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Electronic Supplementary Information

Palladium-catalyzed synthesis of [60]fullerene-fused furochromenones and further electrochemical functionalization

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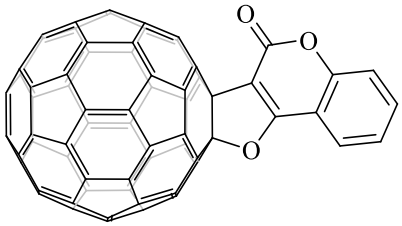
1. General procedure for the synthesis of compounds 2a–l

A mixture of C_{60} (0.05 mmol), **1** (0.15 mmol), $Pd(OAc)_2$ (0.005 mmol), Et_3N (0.15 mmol) and $K_2S_2O_8$ (0.15 mmol) was dissolved in *ortho*-dichlorobenzene (ODCB) (3 mL). Then the solution was vigorously stirred at 140 °C in a sealed tube 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 (4:1 v/v) as the eluent to give recovered C_{60} and the then desired product **2**.

2. Synthesis and spectral data of compounds 2a–l

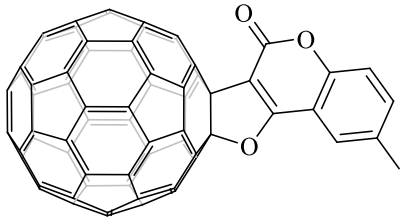
Synthesis and spectral data of compounds 2a



2a

By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1a** (24.4 mg, 0.15 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.3 mg, 0.15 mmol) at 140 °C for 3 h afforded recovered C_{60} (20.9 mg, 58%) and **2a** (16.7 mg, 38%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.18 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.77 (ddd, J_1 = 8.7 Hz, J_2 = 7.4 Hz, J_3 = 1.5 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.52 (td, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 165.16 (1C, *C*=O), 158.24 (1C, O-*C*=C-CO_2), 154.16 (1C, aryl *C*), 147.10 (1C), 146.25 (1C), 145.75, 145.45, 145.35, 145.12, 145.10, 144.98 (4C), 144.51, 144.35, 144.17, 144.04, 143.54, 143.40, 143.02, 141.73, 141.69, 141.65, 141.57, 141.41, 141.28, 141.23, 141.19, 140.71, 140.21, 139.30, 138.78, 136.96, 134.59, 133.06 (1C, aryl *C*), 123.87 (1C, aryl *C*), 123.06 (1C, aryl *C*), 116.35 (1C, aryl *C*), 111.29 (1C, aryl *C*), 105.56 (1C, sp^3-*C* of C_{60}), 102.80 (1C, O-C=*C*-CO_2), 68.22 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1725, 1645, 1507, 1466, 1392, 1095, 1024, 883, 742, 550, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 252 (5.02), 319 (4.64), 416 (3.36), 463 (3.06); MALDI-TOF MS *m*/*z* calcd for $C_{69}H_4O_3$ $[M]^-$ 880.0160, found 880.0171.

Synthesis and spectral data of compound 2b

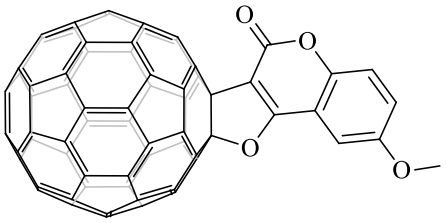


2b

By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (26.4 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.3 mg, 0.15 mmol) at 140 °C for 3 h afforded recovered C_{60} (22.6 mg, 63%) and **2b** (14.1 mg, 32%):

amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$) δ 7.96 (d, J = 1.8 Hz, 1H), 7.57 (dd, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated)δ 164.87 (1C, *C*=O), 157.97 (1C, O-*C*=C-CO_2), 152.40 (1C, aryl *C*), 147.11 (1C), 146.24 (1C), 145.88, 145.46, 145.35, 145.24, 145.10, 144.99 (4C), 144.55, 144.33, 144.18, 144.05, 143.52, 143.46, 143.02, 141.77, 141.73, 141.67, 141.64, 141.45, 141.34, 141.25, 141.21, 140.77, 140.27, 139.32, 138.80, 136.94, 134.50, 134.02 (1C, aryl *C*), 133.72 (1C, aryl *C*), 122.60 (1C, aryl *C*), 116.15 (1C, aryl *C*), 111.07 (1C, aryl *C*), 105.40 (1C, sp^3-*C* of C_{60}), 102.68 (1C, O-C=*C*-CO_2), 68.29 (1C, sp^3-*C* of C_{60}), 20.12 (CH_3); FT-IR ν/cm^{-1} (KBr) 2923, 2849, 1725, 1642, 1466, 1371, 1260, 1092, 1018, 933, 883, 844, 794, 550, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.06), 319 (4.68), 416 (3.26), 456 (2.78); MALDI-TOF MS *m*/*z* calcd for $C_{70}H_6O_3$ $[M]^-$ 894.0317, found 894.0318.

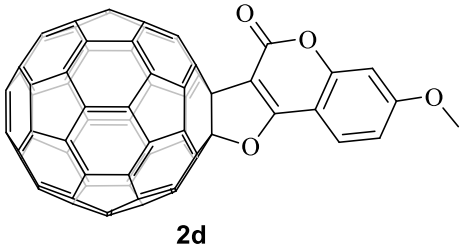
Synthesis and spectral data of compound 2c



2c

By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1c** (28.9 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.4 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (21.1 mg, 58%) and **2c** (14.9 mg, 33%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 7.54 (d, J = 3.0 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.34 (dd, J_1 = 9.2 Hz, J_2 = 3.0 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 164.93 (1C, *C*=O), 158.35 (1C, O-*C*=C-CO_2), 155.28 (1C, aryl *C*), 148.76 (1C, aryl *C*), 147.09 (1C), 146.23 (1C), 145.76, 145.44, 145.34, 145.13, 145.08, 144.97 (4C), 144.49, 144.34, 144.16, 144.03, 143.52, 143.40, 143.00, 141.72, 141.69, 141.64, 141.56, 141.39, 141.27, 141.21, 141.17, 140.69, 140.20, 139.28, 138.76, 136.97, 134.58, 121.75 (1C, aryl *C*), 117.66 (1C, aryl *C*), 111.50 (1C, aryl *C*), 105.49 (1C, sp^3-*C* of C_{60}), 104.04 (1C, aryl *C*), 102.92 (1C, O-C=*C*-CO_2), 68.29 (1C, sp^3-*C* of C_{60}), 55.29 (CH_3); FT-IR ν/cm^{-1} (KBr) 2917, 2846, 1728, 1654, 1636, 1510, 1466, 1257, 1092, 1018, 886, 800, 547, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.04), 317 (4.66), 413 (3.33), 453 (2.78); MALDI-TOF MS *m*/*z* calcd for $C_{70}H_6O_4$ $[M]^-$ 910.0266, found 910.0266.

Synthesis and spectral data of compound 2d

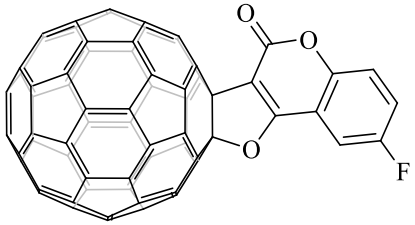


2d

By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (28.9 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.4, 0.15

mmol) at 140 ºC for 3 h afforded recovered C_{60} (21.9 mg, 61%) and **2d** (14.4 mg, 32%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.06 (d, J = 8.6 Hz, 1H), 7.10-703 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 165.39 (1C, *C*=O), 163.51 (1C, aryl *C*), 158.59 (1C, O-*C*=C-CO_2), 156.26 (1C, aryl *C*), 147.09 (1C), 146.25 (1C), 146.16, 145.44, 145.34, 145.07 (4C), 144.97 (4C), 144.47, 144.36, 144.16, 144.01, 143.56, 143.42, 143.02, 141.80, 141.72, 141.67, 141.63, 141.46, 141.27, 141.22, 141.18, 140.71, 140.21, 139.28, 138.74, 136.99, 134.51, 124.09 (1C, aryl *C*), 112.41 (1C, aryl *C*), 105.46 (1C, sp^3-*C* of C_{60}), 104.34 (1C, aryl *C*), 100.18 (1C, aryl *C*), 100.03 (1C, O-C=*C*-CO_2), 68.11 (1C, sp^3-*C* of C_{60}), 55.26 (CH_3); FT-IR ν/cm^{-1} (KBr) 2917, 2846, 1722, 1654, 1636, 1613, 1510, 1466, 1404, 1274, 1260, 1186, 1154, 1109, 1095, 1021, 892, 833, 818, 794, 550, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.41), 320 (5.03), 417 (3.41), 465 (2.58); MALDI-TOF MS *m*/*z* calcd for $C_{70}H_6O_4$ [M]$^-$ 910.0266, found 910.0268.

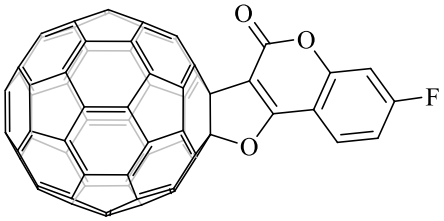
Synthesis and spectral data of compound 2e



2e

By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1e** (27.0 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.5 mg, 0.15 mmol) at 140 ºC for 3.5 h afforded recovered C_{60} (15.1 mg, 42%) and **2e** (20.1 mg, 45%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 7.79–7.71 (m, 1H), 7.58–7.42 (m, 2H); ^{13}C NMR (101 MHz, CS_2 with DMSO-d_6 as the external lock solvent and $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 163.22 (1C, *C*=O), 157.54 (d, J = 247.3 Hz) (1C, aryl *C*), 155.45 (1C, O-*C*=C-CO_2), 150.52 (1C, aryl *C*), 147.09 (1C), 146.20 (1C), 145.62, 145.57, 145.46, 145.36, 145.10, 145.00, 144.99, 144.65, 144.28, 144.18, 144.05, 143.49, 143.47, 142.98, 141.76 (4C), 141.68, 141.40 (6C), 141.26, 141.21, 140.83, 140.29, 139.29, 138.82, 136.89, 134.39, 120.03 (d, J = 23.2 Hz) (1C, aryl *C*), 118.18 (d, J = 7.4 Hz), (1C, aryl *C*), 112.27 (d, J = 9.0 Hz) (1C, aryl *C*), 108.38 (d, J = 24.8 Hz) (1C, aryl *C*), 105.30 (1C, sp^3-*C* of C_{60}), 103.67 (1C, O-C=*C*-CO_2), 68.36 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1736, 1651, 1630, 1507, 1466, 1260, 1089, 1024, 930, 886, 821, 794, 553, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.17), 317 (4.62), 417 (3.53), 459 (3.33); MALDI-TOF MS *m*/*z* calcd for $C_{69}H_3FO_3$ [M]$^-$ 898.0066, found 898.0075.

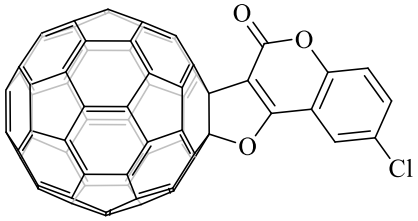
Synthesis and spectral data of compound 2f



2f

By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1f** (26.9 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.5 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (21.2 mg, 59%) and **2f** (13.9 mg, 31%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 7.78–7.73 (m, 1H), 7.57–7.43 (m, 2H); ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 164.85 (d, J = 257.0 Hz) (1C, aryl *C*), 164.35 (1C, *C*=O), 157.07 (1C, O-*C*=C-CO_2), 155.70 (d, J = 13.2 Hz) (1C, aryl *C*), 147.19 (1C), 146.29 (1C), 145.78, 145.54, 145.43, 145.35, 145.16, 145.08, 145.06, 144.69, 144.35, 144.25, 144.12, 143.54, 143.49, 143.05, 141.82 (4C), 141.74, 141.48 (4C), 141.44, 141.31, 141.26, 140.88, 140.31, 139.48, 138.86, 137.02, 134.47, 124.65 (d, J = 10.5 Hz) (1C, aryl *C*), 112.00 (d, J = 23.1 Hz) (1C, aryl *C*), 108.15 (1C, aryl *C*), 105.62 (1C, sp^3-*C* of C_{60}), 104.16 (d, J = 25.5 Hz) (1C, aryl *C*), 101.91 (1C, O-C=*C*-CO_2), 68.18 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1739, 1645, 1513, 1463, 1392, 1260, 1136, 1101, 1021, 892, 809, 550, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.12), 318 (4.77), 417 (3.69), 462 (3.51); MALDI-TOF MS *m*/*z* calcd for $C_{69}H_3FO_3$ $[M]^-$ 898.0066, found 898.0077.

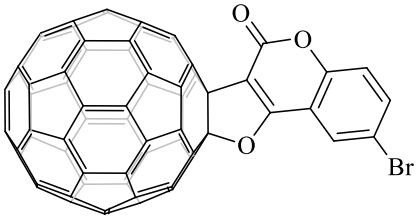
Synthesis and spectral data of compound 2g



2g

By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1g** (29.5, 0.15 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.5 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (19.0 mg, 53%) and **2g** (14.9 mg, 33%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$) δ 8.16 (d, J = 2.5 Hz, 1H), 7.72 (dd, J_1 = 8.9 Hz, J_2 = 2.5 Hz, 1H), 7.53 (d, J = 8.9 Hz, 1H); ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 163.89 (1C, *C*=O), 157.15 (1C, O-*C*=C-CO_2), 152.51 (1C, aryl *C*), 147.13 (1C), 146.27 (1C), 145.48, 145.41, 145.37, 145.15 (4C), 145.03 (4C), 144.61, 144.29, 144.21, 144.08, 143.43, 143.03 (4C), 141.78 (4C), 141.71, 141.40, 141.35, 141.28, 141.24 (4C), 140.78, 140.23, 139.36, 138.86, 136.92, 134.56, 132.86 (1C, aryl *C*), 129.44 (1C, aryl *C*), 122.40 (1C, aryl *C*), 117.86 (1C, aryl *C*), 112.50 (1C, aryl *C*), 105.72 (1C, sp^3-*C* of C_{60}), 103.68 (1C, O-C=*C*-CO_2), 68.14 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1733, 1648, 1630, 1507, 1469, 1374, 1254, 1104, 1027, 886, 818, 794, 721, 700, 547, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (4.94), 319 (4.56), 417 (3.08), 458 (2.60); MALDI-TOF MS *m*/*z* calcd for $C_{69}H_3{}^{35}ClO_3$ $[M]^-$ 913.9771, found 913.9771.

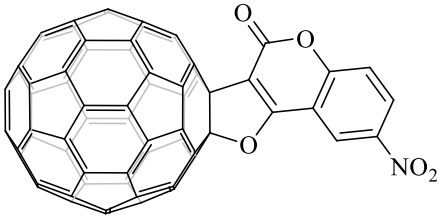
Synthesis and spectral data of compound 2h



2h

By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with **1h** (36.3 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.6 mg, 0.15 mmol) at 140 ºC for 3.5 h afforded recovered C_{60} (12.9 mg, 36%) and **2h** (24.9 mg, 52%): amorphous brown solid; ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ 8.30 (d, J = 2.3 Hz, 1H), 7.85 (dd, J_1 = 8.9 Hz, J_2 = 2.3 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H); FT-IR ν/cm^{-1} (KBr) 1728, 1642, 1507, 1469, 1419, 1374, 1265, 1104, 1015, 900, 880, 794, 727, 703, 550, 521; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.01), 318 (4.61), 417 (3.27), 462 (2.96); MALDI-TOF MS m/z calcd for $C_{69}H_3{}^{79}BrO_3$ $[M]^-$ 957.9266, found 957.9269.

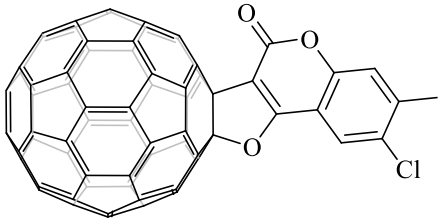
Synthesis and spectral data of compound 2i



2i

By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1i** (31.1 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.4 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (12.1 mg, 34%) and **2i** (21.8 mg, 47%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 9.01 (s, 1H), 8.61 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H); FT-IR ν/cm^{-1} (KBr) 1745, 1648, 1630, 1530, 1492, 1466, 1383, 1330, 1260, 1112, 1024, 885, 847, 797, 723, 559, 523; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 252 (5.12), 316 (4.73), 412 (3.53), 458 (3.24); MALDI-TOF MS m/z calcd for $C_{69}H_3NO_5$ $[M]^-$ 925.0011, found 925.0015.

Synthesis and spectral data of compound 2j

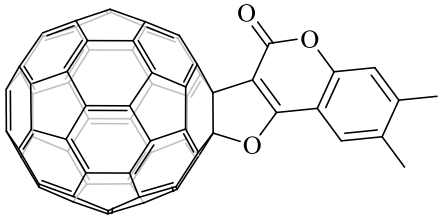


2j

By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (31.5 mg, 0.15 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.4 mg, 0.15 mmol) at 140 ºC for 2.5 h afforded recovered C_{60} (20.0 mg, 56%) and **2j** (16.4 mg, 35%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$) δ 8.11 (s, 1H), 7.46 (s, 1H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ with $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 164.01 (1C, *C*=O), 157.41 (1C, O-*C*=C-CO_2), 152.51 (1C, aryl *C*), 147.13 (1C), 146.27 (1C), 145.61, 145.48, 145.40, 145.18, 145.13, 145.02 (4C), 144.59, 144.31, 144.21, 144.07, 143.47, 143.45, 143.03, 142.19 (1C, aryl *C*), 141.78, 141.76, 141.70, 141.43, 141.40, 141.34, 141.28, 141.23, 140.78, 140.25, 139.34, 138.84, 136.94, 134.53, 129.94 (1C, aryl *C*), 122.55 (1C, aryl *C*), 118.34 (1C, aryl *C*), 110.31 (1C, aryl *C*), 105.66 (1C, sp^3-*C* of C_{60}), 102.82 (1C, O-C=*C*-CO_2), 68.16 (1C, sp^3-*C* of C_{60}), 20.20 (CH_3); FT-IR ν/cm^{-1} (KBr) 2917, 2852, 1731, 1648, 1466, 1421, 1374, 1260, 1174, 1106, 1030, 886, 845, 821, 736, 550, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log

ε) 257 (5.01), 319 (4.63), 417 (3.47), 455 (3.27); MALDI-TOF MS *m*/*z* calcd for $C_{70}H_5{}^{35}ClO_3$ $[M]^-$ 927.9927, found 927.9929.

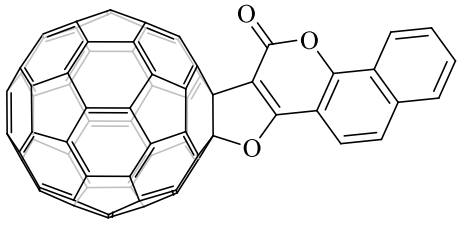
Synthesis and spectral data of compound 2k



2k

By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1k** (28.5 mg, 0.15 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.5 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (13.5 mg, 38%) and **2k** (16.3 mg, 36%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 7.82 (s, 1H), 7.30 (s, 1H), 2.54 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, CS_2 with DMSO-d_6 as the external lock solvent and $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 163.91 (1C, *C*=O), 156.11 (1C, O-*C*=C-CO_2), 153.01 (1C, aryl *C*), 147.08 (1C), 146.31, 146.16 (1C), 145.70, 145.44, 145.30, 145.05, 144.98, 144.94, 144.58, 144.35, 144.15, 144.01, 143.58, 143.54, 142.98, 142.59 (1C, aryl *C*), 141.95, 141.74, 141.72, 141.64, 141.50, 141.41, 141.23, 141.18, 140.83, 140.35, 139.23, 138.75, 136.93, 134.27, 131.99 (1C, aryl *C*), 122.76 (1C, aryl *C*), 117.10 (1C, aryl *C*), 109.11 (1C, aryl *C*), 104.94 (1C, sp^3-*C* of C_{60}), 101.84 (1C, O-C=*C*-CO_2), 68.49 (1C, sp^3-*C* of C_{60}), 19.90 (CH_3), 18.69 (CH_3); FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1721, 1648, 1554, 1504, 1469, 1413, 1380, 1260, 1112, 1101, 1024, 895, 839, 792, 721, 550, 523; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.02), 319 (4.68), 416 (3.16), 458 (2.48); MALDI-TOF MS *m*/*z* calcd for $C_{71}H_8O_3$ $[M]^-$ 908.0473, found 908.0482.

