Ligand design for site-selective installation of Pd and Pt centers to generate homo- and heteropolymetallic motifs

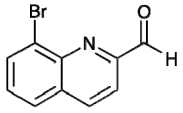
SUPPORTING INFORMATION

Daniel L. M. Suess and Jonas C. Peters*

Experimental Section

General Considerations

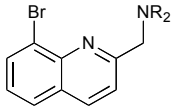
All manipulations were carried out using standard Schlenk or glove box techniques under a dinitrogen atmosphere. Dry, degassed solvents were purged with Ar and passed through an activated alumina column from S. G. Waters (Nashau, NH, USA) prior to use. All other reagents were purchased from commercial vendors and used as received without further purification unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR experiments were performed on Varian 500 MHz spectrometers. ^{1}H NMR spectra were referenced to residual solvent. ^{195}Pt NMR spectra were referenced to K_2PtCl_4. UV/vis spectra were acquired on a Cary 50 instrument. IR spectra were acquired on a Bio-Rad FTS 300 instrument. ESI-MS data were acquired by Ms. Li Li on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer in the MIT Dept. of Chemistry Instrumentation Facility. Combustion analaysis was performed by Midwest Microlab LLC in Indianapolis, IN, USA.



2

8-bromoquinoline-2-carbaldehyde (2): A 200 ml Schlenk tube charged with SeO_2 (10.2 g, 91.8 mmol) and a magnetic stir bar was purged with N_2 for 5 min. 1,4-dioxane (180 ml) was added and the mixture was heated to 80 ˚C before adding 8-bromo-2-methylquinoline[1] (20.2 g, 90.9 mmol) under a stream of N_2. The dark mixture was maintained at 80 ˚C for 12 hr., cooled to room temperature, and filtered through alumina eluting with CH_2Cl_2. Solvent was removed on a rotary evaporator to give a tan solid which was washed with cold acetone (3 x 20 ml). The remaining solid (11.2 g, 52%) was used without further purification. The brown acetone filtrate was condensed and again washed with cold acetone (3 x 10 ml) to give additional product (7.75 g, 36%, total of 88%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 10.31 (s, 1H), 8.34 (dd, J = 8.4 Hz, J = 0.5 Hz, 1H), 8.17 (dd, J = 7.5 Hz, J = 1.3 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 8.2 Hz, J = 1.3 Hz, 1H), 7.55 (dd, J = 8.1 Hz, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 193.4, 153.1, 145.0, 138.2, 134.3, 131.4, 129.6, 127.8, 126.1, 118.1. IR (CCl_4 solution): 1,711 cm^{-1}. ESI-MS: calc. for $C_{10}H_7BrNO$ $(M+H)^+$ 235.9706, found 235.9711. Elemental analysis for $C_{10}H_6BrNO$: calc. C 50.88 H 2.56, found C 50.72 H 2.71.

[1] N. Lin et al., *Nucleic Acids Res.,* **2007**, *35*, 1222-9.



3: R = 2-methoxyethyl
4: R = (1-methylimidazole-2-yl)methyl
5: R = (pyridin-2-yl)methyl

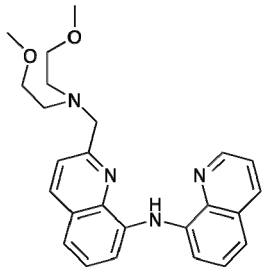
***N*-(8-bromoquinolin-2-methyl)-*N*,*N*-bis(2-methoxyethyl)amine (3)**: A 250 ml flask was charged with a magnetic stir bar, 100 ml 1,2-dichloroethane, **2** (2.18 g, 9.24 mmol), bis(2-methoxyethyl)amine (1.29 g, 9.69 mmol), and one drop of formic acid. The solution was allowed to stir for 30 min. before $NaHB(OAc)_3$ (2.35 g, 11.1 mmol) was added in one portion. The mixture was stirred at room temperature for 24 hr. and quenched with sat. aqueous $NaHCO_3$ (50 ml). The aqueous and organic phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 ml). The combined organics were dried over Na_2SO_4 and condensed on a rotary evaporator to give a dark yellow oil. Purification by flash chromatography (silica gel, 2:2:96 to 4:2:94 CH_3OH:Et_3N:CH_2Cl_2 gradient) gave the product as a viscous, pale yellow oil (2.08 g, 64%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C) δ(ppm) 8.11 (d, J = 8.4 Hz, 1H), 8.02 (dd, J = 7.4 Hz, J = 1.3 Hz, 1H), 7.77 (dd, J = 8.2 Hz, J = 1.3 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 4.36 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H), 4.16 (s, 2H), 3.55 (t, J = 6.0 Hz, 4H), 3.32 (s, 6H), 2.91 (t, J = 6.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 144.6, 136.6, 132.9, 128.6, 127.5, 126.3, 124.6, 121.9, 71.1, 61.5, 58.8, 54.3. ESI-MS: calc. for $C_{16}H_{22}BrN_2O_2Br$ $(M+H)^+$ 353.0865, found 353.0867. Elemental Analysis for $C_{16}H_{21}BrN_2O_2$: calc. C 54.40 H 5.99, found C 54.52 H 5.77.

***N*-(8-bromoquinolin-2-methyl)-*N*,*N*-bis((1-methyl-1*H*-imidazole-2-yl)methyl)amine (4)**: A 250 ml flask was charged with a magnetic stir bar, 100 ml 1,2-dichloroethane, **2** (771 mg, 3.27 mmol), bis((1-methyl-1*H*-imidazole-2-yl)methyl)amine (664 mg, 3.23 mmol),[2] and one drop of formic acid. The solution was allowed to stir for 30 min. before $NaHB(OAc)_3$ (762 mg, 3.59 mmol) was added in one portion. The mixture was stirred at room temperature for 24 hr. and quenched with sat. aqueous $NaHCO_3$ (50 ml). The aqueous and organic phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 ml). The combined organics were dried over Na_2SO_4 and condensed on a rotary evaporator to give a dark yellow oil. Purification by flash chromatography (silica gel, 2:2:96 to 4:2:94 CH_3OH:Et_3N:CH_2Cl_2 gradient) gave the product as a viscous, pale yellow oil which was triterated with pentane to afford a light tan solid (870 mg, 63%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C) δ(ppm) 8.04 (d, J = 8.4 Hz, 1H), 8.03 (dd, J = 7.5 Hz, J = 1.3 Hz, 1H), 7.75 (dd, J = 8.2 Hz, J = 1.3 Hz, 1H), 7.36 (dd, J = 7.5 Hz, J = 8.2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 1.2 Hz, 2H), 6.76 (d, J = 1.2 Hz, 2H), 4.02 (s, 2H), 3.92 (s, 4H), 3.42 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 160.2, 145.0, 133.4, 126.7, 133.0, 128.3, 127.5, 127.1, 127.6, 124.5, 122.6, 121.5, 59.9, 50.1, 32.6. ESI-MS: calc. for $C_{20}H_{22}BrN_6$ $(M+H)^+$ 427.1069, found 427.1052. Elemental analysis for $C_{20}H_{21}BrN_6$: calc C 56.48 H 4.98, found C 55.71 H 4.84.

***N*-(8-bromoquinolin-2-methyl)-*N*,*N*-bis(pyridin-2-ylmethyl)amine (5):** A 250 ml flask was charged with a magnetic stir bar, 100 ml 1,2-dichloroethane, **2** (3.87 g, 16.4 mmol), and 2,2'-

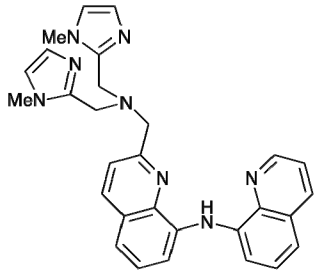
[2] S. R. Banerjee et al., *Inorg. Chem.,* **2002,** *41*, 6417-25.

dipicolylamine (3.11 g, 15.6 mmol). The solution was allowed to stir for 30 min. before $NaHB(OAc)_3$ (3.97 g, 18.7 mmol) was added in one portion. The mixture was stirred at room temperature for 24 hr. and quenched with sat. aqueous $NaHCO_3$ (50 ml). The aqueous and organic phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 ml). The combined organics were dried over Na_2SO_4 and condensed on a rotary evaporator to give a dark yellow oil. Purification by flash chromatography (silica gel, 2:2:96 to 4:2:94 CH_3OH:Et_3N:CH_2Cl_2 gradient) have the product as a viscous, pale yellow oil (4.0 g, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 8.54 (m, 2H), 8.10 (d, J = 8.4 Hz, 1H), 8.02 (dd, J = 7.4 Hz, J = 1.3 Hz, 1H), 7.65-7.76 (m, 6H), 7.35 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.14 (ddd, J = 7.3 Hz, J = 4.9 Hz, J = 1.3 Hz, 2H), 4.10 (s, 2H), 3.97 (s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 161.4, 159.2, 149.1, 144.7, 136.9, 136.8, 133.1, 128.6, 127.5, 126.6, 124.8, 123.5, 122.7, 122.5, 60.3, 60.2. ESI-MS: calc. for $C_{22}H_{20}BrN_4$ $(M+H)^+$ 421.0851, found 421.0850. Elemental analysis for $C_{22}H_{19}BrN_4$: calc. C 63.02 H 4.57, found C 62.74 H 4.67.



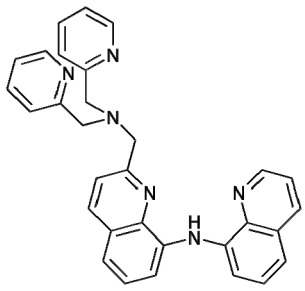
6: $L^{OMe}H$

2-((bis(2-methoxylethyl)amino)methyl)-*N*-(quinolin-8-yl)quinolin-8-amine (6, $L1^{OMe}H$): A 100 ml Schlenk tube charged with a magnetic stir bar, $Pd_2(dba)_3$ (79.8 mg, 0.0871 mmol), and *rac*-BINAP (108.6 mg, 0.174 mmol) was evacuated and back-filled with N_2 three times. Toluene (10 ml) was added and the solution was allowed to stir for 5 min. before **3** (1.54 g, 4.76 mmol), 8-aminoquinoline (755 mg, 5.24 mmol), NaO^tBu (549 mg, 5.71 mmol), and an additional 40 ml toluene were added. The solution was stirred at 110 ˚C for 20 hr., cooled to room temperature, filtered through Celite, and condensed on a rotary evaporator. The resulting brown oil was purified by flash chromatography (silica gel, 4:2:94 CH_3OH:Et_3N:CH_2Cl_2) to give 1.60 g (88%) of the title compound as a viscous yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C) δ(ppm) 10.69 (s, 1H), 8.95 (dd, J = 4.2 Hz, J = 1.7 Hz 1H), 8.16 (dd, J = 8.3 Hz, J = 1.7 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.90 (m, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 7.9 Hz, J = 7.9 Hz, 1H), 7.49 (dd, J = 8.01 Hz, J = 8.01 Hz, 1H), 7.48 (dd, J = 8.51, J = 4.15, 1H), 7.35-7.30 (m, 2H), 4.23 (s, 2H), 3.61 (t, J = 5.9 Hz, 4H), 3.35 (s, 6H), 3.01 (t, J = 5.9 Hz, 4H). ^{13}C NMR ($CDCl_3$, 500 MHz, 20 ˚C) δ(ppm) 158.25, 147.97, 140.25, 139.14, 139.10, 138.65, 136.47, 136.20, 129.11, 127.94, 127.30, 126.64, 121.88, 121.71, 117.76, 117.72, 110.02, 71.51, 61.37, 58.91, 54.41. ESI-MS: calc. for $C_{25}H_{29}N_4O_2$ $(M+H)^+$ 417.2285, found 417.2265. Elemental analysis for $C_{25}H_{28}N_4O_2$: calc. C 72.09 H 6.78, found C 71.27 H 6.78.



7: $L^{im}H$

2-((bis((1-methyl-1*H*-imidazole-2-yl)methyl)amino)methyl)-*N*-(quinolin-8-yl)quinolin-8-amine (7, $L1^{im}H$): A 100 ml Schlenk tube charged with a magnetic stir bar, $Pd_2(dba)_3$ (23.8 mg, 0.026 mmol), and *rac*-BINAP (32.3 mg, 0.052 mmol) was evacuated and back-filled with N_2 three times. Toluene (10 ml) was added and the solution was allowed to stir for 5 min. before **4** (552 mg, 1.30 mmol), 8-aminoquinoline (189 mg, 1.31 mmol), NaO^tBu (150 mg, 1.56 mmol), and an additional 20 ml toluene were added. The solution was stirred at 110 ˚C for 20 hr., cooled to room temperature, filtered through Celite, and condensed on a rotary evaporator. The resulting brown oil was purified by flash chromatography (silica gel, 4:2:94 CH_3OH:Et_3N:CH_2Cl_2) to give 597 mg (94%) of the title compound as a yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 10.65 (s, 1H), 8.74 (dd, J = 4.2 Hz, J = 1.8 Hz, 1H), 8.14 (dd, J = 8.3 Hz, J = 0.7 Hz, 1H), 8.06 (d, 8.4 Hz, 1H), 7.87 (m, 2H), 7.52 (dd, J = 7.9 Hz, 7.9 Hz, 1H), 7.50 (dd, J = 7.9 Hz, J = 7.9 Hz, 1H), 7.44 (8.2 Hz, 4.2 Hz, 1H), 7.28-7.24 (m, 3H), 6.94 (d, J = 1.3 Hz, 2H), 6.74 (d, J = 1.3 Hz, 2H), 4.09 (s, 2H), 4.06 (s, 4H), 3.35 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz, 20 ˚C) δ(ppm) 156.8, 147.8, 145.4, 139.9, 138.9, 138.7, 138.5, 136.6, 136.1, 128.9, 127.7, 127.2, 127.1, 126.9, 122.4, 121.7, 121.4, 117.9, 117.5, 110.1, 109.8, 60.0, 50.2, 32.5. ESI-MS: calc. for $C_{29}H_{29}N_8$ $(M+H)^+$ 489.2515 found 489.2505. Elemental analysis for $C_{29}H_{28}N_8$: calc. C 71.29 H 5.78, found C 70.85 H 5.92.



8: $L^{py}H$

2-((bis((pyridin-2-yl)methyl)amino)methyl)-*N*-(quinolin-8-yl)quinolin-8-amine (8, $L1^{py}H$): A 100 ml Schlenk tube charged with a magnetic stir bar, $Pd_2(dba)_3$ (99 mg, 0.11 mmol), and *rac*-BINAP (135 mg, 0.22 mmol) was evacuated and back-filled with N_2 three times. Toluene (10 ml) was added and the solution was allowed to stir for 5 min. before **5** (2.27 g, 5.42 mmol), 8-aminoquinoline (790 mg, 5.48 mmol), NaO^tBu (573 mg, 5.97 mmol), and an additional 40 ml toluene were added. The solution was stirred at 110 ˚C for 20 hr., cooled to room temperature, filtered through Celite, and condensed on a rotary evaporator. The resulting brown oil was purified by flash chromatography (silica gel, 4:2:94 CH_3OH:Et_3N:CH_2Cl_2) to give 2.38 g (91%) of the title compound as a viscous yellow oil. ^{1}H NMR (CD_3OD, 500 MHz, 20 ˚C): δ(ppm)

8.58 (dd, J = 4.1 Hz, J = 1.6 Hz, 1H), 8.21 (m, 2H), 7.99 (dd, J = 8.3 Hz, J = 1.6 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.62 (dd, J = 7.7 Hz, J = 1.0 Hz, 1H), 7.59 (dd, J = 7.7 Hz, J = 1.0 Hz, 1H), 7.36 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.8 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.21-7.30 (m, 3H), 7.12 (dd, J = 8.2 Hz, J = 0.9 Hz, 1H), 7.05 (dd, J = 8.2 Hz, J = 0.9 Hz, 1H), 6.97 (ddd, J = 7.5 Hz, J = 5.0 Hz, J = 1.0 Hz, 2H), 3.83 (s, 2H), 3.77 (s, 4H). ^{13}C NMR (CD_3OD, 125 MHz, 20 ˚C): δ(ppm) 160.2, 157.9, 149.1, 148.3, 140.8, 130.0, 139.6, 139.3, 138.4, 137.7, 137.3, 130.2, 129.1, 128.3, 127.8, 124.8, 123.6, 122.7, 122.7, 118.8, 118.7, 111.0, 110.5, 61.3, 60.9. ESI-MS: calc. for $C_{31}H_{27}N_6$ $(M+H)^+$ 483.2297, found 483.2293. Elemental analysis for $C_{31}H_{26}N_6$: calc. C 77.16 H 5.43, found C 76.83 H 5.56.

L1^{OMe}PdCl (10): A 25 ml Schlenk tube was charged with **10** (515 mg, 1.24 mmol), (COD)Pd(Me)Cl (328 mg, 1.24 mmol), Et_3N (0.02 ml, 0.12 mmol), 5 ml THF, and a magnetic stirbar. The solution was heated overnight at 60 ˚C. Solvent was removed in vacuo. The solids were dissolved in a minimum volume of dichloromethane and precipitated upon the addition of Et_2O. Additional washing with Et_2O provided the title compound (553 mg, 80%). Single crystals suitable for x-ray diffraction were grown by slow diffusion of Et_2O into a CH_3CN solution. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 9.21 (dd, J = 5.2 Hz, J = 1.1 Hz, 1H), 8.24 (dd, J = 8.3 Hz, J = 1.4 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.70-7.73 (m, 2H), 7.44-7.50 (m, 2H), 7.39 (dd, J = 7.9, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 4.66 (s, 2H), 3.58 (t, J = 5.7 Hz, 4H), 3.29 (s, 6H), 2.97 (t, J = 5.7 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 149.4, 149.2, 148.5, 148.2, 147.5, 139.0, 138.9, 131.0, 129.9, 129.2, 128.4, 122.0, 121.2, 115.3, 115.2, 112.9, 111.1, 71.1, 64.2, 58.8, 55.7. ESI-MS: calc. for $C_{25}H_{28}ClN_4O_2Pd$ $(M+H)^+$ 559.0939, found 559.0933. Elemental analysis for $C_{25}H_{27}ClN_4O_2Pd$: calc. C 53.87 H 4.88, found C 53.50 H 4.85.

[L1^{im}Pd][Cl] (11): A 25 ml Schlenk tube was charged with **7** (96.7 mg, 0.20 mmol), (COD)$PdCl_2$ (56.5 g, 0.20 mmol), Et_3N (0.030 ml, 0.22 mmol), 2 ml $CHCl_3$, and a magnetic stirbar. The solution was heated overnight at 60 ˚C. Solvent was removed in vacuo. Recrystallization by slow diffusion of Et_2O into a dichloromethane solution provided the title compound as red solid (76 mg, 61%). Single crystals suitable for x-ray diffraction were grown by slow diffusion of Et_2O into a $CHCl_3$ solution. ^{1}H NMR ($CDCl_3$, 500 MHz, -50 ˚C): δ(ppm) 8.35 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.82 (dd, J = 7.9 Hz, J = 2.7 Hz, 2H), 7.63 (br, 1H), 7.58 (dd, J = 7.7 Hz, J = 7.7 Hz, 1H), 7.50 (dd, J = 7.9 Hz, J = 5.5 Hz, 1H), 7.46 (dd, J = 7.9 Hz, J = 7.9 Hz, 1H), 7.41 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.16 (s, 1H), 7.13 (d (br), J = 8.0 Hz, 1H), 6.68 (s, 1H), 6.20 (s, 1H), 4.83 (d, J = 14.7 Hz, 1H), 4.35-4.41 (m, 2H), 4.07 (s, 3H), 4.01 (d, J = 12.8 Hz, 1H), 3.75-3.80 (m, 4H), 3.30 (d, J = 14.8 Hz, 1H). ESI-MS: calc. for $C_{29}H_{27}N_8Pd$ $(M-Cl)^+$ 593.1394, found. Despite several purifications, satisfactory carbon and hydrogen combustion analysis could not be obtained on otherwise spectroscopically-pure samples.

[L1^{py}HPdMe][PF_6] (12). A 20 ml scintillation vial was charged with (COD)Pd(Me)Cl (44 mg, 0.17 mmol), 2 ml acetonitrile, and a magnetic stirbar. Addition of $TlPF_6$ (58 mg, 0.17 mmol) afforded a white precipitate. Dropwise addition of a solution of **8** (80 mg, 0.17 mmol) in 1 ml CH_3CN produced a brilliant yellow solution. After stirring for 1 hr., solvent was removed in vacuo. The resulting solid was suspended in 5 ml CH_2Cl_2 and filtered. The yellow filtrate was treated with Et_2O which resulted in precipitation of a yellow solid which was washed with

pentate and dried to provide analytically pure **12** (. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 10.56 (s, 1H), 9.02 (dd, J = 4.3 Hz, J = 1.7 Hz, 1H), 8.41 (d, J = 7.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 5.0 Hz, 2H), 7.93 (d, J = 7.6 Hz, 1H), 7.78 (dd, J = 8.2 Hz, J = 3.2 Hz, 2H), 7.62-7.70 (m, 4H), 7.53 (d, J = 8.2 Hz, 1H), 7.48 (dd, J = 7.9 Hz, J = 7.9 Hz, 1H), 7.35 (7.8 Hz, 2H), 7.22 (d, J = 8.2 Hz, 1H), 7.16 (br, 2H), 4.92 (d, J = 15.8 Hz, 2H), 4.78 (d, J = 15.8 Hz, 2H), 4.30 (s, 2H), 0.58 (s, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 164.8, 151.4, 148.9, 148.5, 139.8, 139.1, 139.1, 138.3, 138.2, 137.9, 136.9, 136.6, 129.1, 128.0, 127.8, 127.4, 124.2, 124.0, 124.0, 122.2, 118.4, 110.3, 109.9, 64.2, 63.0, 3.6 ESI-MS: calc. for $C_{32}H_{29}N_6Pd$ $(M\text{-}PF_6)^+$ 603.1499, found 603.1476. Elemental analysis for $C_{32}H_{29}F_6N_6PPd$: calc. C 51.31 H 3.90, found C 51.05 H 3.85.

[L1^{py}Pd(Cl)(PdMe)][PF_6] (13): A 25 ml Schlenk tube was charged with **12** (121 mg, 0.162 mmol), (COD)Pd(Me)Cl (85.6 mg, 0.324 mmol), Et_3N (2.2 µl, 0.016 mmol), 2 ml CH_3CN, and a magnetic stirbar. A deep red-purple solution formed upon heating at 80 ˚C overnight. Addition of 10 ml Et_2O precipitated a solid which was redissolved in 1 ml CH_3CN and again precipitated with Et_2O to give a red-purple solid (115 mg, 80%). Single crystals suitable for x-ray diffraction were grown by slow diffusion of Et_2O into a 3:1 CH_2Cl_2/DMSO solution. ^{1}H NMR (CD_3CN, 500 MHz, 20 ˚C): δ(ppm) 8.73 (dd, J = 5.2 Hz, J = 1.4 Hz, 1H), 8.47 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.86 (d (br), J = 4.7 Hz, 2H), 7.73 (dd, J = 7.8 Hz, J = 0.8 Hz, 1H), 7.52-7.62 (m, 6H), 7.27 (d, J = 7.6 Hz, 1H), 7.25 (dd, J = 7.9 Hz, J = 7.9 Hz, 1H), 7.10 (br, 2H), 7.02 (br, 2H), 6.76 (d, J = 7.8 Hz, 1H), 5.12 (br, 2H), 4.90 (d, J = 15.7 Hz, 2H), 4.28 (d, J = 15.7 Hz, 2H), 0.32 (s, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 164.5, 156.8, 149.9, 149.8, 149.6, 149.5, 149.1, 148.9, 141.3, 140.5, 139.2, 132.3, 131.0, 130.7, 130.4, 127.6, 124.7, 124.3, 123.0, 117.1, 115.3, 114.6, 112.3, 66.0, 65.3, 6.3. ESI-MS: calc. for $C_{32}H_{28}ClN_6Pd_2$ $(M\text{-}PF_6)^+$ 745.0147, found 745.0127. Elemental analysis for $C_{32}H_{28}ClF_6N_6PPd_2$: calc. C 43.19 H 3.17, found C 43.07 H 3.45.

[L1^{py}HPtMe][PF_6] (14). A 20 ml scintillation vial was charged with (COD)Pt(Me)Cl (74 mg, 0.21 mmol), 2 ml acetonitrile, and a magnetic stirbar. Addition of $TlPF_6$ (73 mg, 0.21 mmol) afforded a white precipitate. Dropwise addition of a solution of **8** (101 mg, 0.21 mmol) in 2 ml CH_3CN produced a yellow-orange solution. After stirring overnight, solvent was removed in vacuo. The resulting solid was suspended in 5 ml CH_2Cl_2 and filtered. The yellow-brown filtrate was treated with Et_2O which resulted in precipitation of a yellow-brown solid which was washed with pentate and dried to provide analytically pure **14** ^{1}H NMR (CD_3CN, 500 MHz, 20 ˚C): δ(ppm) 10.75 (s, 1H), 9.09 (dd, J = 4.3 Hz, J = 1.7 Hz, 1H), 8.39 (dd, J = 8.2 Hz, J = 1.7 Hz, 1H), 8.30 (d, 5.8Hz, $^{3}J_{PtH}$ = 19.6 Hz, 2H), 8.05 (d, 8.4 Hz, 1H), 7.93 (d, 7.6 Hz, 1H), 7.84 (dd, J = 10.7 Hz, J = 7.8 Hz, 2H), 7.63-7.72 (m, 3H), 7.53 (m, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.15 (dd, J = 6.7 Hz, J = 6.7 Hz, 2H), 5.13 (d, J = 5.6 Hz, 2H), 4.91 (d, J = 5.6 Hz, 2H), 4.51 (s, 2H), 0.69 (s, $^{3}J_{PtH}$ = 37.5 Hz, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 167.0, 151.6, 149.3, 149.2, 140.4, 139.4, 138.8, 138.7, 137.4, 137.3, 129.8, 128.9, 128.4, 128.2, 125.5, 125.1, 124.8, 122.9, 119.1, 111.0, 110.5, 66.1, 64.2, -11.6. ^{195}Pt NMR (CD_3CN, 107 MHz, 20 ˚C): δ(ppm) -3,059. ESI-MS: calc. for $C_{32}H_{29}N_6Pt$ $(M\text{-}PF_6)^+$ 692.2101, found 692.2083. Elemental analysis for $C_{32}H_{29}F_6N_6PPt$: calc. C 45.88 H 3.49, found C 45.82 H 3.55.

[L1^{py}Pd(Cl)(PtMe)][PF_6] (15): A 25 ml Schlenk tube was charged with **14** (55.9 mg, 0.067 mmol), (COD)Pd(Me)Cl (17.7 mg, 0.067 mmol), Et_3N (1 µl, 0.007 mmol), 1 ml CH_3CN, and a

magnetic stirbar. A deep red-purple solution formed upon heating at 80 ˚C overnight. Addition of 10 ml Et_2O precipitated a red-purple solid (62 mg, 95%). Single crystals suitable for x-ray diffraction were grown by slow diffusion of Et_2O into a 3:1 CH_2Cl_2/DMSO solution. ^{1}H NMR (CD_3CN, 500 MHz, 20 ˚C): δ(ppm) 8.72 (dd, J = 5.2 Hz, J = 1.5 Hz, 1H), 8.44 (dd, J = 8.5 Hz, J = 1.4 Hz, 1H), 8.06 (br, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.71 (dd, J = 7.9 Hz, J = 0.9 Hz, 1H), 7.53-7.60 (m, 6H), 7.24 (m, 2H), 7.07 (br, 2H), 6.98 (br, 2H), 6.73 (d, J = 7.9 Hz, 1H), 5.32 (br, 2H), 4.83 (d, J = 15.6 Hz, 2H), 4.43 (d, J = 15.6 Hz, 2H), 0.22 (s, $^3J_{PtH}$ = 34.8 Hz, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 165.6, 155.5, 149.8, 149.4, 149.3, 149.1, 148.7, 141.0, 140.1, 138.4, 132.0, 130.8, 130.5, 130.2, 127.3, 124.8, 124.0, 122.8, 116.8, 115.0, 114.2, 112.1, 65.6, -10.9. ^{195}Pt NMR (CD_3CN, 107 MHz, 20 ˚C): δ(ppm) -3,038. ESI-MS: calc. for $C_{32}H_{28}ClN_6PdPt$ $(M\text{-}PF_6)^+$ 833.0747, found 833.0742. Elemental analysis for $C_{32}H_{28}ClF_6N_6PPdPt$: calc. C 39.28 H 2.88, found C 38.99 H 3.08.

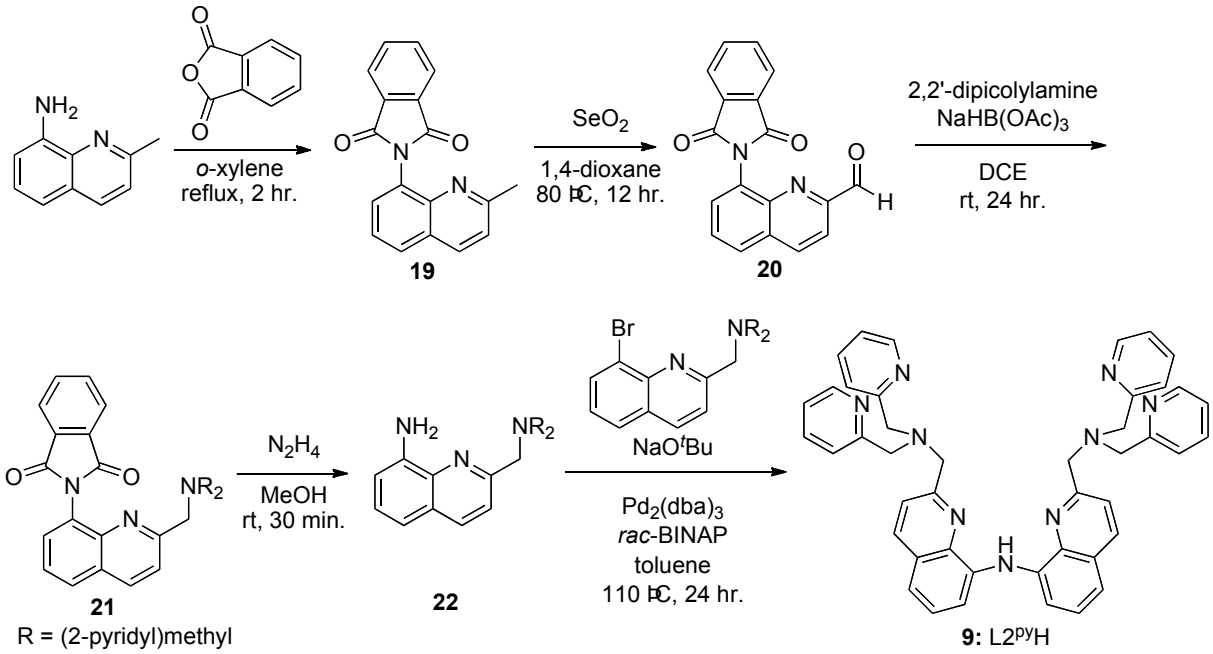
$[L2^{py}(PdBr)_3][BF_4]_2$ (16): A sealable NMR tube (J. Young) was charged with a solution of $[(CH_3CN)_4Pd][BF_4]_2$ (63.0 mg, 0.141 mmol) in 0.5 ml CD_3CN, a solution of $L2^{py}H$ (32.8 mg, 0.047 mmol) in 0.5 ml CD_3CN, and Et_3N (9.9 µl, 0.071 mmol). Upon heating to 50 ˚C for 8 hr., the solution turned deep red-purple. To this solution was added TBABr (45.7 mg, 0.142 mmol) under an inert atmosphere. The solution turned deep purple immediately. The purple product was purified by recrystallization from a CH_3CN solution layered with Et_2O and crushing and drying the crystals (65 mg, 97%). Crystals suitable for x-ray diffraction were grown by slow diffusion of Et_2O into a CH_3CN solution. The ^{1}H and ^{13}C NMR signals are broad owing to at least one fluxional process. Five sharper peaks of similar intensity in the ^{1}H NMR spectrum with δ(ppm) = 8.23 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H), 7.49 (dd, J = 7.8 Hz, J = 7.8 Hz, 2H), and 7.06 (J = 7.9 Hz, 2H) ppm are tentatively assigned as the quinoline peaks; the broad methylene resonances occur between d = 4.0 and 5.6 ppm (see Figure SI38). Elemental analysis for $C_{44}H_{38}B_2Br_3F_8N_9Pd_3$: calc. C 37.07 H 2.69, found C 37.05 H 3.02.

$[(MDPA)PdMe][PF_6]$ (17) (MDPA = *N*-methyl-2,2'-dipicolylamine): A 20 ml scintillation vial was charged with (COD)Pd(Me)Cl (809 mg, 3.05 mmol), a magnetic stirbar, and 10 ml CH_3CN. Addition of $TlPF_6$ (1.07 g, 3.05 mmol) afforded a white precipitate. A solution of MDPA (651 mg, 3.05 mmol) in 5 ml CH_3CN was added dropwise and the mixture was allowed to stir for 15 min. The mixture was then filtered and the TlCl was properly disposed. The filtrate was concentrated *in vacuo*, redissolved in a minimum volume of CH_2Cl_2, and precipated with Et_2O to give a pale yellow solid (1.14 g, 78%). ^{1}H NMR (CD_3CN, 500 MHz, 20 ˚C): δ(ppm) 8.40 (d (br), 2H), 8.04 (ddd, J = 9.4 Hz, J = 7.8 Hz, J = 1.6 Hz, 2H), 7.58 (d (br), 2H), 7.52 (m, 2H), 4.80 (d, J =15.5 Hz, 2H), 4.21 (d, J = 15.5 Hz, 2H), 2.58 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 165.5, 150.6, 141.0, 126.0, 125.4, 65.6, 45.2, 4.0. ESI-MS: calc. for $C_{14}H_{18}N_3Pd$ $(M\text{-}PF_6)^+$ 334.0541, found 334.0539. Elemental analysis for $C_{14}H_{18}F_6N_3PPd$: calc. C 35.05 H 3.78, found C 35.19 H 3.79.

$[(MDPA)PtMe][PF_6]$ (18) (MDPA = *N*-methyl-2,2'-dipicolylamine): A 20 ml scintillation vial was charged with (COD)Pt(Me)Cl (50.6 mg, 0.143 mmol), a magnetic stirbar, and 1 ml CH_3CN. Addition of $TlPF_6$ (49.9 mg, 0.143 mmol) afforded a white precipitate. A solution of MDPA (30.5 mg, 0.143 mmol) in 1 ml CH_3CN was added dropwise and the mixture was allowed to stir overnight. The mixture was then filtered and the TlCl was properly disposed. The filtrate was concentrated *in vacuo*, redissolved in a minimum volume of CH_2Cl_2, and precipated with Et_2O to

give a pale yellow solid (62 mg, 76%). ^{1}H NMR (CD_3CN, 500 MHz, 20 ˚C): δ(ppm) 8.60 (d (br), J = 5.8 Hz, $^3J_{PtH}$ = 25.2 Hz, 2H), 8.10, (ddd, J = 7.8 Hz, J = 7.8 Hz, J = 1.5 Hz, 2H), 7.58 (d (br), 7.8 Hz, 2H), 7.47 (m, 2H), 4.74 (d, J = 15.4 Hz, 2H), 4.41 (d, J = 15.4 Hz, $^3J_{PtH}$ = 11.0 Hz, 2H), 2.73 (s, $^3J_{PtH}$ = 6.5 Hz, 3H), 0.83 (s, $^3J_{PtH}$ = 32.8 Hz, 3H). ^{13}C NMR (CD_3CN, 125 MHz, 20 ˚C): δ(ppm) 166.8, 150.2, 140.6, 126.4, 125.5, 66.8, 46.4. ESI-MS: calc. for $C_{14}H_{18}N_3Pt$ (M-PF_6)$^+$ 423.1139, found 423.1154. Elemental analysis for $C_{14}H_{18}F_6N_3PPt$: calc. C 29.59 H 3.19, found C 29.57 H 3.15.

Bis(2-((bis(pyridin-2-ylmethyl)amino)methyl)quinolin-8-yl)amine (9, L2^{py}H): This ligand was prepared similarly to **8** beginning with 8-amino-2-methylquinoline.



2-(2-methylquinolin-8-yl)isoindoline-1,3-dione (19): A 250 ml flask equipped with a reflux condenser and charged with phthalic anhydride (5.53 g, 37.3 mmol) and 8-amino-2-methylquinoline (5.85 g, 37.0 mmol) was heated to reflux for 2 hr. The brown solution was cooled to room temperature. The off-white microcrystals thus generated were isolated by filtration, washed with cold toluene, and used without further purification (9.01 g, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 8.09 (d, J = 8.4 Hz, 1H), 8.02 (m, 2H), 7.92 (dd, J = 7.3 Hz, J = 1.5 Hz, 1H), 7.83 (m, 2H), 7.71 (dd, J = 7.2 Hz, J = 1.4 Hz, 1H), 7.59 (dd, J = 7.7 Hz, J = 7.7 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 168.3, 160.1, 143.9, 136.3, 134.3, 132.7, 130.3, 129.5, 127.7, 125.4, 124.0, 123.1, 25.8. ESI-MS: calc. for $C_{18}H_{13}N_2O_2$ (M+H)$^+$ 289.0972, found 289.0982. Elemental analysis for $C_{18}H_{12}N_2O_2$: calc. C 74.99 H 4.20, found C 74.91 H 4.31.

