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Electronic Supplementary Information

Palladium Bis-Pincer Complexes with Controlled Rigidity and Inter-Metal Distance

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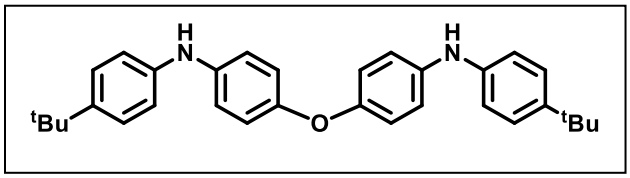
I. General Considerations

General Considerations. Glovebox or standard Schlenk line operations were performed under argon or dinitrogen. Toluene, diethyl ether, *n*-pentane, tetrahydrofuran (THF) and isooctane were dried and deoxygenated (by purging) using a solvent purification system (Innovative Technology Pure Solv MD-5 Solvent Purification System) and stored over molecular sieves in an Ar-filled glovebox. For the synthesis of complex **4**, diethyl ether was dried over Na/K, and distilled under nitrogen before usage. THF was dried over Na, and distilled under nitrogen before usage. C_6D_6 was dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. CH_2Cl_2, $CDCl_3$, and CD_2Cl_2 were dried over CaH_2, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. 2,8-di-*tert*-butyl-5,11-dihydroindolo[3,2-b]carbazole (**4b**) and 2-bromo-5-(triisopropylsilyl)thiazole (**4a**) were synthesized according to a modified procedure from the literature.[1,2] Ferrocenium carba-*closo*-dodecaborate [Fc][$CH_{12}B_{11}$] was synthesized by the procedure from the literature.[3] All other chemicals were used as received from commercial vendors.

Physical Methods. NMR spectra were recorded on a Varian Inova 300, Mercury 300 (^{1}H NMR, 299.952 MHz; ^{13}C NMR, 75.421 MHz; ^{31}P NMR, 121.422 MHz), Bruker 400 (^{1}H NMR, 399.535 MHz; ^{13}C NMR, 100.582 MHz; ^{31}P NMR, 161.734 MHz) and Varian Inova 500 (^{1}H NMR, 499.703 MHz; ^{13}C NMR, 125.697 MHz; ^{31}P NMR, 202.265 MHz) spectrometers. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference (^{1}H NMR: δ 7.16 for C_6D_6, 7.26 for $CDCl_3$; ^{13}C NMR: δ 128.06 for C_6D_6, 77.23 for $CDCl_3$). ^{31}P NMR spectra were referenced externally with 85% phosphoric acid at δ 0. UV-Vis-NIR spectra were collected on a Hitachi U-4100 UV-Vis-NIR spectrophotometer. Electron paramagnetic resonance spectra were recorded in a continuous wave X-band EleXsys EPR

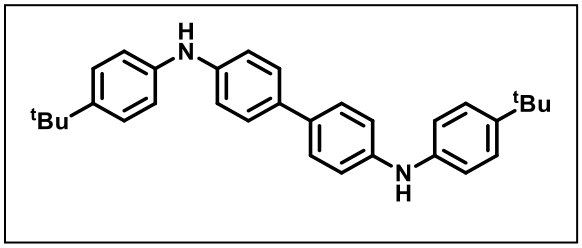
spectrometer at 288 K. Electrochemical studies were carried out using a CH Instruments Model 700 D Series Electrochemical Analyzer and Workstation in conjunction with a three electrode cell. The working electrode was a CHI 104 glassy carbon disk with a 3.0 mm diameter and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was an $Ag/AgNO_3$ electrode. This was prepared as a bulk solution composed of 0.01 M $AgNO_3$ and 0.1 M $[n\text{Bu}_4\text{N}][PF_6]$ in dichloromethane. This was separated from solution by a fine porosity frit. CVs were conducted in dichloromethane with 0.1 M $[n\text{Bu}_4\text{N}][PF_6]$ as the general supporting electrolyte if not specifically mentioned and were reported with a scan rate of 100 mV/s. The concentration of the analyte solutions were approximately 1.00×10^{-3} M. CVs were referenced to $Fe(\eta^5\text{-Cp})_2/ Fe(\eta^5\text{-Cp})^+$ redox couple. ACPI-MS and ESI-MS data were performed by Texas A&M University Chemistry Mass Spectrometry Laboratory. Preparative GPC was performed in chloroform solution at room temperature, using a JAI recycling preparative HPLC (LC-92XXII NEXT SERIES) through a JAIGEL-2H-40 column. Column chromatography was carried out using Biotage® IsoleraTM Prime instrument with various size of SiO_2 Biotage ZIP® cartridge. Elemental analyses were performed by CALI Labs, Inc. (Highland Park, NJ).

II. Synthesis and Characterization of Bis(Pincer) Ligands



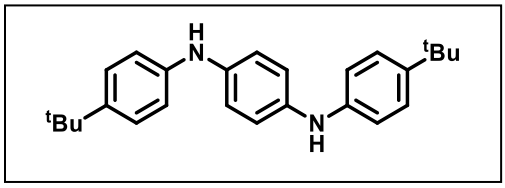
4,4'-oxybis(*N*-(4-(*tert*-butyl)phenyl)aniline) (8).

4,4'-Dibromodiphenyl ether (**5**, 5.0 g, 15.2 mmol) and *tert*-butylaniline (6.8 g, 45.7 mmol) were mixed with 300 mL of toluene in a 1 L flask. In another vial, $Pd_2(dba)_3$ (70 mg, 0.076 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (DPPF, 126 mg, 0.228 mmol) were pre-mixed with 20 mL toluene. Then the yellow suspension solution was combined to the flask. Sodium *tert*-pentoxide (5.0 g, 45.6 mmol) was added into the flask and the solution immediately turned red. The reaction mixture was heated to reflux for two days. After completion, the solution was directly poured into a separation funnel and extracted with water, diluted $HCl_{(aq)}$, and $NaHCO_{3(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel. The filtrate was pumped down under vacuum, re-dissolved in CH_2Cl_2, layered with ethanol and put into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield light yellow powder (6.0 g, 85%). ^{1}H NMR (Figure **S15**, 400 MHz, C_6D_6): δ 7.21 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.98 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.86 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.82 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 4.98 (s, 1H, N-*H*), 1.27 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S16**, 101 MHz, C_6D_6): δ. 152.6 (s, Ar-*C*), 143.4 (s, Ar-*C*), 141.9 (s, Ar-*C*), 139.4 (s, Ar-*C*), 126.4 (s, Ar-*C*), 120.0 (s, Ar-*C*), 119.9 (s, Ar-*C*), 117.6 (s, Ar-*C*), 34.2 (s, *C*Me$_3$), 31.7 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{32}H_{36}N_2O$: 464.2900; Found: 465.2894.



N^4,$N^{4'}$-bis(4-(*tert*-butyl)phenyl)-[1,1'-biphenyl]-4,4'-diamine (9).

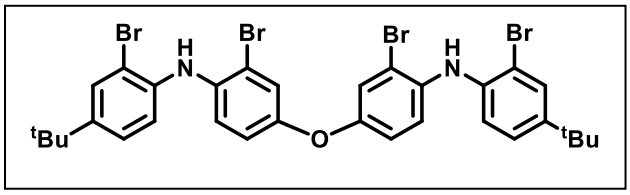
4,4'-Dibromobiphenyl (**6**, 5.0 g, 16.0 mmol) and *tert*-butylaniline (7.2 g, 48.0 mmol) were dissolved in 300 mL of toluene in a 1 L flask. In another vial, $Pd(OAc)_2$ (35.9 mg, 0.16 mmol) and DPPF (133 mg, 0.24 mmol) were pre-mixed with 20 mL toluene. The resultant yellow suspension was added to the flask. Sodium *tert*-pentoxide (5.3 g, 48.0 mmol) was then added into the flask and the contents immediately turned red. The reaction mixture was heated to reflux for two days. After completion, the solution was poured into a separation funnel and extracted with water, diluted $HCl_{(aq)}$, and $NaHCO_{3(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel. The volatiles were removed from the filtrate under vacuum; the residue was re-dissolved in CH_2Cl_2, layered with ethanol and put into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield grey powder (4.9 g, 68%). ^{1}H NMR (Figure **S17**, 400 MHz, C_6D_6): δ 7.48 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 7.24 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.96 (d, $J_{H\text{-}H}$ = 8 Hz, 4H, Ar-*H*), 5.09 (s, 1H, N-*H*), 1.28 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S18**, 101 MHz, C_6D_6): δ. 144.0 (s, Ar-*C*), 143.0 (s, Ar-*C*), 141.0 (s, Ar-*C*), 133.8 (s, Ar-*C*), 127.7 (s, Ar-*C*), 126.4 (s, Ar-*C*), 118.7 (s, Ar-*C*), 118.0 (s, Ar-*C*), 34.2 (s, *C*Me$_3$), 31.7 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{32}H_{36}N_2$: 449.2951; Found: 449.2942.



N^1,N^4-bis(4-(*tert*-butyl)phenyl)benzene-1,4-diamine (10).

1,4-Dibromobenzene (**7**, 5.0 g, 21.2 mmol) and *tert*-butylaniline (9.5 g, 63.6 mmol) were dissolved in 300 mL of toluene in a 1 L flask. In another vial, $Pd(OAc)_2$ (49.4 mg, 0.22 mmol) and DPPF (183 mg, 0.33 mmol) were pre-mixed with 20 mL

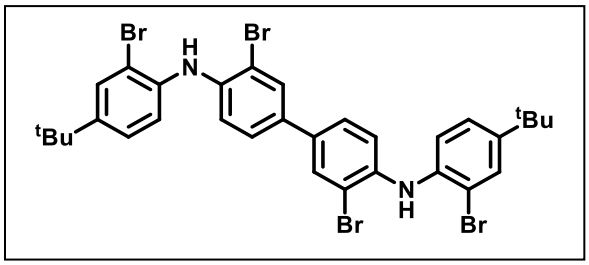
toluene. The resultant yellow suspension was added to the flask, followed by sodium *tert*-pentoxide (7.0 g, 63.6 mmol). The reaction mixture immediately turned red; it was then heated at reflux for two days. Subsequently, the solution was poured into a separation funnel and extracted with water, diluted $HCl_{(aq)}$, and $NaHCO_{3(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel. The volatiles were removed from the filtrate under vacuum, the residue was re-dissolved in CH_2Cl_2, layered with ethanol and placed into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a light-red powder (6.7 g, 85%). ^{1}H NMR (Figure **S19**, 400 MHz, C_6D_6): δ 7.21 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.98 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.86 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.82 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 4.98 (s, 1H, N-*H*), 1.27 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S20**, 101 MHz, C_6D_6): δ. 142.9 (s, Ar-*C*), 142.5 (s, Ar-*C*), 138.0 (s, Ar-*C*), 126.4 (s, Ar-*C*), 120.6 (s, Ar-*C*), 117.1 (s, Ar-*C*), 34.2 (s, *C*Me$_3$), 31.7 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{26}H_{32}N_2$: 372.2560; Found: 372.2554.



4,4'-oxybis(2-bromo-*N*-(2-bromo-4-(*tert*-butyl)phenyl)aniline) (11).

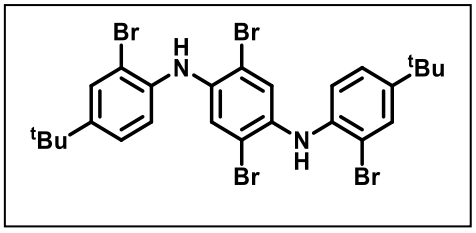
8 (1.0 g, 2.15 mmol) was dissolved in 100 mL of dried, degassed CH_2Cl_2 under argon atmosphere. N-bromosuccinimide (NBS, 1.53 g, 8.61 mmol) was added in 4 portions during 4 h. Three hours after the addition of the final portion, the volatiles were removed under vacuum. The residue was then re-dissolved in 1:1 hexanes/toluene and carefully passed through a plug of silica gel collecting only the light-colored portion. The volatiles were removed from the filtrate under vacuum, the residue was re-dissolved in CH_2Cl_2, layered with ethanol and put into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield light-yellow powder (1.0 g, 60%). ^{1}H NMR (Figure **S21**,

400 MHz, C_6D_6): δ 7.63 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.28 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.00-6.92 (m, 3H, Ar-*H*), 6.67 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 6.37 (s, 1H, N-*H*), 1.12 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S22**, 101 MHz, C_6D_6): δ. 152.3 (s, Ar-*C*), 146.0 (s, Ar-*C*), 138.5 (s, Ar-*C*), 136.9 (s, Ar-*C*), 130.4 (s, Ar-*C*), 125.54 (s, Ar-*C*), 123.7 (s, Ar-*C*), 120.0 (s, Ar-*C*), 118.9 (s, Ar-*C*), 117.9 (s, Ar-*C*), 115.6 (s, Ar-*C*), 114.5 (s, Ar-*C*), 34.2 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{32}H_{32}Br_4N_2O$: 780.9280; Found: 780.9275.



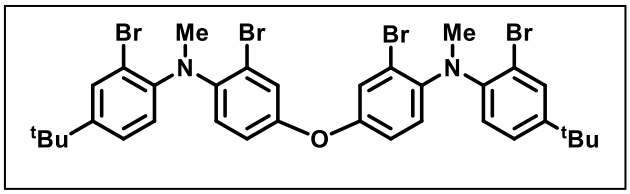
3,3'-dibromo-*N*^{4},*N*$^{4'}$-bis(2-bromo-4-(*tert*-butyl)phenyl)-[1,1'-biphenyl]-4,4'-diamine (12).

9 (1.0 g, 2.22 mmol) was dissolved in 100 mL of dried, degassed CH_2Cl_2 under argon atmosphere. NBS (1.59 g, 8.92 mmol) was added in 4 portions during 4 h. Three hours after the final portion was added, the volatiles were removed under vacuum. The residue was then re-dissolved in 1:1 hexanes/toluene and carefully passed through a plug of silica gel while collecting only the light-colored portion. The volatiles were removed from the filtrate under vacuum; the residue was re-dissolved in CH_2Cl_2, layered with ethanol and put into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield light-yellow powder (1.1 g, 66%). ^{1}H NMR (Figure **S23**, 400 MHz, C_6D_6): δ 7.65 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.64 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.14-6.99 (m, 4H, Ar-*H*), 6.64 (s, 1H, N-*H*), 1.12 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S24**, 101 MHz, C_6D_6): δ. 146.9 (s, Ar-*C*), 140.0 (s, Ar-*C*), 137.7 (s, Ar-*C*), 133.8 (s, Ar-*C*), 131.3 (s, Ar-*C*), 130.5 (s, Ar-*C*), 126.5 (s, Ar-*C*), 125.5 (s, Ar-*C*), 119.5 (s, Ar-*C*), 117.4 (s, Ar-*C*), 115.7 (s, Ar-*C*), 114.3 (s, Ar-*C*), 34.3 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{32}H_{32}Br_4N_2$: 764.9331; Found: 764.5726.



2,5-dibromo-*N*^{1},*N*^{4}-bis(2-bromo-4-(*tert*-butyl)phenyl)benzene-1,4-diamine (13).

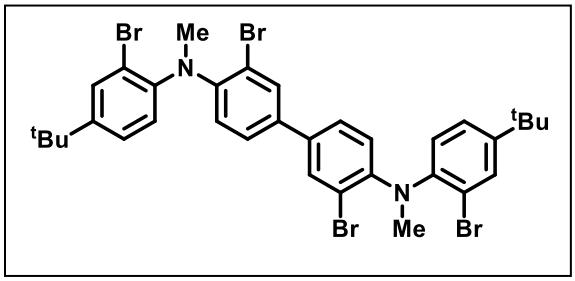
10 (1.0 g, 2.68 mmol) was dissolved in 100 mL of dried, degassed CH_2Cl_2 under argon atmosphere. NBS (1.91 g, 10.74 mmol) was added in 4 portions during 4 h. Three hours after the addition of the final portion, the volatiles were removed under vacuum. The residue was then re-dissolved in 1:1 hexanes/toluene and carefully passed through a plug of silica gel while collecting only the light-colored portion. The volatiles were removed from the filtrate under vacuum, the residue was re-dissolved in CH_2Cl_2, layered with ethanol and placed into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a light-red powder (1.0 g, 54%). ^{1}H NMR (Figure **S25**, 400 MHz, C_6D_6): δ 7.62 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.37 (s, 1H, Ar-*H*), 6.93-6.85 (m, 2H, Ar-*H*), 6.29 (s, 1H, N-*H*), 1.09 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S26**, 101 MHz, C_6D_6): δ. 146.1 (s, Ar-*C*), 138.2 (s, Ar-*C*), 135.9 (s, Ar-*C*), 130.4 (s, Ar-*C*), 125.7 (s, Ar-*C*), 123.4 (s, Ar-*C*), 117.6 (s, Ar-*C*), 114.9 (s, Ar-*C*), 114.2 (s, Ar-*C*), 34.2 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{26}H_{28}Br_4N_2$: 687.8940; Found: 687.8919.



4,4'-oxybis(2-bromo-*N*-(2-bromo-4-(*tert*-butyl)phenyl)-*N*-methylaniline) (14).

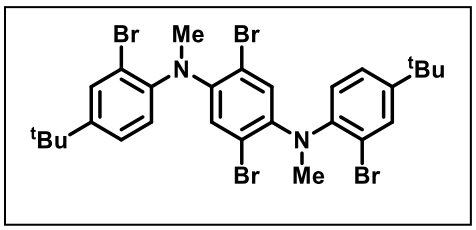
11 (1.0 g, 1.28 mmol) was dissolved in 50 mL of dried, degassed DMF under argon atmosphere. NaH (94 mg, 3.84 mmol) was added slowly. After 10 min, methyl iodide (MeI, 545 mg, 3.84 mmol) was added and the solution was stirred overnight. After completion, the solution was poured into a separation funnel and extracted with water and $NaCl_{(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel and the volatiles were removed from the filtrate under

vacuum to yield a white powder (1.0 g, 97%). ^{1}H NMR (Figure **S27**, 400 MHz, C_6D_6): δ 7.70 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.36 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.08 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 6.77 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 6.67 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 6.61 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 2.93 (s, 3H, N-*Me*), 1.11 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S28**, 101 MHz, C_6D_6): δ. 153.8 (s, Ar-*C*), 148.0 (s, Ar-*C*), 146.5 (s, Ar-*C*), 145.3 (s, Ar-*C*), 131.8 (s, Ar-*C*), 125.3 (s, Ar-*C*), 125.3 (s, Ar-*C*), 124.9 (s, Ar-*C*), 123.2 (s, Ar-*C*), 122.0 (s, Ar-*C*), 120.3 (s, Ar-*C*), 118.5 (s, Ar-*C*), 41.5 (s, N-*Me*), 34.2 (s, *C*Me$_3$), 31.3 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{34}H_{36}Br_4N_2O$: 808.9593; Found: 808.9586.



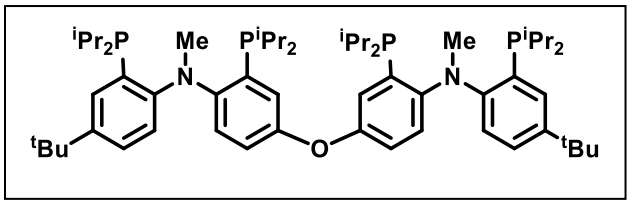
3,3'-dibromo-*N*^{4},*N*$^{4'}$-bis(2-bromo-4-(*tert*-butyl)phenyl)-*N*^{4},*N*$^{4'}$-dimethyl-[1,1'-biphenyl]-4,4'-diamine (15).

12 (1.0 g, 1.31 mmol) was dissolved in 50 mL of dried, degassed DMF under argon atmosphere. NaH (94 mg, 3.92 mmol) was added slowly. After 10 min, MeI (557 mg , 3.92 mmol) was added. The resultant solution was stirred overnight, then poured into a separation funnel and extracted with water and $NaCl_{(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to yield a white powder (1.0 g, 96%). ^{1}H NMR (Figure **S29**, 400 MHz, C_6D_6): δ 7.75 (d, $J_{H\text{-}H}$ = 4 Hz, 2H, Ar-*H*), 7.08 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.79 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 6.77 (d, $J_{H\text{-}H}$ = 8 Hz, 2H, Ar-*H*), 3.00 (s, 3H, N-*Me*), 1.12 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S30**, 101 MHz, C_6D_6): δ. 148.6 (s, Ar-*C*), 148.4 (s, Ar-*C*), 146.5 (s, Ar-*C*), 136.0 (s, Ar-*C*), 132.9 (s, Ar-*C*), 131.7 (s, Ar-*C*), 126.5 (s, Ar-*C*), 125.5 (s, Ar-*C*), 124.2 (s, Ar-*C*), 124.1 (s, Ar-*C*), 121.1 (s, Ar-*C*), 120.9 (s, Ar-*C*), 41.4 (s, N-*Me*), 34.3 (s, *C*Me$_3$), 31.2 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{32}H_{32}Br_4N_2$: 808.9593; Found: 808.9579.



2,5-dibromo-*N*[1],*N*[4]-bis(2-bromo-4-(*tert*-butyl)phenyl)-*N*[1],*N*[4]-dimethylbenzene-1,4-diamine (16).

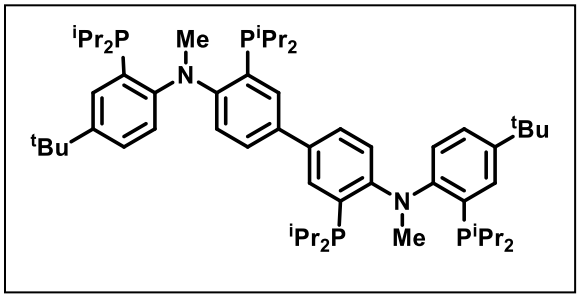
13 (1.0 g, 1.45 mmol) was dissolved in 50 mL of dried, degassed DMF under argon atmosphere. NaH (105 mg , 4.36 mmol) was added slowly. After 10 minutes, MeI (620 mg , 4.36 mmol) was added and the solution was stirred overnight, then poured into a separation funnel, and extracted with water and $NaCl_{(aq)}$. The organic layer was collected and dried with $Na_2SO_{4(s)}$. The solution was then filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to yield a white powder (1.0 g, 97%). ^{1}H NMR (Figure **S31**, 400 MHz, C_6D_6): δ 7.68 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.30 (s, 1H, Ar-*H*), 7.02 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 2H, Ar-*H*), 6.71 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 2.85 (s, 3H, N-*Me*) 1.07 (s, 9H, C*Me*$_3$).^{13}C{^{1}H} NMR (Figure **S32**, 101 MHz, C_6D_6): δ. 148.6 (s, Ar-*C*), 146.2 (s, Ar-*C*), 145.6 (s, Ar-*C*), 131.7 (s, Ar-*C*), 129.0 (s, Ar-*C*), 125.6 (s, Ar-*C*), 124.1 (s, Ar-*C*), 120.9 (s, Ar-*C*), 119.6 (s, Ar-*C*), 41.4 (s, N-*Me*), 34.2 (s, *C*Me$_3$), 31.2 (s, C*Me*$_3$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{28}H_{32}Br_4N_2$: 715.9523; Found: 715.9230.



$^{t\text{Bu}}$PNPOPNP (17).

In a glovebox, **14** (1.0 g, 1.04 mmol) was dissolved in 50 mL of dried, degassed ether in a Schlenk flask and cooled to -35 °C. *n*BuLi (1.83 mL, 4.58 mmol) was added slowly by syringe. After 2 h, ^{i}Pr$_2$PCl (700 mg , 4.58 mmol) was added and the solution was stirred overnight. After completion, the volatiles was removed under vacuum and the residue was re-dissolved in *n*-pentane. The solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to leave behind a colorless oil. The oil was re-dissolved in CH_2Cl_2, layered with acetonitrile and put into a -35 °C freezer for one day. The supernatant was decanted

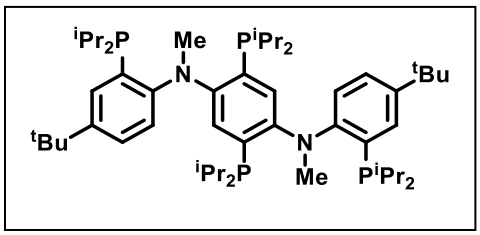
and the solid was dried under vacuum to yield white powder (630 mg, 63%). ^{1}H NMR (Figure **S33**, 400 MHz, C_6D_6): δ 7.55 (s, 1H, Ar-*H*), 7.32 (s, 1H, Ar-*H*), 7.14 (s, 1H, Ar-*H*), 6.89 (m, 3H, Ar-*H*), 3.47 (s, 3H, N-*Me*), 2.13 (m, 2H, C*H*Me$_2$), 1.95 (s, 3H, C*H*Me$_2$),1.28 (s, 9H, C*Me*$_3$), 1.21 (dd, 6H, CH*Me*$_2$), 1.13 (dd, 6H, CH*Me*$_2$) 1.01 (m, 12H, CH*Me*$_2$). ^{31}P{^{1}H} NMR (Figure **S34**, 202 MHz, C_6D_6): δ -5.70 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)), -5.90 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)).^{13}C{^{1}H} NMR (**S35**, 101 MHz, C_6D_6): δ. 158.0 (d, $J_{C\text{-}P}$ = 10 Hz, Ar-*C*), 156.3 (d, $J_{C\text{-}P}$ = 10 Hz, Ar-*C*), 145.1 (s, Ar-*C*), 135.3 (s, Ar-*C*), 132.9 (d, $J_{C\text{-}P}$ = 4 Hz, Ar-*C*), 132.2 (d, $J_{C\text{-}P}$ = 23 Hz, Ar-*C*), 132.0 (d, $J_{C\text{-}P}$ = 23 Hz, Ar-*C*), 131.4 (d, $J_{C\text{-}P}$ = 4 Hz, Ar-*C*), 126.5 (s, Ar-*C*), 124.2 (d, $J_{C\text{-}P}$ = 24 Hz, Ar-*C*), 46.4 (t, $J_{C\text{-}P}$ = 10 Hz, N-*Me*), 34.4 (s, *C*Me$_3$), 31.6 (s, C*Me*$_3$), 25.0 (d, $J_{C\text{-}P}$ = 10 Hz, *C*HMe$_2$), 24.8 (d, $J_{C\text{-}P}$ = 10 Hz, *C*HMe$_2$), 21.2 (dd, $J_{C\text{-}P}$ = 14 Hz, 3 Hz, CH*Me*$_2$), 20.9 (dd, $J_{C\text{-}P}$ = 14 Hz, 3 Hz, CH*Me*$_2$), 20.4 (dd, $J_{C\text{-}P}$ = 7 Hz, 1 Hz, CH*Me*$_2$), 20.2 (dd, $J_{C\text{-}P}$ = 7 Hz, 1 Hz, CH*Me*$_2$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{58}H_{92}N_2OP_4$: 957.6233; Found: 957.6217.



$^{t\text{Bu}}$PNP$_{\text{B}}$PNP (18).

In a glovebox, **15** (1.0 g, 1.26 mmol) was dissolved in 50 mL of dried, degassed ether in a Schlenk flask and cooled to -35^{o}C. *n*BuLi (2.22 mL, 5.54 mmol) was added slowly by syringe. After 2 h, ^{i}Pr$_2$PCl (845 mg, 5.54 mmol) was added and the solution was stirred overnight. Subsequently, the volatiles were removed under vacuum and the residue was re-dissolved in *n*-pentane. The solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuumto result in a colorless oil. The oil was re-dissolved in CH_2Cl_2, layered with acetonitrile and put into a -35 ^{o}C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a white powder (1.0 g, 84%). ^{1}H NMR (Figure **S36**, 400 MHz, C_6D_6): δ 7.91 (s, 1H, Ar-*H*), 7.60 (s, 1H, Ar-*H*), 7.47 (dd,

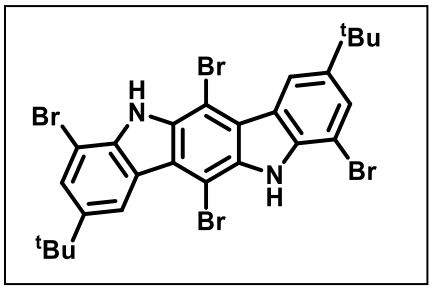
$J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 7.14 (d, $J_{H\text{-}H}$ = 4 Hz, 1H, Ar-*H*), 7.00 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 6.95 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 3.56 (s, 3H, N-*Me*), 2.18 (m, 4H, C*H*Me$_2$), 1.30 (s, 9H, C*Me*$_3$), 1.23 (dd, 12H, CH*Me*$_2$), 1.06 (dd, 12H, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (Figure **S37**, 202 MHz, C_6D_6): δ -5.74 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)), -6.02 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)).$^{13}C\{^1H\}$ NMR (Figure **S38**, 101 MHz, C_6D_6): δ 157.96 (d, $J_{C\text{-}P}$ = 10 Hz, Ar-*C*), 156.28 (d, $J_{C\text{-}P}$ = 10 Hz, Ar-*C*), 145.14 (s, Ar-*C*), 135.34 (s, Ar-*C*), 132.85 (d, $J_{C\text{-}P}$ = 4 Hz, Ar-*C*), 132.24 (d, $J_{C\text{-}P}$ = 23 Hz, Ar-*C*), 132.00 (d, $J_{C\text{-}P}$ = 23 Hz, Ar-*C*), 131.41 (d, $J_{C\text{-}P}$ = 4 Hz, Ar-*C*), 126.46 (s, Ar-*C*), 124.22 (d, $J_{C\text{-}P}$ = 24 Hz, Ar-*C*), 46.21 (t, $J_{C\text{-}P}$ = 10 Hz, N-*Me*), 34.46 (s, *C*Me$_3$), 31.61 (s, C*Me*$_3$), 24.91 (d, $J_{C\text{-}P}$ = 20 Hz, *C*HMe$_2$), 24.71(d, $J_{C\text{-}P}$ = 20 Hz, *C*HMe$_2$), 21.12 (dd, $J_{C\text{-}P}$ = 6 Hz, 2 Hz, CH*Me*$_2$), 20.98 (dd, $J_{C\text{-}P}$ = 6 Hz, 2 Hz, CH*Me*$_2$), 20.34 (s, CH*Me*$_2$), 20.17(s, CH*Me*$_2$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{58}H_{92}N_2P_4O$: 957.6233; Found: 957.6212.



$^{t\text{Bu}}$PNPPNP (19).

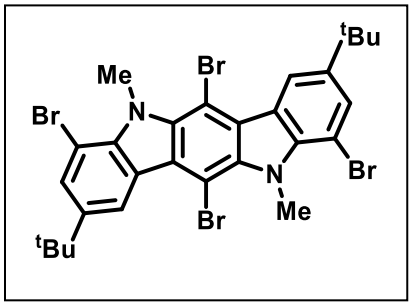
In a glovebox, **16** (1.0 g, 1.40 mmol) was dissolved in 50 mL of dried, degassed ether in a Schlenk flask and cooled to -35 °C. *n*BuLi (2.46 mL , 6.16 mmol) was added slowly by syringe. After 2 h, ^{i}Pr$_2$PCl (940 mg, 6.16 mmol) was added and the solution was stirred overnight. Subsequently, the volatiles were removed under vacuum and the residue was re-dissolved in *n*-pentane. The resultant solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to produce a colorless oil. The oil was re-dissolved in CH_2Cl_2, layered with acetonitrile and placed into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a light-brown powder (800 mg, 66%). ^1H NMR (Figure **S39**, 400 MHz, C_6D_6): δ 7.57 (s, 1H, Ar-*H*), 7.27 (s, 1H, Ar-*H*), 7.19 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 7.02 (dd, $J_{H\text{-}H}$ = 8 Hz, 4Hz, 1H, Ar-*H*), 3.59 (s, 3H, N-*Me*), 2.25 (m, 2H, C*H*Me$_2$), 2.00 (m, 2H, C*H*Me$_2$), 1.30 (s, 9H, C*Me*$_3$),

1.59 (m, 6H, CH*Me*$_2$), 1.13 (m, 12H, CH*Me*$_2$), 1.01 (dd, $J_{H\text{-}H}$ = 12 Hz, 8 Hz, 6H, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR (Figure **S40**, 202 MHz, C_6D_6): δ -4.34 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)), -6.54 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)). $^{13}C\{^1H\}$ NMR (Figure **S41**, 101 MHz, C_6D_6): δ 156.6 (d, $J_{C\text{-}P}$ = 5 Hz Ar-*C*), 153.3 (d, $J_{C\text{-}P}$ = 5 Hz Ar-*C*), 144.7 (s, Ar-*C*), 134.5 (d, $J_{C\text{-}P}$ = 13 Hz, Ar-*C*), 131.3 (s, Ar-*C*), 131.0 (s, Ar-*C*), 129.9 (s, Ar-*C*), 126.1 (s, Ar-*C*), 124.1 (m, Ar-*C*), 46.5 (m, N-*Me*), 34.4 (s, *C*Me$_3$), 31.6 (s, C*Me*$_3$), 24.8 (d, $J_{C\text{-}P}$ = 17 Hz, *C*HMe$_2$), 21.0 (d, $J_{C\text{-}P}$ = 13 Hz, *C*HMe$_2$), 20.4 (d, $J_{C\text{-}P}$ = 18 Hz, CH*Me*$_2$), 20.2 (d, $J_{C\text{-}P}$ = 18 Hz, CH*Me*$_2$). ESI-MS: m/z $[M+H]^+$ Calcd. For $C_{52}H_{88}N_2P_4$: 865.5971; Found: 865.5953.



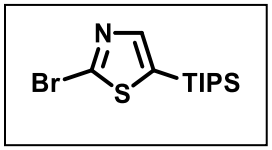
4,6,10,12-tetrabromo-2,8-di-*tert*-butyl-5,11-dihydroindolo[3,2-b]carbazole (21).