Synthesis and spectral data of compound 2l



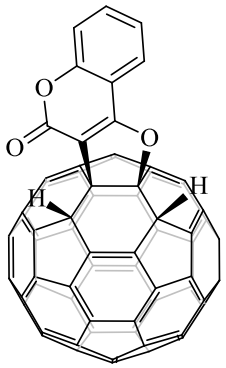
2l

By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1l** (31.8 mg, 0.15 mmol), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol), Et_3N (21 μL, 0.15 mmol) and $K_2S_2O_8$ (40.6 mg, 0.15 mmol) at 140 ºC for 3 h afforded recovered C_{60} (18.5 mg, 51%) and **2l** (21.3 mg, 46%): amorphous brown solid; ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 8.68–8.63 (m, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 8.00–7.95 (m, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.77–7.72 (m, 2H); ^{13}C NMR (101 MHz, CS_2 with DMSO-d_6 as the external lock solvent and $Cr(acac)_3$ as the relaxation reagent) (all 2C unless indicated) δ 164.94 (1C, *C*=O), 155.79 (1C, O-*C*=C-CO_2), 152.39 (1C, aryl *C*), 147.08 (1C), 146.18 (1C), 146.16, 145.61, 145.45, 145.33, 145.07, 144.99, 144.96, 144.62, 144.33, 144.16, 144.02, 143.58, 143.53, 142.99, 141.80, 141.76, 141.73, 141.65, 141.49, 141.40, 141.24, 141.20, 140.85, 140.35, 139.29, 138.77, 136.95, 134.76 (1C, aryl *C*), 134.38, 128.54 (1C, aryl *C*), 127.23 (1C, aryl *C*), 126.72 (1C, aryl *C*), 123.67 (1C, aryl *C*), 122.46

(1C, aryl *C*), 122.27 (1C, aryl *C*), 117.86 (1C, aryl *C*), 106.56 (1C, aryl *C*), 105.19 (1C, sp^3-*C* of C_{60}), 102.10 (1C, O-C=*C*-CO_2), 68.37 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1728, 1645, 1616, 1466, 1374, 1260, 1104, 1086, 1018, 939, 844, 809, 794, 750, 550, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (4.96), 319 (4.56), 414 (3.50), 462 (3.28); MALDI-TOF MS *m*/*z* calcd for $C_{73}H_6O_3$ $[M]^-$ 930.0317, found 930.0319.

3. Synthesis and spectral data of compounds 3a–b

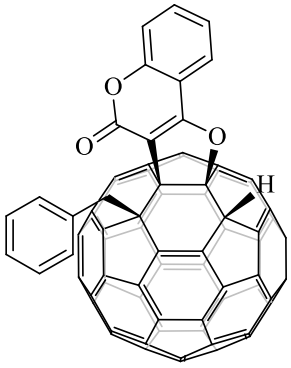
Synthesis and spectral data of compound 3a



3a

20.0 mg (0.023 mmol) of **2a** was electroreduced by controlled potential electrolysis (CPE) at –1.0 V vs saturated calomel electrode (SCE) in 30 mL of ODCB containing 0.1 M *n*-butylammonium perchlorate (TBAP) under an argon atmosphere at 25 ºC. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of **2a** to $\mathbf{2a}^{2-}$ was reached. Then, the dianionic $\mathbf{2a}^{2-}$ was reacted with trifluoroacetic acid (5 μL, 0.063 mmol) at room temperature for 15 min, and reaction mixture was filtered through a silica gel (200–300 mesh) plug with CS_2/CH_2Cl_2 (1:1, v/v) to remove the electrolyte. After evaporation in *vacuo*, the residue was separated by silica gel (400–500 mesh) column with CS_2/CH_2Cl_2 (4:1, v/v) to afford **3a** (18.9 mg, 94%). ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 8.04 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H), 7.74 (ddd, J_1 = 8.8 Hz, J_2 = 7.4 Hz, J_3 = 1.6 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.47 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 6.54 (d, J = 1.8 Hz, 1H), 6.40 (d, J = 1.8 Hz, 1H); ^{13}C NMR (101 MHz, CS_2 with DMSO-d_6 as the external lock solvent) (all 1C unless indicated) δ 162.55 (*C*=O), 156.26 (O-*C*=C-CO_2), 154.45 (aryl *C*), 149.48, 147.81, 147.41, 147.25, 147.00, 146.44, 146.37, 146.11, 146.08, 145.93, 145.80, 145.33, 145.28, 144.83, 144.69, 144.20, 144.15, 143.90, 143.83, 143.70, 143.67, 143.48, 143.40, 143.36, 143.34, 143.23, 143.13 (2C), 143.12, 143.05, 142.99, 142.84, 142.72, 142.70 (2C), 142.69, 142.51, 142.23. 142.10, 141.72, 141.46, 141.36, 141.30, 141.26, 141.16, 140.73, 140.49, 140.18, 140.14 (2C), 138.91, 138.15, 137.98, 136.08, 135.64, 134.75, 132.14 (aryl *C*), 123.24 (aryl *C*), 122.54 (aryl *C*), 116.40 (aryl *C*), 111.60 (aryl *C*), 107.87 (O-C=*C*-CO_2), 100.60 (sp^3-*C* of C_{60}), 62.83 (sp^3-*C* of C_{60}), 55.30 (sp^3-*C* of C_{60}), 53.11 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2955, 2920, 2849, 1731, 1645, 1463, 1374, 1262, 1089, 1030, 895, 803, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.02), 350 (4.39), 435 (3.70); MALDI-TOF MS *m*/*z* calcd for $C_{69}H_6O_3$ $[M]^-$ 882.0317, found 882.0321.

Synthesis and spectral data of compound 3b



3b

20.0 mg (0.023 mmol) of **2a** was electroreduced by CPE at –1.0V vs SCE in 30 mL of ODCB containing 0.1M TBAP under an argon atmosphere at room temperature. The electrolysis was terminated when the theoretical number of coulombs required for a full conversion of **2a** to **2a**$^{2-}$ was reached. Then, the dianionic **2a**$^{2-}$ was reacted with benzyl bromide (54 μL, 0.46 mmol) at 30 ^{o}C for 20 h and reaction mixture was filtered through a silica gel (200–300 mesh) plug with CS_2/CH_2Cl_2 (1:1, v/v) to remove the electrolyte. After evaporation in *vacuo*, the residue was separated by silica gel (400–500 mesh) column with CS_2/CH_2Cl_2 (4:1, v/v) to afford **3b** (17.3 mg, 78%). ^{1}H NMR (400 MHz, CS_2 with DMSO-d_6 as the external lock solvent) δ 7.76–7.69 (m, 2H), 7.58 (d, J = 7.3 Hz, 2H), 7.48–7.39 (m, 2H), 6.96 (t, J = 7.6 Hz, 2H), 6.48 (t, J = 7.4 Hz, 1H), 5.69 (s, 1H), 4.43 (d, J = 13.2 Hz, 1H), 4.23 (d, J = 13.2 Hz, 1H); ^{13}C NMR (101 MHz, $CS_2/CDCl_2CDCl_2$) δ 163.42 (*C*=O), 157.32 (O-*C*=C-CO_2), 153.94 (aryl *C*), 151.38, 151.08, 148.17, 147.99, 147.27, 146.36, 146.13, 146.03, 145.94, 145.86, 145.68, 145.54, 145.33, 145.20, 145.15, 145.05, 144.90, 144.88, 144.52, 144.03, 143.92, 143.87, 143.75, 143.67, 143.63, 143.58, 143.53, 143.31, 143.26, 143.17 (2C), 143.08, 142.92, 142.80, 142.76, 142.72, 142.45, 142.40, 142.39, 141.99, 141.85, 141.61, 141.54, 141.48, 141.06, 140.71, 140.66, 140.51, 140.46, 139.71, 137.42, 137.31, 136.76, 134.61, 134.32, 133.73, 133.17 (aryl *C*), 132.23 (aryl *C*), 129.92 (2C, aryl *C*), 127.38 (2C, aryl *C*), 126.02 (aryl *C*), 123.15 (aryl *C*), 122.41 (aryl *C*), 115.99 (aryl *C*), 111.93 (aryl *C*), 101.71 (O-C=*C*-CO_2), 101.48 (sp^3-*C* of C_{60}), 64.65 (sp^3-*C* of C_{60}), 61.42 (sp^3-*C* of C_{60}), 58.68 (sp^3-*C* of C_{60}), 51.36 (CH_2); FT-IR ν/cm^{-1} (KBr) 2961, 2920, 2846, 1733, 1651, 1604, 1495, 1454, 1407, 1318, 1274, 1101, 1036, 895, 812, 759, 700, 555, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.02), 332 (4.50), 428 (3.63); MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{12}O_3$ [M]$^-$ 972.0786, found 972.0788.

Note: Complete removal of petroleum ether/grease from the samples was difficult for the ^{1}H NMR and ^{13}C NMR spectra due to the poor solubility of these compounds. The ^{13}C NMR spectra of **2h** and **2i** were unavailable due to their extremely low solubility.

