Supporting Information

A Facile Access to Novel [60]Fullerenyl Diethers and [60]Fullerene-Sugar Conjugates via Annulation of Diol Moieties

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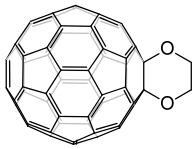
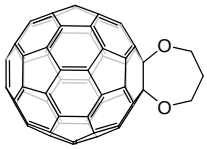
General Procedure for the Reaction of C_{60} with Diols 1a–o.

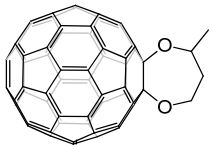
Firstly, C_{60} (0.05 mmol) was dissolved in anhydrous chlorobenzene (7 mL) by sonication, then iron salt (0.15 mmol $FeCl_2$ for **1a**–**g**, **1i**, **1k**, **1l**, **1n** and **1o**; 0.15 mmol $FeCl_3$ for **1h**; 0.10 mmol $FeCl_3$ for **1j** and **1m**), the hypervalent iodine(III) reagent (0.075 mmol/0.075 mmol PIDA/PIFA for **1a**–**e**, **1g**–**i**, **1k**, **1l** and **1n**; 0.15 mmol PIDA for **1f** and **1o**; 0.10 mmol PIDA for **1j** and **1m**) and diol (0.25 mmol for **1a**–**f**, **1k**–**o**; 0.50 mmol for **1g** and **1i**; 0.10 mmol for **1h**; 0.15 mmol for **1j**) were added. After being stirred at the designated reaction time and temperature, then the reaction mixture was directly separated on a silica gel column with CS_2/CH_2Cl_2 or CS_2/EtOAc as the eluent. The desired product **2** was obtained along with recovered C_{60}.



By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (14 μL, 0.25 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (33 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2a**[1] (14.9 mg, 38%) and recovered C_{60} (20.3 mg, 56%): amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.99 (s, 4H).

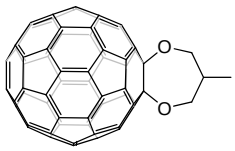


By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1b** (18 μL, 0.25 mmol), $FeCl_2$ (20 mg, 0.15 mmol), PIDA (25 mg, 0.075 mmol) and PIFA (34 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2b**[1] (19.8 mg, 50%) and recovered C_{60} (10.1 mg, 28%): amorphous brown solid.^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 5.06-5.02 (m, 4H), 2.68-2.61 (m, 2H).

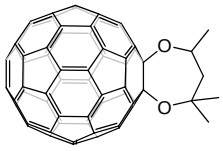


By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (23 μL, 0.25 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (32 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2c**[1] (15.5 mg, 38%) and recovered C_{60} (14 mg, 39%): amorphous brown solid. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 5.40-5.31 (m, 1H), 5.15 (td, J = 12.8, 2.0 Hz, 1H), 4.87

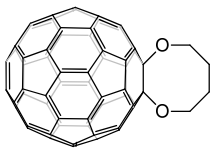
(ddd, J = 12.8, 4.6, 2.0 Hz, 1H), 2.82-2.70 (m, 1H), 2.31 (dq, J = 14.4, 2.0 Hz, 1H), 1.74 (d, J = 6.0 Hz, 3H).



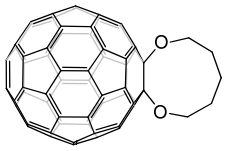
By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (22 μL, 0.25 mmol), $FeCl_2$ (19.2 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (32 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2d** (16.3 mg, 40%) and recovered C_{60} (14.1 mg, 39%): amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$, broad peaks due to ring flipping) δ 4.98-4.73 (br s, 2H), 4.73-4.64 (m, 2H), 3.00-2.80 (br s, 1H), 1.41-1.24 (br s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, –60 ^{o}C) δ 150.71, 148.31, 148.13, 146.18, 146.15, 145.80, 145.78, 145.74, 145.54, 145.11, 145.01, 144.98, 144.80, 144.74, 144.40, 144.22, 144.17, 142.20, 142.17, 141.94, 141.92, 141.51, 141.34, 140.98, 140.27, 139.05, 138.91, 138.47, 135.67, 91.60 (sp^3-*C* of C_{60}), 53.76, 35.70, 11.48; FT-IR ν/cm^{-1} (KBr) 2925, 2863, 1457, 1430, 1389, 1168, 1124, 1089, 1024, 980, 909, 598, 526, 501; UV-vis ($CHCl_3$) λ_{max}/nm 259, 318, 415; HRMS (MALDI-TOF) m/z calcd for $C_{64}H_8O_2$ [M^+] 808.0519, found 808.0545.



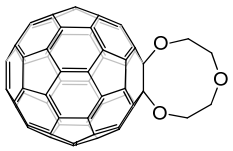
By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (32 μL, 0.25 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (32.3 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2e** (8.9 mg, 21%) and recovered C_{60} (15 mg, 42%): amorphous brown solid. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 5.40-5.28 (m, 1H), 3.37 (dd, J = 15.8, 7.7 Hz, 1H), 3.01 (dd, J = 15.8, 4.4 Hz, 1H), 1.93 (s, 3H), 1.91 (s, 3H), 1.87 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 152.92, 152.78, 152.57, 151.60, 148.54, 146.52, 146.46, 146.42, 146.16, 146.12, 145.94, 145.91, 145.84, 145.80, 145.41, 145.35, 145.28, 145.24, 145.08, 145.03, 144.90, 144.82, 142.69, 142.67, 142.64, 142.63, 142.60, 142.35, 141.59, 141.56, 141.52, 141.51, 141.46, 141.39, 141.28, 139.53, 139.51, 139.42, 139.38, 136.79, 136.62, 136.33, 136.19, 88.75 (sp^3-*C* of C_{60}), 88.49 (sp^3-*C* of C_{60}), 80.65, 74.66, 43.56, 31.62, 30.91, 23.93; FT-IR ν/cm^{-1} (KBr) 2969, 2922, 2860, 1434, 1368, 1152, 1061, 953, 573, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258, 318 , 415; HRMS (MALDI-TOF) m/z calcd for $C_{66}H_{12}O_2$ [M^+] 836.0832, found 836.0810.



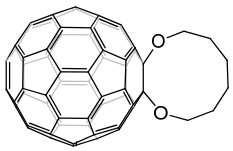
By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1f** (23 μL, 0.25 mmol), $FeCl_2$ (19.8 mg, 0.15 mmol) and PIDA (49.7 mg, 0.15 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2f** (9.3 mg, 23%) and recovered C_{60} (24.2 mg, 68%): amorphous brown solid. ^{1}H NMR (300 MHz, CS_2/$CDCl_3$, broad peaks due to ring flipping) δ 5.70-4.54 (br s, 4H), 2.51-2.30 (br s, 4H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, –60 ^{o}C) δ 150.63, 149.97, 148.10, 146.14, 146.08, 145.83, 145.79, 145.74, 145.53, 145.38, 145.07, 144.84, 144.82, 144.56, 144.19, 144.07, 142.22, 142.13, 142.07, 141.93, 141.85, 141.46, 141.15, 141.13, 140.83, 139.14, 139.09, 137.93, 135.32, 87.26 (sp^3-*C* of C_{60}), 69.21, 27.81; FT-IR ν/cm^{-1} (KBr) 2921, 2867, 1461, 1431, 1372, 1221, 1127, 1091, 1071, 976, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 259, 318, 415; HRMS (MALDI-TOF) m/z calcd for $C_{64}H_8O_2$ [M^+] 808.0519, found 808.0491.



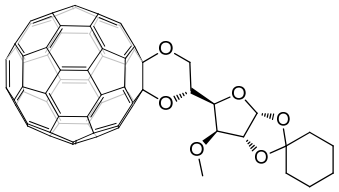
By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (52 μL, 0.5 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (32 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2g** (8.1 mg, 20%) and recovered C_{60} (19.6 mg, 54%): amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 5.06-5.01 (m, 4H), 2.32-2.26 (m, 6H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$,) δ 151.25, 148.56, 146.51, 146.20, 145.95, 145.52, 145.47, 145.29, 144.78, 142.59, 142.57, 142.34, 141.58, 141.54, 139.47, 137.36, 89.18 (sp^3-*C* of C_{60}), 71.20, 29.93, 26.31; FT-IR ν/cm^{-1} (KBr) 2916, 2867, 1508, 1463, 1430, 1180, 1124, 1095, 1041, 601, 573, 565, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257, 316, 415; HRMS (MALDI-TOF) m/z calcd for $C_{65}H_{10}O_2$ [M^+] 822.0675, found 822.0699.



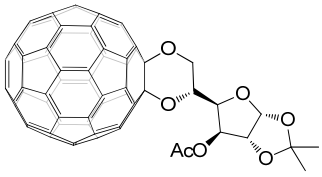
By following the general procedure, the reaction of C_{60} (37.0 mg, 0.05 mmol) with **1h** (10 μL, 0.10 mmol), $FeCl_3$ (30 mg, 0.15 mmol), PIDA (25.5 mg, 0.075 mmol) and PIFA (32.8 mg, 0.075 mmol) in anhydrous CB (7 mL) at 130 °C for 2.5 h afforded **2h** (4.0 mg, 10%) and recovered C_{60} (19 mg, 53%): amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 4.99 (s, 8H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6) δ 148.30, 148.11, 146.16, 145.84, 145.81, 145.13, 144.97, 144.85, 144.40, 142.26, 142.18, 141.90, 141.38, 141.06, 139.24, 137.40, 86.68 (sp^3-*C* of C_{60}), 60.91; FT-IR ν/cm^{-1} (KBr) 2969, 2923, 2869, 1511, 1462, 1428, 1265, 1182, 1132, 1092, 1007, 942, 897, 846, 768, 694, 663, 594, 568, 527, 497; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257, 318, 423; HRMS (MALDI-TOF) m/z calcd for $C_{62}H_4O_2$ [M-OC_2H_4]$^+$ 780.0206, found 780.0173.



By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (62 mg, 0.50 mmol), $FeCl_2$ (19.3 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and PIFA (32 mg, 0.075 mmol) in anhydrous CB (7 mL) at 100 °C for 1 h afforded **2i** (6.9 mg, 17%) and recovered C_{60} (19.5 mg, 54%): amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/C_6D_6) δ 5.36 (t, J = 5.0 Hz, 4H), 2.47-2.36 (m, 8H). ^{13}C NMR (100 MHz, CS_2/C_6D_6) δ 152.59, 149.37, 147.32, 147.01, 146.75, 146.35, 146.29, 146.10, 145.62, 143.43, 143.20, 142.37, 142.33, 140.24, 137.99, 90.12 (sp^3-*C* of C_{60}), 69.29, 31.24, 20.99; FT-IR ν/cm^{-1} (KBr) 2925, 2866, 1510, 1428, 1182, 1122, 1098, 1066, 963, 598, 569, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258, 317, 415; HRMS (MALDI-TOF) m/z calcd for $C_{66}H_{12}O_2$ [M^+] 836.0832, found 836.0863.

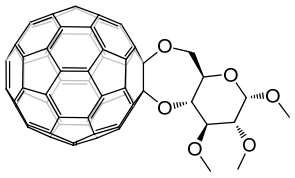


By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (41 mg, 0.15 mmol), $FeCl_3$ (16.3 mg, 0.10 mmol), and PIDA (33.3 mg, 0.10 mmol) at 100 °C for 2 h afforded **2j** (12.7 mg, 25%) and recovered C_{60} (19.7 mg, 55%): amorphous brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (d, J = 3.6 Hz, 1H), 5.49-5.41 (m, 1H), 5.16 (dd, J = 11.8, 7.0 Hz, 1H), 5.00 (dd, J = 11.8, 7.0 Hz, 1H), 4.96 (dd, J = 7.6, 3.0 Hz, 1H), 4.71 (d, J = 3.6 Hz, 1H), 4.20 (d, J = 3.0 Hz, 1H), 1.93-1.83 (m, 2H), 1.81-1.69 (m, 2H), 1.69-1.61 (m, 4H), 1.51-1.41 (m, 2H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 148.90, 148.71, 148.54, 148.49, 148.39, 148.26, 146.57, 146.54, 146.51, 146.25, 146.22, 146.19, 146.16, 146.08, 145.65, 145.50, 145.39, 145.31, 145.20, 145.18, 145.15, 144.81, 144.72, 142.67, 142.65, 142.62, 142.57, 142.30, 142.23, 141.83, 141.81, 141.74, 141.72, 141.70, 141.65, 141.62, 139.68, 139.65, 139.59, 139.56, 138.57, 138.47, 137.27, 137.07, 112.55, 105.04, 87.11 (sp^3-*C* of C_{60}), 87.04 (sp^3-*C* of C_{60}), 84.01, 82.22, 81.86, 68.40, 64.53, 58.60, 36.90, 36.12, 25.35, 24.29, 24.02; FT-IR ν/cm^{-1} (KBr) 2928, 2859, 1451, 1437, 1366, 1159, 1121, 1087, 1023, 935, 839, 753, 709, 562, 526; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 258, 317, 423; HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{20}O_6$ [M^+] 992.1254, found 992.1295.

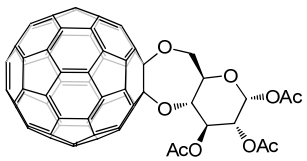


By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1k** (65.5 mg, 0.25 mmol), $FeCl_2$ (19.1 mg, 0.15 mmol), PIDA (24 mg, 0.075 mmol) and

PIFA (31.8 mg, 0.075 mmol) at 80 °C for 1.5 h afforded **2k** (11.3 mg, 23%) and recovered C_{60} (19.8 mg, 55%): brown amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, J = 3.6 Hz, 1H), 5.68 (d, J = 3.0 Hz, 1H), 5.29 (dt, J = 8.4, 6.6 Hz, 1H), 5.11 (dd, J = 11.8, 7.0 Hz, 1H), 4.98 (dd, J = 8.4, 3.0 Hz, 1H), 4.90 (dd, J = 11.8, 6.2 Hz, 1H), 4.60 (d, J = 3.6 Hz, 1H), 1.91 (s, 3H), 1.66 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 168.43, 148.62, 148.59, 148.19, 148.14, 147.75, 146.66, 146.65, 146.58, 146.34, 146.33, 146.25, 146.11, 145.70, 145.55, 145.45, 145.44, 145.33, 145.25, 145.20, 145.15, 144.90, 144.82, 144.80, 144.77, 142.77, 142.75, 142.71, 142.70, 142.64, 142.63, 142.38, 142.36, 142.33, 142.25, 142.06, 141.91, 141.82, 141.77, 141.64, 141.16, 140.93, 139.79, 139.75, 139.68, 139.56, 138.49, 138.32, 137.40, 137.07, 112.44, 105.31, 87.31 (sp^3-*C* of C_{60}), 86.88 (sp^3-*C* of C_{60}), 83.56, 81.21, 75.53, 67.99, 64.86, 26.90, 26.30, 20.35; FT-IR ν/cm^{-1} (KBr) 2980, 2922, 1751, 1460, 1429, 1373, 1220, 1160, 1093, 1029, 935, 528; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 257, 318, 424; HRMS (MALDI-TOF) *m/z* calcd for $C_{71}H_{16}O_7$ [M^+] 980.0891, found 980.0889.

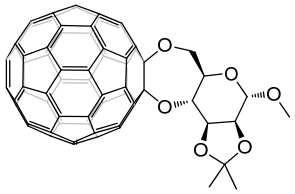


By following the general procedure, the reaction of C_{60} (36.3 mg, 0.05 mmol) with **1l** (56 mg, 0.25 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (23.5 mg, 0.075 mmol) and PIFA (32 mg, 0.075 mmol) at 100 °C for 2 h afforded **2l** (13.3 mg, 28%) and recovered C_{60} (7 mg, 19%): brown amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (d, J = 3.6 Hz, 1H), 4.99 (dd, J = 12.0, 10.4 Hz, 1H), 4.88 (dd, J = 10.4, 9.2 Hz, 1H), 4.99 (dd, J = 12.0, 4.8 Hz, 1H), 4.64 (ddd, J = 10.4, 10.4, 4.8 Hz, 1H), 4.09 (t, J = 9.2 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 3.49 (dd, J = 9.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.09, 150.90, 149.06, 148.99, 148.96, 148.30, 146.90, 146.81, 146.55, 146.51, 146.47, 146.45, 146.26, 146.24, 145.83, 145.73, 145.70, 145.69, 145.54, 145.50, 145.43, 145.42, 145.10, 145.06, 144.98, 144.89, 144.87, 144.80, 142.89, 142.86, 142.84, 142.83, 142.62, 142.56, 142.55, 142.11, 142.05, 141.93, 141.72, 141.69, 141.14, 140.05, 139.77, 139.72, 139.60, 139.26, 138.64, 136.36, 136.13, 98.20, 91.72 (sp^3-*C* of C_{60}), 91.54 (sp^3-*C* of C_{60}), 84.67, 81.99, 81.65, 72.67, 66.83, 62.01, 59.86, 55.67; FT-IR ν/cm^{-1} (KBr) 2922, 2818, 1455, 1437, 1378, 1192, 1088, 1052, 967, 911, 769, 528; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 257, 318, 423; HRMS (MALDI-TOF) *m/z* calcd for $C_{69}H_{16}O_6$ [M^+] 940.0941, found 940.0979.

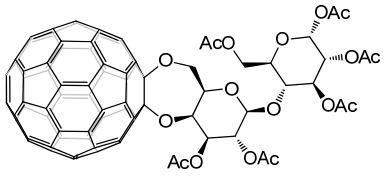


By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1m** (78.7 mg, 0.25 mmol), $FeCl_3$ (16.1 mg, 0.10 mmol), and PIDA (32 mg, 0.10

mmol) at 80 °C for 3 h afforded **2m** (8.5 mg, 17%) and recovered C_{60} (12.1 mg, 33%): brown amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, J = 3.6 Hz, 1H), 6.03 (t, J = 9.8 Hz, 1H), 5.37 (dd, J = 9.8, 3.6 Hz, 1H), 5.11 (t, J = 9.8 Hz, 1H), 5.02 (td, J = 11.6, 1.4 Hz, 1H), 4.95-4.85 (m, 2H), 2.36 (s, 3H), 2.10 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.17, 170.13, 169.39, 150.68, 150.17, 149.04, 149.03, 147.97, 147.93, 146.94, 146.89, 146.63, 146.59, 146.57, 146.52, 146.44, 146.33, 146.28, 145.79, 145.77, 145.70, 145.57, 145.55, 145.35, 145.15, 145.03, 144.93, 144.88, 144.83, 144.71, 144.29, 142.99, 142.95, 142.94, 142.92, 142.89, 142.66, 142.62, 142.53, 142.13, 142.08, 142.04, 141.76, 141.61, 141.12, 141.09, 139.92, 139.81, 139.77, 139.67, 139.00, 138.91, 136.61, 136.17, 91.68 (sp^3-*C* of C_{60}), 91.58 (sp^3-*C* of C_{60}), 89.54, 81.28, 71.90, 70.23, 69.98, 69.22, 21.25, 21.12, 20.74; FT-IR ν/cm^{-1} (KBr) 2954, 1755, 1427, 1370, 1212, 1138, 1064, 1012, 979, 935, 773, 731, 599, 526, 484; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 257, 318, 424; HRMS (MALDI-TOF) *m/z* calcd for $C_{72}H_{16}O_9$ [M^+] 1024.0789, found 1024.0766.



By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1n** (58.5 mg, 0.25 mmol), $FeCl_2$ (19 mg, 0.15 mmol), PIDA (24.5 mg, 0.075 mmol), and PIFA (33 mg, 0.075 mmol) at 120 °C for 1.5 h afforded **2n** (12.6 mg, 26%) and recovered C_{60} (8.8 mg, 24%): brown amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (s, 1H), 5.12-5.03 (m, 2H), 4.91 (dd, J = 12.4, 5.2 Hz, 1H), 4.71 (dd, J = 7.6, 5.2 Hz, 1H), 4.57-4.49 (m, 1H), 4.41 (d, J = 5.2 Hz, 1H), 3.61 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.03, 150.90, 149.28, 149.02, 148.99, 148.38, 146.96, 146.93, 146.91, 146.59, 146.57, 146.53, 146.44, 146.31, 145.78, 145.75, 145.72, 145.52, 145.45, 145.33, 145.15, 145.10, 145.00, 144.94, 144.90, 142.94, 142.91, 142.90, 142.87, 142.83, 142.65, 142.60, 142.17, 142.12, 142.01, 141.75, 141.71, 141.07, 140.94, 139.97, 139.77, 139.59, 139.18, 138.43, 136.47, 136.34, 109.80, 98.48, 91.83 (sp^3-*C* of C_{60}), 91.56 (sp^3-*C* of C_{60}), 82.56, 76.57, 76.34, 72.45, 65.01, 55.50, 27.55, 26.59; FT-IR ν/cm^{-1} (KBr) 2990, 2982, 1454, 1432, 1376, 1218, 1126, 1086, 1029, 977, 903, 853, 776, 600, 562, 526, 479; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 258, 318, 422; HRMS (MALDI-TOF) *m/z* calcd for $C_{70}H_{16}O_6$ [M^+] 952.0941, found 952.0908.



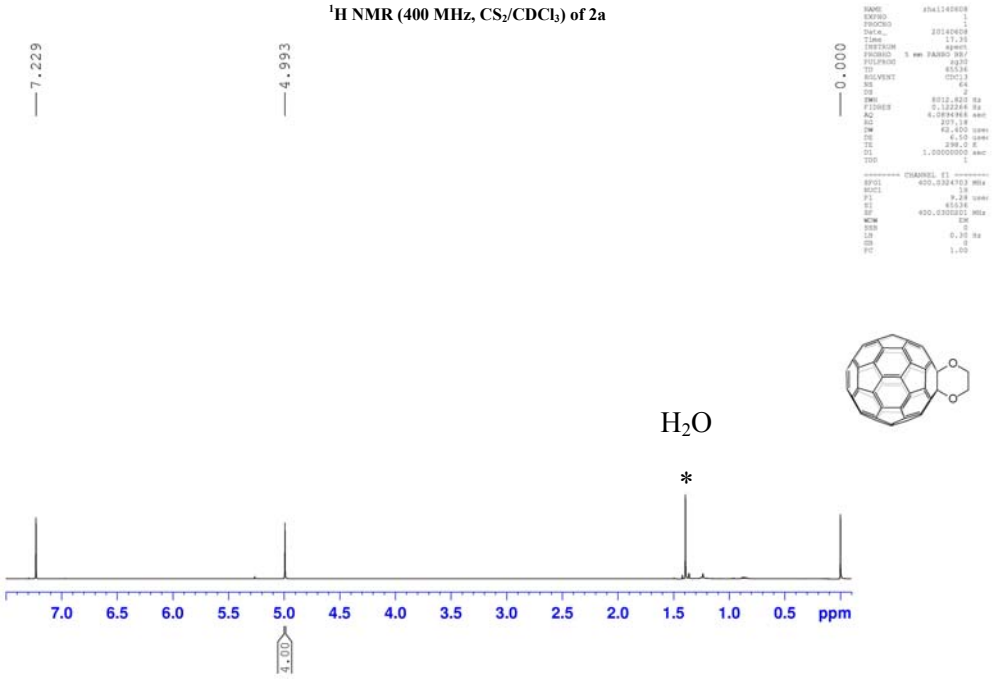
By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1o** (149 mg, 0.25 mmol), $FeCl_2$ (18.9 mg, 0.15 mmol), and PIDA (48.3 mg, 0.15 mmol) at 100 °C for 2 h afforded **2o** (9.7 mg, 15%) and recovered C_{60} (18.4 mg, 51%):

brown amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, J = 3.6 Hz, 1H), 5.86 (d, J = 3.6 Hz, 1H), 5.73 (dd, J = 10.6, 8.0 Hz, 1H), 5.68 (dd, J = 10.0, 9.2 Hz, 1H), 5.31 (d, J = 13.6 Hz, 1H), 5.18 (dd, J = 10.0, 3.6 Hz, 1H), 5.15 (dd, J = 10.0, 3.6 Hz, 1H), 5.01 (dd, J = 13.6, 1.6 Hz, 1H), 4.77 (d, J = 8.0 Hz, 1H), 4.57 (dd, J = 12.0, 2.0 Hz, 1H), 4.29 (dd, J = 12.0, 4.4 Hz, 1H), 4.21-4.14 (m, 2H), 4.09 (dd, J = 10.0, 9.2 Hz, 1H), 2.53 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.91, 170.80, 170.55, 170.24, 169.30, 169.24, 151.06, 150.80, 149.00, 148.98, 148.10, 147.87, 146.97, 146.93, 146.90, 146.63, 146.60, 146.52, 146.46, 146.41, 146.36, 146.23, 145.81, 145.78, 145.76, 145.71, 145.51, 145.26, 145.16, 145.15, 144.85, 144.82, 144.77, 144.72, 144.69, 142.97, 142.89, 142.88, 142.62, 142.60, 142.54, 142.34, 142.31, 142.24, 142.09, 141.68, 141.52, 141.02, 140.94, 139.85, 139.67, 139.58, 139.21, 138.95, 136.98, 136.58, 101.65, 93.23 (sp^3-*C* of C_{60}), 92.45 (sp^3-*C* of C_{60}), 89.35, 77.88, 75.61, 73.39, 72.93, 71.94, 71.23, 69.67, 69.54, 61.89, 21.53, 21.19, 21.08, 21.04, 20.99, 20.75; FT-IR ν/cm^{-1} (KBr) 1750, 1429, 1367, 1219, 1150, 1046, 936, 907, 769, 744, 682, 601, 561, 528; UV-vis ($CHCl_3$) λ_{max} nm (log ε) 257, 318, 424; HRMS (MALDI-TOF) *m/z* calcd for $C_{73}H_{20}O_6$ [M^+] 1312.1634, found 1312.1649.

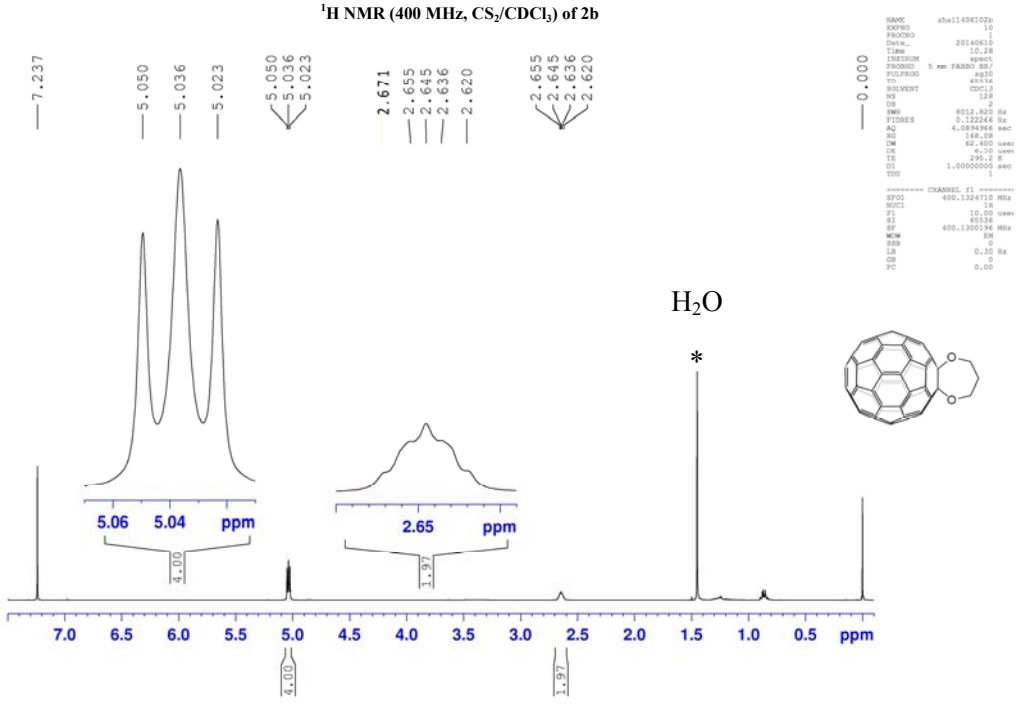
Reference

(1) Li, F.-B.; You, X.; Liu, T.-X.; Wang, G.-W. *Org. Lett.* **2012**, *14*, 1800.

