Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Material

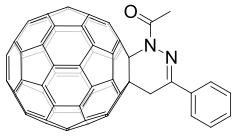
Synthesis of fullerotetrahydropyridazines *via* copper-catalyzed heteroannulation of [60]fullerene with hydrazones

Sheng-Peng Jiang,[a] Zhan Liu,[a] Wen-Qiang Lu[a] and Guan-Wu Wang*[,a,b]

[a] *CAS Key Laboratory of Soft Matter Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*
E-mail: gwang@ustc.edu.cn; Fax: +86 551 3607864; Tel: +86 551 3607864
[b] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China*

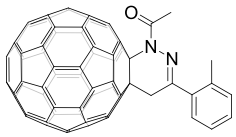
Table of contents

General procedure for the synthesis of 2a–2o from the $Cu(OAc)_2·H_2O$-catalyzed reaction of C_{60} with 1a–1o. A mixture of C_{60} (0.05 mmol), hydrazone **1** (0.15 mmol), $Cu(OAc)_2·H_2O$ (0.01 mmol), 1,10-phenanthroline (0.02 mmol) and KOAc (0.10 mmol) was dissolved in chlorobenzene (6 mL) under an open-air atmosphere. Then the solution was vigorously stirred at the desired temperature and stopped at the designated time. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column. The recovered C_{60} was firstly collected with CS_2 as the eluent. Then the eluent was changed to CS_2/CH_2Cl_2 (6:1 v/v unless specified) to give the desired product **2**.



2a

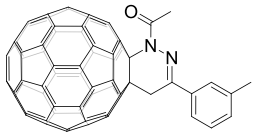
Fullerotetrahydropyridazine 2a. By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with *N*-(1-phenylethylidene)acetohydrazide **1a** (26.0 mg, 0.15 mmol), $Cu(OAc)_2·H_2O$ (2.1 mg, 0.01 mmol), 1,10-phenanthroline (3.9 mg, 0.02 mmol) and KOAc (10.2 mg, 0.10 mmol) at 120 °C for 2 h afforded recovered C_{60} (14.8 mg, 41%) and **2a** (17.0 mg, 38%) as an amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.18–8.14 (m, 2H), 7.58–7.52 (m, 3H), 4.58 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 172.24 (*C*=*O*), 168.12 (*C*=*N*), 153.02, 149.32, 147.92, 147.51, 146.46, 146.41, 146.20, 146.03, 145.97, 145.65, 145.56, 145.46, 145.33, 145.16, 144.65, 144.34, 144.20, 142.82, 142.76, 142.65, 142.54, 142.07, 141.79, 141.74, 141.73, 141.57, 140.35, 138.35, 136.21, 134.43, 134.39, 131.60, 129.09, 126.71, 78.83 (sp^3-*C* of C_{60}), 69.32 (sp^3-*C* of C_{60}), 39.11, 24.52; FT-IR ν/cm^{-1} (KBr) 2920, 2854, 1673, 1611, 1512, 1427, 1361, 1297, 1266, 1184, 1037, 811, 568, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.06), 316 (4.61), 434 (3.45); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{70}H_{10}N_2O$ $[M]^+$ 894.0788, found 894.0771.



2b

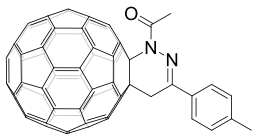
Fullerotetrahydropyridazine 2b. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(1-(*o*-tolyl)phenylethylidene)acetohydrazide **1b** (28.4 mg, 0.15 mmol), $Cu(OAc)_2·H_2O$ (1.9 mg, 0.01 mmol), 1,10-phenanthroline (3.7 mg, 0.02 mmol) and KOAc (10.5 mg, 0.10 mmol) at 120 °C for 1 h afforded recovered C_{60} (18.7 mg, 52%) and **2b** (10.7 mg, 24%) as an amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) δ 7.73 (d, *J* = 7.4 Hz, 1H), 7.45–7.30 (m, 3H), 4.55 (s, 2H), 2.84 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) δ 171.39 (*C*=*O*), 169.57 (*C*=*N*),

151.90, 148.04, 146.69, 146.26, 145.23, 145.16, 144.97, 144.81, 144.68, 144.39, 144.30, 144.23, 144.09, 143.93, 143.37, 143.08, 142.98, 141.60, 141.54, 141.38, 141.32, 140.83, 140.57, 140.50, 140.49, 140.34, 139.12, 137.11, 135.81, 134.74, 133.51, 133.09, 130.63, 129.20, 128.08, 125.24, 77.37 (sp^3-*C* of C_{60}), 68.22 (sp^3-*C* of C_{60}), 41.03, 23.66, 20.96; FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1683, 1456, 1425, 1361, 1299, 1256, 1185, 1165, 1117, 1084, 1033, 954, 878, 752, 718, 613, 570, 558, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.08), 316 (4.62), 433 (3.48); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{12}N_2O$ $[M]^+$ 908.0944, found 908.0933.



2c

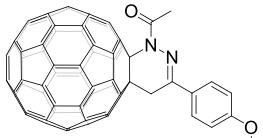
Fullerotetrahydropyridazine 2c. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(1-(*m*-tolyl)phenylethylidene)acetohydrazide **1c** (28.5 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.8 mg, 0.01 mmol), 1,10-phenanthroline (3.8 mg, 0.02 mmol) and KOAc (10.4 mg, 0.10 mmol) at 120 °C for 1 h afforded recovered C_{60} (15.6 mg, 43%) and **2c** (15.7 mg, 35%) as an amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) δ 7.98 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 4.55 (s, 2H), 2.63 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) δ 171.86 (*C*=*O*), 168.40 (*C*=*N*), 151.95, 148.11, 146.85, 146.39, 145.35, 145.26, 145.07, 144.94, 144.62, 144.51, 144.37, 144.32, 144.22, 144.06, 143.46, 143.31, 143.13, 141.71, 141.62, 141.46, 141.42, 140.96, 140.71, 140.60, 140.46, 139.21, 137.89, 137.28, 134.99, 133.38, 133.13, 131.62, 128.01, 126.11, 123.06, 77.72 (sp^3-*C* of C_{60}), 68.04 (sp^3-*C* of C_{60}), 38.08, 23.64, 20.53; FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1677, 1427, 1360, 1306, 1269, 1185, 1090, 1042, 1002, 949, 883, 782, 742, 692, 614, 556, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.05), 317 (4.62), 433 (3.45); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{12}N_2O$ $[M]^+$ 908.0944, found 908.0926.



2d

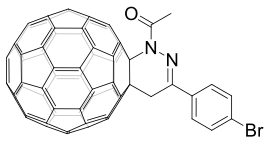
Fullerotetrahydropyridazine 2d. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(1-(*p*-tolyl)phenylethylidene)acetohydrazide **1d** (28.5 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.1 mg, 0.01 mmol), 1,10-phenanthroline (4.1 mg, 0.02 mmol) and KOAc (9.6 mg, 0.10 mmol) at 120 °C for 1 h afforded recovered C_{60} (12.7 mg, 35%) and **2d** (14.5 mg, 32%) as an amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.55 (s, 2H), 2.62 (s,

3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 172.14 (*C=O*), 168.23 (*C=N*), 153.08, 149.40, 147.89, 147.49, 146.43, 146.38, 146.18, 146.01, 145.96, 145.65, 145.52, 145.43, 145.31, 145.14, 144.64, 144.37, 144.19, 142.80, 142.74, 142.63, 142.52, 142.06, 141.98, 141.78, 141.73, 141.55, 140.31, 138.35, 136.21, 134.38, 131.71, 129.82, 126.76, 78.77 (sp^3-*C* of C_{60}), 69.25 (sp^3-*C* of C_{60}), 39.01, 24.48, 21.70; FT-IR ν/cm^{-1} (KBr) 2926, 2855, 1677, 1605, 1510, 1459, 1423, 1361, 1301, 1252, 1174, 1116, 1026, 827, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.06), 315 (4.63), 434 (3.47); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{12}N_2O$ $[M]^+$ 908.0944, found 908.0958.



2e

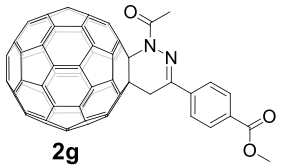
Fullerotetrahydropyridazine 2e. By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(1-(4-methoxyphenyl)ethylidene)acetohydrazide **1e** (30.1 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (3.9 mg, 0.02 mmol) and KOAc (10.1 mg, 0.10 mmol) at 120 °C for 1 h afforded recovered C_{60} (11.2 mg, 31%) and **2e** (15.0 mg, 33%) as an amorphous brown solid with CS_2/CH_2Cl_2 (4:1, v/v) as the eluent for silica gel column purification; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 4.54 (s, 2H), 3.89 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 171.97 (*C=O*), 167.86 (*C=N*), 162.47, 153.11, 149.47, 147.89, 147.51, 146.43, 146.39, 146.19, 146.02, 145.96, 145.65, 145.52, 145.44, 145.32, 145.15, 144.66, 144.39, 144.19, 142.81, 142.75, 142.64, 142.52, 142.07, 141.78, 141.74, 141.55, 140.30, 138.38, 136.25, 134.36, 128.38, 126.86, 114.48, 78.74 (sp^3-*C* of C_{60}), 69.18 (sp^3-*C* of C_{60}), 55.09, 38.93, 24.44; FT-IR ν/cm^{-1} (KBr) 2925, 2854, 1718, 1671, 1513, 1430, 1359, 1301, 1268, 1186, 1109, 956, 872, 770, 609, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.08), 316 (4.71), 433 (3.53); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{12}N_2O_2$ $[M]^+$ 924.0893, found 924.0881.



2f

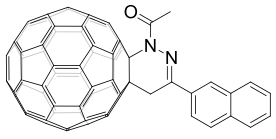
Fullerotetrahydropyridazine 2f. By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with *N*-(1-(4-bromophenyl)ethylidene)acetohydrazide **1f** (38.1 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.1 mg, 0.01 mmol), 1,10-phenanthroline (3.9 mg, 0.02 mmol) and KOAc (9.6 mg, 0.10 mmol) at 120 °C for 2 h afforded recovered C_{60} (9.4 mg, 26%) and **2f** (13.9 mg, 29%) as an amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 4.56 (s, 2H), 2.62 (s, 3H); ^{13}C

NMR (100 MHz, $CS_2/CDCl_3$) δ 172.24 (*C*=*O*), 166.99 (*C*=*N*), 152.78, 149.13, 147.91, 147.51, 146.46, 146.41, 146.21, 146.04, 145.90, 145.60, 145.57, 145.47, 145.33, 145.16, 144.63, 144.20, 144.18, 142.82, 142.77, 142.63, 142.55, 142.03, 141.78, 141.73, 141.67, 141.57, 140.36, 138.33, 136.16, 134.34, 133.22, 132.38, 128.01, 126.92, 78.88 (sp^3-*C* of C_{60}), 69.31 (sp^3-*C* of C_{60}), 38.98, 24.52; FT-IR ν/cm^{-1} (KBr) 2925, 2854, 1684, 1631, 1577, 1511, 1466, 1426, 1366, 1295, 1266, 1040, 783, 731, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.11), 316 (4.69), 433 (3.51); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{70}H_9N_2O^{79}Br$ $[M]^+$ 971.9893, found 971.9880.



2g

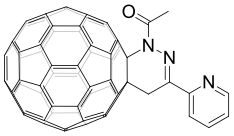
Fullerotetrahydropyridazine 2g. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(1-(4-methoxycarbonylphenyl)ethylidene)acetohydrazide **1g** (35.0 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (3.7 mg, 0.02 mmol) and KOAc (9.8 mg, 0.10 mmol) at 120 °C for 1 h afforded recovered C_{60} (14.8 mg, 41%) and **2g** (14.5 mg, 31%) as an amorphous brown solid with CS_2/CH_2Cl_2 (4:1, v/v) as the eluent for silica gel column purification; ^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) δ 8.22 (d, *J* = 8.2 Hz, 2H), 8.18 (d, *J* = 8.2 Hz, 2H), 4.59 (s, 2H), 3.92 (s, 3H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) δ 172.07 (*C*=*O*), 166.69 (*C*=*N*), 164.80 (*C*=*O*), 151.83, 148.04, 147.01, 146.55, 145.54, 145.45, 145.26, 145.11, 144.80, 144.64, 144.59, 144.52, 144.39, 144.23, 143.62, 143.29, 143.27, 141.88, 141.82, 141.64, 141.61, 141.08, 140.86, 140.76, 140.72, 140.64, 139.44, 137.38, 137.20, 135.12, 133.49, 131.76, 129.36, 125.73, 78.08 (sp^3-*C* of C_{60}), 68.36 (sp^3-*C* of C_{60}), 51.31, 38.26, 23.84; FT-IR ν/cm^{-1} (KBr) 2923, 2854, 1675, 1587, 1512, 1427, 1362, 1308, 1292, 1263, 1071, 988, 610, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.04), 316 (4.63), 433 (3.42); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{72}H_{12}N_2O_3$ $[M]^+$ 952.0842, found 952.0823.



2h

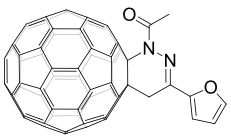
Fullerotetrahydropyridazine 2h. By following the general procedure, the reaction of C_{60} (35.6 mg, 0.05 mmol) with *N*-(1-(naphthalene-2-yl)ethylidene)acetohydrazide **1h** (34.2 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.9 mg, 0.01 mmol), 1,10-phenanthroline (3.9 mg, 0.02 mmol) and KOAc (10.0 mg, 0.10 mmol) at 120 °C for 2 h afforded recovered C_{60} (10.7 mg, 30%) and **2h** (17.2 mg, 37%) as an amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.52 (s, 1H), 8.45 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H),

7.97 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.62–7.53 (m, 2H), 4.73 (s, 2H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 172.55 (*C*=*O*), 168.09 (*C*=*N*), 153.04, 149.31, 147.94, 147.53, 146.48, 146.41, 146.22, 146.05, 145.94, 145.67, 145.57, 145.49, 145.34, 145.18, 144.65, 144.41, 144.22, 142.83, 142.78, 142.66, 142.56, 142.10, 141.82, 141.77, 141.75, 141.59, 140.37, 138.40, 136.24, 134.86, 134.46, 132.98, 131.69, 129.14, 128.98, 127.97, 127.94, 127.59, 127.06, 123.04, 78.96 (sp^3-*C* of C_{60}), 69.26 (sp^3-*C* of C_{60}), 38.93, 24.70; FT-IR ν/cm^{-1} (KBr) 2922, 2854, 1674, 1506, 1424, 1361, 1299, 1264, 1168, 1083, 1046, 763, 729, 691, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.10), 315 (4.68), 434 (3.43); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{74}H_{12}N_2O$ $[M]^+$ 944.0944, found 944.0959.



2i

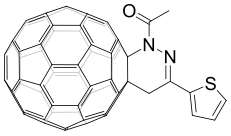
Fullerotetrahydropyridazine 2i. By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with *N*-(1-(pyridin-2-yl)ethylidene)acetohydrazide **1i** (26.2 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (4.3 mg, 0.02 mmol) and KOAc (10.0 mg, 0.10 mmol) at 100 °C for 2 h afforded recovered C_{60} (10.4 mg, 29%) and **2i** (16.1 mg, 36%) as an amorphous brown solid with CS_2/CH_2Cl_2 (4:1, v/v) as the eluent for silica gel column purification; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.73 (ddd, *J* = 4.8, 1.6, 0.9 Hz, 1H), 8.56 (ddd, *J* = 7.8, 1.1, 0.9 Hz, 1H), 7.92 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 7.48 (ddd, *J* = 7.8, 4.8, 1.1 Hz, 1H), 4.89 (s, 2H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 172.54 (*C*=*O*), 168.66 (*C*=*N*), 153.67, 151.85, 149.52, 149.28, 147.96, 147.47, 146.50, 146.38, 146.20, 146.05, 146.00, 145.68, 145.59, 145.42, 145.30, 145.18, 144.68, 144.56, 144.30, 142.80, 142.73, 142.61, 142.55, 142.11, 141.88, 141.72, 141.67, 141.59, 140.38, 138.24, 136.56, 135.74, 134.57, 125.57, 120.59, 79.09 (sp^3-*C* of C_{60}), 69.26 (sp^3-*C* of C_{60}), 36.50, 24.75; FT-IR ν/cm^{-1} (KBr) 2921, 2854, 1678, 1508, 1426, 1360, 1299, 1187, 1167, 1129, 855, 818, 744, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.08), 315 (4.67), 434 (3.50); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{69}H_9N_3O$ $[M]^+$ 895.0740, found 895.0724.



2j

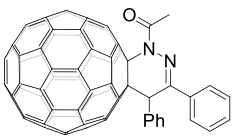
Fullerotetrahydropyridazine 2j. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with *N*-(1-(furan-2-yl)ethylidene)acetohydrazide **1j** (24.9 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.1 mg, 0.01 mmol), 1,10-phenanthroline (4.0 mg, 0.02 mmol) and KOAc (9.5 mg, 0.10 mmol) at 100 °C for 3 h afforded recovered C_{60} (18.4 mg, 51%) and **2j** (7.7 mg,

17%) as an amorphous brown solid with CS_2/CH_2Cl_2 (4:1, v/v) as the eluent for silica gel column purification; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.71 (d, J = 1.7 Hz, 1H), 7.32 (d, J = 3.5 Hz, 1H), 6.68 (dd, J = 3.5, 1.7 Hz, 1H), 4.53 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 172.32 (*C*=*O*), 159.82 (*C*=*N*), 152.94, 149.26, 149.23, 147.97, 147.58, 146.51, 146.46, 146.25, 146.09, 145.87, 145.71, 145.60, 145.52, 145.38, 145.22, 144.69, 144.42, 144.25, 142.86, 142.81, 142.69, 142.59, 142.10, 141.86, 141.80, 141.74, 141.62, 140.35, 138.42, 136.25, 134.44, 113.34, 112.79, 79.17 (sp^3-*C* of C_{60}), 68.87 (sp^3-*C* of C_{60}), 38.42, 24.53; FT-IR ν/cm^{-1} (KBr) 2922, 1674, 1425, 1362, 1295, 1168, 1111, 1047, 905, 728, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.09), 316 (4.61), 434 (3.51); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{68}H_8N_2O_2$ $[M]^+$ 884.0580, found 884.0565.



2k

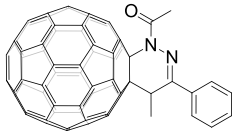
Fullerotetrahydropyridazine 2k. By following the general procedure, the reaction of C_{60} (35.8 mg, 0.05 mmol) with *N*-(1-(thiophen -2-yl)ethylidene)acetohydrazide **1k** (27.7 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.2 mg, 0.01 mmol), 1,10-phenanthroline (4.2 mg, 0.02 mmol) and KOAc (9.7 mg, 0.10 mmol) at 120 ºC for 3.5 h afforded recovered C_{60} (20.2 mg, 56%) and **2k** (6.2 mg, 14%) as an amorphous brown solid with CS_2/CH_2Cl_2 (4:1, v/v) as the eluent for silica gel column purification; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.73 (d, J = 3.8, 0.8 Hz, 1H), 7.59 (d, J = 5.0, 0.8 Hz, 1H), 7.19 (J = 5.0, 3.8 Hz, 1H), 4.56 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 171.77 (*C*=*O*), 163.76 (*C*=*N*), 151.90, 148.16, 146.98, 146.51, 145.44, 145.37, 145.18, 145.06, 144.67, 144.60, 144.44, 144.41, 144.34, 144.17, 143.56, 143.39, 143.23, 141.82, 141.71, 141.55, 141.52, 141.06, 140.82, 140.73, 140.68, 140.56, 139.29, 137.39, 135.08, 133.50, 130.42, 129.19, 127.45, 78.09 (sp^3-*C* of C_{60}), 67.71 (sp^3-*C* of C_{60}), 39.02, 23.74; FT-IR ν/cm^{-1} (KBr) 2920, 1670, 1513, 1435, 1367, 1299, 1167, 1063, 953, 876, 855, 763, 703, 558, 527; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.01), 317 (4.61), 434 (3.40); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{68}H_8N_2OS$ $[M]^+$ 900.0352, found 900.0353.



2l

Fullerotetrahydropyridazine 2l. By following the general procedure, the reaction of C_{60} (36.2 mg, 0.05 mmol) with *N*-(1,2-diphenylethylidene)acetohydrazide **1l** (37.2 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.9 mg, 0.01 mmol), 1,10-phenanthroline (4.1 mg, 0.02 mmol) and KOAc (10.5 mg, 0.10 mmol) at 120 ºC for 1.5 h afforded recovered C_{60} (20.7 mg, 57%) and **2l** (16.2 mg, 33%) as an amorphous brown solid;

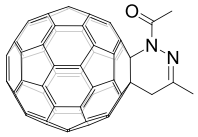
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.09 (d, J = 7.1 Hz, 1H), 7.86 (d, J = 7.1 Hz, 1H), 7.56–7.46 (m, 3H), 7.46–7.35 (m, 3H), 6.04 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) δ 171.13 (*C*=*O*), 167.25 (*C*=*N*), 151.13, 150.93, 149.03, 147.85, 147.56, 147.48, 146.46, 146.36, 146.31, 145.26, 146.09, 145.98, 145.75, 145.69, 145.60, 145.38, 145.29, 145.22, 144.90, 144.82, 144.71, 144.55, 144.30, 144.23, 144.01, 143.61, 142.95, 142.70, 142.67, 142.65, 142.57, 142.51, 142.40, 141.86, 141.72, 141.63, 141.60, 141.51, 141.49, 141.40, 141.34, 140.16, 139.97, 139.02, 137.63, 137.35, 135.44, 135.03, 134.92, 134.49, 133.72, 131.26, 129.81, 129.01, 128.86, 128.41, 126.92, 81.78 (sp^3-*C* of C_{60}), 71.62 (sp^3-*C* of C_{60}), 53.72, 24.35; (*It should be noted that the low solubility of* ***2k*** *prevented us from obtaining a* ^{13}*C NMR spectrum with a good signal-to-noise ratio at –60* °C); FT-IR ν/cm^{-1} (KBr) 2923, 1675, 1493, 1425, 1364, 1291, 1185, 1161, 1077, 1027, 953, 899, 765, 745, 692, 569, 610, 569, 554, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.09), 318 (4.67), 434 (3.48); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{76}H_{14}N_2O$ $[M]^+$ 970.1101, found 970.1124.



2m

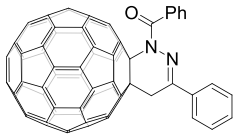
Fullerotetrahydropyridazine 2m. By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with *N*-(1-phenylpropylidene)acetohydrazide **1m** (27.8 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (5.0 mg, 0.025 mmol), 1,10-phenanthroline (9.7 mg, 0.05 mmol) and KOAc (10.3 mg, 0.10 mmol) at 140 °C for 0.5 h afforded recovered C_{60} (13.6 mg, 38%) and **2m** (12.2 mg, 27%) as an amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.12 (d, J = 5.9 Hz, 2H), 7.59–7.50 (m, 3H), 4.81 (q, J = 7.1 Hz, 1H), 2.60 (s, 3H), 2.36 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) δ 170.97 (*C*=*O*), 170.31 (*C*=*N*), 155.50, 150.83, 150.51, 149.44, 147.84, 147.45, 146.44, 146.37, 146.33, 146.27, 146.08, 145.96, 145.77, 145.75, 145.60, 145.42, 145.36, 145.31, 145.23, 144.91, 144.89, 144.66, 144.53, 144.27, 143.97, 142.97, 142.68, 142.63, 142.54, 142.52, 142.49, 142.36, 141.92, 141.89, 141.87, 141.83, 141.81, 141.68, 141.54, 141.52, 141.35, 141.22, 140.37, 140.04, 139.14, 137.46, 137.25, 135.19, 134.92, 134.55, 133.38, 131.44, 129.01, 126.41, 80.80 (sp^3-*C* of C_{60}), 71.11 (sp^3-*C* of C_{60}), 42.99, 24.28, 16.36; ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 213.1 K) δ 171.75 (*C*=*O*), 170.81 (*C*=*N*), 154.88, 150.19, 149.94, 148.59, 147.42, 147.00, 146.65, 146.05, 145.94, 145.85, 145.68, 145.54, 145.37, 145.30, 145.25, 145.03, 144.92, 144.84, 144.55, 144.48, 144.17, 144.06, 143.87, 143.53, 143.51, 143.48, 142.57, 142.26, 142.24, 142.17, 142.12, 142.03, 141.95, 141.47, 141.40, 141.28, 141.16, 141.02, 140.82, 140.00, 139.63, 138.89, 137.05, 137.01, 134.60, 133.66, 133.02, 131.67, 128.86, 126.12, 76.15 (sp^3-*C* of C_{60}), 70.23 (sp^3-*C* of C_{60}), 42.51, 24.82, 16.08; FT-IR ν/cm^{-1} (KBr) 2926, 1670, 1509, 1444, 1425, 1382, 1360, 1313, 1299, 1251, 1185, 1164, 989, 959, 768, 689, 646, 610, 570, 552, 526; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.08), 316 (4.64), 434 (3.50);

HRMS (MALDI-TOF) *m*/*z* calcd for $C_{71}H_{12}N_2O$ $[M]^+$ 908.0944, found 908.0926.



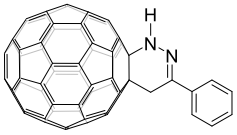
2n

Fullerotetrahydropyridazine 2n. By following the general procedure, the reaction of C_{60} (35.7 mg, 0.05 mmol) with *N*-(propan-2-ylidene)acetohydrazide **1n** (17.2 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (4.1 mg, 0.02 mmol) and KOAc (9.7 mg, 0.10 mmol) at 120 °C for 2 h afforded recovered C_{60} (11.1 mg, 31%) and **2n** (3.1 mg, 8%) as an amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 4.12 (s, 2H), 2.71 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 171.31 (*C*=*O*), 170.87 (*C*=*N*), 152.98, 149.36, 147.85, 147.50, 146.40, 146.17, 146.01, 145.92, 145.62, 145.49, 145.43, 145.31, 145.12, 144.63, 144.31, 144.15, 142.81, 142.73, 142.61, 142.51, 142.05, 141.74, 141.69, 141.53, 140.25, 138.34, 136.11, 134.20, 78.09 (sp^3-*C* of C_{60}), 68.78 (sp^3-*C* of C_{60}), 42.05, 24.23, 23.69; FT-IR ν/cm^{-1} (KBr) 2924, 1662, 1509, 1424, 1383, 1361, 1311, 1175, 960, 863, 763, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.07), 316 (4.59), 434 (3.48); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{65}H_8N_2O$ $[M]^+$ 832.0631, found 832.0648.



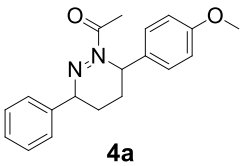
2o

Fullerotetrahydropyridazine 2o. By following the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with *N*-(1-phenylethylidene)benzohydrazide **1o** (35.3 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.9 mg, 0.01 mmol), 1,10-phenanthroline (3.8 mg, 0.02 mmol) and KOAc (9.8 mg, 0.10 mmol) at 120 °C for 2 h afforded recovered C_{60} (11.1 mg, 31%) and **2o** (19.2 mg, 40%) as an amorphous brown solid; ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.99–7.94 (m, 2H), 7.81–7.76 (m, 2H), 7.53–7.40 (m, 6H), 4.71 (s, 2H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 171.28 (*C*=*O*), 167.81 (*C*=*N*), 153.18, 148.53, 147.93, 147.52, 146.62, 146.54, 146.50, 146.26, 146.06, 145.78, 145.70, 145.49, 145.34, 145.25, 144.69, 144.32, 144.27, 142.84, 142.79, 142.75, 142.61, 142.12, 141.85, 141.76, 141.68, 141.62, 140.46, 138.11, 136.48, 136.18, 135.08, 134.26, 131.52, 130.71, 129.59, 129.05, 127.64, 126.80, 79.95 (sp^3-*C* of C_{60}), 69.25 (sp^3-*C* of C_{60}), 39.32; FT-IR ν/cm^{-1} (KBr) 2923, 1661, 1508, 1439, 1424, 1361, 1296, 1267, 1180, 1150, 904, 763, 729, 691, 524; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.14), 317 (4.69), 434 (3.51); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{75}H_{12}N_2O$ $[M]^+$ 956.0944, found 956.0961.



3

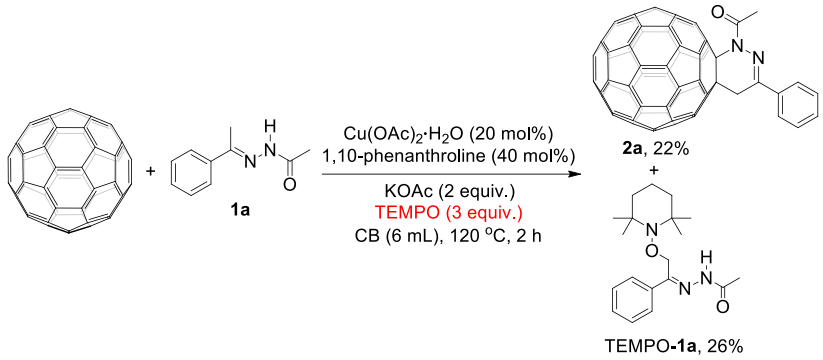
Fullerotetrahydropyridazine 3. The reaction mixture of **2a** (8.9 mg, 0.01 mmol) with TfOH (3.6 μL, 0.04 mmol) in chlorobenzene (2 mL) at 15 °C for 5 min afforded **3** (7.1 mg, 84%) as an amorphous brown solid. Similarly, the reaction mixture of **2n** (9.6 mg, 0.01 mmol) with TfOH (3.6 μL, 0.04 mmol) in chlorobenzene (2 mL) at 15 °C for 5 min afforded **3** (4.8 mg, 56%) as an amorphous brown solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 8.04–7.98 (m, 2H), 7.49 (s, 1H), 7.48–7.42 (m, 3H), 4.49 (s, 2H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) δ 161.27 (*C*=*N*), 153.73, 150.41, 147.86, 147.50, 146.40, 146.39, 146.05, 146.02, 145.91, 145.45, 145.19, 145.18, 144.55, 144.53, 144.48, 144.45, 142.83, 142.55, 142.48, 142.26, 142.14, 141.97, 141.94, 141.79, 141.49, 140.17, 139.97, 136.81, 136.23, 136.02, 129.75, 128.68, 125.74, 78.43 (sp^3-*C* of C_{60}), 66.56 (sp^3-*C* of C_{60}), 36.82; FT-IR ν/cm^{-1} (KBr) 2920, 1510, 1424, 1350, 1178, 1062, 1001, 965, 946, 881, 832, 805, 746, 689, 557, 525; UV-vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.05), 318 (4.59), 433 (3.41); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{68}H_8N_2$ $[M]^+$ 852.0682, found 852.0676.



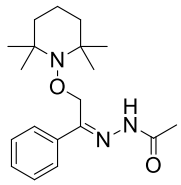
4a

Preparation of 4a. A mixture of *N*-(1-phenylethylidene)acetohydrazide **1a** (70.4 mg, 0.40 mmol), 4-methoxystyrene (160.8 μL, 1.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (7.9 mg, 0.04 mmol), 1,10-phenanthroline (15.8 mg, 0.08 mmol) and KOAc (39.2 mg, 0.40 mmol) in chlorobenzene (6 mL) was heated at 120 °C for 6 h. Then the reaction mixture was cooled to room temperature and most of the solvent was evaporated in *vacuo*. The residue was purified by column chromatography (SiO_2, PE/EtOAc = 3:1) to afford **4a** as colorless oil (45.7 mg, 37%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.44–7.33 (m, 3H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.89 (s, 1H), 3.74 (s, 3H), 2.67–2.59 (m, 1H), 2.54 (s, 3H), 2.28–2.03 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (*C*=*O*), 158.7 (*C*=*N*), 146.7, 137.4, 132.2, 129.3, 128.5, 126.6, 125.3, 114.1, 55.3, 50.3, 23.9, 21.7, 18.7; HRMS (MALDI-TOF) *m*/*z* calcd for $C_{19}H_{21}N_2O_2$ $[M + H]^+$ 309.1598, found 309.1596.

