-Electronic Supplementary Information-

Electron-rich Carbon Nanorings as Macrocyclic Hosts for Fullerenes

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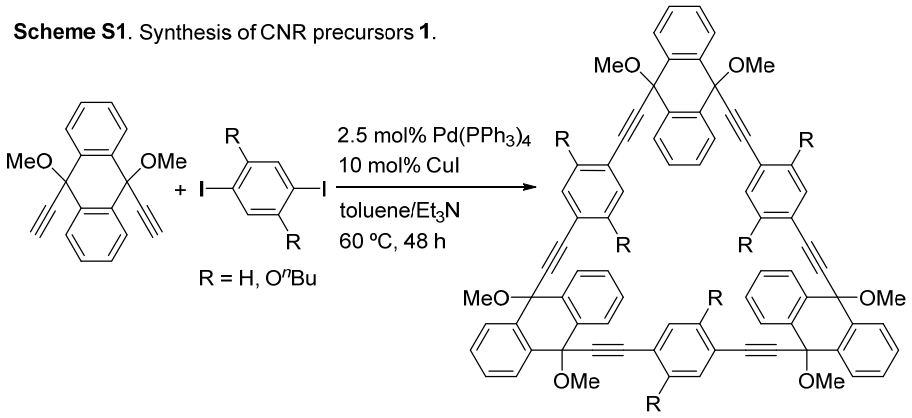
General Procedures. All solvents were dried by the usual methods and distilled before use. Organic reagents were used as purchased. All catalytic reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Column chromatographies were performed on silica gel (230-400 mesh). Analytical TLC was performed on ready-made plates coated with silica gel on glass. Gel permeation chromatography (GPC: LC-908 equipped with JAIGEL-1H and JAIGEL-2H as size exclusion columns, Japan Analytical Industry Co., Ltd.) with $CHCl_3$ as an eluent was performed to purify macrocycles. The NMR spectra were measured for solutions in $CDCl_3$ and CD_2Cl_2 with Me_4Si as an internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. 9,10-Diethynyl-9,10-dimethoxy-9,10-dihydroanthracene were synthesized by the reported procedure.[1] Fullerene was purchased from Matsubo Co., Japan.

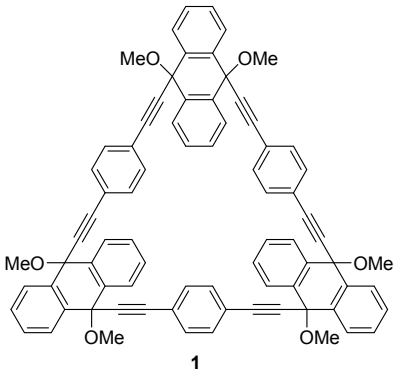
Synthesis of cyclotrimers 1.

In both cases, cyclodimers, cyclotetramers and larger size of macrocycles were detected but difficult to be isolated even by recycle GPC purification.

Scheme S1. Synthesis of CNR precursors **1**.

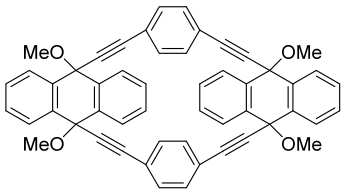


Synthesis of cyclotrimer 1.



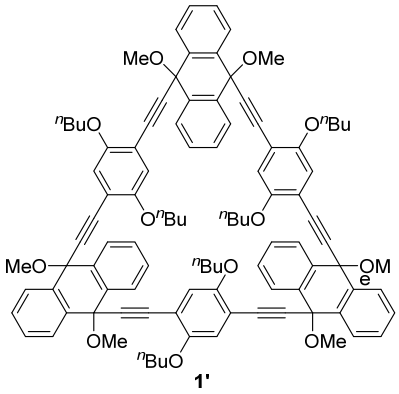
A solution of 9,10-diethynyl-9,10-dimethoxy-9,10-dihydroanthracene (0.58 g, 2.0 mmol) and 1,4-diiodobenzene (0.66 g, 2.0 mmol) in toluene/Et_3N (v:v = 4:1, 200 mL, 0.01 M) was degassed. To this solution were added CuI (38 mg, 0.20 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) at room temperature. After stirring for 48 h at 60 ºC, the reaction mixture was cooled and washed with saturated NH_4Cl aqueous solution. The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give cyclotrimer **1** (0.11 g, 0.10 mmol, 15%) as a pale yelow solid. Under the present reaction conditions, cyclodimer was also obtained in 3% yield. mp > 250 °C; IR (KBr) 2929, 2226 (C≡C), 1507, 1448, 1241, 1079, 1041, 953, 912, 837, 776, 755, 739, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25°C) δ 2.75 (s, 18H), 7.12 (s, 12H), 7.49 (dd, J = 3.3, 5.9 Hz, 12H), 7.91 (dd, J = 3.3, 5.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 50.6, 71.1, 85.2, 93.8, 122.4, 128.1, 129.4, 131.4, 134.9. HRMS (FAB) calcd for $C_{78}H_{55}O_6$ ($M+H^+$): 1087.3999. Found: 1087.4009.

Cyclodimer:



A white solid (21 mg, 3%); mp > 250 °C; IR (KBr) 2927, 2223 (C≡C), 1637, 1449, 1267, 1230, 1085, 1041, 966, 908, 836, 777, 719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.04 (s, 12H), 6.52 (s, 8H), 7.50 (dd, J = 3.3, 5.9 Hz, 8H), 7.85 (dd, J = 3.3, 5.9 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 51.7, 71.9, 86.7, 91.9, 122.1, 126.6, 128.9, 130.9, 135.7. HRMS calcd for $C_{52}H_{37}O_4$ ($M+H^+$): 725.2692. Found: 725.2701.

Synthesis of cyclotrimer 1′.

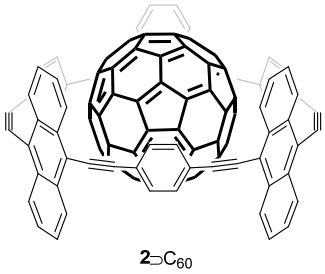


1'

Cyclotrimer **1′** was obtained from 9,10-diethynyl-9,10-dimethoxy-9,10-dihydroanthracene and 2,5-di-*n*-butoxy-1,4-diiodobenzene[2] in the same procedure shown above. A pale yellow solid (15%); mp > 250 °C; IR(KBr) 2956, 2931, 2871, 2227 (C≡C), 1499, 1412, 1218, 1077, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.74 (t, J = 7.3 Hz, 18H), 1.09-1.21 (m, 12H), 1.37-1.46 (m, 12H), 2.76 (s, 18H), 3.58 (q, J = 6.2 Hz, 12H), 6.58 (s, 6H), 7.46 (dd, J = 3.3, 5.9 Hz, 12H), 7.93 (dd, J = 3.3, 5.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 13.8, 18.9, 31.2, 50.6, 68.9, 71.3, 82.0, 97.2, 113.4, 116.9, 128.2, 129.1, 135.1, 153.8. HRMS (FAB) calcd for $C_{102}H_{103}O_{12}$ ($M+H^+$): 1519.7450. Found: 1519.7451.

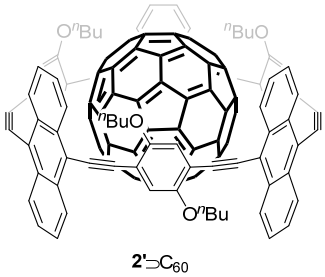
Reductive aromatization of cyclotrimers 1 with C_{60}

Synthesis of 2⊃C_{60}.



A solution of **1** (0.030 g, 0.028 mmol) in CH_2Cl_2 (25 mL) was degassed by bubbling of N_2 gas for 15 min. A solution of $SnCl_2 \cdot 2H_2O$ (0.63 g, 2.8 mmol) in 1N HCl aqueous solution (45 mL) was also degassed by bubbling of N_2 gas for 15 min. C_{60} (0.020 g, 0.028 mmol) and this aqueous solution were successively added to the organic solution and gently stirred at room temperature in dark for 18 h (the color of the reaction mixture changed to redish brown). The aqueous solution was extracted with CH_2Cl_2 (15 mL x 2). The combined organic solution was washed with sat. $NaHCO_3$ aqueous solution and dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give 1:1 complex **2⊃C_{60}** (23 mg, 0.014 mmol, 51%) as a dark red-brown solid. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 7.57-7.60 (m, 24H), 8.53 (dd, J = 3.3, 6.3 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 97.4, 106.3, 119.3, 124.2, 127.0, 127.2, 131.8, 132.6, 142.3, 142.5, 142.8, 142.9, 143.1, 143.2, 143.3, 143.8. HRMS (FAB) calcd for $C_{132}H_{37}$ (M^+): 1621.2895. Found: 1621.2911. FAB mass spectra and variable temperature ^{1}H NMR data are shown in Figures S1 and S2a.

Synthesis of 2′⊃C_{60}.



The 1:1 complex **2′⊃C_{60}** was obtained from **1′** and fullerene under the same reaction conditions shown above. **2′⊃C_{60}**: a black solid (17 mg, 35%); IR(KBr) 2954, 2927, 2869, 2146 (C≡C), 1495, 1465, 1421, 1378, 1216, 1200, 1026, 763, 634, 527 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.13 (t, J = 7.3 Hz, 18H), 1.65-1.78 (m, 12H), 1.97-2.07 (m, 12H), 4.15 (t, J = 6.3 Hz, 12H), 7.01 (s, 6H), 7.53-7.61 (m, 12H), 8.55 (d, J = 6.9 Hz, 6H), 8.71 (d, J = 7.2 Hz, 6H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 14.3, 19.6, 31.7, 69.0, 98.2, 104.2, 114.7, 116.2, 119.6, 126.3, 126.4, 126.5, 126.7, 128.1, 128.3, 132.7, 141.4, 153.7. HRMS (FAB) calcd for $C_{156}H_{85}O_6$ (M^+): 2053.6301. Found: 2053.6292. FAB mass spectra and variable temperature ^{1}H NMR data are shown in Figures S2b and S3.