4. NMR spectra of compounds 2a–l and 3a–b

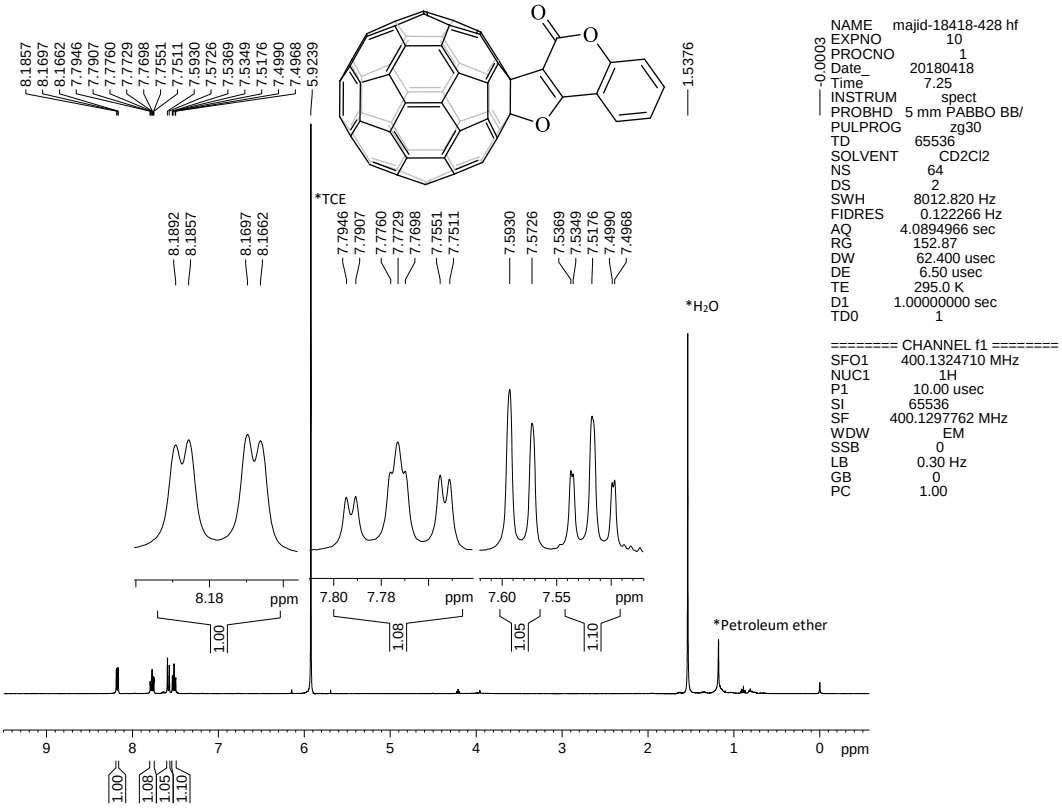


Figure S1 ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) of compound 2a

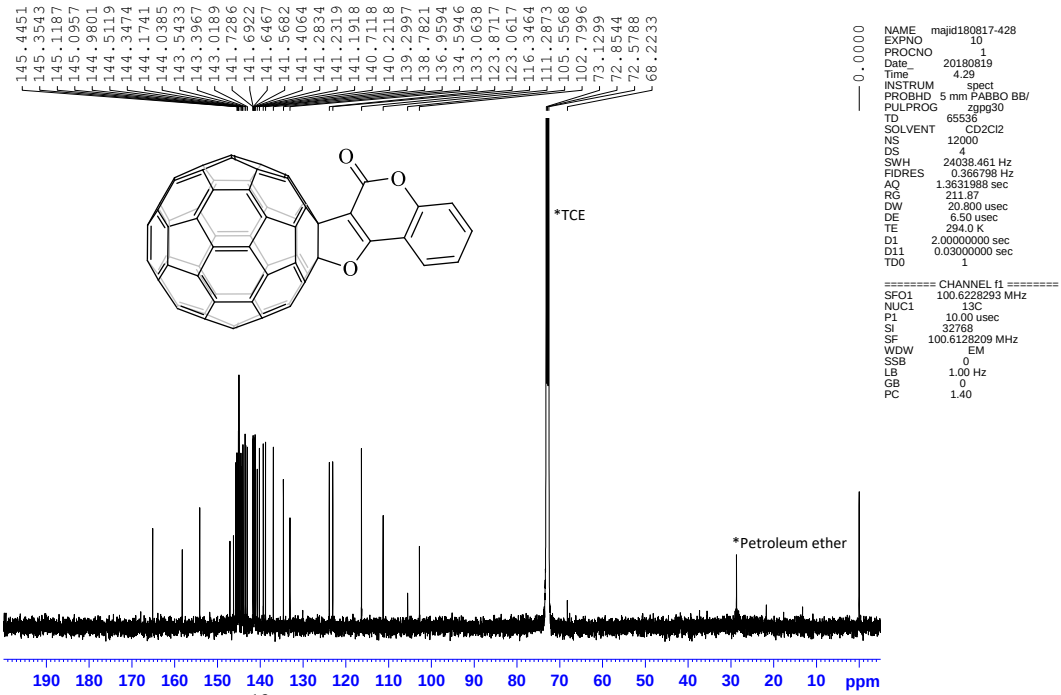


Figure S2 ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2a

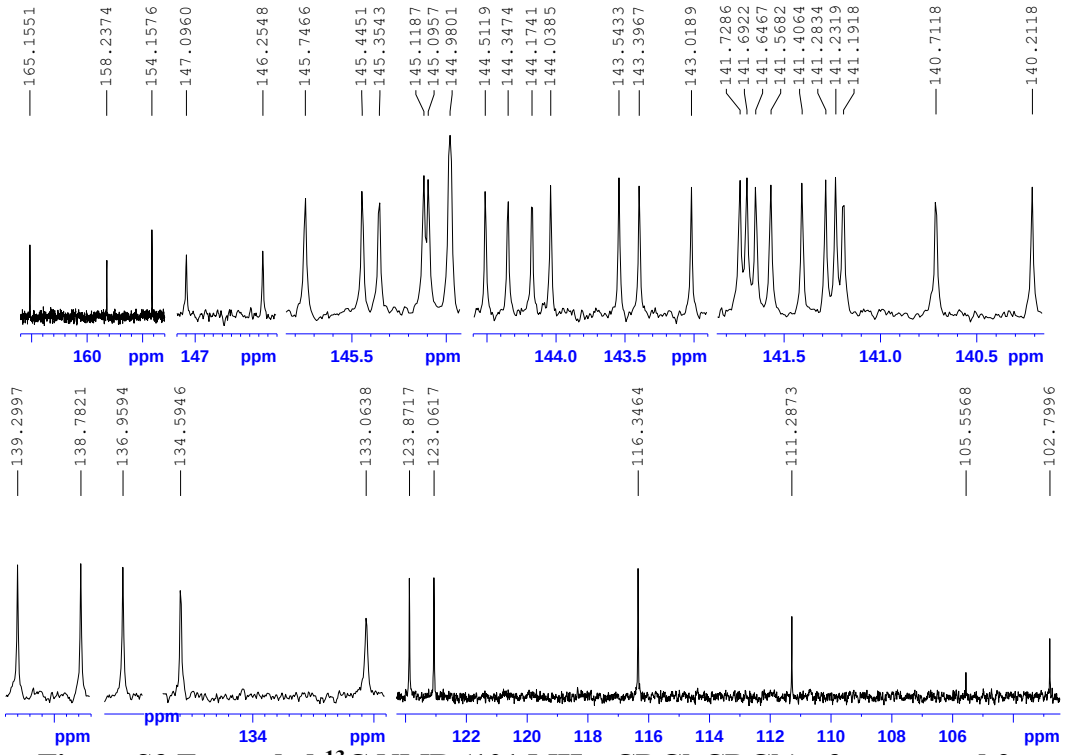


Figure S3 Expanded ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2a

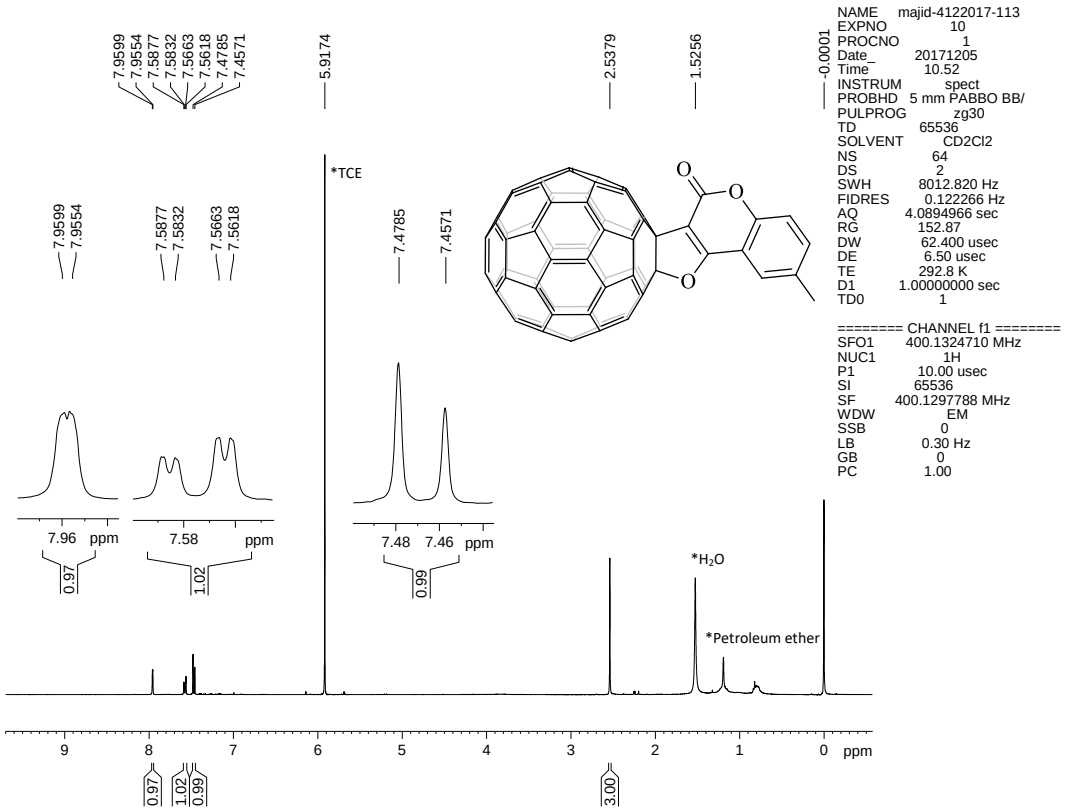


Figure S4 ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2b

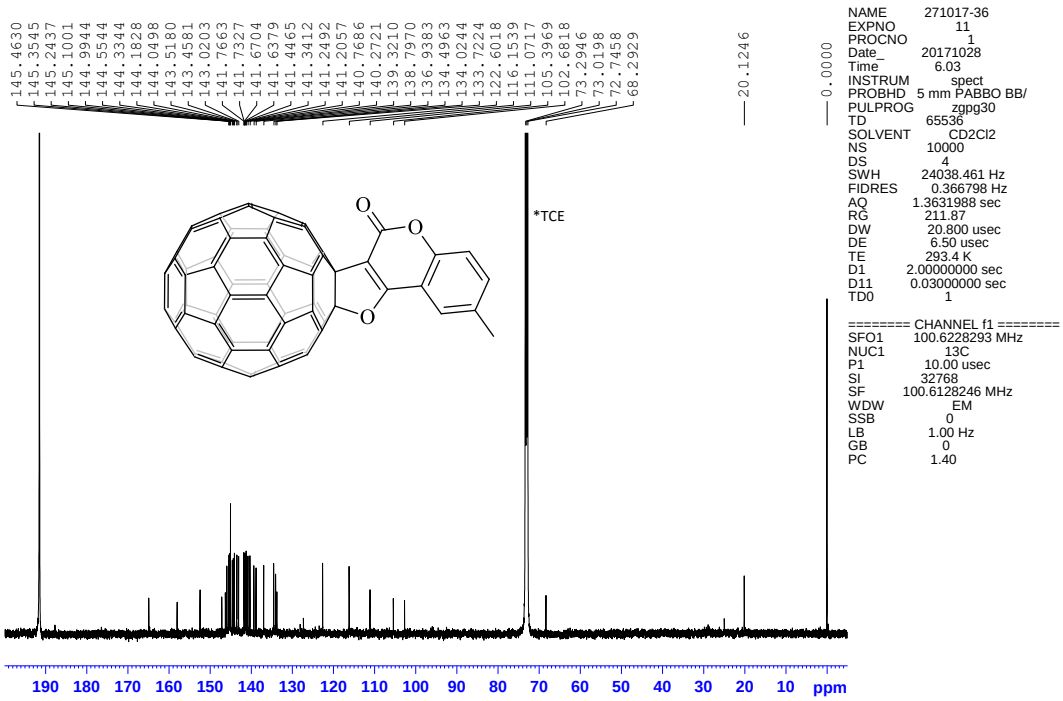


Figure S5 ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2b

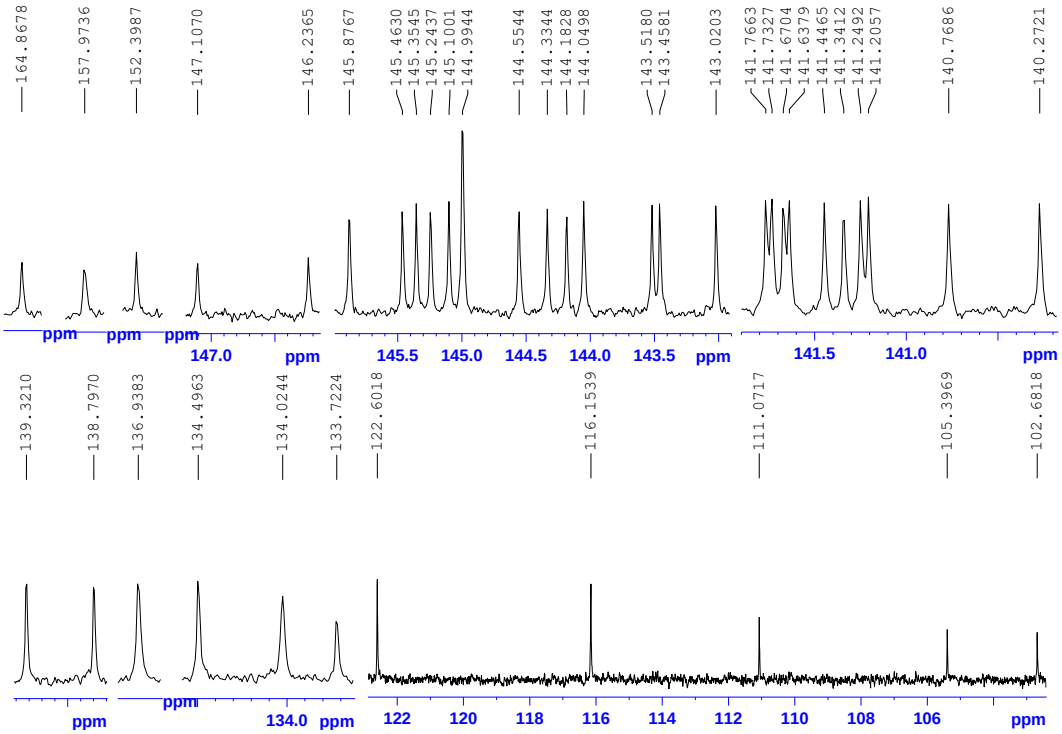


Figure S6 Expanded ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2b

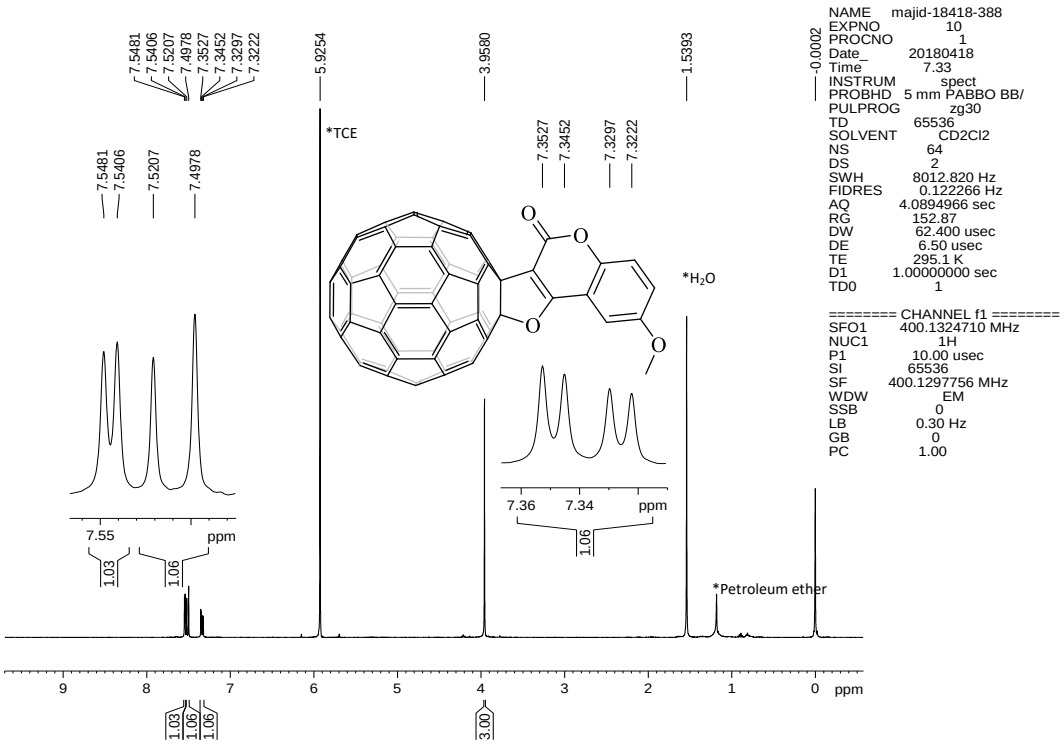


Figure S7 ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) of compound 2c

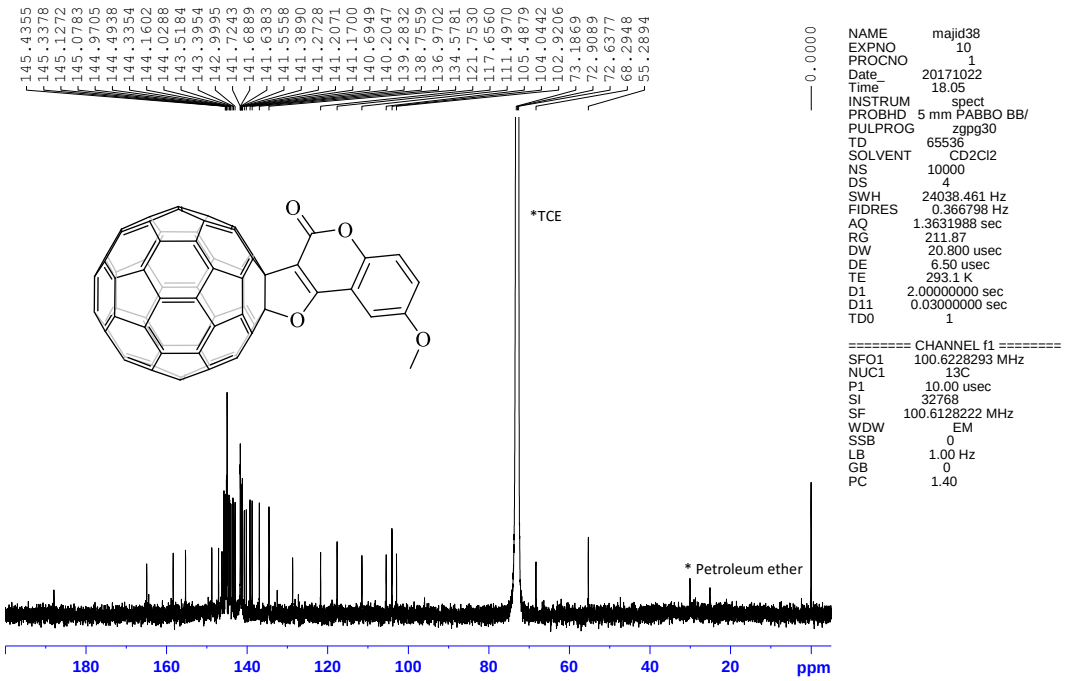


Figure S8 ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2c