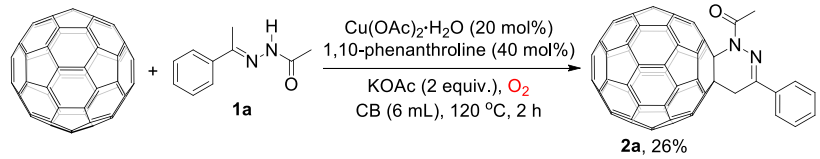
Control experiments.



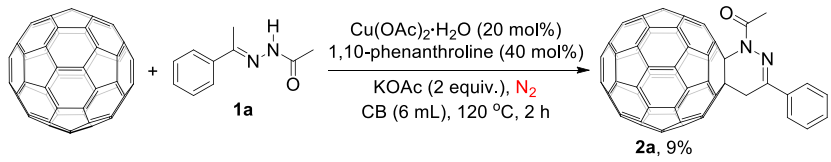
A mixture of C_{60} (36.7 mg, 0.05 mmol), *N*-(1-phenylethylidene)acetohydrazide **1a** (26.7 mg, 0.15 mmol), $Cu(OAc)_2·H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (3.9 mg, 0.02 mmol), KOAc (10.5 mg, 0.10 mmol) and TEMPO (22.3 mg, 0.15 mmol) was dissolved in chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 °C for 2 h. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (22.4 mg, 61%) and then **2a** (10.2 mg, 22%) with CS_2/CH_2Cl_2 (6:1 v/v) as the eluent. Finally, TEMPO-**1a** was separated out using PE/EtOAc = 4:1 as the eluent.



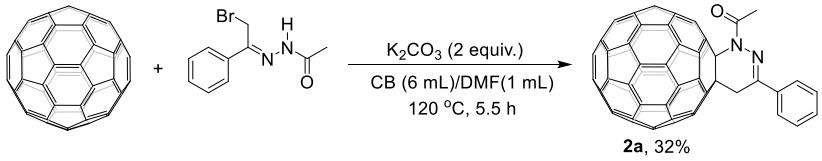
TEMPO–**1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.72–7.66 (m, 2H), 7.41–7.34 (m, 3H), 5.02 (s, 2H), 2.37 (s, 3H), 1.63–1.47 (m, 5H), 1.41–1.31 (m, 1H), 1.22 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 145.4, 136.3, 129.4, 128.6, 126.3, 75.5, 60.4, 39.8, 33.1, 20.6, 20.2, 17.0; HRMS (MALDI-TOF) *m*/*z* calcd for $C_{19}H_{30}N_3O_2$ $[M + H]^+$ 332.2333, found 332.2337.



A mixture of C_{60} (35.9 mg, 0.05 mmol), *N*-(1-phenylethylidene)acetohydrazide **1a** (26.5 mg, 0.15 mmol), $Cu(OAc)_2·H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (4.2 mg, 0.02 mmol), KOAc (10.4 mg, 0.10 mmol) was dissolved in chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 °C for 2 h under an oxygen atmosphere. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (19.4 mg, 54%) and then **2a** (11.7 mg, 26%) with CS_2/CH_2Cl_2 (6:1 v/v) as the eluent.



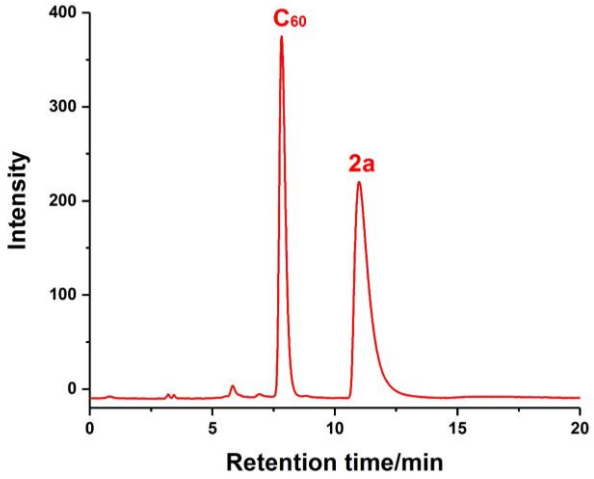
A mixture of C_{60} (36.2 mg, 0.05 mmol), *N*-(1-phenylethylidene)acetohydrazide **1a** (26.0 mg, 0.15 mmol), $Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), 1,10-phenanthroline (4.0 mg, 0.02 mmol), KOAc (9.7 mg, 0.10 mmol) was dissolved in chlorobenzene (6 mL). Then the solution was vigorously stirred at 120 °C for 2 h under a nitrogen atmosphere. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (26.2 mg, 72%) and then **2a** (4.1 mg, 9%) with CS_2/CH_2Cl_2 (6:1 v/v) as the eluent.



A mixture of C_{60} (36.0 mg, 0.05 mmol), *N*-(2-bromo-1-phenylethylidene)acetohydrazide (30.4 mg, 0.15 mmol), K_2CO_3 (13.6 mg, 0.10 mmol) was dissolved in a mixture of chlorobenzene (6 mL) and DMF (1 mL). Then the solution was vigorously stirred at 120 °C for 5.5 h under an open-air atmosphere. The resulting solution was evaporated in *vacuo*, and the residue was then separated on a silica gel column with CS_2 as the eluent to give the recovered C_{60} (20.2 mg, 56%) and then **2a** (14.1 mg, 32%) with CS_2/CH_2Cl_2 (6:1 v/v) as the eluent.

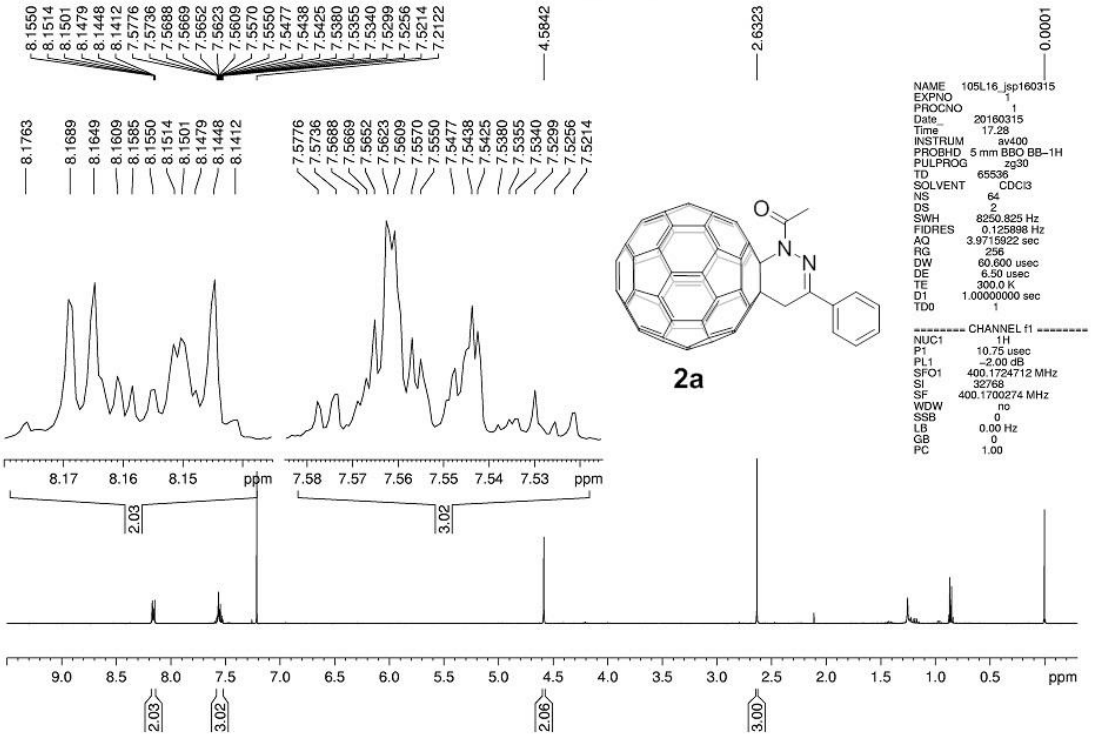
HPLC chart for the reaction mixture of C_{60} with 1a

The HPLC chart for the reaction mixture of C_{60} with **1a** under the optimized conditions on a Cosmosil Buckyprep column (4.6 × 250 mm) using toluene as the eluent is shown below.

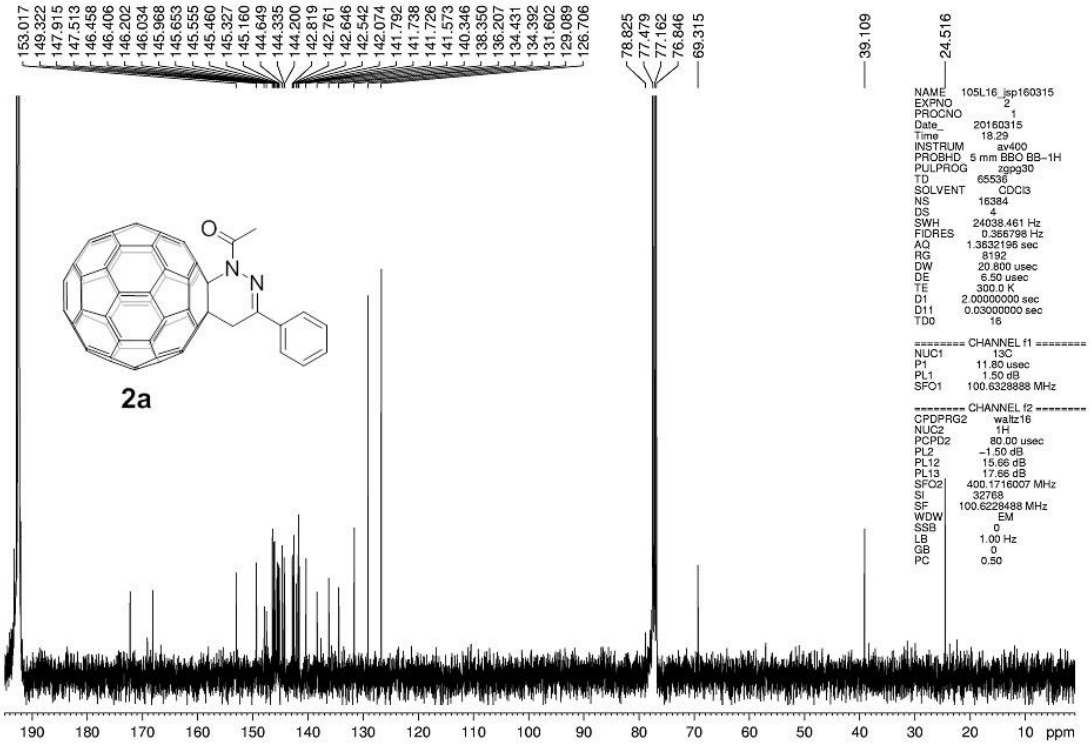


HPLC chart for the formation of **2a**

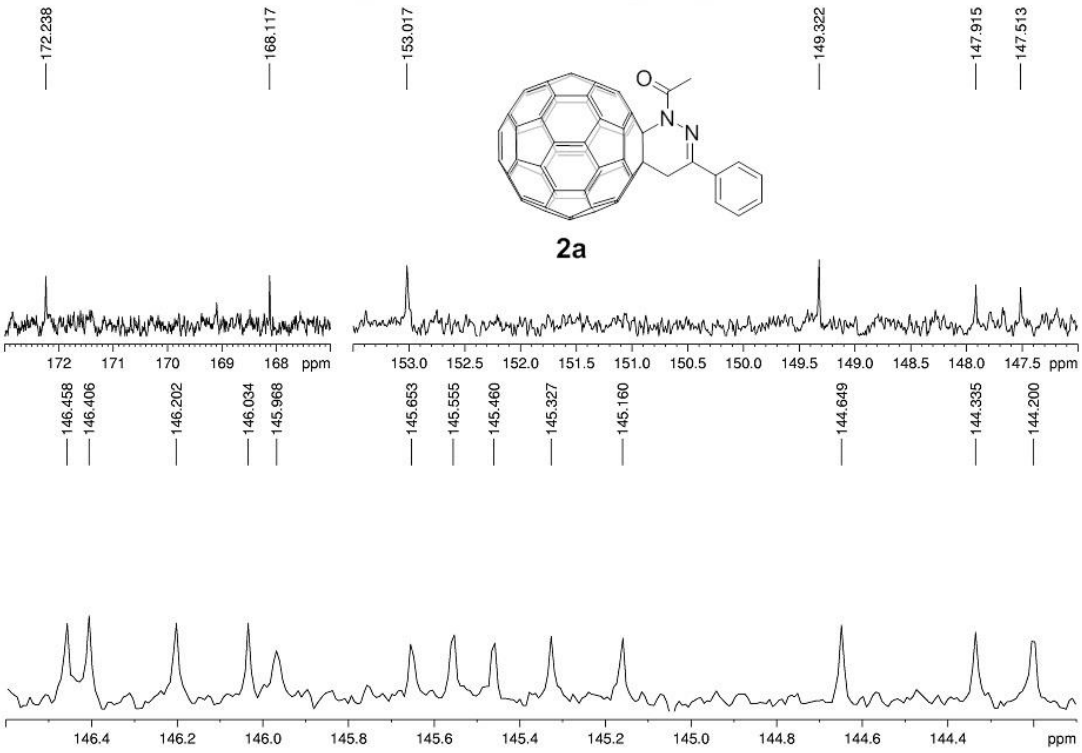
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2a



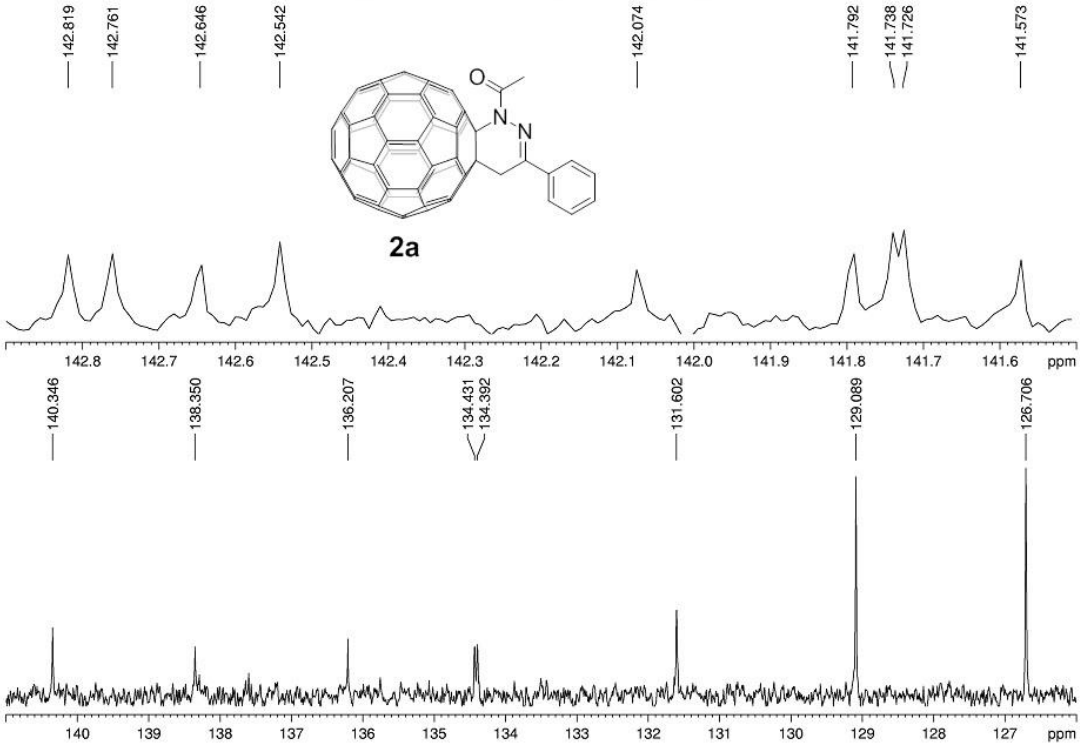
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2a



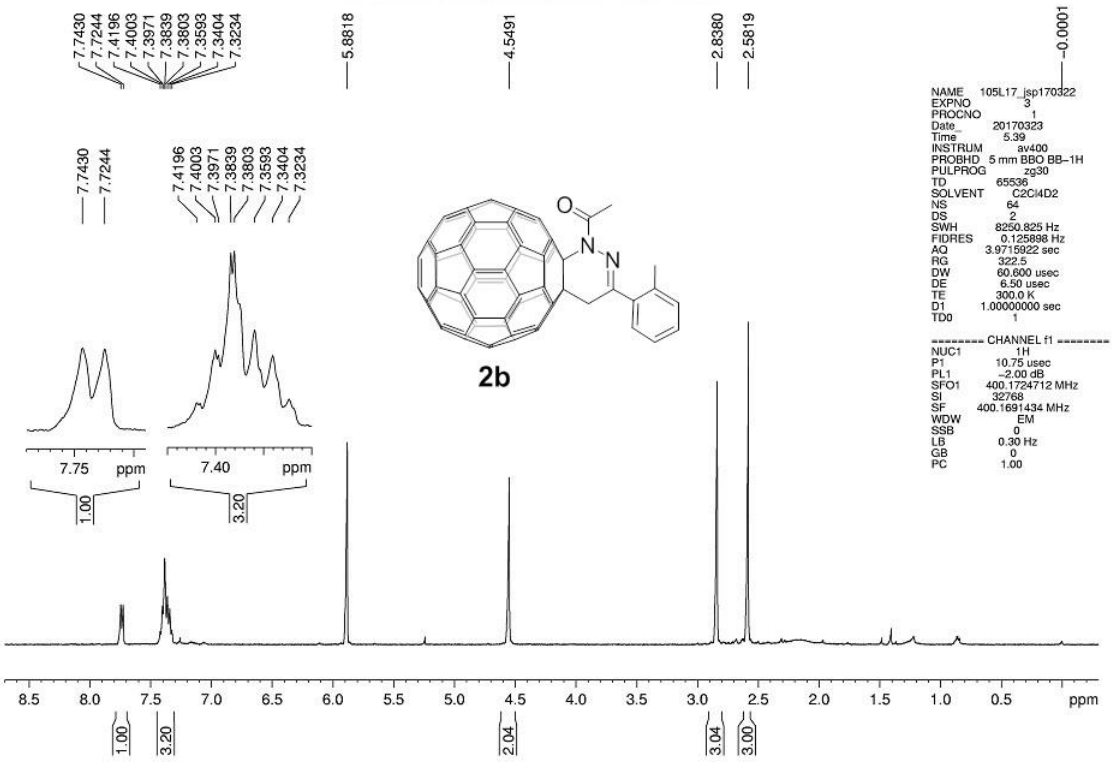
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2a



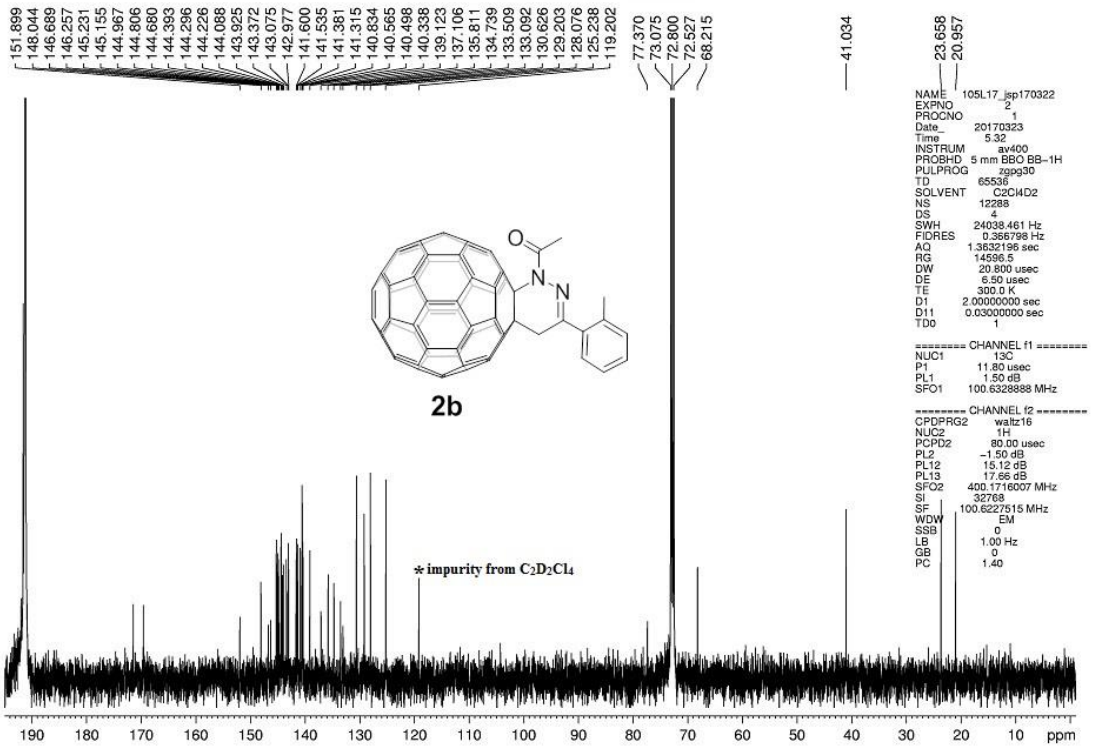
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2a



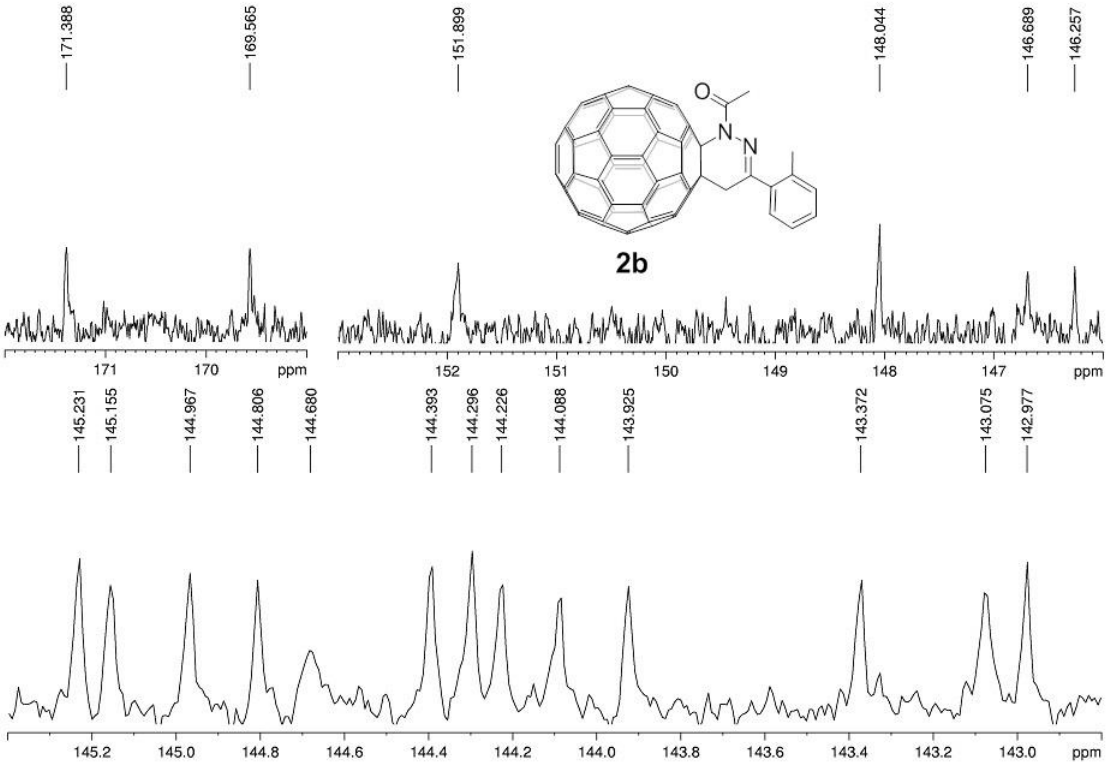
^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2b



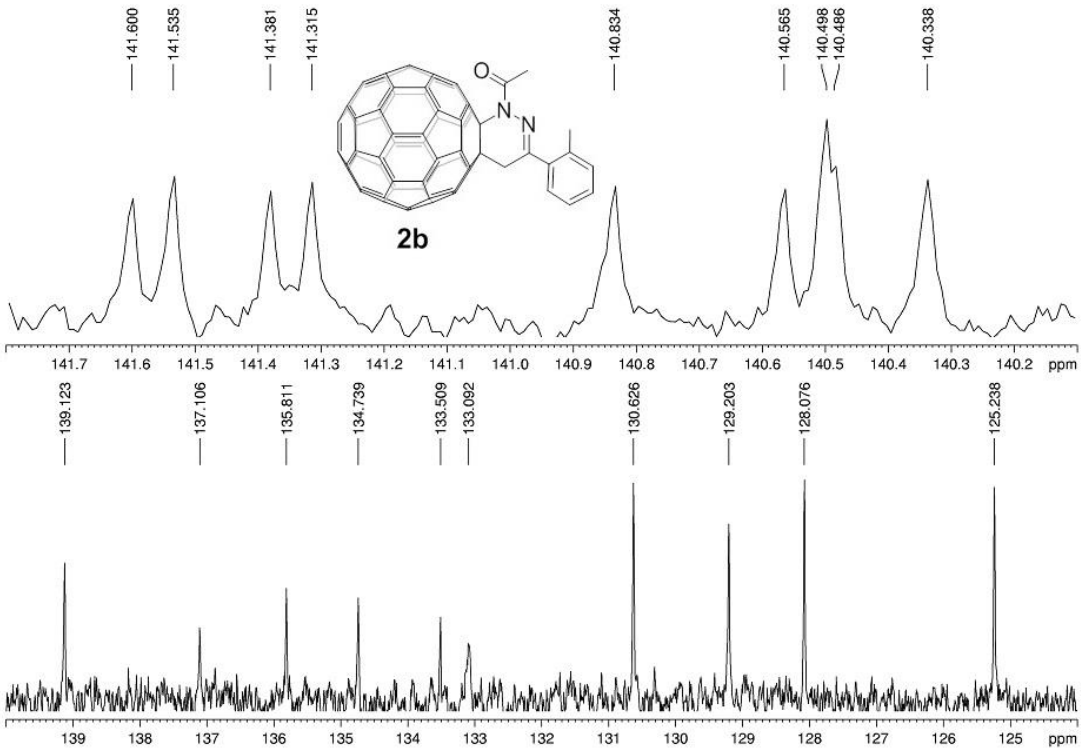
^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2b



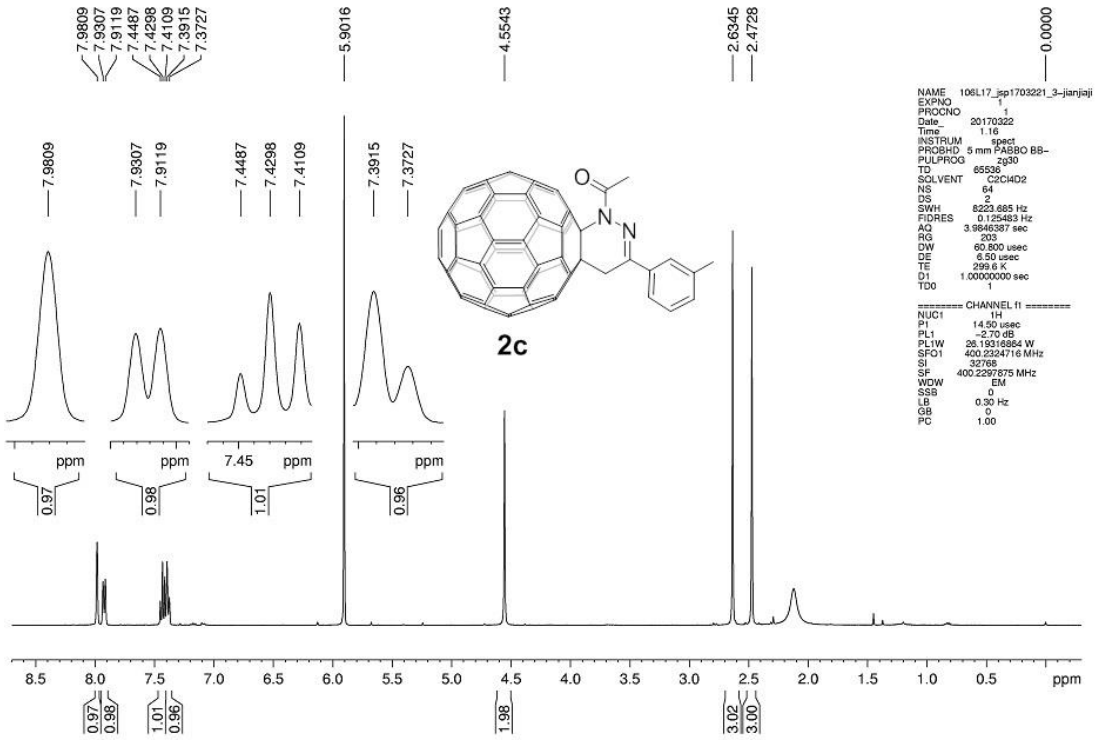
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2b



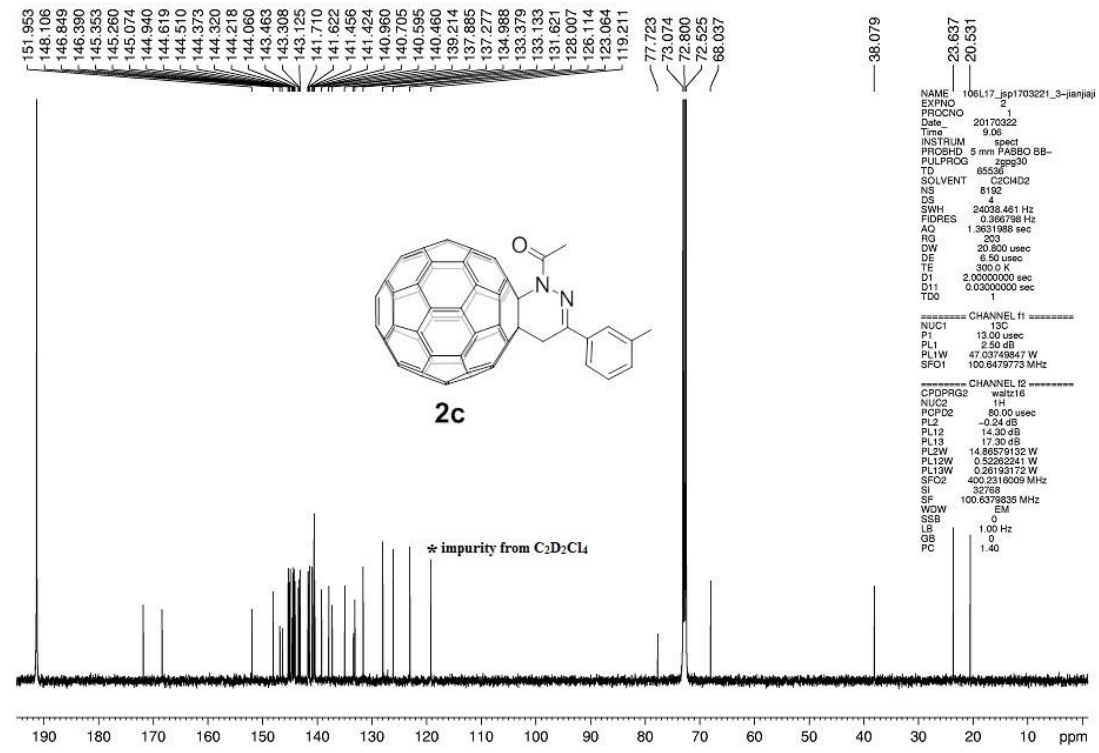
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2b