8-(1,3-dioxoisoindolin-2-yl)quinoline-2-carbaldehyde (**20**): A 200 ml Schlenk tube charged with SeO_2 (3.47 g, 31.3 mmol) and a magnetic stir bar was purged with N_2 for 5 min. 1,4-dioxane (180 ml) was added and the mixture was heated to 80 ˚C before adding **19** (9.01 g, 31.3 mmol) under a stream of N_2. The dark mixture was maintained at 80 ˚C for 12 hr., cooled to

room temperature, and filtered through alumina eluting with CH_2Cl_2. Solvent was removed on a rotary evaporator to give a tan solid (9.35 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 9.96 (d, J = 0.8 Hz, 1H), 8.40 (dd, J = 8.5 Hz, J = 0.8 Hz, 1H), 8.03-8.08 (m, 4H), 7.82-7.88 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 193.8, 168.0, 153.8, 144.2, 138.0, 134.6, 132.5, 131.5, 131.2, 129.7, 129.0, 124.2, 124.0, 118.3. ESI-MS: calc. for $C_{18}H_{11}N_2O_3$ $(M+H)^+$ 303.0764, found 303.0770. Elemental analysis for $C_{18}H_{10}N_2O_3$: calc. C 71.52 H 3.33, found C 71.14 H 3.68.

2-(2-((bis(pyridin-2-ylmethyl)amino)methyl)quinolin-8-yl)isoindoline-1,3-dione (**21**): A 250 ml flask was charged with a magnetic stir bar, 100 ml 1,2-dichloroethane, **20** (4.43 g, 14.7 mmol), and 2,2'-dipicolylamine (2.89 g, 14.5 mmol). The solution was allowed to stir for 30 min. before $NaHB(OAc)_3$ (3.42 g, 16.1 mmol) was added in one portion. The mixture was stirred at room temperature for 24 hr. and quenched with sat. aqueous $NaHCO_3$ (50 ml). The aqueous and organic phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 ml). The combined organics were dried over Na_2SO_4 and condensed on a rotary evaporator to give a dark yellow oil. Purification by flash chromatography (silica gel, 2:2:96 to 6:2:92 CH_3OH:Et_3N:CH_2Cl_2 gradient) have the product as a tan solid (5.41 g, 76%). The product may be recrystallized by slow evaporation from a CH_2Cl_2/hexanes solution to give yellow needles. ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 8.48 (m, 2H), 8.17 (d, J = 8.4 Hz, 1H), 7.99 (m, 2H), 7.93 (dd, J = 8.3 Hz, J = 1.5 Hz, 1H), 7.83 (m, 2H), 7.72 (dd, J = 7.2 Hz, J = 1.4 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.63 (dd, J = 8.2 Hz, J = 7.2 Hz, 1H), 7.46-7.51 (m, 4H), 7.08 (m, 2H), 3.82 (two overlapping singlets, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 168.2, 161.0, 159.4, 149.2, 143.8, 136.6, 136.4, 134.4, 132.7, 130.3, 129.8, 129.5, 128.5, 125.9, 124.0, 123.4, 122.2, 122.1, 60.4, 60.2. ESI-MS: calc. for $C_{30}H_{24}N_5O_2$ $(M+H)^+$ 486.1925, found 486.1916. Elemental analysis for $C_{30}H_{23}N_5O_2$: calc. C 74.21 H 4.77, found C 73.21 H 4.99.

2-((bis(pyridin-2-ylmethyl)amino)methyl)quinolin-8-amine (**22**): A 50 ml flask was charged with **21** (209 mg, 0.43 mmol) and 5 ml methanol. To this mixture was added 1 ml N_2H_4•H_2O in one portion. The resulting yellow solution was allowed to sit at room temperature for 30 min. Then 50 ml dichloromethane was added followed by 1 M NaOH until the pH reached >12. The phases were separated and the aqueous phase was washed with dichloromethane (3 x 30 ml). The aqueous phase was properly disposed. The combined organics were dried over Na_2SO_4 and condensed on a rotary evaporator to give pure product as a bright yellow oil (153 mg, 100%). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 8.54 (m, 2H), 8.02 (d, J = 8.5 Hz, 1H), 7.60-7.68 (m, 5H), 7.28 (dd, J = 8.0 Hz, J = 7.4 Hz, 1H), 7.10-7.15 (m, 3H), 6.90 (dd, J = 7.4 Hz, J = 1.2 Hz, 1H), 5.01 (s (br), 2H), 4.00 (s, 2H), 3.93 (s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 159.7, 157.0, 149.3, 144.0, 137.7, 136.6, 136.5, 127.9, 127.1, 123.1, 122.2, 121.4, 115.9, 110.2, 60.7, 60.5. ESI-MS: calc. for $C_{22}H_{22}N_5$ $(M+H)^+$ 356.1870, found 356.1876. Since the product is somewhat hygroscopic and the phthalimide deprotection is quantitative by NMR spectroscopy, the product is typically stored as phthalimide-protected **22** and used in the cross-coupling step immediately after deprotection.

Bis(2-((bis(pyridin-2-ylmethyl)amino)methyl)quinolin-8-yl)amine (9, L2^{py}H): A 100 ml Schlenk tube charged with a magnetic stir bar, $Pd_2(dba)_3$ (7.9 mg, 0.009 mmol), and *rac*-BINAP (10.8 mg, 0.017 mmol) was evacuated and back-filled with N_2 three times. Toluene (2 ml) was added and the solution was allowed to stir for 5 min. before **22** (153 mg, 0.43 mmol), **5** (182 mg,

0.43 mmol), NaO^{t}Bu (50.1 mg, 0.52 mmol), and 3 ml toluene were added. The solution was stirred at 110 ˚C for 24 hr., cooled to room temperature, filtered through Celite, and condensed on a rotary evaporator. The resulting brown oil was purified by flash chromatography (silica gel, 4:2:94 CH_3OH:Et_3N:CH_2Cl_2) to give 287 g (96%) of **9** as a yellow solid. In spite of a slight (~1%) and persistent impurity revealed by ^{1}H NMR, samples of **9** were sufficiently pure for further reactions to generate analytically pure compounds (such as **16**). ^{1}H NMR ($CDCl_3$, 500 MHz, 20 ˚C): δ(ppm) 10.61 (s, 1H), 8.48 (m, 4H), 8.08 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 7.7 Hz, J = 1.1 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.59 (d (br), J = 7.9 Hz, 4H), 7.51 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 1.8 Hz, 4H), 7.43 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H), 7.25 (dd, J = 8.2 Hz, J = 0.9 Hz, 2H), 7.05 (ddd, J = 7.4 Hz, J = 4.9 Hz, J = 1.2 Hz, 4H), 4.04 (s, 4H), 3.90 (s, 8H). ^{13}C NMR ($CDCl_3$, 125 MHz, 20 ˚C): δ(ppm) 159.5, 157.5, 149.1, 139.2, 138.7, 136.6, 136.4, 128.0, 126.7, 123.2, 122.0, 121.6, 117.5, 110.1, 60.9, 60.9. ESI-MS: calc. for $C_{44}H_{40}N_9$ $(M+H)^+$ 694.3401, found 694.3407.

Computational Details

DFT calculations were performed using the Gaussian 03 software package,[3] the B3LYP functional, the LANL2DZ basis set for Pt, Pd, and Cl atoms, and the 6-31+G* basis set for all other atoms. Atom coordinates were taken from the solid-state structures as determined by x-ray crystallography. Molecular orbital contours are shown at the 0.04 isovalue level.

[3] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004

UV/vis spectroscopy

Figure S1. Comparison of [L1^{py}Pd(Cl)(PdMe)][PF_6] (**13**), (BQA)PdCl, and [(MDPA)PdMe][PF_6] (**17**)

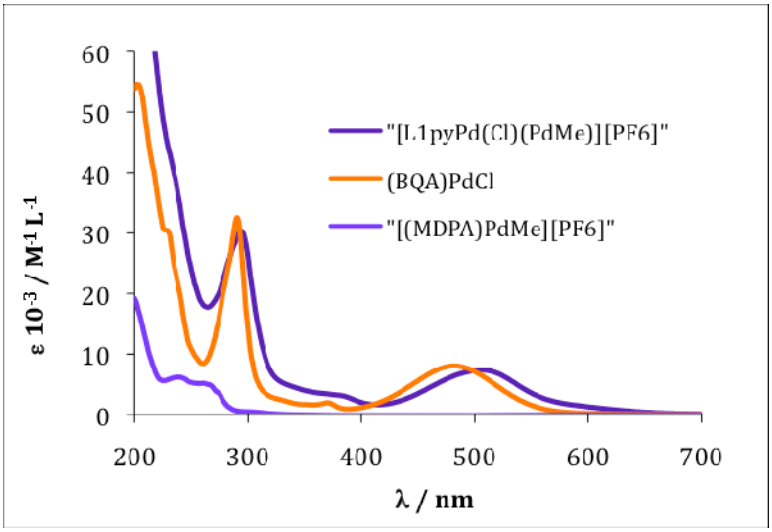
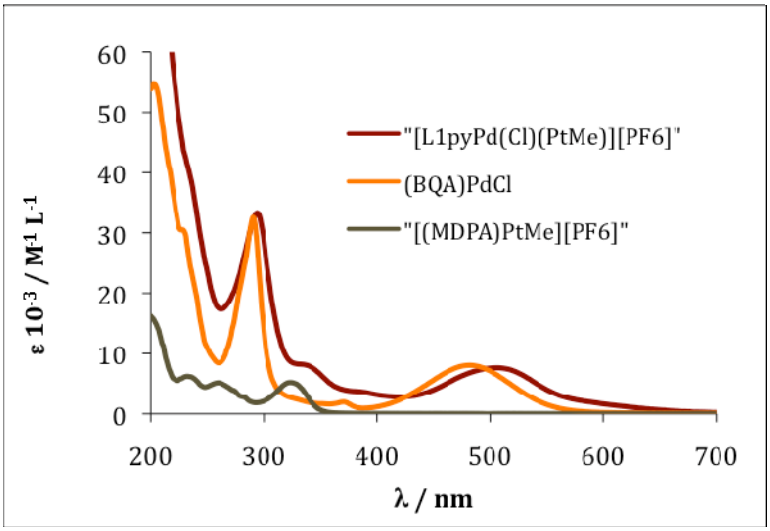


Figure S2. Comparison of [L1^{py}Pd(Cl)(PdMe)][PF_6] (**15**), (BQA)PdCl, and [(MDPA)PtMe][PF_6] (**18**)



Variable Temperature NMR studies of $[L1^{im}Pd]Cl$ (**11**) and $[L1^{py}Pd(Cl)(PdMe)][PF_6]$ (**13**)

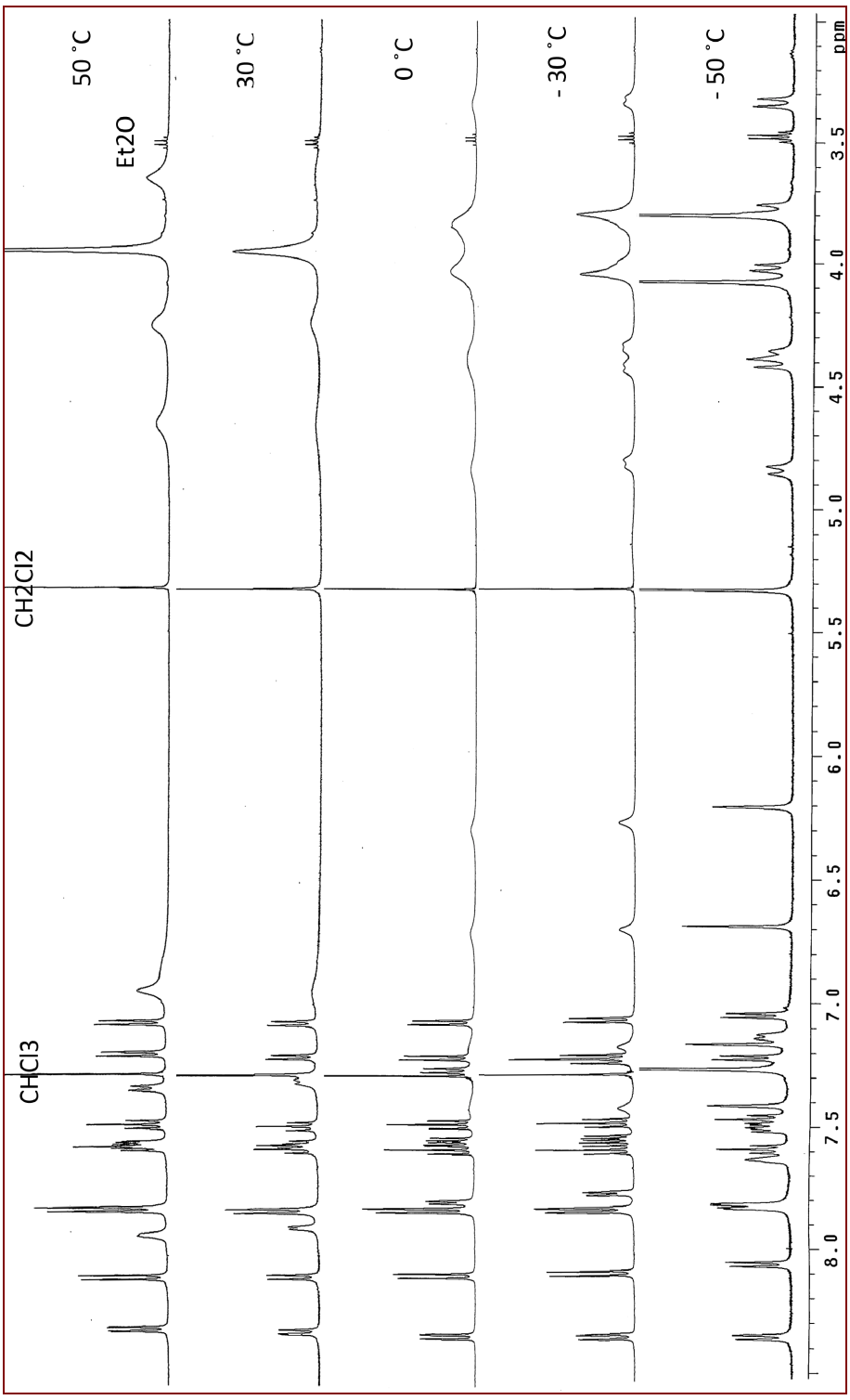


Figure S3. ^{1}H VT-NMR of $[L1^{im}Pd]Cl$ (**11**)

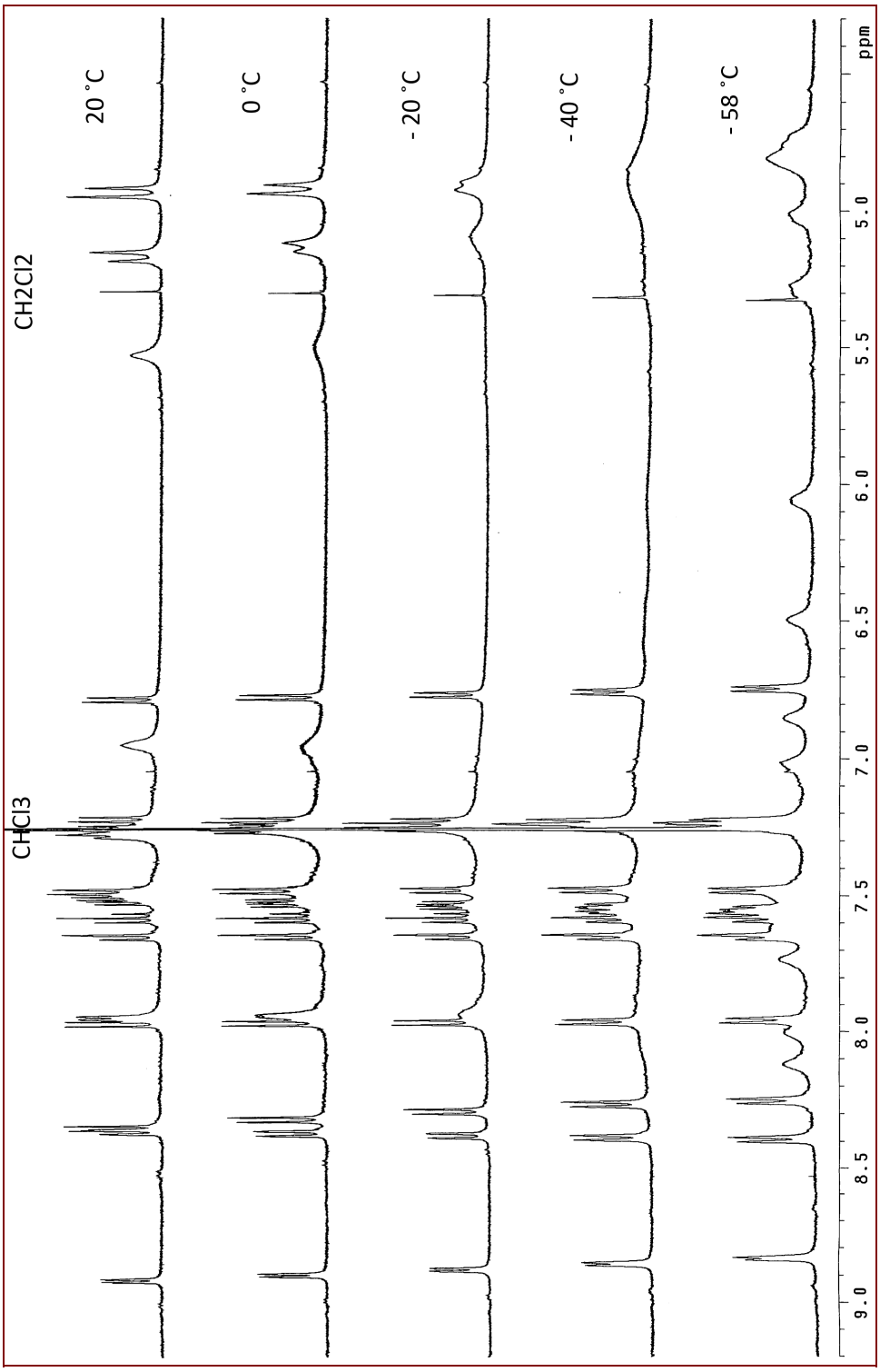


Figure S4. ^{1}H VT-NMR of [L1^{py}Pd(Cl)(PdMe)][PF_6] (**13**)

X-ray Crystallography

Low-temperature x-ray diffraction data were collected on a Siemens or Bruker Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo or Cu Kα radiation (λ = 0.71073 or 1.54178 Å, respectively), performing φ- and ω-scans. The structures were solved by direct or Patterson methods using SHELXS[4] and refined against $F2$ on all data by full- matrix least squares with SHELXL-97.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except the amine hydrogen in **12**) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Each asymmetric unit of **13** contains 1.5 molecules of DMSO. The half molecule of DMSO lies on a two-fold rotational axis and is therefore disordered over two positions in the lattice. The full molecule of DMSO is best modeled as a disorder with the following features: the carbon atoms (C100 and C101) are not disordered, the sulfur atoms (S1, S2, and S3) are disordered over three positions, and the oxygen atoms (O100 and O101) are disordered over two positions. Thus, the disorder has three components (each of which contains C100 and C101): S2 bound to O101, S3 bound to O101, and S1 bound to O100. The occupancies of each sulfur and oxygen atom were assigned free variables and refined while restraining the sums of the occupancies of the sulfur atoms and of the oxygen atoms each to be unity. As such, a representation of *all six* components from the 1.5 molecules of DMSO shows close contact between certain atoms, particularly O100 and O200; however, it is reasonable to assume that asymmetric units containing a component with O100 will not contain a component with O200 and vice versa.

[4] Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467-473.
[5] Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Crystallographic Data for **10**

Figure S5. Thermal ellipsoid plot of **10** at the 40% probability level. Hydrogen atoms have been omitted for clarity

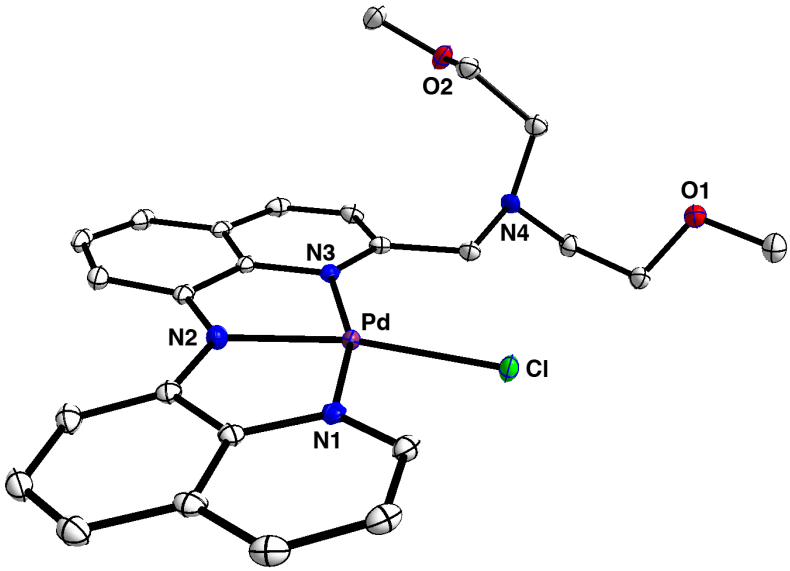


Table S1. Crystal data and structure refinement for **10**.

Identification code	**10**	
Empirical formula	C25 H27 Cl N4 O2 Pd	
Formula weight	557.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 5.1225(2) Å	α= 90°.
	b = 17.5023(7) Å	β= 90.583(2)°.
	c = 24.8571(10) Å	γ = 90°.
Volume	2228.46(15) $Å^3$	
Z	4	
Density (calculated)	1.661 Mg/m^3	
Absorption coefficient	8.078 mm^{-1}	
F(000)	1136	
Crystal size	0.25 x 0.15 x 0.12 mm^3	
Theta range for data collection	3.09 to 68.91°.	
Index ranges	-4<=h<=5, -21<=k<=21, -30<=l<=30	
Reflections collected	42087	
Independent reflections	3997 [R(int) = 0.0226]	
Completeness to theta = 68.91°	96.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4440 and 0.2373	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3997 / 0 / 300	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0553	
R indices (all data)	R1 = 0.0216, wR2 = 0.0553	
Largest diff. peak and hole	0.485 and -0.463 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **10**.

Pd(1)-N(2)	1.9704(17)
Pd(1)-N(1)	2.0194(17)
Pd(1)-N(3)	2.0858(17)
Pd(1)-Cl(1)	2.3510(5)
N(1)-C(1)	1.327(3)
N(1)-C(9)	1.383(3)
N(3)-C(18)	1.339(3)
N(3)-C(10)	1.396(3)
C(18)-C(17)	1.417(3)
C(18)-C(19)	1.512(3)
N(2)-C(11)	1.377(3)
N(2)-C(8)	1.380(3)
C(8)-C(7)	1.394(3)
C(8)-C(9)	1.435(3)
C(1)-C(2)	1.406(3)
C(1)-H(1)	0.9500
C(11)-C(12)	1.397(3)
C(11)-C(10)	1.430(3)
C(19)-N(4)	1.464(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(9)-C(4)	1.416(3)
C(10)-C(15)	1.414(3)
C(3)-C(2)	1.367(3)
C(3)-C(4)	1.413(3)
C(3)-H(3)	0.9500
C(6)-C(5)	1.376(3)
C(6)-C(7)	1.405(3)
C(6)-H(6)	0.9500
C(2)-H(2)	0.9500
C(16)-C(17)	1.359(3)
C(16)-C(15)	1.414(3)
C(16)-H(16)	0.9500
C(4)-C(5)	1.417(3)

C(13)-C(14)	1.366(3)
C(13)-C(12)	1.407(3)
C(13)-H(13)	0.9500
C(17)-H(17)	0.9500
C(15)-C(14)	1.415(3)
C(14)-H(14)	0.9500
C(12)-H(12)	0.9500
C(7)-H(7)	0.9500
O(1)-C(25)	1.416(3)
O(1)-C(24)	1.426(3)
O(2)-C(21)	1.417(3)
O(2)-C(22)	1.423(3)
N(4)-C(23)	1.464(3)
N(4)-C(20)	1.467(3)
C(20)-C(21)	1.525(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(24)-C(23)	1.513(3)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(5)-H(5)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

N(2)-Pd(1)-N(1)	81.84(7)
N(2)-Pd(1)-N(3)	81.90(7)
N(1)-Pd(1)-N(3)	163.62(7)
N(2)-Pd(1)-Cl(1)	170.13(5)

N(1)-Pd(1)-Cl(1)	90.42(5)
N(3)-Pd(1)-Cl(1)	105.96(5)
C(1)-N(1)-C(9)	119.35(17)
C(1)-N(1)-Pd(1)	128.81(14)
C(9)-N(1)-Pd(1)	111.84(13)
C(18)-N(3)-C(10)	118.59(17)
C(18)-N(3)-Pd(1)	131.76(14)
C(10)-N(3)-Pd(1)	109.65(13)
N(3)-C(18)-C(17)	121.60(19)
N(3)-C(18)-C(19)	119.03(18)
C(17)-C(18)-C(19)	119.36(18)
C(11)-N(2)-C(8)	128.94(17)
C(11)-N(2)-Pd(1)	115.77(13)
C(8)-N(2)-Pd(1)	114.97(14)
N(2)-C(8)-C(7)	129.5(2)
N(2)-C(8)-C(9)	113.78(18)
C(7)-C(8)-C(9)	116.74(19)
N(1)-C(1)-C(2)	122.23(19)
N(1)-C(1)-H(1)	118.9
C(2)-C(1)-H(1)	118.9
N(2)-C(11)-C(12)	127.51(19)
N(2)-C(11)-C(10)	114.79(17)
C(12)-C(11)-C(10)	117.64(19)
N(4)-C(19)-C(18)	113.72(17)
N(4)-C(19)-H(19A)	108.8
C(18)-C(19)-H(19A)	108.8
N(4)-C(19)-H(19B)	108.8
C(18)-C(19)-H(19B)	108.8
H(19A)-C(19)-H(19B)	107.7
N(1)-C(9)-C(4)	121.11(18)
N(1)-C(9)-C(8)	116.68(18)
C(4)-C(9)-C(8)	122.20(19)
N(3)-C(10)-C(15)	121.79(19)
N(3)-C(10)-C(11)	117.83(18)
C(15)-C(10)-C(11)	120.37(18)
C(2)-C(3)-C(4)	120.0(2)

C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(5)-C(6)-C(7)	122.5(2)
C(5)-C(6)-H(6)	118.8
C(7)-C(6)-H(6)	118.8
C(3)-C(2)-C(1)	119.5(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(17)-C(16)-C(15)	120.1(2)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(3)-C(4)-C(9)	117.67(19)
C(3)-C(4)-C(5)	123.8(2)
C(9)-C(4)-C(5)	118.6(2)
C(14)-C(13)-C(12)	121.6(2)
C(14)-C(13)-H(13)	119.2
C(12)-C(13)-H(13)	119.2
C(16)-C(17)-C(18)	120.3(2)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(16)-C(15)-C(10)	117.57(19)
C(16)-C(15)-C(14)	122.5(2)
C(10)-C(15)-C(14)	119.9(2)
C(13)-C(14)-C(15)	119.2(2)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(11)-C(12)-C(13)	121.1(2)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(8)-C(7)-C(6)	120.8(2)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(25)-O(1)-C(24)	112.40(18)
C(21)-O(2)-C(22)	110.49(16)
C(23)-N(4)-C(19)	112.58(17)
C(23)-N(4)-C(20)	114.40(17)

C(19)-N(4)-C(20)	112.52(16)
N(4)-C(20)-C(21)	117.16(18)
N(4)-C(20)-H(20A)	108.0
C(21)-C(20)-H(20A)	108.0
N(4)-C(20)-H(20B)	108.0
C(21)-C(20)-H(20B)	108.0
H(20A)-C(20)-H(20B)	107.3
O(2)-C(21)-C(20)	110.17(17)
O(2)-C(21)-H(21A)	109.6
C(20)-C(21)-H(21A)	109.6
O(2)-C(21)-H(21B)	109.6
C(20)-C(21)-H(21B)	109.6
H(21A)-C(21)-H(21B)	108.1
O(1)-C(24)-C(23)	109.25(18)
O(1)-C(24)-H(24A)	109.8
C(23)-C(24)-H(24A)	109.8
O(1)-C(24)-H(24B)	109.8
C(23)-C(24)-H(24B)	109.8
H(24A)-C(24)-H(24B)	108.3
N(4)-C(23)-C(24)	112.90(18)
N(4)-C(23)-H(23A)	109.0
C(24)-C(23)-H(23A)	109.0
N(4)-C(23)-H(23B)	109.0
C(24)-C(23)-H(23B)	109.0
H(23A)-C(23)-H(23B)	107.8
C(6)-C(5)-C(4)	119.0(2)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5
O(1)-C(25)-H(25A)	109.5
O(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(2)-C(22)-H(22A)	109.5
O(2)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5
O(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Figure S6. Thermal probability ellipsoids of **11** at the 40% probability level. Hydrogen atoms, solvent molecules, and counteranions have been omitted for clarity.

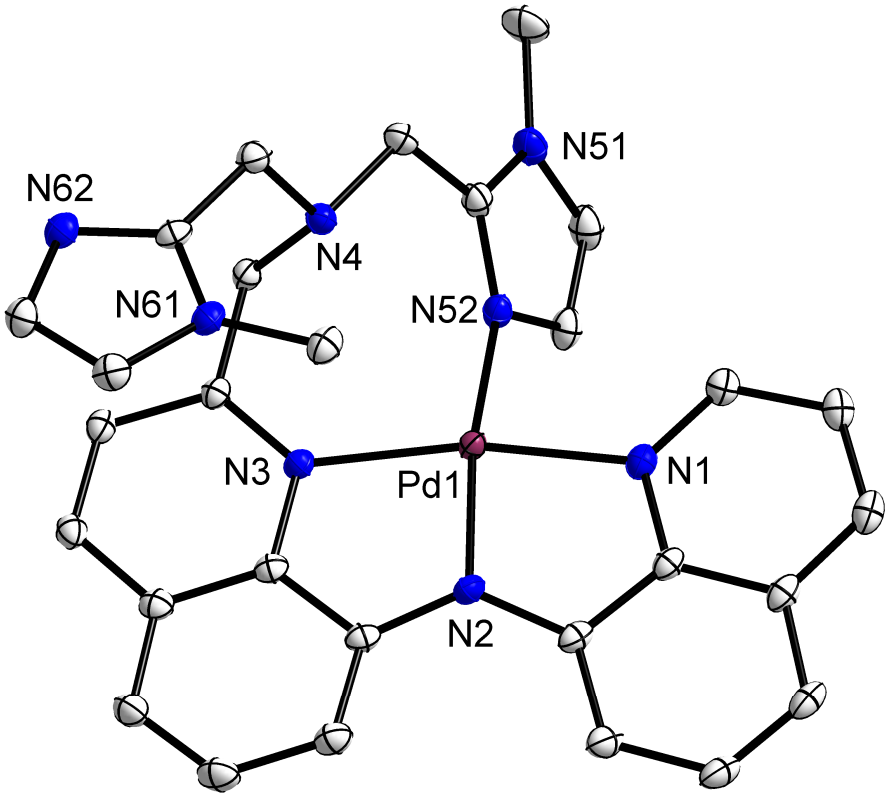


Table S3. Crystal data and structure refinement for **11 • $2H_2O$ • $2CHCl_3$**.

Identification code	**11 • $2H_2O$ • $2CHCl_3$**	
Empirical formula	C31 H33 Cl7 N8 O2 Pd	
Formula weight	904.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.3314(7) Å	α= 84.743(2)°.
	b = 13.8105(13) Å	β= 88.483(2)°.
	c = 18.3307(18) Å	γ = 82.262(2)°.
Volume	1831.2(3) $Å^3$	
Z	2	
Density (calculated)	1.640 Mg/m^3	
Absorption coefficient	1.060 mm^{-1}	
F(000)	912	
Crystal size	0.28 x 0.20 x 0.05 mm^3	
Theta range for data collection	1.12 to 29.13°.	
Index ranges	-10<=h<=10, -18<=k<=18, -25<=l<=25	
Reflections collected	47572	
Independent reflections	9810 [R(int) = 0.0404]	
Completeness to theta = 29.13°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9489 and 0.7557	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9810 / 490 / 513	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0825	
R indices (all data)	R1 = 0.0414, wR2 = 0.0873	
Largest diff. peak and hole	1.379 and -0.712 $e.Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for **11**.

