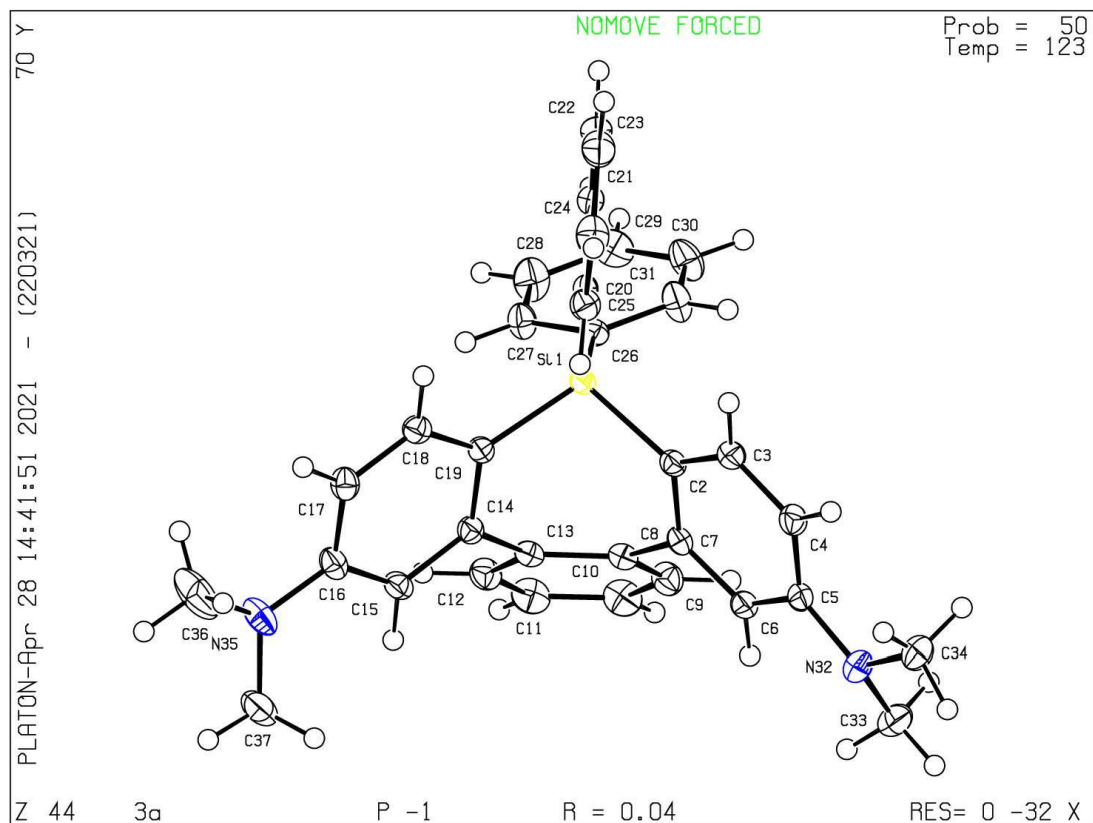


Figure S2. UV absorption (solid line) and photoluminescence (dot line) spectra of **3a**, **3f**, **5**, and **9** in toluene (5.0×10^{-5} M).

6. X-ray structures of compounds 3a, 5, 9

6-1. X-ray Structure of compound 3a

A single crystal of N^6, N^6, N^{12}, N^{12} -tetramethyl-9,9-diphenyl-9*H*-tribenzo[*b,d,f*]silepin-6,12-diamine ($C_{34}H_{32}N_2Si$) (**3a**) was prepared by recrystallization from the dichloromethane/ethanol solution. A suitable crystal was selected, and the X-ray diffraction was collected on an Rigaku AFC HyPix-6000 diffractometer: fixed-chi single diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). The crystal was kept at 123 K during data collection. The data were collected using ω scan in the θ range of $5.182 \leq \theta \leq 54.964$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,¹³ and expanded using Fourier techniques.¹⁴ Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 12122 observed reflections. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ All calculations were performed using the Olex-2 crystallographic software package except for refinement,¹⁶ which was performed using version 2018/3 of ShelXL (Sheldrick, 2015) of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.



Crystal structure determination of **3a**

$C_{34}H_{32}N_2Si$ ($M = 496.70$ g/mol): triclinic, space group P-1 (no. 2), $a = 9.8113(2)$ Å, $b = 12.0833(4)$ Å, $c = 12.1527(3)$ Å, $\alpha = 82.005(2)^\circ$, $\beta = 82.769(2)^\circ$, $\gamma = 71.726(3)^\circ$, $V = 1349.59(7)$ Å³, $Z = 2$, $T = 123$ K, $\mu(\text{Mo K}\alpha) = 0.113$ mm⁻¹, $D_{\text{calc}} = 1.222$ g/cm³, 20753 reflections measured ($5.182^\circ \leq 2\theta \leq 54.964^\circ$), 6188 unique ($R_{\text{int}} = 0.0182$, $R_{\text{sigma}} = 0.0186$) which were used in all calculations. The final R_1 was 0.0353 ($I > 2\sigma(I)$) and wR_2 was 0.0950 (all data).

Table S1. Crystal data and structure refinement for **3a**

Empirical formula	$C_{34}H_{32}N_2Si$
Formula weight	496.70
Temperature/K	123
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	9.8113(2)
$b/\text{\AA}$	12.0833(4)
$c/\text{\AA}$	12.1527(3)
$\alpha/^\circ$	82.005(2)
$\beta/^\circ$	82.769(2)
$\gamma/^\circ$	71.726(3)
Volume/Å ³	1349.59(7)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.222
μ/mm^{-1}	0.113
$F(000)$	528.0
Crystal size/mm ³	$0.5 \times 0.4 \times 0.4$
Radiation	Mo K α ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	5.182 to 54.964
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	20753
Independent reflections	6188 [$R_{\text{int}} = 0.0182$, $R_{\text{sigma}} = 0.0186$]
Data/restraints/parameters	6188/0/338
Goodness-of-fit on F^2	1.046
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0929$
Final R indexes [all data]	$R_1 = 0.0386$, $wR_2 = 0.0950$

Largest diff. peak/hole / e Å⁻³ 0.38/-0.28

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Si1	6746.1(3)	4082.5(2)	3022.0(2)	15.30(8)
N32	11465.1(11)	1937.6(9)	-515.6(9)	26.6(2)
N35	8314.5(13)	-68.4(9)	6567.6(9)	30.0(2)
C20	7029.9(12)	5405.3(9)	3484.1(9)	17.8(2)
C26	4883.4(11)	4513.4(9)	2574.3(9)	17.9(2)
C7	8141.1(12)	2482.0(9)	1431.8(9)	17.7(2)
C8	7011.7(12)	1886.3(9)	1781.1(9)	18.8(2)
C3	9206.9(12)	4003.2(10)	1450.1(9)	20.3(2)
C19	7128.2(11)	2837.7(9)	4133.0(9)	16.5(2)
C2	8114.9(11)	3511.9(9)	1865.8(9)	17.4(2)
C14	7166.2(11)	1711.9(9)	3916.4(9)	17.6(2)
C18	7532.4(12)	2941.6(10)	5166.1(9)	19.4(2)
C25	8366.9(13)	5387.4(10)	3786.8(10)	22.4(2)
C13	6603.6(12)	1516.7(9)	2893.4(9)	18.5(2)
C5	10334.4(12)	2493.6(10)	228.9(9)	20.7(2)
C16	7975.8(12)	874.7(10)	5762.2(10)	21.5(2)
C6	9214.0(12)	2010.9(10)	609.5(9)	19.8(2)
C12	5566.1(13)	921.9(10)	3079.1(10)	23.7(2)
C15	7597.7(12)	755.1(10)	4718.0(9)	20.2(2)
C17	7945.3(12)	1998.9(10)	5967.5(9)	21.8(2)
C9	6348.0(13)	1646.5(11)	923.6(10)	24.9(2)
C27	3764.2(13)	4231.7(11)	3251.6(10)	24.2(2)
C4	10303.8(12)	3515.1(10)	662.0(9)	21.9(2)
C21	5911.2(13)	6460.5(10)	3508.5(9)	21.5(2)
C11	4931.1(14)	692.6(11)	2219.5(11)	28.3(3)
C31	4559.1(14)	5186.6(12)	1556.7(11)	29.1(3)
C24	8587.4(15)	6390.4(12)	4066.4(10)	29.2(3)
C30	3164.7(15)	5577.2(12)	1236.7(11)	33.2(3)
C22	6119.5(15)	7460.8(11)	3808.1(10)	28.8(3)
C29	2068.0(14)	5302.7(12)	1931.0(12)	30.9(3)
C10	5323.4(14)	1063.3(11)	1131.7(11)	29.3(3)
C34	12557.5(14)	2507.1(12)	-920.4(11)	30.7(3)
C23	7459.8(17)	7424.0(12)	4069.9(11)	32.7(3)
C37	8686.9(16)	-1254.7(11)	6268.7(12)	33.8(3)
C33	11149.0(16)	1297.2(12)	-1324.4(11)	34.4(3)

Atom	x	y	z	U_{eq}
C28	2369.8(14)	4620.0(13)	2931.6(12)	32.8(3)
C36	8741(2)	73.1(15)	7609.9(14)	52.4(5)

Table S3. Anisotropic Displacement Parameters ($\times 10^4$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	13.78(14)	13.97(14)	17.33(14)	0.08(10)	-0.89(10)	-3.94(11)
N32	27.4(5)	26.1(5)	23.0(5)	-4.2(4)	6.6(4)	-5.9(4)
N35	36.4(6)	24.3(5)	29.0(5)	9.5(4)	-13.3(5)	-9.9(5)
C20	19.3(5)	17.2(5)	16.6(5)	-0.7(4)	1.7(4)	-6.8(4)
C26	16.4(5)	16.7(5)	20.0(5)	-1.1(4)	-2.5(4)	-4.3(4)
C7	19.1(5)	17.0(5)	16.1(5)	2.2(4)	-4.2(4)	-4.7(4)
C8	19.5(5)	15.2(5)	21.2(5)	-1.1(4)	-3.3(4)	-4.5(4)
C3	21.7(5)	17.7(5)	21.0(5)	-1.0(4)	-0.3(4)	-6.4(4)
C19	13.2(5)	16.6(5)	18.2(5)	0.2(4)	-0.4(4)	-3.6(4)
C2	16.9(5)	15.9(5)	17.7(5)	1.0(4)	-2.0(4)	-3.5(4)
C14	15.3(5)	18.2(5)	18.4(5)	-0.4(4)	0.2(4)	-5.2(4)
C18	17.7(5)	19.1(5)	21.2(5)	-2.0(4)	-1.0(4)	-5.5(4)
C25	21.9(5)	22.9(6)	23.1(5)	-1.4(4)	-1.5(4)	-8.3(4)
C13	18.3(5)	14.7(5)	22.0(5)	-0.9(4)	-2.4(4)	-4.3(4)
C5	21.8(5)	19.3(5)	16.6(5)	1.6(4)	-0.1(4)	-1.8(4)
C16	18.2(5)	21.9(5)	22.4(5)	4.7(4)	-3.4(4)	-5.7(4)
C6	24.4(5)	16.8(5)	17.2(5)	-0.5(4)	-2.9(4)	-4.7(4)
C12	23.0(6)	22.0(6)	27.2(6)	-0.8(4)	-0.9(4)	-9.6(5)
C15	20.4(5)	16.1(5)	23.2(5)	0.9(4)	-1.0(4)	-6.0(4)
C17	20.8(5)	25.7(6)	18.9(5)	0.1(4)	-4.3(4)	-7.4(4)
C9	29.3(6)	24.5(6)	22.5(5)	-0.9(4)	-6.2(5)	-9.5(5)
C27	20.3(5)	29.7(6)	21.8(5)	3.2(5)	-2.7(4)	-8.8(5)
C4	20.8(5)	22.1(5)	22.0(5)	0.7(4)	1.7(4)	-7.9(4)
C21	23.1(5)	19.8(5)	19.2(5)	-1.1(4)	2.8(4)	-5.2(4)
C11	25.3(6)	26.7(6)	37.9(7)	-3.3(5)	-4.9(5)	-14.1(5)
C31	24.5(6)	34.9(7)	26.1(6)	9.4(5)	-4.5(5)	-10.8(5)
C24	35.2(7)	34.9(7)	25.3(6)	-2.5(5)	-3.4(5)	-21.6(6)
C30	31.5(7)	35.0(7)	30.8(7)	10.6(5)	-14.6(5)	-8.1(6)
C22	39.7(7)	18.1(5)	25.0(6)	-4.3(4)	4.2(5)	-5.2(5)
C29	20.6(6)	33.2(7)	39.5(7)	-0.2(5)	-13.0(5)	-6.5(5)
C10	31.6(7)	29.0(6)	32.3(6)	-4.1(5)	-11.5(5)	-12.7(5)
C34	25.7(6)	31.7(7)	28.7(6)	-2.4(5)	8.2(5)	-4.5(5)
C23	53.9(8)	25.0(6)	25.8(6)	-5.8(5)	0.6(6)	-21.6(6)
C37	35.1(7)	23.2(6)	37.9(7)	8.4(5)	-5.1(6)	-5.6(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C33	43.6(8)	27.2(6)	30.2(7)	-9.9(5)	10.0(6)	-9.7(6)
C28	19.5(6)	45.0(8)	35.0(7)	2.6(6)	-2.7(5)	-14.0(6)
C36	82.5(13)	39.8(8)	42.2(9)	17.3(7)	-40.1(9)	-24.8(9)

Table S4. Bond Lengths in Å for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C20	1.8749(11)	C19	C14	1.4095(15)
Si1	C26	1.8660(11)	C19	C18	1.3964(15)
Si1	C19	1.8534(11)	C14	C13	1.4972(15)
Si1	C2	1.8620(11)	C14	C15	1.3959(15)
N32	C5	1.3963(14)	C18	C17	1.3825(16)
N32	C34	1.4492(17)	C25	C24	1.3887(17)
N32	C33	1.4491(17)	C13	C12	1.3999(16)
N35	C16	1.3788(15)	C5	C6	1.4005(16)
N35	C37	1.4503(18)	C5	C4	1.3982(16)
N35	C36	1.4308(18)	C16	C15	1.4042(16)
C20	C25	1.3994(16)	C16	C17	1.4055(17)
C20	C21	1.3986(15)	C12	C11	1.3815(17)
C26	C27	1.3885(16)	C9	C10	1.3790(18)
C26	C31	1.3961(16)	C27	C28	1.3870(17)
C7	C8	1.4909(15)	C21	C22	1.3898(17)
C7	C2	1.4095(15)	C11	C10	1.3827(19)
C7	C6	1.3959(15)	C31	C30	1.3870(18)
C8	C13	1.4124(15)	C24	C23	1.385(2)
C8	C9	1.4025(16)	C30	C29	1.377(2)
C3	C2	1.3909(15)	C22	C23	1.377(2)
C3	C4	1.3867(16)	C29	C28	1.3803(19)

Table S5. Bond Angles in ° for **3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C26	Si1	C20	108.00(5)	C19	C14	C13	121.94(9)
C19	Si1	C20	110.70(5)	C15	C14	C19	120.09(10)
C19	Si1	C26	113.96(5)	C15	C14	C13	117.63(10)
C19	Si1	C2	102.46(5)	C17	C18	C19	122.79(10)
C2	Si1	C20	110.54(5)	C24	C25	C20	121.20(11)

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C2	Si1	C26	111.14(5)	C8	C13	C14	126.09(10)
C5	N32	C34	118.13(10)	C12	C13	C8	118.14(10)
C5	N32	C33	117.96(11)	C12	C13	C14	115.76(10)
C34	N32	C33	114.26(10)	N32	C5	C6	120.66(11)
C16	N35	C37	120.39(11)	N32	C5	C4	121.87(11)
C16	N35	C36	119.76(11)	C4	C5	C6	117.41(10)
C36	N35	C37	117.02(11)	N35	C16	C15	121.11(11)
C25	C20	Si1	121.70(8)	N35	C16	C17	121.39(11)
C21	C20	Si1	120.73(9)	C15	C16	C17	117.46(10)
C21	C20	C25	117.55(10)	C7	C6	C5	122.13(10)
C27	C26	Si1	121.89(8)	C11	C12	C13	122.47(11)
C27	C26	C31	117.73(10)	C14	C15	C16	122.03(10)
C31	C26	Si1	120.31(9)	C18	C17	C16	120.28(11)
C2	C7	C8	122.35(10)	C10	C9	C8	122.30(11)
C6	C7	C8	117.43(10)	C28	C27	C26	120.97(11)
C6	C7	C2	120.17(10)	C3	C4	C5	120.19(11)
C13	C8	C7	125.16(10)	C22	C21	C20	121.43(12)
C9	C8	C7	116.51(10)	C12	C11	C10	119.31(11)
C9	C8	C13	118.30(10)	C30	C31	C26	121.35(11)
C4	C3	C2	123.11(11)	C23	C24	C25	119.69(12)
C14	C19	Si1	120.37(8)	C29	C30	C31	119.86(12)
C18	C19	Si1	121.97(8)	C23	C22	C21	119.62(12)
C18	C19	C14	117.33(10)	C30	C29	C28	119.72(11)
C7	C2	Si1	119.79(8)	C9	C10	C11	119.48(11)
C3	C2	Si1	123.12(8)	C22	C23	C24	120.46(12)
C3	C2	C7	116.90(10)	C29	C28	C27	120.35(12)

Table S6. Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H3	9200.95	4706.5	1718.87	24
H18	7523.37	3691.84	5325.11	23
H25	9137.88	4676.2	3801.25	27

Atom	x	y	z	U_{eq}
H6	9183.29	1341.19	297.92	24
H12	5288.16	666.27	3824.19	28
H15	7636.83	-0.3	4552.04	24
H17	8209.49	2111.52	6659.83	26
H9	6613.57	1894.49	173.21	30
H27	3956.41	3766.04	3944.31	29
H4	11036.64	3875.75	415.71	26
H21	4988.93	6494.24	3316.18	26
H11	4232.26	284.48	2374.26	34
H31	5308.94	5381.13	1073.6	35
H24	9507.53	6367.58	4254.32	35
H30	2966.37	6033.07	540.11	40
H22	5341.98	8165.96	3832.21	35
H29	1108.05	5582	1722.13	37
H10	4890.54	917.43	532.39	35
H34A	12137.35	3220.33	-1408.03	46
H34B	13352.48	1973.73	-1340.48	46
H34C	12921.35	2712.44	-286.53	46
H23	7611.67	8112.52	4254.17	39
H37A	7821.38	-1403.79	6082.64	51
H37B	9087.39	-1811.08	6899.26	51
H37C	9403.74	-1350.86	5622.21	51
H33A	10783.27	667.66	-933.96	52
H33B	12029.83	959.25	-1795.32	52
H33C	10420.04	1831.6	-1790.82	52
H28	1618.32	4415	3403.61	39
H36A	9695.99	188.35	7492.92	79
H36B	8776.52	-629.15	8131.4	79
H36C	8042.37	757.1	7919.15	79

6-2. X-ray structure of compound 5

A single crystal of (N^6, N^6, N^{12}, N^{12} -tetramethyl-9,9-diphenyl-9*H*-6,12-diamine) tribenzo[*b,d,f*]bissilepin ($C_{62}H_{58}N_4Si_2$) (**5**) was prepared by recrystallization from the dichloromethane/ethanol solution. A suitable crystal was selected, and the X-ray diffraction was collected on an Rigaku AFC HyPix-6000 diffractometer: fixed-chi single diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). The crystal was kept at 173 K during data collection. The data were collected using ω scan in the θ range of $4.476 \leq \theta \leq 54.966$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,¹³ and expanded using Fourier techniques.¹⁴ Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 26837 observed

reflections. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ All calculations were performed using the Olex-2 crystallographic software package except for refinement,¹⁶ which was performed using version 2018/3 of ShelXL (Sheldrick, 2015) of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.

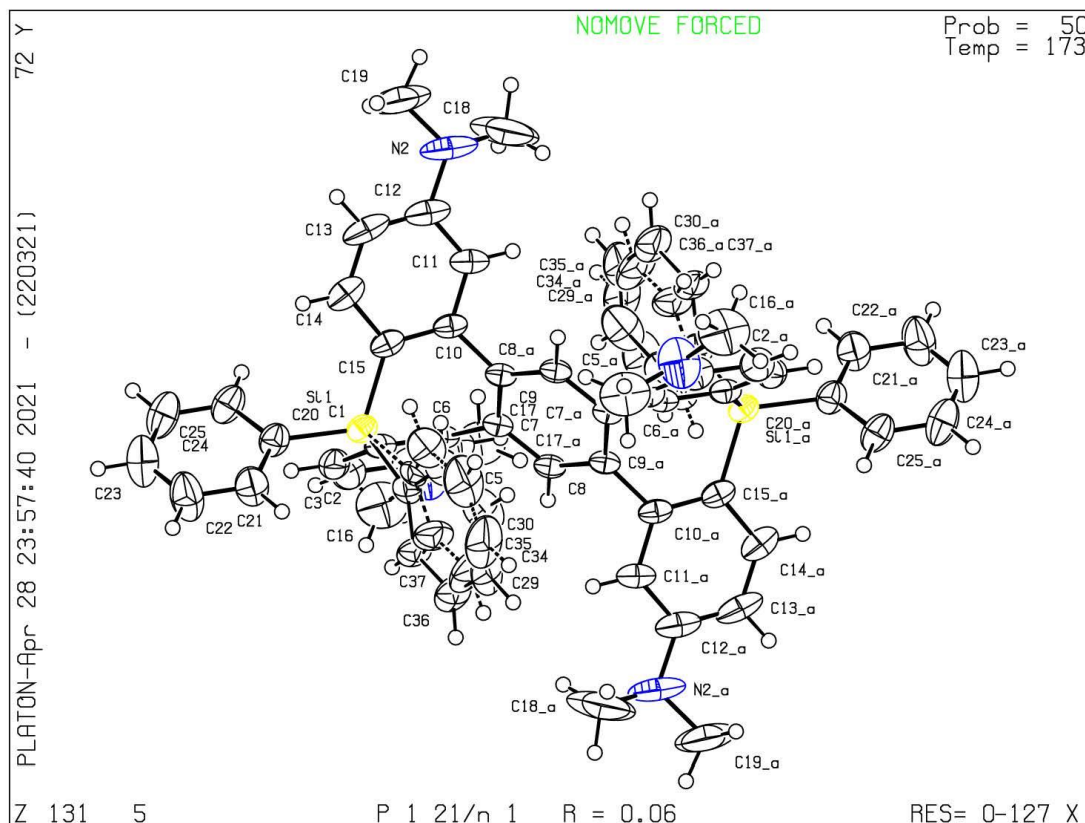


Table S7. Crystal data and structure refinement for **5**

Empirical formula	$C_{62}H_{58}N_4Si_2$
Formula weight	915.30
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	15.3334(8)
$b/\text{\AA}$	11.1613(8)
$c/\text{\AA}$	15.7358(9)
$\alpha/^\circ$	90
$\beta/^\circ$	91.890(5)
$\gamma/^\circ$	90

Volume/Å ³	2691.6(3)
Z	50
ρ _{calc} /cm ³	28.234
μ/mm ⁻¹	2.689
F(000)	24300.0
Crystal size/mm ³	0.24 × 0.09 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.476 to 54.966
Index ranges	-19 ≤ h ≤ 19, -14 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	26837
Independent reflections	6128 [R _{int} = 0.0504, R _{sigma} = 0.0491]
Data/restraints/parameters	6128/108/366
Goodness-of-fit on F ²	1.052
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0615, wR ₂ = 0.1631
Final R indexes [all data]	R ₁ = 0.0791, wR ₂ = 0.1720
Largest diff. peak/hole / e Å ⁻³	0.50/-0.27

Table S8. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Si1	5956.9(3)	4776.0(5)	7395.1(4)	36.19(17)
C9	5105.9(11)	5771.0(16)	5709.9(12)	31.5(4)
C7	4686.3(11)	4661.1(16)	5801.7(12)	30.7(4)
C10	5273.0(12)	6668.1(16)	6394.2(13)	34.5(4)
C8	4597.5(12)	3937.8(16)	5088.8(13)	32.0(4)
C6	4326.6(12)	4191.7(16)	6605.8(13)	33.7(4)
C1	4849.4(13)	4082.3(17)	7350.8(13)	36.2(4)
C15	5728.6(13)	6372.9(18)	7147.2(14)	37.9(4)
C5	3475.1(14)	3756.8(19)	6569.8(14)	40.8(5)
C11	5015.6(14)	7847.7(18)	6222.0(16)	44.1(5)
C2	4479.0(15)	3512(2)	8037.9(14)	44.9(5)
N2	4930.8(19)	9946.6(19)	6589(2)	82.1(9)
C20	6461.4(14)	4569(2)	8480.3(14)	43.7(5)
N1	2281.8(15)	2707(3)	7206.1(17)	76.7(8)

Atom	x	y	z	U(eq)
C14	5934.7(15)	7320(2)	7701.7(17)	51.5(6)
C4	3116.9(15)	3176(2)	7266.7(15)	49.2(6)
C12	5203.0(16)	8767(2)	6786.8(19)	55.0(6)
C3	3638.4(17)	3072(2)	8000.4(15)	51.5(6)
C25	6072.3(16)	5018(2)	9204.0(15)	53.6(6)
C13	5677.1(17)	8493(2)	7515(2)	61.1(7)
C21	7227.4(17)	3914(3)	8607.7(16)	60.0(7)
C24	6428.8(19)	4813(3)	10006.9(16)	67.3(8)
C17	1658.8(17)	3185(3)	6612(2)	78.0(9)
C22	7587(2)	3721(4)	9413.4(19)	80.1(10)
C16	1986(2)	1923(3)	7851(2)	87.1(11)
C23	7181(2)	4163(4)	10111.8(18)	78.2(9)
C19	4973(4)	10789(3)	7274(3)	138(2)
C18	4224(4)	10117(3)	5980(4)	152(2)
C28	7873(9)	4662(19)	5616(7)	92(4)
C29	7810(9)	3520(20)	5317(8)	99(4)
C31	6666(8)	3127(12)	6228(10)	64(3)
C27	7328(8)	5034(13)	6243(9)	61(3)
C26	6666(13)	4270(11)	6536(12)	38(2)
C30	7229(10)	2740(20)	5608(11)	96(5)
C36	7028(8)	2188(12)	5856(8)	73(3)
C37	6589(6)	2744(11)	6490(7)	51(2)
C33	7130(8)	4628(13)	6047(8)	60(3)
C35	7510(12)	2820(17)	5317(7)	89(4)
C34	7569(11)	4047(16)	5394(9)	97(5)
C32	6662(11)	3957(13)	6611(11)	40(2)