2,8-di-*tert*-butyl-5,11-dihydroindolo[3,2-b]carbazole (**20**, 1.0 mmol, 369 mg) was dissolved in anhydrous THF (20 mL) at 0 °C. A solution of NBS (6.0 mmol, 1.07 g) in anhydrous THF (15 mL) was added. The resulting mixture was warmed up to room temperature and stirred overnight. After removal of volatiles under reduced pressure, the crude product was washed with methanol, to give **21** (568 mg, 83%) as a grey solid. ^1H NMR (Figure **S42**, 500 MHz, $CDCl_3$): δ 8.74 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 8.27 (s, 2H, N-*H*), 7.73 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 1.48 (s, 18H, C*Me*$_3$). $^{13}C\{^1H\}$ NMR (Figure **S43**, 100 MHz, $CDCl_3$): δ 144.7 (s, Ar-*C*), 137.3 (s, Ar-*C*), 134.9 (s, Ar-*C*), 127.6 (s, Ar-*C*), 124.4 (s, Ar-*C*), 122.0 (s, Ar-*C*), 118.3 (s, Ar-*C*), 35.2 (s, *C*Me$_3$), 32.1 (s, C*Me*$_3$). APCI-MS: m/z $[M+H]^+$ Calcd. for $C_{26}H_{25}Br_4N_2$: 684.8707; Found: 684.8701.



22.

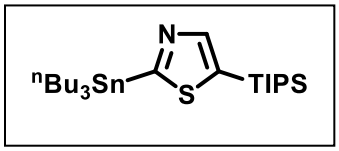
21 (1.10 g, 1.61 mmol) was dissolved in a mixed solvent of DMF (100 mL) and THF (20 mL) at room temperature. NaH powder (116 mg, 4.83 mmol) was added in one portion. The mixture was stirred at room temperature for 30 min before MeI (680 mg, 4.79 mmol) was added. After the addition of MeI, a yellow precipitate was formed, and the suspension was stirred overnight. The suspension was filtered, and the resulting yellow solids were washed extensively with water and acetone, to give **22** (1.10 g, 96%). ^{1}H NMR (Figure **S44**, 500 MHz, $CDCl_3$): δ 9.01 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 7.75 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 4.30 (s, 6H, N-*Me*), 1.45 (s, 18H, C*Me*$_3$). ^{13}C{^{1}H} NMR (Figure **S45**, 125 MHz, $CDCl_3$): δ 145.0 (s, Ar-*C*), 142.4 (s, Ar-*C*), 141.1 (s, Ar-*C*), 130.4 (s, Ar-*C*), 127.4 (s, Ar-*C*), 125.0 (s, Ar-*C*), 119.2 (s, Ar-*C*), 104.6 (s, Ar-*C*), 98.8 (s, Ar-*C*), 39.1 (s, N-*Me*), 35.0 (s, *C*Me$_3$), 32.0 (s, C*Me*$_3$). APCI-MS: m/z $[M+H]^+$ Calcd. For $C_{28}H_{29}Br_4N_2$: 712.9021; Found: 712.9002.



2-bromo-5-(triisopropylsilyl)thiazole (23a).[1]

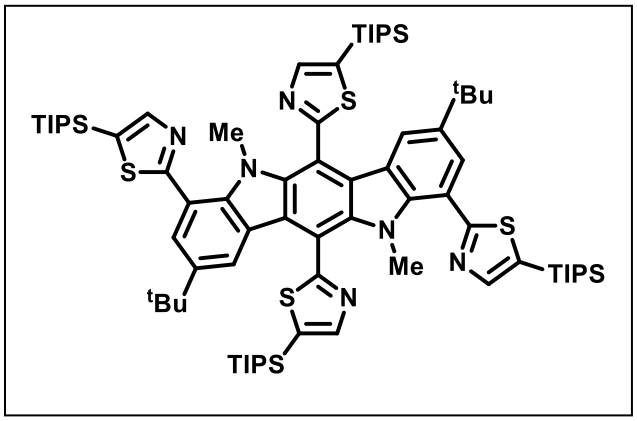
To a solution of ^{i}PrMgCl•LiCl (12.0 mL, 15.6 mmol, 1.3 M in THF), anhydrous 2,2,6,6-tetramethylpiperidine (TMPH, 16.0 mmol, 2.26 g) was added dropwise at room temperature. The resulting mixture was stirred for 2 d to give a TMPMgCl•LiCl THF solution, which is directly used for the following synthesis. A solution of 2-bromothiazole (10.0 mmol, 1.64 g) in anhydrous THF (20 mL) was stirred at −78 °C. The freshly prepared TMPMgCl•LiCl solution was added dropwise over 15 min. The resulting mixture was stirred at −78 °C for 2 h, and triisopropylsilylchloride was added in one portion. The mixture was slowly warmed up to room temperature and stirred overnight. The reaction mixture was extracted with CH_2Cl_2. The organic solution was washed with water extensively, and dried over $MgSO_4$. The crude product was

purified by column chromatography (SiO_2, hexane/CH_2Cl_2 = 2/1), to give **23a** as pale yellow oil (1.73 g, 54%). ^{1}H NMR (Figure **S46**, 500 MHz, $CDCl_3$): δ 7.63 (s, 1H, Ar-*H*), 1.30 (sept, $J_{H\text{-}H}$ = 7.5 Hz, 3H, C*H*Me$_2$), 1.09 (d, $J_{H\text{-}H}$ = 7.5 Hz, 18H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (Figure **S47**, 101 MHz, $CDCl_3$): δ 150.1 (s, Ar-*C*), 140.6 (s, Ar-*C*), 132.9 (s, Ar-*C*), 18.6 (m, *C*HMe$_2$), 11.8 (m, *C*H*Me$_2$*). APCI-MS: m/z [M+H]$^+$ Calcd. for $C_{12}H_{23}BrNSSi$: 320.0498; Found: 320.0489.



2-(tributylstannyl)-5-(triisopropylsilyl)thiazole (23).

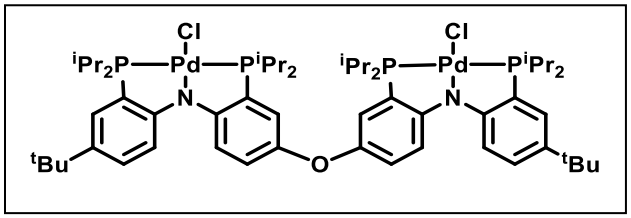
To a solution of **23a** (1.19 mmol, 380 mg) in anhydrous Et_2O (3 mL) at −78 °C, *n*BuLi (1.0 mL, 1.6 M in hexane) was added dropwise. After the addition of *n*BuLi, anhydrous THF (0.3 mL) was added. The resulting mixture was stirred at −78 °C for 1 h, before ^{n}Bu$_3$SnCl (1.6 mmol, 520 mg) was added in one portion. The mixture was slowly warmed up to room temperature and stirred overnight. The reaction mixture was extracted with CH_2Cl_2. The organic solution was washed with water extensively, and dried over $MgSO_4$. The crude product was purified by GPC, to give **23** as brown oil (500 mg, 79%). ^{1}H NMR (Figure **S48**, 500 MHz, $CDCl_3$): δ 8.22 (s, 1H, Ar-*H*), 1.60 (m, 6H), 1.36~1.31 (m, 9H), 1.22 (m, 6H), 1.09 (d, $J_{H\text{-}H}$ = 7.5 Hz, 18H, CH*Me$_2$*), 0.88 (t, $J_{H\text{-}H}$ = 7.5 Hz, 9H, Sn*^{n}Bu$_3$*). ^{13}C{^{1}H} NMR (Figure **S49**, 101 MHz, $CDCl_3$): δ 178.4 (s, Ar-*C*), 152.4 (s, Ar-*C*), 128.6 (s, Ar-*C*), 29.1, 27.4, 18.7, 13.8, 12.2, 11.4. APCI-MS: m/z [M+H]$^+$ Calcd. for $C_{24}H_{50}NSSiSn$: 532.2450; Found: 532.2434.



24

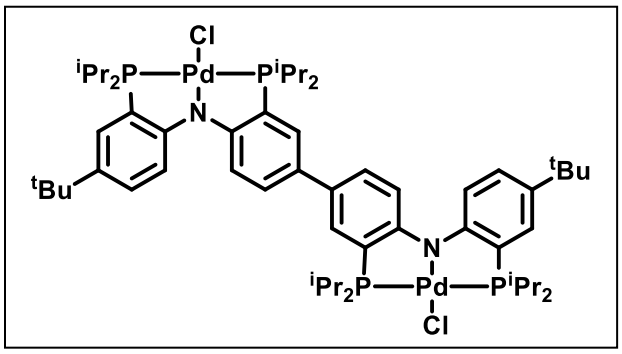
A thick-wall reaction vessel filled with **22** (99.7 mg, 0.14 mmol) and **23** (509.2 mg, 0.96 mmol) was taken into an N_2-filled glovebox, where $Pd(PPh_3)_4$ (40.4 mg, 0.035 mmol), CuI (6.7 mg, 0.035 mmol) and toluene (4 mL) were added. The reaction vessel was sealed and taken out of the glovebox. The reaction mixture was stirred at 140 °C for 3 d. After cooling to room temperature, volatiles were removed under reduced pressure. The mixture was further extracted with CH_2Cl_2. The organic solution was washed with water extensively, and dried over $MgSO_4$. The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate = 19/1 ~ 7/3), to give **24** as yellow solids (148 mg, 78%). ^{1}H NMR (Figure **S50**, 500 MHz, $CDCl_3$): δ 8.26 (s, 2H, Ar-*H*), 7.91 (s, 2H, Ar-*H*), 7.53 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 7.05 (d, $J_{H\text{-}H}$ = 1.5 Hz, 2H, Ar-*H*), 2.94 (s, 6H, N-*Me*), 1.45 (sept, 6H, C*H*Me$_2$), 1.36 (sept, 6H, C*H*Me$_2$), 1.24 (s, 18H, C*Me$_3$*), 1.18 (d, $J_{H\text{-}H}$ = 7.5 Hz, 36H, CH*Me$_2$*), 1.12 (d, $J_{H\text{-}H}$ = 7.5 Hz, 36H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (Figure **S51**, 125 MHz, $CDCl_3$): δ 171.5 (s, Ar-*C*), 169.4 (s, Ar-*C*), 150.4 (s, Ar-*C*), 150.0 (s, Ar-*C*), 141.6 (s, Ar-*C*), 140.6 (s, Ar-*C*), 137.9 (s, Ar-*C*), 131.0 (s, Ar-*C*), 128.5 (s, Ar-*C*), 127.2 (s, Ar-*C*), 124.3 (s, Ar-*C*), 123.3 (s, Ar-*C*), 120.5 (s, Ar-*C*), 117.2 (s, Ar-*C*), 111.8 (s, Ar-*C*), 36.3 (s, N-*Me*), 34.6, 32.0, 18.8 (two s), 12.0. APCI-MS: m/z $[M+H]^+$ Calcd. for $C_{76}H_{117}N_6S_4Si_4$: 1354.7300; Found: 1354.7334.

III. Synthesis and Characterization of Bis(Pincer) Palladium Complexes 1-4



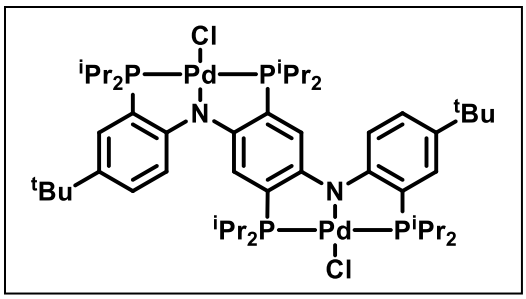
$^{t\mathrm{Bu}}$(PNPOPNP)PdCl (1).

In a glovebox, **17** (200 mg, 209 μmol) was dissolved in 10 mL of dried, degassed toluene in a screw cap culture tube. $Pd(COD)Cl_2$ (119 mg, 417 μmol) was added and the tube was brought outside the glovebox. After heating at 100 °C for 3 h, the tube was taken in the glovebox. Volatiles were then removed under vacuum and the residue was re-dissolved in ether. The solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to give a red powder. The powder can be further purified by re-dissolving in CH_2Cl_2, layering with acetonitrile and placing into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a red powder (253 mg, 72%). ^{1}H NMR (Figure **S4**, 400 MHz, C_6D_6): δ 7.66 (m, 2H, Ar-*H*), 7.13 (s, 1H, Ar-*H*), 7.04 (d, 1H, $J_{H\text{-}H}$ = 8 Hz, Ar-*H*), 6.91 (m, 2H, Ar-*H*), 2.37 (m, 2H, C*H*Me$_2$), 2.21 (m, 2H, C*H*Me$_2$), 1.42 (m, 12H, CH*Me*$_2$),1.25 (s, 9H, C*Me*$_3$), 1.13 (m, 12H, CH*Me*$_2$). ^{31}P{^{1}H} NMR (Figure **S5**, 202 MHz, C_6D_6): δ 49.45 (d, $J_{P\text{-}P}$ = 418 Hz, 1P, Ar-*P*(^{i}Pr$_2$)), 47.50 (d, $J_{P\text{-}P}$ = 418 Hz, 1P, Ar-*P*(^{i}Pr$_2$)).^{13}C{^{1}H} NMR (**S6**, 101 MHz, C_6D_6): δ 162.0 (dd, $J_{C\text{-}P}$ = 5 Hz, 17 Hz, Ar-*C*), 160.2 (dd, $J_{C\text{-}P}$ = 5 Hz, 17 Hz, Ar-*C*), 149.1 (dd, $J_{C\text{-}P}$ = 6 Hz, 2 Hz, Ar-*C*), 139.7 (d, $J_{C\text{-}P}$ = 5 Hz, Ar-*C*), 129.1 (d, $J_{C\text{-}P}$ = 6 Hz, Ar-*C*), 122.1 (d, $J_{C\text{-}P}$ = 5 Hz, Ar-*C*), 120.8 (dd, $J_{C\text{-}P}$ = 10 Hz, 5 Hz, Ar-*C*), 119.2 (dd, $J_{C\text{-}P}$ = 10 Hz, 5 Hz, Ar-*C*), 116.9 (d, $J_{C\text{-}P}$ = 13 Hz, Ar-*C*), 115.7 (d, $J_{C\text{-}P}$ = 10 Hz, Ar-*C*), 33.9 (s, *C*Me$_3$), 31.6 (s, C*Me*$_3$), 25.1 (dd, $J_{C\text{-}P}$ = 4 Hz, 8Hz, *C*HMe$_2$), 18.7 (dd, $J_{C\text{-}P}$ = 4 Hz, 8Hz, *C*HMe$_2$), 18.0 (s, CH*Me*$_2$). Elem. Anal. Calcd for $C_{56}H_{86}Cl_2N_2OP_4Pd_2$: C, 55.54; H, 7.16; N, 2.31. Found: C, 55.48; H, 7.15; N, 2.18.



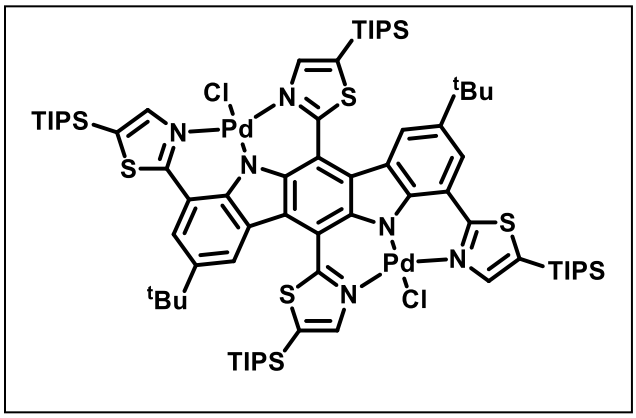
$^{t\mathrm{Bu}}$PNP$_{\mathrm{B}}$PNPPdCl (2).

In a glovebox, **18** (200 mg, 212 μmol) was dissolved in 10 mL of dried, degassed toluene in a screw cap culture tube. $Pd(COD)Cl_2$ (121 mg, 425 μmol) was added to the solution and the tube was brought outside the glovebox. After heating at 100 °C for 3 h, the tube was taken in the glovebox. Volatiles were then removed under vacuum and the residue was re-dissolved in ether. The solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to give a red powder. The powder was further purified by re-dissolving it in THF, layering with *n*-pentane and placing in a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield red powder (180 mg, 71%). ^{1}H NMR (Figure **S7**, 400 MHz, C_6D_6): δ 7.88 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 7.81 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 7.43 (s, 1H, Ar-*H*), 7.37 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 7.16 (s, 1H, Ar-*H*), 7.10 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, Ar-*H*), 2.41 (m, 4H, C*H*Me$_2$), 1.45 (dd, $J_{H\text{-}P}$ = 20 Hz, $J_{H\text{-}H}$ = 8 Hz, 12H, CH*Me*$_2$), 1.26 (s, 9H, C*Me*$_3$), 1.19 (m, 12H, CH*Me*$_2$). ^{31}P{^{1}H} NMR (Figure **S8**, 202 MHz, C_6D_6): δ 48.86 (s, 1P, Ar-*P*(^{i}Pr$_2$)), 48.83 (s, 1P, Ar-*P*(^{i}Pr$_2$)). ^{13}C{^{1}H} NMR (Figure **S9**, 101 MHz, C_6D_6): δ 162.9 (dd, $J_{C\text{-}P}$ = 12 Hz, 9 Hz, Ar-*C*), 161.7 (dd, $J_{C\text{-}P}$ = 12 Hz, 9 Hz, Ar-*C*), 140.3 (s, Ar-*C*), 130.4 (s, Ar-*C*), 130.2 (t, $J_{C\text{-}P}$ = 3 Hz, Ar-*C*), 129.8 (s, Ar-*C*), 129.2 (s, Ar-*C*), 129.0 (s, Ar-*C*), 128.6 (s, Ar-*C*), 120.6 (dd, $J_{C\text{-}P}$ = 20 Hz, 14 Hz, Ar-*C*), 119.7 (dd, $J_{C\text{-}P}$ = 20 Hz, 15 Hz, Ar-*C*), 116.8 (dd, $J_{C\text{-}P}$ = 7 Hz, 6 Hz, Ar-*C*), 116.5 (dd, $J_{C\text{-}P}$ = 7 Hz, 6 Hz, Ar-*C*), 34.0 (s, *C*Me$_3$), 31.6 (s, C*Me*$_3$), 25.1 (m, *C*HMe$_2$), 18.7 (s, CH*Me*$_2$), 18.0 (s, CH*Me*$_2$). Elem. Anal. Calcd. for $C_{56}H_{86}Cl_2N_2P_4Pd_2$: C, 56.29; H, 7.25; N, 2.34. Found: C, 56.56; H, 7.26; N, 2.29.



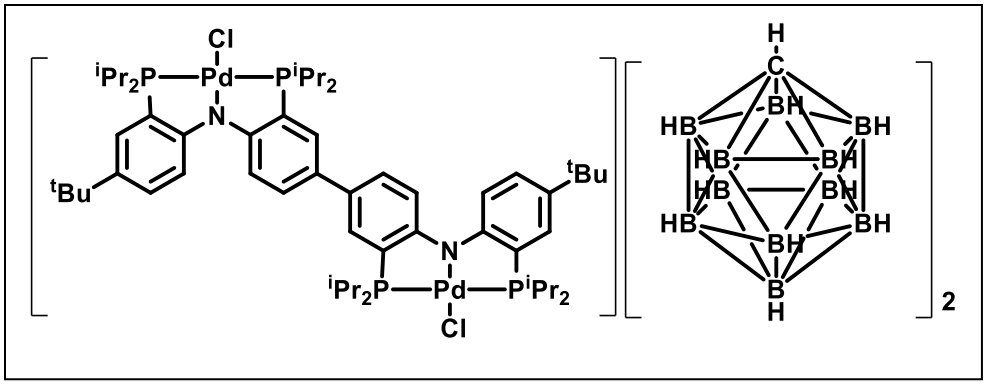
$^{t\text{Bu}}$(PNPPNP)PdCl (3).

In a glovebox, **19** (200 mg, 231 μmol) was dissolved in 10 mL of dried, degassed toluene in a screw cap culture tube followed by the addition of $Pd(COD)Cl_2$ (132 mg, 462 μmol). The tube was taken out of the glovebox and was heated at 100 °C for 3 h. After heating, the tube was taken in the glovebox. The volatiles were then removed under vacuum and the residue was re-dissolved in THF. The resultant solution was filtered through a plug of silica gel and the volatiles were removed from the filtrate under vacuum to give a purple powder. The powder was further purified by re-dissolving in THF, layering with *n*-pentane and placing into a -35 °C freezer for one day. The supernatant was decanted and the solid was dried under vacuum to yield a purple powder (212 mg, 82%). ^{1}H NMR (Figure **S10**, 400 MHz, C_6D_6): δ 7.74 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 7.57 (dd, $J_{H\text{-}H}$ = 8 Hz, 4 Hz, 1H, Ar-*H*), 7.21 (d, $J_{H\text{-}H}$ = 12 Hz, 1H, Ar-*H*), 2.45 (m, 2H, C*H*Me$_2$), 2.13 (m, 2H, C*H*Me$_2$), 1.49 (dd, $J_{H\text{-}H}$ = 16 Hz, 8 Hz, 6H, CH*Me$_2$*), 1.41 (dd, $J_{H\text{-}H}$ = 16 Hz, 8 Hz, 6H, CH*Me$_2$*), 1.25 (s, 9H, C*Me$_3$*), 1.20 (dd, $J_{H\text{-}H}$ = 16 Hz, 8 Hz, 6H, CH*Me$_2$*), 1.11 (dd, $J_{H\text{-}H}$ = 16 Hz, 8 Hz, 6H, CH*Me$_2$*). ^{31}P{^{1}H} NMR (Figure **S11**, 202 MHz, C_6D_6): δ 49.49 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)), 44.66 (d, $J_{P\text{-}P}$ = 10 Hz, 1P, Ar-*P*(^{i}Pr$_2$)). ^{13}C{^{1}H} NMR (Figure **S12**, 126 MHz, THF with trace amount of C_6D_6): δ 161.4 (d, $J_{C\text{-}P}$ = 21 Hz, Ar-*C*), 155.2 (dd, $J_{C\text{-}P}$ = 6 Hz, 21 Hz, Ar-*C*), 138.2 (d, $J_{C\text{-}P}$ = 5 Hz, Ar-*C*), 129.0 (s, Ar-*C*), 128.1 (s, Ar-*C*), 122.5 (d, $J_{C\text{-}P}$ = 37 Hz, Ar-*C*), 118.4 (d, $J_{C\text{-}P}$ = 15 Hz, Ar-*C*), 117.1 (d, $J_{C\text{-}P}$ = 37 Hz, Ar-*C*), 114.5 (d, $J_{C\text{-}P}$ = 13 Hz, Ar-*C*), 33.4 (s, *C*Me$_3$), 30.9 (s, C*Me$_3$*), 17.9 (d, $J_{C\text{-}P}$ = 5 Hz, CH*Me$_2$*), 17.8 (d, $J_{C\text{-}P}$ = 5 Hz, CH*Me$_2$*), 17.3 (d, $J_{C\text{-}P}$ = 3 Hz, CH*Me$_2$*), 17.2 (d, $J_{C\text{-}P}$ = 3 Hz, CH*Me$_2$*). Elemental Analysis: C, 53.68; H, 7.39; N, 2.50. Found: C, 53.44; H, 7.51; N, 2.56.



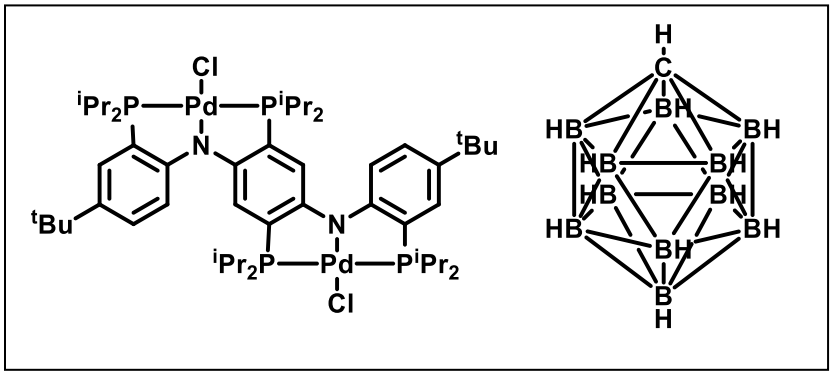
(4)

24 (13.5 mg, 0.01 mmol) was mixed with $Pd(COD)Cl_2$ (6.3 mg, 0.022 mmol) in anhydrous toluene (1.0 mL). The mixture was stirred at 120 °C for two days. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was extracted with CH_2Cl_2. The organic solution was washed with water extensively, and dried over $MgSO_4$. The crude product was purified by column chromatography (SiO_2, hexane/ CH_2Cl_2 = 9/1 ~ 8/2), to give **4** as green solids (13.2 mg, 82%). ^1H NMR (Figure **S13**, 500 MHz, $CDCl_3$): δ 9.33 (s, 2H, Ar-*H*), 9.14 (d, J_{H-H} = 1.5 Hz, 2H, Ar-*H*), 9.11 (s, 2H, Ar-*H*), 8.08 (d, J_{H-H} = 1.5 Hz, 2H, Ar-*H*), 1.48 (s, 18H, C*Me*$_3$), 1.44 (m, 6H, C*H*Me$_2$), 1.37 (m, 6H, C*H*Me$_2$), 1.20 (d, J_{H-H} = 7.5 Hz, 36H, CH*Me*$_2$), 1.14 (d, J_{H-H} = 7.5 Hz, 36H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (Figure **S14**, 125 MHz, $CDCl_3$): δ 168.7 (s, Ar-*C*), 164.0 (s, Ar-*C*), 153.2 (s, Ar-*C*), 152.8 (s, Ar-*C*), 140.4 (s, Ar-*C*), 138.4 (s, Ar-*C*), 137.2 (s, Ar-*C*), 124.4 (s, Ar-*C*), 124.2 (s, Ar-*C*), 124.1 (s, Ar-*C*), 123.7 (s, Ar-*C*), 122.5 (s, Ar-*C*), 121.4 (s, Ar-*C*), 114.5 (s, Ar-*C*), 112.5 (s, Ar-*C*), 35.0, 32.3, 18.7, 18.7, 11.9. Elemental Analysis: C, 55.27; H, 6.90; N, 5.23. Found: C, 54.79; H, 6.79; 5.07.



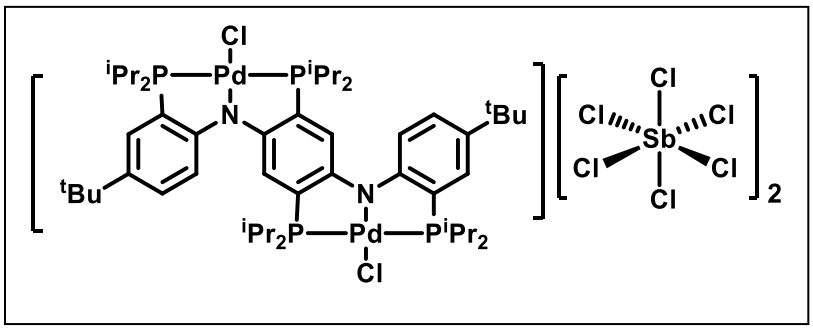
[2][$CH_{12}B_{11}$]$_2$ crystal.

In a glovebox, **2e** (10 mg, 8 μmol) was dissolved in CH_2Cl_2 and mixed with approximately 1 equiv. of ferrocenium carba-*closo*-dodecaborate (2.6 mg, 8 μmol) in a glass vial. The solution color changed from red to black immediately. The reaction mixture was layered with isooctane and placed into a -35 ºC freezer overnight, yielding black crystals. A suitable crystal was selected and subjected to an X-ray diffraction study.



[3][$CH_{12}B_{11}^-$] crystal.

In a glovebox, **3e** (10 mg, 9 μmol) was dissolved in CH_2Cl_2 and mixed with approximately 0.9 equiv. of ferrocenium carba-*closo*-dodecaborate (2.6 mg, 8 μmol) in a glass vial. The solution color changed from purple to black immediately. The reaction mixture was layered with isooctane and placed into a -35 ºC freezer overnight, yielding black crystals. A suitable crystal was selected and subjected to an X-ray diffraction study.



[3][$SbCl_6$]$_2$ crystal.

In a glovebox, **3e** (10 mg, 9 μmol) was dissolved in CH_2Cl_2 and mixed with approximately 2.2 equiv. of tris(4-bromophenyl)aminium hexachloroantimonate, [(4-BrC_6H_4)$_3$N]$SbCl_6$ (16 mg, 18 μmol), in a glass vial. The solution color changed from purple to deep blue immediately. The reaction mixture was layered with isooctane and placed into a -35 ºC freezer overnight, yielding blue crystals. A suitable crystal was selected and subjected to an X-ray diffraction study.

IV. X-Ray Structural Determination Details

X-Ray data collection, solution, and refinement for (1). (CCDC number: 2003991)

A Leica MZ 75 microscope was used to identify a suitable red block with very well defined faces with dimensions (max, intermediate, and min) 0.182 x 0.153 x 0.124 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.71073Å with a potential of 40 kV and a current of 40 mA). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[4] An absorption correction was applied using SADABS.[5] Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using XT/XS in APEX3.[4,6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.[6,7] ORTEP-3 and POV-Ray were employed for the final data presentation and structure plots.[8,9]

X-Ray data collection, solution, and refinement for [2][$CH_{12}B_{11}$]$_2$. (CCDC number: 2003992)

A Leica MZ 75 microscope was used to identify a suitable brown plate with very well defined faces with dimensions (max, intermediate, and min) 0.132 x 0.052 x 0.013 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 140 K. A BRUKER Venture X-ray (kappa

geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418Å with a potential of 50 kV and a current of 1.0mA). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[4] An absorption correction was applied using SADABS.[5] Systematic reflection conditions and statistical tests of the data suggested the space group *P*-1. A solution was obtained readily (Z=1; Z'=0.5) using XT/XS in APEX3.[4,6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure showed presence of partially occupied and/or disordered solvent molecules; both dichloromethane and *n*-pentane. Our efforts to model the solvents resulted in high reliability factors. For the final refinement cycles, these solvent molecules were MASKed using OLEX2.[7] Absence of additional symmetry or void were confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.[6,7] ORTEP-3 and POV-Ray were employed for the final data presentation and structure plots.[8,9]

X-Ray data collection, solution, and refinement for (3). (CCDC number: 1915569)

A Leica MZ 75 microscope was used to identify a suitable dark brown block with very well defined faces with dimensions (max, intermediate, and min) 0.182 x 0.042 x 0.027 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418Å with a potential of 50 kV and a current of 1.0mA). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[4] An

absorption correction was applied using SADABS.[5] Systematic reflection conditions and statistical tests of the data suggested the space group *P*-1. A solution was obtained readily using XT/XS in APEX3.[4,6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. PLATON suggests presence of voids (~47 $Å^3$), however with no electron density. Additionally, no residual electron density were found corresponding at the voids. Absence of additional symmetry was confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.[6,7] ORTEP-3 and POV-Ray were employed for the final data presentation and structure plots.[8,9]

X-Ray data collection, solution, and refinement for [3][$CH_{12}B_{11}$]. (CCDC number: 1915570)

A Leica MZ 75 microscope was used to identify a suitable black block with very well defined faces with dimensions (max, intermediate, and min) 0.402 x 0.385 x 0.376 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.71073Å with a potential of 40 kV and a current of 40 mA). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[4] An absorption correction was applied using SADABS.[5] Systematic reflection conditions and statistical tests of the data suggested the space group *C*2/*c*. A solution was obtained readily (*Z*=4; Z'=0.5) using XT/XS in APEX3.[4,6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. The C1a atom of the carborane could not be located due to the symmetry. Initially all the carborane atoms were assigned boron. C1a was assigned

based on the thermal ellipsoid and was set as disorder. Hydrogen atoms could not be located on the carborane from the residual electron density map, and were placed only to satisfy geometry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Solvent molecules (dichloromethane) which were partially occupied and disordered, could not be modeled and were MASKed using OLEX2.[7] Absence of additional symmetry were confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.[6,7] ORTEP-3 and POV-Ray were employed for the final data presentation and structure plots.[8,9]

X-Ray data collection, solution, and refinement for [3][$SbCl_6$]$_2$. (CCDC number: 1915571)

A Leica MZ 75 microscope was used to identify a suitable brown needle with very well defined faces with dimensions (max, intermediate, and min) 0.192 x 0.042 x 0.027 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with a PHOTON II detector was employed for crystal screening, unit cell determination, and data collection. The X-ray radiation employed was generated from a Mo-Iμs X-ray tube (K_α = 0.71073Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software.[4] An absorption correction was applied using SADABS.[5] Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily (Z=2; Z'=0.5) using XT/XS in APEX3.[4,6] A molecule of dichloromethane was found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated ellipsoids on atoms C25, C20-C22, and the solvent Cl1s, Cl2s, C3s suggested disorder which were successfully modeled between

two positions each with an occupancy ratio of 0.64:0.36. Appropriate restraints and constraints were applied to keep the bond distances, angles, and thermal ellipsoids meaningful. Final formula: $C_{50}H_{82}Cl_2N_2P_4Pd_2 \cdot 2(CH_2Cl_2) \cdot 2(SbCl_6)$. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.[6,7] ORTEP-3 and POV-Ray were employed for the final data presentation and structure plots.[8,9]

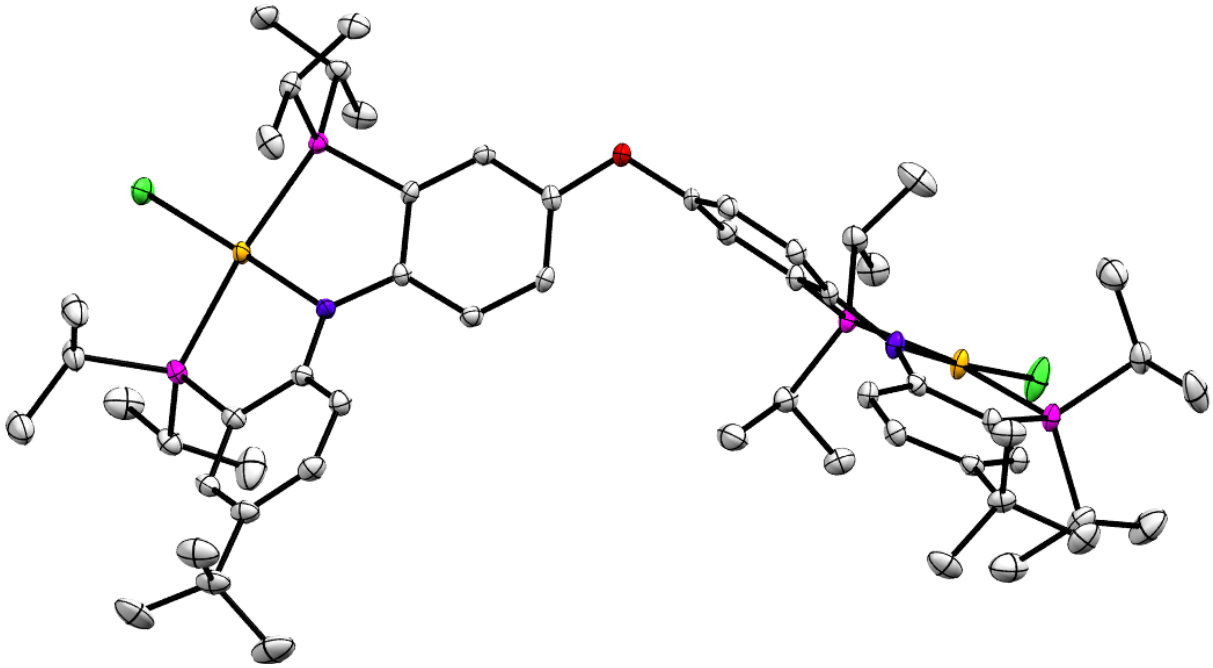


Figure S1: ORTEP of complex **1**. The ellipsoids are set at the 50% probability level, and hydrogen atoms are omitted for clarity. Grey: carbon; yellow: palladium; pink: phosphorus; blue: nitrogen; green: chlorine; red: oxygen.