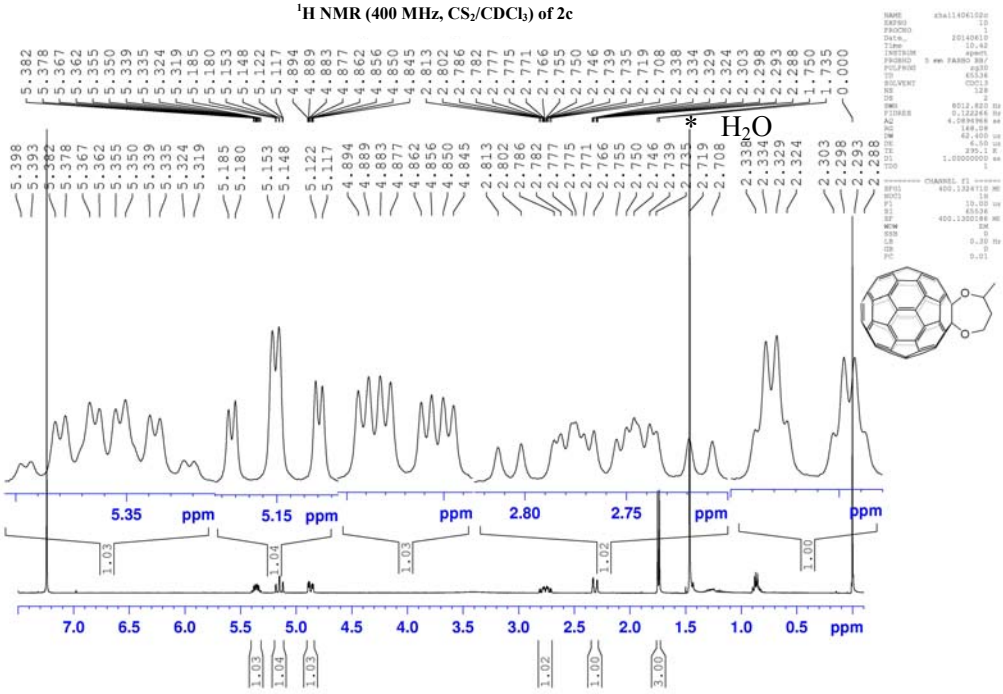
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) of 2a



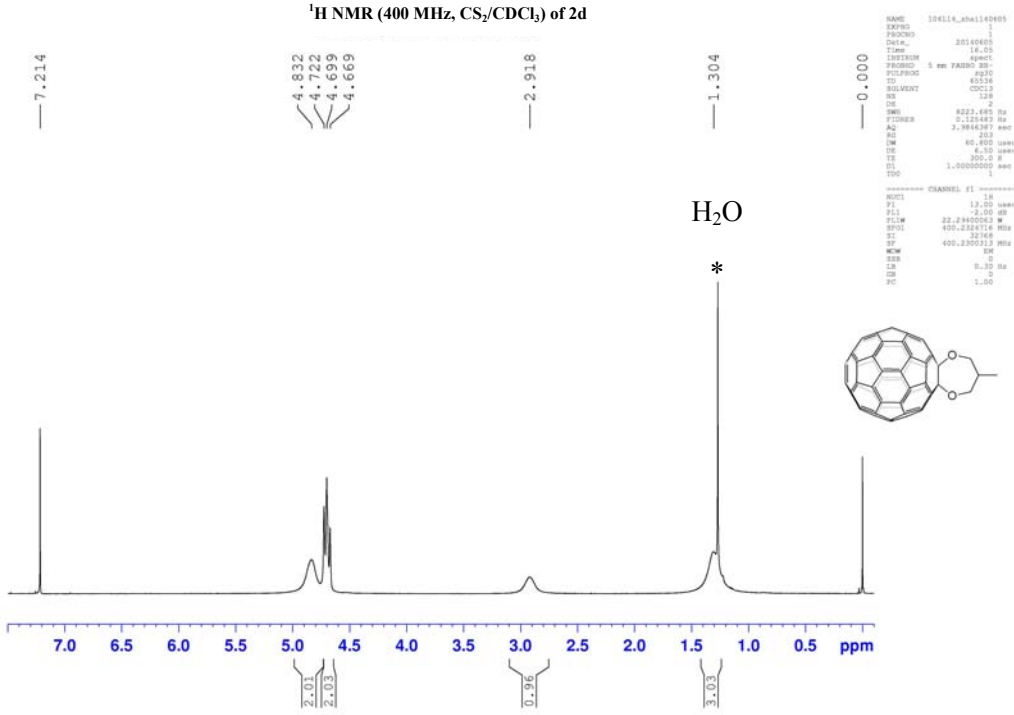
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) of 2b



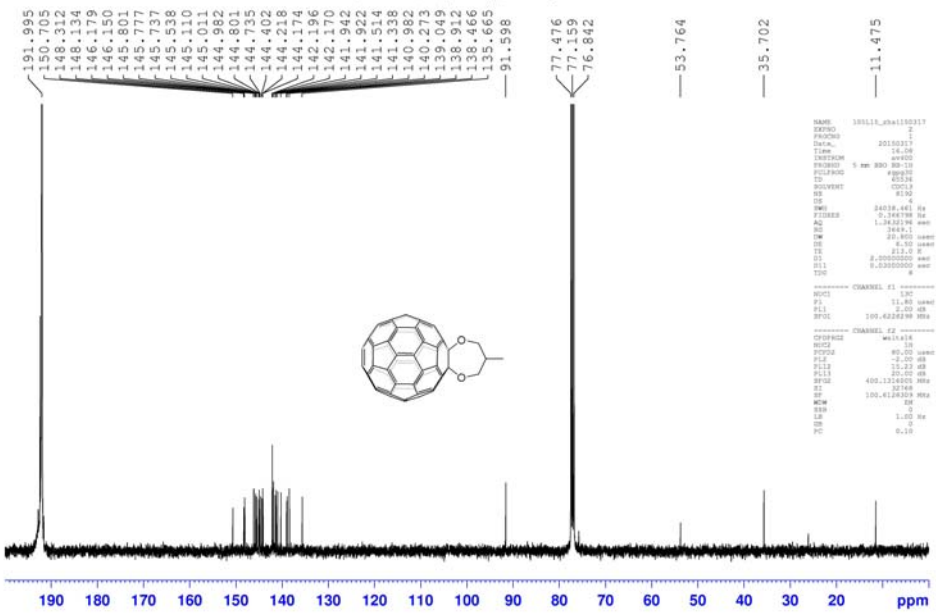
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) of 2c



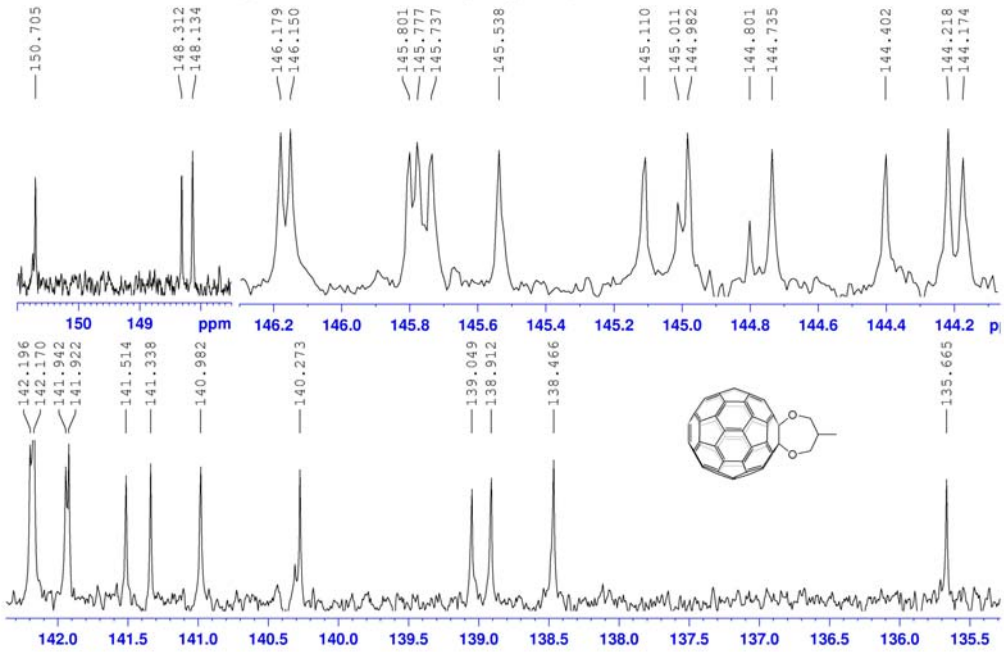
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) of 2d



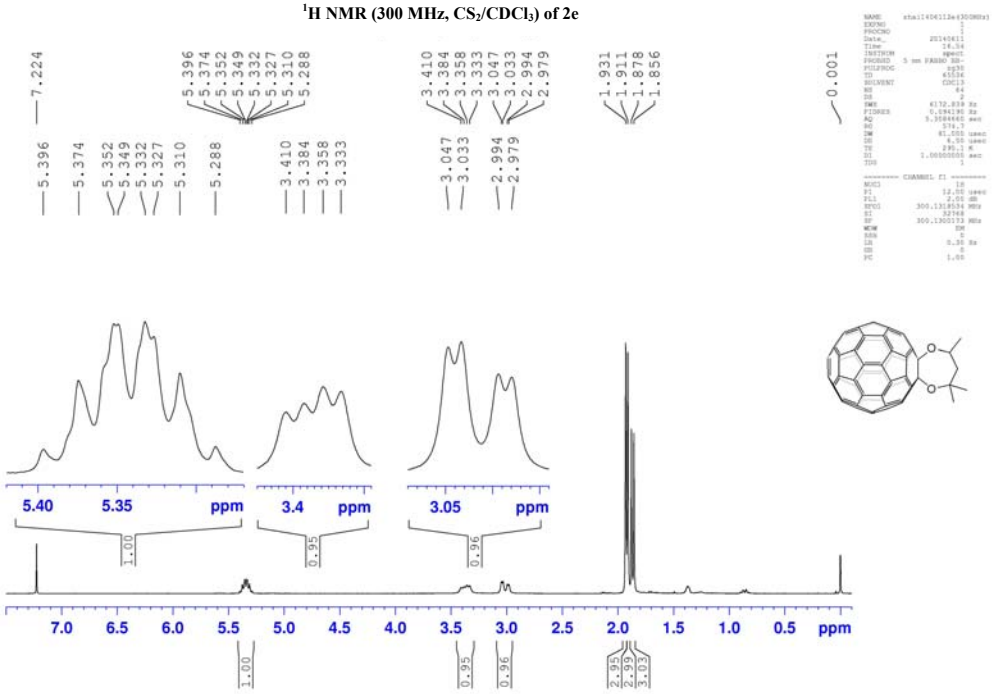
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of compound 2e at −60 °C



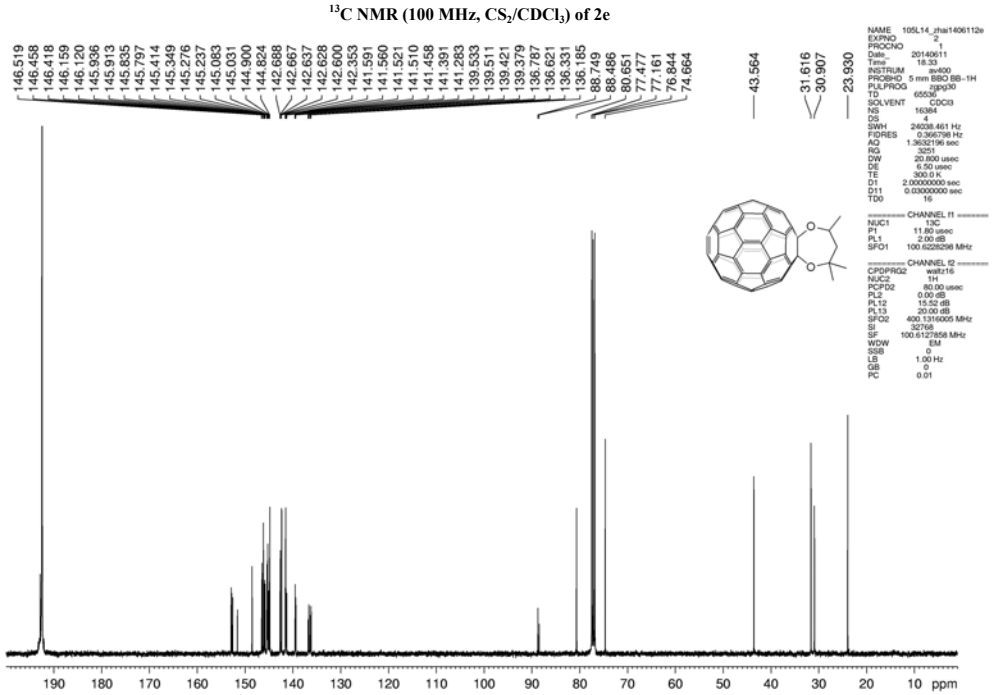
Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of compound 2e at −60 °C



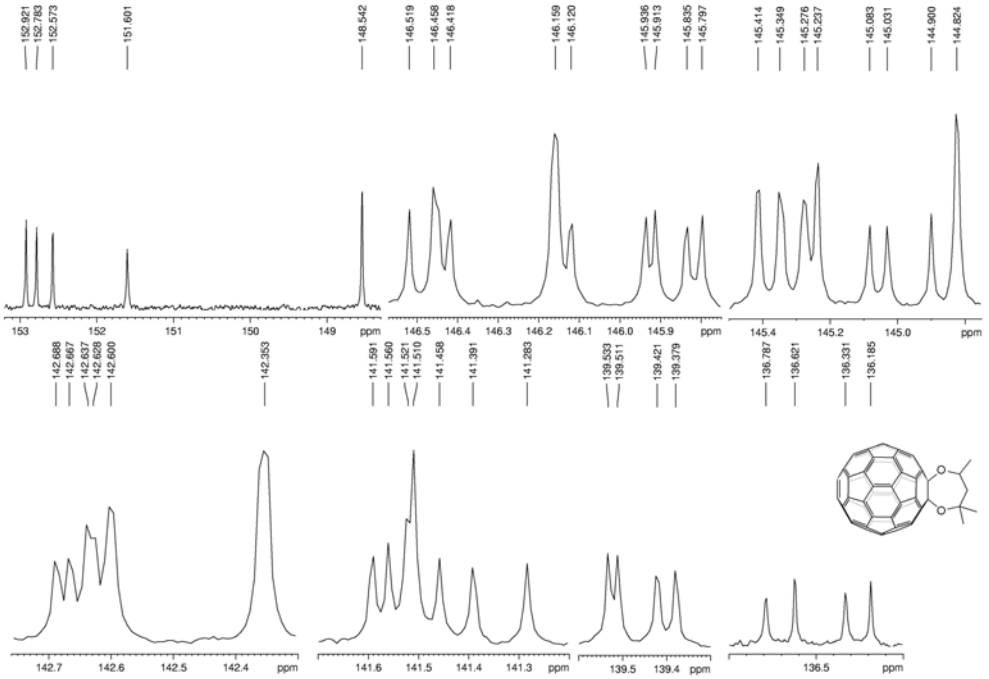
^{1}H NMR (300 MHz, CS_2/$CDCl_3$) of 2e



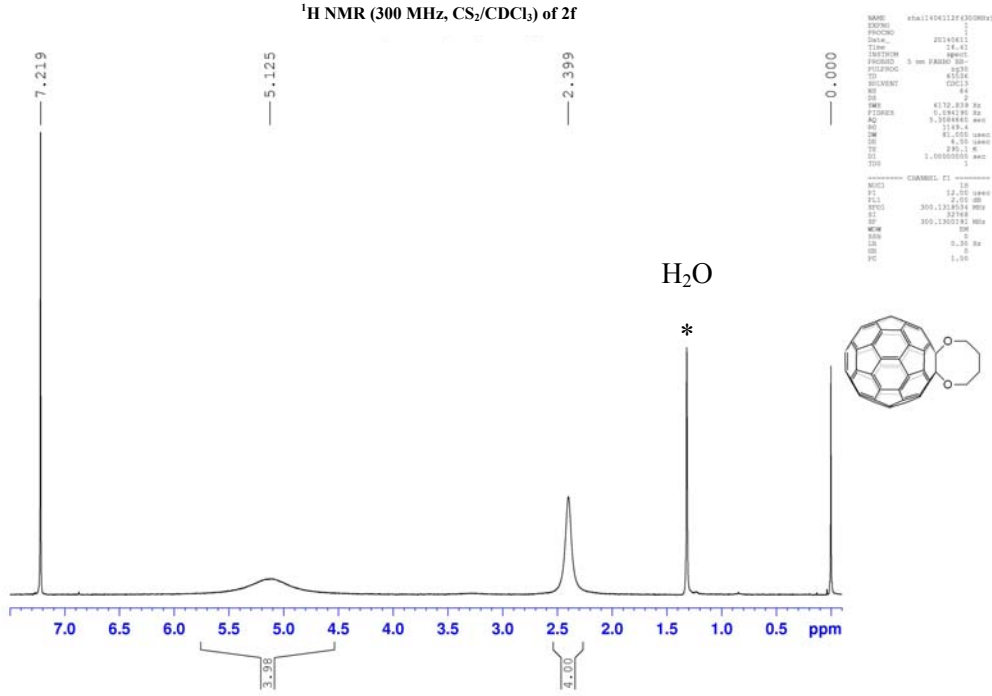
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of 2e

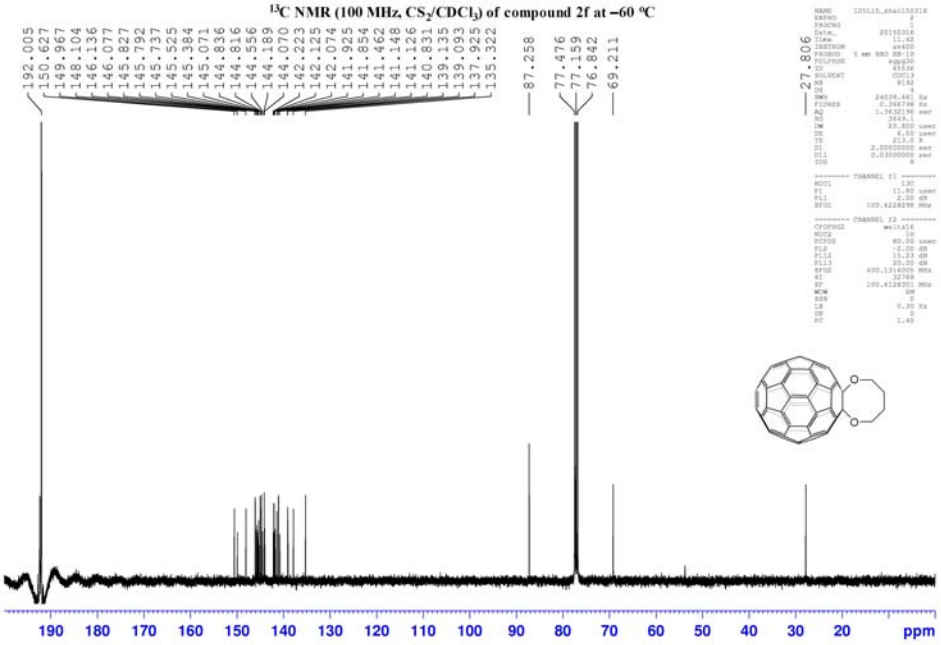


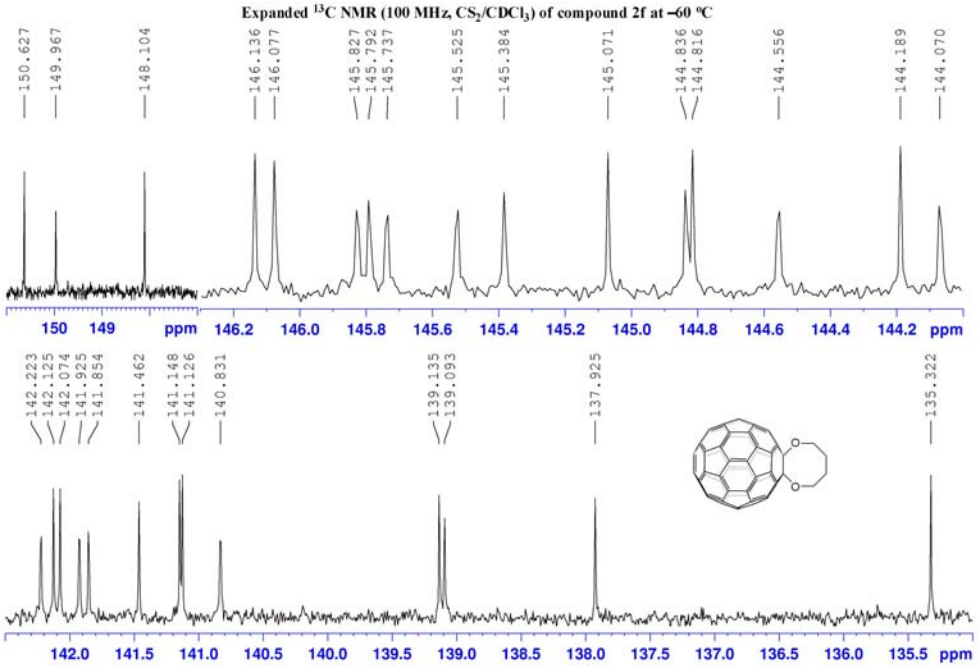
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2e



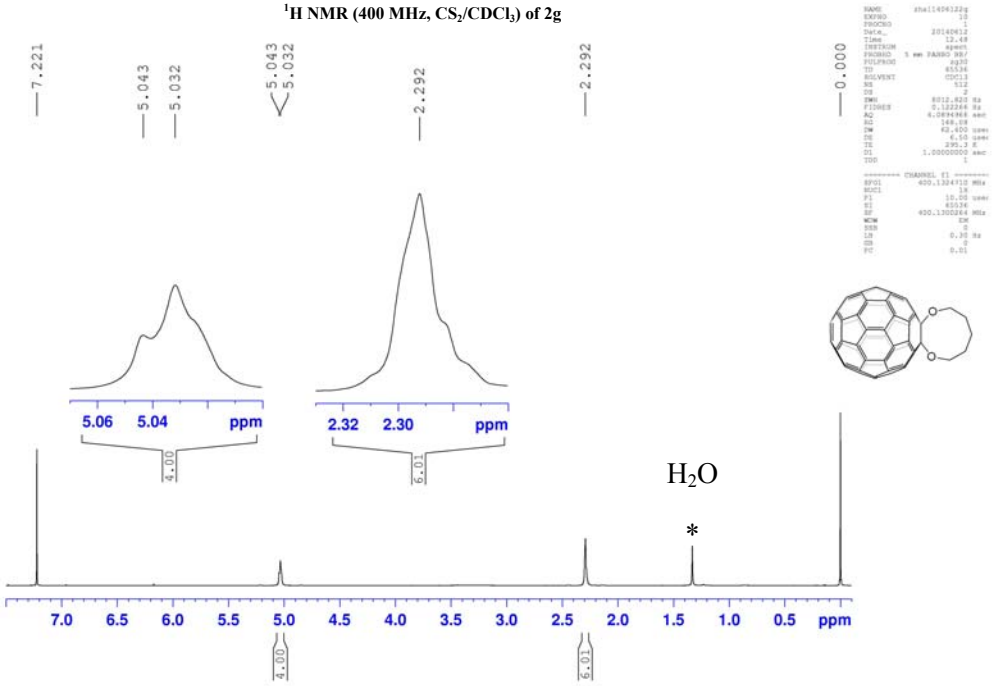
^1H NMR (300 MHz, $CS_2/CDCl_3$) of 2f



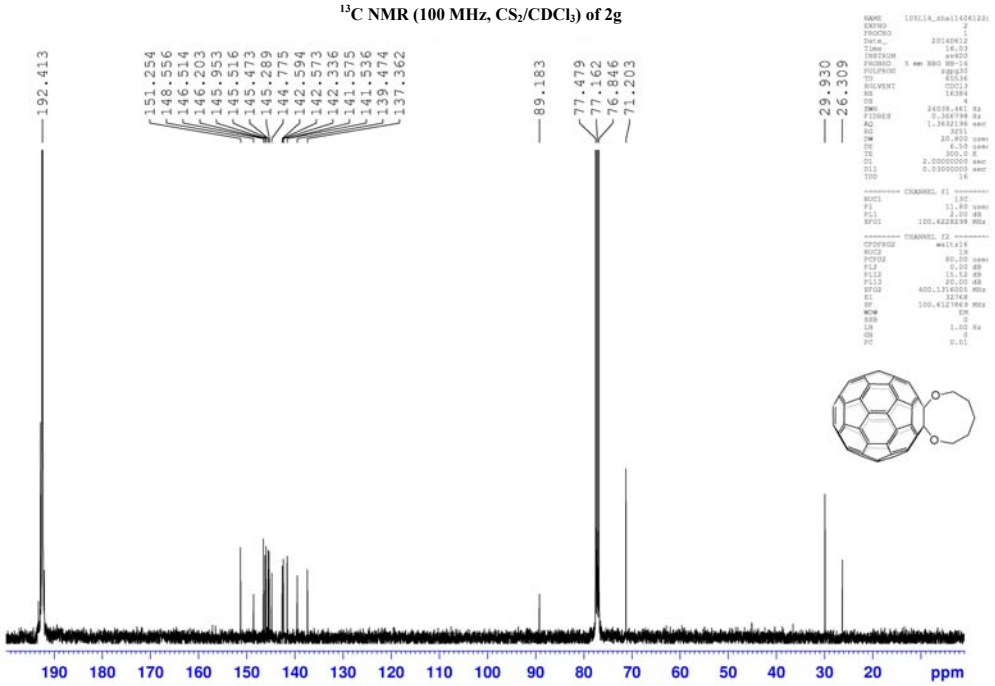

^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of compound 2f at –60 °C
192.005
150.627
149.967
148.104
146.136
146.077
145.827
145.792
145.737
145.525
145.384
145.071
144.836
144.816
144.556
144.189
144.070
142.223
142.125
142.074
141.925
141.854
141.462
141.148
141.126
140.831
139.135
139.093
137.925
135.322
87.258
77.476
77.159
76.842
69.211
27.806
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of compound 2f at –60 °C
150.627
149.967
148.104
146.136
146.077
145.827
145.792
145.737
145.525
145.384
145.071
144.836
144.816
144.556
144.189
144.070
150 149 ppm 146.2 146.0 145.8 145.6 145.4 145.2 145.0 144.8 144.6 144.4 144.2 ppm
142.223
142.125
142.074
141.925
141.854
141.462
141.148
141.126
140.831
139.135
139.093
137.925
135.322
142.0 141.5 141.0 140.5 140.0 139.5 139.0 138.5 138.0 137.5 137.0 136.5 136.0 135.5 ppm