Table S9. Anisotropic Displacement Parameters ($\times 10^4$) for **5**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Si1	32.2(3)	38.9(3)	38.0(3)	-6.0(2)	8.4(2)	5.8(2)
C9	26.8(8)	24.5(9)	43.3(10)	1.7(8)	5.8(7)	2.3(7)
C7	27.6(9)	24.5(9)	40.2(10)	3.0(7)	5.8(7)	1.7(7)
C10	29.7(9)	26.4(9)	48.4(11)	-4.2(8)	14.9(8)	-1.3(7)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C8	28.7(9)	22.3(8)	45.4(11)	3.3(8)	5.3(8)	-3.3(7)
C6	35.4(9)	22.8(9)	43.6(11)	1.2(8)	12.1(8)	1.0(7)
C1	40.2(10)	26.4(9)	42.6(11)	-1.3(8)	11.3(8)	2.0(8)
C15	31.4(9)	34.9(10)	48.0(11)	-10.2(9)	11.3(8)	-4.1(8)
C5	38.3(10)	37.1(11)	47.8(12)	2.9(9)	10.5(9)	-6.5(9)
C11	41.3(11)	26.2(10)	65.9(14)	-1.2(9)	17.1(10)	1.4(8)
C2	55.1(13)	41.1(12)	38.9(11)	-0.1(9)	9.1(9)	0.3(10)
N2	84.1(17)	26.5(10)	138(3)	-21.5(13)	38.7(17)	0.2(11)
C20	38.5(11)	53.7(13)	39.4(11)	-5.4(10)	6.6(8)	3.4(10)
N1	54.5(13)	99(2)	77.9(16)	21.8(14)	13.6(12)	-36.7(13)
C14	46.9(12)	51.9(14)	56.5(14)	-20.7(11)	13.1(10)	-11.7(10)
C4	47.1(12)	45.3(13)	56.2(14)	1.8(10)	19.0(10)	-12.2(10)
C12	52.5(13)	29.6(11)	84.7(18)	-11.6(11)	28.5(13)	-4.0(10)
C3	64.8(15)	44.9(13)	45.9(13)	4.3(10)	20.3(11)	-10.9(11)
C25	44.0(12)	71.0(17)	46.3(13)	-15.1(12)	10.7(10)	-1.6(11)
C13	56.8(14)	42.1(13)	86.1(19)	-32.9(13)	29.0(13)	-16.3(11)
C21	51.3(14)	80.4(19)	48.6(14)	2.5(13)	7.1(11)	18.6(13)
C24	63.8(16)	97(2)	42.0(13)	-13.6(14)	13.9(12)	-15.2(16)
C17	42.0(14)	83(2)	110(3)	-3.2(19)	20.3(16)	-12.7(14)
C22	62.2(17)	123(3)	54.8(16)	13.1(17)	-3.5(13)	23.9(18)
C16	75(2)	84(2)	105(3)	12.8(19)	45.3(19)	-29.8(17)
C23	68.2(19)	120(3)	46.5(15)	8.8(17)	-2.8(13)	-6.7(19)
C19	243(6)	36.0(17)	139(4)	-22(2)	72(4)	10(3)
C18	169(5)	45(2)	240(7)	8(3)	-45(5)	43(3)
C28	76(6)	144(10)	60(5)	14(6)	32(4)	41(6)
C29	78(6)	165(13)	55(5)	-21(7)	12(4)	65(7)
C31	67(4)	52(5)	74(7)	-15(5)	2(4)	24(4)
C27	45(5)	79(6)	60(6)	11(4)	23(4)	15(4)
C26	46(4)	37(5)	31(4)	5(4)	0(3)	25(4)
C30	95(8)	124(11)	69(9)	-52(8)	-2(5)	51(7)
C36	69(5)	86(6)	63(5)	-29(4)	-8(3)	45(4)
C37	47(3)	51(5)	55(5)	-15(3)	1(3)	23(3)
C33	50(5)	76(6)	55(5)	10(4)	20(4)	24(4)
C35	105(9)	128(8)	37(4)	-3(5)	17(4)	79(7)

	Atom U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C34	105(9)	123(8)	64(6)	28(6)	48(6)	70(7)
C32	35(3)	49(6)	37(4)	2(5)	4(3)	27(4)

Table S10. Bond Lengths in Å for **5**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C1	1.866(2)	C20	C21	1.392(3)
Si1	C15	1.855(2)	N1	C4	1.384(3)
Si1	C20	1.866(2)	N1	C17	1.419(4)
Si1	C26	1.852(17)	N1	C16	1.426(4)
Si1	C32	1.901(16)	C14	C13	1.396(4)
C9	C7	1.406(3)	C4	C3	1.387(4)
C9	C10	1.486(3)	C12	C13	1.371(4)
C9	C8 ¹	1.389(3)	C25	C24	1.379(4)
C7	C8	1.385(3)	C21	C22	1.382(4)
C7	C6	1.492(3)	C24	C23	1.369(5)
C10	C15	1.395(3)	C22	C23	1.372(4)
C10	C11	1.398(3)	C28	C29	1.366(17)
C6	C1	1.404(3)	C28	C27	1.378(13)
C6	C5	1.392(3)	C29	C30	1.335(18)
C1	C2	1.392(3)	C31	C26	1.364(14)
C15	C14	1.400(3)	C31	C30	1.393(15)
C5	C4	1.401(3)	C27	C26	1.414(17)
C11	C12	1.382(3)	C36	C37	1.370(11)
C2	C3	1.379(3)	C36	C35	1.343(15)
N2	C12	1.412(3)	C37	C32	1.370(13)
N2	C19	1.431(5)	C33	C34	1.406(13)
N2	C18	1.435(6)	C33	C32	1.382(15)
C20	C25	1.396(3)	C35	C34	1.378(17)

Table S11. Bond Angles in ° for **5**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Si1	C20	109.41(10)	C21	C20	Si1	121.28(17)
C1	Si1	C32	108.2(6)	C21	C20	C25	116.9(2)

Atom Atom Atom Angle/°

C15	Si1	C1	103.04(9)
C15	Si1	C20	112.40(10)
C15	Si1	C32	115.7(5)
C20	Si1	C32	107.9(6)
C26	Si1	C1	113.7(6)
C26	Si1	C15	104.5(4)
C26	Si1	C20	113.3(6)
C7	C9	C10	126.00(17)
C8 ¹	C9	C7	117.63(17)
C8 ¹	C9	C10	116.36(16)
C9	C7	C6	125.45(17)
C8	C7	C9	117.62(17)
C8	C7	C6	116.94(16)
C15	C10	C9	121.71(17)
C15	C10	C11	121.14(19)
C11	C10	C9	116.94(19)
C7	C8	C9 ¹	124.75(17)
C1	C6	C7	121.47(17)
C5	C6	C7	117.40(18)
C5	C6	C1	120.84(18)
C6	C1	Si1	119.29(14)
C2	C1	Si1	123.71(17)
C2	C1	C6	116.89(19)
C10	C15	Si1	119.42(14)
C10	C15	C14	116.6(2)
C14	C15	Si1	123.85(19)
C6	C5	C4	121.4(2)
C12	C11	C10	121.6(2)
C3	C2	C1	122.3(2)
C12	N2	C19	116.1(3)
C12	N2	C18	118.8(3)
C19	N2	C18	115.4(4)
C25	C20	Si1	121.79(18)

Atom Atom Atom Angle/°

C4	N1	C17	120.3(2)
C4	N1	C16	119.9(3)
C17	N1	C16	118.5(2)
C13	C14	C15	121.3(3)
N1	C4	C5	120.4(2)
N1	C4	C3	122.2(2)
C3	C4	C5	117.4(2)
C11	C12	N2	119.8(3)
C13	C12	C11	117.7(2)
C13	C12	N2	122.5(2)
C2	C3	C4	121.2(2)
C24	C25	C20	121.4(2)
C12	C13	C14	121.6(2)
C22	C21	C20	121.5(2)
C23	C24	C25	120.4(2)
C23	C22	C21	120.1(3)
C24	C23	C22	119.7(3)
C29	C28	C27	119.4(11)
C30	C29	C28	122.0(10)
C26	C31	C30	123.1(12)
C28	C27	C26	120.7(11)
C31	C26	Si1	123.4(11)
C31	C26	C27	116.1(13)
C27	C26	Si1	120.0(10)
C29	C30	C31	118.3(12)
C35	C36	C37	121.0(9)
C36	C37	C32	120.6(10)
C32	C33	C34	119.4(10)
C36	C35	C34	120.2(8)
C35	C34	C33	119.4(10)
C37	C32	Si1	121.4(9)
C37	C32	C33	119.2(12)
C33	C32	Si1	118.3(8)

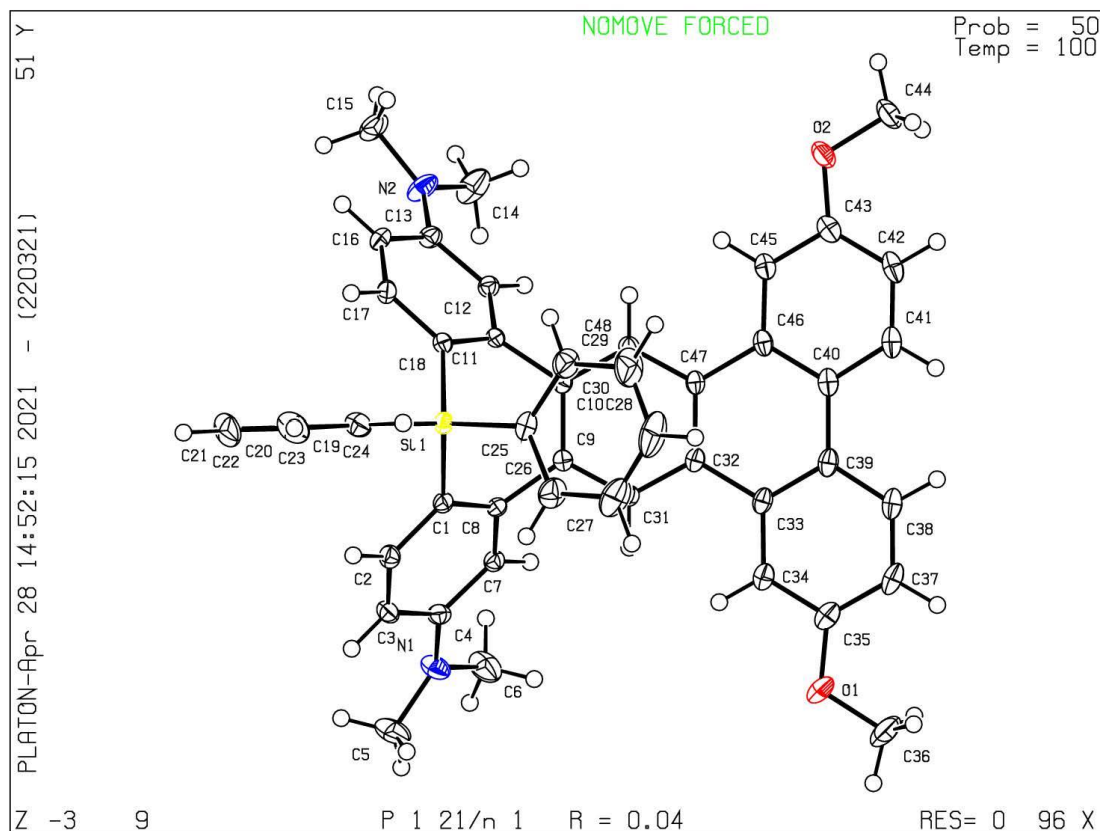
Table S12. Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H8	4313.06	3188.15	5150.62	38
H5	3129.74	3855.61	6062.21	49
H11	4704.64	8020.91	5704.36	53
H2	4817.11	3423.73	8550.89	54
H14	6256.38	7161.12	8215.65	62
H3	3412.28	2690.15	8485.66	62
H25	5550.85	5473.42	9142.14	64
H13	5834.22	9115.89	7901.6	73
H21	7509.86	3593.41	8130	72
H24	6150.46	5124.67	10489.86	81
H17A	1625.1	4056.1	6684.26	117
H17B	1086.17	2829.3	6707.43	117
H17C	1834.93	3001.27	6033.16	117
H22	8114.65	3281.31	9483.41	96
H16A	2417.79	1286.95	7953.9	131
H16B	1427.69	1566.16	7666.6	131
H16C	1910.51	2376.38	8377.04	131
H23	7422.47	4017.69	10666.2	94
H19A	4633.77	10486.99	7745.85	207
H19B	4730.7	11558.2	7079.57	207
H19C	5581.78	10899.36	7465.95	207
H18A	4402.09	9847.58	5419.23	228
H18B	4069.44	10968.56	5953.65	228
H18C	3717.44	9651.56	6152.45	228
H28	8289.26	5198.5	5393.46	111
H29	8192.23	3262.29	4888.66	119
H31	6263.82	2569.13	6448.24	77
H27	7397.86	5811.46	6480.74	73
H30	7199.21	1942.19	5396.39	116
H36	6990.92	1342.19	5796.84	88

Atom	x	y	z	U(eq)
H37	6231.92	2285.18	6849.09	61
H33	7156.14	5475.24	6100.61	72
H35	7810.23	2419.88	4881.45	107
H34	7903.79	4496.73	5008.72	116

6-3. X-ray structure of compound 9

A single crystal of 3,17-dimethoxy-*N*⁷,*N*⁷,*N*¹³,*N*¹³-tetramethyl-10,10-diphenyl-10*H*-dibenzo[*b,f*]triphenylene[2,3-*d*]silepin-7,13-diamine (C₄₈H₄₂N₂O₂Si) (**9**) was prepared by recrystallization from the dichloromethane/ethanol solution. A suitable crystal was selected, and the X-ray diffraction was collected on an Rigaku AFC HyPix-6000 diffractometer: fixed-chi single diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{\AA}$). The crystal was kept at 100 K during data collection. The data were collected using ω scan in the θ range of $4.038 \leq \theta \leq 54.968$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,¹³ and expanded using Fourier techniques.¹⁴ Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 44667 observed reflections. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ All calculations were performed using the Olex-2 crystallographic software package except for refinement,¹⁶ which was performed using version 2018/3 of ShelXL (Sheldrick, 2015) of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.



Crystal structure determination of **9**

$\text{C}_{48}\text{H}_{42}\text{N}_2\text{O}_2\text{Si}$ ($M = 706.92$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 9.1920(3)$ Å, $b = 20.3292(6)$ Å, $c = 20.1781(5)$ Å, $\beta = 90.337(2)$, $V = 3770.54(19)$ Å³, $Z = 4$, $T = 100$ K, $\mu(\text{Mo K}\alpha) = 0.105$ mm⁻¹, $D_{\text{calc}} = 1.245$ g/cm³, 44667 reflections measured ($4.038^\circ \leq 2\theta \leq 54.968^\circ$), 8637 unique ($R_{\text{int}} = 0.0329$, $R_{\text{sigma}} = 0.0259$) which were used in all calculations. The final R_1 was 0.0389 ($I > 2\sigma(I)$) and wR_2 was 0.1042 (all data).

Table S13. Crystal data and structure refinement for **9**

Empirical formula	$\text{C}_{48}\text{H}_{42}\text{N}_2\text{O}_2\text{Si}$
Formula weight	706.92
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{Å}$	9.1920(3)
$b/\text{Å}$	20.3292(6)
$c/\text{Å}$	20.1781(5)
$\alpha/^\circ$	90

$\beta/^\circ$	90.337(2)
$\gamma/^\circ$	90
Volume/ \AA^3	3770.54(19)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.245
μ/mm^{-1}	0.105
F(000)	1496.0
Crystal size/ mm^3	$0.305 \times 0.19 \times 0.109$
Radiation	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.038 to 54.968
Index ranges	$-11 \leq h \leq 11, -26 \leq k \leq 23, -26 \leq l \leq 25$
Reflections collected	44667
Independent reflections	8637 [$R_{\text{int}} = 0.0329, R_{\text{sigma}} = 0.0259$]
Data/restraints/parameters	8637/0/484
Goodness-of-fit on F^2	1.051
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0389, wR_2 = 0.0998$
Final R indexes [all data]	$R_1 = 0.0470, wR_2 = 0.1042$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.36/-0.35

Table S14. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **9**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Si1	3302.1(3)	6608.3(2)	4351.2(2)	13.65(8)
O1	6425.3(12)	9918.6(5)	2082.7(5)	32.3(2)
O2	7101.2(11)	9552.2(5)	6931.9(5)	25.3(2)
N1	-473.9(13)	7942.2(6)	2263.8(6)	25.2(3)
N2	-399.6(14)	7621.3(6)	6615.2(6)	27.4(3)
C1	2249.2(13)	7004.4(6)	3668.2(6)	14.8(2)
C2	1543.4(13)	6655.6(6)	3162.4(6)	17.5(2)
C3	683.3(14)	6959.4(6)	2689.5(6)	19.6(3)
C4	436.8(13)	7641.2(6)	2714.9(6)	17.5(2)
C5	-829.5(19)	7594.0(8)	1663.2(7)	35.5(4)
C6	-793.8(19)	8630.9(8)	2317.0(8)	35.9(4)
C7	1158.8(13)	8002.0(6)	3214.1(6)	15.8(2)

Atom	x	y	z	U(eq)
C8	2063.6(12)	7692.9(6)	3673.2(6)	14.0(2)
C9	2979.3(12)	8112.7(6)	4114.1(6)	13.8(2)
C10	3027.3(12)	8072.8(6)	4813.2(6)	13.5(2)
C11	2159.8(12)	7590.3(6)	5206.6(6)	14.0(2)
C12	1252.8(13)	7822.7(6)	5701.4(6)	15.8(2)
C13	539.3(13)	7390.2(6)	6137.8(6)	18.1(2)
C14	-675(2)	8307.8(8)	6677.6(9)	37.8(4)
C15	-823.8(17)	7190.6(7)	7148.5(7)	30.0(3)
C16	817.7(14)	6714.6(6)	6071.3(6)	18.8(3)
C17	1691.4(13)	6487.8(6)	5563.1(6)	17.2(2)
C18	2370.9(13)	6908.6(6)	5111.3(6)	14.7(2)
C19	3090.3(14)	5695.3(6)	4282.6(6)	17.6(2)
C20	1695.0(15)	5416.4(7)	4266.8(7)	24.4(3)
C21	1497.6(18)	4743.8(7)	4200.6(8)	32.3(3)
C22	2689.6(19)	4333.3(7)	4150.8(8)	34.8(4)
C23	4077.7(18)	4594.3(7)	4169.8(7)	31.2(3)
C24	4274.4(15)	5271.0(7)	4235.9(6)	21.8(3)
C25	5250.8(13)	6862.2(6)	4312.3(6)	18.4(2)
C26	5926.8(16)	6942.4(8)	3698.1(8)	29.0(3)
C27	7349.7(17)	7156.2(9)	3649.4(9)	39.6(4)
C28	8137.8(17)	7291.0(9)	4219.2(10)	43.6(4)
C29	7493.2(18)	7224.1(9)	4832.9(10)	42.8(4)
C30	6059.4(15)	7013.6(8)	4877.4(8)	29.0(3)
C31	3899.1(13)	8555.3(6)	3804.3(6)	15.1(2)
C32	4911.4(13)	8945.4(6)	4143.2(6)	15.2(2)
C33	5889.1(13)	9387.8(6)	3784.3(6)	17.1(2)
C34	5786.2(14)	9459.1(6)	3096.4(7)	20.8(3)
C35	6644.0(15)	9899.2(7)	2754.5(7)	24.0(3)
C36	7149(2)	10423.0(10)	1724.4(8)	43.1(4)
C37	7646.1(15)	10283.4(7)	3102.2(7)	27.6(3)
C38	7777.6(15)	10207.5(7)	3780.2(7)	24.8(3)
C39	6919.6(13)	9763.8(6)	4142.1(7)	19.0(3)
C40	7028.5(13)	9700.1(6)	4863.3(6)	18.2(2)
C41	8067.3(14)	10049.9(6)	5235.4(7)	22.2(3)

Atom	x	y	z	U(eq)
C42	8144.5(14)	10013.9(6)	5918.1(7)	23.1(3)
C43	7152.4(14)	9620.0(6)	6255.1(7)	20.8(3)
C44	8008.1(17)	9972.6(7)	7317.5(8)	30.7(3)
C45	6131.1(14)	9260.3(6)	5904.1(6)	19.3(3)
C46	6048.8(13)	9289.5(6)	5210.5(6)	16.7(2)
C47	4967.2(13)	8905.7(6)	4838.8(6)	15.0(2)
C48	3987.9(13)	8479.4(6)	5154.8(6)	15.0(2)

Table S15. Anisotropic Displacement Parameters ($\times 10^4$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Si1	12.79(16)	12.87(16)	15.30(16)	-0.46(12)	1.57(11)	-1.09(11)
O1	36.0(6)	35.9(6)	25.2(5)	10.4(4)	6.7(4)	-11.5(5)
O2	29.7(5)	21.9(5)	24.3(5)	-2.8(4)	-10.2(4)	-5.1(4)
N1	29.0(6)	25.9(6)	20.5(5)	-2.5(5)	-9.1(5)	3.9(5)
N2	34.9(7)	22.7(6)	24.9(6)	4.3(5)	16.8(5)	4.7(5)
C1	13.6(6)	16.2(6)	14.6(5)	-0.6(4)	3.0(4)	-1.4(4)
C2	18.1(6)	15.7(6)	18.8(6)	-2.8(5)	3.2(5)	-1.1(5)
C3	20.1(6)	22.2(6)	16.6(6)	-4.8(5)	-0.4(5)	-3.8(5)
C4	15.2(6)	23.4(6)	14.0(5)	0.5(5)	0.3(4)	-0.8(5)
C5	42.7(9)	39.9(9)	23.8(7)	-2.8(6)	-16.2(6)	5.9(7)
C6	45.1(9)	26.7(8)	35.6(8)	1.5(6)	-21.2(7)	5.1(7)
C7	16.2(6)	15.7(6)	15.4(5)	-0.3(4)	2.6(4)	-1.1(4)
C8	13.1(5)	16.8(6)	12.3(5)	-0.6(4)	3.2(4)	-2.1(4)
C9	12.7(5)	13.2(5)	15.5(5)	-1.0(4)	0.7(4)	0.4(4)
C10	13.2(5)	11.9(5)	15.4(5)	0.2(4)	1.7(4)	0.3(4)
C11	12.7(5)	16.6(6)	12.8(5)	0.6(4)	-1.7(4)	-2.9(4)
C12	17.0(6)	14.6(6)	15.8(6)	0.1(4)	0.7(4)	0.0(4)
C13	16.7(6)	21.5(6)	16.2(6)	-0.1(5)	3.1(4)	-0.7(5)
C14	47.8(10)	24.5(8)	41.5(9)	-0.1(7)	27.8(8)	5.3(7)
C15	37.0(8)	28.1(7)	25.2(7)	0.9(6)	16.9(6)	-3.3(6)
C16	20.1(6)	18.9(6)	17.4(6)	3.0(5)	3.9(5)	-4.4(5)
C17	17.3(6)	14.9(6)	19.6(6)	0.1(5)	0.8(5)	-3.0(4)
C18	13.3(5)	16.2(6)	14.5(5)	-0.3(4)	-1.0(4)	-1.7(4)

Atom	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C19	21.6(6)	15.7(6)	15.5(6)	-0.6(5)	0.8(5)	-0.9(5)
C20	24.7(7)	19.3(6)	29.2(7)	-1.4(5)	1.2(5)	-3.6(5)
C21	36.0(8)	21.8(7)	39.0(8)	0.5(6)	-5.9(6)	-10.4(6)
C22	51.2(10)	14.2(7)	38.8(8)	-1.5(6)	-13.0(7)	-2.9(6)
C23	40.5(9)	20.1(7)	33.0(8)	-4.7(6)	-10.0(6)	9.6(6)
C24	25.9(7)	20.0(6)	19.5(6)	-1.6(5)	-3.0(5)	2.3(5)
C25	14.2(6)	14.3(6)	26.8(7)	2.5(5)	3.0(5)	1.5(4)
C26	22.7(7)	32.4(8)	31.9(8)	-1.6(6)	8.9(6)	-0.9(6)
C27	24.8(8)	42.1(9)	52.1(10)	5.6(8)	17.9(7)	-1.5(7)
C28	15.2(7)	41.3(10)	74.4(13)	13.9(9)	6.2(7)	-5.0(6)
C29	23.5(8)	48.8(10)	56.0(11)	11.6(8)	-14.6(7)	-11.0(7)
C30	20.4(7)	34.4(8)	32.0(8)	8.2(6)	-4.3(5)	-4.5(6)
C31	15.6(6)	14.3(6)	15.3(5)	-0.2(4)	2.3(4)	0.2(4)
C32	13.4(6)	12.4(5)	19.8(6)	0.5(5)	2.4(4)	0.4(4)
C33	14.2(6)	13.4(6)	23.9(6)	1.0(5)	4.0(5)	0.3(4)
C34	18.7(6)	18.6(6)	25.1(6)	1.3(5)	3.3(5)	-3.3(5)
C35	23.0(7)	22.7(7)	26.4(7)	4.9(5)	6.5(5)	-0.5(5)
C36	43.2(10)	51.3(11)	34.8(9)	20.1(8)	5.9(7)	-17.1(8)
C37	23.0(7)	24.5(7)	35.3(8)	6.4(6)	8.3(6)	-7.6(5)
C38	18.5(6)	21.3(7)	34.7(7)	1.5(6)	2.2(5)	-6.4(5)
C39	14.0(6)	15.1(6)	28.0(7)	0.2(5)	3.3(5)	-0.5(4)
C40	13.7(6)	13.8(6)	27.2(6)	-1.3(5)	-0.5(5)	0.5(4)
C41	15.4(6)	16.5(6)	34.6(7)	-1.2(5)	-0.6(5)	-2.5(5)
C42	17.7(6)	17.2(6)	34.3(7)	-4.2(5)	-8.1(5)	-0.8(5)
C43	20.5(6)	16.6(6)	25.3(6)	-2.6(5)	-6.3(5)	2.7(5)
C44	36.3(8)	25.1(7)	30.5(7)	-4.2(6)	-14.0(6)	-7.1(6)
C45	18.1(6)	15.7(6)	24.1(6)	-0.8(5)	-2.9(5)	-1.3(5)
C46	13.9(6)	12.2(6)	24.1(6)	-1.7(5)	-1.8(5)	0.8(4)
C47	13.5(5)	11.9(6)	19.5(6)	-0.7(4)	-0.4(4)	-0.2(4)
C48	16.2(6)	13.8(6)	15.0(5)	-0.7(4)	-0.3(4)	0

Table S16. Bond Lengths in Å for **9**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C1	1.8625(12)	C19	C20	1.4024(18)

Atom Atom Length/Å			Atom Atom Length/Å		
Si1	C18	1.8637(12)	C19	C24	1.3924(18)
Si1	C19	1.8711(13)	C20	C21	1.386(2)
Si1	C25	1.8662(13)	C21	C22	1.381(2)
O1	C35	1.3698(17)	C22	C23	1.382(2)
O1	C36	1.4222(17)	C23	C24	1.394(2)
O2	C43	1.3736(16)	C25	C26	1.3992(19)
O2	C44	1.4224(16)	C25	C30	1.3918(19)
N1	C4	1.3764(16)	C26	C27	1.382(2)
N1	C5	1.4394(18)	C27	C28	1.383(3)
N1	C6	1.4349(19)	C28	C29	1.383(3)
N2	C13	1.3797(16)	C29	C30	1.389(2)
N2	C14	1.4241(19)	C31	C32	1.3983(17)
N2	C15	1.4428(17)	C32	C33	1.4659(16)
C1	C2	1.3990(17)	C32	C47	1.4064(17)
C1	C8	1.4100(17)	C33	C34	1.3982(18)
C2	C3	1.3813(18)	C33	C39	1.4124(18)
C3	C4	1.4056(18)	C34	C35	1.3801(18)
C4	C7	1.4090(17)	C35	C37	1.394(2)
C7	C8	1.3913(17)	C37	C38	1.381(2)
C8	C9	1.4900(16)	C38	C39	1.4054(18)
C9	C10	1.4133(16)	C39	C40	1.4639(18)
C9	C31	1.3861(16)	C40	C41	1.4045(18)
C10	C11	1.4952(16)	C40	C46	1.4164(17)
C10	C48	1.3895(16)	C41	C42	1.381(2)
C11	C12	1.3874(17)	C42	C43	1.394(2)
C11	C18	1.4126(17)	C43	C45	1.3821(17)
C12	C13	1.4092(17)	C45	C46	1.4023(18)
C13	C16	1.4036(18)	C46	C47	1.4667(16)
C16	C17	1.3852(17)	C47	C48	1.4053(16)
C17	C18	1.3999(17)			

Table S17. Bond Angles in ° for **9**.

