Supporting Information

Cascade Radical Reaction of *N*-Sulfonyl-2-allylanilines with [60]Fullerene: Synthesis and Functionalization of (2-Indolinyl)methylated Hydrofullerenes

Sheng-Peng Jiang,[†] Mengmeng Zhang,[‡] Cheng-Yu Wang,[†] Shangfeng Yang,*[,‡] and Guan-Wu Wang*[,†,§]

[†]CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Collaborative Innovation Center of Chemistry for Energy Materials (*i*ChEM), and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
E-mail: gwang@ustc.edu.cn; Fax: +86 551 3607864; Tel: +86 551 3607864
[‡]Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion, and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China E-mail: sfyang@ustc.edu.cn

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

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Optimization for the Synthesis of 2a

The combination of Cu(II) and K_2CO_3 has proven to be effective for coupling reactions of *N*-sulfonyl-2-allylanilines **1**.[1] Therefore, we initially studied the reaction of C_{60} (0.05 mmol) with *N*-tosyl-2-allylaniline **1a** (2.0 equiv) by using $CuCl_2 \cdot 2H_2O$ (2.0 equiv) and K_2CO_3 (2.0 equiv) in anhydrous chlorobenzene (CB) at 120 °C under an open-air atmosphere. To our delight, the desired product **2a** was obtained in 9% yield after 1.5 h (Table S1, entry1). Encouraged by this result, different copper salts were next evaluated to improve the product yield. To our satisfaction, when $Cu(OTf)_2$ was used, the yield of **2a** was significantly increased to 23%, while other Cu(II) salts such as $Cu(OAc)_2 \cdot H_2O$, $CuBr_2$, CuF_2, and $Cu(acac)_2$ could not induce the reaction (Table S1, entries 2–6). Other carbonates including Na_2CO_3 and Li_2CO_3 did not give a better result, delivering **2a** in 19% and 17% yields, respectively (Table S1, entries 7 and 8). However, no desired product was observed when Cs_2CO_3 was used as the base (Table S1, entry 9). Acetate such as KOAc and NaOAc were not beneficial to the improvement of the yield either, giving **2a** in 11% and 17% yields, respectively (Table S1, entries 10 and 11). Unexpectedly, an obviously increased yield of 30% was observed when K_2CO_3 was replaced by 4-dimethylaminopyridine (DMAP) (Table S1, entry 12). Decreasing the loadings of $Cu(OTf)_2$ and DMAP to 1.0 equiv could provide a slightly better yield of 33% (Table S1, entry 13). Reducing the reaction temperature from 120 °C to 110 °C and 100 °C could still afford **2a** in a comparable yield of 32% (Table S1, entries 14 and 15 vs. entry 13). Further reducing the temperature to 90 °C resulted in only 23% yield (Table S1, entry 16). Therefore, the optimal reaction temperature was chosen to be 100 °C. Under the best reaction temperature, reducing the amounts of $Cu(OTf)_2$ and DMAP to 0.5 equiv delivered **2a** in 26% yield (Table S1, entry 17). However, increasing the amounts of $Cu(OTf)_2$ and DMAP to 1.5 equiv delivered a slightly decreased yield of 30% (Table S1, entry 18 vs. entry 15). The decrease of the amount of substrate **1a** to 1.5 equiv gave a lower yield of 27% (Table S1, entry 19), and only a comparable yield of 34% was obtained when the amount of substrate **1a** was increased to 2.5 equiv (Table S1, entry 20 vs. entry 15). The reaction time was also varied, and it was found that 1.5 h was still the best choice (Table S1, entry 15 vs. entries 21 and 22). Furthermore, control experiments confirmed that the reaction was totally shut down in the absence of $Cu(OTf)_2$, and the product yield was only 7% without DMAP (Table S1, entries 23 and 24). These observations suggested that the copper species was indispensable and DMAP played an important role in this reaction. Thus, the optimal reaction conditions were a molar ratio of 1/2/1/1 for the reagents C_{60}, **1a**, $Cu(OTf)_2$, and DMAP, and carrying out the reaction at 100 °C for 1.5 h in anhydrous CB under an open-air atmosphere (Table S1, entry 15).

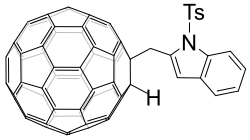
Table S1. Optimization of the Reaction Conditions[a]

entry	copper/base	molar ratio[b]	temp. (°C)	yield (%)[c]
1	$CuCl_2 \cdot 2H_2O/K_2CO_3$	1:2:2:2	120	9 (53)
2	$Cu(OAc)_2 \cdot H_2O/K_2CO_3$	1:2:2:2	120	0 (0)
3	$CuBr_2/K_2CO_3$	1:2:2:2	120	0 (0)
4	CuF_2/K_2CO_3	1:2:2:2	120	0 (0)
5	$Cu(acac)_2/K_2CO_3$	1:2:2:2	120	0 (0)
6	$Cu(OTf)_2/K_2CO_3$	1:2:2:2	120	23 (47)
7	$Cu(OTf)_2/Na_2CO_3$	1:2:2:2	120	19 (86)
8	$Cu(OTf)_2/Li_2CO_3$	1:2:2:2	120	17 (77)
9	$Cu(OTf)_2/Cs_2CO_3$	1:2:2:2	120	0 (0)
10	$Cu(OTf)_2$/KOAc	1:2:2:2	120	11 (79)
11	$Cu(OTf)_2$/NaOAc	1:2:2:2	120	17 (55)
12	$Cu(OTf)_2$/DMAP	1:2:2:2	120	30 (38)
13	$Cu(OTf)_2$/DMAP	1:2:1:1	120	33 (46)
14	$Cu(OTf)_2$/DMAP	1:2:1:1	110	32 (55)
15	**$Cu(OTf)_2$/DMAP**	**1:2:1:1**	**100**	**32 (71)**
16	$Cu(OTf)_2$/DMAP	1:2:1:1	90	23 (64)
17	$Cu(OTf)_2$/DMAP	1:2:0.5:0.5	100	26 (76)
18	$Cu(OTf)_2$/DMAP	1:2:1.5:1.5	100	30 (54)
19	$Cu(OTf)_2$/DMAP	1:1.5:1:1	100	27 (71)
20	$Cu(OTf)_2$/DMAP	1:2.5:1:1	100	34 (60)
21[d]	$Cu(OTf)_2$/DMAP	1:2:1:1	100	31 (61)
22[e]	$Cu(OTf)_2$/DMAP	1:2:1:1	100	28 (70)
23	$Cu(OTf)_2$/DMAP	1:2:0:1	100	0 (0)
24	$Cu(OTf)_2$/DMAP	1:2:1:0	100	7 (54)

[a]Unless otherwise noted, the reactions were performed in anhydrous CB under an open-air atmosphere for 1.5 h. [b]Molar ratio refers to C_{60}/**1a**/copper/base. [c]Isolated yields. Values in parentheses were based on consumed C_{60}. [d]The reaction time was 2 h. [e]The reaction time was 1 h.

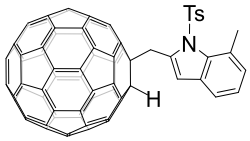
Experimental Procedures

General Procedure for the Synthesis of 2a–r from the $Cu(OTf)_2$-Promoted Reaction of C_{60} with 1a–r. A mixture of C_{60} (0.05 mmol), *N*-sulfonyl-2-allylanilines **1** (0.10 mmol), $Cu(OTf)_2$ (0.05 mmol), and DMAP (0.05 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at the desired temperature and stopped at the designated time. The resulting solution was evaporated in *vacuo* and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} and then the desired product **2**.



2a

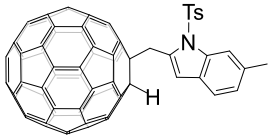
Preparation of **2a**: By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1a** (28.9 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.3 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (19.9 mg, 55%) and **2a** (16.2 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.36–7.31 (m, 2H), 7.29–7.23 (m, 3H), 6.77 (s, 1H), 5.28 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, all 2C unless indicated) δ 154.77, 153.67, 147.46 (1C), 147.23 (1C), 146.90, 146.34 (4C), 146.17, 146.13, 145.99, 145.75, 145.52, 145.38, 145.36, 145.33, 144.89 (1C, aryl *C*), 144.69, 144.49, 143.18, 142.53, 142.51, 142.19, 142.03, 141.96, 141.75, 141.62 (4C), 140.24, 140.02, 137.69 (1C, aryl *C*), 136.24 (4C), 136.20 (1C, aryl *C*), 136.05 (1C, aryl *C*), 129.87 (aryl *C*), 129.73 (1C, aryl *C*), 126.54 (aryl *C*), 125.11 (1C, aryl *C*), 124.33 (1C, aryl *C*), 121.00 (1C, aryl *C*), 115.81 (1C, aryl *C*), 114.00 (1C, aryl *C*), 64.96 (1C, sp^3-*C* of C_{60}), 58.67 (1C, sp^3-*C* of C_{60}), 44.08 (1C), 21.70 (1C). FT-IR ν/cm^{-1} (KBr) 2920, 2854, 1596, 1509, 1445, 1367, 1306, 1216, 1174, 1088, 1046, 808, 744, 704, 668, 578, 528. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.17), 308 (4.66), 327 (4.62), 433 (3.63), 707 (2.54). MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{16}NO_2S$ $[M+H]^+$ 1006.0896, found 1006.0881.



2b

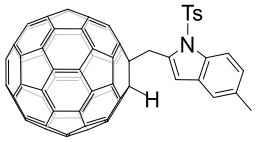
Preparation of **2b**: By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30.5 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 120 °C for 1.0 h afforded recovered C_{60} (10.4 mg, 29%) and **2b** (16.5 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.38 (d, J = 8.2 Hz, 2H), 7.26–7.18 (m, 3H), 7.12 (d, J = 8.2 Hz, 2H), 7.08 (s, 1H), 6.85 (s, 1H), 5.14 (s, 2H), 2.82 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100

MHz, $CS_2/CDCl_3$, all 2C unless indicated) δ 155.00, 153.67, 147.41 (1C), 147.18 (1C), 146.95, 146.28 (4C), 146.12, 146.09, 145.94, 145.71, 145.43, 145.30 (6C), 144.64, 144.47 (1C, aryl *C*), 144.36, 143.12, 142.48 (4C), 142.15, 141.97, 141.93, 141.75, 141.56 (4C), 140.90 (1C, aryl *C*), 140.63 (1C, aryl *C*), 140.18, 139.98, 136.16, 136.03, 133.56 (1C, aryl *C*), 133.44 (1C, aryl *C*), 130.39 (1C, aryl *C*), 129.20 (1C, aryl *C*), 128.98 (aryl *C*), 126.72 (aryl *C*), 125.79 (1C, aryl *C*), 120.11 (1C, aryl *C*), 118.59 (1C, aryl *C*), 65.11 (1C, sp^3-*C* of C_{60}), 58.38 (1C, sp^3-*C* of C_{60}), 46.10 (1C), 22.05 (1C), 21.67 (1C). FT-IR ν/cm^{-1} (KBr) 2962, 2922, 2859, 1638, 1595, 1508, 1427, 1362, 1169, 1138, 1086, 806, 745, 675, 621, 578, 524. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.11), 312 (4.63), 328 (4.56), 434 (3.58), 707 (2.54). MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{18}NO_2S$ $[M+H]^+$ 1020.1053, found 1020.1025.



2c

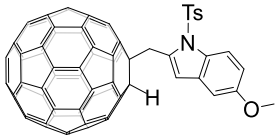
Preparation of **2c**: By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1c** (30.2 mg, 0.10 mmol), $Cu(OTf)_2$ (17.9 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (15.9 mg, 44%) and **2c** (17.2 mg, 34%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.05 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.22 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 5.23 (s, 2H), 2.52 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, all 2C unless indicated) δ 154.74, 153.62, 147.35 (1C), 147.13 (1C), 146.83, 146.24 (4C), 146.07, 146.03, 145.92, 145.66, 145.42, 145.29, 145.25, 145.23, 144.60, 144.58 (1C, aryl *C*), 144.41, 143.09, 142.44, 142.42, 142.10, 141.94, 141.88, 141.67, 141.53 (4C), 140.15, 139.92, 138.10 (1C, aryl *C*), 136.21 (1C, aryl *C*), 136.18, 136.08, 135.38 (1C, aryl *C*), 134.88 (1C, aryl *C*), 129.72 (aryl *C*), 127.39 (1C, aryl *C*), 126.44 (aryl *C*), 125.76 (1C, aryl *C*), 120.57 (1C, aryl *C*), 115.98 (1C, aryl *C*), 113.96 (1C, aryl *C*), 64.96 (1C, sp^3-*C* of C_{60}), 58.58 (1C, sp^3-*C* of C_{60}), 44.06 (1C), 22.22 (1C), 21.68 (1C). FT-IR ν/cm^{-1} (KBr) 2915, 2857, 1639, 1596, 1508, 1425, 1365, 1172, 1135, 1090, 1042, 812, 704, 663, 594, 578, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.11), 309 (4.63), 328 (4.56), 434 (3.58), 707 (2.65). MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{18}NO_2S$ $[M+H]^+$ 1020.1053, found 1020.1038.



2d

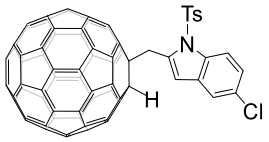
Preparation of **2d**: By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1d** (29.9 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.0 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (18.7 mg, 52%)

and **2d** (19.1 mg, 37%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.12 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.38 (s, 1H), 7.29 (s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.17 (dd, J = 8.7, 1.4 Hz, 2H), 6.68 (s, 1H), 5.23 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$, all 2C unless indicated) δ 153.86, 152.69, 146.35 (1C), 146.13 (1C), 145.83, 145.21 (4C), 145.05, 145.00 (4C), 144.64, 144.33 (2C + 1C, aryl C), 144.23, 144.21, 144.18, 143.56, 143.36, 142.03, 141.38, 141.36, 141.07, 140.87, 140.82, 140.63, 140.46, 140.45, 139.01, 138.80, 135.17 (1C, aryl *C*), 135.11, 135.02, 134.70 (1C, aryl *C*), 134.51 (1C, aryl *C*), 132.75 (1C, aryl *C*), 129.08 (aryl *C*), 128.90 (1C, aryl *C*), 125.40 (1C, aryl *C*), 125.31 (aryl *C*), 120.01 (1C, aryl *C*), 114.13 (1C, aryl *C*), 112.73 (1C, aryl *C*), 63.88 (1C, sp^3-*C* of C_{60}), 57.61 (1C, sp^3-*C* of C_{60}), 42.81 (1C), 20.63 (1C), 20.26 (1C). FT-IR ν/cm^{-1} (KBr) 2924, 2857, 1631, 1509, 1434, 1364, 1219, 1171, 1090, 1048, 804, 766, 703, 665, 598, 558, 526. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.12), 308 (4.65), 328 (4.57), 434 (3.58), 707 (2.65). ESI FT-ICR MS m/z calcd for $C_{77}H_{18}NO_2S$ $[M+H]^+$ 1020.1053, found 1020.1032.



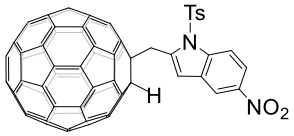
2e

Preparation of **2e**: By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1e** (31.5 mg, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 120 °C for 1.0 h afforded recovered C_{60} (16.1 mg, 45%) and **2e** (16.6 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.14 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.20 (s, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.92 (dd, J = 9.0, 2.4 Hz, 1H), 6.78 (s, 1H), 5.24 (s, 2H), 3.81 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 156.98 (1C, aryl *C*), 154.76, 153.68, 147.44 (1C), 147.20 (1C), 146.90, 146.32 (4C), 146.15, 146.11, 145.96, 145.73, 145.50, 145.36, 145.34, 145.31, 144.74 (1C, aryl *C*), 144.68, 144.48, 143.16, 142.50 (4C), 142.18, 142.01, 141.94, 141.74, 141.59 (4C), 140.22, 140.00, 136.87, 136.22 (1C, aryl *C*), 136.18, 135.86 (1C, aryl *C*), 132.25 (1C, aryl *C*), 130.78 (1C, aryl *C*), 129.77 (aryl *C*), 126.50 (aryl *C*), 116.79 (1C, aryl *C*), 114.36 (1C, aryl *C*), 114.04 (1C, aryl *C*), 103.26 (1C, aryl *C*), 65.02 (1C, sp^3-*C* of C_{60}), 58.57 (1C, sp^3-*C* of C_{60}), 55.23 (1C), 44.11 (1C), 21.69 (1C). FT-IR ν/cm^{-1} (KBr) 2977, 2922, 2824, 1602, 1510, 1464, 1431, 1365, 1208, 1163, 1091, 1047, 769, 666, 631, 598, 551, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.13), 312 (4.66), 434 (3.58), 708 (2.65). MALDI-TOF MS m/z calcd for $C_{77}H_{18}NO_3S$ $[M+H]^+$ 1036.1002, found 1036.0989.



2f

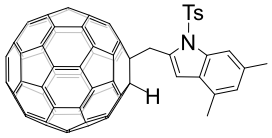
Preparation of **2f**: By following the general procedure, the reaction of C_{60} (35.6 mg, 0.05 mmol) with **1f** (31.7 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), and DMAP (6.3 mg, 0.05 mmol) at 100 °C for 2.5 h afforded recovered C_{60} (15.1 mg, 42%) and **2f** (16.4 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.19 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 2.1 Hz, 1H), 7.31 (dd, J = 9.0, 2.1 Hz, 1H), 7.29 (s, 1H), 7.27 (d, J = 8.3 Hz, 2H), 6.65 (s, 1H), 5.23 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$, all 2C unless indicated) δ 153.47, 152.47, 146.36 (1C), 146.13 (1C), 145.76, 145.22 (4C), 145.06, 145.01, 144.88, 144.78 (1C, aryl *C*), 144.62, 144.36, 144.24, 144.21, 144.19, 143.55, 143.34, 142.03, 141.40, 141.37, 141.05, 140.88, 140.81, 140.59, 140.47, 140.45, 139.04, 138.78, 136.74 (1C, aryl *C*), 135.06, 135.02, 134.83 (1C, aryl *C*), 134.07 (1C, aryl *C*), 129.86 (1C, aryl *C*), 129.25 (aryl *C*), 128.65 (1C, aryl *C*), 125.27 (aryl *C*), 124.12 (1C, aryl *C*), 119.66 (1C, aryl *C*), 115.56 (1C, aryl *C*), 112.14 (1C, aryl *C*), 63.73 (1C, sp^3-*C* of C_{60}), 57.69 (1C, sp^3-*C* of C_{60}), 42.82 (1C), 20.69 (1C). FT-IR ν/cm^{-1} (KBr) 2923, 2858, 1633, 1595, 1509, 1436, 1367, 1219, 1171, 1144, 1091, 1046, 803, 719, 663, 588, 549, 524. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 307 (4.59), 328 (4.53), 434 (3.53), 707 (2.65). MALDI-TOF MS m/z calcd for $C_{76}H_{15}NO_2S^{35}Cl$ $[M+H]^+$ 1040.0507, found 1040.0520.



2g

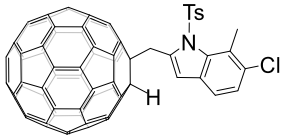
Preparation of **2g**: By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1g** (32.9 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) at 120 °C for 1.0 h afforded recovered C_{60} (16.7 mg, 47%) and **2g** (16.3 mg, 31%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.47 (d, J = 2.3 Hz, 1H), 8.42 (d, J = 9.3 Hz, 1H), 8.23 (dd, J = 9.3, 2.3 Hz, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.52 (s, 1H), 7.32 (d, J = 8.2 Hz, 2H), 6.67 (s, 1H), 5.31 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 153.93, 153.12, 147.46 (1C), 147.21 (1C), 146.64, 146.35, 146.33, 146.17, 146.13, 145.80, 145.65, 145.62 (1C, aryl *C*), 145.55, 145.40, 145.36, 145.31, 144.70 (1C, aryl *C*), 144.66, 144.40, 143.19, 142.56, 142.53, 142.08, 142.00, 141.89, 141.62, 141.60, 141.58, 140.29, 140.12 (1C, aryl *C*), 139.99, 139.56 (1C, aryl *C*), 136.19, 136.07, 135.67 (1C, aryl *C*), 130.22 (aryl *C*), 129.41 (1C, aryl *C*), 126.59 (aryl *C*), 119.90 (1C, aryl *C*), 116.92 (1C, aryl *C*), 115.63 (1C, aryl *C*), 113.28 (1C, aryl *C*), 64.47 (1C, sp^3-*C* of C_{60}), 58.80 (1C, sp^3-*C* of C_{60}), 43.93 (1C), 21.73 (1C). FT-IR ν/cm^{-1} (KBr) 2923, 2857, 1600, 1514, 1444, 1373, 1339, 1276, 1226, 1174, 1086, 1044, 893, 808,

745, 707, 663, 587, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.13), 311 (4.65), 328 (4.58), 433 (3.68), 707 (2.54). ESI FT-ICR MS *m*/*z* calcd for $C_{76}H_{15}N_2O_4S$ $[M+H]^+$ 1051.0747, found 1051.0731.



2h

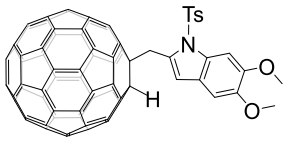
Preparation of **2h**: By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with **1h** (31.5 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (14.6 mg, 41%) and **2h** (21.0 mg, 41%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.89 (s, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.32 (s, 1H), 7.26 (d, J = 8.3 Hz, 2H), 6.92 (s, 1H), 6.69 (s, 1H), 5.23 (s, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$, all 2C unless indicated) δ 154.04, 152.83, 146.40 (1C), 146.19 (1C), 145.91, 145.27 (4C), 145.13, 145.11, 145.06, 144.73, 144.39, 144.35 (1C, aryl *C*), 144.29, 144.27, 144.24, 143.61, 143.42, 142.08, 141.44, 141.43, 141.14, 140.94, 140.89, 140.70, 140.51 (4C), 139.07, 138.83, 136.76 (1C, aryl *C*), 135.15, 135.02, 134.76 (1C, aryl *C*), 134.21 (1C, aryl *C*), 133.83 (1C, aryl *C*), 129.15 (aryl *C*), 129.06 (1C, aryl *C*), 126.05 (1C, aryl *C*), 125.41 (aryl *C*), 125.17 (1C, aryl *C*), 112.13 (1C, aryl *C*), 111.34 (1C, aryl *C*), 64.10 (1C, sp^3-*C* of C_{60}), 57.75 (1C, sp^3-*C* of C_{60}), 43.03 (1C), 21.14 (1C), 20.70 (1C), 17.63 (1C). FT-IR ν/cm^{-1} (KBr) 2921, 2859, 1600, 1510, 1435, 1366, 1299, 1171, 1102, 1033, 810, 760, 706, 664, 583, 528. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.08), 310 (4.59), 329 (4.53), 433 (3.53). MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{20}NO_2S$ $[M+H]^+$ 1034.1209, found 1034.1189.



2i

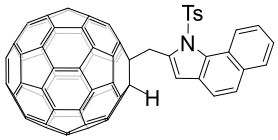
Preparation of **2i**: By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1i** (33.4 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 120 °C for 1.5 h afforded recovered C_{60} (16.6 mg, 46%) and **2i** (16.4 mg, 31%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.37–7.32 (m, 3H), 7.18 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.97 (s, 1H), 6.85 (s, 1H), 5.09 (s, 2H), 2.81 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.73, 153.50, 147.44 (1C), 147.19 (1C), 146.89, 146.31 (4C), 146.14, 146.11, 145.81, 145.68, 145.45, 145.33 (4C), 145.30, 144.72 (1C, aryl *C*), 144.66, 144.45, 143.14, 142.51, 142.50, 142.27 (1C, aryl *C*), 142.14, 141.99, 141.92, 141.88 (1C, aryl *C*), 141.73, 141.58, 141.56, 140.23, 140.00, 136.08, 136.04, 133.86 (1C, aryl *C*), 132.81 (1C, aryl *C*), 132.31 (1C, aryl *C*), 129.79 (1C, aryl *C*), 129.05 (aryl *C*), 127.33 (1C, aryl *C*), 126.84 (aryl *C*), 119.92 (1C, aryl *C*), 118.83 (1C,

aryl *C*), 65.00 (1C, sp^3-*C* of C_{60}), 58.35 (1C, sp^3-*C* of C_{60}), 46.07 (1C), 21.71 (1C), 19.95 (1C). FT-IR ν/cm^{-1} (KBr) 2961, 2921, 1593, 1509, 1452, 1430, 1395, 1367, 1171, 1088, 1004, 806, 711, 671, 588, 526. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.05), 310 (4.56), 328 (4.49), 433 (3.53), 707 (2.65). MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{17}NO_2S^{35}Cl$ $[M+H]^+$ 1054.0663, found 1054.0648.



2j

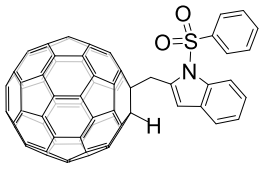
Preparation of **2j**: By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1j** (34.5 mg, 0.10 mmol), $Cu(OTf)_2$ (36.5 mg, 0.10 mmol), and DMAP (12.0 mg, 0.10 mmol) at 120 °C for 1.0 h afforded recovered C_{60} (18.5 mg, 51%) and **2j** (9.9 mg, 19%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.85 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.18 (s, 1H), 6.95 (s, 1H), 6.78 (s, 1H), 5.22 (s, 2H), 4.00 (s, 3H), 3.89 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.99, 153.81, 148.35 (1C, aryl *C*), 147.79 (1C, aryl *C*), 147.49 (1C), 147.26 (1C), 146.97, 146.37 (4C), 146.21, 146.16, 146.10, 145.79, 145.52, 145.39 (4C), 145.36, 144.93 (1C, aryl *C*), 144.72, 144.53, 143.21, 142.56, 142.55, 142.24, 142.05, 142.00, 141.81, 141.64 (4C), 140.25, 140.04, 136.29, 136.18, 135.86 (1C, aryl *C*), 134.75 (1C, aryl *C*), 132.20 (1C, aryl *C*), 129.87 (aryl *C*), 126.40 (aryl *C*), 122.85 (1C, aryl *C*), 114.55 (1C, aryl *C*), 102.41 (1C, aryl *C*), 99.95 (1C, aryl *C*), 65.28 (1C, sp^3-*C* of C_{60}), 58.64 (1C, sp^3-*C* of C_{60}), 56.21 (1C), 55.93 (1C), 44.27 (1C), 21.71 (1C). FT-IR ν/cm^{-1} (KBr) 2923, 1621, 1548, 1510, 1483, 1461, 1429, 1363, 1323, 1259, 1158, 1118, 1090, 1047, 804, 703, 665, 593, 524. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.09), 312 (4.62), 328 (4.58), 433 (3.60), 707 (2.74). MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{19}NO_4SNa$ $[M+Na]^+$ 1088.0927, found 1088.0908.



2k

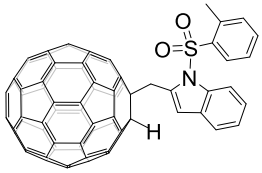
Preparation of **2k**: By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1k** (33.4 mg, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 100 °C for 2.0 h afforded recovered C_{60} (20.4 mg, 57%) and **2k** (16.4 mg, 31%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.95 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.62 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.53–7.47 (m, 2H), 7.24–7.21 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 5.28 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.98, 153.65, 147.41 (1C), 147.18 (1C), 146.95, 146.28 (4C), 146.13, 146.08, 145.98, 145.71, 145.45, 145.30 (4C), 145.28,

144.64, 144.55 (1C, aryl *C*), 144.47, 143.11, 142.47 (4C), 142.16, 141.97, 141.94, 141.78, 141.56 (4C), 140.60 (1C, aryl *C*), 140.17, 140.01, 136.89 (1C, aryl *C*), 136.16, 136.11, 132.98 (1C, aryl *C*), 132.60 (1C, aryl *C*), 130.42 (1C, aryl *C*), 128.90 (aryl *C*), 128.27 (1C, aryl *C*), 127.56 (1C, aryl *C*), 126.63 (aryl *C*), 126.36 (1C, aryl *C*), 126.13 (1C, aryl *C*), 125.87 (1C, aryl *C*), 125.46 (1C, aryl *C*), 120.21 (1C, aryl *C*), 119.07 (1C, aryl *C*), 65.37 (1C, sp^3-*C* of C_{60}), 58.38 (1C, sp^3-*C* of C_{60}), 46.31 (1C), 21.65 (1C). FT-IR ν/cm^{-1} (KBr) 2918, 1624, 1592, 1508, 1425, 1366, 1262, 1168, 1086, 805, 741, 698, 652, 589, 524. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.10), 311 (4.58), 328 (4.54), 433 (3.51), 707 (2.54). MALDI-TOF MS *m*/*z* calcd for $C_{80}H_{18}NO_2S$ $[M+H]^+$ 1056.1053, found 1056.1031.



2l

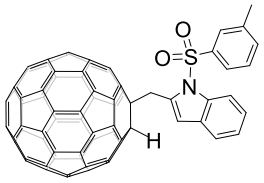
Preparation of **2l**: By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1l** (27.4 mg, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) at 100 °C for 3.0 h afforded recovered C_{60} (17.3 mg, 48%) and **2l** (17.0 mg, 34%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 1H), 7.94–7.88 (m, 2H), 7.62–7.54 (m, 2H), 7.52–7.45 (m, 2H), 7.39–7.33 (m, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.79 (s, 1H), 5.30 (s, 2H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.63, 153.56, 147.41 (1C), 147.18 (1C), 146.85, 146.30 (4C), 146.13, 146.08, 145.91, 145.70, 145.49, 145.35, 145.31, 145.28, 144.65, 144.45, 143.14, 142.49, 142.47, 142.14, 141.99, 141.92, 141.70, 141.57 (4C), 140.21, 139.98, 138.84 (1C, aryl *C*), 137.62 (1C, aryl *C*), 136.20, 136.18, 136.16 (1C, aryl *C*), 133.66 (1C, aryl *C*), 129.68 (1C, aryl *C*), 129.17 (aryl *C*), 126.37 (aryl *C*), 125.19 (1C, aryl *C*), 124.44 (1C, aryl *C*), 121.02 (1C, aryl *C*), 115.76 (1C, aryl *C*), 114.19 (1C, aryl *C*), 64.90 (1C, sp^3-*C* of C_{60}), 58.65 (1C, sp^3-*C* of C_{60}), 44.08 (1C). FT-IR ν/cm^{-1} (KBr) 2922, 1509, 1445, 1363, 1209, 1174, 1087, 1045, 807, 745, 726, 681, 649, 588, 570, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.04), 308 (4.54), 330 (4.48), 434 (3.49), 707 (2.48). MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{14}NO_2S$ $[M+H]^+$ 992.0740, found 992.0721.



2m

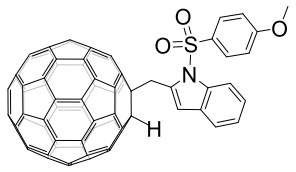
Preparation of **2m**: By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1m** (28.5 mg, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 120 °C for 40 min afforded recovered C_{60} (17.9 mg, 50%) and **2m** (15.8 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz,

$CS_2/CDCl_3$) δ 8.04–7.99 (m, 1H), 7.68–7.62 (m, 1H), 7.52–7.47 (m, 2H), 7.45 (dd, J = 7.5, 1.2 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.30–7.24 (m, 3H), 6.70 (s, 1H), 5.21 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, all 2C unless indicated) δ 154.61, 153.56, 147.44 (1C), 147.22 (1C), 146.85, 146.33 (4C), 146.16, 146.12, 145.98, 145.72, 145.52, 145.35 (4C), 145.32, 144.67, 144.48, 143.17, 142.50 (4C), 142.14, 142.02, 141.95, 141.67, 141.60 (4C), 140.23, 139.96, 139.30 (1C, aryl *C*), 137.82 (1C, aryl *C*), 137.61 (1C, aryl *C*), 137.02 (1C, aryl *C*), 136.25, 136.18, 133.41 (1C, aryl *C*), 133.01 (1C, aryl *C*), 128.69 (1C, aryl *C*), 127.48 (1C, aryl *C*), 126.45 (1C, aryl *C*), 124.97 (1C, aryl *C*), 124.02 (1C, aryl *C*), 121.11 (1C, aryl *C*), 115.32 (1C, aryl *C*), 112.05 (1C, aryl *C*), 64.74 (1C, sp^3-*C* of C_{60}), 58.93 (1C, sp^3-*C* of C_{60}), 43.98 (1C), 20.22 (1C). FT-IR ν/cm^{-1} (KBr) 2922, 2857, 1634, 1507, 1451, 1354, 1214, 1165, 1066, 1043, 806, 746, 704, 587, 526. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.08), 309 (4.58), 327 (4.53), 434 (3.55), 709 (2.60). MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{16}NO_2S$ $[M+H]^+$ 1006.0896, found 1006.0875.



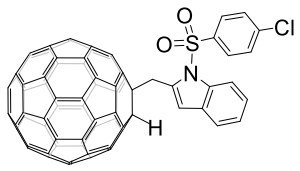
2n

Preparation of **2n**: By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1n** (28.3 mg, 0.10 mmol), $Cu(OTf)_2$ (18.3 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (15.6 mg, 43%) and **2n** (17.7 mg, 35%) as an amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.68 (d, J = 7.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.39–7.31 (m, 4H), 7.27 (t, J = 7.1 Hz, 1H), 6.77 (s, 1H), 5.29 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, all 2C unless indicated) δ 154.77, 153.65, 147.47 (1C), 147.24 (1C), 146.90, 146.36 (4C), 146.18, 146.15, 145.99, 145.76, 145.54, 145.37 (4C), 145.35, 144.70, 144.50, 143.19, 142.53 (4C), 142.20, 142.04, 141.98, 141.76, 141.63 (4C), 140.25, 140.03, 139.62 (1C, aryl *C*), 138.93 (1C, aryl *C*), 137.69 (1C, aryl *C*), 136.25 (4C), 136.22 (1C, aryl *C*), 134.62 (1C, aryl *C*), 129.70 (1C, aryl *C*), 129.17 (1C, aryl *C*), 126.74 (1C, aryl *C*), 125.13 (1C, aryl *C*), 124.36 (1C, aryl *C*), 123.63 (1C, aryl *C*), 121.03 (1C, aryl *C*), 115.76 (1C, aryl *C*), 113.95 (1C, aryl *C*), 64.96 (1C, sp^3-*C* of C_{60}), 58.70 (1C, sp^3-*C* of C_{60}), 44.08 (1C), 21.49 (1C). FT-IR ν/cm^{-1} (KBr) 2920, 2855, 1634, 1512, 1447, 1366, 1308, 1216, 1170, 1147, 1087, 1042, 744, 704, 593, 524. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.07), 309 (4.56), 329 (4.50), 434 (3.52), 707 (2.40). MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{16}NO_2S$ $[M+H]^+$ 1006.0896, found 1006.0881.



2o

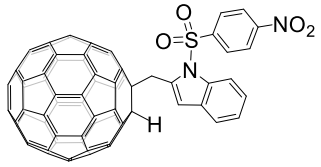
Preparation of **2o**: By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with **1o** (30.8 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (16.4 mg, 46%) and **2o** (16.0 mg, 32%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.27 (dd, J = 8.4, 0.7 Hz, 1H), 7.83 (d, J = 9.0 Hz, 2H), 7.53 (dd, J = 7.4, 0.9 Hz, 1H), 7.33 (ddd, J = 8.4, 7.4, 0.9 Hz, 1H), 7.30 (s, 1H), 7.26 (td, J = 7.4, 0.7 Hz, 1H), 6.89 (d, J = 9.0 Hz, 2H), 6.77 (s, 1H), 5.27 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 163.68 (1C, aryl *C*), 154.79, 153.67, 147.44 (1C), 147.21 (1C), 146.89, 146.32 (4C), 146.13 (4C), 145.97, 145.73, 145.50, 145.33 (6C), 144.68, 144.48, 143.16, 142.51 (4C), 142.18, 142.01, 141.95, 141.74, 141.60 (4C), 140.22, 140.01, 137.69 (1C, aryl *C*), 136.19 (4C + 1C, aryl *C*), 130.56 (1C, aryl *C*), 129.74 (1C, aryl *C*), 128.67 (aryl *C*), 125.05 (1C, aryl *C*), 124.26 (1C, aryl *C*), 120.97 (1C, aryl *C*), 115.81 (1C, aryl *C*), 114.37 (aryl *C*), 113.90 (1C, aryl *C*), 64.96 (1C, sp^3-*C* of C_{60}), 58.63 (1C, sp^3-*C* of C_{60}), 55.36 (1C), 44.07 (1C). FT-IR ν/cm^{-1} (KBr) 2924, 2838, 1633, 1591, 1497, 1449, 1362, 1309, 1262, 1217, 1165, 1119, 1091, 1024, 910, 828, 804, 743, 704, 673, 629, 578, 554, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.10), 308 (4.56), 327 (4.52), 434 (3.50), 707 (2.40). MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{16}NO_3S$ $[M+H]^+$ 1022.0845, found 1022.0830.



2p

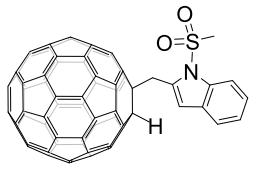
Preparation of **2p**: By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1p** (30.3 mg, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 100 °C for 2.0 h afforded recovered C_{60} (20.2 mg, 56%) and **2p** (17.9 mg, 35%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.41–7.35 (m, 2H), 7.31 (td, J = 7.5, 0.8 Hz, 1H), 6.78 (s, 1H), 5.29 (s, 2H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.50, 153.46, 147.46 (1C), 147.23 (1C), 146.84, 146.34 (4C), 146.17, 146.13, 145.91, 145.72, 145.53, 145.35 (6C), 144.68, 144.47, 143.18, 142.53 (4C), 142.16, 142.02, 141.96, 141.71, 141.62 (4C), 140.86 (1C, aryl *C*), 140.26, 140.01, 137.62 (1C, aryl *C*), 137.03 (1C, aryl *C*), 136.21 (4C + 1C, aryl *C*), 129.81 (1C, aryl *C*), 129.52 (aryl *C*), 127.80 (aryl *C*), 125.39 (1C, aryl *C*), 124.70 (1C, aryl *C*), 121.20 (1C, aryl *C*), 115.76 (1C, aryl *C*), 114.77 (1C, aryl *C*), 64.92 (1C, sp^3-*C* of C_{60}), 58.74 (1C, sp^3-*C* of C_{60}), 44.22 (1C). FT-IR ν/cm^{-1} (KBr) 2922, 1640, 1578, 1510, 1474, 1451, 1426, 1371, 1211, 1177, 1147, 1089, 1048, 1015, 820, 754, 704, 619, 574, 525.

UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.04), 309 (4.54), 330 (4.48), 434 (3.49), 707 (2.48). MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{13}NO_2S^{35}Cl$ $[M+H]^+$ 1026.0350, found 1026.0331.



2q

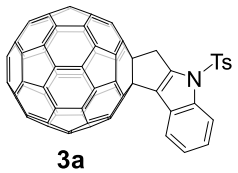
Preparation of **2q**: By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with **1q** (31.7 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) at 110 °C for 1.5 h afforded recovered C_{60} (16.9 mg, 47%) and **2q** (18.9 mg, 37%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.28 (d, J = 8.9 Hz, 2H), 8.22 (dd, J = 8.3, 0.7 Hz, 1H), 8.05 (d, J = 8.9 Hz, 2H), 7.55 (dd, J = 7.5, 0.6 Hz, 1H), 7.41–7.35 (m, 2H), 7.31 (td, J = 7.5, 0.7 Hz, 1H), 6.75 (s, 1H), 5.29 (s, 2H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.21, 153.24, 150.53 (1C, aryl *C*), 147.46 (1C), 147.23 (1C), 146.77, 146.35 (4C), 146.19, 146.14, 145.84, 145.68, 145.55, 145.41, 145.36, 145.33, 144.67, 144.45, 143.37 (1C, aryl *C*), 143.19, 142.56, 142.54, 142.13, 142.02, 141.95, 141.67, 141.64, 141.60, 140.29, 139.99, 137.47 (1C, aryl *C*), 136.25 (1C, aryl *C*), 136.17, 136.14, 129.85 (1C, aryl *C*), 127.65 (aryl *C*), 125.75 (1C, aryl *C*), 125.17 (1C, aryl *C*), 124.35 (aryl *C*), 121.46 (1C, aryl *C*), 115.70 (1C, aryl *C*), 115.64 (1C, aryl *C*), 64.86 (1C, sp^3-*C* of C_{60}), 58.84 (1C, sp^3-*C* of C_{60}), 44.38 (1C). FT-IR ν/cm^{-1} (KBr) 2921, 2860, 1604, 1529, 1449, 1429, 1374, 1347, 1312, 1178, 1147, 1088, 1048, 852, 809, 743, 681, 610, 573, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.09), 307 (4.58), 326 (4.53), 433 (3.54), 706 (2.65). MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{13}N_2O_4S$ $[M+H]^+$ 1037.0591, found 1037.0572.



2r

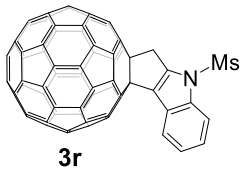
Preparation of **2r**: By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with **1r** (17.0 μL, 0.10 mmol), $Cu(OTf)_2$ (18.2 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) at 100 °C for 1.5 h afforded recovered C_{60} (21.9 mg, 61%) and **2r** (14.1 mg, 31%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 7.4 Hz, 1H), 7.41–7.30 (m, 3H), 6.76 (s, 1H), 5.28 (s, 2H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 154.51, 153.50, 147.47 (1C), 147.23 (1C), 146.87, 146.36 (4C), 146.19, 146.14, 146.09, 145.75, 145.53, 145.41, 145.37, 145.34, 144.71, 144.48, 143.20, 142.58, 142.54, 142.17, 142.06, 141.96, 141.69, 141.66, 141.61, 140.28, 139.91, 137.21 (1C, aryl *C*), 136.28 (4C), 136.20 (1C, aryl *C*), 129.51 (1C, aryl *C*), 125.34 (1C, aryl *C*), 124.44 (1C, aryl *C*), 121.30 (1C, aryl *C*), 114.89 (1C, aryl *C*),

113.64 (1C, aryl *C*), 64.95 (1C, sp^3-*C* of C_{60}), 59.23 (1C, sp^3-*C* of C_{60}), 44.04 (1C), 40.34 (1C). FT-IR ν/cm^{-1} (KBr) 2923, 2858, 1614, 1537, 1506, 1451, 1365, 1323, 1216, 1170, 1053, 959, 904, 809, 733, 627, 523. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.06), 307 (4.56), 327 (4.51), 434 (3.54), 707 (2.70). MALDI-TOF MS *m*/*z* calcd for $C_{70}H_{12}NO_2S$ $[M+H]^+$ 930.0583, found 930.0568.



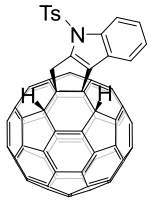
3a

Preparation of **3a**: the reaction mixture of **2a** (10.4 mg, 0.01 mmol) with $KMnO_4$ (15.6 mg, 0.10 mmol), and TFA (14.8 μL, 0.20 mmol) in CB (2 mL) at 25 °C for 2.0 h afforded **3a** (7.9 mg, 76%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.40–7.34 (m, 3H), 7.29–7.23 (m, 1H), 5.19 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 2C unless indicated) δ 155.79, 150.54, 147.36 (1C), 147.19 (1C), 146.09, 146.06 (1C, aryl *C*), 145.97, 145.96, 145.71, 145.63, 145.33, 145.22 (4C), 145.18, 145.10, 145.06, 144.41, 144.27, 143.07, 142.60, 142.50, 142.30, 142.11, 141.93, 141.91, 141.88, 141.59, 140.90, 140.55, 140.06 (1C, aryl *C*), 139.42 (1C, aryl *C*), 136.03, 135.75, 135.09 (1C, aryl *C*), 130.07 (aryl *C*), 126.96 (aryl *C*), 126.08 (1C, aryl *C*), 125.56 (1C, aryl *C*), 124.75 (1C, aryl *C*), 124.04 (1C, aryl *C*), 119.20 (1C, aryl *C*), 114.74 (1C, aryl *C*), 74.05 (1C, sp^3-*C* of C_{60}), 69.98 (1C, sp^3-*C* of C_{60}), 42.27 (1C), 21.77 (1C). FT-IR ν/cm^{-1} (KBr) 2922, 2856, 1604, 1509, 1438, 1374, 1218, 1175, 1121, 1089, 1018, 746, 665, 571, 531. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.10), 309 (4.56), 323 (4.53), 430 (3.51), 702 (2.60). MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{13}NO_2S$ $[M]^+$ 1003.0662, found 1003.0652.



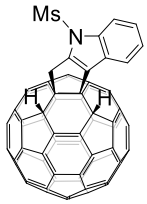
3r

Preparation of **3r**: the reaction mixture of **2r** (9.3 mg, 0.01 mmol) with $KMnO_4$ (15.6 mg, 0.10 mmol), and TFA (14.8 μL, 0.20 mmol) in CB (2 mL) at 25 °C for 2.0 h afforded **3r** (6.3 mg, 68%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 4.91 (s, 2H), 3.17 (s, 3H). (*It should be noted that the very low solubility of* ***3r*** *prevented us from obtaining a* ^{13}*C NMR spectrum with a good signal-to noise ratio*). FT-IR ν/cm^{-1} (KBr) 2923, 2848, 1618, 1509, 1442, 1398, 1368, 1324, 1286, 1221, 1171, 1146, 1120, 1088, 1019, 961, 931, 905, 869, 784, 744, 632, 602, 570, 533. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.06), 311 (4.50), 325 (4.48), 430 (3.48), 701 (2.65). MALDI-TOF MS *m*/*z* calcd for $C_{70}H_9NO_2S$ $[M]^+$ 927.0349, found 927.0330.



4a

Preparation of **4a**: the reaction mixture of **2a** (10.0 mg, 0.01 mmol) with TfOH (8.8 μL, 0.10 mmol) in CB (2 mL) at 0 °C for 5 min afforded **4a** (4.1 mg, 41%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.15–8.10 (m, 1H), 8.00–7.96 (m, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.42–7.33 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.36 (s, 2H), 4.74 (d, J = 18.1 Hz, 1H), 4.70 (d, J = 18.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, all 1C unless indicated) δ 149.24, 149.20, 149.13, 148.84, 148.47, 148.30, 148.21, 148.12, 147.57, 146.99, 146.93, 146.63, 146.56, 146.54, 146.40, 146.28, 145.91, 145.77, 145.17, 145.08, 145.03, 144.97 (2C), 144.94, 144.78 (3C), 144.63, 144.55, 144.53, 144.36, 144.09 (2C), 144.08, 144.04, 143.79, 143.64, 143.09, 143.04, 142.95, 142.78, 142.63 (2C), 142.61, 142.52, 142.35, 142.29, 142.02, 141.65, 141.37, 141.23, 140.59, 139.67, 138.26, 136.19, 136.12, 135.99, 134.79, 134.39, 133.46, 130.43 (aryl *C*), 129.98 (2C, aryl *C*), 126.83 (2C, aryl *C*), 124.87 (aryl *C*), 124.66 (aryl *C*), 124.26 (aryl *C*), 118.50 (aryl *C*), 114.92 (aryl *C*), 66.71 (sp^3-*C* of C_{60}), 62.45 (sp^3-*C* of C_{60}), 61.46 (sp^3-*C* of C_{60}), 54.91 (sp^3-*C* of C_{60}), 51.71, 21.71. FT-IR ν/cm^{-1} (KBr) 2917, 2852, 1510, 1442, 1368, 1216, 1172, 1120, 1089, 809, 743, 702, 666, 573, 525. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.08), 333 (4.45), 433 (3.75). MALDI-TOF MS m/z calcd for $C_{76}H_{15}NO_2S$ $[M]^+$ 1005.0818, found 1005.0802.



