Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Heteroannulation of [60]Fullerene with *N*-(2-Arylethyl) Sulfonamides via C–H Bond Activation

Yi-Tan Su,[a] You-Liang Wang[a] and Guan-Wu Wang*[a,b]

[a]*Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry, and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; E-mail: gwang@ustc.edu.cn*

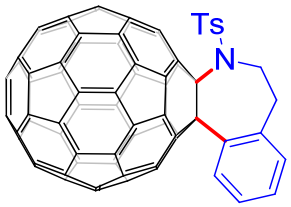
[b]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China*

gwang@ustc.edu.cn

Table of Contents

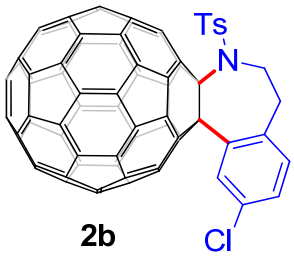
Experimental procedures and characterization data.

General procedure for the preparation of C_{60}-fused tetrahydrobenzazepines 2a-2i: To a 15 mL sealed tube containing C_{60} (36 mg, 0.050 mol), *N*-(2-arylethyl) sulfonamide derivative **1a** (**1b-1i**, 0.15 mmol), $Cu(OAc)_2$ (27.2 mg, 0.15 mmol) and $Pd(OAc)_2$ (2.2 mg, 0.010 mmol) were added ODCB (6 mL) and TFA (0.2 mL). After being stirred at 80 ^oC for 10 h (6 h for **1f)**, the reaction mixture was filtered through a silica gel plug to remove any insoluble material. After evaporation in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60}, and subsequent elution with carbon disulfide/dichloromethane provided **2a** (**2b-2i**).



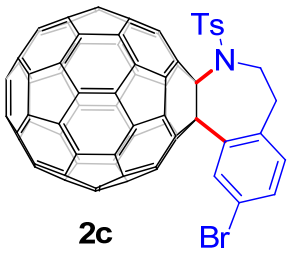
2a

C_{60}-fused tetrahydrobenzazepine 2a: According to the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1a** (41.0 mg, 0.15 mmol) afforded first recovered C_{60} (16.5 mg, 46%) and then **2a** (15.8 mg, 32%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.28 (d, 8.0 Hz, 1H), 7.60-7.53 (m, 5H), 7.09 (d, J = 8.4 Hz, 2H), 5.33-5.23 (m, 1H), 5.15-5.06 (m, 1H), 4.63 (dd, J = 13.6, 7.6 Hz, 1H), 3.43 (dd, J = 14.4, 6.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 154.40, 153.83, 150.03, 149.61, 147.86, 147.27, 146.23, 146.16 (2C), 145.81, 145.76 (2C), 145.72, 145.66, 145.50, 145.34 (2C), 145.31, 145.23, 145.11, 145.00, 144.95 (3C), 144.79, 144.71, 144.49, 144.45, 144.31, 144.20, 144.08, 143.93, 142.80, 142.64, 142.52, 142.34 (2C), 142.15 (2C), 142.00, 141.90, 141.85, 141.83, 141.77, 141.70, 141.35 (2C), 141.15, 141.07, 140.91, 140.85, 139.91, 139.83, 139.67, 139.40, 139.10, 139.01, 137.77, 137.70, 137.27 (aryl *C*), 136.03, 133.82, 130.81 (aryl *C*), 129.56 (aryl *C*), 128.93 (aryl *C*), 128.81 (2C, aryl *C*), 128.09 (aryl *C*), 126.25 (2C, aryl *C*), 78.60 (sp^3-*C* of C_{60}), 71.68 (sp^3-*C* of C_{60}), 50.00 (CH_2), 33.60 (CH_2), 21.24 (CH_3); FT-IR ν/cm^{-1} (KBr) 2915, 1456, 1431, 1344, 1155, 1117, 1091, 1048, 990, 744, 670, 562, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (4.99), 322 (4.53), 435 (3.41), 694 (2.43); (-)ESI-MS m/z calcd for $C_{75}H_{15}NO_2S$ [M^-] 993.0829, found 993.0839.



2b

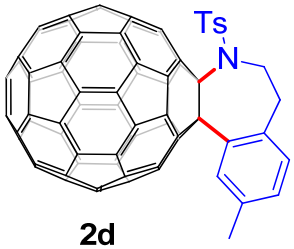
C_{60}-fused tetrahydrobenzazepine 2b: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (46.5 mg, 0.15 mmol) afforded first recovered C_{60} (13.5 mg, 38%) and then **2b** (12.5 mg, 24%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.28 (d, J = 2.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.0, 2.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 5.30-5.21 (m, 1H), 5.17-5.08 (m, 1H), 4.65 (dd, J = 13.4, 7.4 Hz, 1H), 3.43 (dd, J = 14.6, 7.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR [75 MHz, CS_2/ODCB-d_4 with Cr(acac)$_3$ as relaxation reagent] (all 1C unless indicated) δ 153.82, 152.92, 150.23, 149.56, 148.07, 147.53, 146.43, 146.39, 146.37, 146.04, 145.99 (4C), 145.90, 145.72, 145.68, 145.45, 145.43, 145.32, 145.23, 145.20 (2C), 145.13, 145.10, 144.80, 144.56, 144.46, 144.38 (2C), 144.29, 144.18, 142.97, 142.84, 142.80, 142.72, 142.56 (2C), 142.48, 142.40, 142.29, 142.18, 142.13, 142.07, 141.95, 141.77, 141.53, 141.39, 141.21, 141.14, 141.11, 140.15, 139.98, 139.92, 139.79, 139.30, 139.15, 138.18, 137.75 (aryl *C*), 136.55 (aryl *C*), 136.48, 134.42 (aryl *C*), 134.08, 129.23 (2C, aryl *C*), 129.00 (aryl *C*), 126.60 (2C, aryl *C*), 79.01 (sp^3-*C* of C_{60}), 71.64 (sp^3-*C* of C_{60}), 50.12 (*C*H_2), 33.31 (*C*H_2), 21.36 (*C*H_3) (Note: 2C of the phenyl ring were overlapped by very strong signals of the bulk ODCB-d_4); FT-IR ν/cm^{-1} (KBr) 2920, 1455, 1344, 1263, 1157, 1092, 1067, 1024, 811, 670, 561, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (4.99), 321 (4.47), 435 (3.43), 693 (2.44); (-)ESI-MS m/z calcd for $C_{75}H_{14}{}^{35}ClNO_2S$ [M$^-$] 1027.0439, found 1027.0432.



2c

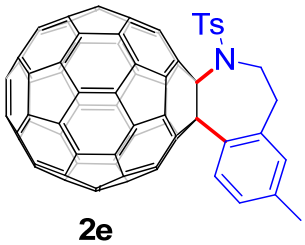
C_{60}-fused tetrahydrobenzazepine 2c: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (53.1 mg, 0.15 mmol) afforded first recovered C_{60} (23.3 mg, 65%) and then **2c** (6.4 mg, 12%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.36 (d, J = 2.0 Hz, 1H), 7.69 (dd, J = 8.0, 2.0 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.2 Hz, 2H), 5.26-5.16 (m, 1H), 5.13-5.04 (m, 1H), 4.61 (dd, J = 13.2, 7.2 Hz, 1H), 3.40 (dd, J = 14.4, 6.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent] (all 1C unless indicated) δ 153.60, 152.66, 149.75, 149.25, 147.89, 147.31, 146.25, 146.21 (2C), 145.86, 145.82, 145.80, 145.77, 145.69,

145.52, 145.36, 145.29, 145.26, 145.13, 145.11, 145.07 (2C), 144.98, 144.93, 144.90, 144.69, 144.41, 144.26, 144.21, 144.18, 143.94, 143.92, 142.82, 142.66, 142.65, 142.55, 142.38 (2C), 142.21, 142.16, 142.09, 142.01, 141.90, 141.86, 141.73, 141.69, 141.38, 141.26, 140.95, 140.85, 140.61, 139.91, 139.85, 139.64, 139.47, 139.17, 138.94, 137.87, 137.51, 136.27, 136.24, 134.01, 132.38 (aryl *C*), 132.25 (aryl *C*), 131.62 (aryl *C*), 128.88 (2C, aryl *C*), 126.31 (2C, aryl *C*), 122.32 (aryl *C*), 78.59 (sp^3-*C* of C_{60}), 71.16 (sp^3-*C* of C_{60}), 49.73 (*C*H_2), 33.08 (*C*H_2), 21.28 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2922, 1463, 1345, 1266, 1157, 1089, 1067, 990, 809, 670, 562, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (4.99), 323 (4.48), 435 (3.42), 693 (2.45); (-)ESI-MS m/z calcd for $C_{75}H_{14}{}^{79}BrNO_2S$ [M^-] 1070.9934, found 1070.9933.



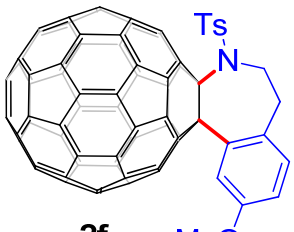
2d

C_{60}-fused tetrahydrobenzazepine 2d: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (43.5 mg, 0.15 mmol) afforded first recovered C_{60} (13.7 mg, 38%) and then **2d** (20.2 mg, 40%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.11 (s, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.10 (d, J= 8.4 Hz, 2H), 5.29-5.20 (m, 1H), 5.17-5.09 (m, 1H), 4.65 (dd, J = 13.2, 7.2 Hz, 1H), 3.43 (dd, J = 14.2, 6.6 Hz, 1H), 2.52 (s, 3H), 2.30 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 154.69, 154.06, 150.20, 149.82, 148.00, 147.41, 146.35, 146.28 (2C), 145.94, 145.89 (2C), 145.85, 145.79, 145.60 (2C), 145.49, 145.45, 145.36, 145.25, 145.11 (2C), 145.08, 145.05, 144.86, 144.83, 144.64, 144.60, 144.40, 144.33, 144.24, 144.06, 142.93, 142.77, 142.65, 142.47 (2C), 142.28 (2C), 142.12, 142.10, 142.03, 141.98, 141.97, 141.82, 141.48, 141.33, 141.25 (2C), 140.99 (2C), 140.02, 139.96, 139.80, 139.50, 139.18, 139.14, 137.88 (2C), 137.68 (aryl *C*), 136.08, 134.38 (aryl *C*), 133.87, 130.84 (aryl *C*), 130.32 (aryl *C*), 129.64 (aryl *C*), 128.96 (2C, aryl *C*), 126.35 (2C, aryl *C*), 78.77 (sp^3-*C* of C_{60}), 71.80 (sp^3-*C* of C_{60}), 50.15 (*C*H_2), 33.20 (*C*H_2), 21.45 (*C*H_3), 21.29 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2919, 1450, 1330, 1156, 1090, 1070, 986, 810, 669, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.00), 322 (4.41), 435 (3.36), 693 (2.38); (-)ESI-MS m/z calcd for $C_{76}H_{17}NO_2S$ [M^-] 1007.0985, found 1007.0992.



2e

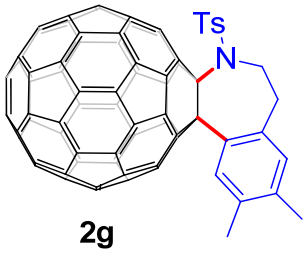
C_{60}-fused tetrahydrobenzazepine 2e: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (43.4 mg, 0.15 mmol) afforded first recovered C_{60} (14.0 mg, 39%) and then **2e** (18.8 mg, 37%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 1.6 Hz, 1H), 7.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 5.31-5.22 (m, 1H), 5.19-5.11 (m, 1H), 4.67 (dd, J = 13.0, 7.0 Hz, 1H), 3.41 (dd, J = 14.2, 6.6 Hz, 1H), 2.55 (s, 3H), 2.29 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 155.10, 154.40, 150.29, 150.10, 148.29, 147.69, 146.61, 146.54, 146.53, 146.20, 146.15 (2C), 146.10, 146.06, 145.84, 145.81, 145.76, 145.70, 145.63, 145.53, 145.39, 145.37, 145.35, 145.27, 145.07, 145.06, 144.87 (2C), 144.62, 144.60, 144.54, 144.33, 143.17, 143.02, 142.89, 142.72 (2C), 142.53 (4C), 142.36, 142.28 (2C), 142.21, 142.09, 141.72, 141.50 (2C), 141.21, 141.13, 140.30, 140.26, 140.10, 139.72 (aryl *C*), 139.48, 139.42, 139.17, 138.16, 138.09, 137.49 (aryl *C*), 136.31, 134.11, 131.95 (aryl *C*), 129.24 (2C, aryl *C*), 128.99 (aryl *C*), 128.98 (aryl *C*), 126.58 (2C, aryl *C*), 78.96 (sp^3-*C* of C_{60}), 71.90 (sp^3-*C* of C_{60}), 50.41 (*C*H_3), 33.65 (*C*H_2), 21.44 (*C*H_3), 21.23 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2919, 1449, 1335, 1261, 1155, 1120, 1082, 807, 748, 668, 554, 523; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.00), 321 (4.52), 435 (3.44), 693 (2.55); (-)ESI-MS m/z calcd for $C_{76}H_{17}NO_2S$ [M^-] 1007.0985, found 1007.0981.



2f

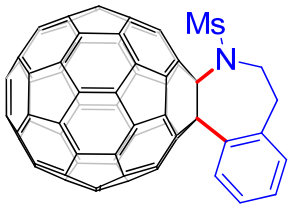
C_{60}-fused tetrahydrobenzazepine 2f: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (45.8 mg, 0.15 mmol) afforded first recovered C_{60} (26.8 mg, 74%) and then **2f** (10.0 mg, 20%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.90 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.15 (dd, J = 8.0, 2.0 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 5.26-5.09 (m, 2H), 4.71-4.59 (m, 1H), 3.91 (s, 3H), 3.49-3.37 (m, 1H), 2.30 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 159.66 (aryl *C*), 154.71, 153.95, 150.41, 149.98, 148.29, 147.71, 146.62, 146.54 (2C), 146.21, 146.17 (2C), 146.12, 146.05, 145.84, 145.82, 145.75, 145.71, 145.63, 145.52, 145.40, 145.36 (2C), 145.30, 145.12, 145.07, 144.86,

144.84, 144.61, 144.59, 144.48, 144.35, 143.16, 143.12, 143.02 (2C), 142.88, 142.72 (2C), 142.55 (2C), 142.36, 142.28, 142.21 (2C), 142.10, 141.71, 141.51, 141.48, 141.19, 141.09, 140.32, 140.21, 140.08, 139.75, 139.41, 139.34, 138.16, 138.11, 136.37, 134.22, 131.88 (aryl *C*), 129.94 (aryl *C*), 129.25 (2C, aryl *C*), 126.60 (2C, aryl *C*), 116.90 (aryl *C*), 113.37 (aryl *C*), 79.05 (sp^3-*C* of C_{60}), 71.99 (sp^3-*C* of C_{60}), 55.41 (*C*H_3O), 50.48 (*C*H_2), 32.78 (*C*H_2), 21.44 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2921, 1456, 1434, 1342, 1260, 1154, 1111, 1090, 1046, 807, 669, 560, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (4.98), 323 (4.48), 435 (3.33), 693 (2.46); (-)ESI-MS m/z calcd for $C_{76}H_{17}NO_3S$ [M^-] 1023.0935, found 1023.0938.



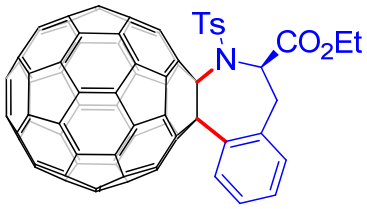
2g

C_{60}-fused tetrahydrobenzazepine 2g: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (45.5 mg, 0.15 mmol) for 6 h afforded first recovered C_{60} (8.9 mg, 25%) and then **2g** (24.1 mg, 47%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.03 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 7.09 (d, J = 8.4 Hz, 2H), 5.25-5.10 (m, 2H), 4.70-4.61 (m, 1H), 3.44-3.34 (m, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.29 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 155.21, 154.44, 150.33, 150.14, 148.21, 147.61, 146.55, 146.49, 146.47, 146.14, 146.09 (2C), 146.03, 145.99, 145.90, 145.78, 145.71, 145.67, 145.56, 145.47, 145.33, 145.31, 145.28, 145.22, 145.02, 144.97, 144.83, 144.82, 144.58, 144.54, 144.50, 144.26, 143.12, 142.95, 142.83, 142.65 (2C), 142.47 (2C), 142.35, 142.31, 142.27, 142.22, 142.16, 142.00, 141.67, 141.49, 141.45, 141.20, 141.16, 140.21 (2C), 140.04, 139.64, 139.40, 139.34, 139.12, 138.16, 138.11, 138.02, 136.39 (aryl *C*), 136.23, 134.75 (aryl *C*), 133.86, 132.43 (aryl *C*), 130.16 (aryl *C*), 129.14 (2C, aryl *C*), 126.55 (2C, aryl *C*), 78.84 (sp^3-*C* of C_{60}), 71.77 (sp^3-*C* of C_{60}), 50.33 (*C*H_2), 33.23 (*C*H_2), 21.42 (*C*H_3), 19.85 (*C*H_3), 19.53 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2915, 1447, 1432, 1341, 1262, 1154, 1089, 982, 808, 728, 669, 562, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (4.99), 322 (4.49), 437 (3.45), 695 (2.45); (-)ESI-MS m/z calcd for $C_{77}H_{19}NO_2S$ [M^-] 1021.1142, found 1021.1148.



2h

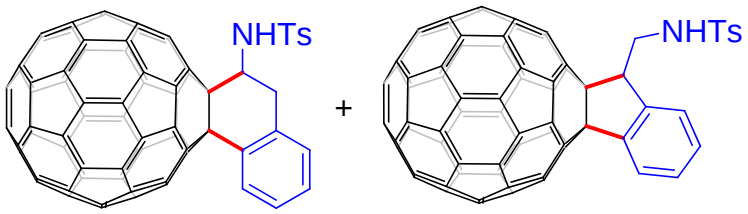
C_{60}-fused tetrahydrobenzazepine 2h: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (30.1 mg, 0.15 mmol) afforded first recovered C_{60} (12.3 mg, 34%) and then **2h** (17.1 mg, 37%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.28 (d, J = 7.8 Hz, 1H), 7.64-7.51 (m, 3H), 5.32-5.22 (m, 1H), 4.90-4.81 (m, 1H), 4.59 (dd, J = 14.0, 7.6 Hz, 1H), 3.39 (dd, J = 14.8, 7.2 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR [75 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 154.33, 154.23, 150.23, 149.89, 148.35, 147.79, 146.68, 146.63, 146.57, 146.29, 146.19 (3C), 146.16, 146.05, 145.72 (2C), 145.69, 145.57, 145.55, 145.48, 145.42, 145.38, 145.28, 145.20, 145.17, 144.92 (2C), 144.76, 144.67, 144.42, 144.21, 143.25, 143.15, 143.02, 142.95, 142.83, 142.79, 142.69, 142.60, 142.45, 142.34 (2C), 142.19, 142.15, 141.92, 141.69, 141.55, 141.54, 140.75, 140.27, 140.21, 139.93, 139.90, 139.41, 139.18, 138.16, 137.77 (aryl *C*), 136.38, 134.19, 131.33 (aryl *C*), 129.94 (aryl *C*), 129.11 (aryl *C*), 128.35 (aryl *C*), 79.50 (sp^3-*C* of C_{60}), 71.85 (sp^3-*C* of C_{60}), 49.75 (*C*H_2), 44.90 (*C*H_3), 33.45 (*C*H_2); FT-IR ν/cm^{-1} (KBr) 2924, 1454, 1431, 1338, 1262, 1148, 1117, 1071, 1046, 951, 748, 551, 521; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (4.99), 320 (4.50), 434 (3.42), 693 (2.50); (-)ESI-MS m/z calcd for $C_{69}H_{11}NO_2S$ [M$^-$] 917.0516, found 917.0515.



2i

C_{60}-fused tetrahydrobenzazepine 2i: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (52.1 mg, 0.15 mmol) afforded first recovered C_{60} (23.5 mg, 65%) and then **2i** (12.8 mg, 24%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.60-7.49 (m, 3H), 7.04 (d, J = 8.4 Hz, 2H), 6.03 (dd, J = 12.0, 6.8 Hz, 1H), 5.43 (dd, J = 15.0, 12.0 Hz, 1H), 4.21 (dq, J = 10.8, 7.2 Hz, 1H), 3.95 (dq, J = 10.8, 7.2 Hz, 1H), 3.86 (dd, J =15.0, 6.8 Hz, 1H), 2.30 (s, 3H), 1.16 (t, 7.2 Hz, 3H); ^{13}C NMR [100 MHz, CS_2/$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 170.73 (*C*=O), 154.93, 153.88, 149.94, 147.91, 147.68, 147.25, 146.32, 146.26, 146.15, 145.90, 145.81, 145.79, 145.76 (2C), 145.58, 145.54, 145.51, 145.40 (2C), 145.31, 145.14, 145.07, 145.00, 144.93 (2C), 144.77, 144.67, 144.46, 144.39, 144.21, 144.03, 143.89, 142.78, 142.62, 142.58, 142.41, 142.38, 142.27, 142.23, 142.12, 142.05, 142.03, 142.01, 141.78, 141.72, 141.62, 141.44, 141.28,

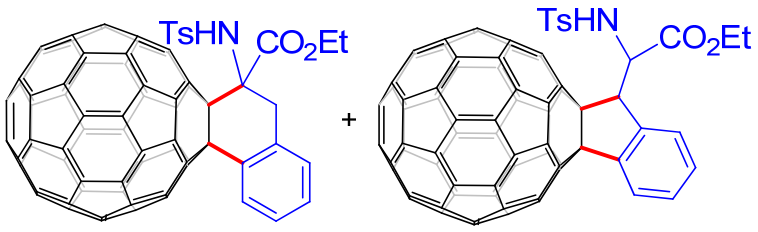
141.18, 141.07, 140.03, 139.58, 139.56, 139.13, 139.06, 139.03, 138.35, 138.27, 138.05, 137.01 (aryl *C*), 135.84, 133.30, 130.60 (aryl *C*), 129.39 (aryl *C*), 129.23 (aryl *C*), 128.39 (aryl *C*), 128.36 (2C, aryl *C*), 128.20 (2C, aryl *C*), 78.89 (sp^3-*C* of C_{60}), 71.07 (sp^3-*C* of C_{60}), 62.45 (*C*H_2), 61.57 (*C*H_2), 35.09 (*C*H_2), 21.27 (*C*H_3), 14.02 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2926, 1727, 1449, 1330, 1232, 1153, 1088, 1020, 812, 748, 557, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.00), 321 (4.53), 433 (3.36), 690 (2.52); (-)ESI-MS m/z calcd for $C_{78}H_{19}NO_4S$ [M^-] 1065.1040, found 1065.1046. $[a]^{25\ °C}{}_D$ = + 5.82 ($CHCl_3$).



3a **4a**

3a:**4a** = 4:1

Transformation of 2a to fullerotetrahydronaphthalene 3a and fulleroindane 4a: A mixture of **2a** (19.9 mg, 0.02 mmol) and TfOH (18.0 μL, 0.20 mmol) in ODCB (6 mL) was stirred at 25 °C for 45 min. After evaporation in vacuo, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to give unreacted **2a** (2.0 mg, 10%) and rearrangement products fullerotetrahydronaphthalene **3a** and fulleroindane **4a** (16.3 mg, 82%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.43-8.38 (m, 0.80 × 1H, **3a**), 8.36-8.33 (m, 0.20 × 1H, **4a**), 7.65 (d, *J* = 8.2 Hz, 0.80 × 2H, **3a**), 7.63 (d, *J* = 8.4 Hz, 0.20 × 2H, **4a**), 7.54-7.42 (m, 3H, **3a** + **4a**,), 7.12 (d, *J* = 8.2 Hz, 2H, **3a** + **4a**), 5.46 (ddd, *J* = 10.2, 4.0, 2.0 Hz, 0.80 × 1H, **3a**), 5.29 (d, *J* = 11.2 Hz, 0.20 × 1H, **4a**), 5.25 (d, *J* = 10.2 Hz, 0.80 × 1H, **3a**), 5.07-5.01 (m, 0.20 × 1H, **4a**), 4.47 (d, *J* = 15.2 Hz, 0.80 × 1H, **3a**), 4.19-4.12 (m, 0.20 × 1H, **4a**), 3.52-3.47 (m, 0.20 × 1H, **4a**), 3.49 (dd, *J* = 15.2, 4.0 Hz, 0.80 × 1H, **3a**), 2.36 (s, 0.20 × 3H, **4a**), 2.35 (s, 0.80 × 3H, **3a**); (-)ESI-MS m/z calcd for $C_{75}H_{15}NO_2S$ [M^-] 993.0829, found 993.0821.



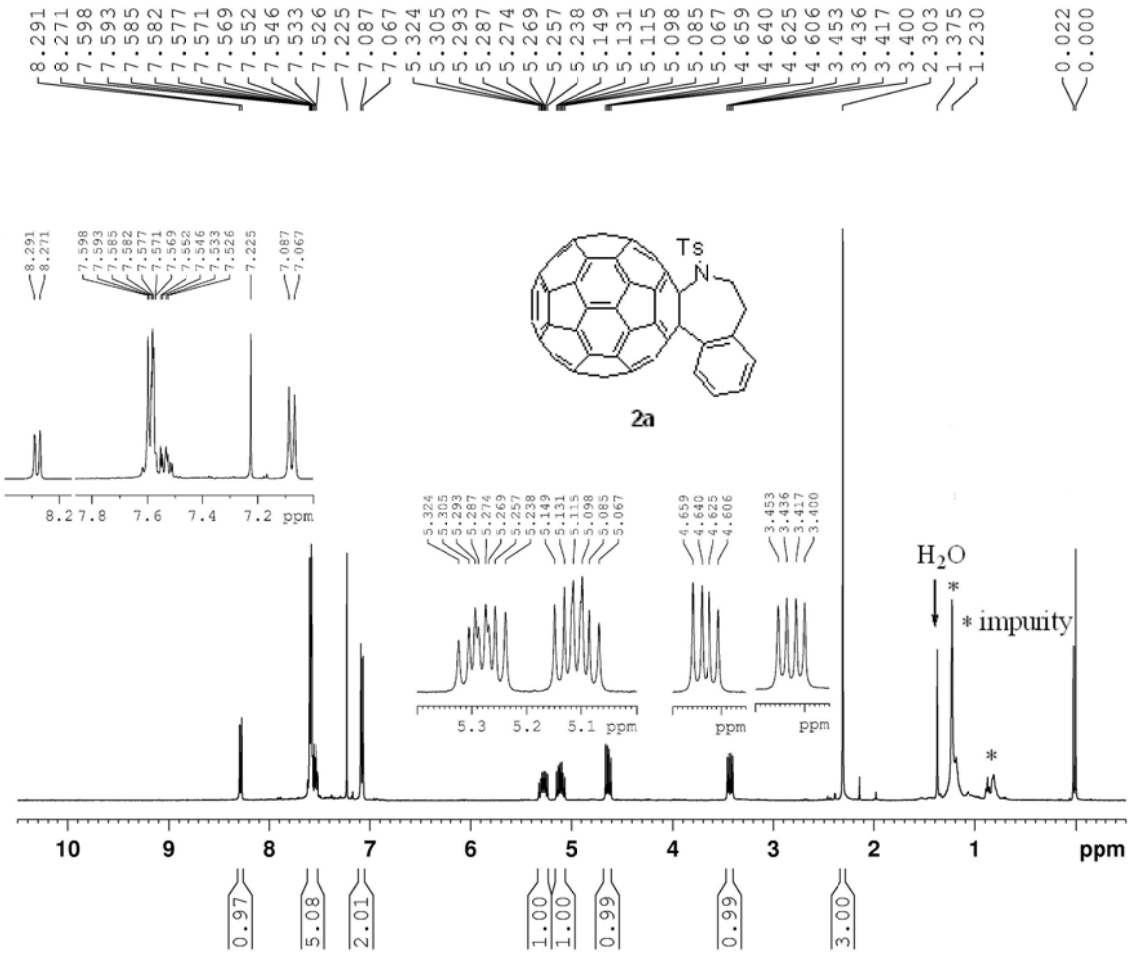
3i **4i**

3i:**4i** = 8.1:1

Transformation of 2i to fullerotetrahydronaphthalene 3i and fulleroindane 4i: A mixture of **2i** (21.3 mg, 0.02 mmol) and TfOH (18.0 μL, 0.20 mmo) in ODCB (6 mL) was stirred at 25 °C for 2 h. After evaporation in vacuo, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent

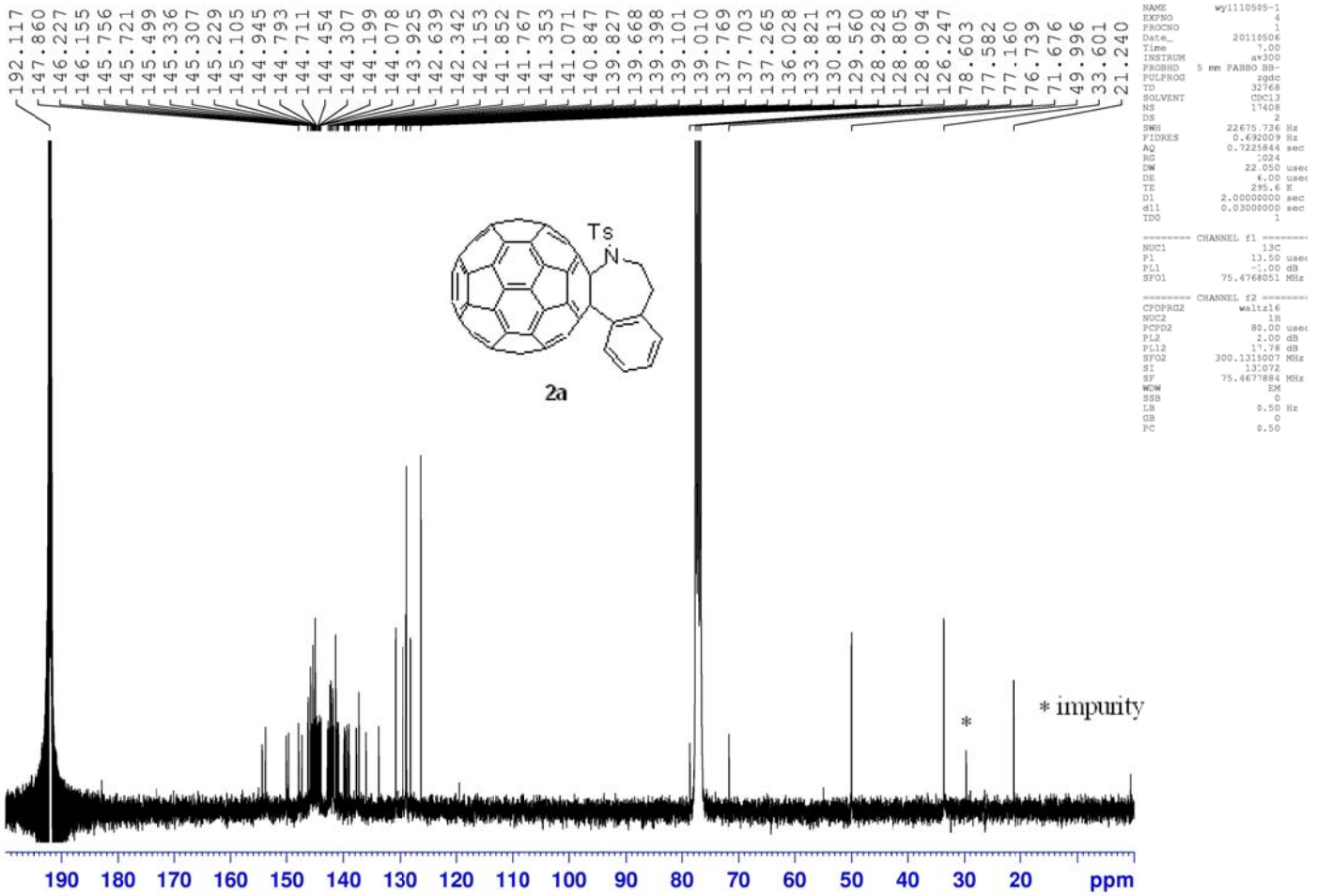
to give unreacted **2i** (7.9 mg, 37%) and rearrangement products fullerotetrahydronaphthalene **3i** and fulleroindane **4i** (11.5 mg, 55%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 9.09 (s, 0.89 × 1H, **3i**), 8.22 (d, J = 8.0 Hz, 0.89 × 1H, **3i**), 8.16 (d, J = 7.2 Hz, 0.11 × 1H, **4i**), 7.78 (d, J = 8.4 Hz, 0.89 × 2H, **3i**), 7.49 (d, J = 7.8 Hz, 0.11 × 2H, **4i**), 7.38-7.26 (m, 0.89 × 5H, **3i**), 7.17 (t, J = 7.8 Hz, 0.11 × 1H, **4i**), 7.05 (d, J = 7.8 Hz, 0.11 × 2H, **4i**), 6.96 (d, J = 7.8 Hz, 0.11 × 1H, **4i**), 6.85 (t, J = 7.4 Hz, 0.11 × 1H, **4i**), 4.74 (d, J = 14.8 Hz, 0.89 × 1H, **3i**), 4.69 (d, J = 16.4 Hz, 0.11 × 1H, **4i**), 4.17 (d, J = 16.4 Hz, 0.11 × 1H, **4i**), 4.09-4.02 (m, 0.11 × 2H, **4i**), 3.86 (dq, J = 10.8, 7.2 Hz, 0.89 × 1H, **3i**), 3.57 (d, J = 14.8 Hz, 1H × 0.89, **3i**), 3.51 (dq, J = 10.8, 7.2 Hz, 0.89 × 1H, **3i**), 2.48 (s, 0.89 × 3H, **3i**), 2.43 (s, 0.11 × 3H, **4i**), 1.12 (t, J = 7.2 Hz, 0.11 × 3H, **4i**), 0.74 (t, J = 7.2 Hz, 0.89 × 3H, **3i**); ^{13}C NMR of **3i** [100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent] (all 1C unless indicated) δ 166.99 (*C*═O), 159.55, 153.27, 152.45, 151.86, 148.35, 147.10, 146.55, 146.38, 146.30, 145.27 (2C), 145.17, 145.11, 145.10, 144.93, 144.80, 144.73, 144.70, 144.67, 144.31, 144.03 (2C), 143.97 (2C), 143.92, 143.86, 143.81, 143.67, 143.46, 143.42, 143.35, 142.48, 141.86, 141.73, 141.47 (2C), 141.33 (2C), 141.19, 141.17, 141.09, 140.92, 140.87, 140.80, 140.53, 140.39, 140.23, 140.20 (2C), 140.04, 139.88, 139.75, 138.91, 137.47, 137.29, 137.26, 137.10, 137.02, 136.70, 135.72, 133.98, 130.60 (aryl *C*), 129.17 (aryl *C*), 127.83 (2C, aryl *C*), 127.49 (aryl *C*), 126.10 (aryl *C*), 125.85 (aryl *C*), 125.32 (2C, aryl *C*), 71.95 (sp^3-*C* of C_{60}), 69.06 (sp^3-*C* of C_{60}), 67.52, 60.22 (O*C*H_2), 38.65 (*C*H_2), 20.64 (*C*H_3), 12.54 (*C*H_3); FT-IR ν/cm^{-1} (KBr) 2922, 1740, 1433, 1329, 1245, 1187, 1159, 1092, 1047, 811, 743, 662, 551, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.00), 318 (4.59), 435 (3.42), 693 (2.42); (-)ESI-MS m/z calcd for $C_{78}H_{19}NO_4S$ [M^-] 1065.1040, found 1065.1036.

^{1}H NMR (400 M, $CS_2/CDCl_3$) spectrum of compound **2a**

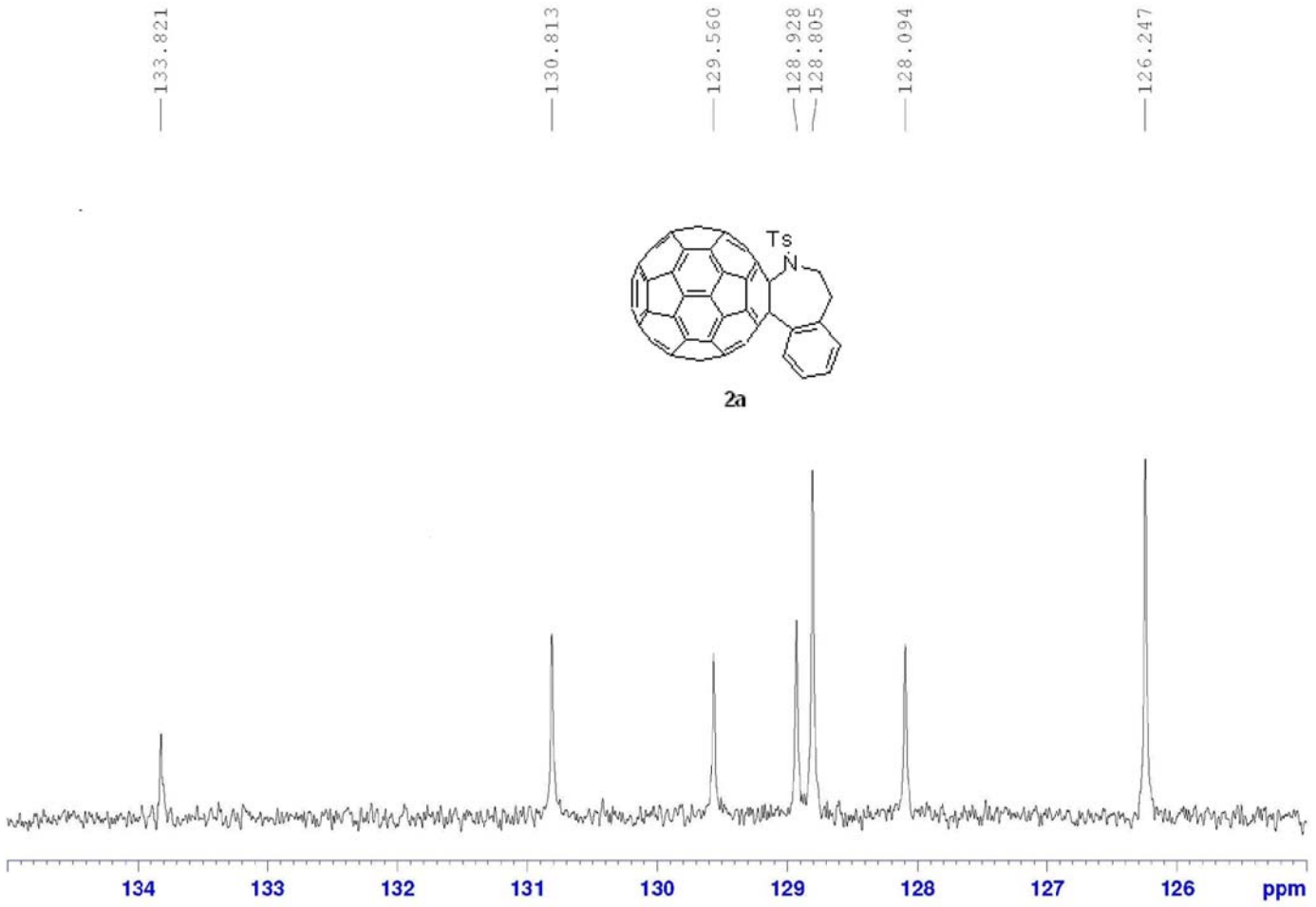


NAME	syt 140505-01
EXPNO	10
PROCNO	1
Date_	20140506
Time	11.31
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	152.87
DW	62.400 usec
DE	6.50 usec
TE	294.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.00 usec
SI	65536
SF	400.1300247 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

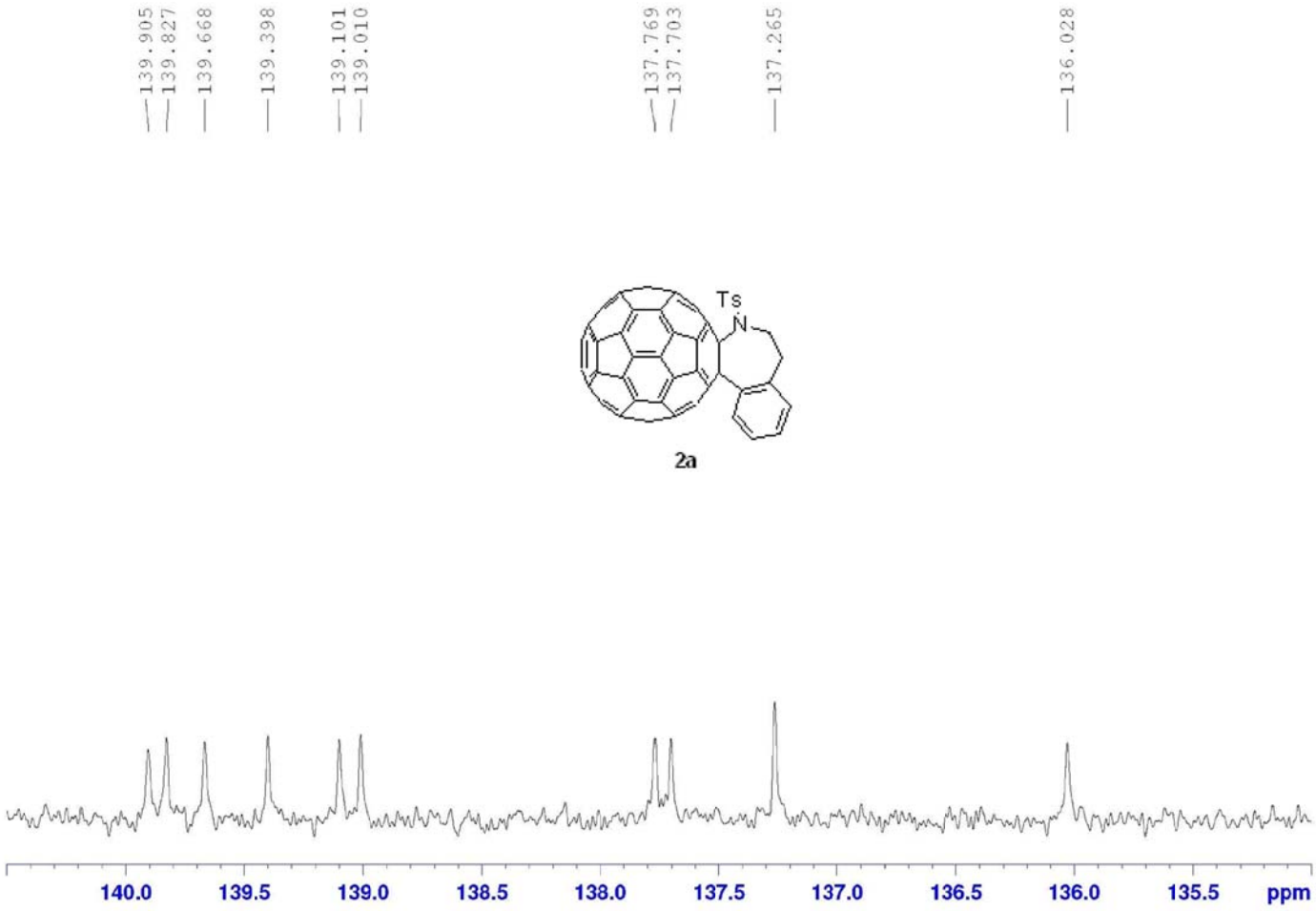
^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2a**