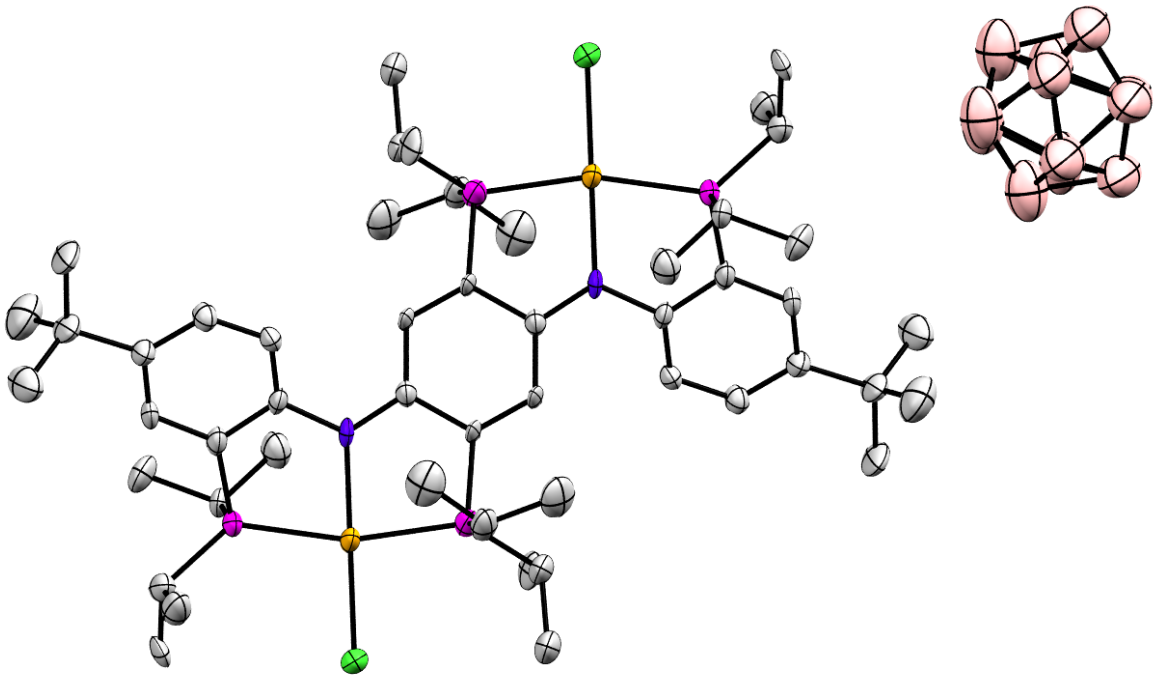


Fig. S2: ORTEP of complex [**3**]$CH_{12}B_{11}$. The ellipsoids are set at the 50% probability level, and hydrogen atoms are omitted for clarity. Grey: carbon; yellow: palladium; pink: phosphorus; blue: nitrogen; green: chlorine; beige: boron.

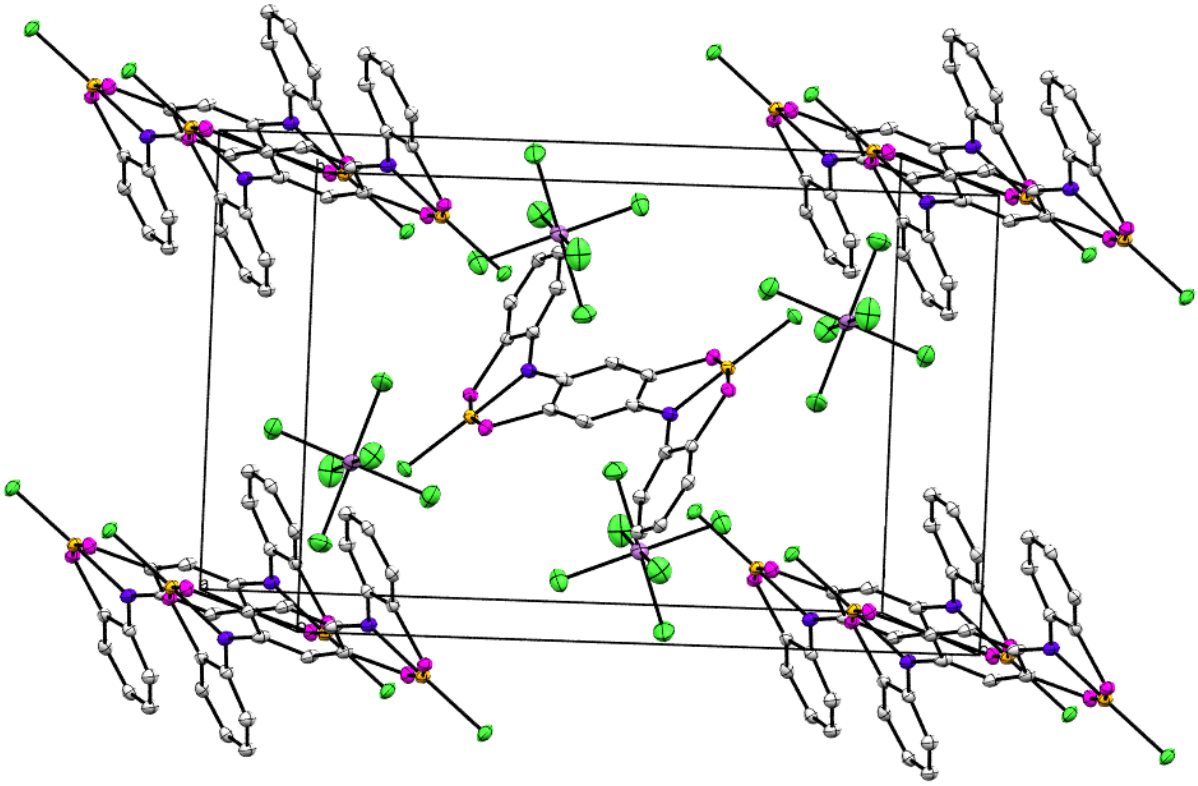


Figure S3: ORTEP of **[3][SbCl$_6$]$_2$** unit cell. The ellipsoids are set at the 50% probability level. The diisopropryl groups on phosphine, *tert*-butyl groups, solvents and hydrogen atoms are omitted for clarity. Grey: carbon; yellow: palladium; pink: phosphorus; blue: nitrogen; green: chlorine; purple; antimony.

V. NMR Spectra

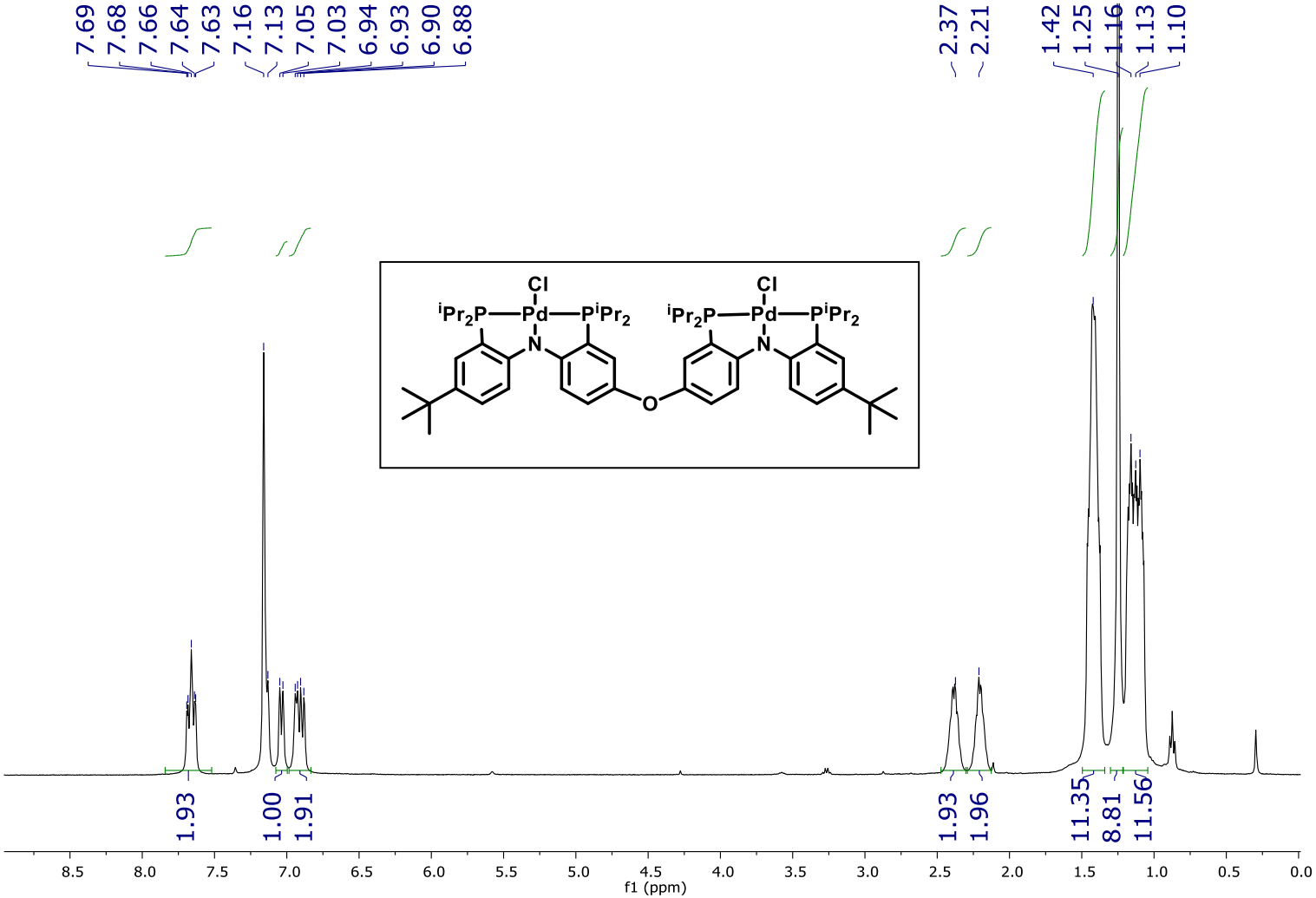


Figure S4. ^{1}H NMR spectrum of **1** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

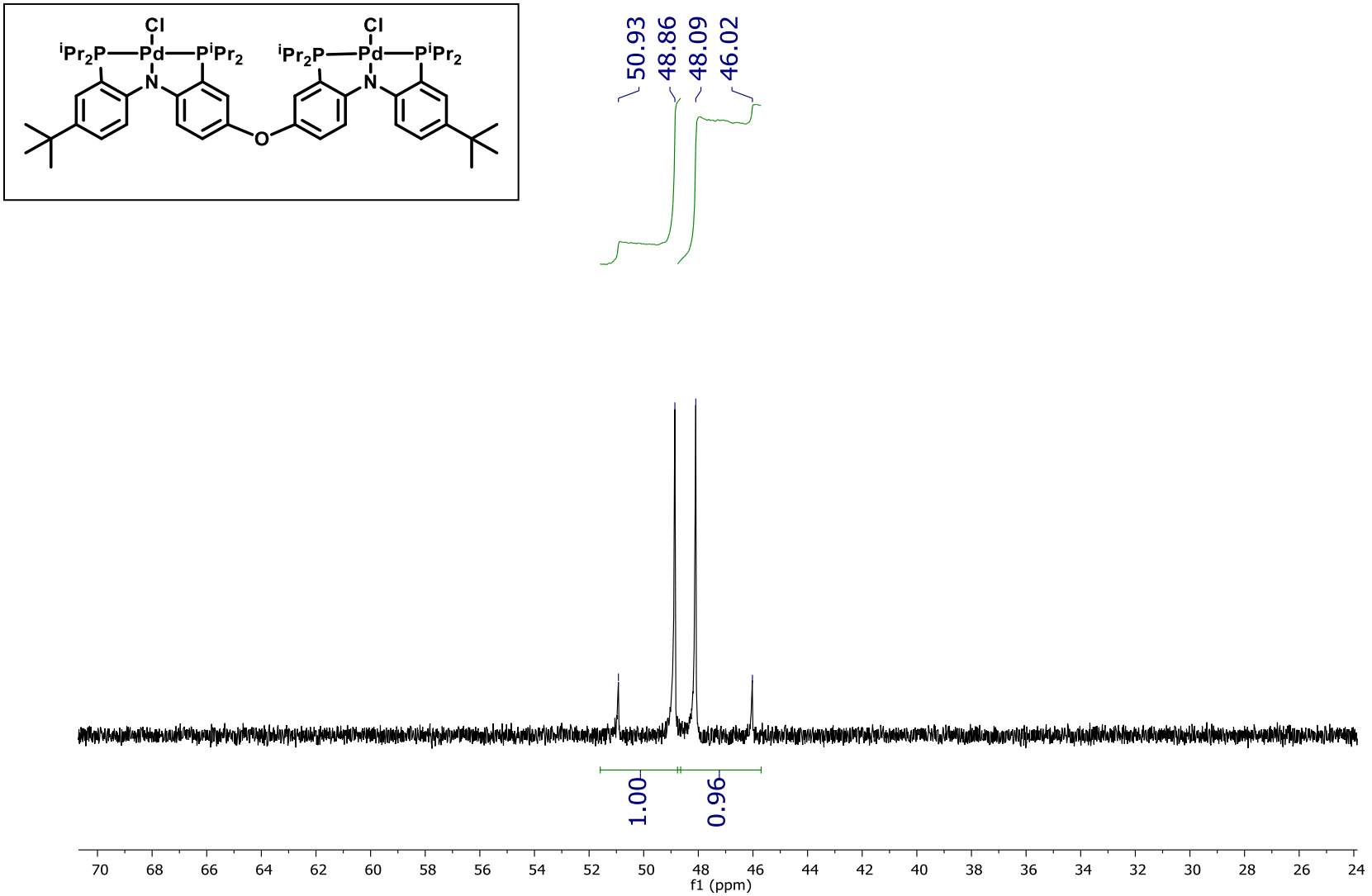


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

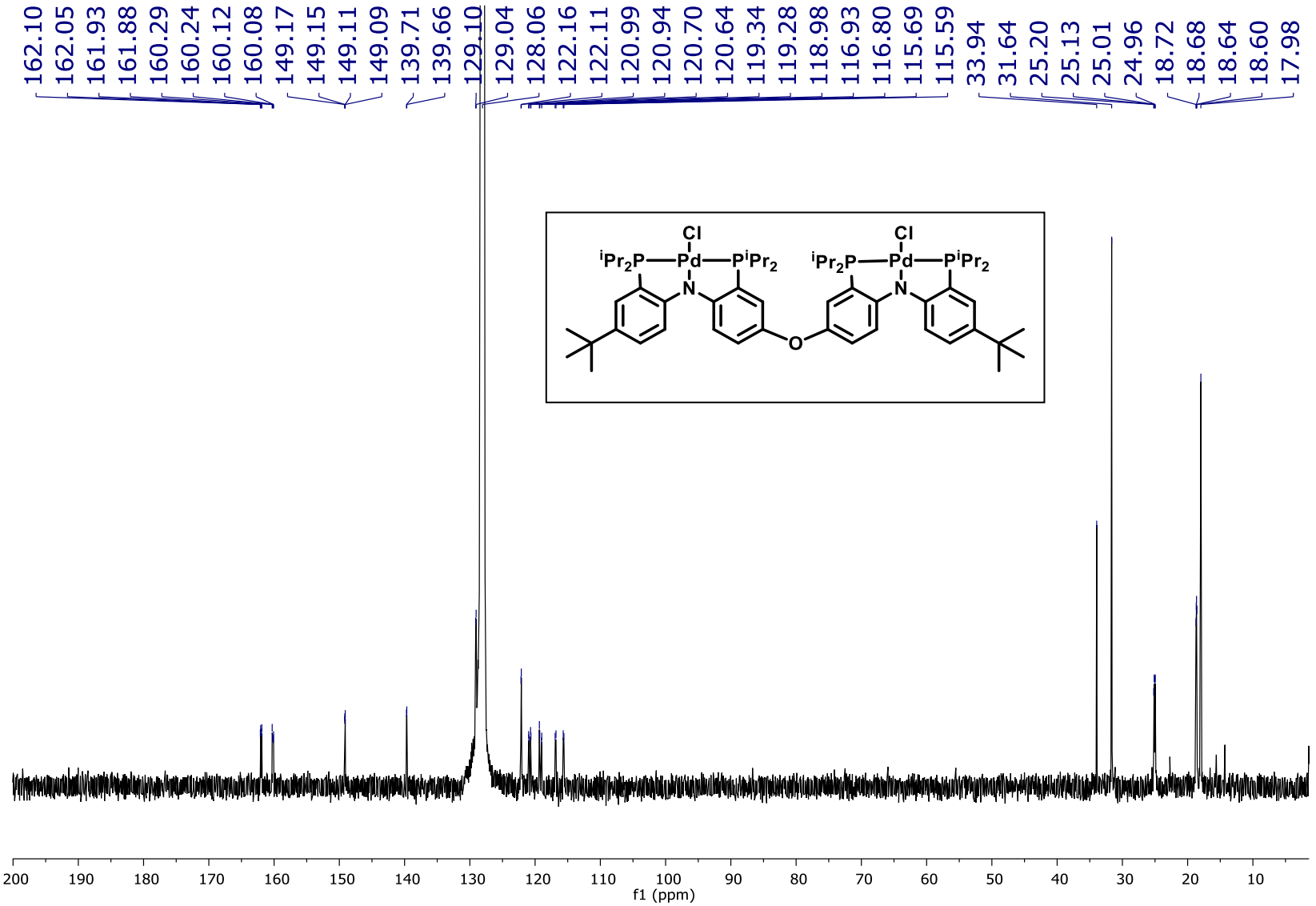


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

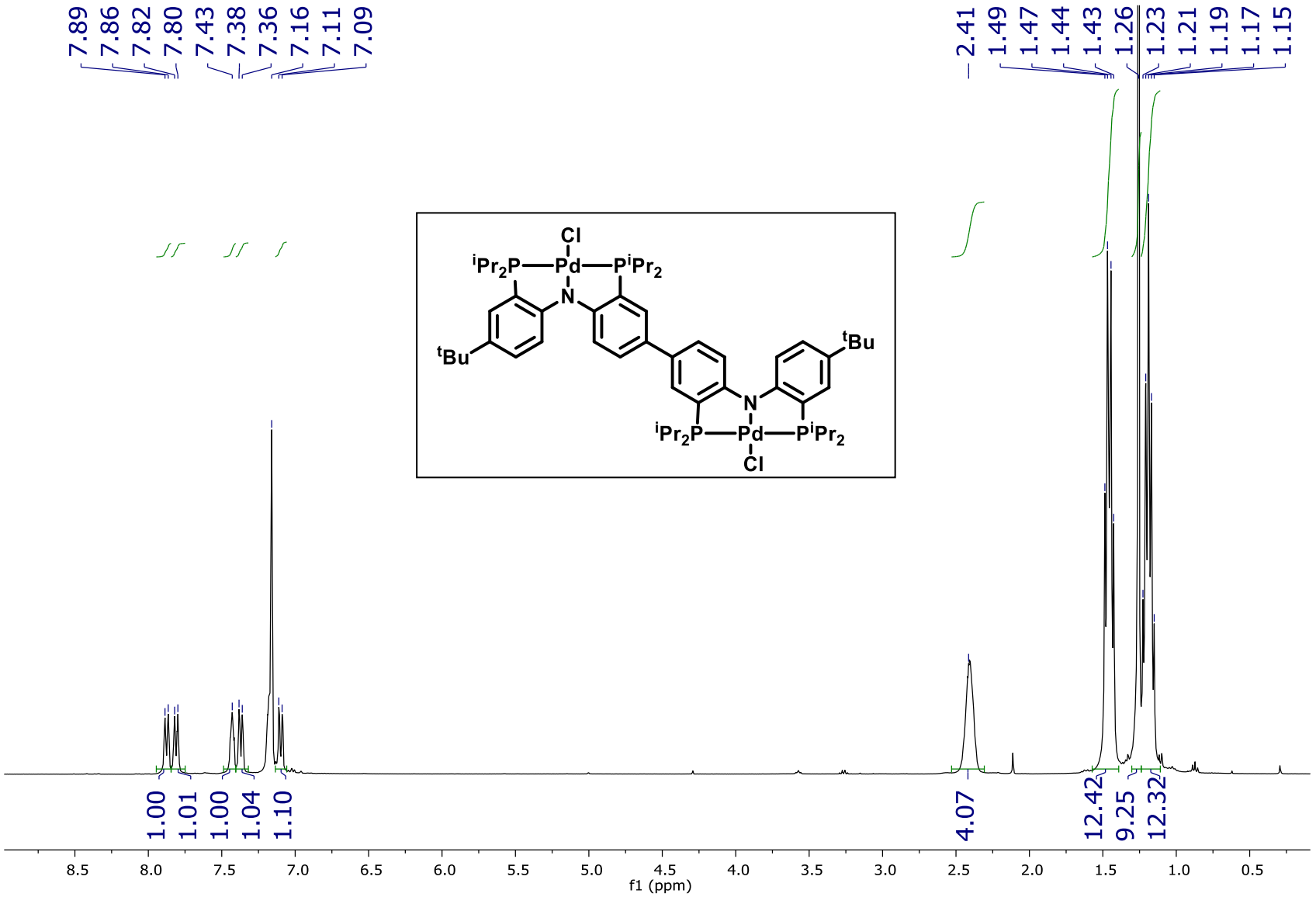


Figure S7. ^{1}H NMR spectrum of **2** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

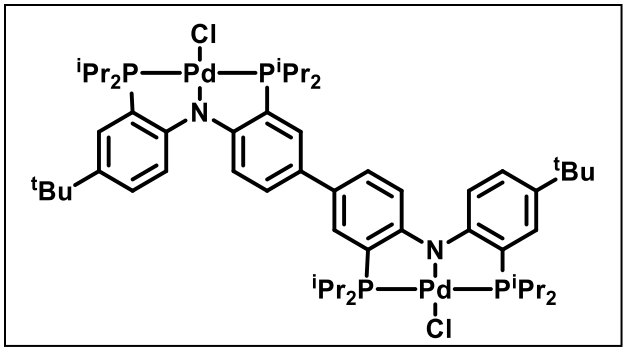


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

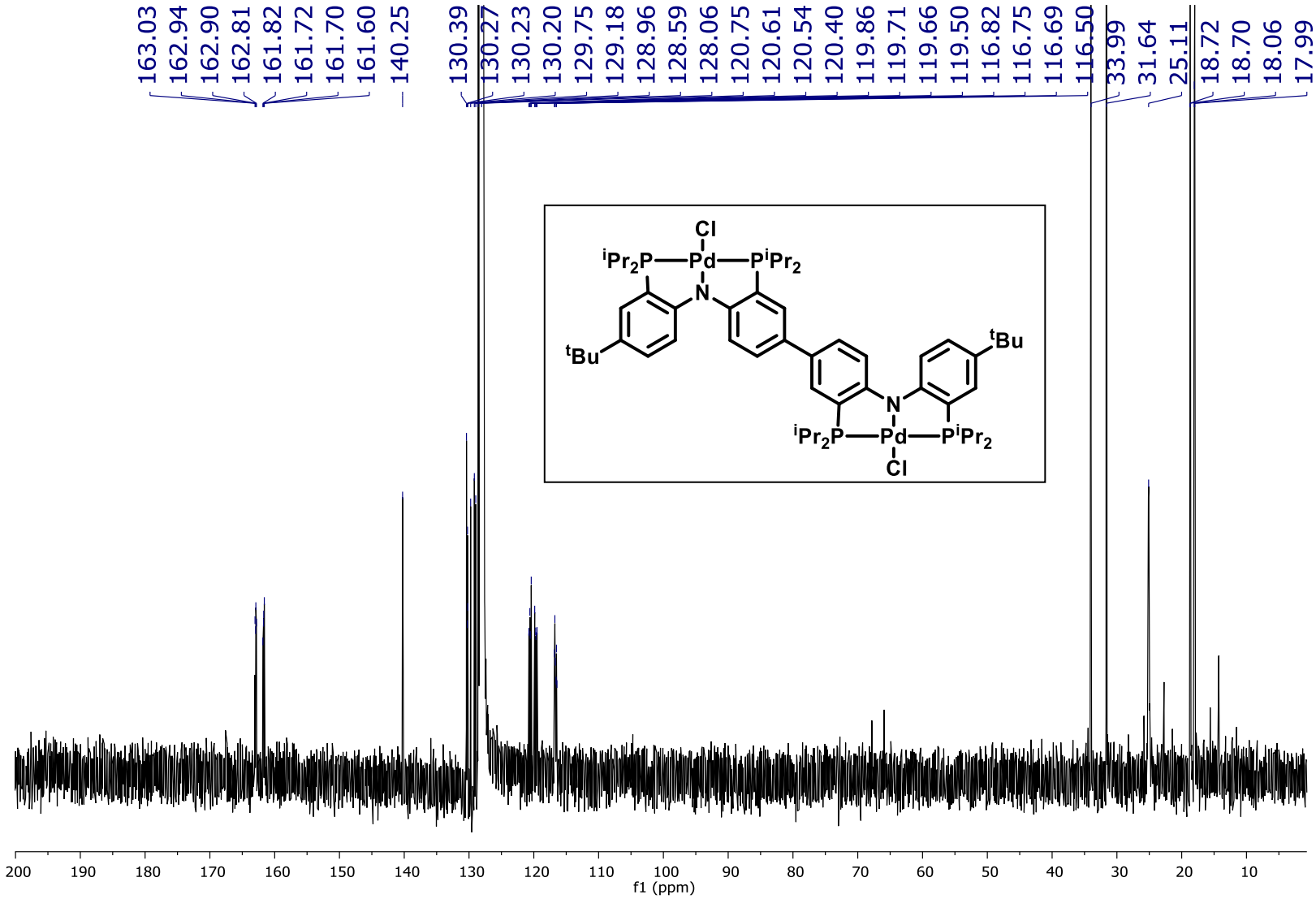


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

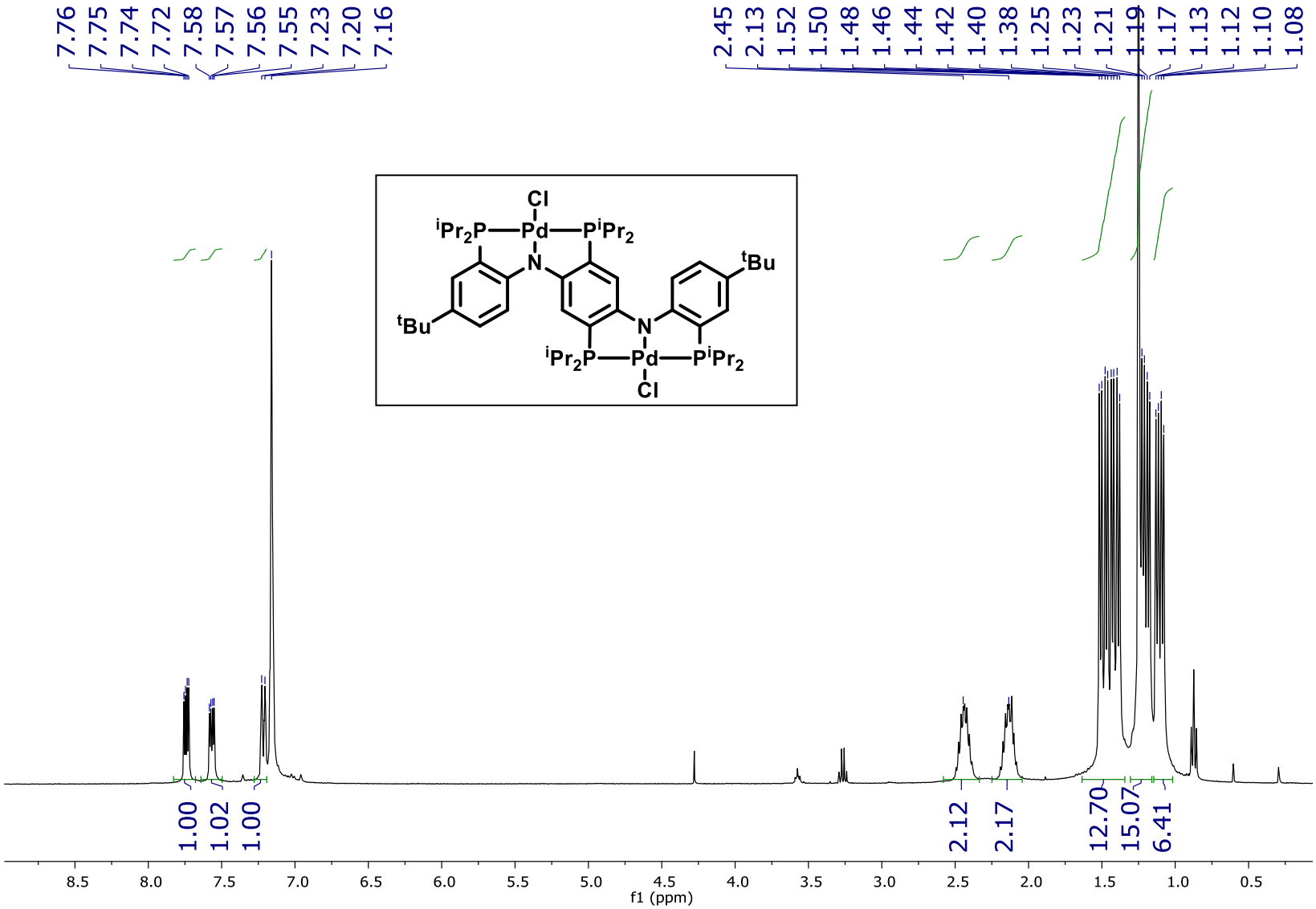


Figure S10. ^{1}H NMR spectrum of **3** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