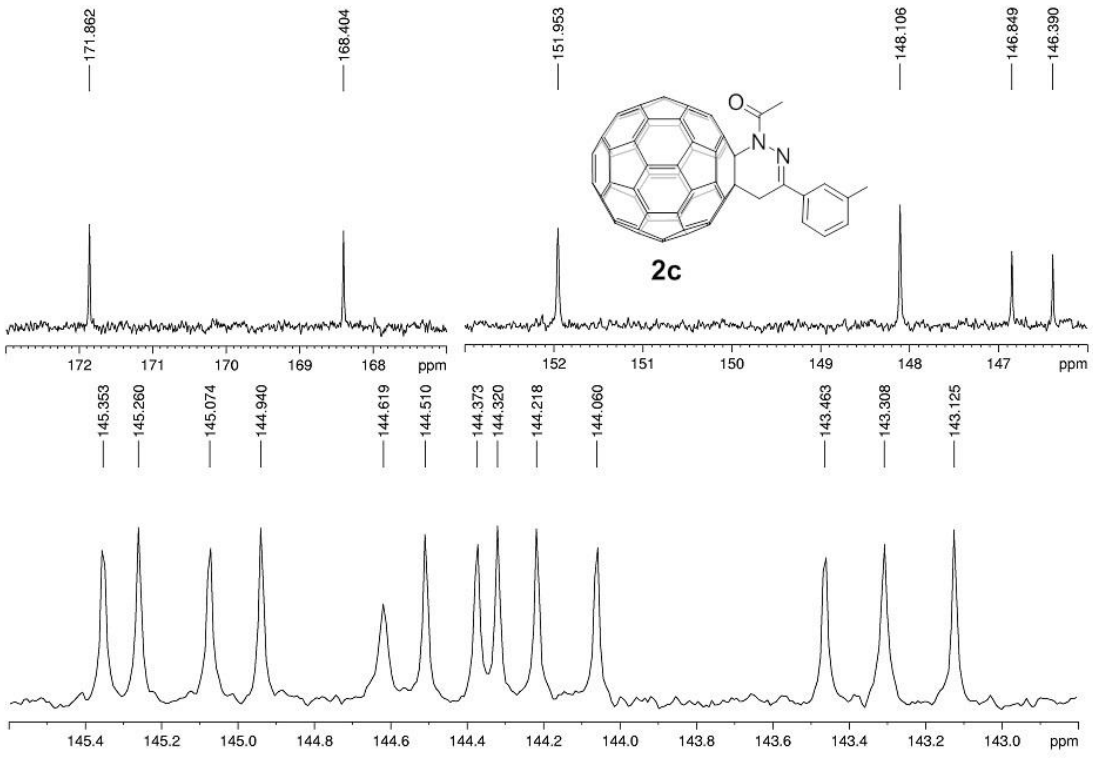
^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2c



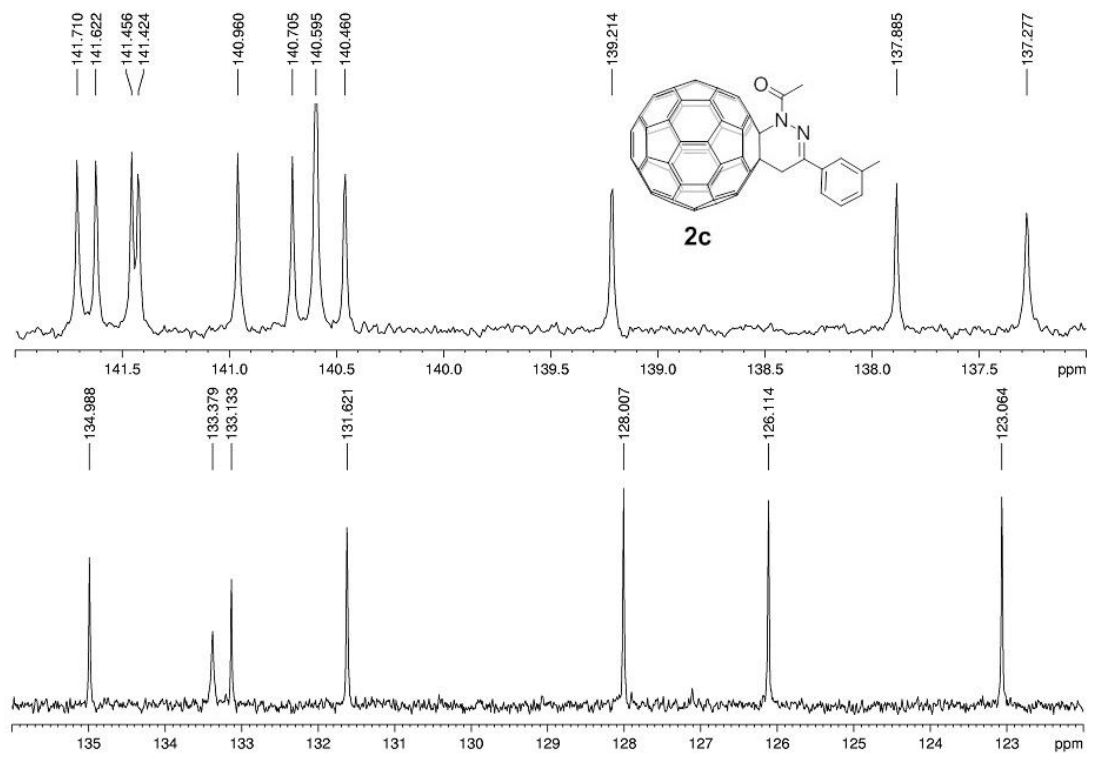
^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2c



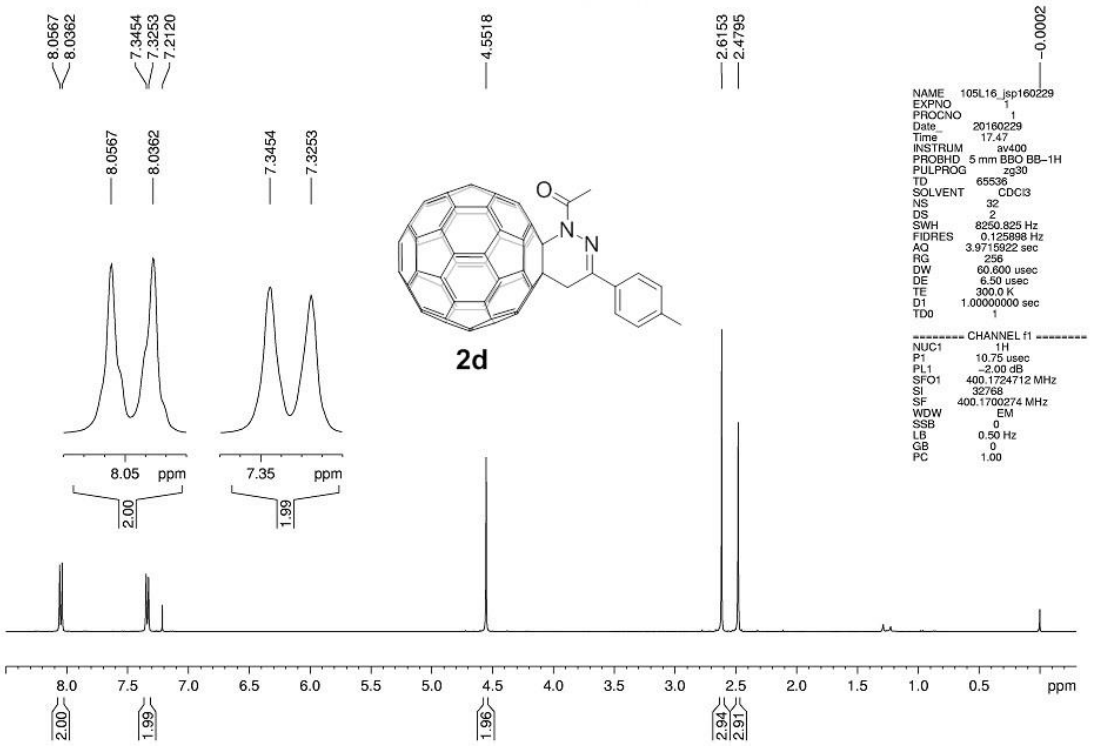
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2c



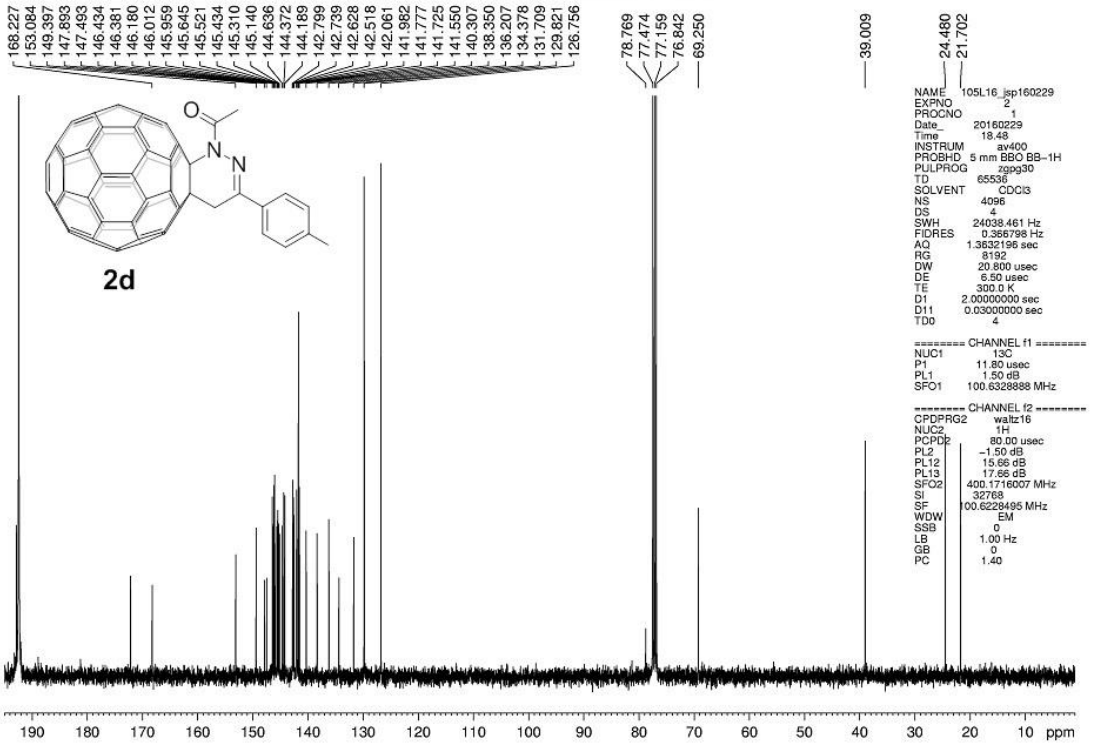
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2c



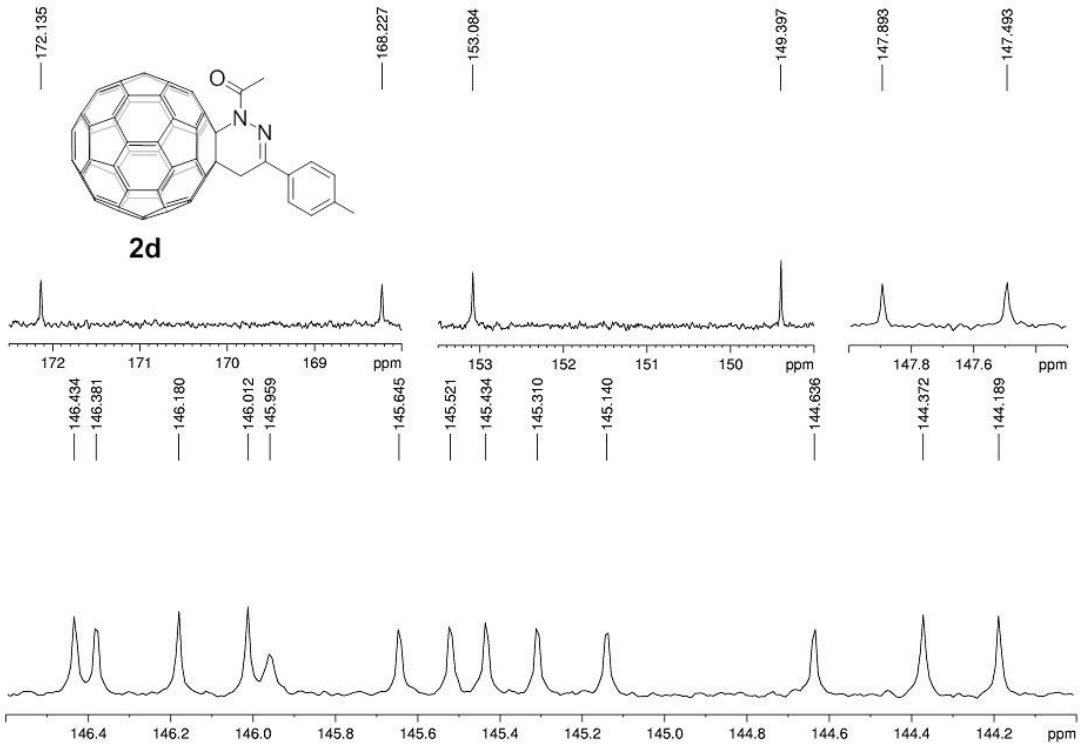
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2d



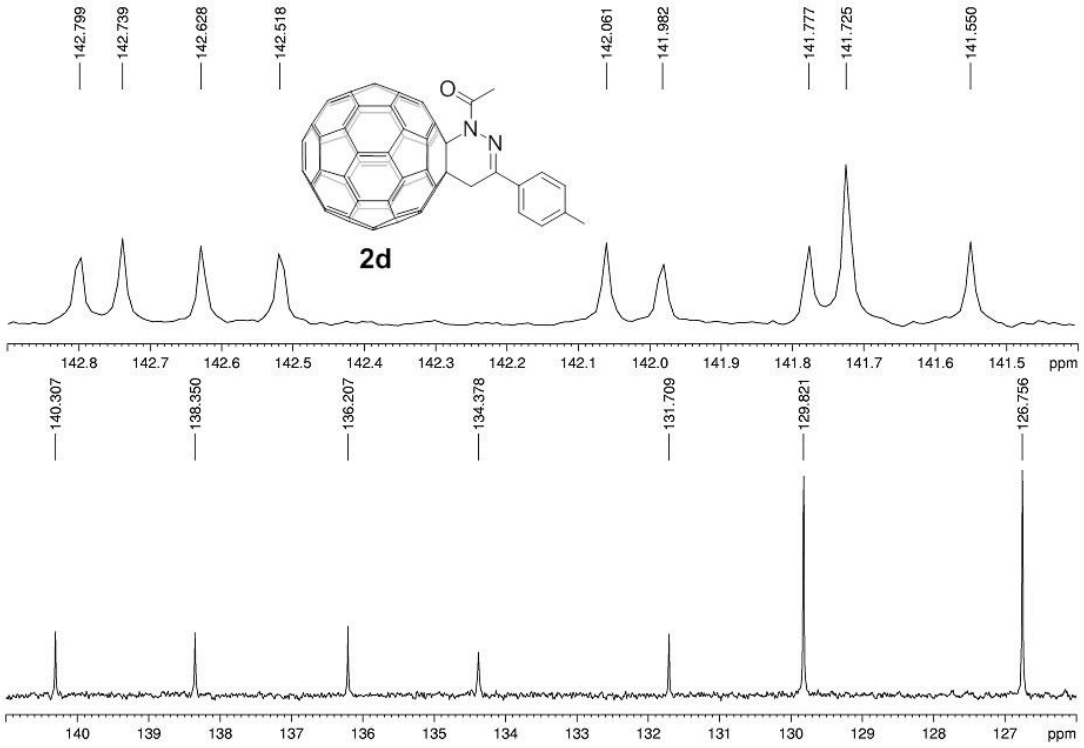
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2d



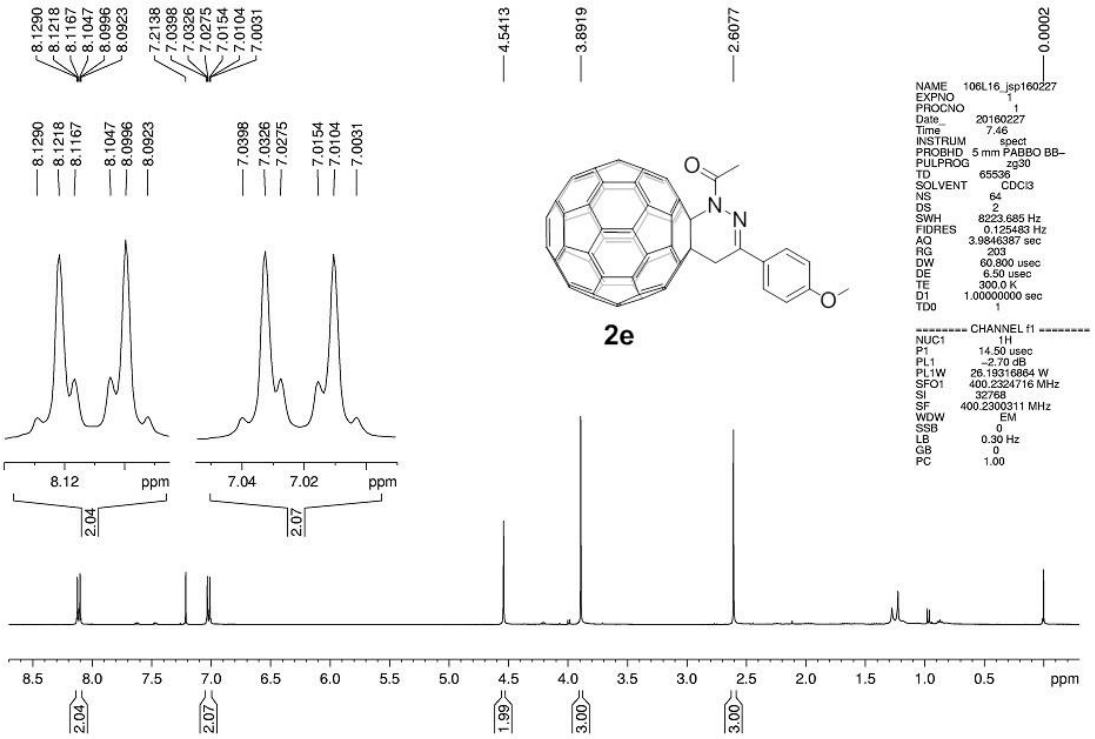
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2d



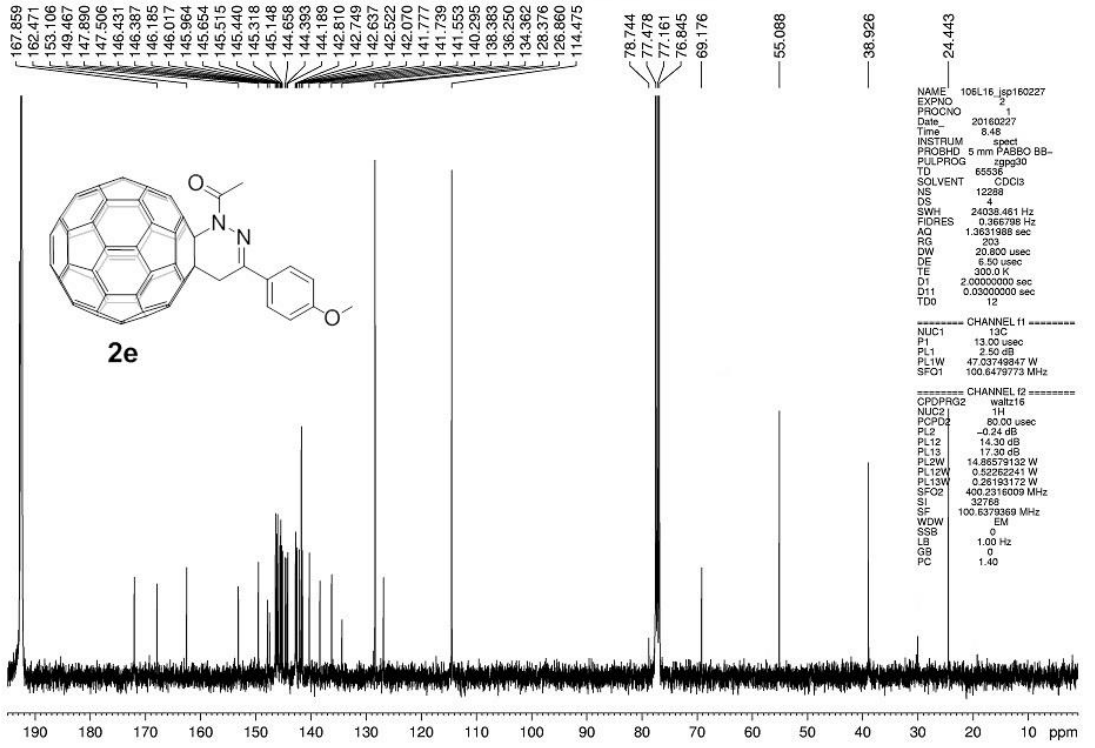
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2d



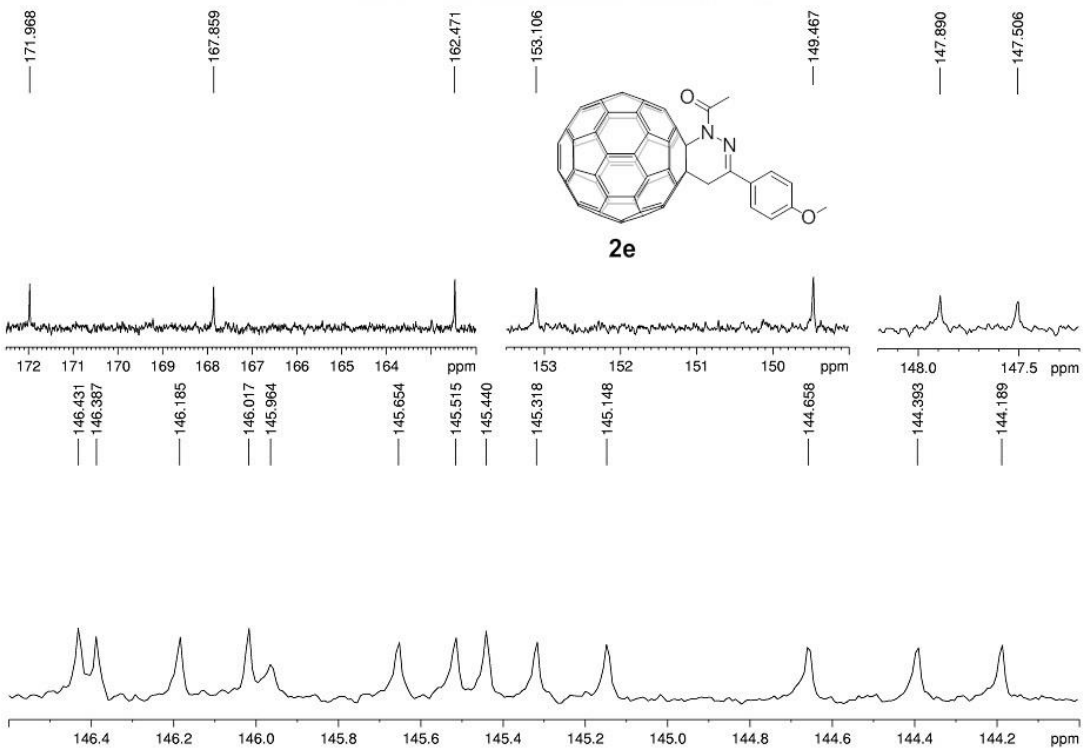
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2e



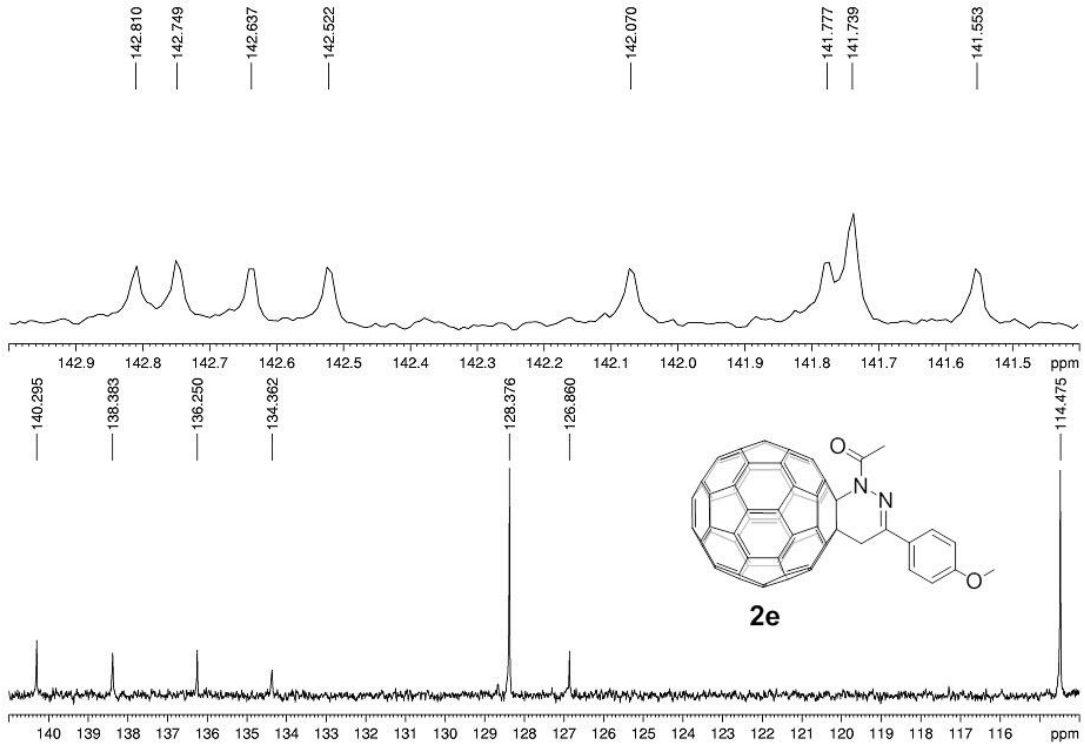
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2e



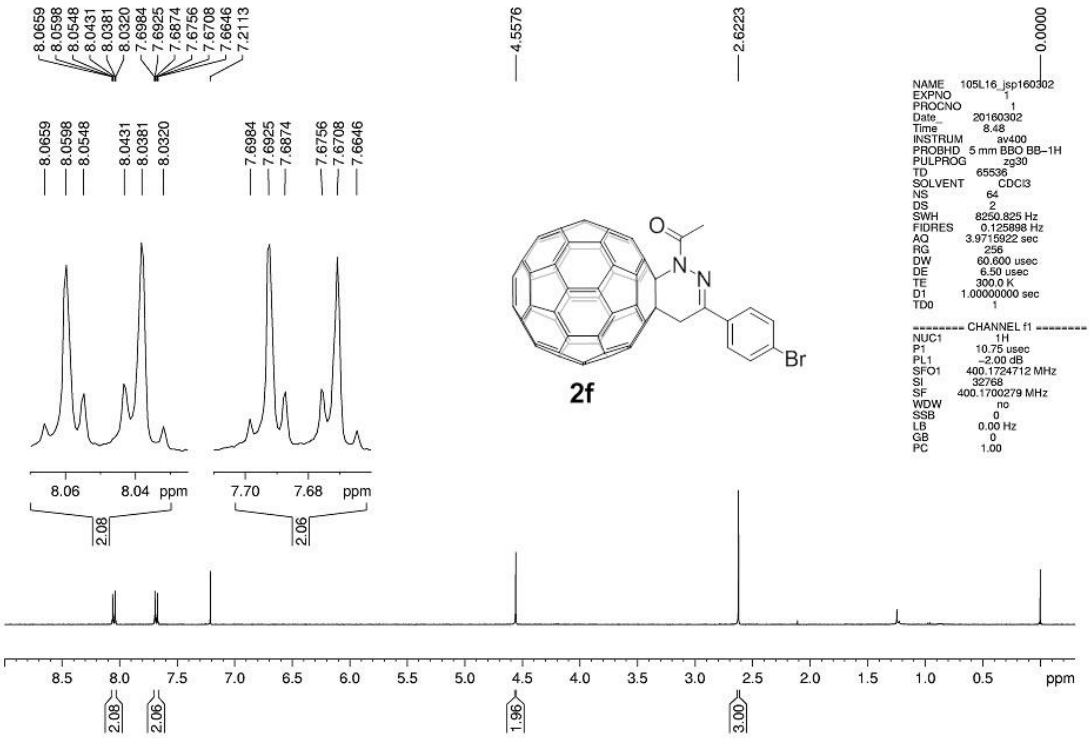
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2e



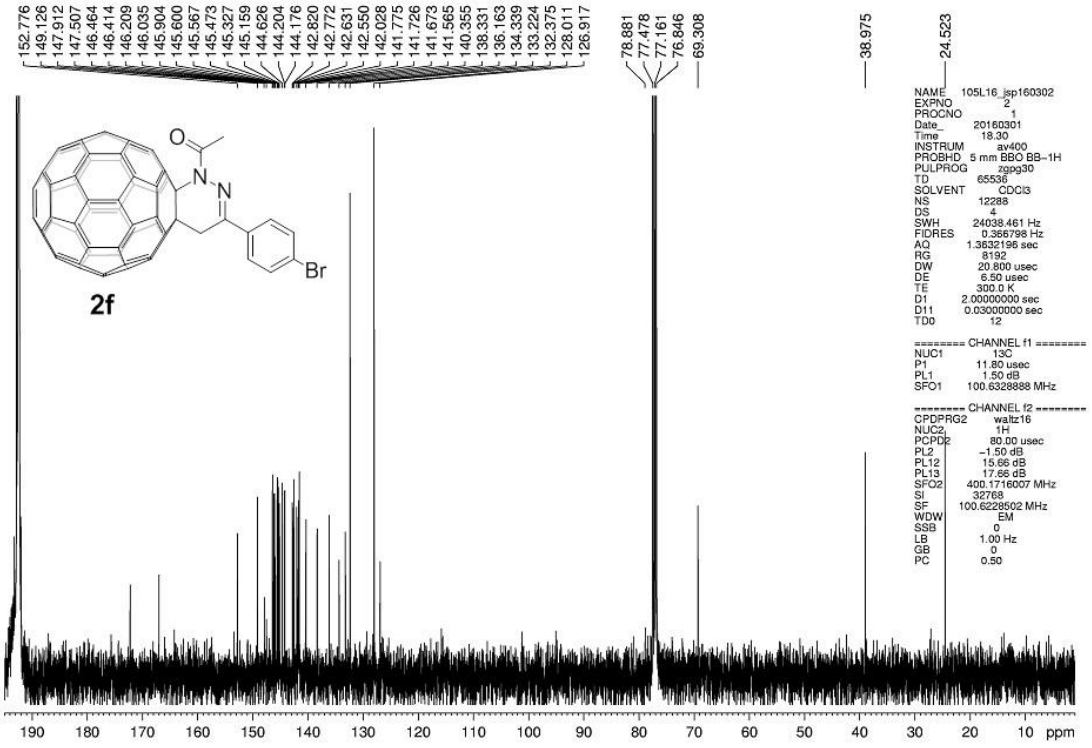
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2e



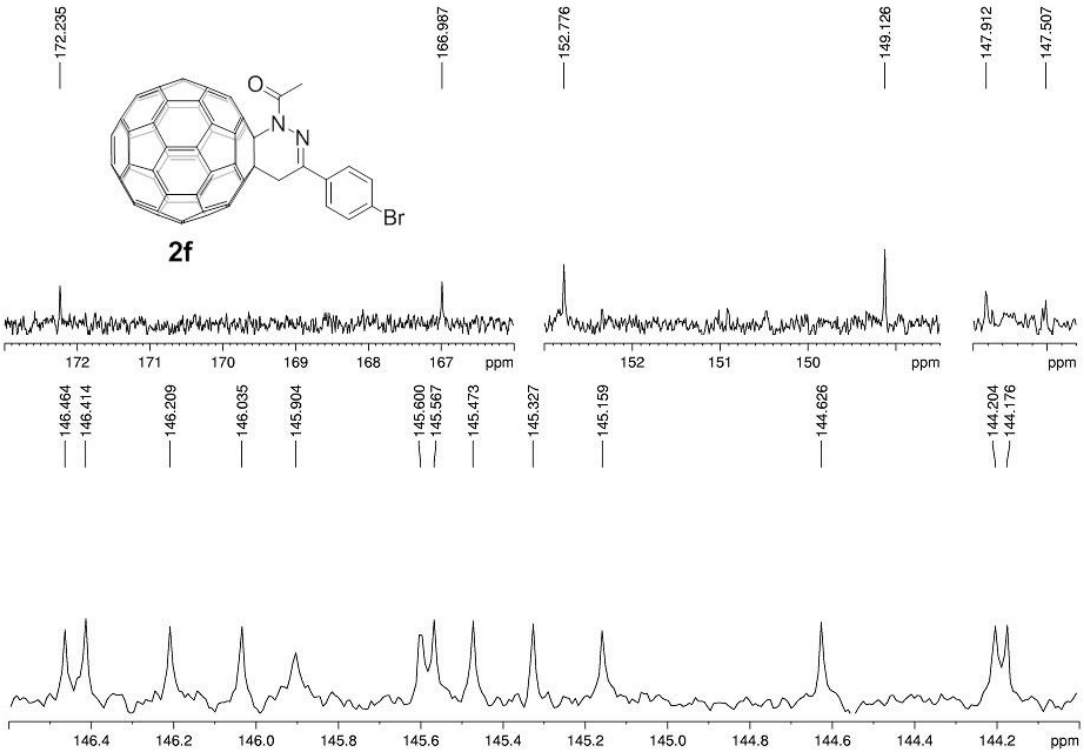
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2f