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C1	Si1	C18	103.19(5)	C24	C19	C20	117.59(12)

Atom Atom Atom Angle/°

C1	Si1	C19	108.71(6)
C1	Si1	C25	110.12(6)
C18	Si1	C19	109.74(5)
C18	Si1	C25	112.93(6)
C25	Si1	C19	111.76(6)
C35	O1	C36	117.22(12)
C43	O2	C44	117.39(11)
C4	N1	C5	118.20(12)
C4	N1	C6	120.56(11)
C6	N1	C5	119.81(12)
C13	N2	C14	120.53(11)
C13	N2	C15	119.14(12)
C14	N2	C15	118.67(12)
C2	C1	Si1	123.87(9)
C2	C1	C8	116.91(11)
C8	C1	Si1	119.10(9)
C3	C2	C1	122.58(12)
C2	C3	C4	120.49(11)
N1	C4	C3	120.78(11)
N1	C4	C7	121.56(12)
C3	C4	C7	117.65(11)
C8	C7	C4	121.20(11)
C1	C8	C9	120.32(10)
C7	C8	C1	121.04(11)
C7	C8	C9	118.18(11)
C10	C9	C8	125.27(10)
C31	C9	C8	116.51(10)
C31	C9	C10	118.15(11)
C9	C10	C11	123.63(10)
C48	C10	C9	118.49(11)
C48	C10	C11	117.79(10)
C12	C11	C10	118.90(11)
C12	C11	C18	121.04(11)
C18	C11	C10	119.81(10)

Atom Atom Atom Angle/°

C21	C20	C19	121.35(13)
C22	C21	C20	119.98(14)
C21	C22	C23	119.91(14)
C22	C23	C24	120.04(14)
C19	C24	C23	121.13(13)
C26	C25	Si1	120.06(11)
C30	C25	Si1	122.33(10)
C30	C25	C26	117.52(13)
C27	C26	C25	121.67(15)
C26	C27	C28	119.64(15)
C29	C28	C27	120.00(14)
C28	C29	C30	119.99(16)
C29	C30	C25	121.17(15)
C9	C31	C32	123.61(11)
C31	C32	C33	120.97(11)
C31	C32	C47	118.41(11)
C47	C32	C33	120.63(11)
C34	C33	C32	121.06(11)
C34	C33	C39	119.51(11)
C39	C33	C32	119.39(11)
C35	C34	C33	121.86(12)
O1	C35	C34	115.62(12)
O1	C35	C37	125.08(12)
C34	C35	C37	119.31(13)
C38	C37	C35	119.31(12)
C37	C38	C39	122.69(13)
C33	C39	C40	120.13(11)
C38	C39	C33	117.29(12)
C38	C39	C40	122.55(12)
C41	C40	C39	121.93(12)
C41	C40	C46	117.79(12)
C46	C40	C39	120.26(11)
C42	C41	C40	122.50(12)
C41	C42	C43	119.16(12)

Atom Atom Atom Angle/°				Atom Atom Atom Angle/°			
C11	C12	C13	121.40(11)	O2	C43	C42	124.69(12)
N2	C13	C12	121.27(12)	O2	C43	C45	115.42(12)
N2	C13	C16	121.01(11)	C45	C43	C42	119.89(12)
C16	C13	C12	117.72(11)	C43	C45	C46	121.44(12)
C17	C16	C13	120.21(11)	C40	C46	C47	119.44(11)
C16	C17	C18	122.79(12)	C45	C46	C40	119.20(11)
C11	C18	Si1	119.84(9)	C45	C46	C47	121.35(11)
C17	C18	Si1	122.99(9)	C32	C47	C46	120.03(11)
C17	C18	C11	116.66(11)	C48	C47	C32	117.94(11)
C20	C19	Si1	119.83(10)	C48	C47	C46	122.01(11)
C24	C19	Si1	122.57(10)	C10	C48	C47	123.27(11)

Table S18. Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **9**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U(eq)
H2	1660.25	6191.7	3143.48	21
H3	255.24	6705.51	2344.53	24
H5A	66.87	7438.92	1454.12	53
H5B	-1346.62	7889.46	1358.8	53
H5C	-1450.88	7216.76	1767.7	53
H6A	-1096.61	8731.71	2770.65	54
H6B	-1580.09	8744.67	2007.56	54
H6C	76.79	8886.76	2209.09	54
H7	1025.36	8464.83	3237.67	19
H12	1109.78	8283.29	5746.92	19
H14A	201.37	8528.97	6843.32	57
H14B	-1475.15	8377.66	6988.87	57
H14C	-942.36	8489.11	6243.64	57
H15A	-1387.88	6821.66	6968.83	45
H15B	-1419.43	7435.16	7465.49	45
H15C	47.77	7022.25	7373.27	45
H16	405.64	6411.84	6375.83	23
H17	1835.47	6027.17	5519.21	21

Atom	x	y	z	U(eq)
H20	868.21	5694.37	4302.1	29
H21	542.84	4565.09	4189.55	39
H22	2555.35	3872.32	4103.53	42
H23	4898.33	4312.2	4137.69	37
H24	5232.62	5445.76	4249.42	26
H26	5394.5	6847.41	3304.64	35
H27	7783.75	7210.34	3226.77	48
H28	9122.26	7429.53	4188.99	52
H29	8030.73	7322.2	5224.15	51
H30	5622.98	6972.24	5300.94	35
H31	3838.31	8595.77	3335.93	18
H34	5106.68	9197.06	2857.58	25
H36A	6877.59	10395.76	1254.85	65
H36B	8203.89	10367.56	1771.42	65
H36C	6865.13	10853.41	1900.1	65
H37	8232.58	10594.21	2875.29	33
H38	8476.57	10465.72	4011.4	30
H41	8742.45	10321.51	5008.81	27
H42	8864.68	10254.63	6155.03	28
H44A	7795.25	10432.27	7207.35	46
H44B	9030.69	9877.71	7221.44	46
H44C	7823.29	9897.46	7789.26	46
H45	5470.38	8987.26	6137.72	23
H48	3982.3	8468.65	5625.51	18

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8. NMR Spectra

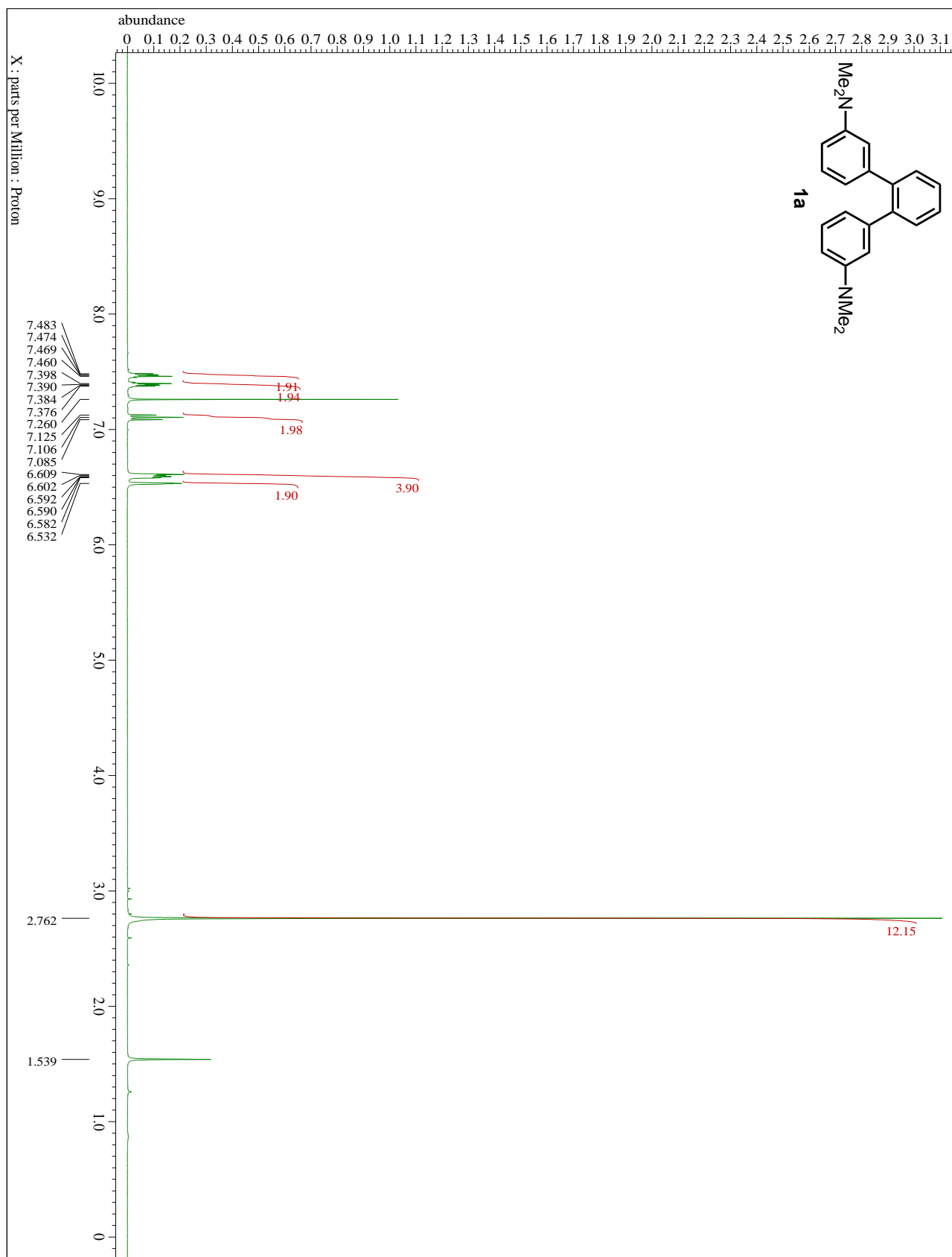


Figure S3. ^1H NMR of **1a** in CDCl_3 .

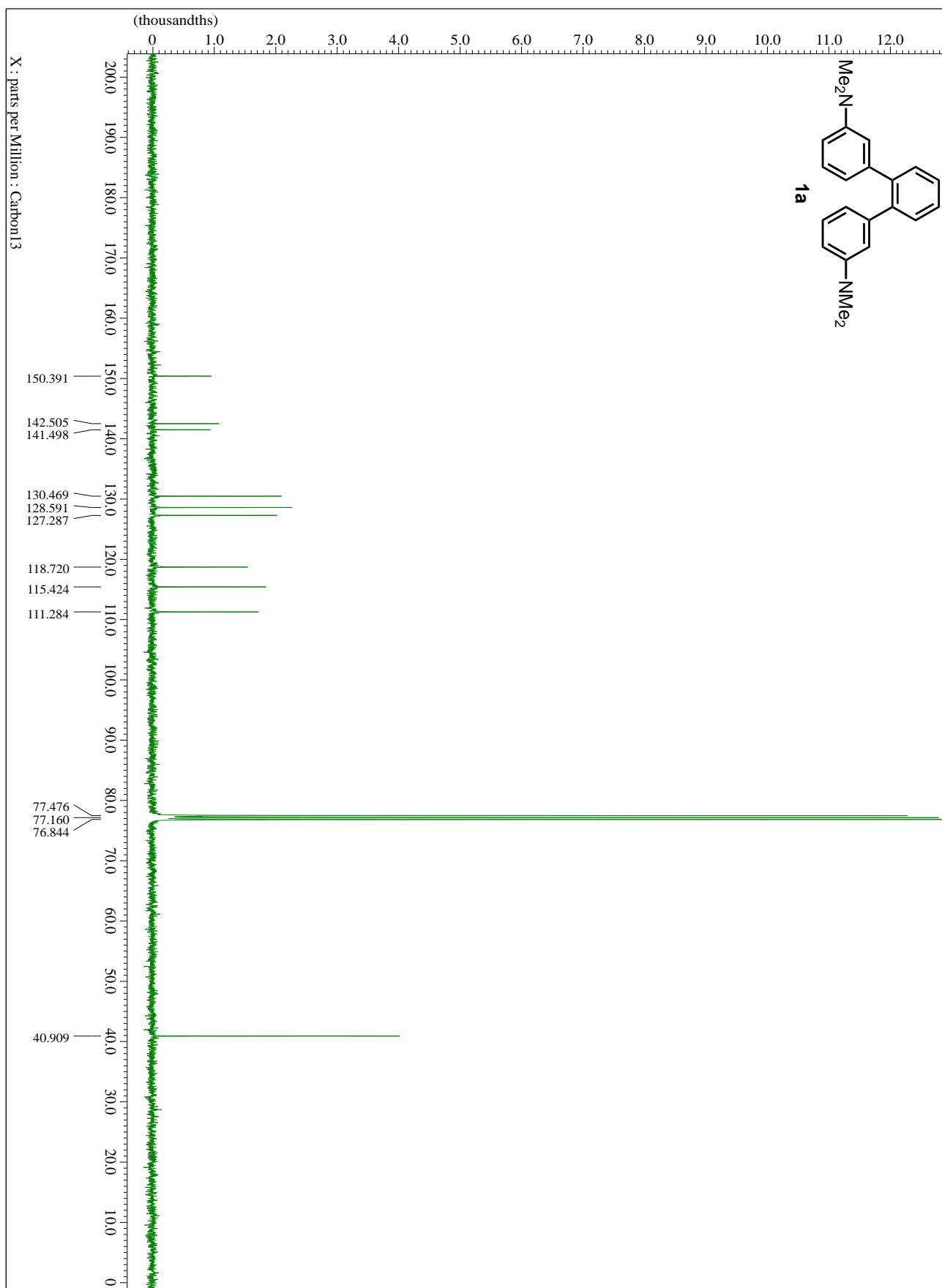


Figure S4. ^{13}C NMR of **1a** in CDCl_3 .

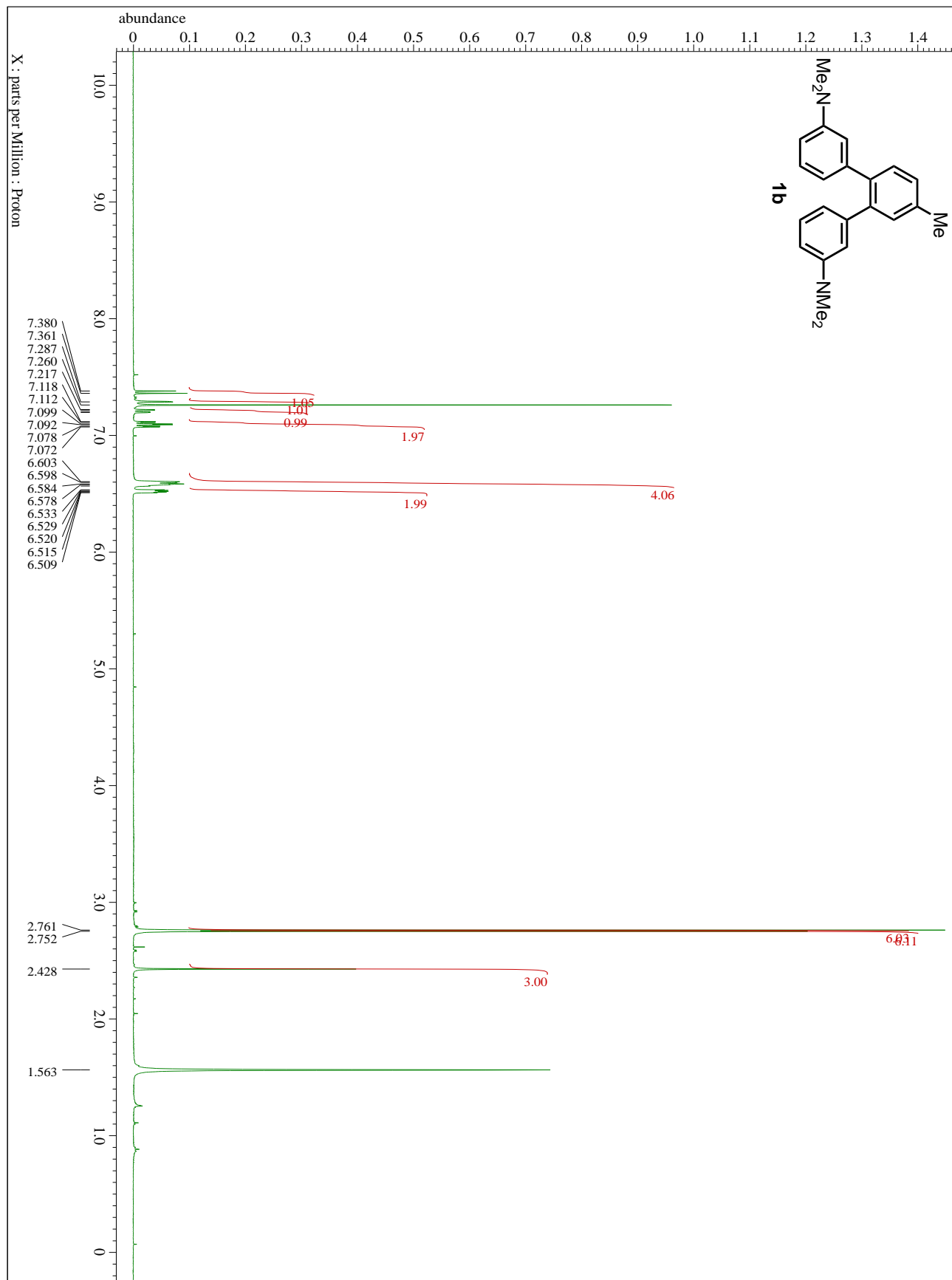


Figure S5. ¹H NMR of **1b** in CDCl₃.

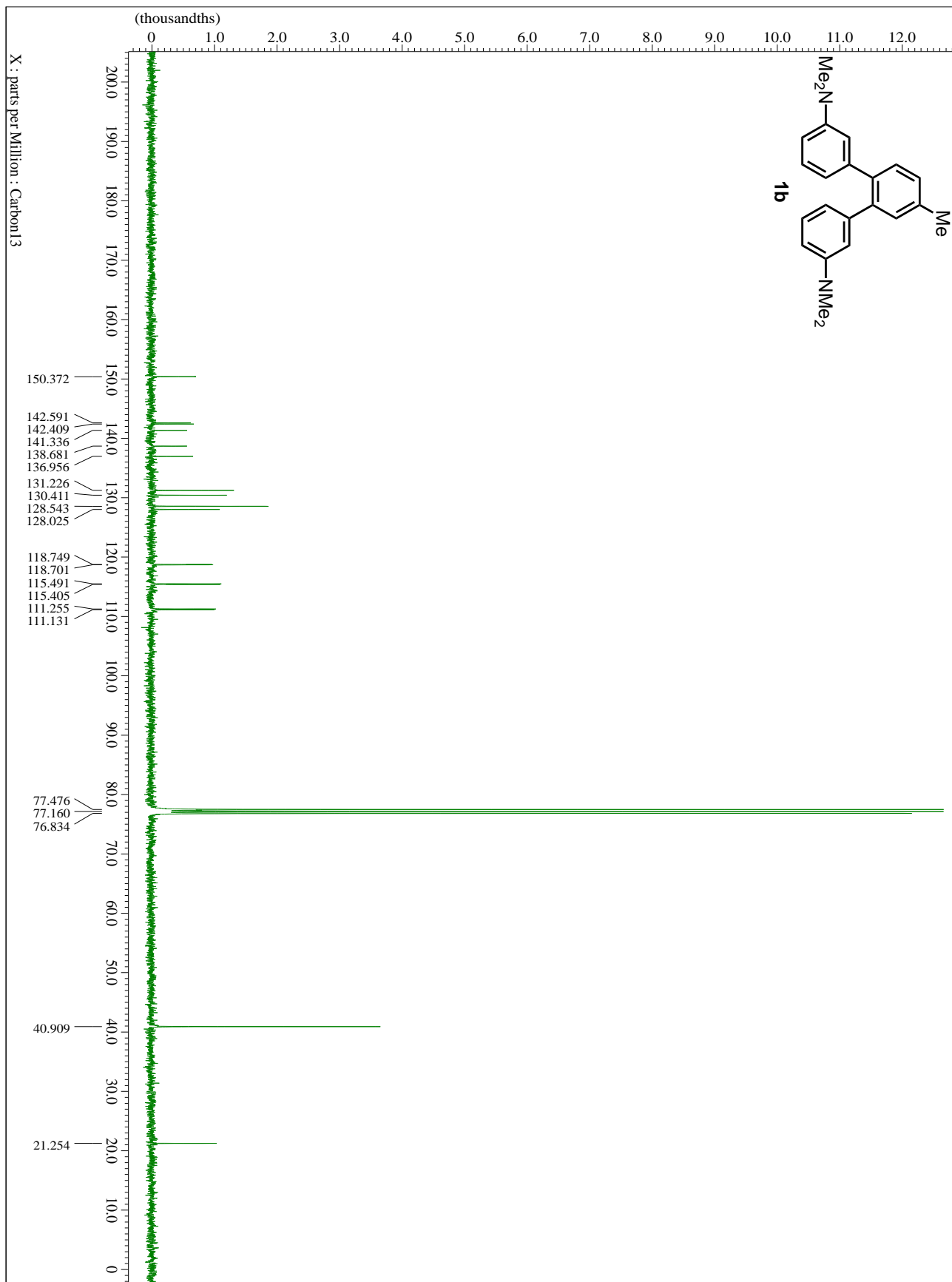


Figure S6. ^{13}C NMR of **1b** in CDCl_3 .

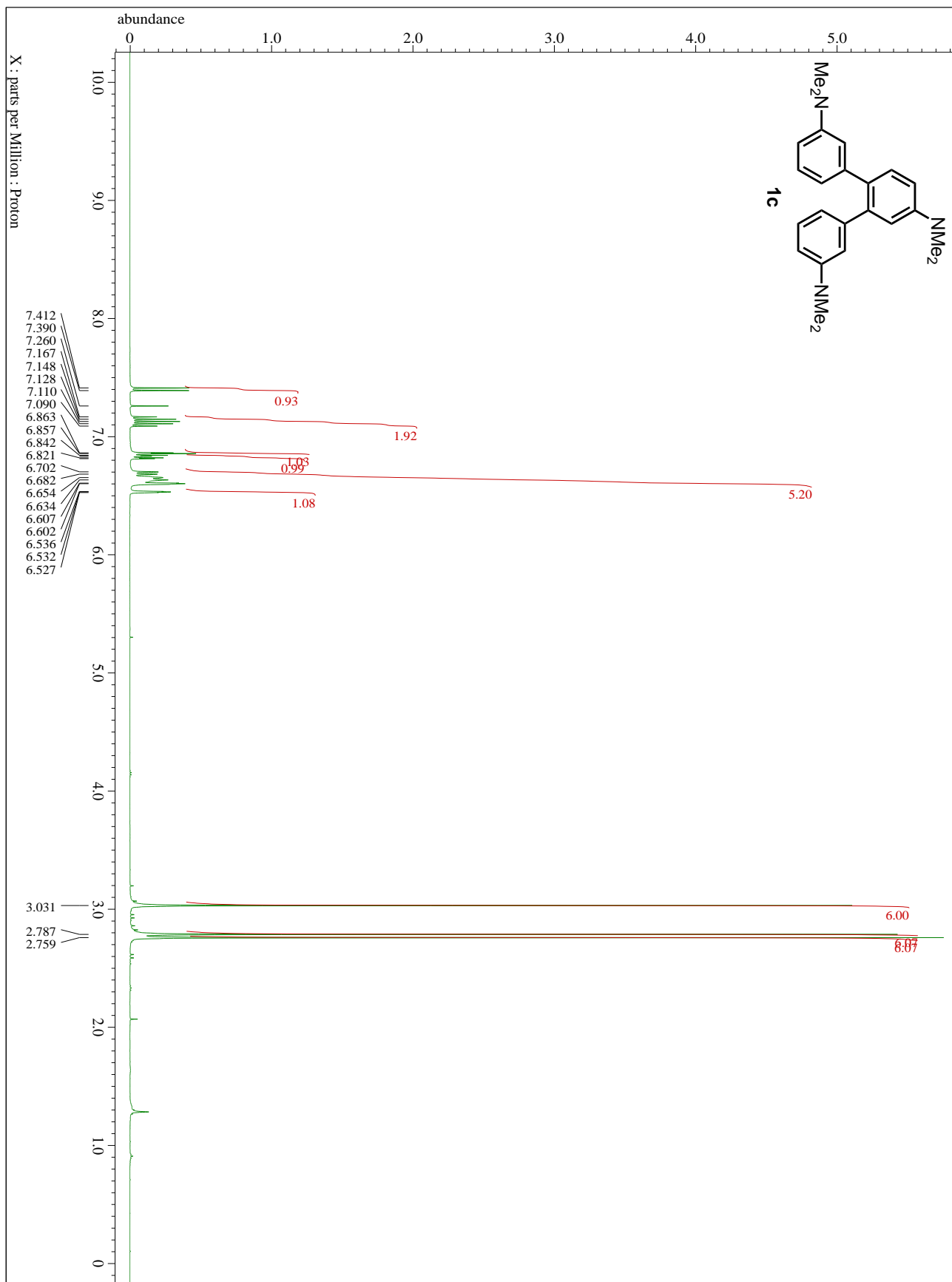


Figure S7. ^1H NMR of **1c** in CDCl_3 .