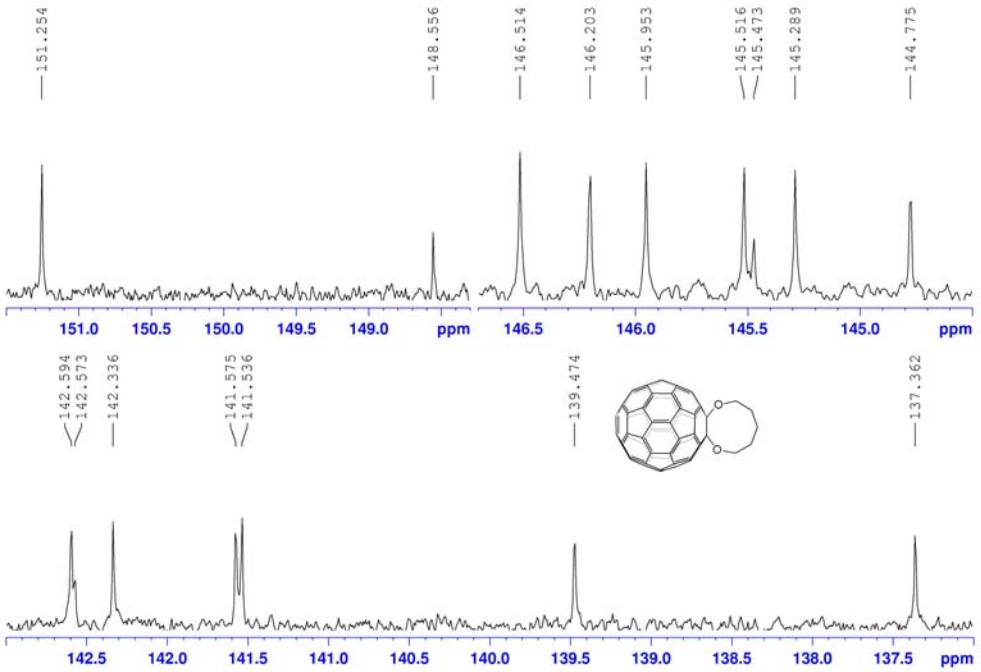
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) of 2g



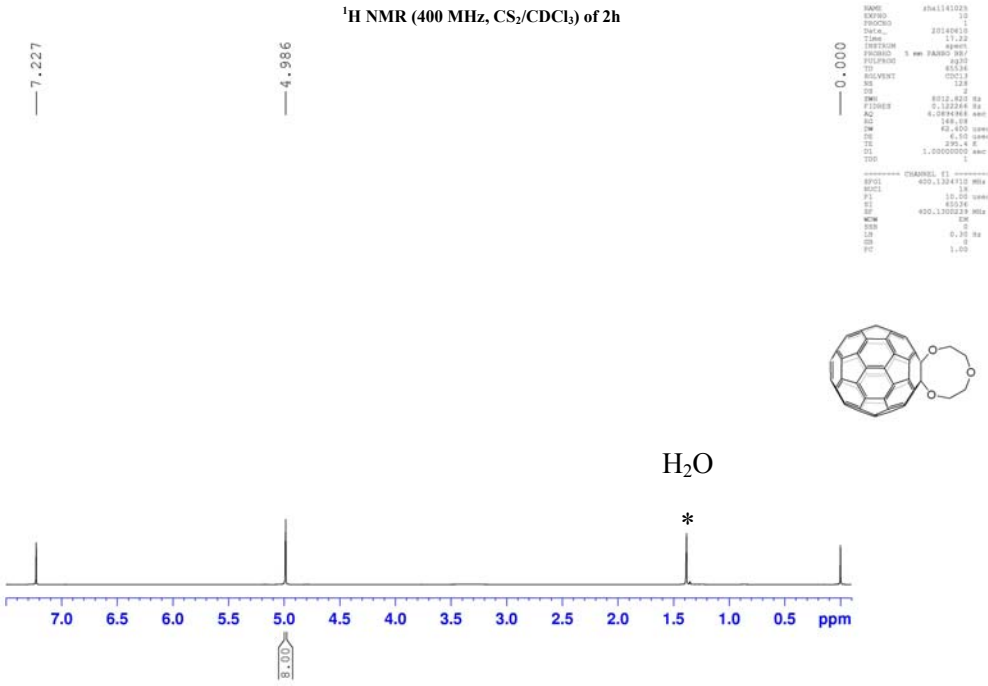
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of 2g



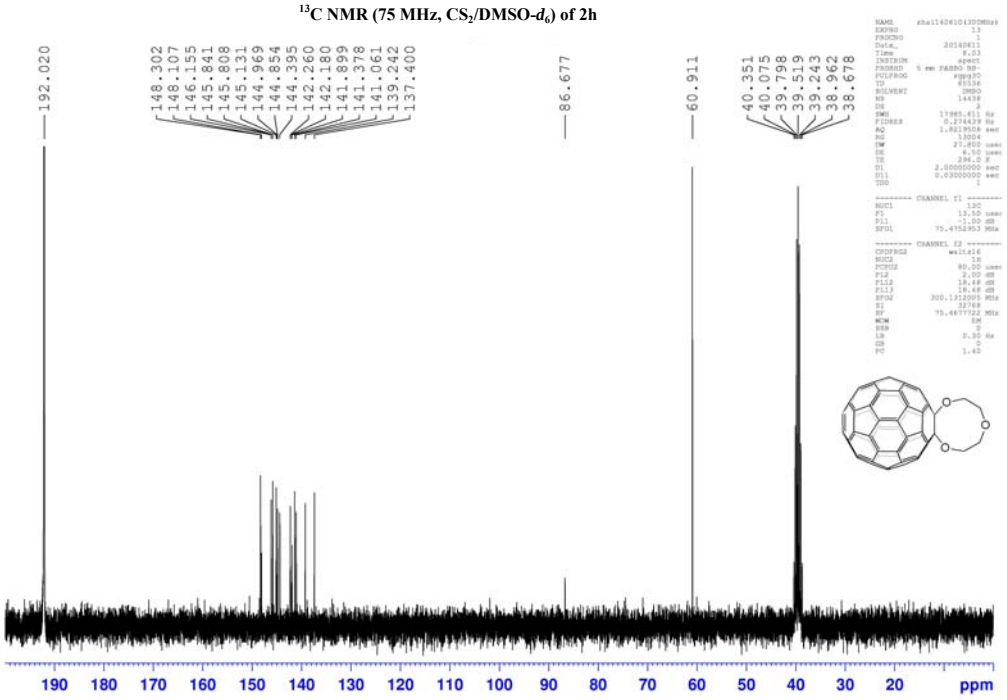
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2g



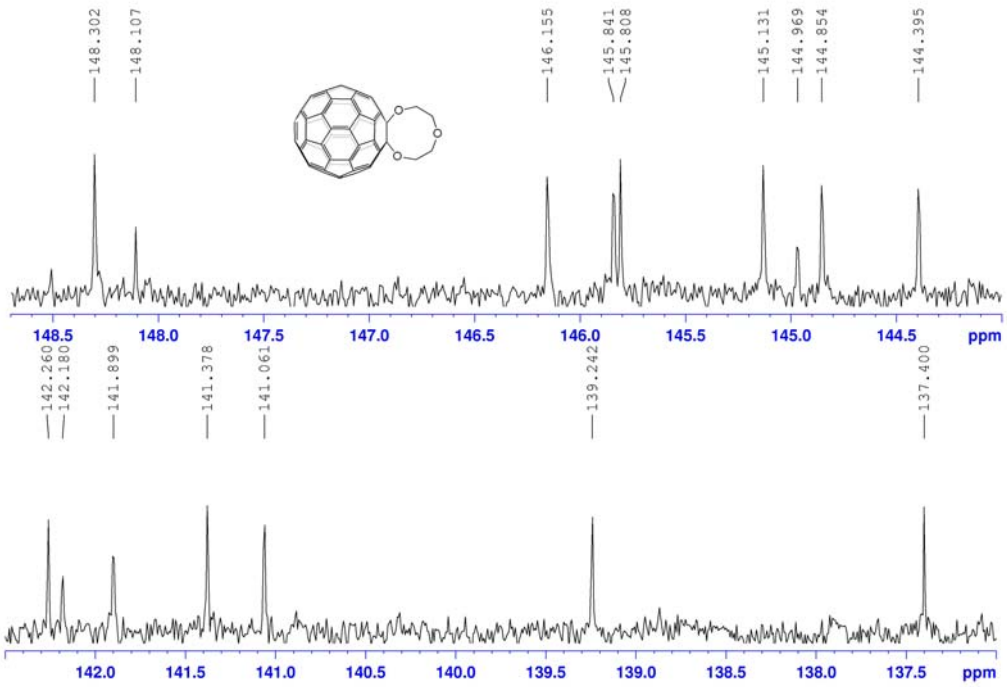
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) of 2h



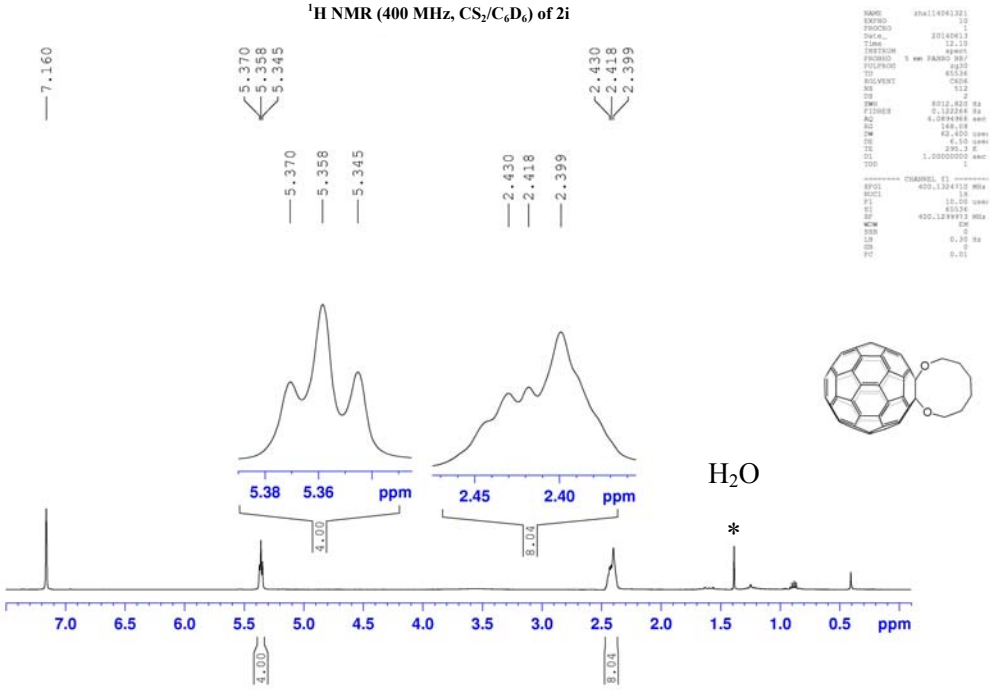
^{13}C NMR (75 MHz, CS_2/DMSO-d_6) of 2h



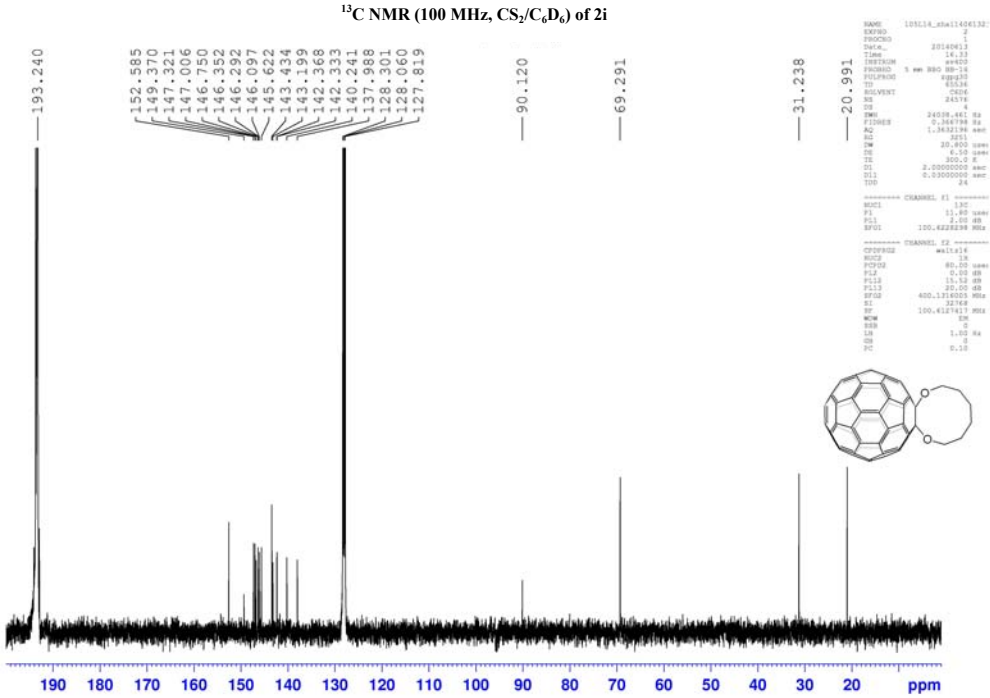
Expanded ^{13}C NMR (75 MHz, CS_2/DMSO-d_6) of 2h



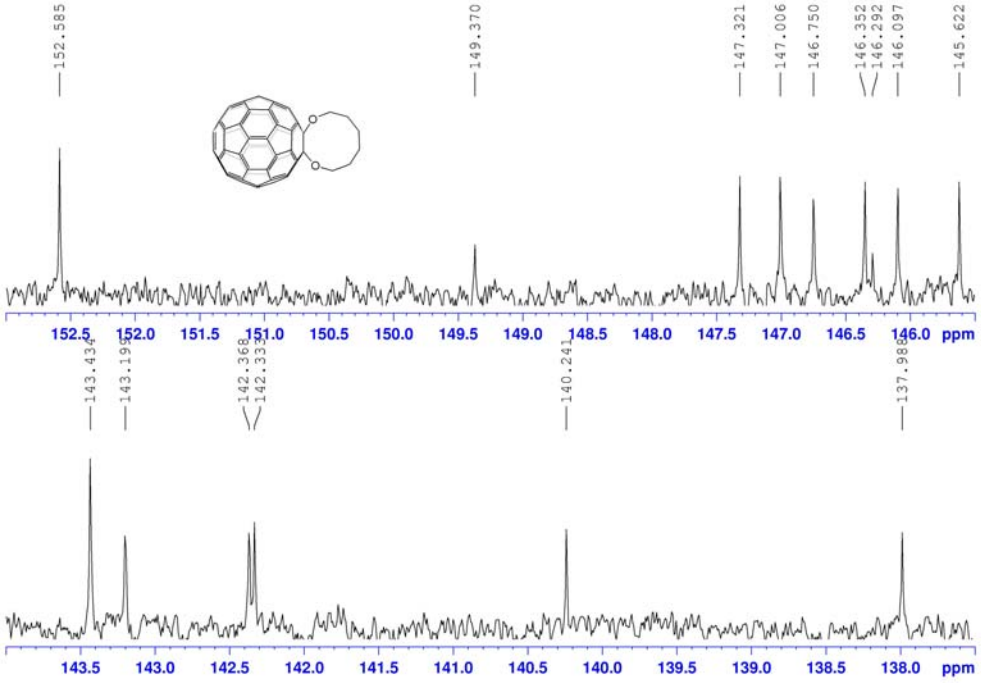
^{1}H NMR (400 MHz, CS_2/C_6D_6) of 2i



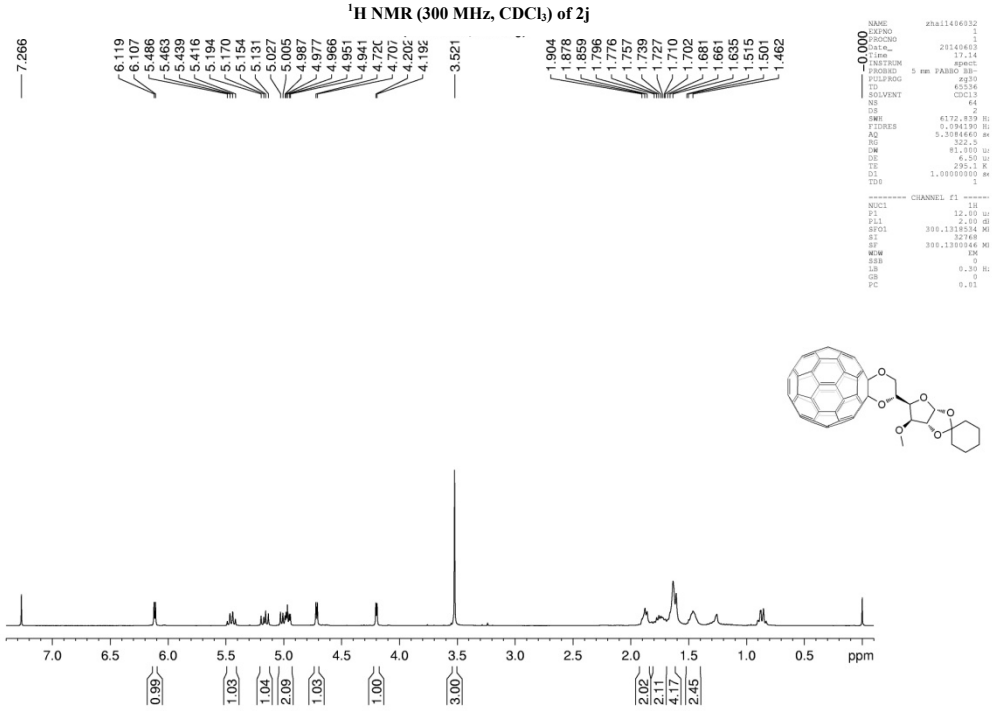
^{13}C NMR (100 MHz, CS_2/C_6D_6) of 2i



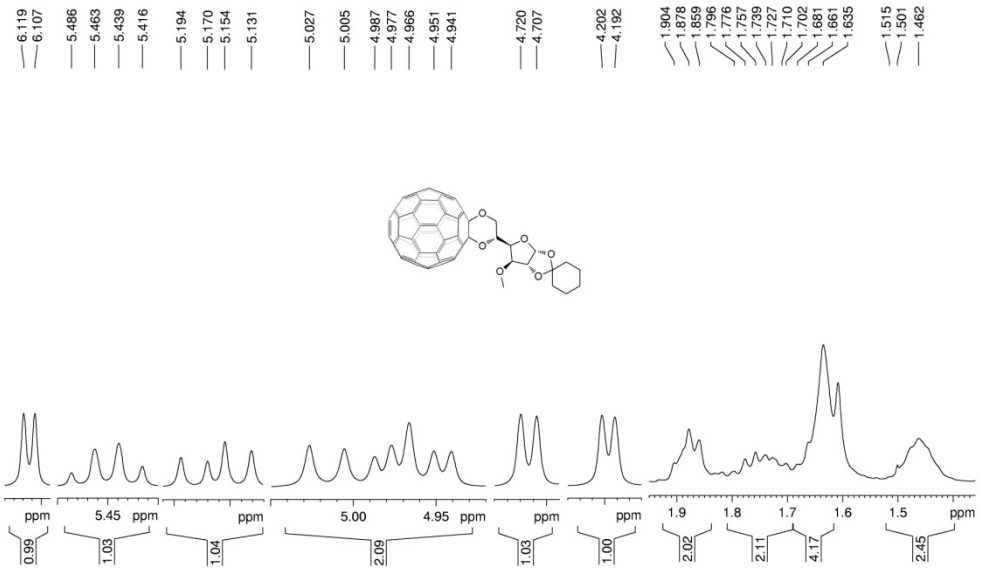
Expanded ^{13}C NMR (100 MHz, CS_2/C_6D_6) of 2i



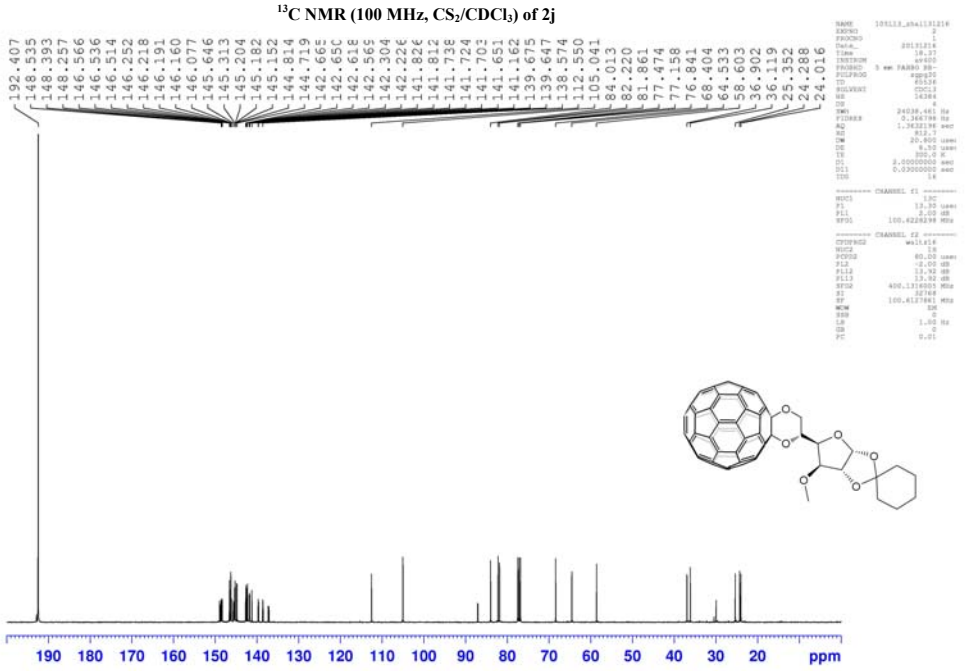
^1H NMR (300 MHz, $CDCl_3$) of 2j

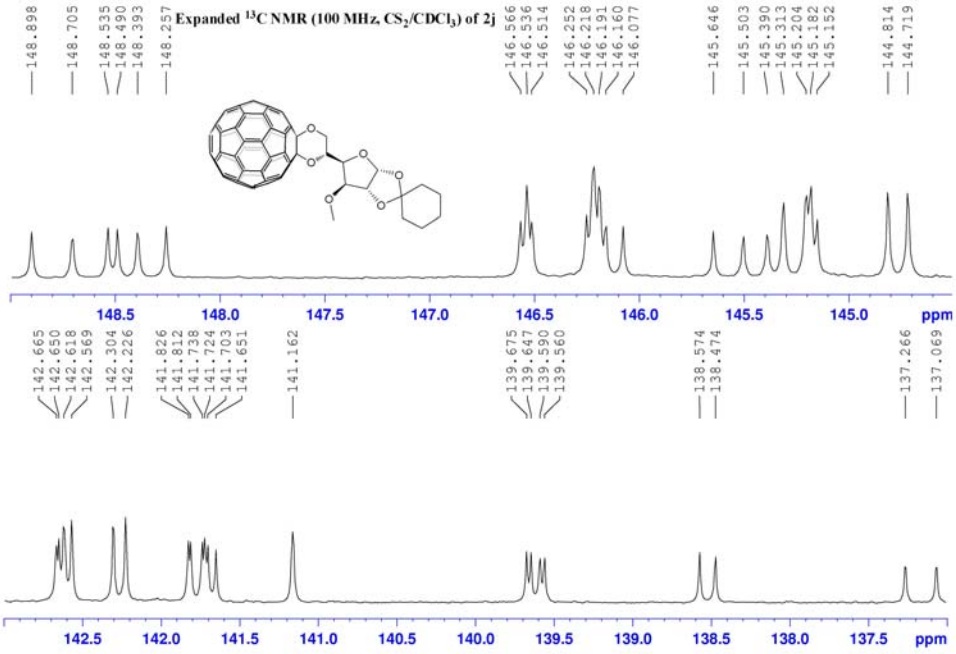


Expanded ^{1}H NMR (300 MHz, $CDCl_3$) of 2j



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




Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of 2j
148.898
148.705
148.535
148.490
148.393
148.257
146.566
146.536
146.514
146.252
146.218
146.191
146.160
146.077
145.646
145.503
145.390
145.313
145.204
145.182
145.152
144.814
144.719
148.5
148.0
147.5
147.0
146.5
146.0
145.5
145.0
ppm
142.665
142.650
142.618
142.569
142.304
142.226
141.826
141.812
141.738
141.724
141.703
141.651
141.162
139.675
139.647
139.590
139.560
138.574
138.474
137.266
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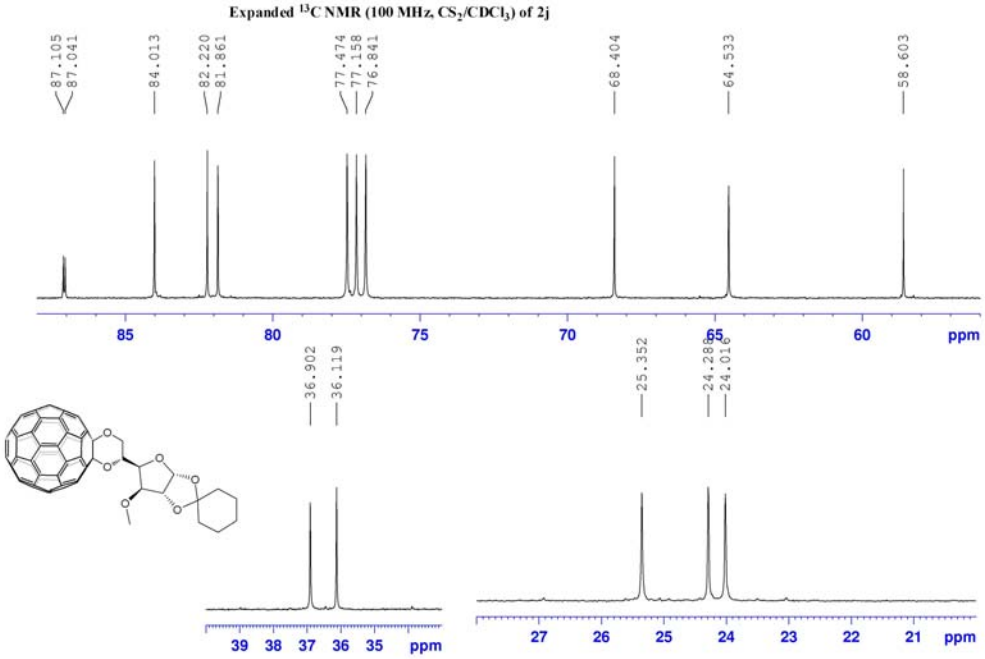
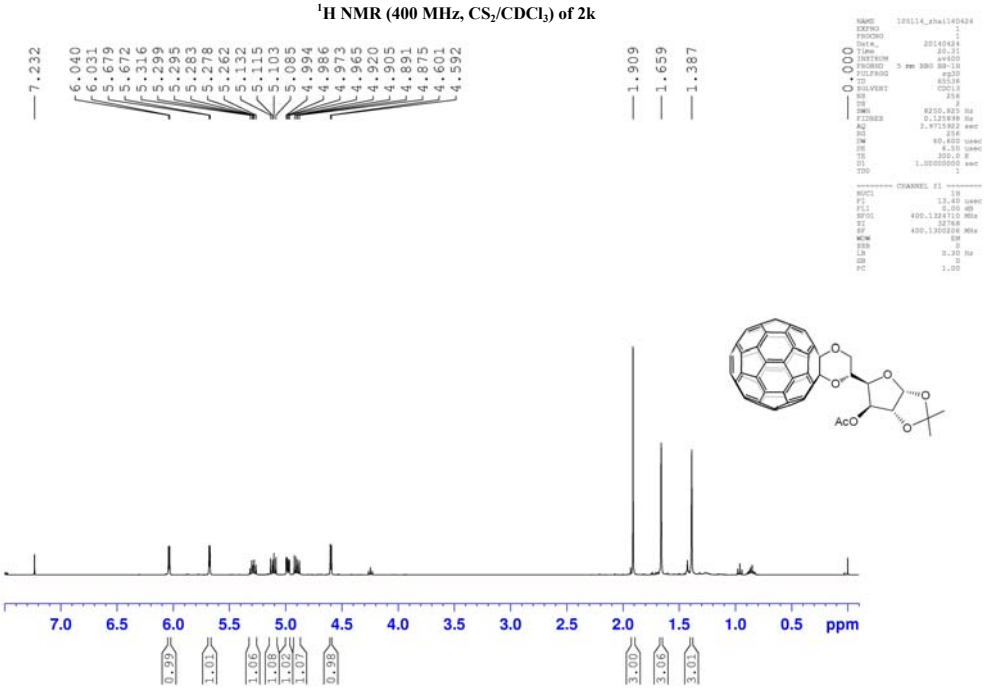
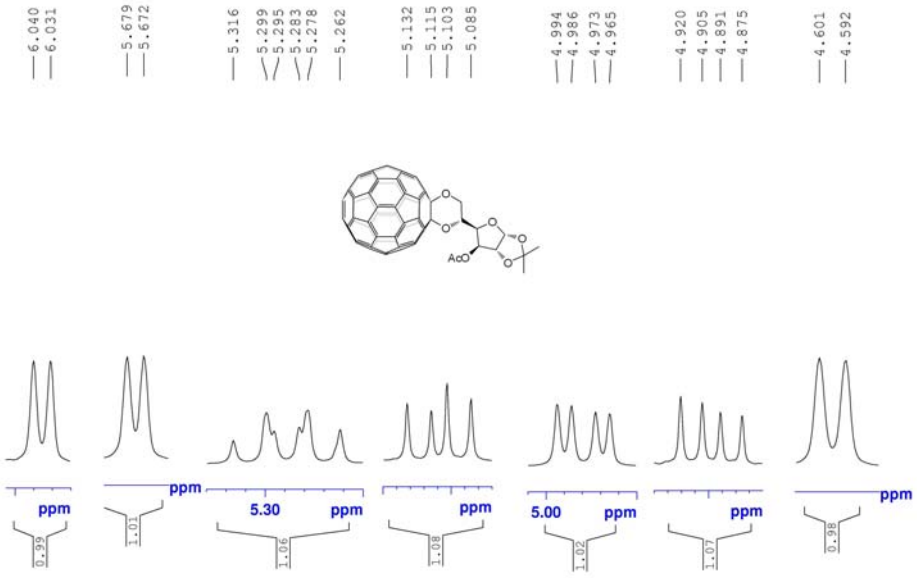
139.5
139.0
138.5
138.0
137.5
ppm


Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) of 2j
87.105
87.041
84.013
82.220
81.861
77.474
77.158
76.841
68.404
64.533
58.603
85
80
75
70
65
60
ppm
36.902
36.119
25.352
24.285
24.016
39
38
37
36
35
ppm
27
26
25
24
23
22
21
ppm

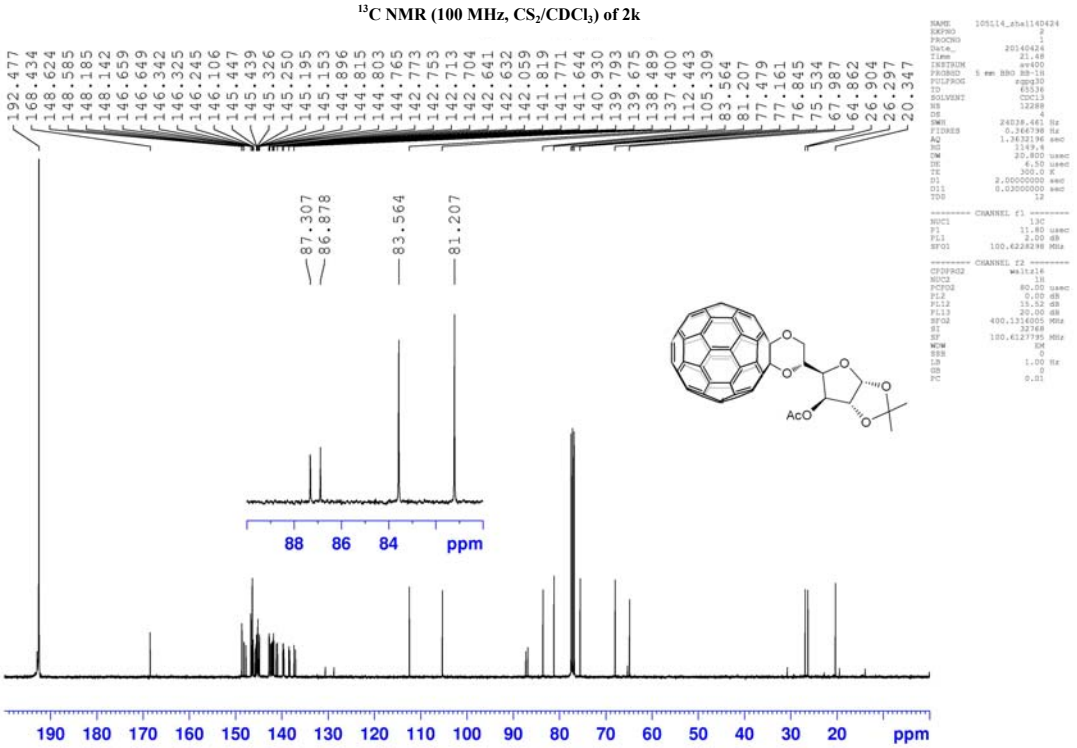
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) of 2k



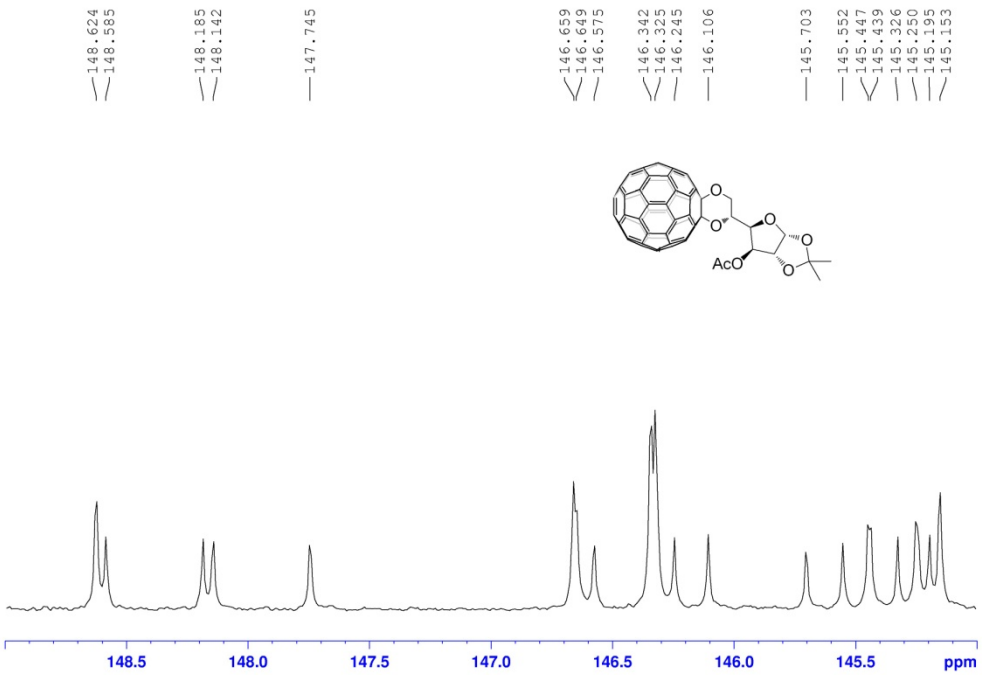
Expanded ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) of 2k



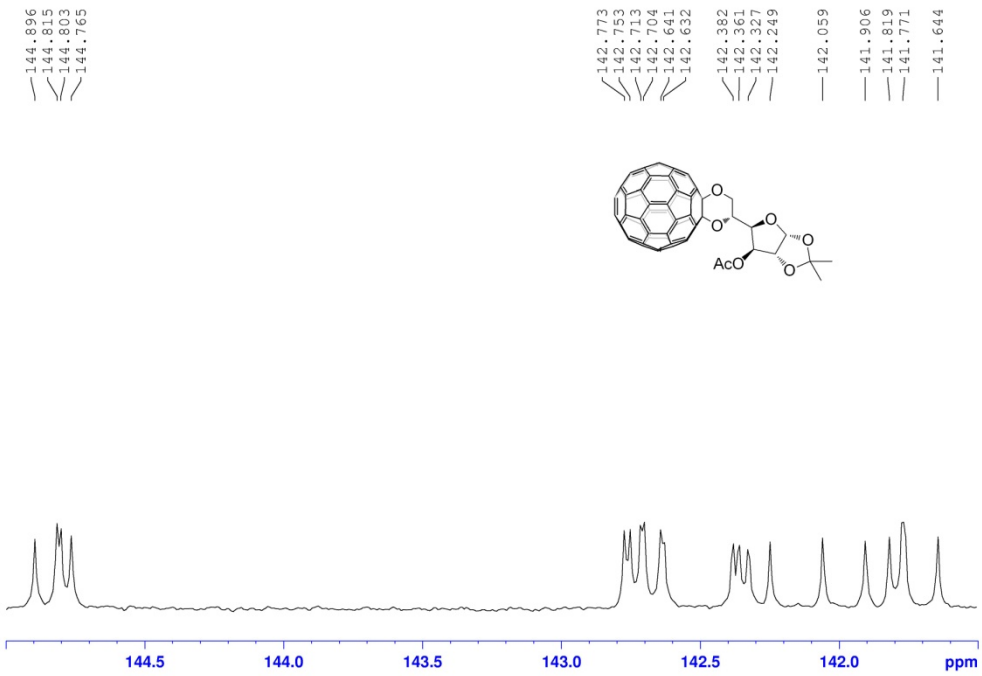
^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2k



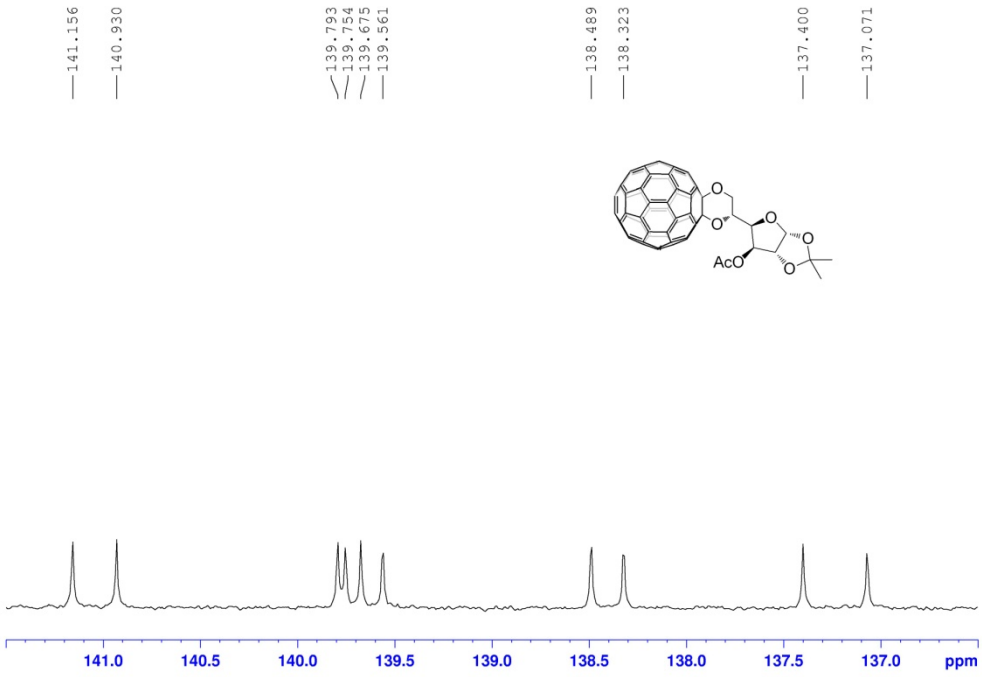
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2k



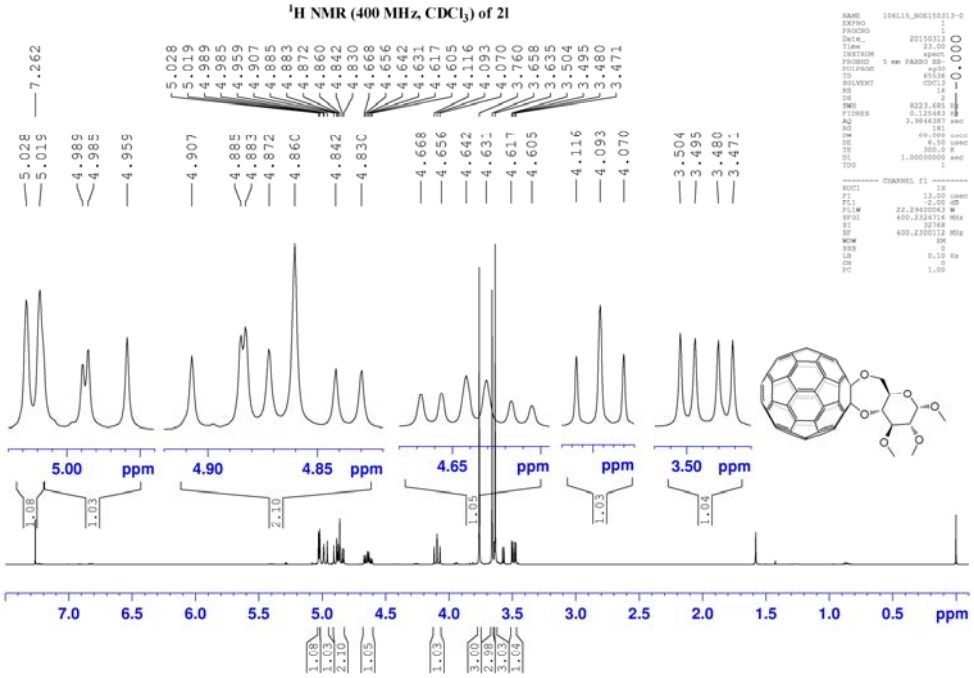
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2k



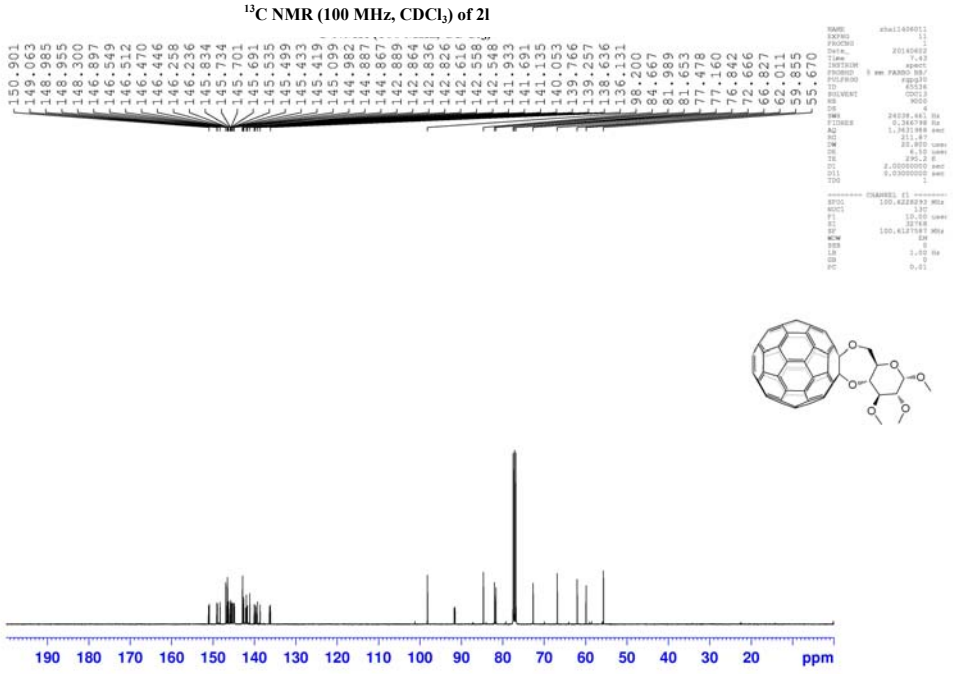
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) of 2k



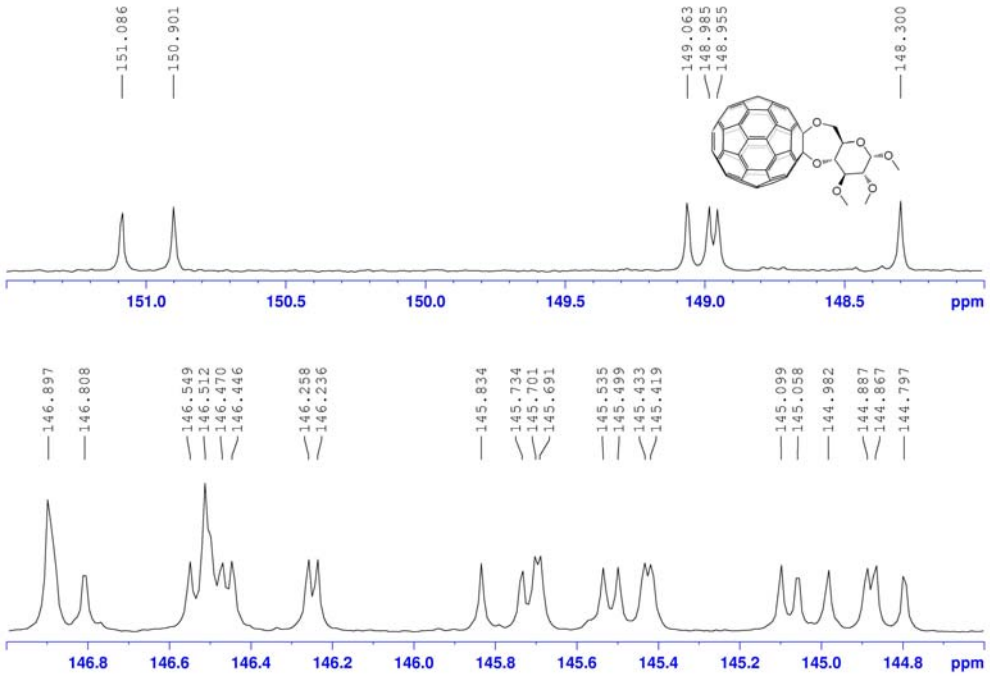
^{1}H NMR (400 MHz, $CDCl_3$) of 2l



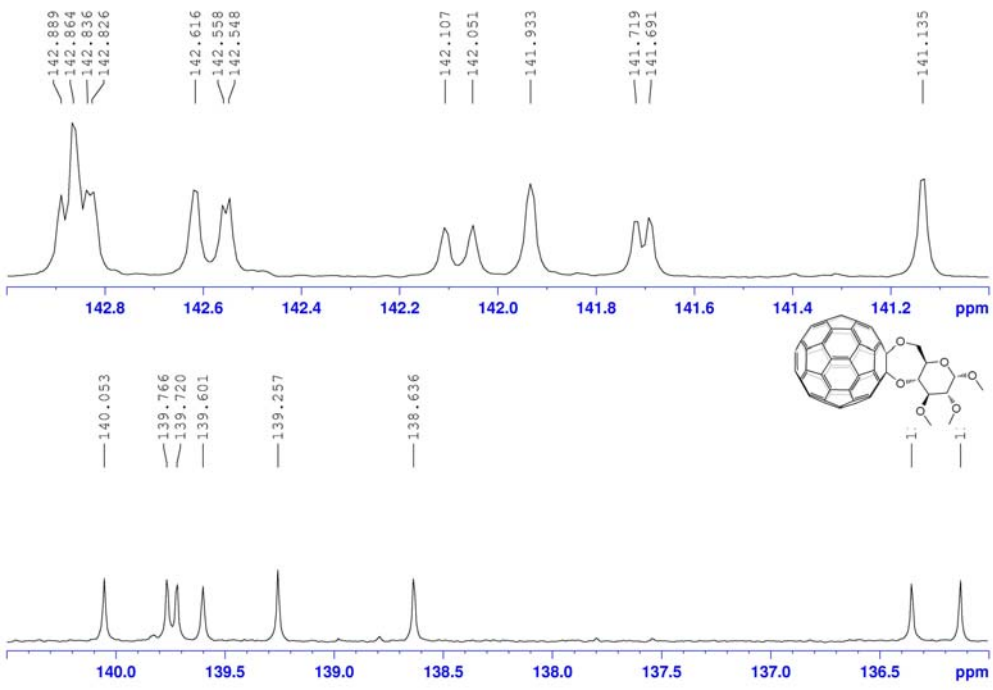
^{13}C NMR (100 MHz, $CDCl_3$) of 2l



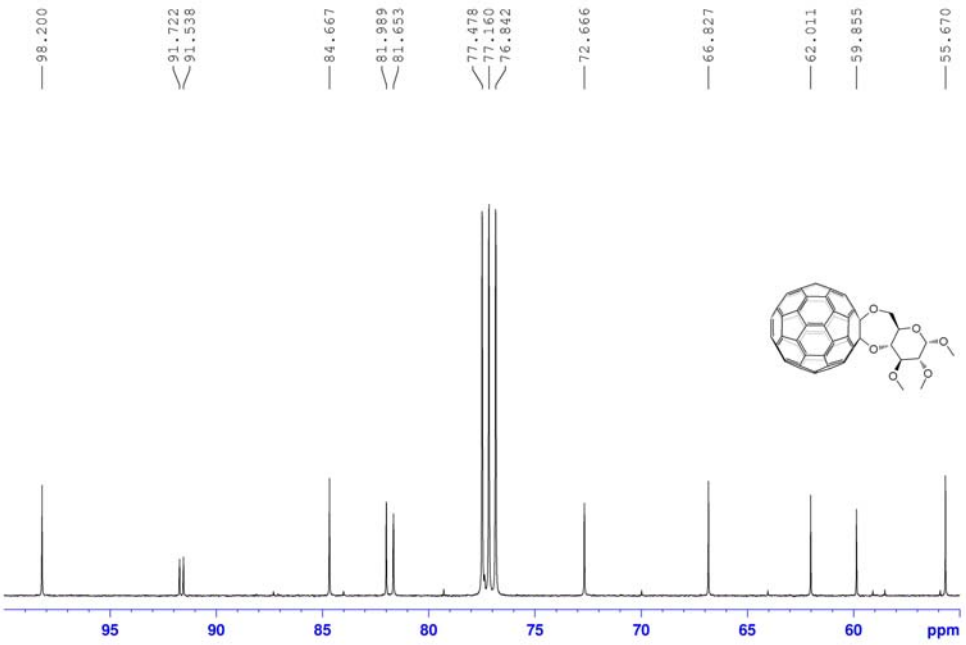
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2l



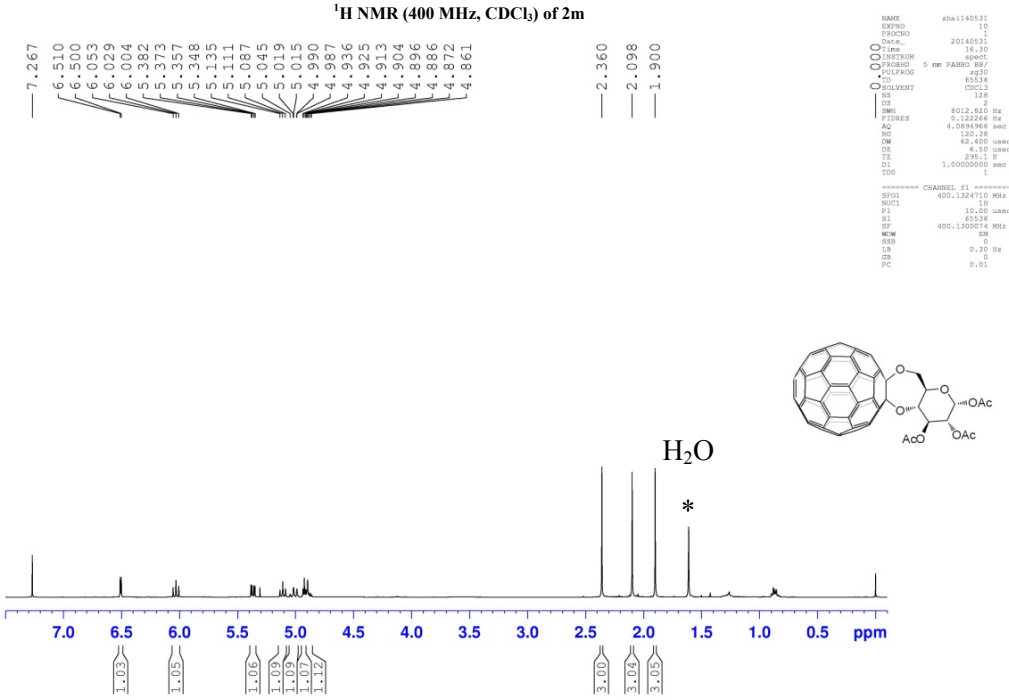
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2l



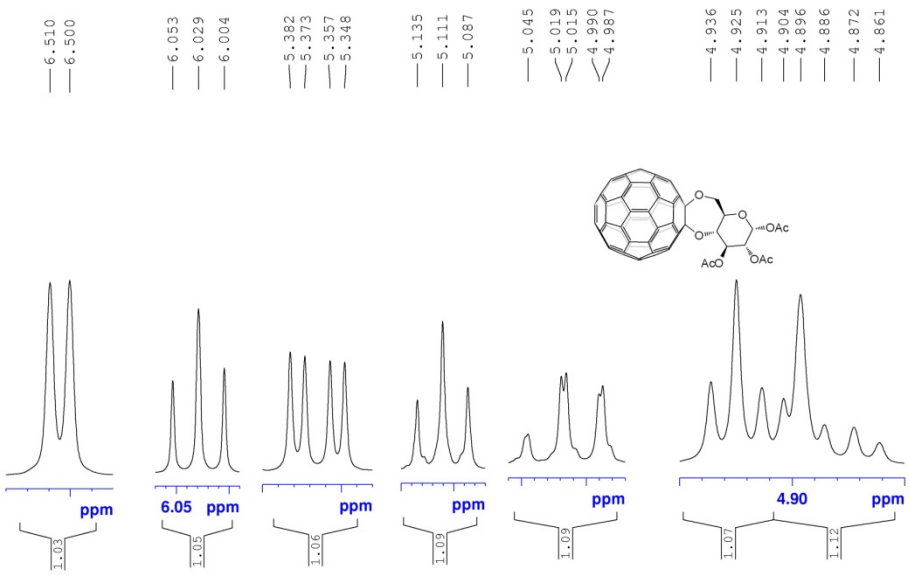
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2l