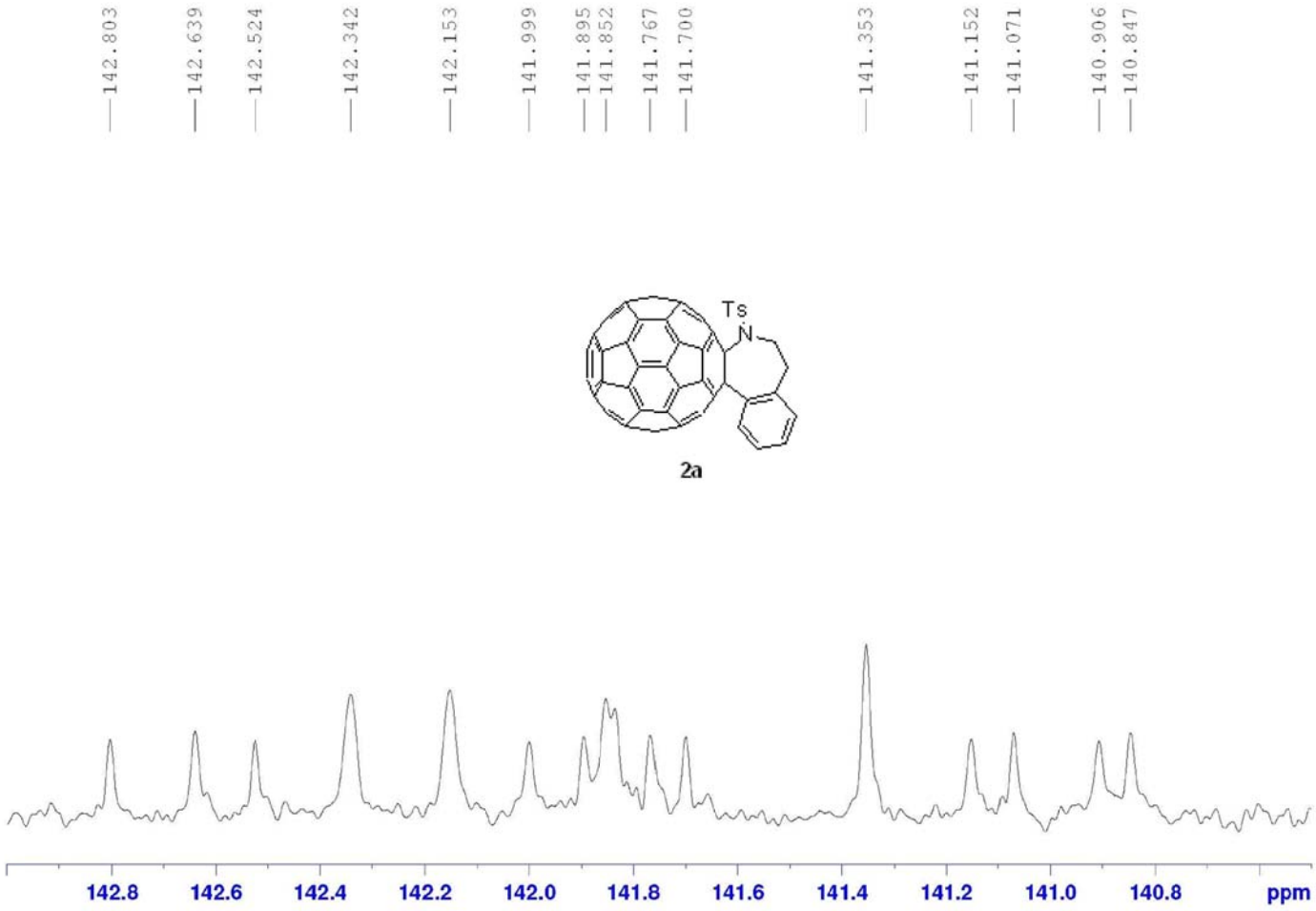
The detailed ^{13}C NMR spectrum of compound **2a** (135–125 ppm)



The detailed ^{13}C NMR spectrum of compound **2a** (140–135 ppm)

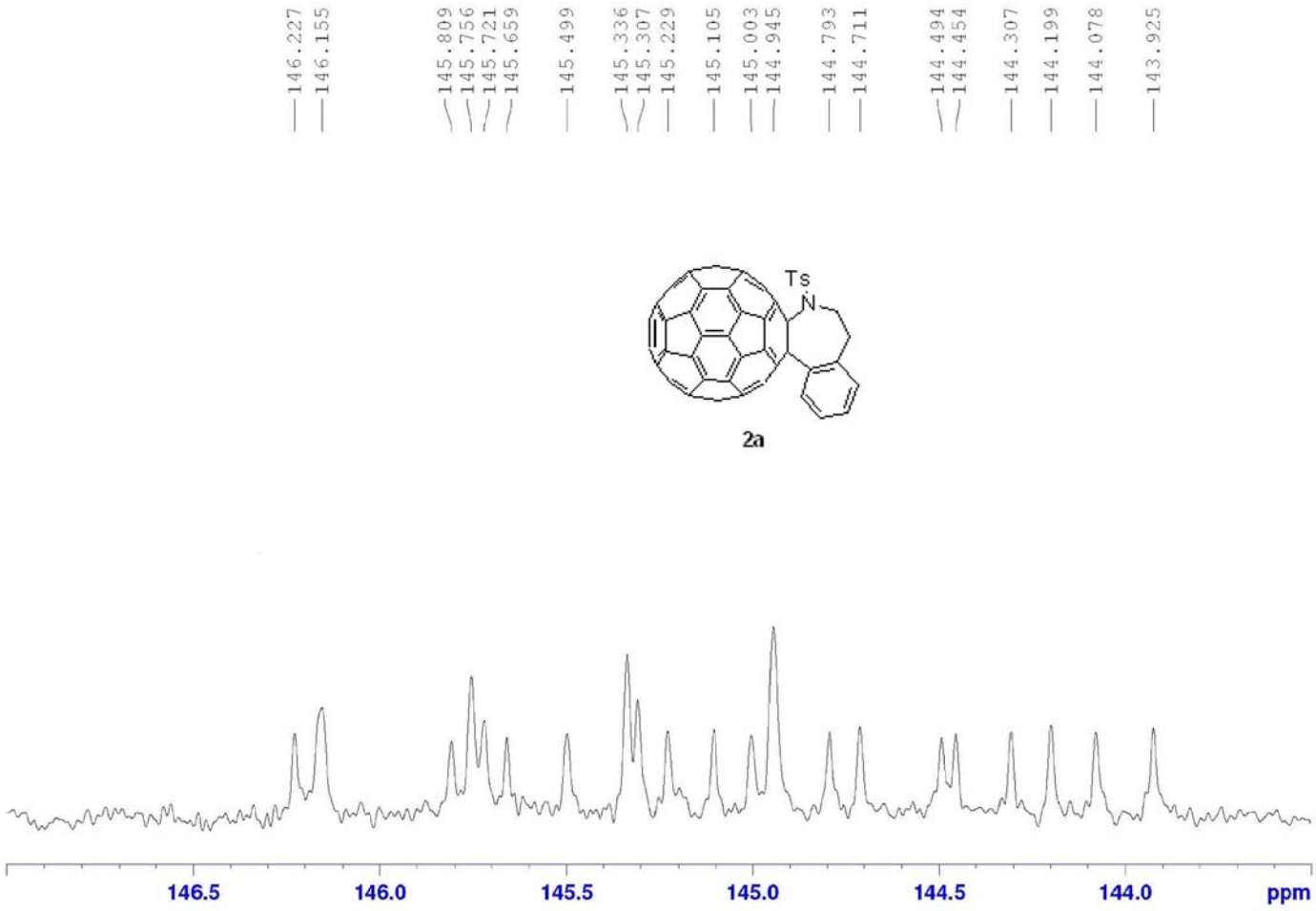


The detailed ^{13}C NMR spectrum of compound **2a** (143–140 ppm)

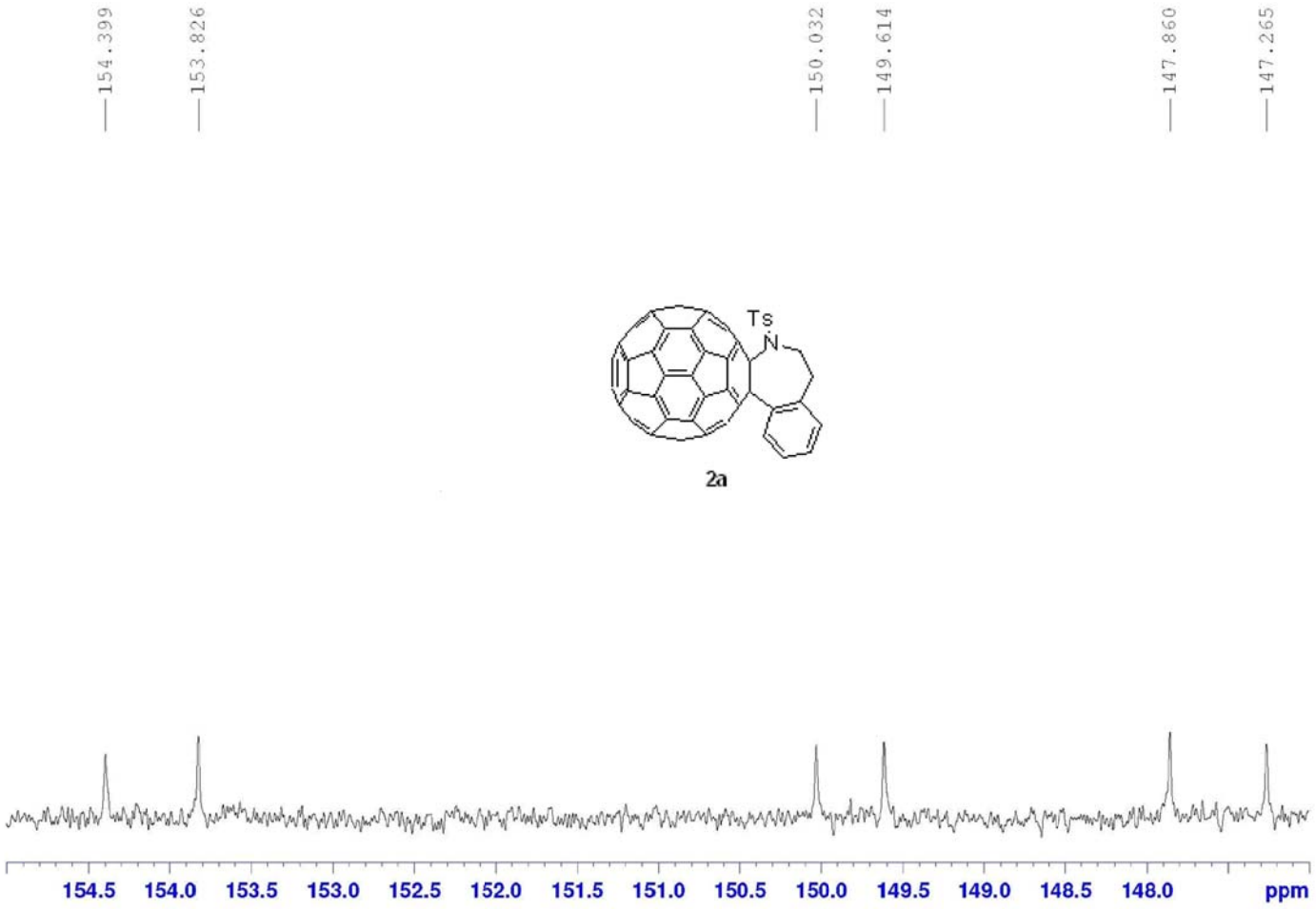


2a

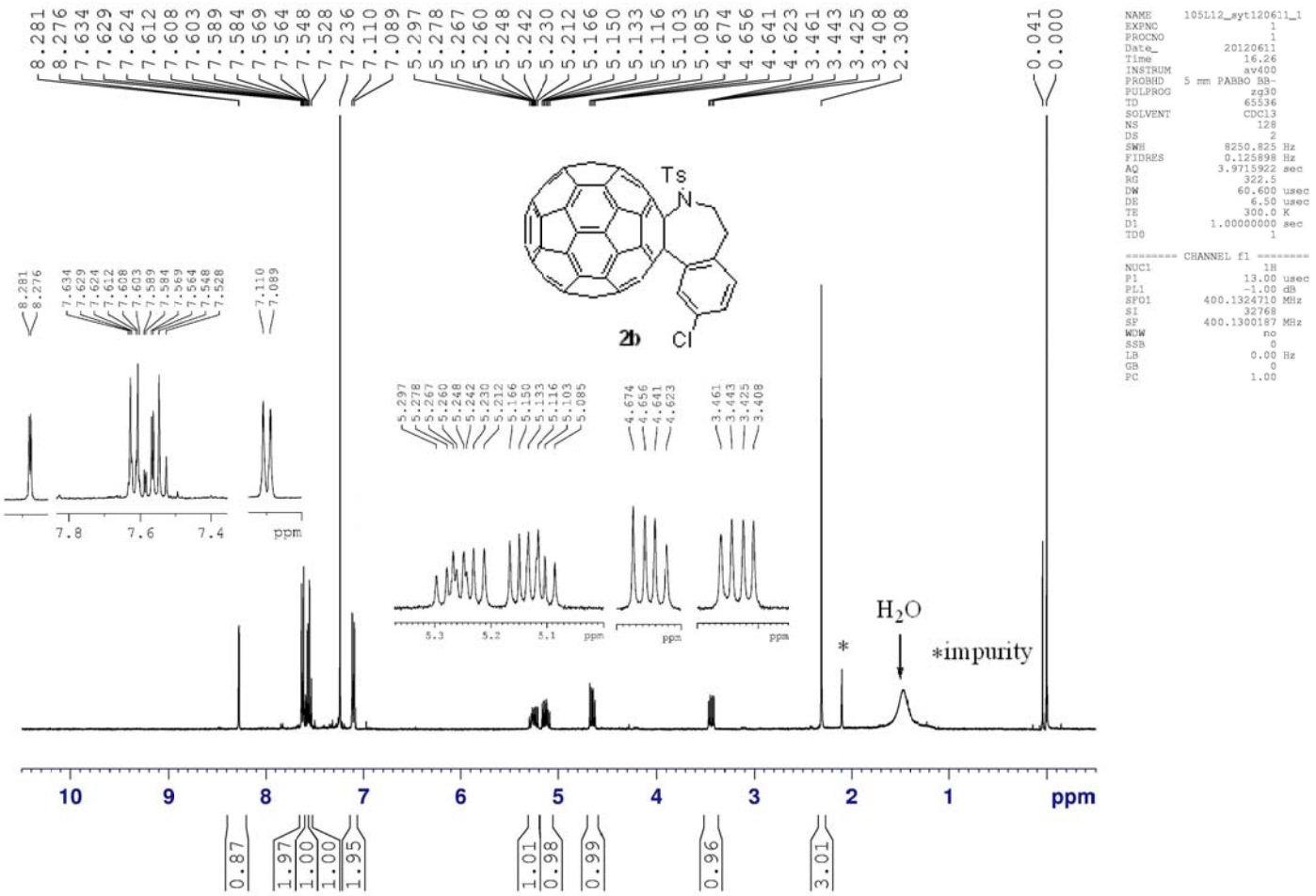
The detailed ^{13}C NMR spectrum of compound **2a** (147–143 ppm)



The detailed ^{13}C NMR spectrum of compound **2a** (155–147 ppm)



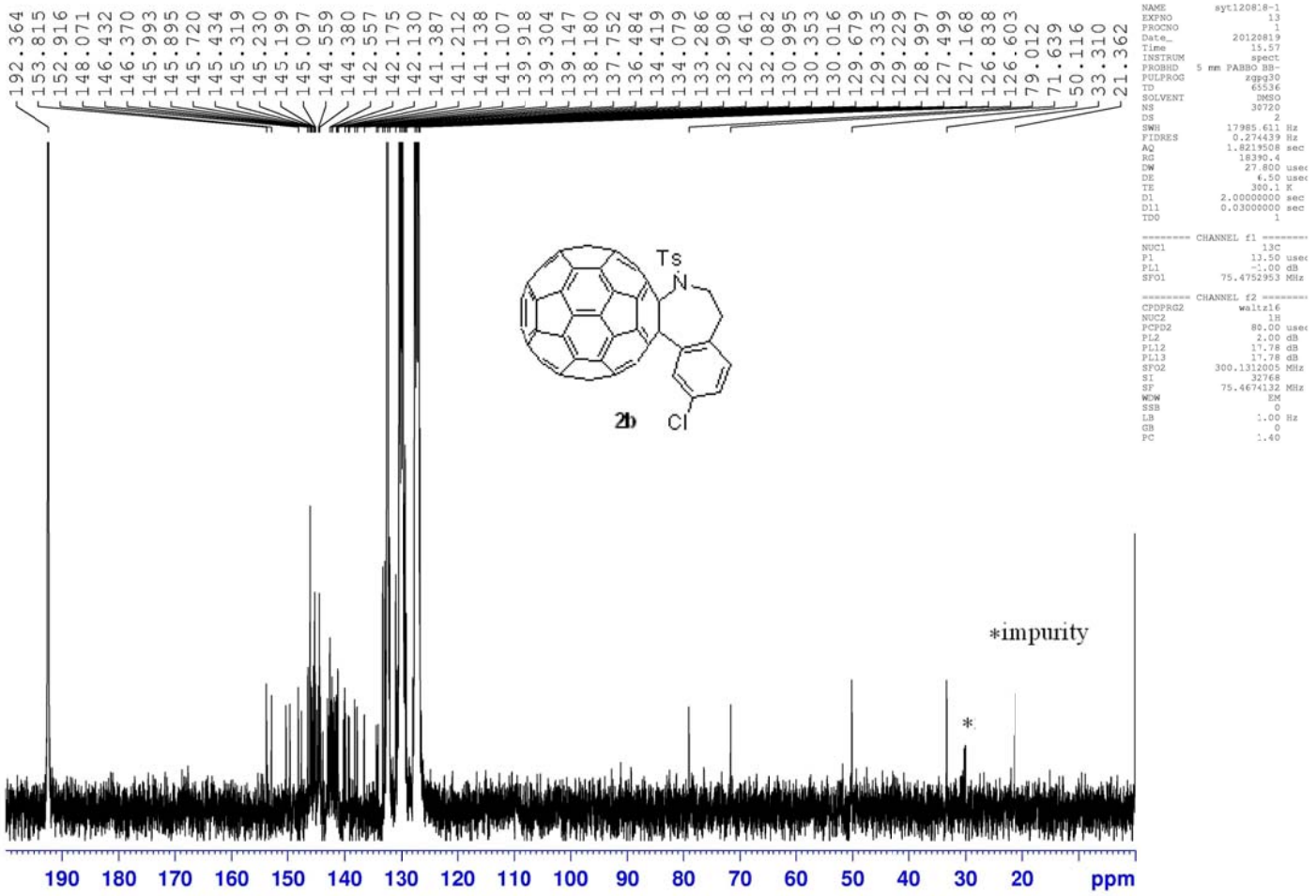
^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2b**



NAME 105L12_syt120611_1
EXPNO 1
PROCNO 1
Date_ 20120611
Time 16.26
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 8250.825 Hz
FIDRES 0.125898 Hz
AQ 3.9715922 sec
RG 322.5
DW 60.600 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300187 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

^{13}C NMR (75 M, CS_2/ODCB-d_4) spectrum of compound **2b**

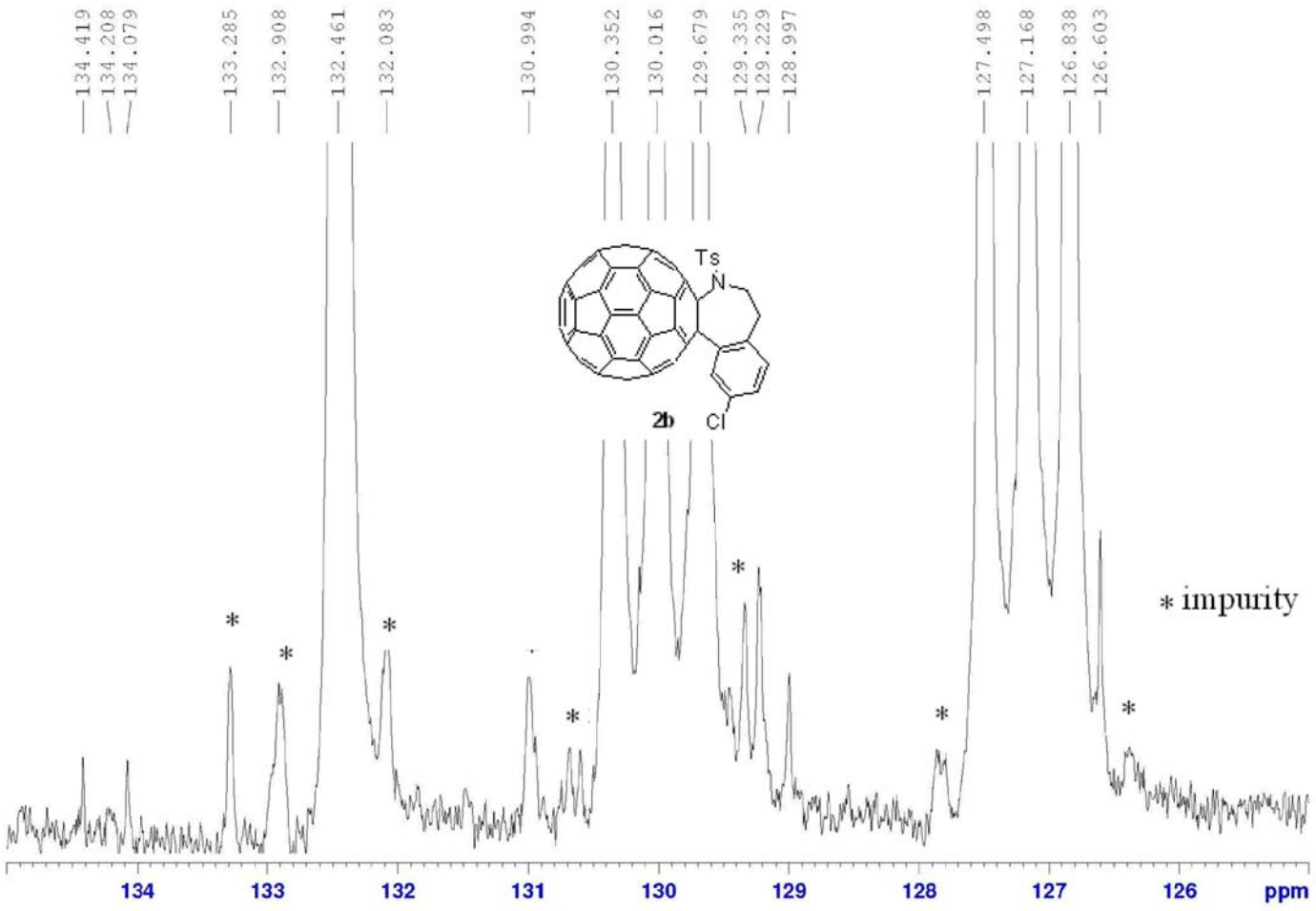


NAME syt120818-1
EXPNO 13
PROCNO 1
Date_ 20120819
Time 15.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 30720
DS 2
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 18390.4
DW 27.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

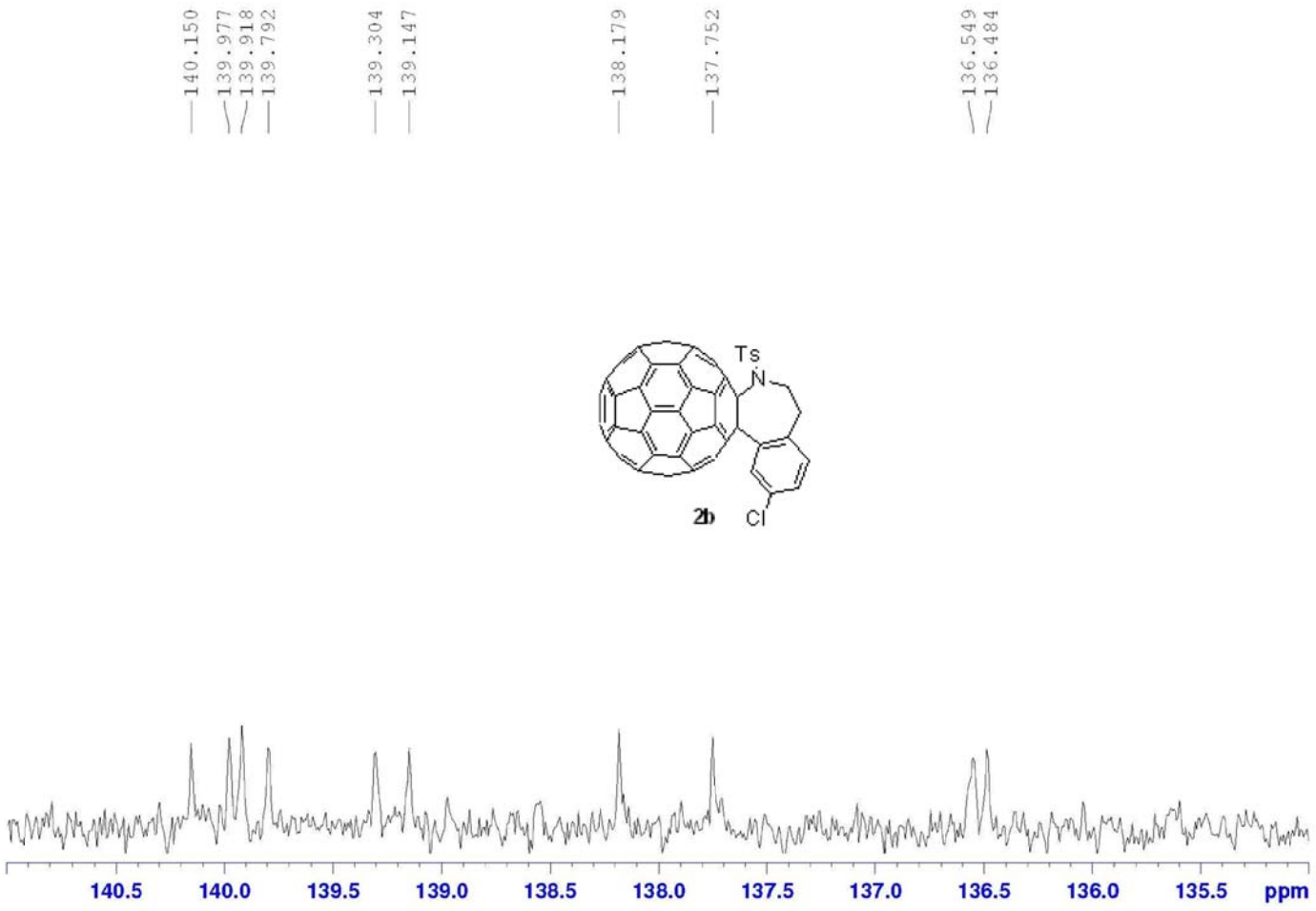
======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
PL1 -1.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 2.00 dB
PL12 17.78 dB
PL13 17.78 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4674132 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

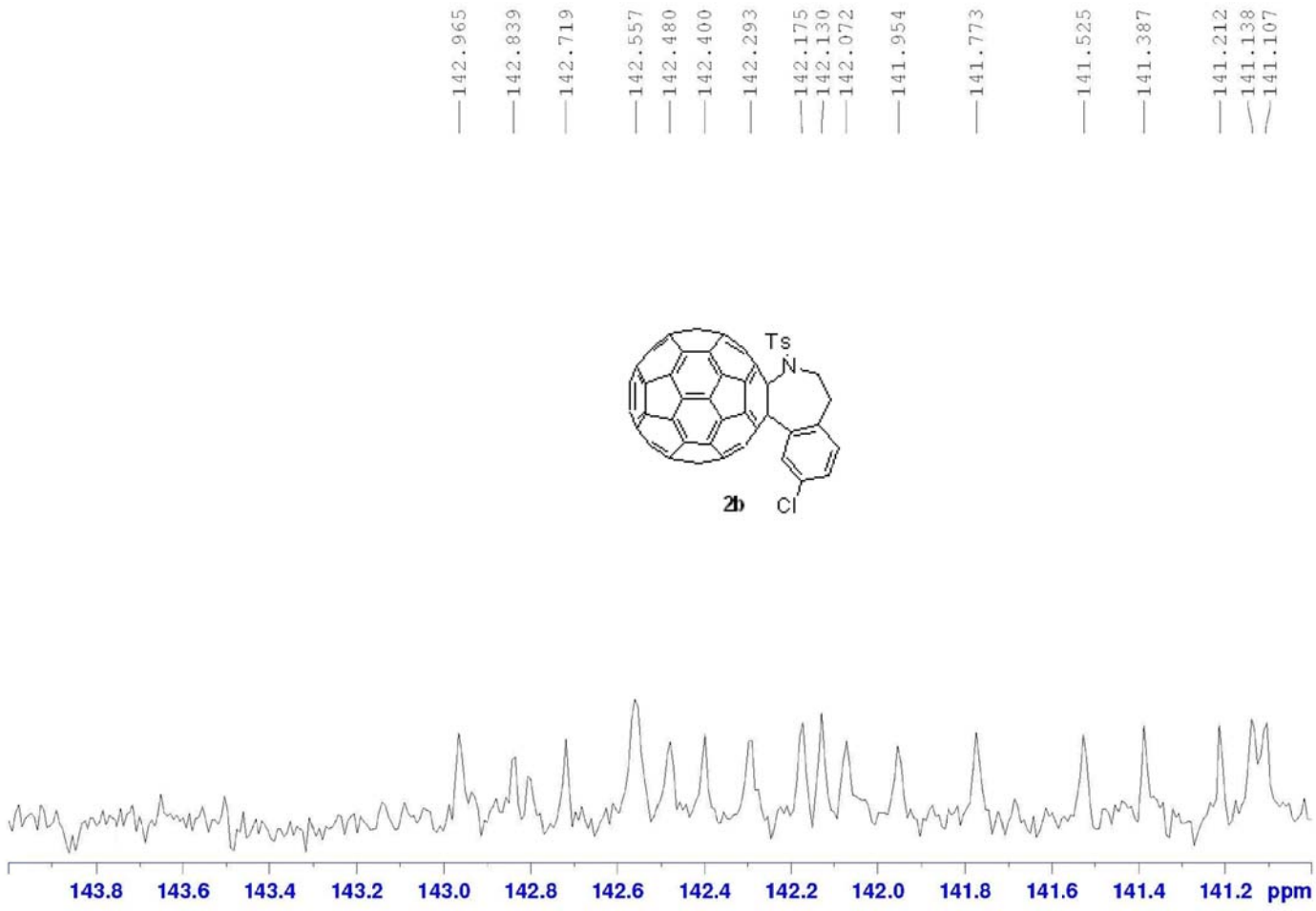
The detailed ^{13}C NMR spectrum of compound **2b** (135–125 ppm)



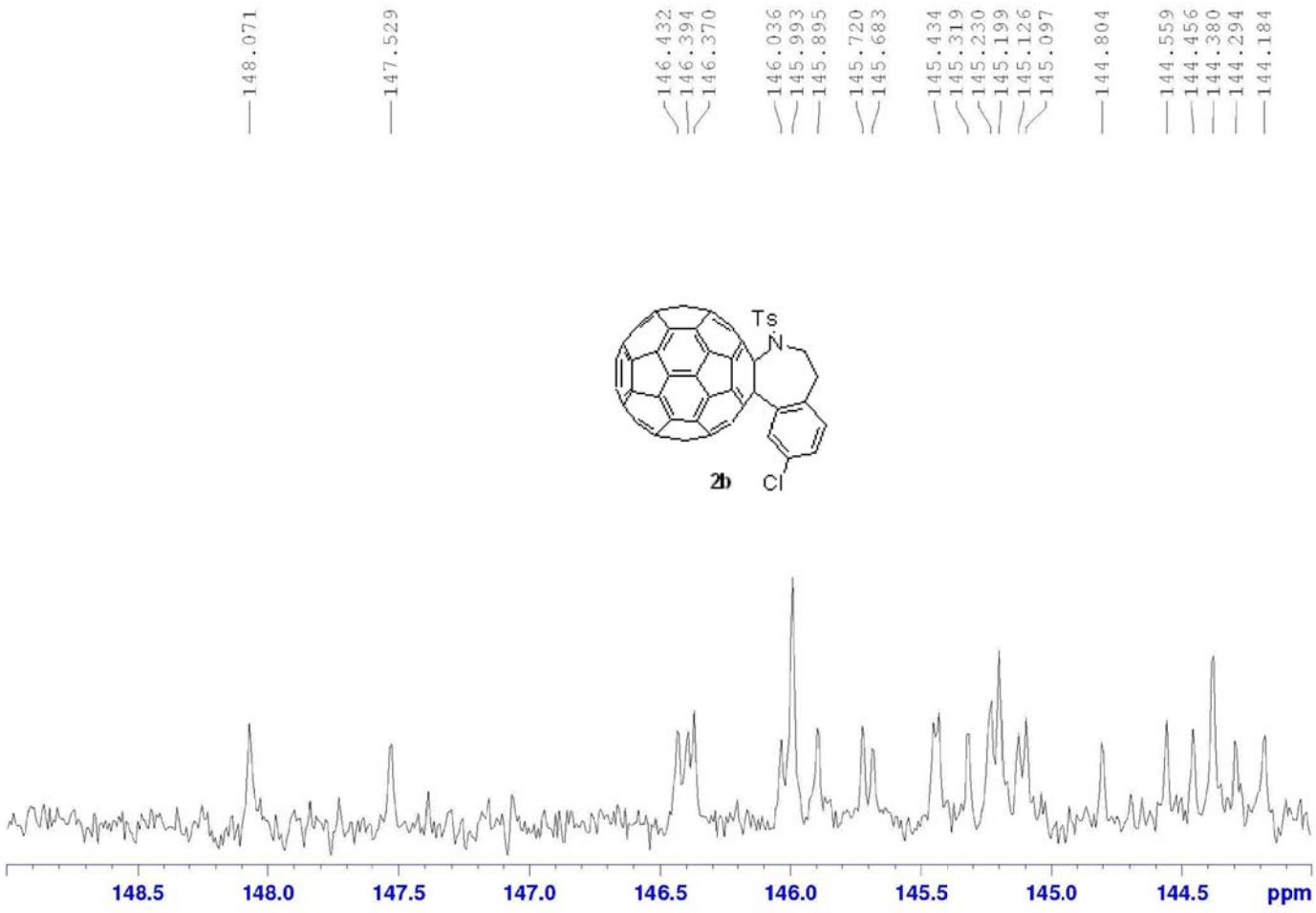
The detailed ^{13}C NMR spectrum of compound **2b** (141–135 ppm)



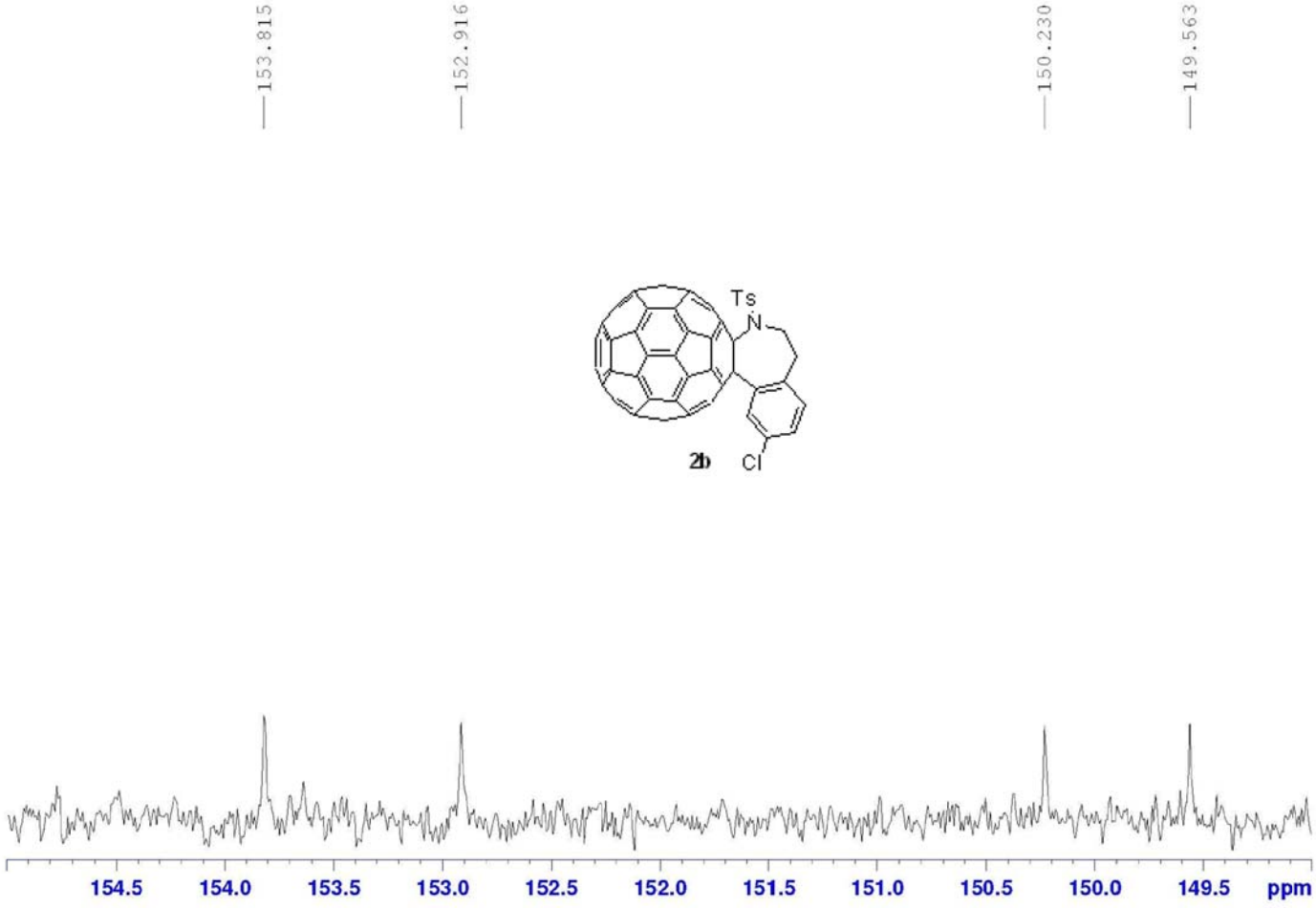
The detailed ^{13}C NMR spectrum of compound **2b** (144–141 ppm)



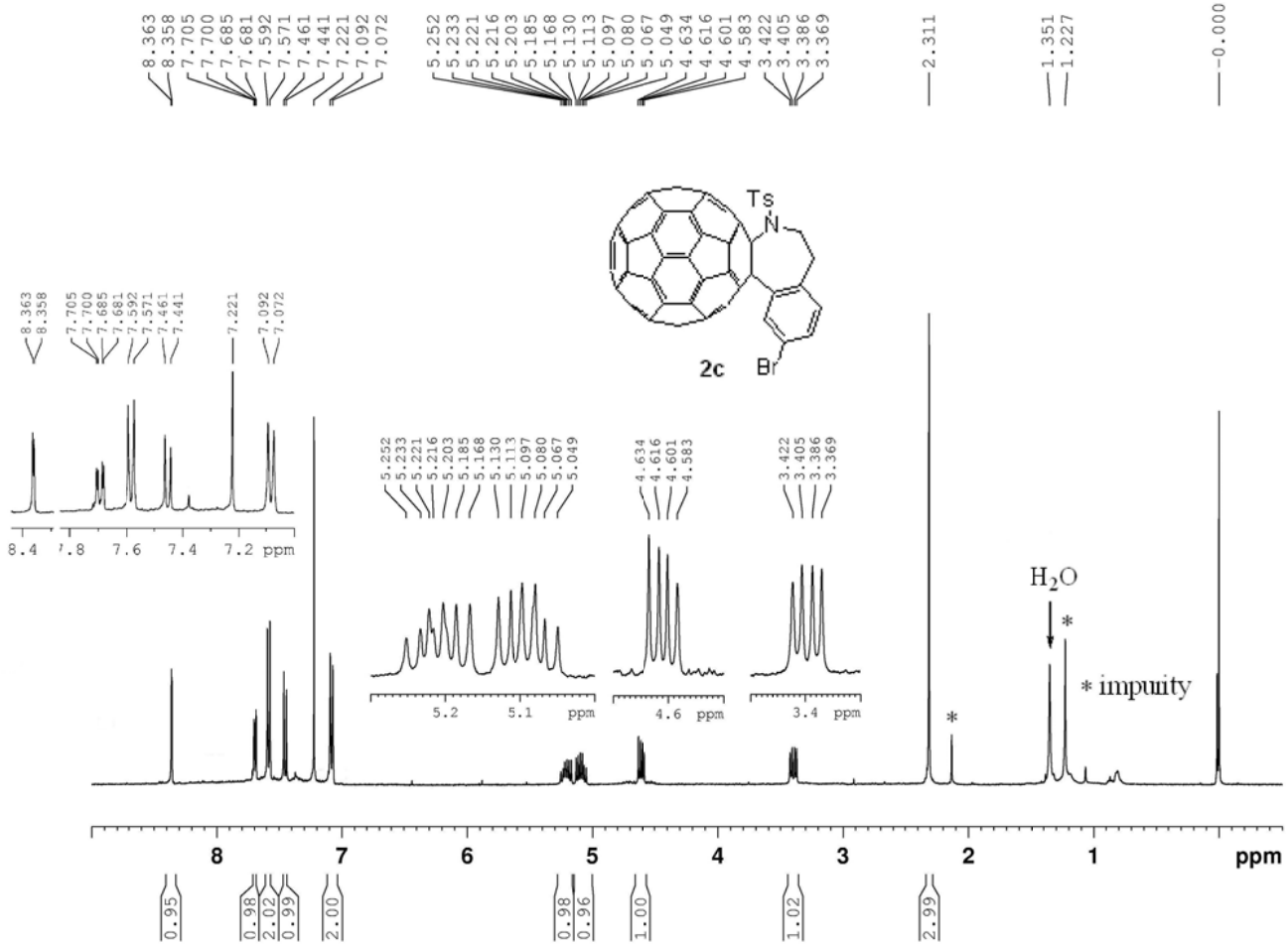
The detailed ^{13}C NMR spectrum of compound **2b** (149–144 ppm)



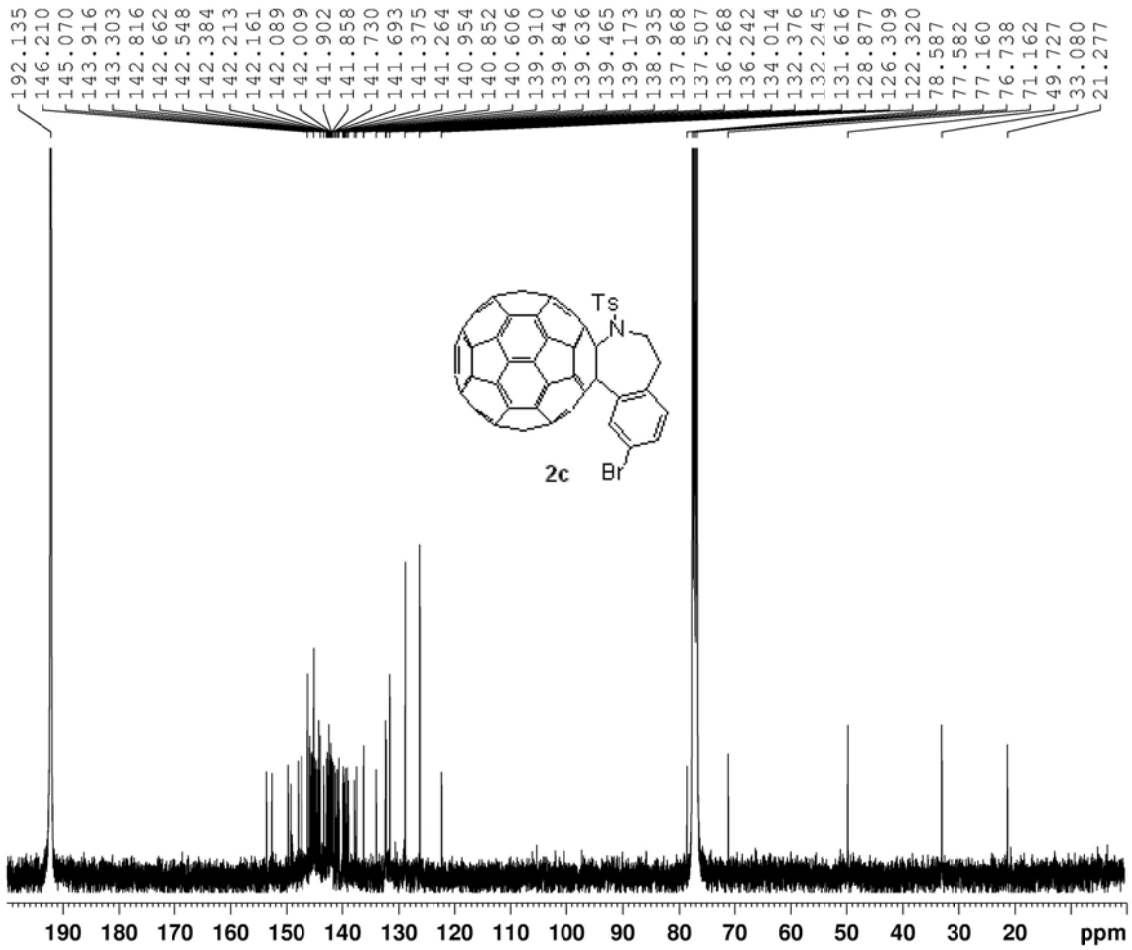
The detailed ^{13}C NMR spectrum of compound **2b** (155–150 ppm)



