Electronic Supplementary Information

Metal-free-mediated synthesis of fulleropyrrolines by the reaction of [60]fullerene with β-substituted ethylamines

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Experimental section

General methods

All reagents and solvents were commercially available and were used as received without further purification. The UV-vis spectra were measured in $CHCl_3$. IR spectra were taken with KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a 400, 500 or 600 MHz NMR spectrometer. Chemical shifts in ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, yet chemical shifts in ^{13}C NMR spectra were referenced to residual DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

General procedure for the preparation of fulleropyrrolines 2

C_{60} (36.0 mg, 0.05 mmol) and a chosen β-substituted ethylamine **1** (1.00 mmol, 2.50 mmol for **1g**) were added to a 50 mL three-neck flask. After the mixed compounds were completely dissolved in 10 mL chlorobenzene by sonication, the resulting solution was put into an oil bath preset at 120 ^{o}C to heat and stir under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. Insoluble materials were first removed from the reaction mixture by filtering through a silica gel plug. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60} and then fulleropyrrolines **2**. It should be noted that column chromatography should be carried out in dark due to the inherent light sensitive properties of fulleropyrrolidines

2, especially for those bearing electron-withdrawing groups, and the addition of drops of Et_3N to the silica gel would be highly efficient to avoid the decomposition and/or absorption of fulleropyrrolines **2** on the silica gel.

Fulleropyrroline 2a

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (148 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 19 h afforded first unreacted C_{60} (9.0 mg, 25%) and then **2a** (21.4 mg, 43%) as an amorphous brown solid: mp >300 °C. ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.47 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 6.89 (s, 1H), 6.75 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 4.11 (t, J = 7.3 Hz, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.20 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 157.35 (1C, aryl *C*), 157.12 (1C, aryl *C*), 148.76, 146.75 (1C), 146.23 (1C), 145.23, 145.12, 145.09, 144.99, 144.81 (4C), 144.55, 144.14, 144.00, 143.94 (6C), 143.46, 143.20, 142.04, 141.65, 141.58 (4C), 141.41, 141.23, 141.12, 141.05, 140.63, 138.96, 138.68, 135.34, 134.58 (1C), 134.42, 129.82 (1C, aryl *C*), 129.22 (aryl *C*), 128.87 (aryl *C*), 126.59 (1C, aryl *C*), 113.23 (4C, aryl *C*), 107.31 (1C), 88.11 (1C, sp^3-*C* of C_{60}), 77.97 (1C, sp^3-*C* of C_{60}), 54.07, 48.42 (1C), 35.53 (1C); FT-IR ν/cm^{-1} (KBr) 2923 (m), 2852 (w), 1607 (m), 1509 (m), 1459 (w), 1438 (w), 1430 (w), 1387 (w), 1354 (w), 1244 (s), 1176 (m), 1127 (w), 1037 (m), 823 (m), 526 (m); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 257 (5.14), 307 (4.73), 428 (3.91); MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{19}NO_2$ $[M + H]^+$ 1002.1494, found 1002.1479.

Fulleropyrroline 2b

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (147 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 9 h afforded first unreacted C_{60} (19.4 mg, 54%) and then **2b** (14.8 mg, 30%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.19-7.10 (m, 5H), 6.85-6.84 (m, 2H), 6.67 (dd, J = 8.4, 1.5 Hz, 1H), 6.62 (dd, J = 8.4, 1.6 Hz, 1H), 4.20 (t, J = 7.4 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.26 (t, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 158.90 (1C, aryl *C*), 158.76 (1C, aryl *C*), 148.76, 146.86 (1C), 146.37 (1C), 145.38, 145.24 (4C), 145.13, 144.95 (4C), 144.70, 144.10 (4C), 144.08 (6C), 143.59, 143.33, 142.16, 141.79, 141.72, 141.70, 141.46, 141.41, 141.24, 141.19, 140.76, 139.55 (1C, aryl *C*), 138.92, 138.85, 136.14 (1C), 135.94 (1C, aryl *C*), 135.50, 134.53, 128.86 (1C, aryl *C*), 128.63 (1C, aryl *C*), 120.67 (1C, aryl *C*), 119.64 (1C, aryl *C*), 114.23 (1C, aryl *C*), 112.91 (1C, aryl *C*), 111.41 (1C, aryl *C*), 110.57 (1C, aryl *C*), 107.09 (1C), 88.49 (1C, sp^3-*C* of C_{60}), 77.56 (1C, sp^3-*C* of C_{60}), 54.03 (1C), 54.01 (1C), 48.00 (1C), 36.53 (1C); FT-IR ν/cm^{-1} (KBr) 2899 (w), 2827 (w), 1594 (s), 1488 (w), 1459 (w), 1423 (m), 1384 (w), 1355 (w), 1286 (w), 1259 (m), 1219 (w), 1163 (m), 1043 (m), 854 (w), 777 (m), 695 (m), 526 (m); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (5.08), 308 (4.64), 428 (3.40); MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{19}NO_2$ $[M + H]^+$ 1002.1494, found 1002.1479.

Fulleropyrroline 2c

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (169 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 8 h afforded first unreacted C_{60} (13.0 mg, 36%) and then **2c** (23.0 mg, 43%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.10 (dd, J = 8.5, 2.0 Hz, 1H), 7.01 (d, J = 1.9 Hz, 1H), 6.96 (s, 1H), 6.84 (d, J = 1.7 Hz, 1H), 6.78 (dd, J = 8.4, 1.8 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 4.16 (t, J = 7.1 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.18 (t, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.77, 148.57 (1C), 148.50 (1C), 147.31 (1C), 147.07 (1C), 146.83 (1C), 146.32 (1C), 145.35, 145.21, 145.18, 145.08, 144.89 (4C), 144.59, 144.15, 144.02 (8C), 143.54, 143.28, 142.13, 141.75, 141.69, 141.64, 141.48, 141.33, 141.20, 141.14, 140.70, 138.90, 138.73, 135.32, 134.93 (1C), 134.41, 130.71 (1C, aryl *C*), 127.37 (1C, aryl *C*), 120.52 (1C, aryl *C*), 119.94 (1C, aryl *C*), 112.77 (1C, aryl *C*), 112.10 (1C, aryl *C*), 111.66 (1C, aryl *C*), 111.60 (1C, aryl *C*), 106.96 (1C), 88.24 (1C, sp^3-*C* of C_{60}), 77.90 (1C, sp^3-*C* of C_{60}), 54.88 (1C), 54.82 (1C), 54.75, 48.13 (1C), 36.01 (1C); FT-IR ν/cm^{-1} (KBr) 2920 (m), 2850 (w), 1618 (m), 1510 (s), 1454 (m), 1440 (m), 1411 (w), 1383 (w), 1351 (w), 1297 (w), 1252 (m), 1233 (s), 1177 (w), 1140 (m), 1101 (w), 1026 (s), 826 (m), 799 (m), 763 (m), 733 (m), 525 (m); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 258 (5.07), 309 (4.70), 428 (3.62); MALDI-TOF MS *m*/*z* calcd for $C_{80}H_{23}NO_4$ $[M + H]^+$ 1062.1705, found 1062.1693.

Fulleropyrroline 2d

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (126 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 19 h afforded first unreacted C_{60} (13.8 mg, 38%) and then **2d** (18.0 mg, 38%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.62 (d, J = 7.0 Hz, 2H), 7.30-7.17 (m, 8H), 7.10 (t, $J = 6.3$ Hz, 1H), 4.20 (t, $J = 6.8$ Hz, 2H), 3.30 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.75, 146.83 (1C), 146.33 (1C), 145.29, 145.20 (4C), 145.09, 144.91 (4C), 144.69, 144.07 (6C), 144.05 (4C), 143.55, 143.28, 142.14, 141.76, 141.69, 141.67, 141.43, 141.35, 141.20, 141.15, 140.74, 138.99, 138.83, 138.01 (1C, aryl *C*), 135.81 (1C, aryl *C*), 135.51, 134.54 (3C), 128.36 (aryl *C*), 127.92 (aryl *C*), 127.77 (aryl *C*), 127.24 (aryl *C*), 125.90 (1C, aryl *C*), 125.17 (1C, aryl *C*), 107.57 (1C), 88.40 (1C, sp^3-*C* of C_{60}), 77.61 (1C, sp^3-*C* of C_{60}), 48.25 (1C), 36.51 (1C); FT-IR *ν*/cm^{-1} (KBr) 2915 (m), 2849 (w), 1612 (s), 1593 (s), 1493 (m), 1451 (m), 1425 (m), 1392 (m), 1355 (m), 1180 (m), 1163 (m), 1073 (w), 872 (m), 751 (s), 695 (s), 526 (s); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 257 (5.21), 307 (4.79), 428 (3.65); MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{15}N$ $[M + H]^+$ 942.1283, found 942.1270.

Fulleropyrroline 2e

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (131 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 15 h afforded first unreacted C_{60} (20.3 mg, 56%) and then **2e** (12.0 mg, 25%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.61 (dd, $J = 8.9, 5.5$ Hz, 2H), 7.30 (dd, $J = 8.5, 5.5$ Hz, 2H), 7.02-6.99 (m, 4H), 6.89 (s, 1H), 4.20 (t, $J = 7.4$ Hz, 2H), 3.29 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 160.67 (d, $J_{C-F} = 244$ Hz, 1C, aryl *C*), 160.27 (d, $J_{C-F} = 246$ Hz, 1C, aryl *C*), 148.52, 146.83 (1C), 146.33 (1C), 145.20, 145.13, 145.08, 145.07, 144.92 (4C), 144.68, 144.04 (6C), 143.91 (4C), 143.52, 143.26, 142.13, 141.75, 141.70, 141.61, 141.39, 141.30, 141.18, 141.12, 140.73, 139.08, 138.81, 135.90 (1C), 135.44, 134.53, 133.81 (1C, aryl *C*), 130.57 (1C, aryl *C*), 129.92 (d, $J_{C\text{–}F}$ = 5 Hz, aryl *C*), 129.08 (aryl *C*), 114.67 (aryl *C*), 114.51 (aryl *C*), 106.671 (1C), 88.28 (1C, sp^3-*C* of C_{60}), 77.66 (1C, sp^3-*C* of C_{60}), 48.21 (1C), 35.53 (1C); FT-IR *ν*/cm^{-1} (KBr) 2914 (w), 2862 (w), 1624 (s), 1602 (s), 1508 (s), 1453 (w), 1384 (m), 1354 (m), 1228 (s), 1188 (m), 1156 (m), 1012 (w), 826 (s), 526 (m); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 257 (5.25), 306 (4.79), 428 (3.65); MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{13}F_2N$ [M + H]$^+$ 978.1094, found 978.1082.

Fulleropyrroline 2f

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (140 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 11.5 h afforded first unreacted C_{60} (23.2 mg, 64%) and then **2f** (10.2 mg, 20%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) *δ* 7.59 (d, *J* = 8.8 Hz, 2H), 7.29-7.25 (m, 6H), 6.93 (s, 1H), 4.22 (t, *J* = 7.4 Hz, 2H), 3.29 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) *δ* 148.36, 146.83 (1C), 146.35 (1C), 145.21, 145.15, 145.10, 145.04, 144.93 (4C), 144.67, 144.10, 144.05 (4C), 143.88, 143.82, 143.52, 143.28, 142.14, 141.77, 141.71, 141.62, 141.35 (4C), 141.19, 141.14, 140.73, 139.01, 138.81, 136.68 (1C, aryl *C*), 136.62 (1C), 135.43, 134.60, 133.34 (1C, aryl *C*), 131.72 (1C, aryl *C*), 130.42 (1C, aryl *C*), 129.97 (aryl *C*), 128.15 (aryl *C*), 127.91 (aryl *C*), 127.83 (aryl *C*), 106.15 (1C), 88.44 (1C, sp^3-*C* of C_{60}), 77.31 (1C, sp^3-*C* of C_{60}), 47.80 (1C), 35.69 (1C); FT-IR *ν*/cm^{-1} (KBr) 2919 (m), 2851 (w), 1610 (s), 1510 (w), 1489 (s), 1426 (w), 1405 (m), 1354 (m), 1225 (w), 1180 (m), 1163 (m), 1128 (w), 1091 (s), 1013 (m), 872 (w), 820 (m), 806 (m), 526 (s); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 257 (5.02), 312 (4.57), 427 (3.29); MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{13}Cl_2N$ $[M + H]^+$ 1010.0503, found 1010.0490.

Fulleropyrroline 2g

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (377 μL, 2.50 mmol) in chlorobenzene (10 mL) at 120 °C for 10 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **2g** (13.6 mg, 25%) as an amorphous brown solid: mp >300 °C. ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 1H), 7.46 (d, J = 1.9 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 1.7 Hz, 1H), 7.22-7.21 (m, 1H), 7.17 (dd, J = 8.5, 1.8 Hz, 1H), 6.94 (s, 1H), 4.25 (t, J = 7.1 Hz, 2H), 3.39 (t, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 147.94, 146.77 (1C), 146.26 (1C), 145.10, 145.04, 144.94, 144.82 (4C), 144.59, 144.45, 143.95 (8C), 143.40, 143.14, 142.80, 142.05, 141.59 (3C), 141.55 (3C), 141.31, 141.10 (4C), 140.95, 140.64, 139.21, 138.53, 137.77 (1C, aryl *C*), 136.11 (1C), 135.35, 134.34, 134.29 (1C, aryl *C*), 134.15 (1C, aryl *C*), 133.20 (1C, aryl *C*), 132.85 (1C, aryl *C*), 132.56 (1C, aryl *C*), 132.18 (1C, aryl *C*), 130.85 (1C, aryl *C*), 129.00 (1C, aryl *C*), 128.34 (1C, aryl *C*), 126.55 (1C, aryl *C*), 126.02 (1C, aryl *C*), 102.37 (1C), 87.40 (1C, sp^3-*C* of C_{60}), 78.63 (1C, sp^3-*C* of C_{60}), 45.23 (1C), 33.77 (1C); FT-IR ν/cm^{-1} (KBr) 2918 (w), 2852 (w), 1624 (w), 1579 (m), 1469 (w), 1453 (m), 1428 (m), 1375 (w), 1352 (w), 1241 (w), 1180 (w), 1162 (w), 1123 (m), 1098 (m), 1049 (w), 1033 (w), 865 (s), 818 (s), 782 (w), 745 (s), 525 (s); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 258 (5.36), 309 (4.77), 428 (3.54); MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{11}Cl_4N$

$[M + H]^+$ 1077.9724, found 1077.9711.

Fulleropyrroline 2h

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (117 μL, 1.00 mmol) in chlorobenzene (10 mL) at 120 °C for 24 h afforded first unreacted C_{60} (14.2 mg, 39%) and then **2h** (7.5 mg, 16%) as an amorphous brown solid: mp >300 °C. ^1H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.28 (s, 1H), 7.14-7.13 (m, 2H), 7.04 (d, J = 5.1 Hz, 1H), 6.93 (d, J = 2.4 Hz, 1H), 6.91-6.88 (m, 2H), 4.26 (t, J = 7.1 Hz, 2H), 3.52 (t, J = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.24, 147.00 (1C), 146.48 (1C), 145.63, 145.39, 145.28, 145.23, 145.07 (4C), 144.93, 144.41, 144.30, 144.20 (4C), 144.04, 143.72, 143.42, 142.26, 141.90, 141.84, 141.72, 141.53 (4C), 141.33 (4C), 140.90, 139.95 (1C, aryl *C*), 139.10, 138.95, 137.34 (1C), 135.73, 135.67 (1C, aryl *C*), 134.74, 126.72 (1C, aryl *C*), 126.52 (1C, aryl *C*), 125.30 (1C, aryl *C*), 123.72 (1C, aryl *C*), 122.70 (1C, aryl *C*), 121.59 (1C, aryl *C*), 101.95 (1C), 88.06 (1C, sp^3-*C* of C_{60}), 77.15 (1C, sp^3-*C* of C_{60}), 48.23 (1C), 30.49 (1C); FT-IR ν/cm^{-1} (KBr) 2916 (m), 2848 (w), 1611 (s), 1538 (w), 1511 (w), 1428 (m), 1388 (m), 1362 (w), 1259 (w), 1217 (m), 1182 (m), 1164 (m), 1075 (w), 812 (w), 800 (m), 691 (s), 526 (s); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 258 (5.39), 313 (4.73), 427 (3.63); MALDI-TOF MS *m*/*z* calcd for $C_{72}H_{11}NS_2$ $[M + H]^+$ 954.0411, found 954.0400.