4r

Preparation of **4r**: the reaction mixture of **3r** (9.3 mg, 0.01 mmol) with TfOH (8.8 μL, 0.10 mmol) in CB (2 mL) at 0 °C for 5 min afforded **4r** (7.3 mg, 78%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.10–8.06 (m, 1H), 8.05–8.01 (m, 1H), 7.47–7.43 (m, 2H), 6.43 (d, J = 1.7 Hz, 1H), 6.37 (d, J = 1.7 Hz, 1H), 4.67 (d, J = 18.1 Hz, 1H), 4.63 (d, J = 18.1 Hz, 1H), 3.26 (s, 3H). (*It should be noted that the very low solubility of* ***4r*** *prevented us from obtaining a* ^{13}*C NMR spectrum with a good signal-to-noise ratio*). FT-IR ν/cm^{-1} (KBr) 2923, 2846, 1617, 1508, 1442, 1364, 1323, 1262, 1221, 1169, 1119, 1017, 958, 830, 775, 745, 564, 537. UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.00), 333 (4.38), 436 (3.68). MALDI-TOF MS m/z calcd for $C_{70}H_{11}NO_2S$ $[M]^+$ 929.0505, found 929.0486.

Scale-Up Reaction

A mixture of C_{60} (359.9 mg, 0.5 mmol), **1h** (316.8 mg, 1.0 mmol), $Cu(OTf)_2$ (180.6 mg, 0.5 mmol), and DMAP (61.4 mg, 0.5 mmol) was dissolved in CB (60 mL). Then the solution was vigorously stirred at 100 ^oC for 2 h. The resulting solution was evaporated in *vacuo* and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (107.4 mg, 30%) and then the desired product **2h** (205.6 mg, 40%).

Single-Crystal X-Ray Crystallography of 4a

Black block crystals of **4a** was obtained by slow evaporation of a saturated solution in carbon disulfide at 15 ºC. Single-crystal X-ray diffraction data were collected on a diffractometer (Gemini S Ultra, Agilent Technologies) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 6.46° < 2θ < 132.06°. The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares refinement using the SHELXL-97 program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 1557961.

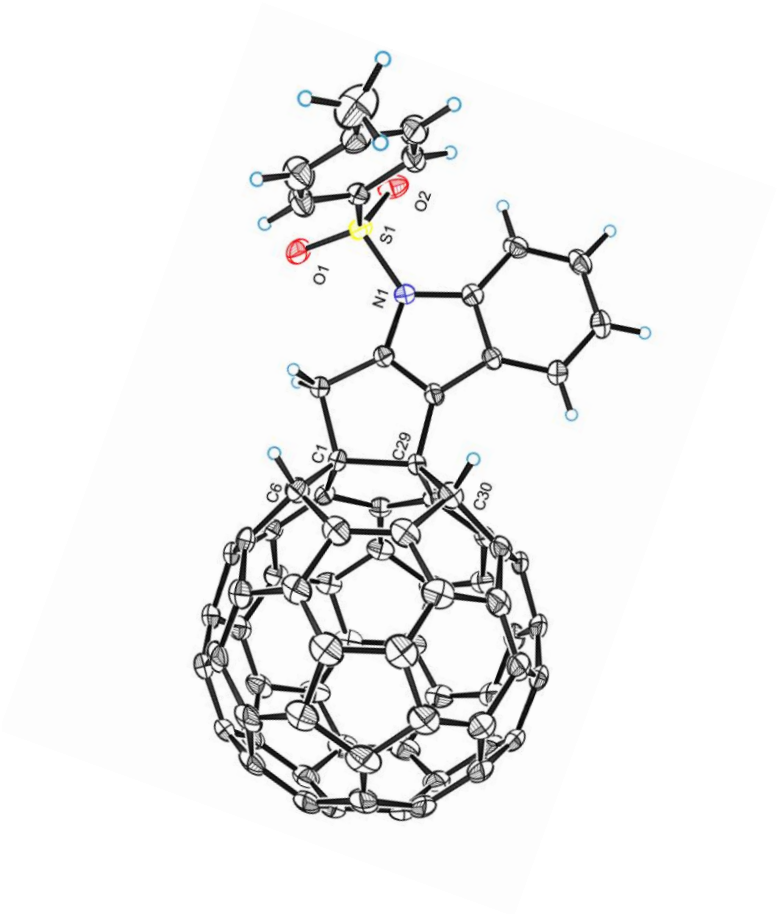


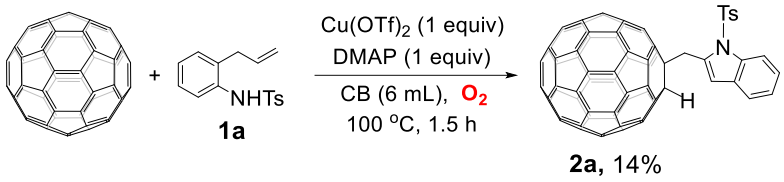
Figure S1. ORTEP Diagrams of **4a** with 20% Thermal Ellipsoids. The Carbon Disulfide Molecule is Omitted for Clarity.

Table S2. Crystal Data and Structure Refinement for 4a

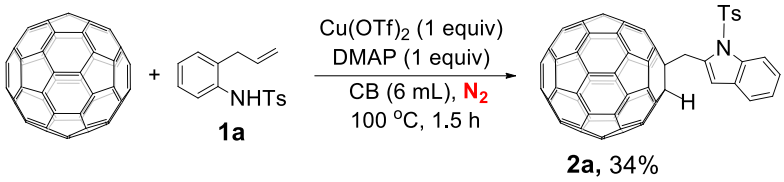
Identification code	1557961
Empirical formula	$C_{77}H_{15}NO_2S_3$
Formula weight	1082.08
Temperature/K	292(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.9333(2)
b/Å	32.2929(6)
c/Å	28.6843(6)
α/°	90
β/°	96.813(2)
γ/°	90
Volume/Å^3	9136.2(3)
Z	8
ρ_{calc} g/cm^3	1.573
μ/mm^{-1}	1.981
F(000)	4384.0
Crystal size/mm^3	0.320 × 0.300 × 0.210
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.278 to 143.052
Index ranges	$-11 \le h \le 10$, $-39 \le k \le 27$, $-34 \le l \le 24$
Reflections collected	37361
Independent reflections	17231 [R_{int} = 0.0311, R_{sigma} = 0.0356]
Data/restraints/parameters	17231/0/1497
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0714, wR_2 = 0.1767
Final R indexes [all data]	R_1 = 0.0880, wR_2 = 0.1869
Largest diff. peak/hole / e Å^{-3}	0.50/–0.74

Mechanism Studies

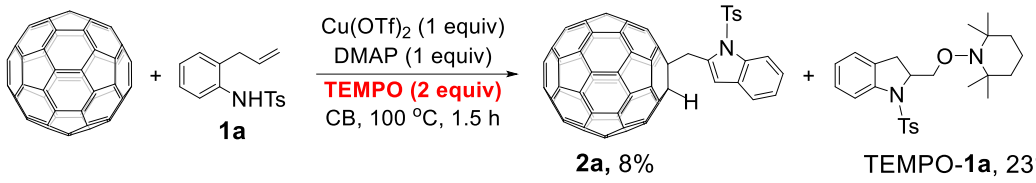
Control Experiments



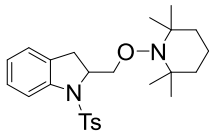
A mixture of C_{60} (36.1 mg, 0.05 mmol), **1a** (28.7 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), and DMAP (6.1 mg, 0.05 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h under the oxygen atmosphere (an oxygen balloon was used to supply the oxygen atmosphere). The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (27.7 mg, 77%) and then the desired product **2a** (7.1 mg, 14%).



A mixture of C_{60} (35.9 mg, 0.05 mmol), **1a** (28.9 mg, 0.10 mmol), $Cu(OTf)_2$ (18.3 mg, 0.05 mmol), and DMAP (6.2 mg, 0.05 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h under the nitrogen atmosphere (a nitrogen balloon was used to supply the nitrogen atmosphere). The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (16.6 mg, 46%) and then the desired product **2a** (17.1 mg, 34%).

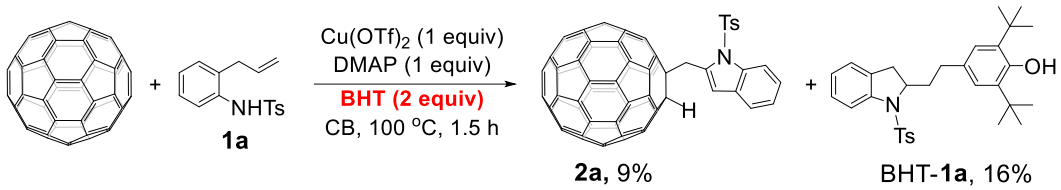


A mixture of C_{60} (36.0 mg, 0.05 mmol), **1a** (28.3 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), DMAP (6.2 mg, 0.05 mmol), and TEMPO (16.1 mg, 0.10 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h. The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (30.0 mg, 83%) and then the desired product **2a** (4.2 mg, 8%). Finally, the TEMPO-**1a** (10.1 mg, 23%) was isolated using PE/EtOAc = 15:1 as the eluent.

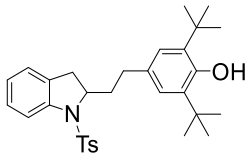


TEMPO-**1a**

TEMPO-**1a**.[1b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.21–7.13 (m, 3H), 7.05 (d, J = 6.9 Hz, 1H), 7.00 (td, J = 7.3, 0.7 Hz, 1H), 4.38–4.30 (m, 1H), 4.01 (dd, J = 9.0, 4.8 Hz, 1H), 3.94 (dd, J = 9.0, 6.6 Hz, 1H), 2.83 (dd, J = 16.0, 2.6 Hz, 1H), 2.74 (dd, J = 16.0, 9.2 Hz, 1H), 2.35 (s, 3H), 1.38–1.31 (m, 6H), 1.18 (s, 3H), 1.13 (s, 3H), 0.98 (s, 3H), 0.87 (s, 3H).

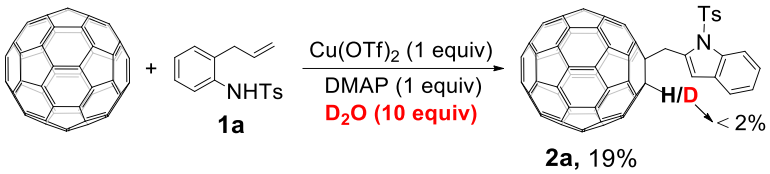


A mixture of C_{60} (35.9 mg, 0.05 mmol), **1a** (28.6 mg, 0.10 mmol), $Cu(OTf)_2$ (18.0 mg, 0.05 mmol), DMAP (6.1 mg, 0.05 mmol), and BHT (22.2 mg, 0.10 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h. The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (29.5 mg, 82%) and then the desired product **2a** (4.5 mg, 9%). Finally, the BHT-**1a** (8.0 mg, 16%) was isolated using PE/EtOAc = 15:1 as the eluent.

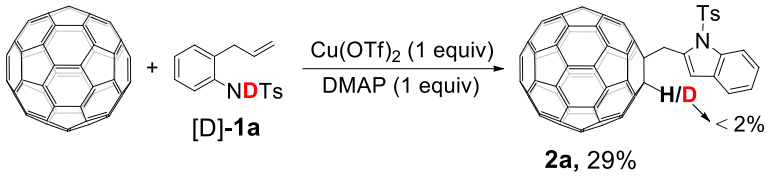


BHT-**1a**

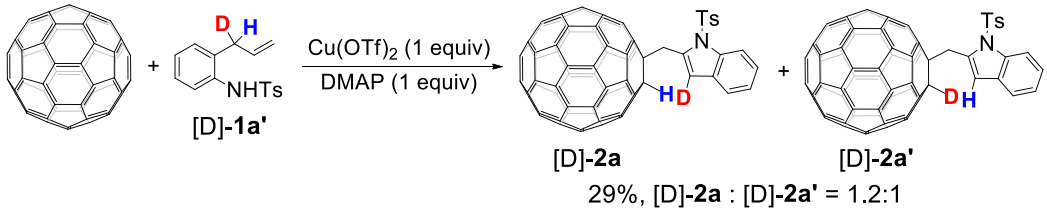
BHT-**1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 6.8 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.73 (s, 2H), 6.60 (d, J = 7.7 Hz, 1H), 5.28–5.15 (m, 1H), 5.13 (s, 1H), 4.98 (d, J = 12.8 Hz, 1H), 4.89 (s, 1H), 4.88–4.83 (m, 1H), 4.08 (d, J = 12.8 Hz, 1H), 3.22 (dd, J = 15.9, 7.5 Hz, 1H), 3.00 (dd, J = 15.9, 6.3 Hz, 1H), 2.46 (s, 3H), 1.27 (s, 18H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.65, 143.47, 142.82, 137.29, 136.97, 136.57, 135.72, 130.03, 129.65, 128.36, 128.29, 128.09, 126.87, 126.42, 125.49, 116.15, 56.52, 35.06, 34.21, 30.21, 21.72.



D₂O-Labeled Experiments: A mixture of C_{60} (35.6 mg, 0.05 mmol), **1a** (28.6 mg, 0.10 mmol), $Cu(OTf)_2$ (17.8 mg, 0.05 mmol), DMAP (6.6 mg, 0.05 mmol), and D_2O (9.0 μL, 0.50 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h. The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (20.0 mg, 56%) and then the desired product **2a** with less than 2% deuterium incorporation (9.6 mg, 19%).



[D]-1a-Labeled Experiments: A mixture of C_{60} (36.0 mg, 0.05 mmol), [D]-**1a** (28.8 mg, 0.10 mmol), $Cu(OTf)_2$ (18.4 mg, 0.05 mmol), and DMAP (6.4 mg, 0.05 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h. The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (20.3 mg, 56%) and then the desired product **2a** with less than 2% deuterium incorporation (14.4 mg, 29%).



[D]-1a'-Labeled Experiments: A mixture of C_{60} (36.0 mg, 0.05 mmol), [D]-**1a'** (28.7 mg, 0.10 mmol), $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), and DMAP (6.3 mg, 0.05 mmol) was dissolved in CB (6 mL). Then the solution was vigorously stirred at 100 °C for 1.5 h. The resulting solution was evaporated in vacuo and then separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent to give recovered C_{60} (19.3 mg, 54%) and then the desired product [D]-**2a** and [D]-**2a'** with a molar ratio of 1.2:1 (14.4 mg, 29%).

Table S3. Half-Wave Reduction Potentials[a]

compound	E_1	E_2
C_{60}	–1.080	–1.473
PCBM	–1.160	–1.538
2a	–1.177	–1.550
2b	–1.185	–1.556
2c	–1.177	–1.545
2d	–1.180	–1.550
2e	–1.175	–1.550
2f	–1.162	–1.535
2g	–1.155	–1.547
2h	–1.180	–1.560
2i	–1.172	–1.540
2j	–1.177	–1.542
2k	–1.185	–1.563
2l	–1.175	–1.545
2m	–1.178	–1.552
2n	–1.181	–1.559
2o	–1.181	–1.566
2p	–1.174	–1.536
2q	–1.174	–1.371
2r	–1.174	–1.552
3a	–1.144	–1.527
3r[b]	–1.144	–1.522
4a	–1.223	–1.603
4r	–1.220	–1.600

[a]Versus ferrocene/ferrocenium couple. Experimental conditions: 1 mM of **2a** (or **2b**–**r**, **3a**, **4a**, C_{60}, PCBM) and 0.1 M of *n*-Bu_4NClO_4 in anhydrous ODCB; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 20 mV s^{-1}. [b]Saturated solution.

Device Fabrication. The ITO-coated glass substrate with a sheet resistance of 10 $\Omega \cdot \square^{-1}$ (purchased from Shenzhen Nan Bo Group, China) was ultrasonicated in a detergent (2% RBS aqueous solution, v/v), deionized water, acetone and isopropanol for 15 min every time, and subsequently dried in an oven at 60 ^{o}C overnight. 0.1 M zinc acetate dihydrate was dissolved in a mixture of 2-methoxyethanol (10 mL) and ethanolamine under stirring for 10 h at 60 ^{o}C for the hydrolysis reaction. The ZnO precursor solution was spin-coated onto the cleaned ITO-coated substrate at 2000 rpm for 30 s, and then heated at 200 ^{o}C for 10 min in N_2 and 200 ^{o}C for 60 min in air to form a ZnO film (~ 40 nm). For active layer deposition, P3HT:PCBM (1:0.8, w/w; 36 mg/mL in total) dissolved in *o*-dichlorobenzene (*o*-DCB) was spin-coated onto the ZnO layer at 800 rpm for 60 s in a glovebox, followed by evaporation of the *o*-DCB solvent in a vacuum for 2 h to form a thin active layer (~ 170 nm), and then the P3HT:PCBM film was annealed at 135 ^{o}C for 10 min. Finally, the device was transferred into a vacuum chamber (~ 10^{-5} Torr), and MoO_3 (~ 10 nm) and the Ag electrode (~ 100 nm) were sequentially deposited thermally atop the active layer. The active areas of P3HT:PCBM devices were all defined as 2 × 5 mm^2. For active layer deposition, P3HT:**2a** and P3HT:**2r** were fabricated by the above procedure.

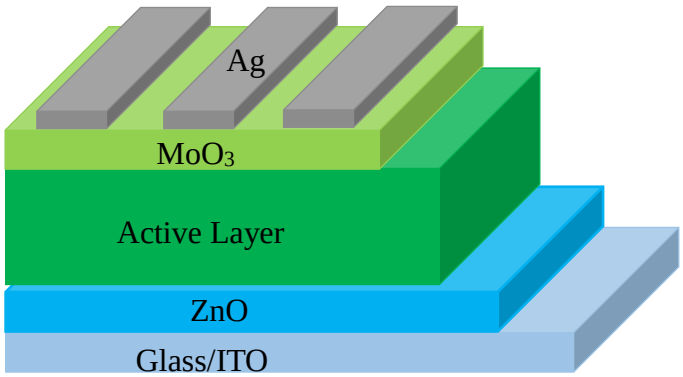


Figure S2. Schematic Structures of the ITO/ZnO/Active Layer/MoO_3/Ag BHJ-iPSC Devices.

Measurement and Characterization. The current density–voltage (*J–V*) characterization of BHJ-iPSC devices was carried out by using a Keithley 2400 source measurement unit under simulated AM 1.5 irradiation (100 mW cm^{-2}) with a standard xenon-lamp-based solar simulator (Oriel Sol 3A, USA). The solar simulator illumination intensity was calibrated by using a monocrystalline silicon reference cell (Oriel P/N 91 150 V, with KG-5 visible colour filter) calibrated by the National Renewable Energy Laboratory (NREL). All the measurements were carried out in a glovebox and a mask with a well-defined area size of 10 mm^2 was attached onto the cell to define the effective area so as to ensure accurate measurements.

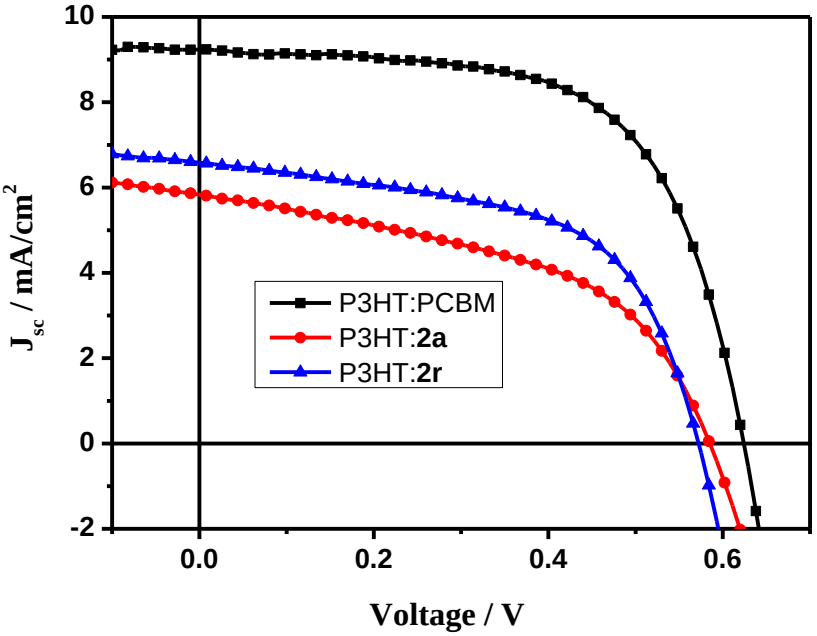


Figure S3. *J–V* Curves of Different Active Layer Systems Including P3HT:PCBM, P3HT:**2a** and P3HT:**2r**. The Measurements were Carried Out under Illumination of an AM 1.5 Solar Simulator (100 mW cm^{-2}) in a Glovebox.

Table S4. Photovoltaic Parameters of OPVs Based on a Blend of P3HT with Different Acceptors Measured under AM 1.5G Illumination of 100 mW/cm^2.[a]

P3HT:acceptor	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
P3HT:PCBM[b]	0.62 ± 0.00	9.24 ± 0.14	63.28 ± 0.84	3.62 ± 0.05
P3HT:**2a**	0.57 ± 0.02	5.93 ± 0.24	47.93 ± 3.14	1.63 ± 0.20
P3HT:**2r**	0.57 ± 0.01	6.51 ± 0.15	58.92 ± 1.53	2.15 ± 0.06

[a]In all cases, the values were averaged around ten independent devices. [b]P3HT:PCBM (1:0.8, w/w; 36 mg/mL in total) as a reference device.

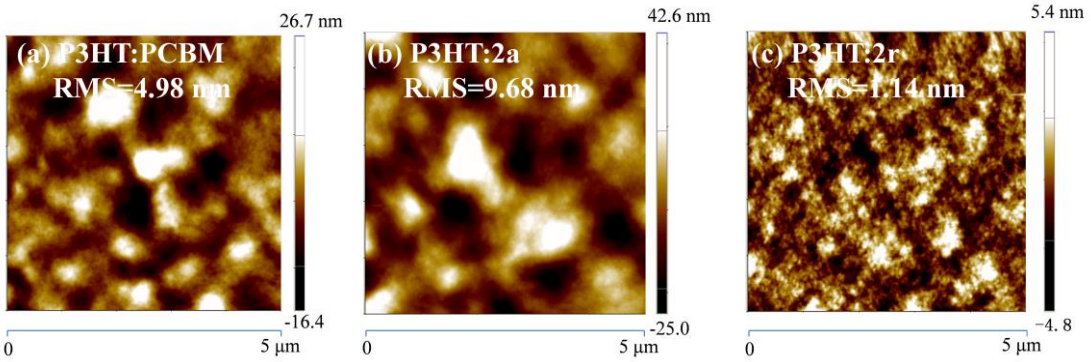
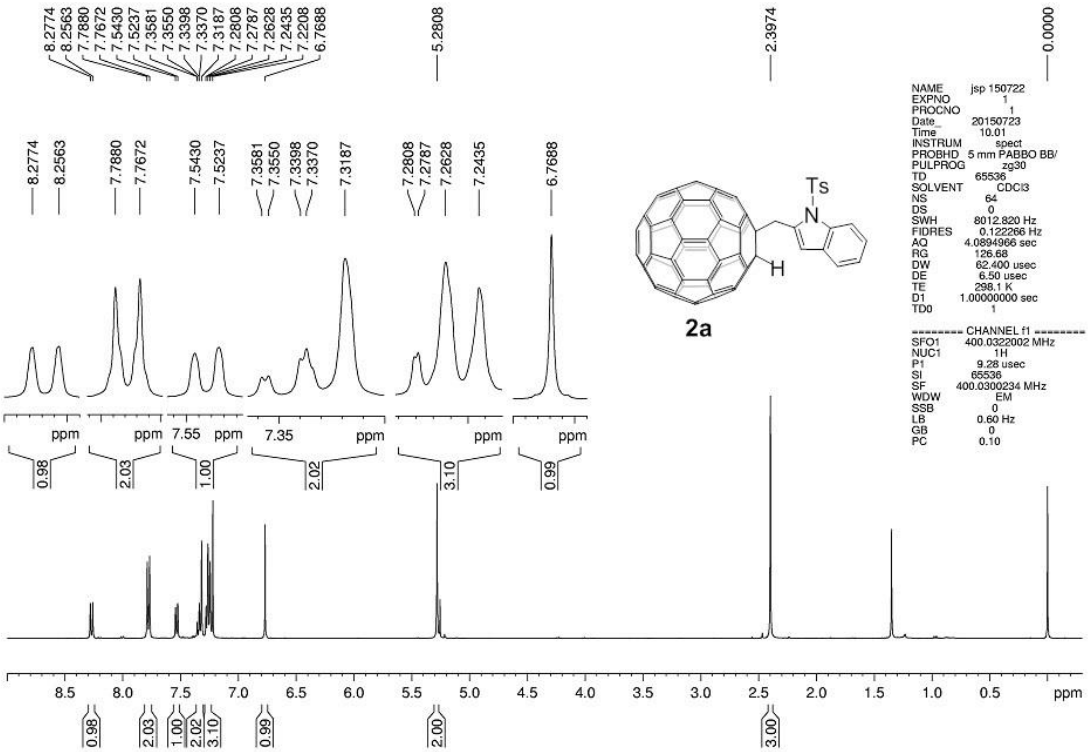


Figure S4. AFM Topographic Images (5 μm × 5 μm) of Photoactive Films Based on P3HT Blended with Different Acceptors.

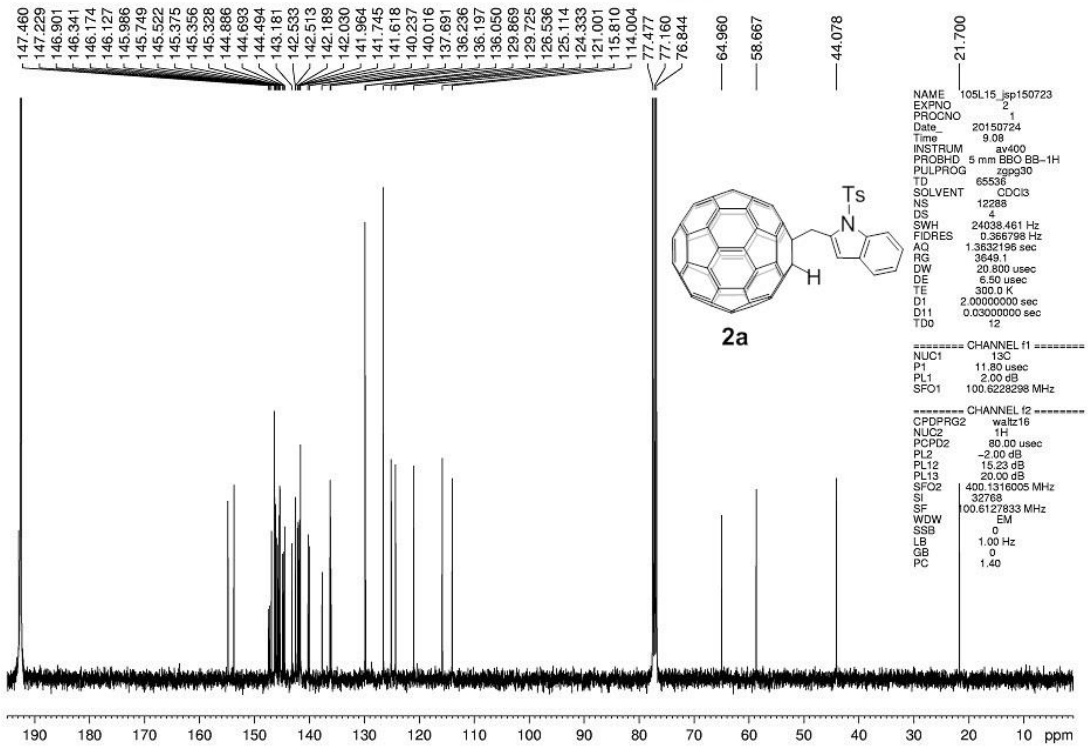
Theoretically, the V_{oc} value is linearly correlated with the difference between and the LUMO level of the acceptor and the HOMO level of donor in bulk heterojunction polymer solar cells. However, for the practical device, the actual V_{oc} value is sensitively affected by the shunt resistance of the device, interface dipole, active layer morphology, and imperfect contacts with the electrodes.[2]

In order to unveil the reason responsible for the lower V_{oc} of devices based on **2a** and **2r** acceptors, we carried out an additional study on the morphologies of the photoactive films based on different acceptors measured by atomic force microscopy (AFM). According to the comparison of the AFM images based on three different acceptors (Figure S4), obviously the P3HT:**2a** film is much rougher than P3HT:PCBM as reflected from its much larger root-mean-square (RMS) roughness, suggesting that phase separation within the P3HT:**2a** photoactive layer is too large for efficient exciton separations (ideally 20 nm).[2] This would result in insufficient exciton separation and consequently the decrease of V_{oc} value. On the other hand, for P3HT:**2r** film, its RMS roughness (1.14 nm) is even much smaller than that of P3HT:PCBM (4.98 nm). This suggests too small phase separation within the P3HT:**2r** photoactive layer, which would lead to enhanced probability of charge carrier recombination, and consequently the decrease of V_{oc} value as well. In this regard, the phase separation within the P3HT:PCBM photoactive layer seems to be optimum for efficient exciton separations.

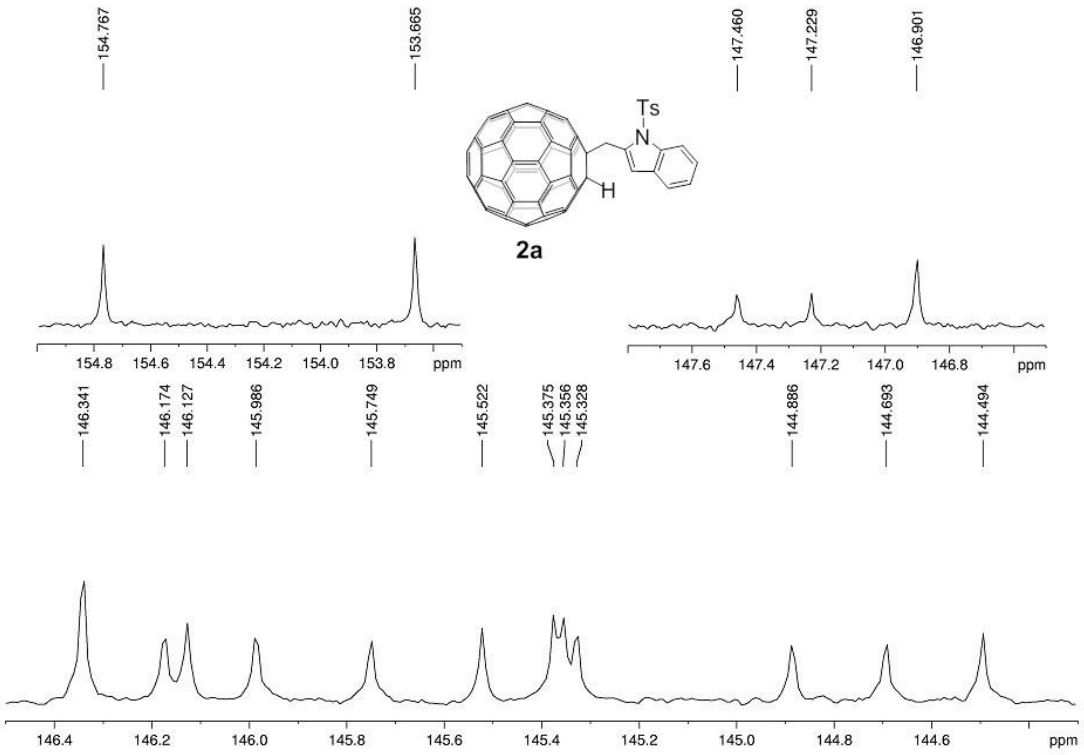
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2a



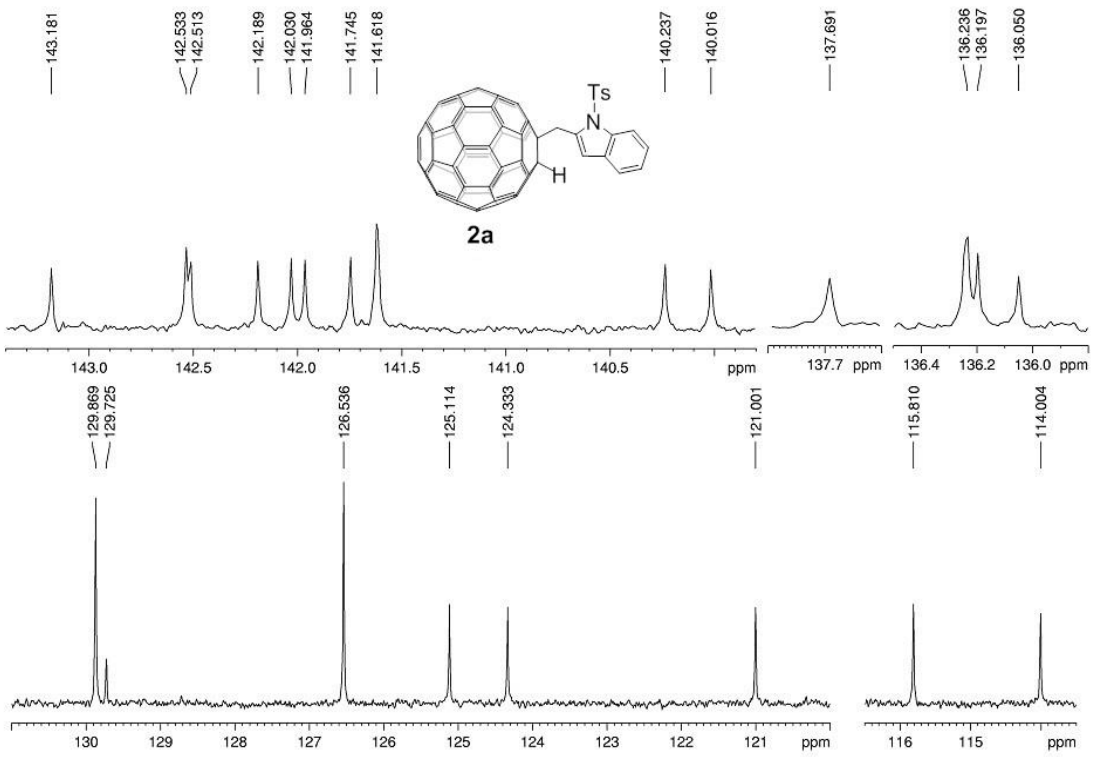
^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2a



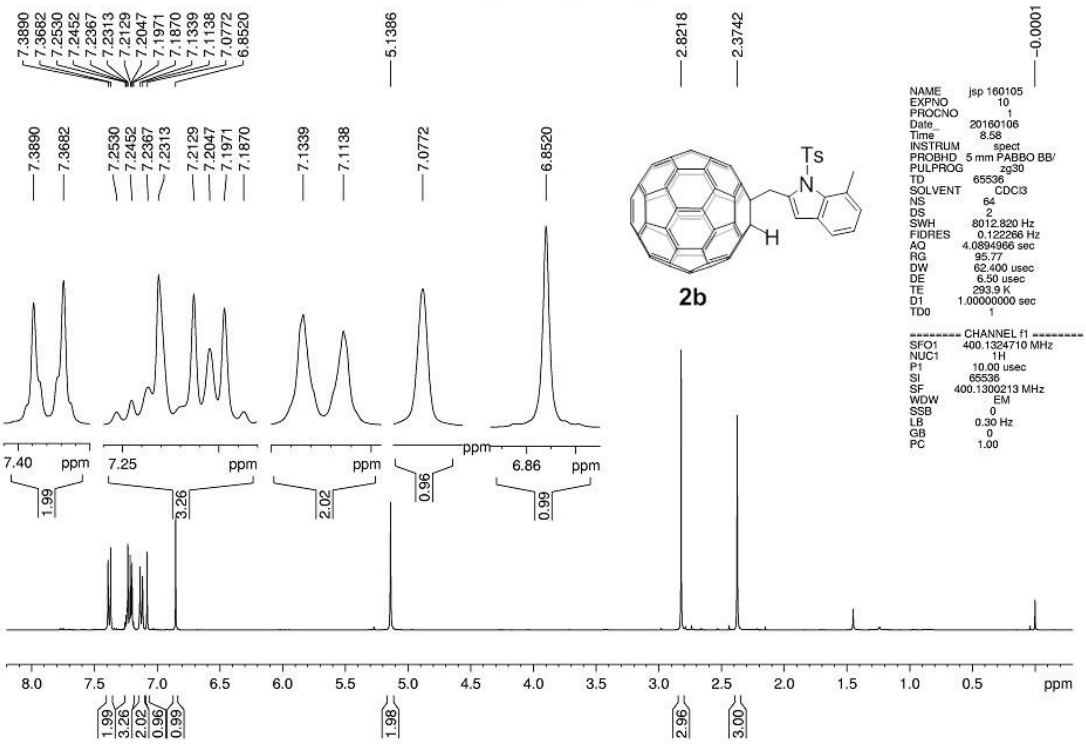
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2a



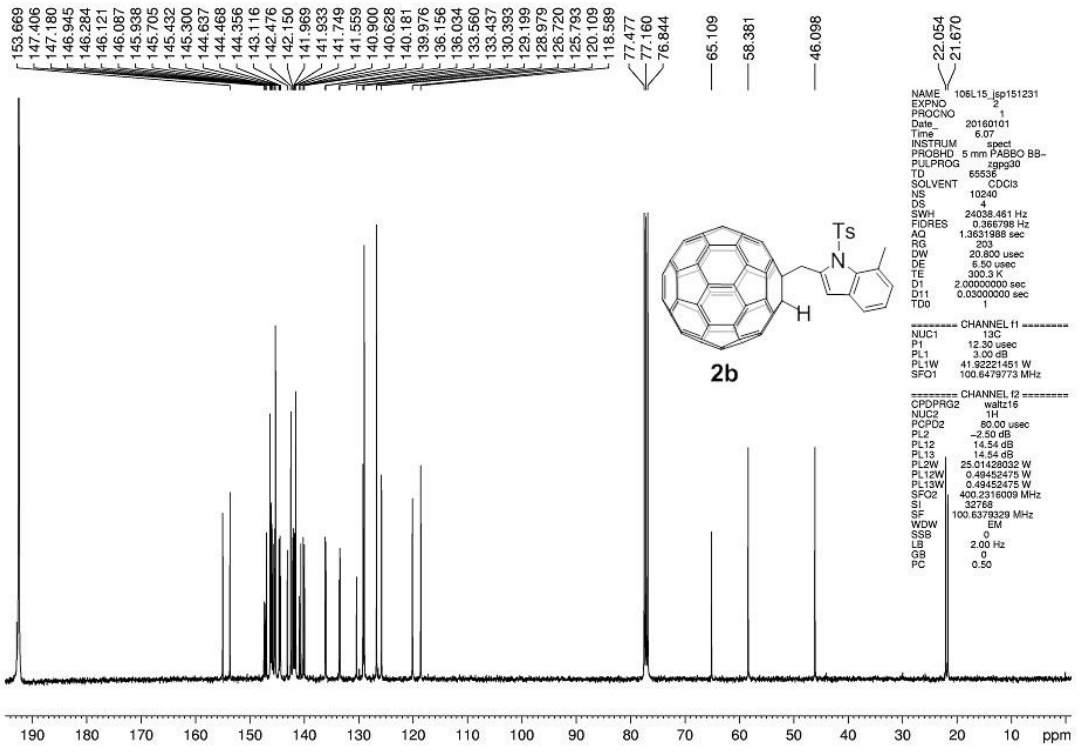
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2a



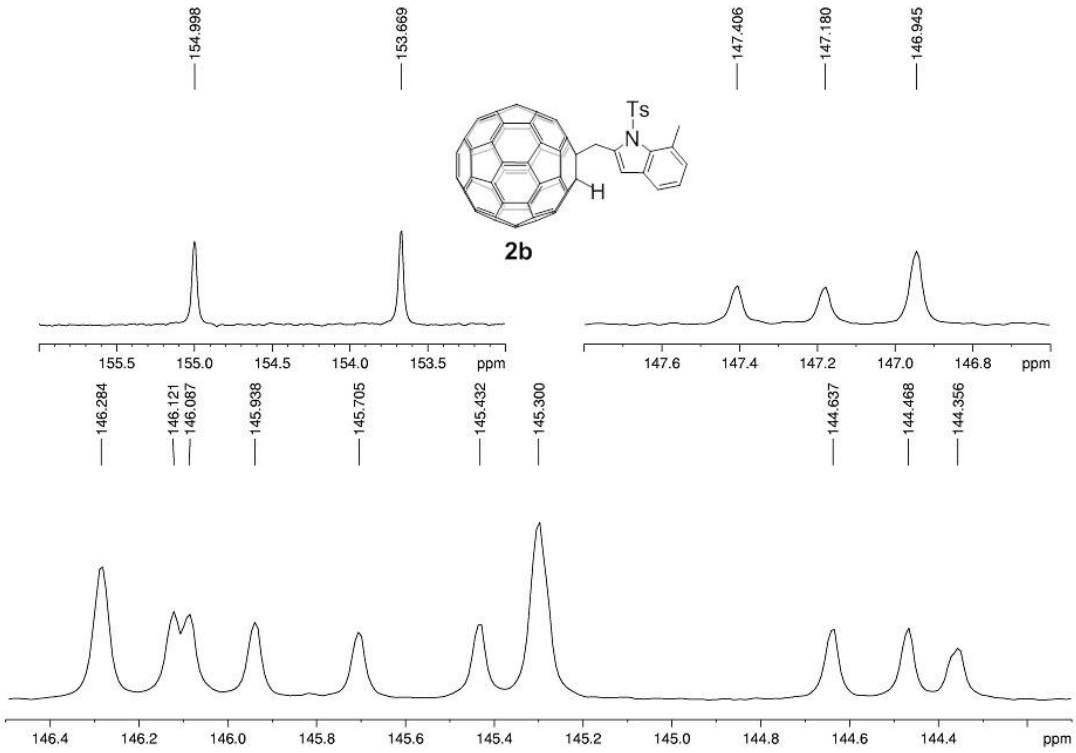
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2b



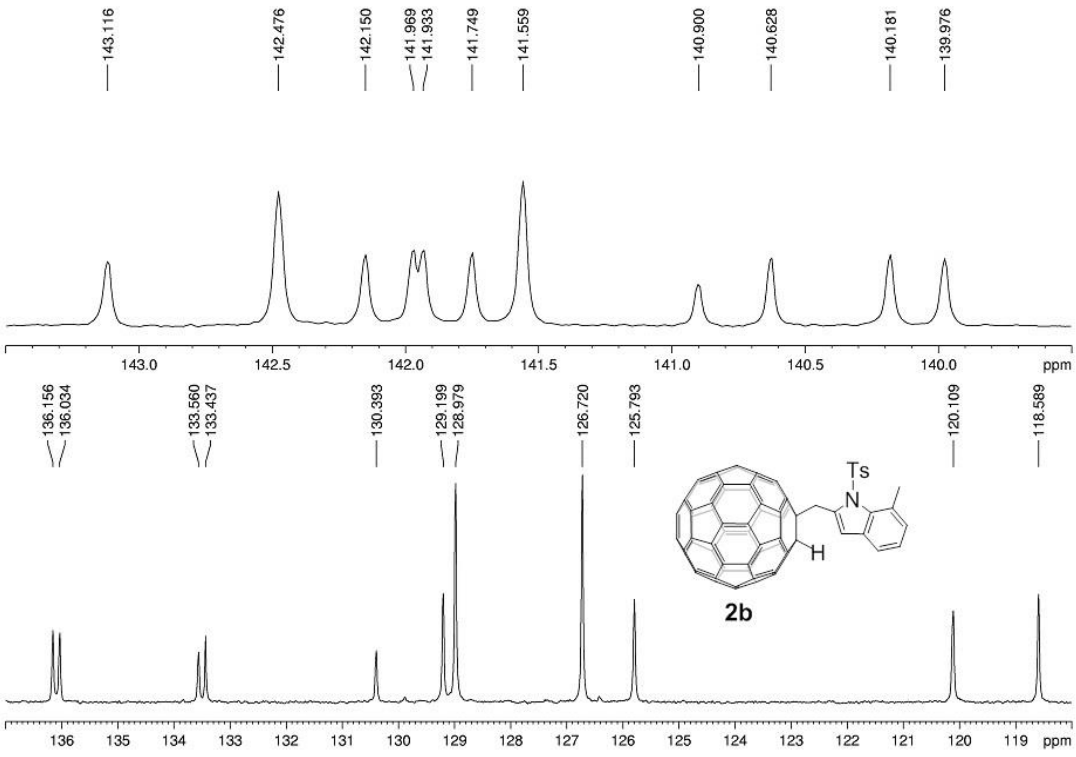
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2b



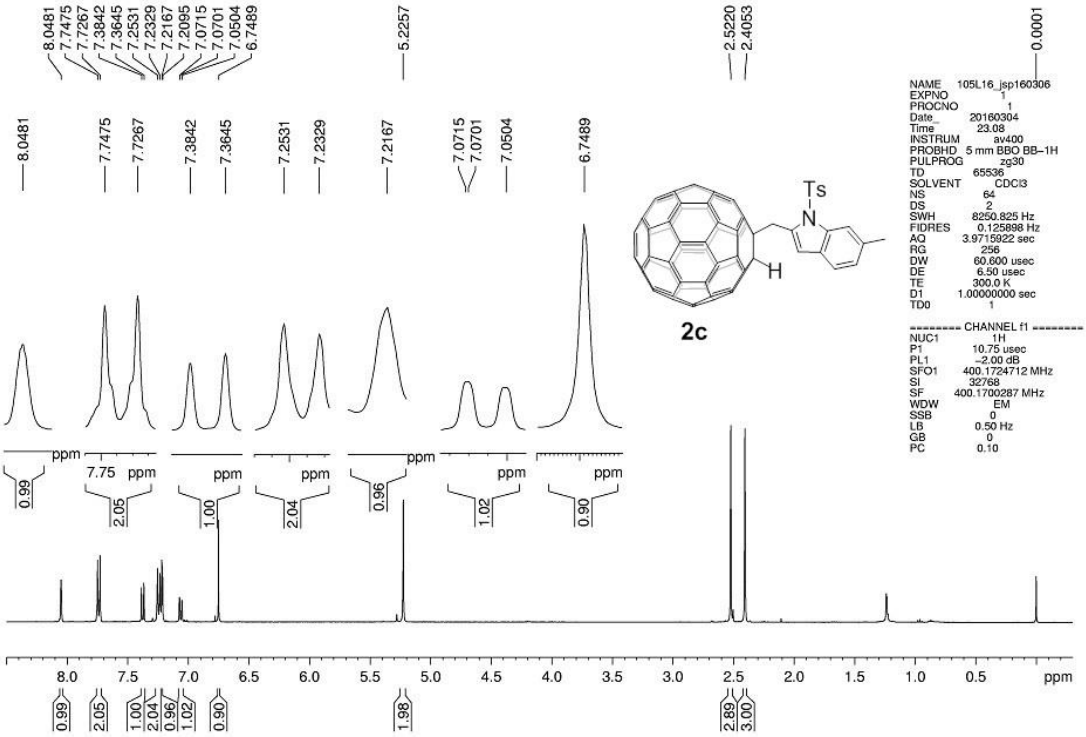
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2b