^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2c**

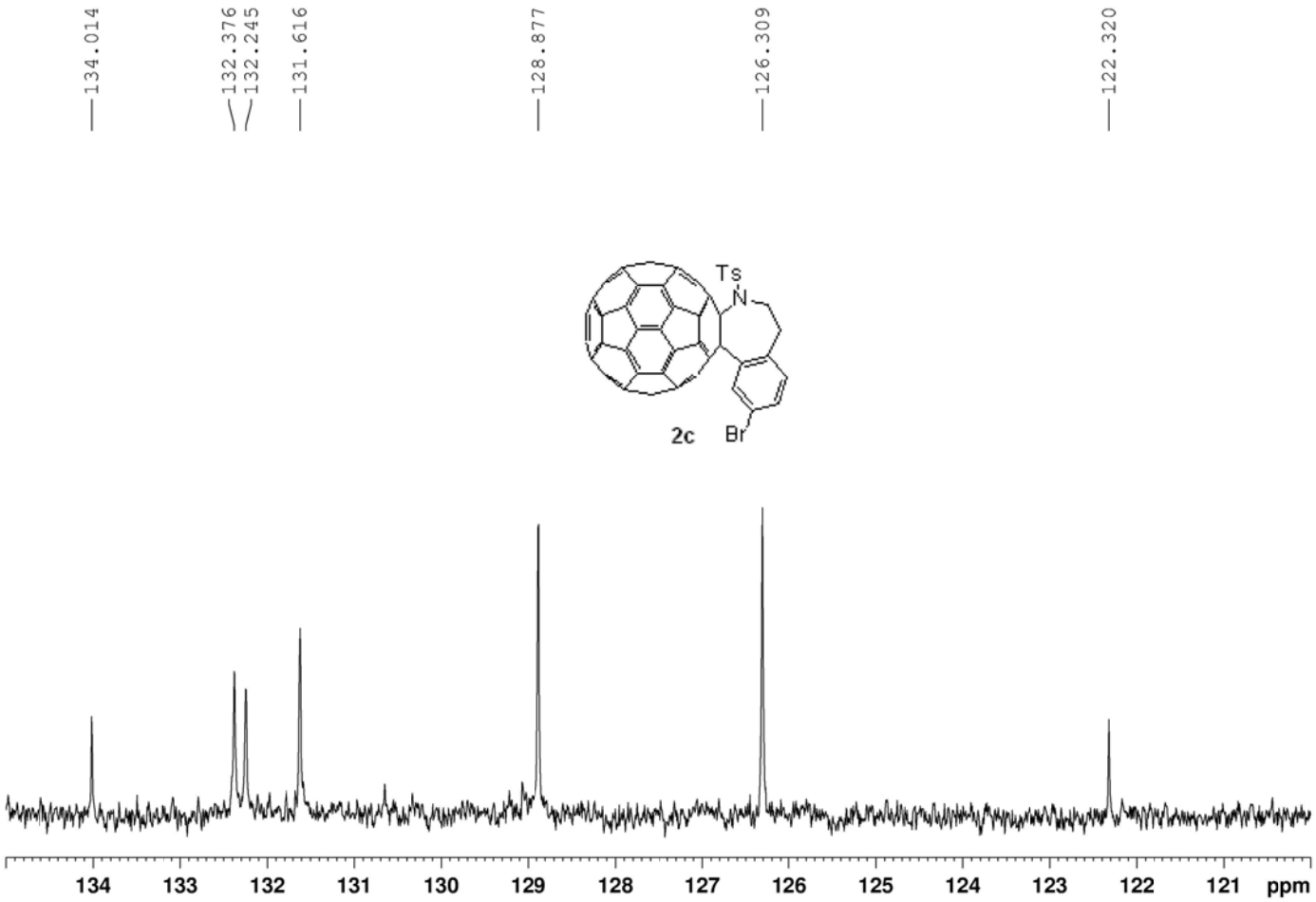


^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2c**

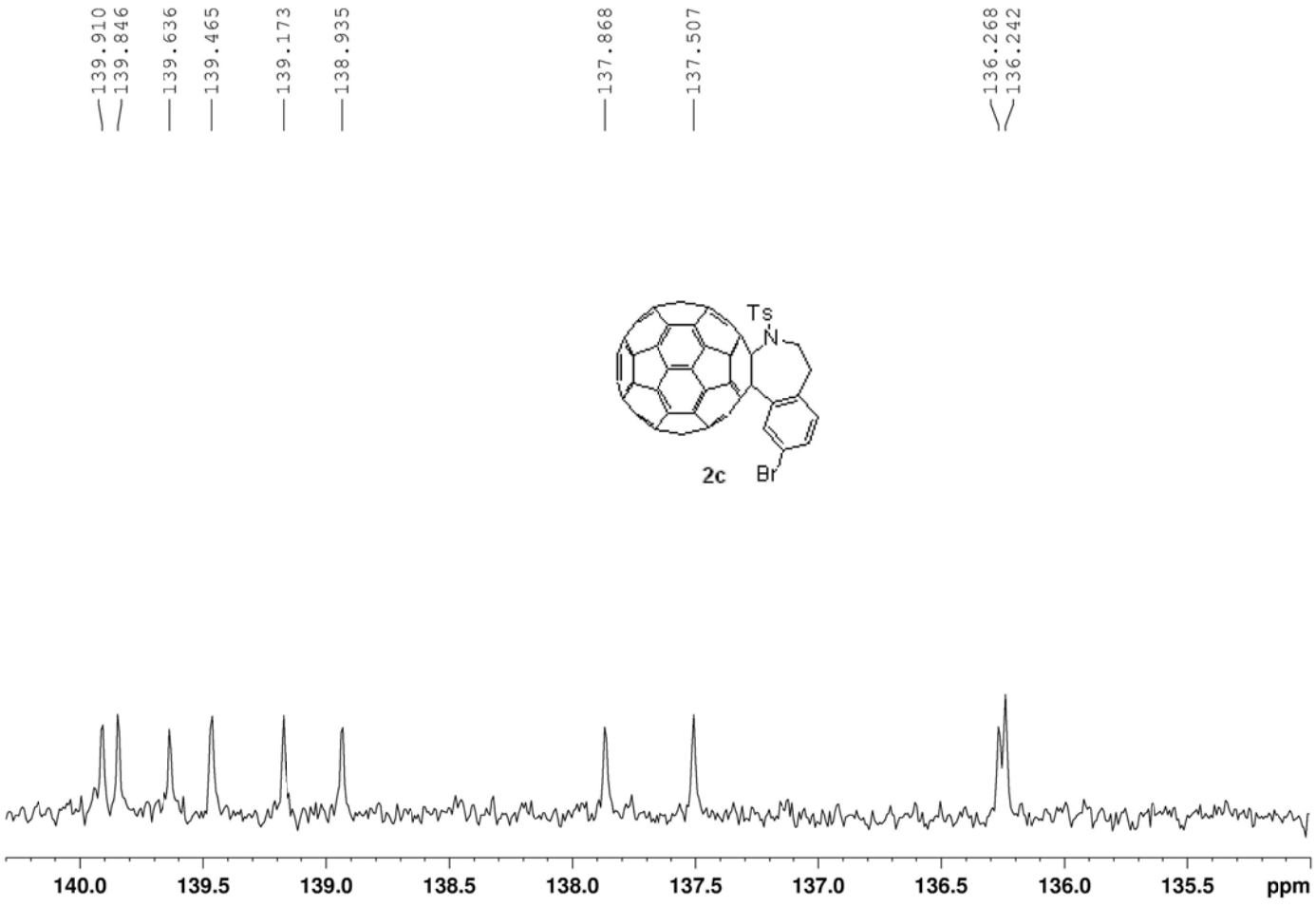


NAME	syt140509
EXPNO	13
PROCNO	1
Date_	20140511
Time	6.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	34153
DS	2
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	9195.2
DW	27.800 usec
DE	6.50 usec
TE	295.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	13.50 usec
PL1	-1.00 dB
SFO1	75.4768051 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	2.00 dB
PL12	18.48 dB
PL13	18.48 dB
SFO2	300.1312005 MHz
SI	32768
SF	75.4677866 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	0.50

The detailed ^{13}C NMR spectrum of compound **2c** (135–121 ppm)

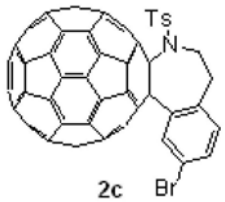


The detailed ^{13}C NMR spectrum of compound **2c** (140–135 ppm)

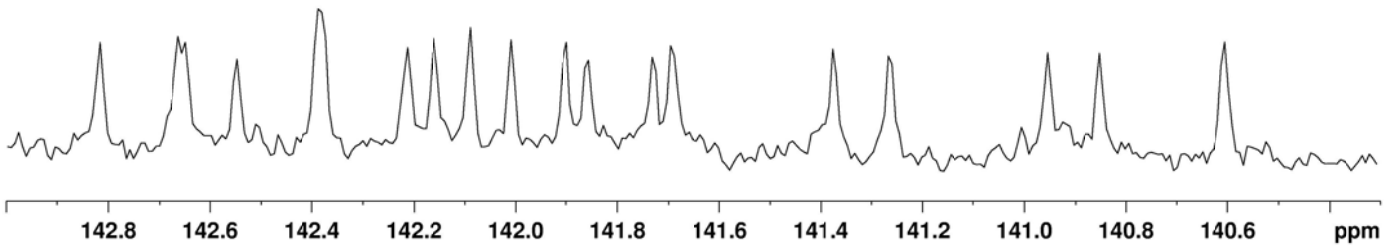


The detailed ^{13}C NMR spectrum of compound **2c** (143–140 ppm)

142.816
142.662
142.548
142.384
142.213
142.161
142.089
142.009
141.902
141.858
141.730
141.693
141.375
141.264
140.954
140.852
140.606

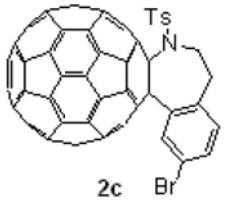


2c

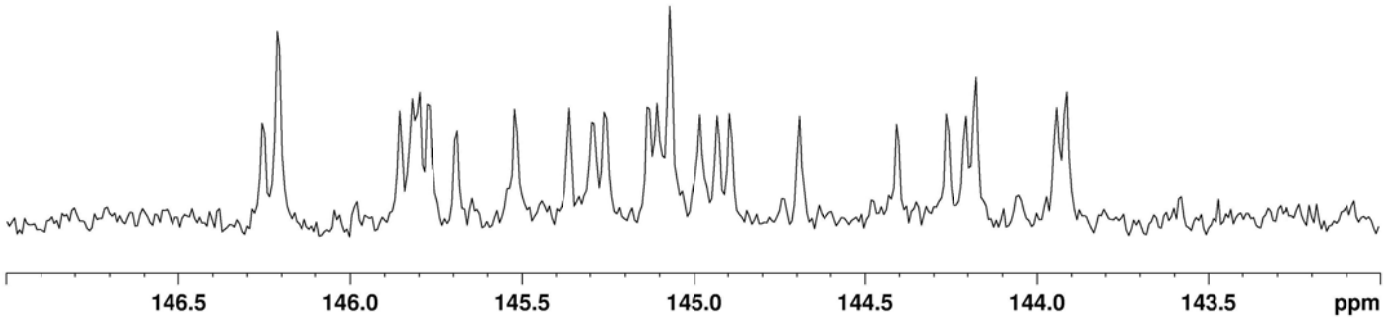


The detailed ^{13}C NMR spectrum of compound **2c** (147–143 ppm)

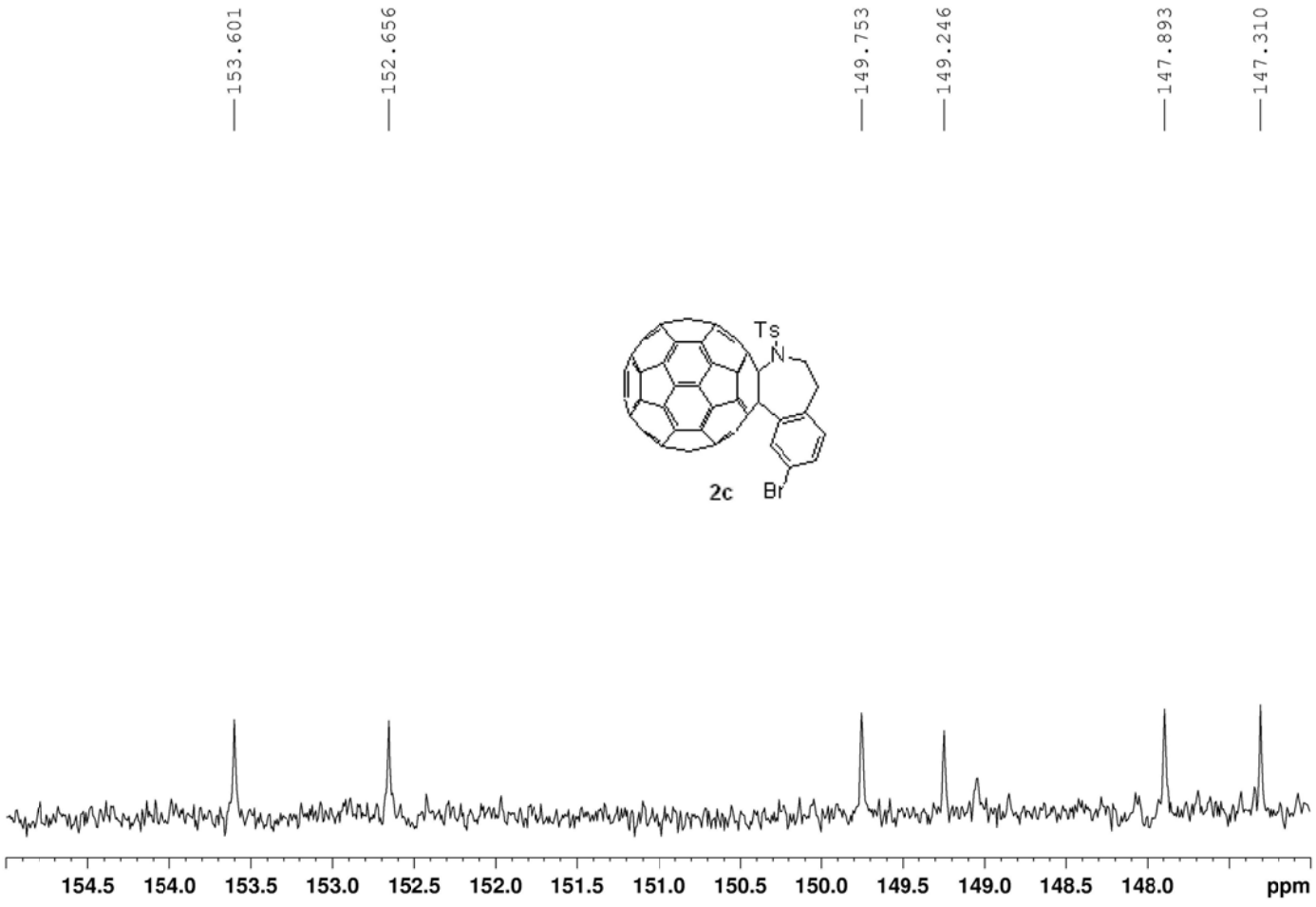
146.254
146.210
145.855
145.819
145.800
145.773
145.691
145.520
145.362
145.293
145.257
145.133
145.107
145.070
144.983
144.931
144.895
144.693
144.407
144.261
144.206
144.177
143.944
143.916



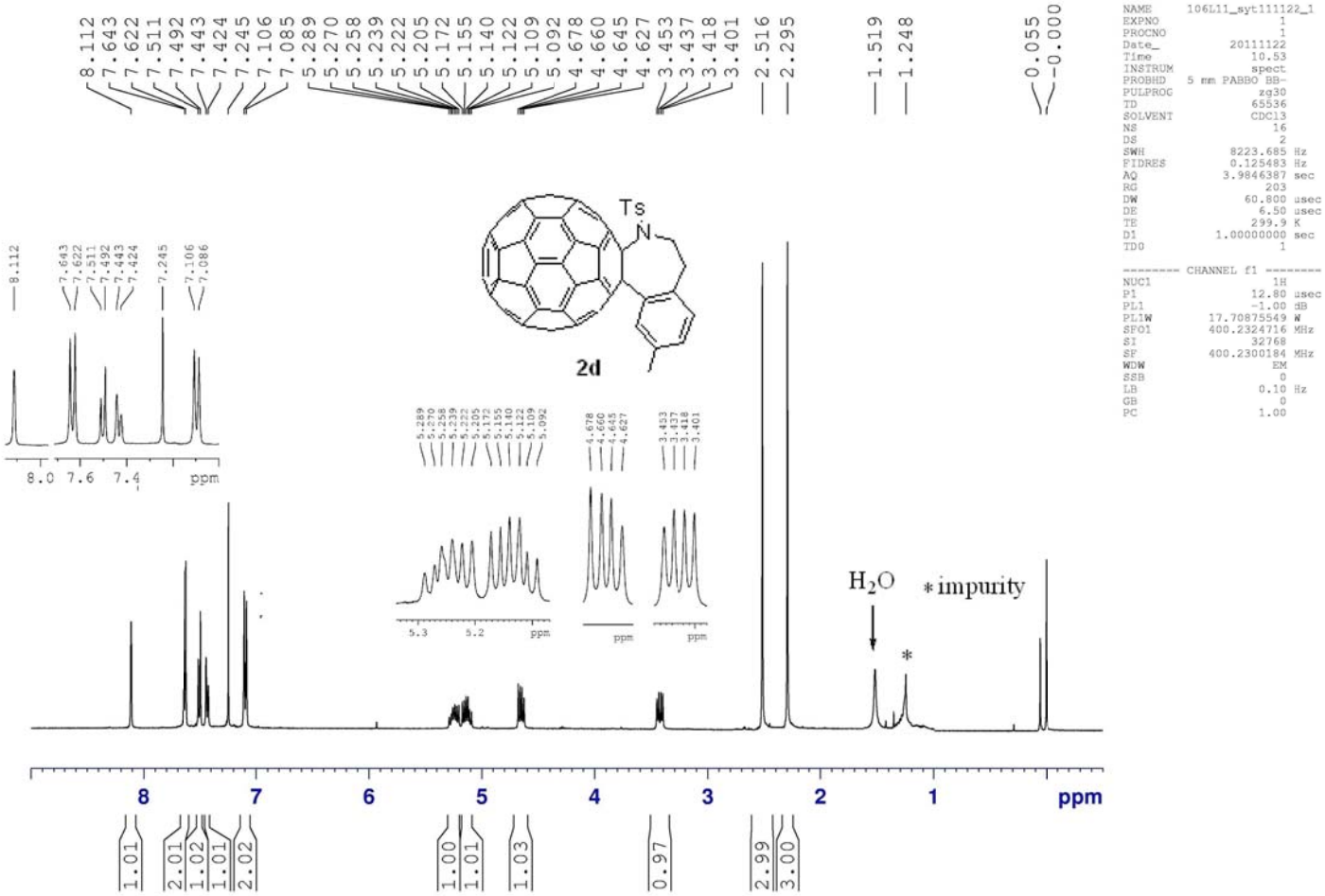
2c



The detailed ^{13}C NMR spectrum of compound **2c** (155–147 ppm)

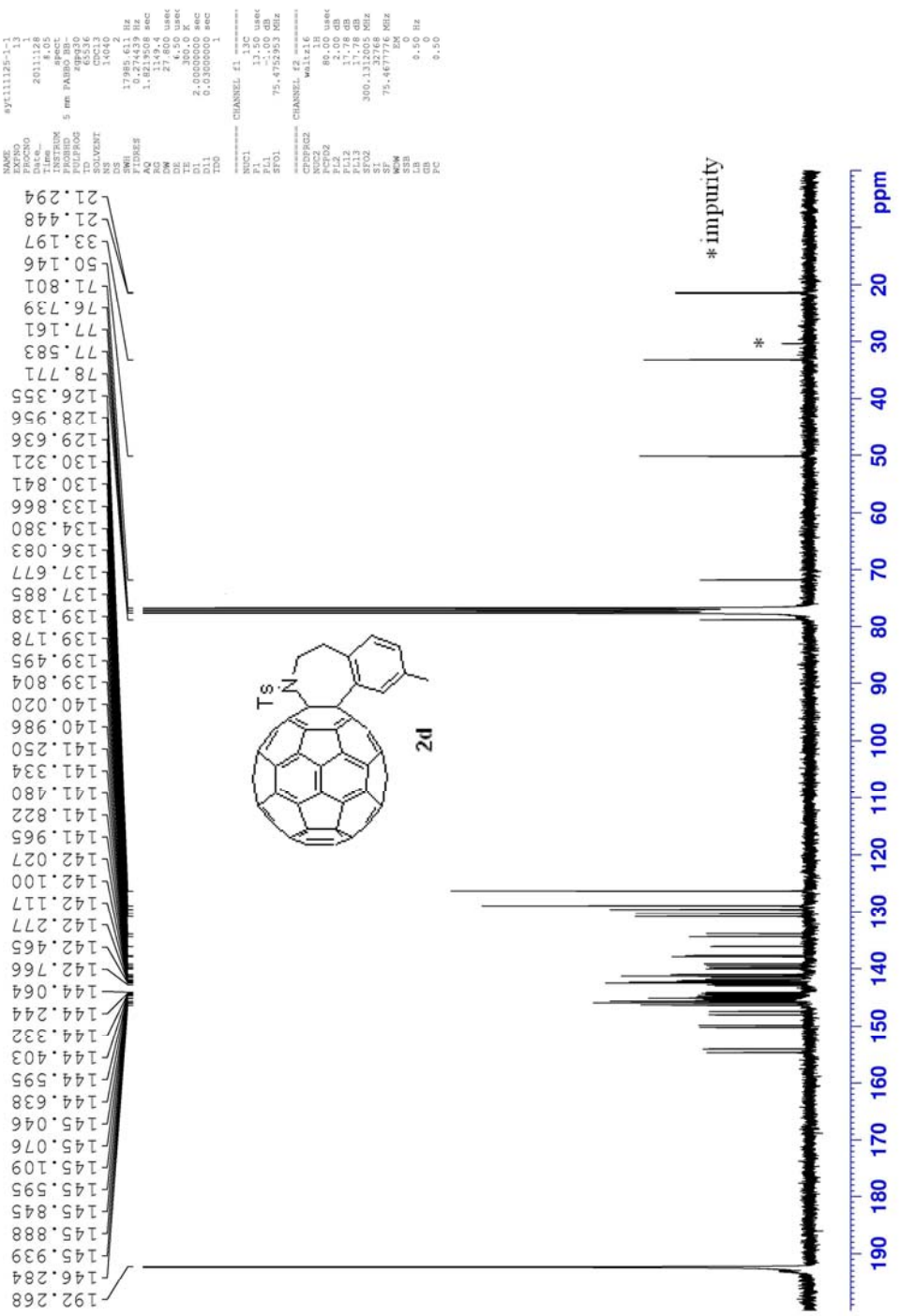


^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2d**

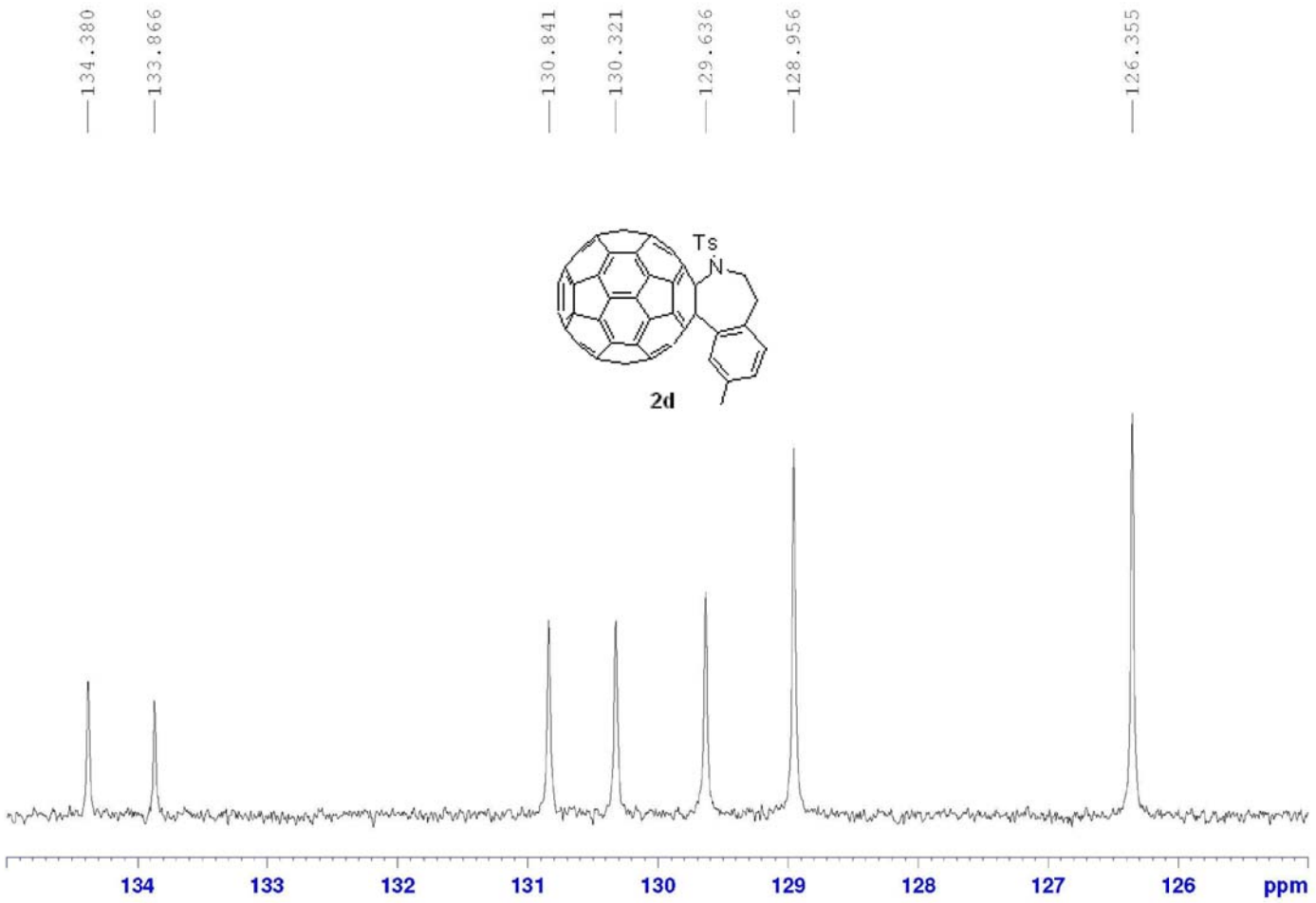



```
NAME        106L11_syt111122_1
EXPNO                        1
PROCNO                       1
Date_                 20111122
Time                     10.53
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         203
DW                    60.800 usec
DE                     6.50 usec
TE                     299.9 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                    12.80 usec
PL1                   -1.00 dB
PL1W             17.70875549 W
SFO1            400.2324716 MHz
SI                       32768
SF              400.2300184 MHz
WDW                        EM
SSB                         0
LB                    0.10 Hz
GB                          0
PC                       1.00
```

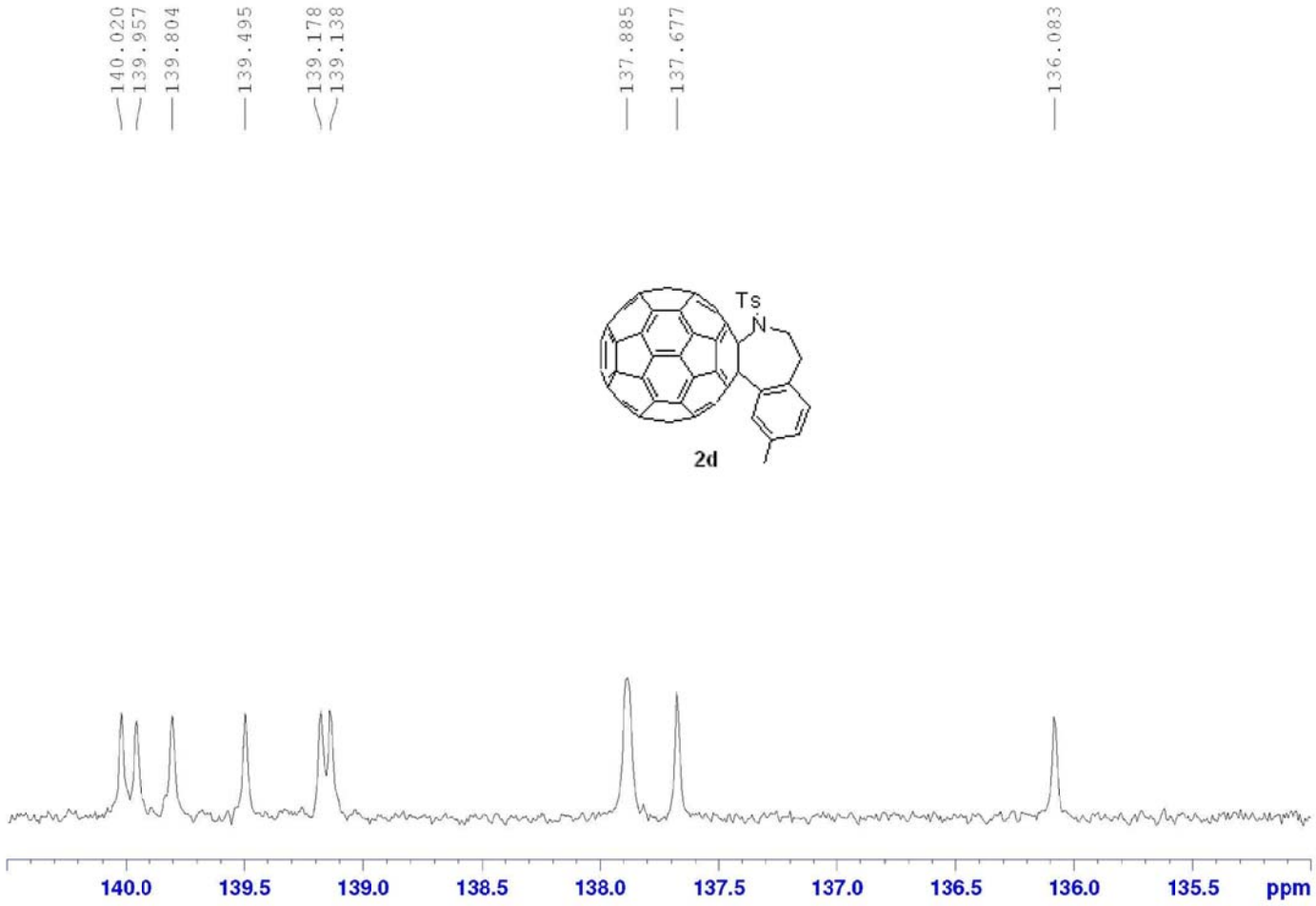
^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2d**



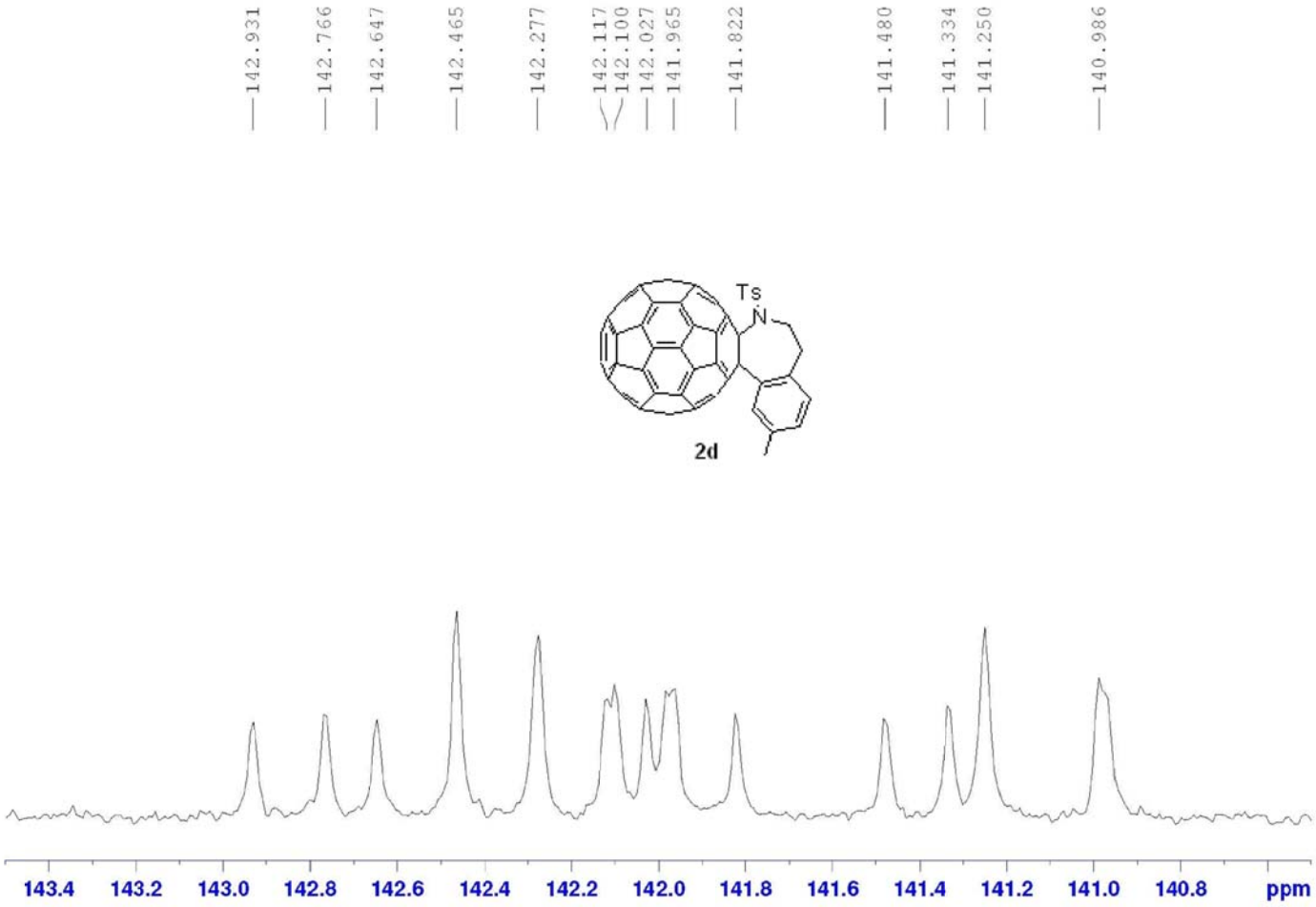
The detailed ^{13}C NMR spectrum of compound **2d** (135–125 ppm)



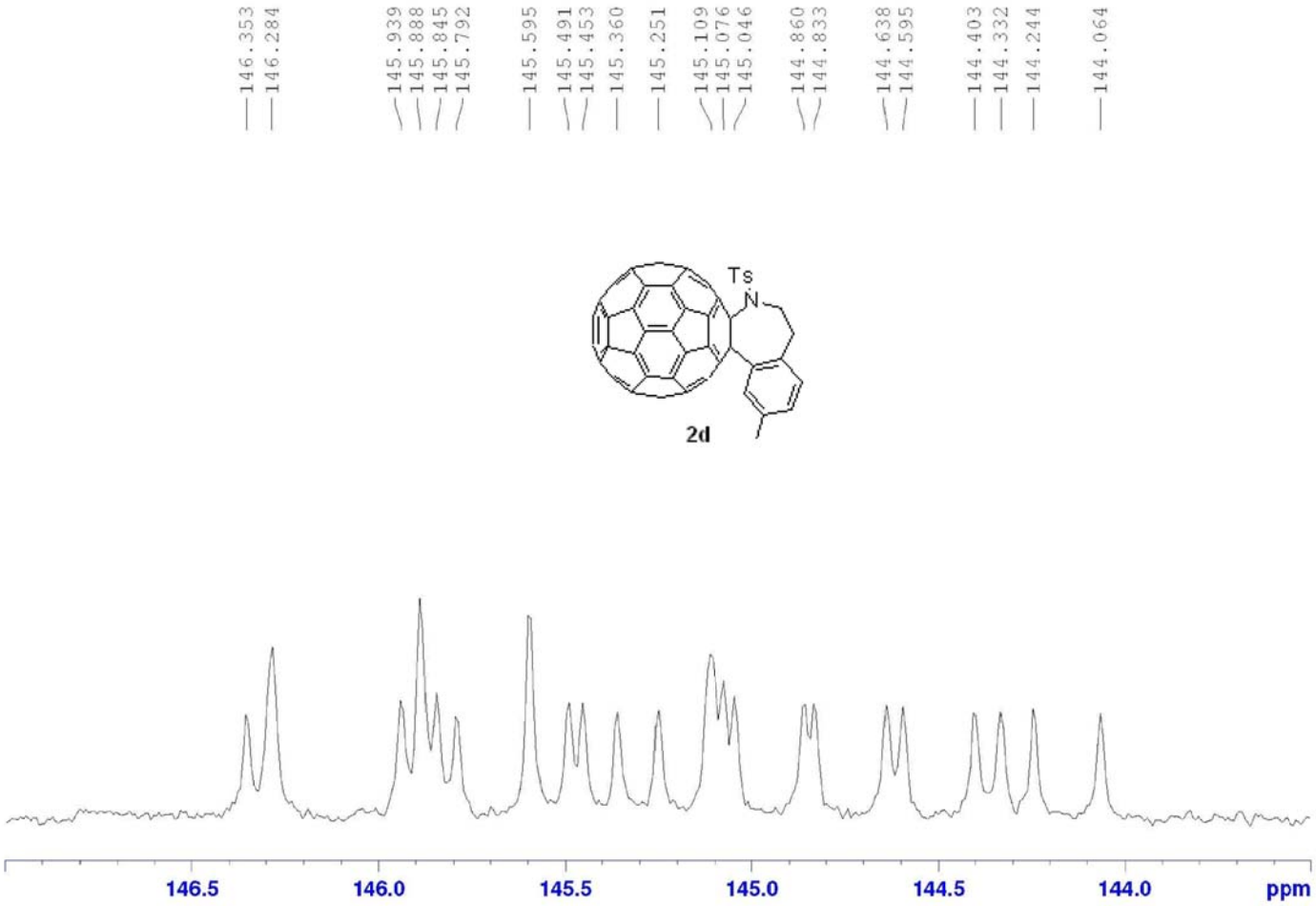
The detailed ^{13}C NMR spectrum of compound **2d** (141–135 ppm)



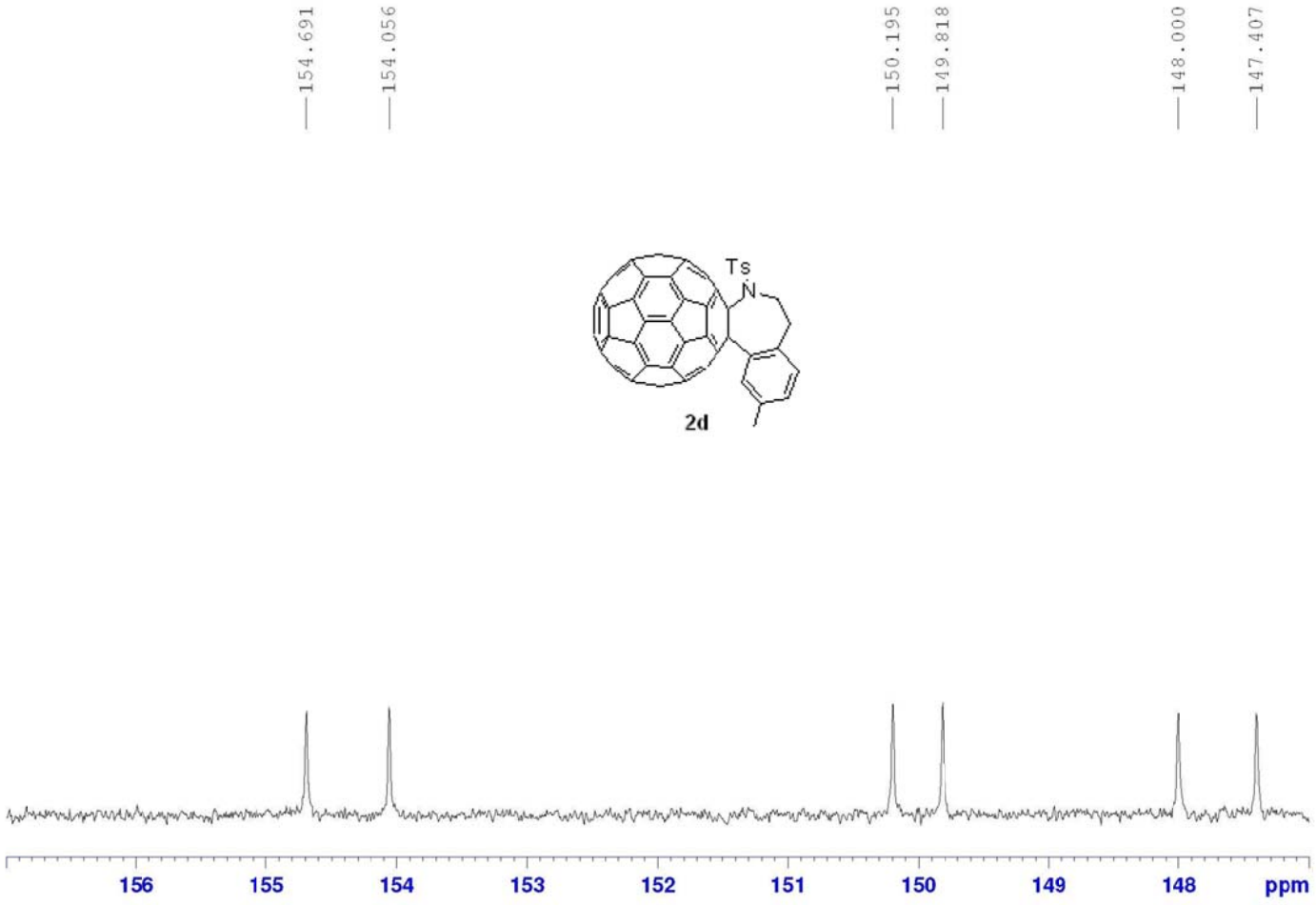
The detailed ^{13}C NMR spectrum of compound **2d** (143–140 ppm)