Fulleropyrroline 2i

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (355 μL, 2.50 mmol) in chlorobenzene (10 mL) at 120 °C for 29 h afforded first unreacted C_{60} (14.4 mg, 40%) and then **2i** (14.6 mg, 30%) as an amorphous brown solid: mp >300 °C. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.38 (d, J = 7.3 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.17-7.09 (m, 5H), 7.04 (t, J = 7.0 Hz, 1H), 6.40 (s, 1H), 3.95 (s, 2H), 3.77 (t, J = 7.6 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 2.25-2.19 (m, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.99, 146.89 (1C), 146.32 (1C), 145.90, 145.22, 145.09, 145.03, 144.98, 144.90, 144.88, 144.80, 144.34, 144.19, 144.07 (4C), 143.59, 143.33, 142.15, 141.71, 141.68, 141.66, 141.50, 141.27, 141.17, 141.13, 140.78, 140.24 (1C, aryl *C*), 139.32, 138.63, 138.34 (1C, aryl *C*), 135.52, 134.51, 133.42 (1C), 128.73 (aryl *C*), 127.78 (aryl *C*), 127.74 (aryl *C*), 127.70 (aryl *C*), 125.79 (1C, aryl *C*), 125.30 (1C, aryl *C*), 107.78 (1C), 87.69 (1C, sp^3-*C* of C_{60}), 78.36 (1C, sp^3-*C* of C_{60}), 47.02 (1C), 33.52 (1C), 32.62 (1C), 31.15 (1C); FT-IR ν/cm^{-1} (KBr) 3057 (w), 3022 (w), 2916 (m), 2847 (w), 1648 (m), 1602 (w), 1493 (m), 1451 (m), 1427 (m), 1383 (w), 1181 (m), 1163 (m), 1120 (m), 1074 (w), 1029 (w), 906 (w), 743 (m), 697 (s), 526 (s); UV-vis ($CHCl_3$) λ_{max}/nm (log ϵ) 256 (5.18), 307 (4.63), 429 (3.56); MALDI-TOF MS *m/z* calcd for $C_{78}H_{19}N$ $[M + H]^+$ 970.1596, found 970.1584.

Transformation of 2d to 3 in the presence of TsOH·H$_2$O

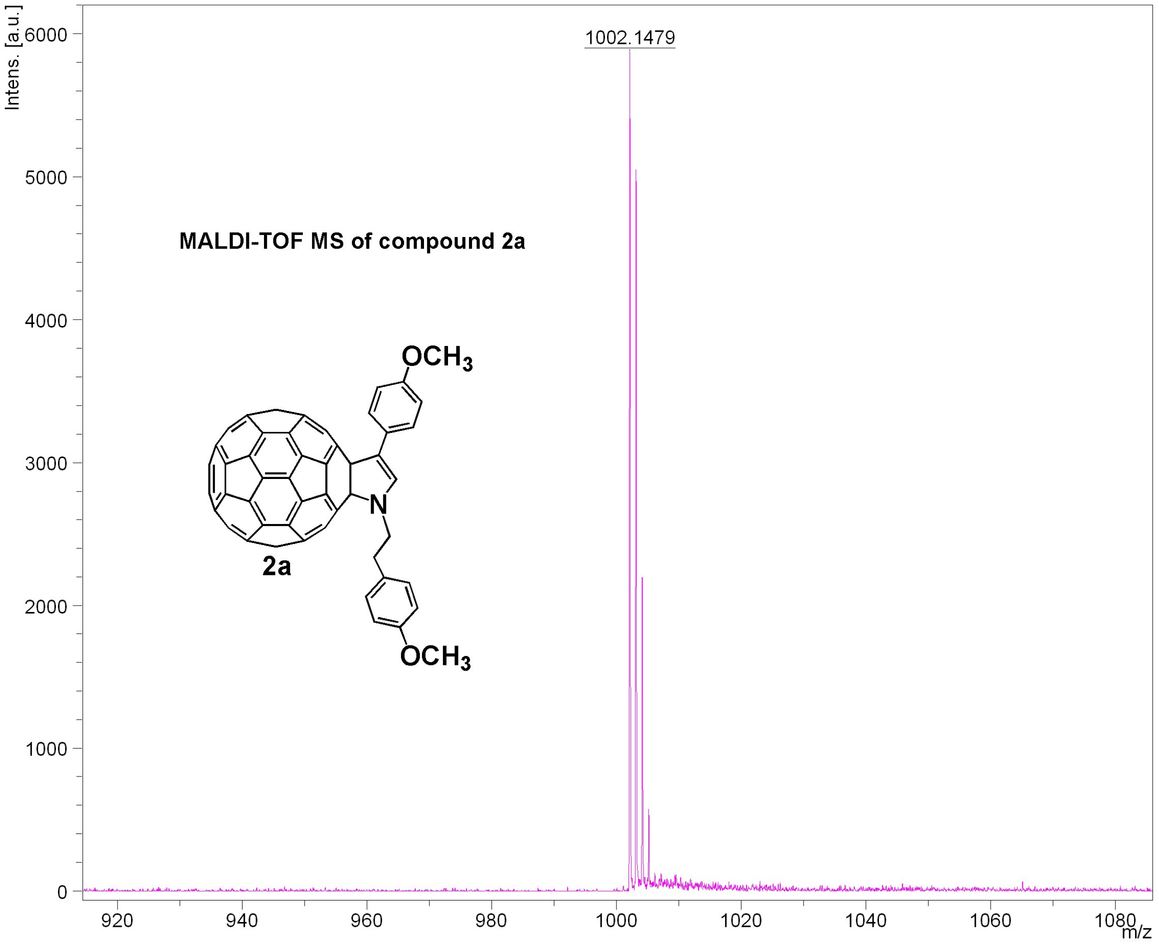
By the same procedure as for the preparation of fulleropyrrolines **2**, the reaction of fulleropyrroline **2d** (18.8 mg, 0.02 mmol), 1,3-propanediol (3 μL, 0.04 mmol) and TsOH·H$_2$O (19.0 mg, 0.10 mmol) in chlorobenzene (6 mL) at 120 °C for 0.5 h afforded C_{60}-fused dioxygenated ring compound **3**[1] (11.0 mg, 69%) together with a trace amount of unreacted fulleropyrroline **2d**.

Transformation of 2d to C_{60} in the presence of TsOH·H$_2$O

By the same procedure as for the preparation of fulleropyrrolines **2**, the reaction of fulleropyrroline **2d** (18.8 mg, 0.02 mmol) and $TsOH \cdot H_2O$ (7.6 mg, 0.04 mmol) in chlorobenzene (6 mL) at 120 ^{o}C for 0.5 h afforded C_{60} (13.2 mg, 92%) together with a trace amount of unreacted fulleropyrroline **2d**.

Notes and references

1 (*a*) F.-B. Li, X. You, T.-X. Liu and G.-W. Wang, *Org. Lett.,* 2012, **14**, 1800; (*b*) W.-Q. Zhai, S.-P. Jiang, R.-F. Peng, B. Jin and G.-W. Wang, *Org. Lett.,* 2015, **17**, 1862. (*c*) X.-F. Zhang, F.-B. Li, J. Wu, J.-L. Shi, Z. Liu and L. Liu, *J. Org. Chem.,* 2015, **80**, 6037; (*d*) J. Wu, F.-B. Li, X.-F. Zhang, J.-L. Shi and L. Liu, *RSC Adv.,* 2015, **5**, 30549.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MALDI-TOF MS of compound 2a
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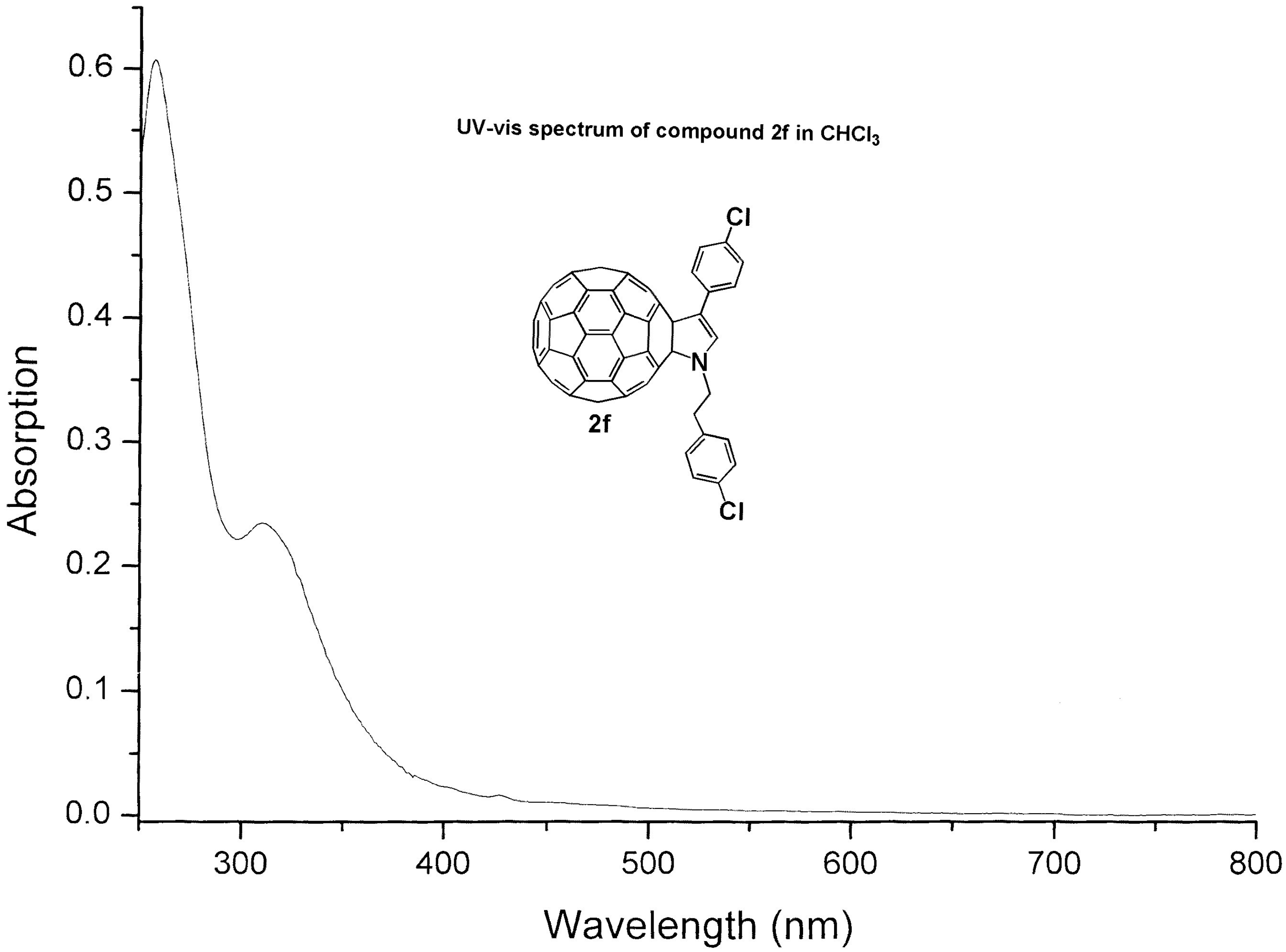
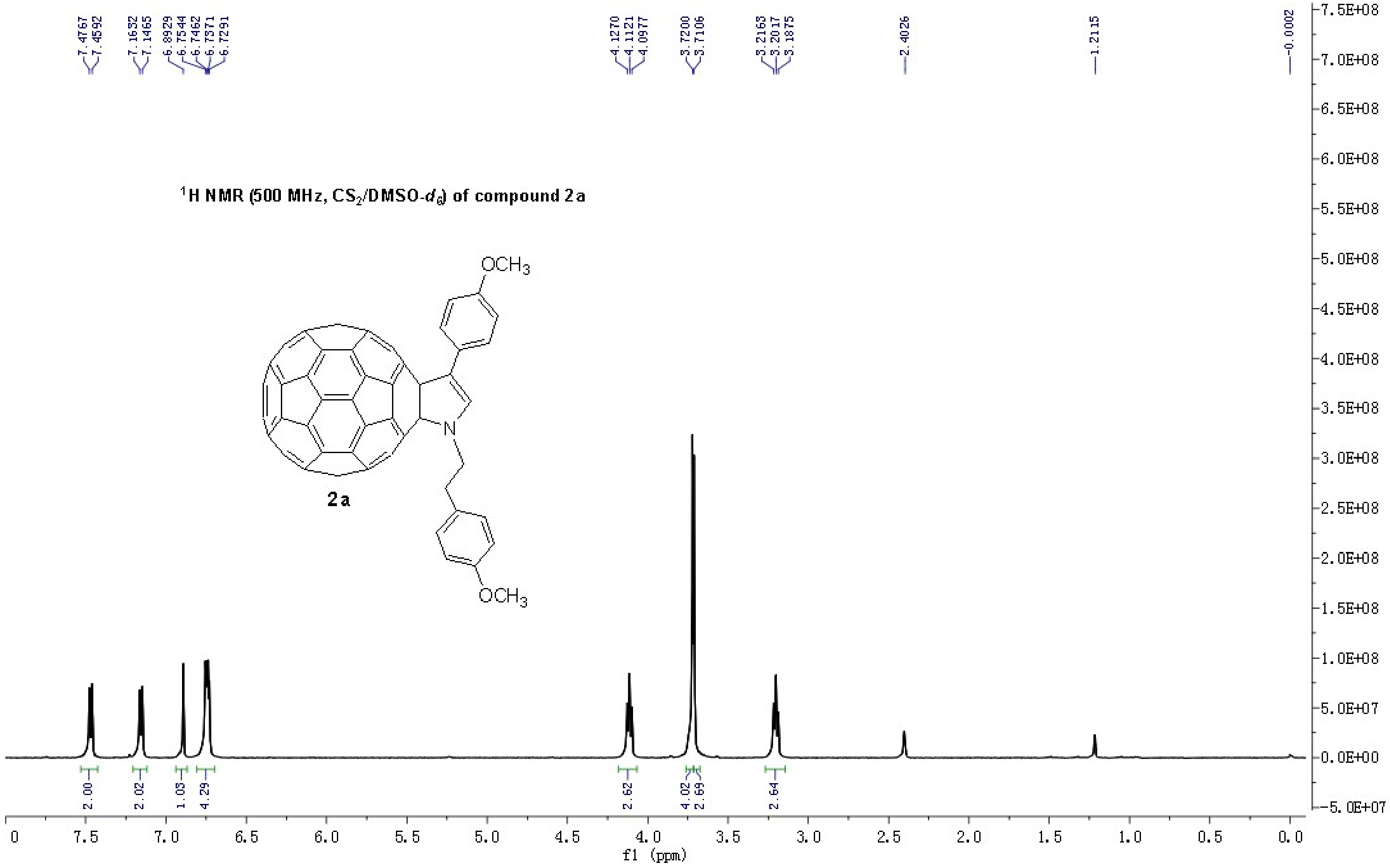
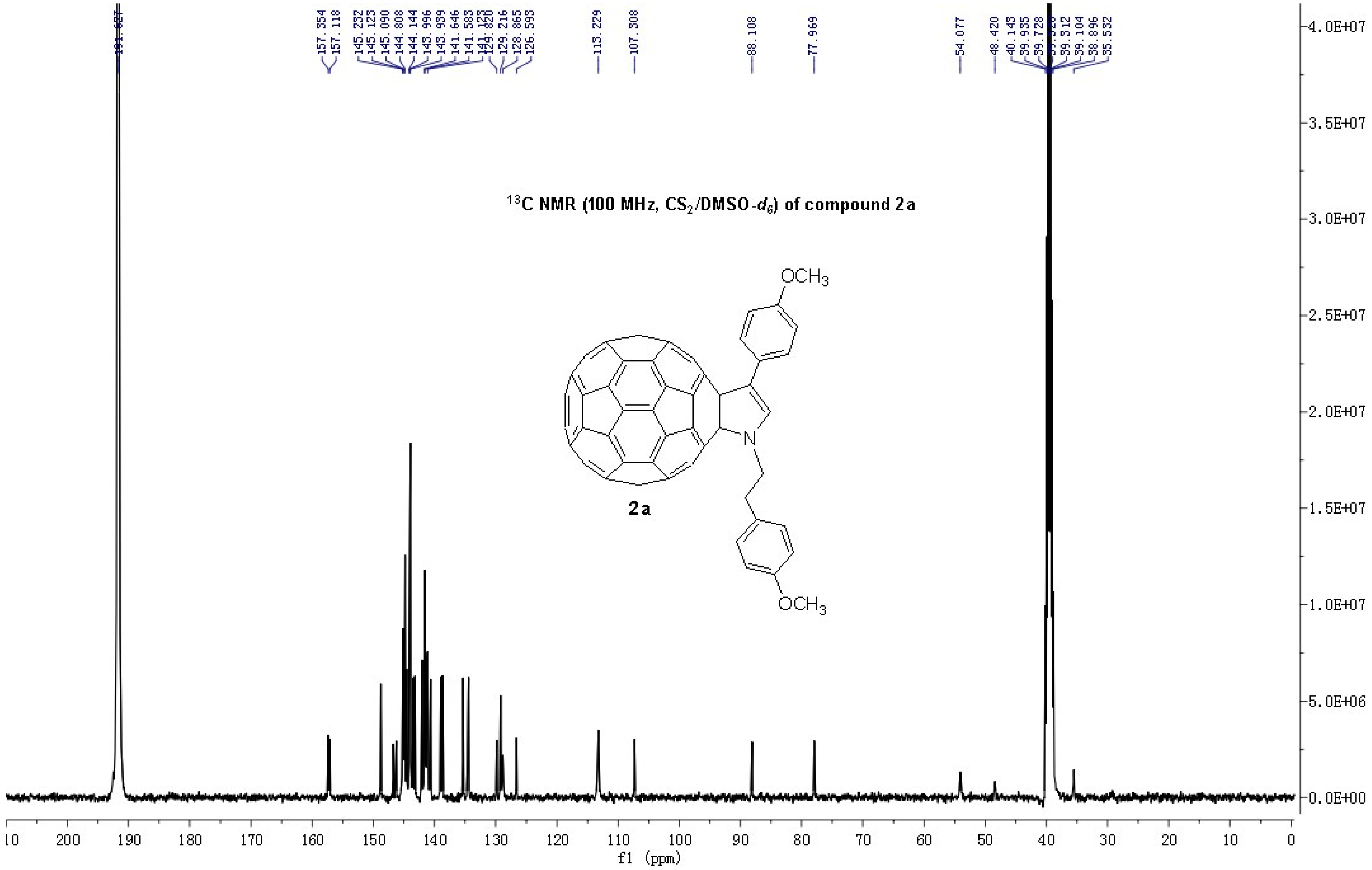
N
OCH3
2a
920
940
960
980
1000
1020
1040
1060
1080
m/z



