Supplementary Information

Lewis Acid-Catalyzed Synthesis of Silafluorene Derivatives from Biphenyls and Dihydrosilanes via Double Sila-Friedel-Crafts Reaction

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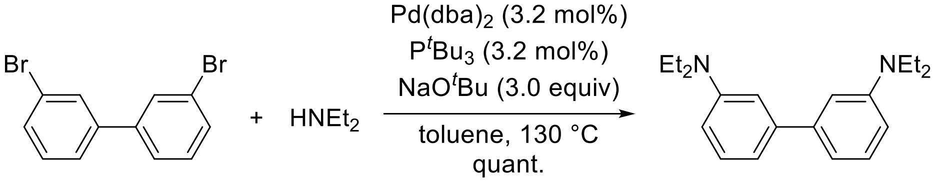
Contents

1. General

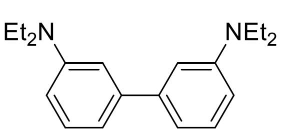
All reactions were carried out using standard Schlenk techniques under an inert atmosphere. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECA600 (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR), JEOL ECZ-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR), JEOL JNM-LA400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometers. Proton and carbon chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.00 (^{1}H NMR, ^{13}C NMR)) or the residual solvent ($CHCl_3$ (δ 7.26 for ^{1}H NMR or δ 77.16 for ^{13}C NMR), CH_2Cl_2 (δ 5.23 for ^{1}H NMR or δ 53.84 for ^{13}C NMR)) used as an internal reference. HRMS were measured on a JEOL JMS-700 spectrometer. Di-*p*-tolylsilane, bis(4-fluorophenyl)silane, bis(4-bromophenyl)silane, di(naphthalen-2-yl)silane, 5*H*-dibenzo[*b*,*d*]silole were prepared according to the literature procedures or modified procedures.[1a] 9,9-Dihydro-5-silafluorene was synthesized according to the literature procedure.[1b]

2. Synthesis and Characterization of Substrates

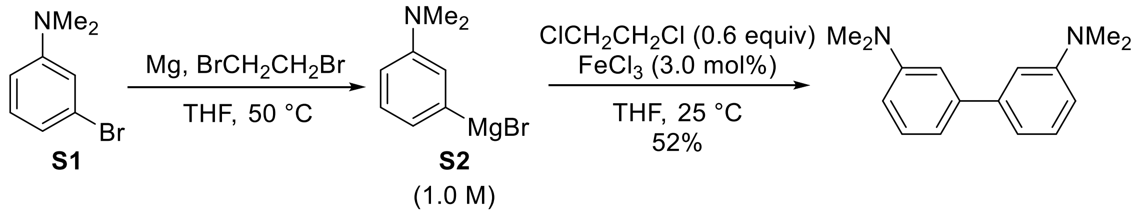


Scheme S1. Synthesis of biphenyl **1a**

Biphenyl 1a

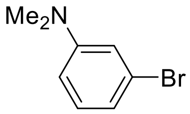


Compound **1a** was synthesized according to the reported method.[2] Schlenk flask was charged with 3,3'-dibromobiphenyl (1.87 g, 6.00 mmol, 1.0 equiv), $HNEt_2$ (878 mg, 12.0 mmol, 2.0 equiv), NaO^tBu (1.73 g, 18.0 mmol, 3.0 equiv), $Pd(dba)_2$ (138 mg, 0.240 mmol, 4.0 mol%), P^tBu_3 (39.2 mg, 0.190 mmol, 3.2 mol%), and toluene (12 mL) under N_2. The flask was immersed in an oil bath and heated to 130 °C with stirring overnight. The mixture was cooled to room temperature, filtered over Celite, and concentrated. The crude product was then purified by column chromatography (eluent: ethyl acetate) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1a** as pale yellow solid (1.78 g, quant). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 8.1 Hz, 2H), 6.86 -6.83 (m, 4H), 6.67 (dd, J = 8.1, 2.3 Hz, 2H), 3.40 (q, J = 7.0 Hz, 8H), 1.19 (t, J = 7.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 144.0, 129.5, 114.9, 111.2, 110.6, 44.6, 12.8; HRMS(EI$^+$) Calcd for $C_{20}H_{28}N_2$ ([M]$^+$) 296.2252, Found 296.2253.



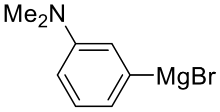
Scheme S2. Synthesis of biphenyl **1b**

Compound S1



Compound **S1** was synthesized according to the reported method.[3] A mixture of aniline (10 mmol), iodomethane (22 mmol) and K_2CO_3 (22 mmol) in DMF (80 mL) was refluxed at 75 °C. After completion of the reaction monitored by TLC, the mixture was poured into aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel afford *N*,*N*-dimethylanilines (1.80 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, J = 8.2 Hz, 1H), 6.84-6.81 (m, 2H), 6.64-6.61 (m, 1H), 2.94 (s, 6H). The analytical data is in accordance with the previous report.[4]

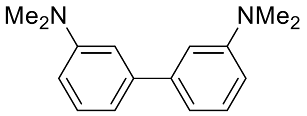
Compound S2[5]



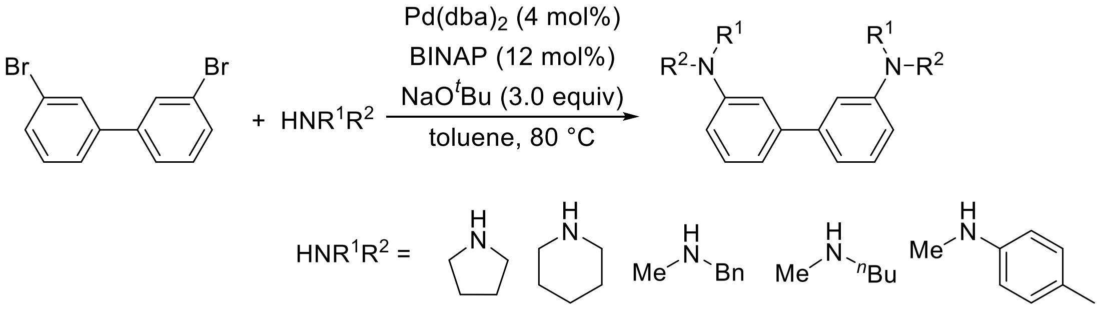
To an oven dried two-necked round bottom flask equipped with a magnetic stir bar and a constant-pressure dropping funnel, activated magnesium turnings (613 mg, 25.2 mmol, 1.05 equiv) was added. The equipment was sealed with rubber septum, evacuated, and back filled with nitrogen. To the funnel were added 24 drops of 1,2-dibromoethane and 1 M solution of 3-bromide-

N,*N*-dimethylaniline (3.28 g, 16.4 mmol, 1.0 equiv) in THF (16.4 mL) by a syringe at room temperature within 30 min. Upon the addition, the flask was immersed in a preheated oil-bath at 50 °C for 2 h. The prepared 3-(*N*,*N*-dimethylamino)phenyl magnesium bromide (1.0 M in THF) was stored in nitrogen atmosphere and used in the next step.

Biphenyl 1b

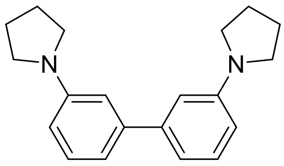


Compound **1b** was synthesized according to the reported method.[6] Dried two-necked flask equipped with a magnetic stirrer was charged under nitrogen with THF (32 mL) with a solution of $FeCl_3$ (79.8 mg, 0.490 mmol, 3.0 mol%) and 1,2-dichloroethane (974 mg, 9.84 mmol, 0.60 equiv). A solution of the 3-(*N*,*N*-dimethylamino)phenyl magnesium bromide **S2** in THF (1.0 M, 12 mmol) was added via a syringe. The color immediately changed to dark brown and the temperature increased. The resulting mixture was stirred at room temperature for 1 h then quenched with H_2O (30 mL). After extraction with CH_2Cl_2 (3 × 50 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: hexane/ethyl acetate = 100:0 to 19:1) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1b** as brown oil (2.06 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 8.0 Hz, 2H), 6.96-6.94 (m, 4H) 6.76-6.73 (m, 2H), 3.00 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.5, 129.4, 116.3, 112.1, 111.7, 40.9; HRMS(EI$^+$) Calcd for $C_{16}H_{20}N_2$ ([M]$^+$) 240.1626, Found 240.1622. The analytical data is in accordance with the previous report.[7]



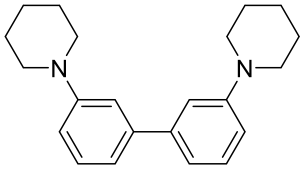
Scheme S3. Synthesis of biphenyl **1c-1f**

Biphenyl 1c



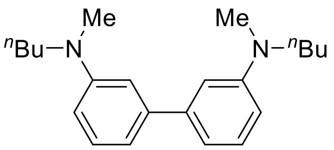
Compound **1c** was synthesized according to the reported method.[8] A Schlenk flask was charged with 3,3'-dibromobiphenyl (624 mg, 2.00 mmol, 1.0 equiv), pyrrolidine (427 mg, 6.00 mmol, 3.0 equiv), NaO^{t}Bu (577 mg, 6.00 mmol, 3.0 equiv), Pd(dba)$_2$ (46.0 mg, 0.08 mmol, 4.0 mol%), BINAP (149 mg, 0.240 mmol, 12 mol%), and toluene (4.0 mL) under N_2. The flask was immersed in an oil bath and heated to 80 °C with stirring overnight. The mixture was cooled to room temperature, filtered over Celite, and concentrated. The crude product was then purified by column chromatography (eluent: ethyl acetate) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1c** as white yellow solid (601 mg, quant). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz 2H), 6.90 (d, *J* = 7.3 Hz, 2H), 6.79 (s, 2H), 6.57 (d, *J* = 8.2 Hz, 2H), 3.35 (t, *J* = 6.4 Hz, 8H), 2.04-2.01 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ148.3, 143.7, 129.4, 115.1, 111.0, 110.7, 47.9, 25.6; HRMS(EI$^+$) Calcd for $C_{20}H_{24}N_2$ ([M]$^+$) 292.1939, Found 292.1938.

Biphenyl 1d



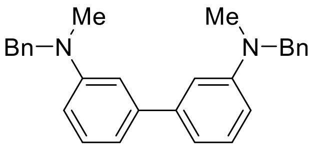
The same method as **1c**. 3,3'-Dibromobiphenyl (624 mg, 2.00 mmol, 1.0 equiv), piperidine (427 mg, 6.00 mmol, 3.0 equiv), NaO^{t}Bu (577 mg, 6.00 mmol, 3.0 equiv), Pd(dba)$_2$ (46.0 mg, 0.0800 mmol, 4.0 mol%), BINAP (149 mg, 0.240 mmol, 12 mol%), and toluene (4.0 mL). **1d** was obtained as yellow solid (682 mg, quant). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 2.0 Hz, 2H), 7.03 (dd, *J* = 6.4, 1.4 Hz, 2H), 6.92 (dd, *J* = 8.1, 2.0 Hz, 2H), 3.21 (t, *J* = 5.7 Hz, 8H), 1.74 (quint, 5.7 Hz, 8H), 1.60 (quint, *J* = 5.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 143.1, 129.3, 118.7, 116.0, 115.5, 51.0, 26.1, 24.5; HRMS(EI$^+$) Calcd for $C_{22}H_{28}N_2$ ([M]$^+$) 320.2252, Found 320.2251.

Biphenyl 1e



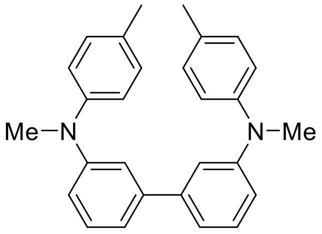
The same method as **1c**. 3,3’-Dibromobiphenyl (624 mg, 2.00 mmol, 1.0 equiv), *N*-methylbutan-1-amine (419 mg, 4.80 mmol, 2.4 equiv), NaO^{t}Bu (577 mg, 6.00 mmol, 3.0 equiv), Pd(dba)$_2$ (46.0 mg, 0.0800 mmol, 4.0 mol%), BINAP (149 mg, 0.240 mmol, 12 mol%), and toluene (4.0 mL). The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 9:1) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1e** as pale yellow solid (289 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 2H), 6.89-6.87 (m, 4H), 6.68 (dd, *J* = 8.5, 2.5 Hz, 2H), 3.35 (t, *J* = 7.5 Hz, 4H), 2.97 (s, 6H), 1.61-1.55 (m, 4H), 1.36 (q, *J* = 7.5 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.7, 129.4, 115.4, 111.5, 111.0, 52.8, 38.6, 29.1, 20.6, 14.2; HRMS(EI$^+$) Calcd for $C_{22}H_{32}N_2$ ([M]$^+$) 324.2565, Found 324.2564.

Biphenyl 1f

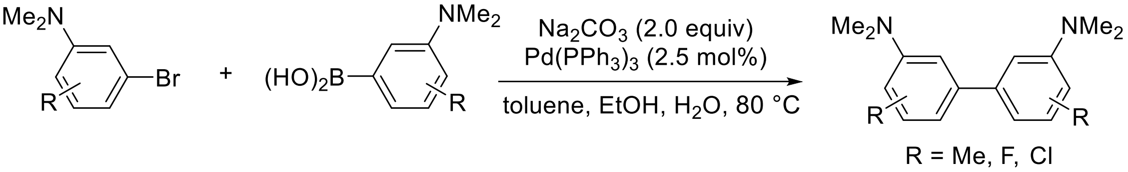


The same method as **1c**. 3,3’-Dibromobiphenyl (624 mg, 2.00 mmol, 1.0 equiv), *N*-metylbenzylamine (582 mg, 4.80 mmol, 2.4 equiv), NaO^{t}Bu (577 mg, 6.00 mmol, 3.0 equiv), Pd(dba)$_2$ (46.0 mg, 0.0800 mmol, 4.0 mol%), BINAP (149 mg, 0.240 mmol, 12 mol%), and toluene (4.0 mL). The crude product was then purified further by column chromatography (eluent: hexane/ethyl acetate = 19:1) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1f** as pale yellow oil (740 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 7.27-7.15 (m, 8H), 6.91-6.89 (m, 4H), 6.74-6.71 (m, 2H), 4.55 (s, 4H), 3.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 143.4, 139.1, 129.4, 128.6, 126.9, 126.9, 116.0, 111.7, 111.4, 56.9, 38.7; HRMS(EI$^+$) Calcd for $C_{20}H_{28}N_2$ ([M]$^+$) 392.2252, Found 392.2251.

Biphenyl 1g

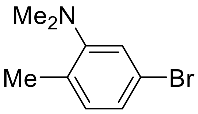


The same method as **1c**. 3,3'-Dibromobiphenyl (624 mg, 2.00 mmol 1.0 equiv), *N*-methyl-*p*-toluidine (582 mg, 4.80 mmol, 2.4 equiv), NaO^{t}Bu (577 mg, 6.00 mmol, 3.0 equiv), Pd(dba)$_2$ (46.0 mg, 0.0800 mmol, 4.0 mol%), BINAP (149 mg, 0.240 mmol, 12 mol%), and toluene (4.0 mL). The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 19:1) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1g** as a white solid (665 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (t, *J* = 7.6 Hz, 2H), 7.11-7.07 (m, 6H), 7.03-7.00 (m, 6H), 6.86-6.84 (ddd, *J* = 0.8, 2.8, 8.4 Hz, 2H), 3.31 (s, 6H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 143.4, 139.1, 129.4, 128.6, 126.9, 126.9, 116.0, 111.7, 111.4, 56.9, 38.7; HRMS(EI$^+$) Calcd for $C_{28}H_{28}N_2$ ([M]$^+$) 392.2252, Found 392.2252.



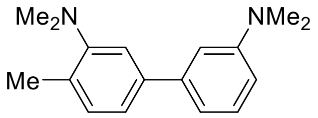
Scheme S4. Synthesis of biphenyl **1h-1l**

5-Bromo-*N*,*N*,2-trimethylaniline

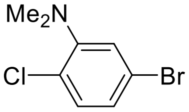


To a solution of 5-bromo-2-methylaniline (1.12 g, 6.00 mmol, 1.0 equiv) in dry DMF (30 mL) were added MeI (4.26 g, 30.0 mmol, 5.0 equiv) and NaH (720 mg, 18.0 mmol, 3.0 equiv; 60 wt% in mineral oil). After 1 h, the reaction was quenched with water (5 mL). Brine (25 mL) and Et_2O (25 mL) were added. The organic layer was separated, washed with brine (2 × 25 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 19:1) on silica gel to give 5-bromo-*N*,*N*,2-trimethylaniline as colorless oil (964 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 1.8 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 2.68 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 132.5, 130.9, 125.3, 121.8, 119.7, 44.1, 18.2; HRMS(EI$^+$) Calcd for $C_9H_{12}BrN$ ([M]$^+$) 213.0153, Found 213.0152.

Biphenyl 1h

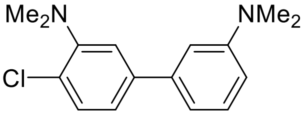


A mixture of (3-(dimethylamino)phenyl)boronic acid (330 mg, 2.00 mmol, 1.0 equiv), 5-bromo-*N*,*N*,2-trimethylaniline (428 mg, 2.00 mmol, 1.0 equiv), Na_2CO_3 (424 mg, 4.00 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (57.8 mg, 0.0500 mmol, 2.5 mol%) in a mixture of toluene (25 mL), water (4 mL) and ethanol (8 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 x 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate 20:1) on silica gel to give **1h** (208 mg, 60%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.8 Hz, 1H), 7.25-7.19 (m, 3H), 6.93 (d, J = 7.8 Hz, 2H), 6.75-6.73 (m, 1H), 3.00 (s, 6H), 2.77 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 151.1, 142.8, 140.9, 131.5, 131.1, 129.4, 121.6, 117.7, 116.0, 111.8, 111.6, 44.4, 40.9, 18.3; HRMS(EI$^+$) Calcd for $C_{17}H_{22}N_2$ ($[M]^+$) 254.1783, Found 254.1783.

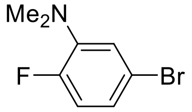


The same method as 5-bromo-*N*,*N*,2-trimethylaniline. 5-Bromo-2-chloroaniline (1.03 g, 5.00 mmol, 1.0 equiv), MeI (1.55 mL, 25.0 mmol, 5.0 equiv) and NaH (600 mg, 15.0 mmol, 3.0 equiv; 60 wt% in mineral oil) were used. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 19:1) on silica gel to give the desired compound as colorless oil (1.022 g, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.2 Hz, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.05 (dd, J = 8.2, 2.3 Hz, 1H), 2.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 131.9, 127.1, 126.0, 123.4, 120.9, 43.7; HRMS(EI$^+$) Calcd for C_8H_9BrClN ($[M]^+$) 232.9607, Found 232.9609.

Biphenyl 1i

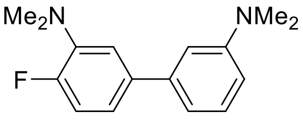


The same method as **1h**. A mixture of (3-(dimethylamino)phenyl)boronic acid (248 mg, 1.50 mmol, 1.0 equiv), 5-bromo-2-chloro-*N*,*N*-dimethylaniline (352 mg, 1.50 mmol, 1.0 equiv), Na_2CO_3 (318 mg, 3.00 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (43.3 mg, 0.0375 mmol, 2.5 mol%) in a mixture of toluene (20 mL), water (2 mL) and ethanol (4 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 × 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 15:1) on silica gel to give **1i** (323 mg, 78%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.16 (dd, J = 8.0, 2.1 Hz, 1H), 6.91-6.86 (m, 2H), 6.76 (dd, J = 8.2, 1.8 Hz, 1H), 3.01 (s, 6H), 2.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 150.5, 142.0, 141.8, 130.9, 129.6, 127.3, 122.2, 119.2, 115.8, 112.0, 111.5, 44.0, 40.8; HRMS(EI$^+$) Calcd for $C_{16}H_{19}ClN_2$ ([M]$^+$) 274.1237, Found 274.1236.

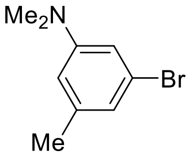


The same method as 5-bromo-*N*,*N*,2-trimethylaniline. 5-Bromo-2-fluoroaniline (1.52 g, 8.00 mmol, 1.0 equiv), MeI (5.68 g, 40.0 mmol, 5.0 equiv) and NaH (960 mg, 24.0 mmol, 3.0 equiv; 60 wt% in mineral oil) were used. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 19:1) on silica gel to give the desired compound as colorless oil (1.30 g, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.98-6.84 (m, 3H), 2.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 ($J_{C\text{-}F}$ = 243.4 Hz), 142.1 ($J_{C\text{-}F}$ = 9.6 Hz), 123.2 ($J_{C\text{-}F}$ = 7.7 Hz), 121.1 ($J_{C\text{-}F}$ = 2.9 Hz), 117.5 ($J_{C\text{-}F}$ = 22.0 Hz), 116.8, 42.6 ($J_{C\text{-}F}$ = 4.8 Hz); HRMS(EI$^+$) Calcd for C_8H_9BrFN ([M]$^+$) 216.9902, Found 216.9903.

Biphenyl 1j.

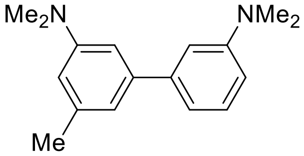


The same method as **1h**. A mixture of (3-(dimethylamino)phenyl)boronic acid (330 mg, 2.00 mmol, 1.0 equiv), 5-bromo-2-fluoro-*N*,*N*-dimethylaniline (436 mg, 2.00 mmol, 1.0 equiv), Na_2CO_3 (424 mg, 4.00 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (57.8 mg, 0.0500 mmol, 2.5 mol%) in a mixture of toluene (25 mL), water (4 mL) and ethanol (8 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 × 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 10:1) on silica gel to give **1j** (421 mg, 81%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.8 Hz, 1H), 7.11-7.05 (m, 3H), 6.90-6.86 (m, 2H), 6.74 (dd, J = 8.2, 2.7 Hz, 1H), 3.01 (s, 6H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 ($J_{C\text{-}F}$ = 244.4 Hz), 151.0, 142.2, 140.8 ($J_{C\text{-}F}$ = 9.6 Hz), 138.90, 138.87, 129.5, 120.1 ($J_{C\text{-}F}$ = 6.7 Hz), 117.7, 116.3 ($J_{C\text{-}F}$ = 22.0 Hz), 116.0, 111.7, 43.0, 40.9; HRMS(EI$^+$) Calcd for $C_{16}H_{19}FN_2$ ([M]$^+$) 258.1532, Found 258.1531.



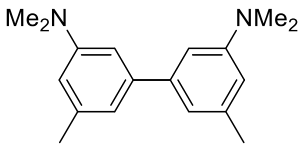
The same method as 5-bromo-*N*,*N*,2-trimethylaniline. 3-Bromo-5-methylaniline (1.12 g, 6.00 mmol, 1.0 equiv), K_2CO_3 (7.50 g, 54.0 mmol, 9.0 equiv), MeI (4.26 g, 30.0 mmol, 5.0 equiv) and DMF (15 mL). The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 9:1) on silica gel to give the desired compound as a colorless oil (1.00 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67-6.65 (m, 2H), 6.43 (s, 1H), 2.92 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 140.5, 123.3, 120.2, 112.6, 111.9, 40.6, 21.8; HRMS(EI$^+$) Calcd for $C_9H_{12}BrN$ ([M]$^+$) 213.0153, Found 213.0154.

Biphenyl 1k



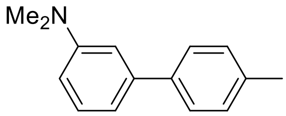
The same method as **1h**. A mixture of (3-(dimethylamino)phenyl)boronic acid (330 mg, 2.00 mmol, 1.0 equiv), 3-bromo-*N*,*N*,5-trimethylaniline (428 mg, 2.00 mmol, 1.0 equiv), Na_2CO_3 (424 mg, 4.00 mmol, 2.0 equiv) and $Pd(PPh_3)_4$ (57.8 mg, 0.0500 mmol, 2.5 mol%) in a mixture of toluene (25 mL), water (4 mL) and ethanol (8 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 × 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 25:1) on silica gel to give **1k** (399 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 8.0 Hz, 1H), 6.95-6.93 (m, 2H), 6.78-6.73 (m, 3H), 6.57 (s, 1H), 3.00 (s, 6H), 2.99 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 151.0, 143.6, 143.5, 139.0, 129.3, 117.4, 116.3, 112.6, 112.1, 111.7, 109.5, 41.0, 40.9, 22.1; HRMS(EI$^+$) Calcd for $C_{17}H_{22}N_2$ ([M]$^+$) 254.1783, Found 254.1779.

Biphenyl 1l



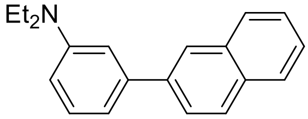
The same method as **1h**. A mixture of (3-(dimethylamino)-5-methylphenyl)boronic acid (269 mg, 1.50 mmol, 1.0 equiv), 3-bromo-*N*,*N*,5-trimethylaniline (321 mg, 1.50 mmol, 1.0 equiv), Na_2CO_3 (318 mg, 3.00 mmol, 2.0 equiv) and $PdCl_2(PPh_3)_2$ (26.3 mg, 0.0380 mmol, 2.5 mol%) in a mixture of toluene (15 mL), water (2 mL) and ethanol (4 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 × 30 mL). The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 30:1) on silica gel to give **1l** (295 mg, 73%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77-6.75 (m, 4H), 6.56 (s, 2H), 2.98 (s, 12H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.6, 138.9, 117.4, 112.5, 109.6, 41.0, 22.1; HRMS(EI$^+$) Calcd for $C_{18}H_{24}N_2$ ([M]$^+$) 268.1939, Found 268.1939.

Biphenyl 1m



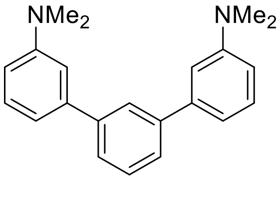
A mixture of 3-(*N*,*N*-dimethylamino)phenylboronic acid (330 mg, 2.00 mmol, 1.0 equiv), *p*-bromotoluene (342 mg, 2.00 mmol, 1.0 equiv), K_2CO_3 (829 mg, 6.00 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (57.8 mg, 0.0500 mmol, 2.5 mol%) in a mixture of water (1.4 mL) and dimethoxyethane (0.7 mL) was heated to 80 °C under nitrogen overnight. After cooled to room temperature, the mixture was diluted with water and EtOAc. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in ethanol. Water was added and the mixture was evaporated to dryness. The crude product was then purified by column chromatography (eluent: hexane/ethyl acetate = 9:1) on silica gel (pretreated with 1% NEt_3 in hexane) to give **1l** (419 mg, 99%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, J = 8.3, 1.9 Hz, 2H), 7.31 (t, J = 8.1 Hz, 1H), 7.25 (d, J = 8.3 Hz, 2H), 6.97-6.89 (m, 2H), 6.74 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.01 (s, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 142.3, 139.5, 137.0, 129.5, 129.5, 127.3, 115.8, 111.6, 111.5, 40.9, 21.3; HRMS(MALDI$^+$) Calcd for $C_{22}H_{24}N_2$ ([M]$^+$) 316.1939, Found 316.1936.

Biphenyl 1n



The same method as **1m**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 0.7 Hz, 1H), 7.91-7.85 (m, 3H), 7.75 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.52-7.45 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.99-6.98 (m, 2H), 6.74-6.71 (m, 1H), 3.44 (q, *J* = 7.0 Hz, 4H), 1.23 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 142.5, 140.0, 135.7, 133.7, 132.7, 129.8, 128.3, 128.0, 127.7, 126.2, 126.1, 125.9, 125.8, 115.0, 111.1, 44.6, 12.8; HRMS(EI$^+$) Calcd for $C_{20}H_{21}N$ ([M]$^+$) 275.1674, Found 275.1676.

***N*^{3},*N*^{3},*N*$^{3''}$,*N*$^{3''}$-tetramethyl-[1,1':3',1''-terphenyl]-3,3''-diamine 6**

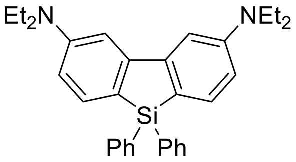


The same method as **1h**. A mixture of (3-(dimethylamino)phenyl)boronic acid (545 mg, 3.30 mmol, 2.2 equiv), 1,3-dibromobenzene (354 mg, 1.50 mmol, 1.0 equiv), Na_2CO_3 (795 mg, 7.50 mmol, 5.0 equiv) and $Pd(PPh_3)_4$ (87.0 mg, 0.0750 mmol, 5.0 mol%) in a mixture of toluene (15 mL), water (2 mL) and ethanol (4 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 is extracted with EtOAc (3 × 30 mL). The combined organic phases are 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 **6** (354 mg, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.6 Hz, 1H), 7.58-7.55 (m, 2H), 7.48 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.01-6.97 (m, 4H), 6.77 (dd, *J* = 8.2, 2.3 Hz, 2H), 3.01 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 142.8, 142.5, 129.6, 129.0, 126.7, 126.3, 116.1, 111.9, 40.9 (one carbon is missing); HRMS(EI$^+$) Calcd for $C_{22}H_{24}N_2$ ([M]$^+$) 316.1939, Found 316.1940.

3. General Procedure for Boron-catalyzed Double Sila-Friedel-Crafts reaction[9]

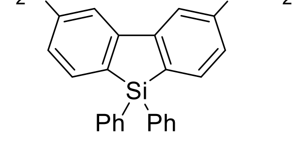
To a test tube with a screw cap equipped with a magnetic stir bar was charged biphenyl **1a** (74.1 mg, 0.250 mmol, 1.0 equiv) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 6.4 mg, 0.013 mmol, 5.0 mol%). The test tube was evacuated and filled with nitrogen. Chlorobenzene (0.50 mL) was added via syringe. Diphenylsilane **2a** (0.14 mL, 138 mg, 0.750 mmol, 3.0 equiv) and 2,6-lutidine (2.2 μL, 2.0 mg, 0.019 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 completion of the reaction, the mixture was cooled to room temperature. The resulting mixture was subjected to ^{1}H NMR spectroscopy. The crude NMR yields were calculated on the basis of 1,1,2,2-tetrachloroethane (26.4 μL, 42.0 mg, 0.25 mmol, 1.0 equiv). The desired silafluorene **3a** was obtained by column chromatography (eluent: hexane/ethyl acetate) on silica gel (pretreated with 1% NEt_3 in hexane) in 87% isolated yield.

Silafluorene 3a



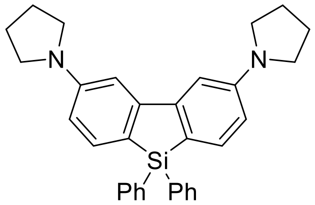
3a was obtained as white solid (104.1 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 4H), 7.57 (d, J = 8.2 Hz, 2H), 7.38-7.28 (m, 6H), 7.16 (s, 2H), 6.64 (d, J = 8.2 Hz, 2H), 3.45 (q, J = 7.1 Hz, 8H), 1.22 (t, J = 7.1 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.9, 135.6, 135.3, 134.8, 129.5, 127.9, 121.4, 111.5, 104.3, 44.6, 12.8; HRMS(EI$^+$) Calcd for $C_{32}H_{36}N_2Si$ ([M]$^+$) 476.2648, Found 476.2647.