Pd(1)-N(2)	1.9646(18)
Pd(1)-N(1)	2.0105(19)
Pd(1)-N(3)	2.0511(18)
Pd(1)-N(52)	2.0694(19)
N(2)-C(11)	1.381(3)
N(2)-C(8)	1.387(3)
N(61)-C(212)	1.362(3)
N(61)-C(214)	1.371(3)
N(61)-C(213)	1.458(3)
N(4)-C(201)	1.460(3)
N(4)-C(211)	1.476(3)
N(4)-C(19)	1.477(3)
N(52)-C(202)	1.333(3)
N(52)-C(205)	1.391(3)
N(1)-C(1)	1.327(3)
N(1)-C(9)	1.377(3)
N(3)-C(18)	1.335(3)
N(3)-C(10)	1.386(3)
C(17)-C(16)	1.368(3)
C(17)-C(18)	1.407(3)
C(17)-H(17)	0.9500
C(212)-N(62)	1.323(3)
C(212)-C(211)	1.495(3)
N(51)-C(202)	1.348(3)
N(51)-C(204)	1.373(3)
N(51)-C(203)	1.462(3)
C(202)-C(201)	1.496(3)
N(62)-C(215)	1.380(3)
C(16)-C(15)	1.413(3)
C(16)-H(16)	0.9500
C(18)-C(19)	1.506(3)
C(211)-H(21A)	0.9900
C(211)-H(21B)	0.9900
C(3)-C(2)	1.371(3)

C(3)-C(4)	1.412(3)
C(3)-H(3)	0.9500
C(4)-C(9)	1.417(3)
C(4)-C(5)	1.418(3)
C(14)-C(13)	1.367(4)
C(14)-C(15)	1.419(3)
C(14)-H(14)	0.9500
C(9)-C(8)	1.433(3)
C(214)-C(215)	1.361(3)
C(214)-H(214)	0.9500
C(213)-H(21C)	0.9800
C(213)-H(21D)	0.9800
C(213)-H(21E)	0.9800
C(1)-C(2)	1.402(3)
C(1)-H(1)	0.9500
C(15)-C(10)	1.413(3)
C(11)-C(12)	1.395(3)
C(11)-C(10)	1.437(3)
C(2)-H(2)	0.9500
C(7)-C(8)	1.396(3)
C(7)-C(6)	1.411(3)
C(7)-H(7)	0.9500
C(6)-C(5)	1.366(4)
C(6)-H(6)	0.9500
C(215)-H(215)	0.9500
C(5)-H(5)	0.9500
C(204)-C(205)	1.349(3)
C(204)-H(204)	0.9500
C(205)-H(205)	0.9500
C(12)-C(13)	1.406(4)
C(12)-H(12)	0.9500
C(201)-H(20A)	0.9900
C(201)-H(20B)	0.9900
C(13)-H(13)	0.9500
C(203)-H(20C)	0.9800
C(203)-H(20D)	0.9800

C(203)-H(20E)	0.9800
Cl(30)-C(301)	1.765(2)
Cl(32)-C(301)	1.761(3)
Cl(31)-C(301)	1.761(3)
Cl(7A)-C(401)	1.691(5)
Cl(8A)-C(401)	1.713(4)
Cl(9A)-C(401)	1.836(4)
Cl(8B)-C(401)	1.803(7)
Cl(7B)-C(401)	1.787(6)
Cl(9B)-C(401)	1.698(6)
Cl(8C)-C(401)	1.862(11)
Cl(7C)-C(401)	1.577(11)
Cl(9C)-C(401)	1.663(8)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(301)-H(301)	1.0000
C(401)-H(401)	1.0000
O(1)-H(101)	0.834(18)
O(1)-H(102)	0.812(18)
O(2)-H(201)	0.839(18)
O(2)-H(202)	0.804(18)

N(2)-Pd(1)-N(1)	82.67(8)
N(2)-Pd(1)-N(3)	81.90(8)
N(1)-Pd(1)-N(3)	164.28(7)
N(2)-Pd(1)-N(52)	168.17(8)
N(1)-Pd(1)-N(52)	90.79(8)
N(3)-Pd(1)-N(52)	104.93(7)
C(11)-N(2)-C(8)	129.18(19)
C(11)-N(2)-Pd(1)	115.73(14)
C(8)-N(2)-Pd(1)	114.20(15)
C(212)-N(61)-C(214)	107.0(2)
C(212)-N(61)-C(213)	126.7(2)
C(214)-N(61)-C(213)	126.3(2)
C(201)-N(4)-C(211)	108.41(18)
C(201)-N(4)-C(19)	112.02(18)

C(211)-N(4)-C(19)	111.77(18)
C(202)-N(52)-C(205)	105.97(19)
C(202)-N(52)-Pd(1)	134.34(16)
C(205)-N(52)-Pd(1)	118.75(16)
C(1)-N(1)-C(9)	120.1(2)
C(1)-N(1)-Pd(1)	128.39(16)
C(9)-N(1)-Pd(1)	111.46(15)
C(18)-N(3)-C(10)	119.22(19)
C(18)-N(3)-Pd(1)	130.07(15)
C(10)-N(3)-Pd(1)	110.71(14)
C(16)-C(17)-C(18)	120.1(2)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
N(62)-C(212)-N(61)	111.5(2)
N(62)-C(212)-C(211)	124.8(2)
N(61)-C(212)-C(211)	123.7(2)
C(202)-N(51)-C(204)	107.9(2)
C(202)-N(51)-C(203)	126.0(2)
C(204)-N(51)-C(203)	126.1(2)
N(52)-C(202)-N(51)	110.3(2)
N(52)-C(202)-C(201)	126.6(2)
N(51)-C(202)-C(201)	123.0(2)
C(212)-N(62)-C(215)	105.1(2)
C(17)-C(16)-C(15)	119.8(2)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
N(3)-C(18)-C(17)	121.4(2)
N(3)-C(18)-C(19)	118.59(19)
C(17)-C(18)-C(19)	119.96(19)
N(4)-C(211)-C(212)	112.12(19)
N(4)-C(211)-H(21A)	109.2
C(212)-C(211)-H(21A)	109.2
N(4)-C(211)-H(21B)	109.2
C(212)-C(211)-H(21B)	109.2
H(21A)-C(211)-H(21B)	107.9
C(2)-C(3)-C(4)	119.9(2)

C(2)-C(3)-H(3)	120.0
C(4)-C(3)-H(3)	120.0
C(3)-C(4)-C(9)	118.1(2)
C(3)-C(4)-C(5)	123.3(2)
C(9)-C(4)-C(5)	118.6(2)
C(13)-C(14)-C(15)	118.9(2)
C(13)-C(14)-H(14)	120.6
C(15)-C(14)-H(14)	120.6
N(1)-C(9)-C(4)	120.4(2)
N(1)-C(9)-C(8)	117.20(19)
C(4)-C(9)-C(8)	122.4(2)
C(215)-C(214)-N(61)	106.0(2)
C(215)-C(214)-H(214)	127.0
N(61)-C(214)-H(214)	127.0
N(61)-C(213)-H(21C)	109.5
N(61)-C(213)-H(21D)	109.5
H(21C)-C(213)-H(21D)	109.5
N(61)-C(213)-H(21E)	109.5
H(21C)-C(213)-H(21E)	109.5
H(21D)-C(213)-H(21E)	109.5
N(1)-C(1)-C(2)	122.1(2)
N(1)-C(1)-H(1)	118.9
C(2)-C(1)-H(1)	118.9
C(16)-C(15)-C(10)	117.6(2)
C(16)-C(15)-C(14)	122.8(2)
C(10)-C(15)-C(14)	119.6(2)
N(2)-C(11)-C(12)	129.3(2)
N(2)-C(11)-C(10)	113.82(19)
C(12)-C(11)-C(10)	116.9(2)
N(3)-C(10)-C(15)	121.4(2)
N(3)-C(10)-C(11)	117.4(2)
C(15)-C(10)-C(11)	121.2(2)
C(3)-C(2)-C(1)	119.3(2)
C(3)-C(2)-H(2)	120.4
C(1)-C(2)-H(2)	120.4
C(8)-C(7)-C(6)	120.9(2)

C(8)-C(7)-H(7)	119.5
C(6)-C(7)-H(7)	119.5
C(5)-C(6)-C(7)	122.5(2)
C(5)-C(6)-H(6)	118.8
C(7)-C(6)-H(6)	118.8
C(214)-C(215)-N(62)	110.3(2)
C(214)-C(215)-H(215)	124.8
N(62)-C(215)-H(215)	124.8
C(6)-C(5)-C(4)	119.1(2)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5
C(205)-C(204)-N(51)	106.7(2)
C(205)-C(204)-H(204)	126.6
N(51)-C(204)-H(204)	126.6
C(204)-C(205)-N(52)	109.1(2)
C(204)-C(205)-H(205)	125.4
N(52)-C(205)-H(205)	125.4
C(11)-C(12)-C(13)	121.4(2)
C(11)-C(12)-H(12)	119.3
C(13)-C(12)-H(12)	119.3
N(4)-C(201)-C(202)	110.51(19)
N(4)-C(201)-H(20A)	109.5
C(202)-C(201)-H(20A)	109.5
N(4)-C(201)-H(20B)	109.5
C(202)-C(201)-H(20B)	109.5
H(20A)-C(201)-H(20B)	108.1
C(14)-C(13)-C(12)	122.0(2)
C(14)-C(13)-H(13)	119.0
C(12)-C(13)-H(13)	119.0
N(2)-C(8)-C(7)	129.7(2)
N(2)-C(8)-C(9)	113.86(19)
C(7)-C(8)-C(9)	116.4(2)
N(51)-C(203)-H(20C)	109.5
N(51)-C(203)-H(20D)	109.5
H(20C)-C(203)-H(20D)	109.5
N(51)-C(203)-H(20E)	109.5

H(20C)-C(203)-H(20E)	109.5
H(20D)-C(203)-H(20E)	109.5
N(4)-C(19)-C(18)	110.74(17)
N(4)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19A)	109.5
N(4)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	108.1
Cl(31)-C(301)-Cl(32)	110.25(14)
Cl(31)-C(301)-Cl(30)	110.07(14)
Cl(32)-C(301)-Cl(30)	110.34(13)
Cl(31)-C(301)-H(301)	108.7
Cl(32)-C(301)-H(301)	108.7
Cl(30)-C(301)-H(301)	108.7
Cl(7C)-C(401)-Cl(9C)	121.6(10)
Cl(7C)-C(401)-Cl(7A)	44.7(12)
Cl(9C)-C(401)-Cl(7A)	138.9(5)
Cl(7C)-C(401)-Cl(9B)	80.3(11)
Cl(9C)-C(401)-Cl(9B)	43.9(8)
Cl(7A)-C(401)-Cl(9B)	116.8(3)
Cl(7C)-C(401)-Cl(8A)	136.6(6)
Cl(9C)-C(401)-Cl(8A)	39.9(7)
Cl(7A)-C(401)-Cl(8A)	116.1(3)
Cl(9B)-C(401)-Cl(8A)	80.2(5)
Cl(7C)-C(401)-Cl(7B)	29.1(11)
Cl(9C)-C(401)-Cl(7B)	142.4(7)
Cl(7A)-C(401)-Cl(7B)	17.8(2)
Cl(9B)-C(401)-Cl(7B)	107.6(3)
Cl(8A)-C(401)-Cl(7B)	131.8(3)
Cl(7C)-C(401)-Cl(8B)	123.4(9)
Cl(9C)-C(401)-Cl(8B)	77.7(7)
Cl(7A)-C(401)-Cl(8B)	84.4(4)
Cl(9B)-C(401)-Cl(8B)	113.4(4)
Cl(8A)-C(401)-Cl(8B)	37.9(4)
Cl(7B)-C(401)-Cl(8B)	102.1(4)
Cl(7C)-C(401)-Cl(9A)	63.5(12)

Cl(9C)-C(401)-Cl(9A)	68.1(8)
Cl(7A)-C(401)-Cl(9A)	107.3(2)
Cl(9B)-C(401)-Cl(9A)	26.5(5)
Cl(8A)-C(401)-Cl(9A)	106.3(2)
Cl(7B)-C(401)-Cl(9A)	92.6(3)
Cl(8B)-C(401)-Cl(9A)	139.3(4)
Cl(7C)-C(401)-Cl(8C)	104.9(10)
Cl(9C)-C(401)-Cl(8C)	100.3(7)
Cl(7A)-C(401)-Cl(8C)	62.2(7)
Cl(9B)-C(401)-Cl(8C)	129.1(6)
Cl(8A)-C(401)-Cl(8C)	61.3(6)
Cl(7B)-C(401)-Cl(8C)	79.9(6)
Cl(8B)-C(401)-Cl(8C)	23.7(6)
Cl(9A)-C(401)-Cl(8C)	149.5(5)
Cl(7C)-C(401)-H(401)	114.2
Cl(9C)-C(401)-H(401)	111.0
Cl(7A)-C(401)-H(401)	109.0
Cl(9B)-C(401)-H(401)	122.8
Cl(8A)-C(401)-H(401)	109.0
Cl(7B)-C(401)-H(401)	105.7
Cl(8B)-C(401)-H(401)	103.2
Cl(9A)-C(401)-H(401)	109.0
Cl(8C)-C(401)-H(401)	101.5
H(101)-O(1)-H(102)	105(3)
H(201)-O(2)-H(202)	103(4)

Figure S7. Thermal ellipsoid plot of **12** at the 40% probability level. Hydrogen atoms, solvent molecules, and counteranions have been omitted for clarity.

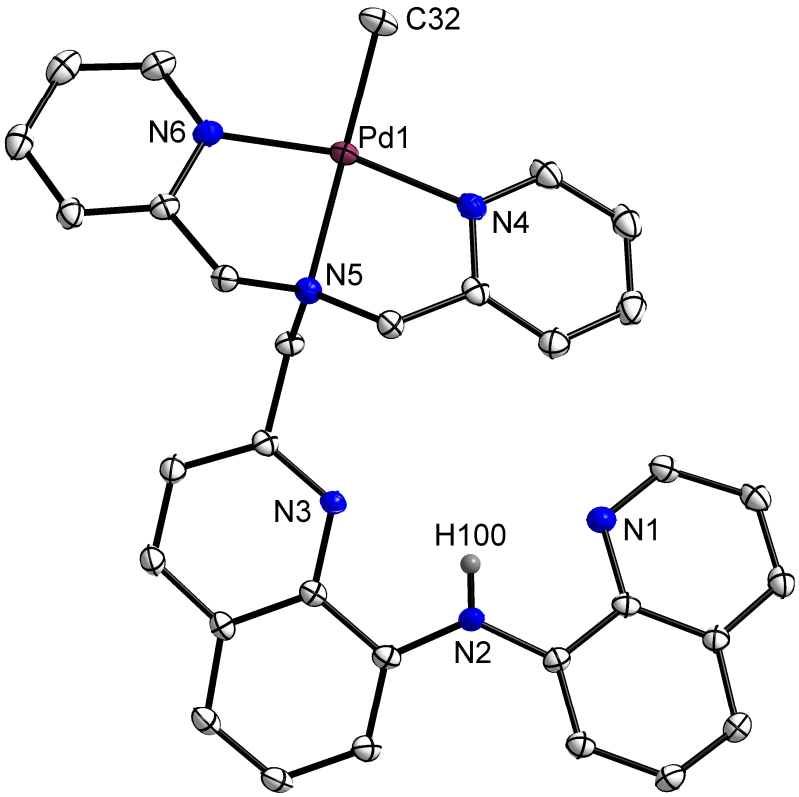


Table S5. Crystal data and structure refinement for **12** • CH_3CN.

Identification code	**12** • CH_3CN	
Empirical formula	C34 H32 F6 N7 P Pd	
Formula weight	790.04	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.6795(13) Å	α= 90°.
	b = 13.2225(11) Å	β= 91.096(2)°.
	c = 16.7504(14) Å	γ = 90°.
Volume	3250.7(5) $Å^3$	
Z	4	
Density (calculated)	1.614 Mg/m^3	
Absorption coefficient	0.692 mm^{-1}	
F(000)	1600	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.39 to 30.51°.	
Index ranges	-20<=h<=20, -18<=k<=18, -23<=l<=23	
Reflections collected	74757	
Independent reflections	9886 [R(int) = 0.0502]	
Completeness to theta = 30.51°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8739 and 0.8459	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9886 / 0 / 448	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0767	
R indices (all data)	R1 = 0.0493, wR2 = 0.0861	
Largest diff. peak and hole	0.569 and -0.565 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for **12**.

Pd(1)-C(32)	2.022(2)
Pd(1)-N(6)	2.0228(17)
Pd(1)-N(4)	2.0274(18)
Pd(1)-N(5)	2.1315(16)
N(3)-C(18)	1.327(2)
N(3)-C(10)	1.366(2)
N(2)-C(11)	1.381(2)
N(2)-C(8)	1.389(3)
N(2)-H(100)	0.82(3)
C(8)-C(7)	1.387(3)
C(8)-C(9)	1.436(3)
N(6)-C(31)	1.343(3)
N(6)-C(27)	1.361(2)
N(5)-C(20)	1.485(2)
N(5)-C(26)	1.488(2)
N(5)-C(19)	1.496(2)
C(12)-C(11)	1.385(3)
C(12)-C(13)	1.412(3)
C(12)-H(12)	0.9500
C(27)-C(28)	1.380(3)
C(27)-C(26)	1.515(3)
C(18)-C(17)	1.413(3)
C(18)-C(19)	1.516(2)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(9)-N(1)	1.370(2)
C(9)-C(4)	1.417(3)
C(10)-C(15)	1.423(3)
C(10)-C(11)	1.440(3)
C(20)-C(21)	1.516(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900

C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
N(1)-C(1)	1.320(3)
C(3)-C(2)	1.371(3)
C(3)-C(4)	1.415(3)
C(3)-H(3)	0.9500
C(15)-C(16)	1.409(3)
C(15)-C(14)	1.424(3)
C(1)-C(2)	1.410(3)
C(1)-H(1)	0.9500
C(21)-N(4)	1.359(2)
C(21)-C(22)	1.384(3)
C(6)-C(5)	1.363(3)
C(6)-C(7)	1.410(3)
C(6)-H(6)	0.9500
C(13)-C(14)	1.369(3)
C(13)-H(13)	0.9500
C(17)-C(16)	1.371(3)
C(17)-H(17)	0.9500
C(16)-H(16)	0.9500
C(5)-C(4)	1.424(3)
C(5)-H(5)	0.9500
C(14)-H(14)	0.9500
C(22)-C(23)	1.395(3)
C(22)-H(22)	0.9500
C(28)-C(29)	1.398(3)
C(28)-H(28)	0.9500
C(7)-H(7)	0.9500
N(4)-C(25)	1.352(3)
C(2)-H(2)	0.9500
C(31)-C(30)	1.385(3)
C(31)-H(31)	0.9500
C(25)-C(24)	1.374(3)
C(25)-H(25)	0.9500
C(29)-C(30)	1.380(3)

C(29)-H(29)	0.9500
C(23)-C(24)	1.380(3)
C(23)-H(23)	0.9500
C(30)-H(30)	0.9500
C(24)-H(24)	0.9500
P(1)-F(4)	1.5901(14)
P(1)-F(3)	1.5984(14)
P(1)-F(2)	1.5991(14)
P(1)-F(6)	1.6011(13)
P(1)-F(1)	1.6062(14)
P(1)-F(5)	1.6142(13)
N(7)-C(33)	1.138(3)
C(33)-C(34)	1.453(4)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800

C(32)-Pd(1)-N(6)	96.77(9)
C(32)-Pd(1)-N(4)	97.55(9)
N(6)-Pd(1)-N(4)	165.68(6)
C(32)-Pd(1)-N(5)	176.75(8)
N(6)-Pd(1)-N(5)	83.00(6)
N(4)-Pd(1)-N(5)	82.73(6)
C(18)-N(3)-C(10)	118.32(16)
C(11)-N(2)-C(8)	130.70(17)
C(11)-N(2)-H(100)	114(2)
C(8)-N(2)-H(100)	115(2)
C(7)-C(8)-N(2)	126.06(18)
C(7)-C(8)-C(9)	118.20(18)
N(2)-C(8)-C(9)	115.69(16)
C(31)-N(6)-C(27)	119.28(19)
C(31)-N(6)-Pd(1)	128.05(15)
C(27)-N(6)-Pd(1)	111.94(13)
C(20)-N(5)-C(26)	115.64(15)
C(20)-N(5)-C(19)	111.82(15)
C(26)-N(5)-C(19)	112.61(15)

C(20)-N(5)-Pd(1)	102.75(11)
C(26)-N(5)-Pd(1)	102.34(11)
C(19)-N(5)-Pd(1)	110.71(11)
C(11)-C(12)-C(13)	120.80(19)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
N(6)-C(27)-C(28)	121.30(18)
N(6)-C(27)-C(26)	116.01(17)
C(28)-C(27)-C(26)	122.67(18)
N(3)-C(18)-C(17)	122.96(17)
N(3)-C(18)-C(19)	116.45(16)
C(17)-C(18)-C(19)	120.51(17)
N(5)-C(19)-C(18)	115.11(15)
N(5)-C(19)-H(19A)	108.5
C(18)-C(19)-H(19A)	108.5
N(5)-C(19)-H(19B)	108.5
C(18)-C(19)-H(19B)	108.5
H(19A)-C(19)-H(19B)	107.5
N(1)-C(9)-C(4)	122.51(17)
N(1)-C(9)-C(8)	117.24(17)
C(4)-C(9)-C(8)	120.25(17)
N(3)-C(10)-C(15)	122.46(17)
N(3)-C(10)-C(11)	117.46(17)
C(15)-C(10)-C(11)	119.92(16)
N(2)-C(11)-C(12)	125.65(18)
N(2)-C(11)-C(10)	115.85(16)
C(12)-C(11)-C(10)	118.39(18)
N(5)-C(20)-C(21)	109.75(15)
N(5)-C(20)-H(20A)	109.7
C(21)-C(20)-H(20A)	109.7
N(5)-C(20)-H(20B)	109.7
C(21)-C(20)-H(20B)	109.7
H(20A)-C(20)-H(20B)	108.2
N(5)-C(26)-C(27)	109.06(15)
N(5)-C(26)-H(26A)	109.9
C(27)-C(26)-H(26A)	109.9

N(5)-C(26)-H(26B)	109.9
C(27)-C(26)-H(26B)	109.9
H(26A)-C(26)-H(26B)	108.3
Pd(1)-C(32)-H(32A)	109.5
Pd(1)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
Pd(1)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(1)-N(1)-C(9)	117.81(18)
C(2)-C(3)-C(4)	119.54(19)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(16)-C(15)-C(10)	117.25(17)
C(16)-C(15)-C(14)	123.11(18)
C(10)-C(15)-C(14)	119.62(18)
N(1)-C(1)-C(2)	123.87(19)
N(1)-C(1)-H(1)	118.1
C(2)-C(1)-H(1)	118.1
N(4)-C(21)-C(22)	121.13(19)
N(4)-C(21)-C(20)	116.57(17)
C(22)-C(21)-C(20)	122.29(18)
C(5)-C(6)-C(7)	122.20(19)
C(5)-C(6)-H(6)	118.9
C(7)-C(6)-H(6)	118.9
C(14)-C(13)-C(12)	121.87(18)
C(14)-C(13)-H(13)	119.1
C(12)-C(13)-H(13)	119.1
C(16)-C(17)-C(18)	119.08(19)
C(16)-C(17)-H(17)	120.5
C(18)-C(17)-H(17)	120.5
C(17)-C(16)-C(15)	119.87(18)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
C(6)-C(5)-C(4)	119.01(19)
C(6)-C(5)-H(5)	120.5

C(4)-C(5)-H(5)	120.5
C(13)-C(14)-C(15)	119.15(18)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(21)-C(22)-C(23)	119.6(2)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(27)-C(28)-C(29)	119.2(2)
C(27)-C(28)-H(28)	120.4
C(29)-C(28)-H(28)	120.4
C(8)-C(7)-C(6)	120.70(18)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(25)-N(4)-C(21)	118.72(18)
C(25)-N(4)-Pd(1)	128.74(15)
C(21)-N(4)-Pd(1)	112.04(13)
C(3)-C(2)-C(1)	118.77(19)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
N(6)-C(31)-C(30)	121.9(2)
N(6)-C(31)-H(31)	119.0
C(30)-C(31)-H(31)	119.0
N(4)-C(25)-C(24)	122.4(2)
N(4)-C(25)-H(25)	118.8
C(24)-C(25)-H(25)	118.8
C(30)-C(29)-C(28)	119.0(2)
C(30)-C(29)-H(29)	120.5
C(28)-C(29)-H(29)	120.5
C(3)-C(4)-C(9)	117.49(18)
C(3)-C(4)-C(5)	122.88(18)
C(9)-C(4)-C(5)	119.62(18)
C(24)-C(23)-C(22)	118.8(2)
C(24)-C(23)-H(23)	120.6
C(22)-C(23)-H(23)	120.6
C(29)-C(30)-C(31)	119.2(2)
C(29)-C(30)-H(30)	120.4

C(31)-C(30)-H(30)	120.4
C(25)-C(24)-C(23)	119.3(2)
C(25)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
F(4)-P(1)-F(3)	90.56(8)
F(4)-P(1)-F(2)	90.39(8)
F(3)-P(1)-F(2)	90.39(8)
F(4)-P(1)-F(6)	90.68(8)
F(3)-P(1)-F(6)	90.06(8)
F(2)-P(1)-F(6)	178.84(8)
F(4)-P(1)-F(1)	90.79(8)
F(3)-P(1)-F(1)	178.63(9)
F(2)-P(1)-F(1)	89.82(8)
F(6)-P(1)-F(1)	89.70(8)
F(4)-P(1)-F(5)	179.87(10)
F(3)-P(1)-F(5)	89.55(8)
F(2)-P(1)-F(5)	89.65(7)
F(6)-P(1)-F(5)	89.28(7)
F(1)-P(1)-F(5)	89.10(8)
N(7)-C(33)-C(34)	178.6(3)
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

Figure S8. Thermal ellipsoid plot of **13** at the 40% probability level. Hydrogen atoms, solvent molecules, and counteranions have been omitted for clarity.

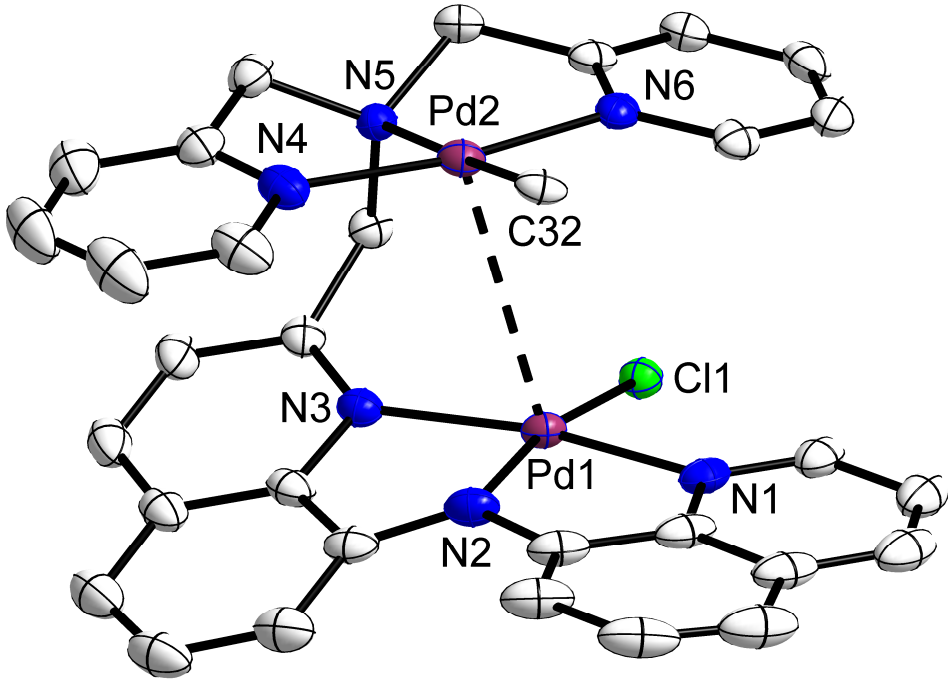


Table S7. Crystal data and structure refinement for **13** • 1.5 DMSO.

Identification code	**13** • 1.5 DMSO	
Empirical formula	C35 H28 Cl F6 N6 O1.50 P Pd2 S1.50	
Formula weight	997.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 16.542(3) Å	α= 90°.
	b = 32.618(5) Å	β= 109.131(2)°.
	c = 14.722(2) Å	γ = 90°.
Volume	7505(2) $Å^3$	
Z	8	
Density (calculated)	1.767 Mg/m^3	
Absorption coefficient	1.226 mm^{-1}	
F(000)	3952	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.25 to 26.37°.	
Index ranges	-20<=h<=20, -40<=k<=40, -18<=l<=18	
Reflections collected	58464	
Independent reflections	7673 [R(int) = 0.0500]	
Completeness to theta = 26.37°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8872 and 0.7916	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7673 / 122 / 536	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1070	
R indices (all data)	R1 = 0.0551, wR2 = 0.1182	
Largest diff. peak and hole	1.683 and -0.922 $e.Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for **13**.

Pd(1)-N(2)	1.968(4)
Pd(1)-N(1)	2.015(4)
Pd(1)-N(3)	2.054(4)
Pd(1)-Cl(1)	2.3329(11)
Pd(1)-Pd(2)	3.1909(7)
Pd(2)-N(6)	2.023(4)
Pd(2)-N(4)	2.032(4)
Pd(2)-C(32)	2.083(4)
Pd(2)-N(5)	2.129(4)
P(1)-F(3)	1.516(6)
P(1)-F(6)	1.572(4)
P(1)-F(1)	1.576(5)
P(1)-F(2)	1.579(5)
P(1)-F(5)	1.589(5)
P(1)-F(4)	1.619(5)
N(5)-C(26)	1.493(6)
N(5)-C(20)	1.494(6)
N(5)-C(19)	1.505(6)
N(6)-C(31)	1.344(6)
N(6)-C(27)	1.371(6)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
N(3)-C(18)	1.343(6)
N(3)-C(10)	1.381(6)
N(2)-C(11)	1.375(7)
N(2)-C(8)	1.387(7)
N(1)-C(1)	1.322(7)
N(1)-C(9)	1.386(6)
C(26)-C(27)	1.502(7)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(18)-C(17)	1.411(6)
C(18)-C(19)	1.501(6)

C(27)-C(28)	1.384(7)
N(4)-C(25)	1.354(7)
N(4)-C(21)	1.359(7)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(8)-C(7)	1.402(7)
C(8)-C(9)	1.434(8)
C(28)-C(29)	1.397(7)
C(28)-H(28)	0.9500
C(31)-C(30)	1.374(7)
C(31)-H(31)	0.9500
C(29)-C(30)	1.376(8)
C(29)-H(29)	0.9500
C(15)-C(16)	1.406(8)
C(15)-C(14)	1.418(7)
C(15)-C(10)	1.423(7)
C(16)-C(17)	1.368(7)
C(16)-H(16)	0.9500
C(11)-C(12)	1.388(7)
C(11)-C(10)	1.440(7)
C(17)-H(17)	0.9500
C(21)-C(22)	1.389(8)
C(21)-C(20)	1.510(7)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(1)-C(2)	1.411(7)
C(1)-H(1)	0.9500
C(30)-H(30)	0.9500
C(12)-C(13)	1.405(9)
C(12)-H(12)	0.9500
C(9)-C(4)	1.413(7)
C(6)-C(5)	1.350(10)
C(6)-C(7)	1.418(9)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(25)-C(24)	1.381(9)

C(25)-H(25)	0.9500
C(13)-C(14)	1.376(9)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(4)-C(3)	1.409(9)
C(4)-C(5)	1.423(9)
C(5)-H(5)	0.9500
C(23)-C(24)	1.368(10)
C(23)-C(22)	1.387(9)
C(23)-H(23)	0.9500
C(22)-H(22)	0.9500
C(2)-C(3)	1.356(9)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(24)-H(24)	0.9500
S(1)-C(101)	1.596(10)
S(1)-C(100)	1.785(9)
S(2)-C(100)	1.591(10)
S(2)-C(101)	1.762(9)
S(3)-C(100)	1.797(10)
S(3)-C(101)	1.858(10)
S(200)-O(200)	1.444(11)
S(200)-C(200)	1.839(14)
S(200)-C(201)	1.848(14)

N(2)-Pd(1)-N(1)	82.82(18)
N(2)-Pd(1)-N(3)	81.80(16)
N(1)-Pd(1)-N(3)	164.60(16)
N(2)-Pd(1)-Cl(1)	168.84(12)
N(1)-Pd(1)-Cl(1)	92.95(12)
N(3)-Pd(1)-Cl(1)	102.02(11)
N(2)-Pd(1)-Pd(2)	92.86(11)
N(1)-Pd(1)-Pd(2)	109.96(10)
N(3)-Pd(1)-Pd(2)	71.73(10)
Cl(1)-Pd(1)-Pd(2)	98.30(3)
N(6)-Pd(2)-N(4)	165.94(17)

N(6)-Pd(2)-C(32)	97.60(17)
N(4)-Pd(2)-C(32)	95.97(18)
N(6)-Pd(2)-N(5)	83.12(15)
N(4)-Pd(2)-N(5)	83.18(16)
C(32)-Pd(2)-N(5)	177.70(16)
N(6)-Pd(2)-Pd(1)	82.05(10)
N(4)-Pd(2)-Pd(1)	101.66(11)
C(32)-Pd(2)-Pd(1)	89.91(12)
N(5)-Pd(2)-Pd(1)	92.35(10)
F(3)-P(1)-F(6)	176.0(3)
F(3)-P(1)-F(1)	92.3(4)
F(6)-P(1)-F(1)	89.6(3)
F(3)-P(1)-F(2)	91.2(3)
F(6)-P(1)-F(2)	85.2(3)
F(1)-P(1)-F(2)	91.2(4)
F(3)-P(1)-F(5)	89.5(3)
F(6)-P(1)-F(5)	88.7(3)
F(1)-P(1)-F(5)	176.6(4)
F(2)-P(1)-F(5)	91.6(3)
F(3)-P(1)-F(4)	90.8(3)
F(6)-P(1)-F(4)	92.7(3)
F(1)-P(1)-F(4)	89.5(3)
F(2)-P(1)-F(4)	177.8(3)
F(5)-P(1)-F(4)	87.7(3)
C(26)-N(5)-C(20)	113.3(3)
C(26)-N(5)-C(19)	108.8(3)
C(20)-N(5)-C(19)	112.1(4)
C(26)-N(5)-Pd(2)	101.8(3)
C(20)-N(5)-Pd(2)	103.2(3)
C(19)-N(5)-Pd(2)	117.3(3)
C(31)-N(6)-C(27)	118.3(4)
C(31)-N(6)-Pd(2)	129.5(3)
C(27)-N(6)-Pd(2)	111.6(3)
Pd(2)-C(32)-H(32A)	109.5
Pd(2)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5

Pd(2)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(18)-N(3)-C(10)	119.6(4)
C(18)-N(3)-Pd(1)	131.7(3)
C(10)-N(3)-Pd(1)	108.6(3)
C(11)-N(2)-C(8)	128.9(4)
C(11)-N(2)-Pd(1)	113.1(3)
C(8)-N(2)-Pd(1)	114.3(3)
C(1)-N(1)-C(9)	120.1(4)
C(1)-N(1)-Pd(1)	128.4(3)
C(9)-N(1)-Pd(1)	111.5(3)
N(5)-C(26)-C(27)	109.8(4)
N(5)-C(26)-H(26A)	109.7
C(27)-C(26)-H(26A)	109.7
N(5)-C(26)-H(26B)	109.7
C(27)-C(26)-H(26B)	109.7
H(26A)-C(26)-H(26B)	108.2
N(3)-C(18)-C(17)	120.3(4)
N(3)-C(18)-C(19)	119.5(4)
C(17)-C(18)-C(19)	119.9(4)
N(6)-C(27)-C(28)	121.3(4)
N(6)-C(27)-C(26)	116.0(4)
C(28)-C(27)-C(26)	122.6(4)
C(25)-N(4)-C(21)	119.1(5)
C(25)-N(4)-Pd(2)	128.5(4)
C(21)-N(4)-Pd(2)	112.2(3)
C(18)-C(19)-N(5)	110.9(4)
C(18)-C(19)-H(19A)	109.5
N(5)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
N(5)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	108.0
N(2)-C(8)-C(7)	128.0(5)
N(2)-C(8)-C(9)	114.5(4)
C(7)-C(8)-C(9)	117.4(5)

C(27)-C(28)-C(29)	119.0(5)
C(27)-C(28)-H(28)	120.5
C(29)-C(28)-H(28)	120.5
N(6)-C(31)-C(30)	123.1(5)
N(6)-C(31)-H(31)	118.5
C(30)-C(31)-H(31)	118.5
C(30)-C(29)-C(28)	119.5(5)
C(30)-C(29)-H(29)	120.3
C(28)-C(29)-H(29)	120.3
C(16)-C(15)-C(14)	123.6(5)
C(16)-C(15)-C(10)	117.0(4)
C(14)-C(15)-C(10)	119.3(5)
C(17)-C(16)-C(15)	120.4(5)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
N(2)-C(11)-C(12)	128.6(5)
N(2)-C(11)-C(10)	113.7(4)
C(12)-C(11)-C(10)	117.7(5)
C(16)-C(17)-C(18)	120.5(5)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
N(4)-C(21)-C(22)	121.0(5)
N(4)-C(21)-C(20)	116.9(4)
C(22)-C(21)-C(20)	122.1(5)
N(3)-C(10)-C(15)	121.5(4)
N(3)-C(10)-C(11)	117.6(4)
C(15)-C(10)-C(11)	120.9(4)
N(5)-C(20)-C(21)	111.0(4)
N(5)-C(20)-H(20A)	109.4
C(21)-C(20)-H(20A)	109.4
N(5)-C(20)-H(20B)	109.4
C(21)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
N(1)-C(1)-C(2)	121.0(5)
N(1)-C(1)-H(1)	119.5
C(2)-C(1)-H(1)	119.5

C(31)-C(30)-C(29)	118.9(5)
C(31)-C(30)-H(30)	120.6
C(29)-C(30)-H(30)	120.6
C(11)-C(12)-C(13)	120.4(5)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
N(1)-C(9)-C(4)	121.2(5)
N(1)-C(9)-C(8)	116.9(4)
C(4)-C(9)-C(8)	121.9(5)
C(5)-C(6)-C(7)	123.0(6)
C(5)-C(6)-H(6)	118.5
C(7)-C(6)-H(6)	118.5
C(8)-C(7)-C(6)	119.5(6)
C(8)-C(7)-H(7)	120.3
C(6)-C(7)-H(7)	120.3
N(4)-C(25)-C(24)	121.4(6)
N(4)-C(25)-H(25)	119.3
C(24)-C(25)-H(25)	119.3
C(14)-C(13)-C(12)	123.0(5)
C(14)-C(13)-H(13)	118.5
C(12)-C(13)-H(13)	118.5
C(13)-C(14)-C(15)	118.4(5)
C(13)-C(14)-H(14)	120.8
C(15)-C(14)-H(14)	120.8
C(3)-C(4)-C(9)	116.9(5)
C(3)-C(4)-C(5)	124.9(6)
C(9)-C(4)-C(5)	118.3(6)
C(6)-C(5)-C(4)	119.7(6)
C(6)-C(5)-H(5)	120.1
C(4)-C(5)-H(5)	120.1
C(24)-C(23)-C(22)	119.0(6)
C(24)-C(23)-H(23)	120.5
C(22)-C(23)-H(23)	120.5
C(23)-C(22)-C(21)	119.5(6)
C(23)-C(22)-H(22)	120.3
C(21)-C(22)-H(22)	120.3

C(3)-C(2)-C(1)	119.9(6)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(2)-C(3)-C(4)	120.8(5)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(23)-C(24)-C(25)	120.0(6)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(101)-S(1)-C(100)	115.2(6)
C(100)-S(2)-C(101)	116.7(5)
C(100)-S(3)-C(101)	102.7(6)
S(2)-C(100)-S(1)	59.3(4)
S(2)-C(100)-S(3)	41.1(4)
S(1)-C(100)-S(3)	37.4(3)
S(1)-C(101)-S(2)	59.7(4)
S(1)-C(101)-S(3)	37.9(3)
S(2)-C(101)-S(3)	38.8(4)
O(200)-S(200)-C(200)	103.9(9)
O(200)-S(200)-C(201)	102.4(8)
C(200)-S(200)-C(201)	99.8(9)

Figure S9. Thermal ellipsoid plot of **15** at the 40% probability level. Hydrogen atoms, solvent molecules, and conteranions have been omitted for clarity.

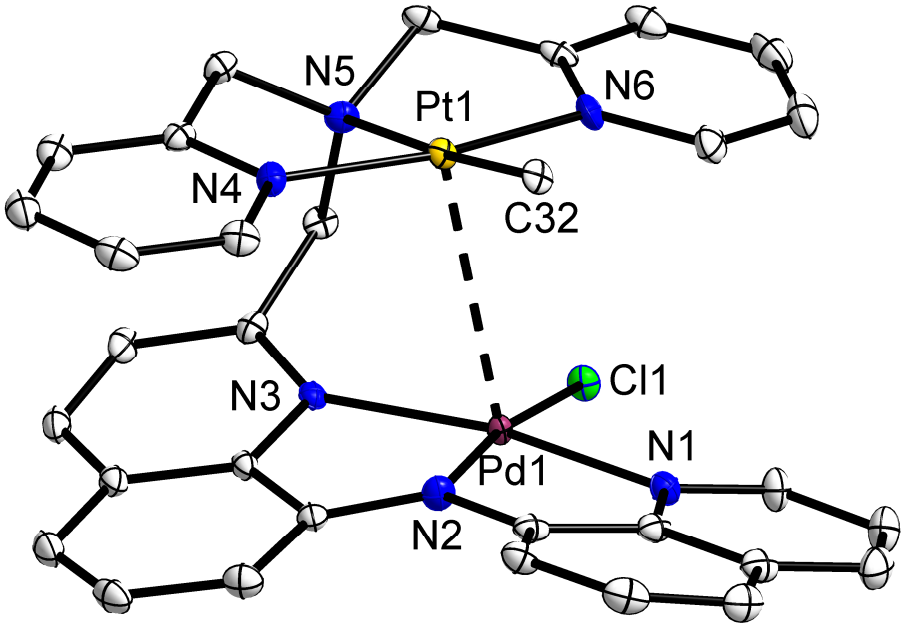


Table S9. Crystal data and structure refinement for **15** • CH_2Cl_2.