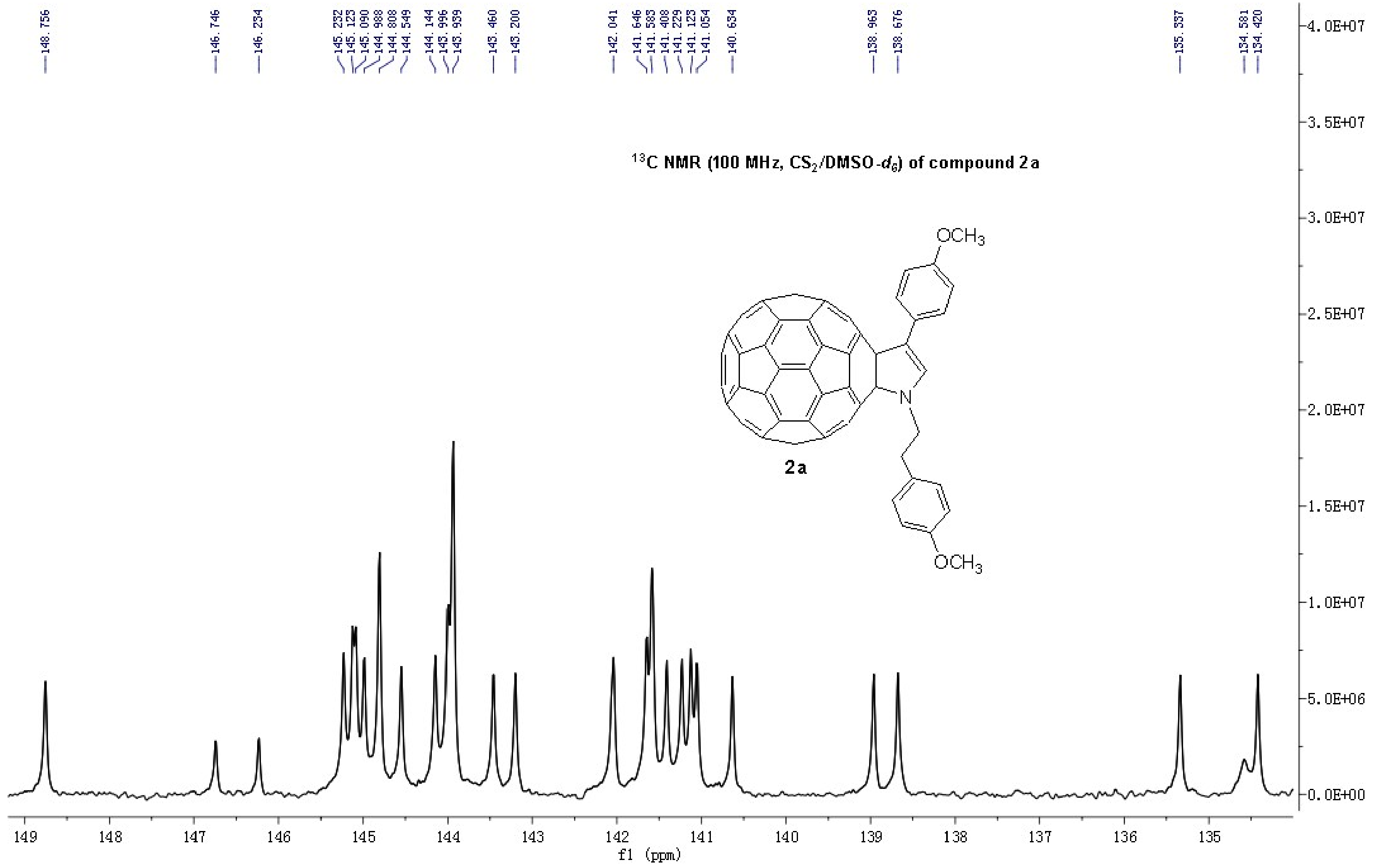
UV-vis spectrum of compound 2f in $CHCl_3$



^{1}H NMR (500 MHz, CS_2/DMSO-d_6) of compound **2a**

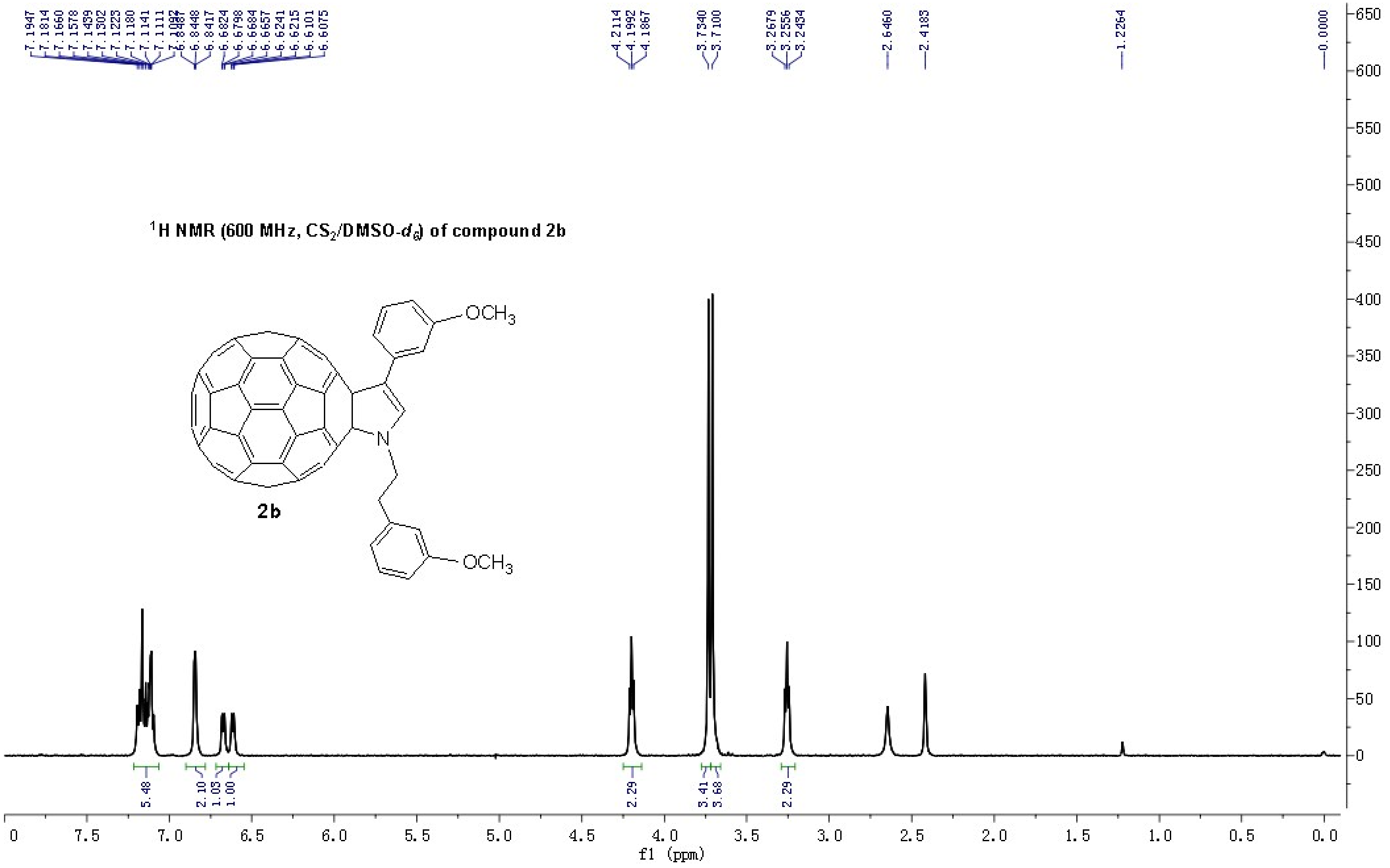


^{13}C NMR (100 MHz, CS_2/DMSO-d_6) of compound 2a



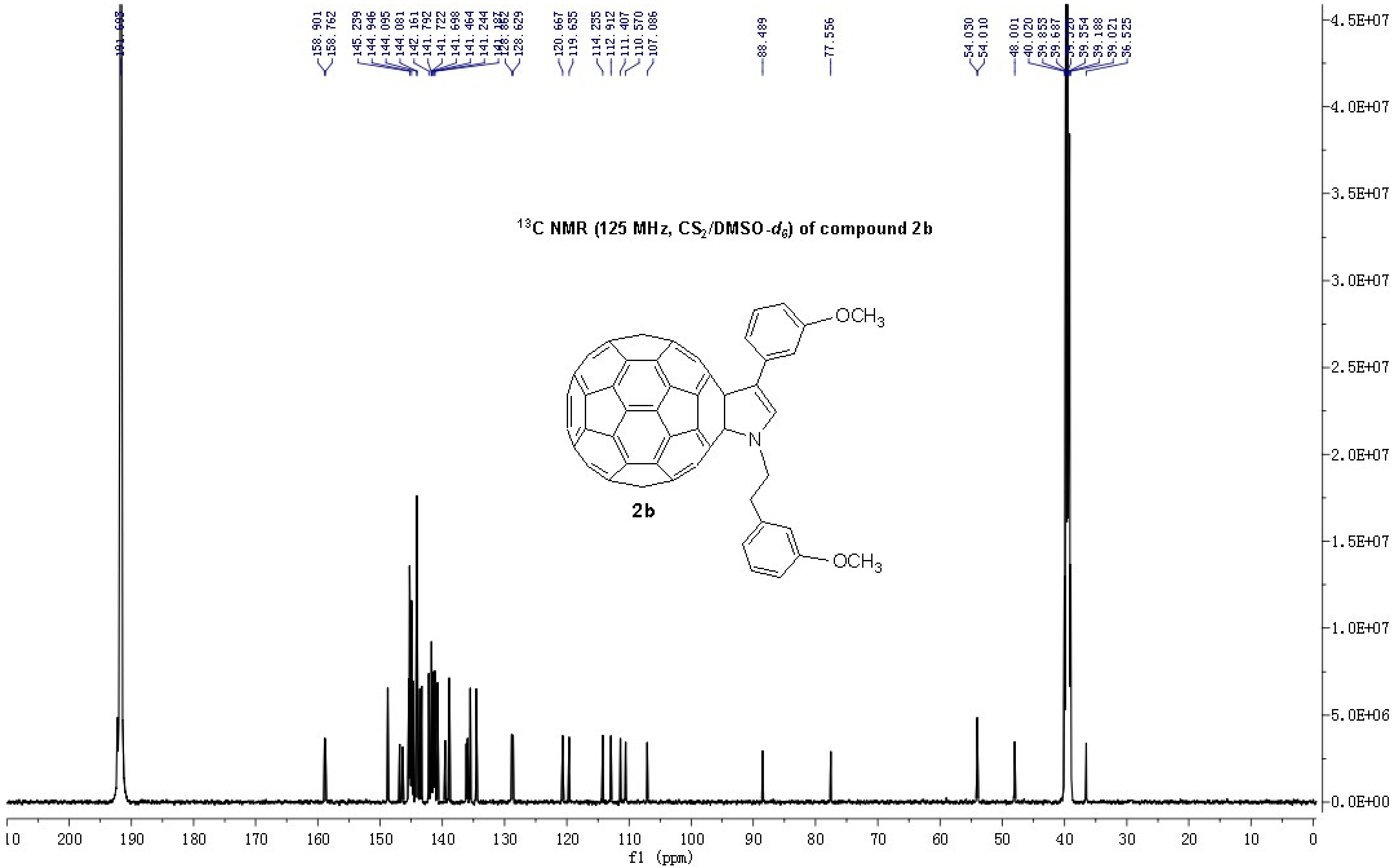
^{13}C NMR (100 MHz, CS_2/DMSO-d_6) of compound **2a**

2a



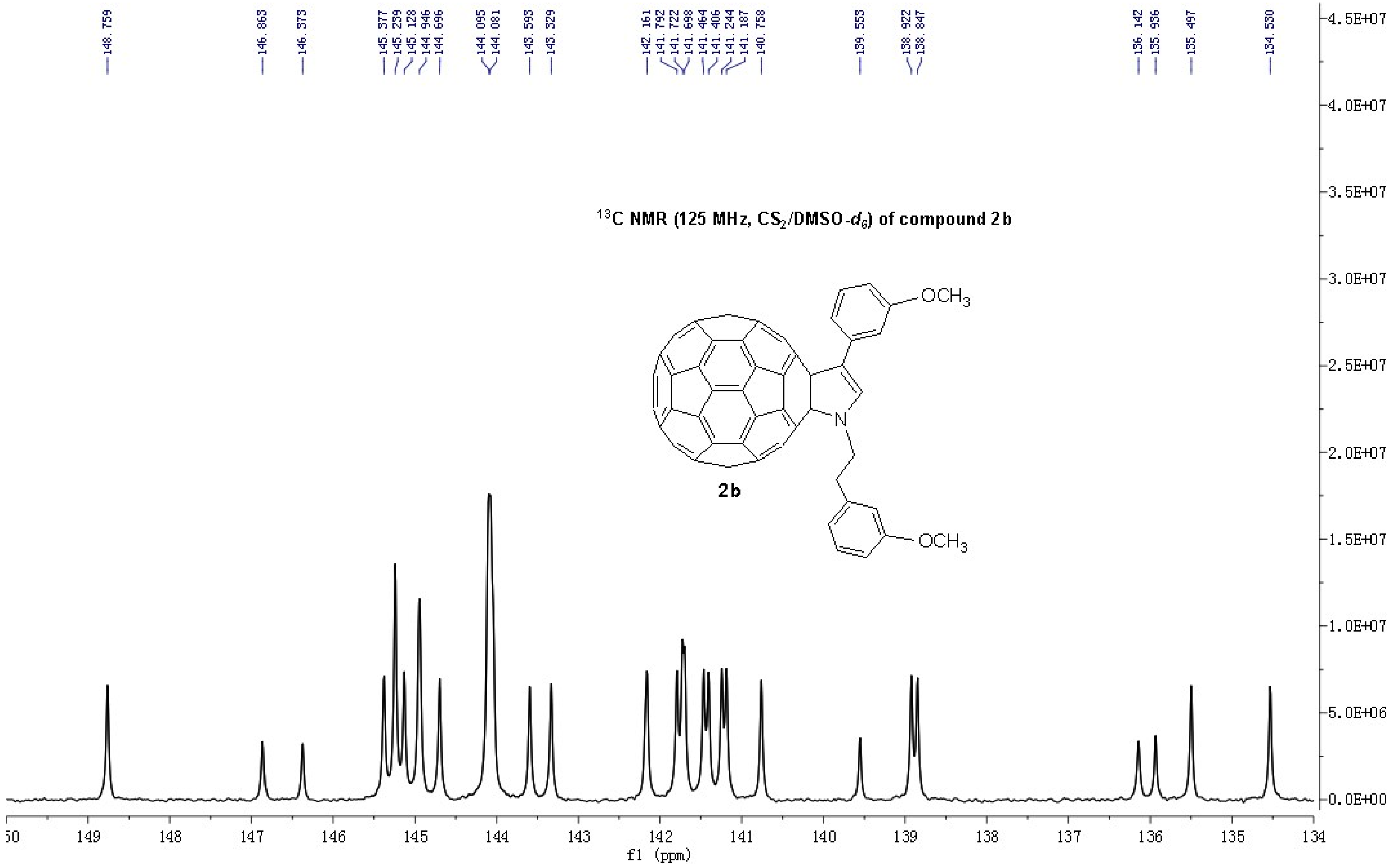
^{1}H NMR (600 MHz, CS_2/DMSO-d_6) of compound **2b**