Silafluorene 3b



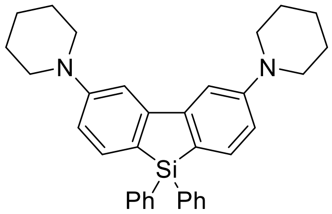
3b was obtained as white solid (1.68 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.0, 1.6 Hz, 4H), 7.62 (d, J = 8.1 Hz, 2H), 7.43-7.28 (m, 6H), 7.26 (d, J = 2.4 Hz, 2H), 6.71 (dd, J = 8.1, 2.4 Hz, 2H), 3.08 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 150.5, 135.6, 134.9, 134.6, 129.6, 127.9, 122.7, 112.2, 105.0, 40.7; HRMS(EI$^+$) Calcd for $C_{28}H_{28}N_2Si$ ([M]$^+$) 420.2022, Found 420.2024.

Silafluorene 3c



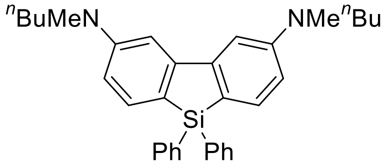
3c was obtained as white solid (106.9 mg, 90%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, *J* = 7.8, 1.4 Hz, 4H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.40-7.23 (m, 6H), 7.07 (d, *J* = 2.3 Hz, 2H), 6.54 (dd, *J* = 7.8, 2.3 Hz, 2H), 3.42 (t, *J* = 6.6 Hz, 8H), 2.02 (quint, *J* = 6.6 Hz, 8H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.7, 150.0, 135.7, 134.6, 129.5, 127.9, 121.7, 112.0, 111.7, 104.5, 47.8, 25.6; HRMS(EI$^+$) Calcd for $C_{32}H_{32}N_2Si$ ([M]$^+$) 472.2335, Found 472.2337.

Silafluorene 3d



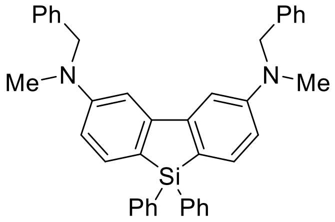
3d was obtained as white solid (101 mg, 81%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (dd, *J* = 6.4, 1.6 Hz, 4H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 1.8 Hz, 2H), 7.43-7.28 (m, 6H), 6.90 (dd, J = 8.0, 2.1 Hz, 2H), 3.30 (t, *J* = 5.5 Hz, 8H), 1.79 (quin, *J* = 5.5 Hz, 8H), 1.63 (quin, *J* = 5.5 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.5, 150.4, 135.6, 134.6, 134.5, 129.7, 128.0, 125.7, 115.8, 109.2, 50.5, 26.0, 24.5; HRMS(EI$^+$) Calcd for $C_{34}H_{36}N_2Si$ ([M]$^+$) 500.2648, Found 500.2649.

Silafluorene 3e



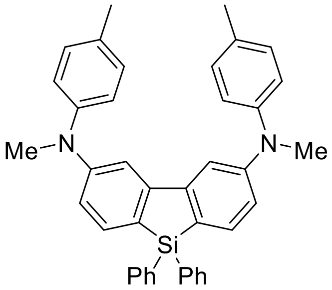
3e was obtained as white solid (105 mg, 82%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66-7.64 (m, 4H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.36-7.29 (m, 6H), 7.20 (d, *J* = 1.8 Hz, 2H), 6.66 (dd, *J* = 8.0, 2.1 Hz, 2H), 3.42 (t, *J* = 7.5 Hz, 4H), 3.05 (s, 6H), 1.63 (q, *J* = 7.5 Hz, 4H), 1.40 (q, *J* = 7.5 Hz, 4H), 0.99 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.4, 150.7, 135.6, 135.2, 134.6, 129.5, 127.9, 121.8, 111.7, 104.5, 52.6, 38.6, 29.1, 20.5, 14.2; HRMS (EI$^+$) Calcd for $C_{34}H_{40}N_2Si$ ([M]$^+$) 504.2961, Found 504.2959.

Silafluorene 3f



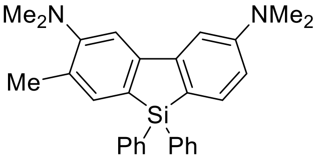
3f was obtained as white solid (111 mg, 78%). ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.64 (dd, *J* = 7.8, 1.4 Hz, 4H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.37-7.23 (m, 16H), 7.15 (d, *J* = 2.5 Hz, 2H), 6.69 (dd, *J* = 7.8, 2.3 Hz, 2H), 4.59 (s, 4H), 3.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 151.9, 150.5, 139.2, 135.6, 135.0, 134.7, 129.6, 128.8, 127.9, 127.1, 126.9, 122.8, 112.2, 105.1, 56.9, 38.9; HRMS(FAB$^+$) Calcd for $C_{40}H_{36}N_2Si$ ([M]$^+$) 572.2648, Found 572.2649.

Silafluorene 3g



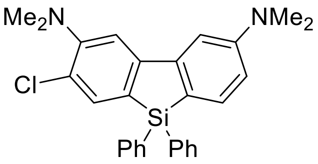
3g was obtained as white solid (48.6 mg, 34%). ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.67-7.65 (m, 4H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.38-7.30 (m, 8H), 7.13 (d, *J* = 8.2 Hz, 4H), 7.05 (dd, *J* = 6.4, 1.8 Hz, 4H), 6.81 (dd, *J* = 8.0, 2.1 Hz, 2H), 3.35 (s, 6H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 151.6, 150.3, 146.2, 135.6, 134.5, 134.3, 132.8, 130.0, 129.8, 128.0, 126.0, 123.4, 117.3, 110.0, 40.4, 20.9; HRMS(EI$^+$) Calcd for $C_{40}H_{36}N_2Si$ ([M]$^+$) 572.2648, Found 572.2648.

Silafluorene 3h



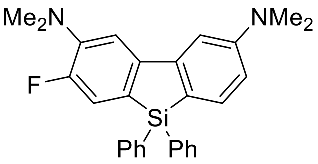
General Procedure using *N*^{3},*N*^{3},*N*$^{3'}$,*N*$^{3'}$,4-pentamethyl-[1,1'-biphenyl]-3,3'-diamine (63.6 mg, 0.250 mmol) and diphenylsilane (138 mg, 0.750 mmol) at 100 °C for 24 h. The desired compound **3h** was obtained as white powder (91.0 mg, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.66-7.64 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 3.7 Hz, 2H), 7.37-7.29 (m, 6H), 7.20 (d, *J* = 1.8 Hz, 1H), 6.68 (dd, *J* = 7.8, 2.3 Hz, 1H), 3.08 (s, 6H), 2.80 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 155.1, 152.7, 150.6, 148.1, 136.5, 135.6, 134.7, 134.5, 131.4, 130.2, 129.7, 128.0, 121.5, 111.9, 110.8, 104.8, 44.1, 40.6, 18.8; HRMS (EI$^+$) Calcd for $C_{29}H_{30}N_2Si$ ([M]$^+$) 434.2178, Found 434.2179.

Silafluorene 3i



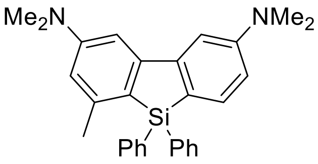
General Procedure using 4-chloro-N^3,N^3,$N^{3'}$,$N^{3'}$-tetramethyl-[1,1'-biphenyl]-3,3'-diamine (68.7 mg, 0.250 mmol) and diphenylsilane (138 mg, 0.750 mmol) at 100 °C for 24 h. The desired compound **3i** was obtained as a white powder (111 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.61 (m, 6H), 7.54 (s, 1H), 7.40-7.32 (m, 6H), 7.17 (d, J = 2.3 Hz, 1H), 6.72 (dd, J = 8.2, 2.3 Hz, 1H), 3.09 (s, 6H), 2.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.4, 149.5, 148.9, 135.6, 135.5, 134.9, 133.6, 131.9, 130.0, 128.1, 127.8, 121.3, 112.6, 112.4, 105.0, 43.9, 40.6; HRMS (EI$^+$) Calcd for $C_{28}H_{27}ClN_2Si$ ([M]$^+$) 454.1632, Found 454.1630.

Silafluorene 3j



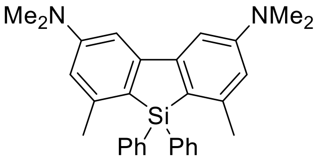
General Procedure using 4-fluoro-N^3,N^3,$N^{3'}$,$N^{3'}$-tetramethyl-[1,1'-biphenyl]-3,3'-diamine (64.6 mg, 0.250 mmol) and diphenylsilane (138 mg, 0.750 mmol) at 100 °C for 24 h. The desired compound **3j** was obtained as white powder (104 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 4H), 7.60 (d, J = 7.8 Hz, 1H), 7.39-7.31 (m, 8H), 7.14 (d, J = 2.3 Hz, 1H), 6.68 (dd, J = 8.2, 2.3 Hz, 1H), 3.08 (s, 6H), 2.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 ($J_{C\text{-}F}$ = 247.6 Hz), 152.8, 149.8, 145.7 ($J_{C\text{-}F}$ = 1.9 Hz), 142.6 ($J_{C\text{-}F}$ = 9.6 Hz), 135.6, 134.8, 133.9, 129.9, 129.1 ($J_{C\text{-}F}$ = 5.8 Hz), 128.1, 121.4, 120.7 ($J_{C\text{-}F}$ = 20.2 Hz), 111.8, 110.9 ($J_{C\text{-}F}$ = 2.9 Hz), 104.9, 42.9 ($J_{C\text{-}F}$ = 3.8 Hz), 40.6; HRMS (EI$^+$) Calcd for $C_{28}H_{27}FN_2Si$ ([M]$^+$) 438.1928, Found 438.1929.

Silafluorene 3k



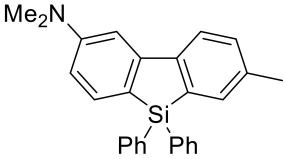
General Procedure using N^3,N^3,$N^{3'}$,$N^{3'}$,5-pentamethyl-[1,1'-biphenyl]-3,3'-diamine (63.6 mg, 0.250 mmol) and diphenylsilane (138 mg, 0.750 mmol) at 100 °C for 24 h. The desired compound **3k** was obtained as a white powder (96 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 4H), 7.50 (d, J = 7.8 Hz, 1H), 7.39-7.29 (m, 6H), 7.23 (d, J = 2.3 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 6.67 (dd, J = 8.0, 2.5 Hz, 1H), 6.49 (d, J = 1.6 Hz, 1H), 3.07 (s, 6H), 3.06 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 152.6, 150.8, 150.6, 144.7, 136.0, 134.4, 129.6, 128.0, 123.3, 122.5, 112.9, 112.3, 105.2, 102.9, 40.7, 24.0 (one carbon is missing); HRMS (EI$^+$) Calcd for $C_{29}H_{30}N_2Si$ ([M]$^+$) 434.2178, Found 434.2181.

Silafluorene 3l



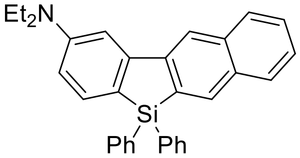
General Procedure using N^3,N^3,$N^{3'}$,$N^{3'}$,5,5'-hexamethyl-[1,1'-biphenyl]-3,3'-diamine (67.1 mg, 0.25 mmol) and diphenylsilane (138 mg, 0.75 mmol) at 100 °C for 24 h. The desired compound **3l** was obtained as a white powder (58.4 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 6.4 Hz, 4H), 7.37-7.30 (m, 6H), 7.11 (d, J = 1.8 Hz, 2H), 6.46 (d, J = 1.6 Hz, 2H), 3.05 (s, 12H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.9, 144.6, 136.2, 133.6, 129.6, 127.9, 122.8, 112.9, 103.0, 40.8, 23.7; HRMS (EI$^+$) Calcd for $C_{30}H_{32}N_2Si$ ([M]$^+$) 448.2335, Found 448.2333.

Silafluorene 3m



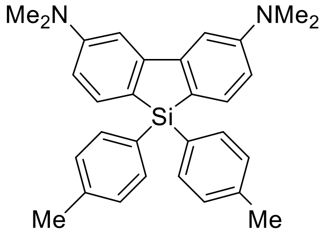
3m was obtained as white solid (39 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.67-7.61 (m, 5H), 7.56 (s, 1H), 7.41-7.31 (m, 6H), 7.27-7.23 (m, 2H), 6.69 (dd, J = 7.8, 2.3 Hz, 1H), 3.07 (s, 6H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 150.4, 146.6, 137.6, 137.3, 135.6, 134.9, 134.5, 134.1, 131.2, 129.9, 128.1, 120.8, 111.9, 105.0, 40.6, 21.5 (one carbon is missing); HRMS(EI$^+$) Calcd for $C_{27}H_{25}NSi$ ([M]$^+$) 391.1756, Found 391.1753.

Silafluorene 3n



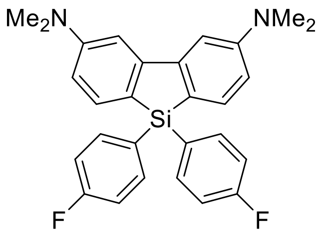
General Procedure using *N,N*-diethyl-3-(naphthalen-2-yl)aniline (68.9 mg, 0.250 mmol) and diphenylsilane (138 mg, 0.750 mmol) at 140 °C. The desired compound **3n** was obtained as white powder (60.4 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 4H), 7.62 (d, J = 7.6 Hz, 1H), 7.38 (dt, J = 35.1, 7.4 Hz, 9H), 6.68 (d, J = 8.2 Hz, 1H), 3.50 (q, J = 6.9 Hz, 4H), 1.28 (t, J = 6.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 150.1, 148.8, 137.0, 136.0, 135.5, 134.9, 133.8, 133.3, 131.3, 129.9, 129.6, 128.8, 128.2, 126.8, 125.5, 120.1, 119.9, 111.3, 104.9, 44.5, 12.9; IR (ATR, ν / cm^{-1}) 3058, 2956, 2925, 2859, 2136, 1729, 1593, 1540, 1466, 1428, 1393, 1374, 1357, 1260, 1201, 1115, 1092, 1076, 1035, 998, 837, 817, 806, 780, 749, 739; HRMS (FAB$^+$) Calcd for $C_{32}H_{29}NSi$ ([M]$^+$) 455.2069, Found 455.2068.

Silafluorene 3o



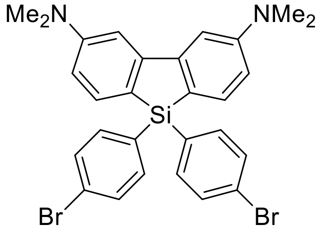
General Procedure using *N*,*N*,*N'*,*N'*-tetramethyl-1,1'-biphenyl-3,3'-diamine (**1b**) (60.1 mg, 0.250 mmol) and di-*p*-tolylsilane (159 mg, 0.750 mmol) at 140 °C. The desired compound **3o** was obtained as yellowish white powder (81.9 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 4H), 7.25 (d, *J* = 1.2 Hz, 2H), 7.15 (d, *J* = 5.2 Hz, 4H), 6.70 (dd, *J* = 4.8, 1.2 Hz, 2H), 3.08 (s, 12H), 2.34 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 150.5, 139.5, 135.7, 134.5, 131.3, 128.8, 123.3, 112.3, 105.1, 40.8, 21.7; IR (ATR, *v* / cm^{-1}); 2924, 2804, 1596, 1544, 1503, 1440, 1426, 1366, 1351, 1309, 1264, 1225, 1184, 1152, 1103, 1057, 1022, 1013, 975, 950, 831, 797, 772, 721; HRMS (FAB$^+$) Calcd for $C_{30}H_{32}N_2Si$ ([M]$^+$) 448.2335, Found 448.2334.

Silafluorene 3p



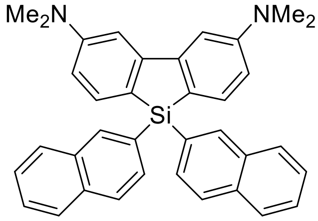
General Procedure using *N*,*N*,*N'*,*N'*-tetramethyl-1,1'-biphenyl-3,3'-diamine **1b** (60.1 mg, 0.250 mmol) and di-*p*-fluorophenylsilane (165 mg, 0.750 mmol) at 140 °C. The desired compound **3p** was obtained as a yellowish white powder (99.3 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.58 (m, 6H), 7.30 (d, *J* = 2.2 Hz, 2H), 7.04 (dd, *J* = 8.4, 8.2 Hz, 4H), 6.72 (dd, *J* = 8.2, 2.2, 2H), 3.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 ($^1J_{C\text{-}F}$ = 247 Hz), 152.7, 150.5, 137.5 ($^3J_{C\text{-}F}$ = 6.8 Hz), 134.4, 130.2 ($^4J_{C\text{-}F}$ = 3.9 Hz), 122.0, 115.2 ($^2J_{C\text{-}F}$ = 20.2 Hz), 112.2, 105.0, 40.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.82 – -110.20 (m); IR (ATR, *v* / cm^{-1}) 1739, 1583, 1542, 1495, 1427, 1359, 1267, 1220, 1158, 1124, 1100, 1055, 1013, 950, 823, 796, 772, 720; HRMS (FAB$^+$) Calcd for $C_{28}H_{26}F_2N_2Si$ ([M]$^+$) 456.1833, Found 456.1834.

Silafluorene 3q



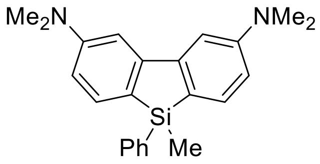
General Procedure using *N*,*N*,*N'*,*N'*-tetramethyl-1,1'-biphenyl-3,3'-diamine **1b** (60.1 mg, 0.250 mmol) and di-*p*-bromophenylsilane (257 mg, 0.750 mmol) at 140 °C. The desired compound **3q** was obtained as white powder (131 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.52-7.47 (m, 8H), 7.26 (d, *J* = 2.4 Hz, 2H), 6.72 (dd, *J* = 8.2, 2.4 Hz, 2H), 3.10 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 150.6, 137.1, 134.4, 133.4, 131.2, 124.8, 121.2, 112.2, 105.0, 40.6; IR (ATR, *v* / cm^{-1}) 2801, 1594, 1545, 1476, 1427, 1369, 1223, 1181, 1106, 1064, 948, 907, 830, 808, 798, 773; HRMS (FAB$^+$) Calcd for $C_{28}H_{26}Br_2N_2Si$ ([M]$^+$) 576.0232, Found 576.0233.

Silafluorene 3r



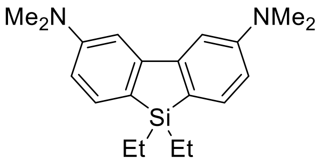
General Procedure using *N*,*N*,*N'*,*N'*-tetramethyl-1,1'-biphenyl-3,3'-diamine **1b** (60.1 mg, 0.250 mmol) and di(naphthalen-2-yl)silane (213 mg, 0.750 mmol) with higher temperature at 140 °C. The desired compound **3r** was obtained as a colorless crystal (105 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.21 (s, 2H), 7.81-7.71 (m, 10H), 7.49-7.41 (m, 4H), 7.29 (d, *J* = 2.3 Hz, 2H), 6.74 (dd, *J* = 8.2, 2.3 Hz, 2H), 3.09 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 152.7, 150.7, 136.7, 134.7, 134.2, 133.1, 132.4, 131.6, 128.4, 127.8, 127.2, 126.6, 125.9, 122.6, 112.3, 105.1, 40.7; IR (ATR, *v* / cm^{-1}) 2922, 2855, 1729, 1592, 1543, 1497, 1443, 1360, 1270, 1224, 1184, 1156, 1085, 1057, 1012, 950, 900, 855, 847, 837, 822, 805, 773, 744, 719; HRMS (FAB$^+$) Calcd for $C_{36}H_{32}N_2Si$ ([M]$^+$) 520.2335, Found 520.2336.

Silafluorene 3s



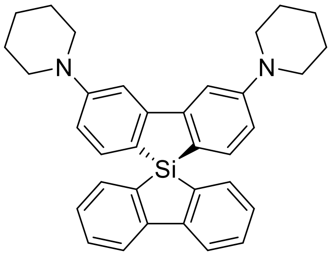
3s was obtained as white solid (71.7 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.57 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.23 (d, *J* = 2.3 Hz, 2H), 6.69 (dd, *J* = 8.2, 2.3 Hz, 2H), 3.07 (s, 12H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 152.5, 150.2, 137.0, 134.6, 134.0, 129.4, 127.9, 124.4, 112.2, 105.0, 40.8, -4.3; HRMS (EI$^+$) Calcd for $C_{23}H_{26}N_2Si$ ([M]$^+$) 358.1865, Found 358.1863.

Silafluorene 3t

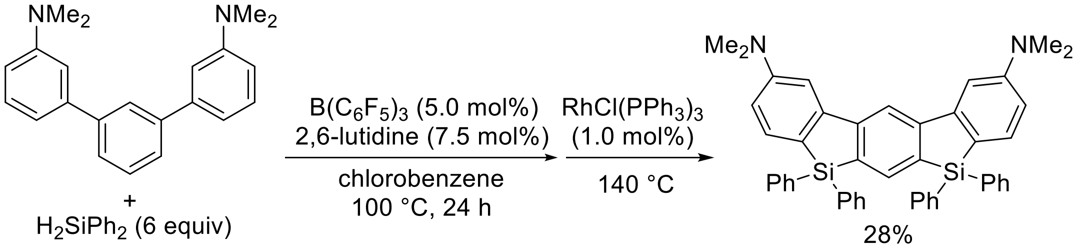


3t was obtained as white solid (70.0 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 2.3 Hz, 2H), 6.69 (dd, *J* = 8.2, 2.3 Hz, 2H), 3.07 (s, 12H), 1.02-0.98 (m, 6H), 0.91-0.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 150.3, 133.8, 124.4, 111.8, 105.0, 40.8, 7.9, 4.6; HRMS(EI$^+$) Calcd for $C_{20}H_{28}N_2Si$ ([M]$^+$) 324.2022, Found 324.2020.

Spirosilabifluorene 5



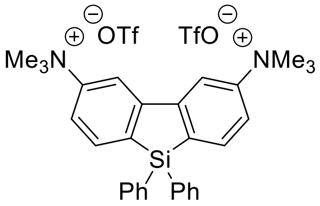
The spirosilabifluorene **5** was synthesized according to the general procedure using 3,3’-di(piperidin-1-yl)-1,1'-biphenyl **1d** (60.1 mg, 0.250 mmol) and 5*H*-dibenzo[*b*,*d*]silole (137 mg, 0.750 mmol) at 100 °C. The desired compound **5** was obtained as white solid (52.0 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.47-7.39 (m, 6H), 7.25-7.16 (m, 4H), 6.76 (dd, *J* = 8.0, 2.1 Hz, 2H), 3.30 (*t*, *J* = 5.5 Hz, 8H), 1.77-1.56 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 151.6, 149.8, 134.9, 134.5, 134.4, 130.9, 127.7, 121.7, 120.8, 115.6, 108.8, 50.3, 26.0, 24.5; HRMS(EI$^+$) Calcd for $C_{34}H_{34}N_2Si$ ([M]$^+$) 498.2491, Found 498.2489.



Scheme S5. Synthesis of the silicon-bridged terphenyl compound **7**

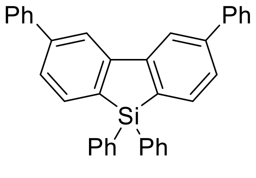
The silicon-bridged terphenyl compound **7** was synthesized according to General Procedure using *N*^{3},*N*^{3},*N*$^{3''}$,*N*$^{3''}$-tetramethyl-[1,1':3',1"-terphenyl]-3,3"-diamine (79.0 mg, 0.250 mmol) and diphenylsilane (276 mg, 1.50 mmol, 6 equiv) at 100 °C. After 24 h, the reaction mixture was cooled to room temperature then 1.0 mol% of $RhCl(PPh_3)_3$ was added. The reaction mixture was heated to 140 °C, and stirred for 24 h. The silicon-bridged terphenyl compound **7** was obtained as white solid (47.0 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.15 (s, 1H), 7.68-7.64 (m, 10H), 7.42-7.29 (m, 14H), 6.76 (dd, J = 8.2, 2.3 Hz, 2H), 3.12 (s, 12H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 151.8, 150.3, 139.3, 136.8, 135.8, 134.9, 134.1, 129.9, 128.1, 122.0, 113.2, 112.7, 105.5, 40.76; HRMS(EI$^+$) Calcd for $C_{46}H_{40}N_2Si_2$ ([M]$^+$) 676.2730, Found 676.2733.

Silafluorene 8



To a dry round bottom flask equipped with a magnetic stir bar was charged **3b** (1.09 g, 2.60 mmol, 1.0 equiv) and CH_2Cl_2 (17 mL). To the resultant stirring solution was added dropwise MeOTf (939 mg, 5.70 mmol, 2.2 equiv) at room temperature. The solution was stirred at room temperature for 2 h. The reaction mixture was concentrated to remove CH_2Cl_2 and the residue was treated with Et_2O (20 mL). The resultant solid was filtered, washed with Et_2O and hexane, and dried under vacuum to give **8** as white solid (1.89 g, 97%). ^{1}H NMR (400 MHz, Acetone-d$_6$) δ 8.96 (d, J = 2.5 Hz, 2H), 8.28 (d, J = 8.2 Hz, 2H), 8.13 (dd, J = 8.2, 2.5 Hz, 2H), 7.71 (dd, J = 7.6, 1.4 Hz, 4H), 7.57-7.49 (m, 2H), 7.45 (t, J = 7.6 Hz, 4H), 3.98 (s, 18H); ^{13}C NMR (100 MHz, Acetone-d$_6$) δ 151.4, 150.3, 139.9, 136.5, 136.1, 135.1, 131.8, 130.9, 129.3, 122.0 (q, J = 8.2, 321.1 Hz), 121.1, 115.7, 57.8; HRMS(FAB$^+$) Calcd for $C_{31}H_{34}F_3N_2O_3SSi^+$ ([M-$^-$OTf]$^+$) 599.2006, Found 599.2012.

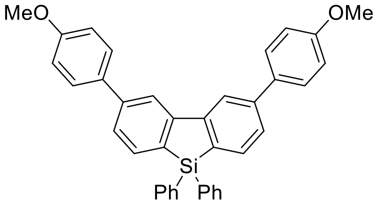
Silafluorene 9



Compound **9** was synthesized according to the reported method. To a dry Schlenk flask equipped with a magnetic stir bar was added the compound **8** (150 mg, 0.200 mmol, 1.0 equiv) and $PdCl_2(PPh_3)_2$ (2.8 mg, 0.0040 mmol, 2.0 mol%). The flask was sealed with a rubber septum, and evacuated/filled with nitrogen. THF (0.4 mL) was added via syringe, and the resultant slurry was stirred for 5 min. Then phenylmagnesium bromide (0.5 M solution in THF, 0.88 mL, 0.44 mmol, 2.2 equiv) was added dropwise at room temperature. After 1 h, the reaction mixture was quenched with water (1 mL) and 6N HCl

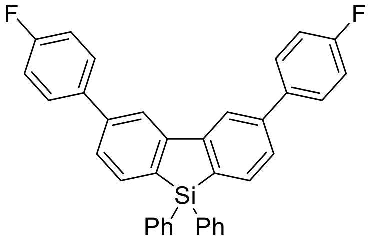
(3 mL), and extracted with Et_2O. The organic extract was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by chromatography on silica gel (eluent: hexane/ethyl acetate = 100:0 to 19:1) to give the compound **9** as white solid (93.2 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 7.92 (d, J = 7.3 Hz, 2H), 7.80-7.71 (m, 8H), 7.61 (d, J = 7.3 Hz, 2H), 7.57-7.37 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 144.0, 141.5, 135.7, 135.1, 134.5, 132.7, 130.3, 129.0, 128.3, 127.8, 127.5, 127.2, 120.3; HRMS(EI$^+$) Calcd for $C_{36}H_{26}Si$ ([M]$^+$) 486.1804, Found 486.1804.

Silafluorene 10



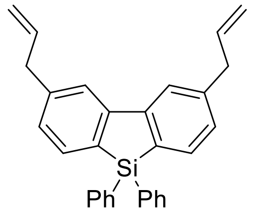
The same method as **9**. The reaction was carried out using 0.15 mmol of **8**. (4-methoxyphenyl)magnesium bromide 1.0 M solutio n in THF, 0.33 mL, 0.33 mmol, 2.2 equiv) were used. The crude product was purified by chromatography on silica gel (eluent: hexane/dichloromethane = 5:1 to 2:1) to give the compound **10** as white solid (43.2 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 1.4 Hz, 2H), 7.84 (d, J = 7.3 Hz, 2H), 7.72-7.70 (m, 4H), 7.63 (dt, J = 9.3, 2.5 Hz, 4H), 7.52 (dd, J = 7.3, 1.4 Hz, 2H), 7.45-7.35 (m, 6H), 7.02 (dt, J = 9.6, 2.5 Hz, 4H), 3.88 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 149.5, 143.6, 135.7, 134.5, 134.0, 133.0, 130.3, 128.5, 128.3, 126.8, 119.8, 114.4, 55.5 (one carbon is missing); HRMS(EI$^+$) Calcd for $C_{38}H_{30}O_2Si$ ([M]$^+$) 546.2015, Found 546.2012.

Silafluorene 11



The same method as **9**. The reaction was carried out using 0.15 mmol of **8**. (4-Fluorophenyl)magnesium bromide (0.5 M solution in THF, 1.2 mL, 0.60 mmol, 4.0 equiv) were used. The crude product was purified by chromatography on silica gel (eluent: hexane/dichloromethane = 5:1) to give the compound **11** as white solid as white solid (55.3 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 1.1 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.70 (dd, J = 7.8, 1.4 Hz, 4H), 7.66-7.63 (m, 4H), 7.51 (dd, J = 7.5, 1.6 Hz, 2H), 7.44-7.36 (m, 6H), 7.20-7.15 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8 ($^1J_{C-F}$ = 245.6 Hz), 149.3, 143.1, 137.6 ($^4J_{C-F}$ = 2.9 Hz), 135.7, 135.3, 134.6, 132.6, 130.4, 129.1 ($^3J_{C\text{-}F}$ = 8.6 Hz), 128.4, 127.1, 120.1, 115.9 ($^2J_{C\text{-}F}$ = 21.5 Hz); HRMS(EI$^+$) Calcd for $C_{36}H_{24}F_2Si$ ([M]$^+$) 522.1615, Found 522.1616.