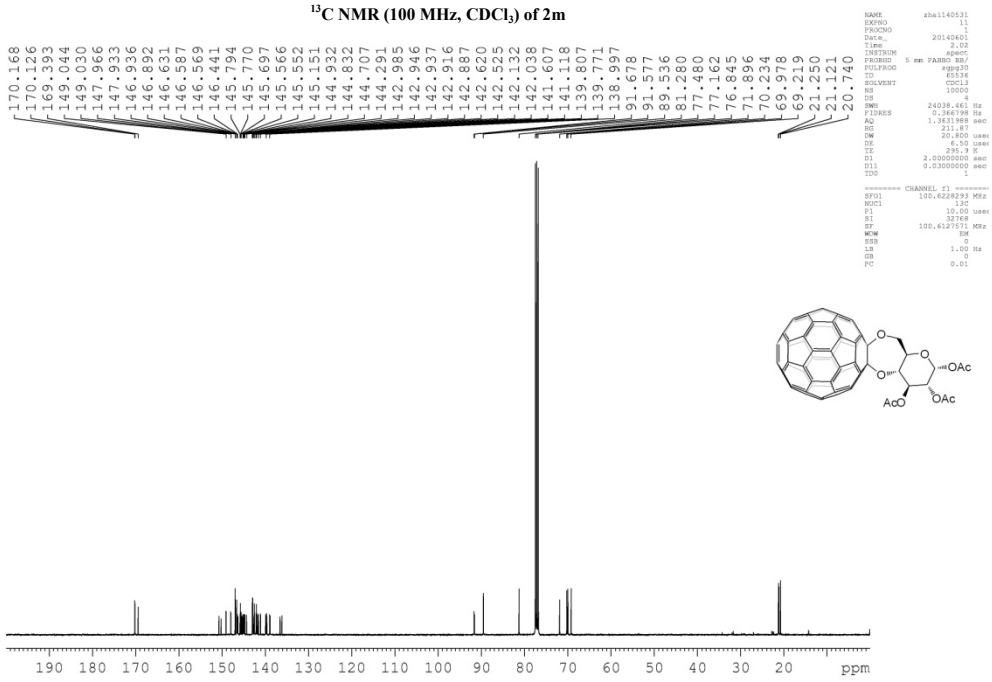
^{1}H NMR (400 MHz, $CDCl_3$) of 2m



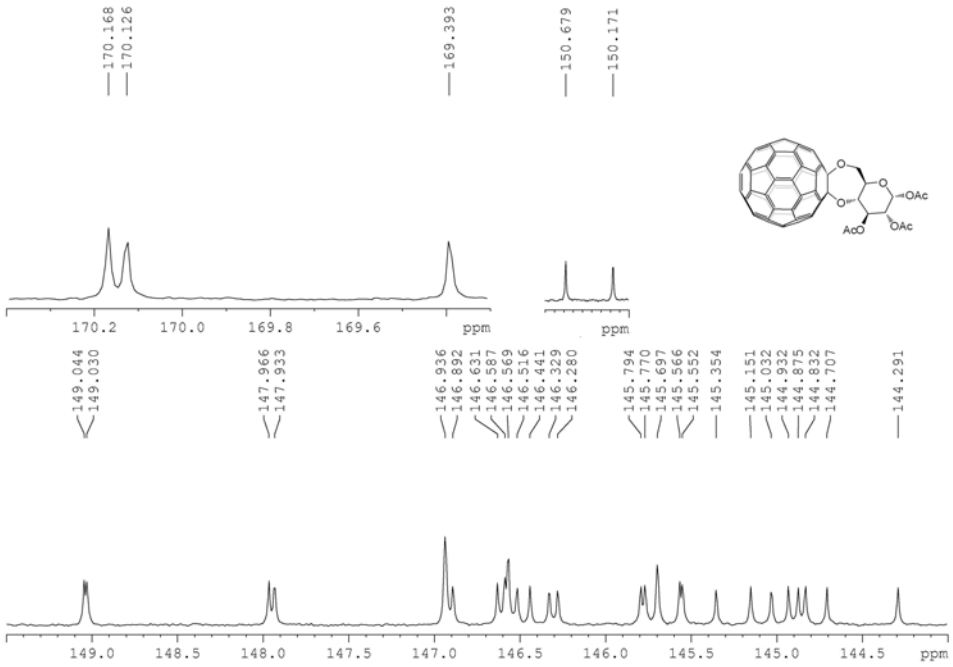
Expanded ^{1}H NMR (400 MHz, $CDCl_3$) of 2m



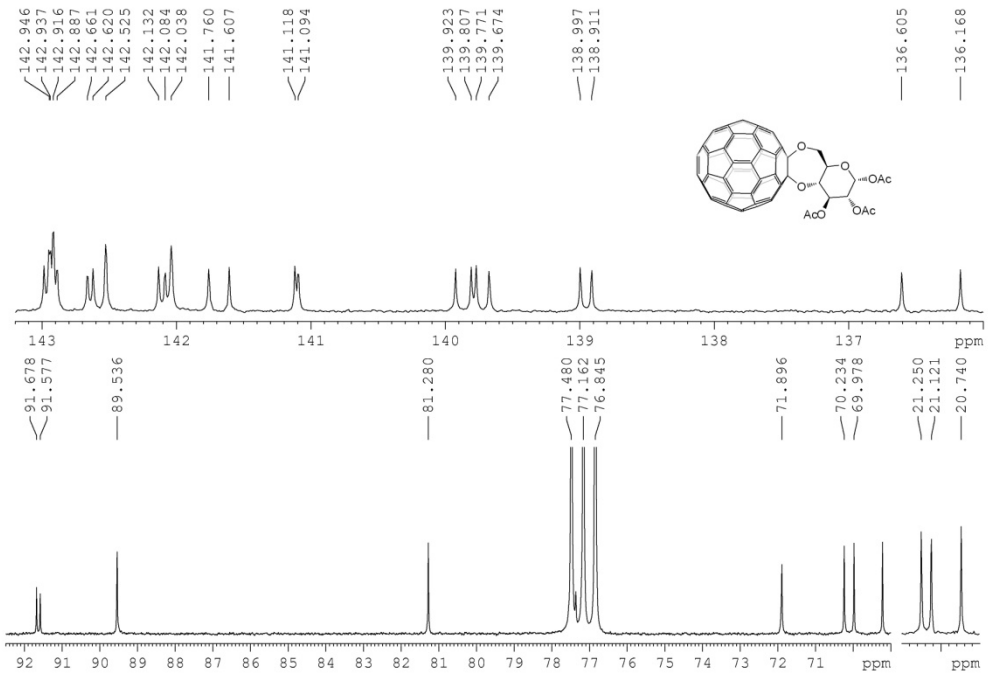
^{13}C NMR (100 MHz, $CDCl_3$) of 2m



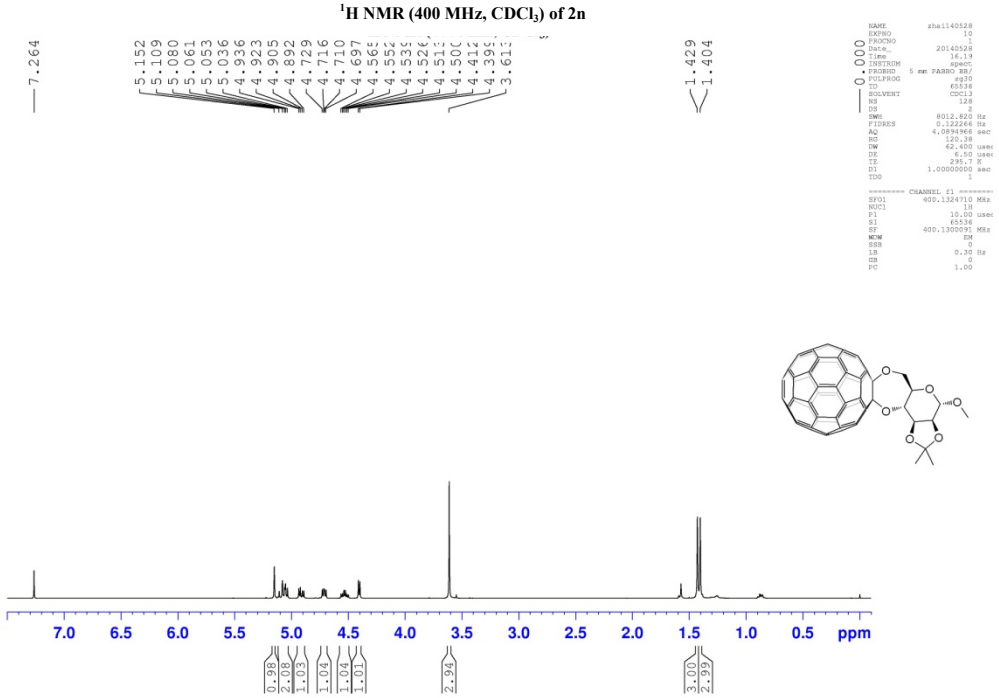
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2m



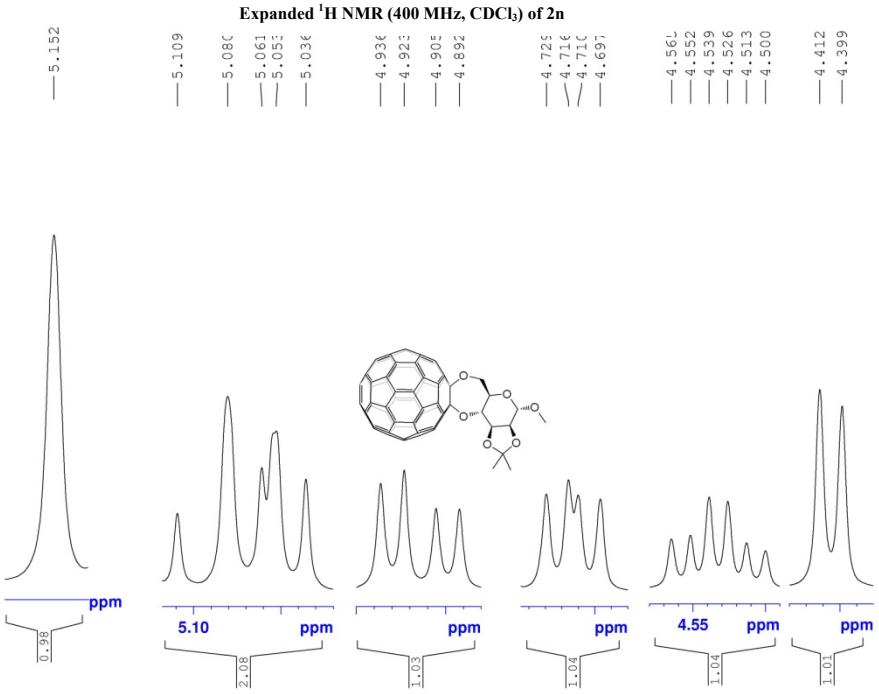
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2m



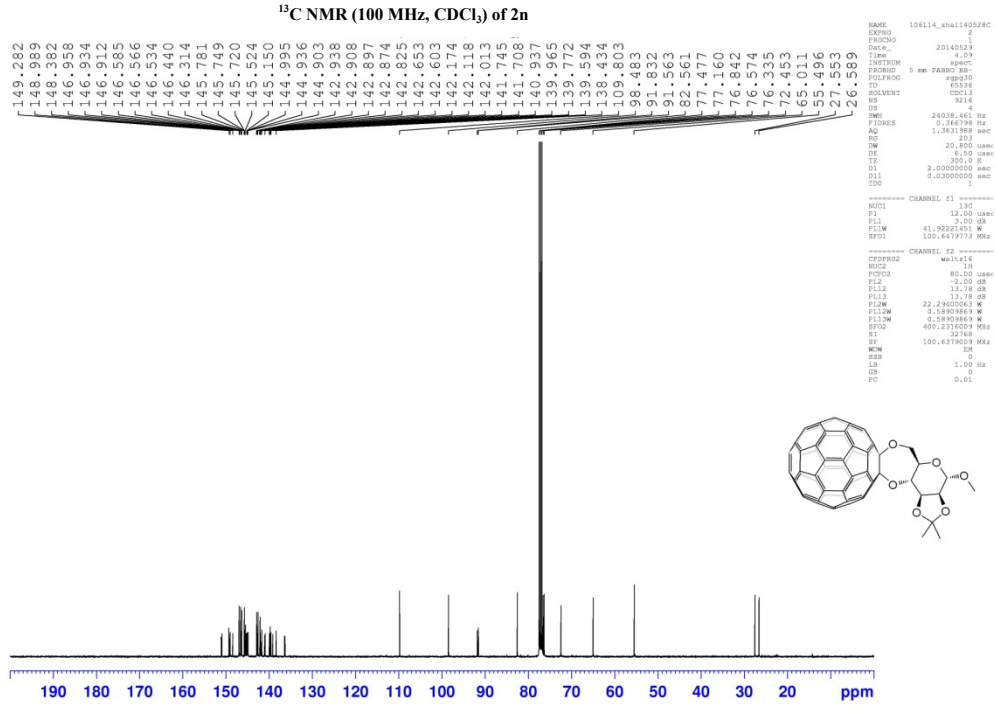
^{1}H NMR (400 MHz, $CDCl_3$) of 2n



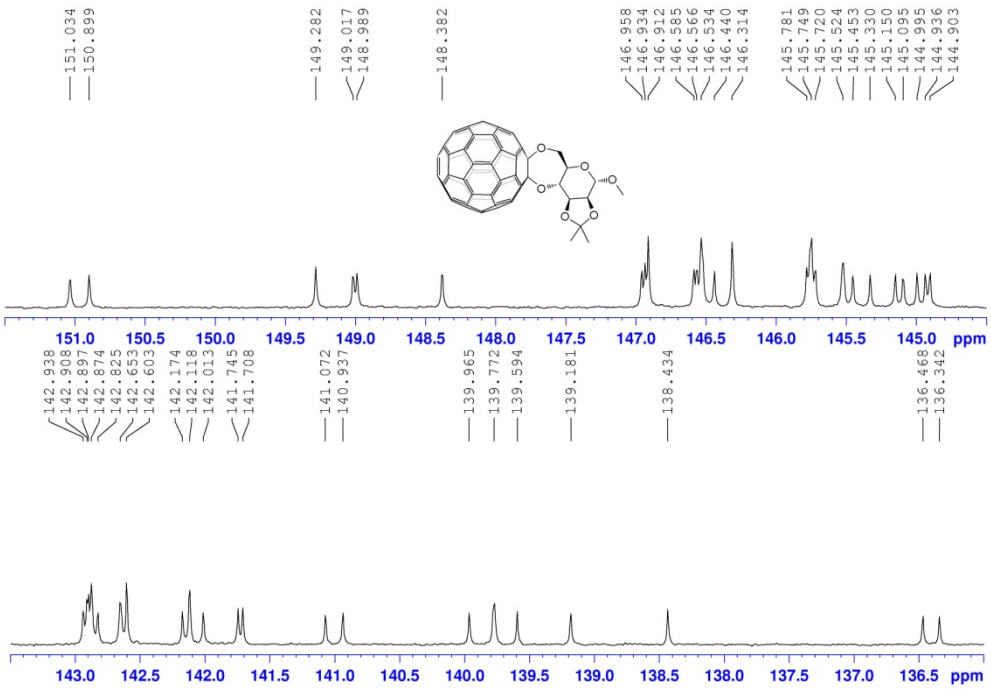
Expanded ^{1}H NMR (400 MHz, $CDCl_3$) of 2n



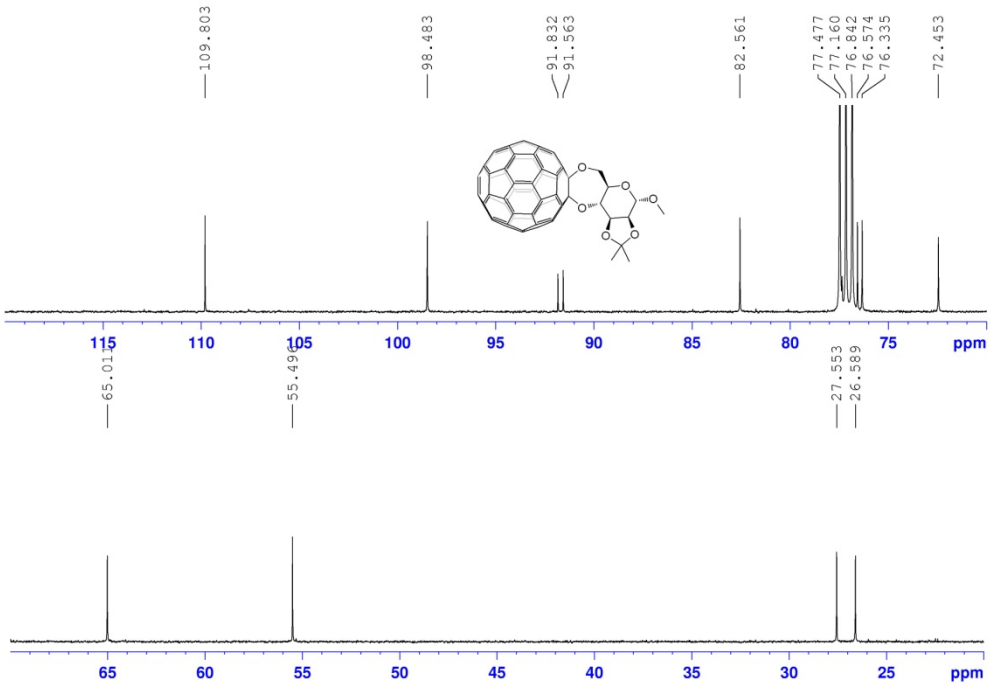
^{13}C NMR (100 MHz, $CDCl_3$) of 2n



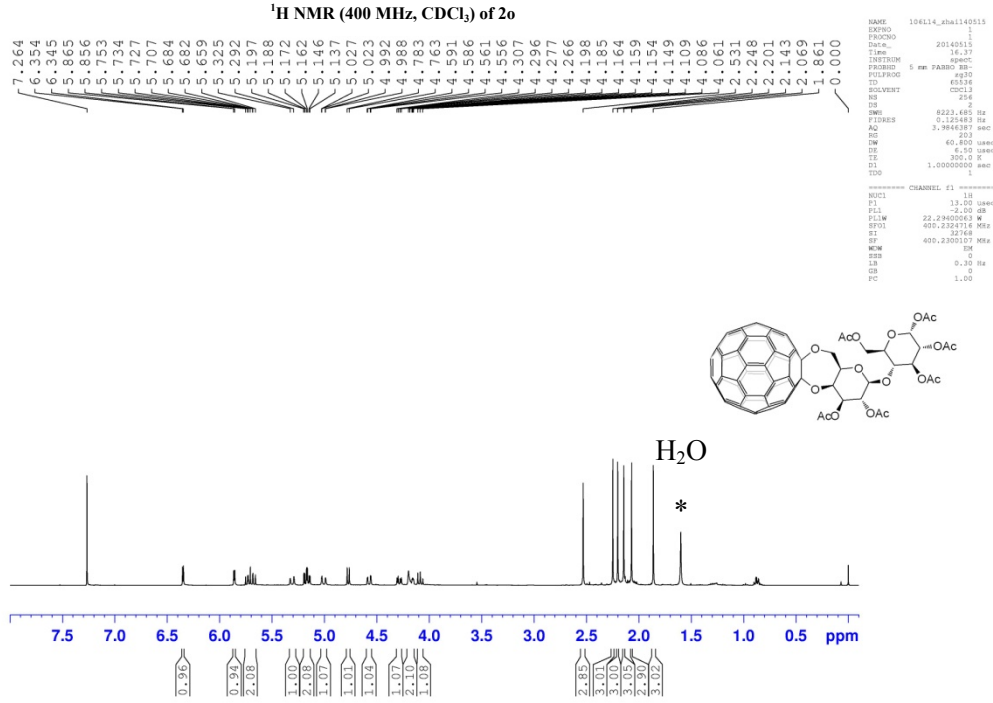
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2n



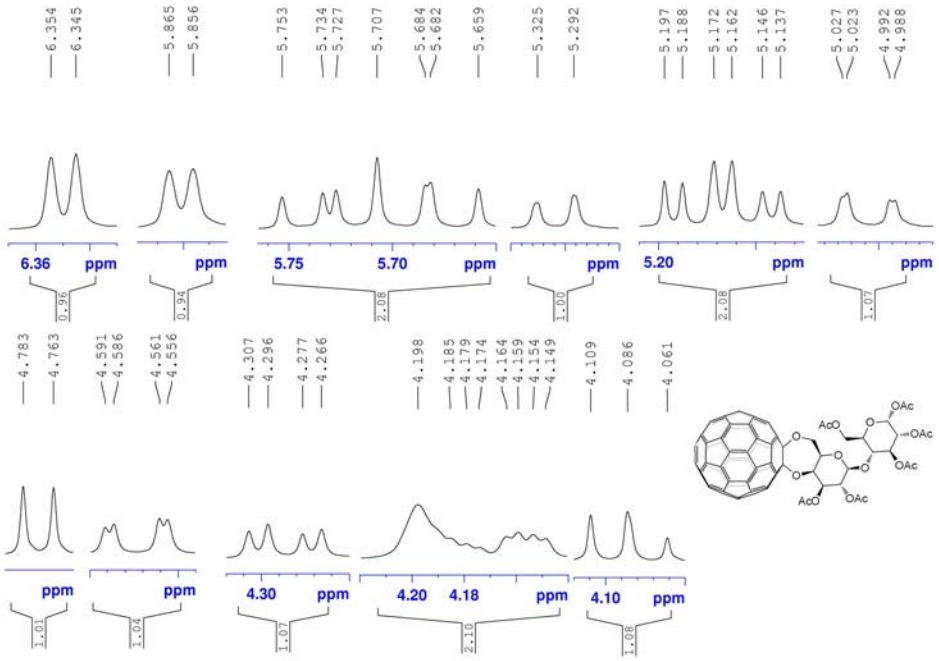
Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2n



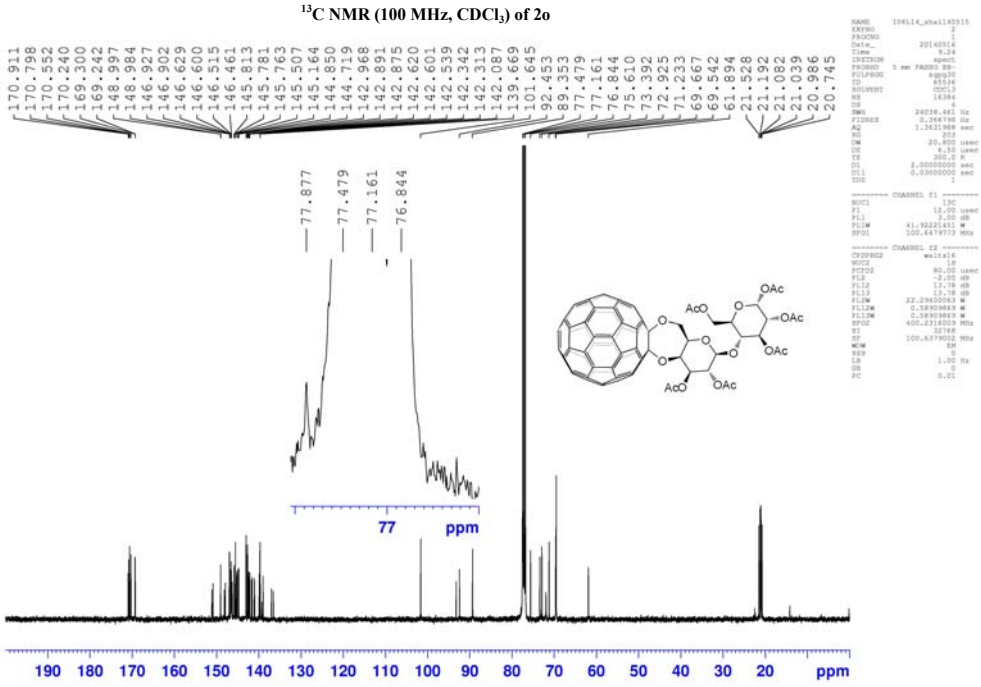
^{1}H NMR (400 MHz, $CDCl_3$) of 2o

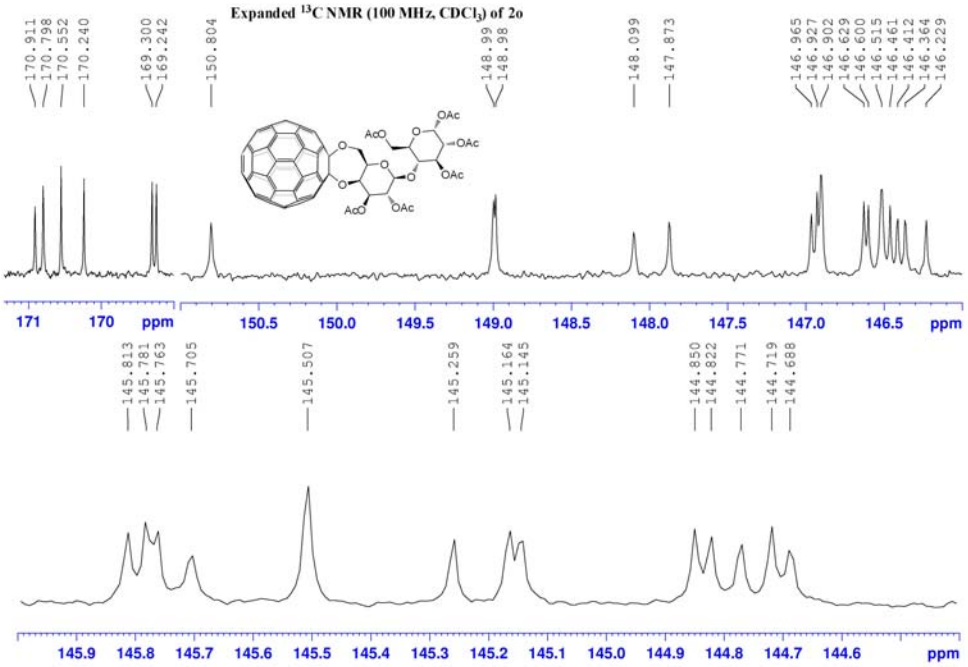


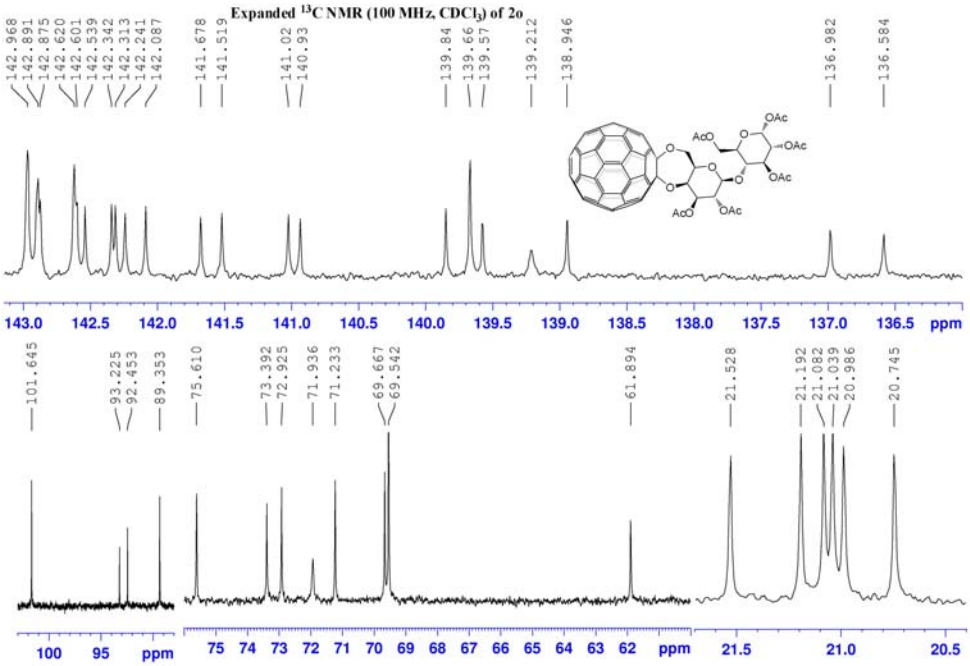
Expanded ^{1}H NMR (400 MHz, $CDCl_3$) of 2o