Identification code	**15** • CH_2Cl_2	
Empirical formula	C33 H30 Cl3 F6 N6 P Pd Pt	
Formula weight	1063.44	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.3949(4) Å	α= 70.729(2)°.
	b = 15.6616(8) Å	β= 81.541(2)°.
	c = 15.8870(9) Å	γ = 86.647(2)°.
Volume	1717.88(16) $Å^3$	
Z	2	
Density (calculated)	2.056 Mg/m^3	
Absorption coefficient	14.927 mm^{-1}	
F(000)	1028	
Crystal size	0.25 x 0.20 x 0.04 mm^3	
Theta range for data collection	2.97 to 68.97°.	
Index ranges	-8<=h<=8, -18<=k<=18, -19<=l<=17	
Reflections collected	33056	
Independent reflections	6077 [R(int) = 0.0318]	
Completeness to theta = 68.97°	95.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5866 and 0.1180	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6077 / 0 / 461	
Goodness-of-fit on F^2	1.170	
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0588	
R indices (all data)	R1 = 0.0234, wR2 = 0.0589	
Largest diff. peak and hole	0.746 and -1.572 e.$Å^{-3}$	

Table S10. Bond lengths [Å] and angles [°] for **15**.

Pt(1)-N(6)	1.998(3)
Pt(1)-N(4)	2.009(3)
Pt(1)-C(32)	2.071(3)
Pt(1)-N(5)	2.133(3)
Pt(1)-Pd(1)	3.1668(3)
Pd(1)-N(2)	1.956(3)
Pd(1)-N(1)	2.012(3)
Pd(1)-N(3)	2.055(3)
Pd(1)-Cl(1)	2.3392(8)
P(1)-F(4)	1.593(2)
P(1)-F(1)	1.594(3)
P(1)-F(5)	1.597(2)
P(1)-F(3)	1.599(2)
P(1)-F(2)	1.603(3)
P(1)-F(6)	1.618(2)
Cl(3)-C(33)	1.763(5)
Cl(2)-C(33)	1.768(5)
N(3)-C(18)	1.336(4)
N(3)-C(10)	1.383(4)
N(4)-C(25)	1.347(4)
N(4)-C(21)	1.361(4)
N(5)-C(20)	1.500(4)
N(5)-C(26)	1.502(4)
N(5)-C(19)	1.514(4)
N(1)-C(1)	1.323(4)
N(1)-C(9)	1.390(4)
N(6)-C(31)	1.351(4)
N(6)-C(27)	1.362(4)
N(2)-C(11)	1.373(4)
N(2)-C(8)	1.389(4)
C(18)-C(17)	1.410(5)
C(18)-C(19)	1.500(4)
C(10)-C(15)	1.424(4)
C(10)-C(11)	1.444(5)

C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(26)-C(27)	1.514(5)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(25)-C(24)	1.383(5)
C(25)-H(25)	0.9500
C(7)-C(8)	1.383(5)
C(7)-C(6)	1.411(5)
C(7)-H(7)	0.9500
C(15)-C(16)	1.414(5)
C(15)-C(14)	1.417(5)
C(4)-C(9)	1.406(5)
C(4)-C(3)	1.413(5)
C(4)-C(5)	1.424(5)
C(31)-C(30)	1.382(5)
C(31)-H(31)	0.9500
C(28)-C(27)	1.377(5)
C(28)-C(29)	1.388(6)
C(28)-H(28)	0.9500
C(17)-C(16)	1.362(5)
C(17)-H(17)	0.9500
C(12)-C(11)	1.396(5)
C(12)-C(13)	1.410(5)
C(12)-H(12)	0.9500
C(14)-C(13)	1.375(5)
C(14)-H(14)	0.9500
C(9)-C(8)	1.431(5)
C(20)-C(21)	1.522(5)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(6)-C(5)	1.368(5)
C(6)-H(6)	0.9500
C(21)-C(22)	1.374(5)
C(22)-C(23)	1.390(5)

C(22)-H(22)	0.9500
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(5)-H(5)	0.9500
C(16)-H(16)	0.9500
C(29)-C(30)	1.383(6)
C(29)-H(29)	0.9500
C(1)-C(2)	1.408(5)
C(1)-H(1)	0.9500
C(24)-C(23)	1.389(5)
C(24)-H(24)	0.9500
C(30)-H(30)	0.9500
C(13)-H(13)	0.9500
C(23)-H(23)	0.9500
C(3)-C(2)	1.374(5)
C(3)-H(3)	0.9500
C(2)-H(2)	0.9500
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900

N(6)-Pt(1)-N(4)	166.64(11)
N(6)-Pt(1)-C(32)	97.45(12)
N(4)-Pt(1)-C(32)	95.42(12)
N(6)-Pt(1)-N(5)	82.97(11)
N(4)-Pt(1)-N(5)	83.95(11)
C(32)-Pt(1)-N(5)	176.07(11)
N(6)-Pt(1)-Pd(1)	83.27(8)
N(4)-Pt(1)-Pd(1)	99.66(8)
C(32)-Pt(1)-Pd(1)	92.89(9)
N(5)-Pt(1)-Pd(1)	91.03(7)
N(2)-Pd(1)-N(1)	82.71(11)
N(2)-Pd(1)-N(3)	81.62(11)
N(1)-Pd(1)-N(3)	164.12(11)
N(2)-Pd(1)-Cl(1)	171.68(9)
N(1)-Pd(1)-Cl(1)	92.97(8)
N(3)-Pd(1)-Cl(1)	102.25(8)

N(2)-Pd(1)-Pt(1)	89.96(8)
N(1)-Pd(1)-Pt(1)	110.94(8)
N(3)-Pd(1)-Pt(1)	71.68(7)
Cl(1)-Pd(1)-Pt(1)	98.23(2)
F(4)-P(1)-F(1)	89.87(17)
F(4)-P(1)-F(5)	90.51(13)
F(1)-P(1)-F(5)	90.99(15)
F(4)-P(1)-F(3)	179.08(14)
F(1)-P(1)-F(3)	90.24(17)
F(5)-P(1)-F(3)	90.40(12)
F(4)-P(1)-F(2)	89.82(16)
F(1)-P(1)-F(2)	178.92(16)
F(5)-P(1)-F(2)	90.05(14)
F(3)-P(1)-F(2)	90.05(17)
F(4)-P(1)-F(6)	89.85(12)
F(1)-P(1)-F(6)	89.44(14)
F(5)-P(1)-F(6)	179.44(14)
F(3)-P(1)-F(6)	89.24(12)
F(2)-P(1)-F(6)	89.53(13)
C(18)-N(3)-C(10)	119.0(3)
C(18)-N(3)-Pd(1)	131.9(2)
C(10)-N(3)-Pd(1)	109.0(2)
C(25)-N(4)-C(21)	118.8(3)
C(25)-N(4)-Pt(1)	128.4(2)
C(21)-N(4)-Pt(1)	112.6(2)
C(20)-N(5)-C(26)	113.1(3)
C(20)-N(5)-C(19)	111.2(2)
C(26)-N(5)-C(19)	108.9(2)
C(20)-N(5)-Pt(1)	102.19(18)
C(26)-N(5)-Pt(1)	101.68(18)
C(19)-N(5)-Pt(1)	119.49(19)
C(1)-N(1)-C(9)	119.7(3)
C(1)-N(1)-Pd(1)	129.2(2)
C(9)-N(1)-Pd(1)	111.1(2)
C(31)-N(6)-C(27)	119.1(3)
C(31)-N(6)-Pt(1)	127.7(2)

C(27)-N(6)-Pt(1)	113.0(2)
C(11)-N(2)-C(8)	129.5(3)
C(11)-N(2)-Pd(1)	114.6(2)
C(8)-N(2)-Pd(1)	114.6(2)
N(3)-C(18)-C(17)	120.9(3)
N(3)-C(18)-C(19)	118.1(3)
C(17)-C(18)-C(19)	120.7(3)
N(3)-C(10)-C(15)	121.6(3)
N(3)-C(10)-C(11)	116.9(3)
C(15)-C(10)-C(11)	121.4(3)
Pt(1)-C(32)-H(32A)	109.5
Pt(1)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
Pt(1)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
N(5)-C(26)-C(27)	109.9(3)
N(5)-C(26)-H(26A)	109.7
C(27)-C(26)-H(26A)	109.7
N(5)-C(26)-H(26B)	109.7
C(27)-C(26)-H(26B)	109.7
H(26A)-C(26)-H(26B)	108.2
N(4)-C(25)-C(24)	122.3(3)
N(4)-C(25)-H(25)	118.9
C(24)-C(25)-H(25)	118.9
C(8)-C(7)-C(6)	120.5(3)
C(8)-C(7)-H(7)	119.8
C(6)-C(7)-H(7)	119.8
C(16)-C(15)-C(14)	124.6(3)
C(16)-C(15)-C(10)	116.5(3)
C(14)-C(15)-C(10)	118.8(3)
C(9)-C(4)-C(3)	118.2(3)
C(9)-C(4)-C(5)	118.4(3)
C(3)-C(4)-C(5)	123.4(3)
N(6)-C(31)-C(30)	121.5(3)
N(6)-C(31)-H(31)	119.2

C(30)-C(31)-H(31)	119.2
C(27)-C(28)-C(29)	119.3(4)
C(27)-C(28)-H(28)	120.3
C(29)-C(28)-H(28)	120.3
N(6)-C(27)-C(28)	121.4(3)
N(6)-C(27)-C(26)	115.8(3)
C(28)-C(27)-C(26)	122.7(3)
C(16)-C(17)-C(18)	120.1(3)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(11)-C(12)-C(13)	121.1(3)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(13)-C(14)-C(15)	119.6(3)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
N(1)-C(9)-C(4)	120.9(3)
N(1)-C(9)-C(8)	117.1(3)
C(4)-C(9)-C(8)	122.1(3)
N(2)-C(11)-C(12)	129.2(3)
N(2)-C(11)-C(10)	113.7(3)
C(12)-C(11)-C(10)	117.1(3)
N(5)-C(20)-C(21)	111.2(3)
N(5)-C(20)-H(20A)	109.4
C(21)-C(20)-H(20A)	109.4
N(5)-C(20)-H(20B)	109.4
C(21)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
C(5)-C(6)-C(7)	122.3(3)
C(5)-C(6)-H(6)	118.9
C(7)-C(6)-H(6)	118.9
N(4)-C(21)-C(22)	121.5(3)
N(4)-C(21)-C(20)	116.3(3)
C(22)-C(21)-C(20)	122.2(3)
C(7)-C(8)-N(2)	128.8(3)
C(7)-C(8)-C(9)	117.4(3)

N(2)-C(8)-C(9)	113.7(3)
C(21)-C(22)-C(23)	119.6(3)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(18)-C(19)-N(5)	110.1(3)
C(18)-C(19)-H(19A)	109.6
N(5)-C(19)-H(19A)	109.6
C(18)-C(19)-H(19B)	109.6
N(5)-C(19)-H(19B)	109.6
H(19A)-C(19)-H(19B)	108.1
C(6)-C(5)-C(4)	119.2(3)
C(6)-C(5)-H(5)	120.4
C(4)-C(5)-H(5)	120.4
C(17)-C(16)-C(15)	120.2(3)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(30)-C(29)-C(28)	119.2(4)
C(30)-C(29)-H(29)	120.4
C(28)-C(29)-H(29)	120.4
N(1)-C(1)-C(2)	121.9(3)
N(1)-C(1)-H(1)	119.0
C(2)-C(1)-H(1)	119.0
C(25)-C(24)-C(23)	118.8(3)
C(25)-C(24)-H(24)	120.6
C(23)-C(24)-H(24)	120.6
C(31)-C(30)-C(29)	119.3(3)
C(31)-C(30)-H(30)	120.3
C(29)-C(30)-H(30)	120.3
C(14)-C(13)-C(12)	122.0(3)
C(14)-C(13)-H(13)	119.0
C(12)-C(13)-H(13)	119.0
C(24)-C(23)-C(22)	119.0(3)
C(24)-C(23)-H(23)	120.5
C(22)-C(23)-H(23)	120.5
C(2)-C(3)-C(4)	119.5(3)
C(2)-C(3)-H(3)	120.2

C(4)-C(3)-H(3)	120.2
C(3)-C(2)-C(1)	119.7(3)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
Cl(3)-C(33)-Cl(2)	111.1(2)
Cl(3)-C(33)-H(33A)	109.4
Cl(2)-C(33)-H(33A)	109.4
Cl(3)-C(33)-H(33B)	109.4
Cl(2)-C(33)-H(33B)	109.4
H(33A)-C(33)-H(33B)	108.0

Figure S10. Thermal ellipsoid plot of **16** at the 40% probability level. Hydrogen atoms, solvent molecules, and counteranions have been omitted for clarity.

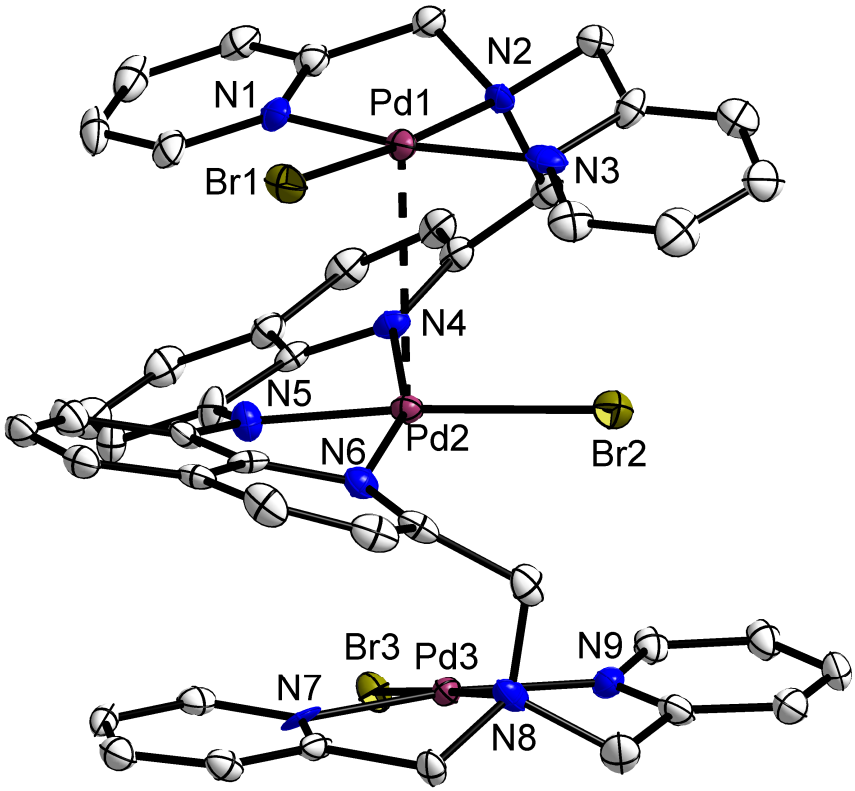


Table S11. Crystal data and structure refinement for **16** • 4 CH_3CN.

Identification code	**16** • 4 CH_3CN	
Empirical formula	C52 H50 B2 Br3 F8 N13 Pd3	
Formula weight	1589.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.8582(13) Å	α= 90°.
	b = 19.3783(19) Å	β= 90°.
	c = 45.245(4) Å	γ = 90°.
Volume	11273.8(19) $Å^3$	
Z	8	
Density (calculated)	1.873 Mg/m^3	
Absorption coefficient	3.150 mm^{-1}	
F(000)	6224	
Crystal size	0.45 x 0.45 x 0.20 mm^3	
Theta range for data collection	0.90 to 29.13°.	
Index ranges	-17<=h<=17, -26<=k<=26, -56<=l<=61	
Reflections collected	221928	
Independent reflections	15158 [R(int) = 0.0708]	
Completeness to theta = 29.13°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5715 and 0.3314	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15158 / 860 / 791	
Goodness-of-fit on F^2	1.258	
Final R indices [I>2sigma(I)]	R1 = 0.0905, wR2 = 0.1983	
R indices (all data)	R1 = 0.1043, wR2 = 0.2045	
Largest diff. peak and hole	1.646 and -2.793 $e.Å^{-3}$	

Table S12. Bond lengths [Å] and angles [°] for **16**.

Pd(3)-N(7)	2.021(8)
Pd(3)-N(9)	2.032(8)
Pd(3)-N(8)	2.044(8)
Pd(3)-Br(3)	2.4297(11)
Pd(3)-Pd(2)	3.4411(10)
Pd(2)-N(5)	1.955(8)
Pd(2)-N(4)	2.084(7)
Pd(2)-N(6)	2.107(8)
Pd(2)-Br(2)	2.4861(13)
Pd(2)-Pd(1)	3.2447(10)
Pd(1)-N(3)	2.013(9)
Pd(1)-N(1)	2.019(9)
Pd(1)-N(2)	2.046(7)
Pd(1)-Br(1)	2.4115(12)
N(6)-C(31)	1.339(12)
N(6)-C(23)	1.393(12)
N(9)-C(44)	1.336(12)
N(9)-C(40)	1.371(13)
N(5)-C(24)	1.362(12)
N(5)-C(21)	1.404(13)
N(7)-C(34)	1.338(12)
N(7)-C(38)	1.357(13)
N(3)-C(12)	1.344(13)
N(3)-C(8)	1.370(13)
N(2)-C(6)	1.496(12)
N(2)-C(7)	1.501(12)
N(2)-C(13)	1.513(12)
N(8)-C(32)	1.488(13)
N(8)-C(39)	1.501(13)
N(8)-C(33)	1.505(11)
C(23)-C(24)	1.424(12)
C(23)-C(28)	1.427(12)
N(4)-C(14)	1.330(11)
N(4)-C(22)	1.397(12)

N(1)-C(1)	1.349(12)
N(1)-C(5)	1.377(12)
C(16)-C(15)	1.358(15)
C(16)-C(17)	1.413(14)
C(16)-H(16)	0.9500
C(14)-C(15)	1.423(12)
C(14)-C(13)	1.508(14)
C(21)-C(20)	1.381(13)
C(21)-C(22)	1.414(13)
C(28)-C(29)	1.406(14)
C(28)-C(27)	1.407(13)
C(34)-C(37)	1.396(13)
C(34)-C(33)	1.493(12)
C(15)-H(15)	0.9500
C(22)-C(17)	1.414(12)
C(7)-C(8)	1.489(14)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(37)-C(36)	1.372(14)
C(37)-H(37)	0.9500
C(27)-C(26)	1.394(15)
C(27)-H(27)	0.9500
C(24)-C(25)	1.417(14)
C(41)-C(42)	1.384(17)
C(41)-C(40)	1.393(15)
C(41)-H(41)	0.9500
C(26)-C(25)	1.393(14)
C(26)-H(26)	0.9500
C(35)-C(38)	1.389(14)
C(35)-C(36)	1.391(14)
C(35)-H(35)	0.9500
C(18)-C(19)	1.357(15)
C(18)-C(17)	1.419(14)
C(18)-H(18)	0.9500

C(31)-C(30)	1.406(13)
C(31)-C(32)	1.516(14)
C(36)-H(36)	0.9500
C(1)-C(2)	1.373(15)
C(1)-H(1)	0.9500
C(8)-C(9)	1.369(15)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(42)-C(43)	1.401(16)
C(42)-H(42)	0.9500
C(39)-C(40)	1.494(14)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(25)-H(25)	0.9500
C(29)-C(30)	1.372(15)
C(29)-H(29)	0.9500
C(9)-C(10)	1.389(16)
C(9)-H(9)	0.9500
C(12)-C(11)	1.373(16)
C(12)-H(12)	0.9500
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(6)-C(5)	1.491(13)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(5)-C(4)	1.390(15)
C(43)-C(44)	1.374(13)
C(43)-H(43)	0.9500
C(20)-C(19)	1.427(13)
C(20)-H(20)	0.9500
C(19)-H(19)	0.9500
C(44)-H(44)	0.9500
C(4)-C(3)	1.382(16)
C(4)-H(4)	0.9500
C(30)-H(30)	0.9500
C(2)-C(3)	1.386(17)

C(2)-H(2)	0.9500
C(11)-C(10)	1.392(17)
C(11)-H(11)	0.9500
C(38)-H(38)	0.9500
C(10)-H(10)	0.9500
C(3)-H(3)	0.9500
F(4)-B(1)	1.361(17)
F(3)-B(1)	1.437(18)
F(7)-B(2)	1.348(14)
N(100)-C(100)	1.118(11)
F(2)-B(1)	1.354(19)
C(100)-C(101)	1.444(13)
F(1)-B(1)	1.369(18)
B(2)-F(101)	1.318(18)
B(2)-F(102)	1.336(17)
B(2)-F(5)	1.345(15)
B(2)-F(8)	1.365(15)
B(2)-F(6)	1.418(15)
B(2)-F(100)	1.537(19)
C(300)-N(300)	1.106(13)
C(300)-C(301)	1.458(14)
C(200)-N(200)	1.120(13)
C(200)-C(201)	1.448(14)
C(201)-H(20A)	0.9800
C(201)-H(20B)	0.9800
C(201)-H(20C)	0.9800
C(301)-H(30A)	0.9800
C(301)-H(30B)	0.9800
C(301)-H(30C)	0.9800
C(101)-H(10A)	0.9800
C(101)-H(10B)	0.9800
C(101)-H(10C)	0.9800
C(500)-C(501)	1.450(16)
C(500)-H(50A)	0.9800
C(500)-H(50B)	0.9800
C(500)-H(50C)	0.9800

C(501)-N(500)	1.126(15)
C(400)-C(401)	1.452(16)
C(400)-H(40A)	0.9800
C(400)-H(40B)	0.9800
C(400)-H(40C)	0.9800
C(401)-N(400)	1.115(15)

N(7)-Pd(3)-N(9)	166.4(3)
N(7)-Pd(3)-N(8)	83.9(3)
N(9)-Pd(3)-N(8)	83.8(3)
N(7)-Pd(3)-Br(3)	97.1(2)
N(9)-Pd(3)-Br(3)	95.2(2)
N(8)-Pd(3)-Br(3)	178.3(2)
N(7)-Pd(3)-Pd(2)	92.5(2)
N(9)-Pd(3)-Pd(2)	94.3(2)
N(8)-Pd(3)-Pd(2)	95.0(2)
Br(3)-Pd(3)-Pd(2)	86.44(3)
N(5)-Pd(2)-N(4)	80.4(3)
N(5)-Pd(2)-N(6)	79.9(3)
N(4)-Pd(2)-N(6)	159.4(3)
N(5)-Pd(2)-Br(2)	173.4(3)
N(4)-Pd(2)-Br(2)	97.7(2)
N(6)-Pd(2)-Br(2)	102.6(2)
N(5)-Pd(2)-Pd(1)	94.7(3)
N(4)-Pd(2)-Pd(1)	72.7(2)
N(6)-Pd(2)-Pd(1)	103.2(2)
Br(2)-Pd(2)-Pd(1)	90.81(3)
N(5)-Pd(2)-Pd(3)	93.6(2)
N(4)-Pd(2)-Pd(3)	120.4(2)
N(6)-Pd(2)-Pd(3)	66.9(2)
Br(2)-Pd(2)-Pd(3)	81.78(3)
Pd(1)-Pd(2)-Pd(3)	165.66(3)
N(3)-Pd(1)-N(1)	167.7(3)
N(3)-Pd(1)-N(2)	83.5(3)
N(1)-Pd(1)-N(2)	84.3(3)
N(3)-Pd(1)-Br(1)	95.9(2)

N(1)-Pd(1)-Br(1)	96.0(2)
N(2)-Pd(1)-Br(1)	175.1(2)
N(3)-Pd(1)-Pd(2)	89.8(2)
N(1)-Pd(1)-Pd(2)	93.6(2)
N(2)-Pd(1)-Pd(2)	95.5(2)
Br(1)-Pd(1)-Pd(2)	89.28(3)
C(31)-N(6)-C(23)	118.3(8)
C(31)-N(6)-Pd(2)	133.2(7)
C(23)-N(6)-Pd(2)	107.5(6)
C(44)-N(9)-C(40)	120.4(8)
C(44)-N(9)-Pd(3)	128.7(7)
C(40)-N(9)-Pd(3)	110.6(6)
C(24)-N(5)-C(21)	129.5(8)
C(24)-N(5)-Pd(2)	116.0(6)
C(21)-N(5)-Pd(2)	114.4(6)
C(34)-N(7)-C(38)	119.6(9)
C(34)-N(7)-Pd(3)	112.2(6)
C(38)-N(7)-Pd(3)	127.9(7)
C(12)-N(3)-C(8)	119.5(9)
C(12)-N(3)-Pd(1)	128.7(7)
C(8)-N(3)-Pd(1)	111.2(7)
C(6)-N(2)-C(7)	113.2(7)
C(6)-N(2)-C(13)	111.6(7)
C(7)-N(2)-C(13)	107.7(7)
C(6)-N(2)-Pd(1)	104.4(5)
C(7)-N(2)-Pd(1)	103.0(6)
C(13)-N(2)-Pd(1)	116.7(5)
C(32)-N(8)-C(39)	109.8(8)
C(32)-N(8)-C(33)	112.9(8)
C(39)-N(8)-C(33)	110.7(7)
C(32)-N(8)-Pd(3)	114.7(6)
C(39)-N(8)-Pd(3)	103.7(6)
C(33)-N(8)-Pd(3)	104.5(5)
N(6)-C(23)-C(24)	116.8(8)
N(6)-C(23)-C(28)	121.5(8)
C(24)-C(23)-C(28)	121.4(9)

C(14)-N(4)-C(22)	117.9(8)
C(14)-N(4)-Pd(2)	133.6(7)
C(22)-N(4)-Pd(2)	108.5(6)
C(1)-N(1)-C(5)	119.0(9)
C(1)-N(1)-Pd(1)	129.0(7)
C(5)-N(1)-Pd(1)	111.6(6)
C(15)-C(16)-C(17)	119.3(9)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
N(4)-C(14)-C(15)	121.3(9)
N(4)-C(14)-C(13)	120.7(8)
C(15)-C(14)-C(13)	117.8(8)
C(20)-C(21)-N(5)	126.0(9)
C(20)-C(21)-C(22)	120.9(9)
N(5)-C(21)-C(22)	113.1(8)
C(29)-C(28)-C(27)	123.1(9)
C(29)-C(28)-C(23)	117.4(9)
C(27)-C(28)-C(23)	119.5(9)
N(7)-C(34)-C(37)	120.7(8)
N(7)-C(34)-C(33)	116.5(9)
C(37)-C(34)-C(33)	122.5(8)
C(16)-C(15)-C(14)	120.6(9)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
N(4)-C(22)-C(17)	122.0(8)
N(4)-C(22)-C(21)	117.4(8)
C(17)-C(22)-C(21)	120.5(9)
C(8)-C(7)-N(2)	109.0(8)
C(8)-C(7)-H(7A)	109.9
N(2)-C(7)-H(7A)	109.9
C(8)-C(7)-H(7B)	109.9
N(2)-C(7)-H(7B)	109.9
H(7A)-C(7)-H(7B)	108.3
C(14)-C(13)-N(2)	111.5(7)
C(14)-C(13)-H(13A)	109.3
N(2)-C(13)-H(13A)	109.3

C(14)-C(13)-H(13B)	109.3
N(2)-C(13)-H(13B)	109.3
H(13A)-C(13)-H(13B)	108.0
C(36)-C(37)-C(34)	120.6(9)
C(36)-C(37)-H(37)	119.7
C(34)-C(37)-H(37)	119.7
C(26)-C(27)-C(28)	118.1(8)
C(26)-C(27)-H(27)	120.9
C(28)-C(27)-H(27)	120.9
N(5)-C(24)-C(25)	128.0(9)
N(5)-C(24)-C(23)	114.0(8)
C(25)-C(24)-C(23)	117.9(9)
C(42)-C(41)-C(40)	120.8(11)
C(42)-C(41)-H(41)	119.6
C(40)-C(41)-H(41)	119.6
C(25)-C(26)-C(27)	123.7(10)
C(25)-C(26)-H(26)	118.2
C(27)-C(26)-H(26)	118.2
C(38)-C(35)-C(36)	119.6(9)
C(38)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2
C(19)-C(18)-C(17)	119.6(9)
C(19)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
N(6)-C(31)-C(30)	121.5(10)
N(6)-C(31)-C(32)	119.6(8)
C(30)-C(31)-C(32)	118.5(9)
C(37)-C(36)-C(35)	118.2(9)
C(37)-C(36)-H(36)	120.9
C(35)-C(36)-H(36)	120.9
N(1)-C(1)-C(2)	122.7(10)
N(1)-C(1)-H(1)	118.6
C(2)-C(1)-H(1)	118.6
C(9)-C(8)-N(3)	120.0(10)
C(9)-C(8)-C(7)	124.5(10)
N(3)-C(8)-C(7)	115.4(9)

C(34)-C(33)-N(8)	110.4(7)
C(34)-C(33)-H(33A)	109.6
N(8)-C(33)-H(33A)	109.6
C(34)-C(33)-H(33B)	109.6
N(8)-C(33)-H(33B)	109.6
H(33A)-C(33)-H(33B)	108.1
C(41)-C(42)-C(43)	117.5(10)
C(41)-C(42)-H(42)	121.3
C(43)-C(42)-H(42)	121.3
C(40)-C(39)-N(8)	109.6(8)
C(40)-C(39)-H(39A)	109.8
N(8)-C(39)-H(39A)	109.8
C(40)-C(39)-H(39B)	109.8
N(8)-C(39)-H(39B)	109.8
H(39A)-C(39)-H(39B)	108.2
C(26)-C(25)-C(24)	119.4(10)
C(26)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3
N(9)-C(40)-C(41)	119.6(10)
N(9)-C(40)-C(39)	116.2(9)
C(41)-C(40)-C(39)	124.0(10)
C(16)-C(17)-C(22)	117.6(9)
C(16)-C(17)-C(18)	124.0(9)
C(22)-C(17)-C(18)	118.3(9)
C(30)-C(29)-C(28)	119.4(8)
C(30)-C(29)-H(29)	120.3
C(28)-C(29)-H(29)	120.3
C(8)-C(9)-C(10)	120.8(11)
C(8)-C(9)-H(9)	119.6
C(10)-C(9)-H(9)	119.6
N(3)-C(12)-C(11)	122.1(11)
N(3)-C(12)-H(12)	118.9
C(11)-C(12)-H(12)	118.9
N(8)-C(32)-C(31)	111.7(8)
N(8)-C(32)-H(32A)	109.3
C(31)-C(32)-H(32A)	109.3

N(8)-C(32)-H(32B)	109.3
C(31)-C(32)-H(32B)	109.3
H(32A)-C(32)-H(32B)	107.9
C(5)-C(6)-N(2)	111.2(7)
C(5)-C(6)-H(6A)	109.4
N(2)-C(6)-H(6A)	109.4
C(5)-C(6)-H(6B)	109.4
N(2)-C(6)-H(6B)	109.4
H(6A)-C(6)-H(6B)	108.0
N(1)-C(5)-C(4)	120.3(9)
N(1)-C(5)-C(6)	115.3(8)
C(4)-C(5)-C(6)	124.3(9)
C(44)-C(43)-C(42)	120.4(10)
C(44)-C(43)-H(43)	119.8
C(42)-C(43)-H(43)	119.8
C(21)-C(20)-C(19)	117.3(9)
C(21)-C(20)-H(20)	121.4
C(19)-C(20)-H(20)	121.4
C(18)-C(19)-C(20)	123.3(10)
C(18)-C(19)-H(19)	118.4
C(20)-C(19)-H(19)	118.4
N(9)-C(44)-C(43)	121.2(10)
N(9)-C(44)-H(44)	119.4
C(43)-C(44)-H(44)	119.4
C(3)-C(4)-C(5)	119.4(10)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(29)-C(30)-C(31)	120.5(9)
C(29)-C(30)-H(30)	119.7
C(31)-C(30)-H(30)	119.7
C(1)-C(2)-C(3)	118.4(10)
C(1)-C(2)-H(2)	120.8
C(3)-C(2)-H(2)	120.8
C(12)-C(11)-C(10)	119.1(11)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4

N(7)-C(38)-C(35)	121.1(10)
N(7)-C(38)-H(38)	119.4
C(35)-C(38)-H(38)	119.4
C(9)-C(10)-C(11)	118.2(11)
C(9)-C(10)-H(10)	120.9
C(11)-C(10)-H(10)	120.9
C(4)-C(3)-C(2)	120.1(10)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
N(100)-C(100)-C(101)	179.0(14)
F(101)-B(2)-F(102)	114.4(14)
F(101)-B(2)-F(5)	58.0(12)
F(102)-B(2)-F(5)	125.1(15)
F(101)-B(2)-F(7)	118.5(12)
F(102)-B(2)-F(7)	116.3(13)
F(5)-B(2)-F(7)	112.0(10)
F(101)-B(2)-F(8)	127.4(13)
F(102)-B(2)-F(8)	23.7(11)
F(5)-B(2)-F(8)	111.9(11)
F(7)-B(2)-F(8)	112.9(10)
F(101)-B(2)-F(6)	50.5(12)
F(102)-B(2)-F(6)	84.0(14)
F(5)-B(2)-F(6)	108.4(11)
F(7)-B(2)-F(6)	103.8(10)
F(8)-B(2)-F(6)	107.3(10)
F(101)-B(2)-F(100)	102.5(13)
F(102)-B(2)-F(100)	100.7(12)
F(5)-B(2)-F(100)	45.5(11)
F(7)-B(2)-F(100)	100.0(11)
F(8)-B(2)-F(100)	78.3(12)
F(6)-B(2)-F(100)	150.6(14)
N(300)-C(300)-C(301)	177.6(18)
N(200)-C(200)-C(201)	179.3(19)
F(2)-B(1)-F(4)	112.0(11)
F(2)-B(1)-F(1)	112.4(15)
F(4)-B(1)-F(1)	114.9(13)

F(2)-B(1)-F(3)	104.5(13)
F(4)-B(1)-F(3)	106.7(13)
F(1)-B(1)-F(3)	105.4(11)
C(200)-C(201)-H(20A)	109.5
C(200)-C(201)-H(20B)	109.5
H(20A)-C(201)-H(20B)	109.5
C(200)-C(201)-H(20C)	109.5
H(20A)-C(201)-H(20C)	109.5
H(20B)-C(201)-H(20C)	109.5
C(300)-C(301)-H(30A)	109.5
C(300)-C(301)-H(30B)	109.5
H(30A)-C(301)-H(30B)	109.5
C(300)-C(301)-H(30C)	109.5
H(30A)-C(301)-H(30C)	109.5
H(30B)-C(301)-H(30C)	109.5
C(100)-C(101)-H(10A)	109.5
C(100)-C(101)-H(10B)	109.5
H(10A)-C(101)-H(10B)	109.5
C(100)-C(101)-H(10C)	109.5
H(10A)-C(101)-H(10C)	109.5
H(10B)-C(101)-H(10C)	109.5
N(500)-C(501)-C(500)	170(3)
C(401)-C(400)-H(40A)	109.5
C(401)-C(400)-H(40B)	109.5
H(40A)-C(400)-H(40B)	109.5
C(401)-C(400)-H(40C)	109.5
H(40A)-C(400)-H(40C)	109.5
H(40B)-C(400)-H(40C)	109.5
N(400)-C(401)-C(400)	177(5)

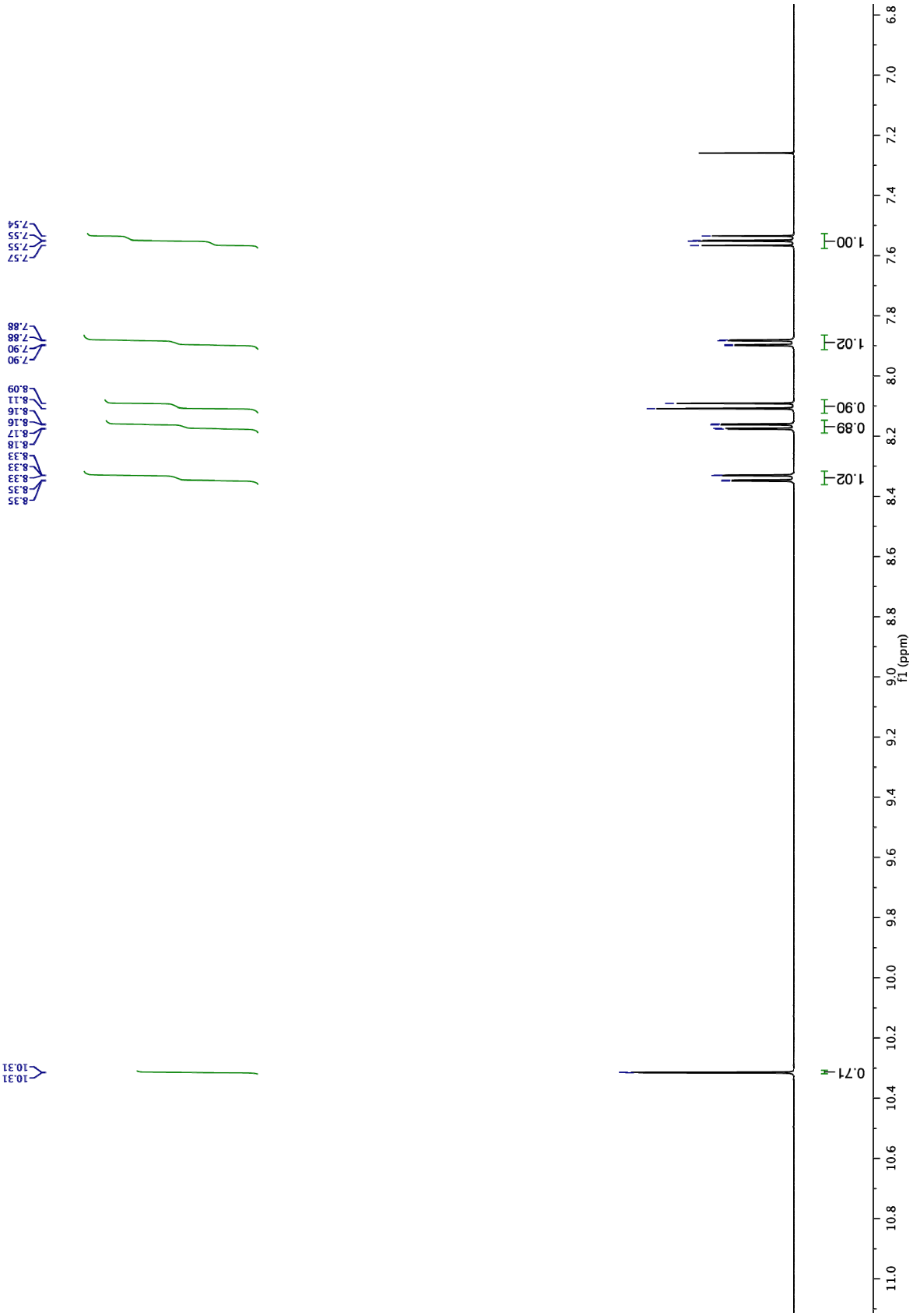


Figure **S11**. ^{1}H NMR spectrum of **2** in $CDCl_3$.