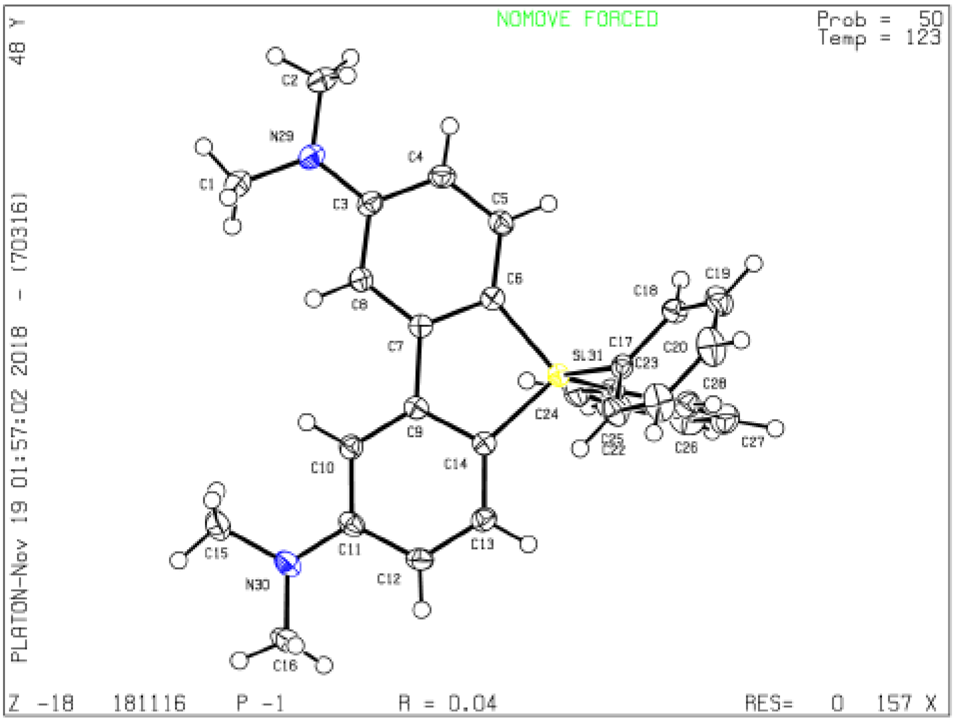
Silafluorene 12



The same method as **9**. The reaction was carried out using 0.15 mmol of **8**. Allylmagnesium bromide (1.0 M solution in THF, 1.2 mL, 0.33 mmol, 2.2 equiv) were used. The crude product was purified by chromatography on silica gel (eluent: hexane/ethyl acetate = 50:1) to give the corresponding silafluorene **12** as white solid (27.6 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 4H), 7.65-7.63 (m, 4H), 7.42-7.31 (m, 6H), 7.15 (dd, J = 7.3, 1.4 Hz, 2H), 6.08-5.98 (m, 2H), 5.19-5.11 (m, 4H), 3.48 (d, J = 6.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 143.0, 137.4, 135.6, 134.2, 133.9, 133.2, 130.1, 128.4, 128.2, 121.7, 116.3, 40.8; HRMS(EI$^+$) Calcd for $C_{30}H_{26}Si$ ([M]$^+$) 414.1804, Found 414.1803.

4. X-ray Structure of Compound 3b

Single crystals of $C_{28}H_{28}N_2Si$, 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene (**3b**), were recrystallized from hot toluene solution. A suitable crystal was selected, and their X-ray diffraction was collected on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71070A). The crystal was kept at 123 K during data collection. The data were collected using ω scan in the θ range of $4.752 \leq \theta \leq 62.052$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,[11] and expanded using Fourier techniques.[12] Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F2 was based on 19804 observed reflections and 6081 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[13] All calculations were performed using the Olex-2 crystallographic software package except for refinement,[14] which was performed using SHELXL-97.5 Details[15] 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 [4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene] (3b)

Crystal Data for $C_{28}H_{28}N_2Si$ (M =420.61 g/mol): triclinic, space group P-1 (no. 2), a = 9.4768(4) Å, b = 10.9099(4) Å, c = 13.1313(5) Å, α = 113.798(3)°, β = 91.992(4)°, γ = 112.004(4)°, V = 1123.73(8) Å^3, Z = 2, T = 123 K, μ(MoKα) = 0.123 mm^{-1}, $Dcalc$ = 1.243 g/cm^3, 19804 reflections measured (4.752° ≤ 2Θ ≤ 62.052°), 6081 unique (R_{int} = 0.0303, R_{sigma} = 0.0328) which were used in all calculations. The final R_1 was 0.0402 (I > 2σ(I)) and wR_2 was 0.1100 (all data).

Table S1. Crystal data and structure refinement for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene (**3b**) .

Identification code	4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene
Empirical formula	$C_{28}H_{28}N_2Si$
Formula weight	420.61
Temperature/K	123
Crystal system	triclinic
Space group	P-1
a/Å	9.4768(4)
b/Å	10.9099(4)
c/Å	13.1313(5)
α/°	113.798(3)
β/°	91.992(4)
γ/°	112.004(4)
Volume/Å^3	1123.73(8)

Z	2
ρ_{calc}g/cm^3	1.243
μ/mm^1	0.123
F(000)	448.0
Crystal size/mm^3	0.359 × 0.274 × 0.133
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.752 to 62.052
Index ranges	$-13 \leq h \leq 12$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$
Reflections collected	19804
Independent reflections	6081 [R_{int} = 0.0303, R_{sigma} = 0.0328]
Data/restraints/parameters	6081/0/284
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0402, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.1100
Largest diff. peak/hole / e Å^{-3}	0.34/-0.27

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si31	2484.7(3)	8754.1(3)	2548.1(3)	16.61(9)
C14	1136.7(13)	8151.3(12)	1210.4(9)	17.8(2)
C9	-187.8(13)	6850.7(12)	997.0(9)	17.4(2)

N29	-2303.6(13)	3266.8(12)	2600.7(9)	28.0(2)
C6	1196.8(13)	7135.5(12)	2736.5(10)	18.7(2)
C23	2711.5(13)	10575.8(13)	3697.0(9)	18.9(2)
N30	-2728.2(13)	6366.3(12)	-1463.7(9)	27.1(2)
C7	-144.1(13)	6267.4(12)	1842.0(9)	17.7(2)
C17	4449.0(13)	8795.5(12)	2384.8(10)	18.1(2)
C27	4234.8(17)	13169.4(14)	4997.2(11)	29.7(3)
C3	-1140.1(14)	4507.2(13)	2609.9(10)	21.6(2)
C18	5509.8(14)	9046.6(13)	3294.6(10)	21.9(2)
C10	-1434.2(14)	6225.0(12)	85.9(10)	20.1(2)
C13	1157.8(14)	8767.0(13)	461.4(10)	21.3(2)
C11	-1422.7(14)	6894.3(13)	-633.7(10)	21.0(2)
C5	1352.5(14)	6636.2(13)	3535.6(10)	22.2(2)
C16	-2604.7(18)	6854.3(16)	-2339.3(11)	32.2(3)
C12	-76.3(15)	8160.4(13)	-443.3(10)	22.9(2)
C8	-1292.2(14)	4981.2(13)	1780.4(10)	20.6(2)
C25	1478.3(17)	12090.9(16)	4839.9(12)	33.4(3)
C28	4134.7(14)	11817.8(13)	4194.3(10)	23.2(2)
C22	4867.9(14)	8468.2(14)	1331.8(10)	25.1(3)
C4	221.4(15)	5348.7(14)	3477.1(10)	23.4(2)
C26	2903.9(18)	13305.5(15)	5313.7(11)	31.7(3)
C2	-1909.3(17)	2556.5(16)	3212.9(13)	35.1(3)

C19	6927.1(15)	8977.2(15)	3156.1(12)	28.4(3)
C1	-3662.4(16)	2360.0(15)	1680.9(12)	31.5(3)
C20	7317.2(16)	8661.3(16)	2101.0(12)	33.6(3)
C24	1384.6(15)	10741.8(15)	4045.0(11)	27.3(3)
C21	6291.4(16)	8406.7(17)	1189.9(12)	33.7(3)
C15	-4033.7(17)	4992.7(15)	-1701.5(13)	34.5(3)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Si31	16.06(15)	16.55(15)	16.44(15)	7.01(12)	2.91(11)	6.63(12)
C14	18.7(5)	17.3(5)	17.8(5)	7.0(4)	4.2(4)	8.9(4)
C9	19.5(5)	17.3(5)	16.9(5)	6.7(4)	4.5(4)	10.2(4)
N29	30.0(6)	23.6(5)	25.7(5)	14.4(4)	2.7(4)	3.3(4)
C6	18.9(5)	18.6(5)	18.6(5)	8.1(4)	4.8(4)	8.2(4)
C23	21.0(5)	20.3(5)	16.6(5)	8.1(4)	3.3(4)	10.1(4)
N30	28.3(5)	27.4(5)	21.9(5)	10.8(4)	-3.3(4)	9.3(5)
C7	19.4(5)	17.6(5)	17.3(5)	7.5(4)	5.2(4)	9.3(4)
C17	17.9(5)	14.9(5)	20.0(5)	6.8(4)	3.1(4)	6.7(4)
C27	36.5(7)	19.4(6)	25.8(6)	7.1(5)	4.0(5)	8.2(5)
C3	24.8(6)	18.9(5)	20.2(5)	9.2(4)	7.3(5)	7.9(5)

C18	22.6(6)	22.4(6)	21.9(5)	10.8(5)	3.5(4)	9.9(5)
C10	20.9(5)	17.4(5)	20.0(5)	7.0(4)	2.5(4)	7.8(4)
C13	23.1(6)	18.5(5)	22.6(6)	10.0(4)	5.2(5)	8.3(5)
C11	25.3(6)	20.3(5)	16.6(5)	5.3(4)	1.4(4)	12.4(5)
C5	22.3(6)	24.0(6)	18.6(5)	9.4(5)	2.7(4)	8.5(5)
C16	42.1(8)	30.7(7)	23.4(6)	12.0(5)	-3.3(6)	16.2(6)
C12	30.4(6)	21.6(6)	20.7(5)	11.7(5)	4.4(5)	12.8(5)
C8	21.2(5)	19.4(5)	18.9(5)	7.9(4)	2.8(4)	7.2(5)
C25	37.9(7)	40.0(8)	30.3(7)	12.4(6)	11.5(6)	27.8(7)
C28	23.9(6)	21.2(6)	23.0(6)	9.0(5)	5.5(5)	9.0(5)
C22	23.0(6)	29.7(6)	18.8(5)	6.9(5)	2.9(5)	11.9(5)
C4	28.4(6)	24.6(6)	19.2(5)	12.5(5)	5.9(5)	10.4(5)
C26	50.3(8)	25.5(6)	21.7(6)	6.4(5)	7.8(6)	23.2(6)
C2	36.3(7)	31.9(7)	36.0(7)	24.2(6)	4.2(6)	3.9(6)
C19	24.3(6)	28.7(6)	31.1(7)	10.8(5)	-0.8(5)	13.7(5)
C1	30.3(7)	26.2(6)	30.5(7)	15.7(5)	2.1(5)	1.7(5)
C20	22.8(6)	36.3(7)	36.2(7)	6.6(6)	5.9(5)	17.8(6)
C24	22.6(6)	29.7(6)	26.8(6)	8.5(5)	3.5(5)	13.1(5)
C21	28.4(7)	40.2(8)	25.1(6)	5.1(6)	9.4(5)	17.3(6)
C15	32.9(7)	26.2(7)	33.3(7)	10.8(6)	-10.2(6)	5.9(6)

Table S4. Bond Lengths for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Si31	C14	1.8526(12)	C7	C8	1.3848(16)
Si31	C6	1.8514(12)	C17	C18	1.3997(16)
Si31	C23	1.8735(12)	C17	C22	1.3939(16)
Si31	C17	1.8671(12)	C27	C28	1.3887(17)
C14	C9	1.4098(16)	C27	C26	1.383(2)
C14	C13	1.3941(16)	C3	C8	1.4052(16)
C9	C7	1.4913(15)	C3	C4	1.4038(17)
C9	C10	1.3896(16)	C18	C19	1.3874(17)
N29	C3	1.3838(15)	C10	C11	1.4065(16)
N29	C2	1.4440(17)	C13	C12	1.3806(17)
N29	C1	1.4383(17)	C11	C12	1.4060(17)
C6	C7	1.4100(16)	C5	C4	1.3809(17)
C6	C5	1.3893(16)	C25	C26	1.379(2)
C23	C28	1.3917(17)	C25	C24	1.3855(18)
C23	C24	1.4024(16)	C22	C21	1.3908(18)
N30	C11	1.3841(15)	C19	C20	1.386(2)
N30	C16	1.4407(17)	C20	C21	1.379(2)
N30	C15	1.4423(17)			

Table S5. Bond Angles for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C14	Si31	C23	112.68(5)	C8	C7	C6	121.09(10)
C14	Si31	C17	115.18(5)	C18	C17	Si31	121.14(9)
C6	Si31	C14	91.83(5)	C22	C17	Si31	121.21(9)
C6	Si31	C23	113.97(5)	C22	C17	C18	117.48(10)
C6	Si31	C17	112.72(5)	C26	C27	C28	120.11(12)
C17	Si31	C23	109.63(5)	N29	C3	C8	121.68(11)
C9	C14	Si31	109.49(8)	N29	C3	C4	120.13(11)
C13	C14	Si31	132.95(9)	C4	C3	C8	118.18(11)
C13	C14	C9	117.45(10)	C19	C18	C17	121.34(11)
C14	C9	C7	114.59(10)	C9	C10	C11	120.74(11)
C10	C9	C14	121.09(10)	C12	C13	C14	122.01(11)
C10	C9	C7	124.28(10)	N30	C11	C10	120.83(11)
C3	N29	C2	118.79(11)	N30	C11	C12	121.15(11)
C3	N29	C1	120.18(11)	C12	C11	C10	117.93(11)
C1	N29	C2	116.47(11)	C4	C5	C6	121.51(11)
C7	C6	Si31	109.64(8)	C13	C12	C11	120.66(11)
C5	C6	Si31	132.42(9)	C7	C8	C3	120.49(11)
C5	C6	C7	117.88(10)	C26	C25	C24	119.87(12)
C28	C23	Si31	123.28(9)	C27	C28	C23	121.32(12)
C28	C23	C24	117.32(11)	C21	C22	C17	121.42(12)

C24	C23	Si31	119.32(9)	C5	C4	C3	120.80(11)
C11	N30	C16	119.94(11)	C25	C26	C27	119.85(12)
C11	N30	C15	119.43(11)	C20	C19	C18	119.88(12)
C16	N30	C15	117.13(11)	C21	C20	C19	119.93(12)
C6	C7	C9	114.39(10)	C25	C24	C23	121.52(12)
C8	C7	C9	124.51(10)	C20	C21	C22	119.94(12)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4,6-bis(dimethylamino)-9,9-diphenyl-9H-9-silafluorene.

Atom	***x***	***y***	***z***	**U(eq)**
H8AA	5198.41	13984.42	5322.58	36
H0BA	5259.54	9264.35	4006.49	26
H1BA	-2285.6	5353.83	-49.46	24
H2BA	2029.71	9612.02	574.57	26
H4BA	2238.74	7181.53	4123.26	27
HA	-2157.99	7915.9	-1991.95	48
HB	-3623.34	6462.62	-2799.43	48
HC	-1950.45	6509.41	-2809.85	48
H5BA	-16.43	8593.65	-931.66	27
H6BA	-2170.35	4427.08	1185.58	25
H7BA	581.74	12177.51	5053.62	40
H8BA	5036.72	11741.11	3984.74	28

H9BA	4180.65	8286.92	710.7	30
H0CA	363.25	5035.29	4018.69	28
H1CA	2969.87	14213.68	5844.78	38
H2CA	-995.82	2414.84	3019.64	53
H2CB	-2762.59	1614.23	3007.51	53
H2CC	-1707.46	3168.23	4018.5	53
H3CA	7614.15	9142.5	3770.2	34
H4CA	-4077.6	2976.74	1552.27	47
H4CB	-4435.61	1672.27	1875.98	47
H4CC	-3381.07	1825.71	1000.68	47
H5CA	8269.64	8620.92	2007.47	40
H6CA	419.51	9927.44	3735.15	33
H7CA	6551.43	8194.21	481.32	40
H8CA	-3707.71	4204.17	-1962.63	52
H8CB	-4850.85	4789.2	-2280.89	52
H8CC	-4411.7	5070.41	-1019.4	52

