Supporting Information

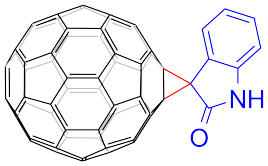
An "umpolung relay" Strategy: One-pot, Twice Polarity Inversion Cascade Synthesis of Diversified [60]Fulleroindoles

Xin-Rui Chen,[†] Ying-Meng Li,[†] Xiang Li,[†] Jun Xuan,[†] Hong-Ping Zhou,[†] Yu-Peng Tian[†] and Fei Li[*,†]

[†]Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei 230039, PR China
lfe@ahu.edu.cn

1. Experimental Procedures and Spectral Data of 2a-5lj

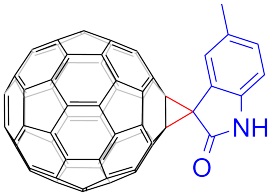
Synthesis of 2a



2a

C_{60} (36.0 mg, 0.05 mmol), indole (7.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (34 mg, 0.15 mmol) was added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (6.0 mg, 17%) and **2a** (15.1 mg, 35%) as black amorphous solid. ^{1}H NMR (600 MHz, CS_2/d_6-DMSO) δ 11.37 (s, N-H, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.42 (td, J = 7.8, 1.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.12 (td, J = 7.8, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 169.25(1C, carbonyl C), 145.3, 144.9, 144.4, 144.35, 144.29, 144.27, 144.25(1C), 144.2, 144.0, 143.9, 143.81, 143.80, 143.7, 143.6(1C), 143.5, 143.4, 143.0, 142.7, 142.31, 142.28, 142.2, 142.1, 142.0, 141.5, 141.4(4C), 140.9, 140.5, 140.3, 140.0, 138.0(1C, aryl C), 128.8(1C, aryl C), 124.6(1C, aryl C), 122.9(1C, aryl C), 121.0(1C, aryl C), 110.1(1C, aryl C), 75.0(sp^3-C of C_{60}), 42.2(1C); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{68}H_5NO$ 851.0371; found 851.0376.

Synthesis of 2b

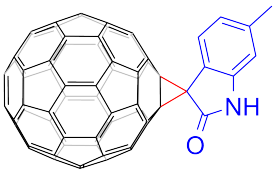


2b

C_{60} (36.0 mg, 0.05 mmol), 5-methyindole (8 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) was added to the mixture and stirred in an oil bath at 100 °C for 60

minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (7.1 mg, 20%) and **2b** (27.8 mg, 64%) as black amorphous solid. ^{1}H NMR (600 MHz, CS_2/d_6-DMSO) δ 11.26 (s, N-H, 1H), 7.98 (s, 1H), 7.22 (d, J = 6.0 Hz, 1H), 7.04 (dd, J = 7.8, 3.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR(150 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 169.3(1C , carbonyl C), 145.5, 144.9, 144.5, 144.38, 144.35, 144.3(4C), 144.2, 144.1, 143.9, 143.8, 143.8, 143.7, 143.6(1C), 143.5, 143.4, 143.0, 142.8, 142.4(1C), 142.32(1C), 142.27, 142.2, 142.1, 141.6, 141.49, 141.45, 141.0, 140.5, 140.4, 140.0, 139.9(1C), 138.0(1C, aryl C), 129.9(1C, aryl C), 129.3(1C, aryl C), 124.8(1C, aryl C), 123.6(1C, aryl C), 109.9(1C, aryl C), 75.1(sp^3-C of C_{60}), 42.2(1C), 21.1(1C, -CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_7NO$ 865.0528; found 865.0532.

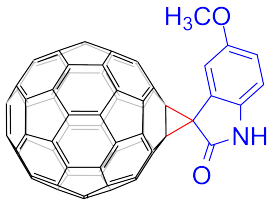
Synthesis of 2c



2c

C_{60} (36.0 mg, 0.05 mmol), 6-methyindole (8 μL, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (45 μL, 0.5 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) was added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (3.3 mg, 9%) and **2c** (10.2 mg, 24%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.29 (s, N-H, 1H), 8.04 (d, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.92 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 169.6(1C, carbonyl C), 145.6, 144.9, 144.5, 144.4, 144.33, 144.31, 144.30, 144.21, 144.17, 143.9, 143.8(4C), 143.73, 143.66(1C), 143.5, 143.4, 143.0, 142.8, 142.4(1C), 142.4(1C), 142.34(1C), 142.26, 142.2, 142.1, 141.5, 141.5, 141.4, 140.9, 140.5, 140.4, 140.1, 138.7 (1C, aryl C), 138.0(1C, aryl C), 122.7(1C, aryl C), 121.8(1C, aryl C), 121.6(1C, aryl C), 111.0(1C, aryl C), 75.1(sp^3-C of C_{60}), 42.3(1C), 21.3(1C, -CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_7NO$ 865.0528; found 865.0530.

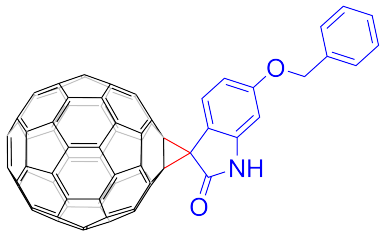
Synthesis of 2d



2d

C_{60} (36.0 mg, 0.05 mmol), 5-methoxyindole (9 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) was added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (8.1 mg, 23%) and **2d** (21.1 mg, 48%) as black amorphous solid. ^{1}H NMR (600 MHz, CS_2/d_6-DMSO) δ 11.17 (s, N-H, 1H), 7.75 (d, J = 3.0 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.4, 2.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 169.24(1C , carbonyl C), 154.3(1C, aryl C), 145.3, 144.9, 144.43, 144.39, 144.33, 144.30, 144.29(1C), 144.2, 144.0, 143.89, 143.86, 143.8, 143.7, 143.6(1C), 143.5, 143.4, 143.0, 142.8, 142.4 (1C), 142.32(1C), 142.27, 142.2, 142.0, 141.6, 141.5, 141.4, 140.9, 140.5, 140.4, 140.0, 137.9, 135.6(1C, aryl C), 125.7 (1C, aryl C), 112.7(1C, aryl C), 111.3(1C, aryl C), 110.1(1C, aryl C), 75.0(sp^3-C of C_{60}), 54.9(1C , -OCH_3), 42.3(1C); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_7NO_2$ 881.0477; found 881.0481.

Synthesis of 2e

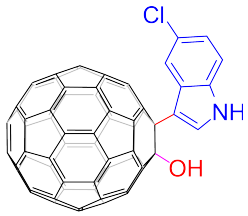


2e

C_{60} (36.0 mg, 0.05 mmol), 6-benzyloxyindole (14 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56

mg, 0.25 mmol) was added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (12.3 mg, 34%) and **2e** (23.1 mg, 48%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.31 (s, N-H, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 6.68 (dd, J = 8.8, 2.4 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR(100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 169.8(1C, carbonyl C), 159.4(1C, aryl C), 145.7, 145.0(1C, aryl C), 144.5, 144.4, 144.32(4C), 144.27, 144.2(4C), 143.9, 143.8(4C), 143.7, 143.7(1C), 143.6(1C), 143.5, 143.4, 143.0, 142.8, 142.33(1C), 142.32(1C), 142.2, 142.1, 142.0, 141.4(4C), 141.4, 140.9, 140.5, 140.4, 140.1, 137.9, 136.1(1C, aryl C), 127.8(aryl C), 127.2(1C, aryl C), 126.7(aryl C), 123.7(1C, aryl C), 116.8(1C, aryl C), 107.0(1C, aryl C), 97.9(1C, aryl C), 75.2(sp^3-C of C_{60}), 69.2(1C, -OCH_2-), 42.3(1C); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{75}H_{11}O_2N$ 957.0790; found 957.0793.

Synthesis of 3f

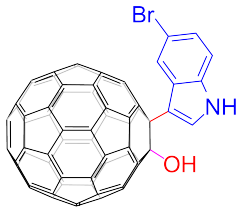


3f

C_{60} (36.0 mg, 0.05 mmol), 5-chloroindole (9 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and H_2O (36 μL, 2 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (5 mg, 14%) and **3f** (17.9 mg, 41%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.42 (s, N-H, 1H), 8.62 (s, 1H), 7.83.-7.82 (m, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.20 (dd, J = 8.8, 1.6 Hz, 1H); ^{13}C NMR(100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 156.0, 153.8, 147.7(1C), 147.1(1C), 145.8, 145.7, 145.4(4C), 145.2(4C), 145.0(4C), 144.63, 144.62, 144.5, 144.20, 144.18, 142.3, 141.9, 141.82, 141.77, 141.62, 141.58, 141.4, 141.0, 140.6, 139.2, 138.7, 135.4, 134.9, 129.5(1C, aryl C), 126.4(1C, aryl C), 124.40(1C, aryl C), 124.36(1C, aryl C), 121.3(1C, aryl C), 119.9(1C, aryl C), 115.0(1C, aryl C), 112.5(1C, aryl C), 86.1(1C, sp^3-C of C_{60}),

65.0(1C, sp^3-C of C_{60}); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{68}H_6ClNO$ 887.0138; found 887.0142.

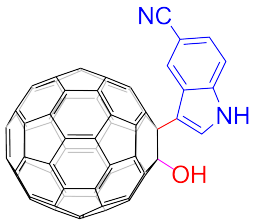
Synthesis of 3g



3g

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and H_2O (36 μL, 2 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (13 mg, 36%) and **3g** (23.2 mg, 50%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.43 (s, N-H, 1H), 8.76 (s, 1H), 7.82 (s, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 8.8 Hz， 1H), 7.32 (dd, J = 8.4, 1.6 Hz, 1H); ^{13}C NMR(100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 156.0, 153.8, 147.8(1C), 147.1(1C), 145.8, 145.7, 145.4(4C), 145.2(4C), 145.0(4C), 144.64, 144.62, 144.5, 144.20, 144.18, 142.3, 141.9, 141.82, 141.77, 141.62, 141.59, 141.4, 141.0, 140.6, 139.2, 138.7, 135.4, 135.2, 134.7(1C, aryl C), 130.2(1C, aryl C), 126.3(1C, aryl C), 123.8(1C, aryl C), 122.9(1C, aryl C), 114.9(1C, aryl C), 113.0(1C, aryl C), 112.5(1C, aryl C), 86.1(1C, sp^3-C of C_{60}), 65.0(1C, sp^3-C of C_{60}); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{68}H_6BrNO$ 930.9633; found 930.9637.

Synthesis of 3h

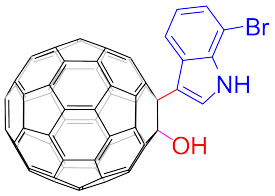


3h

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30

minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and H_2O (36 μL, 2 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane/ethyl acetate(6:2:1) as the eluent to give unreacted C_{60} (13.3 mg, 37%) and **3h** (16 mg, 36%) as black amorphous solid.^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.81 (s, N-H, 1H), 9.00 (s, 1H), 8.00 (d, J = 2.0 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO)(all 2C unless indicated) δ 155.7, 147.7(1C), 147.1(1C), 145.8, 145.7, 145.4(4C), 145.2(4C), 144.9, 144.9(4C), 144.6(4C), 144.5, 144.18, 144.15, 142.2, 141.9, 141.84(4C), 141.76, 141.62, 141.56, 141.4, 141.1, 140.6, 139.2, 138.7, 138.2, 135.3(1C, aryl C), 128.3(1C, aryl C), 127.1(1C, aryl C), 126.1(1C, aryl C), 123.7(1C, aryl C), 119.8(-CN), 116.5(1C, aryl C), 112.6(1C, aryl C), 101.9(1C, aryl C), 86.2(1C, sp^3-C of C_{60}), 64.8(1C, sp^3-C of C_{60}); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_6N_2O$ 878.0480; found 878.0485.

Synthesis of 3i

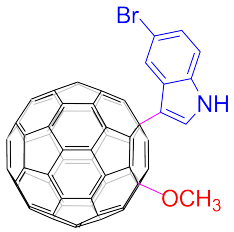


3i

C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (180 μL, 2 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and H_2O (36 μL, 2 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (10 mg, 28%) and **3i** (27 mg, 58%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.38 (s, N-H, 1H), 8.73 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 1.2 Hz, 1H), 7.77 (s, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 156.0, 153.9, 147.7(1C), 147.1(1C), 145.8, 145.7, 145.4(4C), 145.2(4C), 145.03, 145.00, 144.63, 144.61, 144.5, 144.20, 144.18, 142.3, 141.84, 141.82, 141.7, 141.61, 141.59, 141.3, 141.0, 140.6, 139.2, 138.7, 135.4, 134.8, 134.8(1C, aryl C), 130.2(1C, aryl C), 126.2(1C, aryl C),

123.7(1C, aryl C), 120.3(1C, aryl C), 120.0(1C, aryl C), 116.4(1C, aryl C), 104.5(1C, aryl C), 86.2(1C , sp^3-C of C_{60}), 65.2(1C, sp^3-C of C_{60}); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{68}H_6BrNO$ 930.9633; found 930.9637.

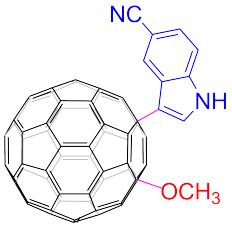
Synthesis of 5ga



5ga

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (2.1 mg, 6 %) and **5ga** (18.9 mg, 40 %) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.59 (s, N-H, 1H), 8.59 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 2.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 4.19 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 154.0, 152.0, 149.0, 148.2, 147.6, 147.1, 146.9, 146.4, 146.24(2C), 146.18(2C), 146.1, 145.9, 145.80, 145.77, 145.0(2C), 144.8, 144.20, 144.18, 143.9, 143.8(2C), 143.7, 143.6, 143.50, 143.47(4C), 143.4, 143.2, 143.0, 142.7, 142.63, 142.58, 142.56, 142.55, 142.4(2C), 142.18(2C), 142.16, 142.03, 142.00, 141.82, 141.80, 141.6, 141.5, 140.3, 140.0, 139.6, 139.1, 138.8, 136.74, 136.67, 135.3(aryl C), 126.7(aryl C), 125.5(aryl C), 124.3(aryl C), 121.8(aryl C), 113.8(aryl C), 113.4(aryl C), 112.9(aryl C), 80.5(sp^3-C of C_{60}), 55.4(sp^3-C of C_{60}), 54.0(-OCH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_8BrNO$ 944.9789; found 944.9794.

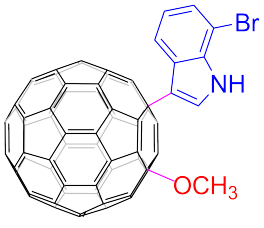
Synthesis of 5ha



5ha

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (10 mg, 28%) and **5ha** (26 mg, 58%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.99 (s, N-H, 1H), 8.94 (s, 1H), 8.00 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 4.23 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 153.8, 153.4, 151.4, 148.6, 147.9, 147.4, 146.8, 146.5, 146.2, 146.01, 145.96, 145.94, 145.89, 145.8, 145.7, 145.53, 145.50, 144.7(2C), 144.6, 144.0, 143.9, 143.6, 143.5, 143.4(2C), 143.3(2C), 143.23, 143.19(3C), 143.1, 143.0, 142.6, 142,5, 142.4, 142.3(3C), 142.14, 142.08, 142.0(2C), 141.9, 141.8, 141.7, 141.6, 141.5, 141.3, 141.2, 140.1, 139.8, 139.5, 138.8, 138.4, 138.0, 136.6, 136.5(aryl C), 126.5(aryl C), 124.6(aryl C), 124.5(aryl C), 123.8(aryl C), 119.0(-CN), 114.8(aryl C), 112.7(aryl C), 102.3(aryl C), 80.2(sp^3-C of C_{60}), 54.8(sp^3-C of C_{60}), 53.6(-OCH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{70}H_8N_2O$ 892.0637; found 892.0639.

Synthesis of 5ia

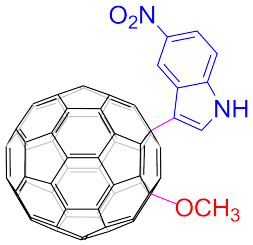


5ia

C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed

from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (8.4 mg, 23%) and **5ia** (17.7 mg, 37%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.55 (s, N-H, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 4.12 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 153.8, 152.0, 149.2, 148.1, 147.6, 147.1, 146.9, 146.4, 146.3, 146.23, 146.17, 146.14, 146.10, 145.9, 145.81, 145.75, 144.9(2C), 144.8, 144.2(2C), 143.9, 143.80, 143.78, 143.7, 143.51, 143.50, 143.45(3C), 143.41, 143.38, 143.3, 143.1, 142.7, 142.63, 142.57, 142.55, 142.5, 142.40, 142.38, 142.21, 142.17(2C), 142.0(2C), 141.79, 141.75, 141.6, 141.5, 140.3, 140.0, 139.7, 139.0, 138.7, 136.82, 136.75, 135.0(aryl C), 126.8(aryl C), 125.4(aryl C), 124.1(aryl C), 120.3(aryl C), 119.0(aryl C), 115.2(aryl C), 105.2(aryl C), 80.5(sp^3-C of C_{60}), 55.5(sp^3-C of C_{60}), 54.2(-$O$$CH_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_8BrNO$ 944.9789; found 944.9792.

Synthesis of 5ja

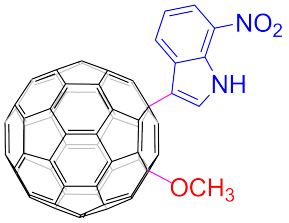


5ja

C_{60} (36.0 mg, 0.05 mmol), 5-nitroindole (9.8 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (10.5 mg, 29%) and **5ja** (15.5 mg, 34%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 12.13 (s, N-H, 1H), 9.54 (s, 1H), 8.13 (dd, J = 8.8, 1.6 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 4.24 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.0, 153.4, 151.5, 148.9, 148.2,

147.7, 147.1, 146.8, 146.4, 146.3, 146.23, 146.20(2C), 146.1, 145.9, 145.81, 145.77, 145.0(2C), 144.8, 144.3, 144.2, 143.81, 143.78, 143.69, 143.67, 143.6, 143.53, 143.50, 143.5(2C), 143.4, 143.2, 142.9, 142.74, 142.65, 142.61, 142.58, 142.56, 142.42, 142.35, 142.3, 142.24, 142.18, 142.03, 141.95, 141.82, 141.81, 141.6, 141.5, 141.1(2C), 140.3, 140.04, 139.98, 139.7(2C), 139.1, 138.6(aryl C), 136.9(aryl C), 136.7(aryl C), 127.8(aryl C), 124.2(aryl C), 116.9(aryl C), 116.7(aryl C), 111.9(aryl C), 80.5(sp^3-C of C_{60}), 55,0sp^3-C of C_{60}), 54.1(-*O*CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_8N_2O_3$ 912.0535; found 912.0538.

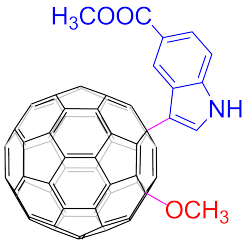
Synthesis of 5ka



5ka

C_{60} (36.0 mg, 0.05 mmol), 5-nitroindole (9.8 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (11 mg, 31%) and **5ka** (16.4 mg, 36%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 12.32 (s, N-H, 1H), 8.94 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 4.15 (s, 3H); ^{13}C NMR (100 MHz, CS_2/ d_6-DMSO) (all 1C unless indicated) δ 154.0, 153.4, 151.5, 148.9, 148.2, 147.7, 147.1, 146.8, 146.4, 146.3, 146.20(2C), 146.16, 146.1, 145.9, 145.79, 145.76, 144.98, 144.96, 144.8, 144.3, 144.2, 143.81, 143.75, 143.71, 143.66, 143.49, 143.47(3C), 143.41(2C), 143.3, 143.2, 143.0, 142.72, 142.66, 142.6(2C), 142.5, 142.44, 142.38, 142.3, 142.2(2C), 141.96, 141.93, 141.81, 141.77, 141.6, 141.5, 140.3, 140.0(2C), 139.0, 138.6, 136.9, 136.8, 132.8(aryl C), 129.4(aryl C), 129.2(aryl C), 127.9(aryl C), 127.5(aryl C), 118.7(aryl C), 118.5(aryl C), 115.7(aryl C), 80.5(sp^3-C of C_{60}), 54.8(sp^3-C of C_{60}), 54.1(-OCH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_8N_2O_3$ 912.0535; found 912.0540.

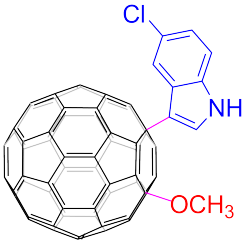
Synthesis of 5la



5la

C_{60} (36.0 mg, 0.05 mmol), methyl indole-5-carboxylate (10.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (34 mg, 0.15 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 120 °C for 30 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (4 mg, 11%) and **5la** (16.6 mg, 36%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.75 (s, N-H, 1H), 9.14 (s, 1H), 7.93 (d, J = 2.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 4.18 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (150 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 166.0(acyl C), 154.6, 154.0, 152.0, 149.1, 148.2, 147.6(2C), 147.1, 146.9, 146.4, 146.3, 146.24, 146.16(5C), 145.9, 145.84, 145.77, 144.9(3C), 144.8, 144.2, 144.0, 143.8(2C), 143.7, 143.6, 143.5(4C), 143.4, 143.2, 143.1, 142.7, 142.6, 142.58, 142.55, 142.4, 142.37, 142.2, 142.18, 142.17, 142.0, 141.8, 141.6, 141.5, 141.1, 140.3, 140.0 139.7, 139.2, 139.1, 138.8, 136.8, 136.7(aryl C), 125.7(aryl C), 124.6(aryl C), 122.8(aryl C), 122.5(aryl C), 121.2(aryl C), 115.6(aryl C), 111.4(aryl C), 80.5(sp^3-C of C_{60}), 55.4(sp^3-C of C_{60}), 54.1(-OCH_3), 50.7(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{71}H_{11}NO_3$ 925.0739; found 925.0743.

Synthesis of 5fa

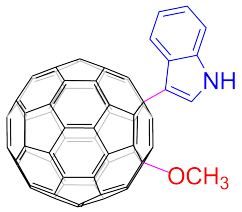


5fa

C_{60} (36.0 mg, 0.05 mmol), 5-chloroindole (9 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred

in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (3 mg, 8%) and **5fa** (18.7 mg, 42%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.58 (s, N-H, 1H), 8.41 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.17 (dd, J = 8.8, 2.0 Hz, 1H), 4.18 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 154.0, 152.0, 149.0, 148.2, 147.6, 147.1, 146.9, 146.4, 146.27, 146.25, 146.2(2C), 146.1, 145.9, 145.82, 145.77, 145.00(2C), 144.8, 144.2, 144.2, 144.0, 143.82, 143.80, 143.7, 143.6, 143.49(3C), 143.48(2C), 143.4, 143.2, 143.1, 142.7, 142.64, 142.58(3C), 142.4(2C), 142.2(3C), 142.04, 142.01, 141.82, 141.81, 141.6, 141.5, 140.3, 140.0, 139.6, 139.1, 138.8, 136.8, 136.7, 135.1(aryl C), 126.1(aryl C), 125.7(aryl C), 124.9(aryl C), 121.7(aryl C), 118.8(aryl C), 113.8(aryl C), 113.0(aryl C), 80.5(sp^3-C of C_{60}), 55.4(sp^3-C of C_{60}), 54.0(-OCH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_8ClNO$ 901.0294; found 901.0298.

Synthesis of 5aa

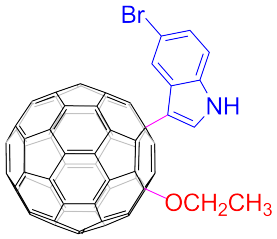


5aa

C_{60} (36.0 mg, 0.05 mmol), indole (7.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (5.5 mg, 15%) and **5aa** (14 mg, 32%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.36 (s, N-H, 1H), 8.34 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 2.4 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.20 (d, J =7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 4.12 (s, 3H); ^{13}C NMR(100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 155.0, 154.3, 152.5, 149.3, 148.1, 147.6, 147.2, 147.0, 146.4, 146.4, 146.22, 146.16, 146.1(2C), 145.9(2C), 145.7, 144.93, 144.92, 144.8, 144.22, 144.15, 144.0, 143.9, 143.8, 143.7, 143.6, 143.53, 143.49, 143.48, 143.43, 143.40(2C), 143.3, 143.2, 142.7, 142.63, 142.56, 142.55, 142.5, 142.4, 142.3, 142.2(2C), 142.1, 142.03, 142.00, 141.79, 141.77,

141.6, 141.5, 140.3, 139.9, 139.5, 139.0, 138.9, 136.73, 136.66, 136.6(aryl C), 125.2(aryl C), 123.9(aryl C), 121.5(aryl C), 119.6(aryl C), 119.2(aryl C), 114.1(aryl C), 111.8(aryl C), 80.6(sp^3-C of C_{60}), 55.8(sp^3-C of C_{60}), 54.2(-OCH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{69}H_9NO$ 867.0684; found 867.0686.

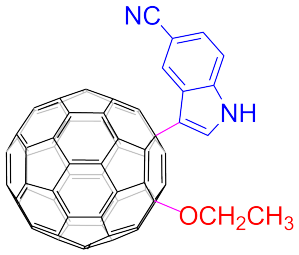
Synthesis of 5gb



5gb

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3CH_2OH (58 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (1.1 mg, 3%) and **5gb** (27.4 mg, 57%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.59 (s, N-H, 1H), 8.53 (s, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.52 (q, J = 6.8 Hz, 2H), 1.60 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 153.7, 151.6, 149.6, 148.1, 147.6, 147.1, 146.9, 146.5, 146.4, 146.3, 146.2, 146.17(2C), 145.9, 145.8, 145.75, 144.9(2C), 144.8, 144.2, 144.17, 144.0, 143.8, 143.76, 143.7, 143.6, 143.5(5C), 143.4, 143.2, 143.0, 142.7, 142.6, 142.59(2C), 142.5, 142.4(2C), 142.2, 142.15(2C), 142.04, 142.0, 141.8(2C), 141.6, 141.5, 140.3, 140.1, 139.92, 138.9, 138.7, 136.8, 136.7, 135.3(aryl C), 126.8(aryl C), 125.6(aryl C), 124.3(aryl C), 121.9(aryl C), 113.6(aryl C), 113.4(aryl C), 112.9(aryl C), 79.9(sp^3-C of C_{60}), 62.5(-OCH_2-), 55.3(sp^3-C of C_{60}), 15.7(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{70}H_{10}BrNO$ 958.9946; found 958.9949.

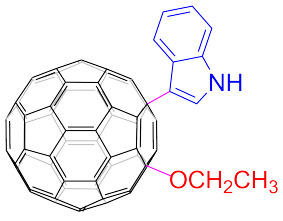
Synthesis of 5hb



5hb

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3CH_2OH (58 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (5.2 mg, 14%) and **5hb** (18.1 mg, 40%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 12.00 (s, N-H, 1H), 8.96 (s, 1H), 8.01 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 4.58 (q, J = 6.8 Hz, 2H), 1.65 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.1, 153.4, 151.2, 149.4, 148.2, 147.7, 147.0, 146.8, 146.5, 146.4, 146.3, 146.24, 146.21, 146.2, 145.9, 145.8, 145.75, 145.0, 144.9, 144.8, 144.3, 144.2, 143.9, 143.8, 143.7, 143.7, 143.6, 143.5(2C), 143.47, 143.4(2C), 143.37, 143.2, 142.9, 142.7, 142.67, 142.62, 142.6, 142.5, 142.4, 142.3, 142.25, 142.2, 142.17, 142.1, 142.0, 141.8(2C), 141.6, 141.5, 140.3, 140.2, 140.0, 139.0, 138.7, 138.2(2C), 136.8(aryl C), 136.7(aryl C), 126.8(aryl C), 124.8(aryl C), 124.1(aryl C), 119.2(-CN), 115.0(aryl C), 112.9(aryl C), 102.6(aryl C), 79.9(sp^3-C of C_{60}), 62.5(-OCH$_2$-), 55.0(sp^3-C of C_{60}), 15.6(-CH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{71}H_{10}N_2O$ 906.0793; found 906.0797.

Synthesis of 5ab

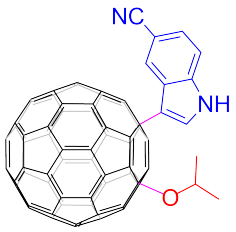


5ab

C_{60} (36.0 mg, 0.05 mmol), indole (7.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90

μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and CH_3CH_2OH (58 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (4.5 mg, 13%) and **5ab** (13.8 mg, 31%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.31 (s, N-H, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.49 (qd, J = 7.2, 3.6 Hz, 2H), 1.58 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 155.0, 154.2, 152.1, 149.7, 148.1, 147.6, 147.1, 147.0, 146.54, 146.46, 146.4, 146.21, 146.17, 146.1, 145.9, 145.8, 145.7, 144.9(2C), 144.8, 144.21, 144.16, 144.1, 143.9, 143.8, 143.64, 143.58, 143.48(2C), 143.46(2C), 143.41, 143.37, 143.3, 143.2, 142.7, 142.62, 142.61, 142.6, 142.5, 142.4, 142.3, 142.14(3C), 142.05(2C), 141.8, 141.75, 141.6, 141.5, 140.3, 139.9, 139.86, 138.8(2C), 136.7, 136.67, 136.6(aryl C), 125.2(aryl C), 124.0(aryl C), 121.5(aryl C), 119.7(aryl C), 119.1(aryl C), 114.0(aryl C), 111.7(aryl C), 80.0(sp^3-C of C_{60}), 62.5(-$O$$CH_2$-), 55.8($sp^3$-C of C_{60}), 15.6(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{70}H_{11}NO$ 881.0841; found 881.0845.

Synthesis of 5hc

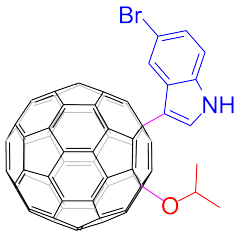


5hc

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3CHOHCH_3$ (76 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (6.7 mg, 19%) and **5hc** (13.9 mg, 30%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.97 (s, N-H, 1H), 9.04 (s, 1H), 8.00 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.14-5.08 (m, 1H), 1.63 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.1,

153.2, 150.8, 149.8, 148.1, 147.7, 147.2, 146.9, 146.8, 146.5, 146.3, 146.2, 145.9, 145.8, 145.6, 145.0, 144.9, 144.8, 144.3, 144.2, 143.9, 143.8, 143.7, 143.6, 143.59, 143.5, 143.45, 143.4(5C), 143.2, 143.0, 142.7(2C), 142.67(2C), 142.5, 142.4, 142.35, 142.3, 142.24, 142.2, 142.1, 142.0, 141.8(2C), 141.6, 141.5, 140.7, 140.3, 140.0, 138.8, 138.6, 138.2(2C), 136.9, 136.9(aryl C), 126.9(aryl C), 125.1(aryl C), 124.7(aryl C), 124.1(aryl C), 119.3(-CN), 114.9(aryl C), 112.8(aryl C), 102.5(aryl C), 79.2(sp^3-C of C_{60}), 69.6(-*O*CH-), 55.0(sp^3-C of C_{60}), 24.1(2C ,-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{72}H_{12}N_2O$ 920.0950; found 920.0955.

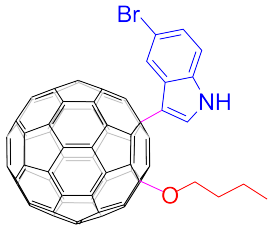
Synthesis of 5gc



5gc

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3CHOHCH_3$ (76 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (3.5 mg, 10%) and **5gc** (18.6 mg, 38%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/*d*$_6$-DMSO)δ 11.58 (s, 1H), 8.57 (s, 1H), 7.87 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.08-5.03 (m, 1H), 1.59 (d, *J* = 5.6 Hz, 6H).^{13}C NMR (100 MHz, CS_2/*d*$_6$-DMSO) (all 1C unless indicated) δ 154.3, 153.5, 151.1, 150.0, 148.1, 147.6, 147.1, 146.9, 146.8, 146.4, 146.37, 146.2, 146.1(2C), 145.8, 145.7, 145.6, 144.9, 144.8, 144.76, 144.2, 144.1, 143.9, 143.8, 143.7, 143.6, 143.5, 143.4(4C), 143.38, 143.3, 143.14, 143.1, 142.6(4C), 142.5, 142.34, 142.32, 142.14(3C), 142.06, 142.0, 141.8(2C), 141.5, 141.4, 140.5, 140.3, 139.9, 138.7, 138.6, 136.8(2C), 135.3(aryl C), 126.6(aryl C), 125.5(aryl C), 124.3(aryl C), 122.0aryl C), 113.6(aryl C), 113.2(aryl C), 112.9(aryl C), 79.2(sp^3-C of C_{60}), 69.3(-OCH-), 55.3(sp^3-C of C_{60}), 24.1(2C, -CH_3).; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{71}H_{12}BrNO$ 973.0102; found 973.0105.

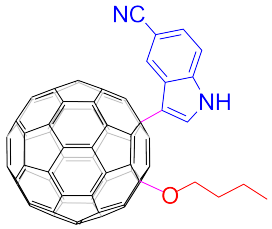
Synthesis of 5gd



5gd

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3CH_2CH_2CH_2OH$ (92 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (2.9 mg, 8%) and **5gd** (24.3 mg, 49%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.60 (s, N-H, 1H), 8.48 (s, 1H), 7.85 (s, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 4.44 (t, J = 6.4 Hz, 2H), 1.97-1.90 (m, 2H), 1.62-1.55 (m, 2H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.4, 153.8, 151.6, 149.6, 148.1, 147.6, 147.1, 146.9, 146.6, 146.4, 146.3, 146.2, 146.2, 146.17, 145.9, 145.8, 145.76, 144.9(2C), 144.8, 144.2, 144.18, 144.0, 143.8(2C), 143.7, 143.6, 143.5(2C), 143.46(3C), 143.4, 143.2, 143.1, 142.7, 142.6, 142.6, 142.59, 142.5, 142.4, 142.35, 142.2, 142.16(2C), 142.1, 142.0, 141.8(2C), 141.6, 141.5, 140.3, 140.1, 140.0, 138.9, 138.7, 136.8, 136.76, 135.3(aryl C), 126.7(aryl C), 125.6(aryl C), 124.3(aryl C), 121.9(aryl C), 113.58(aryl C), 113.37(aryl C), 112.90(aryl C), 79.98(sp^3-C of C_{60}), 66.66(-OCH$_2$-), 55.3(sp^3-C of C_{60}), 32.0(-CH$_2$-), 19.3(-CH$_2$-), 13.7(-CH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{72}H_{14}BrNO$ 987.0259; found 987.0263.

Synthesis of 5hd

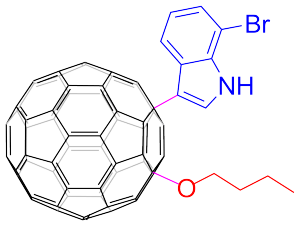


5hd

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30

minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3CH_2CH_2CH_2OH$ (92 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (6.4 mg, 18%) and **5hd** (16.5 mg, 35%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 12.02 (s, N-H, 1H), 8.87 (s, 1H), 8.01 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 4.48 (t, J = 6.0 Hz, 2H), 1.97 (t, J = 7.2 Hz, 2H), 1.59 (q, J = 7.2 Hz, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.0, 153.4, 151.2, 149.4, 148.1, 147.7, 147.0, 146.7, 146.5, 146.4, 146.2, 146.2, 146.17(2C), 145.9, 145.8(2C), 144.9, 144.91, 144.8, 144.2, 144.1, 143.9, 143.8, 143.7(2C), 143.5, 143.47(2C), 143.4(3C), 143.3, 143.2, 142.9, 142.7, 142.6, 142.58(2C), 142.5, 142.4, 142.3, 142.2, 142.17, 142.15, 142.0, 141.95, 141.8(2C), 141.6, 141.5, 140.3, 140.2, 140.0, 139.0, 138.6, 138.2, 136.8, 136.8(aryl C), 126.8(aryl C), 124.8(2C, aryl C), 124.1(aryl C), 119.2(-CN), 114.9(aryl C), 112.8(aryl C), 102.6(aryl C), 79.9(sp^3-C of C_{60}), 66.6(-$O$$CH_2$-), 55.0($sp^3$-C of C_{60}), 31.9(-CH_2-), 19.3(-CH_2-), 13.7(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{73}H_{14}N_2O$ 934.1106; found 934.1109.

Synthesis of 5id

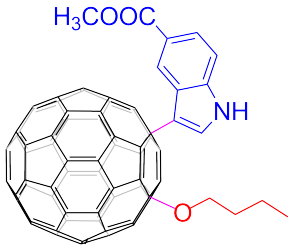


5id

C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3CH_2CH_2CH_2OH$ (92 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (6.1 mg, 17%) and **5id** (21.3 mg, 43%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.51 (s, N-H, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 2.8 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 4.42 (td, J = 6.4, 2.4 Hz, 2H),

1.96-1.89 (m, 2H), 1.64-1.55 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.4, 153.7, 151.6, 149.6, 148.1, 147.6, 147.1, 146.9, 146.5, 146.4, 146.38, 146.2, 146.16, 146.15, 145.9, 145.8, 145.7, 144.9(2C), 144.8, 144.2, 144.17, 144.0, 143.8, 143.7, 143.65, 143.5, 143.45(2C), 143.4(2C), 143.37(2C), 143.2, 143.1, 142.7, 142.6(2C), 142.5, 142.5, 142.4, 142.35, 142.2, 142.1(2C), 142.0(2C), 141.8, 141.7, 141.6, 141.4, 140.3, 140.2, 139.9, 138.9, 138.7, 136.8(2C), 135.0(aryl C), 126.8(aryl C), 125.5(aryl C), 124.1(aryl C), 120.2(aryl C), 119.1(aryl C), 115.1(aryl C), 105.1(aryl C), 80.0(sp^3-C of C_{60}), 66.6(-OCH$_2$-), 55.5(sp^3-C of C_{60}), 32.0(-CH$_2$-), 19.3(-CH$_2$-), 13.7(-CH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{72}H_{14}BrNO$ 987.0259; found 987.0261.

Synthesis of 5ld

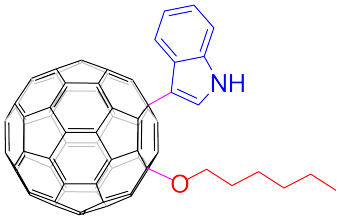


5ld

C_{60} (36.0 mg, 0.05 mmol), methyl indole-5-carboxylate (10.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (34 mg, 0.15 mmol) and $CH_3CH_2CH_2CH_2OH$ (92 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 120 °C for 30 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (7.5 mg, 21%) and **5ld** (19.5 mg, 40%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.71 (s, N-H, 1H), 9.02 (s, 1H), 7.93 (d, J = 2.4 Hz, 1H), 7.88 (dd, J = 8.4, 1.2 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 4.44-4.40 (m, 2H), 3.87 (s, 3H), 1.92-1.85 (m, 2H), 1.60-1.51 (m, 2H), 1.01 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100MHz, CS_2/ d_6-DMSO) (all 1C unless indicated) δ 165.8(acyl C), 154.4, 153.7, 151.6, 149.6, 148.1(2C), 147.6, 147.0, 146.9, 146.5, 146.4, 146.38, 146.2, 146.15, 146.1, 145.8(2C), 145.7, 144.9(2C), 144.8, 144.2, 144.15, 144.0, 143.8(3C), 143.6(2C), 143.5, 143.49, 143.45, 143.4(2C), 143.38(3C), 143.2, 143.1, 142.6, 142.60(2C), 142.2, 142.14, 142.1, 142.0(2C), 141.8(2C), 141.5, 141.4, 140.3, 140.2, 139.9, 139.1, 138.9, 138.7, 136.9, 136.8(aryl C), 125.5(aryl C), 124.6(aryl C), 122.7(aryl C), 122.5(aryl C), 121.1(aryl C), 115.4(aryl C), 111.3(aryl C), 80.0(sp^3-C of C_{60}), 66.6(-OCH$_2$-), 55.3(sp^3-C of C_{60}), 50.6(-CH$_3$), 31.9(-CH$_2$-), 19.2(-CH$_2$-),

13.6(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{74}H_{17}NO_3$ 967.1208; found 967.1213.

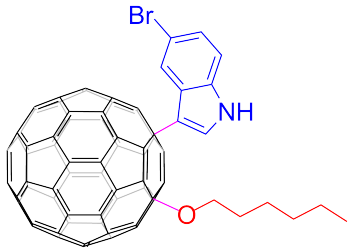
Synthesis of 5ae



5ae

C_{60} (36.0 mg, 0.05 mmol), indole(7.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3(CH_2)_5OH$ (126 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (7.8 mg, 22%) and **5ae** (19 mg, 41%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.27 (s, N-H, 1H), 8.40 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 0.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 4.42-4.38 (m, 2H), 1.95-1.88 (m, 2H), 1.53 (t, J = 6.0 Hz, 2H), 1.39 (t, J = 3.6 Hz, 4H), 0.97 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 155.0, 154.2, 152.0, 149.8, 148.1, 147.6, 147.1, 147.0, 146.6, 146.5, 146.4, 146.2, 146.15, 146.1, 145.8(2C), 145.7, 144.9(2C), 144.7, 144.2, 144.1, 144.0, 143.8, 143.79, 143.6, 143.56, 143.5(2C), 143.44(2C), 143.4, 143.3, 143.23, 143.2, 142.7, 142.6(2C), 142.54, 142.5, 142.4, 142.3, 142.1(3C), 142.0(2C), 141.8, 141.7, 141.6, 141.5, 140.3, 140.0, 139.8, 138.8, 138.78, 136.7, 136.66, 136.6(aryl C), 125.1(aryl C), 123.9(aryl C), 121.5(aryl C), 119.7(aryl C), 119.1(aryl C), 114.0(aryl C), 111.7(aryl C), 80.0(sp^3-C of C_{60}), 67.0(-$O$$CH_2$-), 55.7($sp^3$-C of C_{60}), 31.3(-CH_2-), 29.9(-CH_2-), 25.6(-CH_2-), 22.5(-CH_2-), 13.9(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{74}H_{19}NO$ 937.1467; found 937.1471.

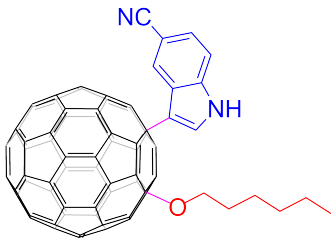
Synthesis of 5ge



5ge

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole(12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3(CH_2)_5OH$ (126 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (3.2 mg, 9%) and **5ge** (24 mg, 47%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.59 (s, N-H, 1H), 8.49 (s, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.42 (t, J = 6.8 Hz, 2H), 1.98-1.91 (m, 2H), 1.56-1.49 (m, 2H), 1.38 (t, J = 3.2 Hz, 4H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 153.7, 151.6, 149.6, 148.1, 147.6, 147.1, 146.9, 146.6, 146.4, 146.29, 146.2, 146.18, 146.16, 145.9, 145.8, 145.75, 144.9(2C), 144.8, 144.2, 144.19, 144.0, 143.8(2C), 143.7, 143.6, 143.5(2C), 143.46(2C), 143.4, 143.39, 143.2, 143.1, 142.7, 142.6, 142.61, 142.6, 142.5, 142.4, 142.35, 142.2, 142.16(2C), 142.1, 142.0, 141.8(2C), 141.6, 141.5, 140.3, 140.1, 139.9, 138.9, 138.7, 136.8, 136.7, 135.3(aryl C), 126.7(aryl C), 125.5(aryl C), 124.3(aryl C), 121.9(aryl C), 113.6(aryl C), 113.3(aryl C), 112.9(aryl C), 80.0(sp^3-C of C_{60}), 67.0(-OCH$_2$-), 55.3(sp^3-C of C_{60}), 31.3(-CH$_2$-), 30.0(-CH$_2$-), 25.6(-CH$_2$-), 22.5(-CH$_2$-), 13.9(-CH$_3$); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{74}H_{18}BrNO$ 1015.0572; found 1015.0574.

Synthesis of 5he

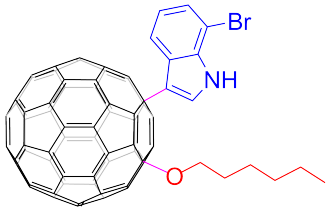


5he

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the

solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3(CH_2)_5OH$ (126 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (8 mg, 22%) and **5he** (19.9 mg, 41%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.99 (s, N-H, 1H), 8.89 (s, 1H), 8.00 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.47 (dd, J = 8.8, 1.6 Hz, 1H), 4.47 (t, J = 6.4 Hz, 2H), 2.02-1.95 (m, 2H), 1.58-1.50 (m, 2H), 1.41-1.37 (m, 4H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.1, 153.4, 151.2, 149.4, 148.2, 147.7, 147.0, 146.8, 146.6, 146.4, 146.3, 146.22, 146.2, 146.18, 145.9, 145.8, 145.78, 145.0, 144.9, 144.8, 144.3, 144.2, 143.9, 143.8, 143.7, 143.68, 143.6, 143.51, 143.5, 143.4(3C), 143.38, 143.2, 142.9, 142.7, 142.66, 142.6(2C), 142.5, 142.4, 142.35, 142.3, 142.2, 142.18, 142.1, 142.0, 141.8(2C), 141.6, 141.5, 140.3, 140.26, 140.0, 139.0, 138.7, 138.3(2C), 136.9(aryl C), 136.8(aryl C), 126.8(aryl C), 124.8(aryl C), 124.1(aryl C), 119.3(-CN), 114.9(aryl C), 112.9(aryl C), 102.6(aryl C), 79.9(sp^3-C of C_{60}), 67.0(-$O$$CH_2$-), 55.0($sp^3$-C of C_{60}), 31.23(-CH_2-), 29.9(-CH_2-), 25.6(-CH_2-), 22.5(-CH_2-), 13.9(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{75}H_{18}N_2O$ 962.1419; found 962.1424.

Synthesis of 5ie

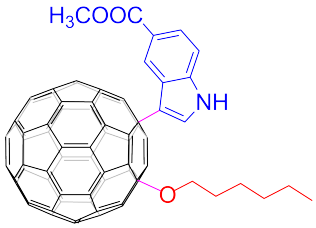


5ie

C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole(12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and $CH_3(CH_2)_5OH$ (126 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (7.1 mg, 20%) and **5ie** (29.4 mg, 58%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.49 (s, N-H, 1H), 8.44 (d, J = 8.0 Hz, 1H), 7.88

(d, J = 2.4 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 4.40 (td, J= 6.8, 2.8 Hz, 2H), 1.95-1.88 (m, 2H), 1.56-1.49 (m, 2H), 1.39-1.35 (m, 4H), 0.96 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 153.7, 151.6, 149.6, 148.1, 147.6, 147.1, 146.9, 146.6, 146.4, 146.3, 146.2, 146.16, 146.1, 145.9, 145.8, 145.7, 144.9(2C), 144.8, 144.2, 144.17, 143.9, 143.8, 143.7, 143.65, 143.5, 143.44(3C), 143.4, 143.36(2C), 143.2, 143.1, 142.7, 142.6(2C), 142.52, 142.5, 142.4, 142.35, 142.2, 142.1(2C), 142.0(2C), 141.8, 141.7, 141.5, 141.4, 140.3, 140.16, 139.9, 138.8, 138.7, 136.8, 136.8, 135.0(aryl C), 126.8(aryl C), 125.5(aryl C), 124.1(aryl C), 120.2(aryl C), 119.1(aryl C), 115.1(aryl C), 105.1(aryl C), 80.0(sp^3-C of C_{60}), 67.0(-OCH_2-), 55.4(sp^3-C of C_{60}), 31.3(-CH_2-), 29.9(-CH_2-), 25.6(-CH_2-), 22.5(-CH_2-), 13.9(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for C74H18BrNO 1015.0572; found 1015.0576.

Synthesis of 5le

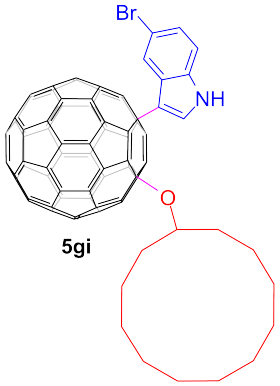


5le

C_{60} (36.0 mg, 0.05 mmol), methyl indole-5-carboxylate (10.2 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (34 mg, 0.15 mmol) and $CH_3(CH_2)_5OH$ (126 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 120 °C for 30 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give unreacted C_{60} (5.1 mg, 14%) and **5le** (20 mg, 40%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.75 (s, N-H, 1H), 9.03 (s, 1H), 7.93 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 4.42-4.38 (m, 2H), 3.87 (s, 3H), 1.91-1.95 (m, 2H), 1.50 (t, J = 7.6 Hz, 2H), 1.35 (s, 4H), 0.95 (t, J = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 165.9(acyl C), 154.5, 153.7, 151.6, 149.7, 148.1, 147.6, 147.1, 146.9, 146.6, 146.4, 146.38, 146.2, 146.18, 146.1, 145.9(2C), 145.8, 144.9(2C), 144.8(2C), 144.2, 144.19(2C), 144.0, 143.8(2C), 143.7, 143.6, 143.5, 143.47(3C), 143.4(2C), 143.2, 143.1, 142.6(2C), 142.58, 142.5, 142.4, 142.36, 142.2, 142.17(2C), 142.0(2C), 141.8(2C), 141.6, 141.5, 140.3, 140.2, 140.0, 139.2, 138.9, 138.7, 136.8(aryl C), 125.5(aryl C), 124.6(aryl C), 122.7(aryl C), 122.5(aryl C), 121.1(aryl C), 115.4(aryl C), 111.4(aryl C), 80.0(sp^3-C of C_{60}), 67.0(-OCH$_2$-), 55.3(sp^3-C of C_{60}), 50.7(-OCH$_3$), 32.7(-CH_2-), 31.3(-CH_2-),

25.6(-CH_2-), 22.5(-CH_2-), 13.9(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{76}H_{21}NO_3$ 995.1521; found 995.1524.

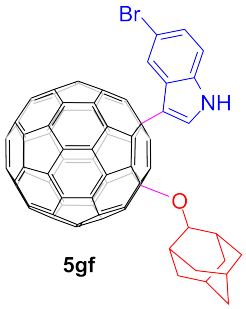
Synthesis of 5gi



5gi

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and cyclododecanol (184 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (4.1mg, 11%) and **5gi** (30 mg, 55%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 10.73 (s, N-H, 1H), 8.61 (s, 1H), 7.91 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 4.91 (s, 1H), 1.55-1.32 (m, 22H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.5, 153.4, 151.0, 150.2, 148.1, 147.6, 147.3, 147.0, 146.8, 146.4, 146.4, 146.2(3C), 145.9, 145.8, 145.6, 144.9, 144.8(2C), 144.2, 144.15, 144.0, 143.8, 143.76, 143.7, 143.6, 143.5, 143.44(2C), 143.4(2C), 143.3, 143.2, 143.15, 142.7(4C), 142.5, 142.4(2C), 142.2, 142.17(2C), 142.1, 142.0, 141.84, 141.8, 141.6, 141.4, 140.7, 140.3, 139.9, 138.7, 138.5, 136.7, 136.7, 135.3(aryl C), 126.7(aryl C), 125.5(aryl C), 124.3(aryl C), 122.0(aryl C), 113.6(aryl C), 113.2(aryl C), 112.9(aryl C), 79.5(sp^3-C of C_{60}), 74.2(-*O*CH-), 55.3(sp^3-C of C_{60}), 31.2, 31.1, 29.7, 29.4, 23.9, 23.9, 23.5, 23.3, 23.2, 21.2, 21.1; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{80}H_{28}BrNO$ 1097.1354; found 1097.1356.

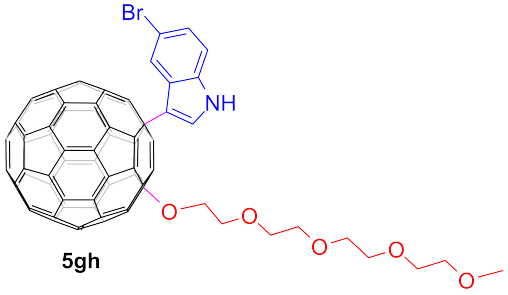
Synthesis of 5gf



5gf

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and 2-adamantanol (152 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (3.9 mg, 11%) and **5gf** (19.4 mg, 36%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.70 (s, N-H, 1H), 8.38 (s, 1H), 7.95 (s, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.33 (d, J = 8.6 Hz, 1H), 4.84 (s, 1H), 2.39 (s, 2H), 1.97-1.87 (m, 6H), 1.67 (t, J = 8.6 Hz, 2H), 1.55 (d, J = 11.6 Hz, 2H), 1.36 (s, 2H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 1C unless indicated) δ 154.6, 153.7, 151.1, 150.4, 148.1, 147.6, 147.4, 147.0, 146.9, 146.4, 146.3, 146.2, 146.19, 146.1, 145.9, 145.8, 145.7, 144.9, 144.8(2C), 144.3, 144.2, 143.9(2C), 143.8, 143.7, 143.6, 143.54, 143.5, 143.47, 143.4(2C), 143.3, 143.2, 143.16, 142.8, 142.7, 142.6, 142.55, 142.5, 142.4, 142.38, 142.3, 142.2, 142.17, 142.1, 142.06, 141.83, 141.82, 141.6, 141.4, 140.9, 140.4, 139.9, 138.6, 138.4, 137.1, 136.8, 135.3(aryl C), 126.7(aryl C), 125.3(aryl C), 124.29(aryl C), 121.8(aryl C), 113.8(aryl C), 113.4(aryl C), 113.0(aryl C), 79.5(sp^3-C of C_{60}), 78.9, 55.2(sp^3-C of C_{60}), 37.3, 36.3(2C), 34.1, 34.0, 31.4, 31.4, 27.37, 27.0; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{78}H_{20}BrNO$ 1065.0728; found 1065.0732.

Synthesis of 5gh

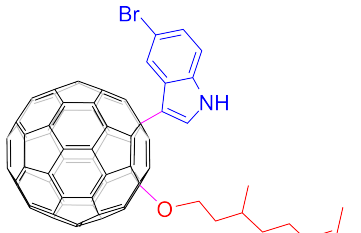


5gh

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar

atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and methyl tetraglycol (210 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane/ethyl acetate(6:2:1) as the eluent to give unreacted C_{60} (4.5 mg, 13%) and **5gh** (18 mg, 32%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 10.59 (s, N-H, 1H), 8.30 (s, 1H), 8.05 (s, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 4.59 (s, 2H), 3.98 – 3.89 (m, 2H), 3.74-3.65 (m, 10H), 3.53 (t, J = 4.4 Hz, 2H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, CS_2/Acetone-d_6) (all 1C unless indicated) δ 155.3, 154.8, 153.2, 150.0, 149.4, 148.9, 148.2, 147.9, 147.7, 147.65, 147.5, 147.42, 147.4, 147.12, 147.1, 147.0, 146.97, 146.2, 146.17, 146.0, 145.6, 145.3, 145.2, 145.1, 145.0, 144.9, 144.8, 144.76, 144.7, 144.69, 144.67(3C), 144.5, 144.3, 143.9, 143.89, 143.8(3C), 143.7, 143.6, 143.4, 143.3(2C), 143.29(2C), 143.0(2C), 142.8, 142.6, 141.5, 141.4, 140.7, 140.6, 140.1, 138.8, 137.9, 136.3(aryl C), 128.0(aryl C), 127.7(aryl C), 125.5(aryl C), 123.1(aryl C), 114.8(aryl C), 114.3(2C, aryl C), 81.1(sp^3-C of C_{60}), 72.4, 71.5, 71.3, 71.3, 71.1, 71.0(2C), 67.7, 59.0(-CH_3), 56.6(sp^3-C of C_{60}); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{77}H_{24}BrNO_5$ 1121.0838; found 1121.0842.

Synthesis of 5gg

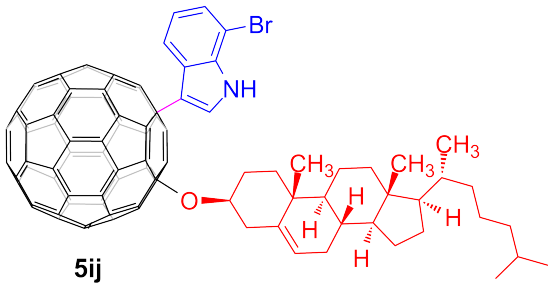


5gg

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and citronellol (182 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (4.5 mg, 13%) and **5gg** (18.1 mg, 34%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 10.61 (s, N-H, 1H), 8.52 (s, 1H), 7.87 (s, 1H), 7.40 (d, J = 8.4 Hz,

1H), 7.29 (d, J = 8.4 Hz, 1H), 5.04 (s, 1H), 4.46-4.39 (m, 2H), 1.98 – 1.96 (m, 2H), 1.72 (d, J = 8.4 Hz, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.39-1.35(m, 1H), 1.27 (m, 2H),0.93 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/Acetone-d_6) (all 1C unless indicated) δ 155.6, 154.8, 152.7, 150.9, 149.5, 149.0, 148.4, 148.2, 147.9, 147.87, 147.8, 147.6, 147.56, 147.5, 147.49, 147.2, 147.1(2C), 146.3, 146.2, 146.1, 145.6, 145.5, 145.3, 145.1, 145.07, 145.0, 144.9, 144.8(2C), 144.76(3C), 144.7, 144.5, 144.4, 144.0, 143.96(2C), 143.9, 143.85, 143.7(2C), 143.6, 143.5(2C), 143.34, 143.3, 143.1(2C), 142.9, 142.8, 141.7, 141.3, 140.2, 140.0, 138.2, 138.1, 136.5(aryl C), 131.1(alkene C), 128.1(aryl C), 126.3(aryl C), 126.0(aryl C), 125.9(alkene C), 123.4(aryl C), 115.8(aryl C), 114.5(aryl C), 114.1(aryl C), 81.3(sp^3-C of C_{60}), 66.6, 56.5(sp^3-C of C_{60}), 38.0(2C), 30.6, 26.4(2C), 20.2(-CH_3), 18.3(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{78}H_{24}BrNO$ 1069.1041; found 1069.1045.