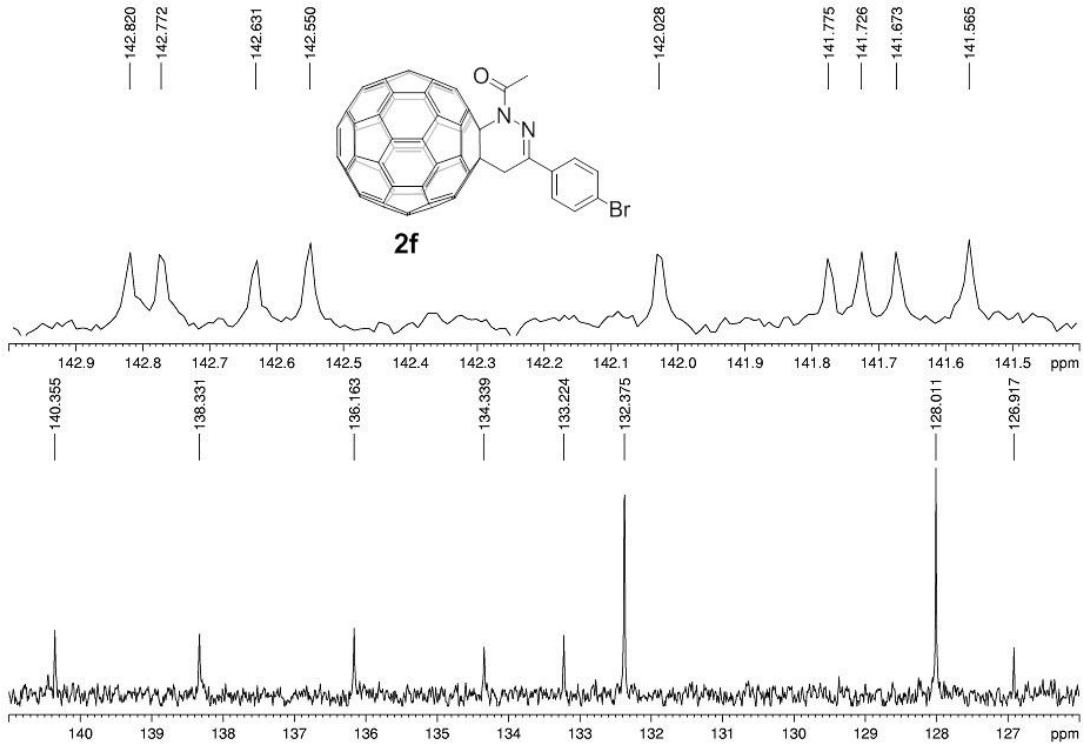
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2f



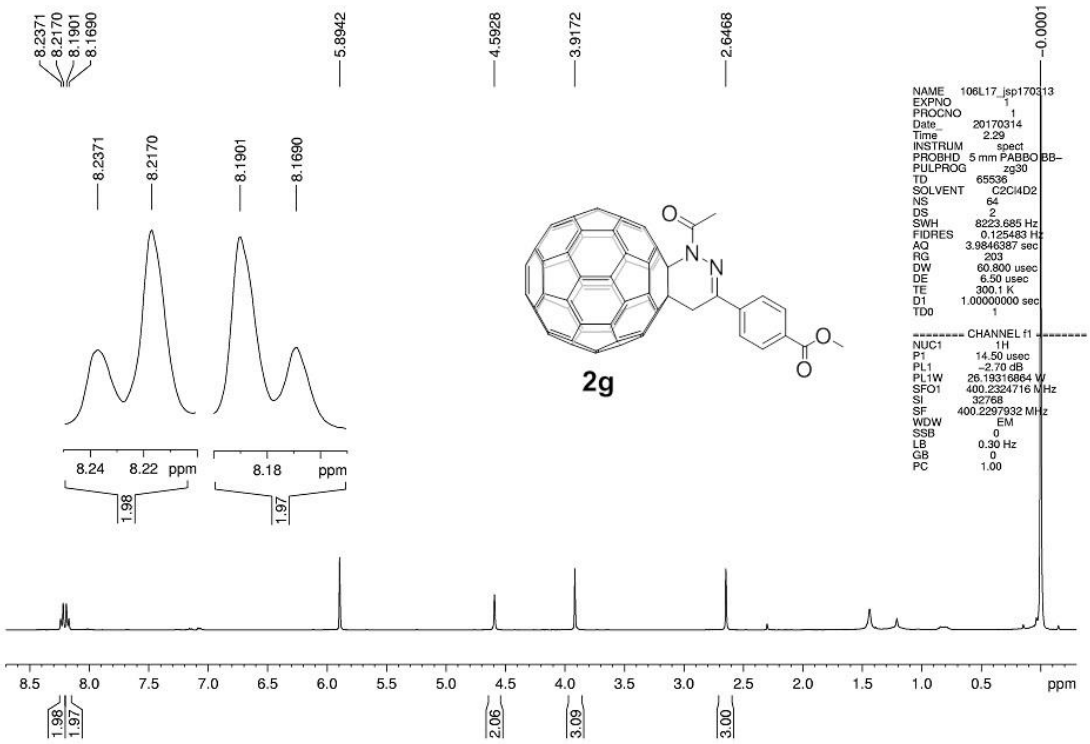
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2f



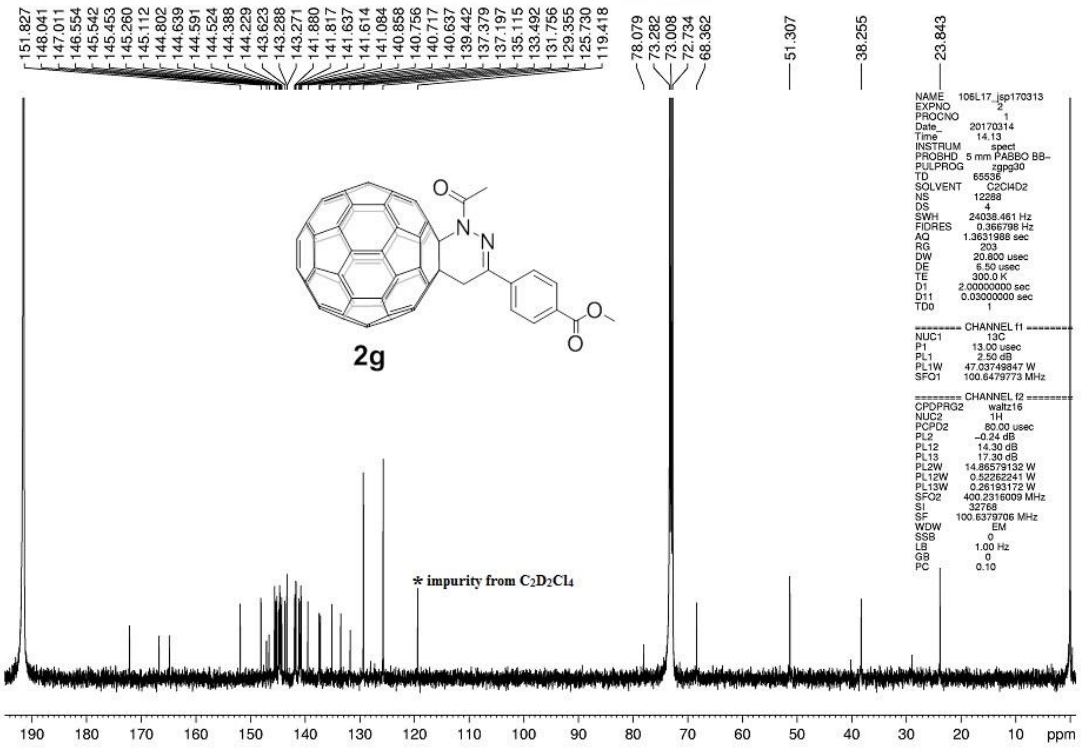
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2f



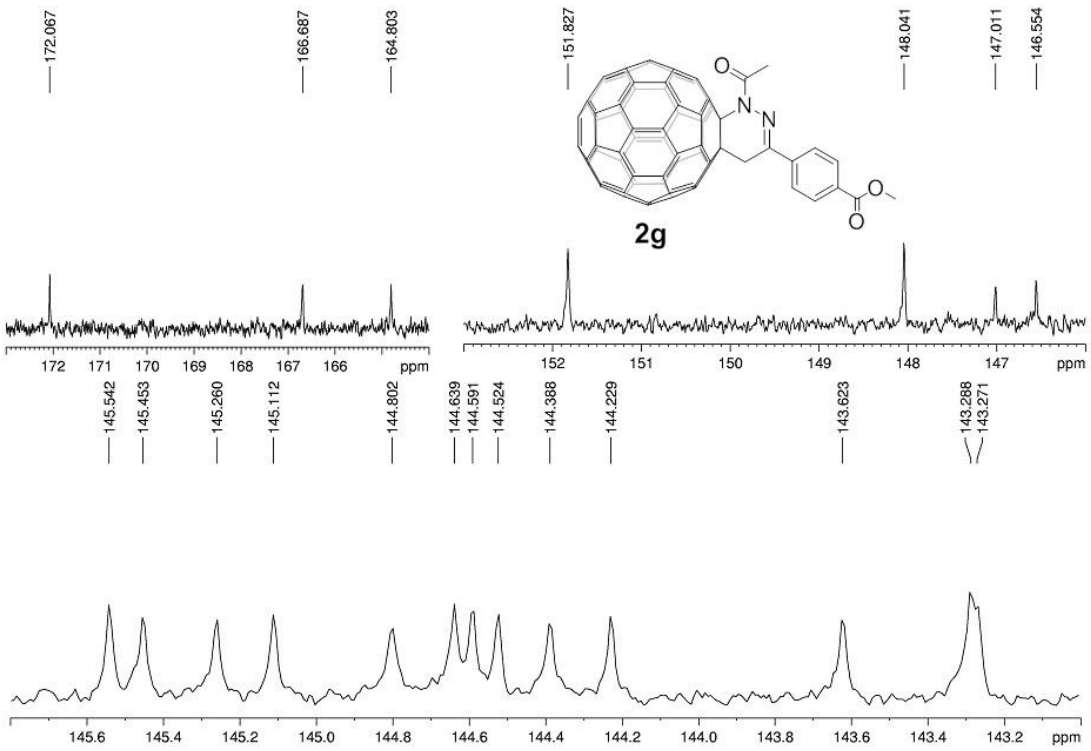
^{1}H NMR (400 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2g



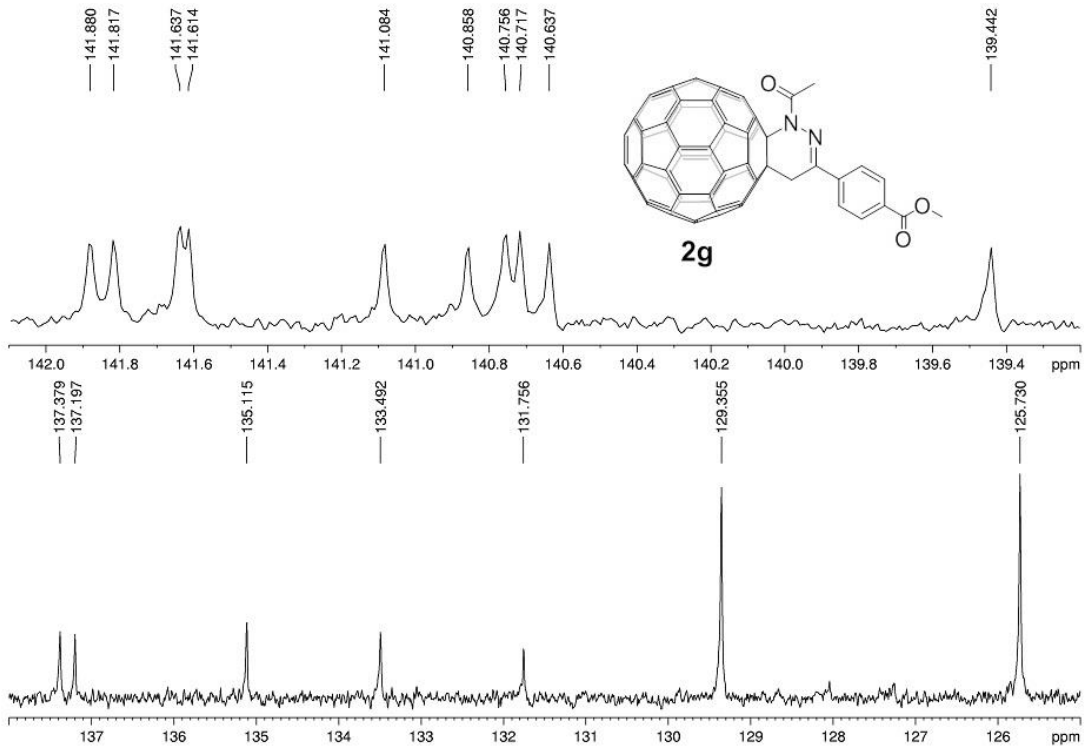
^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2g



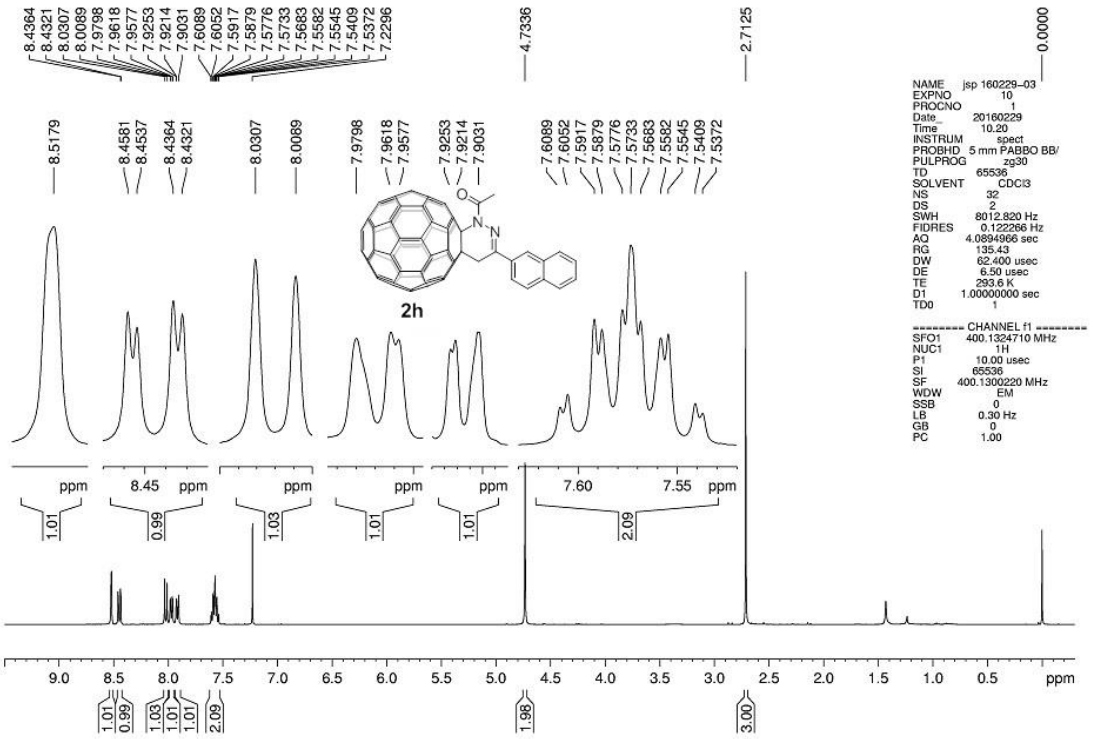
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2g



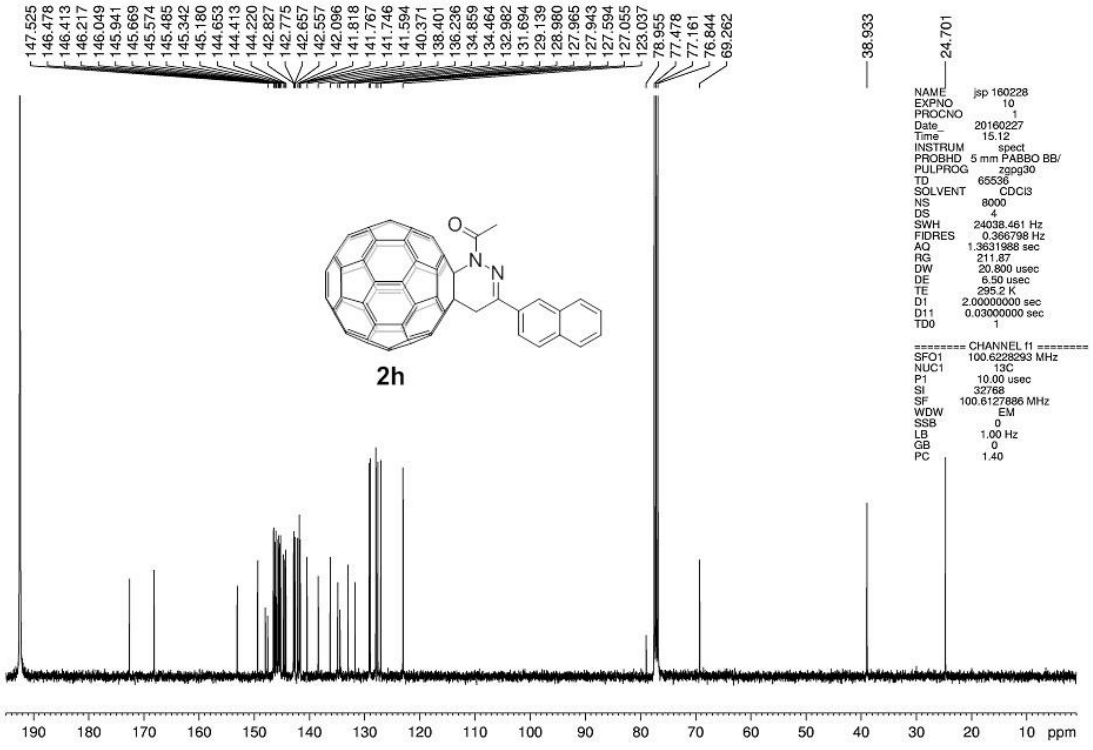
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2g



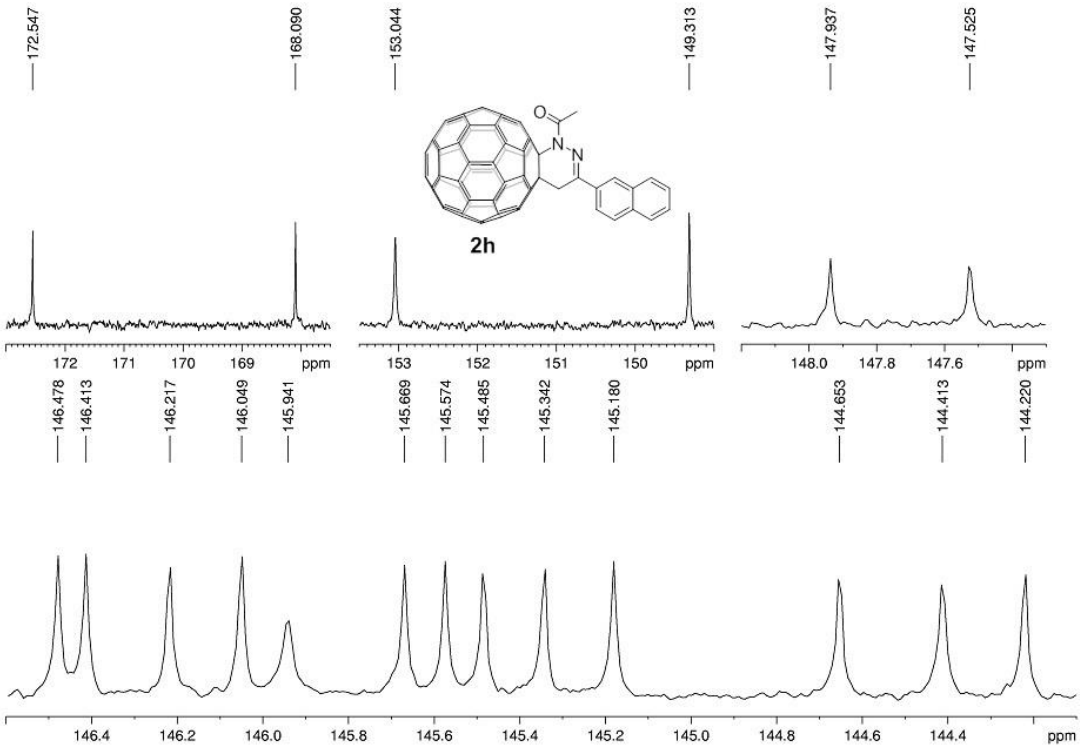
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2h



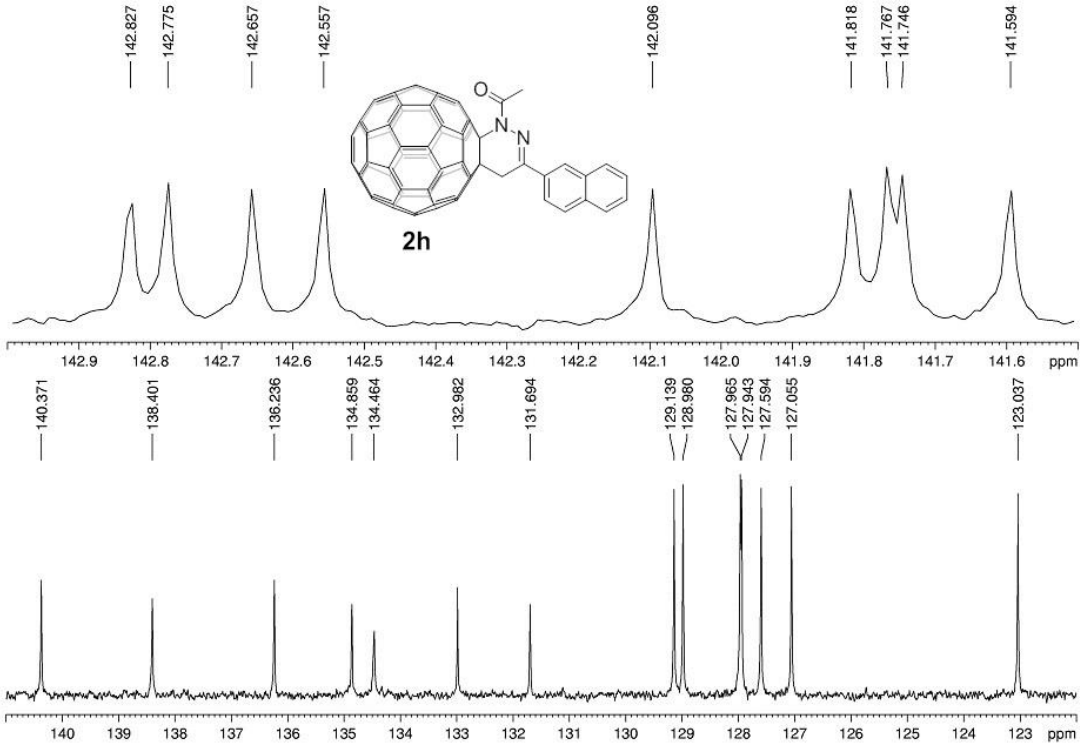
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2h



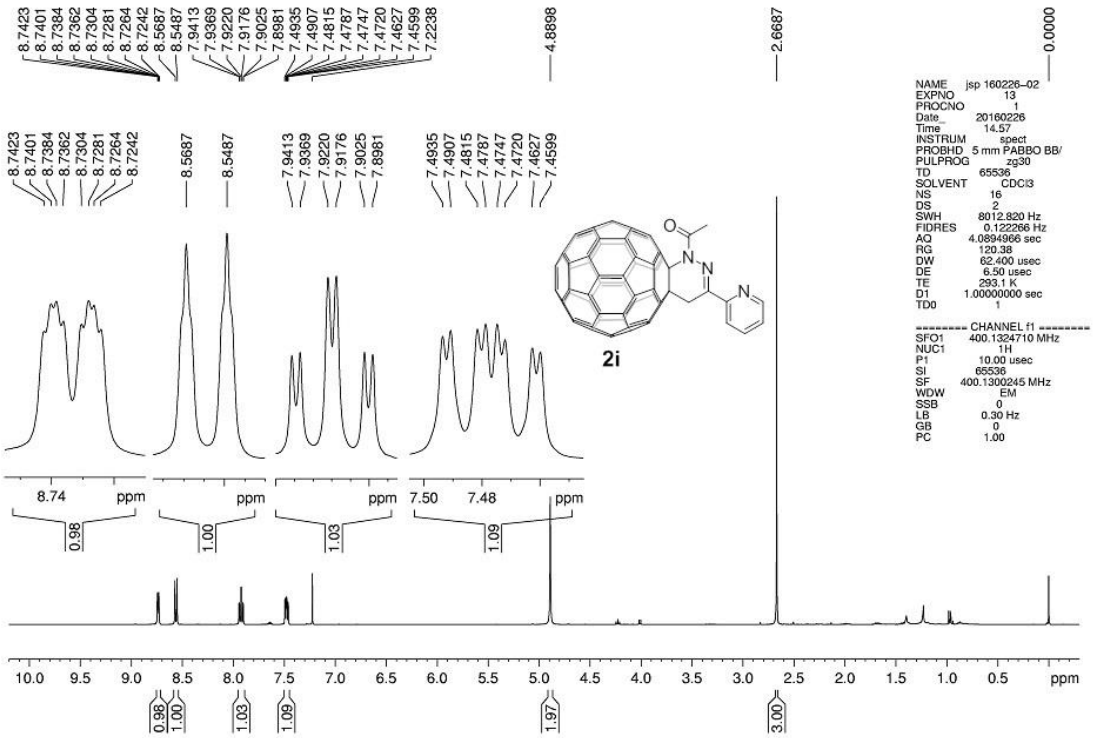
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2h



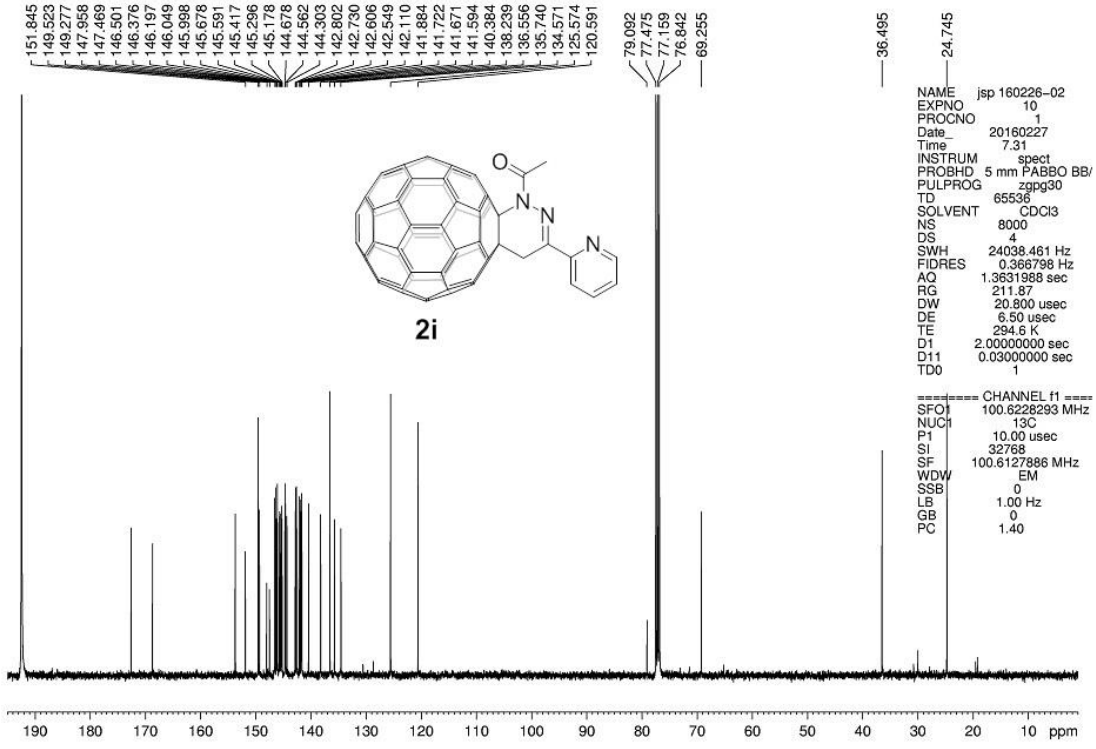
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2h



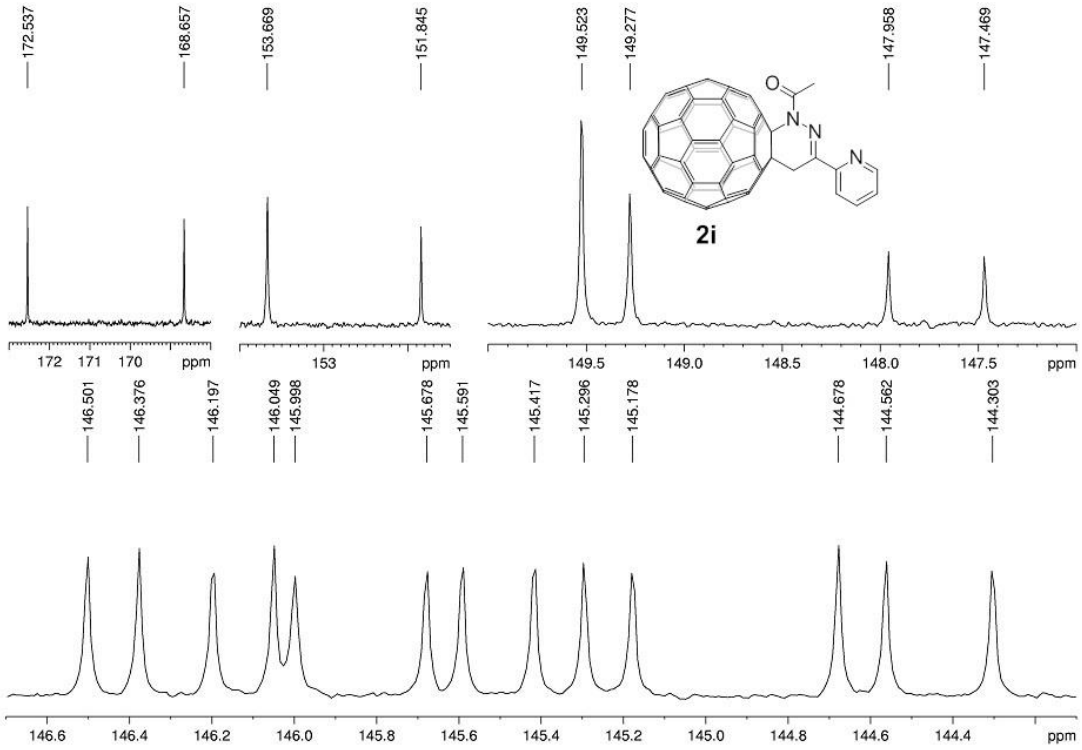
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2i