5. NMR Spectra

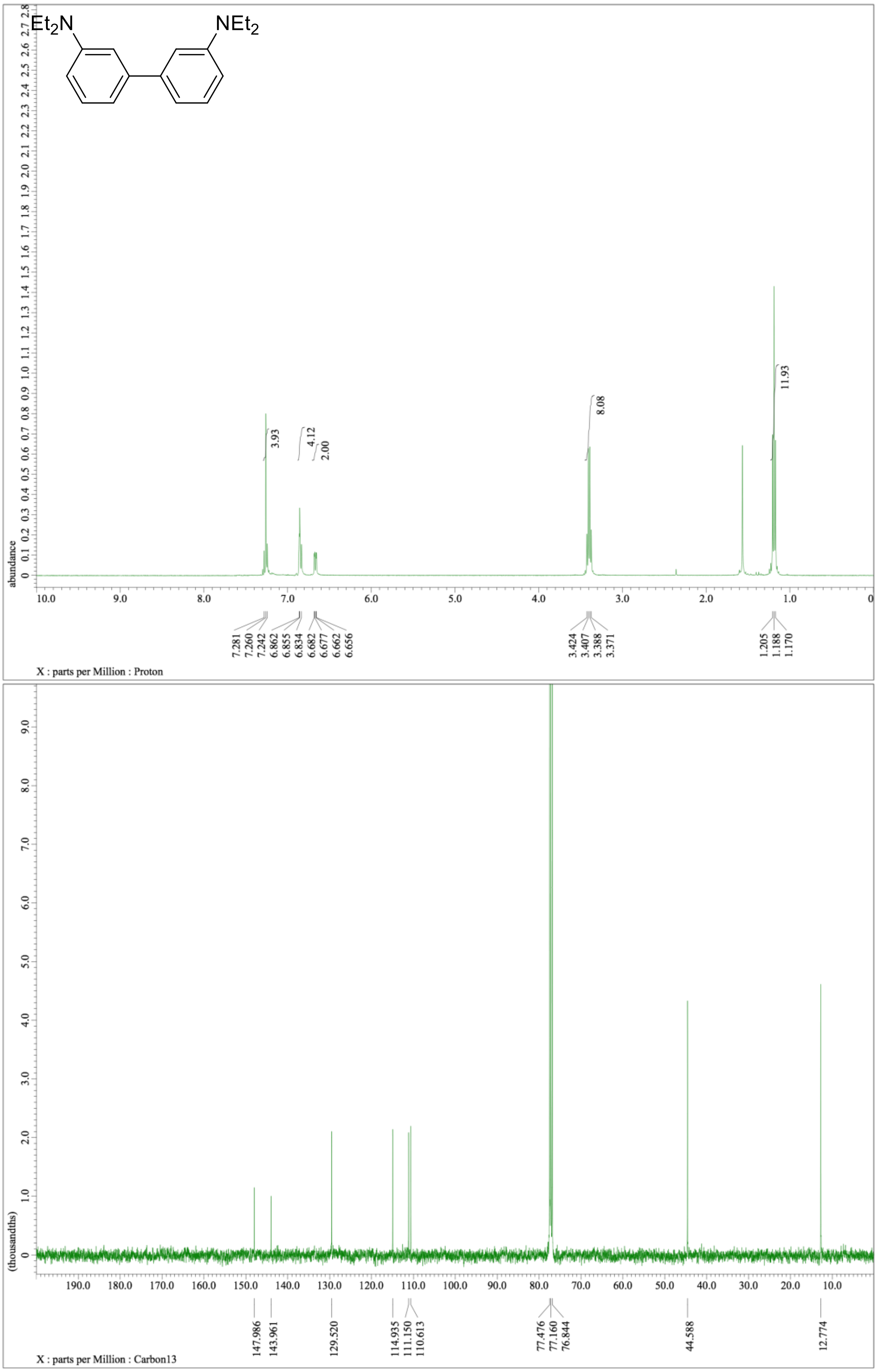


Figure S1. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1a**

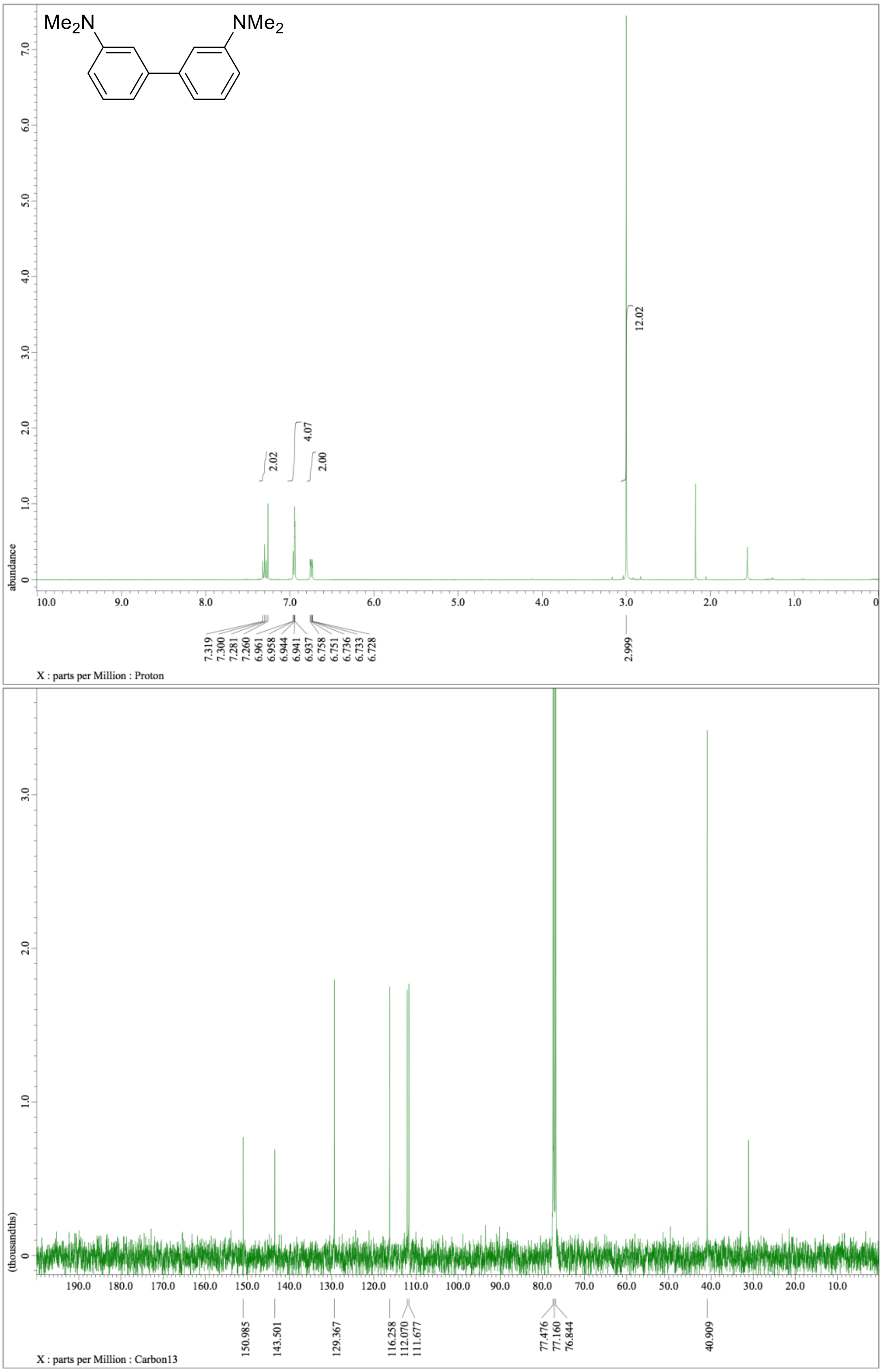


Figure S2. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1b**

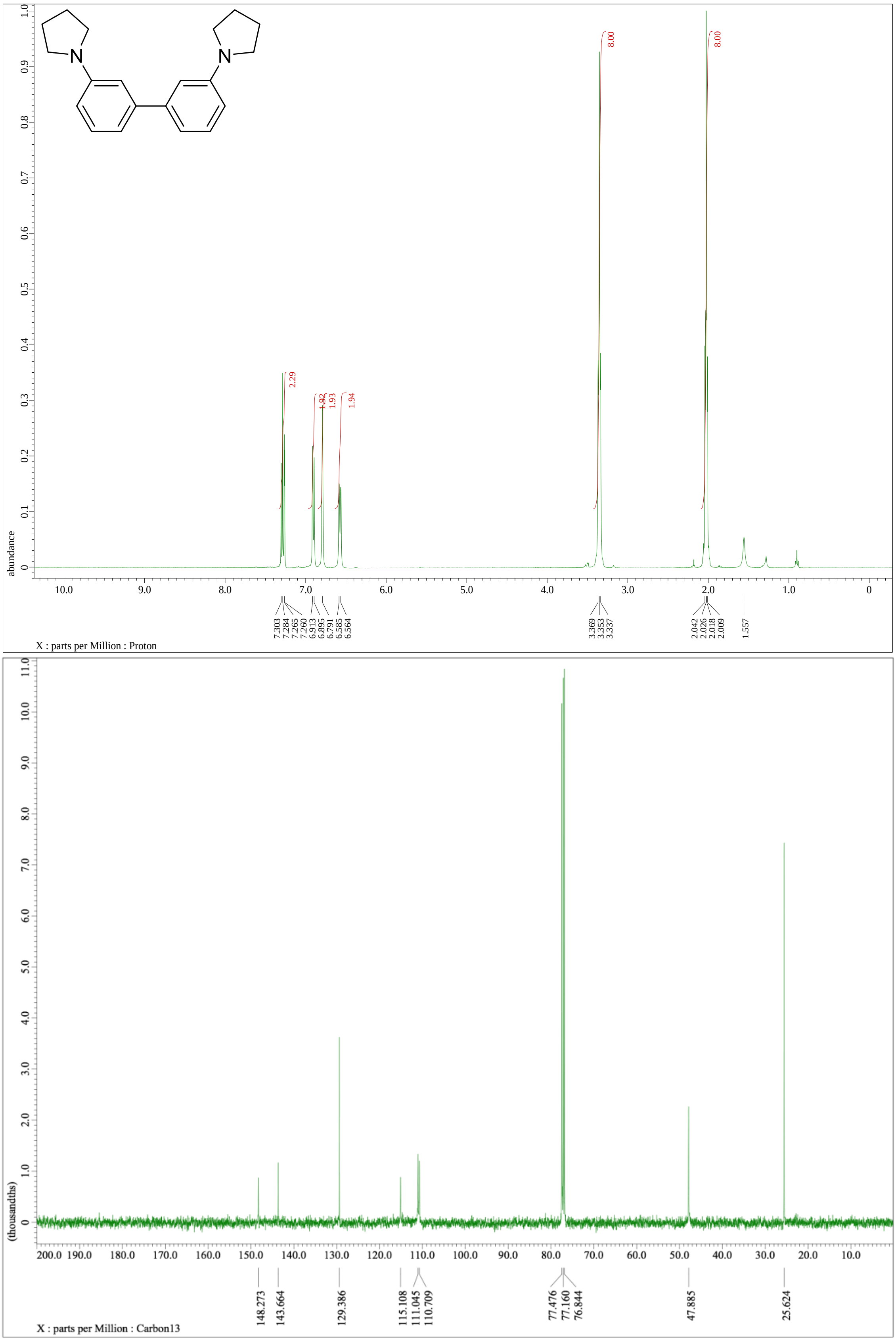


Figure S3. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1c**

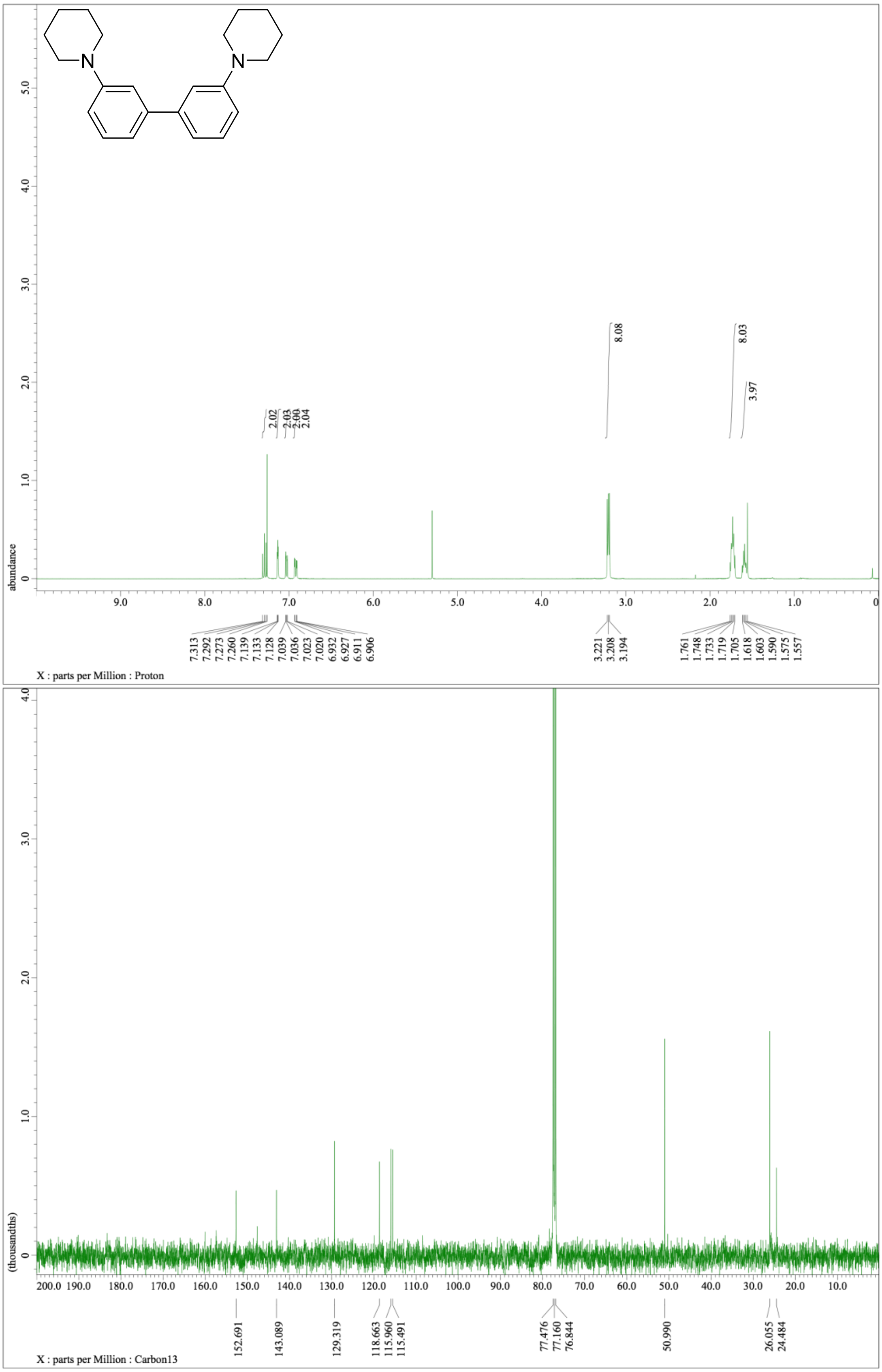


Figure S4. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1d**

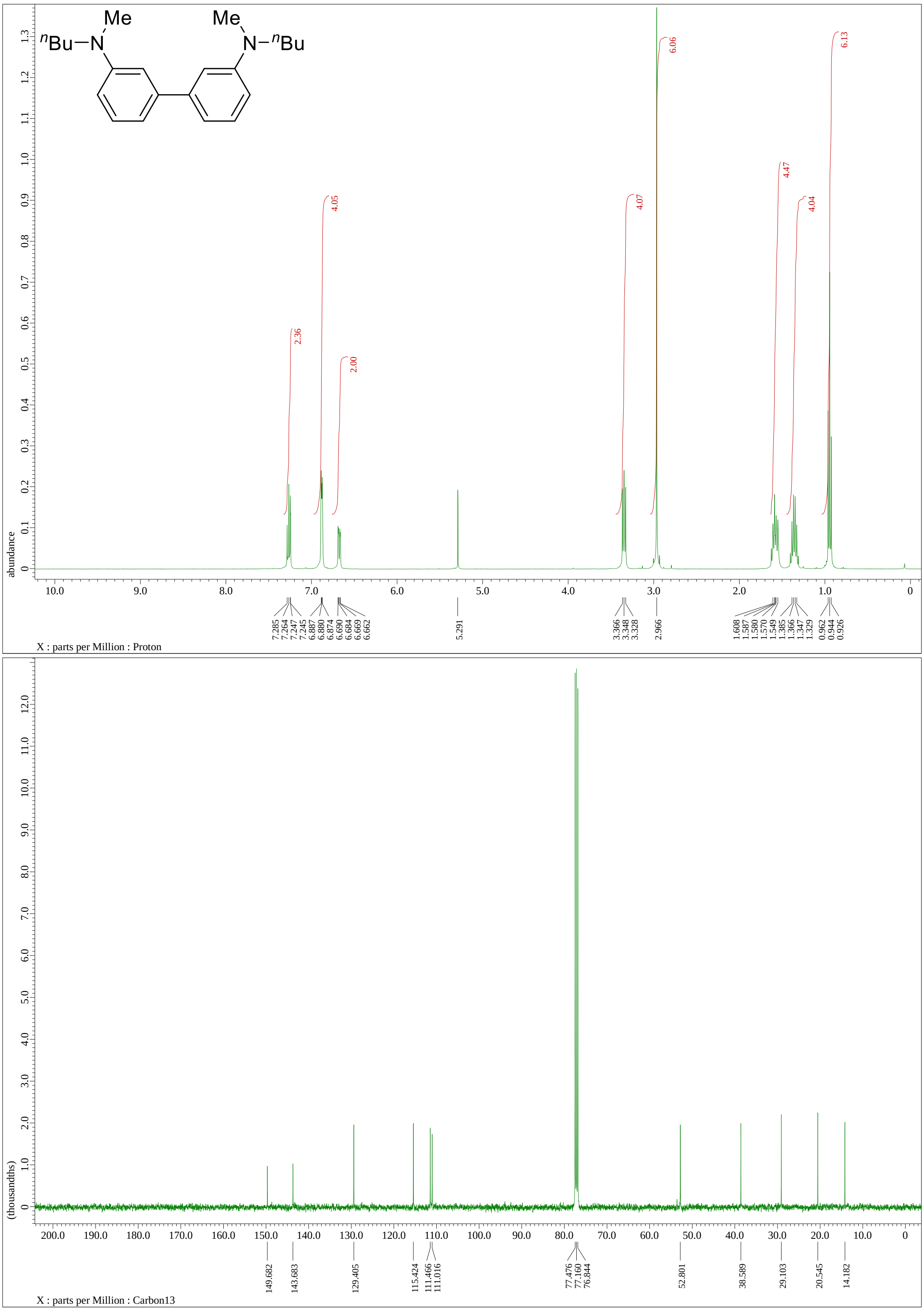


Figure S5. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1e**

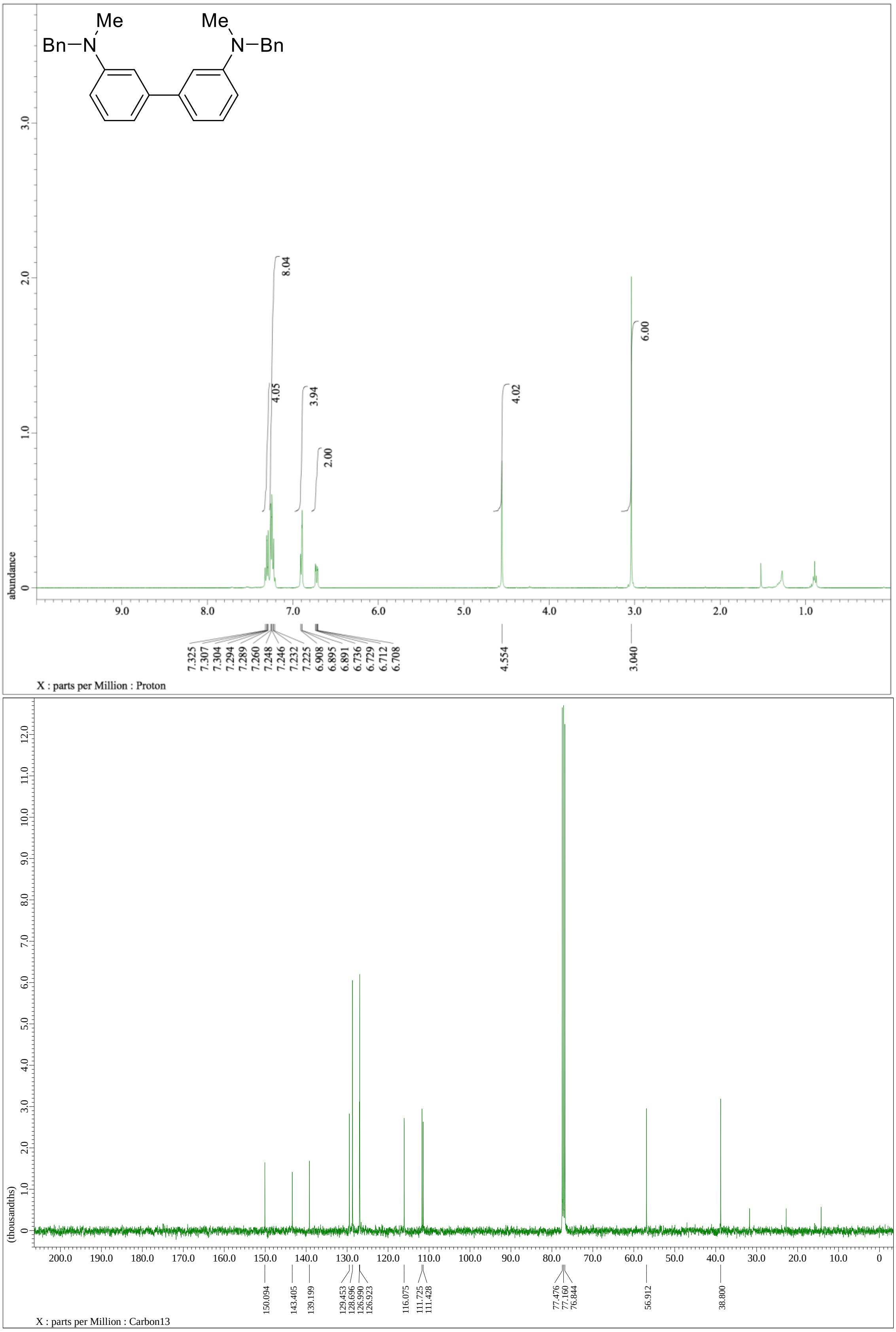


Figure S6. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1f**

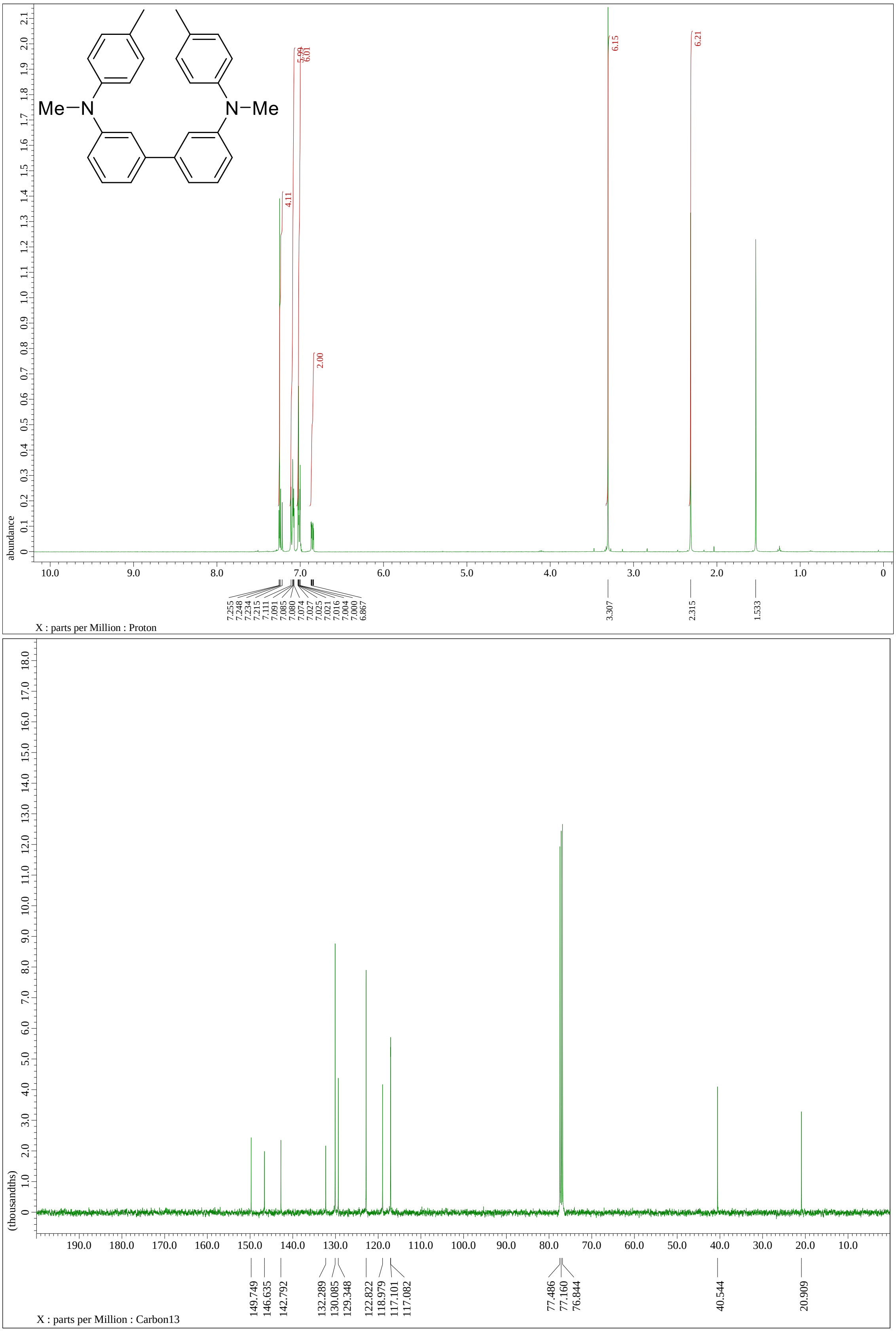


Figure S7. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1g**

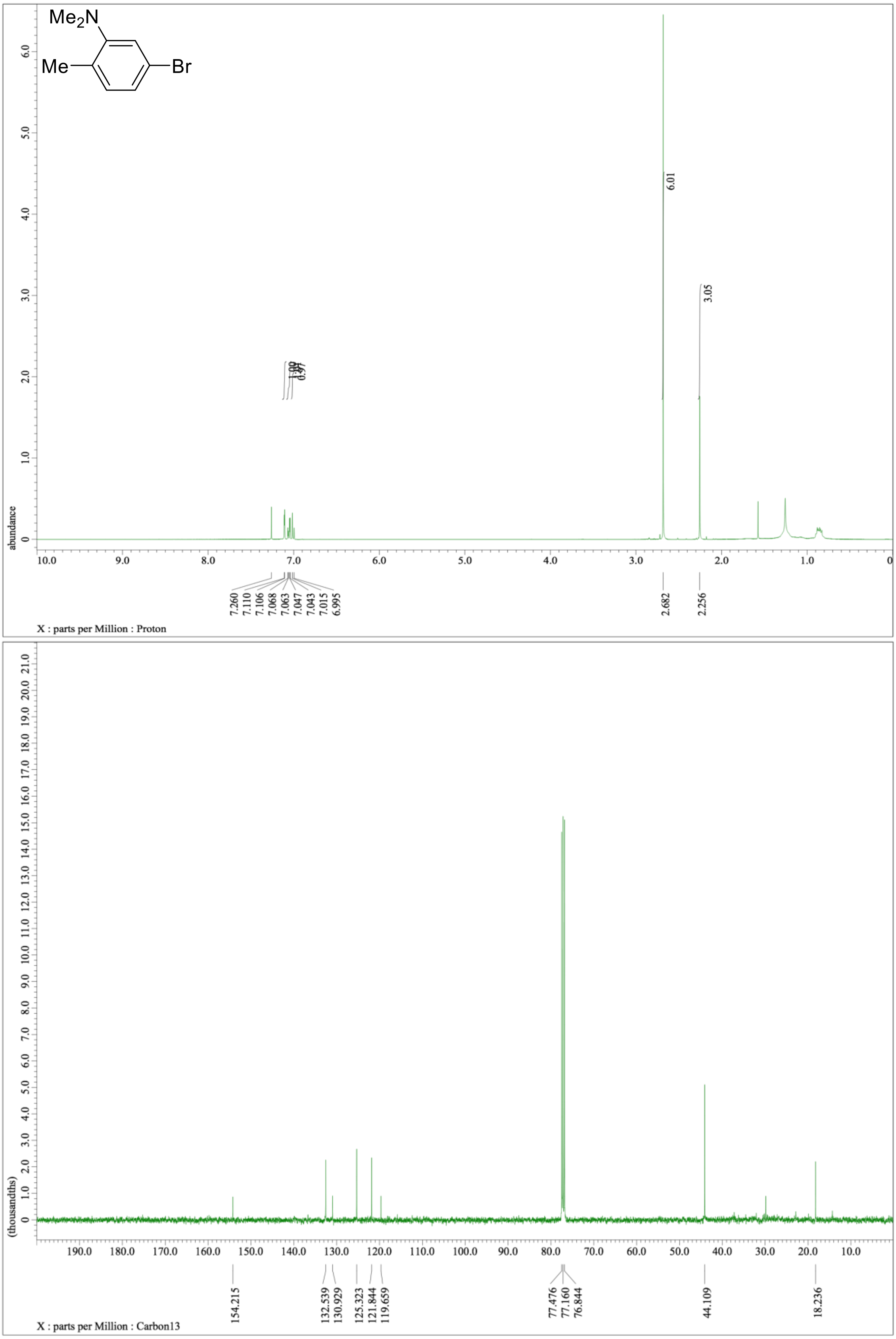


Figure S8. ^{1}H NMR (top) and ^{13}C NMR (bottom) of 5-Bromo-*N*,*N*,2-trimethylaniline

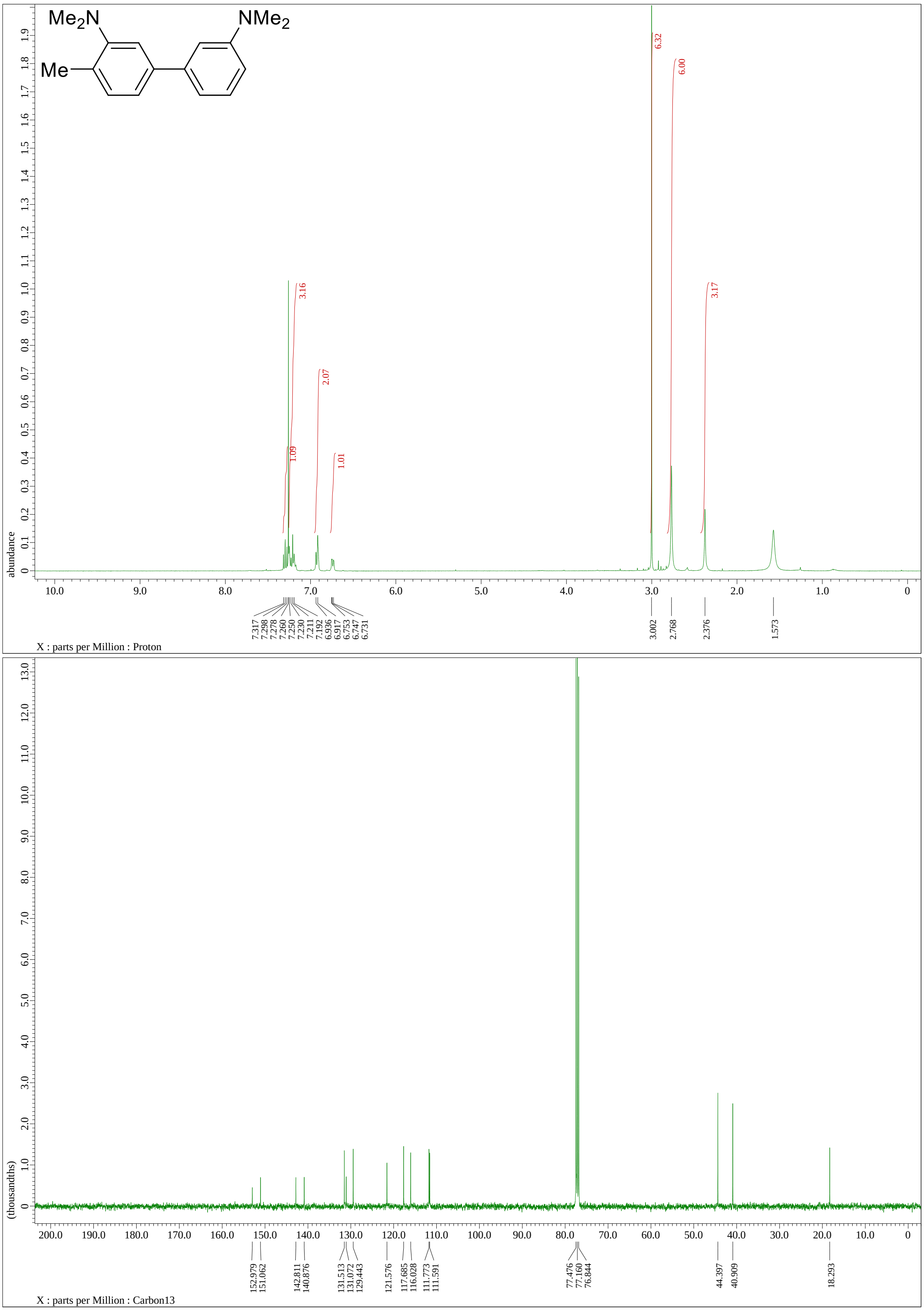


Figure S9. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1h**

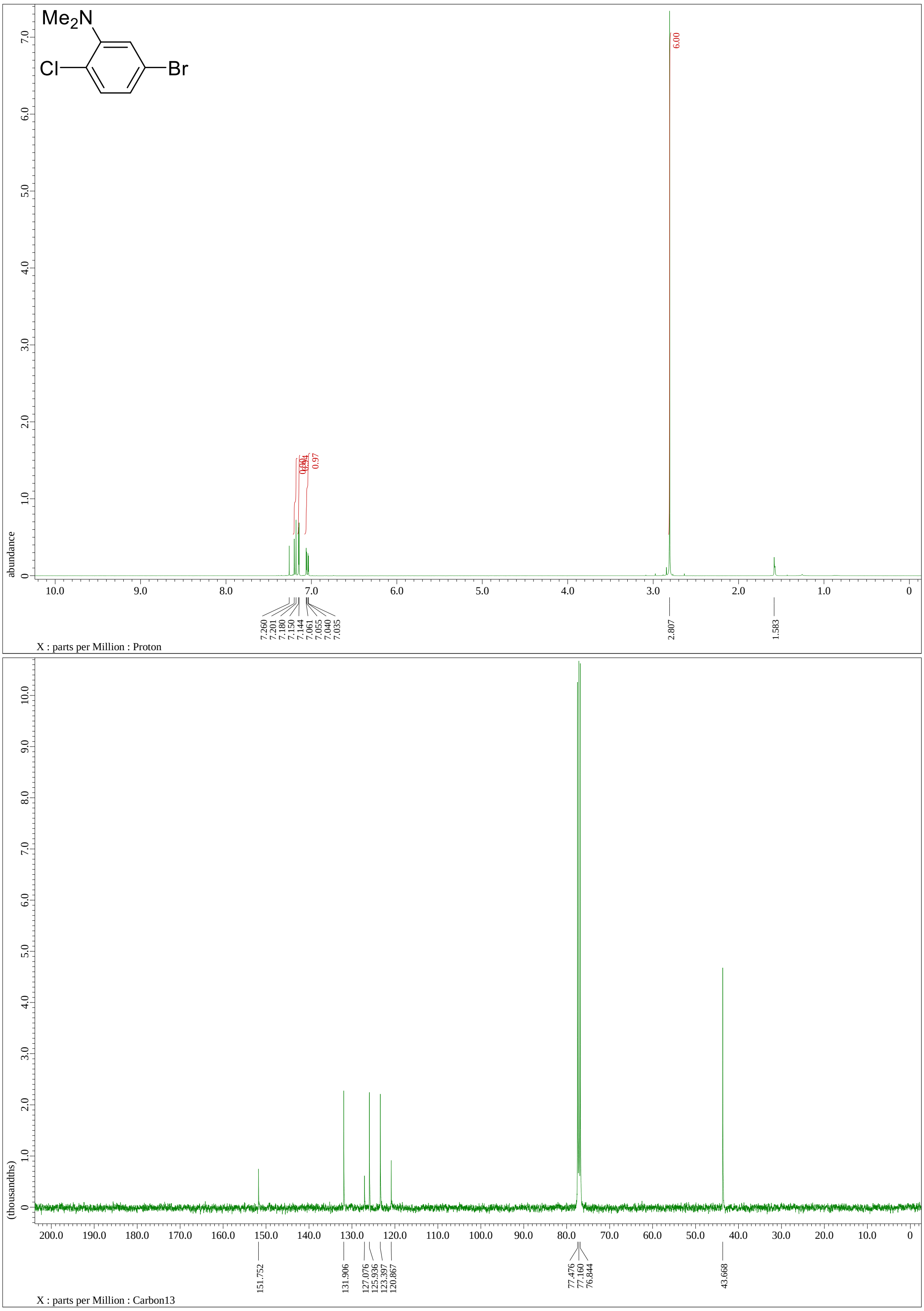


Figure S10. ^{1}H NMR (top) and ^{13}C NMR (bottom) of 5-bromo-2-chloro-*N*,*N*-dimethylaniline

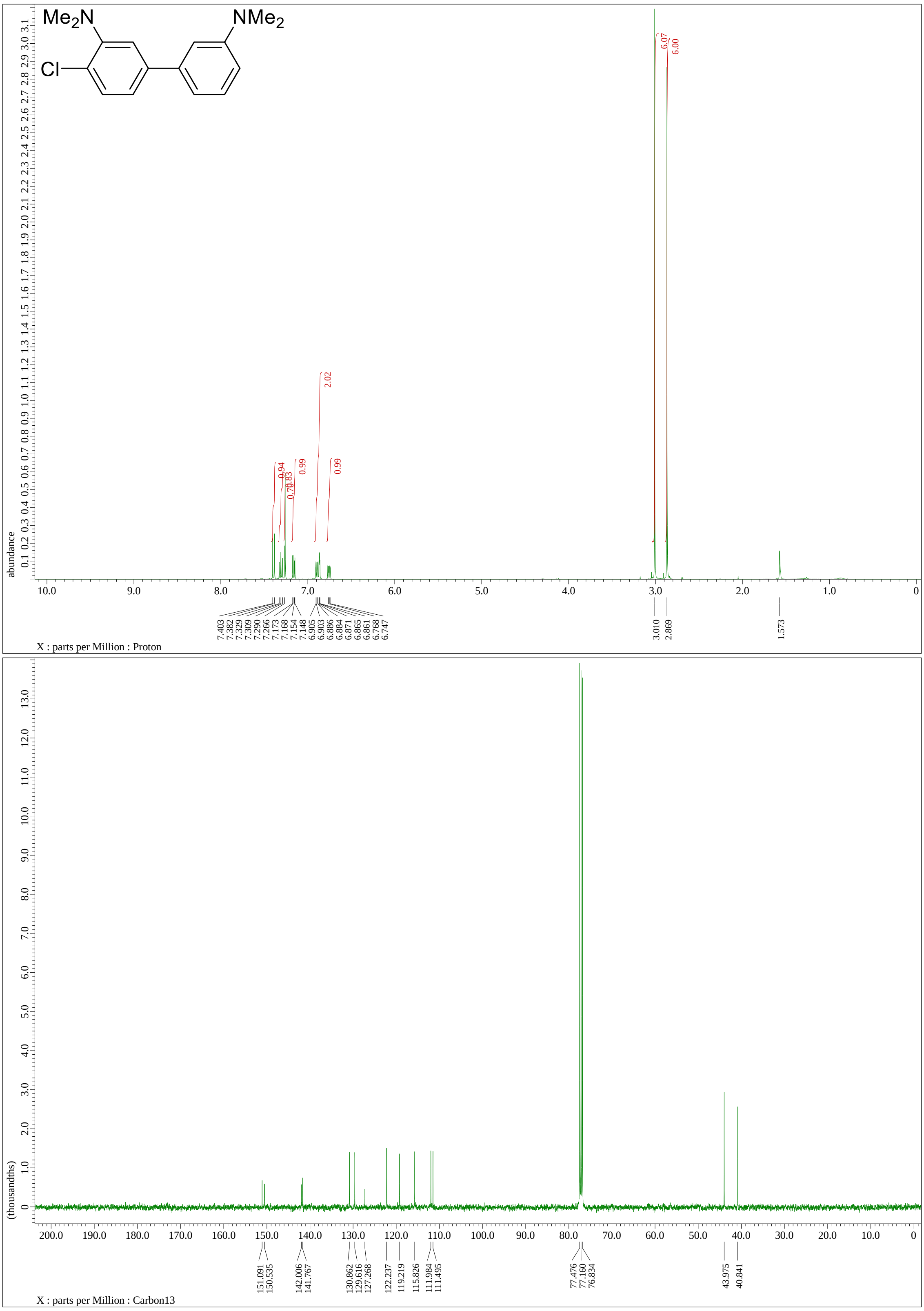


Figure S11. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1i**

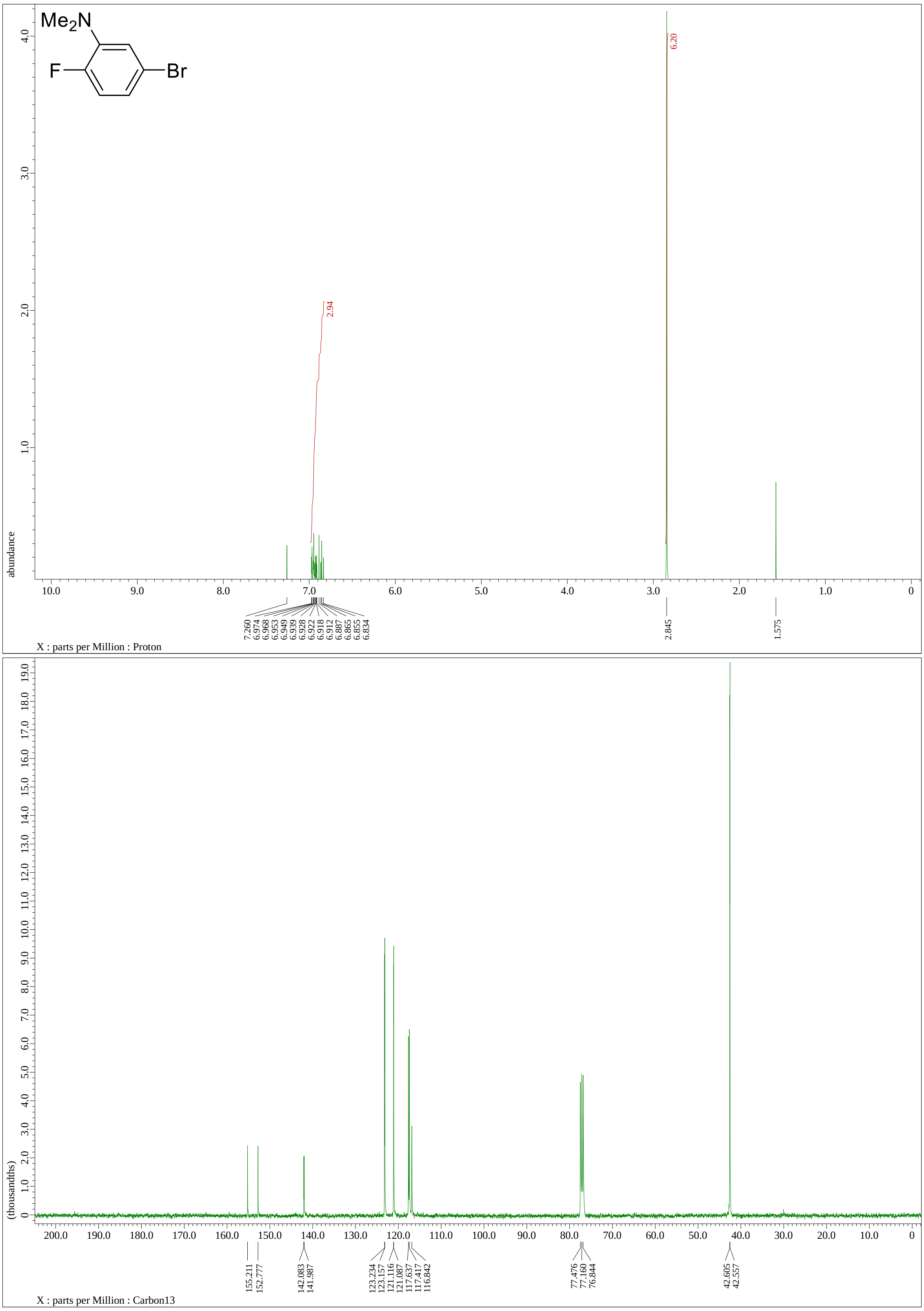


Figure S12. ^{1}H NMR (top) and ^{13}C NMR (bottom) of 5-bromo-2-fluoro-*N*,*N*-dimethylaniline