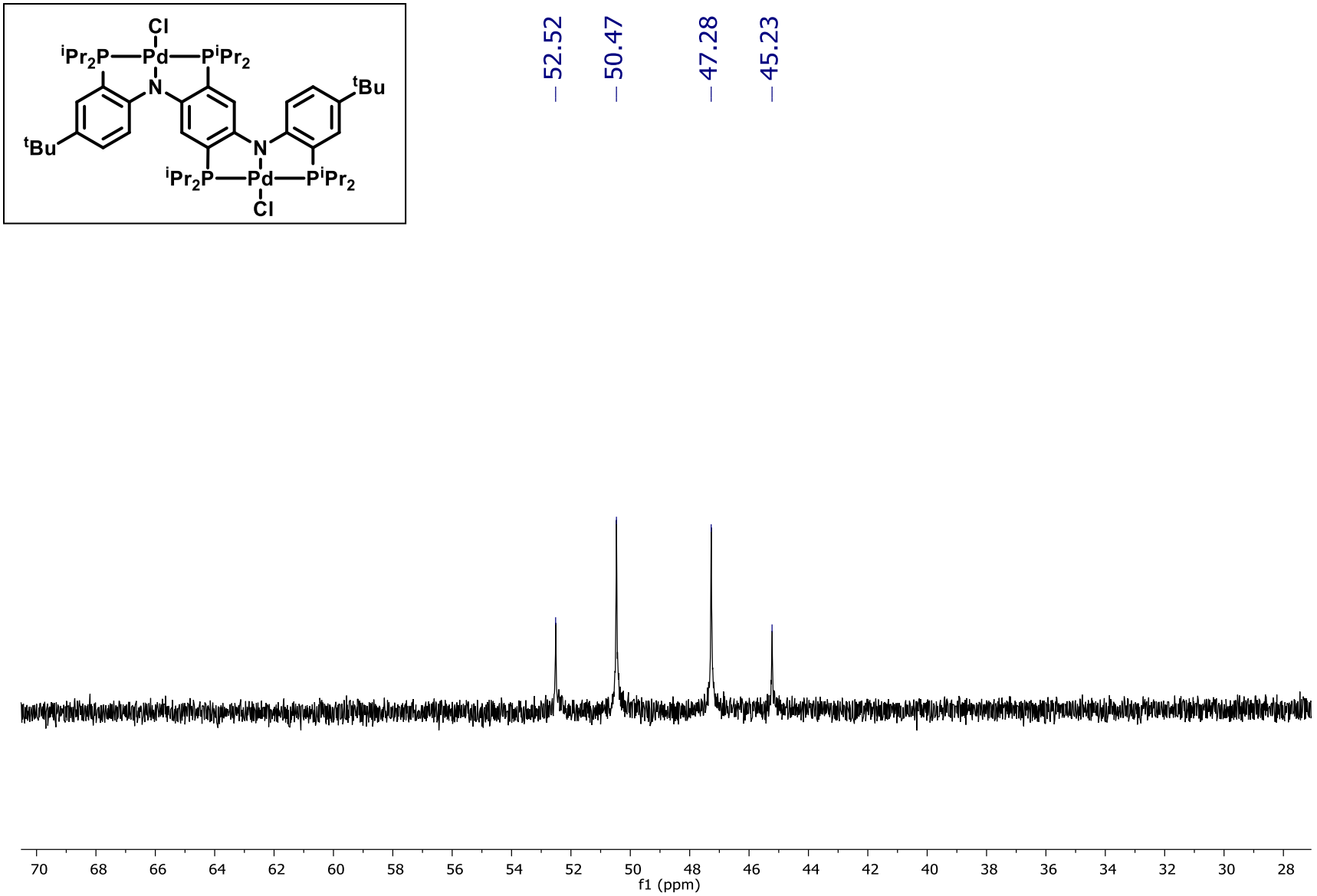


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

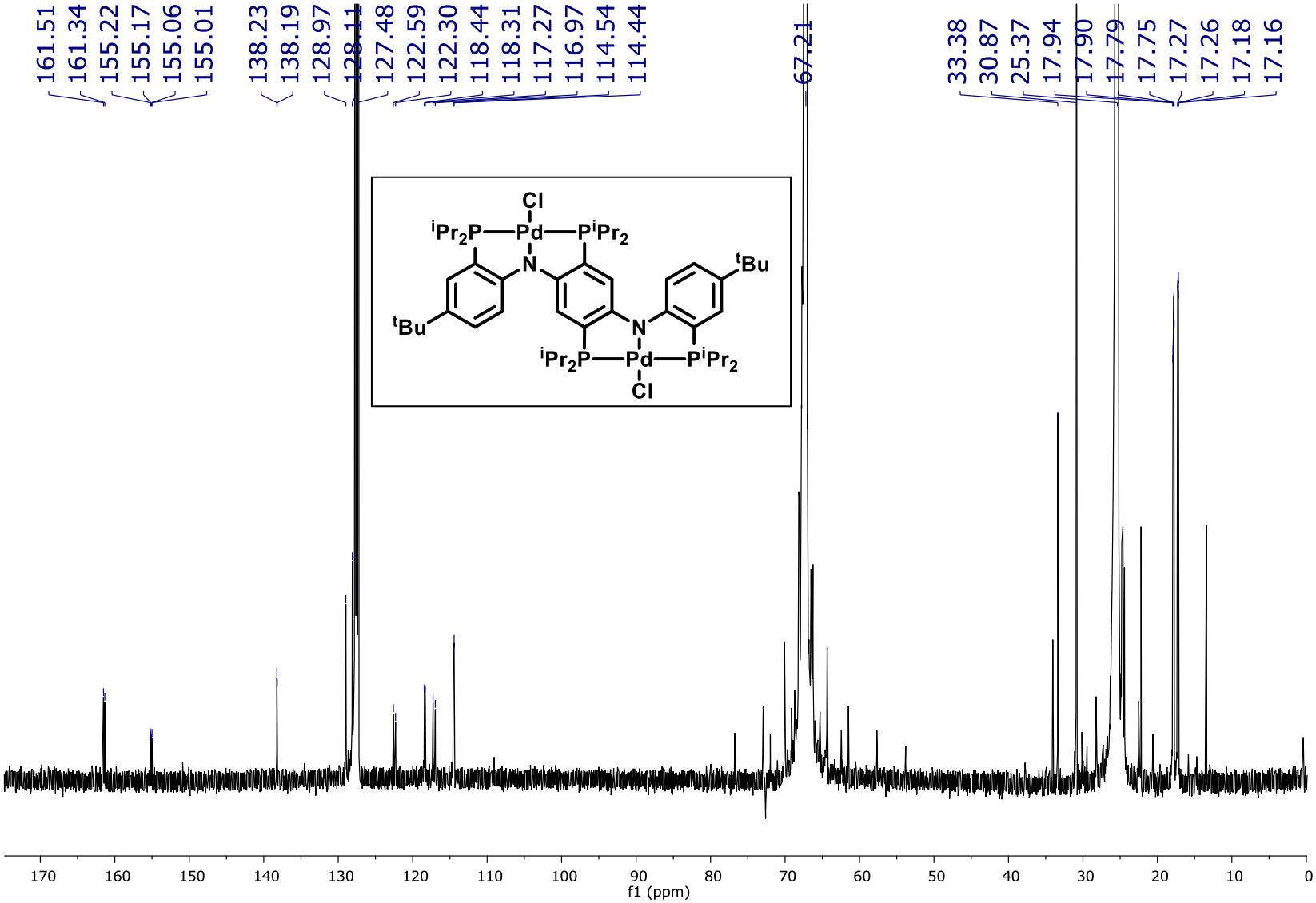


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in THF with C_6D_6 and *n*-pentane measured at RT on a 500 MHz Varian NMR spectrometer.

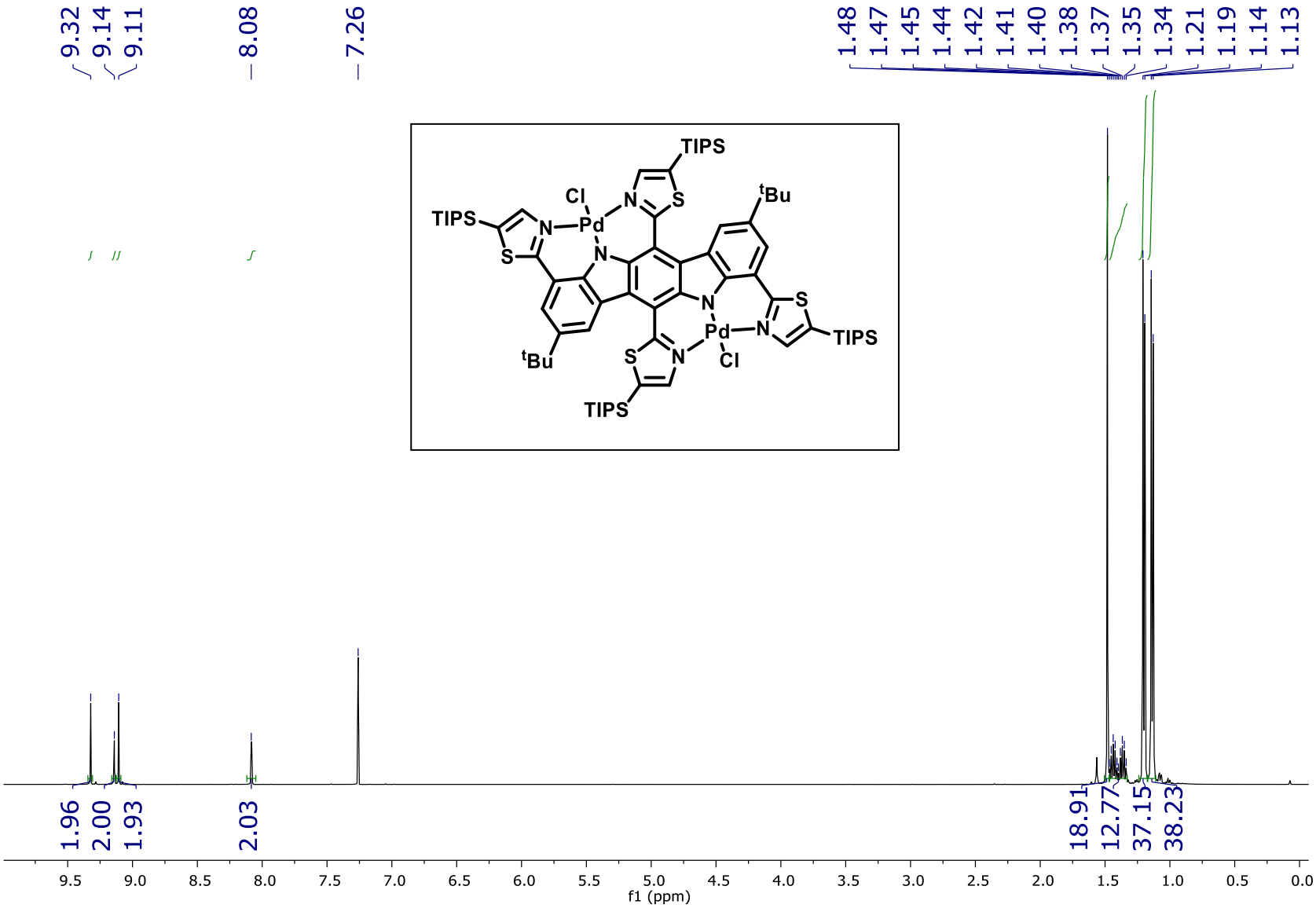


Figure S13. ^{1}H NMR spectrum of **4** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

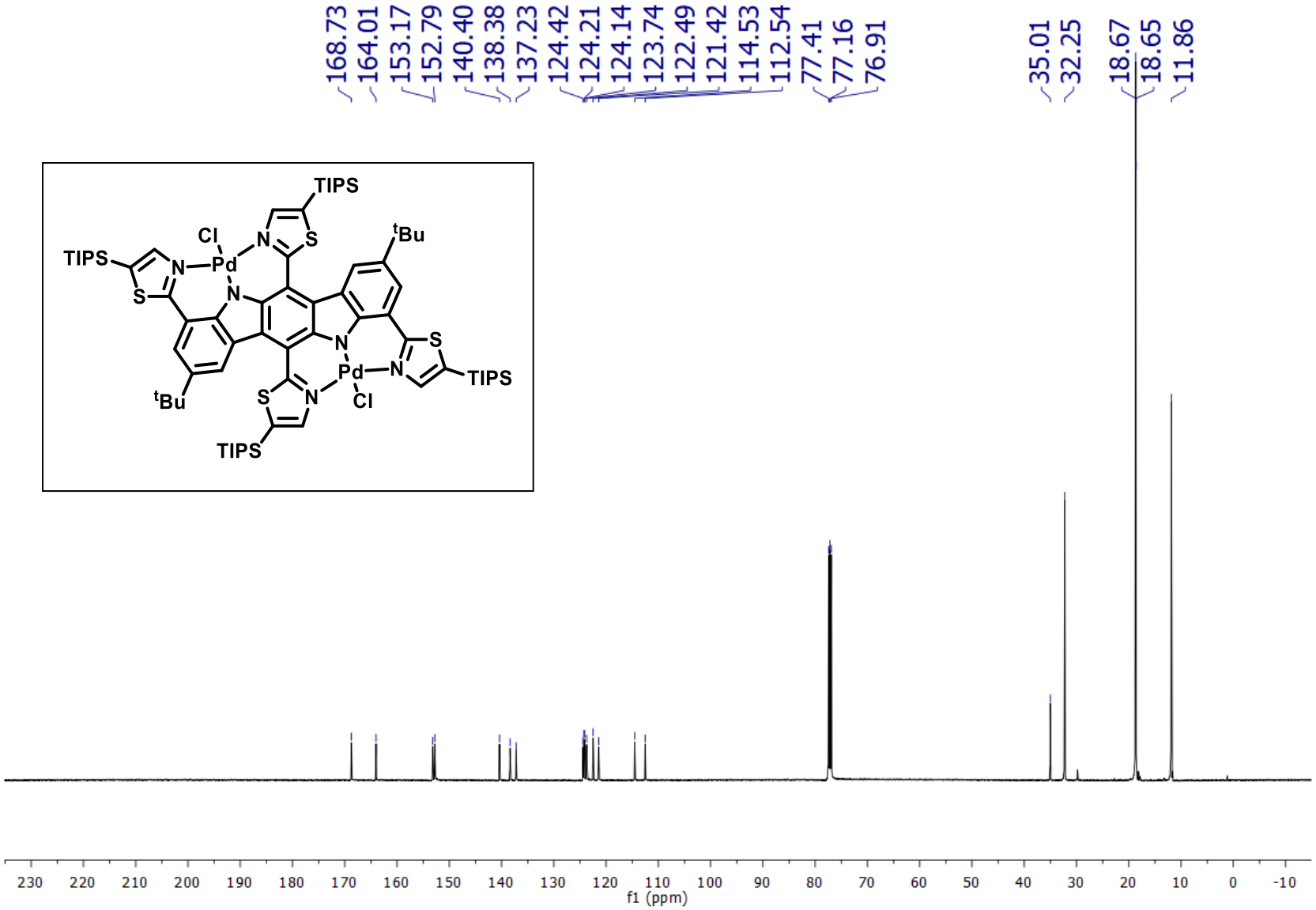


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

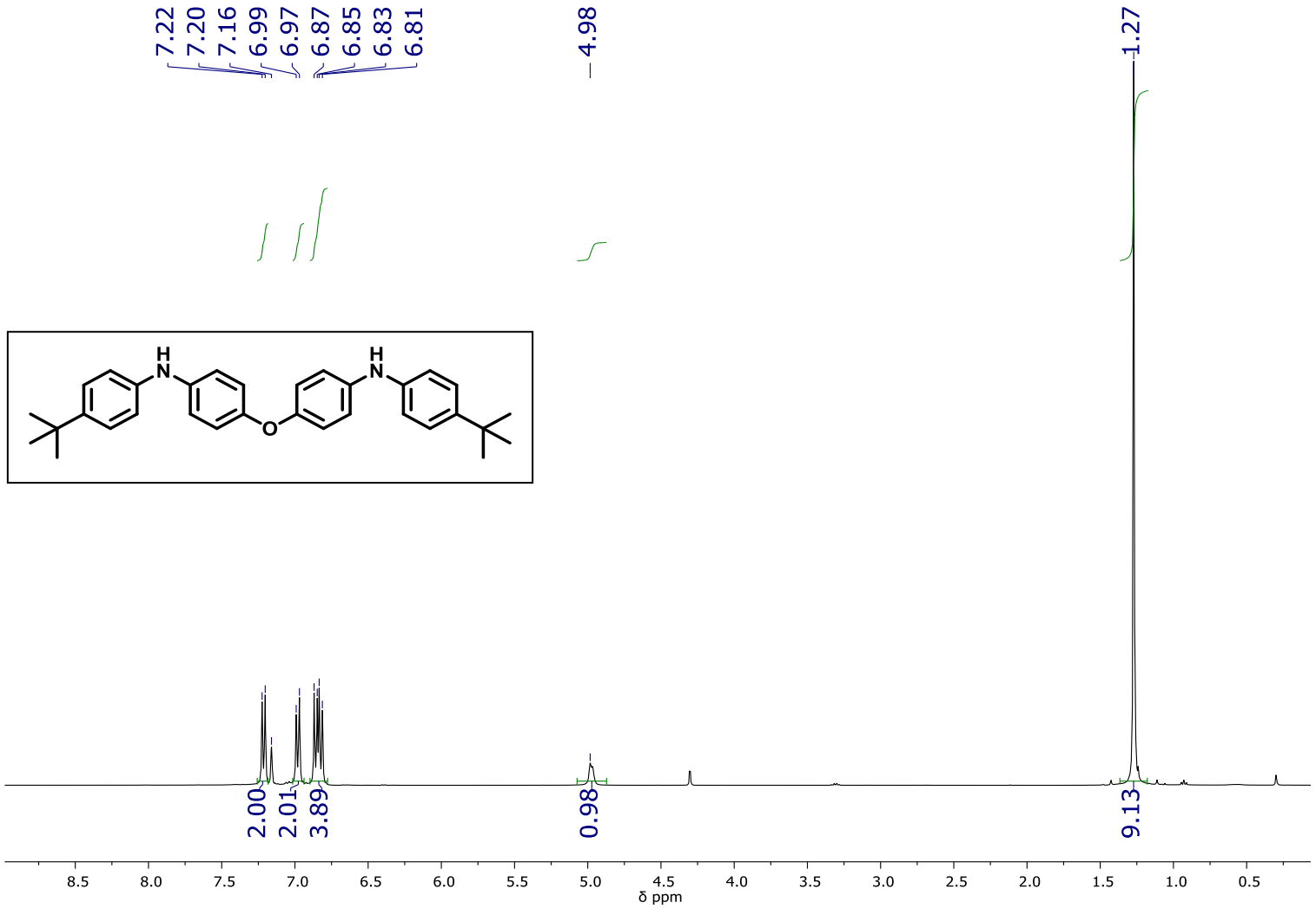


Figure S15. ^{1}H NMR spectrum of **8** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

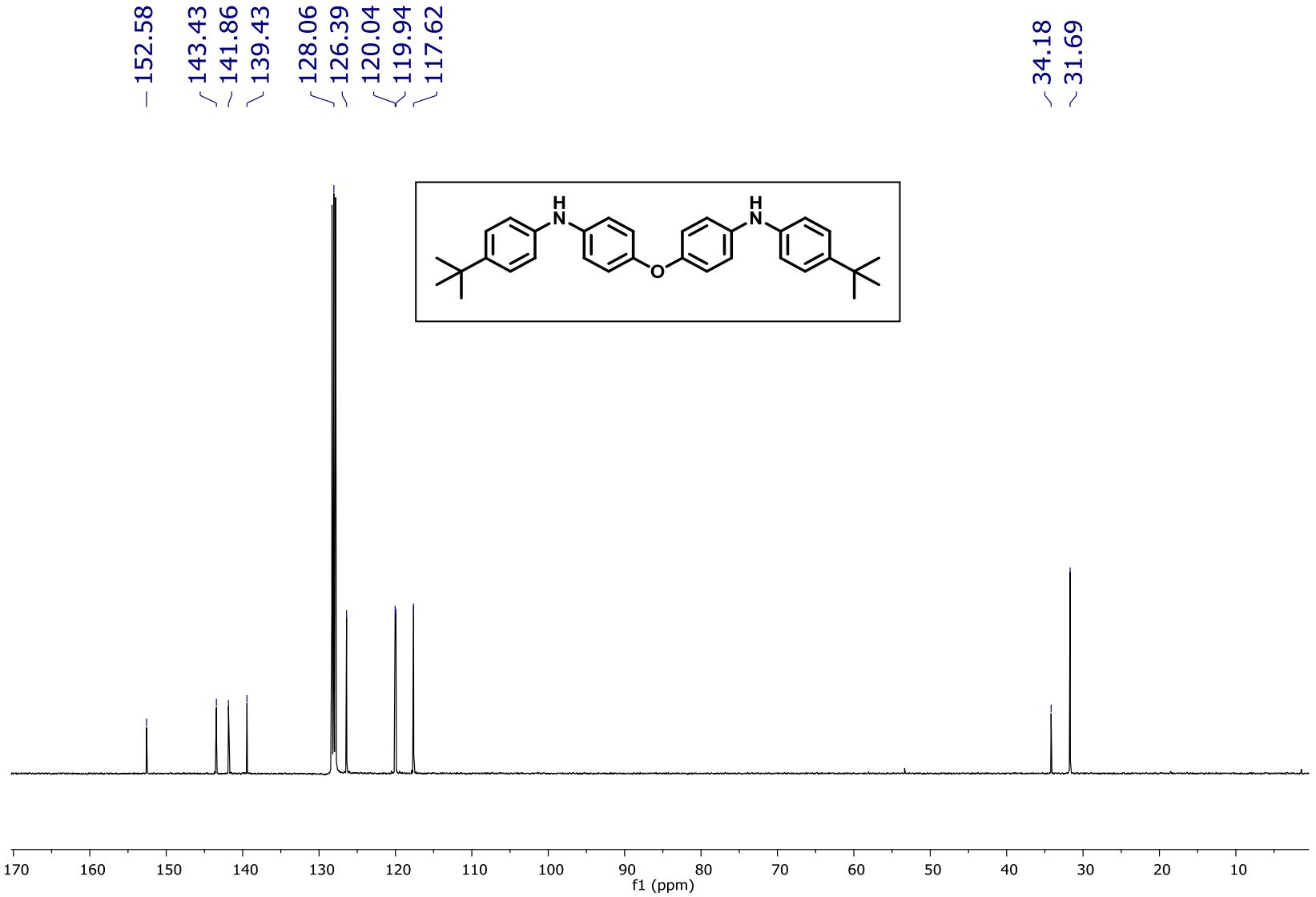


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

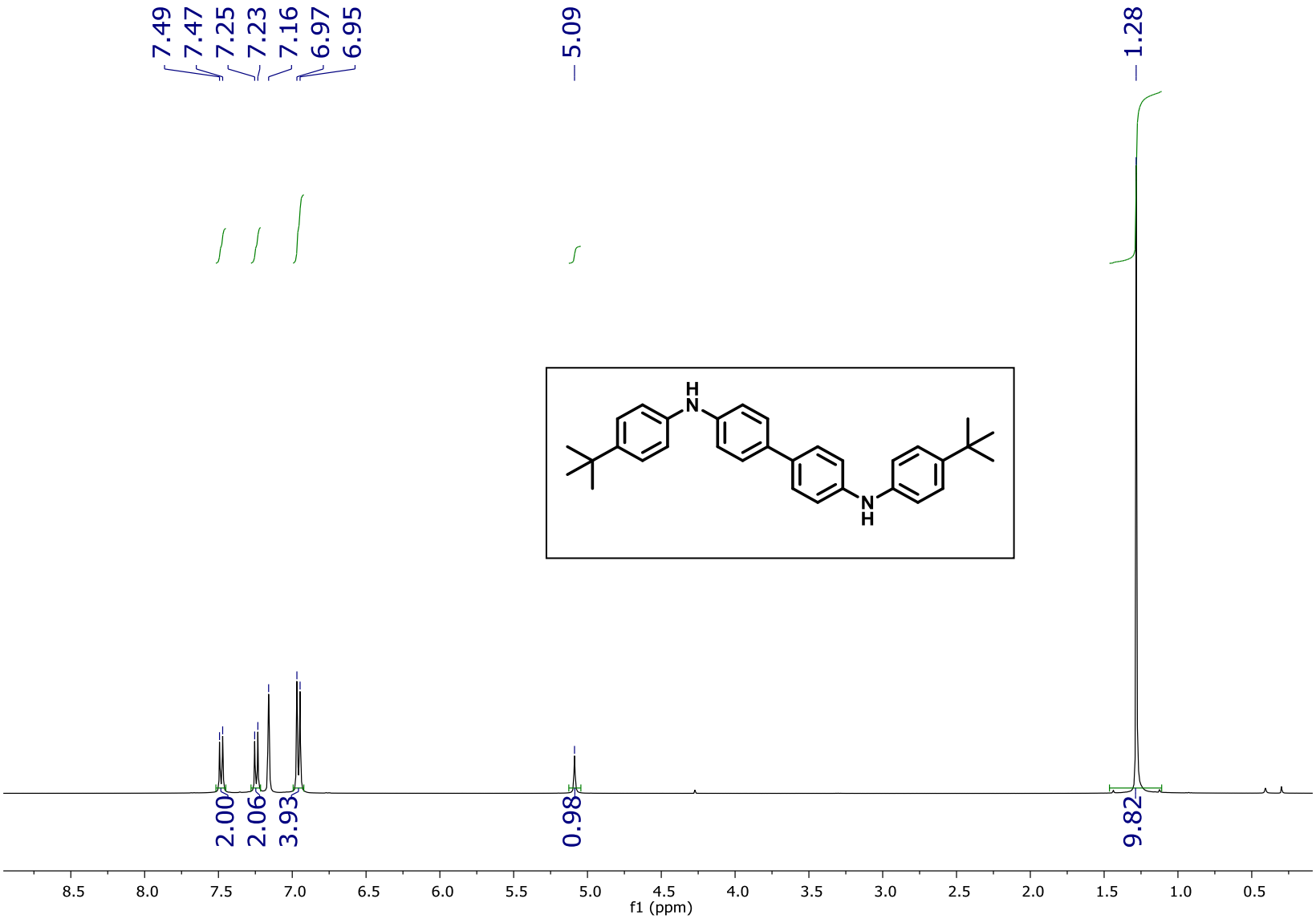


Figure S17. ^{1}H NMR spectrum of **9** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

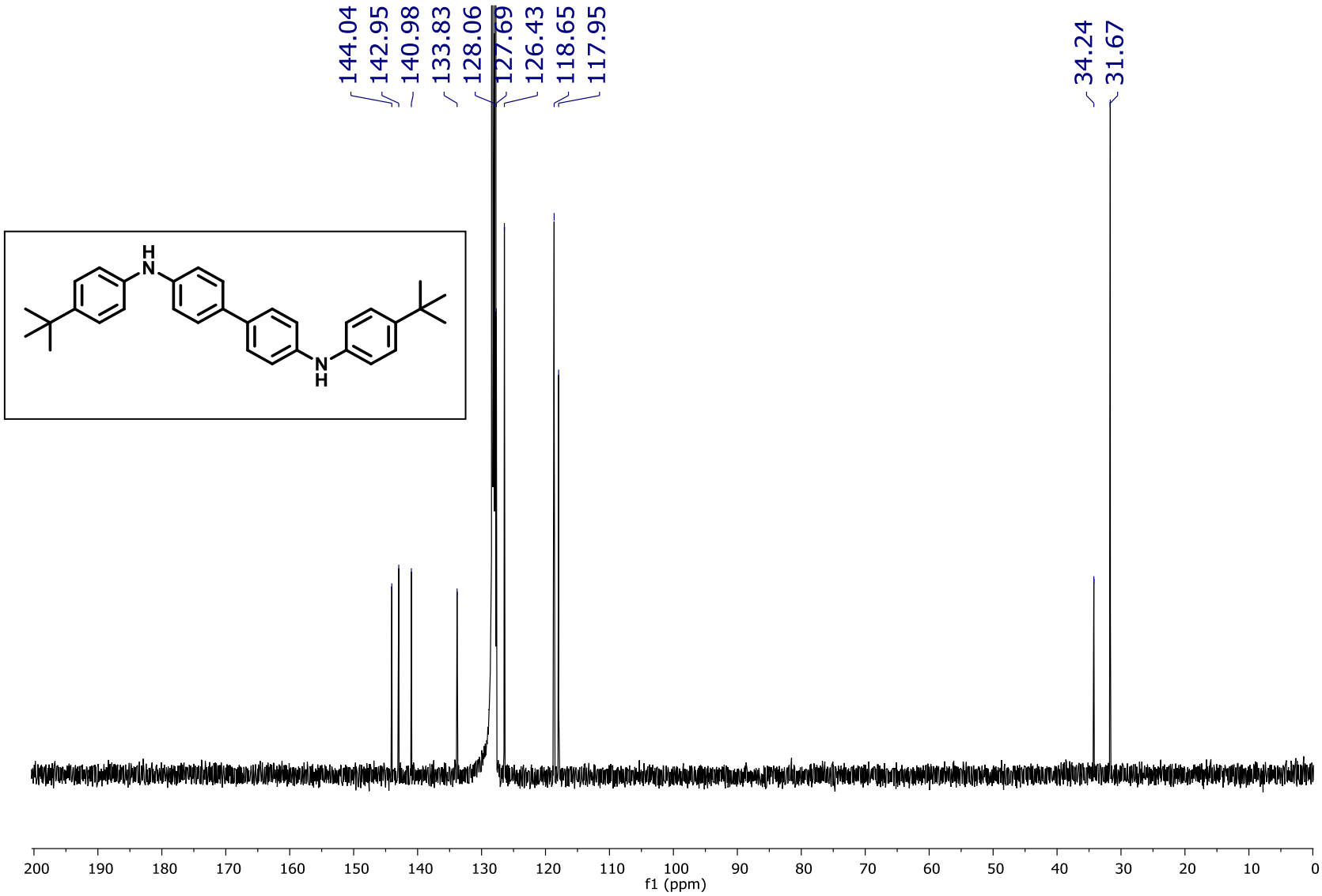


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

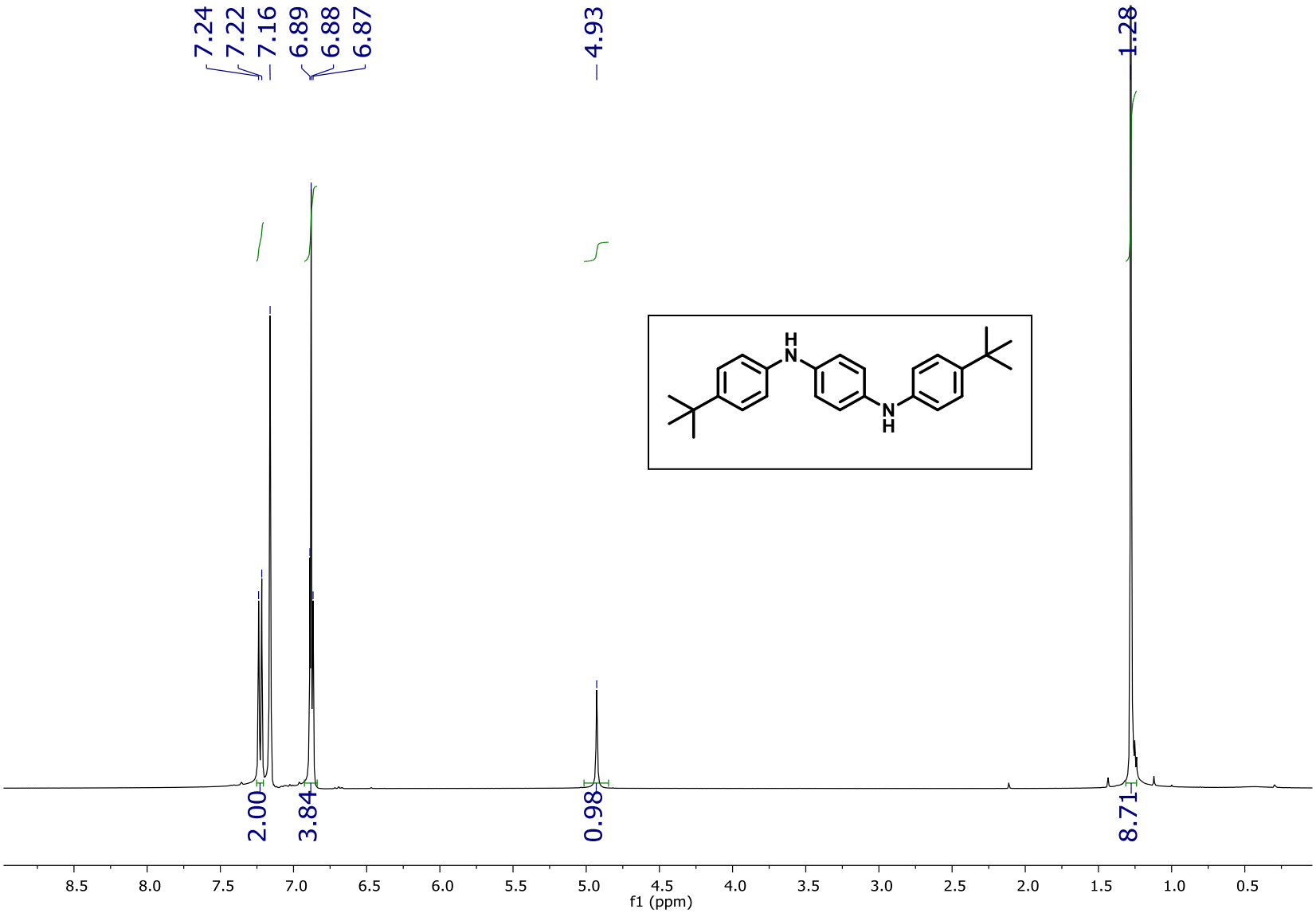


Figure S19. ^{1}H NMR spectrum of **10** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