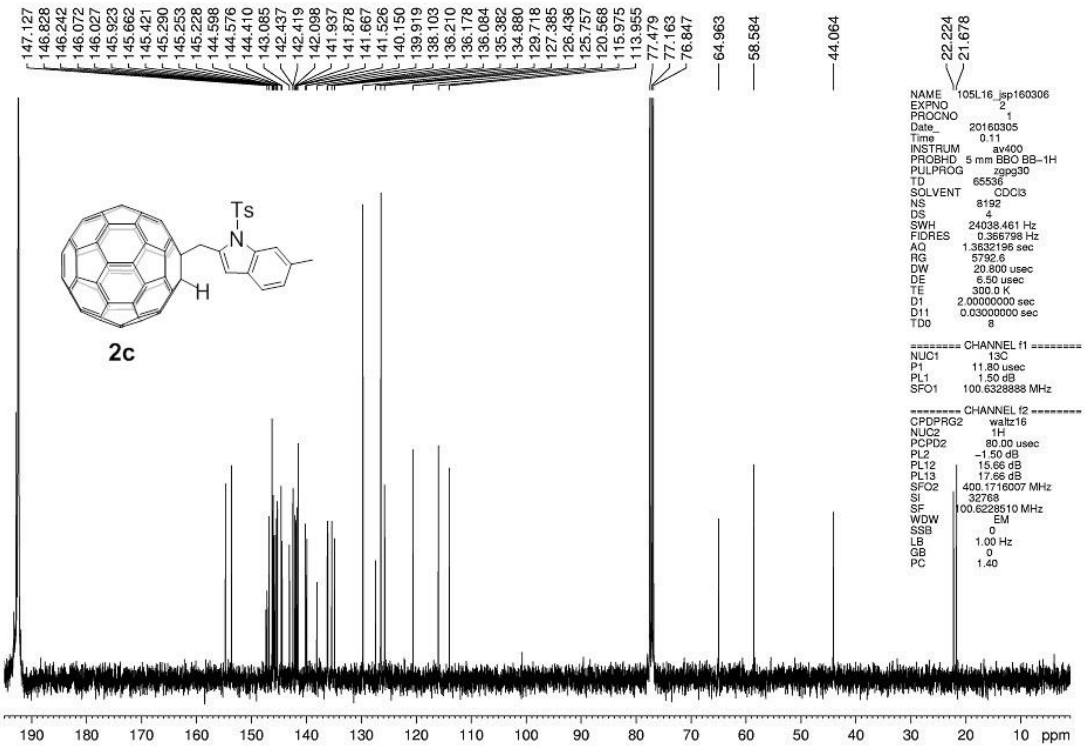
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2b



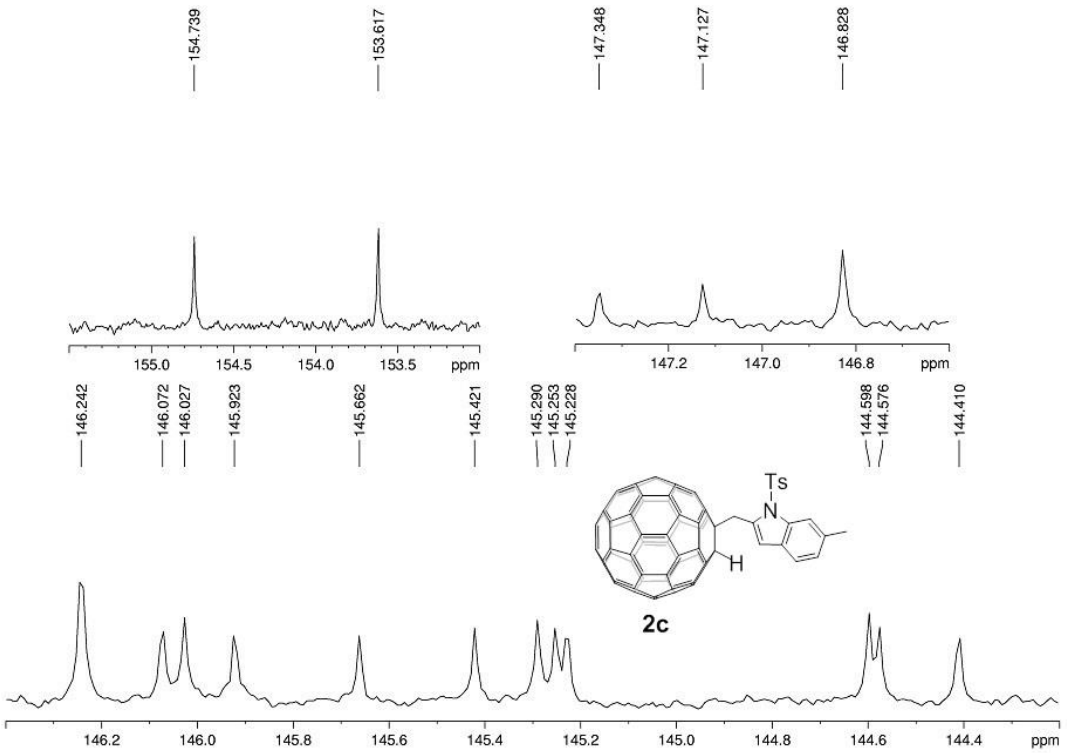
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2c



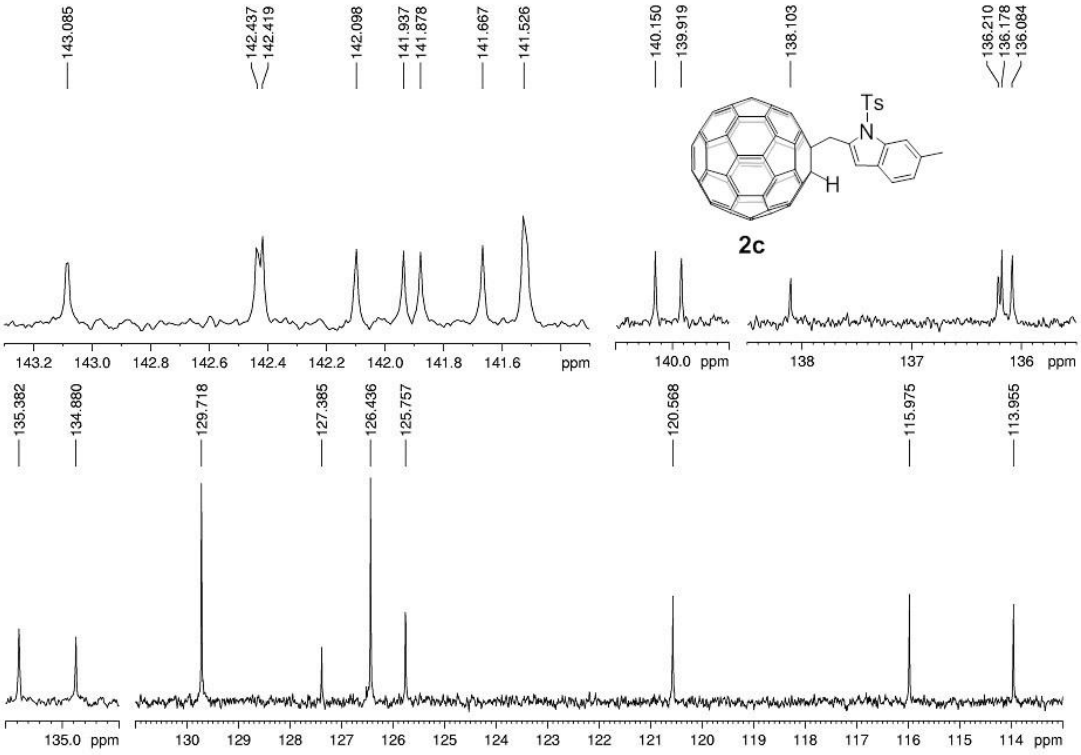
^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2c



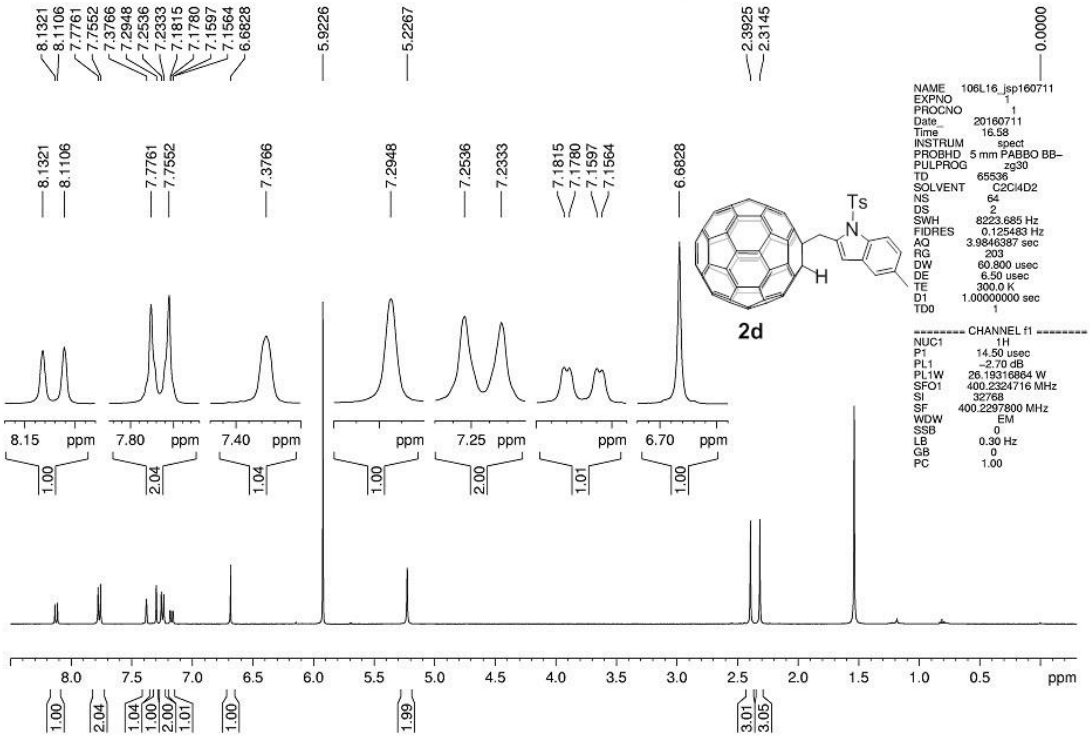
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2c



Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2c



^{1}H NMR (400 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2d



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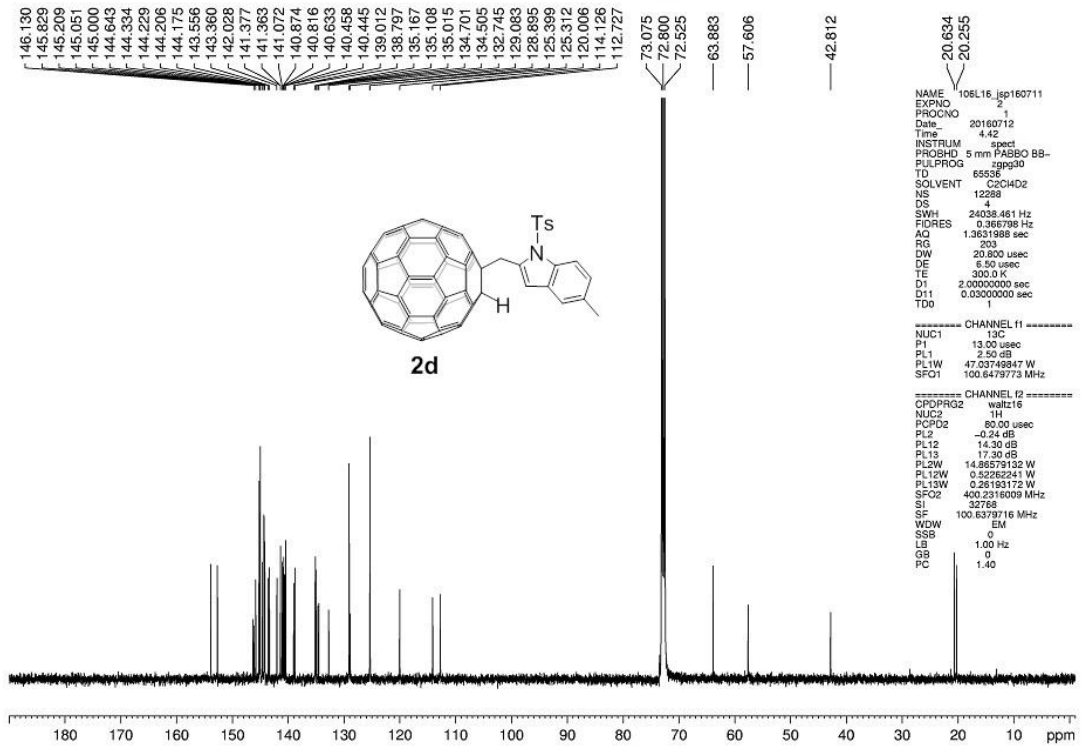
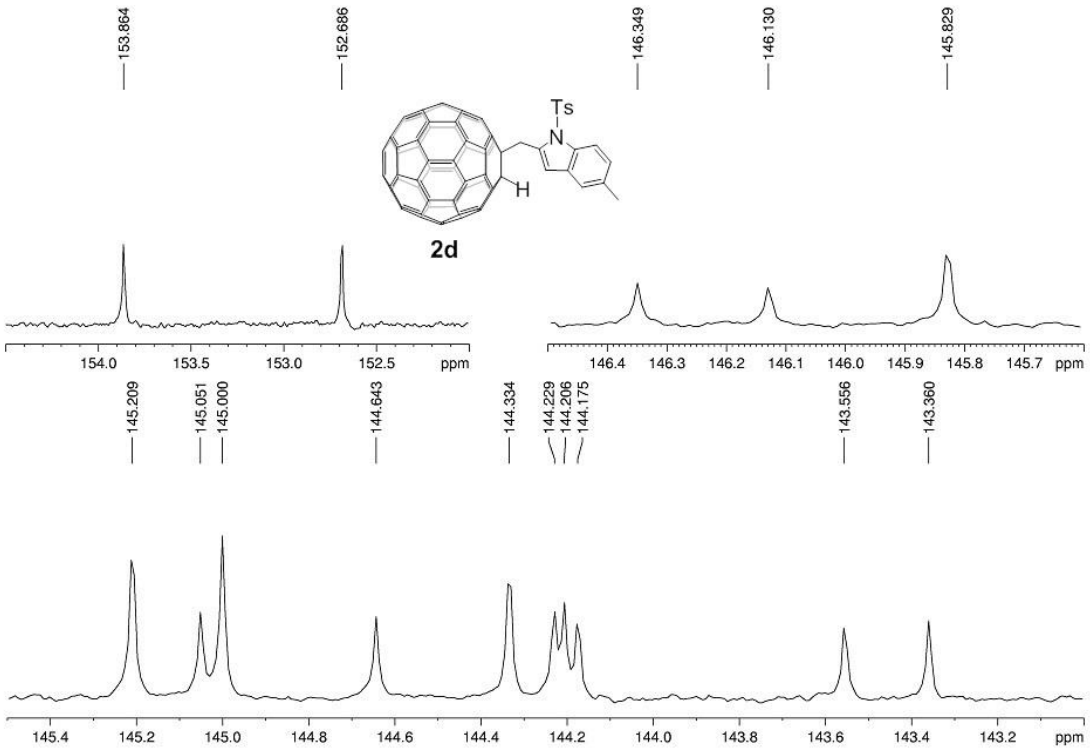


Expanded ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2d



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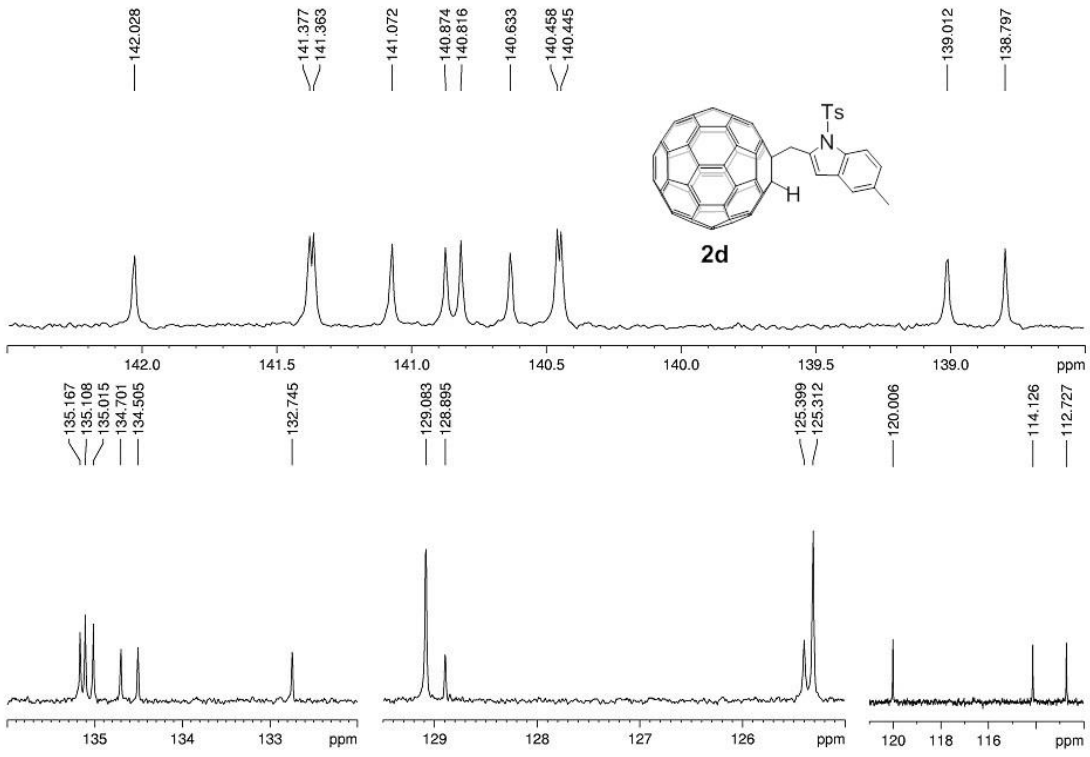

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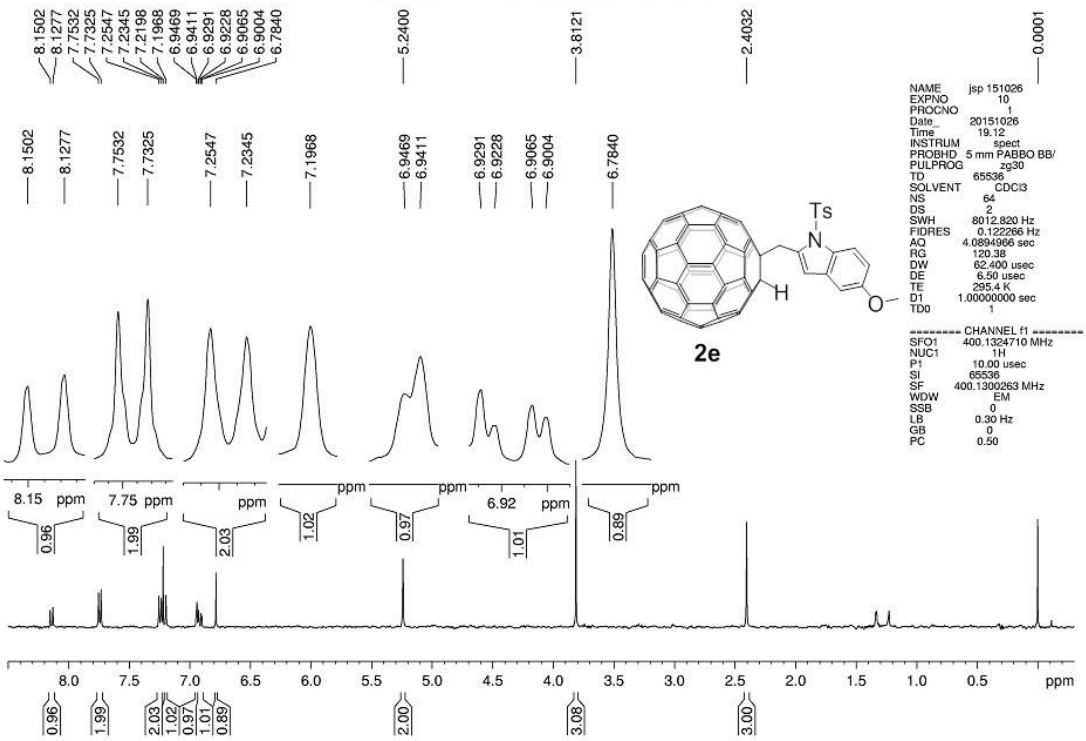

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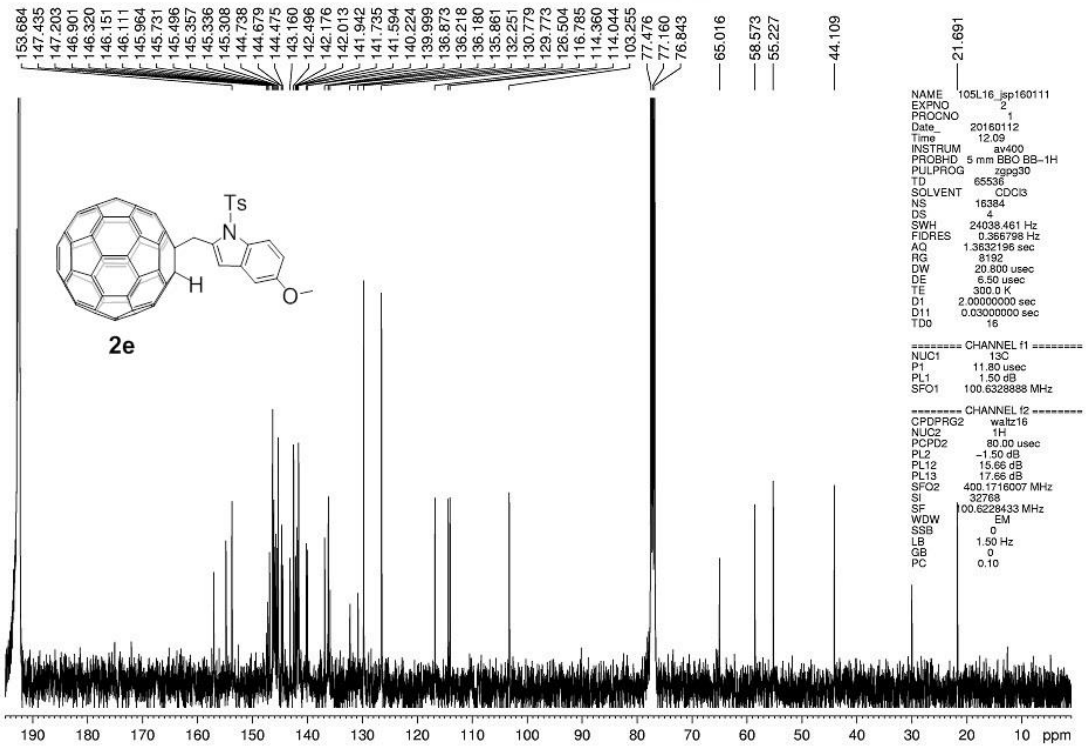
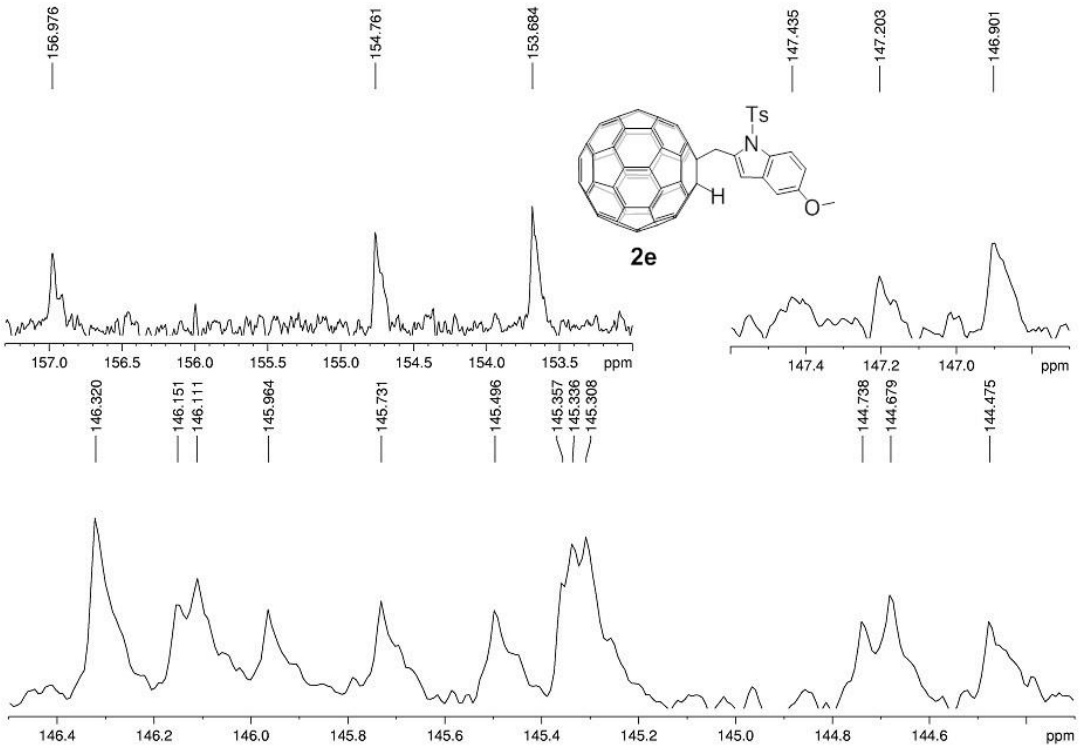
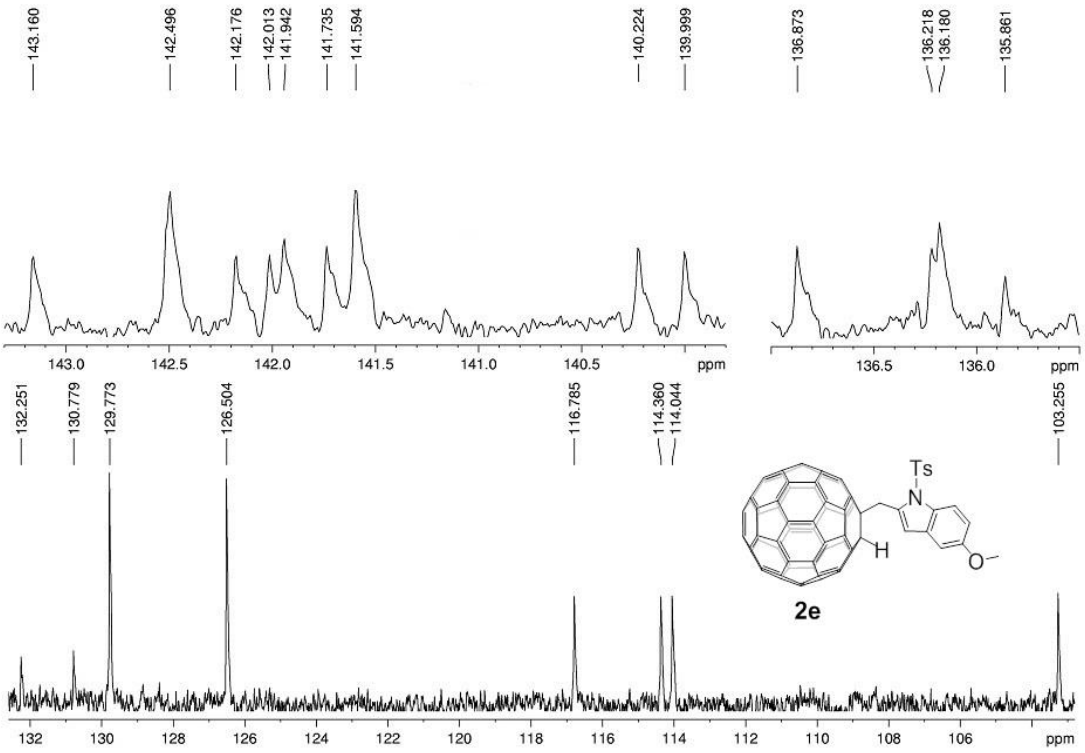


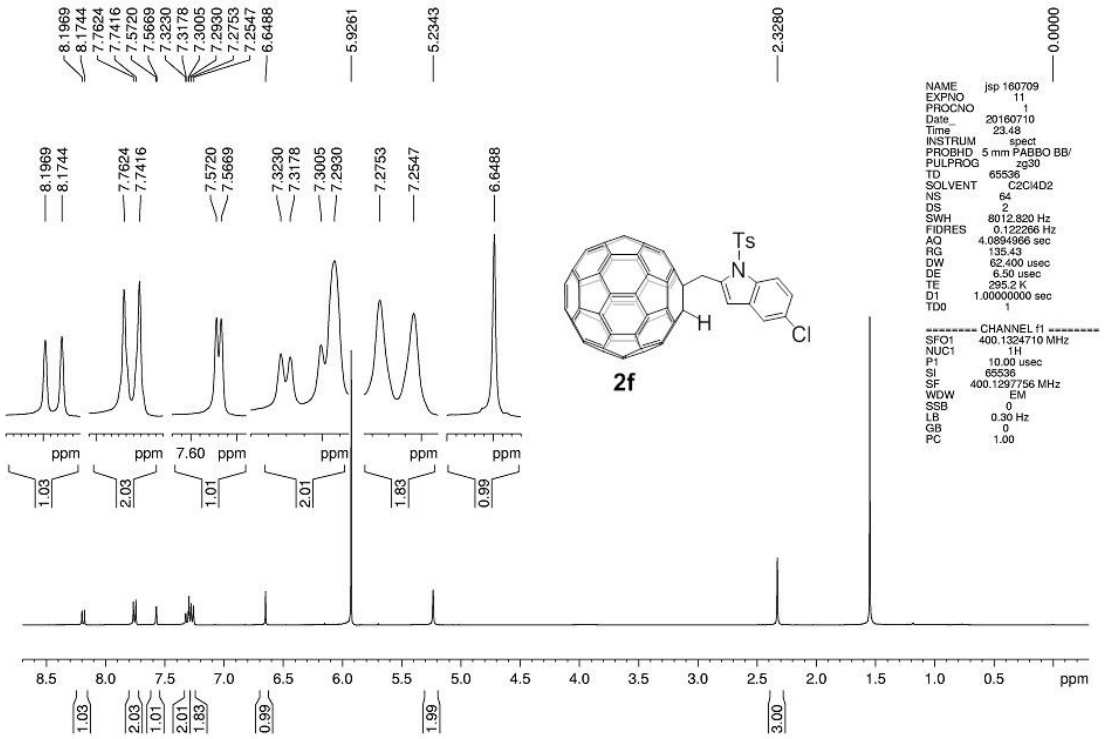
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2e



Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2e



^{1}H NMR (400 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2f



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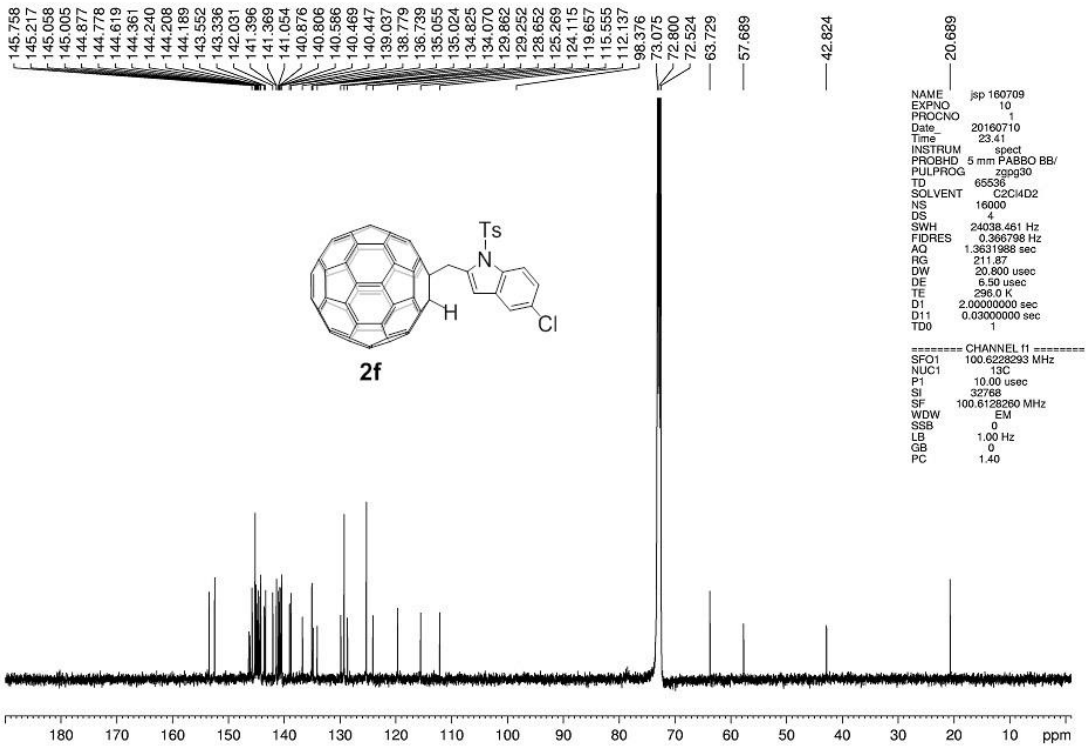
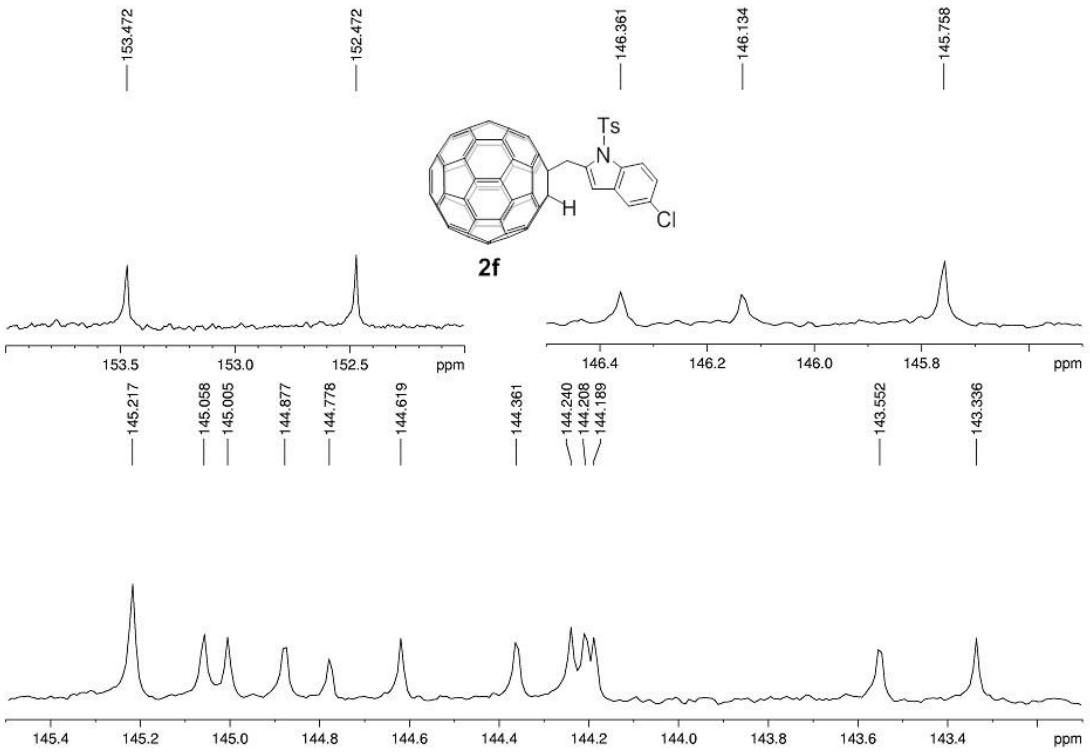
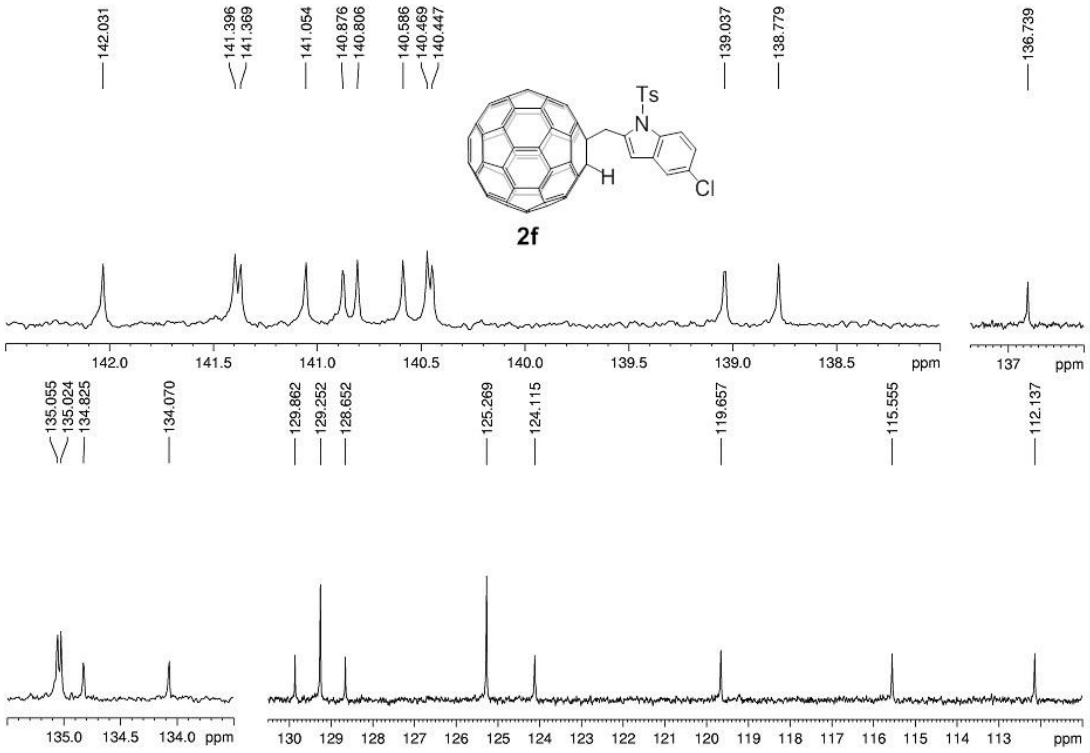


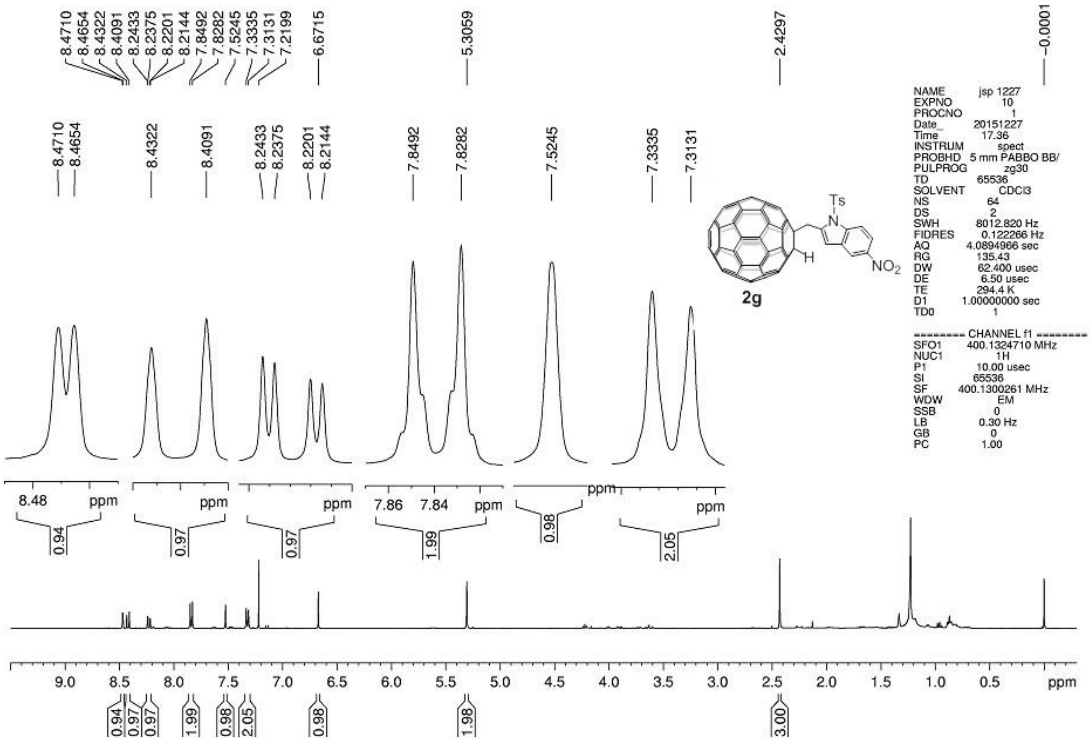
Expanded ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2f



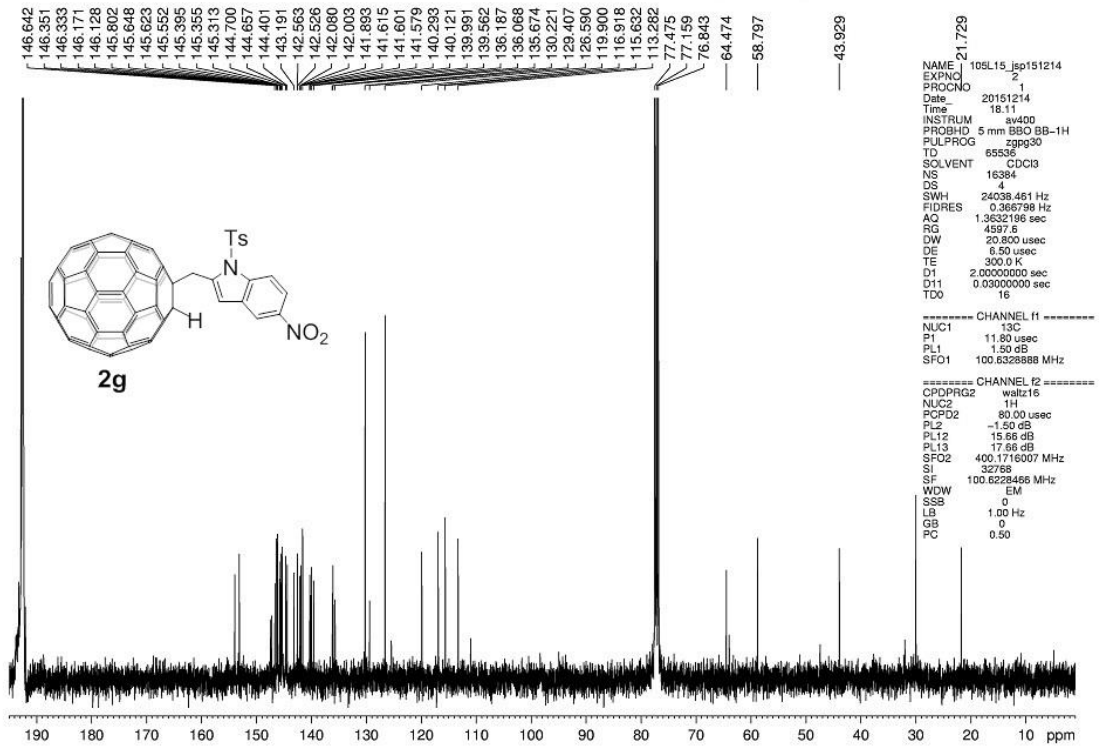
Expanded ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2f



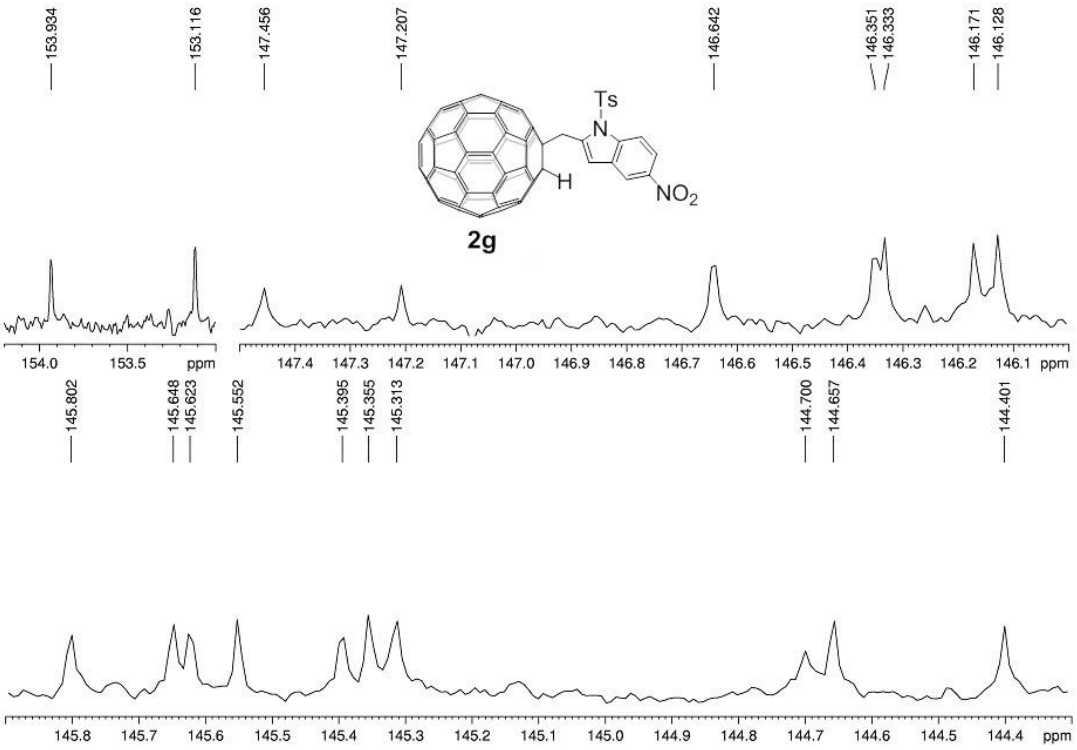
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2g