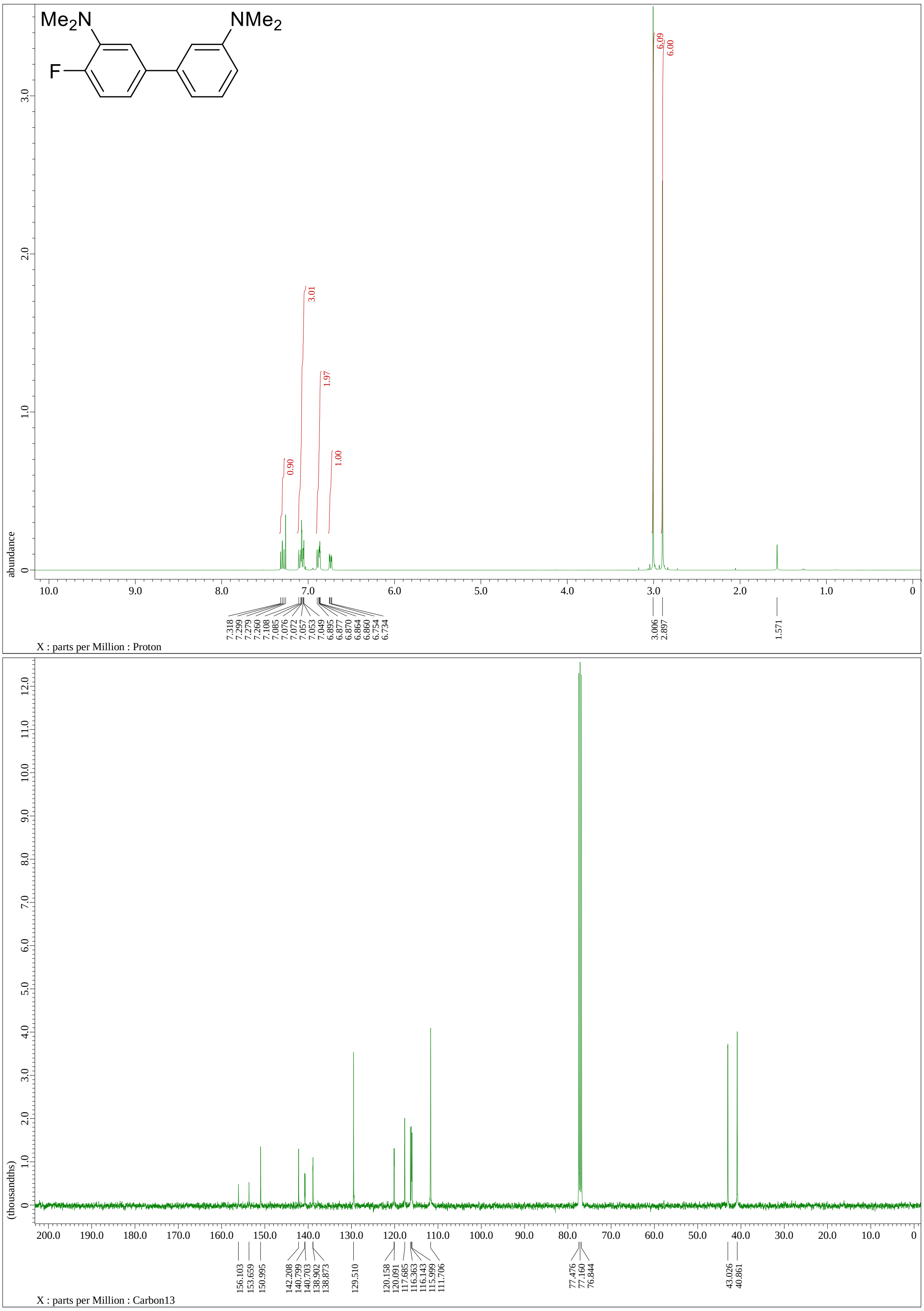


Figure S13. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1j**

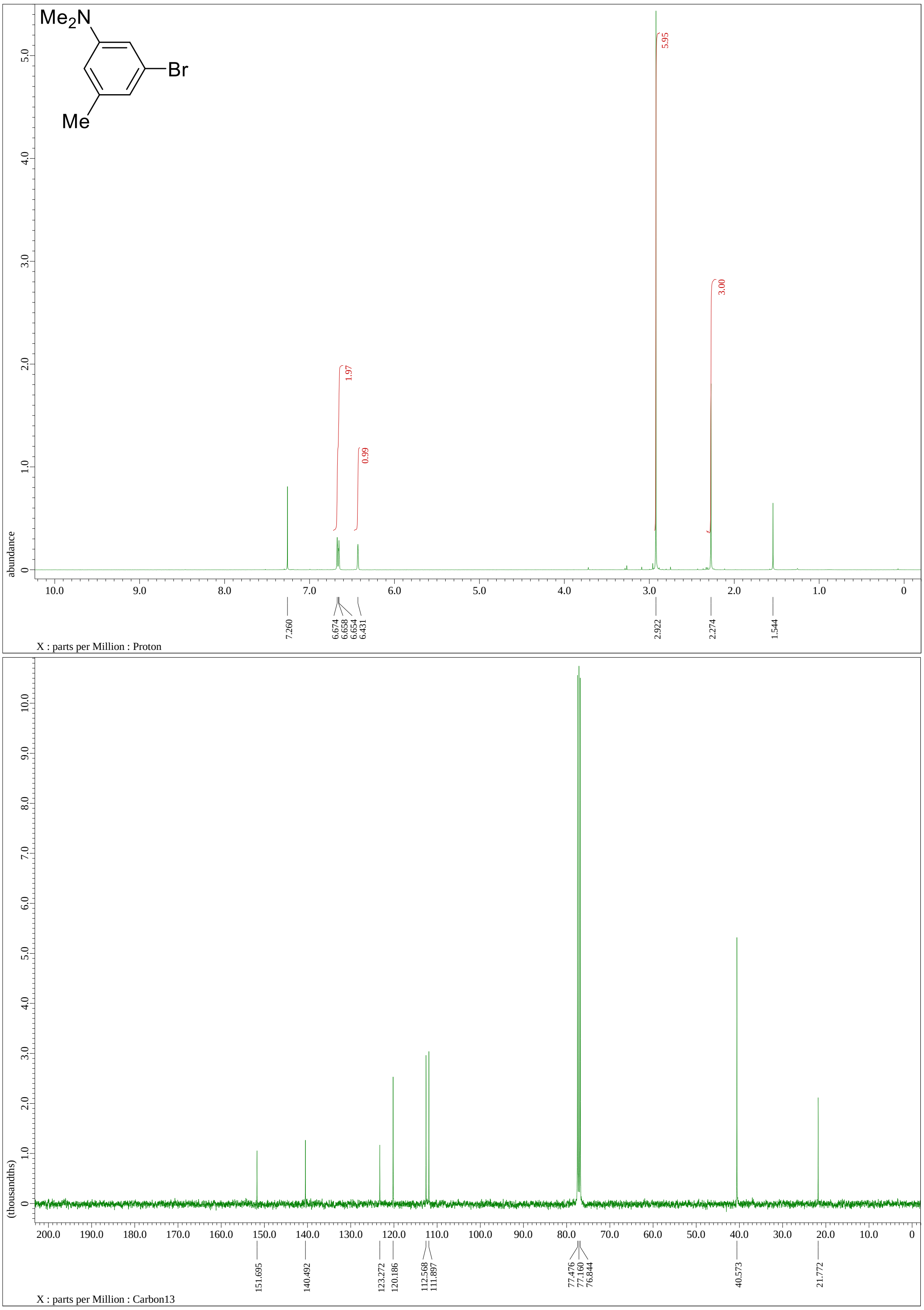


Figure S14. ^{1}H NMR (top) and ^{13}C NMR (bottom) of 3-bromo-*N*,*N*,5-trimethylaniline