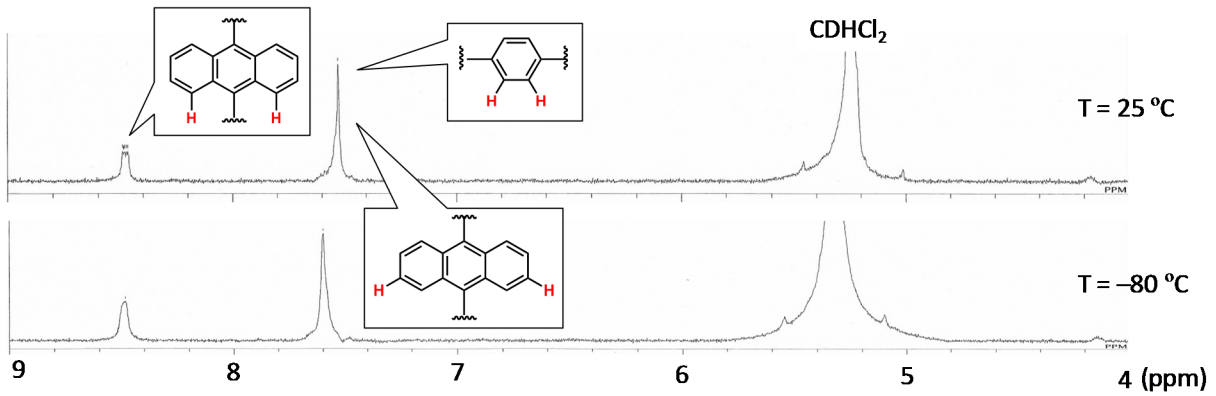


Figure S1. Variable temperature ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of **2⊃C_{60}**.

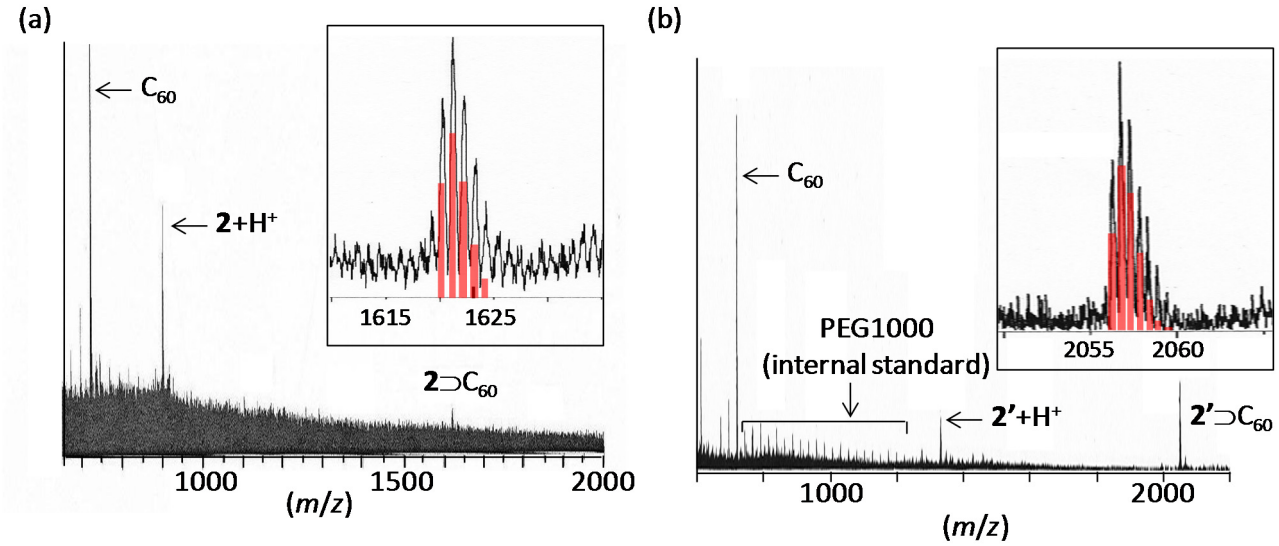


Figure S2. FAB mass spectra of (a) **2**⊃C_{60}., and (b) **2′**⊃C_{60}. Matrix: *m*-nitrobenzyl alcohol (NBA).

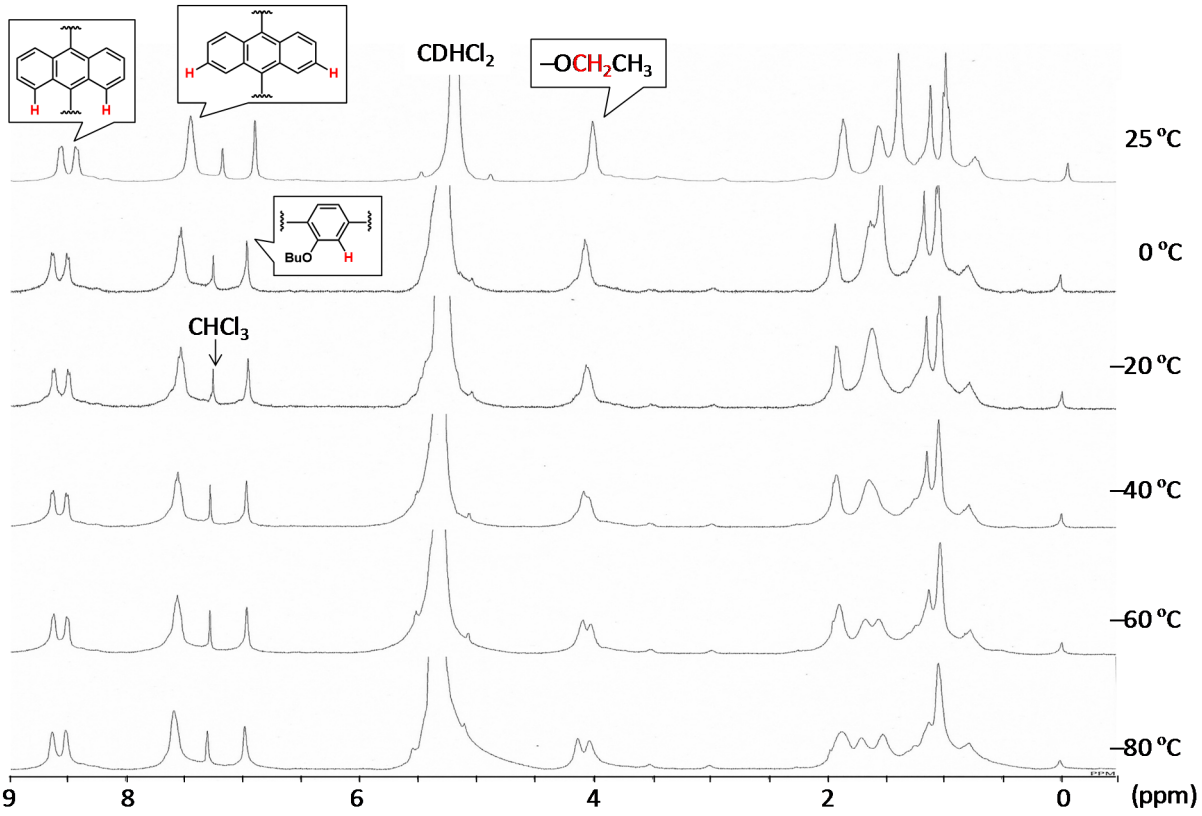
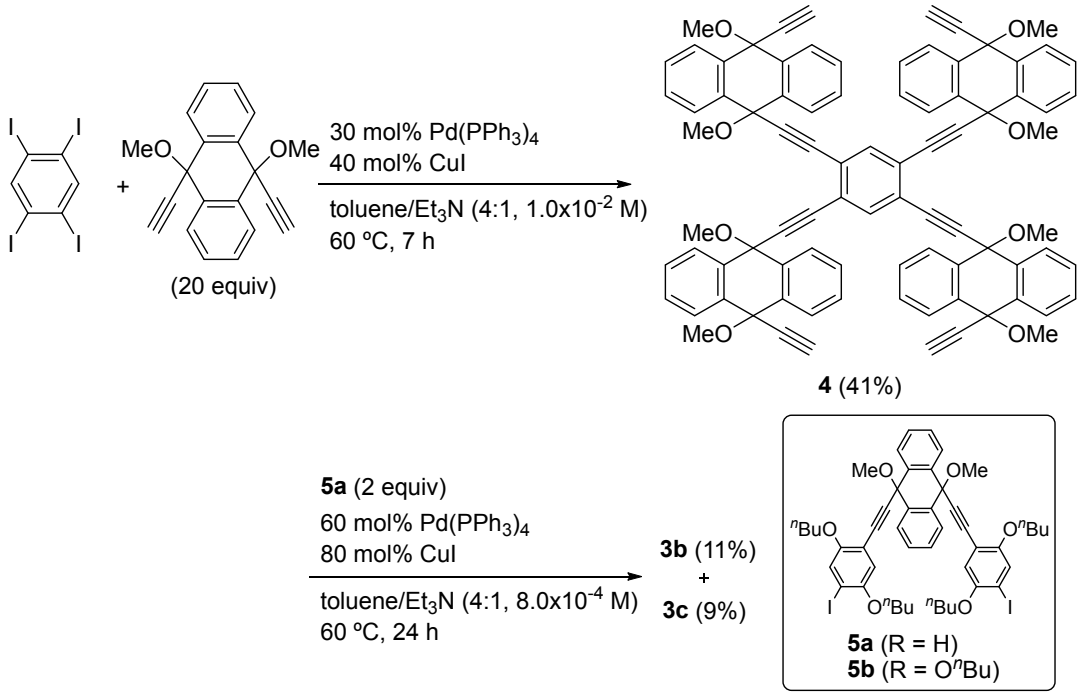


Figure S3. Variable temperature ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of **2′**⊃C_{60}.