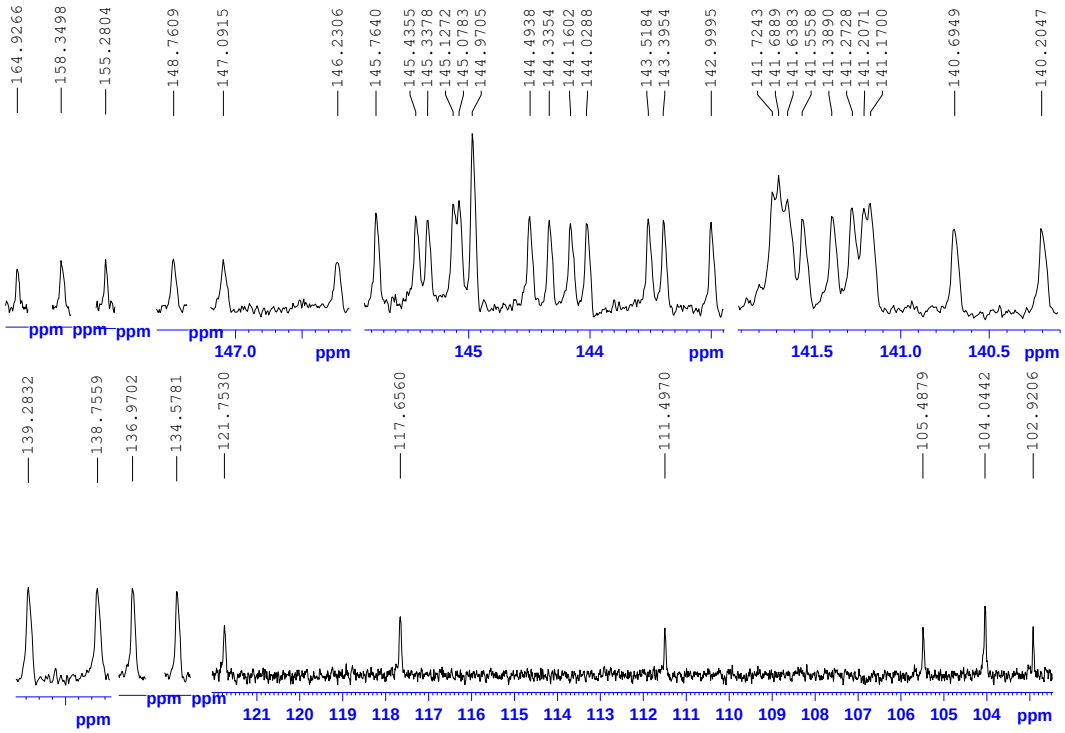


Figure S9 Expanded ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2c

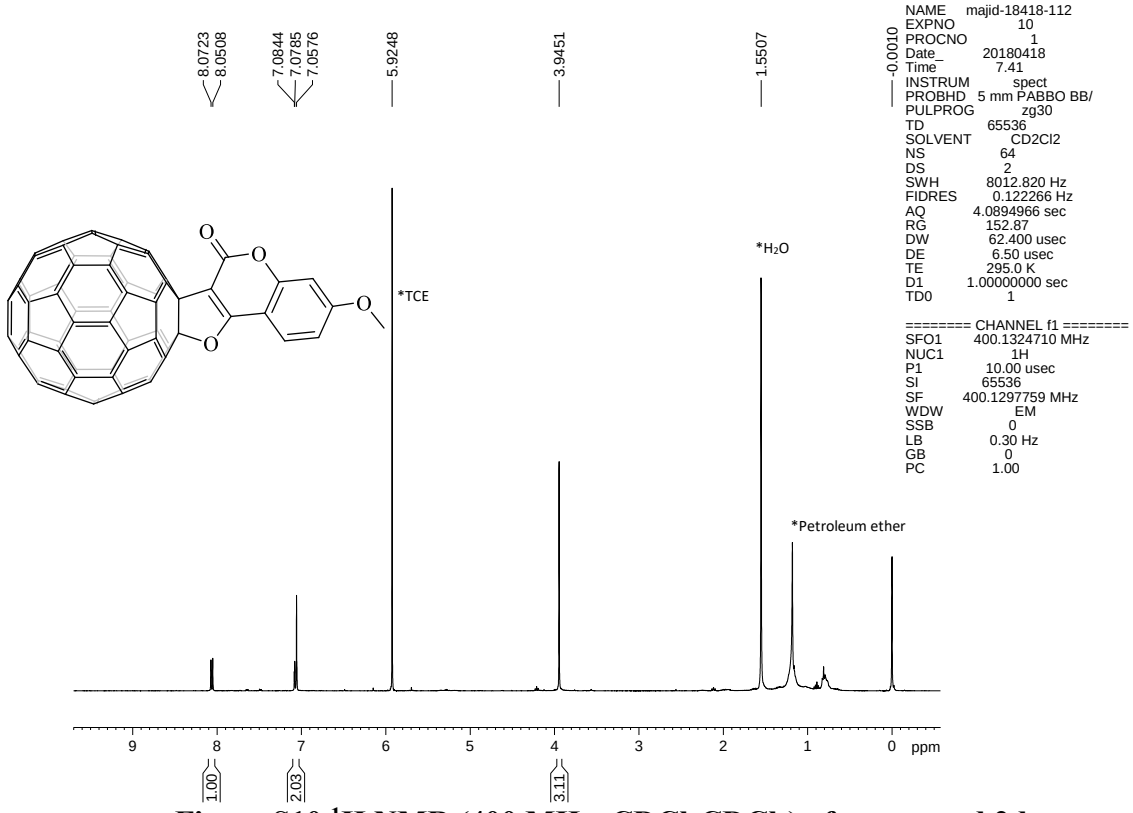


Figure S10 ^1H NMR (400 MHz, $CDCl_2CDCl_2$) of compound 2d

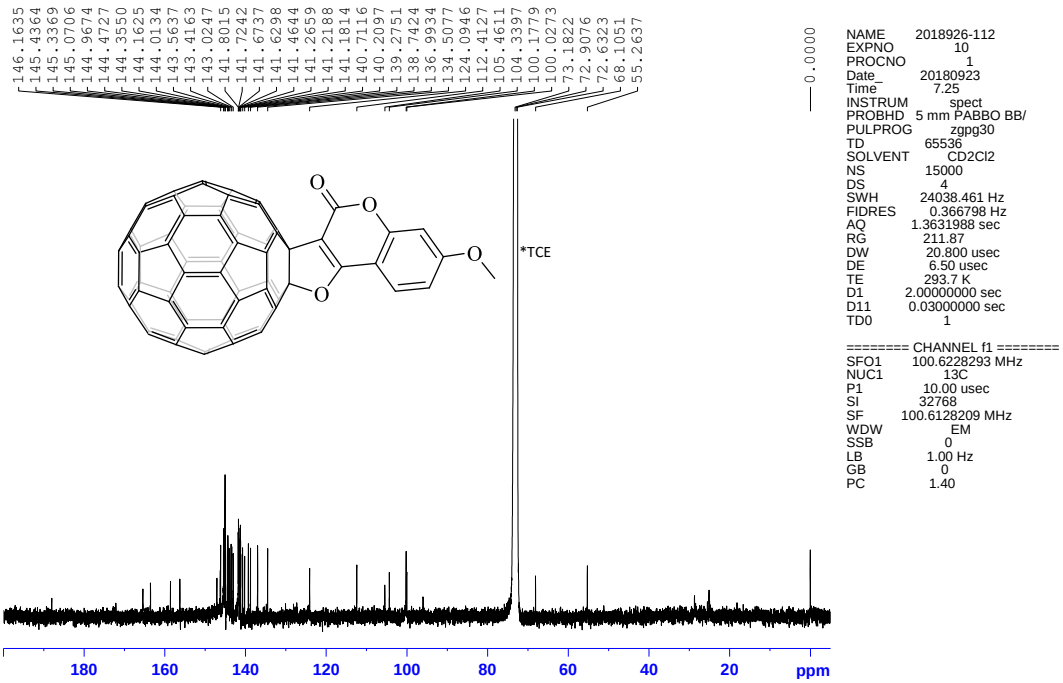


Figure S11 ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2d

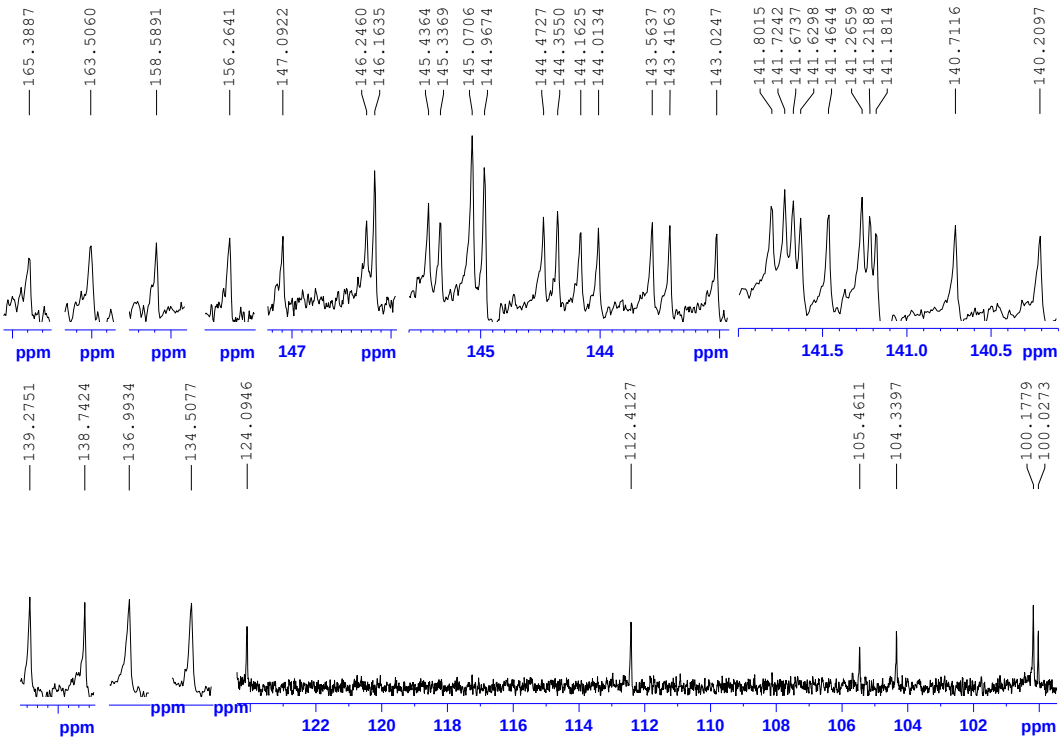


Figure S12 Expanded ^{13}C NMR (101 MHz, $CDCl_2CDCl_2$) of compound 2d

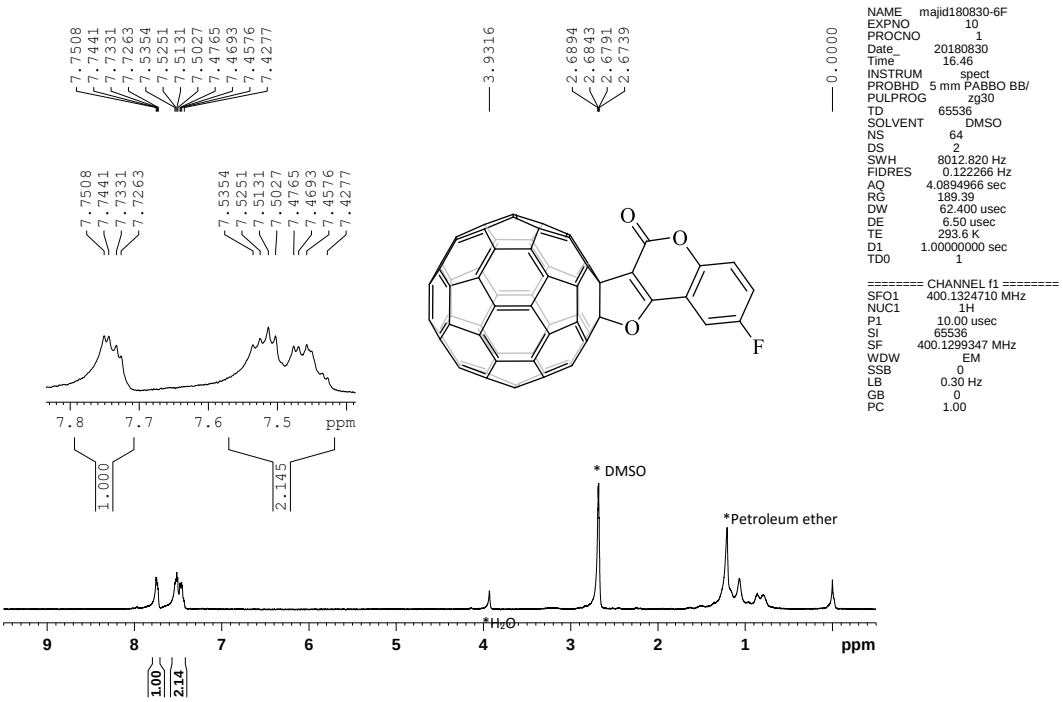


Figure S13 ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) of compound 2e

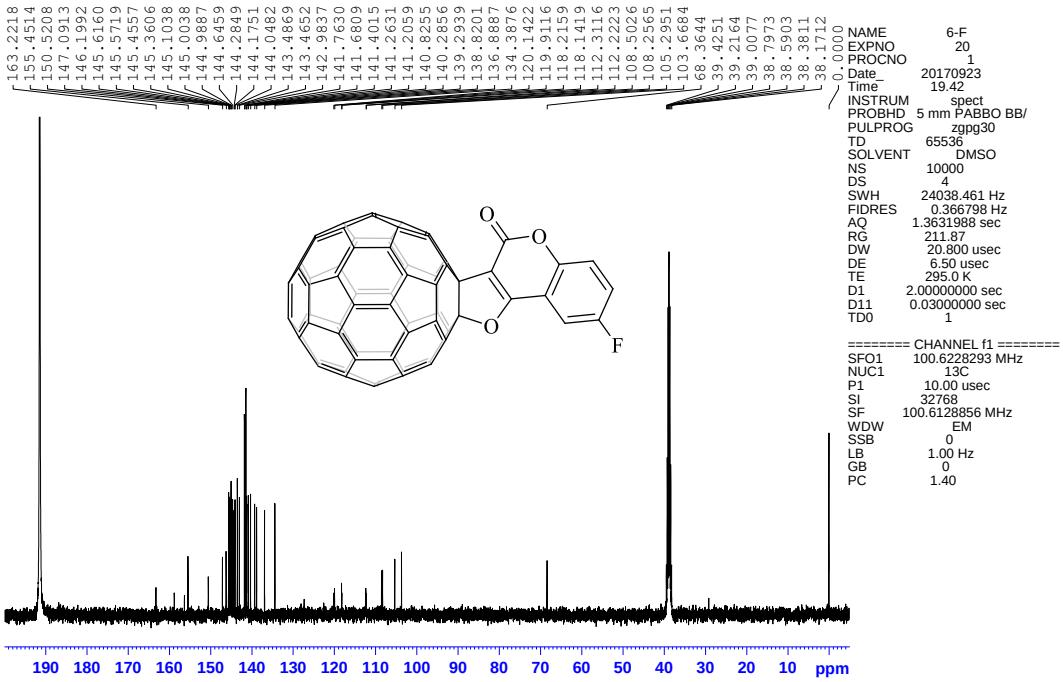


Figure S14 ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 2e

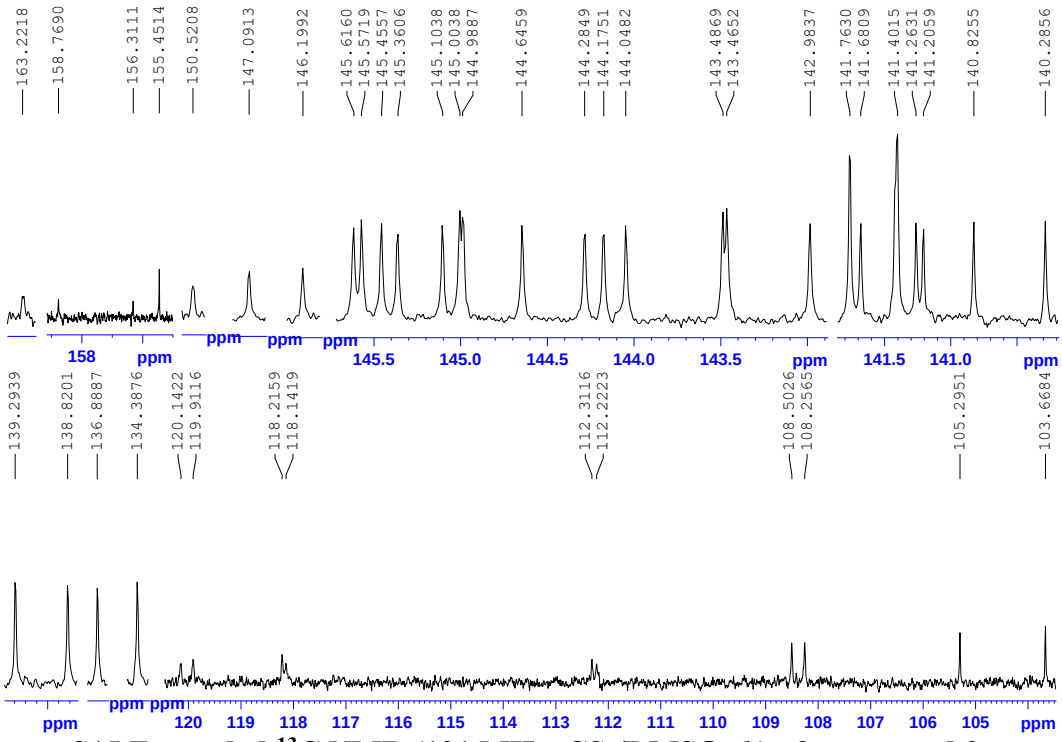


Figure S15 Expanded ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 2e

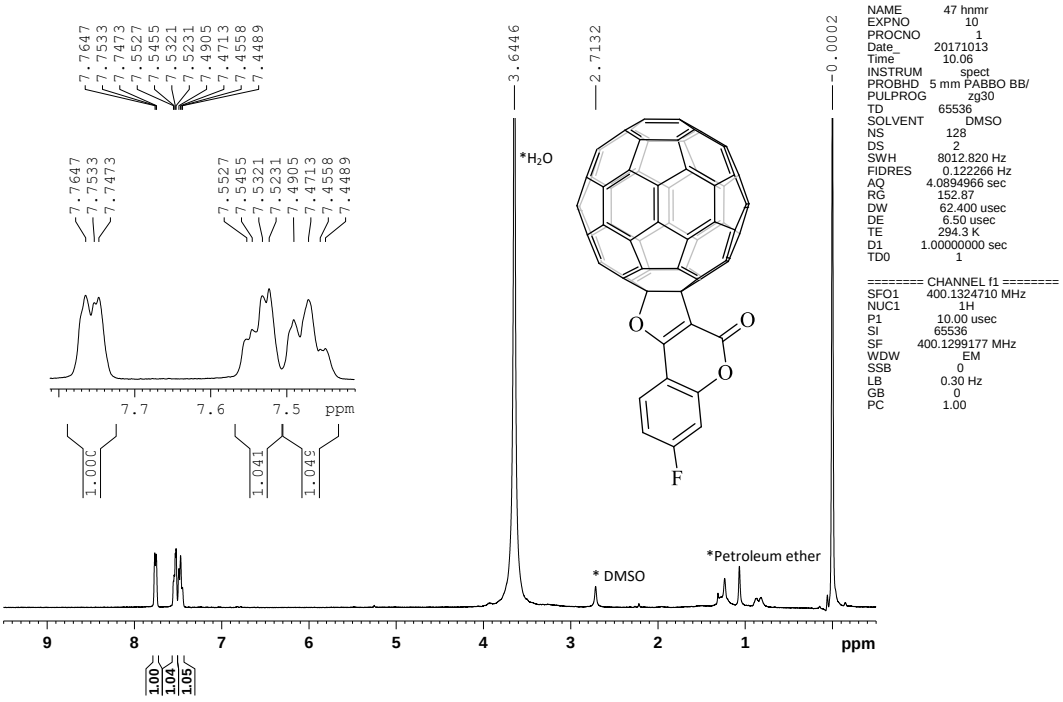


Figure S16 ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) of compound 2f