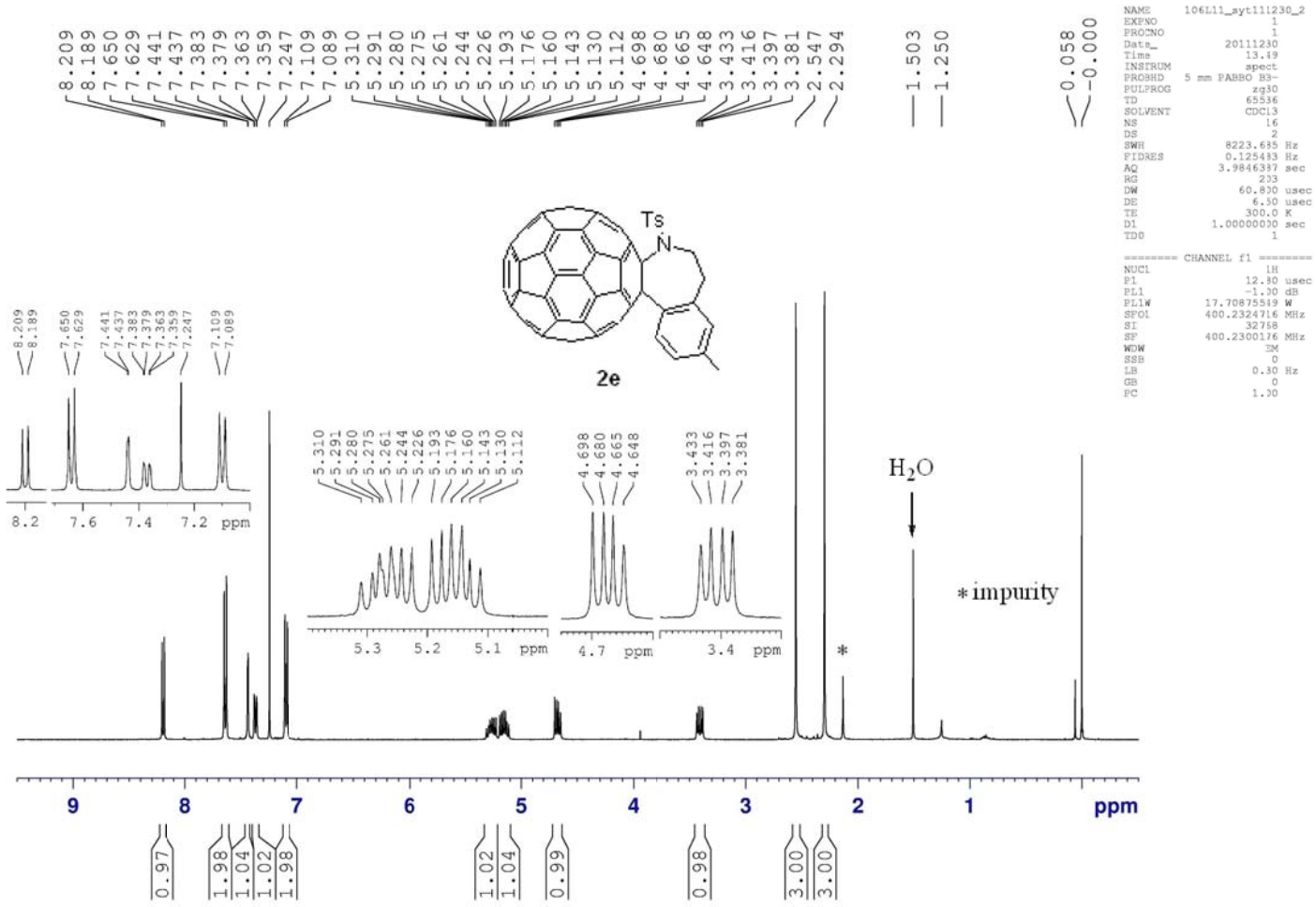
The detailed ^{13}C NMR spectrum of compound **2d** (147–143 ppm)



The detailed ^{13}C NMR spectrum of compound **2d** (157–147 ppm)

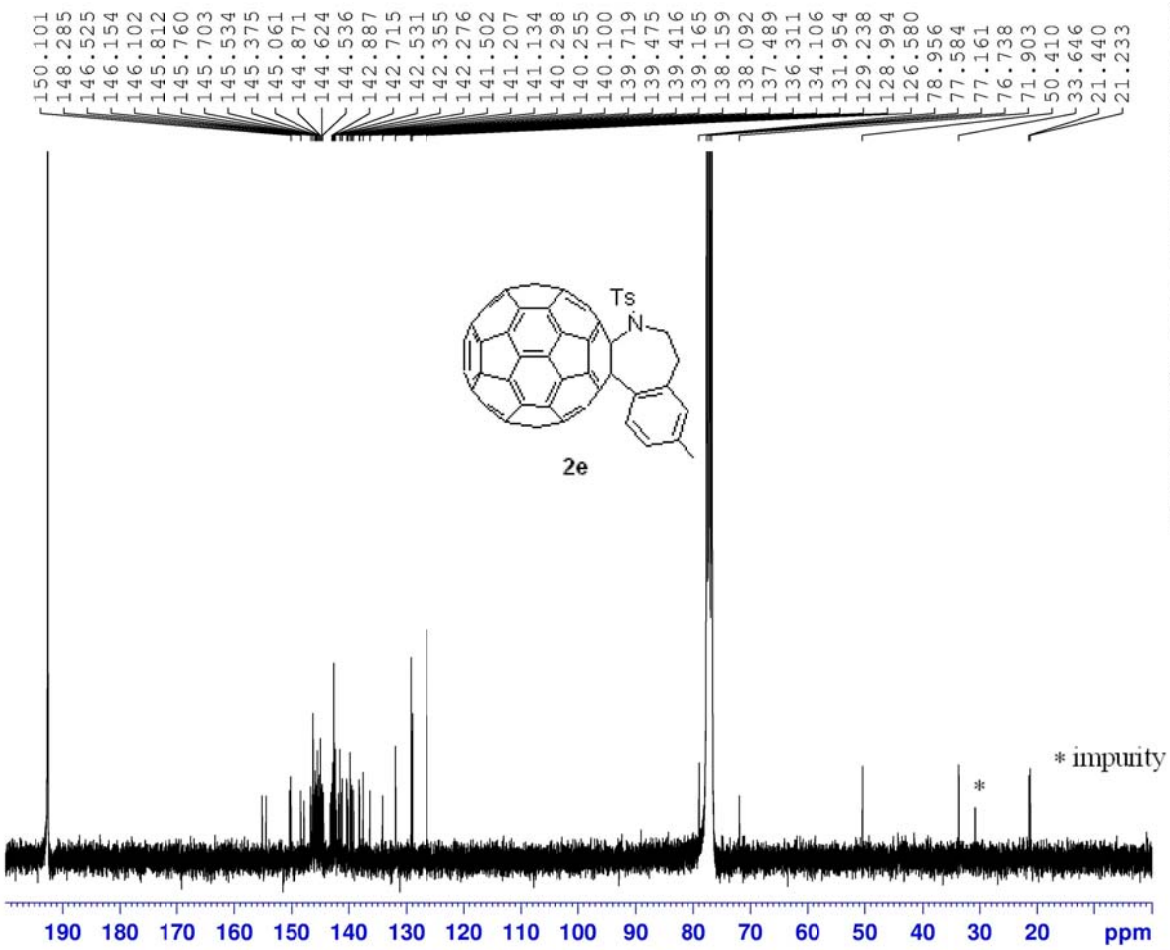


^{1}H NMR (400 M, $CS_2/CDCl_3$) spectrum of compound **2e**



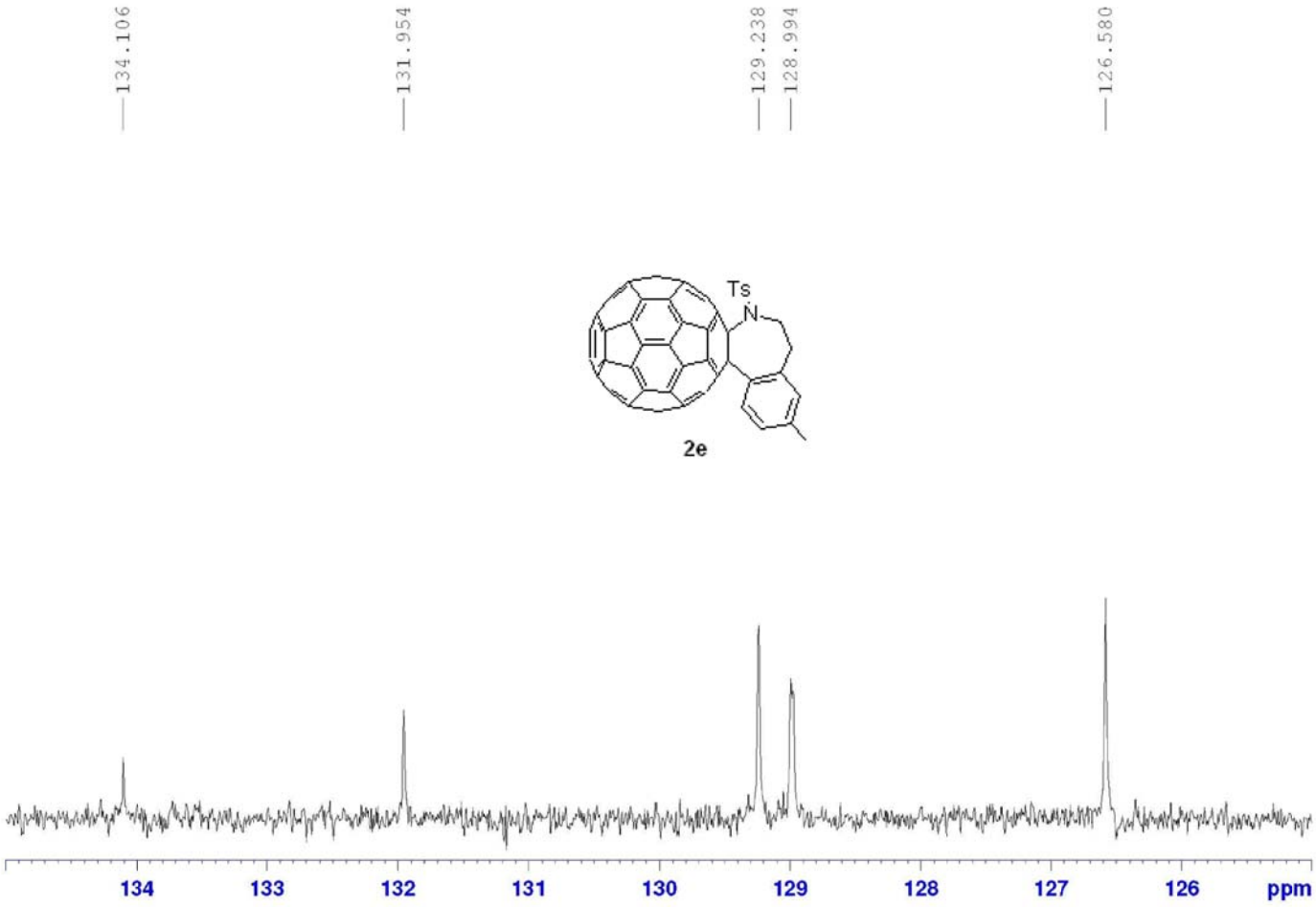

```
NAME        106L11_syt111230_2
EXPNO                        1
PROCNO                       1
Data_                 20111230
Time                     13.49
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         203
DW                    60.830 usec
DE                     6.50 usec
TE                     300.0 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    12.80 usec
PL1                   -1.30 dB
PL1W             17.70875519 W
SFO1             400.2324716 MHz
SI                       32758
SF               400.2300176 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                     1.00
```

^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2e**

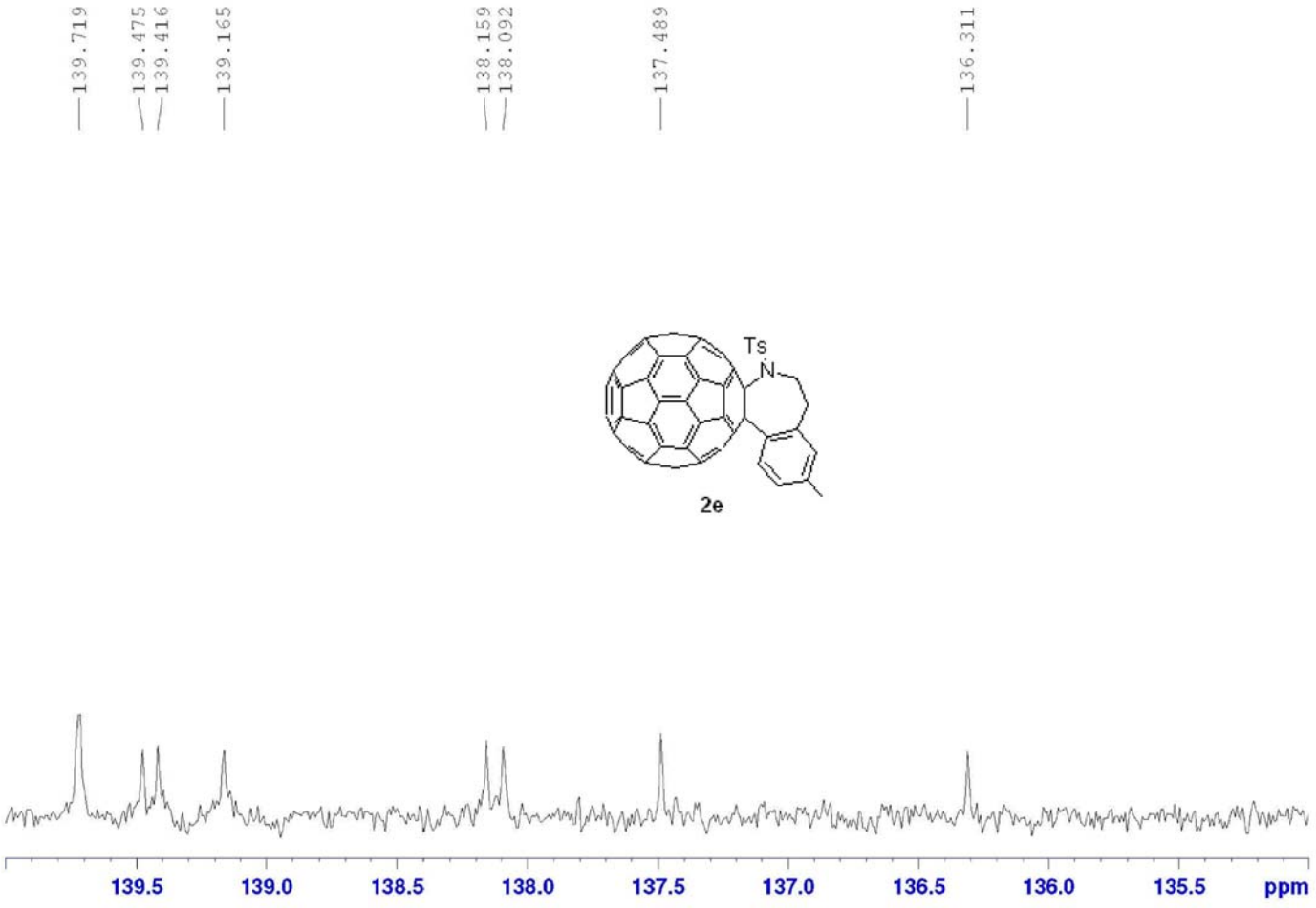



```
NAME          syt111230-2-15
EXPNO                      1
PROCNO                     1
Date_               20120109
Time                    8.04
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                      15864
DS                          2
SWH                17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                   11585.2
DW                    27.800 usec
DE                     6.50 usec
TE                    300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     13.50 usec
PL1                    -1.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     2.00 dB
PL12                   17.78 dB
PL13                   17.78 dB
SFO2             300.1312005 MHz
SI                       32768
SF                75.4677561 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                        1.40
```

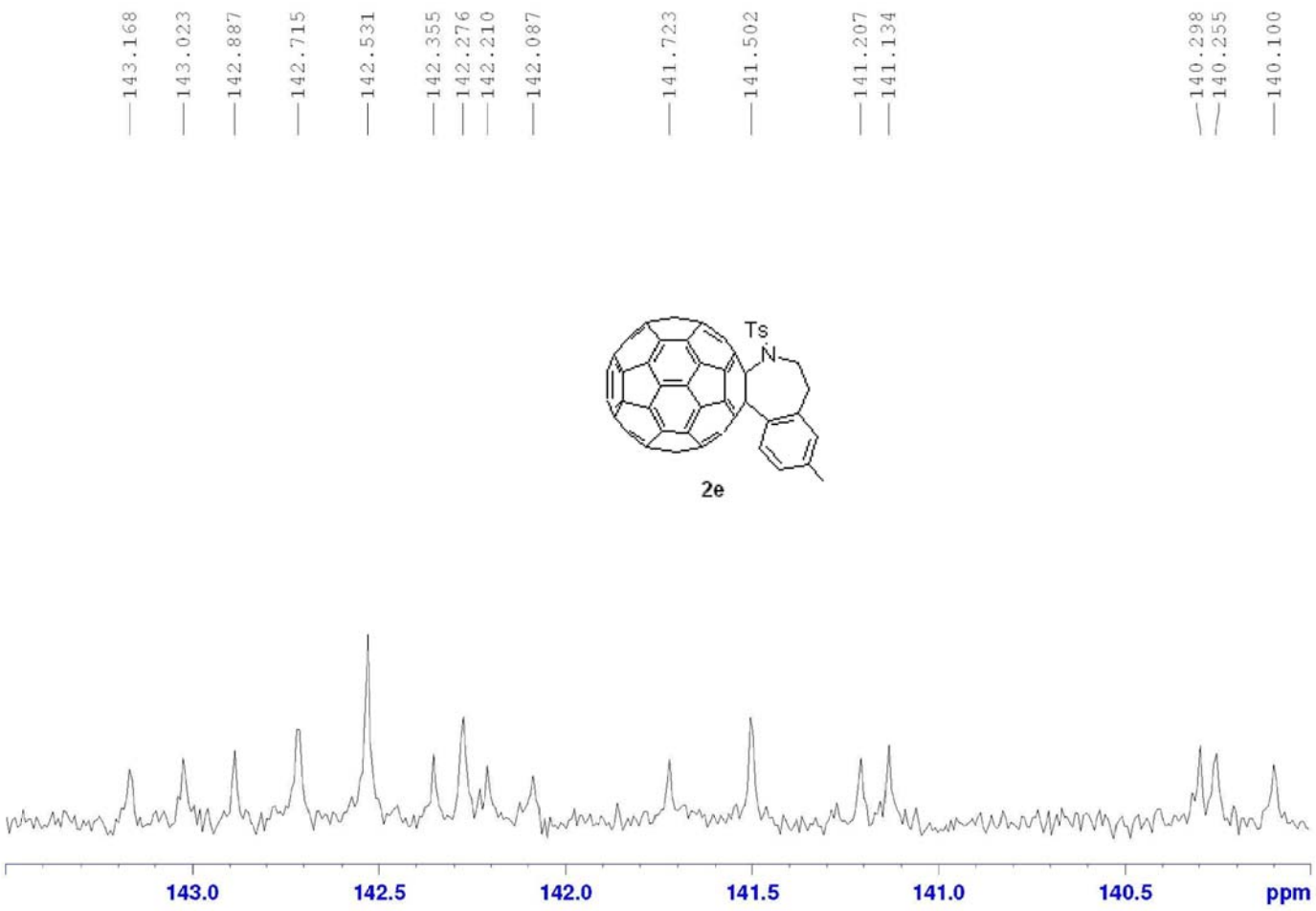
The detailed ^{13}C NMR spectrum of compound **2e** (135–125 ppm)



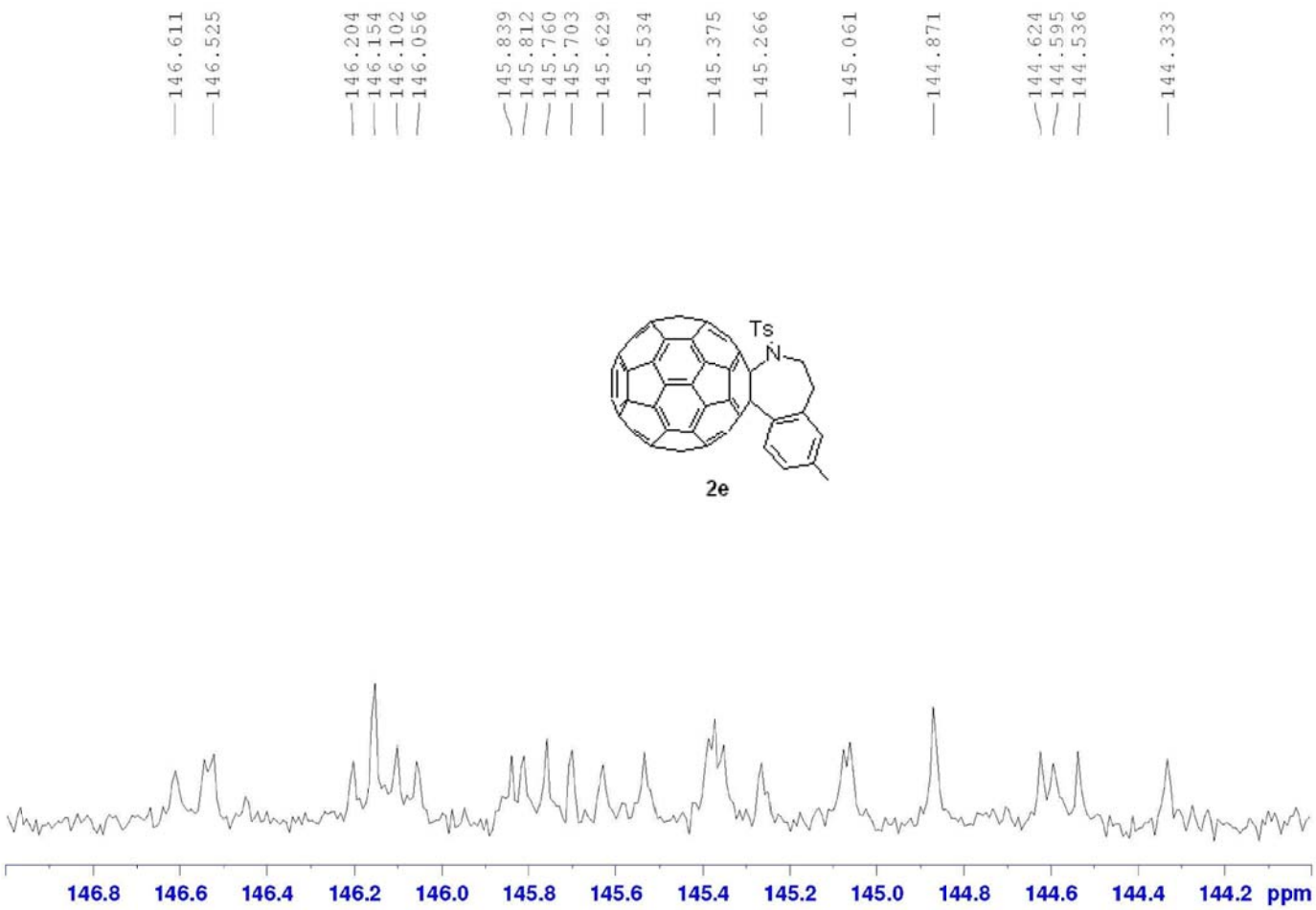
The detailed ^{13}C NMR spectrum of compound **2e** (140–135 ppm)



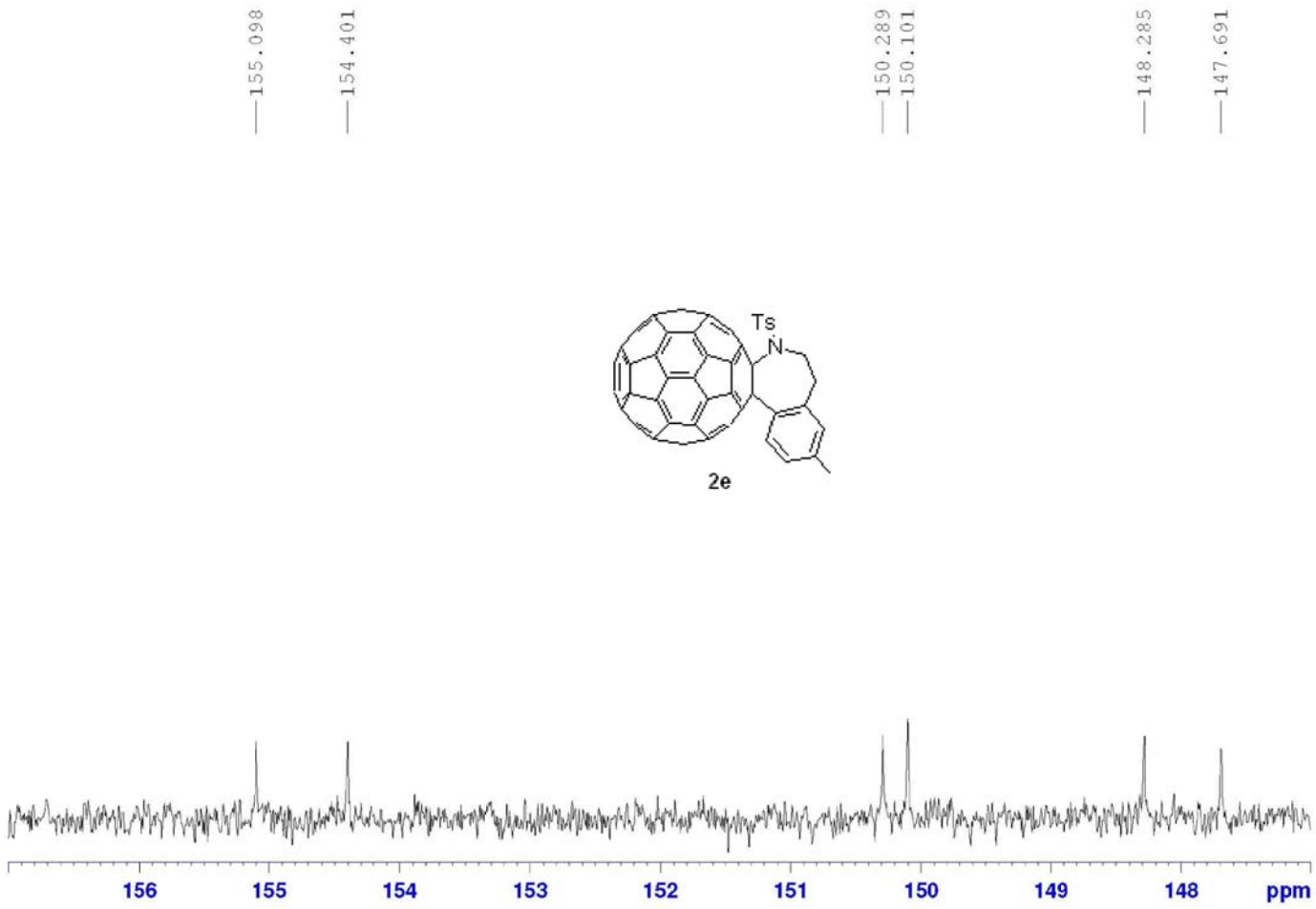
The detailed ^{13}C NMR spectrum of compound **2e** (144–140 ppm)

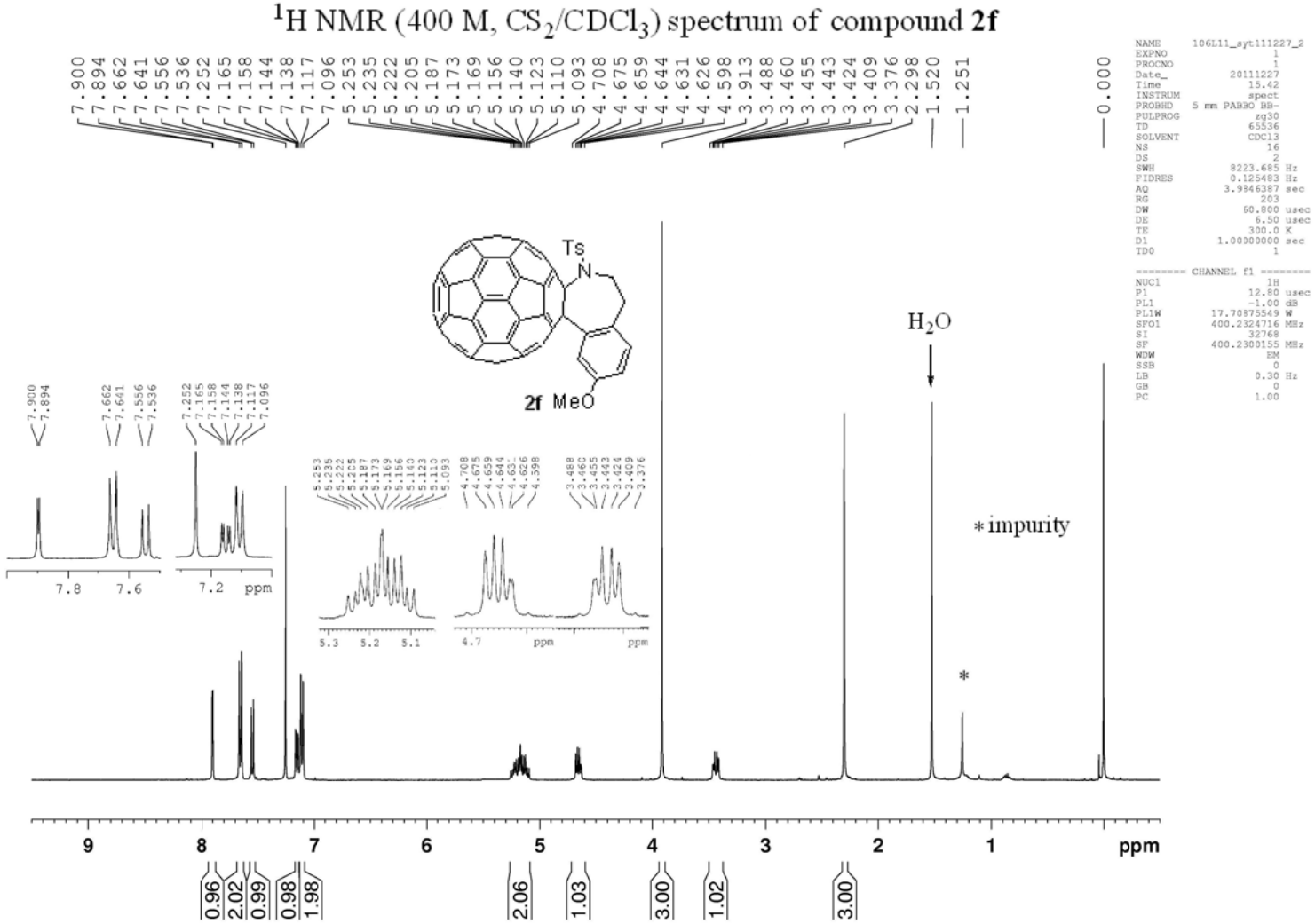


The detailed ^{13}C NMR spectrum of compound **2e** (147–144 ppm)

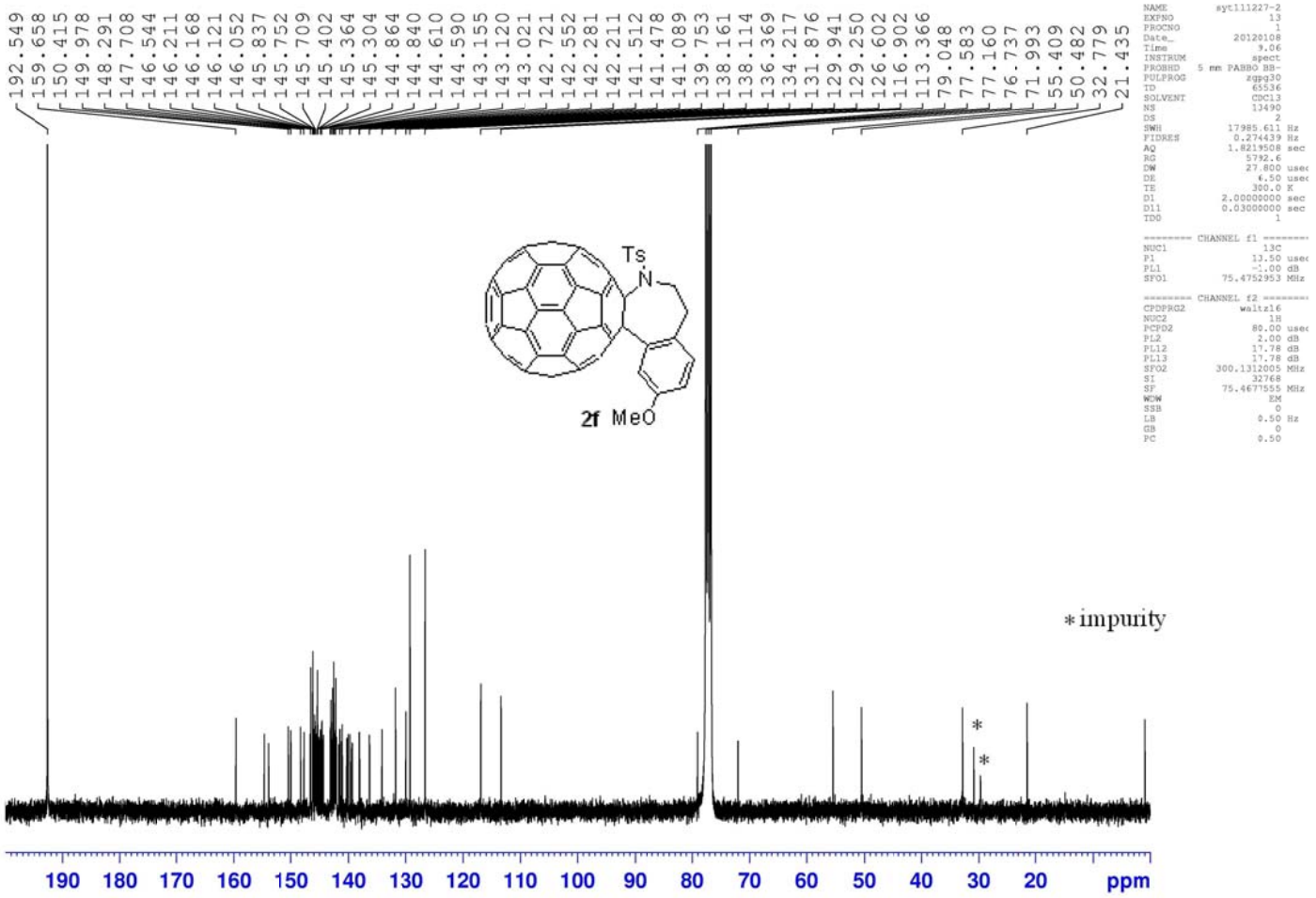


The detailed ^{13}C NMR spectrum of compound **2e** (157–147 ppm)

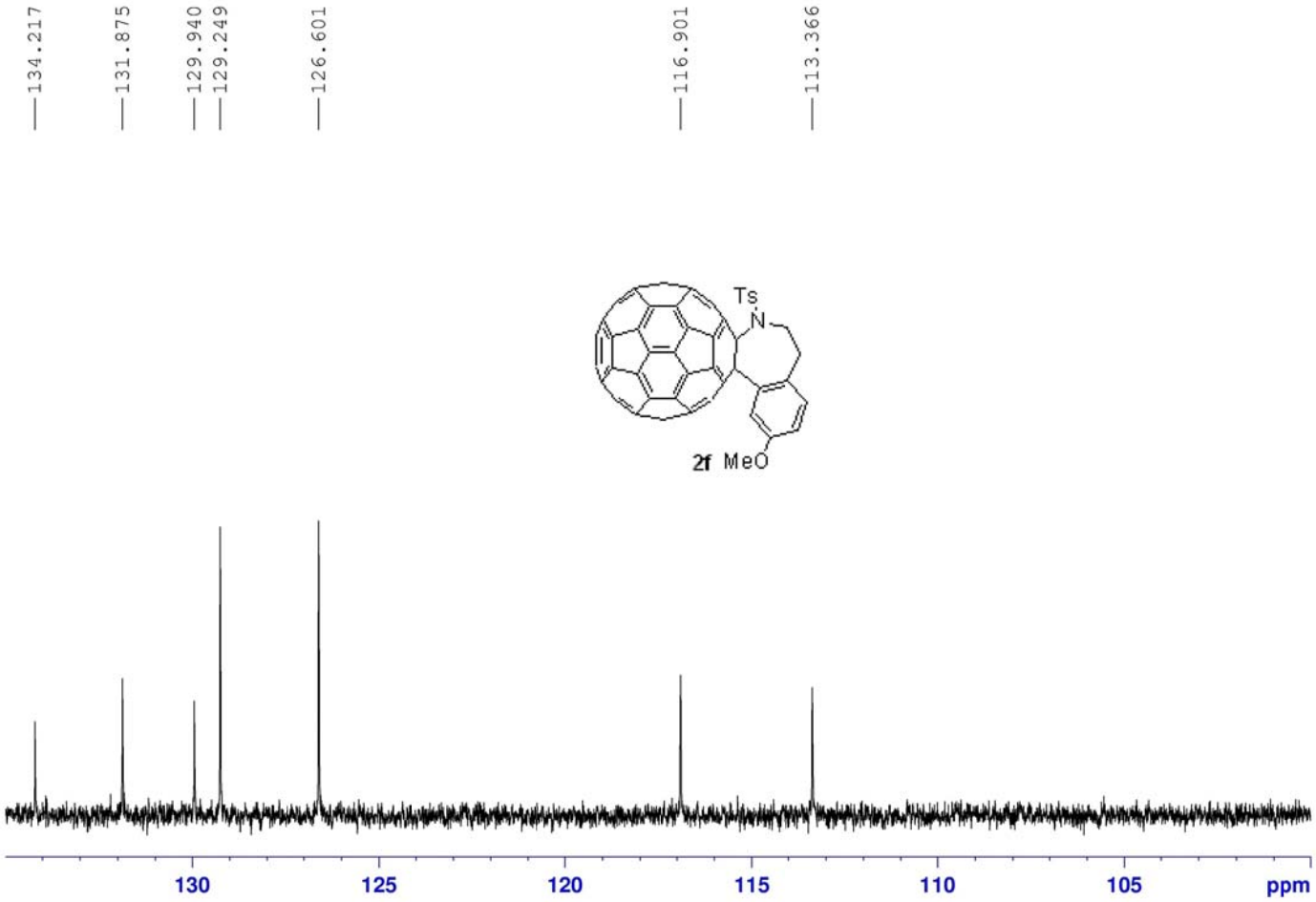



^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2f**
7.900 7.894 7.662 7.641 7.556 7.536 7.252 7.165 7.158 7.144 7.138 7.117 7.096 5.253 5.235 5.222 5.205 5.187 5.173 5.169 5.156 5.140 5.123 5.110 5.093 4.708 4.675 4.659 4.644 4.631 4.626 4.598 3.913 3.488 3.460 3.455 3.443 3.424 3.409 3.376 2.298 1.520 1.251 0.000
Ts
N
2f MeO
H_2O
* impurity
*
7.8 7.6 7.2 ppm
5.3 5.2 5.1 4.7 ppm ppm
9 8 7 6 5 4 3 2 1 ppm
0.96 2.02 0.99 0.98 1.98 2.06 1.03 3.00 1.02 3.00
NAME 106L11_syt111227_2
EXPNO 1
PROCNO 1
Date_ 20111227
Time 15.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 12.80 usec
PL1 -1.00 dB
PL1W 17.70875549 W
SFO1 400.2324716 MHz
SI 32768
SF 400.2300155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

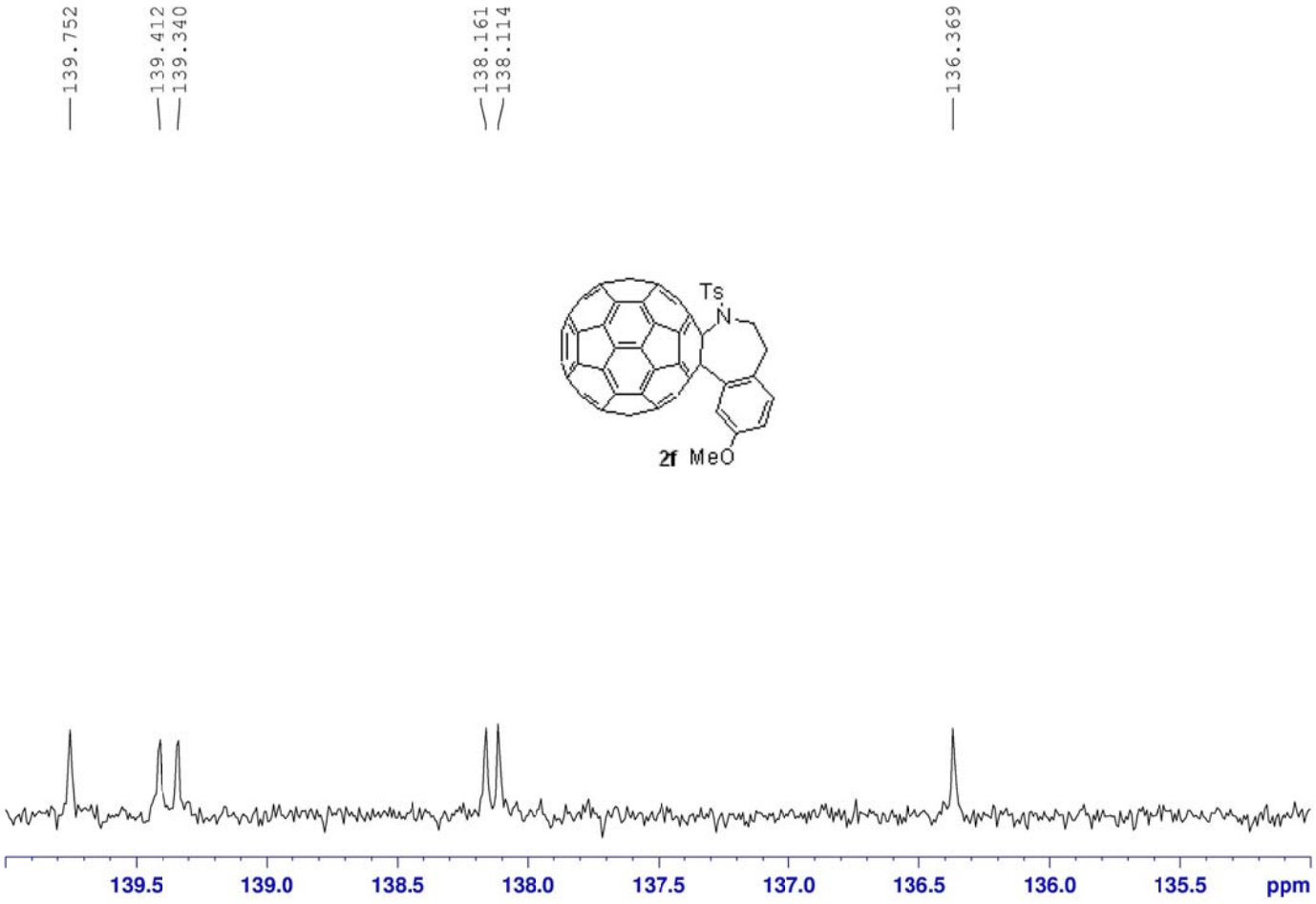
^{13}C NMR (75 M, CS_2/$CDCl_3$) spectrum of compound **2f**



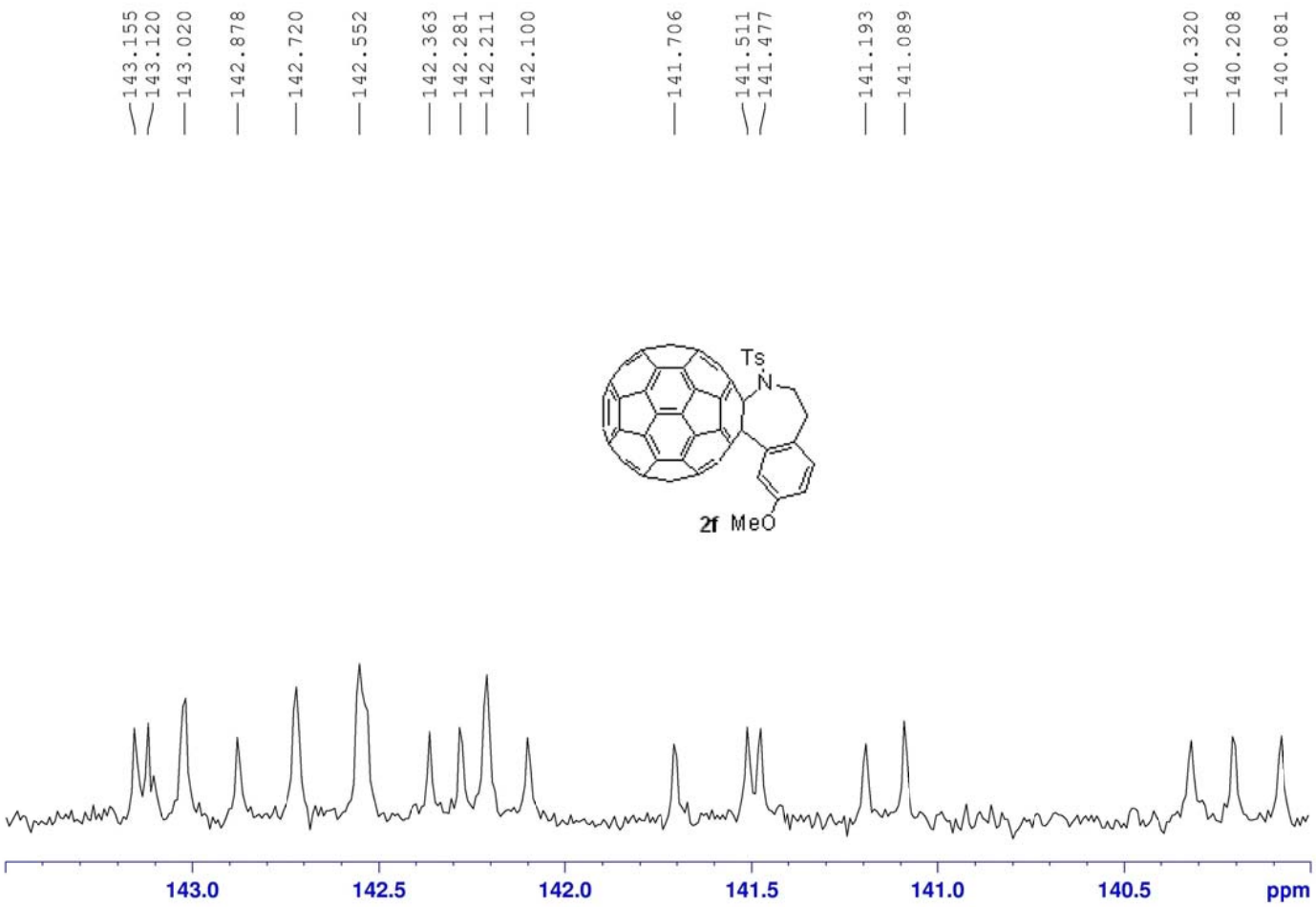
The detailed ^{13}C NMR spectrum of compound **2f** (135–100 ppm)