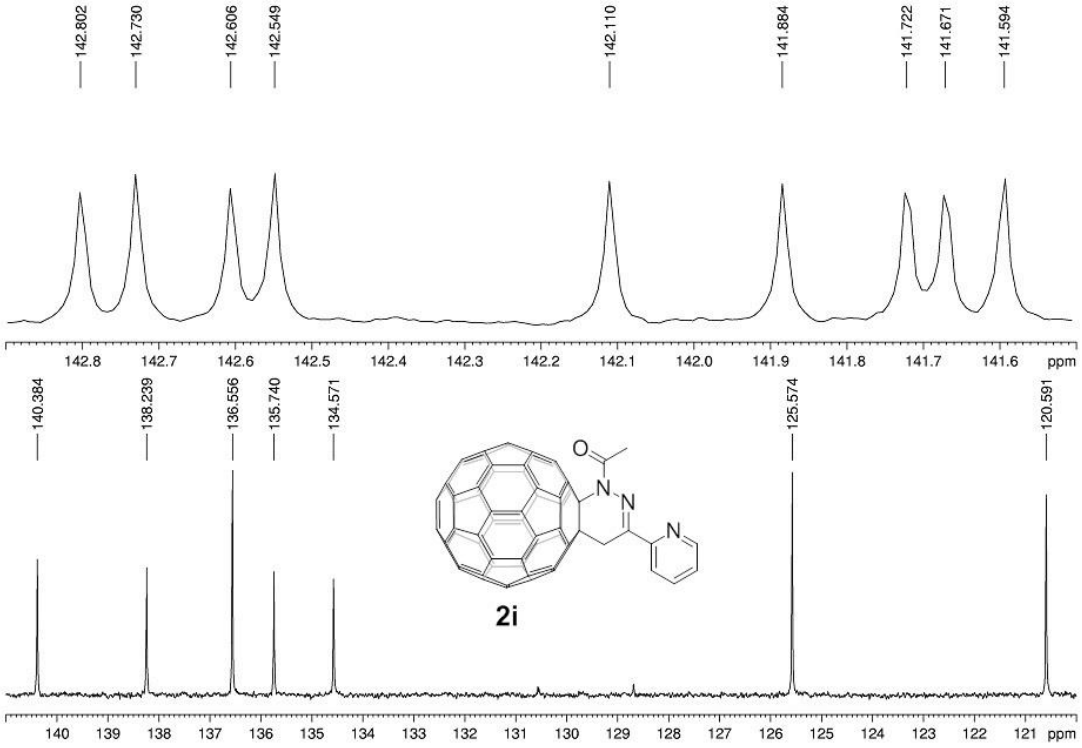
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2i



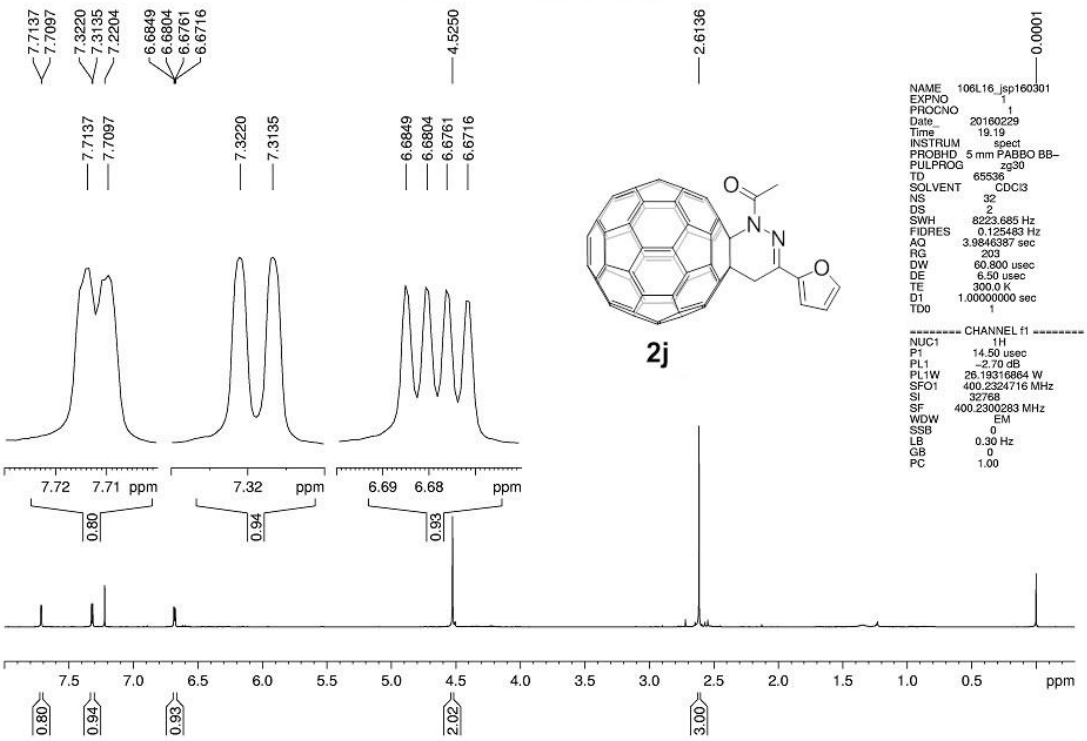
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2i



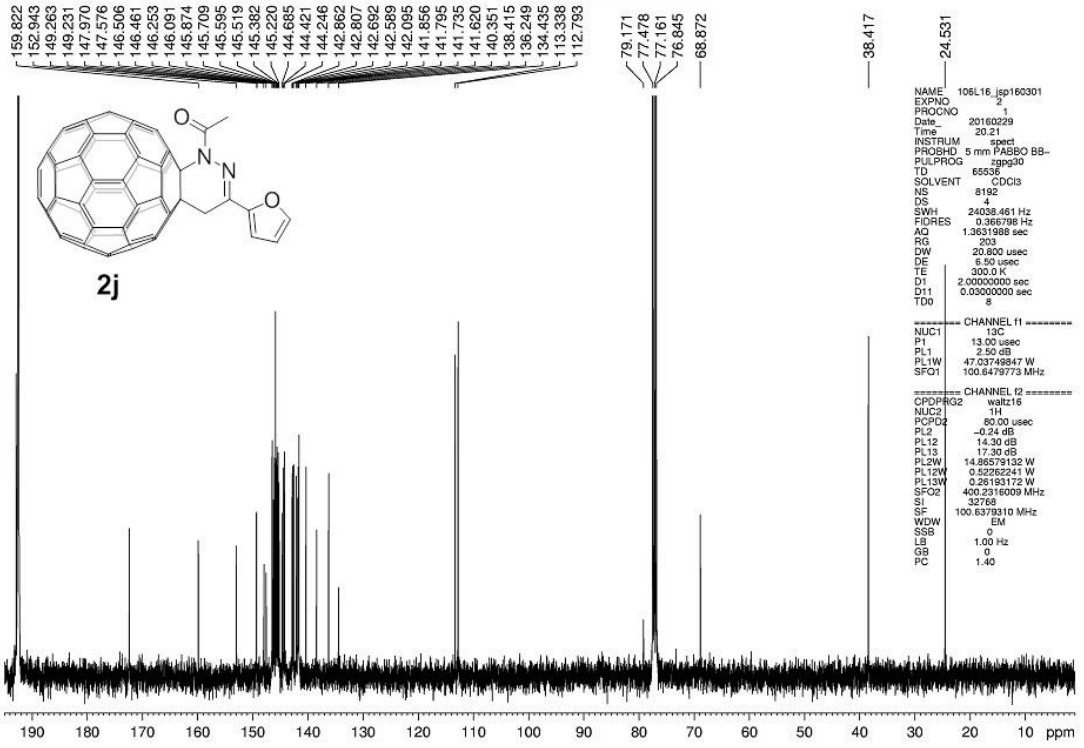
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2i



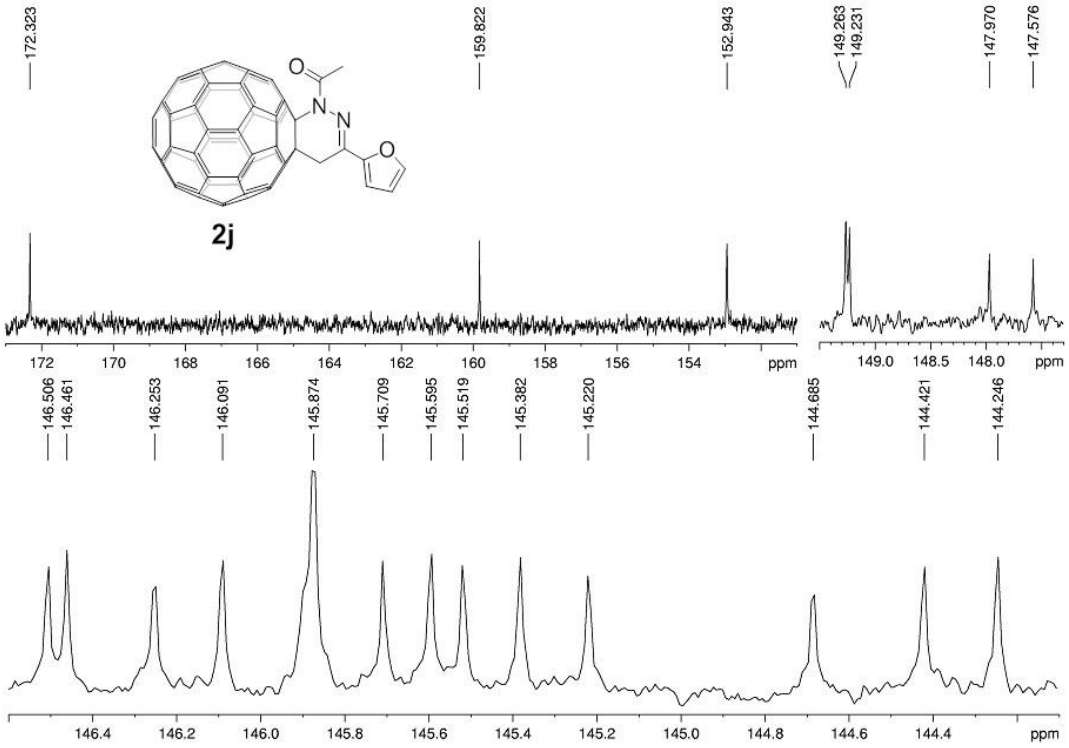
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2j



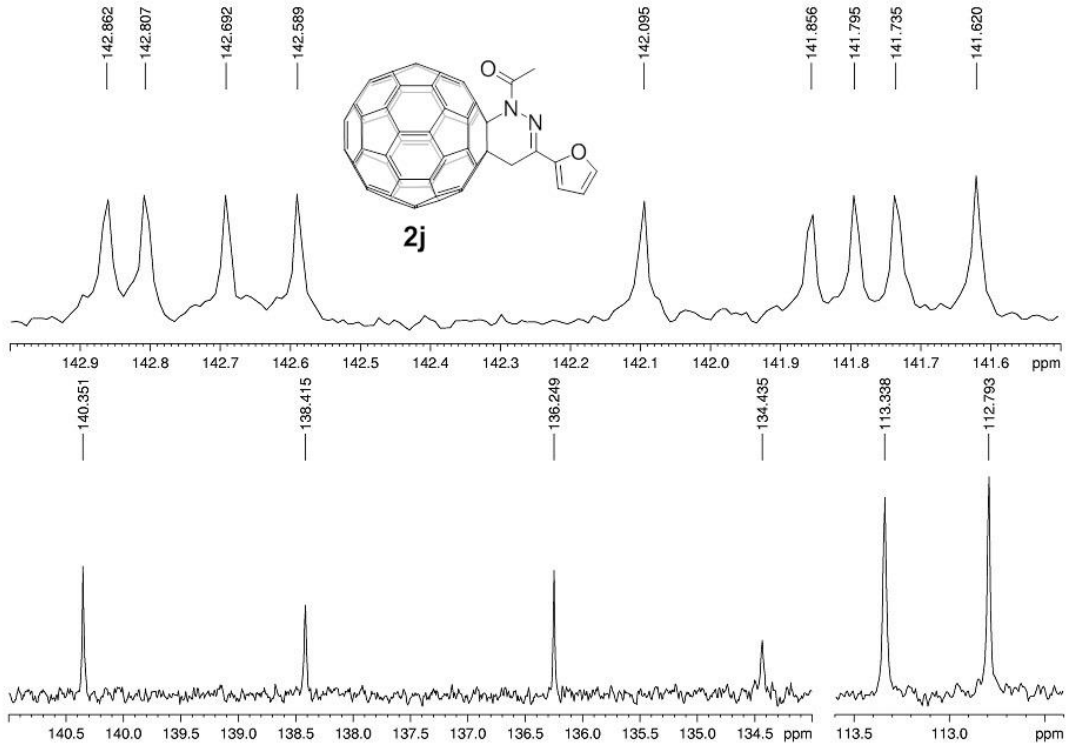
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2j



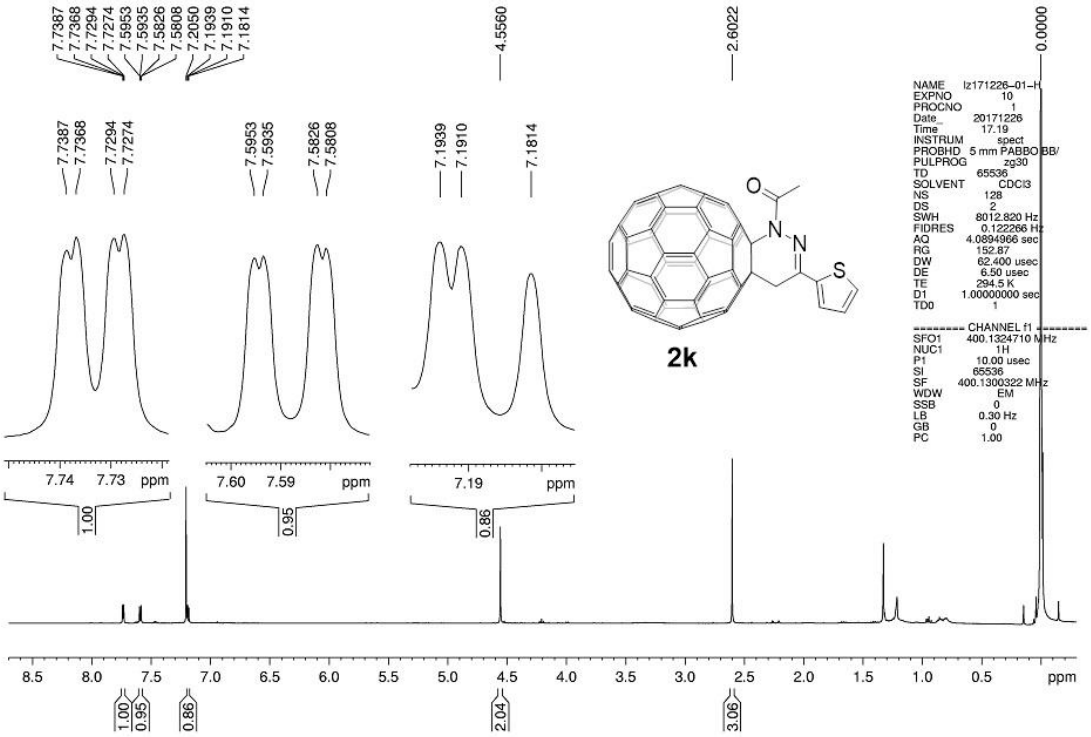
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2j



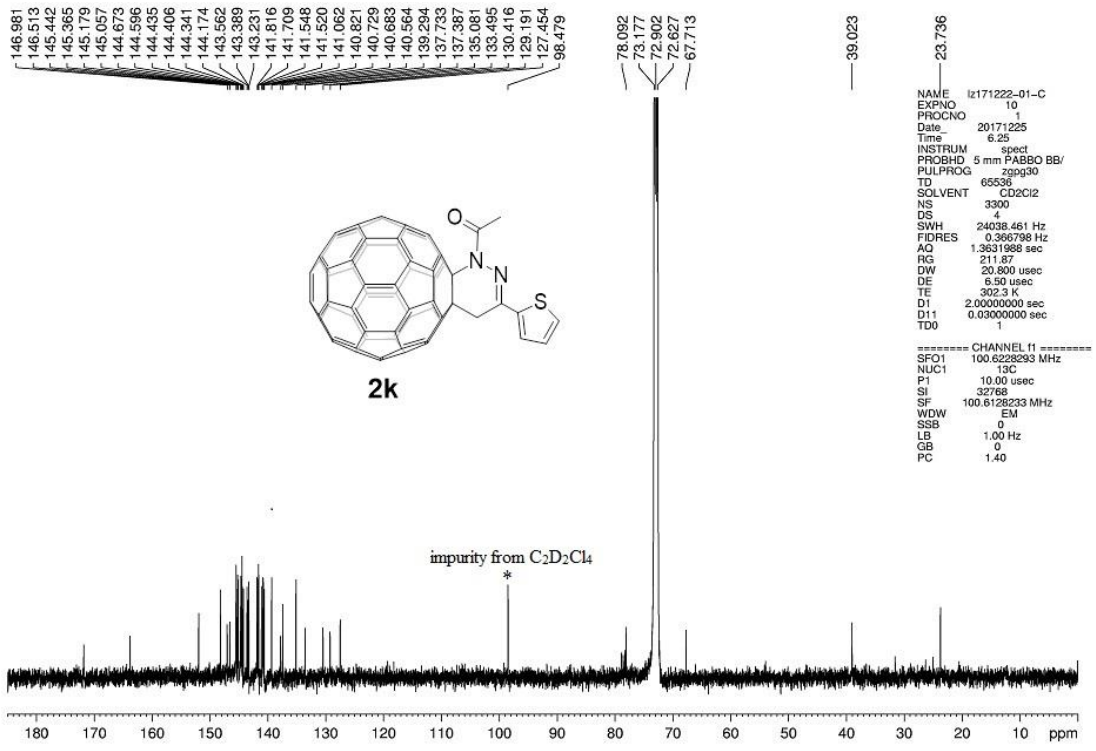
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2j



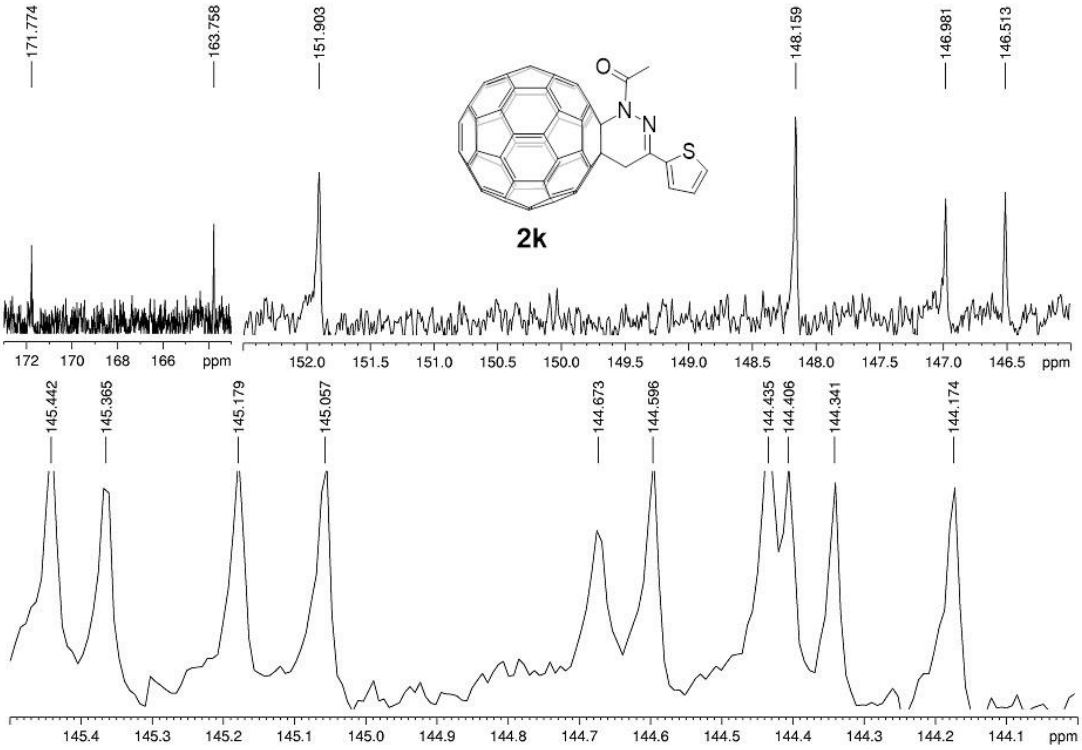
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) spectrum of compound 2k



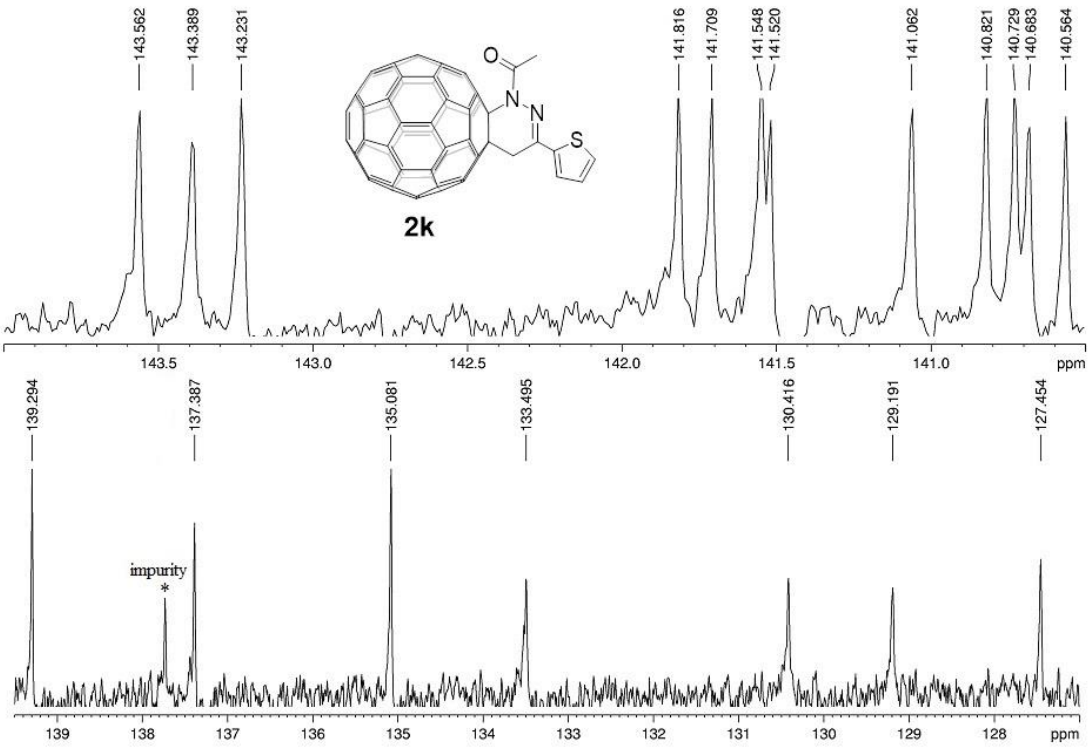
^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2k



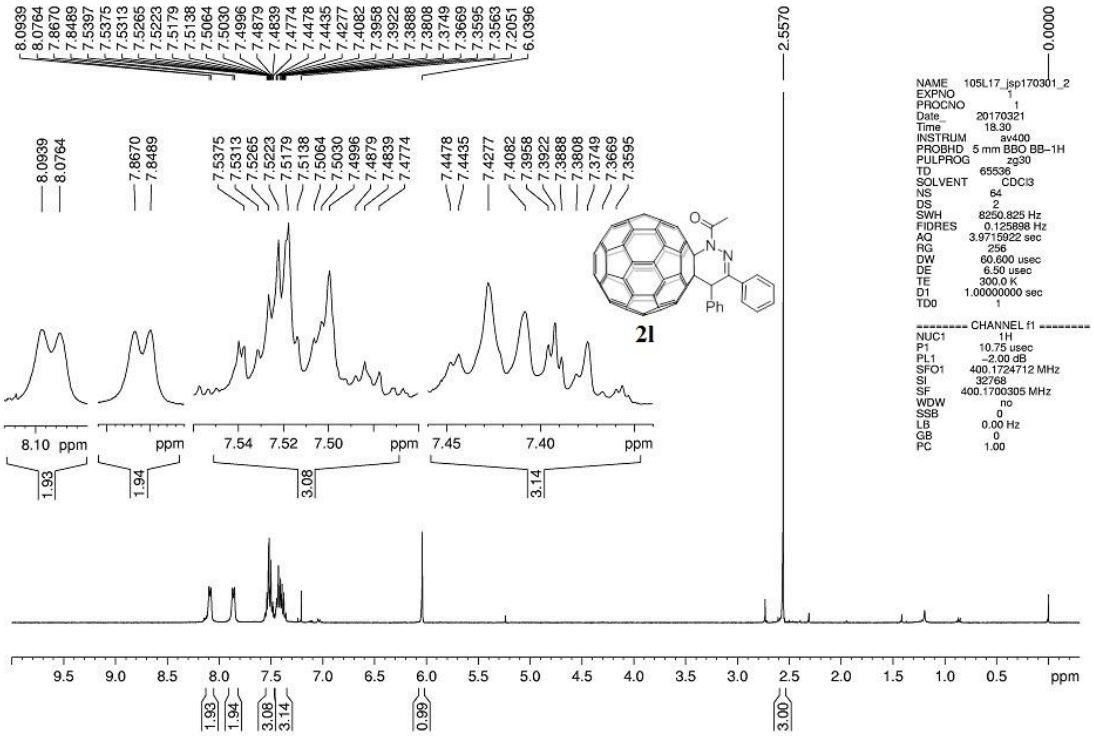
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2k



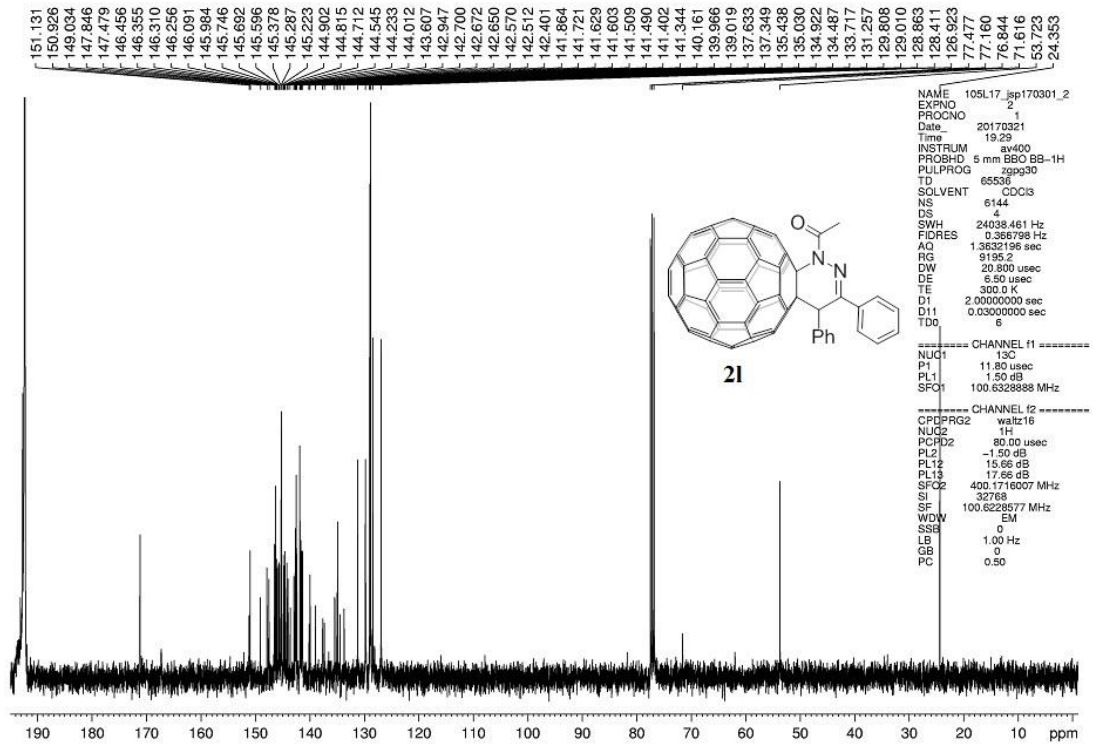
Expanded ^{13}C NMR (100 MHz, $CS_2/C_2D_2Cl_4$) spectrum of compound 2k



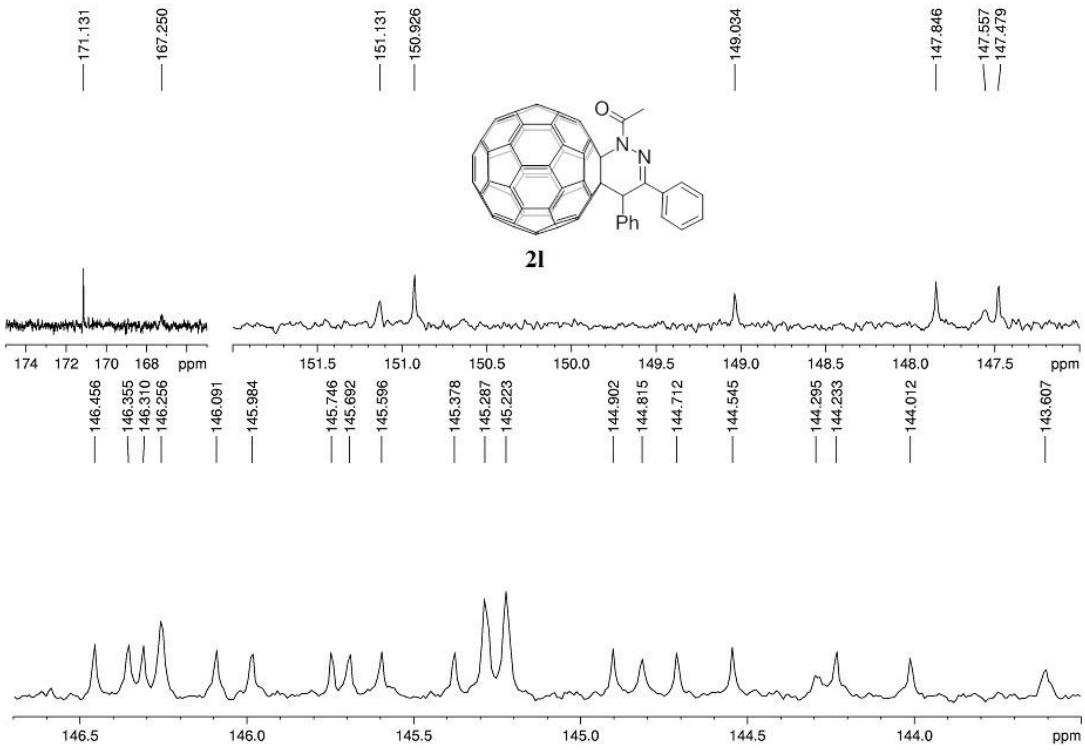
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2l



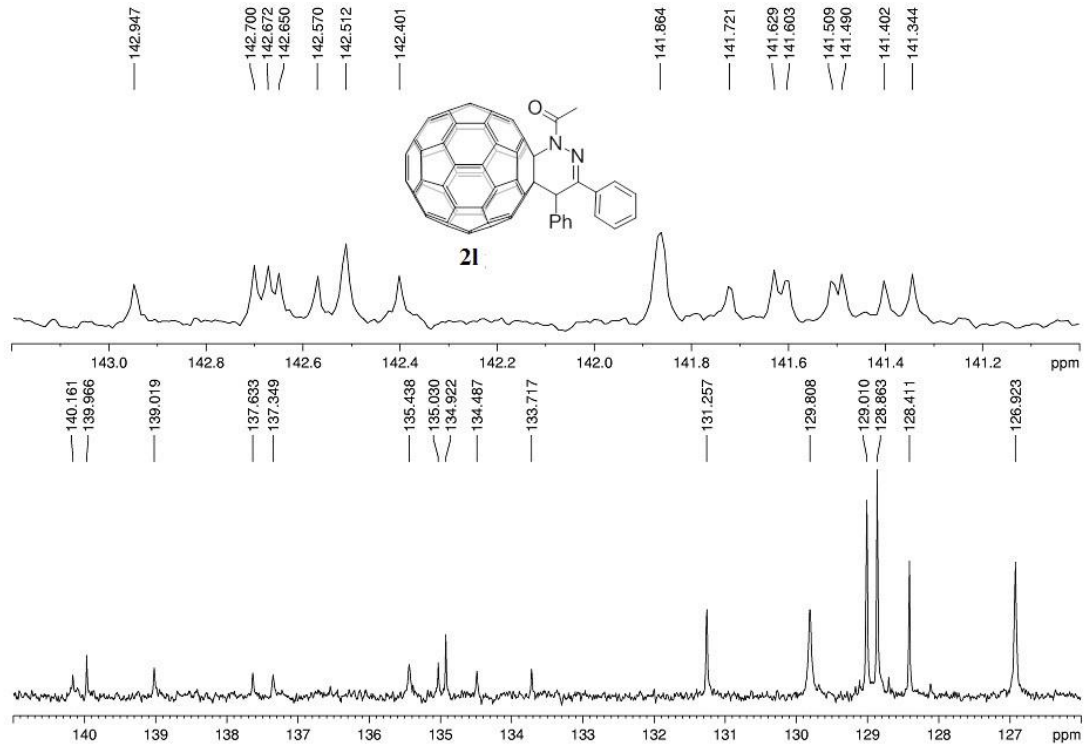
^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) spectrum of compound 2l