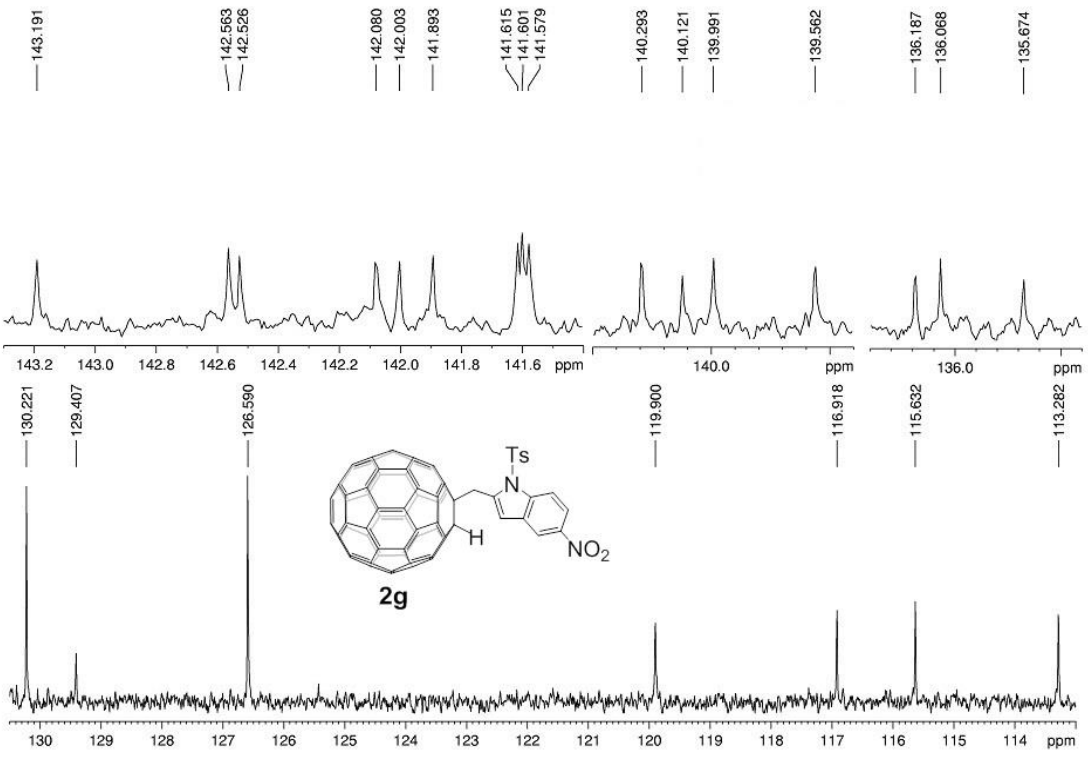
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2g



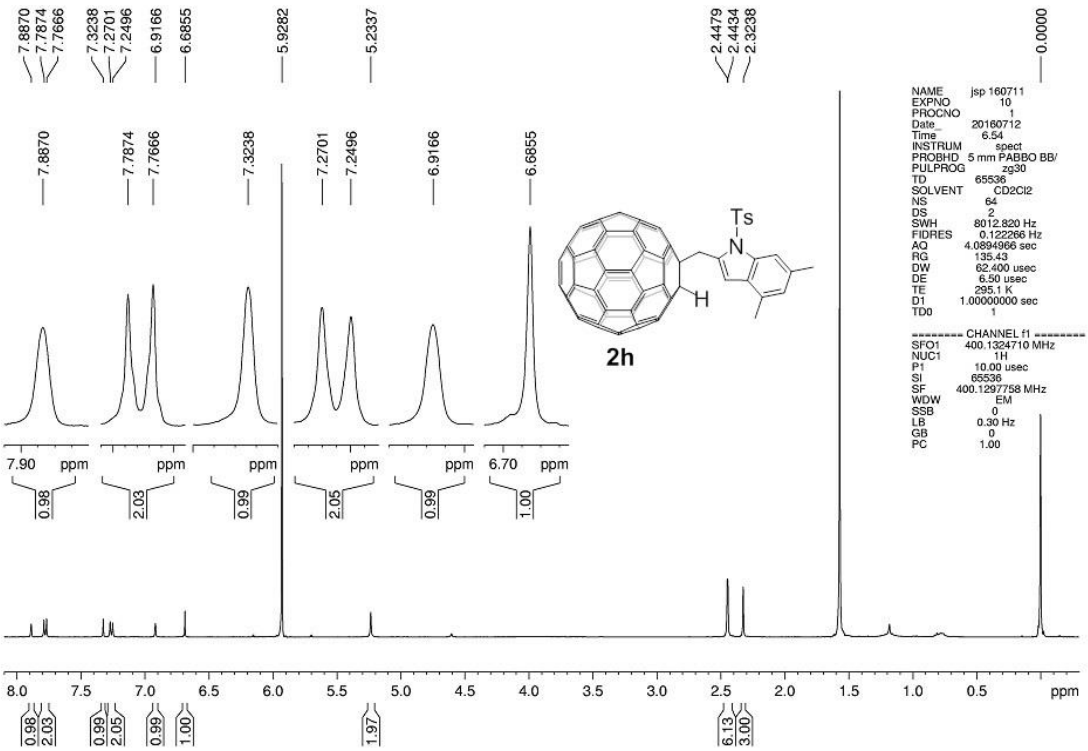
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2g



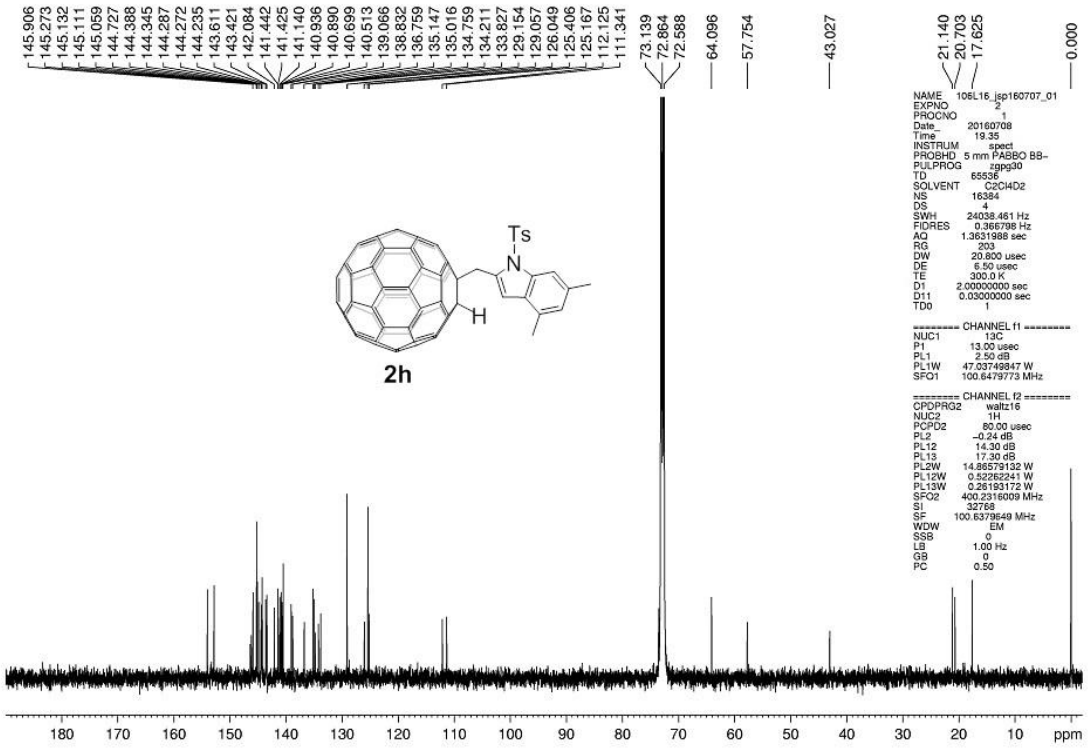
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2g



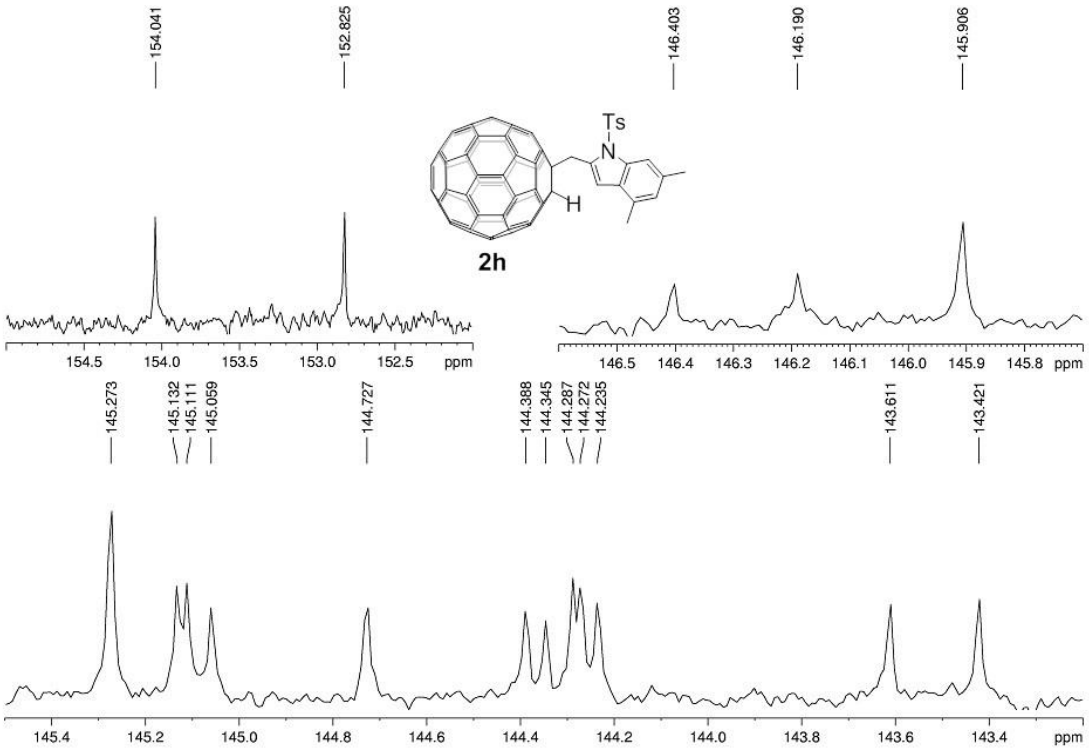
^{1}H NMR (400 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2h



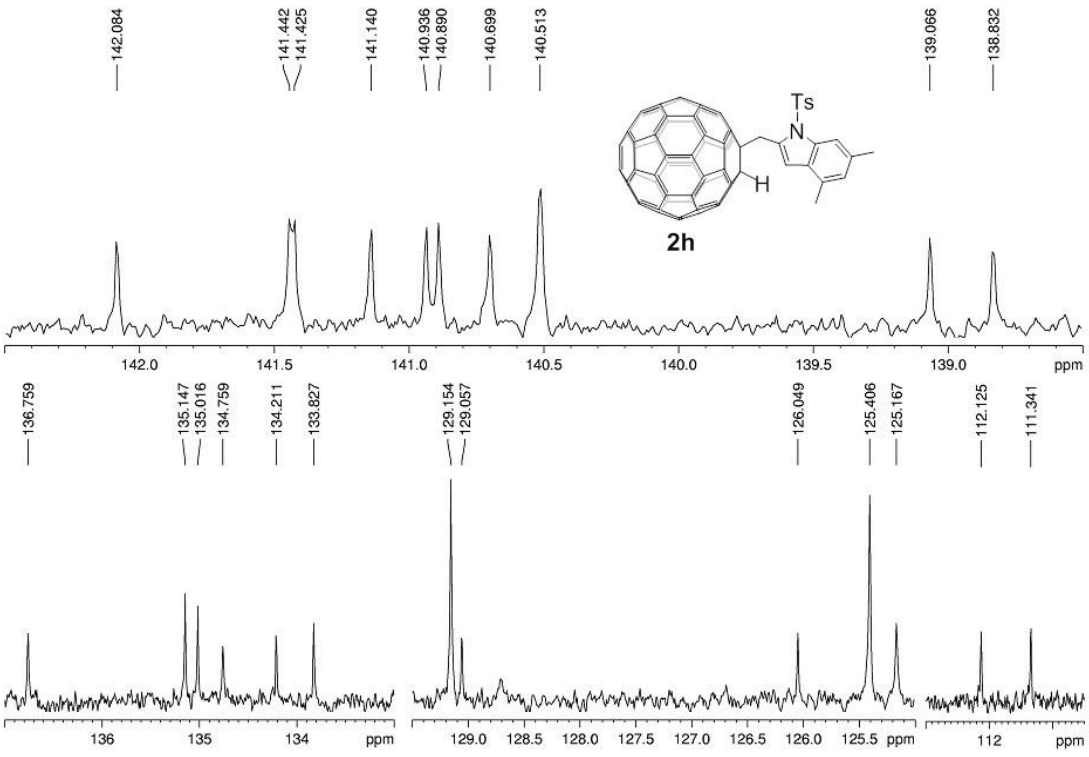
^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2h



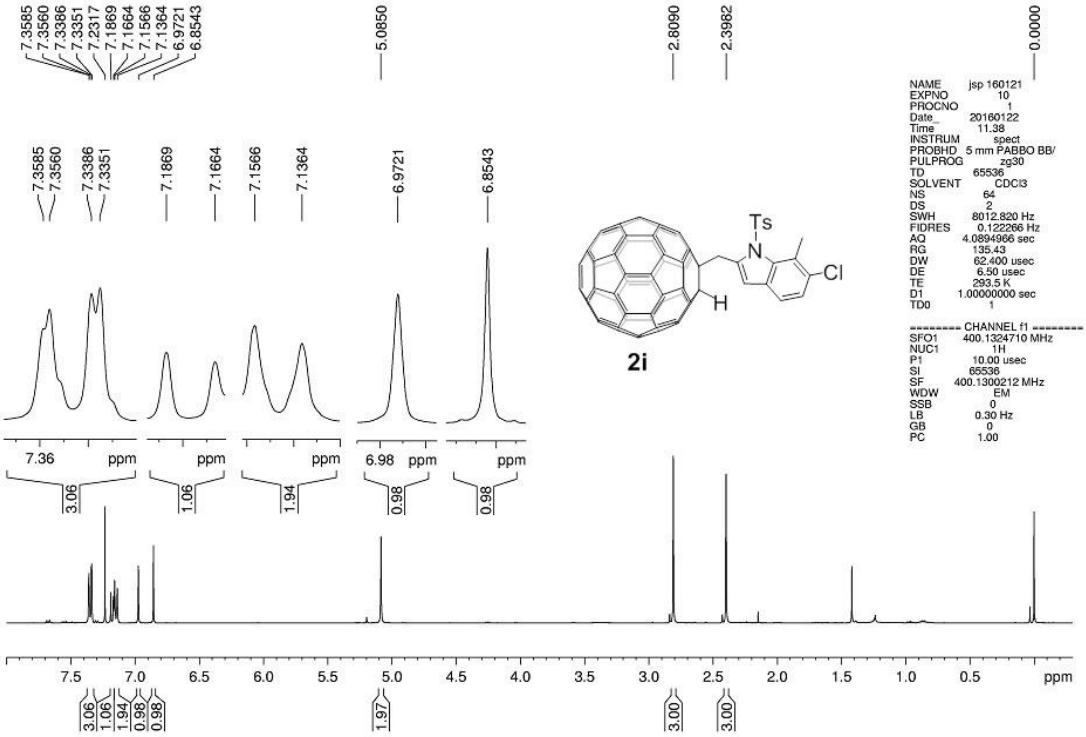
Expanded ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2h



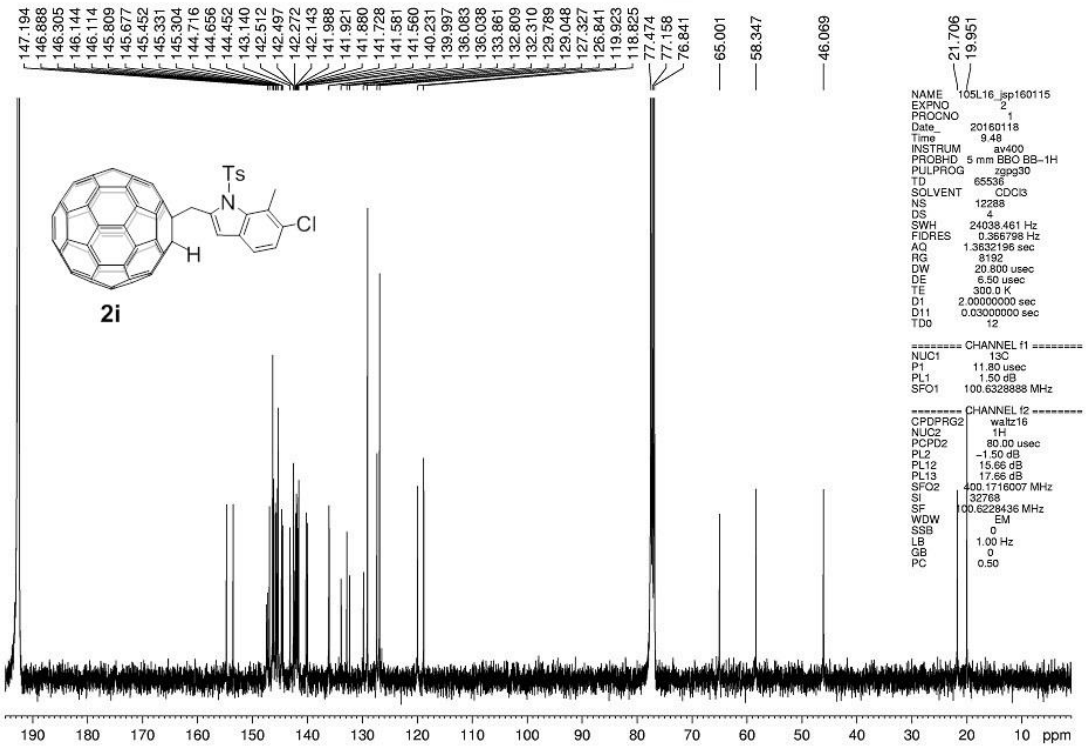
Expanded ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) Spectrum of Compound 2h



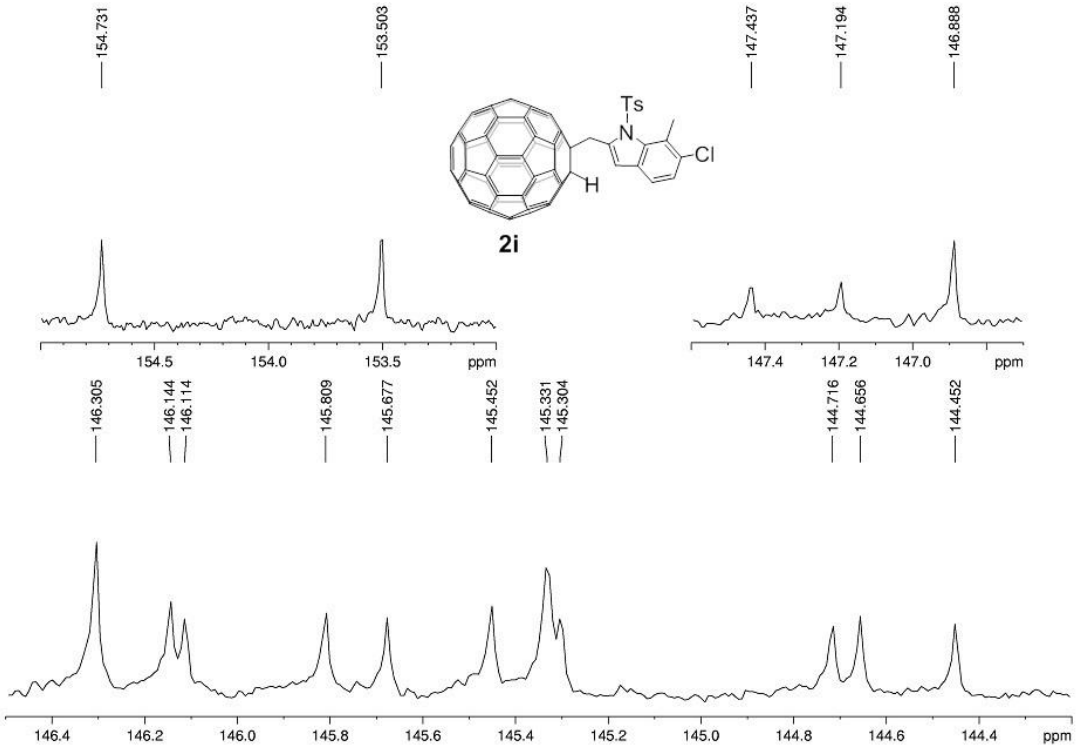
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2i



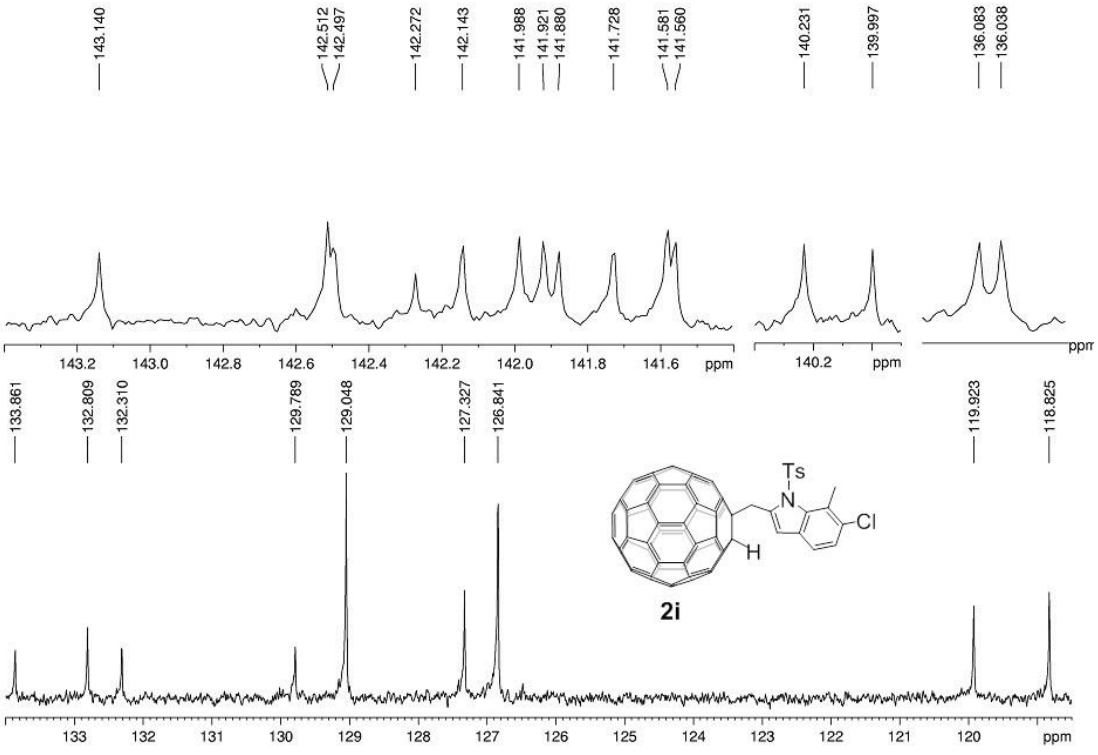
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2i



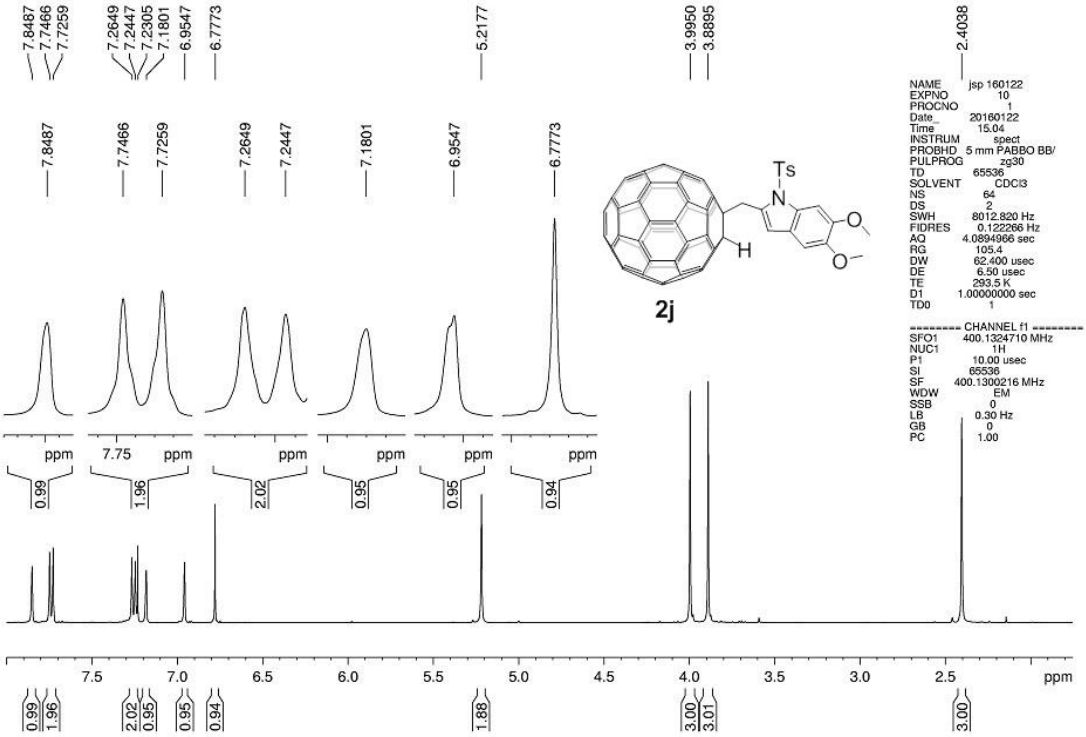
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2i



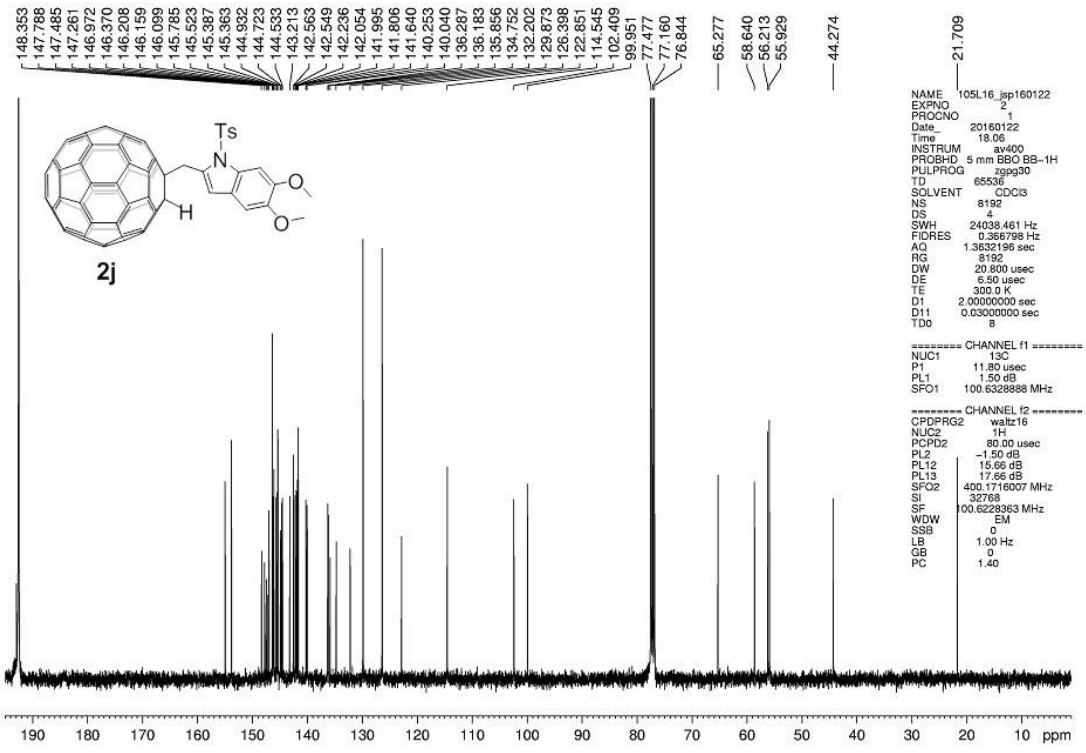
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2i



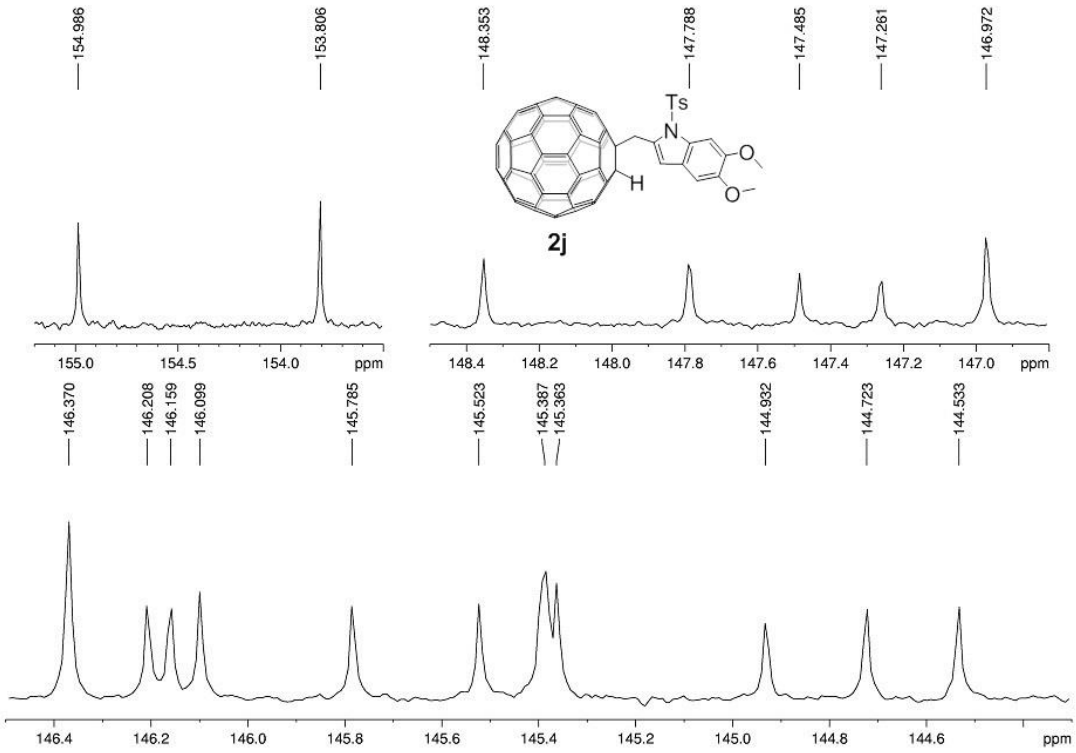
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2j



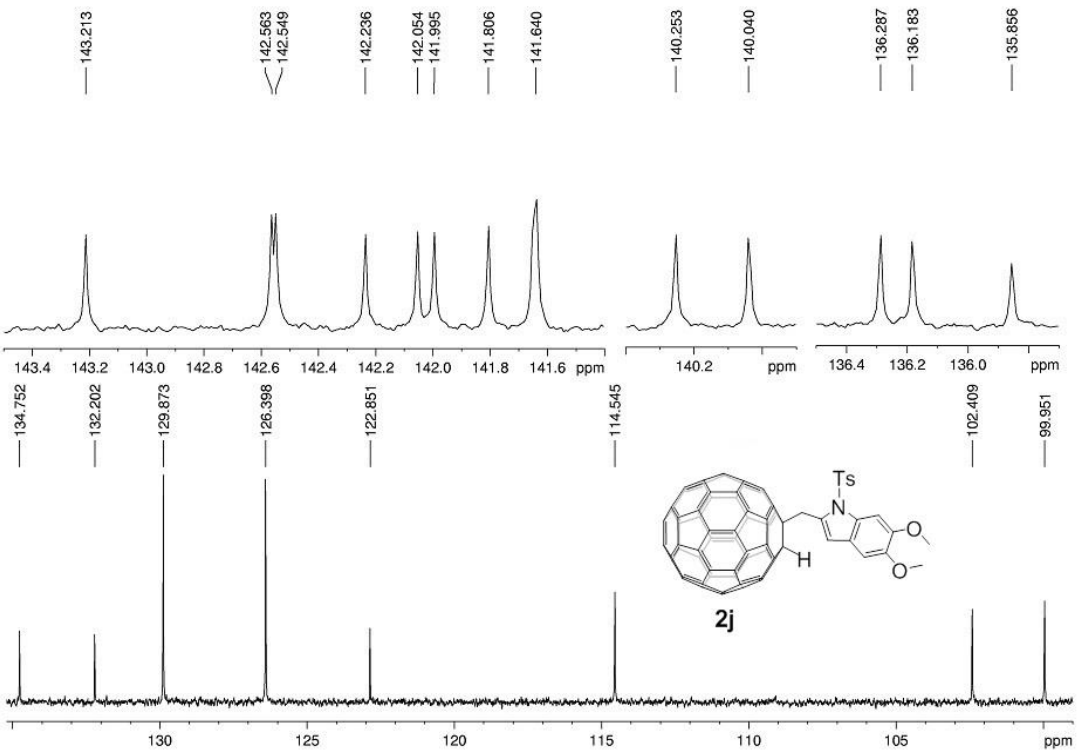
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2j



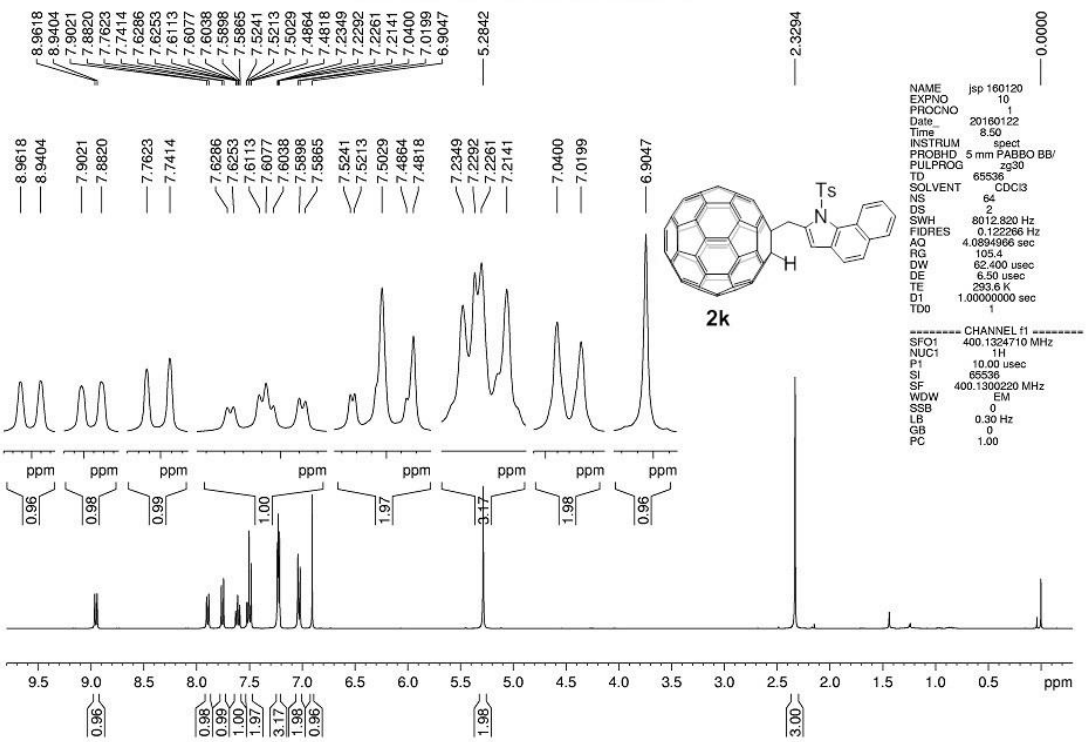
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2j



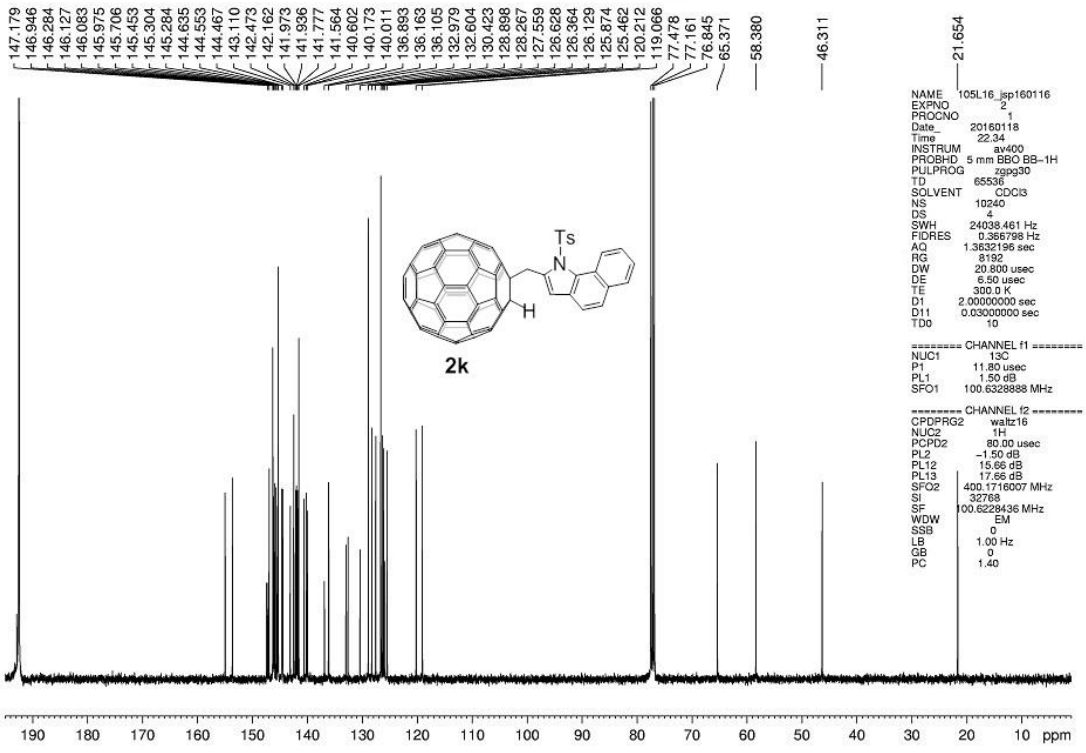
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2j



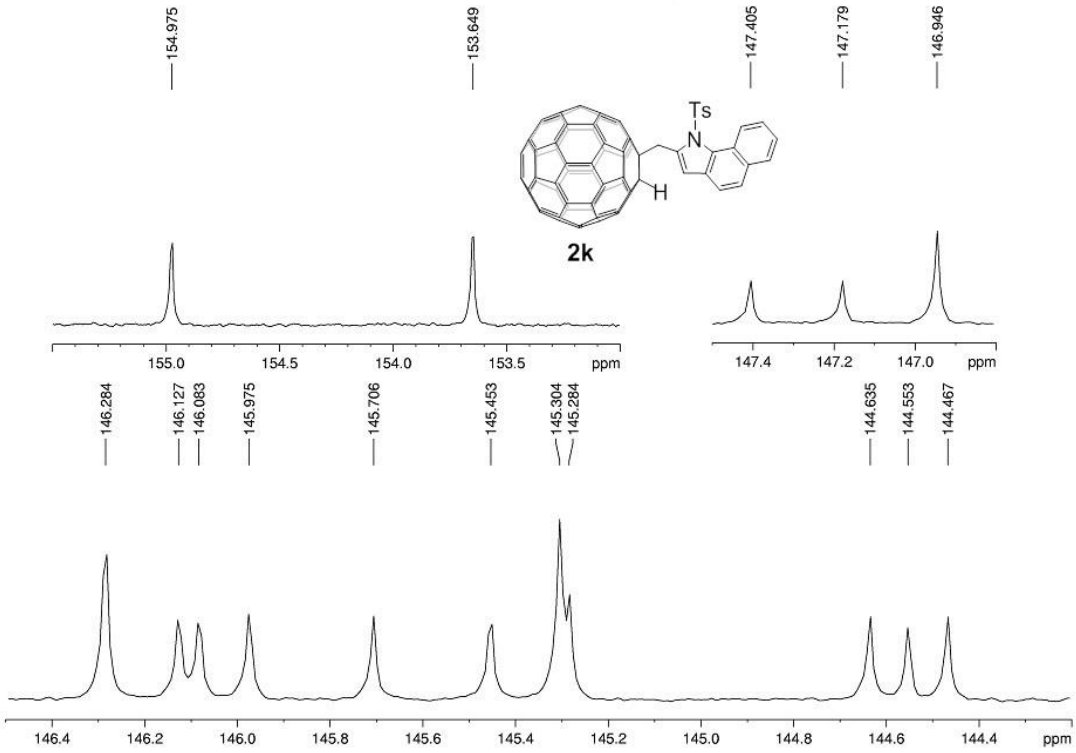
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2k



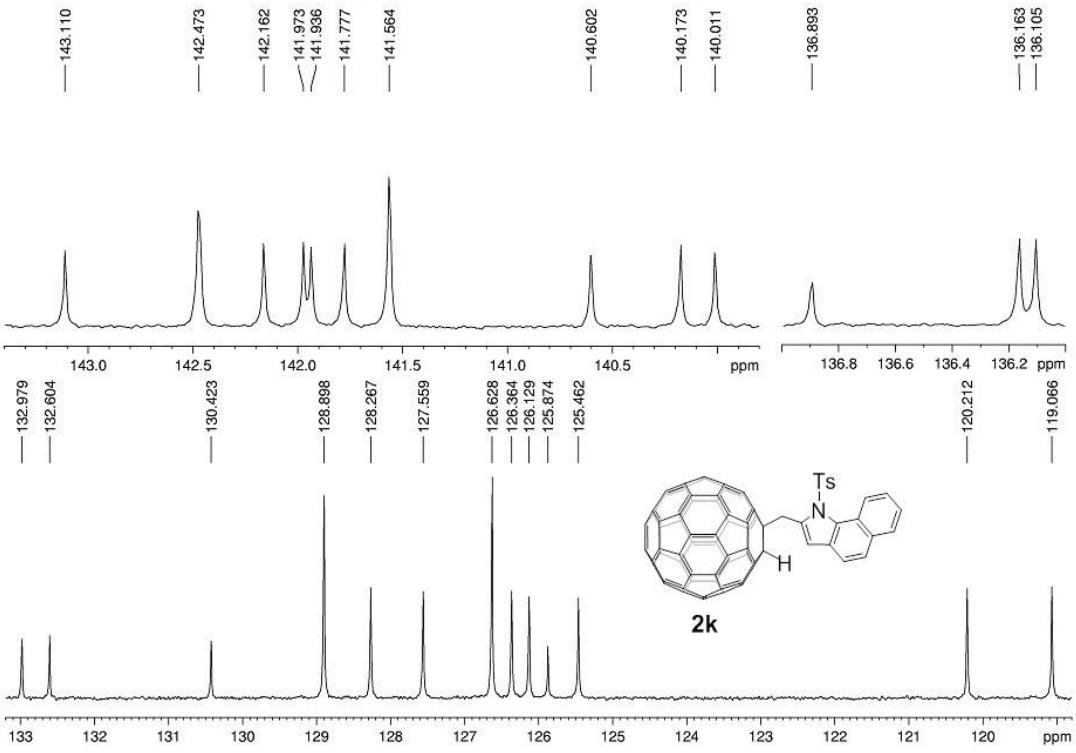
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2k



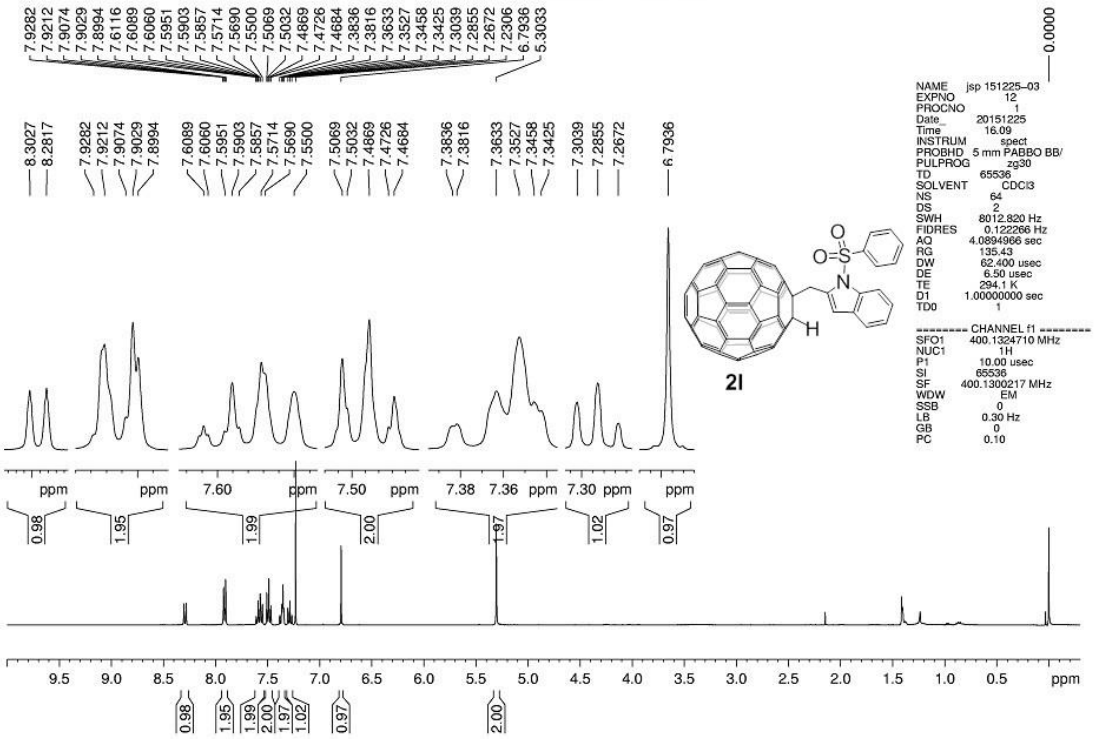
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2k