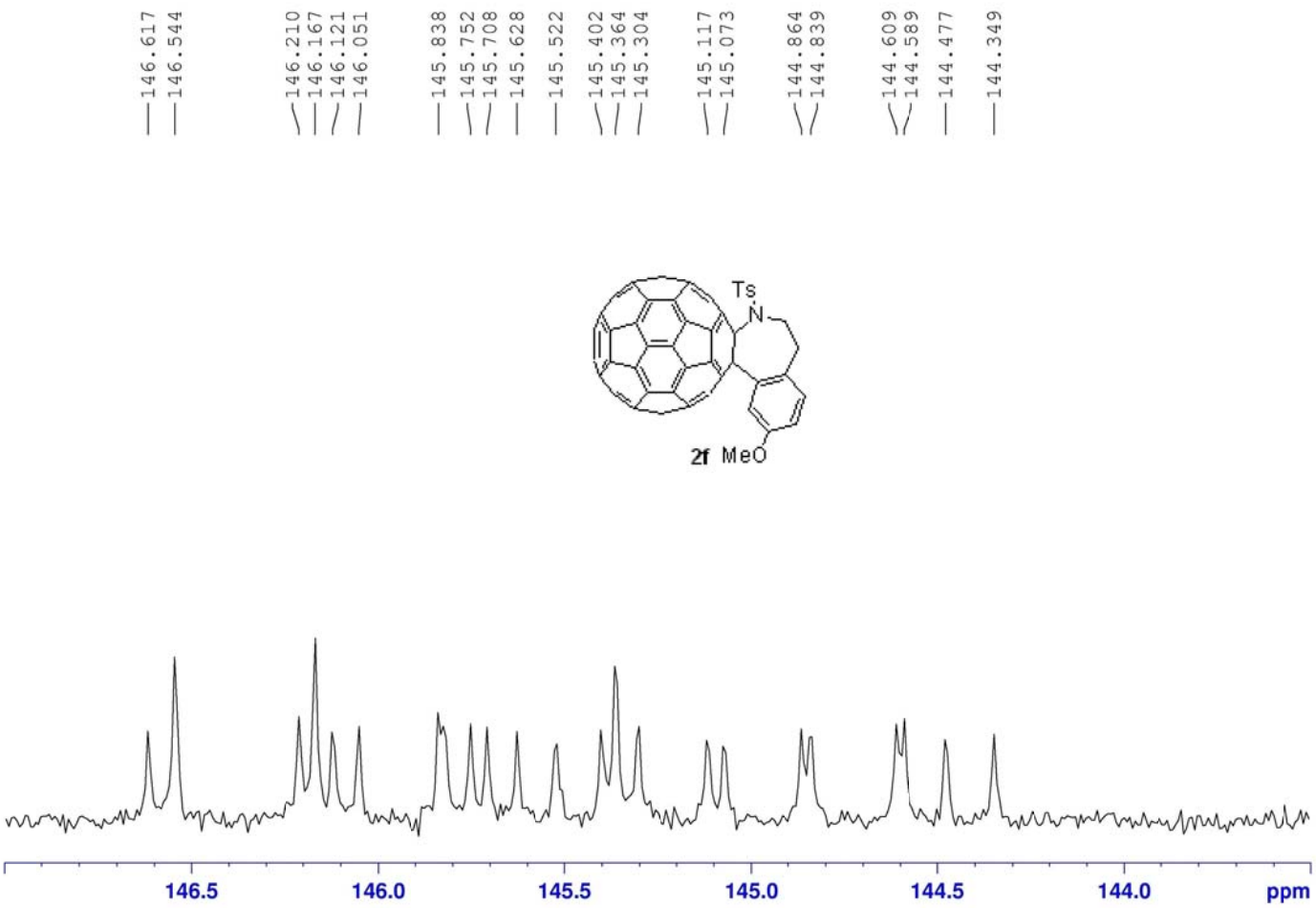
The detailed ^{13}C NMR spectrum of compound **2f** (140–135 ppm)



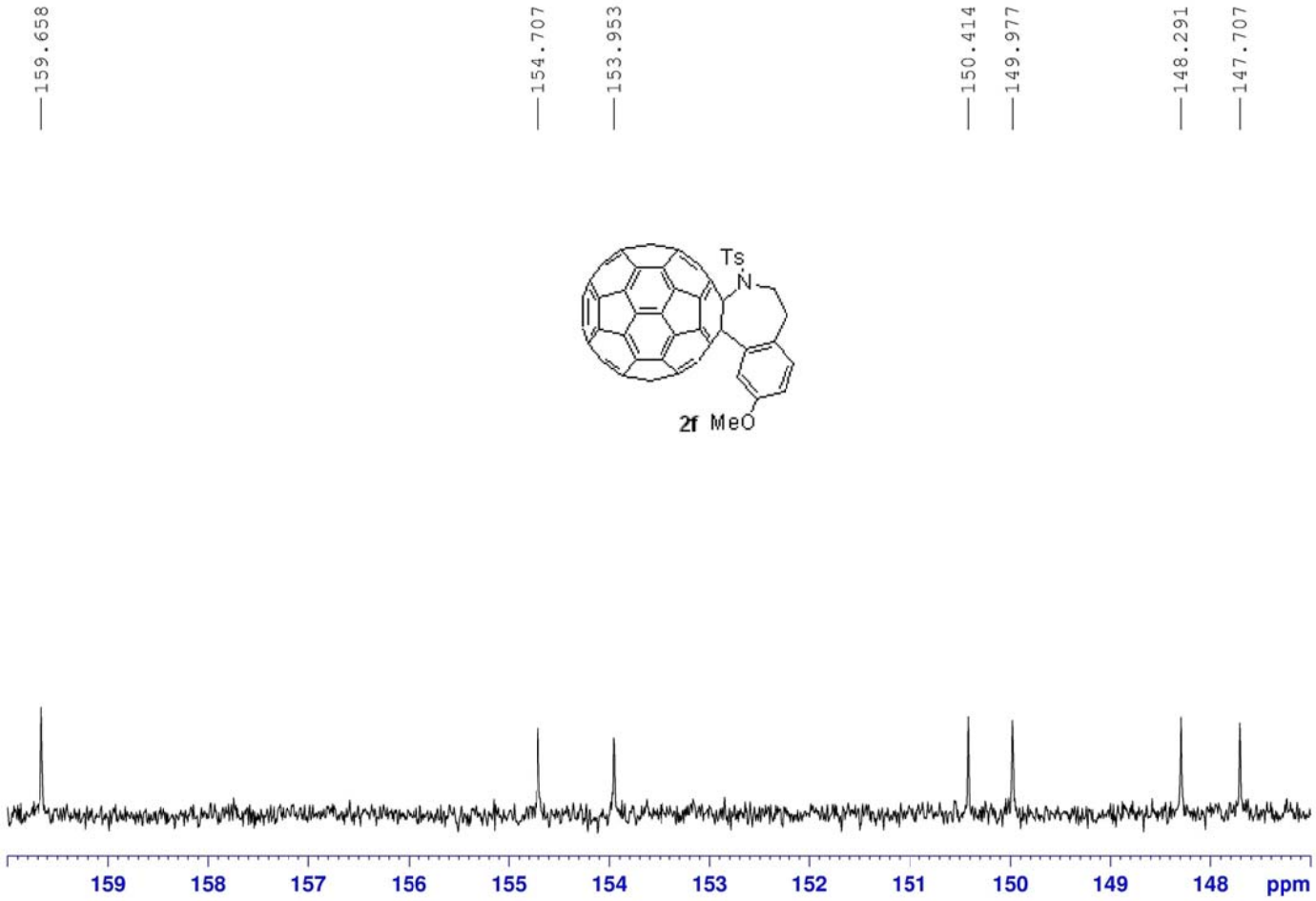
The detailed ^{13}C NMR spectrum of compound **2f** (144–140 ppm)



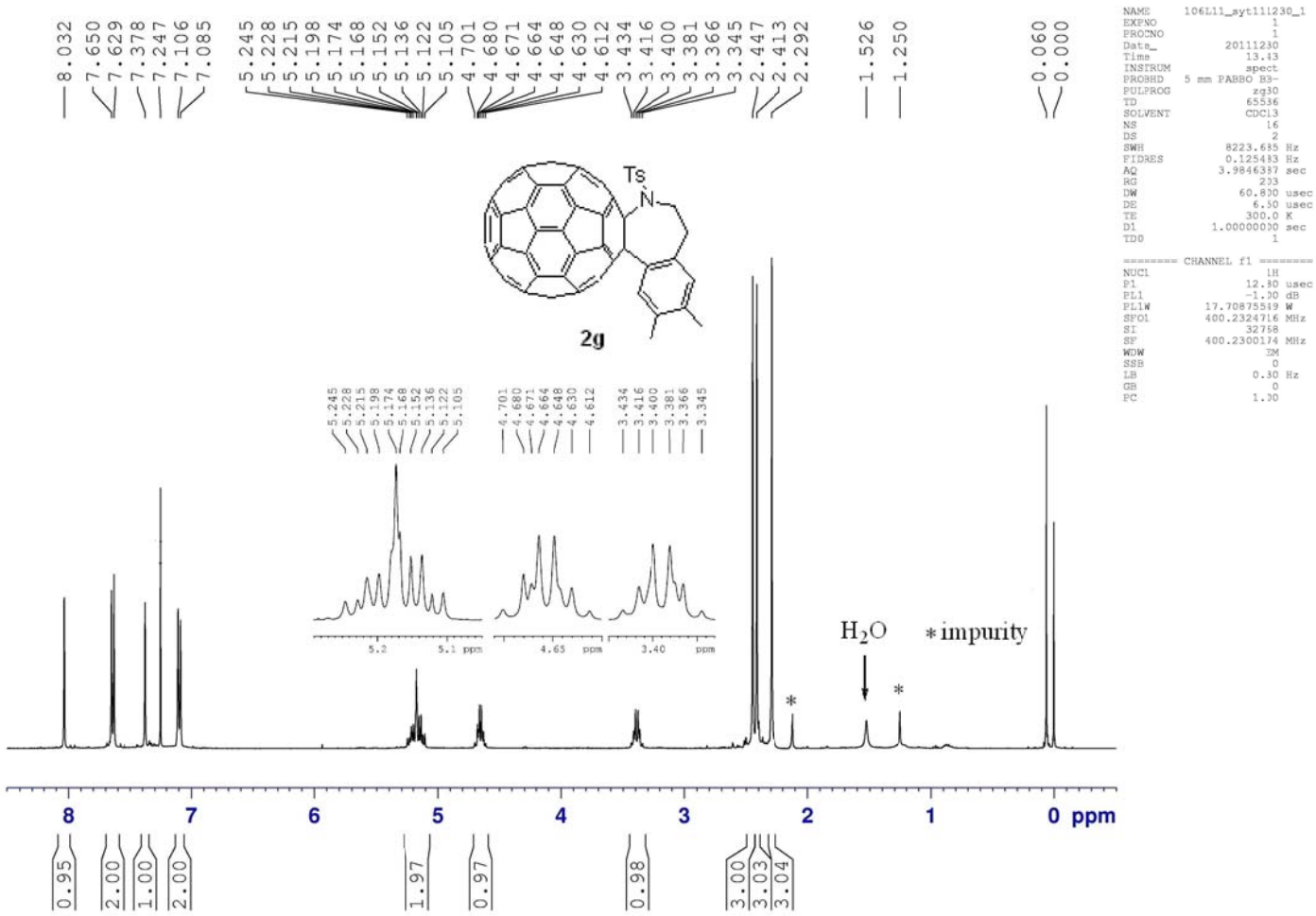
The detailed ^{13}C NMR spectrum of compound **2f** (147–144 ppm)



The detailed ^{13}C NMR spectrum of compound **2f** (160–147 ppm)

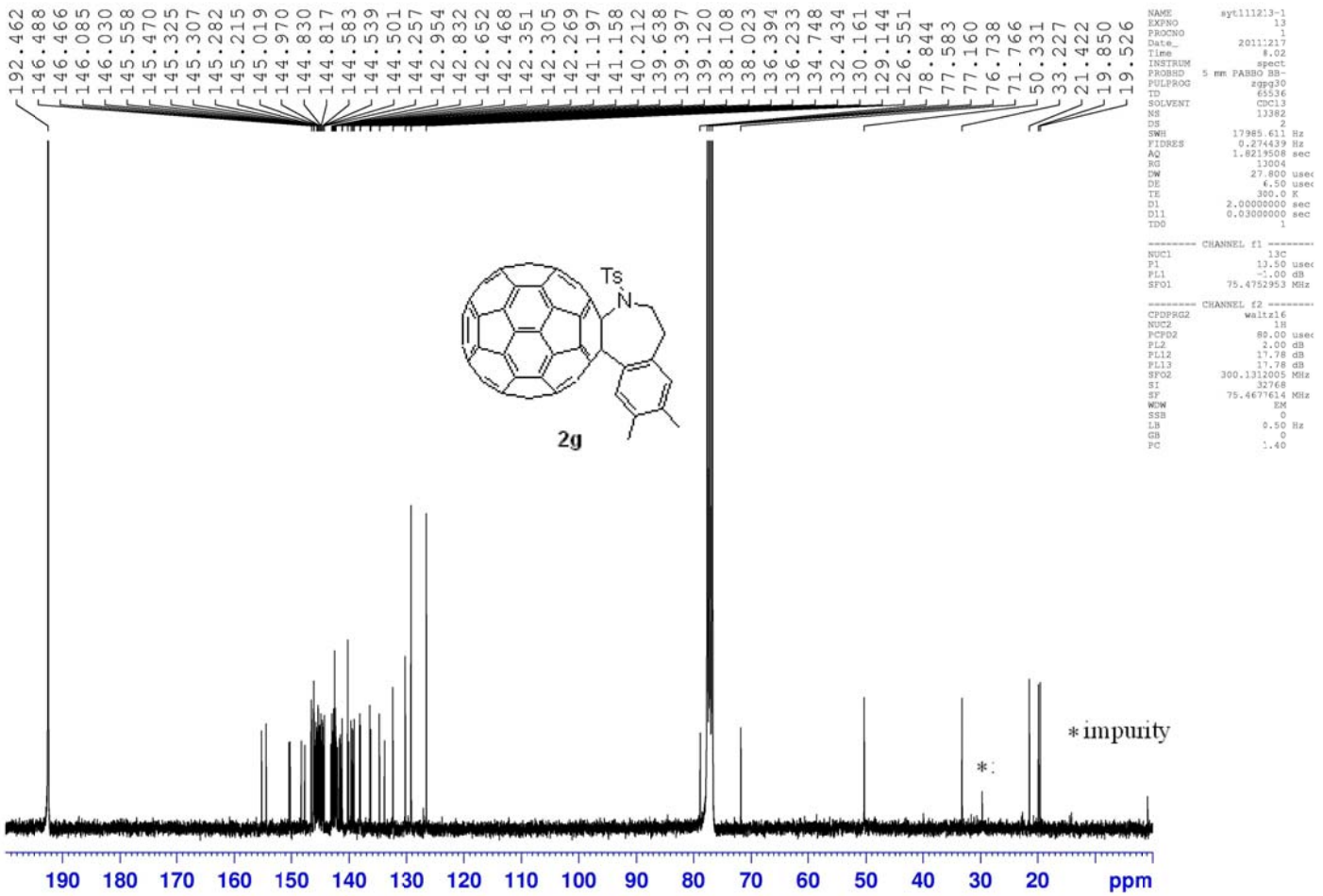


^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2g**

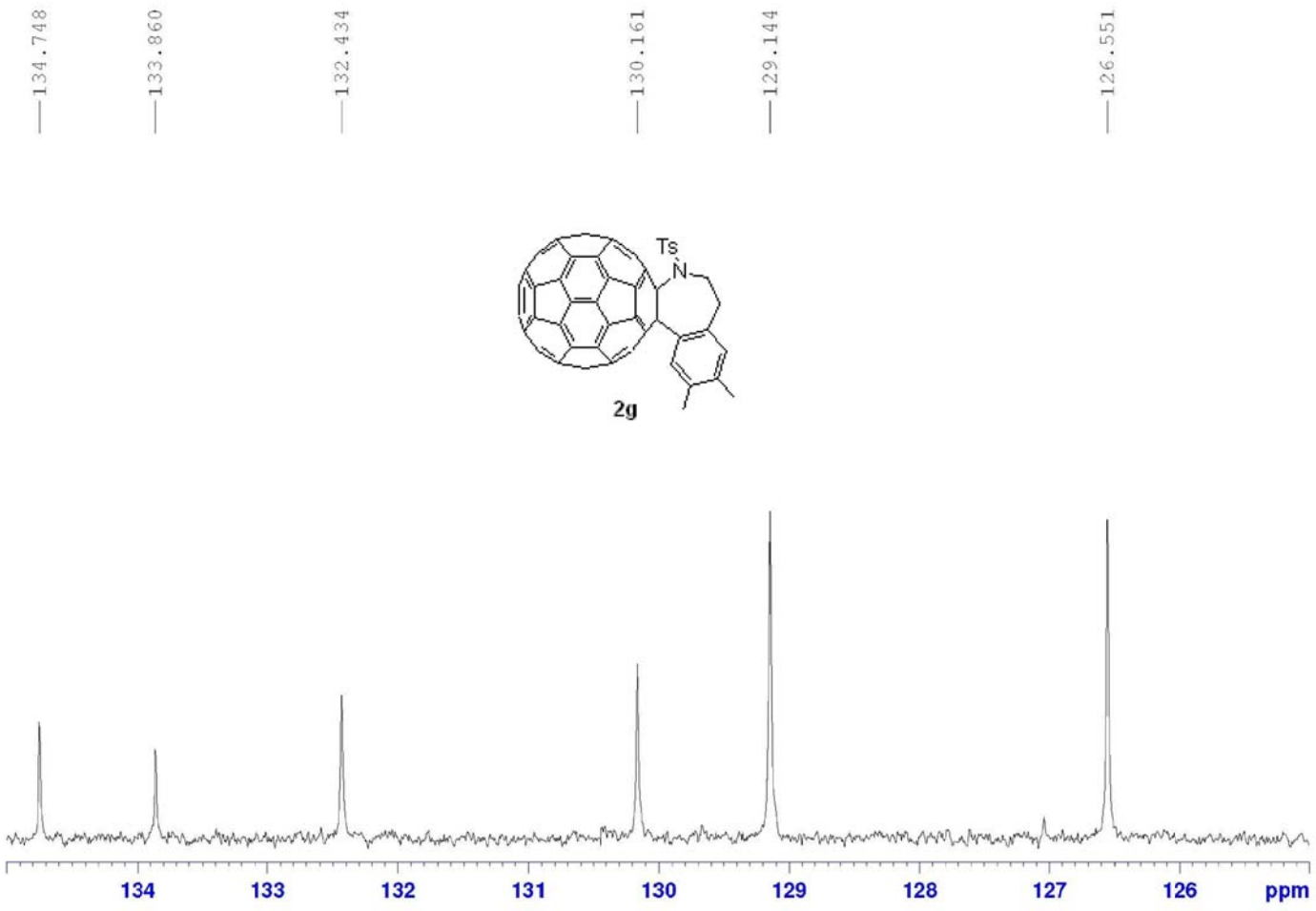



```
NAME        106L11_syt111230_1
EXPNO                        1
PROCNO                       1
Data_                 20111230
Time                     13.43
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                         203
DW                    60.830 usec
DE                     6.50 usec
TE                     300.0 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                    12.80 usec
PL1                   -1.00 dB
PL1W             17.70875519 W
SFO1             400.2324716 MHz
SI                       32758
SF               400.2300174 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                     1.00
```

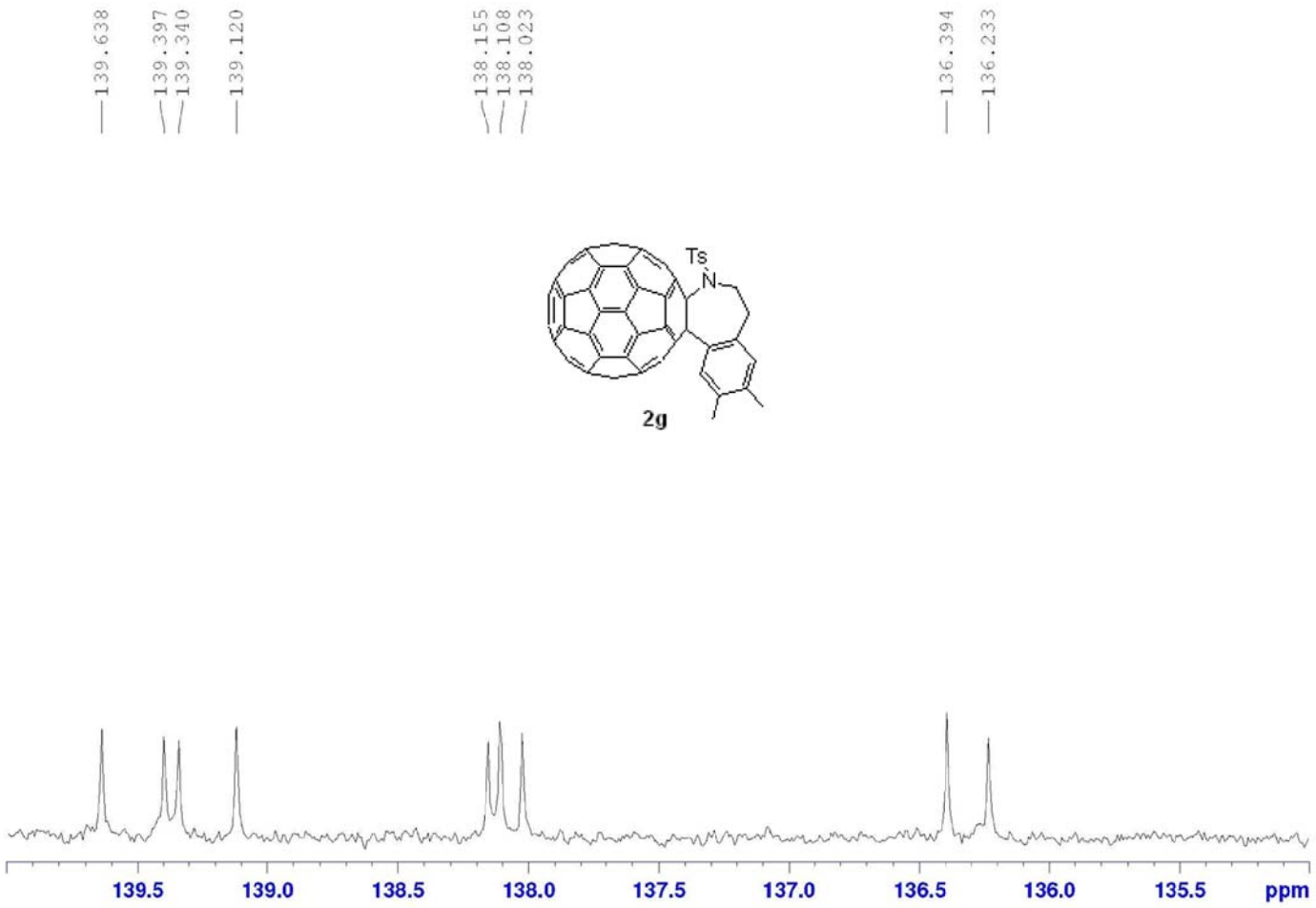
^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2g**



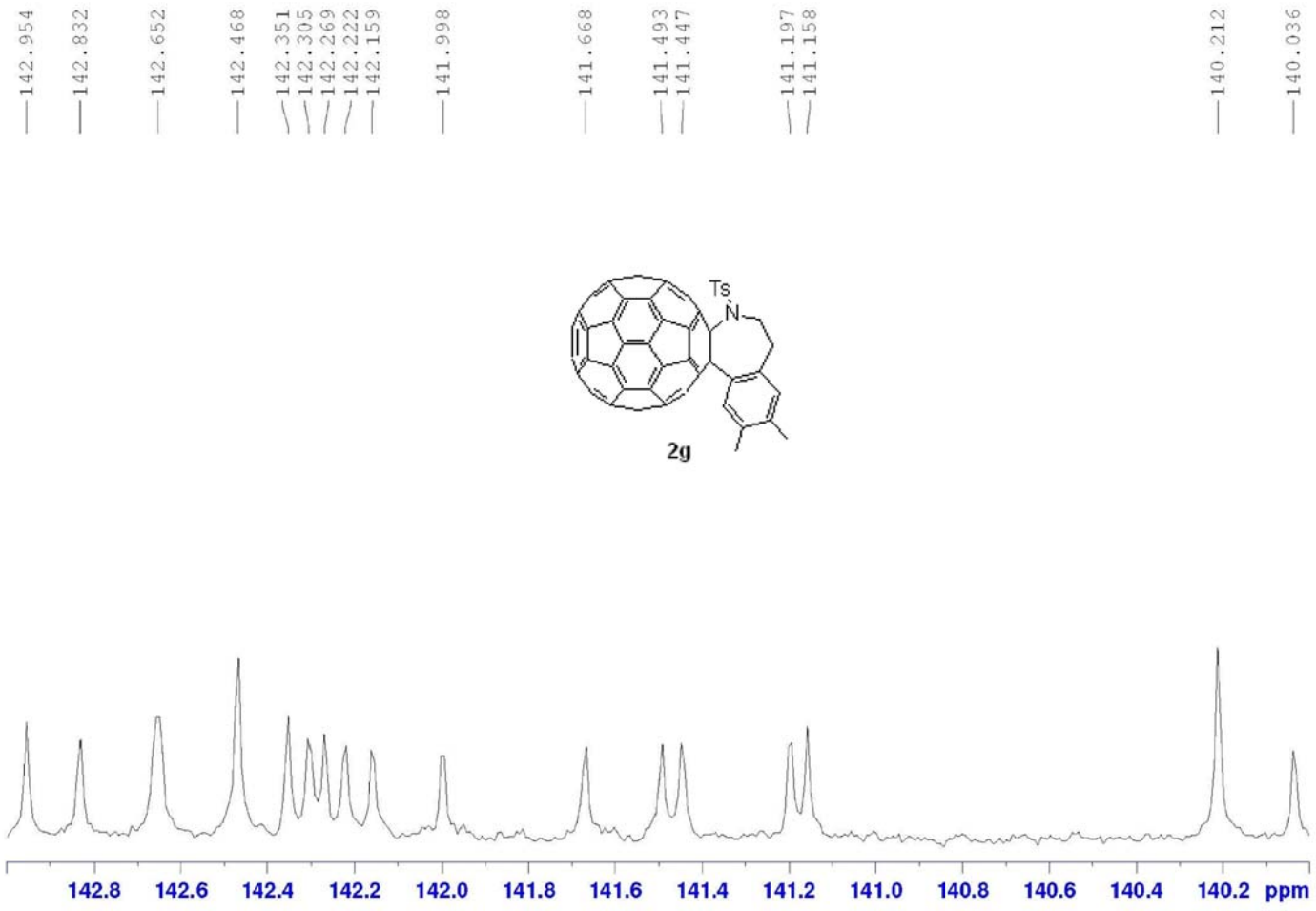
The detailed ^{13}C NMR spectrum of compound **2g** (135–125 ppm)



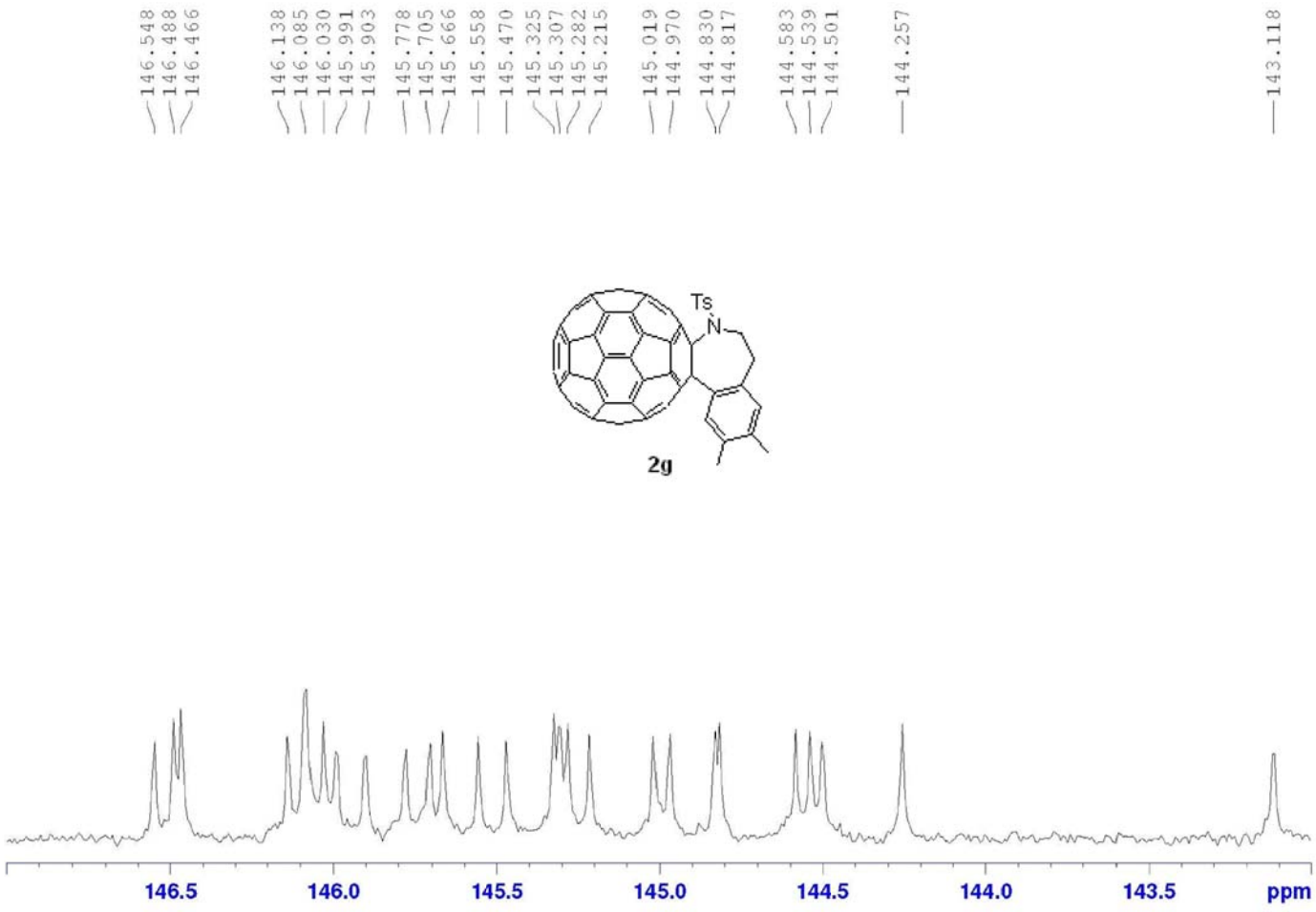
The detailed ^{13}C NMR spectrum of compound **2g** (140–135 ppm)



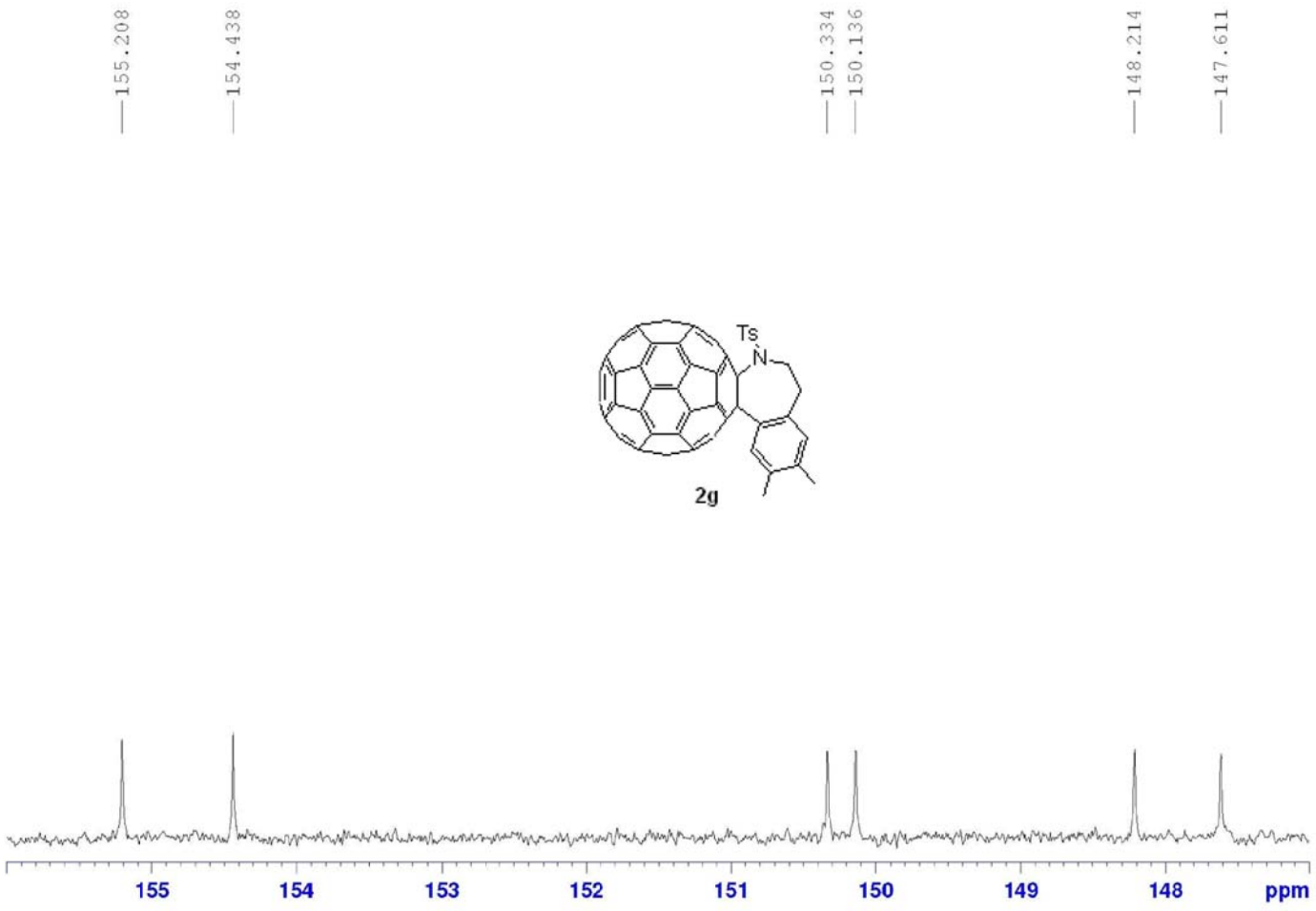
The detailed ^{13}C NMR spectrum of compound **2g** (143–140 ppm)



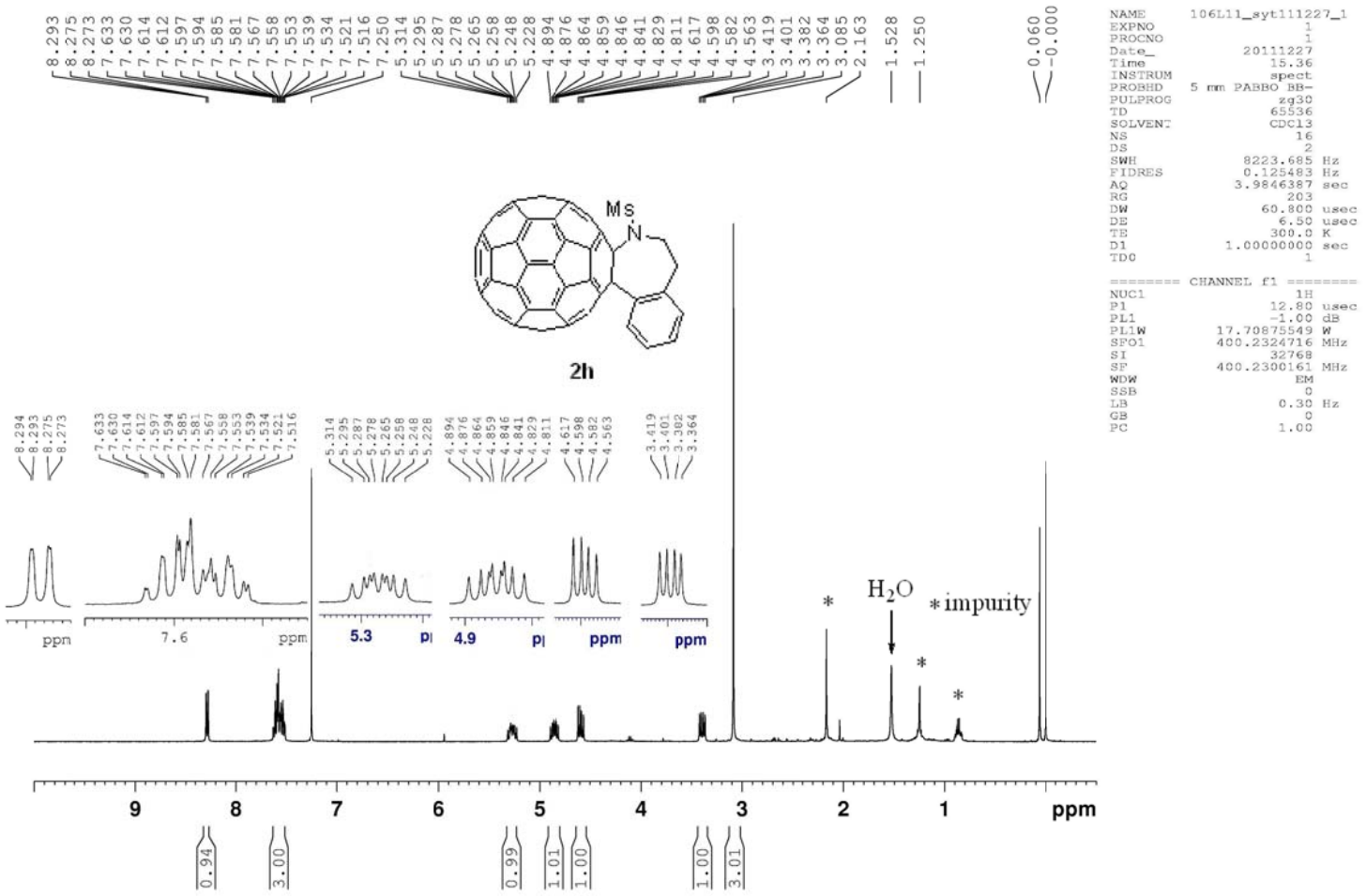
The detailed ^{13}C NMR spectrum of compound **2g** (147–143 ppm)



The detailed ^{13}C NMR spectrum of compound **2g** (156–147 ppm)

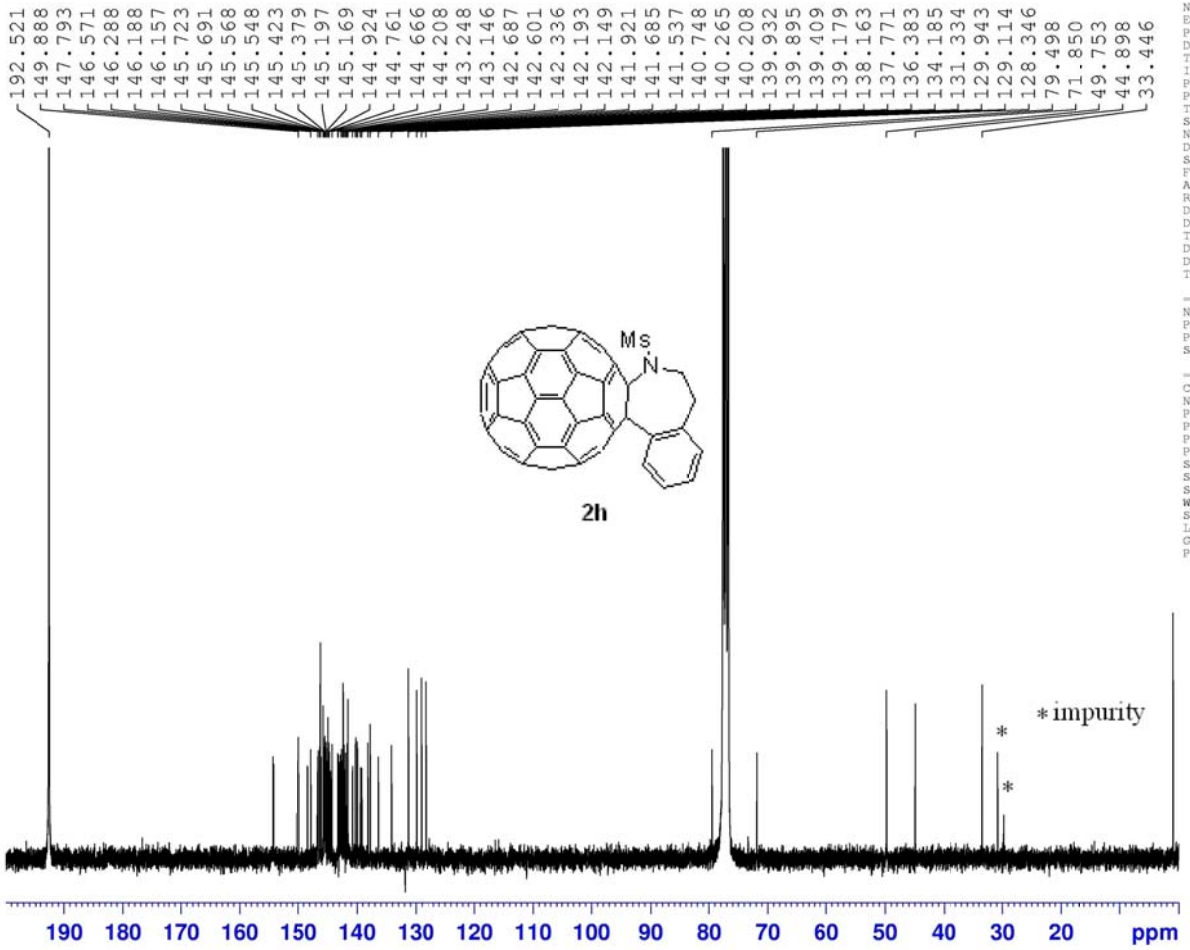


^{1}H NMR (400 M, $CS_2/CDCl_3$) spectrum of compound **2h**



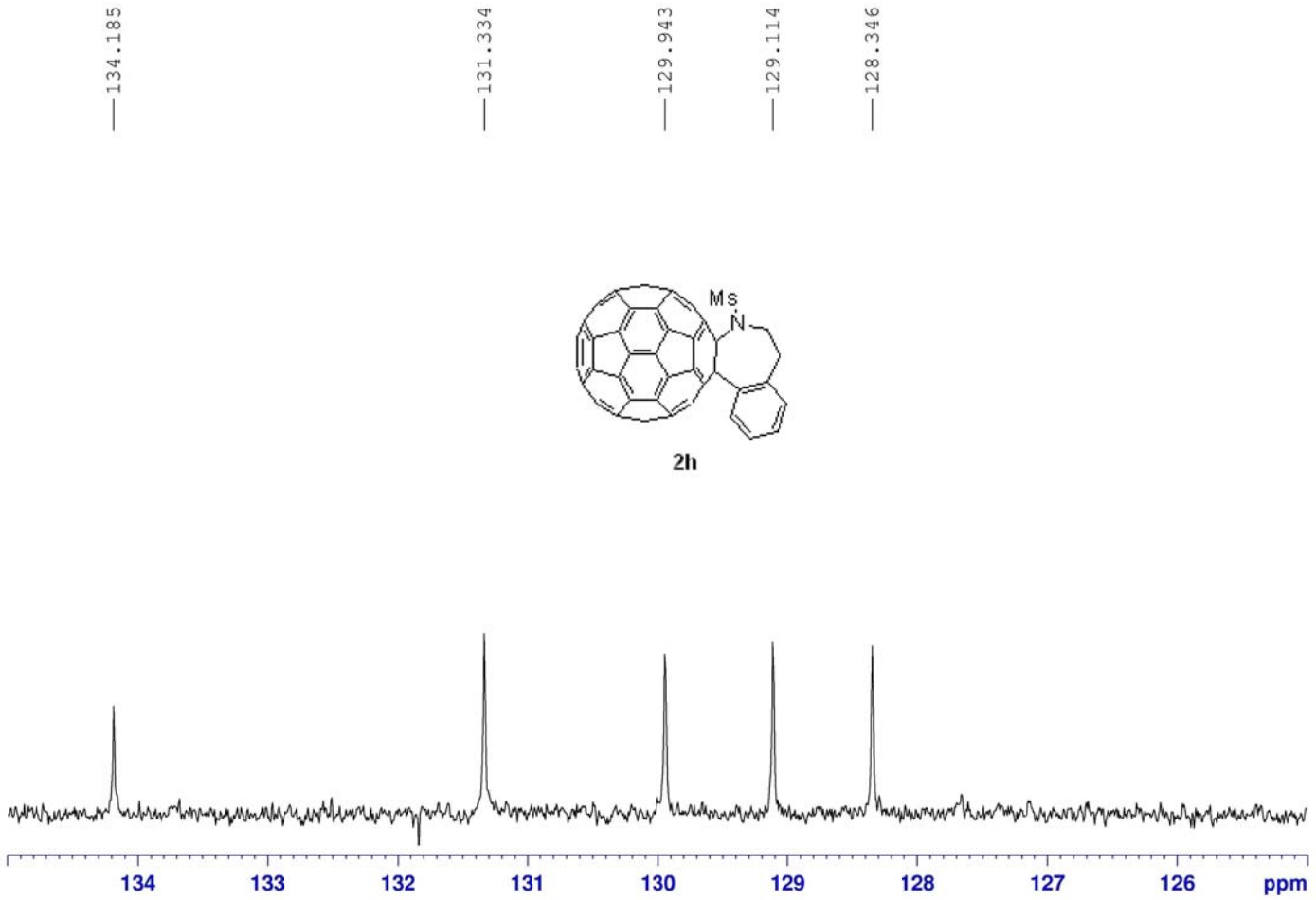
NAME	106L11_syt111227_1
EXPNO	1
PROCNO	1
Date_	20111227
Time	15.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	203
DW	60.800 usec
DE	6.50 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	1H
P1	12.80 usec
PL1	-1.00 dB
PL1W	17.70875549 W
SFO1	400.2324716 MHz
SI	32768
SF	400.2300161 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR (75 M, $CS_2/CDCl_3$) spectrum of compound **2h**