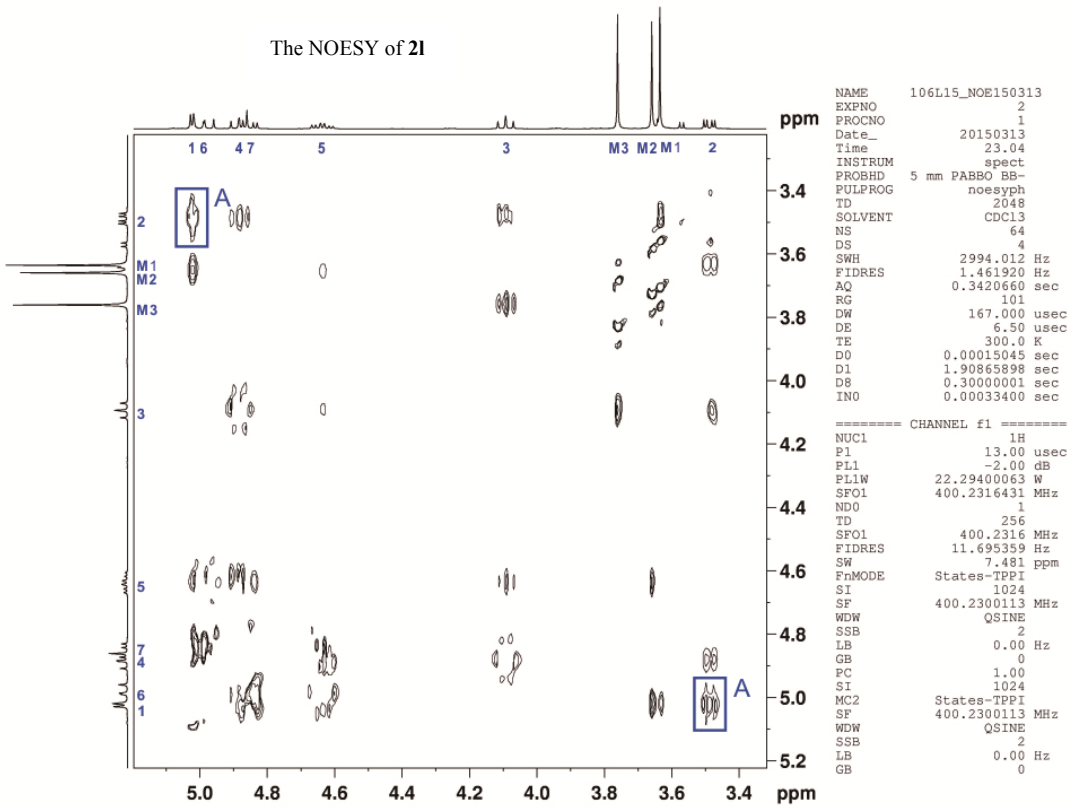
^{13}C NMR (100 MHz, $CDCl_3$) of 2o



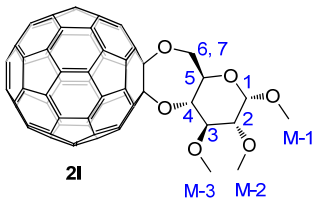

Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2o
170.911
170.798
170.552
170.240
169.300
169.242
150.804
148.99
148.98
148.099
147.873
146.965
146.927
146.902
146.629
146.600
146.515
146.461
146.412
146.364
146.229
OAc
AcO
171
170
ppm
150.5
150.0
149.5
149.0
148.5
148.0
147.5
147.0
146.5
145.813
145.781
145.763
145.705
145.507
145.259
145.164
145.145
144.850
144.822
144.771
144.719
144.688
145.9
145.8
145.7
145.6
145.5
145.4
145.3
145.2
145.1
145.0
144.9
144.8
144.7
144.6


Expanded ^{13}C NMR (100 MHz, $CDCl_3$) of 2o
142.968
142.891
142.875
142.620
142.601
142.539
142.342
142.313
142.241
142.087
141.678
141.519
141.02
140.93
139.84
139.66
139.57
139.212
138.946
136.982
136.584
OAc
AcO
143.0
142.5
142.0
141.5
141.0
140.5
140.0
139.5
139.0
138.5
138.0
137.5
137.0
136.5
ppm
101.645
93.225
92.453
89.353
75.610
73.392
72.925
71.936
71.233
69.667
69.542
61.894
21.528
21.192
21.082
21.039
20.986
20.745
100
95
ppm
75
74
73
72
71
70
69
68
67
66
65
64
63
62
ppm
21.5
21.0
20.5

The NOESY of **2l**



As a representative example, the NOSEY spectrum of **2l** was employed to confirm the stereochemistry. The chemical shift and coupling constant of H-1 at 5.02 ppm (d, J = 3.6 Hz, 1H) agreed with the configuration of the α-isomer, and the cross peak A in its NOESY spectrum was also consistent with the α-isomer. For the β-isomer, the coupling constant of H-1 is generally in 7-9 Hz (Michigami, K.; Hayashi, M. *Tetrahedron* **2013**, *69*, 4221), which did not correlate with the ^{1}H NMR spectrum of **2l**. Then, the peak at 3.49 ppm (dd, J = 9.2, 3.6 Hz, 1H) was assigned to H-2 on the basis of coupling constant. The three methoxy groups were assigned according to a recent report (Matwiejuk, M.; Thiem, J. *Chem. Commun.* **2011**, *47*, 8379). Subsequently, the chemical shifts and stereochemistry of rest protons were assigned according to the ^{1}H NMR and NOESY spectra of **2l**, and were labeled in the NOESY spectrum.



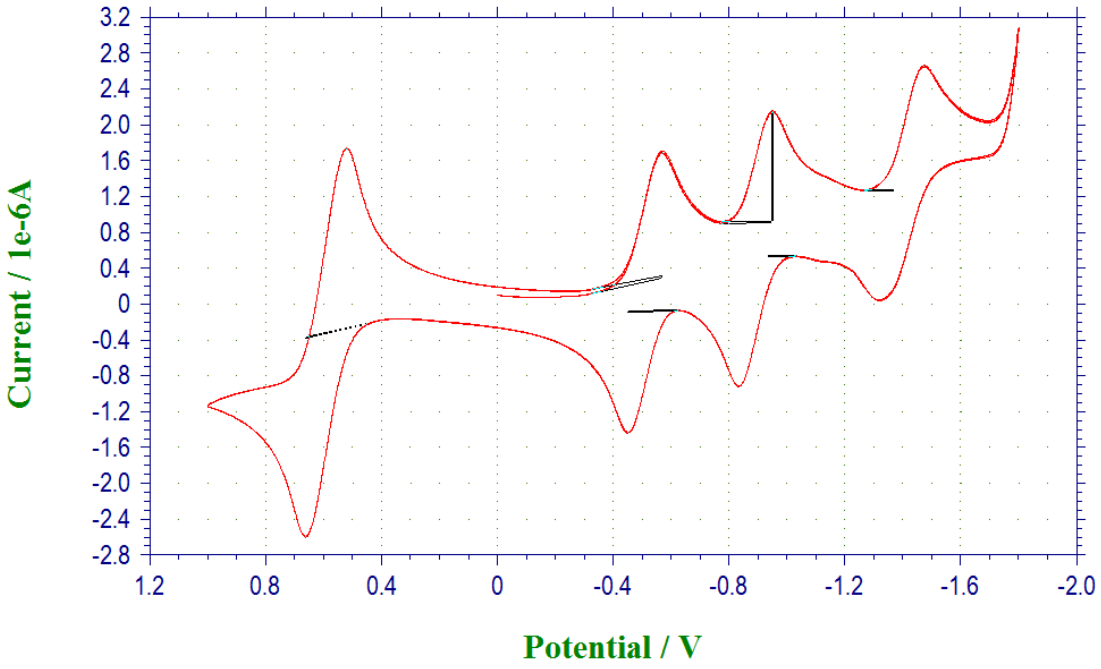
2l

H-1, 5.02 (d, J = 3.6 Hz, 1H)	H-2, 3.49 (dd, J = 9.2, 3.6 Hz, 1H)
H-3, 4.09 (t, J = 9.2 Hz, 1H)	H-4, 4.88 (dd, J = 10.4, 9.2 Hz, 1H)
H-5, 4.64 (ddd, J = 10.4, 10.4, 4.8 Hz, 1H)	H-6, 4.99 (dd, J = 12.0, 10.4 Hz, 1H)
H-7, 4.99 (dd, J = 12.0, 4.8 Hz, 1H)	M-3, 3.76 (s, 3H)
M-2, 3.66 (s, 3H)	M-1, 3.64 (s, 3H)

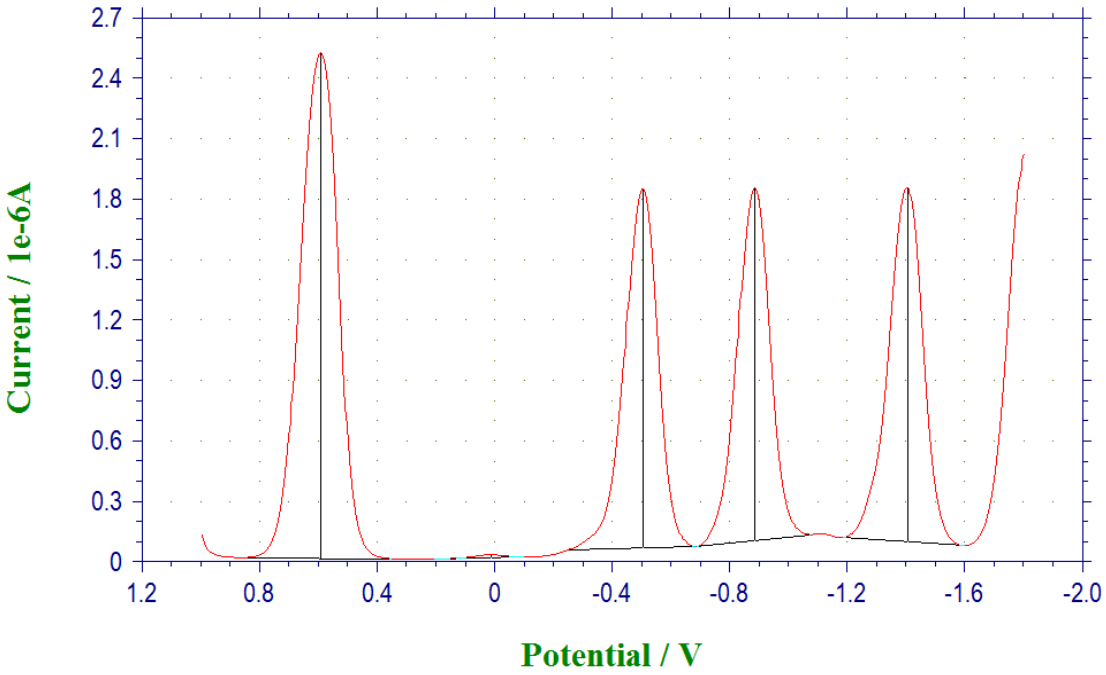
Table S1: Half-wave Reduction Potentials of Compounds **2a–o** and C_{60}[a]

Compd	E_1	E_2	E_3
C_{60}	–1.080	–1.473	–1.934
2a	–1.102	–1.484	–1.990
2b	–1.119	–1.501	–2.032
2c	–1.122	–1.505	–2.036
2d	–1.121	–1.508	–2.043
2e	–1.139	–1.529	–2.075
2f	–1.133	–1.513	–2.048
2g[b]	–1.135	–1.518	–2.054
2h	–1.106	–1.492	–2.014
2i[b]	–1.138	–1.518	–2.044
2j	–1.107	–1.510	–2.052
2k	–1.083	–1.473	–1.977
2l	–1.109	–1.500	–2.019
2m	–1.074	–1.469	–1.981
2n	–1.106	–1.491	–2.001
2o	–1.080	–1.483	–2.024

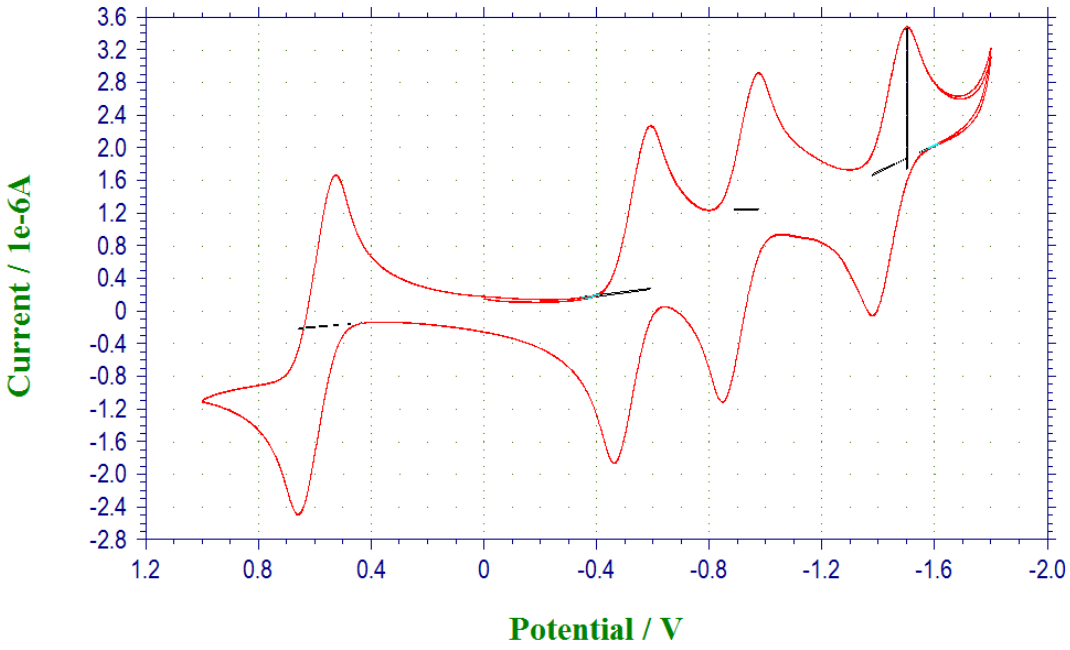
[a]Potential in V versus a ferrocene/ferrocenium couple. Experimental conditions: 0.1 mM of **2a–o**/C_{60} and 0.1 M of $^{n}Bu_4NClO_4$ in anhydrous ODCB; reference electrode, SCE; working electrode, Pt; auxiliary electrode, Pt wire; scanning rate, 20 mV s^{-1}. [b]saturated solution.



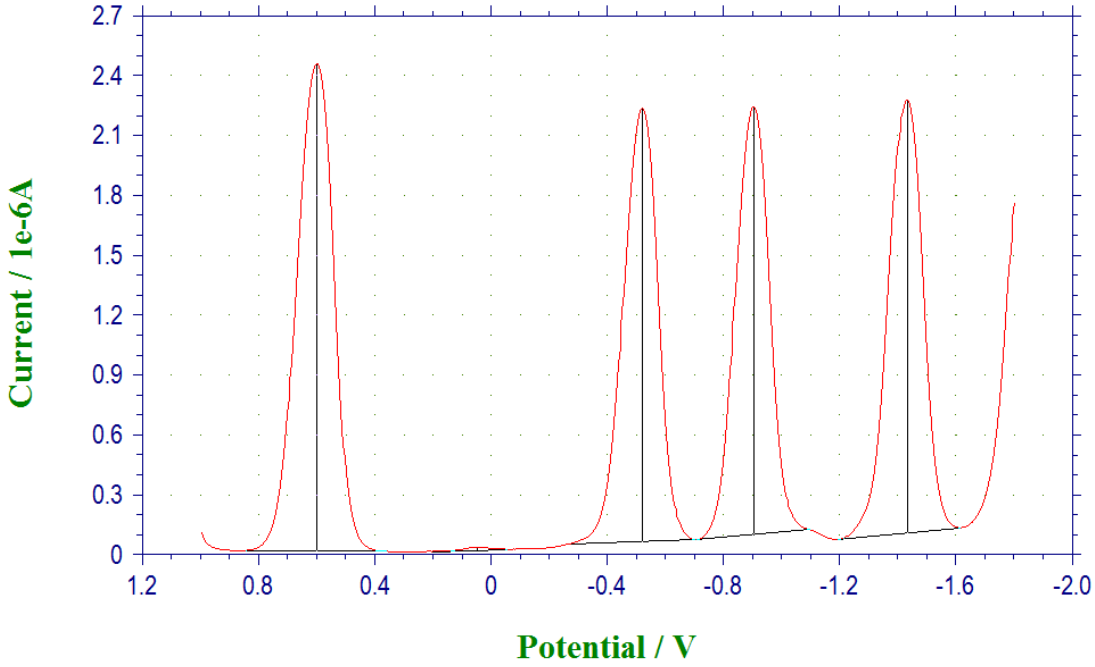
Cyclic Voltammogram of Compound **2a** (scanning rate: 20 mV s^{-1})



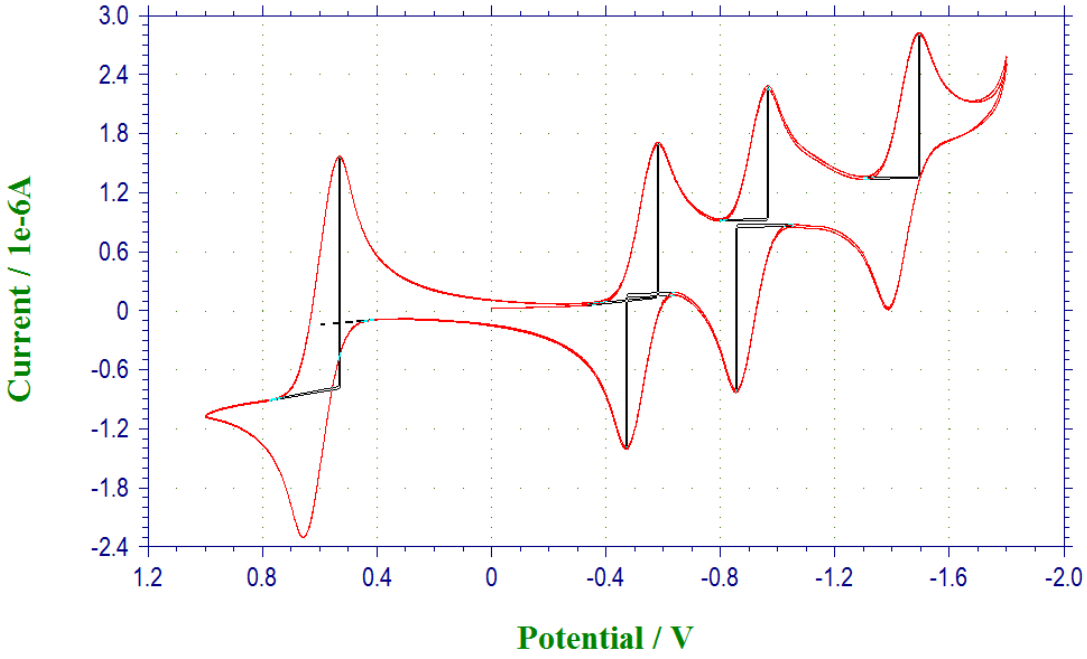
Differential Pulse Voltammogram of Compound **2a**



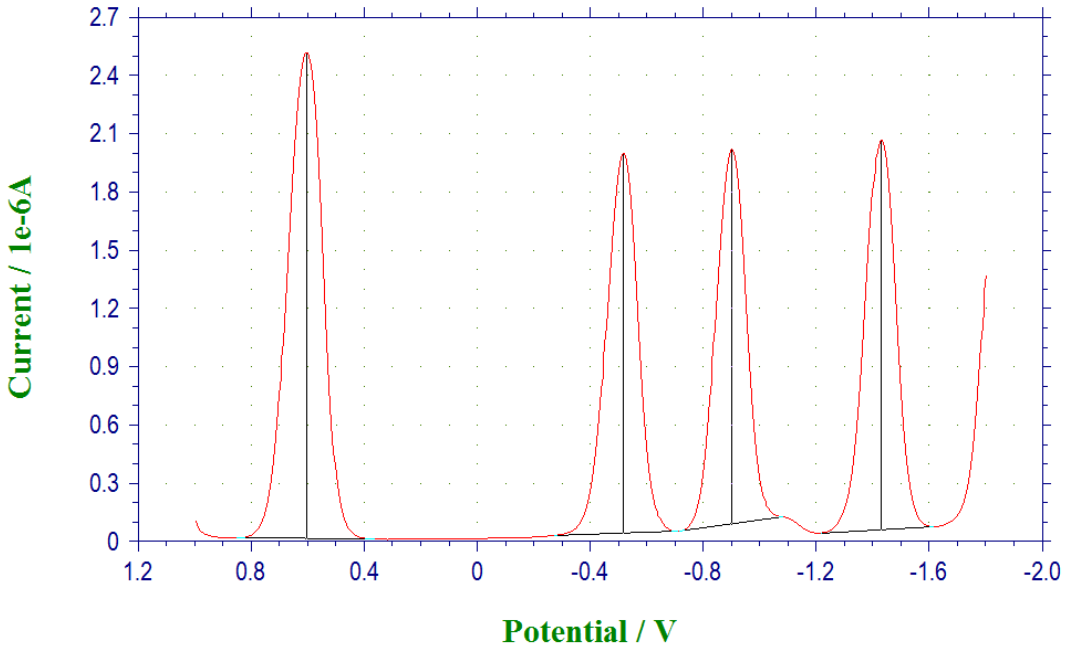
Cyclic Voltammogram of Compound **2b** (scanning rate: 20 mV s^{-1})



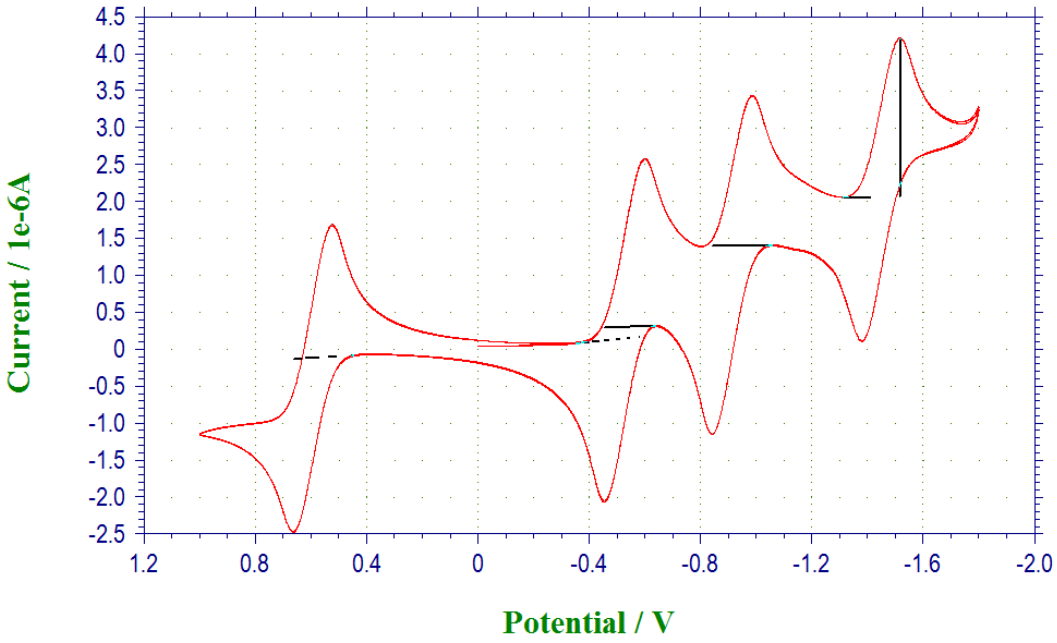
Differential Pulse Voltammogram of Compound **2b**



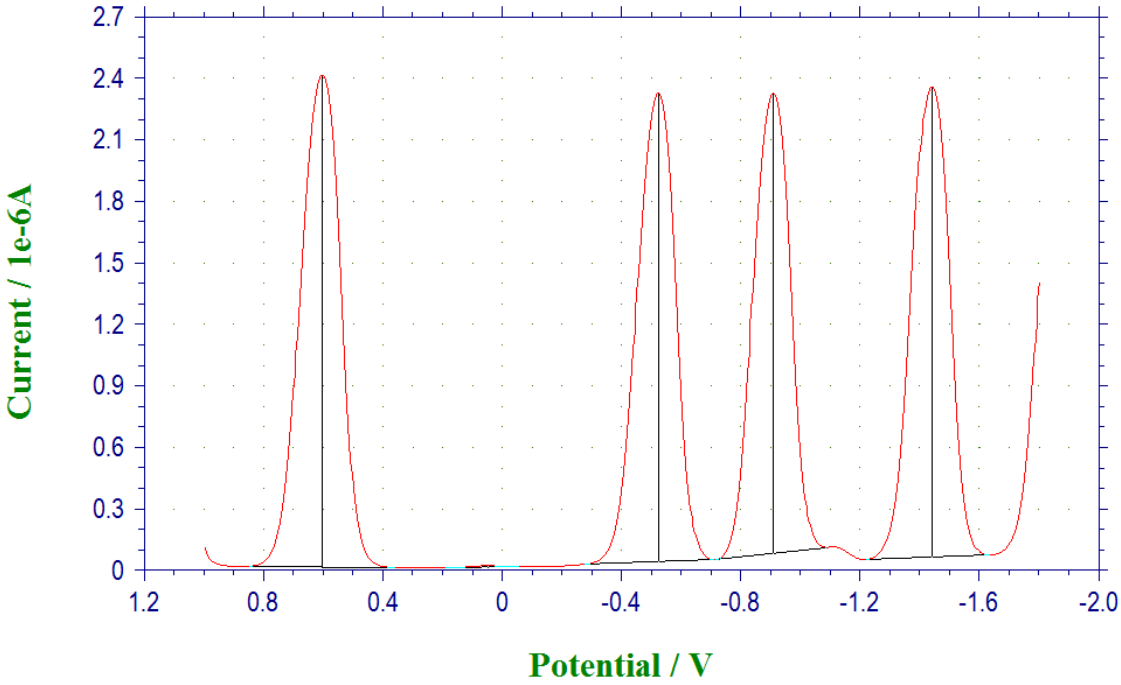
Cyclic Voltammogram of Compound **2c** (scanning rate: 20 mV s^{-1})



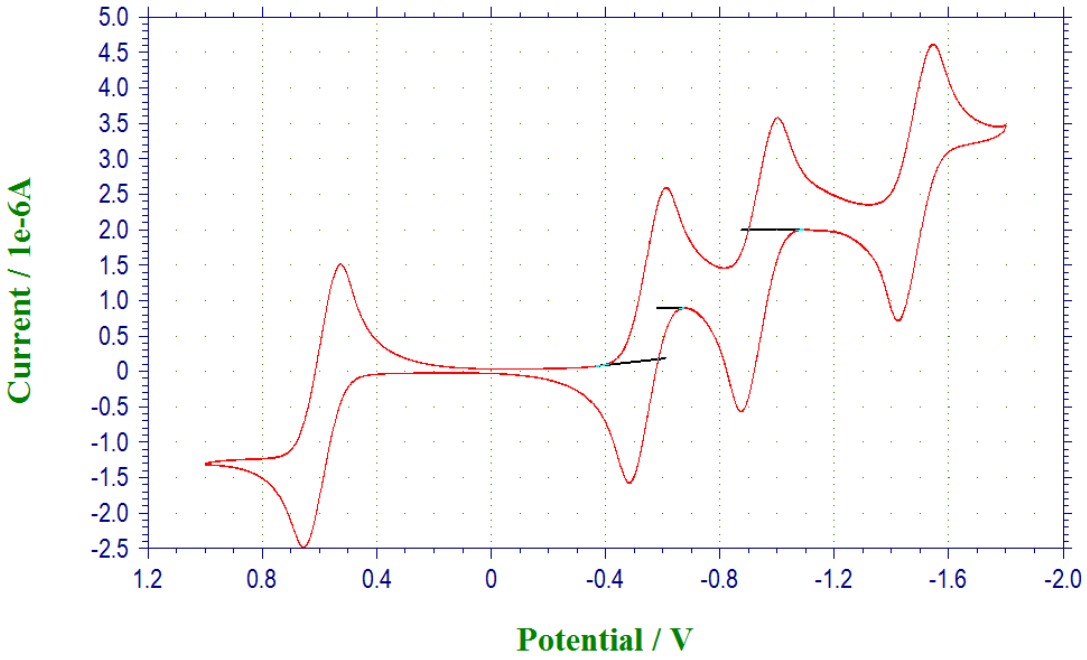
Differential Pulse Voltammogram of Compound **2c**