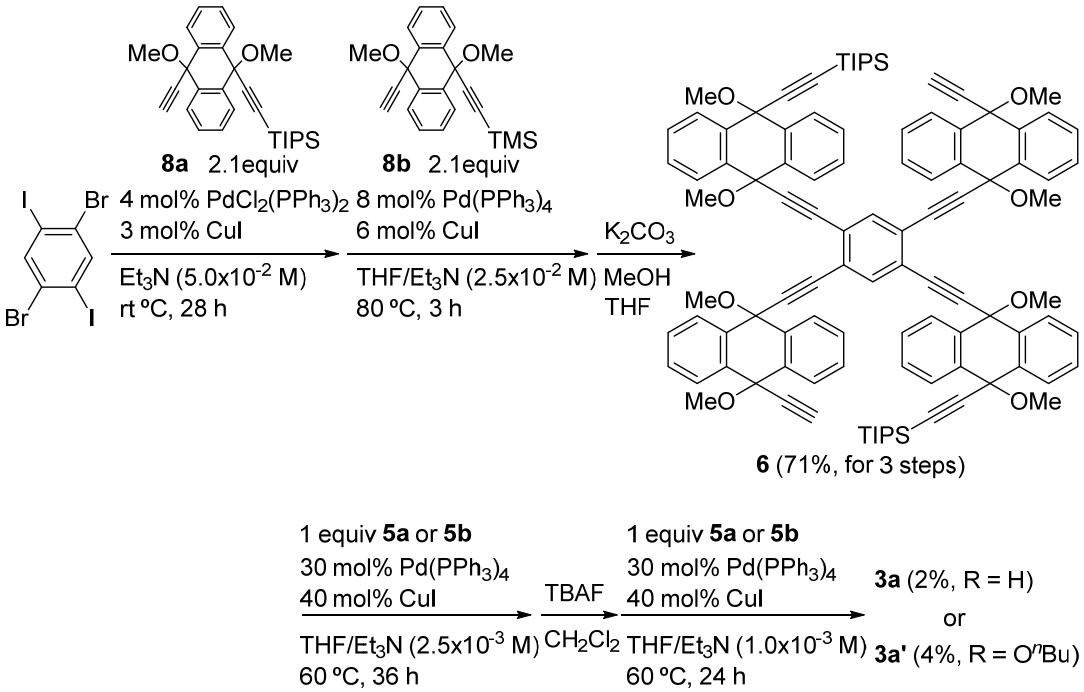
Stepwise synthesis of twin nanoring precursors 3.

Twin nanorings precursors **3** were synthesized from 1,4-dibromo-2,5-diiodobenzene (Schemes S2 and S3).

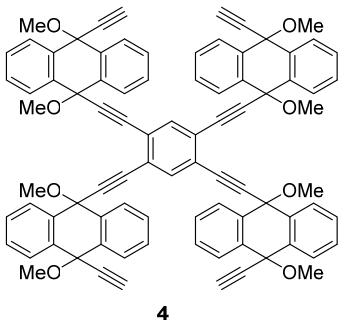
Scheme S2



Scheme S3



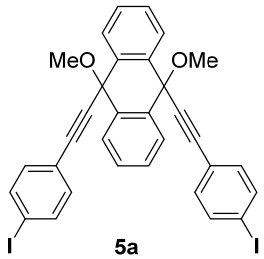
Synthesis of tetraethynylbenzene derivative 4.



4

A solution of 9,10-Diethynyl-9,10-dimethoxy-9,10-dihydroanthracene (1.2 g, 4.0 mmol) and 1,2,4,5-tetraiodobenzene[3] (0.12 g, 0.20 mmol) in THF/Et_3N (v:v = 4:1, 40 mL) was degassed. To this solution were added CuI (15 mg, 0.080 mmol) and $Pd(PPh_3)_4$ (69 mg, 0.060 mmol) at room temperature. After stirring for 7 h at 60 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (40 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give tetraethynylbenzene **4** with small amounts of polymers. From recrystallization using THF/hexane as solvents, **4** was obtained as a white solid (0.092 g, 0.082 mmol, 41%); mp 100.2-102.3 °C; IR (KBr) 2931, 2819, 2111 (C≡C), 1484, 1449, 1243, 1069, 1025, 911, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.81 (s, 4H), 2.96 (s, 12H), 3.00 (s, 12H), 7.26 (dd, J = 7.8, 7.8 Hz, 8H), 7.40 (dd, J = 7.8, 7.8 Hz, 8H), 7.54 (s, 2H), 7.98 (d, J = 7.8 Hz, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 51.7, 51.9, 73.3, 74.0, 84.1, 85.5, 95.7, 124.7, 128.7, 128.9, 129.1, 129.1, 129.1, 135.0, 135.4. One of six ^{13}C signals of alkyne moieties was overlapped with those of $CDCl_3$. HRMS (FAB) calcd for $C_{85}H_{59}O_7$ ($[M–OMe^-]^+$): 1191.4261. Found 1191.4270.

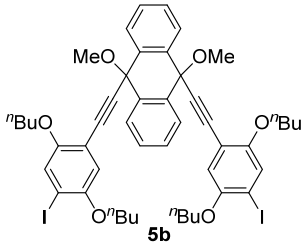
Synthesis of diiodide 5a.



5a

A solution of 9,10-diethynyl-9,10-dimethoxy-9,10- dihydroanthracene (0.058 g, 0.20 mmol) and 1,4-diiodobenzene (0.66 g, 2.0 mmol) in toluene/Et_3N (v:v = 4:1, 20 mL) was degassed. To this solution were added CuI (7.6 mg, 0.040 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) at room temperature. After stirring for 24 h at room temperature, the reaction mixture was washed with saturated NH_4Cl aqueous solution (20 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give diiodide **5a** (0.12 g, 0.17 mmol, 86%) as a pale yellow solid with unreacted 1,4-diiodobenzene (0.53 g, 0.16 mmol, 99% recovered); mp 185.3-187.5 °C; IR (KBr) 2929, 2819, 2227 (C≡C), 1481, 1449, 1388, 1273, 1232, 1085, 1057, 1006, 965, 910, 822, 755 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 3.02 (s, 6H), 7.10 (d, J = 8.2 Hz, 4H), 7.51 (dd, J = 3.6, 5.9 Hz, 4H), 7.57 (d, J = 8.2 Hz, 4H), 8.02 (dd, J = 3.6, 5.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 51.6, 73.0, 86.5, 91.8, 94.5, 121.9, 128.4, 129.1, 133.2, 135.4, 137.3. HRMS (FAB) calcd for $C_{31}H_{19}OI_2$ ($[M–OMe^-]^+$): 660.9525. Found 660.9526.

Synthesis of diiodide 5b.

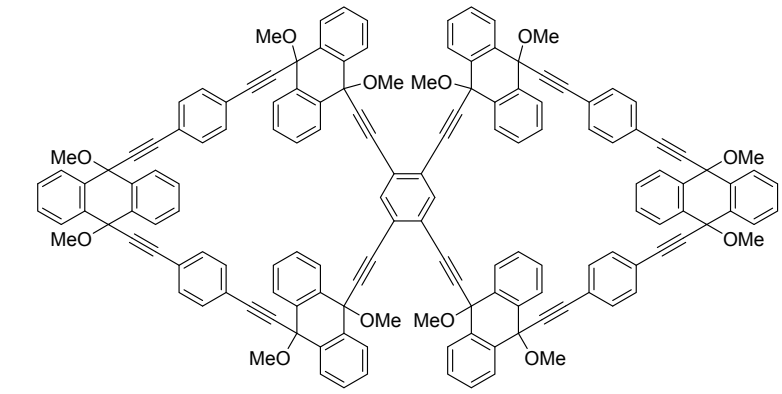


5b

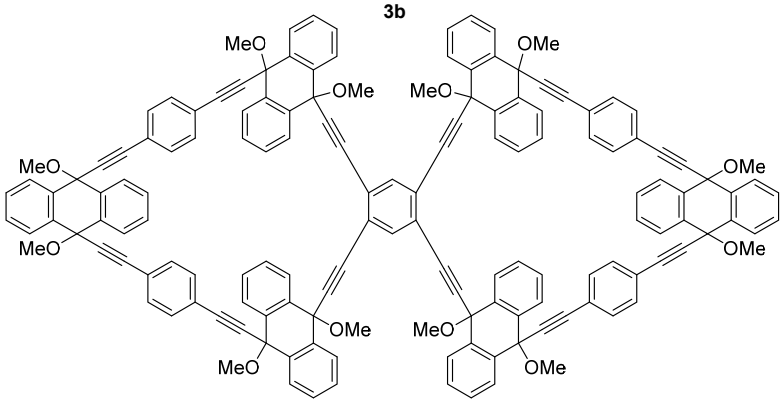
A solution of 9,10-diethynyl-9,10-dimethoxy-9,10- dihydroanthracene (0.29 g, 1.0 mmol) and 2,5-di-*n*-butoxy-1,4-diiodobenzene (4.7 g, 10 mmol) in THF/Et_3N (v:v = 4:1, 100 mL) was degassed. To this solution were added CuI (38 mg, 0.20 mmol) and $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) at room temperature. After stirring for 24 h at 60 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (50 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed

under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/EtOAc (v:v = 20:1 to 10:1) as solvents to afford **5b** (0.48 g, 0.49 mmol, 49%) as a yellowish brown solid. mp = 158.8 °C (dec); IR(KBr) 3289, 2931, 2870, 2820, 2360, 2245, 2226 (C≡C), 1502, 1465, 1450, 1410, 1389, 1244, 1214, 1066, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.89-1.00 (m, 12H), 1.41-1.57 (m, 8H), 1.70-1.83 (m, 8H), 3.17 (s, 6H), 3.90-3.95 (m, 8H), 6.88 (s, 2H), 7.27 (s, 2H), 7.48 (dd, J = 3.3, 5.5 Hz, 4H), 8.20 (dd, J = 3.3, 5.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.7, 13.7, 19.0, 19.2, 31.1, 31.3, 51.9, 69.2, 69.7, 74.6, 84.9, 87.9, 93.7, 112.4, 116.0, 123.0, 128.5, 129.1, 135.8, 151.5, 154.7. HRMS (FAB) calcd for $C_{48}H_{55}I_2O_6$ ($M+H^+$): 981.2088. Found: 981.2071.