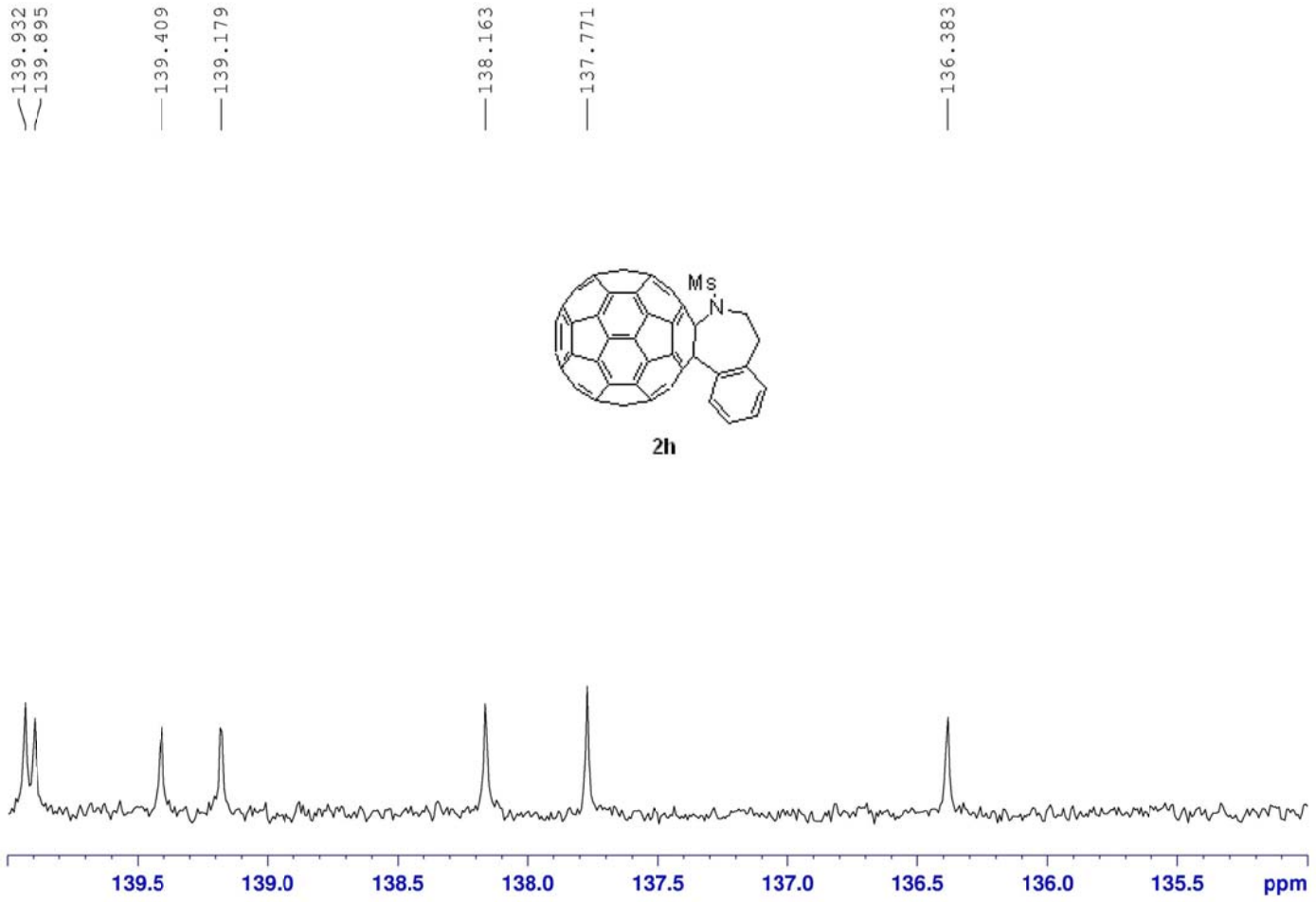


NAME	syt120113-1
EXPNO	13
PROCNO	1
Date_	20120114
Time	15.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	20070
DS	2
SWH	17985.611 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	13004
DW	27.800 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	13.50 usec
PL1	-1.00 dB
SFO1	75.4752953 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	2.00 dB
PL12	17.78 dB
PL13	17.78 dB
SFO2	300.1312005 MHz
SI	32768
SF	75.4677563 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	1.40

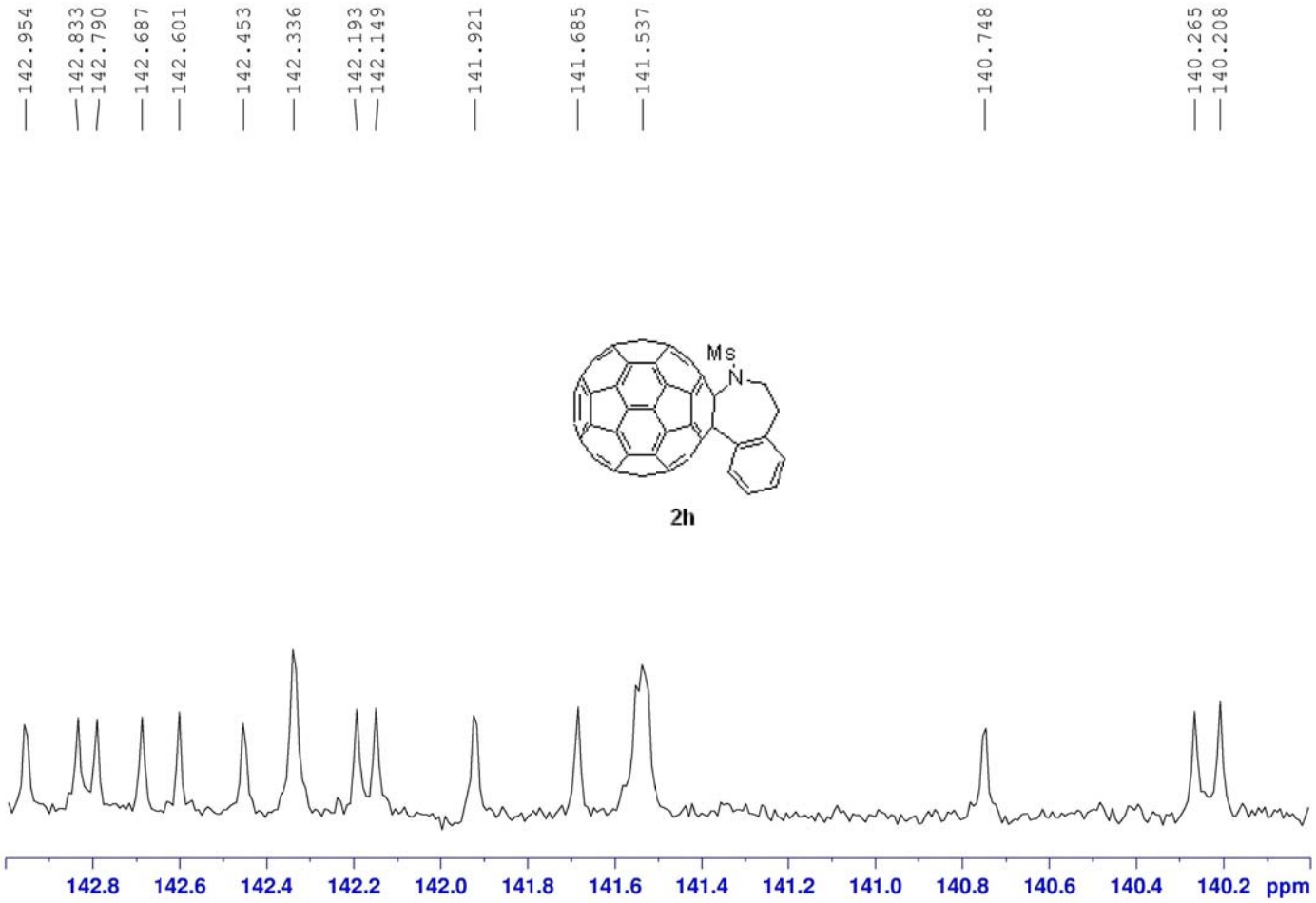
The detailed ^{13}C NMR spectrum of compound **2h** (135–125 ppm)



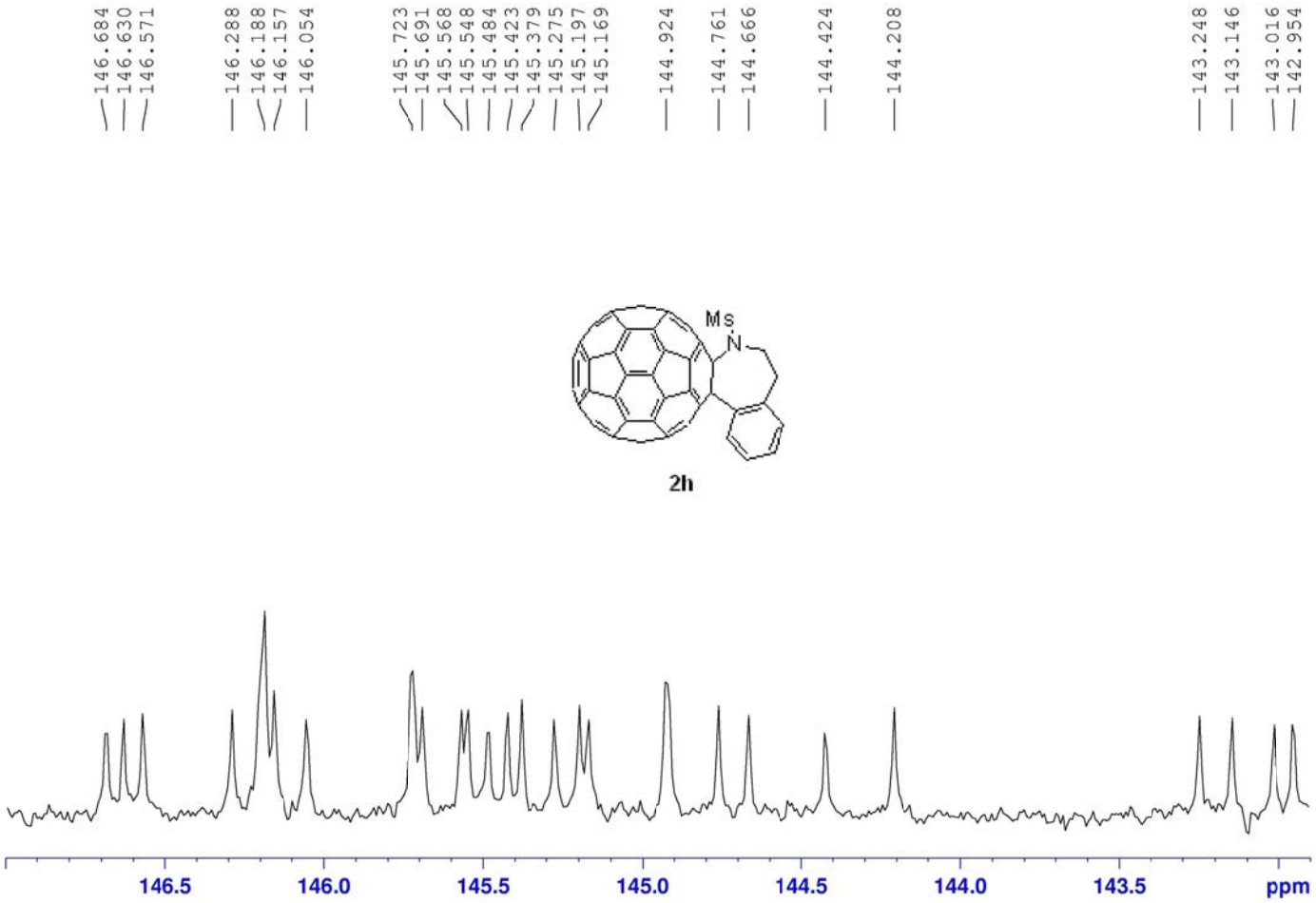
The detailed ^{13}C NMR spectrum of compound **2h** (140–135 ppm)



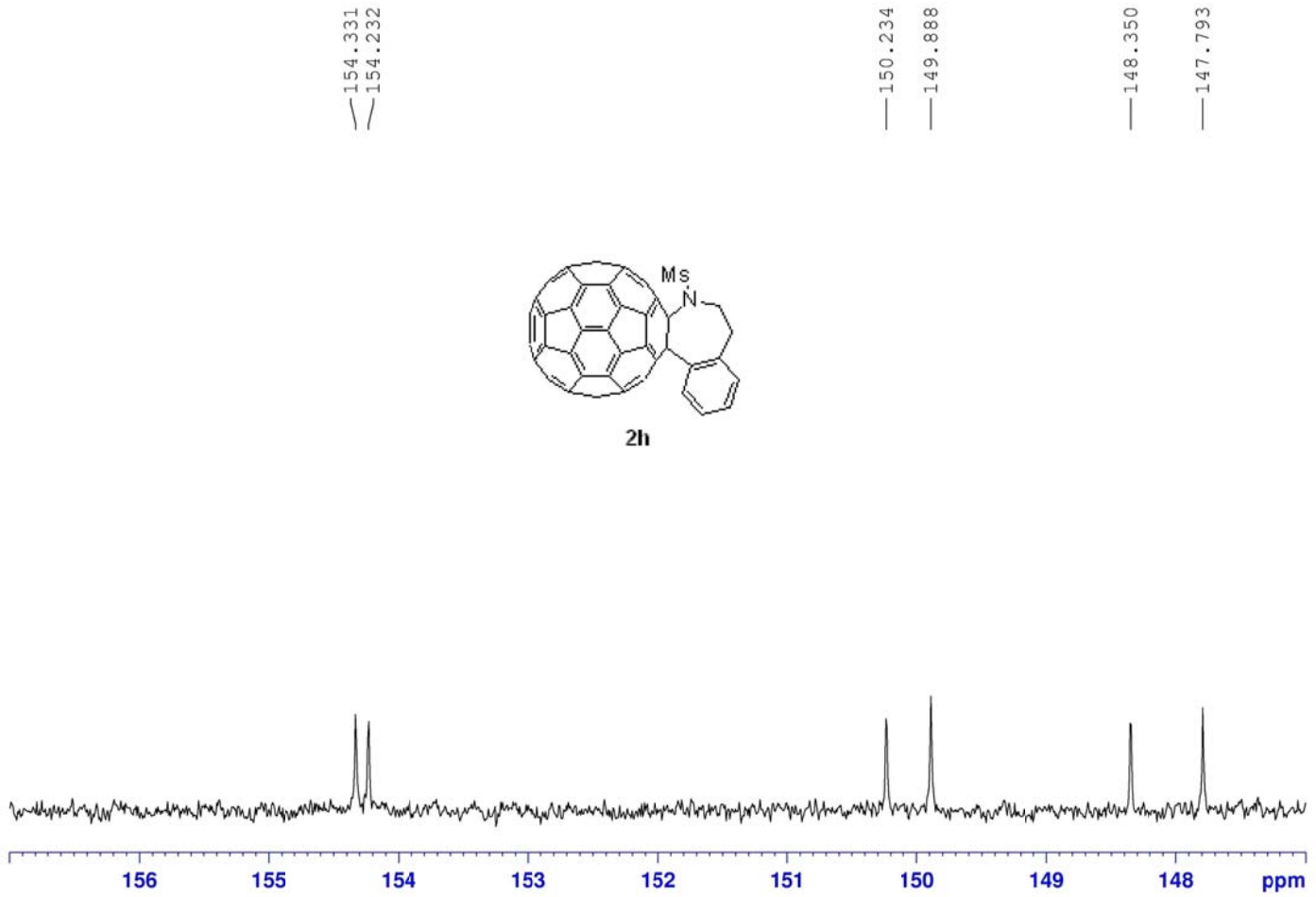
The detailed ^{13}C NMR spectrum of compound **2h** (143–140 ppm)



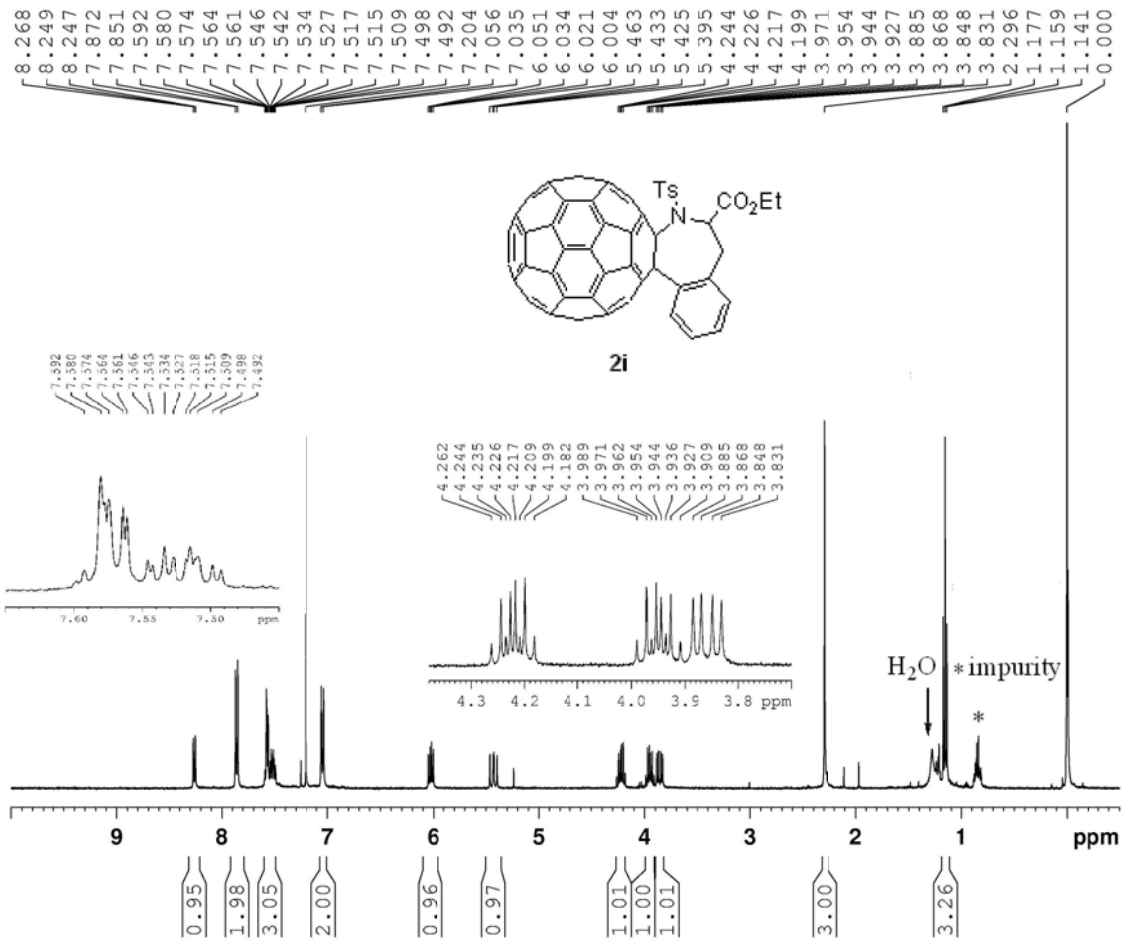
The detailed ^{13}C NMR spectrum of compound **2h** (147–143 ppm)



The detailed ^{13}C NMR spectrum of compound **2h** (157–147 ppm)

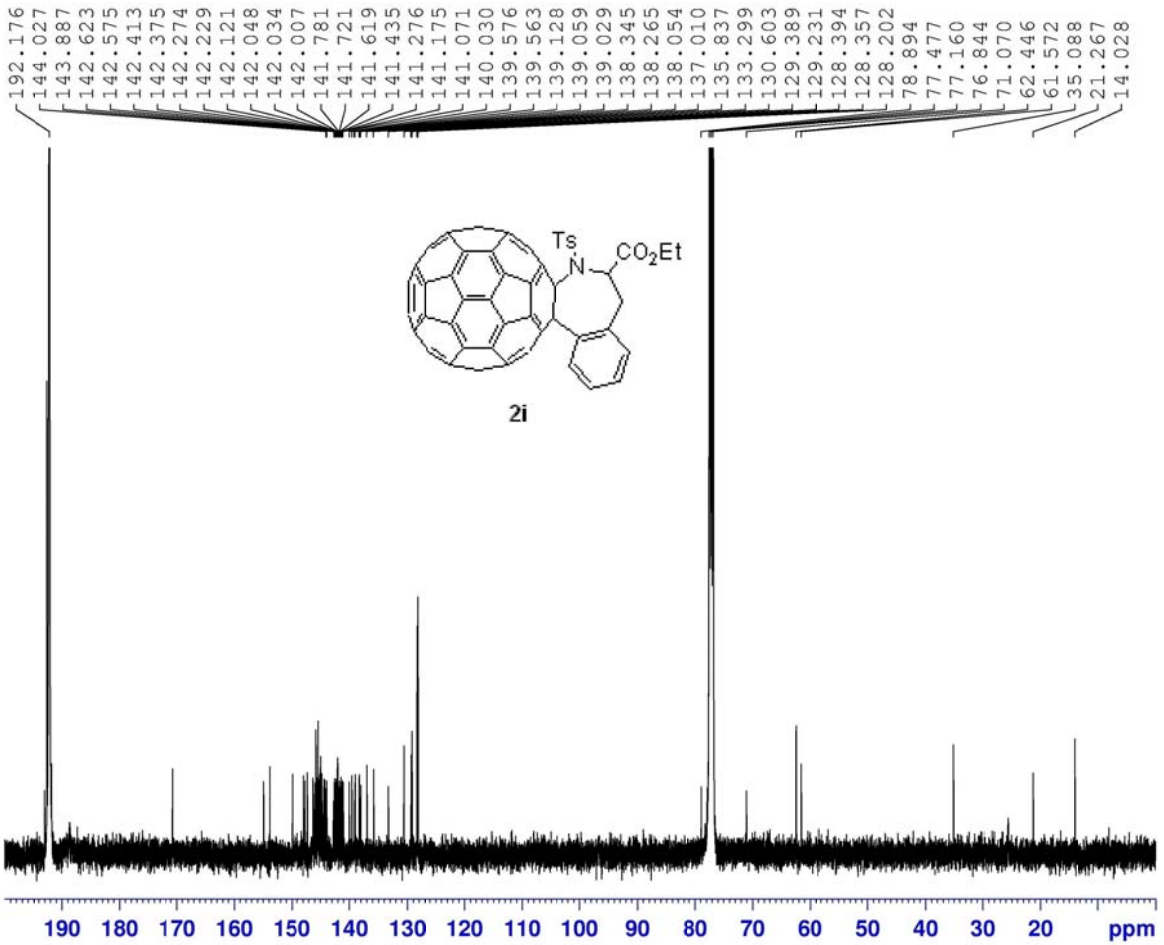


^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compound **2i**



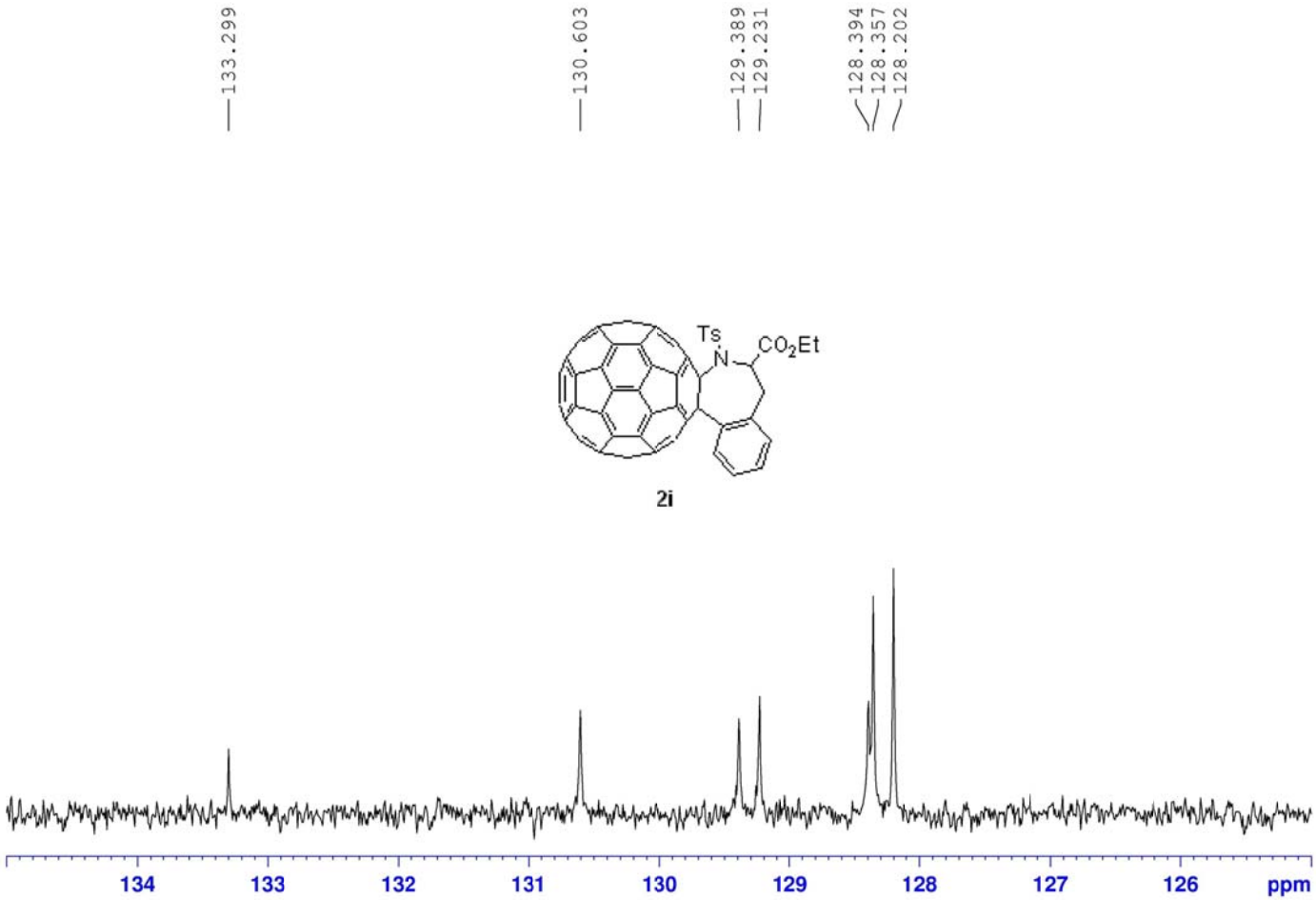

```
NAME            106L12_syt120315_2
EXPNO                            1
PROCNO                           1
Date_                     20120315
Time                         19.30
INSTRUM                      spect
PROBHD   5 mm PABBO BB-
PULPROG                       zg30
TD                           65536
SOLVENT                      CDCl3
NS                              64
DS                               2
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                             203
DW                        60.800 usec
DE                         6.50 usec
TE                        300.0 K
D1                      1.00000000 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                           1H
P1                        12.80 usec
PL1                       -1.00 dB
PL1W                17.70875549 W
SFO1                400.2324716 MHz
SI                           32768
SF                  400.2300351 MHz
WDW                             no
SSB                              0
LB                        0.00 Hz
GB                               0
PC                            1.00
```

^{13}C NMR (100 M, $CS_2/CDCl_3$) spectrum of compound **2i**

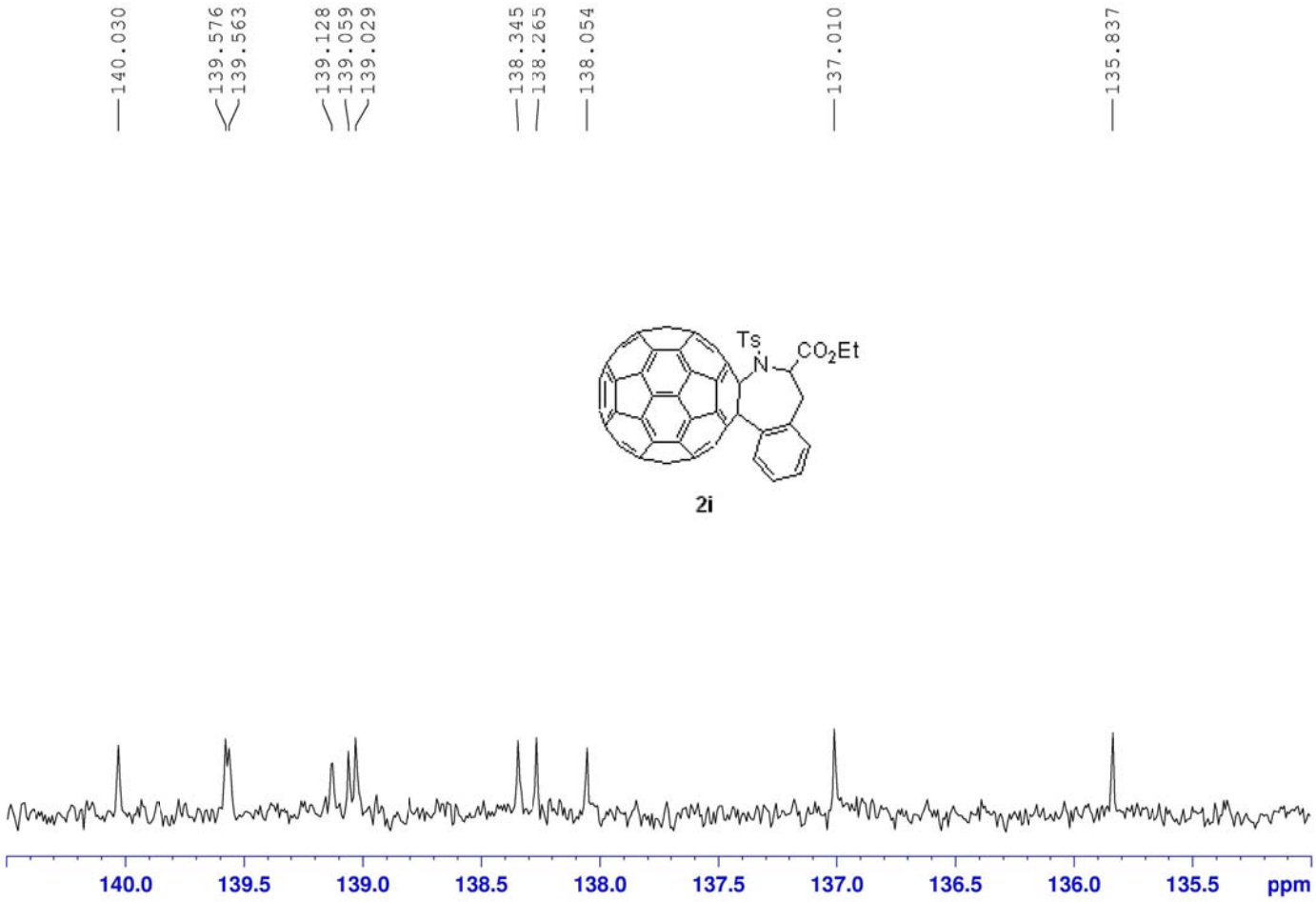


NAME	105L14_syt1405C6_2
EXPNO	2
PROCNO	1
Date_	20140507
Time	16.40
INSTRUM	av400
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	24576
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3632196 sec
RG	1149.4
DW	20.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	24
======== CHANNEL f1 ========	
NUC1	13C
P1	11.80 usec
PL1	2.00 dB
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	15.52 dB
PL13	20.00 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6128158 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	0.10

The detailed ^{13}C NMR spectrum of compound **2i** (135–125 ppm)

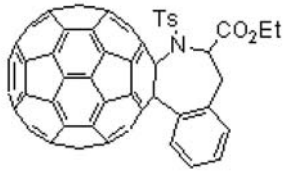


The detailed ^{13}C NMR spectrum of compound **2i** (140–135 ppm)

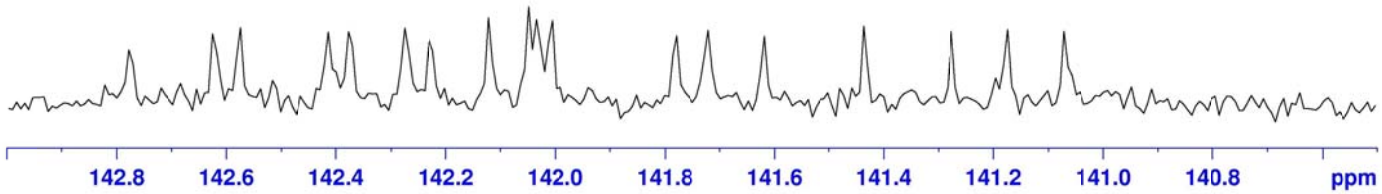


The detailed ^{13}C NMR spectrum of compound **2i** (143–140 ppm)

142.776
142.623
142.575
142.413
142.375
142.274
142.229
142.121
142.048
142.034
142.007
141.781
141.721
141.619
141.435
141.276
141.175
141.071

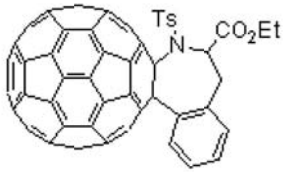


2i

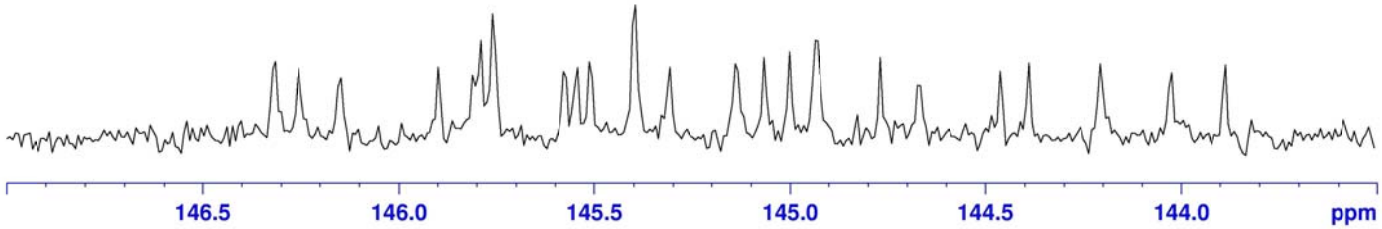


The detailed ^{13}C NMR spectrum of compound **2i** (147–143 ppm)

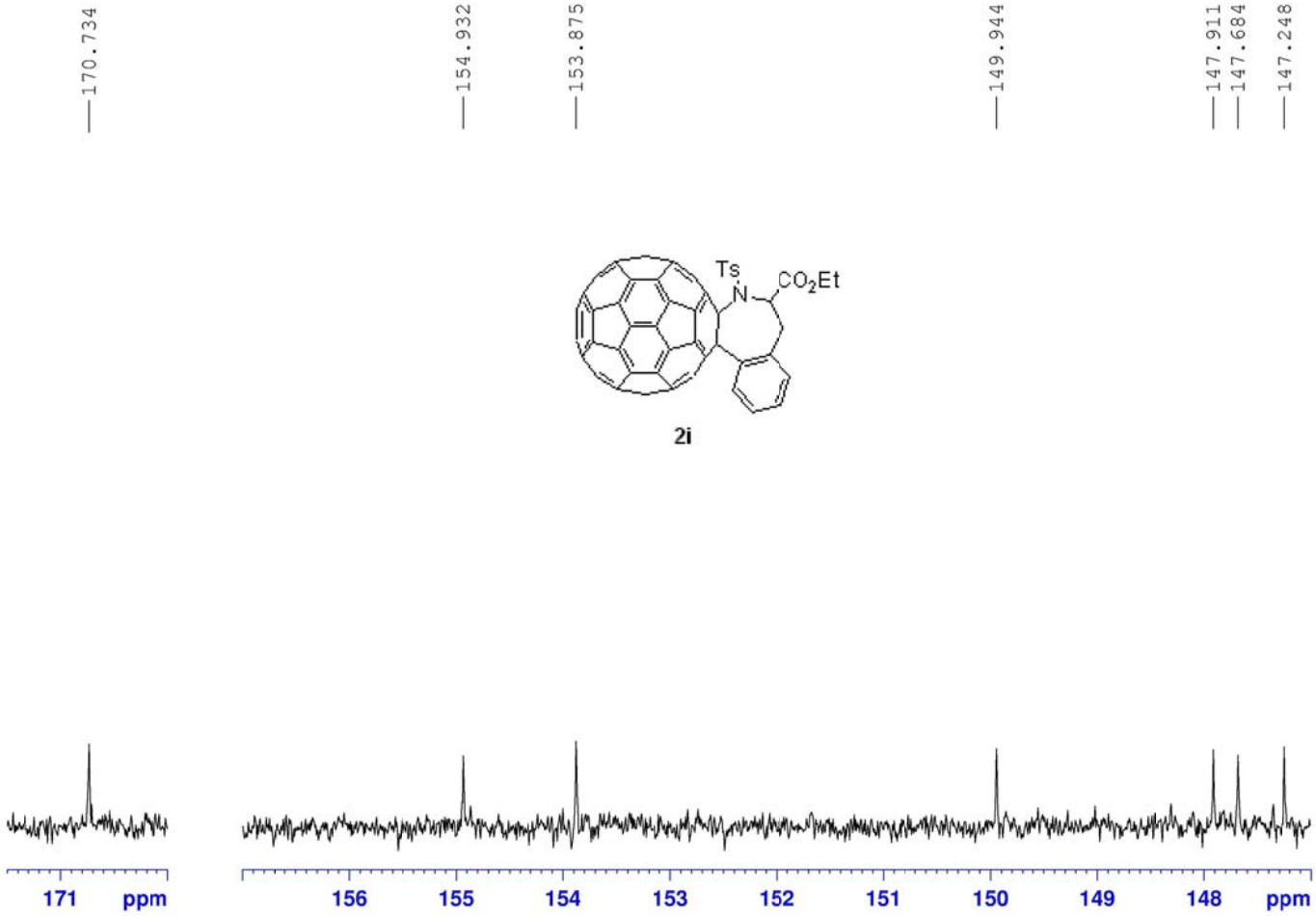
146.317
146.255
146.149
145.898
145.809
145.790
145.759
145.575
145.543
145.510
145.398
145.309
145.138
145.067
145.001
144.933
144.768
144.670
144.462
144.390
144.206
144.027
143.887