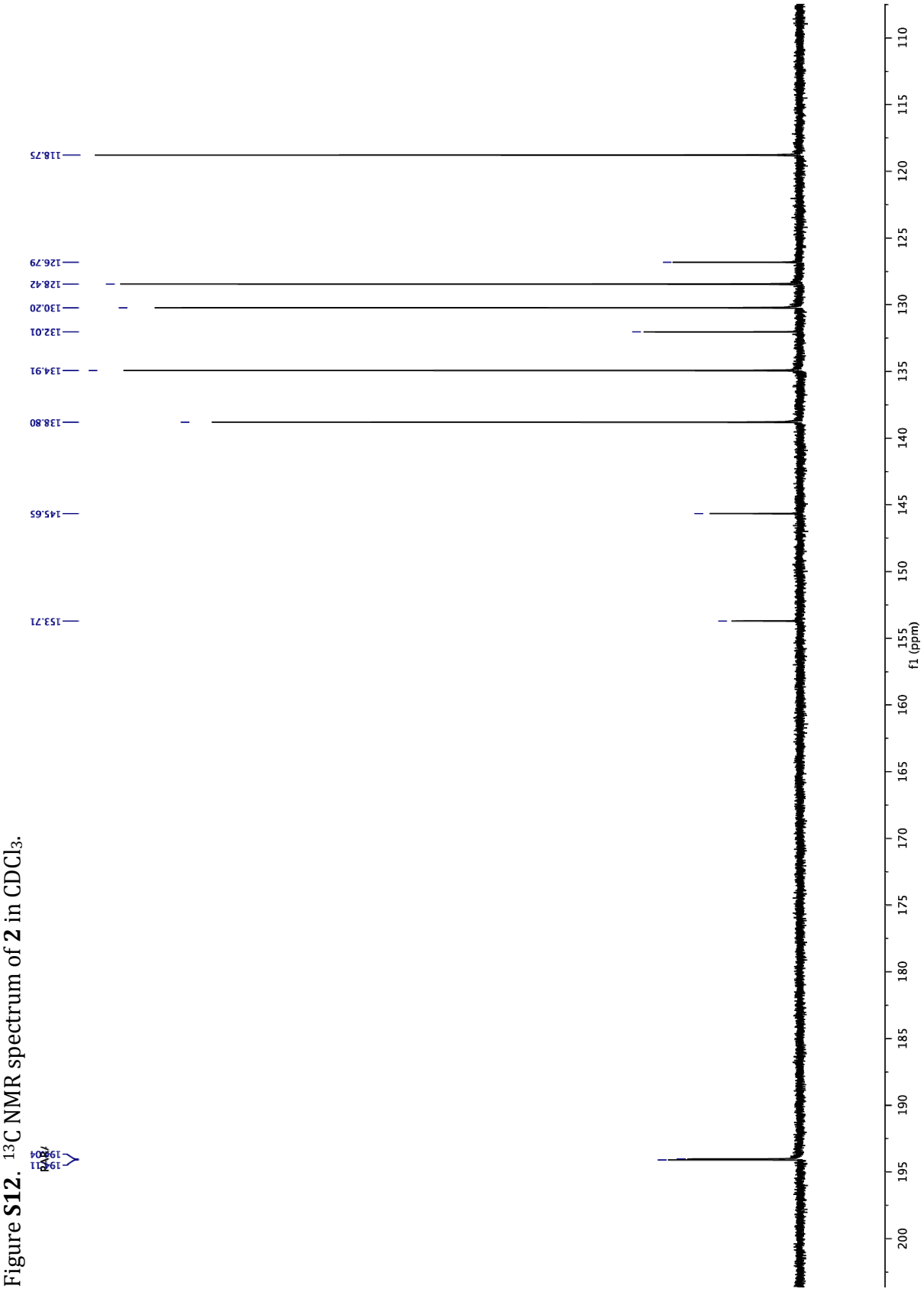


Figure **S12**. ^{13}C NMR spectrum of **2** in $CDCl_3$.

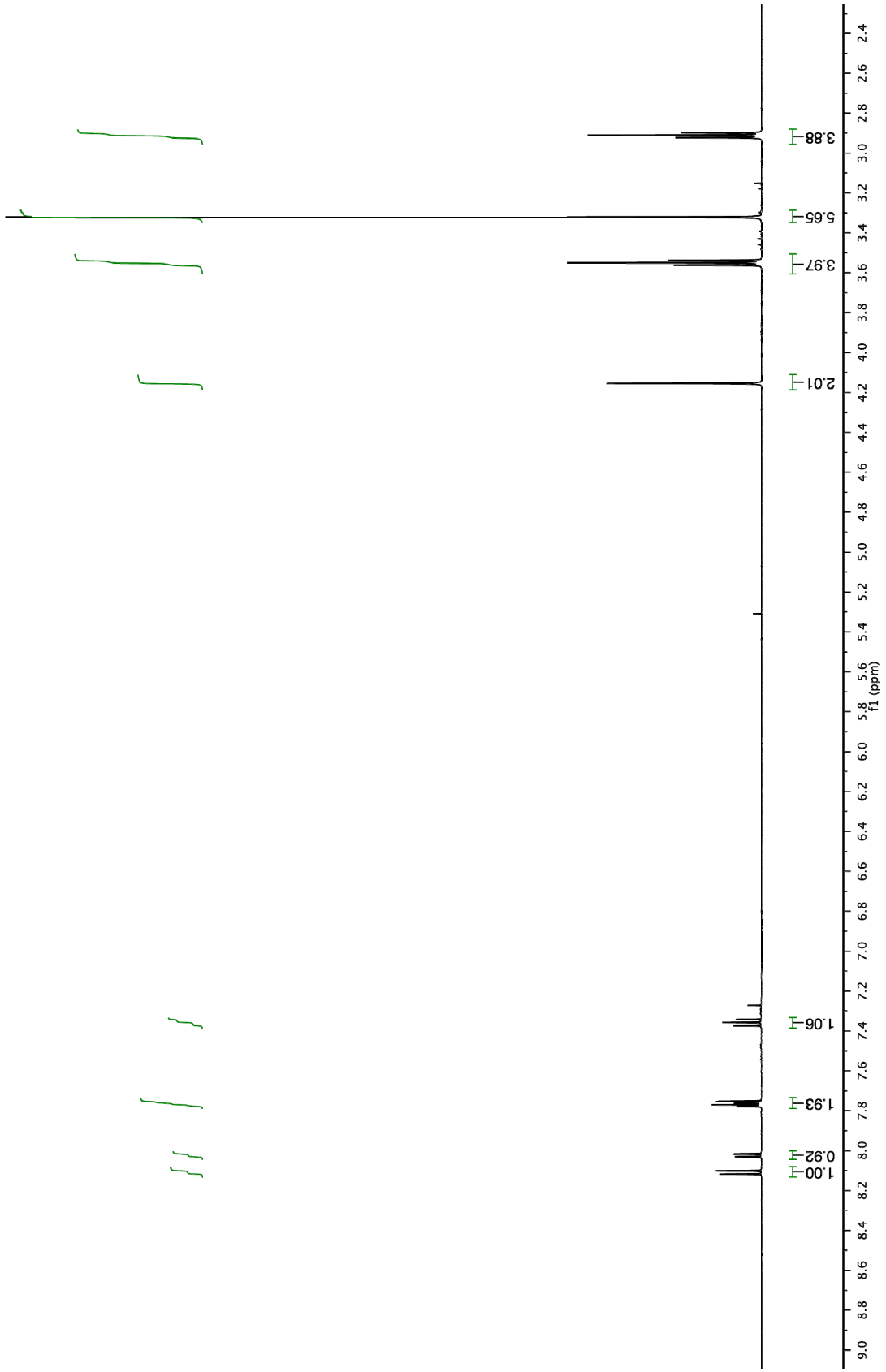


Figure **S13**. ^{1}H NMR spectrum of **3** in $CDCl_3$.
DS-II-232-B
DS-II-244-E

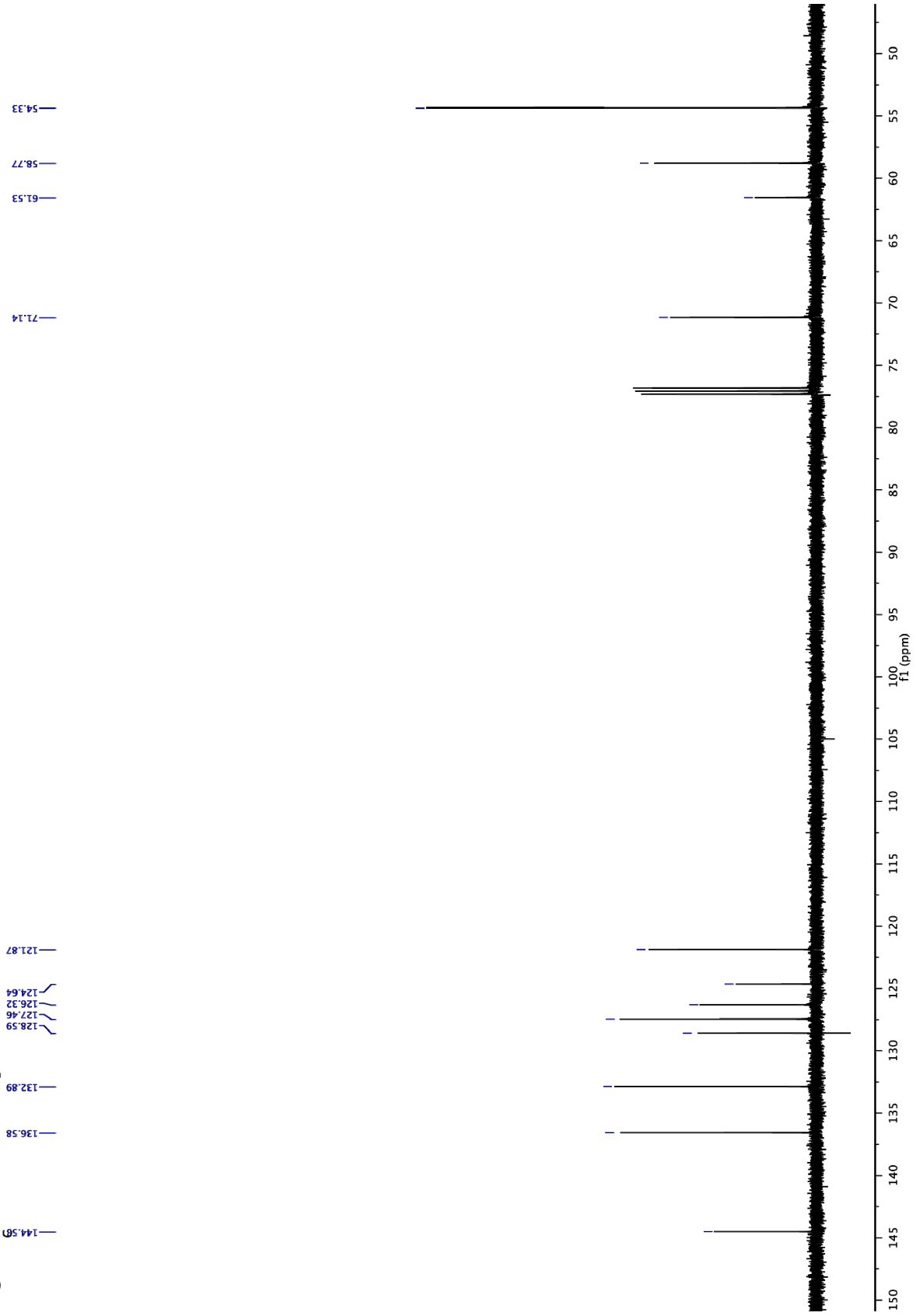


Figure **S14**. ^{13}C NMR spectrum of **3** in $CDCl_3$.

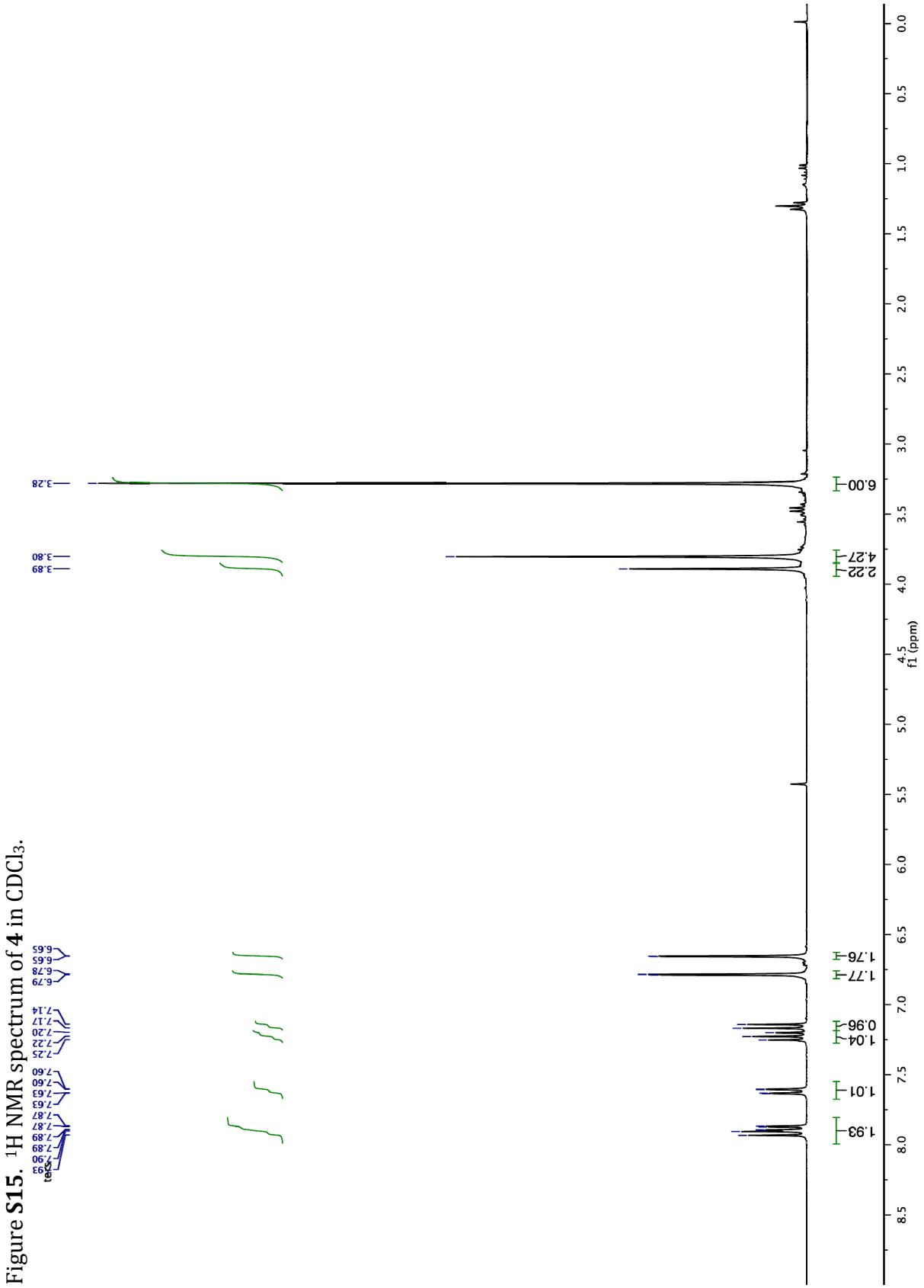


Figure **S15**. ^{1}H NMR spectrum of **4** in $CDCl_3$.

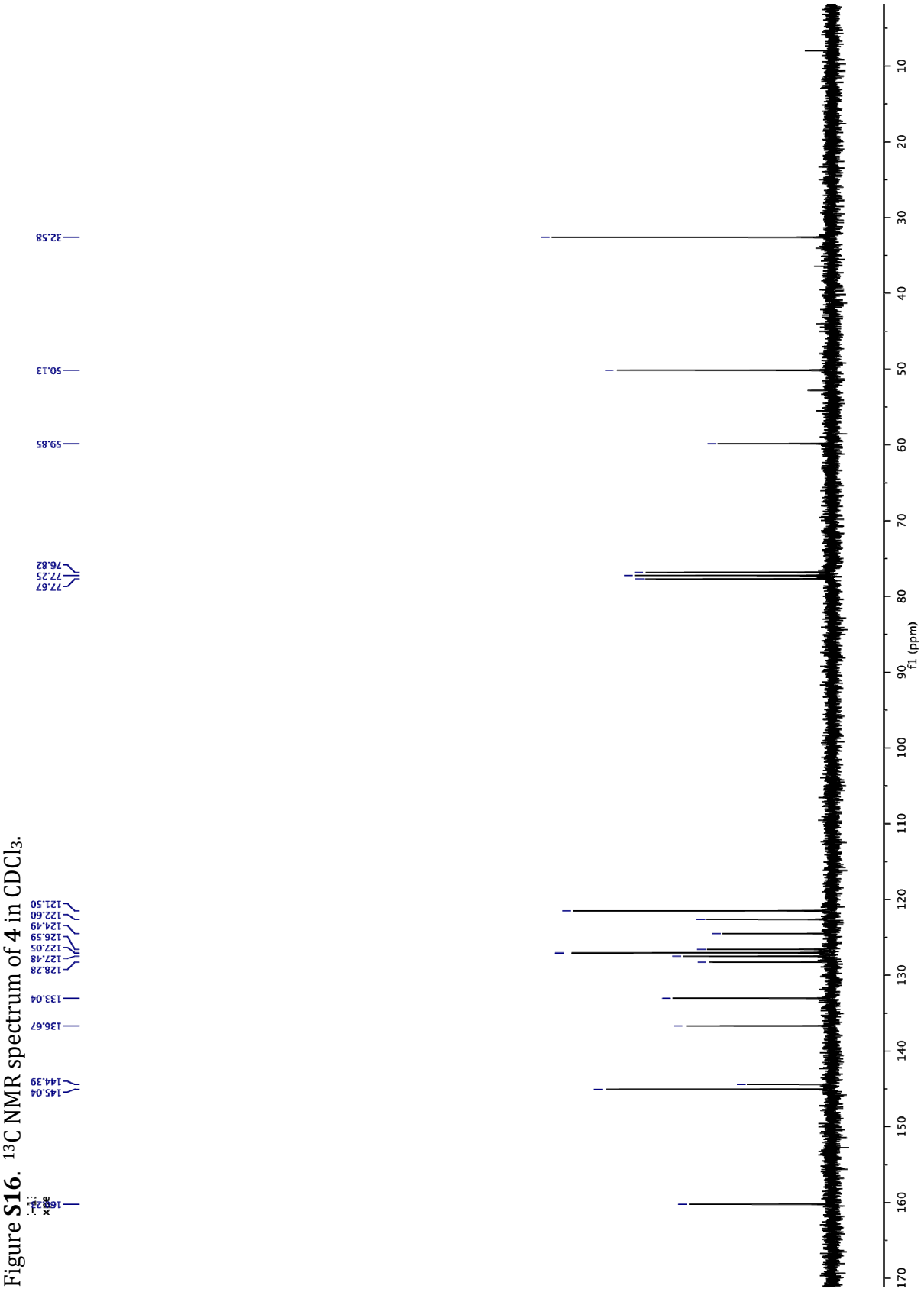


Figure **S16**. ^{13}C NMR spectrum of **4** in $CDCl_3$.

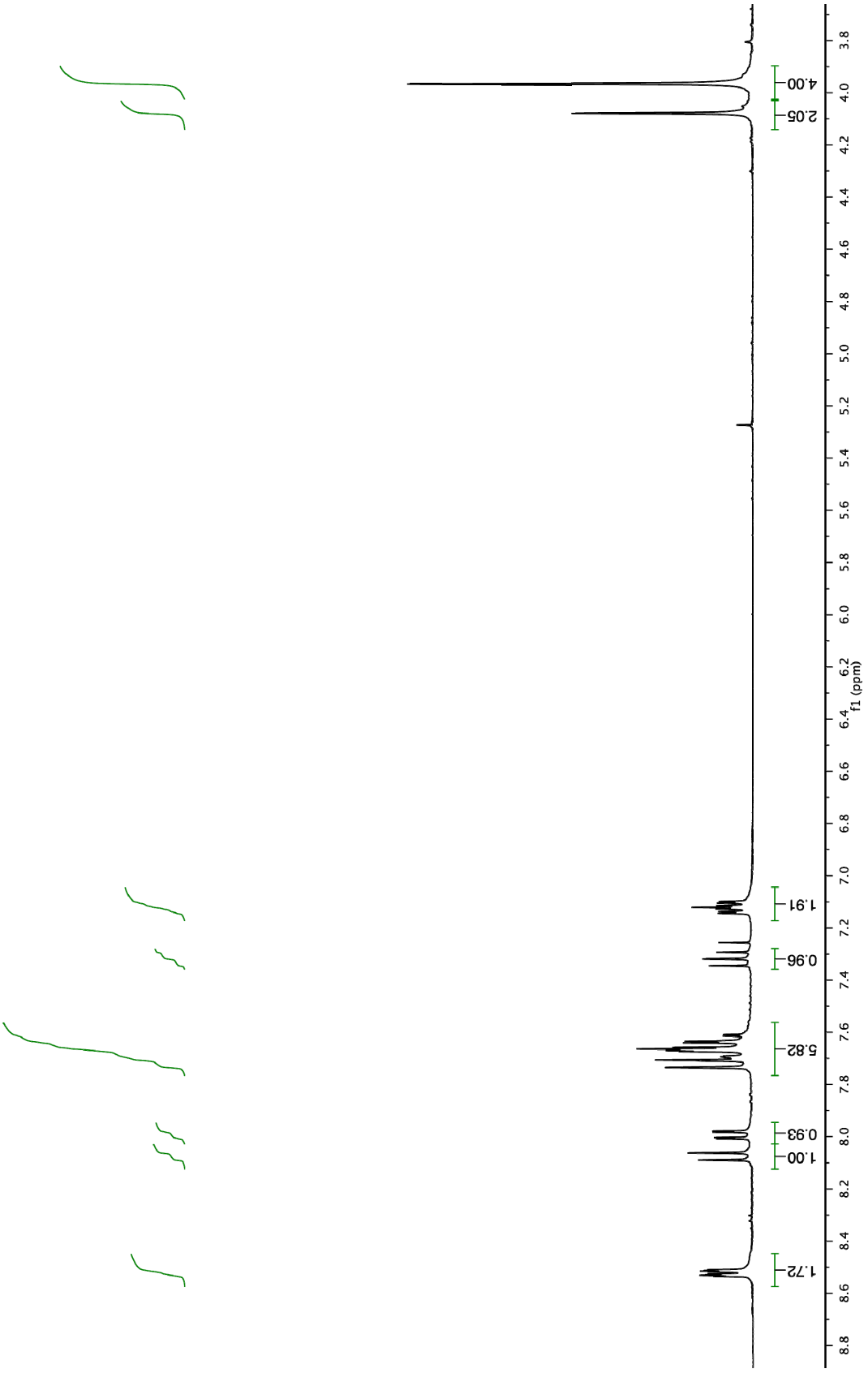


Figure **S17**. ^{1}H NMR spectrum of **5** in $CDCl_3$.

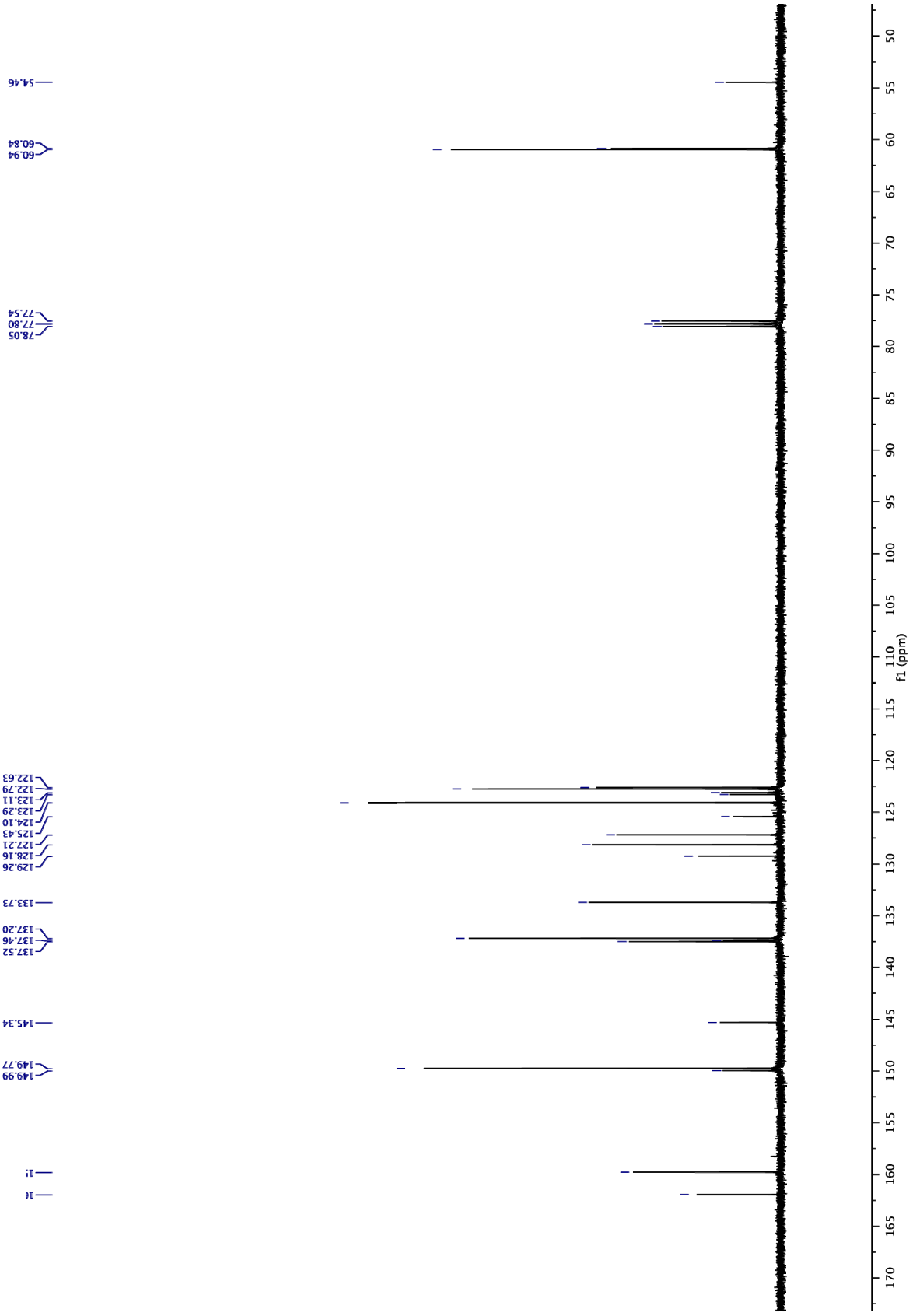


Figure **S18**. ^{13}C NMR spectrum of **5** in $CDCl_3$.

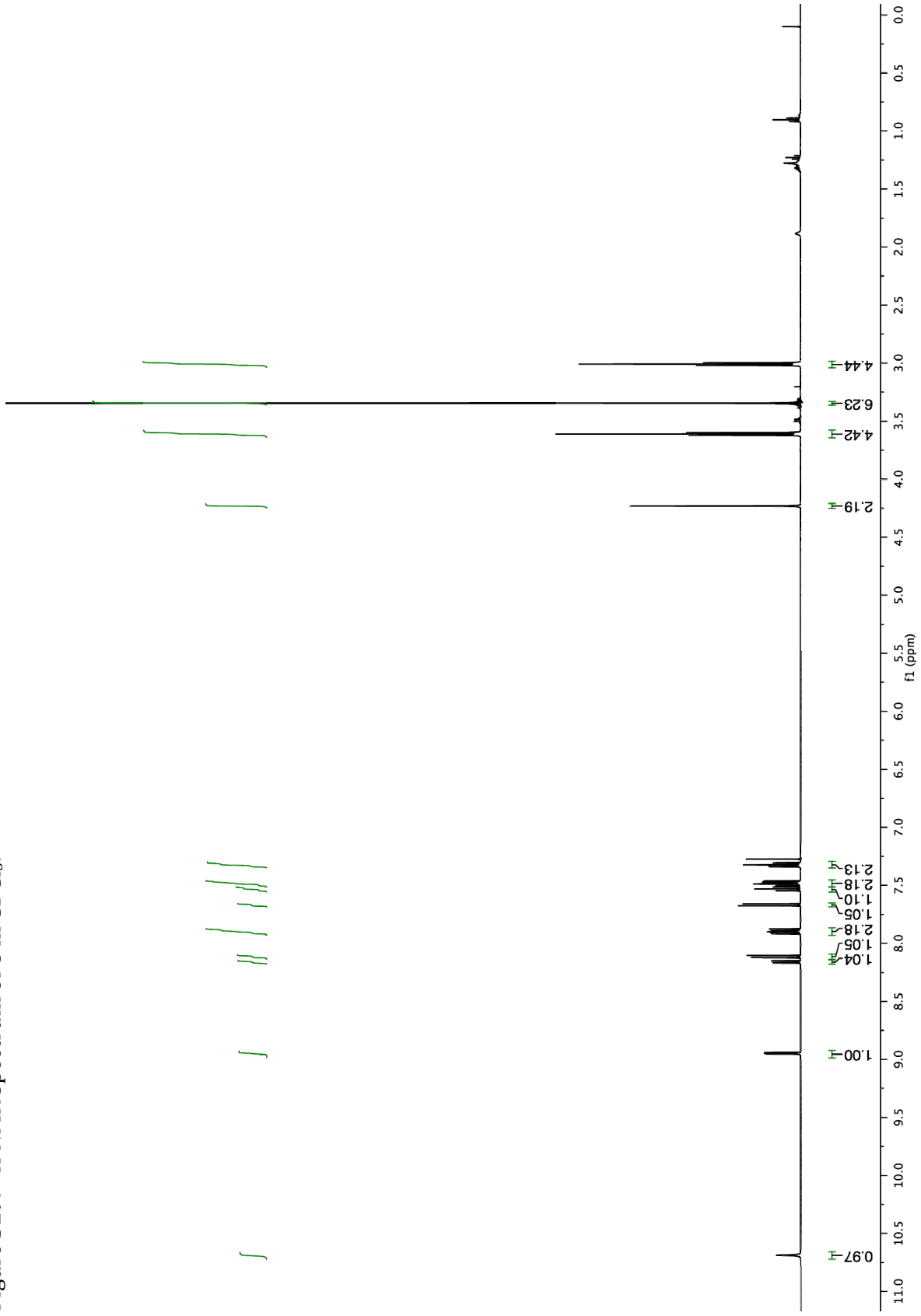


Figure **S19**. ^{1}H NMR spectrum of **6** in $CDCl_3$.

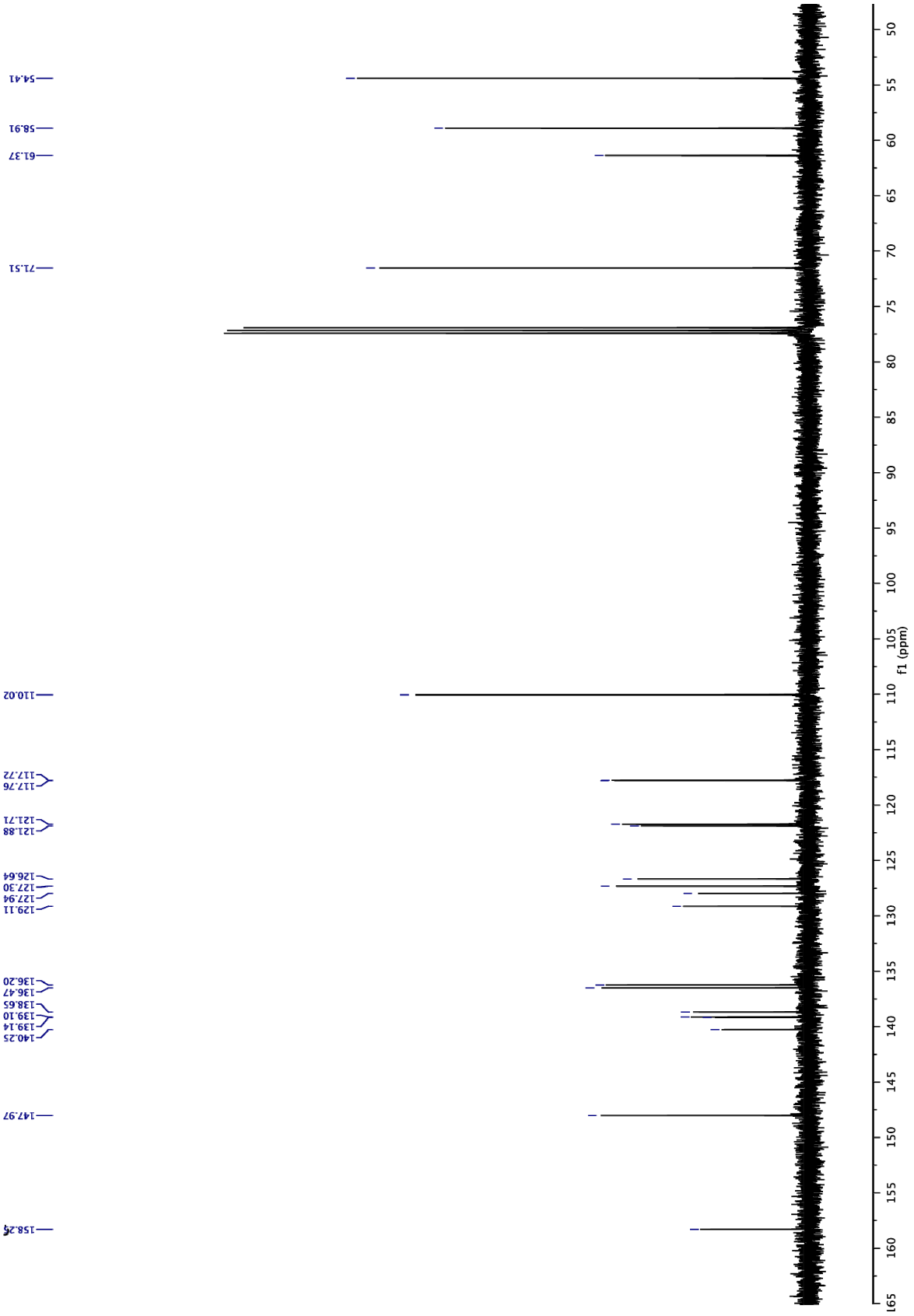


Figure **S20**. ^{13}C NMR spectrum of **6** in $CDCl_3$.

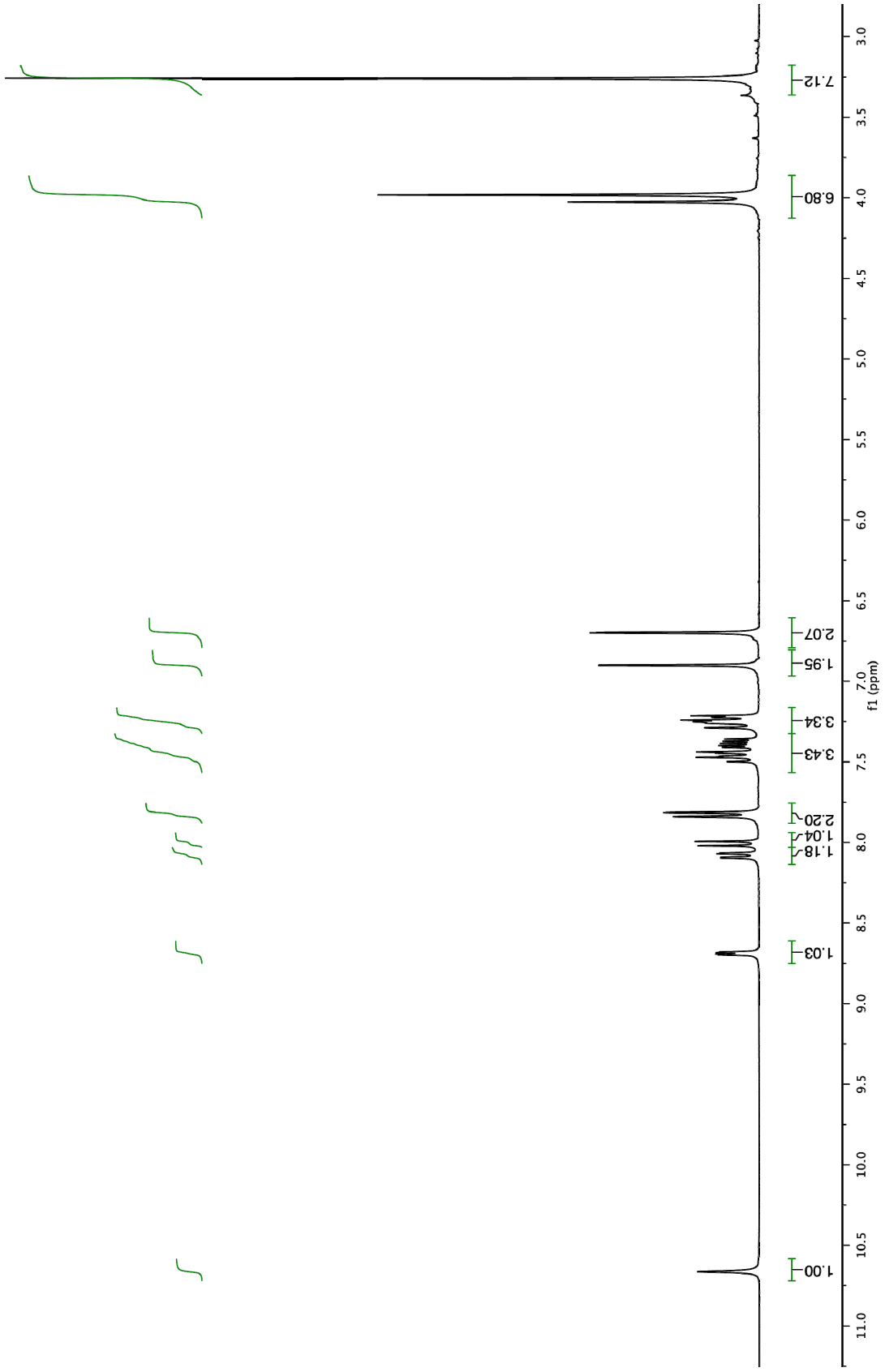


Figure **S21**. ^{1}H NMR spectrum of **7** in $CDCl_3$.