2b



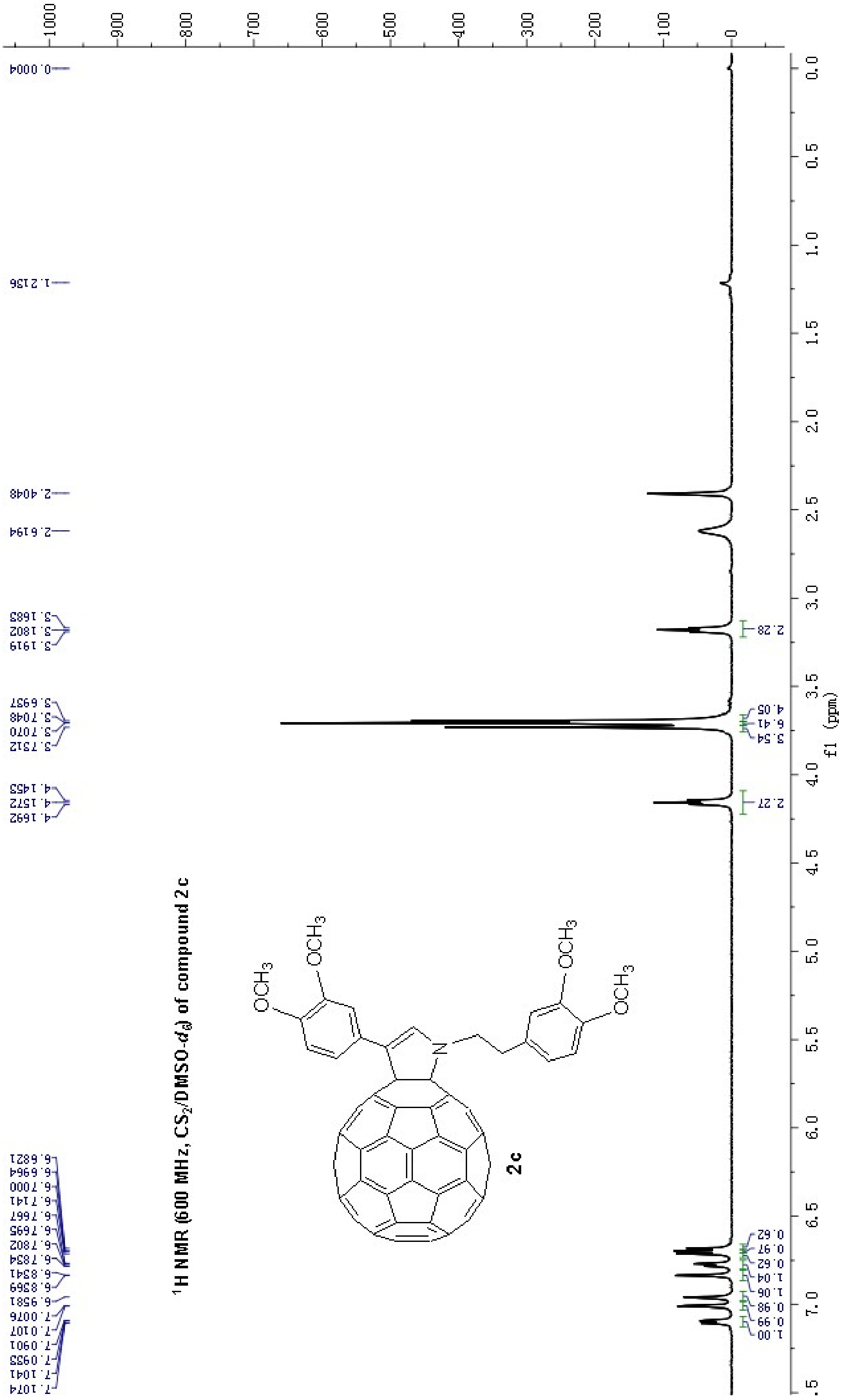
^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2b**

2b

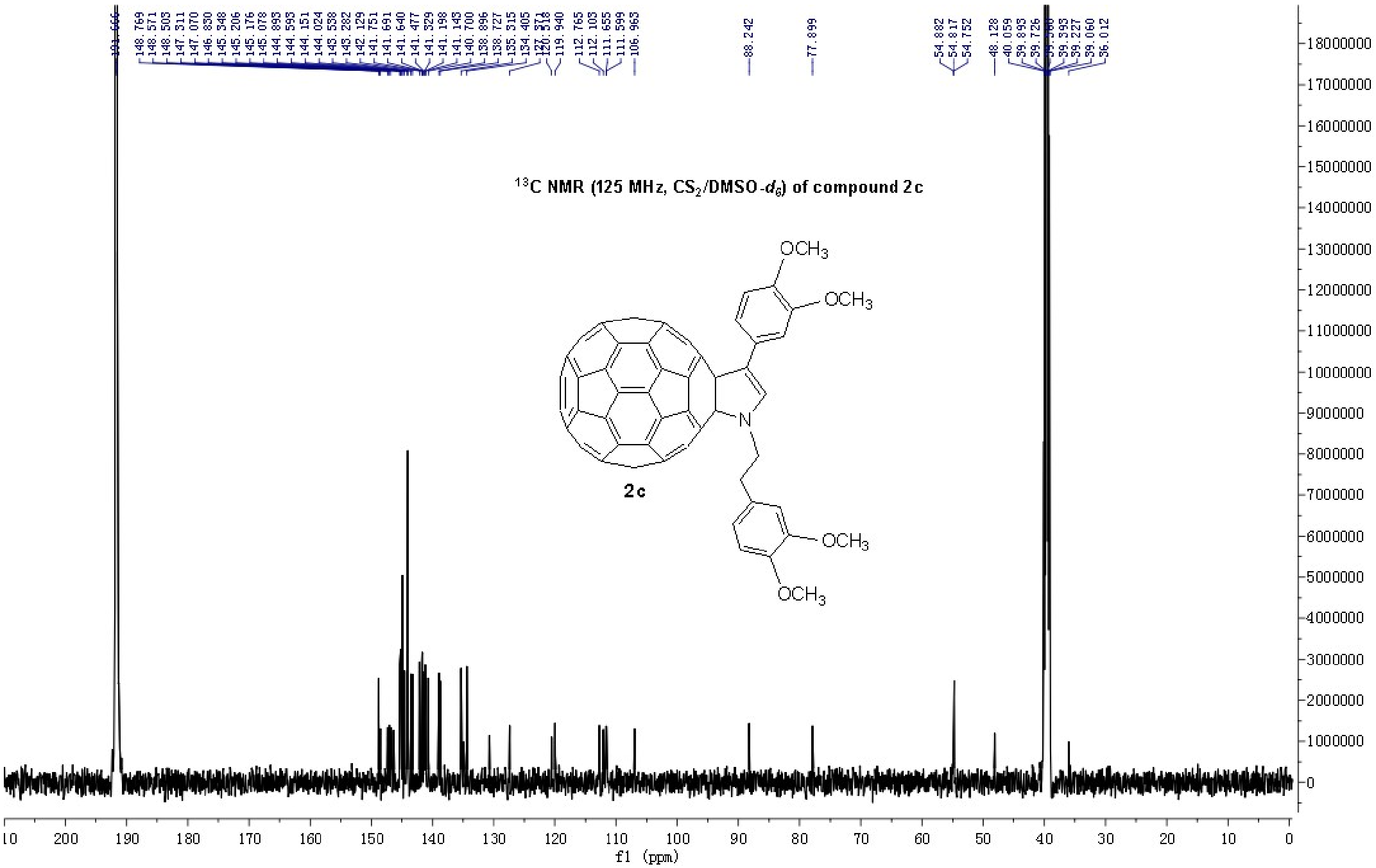


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2b

2b

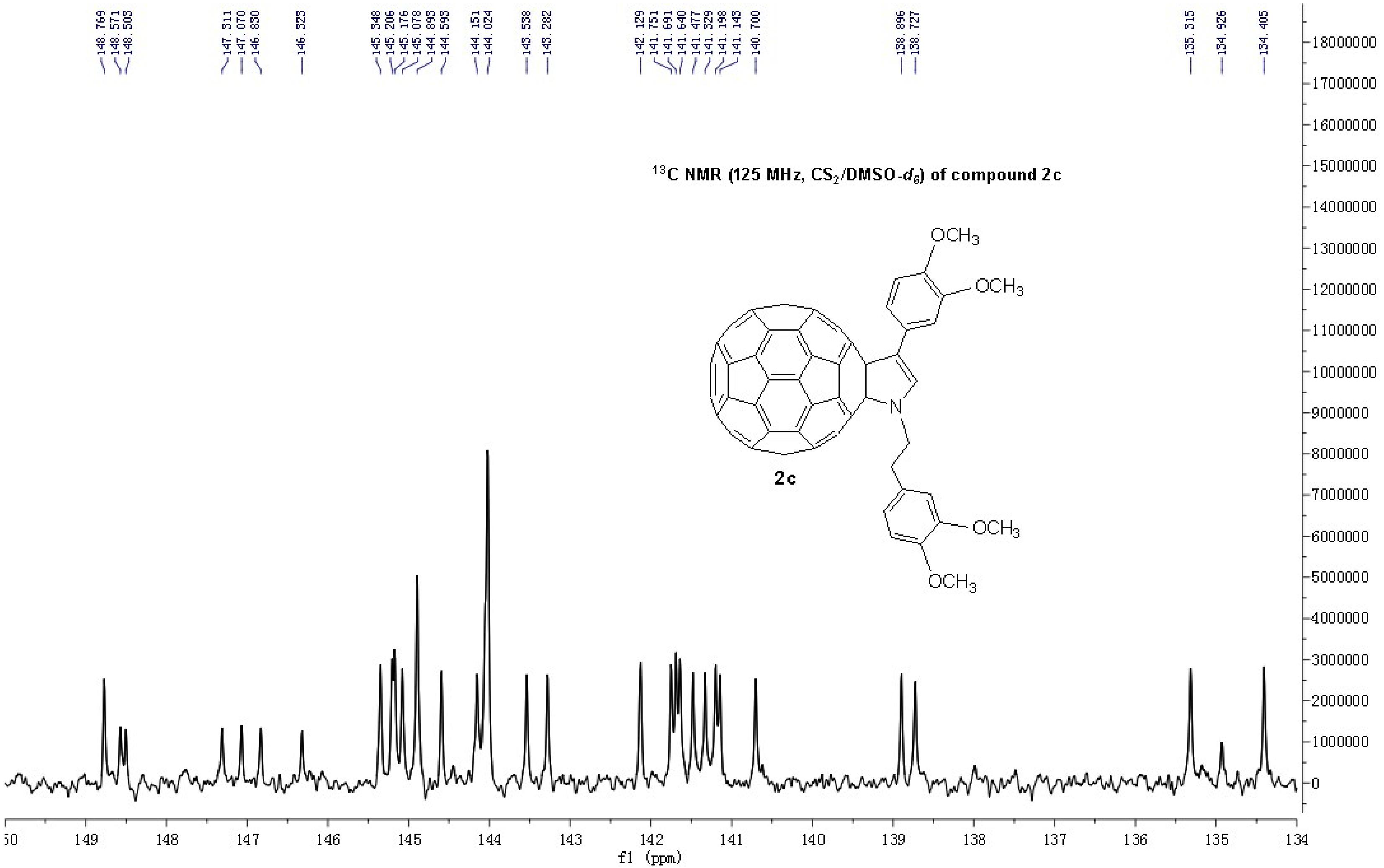


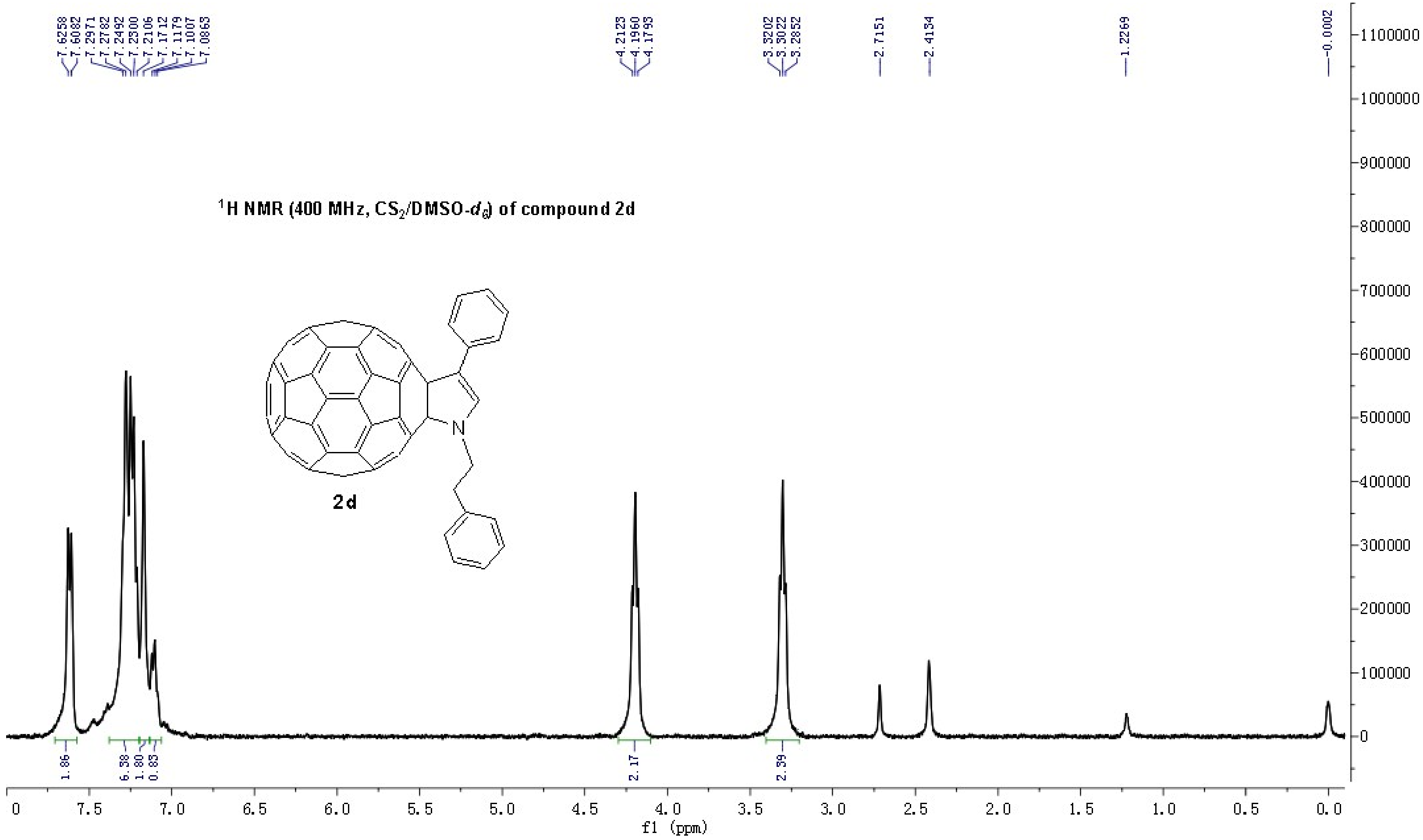
^{1}H NMR (600 MHz, CS_2/DMSO-d_6) of compound **2c**