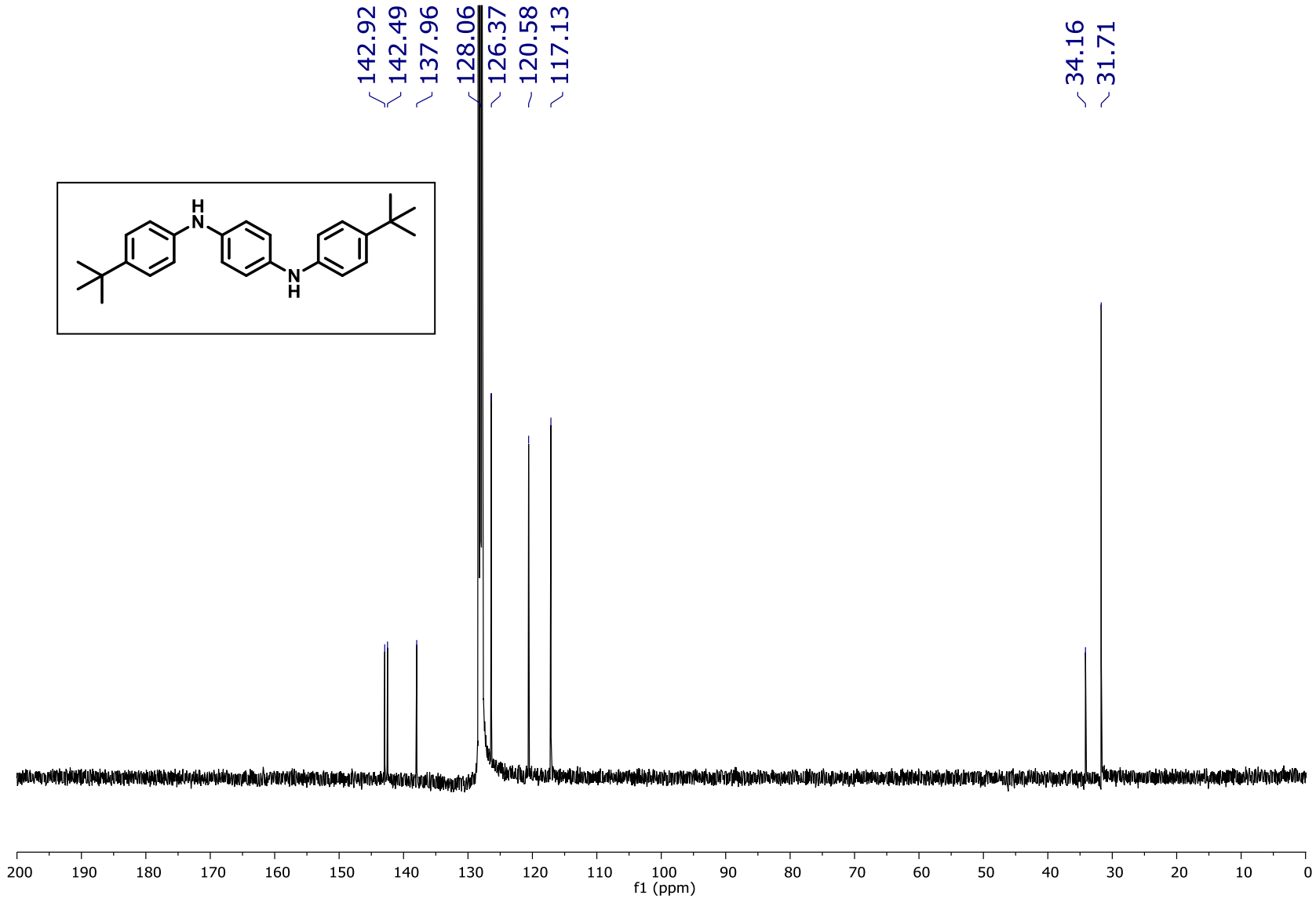


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **10** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

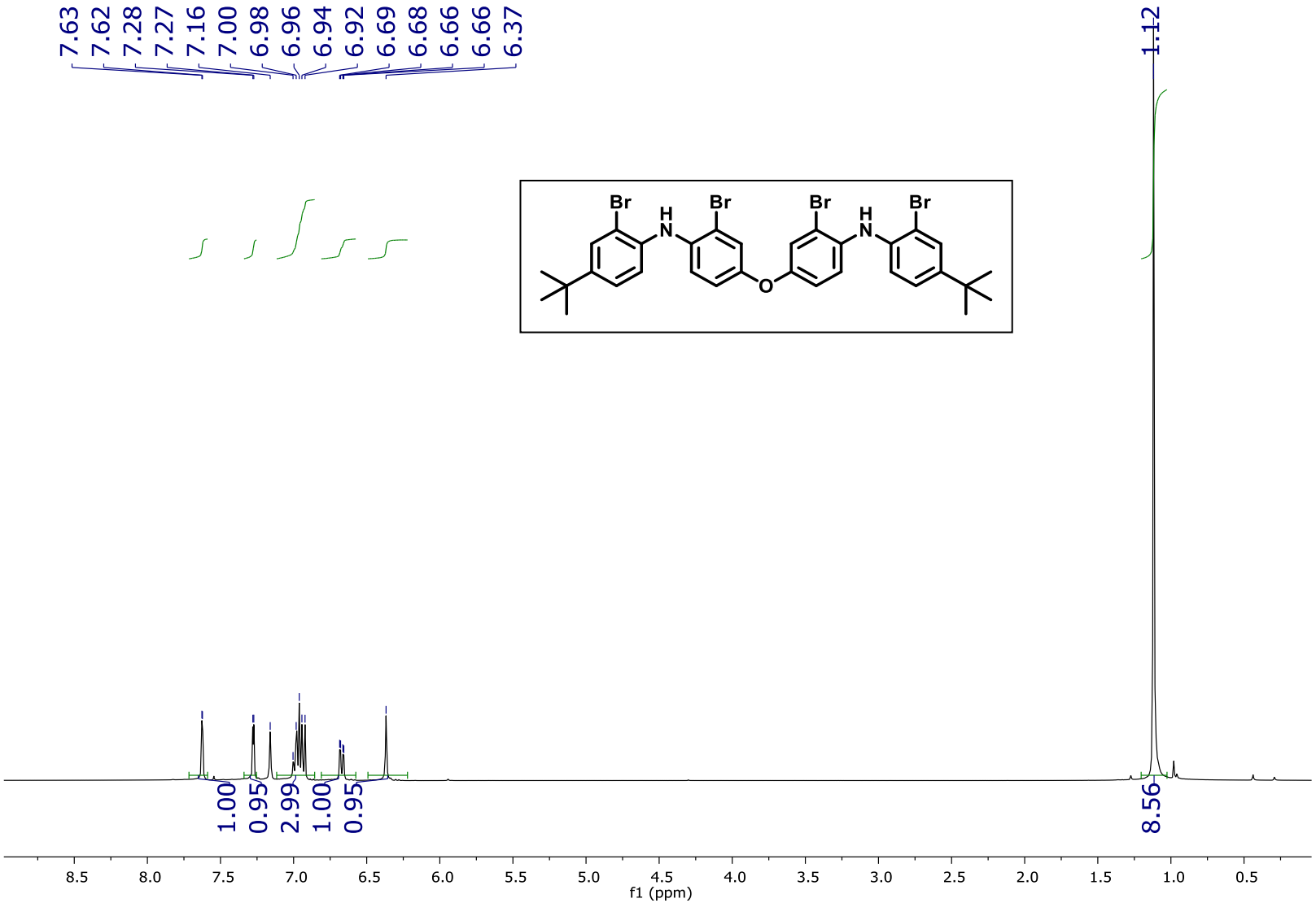


Figure S21. ^{1}H NMR spectrum of **11** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

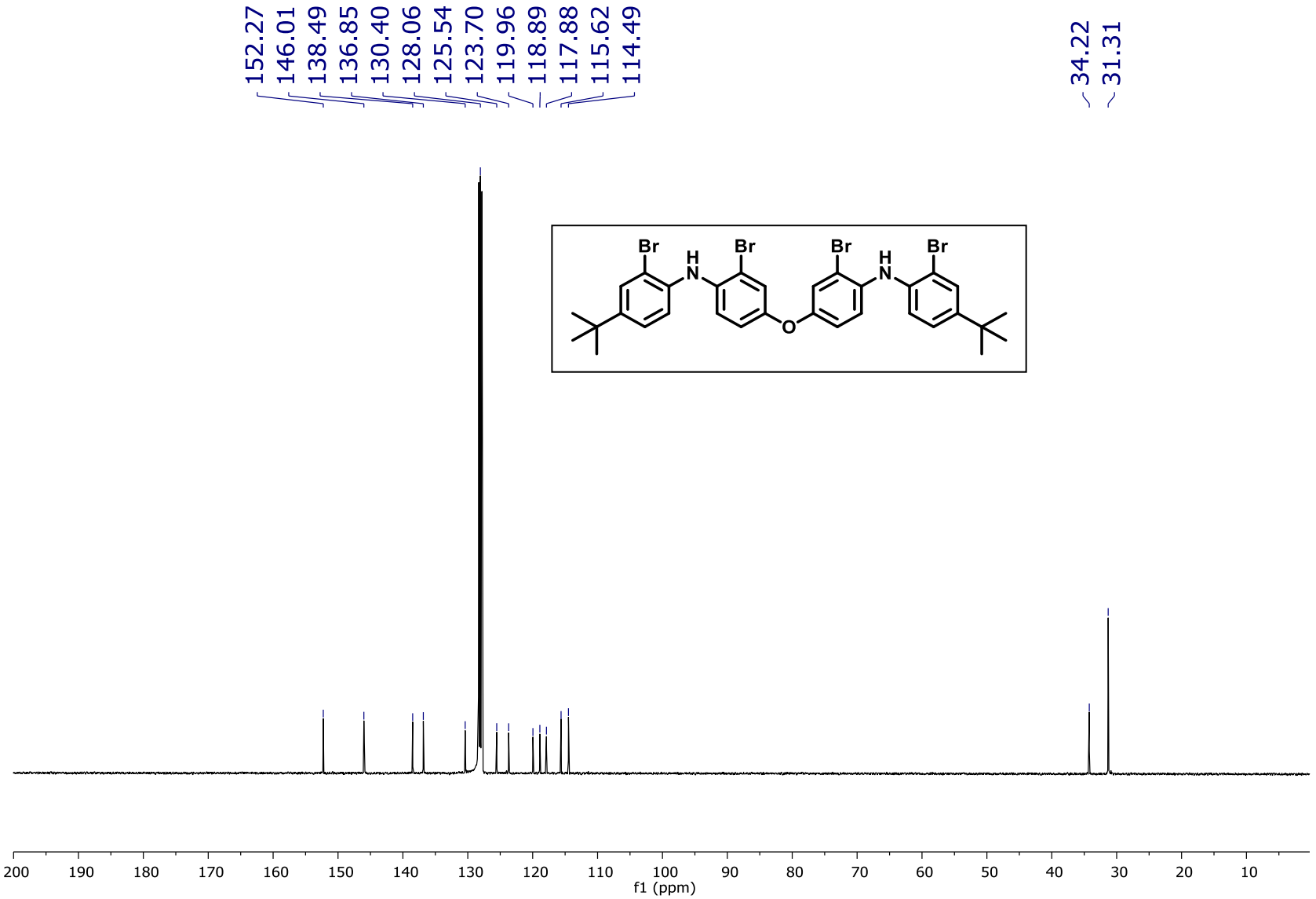


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **11** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

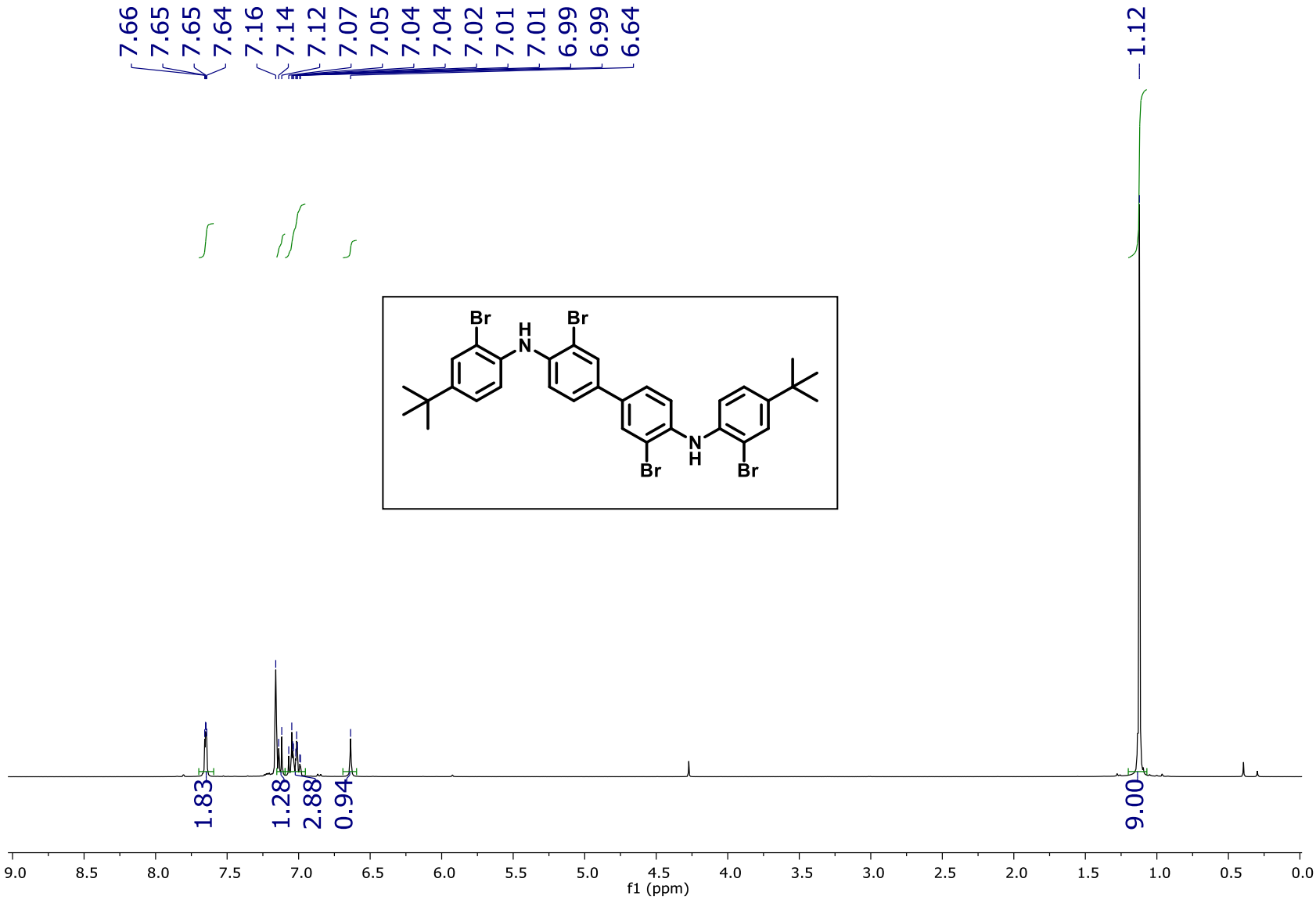


Figure S23. ^{1}H NMR spectrum of **12** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer

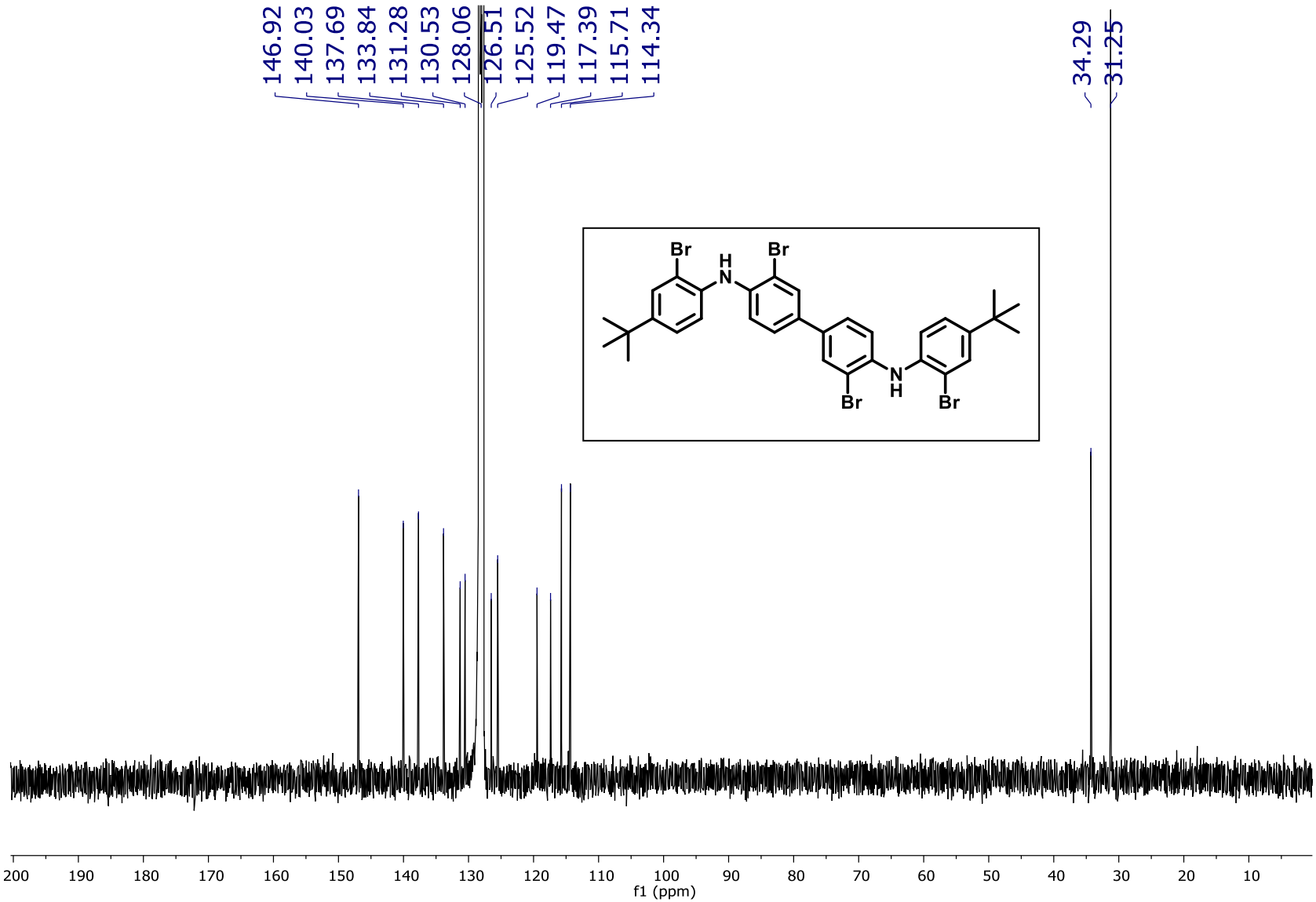


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **12** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer

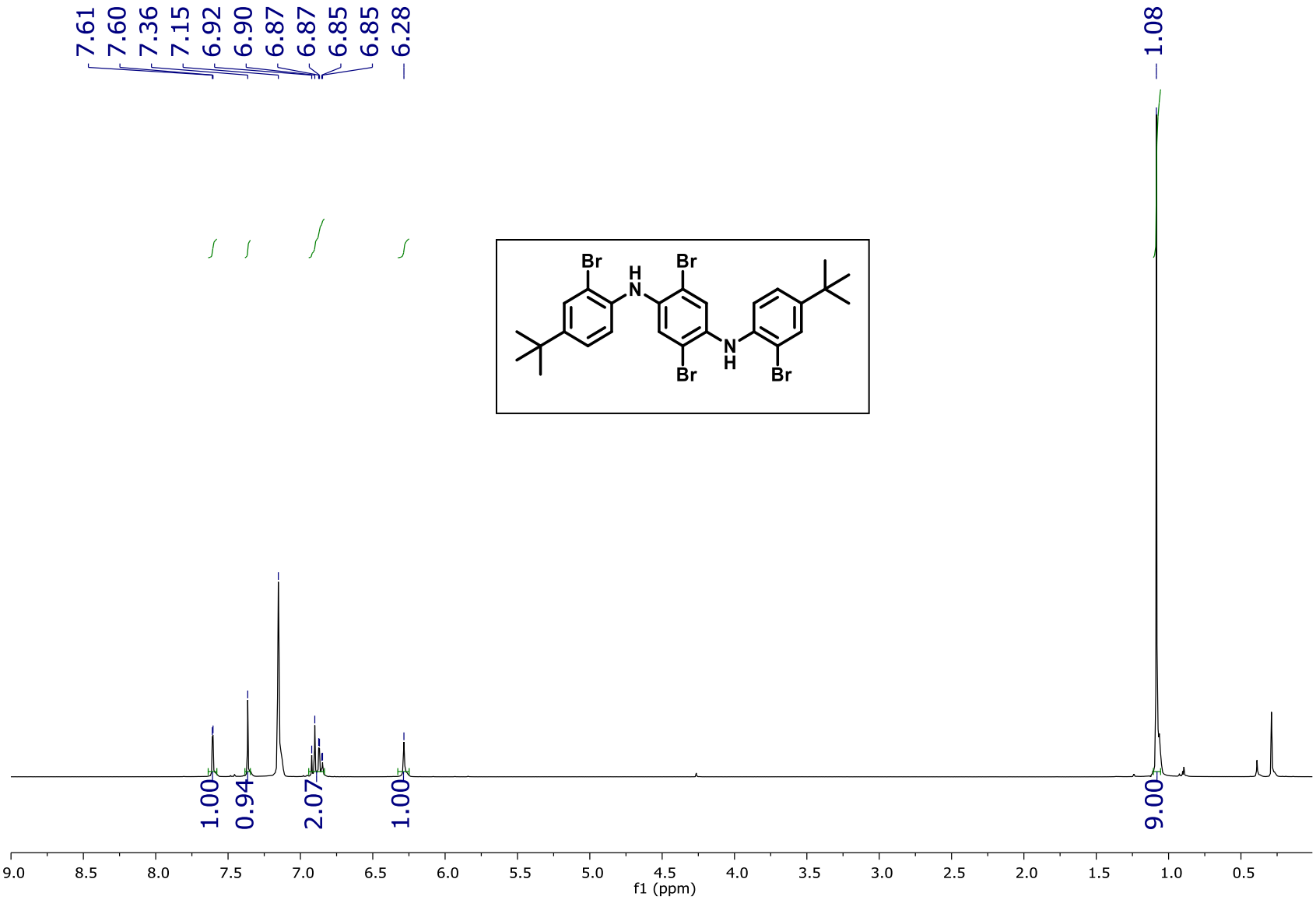


Figure S25. ^{1}H NMR spectrum of **13** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

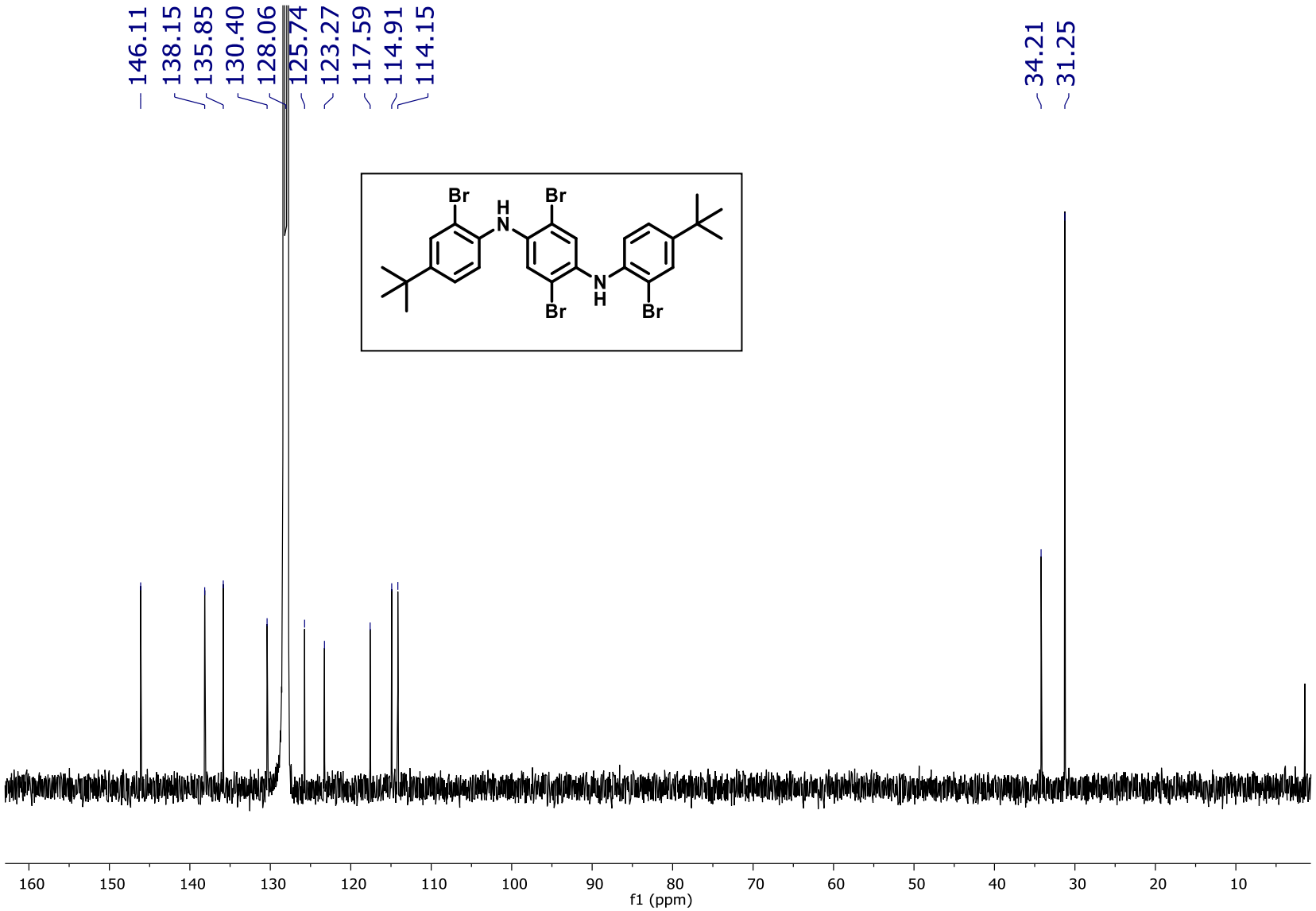


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **13** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

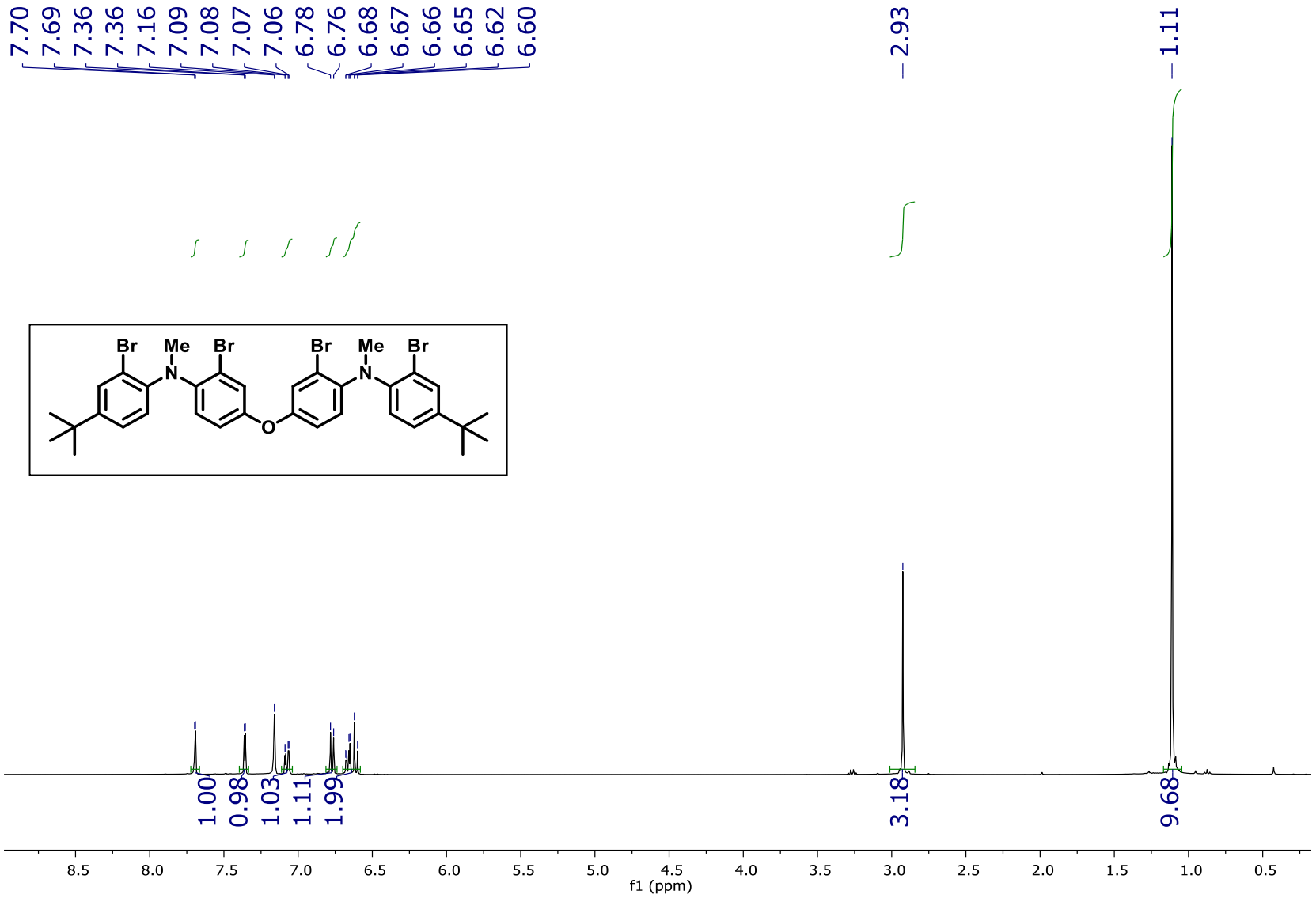


Figure S27. ^{1}H NMR spectrum of **14** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

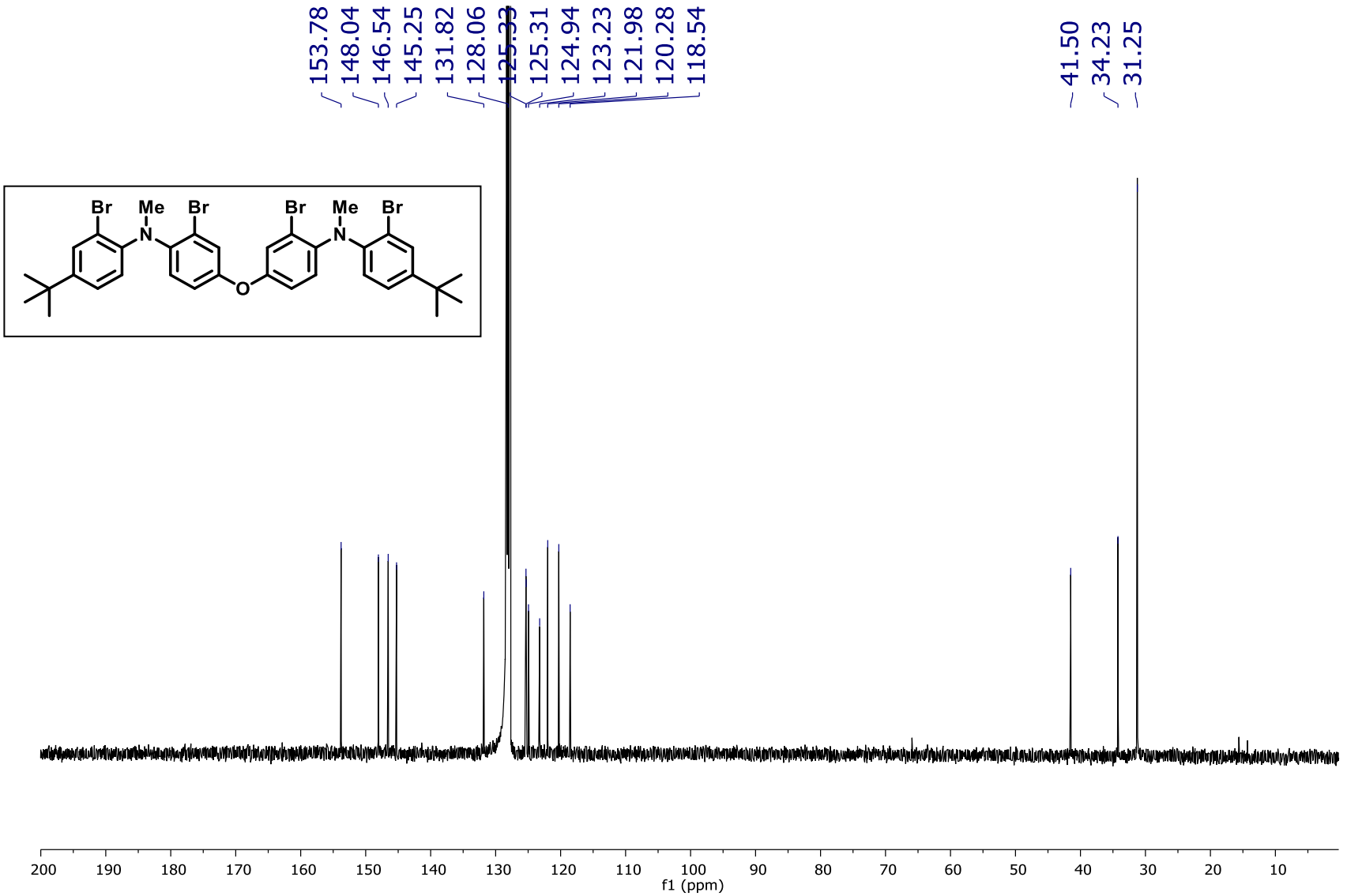


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **14** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