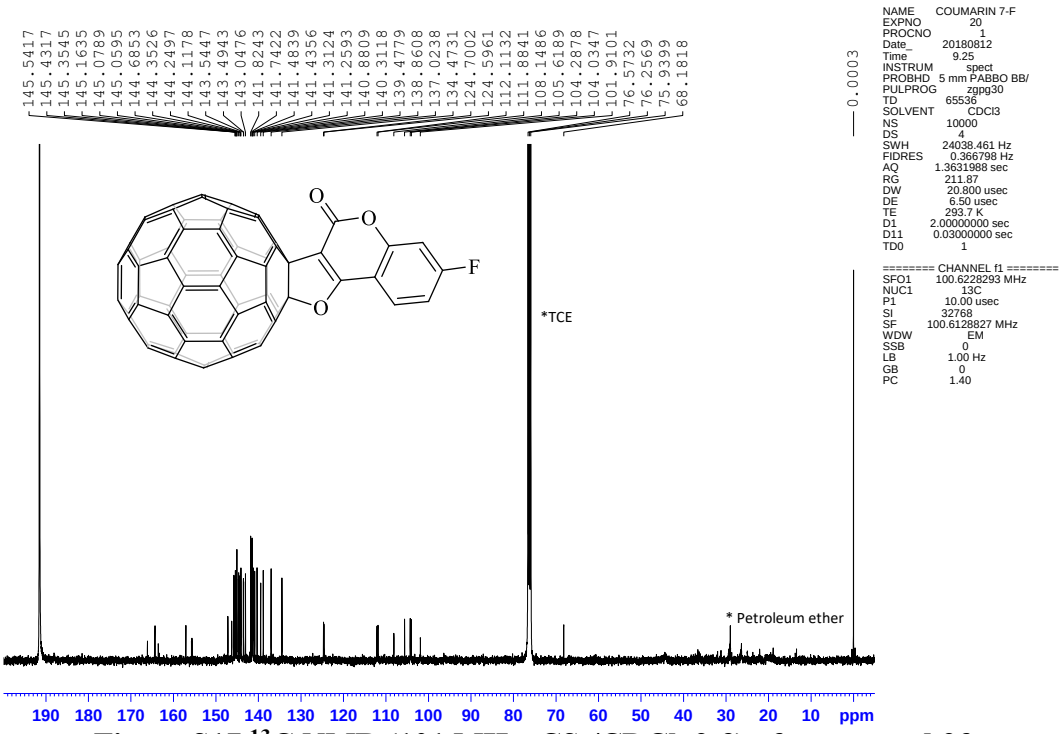


Figure S17 ^{13}C NMR (101 MHz, CS_2/$CDCl_3$ 2:3) of compound 2f

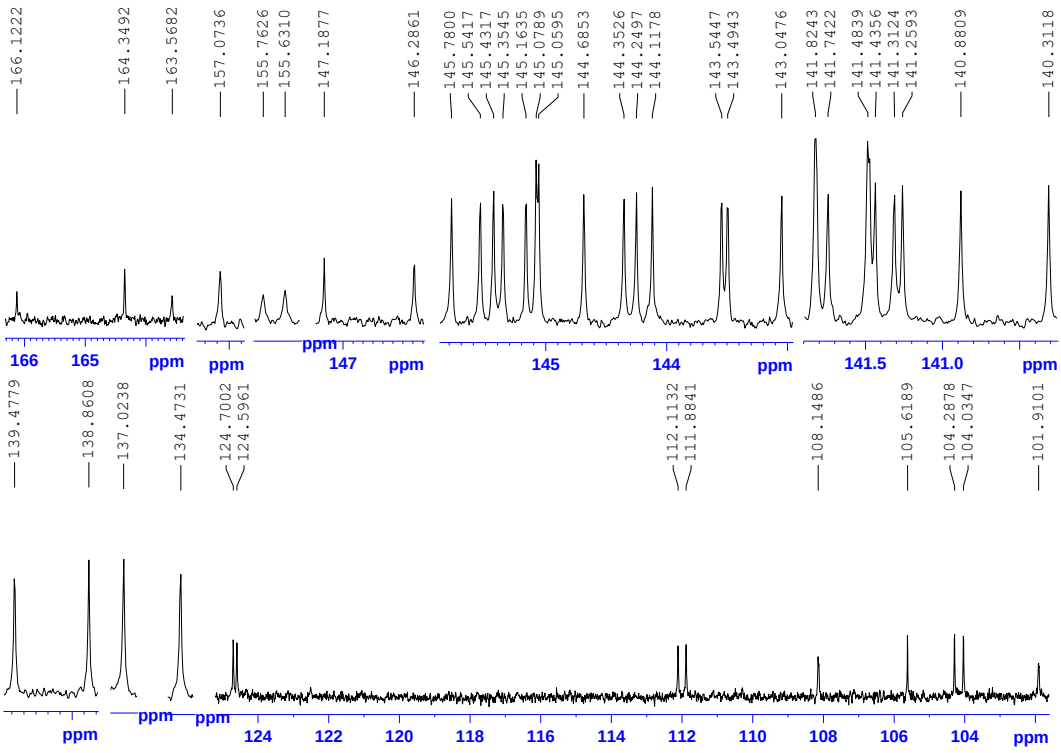


Figure S18 Expanded ^{13}C NMR (101 MHz, CS_2/$CDCl_3$ 2:3) of compound 2f

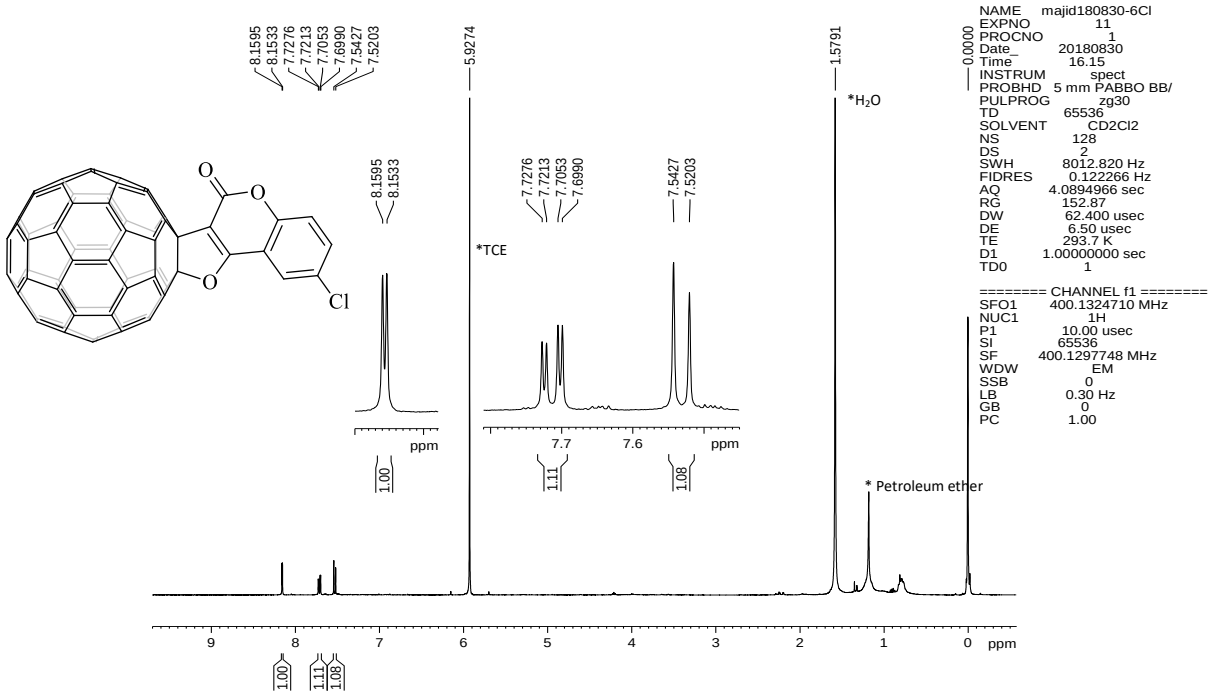


Figure S19 ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2g

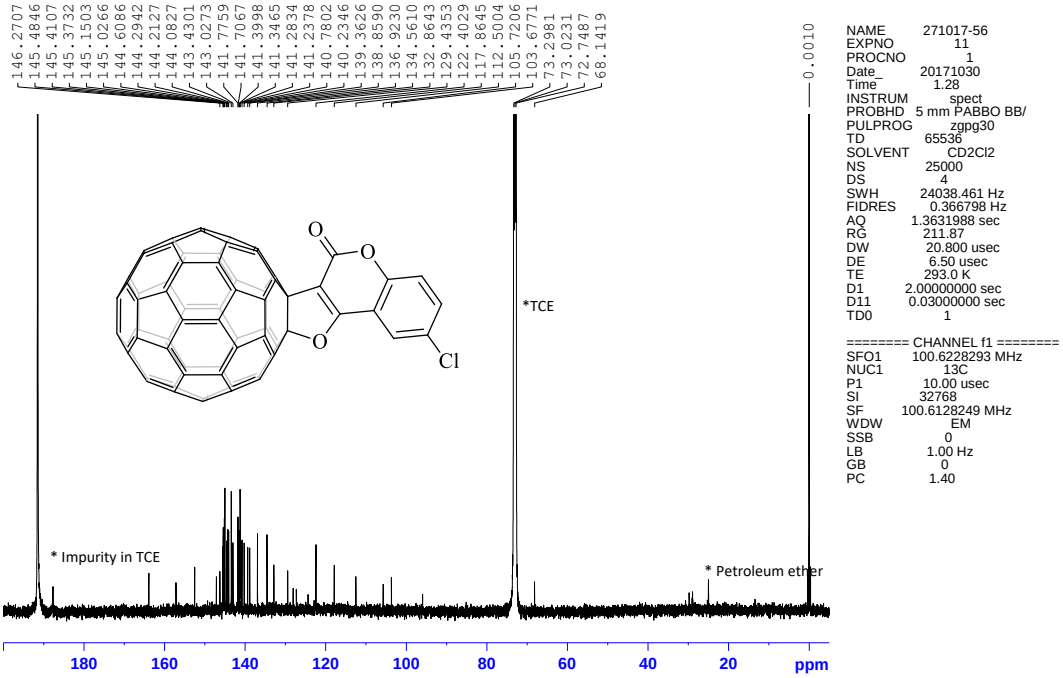


Figure S20 ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2g

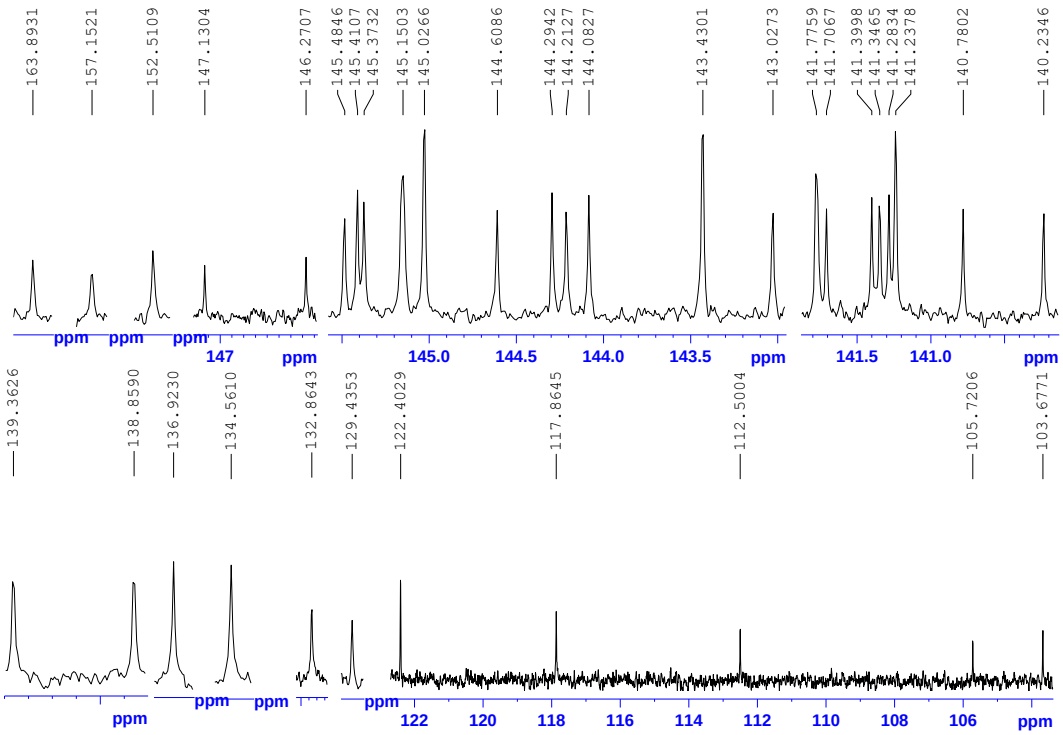


Figure S21 Expanded ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2g

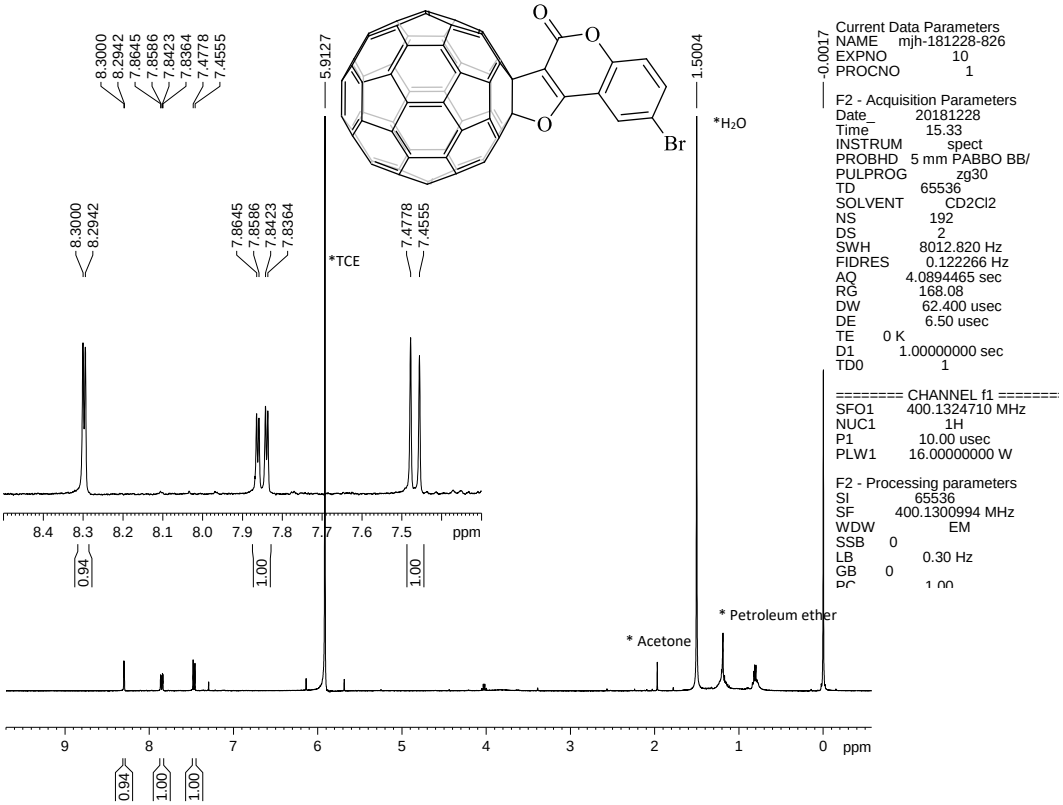


Figure S22 ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) of compound 2h

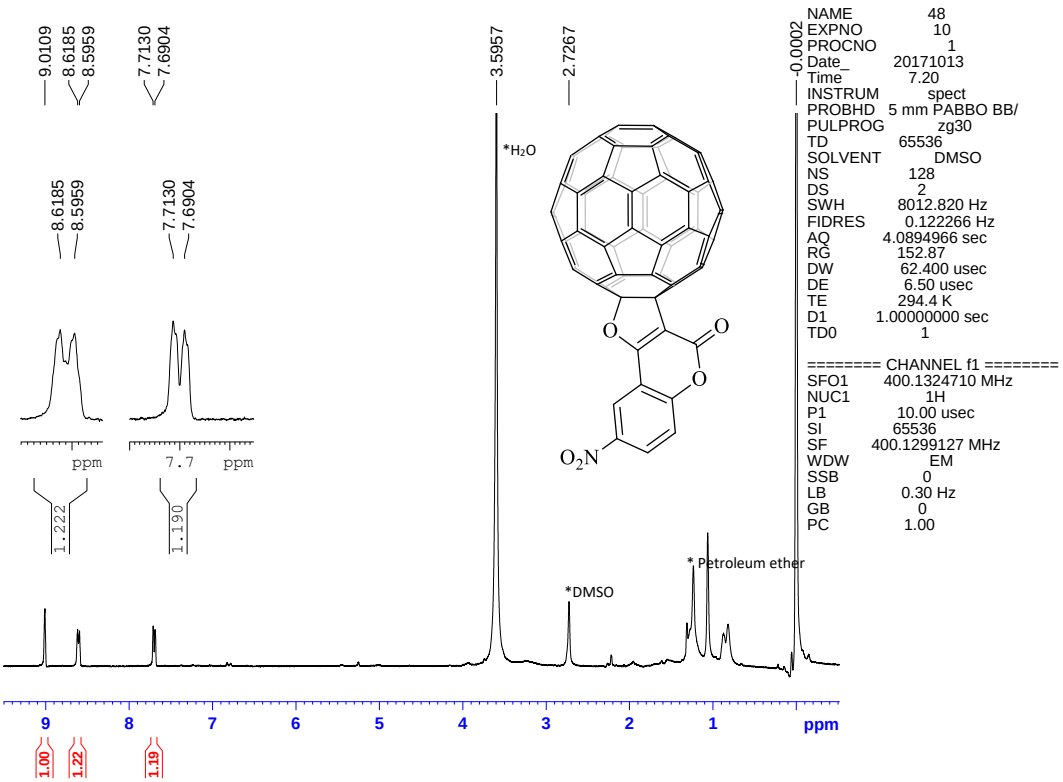


Figure S23 ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) of compound 2i

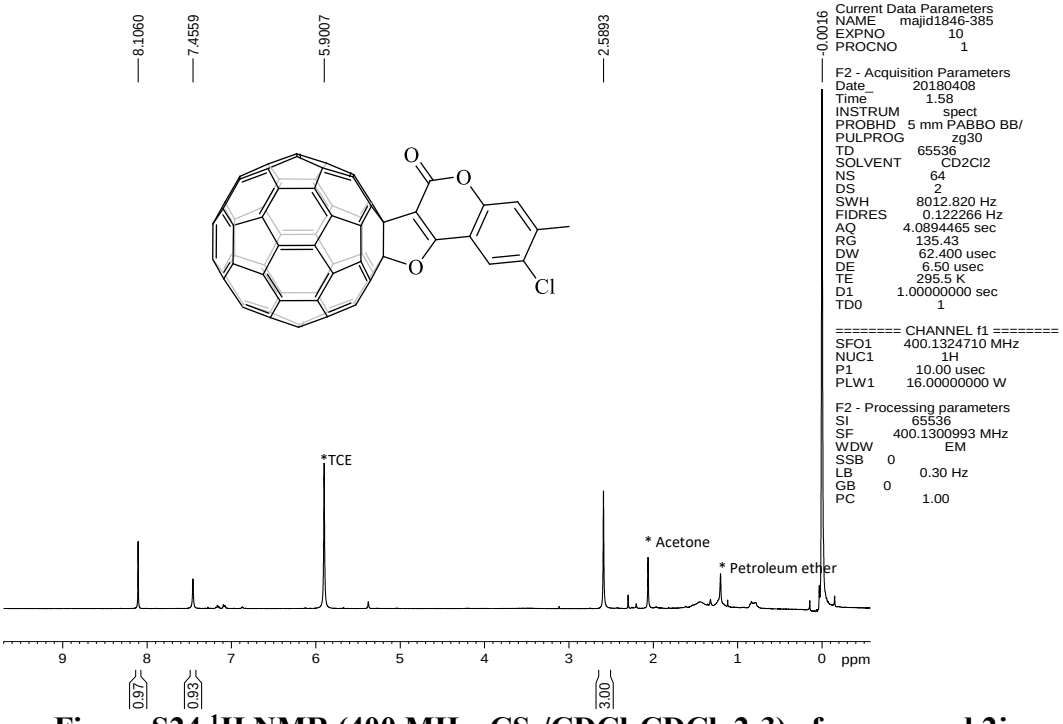


Figure S24 ^{1}H NMR (400 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2j