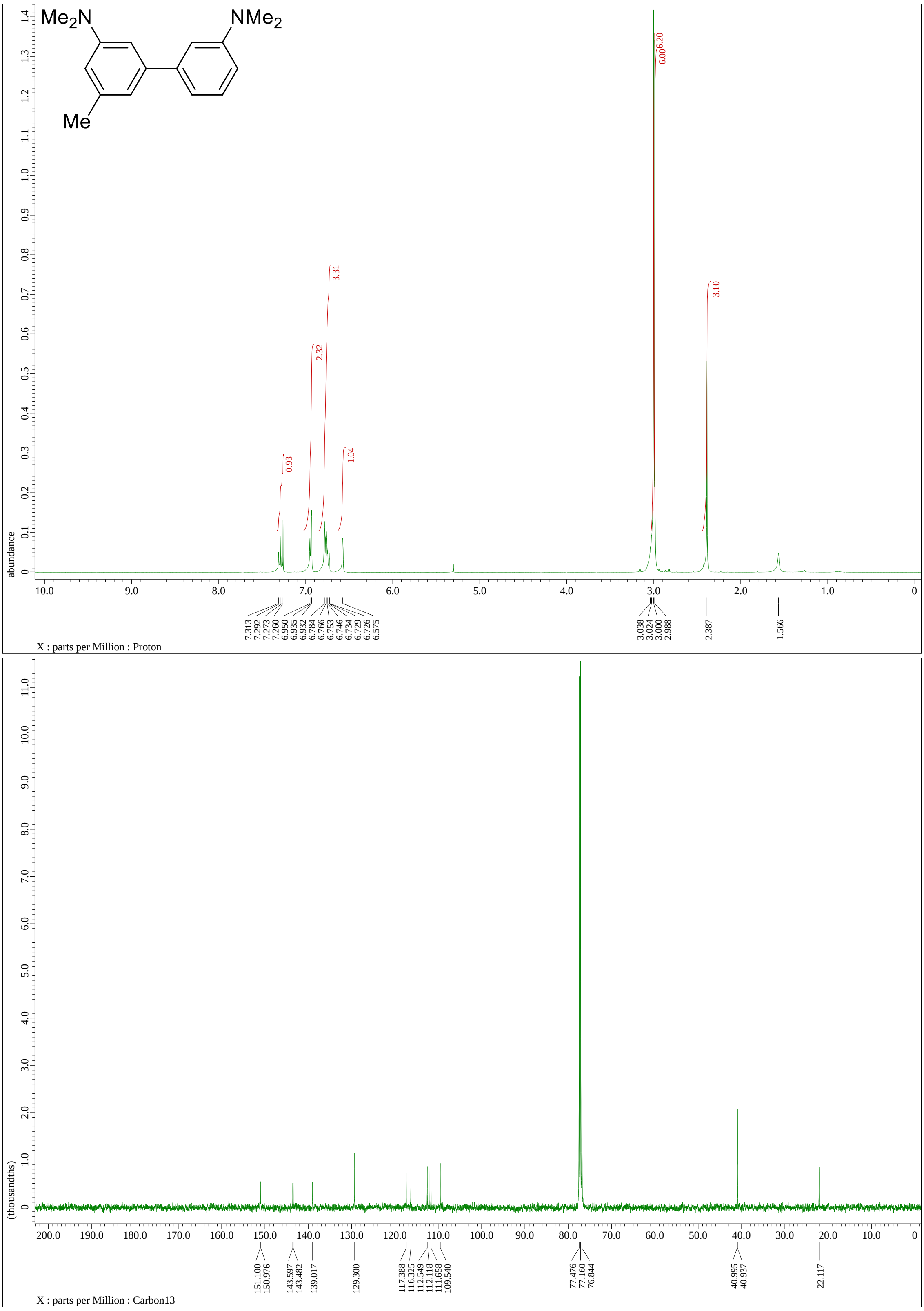


Figure S15. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1k**

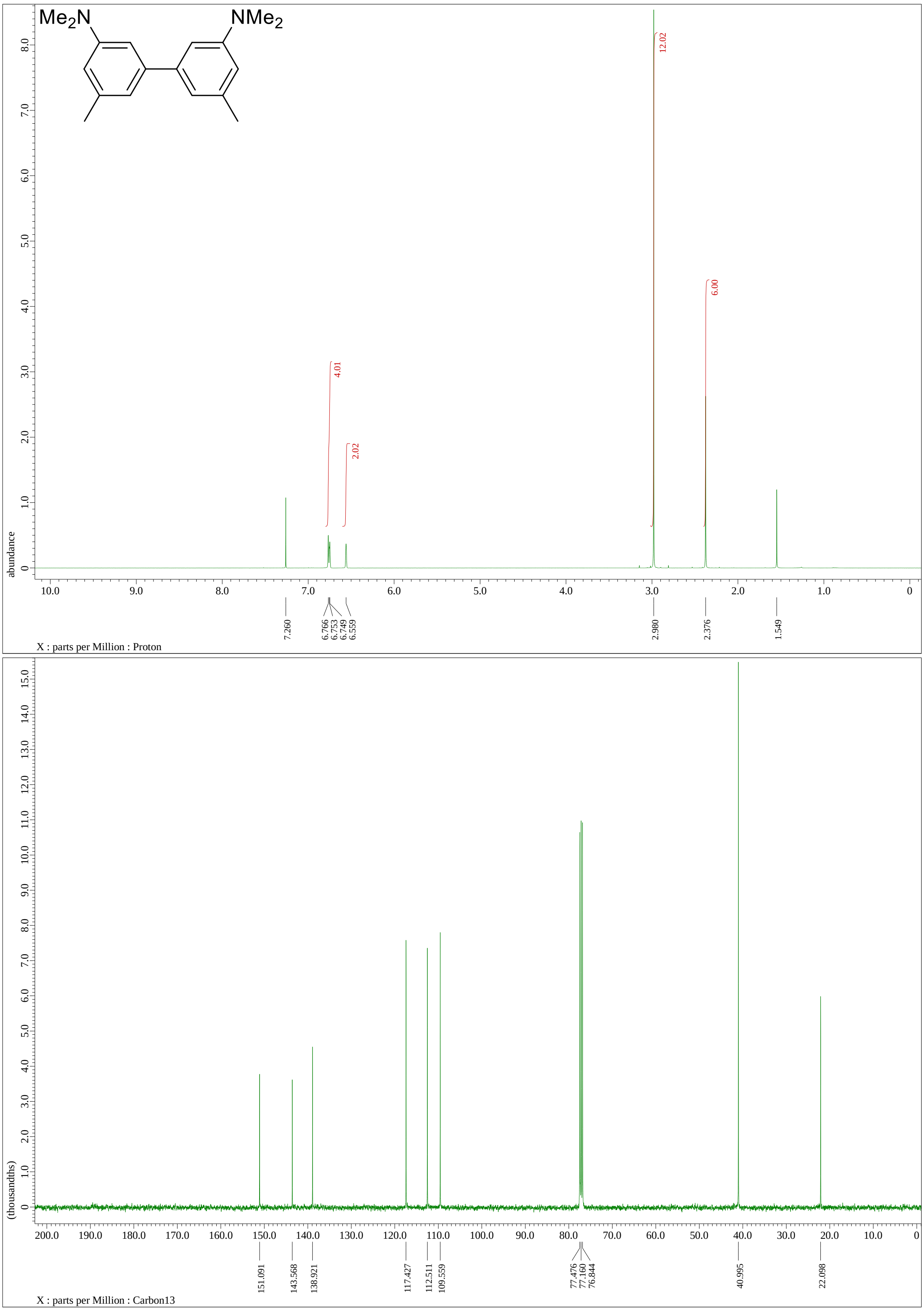


Figure S16. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1l**

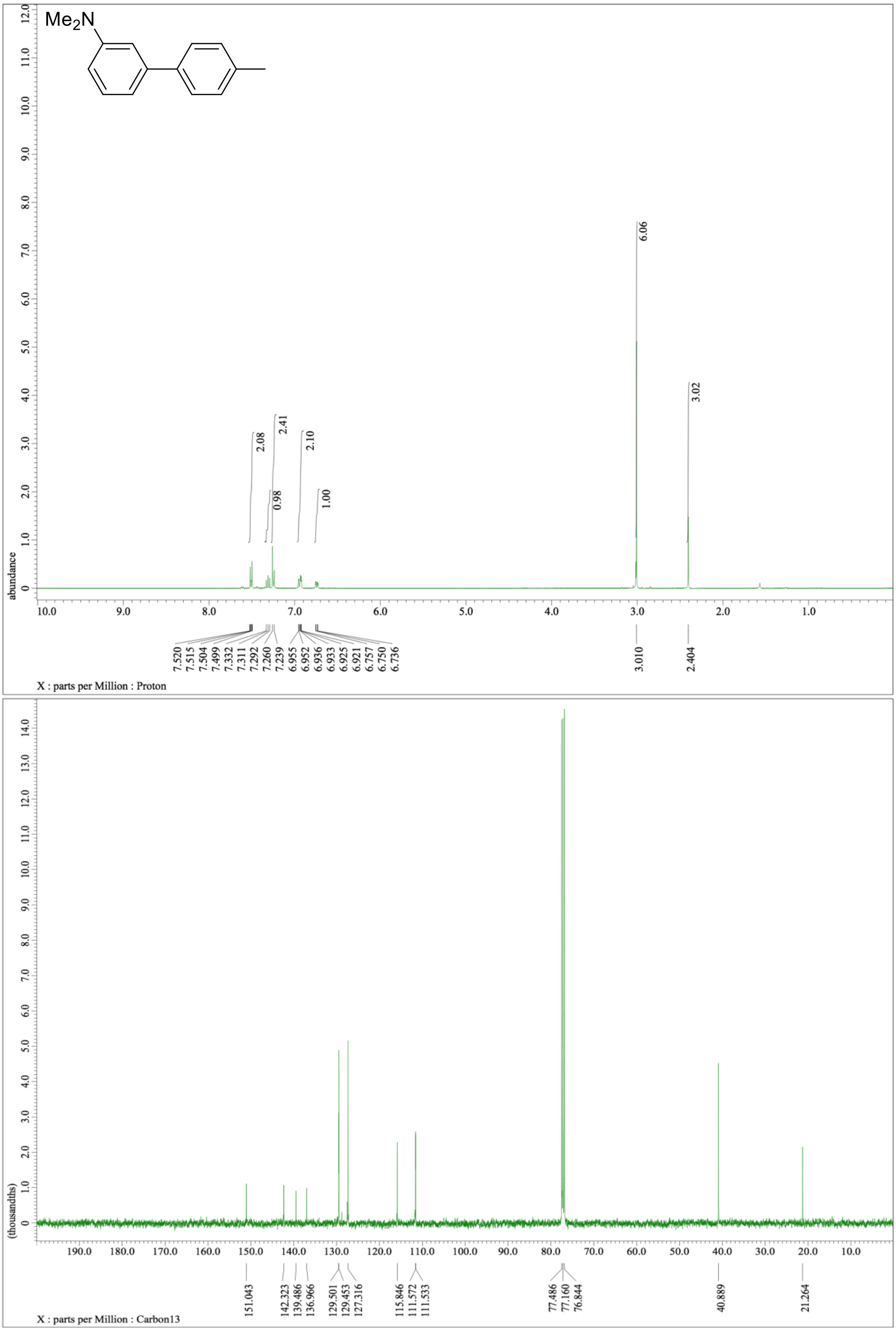


Figure S17. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1m**

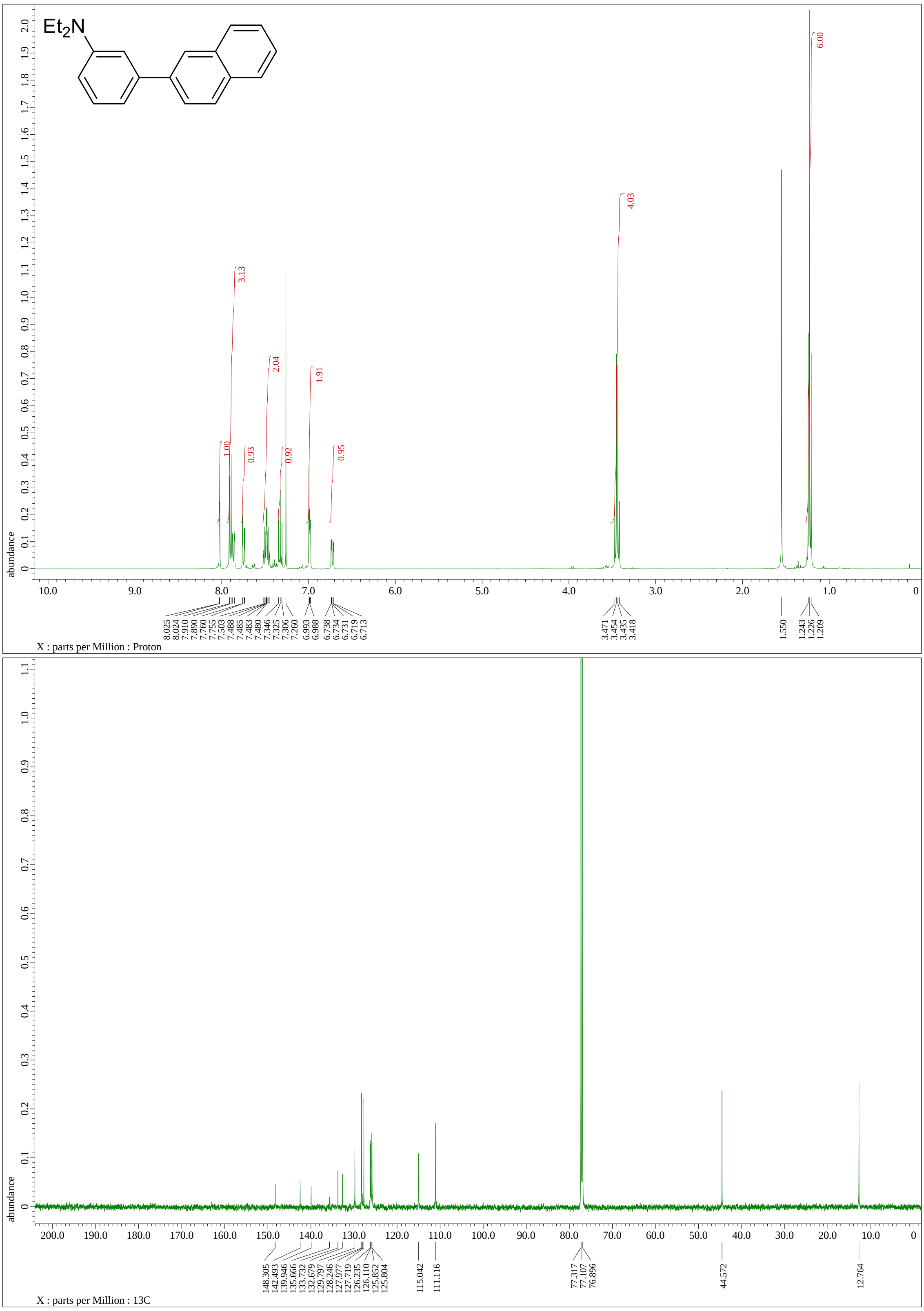


Figure S18. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **1n**

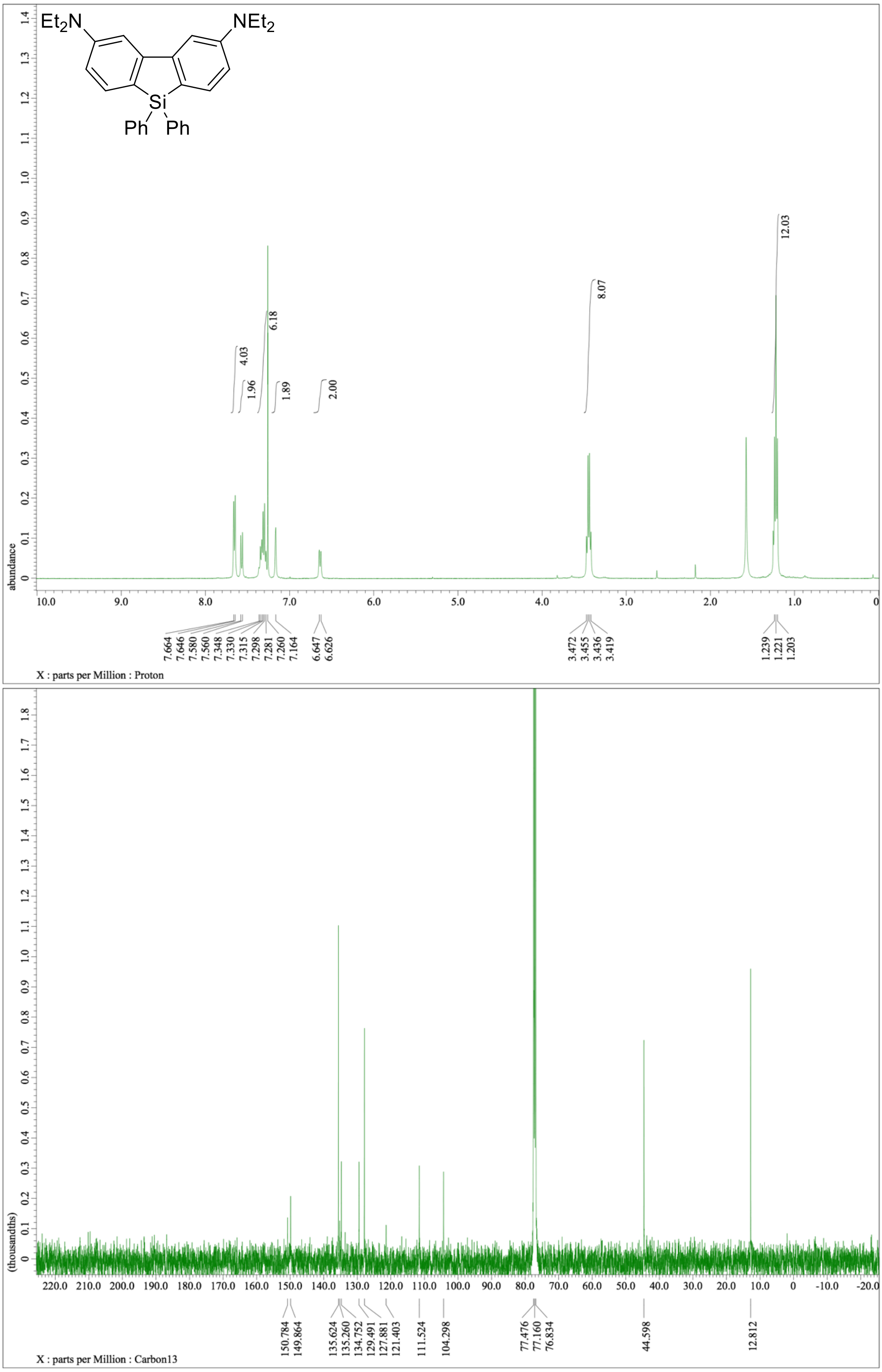


Figure S19. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3a**

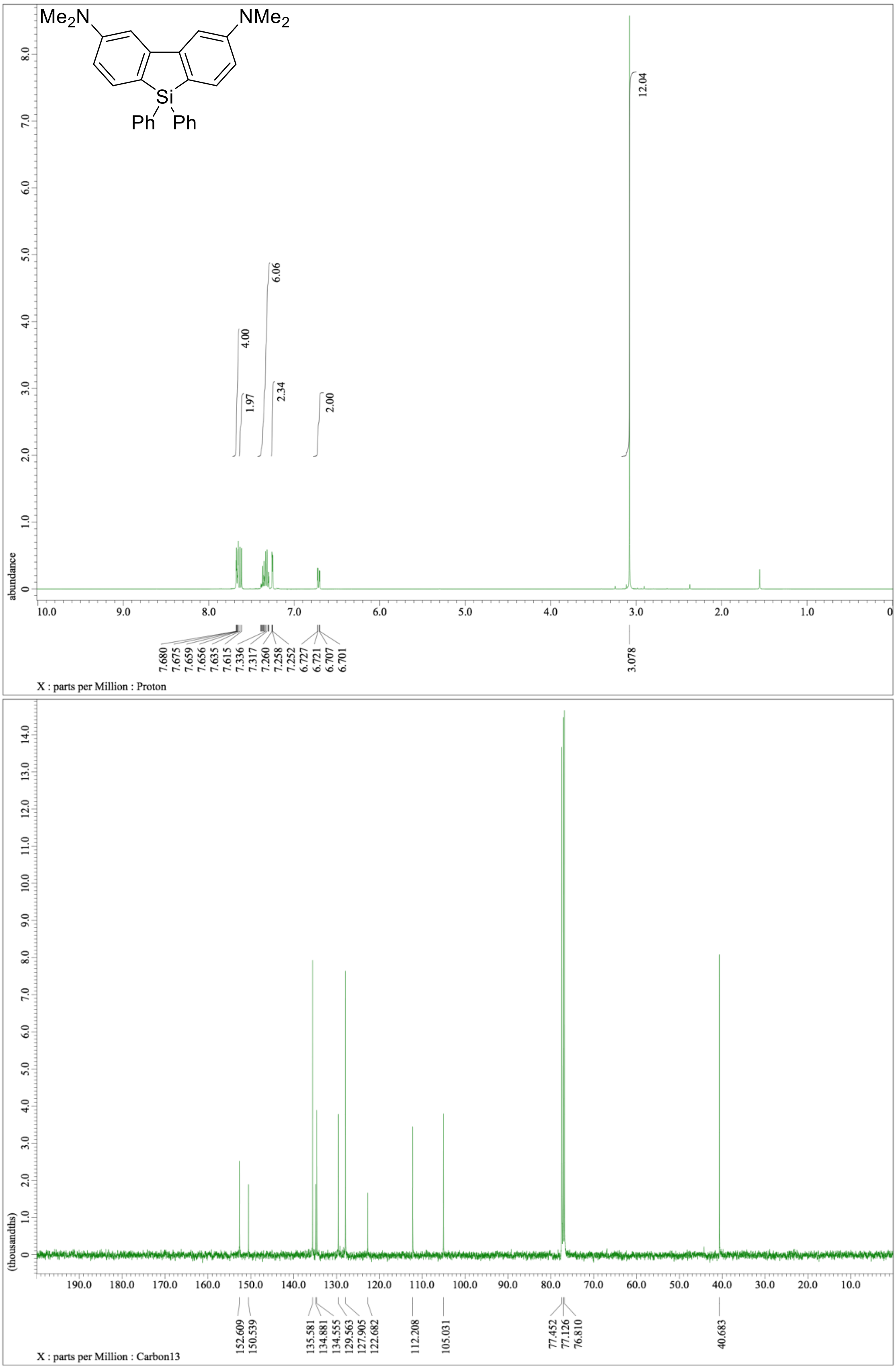


Figure S20. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3b**

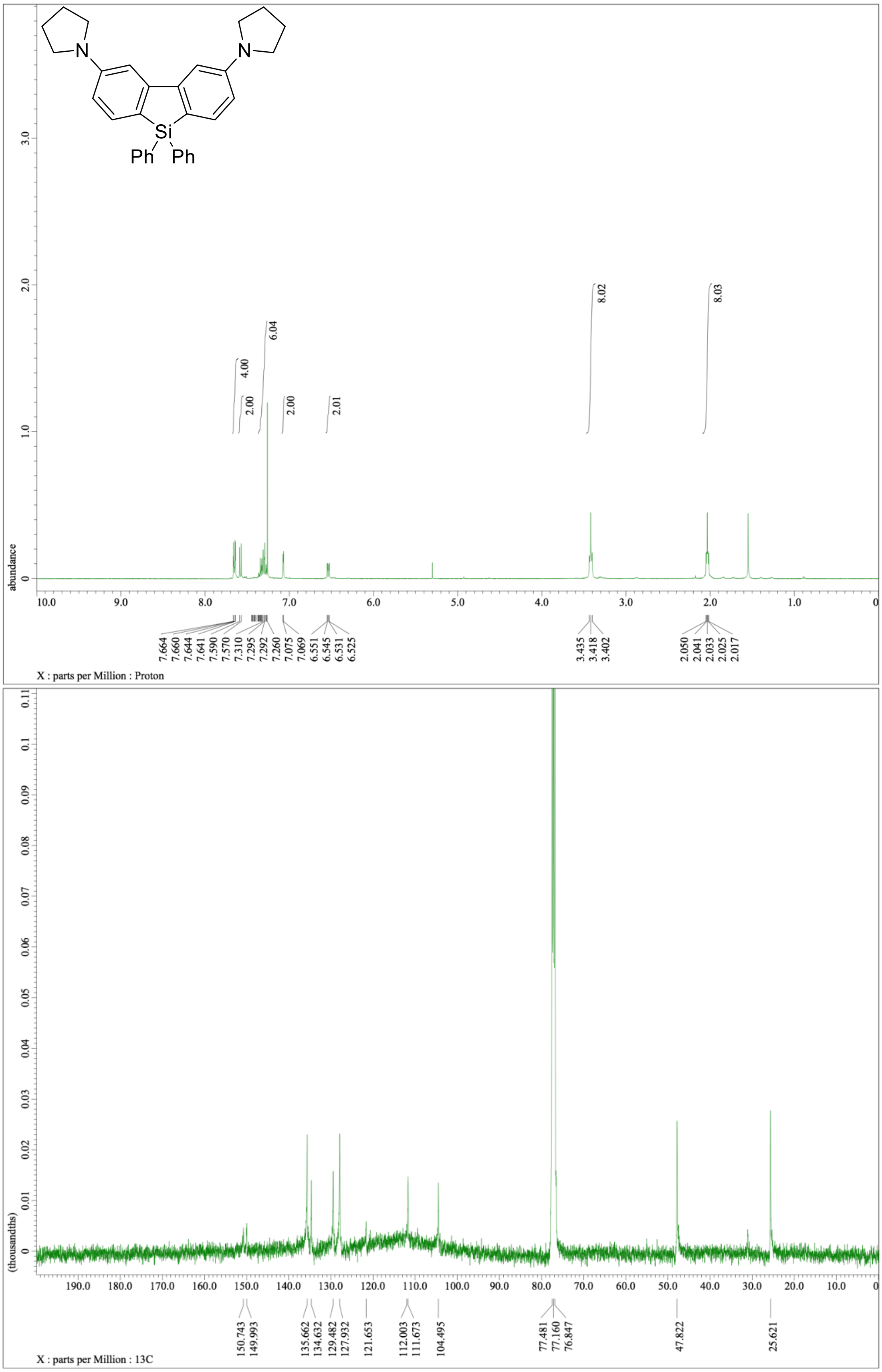


Figure S21. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3c**

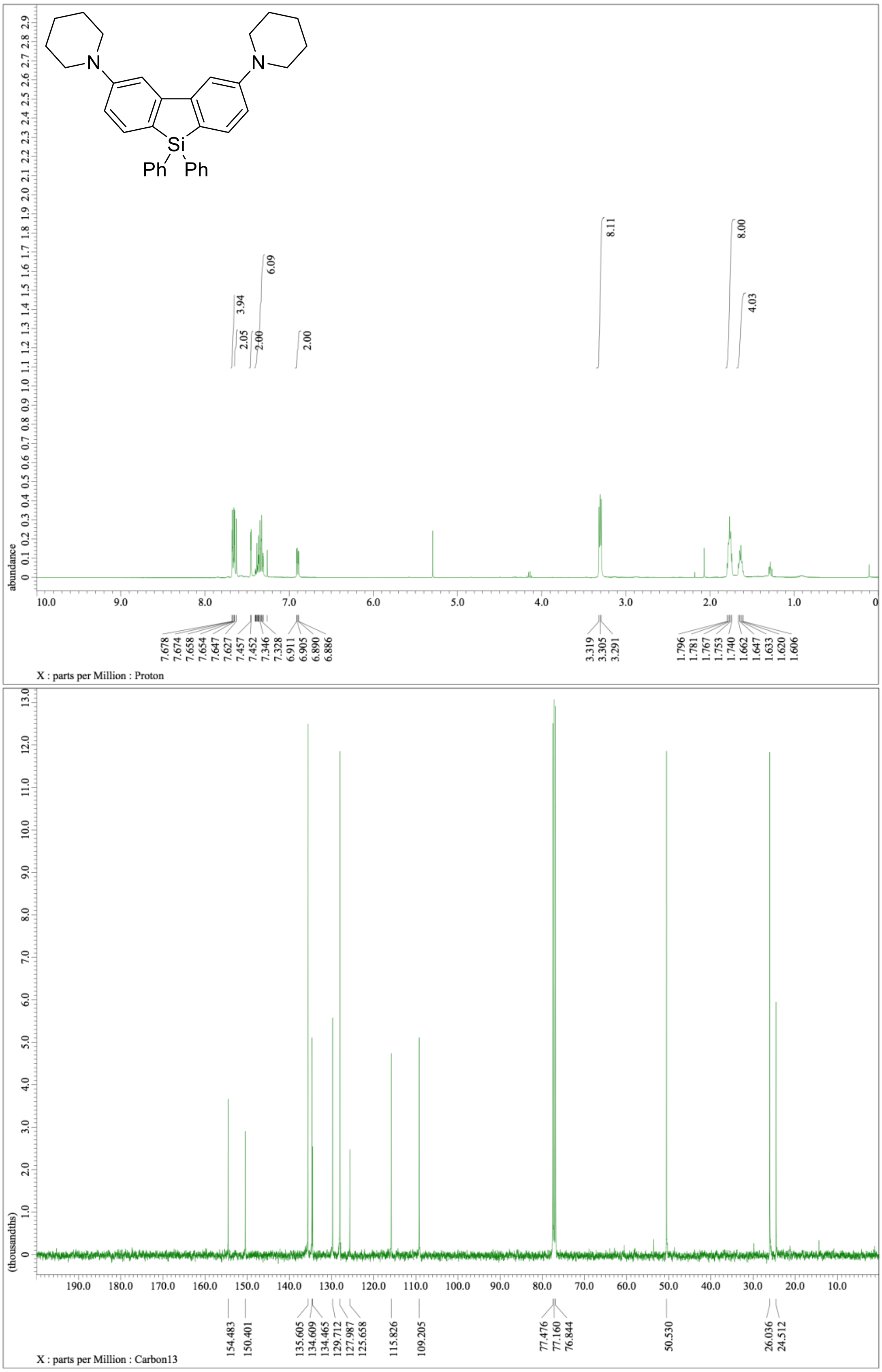


Figure S22. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3d**

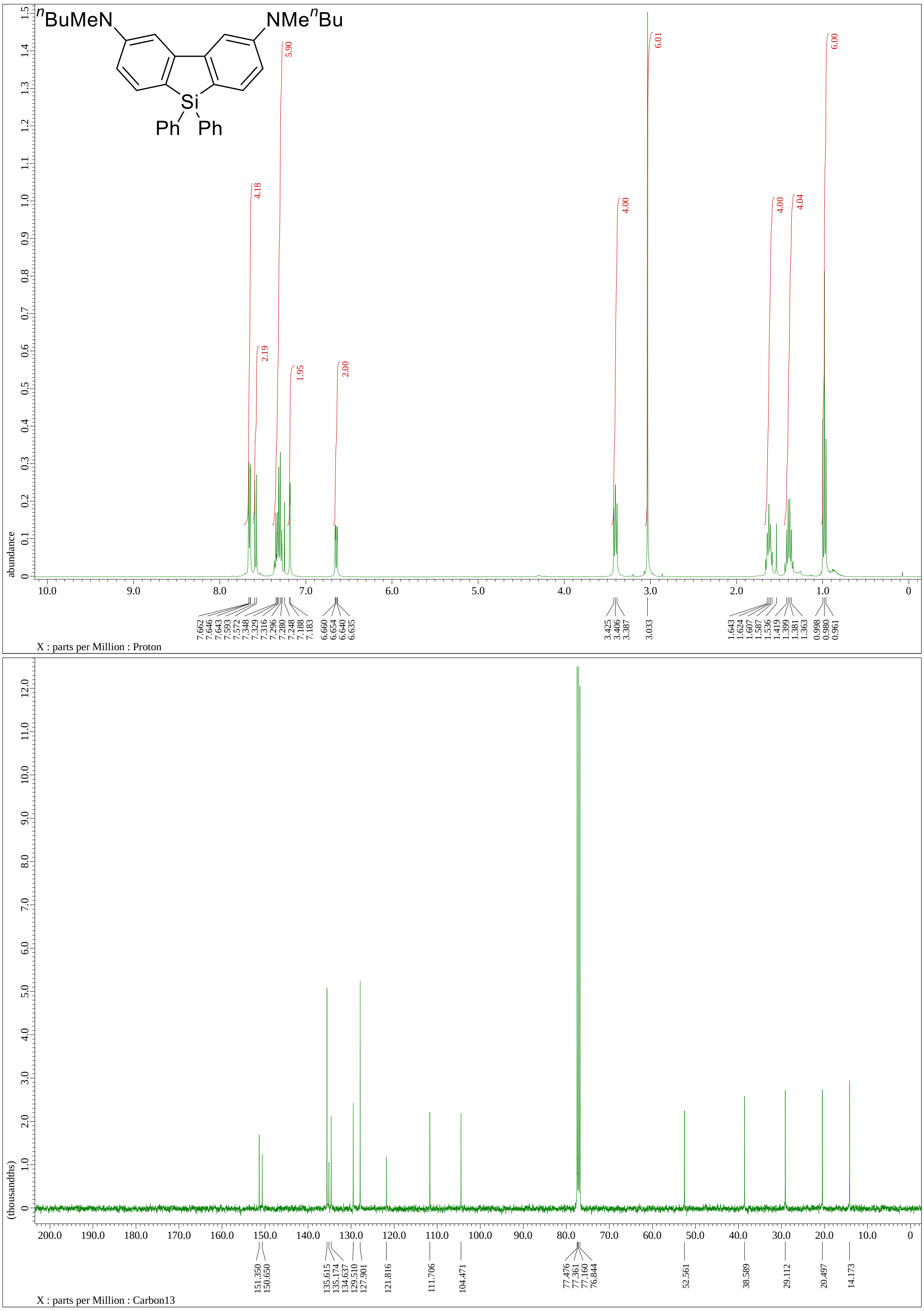


Figure S23. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3e**

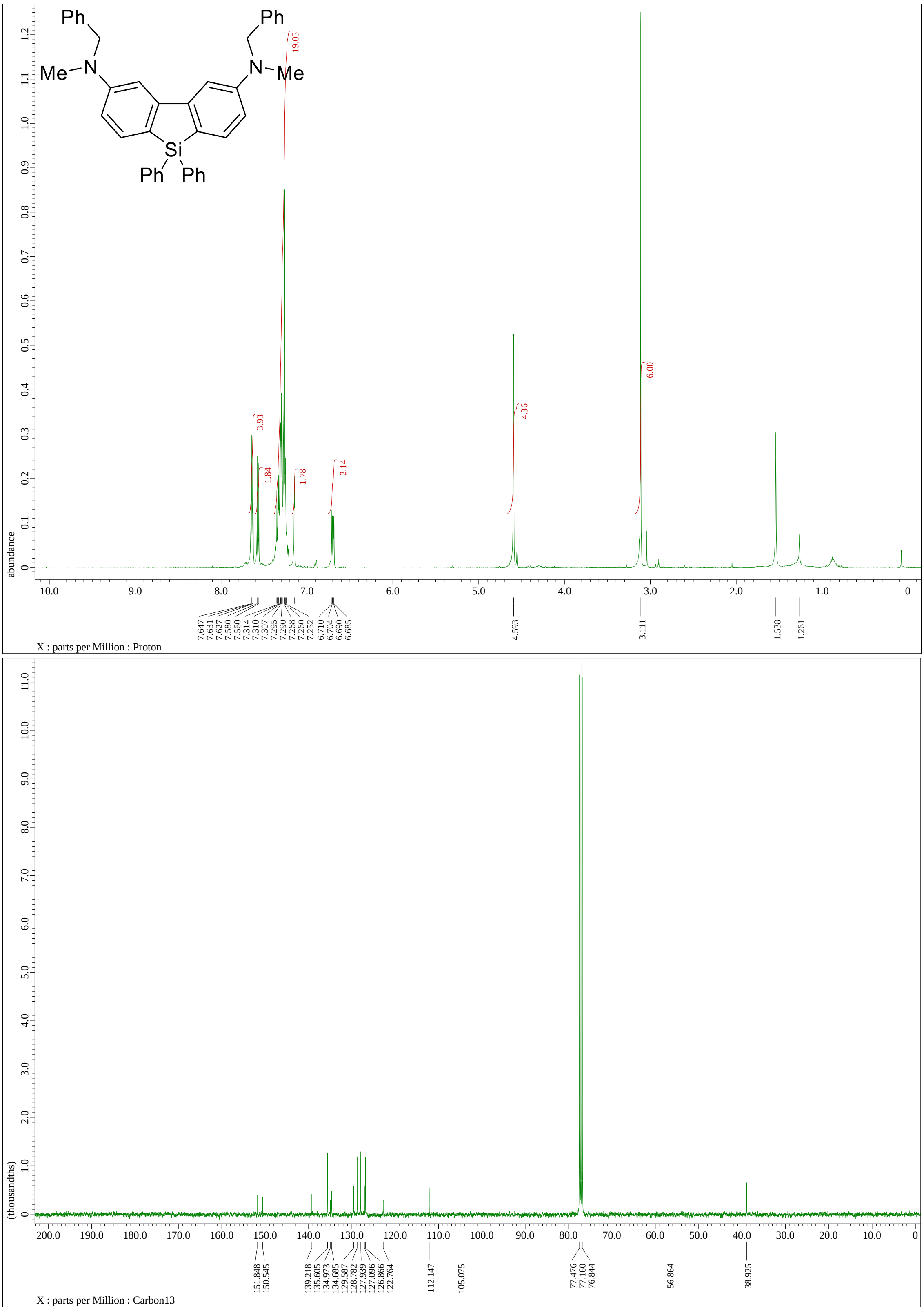


Figure S24. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3f**

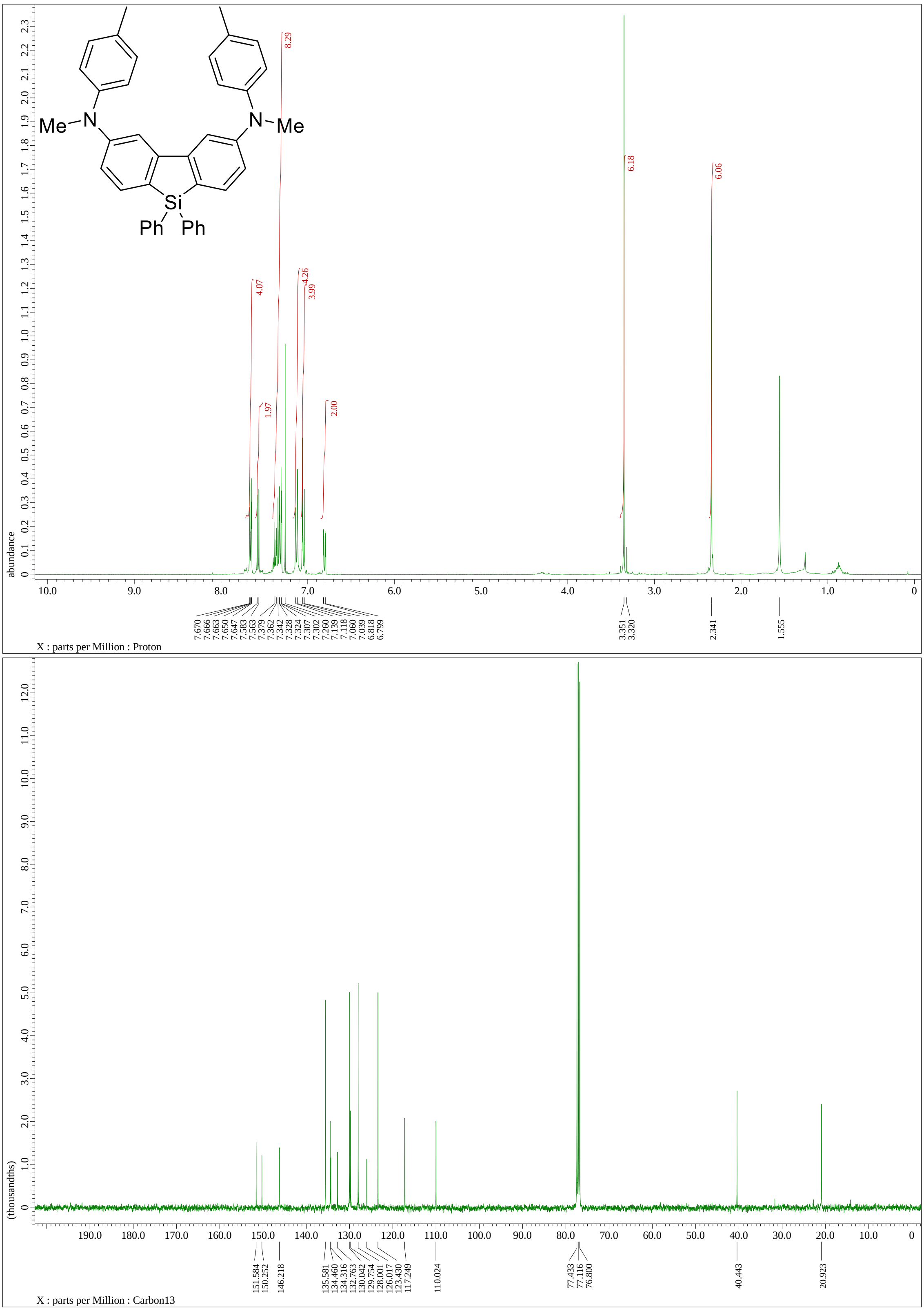


Figure S25. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3g**