Synthesis of 5ij

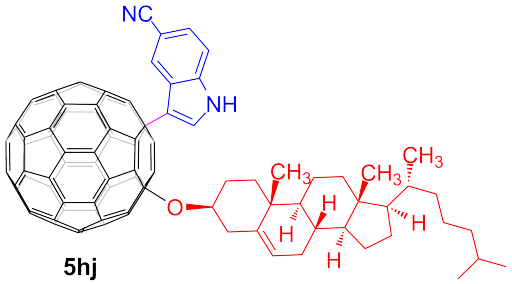


5ij

C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and cholesterol (386 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (4.8 mg, 13%) and **5ij** (25.4 mg, 39%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 10.44 (s, N-H, 1H), 8.28 (dd, J = 7.6, 4.8 Hz, 1H), 7.87 (s, 1H), 7.30 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 5.04 (s, 1H), 4.32-4.30 (m, 1H), 2.48-2.45 (m, 2H), 1.93-1.90 (m, 2H), 1.76-1.63 (m, 4H), 1.51-1.00 (m, 20H), 0.94 (s, 3H), 0.86 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 6.8 Hz, 6H), 0.60 (s, 3H); ^{13}C NMR (100 MHz, CS_2/Acetone-d_6) (all 1C unless indicated) δ 156.0, 155.0, 154.8, 152.4, 152.3, 151.7, 149.5, 149.1, 148.8, 148.5, 148.3, 147.8, 147.6(3C), 147.5, 147.3, 147.2, 147.1, 146.3, 146.2(2C), 145.7(2C), 145.2(3C), 144.9(3C), 144.8(3C), 144.6(2C), 144.1, 144.1, 144.0, 143.9(2C), 143.8(2C), 143.7(2C), 143.6, 143.6, 143.4, 143.2, 143.0, 142.8, 142.4, 142.3, 141.8, 141.3, 140.9(alkene C), 140.0, 139.7, 138.6, 138.1, 136.3(aryl C), 127.9(aryl C), 126.1(aryl C), 125.6(aryl C),

122.6(aryl C), 122.0(alkene C), 120.7(aryl C), 117.5(aryl C), 106.2(aryl C), 80.8(sp^3-C of C_{60}), 77.9, 57.8, 57.1, 56.6(sp^3-C of C_{60}), 50.6, 43.0, 42.0, 40.6, 40.4, 38.3, 37.1, 36.7, 32.8, 32.6, 31.7, 29.0(2C), 25.3, 24.9, 23.5, 23.3(2C, -CH_3), 21.9, 20.0(-CH_3), 19.5(-CH_3), 12.6(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{95}H_{50}BrNO$ 1299.3076; found 1299.3080.

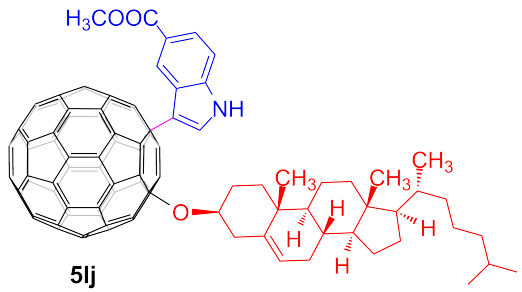
Synthesis of 5hj



5hj

C_{60} (36.0 mg, 0.05 mmol), indole-5-carbonitrile (8.6 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and cholesterol (386 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (7.9 mg, 22%) and **5hj** (27.3 mg, 44%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 11.08 (s, N-H, 1H), 9.06 (s, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 5.24 (s, 1H), 4.60-4.55 (m, 1H), 2.76–2.62 (m, 2H), 2.21 (m, 1H), 2.04 – 1.85 (m, 5H), 1.55 – 1.14 (m, 17H), 1.10 (s, 3H), 1.06-1.00 (m, 3H), 0.96 (d, J = 6.4 Hz, 3H), 0.91–0.89 (m, 6H), 0.72 (s, 3H); ^{13}C NMR (100 MHz, CS_2/Acetone-d_6) (all 1C unless indicated) δ 155.3, 154.4, 154.3, 151.9, 151.1, 149.4, 149.0, 148.5, 148.2, 148.1, 147.8, 147.5(2C), 147.4, 147.2, 147.1, 146.9, 146.3, 146.2, 146.15, 145.6, 145.5, 145.0, 144.99, 144.9, 144.8(2C), 144.7(5C), 144.5, 144.2, 144.0, 143.97(2C), 143.9, 143.8, 143.7, 143.6, 143.58, 143.5, 143.4, 143.3, 143.1(2C), 142.9, 142.8, 142.2, 142.2, 141.7, 141.3, 141.1(alkene C), 141.1, 139.9, 139.85, 139.0, 138.4, 138.1(aryl C), 127.7(aryl C), 126.7(aryl C), 126.1(aryl C), 125.7(aryl C), 122.7(aryl C), 120.3(alkene C), 117.1(-CN), 113.7(aryl C), 104.4(aryl C), 80.5(sp^3-C of C_{60}), 78.0, 57.5, 56.9, 56.1(sp^3-C of C_{60}), 50.8, 43.0, 42.1, 42.0, 40.7, 40.3, 38.4, 37.2, 37.1, 36.6, 32.8, 32.5, 31.7, 28.9, 25.3, 24.7, 23.5(-CH_3), 23.3(-CH_3), 21.9, 20.0(-CH_3), 19.3(-CH_3), 12.6(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z $[M]^-$ calcd for $C_{96}H_{50}N_2O$ 1246.3923; found 1246.3926.

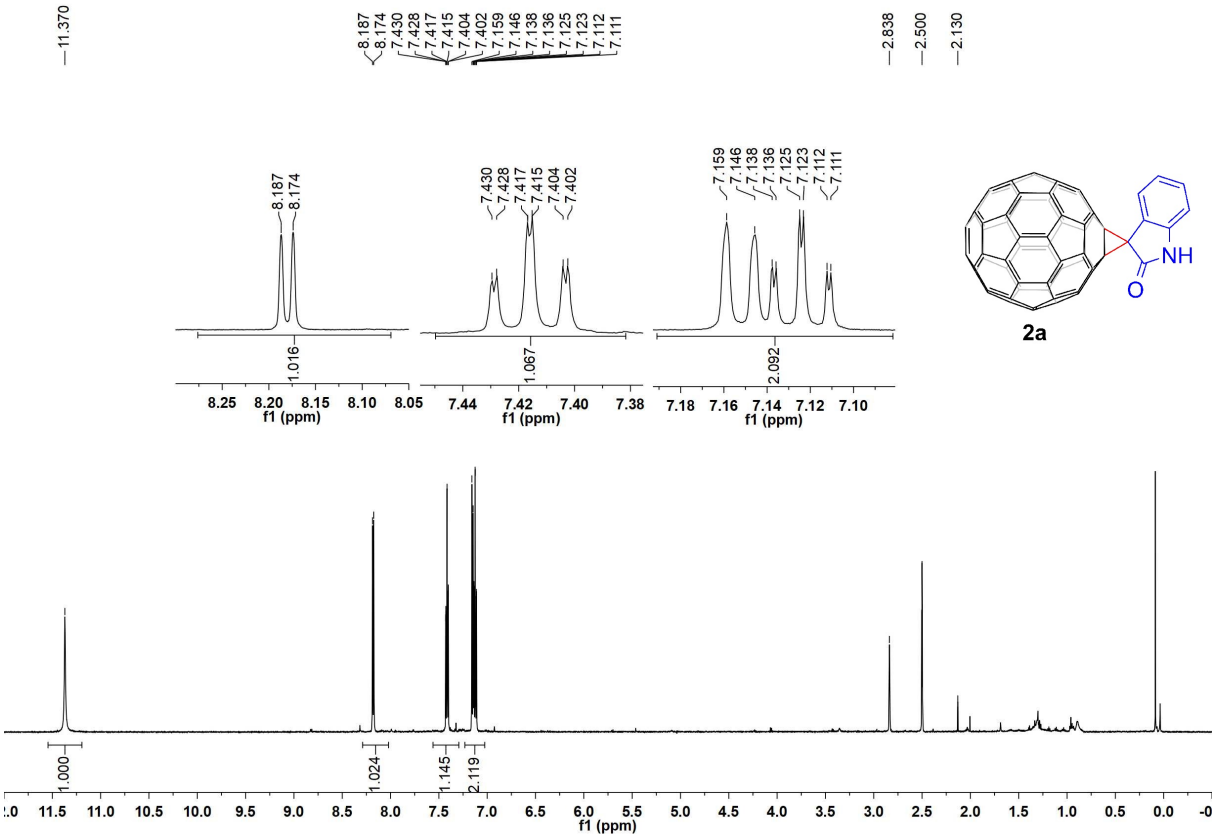
Synthesis of 5lj



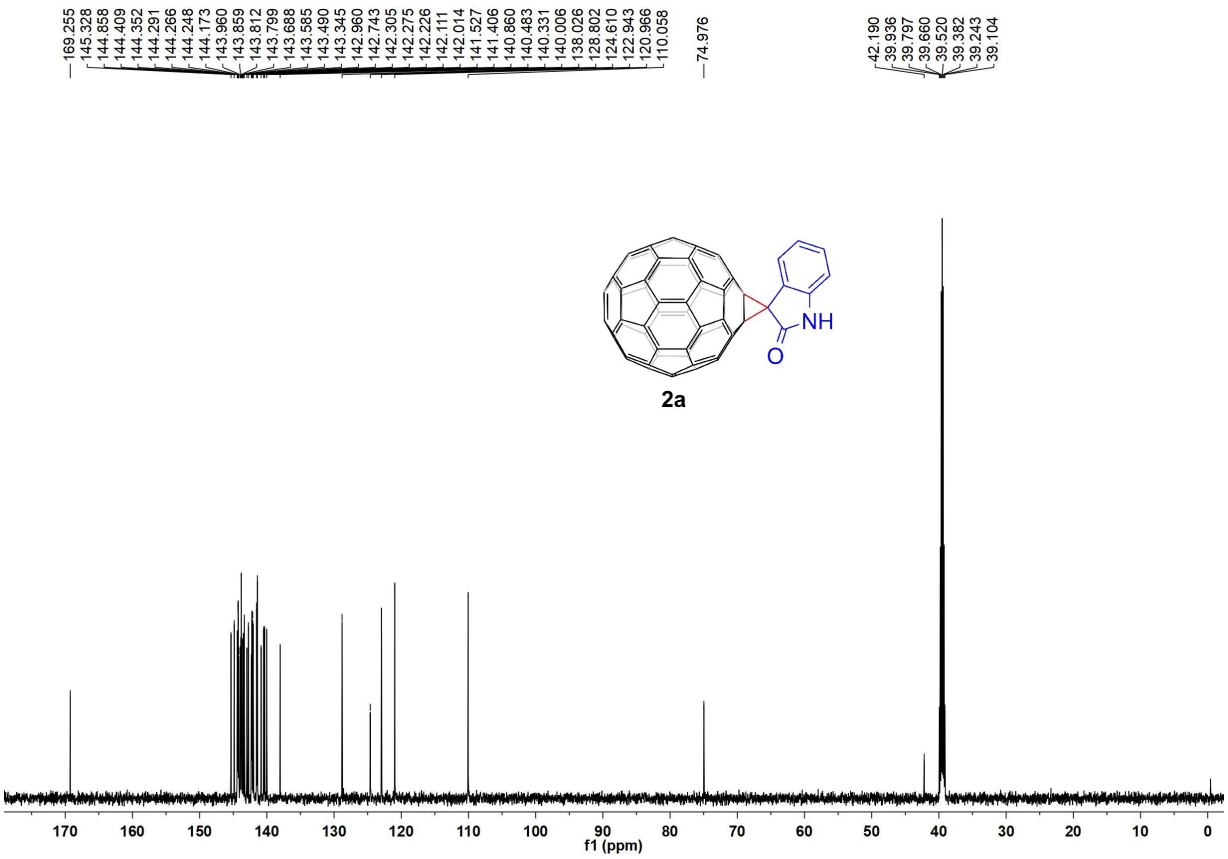
5lj

C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (4 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol) and Cholesterol (386 mg, 1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (6.5 mg, 18%) and **5lj** (32.1 mg, 50%) as black amorphous solid. ^{1}H NMR (400 MHz, CS_2/Acetone-d_6) δ 10.89 (s, N-H, 1H), 9.11 (s, 1H), 7.99 (s, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.54 (d, J = 8.6 Hz, 1H), 5.19 (s, 1H), 4.51- 4.50 (m, 1H), 3.86 (s, 3H), 2.61 – 2.58 (m, 2H), 2.41 – 2.36 (m, 2H), 2.17 (m, 1H), 1.90 – 1.79 (m, 4H), 1.60– 1.40 (m, 19H), 1.05 (s, 3H), 0.97 (d, J = 6.0 Hz, 3H), 0.92 (d, J = 6.4 Hz, 6H), 0.72(s, 3H); ^{13}C NMR (100 MHz, CS_2/Acetone-d_6) (all 1C unless indicated) δ 167.21(acyl C), 155.8, 154.9, 154.8, 152.4, 152.3, 151.5, 149.4, 149.0, 148.6, 148.5, 148.4, 148.2, 147.8, 147.7, 147.6, 147.48, 147.2, 147.1, 147.0, 146.2, 146.16(2C), 145.6, 145.55, 145.1(3C), 145.0, 144.9, 144.8, 144.75(2C), 144.6, 144.5, 144.46, 144.1, 144.0, 143.96, 143.9, 143.8, 143.7, 143.6, 143.5, 143.49, 143.4(2C), 143.1(2C), 142.9, 142.8, 142.3, 142.1, 141.7, 141.3, 141.0(alkene C), 140.3, 140.0, 139.8, 138.4, 138.2(aryl C), 126.6(aryl C), 126.0(aryl C), 124.3(aryl C), 124.1(aryl C), 122.9(aryl C), 122.5(alkene C), 117.5(aryl C), 112.4(aryl C), 80.6(sp^3-C of C_{60}), 77.7, 57.5, 57.0, 56.5, 56.6(sp^3-C of C_{60}), 51.9(-CH_3), 50.6, 43.0, 42.0 41.9, 40.7, 40.3, 38.2, 38.2, 37.1, 32.8, 32.5, 31.6, 28.9, 25.3, 24.8, 23.5(-CH_3), 23.3(-CH_3), 21.9, 19.9(-CH_3), 19.5(-CH_3), 12.6(-CH_3); HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{97}H_{53}NO_3$ 1279.4025; found 1279.4029.

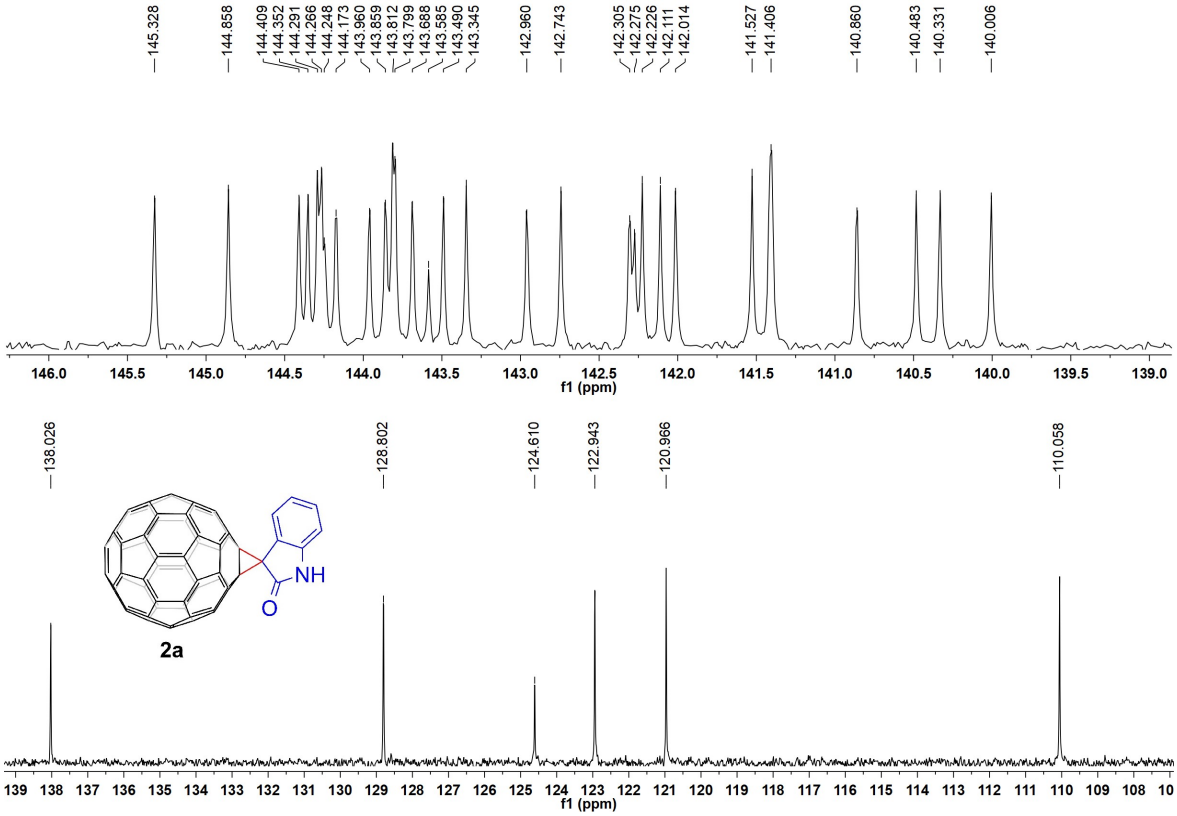
^{1}H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2a



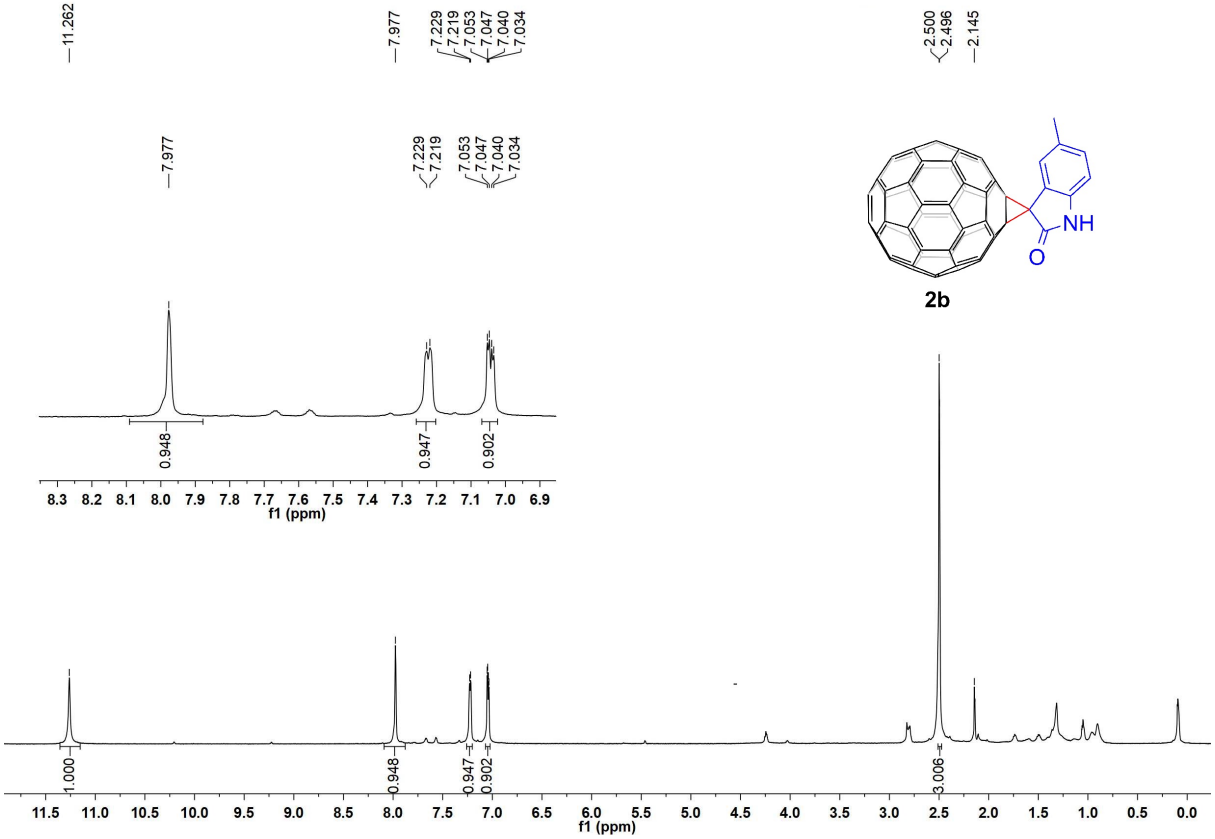
^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2a



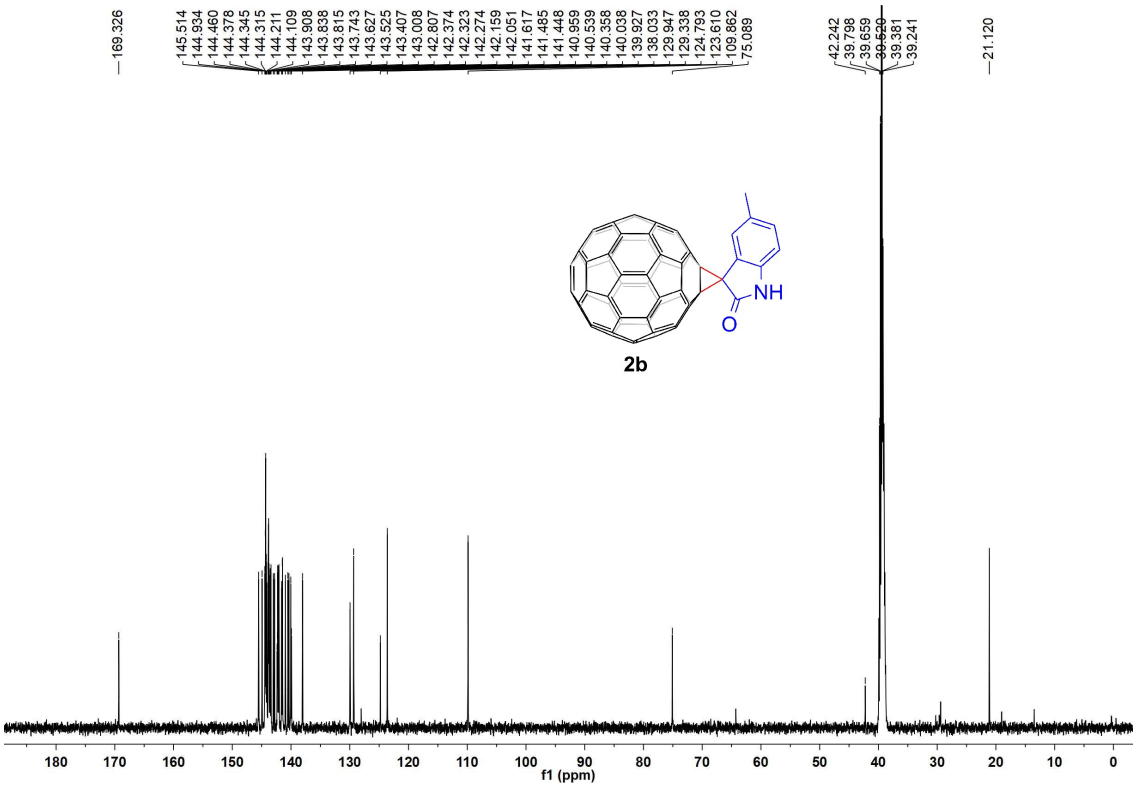
Expanded ^{13}C NMR (150 MHz, d_6-DMSO/CS_2) of compound 2a



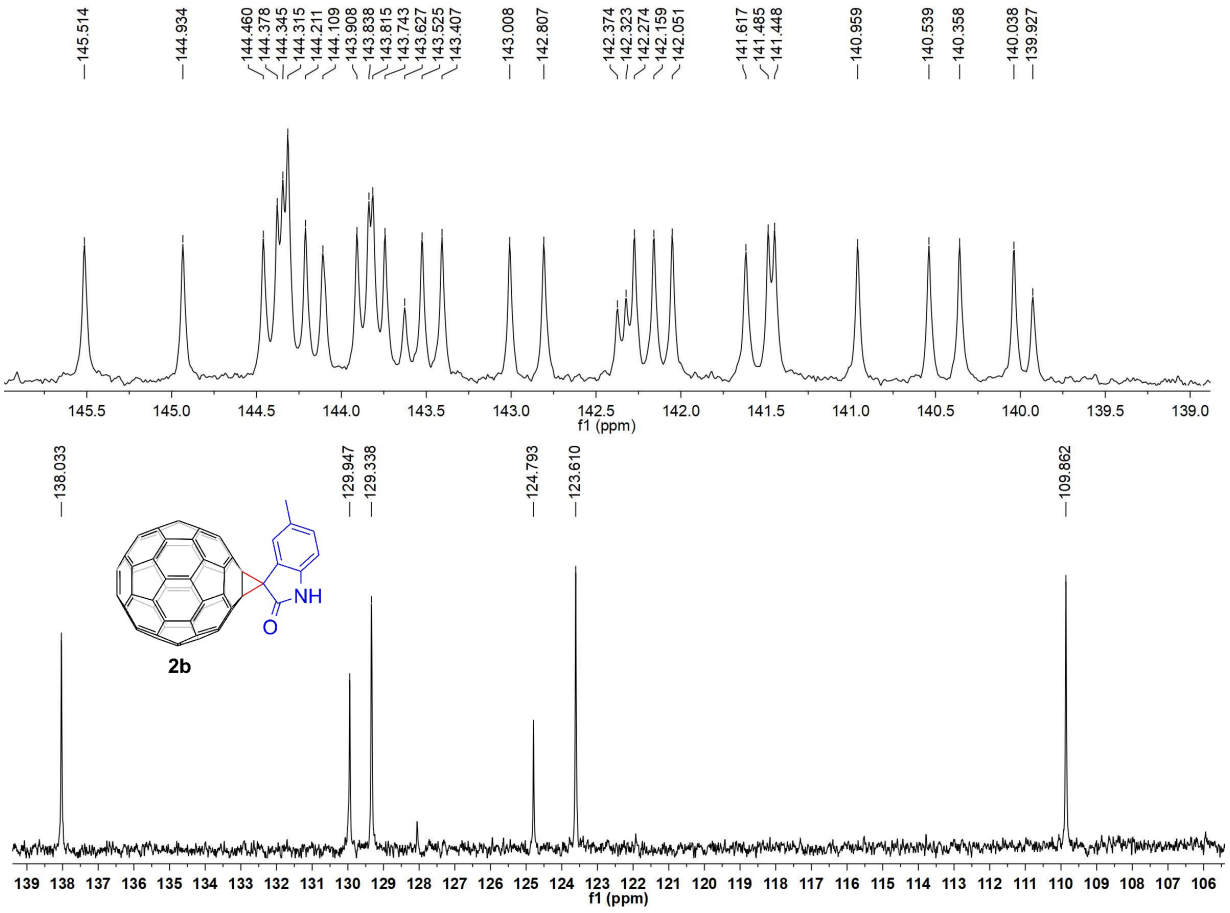
^1H NMR (600 MHz, d_6-DMSO/CS_2) of compound 2b



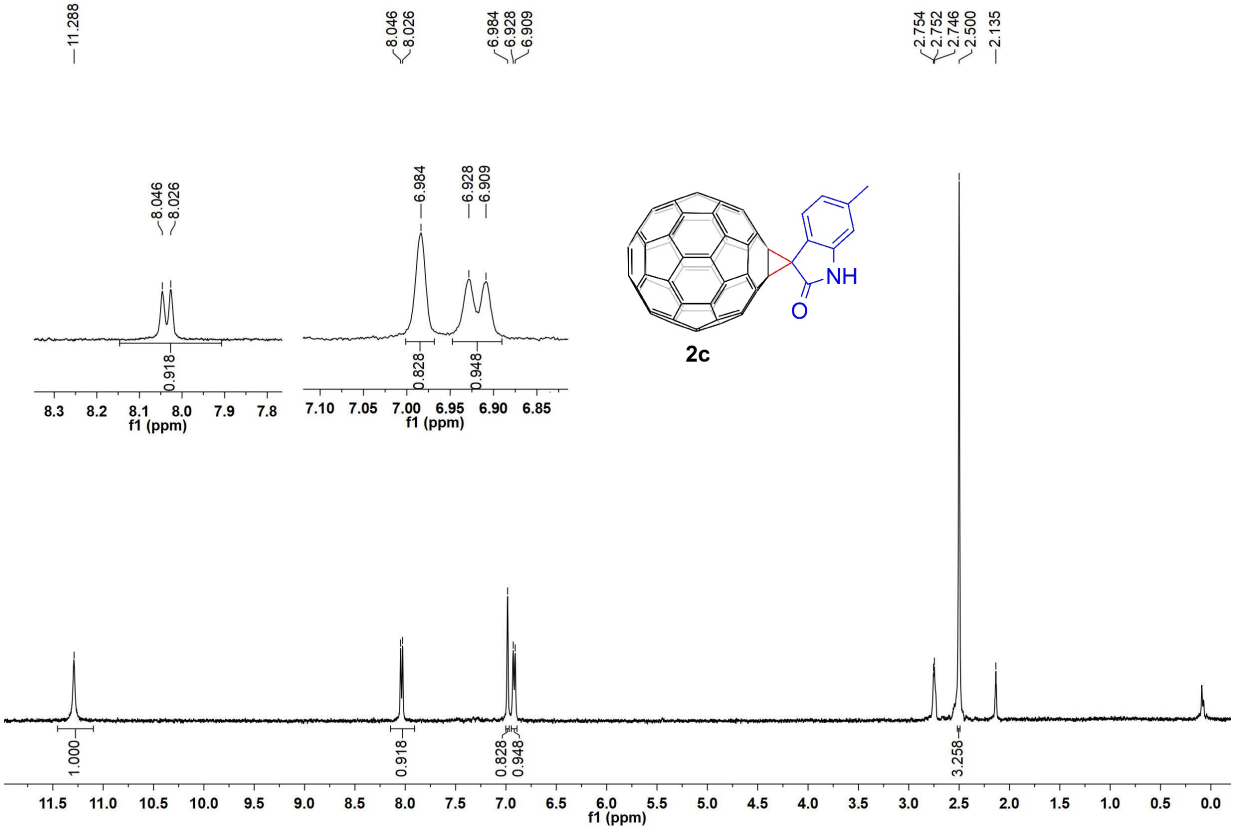
^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 2b



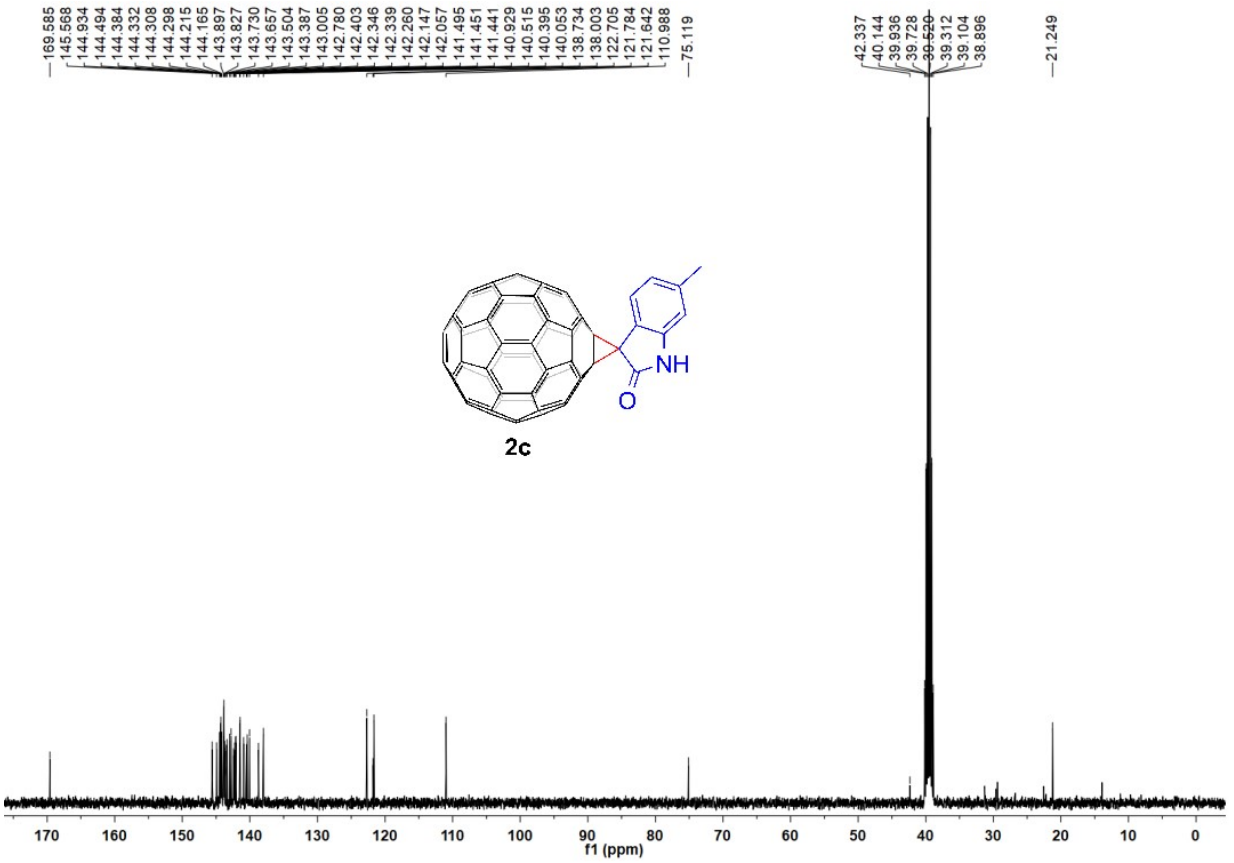
Expanded ^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 2b



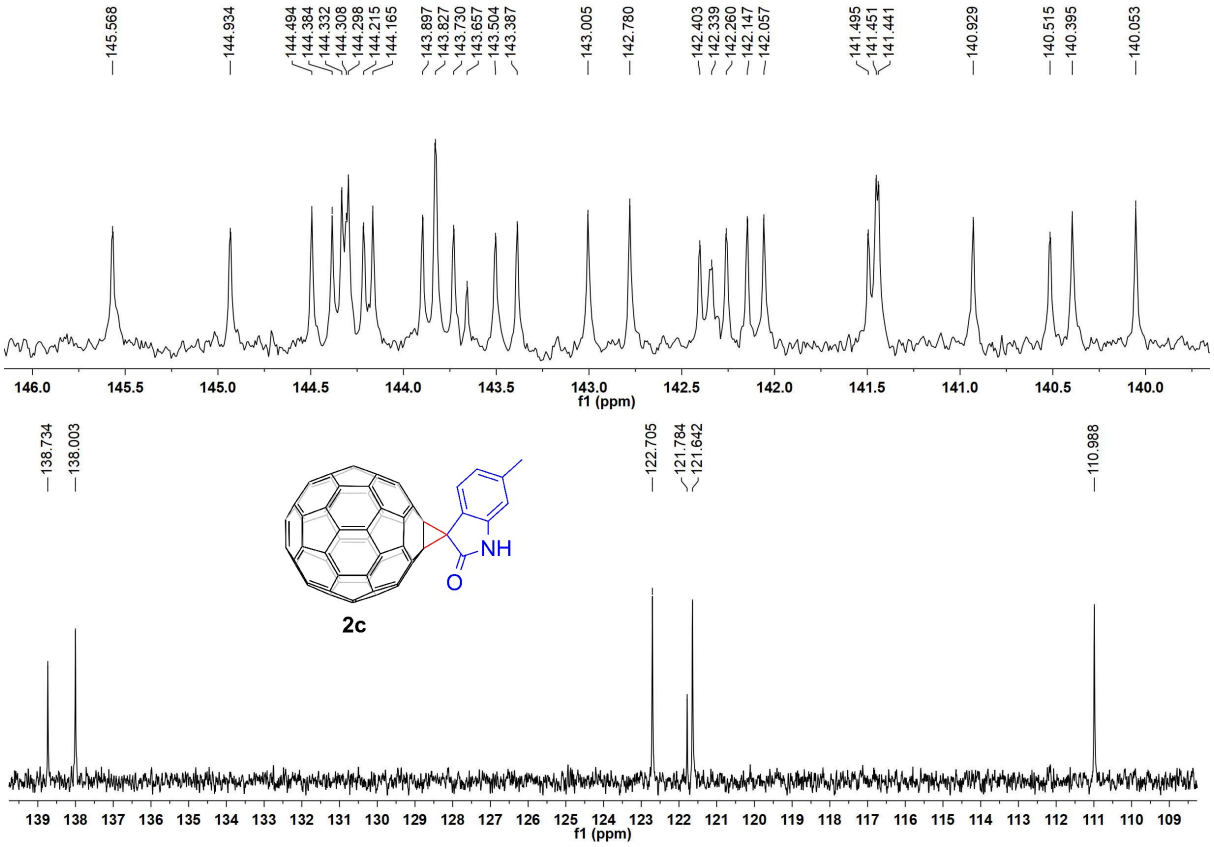
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 2c



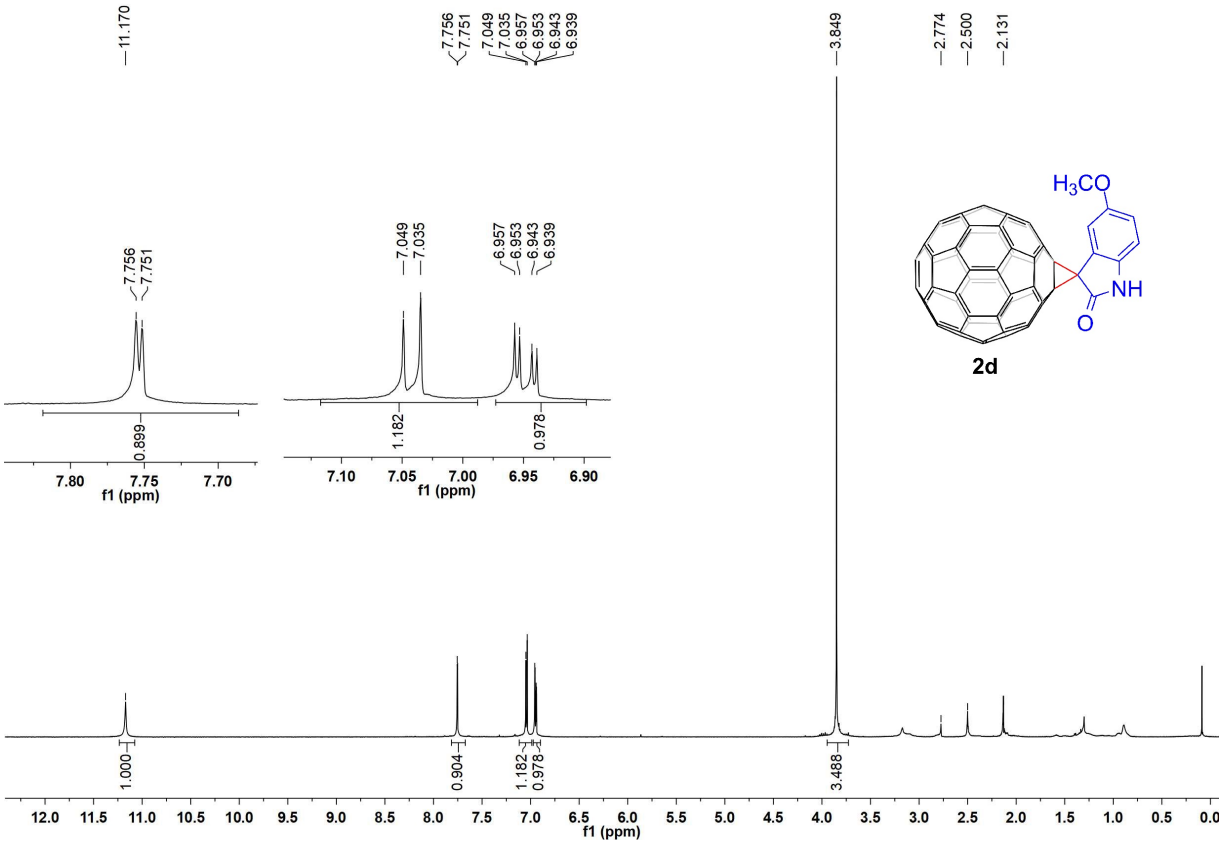
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 2c



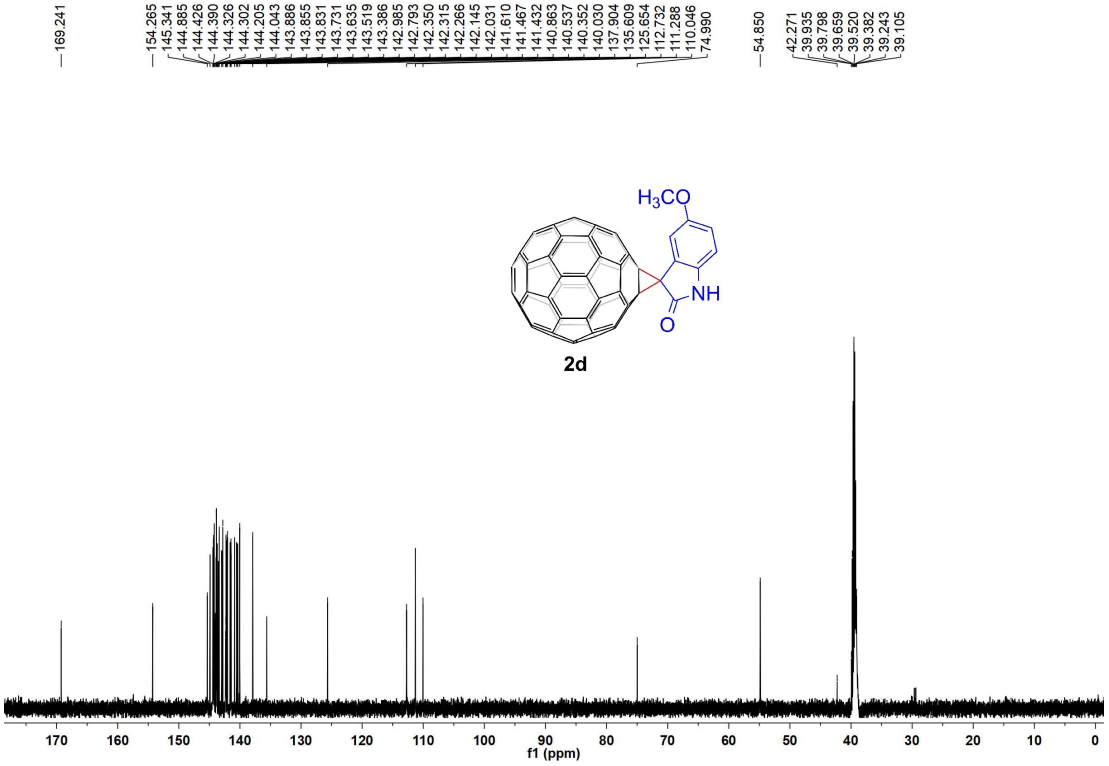
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 2c



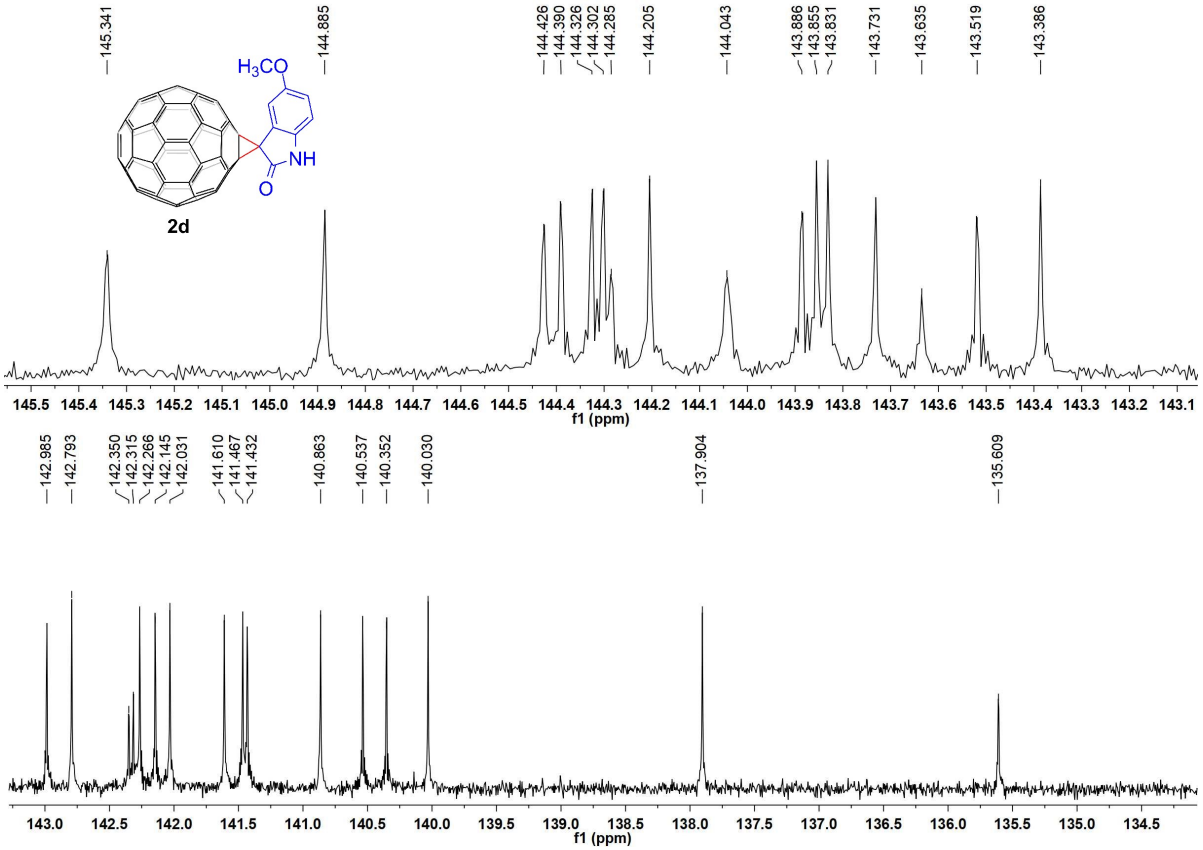
^1H NMR (600 MHz , d_6-DMSO/CS_2) of compound 2d



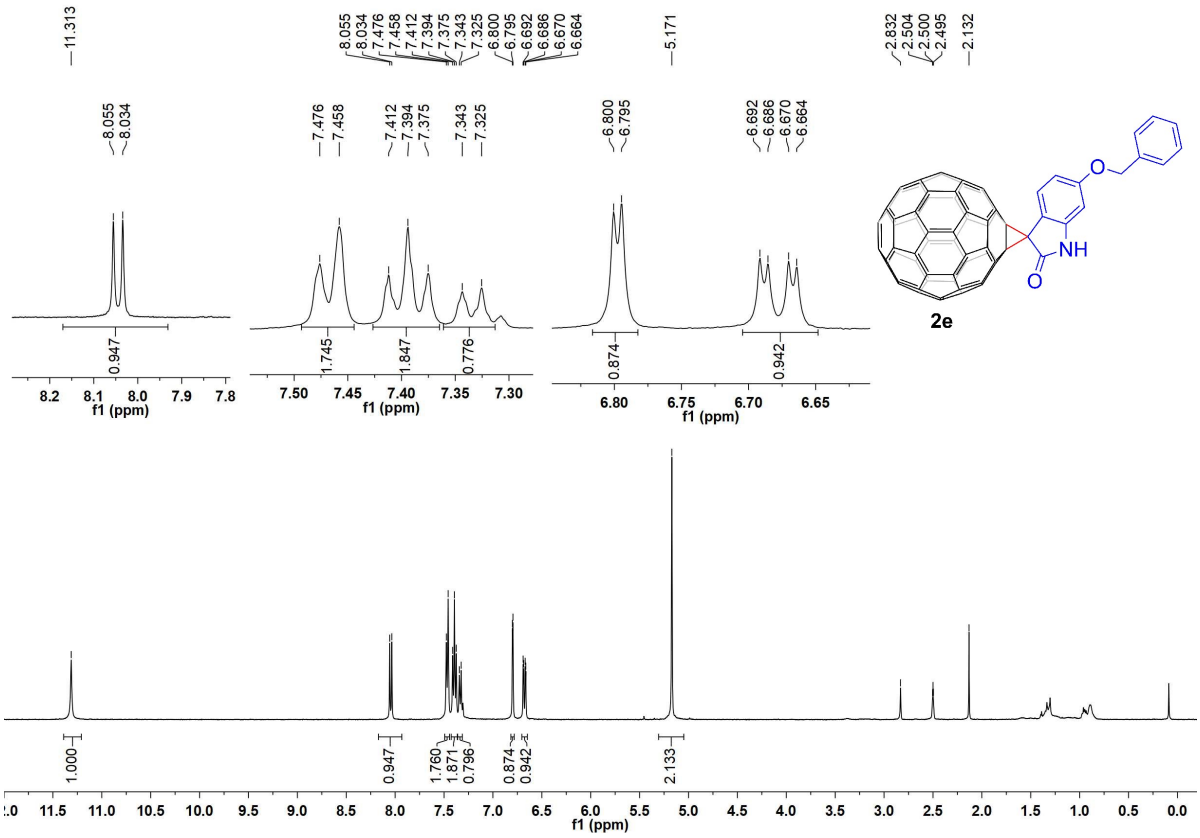
^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 2d



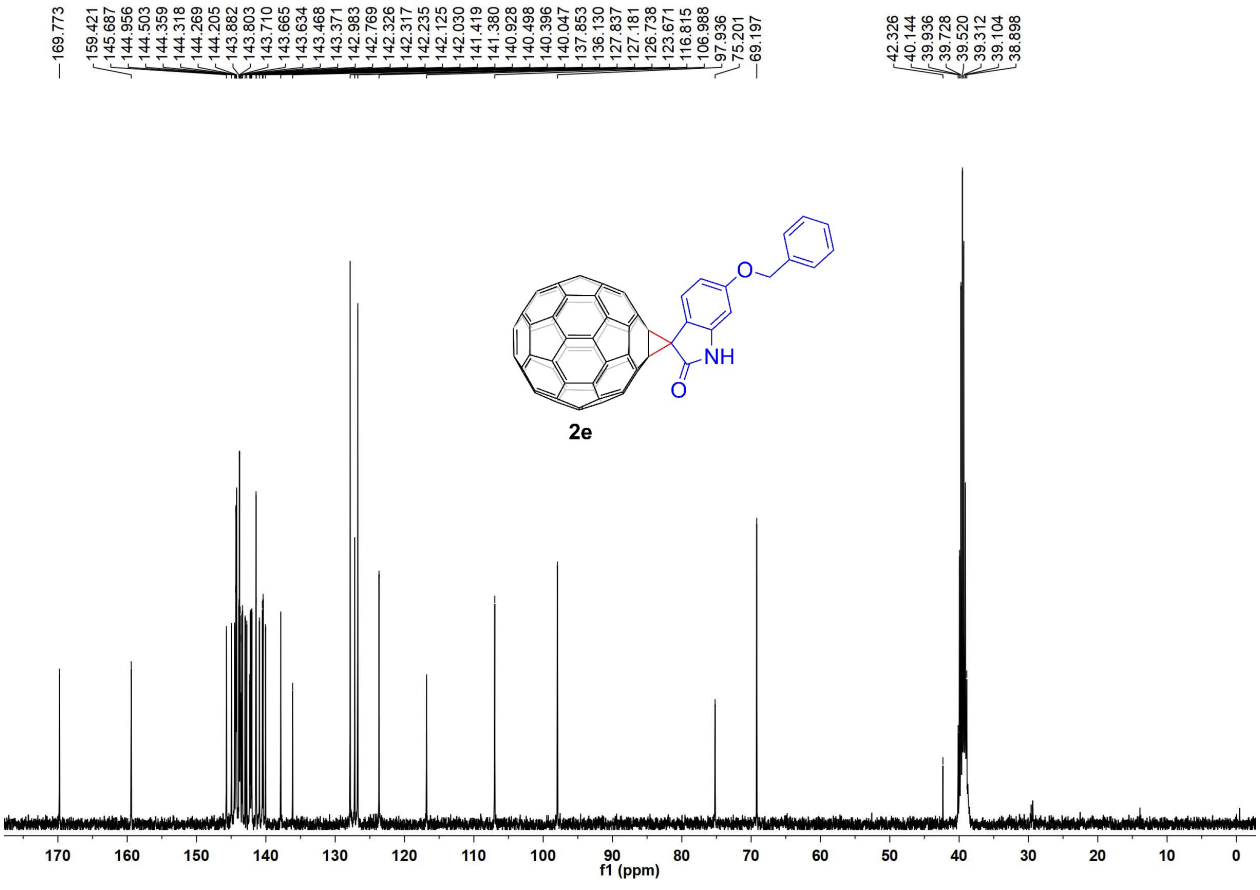
Expanded ^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 2d



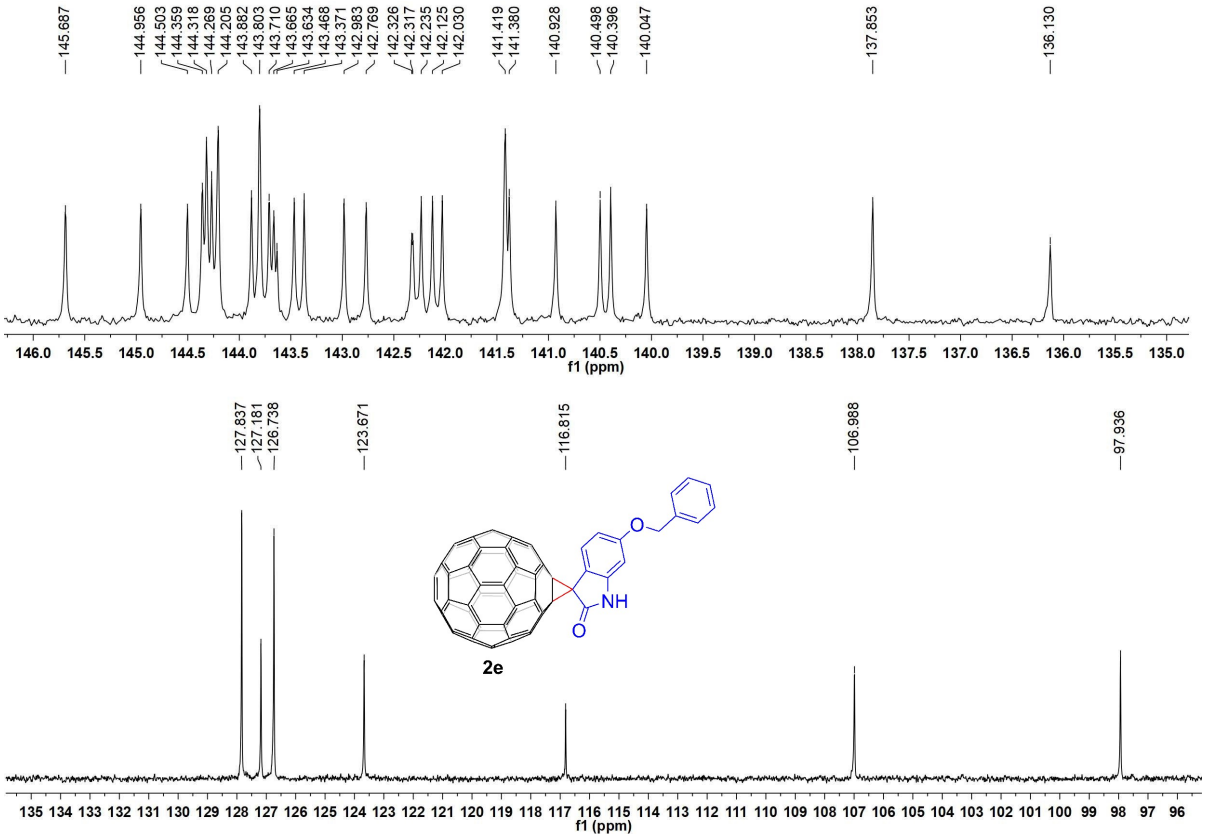
^{1}H NMR (400 MHz, d_6-DMSO/CS_2) of compound 2e



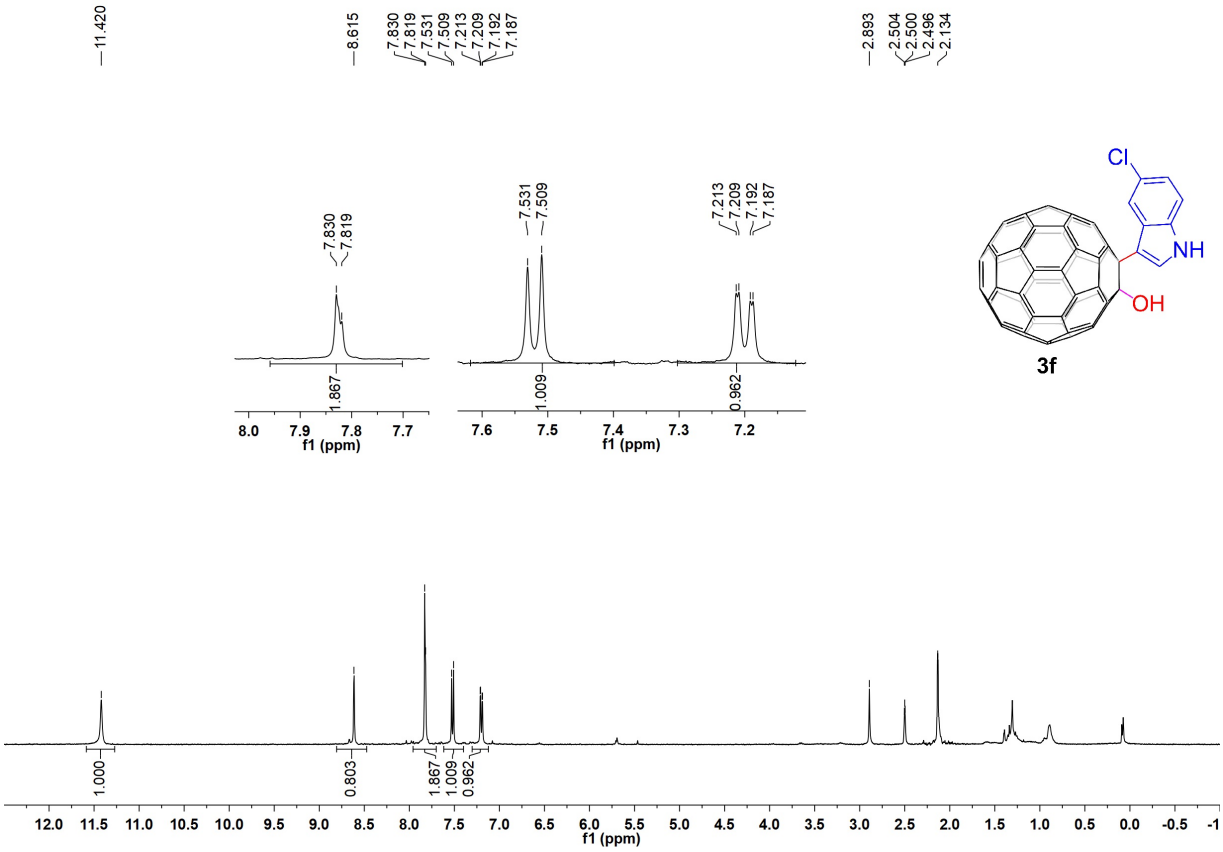
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 2e