Synthesis of twin nanoring precursors 3b and 3c.



3b



3c

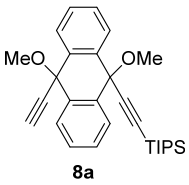
A solution of **4** (0.049 g, 0.040 mmol) and diiodide **5a** (0.055 g, 0.080 mmol) in THF/Et_3N (v:v = 4:1, 50 mL) was degassed. To this solution were added CuI (6.1 mg, 0.032 mmol) and $Pd(PPh_3)_4$ (28 mg, 0.024 mmol) at room temperature. After stirring for 24 h at 60 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (50 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give twin nanoring precursors **3b** and **3c** with small amounts of polymers. From recrystallization of crude **3b** using THF/hexane as solvents, **3b** was obtained as a pale yellow solid (9.2 mg, 4.4 μmol, 11%). From recrystallization of crude **3c** using CH_2Cl_2/MeOH as solvents, **3c** was obtained as a pale yellow solid (7.5 mg, 3.6 μmol, 9%).

3b: a pale yellow solid; mp >300.0 °C (dec); IR (KBr) 3064, 2932, 2821, 2224 (C≡C), 1506, 1448, 1241, 1080, 910, 837, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.87 (s, 12H), 2.97 (s, 12H), 3.01 (s, 12H), 7.10 (d, J = 8.3 Hz, 8H), 7.13 (s, 2H), 7.17 (d, J = 8.3 Hz, 8H), 7.39-7.44 (m, 16H), 7.49 (dd, J = 3.4, 5.9 Hz, 8H),. 7.90-7.93 (m, 16H), 8.03-8.06 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 51.0, 51.4, 51.7, 71.2, 72.7, 72.8, 83.8, 85.8, 86.2, 92.9, 93.3, 97.4, 122.3, 122.5, 124.5, 127.5, 128.9, 129.1, 129.2, 129.3, 129.5, 131.2, 131.3, 134.9, 134.9, 135.0, 136.5. HRMS (FAB) calcd for $C_{149}H_{99}O_{11}$ ([M–OMe^-]$^+$): 2064.7221. Found 2064.7207.

3c: a pale yellow solid; mp >300.0 °C (dec); IR (KBr) 2933, 2820, 2356, 2223 (C≡C), 1476, 1450, 1263, 1244, 1083, 1067, 909, 838, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.99 (s, 12H), 3.08 (s, 12H), 3.10 (s, 12H), 6.45 (dd, J = 7.7, 7.7 Hz, 8H), 7.04 (d, J = 8.4 Hz, 8H), 7.09 (d, J = 7.7 Hz, 8H), 7.26 - 7.29 (m, 8H), 7.58 (dd, J = 3.3, 5.9 Hz, 8H), 7.78 (d, J = 8.1 Hz, 8H), 7.84 (d, J = 8.1 Hz, 8H), 7.97 (dd, J = 3.3, 5.9 Hz, 8H), 8.08 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 51.6, 52.2, 52.6, 71.8, 76.0, 76.1, 86.4, 86.9, 89.5, 90.2, 93.2, 94.3, 122.3,

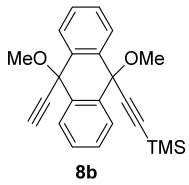
122.9, 124.3, 125.5, 126.9, 127.9, 128.2, 128.6, 129.2, 129.2, 131.1, 132.0, 135.4, 135.5, 135.7. HRMS (FAB) calcd for $C_{149}H_{99}O_{11}$ ([M–OMe$^-$]$^+$): 2064.7221. Found 2064.7207.

Synthesis of diynes 8a and 8b.



8a

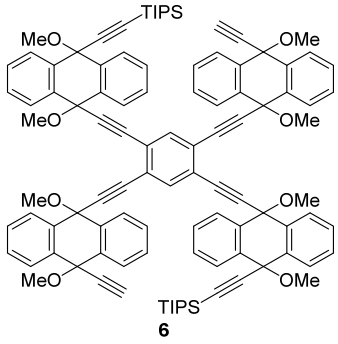
To a solution of 9,10-diethynyl-9,10-dimethoxy-9,10- dihydroanthracene (0.87 g, 3.0 mmol) in THF (40 mL) was added ^{n}BuLi (2.1 mL, 3.3 mmol, 1.6 M in hexane) at -78 ºC. After stirring for 1.5 h, triisopropylsilyl chloride (0.77 mL, 3.6 mmol) was added to this solution at 0 ºC. After stirring for 3 h at 0 ºC and 14 h at room temperature, water (20 mL) was added to this solution. The aqueous solution was extracted with CH_2Cl_2 (10 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give **8a** (0.73 g, 1.7 mmol, 55%) as a pale yellow solid. mp 81.0-82.0 °C ; IR (KBr) 3286, 2955, 2898, 2820, 2166 (C≡C), 2112, 1480, 1449, 1251, 1215, 1089, 857, 844, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.09 (s, 3H), 1.10 (s, 18H), 2.84 (s, 1H), 3.03 (s, 3H), 3.08 (s, 3H), 7.44-7.48 (m, 4H), 8.04-8.06 (m, 2H), 8.07-8.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.2, 18.6, 51.8, 51.9, 73.7, 74.2, 76.4, 83.9, 90.6, 106.6, 128.7, 128.7, 128.8, 128.9, 135.2, 136.0. HRMS (FAB) calcd for $C_{29}H_{37}O_2Si$ (M+H$^+$): 445.2563. Found 445.2554.



8b

To a solution of 9,10-diethynyl-9,10-dimethoxy-9,10- dihydroanthracene (0.87 g, 3.0 mmol) in THF (40 mL) was added ^{n}BuLi (2.6 mL, 4.2 mmol, 1.6 M in hexane) at -78 ºC. After stirring for 1.5 h, triisopropylsilyl chloride (0.52 mL, 6.0 mmol) was added to this solution at 0 ºC. After stirring for 3 h at 0 ºC and 14 h at room temperature, water (20 mL) was added to this solution. The aqueous solution was extracted with CH_2Cl_2 (10 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give **8b** (0.70 g, 1.9 mmol, 65%) as a brown oil; IR (KBr) 3237, 2942, 2864, 2179 (C≡C), 2103, 1448, 1243, 1219, 1092, 914, 779, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.19 (s, 9H), 2.81 (s, 1H), 2.98 (s, 3H), 3.00 (s, 3H), 7.46-7.49 (m, 4H), 8.00-8.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.0, 51.8, 51.9, 73.3, 73.6, 76.3, 84.5, 93.3, 105.4, 128.7, 129.0, 129.0, 129.1, 135.3, 135.8. HRMS (FAB) calcd for $C_{23}H_{25}O_2Si$ (M+H$^+$): 361.1624. Found 361.1612.

Synthesis of tetraethynylbenzene derivative 6.



6

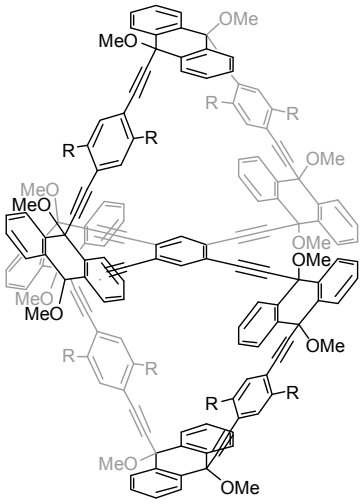
A solution of 1,4-dibromo-2,5-diiodobenzene[4] (14 mg, 0.28 mmol) and **8a** (26 mg, 0.59 mmol) in Et_3N (5.6 mL) was degassed. To this solution were added CuI (1.6 mg, 8.4 μmol) and $PdCl_2(PPh_3)_2$ (7.9 mg, 0.011 mmol) at room temperature. After stirring for 28 h at room temperature, the reaction mixture was washed with saturated NH_4Cl aqueous solution (10 mL). The aqueous solution was extracted with $CHCl_3$ (5 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure. Recrystallization with $CHCl_3$ (1 mL) and MeOH (10 mL) gave dibromobenzene derivative (0.27 g, 0.24 mmol, 87%) as a white solid. mp = 165.2-166.2 °C; IR (KBr) 2941, 2864, 2818, 2360, 2163 (C≡C), 1471, 1349, 1245, 1066, 884, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.08 (s, 6H), 1.09 (s, 36H), 3.11 (s, 6H), 3.13 (s, 6H), 7.45-7.51 (m, 8H), 7.71 (s, 2H), 8.10-8.14 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.3, 18.6, 51.9, 52.2, 74.4, 74.6, 85.4, 90.9, 97.0,

106.6, 124.0, 126.2, 128.8, 128.8, 129.1, 129.2, 135.1, 136.1, 136.4. HRMS (FAB) calcd for $C_{63}H_{69}Br_2O_3Si_2$ ([M–OMe$^-$]$^+$): 1089.3132. Found 1089.3142.