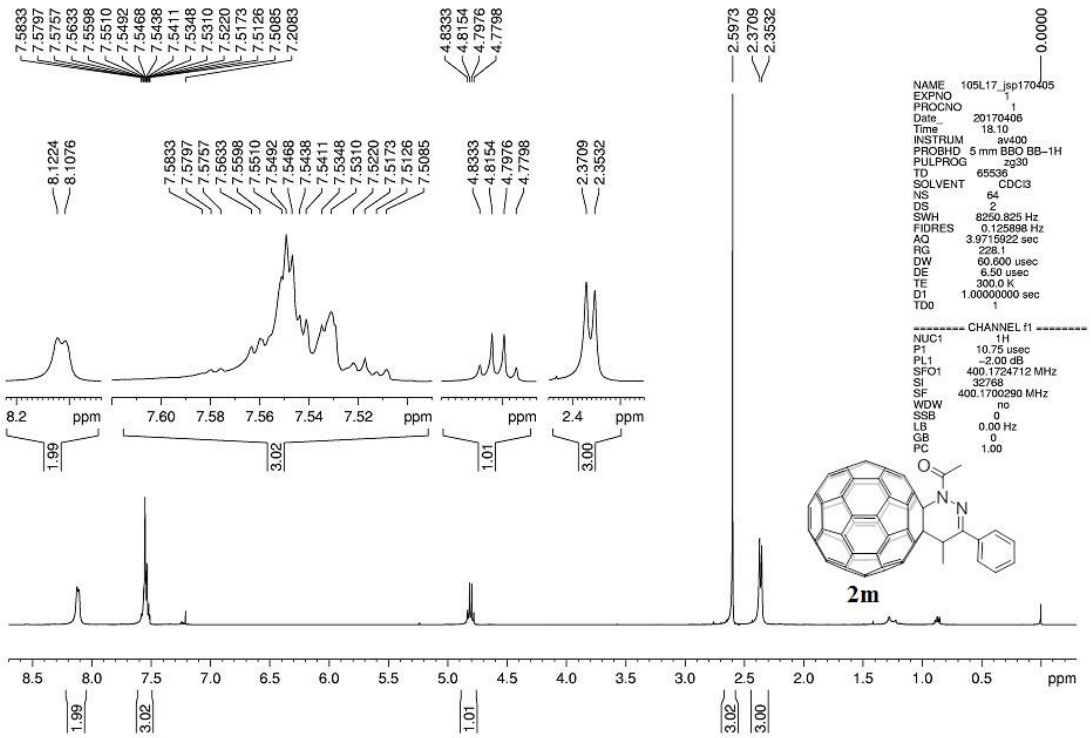
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, 300.0 K) spectrum of compound 2l



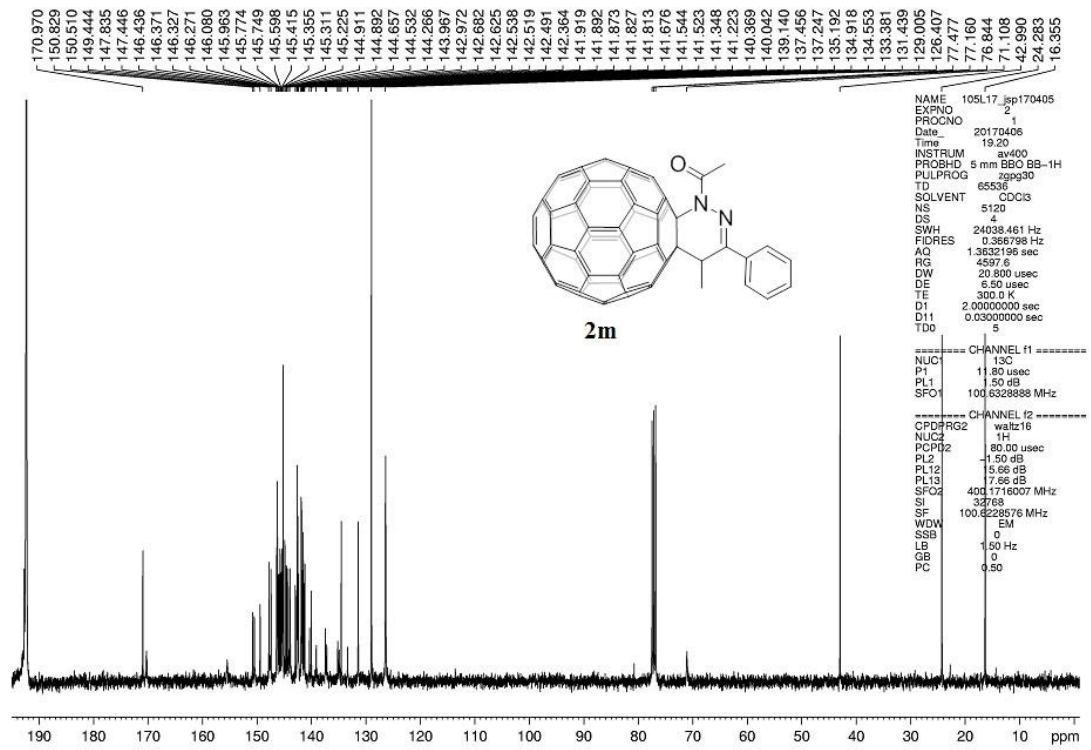
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, 300.0 K) spectrum of compound 2l



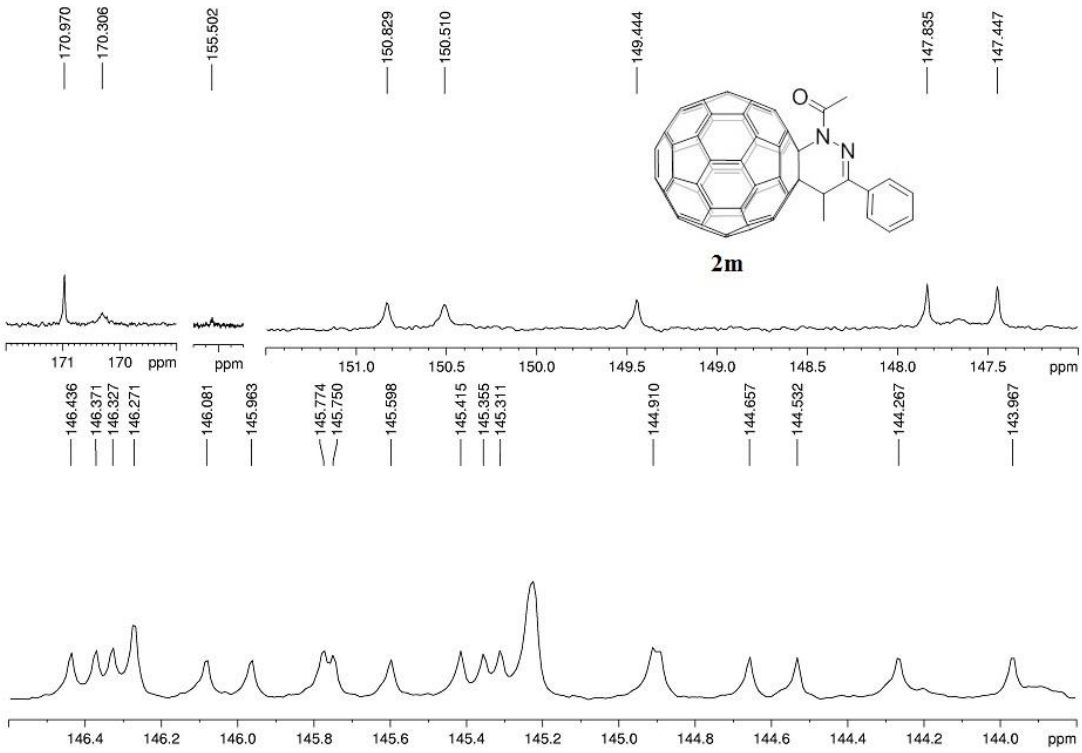
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2m



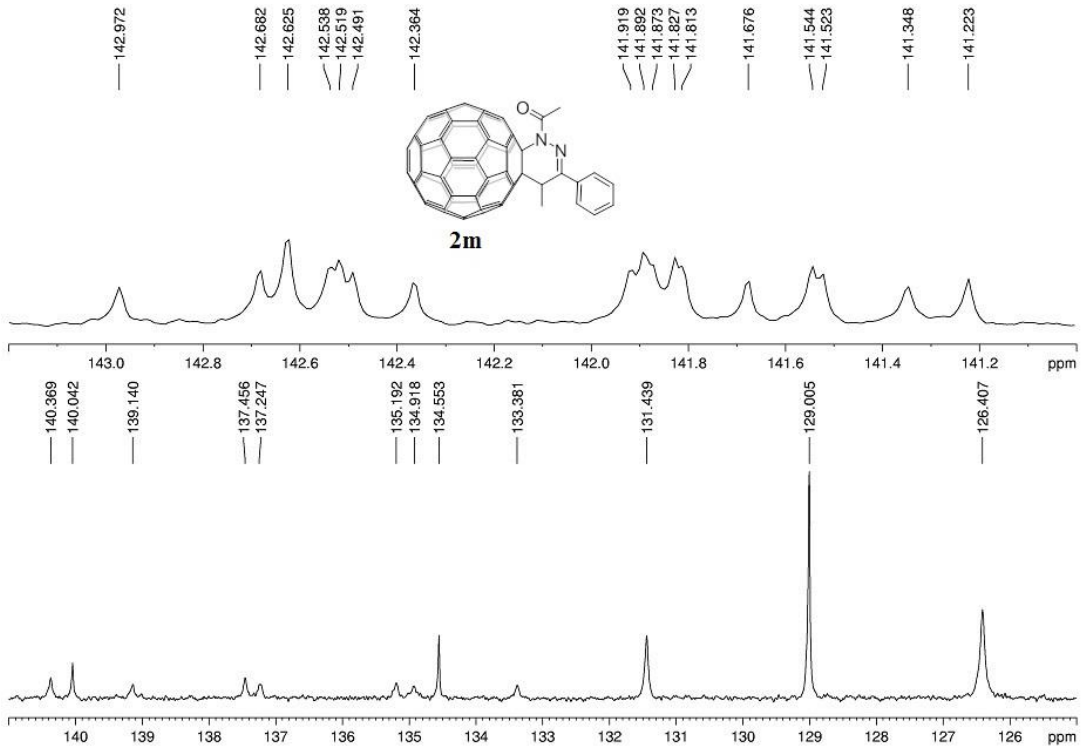
^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) spectrum of compound 2m



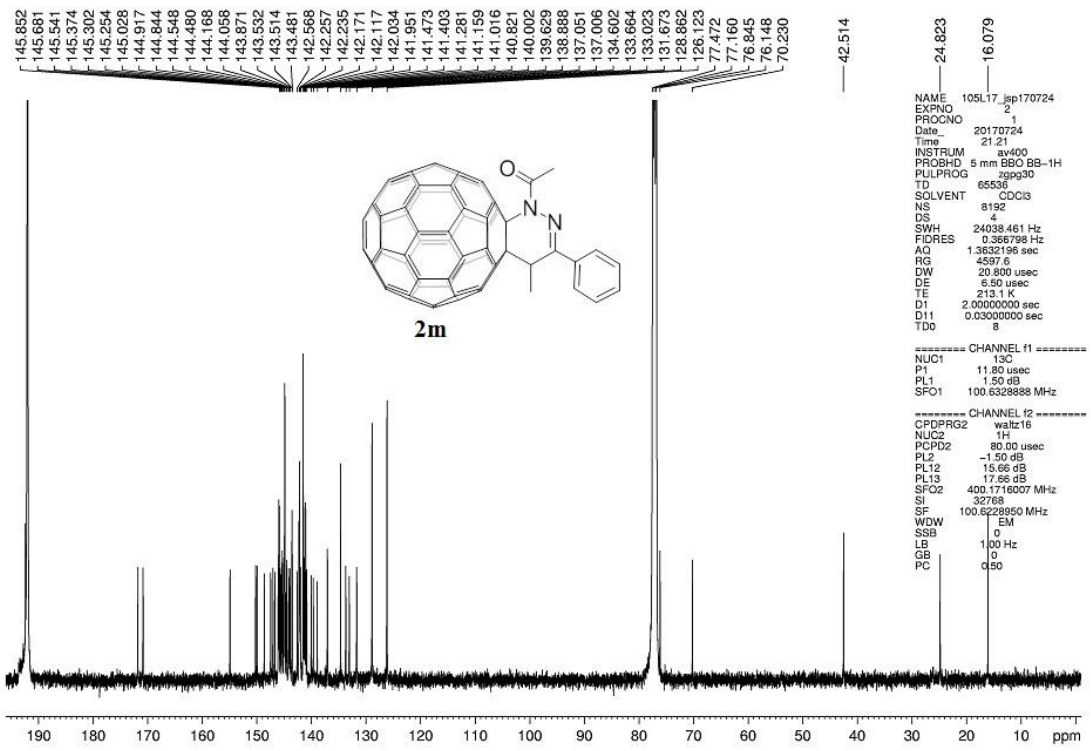
Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) spectrum of compound 2m



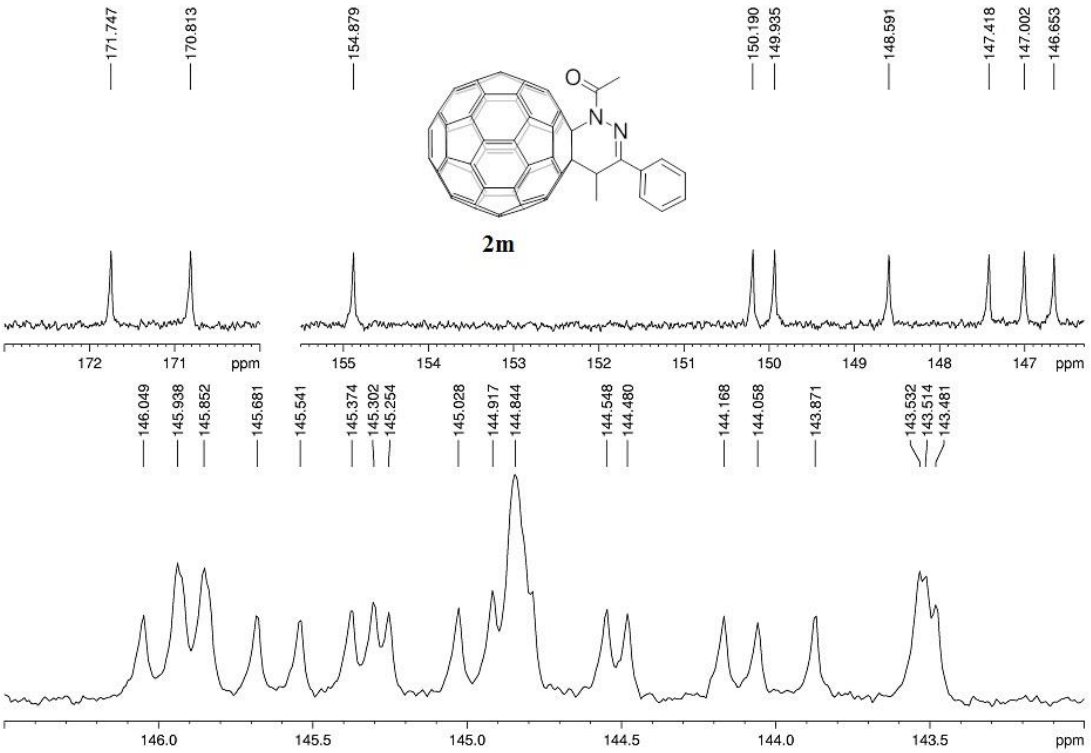
Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 300.0 K) spectrum of compound 2m



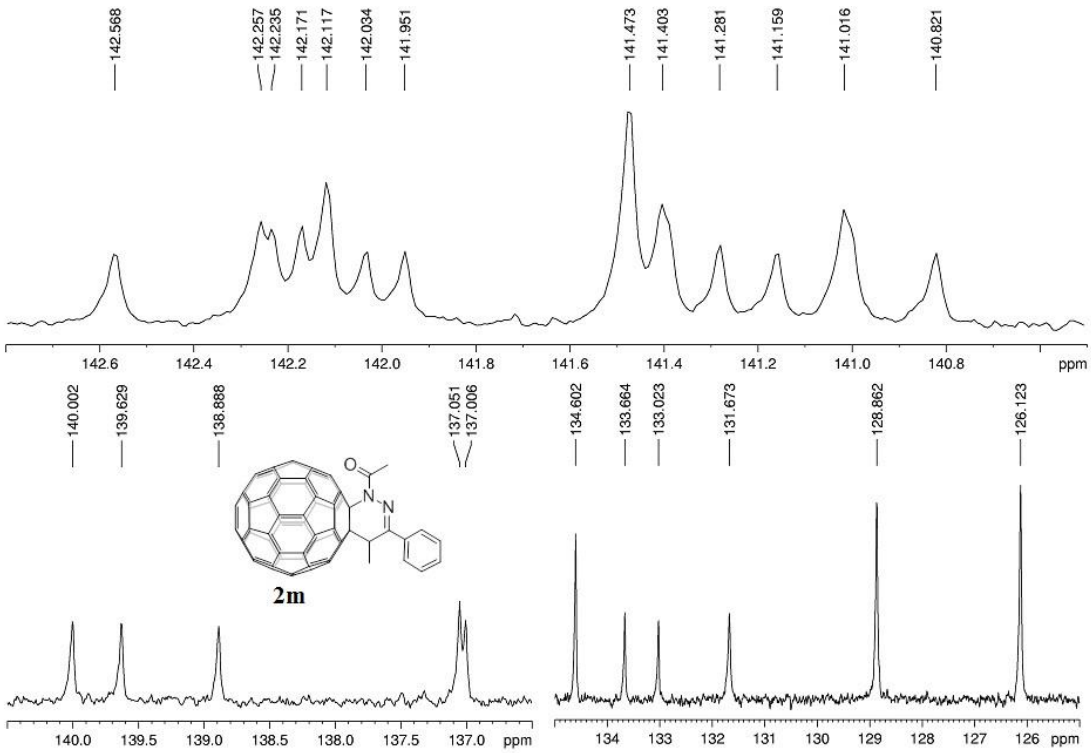
^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 213.1 K) spectrum of compound 2m



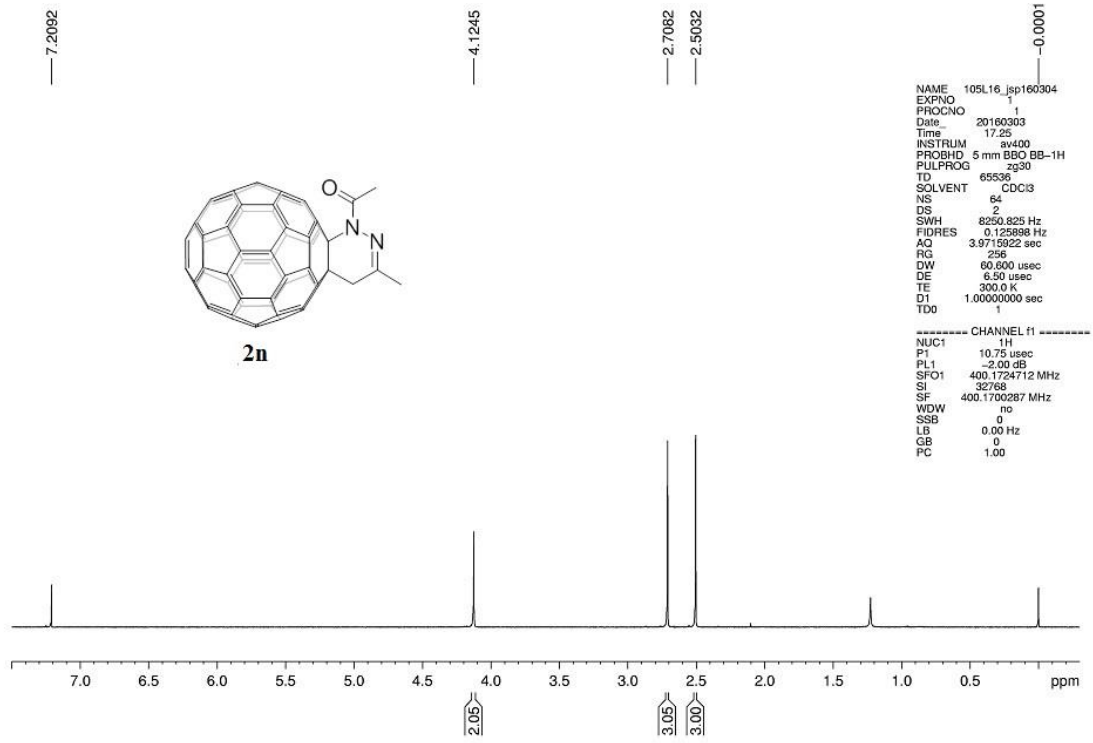
Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$, 213.1 K) spectrum of compound 2m



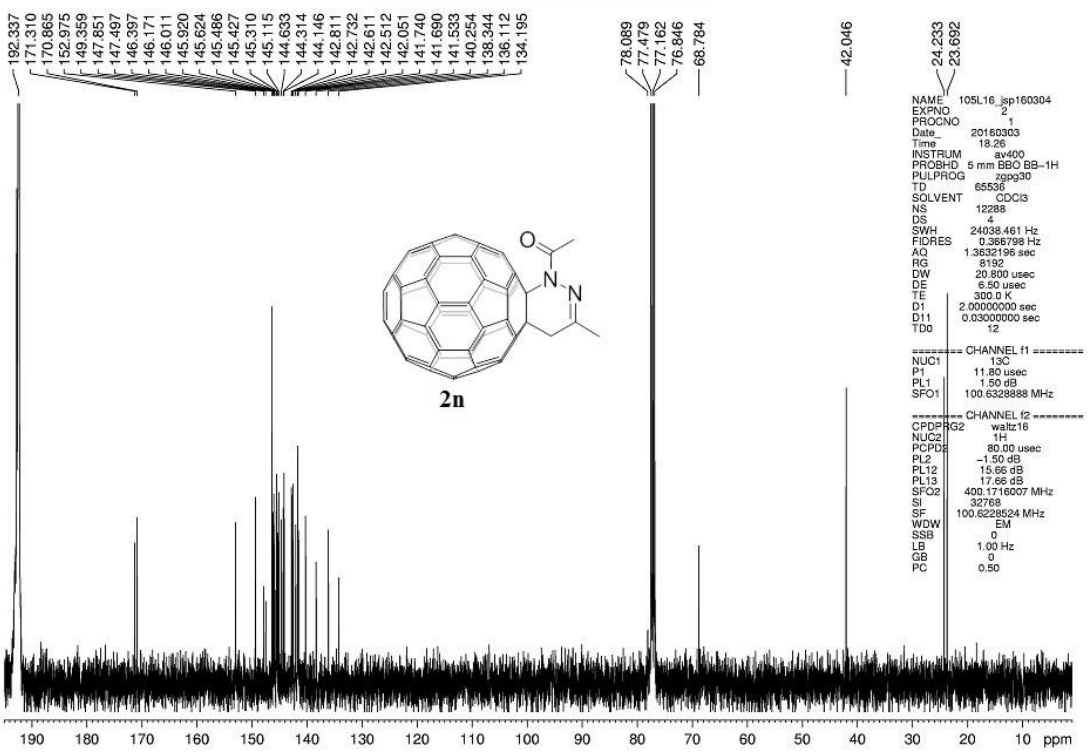
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$, 213.1 K) spectrum of compound 2m



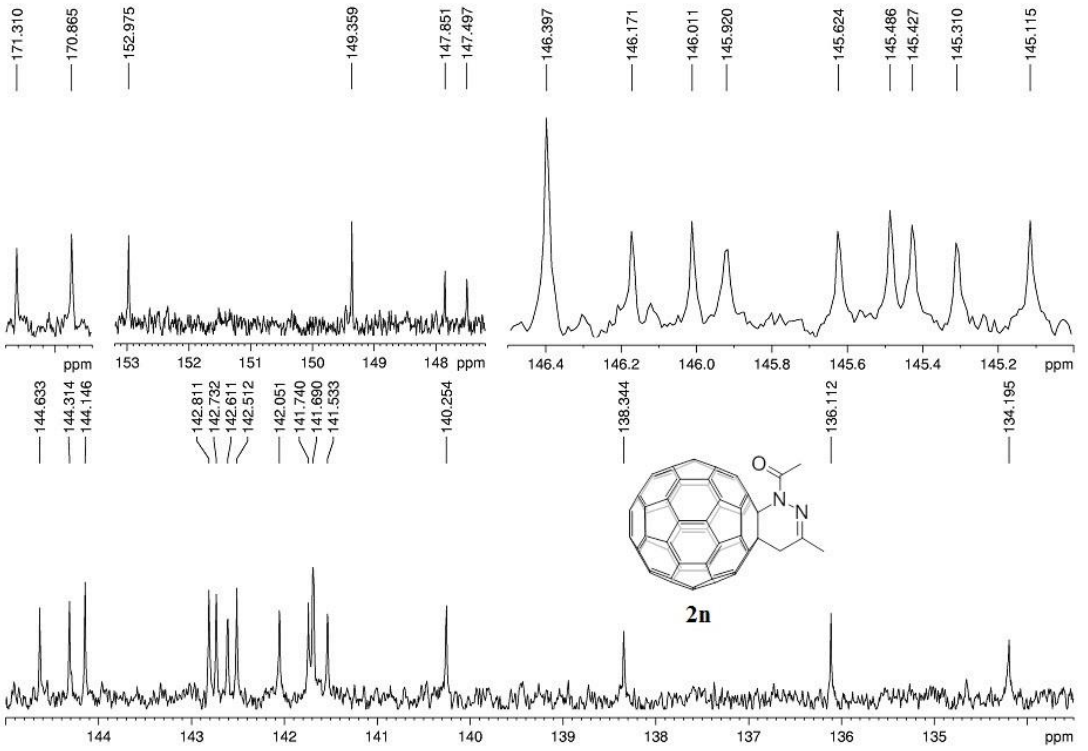
^{1}H NMR (400 MHz, $CS_2/CDCl_3$) spectrum of compound 2n



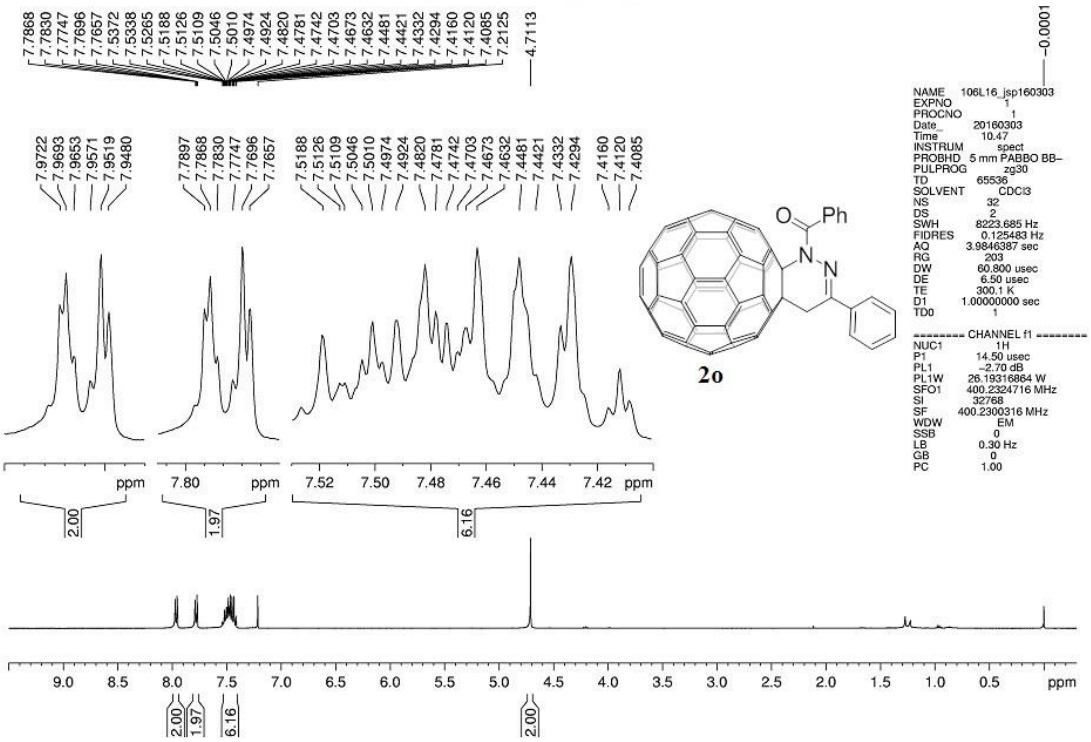
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2n



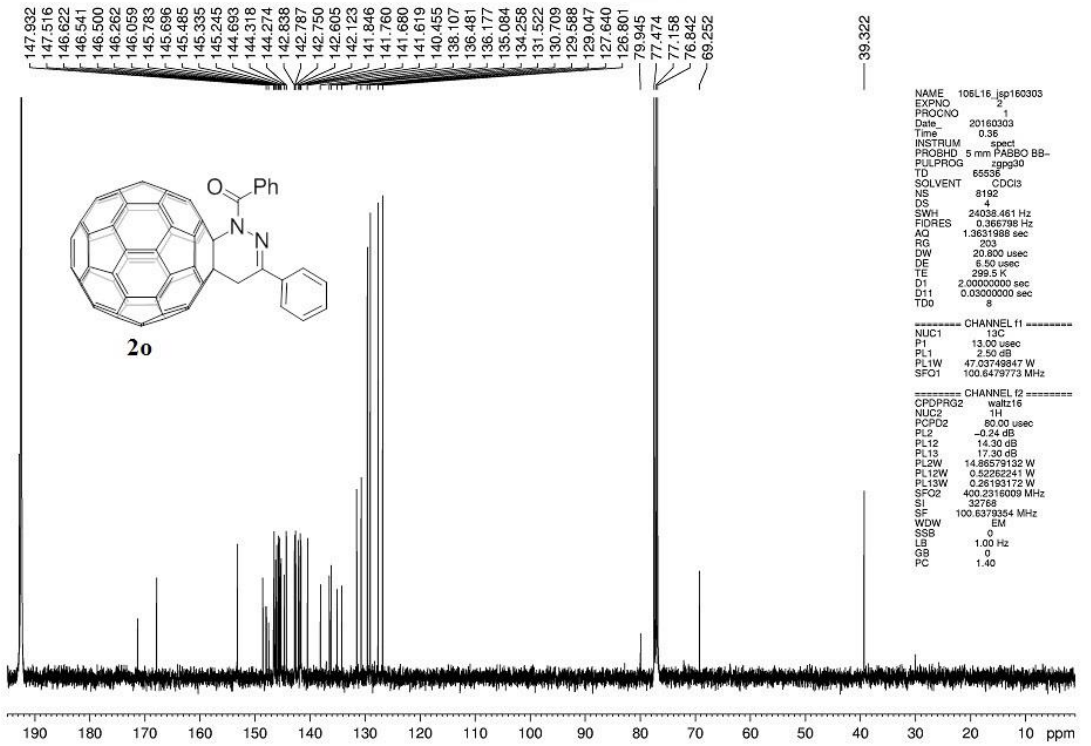
Expanded ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2n