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2c

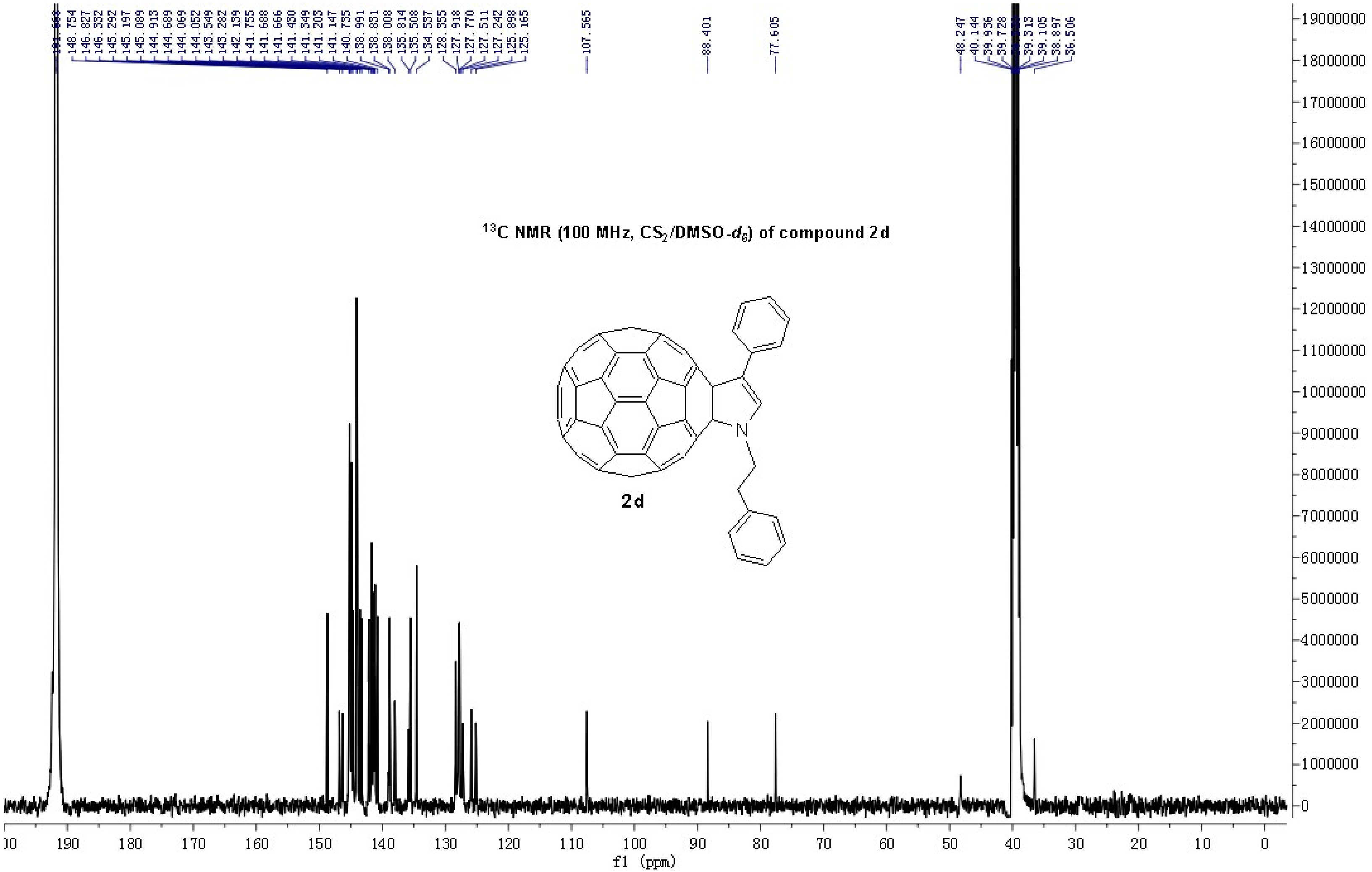
^{13}C NMR (125 MHz, CS$_2$/DMSO-d_6) of compound **2c**





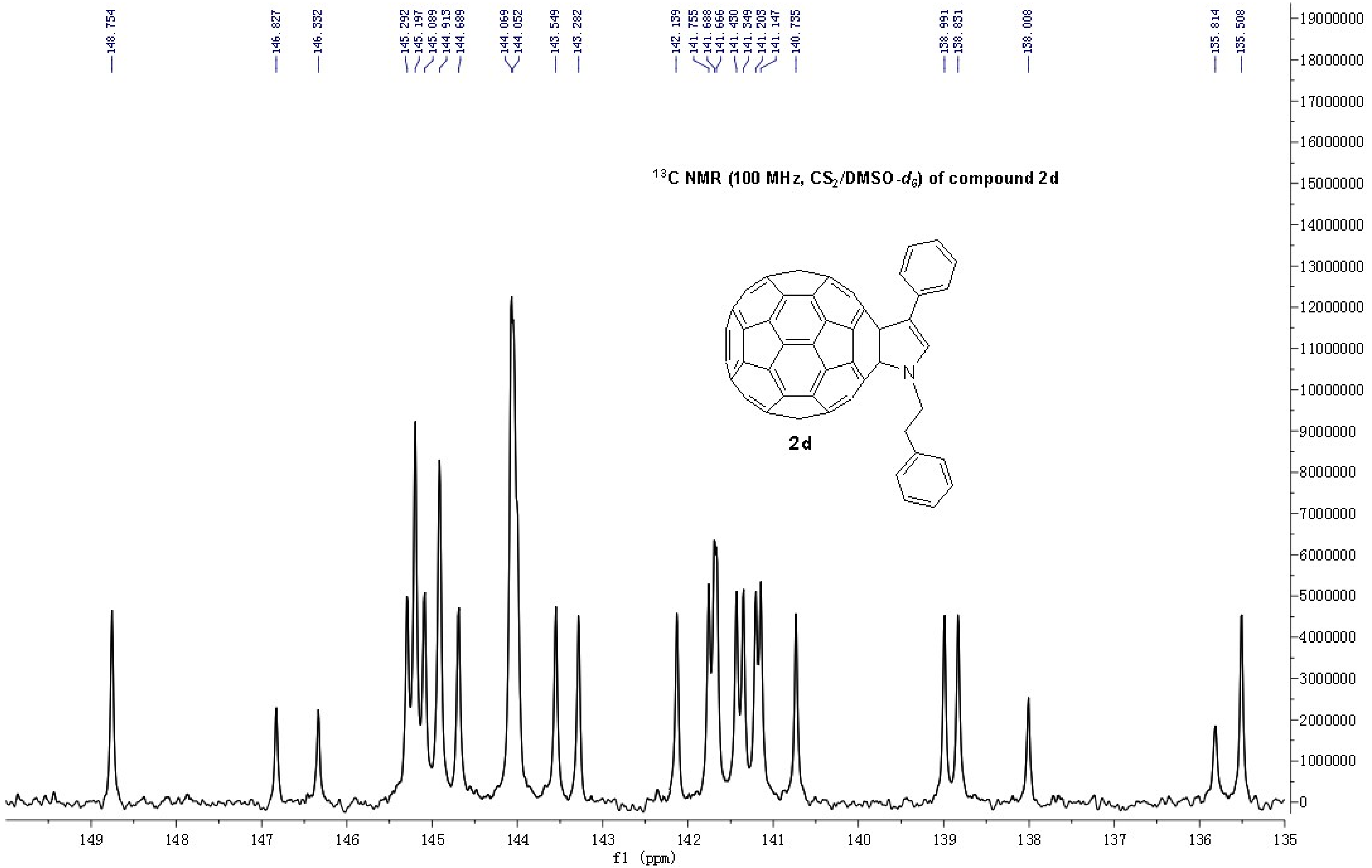
^1H NMR (400 MHz, CS_2/DMSO-d_6) of compound 2d

2d

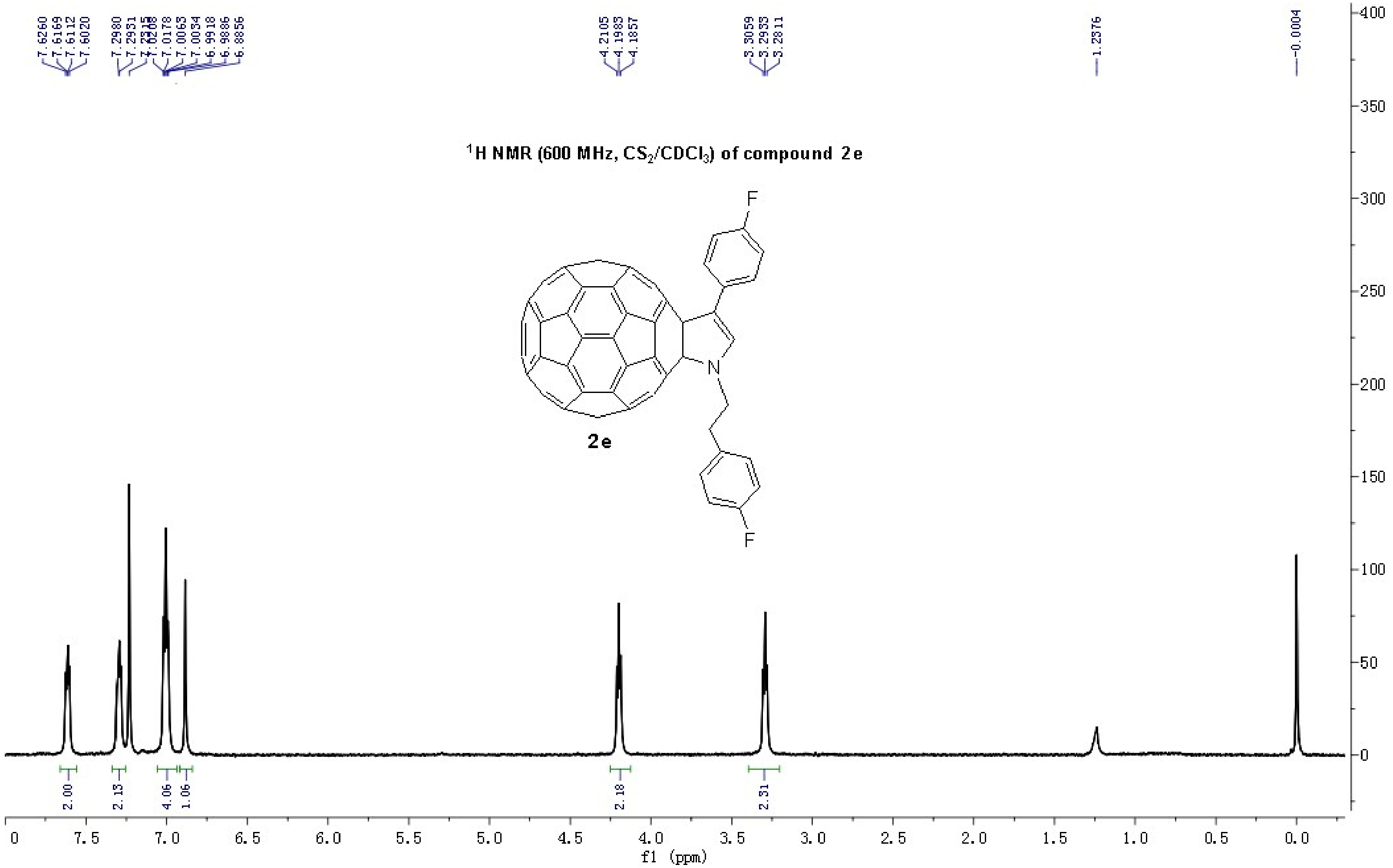


^{13}C NMR (100 MHz, CS_2/DMSO-d_6) of compound 2d

2d

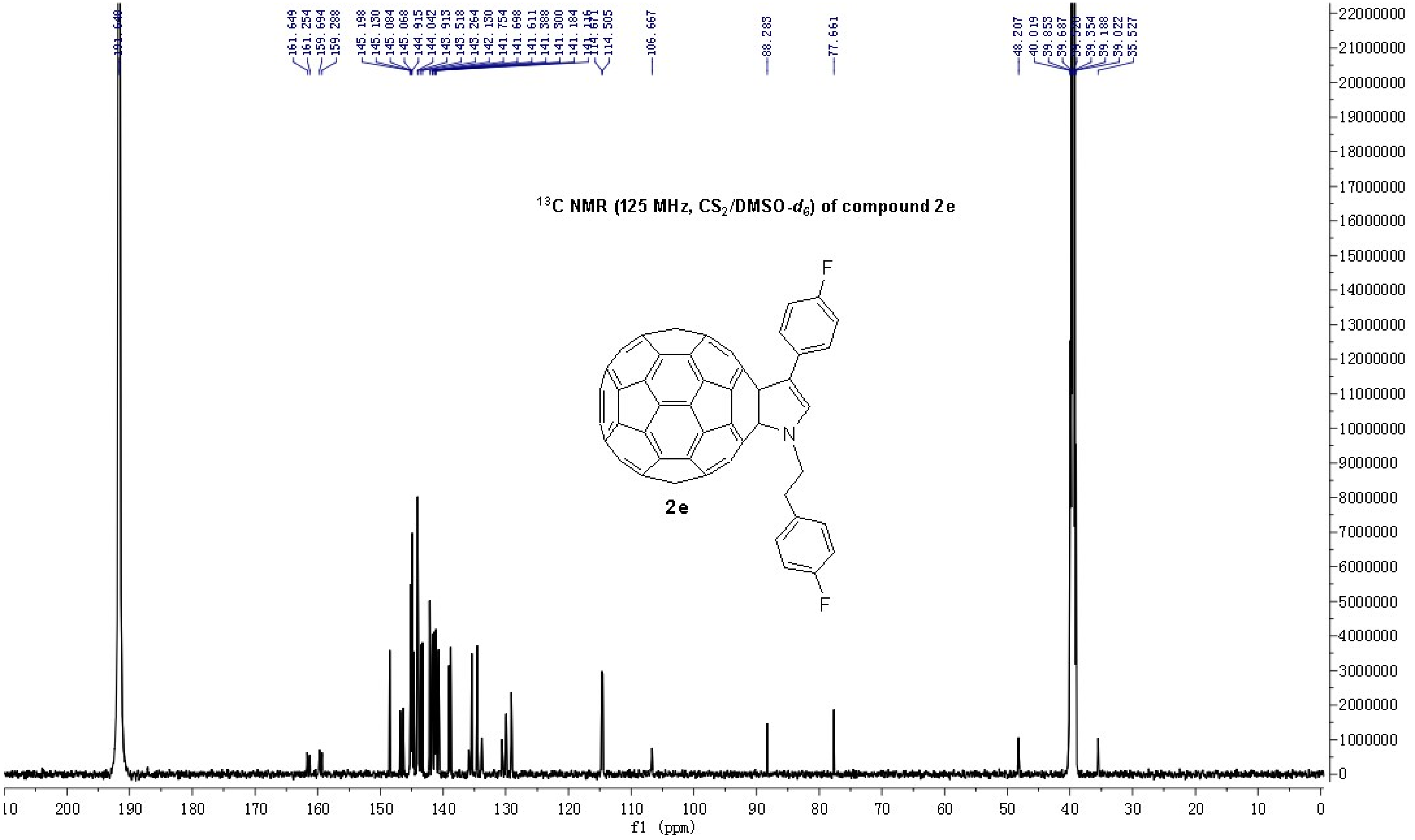


^{13}C NMR (100 MHz, CS_2/DMSO-d_6) of compound 2d



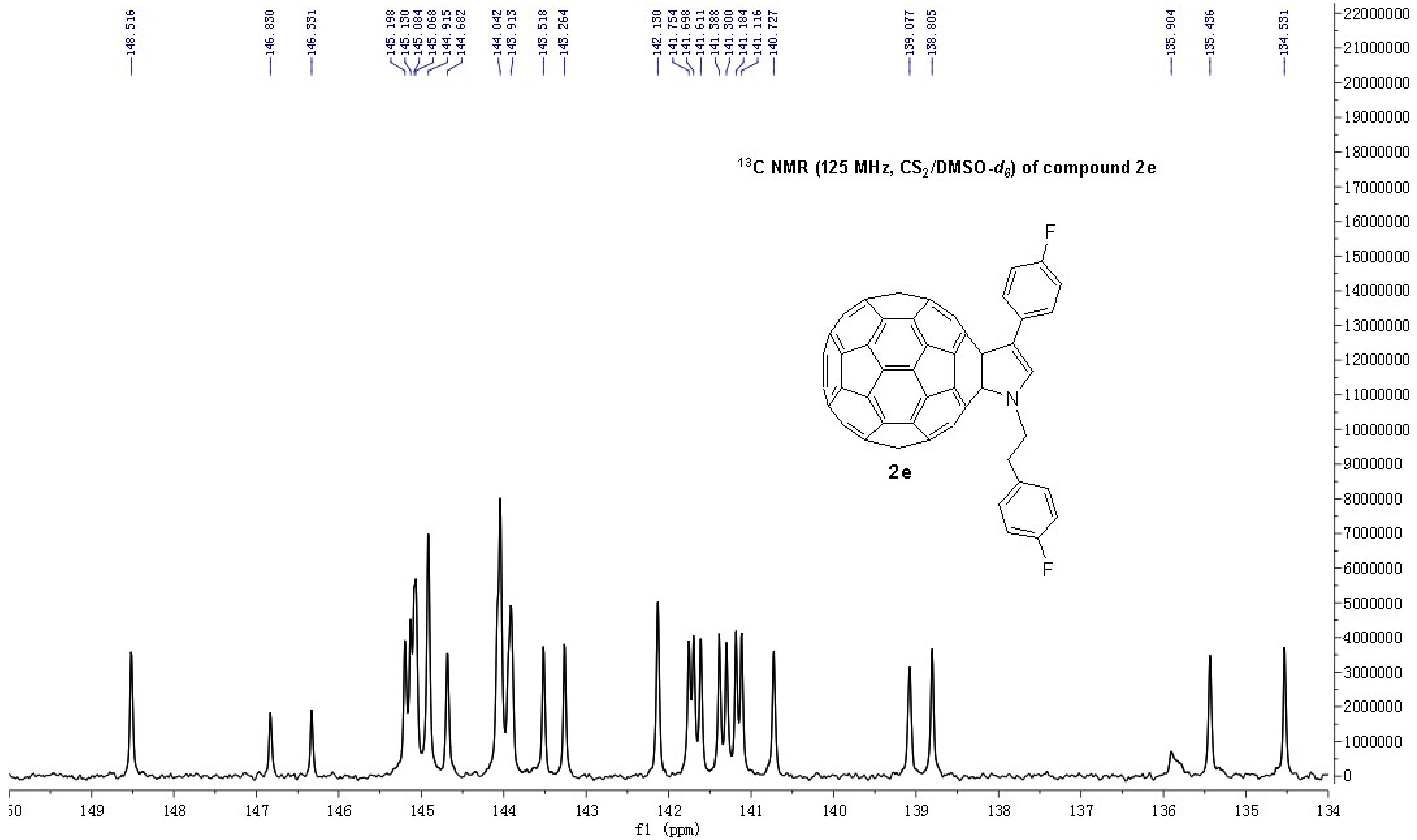
^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2e