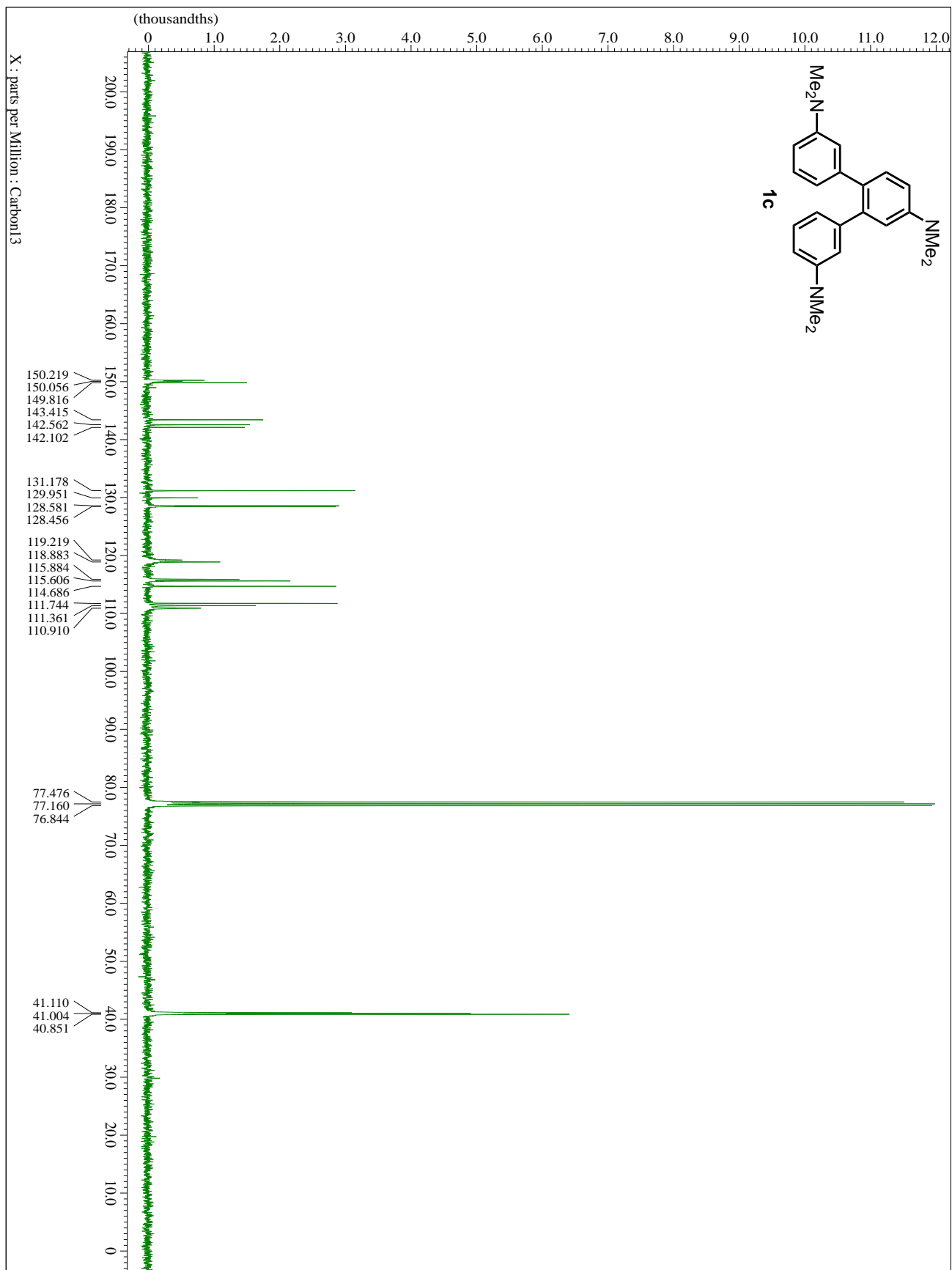


Figure S8. ¹³C NMR of 1c in CDCl₃.

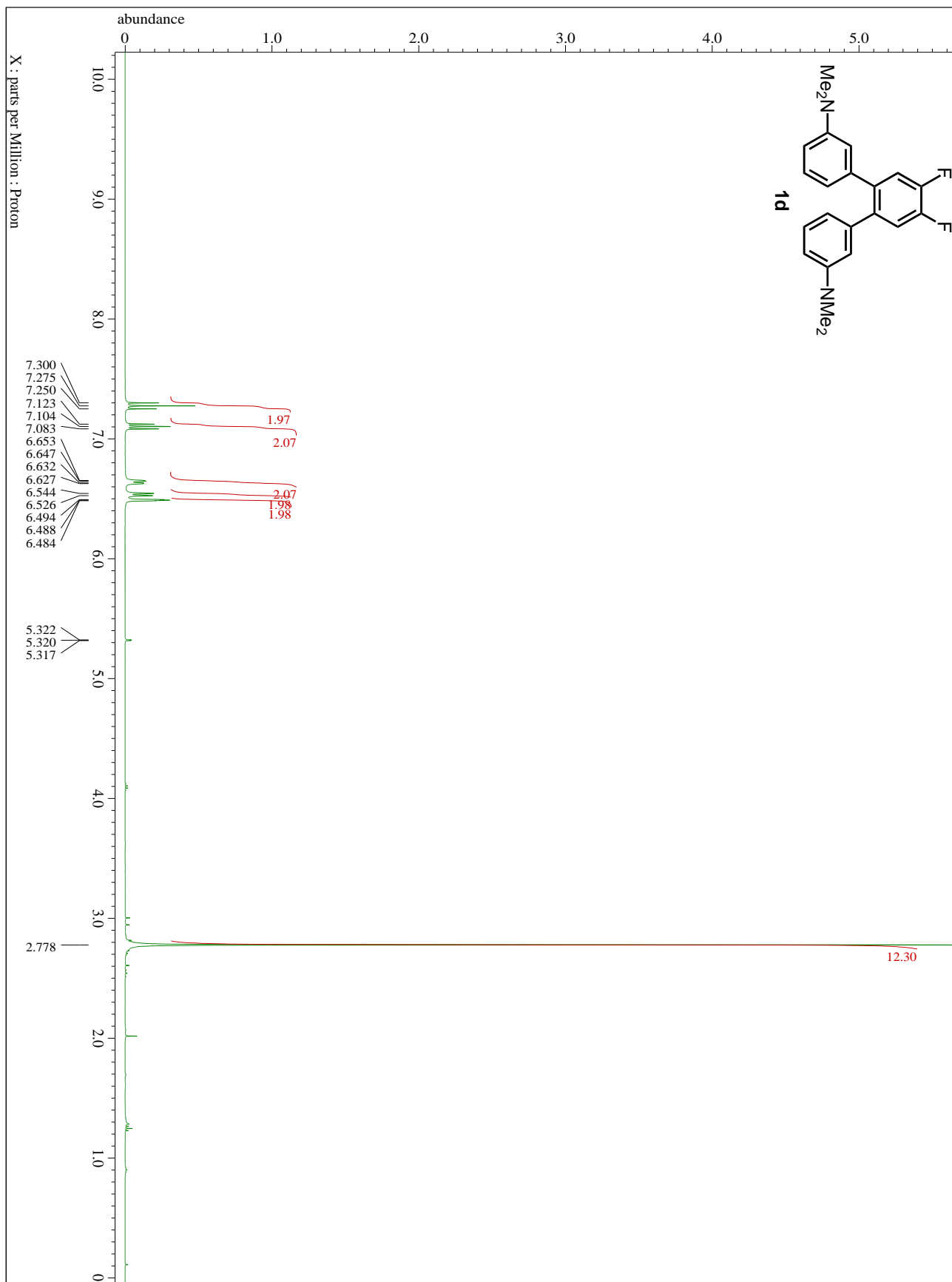


Figure S9. 1H NMR of **1d** in CD_2Cl_2 .

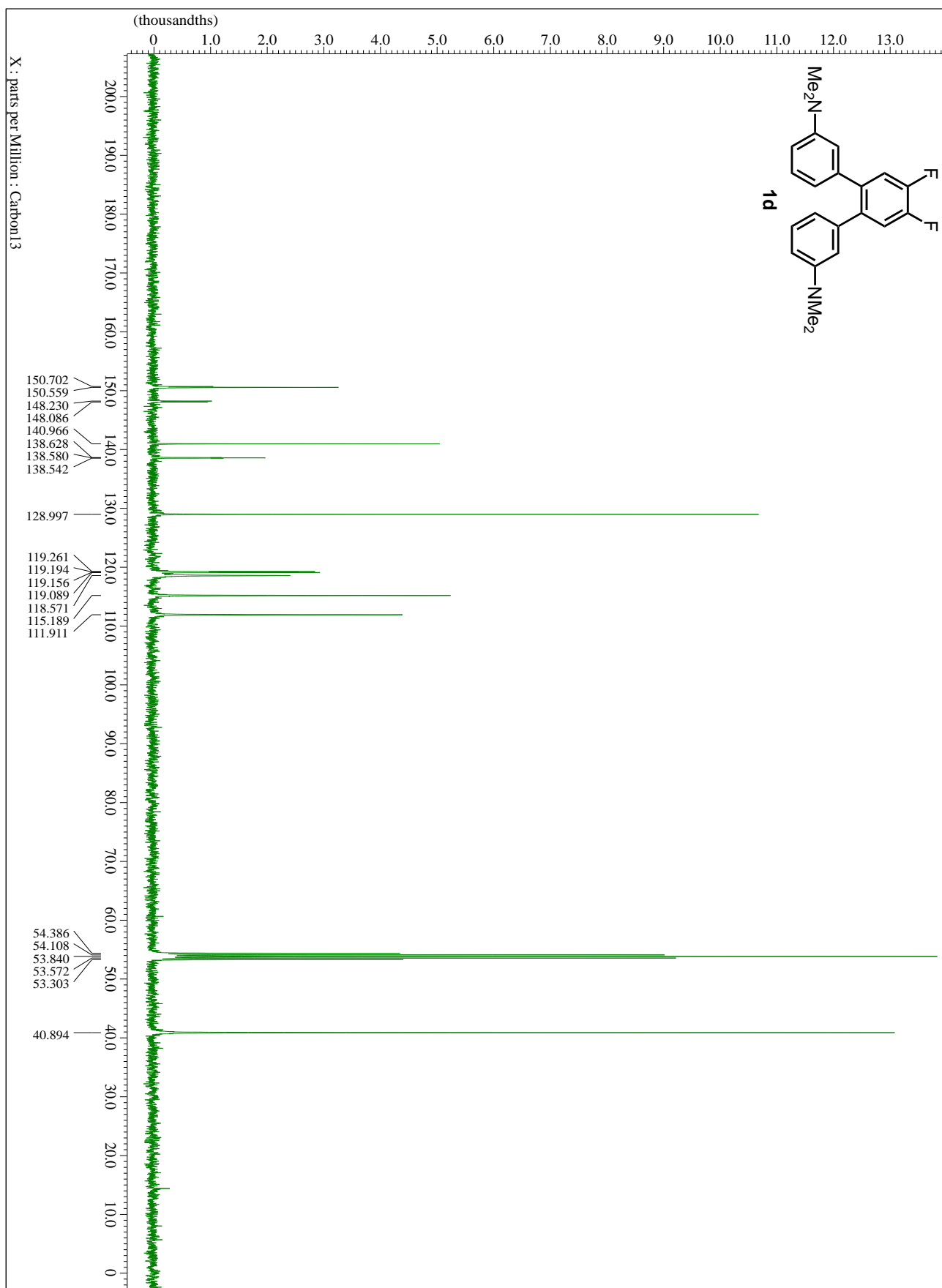


Figure S10. ¹³C NMR of **1d** in CD₂Cl₂.

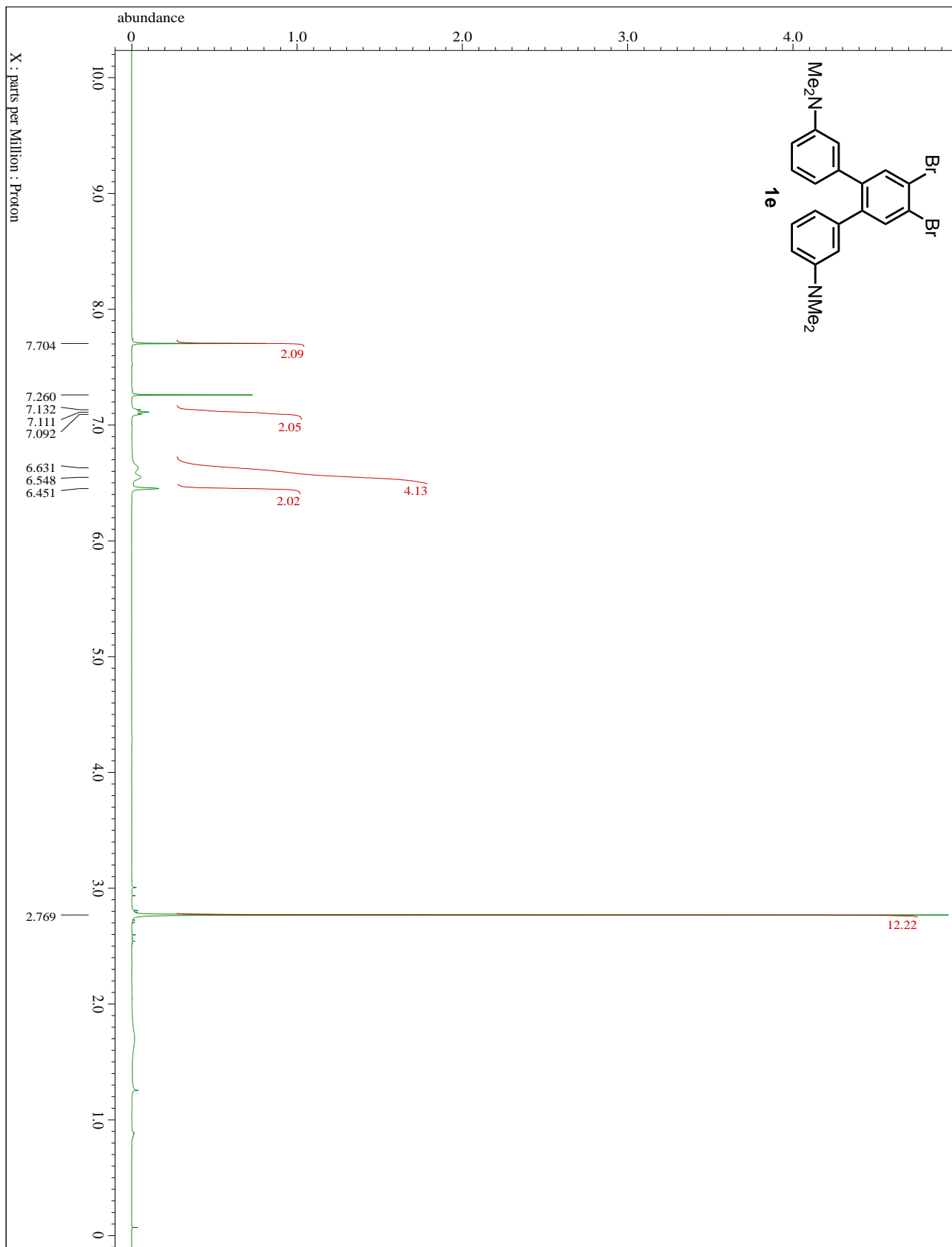


Figure S11. ^1H NMR of **1e** in CDCl_3 .

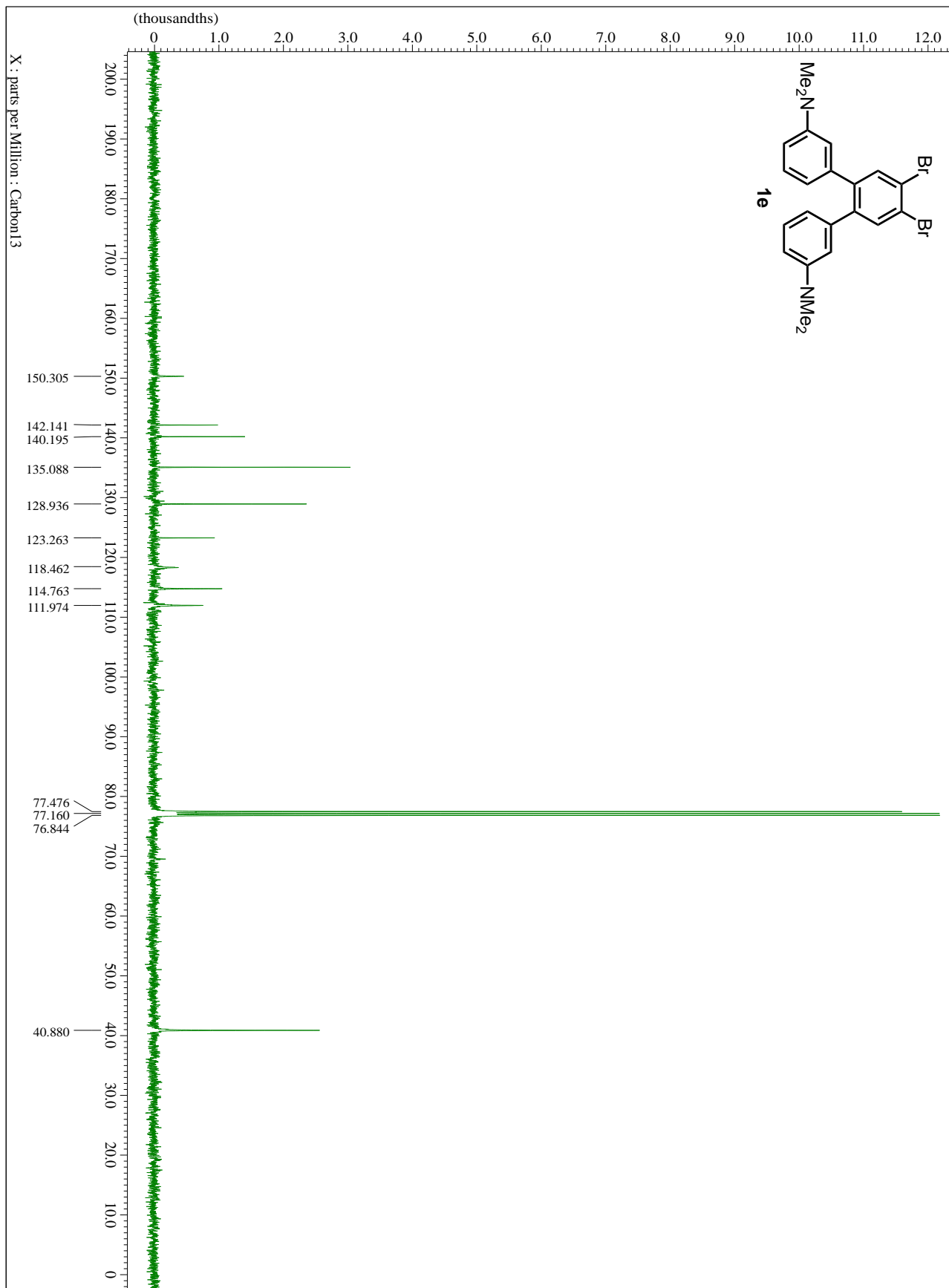


Figure S12. ¹³C NMR of **1e** in CDCl₃.

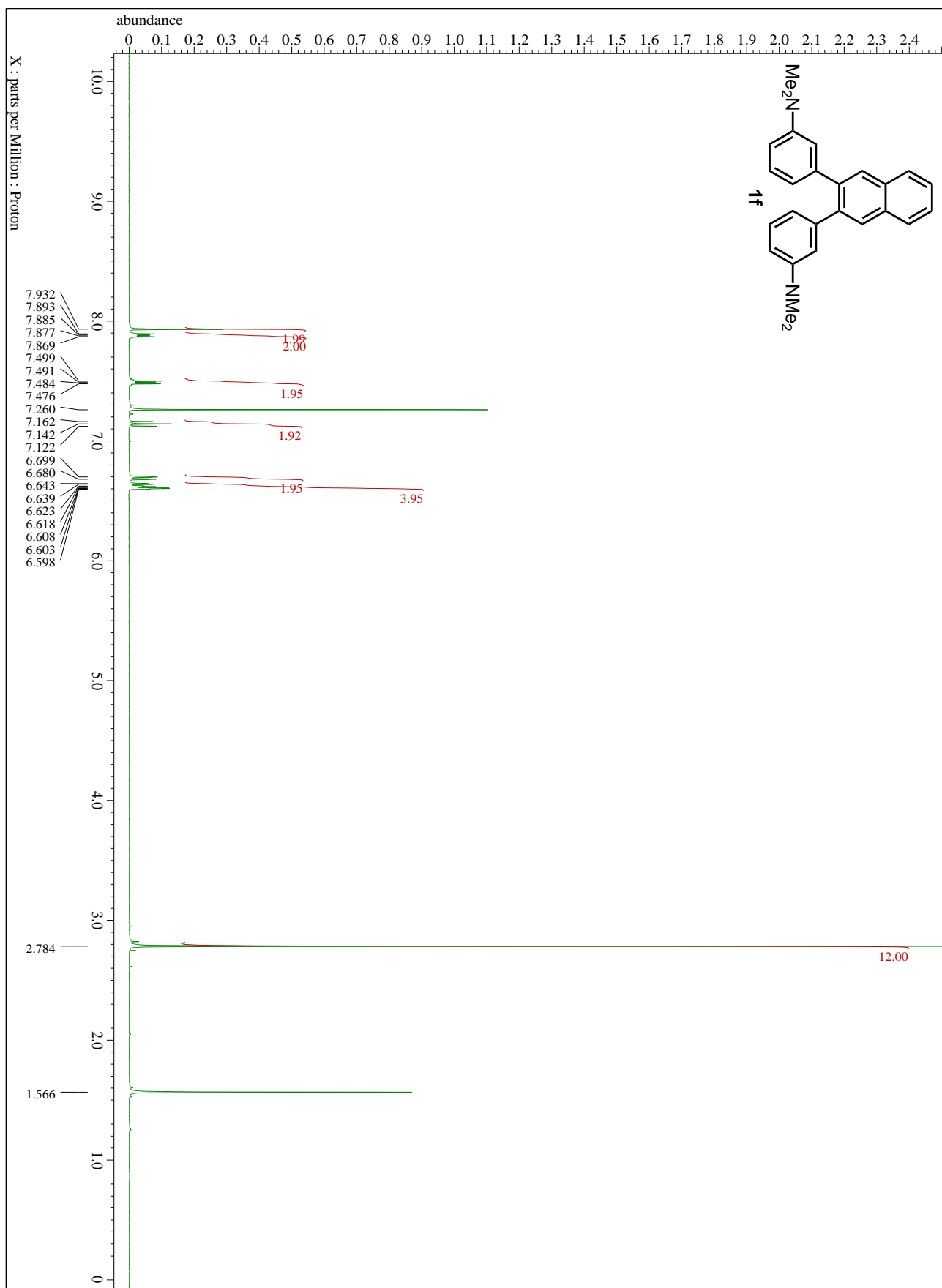


Figure S13. ^1H NMR of **1f** in CDCl_3 .

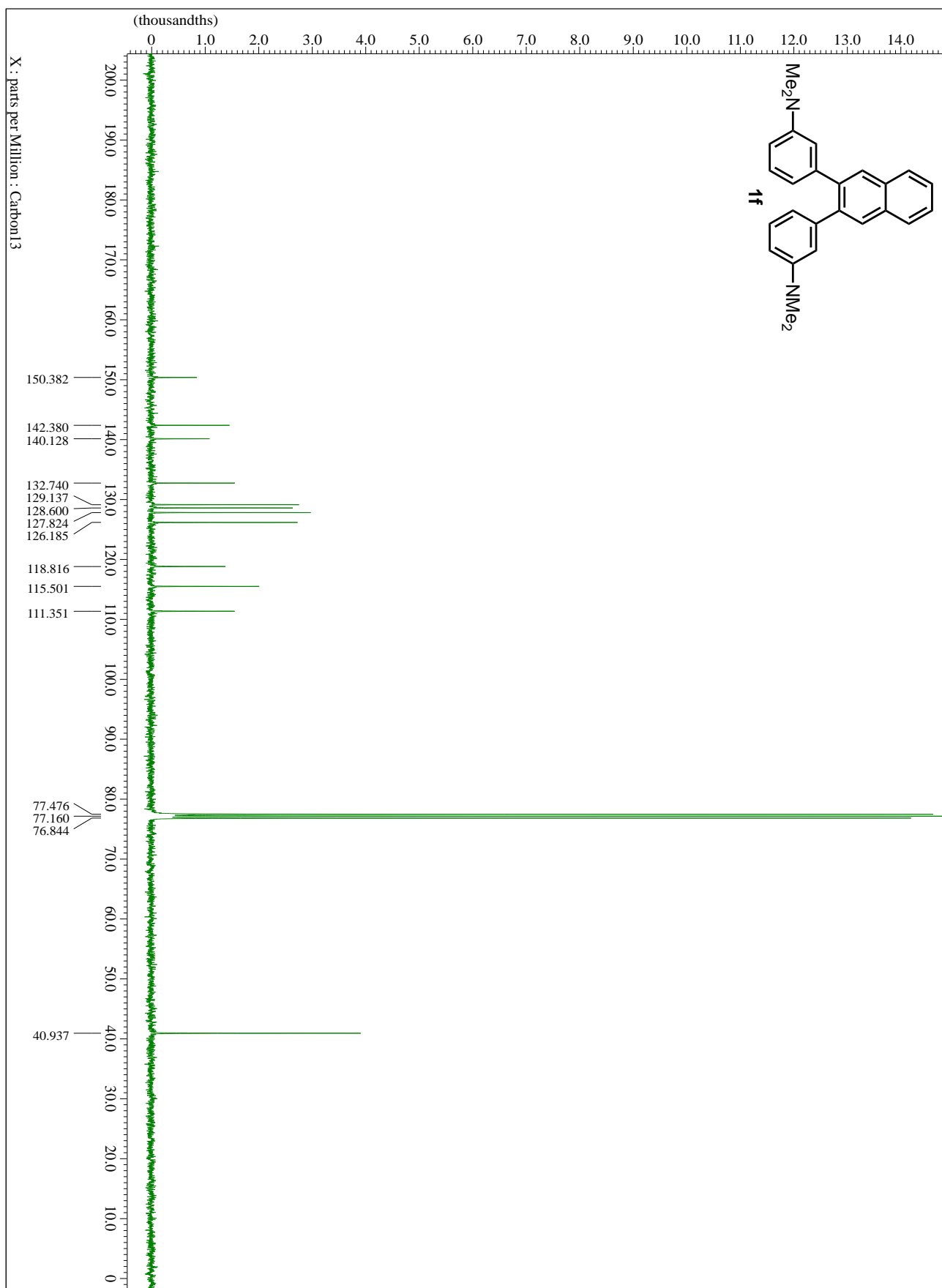


Figure S14. ¹³C NMR of **1f** in CDCl₃.