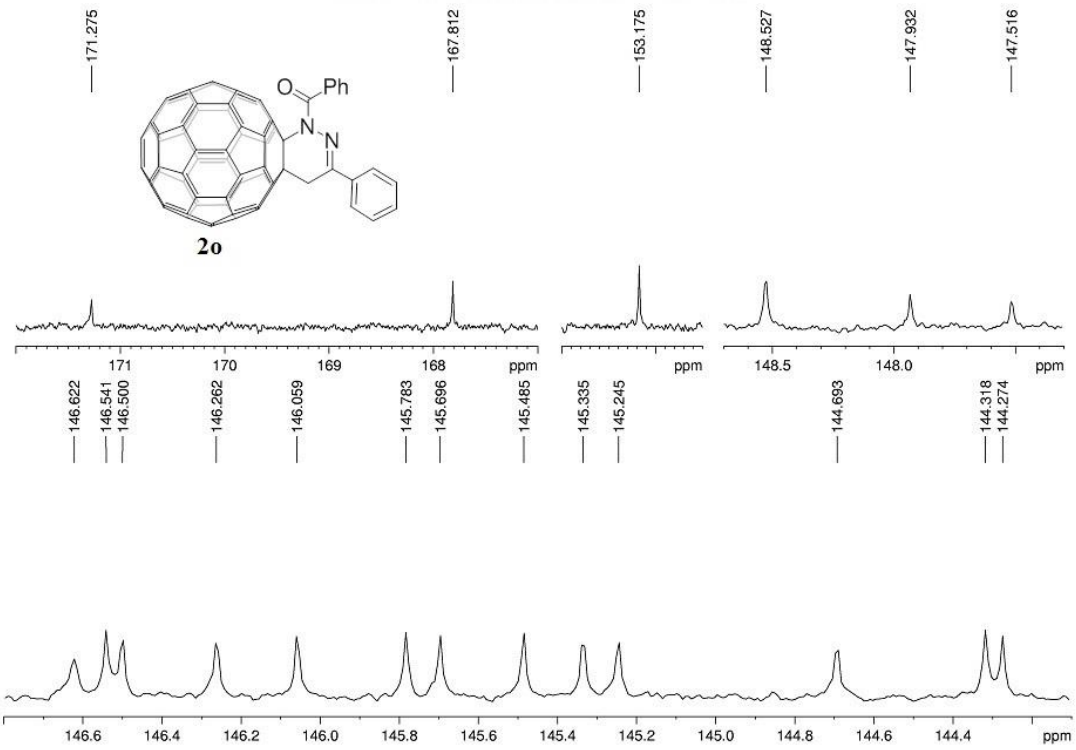
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 2o



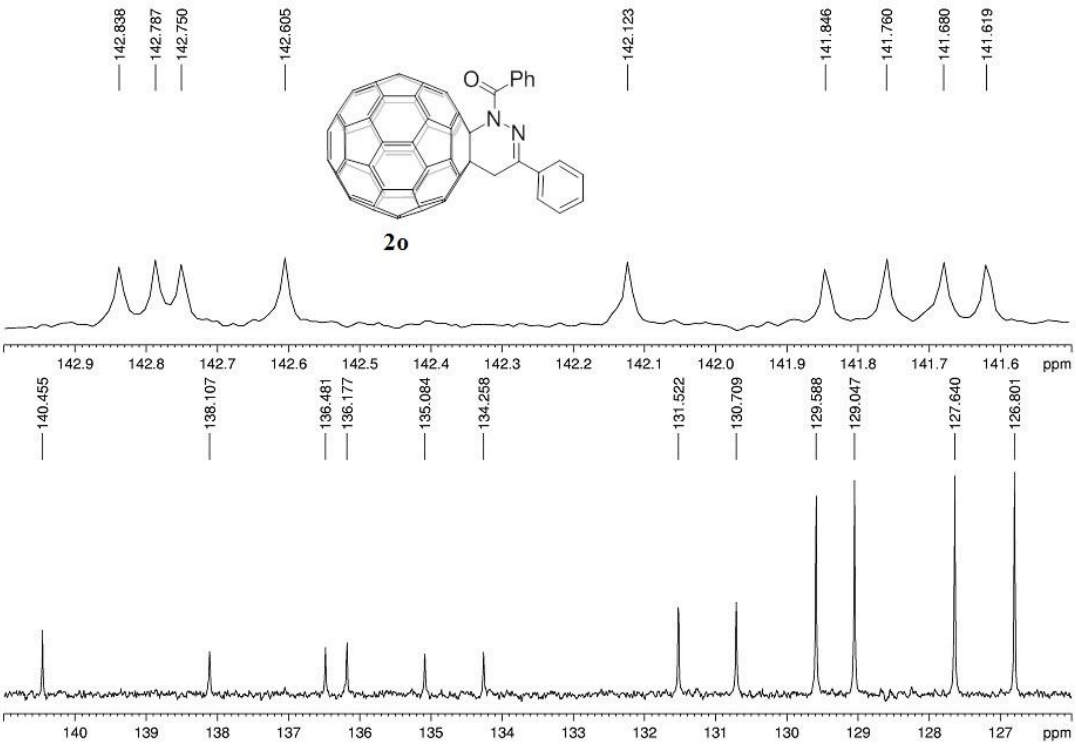
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 2o



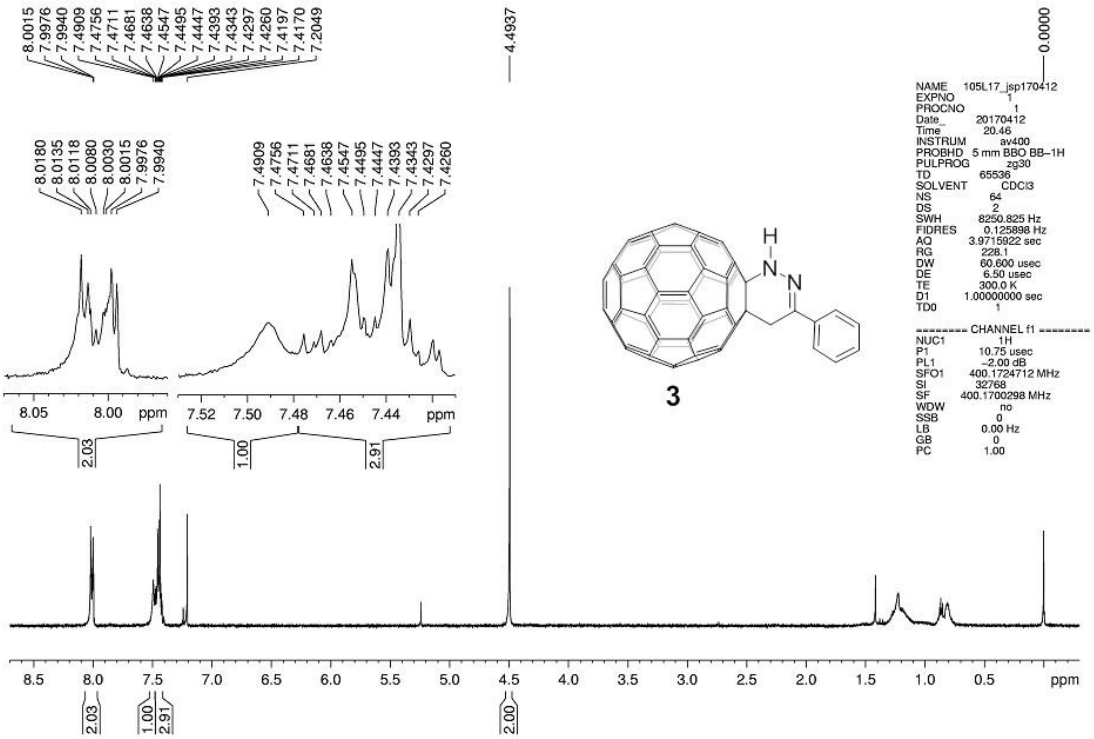
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2o



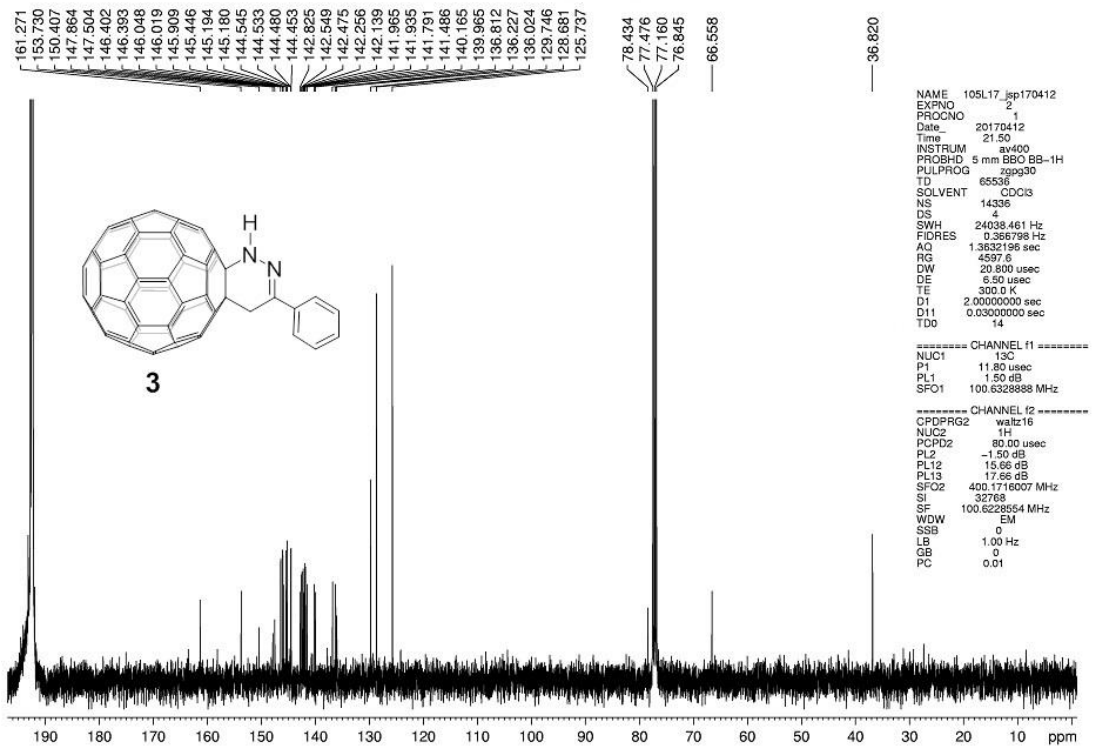
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 2o



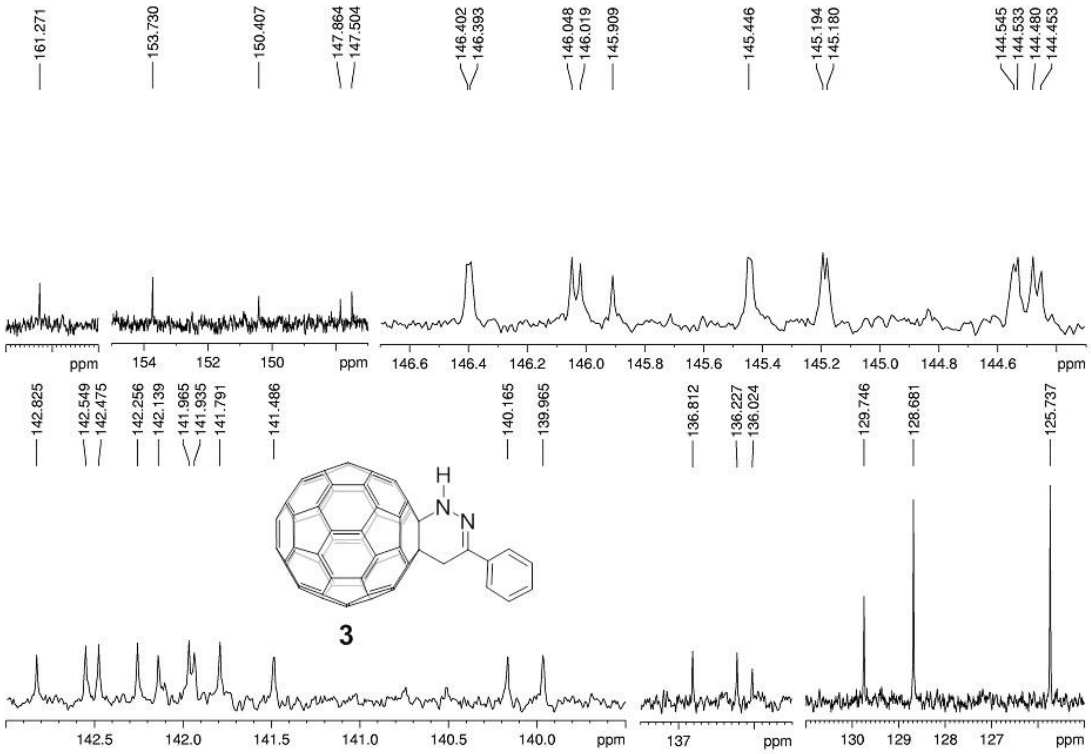
^{1}H NMR (400 MHz, CS_2/$CDCl_3$) spectrum of compound 3



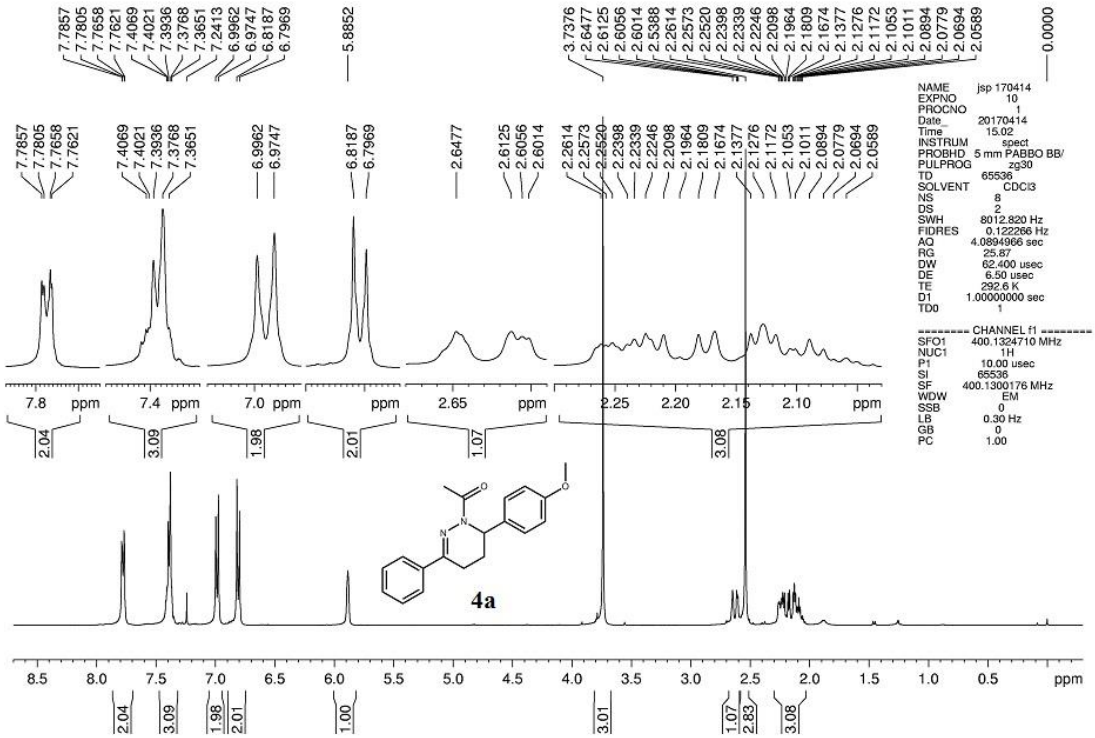
^{13}C NMR (100 MHz, CS_2/$CDCl_3$) spectrum of compound 3



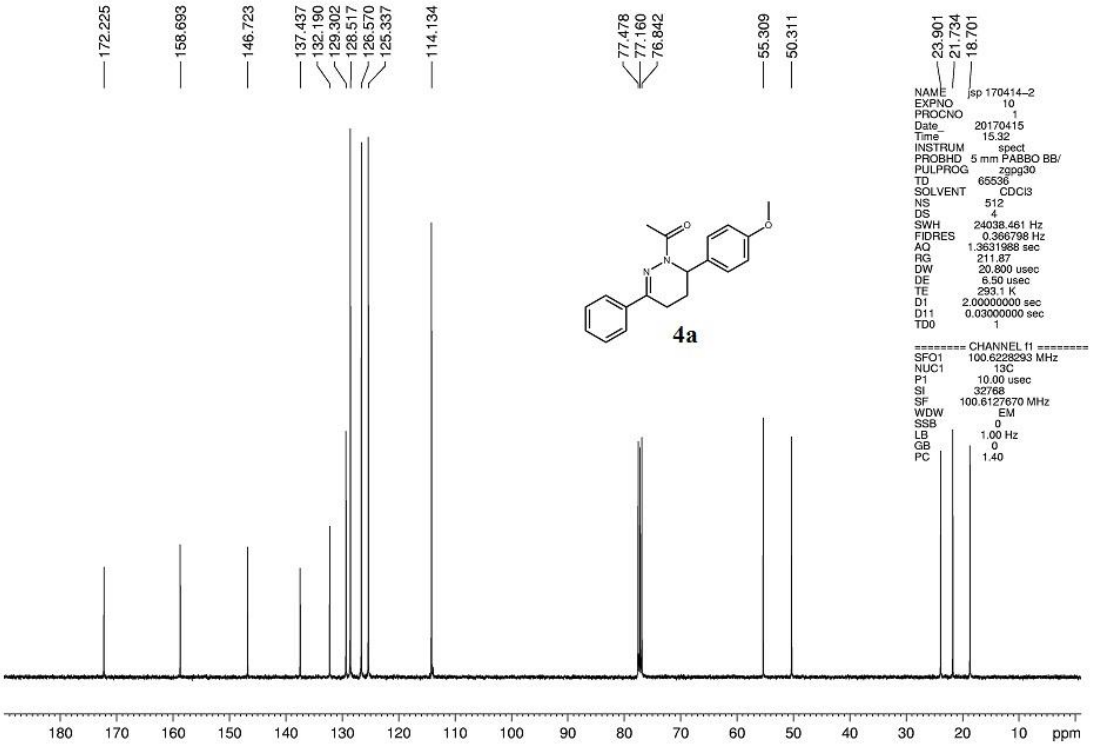
Expanded ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) spectrum of compound 3



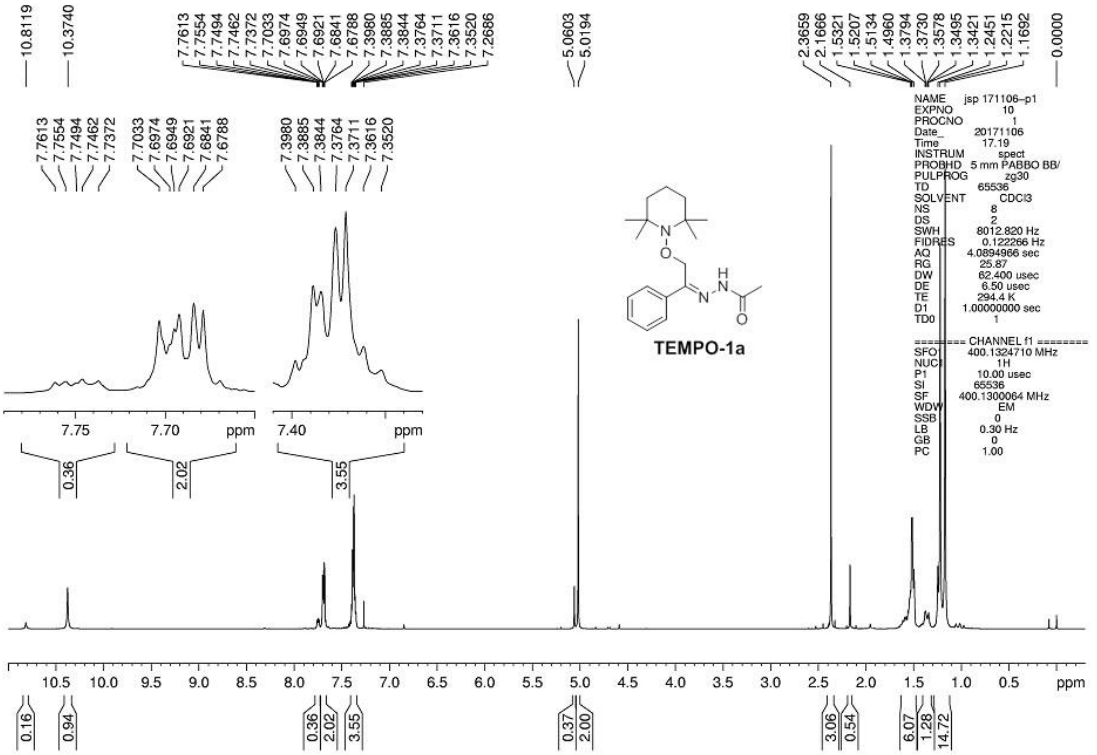
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4a



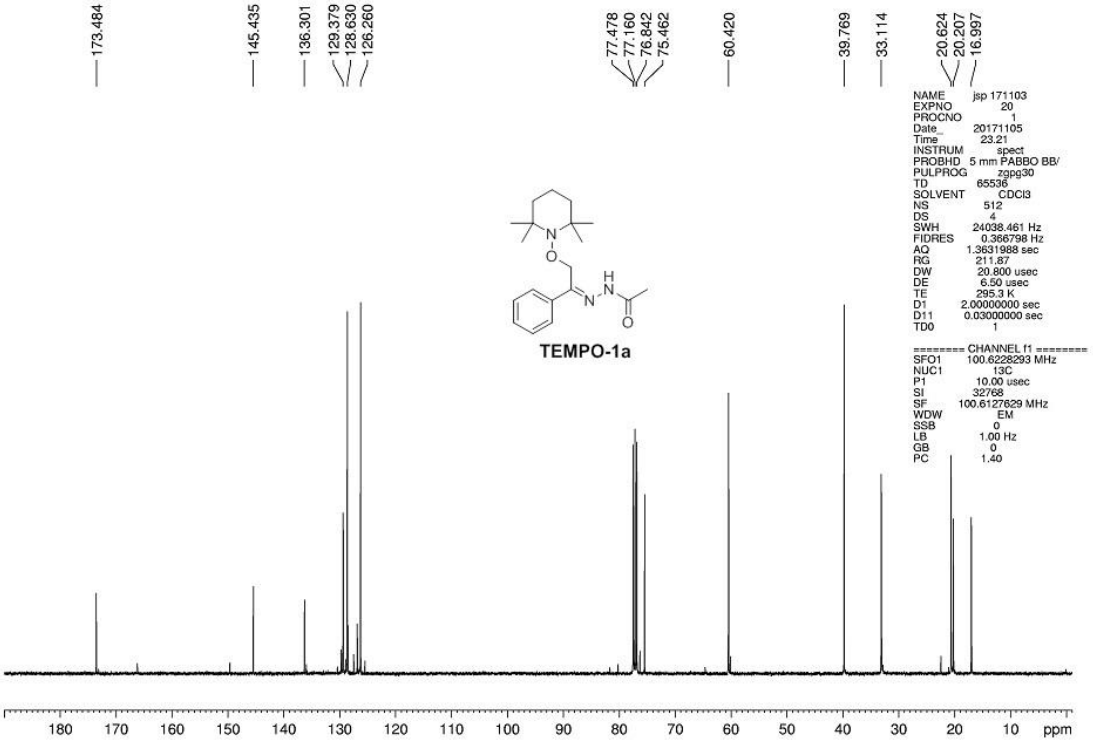
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 4a

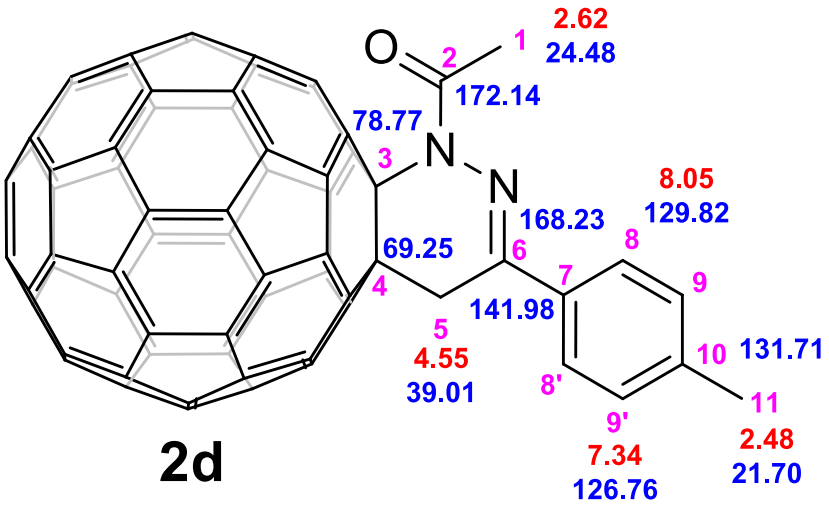


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound TEMPO-1a

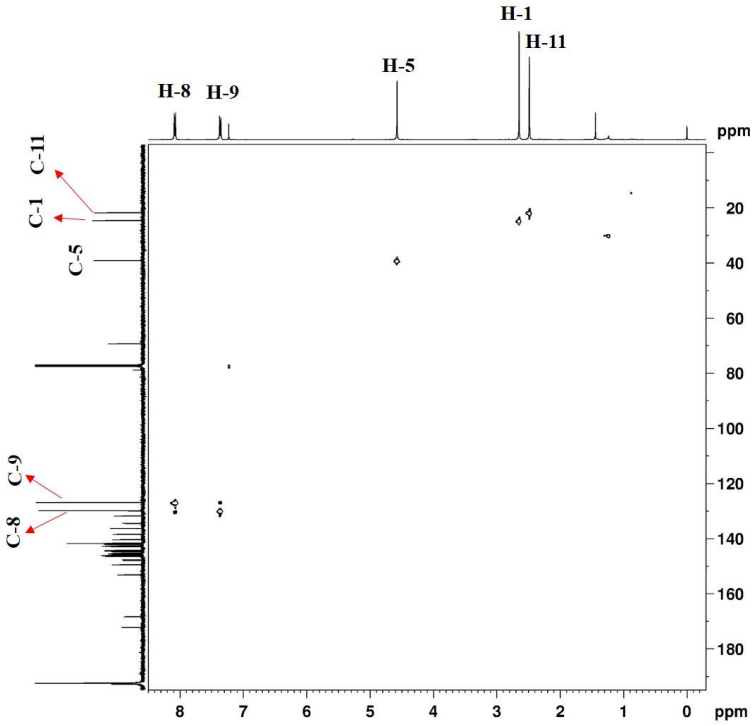


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound TEMPO-1a





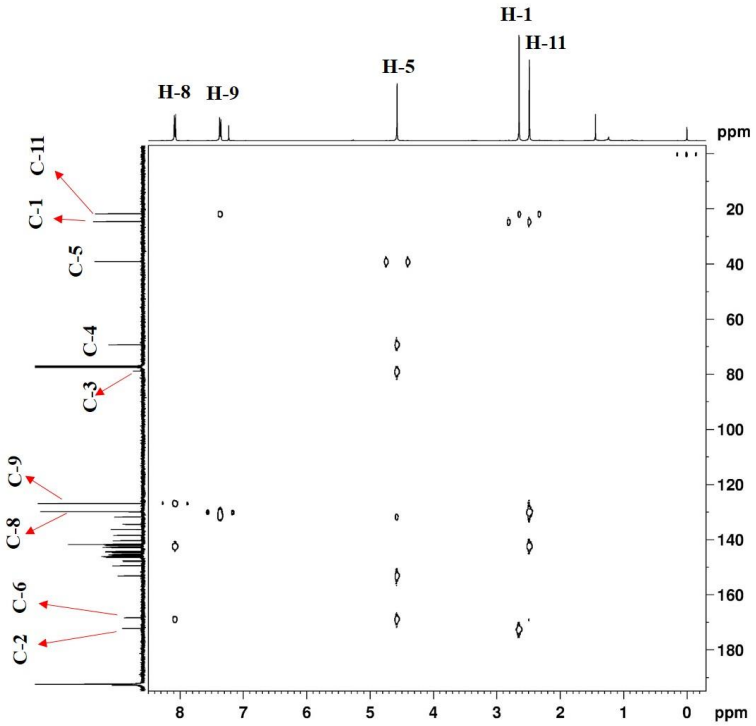
HSQC spectrum of compound **2d**



NAME jsp 170829
EXPNO 11
PROCNO 1
Date_ 20170830
Time 4.56
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hsqcetgp
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3521.127 Hz
FIDRES 3.438600 Hz
AQ 0.1454580 sec
RG 211.87
DW 142.000 usec
DE 6.50 usec
TE 294.6 K
CNST2 145.0000000
D0 0.00000300 sec
D1 1.45043802 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00020000 sec
IN0 0.00003000 sec
ZGOPTNS

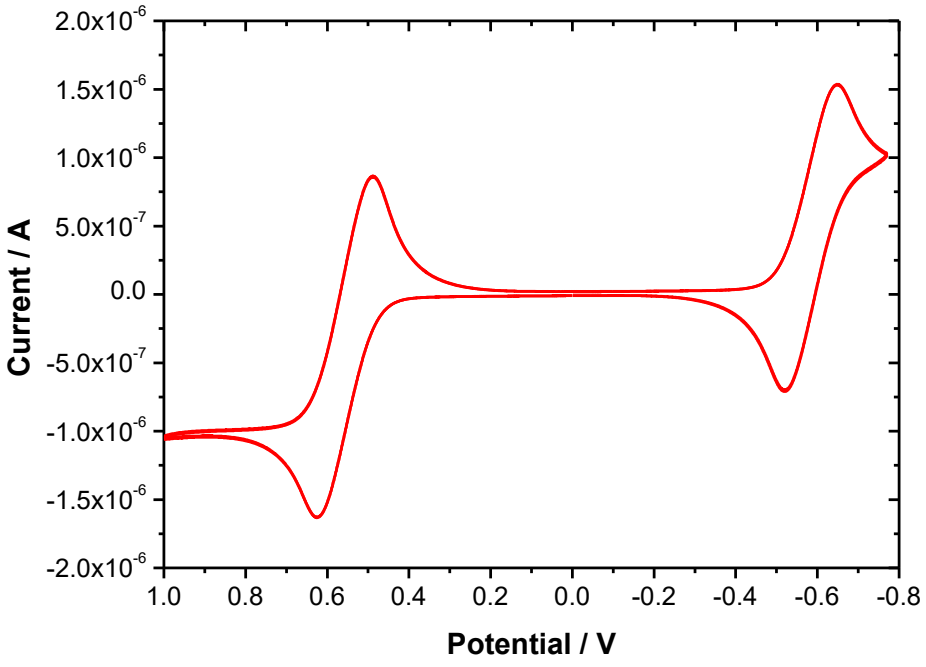
======== CHANNEL f1 ========
SFO1 400.1318278 MHz
NUC1 1H
P1 10.00 usec
P2 20.00 usec
P28 1000.00 usec
ND0 2
TD 256
SFO1 100.6203 MHz
FIDRES 65.104164 Hz
SW 165.639 ppm
FnMODE Echo-Antiecho
SI 1024
SF 400.1300229 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 echo-antiecho
SF 100.6127690 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

HMBC spectrum of compound **2d**

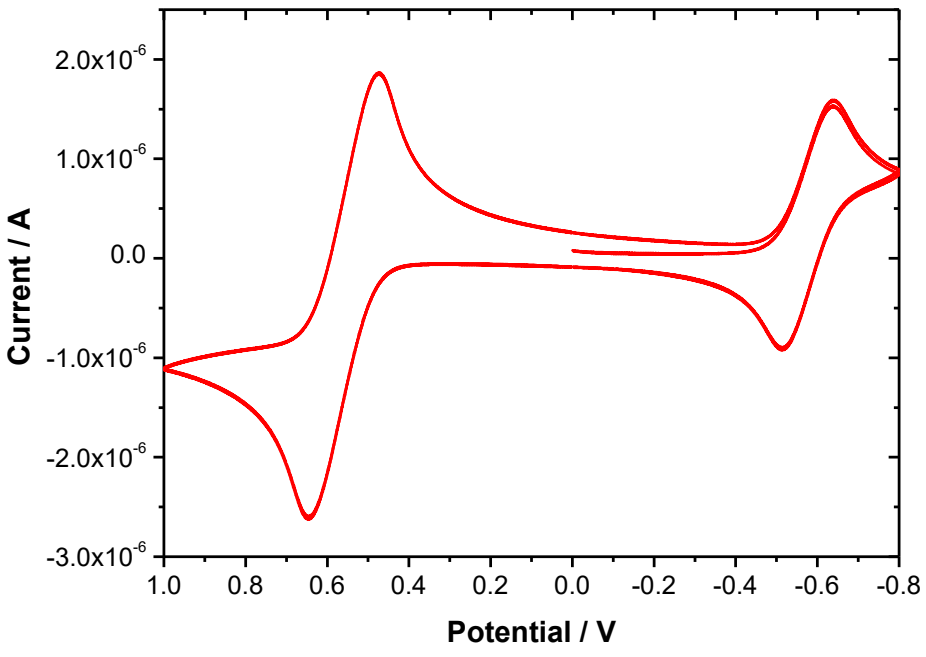


NAME jsp 170831
EXPNO 11
PROCNO 1
Date_ 20170831
Time 22.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hmbcgpndqf
TD 4096
SOLVENT CDCl3
NS 32
DS 16
SWH 4098.361 Hz
FIDRES 1.000576 Hz
AQ 0.4997620 sec
RG 211.87
DW 122.000 usec
DE 6.50 usec
TE 294.3 K
CNST13 8.0000000
D0 0.00000300 sec
D1 1.38449299 sec
D6 0.06250000 sec
D16 0.00020000 sec
IN0 0.00002240 sec