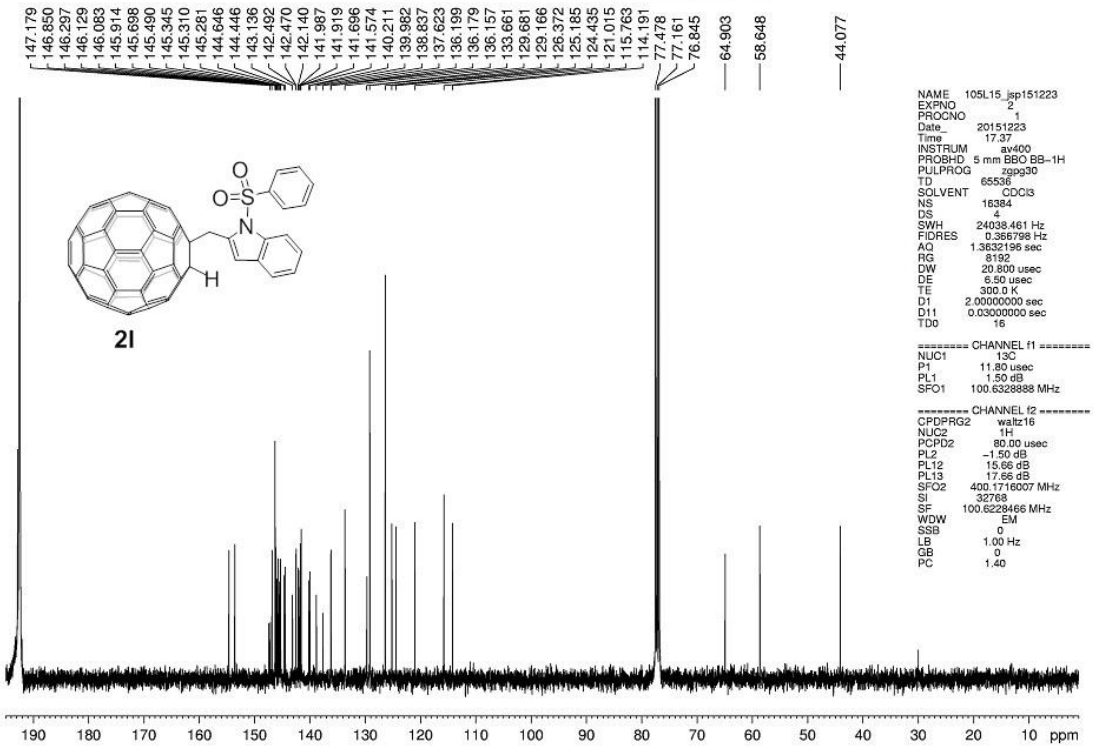
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2k



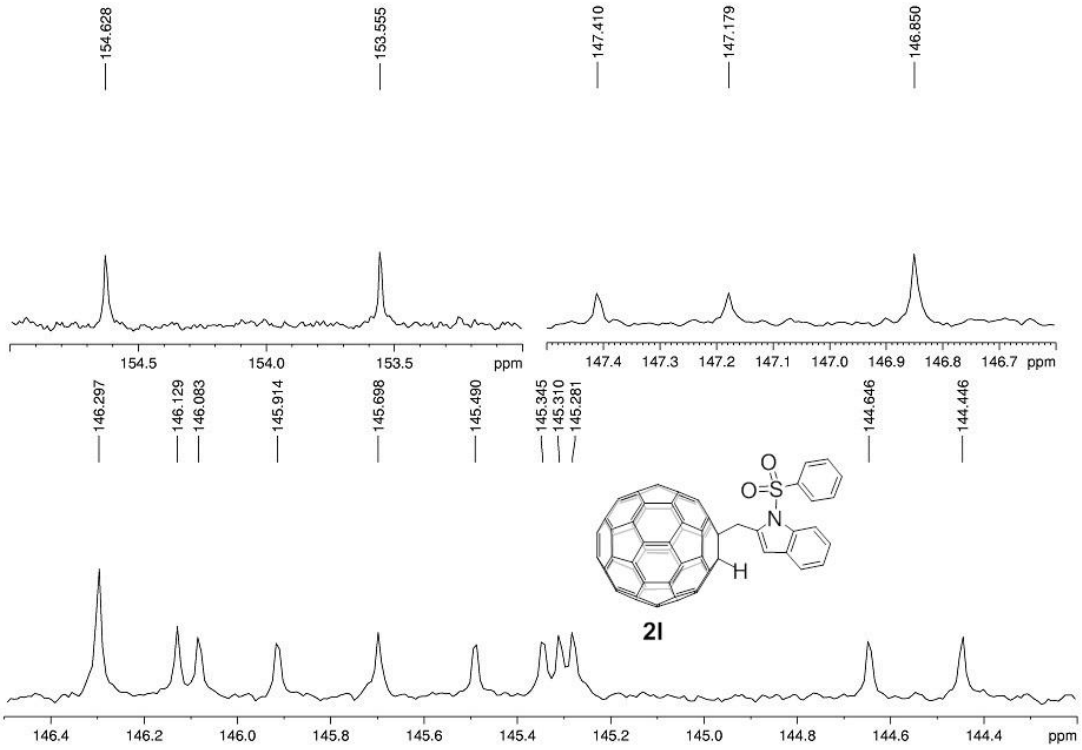
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2l



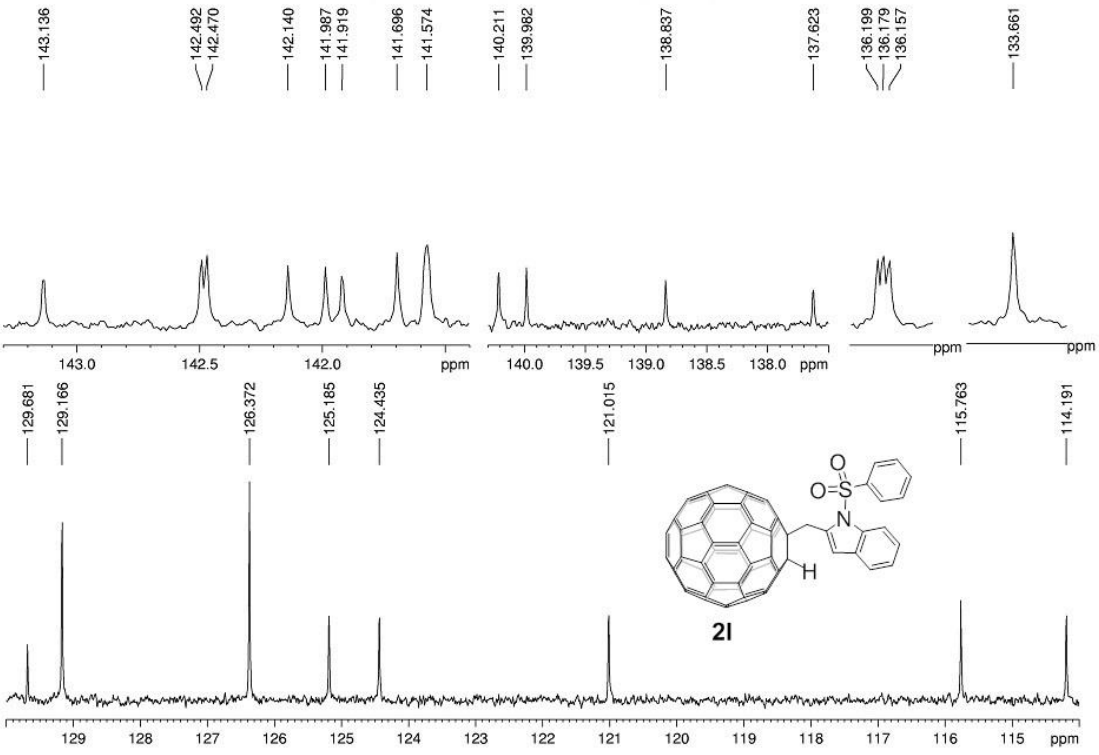
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2l



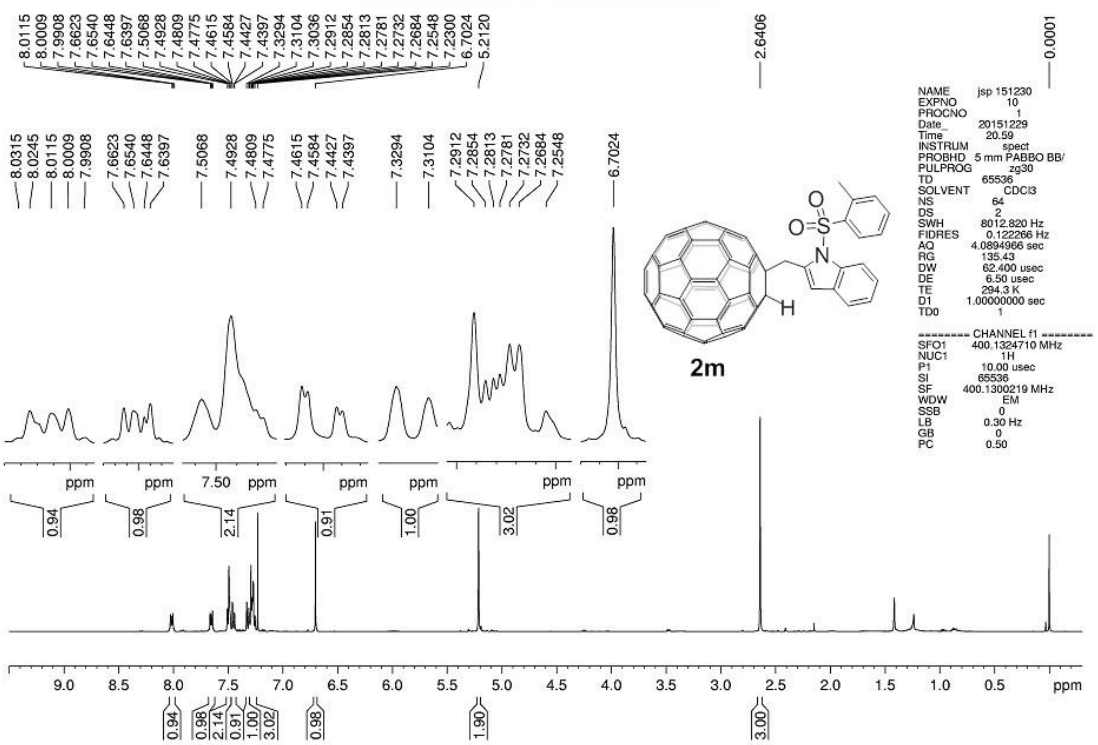
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2l



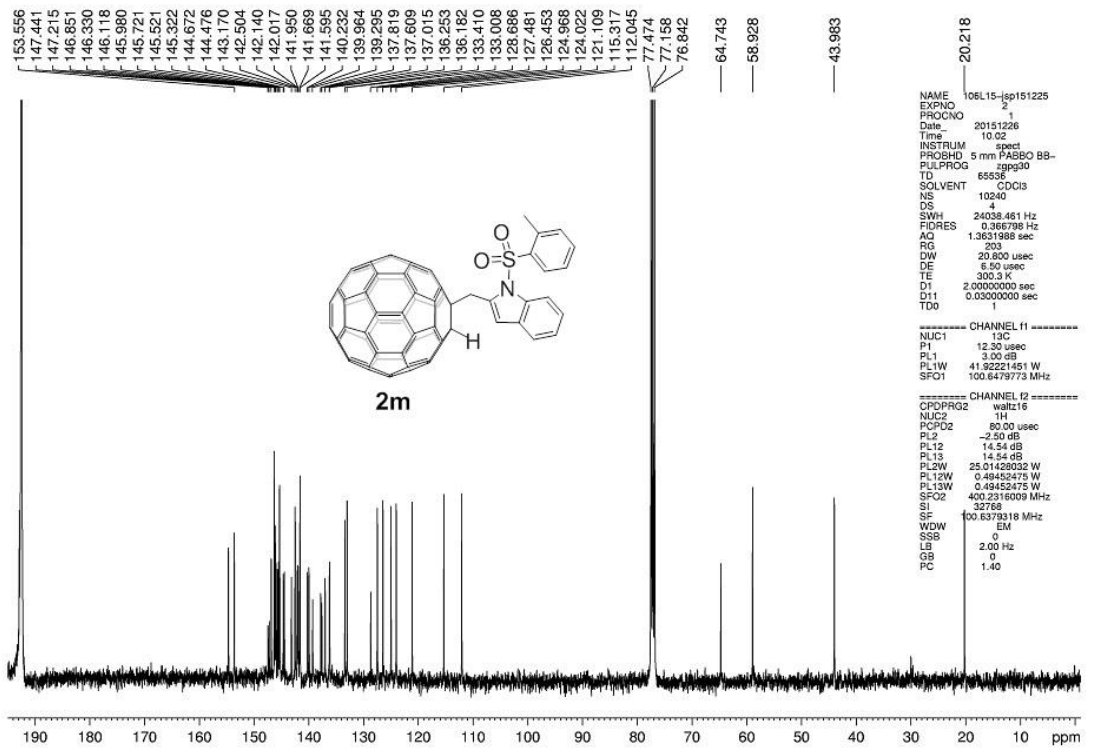
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2l



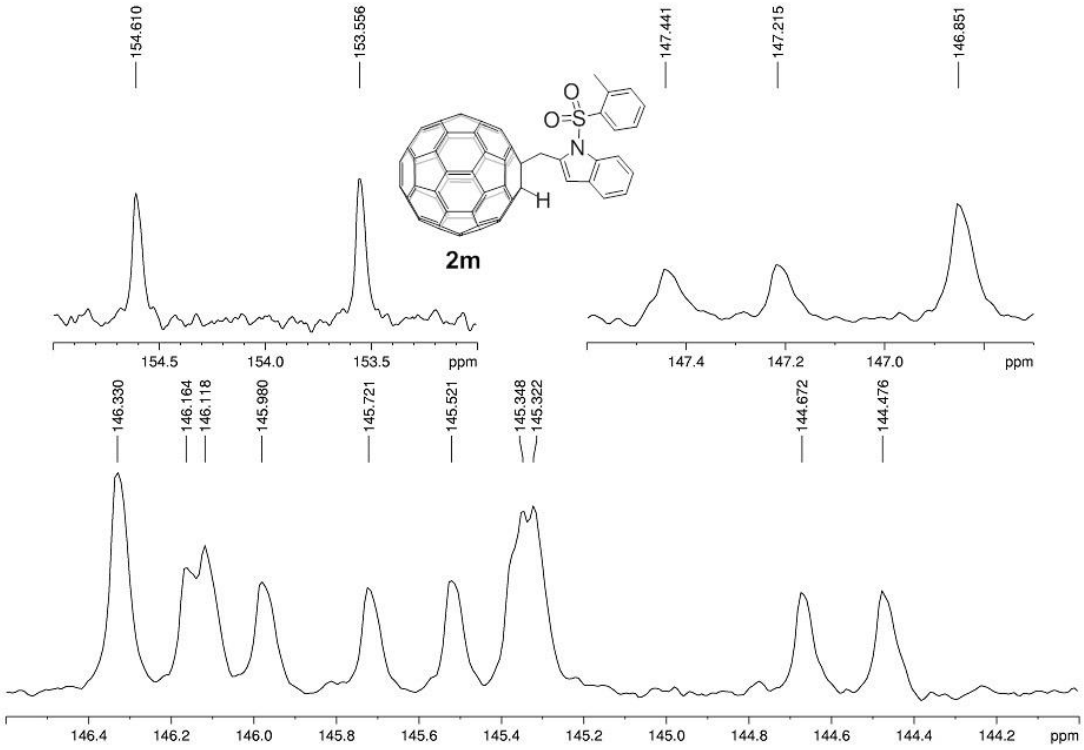
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2m



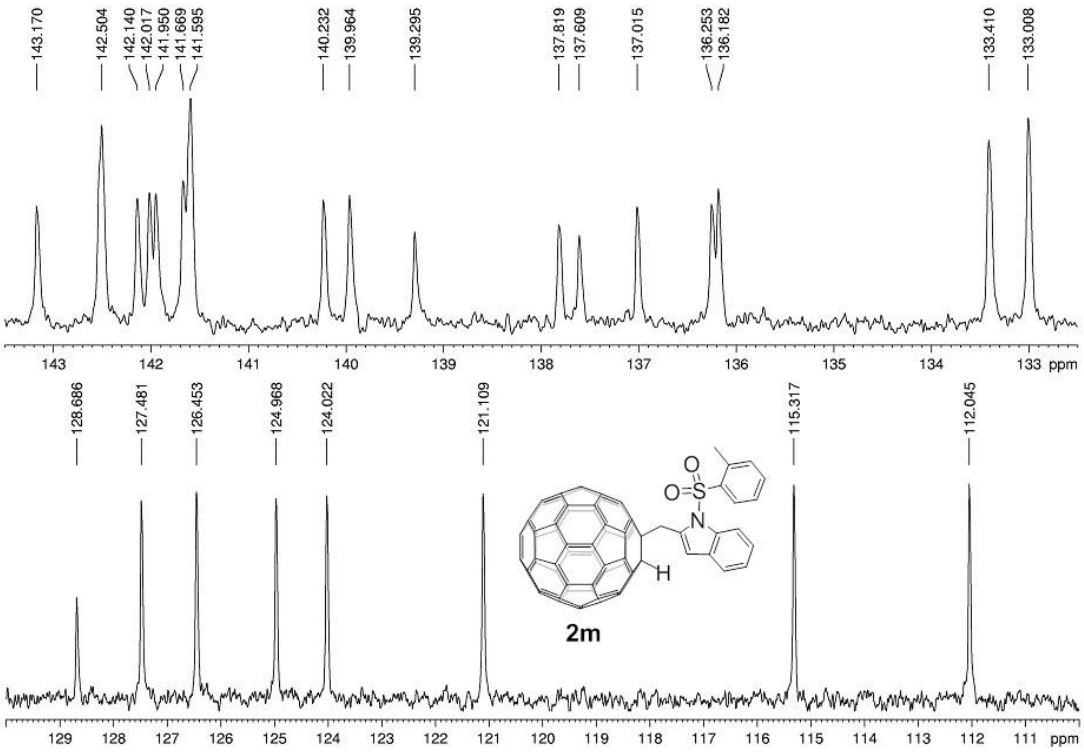
^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2m



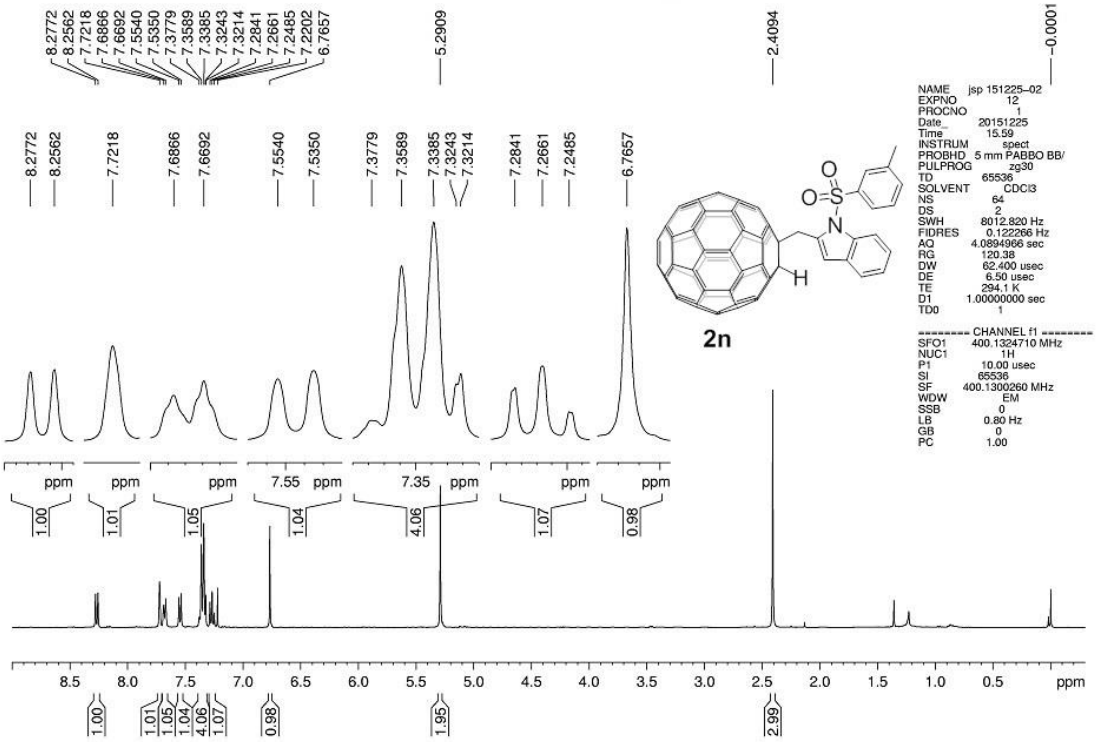
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2m



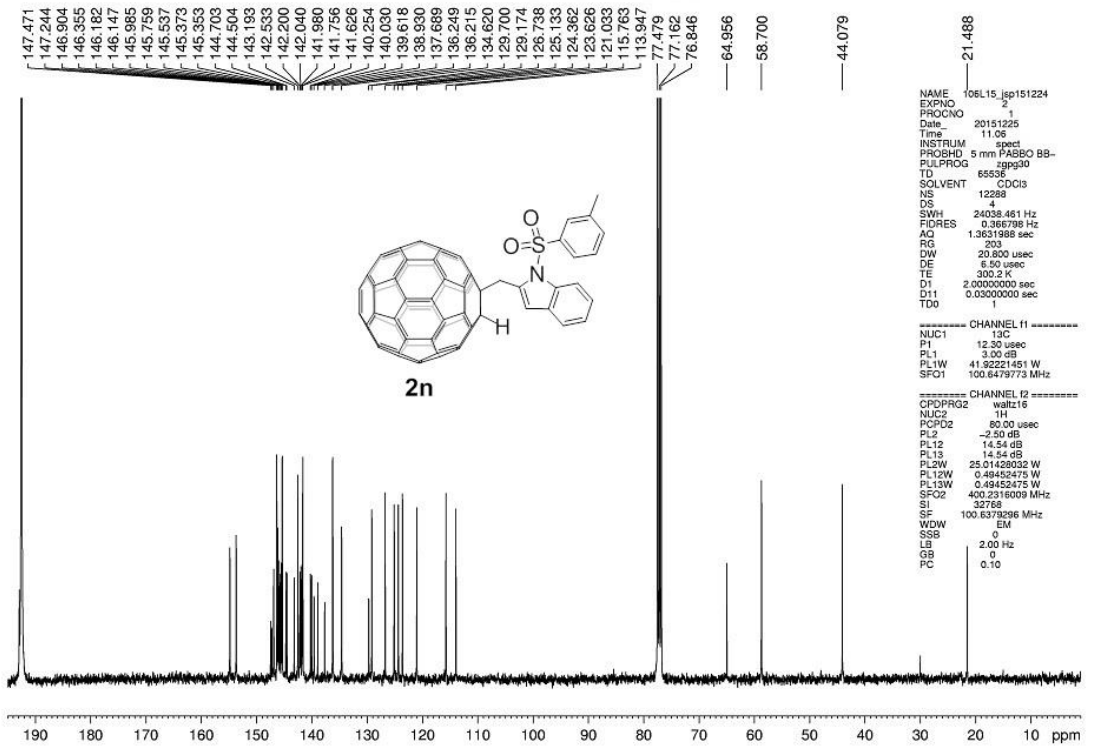
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2m



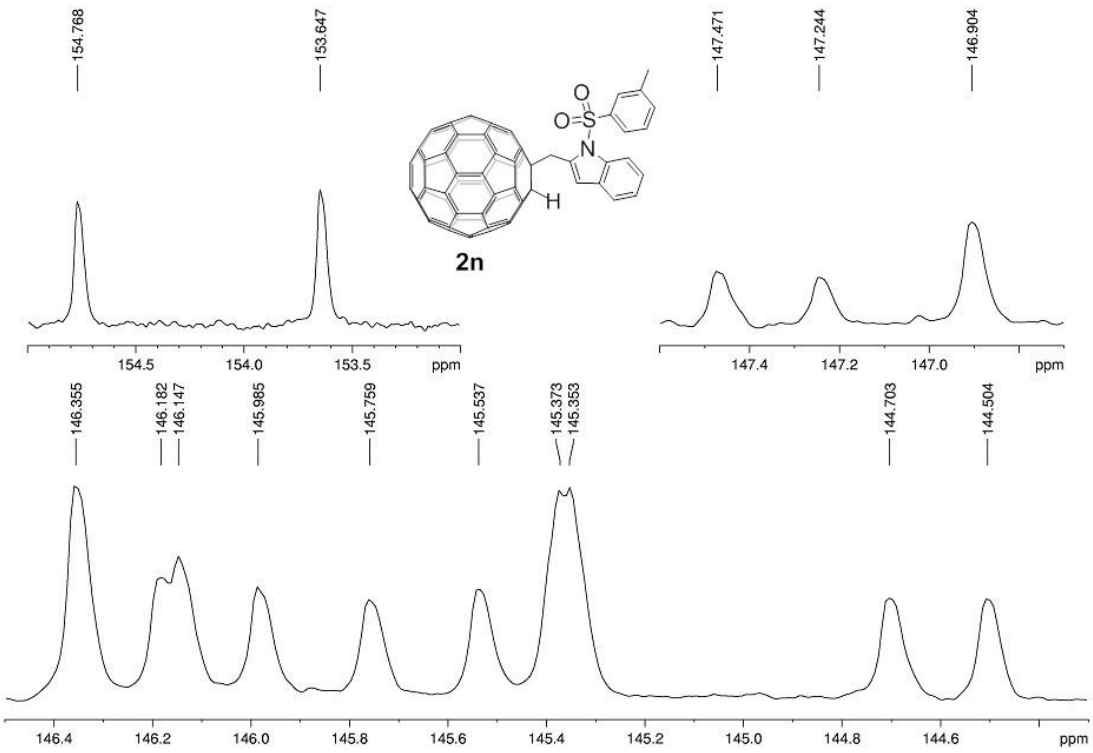
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2n



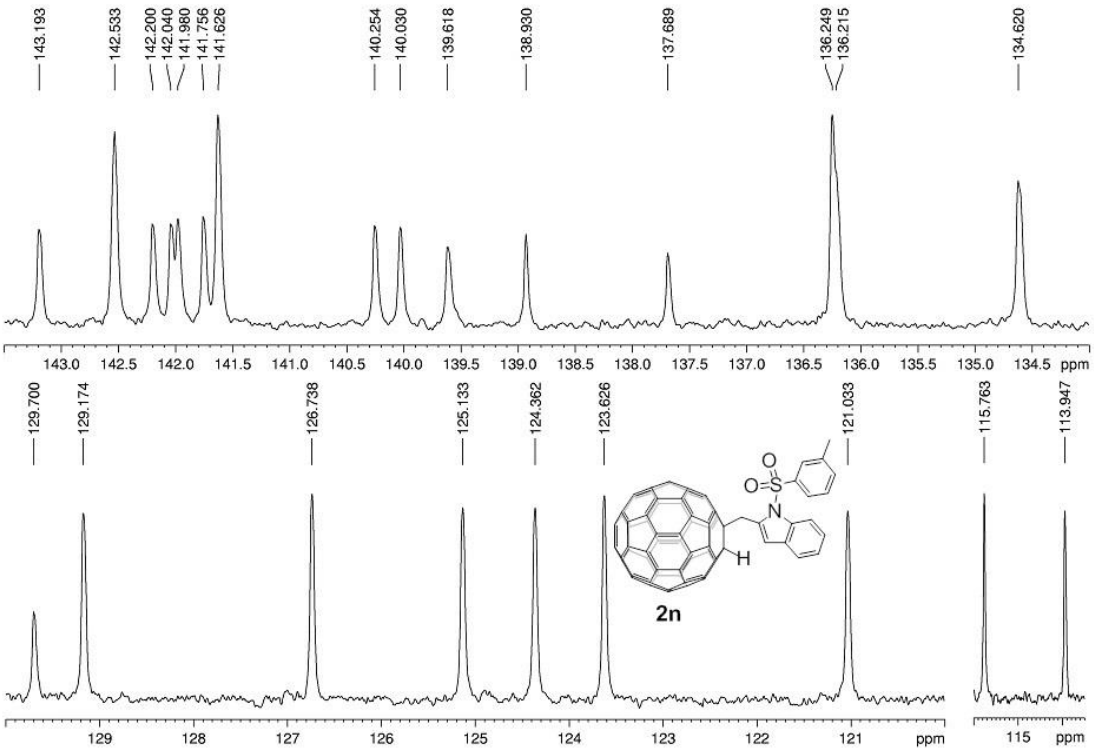
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2n



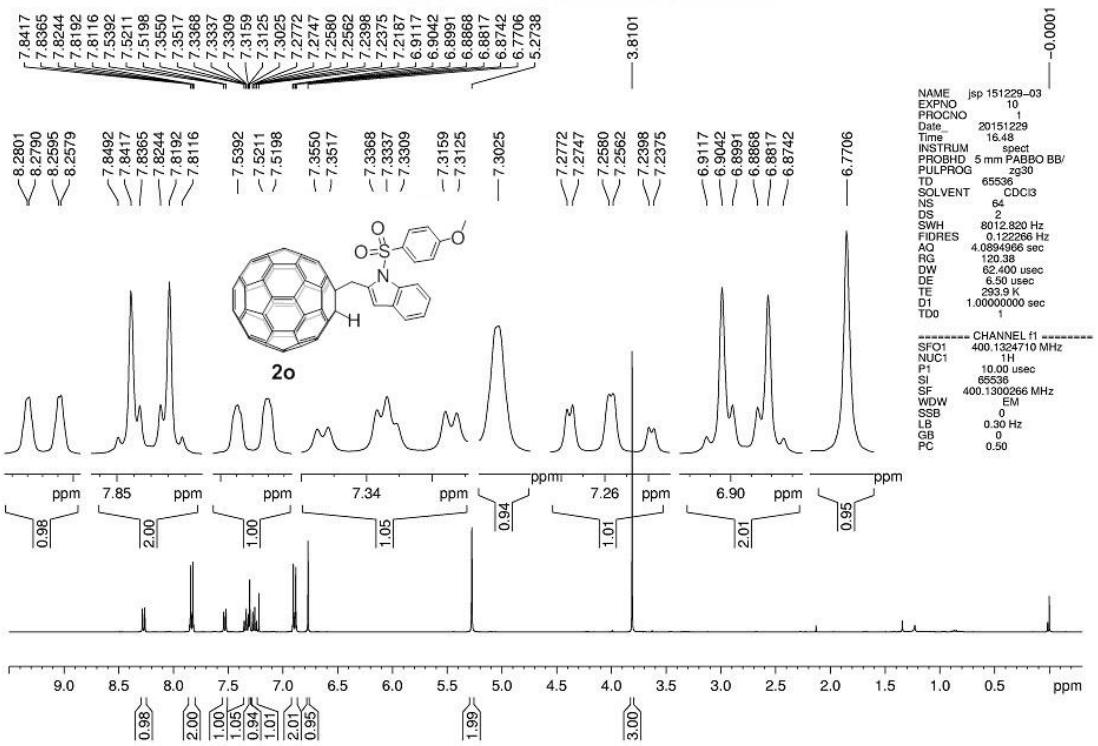
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2n



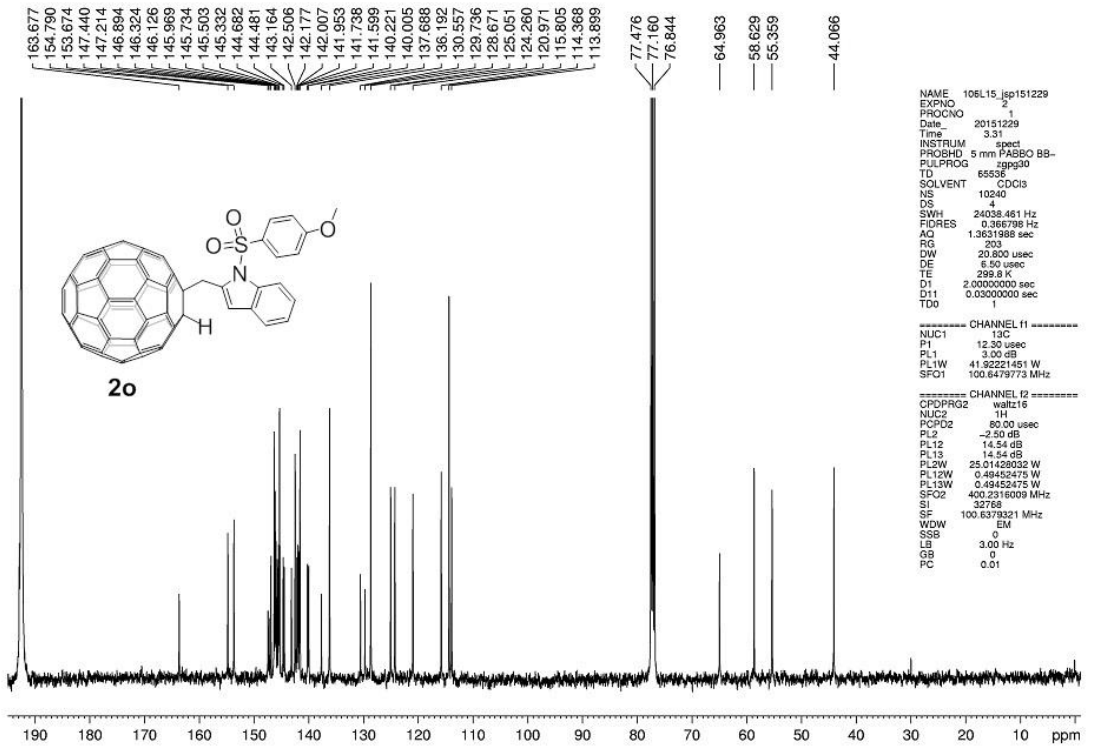
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2n



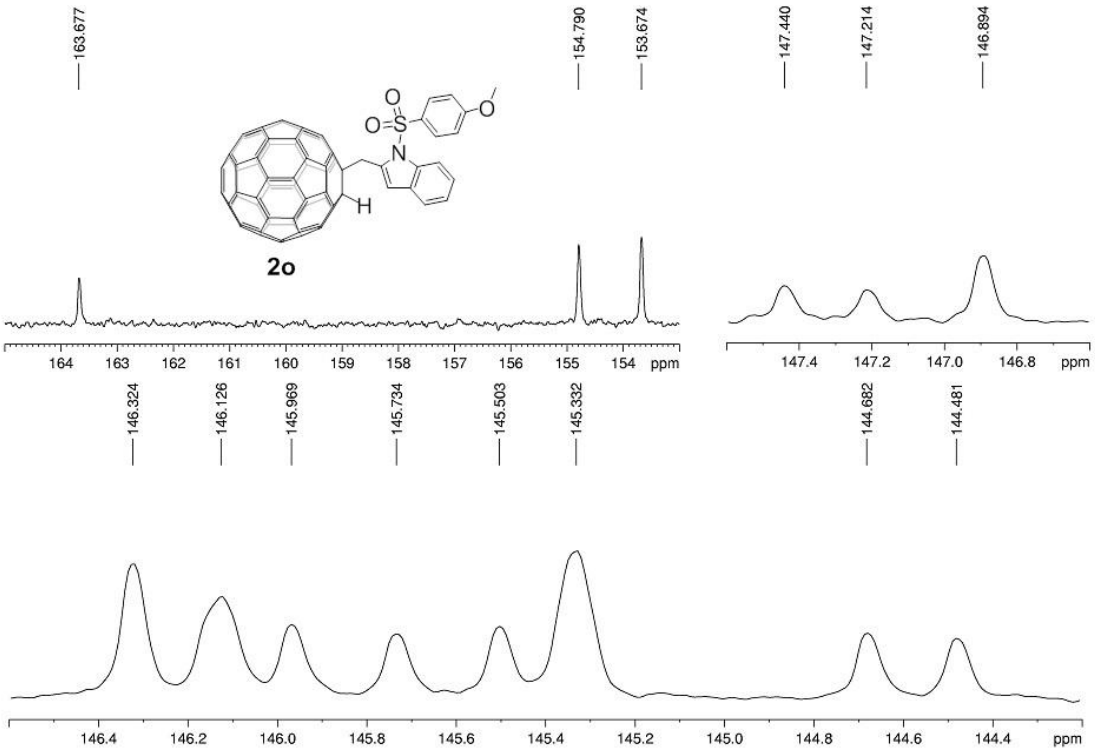
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2o



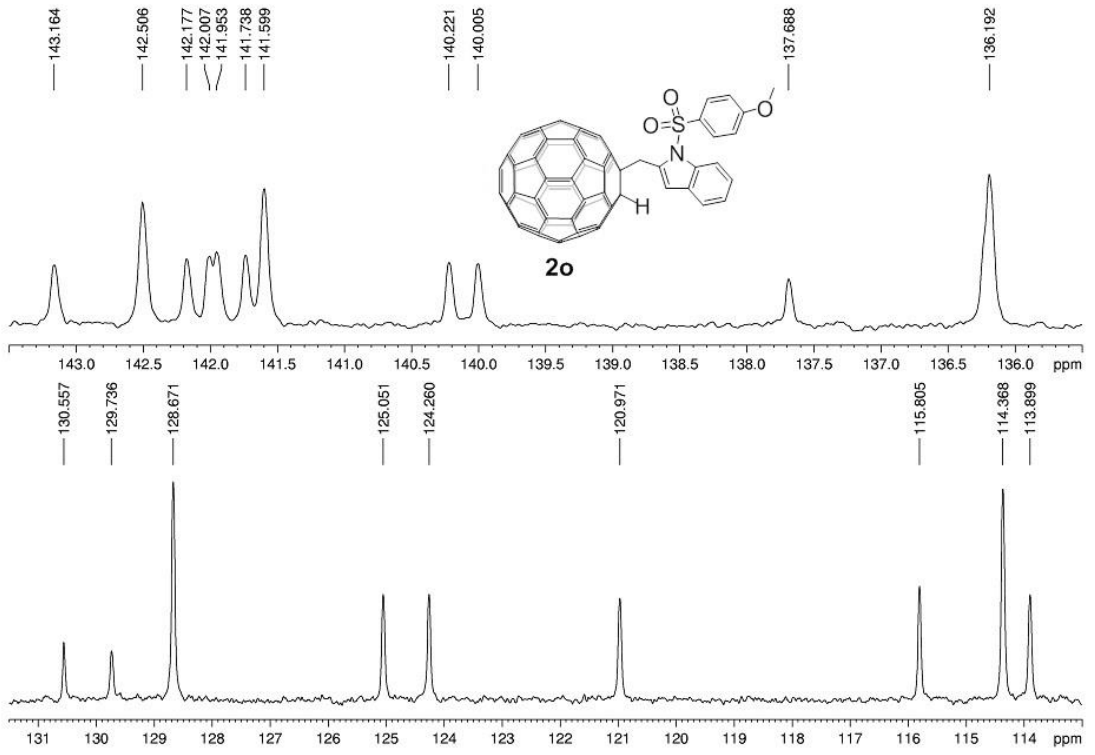
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2o



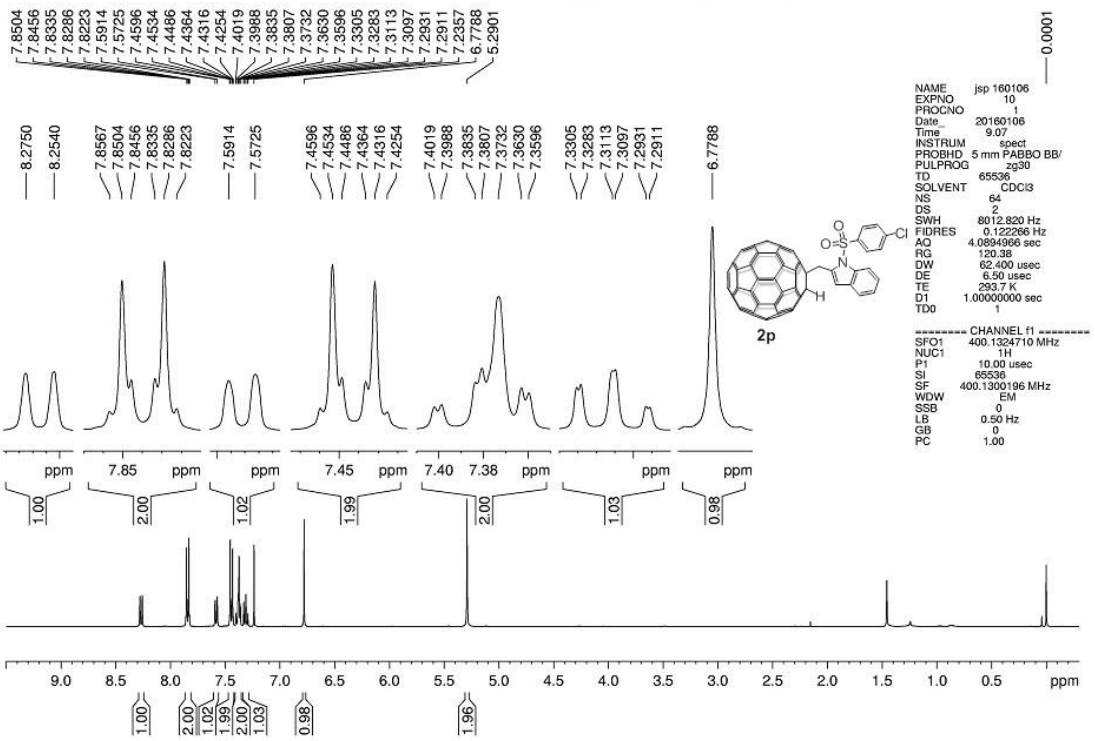
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2o



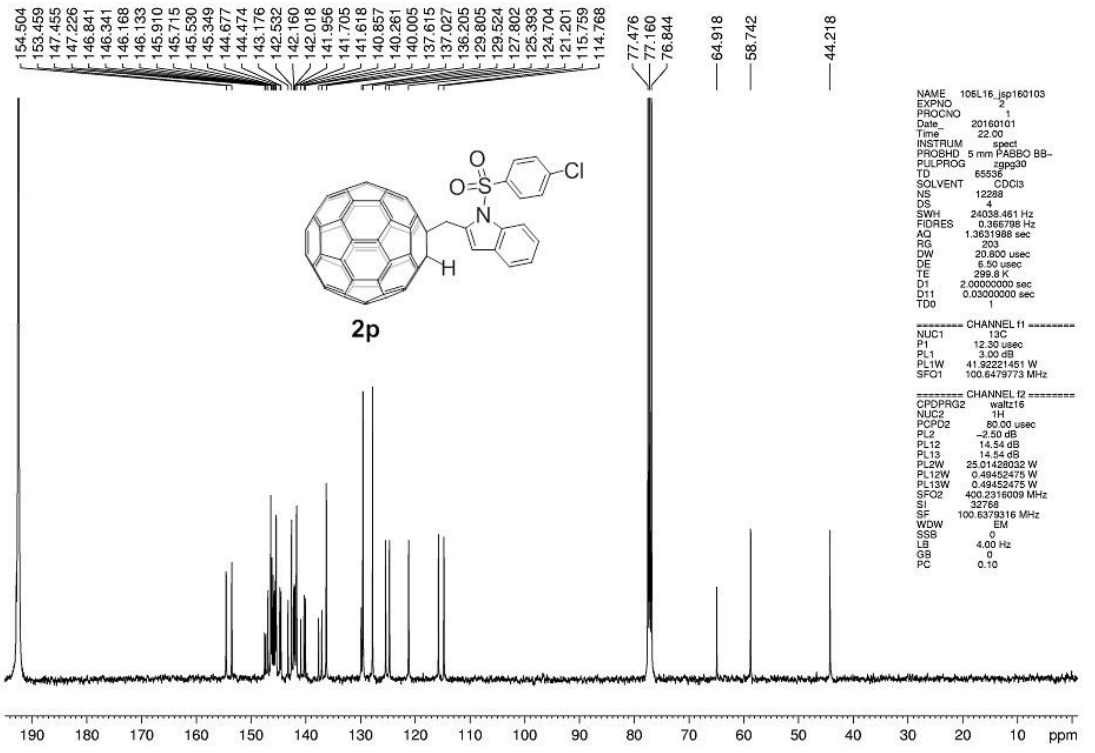
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2o



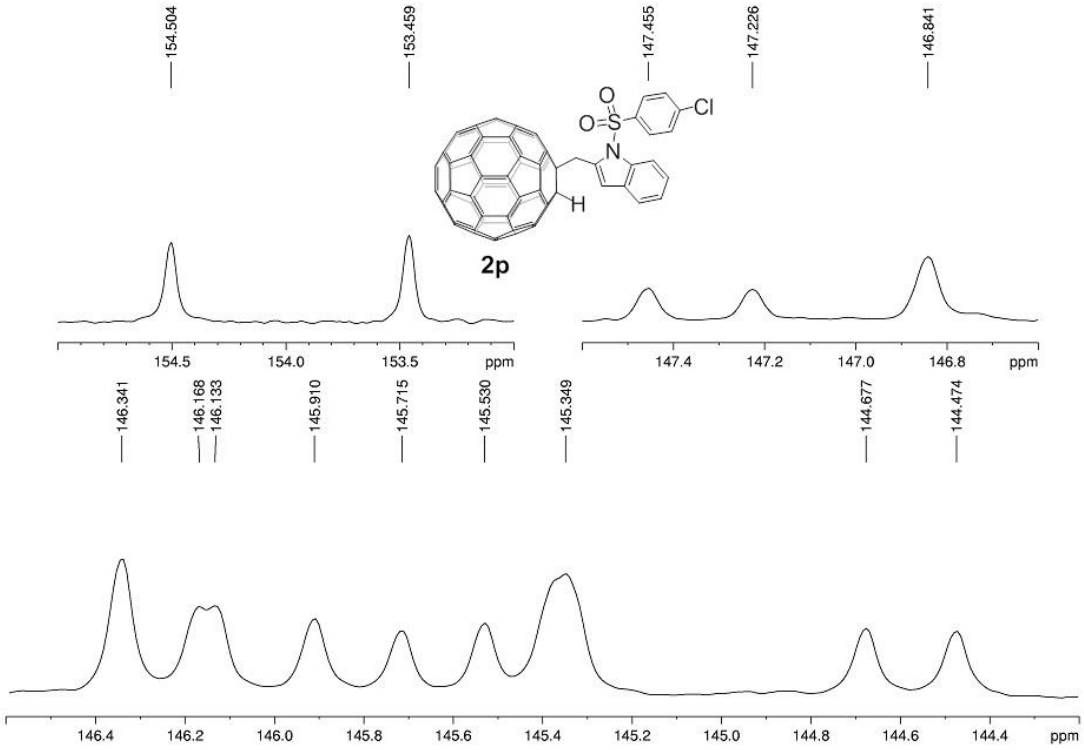
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2p



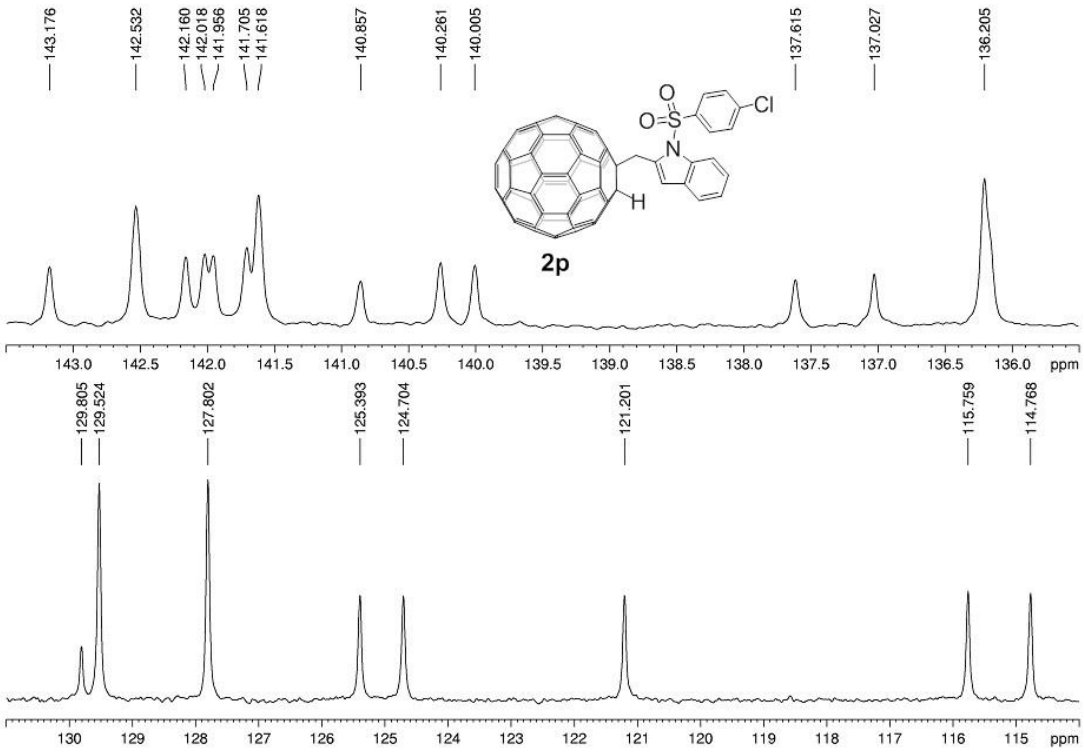
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2p