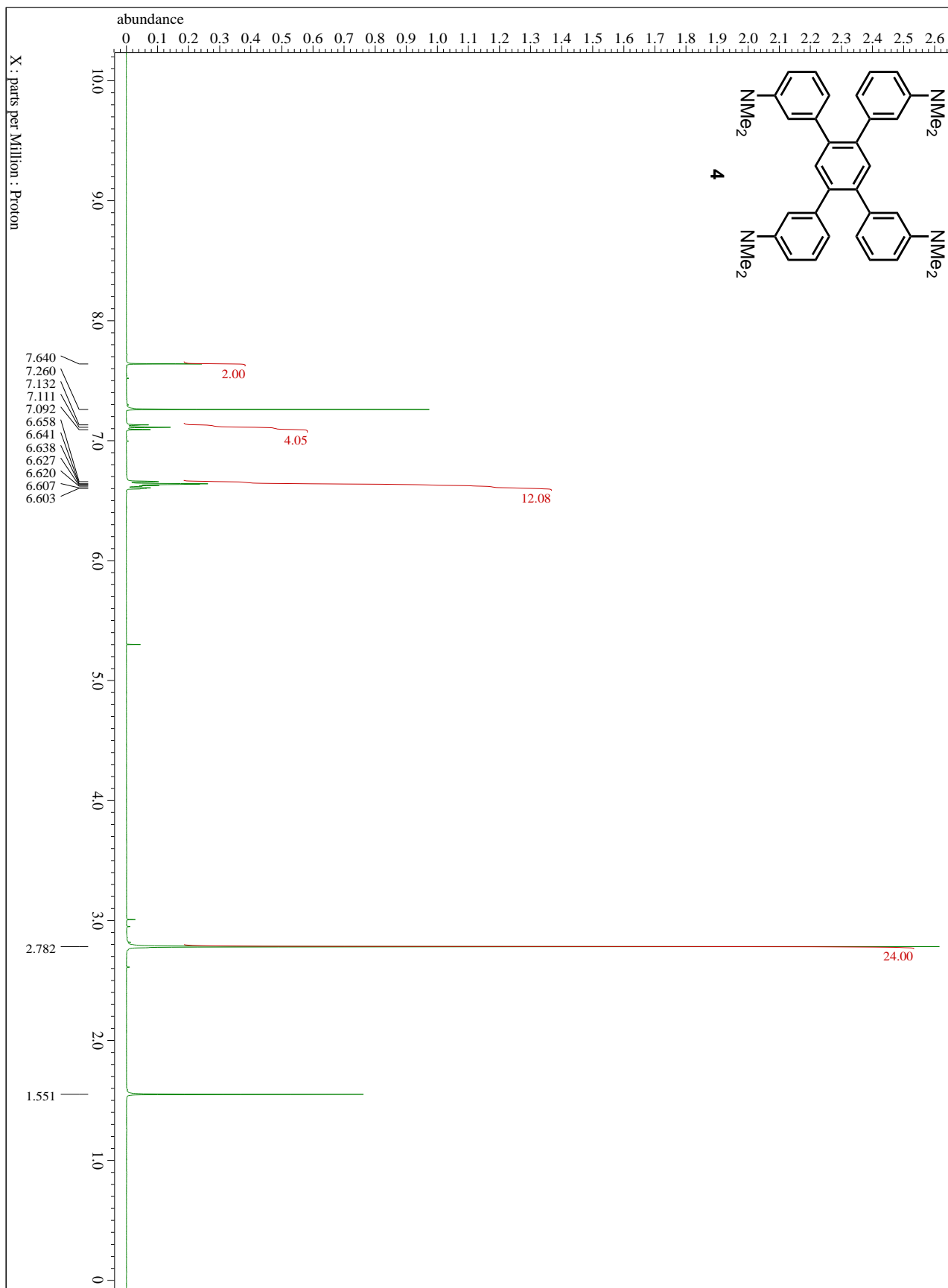


Figure S15. ¹H NMR of **4** in CDCl₃.

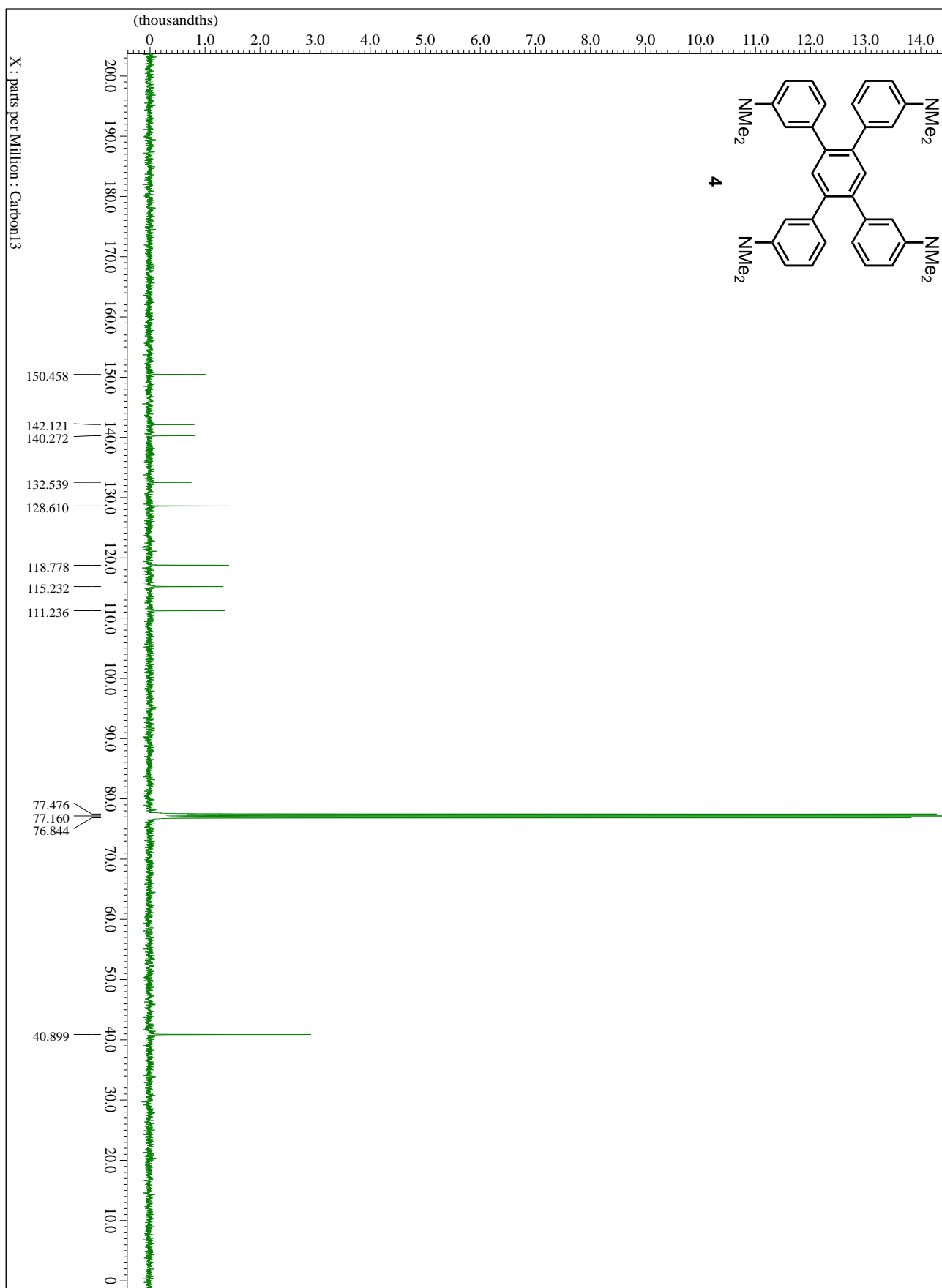


Figure S16. ^{13}C NMR of **4** in CDCl_3 .

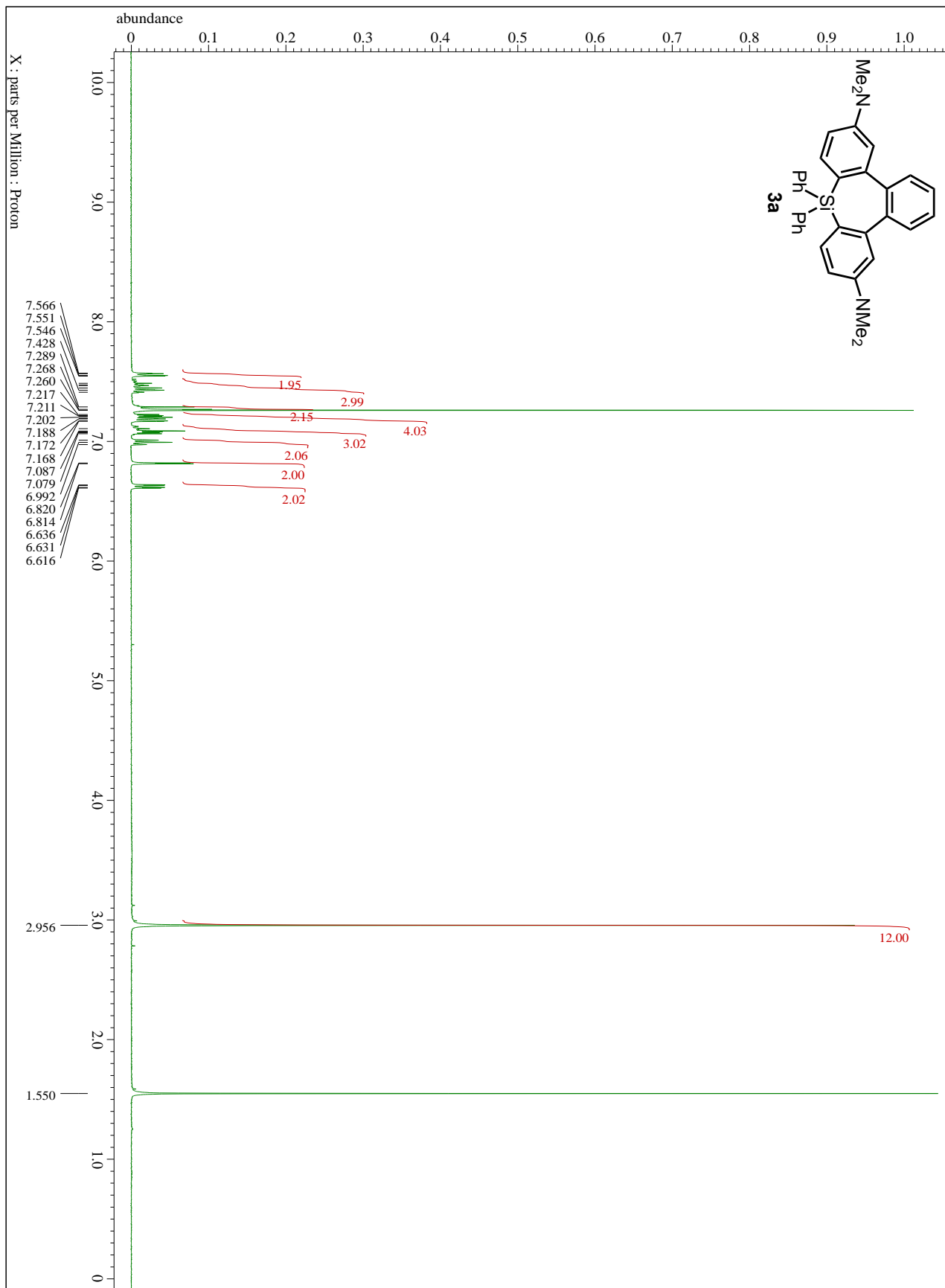


Figure S17. ¹H NMR of **3a** in CDCl₃.

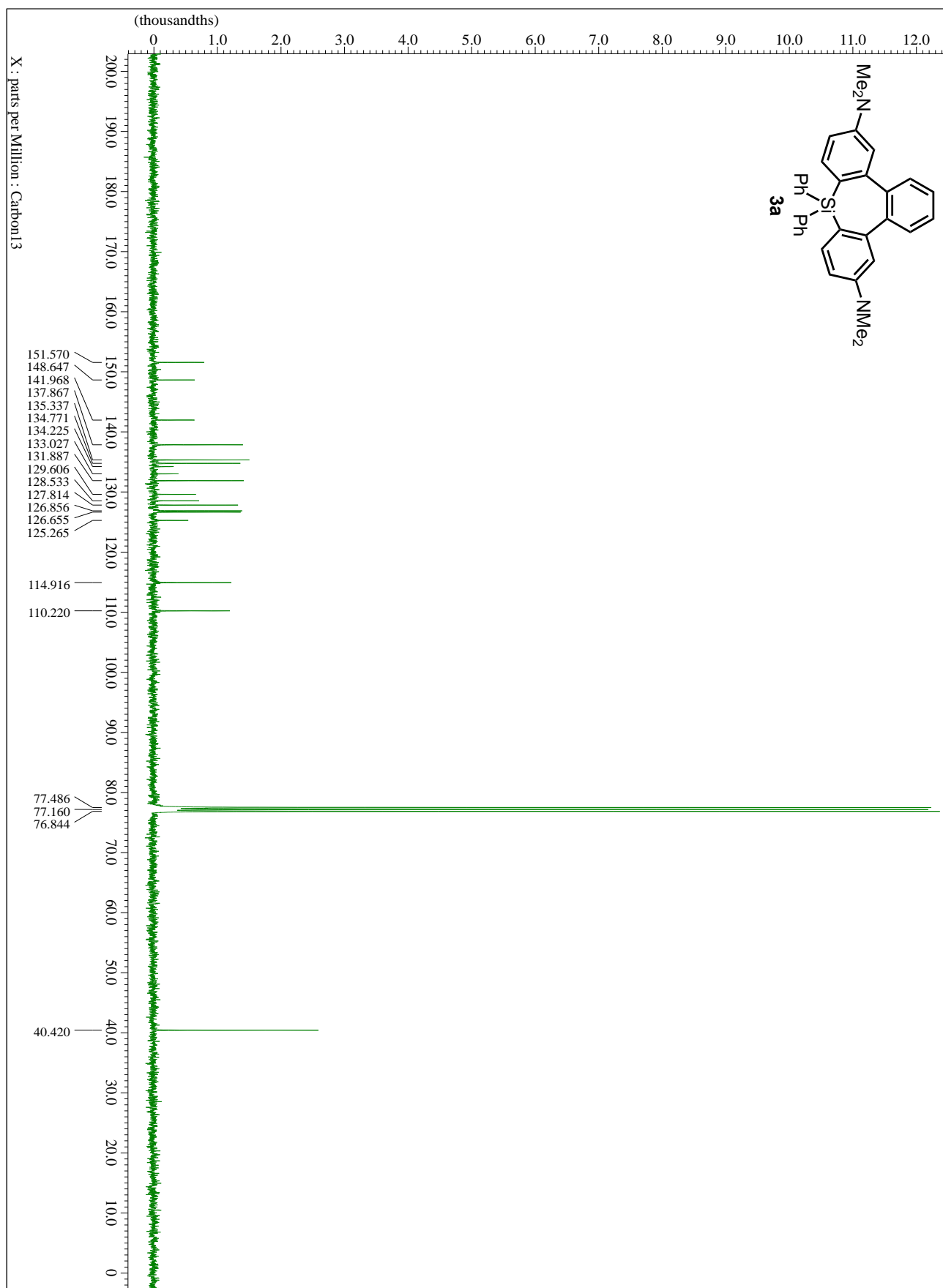


Figure S18. ¹³C NMR of **3a** in CDCl₃.

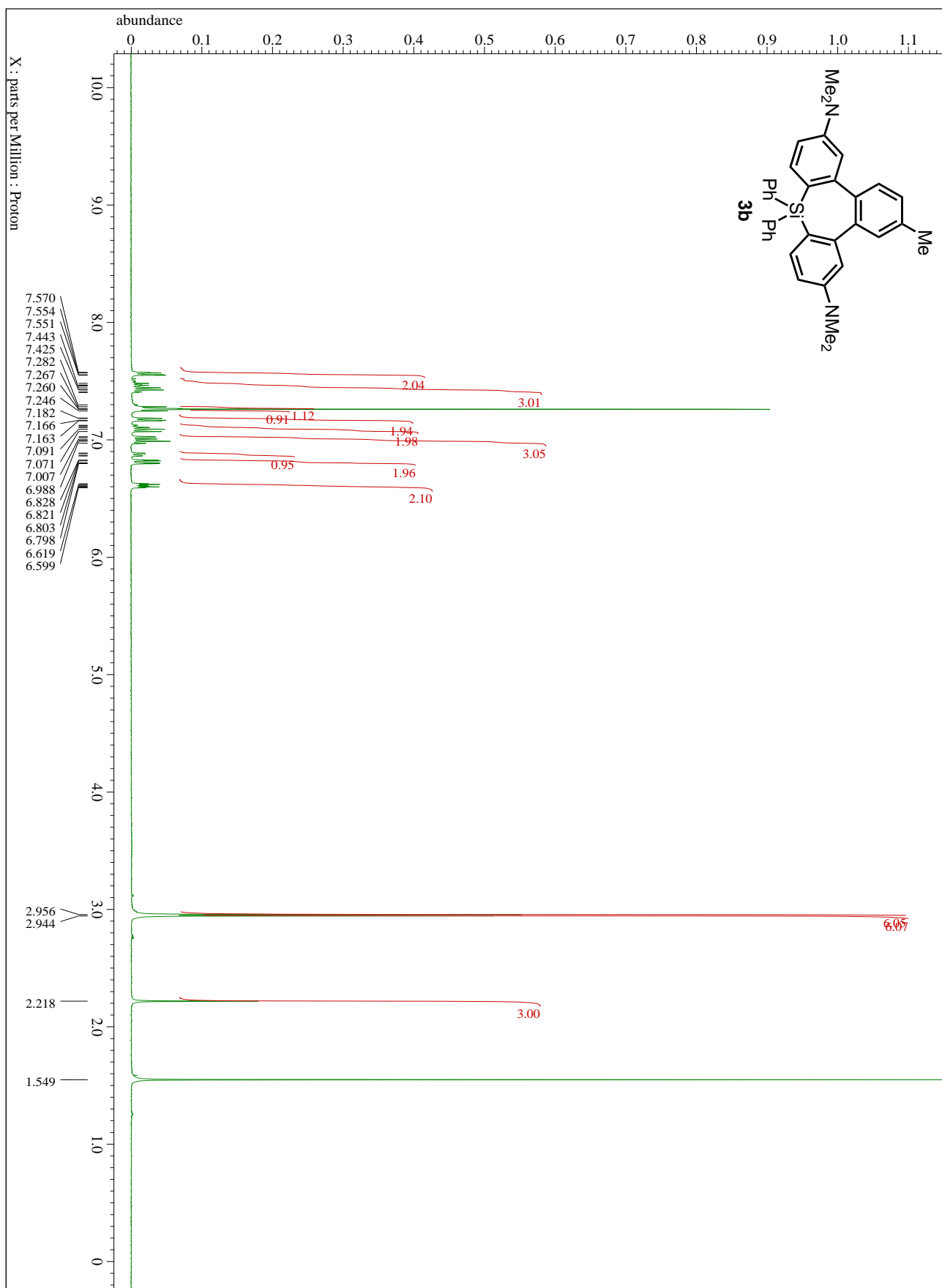


Figure S19. ¹H NMR of **3b** in CDCl₃.

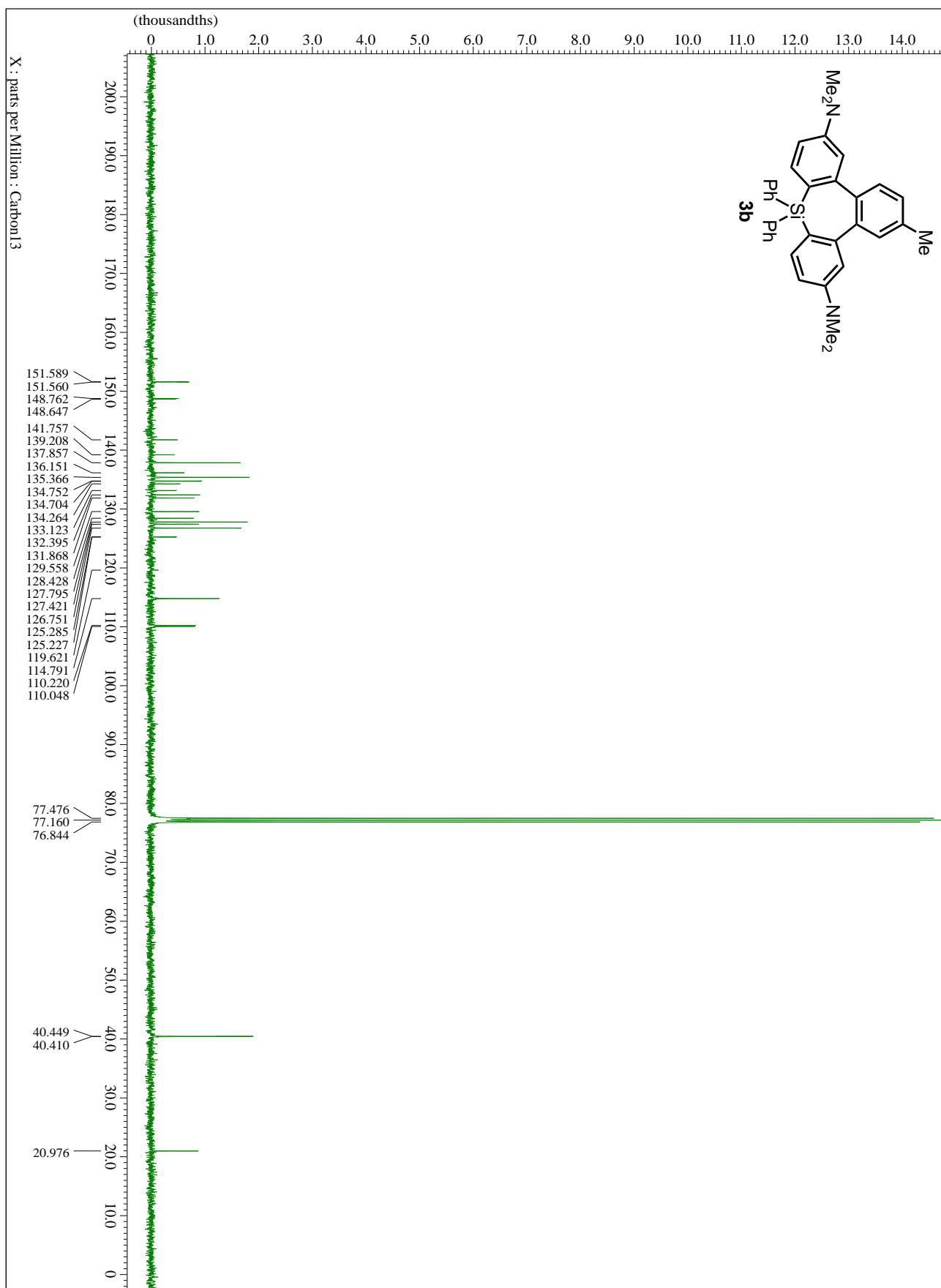


Figure S20. ¹³C NMR of **3b** in CDCl₃.

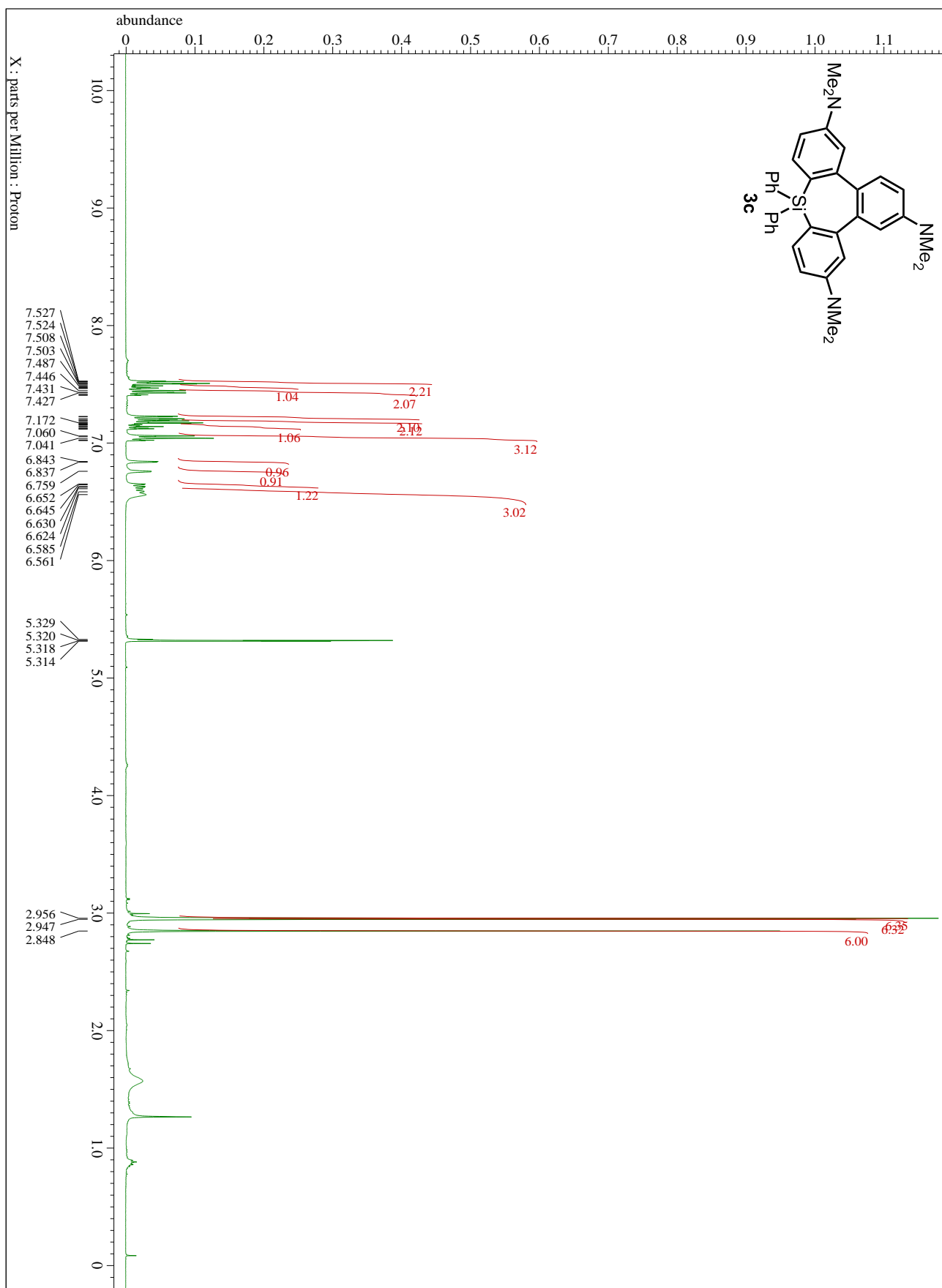


Figure S21. ¹H NMR of **3c** in CD₂Cl₂.