A solution of dibromobenzene derivative (41 mg, 0.37 mmol) and **8b** (28 mg, 0.78 mmol) in THF/Et_3N (v:v = 1:8, 15 mL) was degassed. To this solution were added CuI (4.2 mg, 0.022 mmol) and $Pd(PPh_3)_4$ (35 mg, 4.8 μmol) at room temperature. After stirring for 3 h at 80 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (20 mL). The aqueous solution was extracted with $CHCl_3$ (10 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to short column chromatography on SiO_2 with EtOAc as solvents. The organic solvents were removed under reduced pressure to give tetraethynylbenzene derivative.

To a solution of the tetraethynylbenzene derivative in THF/MeOH (1.9 mL/7.4 mL) was added potassium carbonate (0.20 g, 1.5 mmol) at room temperature. After stirring for 1 h, the organic solvents were removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (10 mL). The organic layer was washed with brine (10 mL) and the aqueous layer was extracted with $CHCl_3$ (5 mL x 2). The combined organic solution was dried over $MgSO_4$ and the organic solvents were removed reduced pressure. Recrystallization with $CHCl_3$ (2 mL) and MeOH (20 mL) gave **6** (0.47 g, 0.31 mmol, 82% from dibromobenzene derivative) as a pale yellow solid. mp 157.2 – 158.2 °C ; IR (KBr) 3303, 2942, 2864, 2819, 2361, 2162 (C≡C), 2112, 1450, 1388, 1243, 1069, 909, 761 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.13 (s, 6H), 1.14 (s, 36H), 2.79 (s, 2H), 2.93 (s, 6H), 2.97 (s, 6H), 3.03 (s, 6H), 3.12 (s, 6H), 7.12 (dd, J = 7.7, 7.7 Hz, 4H), 7.18-7.20 (m, 4H), 7.33 (dd, J = 7.3, 7.3 Hz, 4H), 7.36 (dd, J = 7.0, 7.0 Hz, 4H), 7.66 (s, 2H), 7.93 (d, J = 8.0 Hz, 8H), 8.03 (d, J = 7.7 Hz, 4H), 8.08 (d, J = 7.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.3, 18.7, 51.7, 51.8, 52.1, 52.3, 73.3, 74.0, 75.1, 75.3, 76.3, 84.1, 85.4, 86.2, 91.2, 95.1, 95.9, 106.1, 124.8, 124.9, 128.5, 128.6, 128.6, 128.8, 128.9, 129.0, 129.1, 129.4, 134.9, 135.2, 135.5, 135.9, 136.3. HRMS (FAB) calcd for $C_{103}H_{99}O_7Si_2$ ([M−OMe$^-$]$^+$): 1504.6963. Found 1504.6958.

Synthesis of twin nanoring precursors 3a and 3a′.



3a (R = H)
3a' (R = O^{n}Bu)

A solution of **6** (0.15 g, 0.10 mmol) and **5a** (69 mg, 0.10 mmol) in THF/Et_3N (v:v = 4:1, 20 mL) was degassed. To this solution were added CuI (7.6 mg, 0.040 mmol) and $Pd(PPh_3)_4$ (35 mg, 0.030 mmol) at room temperature. After stirring for 3 h at 60 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (50 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure. To a solution of the residue in CH_2Cl_2 (27 mL) was added tetrabutylammonium fluoride (0.40 mL, 0.40 mmol, 1.0 M in THF) at room temperature. After stirring for 30 min, the organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to afford a macrocyclic compound (51 mg, 0.026 mmol, 26%) as a pale yellow solid. mp 230.0 - 231.0 °C (dec); IR (KBr) 2928, 2227 (C≡C), 1719, 1483, 1448, 1242, 1077, 912, 838, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.66 (s, 6H), 2.71 (s, 6H), 2.78 (s, 6H), 2.84 (s, 6H), 2.88 (s, 2H), 3.02 (s, 6H), 6.82 (d, J = 8.3 Hz, 4H), 6.98 (d, J = 8.3 Hz, 4H), 7.18 - 7.30 (m, 8H), 7.32 (s, 2H), 7.38 (dd, J = 7.8, 7.8 Hz, 8H), 7.56 (dd, J = 3.4, 5.9 Hz, 4H),

7.80 - 7.84 (m, 12H), 7.91 (d, J = 7.8 Hz, 4H), 7.96 (dd, J = 3.4, 5.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 50.4, 50.6, 50.7, 51.8, 52.0, 71.1, 71.2, 71.2, 74.2, 74.7, 83.0, 83.8, 85.4, 85.6, 86.4, 93.5, 93.8, 94.4, 97.9, 122.0, 122.2, 124.0, 124.4, 127.8, 128.3, 128.3, 128.6, 128.8, 128.9, 129.2, 129.5, 129.5, 131.3, 131.5, 131.7, 134.4, 134.9, 135.0, 135.0, 135.9, 137.0. One of ten ^{13}C signals of alkyne moieties was overlapped with those of $CDCl_3$. HRMS (FAB) calcd for $C_{117}H_{79}O_9$ ([M–OMe$^-$]$^+$): 1627.5724. Found 1627.5730.

A solution of this macrocyclic compound (26 mg, 0.016 mmol) and **5a** (11 mg, 0.016 mmol) in THF/Et_3N (v:v = 4:1, 6.4 mL) was degassed. To this solution were added CuI (1.2 mg, 6.4 μmol) and $Pd(PPh_3)_4$ (5.5 mg, 4.8 μmol) at room temperature. After stirring for 3 h at 60 ºC, the reaction mixture was washed with saturated NH_4Cl aqueous solution (50 mL). The aqueous solution was extracted with $CHCl_3$ (20 mL x 2) and the combined organic solution was dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to afford **3a** (2.9 mg, 1.4 μmol, 9%) as a pale yellow solid. mp 259.3-260.3 °C; IR (KBr) 2928, 2817, 2349, 2228 (C≡C), 1634, 1507, 1448, 1242, 1080, 913, 836, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.41 (s, 12H), 2.69 (s, 12H), 2.77 (s, 12H), 7.03 (dd, J = 7.3, 7.3 Hz, 8H), 7.08 (d, J = 8.8 Hz, 8H), 7.11 (d, J = 8.8 Hz, 8H), 7.34-7.47 (m, 18H), 7.53 (dd, J = 7.3, 7.3 Hz, 4H), 7.67 (dd, J = 7.8, 7.8 Hz, 8H), 7.84 (d, J = 7.3 Hz, 4H), 7.88 (d, J = 7.8 Hz, 4H), 7.96 (d, J = 7.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 50.5, 50.6, 50.7, 71.0, 71.2, 71.2, 83.0, 85.2, 85.3, 93.9, 94.0, 97.4, 122.2, 122.6, 124.0, 127.6, 127.8, 128.1, 128.2, 128.8, 129.0, 129.1, 129.2, 129.4, 131.3, 131.5, 134.2, 134.5, 134.8, 134.8, 135.0, 135.1, 136.4. HRMS (FAB) calcd for $C_{149}H_{99}O_{11}$ ([M–OMe$^-$]$^+$): 2063.7187. Found 2063.7170.

3a′ was obtained by the similar synthetic procedure of **3a**. **5b** was used instead of **5a**.

3a′ (a pale yellow solid, 13% yield (The yield of the first macrocyclization was 29%)). mp 164.5-165.5 °C; IR (KBr) 2957, 2931, 2871, 2363, 2224 (C≡C), 1636, 1498, 1448, 1413, 1261, 1243, 1217, 1078 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.33 (t, J = 7.3 Hz, 12H), 0.69-0.73 (m, 8H), 0.79 (t, J = 7.3 Hz, 12H), 1.08-1.11 (m, 8H), 1.19-1.28 (m, 8H), 1.47-1.53 (m, 8H), 2.36 (s, 12H), 2.65 (s, 12H), 2.80 (s, 12H), 3.29 (t, J = 6.4 Hz, 8H), 3.52 - 3.57 (m, 4H), 3.62 - 3.67 (m, 4H), 6.47 (s, 4H), 6.61 (s, 4H), 6.88 (dd, J = 7.3, 7.3 Hz, 4H), 6.96 (dd, J = 7.3, 7.3 Hz, 4H), 7.02 (s, 2H), 7.14 (d, J = 7.3 Hz, 4H), 7.35 (dd, J = 7.6, 7.6 Hz, 4H), 7.42 (dd, J = 7.6, 7.6 Hz, 4H), 7.45 (dd, J = 7.6, 7.6 Hz, 4H), 7.52 (dd, J = 7.6, 7.6 Hz, 4H), 7.59 (d, J = 7.8 Hz, 4H), 7.65 (d, J = 7.8 Hz, 4H), 7.85 (d, J = 7.8 Hz, 4H), 7.92 (d, J = 7.8 Hz, 4H), 7.99 (d, J = 7.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.7, 13.9, 18.6, 19.1, 31.1, 31.4, 50.4, 50.4, 50.7, 68.6, 68.8, 70.9, 71.3, 71.5, 82.0, 82.0, 82.7, 97.2, 97.5, 97.6, 113.1, 113.5, 116.5, 116.8, 123.9, 127.7, 128.1, 128.4, 128.5, 128.8, 128.9, 129.0, 129.1, 129.1, 129.3, 134.2, 134.5, 134.7, 135.0, 135.2, 135.4, 153.6, 153.7. HRMS (FAB) calcd for $C_{181}H_{165}O_{19}$ ([M–OMe$^-$]$^+$): 2641.1822. Found 2641.1829.