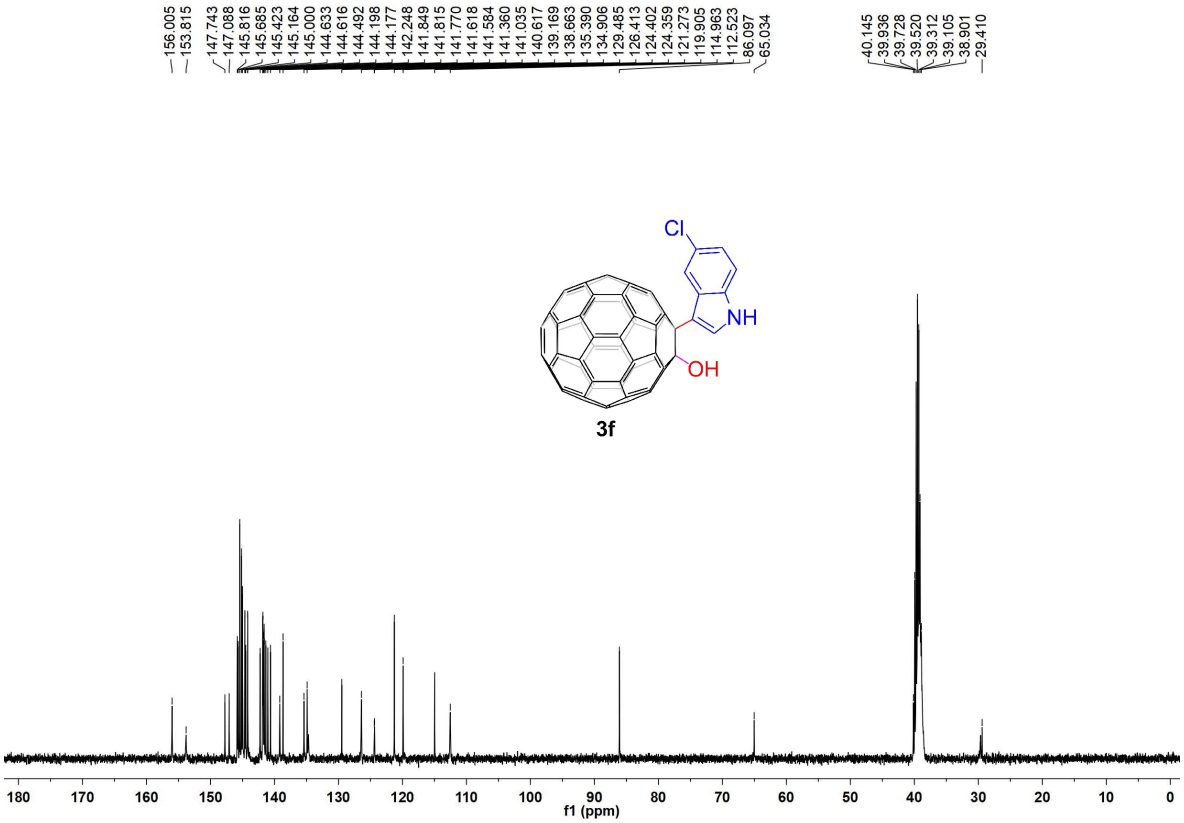
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 2e



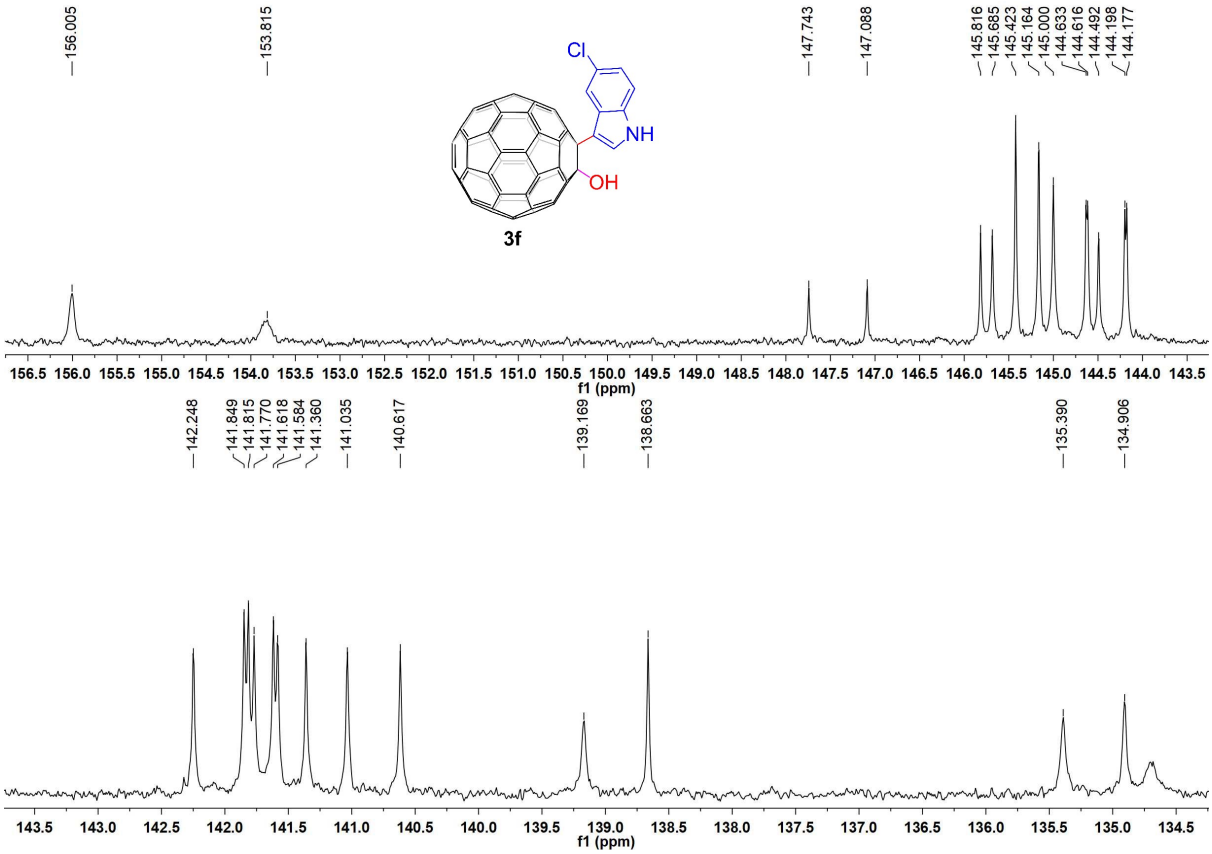
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 3f



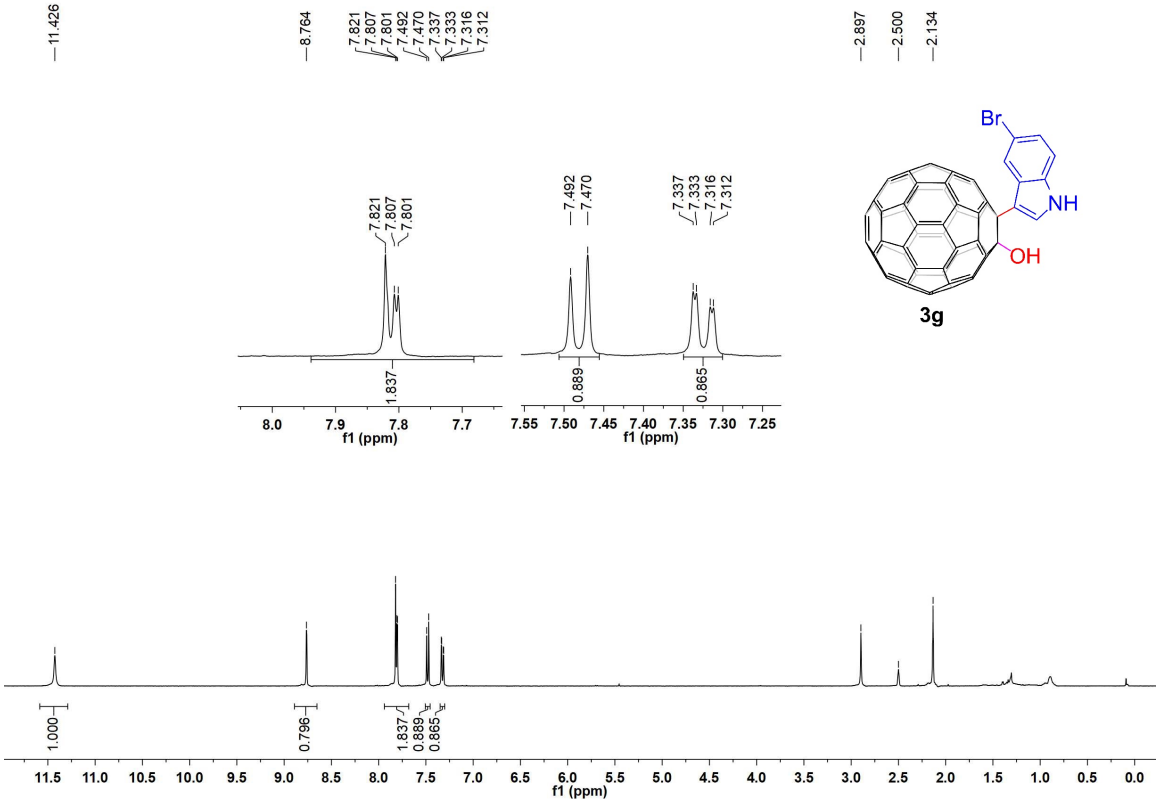
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3f



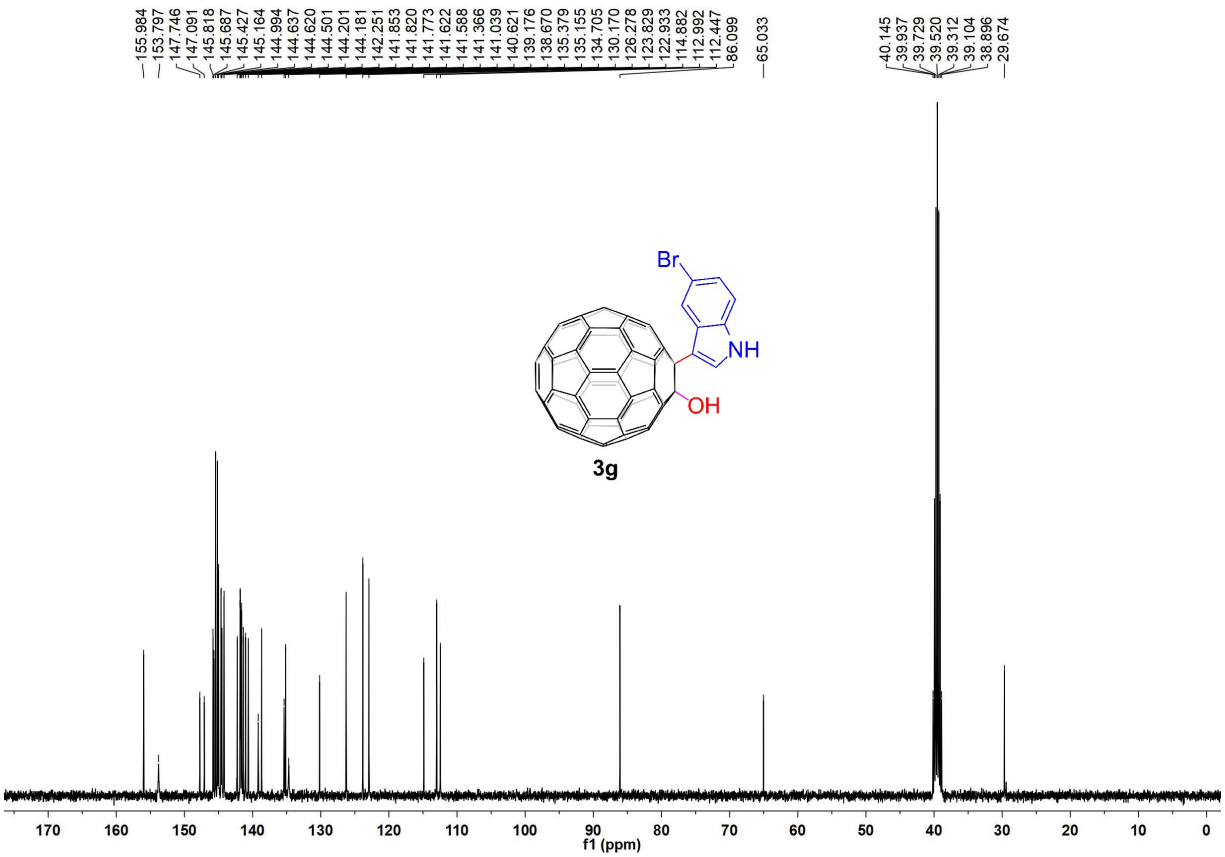
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3f



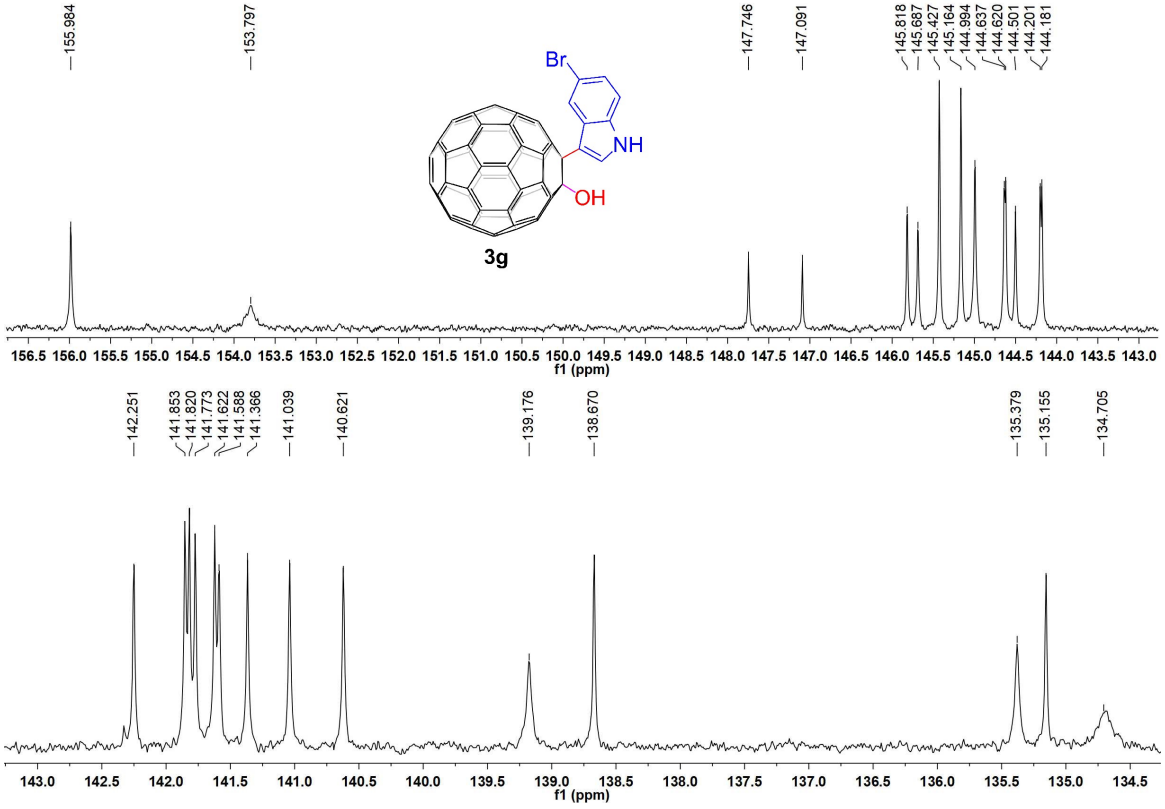
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 3g



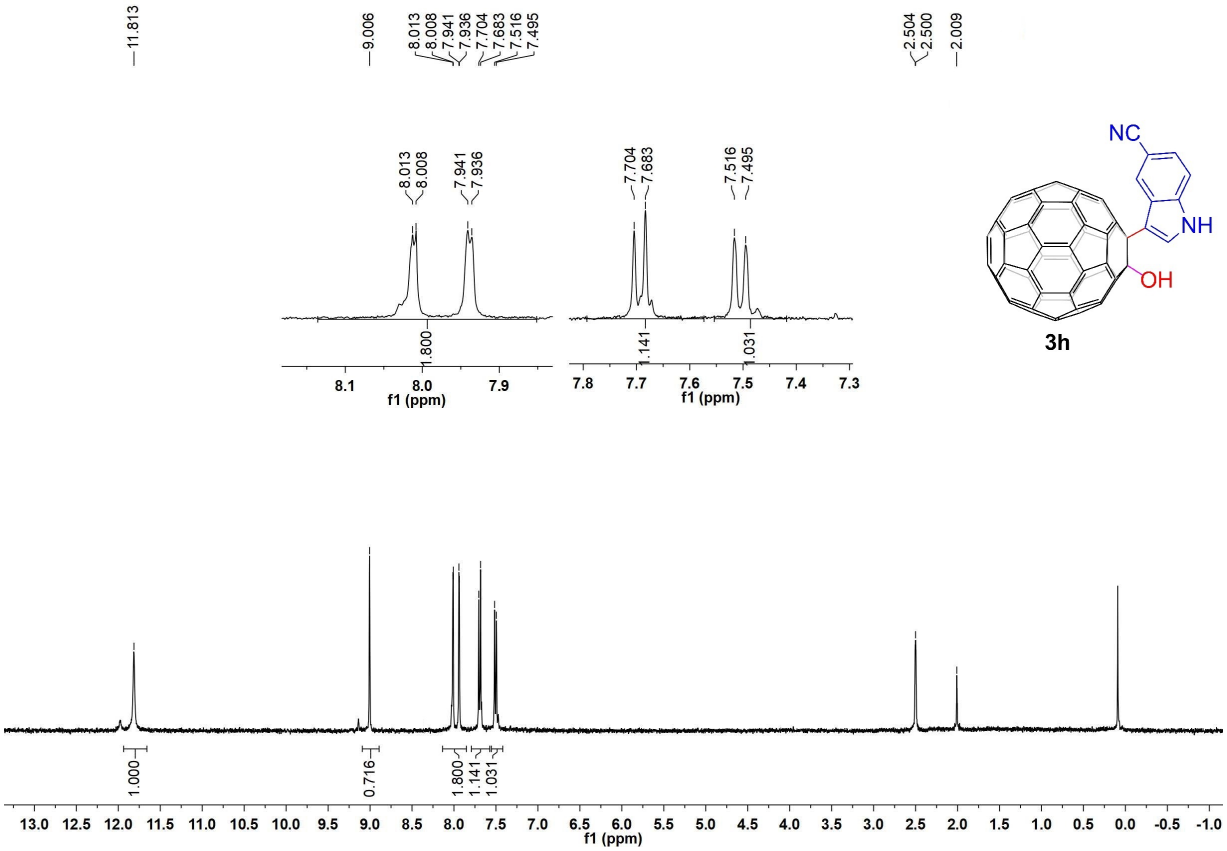
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3g



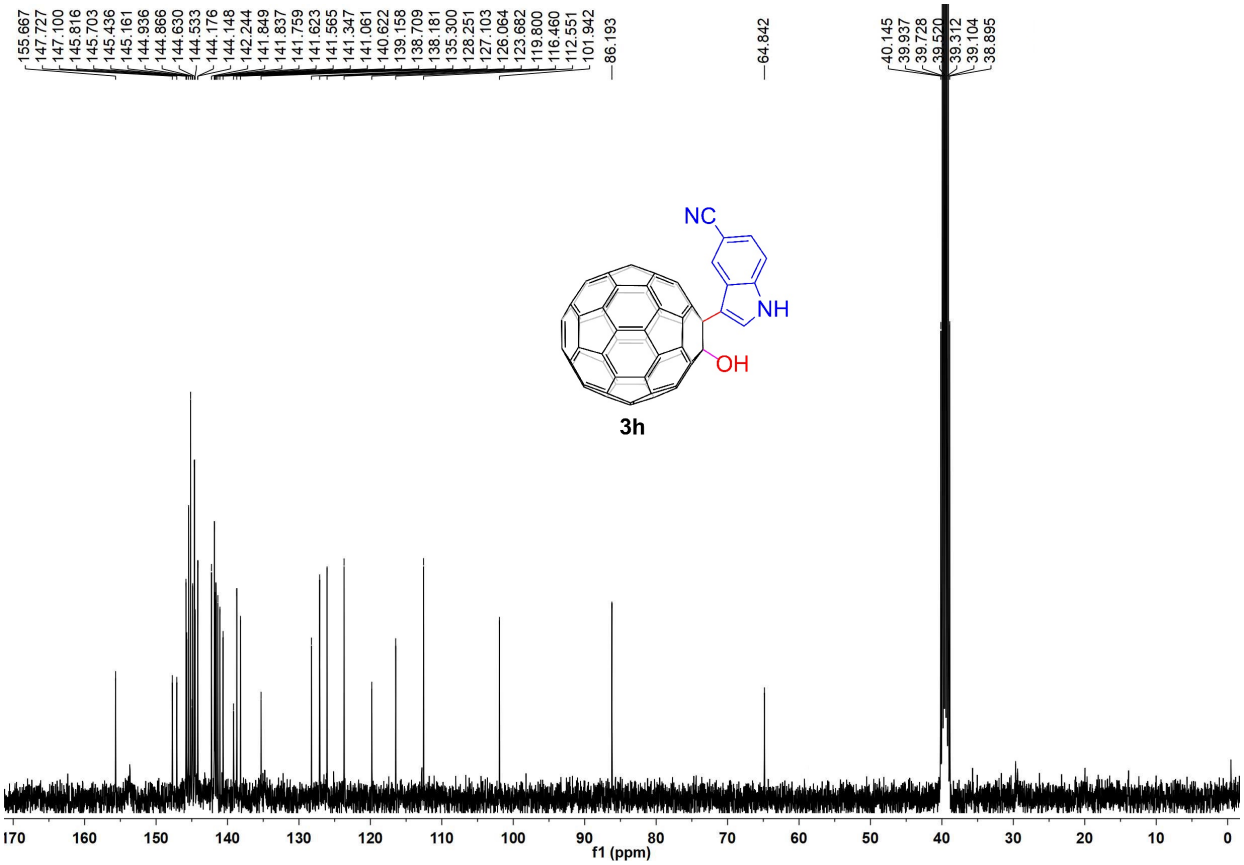
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3g



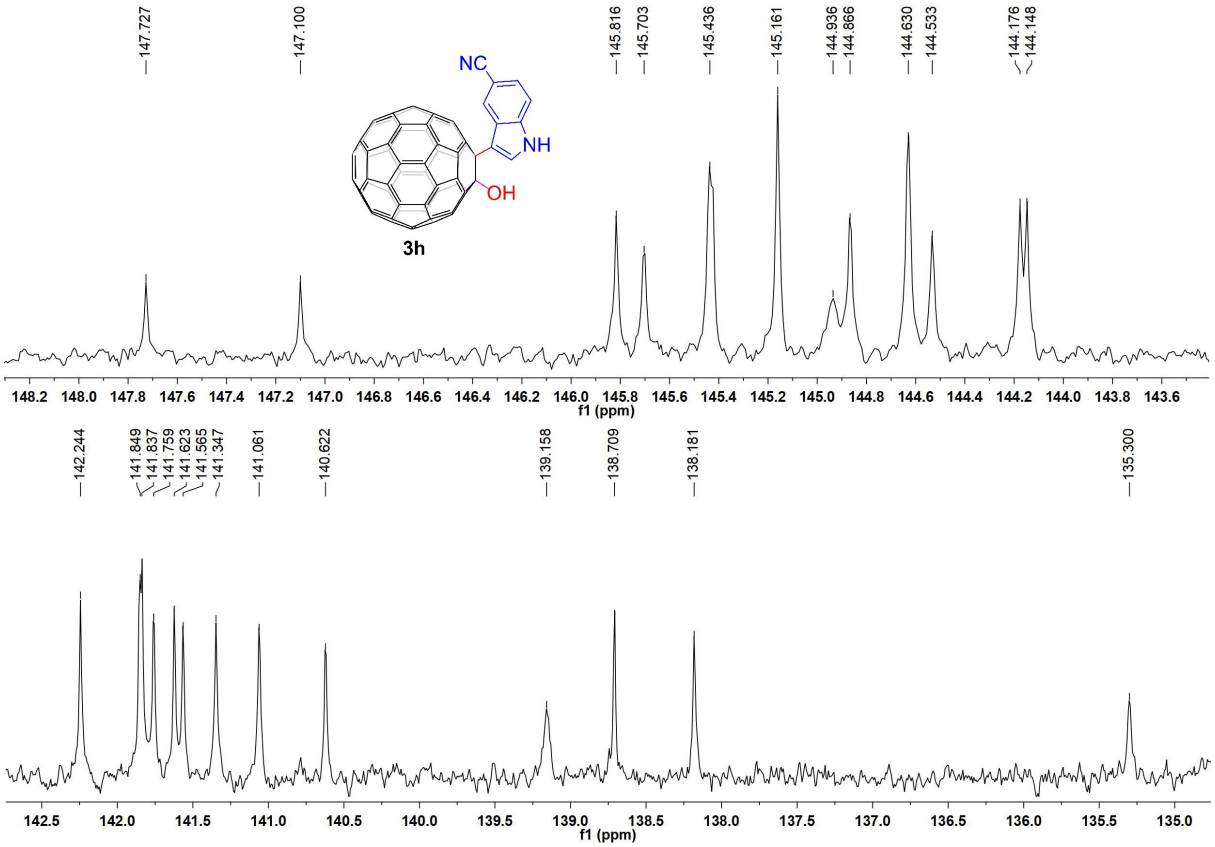
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 3h



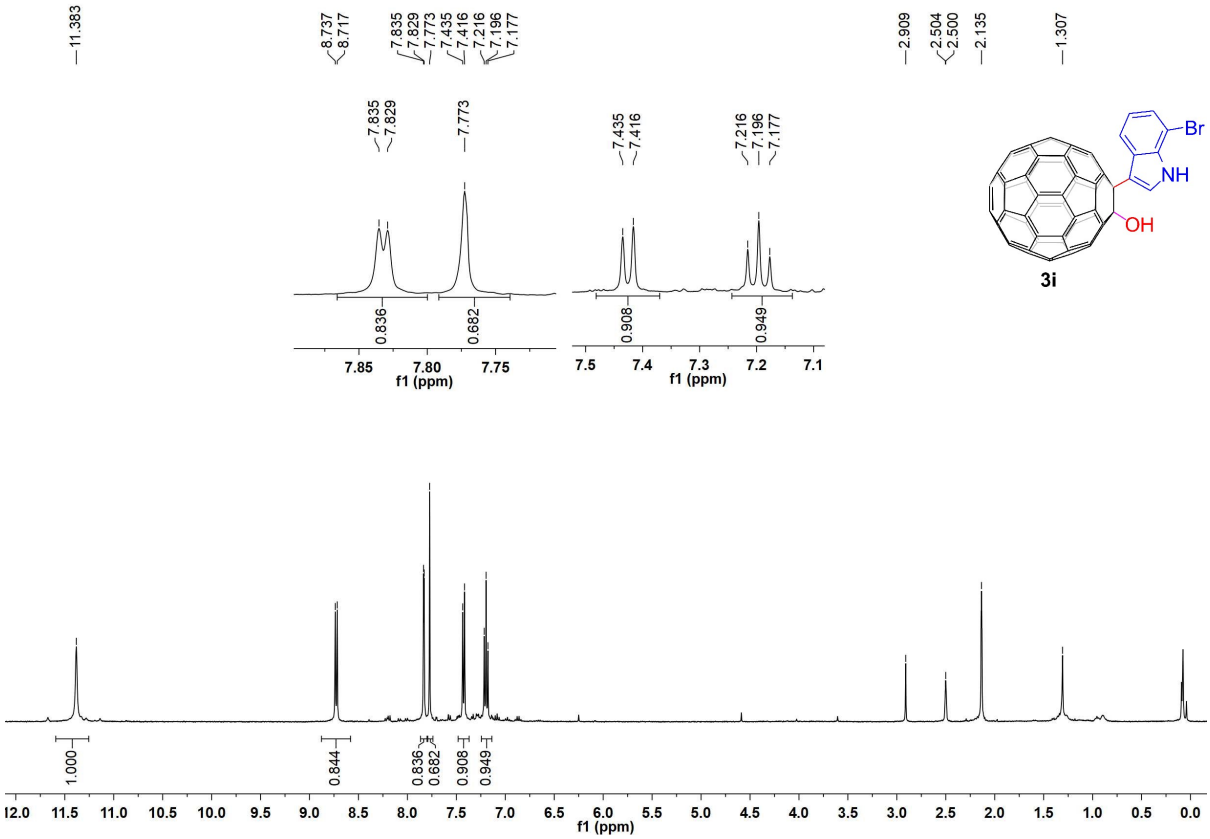
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3h



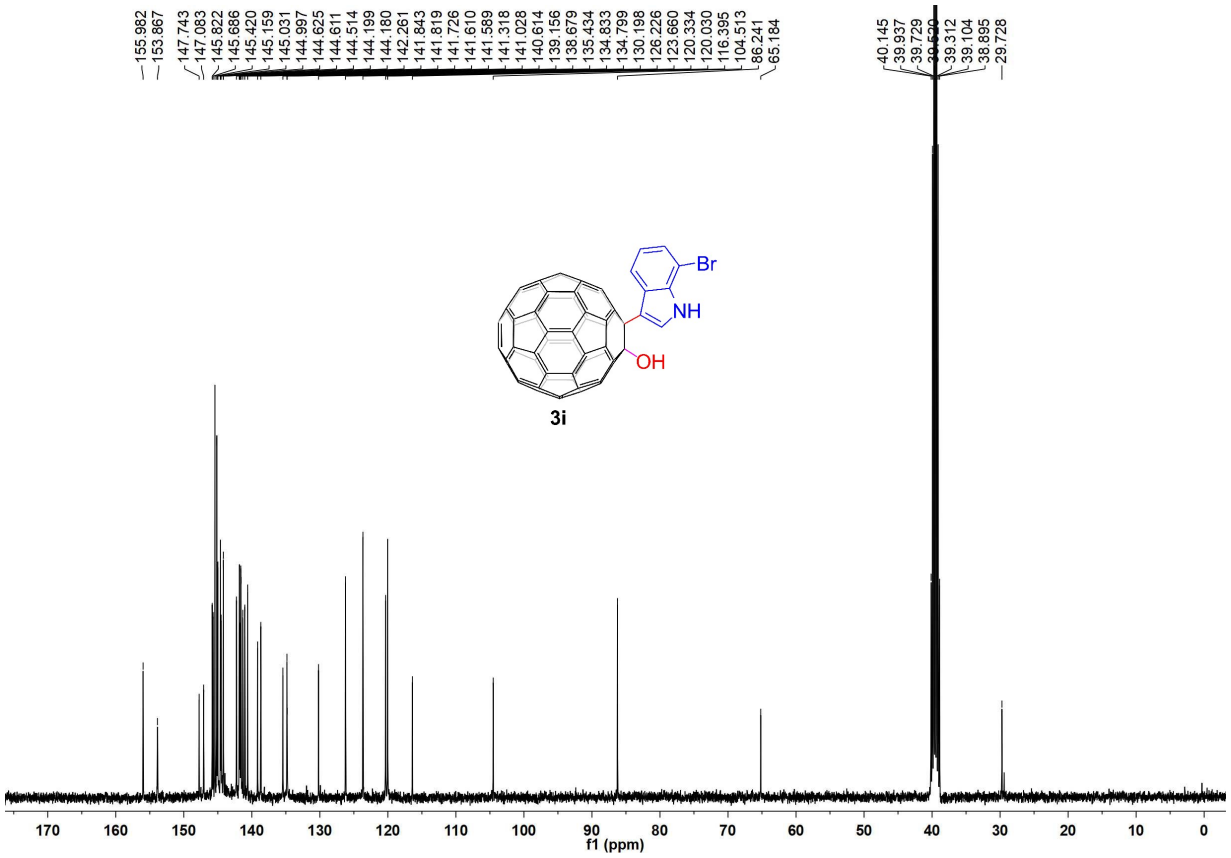
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3h



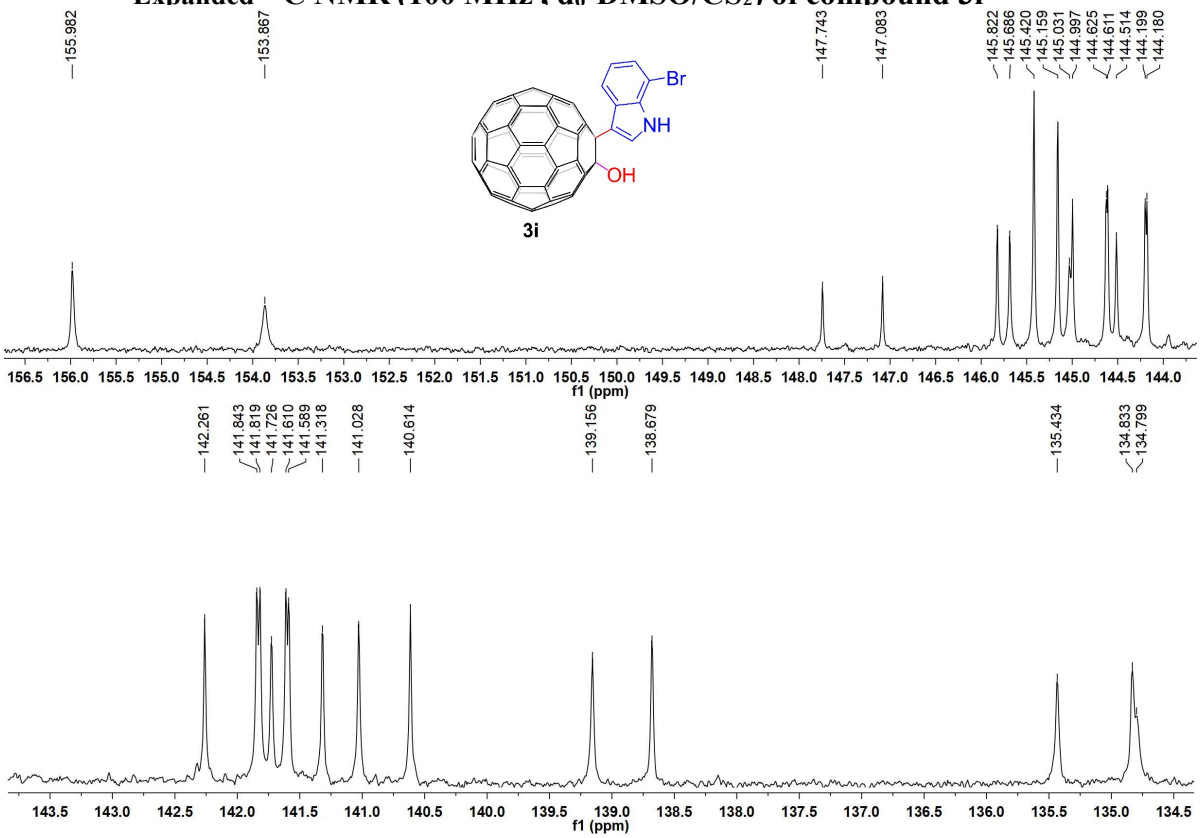
^{1}H NMR (400 MHz , d$_6$-DMSO/CS$_2$) of compound 3i



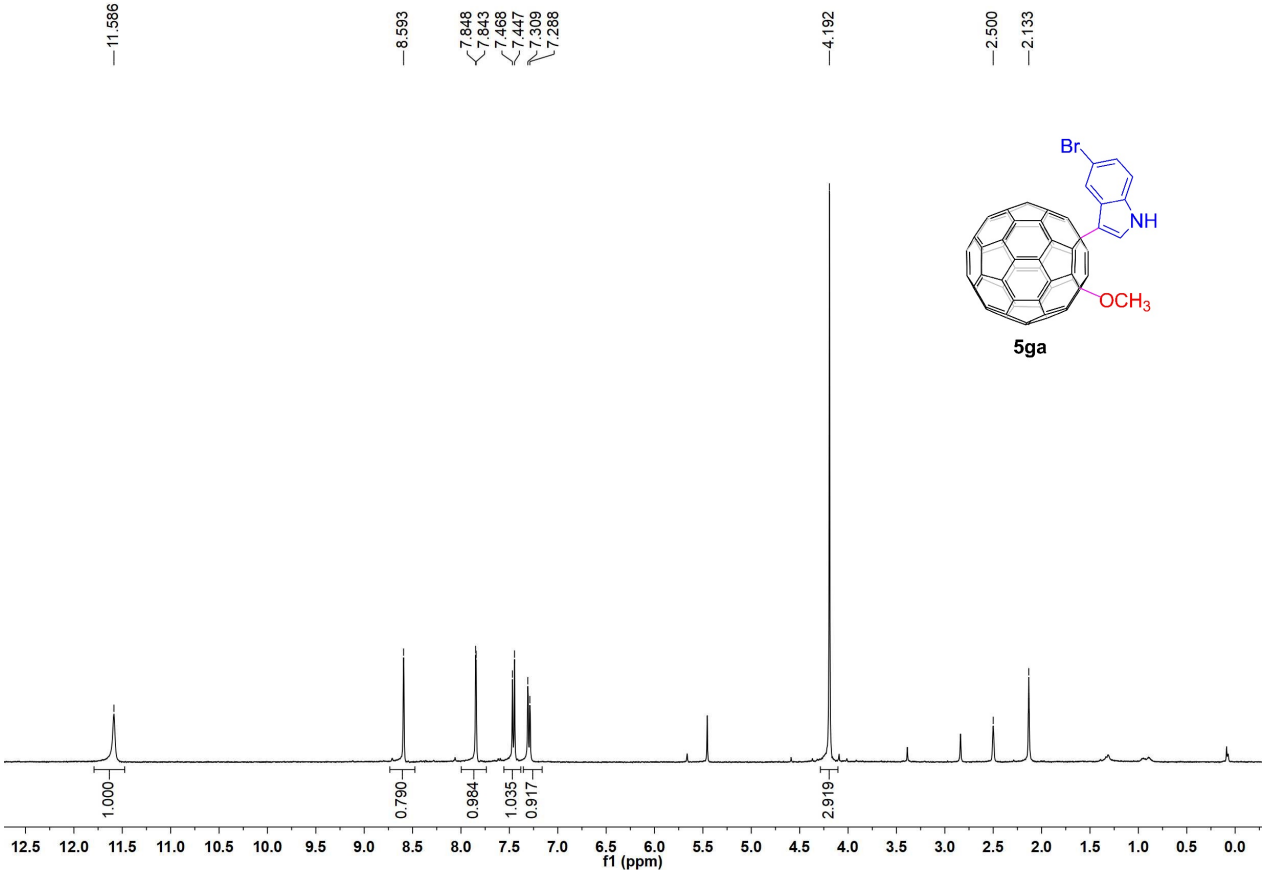
^{13}C NMR (100 MHz , d$_6$-DMSO/CS$_2$) of compound 3i



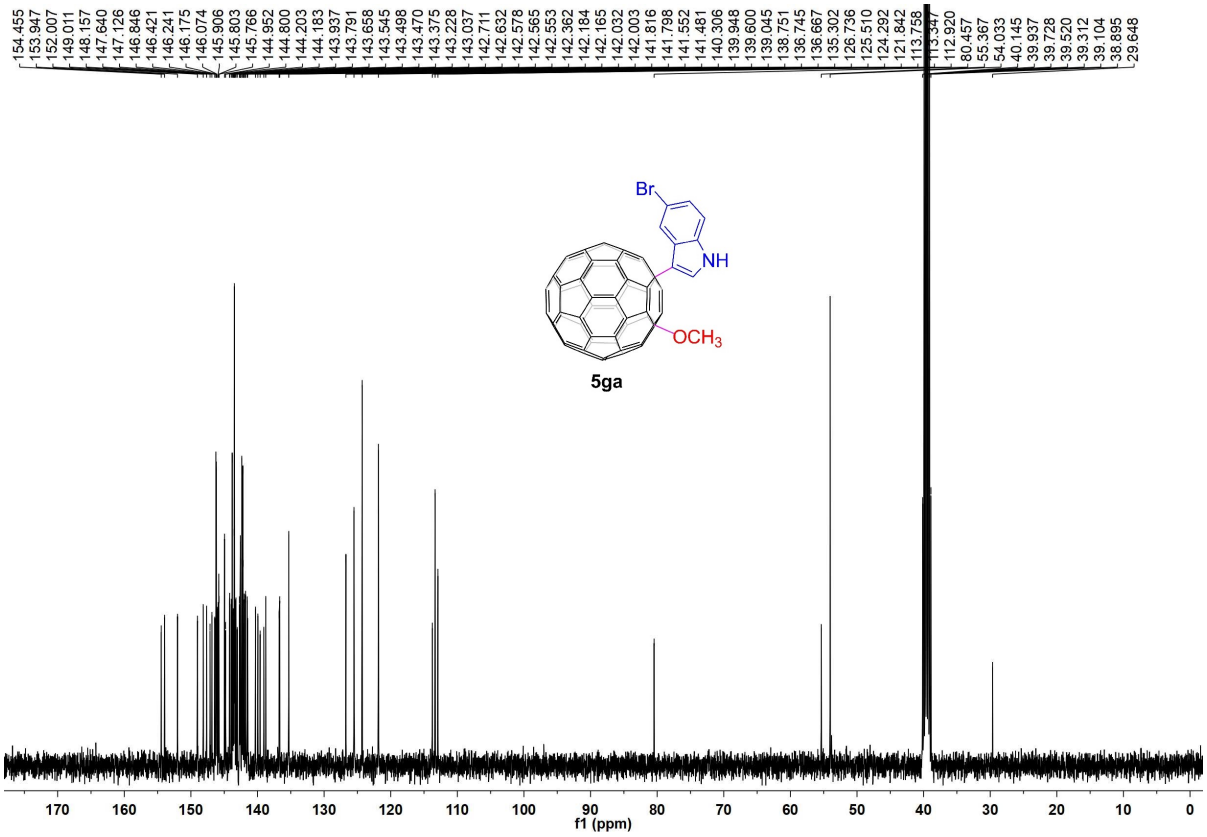
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 3i



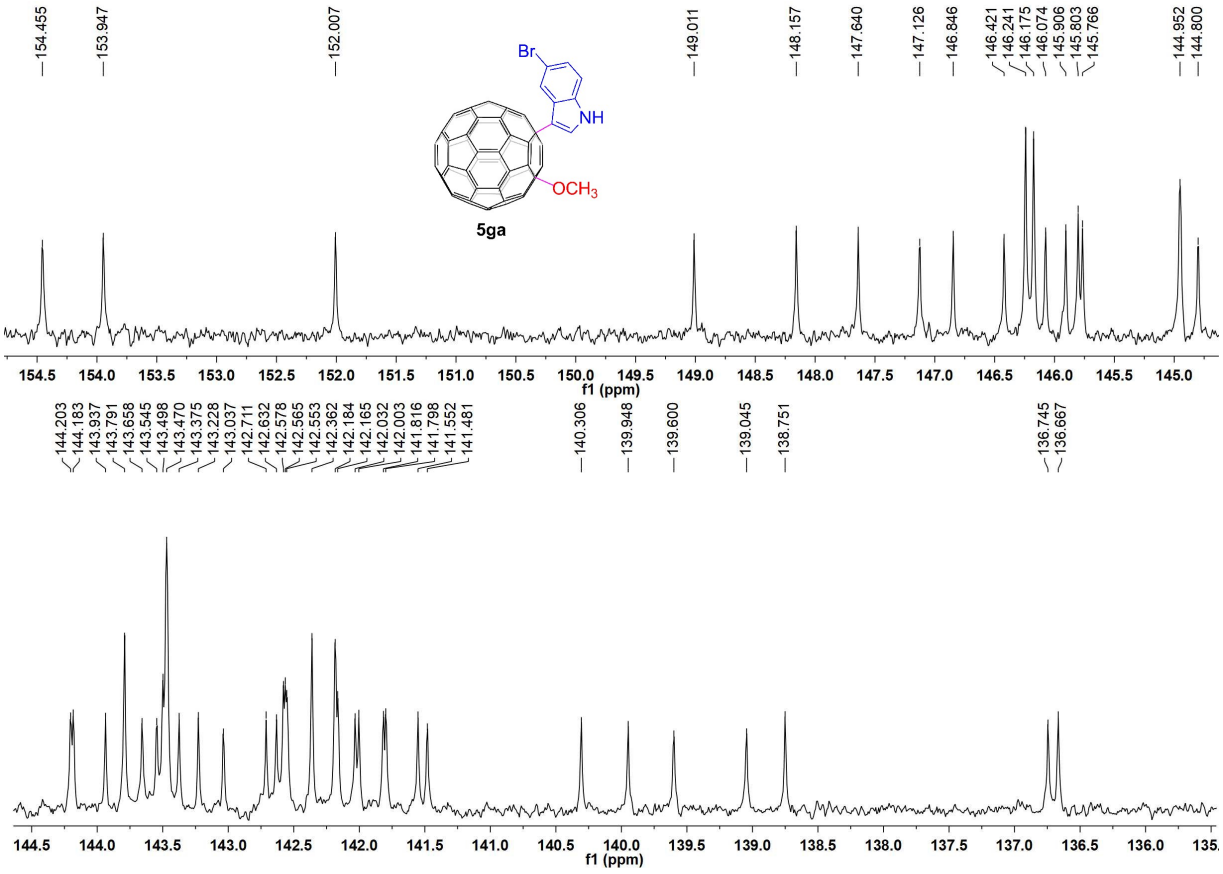
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ga



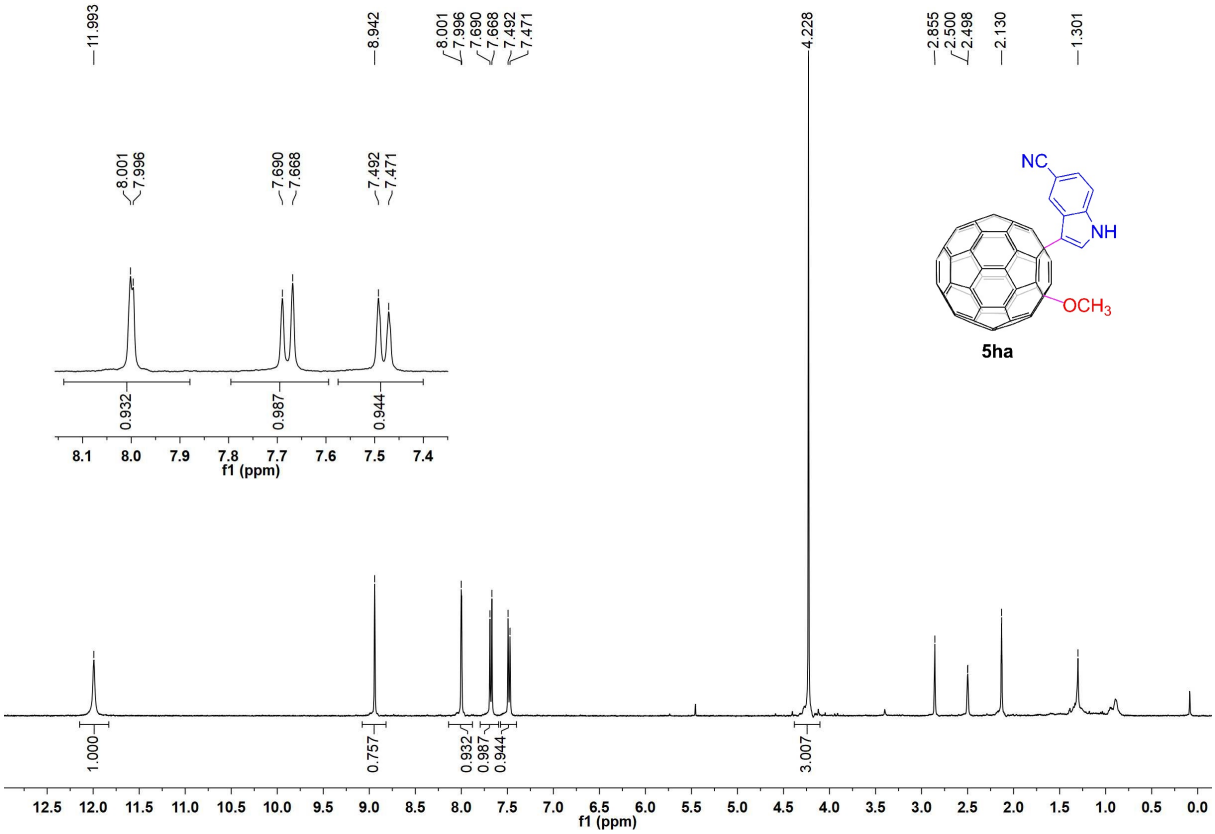
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ga



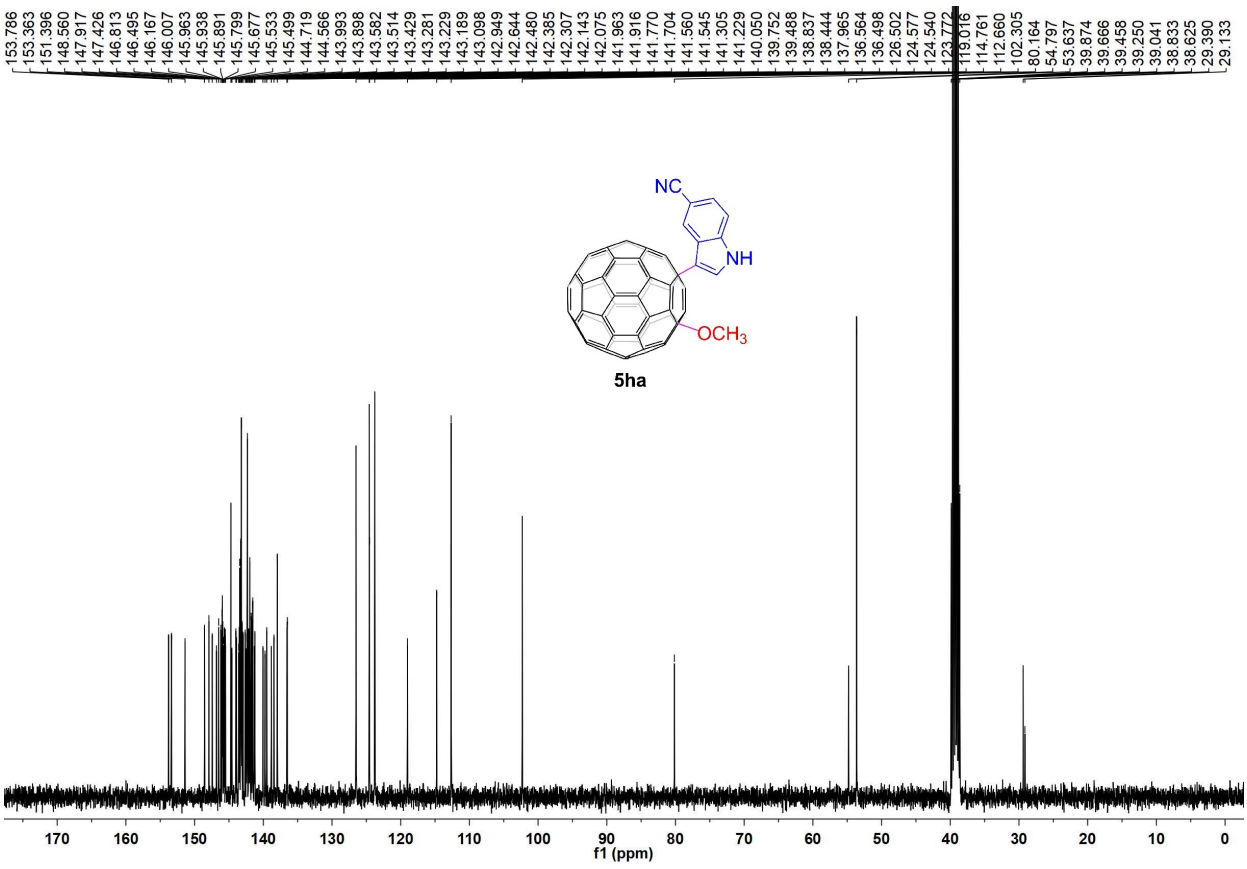
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ga



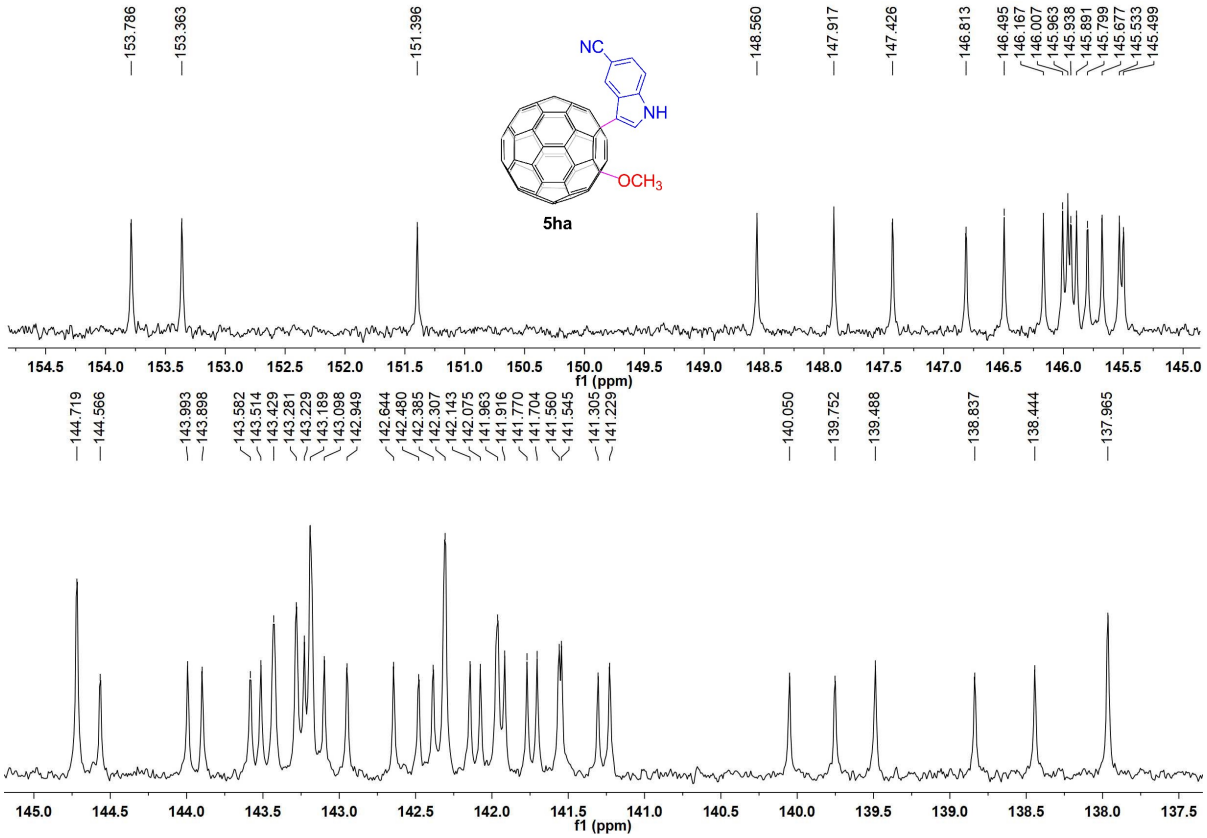
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ha



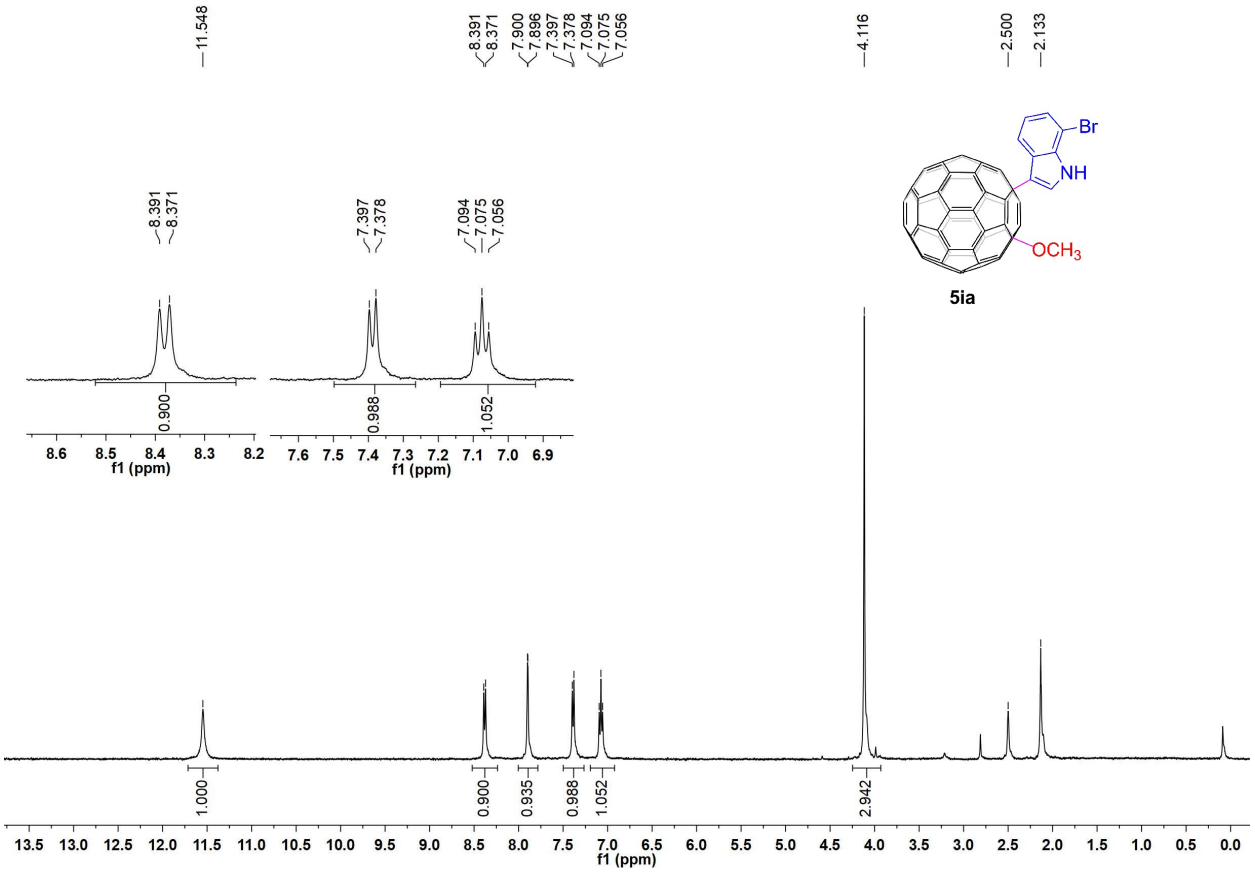
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ha