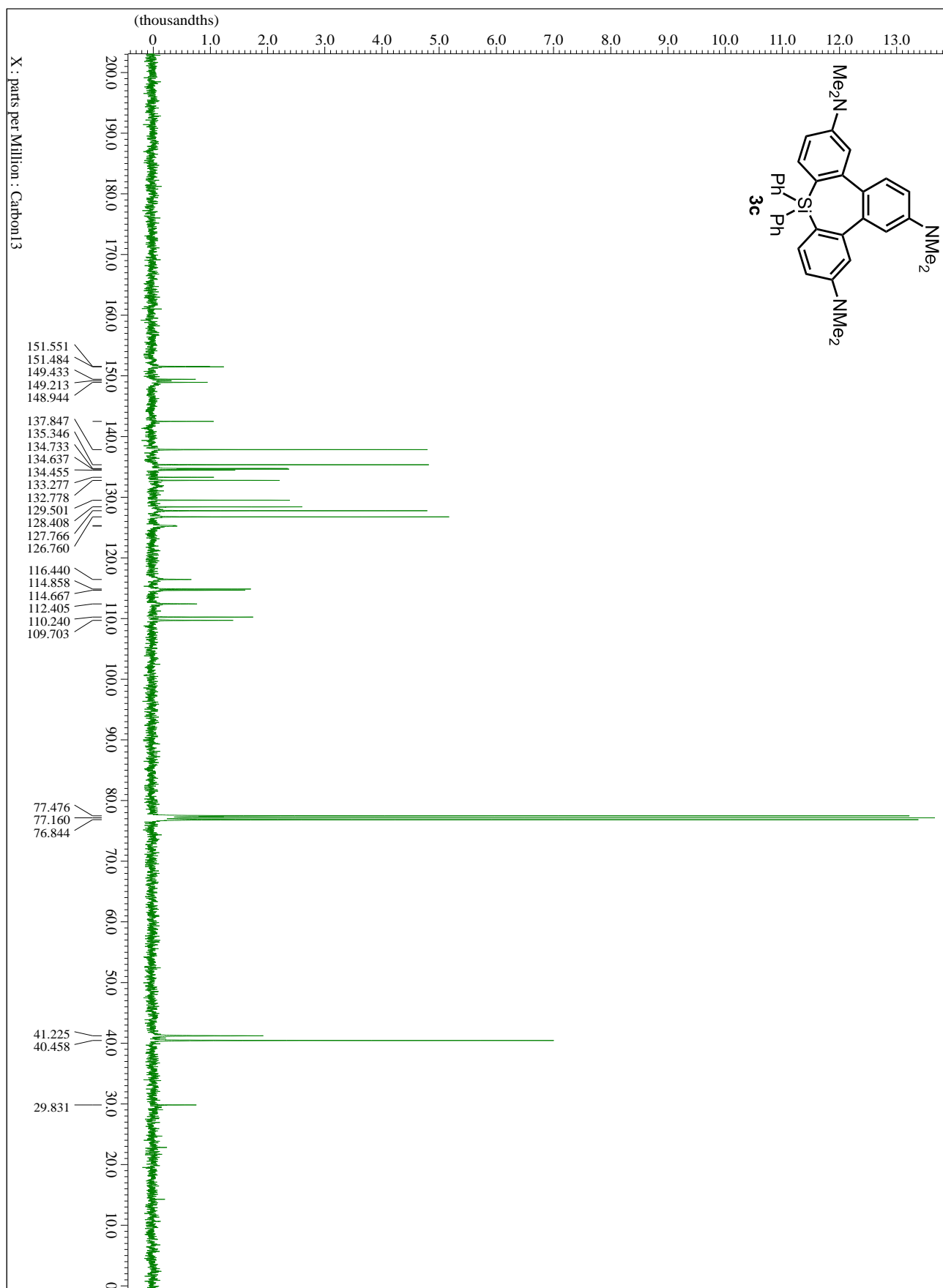


Figure S22. ¹³C NMR of **3c** in CDCl₃.

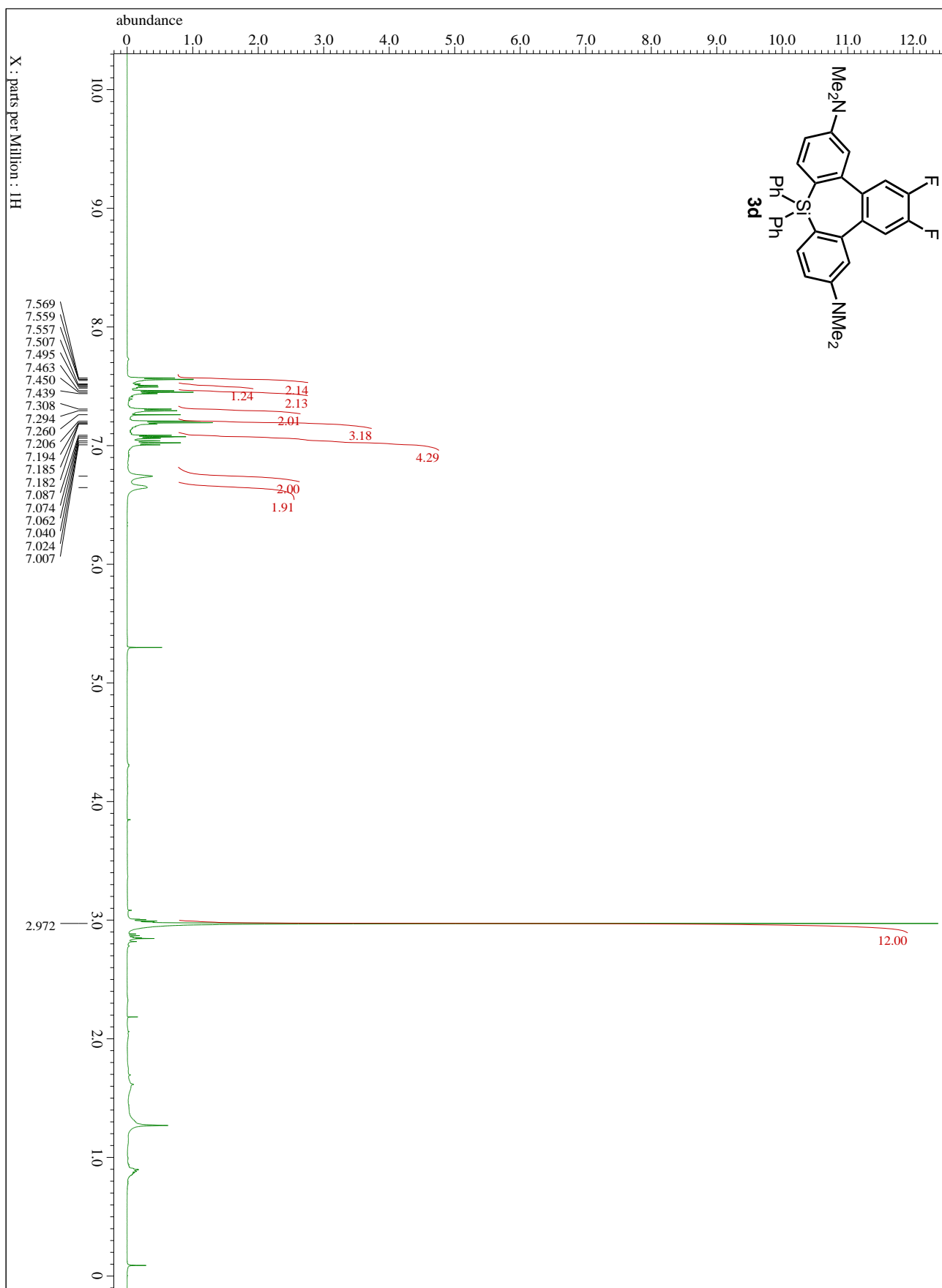


Figure S23. ^1H NMR of **3d** in CDCl_3 .

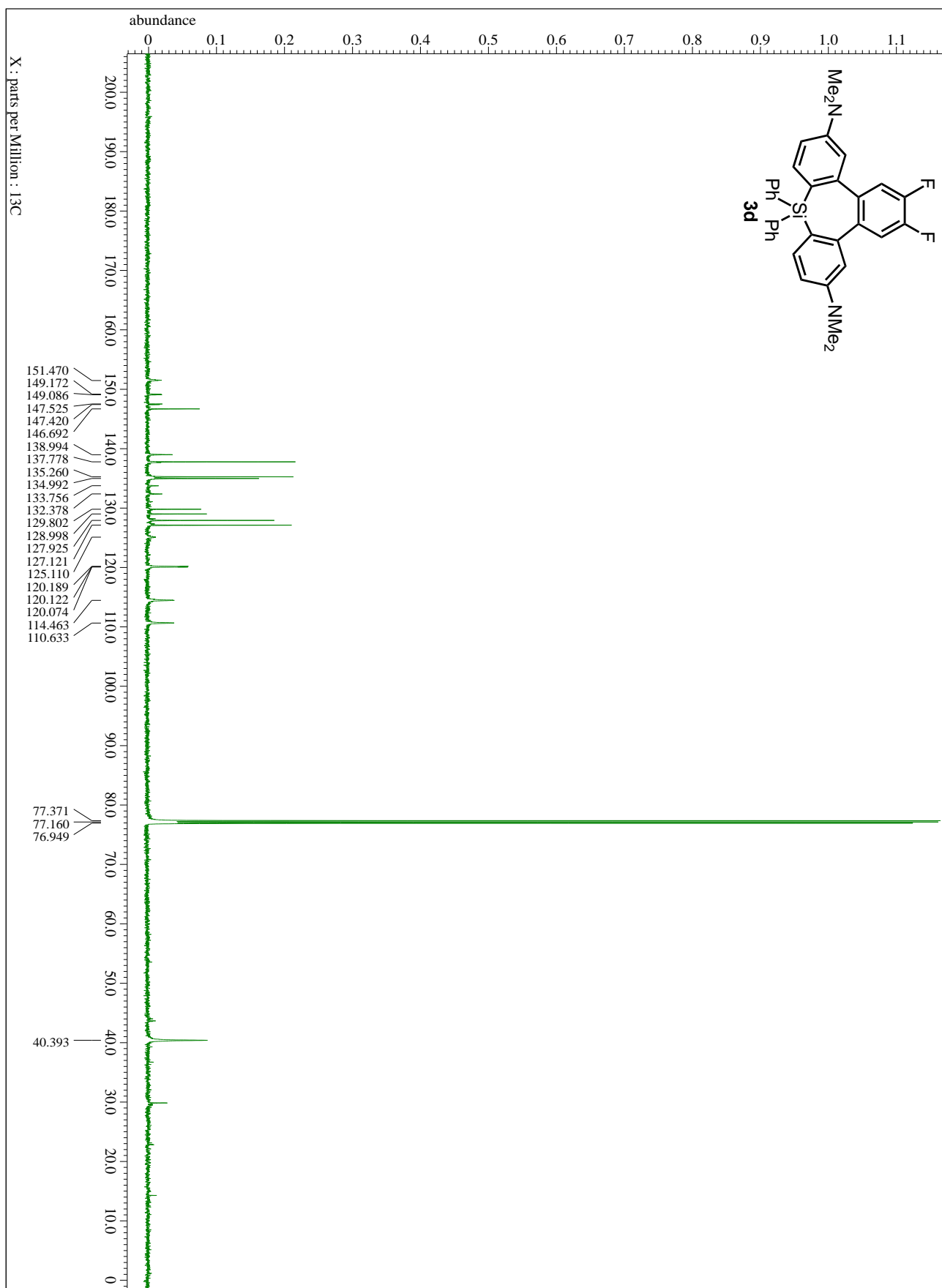


Figure S24. ^{13}C NMR of **3d** in CDCl_3 .

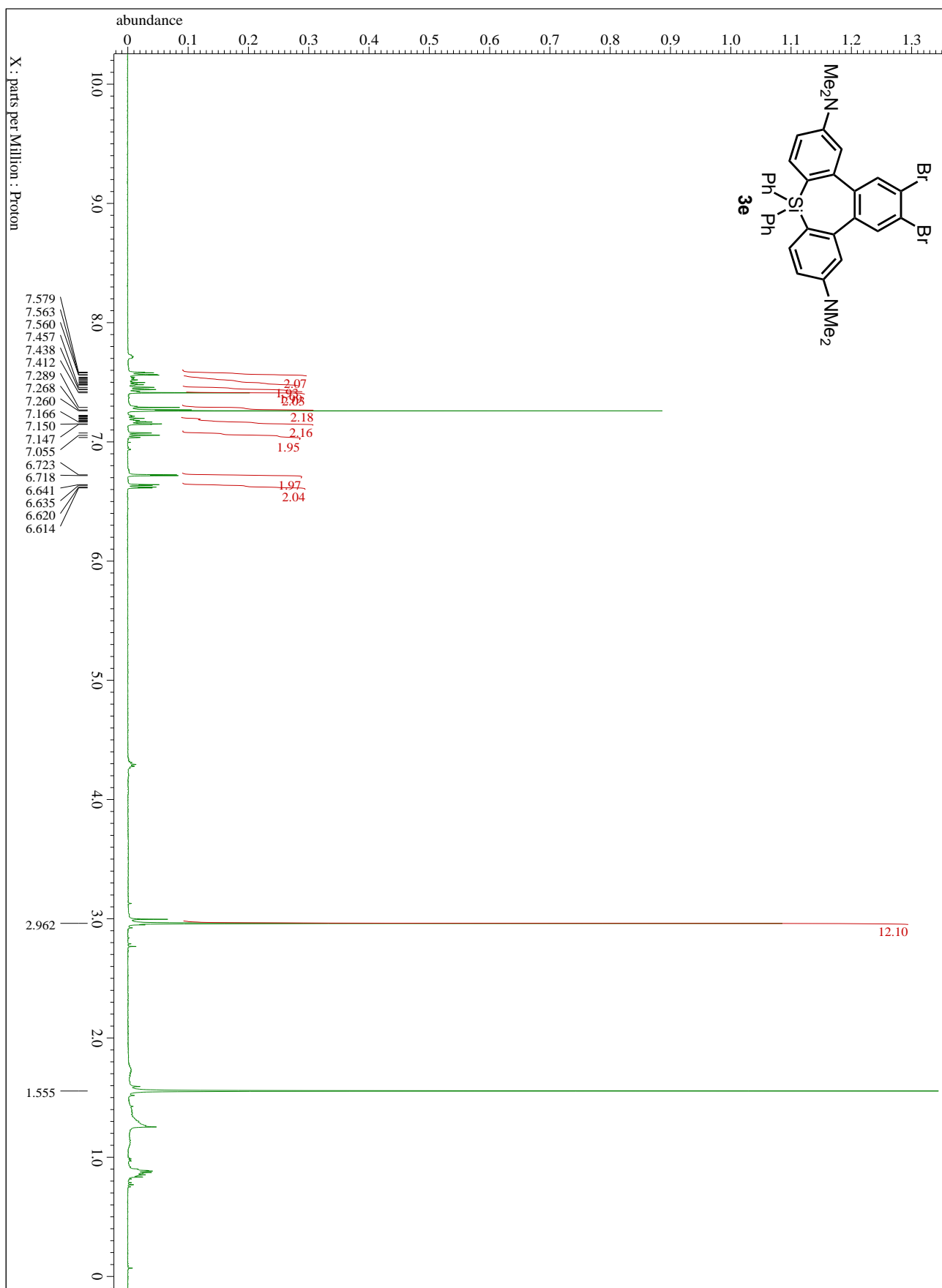


Figure S25. ¹H NMR of **3e** in CDCl₃.

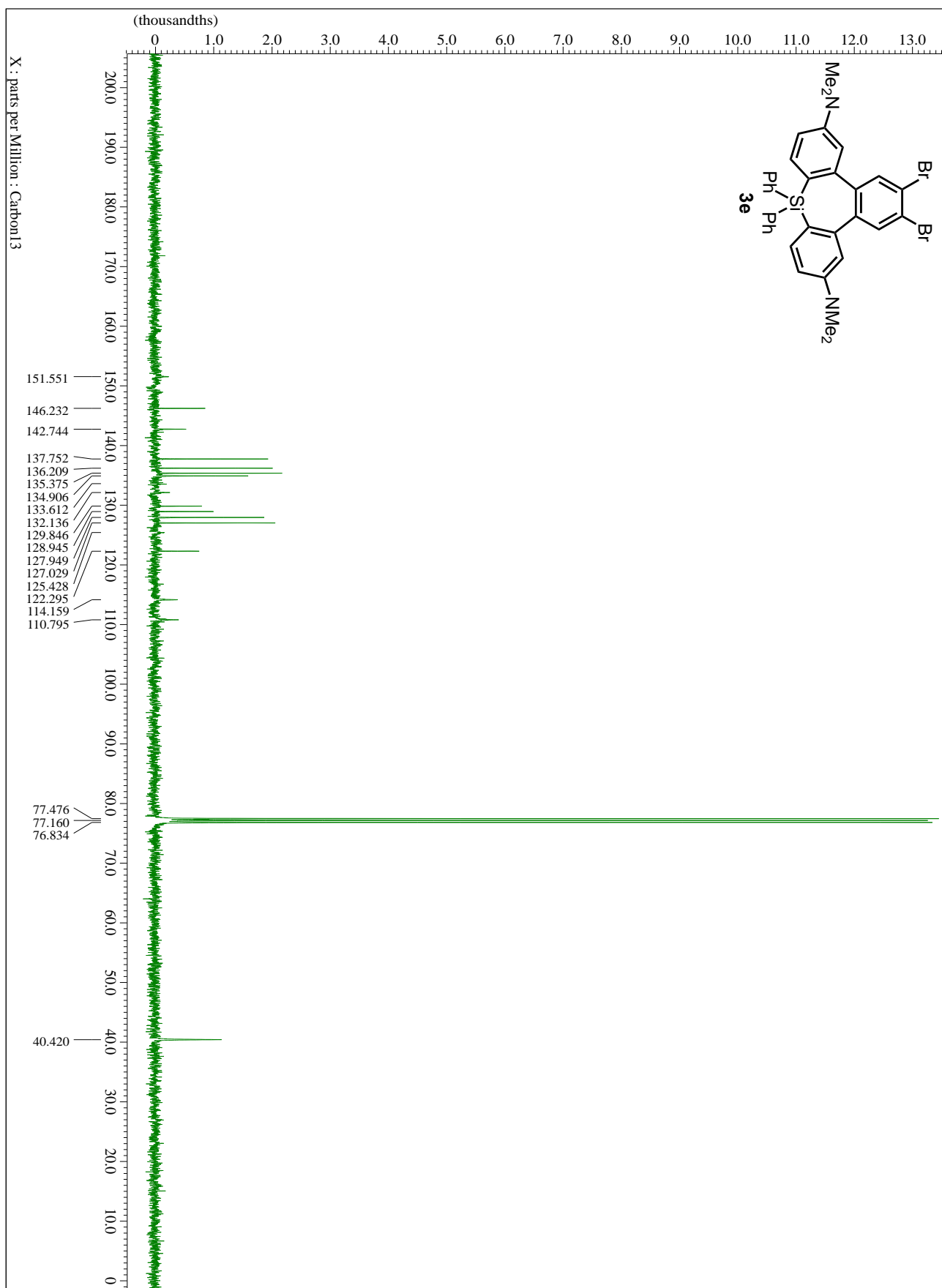


Figure S26. ¹³C NMR of **3e** in CDCl₃.

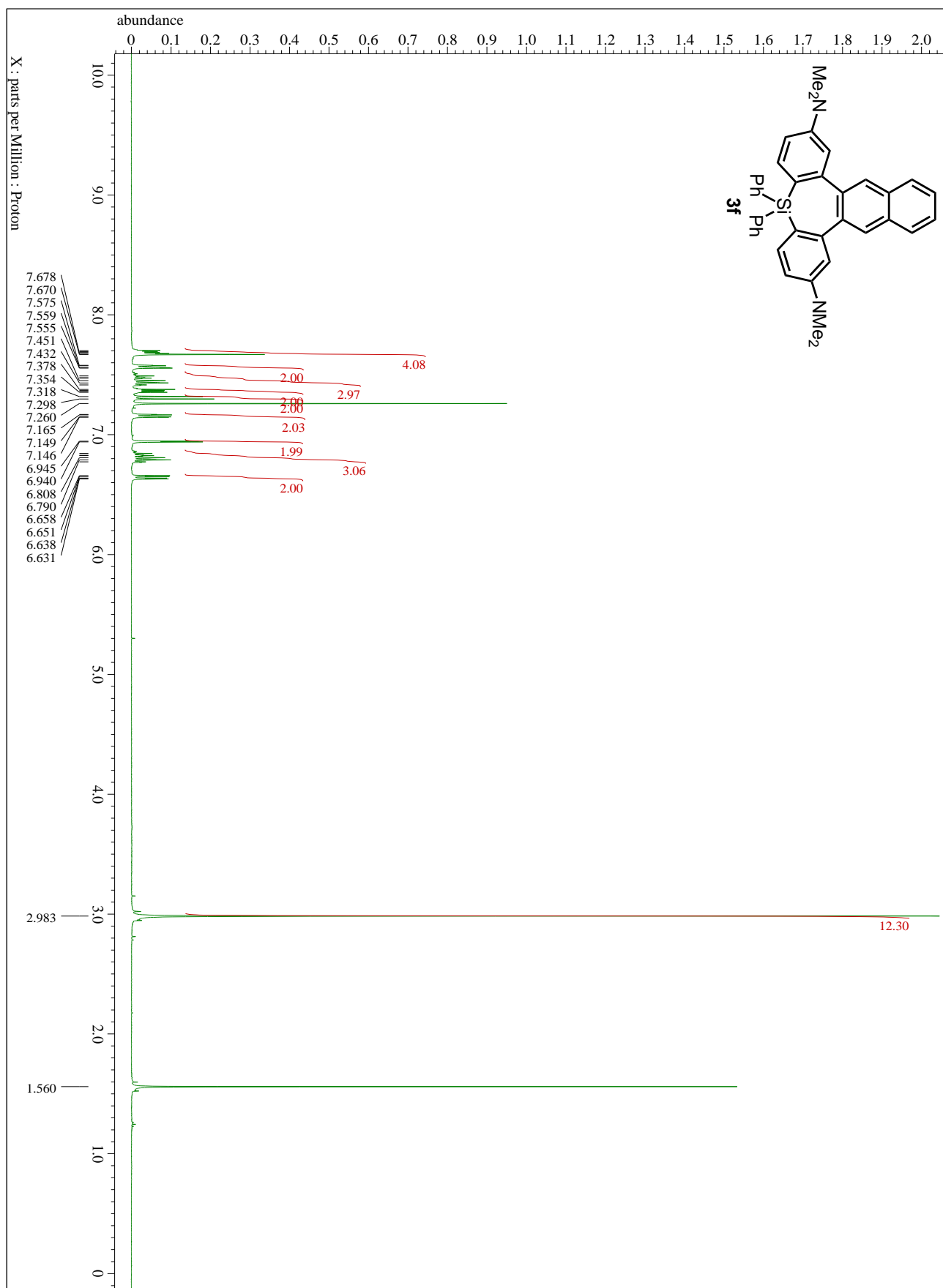


Figure S27. ¹H NMR of **3f** in CDCl₃.

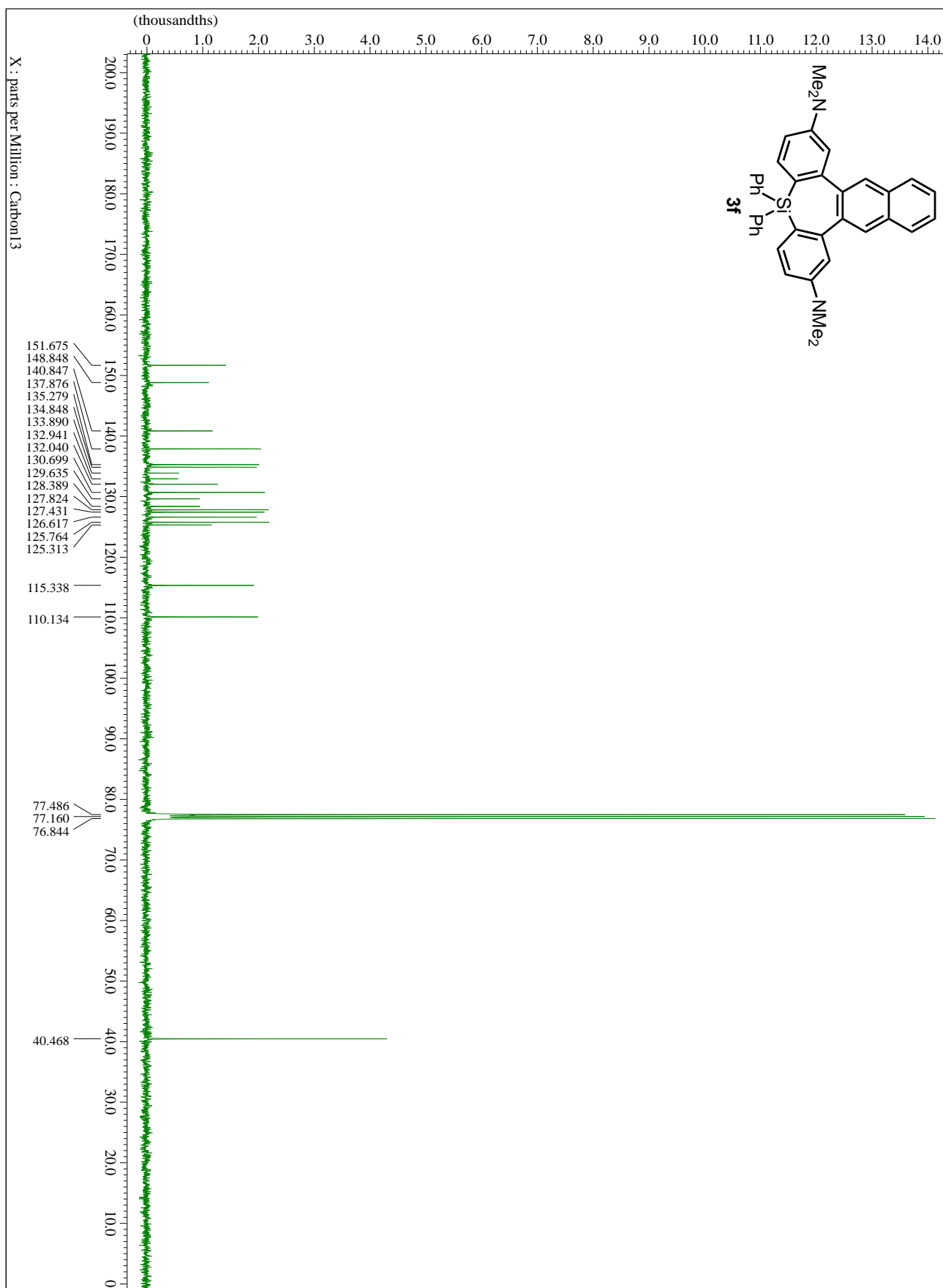


Figure S28. ¹³C NMR of **3f** in CDCl₃.