2e



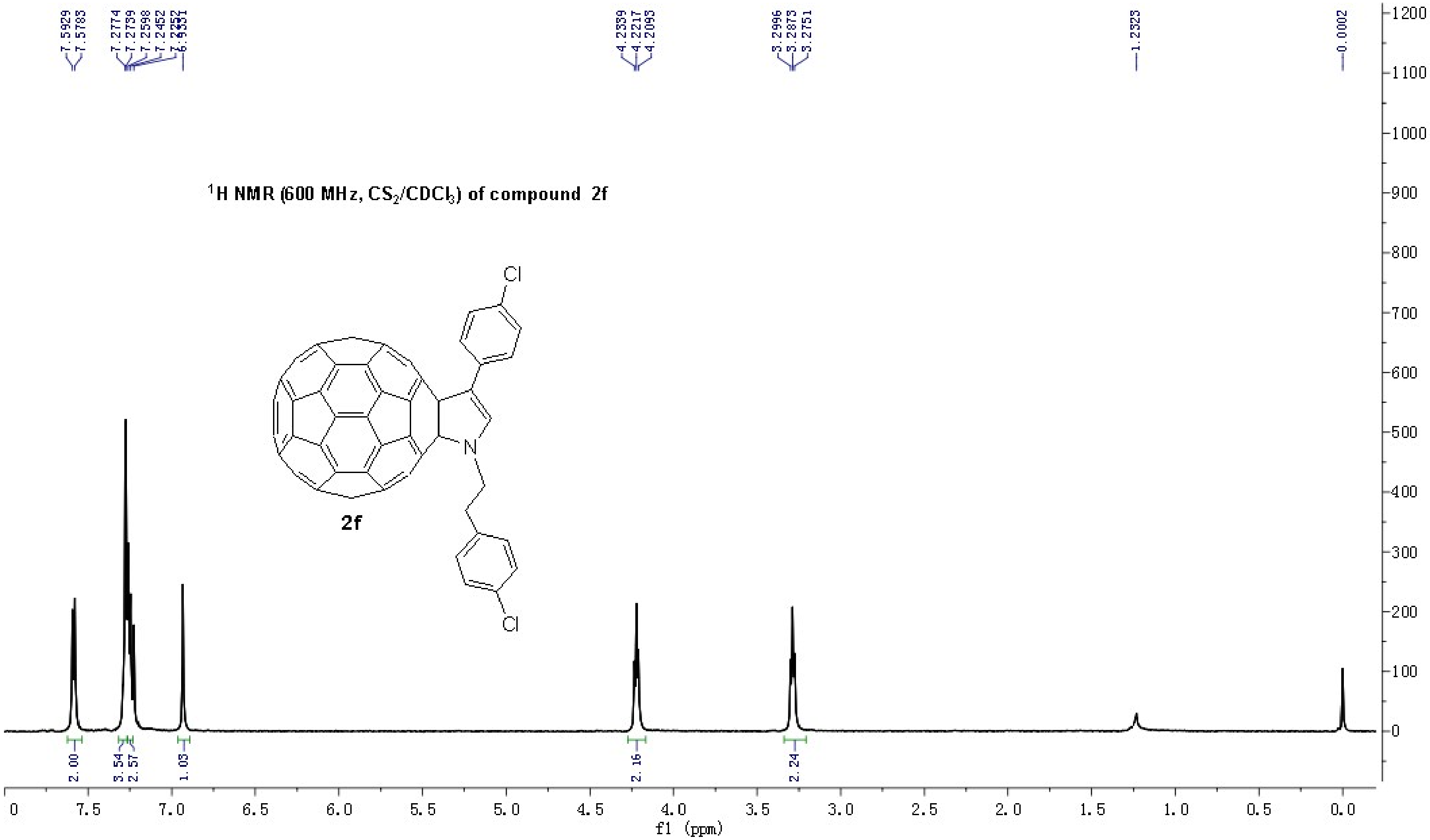
^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2e

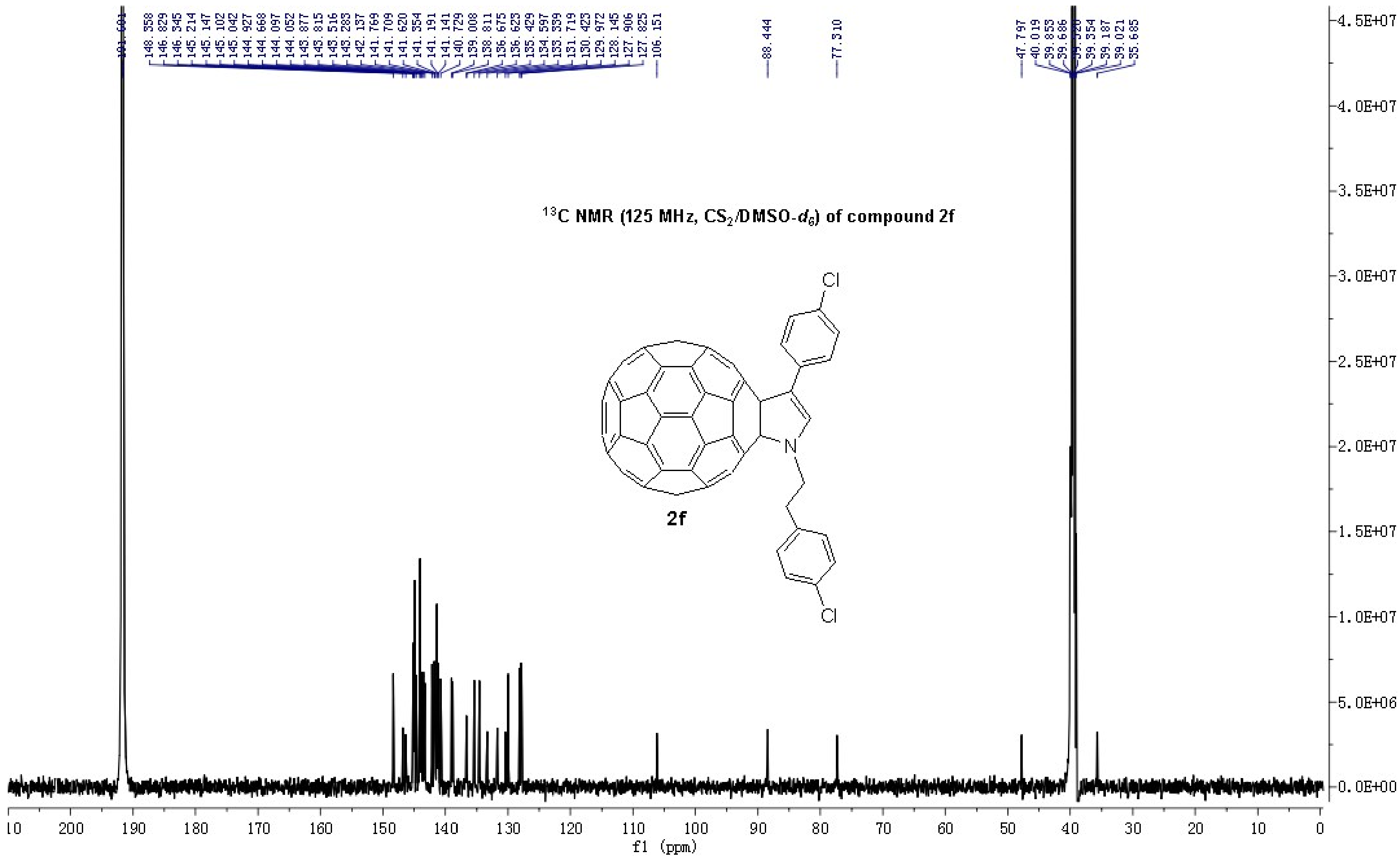
2e



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2e**

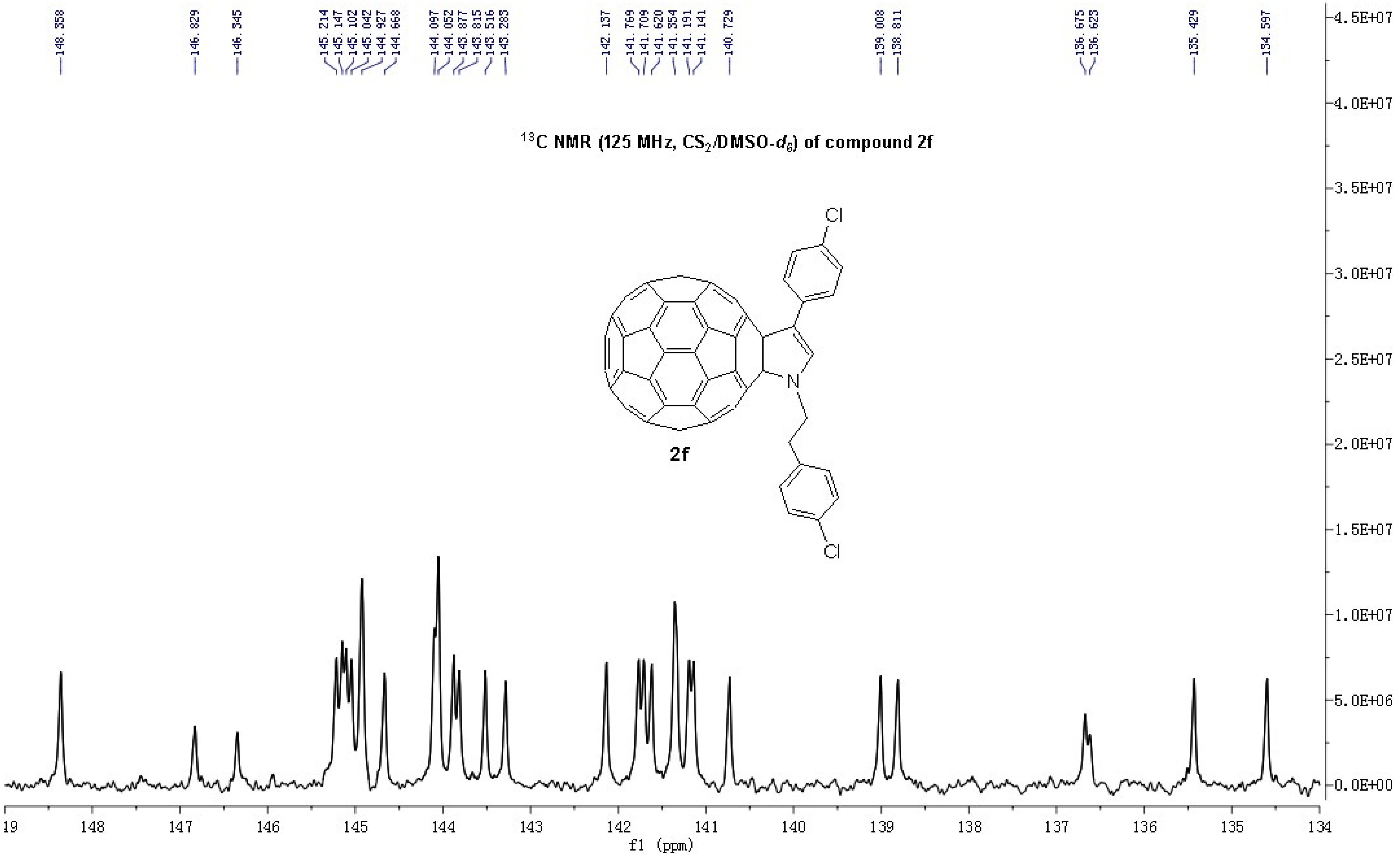
^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound 2f