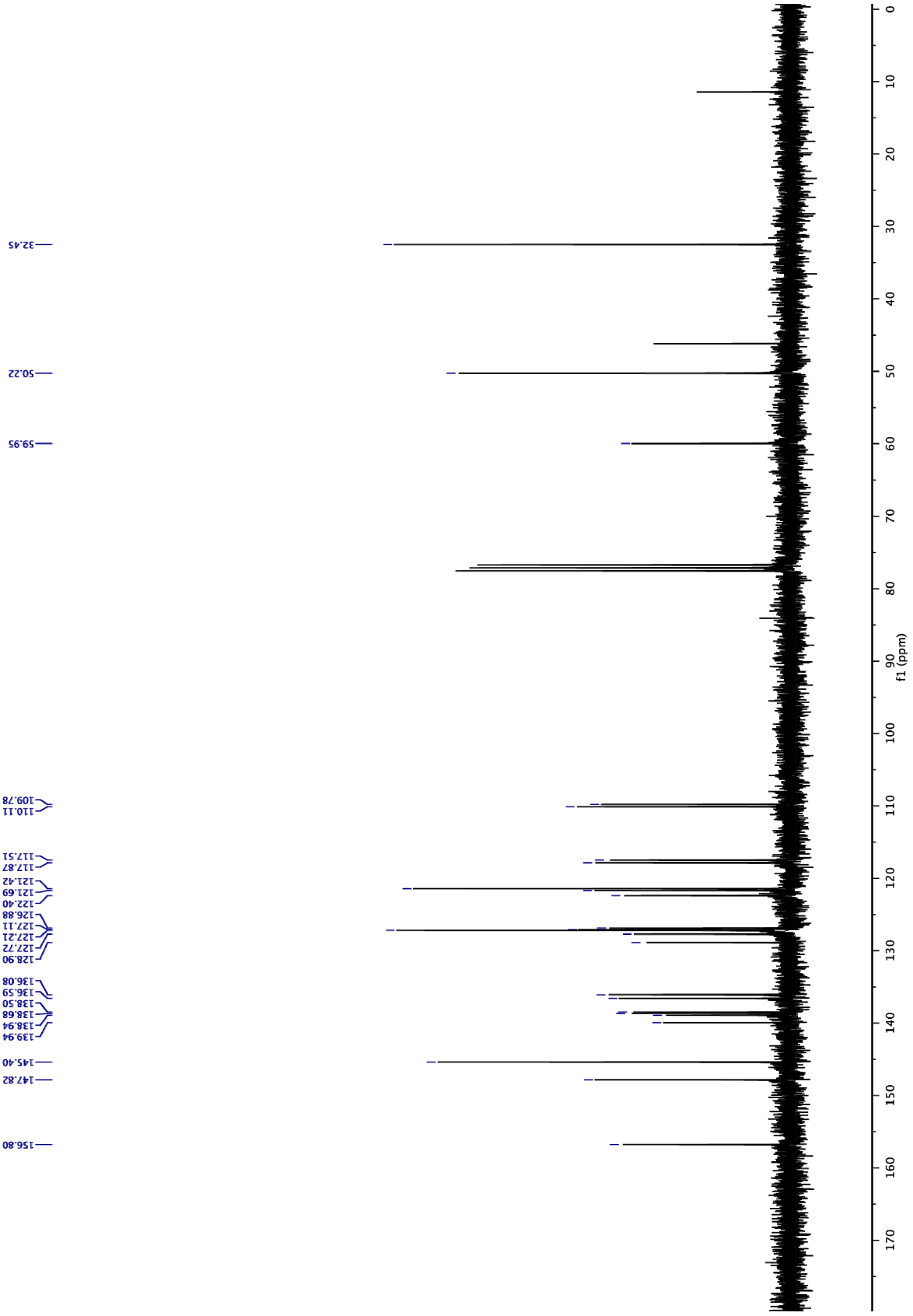


Figure **S22**. ^{13}C NMR spectrum of **7** in $CDCl_3$.

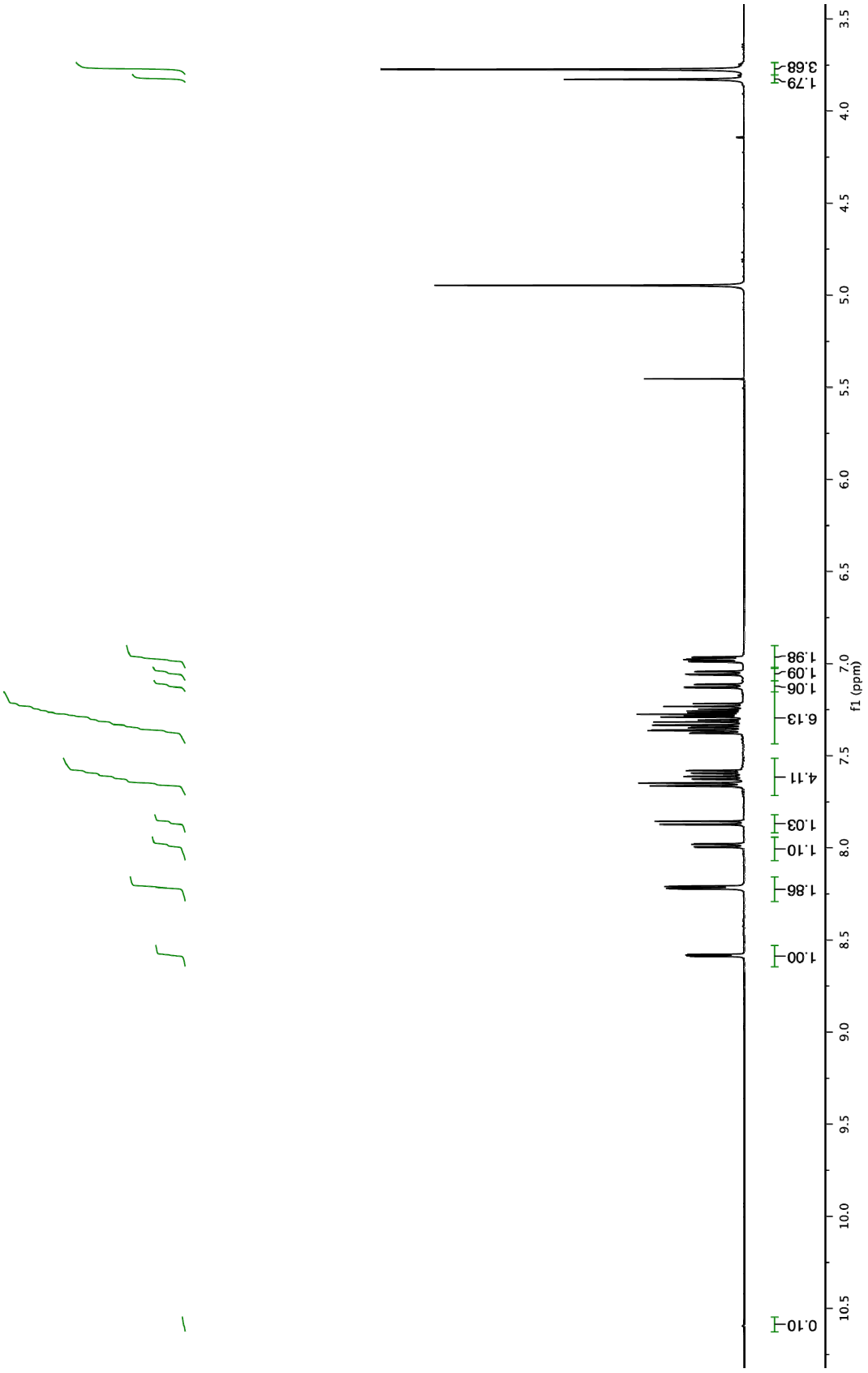


Figure **S23**. ^{1}H NMR spectrum of **8** in CD_3OD.

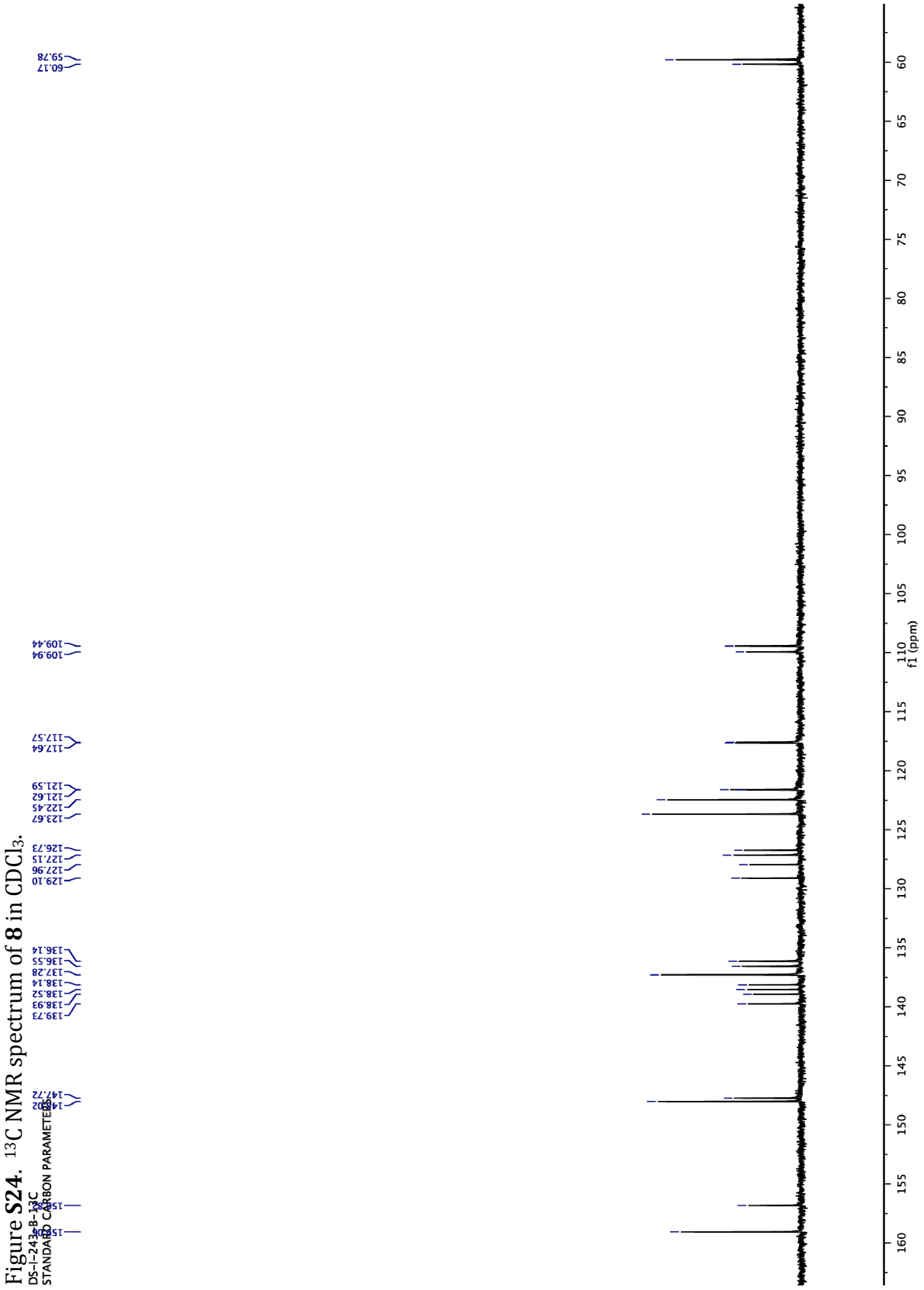


Figure **S24**. ^{13}C NMR spectrum of **8** in $CDCl_3$.

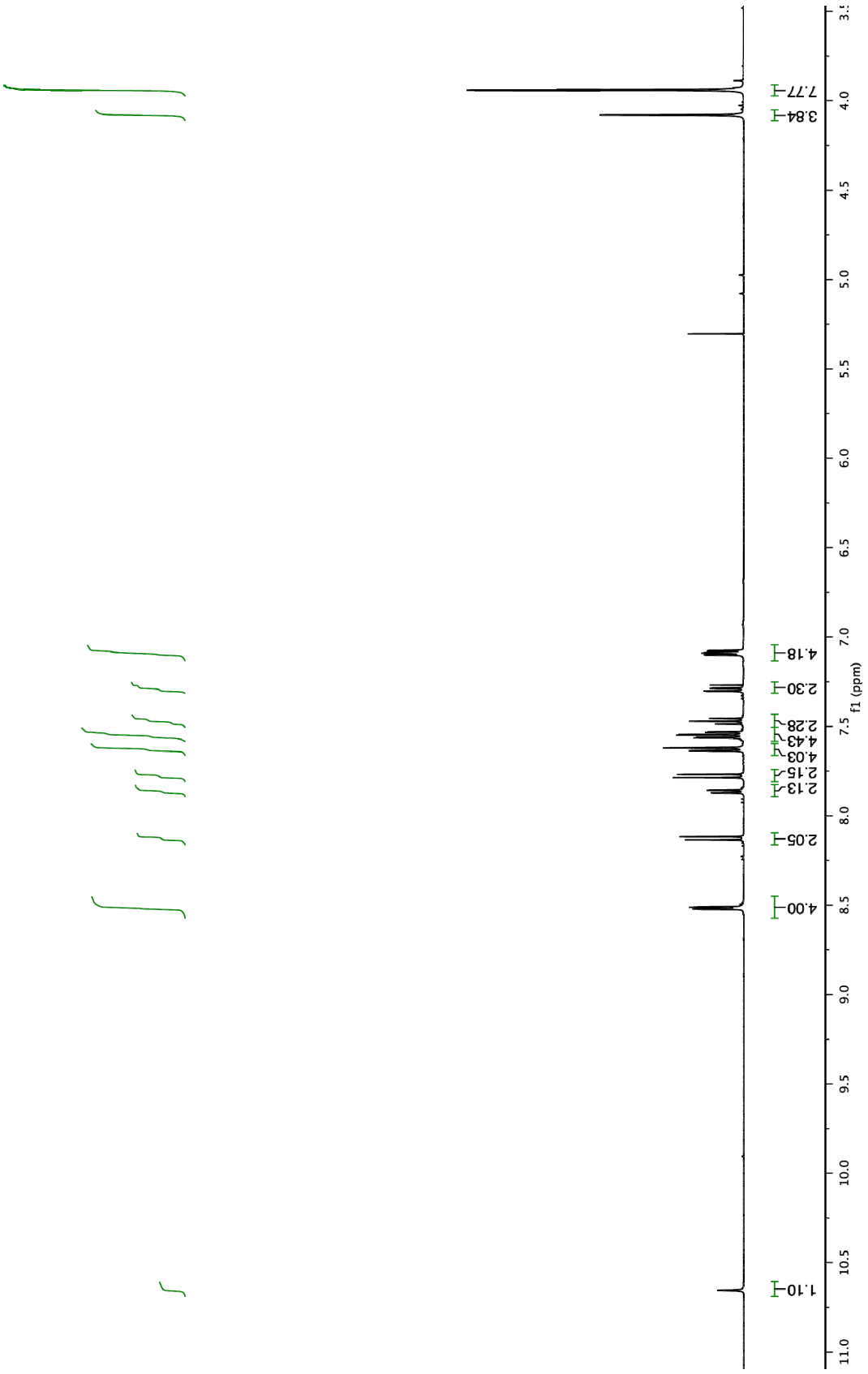


Figure **S25**. ^{1}H NMR spectrum of **9** in $CDCl_3$.

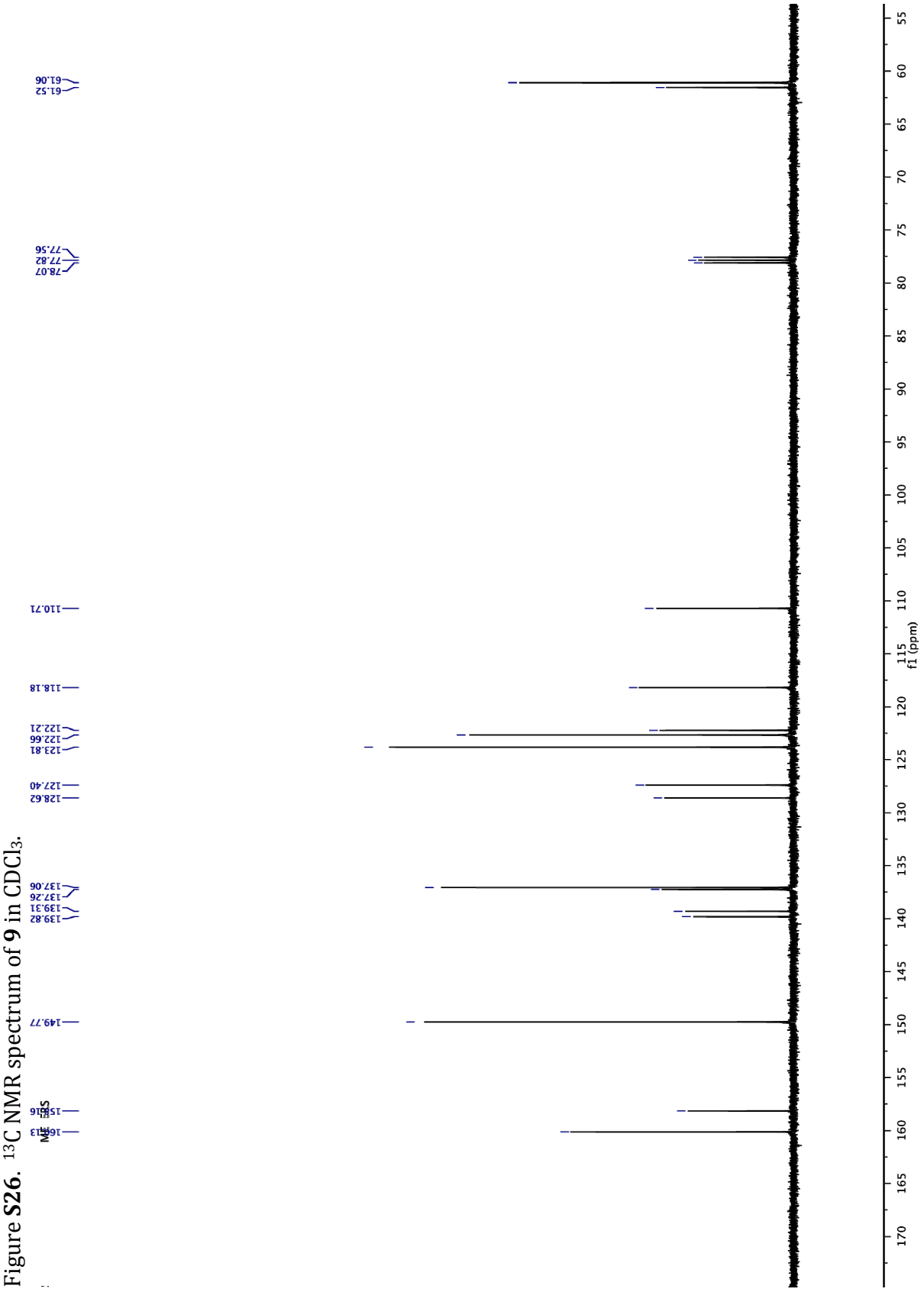


Figure **S26**. ^{13}C NMR spectrum of **9** in $CDCl_3$.

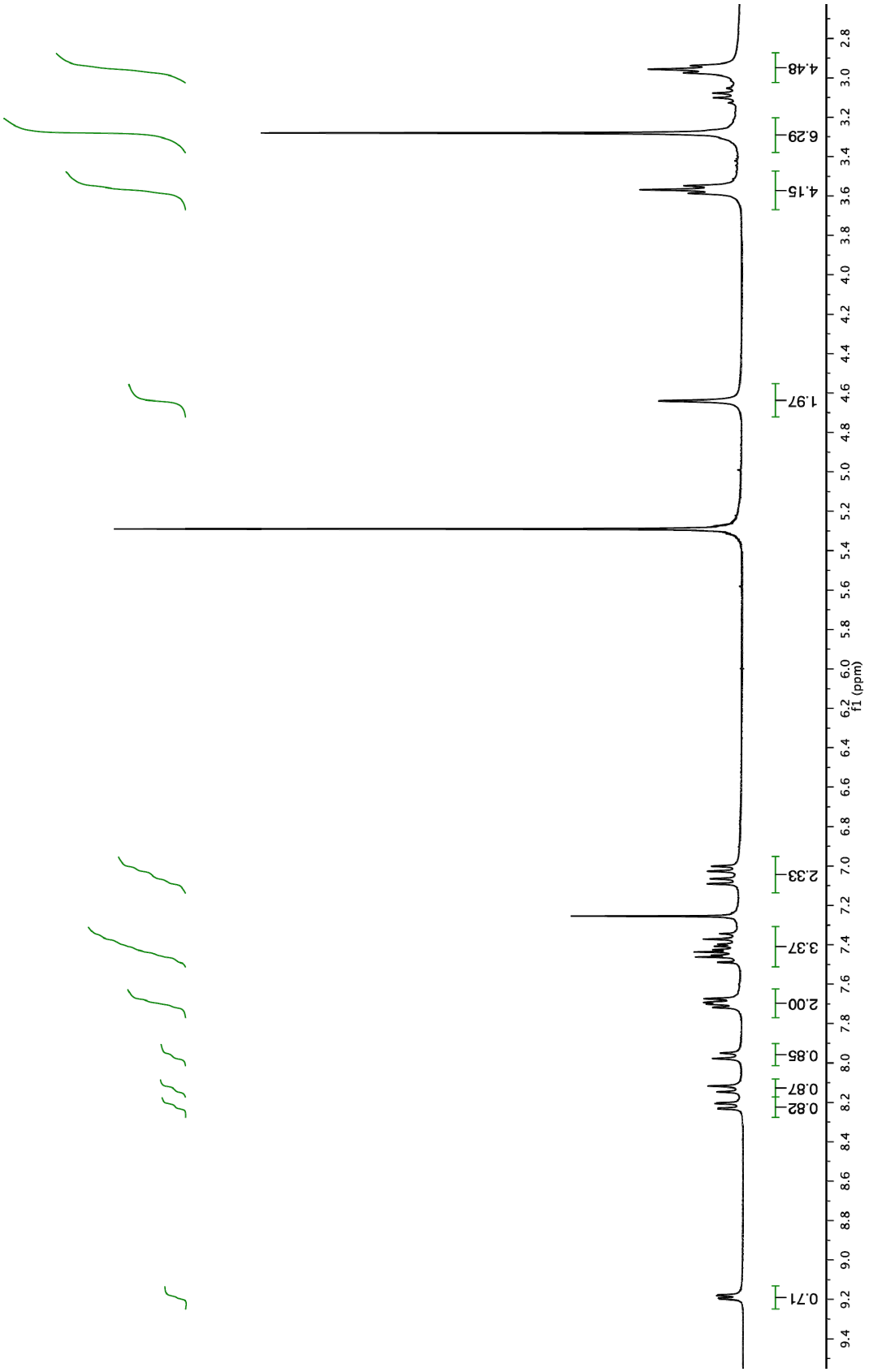


Figure **S27**. ^{1}H NMR spectrum of **10** in $CDCl_3$.

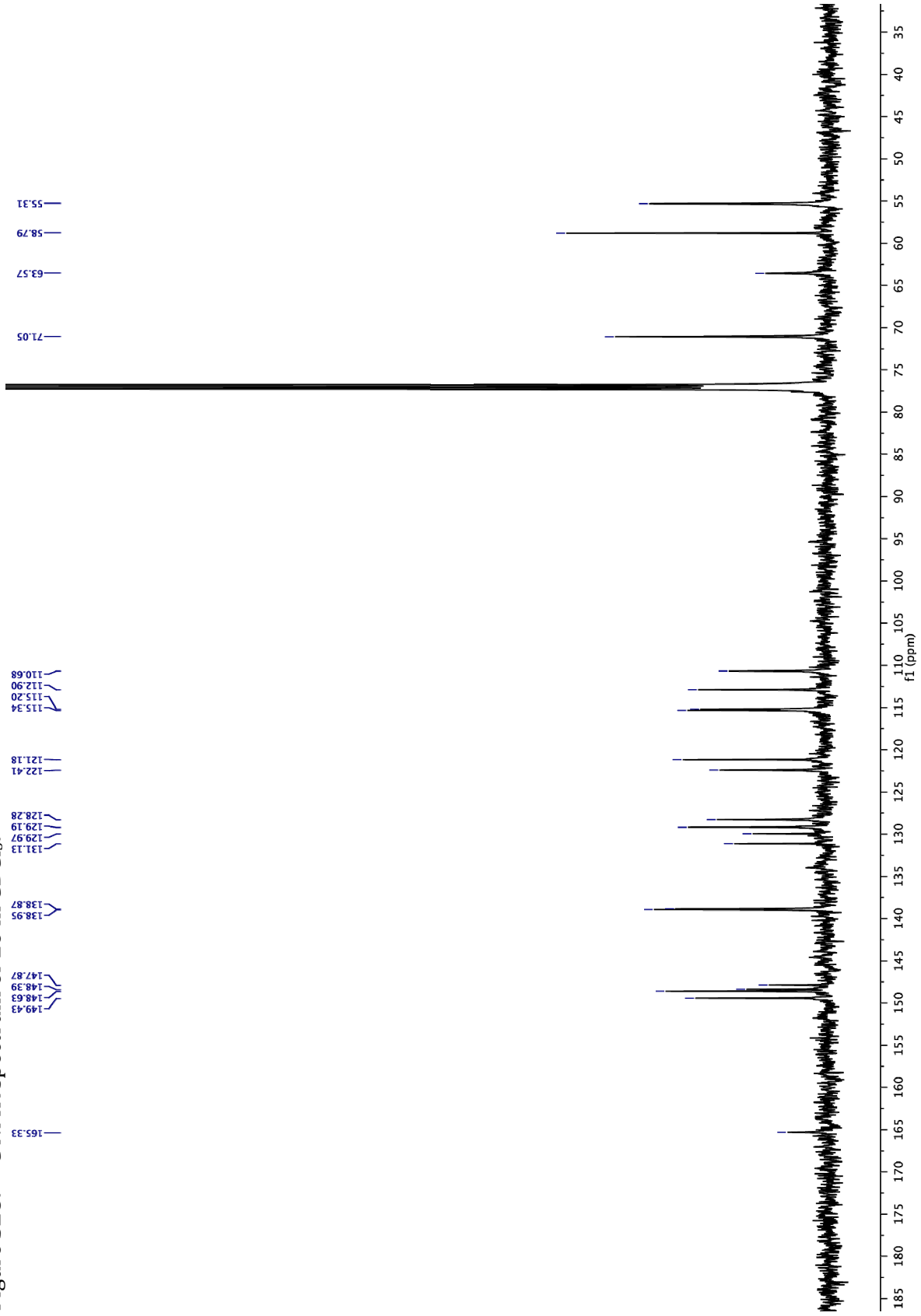


Figure **S28**. ^{13}C NMR spectrum of **10** in $CDCl_3$.

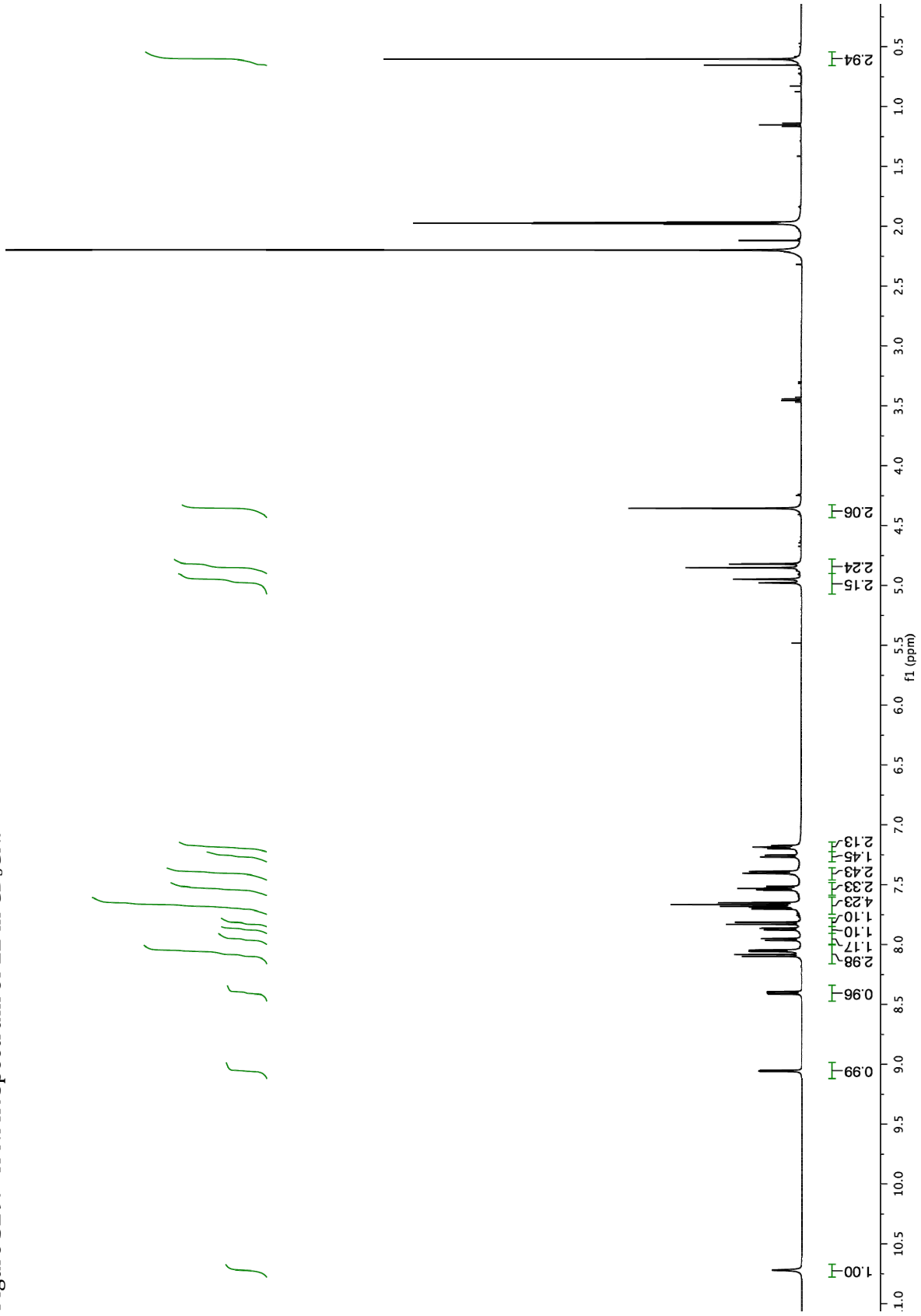


Figure **S29**. ^{1}H NMR spectrum of **12** in CD_3CN.

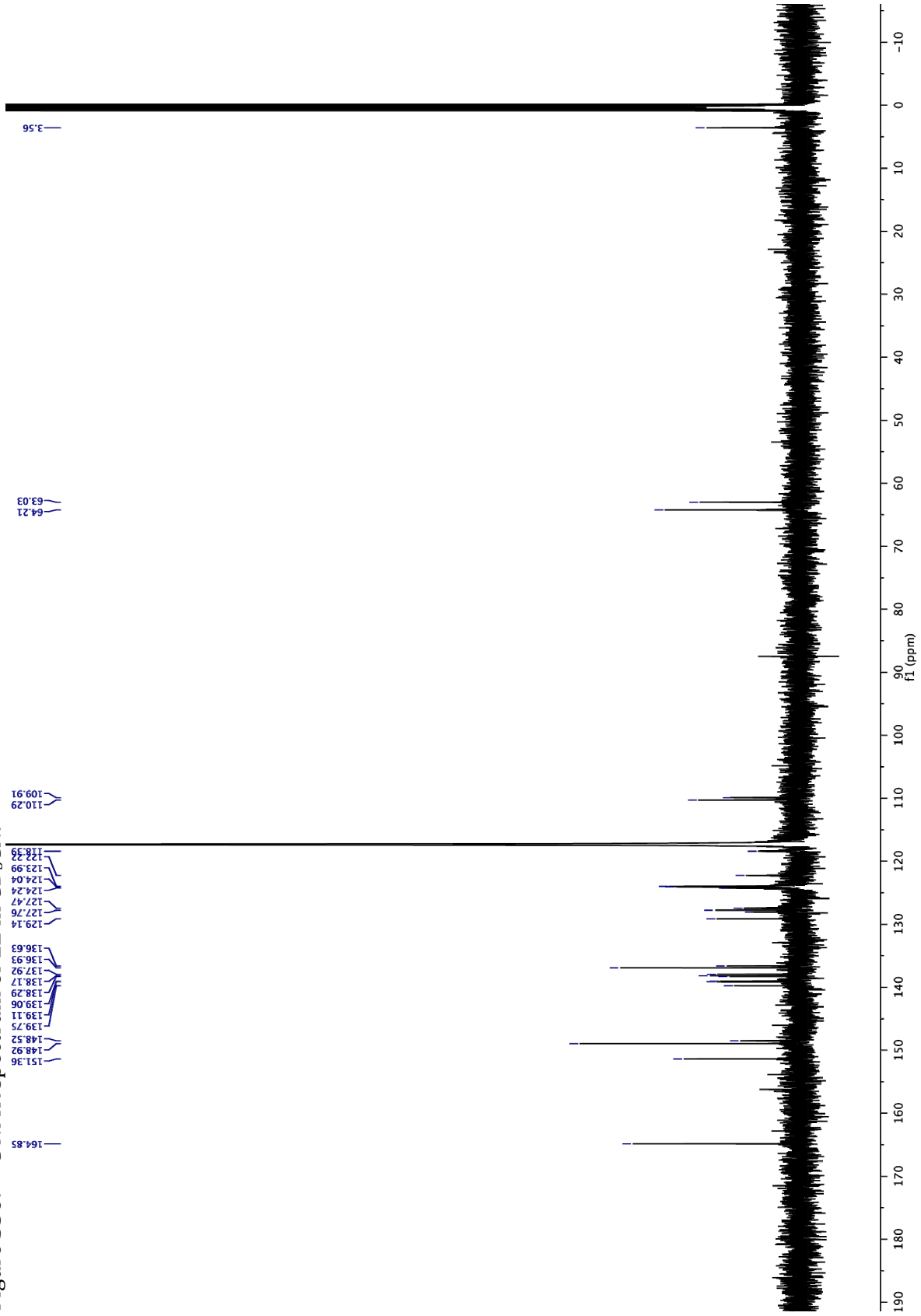


Figure **S30**. ^{13}C NMR spectrum of **12** in CD_3CN.