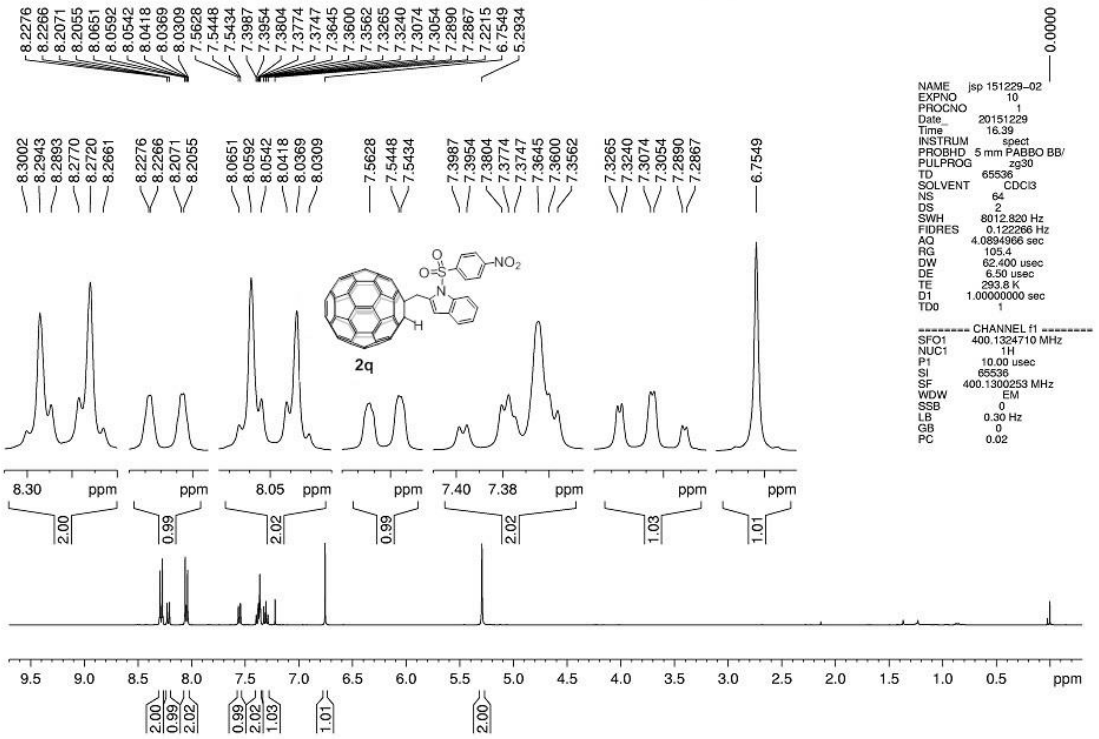
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2p



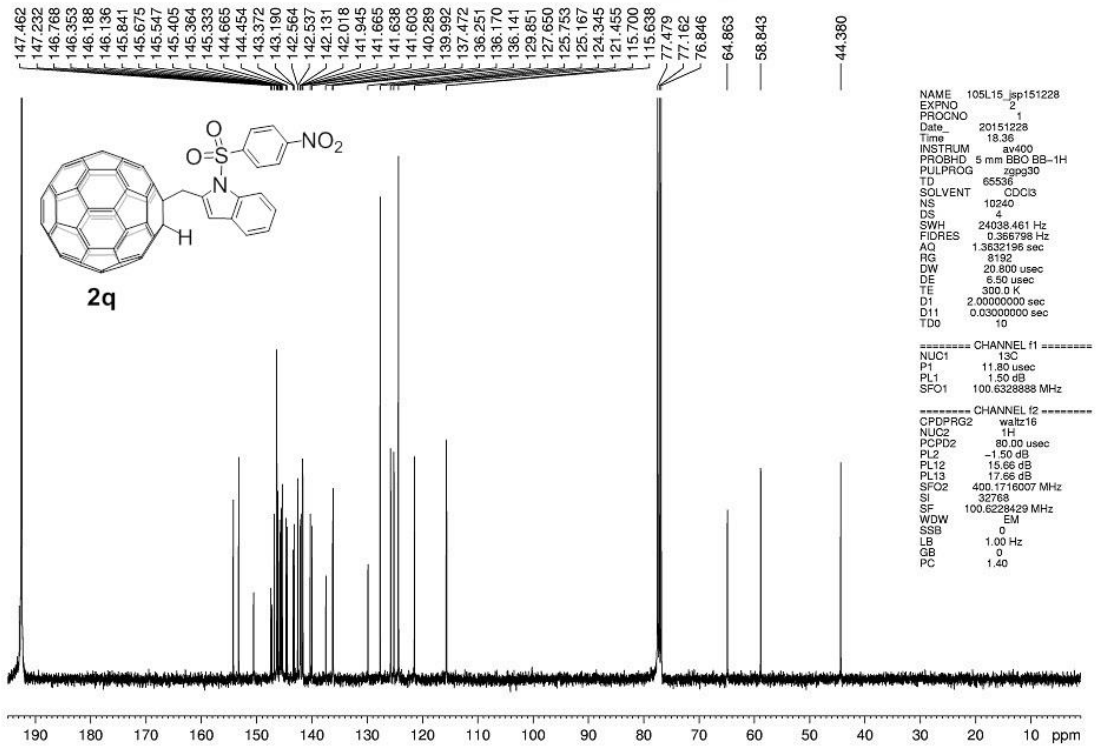
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2p



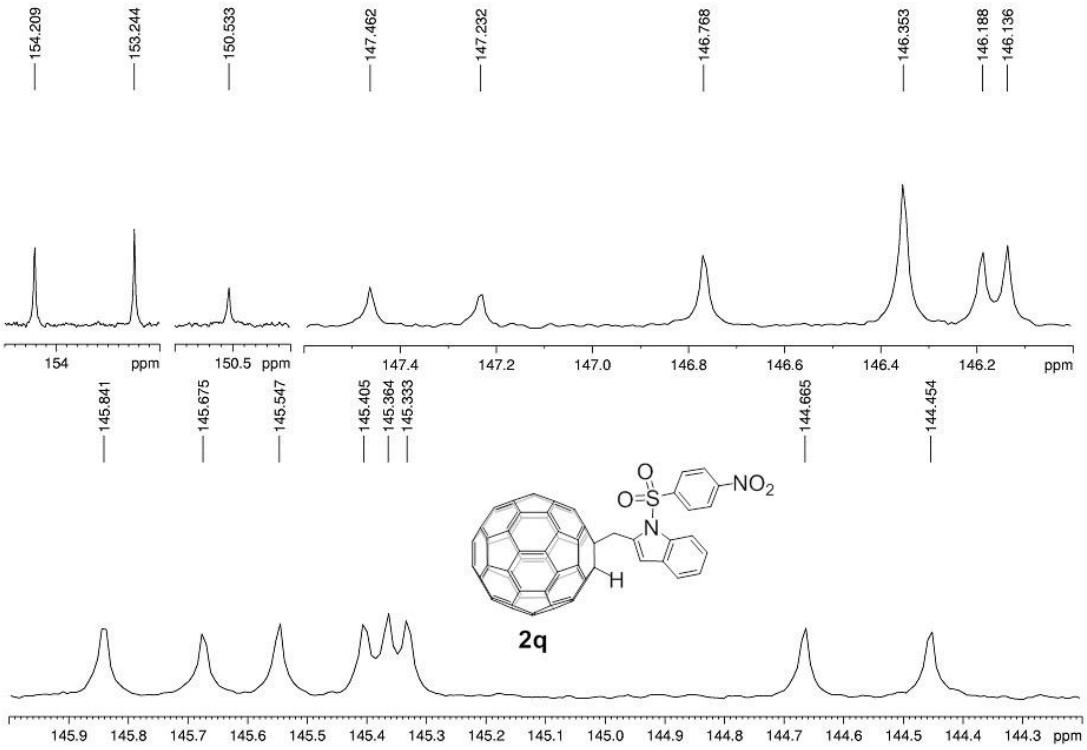
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2q



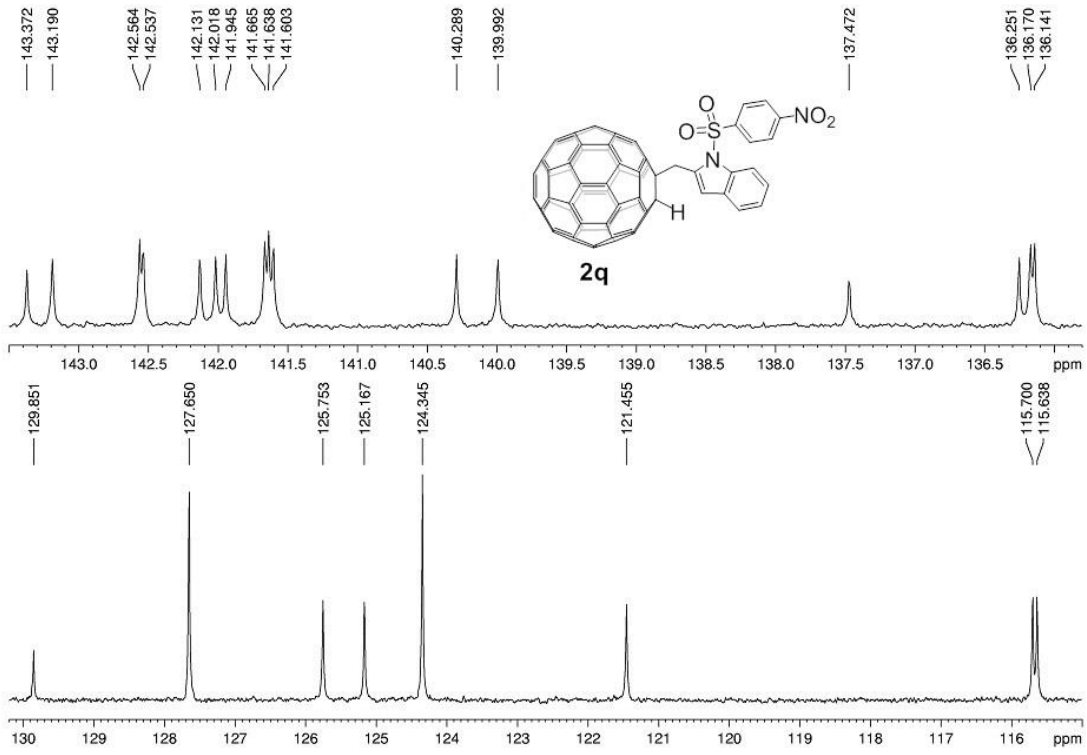
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2q



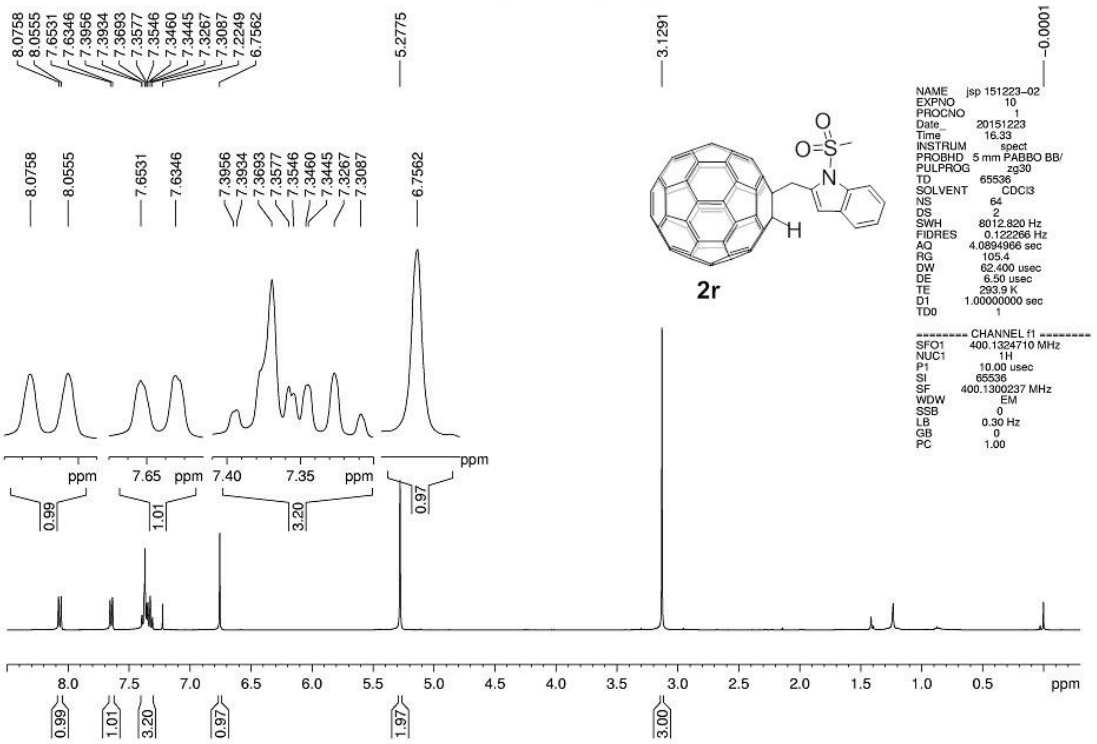
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2q



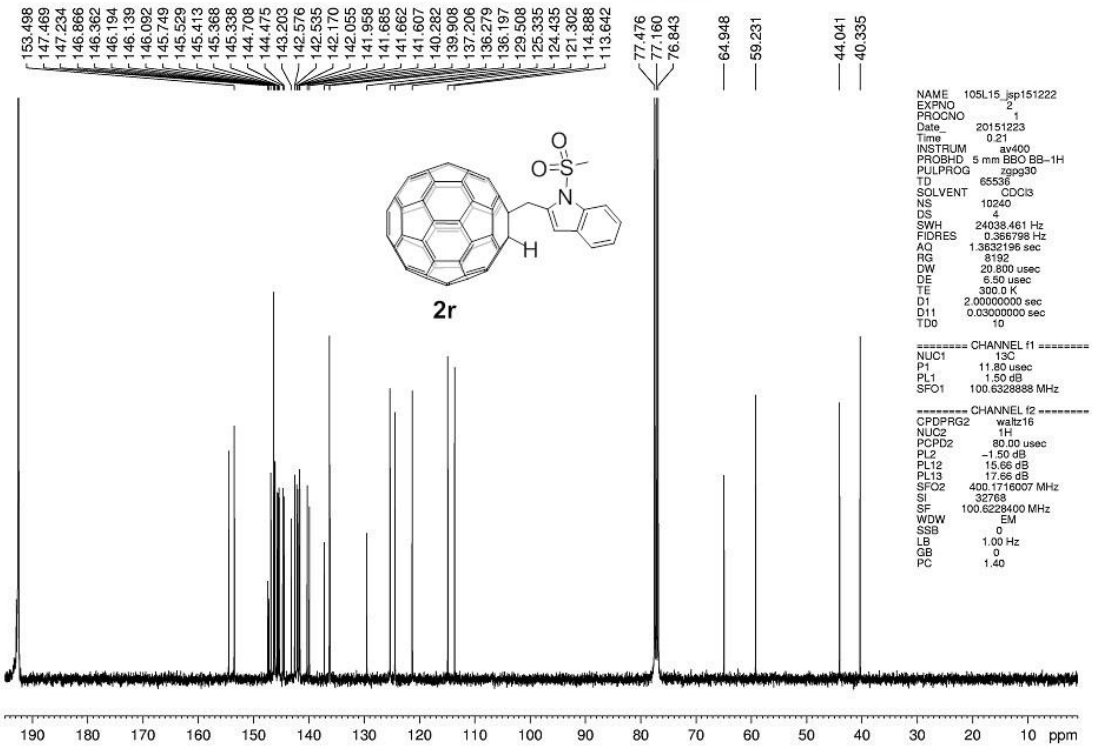
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2q



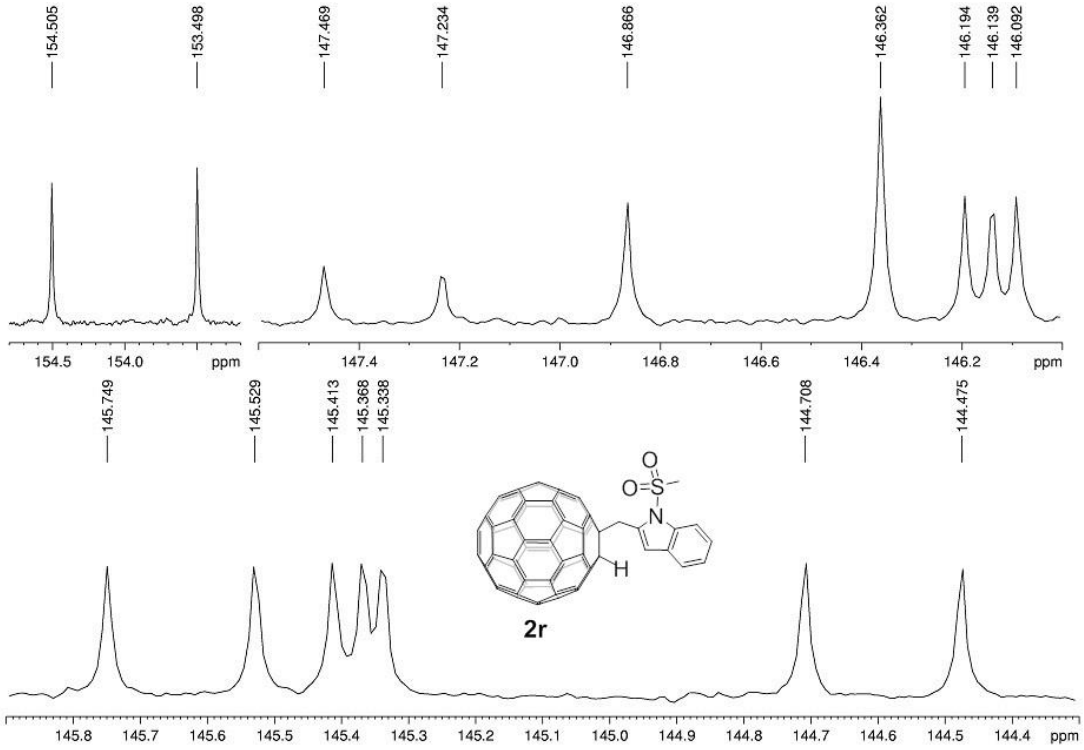
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2r



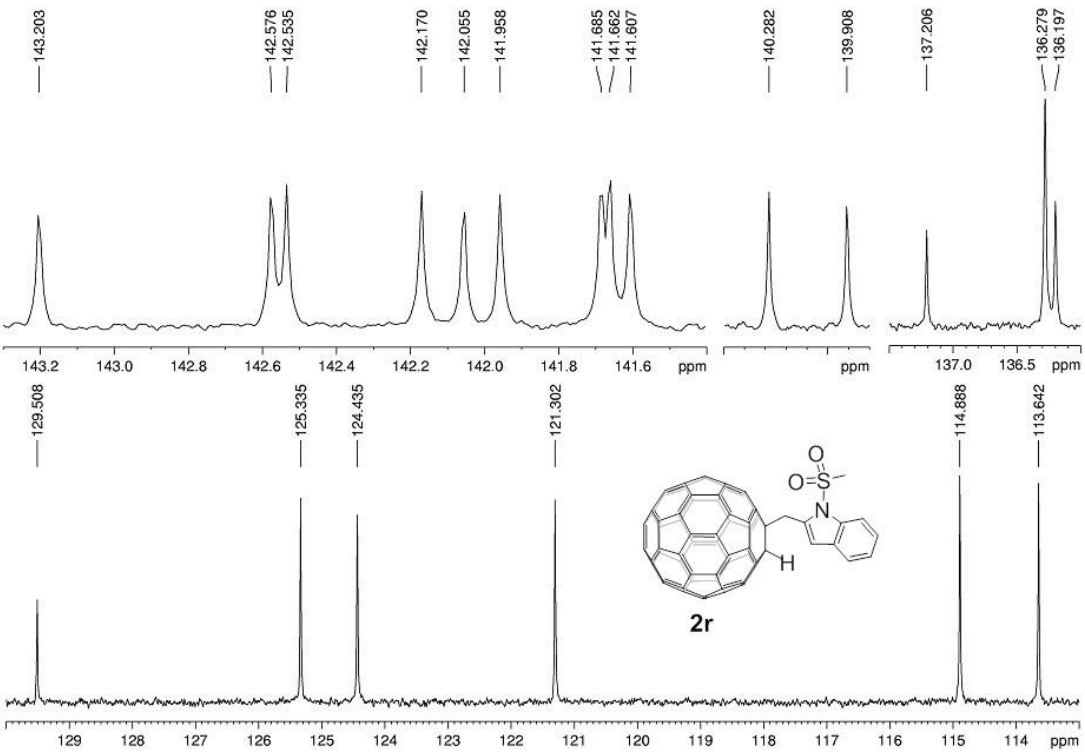
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2r



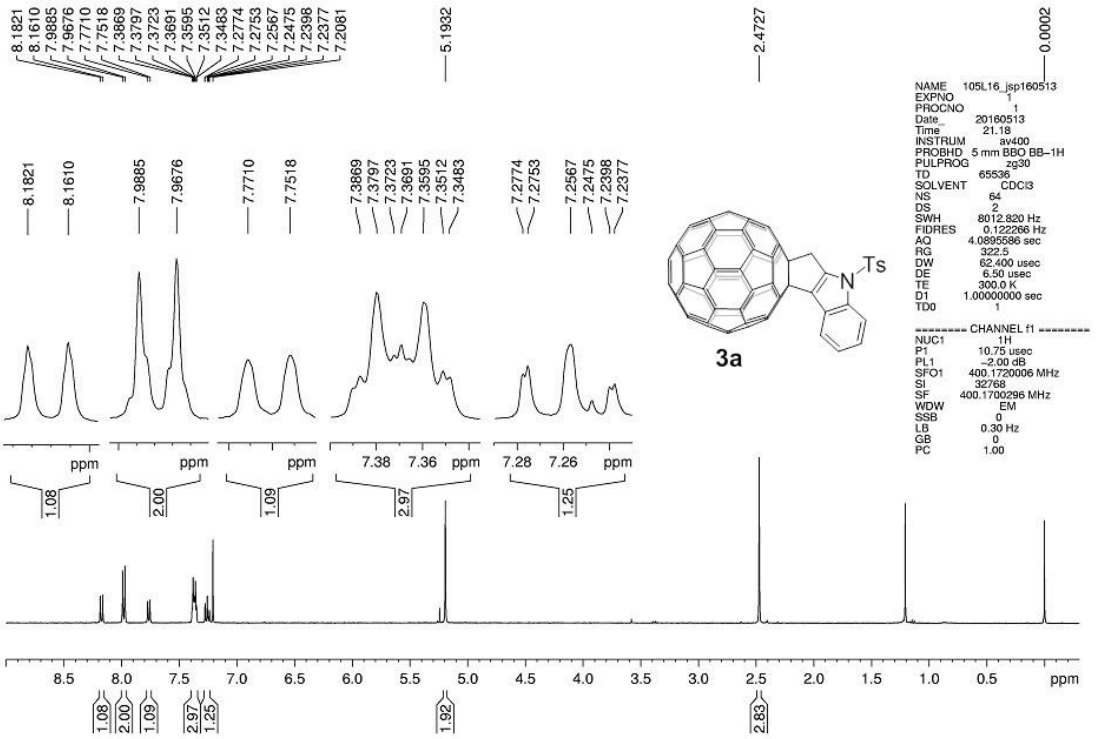
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2r



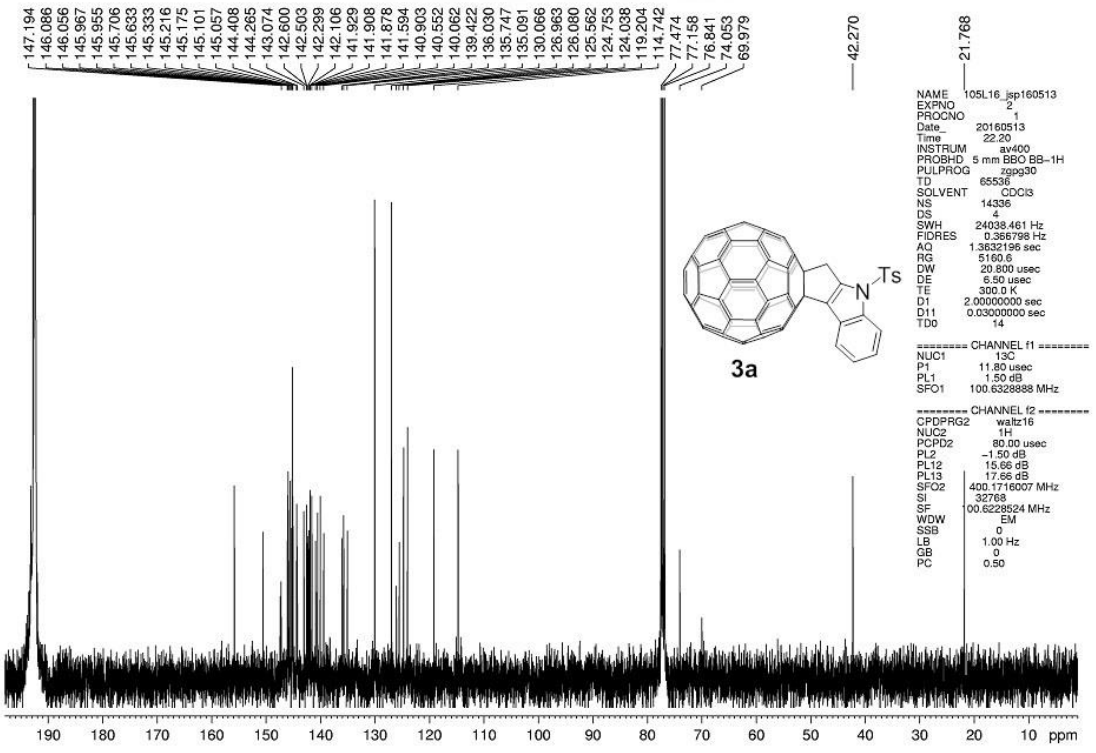
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2r



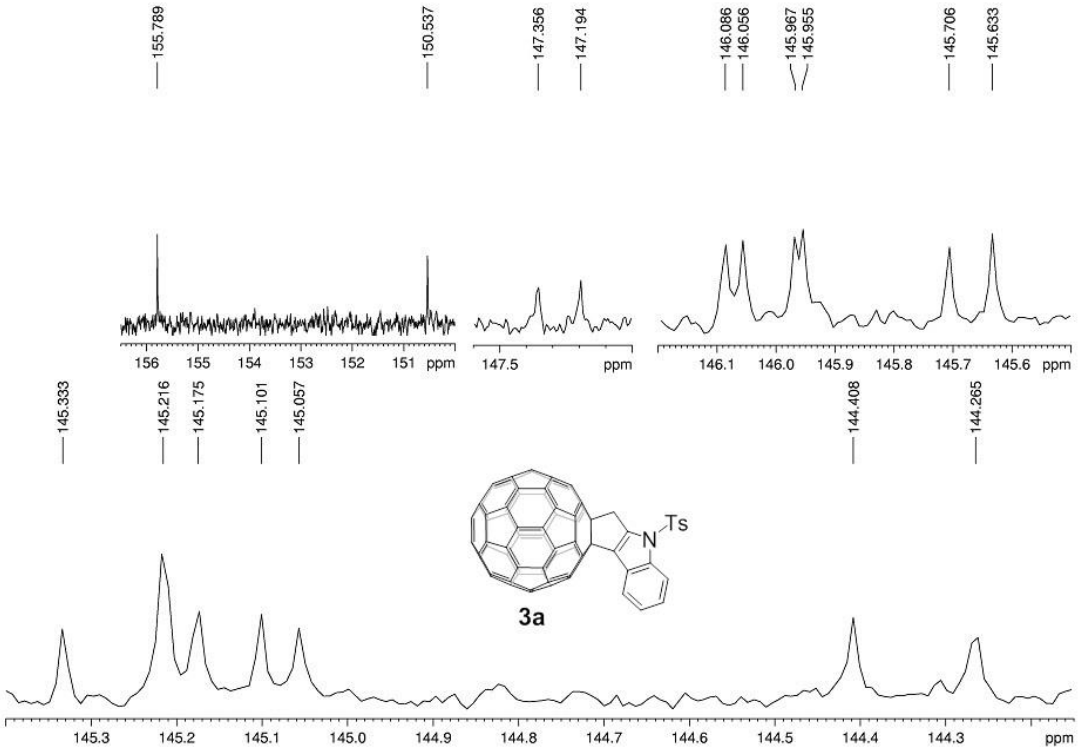
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 3a



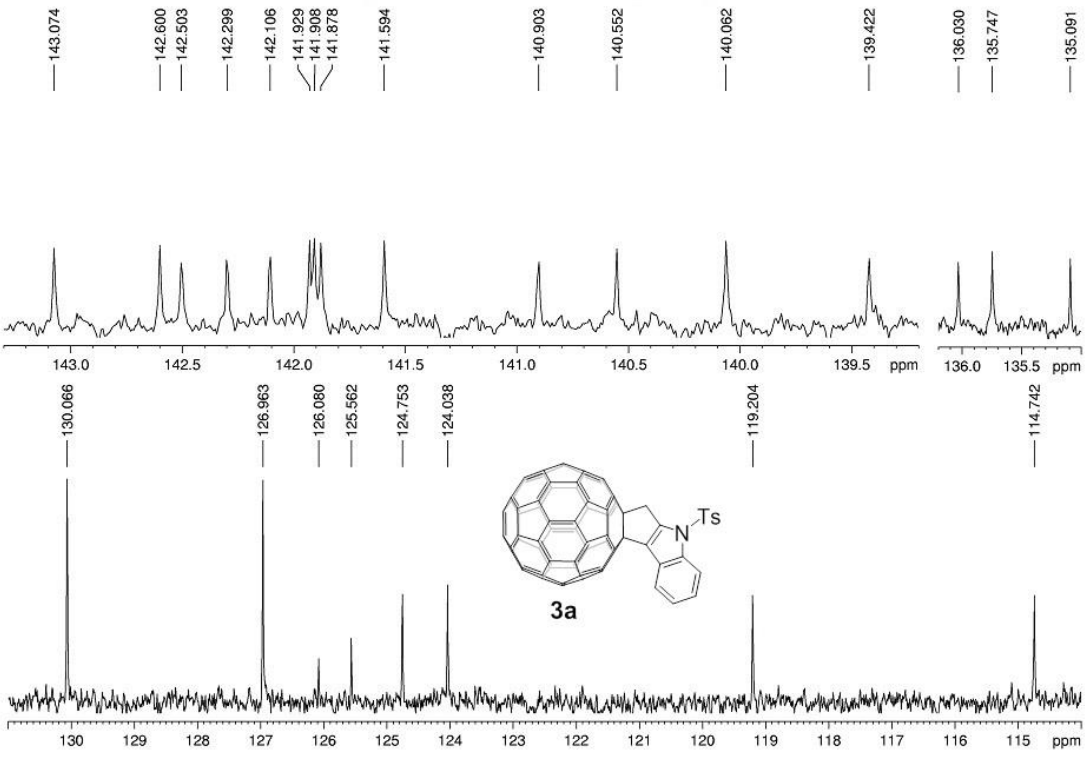
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) Spectrum of Compound 3a



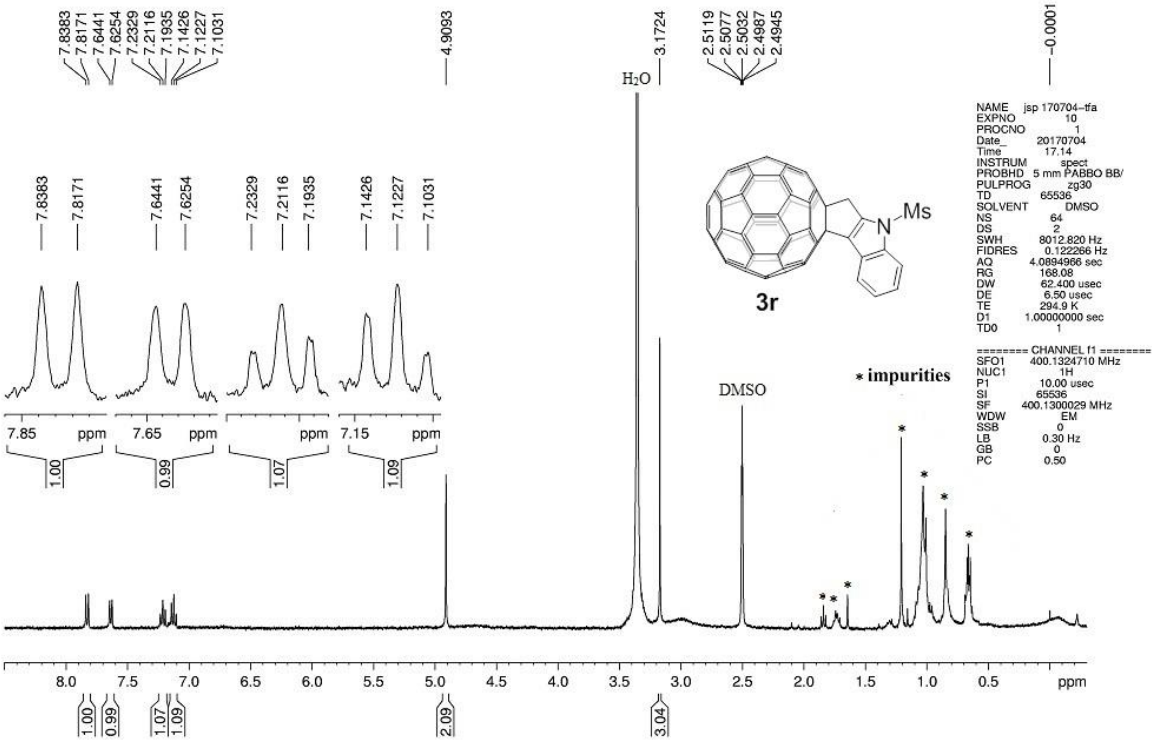
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 3a



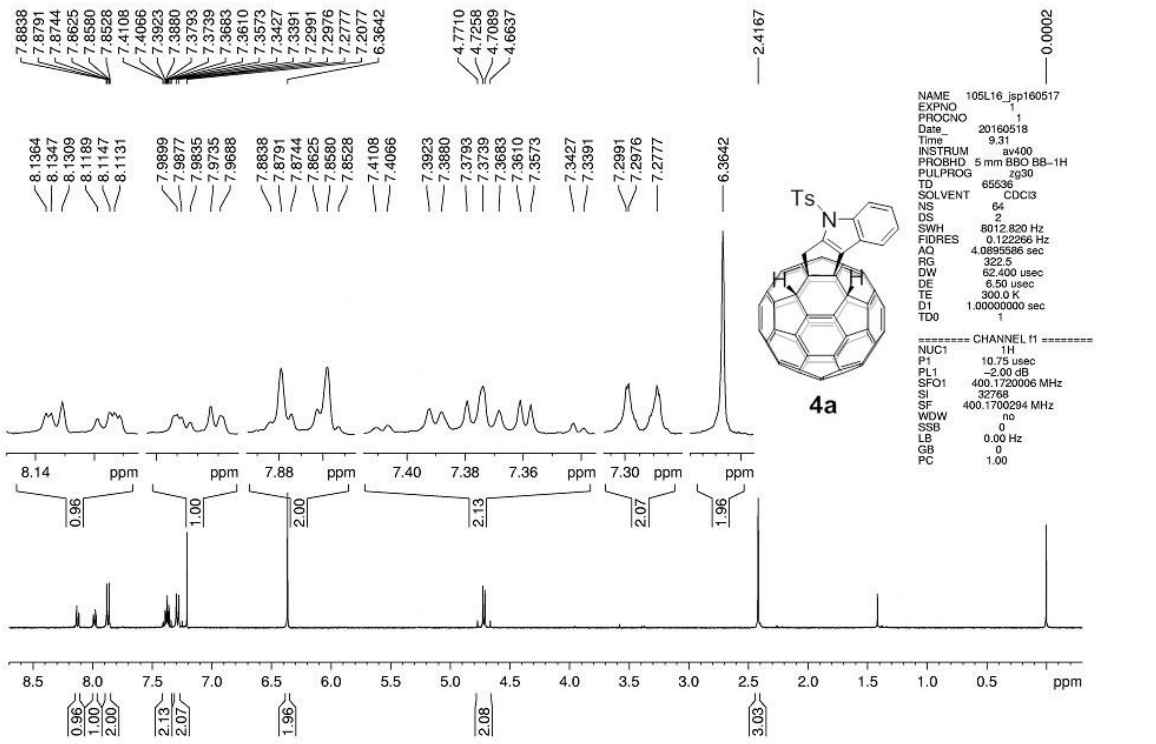
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 3a



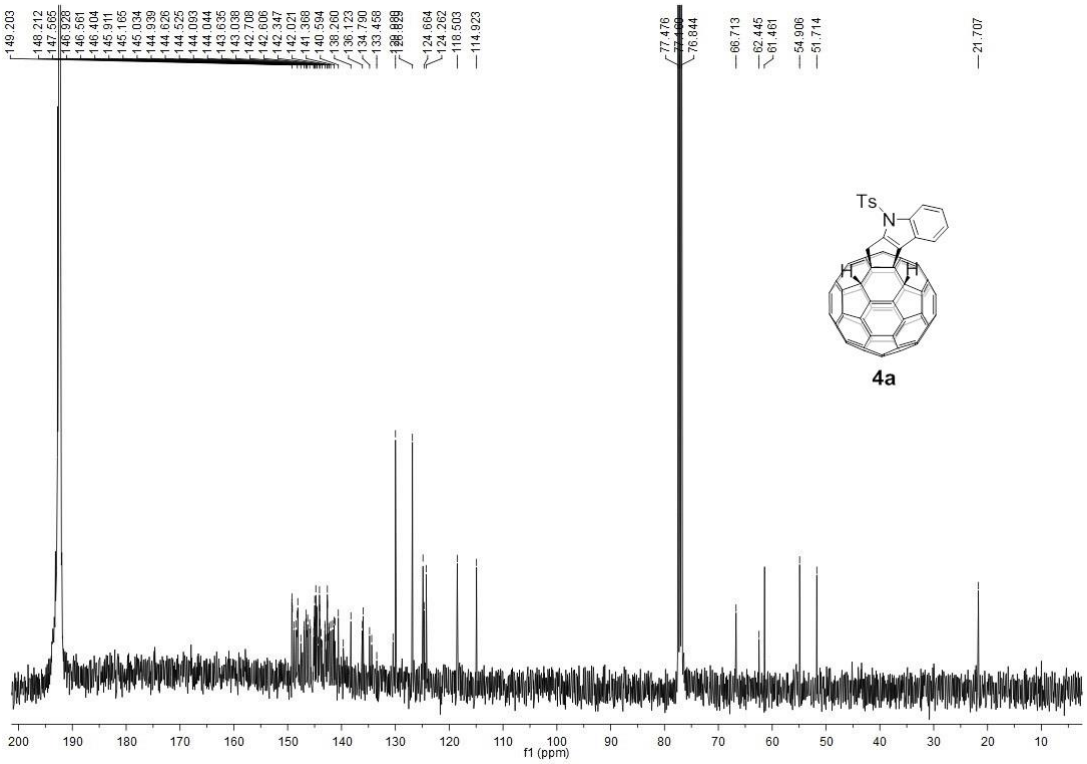
^{1}H NMR (400 MHz, CS_2/DMSO-d_6) Spectrum of Compound 3r



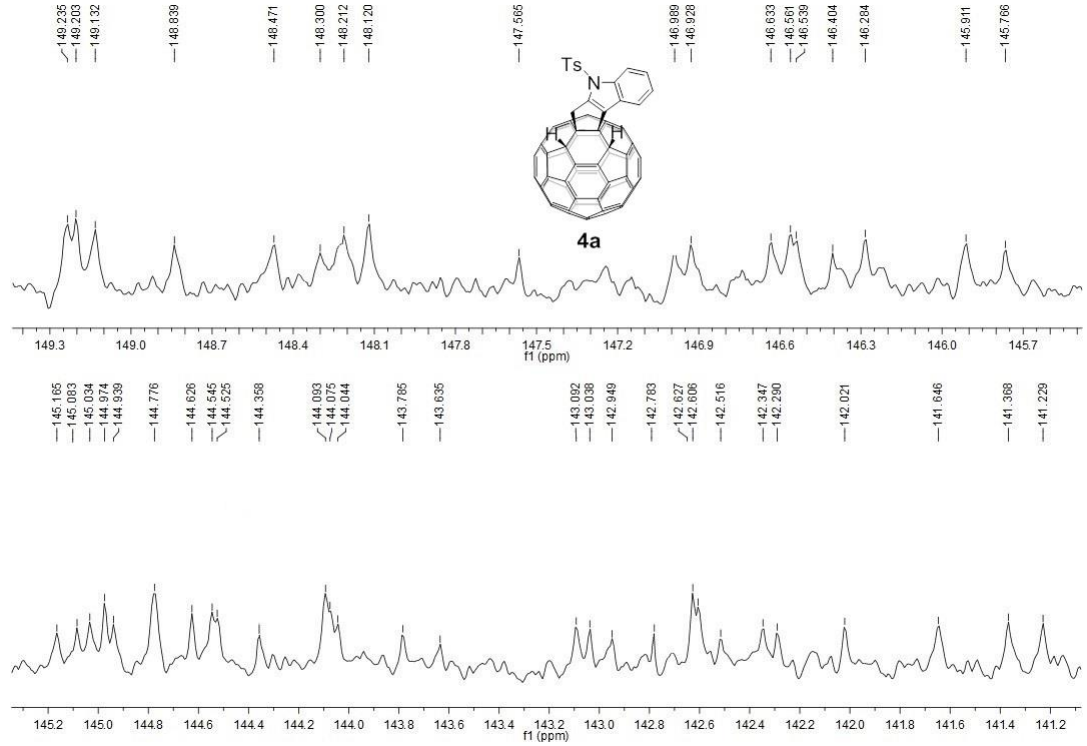
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 4a



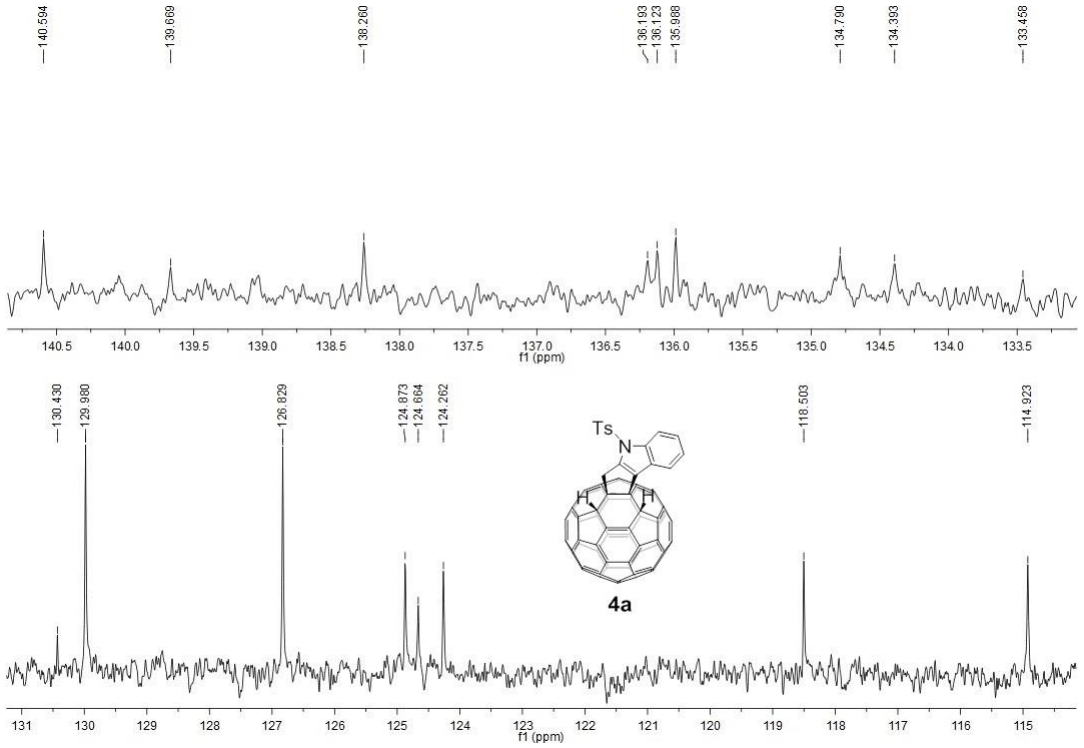
^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 4a



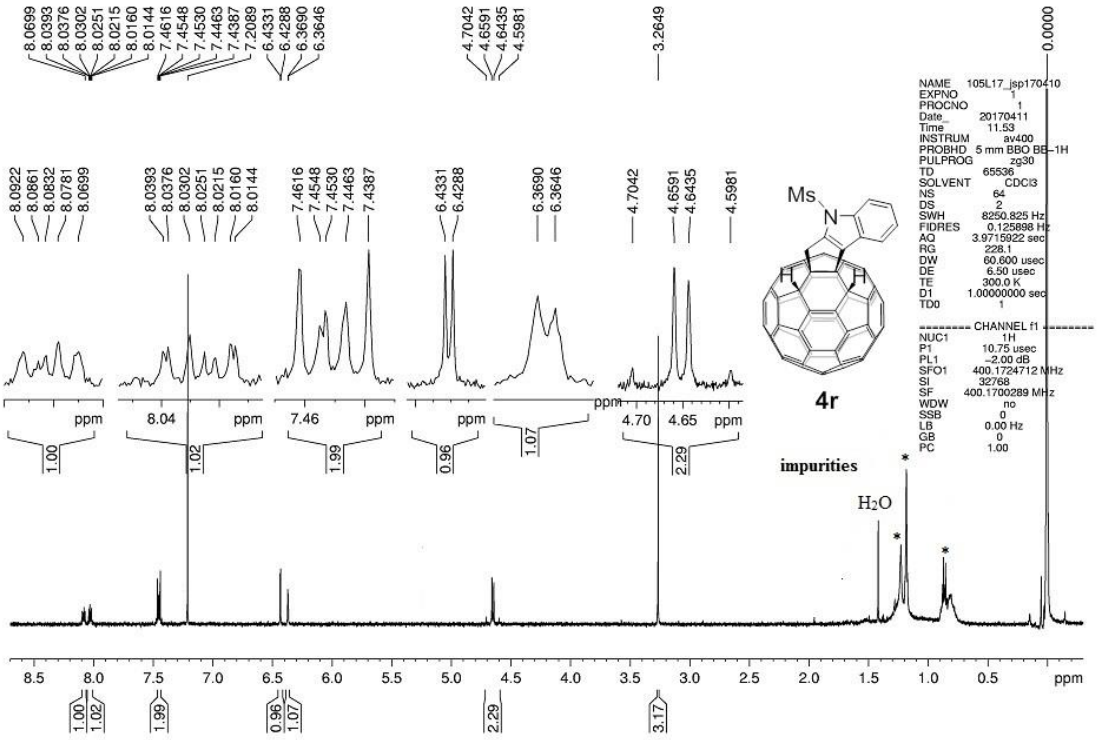
Expaned ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 4a