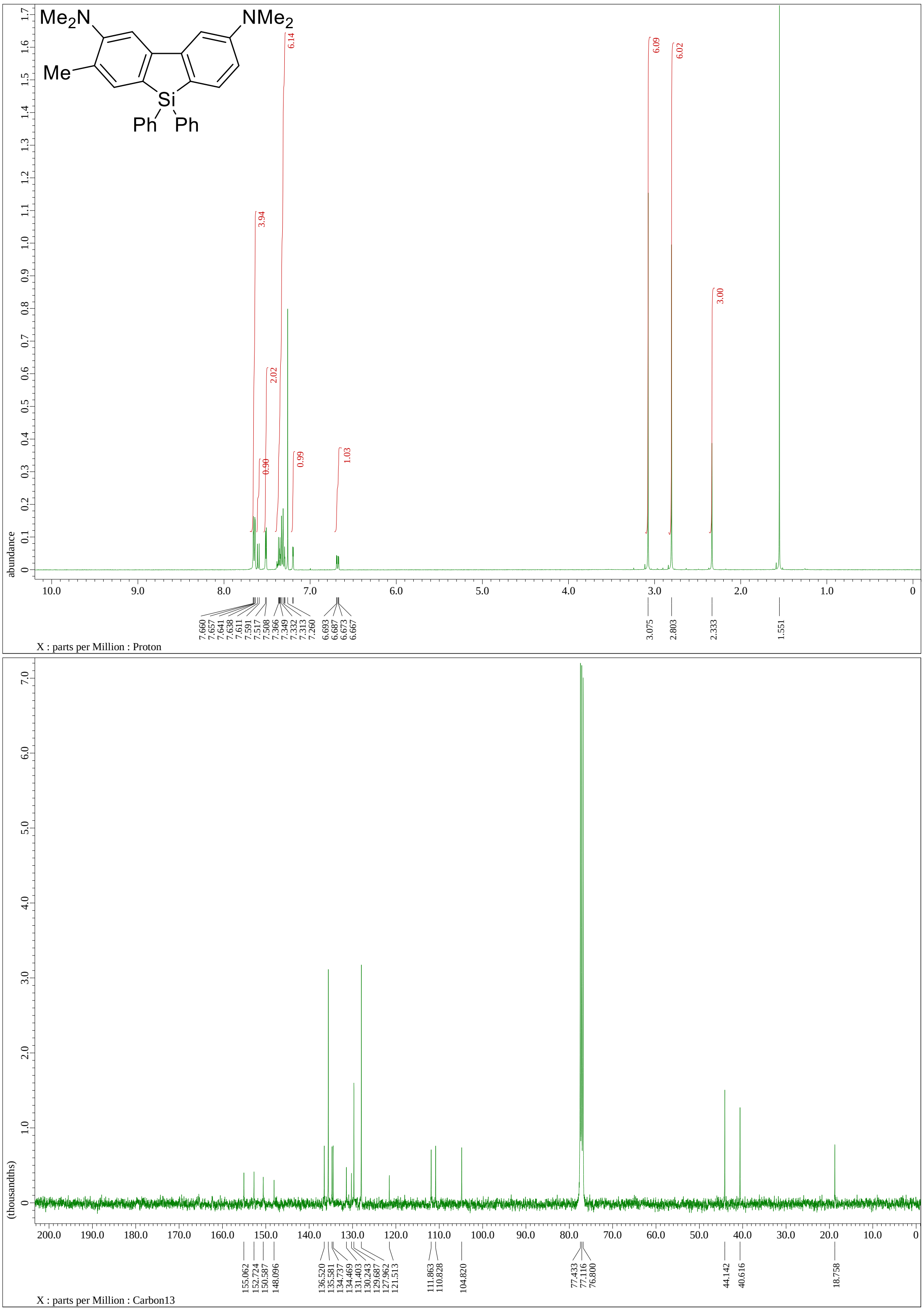


Figure S26. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3h**

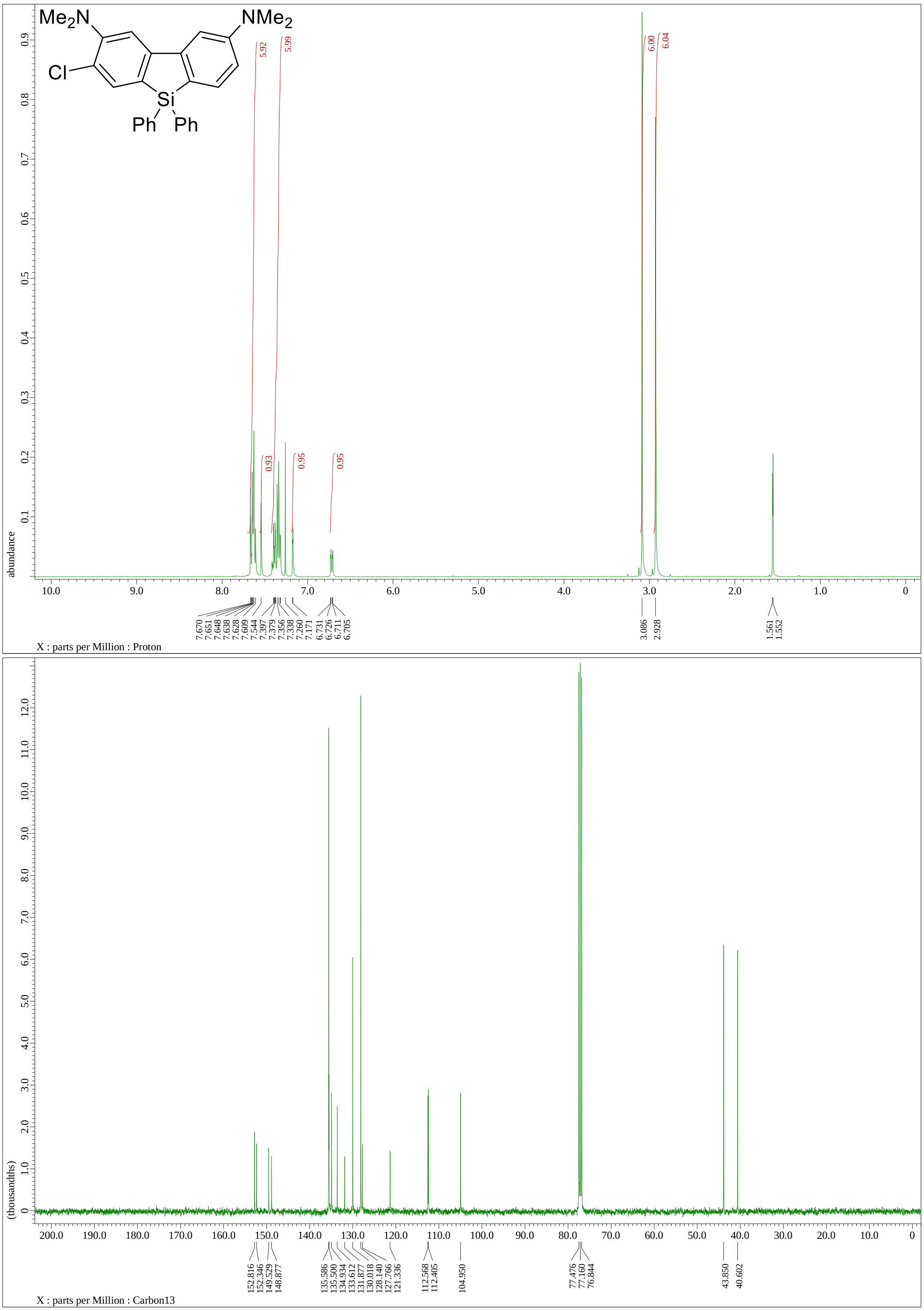


Figure S27. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3i**

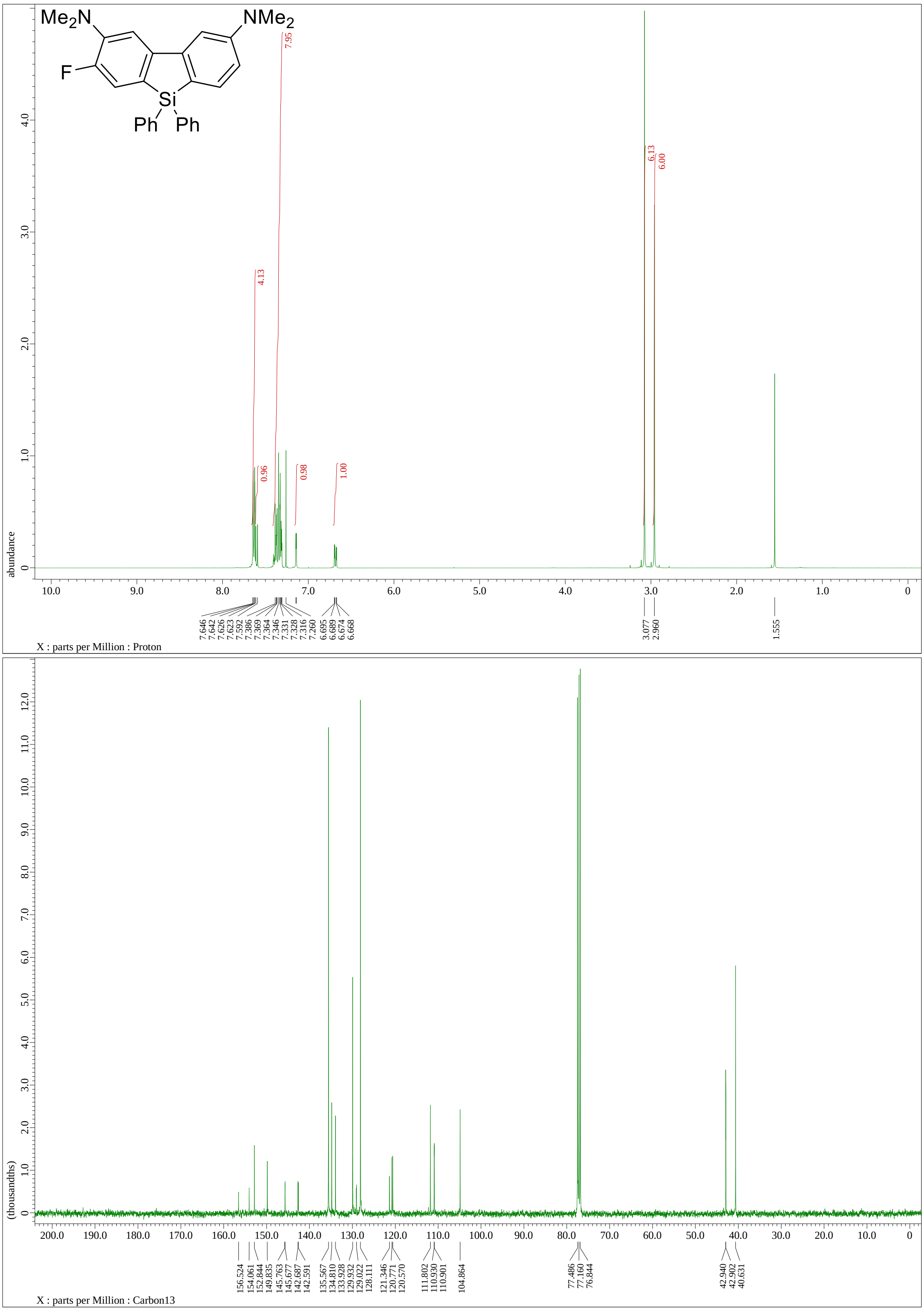


Figure S28. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3j**

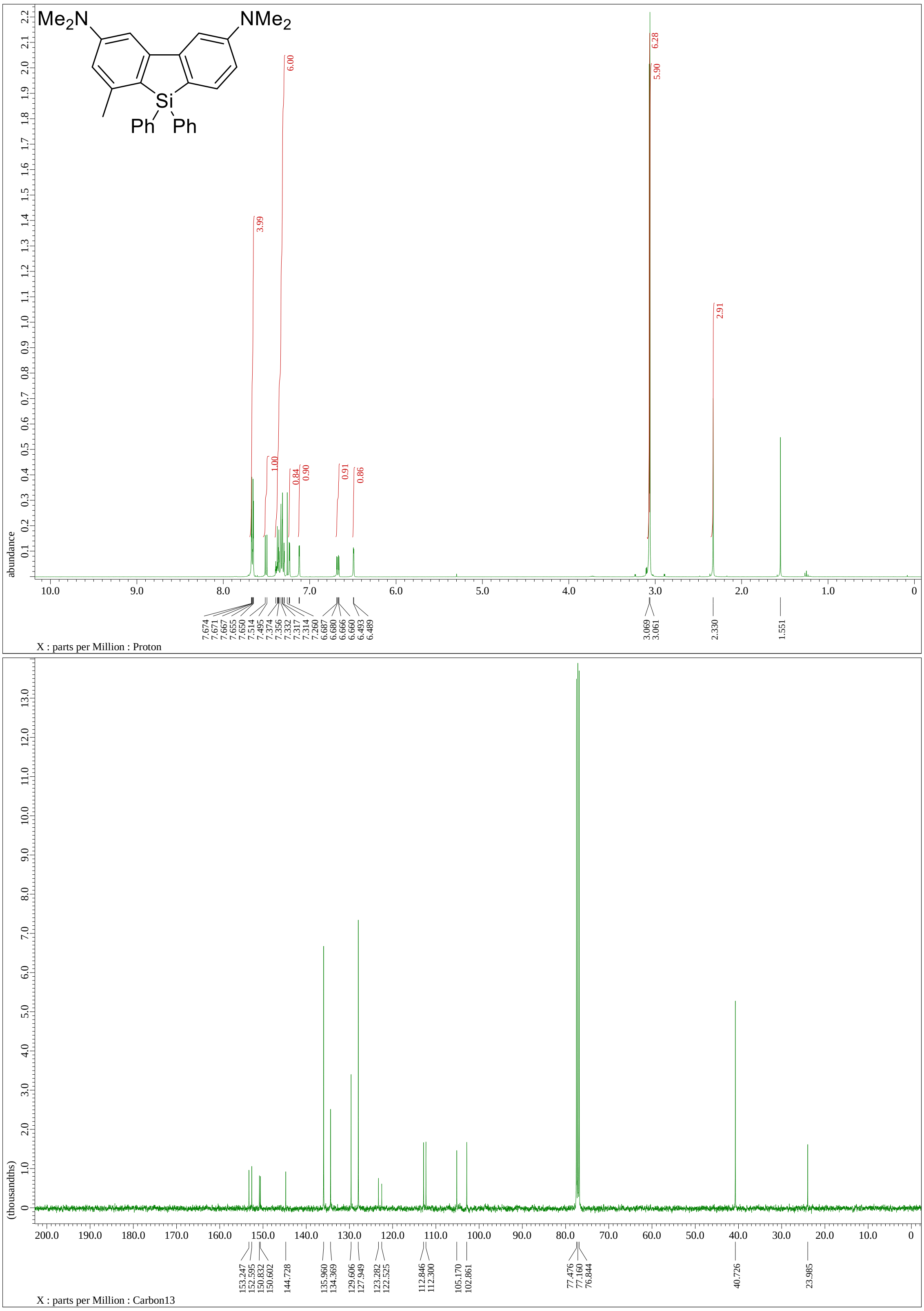


Figure S29. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3k**

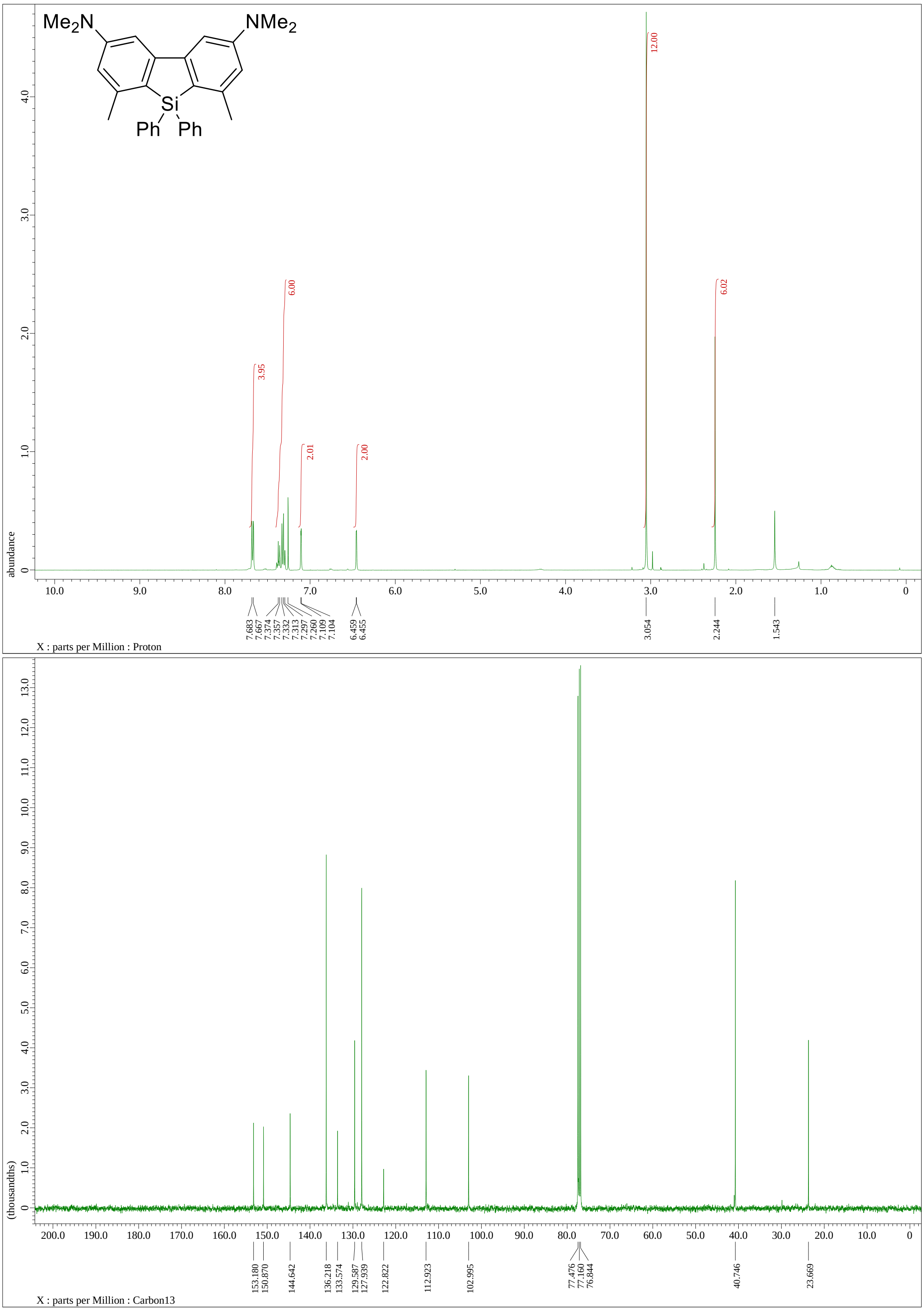


Figure S30. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3l**

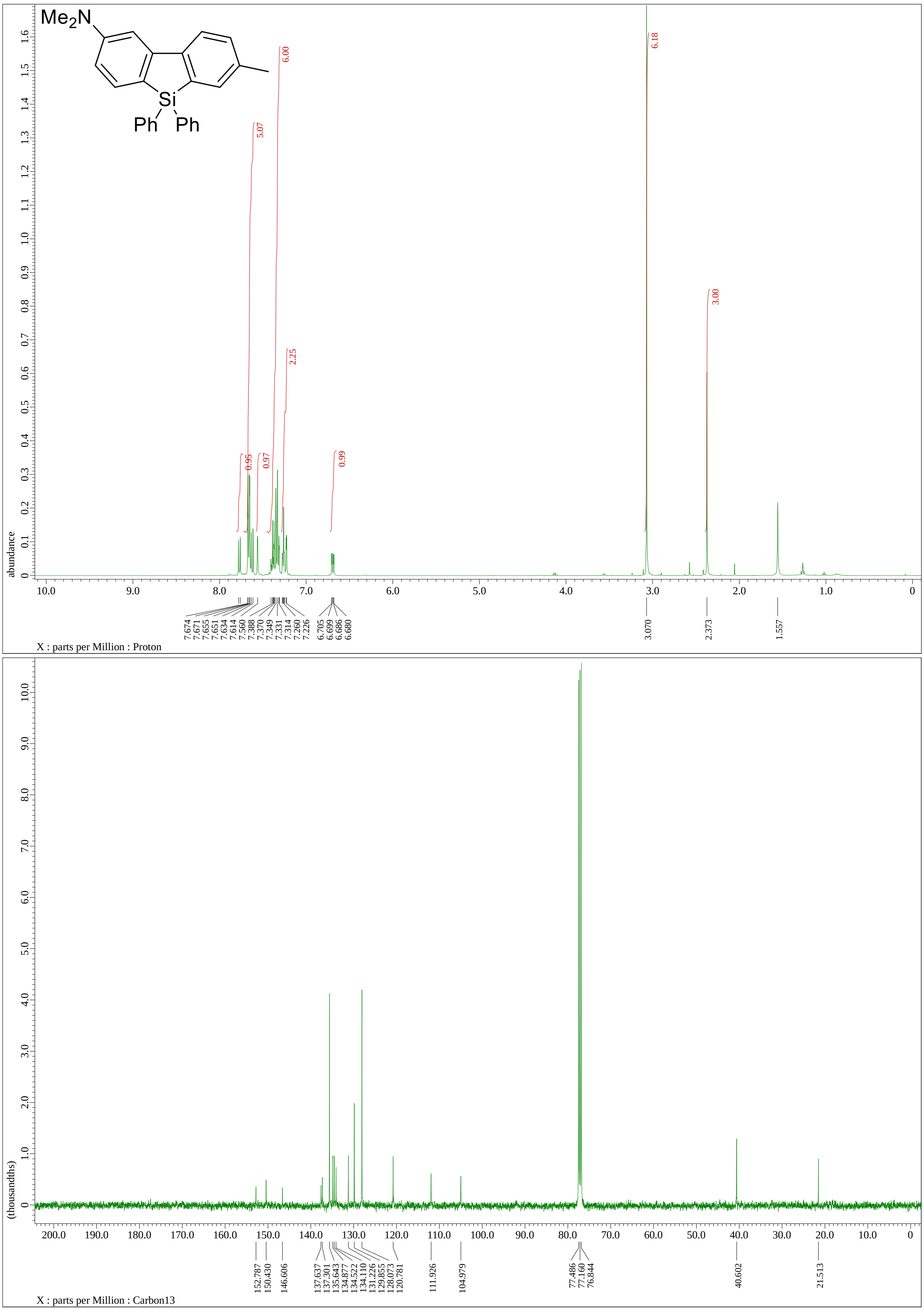


Figure S31. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3m**

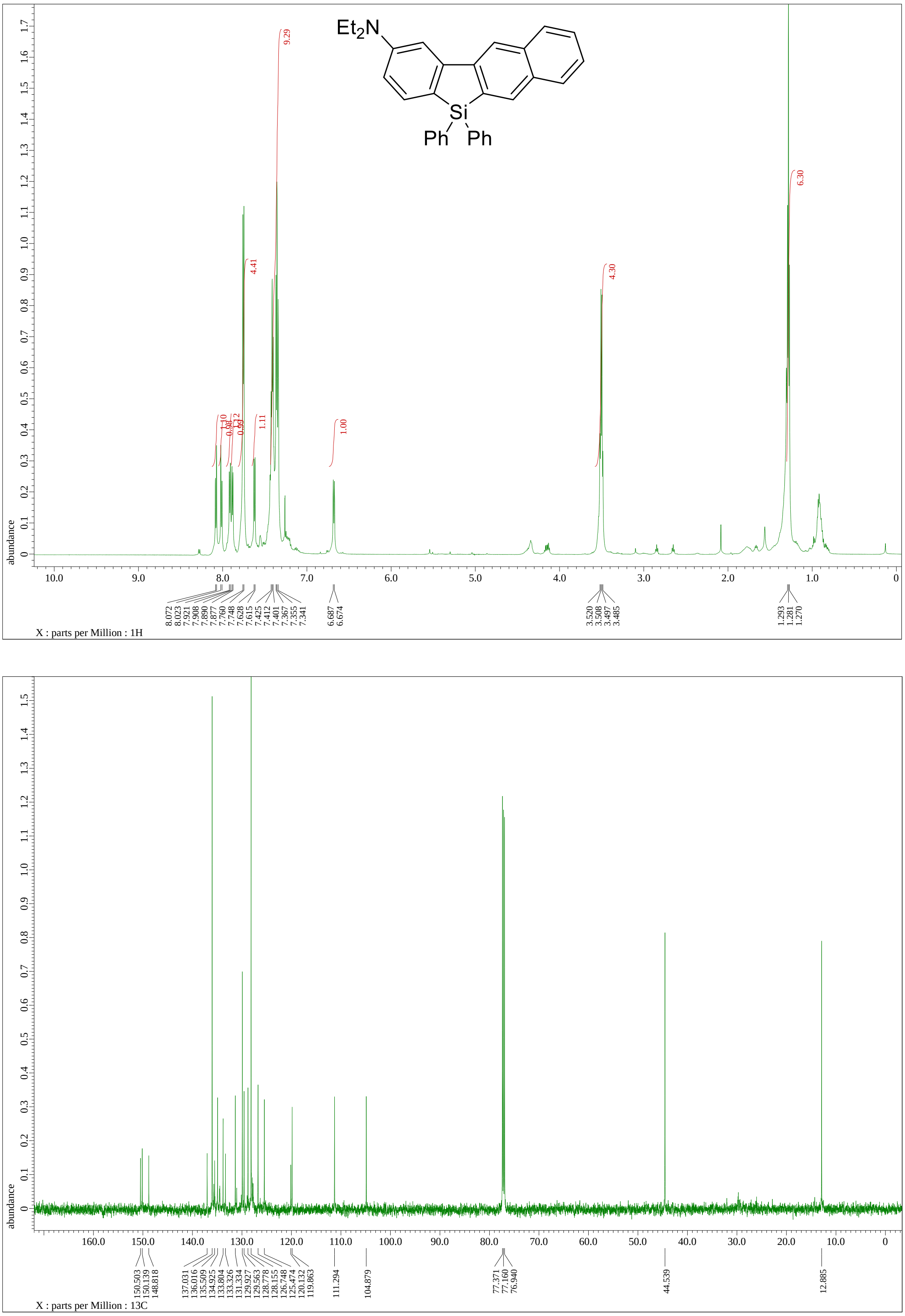


Figure S32. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3n**

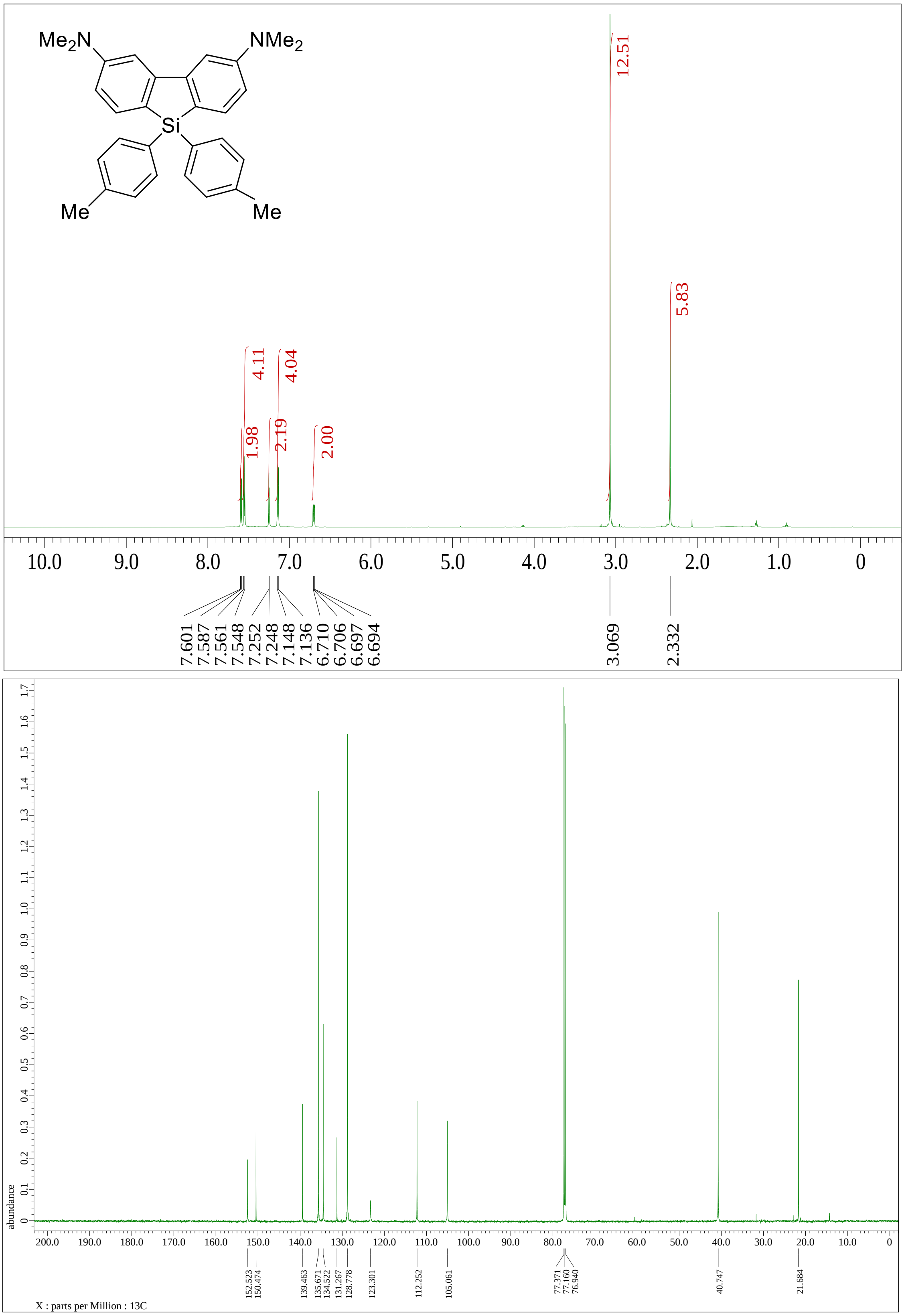


Figure S33. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3o**

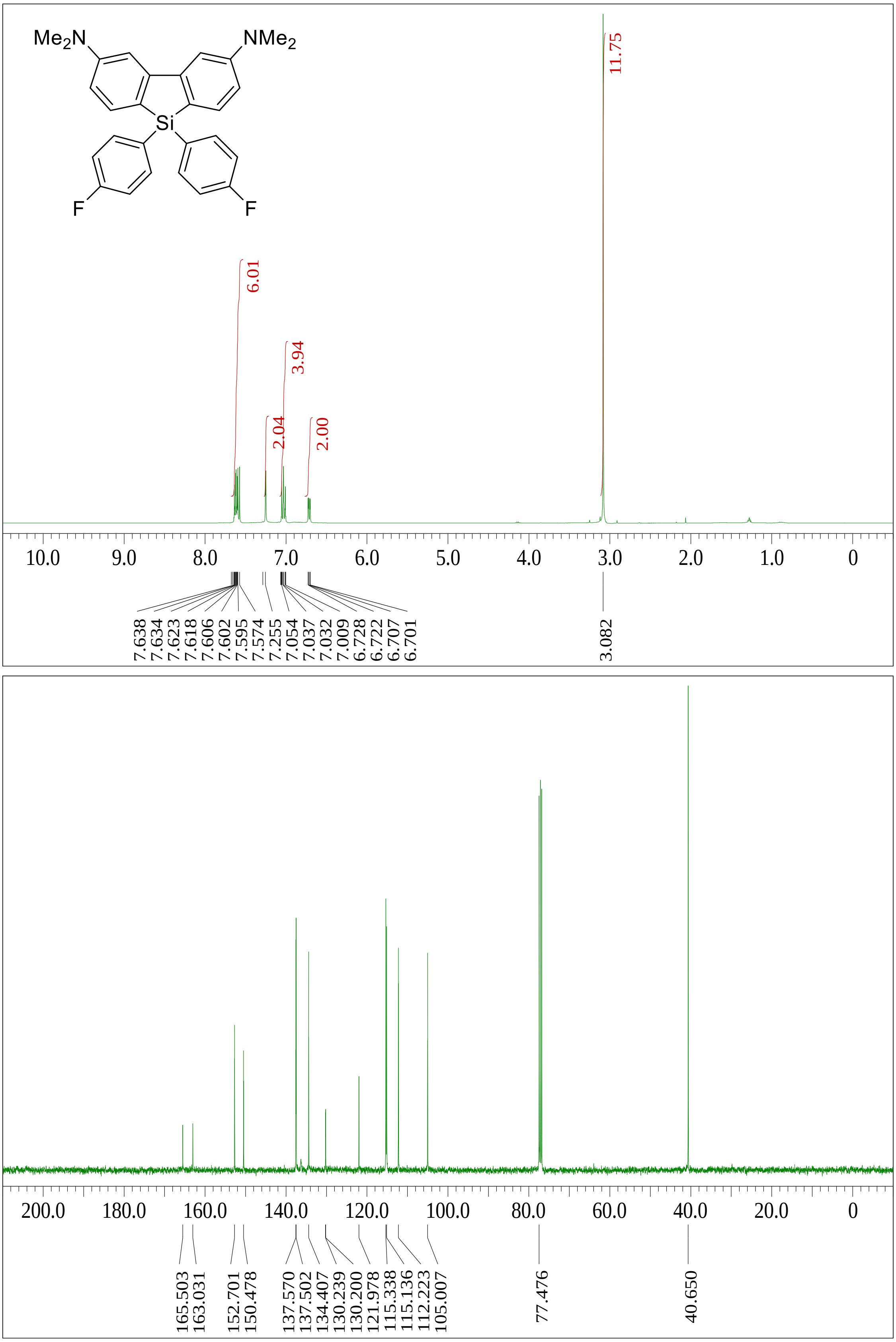


Figure S34. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3p**

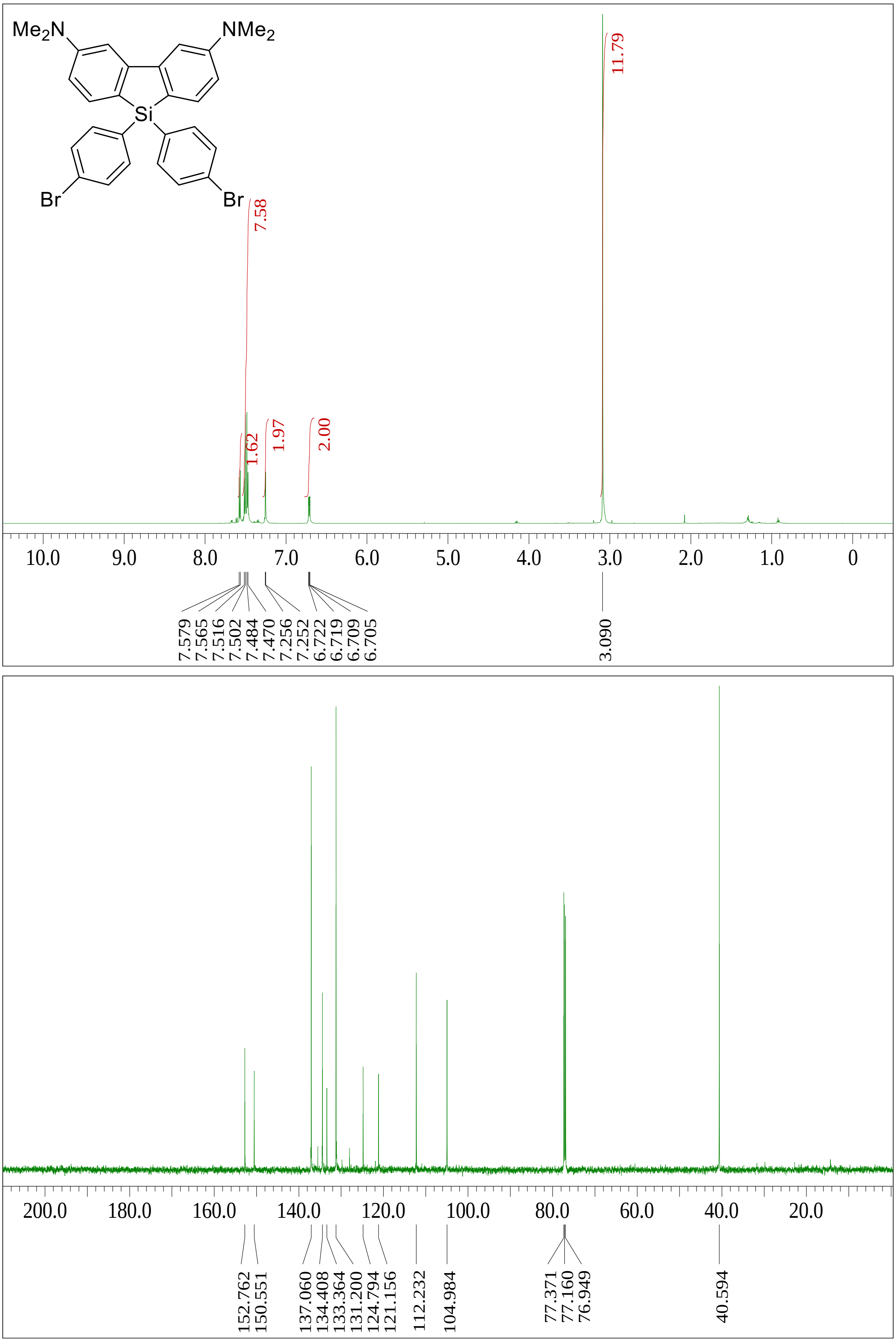


Figure S35. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3q**

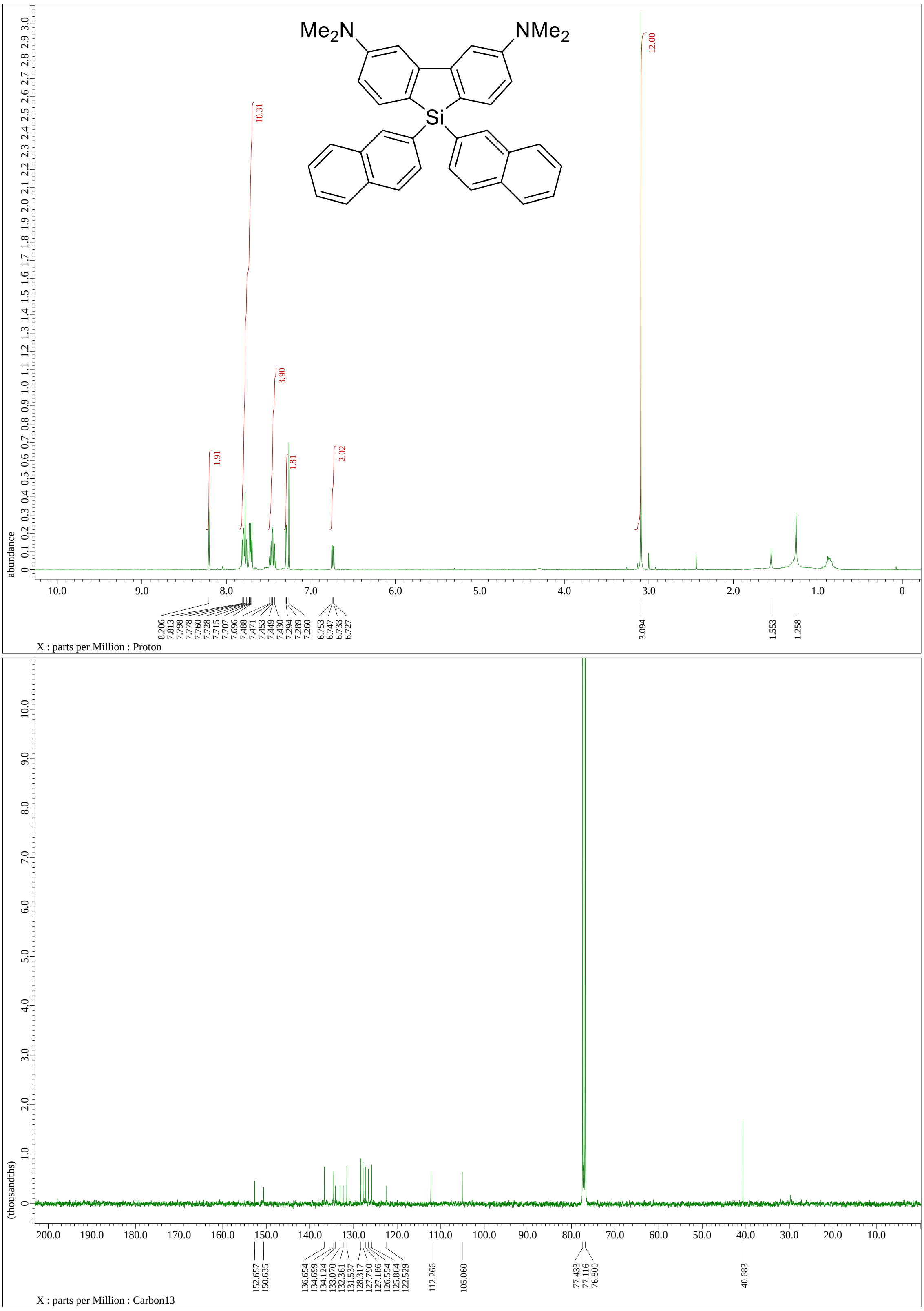