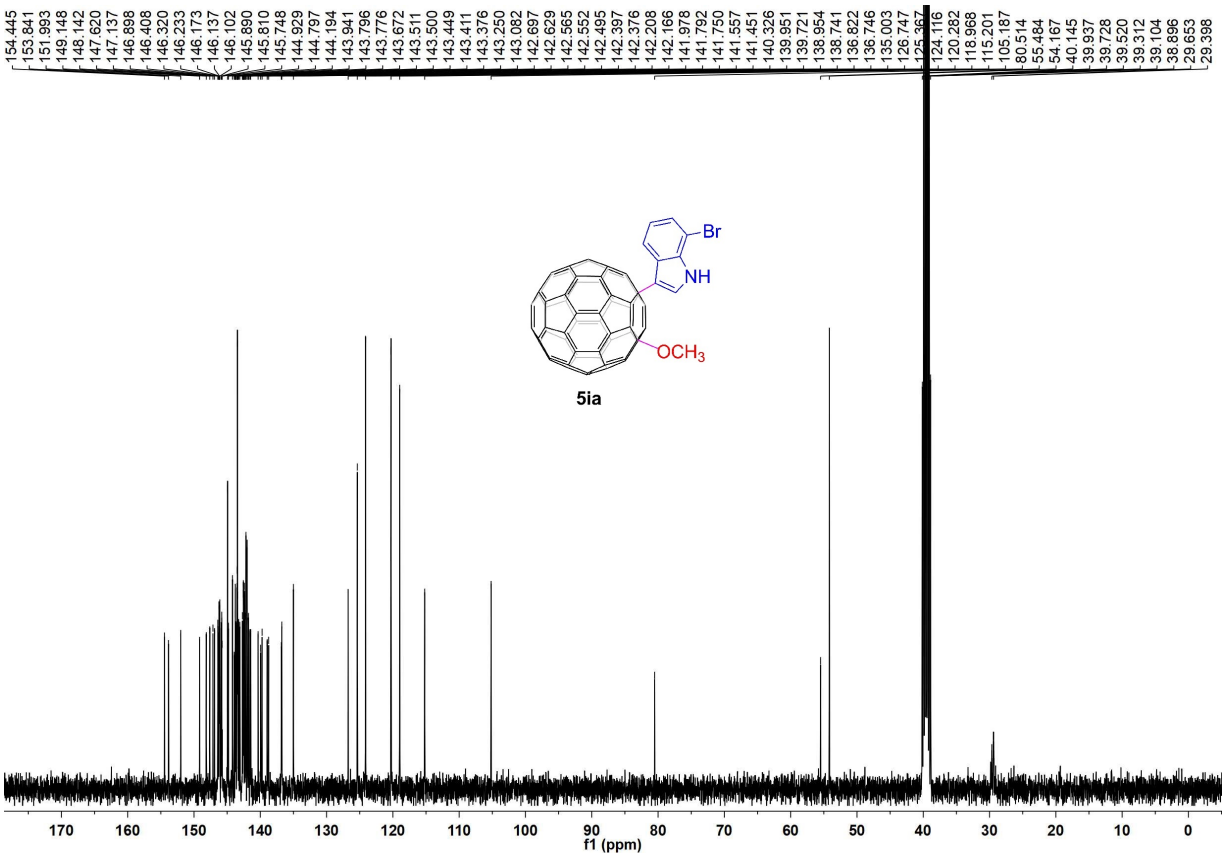
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ha



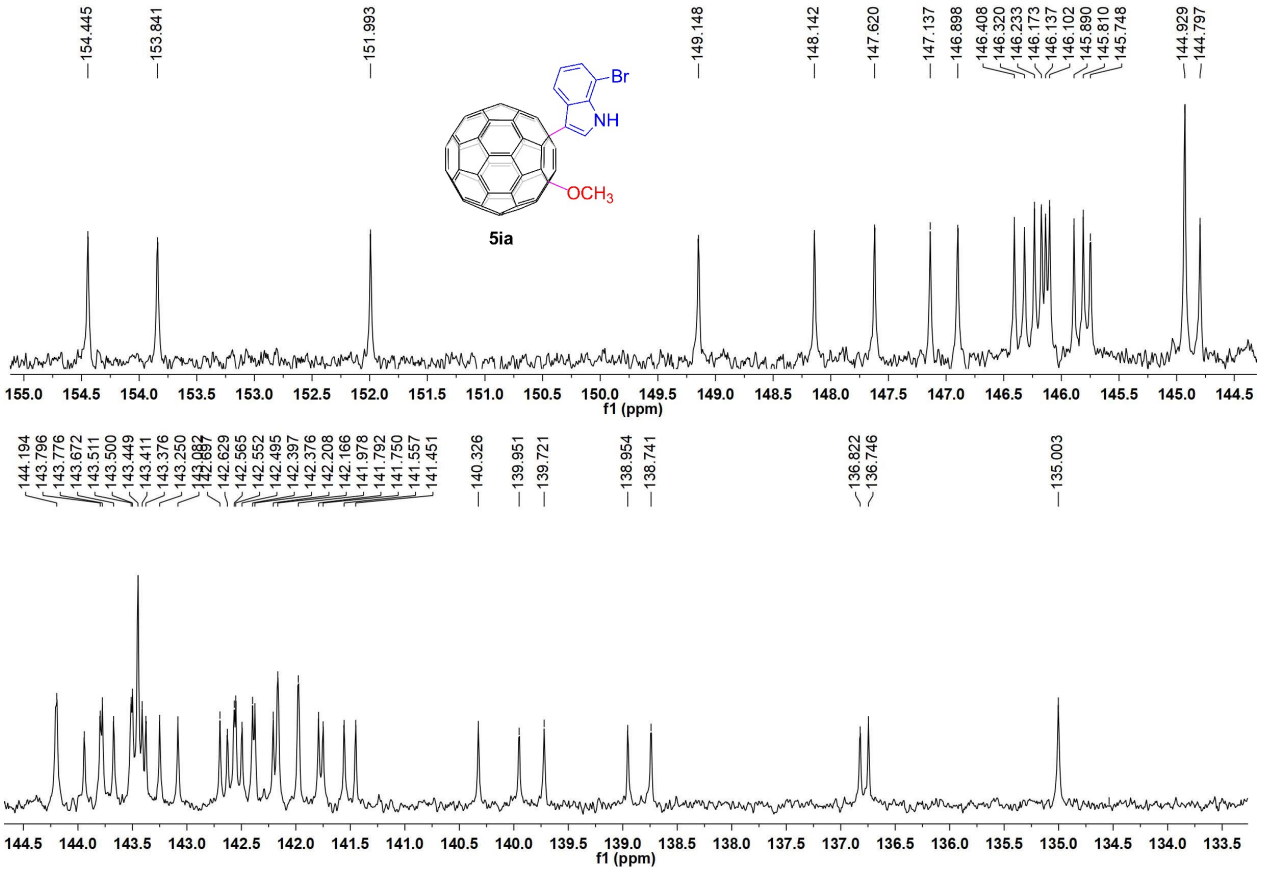
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ia



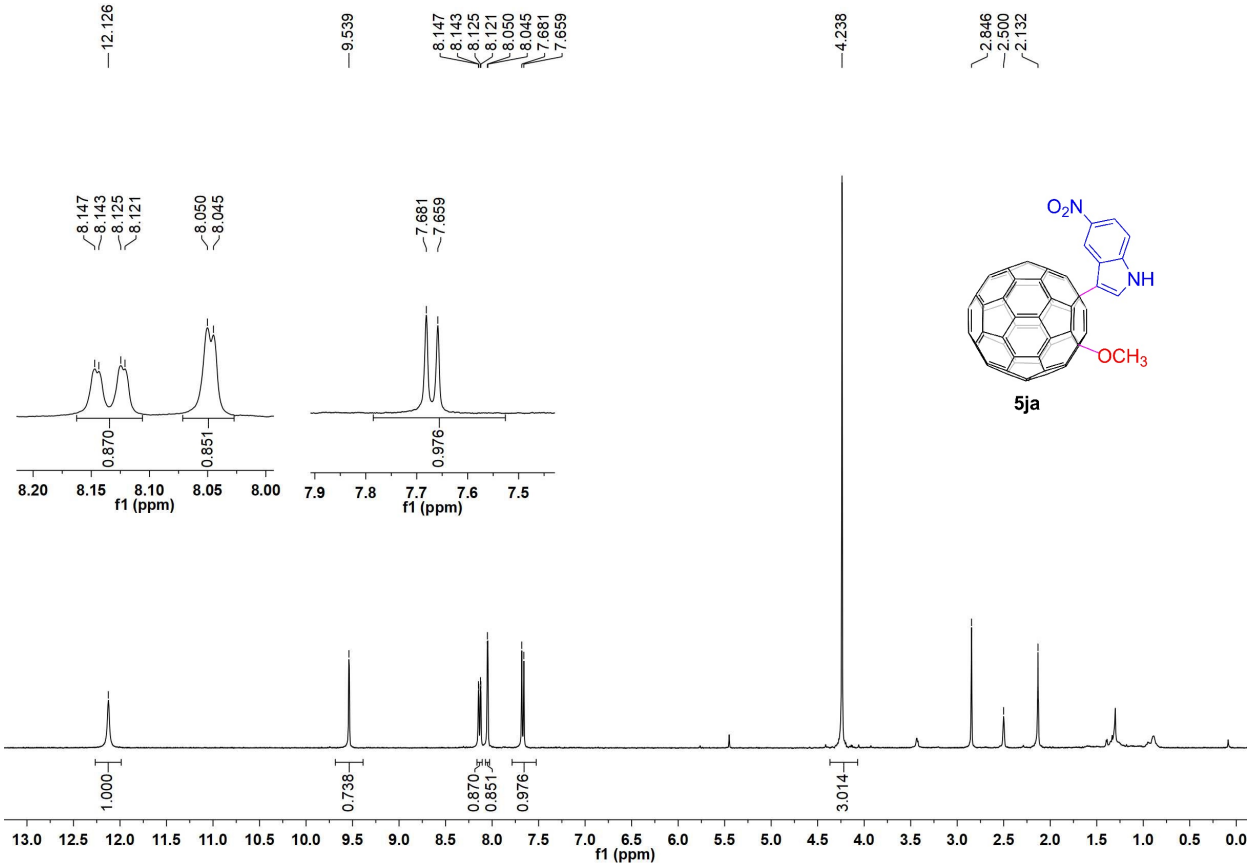
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ia



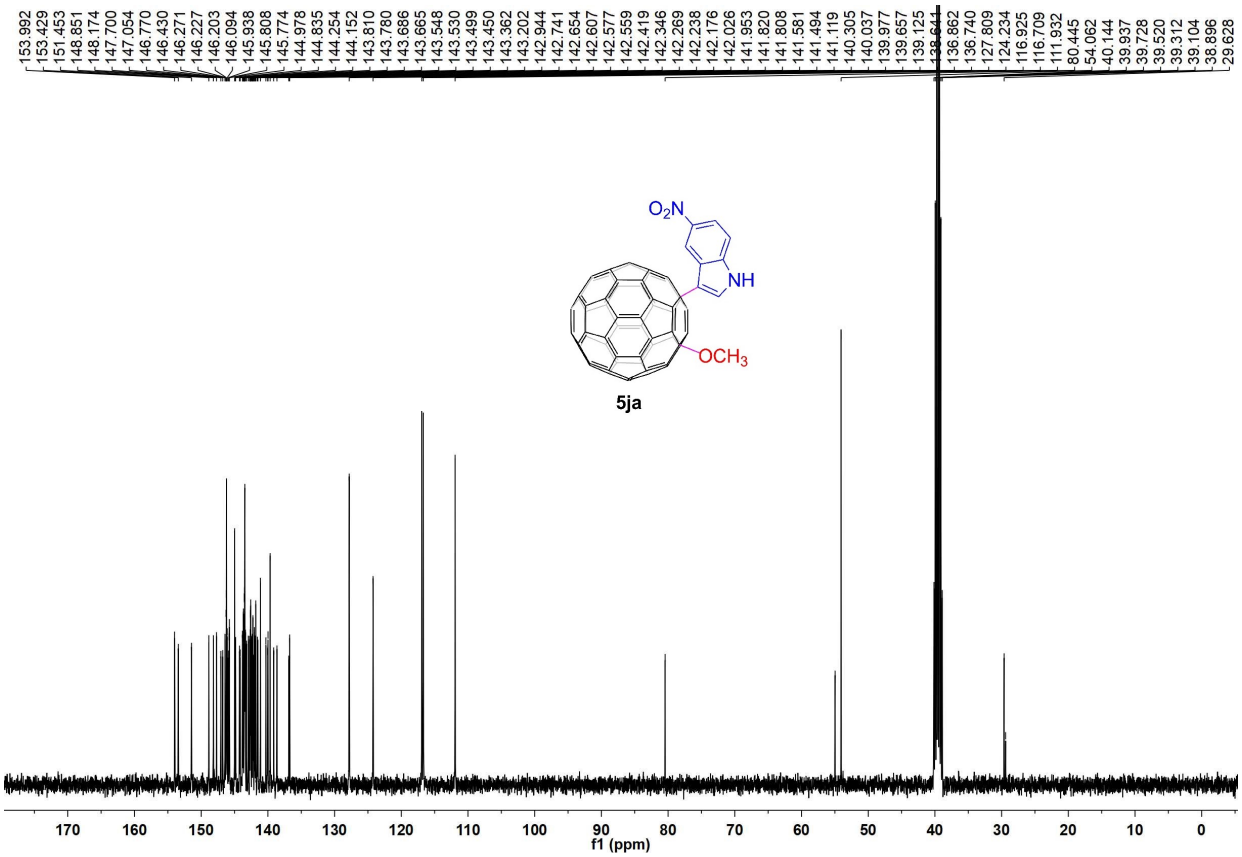
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ia



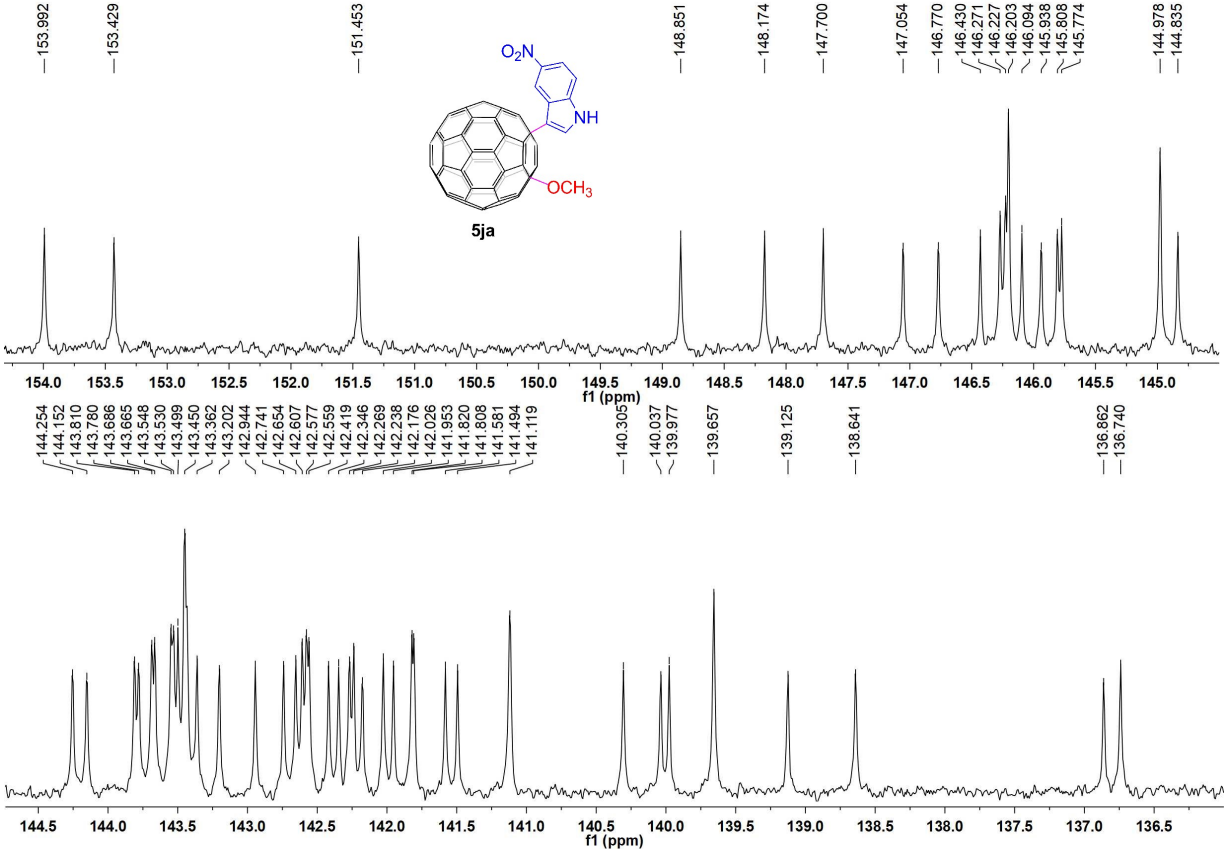
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ja



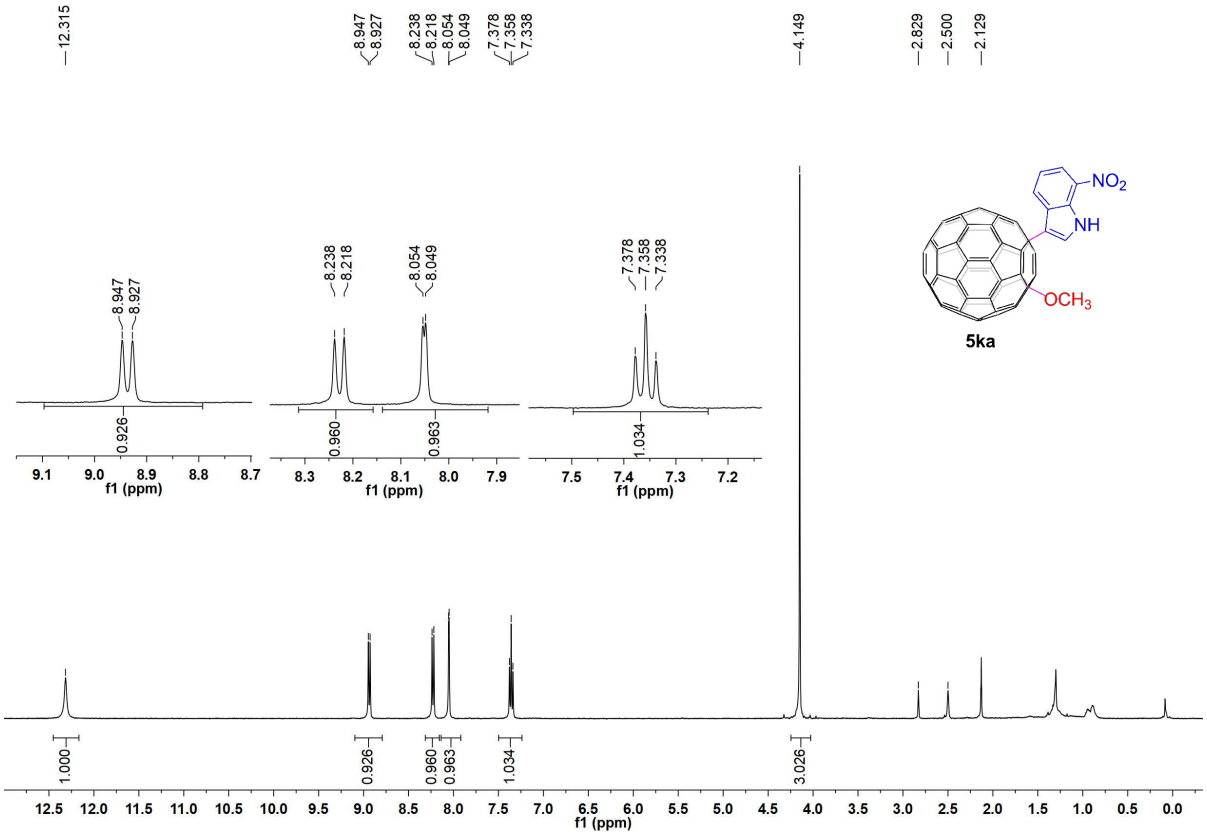
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ja



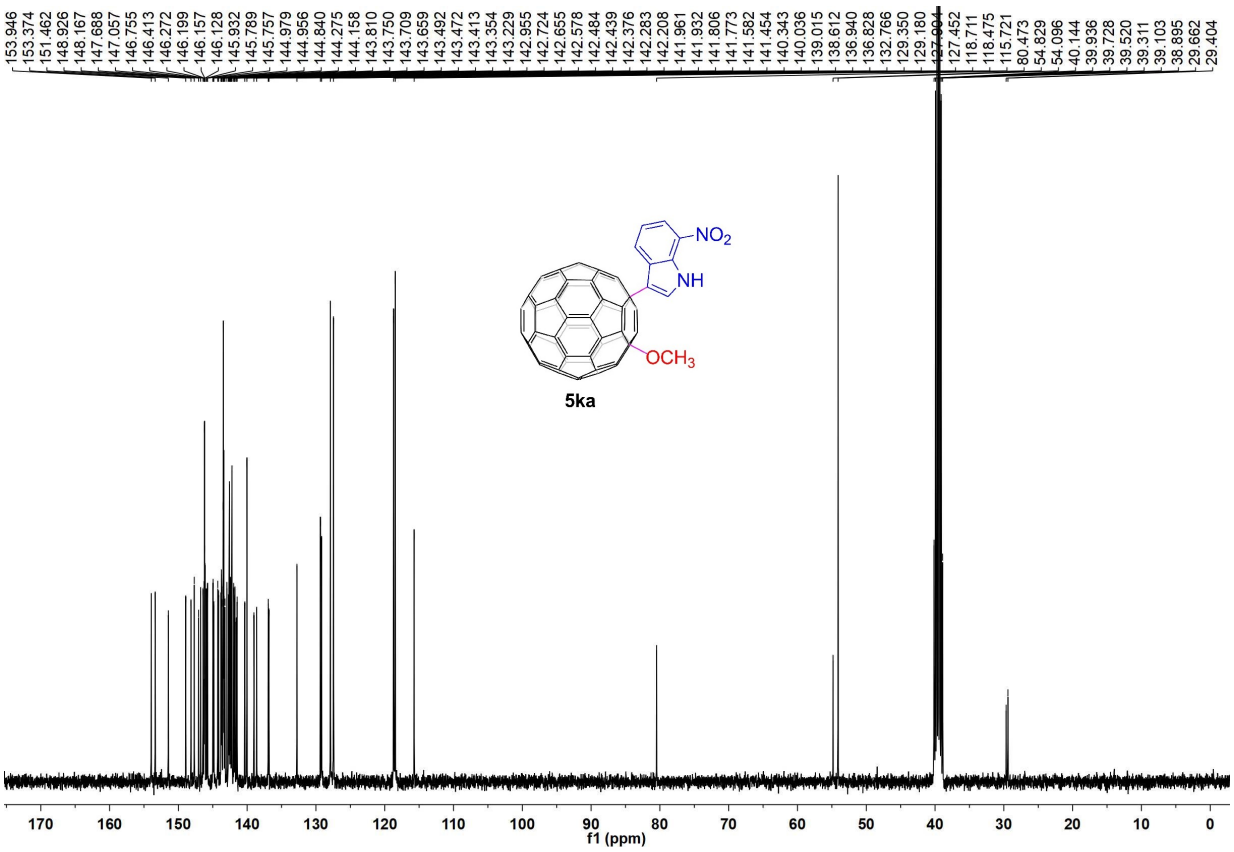
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ja



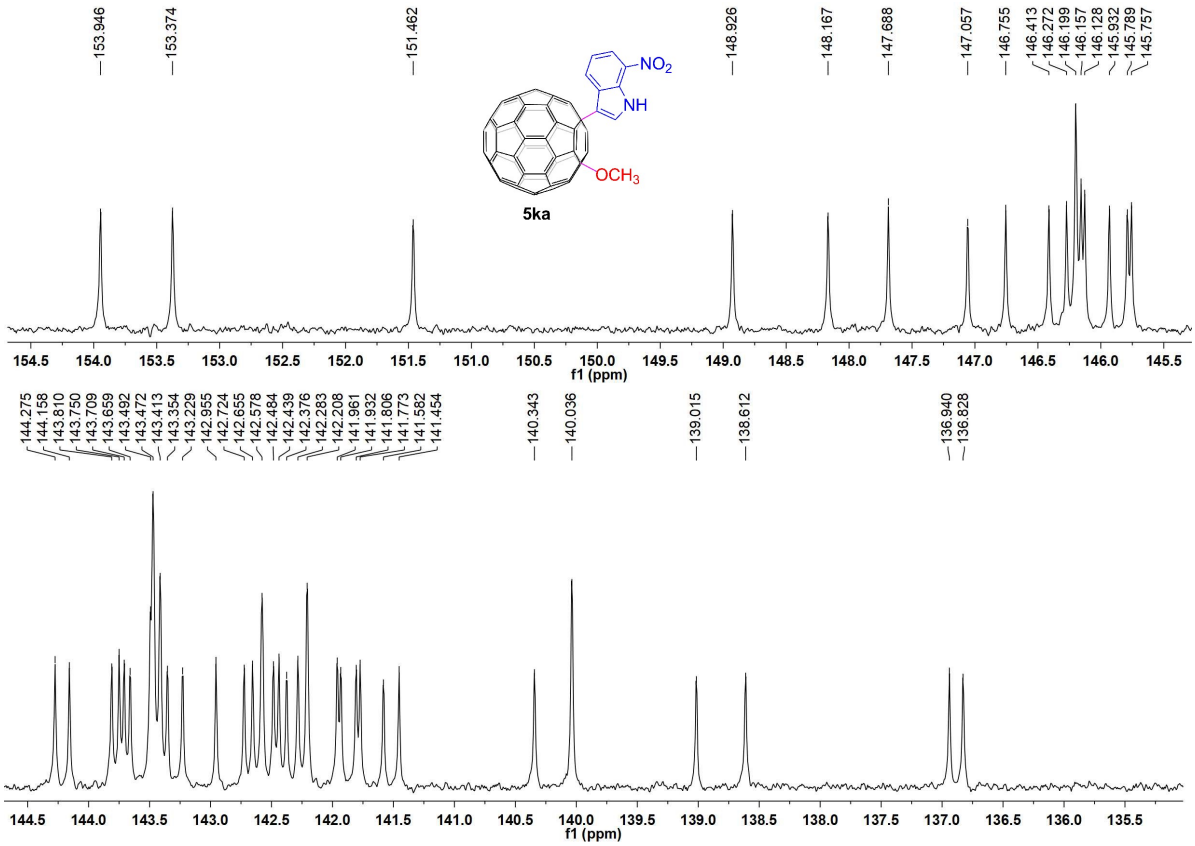
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ka



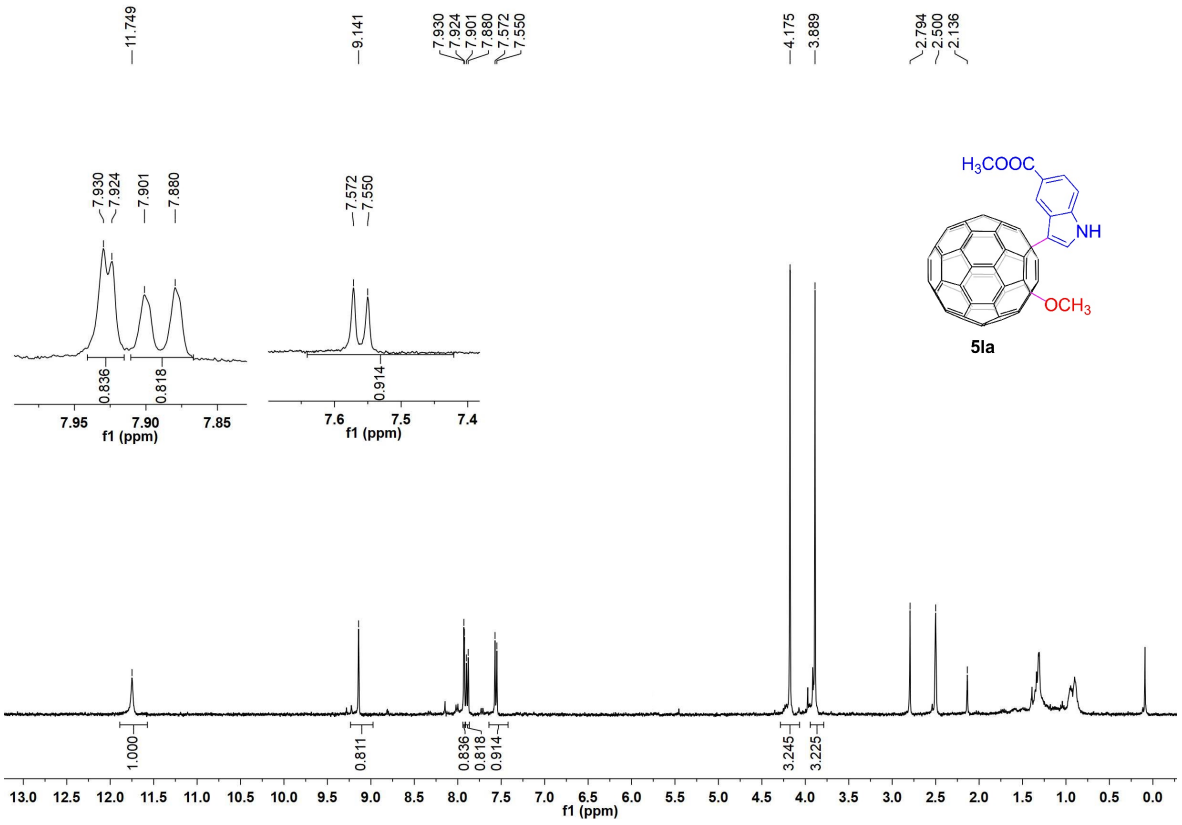
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ka



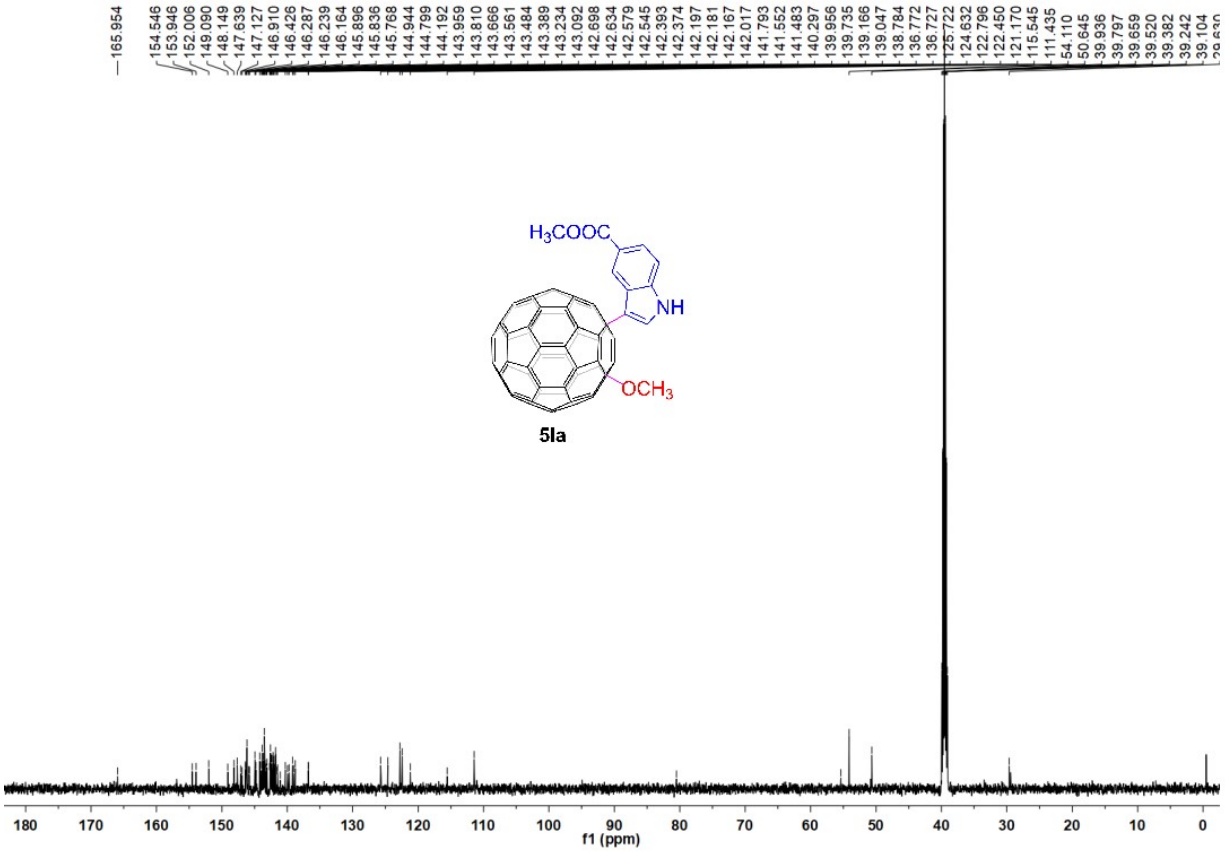
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ka



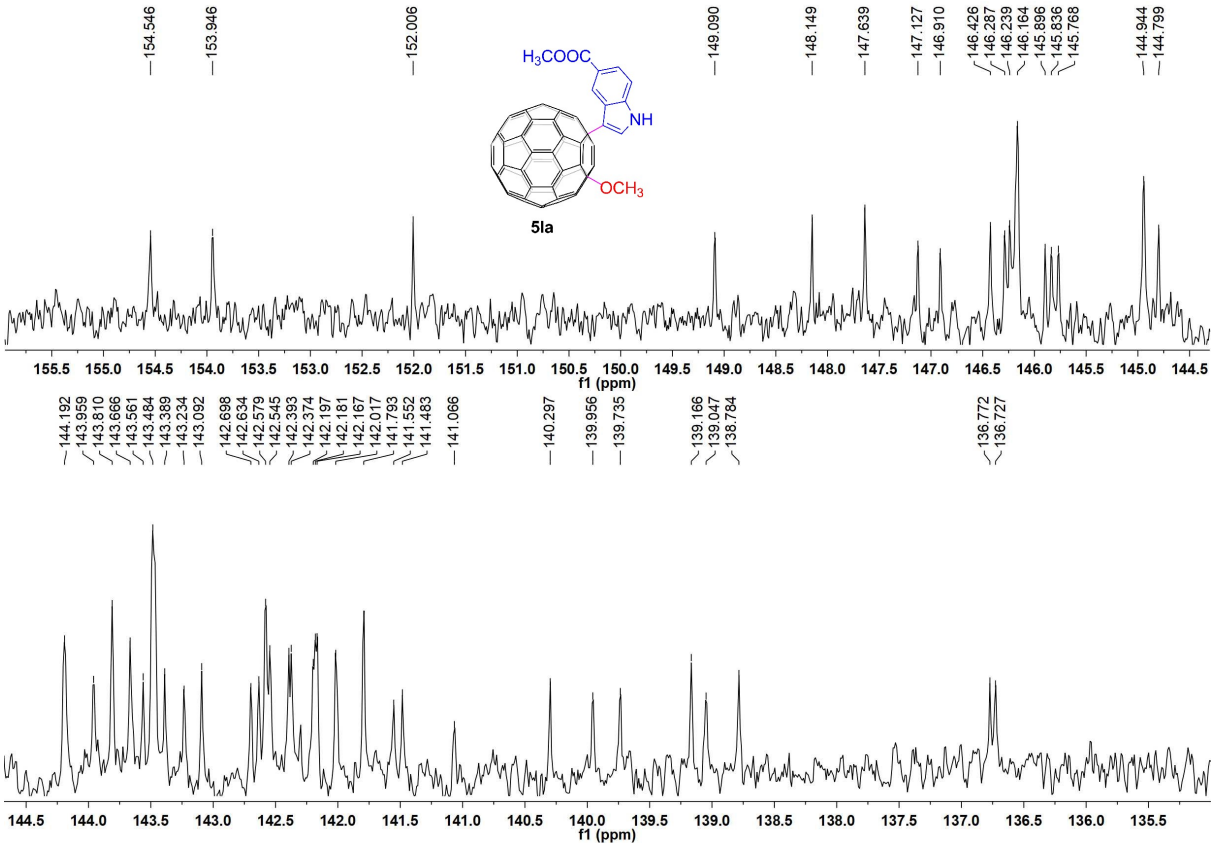
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5la



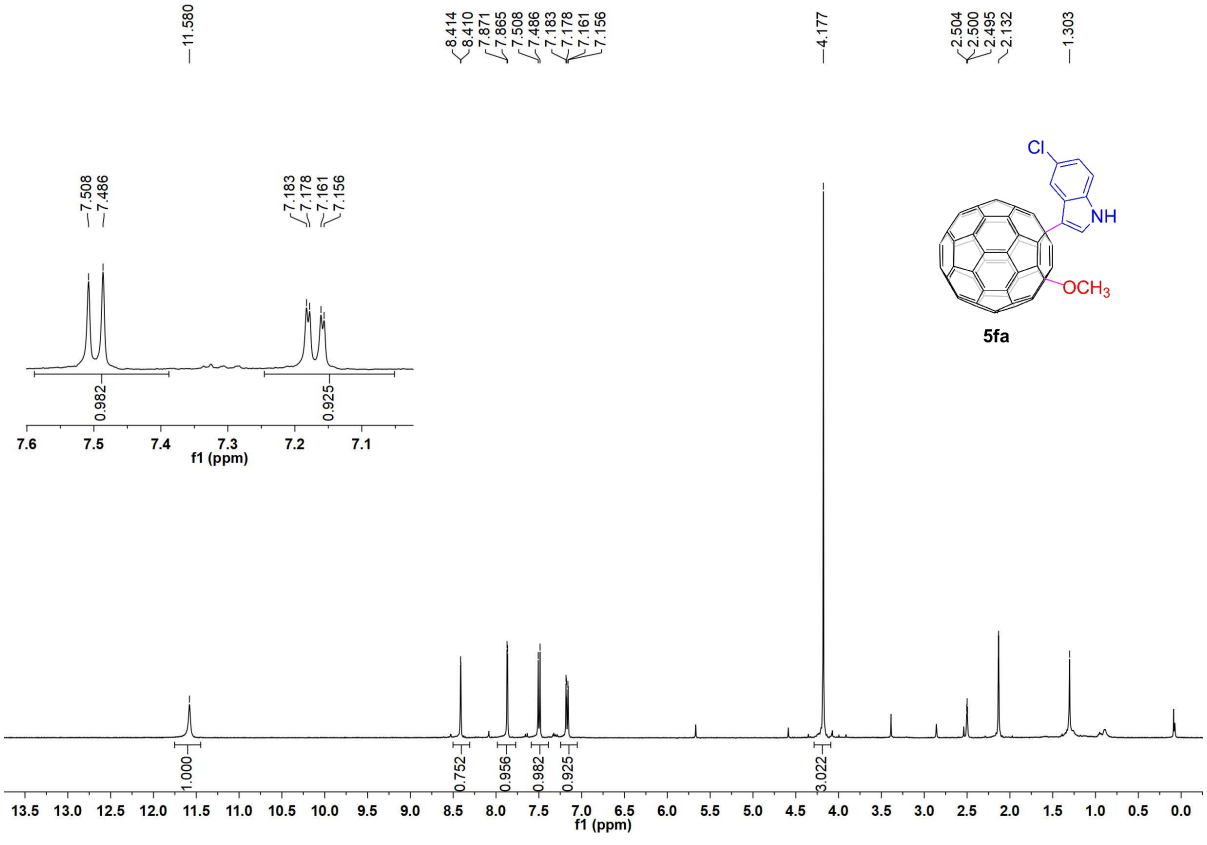
^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 5la



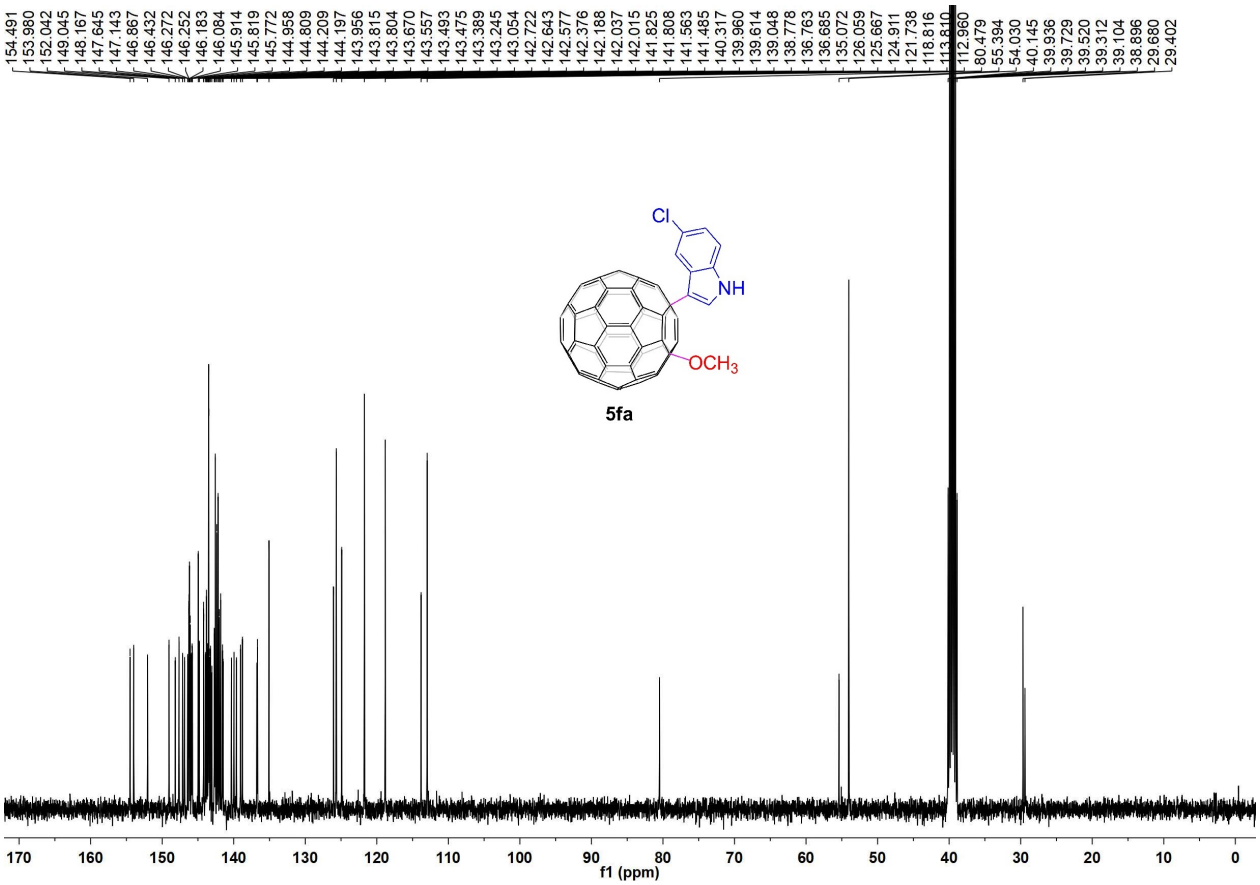
Expanded ^{13}C NMR (150 MHz , d_6-DMSO/CS_2) of compound 5la



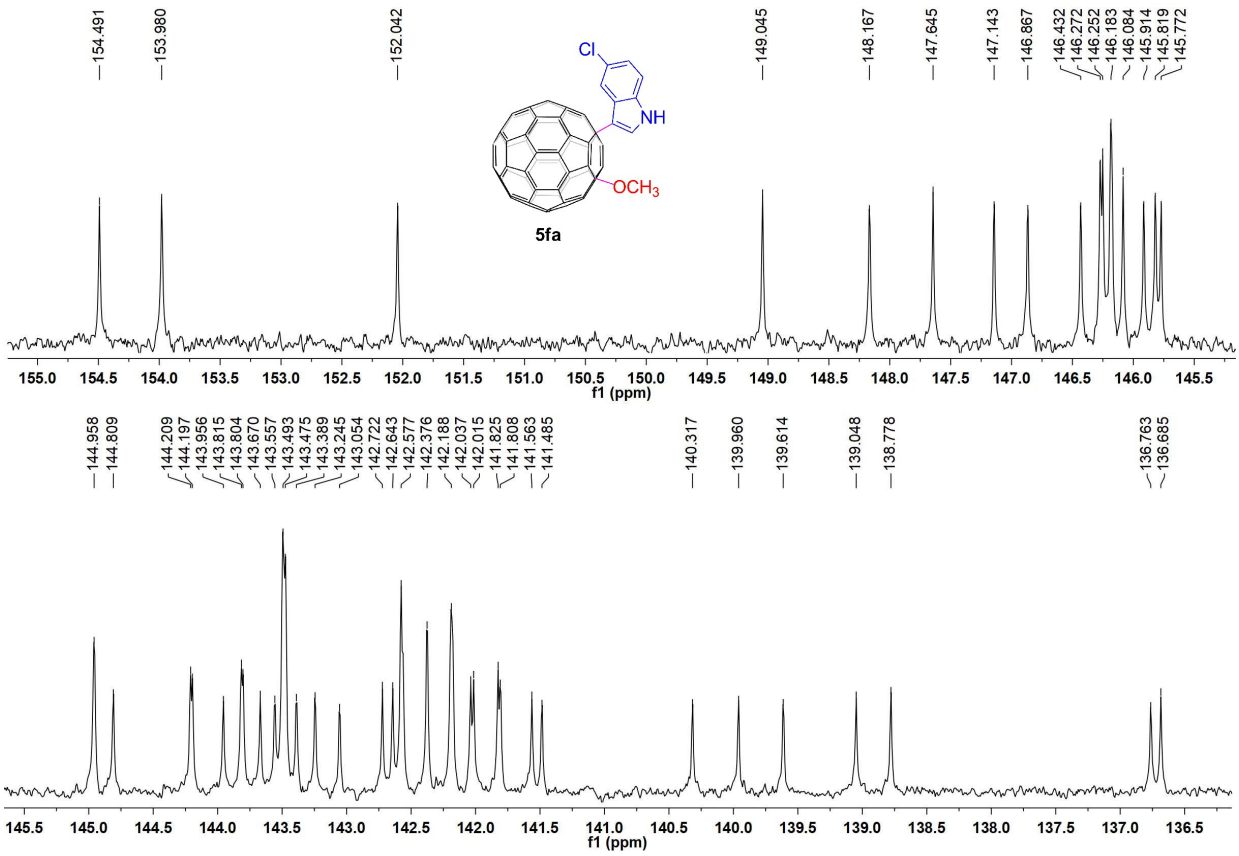
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5fa



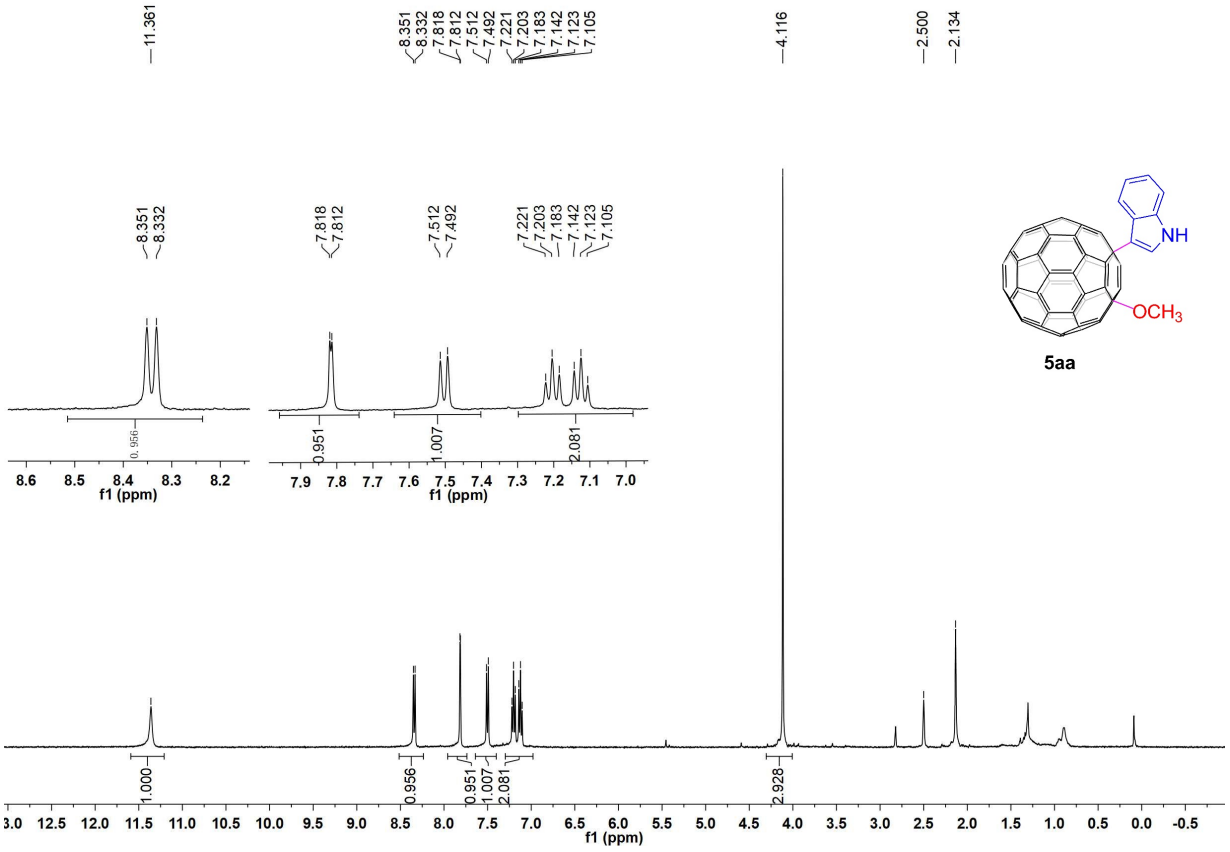
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5fa



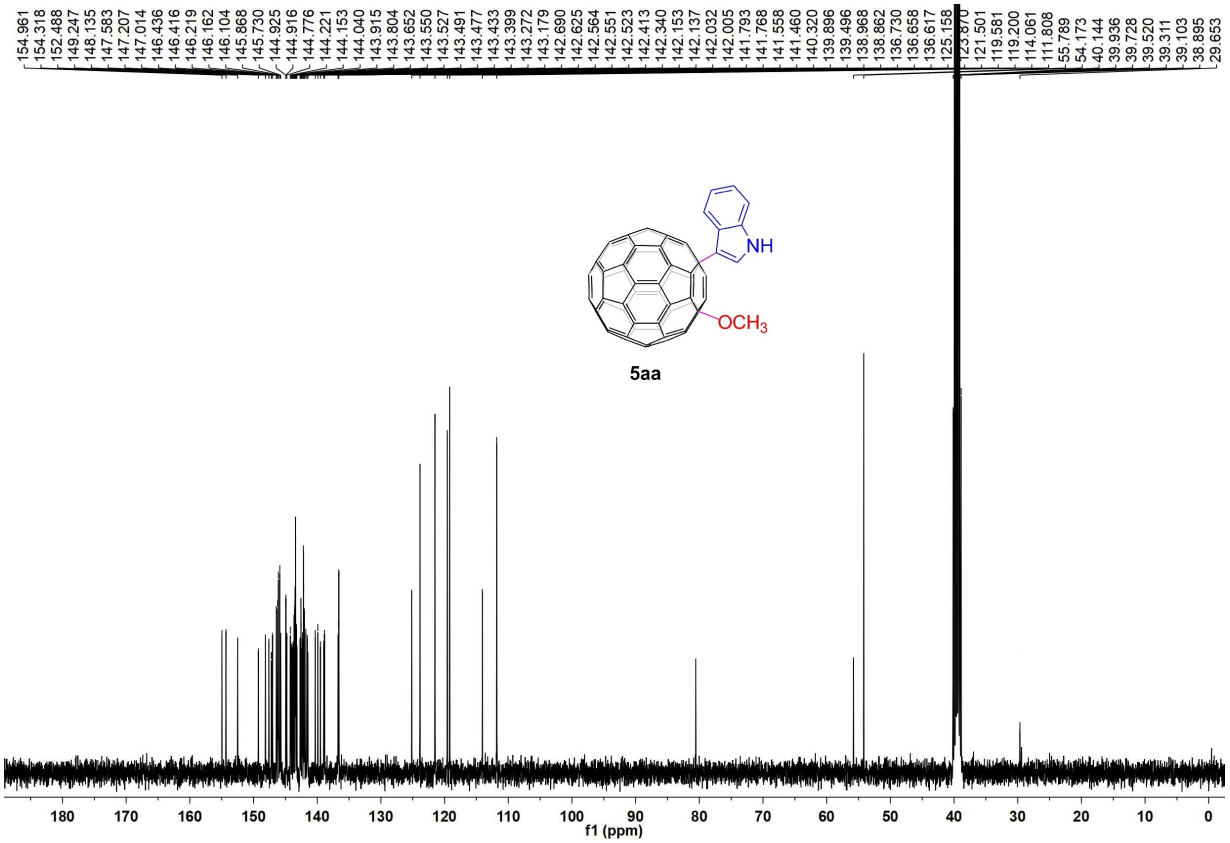
Expanded ^{13}C NMR (100 MHz, d_6-DMSO/CS_2) of compound 5fa



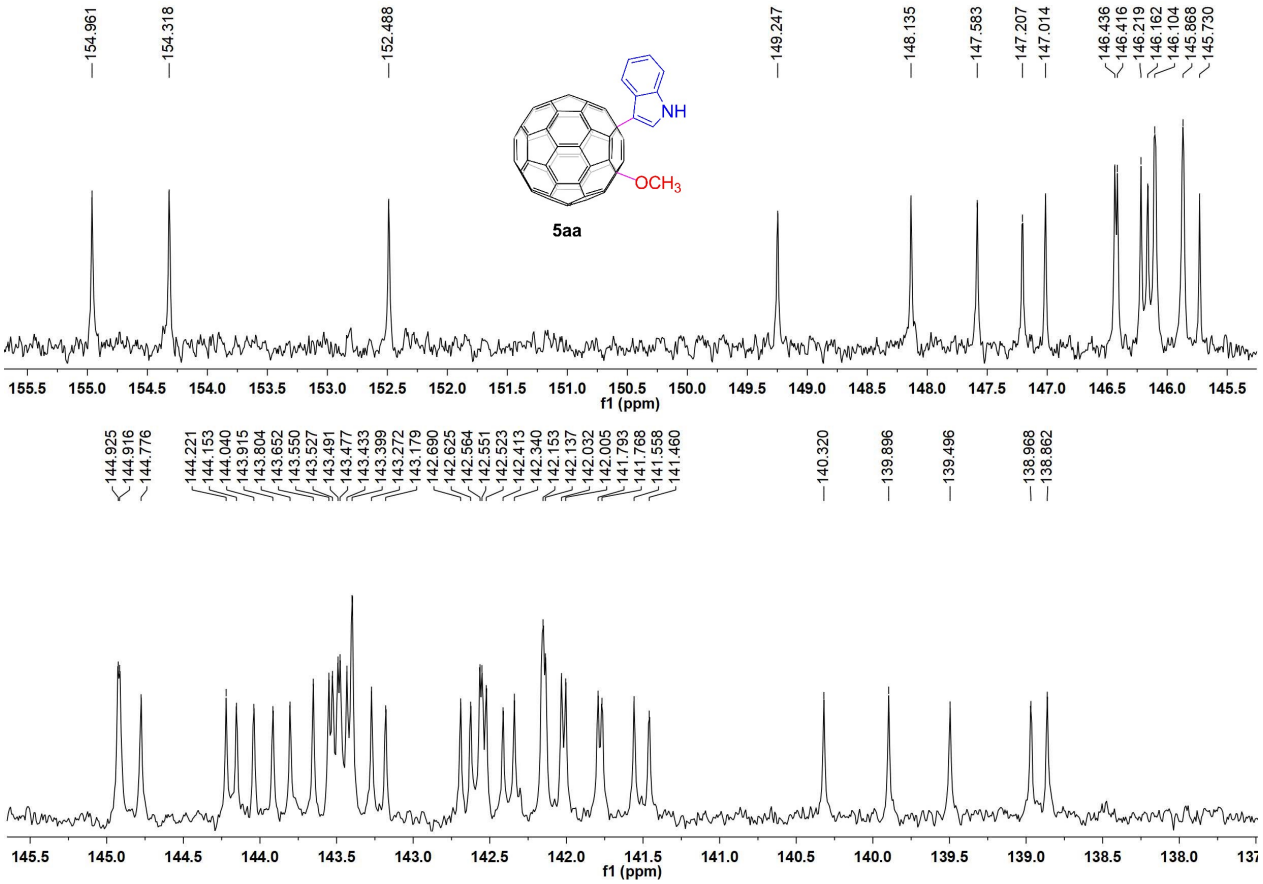
^{1}H NMR (400 MHz , d$_6$-DMSO/CS$_2$) of compound 5aa



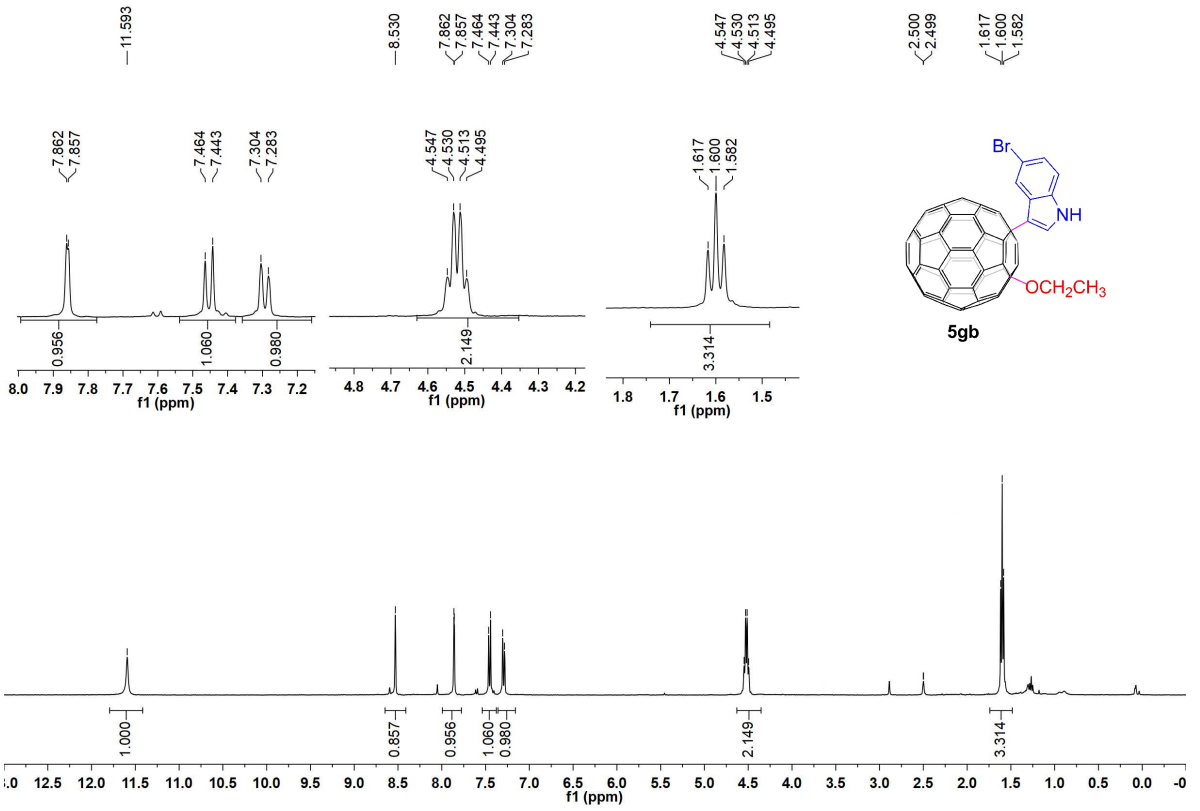
^{13}C NMR (100 MHz , d$_6$-DMSO/CS$_2$) of compound 5aa