Reductive aromatization of twin nanoring precursors 3a and 3a′.

Reductive aromatization of twin nanoring precursors 3a.

The reductive aromatization of **3a** with 5 equivalents of C_{60} smoothly proceeded but the 1:2 complex **7**⊃2C_{60} could not be isolated (the color of the reaction mixture changed to redish brown). The 1:1 and 1:2 complexes with C_{60} could be detected by MALDI-TOF mass spectroscopy (Figure S4).

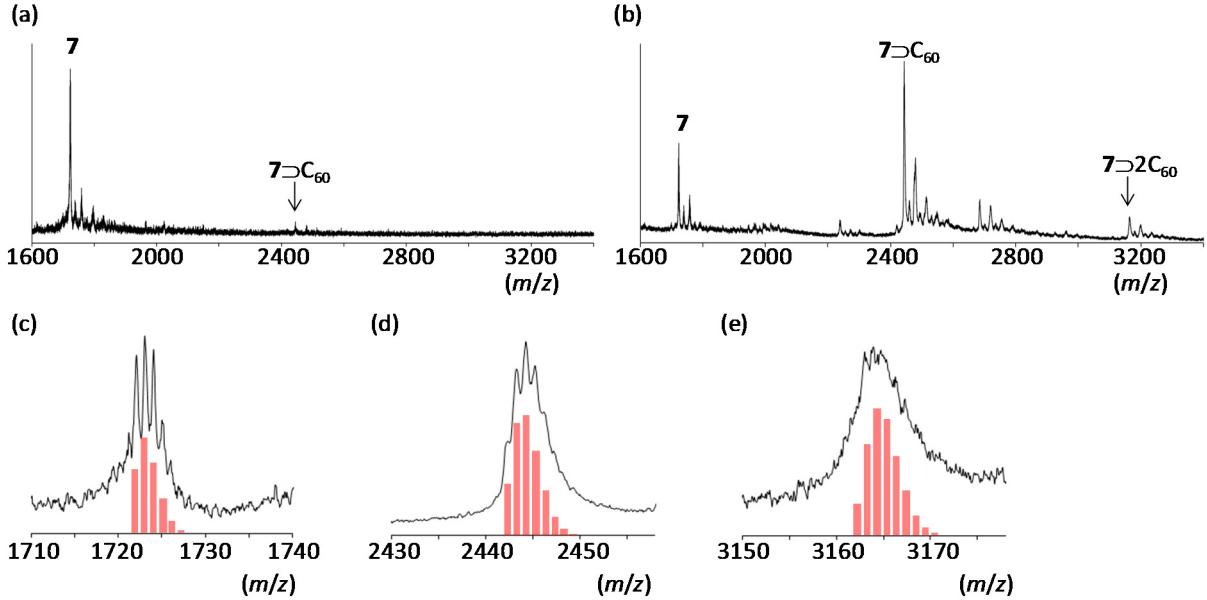
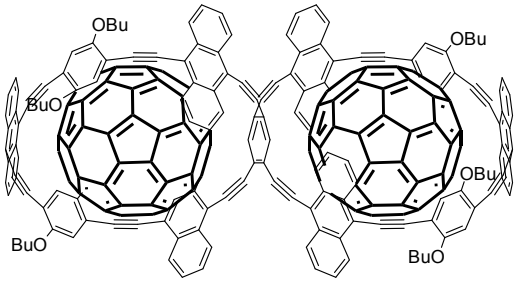


Figure S4. MALDI-TOF mass spectra (matrix: 1,8-dihydroxy-9(10H)-anthracene (dithranol, DIT) or 1,8-dichloroanthraquinone (DCAQ)) measured just after the reductive aromatization of **7** with C_{60}. (a) Positive-ion linear mode, (b) negative-ion linear mode. Enlarged views of molecular ion peaks of (c) twin nanoring **7**, (d) 1:1 complex **7**⊃C_{60}, and (e) 1:2 complex **7**⊃2C_{60} measured by a linear positive mode. Pale red bars indicate theoretical distribution of molecular ion peaks.

Reductive aromatization of twin nanoring precursors 3a′.



7′⊃2C_{60}

A solution of **3a′** (11 mg, 4.0 μmol) in CH_2Cl_2 (10 mL) was degassed by bubbling of N_2 gas for 15 min. A solution of $SnCl_2 \cdot 2H_2O$ (0.18 g, 0.80 mmol) in 1N HCl aqueous solution (18 mL) was also degassed by bubbling of N_2 gas for 15 min. C_{60} (14 mg, 20 μmol) and this aqueous solution were successively added to the organic solution and gently stirred at room temperature in dark for 18 h. The aqueous solution was extracted with CH_2Cl_2 (15 mL x 2). The combined organic solution was washed with sat. $NaHCO_3$ aqueous solution and dried over $MgSO_4$. The organic solvents were removed under reduced pressure and the residue was subjected to GPC with $CHCl_3$ as an eluent to give 1:1 complex **7′**⊃2C_{60} (12 mg, 3.2 μmol, 79%) as a purple solid. IR ($CHCl_3$) 2958, 2927, 2872, 2858, 2197 (C≡C), 1731, 1467, 1376, 1251, 1045, 955 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.06-1.17 (m, 24H), 1.67-1.75 (m, 16H), 1.98-2.07 (m, 16H), 4.13-4.17 (m, 16H), 7.05-7.07 (m, 8H), 7.53-7.60 (m, 16H), 7.67-7.87 (m, 10H), 8.56-8.60 (m, 6H), 8.64-8.80 (m, 14H), 9.08-9.10 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 14.5, 14.5, 20.0, 20.0, 32.1,

32.1, 69.4, 69.4, 98.2, 98.5, 101.1, 104.7, 105.5, 105.6, 115.4, 116.4, 116.5, 116.5, 118.8, 120.0, 121.6, 125.2, 127.0, 127.1, 127.1, 127.2, 127.3, 127.3, 127.5, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.9, 133.1, 133.1, 133.1, 133.2, 143.3, 143.4, 143.4, 154.1, 154.3.

The reductive aromatization of **7′** (31 mg, 7.9 μmol) with **mC$_{60}$** (35 mg, 39 μmol) proceeded to afford the corresponding 1:2 complex **7′**⊃2**mC$_{60}$** (16 mg, 3.9 μmol) as a purple solid in 50% yield. This complex was isolated by GPC with $CHCl_3$ as an eluent, and survives in degassed $CDCl_3$ or CD_2Cl_2 solution for at least several days.

7′⊃2**mC$_{60}$**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 0.75–0.95 (m, 12H), 0.95–1.25 (m, 24H), 1.45-2.25 (m, 32H), 3.81–3.92 (m, 8H), 4.15-4.23 (m, 8H), 4.95-5.00 (m, 8H), 6.77 (br s, 4H), 7.05-7.15 (m, 4H), 7.15-7.70 (m, 26H), 8.20–8.38 (m, 10H), 8.53–8.68 (m, 10H), 8.68-8.95 (m, 4H). For ^{13}C NMR measurement, all signals were observed as broaden peaks at 25 °C probably because of the dynamic behavior of **7′**⊃2**mC$_{60}$**. Peaks were quite weak and broadened even after several thousands of accumulation at low temperature.

By MALDI-TOF mass spectroscopy working in positive-ion reflectron mode, the molecular ion peaks of these 1:2 complexes **7′**⊃2C$_{60}$ and **7′**⊃2**mC$_{60}$** are difficult to be detected (Figure S5-8). The isotropic patterns for these complexes were confirmed by MALDI-TOF mass spectroscopy working in positive-ion linear mode. Both 1:1 and 1:2 complexes were strongly detected by MALDI-TOF mass spectroscopy working in negative-ion linear mode, but isotropic patterns for them were unclear.