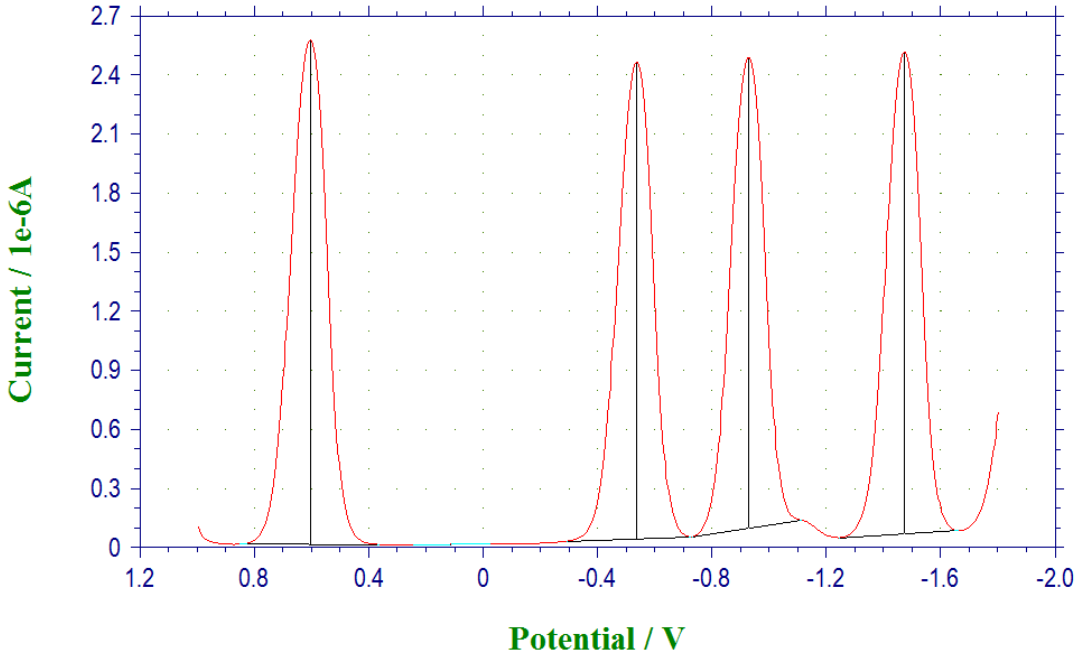
Cyclic Voltammogram of Compound **2d** (scanning rate: 20 mV s^{-1})



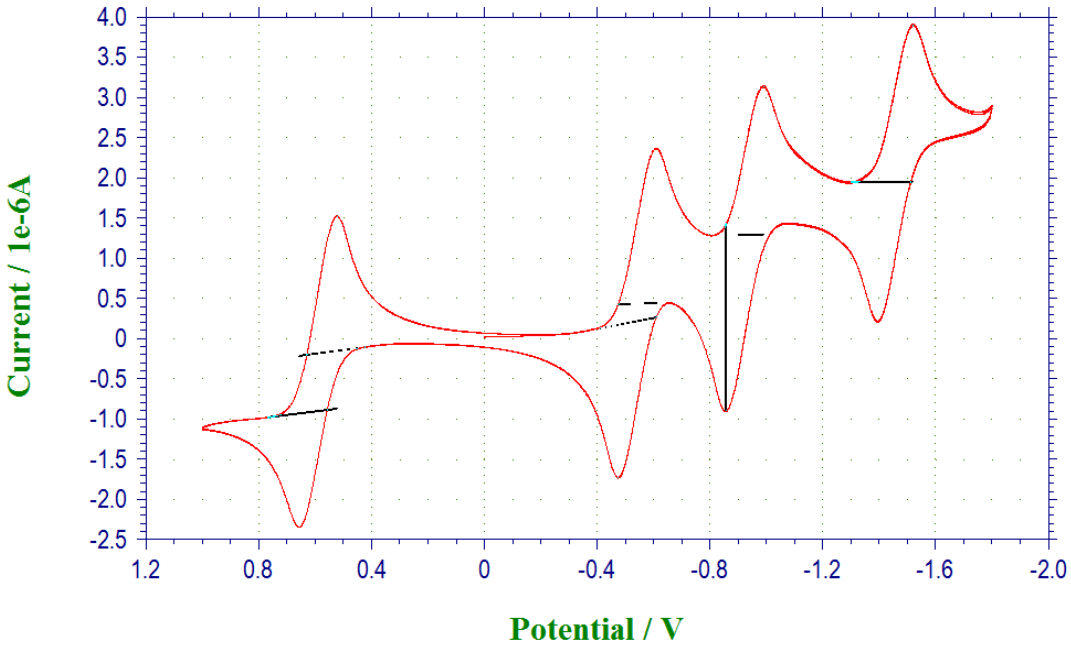
Differential Pulse Voltammogram of Compound **2d**



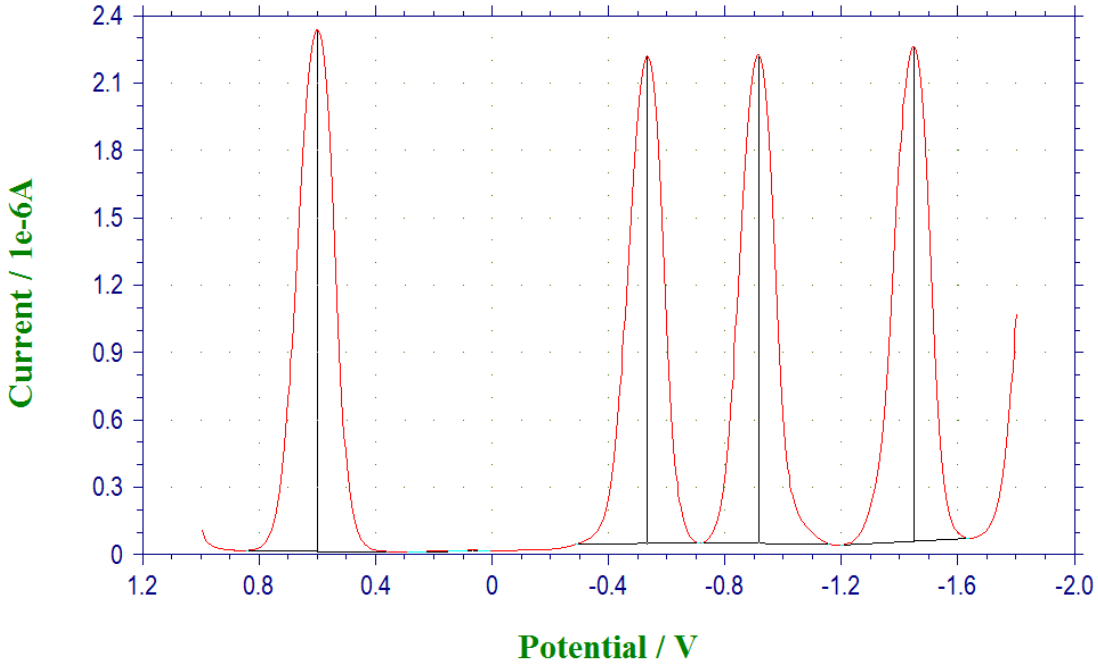
Cyclic Voltammogram of Compound **2e** (scanning rate: 20 mV s^{-1})



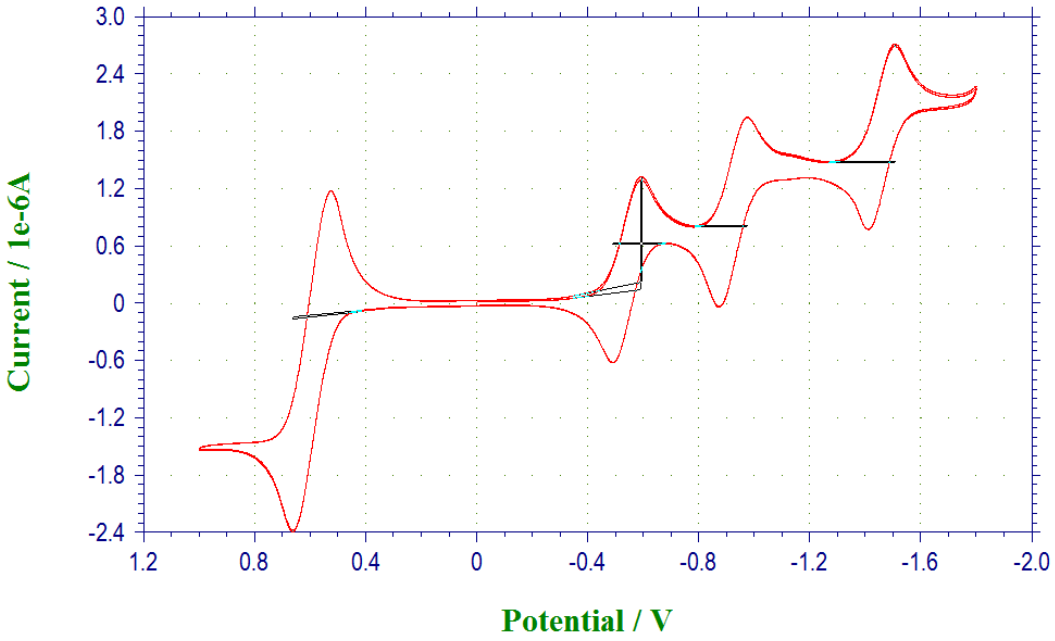
Differential Pulse Voltammogram of Compound **2e**



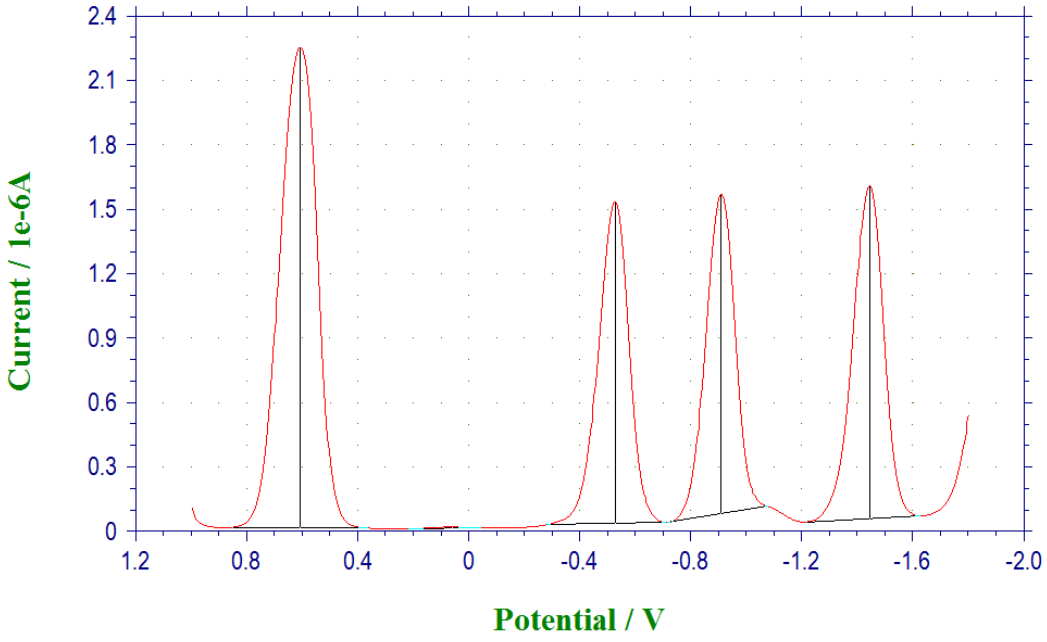
Cyclic Voltammogram of Compound **2f** (scanning rate: 20 mV s^{-1})



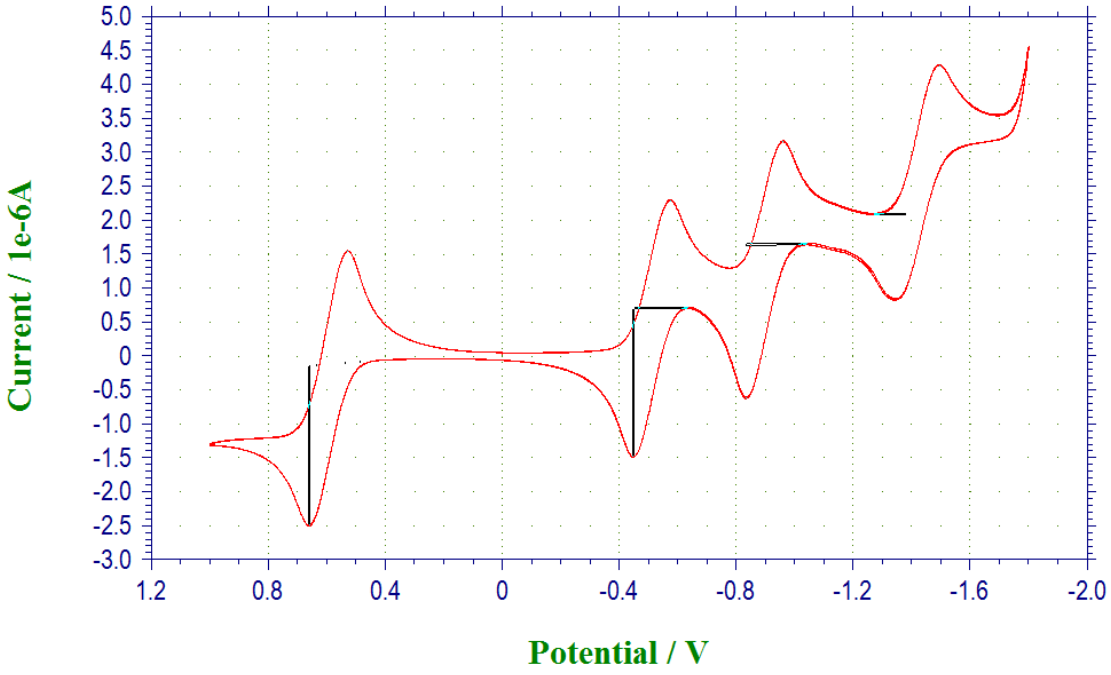
Differential Pulse Voltammogram of Compound **2f**



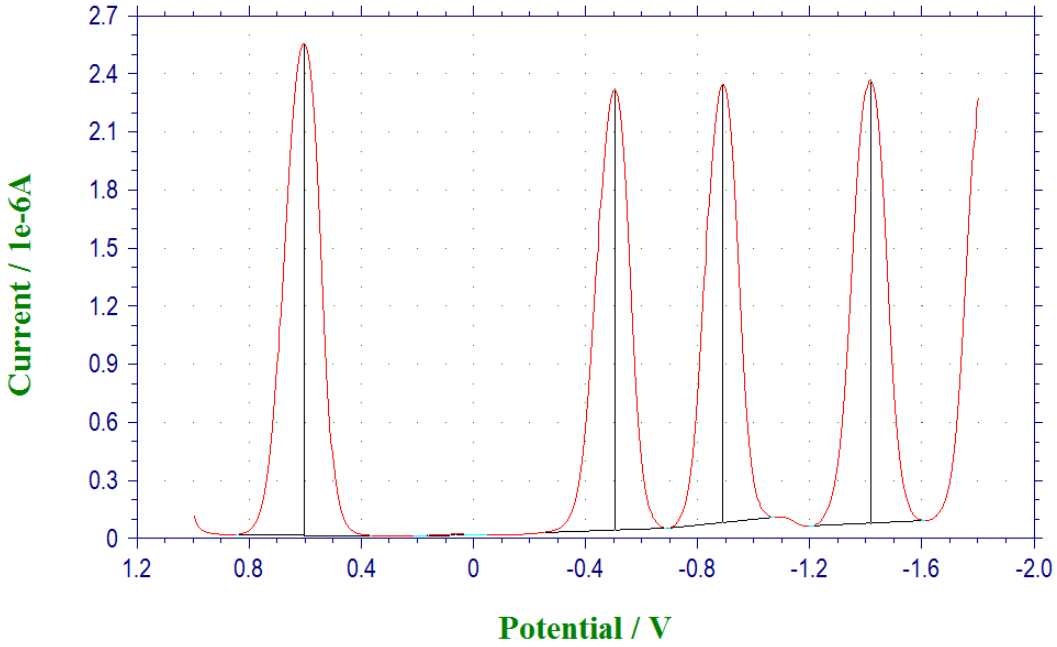
Cyclic Voltammogram of Compound **2g** (scanning rate: 20 mV s^{-1})



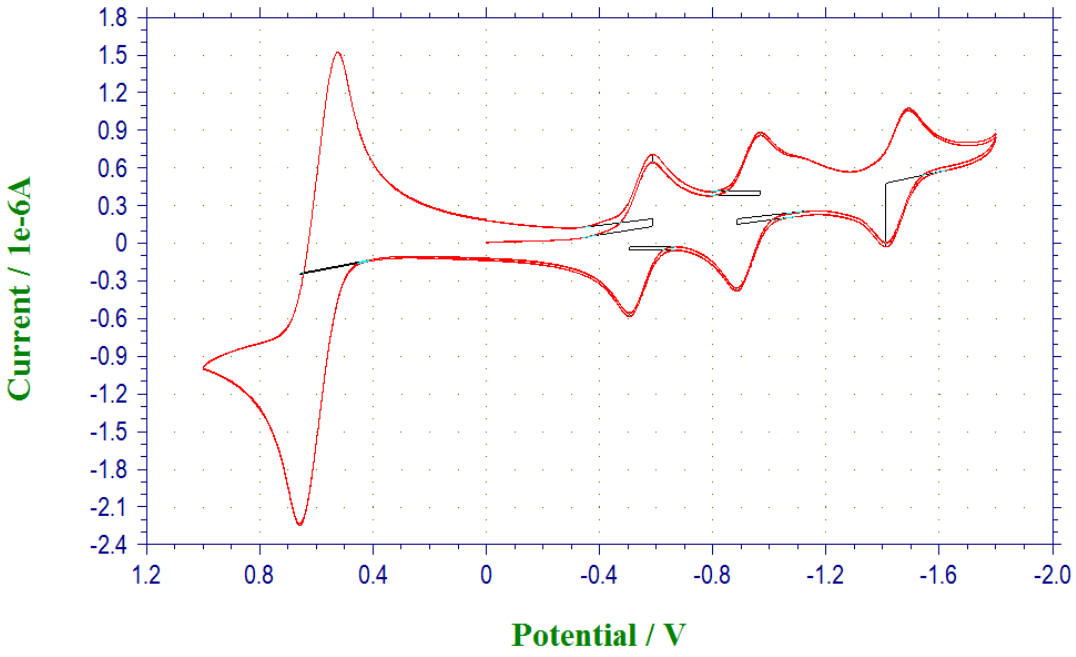
Differential Pulse Voltammogram of Compound **2g**



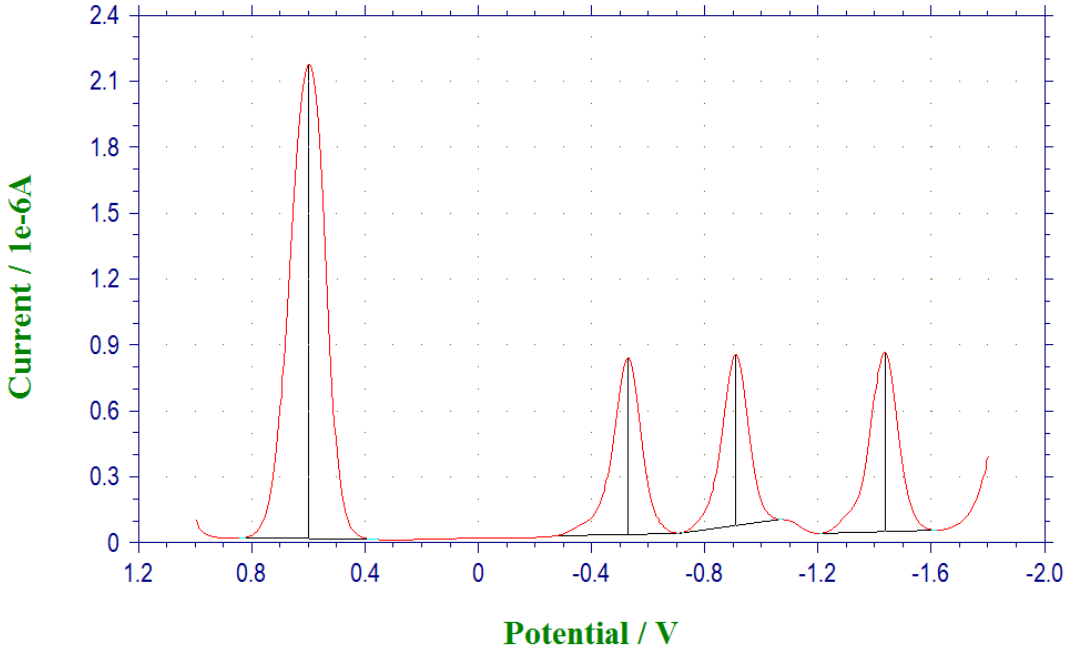
Cyclic Voltammogram of Compound **2h** (scanning rate: 20 mV s^{-1})



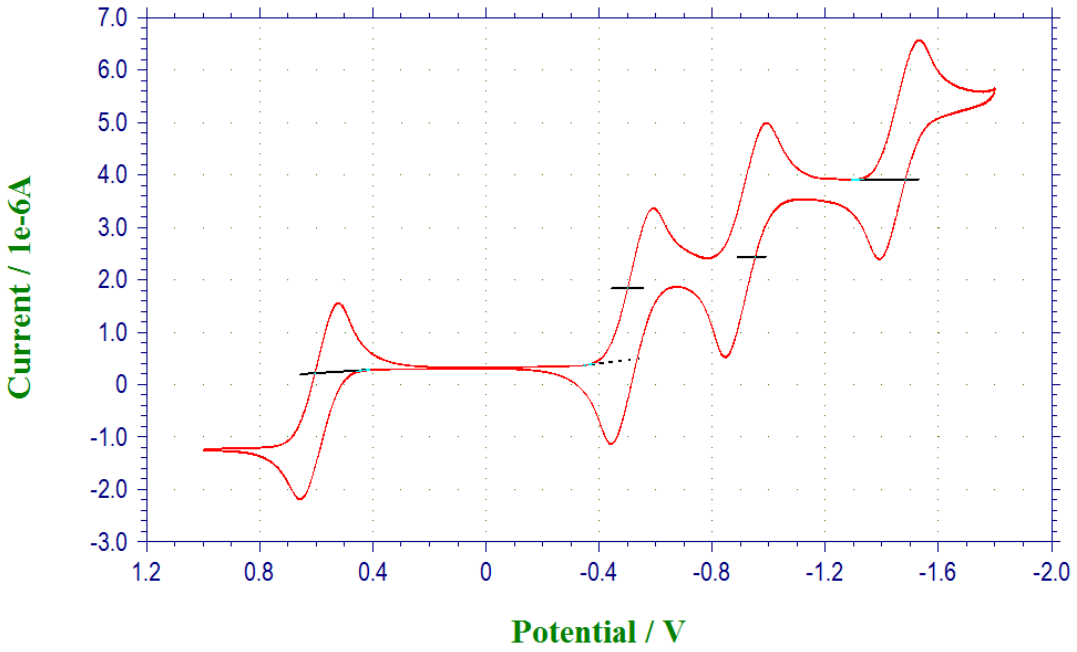
Differential Pulse Voltammogram of Compound **2h**



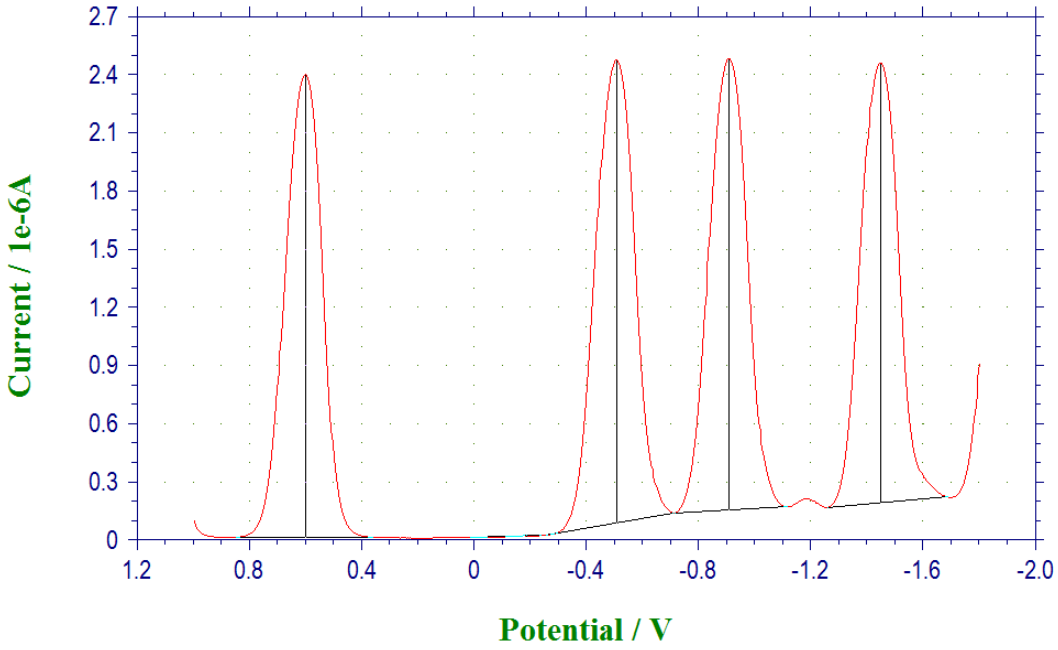
Cyclic Voltammogram of Compound **2i** (scanning rate: 20 mV s^{-1})



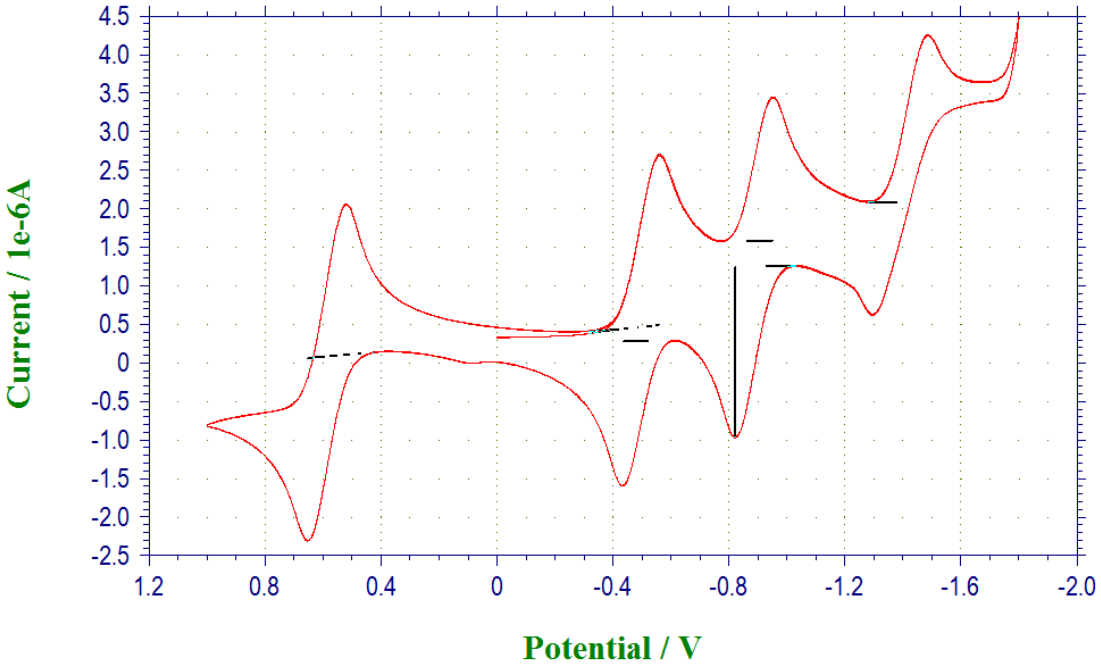
Differential Pulse Voltammogram of Compound **2i**