Figure S36. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3r**

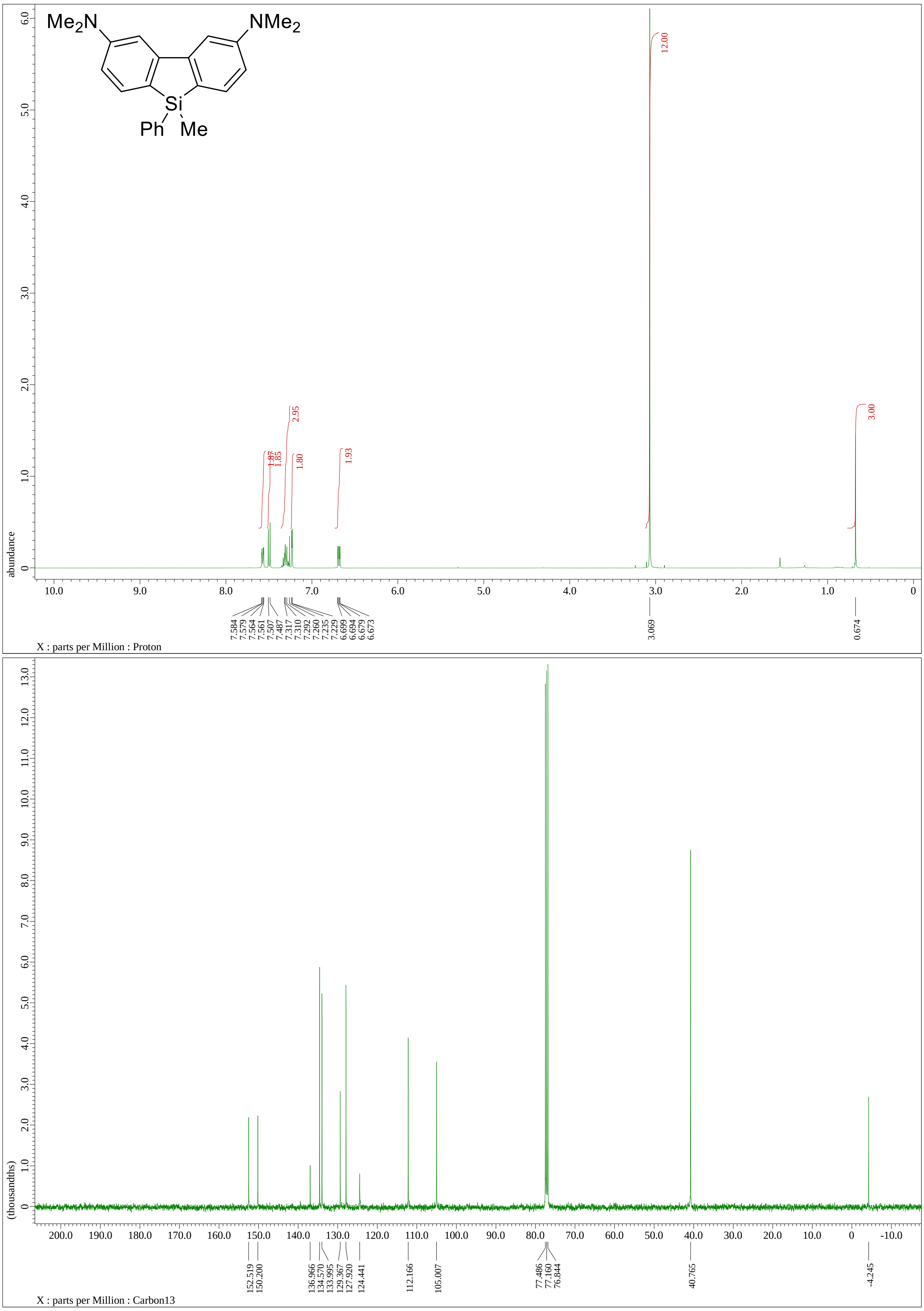


Figure S37. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3s**

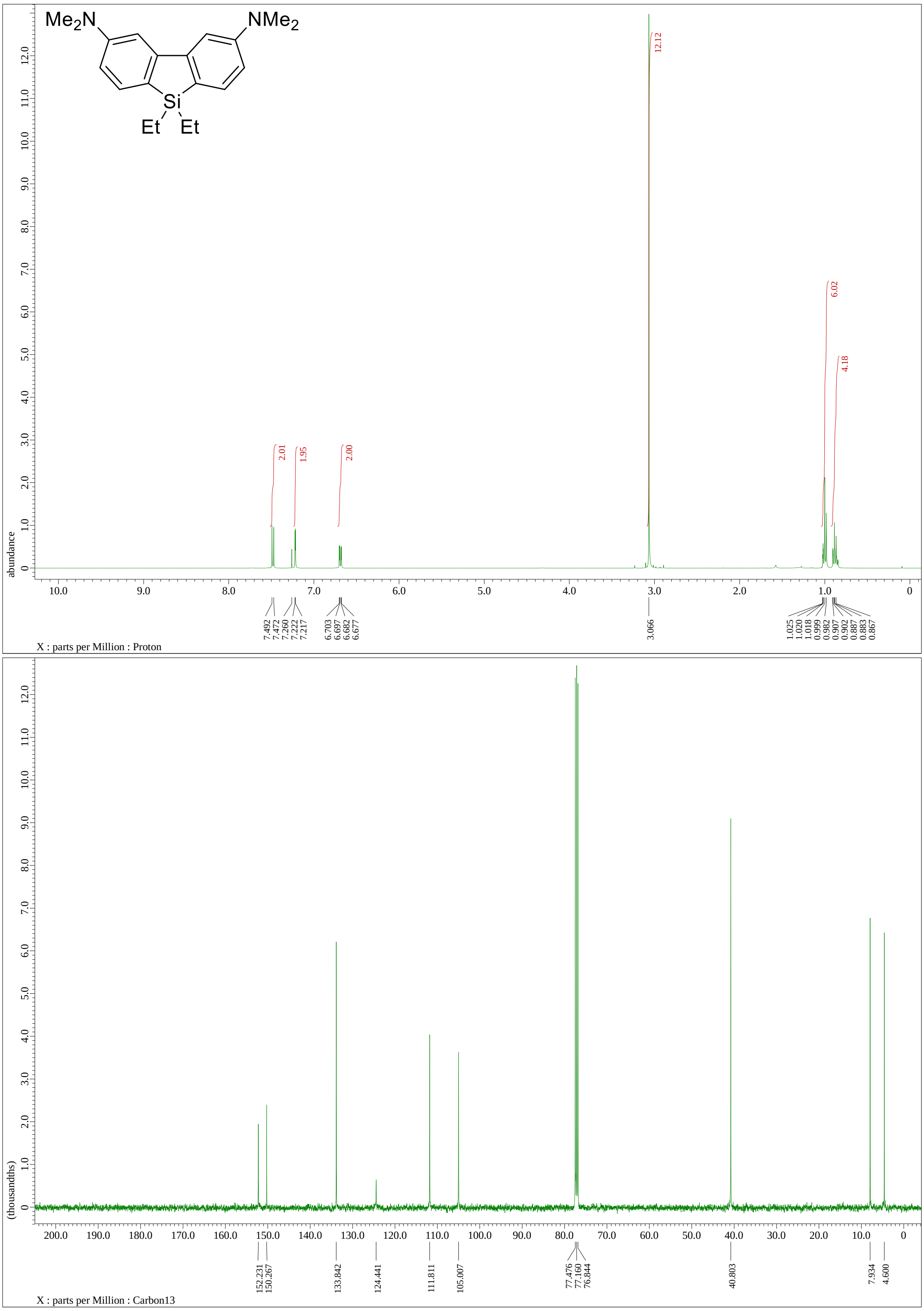


Figure S38. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **3t**

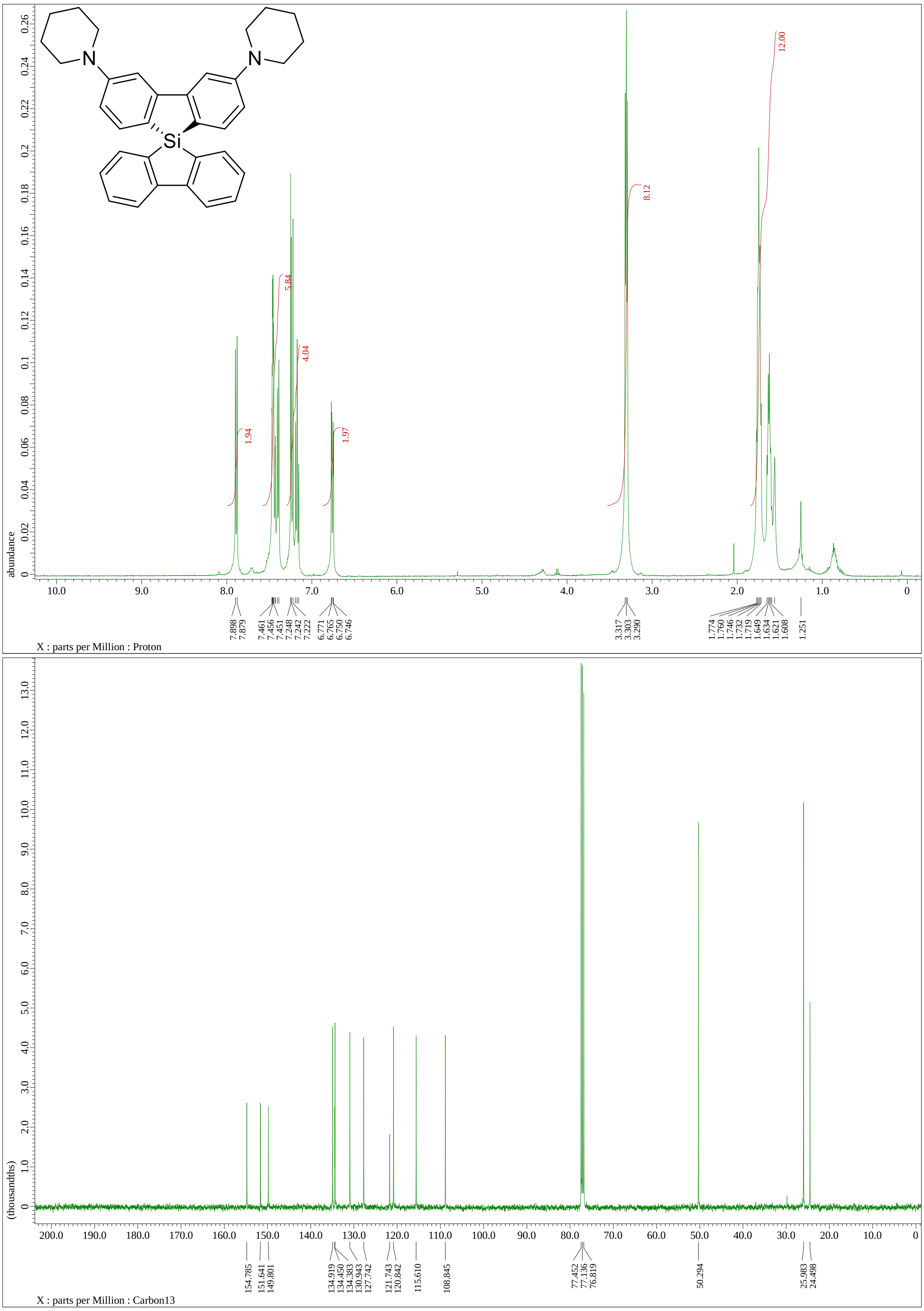


Figure S39. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **5**

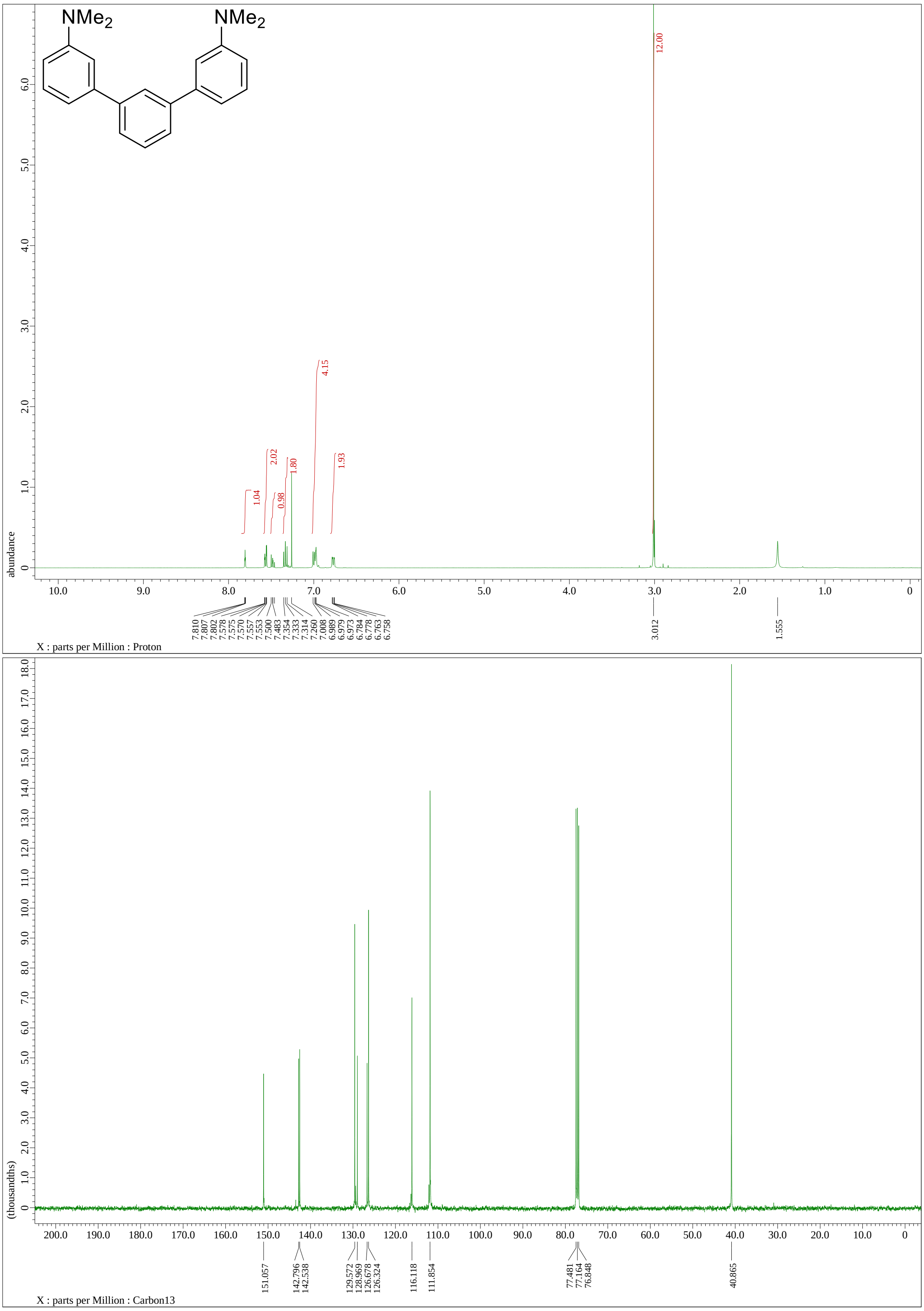


Figure S40. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **6**

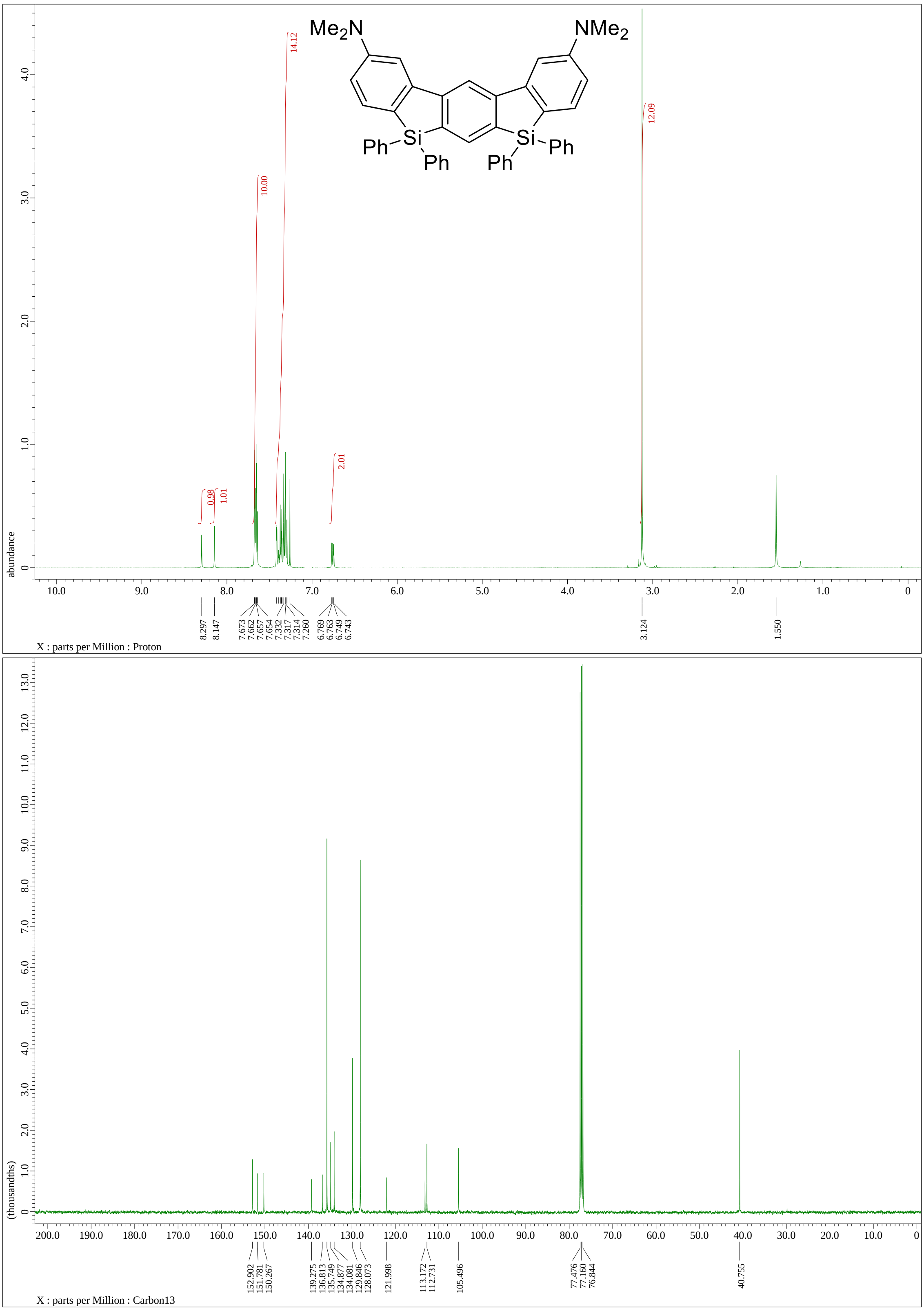


Figure S41. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **7**

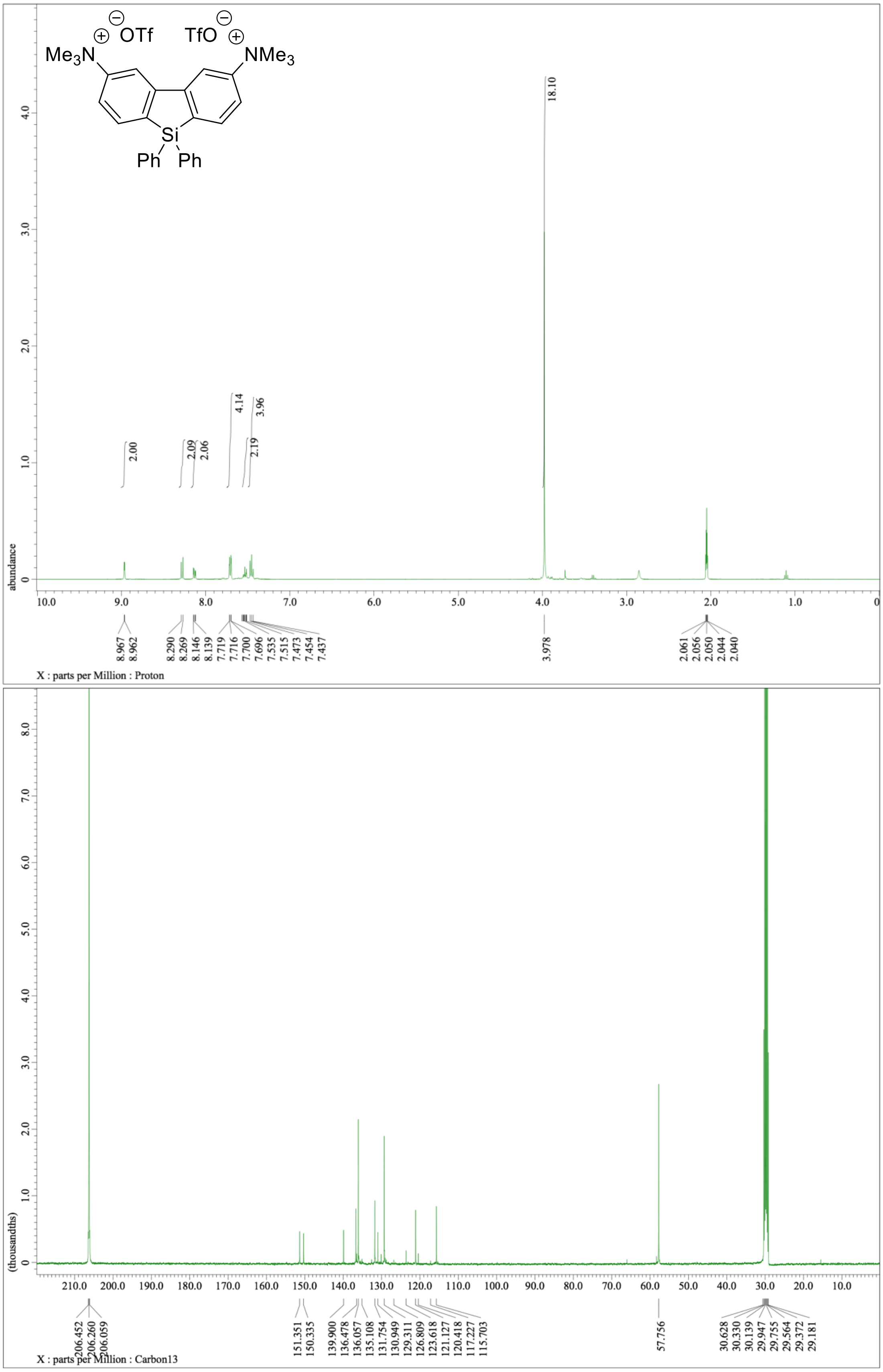


Figure S42. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **9**

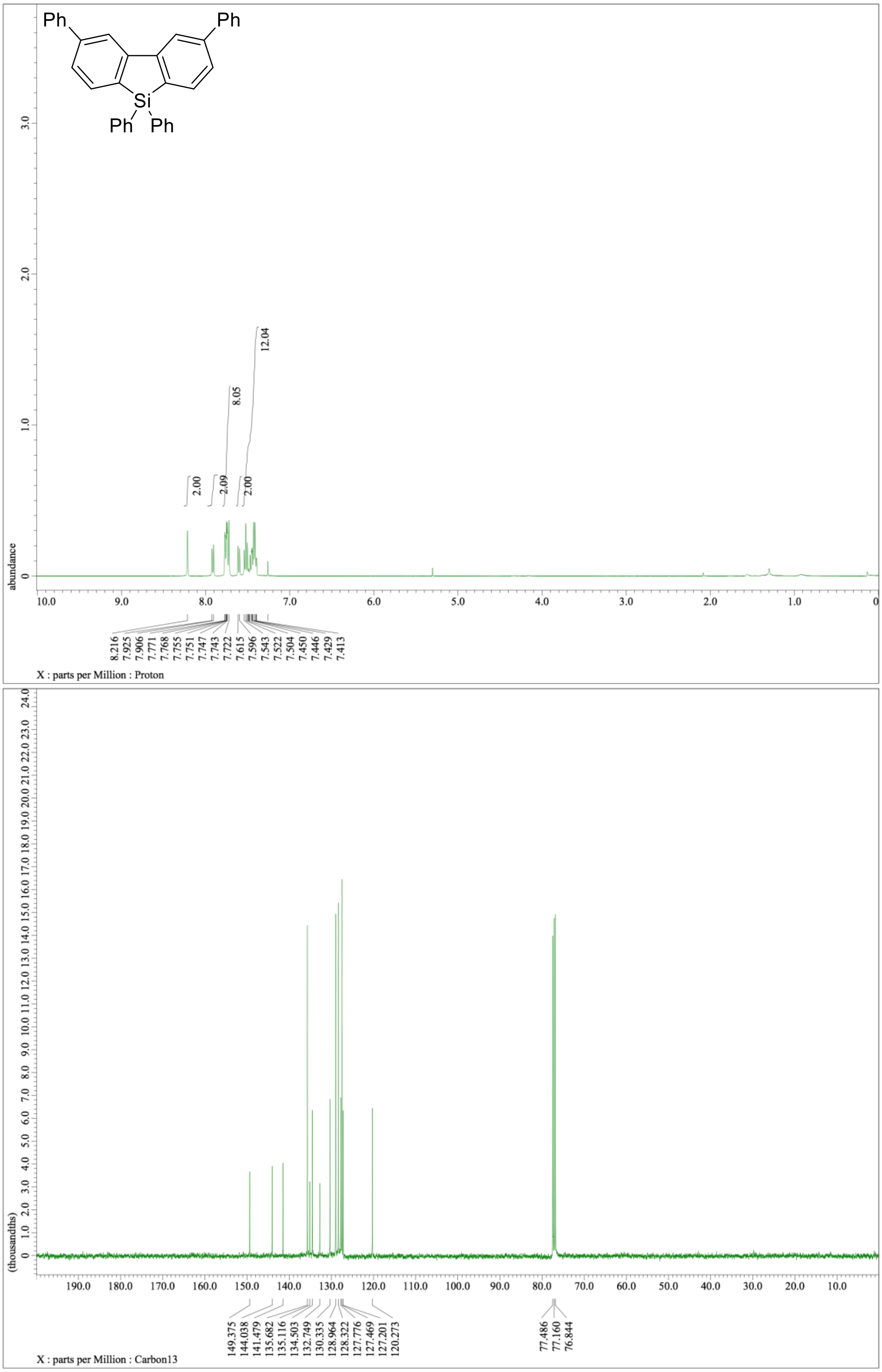


Figure S43. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **9**

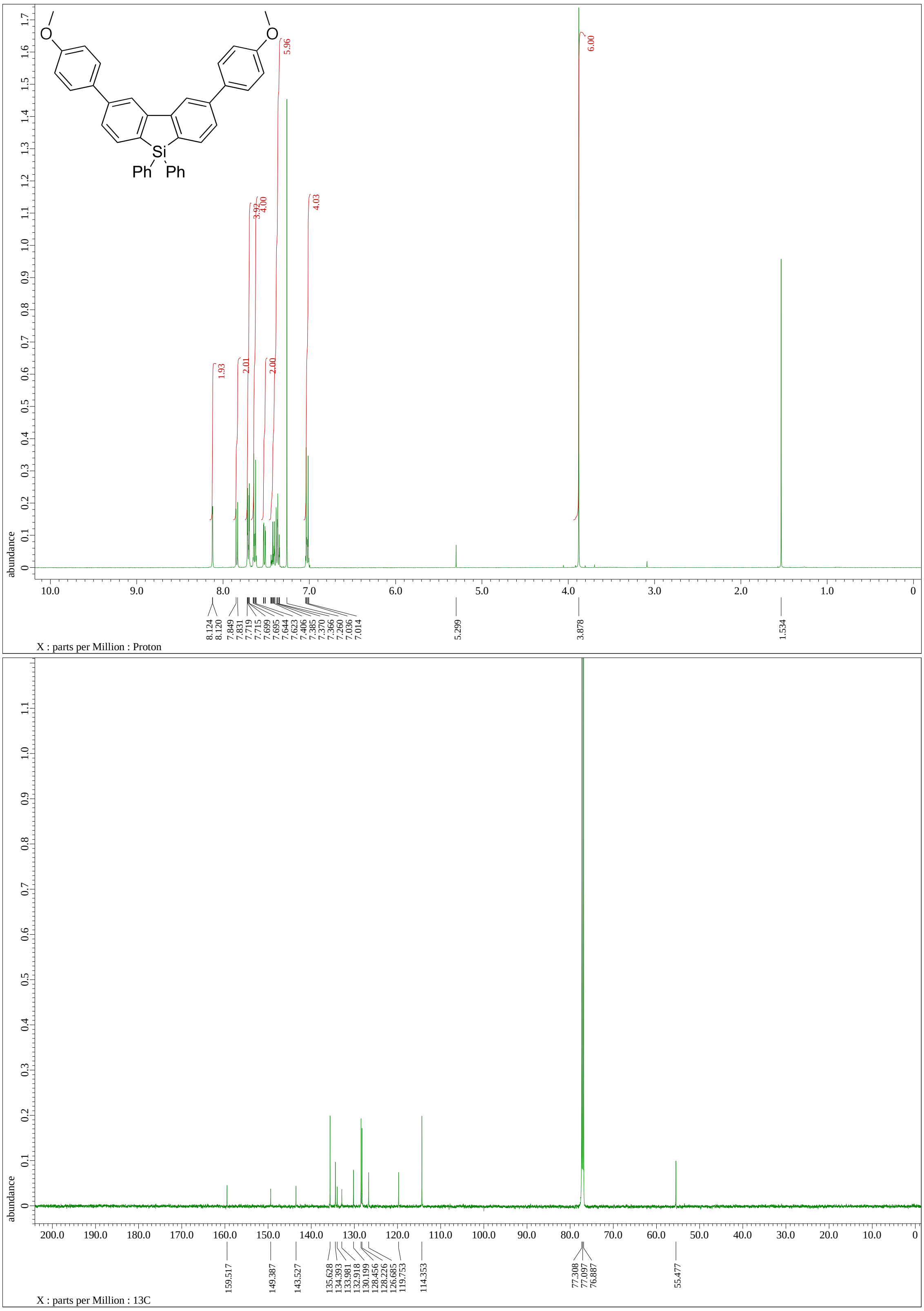


Figure S44. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **10**

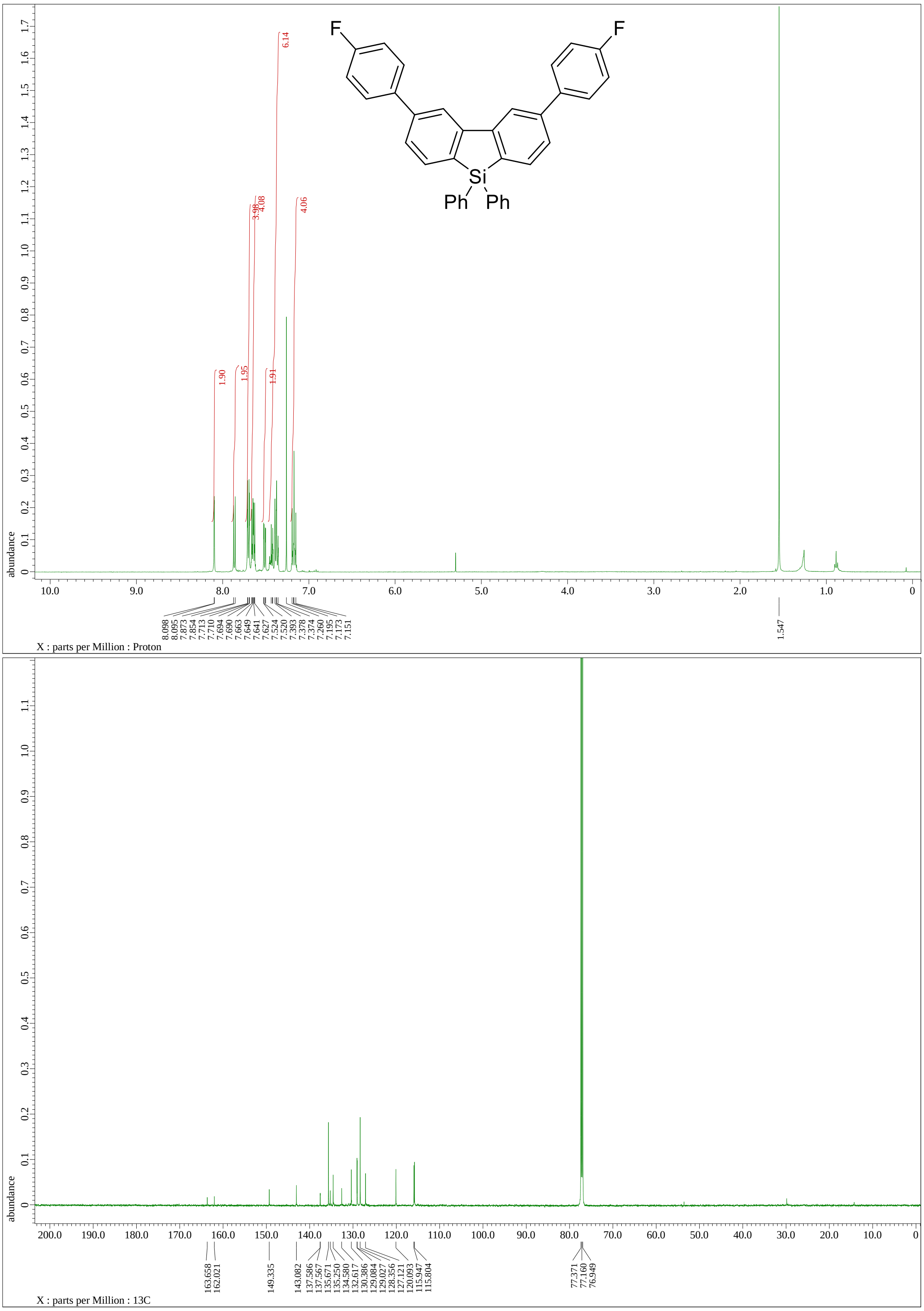


Figure S45. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **11**

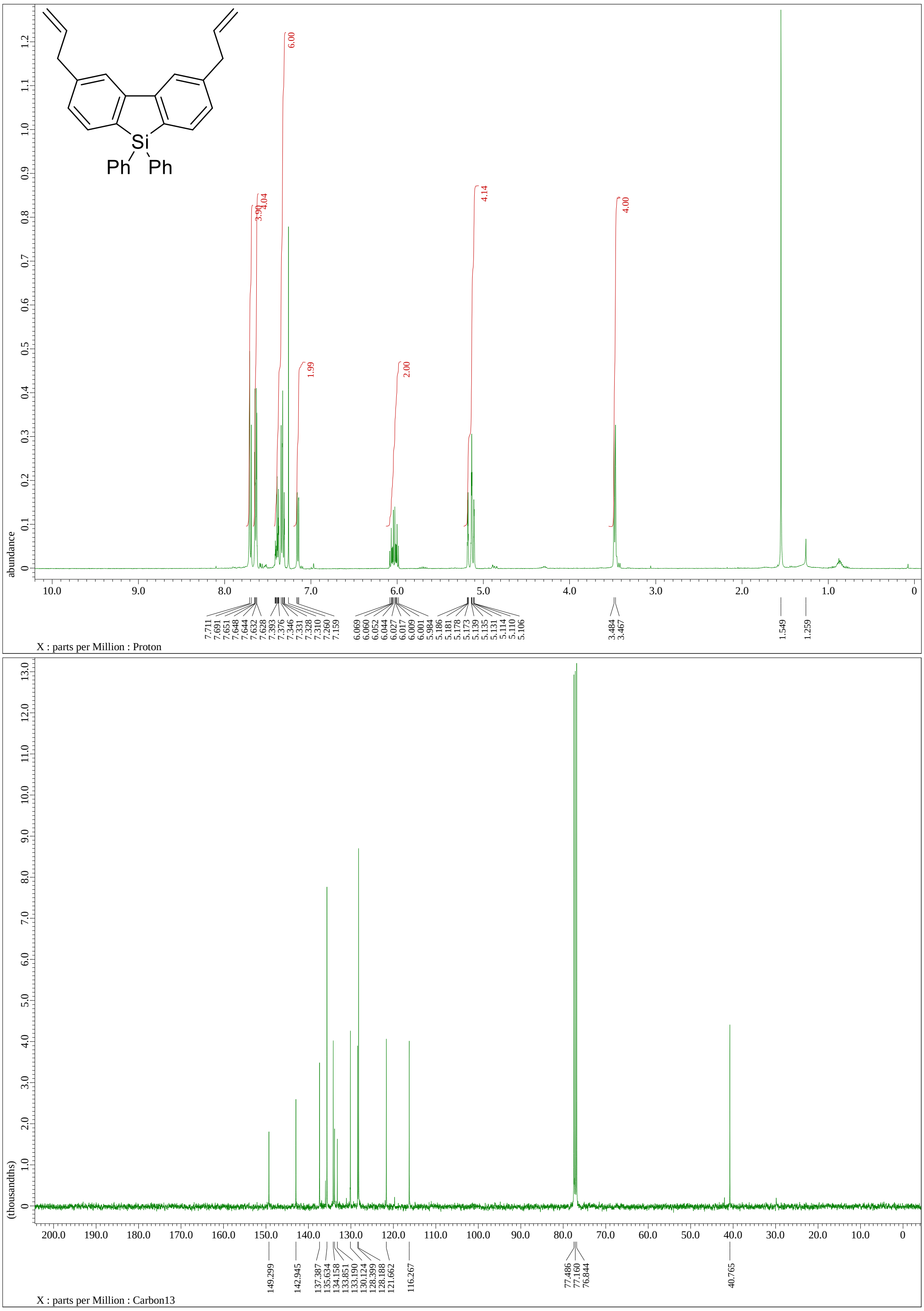


Figure S46. ^{1}H NMR (top) and ^{13}C NMR (bottom) of **12**

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