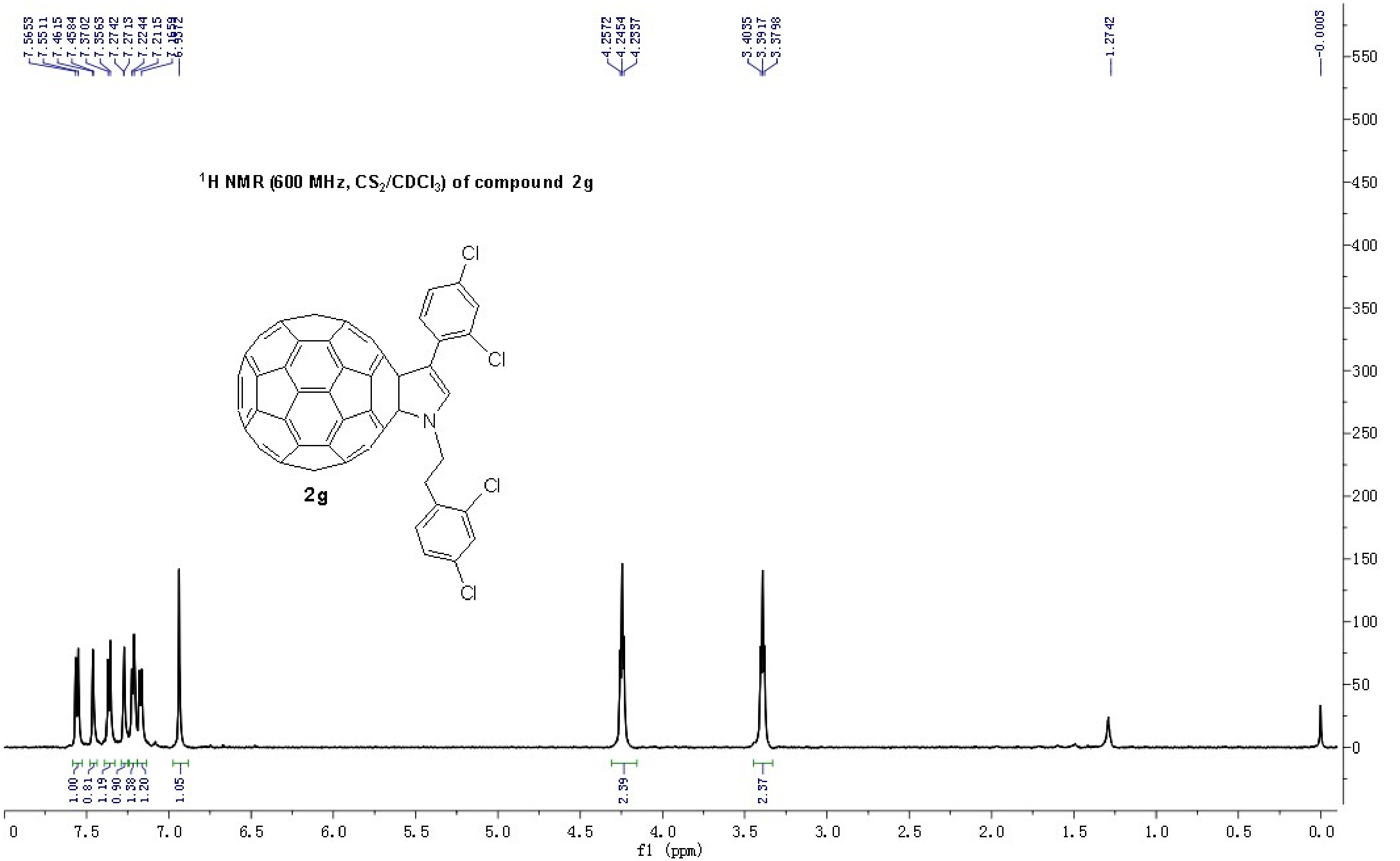


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2f

2f

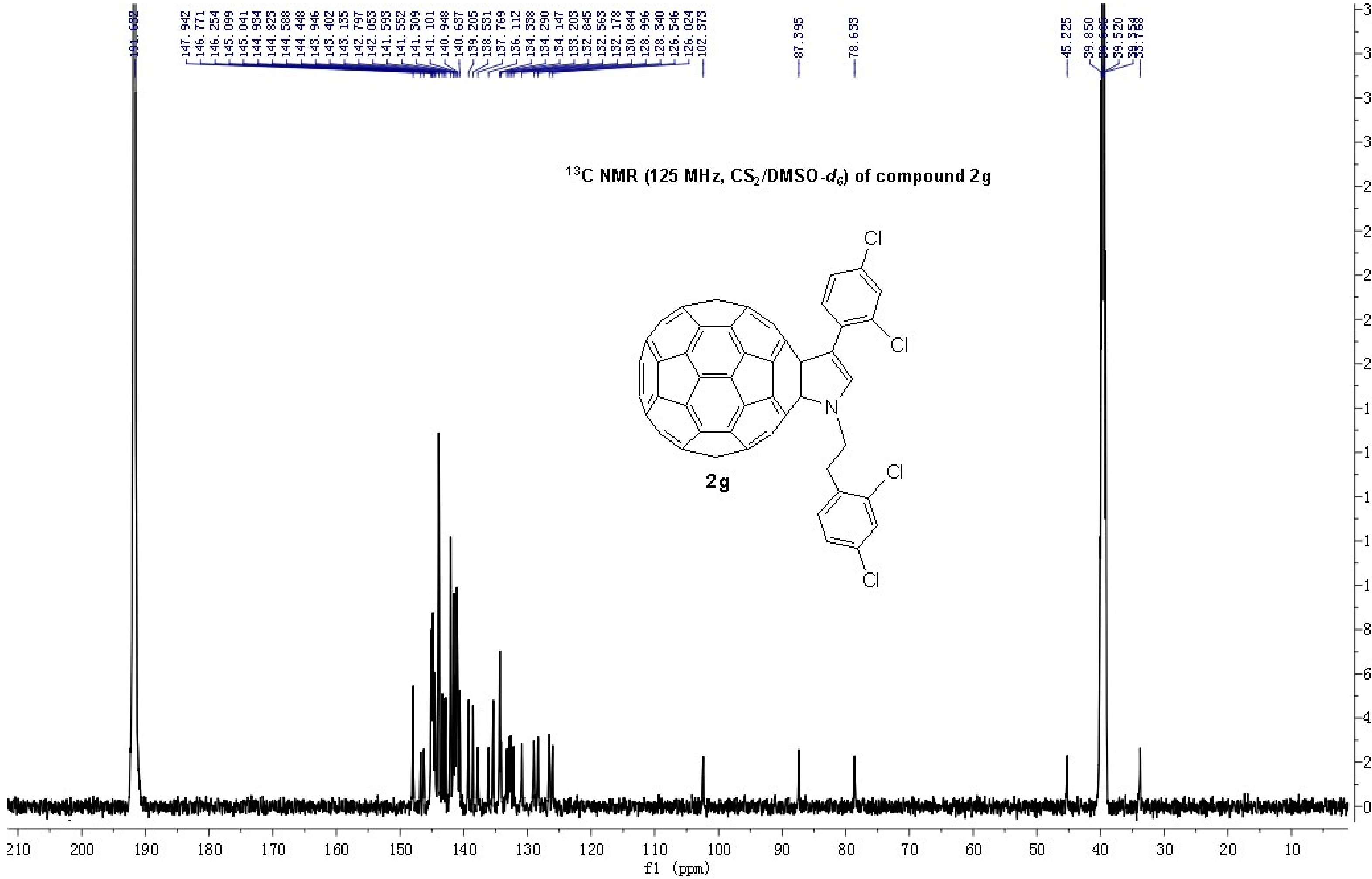


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2f**

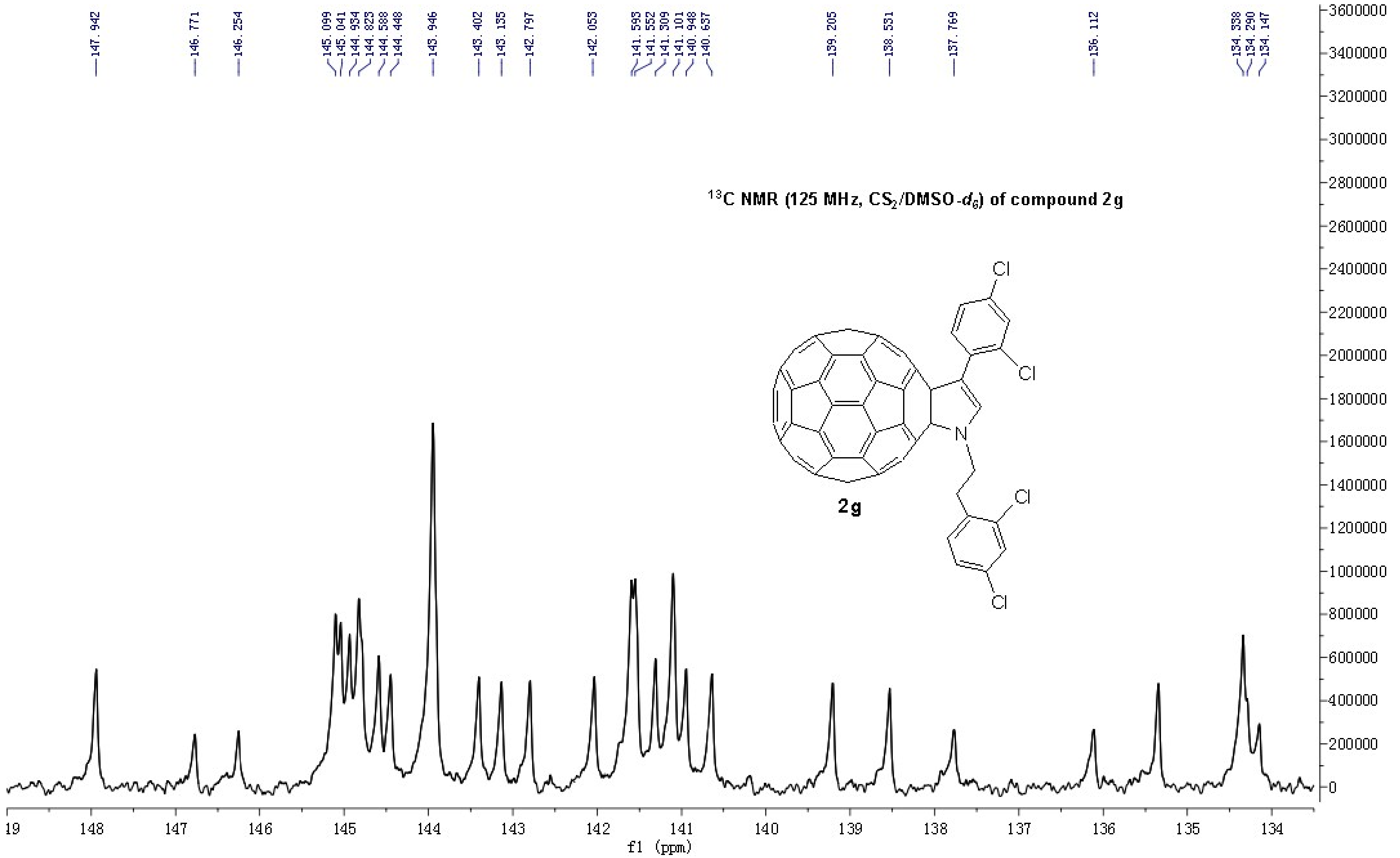


^{1}H NMR (600 MHz, $CS_2/CDCl_3$) of compound **2g**

2g

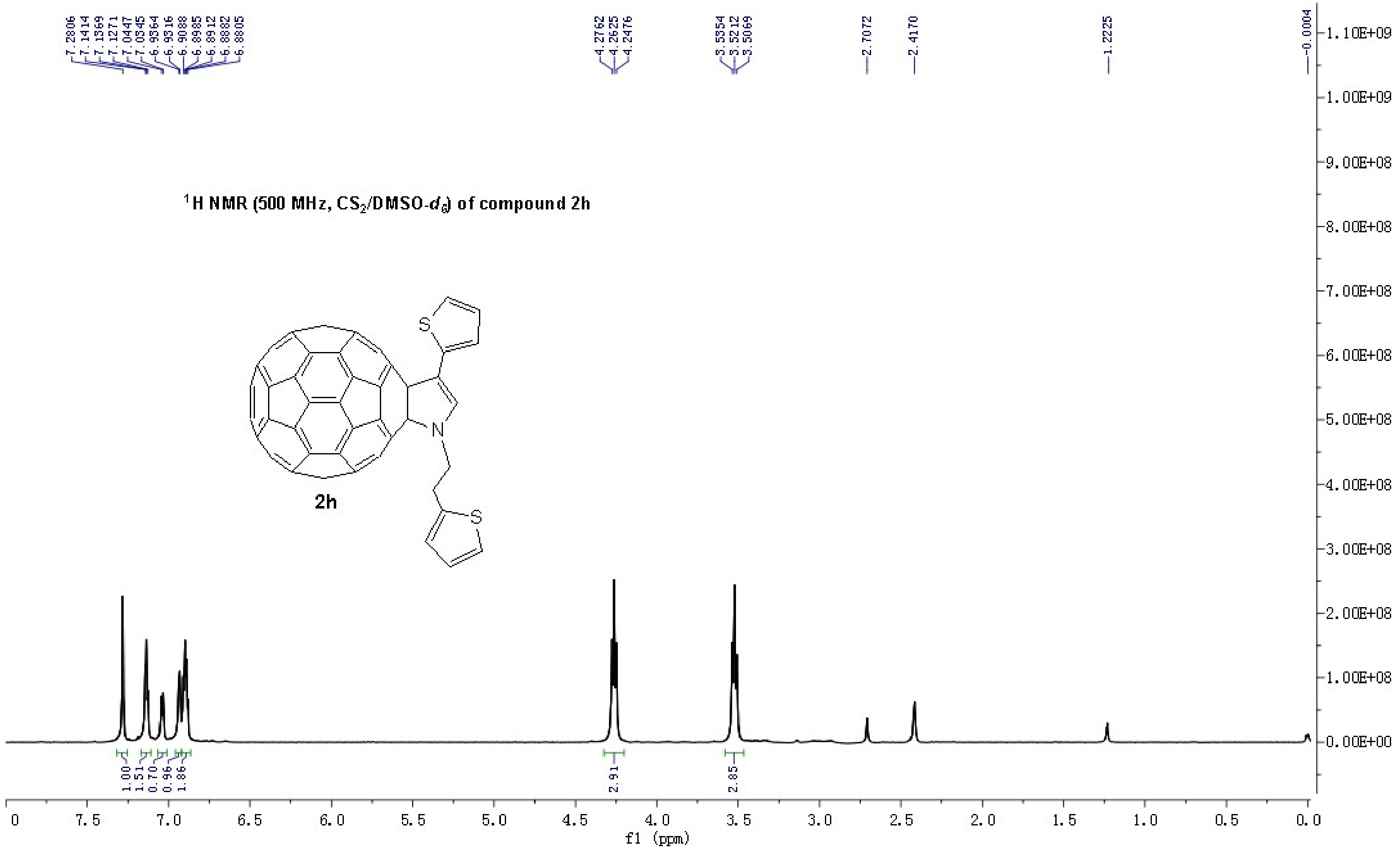

^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2g

2g

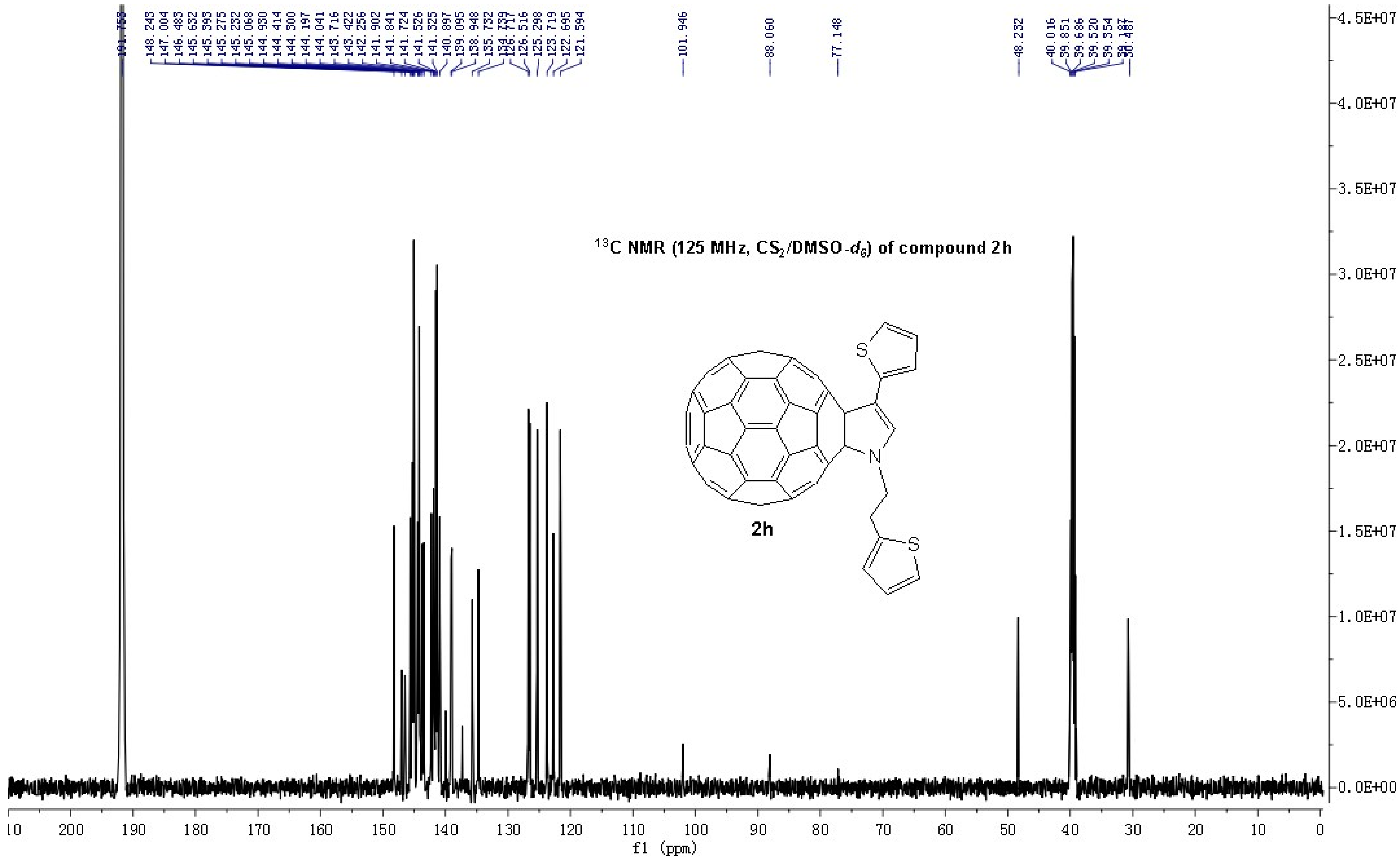


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2g

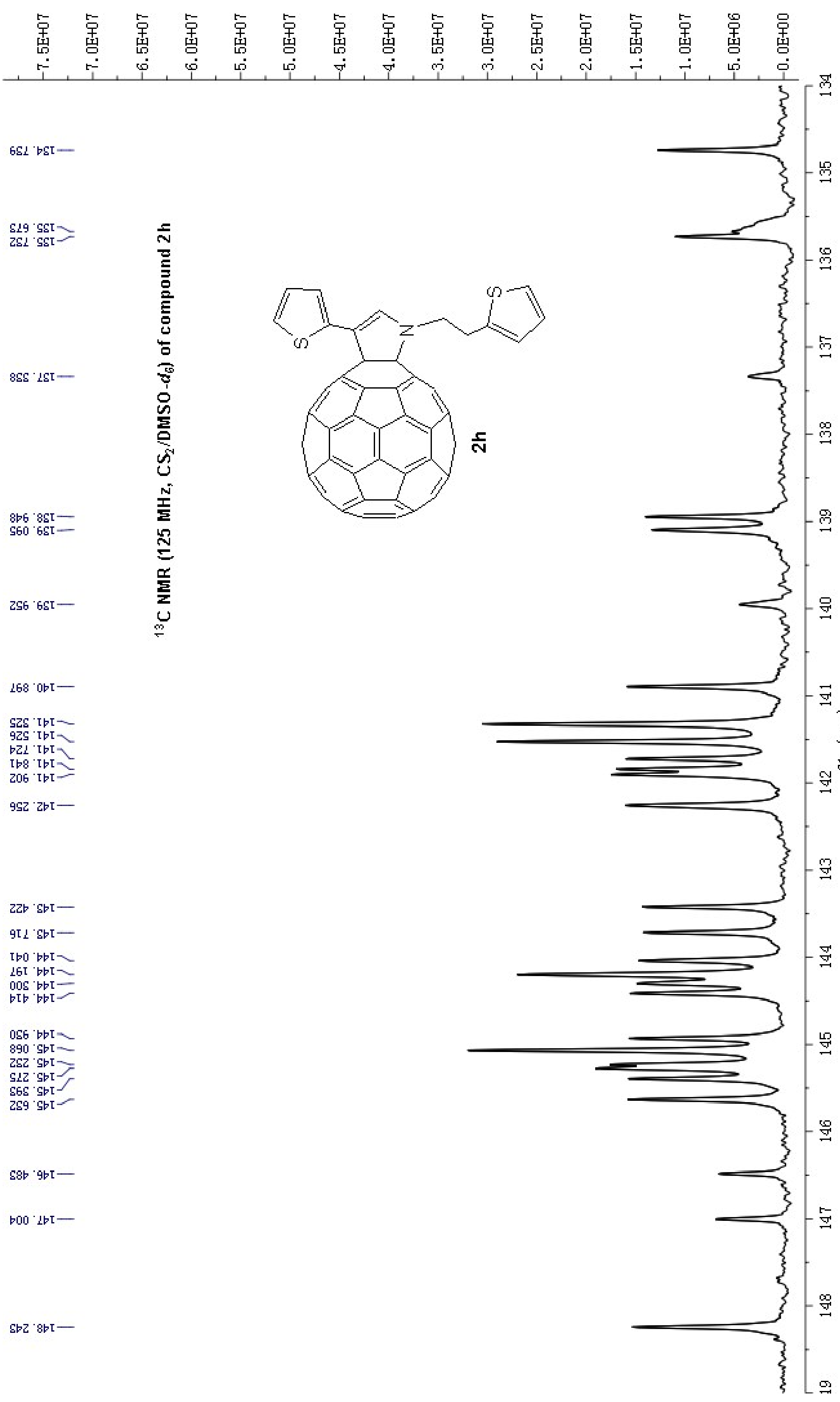
2g