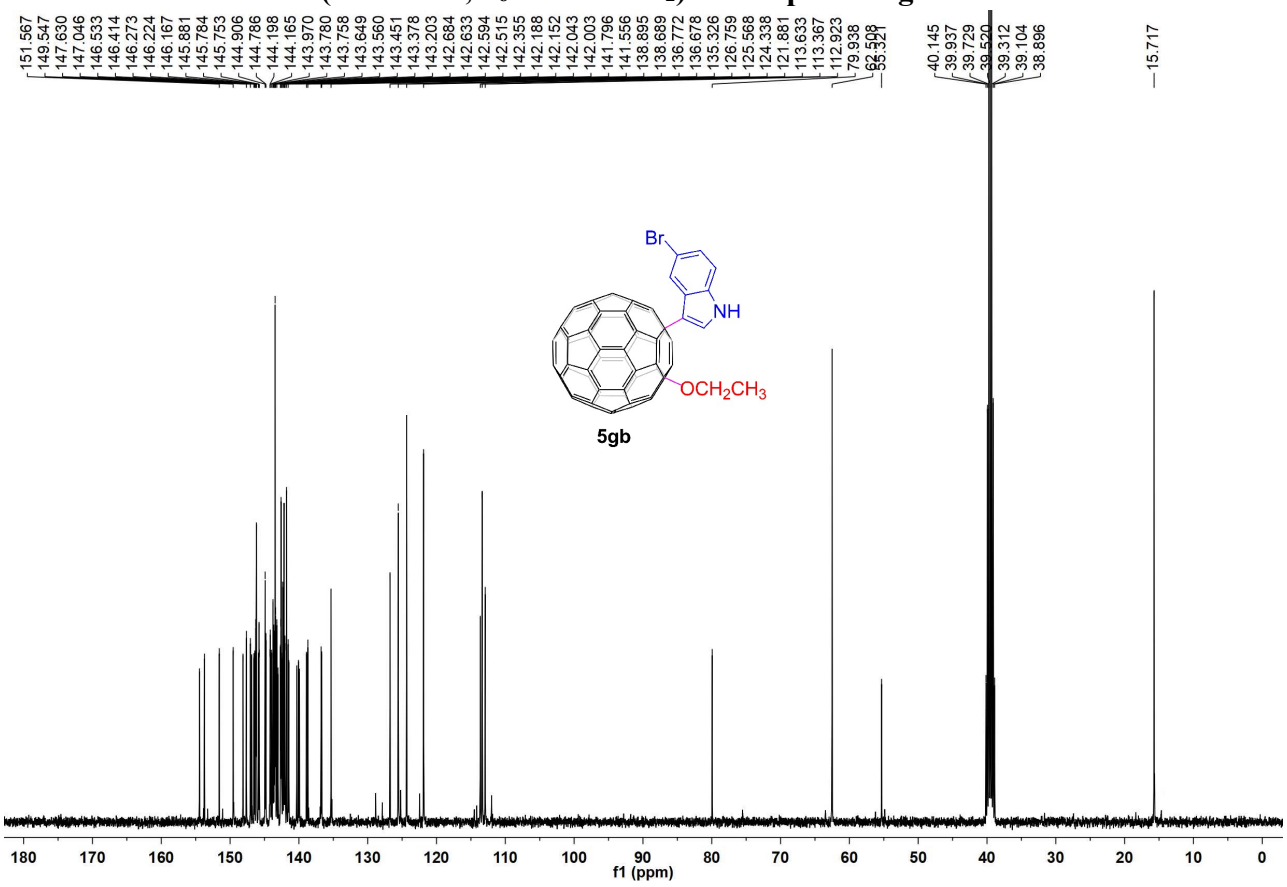
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5aa



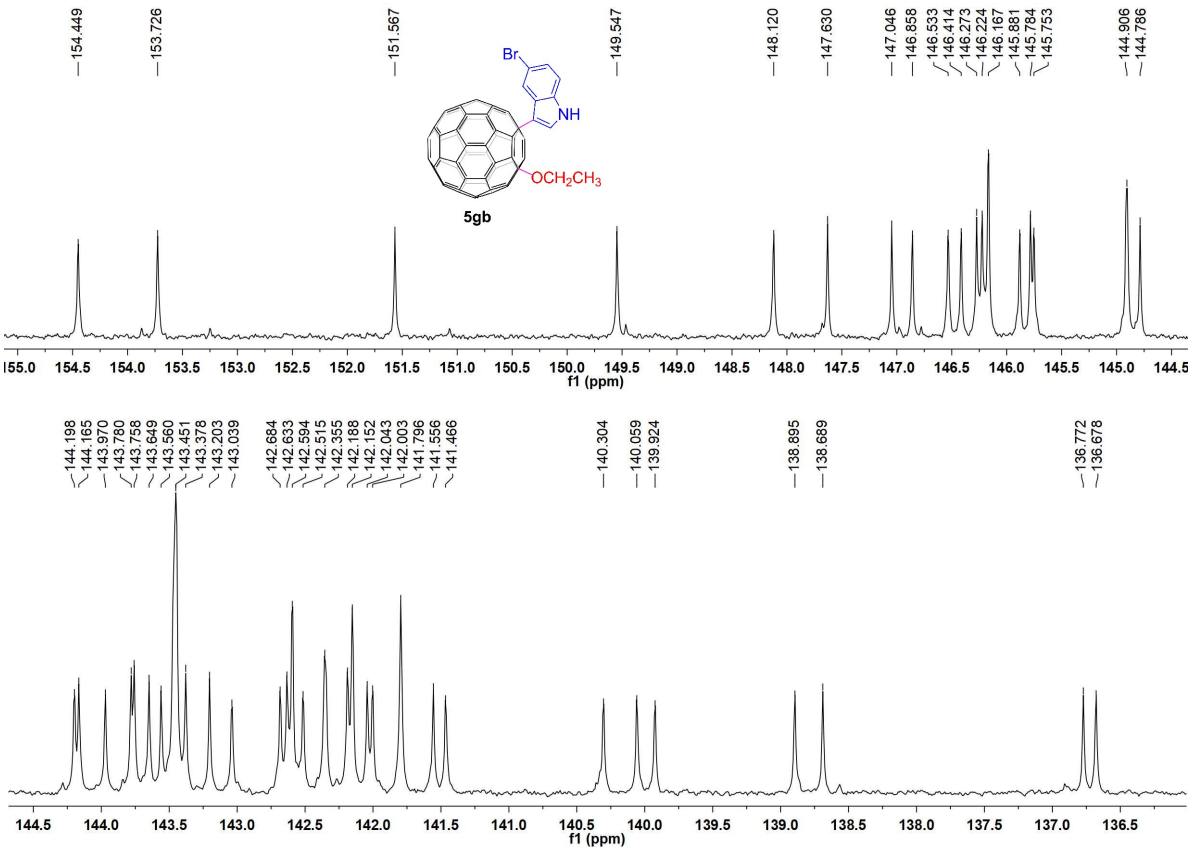
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5gb



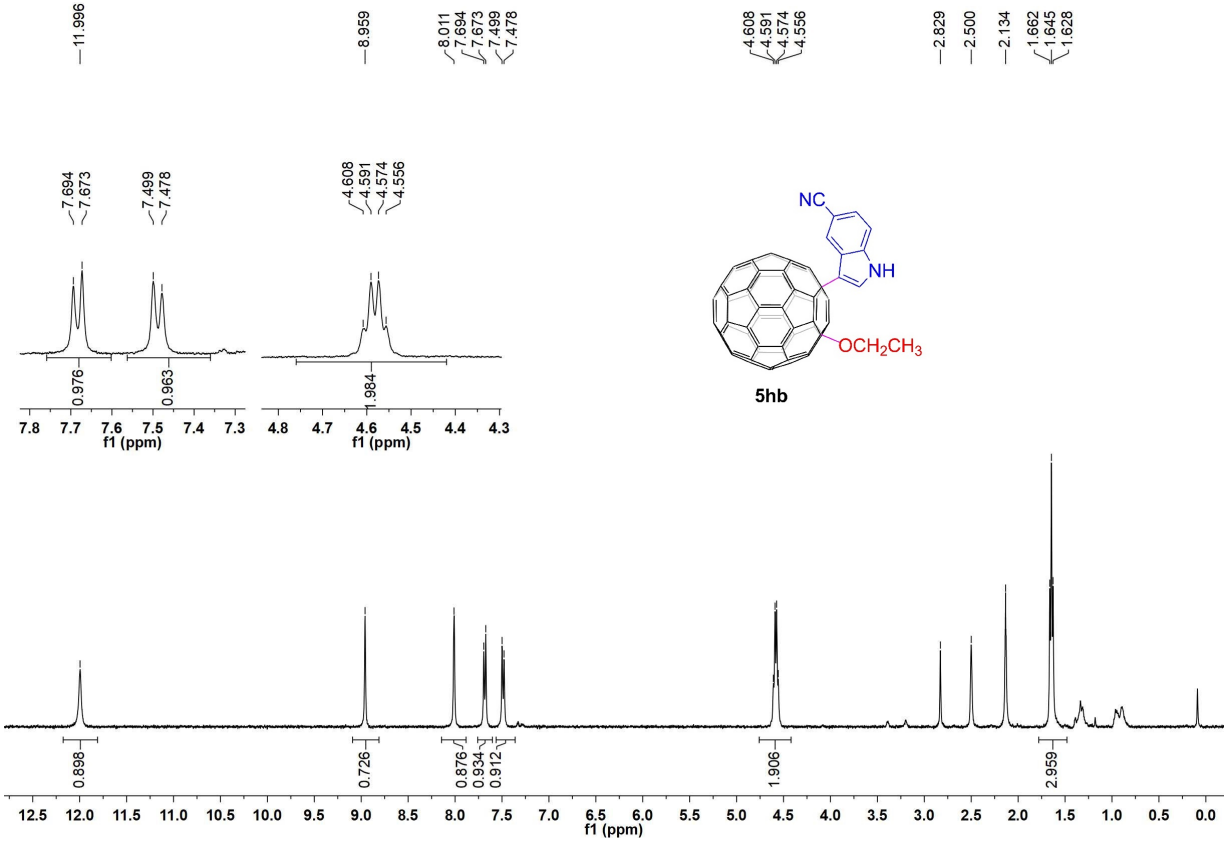
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gb



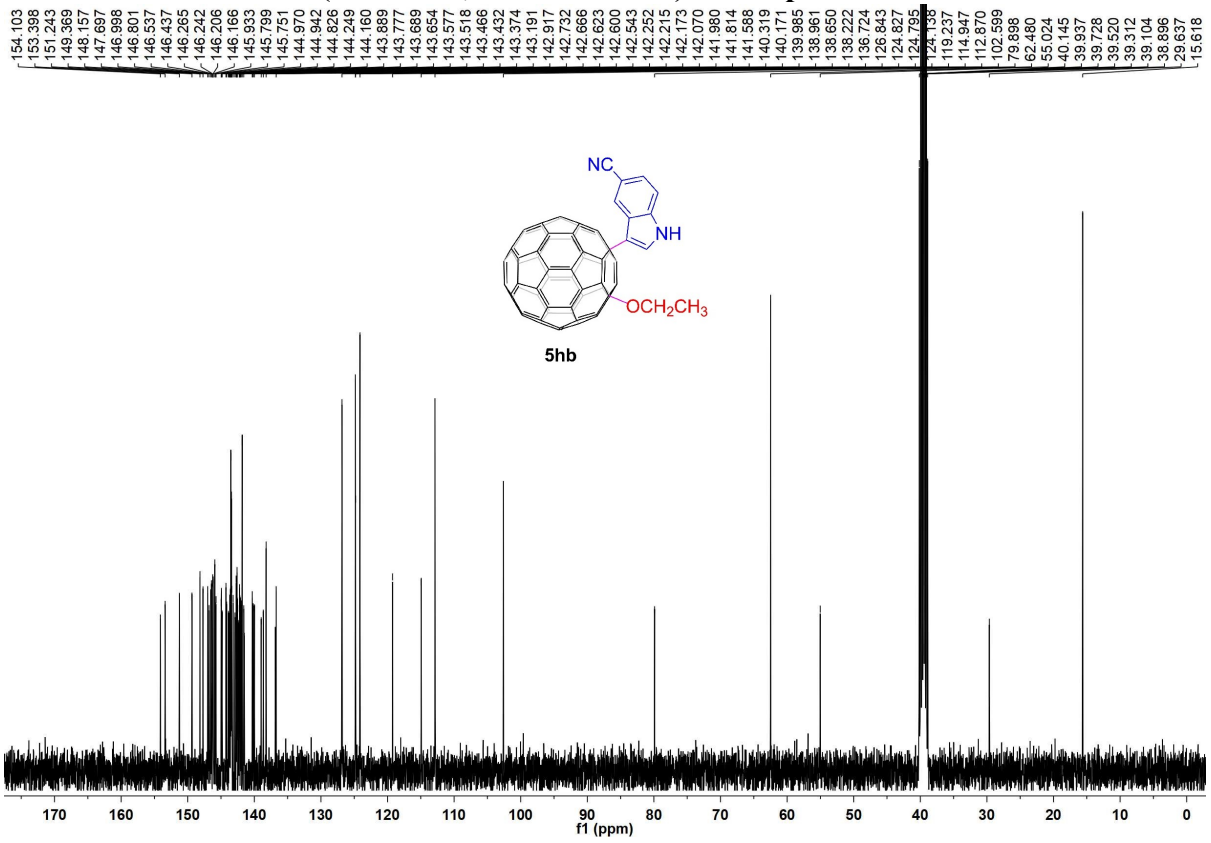
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gb



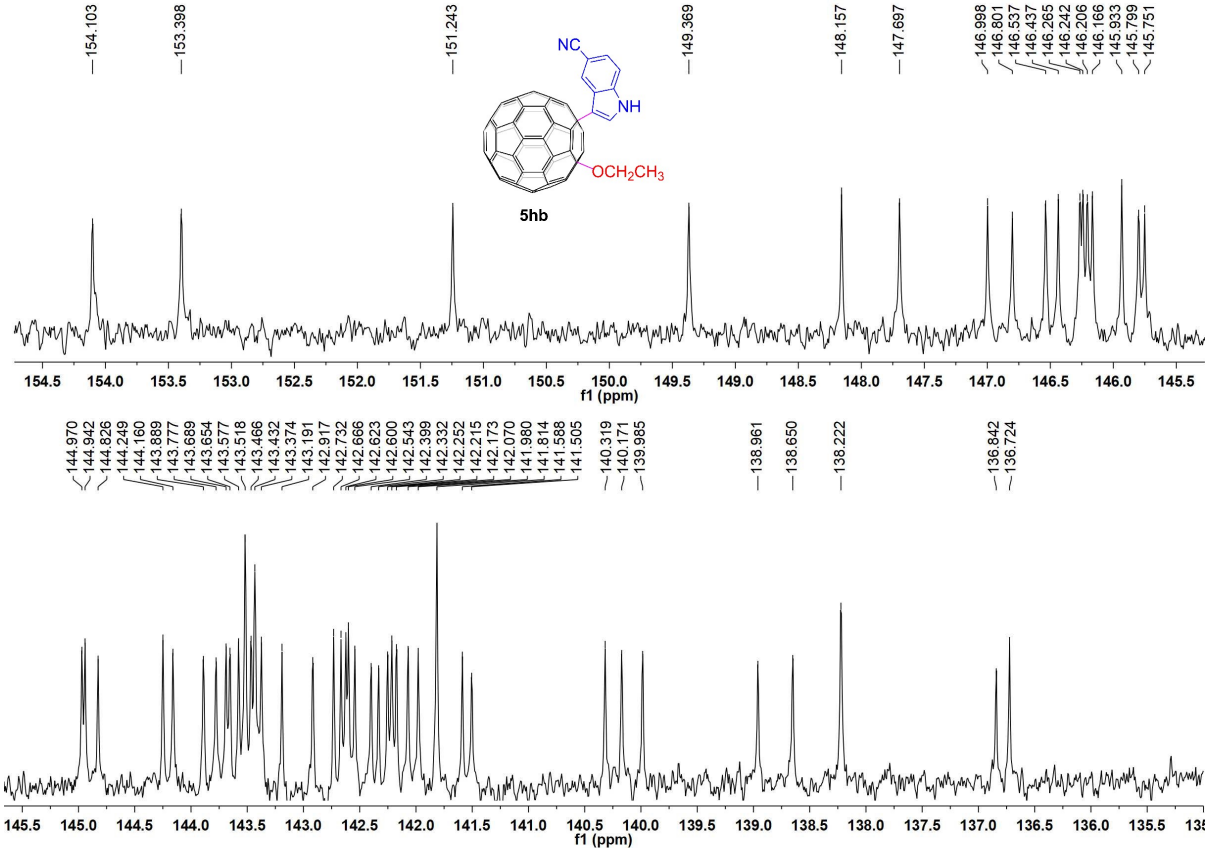
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5hb



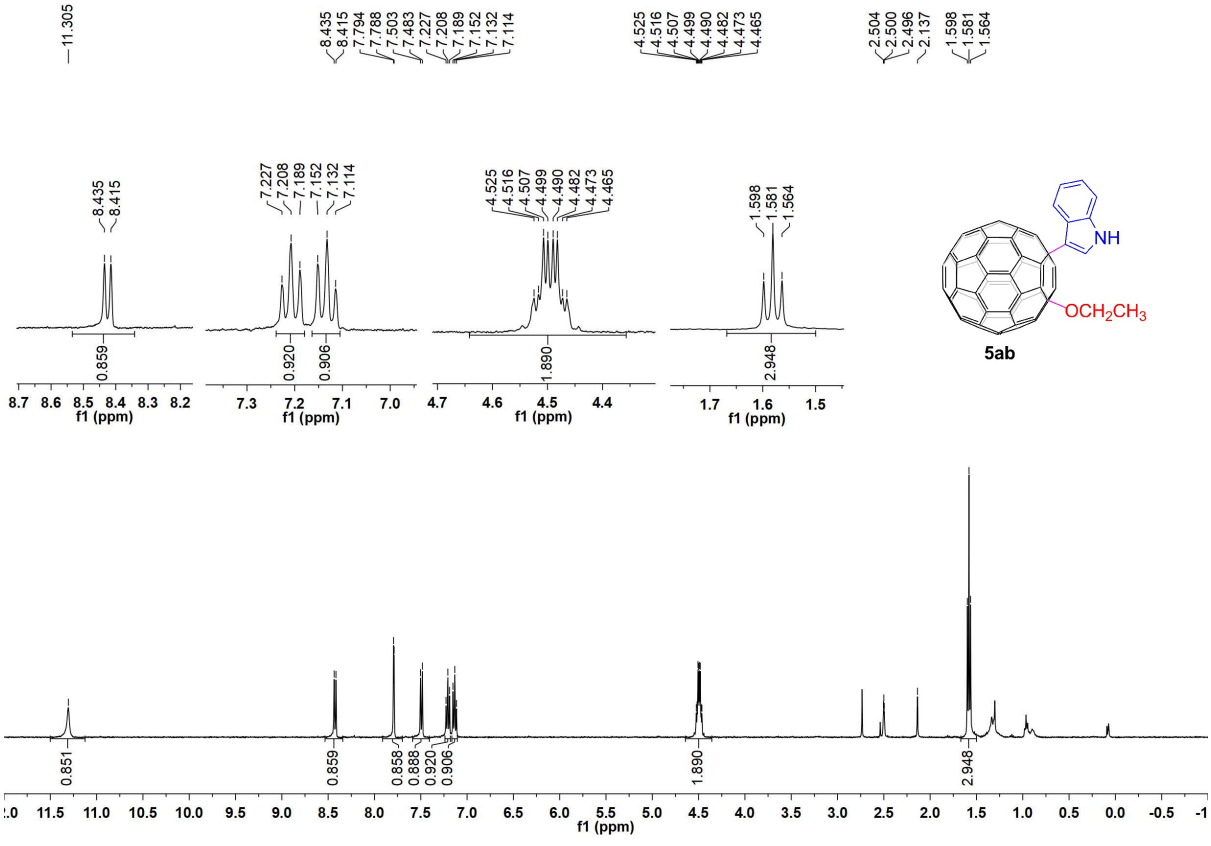
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hb



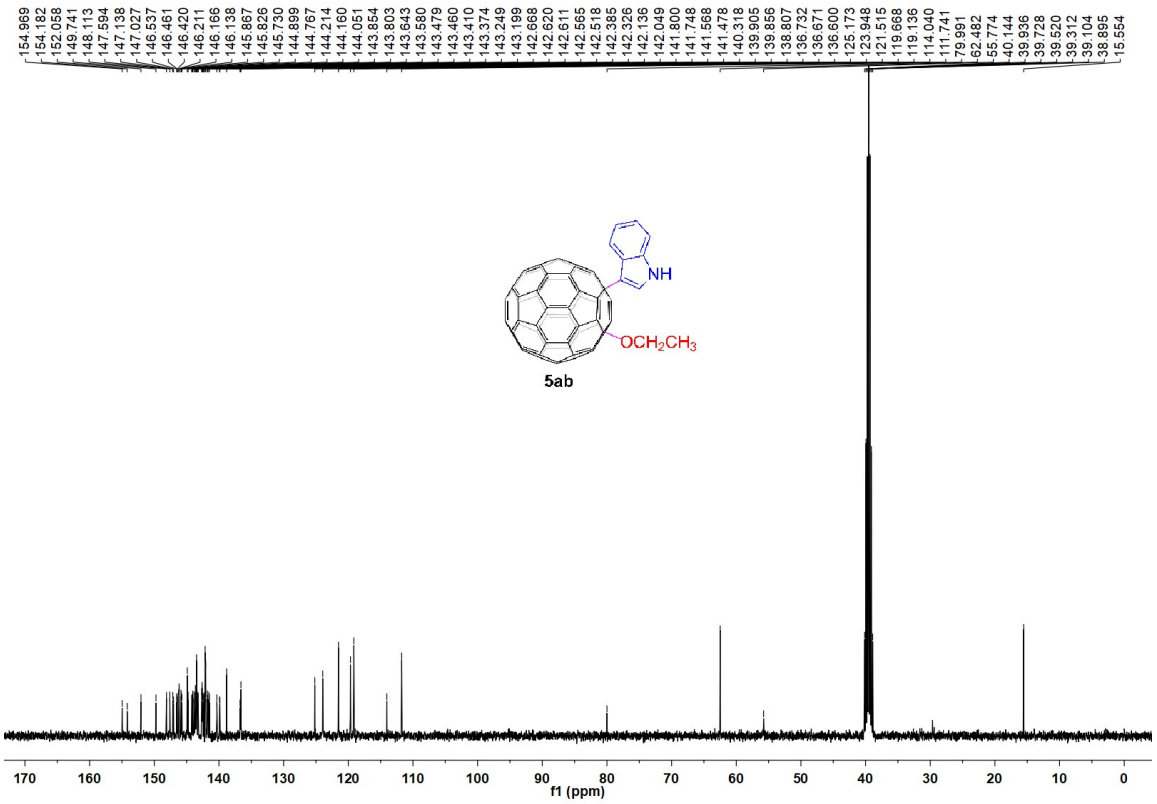
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hb



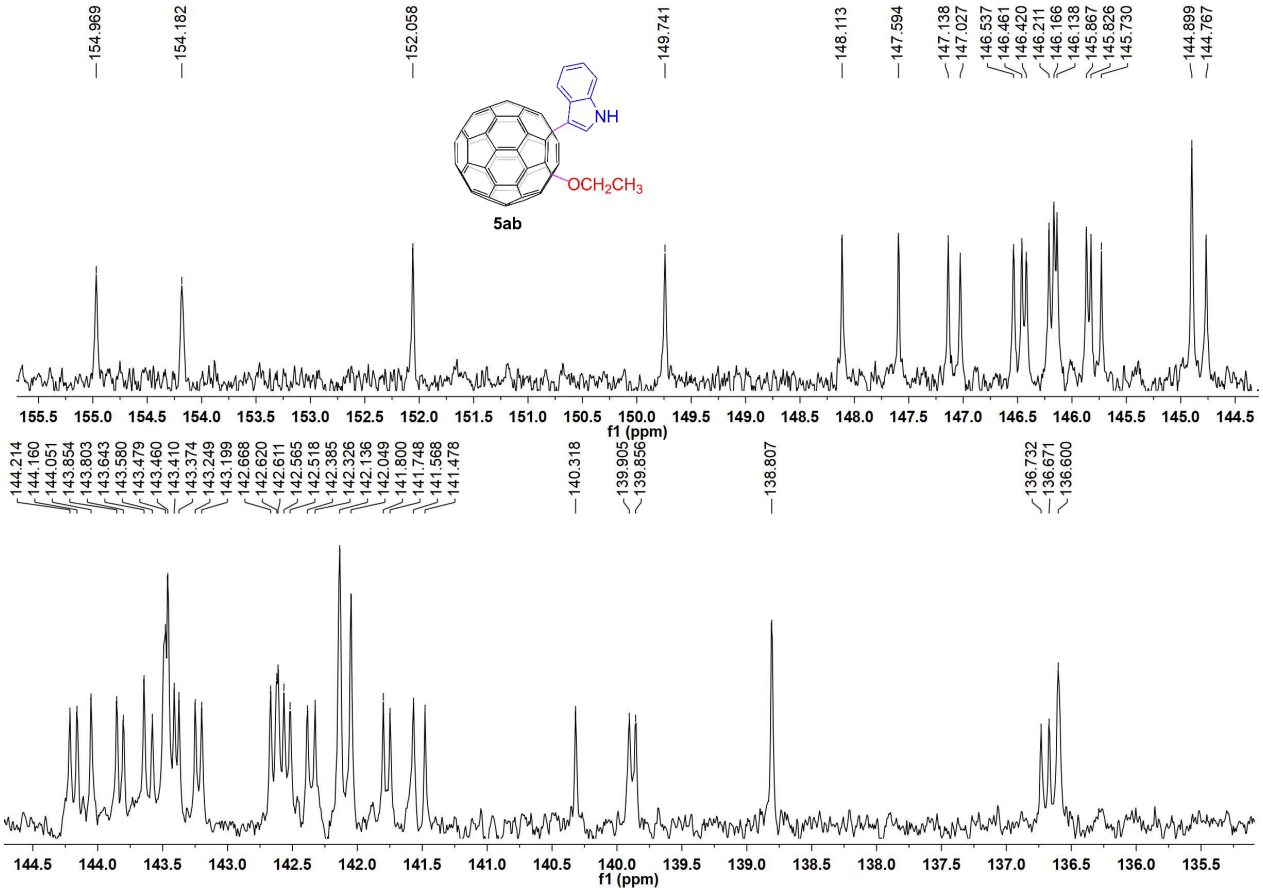
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ab



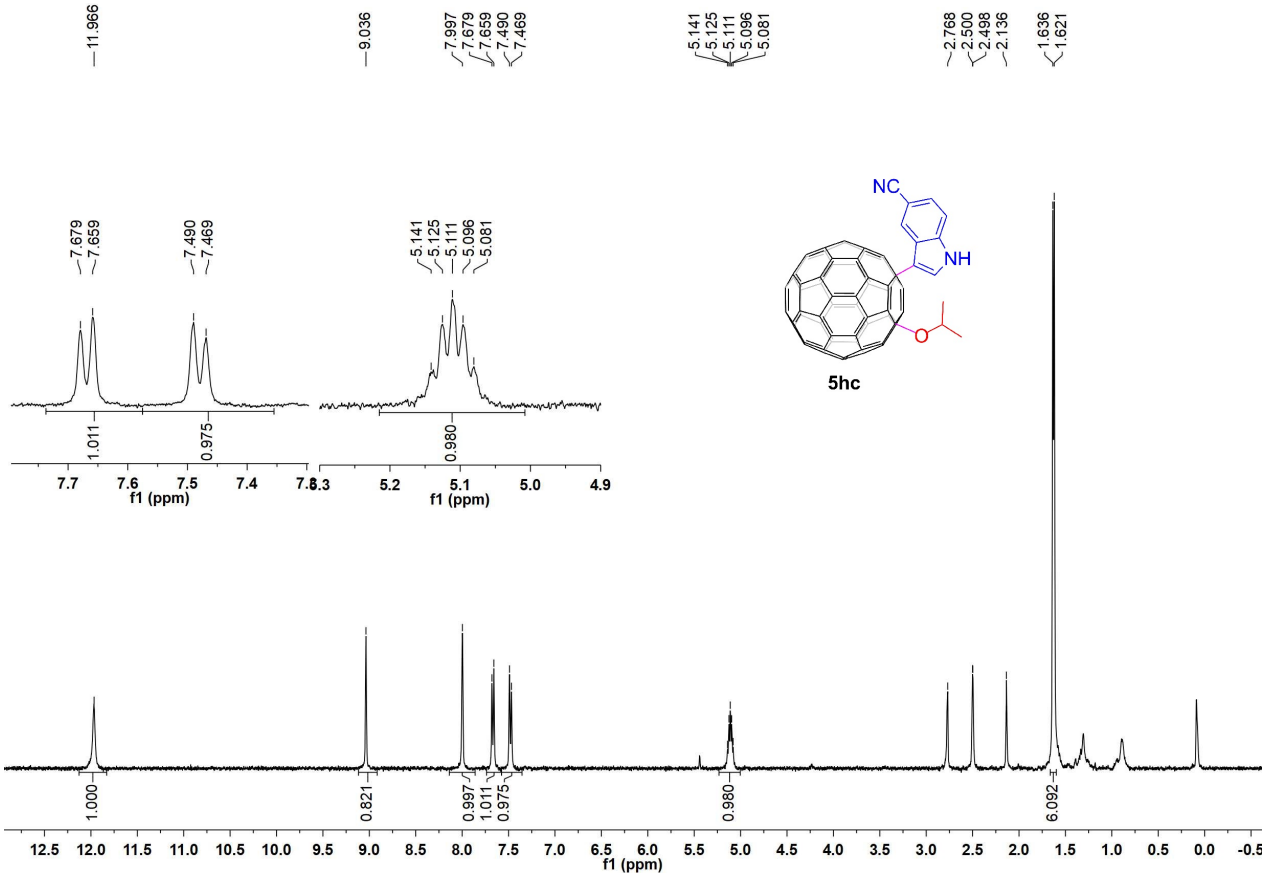
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ab



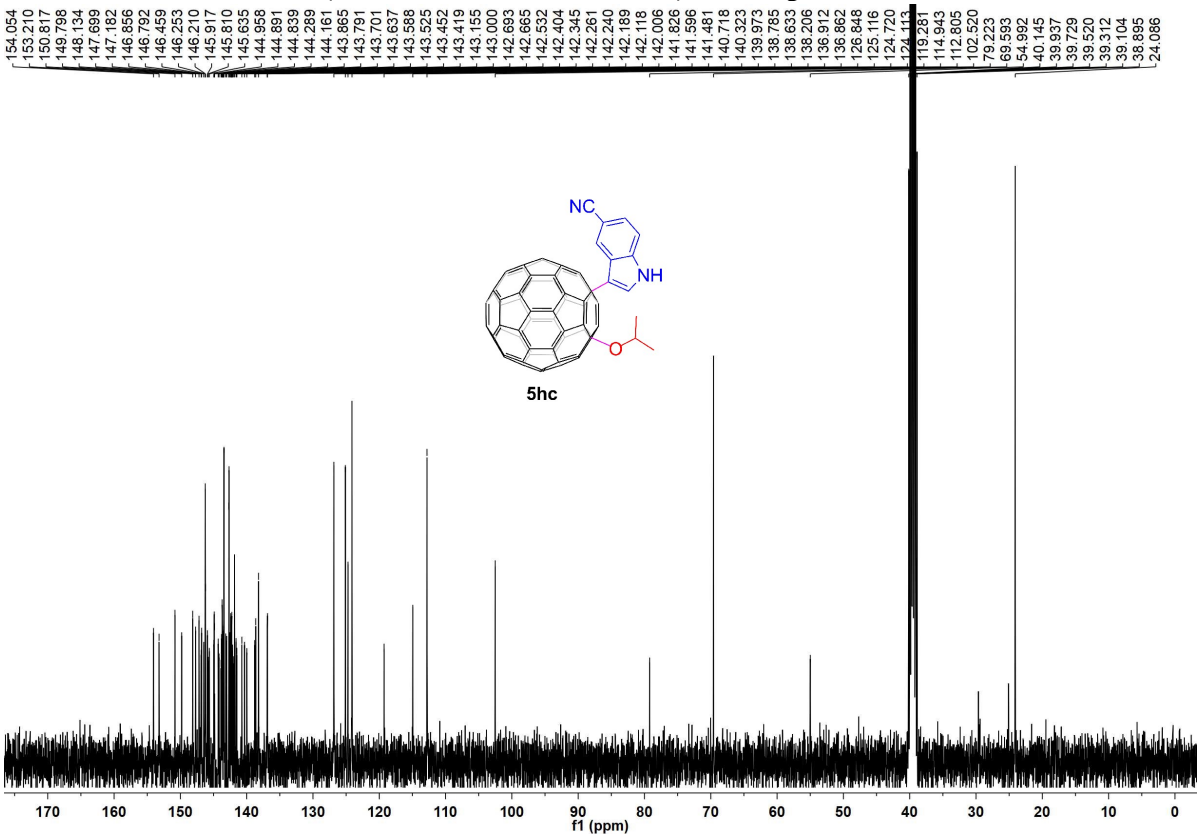
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ab



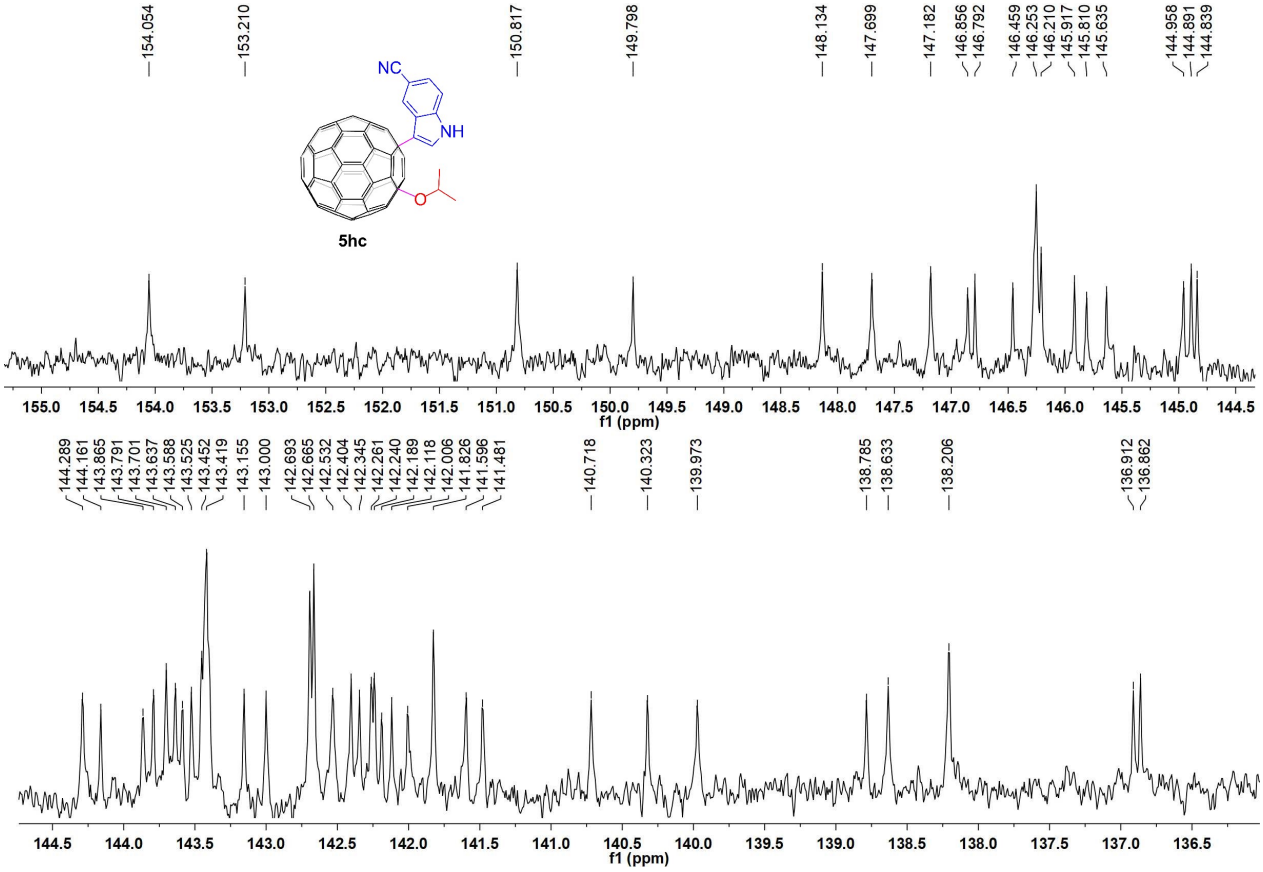
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5hc



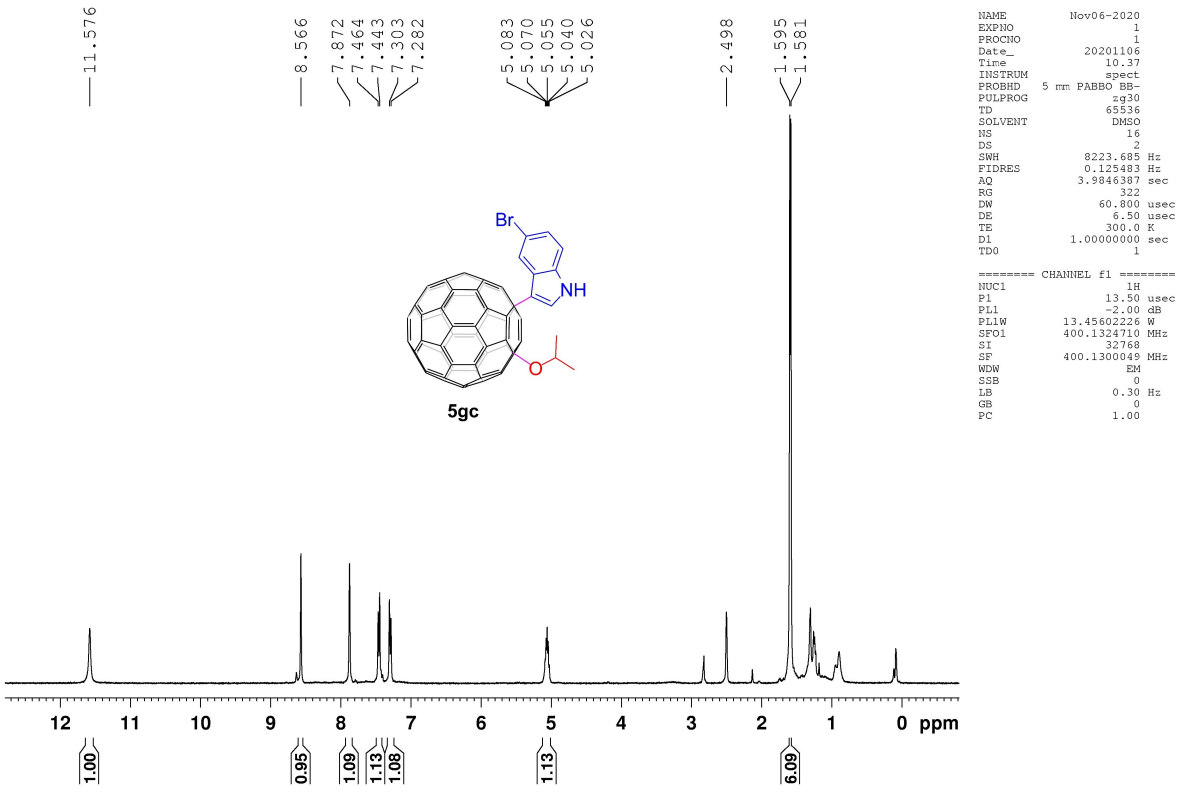
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hc



Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hc



^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5gc

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DS                       2
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FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     322
DW                60.800 usec
DE                 6.50 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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P1                 13.50 usec
PL1                -2.00 dB
PL1W         13.45602226 W
SFO1         400.1324710 MHz
SI                   32768
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PC                   1.00
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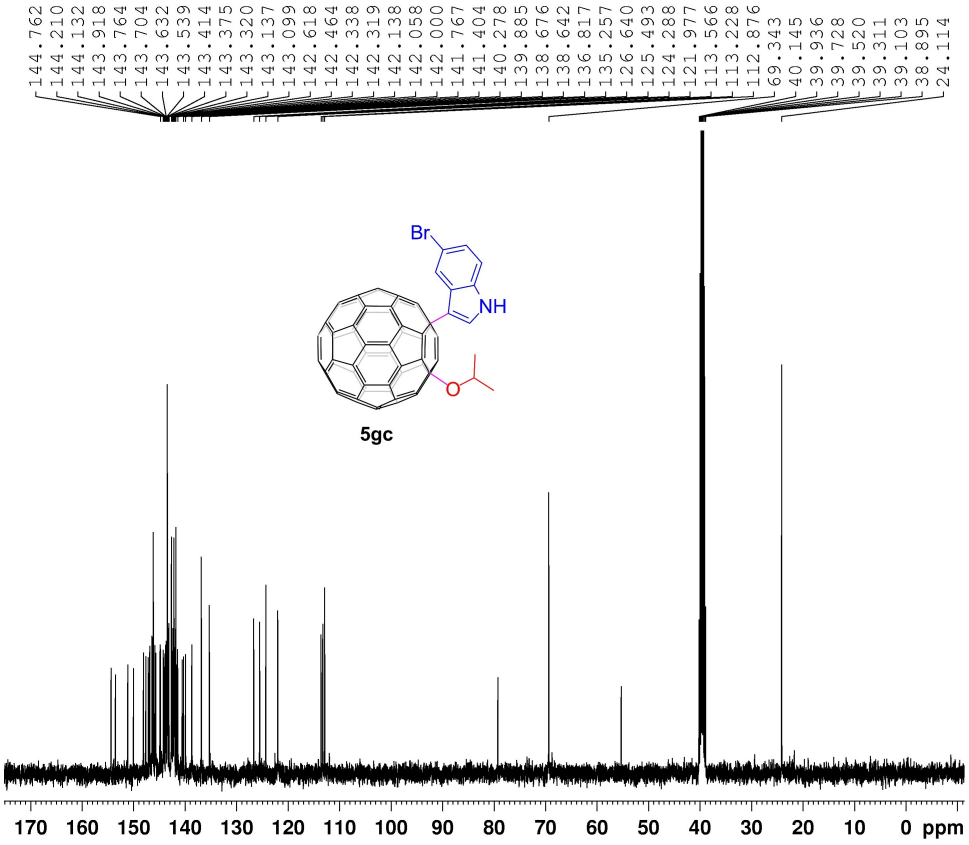
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gc

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TD                 65536
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NS                   20480
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     101
DW                  20.800 usec
DE                   6.50 usec
TE                  300.0 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.30 usec
PL1                  -2.00 dB
PL1W          54.14257431 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 13.46 dB
PL13                120.00 dB
PL2W          13.45602226 W
PL12W          0.38275132 W
PL13W          0.00000000 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6128640 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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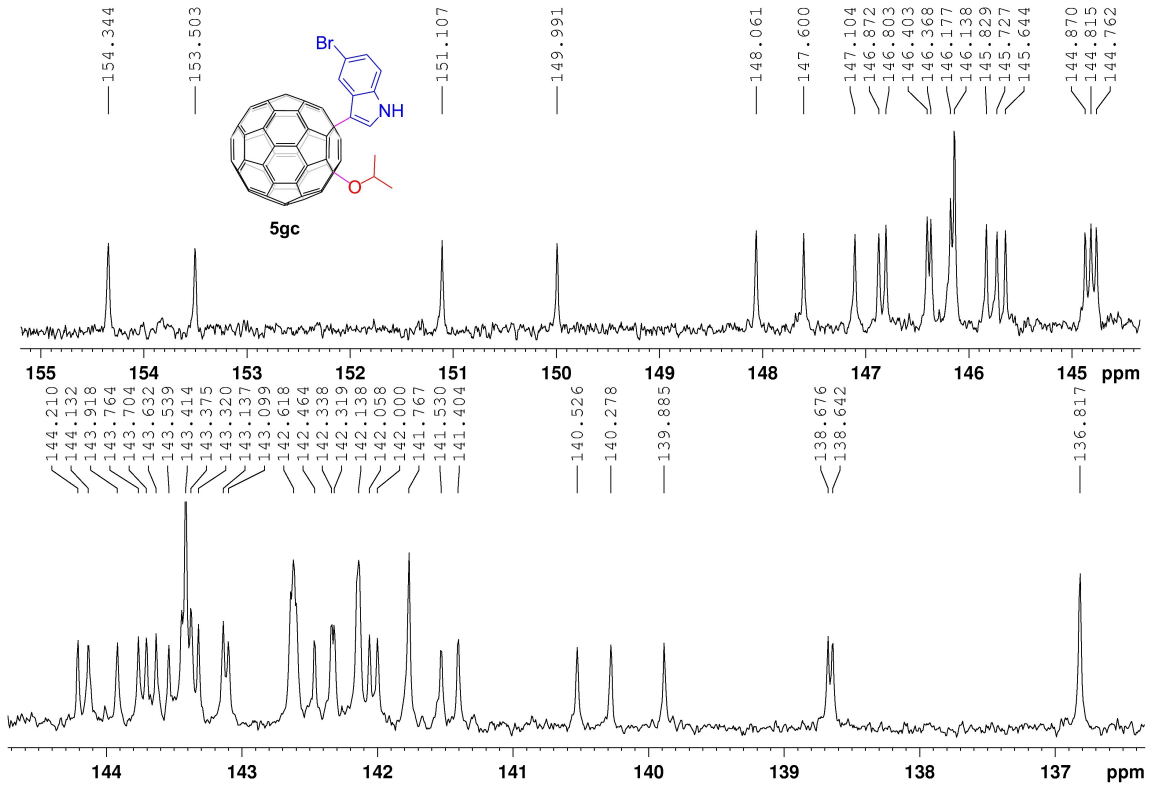
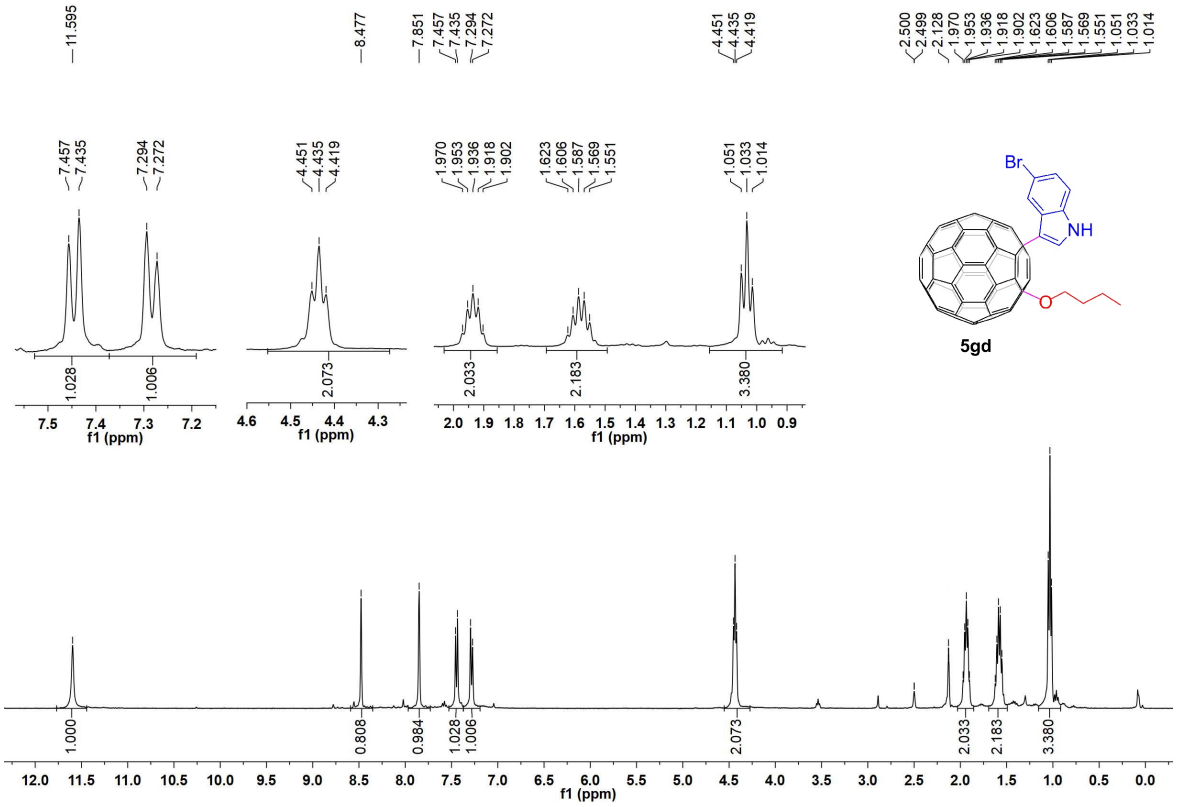
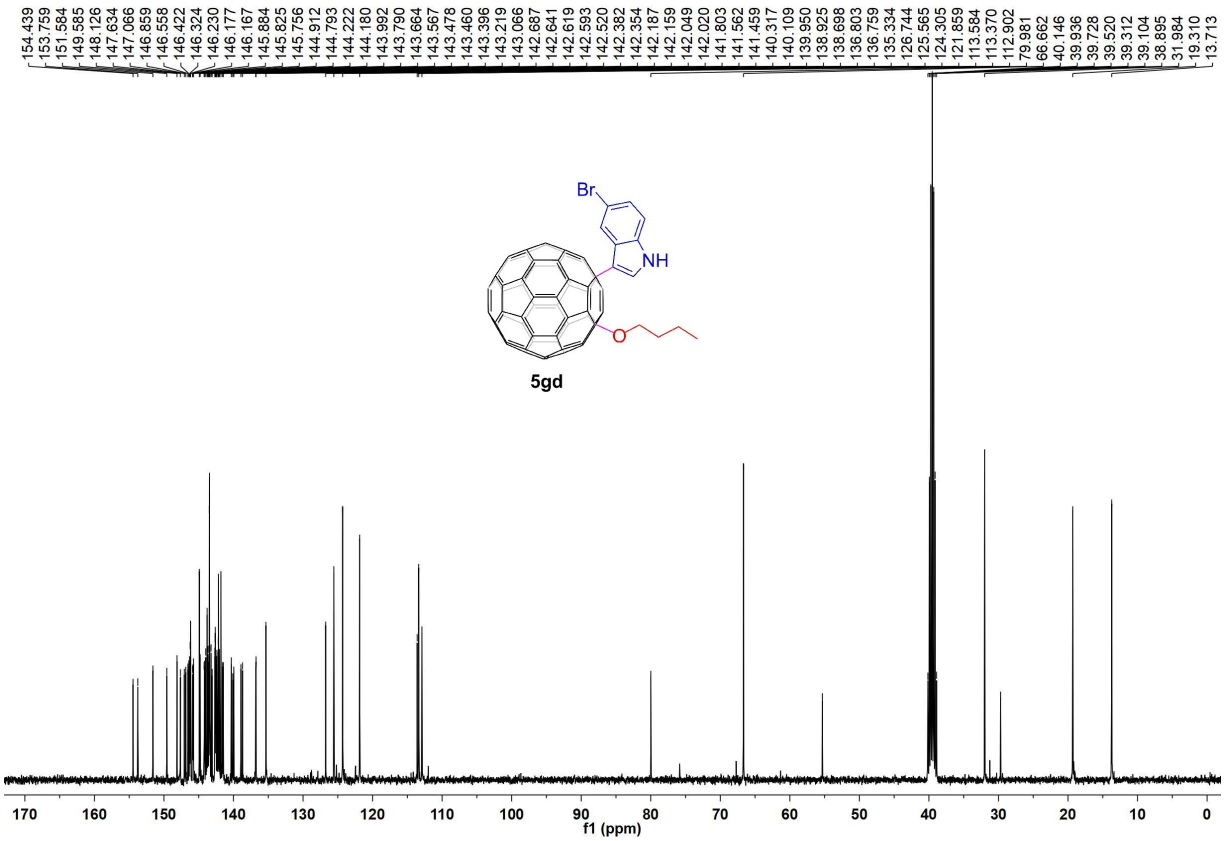
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gc



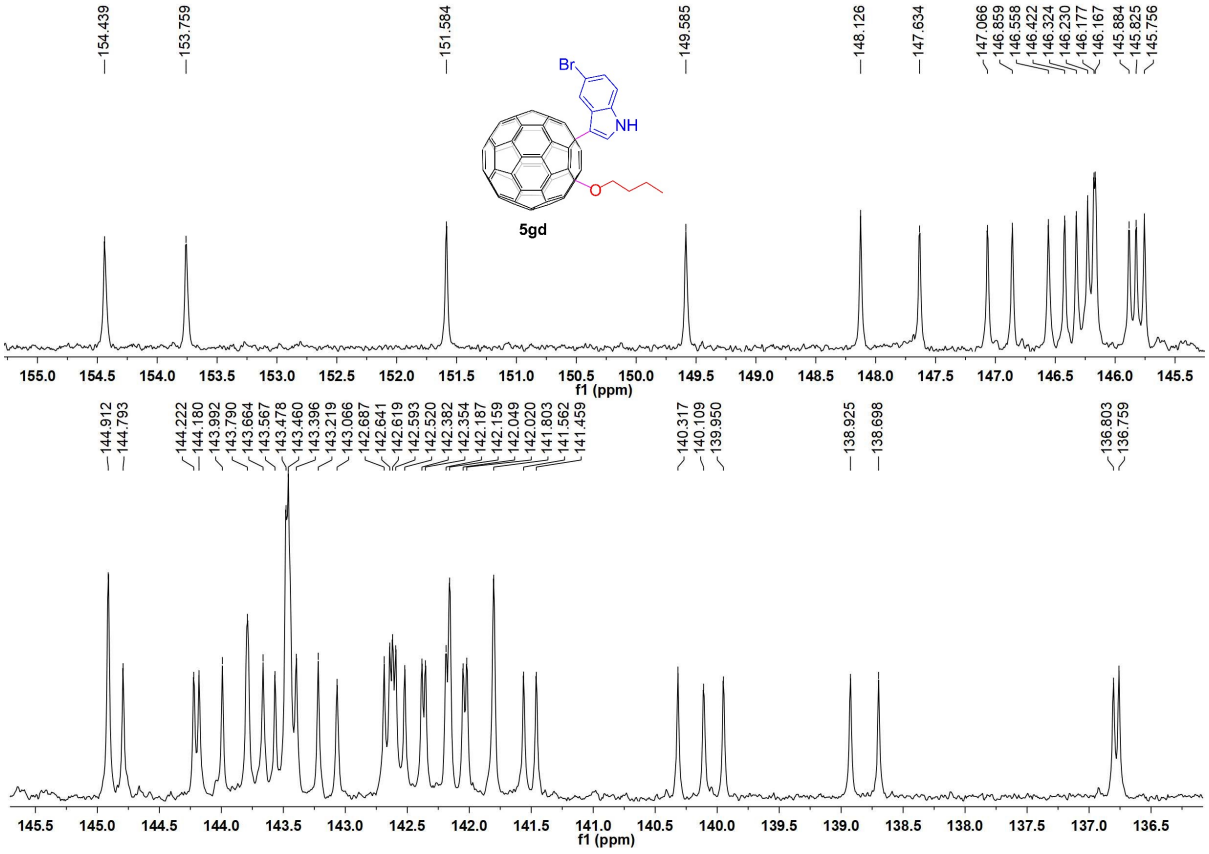
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5gd



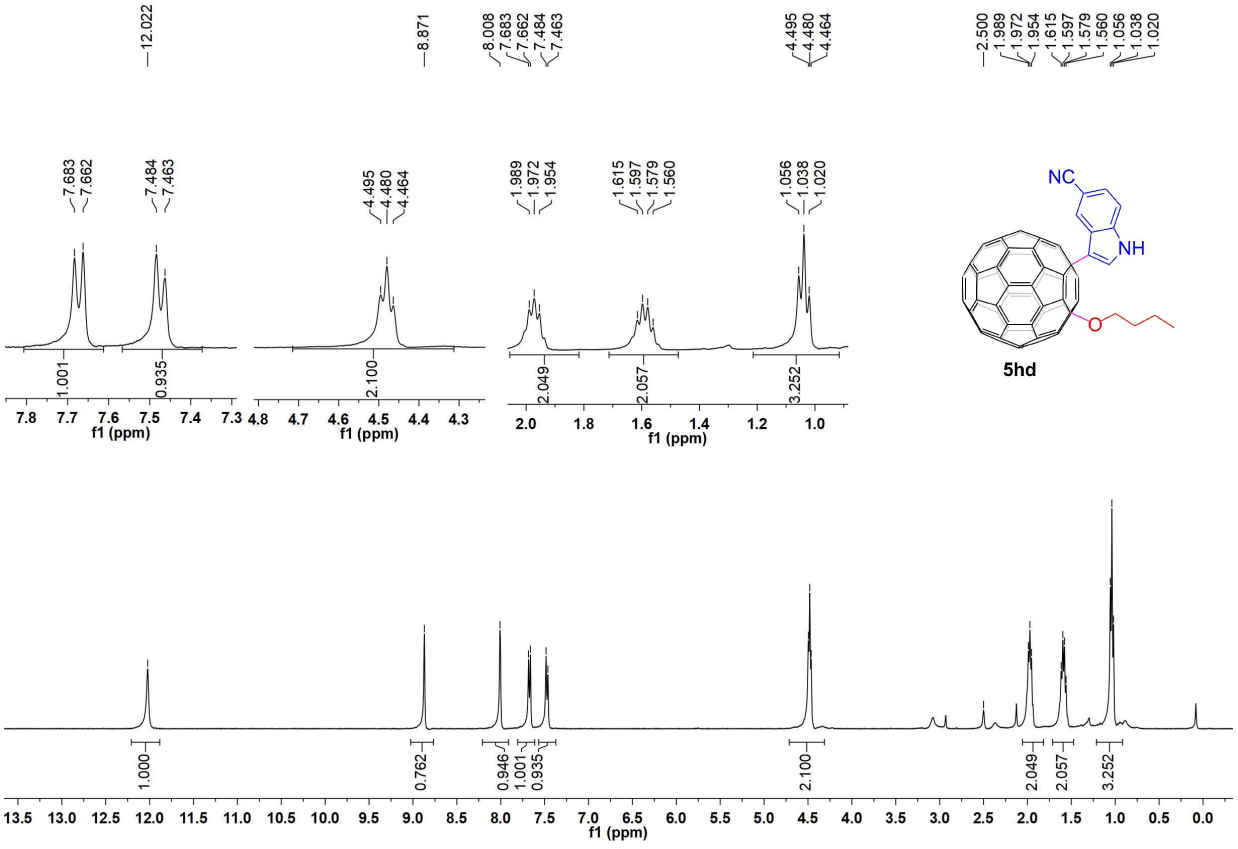
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gd