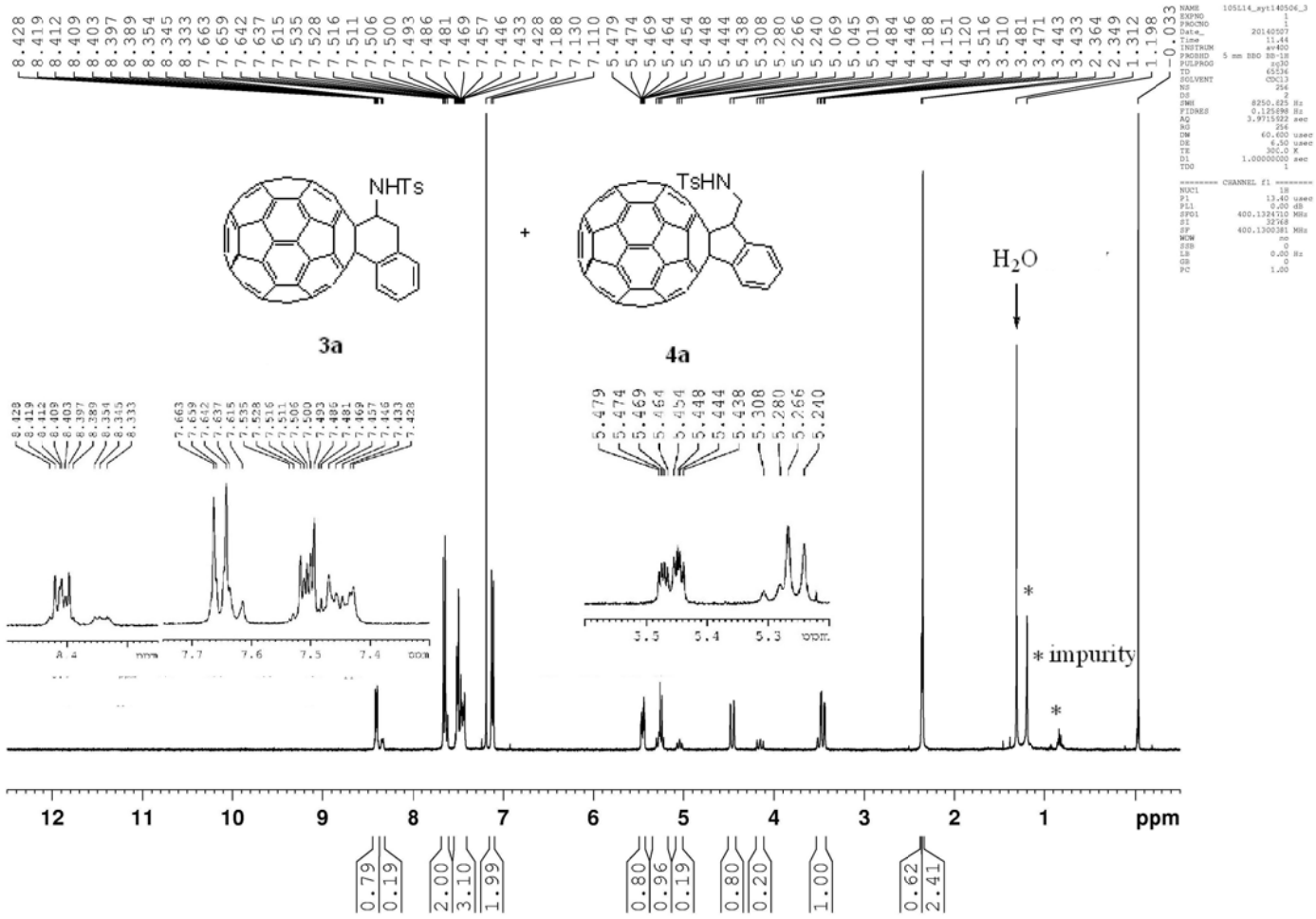
2i



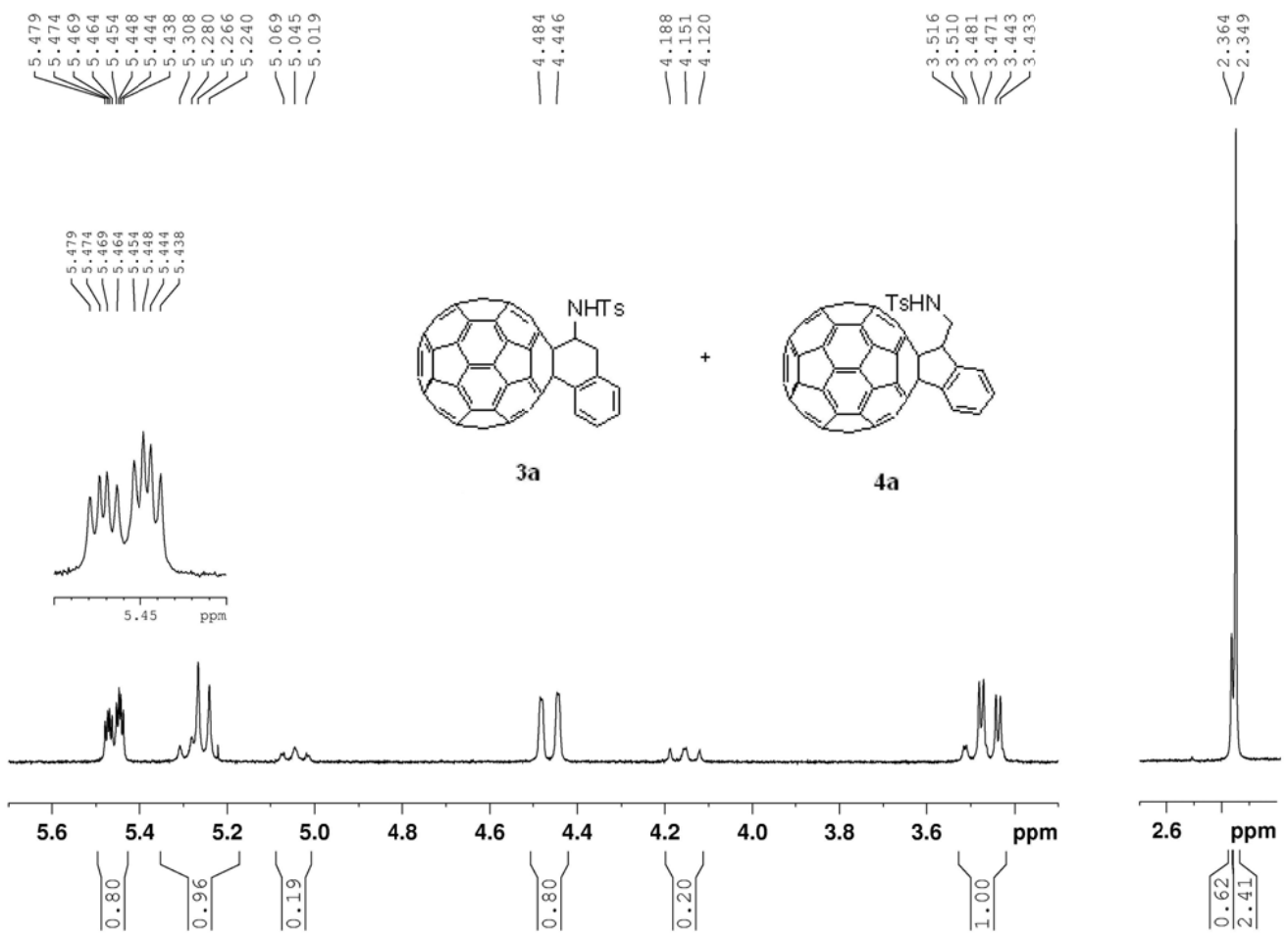
The detailed ^{13}C NMR spectrum of compound **2i** (172–147 ppm)



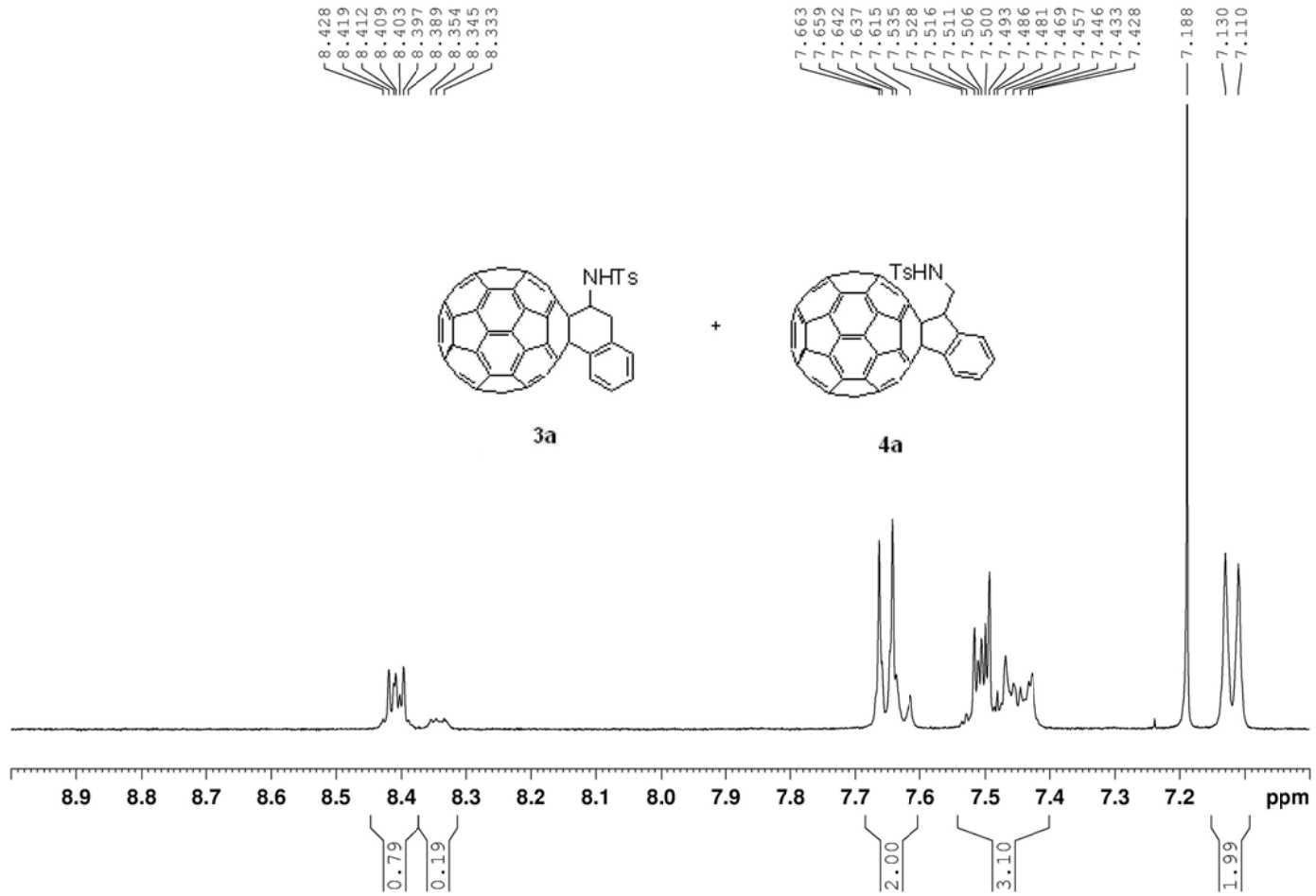
^{1}H NMR (400 M, CS_2/$CDCl_3$) spectrum of compounds **3a** and **4a**



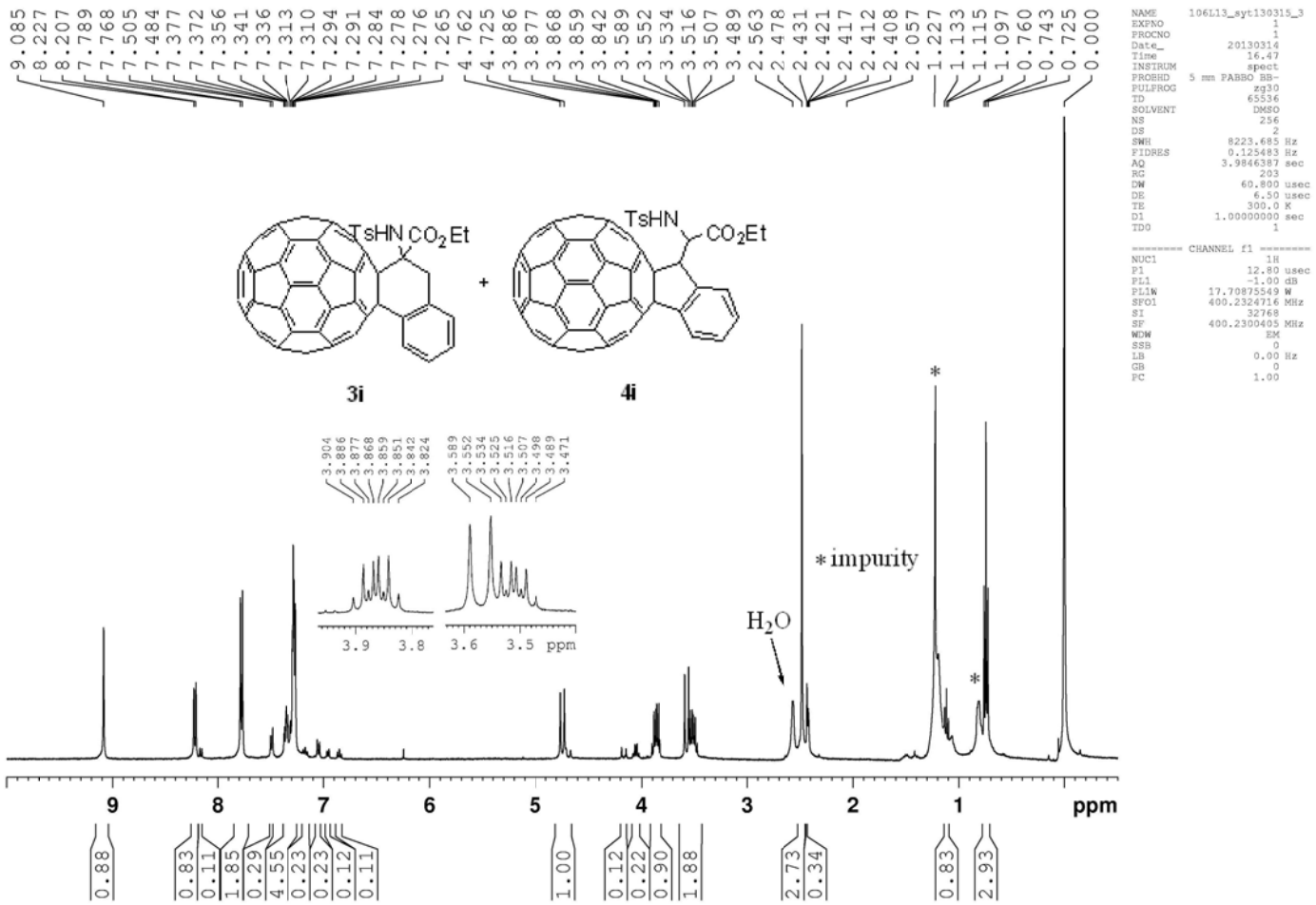
The detailed ^{1}H-NMR spectrum of compounds **3a** and **4a** (5.7 -2.2 ppm)



The detailed ^{1}H-NMR spectrum of compounds **3a** and **4a** (8.7 -7.2 ppm)

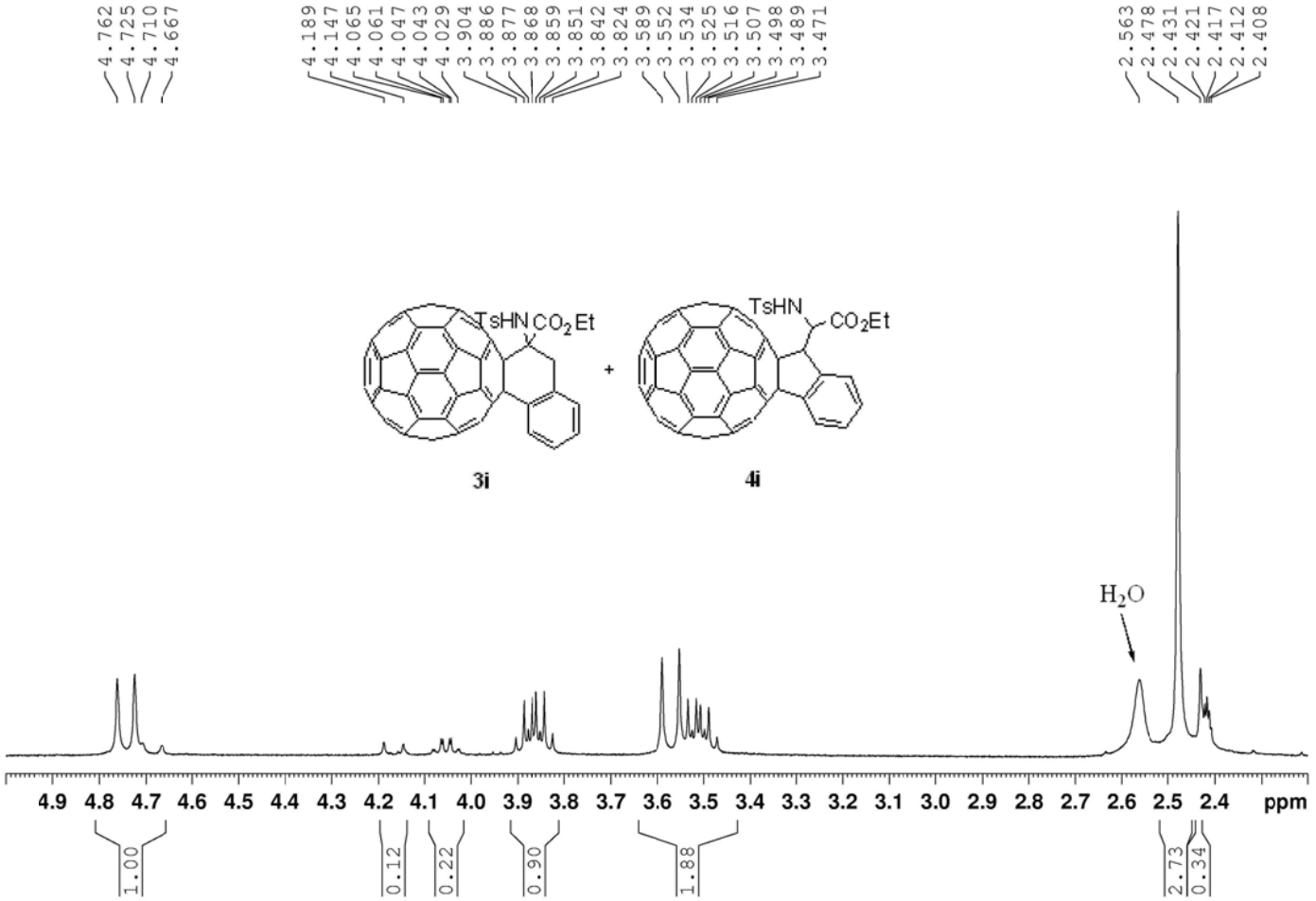


^{1}H NMR (400 M, CS_2/DMSO-d_6) spectrum of compounds **3i** and **4i**.

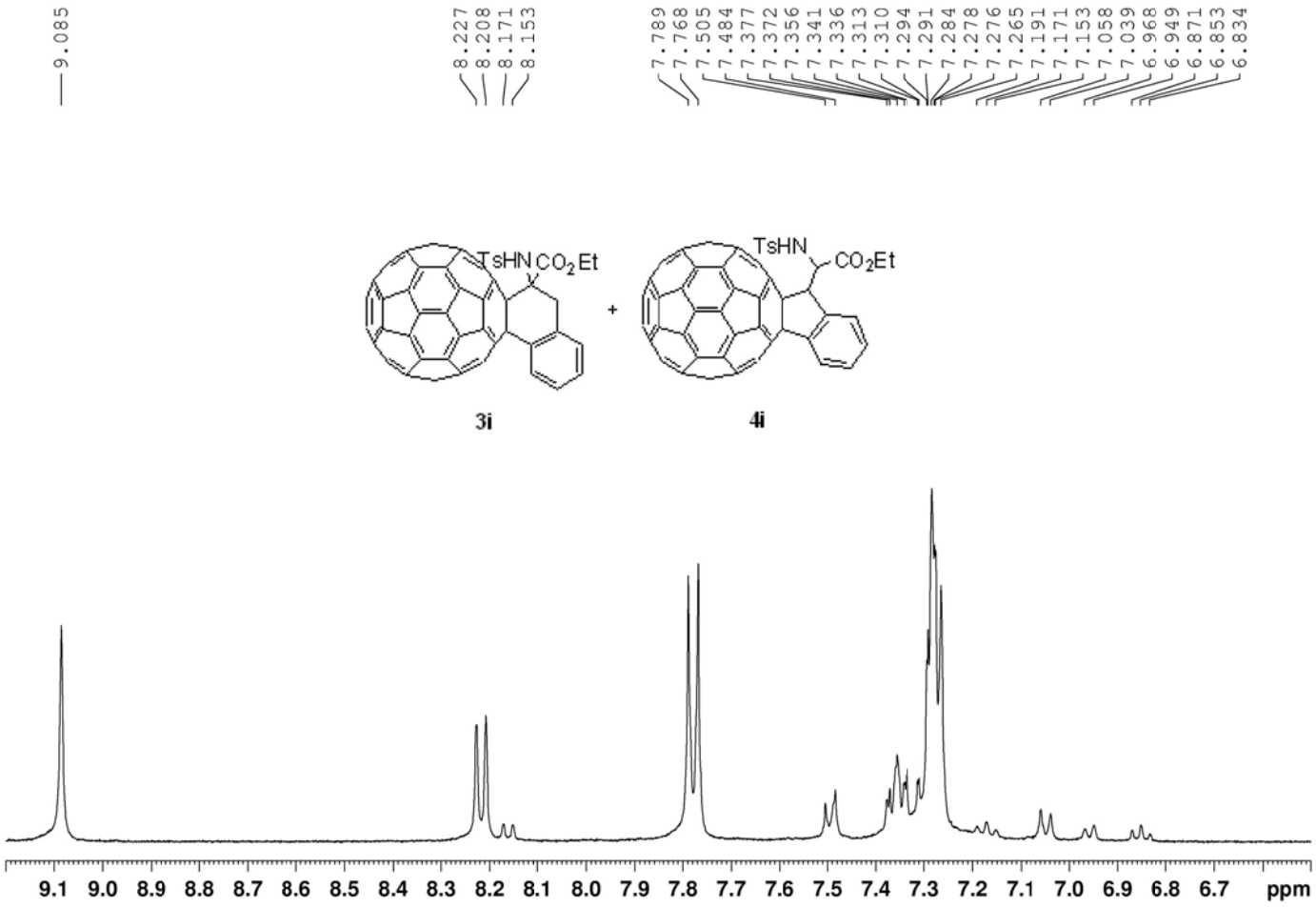



```
NAME          106L13_syt130315_3
EXPNO                          1
PROCNO                         1
Date_                   20130314
Time                       16.47
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                    DMSO
NS                           256
DS                             2
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                           203
DW                        60.800 usec
DE                         6.50 usec
TE                        300.0 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                        12.80 usec
PL1                       -1.00 dB
PL1W                17.70875549 W
SFO1                400.2324716 MHz
SI                         32768
SF                  400.2300405 MHz
WDW                           EM
SSB                            0
LB                         0.00 Hz
GB                             0
PC                          1.00
```

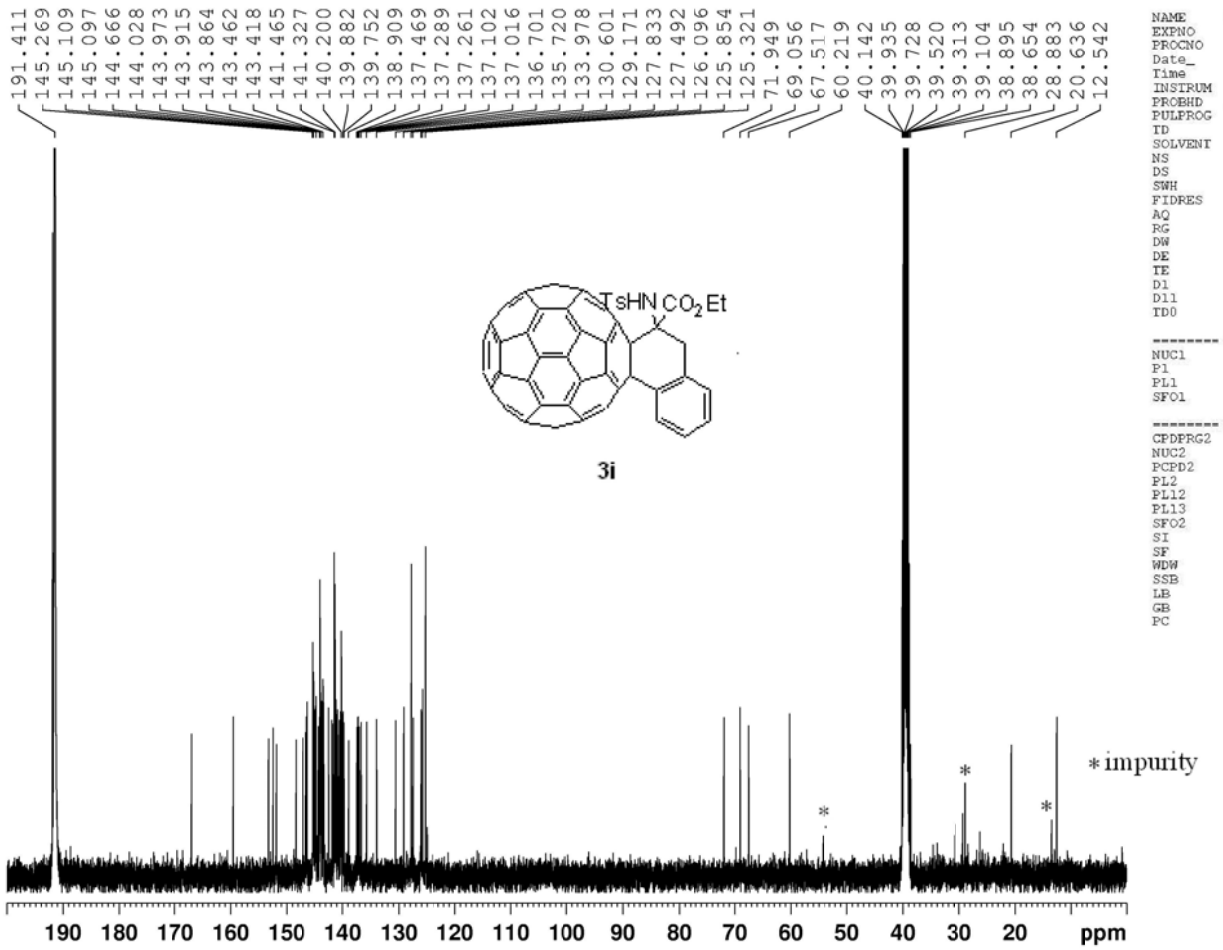
The detailed ^{1}H-NMR spectrum of compounds **3i** and **4i** (5.0 -2.2 ppm)



The detailed ^{1}H-NMR spectrum of compounds **3i** and **4i** (9.2 -6.5 ppm)

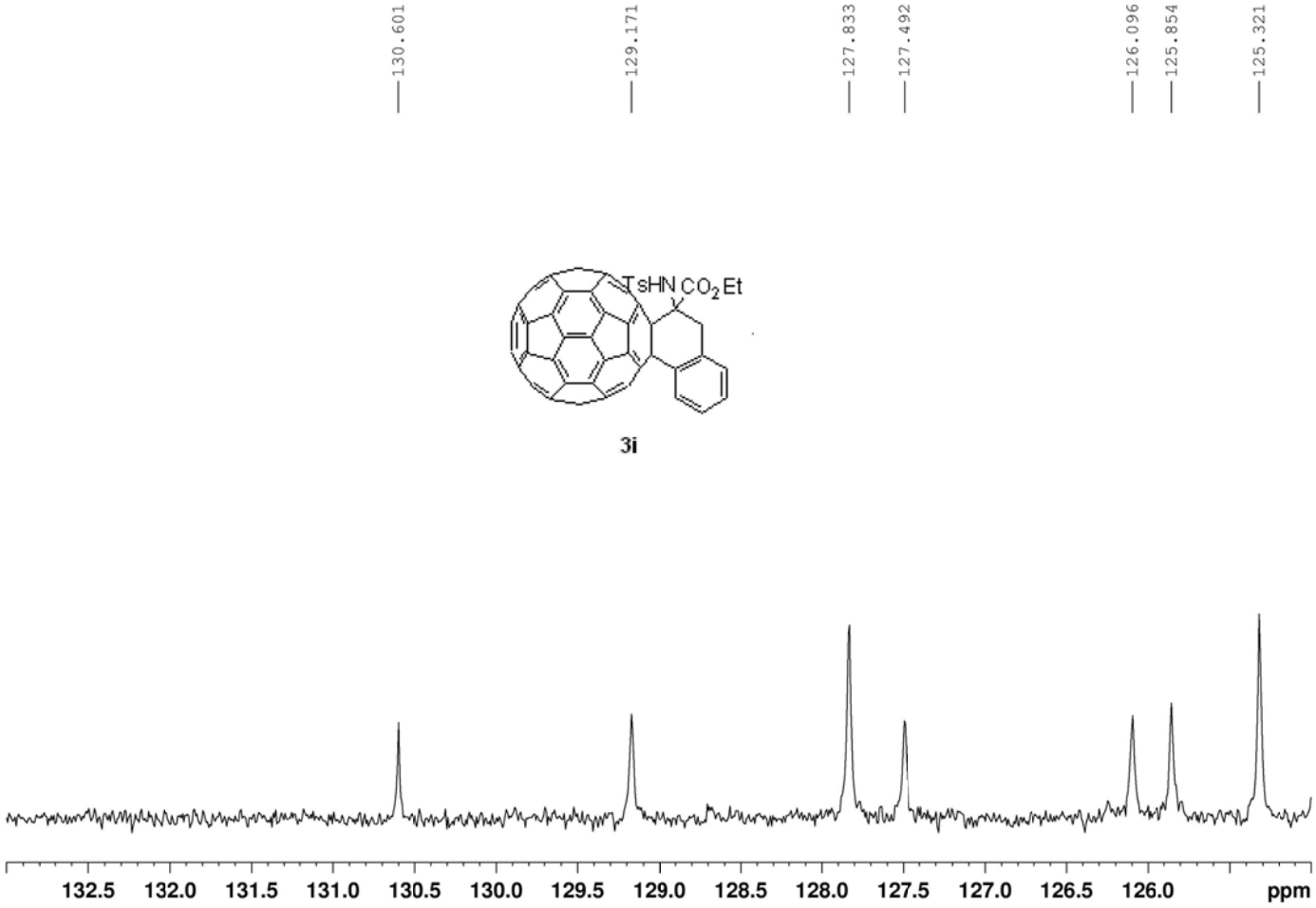


^{13}C NMR (100 M, CS_2/DMSO-d_6) spectrum of compound **3i**

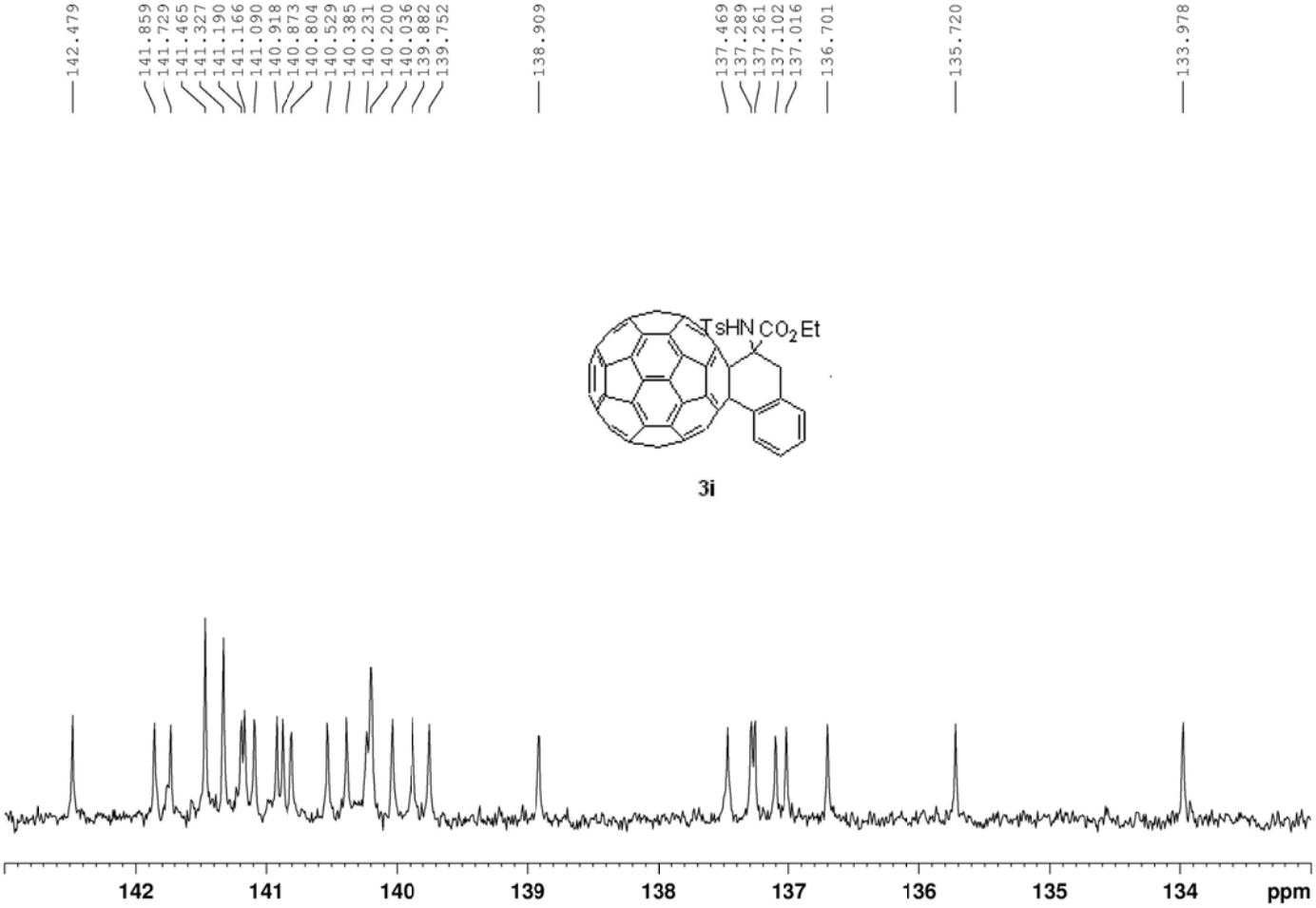


NAME	105L13_syt130305_1
EXPNO	2
PROCNO	1
Date_	20130305
Time	19.16
INSTRUM	av400
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	12288
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3632196 sec
RG	812.7
DW	20.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	12
======== CHANNEL f1 ========	
NUC1	13C
P1	13.40 usec
PL1	2.00 dB
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.78 dB
PL13	14.80 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6129157 MHz
WDW	EM
SSB	0
LB	0.50 Hz
GB	0
PC	0.50

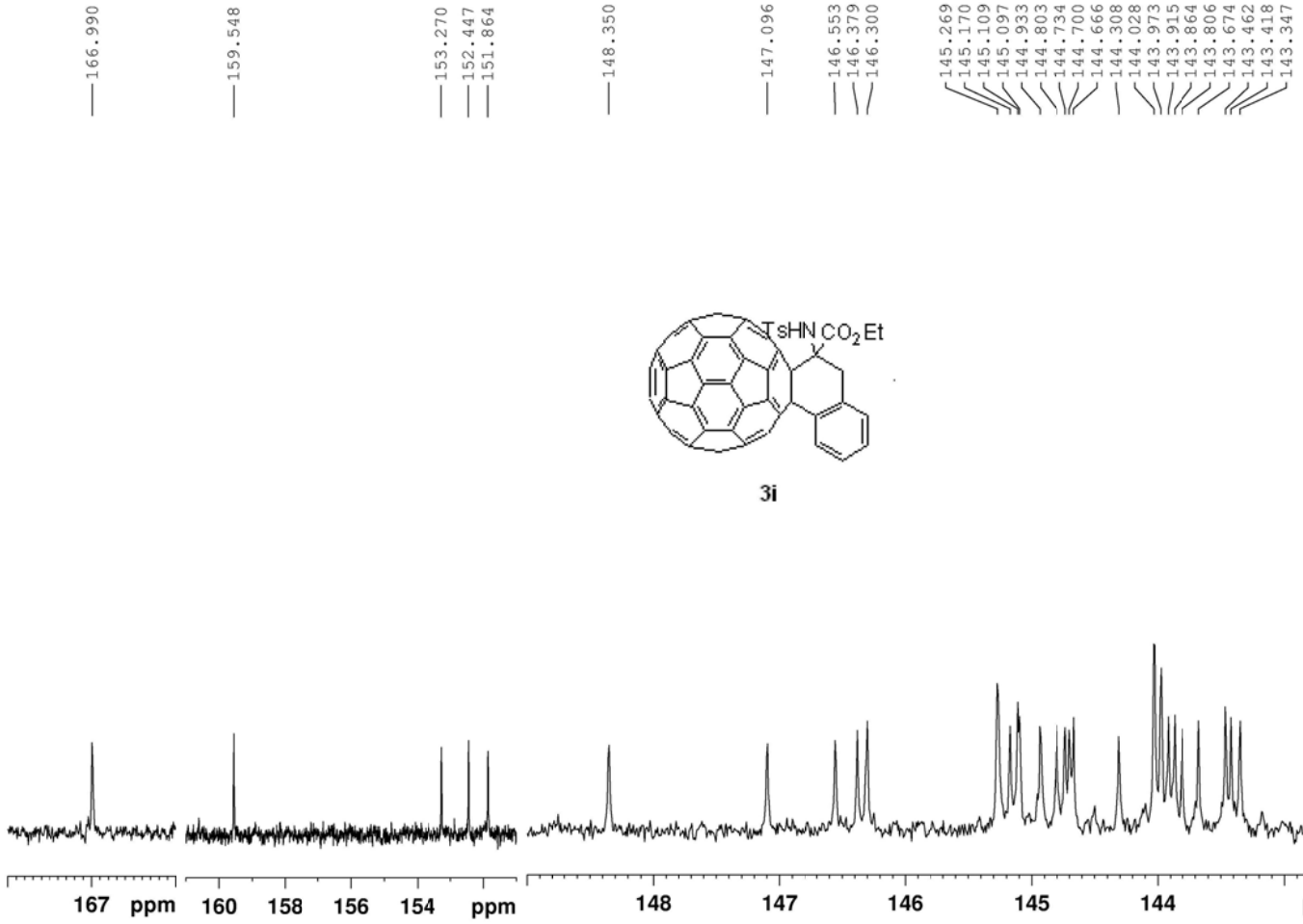
The detailed ^{13}C NMR spectrum of compound **3i** (133–125 ppm)



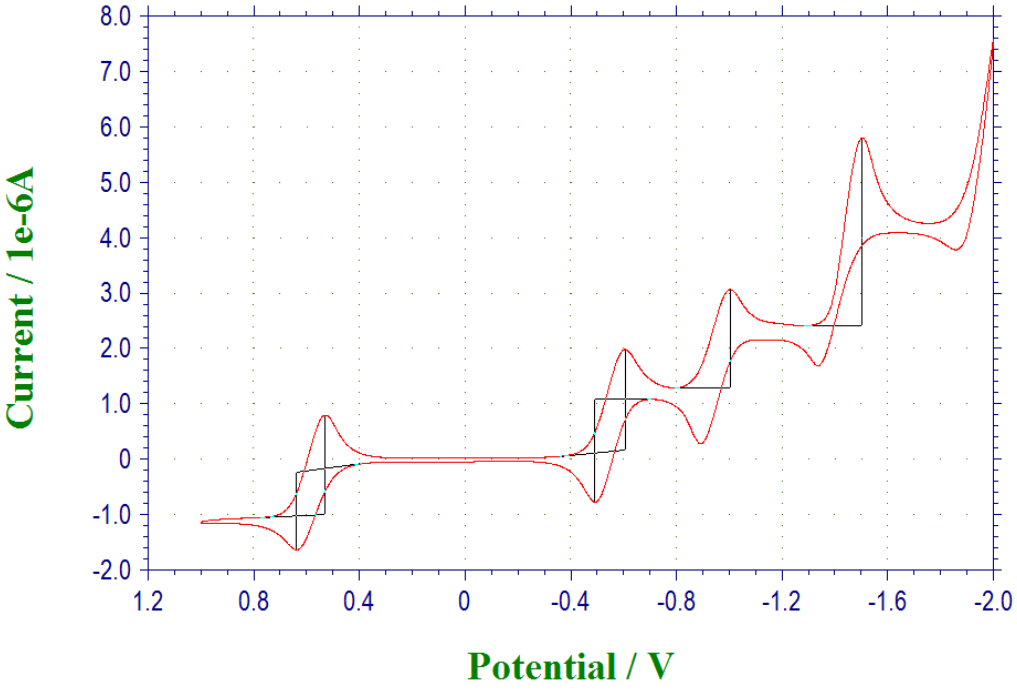
The detailed ^{13}C NMR spectrum of compound **3i** (143–133 ppm)



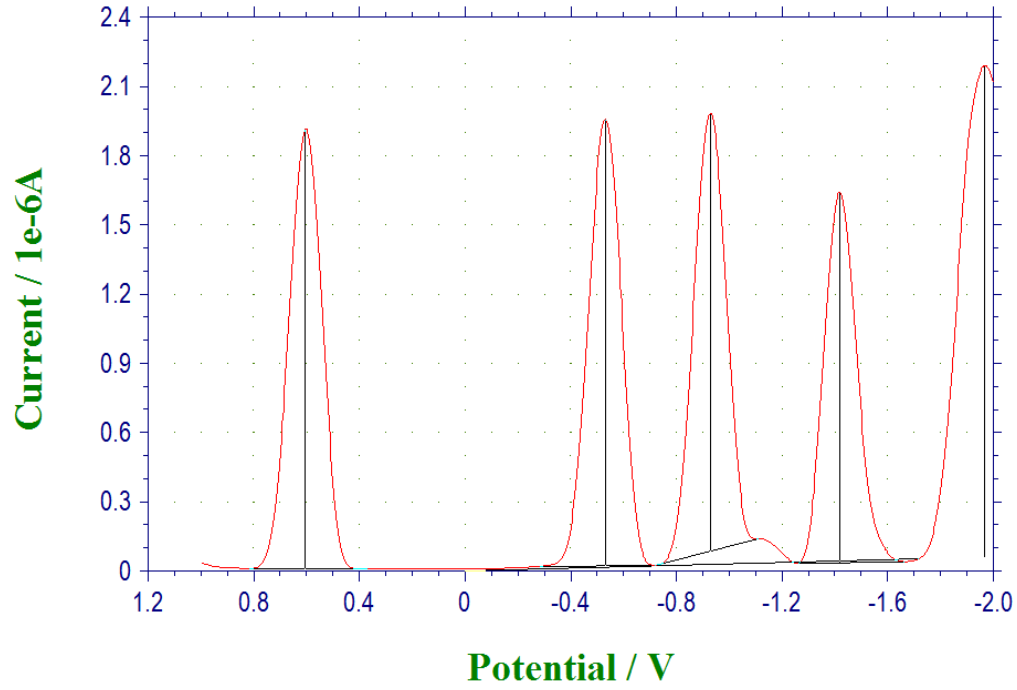
The detailed ^{13}C NMR spectrum of compound **3i** (168–143 ppm)



Voltammograms and data of compounds 2a-i, 5 and C_{60}

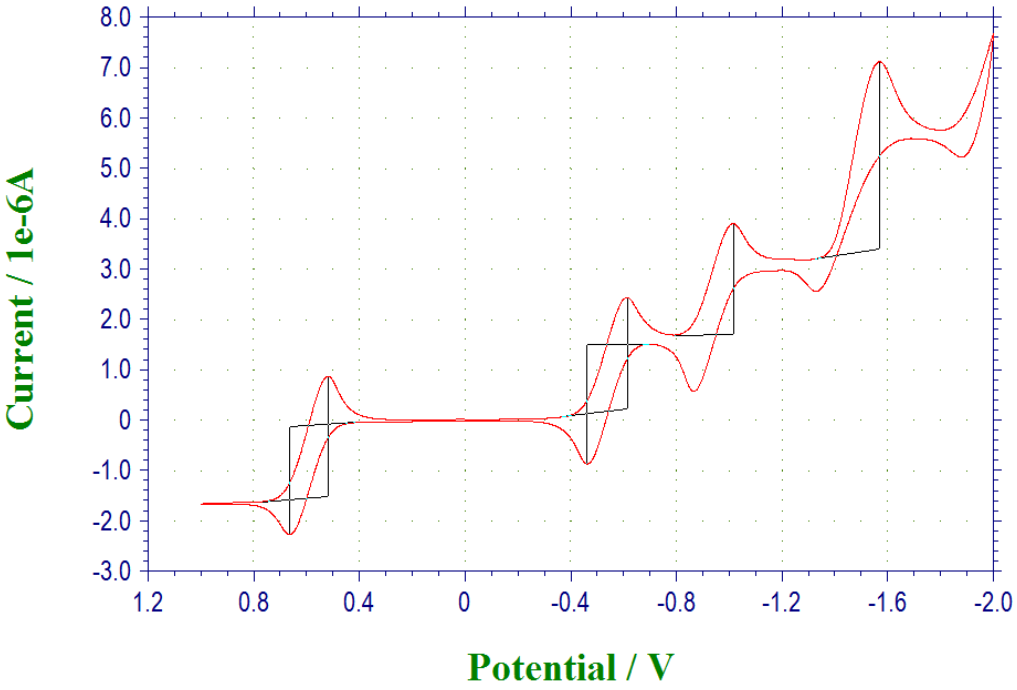


Cyclic voltammogram of compound **2a** (scanning rate: 20 mVs^{-1})

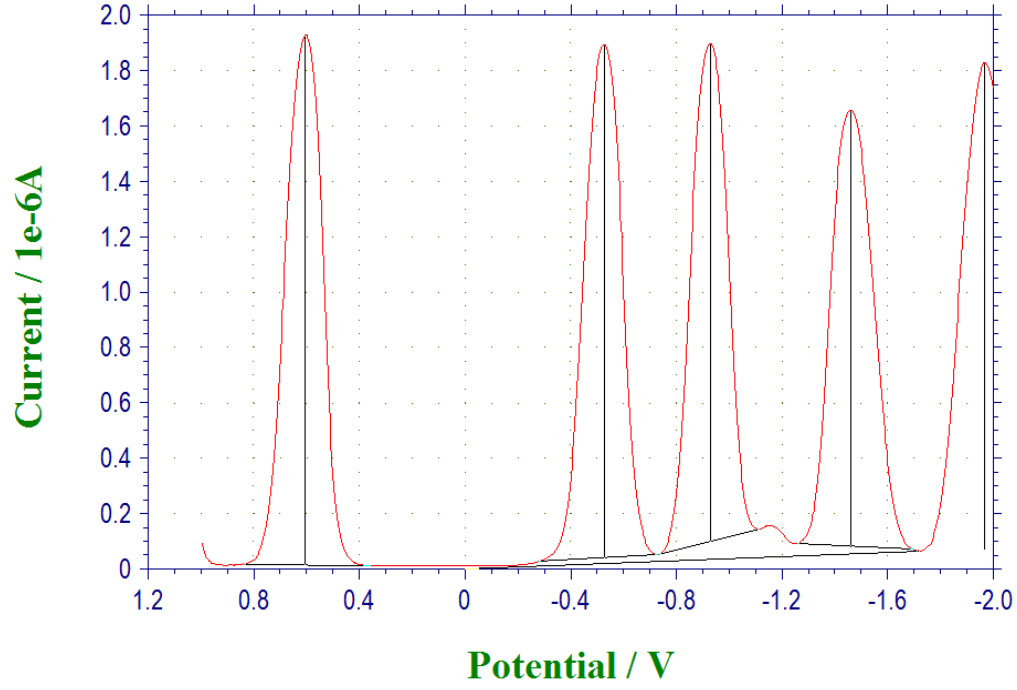


Differential pulse voltammogram of compound **2a**

compound **2a**	E_1	E_2	E_3
CV	–1.133 V	–1.533 V	–2.004 V
DPV	–1.136 V	–1.532 V	–2.024 V