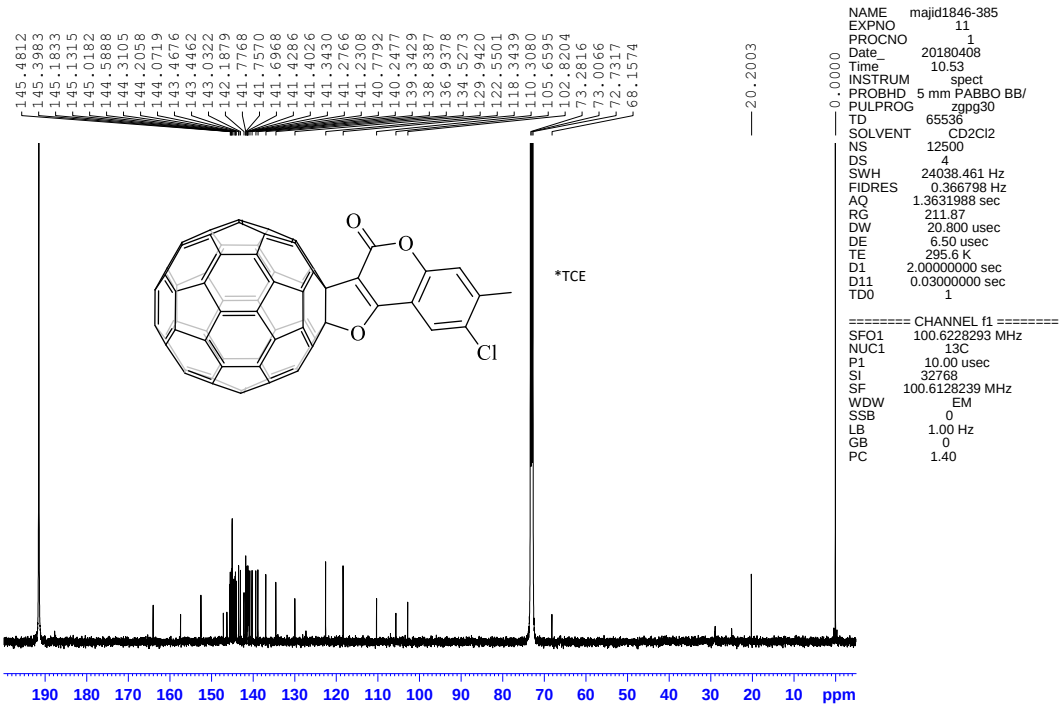


Figure S25 ^{13}C NMR (101 MHz, CS_2/$CDCl_2CDCl_2$ 2:3) of compound 2j

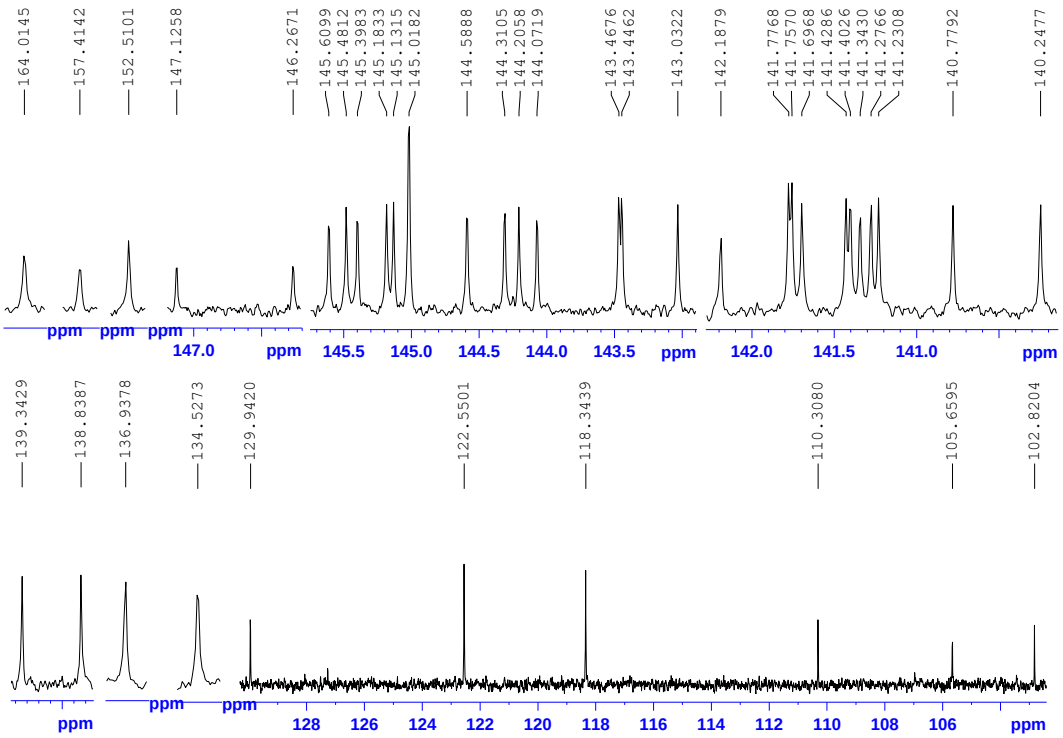


Figure S26 Expanded ^{13}C NMR (101 MHz, 2:3 CS_2/$CDCl_2CDCl_2$) of compound 2j

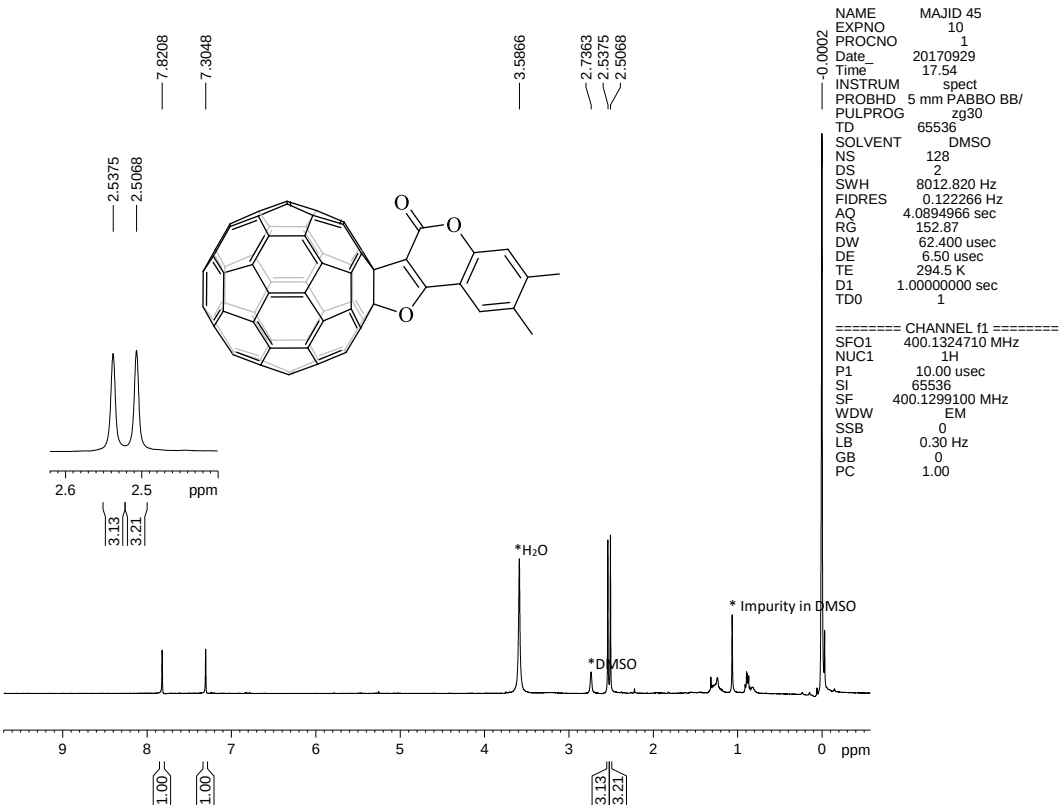


Figure S27 ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) of compound 2k

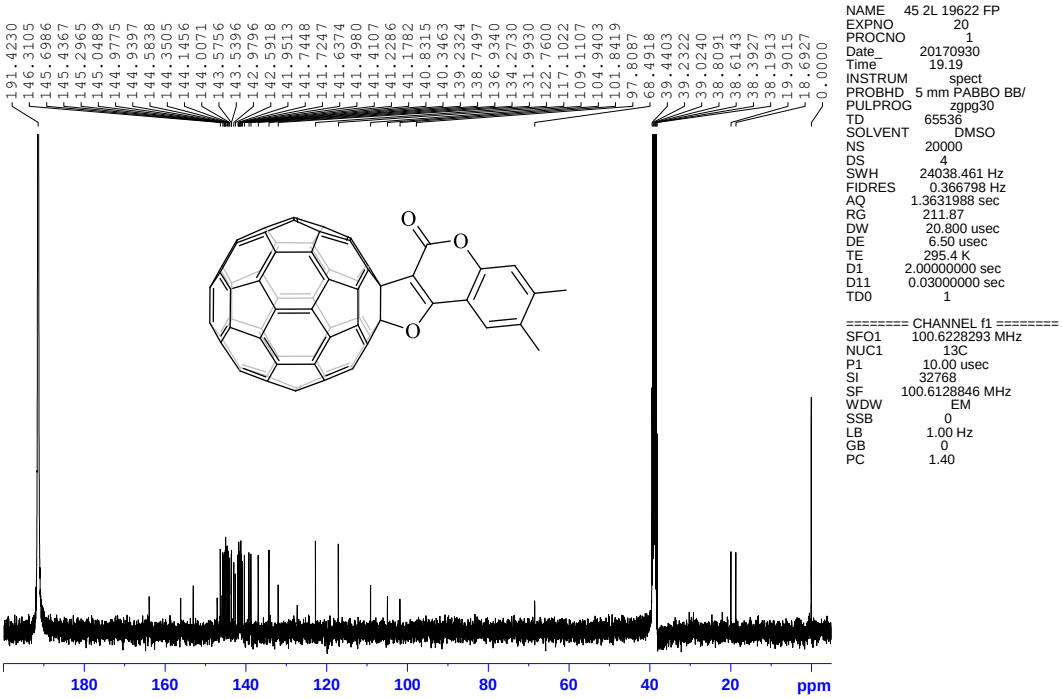


Figure S28 ^{13}C NMR (101 MHz, CS$_2$/DMSO-*d*$_6$) of compound 2k

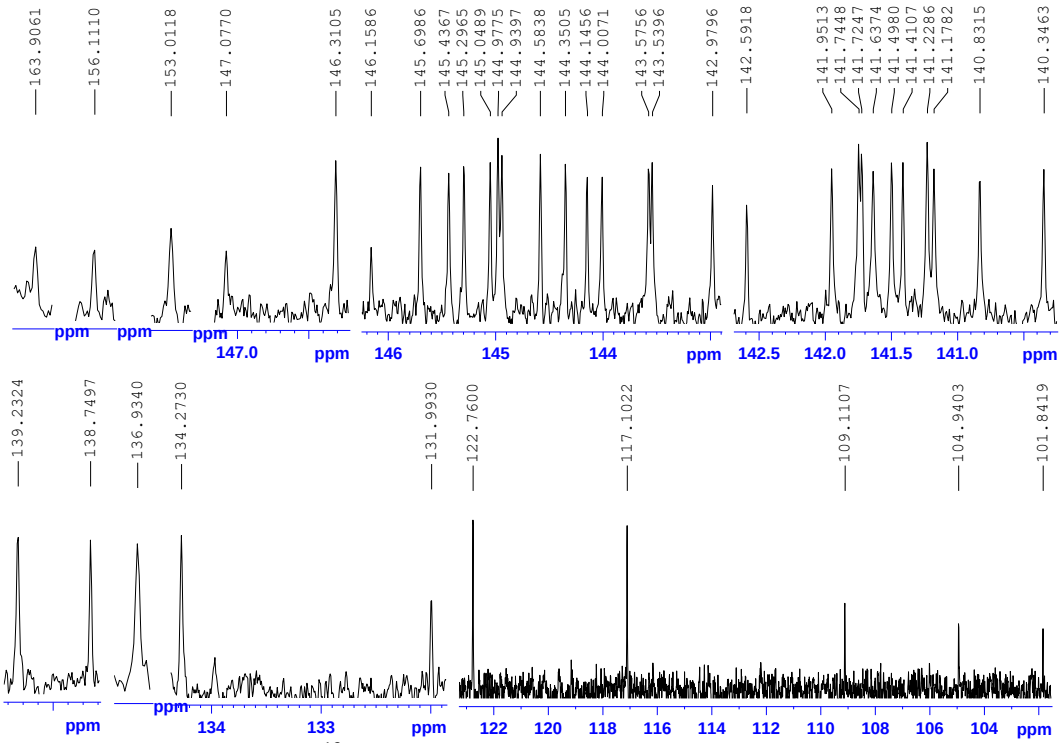


Figure S29 Expanded ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 2k

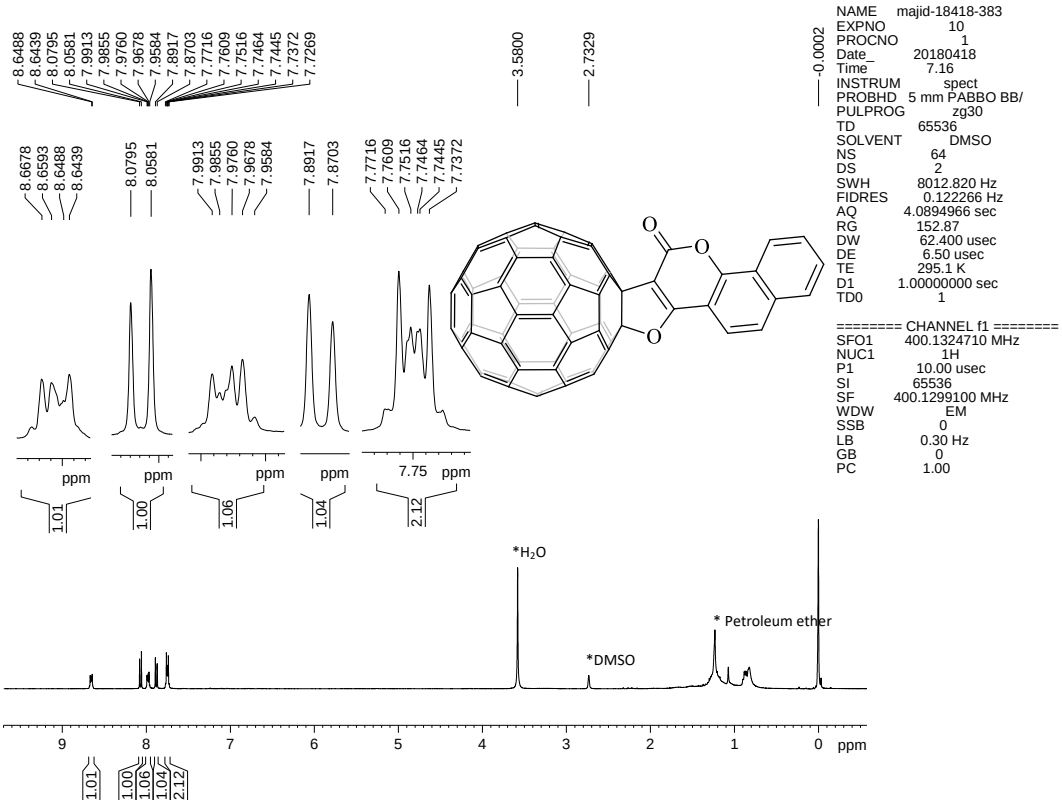


Figure S30 ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) of compound 2l

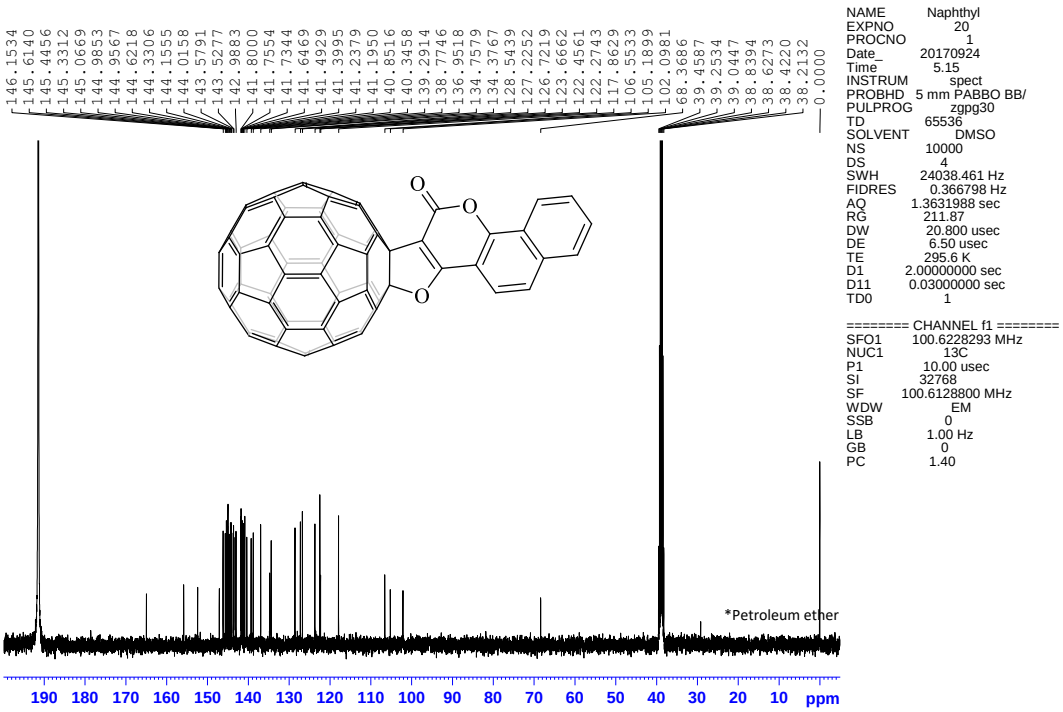


Figure S31 ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 2l

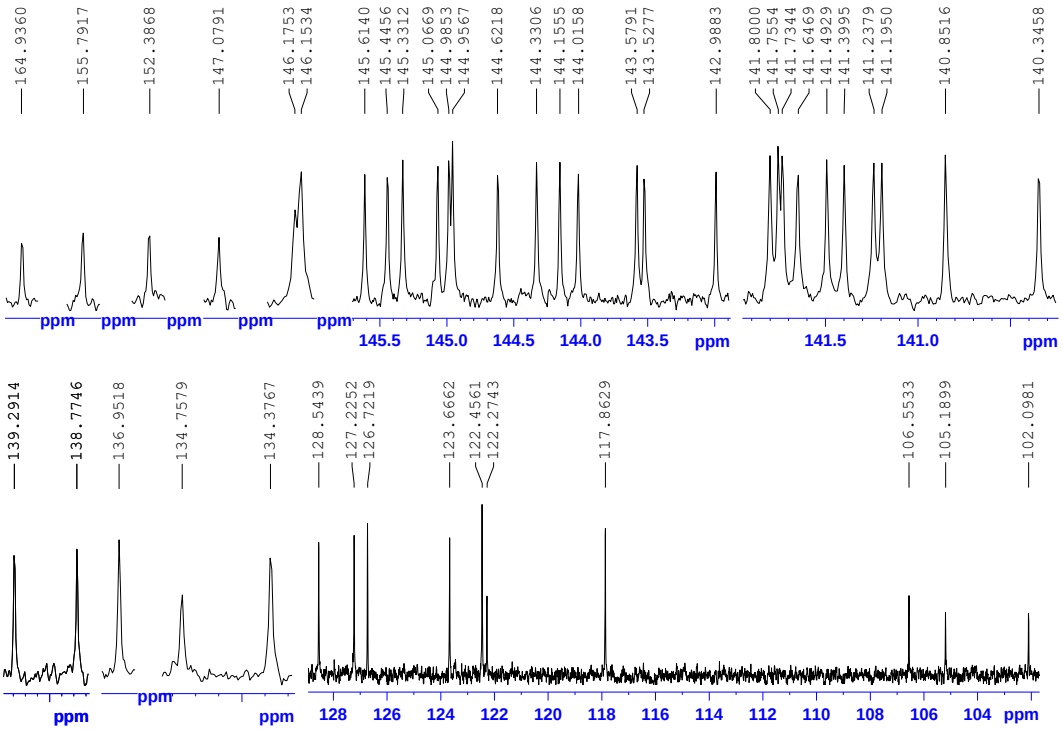


Figure S32 Expanded ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 2l

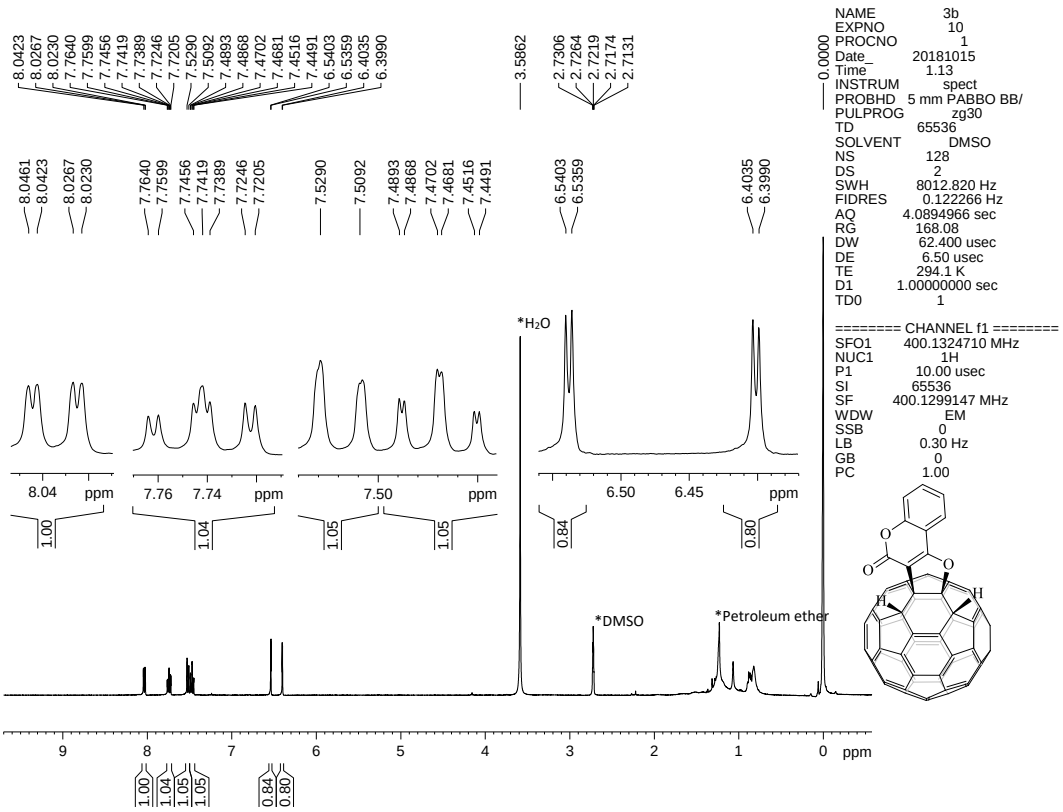