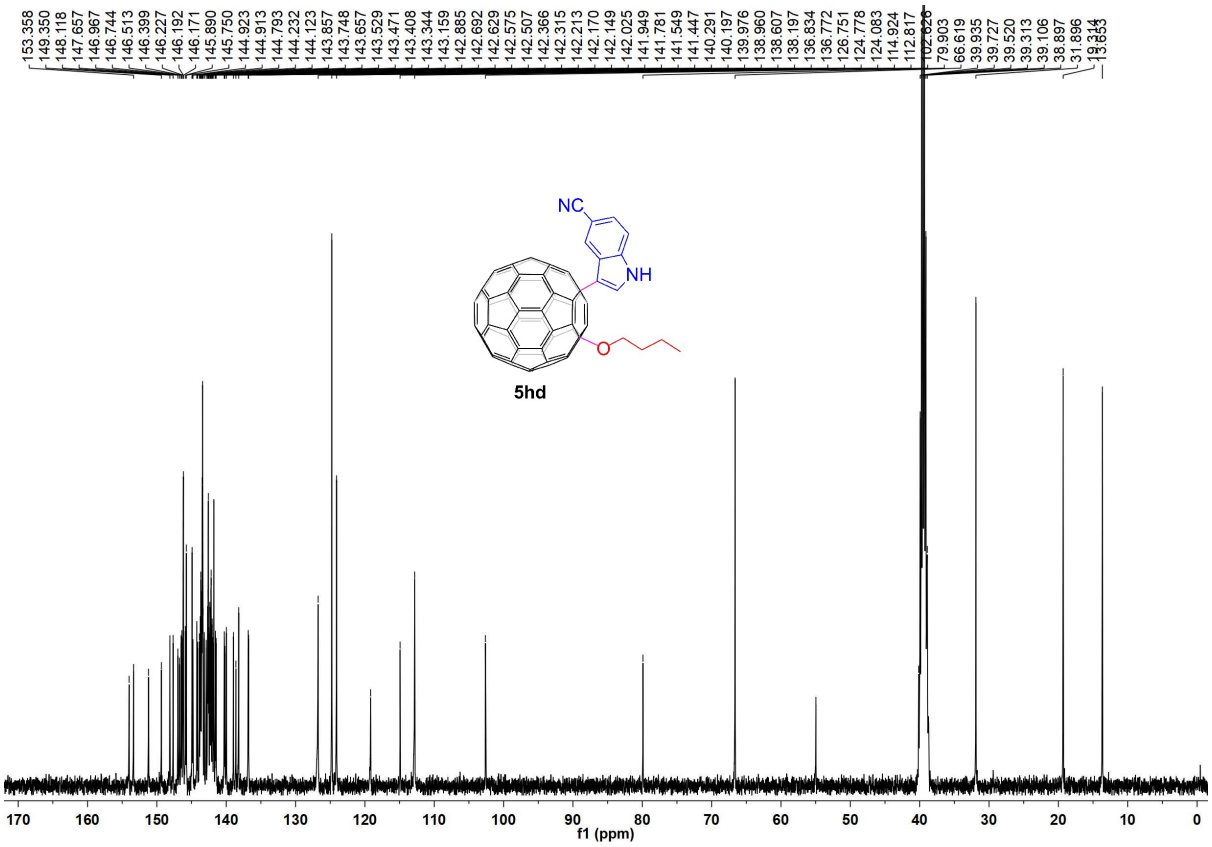
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gd



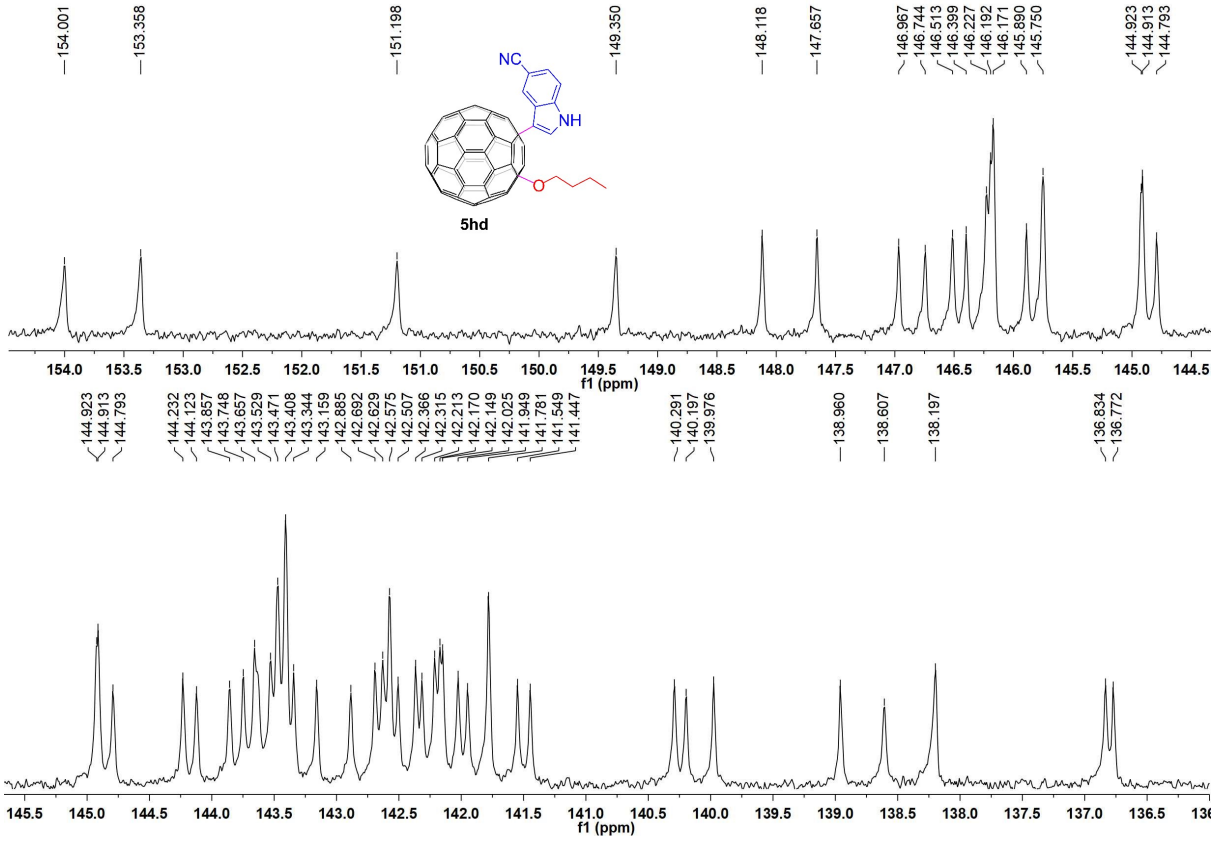
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5hd



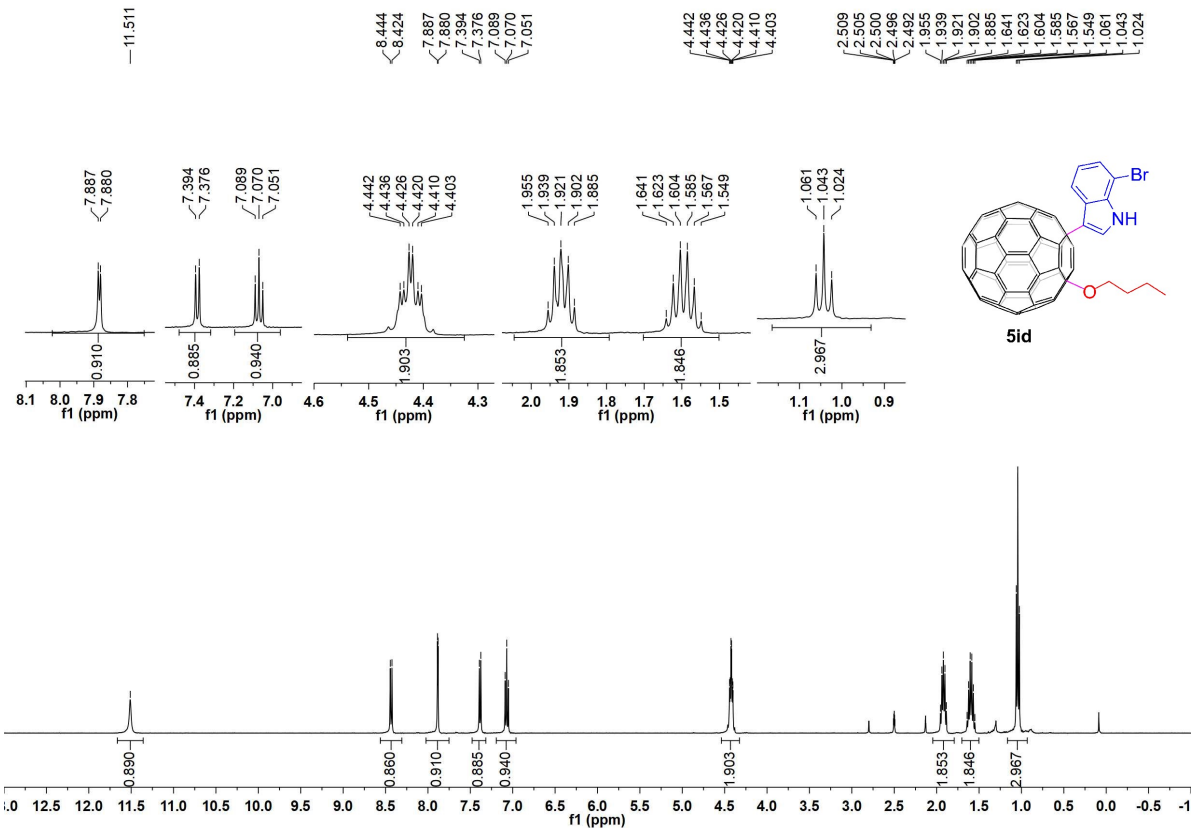
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hd



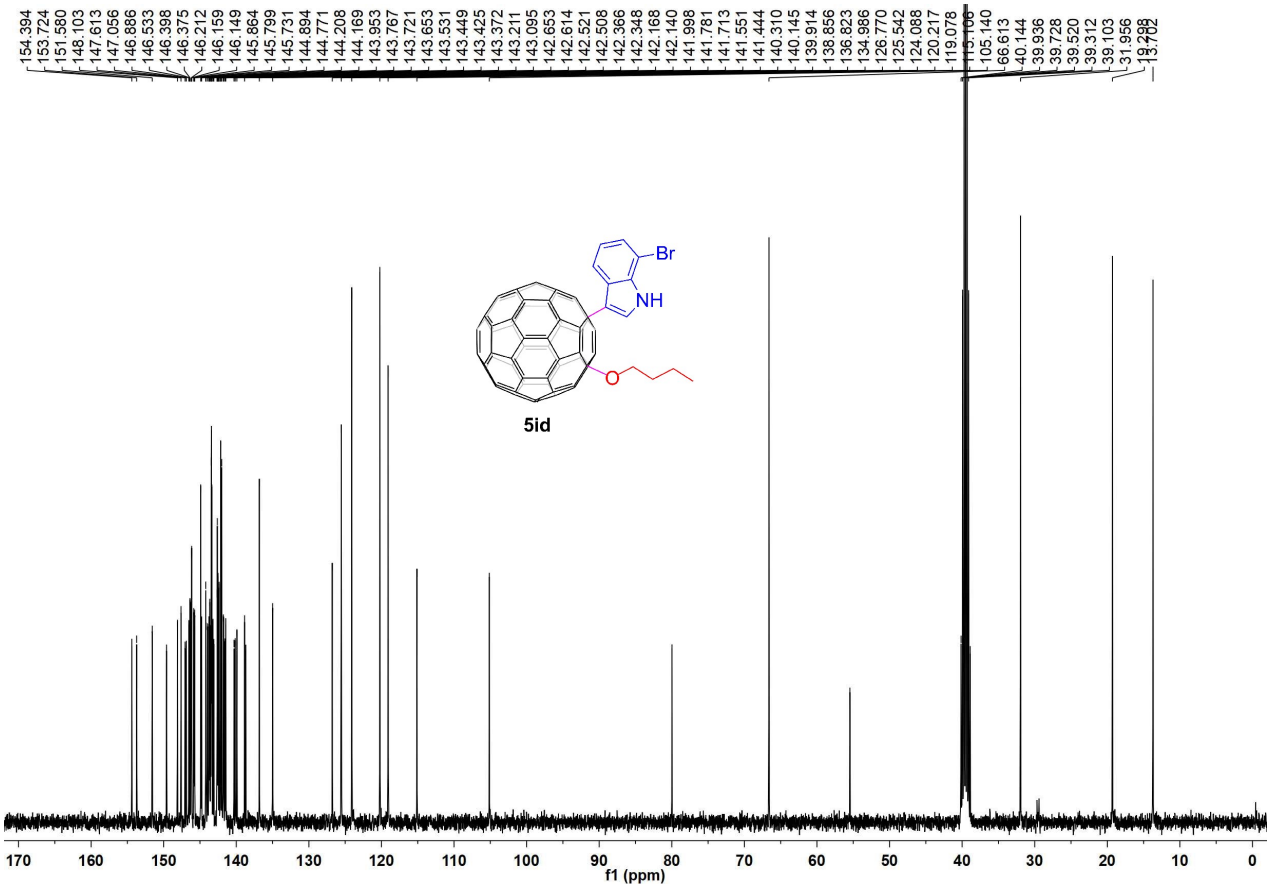
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5hd



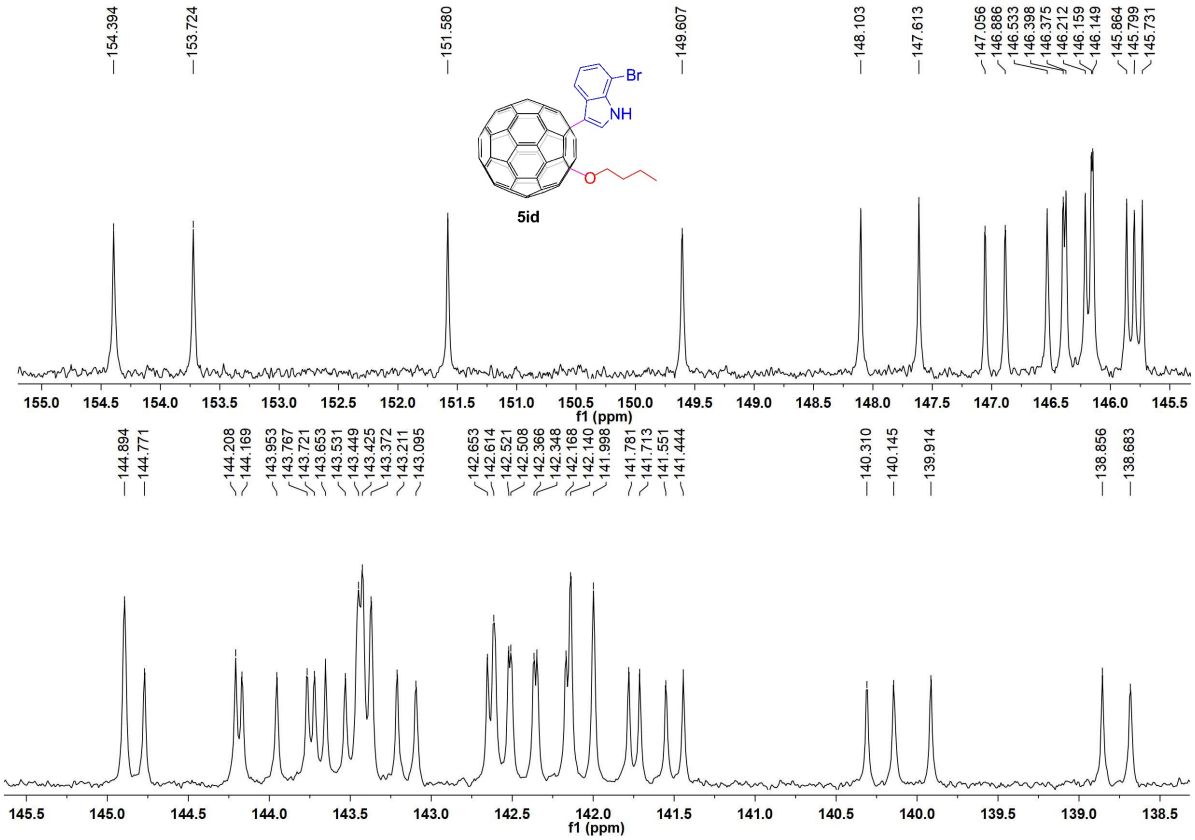
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5id



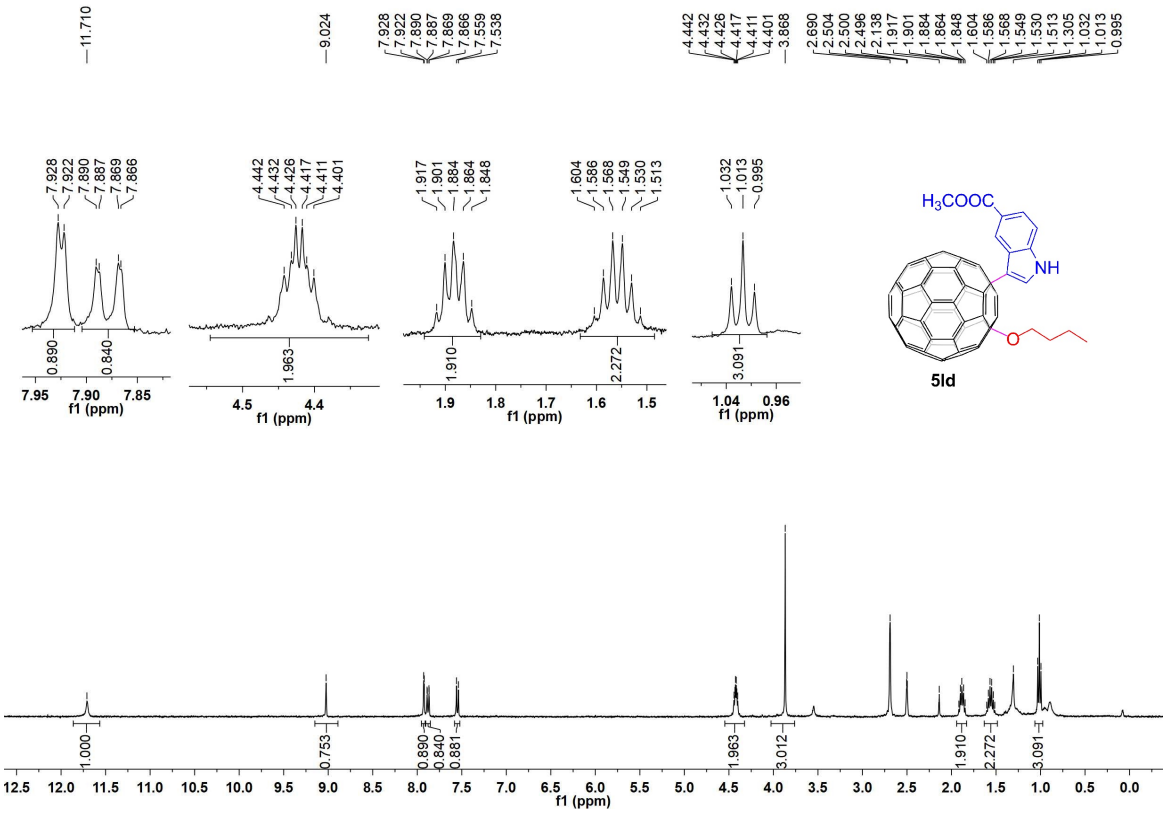
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5id



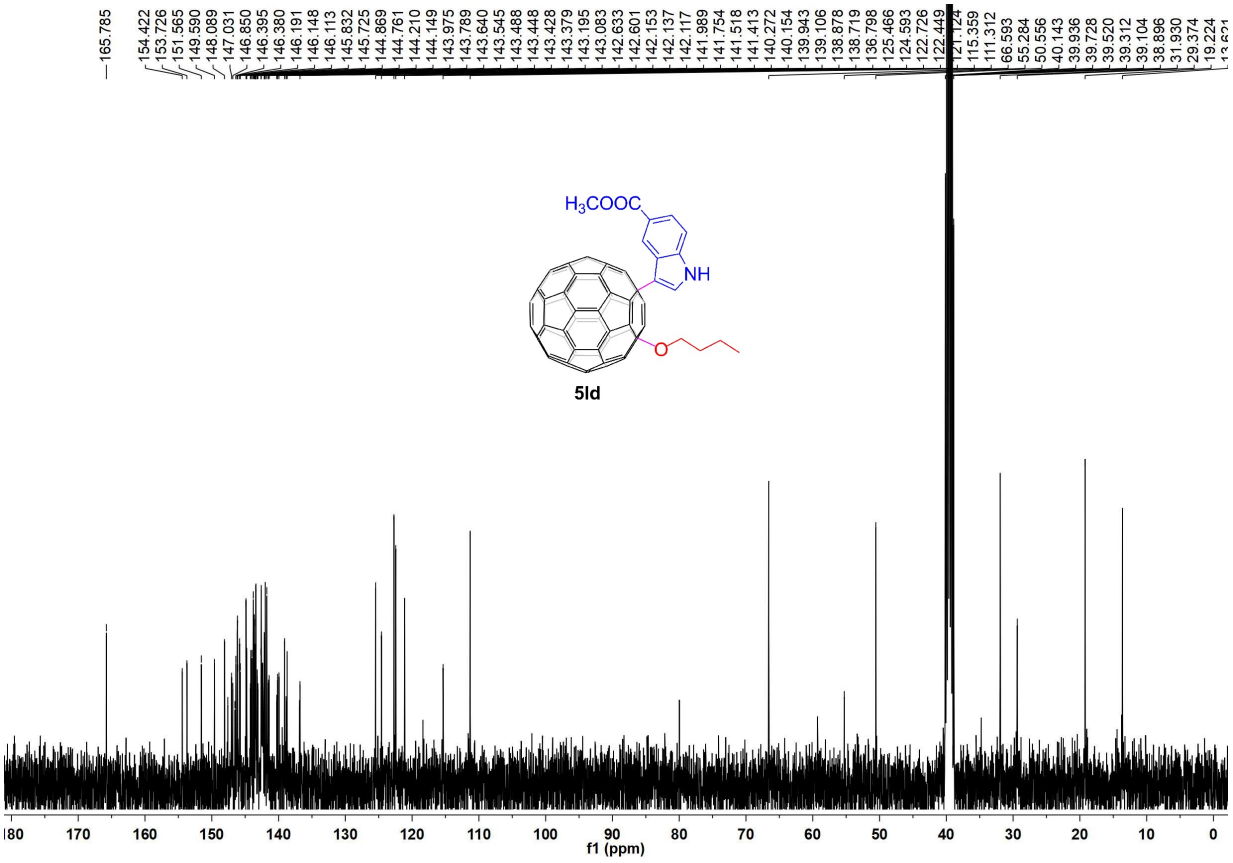
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5id



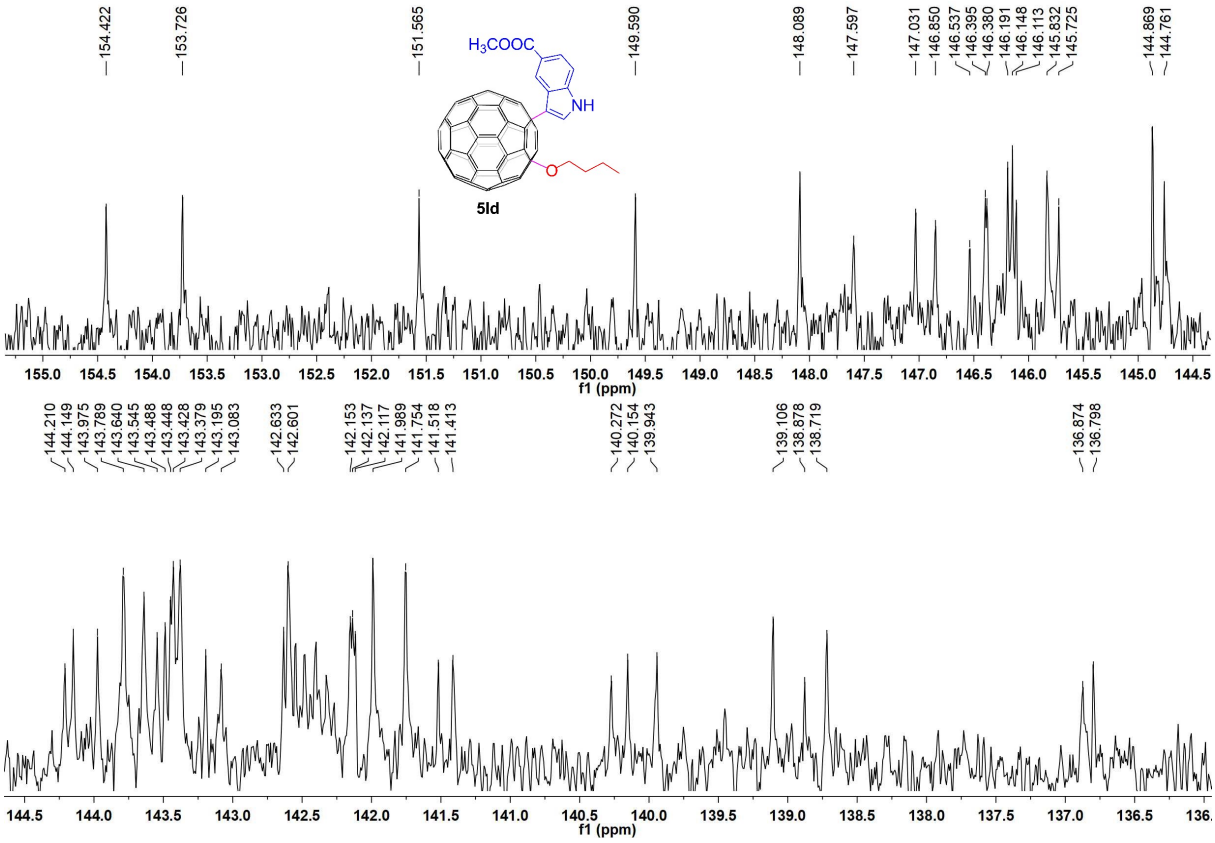
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ld



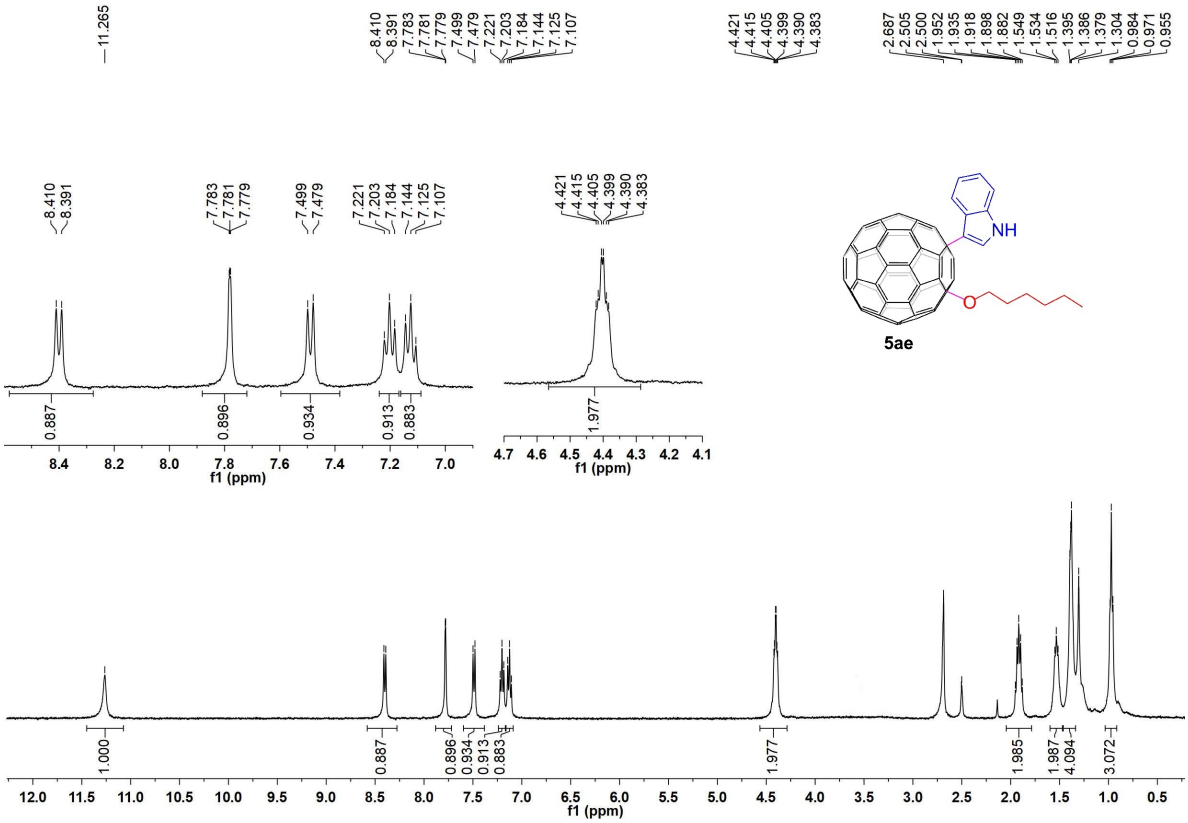
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ld



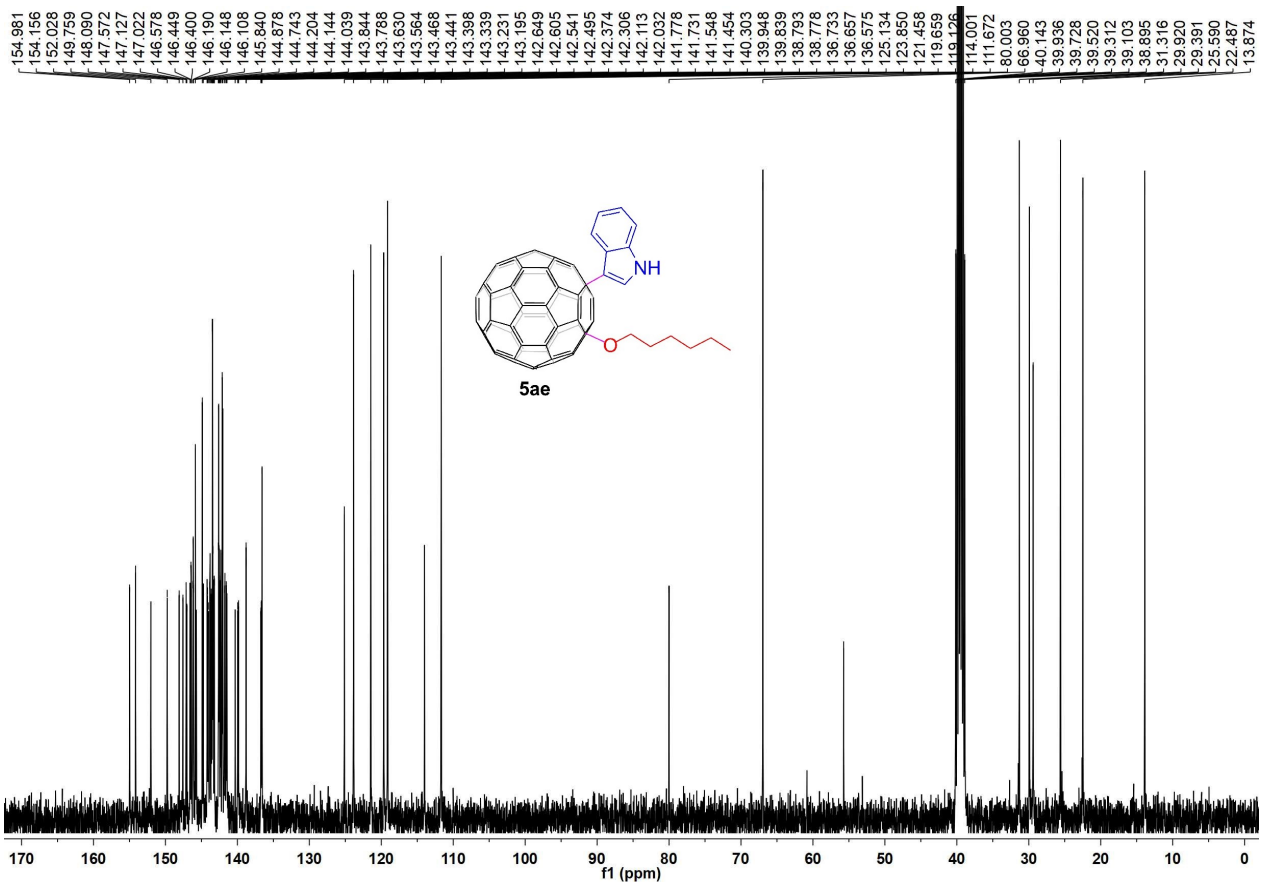
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ld



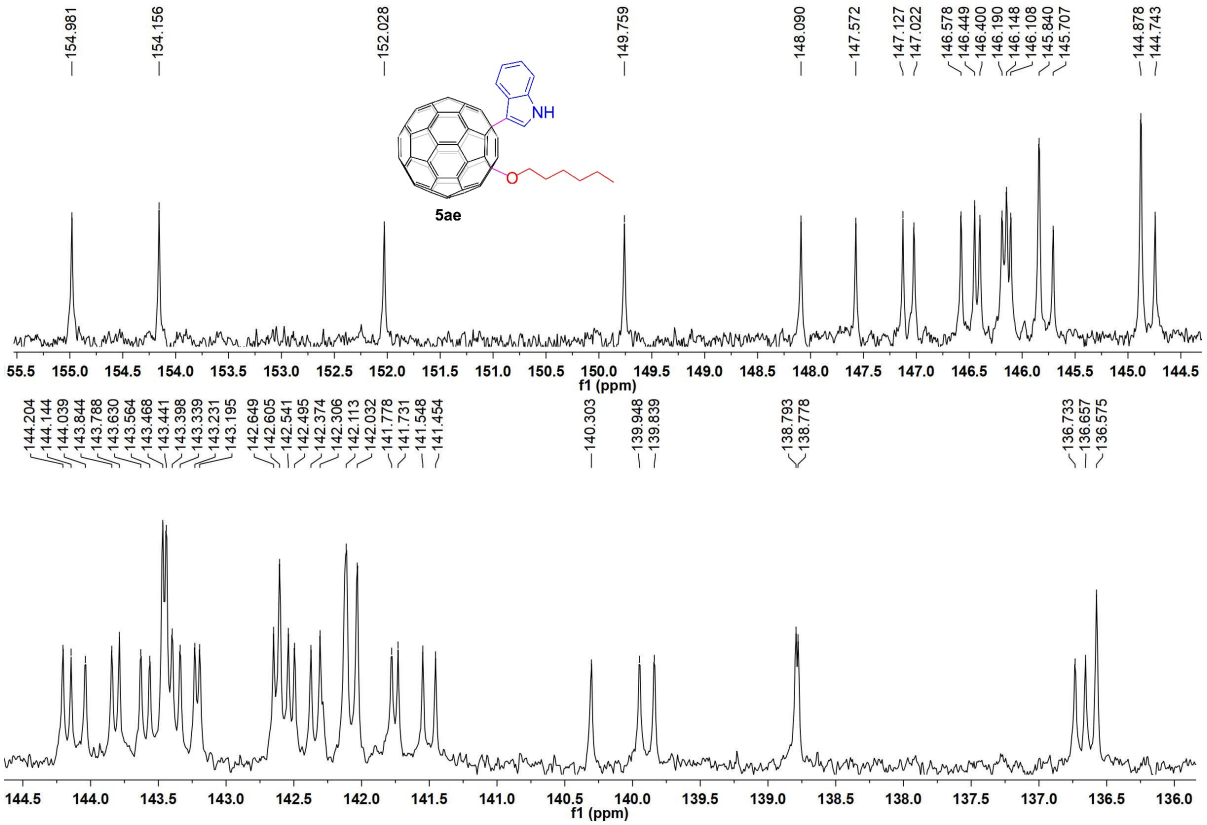
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ae



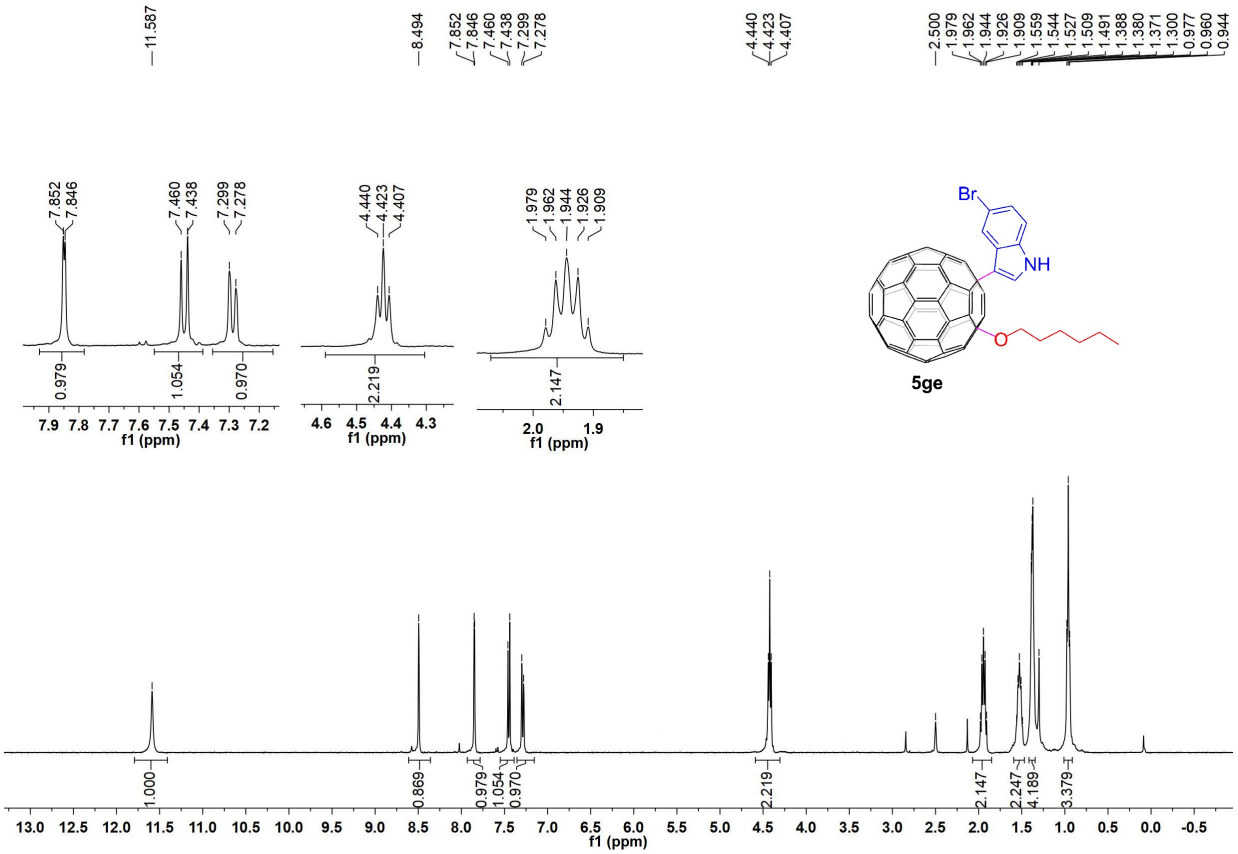
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ae



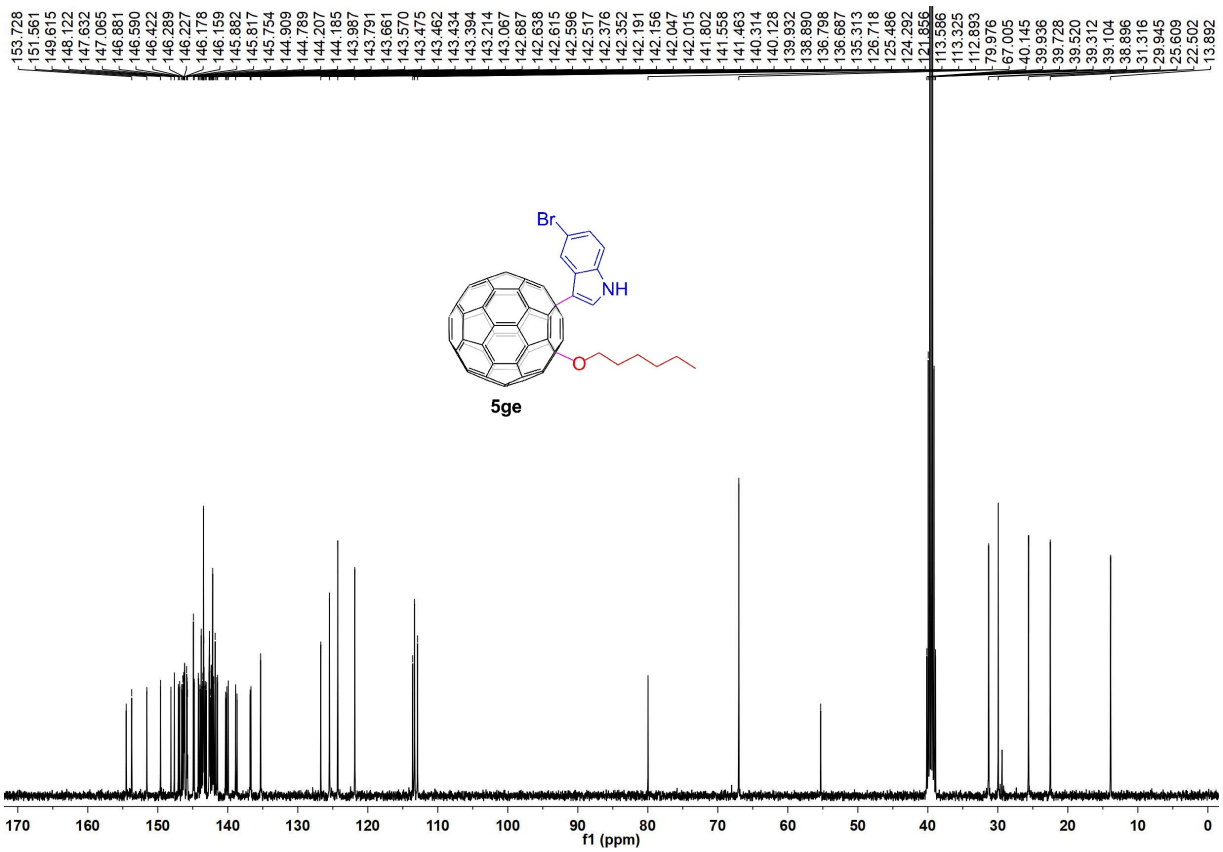
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ae



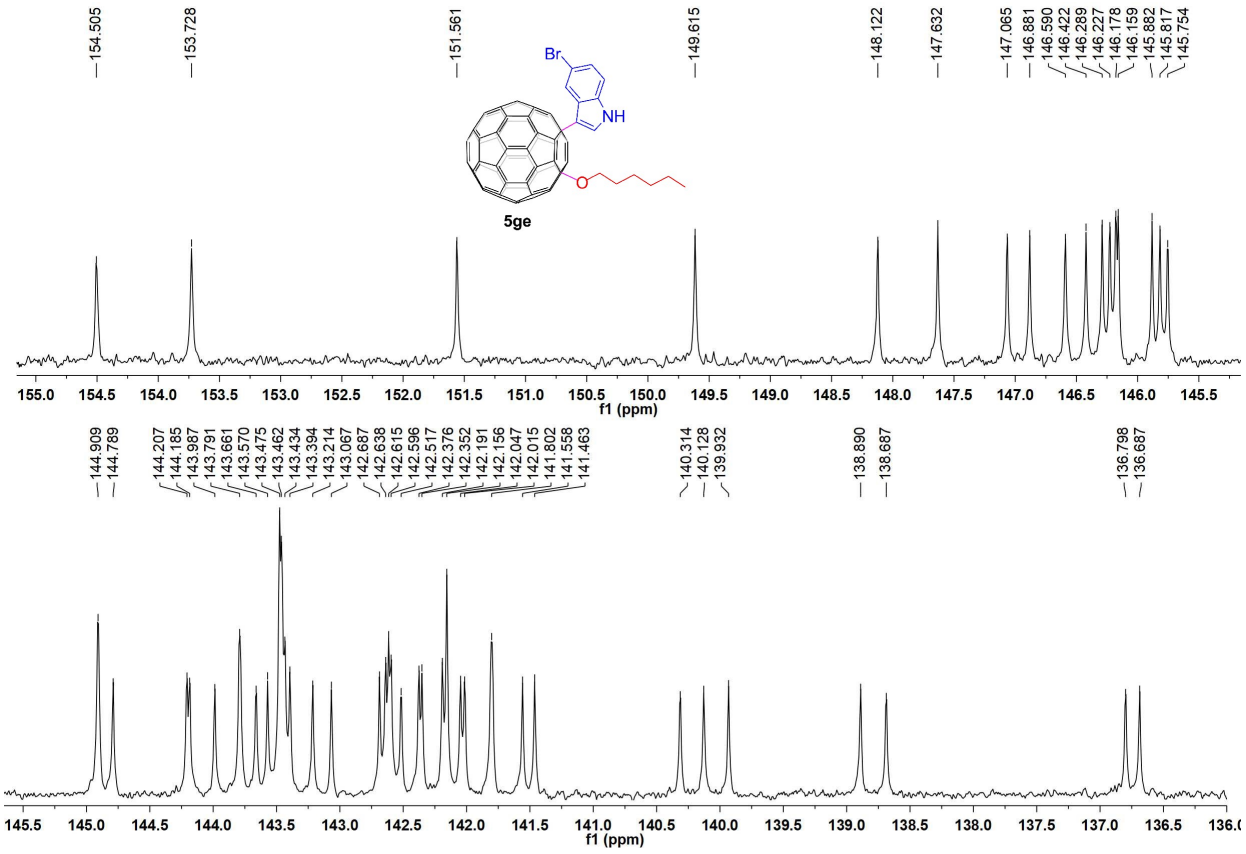
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ge



^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ge



Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ge



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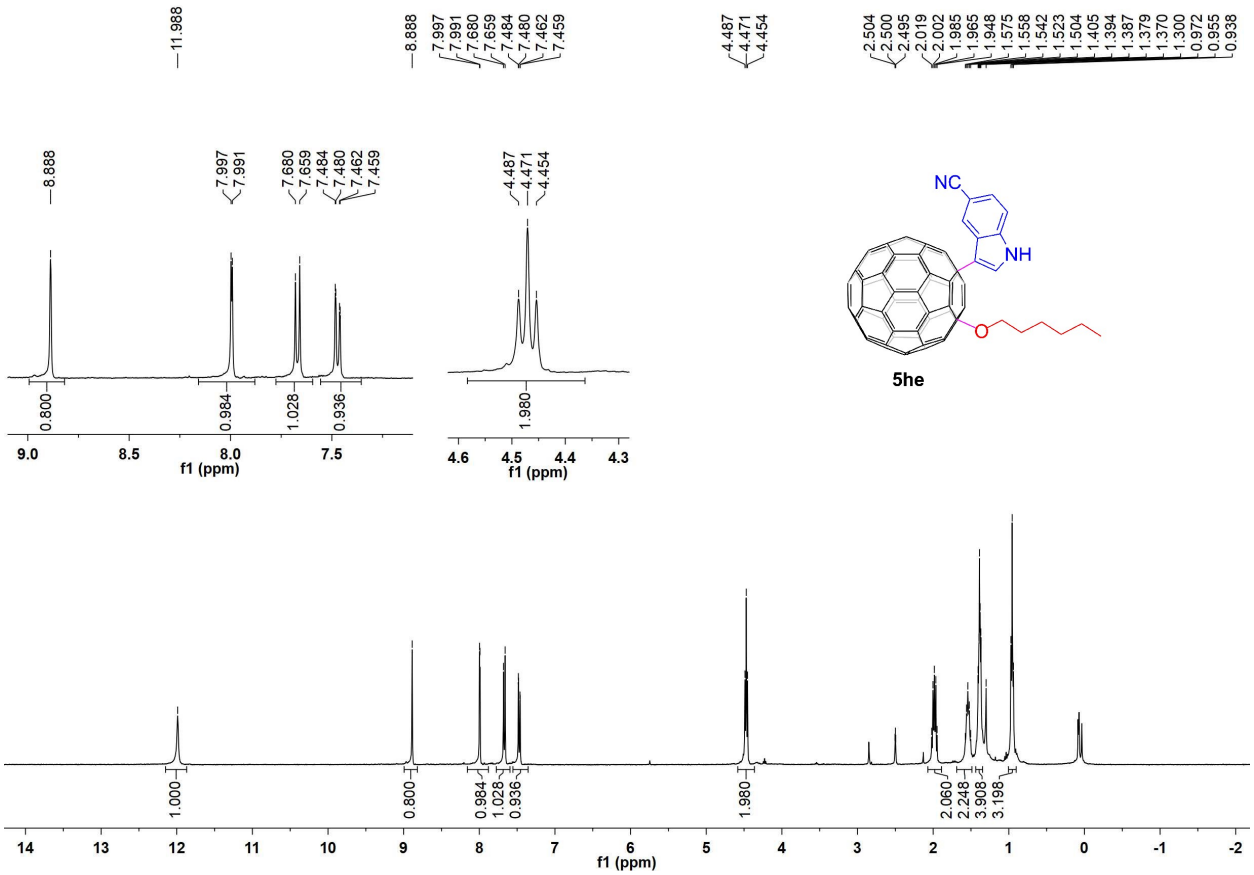
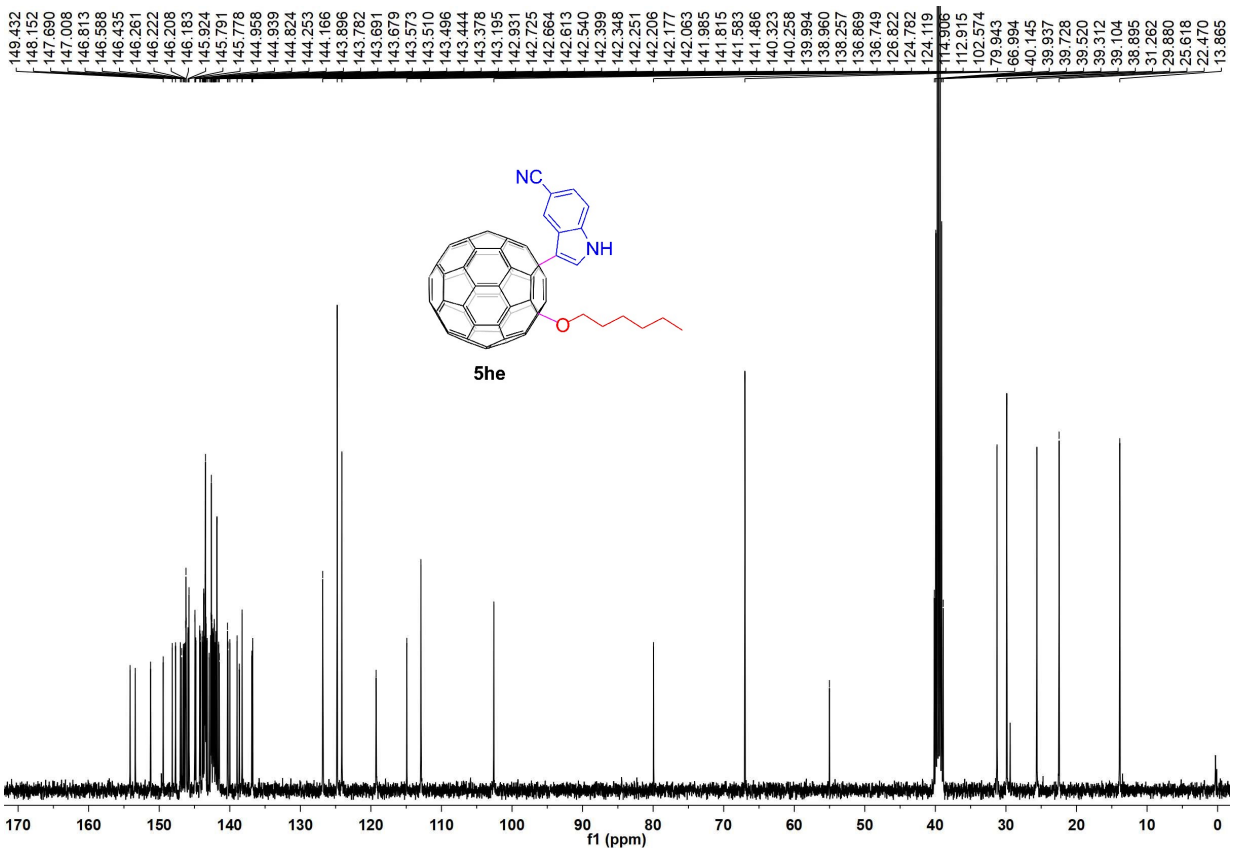
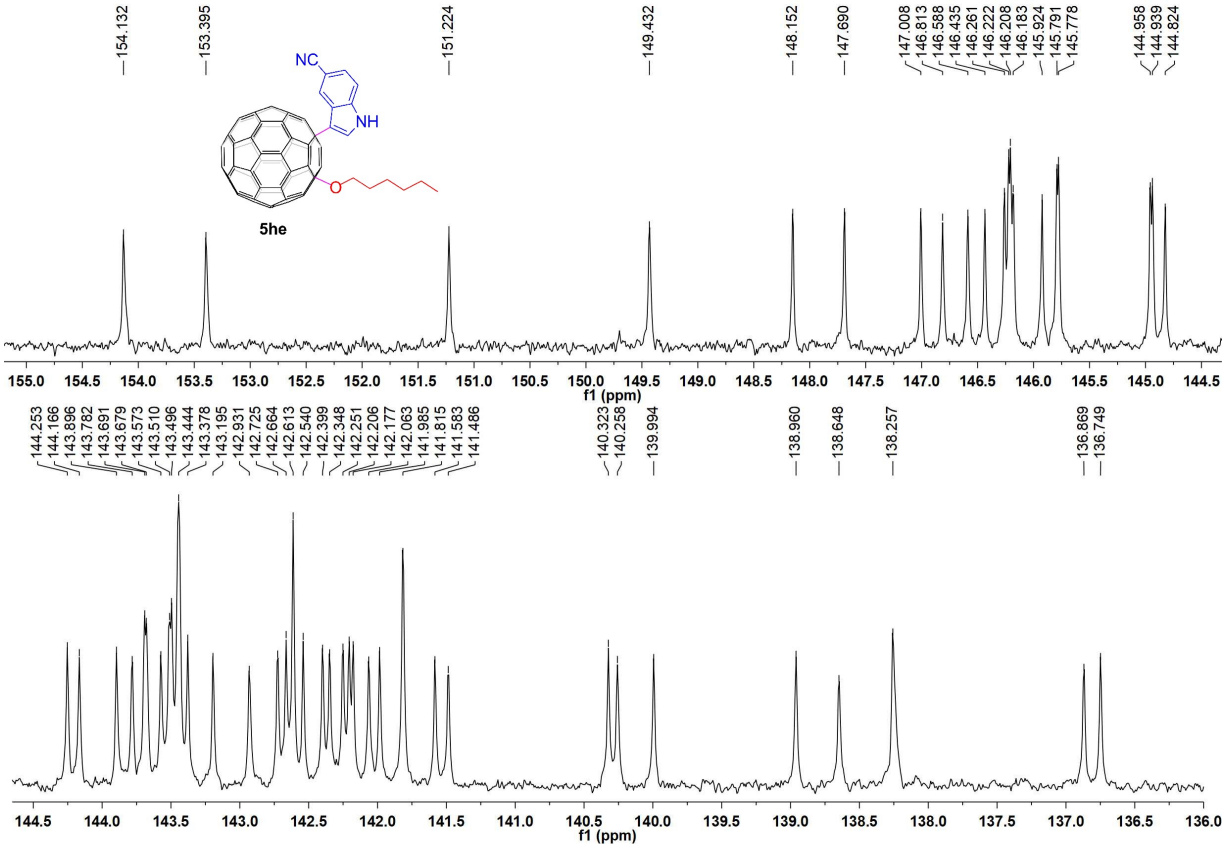


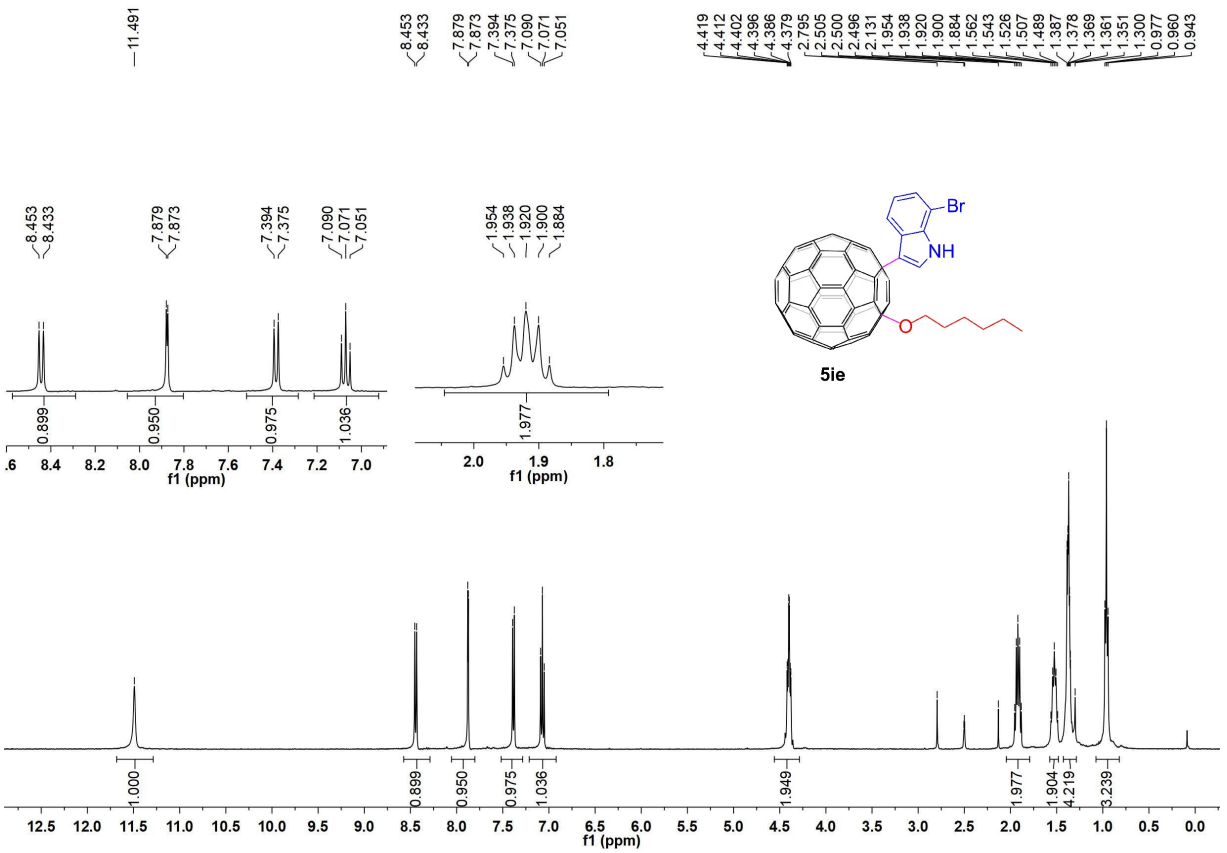
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5he