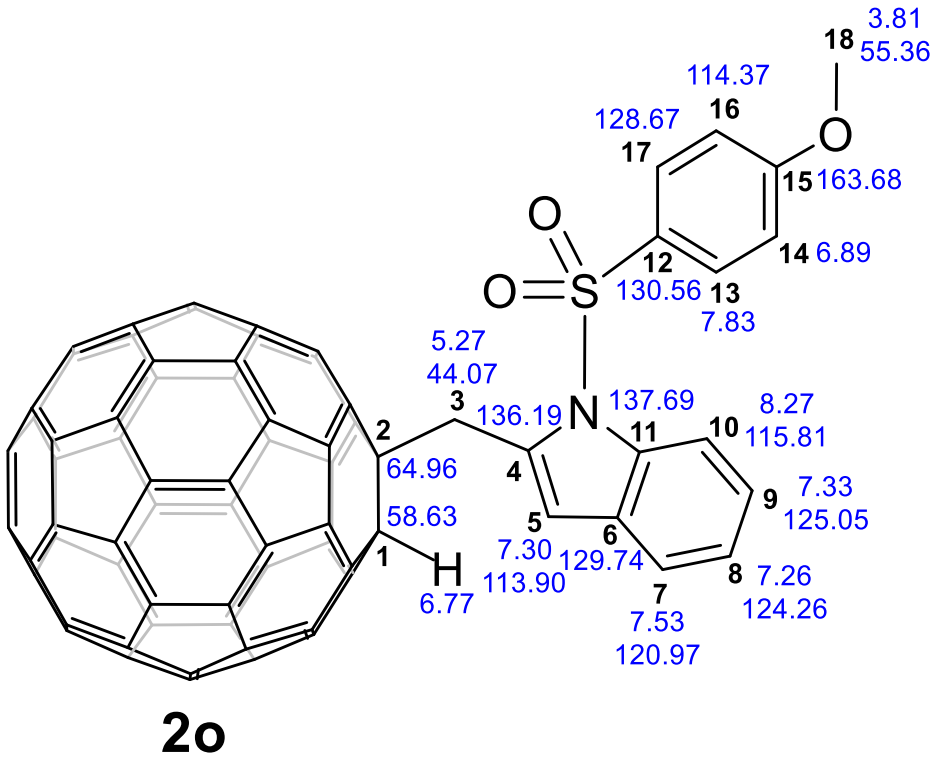


Expaned ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) Spectrum of Compound 4a



^1H NMR (400 MHz, $CS_2/CDCl_3$) Spectrum of Compound 4r





2o

Table S5. The ^{1}H NMR and ^{13}C NMR Chemical Shifts of Compound **2o**

Entry	δ_H [ppm]	δ_C [ppm]	Entry	δ_H [ppm]	δ_C [ppm]
1	6.77	58.63	10	8.27	115.81
2	/	64.96	11	/	137.69
3	5.27	44.07	12	/	130.56
4	/	136.19	13	7.83	128.67
5	7.30	113.90	14	6.89	114.37
6	/	129.74	15	/	163.68
7	7.53	120.97	16	6.89	114.37
8	7.26	124.26	17	7.83	128.67
9	7.33	125.05	18	3.81	55.36

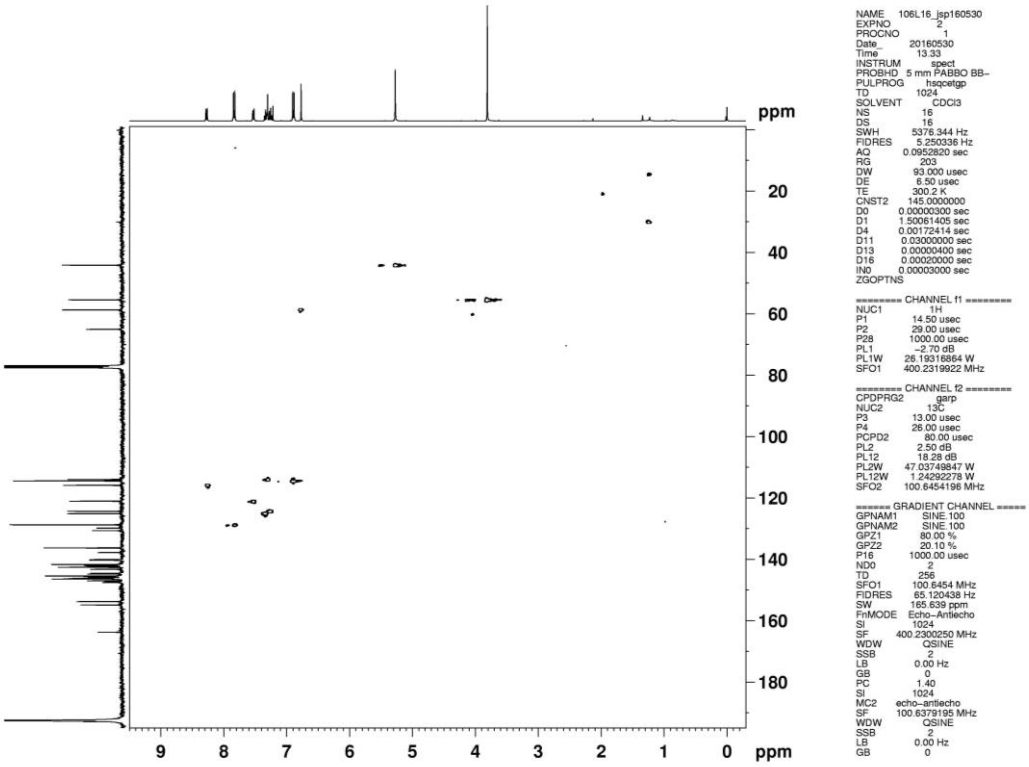


Figure S5. HSQC Spectrum of Compound **2o**

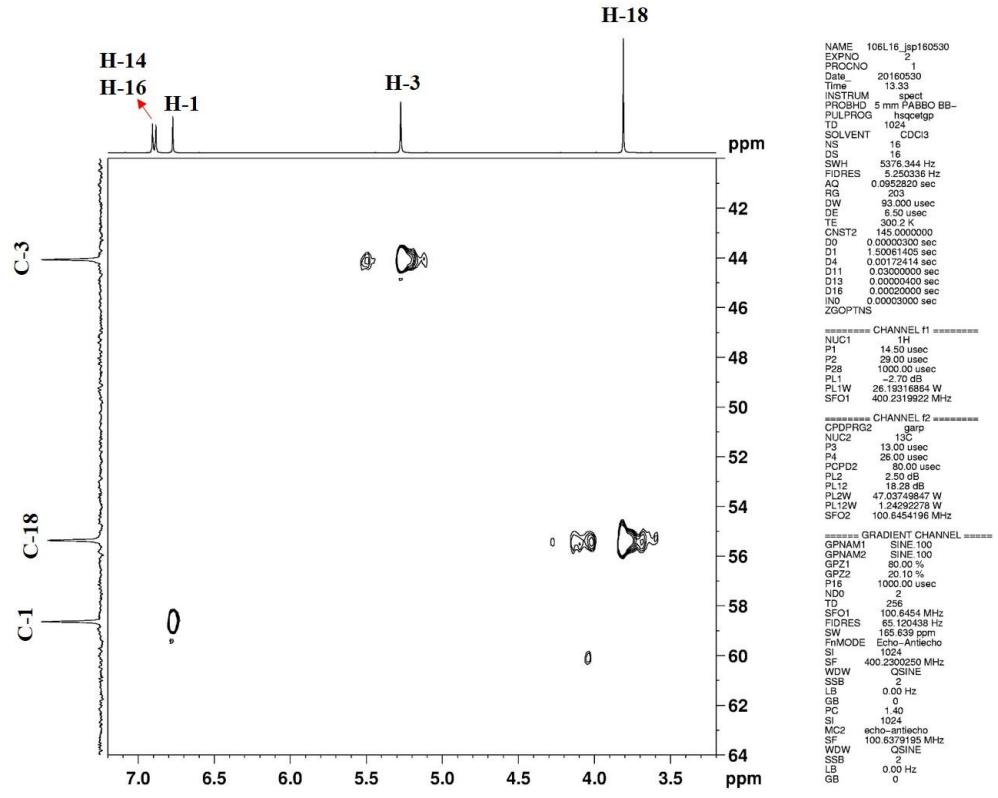


Figure S6. Expanded HSQC Spectrum of Compound **2o**

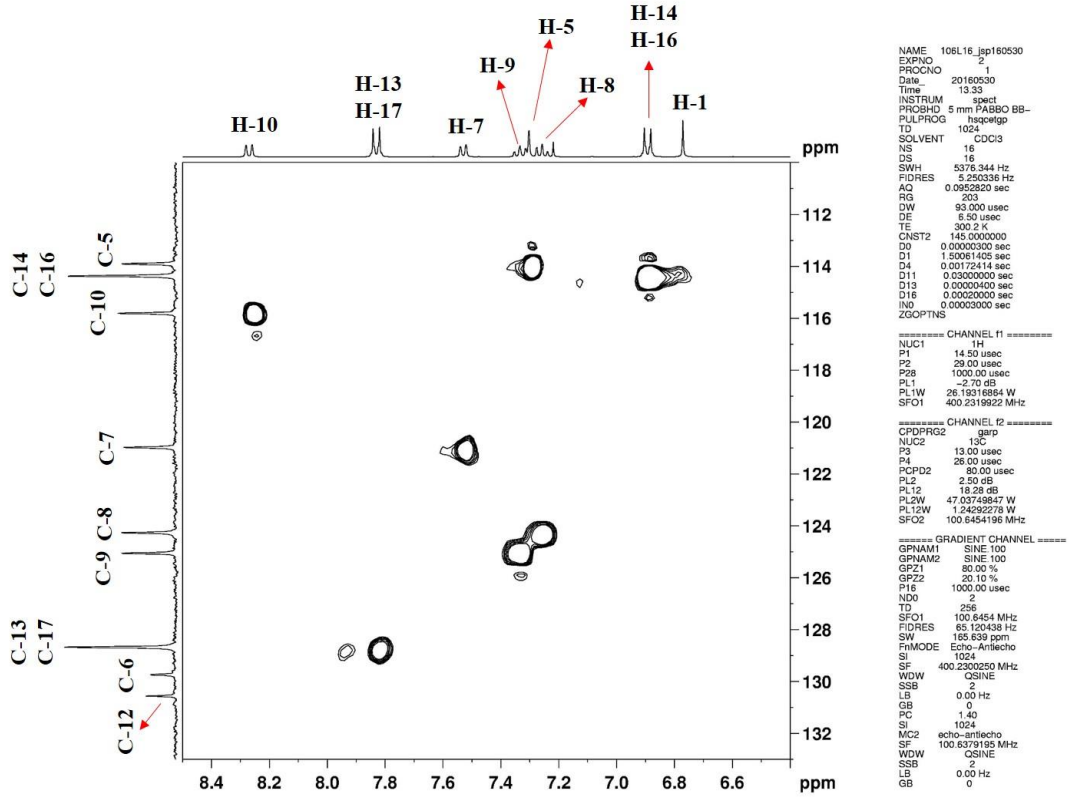


Figure S7. Expanded HSQC Spectrum of Compound **2o**

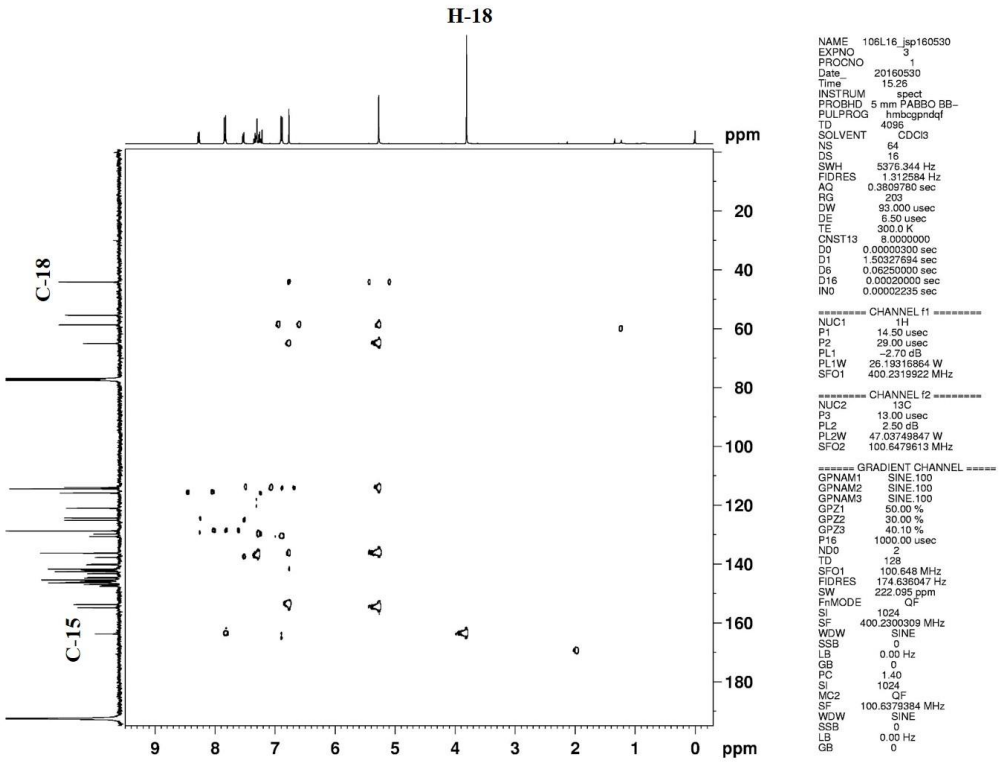


Figure S8. HMBC Spectrum of Compound **2o**

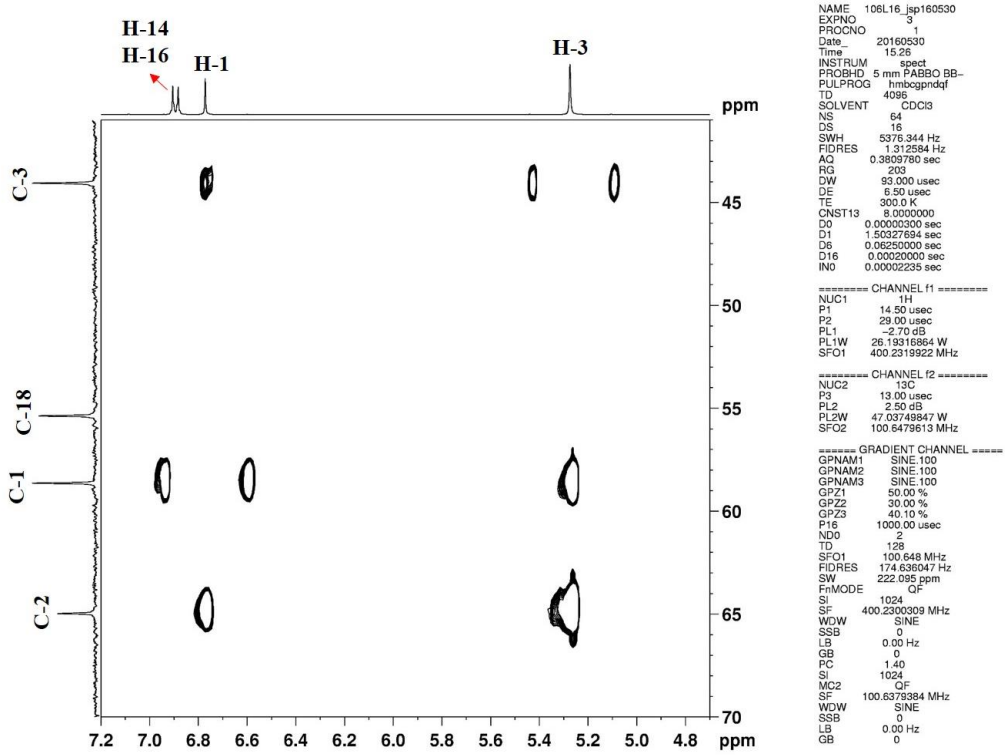


Figure S9. Expanded HMBC Spectrum of Compound **2o**

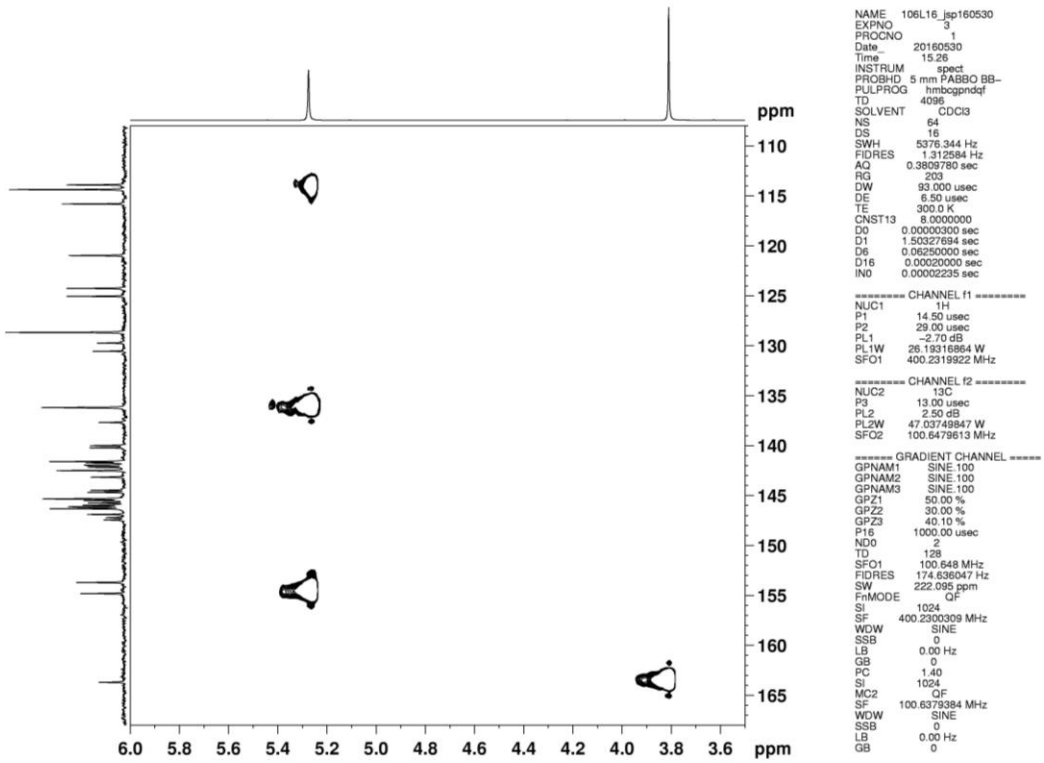


Figure S10. Expanded HMBC Spectrum of Compound **2o**

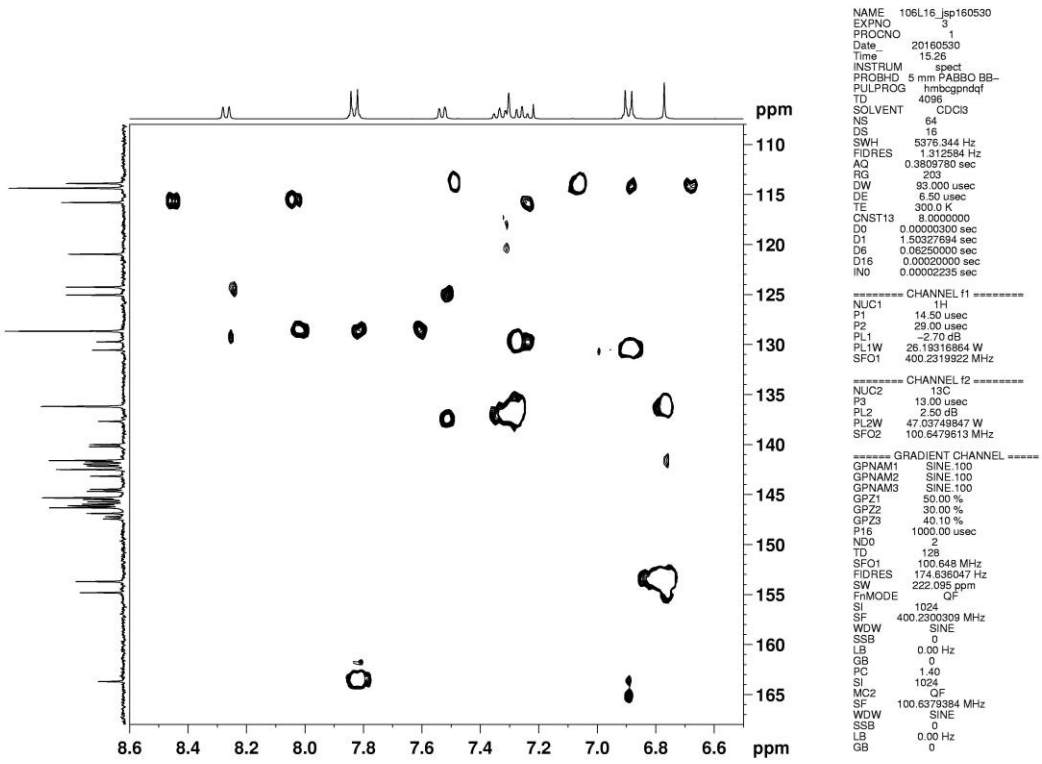
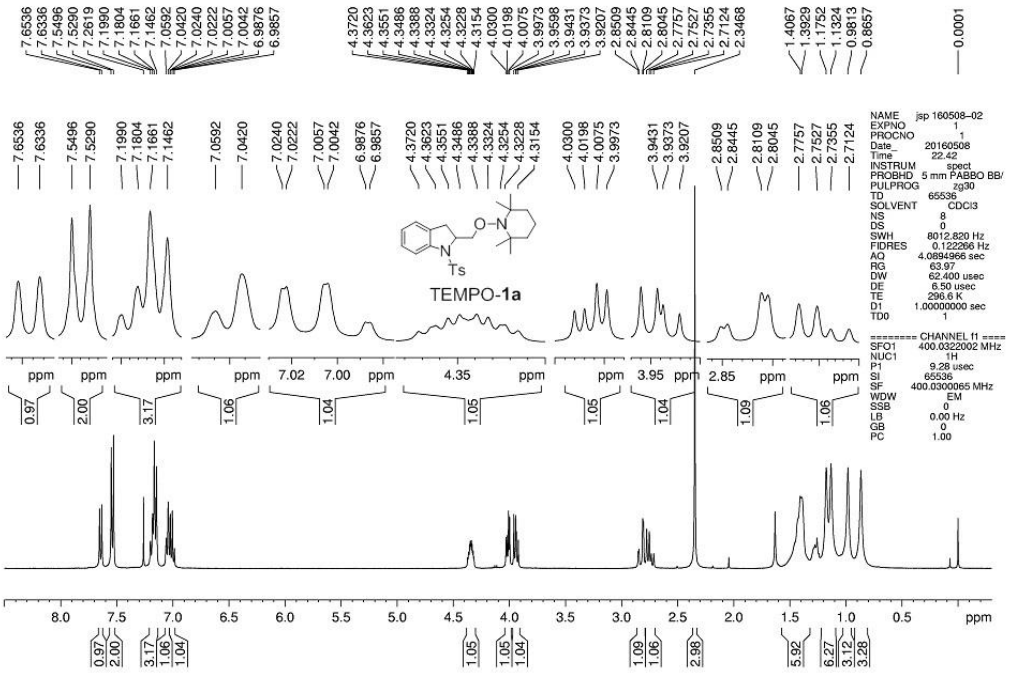
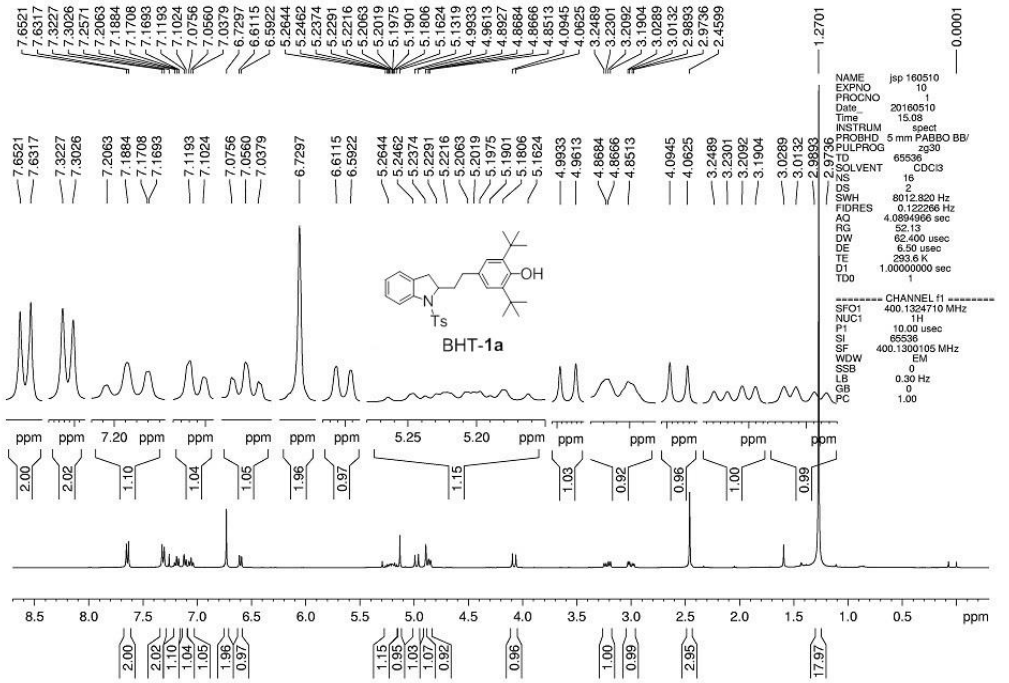


Figure S11. Expanded HMBC Spectrum of Compound **2o**

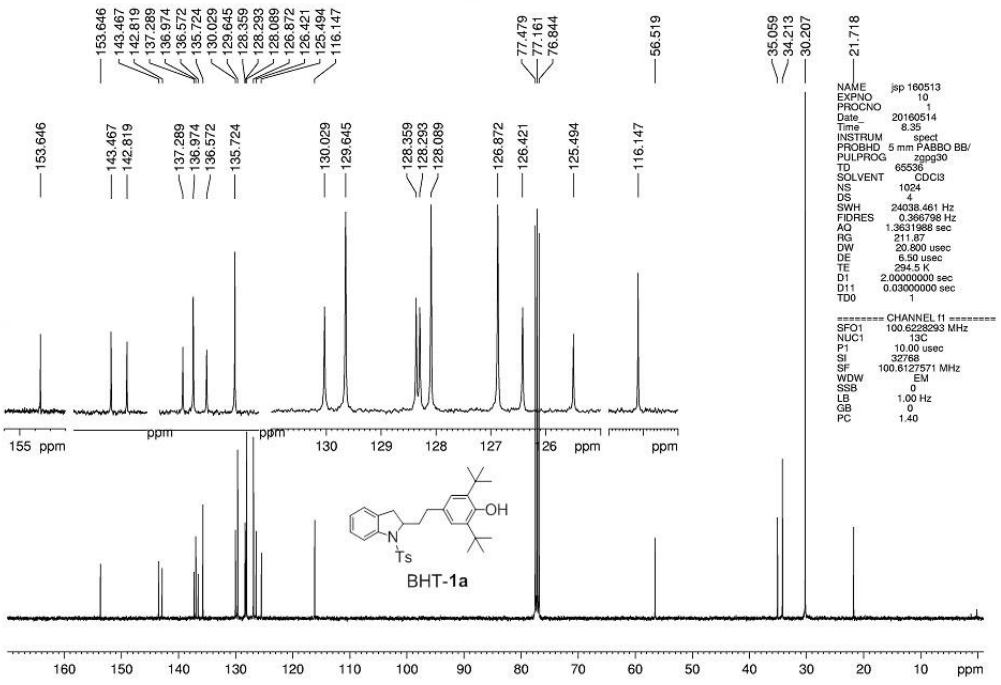
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound TEMPO-1a



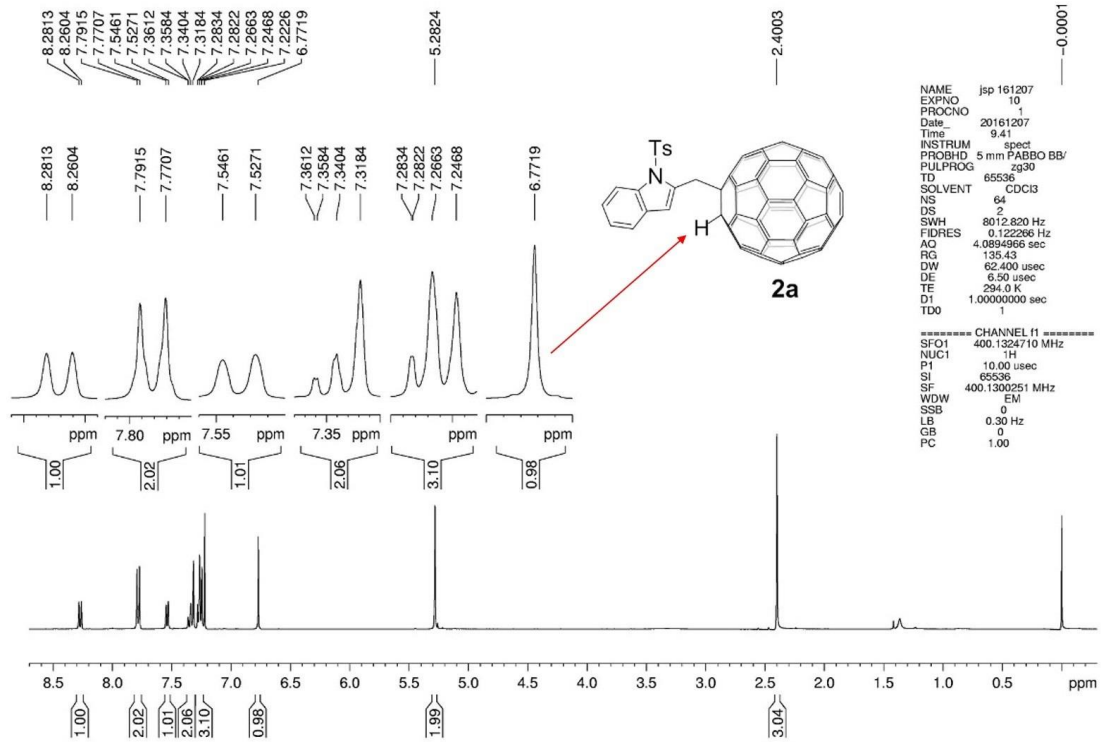
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound BHT-1a



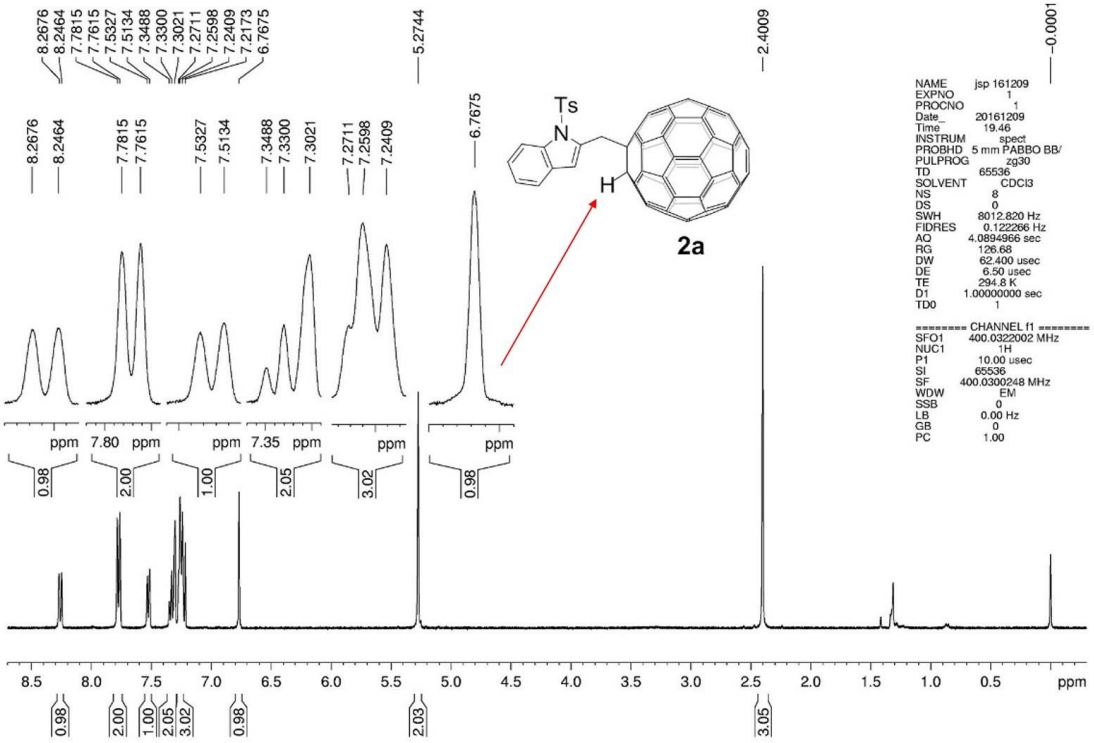
^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound BHT-1a



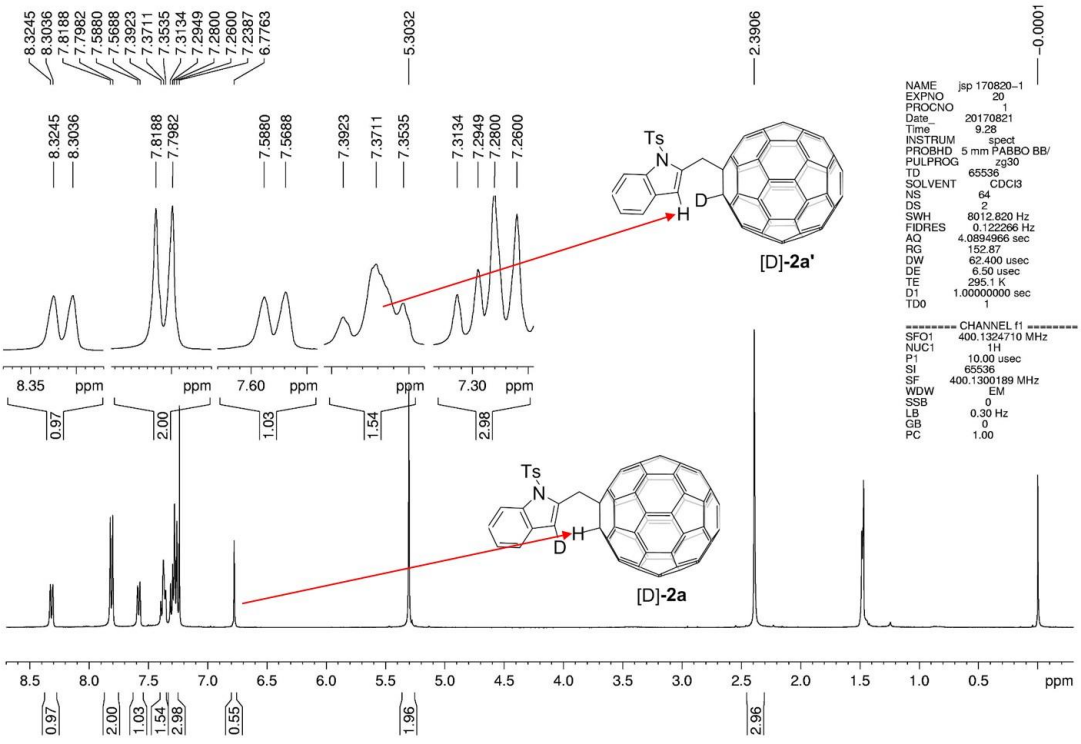
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) Spectrum of Compound 2a Obtained from the D_2O-Labeled Experiment

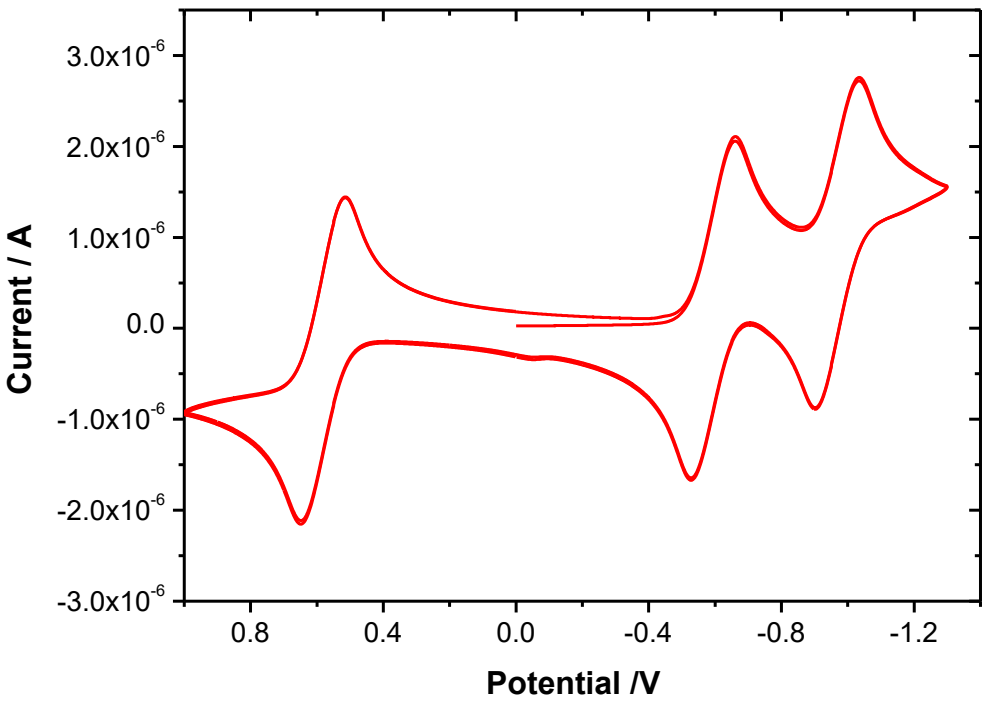


^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2a Obtained from the [D]-1a-Labeled Experiment

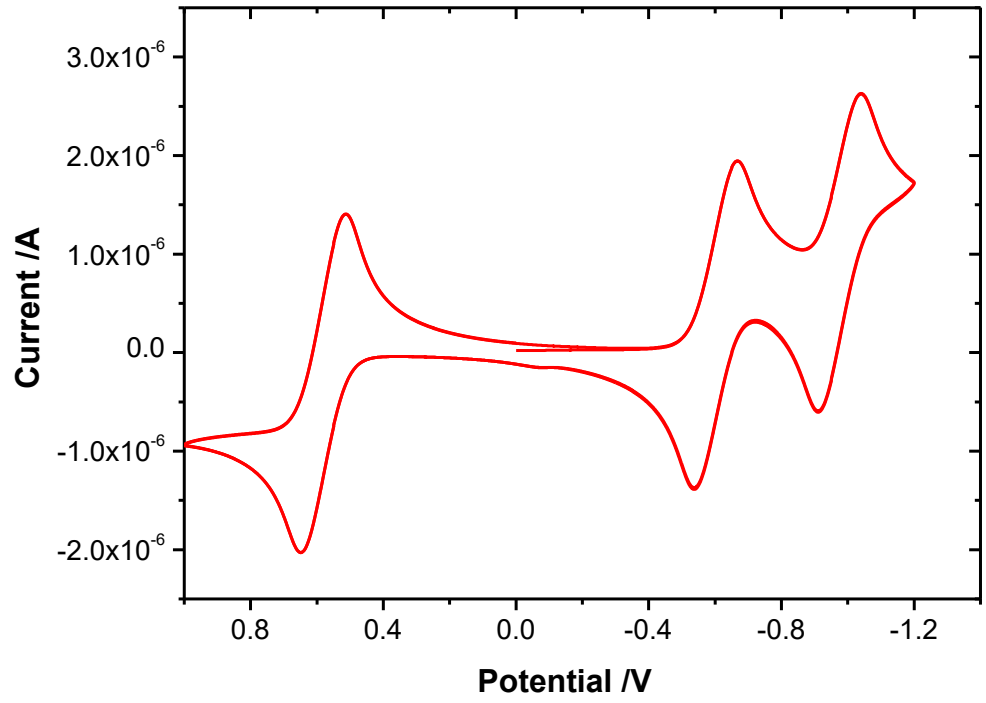


^{1}H NMR (400 MHz, CS_2/$CDCl_3$) Spectrum of Compound 2a Obtained from the [D]-1a'-Labeled Experiment

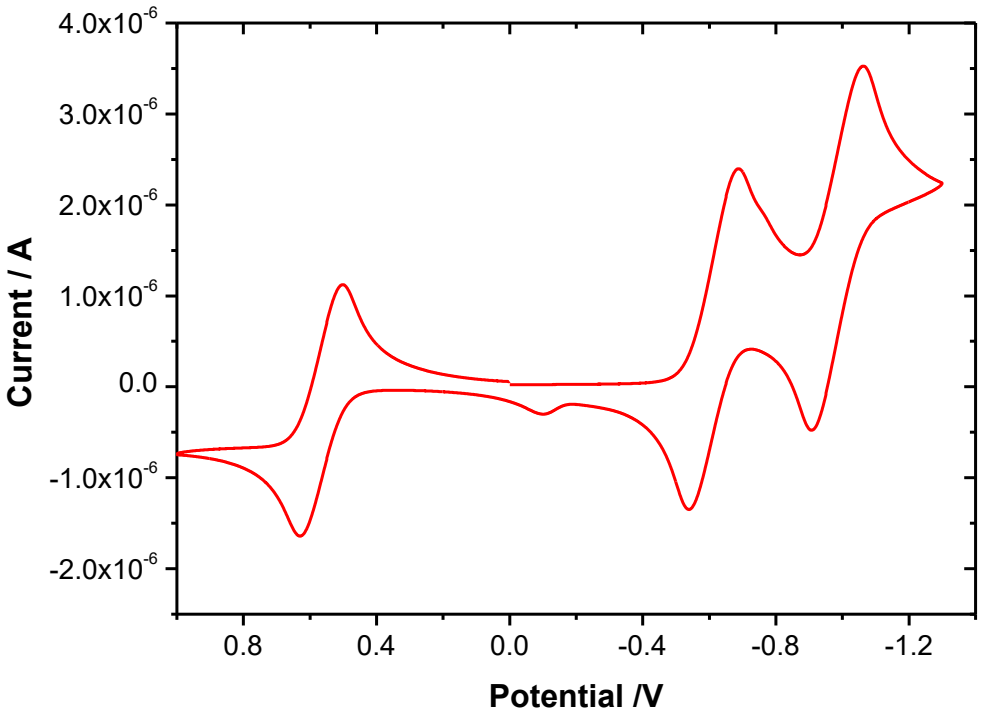




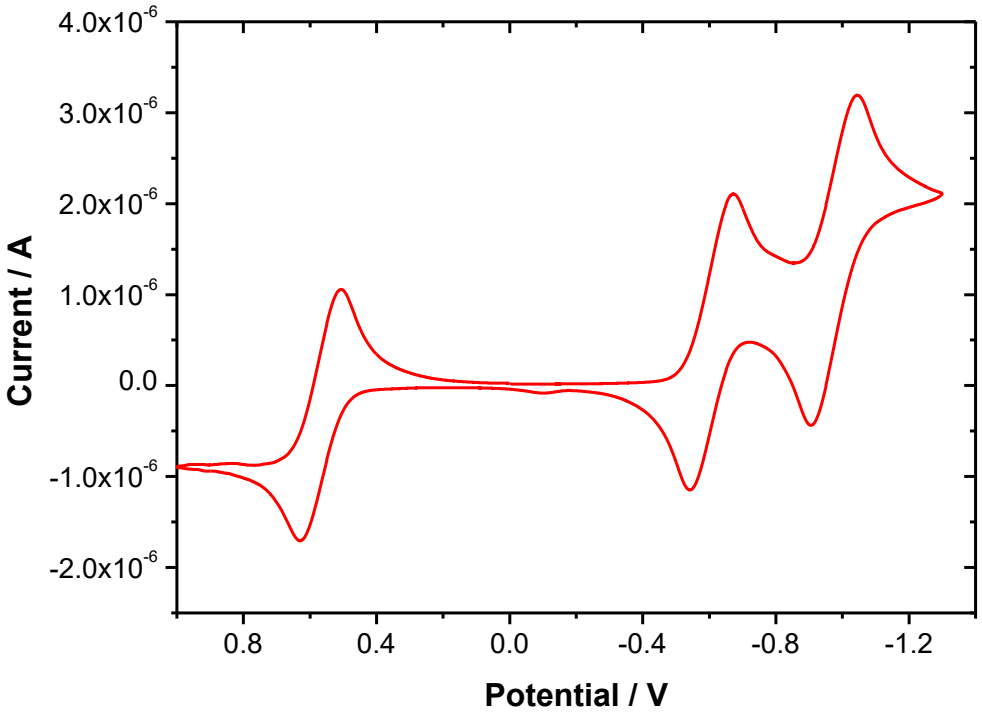
Cyclic Voltammogram of Compound **2a** (scanning rate: 50 mV s^{-1})