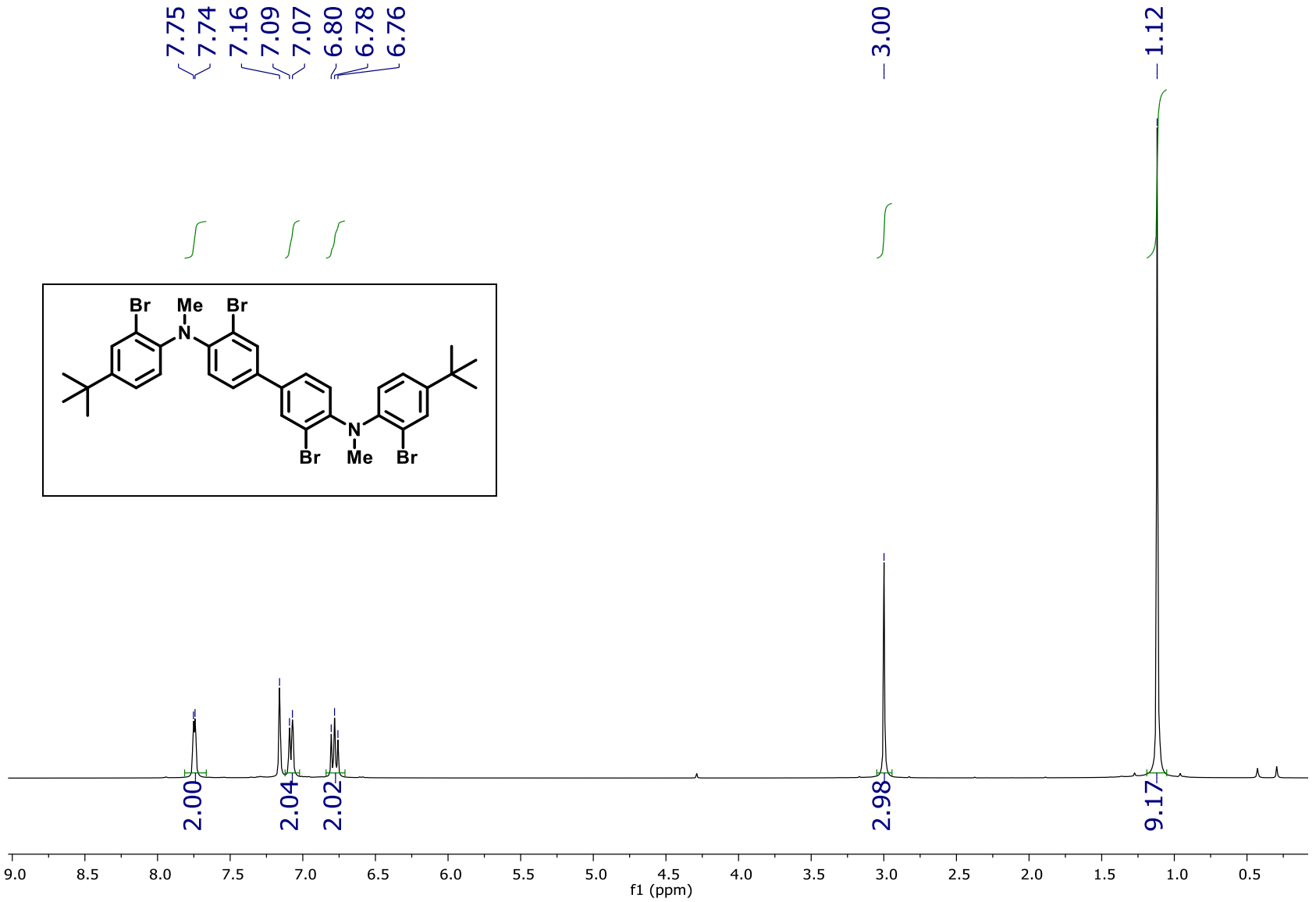


Figure S29. ^{1}H NMR spectrum of **15** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

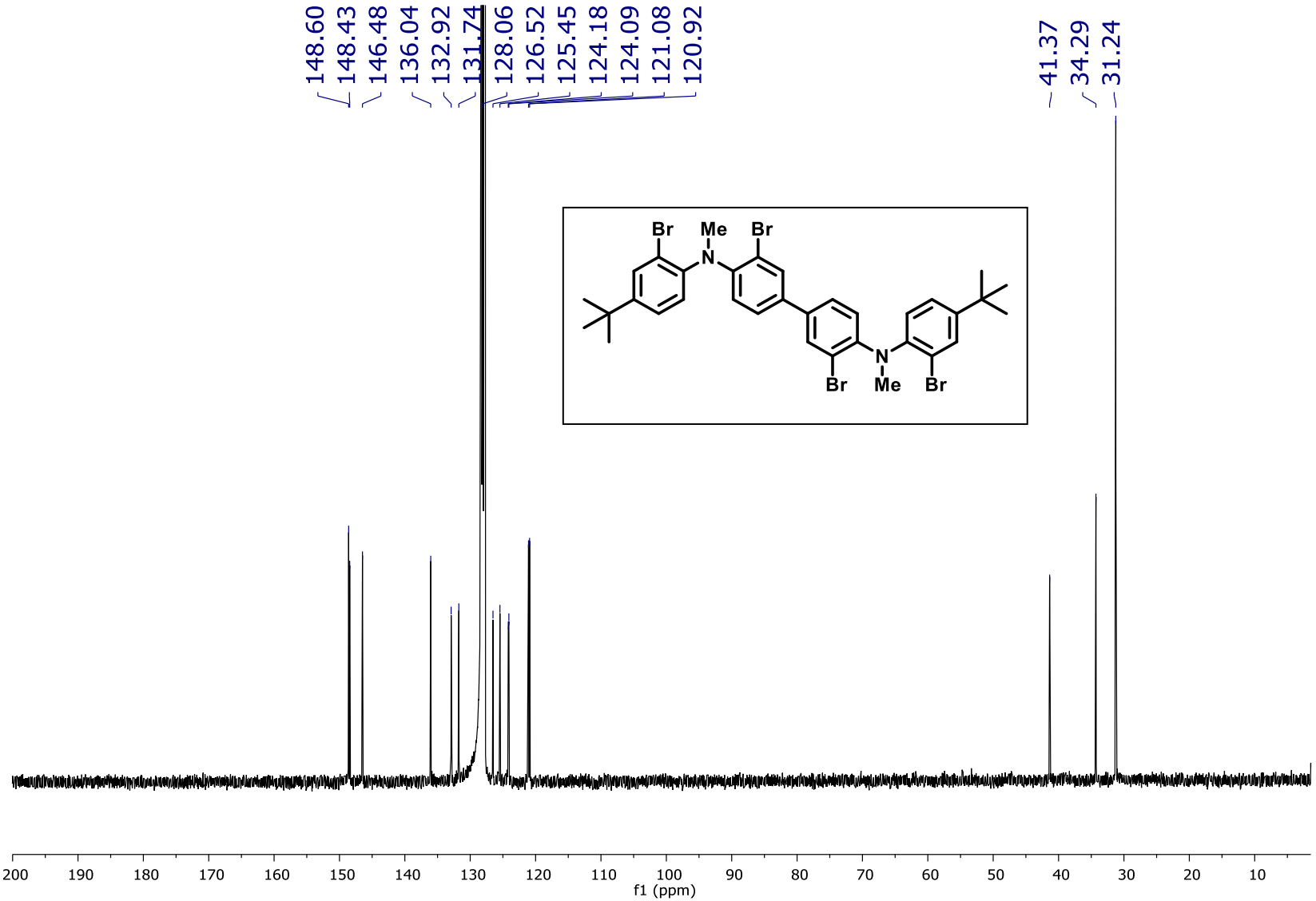


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **15** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

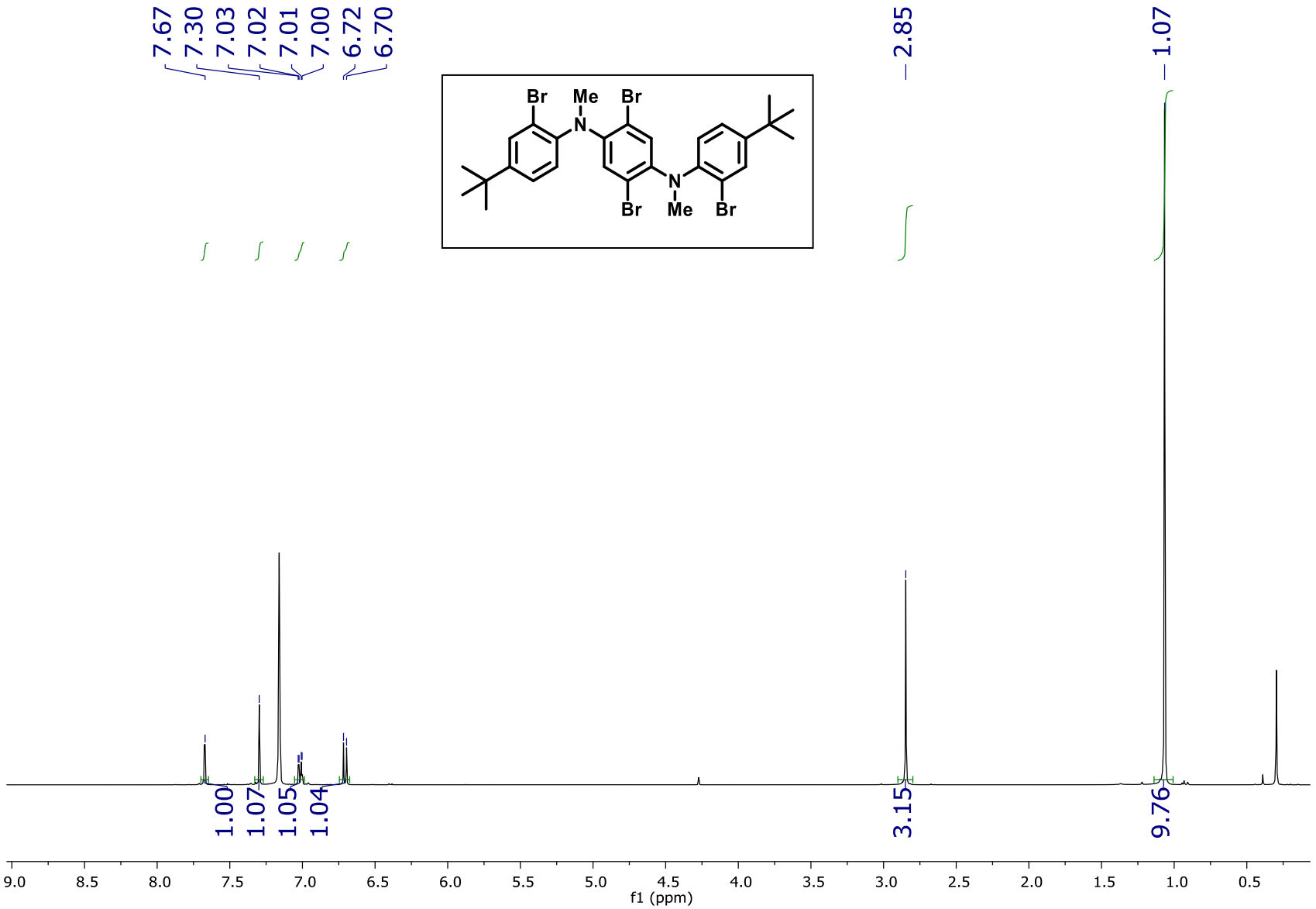


Figure S31. ^{1}H NMR spectrum of **16** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

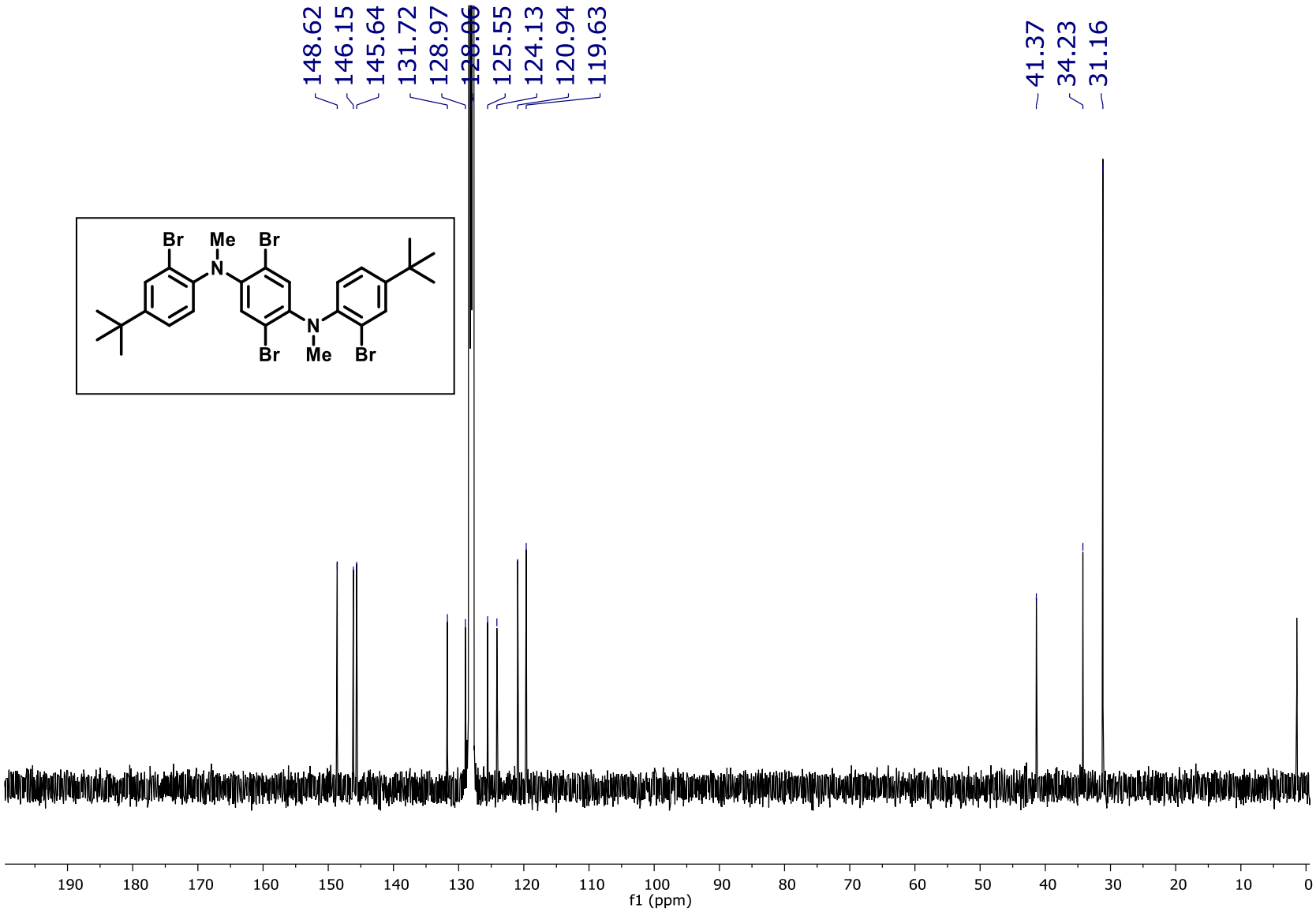


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **16** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

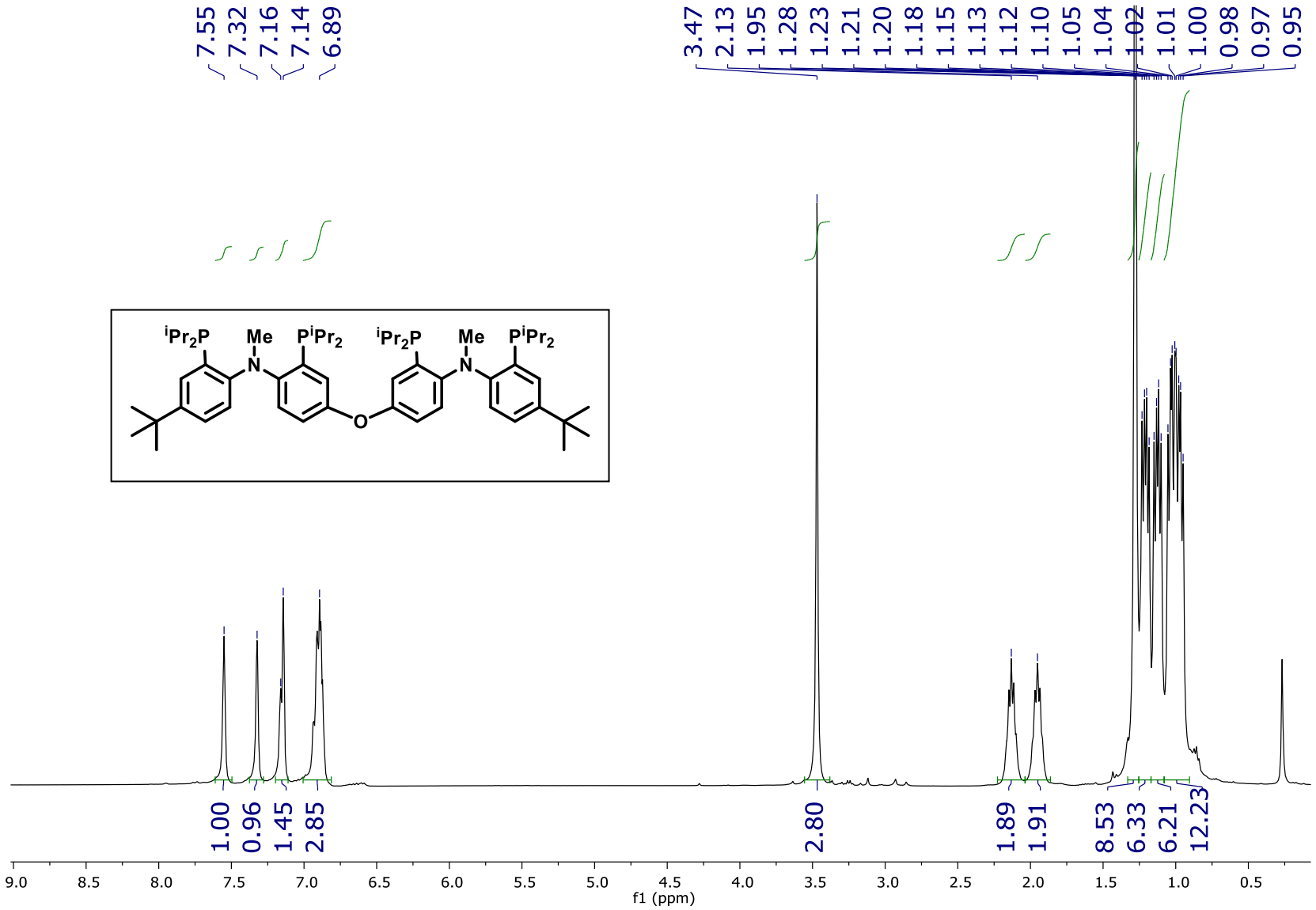


Figure S33. ^{1}H NMR spectrum of **17** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

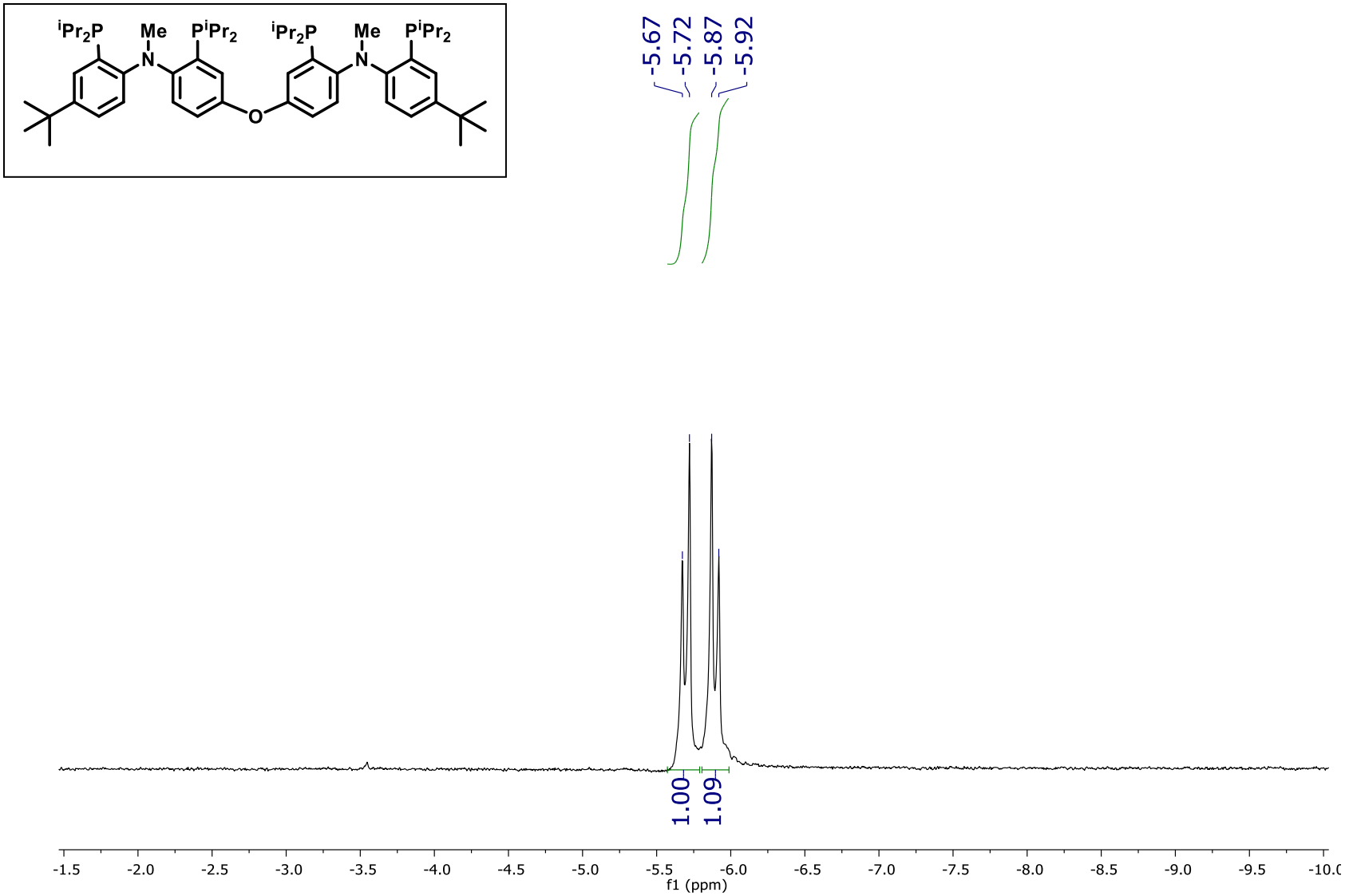


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **17** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

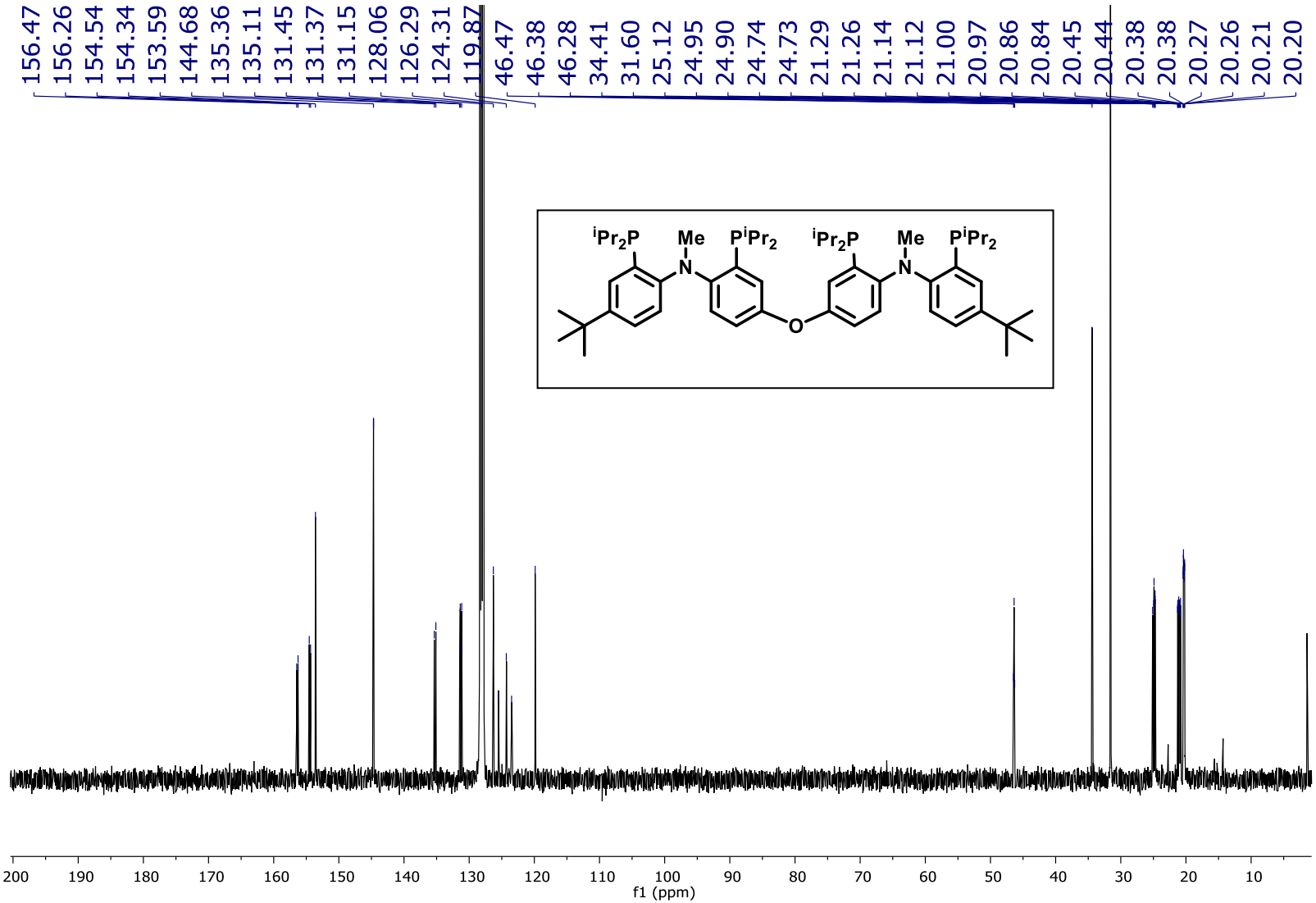


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **17** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer.

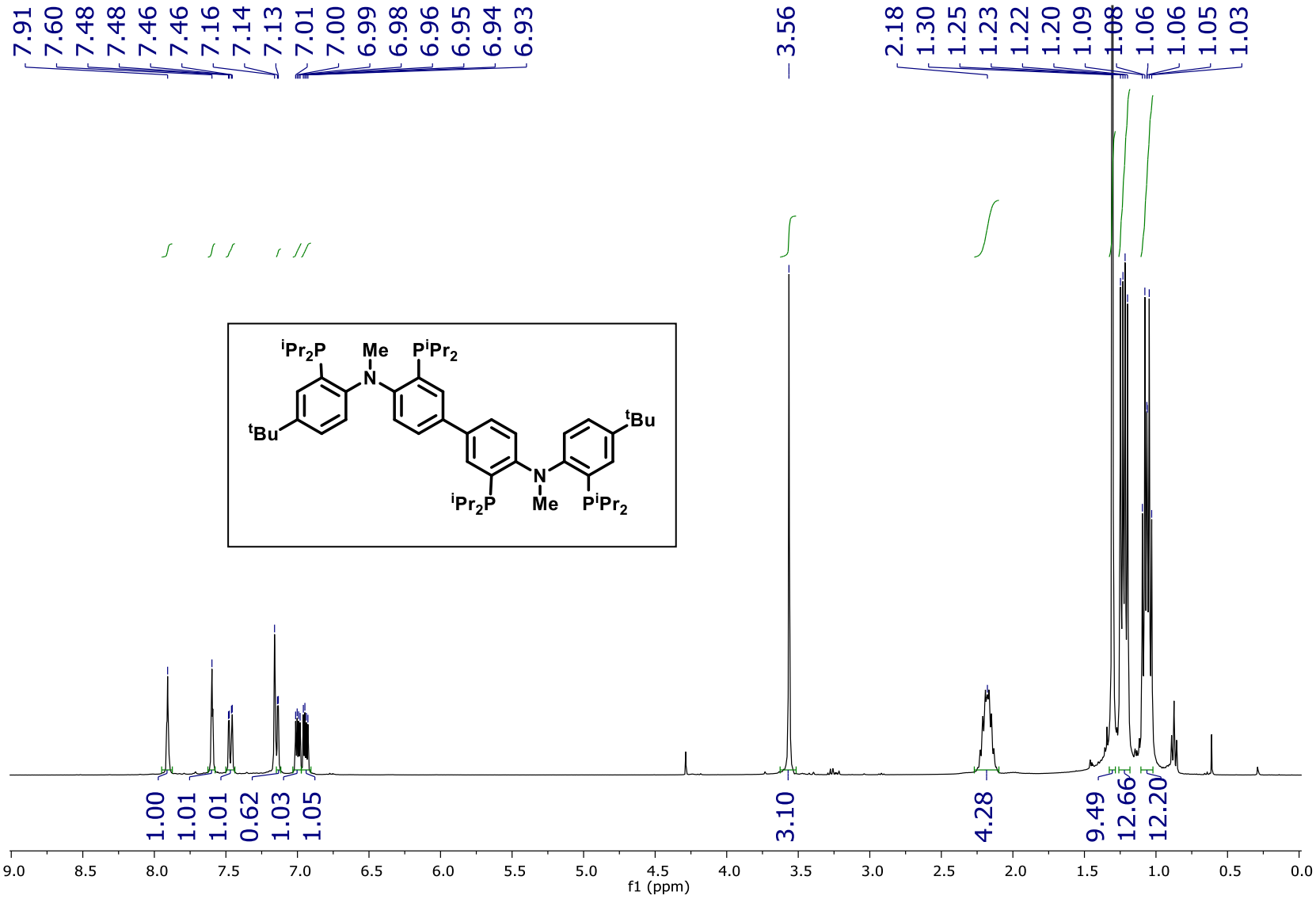


Figure S36. ^{1}H NMR spectrum of **18** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer

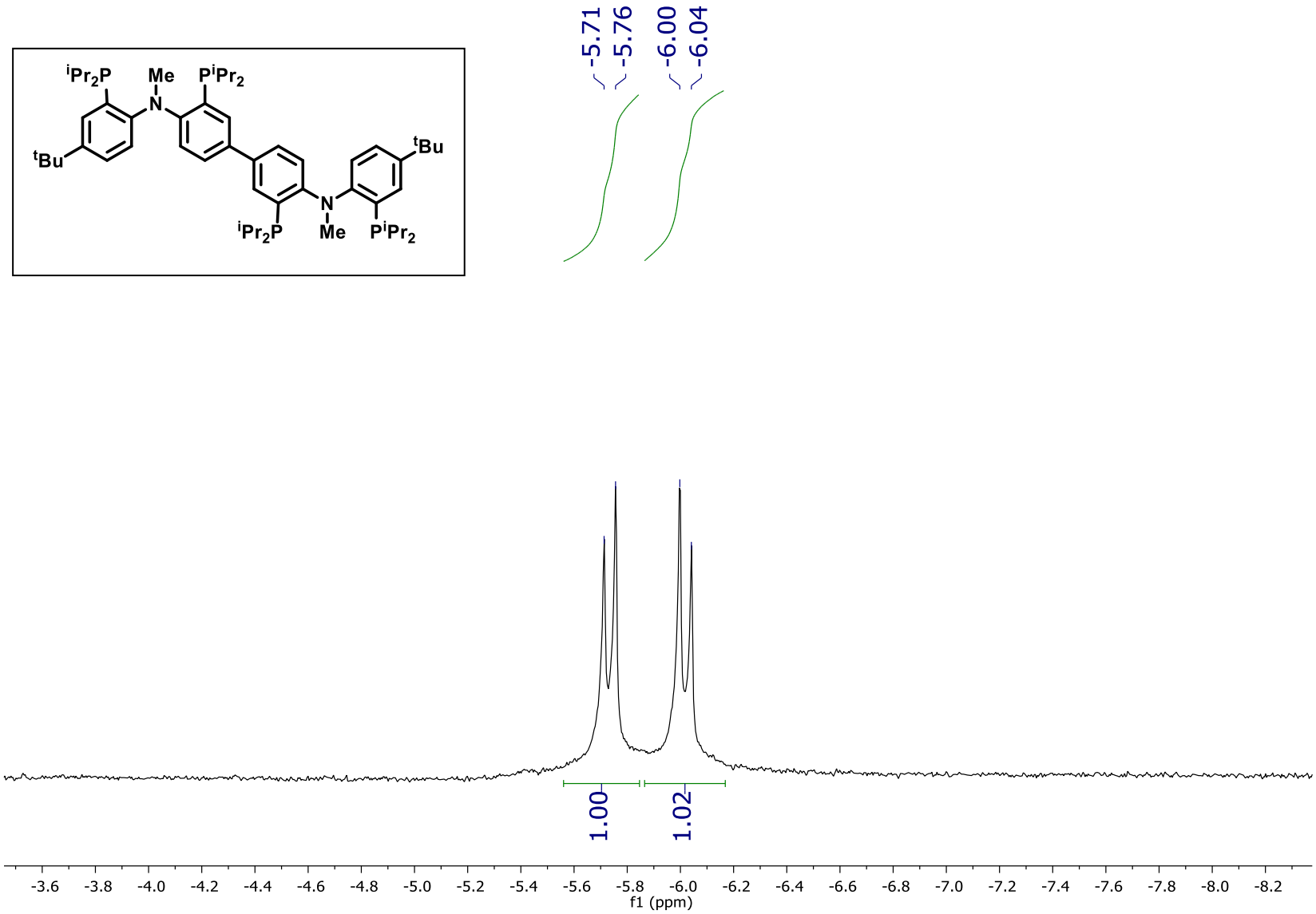


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of **18** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