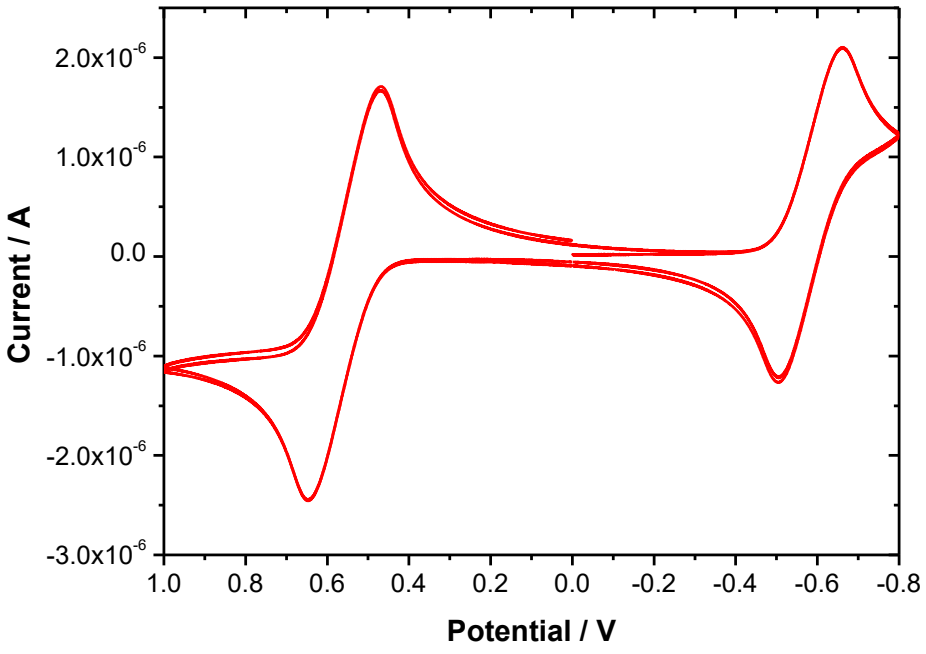
======== CHANNEL f1 ========
SFO1 400.1317389 MHz
NUC1 1H
P1 10.00 usec
P2 20.00 usec
ND0 2
TD 128
SFO1 100.6228 MHz
FIDRES 174.386154 Hz
SW 221.833 ppm
FnMODE QF
SI 1024
SF 400.1300222 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 100.6127690 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0



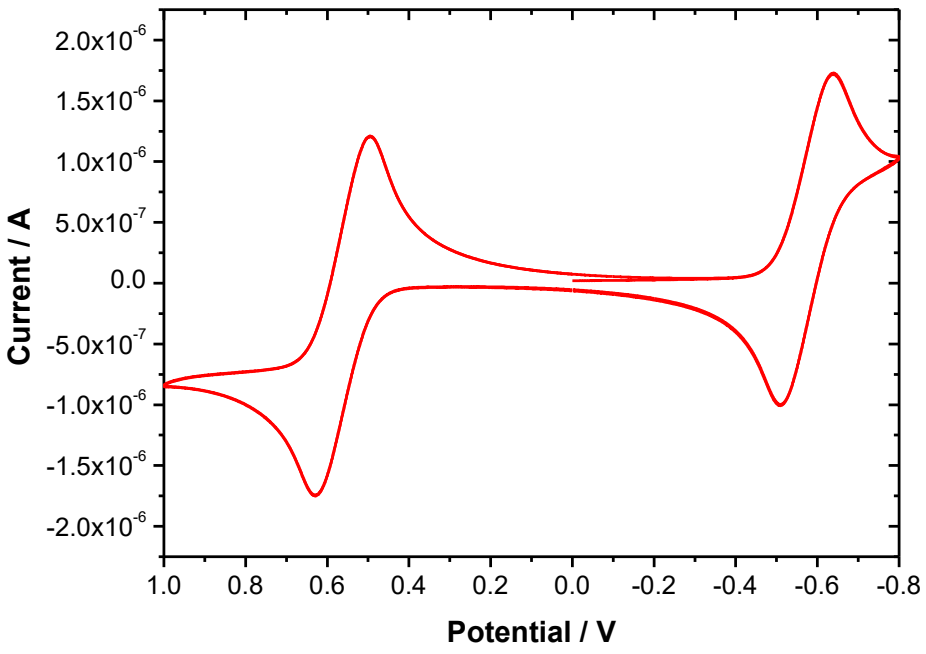
Cyclic voltammogram of compound **2a** (scanning rate: 20 mV s^{-1}**)**



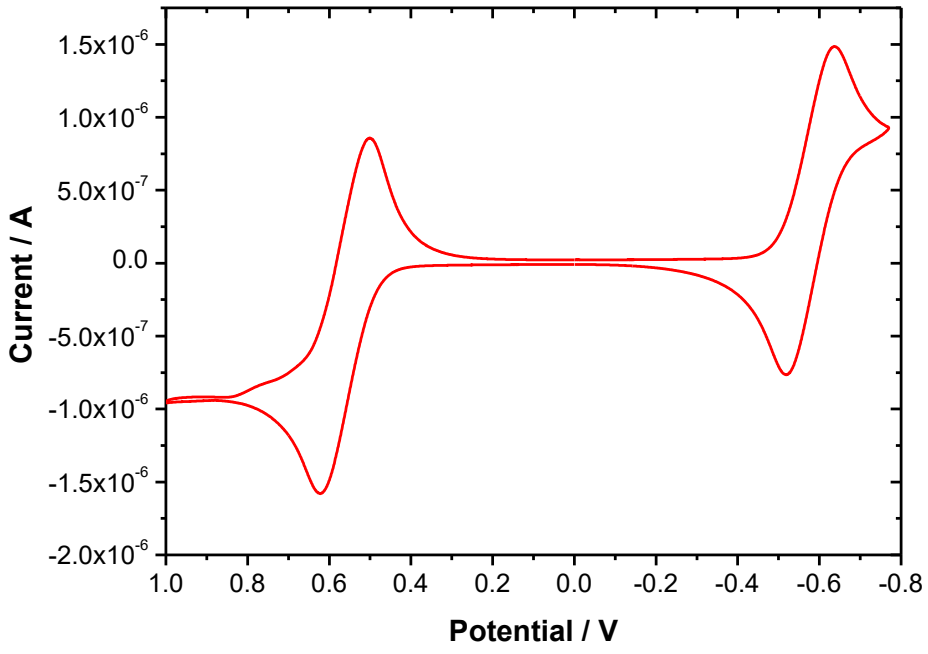
Cyclic voltammogram of compound **2b** (scanning rate: 20 mV s^{-1}**)**



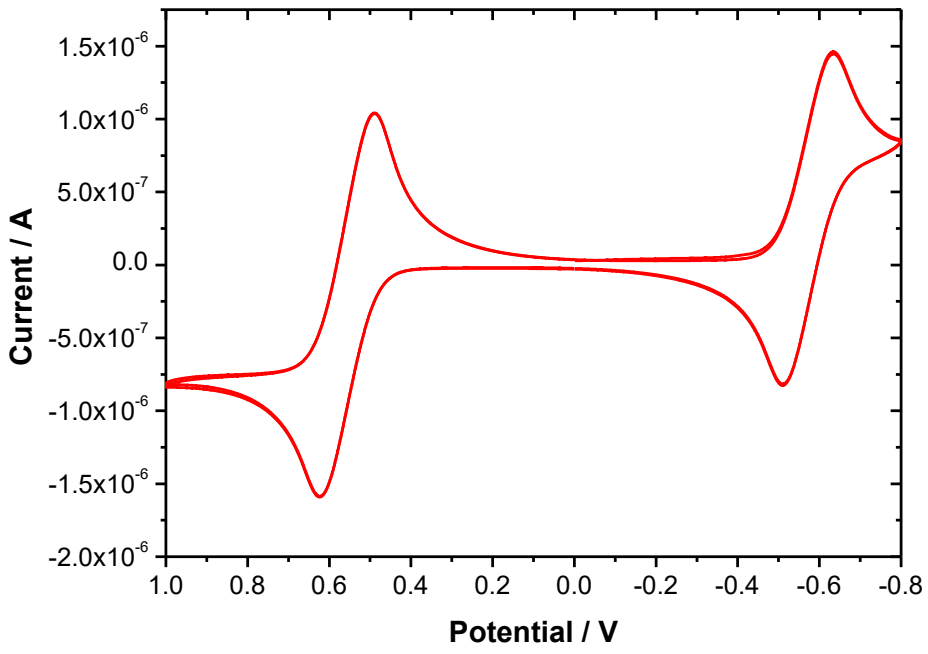
Cyclic voltammogram of compound **2c** (scanning rate: 20 mV s^{-1}**)**



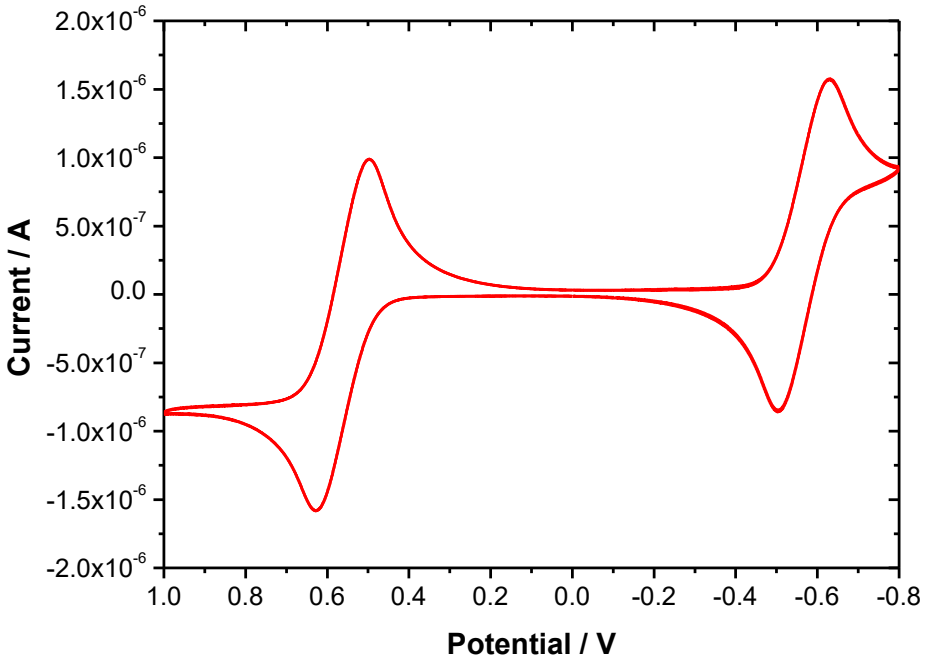
Cyclic voltammogram of compound **2d** (scanning rate: 20 mV s^{-1}**)**



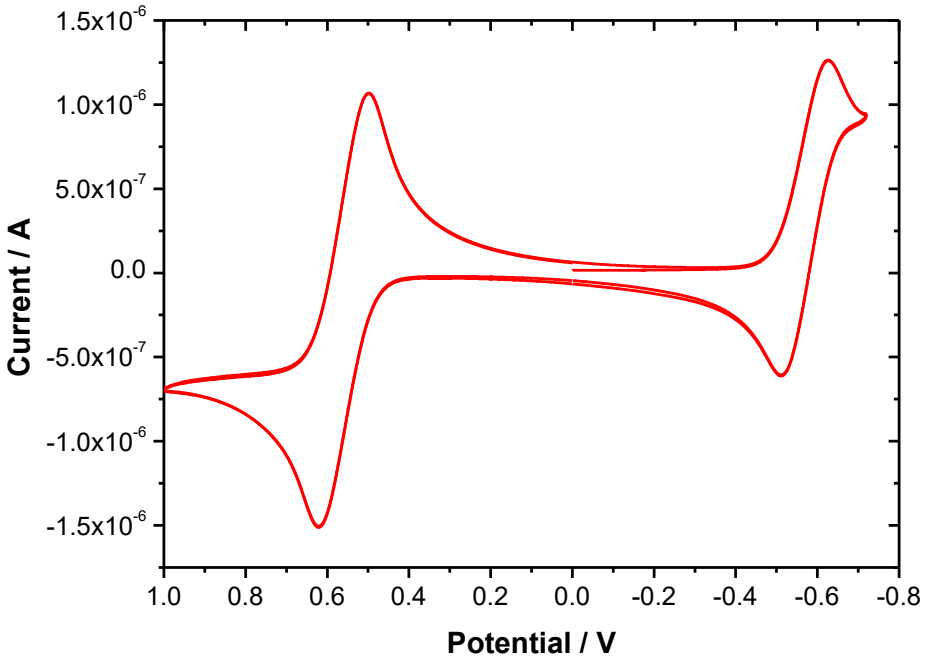
Cyclic voltammogram of compound **2e** (scanning rate: 20 mV s^{-1}**)**



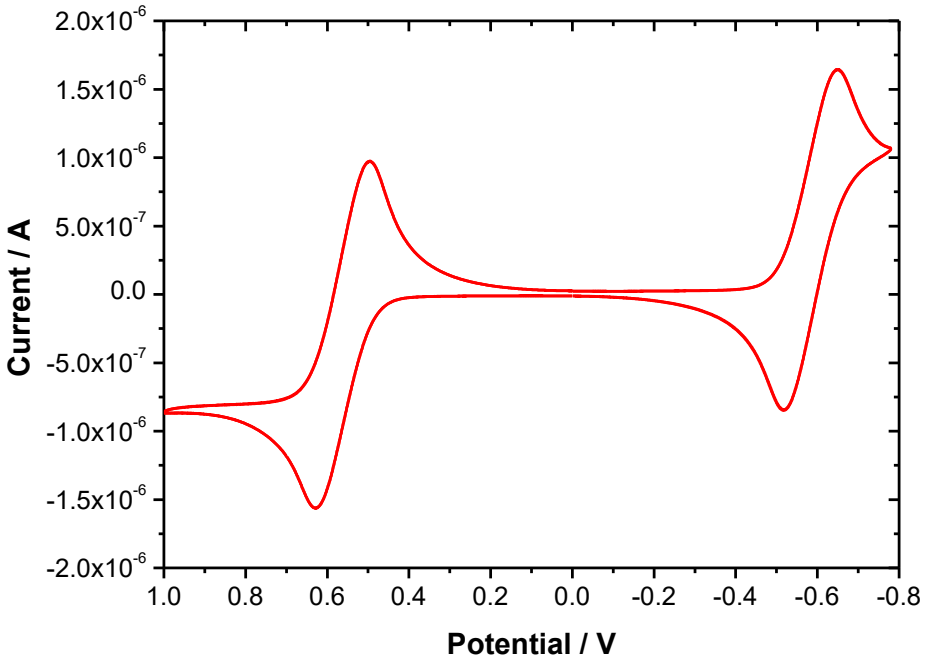
Cyclic voltammogram of compound **2f** (scanning rate: 20 mV s^{-1}**)**



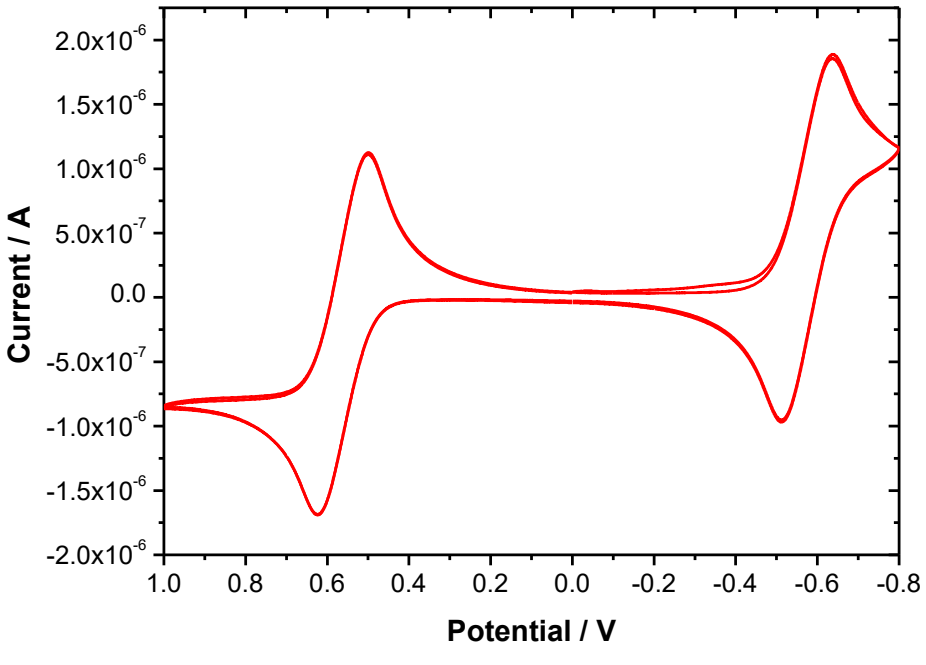
Cyclic voltammogram of compound **2g** (scanning rate: 20 mV s^{-1}**)**



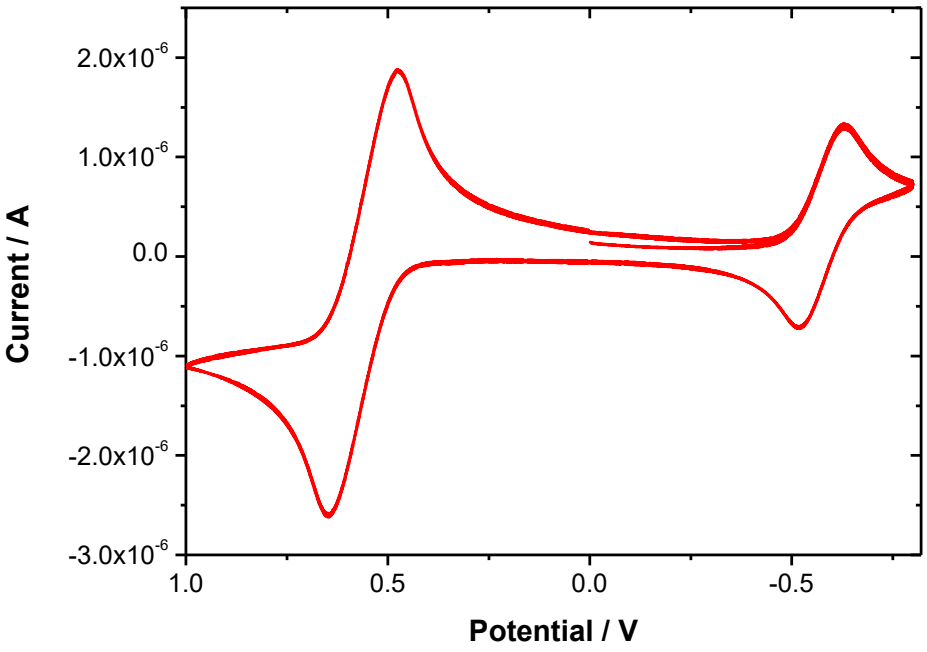
Cyclic voltammogram of compound **2h** (scanning rate: 20 mV s^{-1}**)**



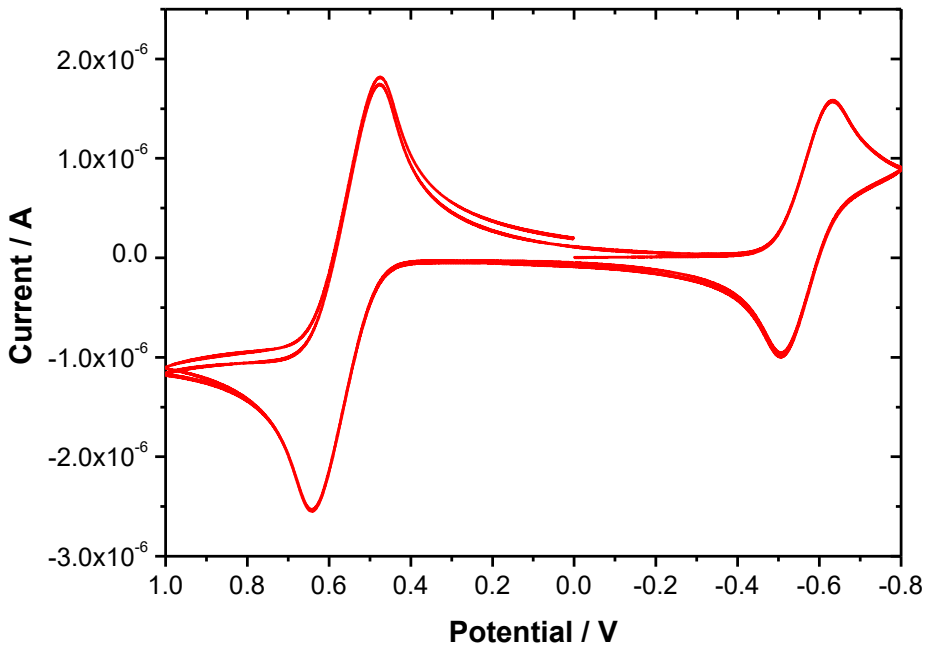
Cyclic voltammogram of compound **2i** (scanning rate: 20 mV s^{-1}**)**



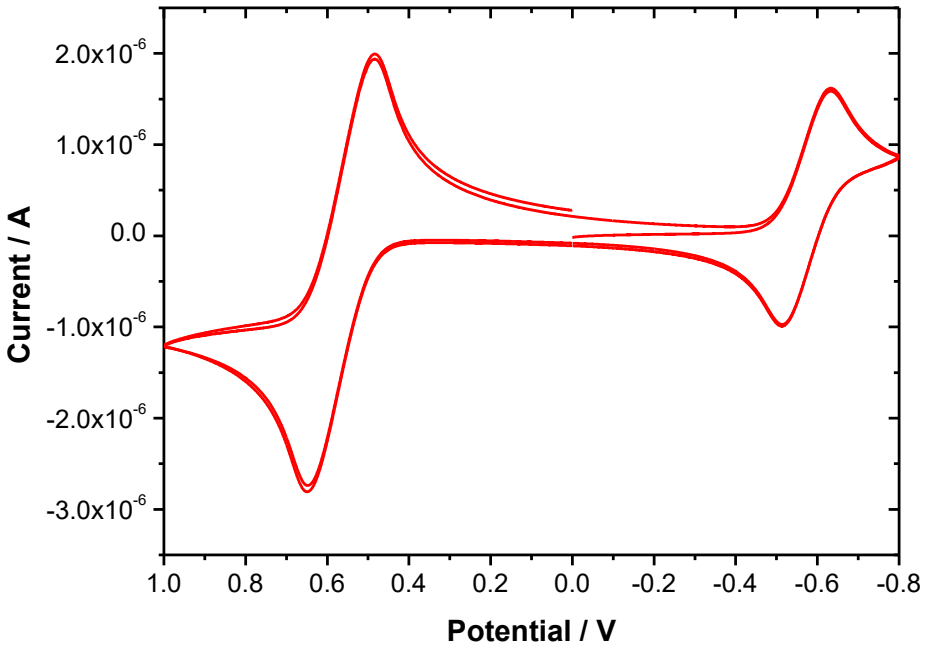
Cyclic voltammogram of compound **2j** (scanning rate: 20 mV s^{-1}**)**



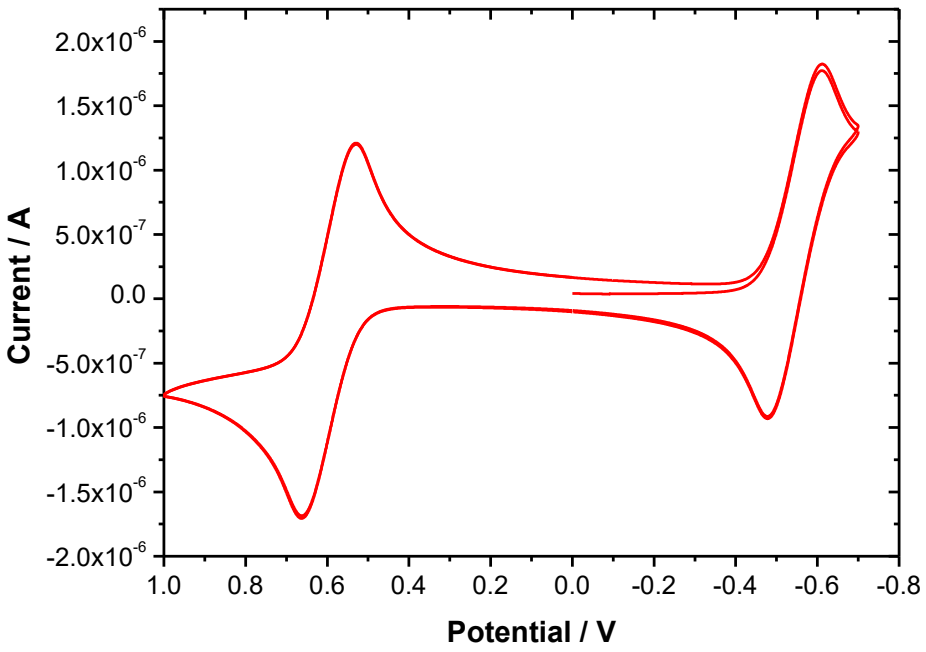
Cyclic voltammogram of compound **2k** (scanning rate: 20 mV s^{-1})



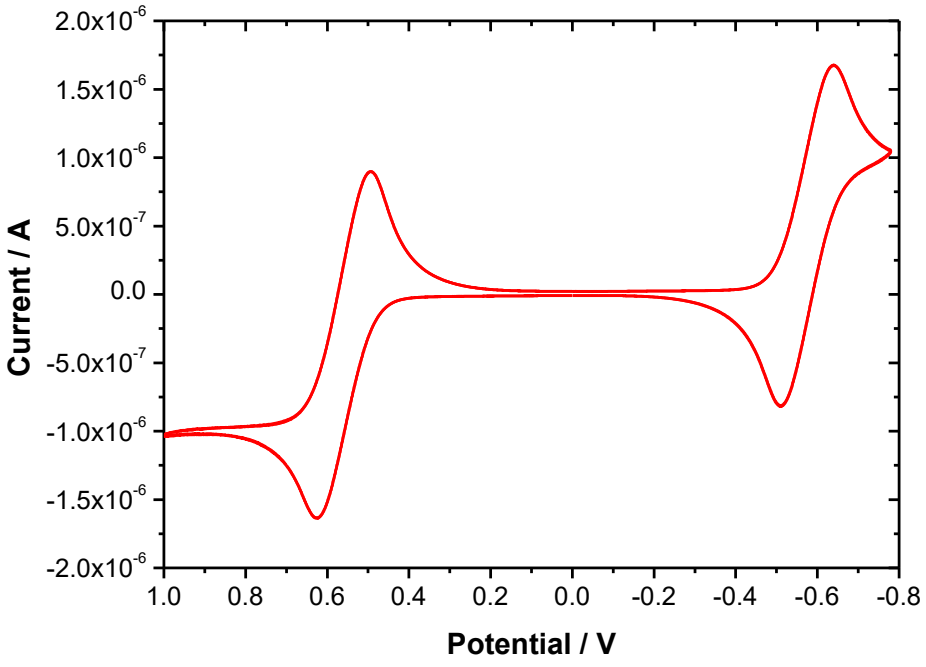
Cyclic voltammogram of compound **2l** (scanning rate: 20 mV s^{-1}**)**



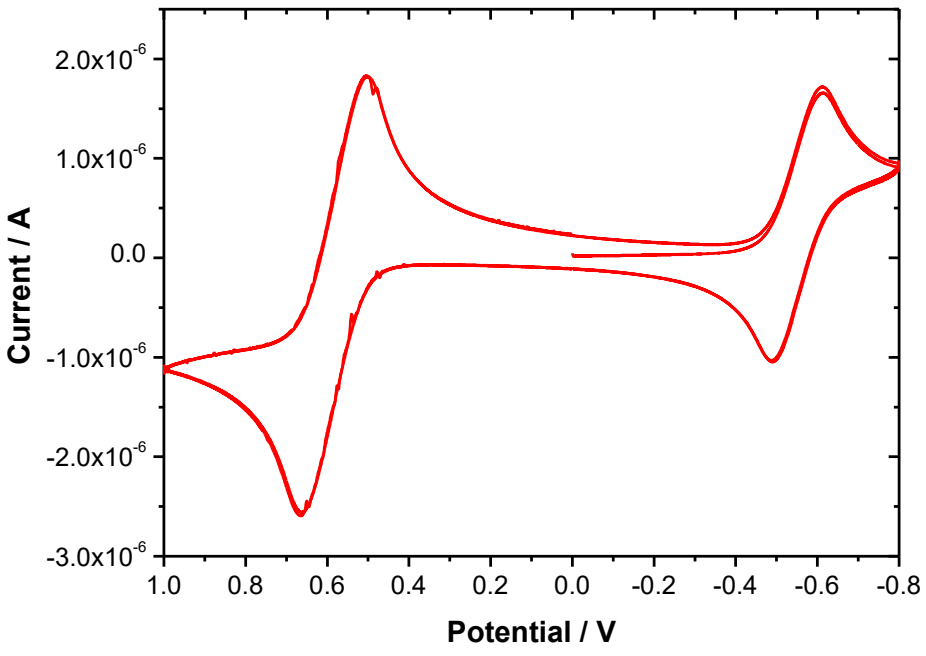
Cyclic voltammogram of compound **2m** (scanning rate: 20 mV s^{-1}**)**



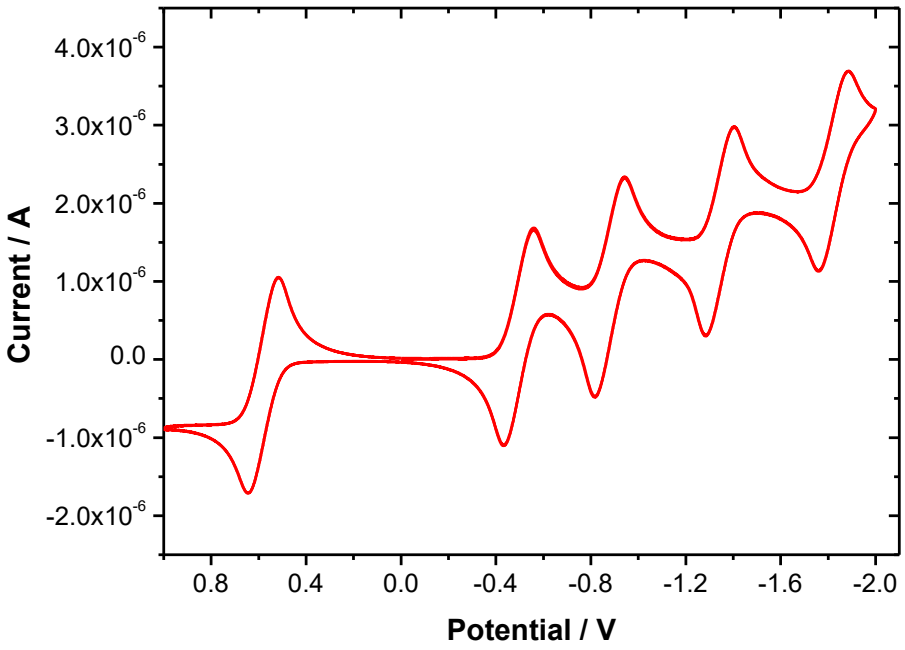
Cyclic voltammogram of compound **2n** (scanning rate: 20 mV s^{-1}**)**



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



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



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