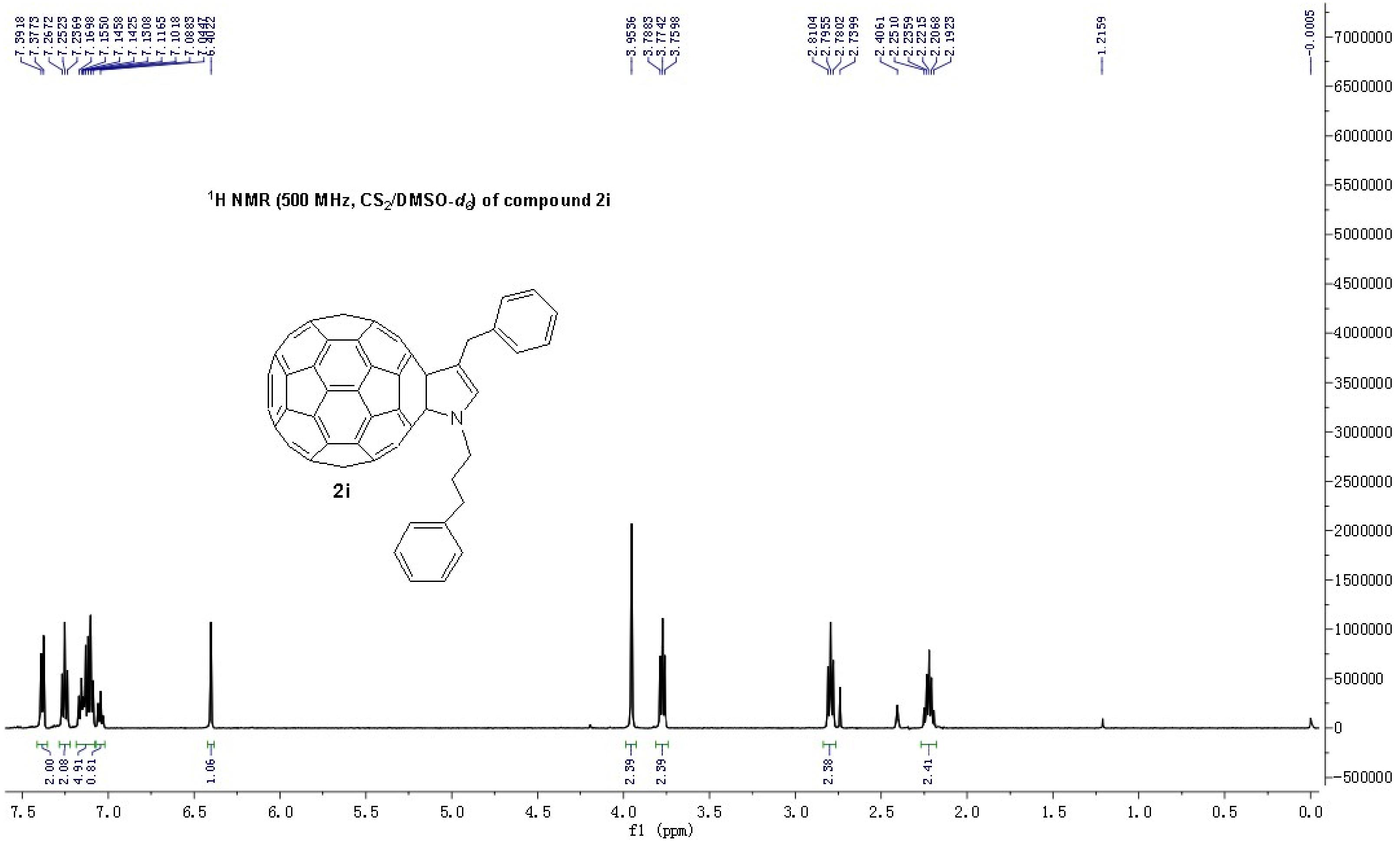
^{1}H NMR (500 MHz, CS_2/DMSO-d_6) of compound 2h



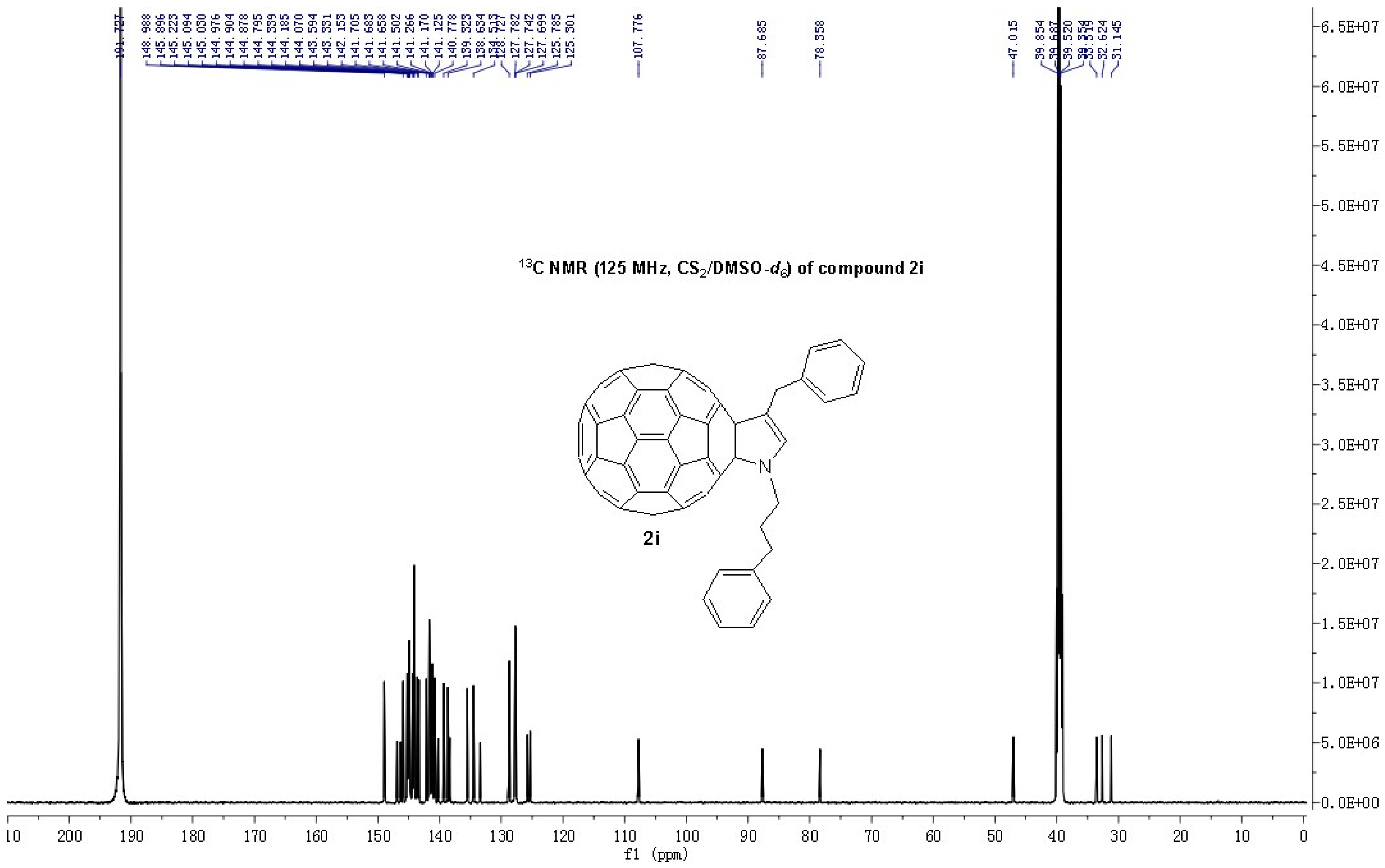
^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound 2h



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2h**

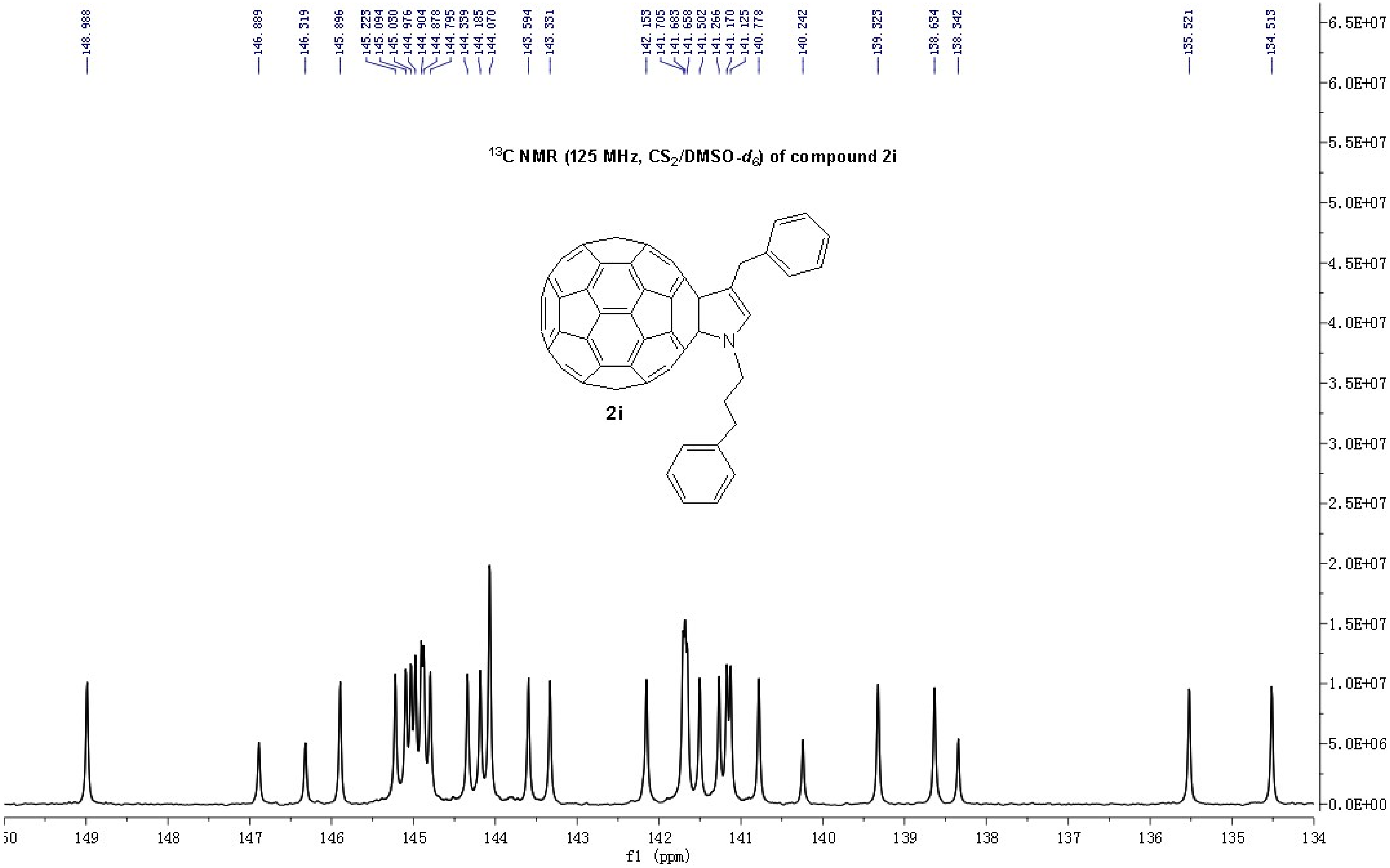


^{1}H NMR (500 MHz, CS_2/DMSO-d_6) of compound **2i**

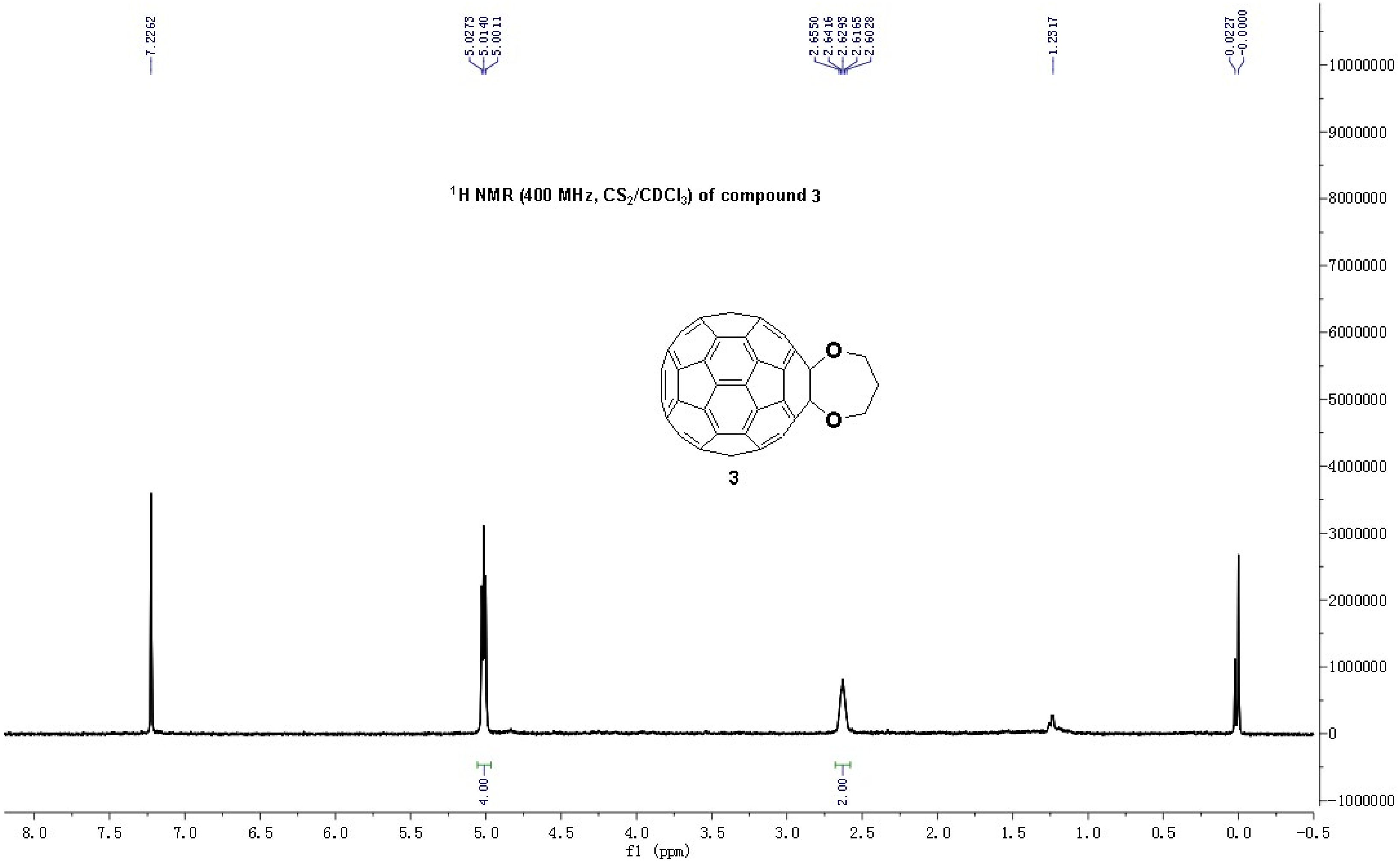


^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2i**

2i



^{13}C NMR (125 MHz, CS_2/DMSO-d_6) of compound **2i**



^1H NMR (400 MHz, $CS_2/CDCl_3$) of compound 3