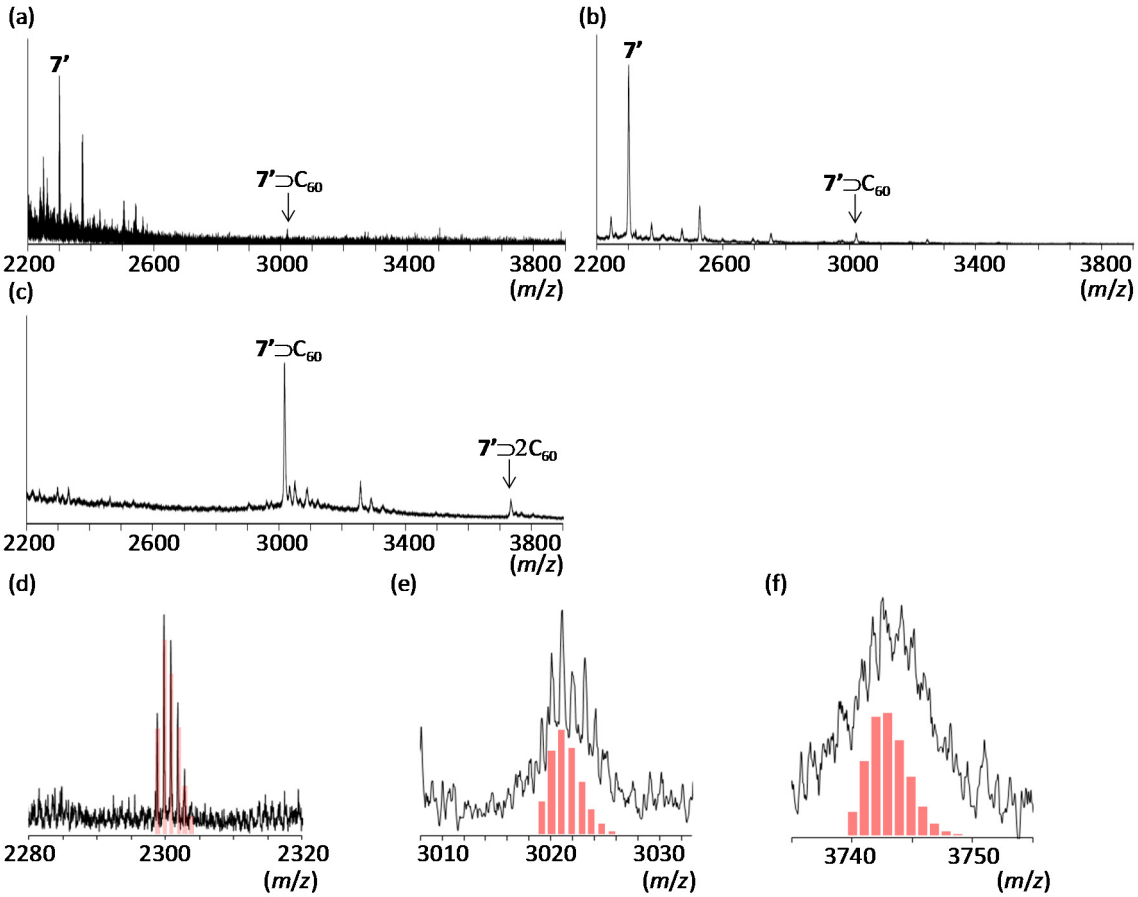


Figure S5. MALDI-TOF mass spectra of **7′**⊃2C$_{60}$. (a) Positive-ion reflectron mode (matrix: DCAQ), (b) positive-ion linear mode (matrix: DIT), and (c) negative-ion linear mode (matrix: DCAQ). Enlarged view of molecular ion peaks of (d) twin nanoring **7′** (positive-ion reflectron mode), (e) 1:1 complex **7′**⊃C$_{60}$ (positive-ion reflectron mode), and (f) 1:2 complex **7′**⊃2C$_{60}$ (positive-ion linear mode). Pale red bars indicate theoretical distribution of molecular ion peaks.

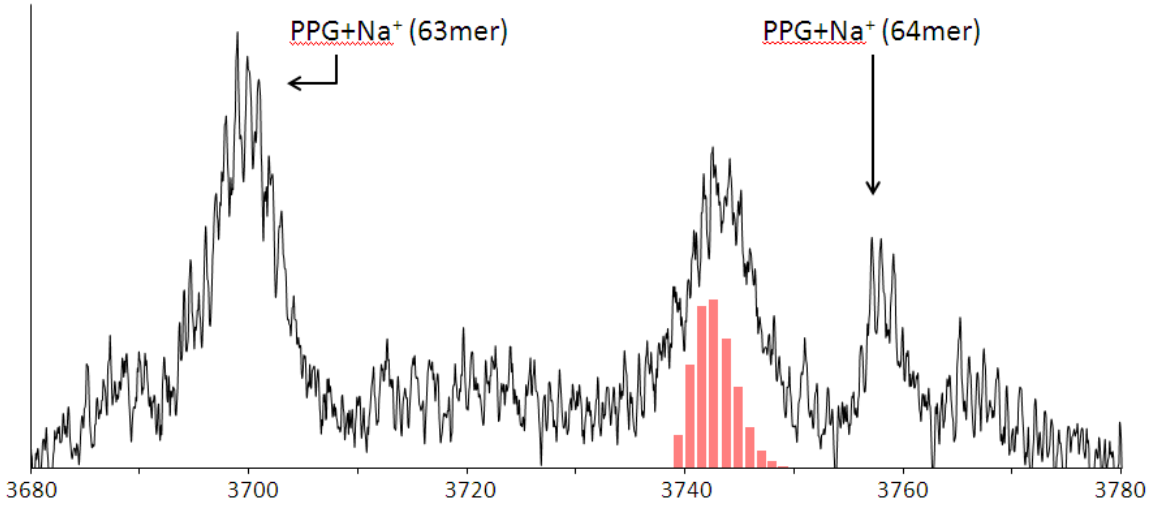


Figure S6. MALDI-TOF mass spectrum (matrix: DIT, positive-ion linear mode) of **7′**⊃2C_{60}. Poly(propylene glycol) (PPG) was used as an internal standard (Na^+). Pale red bars indicate theoretical distribution of molecular ion peaks of **7′**⊃2C_{60}.

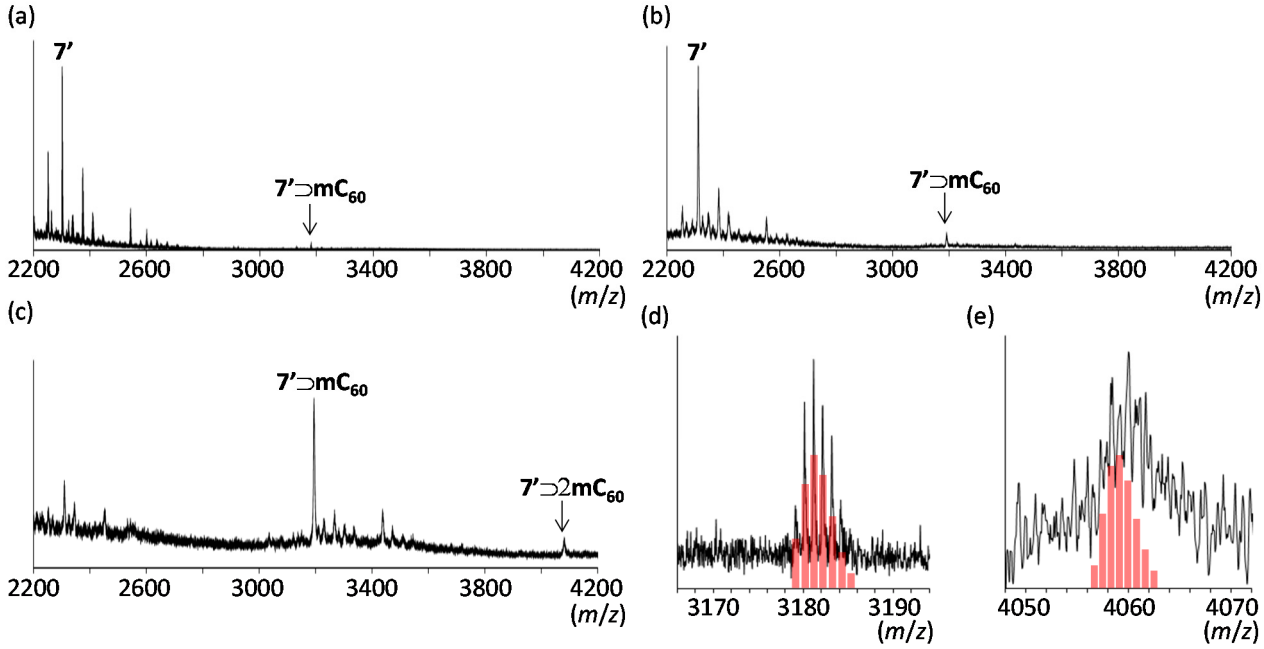


Figure S7. MALDI-TOF mass spectra of **7′**⊃2**mC$_{60}$** (matrix: DCAQ). (a) Positive-ion reflectron mode, (b) positive-ion linear mode, and (c) negative-ion linear mode. Enlarged views of molecular ion peaks of (d) 1:1 complex **7′**⊃**mC$_{60}$** (positive-ion reflectron mode), and (f) 1:2 complex **7′**⊃2**mC$_{60}$** (positive-ion linear mode). Pale red bars indicate theoretical distribution of molecular ion peaks.

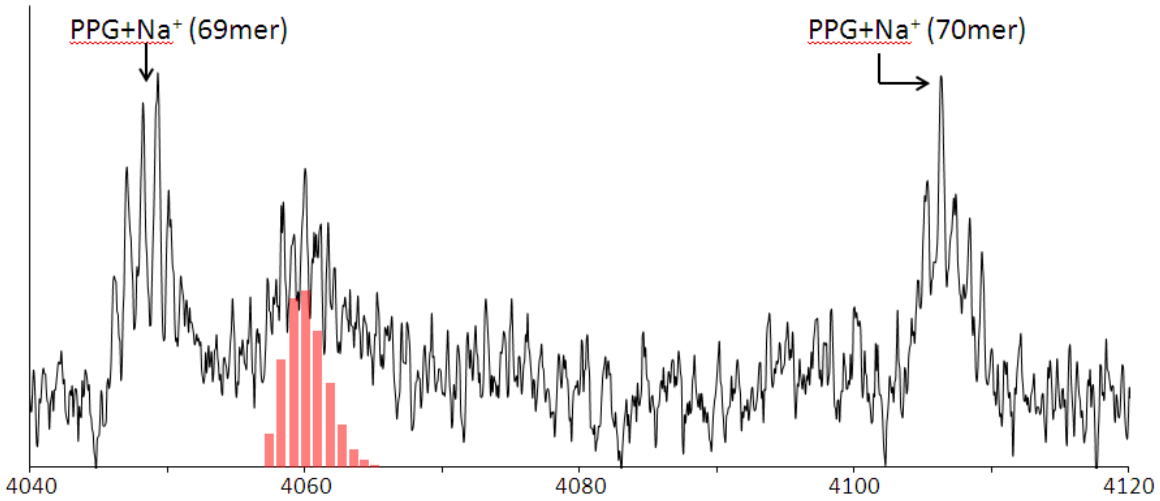


Figure S8. MALDI-TOF mass spectrum (matrix: DIT, positive-ion linear mode) of **7′⊃2mC$_{60}$**. PPG was used as an internal standard (Na^+). Pale red bars indicate theoretical distribution of molecular ion peaks of **7′⊃2mC$_{60}$**.