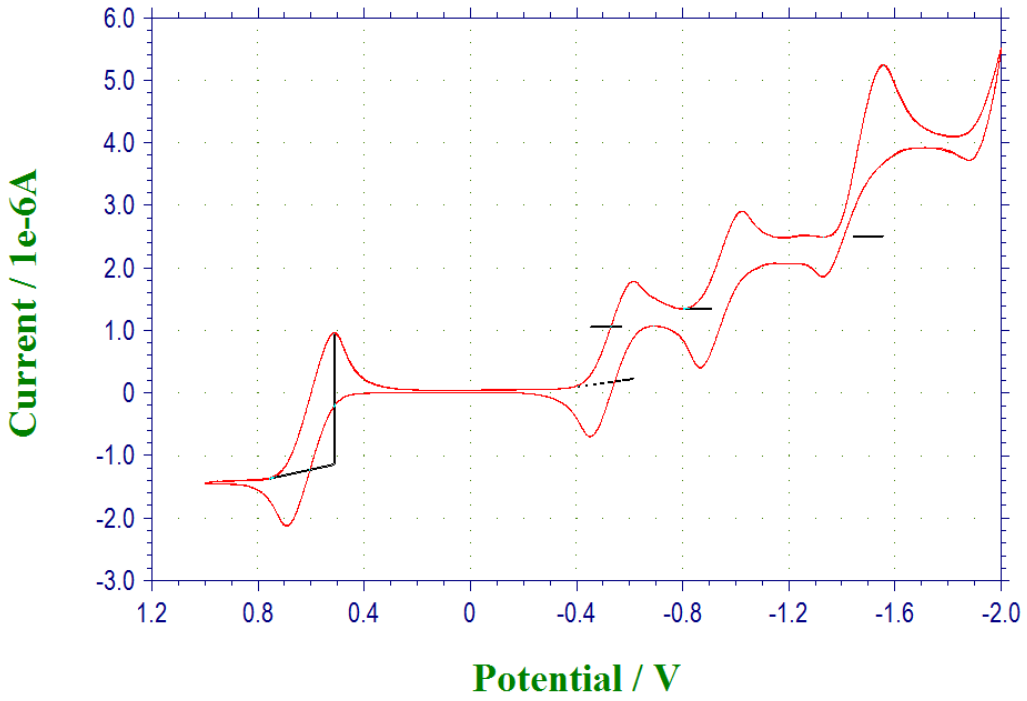


Cyclic voltammogram of compound **2b** (scanning rate: 20 mVs^{-1})

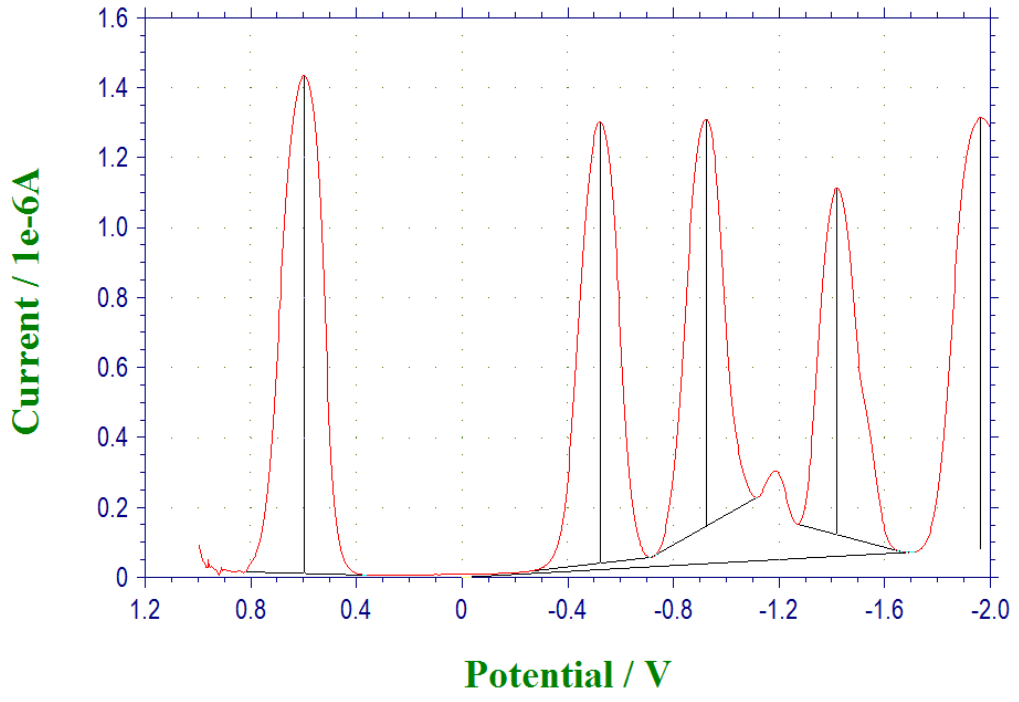


Differential pulse voltammogram of compound **2b**

compound **2b**	E_1	E_2	E_3
CV	–1.128 V	–1.532 V	–2.041 V
DPV	–1.128 V	–1.532 V	–2.064 V

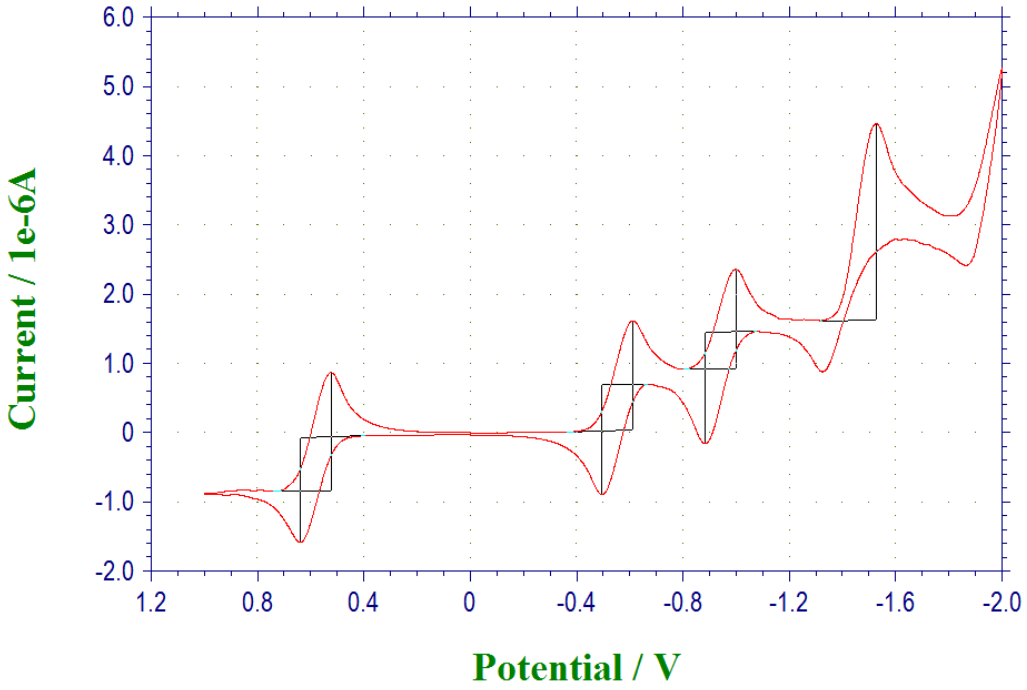


Cyclic voltammogram of compound **2c** (scanning rate: 20 mVs^{-1})

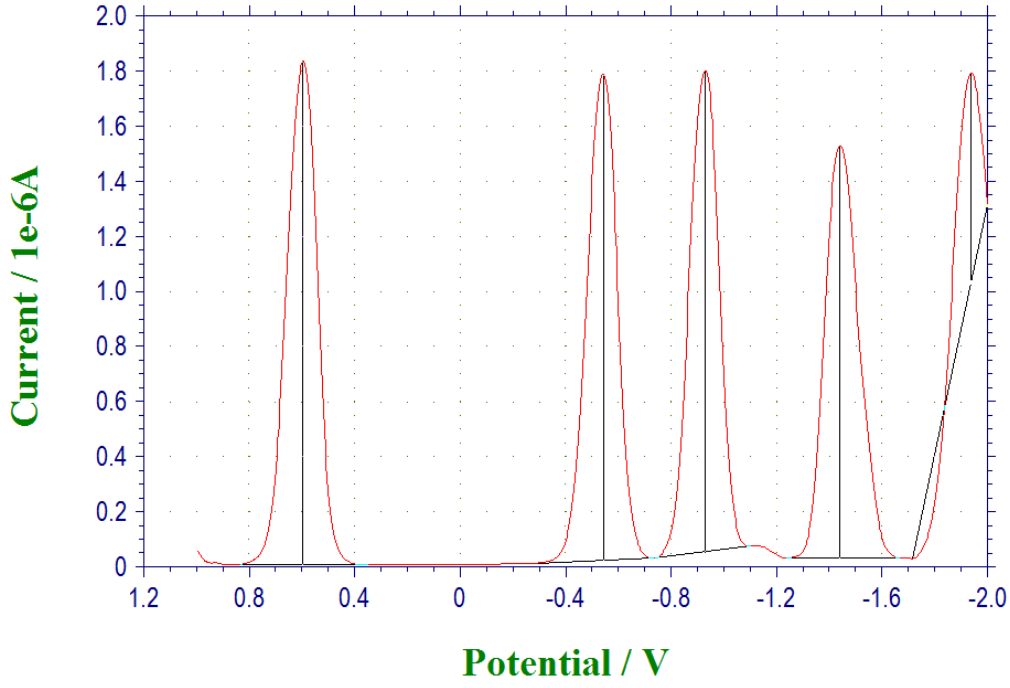


Differential pulse voltammogram of compound **2c**

compound **2c**	E_1	E_2	E_3
CV	–1.124 V	–1.528 V	–2.013 V
DPV	–1.124 V	–1.524 V	–2.020 V

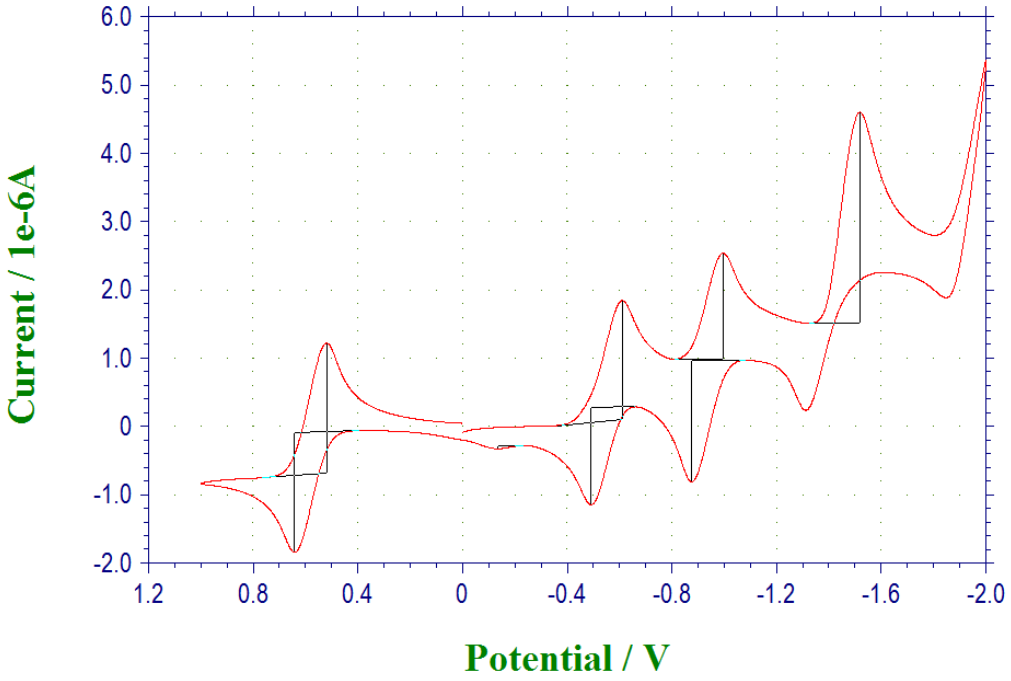


Cyclic voltammogram of compound **2d** (scanning rate: 20 mVs^{-1})

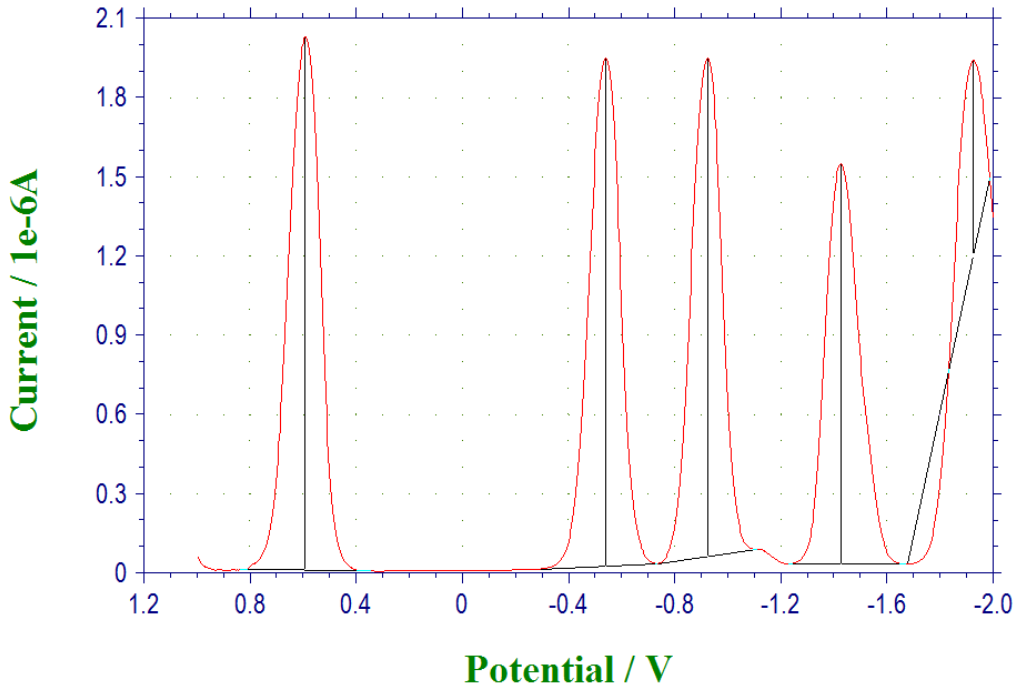


Differential pulse voltammogram of compound **2d**

compound **2d**	E_1	E_2	E_3
CV	–1.135 V	–1.522 V	–2.008 V
DPV	–1.140 V	–1.524 V	–2.036 V

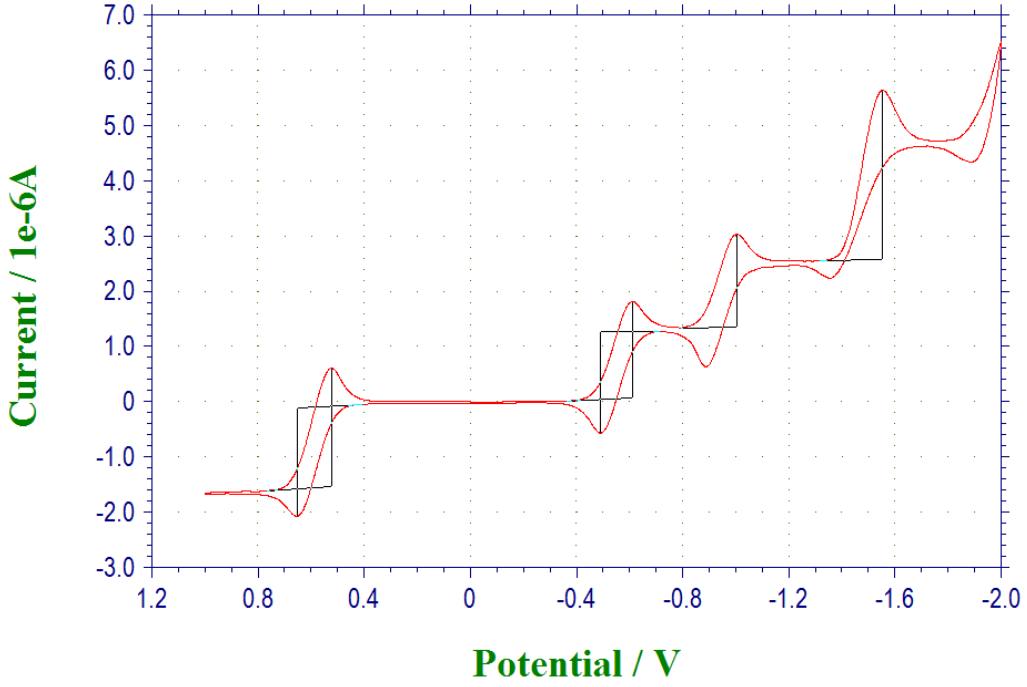


Cyclic voltammogram of compound **2e** (scanning rate: 20 mVs^{-1})

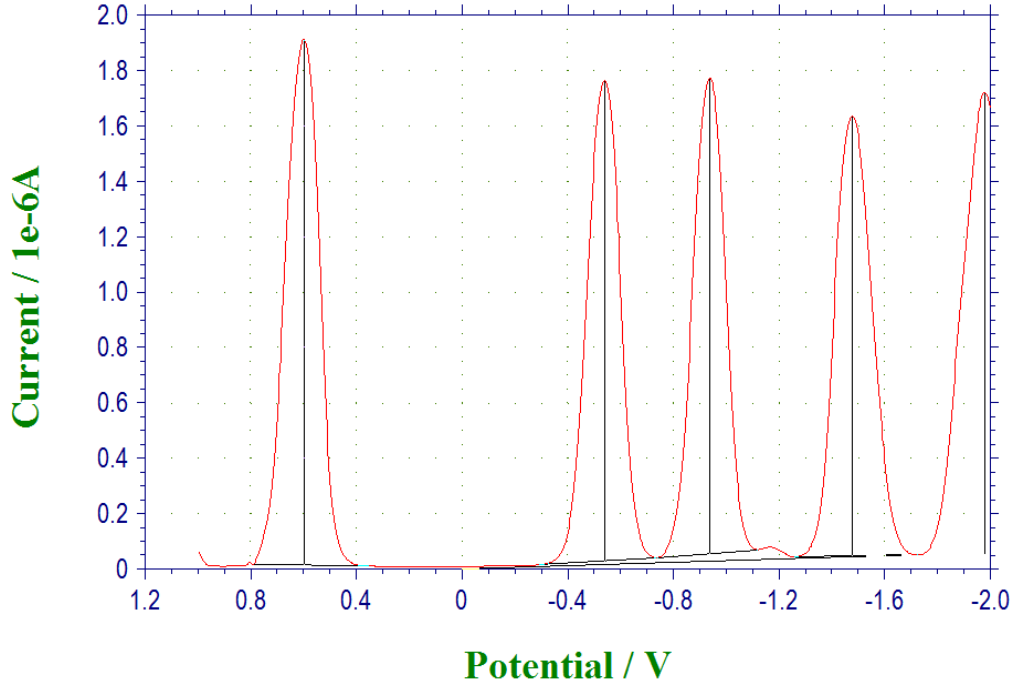


Differential pulse voltammogram of compound **2e**

compound **2e**	E_1	E_2	E_3
CV	–1.132 V	–1.517 V	–1.997 V
DPV	–1.132 V	–1.516 V	–2.020 V

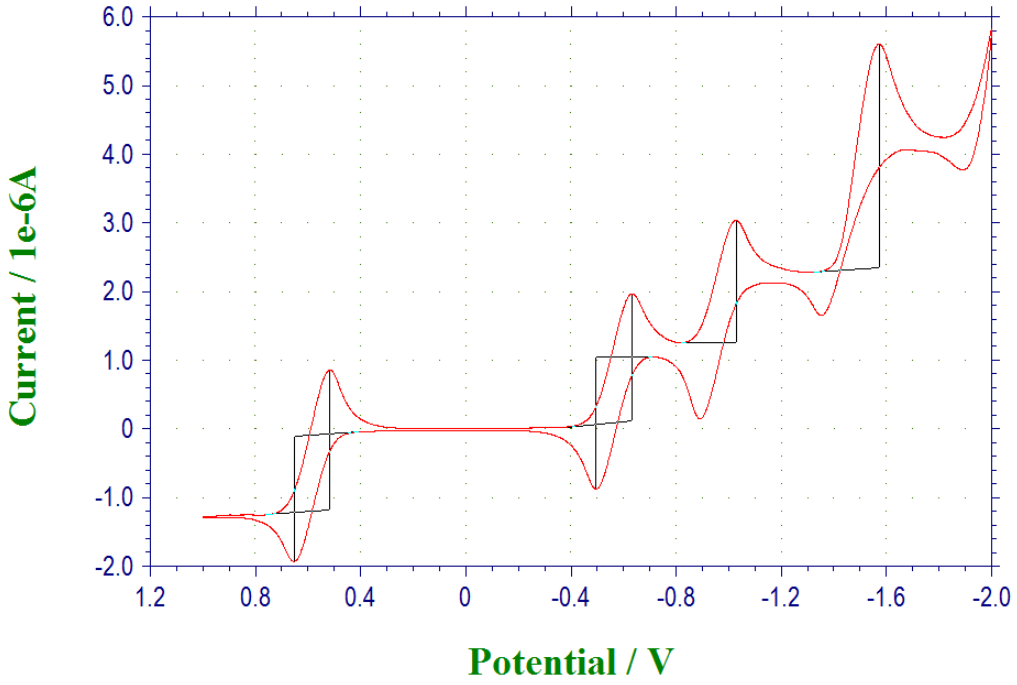


Cyclic voltammogram of compound **2f** (scanning rate: 20 mVs^{-1})

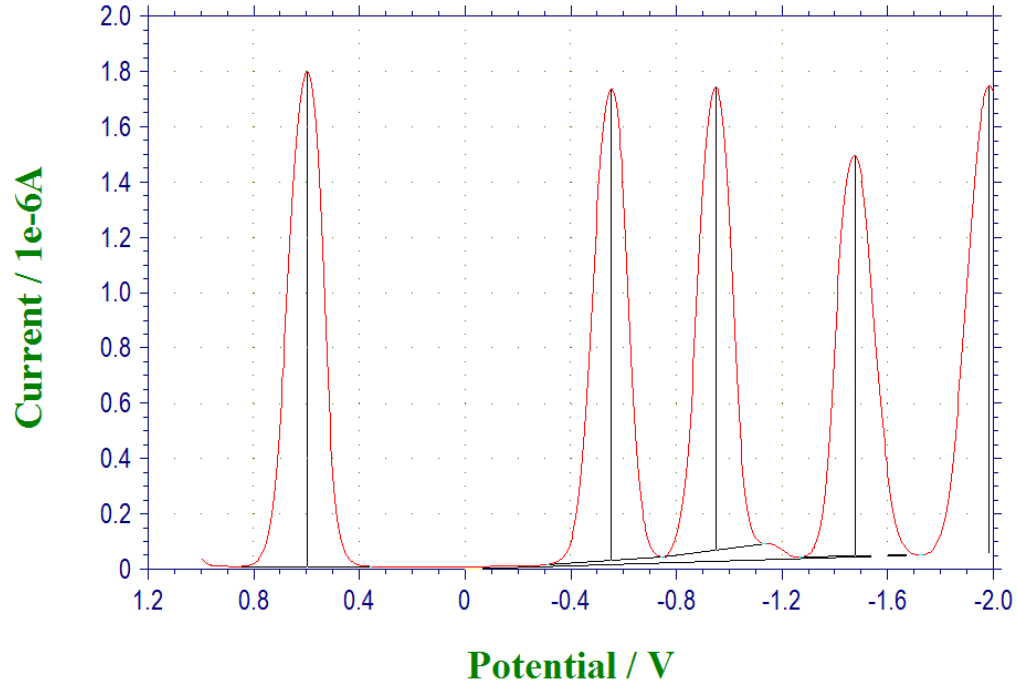


Differential pulse voltammogram of compound **2f**

compound **2f**	E_1	E_2	E_3
CV	–1.140 V	–1.535 V	–2.043 V
DPV	–1.140 V	–1.536 V	–2.076 V

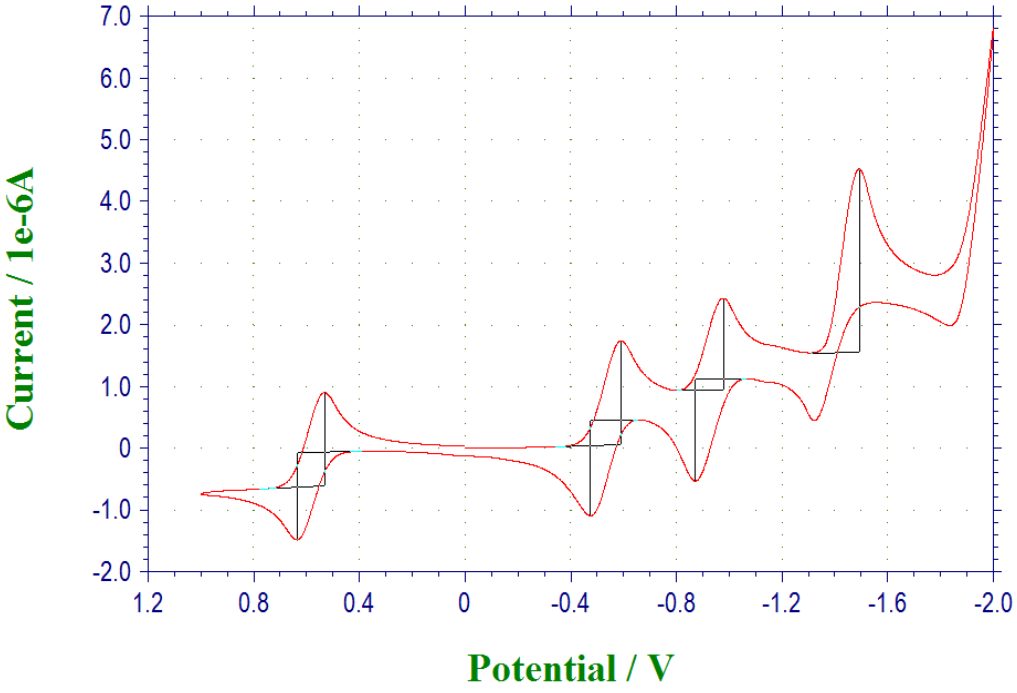


Cyclic voltammogram of compound **2g** (scanning rate: 20 mVs^{-1})

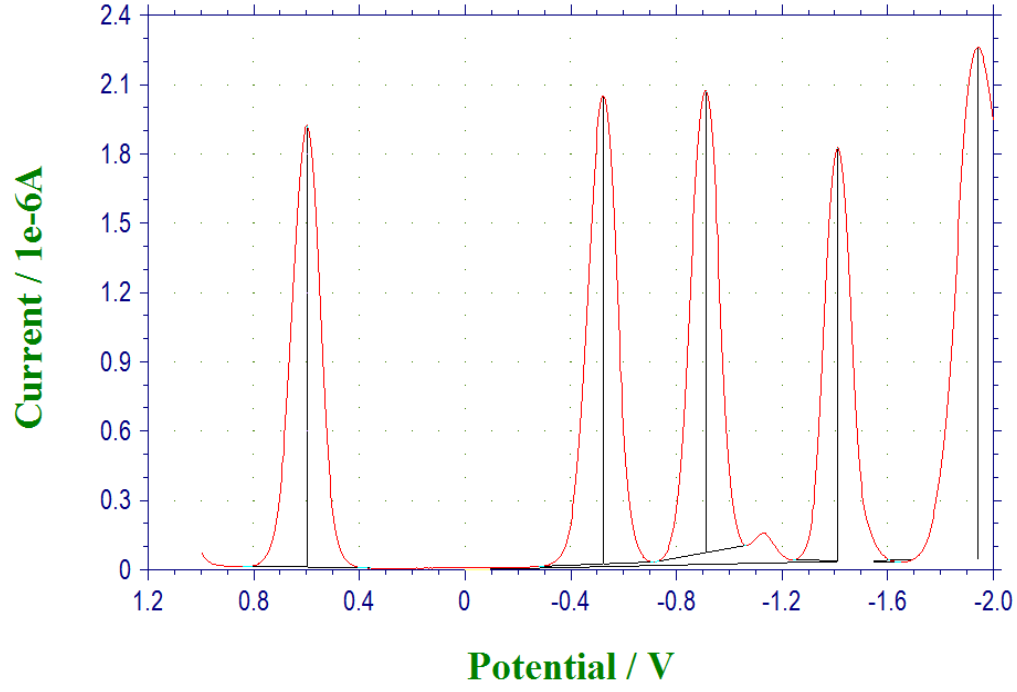


Differential pulse voltammogram of compound **2g**

compound **2g**	E_1	E_2	E_3
CV	–1.149 V	–1.545 V	–2.048 V
DPV	–1.148 V	–1.544 V	–2.072 V

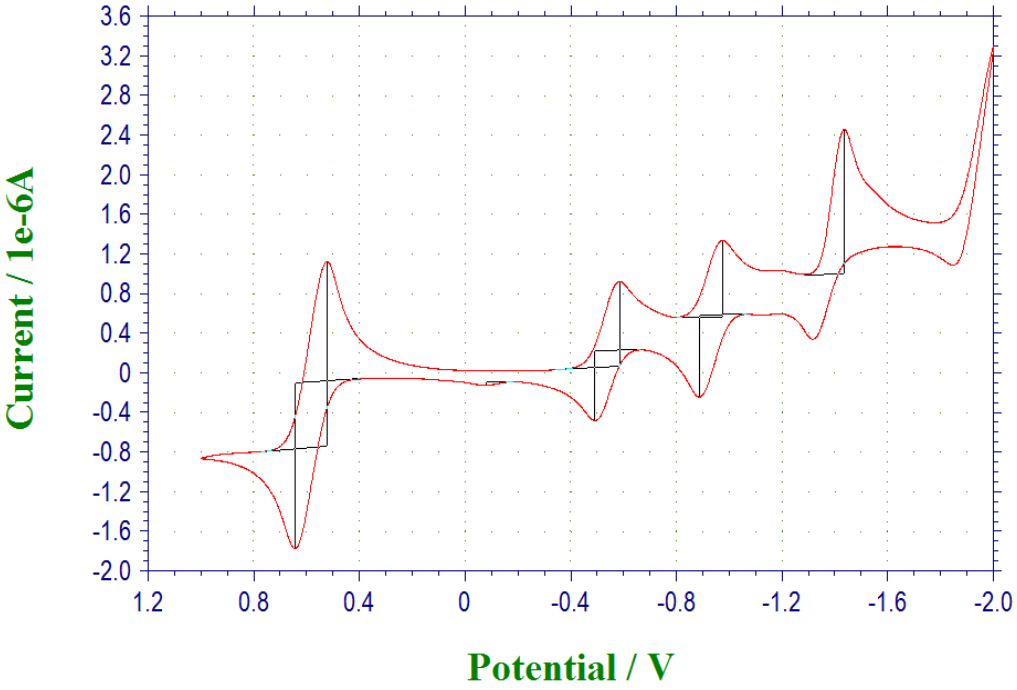


Cyclic voltammogram of compound **2h** (scanning rate: 20 mVs^{-1})

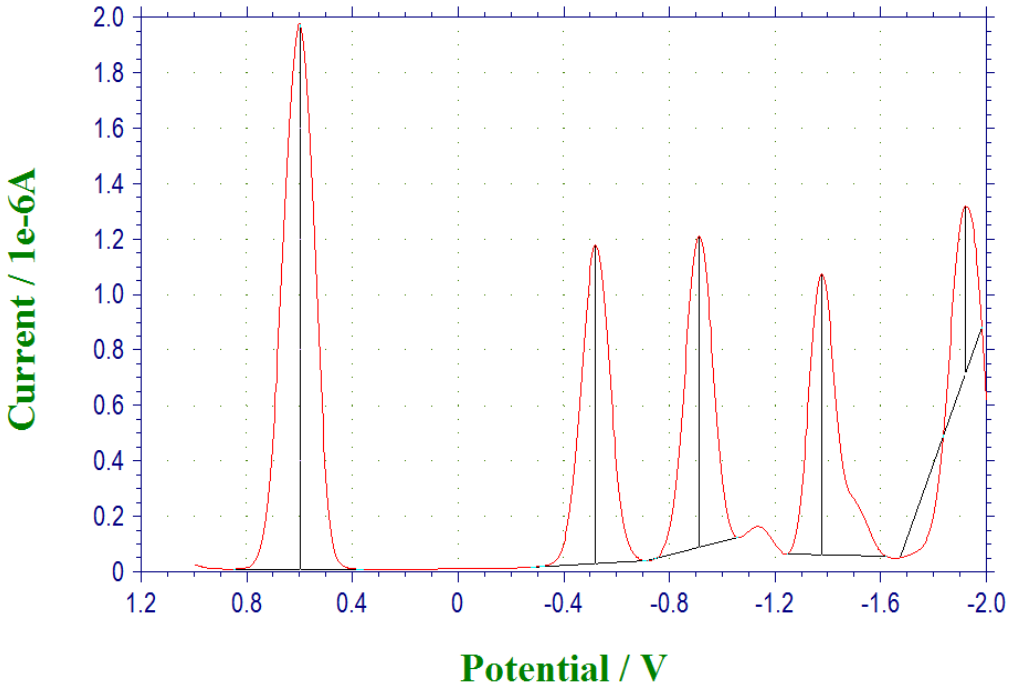


Differential pulse voltammogram of compound **2h**

compound **2h**	E_1	E_2	E_3
CV	–1.118 V	–1.509 V	–1.994 V
DPV	–1.124 V	–1.512 V	–2.012 V

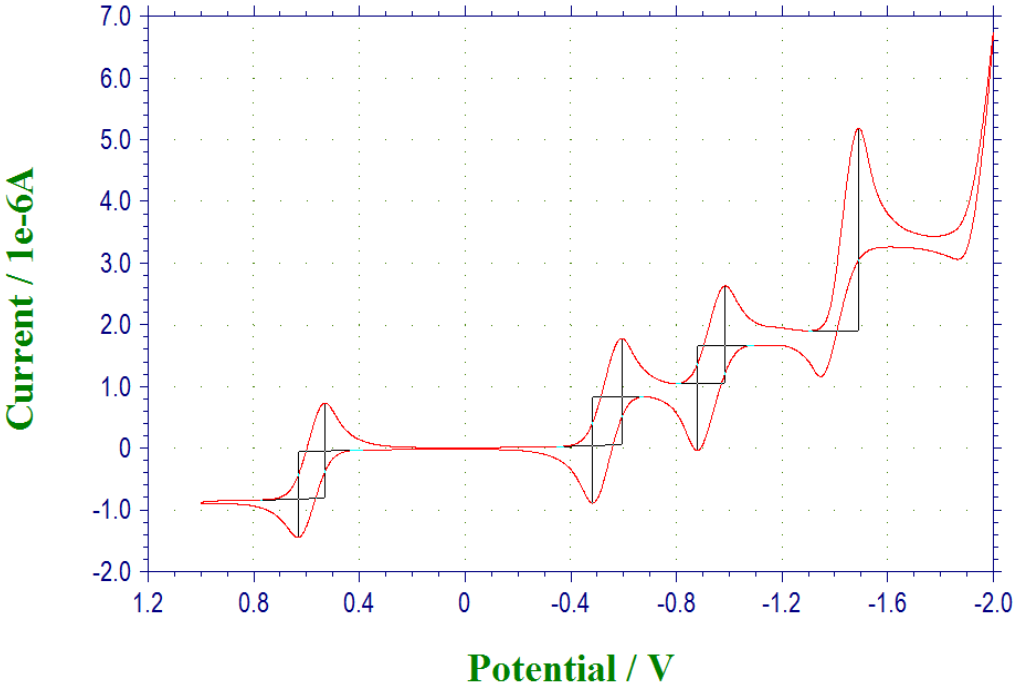


Cyclic voltammogram of compound **2i** (scanning rate: 20 mVs^{-1})

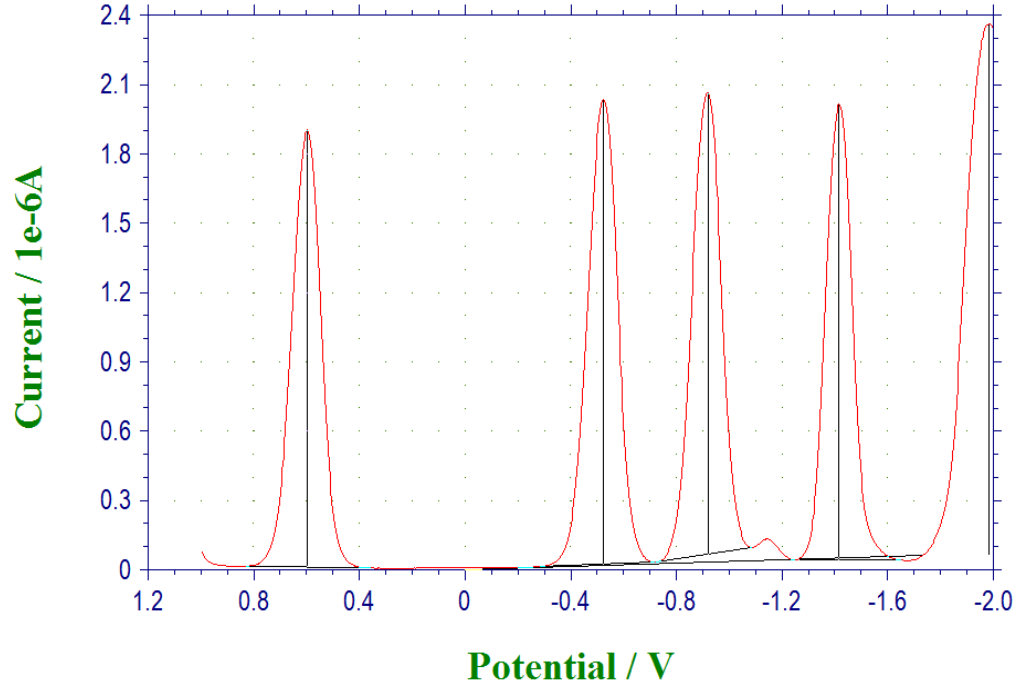


Differential pulse voltammogram of compound **2i**

compound **2i**	E_1	E_2	E_3
CV	–1.122 V	–1.515 V	–1.963 V
DPV	–1.120 V	–1.512 V	–1.976 V

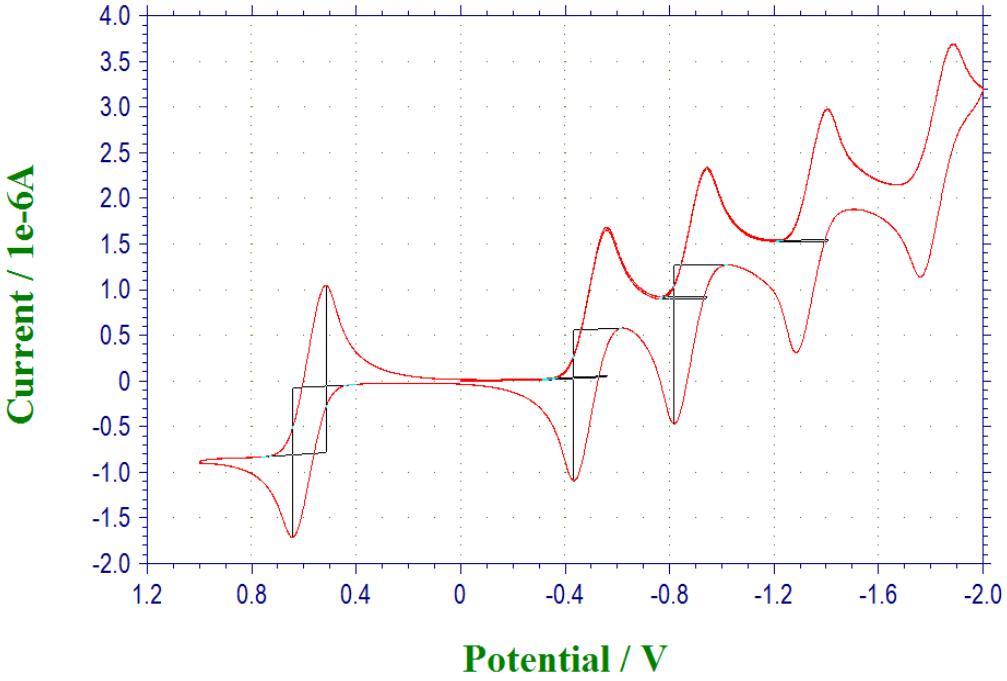


Cyclic voltammogram of compound **5** (scanning rate: 20 mVs^{-1})

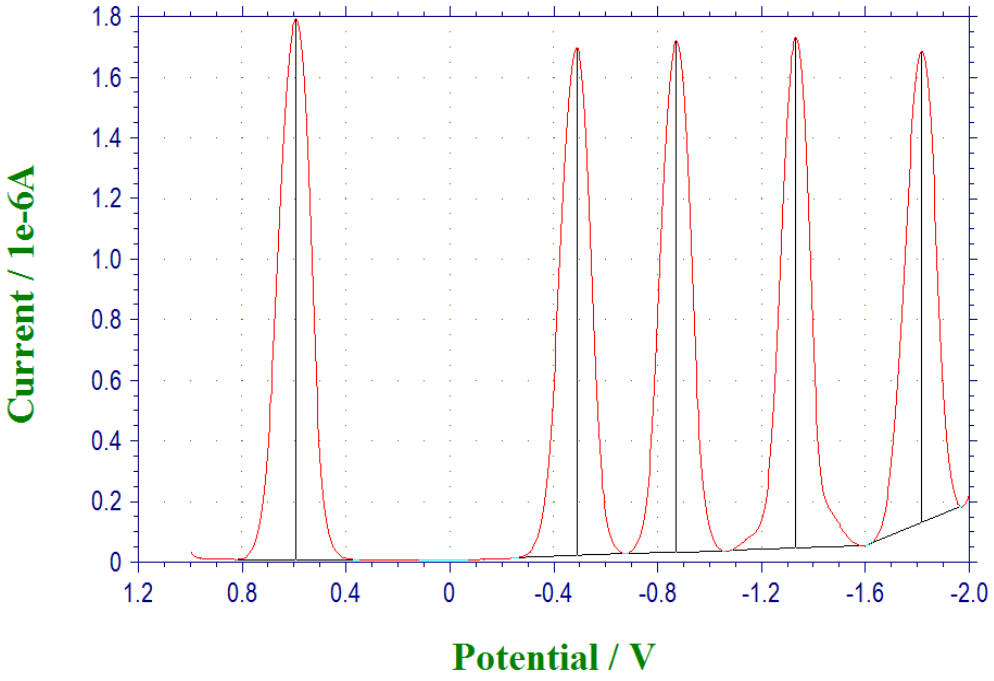


Differential pulse voltammogram of compound **5**

compound **5**	E_1	E_2	E_3
CV	–1.120 V	–1.514 V	–2.000 V
DPV	–1.120 V	–1.516 V	–2.012 V



Cyclic voltammogram of compound C_{60} (scanning rate: 20 mvs^{-1})



Differential pulse voltammogram of compound C_{60}

C_{60}	E_1	E_2	E_3
CV	–1.076 V	–1.460 V	–1.925 V
DPV	–1.080 V	–1.464 V	–1.924 V