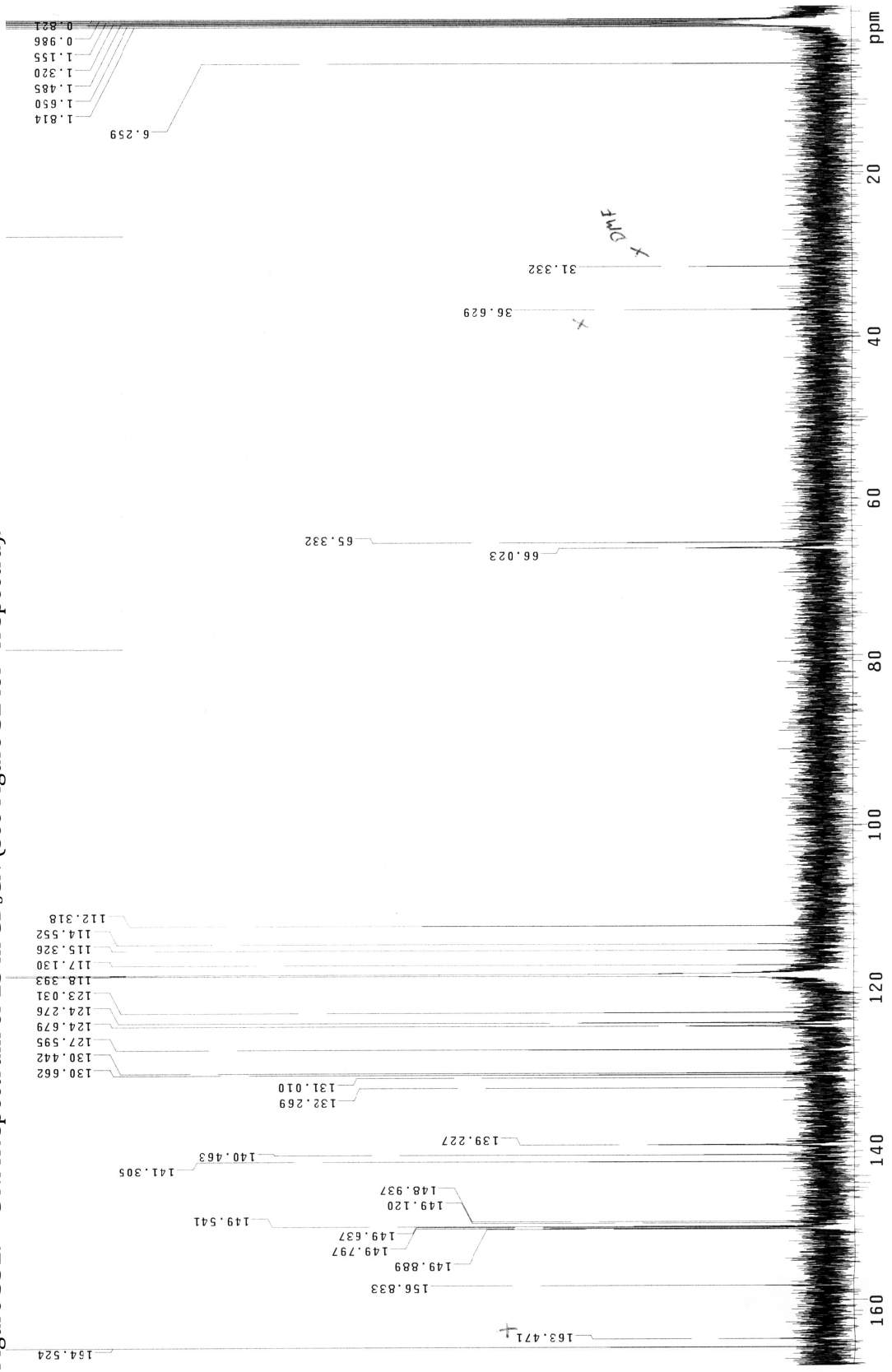


Figure **S31**. ^{13}C NMR spectrum of **13** in CD_3CN (see Figure **S2** for ^{1}H spectra).

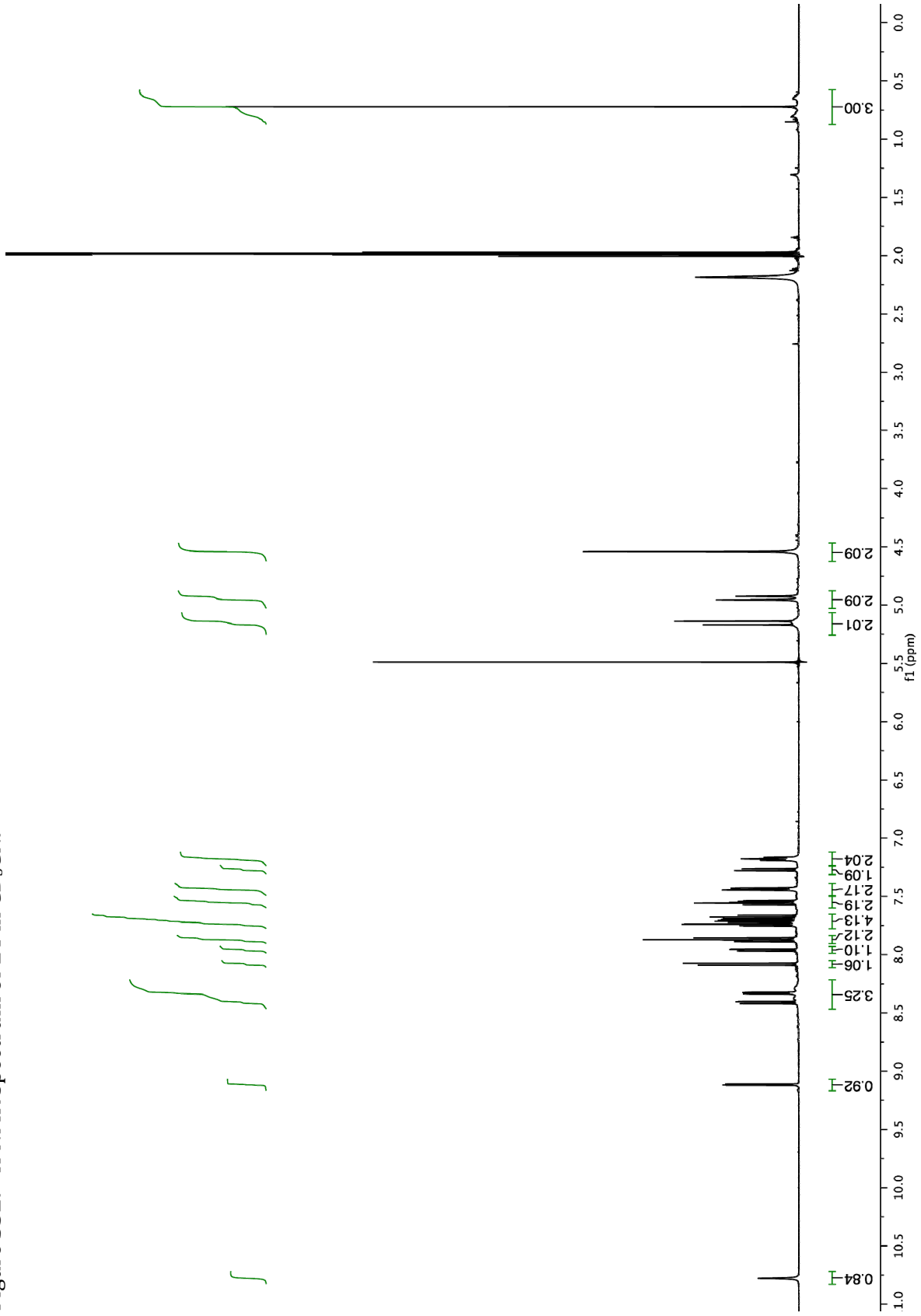


Figure **S32**. ^{1}H NMR spectrum of **14** in CD_3CN.

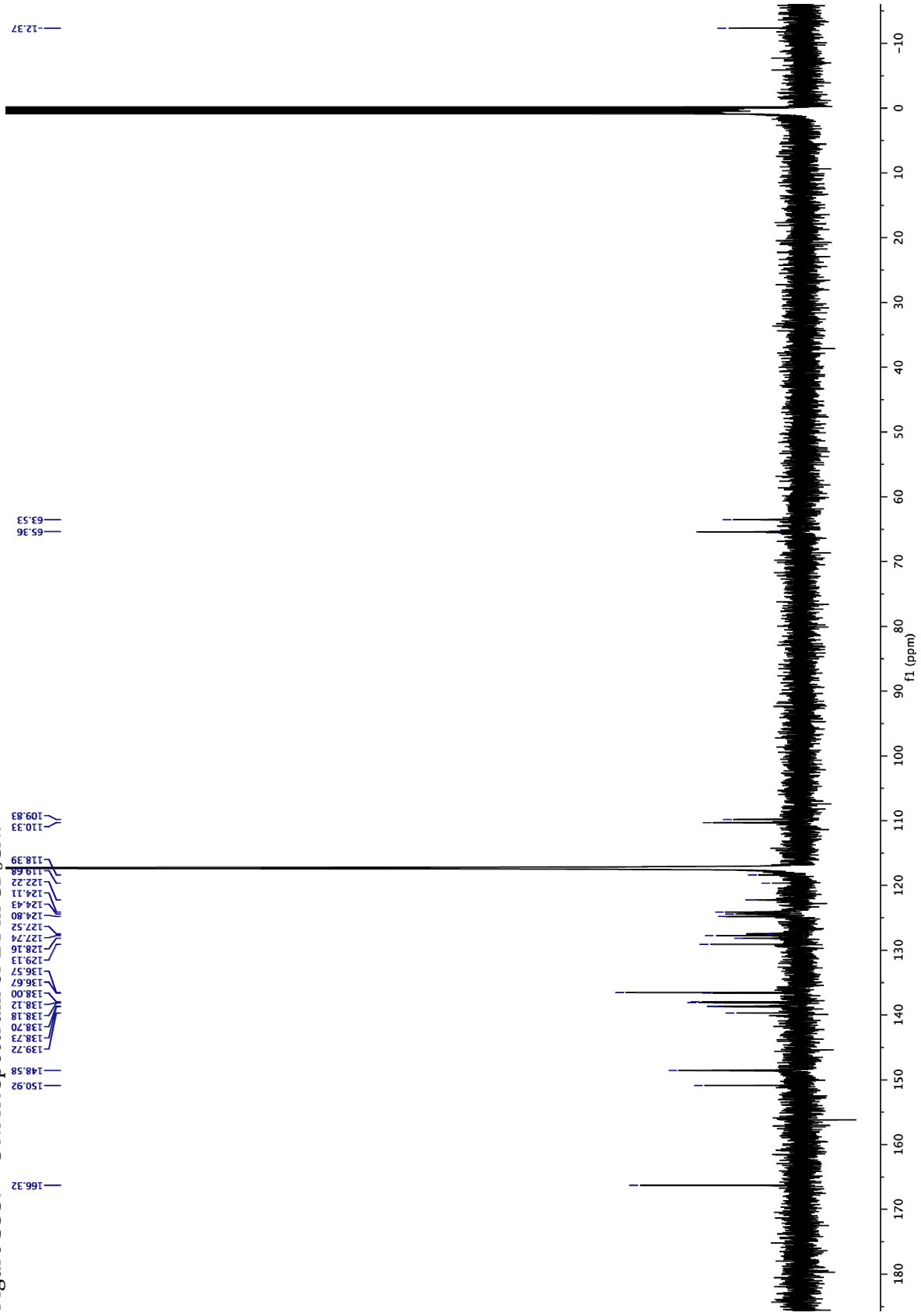


Figure **S33**. ^{13}C NMR spectrum of **14** in CD_3CN.

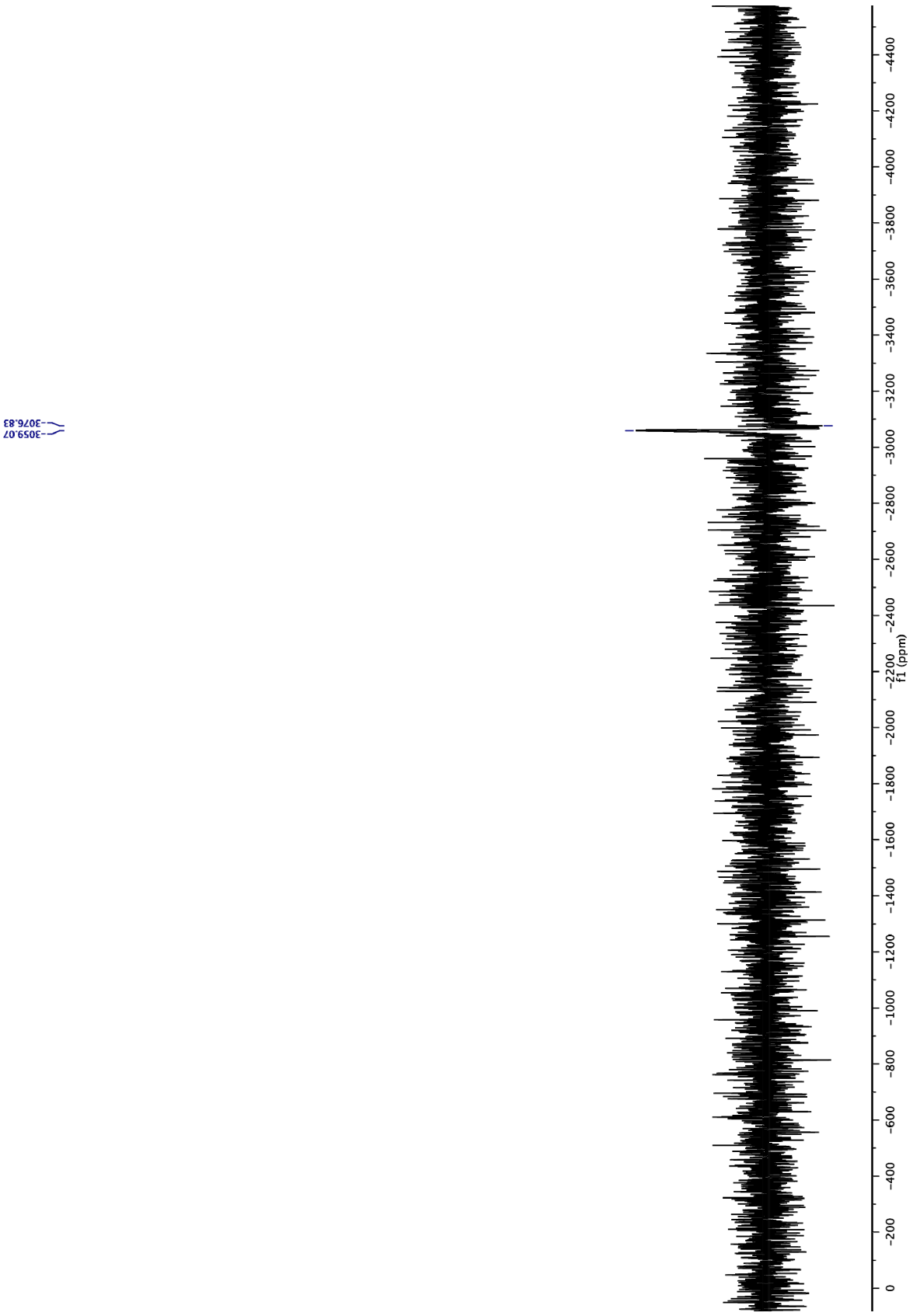


Figure **S34**. ^{195}Pt NMR spectrum of **14** in CD_3CN.

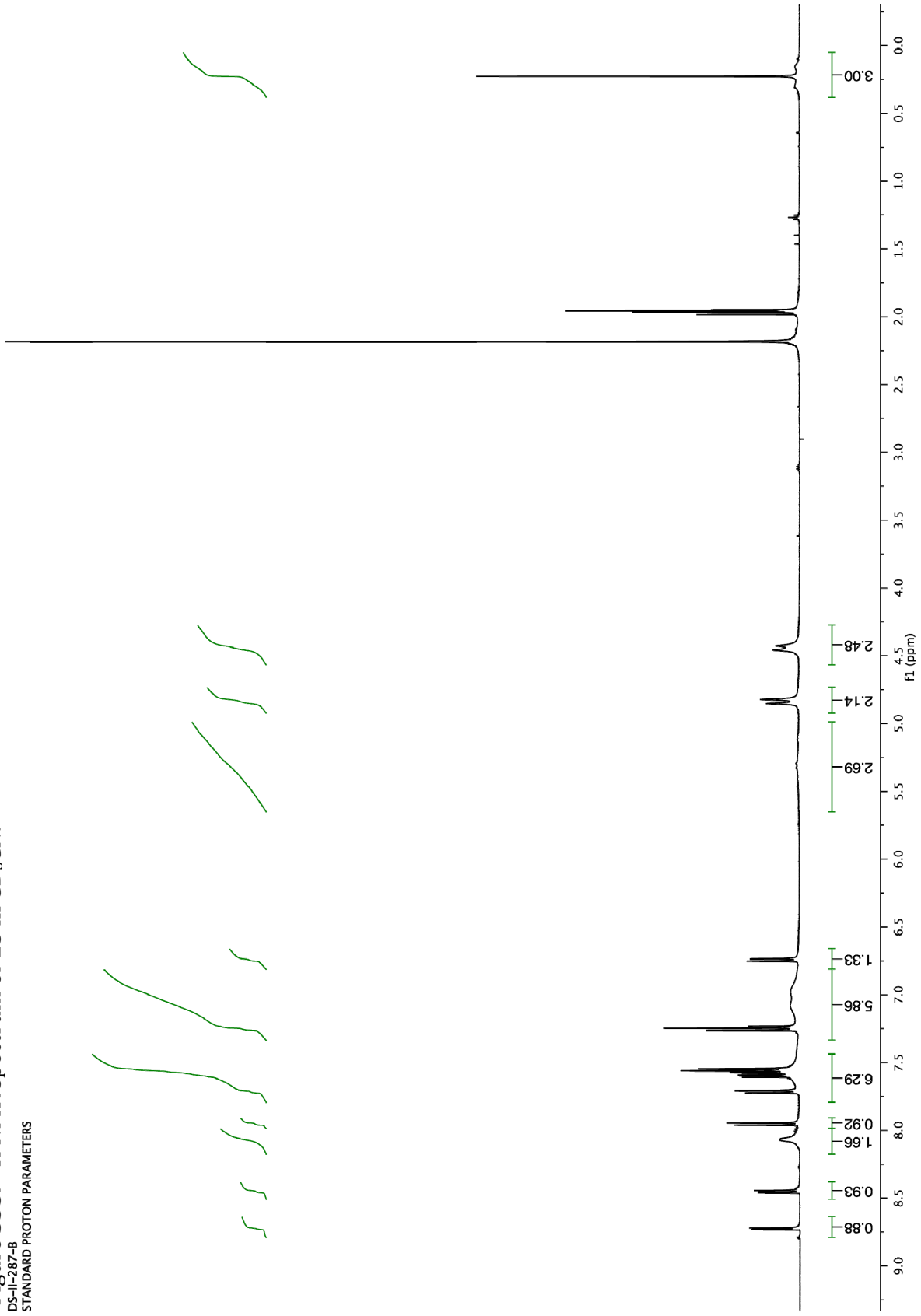


Figure **S35.** ^{1}H NMR spectrum of **15** in CD_3CN.
DS-II-287-B
STANDARD PROTON PARAMETERS

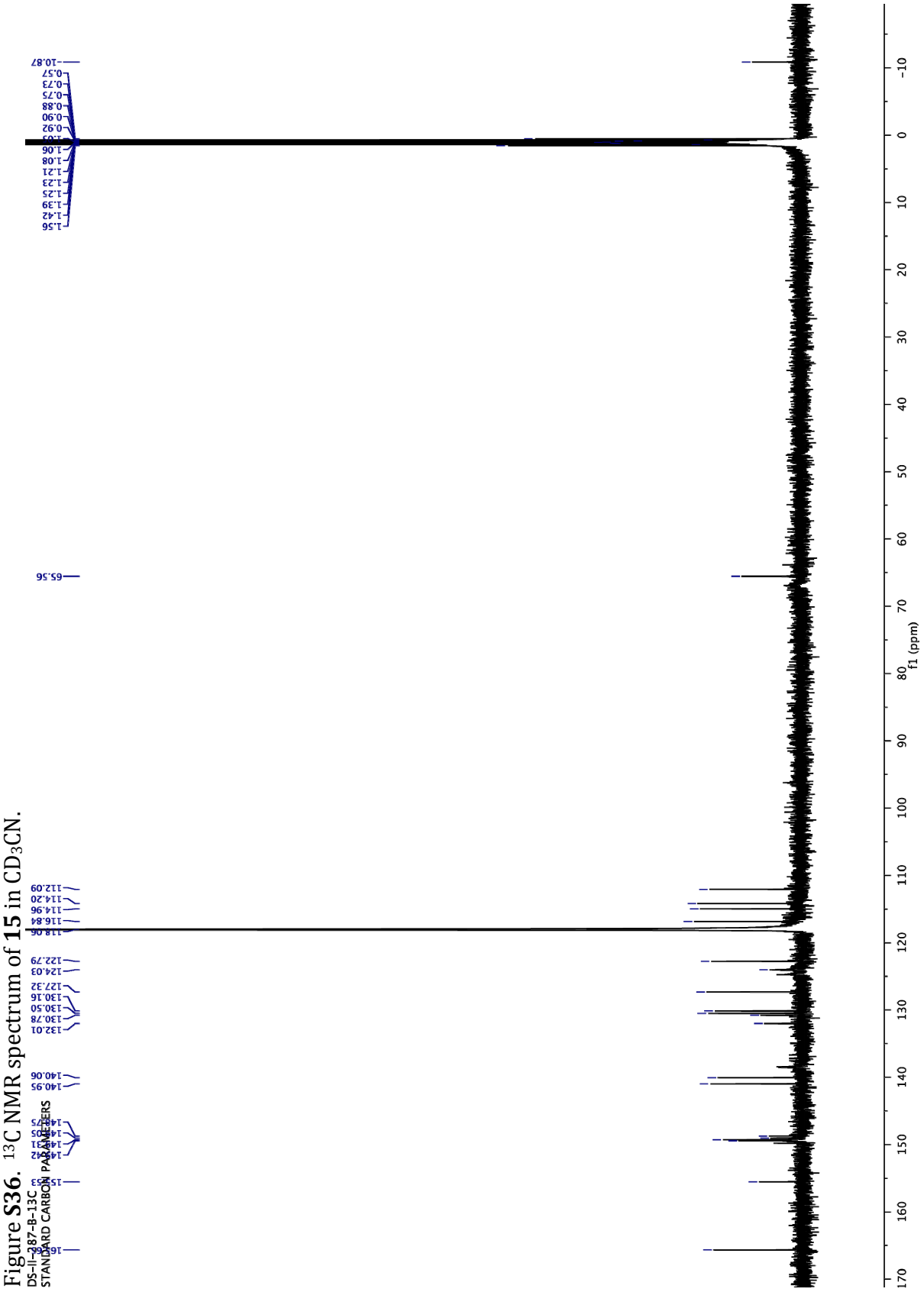


Figure **S36**. ^{13}C NMR spectrum of **15** in CD_3CN.

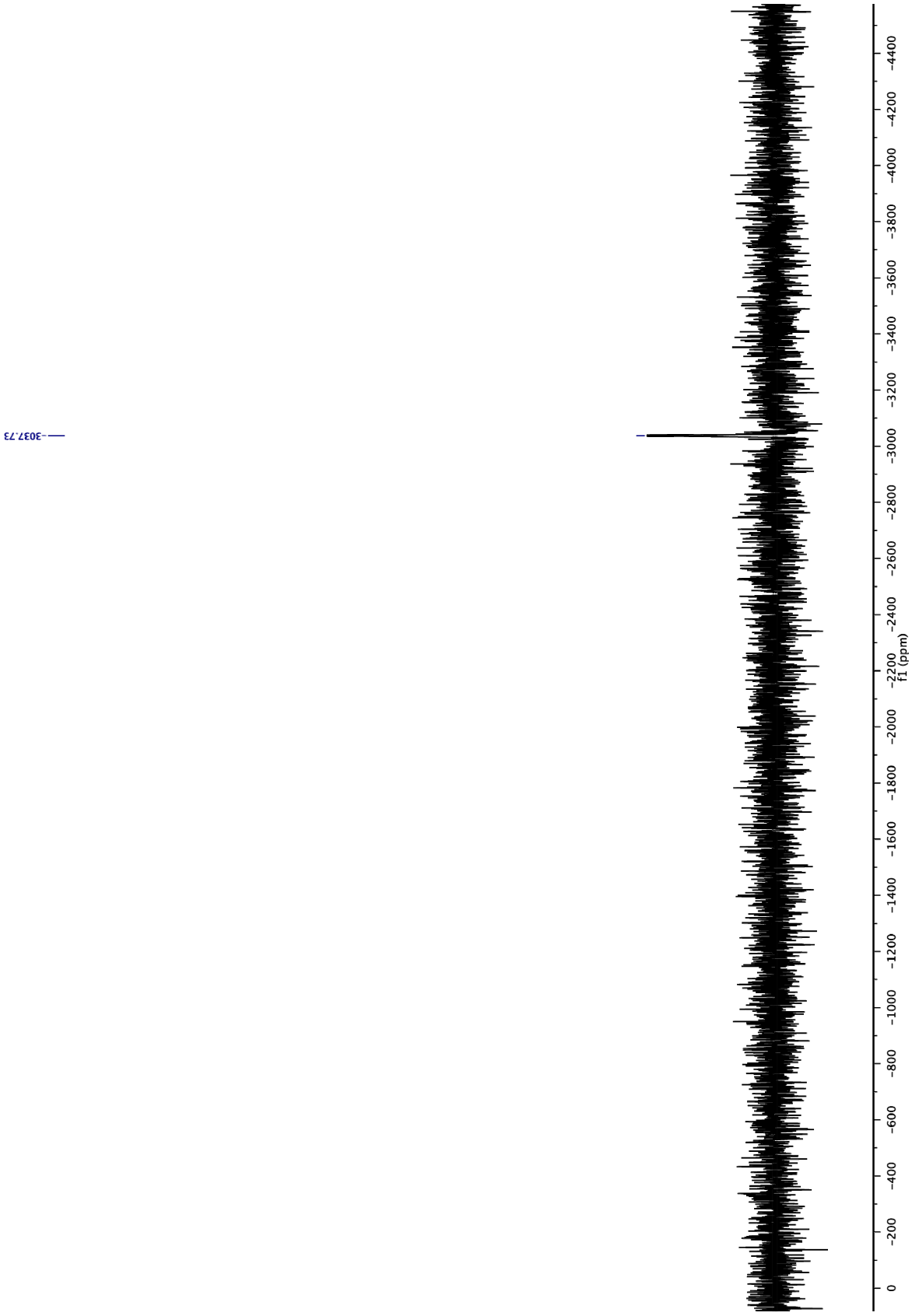


Figure **S37**. ^{195}Pt NMR spectrum of **15** in CD_3CN.

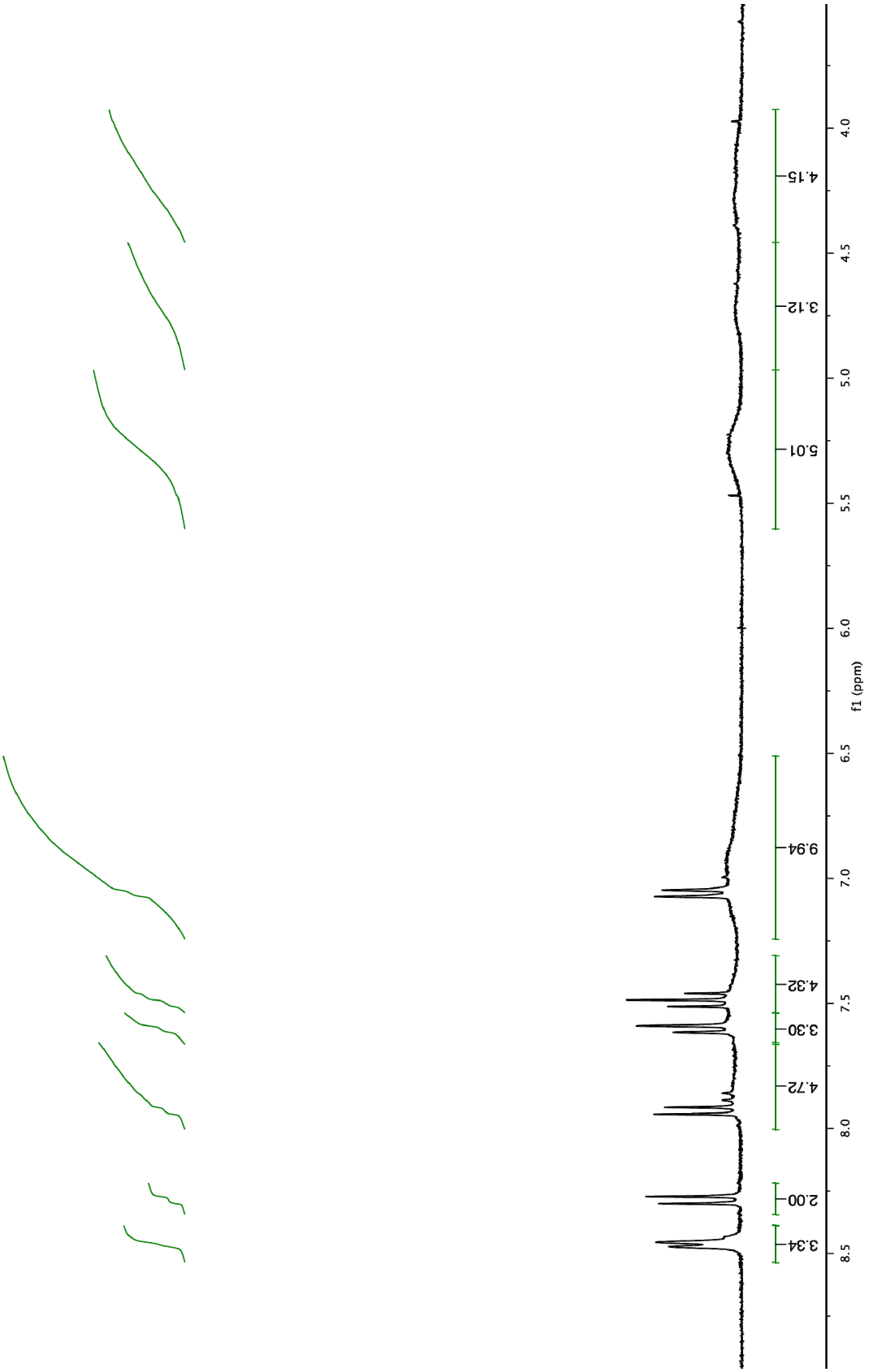


Figure **S38**. ^{1}H NMR spectrum of **16** in CD_3CN.

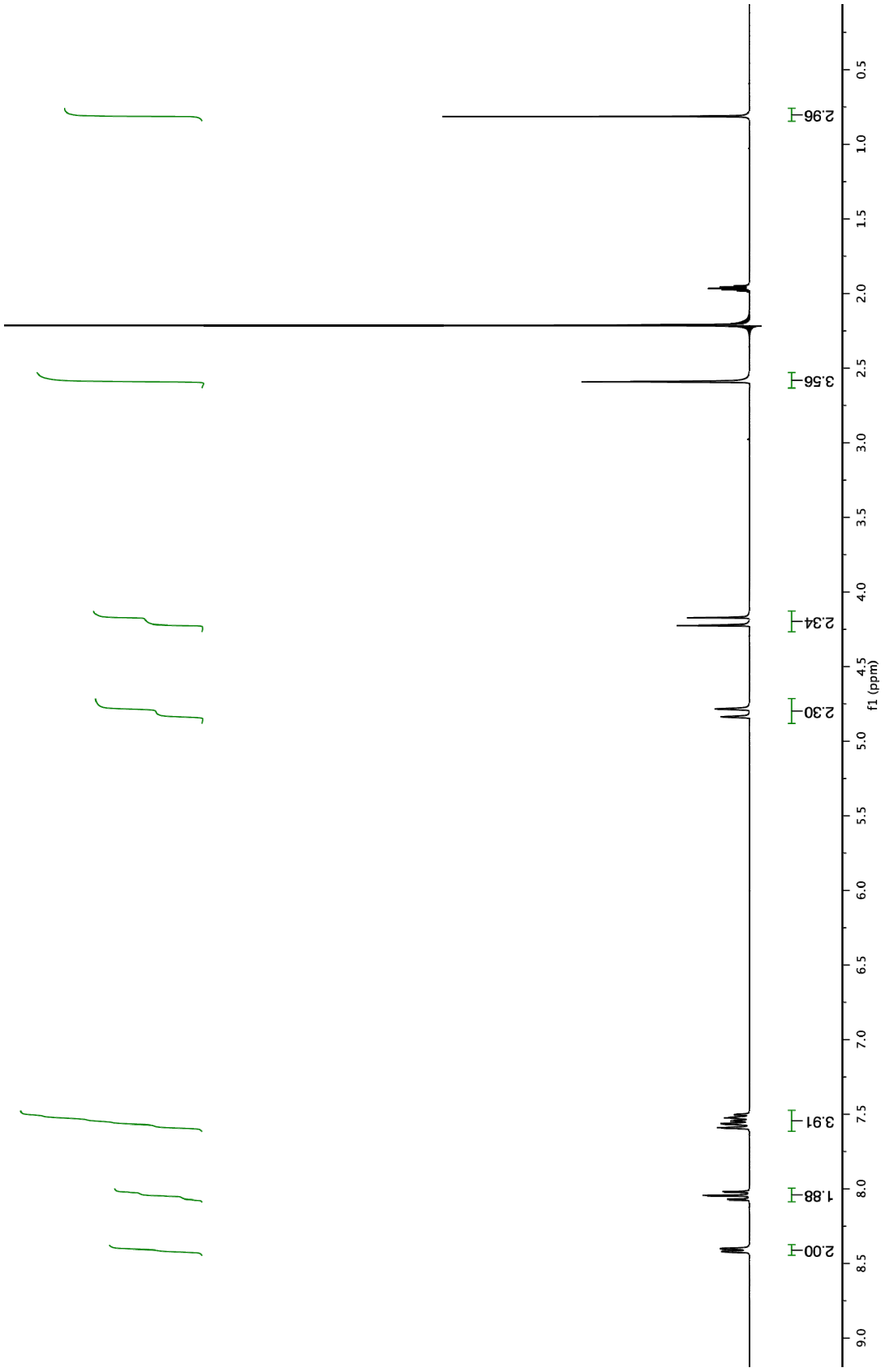


Figure **S39**. ^{1}H NMR spectrum of **17** in CD_3CN.

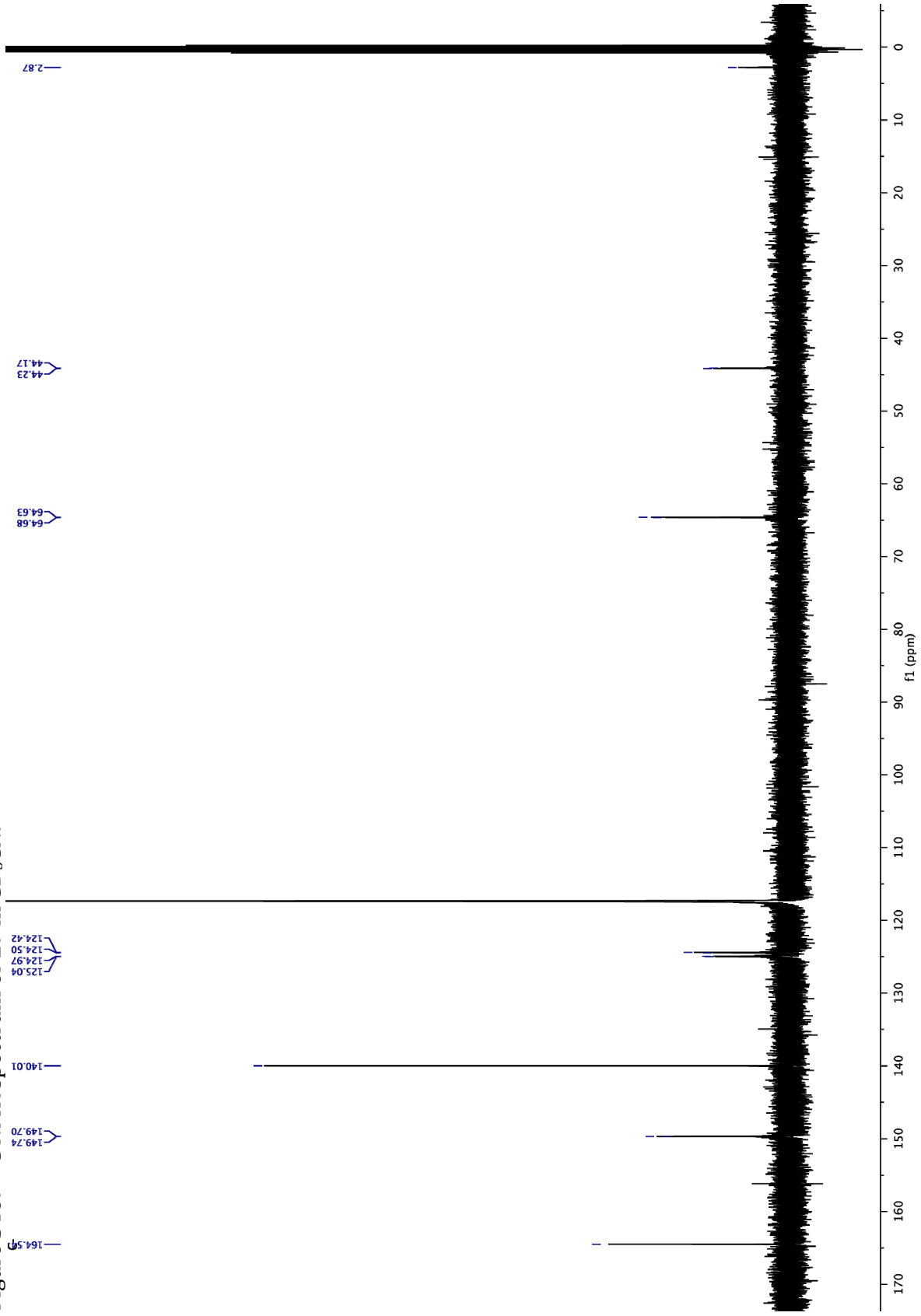


Figure **S40**. ^{13}C NMR spectrum of **17** in CD_3CN.