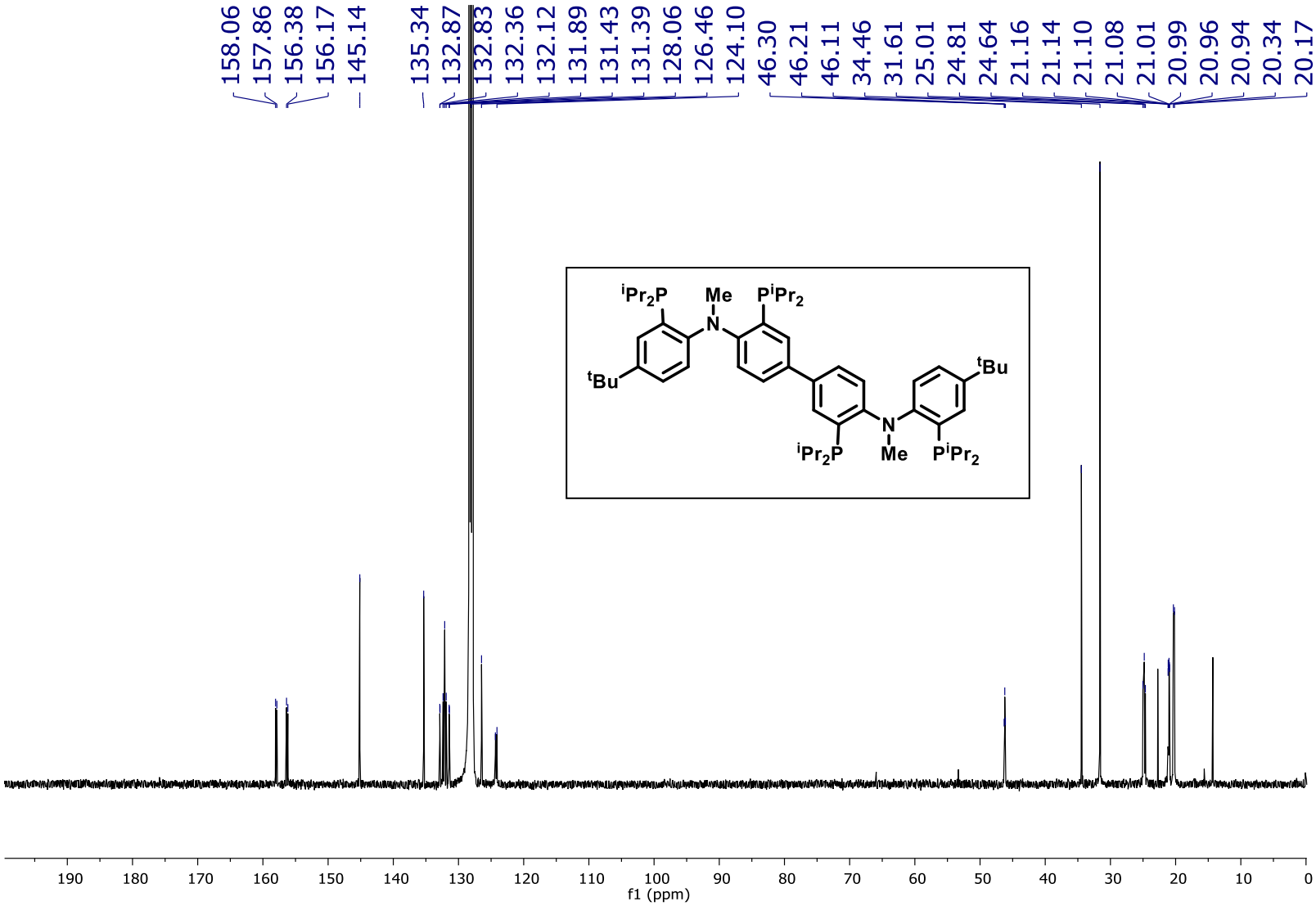


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **18** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer

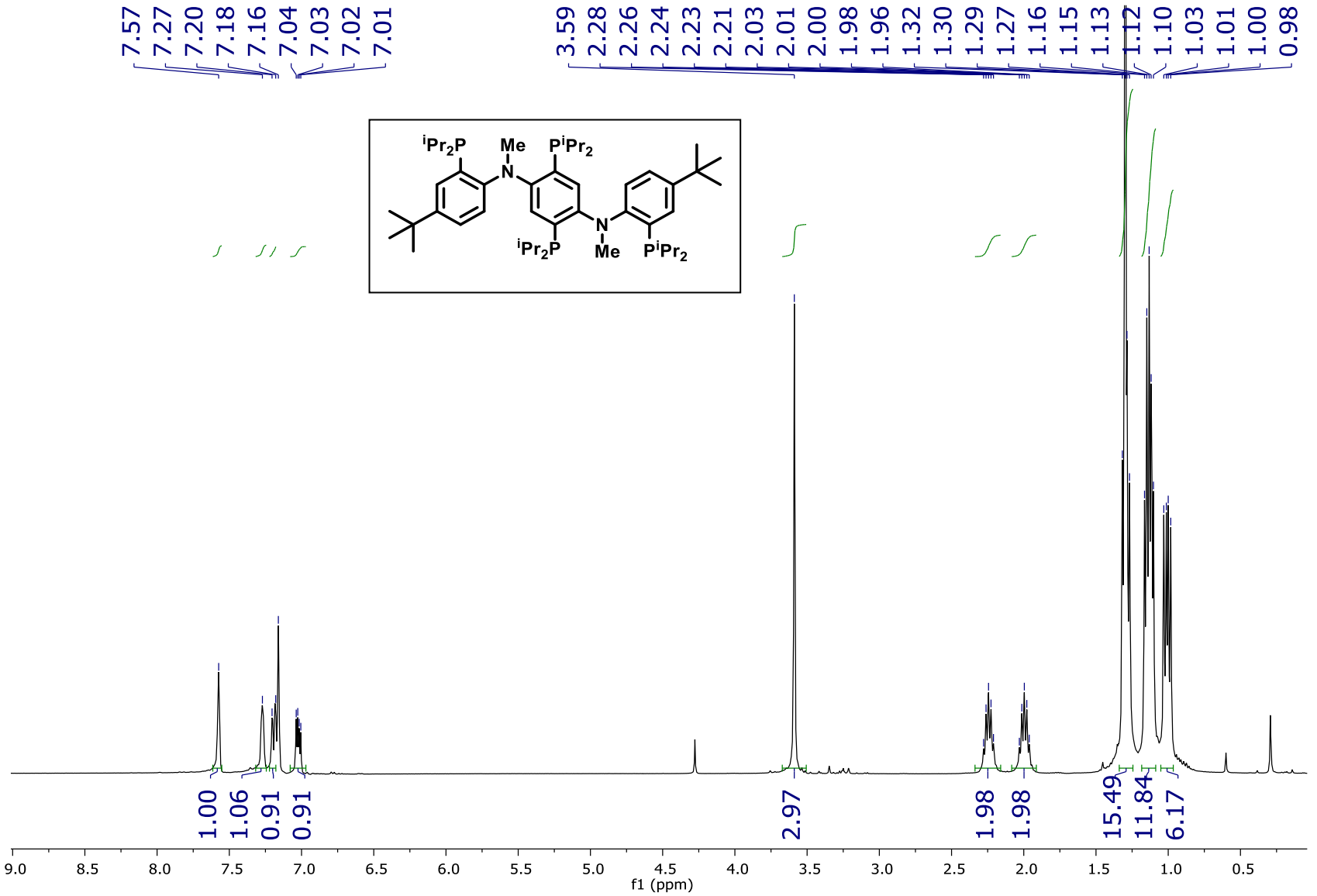


Figure S39. ^{1}H NMR spectrum of **19** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer

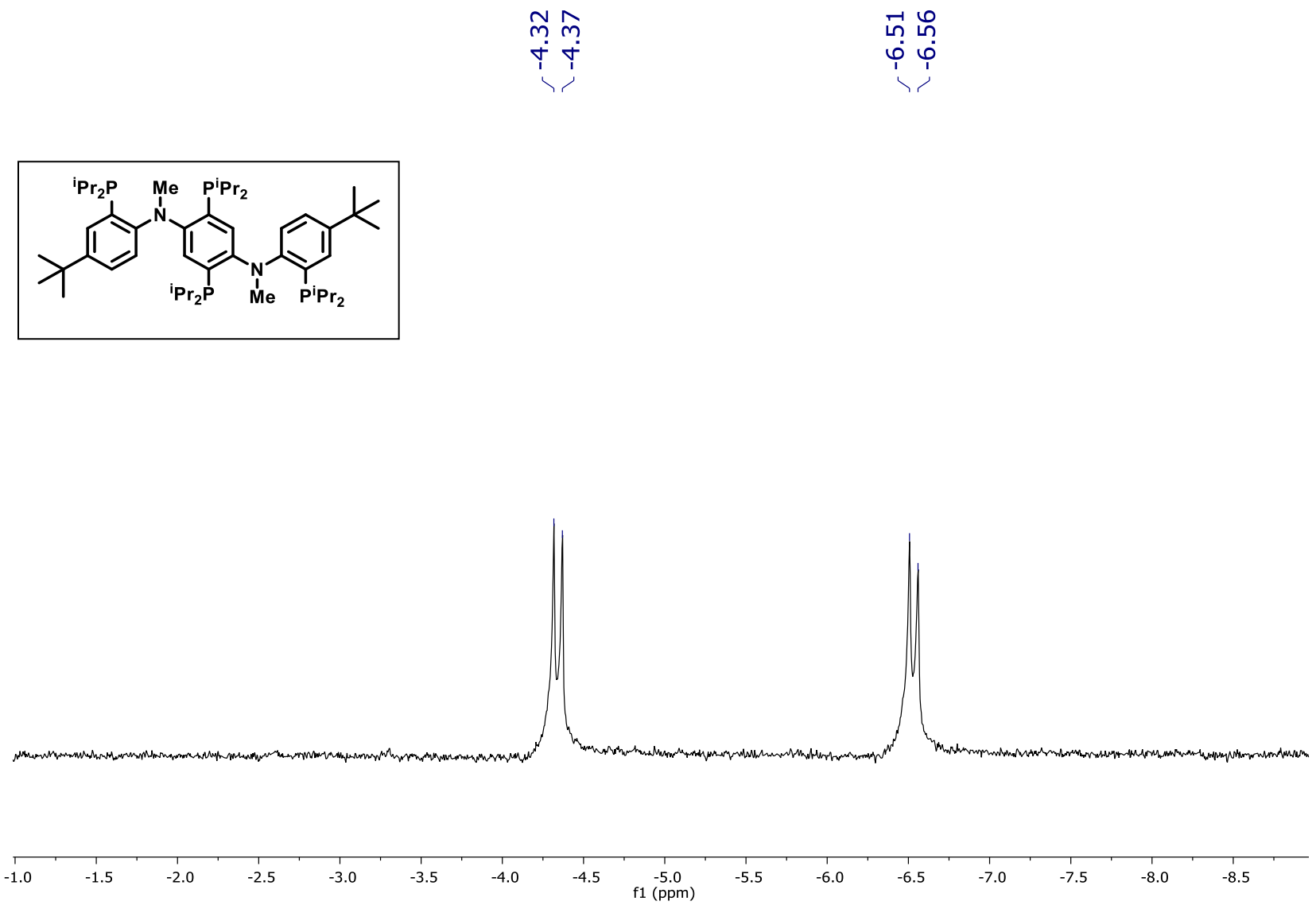


Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum of **19** in C_6D_6 at RT measured on a 500 MHz Varian NMR spectrometer

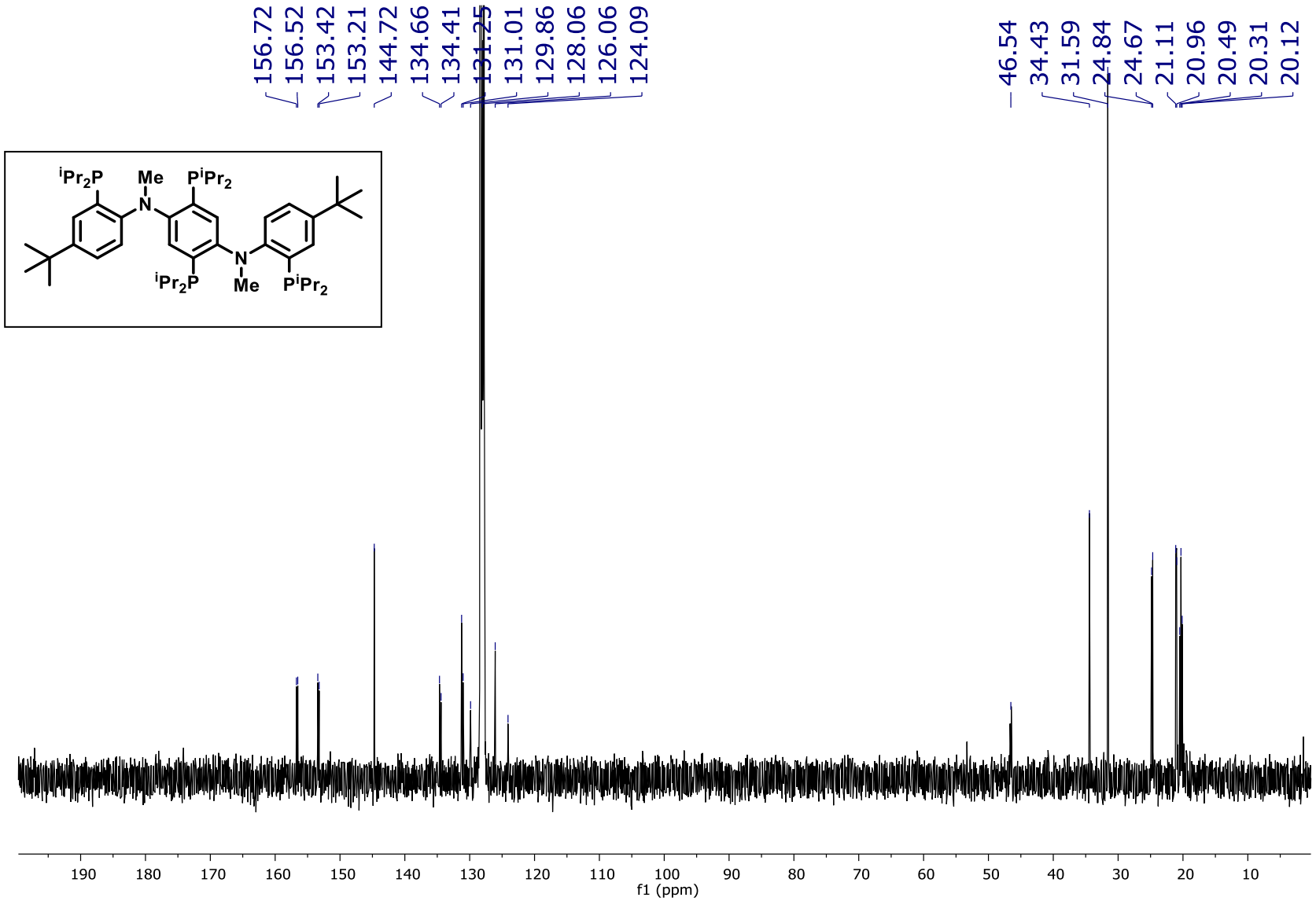


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **19** in C_6D_6 at RT measured on a 400 MHz Varian NMR spectrometer.

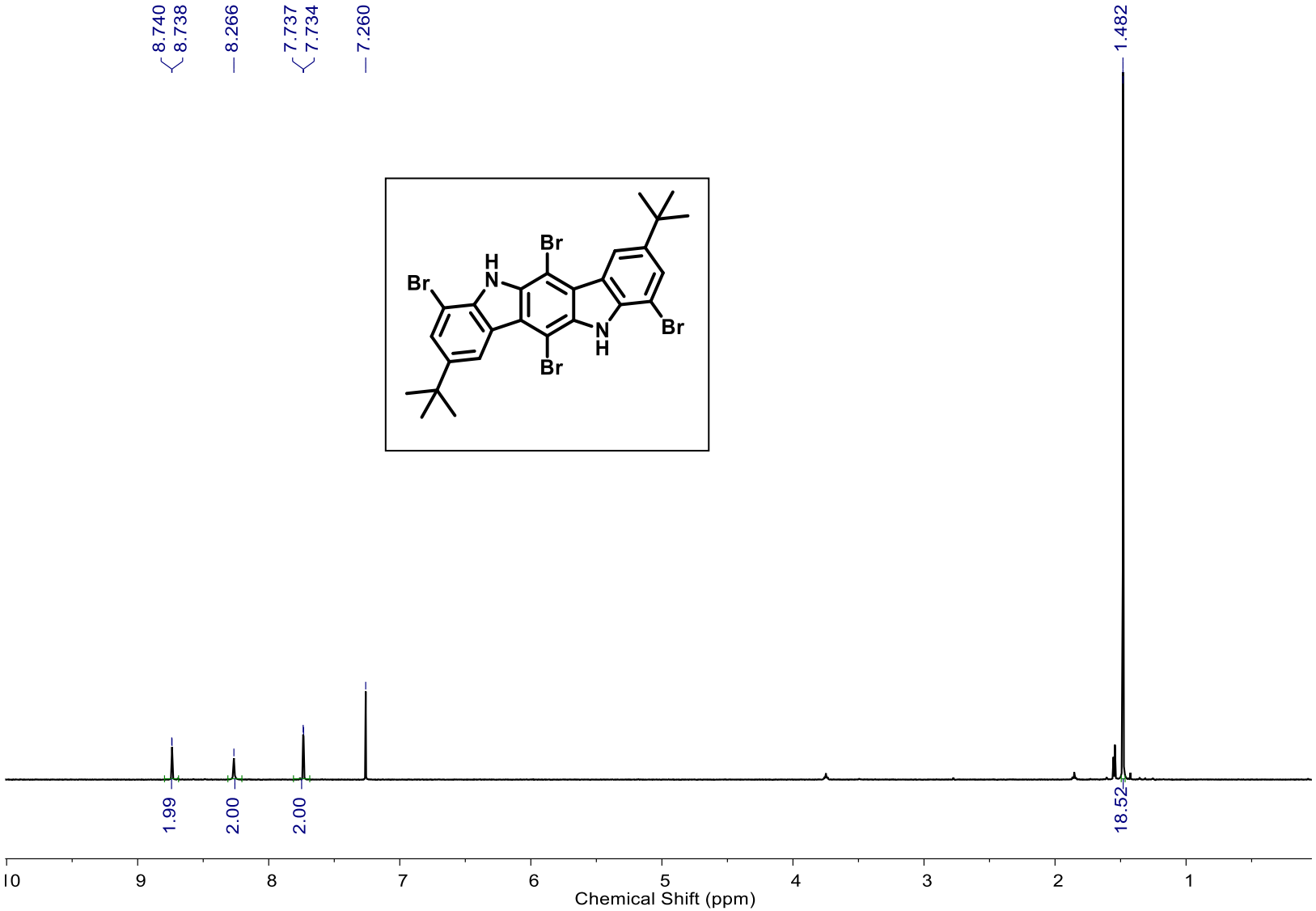


Figure S42. ^{1}H NMR spectrum of **21** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

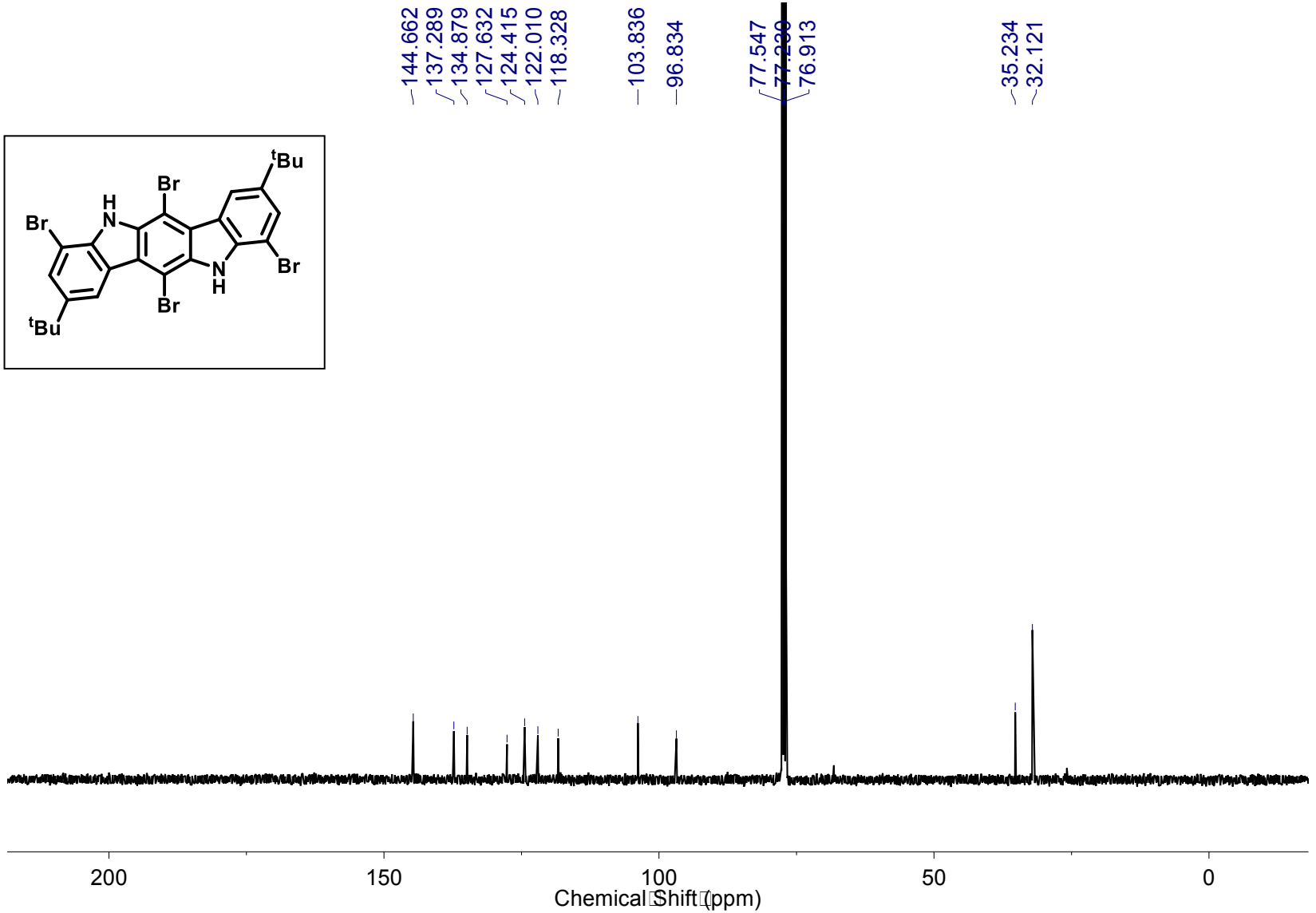


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **21** in $CDCl_3$ at RT measured on a 400 MHz Varian NMR spectrometer.

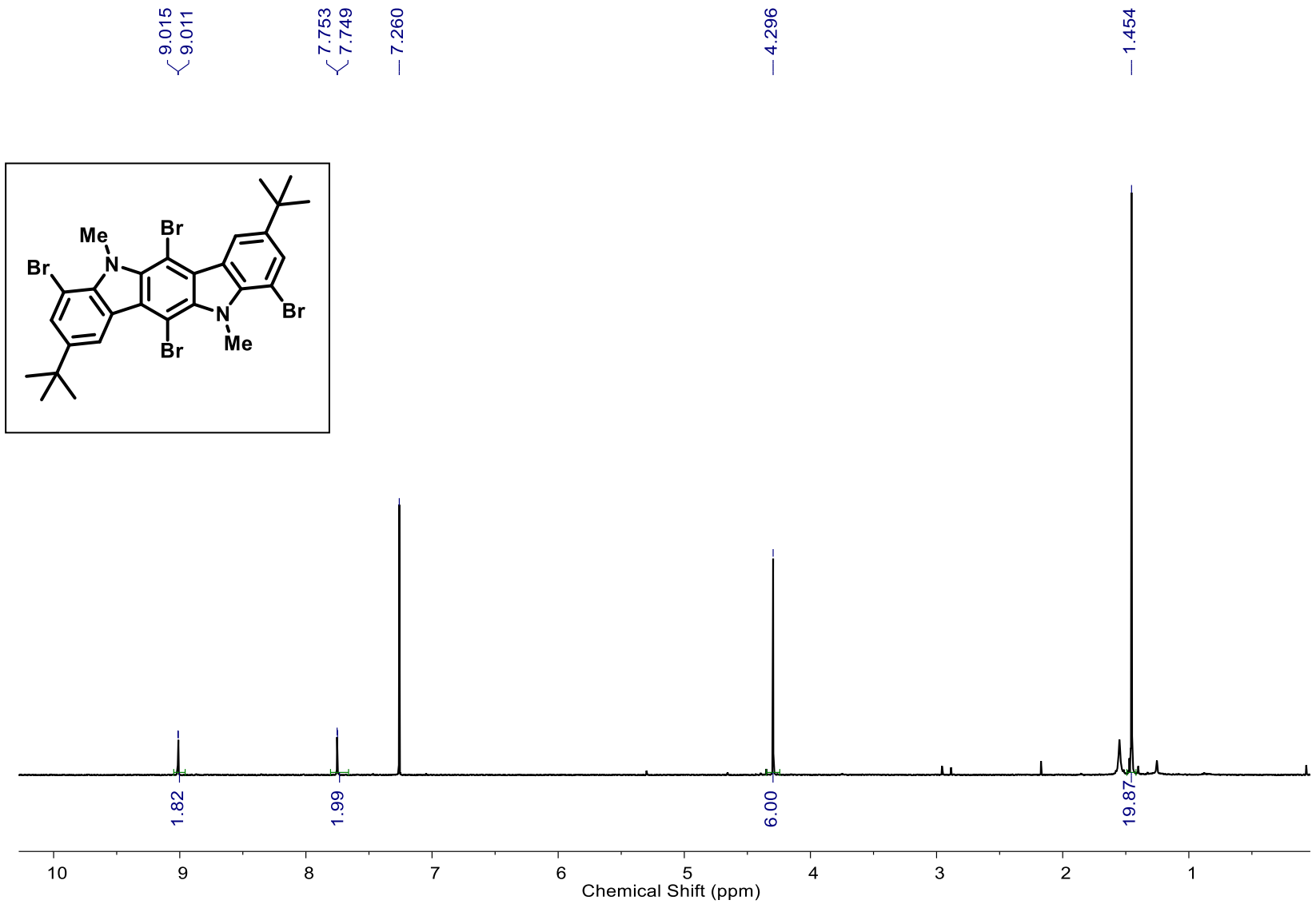


Figure S44. ^{1}H NMR spectrum of **22** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

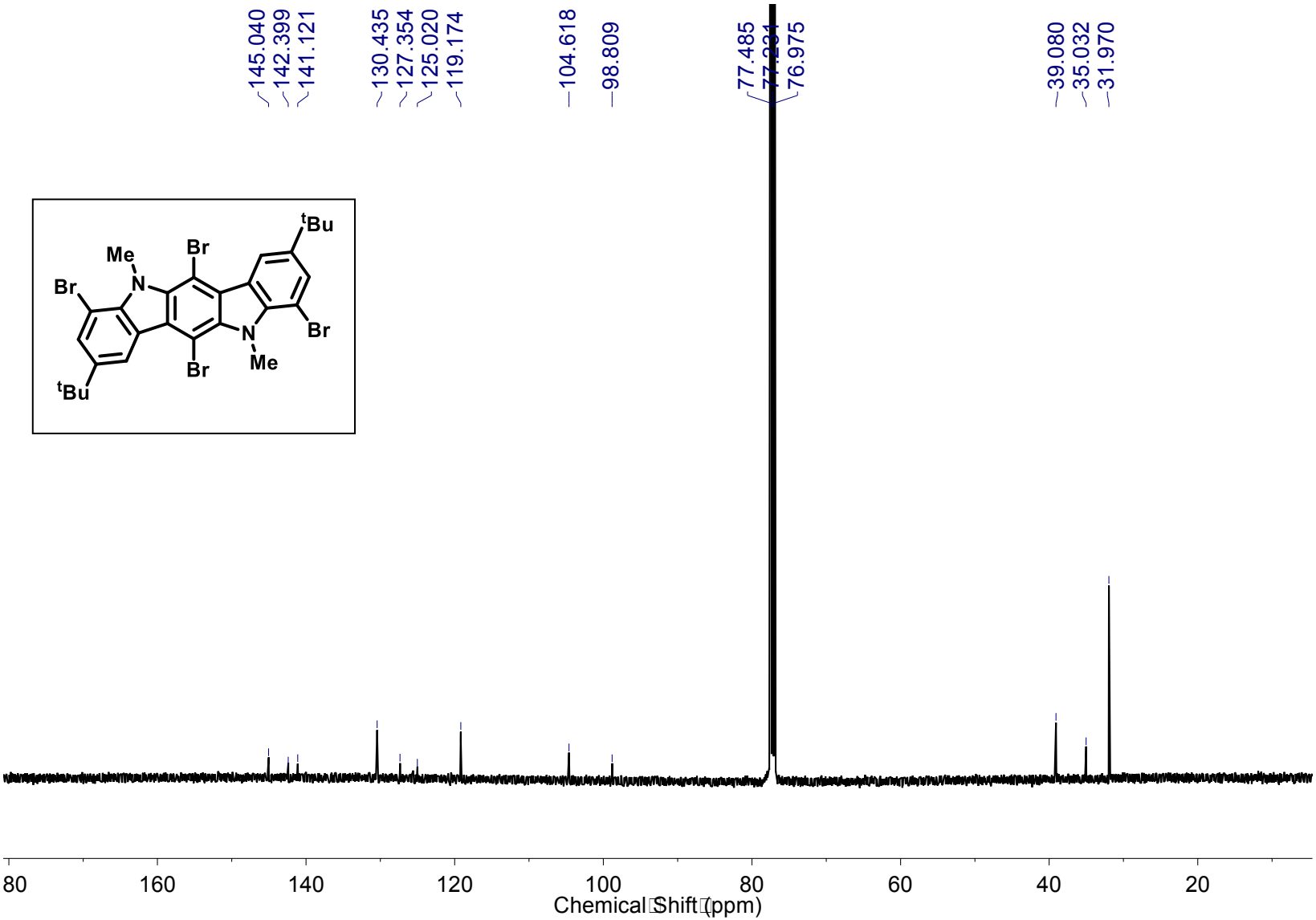


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **22** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

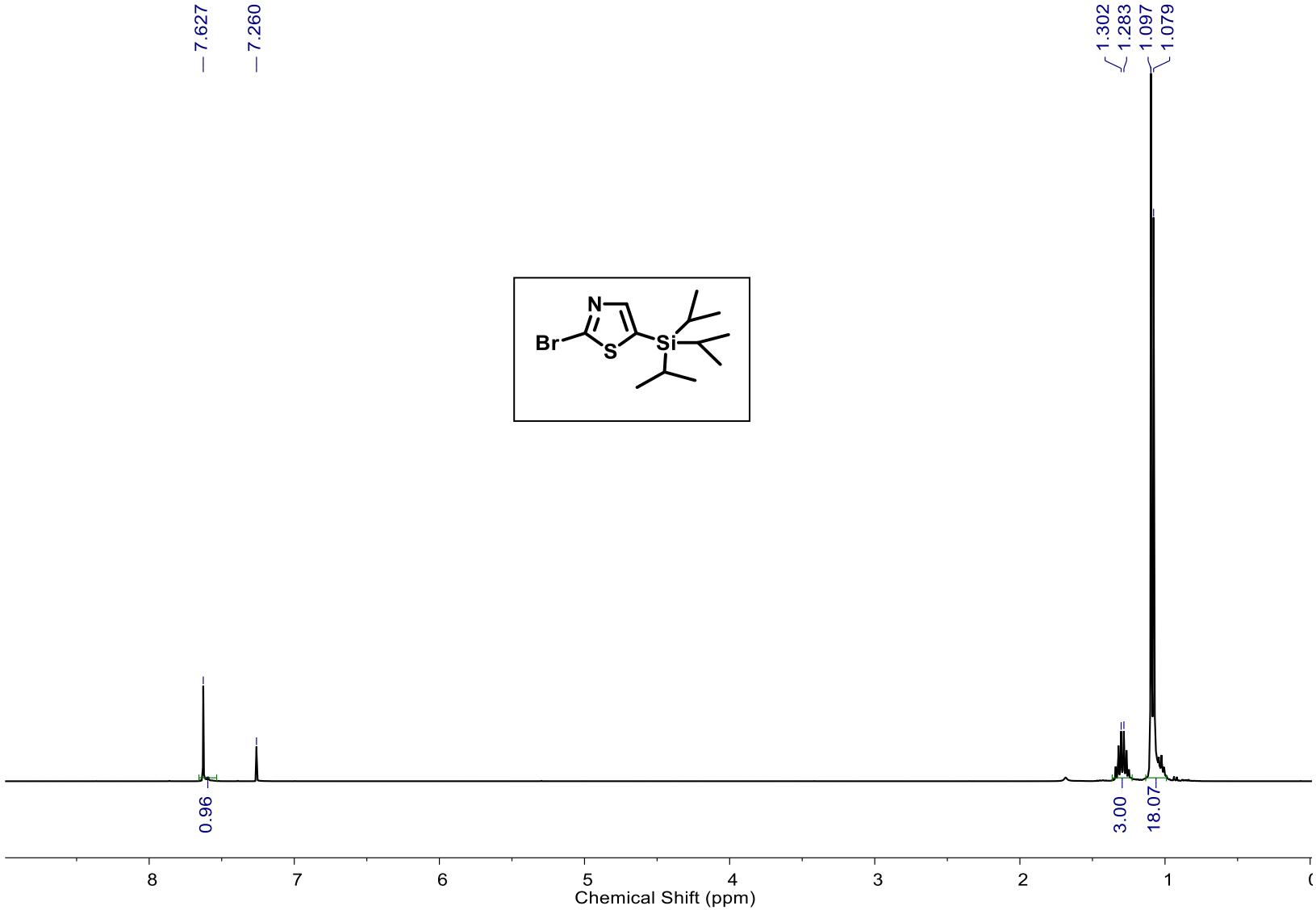


Figure S46. ^{1}H NMR spectrum of **23a** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

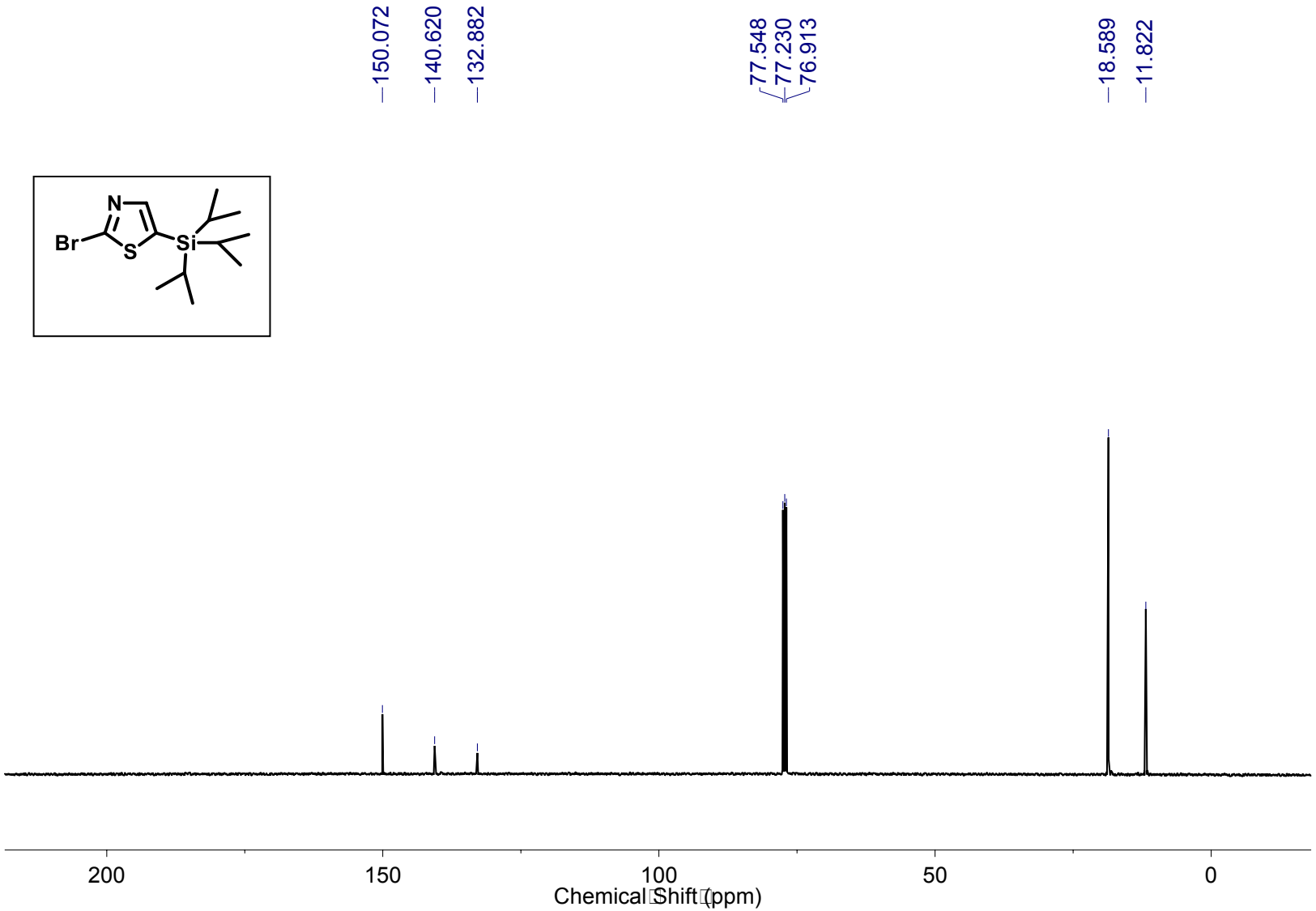


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **23a** in $CDCl_3$ at RT measured on a 400 MHz Varian NMR spectrometer.