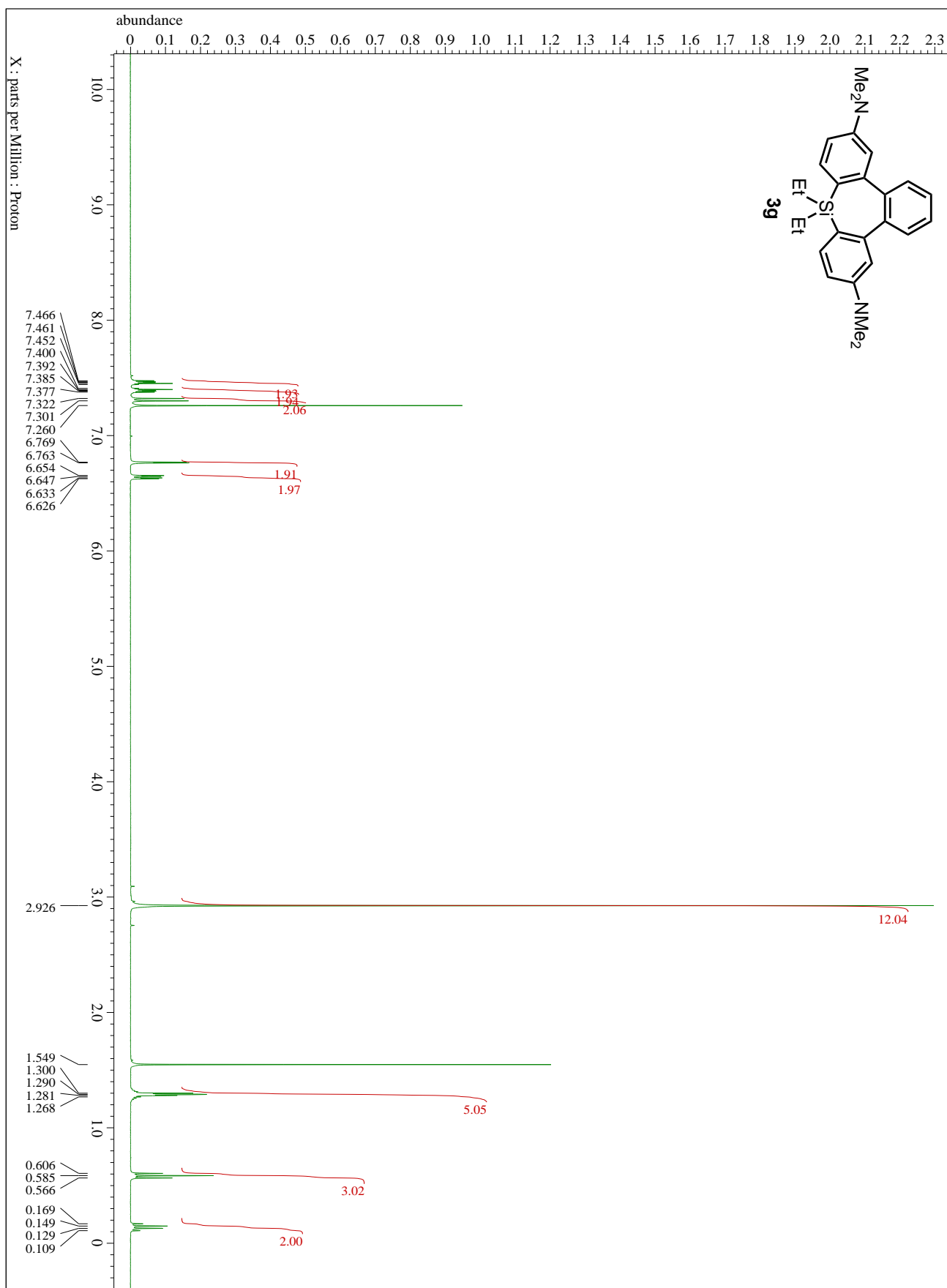


Figure S29. ^1H NMR of **3g** in CDCl_3 .

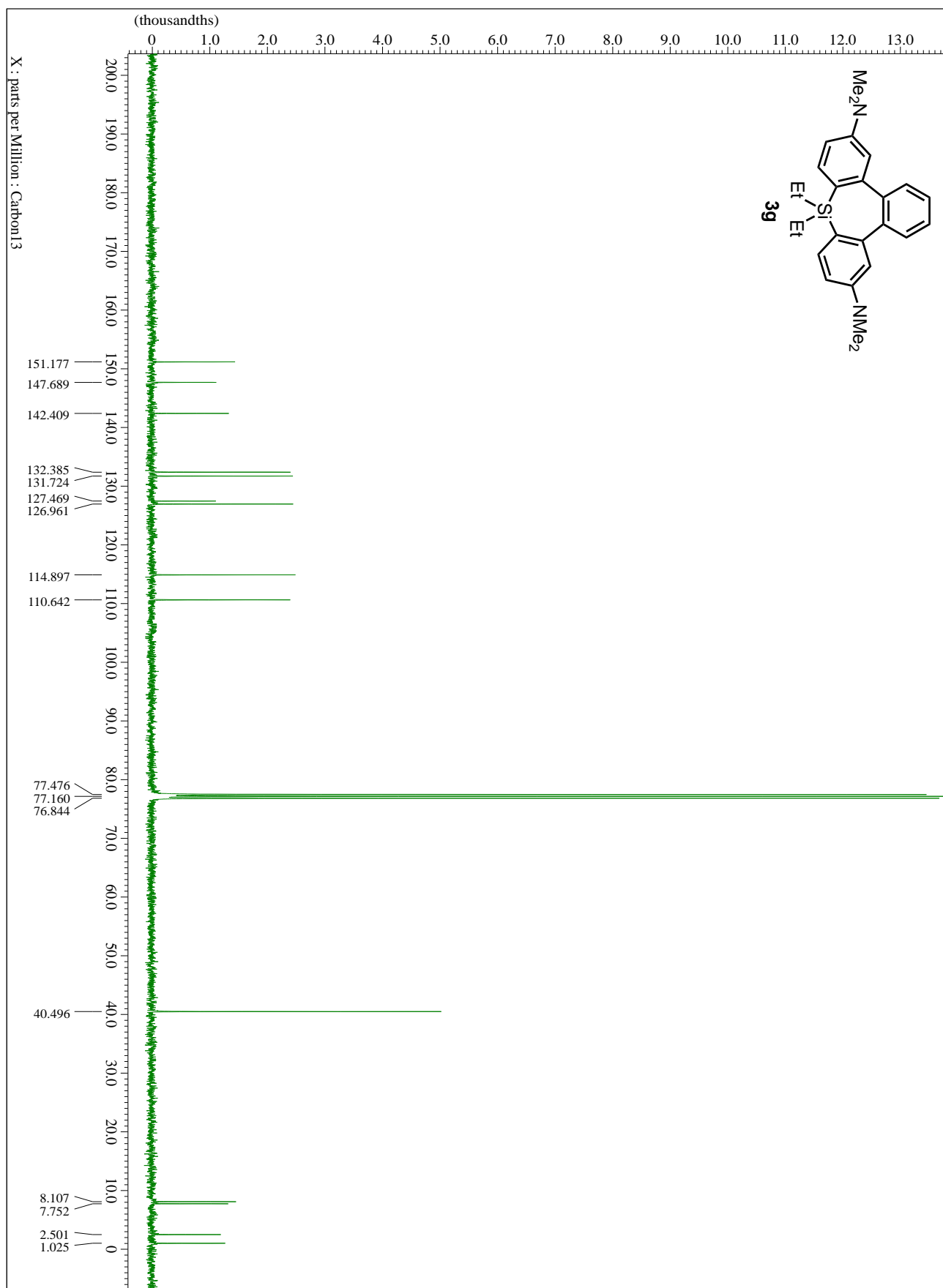


Figure S30. ¹³C NMR of **3g** in CDCl₃.

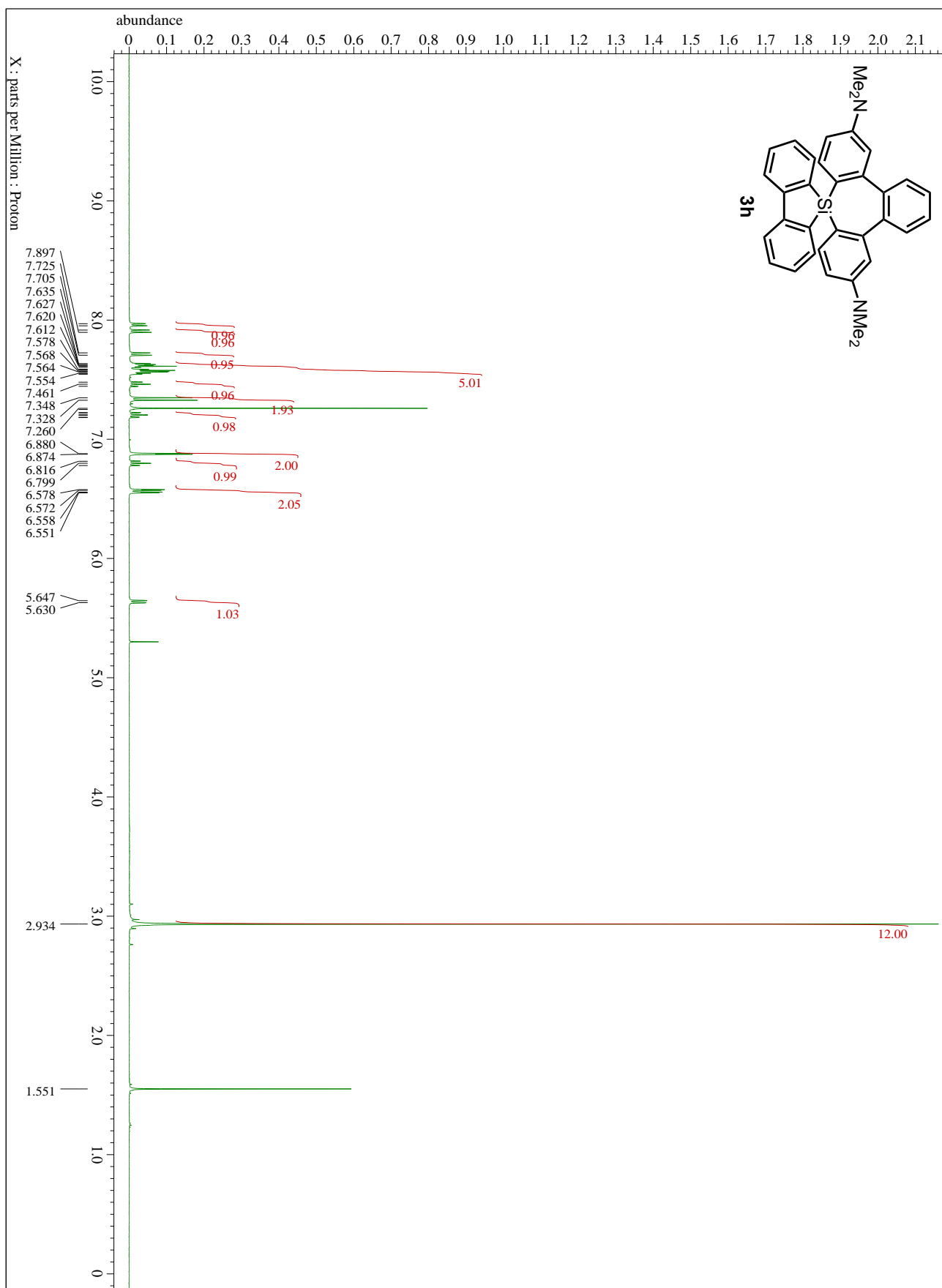


Figure S31. ^1H NMR of **3h** in CDCl_3 .

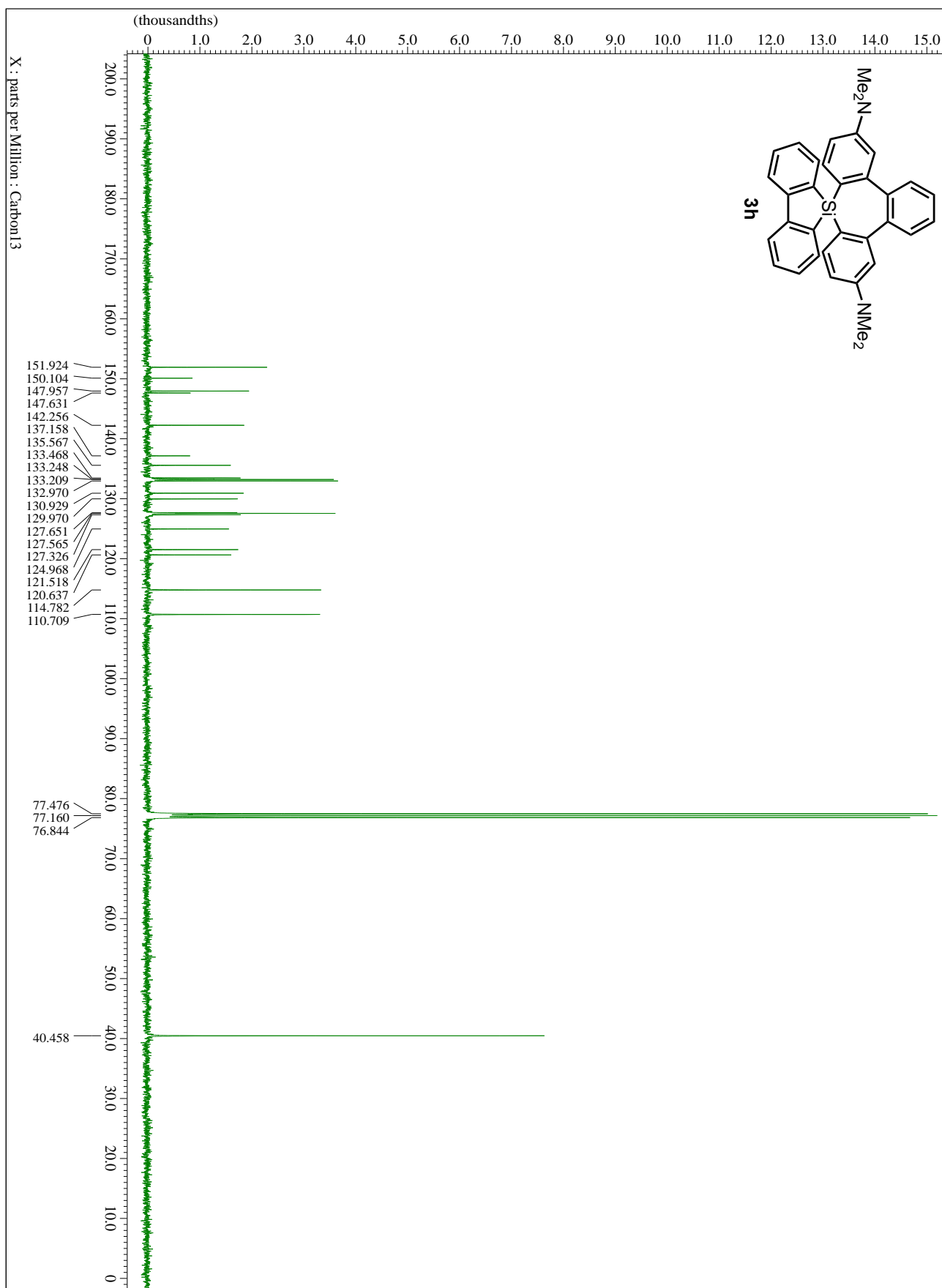


Figure S32. ¹³C NMR of **3h** in CDCl₃.

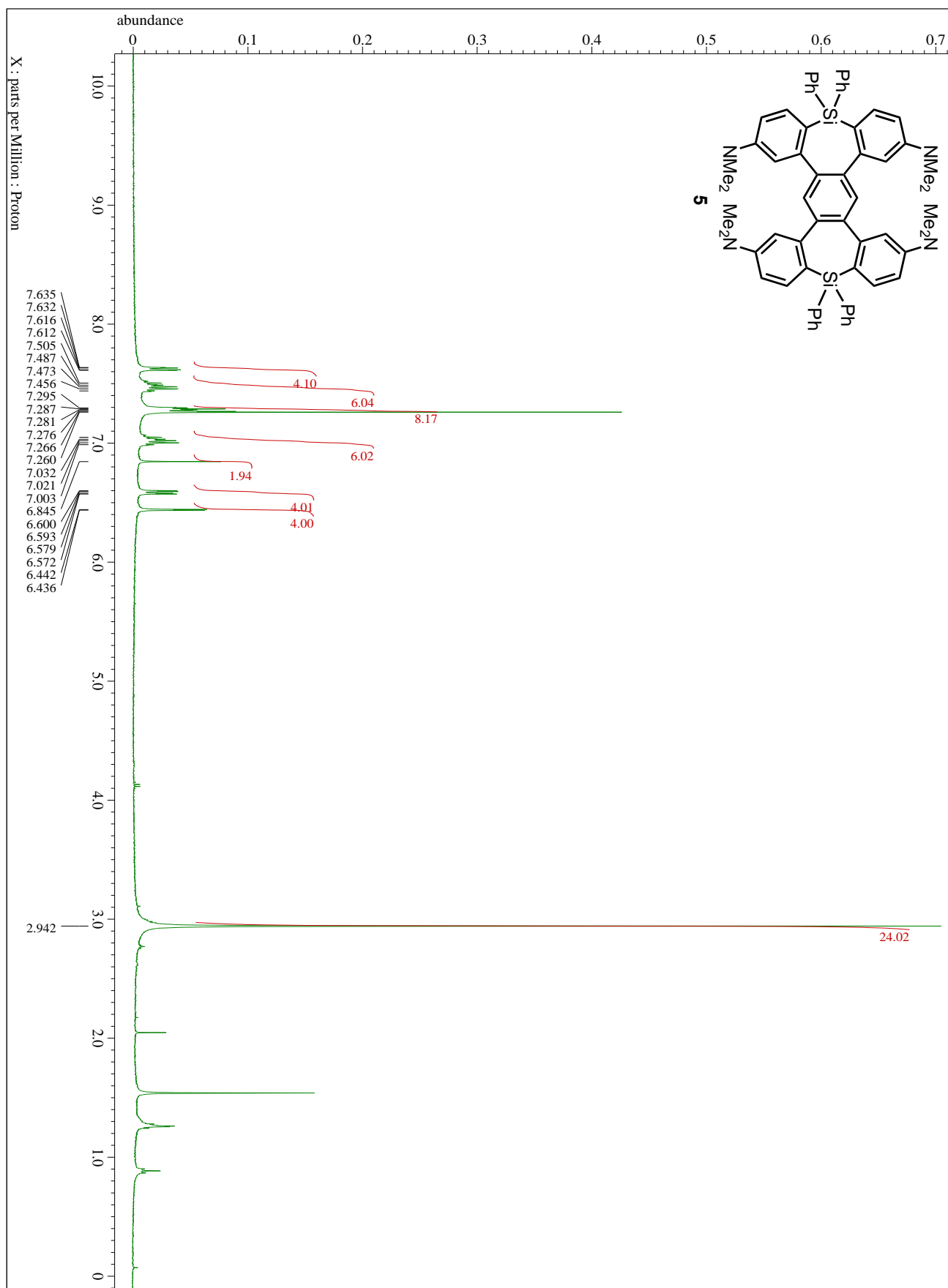


Figure S33. ¹H NMR of **5** in CDCl₃.

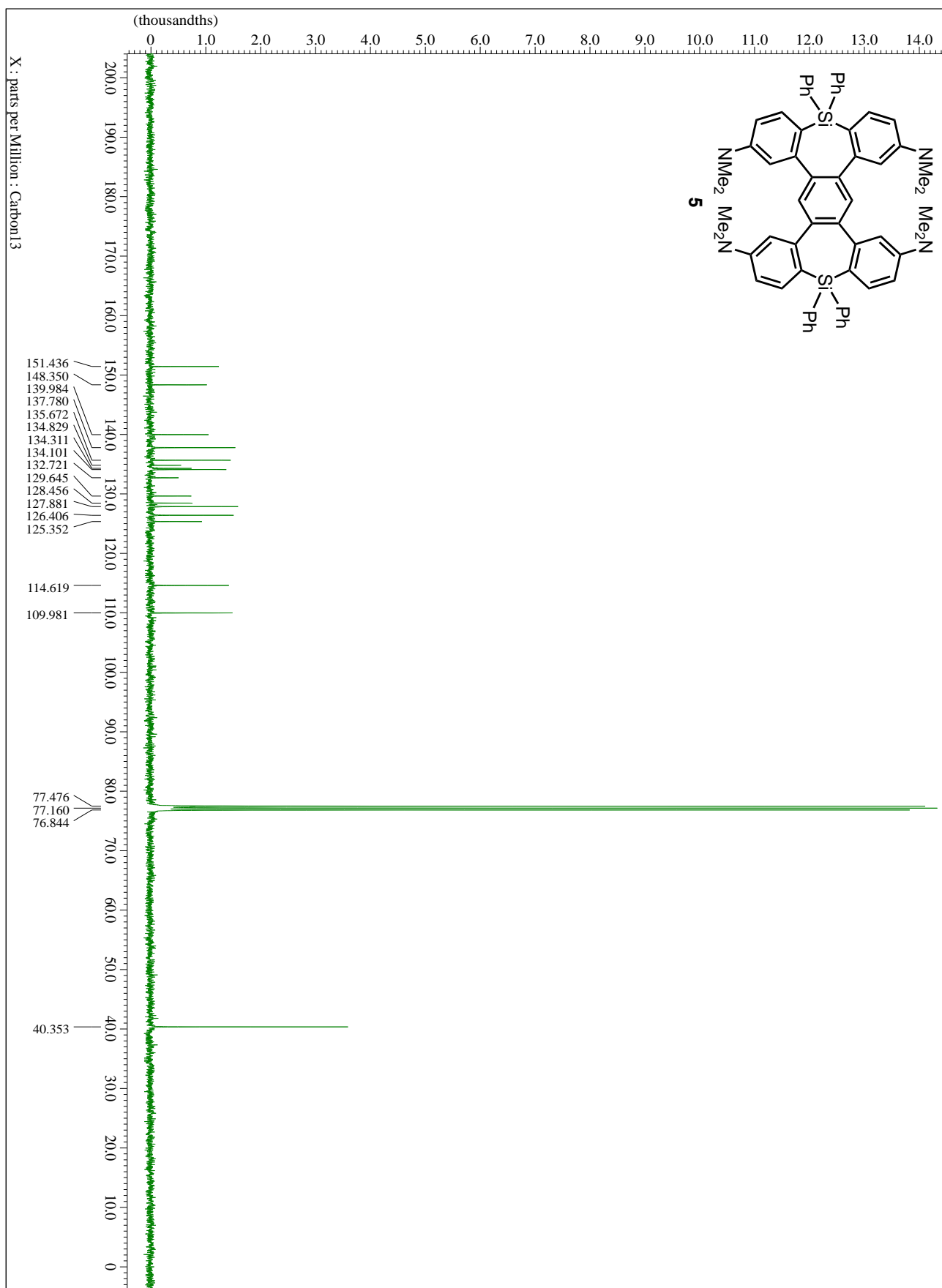


Figure S34. ¹³C NMR of **5** in CDCl₃.

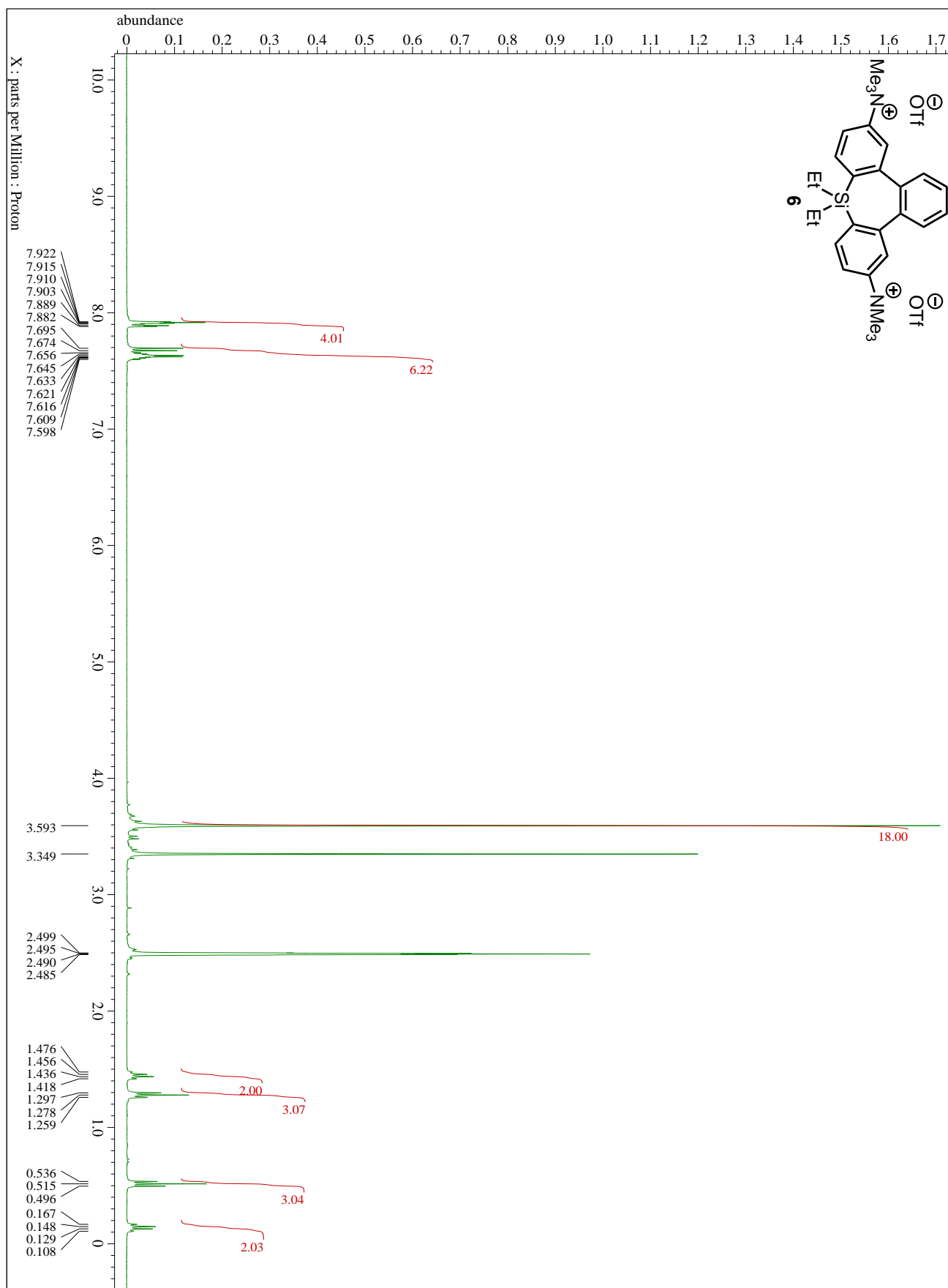


Figure S35. ¹H NMR of **6** in DMSO-*d*₆.