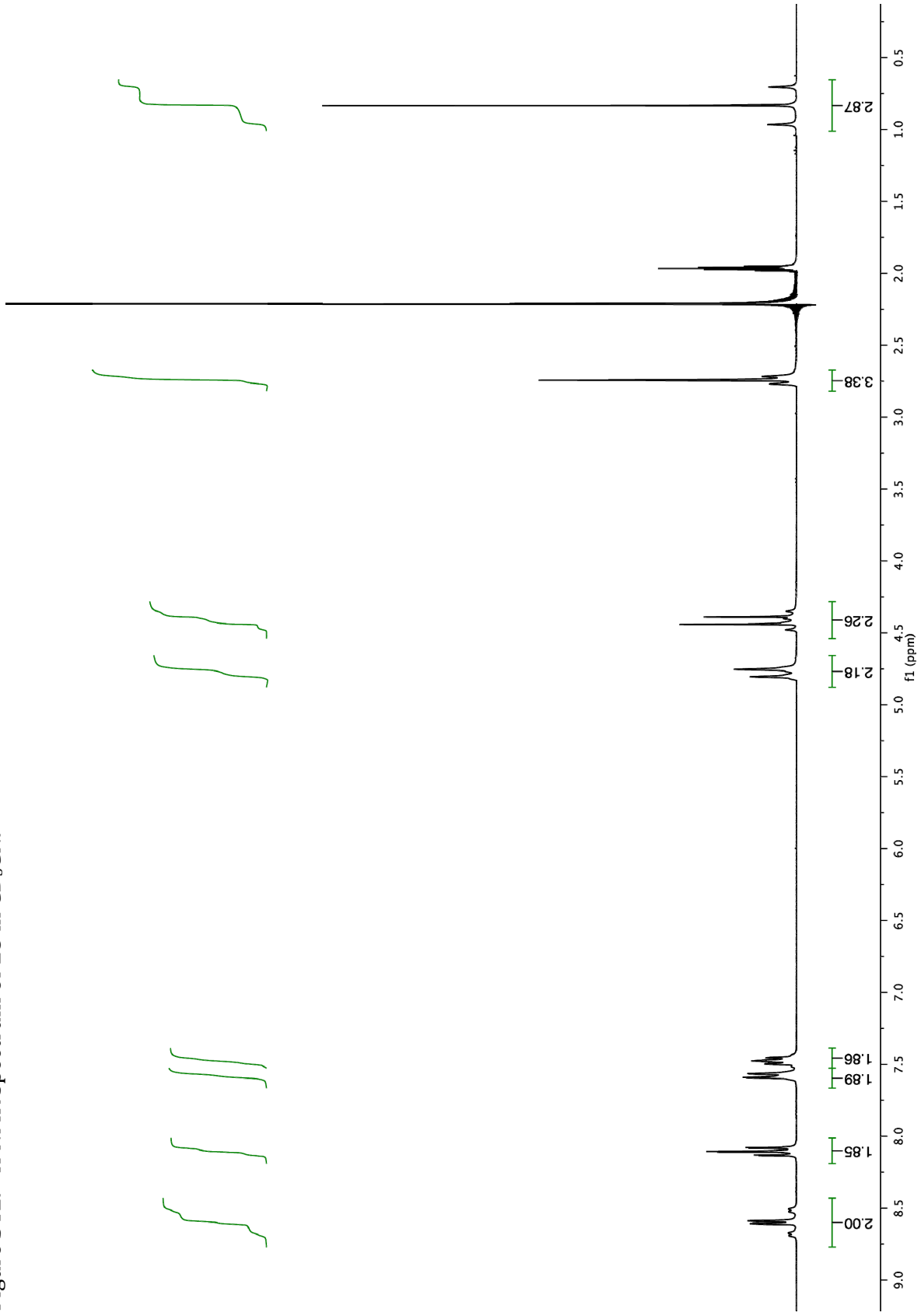


Figure **S41**. ^{1}H NMR spectrum of **18** in CD_3CN.

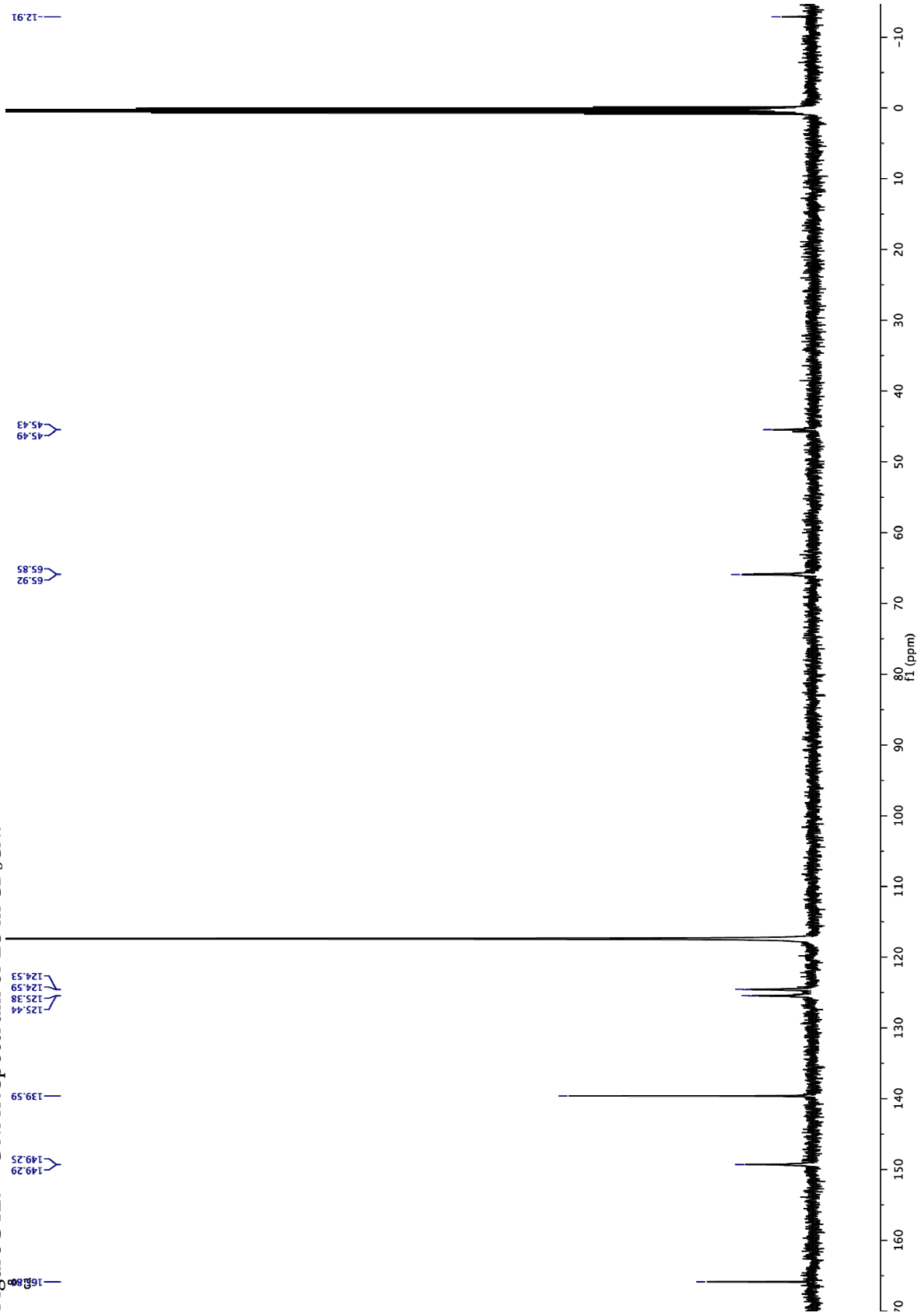


Figure **S42**. ^{13}C NMR spectrum of **18** in CD_3CN.

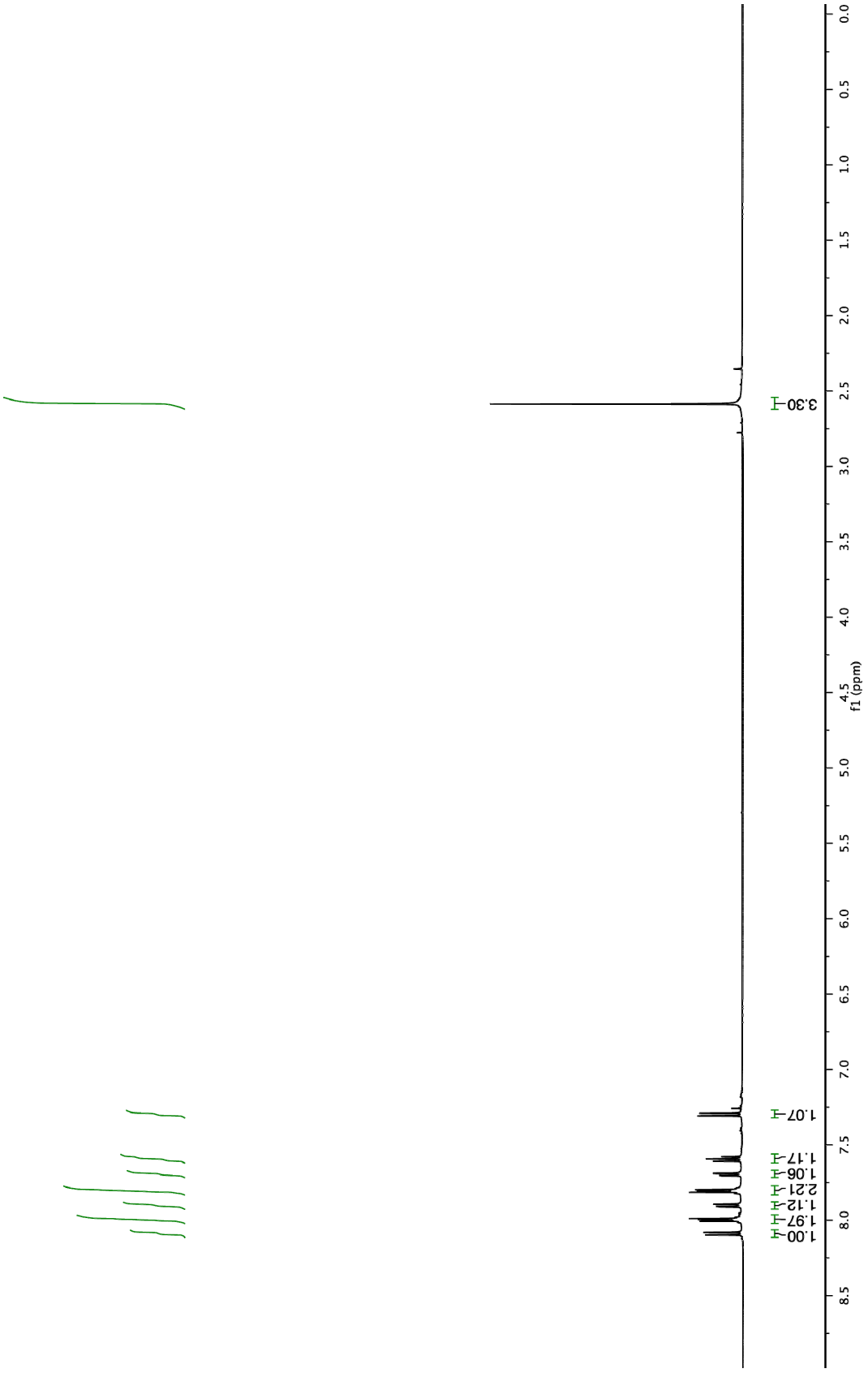


Figure **S43**. ^{1}H NMR spectrum of **19** in $CDCl_3$.

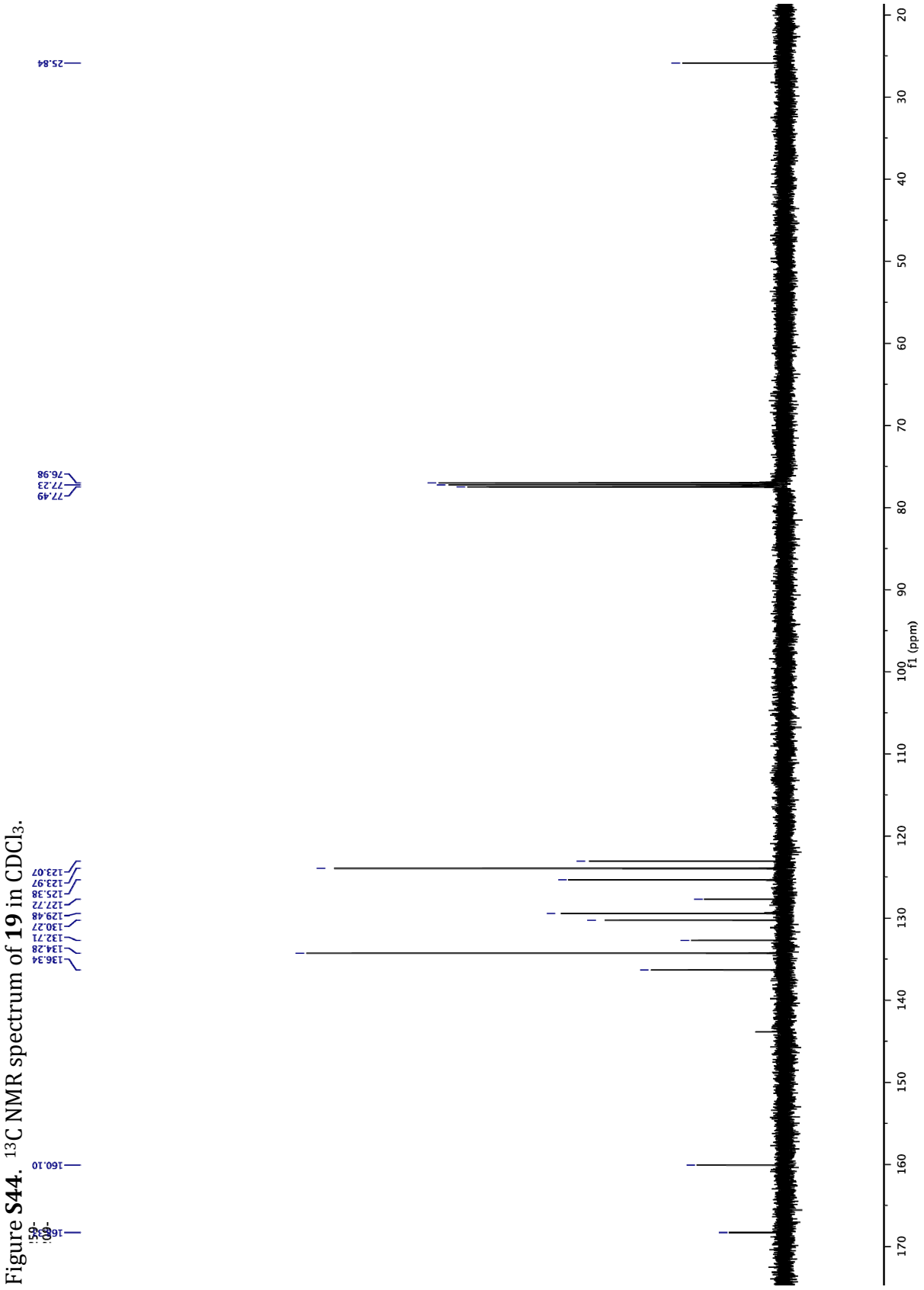


Figure **S44**. ^{13}C NMR spectrum of **19** in $CDCl_3$.

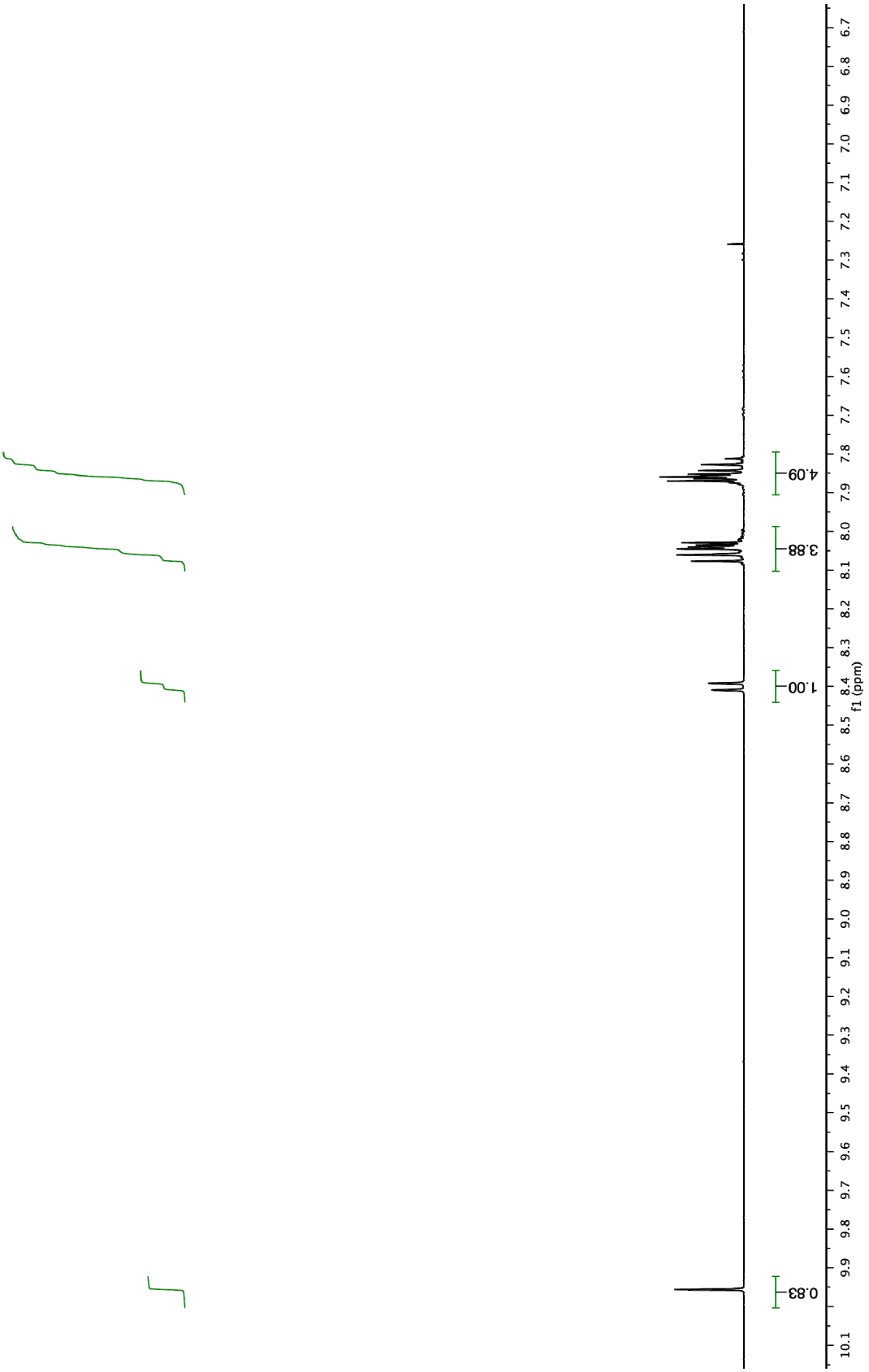


Figure **S45**. ^{1}H NMR spectrum of **20** in $CDCl_3$.

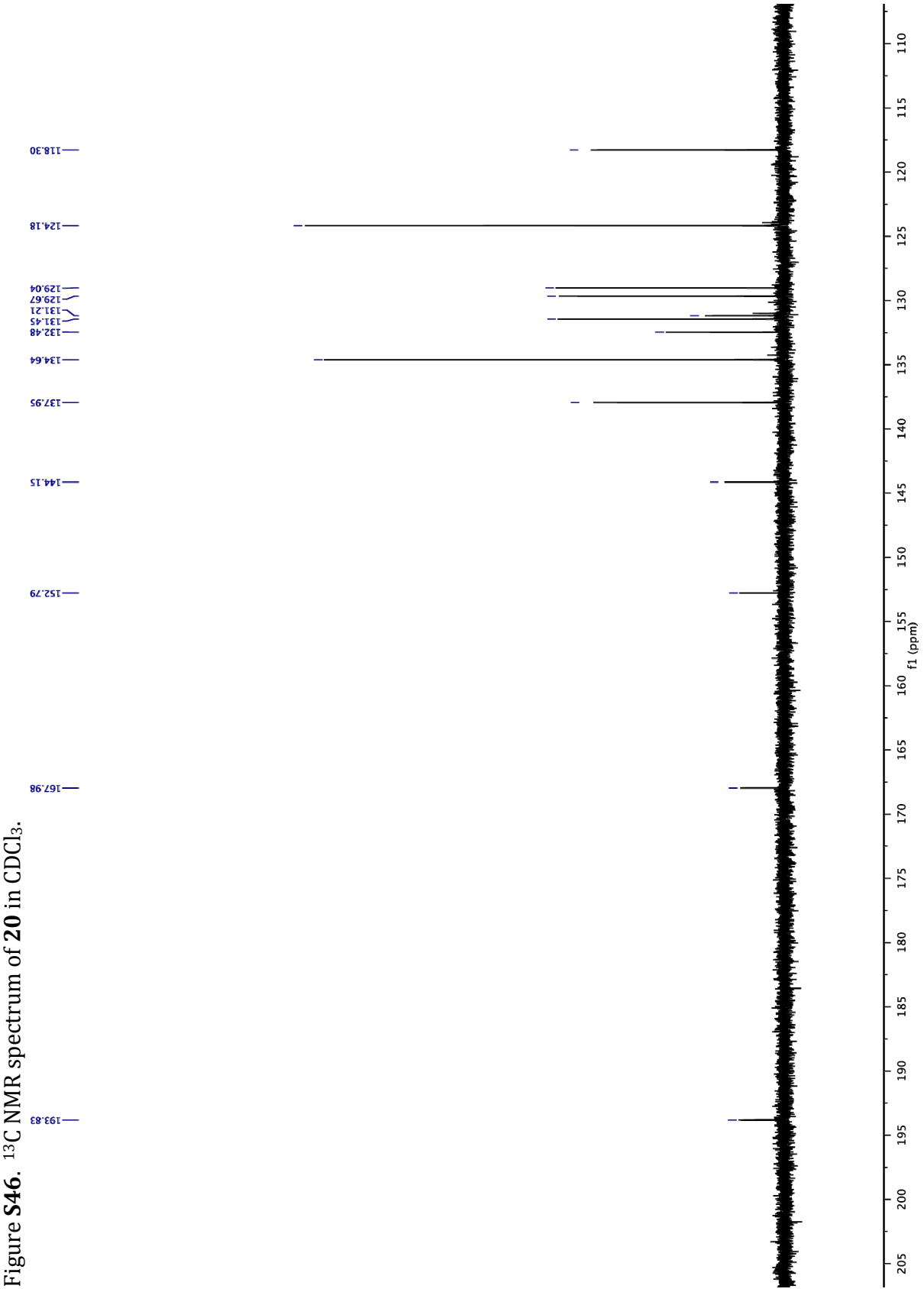


Figure **S46**. ^{13}C NMR spectrum of **20** in $CDCl_3$.

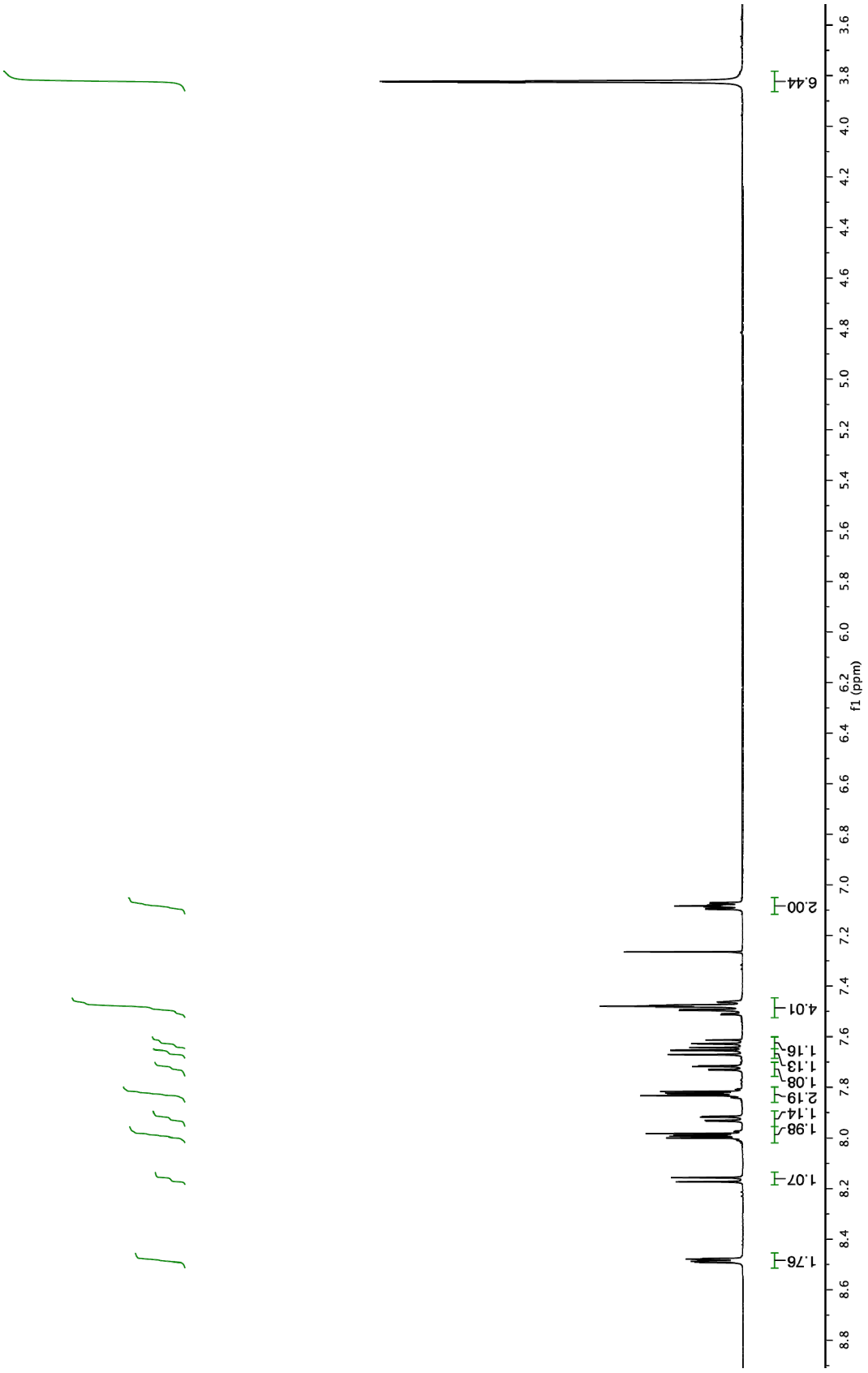


Figure **S47**. ^{1}H NMR spectrum of **21** in $CDCl_3$.

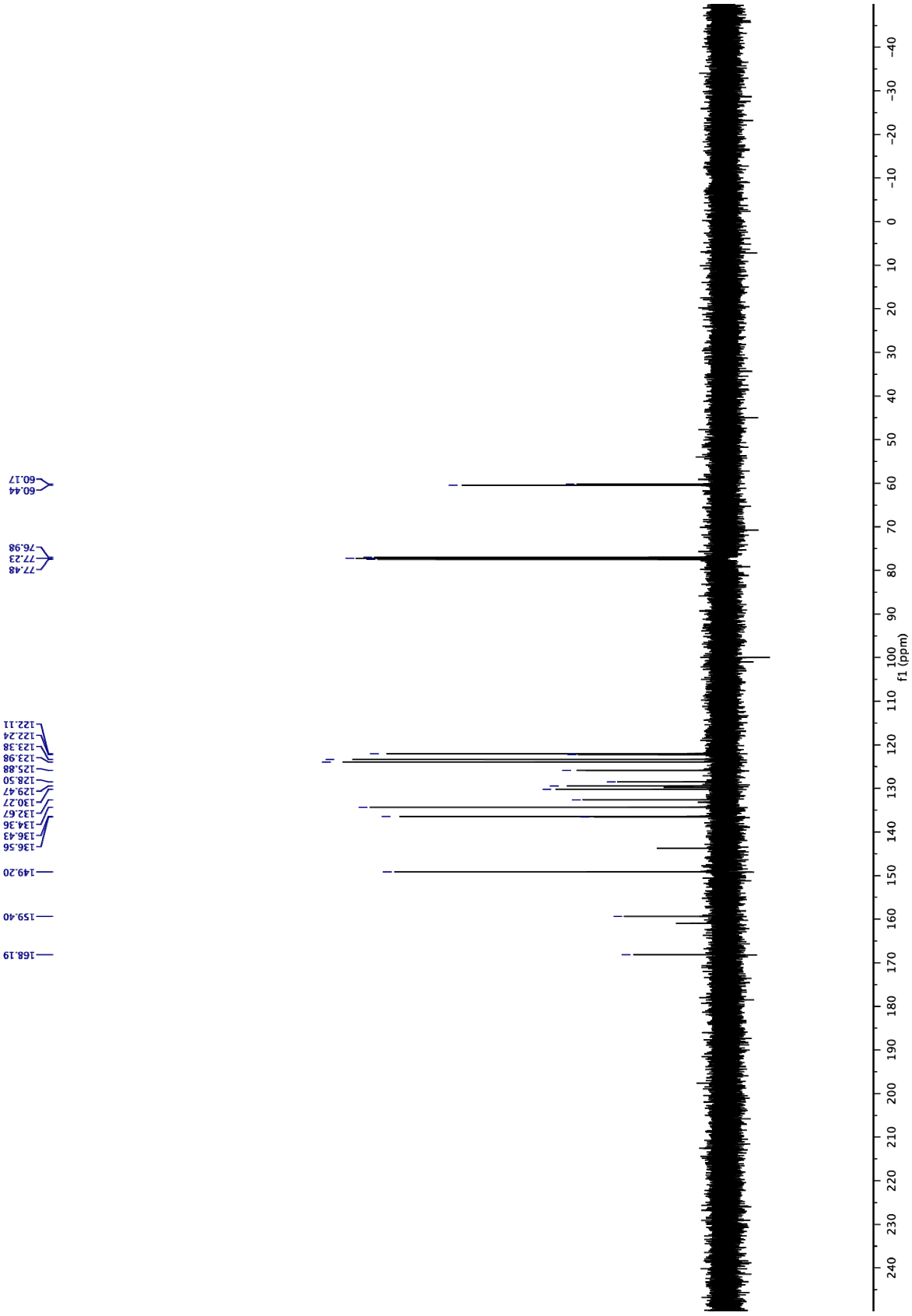


Figure **S48**. ^{13}C NMR spectrum of **21** in $CDCl_3$.

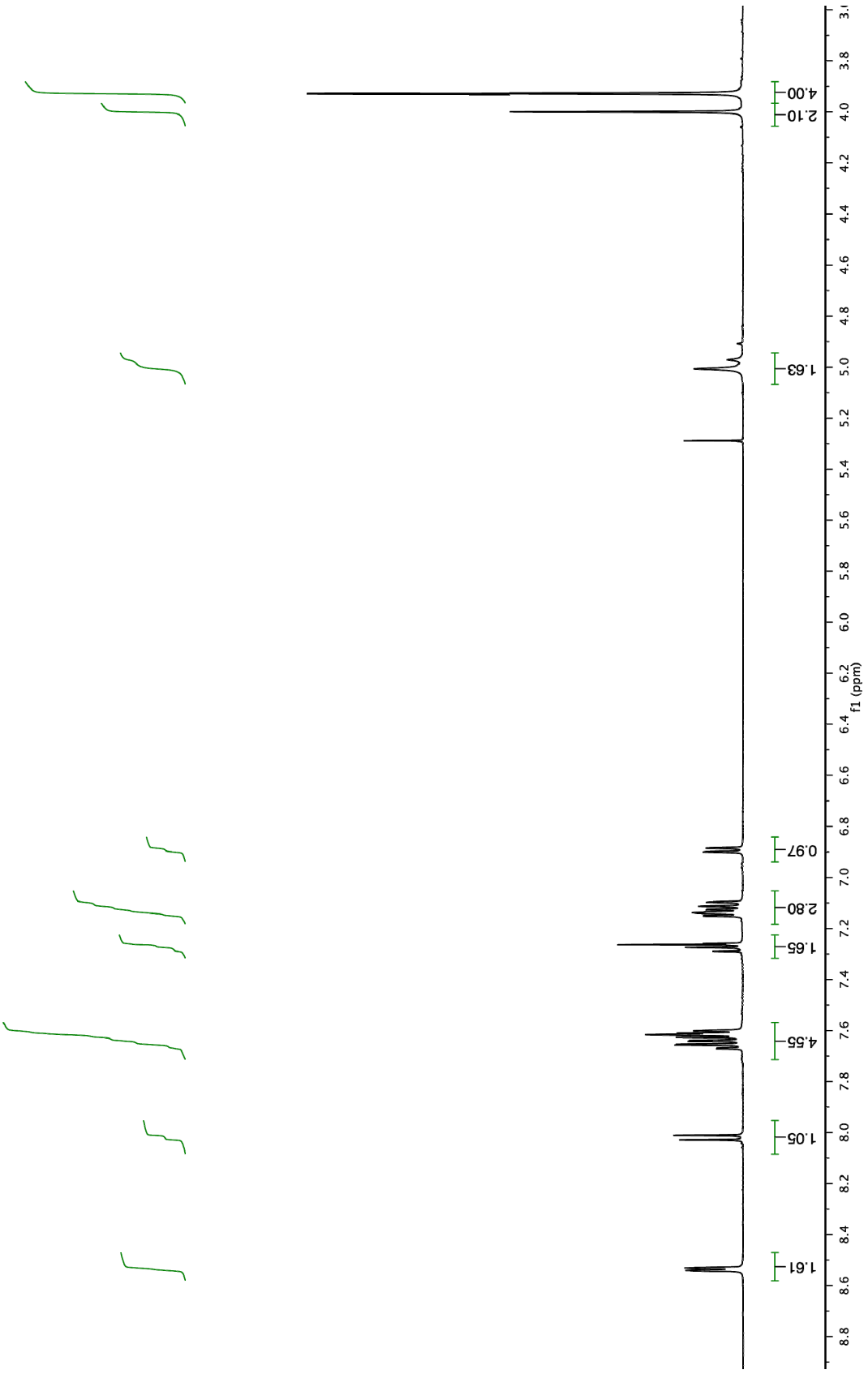


Figure **S49**. ^{13}H NMR spectrum of **22** in $CDCl_3$.

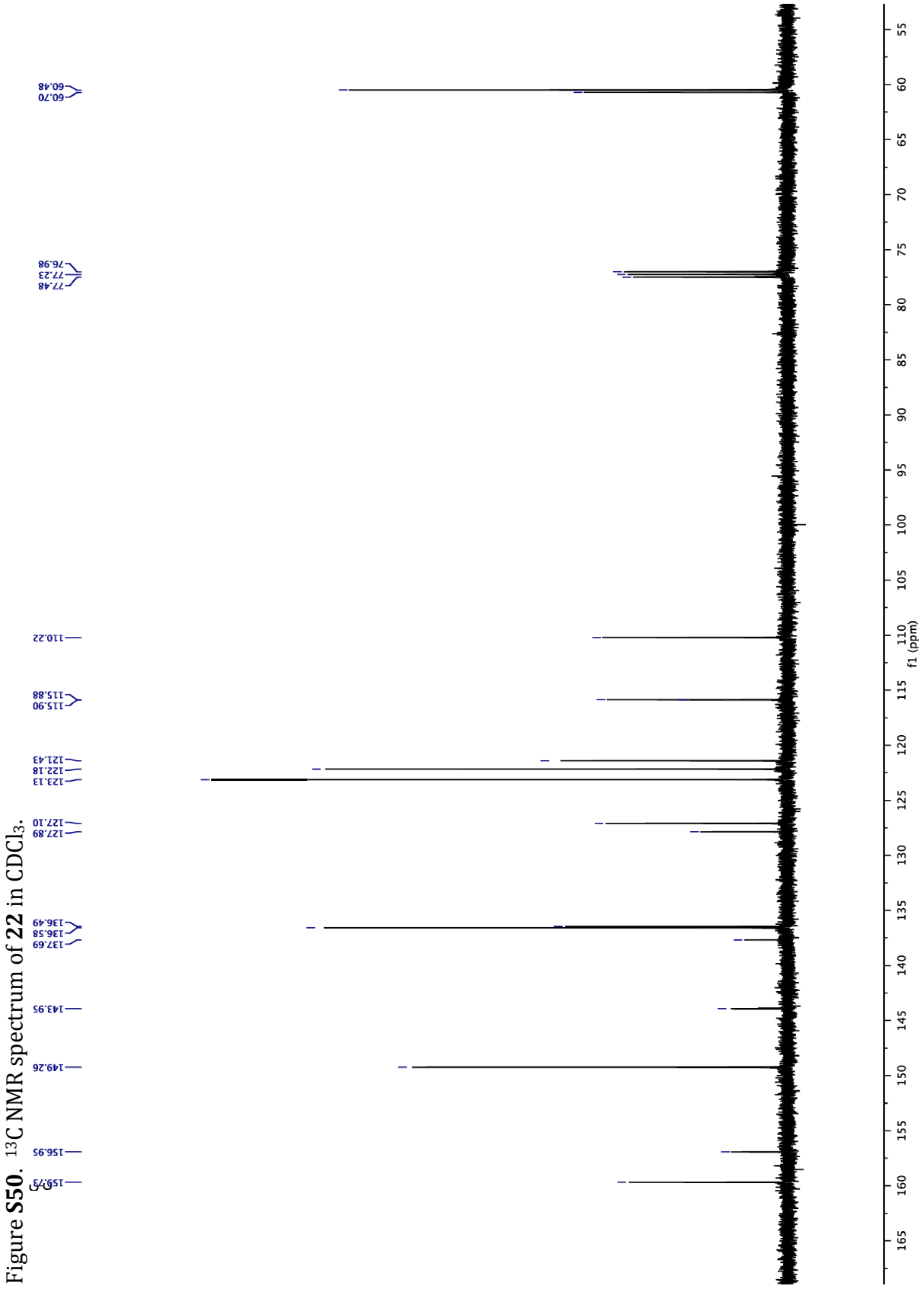


Figure **S50**. ^{13}C NMR spectrum of **22** in $CDCl_3$.