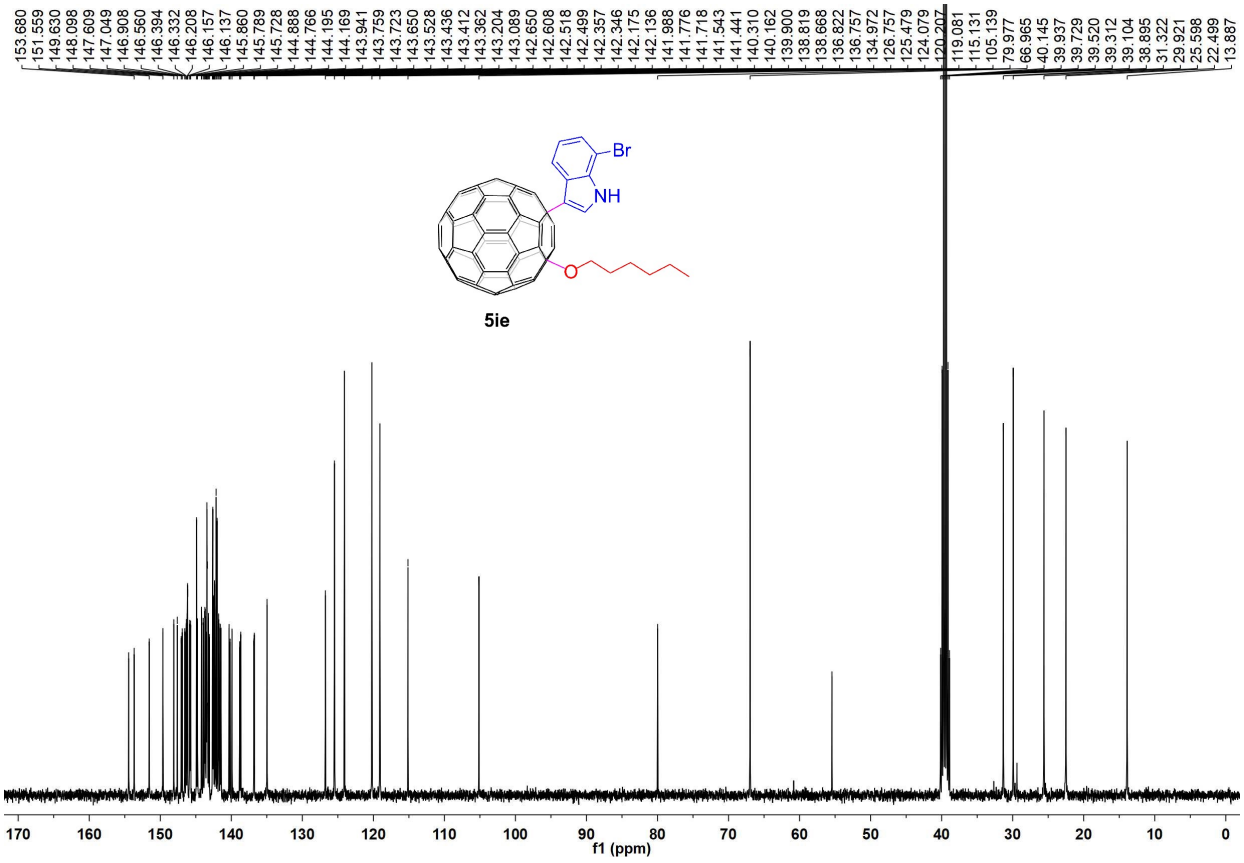
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5he



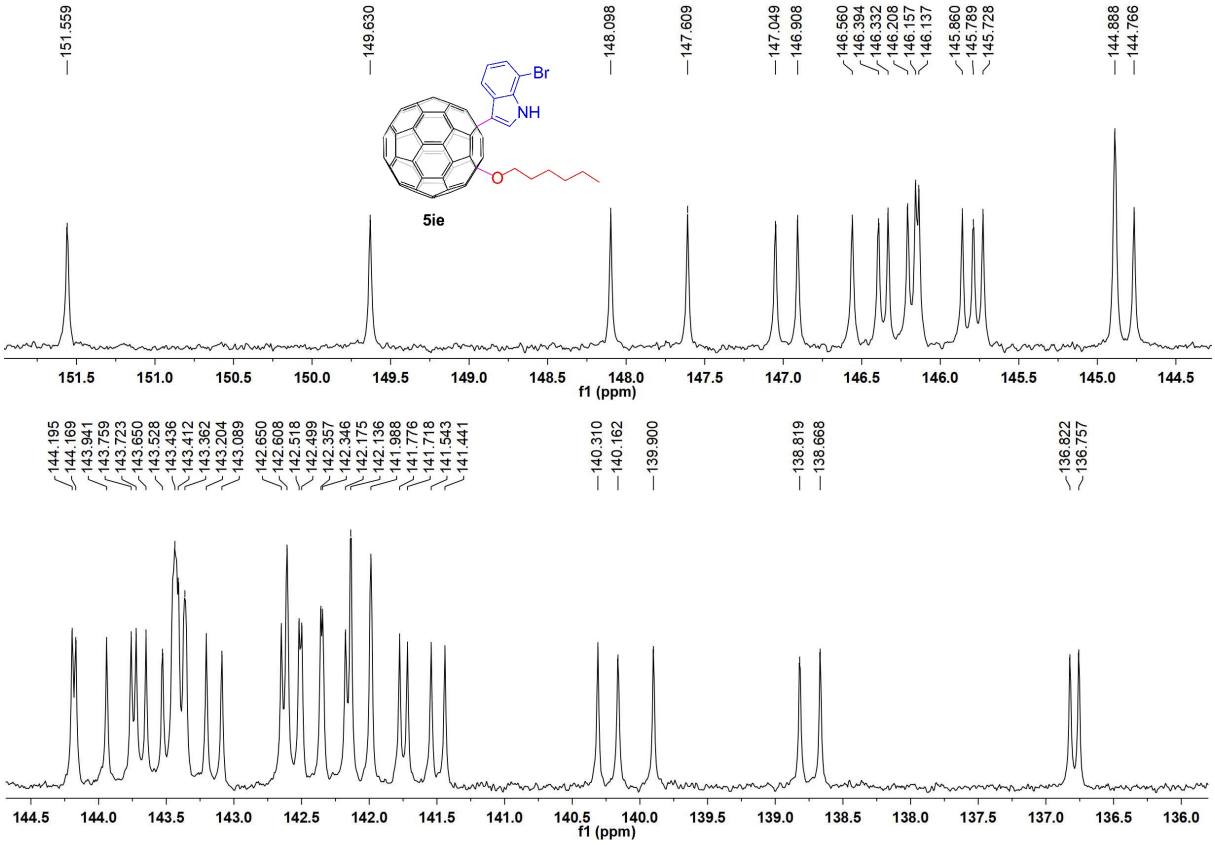
^1H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5ie



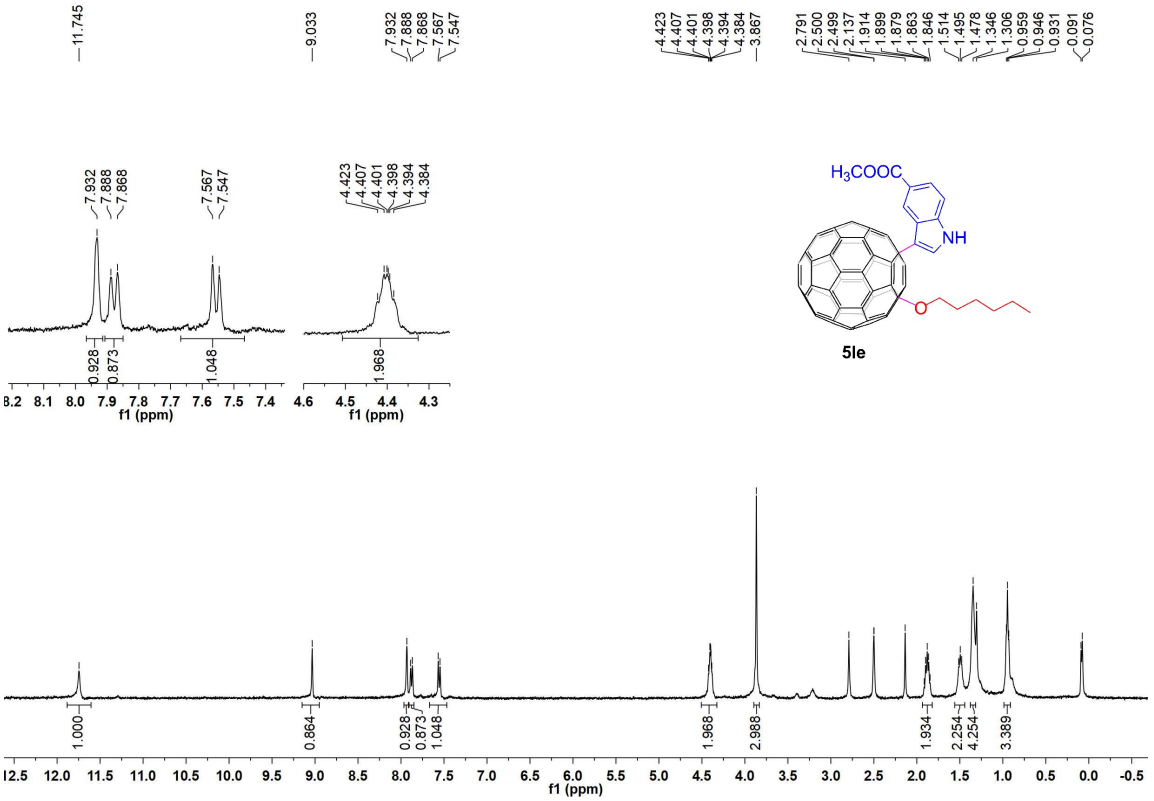
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ie



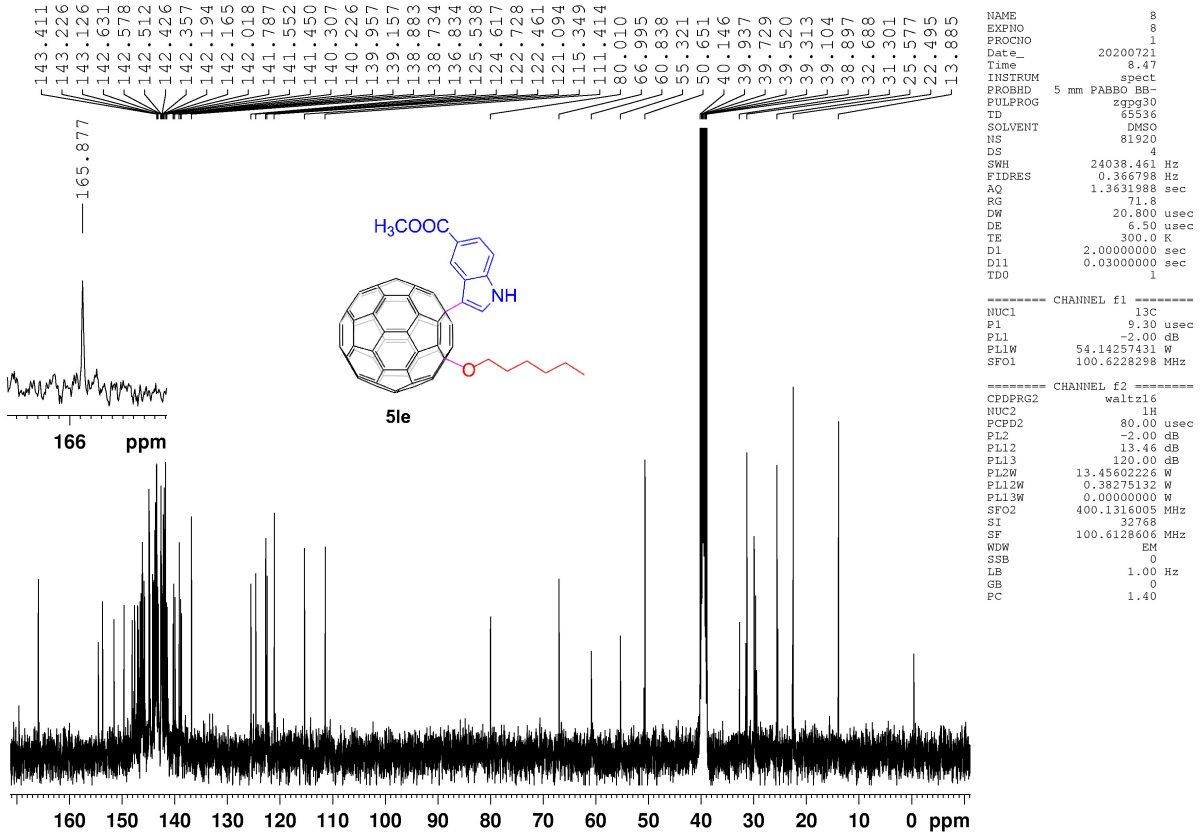
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5ie



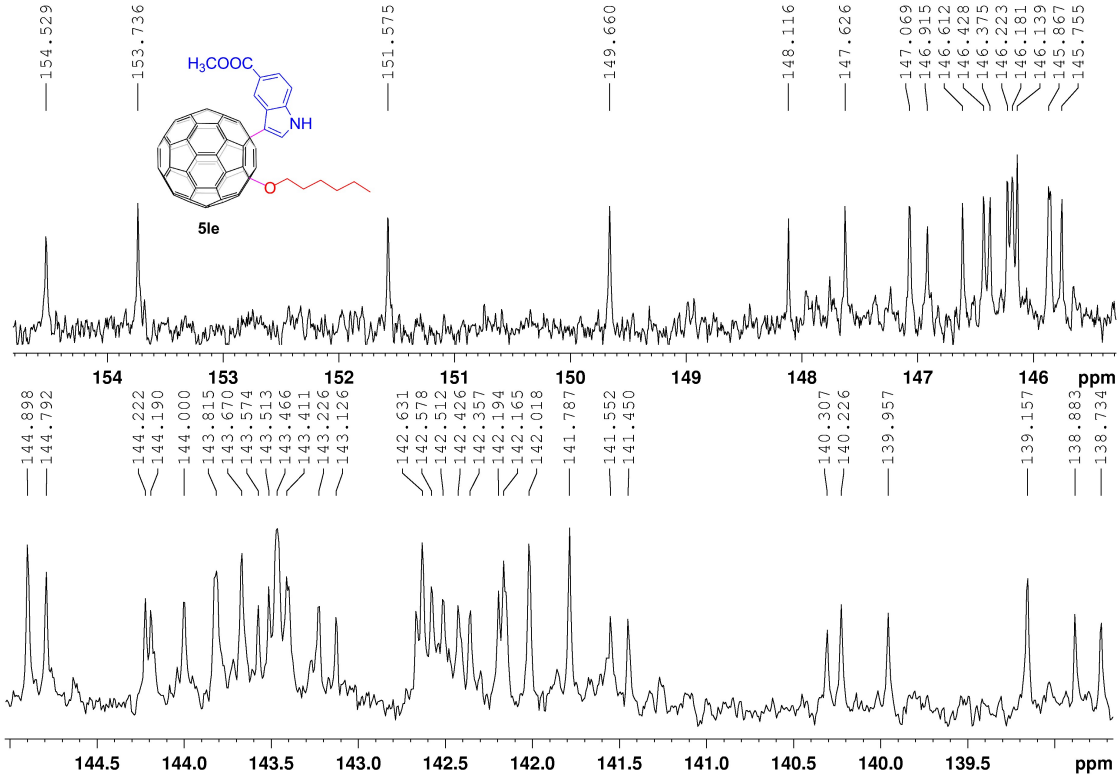
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5le



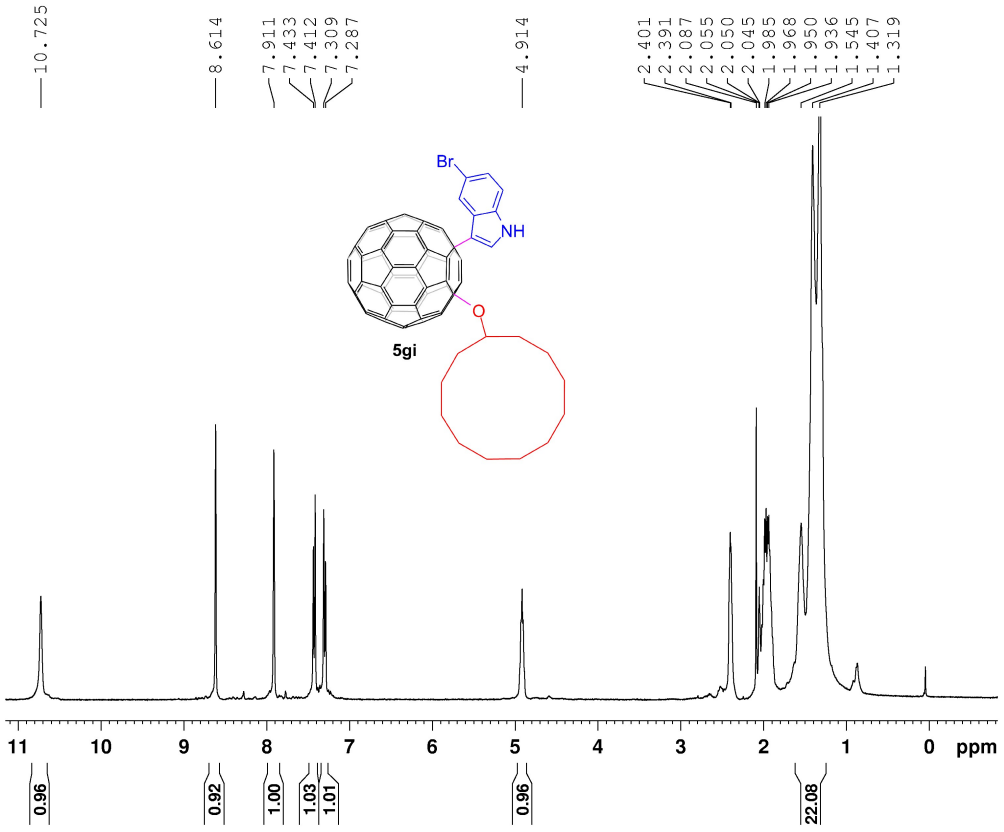
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5le



Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5le



^{1}H NMR (400 MHz , Acetone-d_6/CS_2) of compound 5gi

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DS                       2
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FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     287
DW                  60.800 usec
DE                   6.50 usec
TE                  300.0 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  13.50 usec
PL1                 -2.00 dB
PL1W          13.45602226 W
SFO1          400.1324710 MHz
SI                   32768
SF            400.1300075 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
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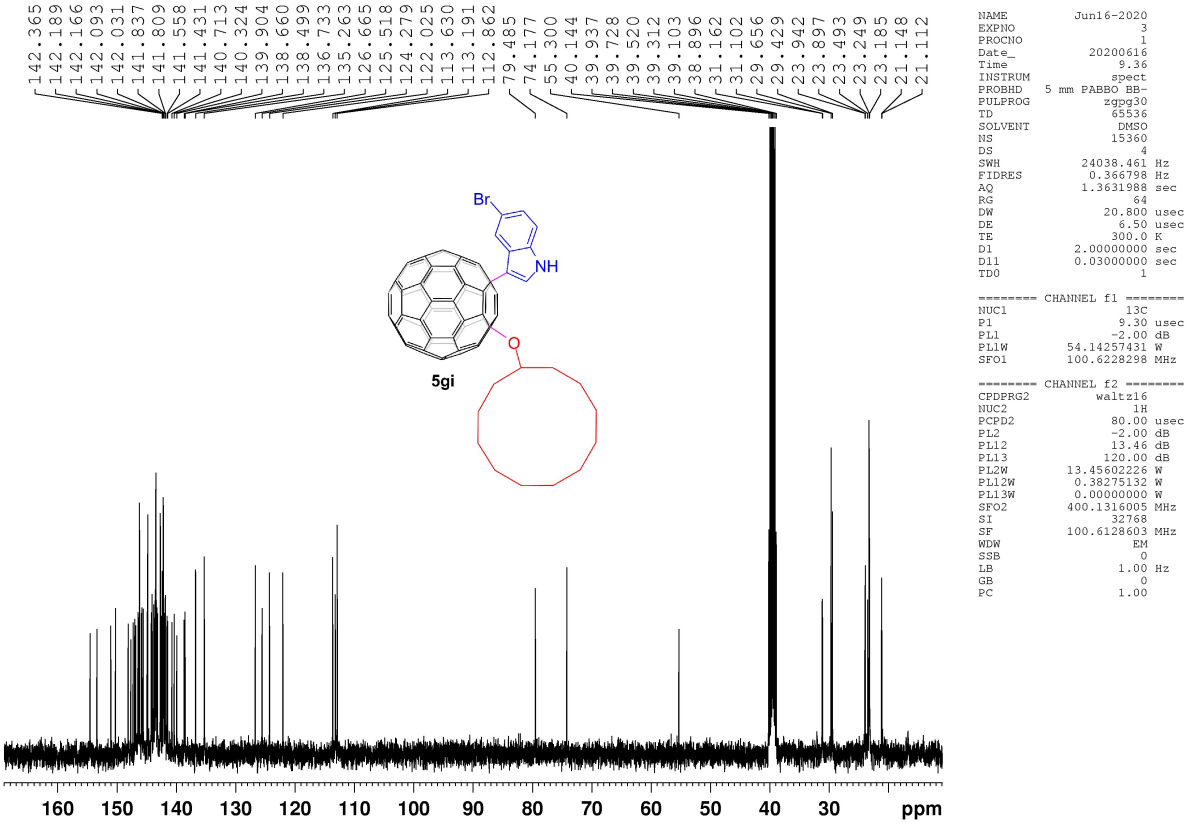
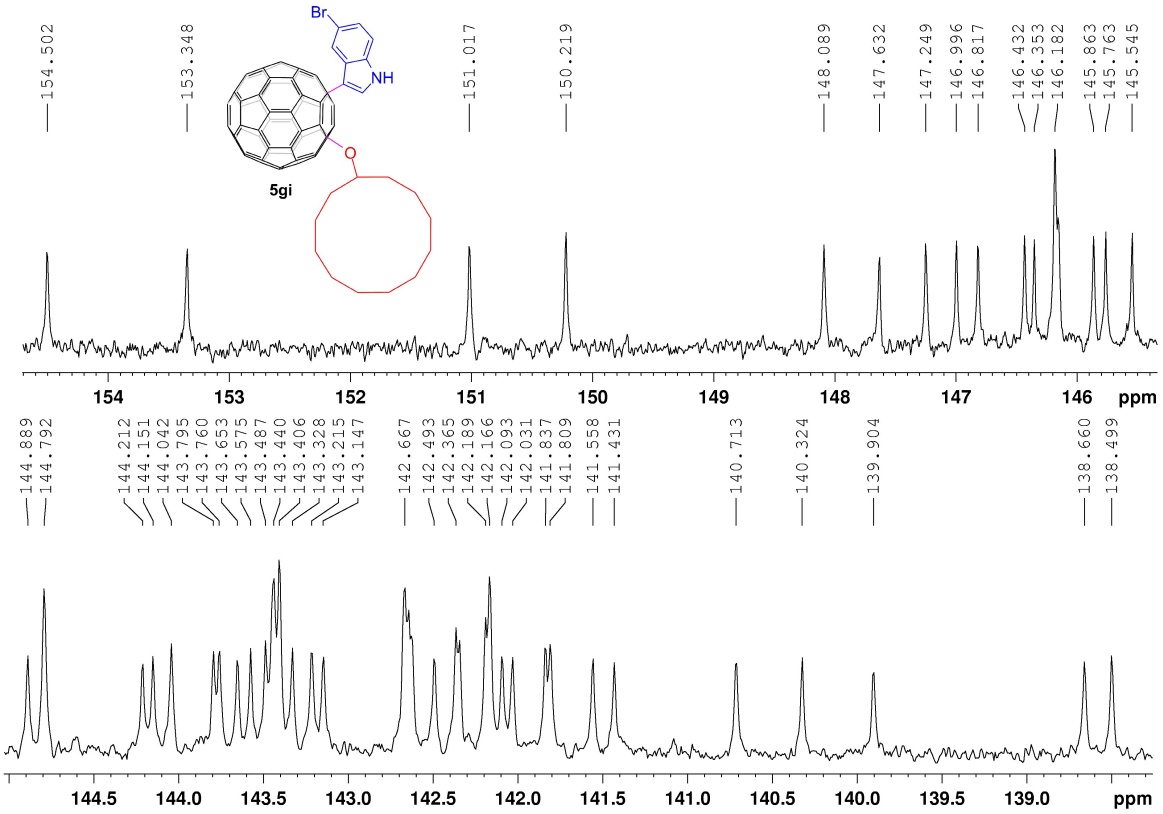
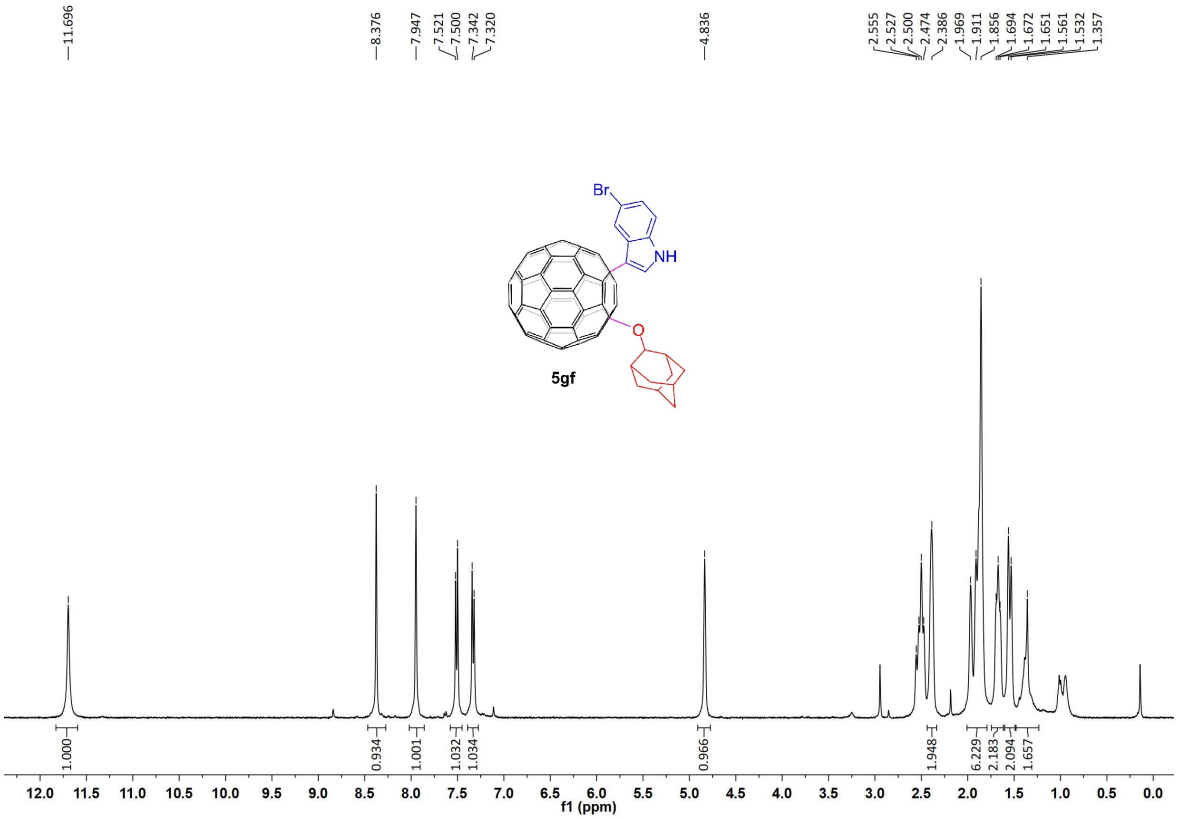
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gi



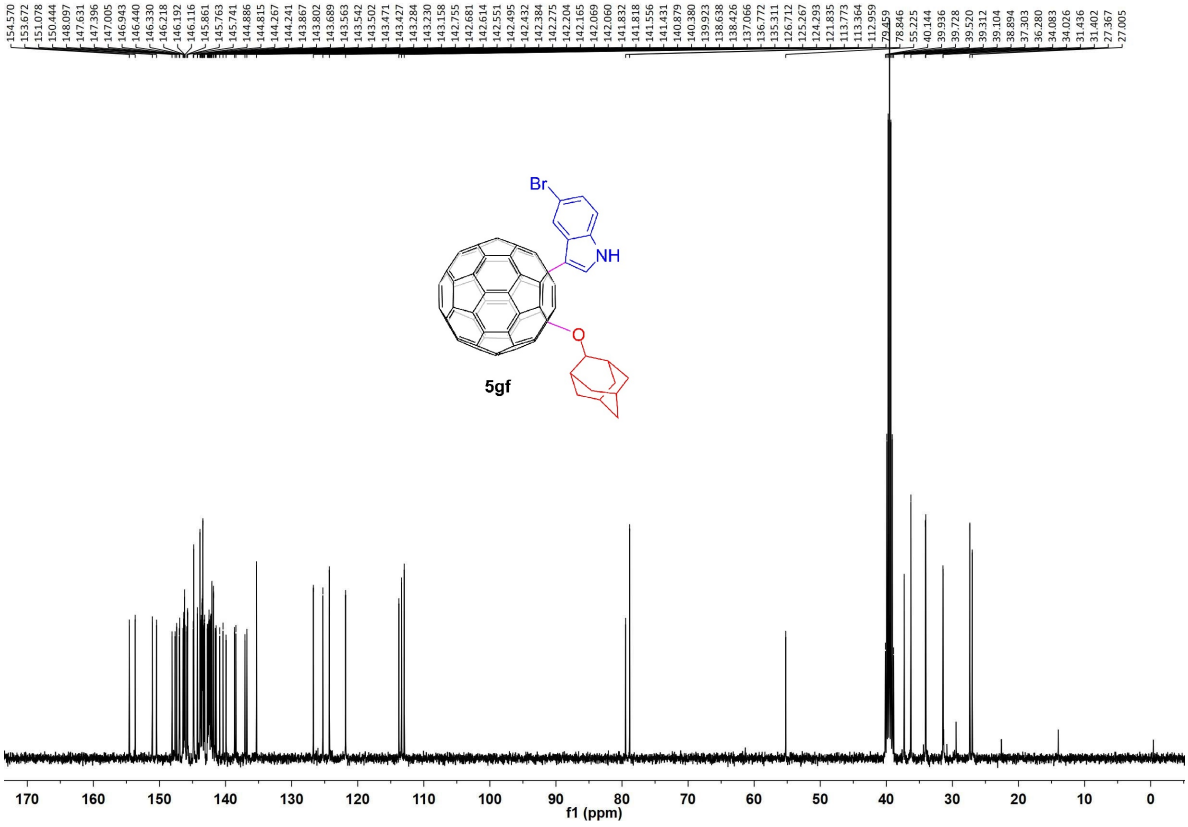
Expanded ^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gi



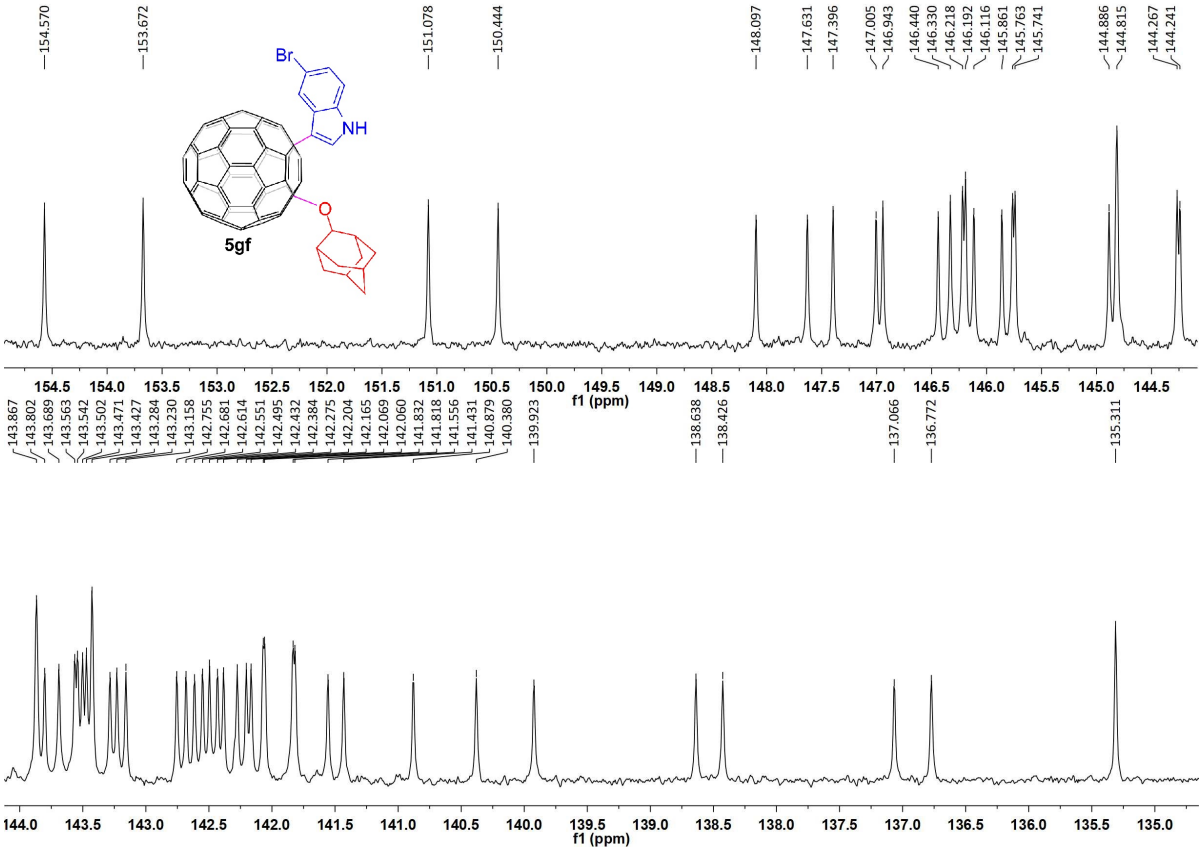
^{1}H NMR (400 MHz , d_6-DMSO/CS_2) of compound 5gf



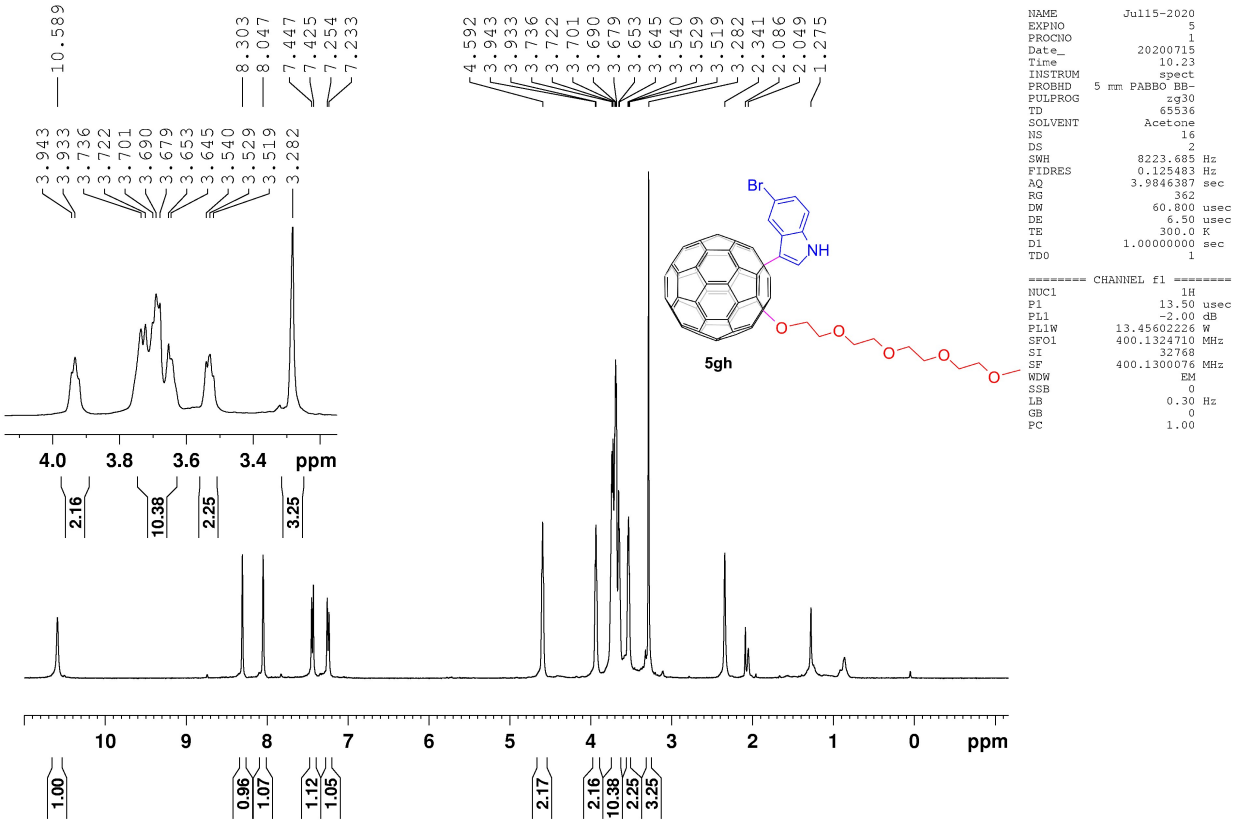
^{13}C NMR (100 MHz , d_6-DMSO/CS_2) of compound 5gf



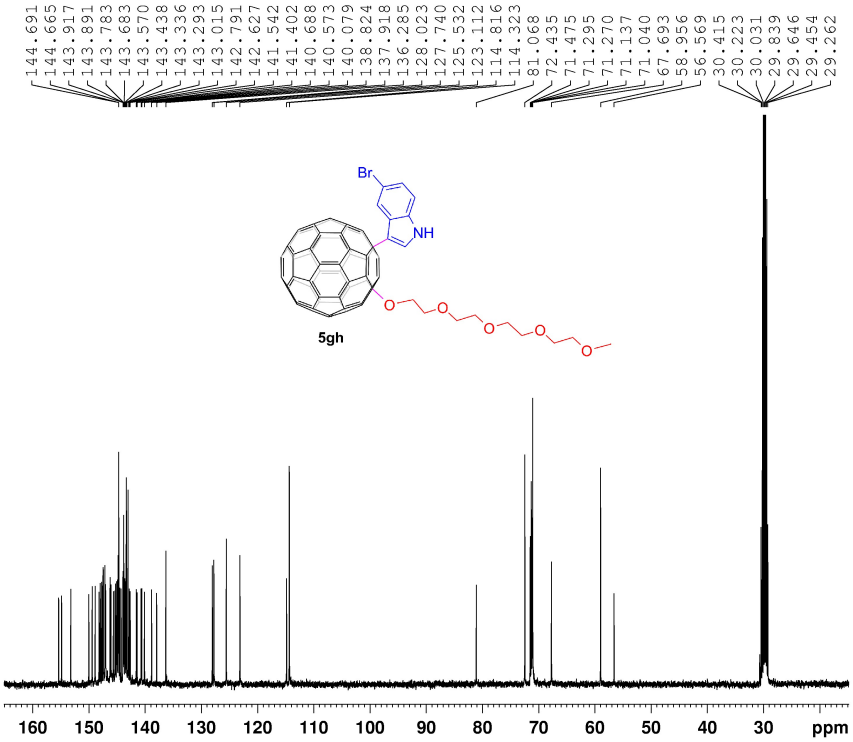
Expanded ^{13}C NMR (100 MHz , d$_6$-DMSO/CS$_2$) of compound 5gf



^{1}H NMR (400 MHz , Acetone-*d*$_6$/CS$_2$) of compound 5gh



^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5gh

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SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    71.8
DW                 20.800 usec
DE                  6.50 usec
TE                 300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   9.30 usec
PL1                 -2.00 dB
PL1W          54.14257431 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                13.46 dB
PL13               120.00 dB
PL2W          13.45602226 W
PL12W          0.38275132 W
PL13W          0.00000000 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127311 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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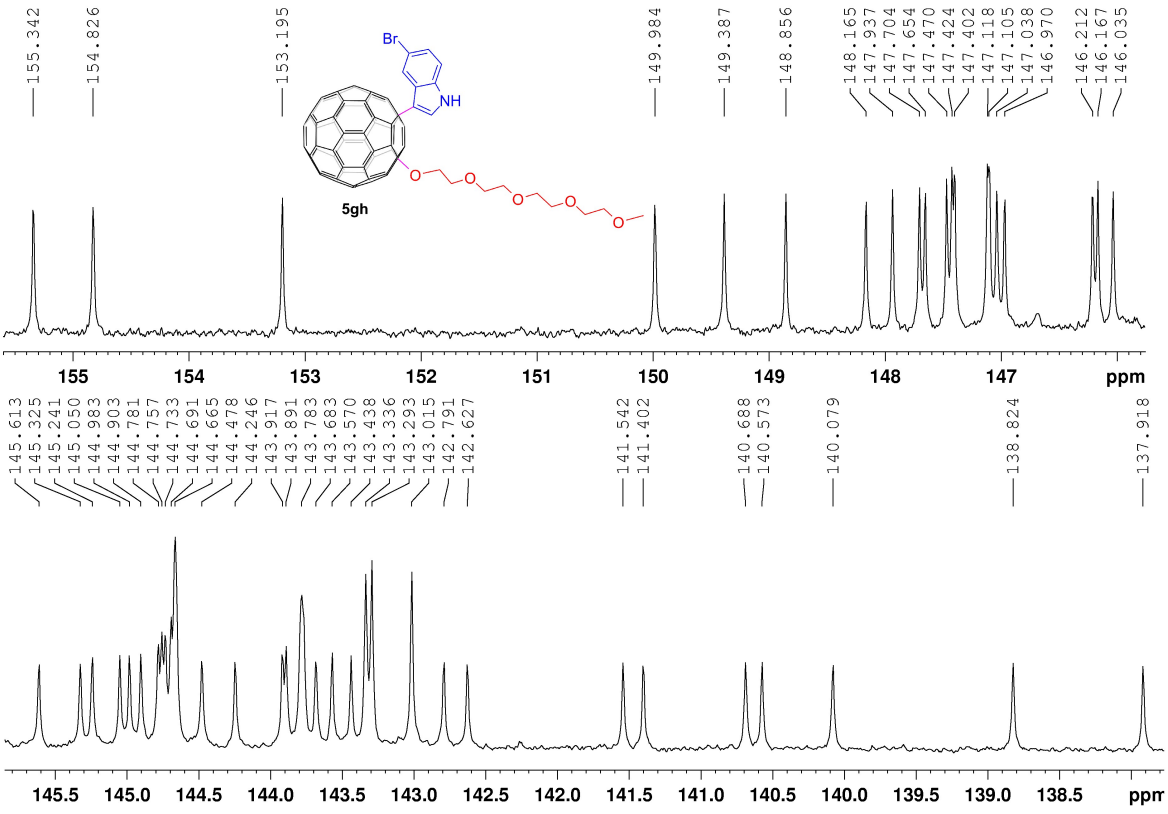
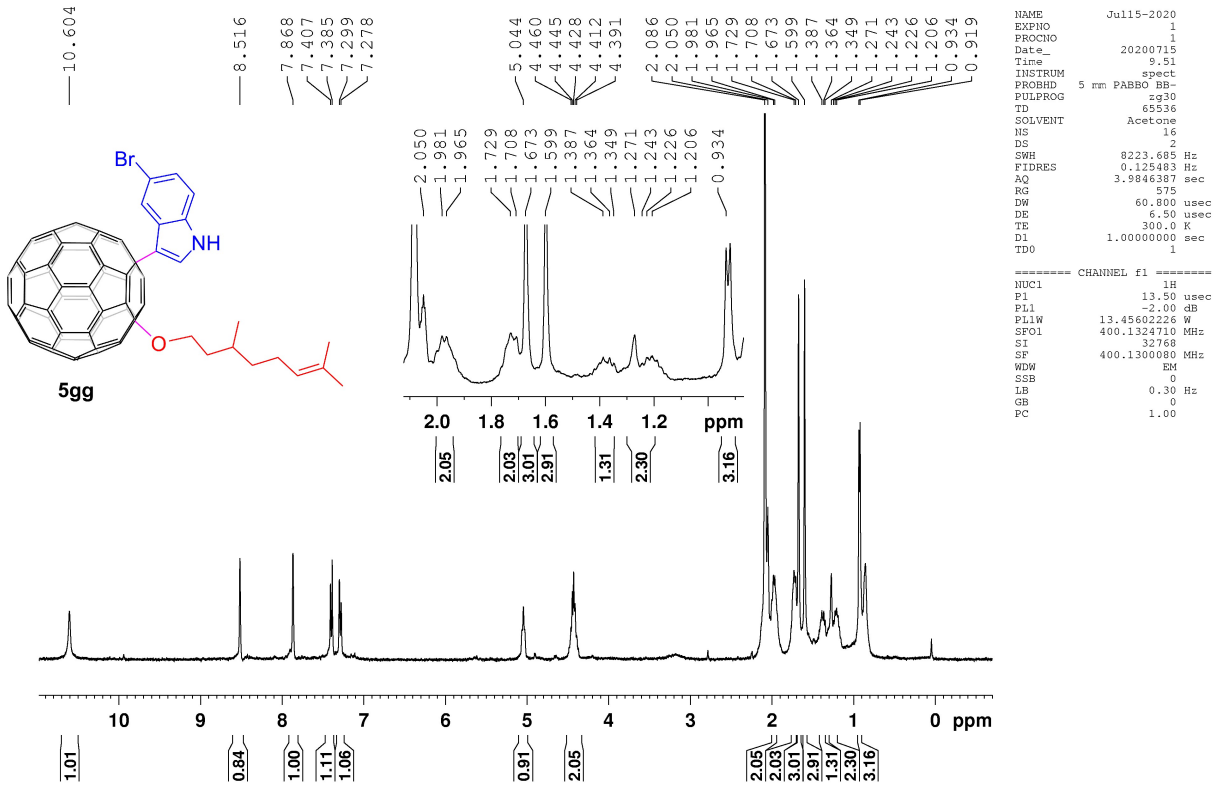
Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5gh

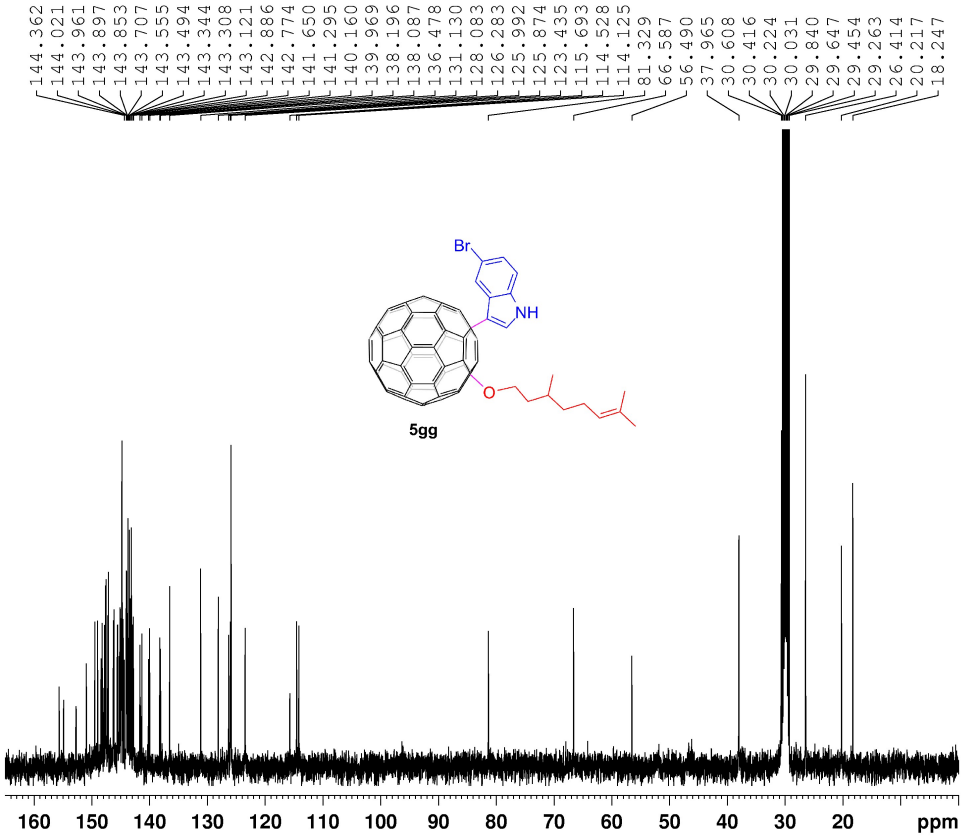


^{1}H NMR (400 MHz , Acetone-d_6/CS_2) of compound 5gg



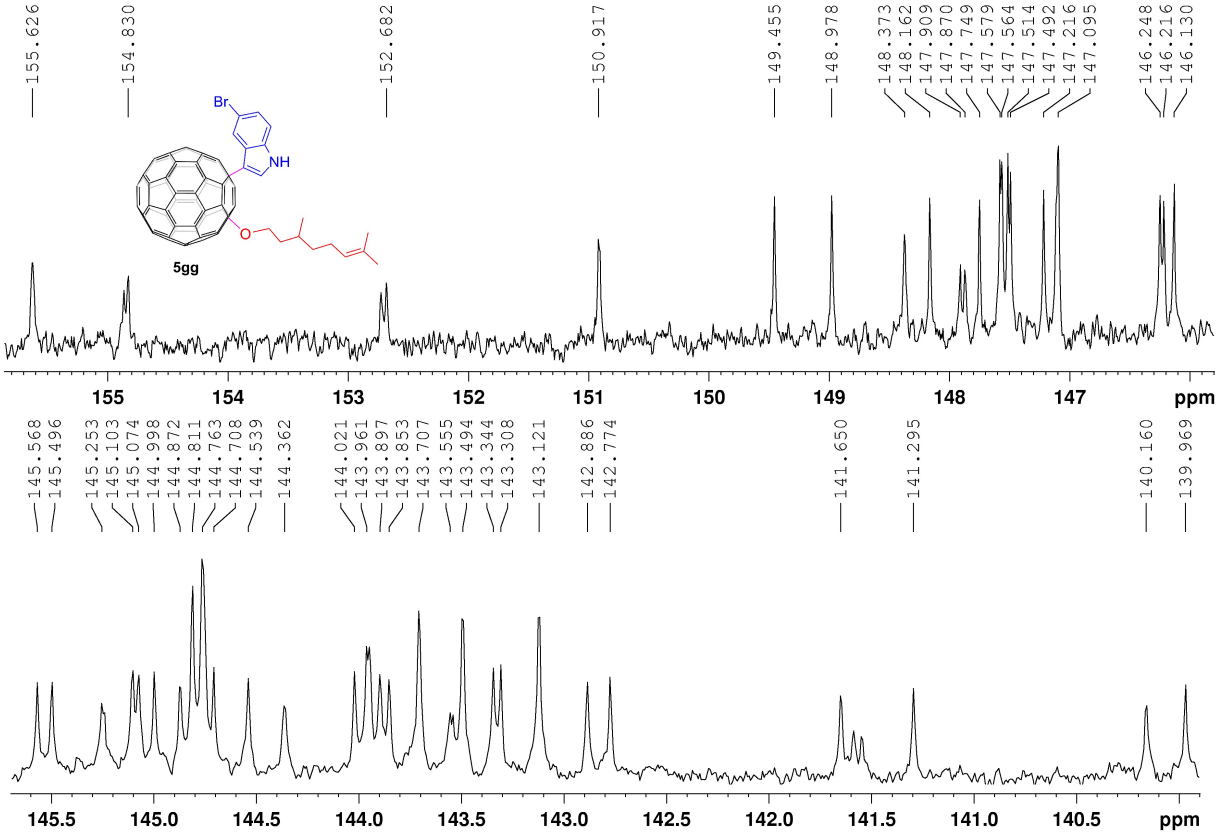

```
NAME            Jul15-2020
EXPNO                    1
PROCNO                   1
Date_             20200715
Time                 9.51
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     575
DW                60.800 usec
DE                 6.50 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.50 usec
PL1                 -2.00 dB
PL1W         13.45602226 W
SFO1         400.1324710 MHz
SI                   32768
SF           400.1300080 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

^{13}C NMR (100 MHz , d$_6$-DMSO/CS_2) of compound 5gg

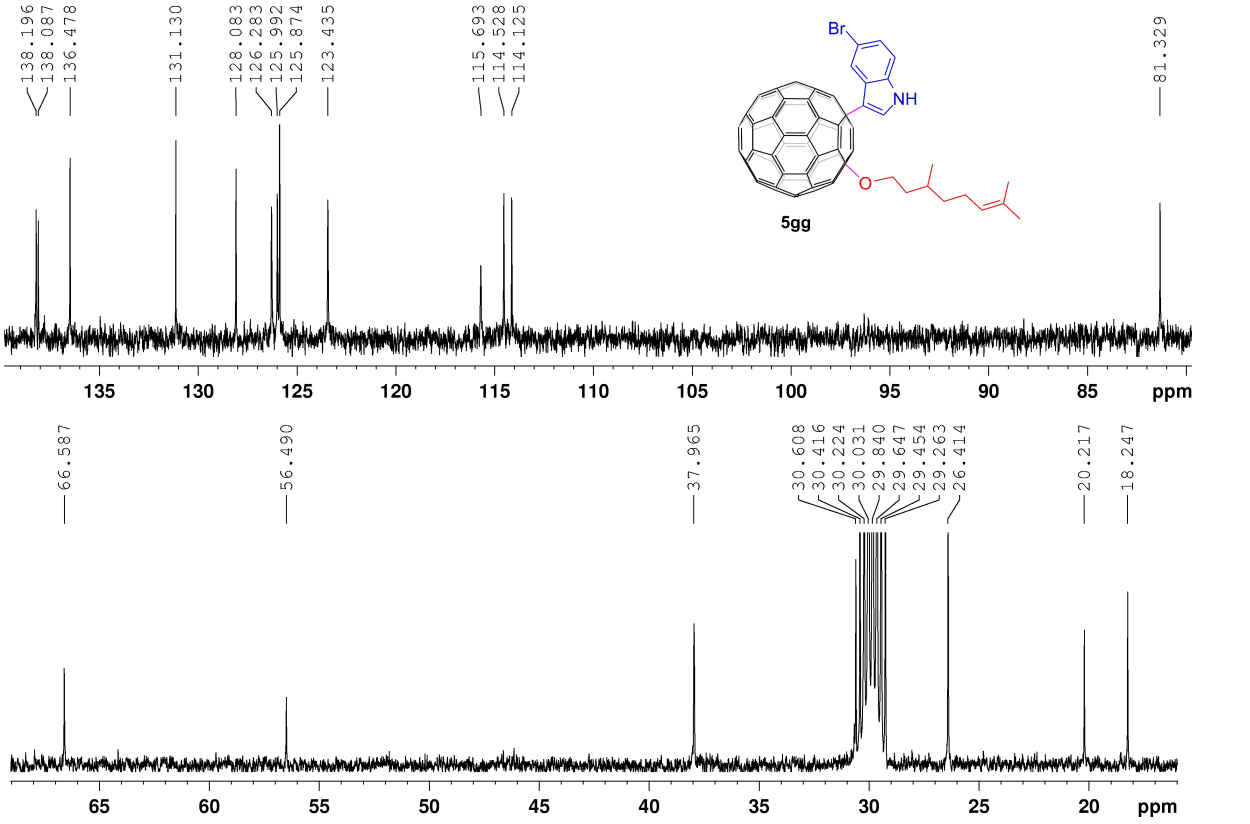