Figure S33 ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) of compound 3a

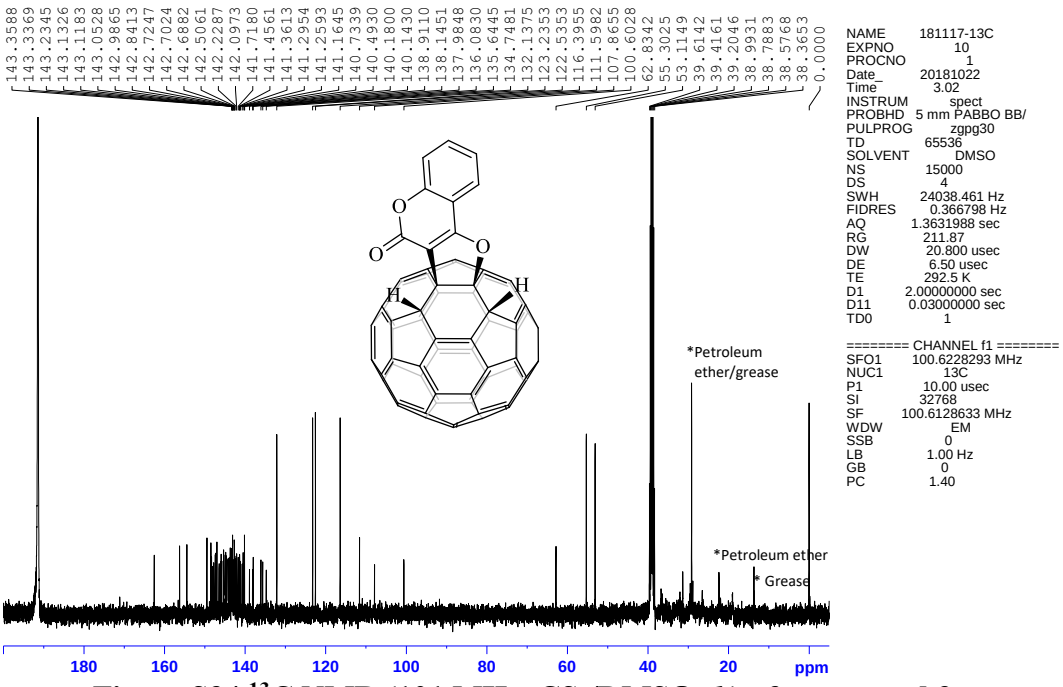


Figure S34 ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 3a

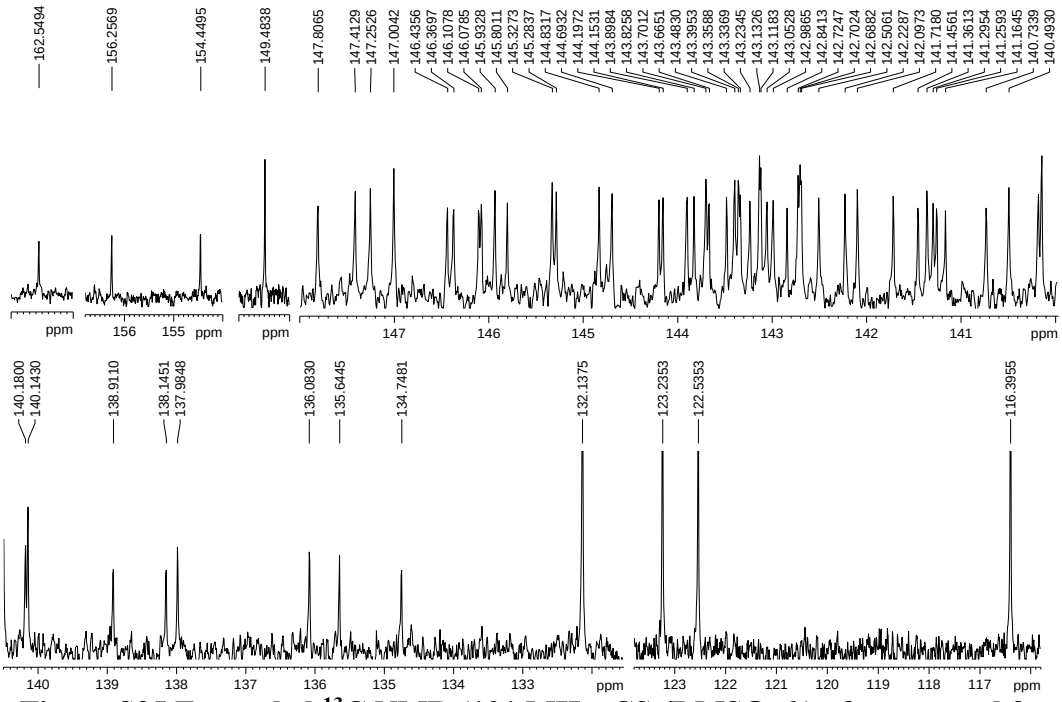


Figure S35 Expanded ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 3a

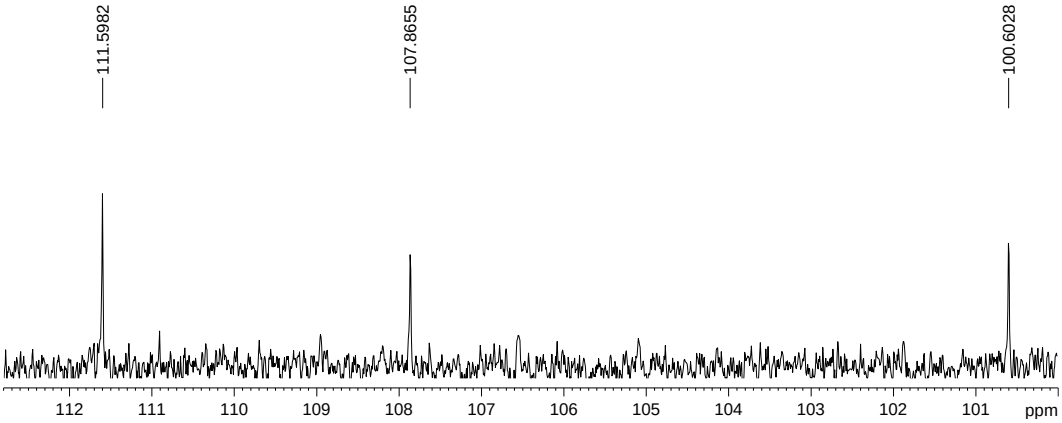


Figure S36 Expanded ^{13}C NMR (101 MHz, CS_2/DMSO-d_6) of compound 3a

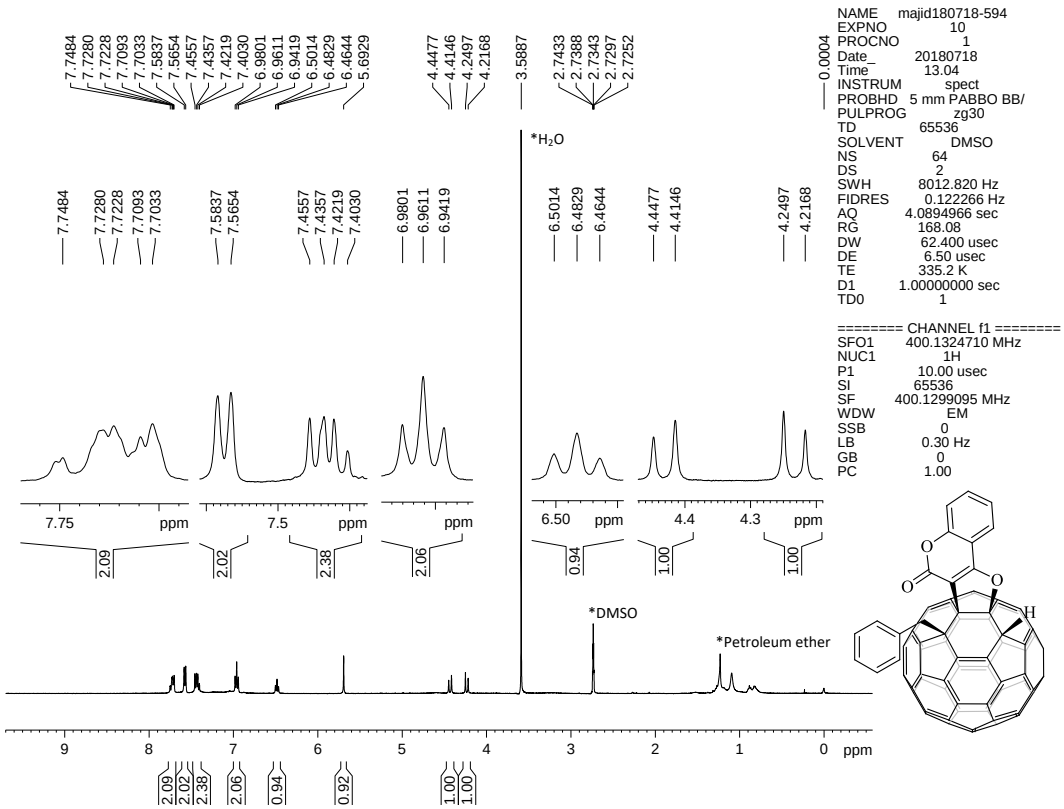


Figure S37 ^{1}H NMR (400 MHz, CS$_2$/DMSO-*d*$_6$) of compound 3b

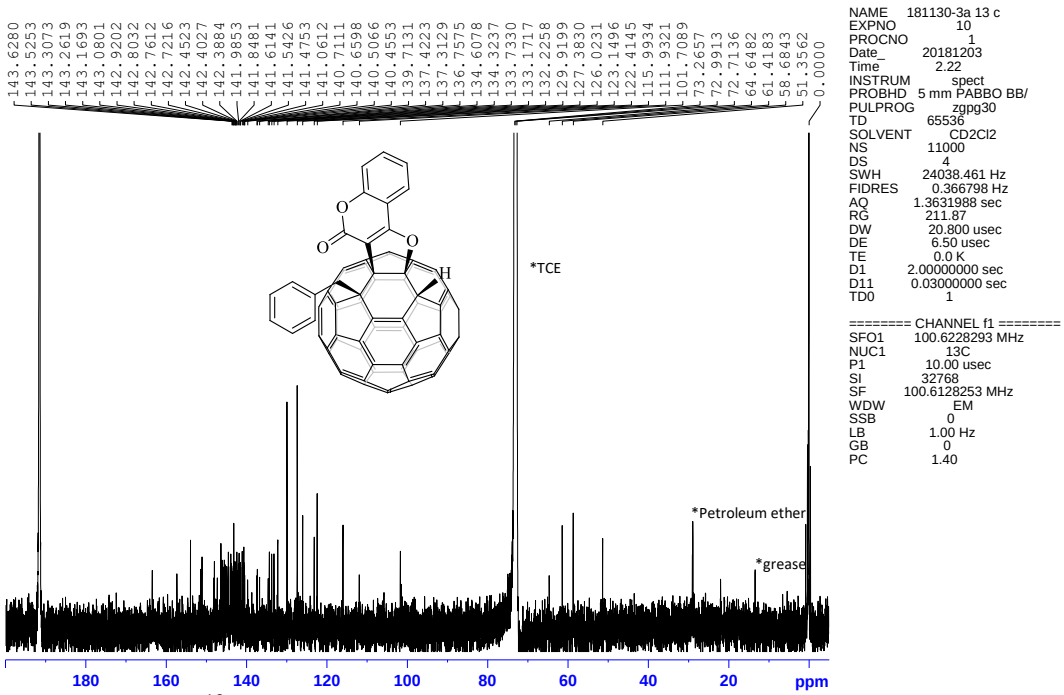


Figure S38 ^{13}C NMR (101 MHz, CS$_2$/CDCl$_2$CDCl$_2$ 2:3) of compound 3b

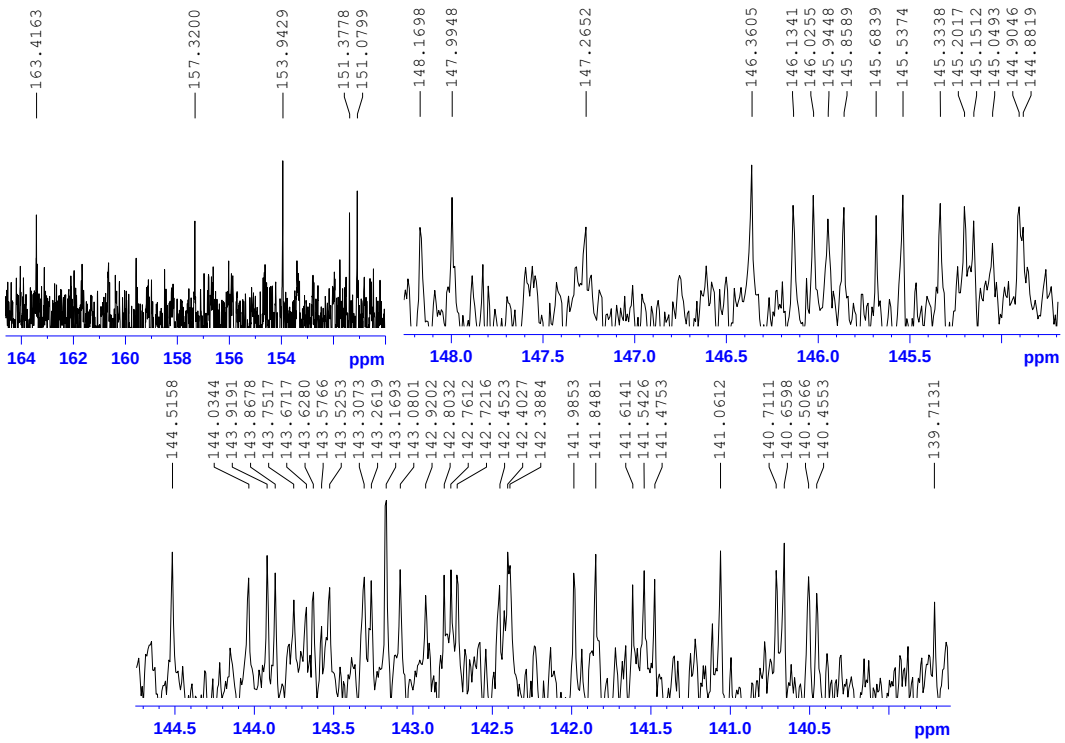


Figure S39 Expanded ^{13}C NMR (101 MHz, $CS_2/CDCl_2CDCl_2$ 2:3) of compound 3b

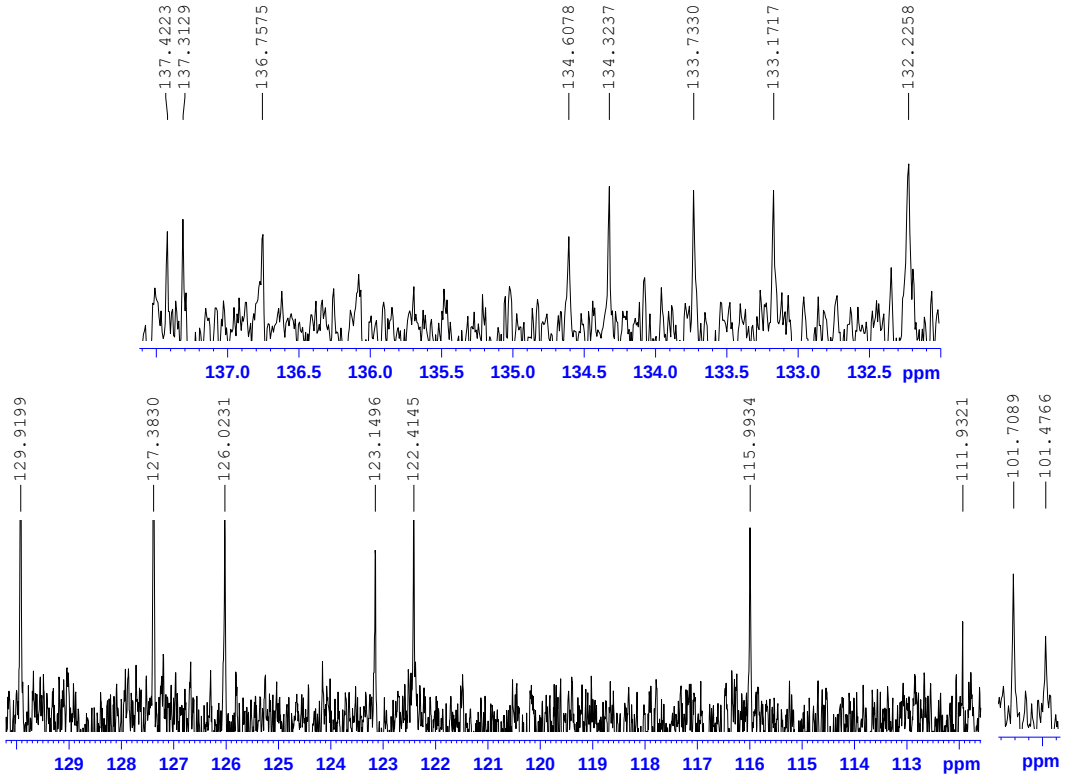


Figure S40 Expanded ^{13}C NMR (101 MHz, $CS_2/CDCl_2CDCl_2$ 2:3) of compound 3b

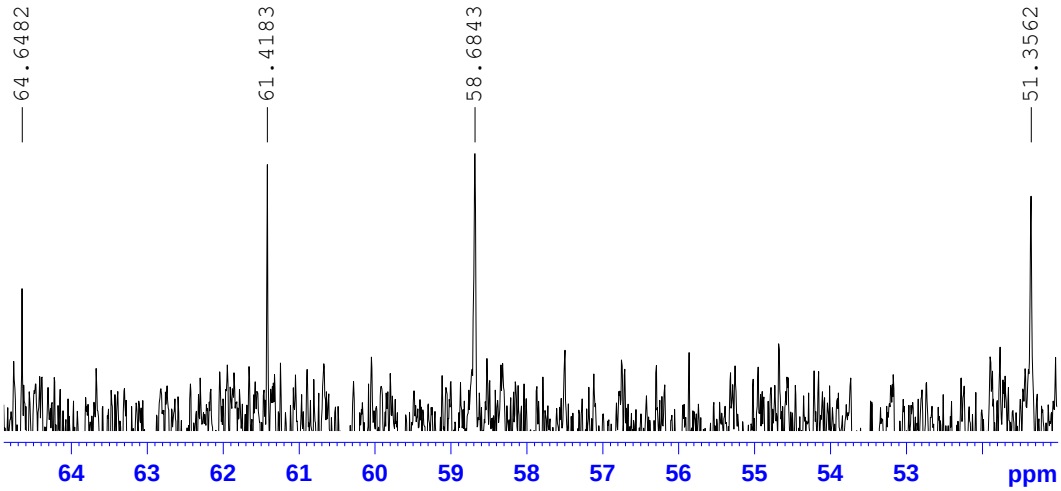


Figure S41 Expanded ^{13}C NMR (101 MHz, 2:3 CS_2/$CDCl_2CDCl_2$ 2:3) of compound 3b