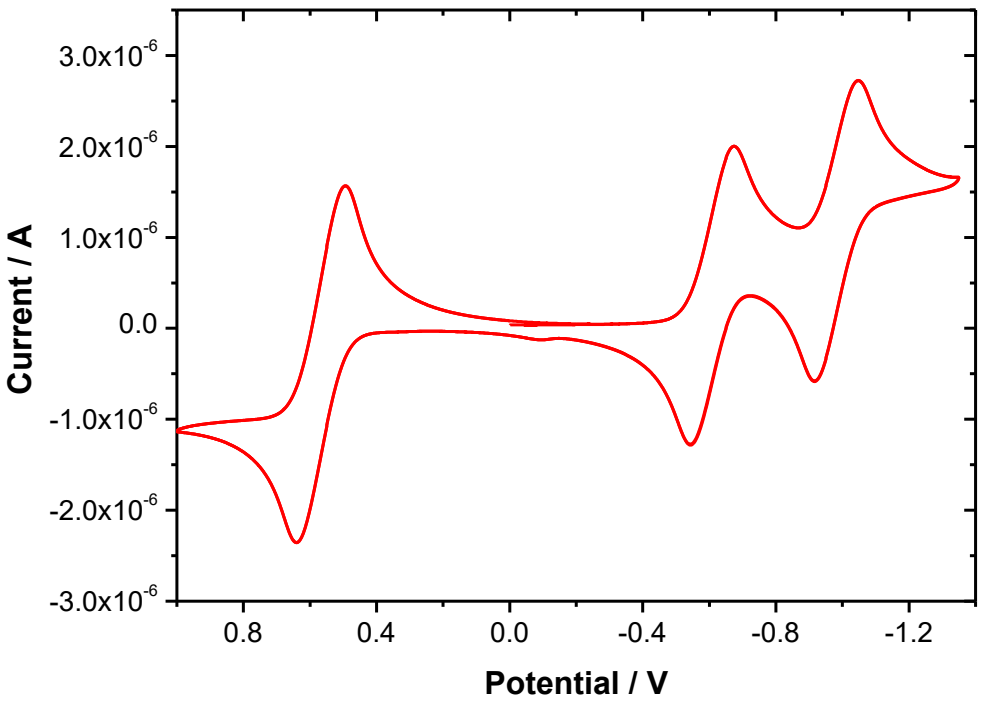
Cyclic Voltammogram of Compound **2b** (scanning rate: 20 mV s^{-1})



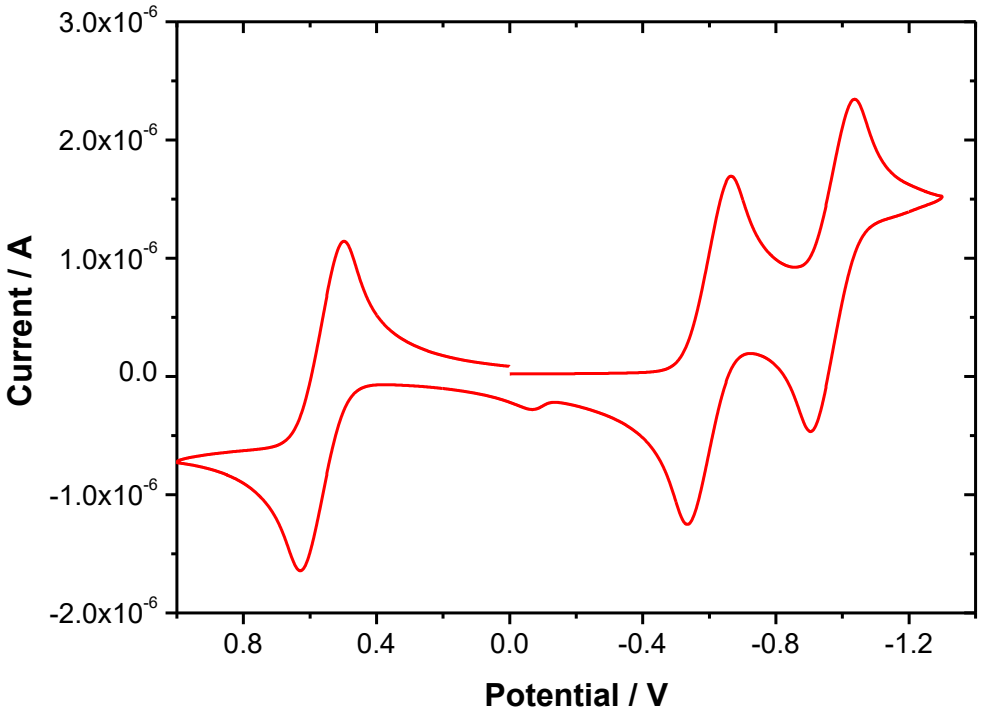
Cyclic Voltammogram of Compound **2c** (scanning rate: 20 mV s^{-1})



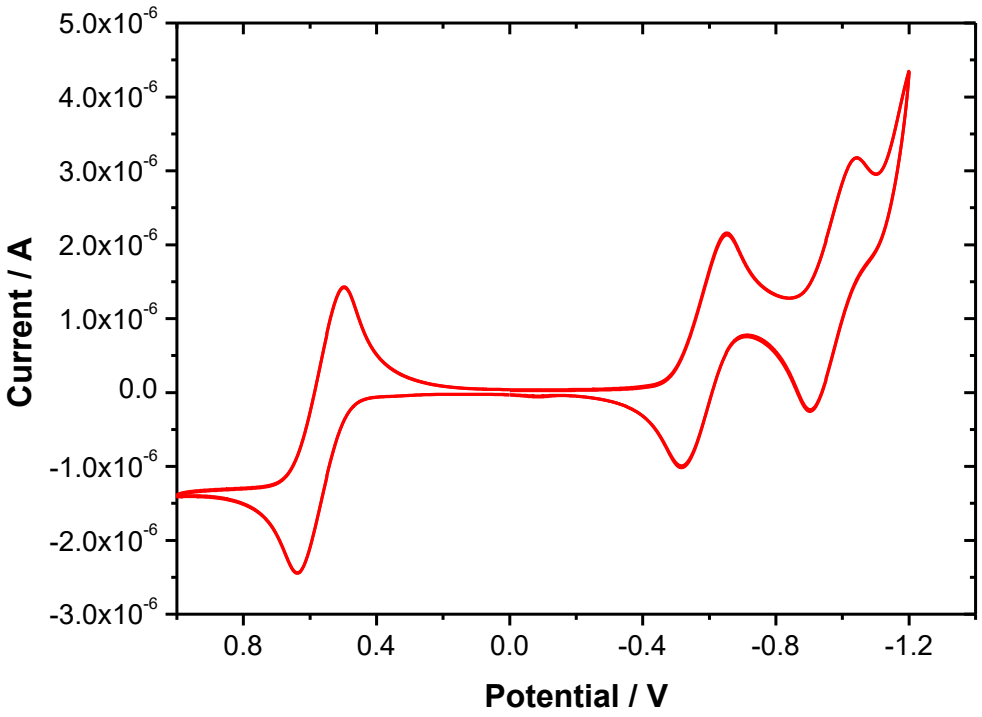
Cyclic Voltammogram of Compound **2d** (scanning rate: 20 mV s^{-1})



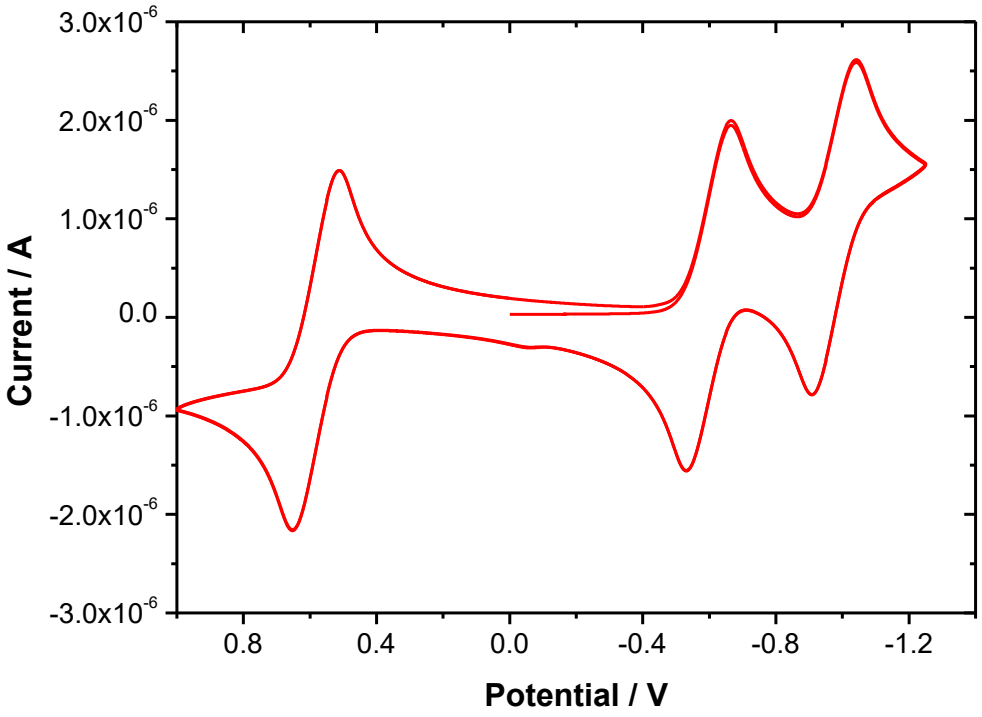
Cyclic Voltammogram of Compound **2e** (scanning rate: 20 mV s^{-1})



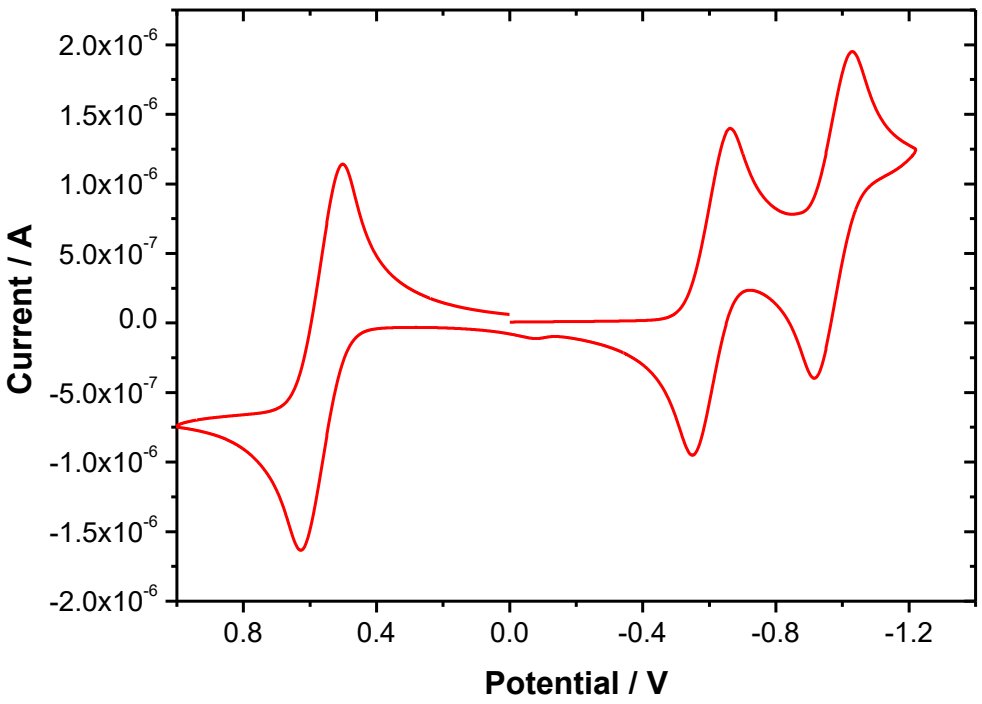
Cyclic Voltammogram of Compound **2f** (scanning rate: 20 mV s^{-1})



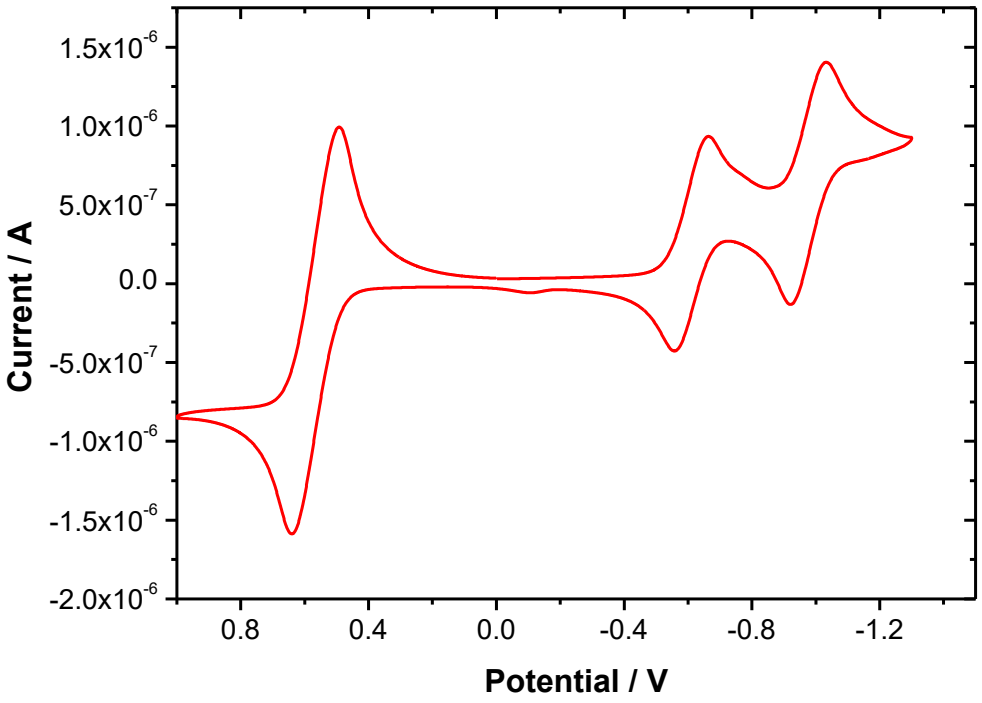
Cyclic Voltammogram of Compound **2g** (scanning rate: 20 mV s^{-1})



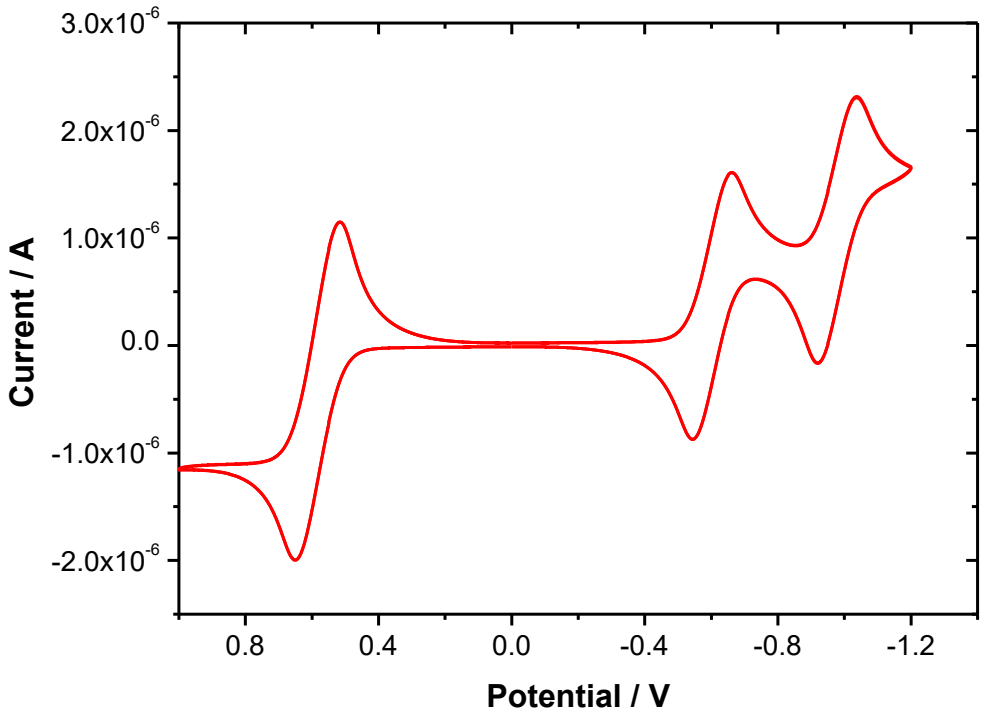
Cyclic Voltammogram of Compound **2h** (scanning rate: 20 mV s^{-1})



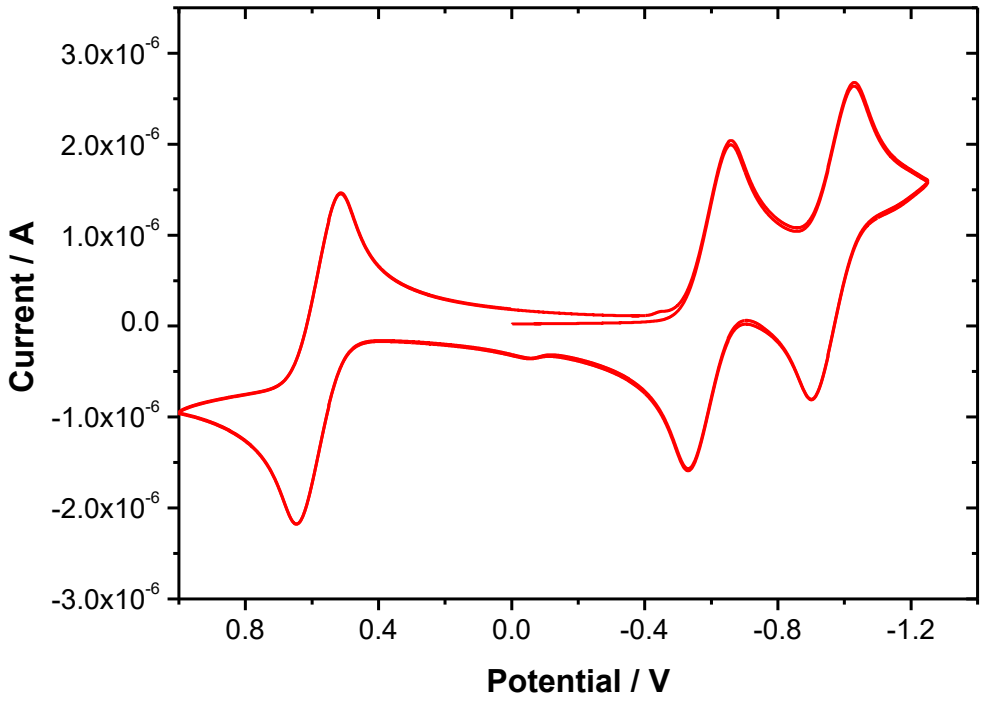
Cyclic Voltammogram of Compound **2i** (scanning rate: 20 mV s^{-1})



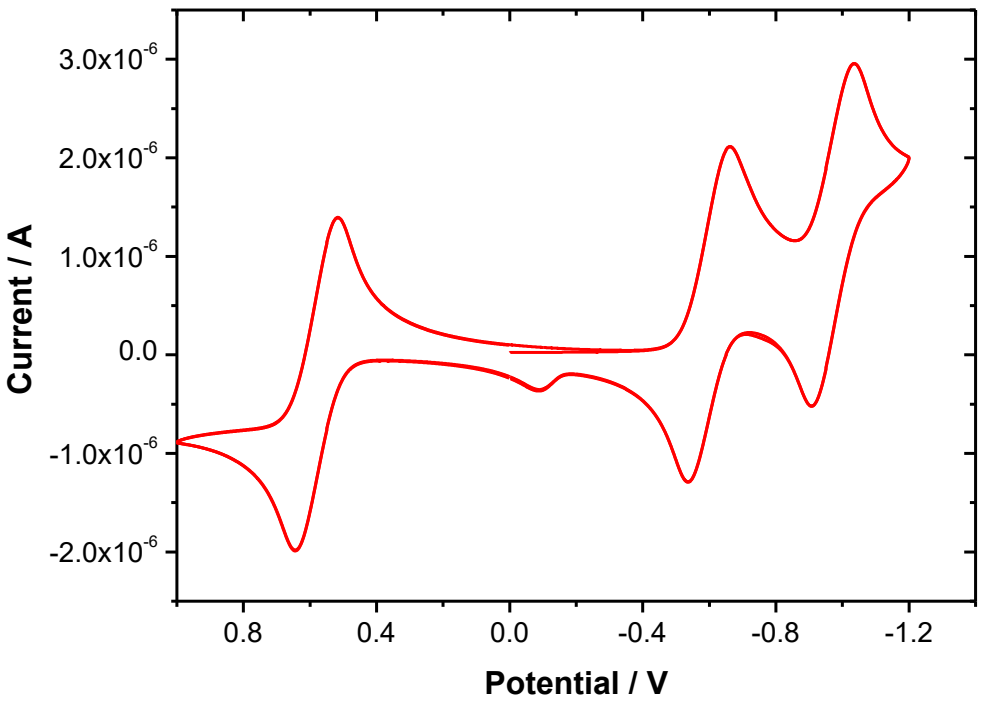
Cyclic Voltammogram of Compound **2j** (scanning rate: 20 mV s^{-1})



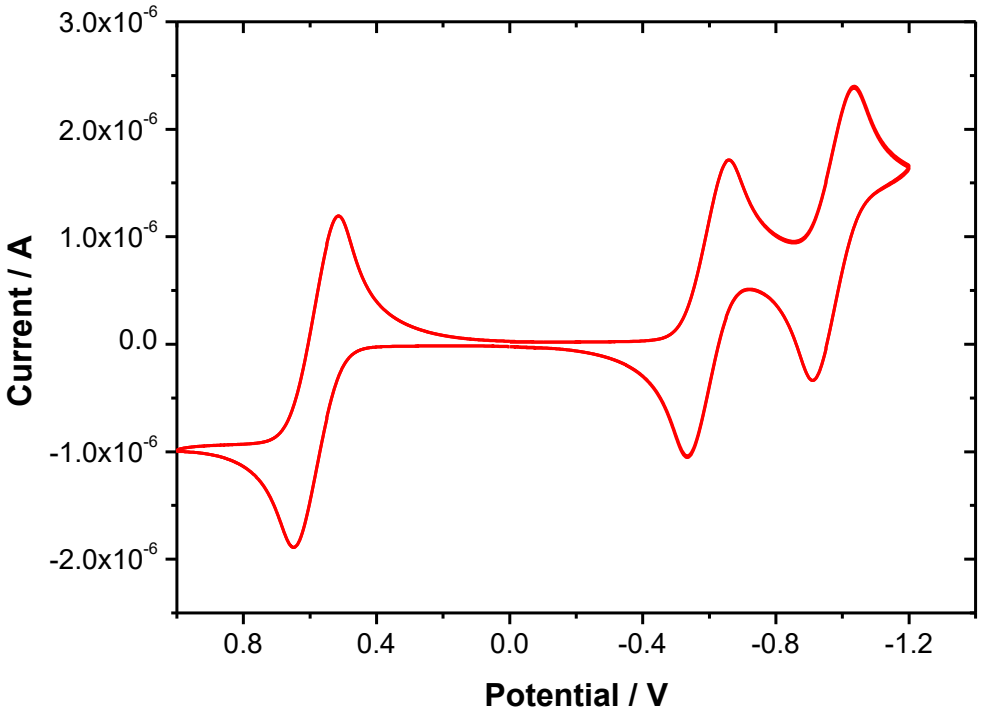
Cyclic Voltammogram of Compound **2k** (scanning rate: 20 mV s^{-1})



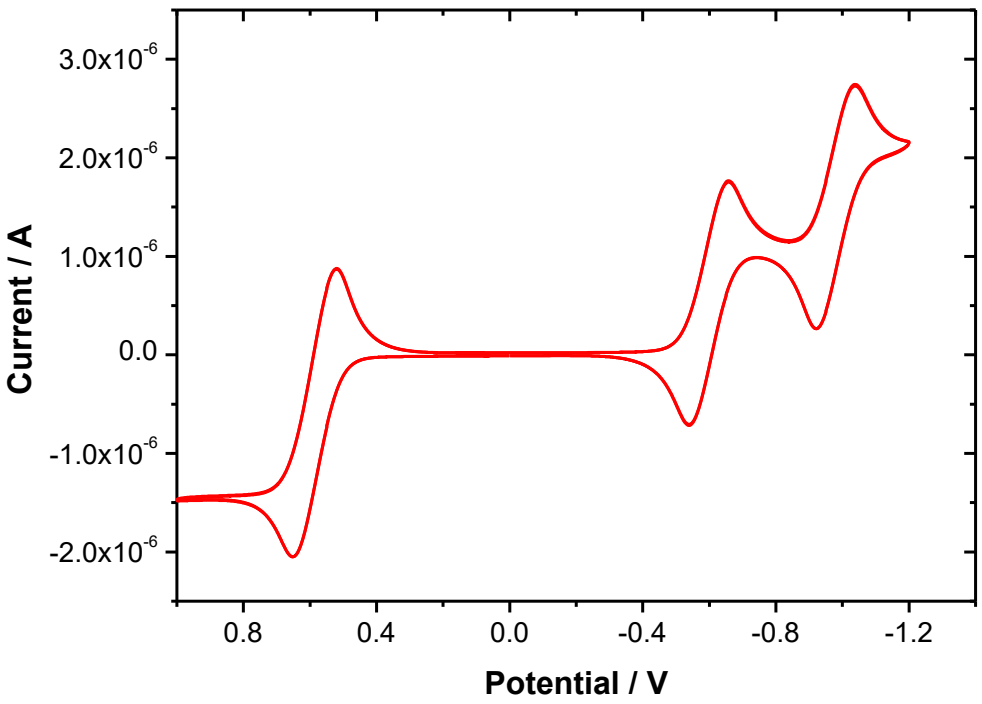
Cyclic Voltammogram of Compound **2l** (scanning rate: 20 mV s^{-1})



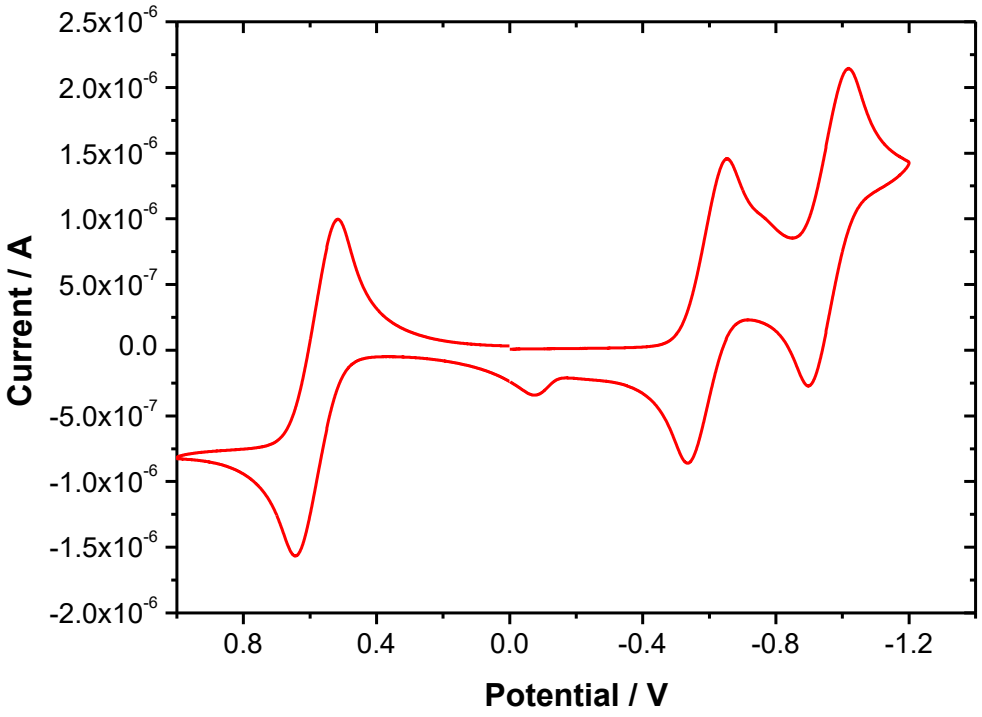
Cyclic Voltammogram of Compound **2m** (scanning rate: 20 mV s^{-1})



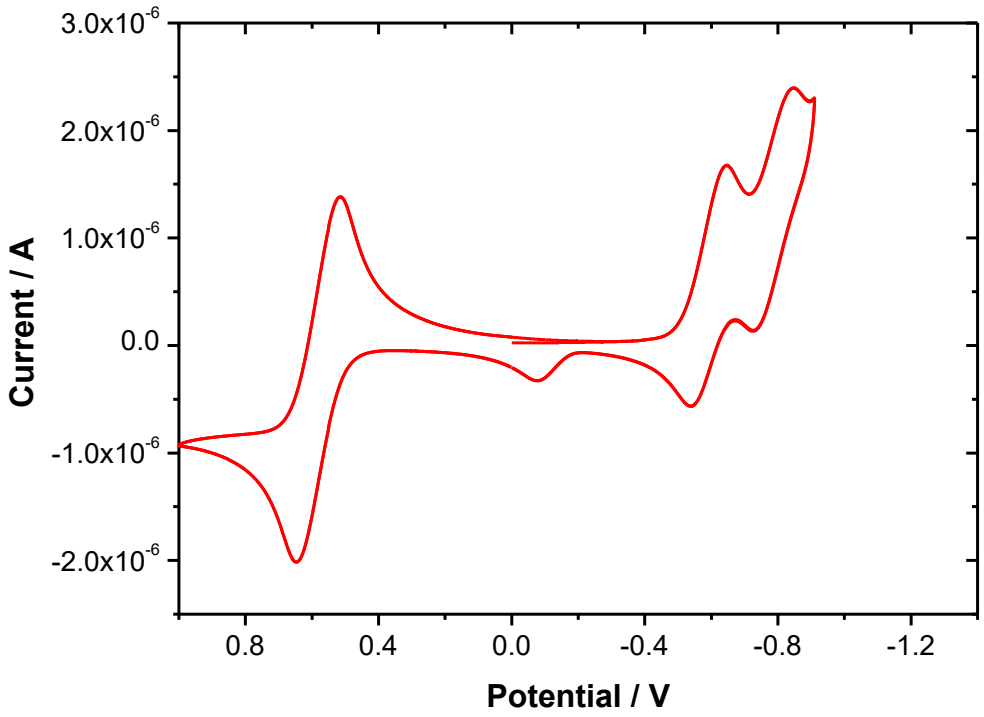
Cyclic Voltammogram of Compound **2n** (scanning rate: 20 mV s^{-1})



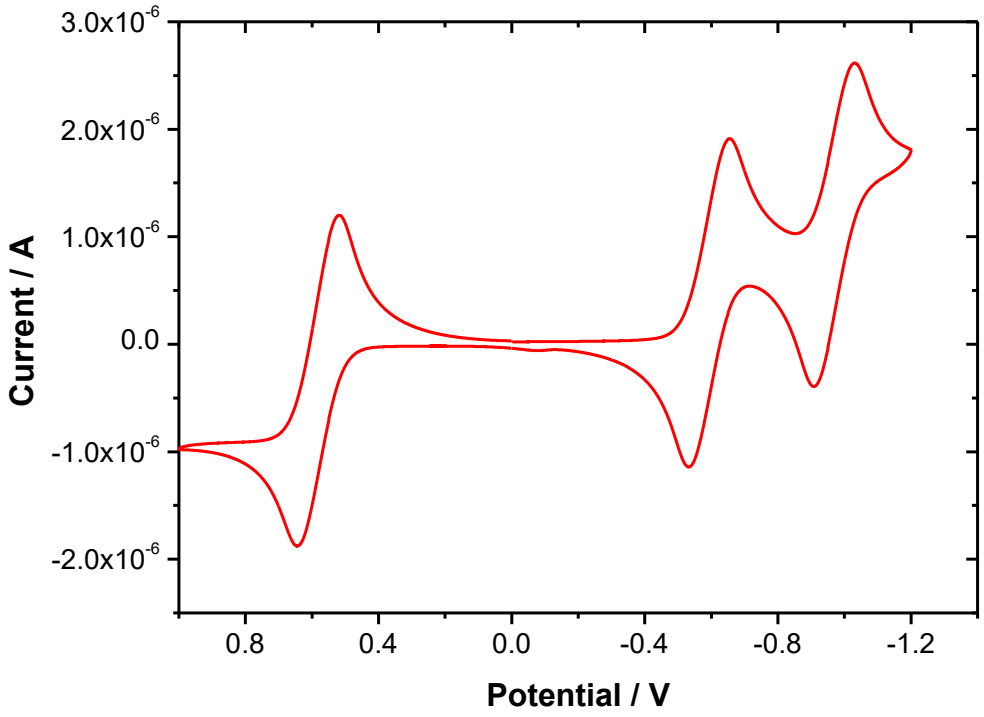
Cyclic Voltammogram of Compound **2o** (scanning rate: 20 mV s^{-1})



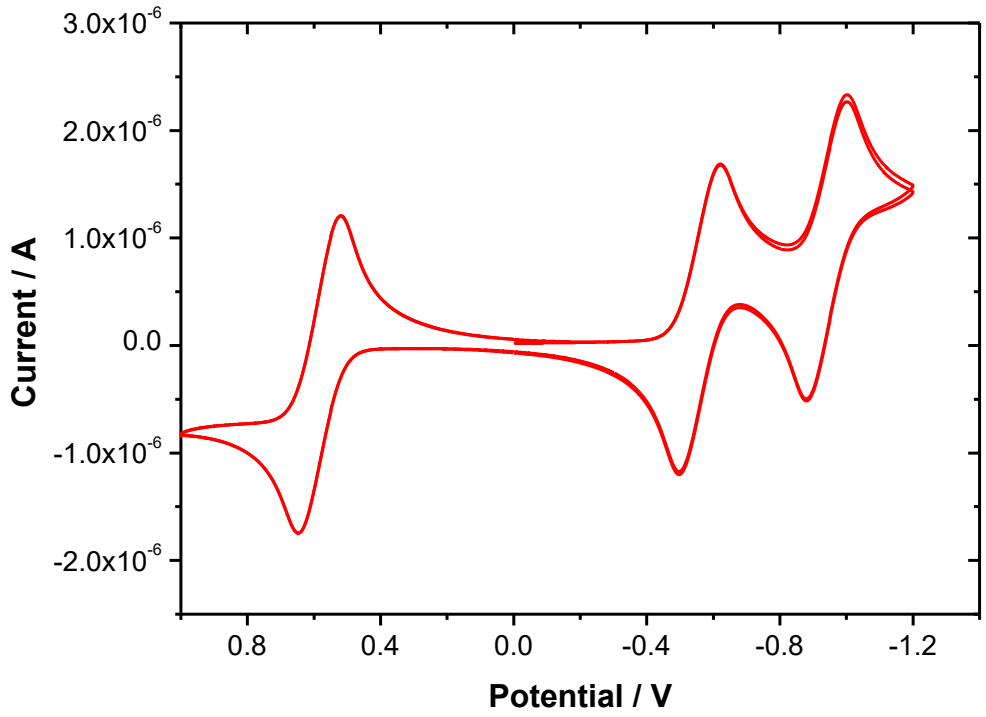
Cyclic Voltammogram of Compound **2p** (scanning rate: 20 mV s^{-1})



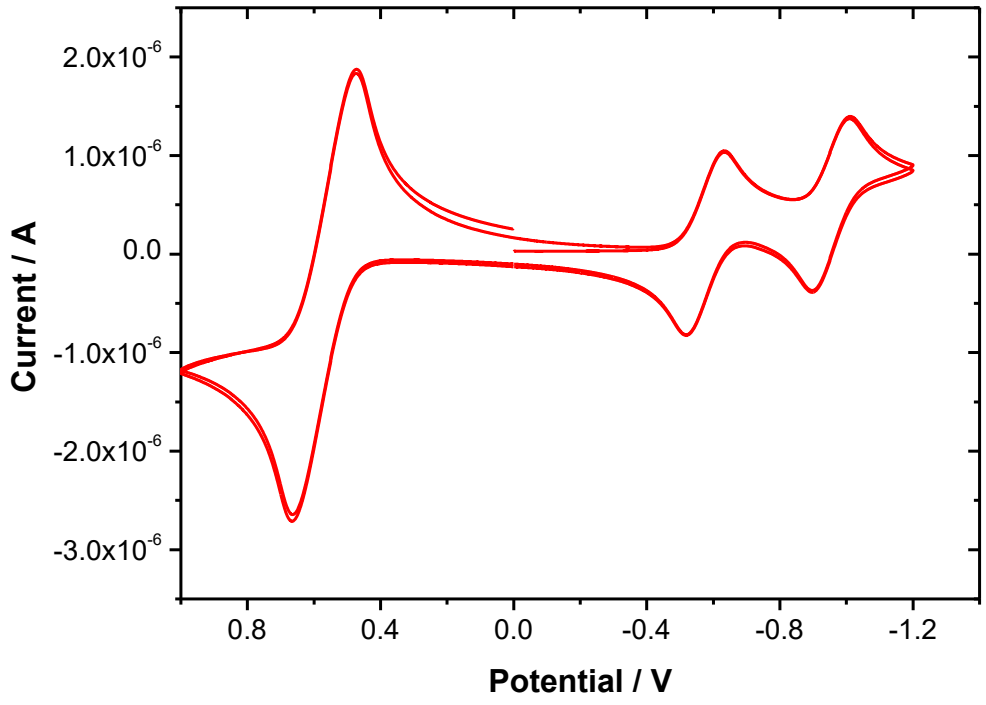
Cyclic Voltammogram of Compound **2q** (scanning rate: 20 mV s^{-1})



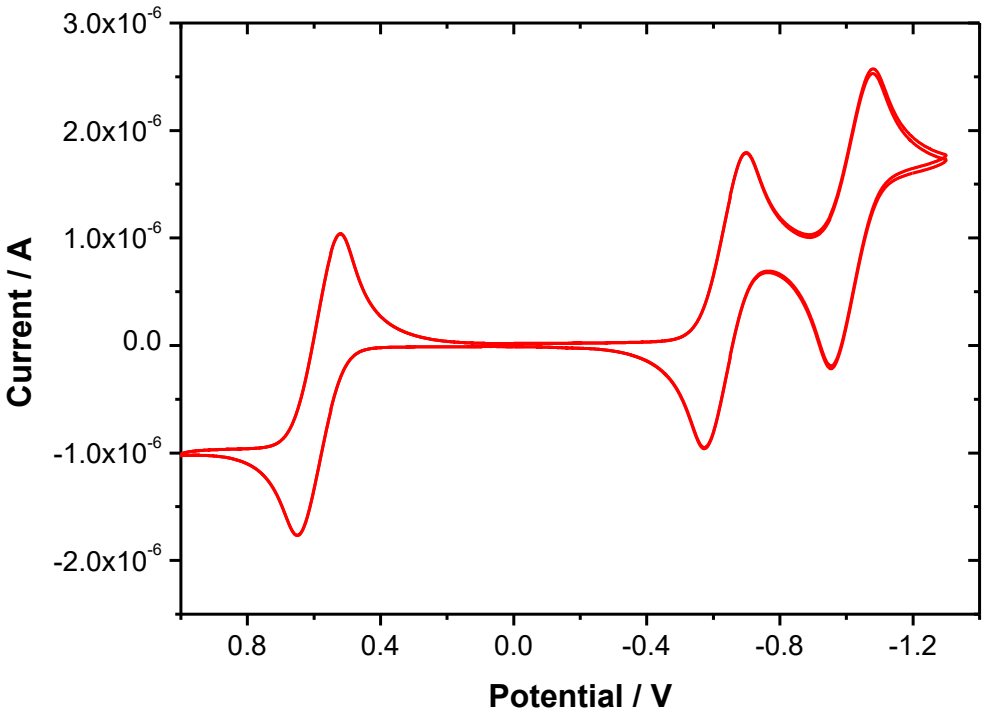
Cyclic Voltammogram of Compound **2r** (scanning rate: 20 mV s^{-1})



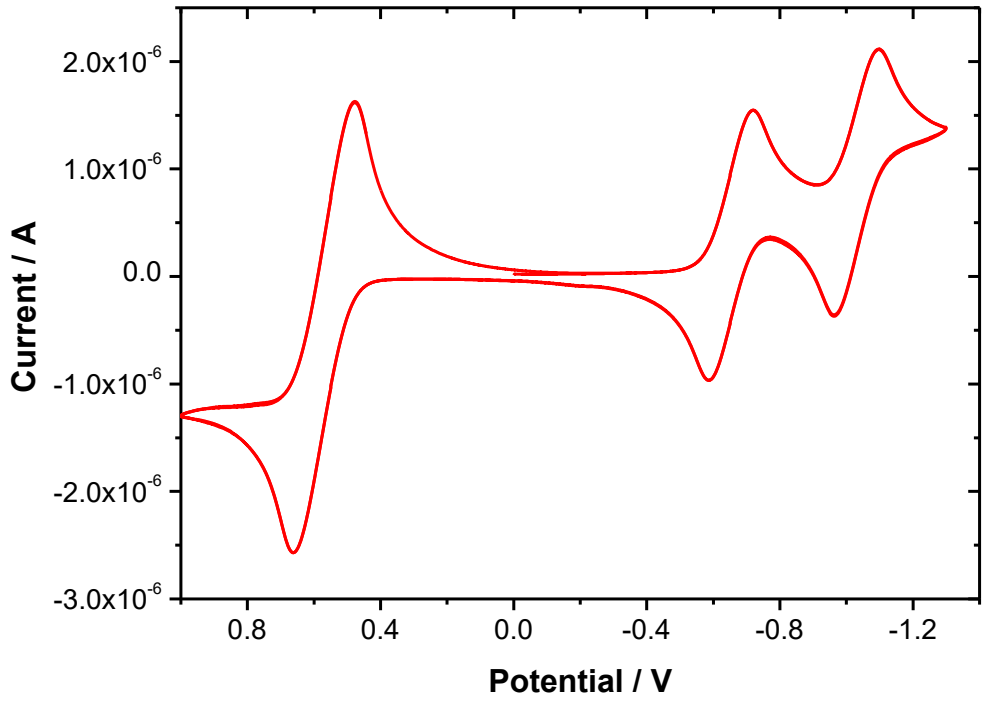
Cyclic Voltammogram of Compound **3a** (scanning rate: 20 mV s^{-1})



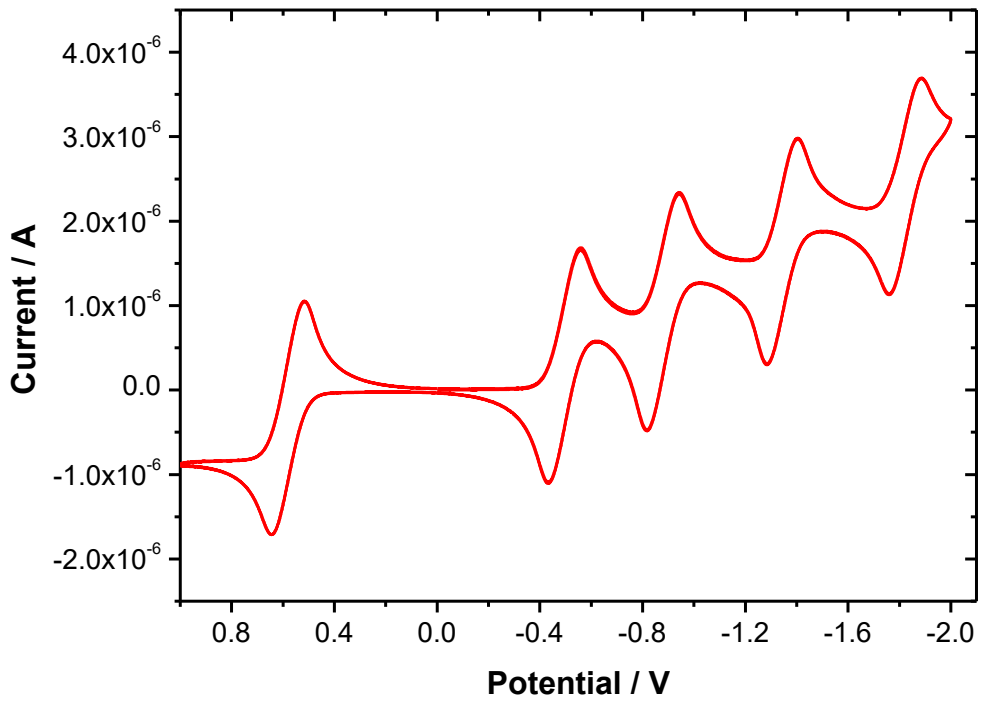
Cyclic Voltammogram of Compound **3r** (scanning rate: 20 mV s^{-1})



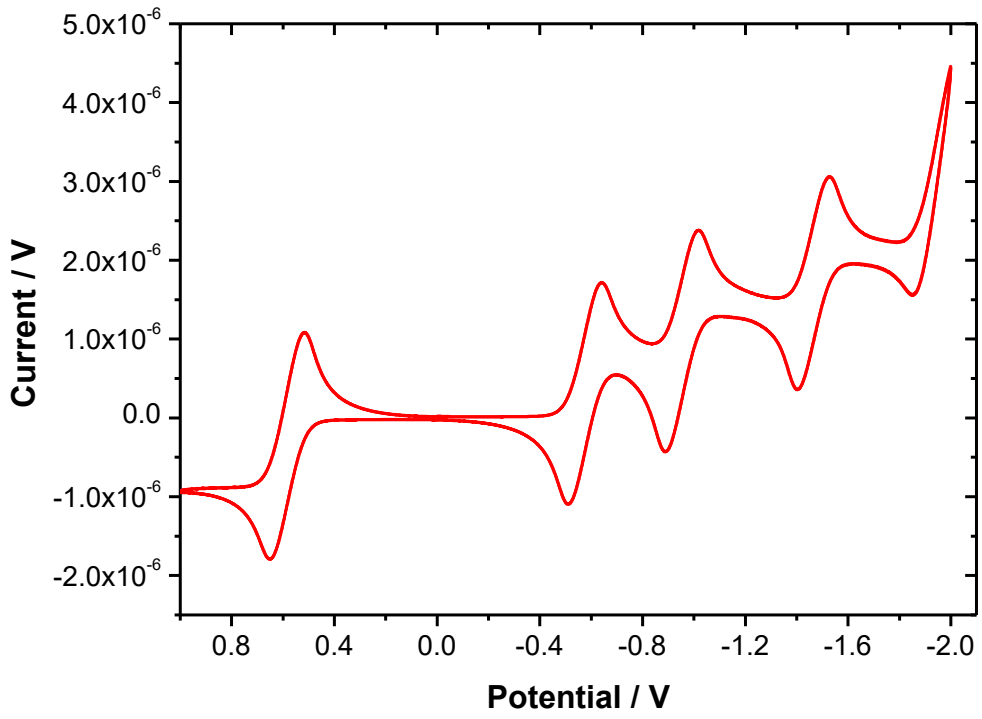
Cyclic Voltammogram of Compound **4a** (scanning rate: 20 mV s^{-1})



Cyclic Voltammogram of Compound **4r** (scanning rate: 20 mV s^{-1})



Cyclic Voltammogram of Compound C_{60} (scanning rate: 20 mV s^{-1})



Cyclic Voltammogram of Compound PCBM (scanning rate: 20 mV s^{-1})

References

(1) (a) Zeng, W.; Chemler, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 12948. (b) Fuller, P. H.; Kim, J.-W.; Chemler, S. R. *J. Am. Chem. Soc.* **2008**, *130*, 17638. (c) Miao, L.; Haque, I.; Manzoni, M. R.; Tham, W. S.; Chemler, S. R. *Org. Lett.* **2010**, *12*, 4739. (d) Paderes, M. C.; Belding, L.; Fanovic, B.; Dudding, T.; Keister, J. B.; Chemler, S. R. *Chem. Eur. J.* **2012**, *18*, 1711. (e) Liwosz, T. W.; Chemler, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 2020. (f) Turnpenny, B. W.; Hy-man, K. L.; Chemler, S. R. *Organometallics* **2012**, *31*, 7819. (g) Dang, L.; Liang, L.; Qian, C.; Fu, M.; Ma, T.; Xu, D.; Jiang, H.; Zeng, W. *J. Org. Chem.* **2014**, *79*, 769.

(2) Nelson, J. *Mater. Today* **2011**, *14*, 462.