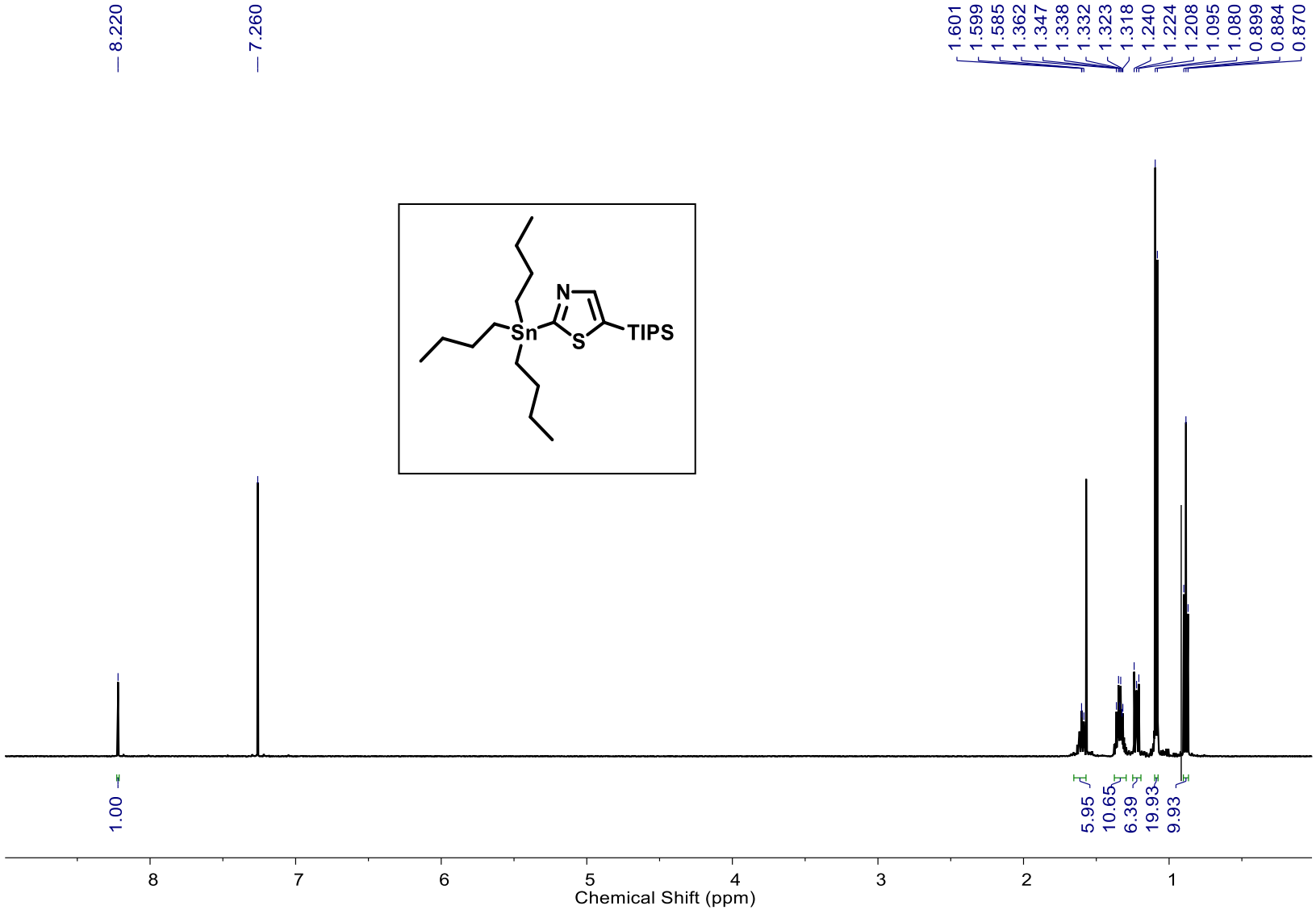


Figure S48. ^{1}H NMR spectrum of **23** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

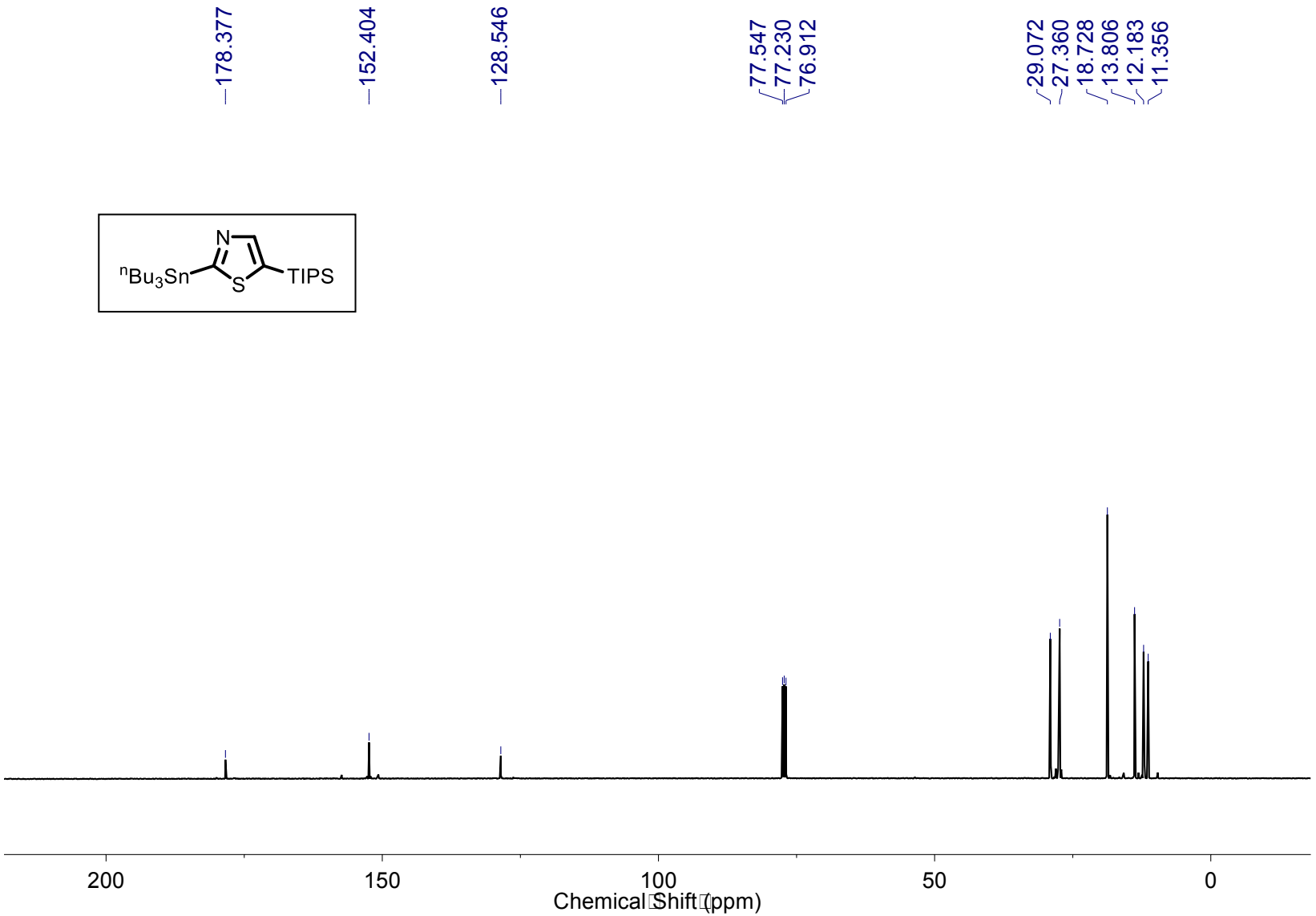


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **23** in $CDCl_3$ at RT measured on a 400 MHz Varian NMR spectrometer.

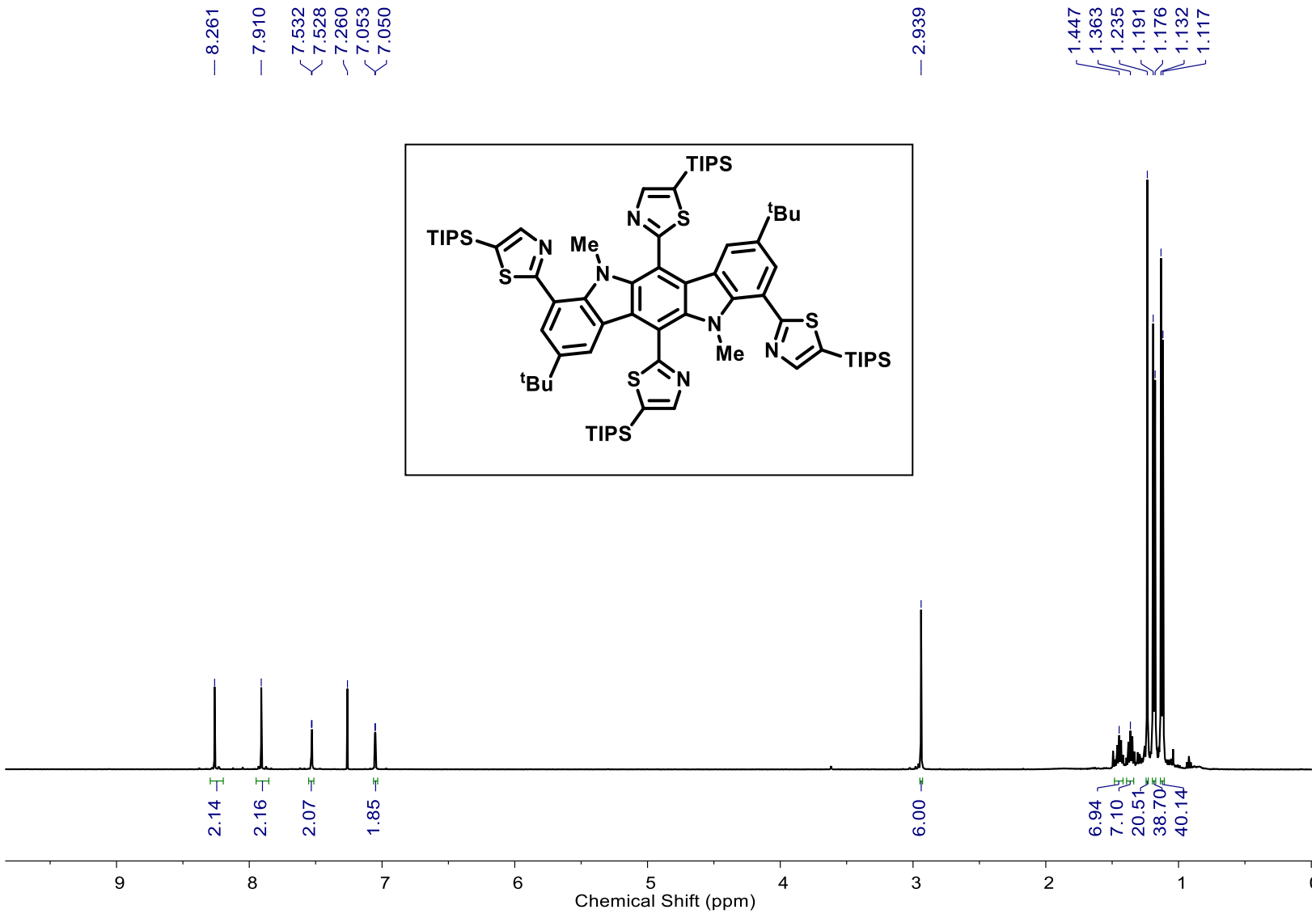


Figure S50. ^{1}H NMR spectrum of **24** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

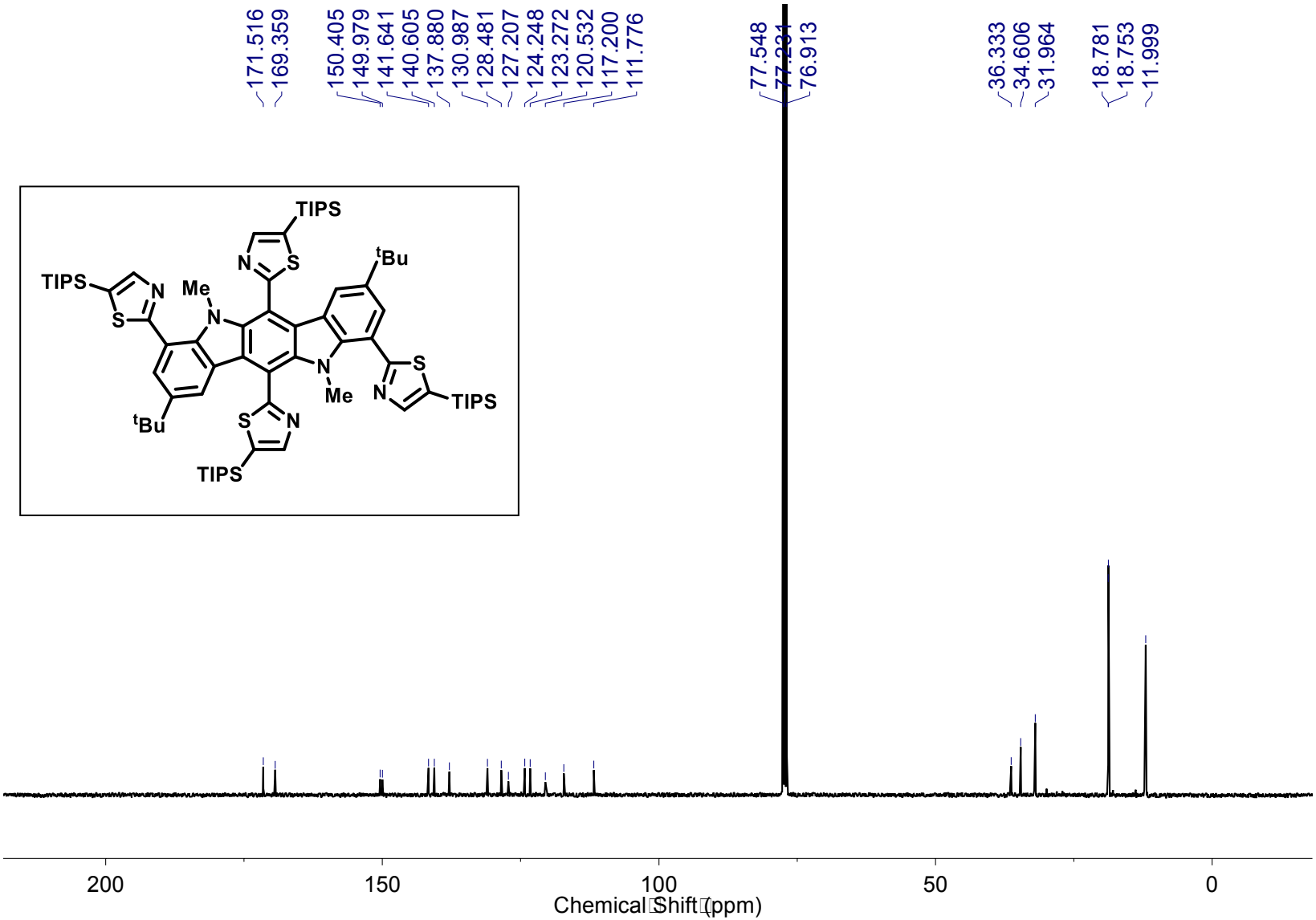


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of **24** in $CDCl_3$ at RT measured on a 500 MHz Varian NMR spectrometer.

VI. UV-Vis/NIR Spectra

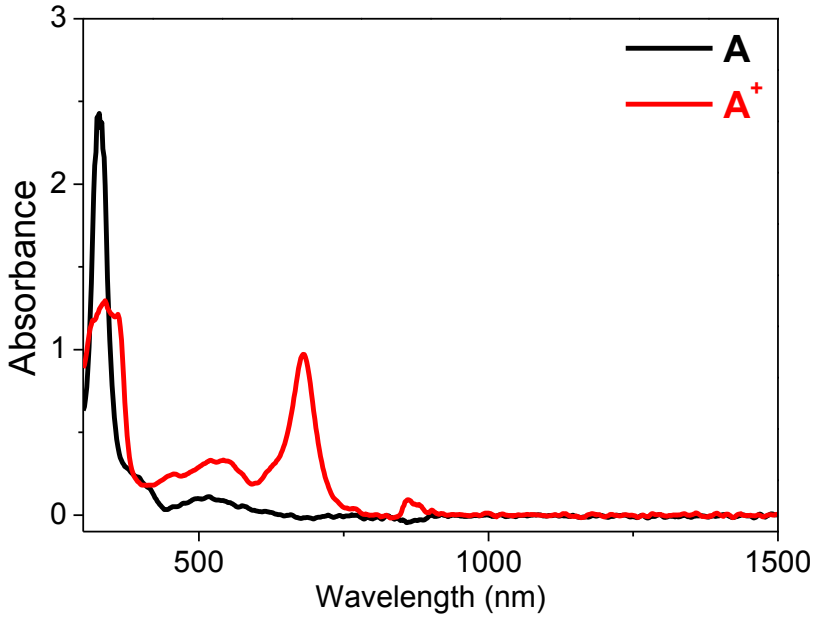


Figure S52. UV-Vis/NIR spectrum of approx. 1 x 10^{-4} M **A** in CH_2Cl_2, where the $\mathbf{A}^+$ was *in situ* generated by addition of 1.2 eq of [Fc]$CH_{12}B_{11}$ as the oxidant.

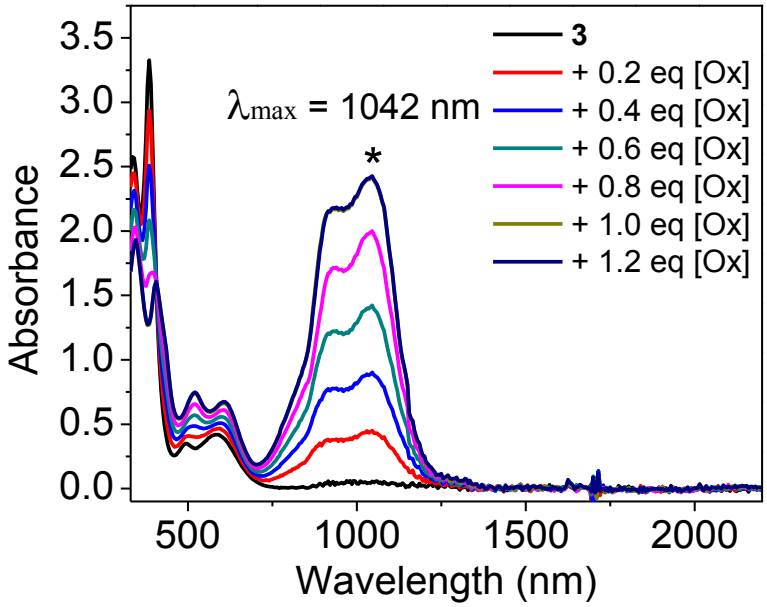


Figure S53. UV-Vis/NIR spectrum of approx. 1 x 10^{-4} M complex **3** in CH_2Cl_2, where the [**3**] $CH_{12}B_{11}$ was *in situ* generated by stepwise addition of 1.2 eq of [Fc]$CH_{12}B_{11}$ as the oxidant [Ox].

VII. Spectroelectrochemical Analysis of Complex 4

Spectroelectrochemical measurements were conducted with a Shimadzu UV3600 UV−vis-NIR spectrophotometer and a 273A potentiostat (Princeton Applied Research). The measurement was carried out in a honeycomb spectroelectrochemical cell (Pine Research Instrumentation, Inc.) composed of a quartz UV-vis cell (path length = 1.7 mm), a gold electrode chip and a mini Ag/AgCl reference electrode. Before taking a scan of an absorption spectrum, the potential was held at a constant voltage for 300 seconds. The range of potentials vs the Ag/AgCl reference electrode applied in these spectroelectrochemical experiments is consistent with the redox potentials vs Fc/Fc^+ determined in cyclic voltammetry experiments.[10]

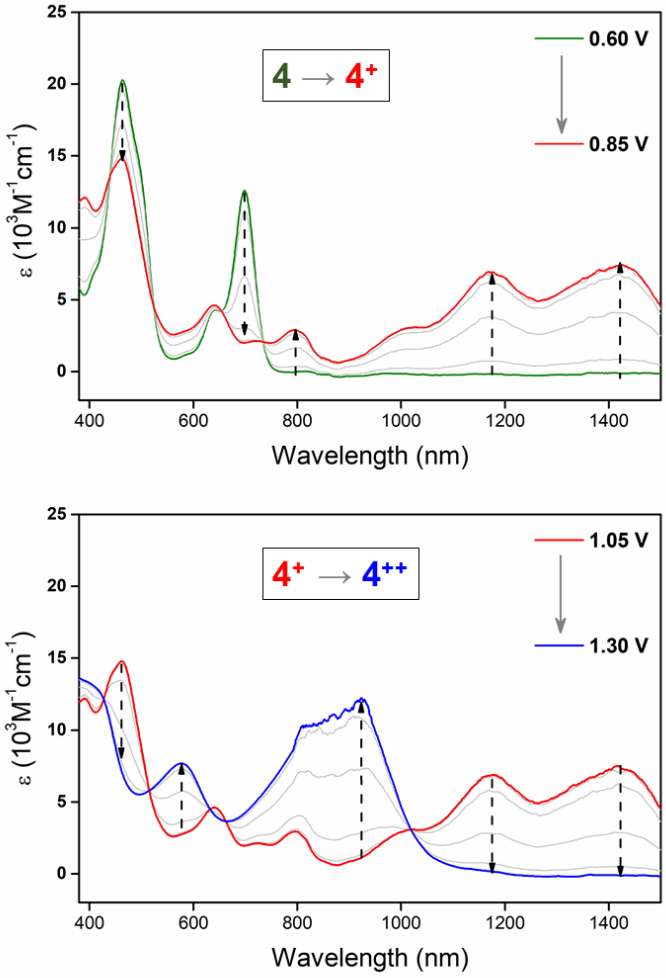


Figure S54. UV-vis-NIR absorption changes of the solution of **4** in CH_2Cl_2 (7.6×10^{-4} M), with 0.10 M [^{n}Bu$_4$N]PF_6 as the electrolyte, upon stepwise applications of potentials on the working electrode (Step height: 0.05 V, *vs* Ag/AgCl) from +0.60 V to +0.85 V (top), +1.05 V to +1.30 V (bottom).

VIII. DFT Calculations

DFT calculations were carried out using Gaussian 09.[11] Geometry optimizations were performed with the M06[12] functional with the LANL2DZp[13] basis set for all atoms. To simplify the computations, –Si(*i*Pr)$_3$ groups were replaced by –Si(CH$_3$)$_3$ groups and the *t*Bu groups were replaced by methyl groups.

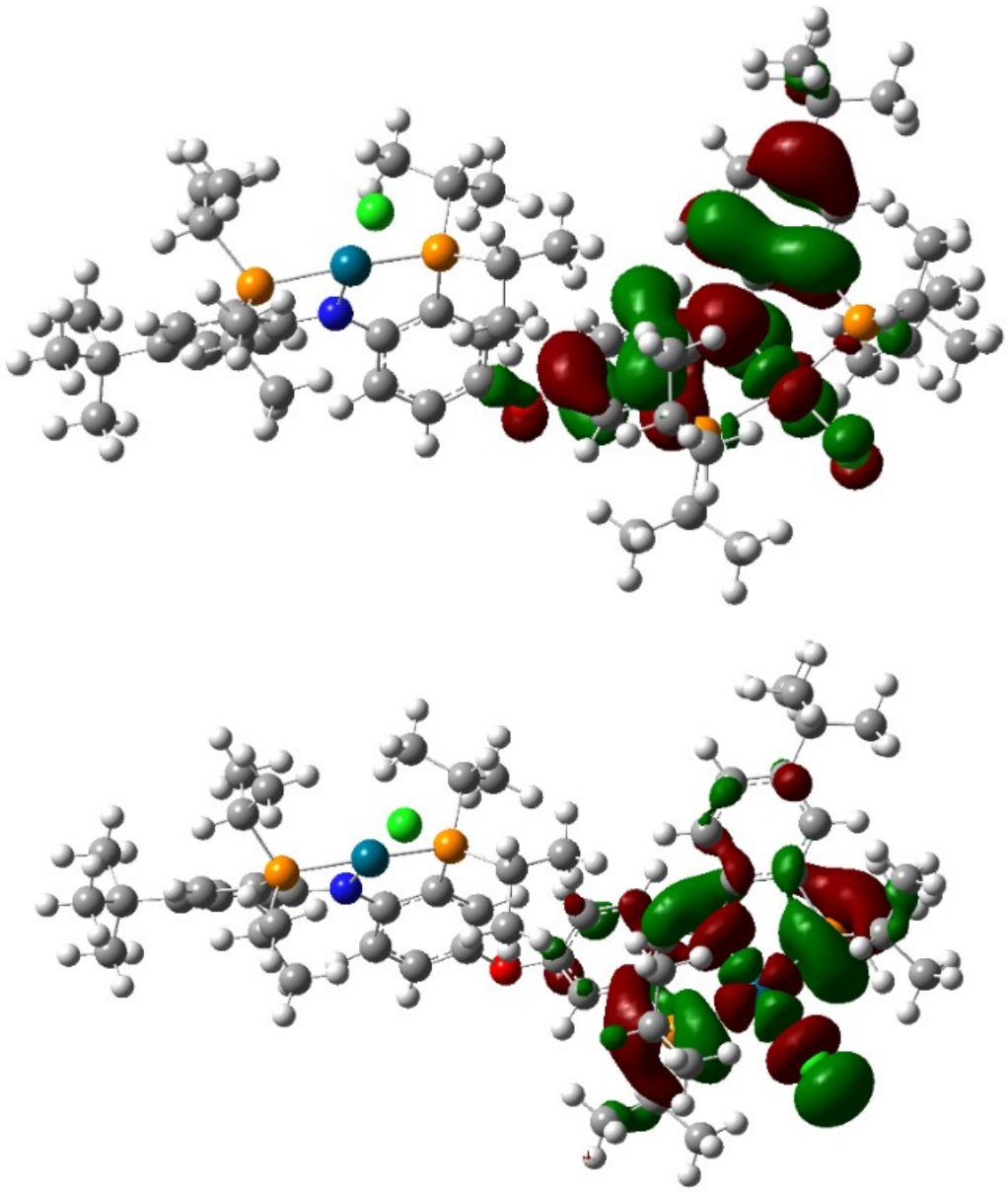


Figure S55. HOMO (upper) and LUMO (lower) for complex **1** (isovalue = 0.02).

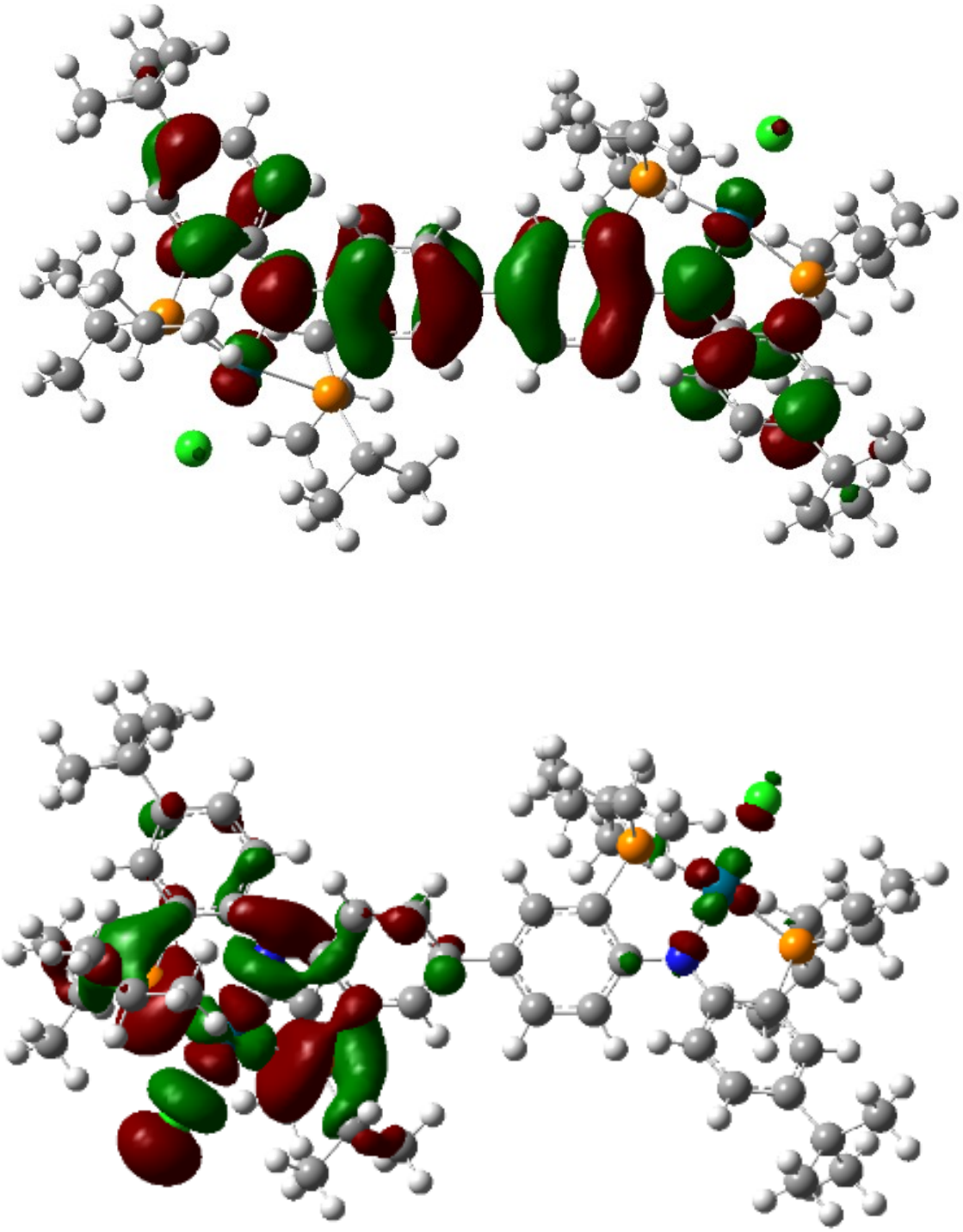


Figure S56. One of the two degenerate HOMOs (upper) and one of the two degenerate LUMOs (lower) for complex **2** (isovalue = 0.02).

IX. ESI References

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