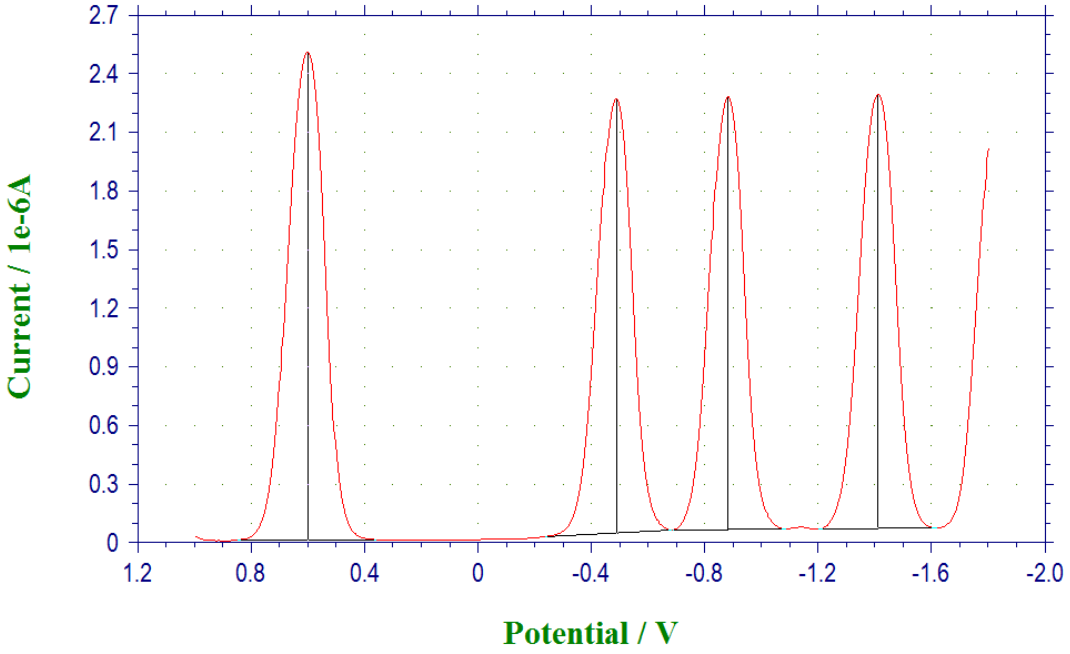
Cyclic Voltammogram of Compound **2j** (scanning rate: 20 mV s^{-1})



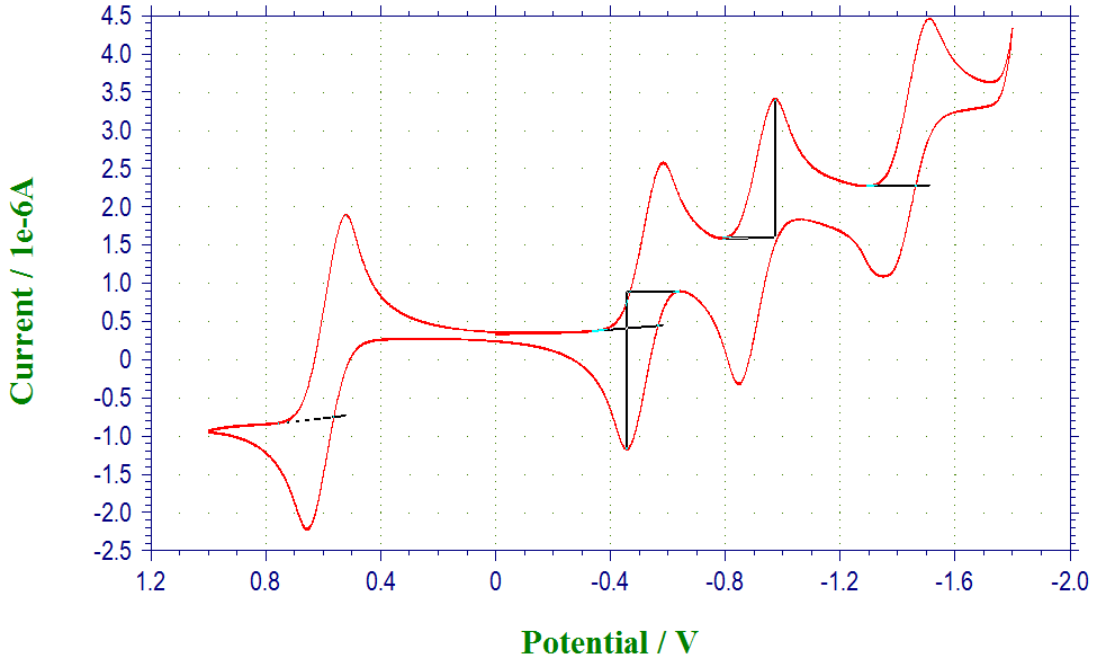
Differential Pulse Voltammogram of Compound **2j**



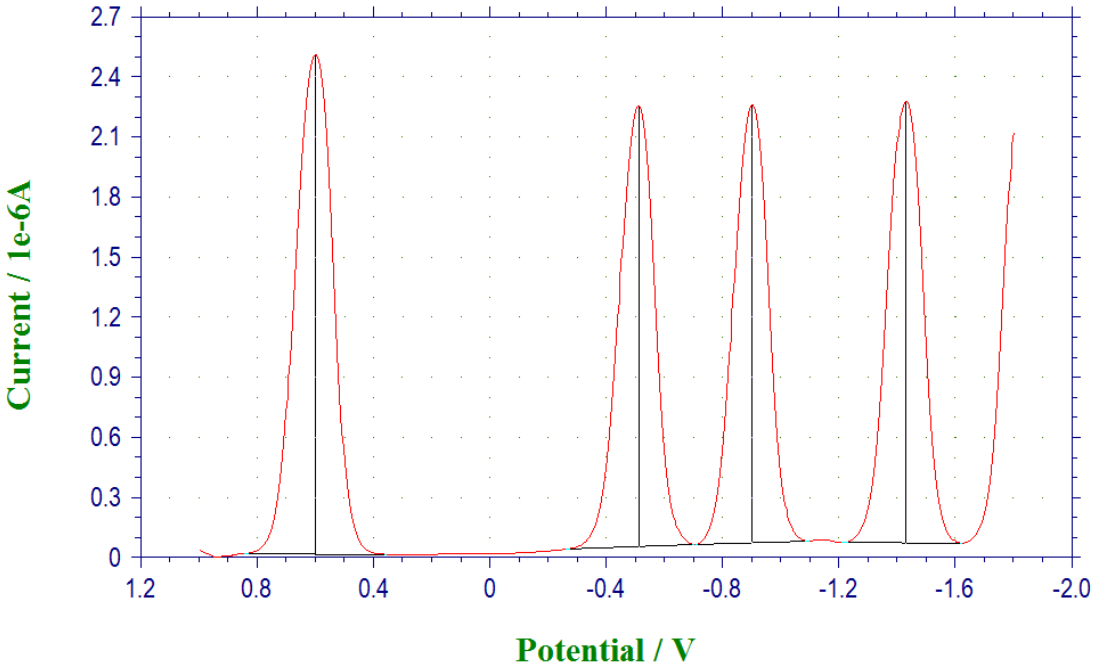
Cyclic Voltammogram of Compound **2k** (scanning rate: 20 mV s^{-1})



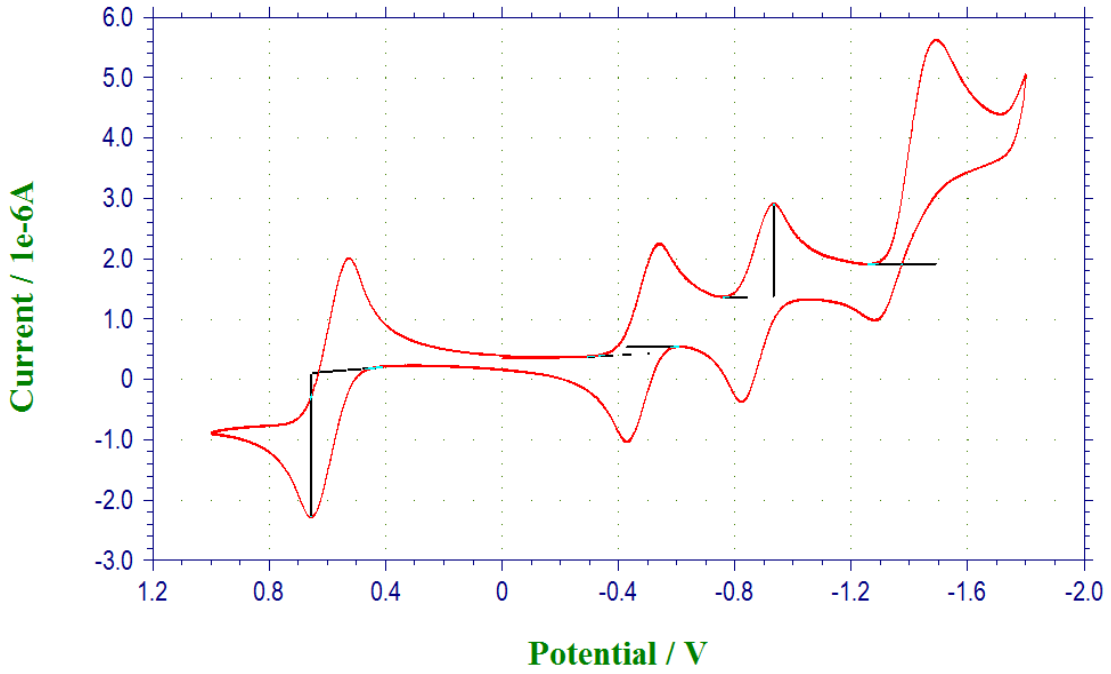
Differential Pulse Voltammogram of Compound **2k**



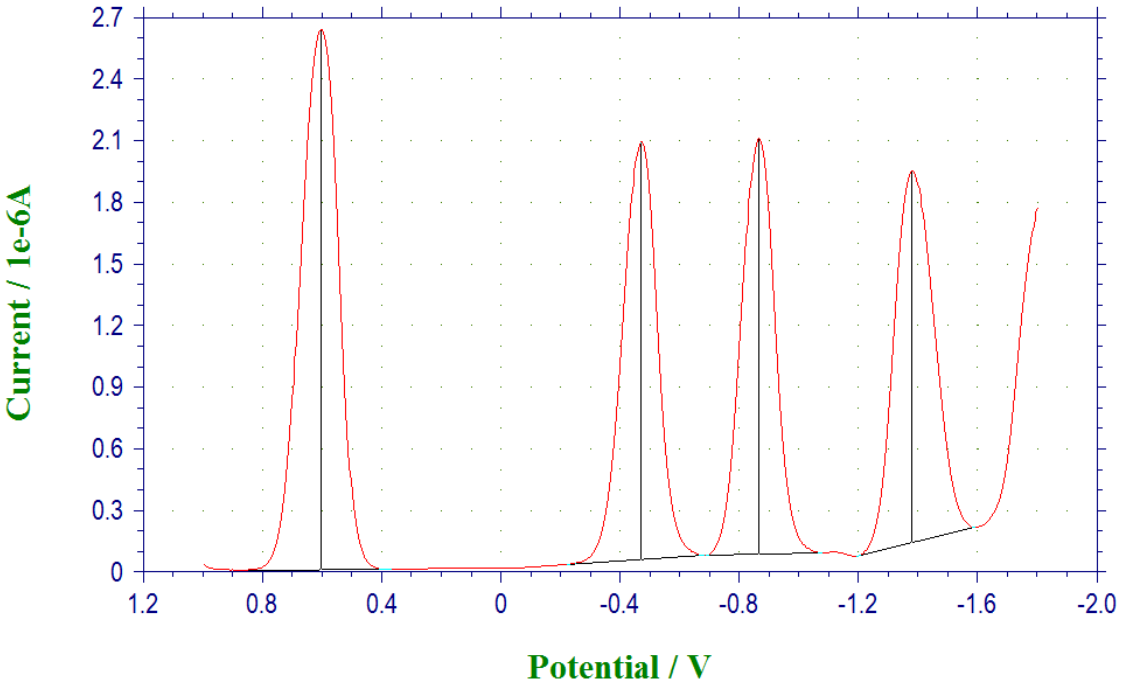
Cyclic Voltammogram of Compound **2l** (scanning rate: 20 mV s^{-1})



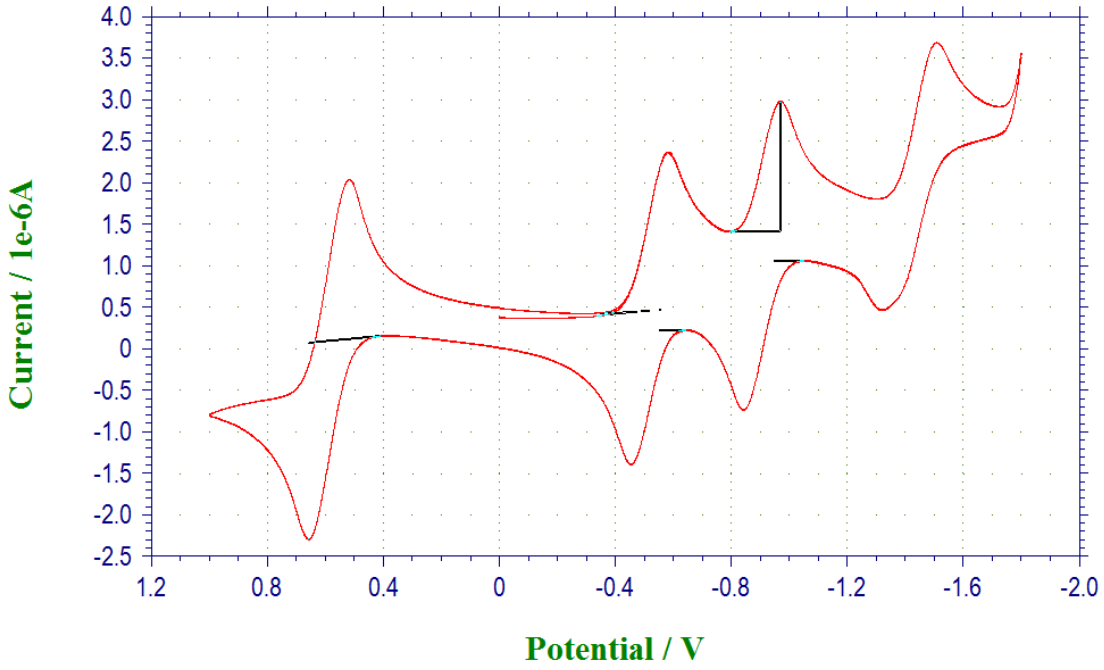
Differential Pulse Voltammogram of Compound **2l**



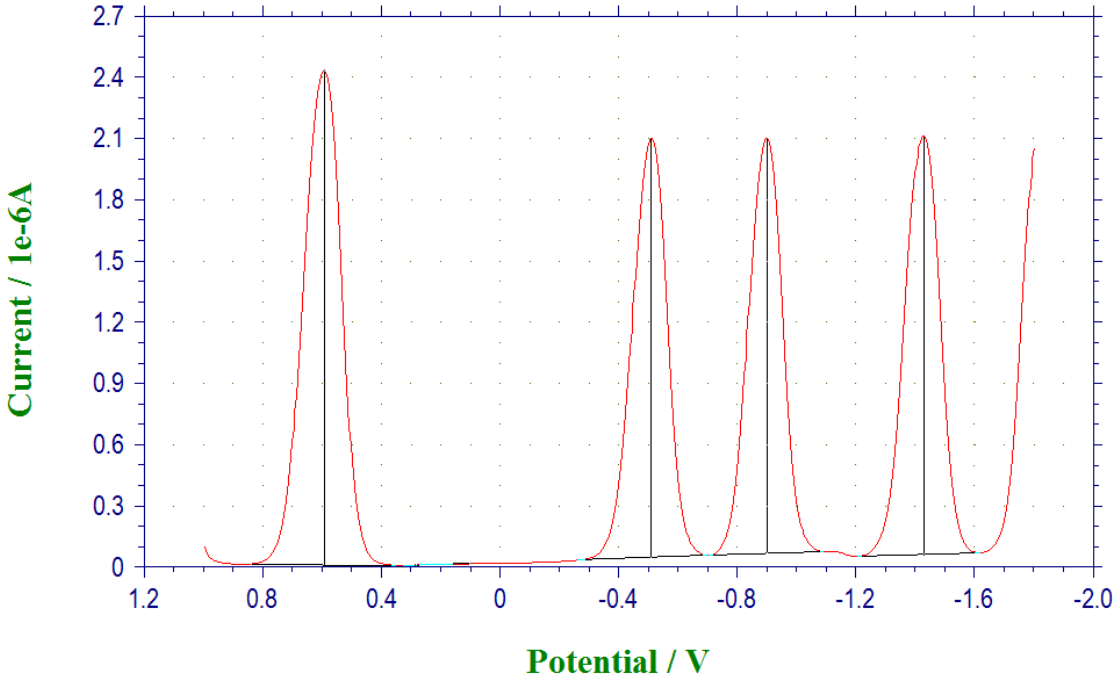
Cyclic Voltammogram of Compound **2m** (scanning rate: 20 mV s^{-1})



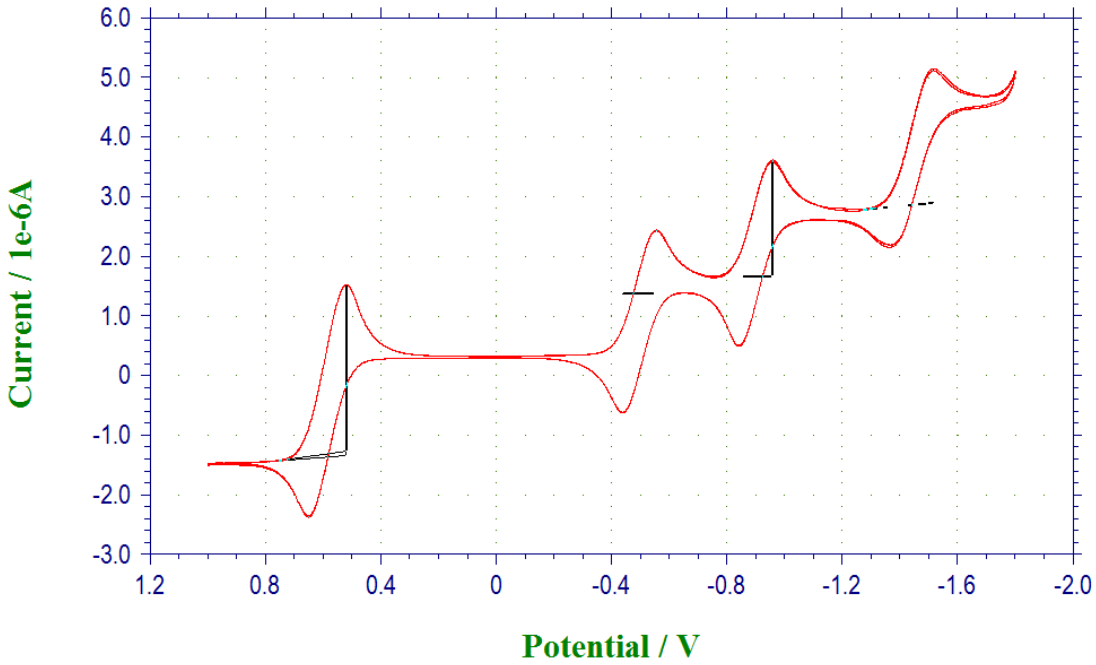
Differential Pulse Voltammogram of Compound **2m**



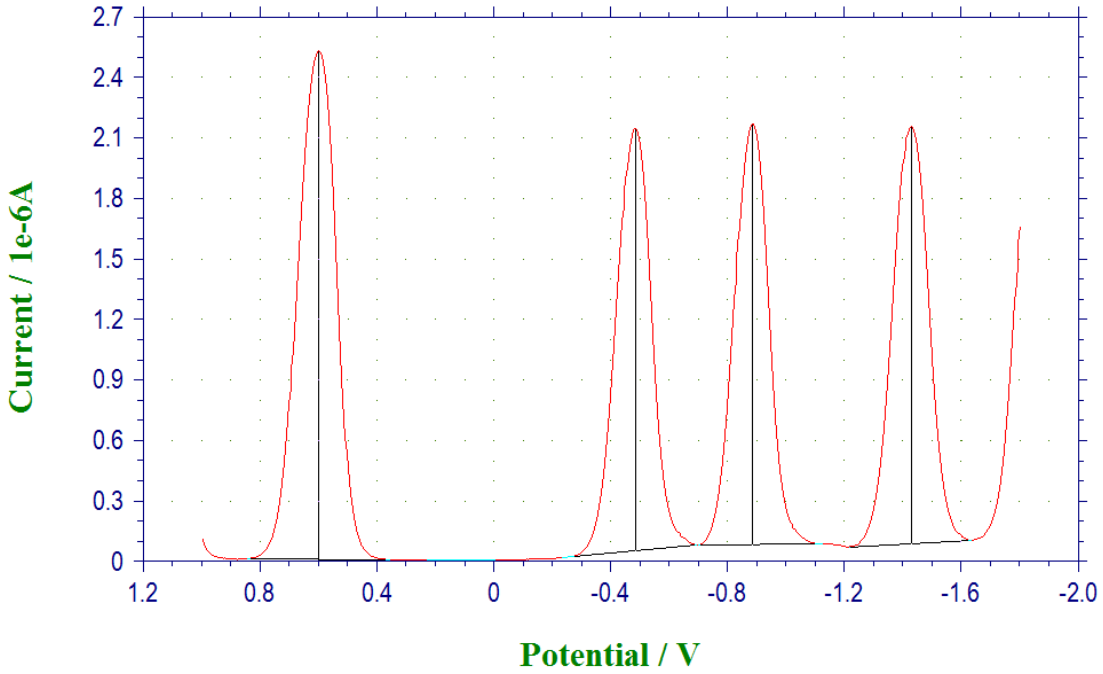
Cyclic Voltammogram of Compound **2n** (scanning rate: 20 mV s^{-1})



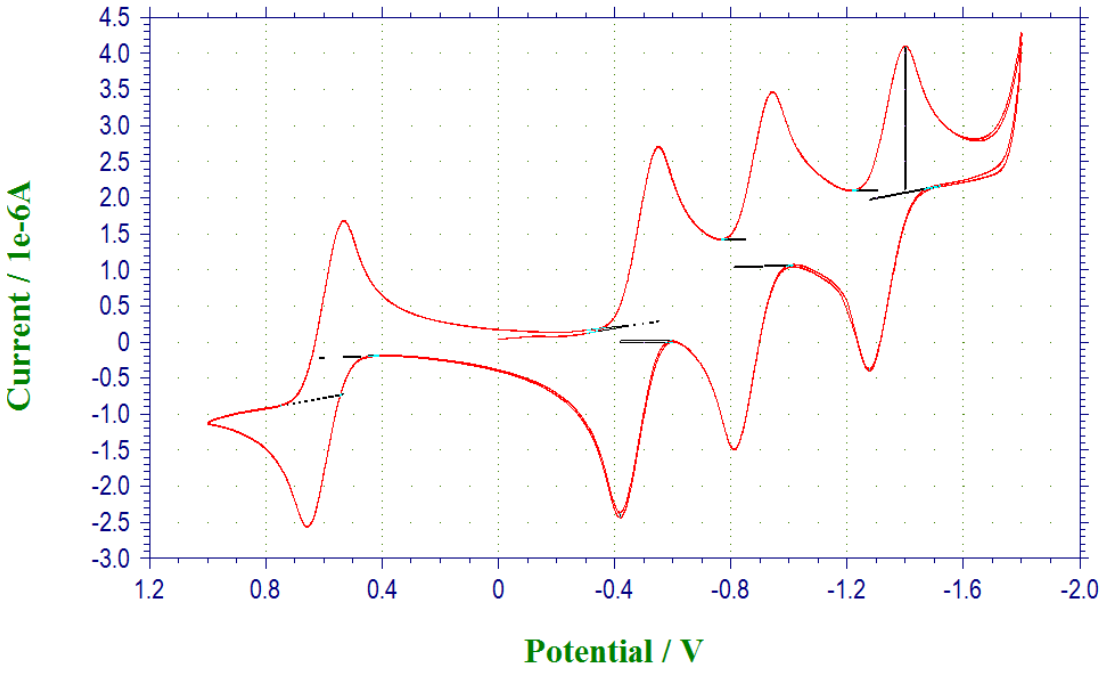
Differential Pulse Voltammogram of Compound **2n**



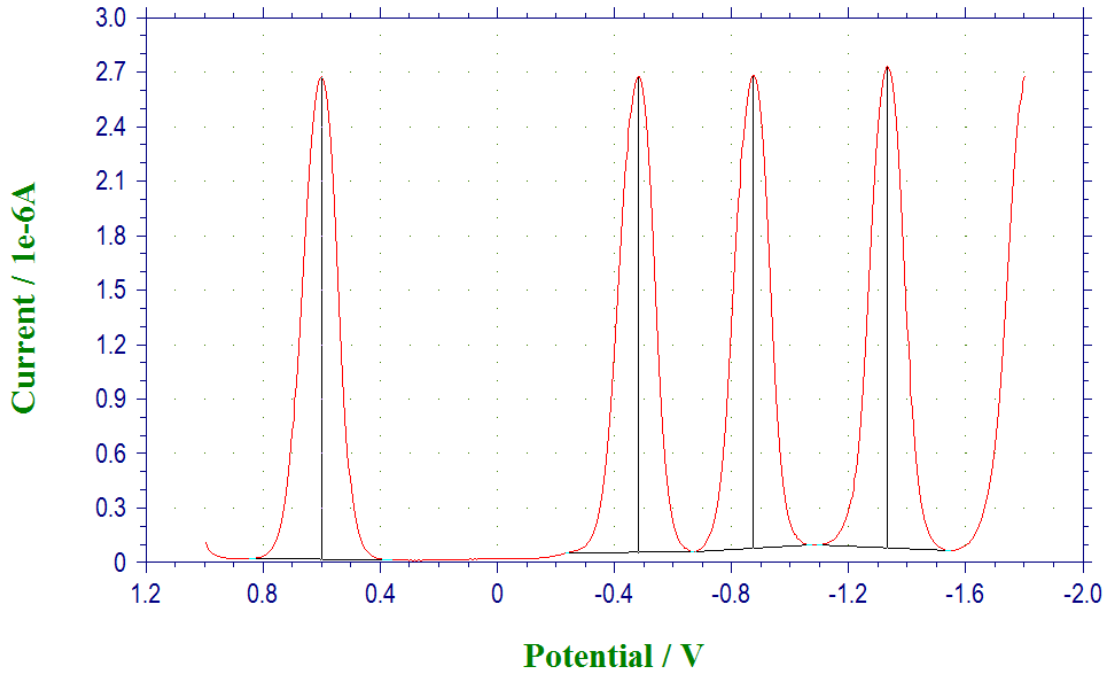
Cyclic Voltammogram of Compound **2o** (scanning rate: 20 mV s^{-1})



Differential Pulse Voltammogram of Compound **2o**



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



Differential Pulse Voltammogram of **C_{60}**