5. UV-vis spectra of compounds 2a–l and 3a–d

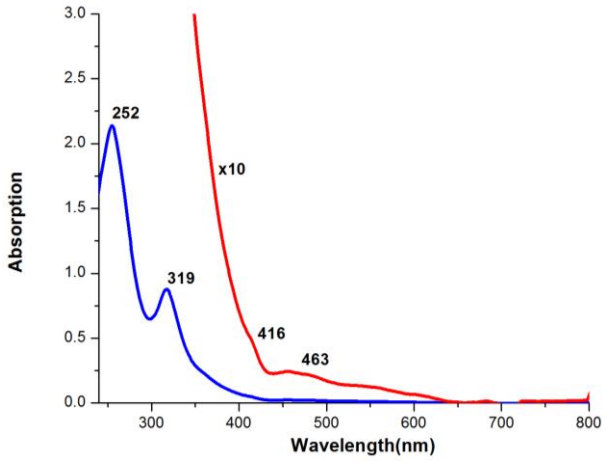


Figure S42 UV-vis absorption of compound 2a

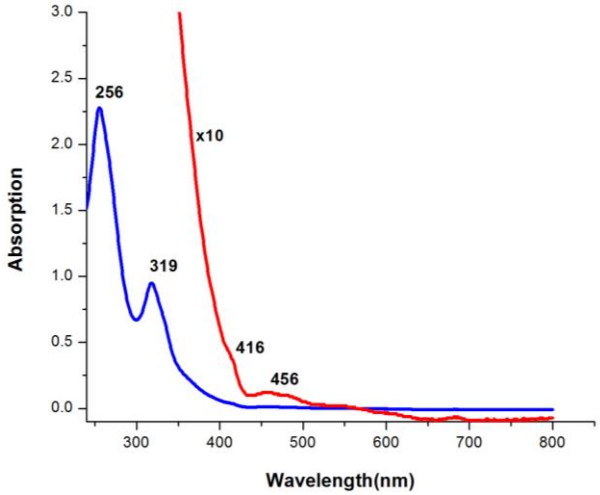


Figure S43 UV-vis absorption of compound 2b

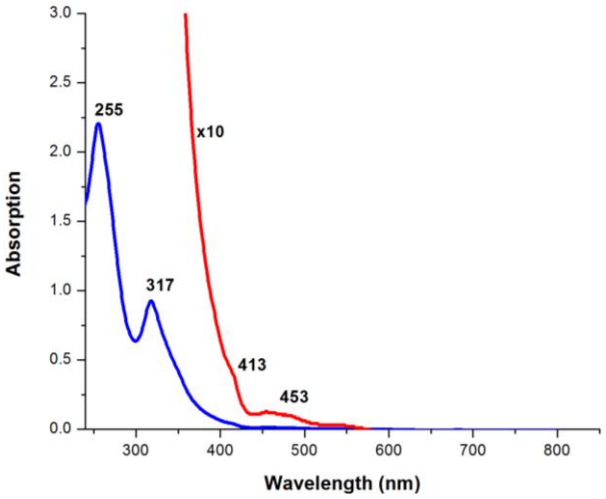


Figure S44 UV-vis absorption of compound 2c

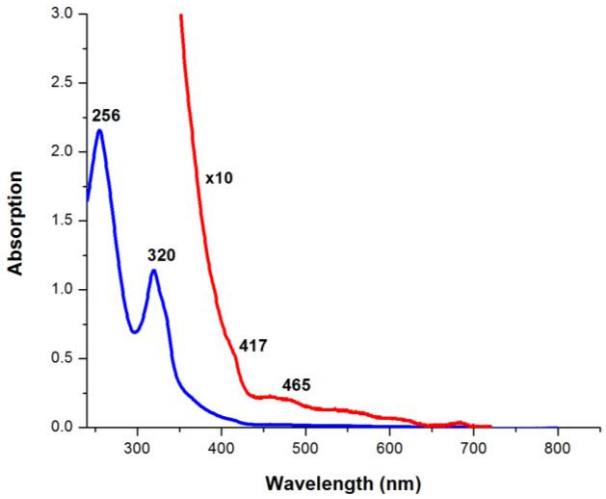


Figure S45 UV-vis absorption of compound 2d

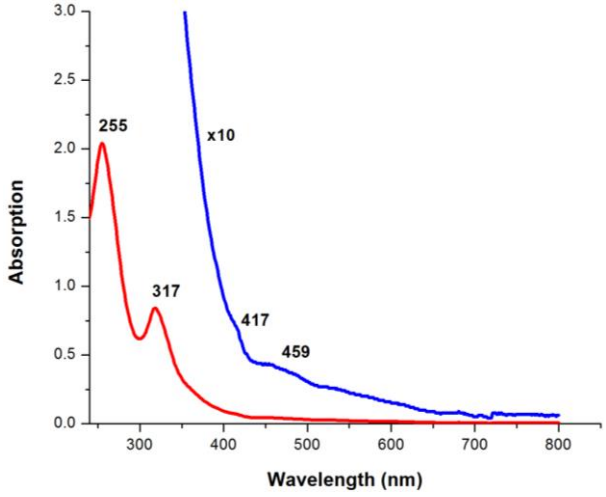


Figure S46 UV-vis absorption of compound 2e

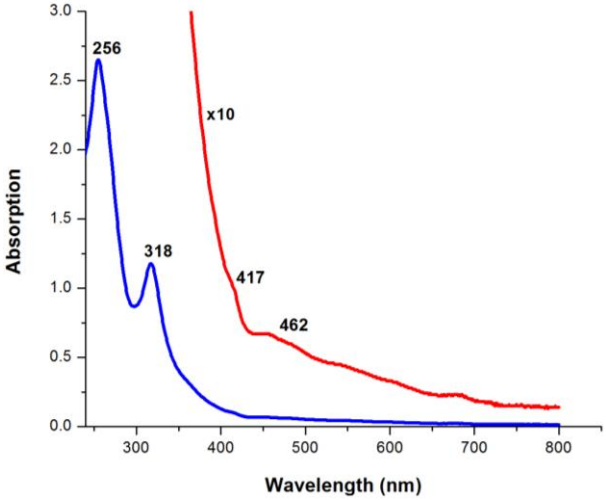


Figure S47 UV-vis absorption of compound 2f

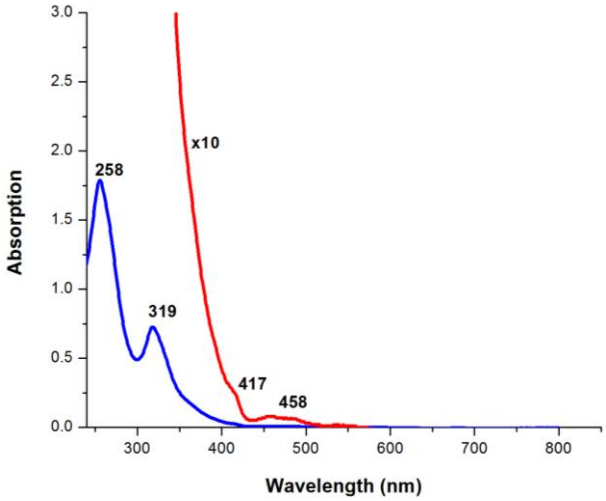


Figure S48 UV-vis absorption of compound 2g

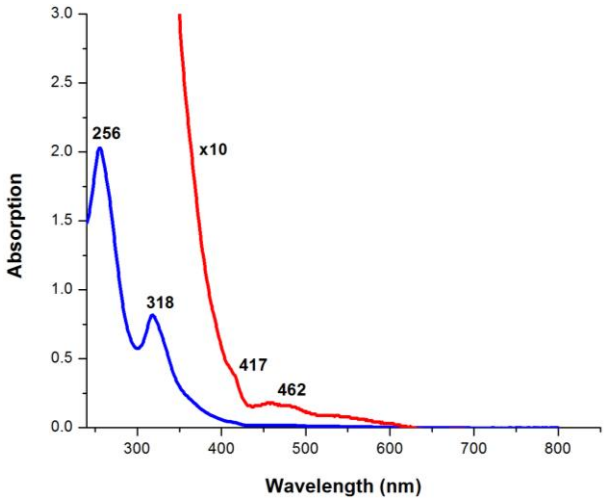


Figure S49 UV-vis absorption of compound 2h

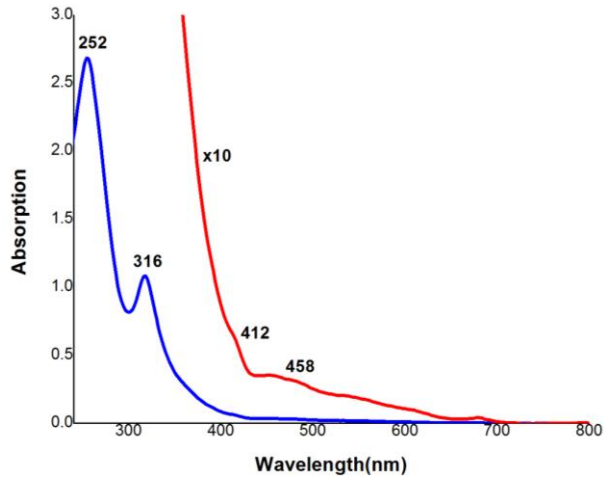


Figure S50 UV-vis absorption of compound 2i

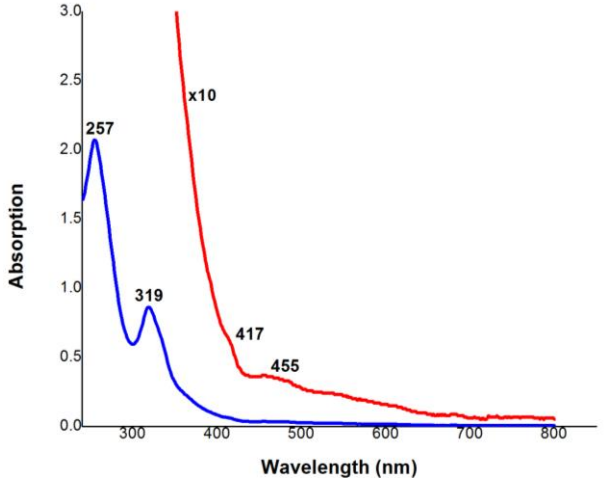


Figure S51 UV-vis absorption of compound 2j

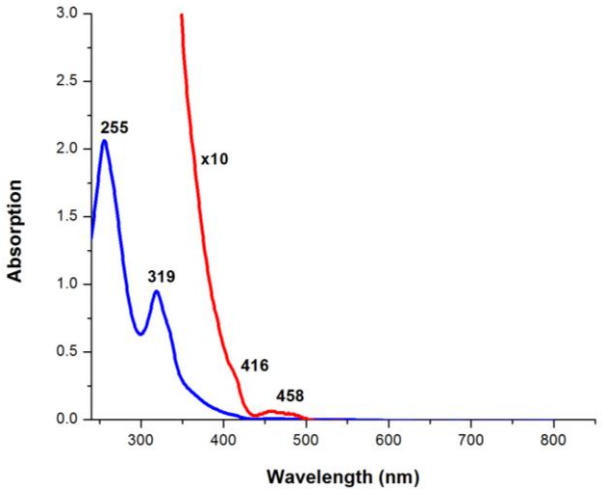


Figure S52 UV-vis absorption of compound 2k

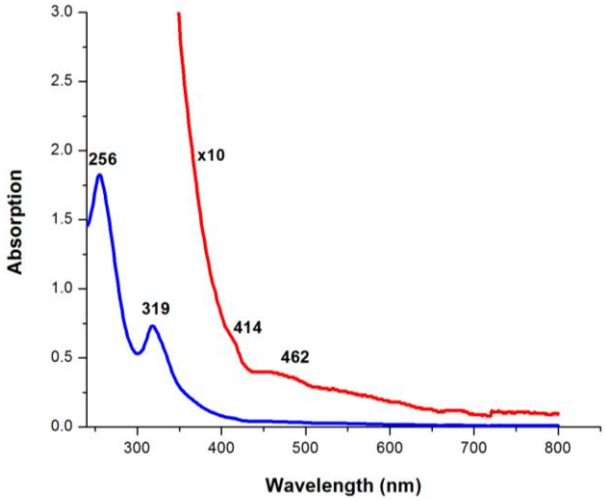


Figure S53 UV-vis absorption of compound 2l

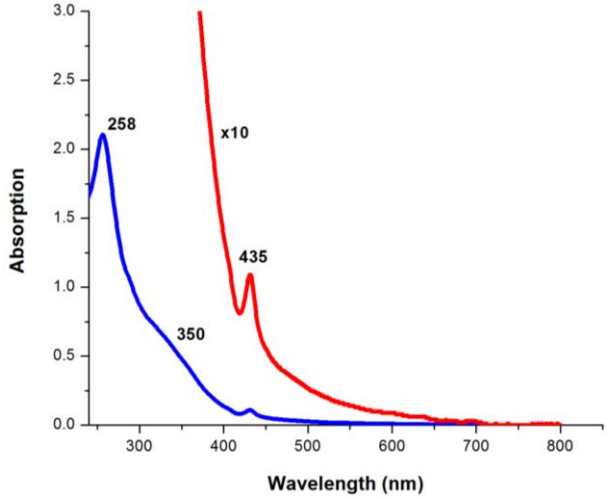


Figure S54 UV-vis absorption of compound 3a

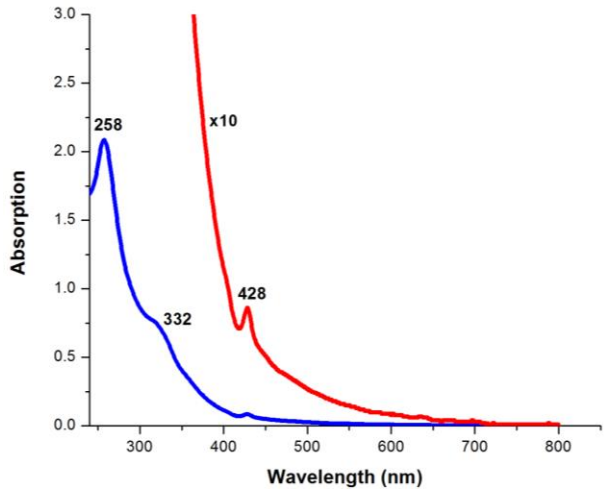


Figure S55 UV-vis absorption of compound 3b

6. CV of compounds 2a–l

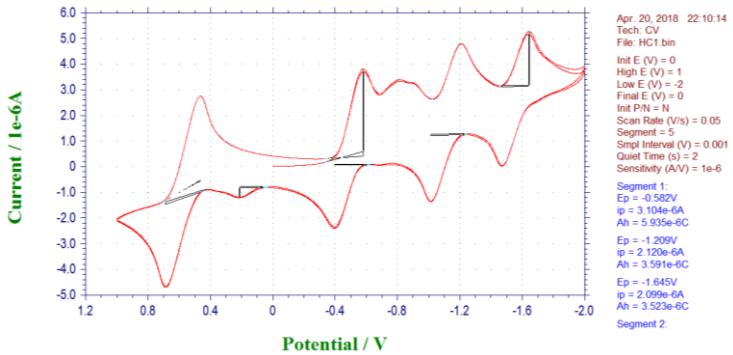


Figure S56 Cyclic voltammogram of compound 2a (scanning rate: 50 mV s^{-1})

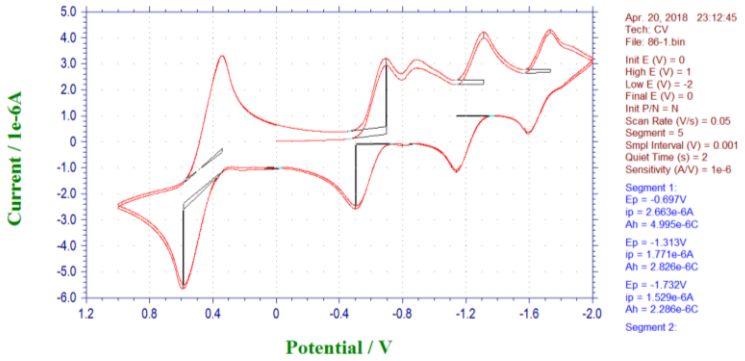


Figure S57 Cyclic voltammogram of compound 2b (scanning rate: 50 mV s^{-1})

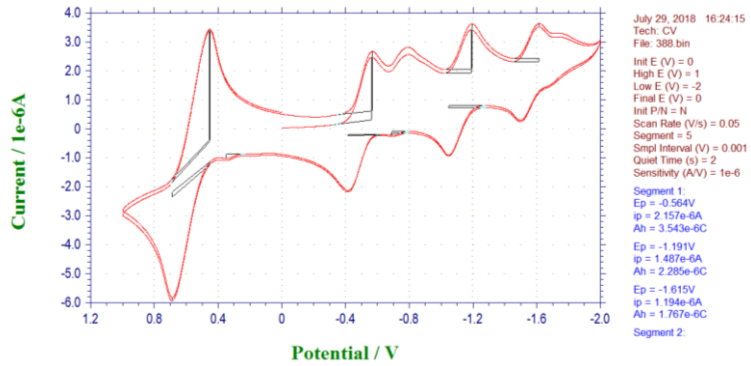


Figure S58 Cyclic voltammogram of compound 2c (scanning rate: 50 mV s^{-1})

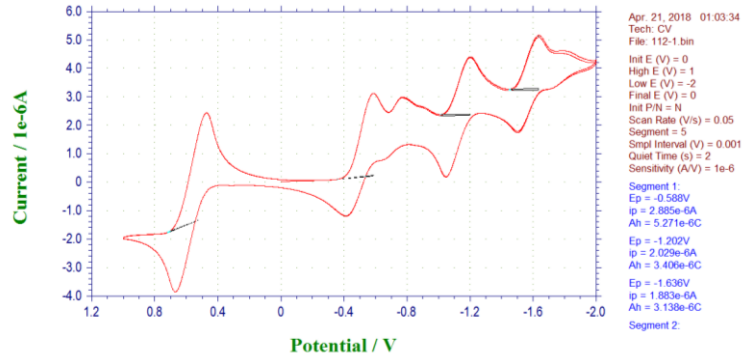


Figure S59 Cyclic voltammogram of compound 2d (scanning rate: 50 mV s^{-1})

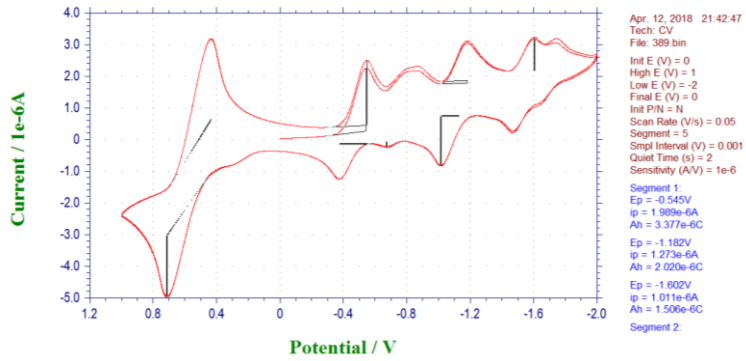


Figure S60 Cyclic voltammogram of compound 2e (scanning rate: 50 mV s^{-1})

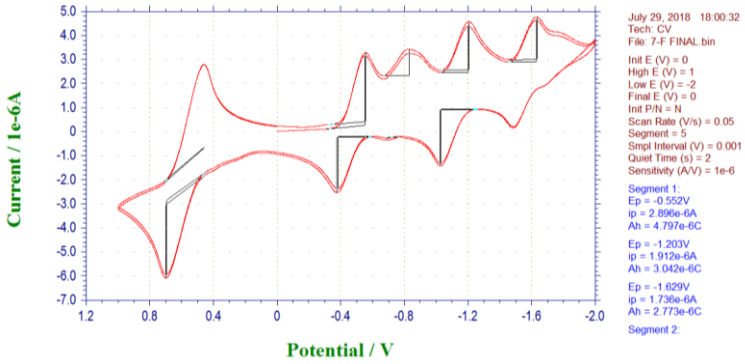


Figure S61 Cyclic voltammogram of compound 2f (scanning rate: 50 mV s^{-1})

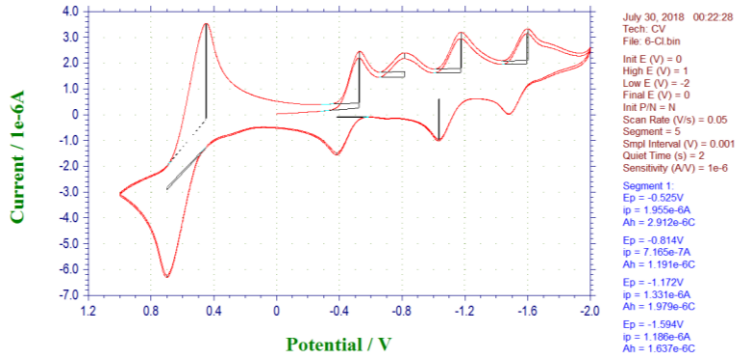


Figure S62 Cyclic voltammogram of compound 2g (scanning rate: 50 mV s^{-1})

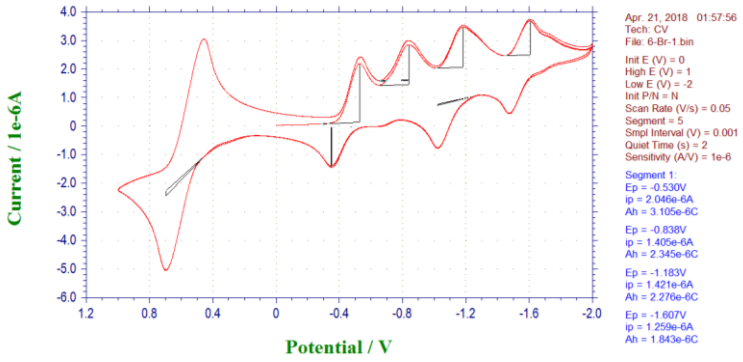


Figure S63 Cyclic voltammogram of compound 2h (scanning rate: 50 mV s^{-1})

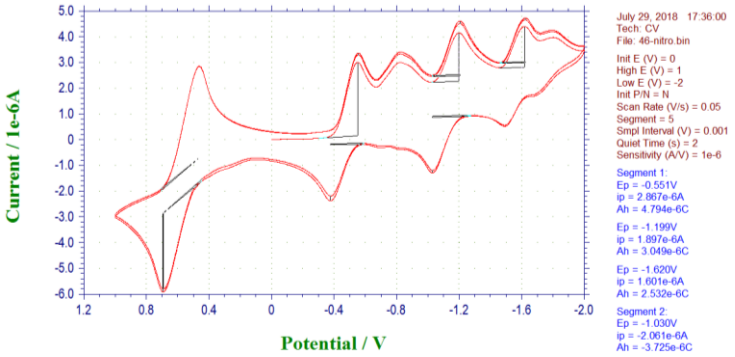


Figure S64 Cyclic voltammogram of compound 2i (scanning rate: 50 mV s^{-1})

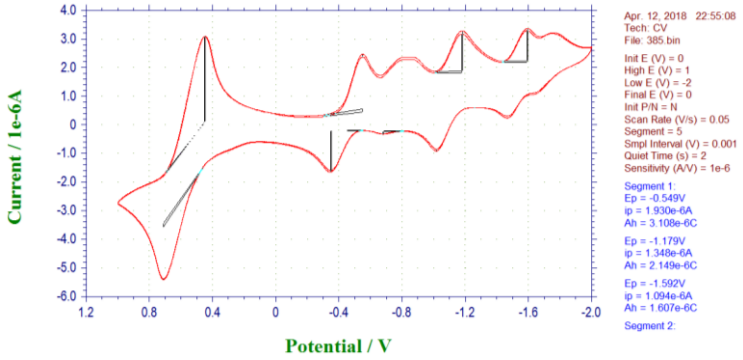


Figure S65 Cyclic voltammogram of compound 2j (scanning rate: 50 mV s^{-1})

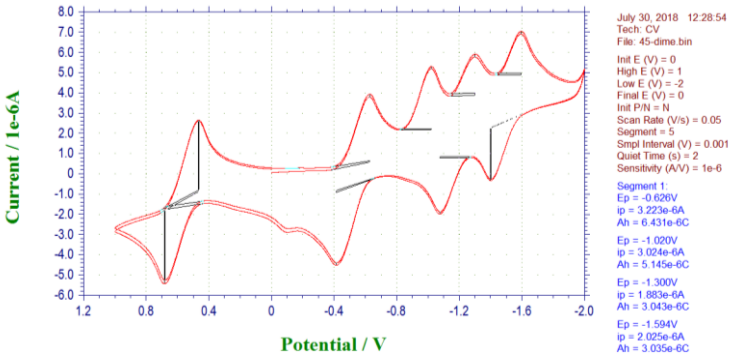


Figure S66 Cyclic voltammogram of compound 2k (scanning rate: 50 mV s^{-1})

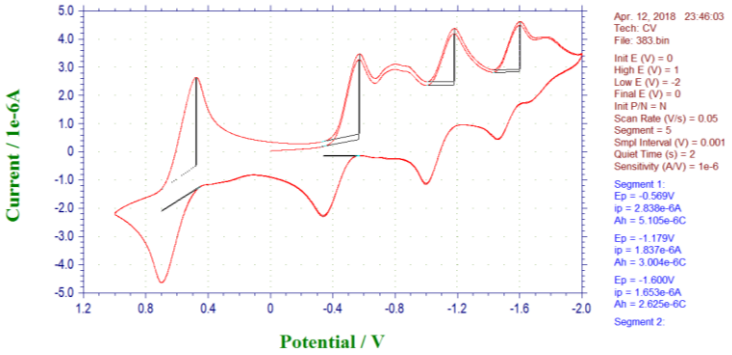


Figure S67 Cyclic voltammogram of compound 2l (scanning rate: 50 mV s^{-1})

7. X-Ray data of compound 2l

Black block crystals of **2l** were obtained by slow evaporation of a saturated solution in carbon disulfide and *n*-hexane (1:2) at 4 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 7.08° < 2θ < 142.47°. 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.

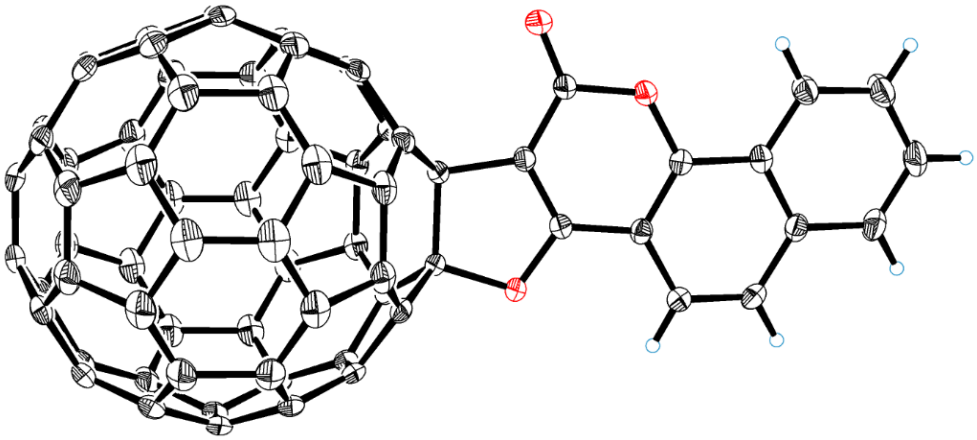


Figure S68 ORTEP diagrams of 2l with 30% thermal ellipsoids. The carbon disulfide molecule is omitted for clarity.

Table S1. Crystal data and structure refinement for 2l	
Identification code	1864794
Empirical formula	$C_{74}H_6O_3S_2$
Formula weight	1006.91
Temperature/K	291(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	18.1547(2)
b/Å	17.1668(2)
c/Å	24.9689(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7781.76(16)
Z	8
ρ_{calc}g/cm^3	1.719
μ/mm^{-1}	1.800
F(000)	4048.0
Crystal size/mm^3	0.300 × 0.270 × 0.260
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.08 to 142.474
Index ranges	$-15 \leq h \leq 21$, $-20 \leq k \leq 20$, $-21 \leq l \leq 30$
Reflections collected	19182
Independent reflections	7358 [R_{int} = 0.0210, R_{sigma} = 0.0188]
Data/restraints/parameters	7358/0/712
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.1244
Final R indexes [all data]	R_1 = 0.0548, wR_2 = 0.1291
Largest diff. peak/hole / e Å^{-3}	0.62/-0.83