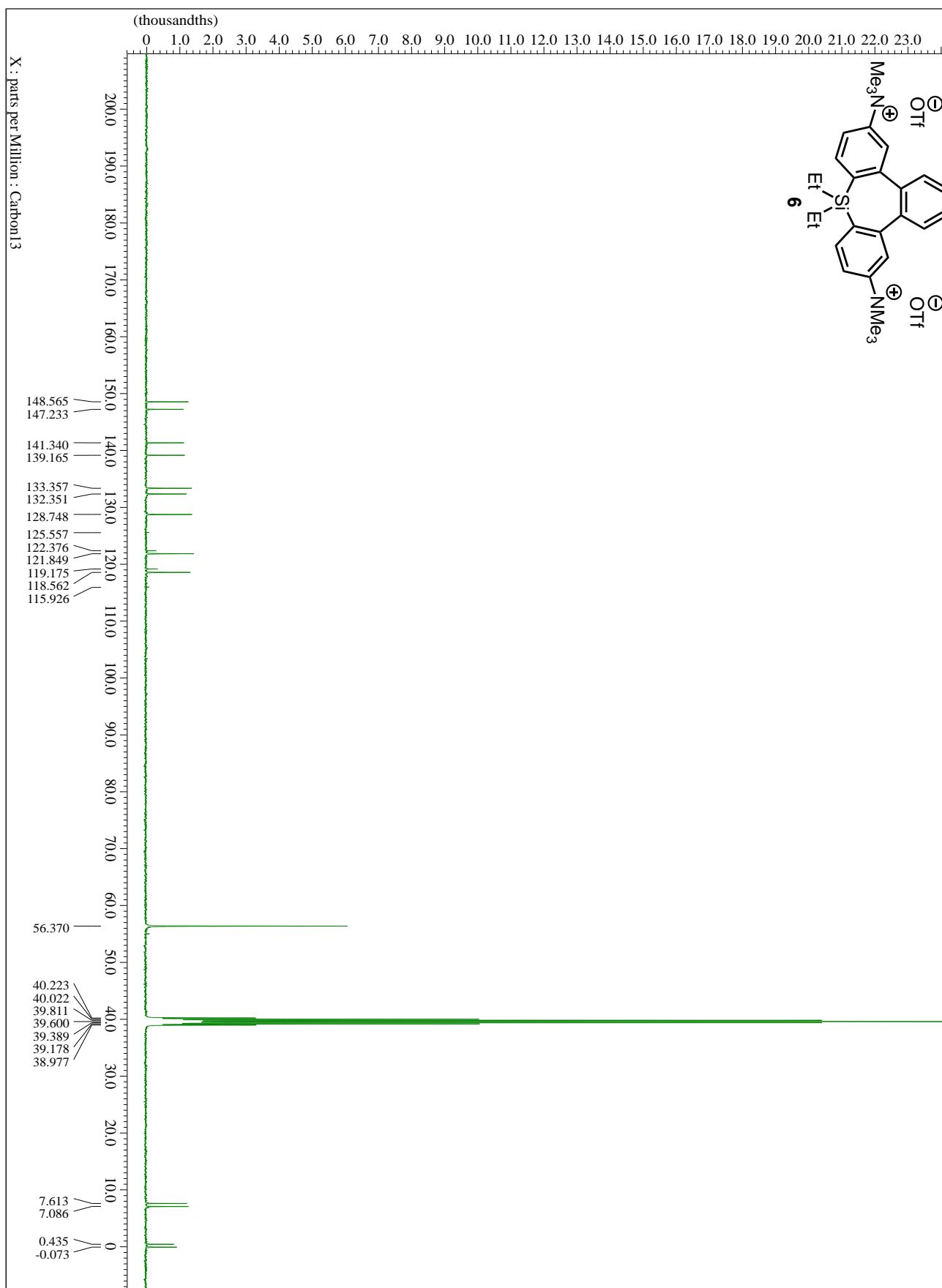


Figure S36. ¹³C NMR of **6** in DMSO-*d*₆.

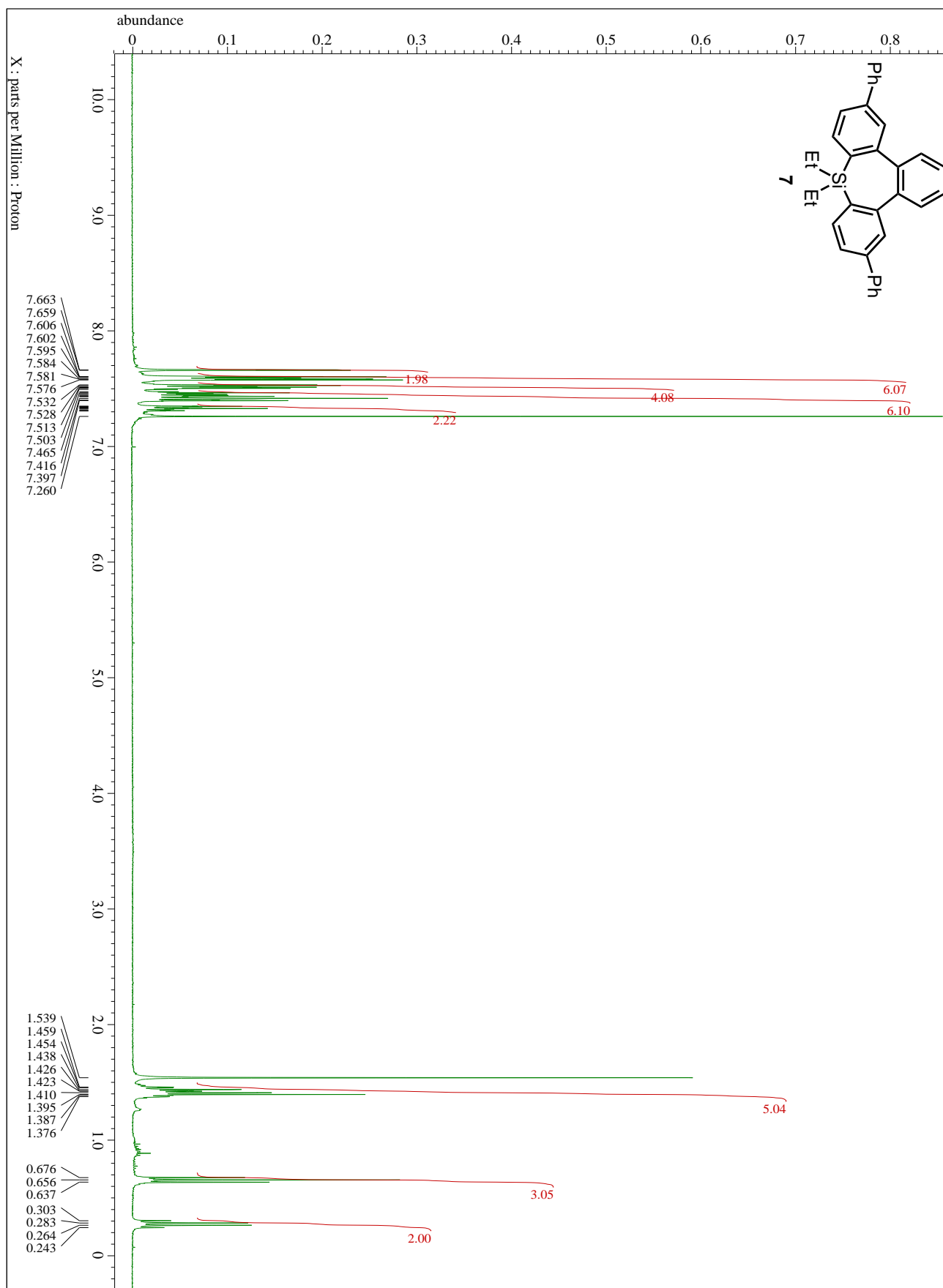


Figure S37. ¹H NMR of 7 in CDCl₃.

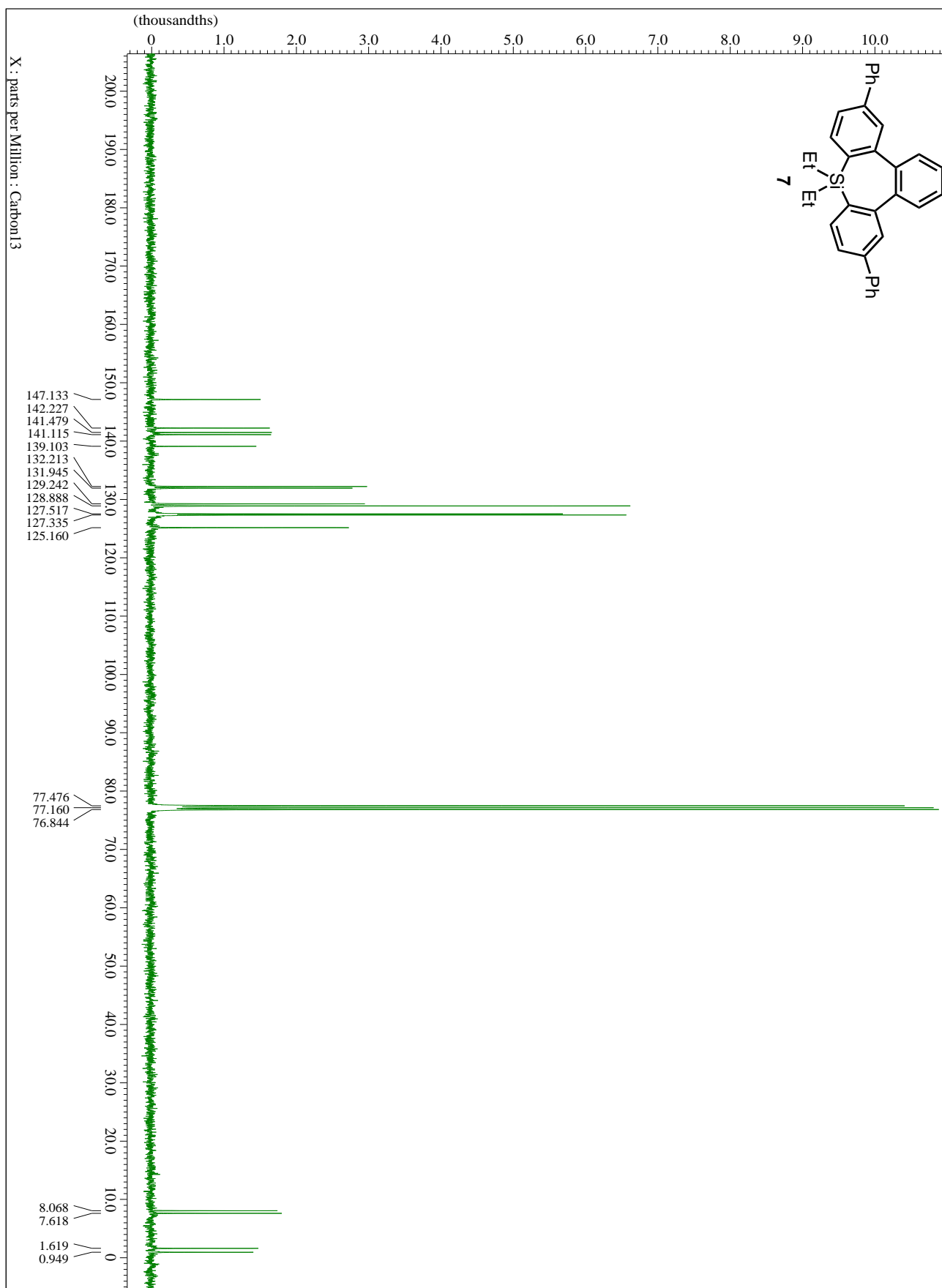


Figure S38. ^{13}C NMR of **7** in CDCl_3 .

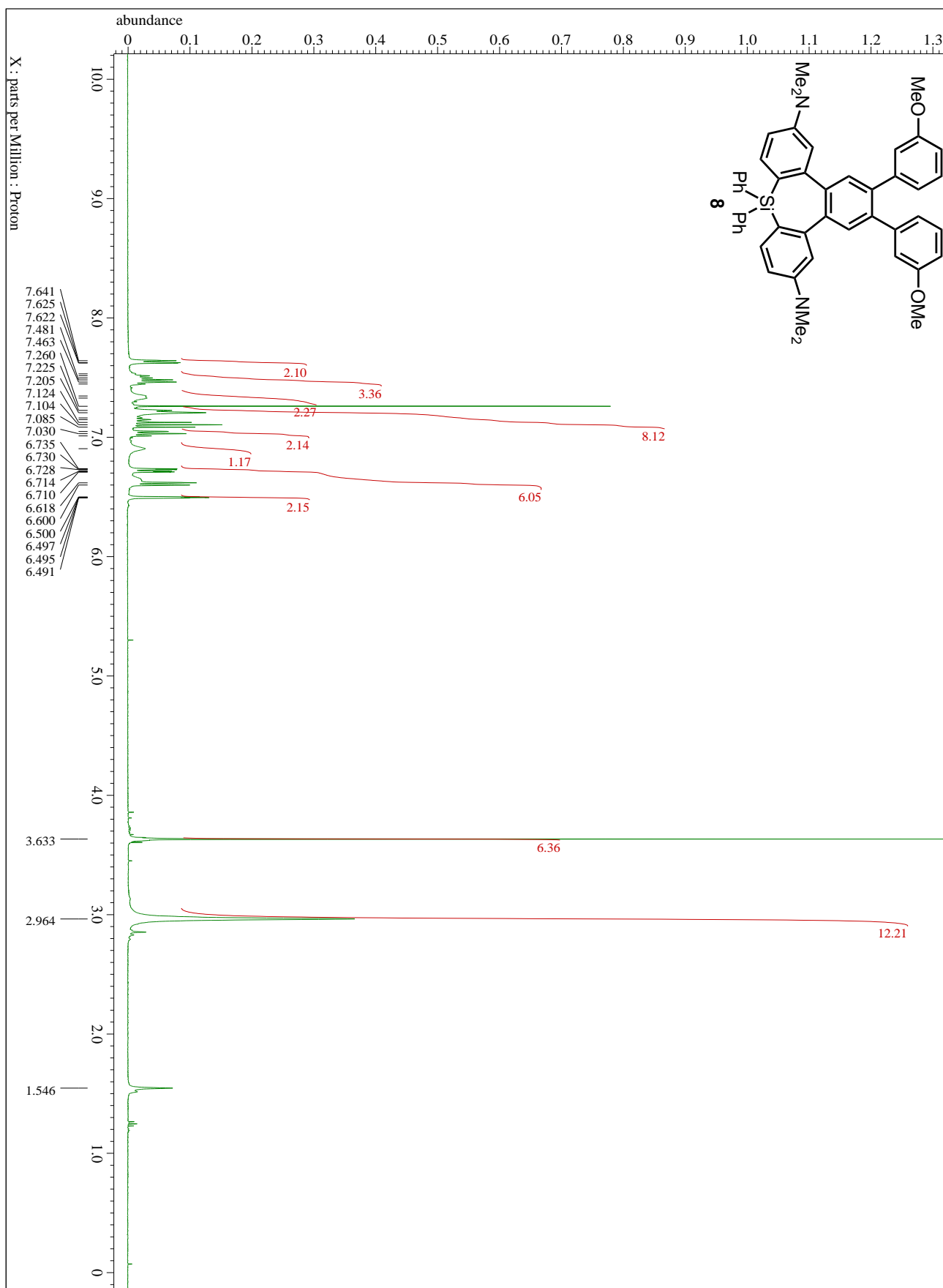


Figure S39. ^1H NMR of **8** in CDCl_3 .

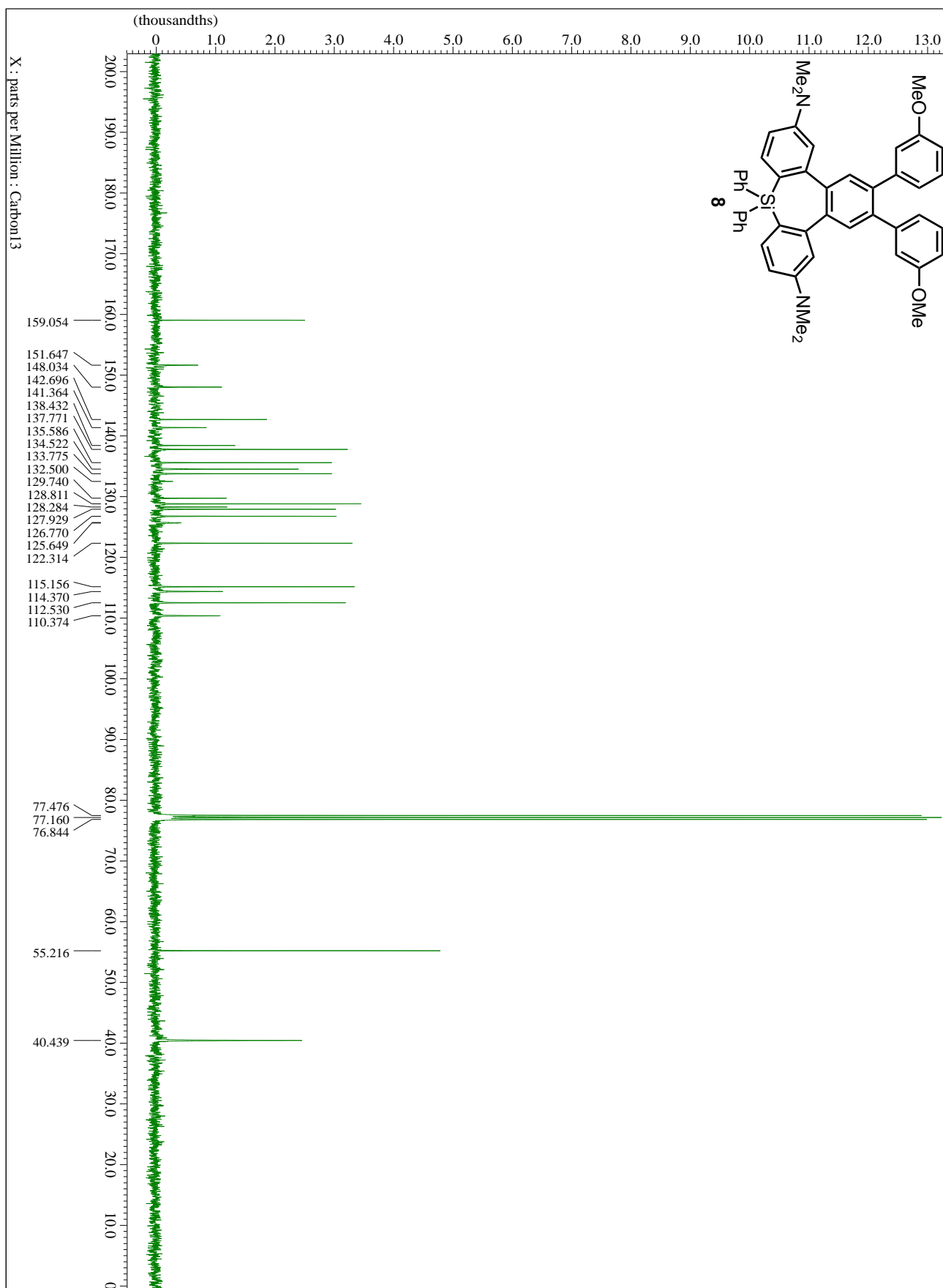


Figure S40. ¹³C NMR of **8** in CDCl₃.

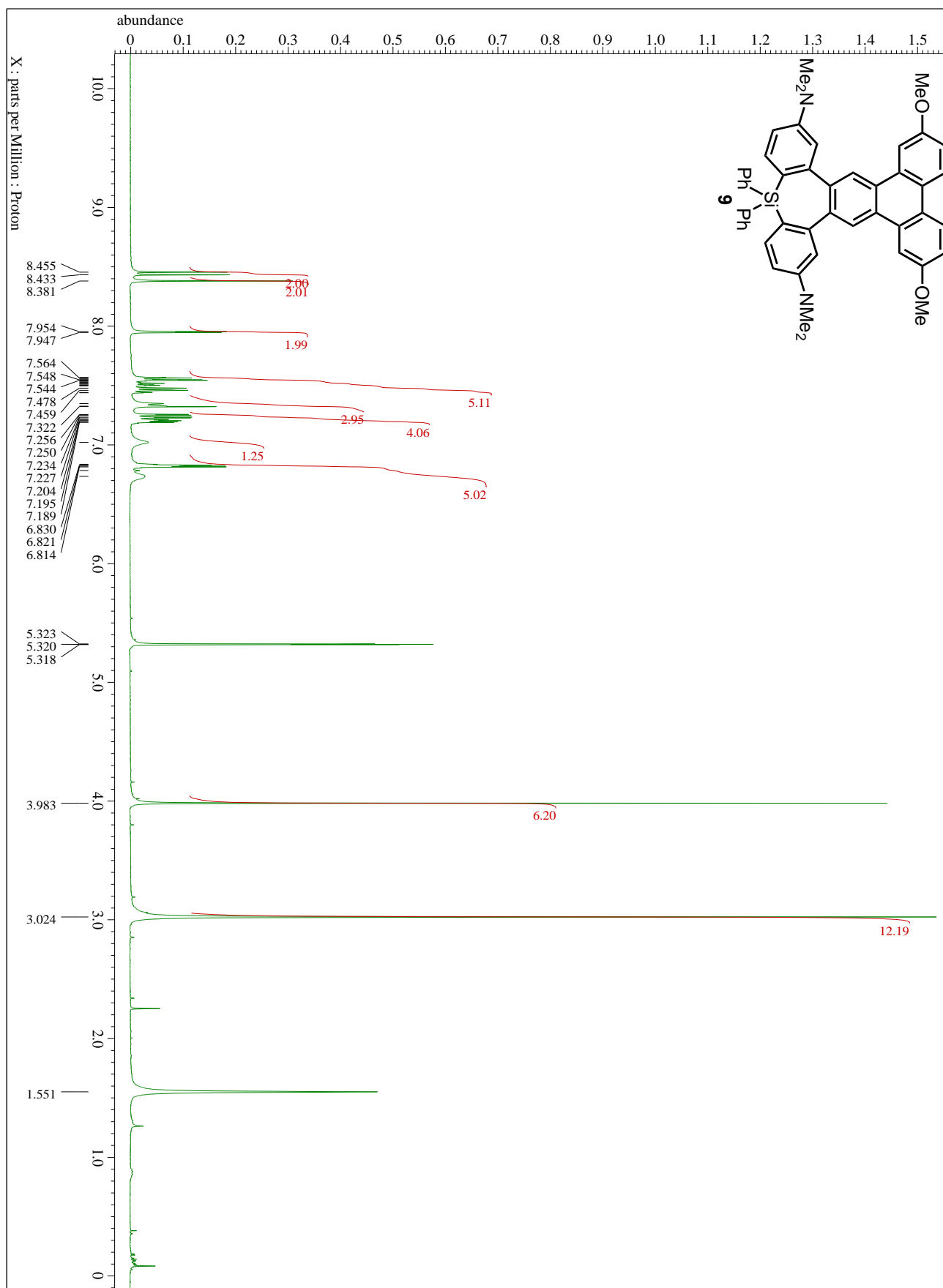


Figure S41. ¹H NMR of **9** in CD₂Cl₂.

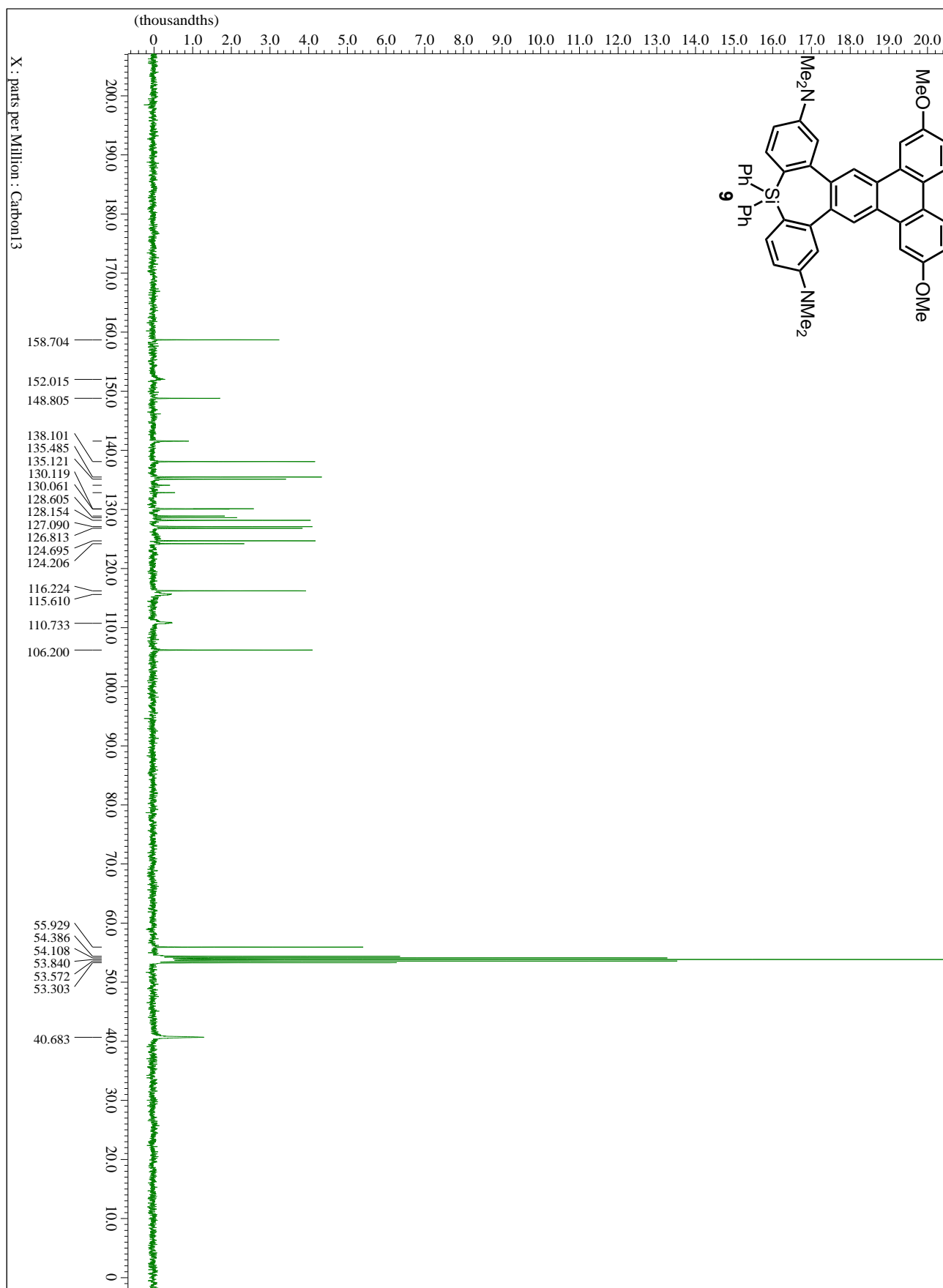


Figure S42. ^{13}C NMR of **9** in CD_2Cl_2 .