```
NAME            Jul07-2020
EXPNO                    2
PROCNO                   1
Date_             20200707
Time                 8.52
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                   20480
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    71.8
DW                20.800 usec
DE                 6.50 usec
TE                 300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.30 usec
PL1                 -2.00 dB
PL1W         54.14257431 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 -2.00 dB
PL12                13.46 dB
PL13               120.00 dB
PL2W         13.45602226 W
PL12W         0.38275132 W
PL13W         0.00000000 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127252 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.20
```

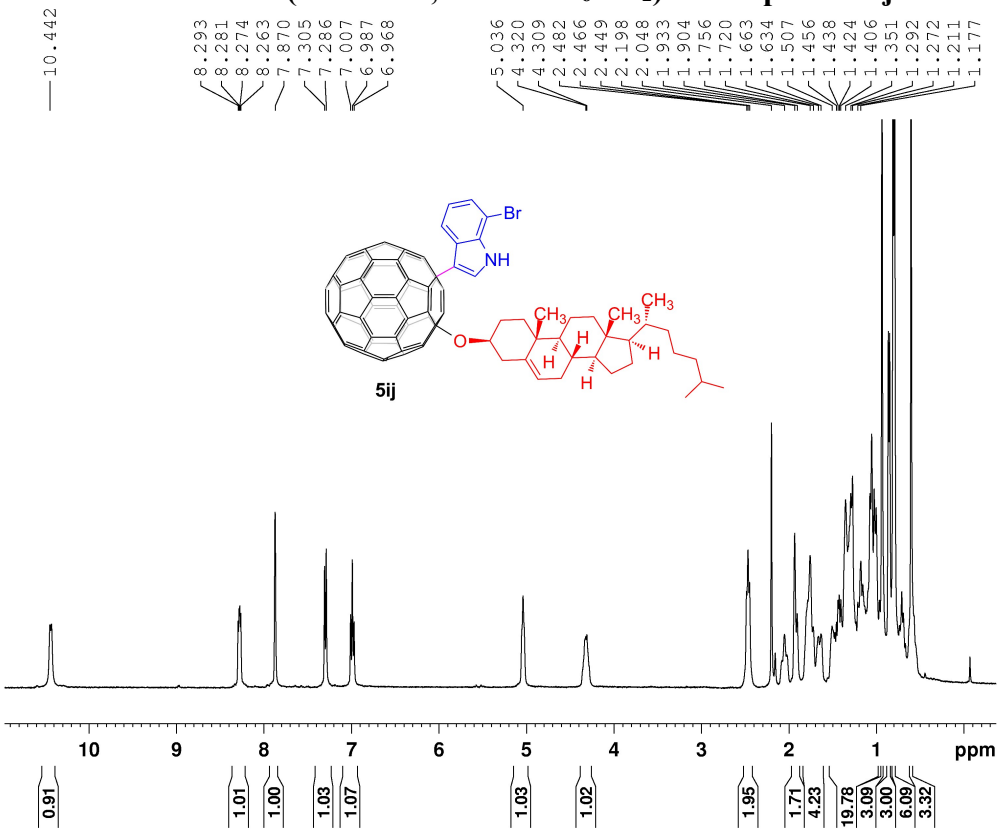
Expanded ^{13}C NMR (100 MHz , d$_6$-DMSO/CS$_2$) of compound 5gg



Expanded ^{13}C NMR (100 MHz , d$_6$-DMSO/CS$_2$) of compound 5gg

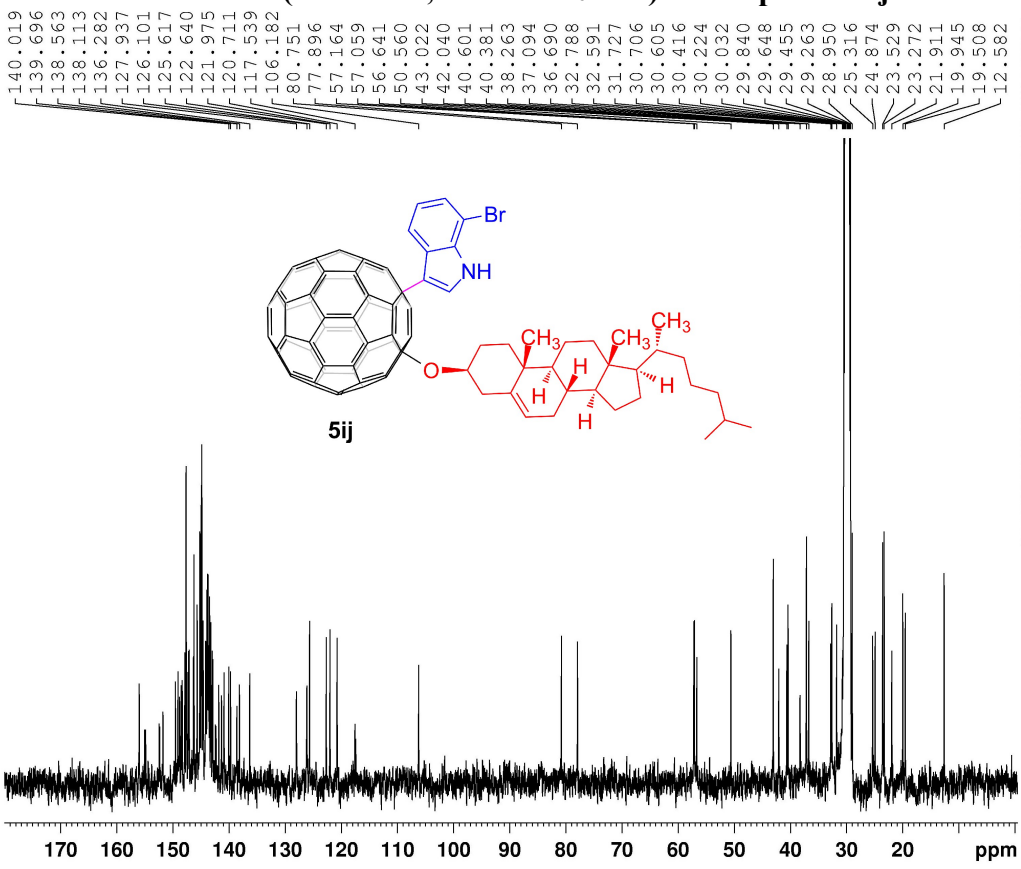


^{1}H NMR (400 MHz , Acetone-d_6/CS_2) of compound 5ij



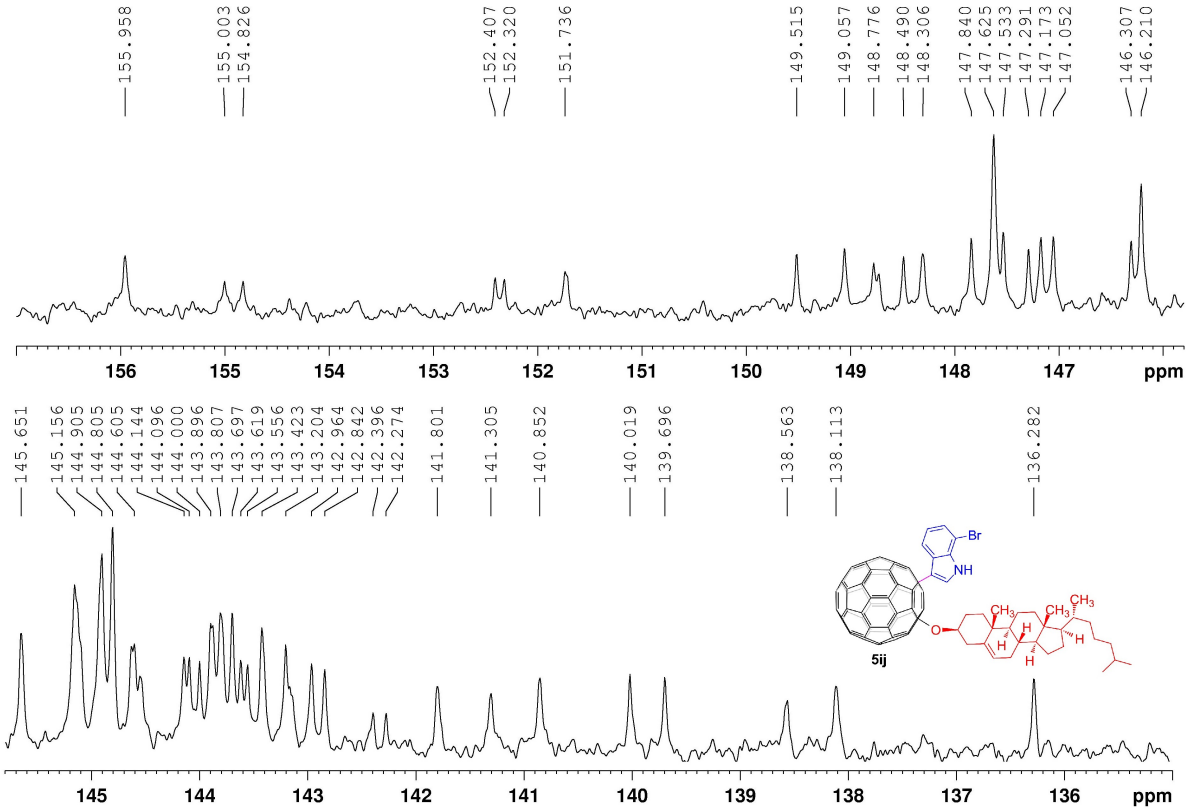

```
NAME            Jul20-2020
EXPNO                    3
PROCNO                   1
Date_             20200720
Time                10.00
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     287
DW                60.800 usec
DE                 6.50 usec
TE                300.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.50 usec
PL1                -2.00 dB
PL1W         13.45602226 W
SFO1        400.1324710 MHz
SI                   32768
SF          400.1300547 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```

^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5ij

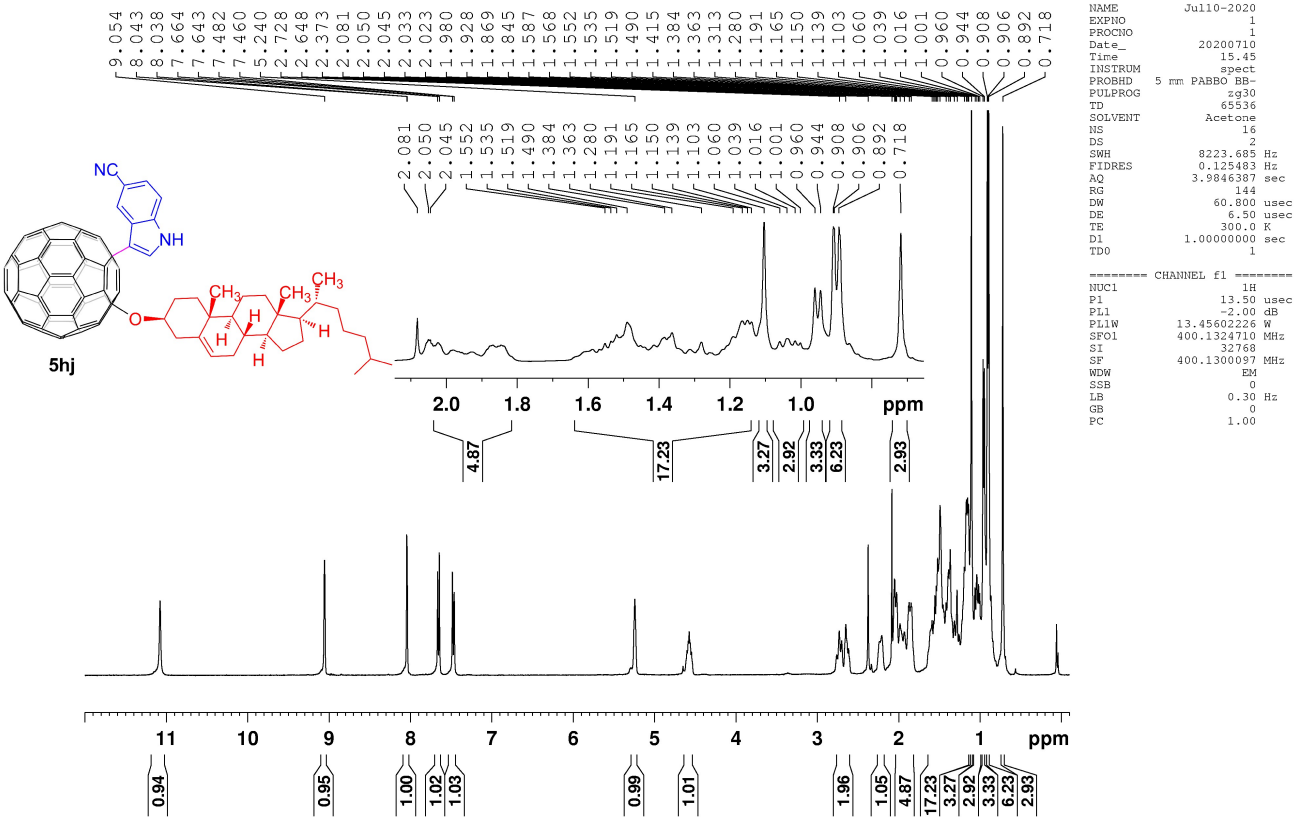



```
NAME          A424-d6-acetone
EXPNO                       2
PROCNO                      1
Date_              20200703
Time                  16.19
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                  20480
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                     64
DW                20.850 usec
DE                 6.50 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.30 usec
PL1                -2.00 dB
PL1W         54.14257431 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.46 dB
PL13              120.00 dB
PL2W         13.45602226 W
PL12W         0.38275132 W
PL13W         0.00000000 W
SFO2        400.1316005 MHz
SI                   32768
SF          100.6127171 MHz
WDW                   EM
SSB                    0
LB                 3.00 Hz
GB                     0
PC                  1.00
```

Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5ij

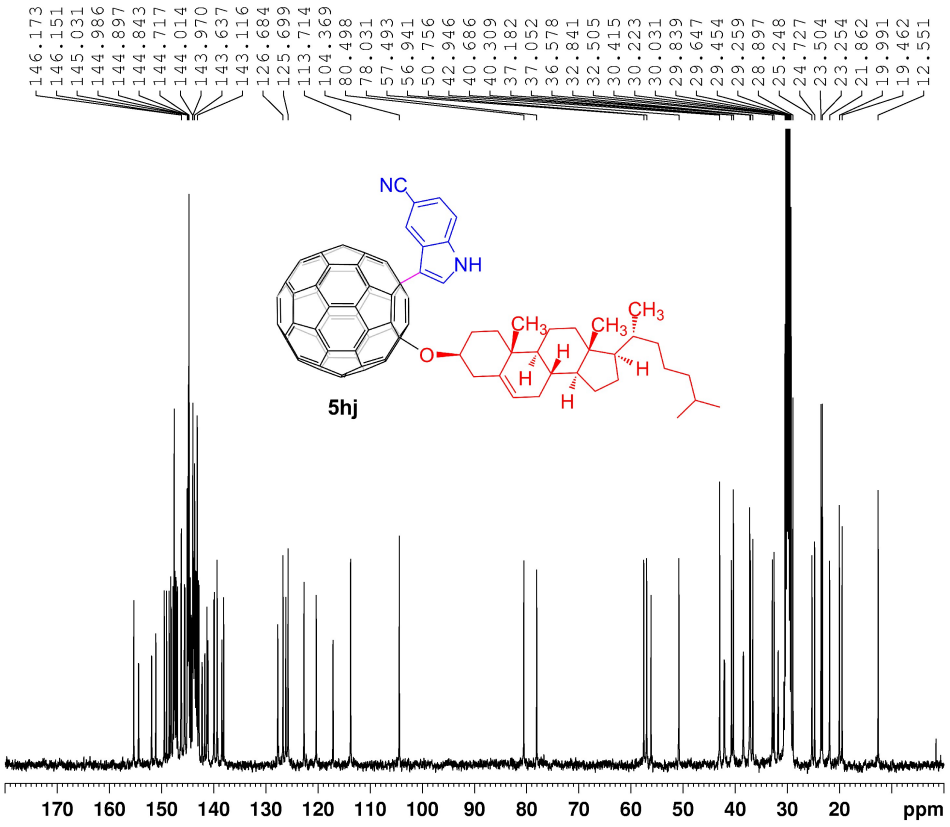


^{1}H NMR (400 MHz , Acetone-d_6/CS_2) of compound 5hj



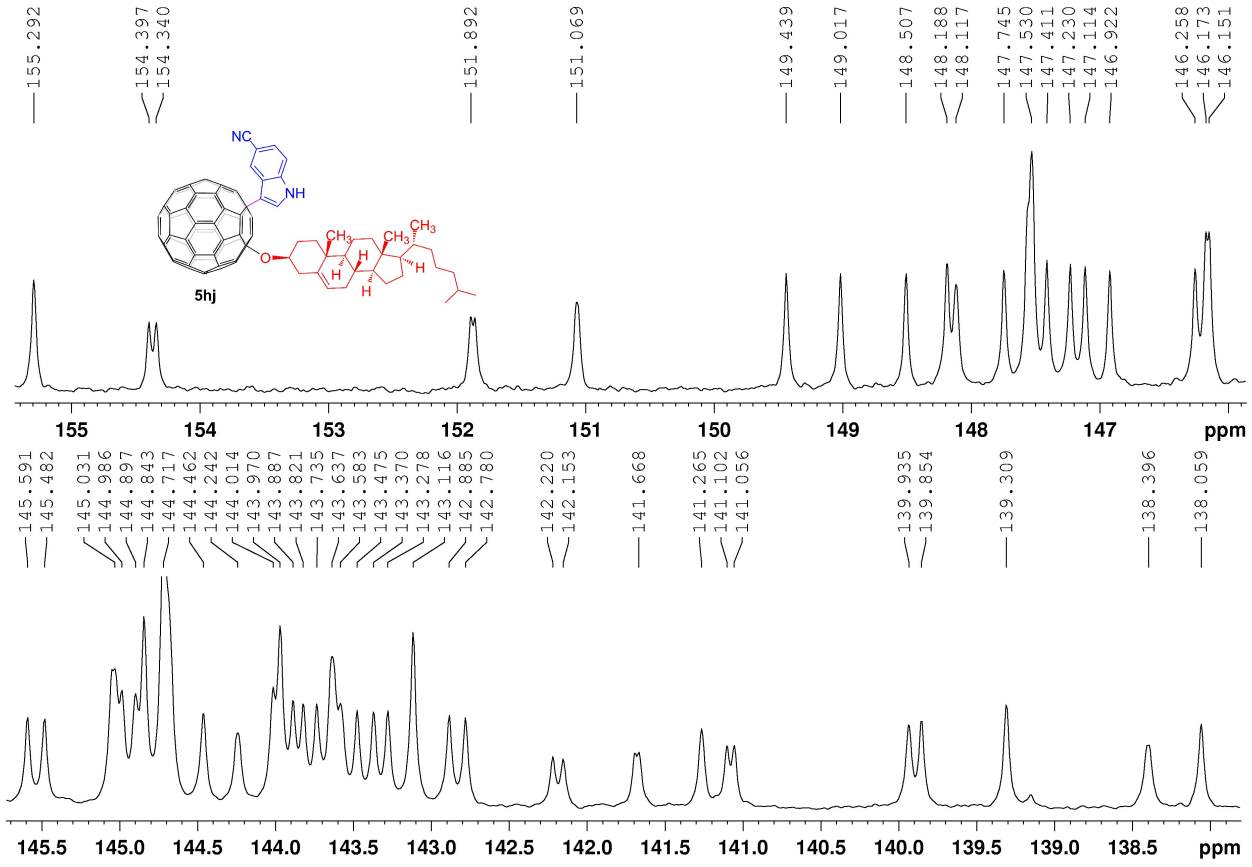

```
NAME                Jul10-2020
EXPNO                        1
PROCNO                       1
Date_                 20200710
Time                     15.45
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT               Acetone
NS                           16
DS                            2
SWH                   8223.685 Hz
FIDRES                0.125483 Hz
AQ                    3.9846387 sec
RG                         144
DW                      60.800 usec
DE                       6.50 usec
TE                      300.0 K
D1                    1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      13.50 usec
PL1                     -2.00 dB
PL1W                13.45602226 W
SFO1                400.1324710 MHz
SI                        32768
SF                  400.1300097 MHz
WDW                         EM
SSB                          0
LB                      0.30 Hz
GB                           0
PC                        1.00
```

^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5hj

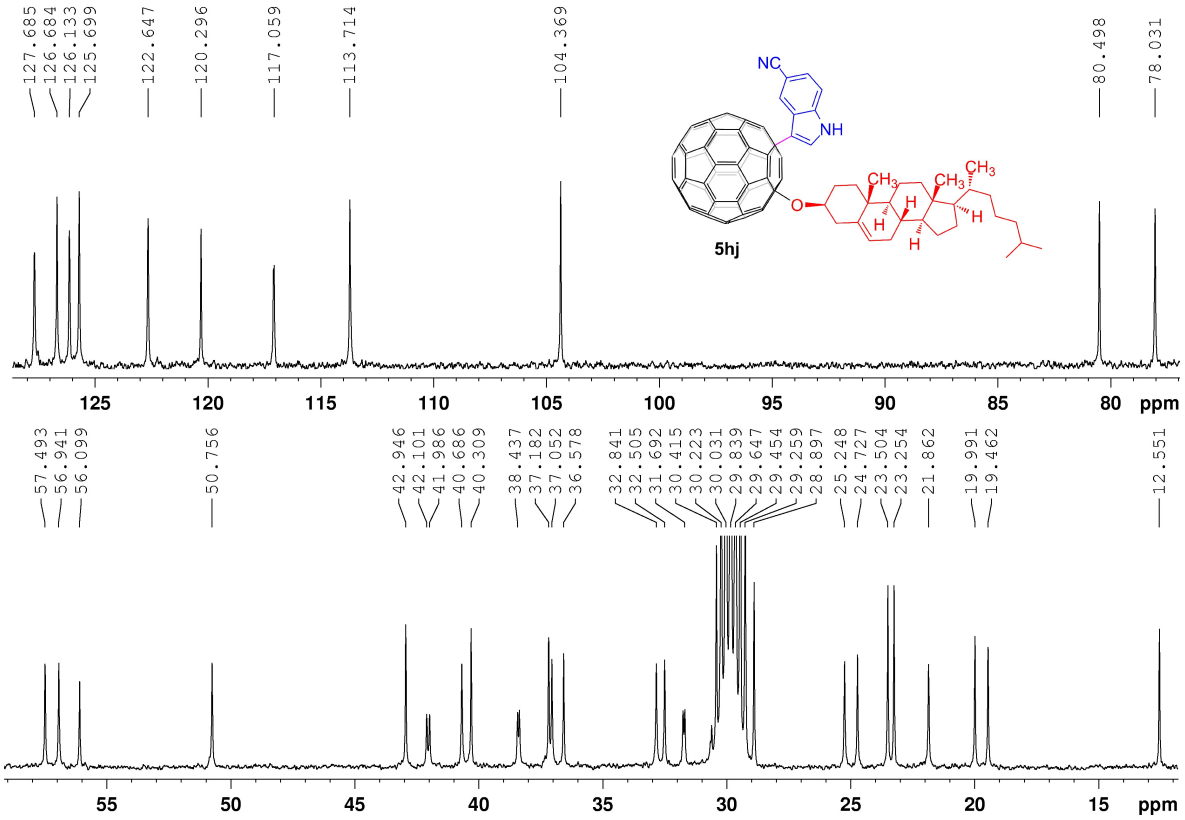



```
NAME            Jul10-2020
EXPNO                    2
PROCNO                   1
Date_             20200710
Time                 15.59
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                   20480
DS                       4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    71.8
DW                20.800 usec
DE                 6.50 usec
TE                 300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  9.30 usec
PL1                -2.00 dB
PL1W          54.14257431 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.46 dB
PL13              120.00 dB
PL2W          13.45602226 W
PL12W          0.38275132 W
PL13W          0.00000000 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127252 MHz
WDW                     EM
SSB                      0
LB                  3.00 Hz
GB                       0
PC                    1.40
```

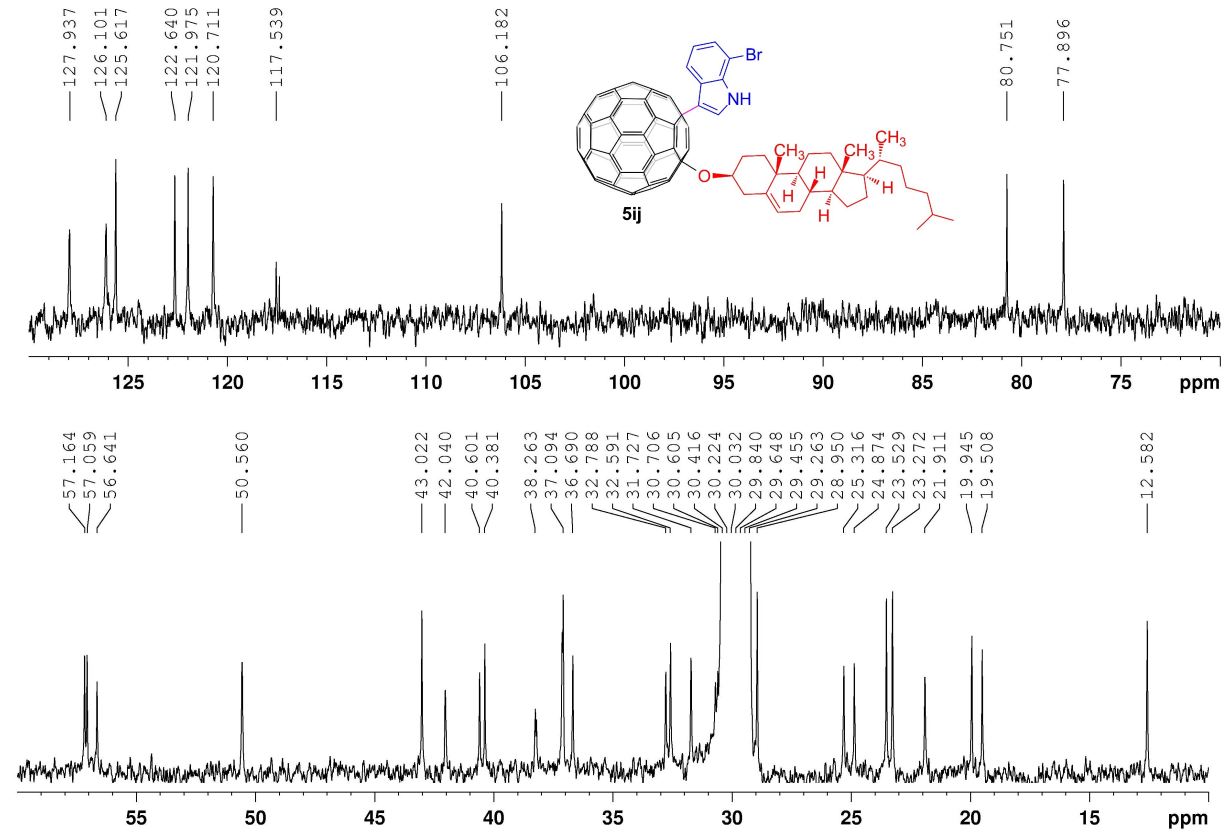
Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5hj



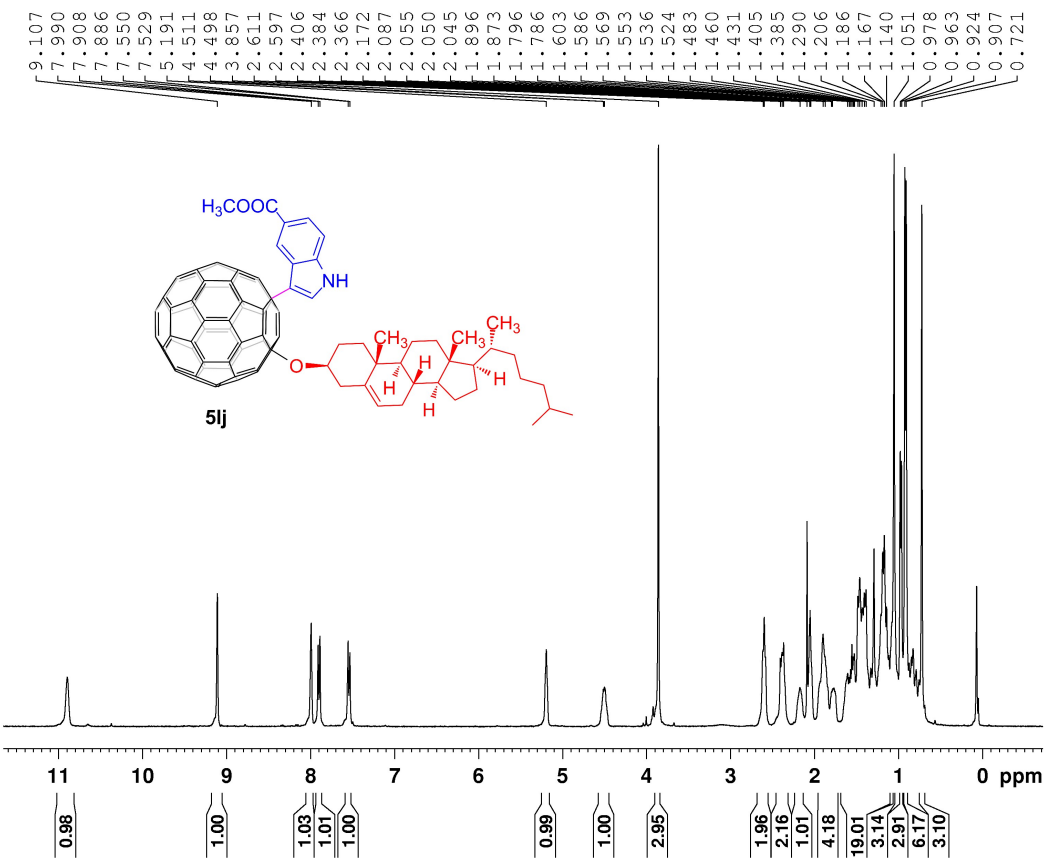
Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5hj



Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5ij

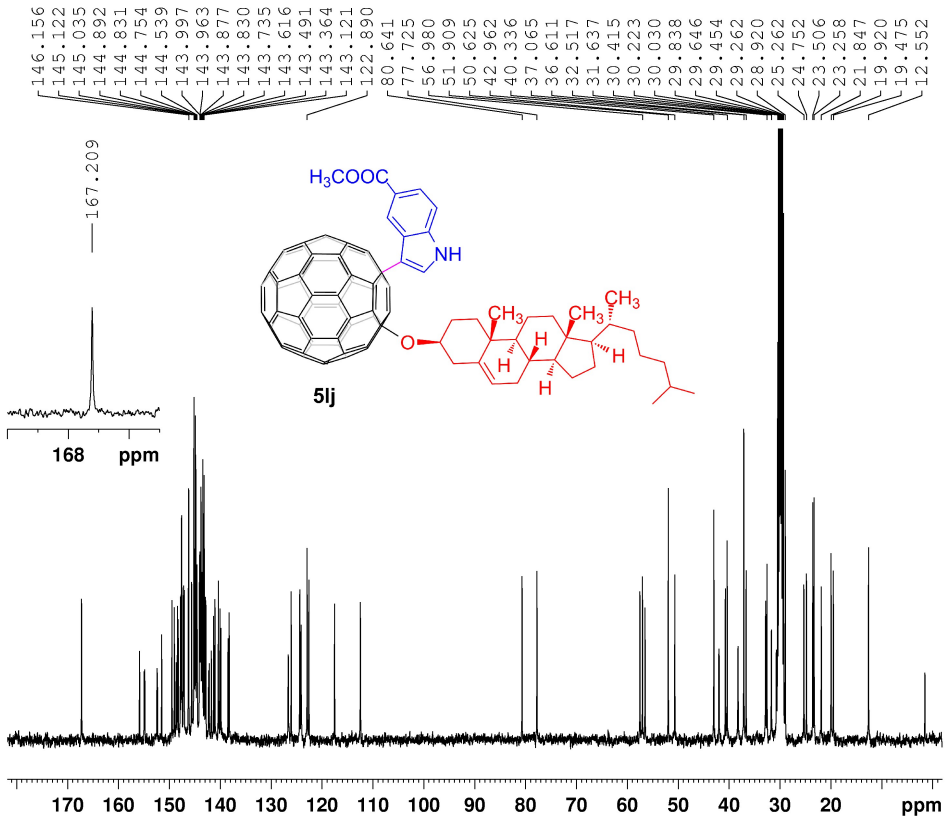


^{1}H NMR (400 MHz , Acetone-d_6/CS_2) of compound 5lj



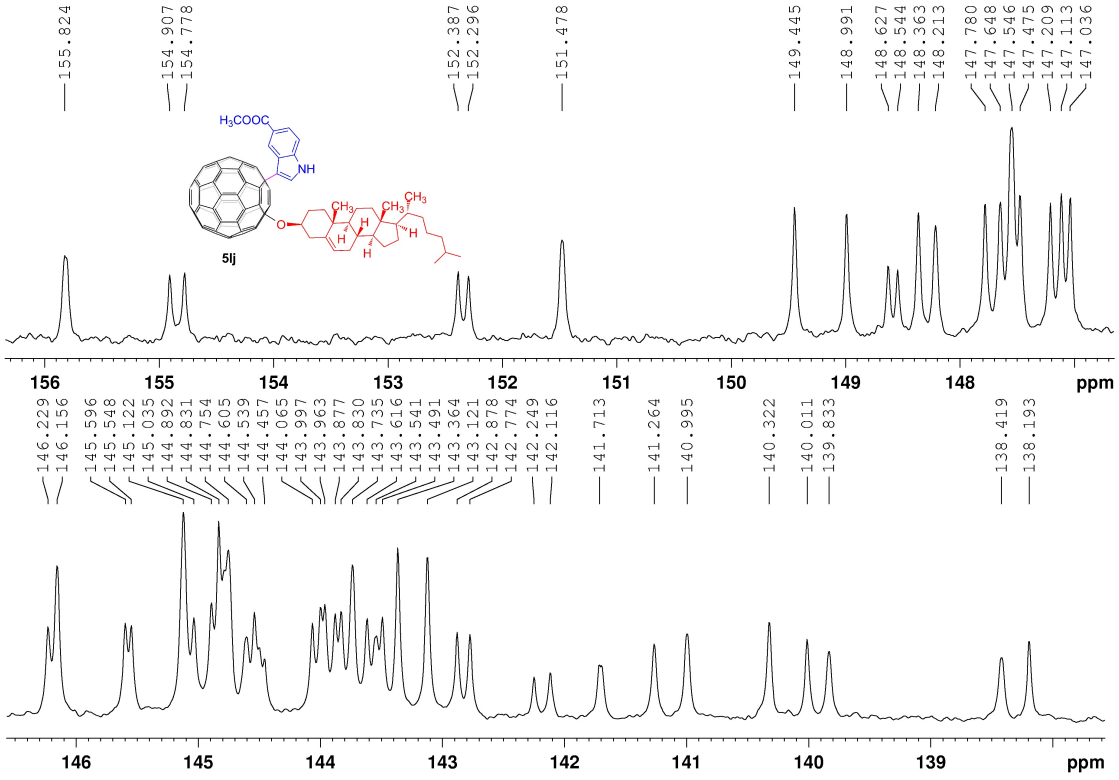

```
NAME            Jul13-2020
EXPNO                    1
PROCNO                   1
Date_             20200713
Time                10.05
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                      16
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     161
DW                60.800 usec
DE                 6.50 usec
TE                300.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.50 usec
PL1                -2.00 dB
PL1W         13.45602226 W
SFO1         400.1324710 MHz
SI                   32768
SF           400.1300075 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```

^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5lj

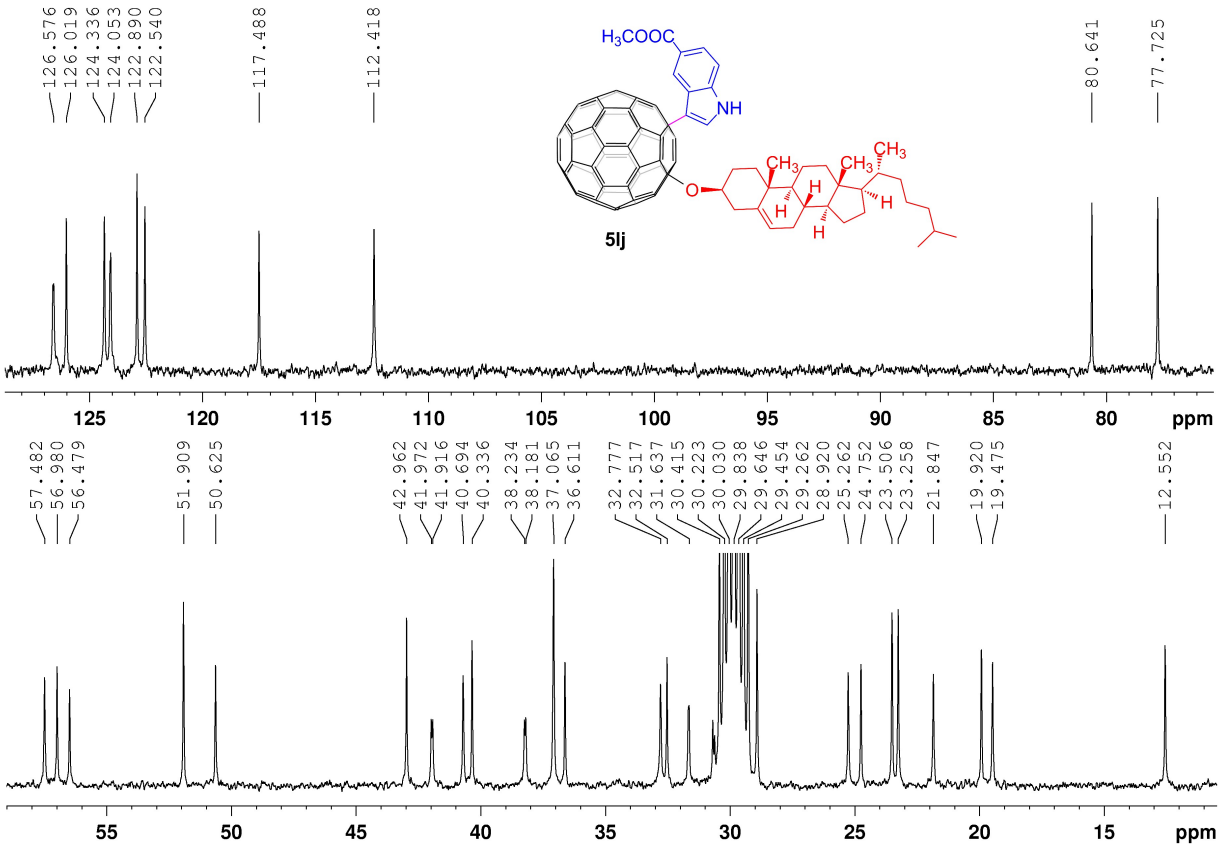



```
NAME            Jul13-2020
EXPNO                    2
PROCNO                   1
Date_             20200713
Time                10.18
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                   20480
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    80.6
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.30 usec
PL1                -2.00 dB
PL1W         54.14257431 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2                -2.00 dB
PL12               13.46 dB
PL13              120.00 dB
PL2W         13.45602226 W
PL12W         0.38275132 W
PL13W         0.00000000 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127222 MHz
WDW                    EM
SSB                     0
LB                 3.00 Hz
GB                      0
PC                   1.40
```

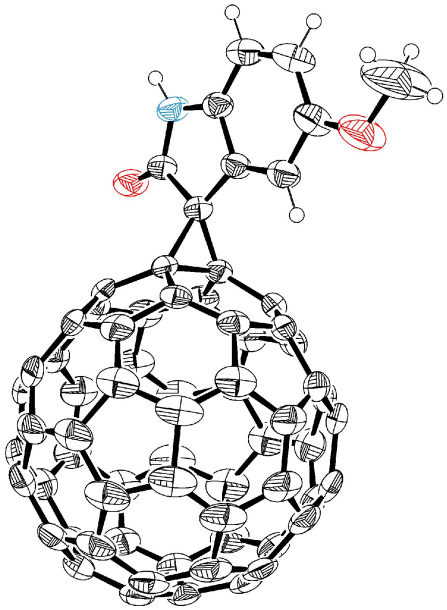
Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5lj



Expanded ^{13}C NMR (100 MHz , Acetone-d_6/CS_2) of compound 5lj



2. Single-Crystal X-Ray Crystallography of 2d, 3g, and 5aa



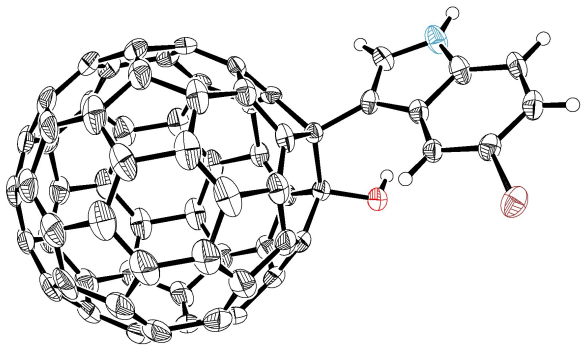
2d: X-ray crystal structure
CCDC number: 2025910

Figure S1 ORTEP diagrams of **2d** with 50% thermal ellipsoids. The solvent molecules are omitted for clarity.

Black block crystals of **2d** suitable for X-ray diffraction were obtained from slow evaporation of its solution in a mixture of CS_2 and DMSO at room temperature. Single-crystal X-ray diffraction data were collected on a diffractometer (DECTRIS PILATUS 300K, STOE & Cie GmbH) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 8.90° < 2θ < 140.22°. The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares refinement using the SHELXL-97 program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2025910.

Table 1 Crystal data and structure refinement for 2d.	
Identification code	**2d**
Empirical formula	$C_{144}H_{26}N_2O_7S_6$
Formula weight	4176.05
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.1194(5)
b/Å	17.9287(10)

c/Å	25.0200(13)
α/°	70.326(4)
β/°	78.550(4)
γ/°	78.428(4)
Volume/Å^3	4145.0(4)
Z	1
ρ_{calc}g/cm^3	1.673
μ/mm^{-1}	2.184
F(000)	2112.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	7.402 to 132.988
Index ranges	-5 ≤ h ≤ 12, -19 ≤ k ≤ 21, -28 ≤ l ≤ 29
Reflections collected	32443
Independent reflections	14135 [R_{int} = 0.0226, R_{sigma} = 0.0217]
Data/restraints/parameters	14135/0/1438
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0856, wR_2 = 0.2462
Final R indexes [all data]	R_1 = 0.1079, wR_2 = 0.2645
Largest diff. peak/hole / e Å^{-3}	1.14/-0.98



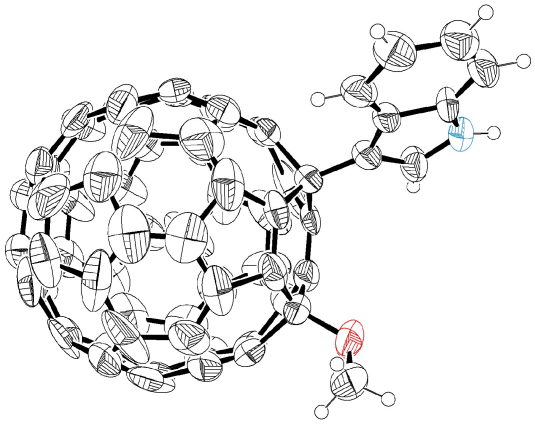
3g: X-ray crystal structure
CCDC number: 2025917

Figure S2 ORTEP diagrams of **3g** with 50% thermal ellipsoids. The solvent molecules are omitted for clarity.

Black block crystals of **3g** suitable for X-ray diffraction were obtained from slow evaporation in a mixture of CS_2 and methanol at room temperature. Single-crystal

X-ray diffraction data were collected on a diffractometer (DECTRIS PILATUS 300K, STOE & Cie GmbH) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 8.90° < 2θ < 140.22°. The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares refinement using the SHELXL-97 program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2025917.

Table 2 Crystal data and structure refinement for 3g.	
Identification code	**3g**
Empirical formula	$C_{68}H_6BrNO$
Formula weight	932.65
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.873(6)
b/Å	10.168(3)
c/Å	19.646(7)
α/°	90
β/°	114.02(2)
γ/°	90
Volume/Å^3	3991(2)
Z	4
ρ_{calc}g/cm^3	1.552
μ/mm^{-1}	1.844
F(000)	1856.0
Crystal size/mm^3	0.23 × 0.21 × 0.07
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	8.852 to 139.354
Index ranges	-20 ≤ h ≤ 26, -11 ≤ k ≤ 5, -23 ≤ l ≤ 20
Reflections collected	16721
Independent reflections	7218 [R_{int} = 0.0552, R_{sigma} = 0.0563]
Data/restraints/parameters	7218/0/641
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0835, wR_2 = 0.2271
Final R indexes [all data]	R_1 = 0.0947, wR_2 = 0.2368
Largest diff. peak/hole / e Å^{-3}	1.44/-1.19



5aa: X-ray crystal structure
CCDC number: 2025919

Figure S3 ORTEP diagrams of **5aa** with 50% thermal ellipsoids. The solvent molecules are omitted for clarity.

Black block crystals of **5aa** suitable for X-ray diffraction were obtained from slow evaporation in a mixture of CS_2 and methanol at room temperature. Single-crystal X-ray diffraction data were collected on a diffractometer (DECTRIS PILATUS 300K, STOE & Cie GmbH) equipped with a CCD area detector using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å) in the scan range 8.90° < 2θ < 140.22°. The structure was solved with direct methods using SHELXS-97 and refined with full-matrix least-squares refinement using the SHELXL-97 program within OLEX2. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC 2025919.

Table 3 Crystal data and structure refinement for 5aa.	
Identification code	**5aa**
Empirical formula	$C_{71}H_9NOS_4$
Formula weight	1020.03
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.1582(5)
b/Å	16.9627(10)
c/Å	23.5264(12)
α/°	90
β/°	95.305(4)
γ/°	90
Volume/Å^3	4036.5(4)

Z	4
ρ_{calc}g/cm^3	1.678
μ/mm^{-1}	2.650
F(000)	2056.0
Crystal size/mm^3	0.3× 0.2 × 0.1
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	9.176 to 139.614
Index ranges	-11 ≤ h ≤ 12, -16 ≤ k ≤ 20, -19 ≤ l ≤ 28
Reflections collected	11433
Independent reflections	5365 [R_{int} = 0.0937, R_{sigma} = 0.0804]
Data/restraints/parameters	5365/0/641
Goodness-of-fit on F^2	0.962
Final R indexes [I>=2σ (I)]	R_1 = 0.0619, wR_2 = 0.1205
Final R indexes [all data]	R_1 = 0.1420, wR_2 = 0.1587
Largest diff. peak/hole / e Å^{-3}	0.17/-0.13

3. HPLC Profiles of the reaction mixtures for the synthesis of 2a, 2e, 3g and 5ie

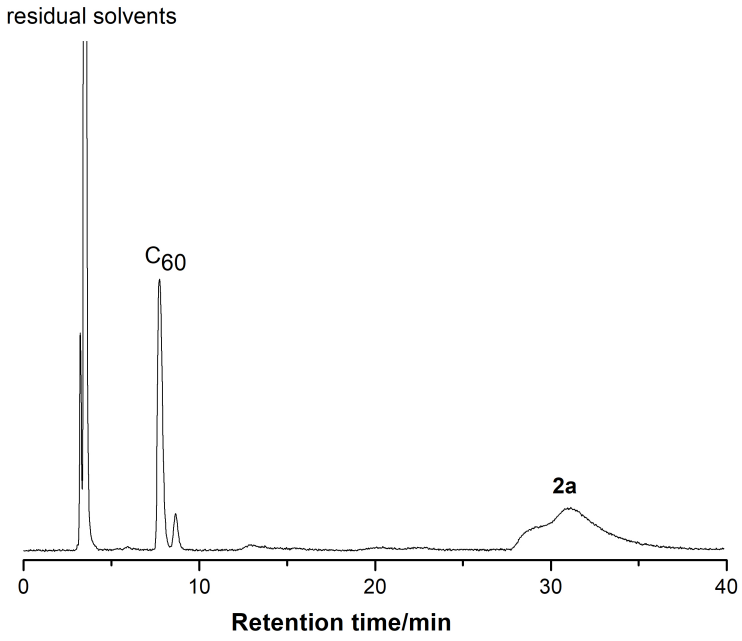


Figure S4. The HPLC profile of the reaction mixtures of toluene solution containing **2a** monitored by HPLC. HPLC column: Cosmosil Buckyprep column (4.6 ×250 mm; toluene, 1 mL/min; 326 nm; 25 °C).

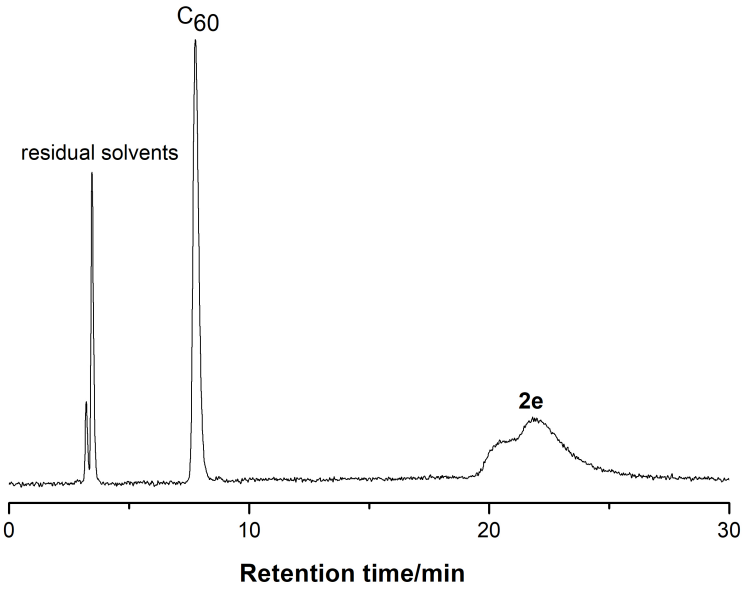


Figure S5. The HPLC profile of the reaction mixtures of toluene solution containing **2e** monitored by HPLC. HPLC column: Cosmosil Buckyprep column (4.6 ×250 mm; toluene, 1 mL/min; 326 nm; 25 °C).

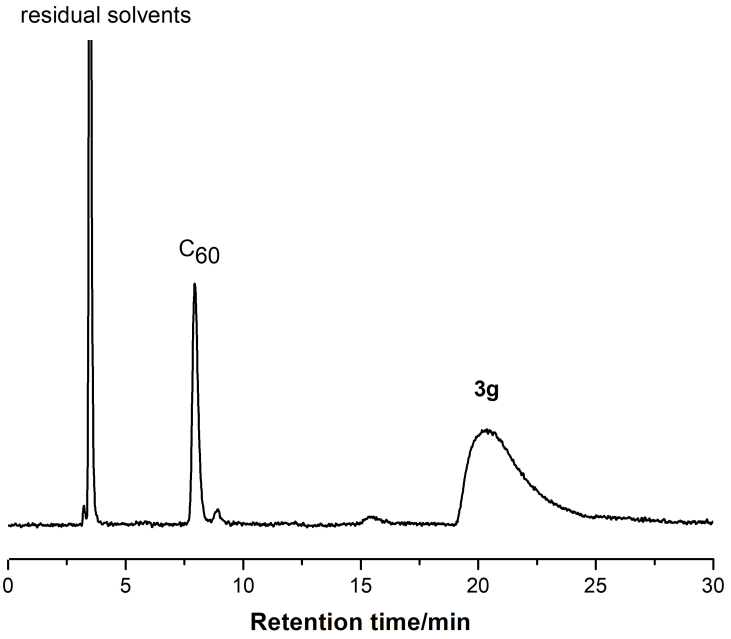


Figure S6. The HPLC profile of the reaction mixtures of toluene solution containing **3g** monitored by HPLC. HPLC column: Cosmosil Buckyprep column (4.6 ×250 mm; toluene, 1 mL/min; 326 nm; 25 °C).

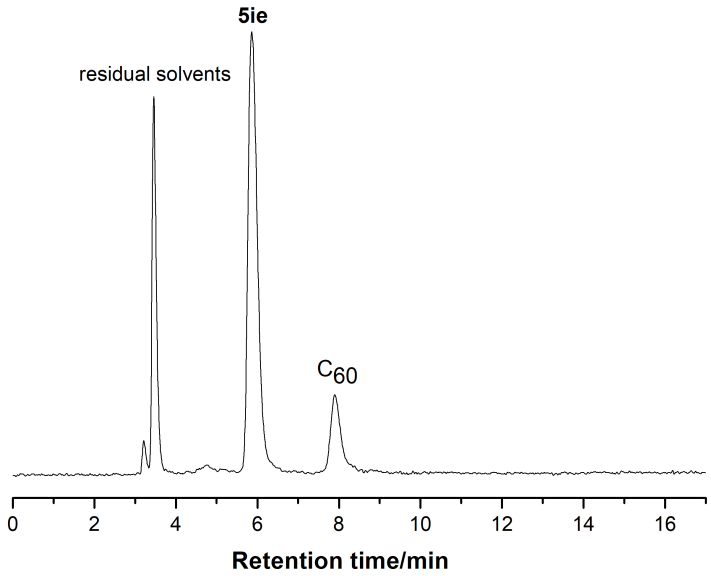
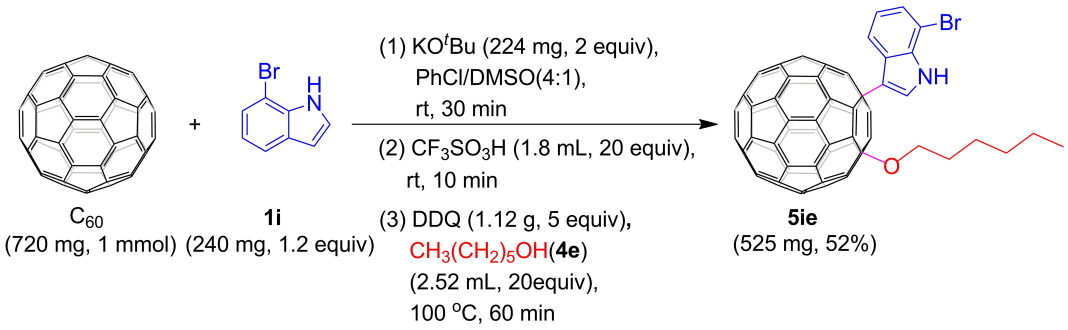


Figure S7. The HPLC profile of the reaction mixtures of toluene solution containing **5ie** monitored by HPLC. HPLC column: Cosmosil Buckyprep column (4.6 ×250 mm; toluene, 1 mL/min; 326 nm; 25 °C).

4. Scale-up procedure for synthesis of 5ie

Scheme S1. Scale-up synthesis of **5ie**

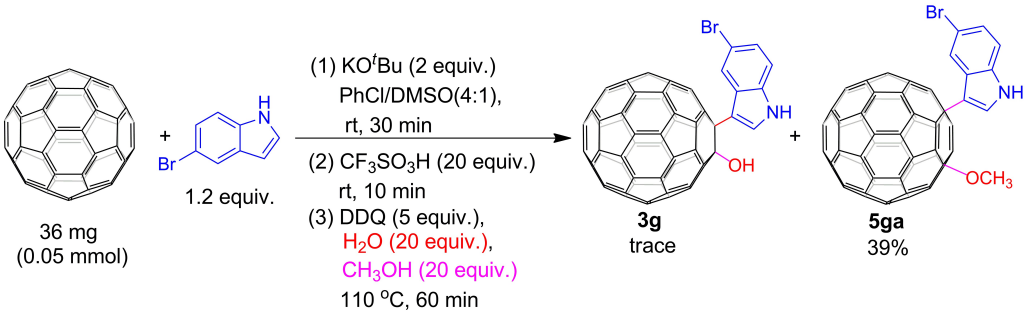


C_{60} (720 mg, 1 mmol), 7-bromoindole (240 mg, 1.2 mmol), KO^{t}Bu (224 mg, 2 mmol) were dissolved in chlorobenzene (160 mL) at room temperature under Ar atmosphere. Then DMSO (40 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (1.8 mL, 20 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (1.12 g, 5 mmol) and $CH_3(CH_2)_5OH$ (2.52 mL, 20 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 400 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the

eluent to give unreacted C_{60} (166 mg, 23%) and **5ie** (525 mg, 52%) as black amorphous solid.

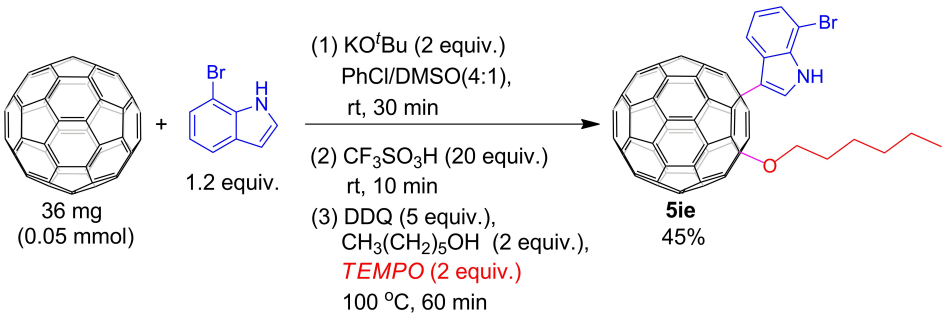
5. Experimental Procedures of Mechanism Studies

Scheme S2. Control experiment for the synthesis of **3g** and **5ga**



C_{60} (36.0 mg, 0.05 mmol), 5-bromoindole (12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol), H_2O (18 μL, 1 mmol) and CH_3OH (40 μL, 1 mmol) were added to the mixture and stirred in an oil bath at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (1.5 mg, 4%) and **5ga** (18.3 mg, 39%) as black amorphous solid.

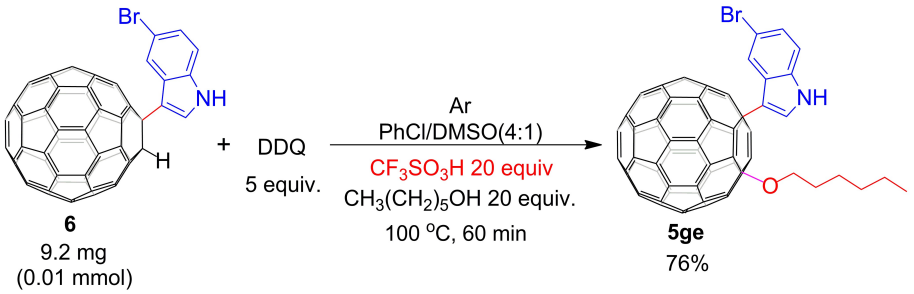
Scheme S3. Control experiment for the synthesis of **5ie**



C_{60} (36.0 mg, 0.05 mmol), 7-bromoindole(12 mg, 0.06 mmol), KO^{t}Bu (11.2 mg, 0.1 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then DMSO (2 mL) was added to the mixture and the color of the solution changed gradually from purple to dark green. After being stirred for 30 minutes, CF_3SO_3H (90 μL, 1 mmol) was added to the mixture and the color changed from dark green to yellowish brown. And after being stirred for 10 minutes, DDQ (56 mg, 0.25 mmol), $CH_3(CH_2)_5OH$ (12.6 μL, 0.1 mmol) and TEMPO

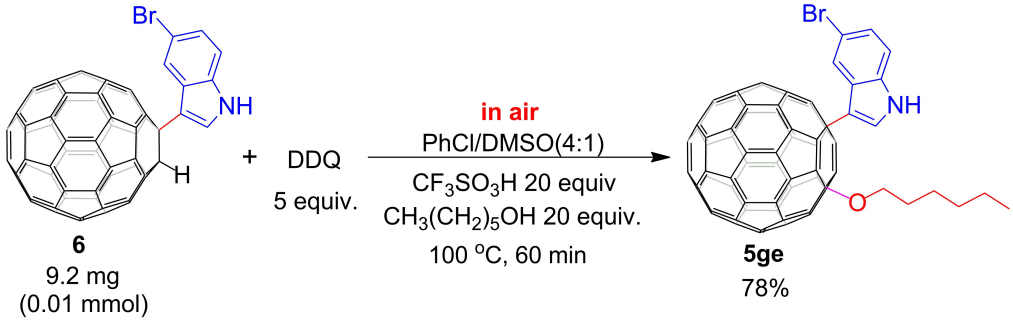
(2,2,6,6-tetramethylpiperidine-1-oxyl) (15.6 mg, 0.1 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 20 mL carbon disulfide. Resulting dark-yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give unreacted C_{60} (3.8 mg, 11%) and **5ie** (22.7 mg, 45%) as black amorphous solid.

Scheme S4. Synthesis of **5ge** from 1,2-(hydro)[60]fulleroindole **6** through DDQ oxidization.



1,2-(Hydro)[60]fulleroindole **6** (9.2 mg, 0.01 mmol) and DDQ (11.5 mg, 0.05 mmol) were dissolved in chlorobenzene (2 mL) and DMSO (0.5 mL) at room temperature under Ar atmosphere. Then CF_3SO_3H (18 μL, 0.2 mmol) and $CH_3(CH_2)_5OH$ (25.2 μL, 0.2 mmol) were added to the mixture and stirred in an oil bath at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 10 mL carbon disulfide. Resulting yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (2:1) as the eluent to give **5ge** (7.7 mg, 76%) as black amorphous solid.

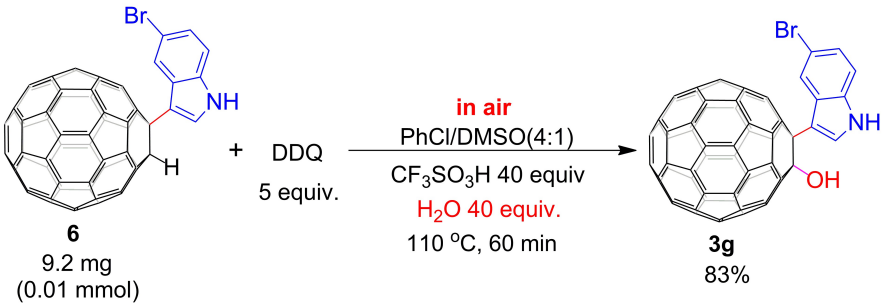
Scheme S5. Synthesis of **5ge** from 1,2-(hydro)[60]fulleroindole **6** through DDQ oxidization in air.



1,2-(Hydro)[60]fulleroindole **6** (9.2 mg, 0.01 mmol) and DDQ (11.5 mg, 0.05 mmol) were dissolved in chlorobenzene (2 mL) and DMSO (0.5 mL) at room temperature in air. Then CF_3SO_3H (18 μL, 0.2 mmol) and $CH_3(CH_2)_5OH$ (25.2 μL, 0.2 mmol) were added to the mixture and stirred in an oil bath in air at 100 °C for 60 minutes. The mixture was cooled to room temperature and then added 10 mL carbon disulfide. Resulting yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon

disulfide/dichloromethane (2:1) as the eluent to give **5ge** (8.0 mg, 78%) as black amorphous solid.

Scheme S6. Synthesis of **3g** from 1,2-(hydro)[60]fulleroindole **6** through DDQ oxidization in air.



1,2-(Hydro)[60]fulleroindole **6** (9.2 mg, 0.01 mmol) and DDQ (11.5 mg, 0.05 mmol) were dissolved in chlorobenzene (2 mL) and DMSO (0.5 mL) at room temperature in air. Then CF_3SO_3H (36 μL, 0.4 mmol) and H_2O (9 μL, 0.4 mmol) were added to the mixture and stirred in an oil bath in air at 110 °C for 60 minutes. The mixture was cooled to room temperature and then added 10 mL carbon disulfide. Resulting yellow solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide/dichloromethane (1:1) as the eluent to give **3g** (7.8 mg, 83%) as black amorphous solid.