Variable temperature ^{1}H NMR of **7′⊃2C$_{60}$** was measured. The data are summarized in Figure S9. No significant changes were observed without methylene protons (OC***H*$_2$**CH$_2$CH$_2$CH$_3$). The ^{1}H NMR spectra of **7′⊃2mC$_{60}$** in $CDCl_3$ and CD_2Cl_2 are summarized in Figure S10.

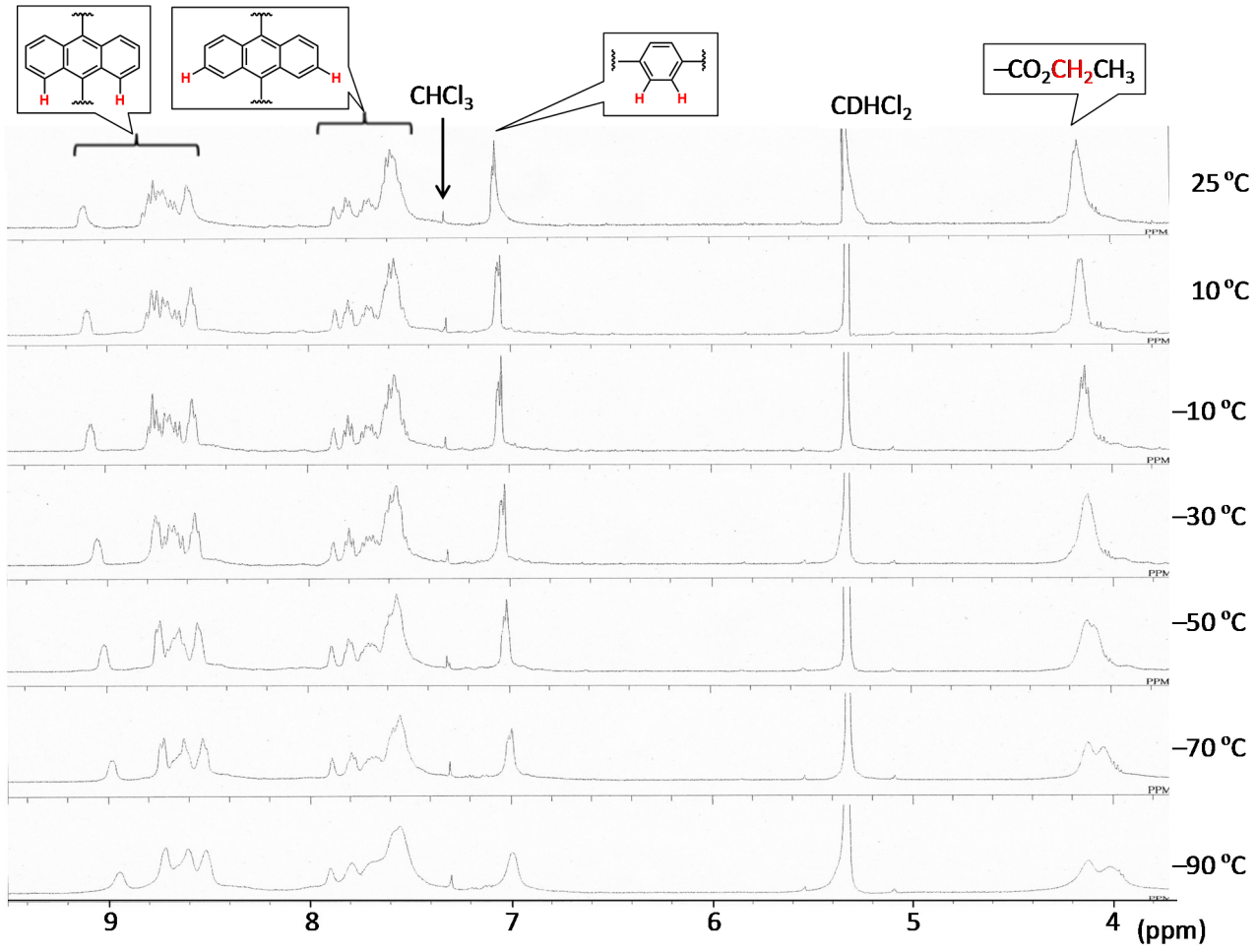


Figure S9. Variable temperature ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of **7′⊃2C$_{60}$**.

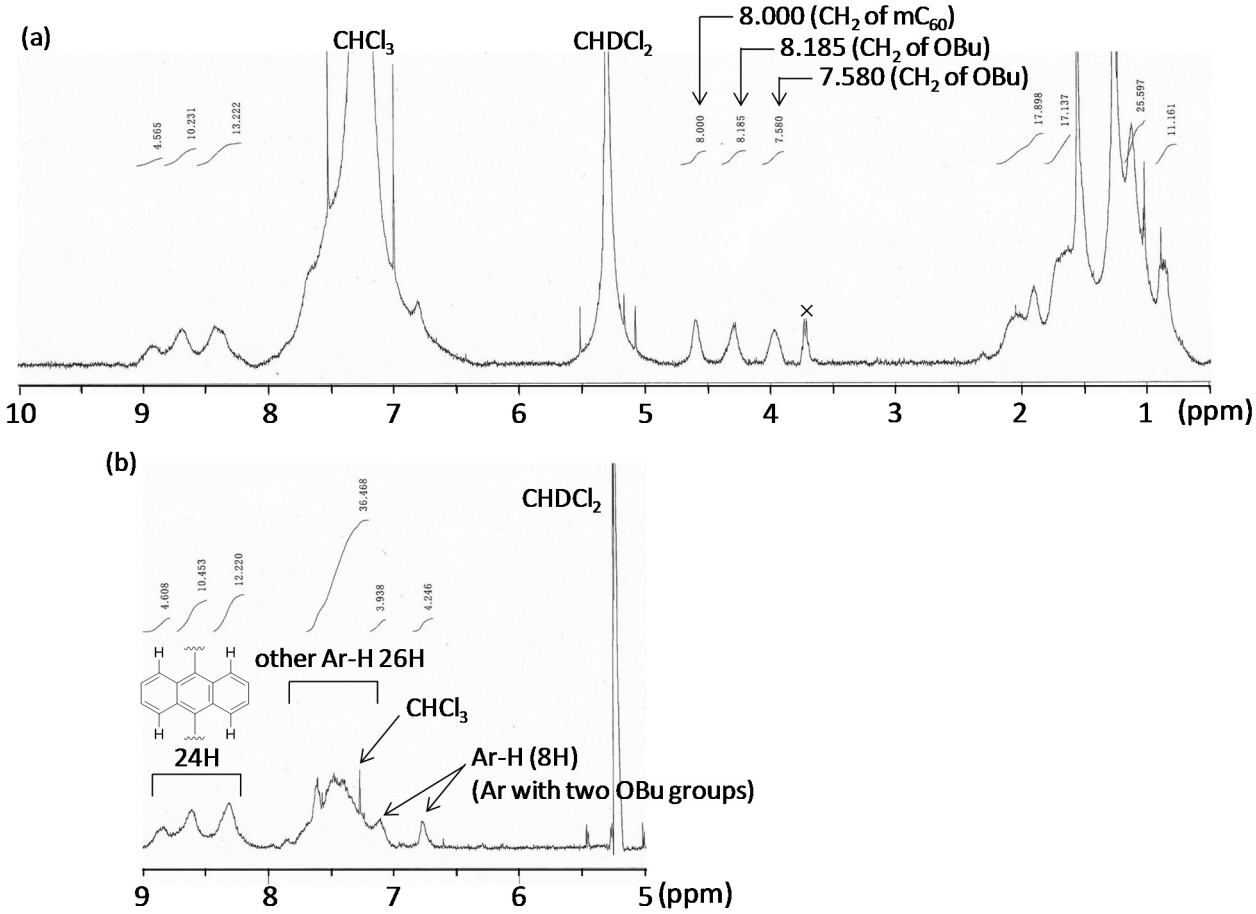
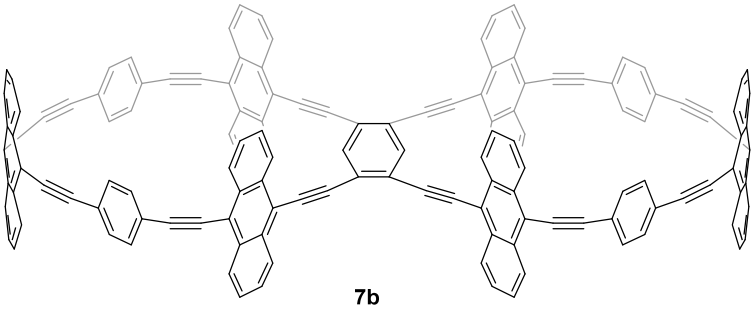


Figure S10. ^{1}H NMR spectra (400 MHz, 25 ºC) of **7′⊃2mC$_{60}$** in (a) $CDCl_3$ and (b) CD_2Cl_2.

Reductive aromatization of twin nanoring precursors 3b and 3c.

When the reductive aromatization of **3c** with 2 equivalents of C_{60} was carried out, neither 1:2 complex with C_{60} nor the corresponding twin carbon nanoring itself detected by MALDI-TOF mass spectroscopy. In the case of **3b**, the corresponding twin carbon nanoring **7b** and its 1:1 complex **7b**⊃C_{60} were detected by MALDI-TOF mass spectroscopy (matrix:DIT, positive ion mode, reflectron mode) (Figure S11). In linear negative ion mode, the corresponding 1:2 complex **7b**⊃2C_{60} was detected as a very weak peak but the molecular ion peaks could not be confirmed.



7b

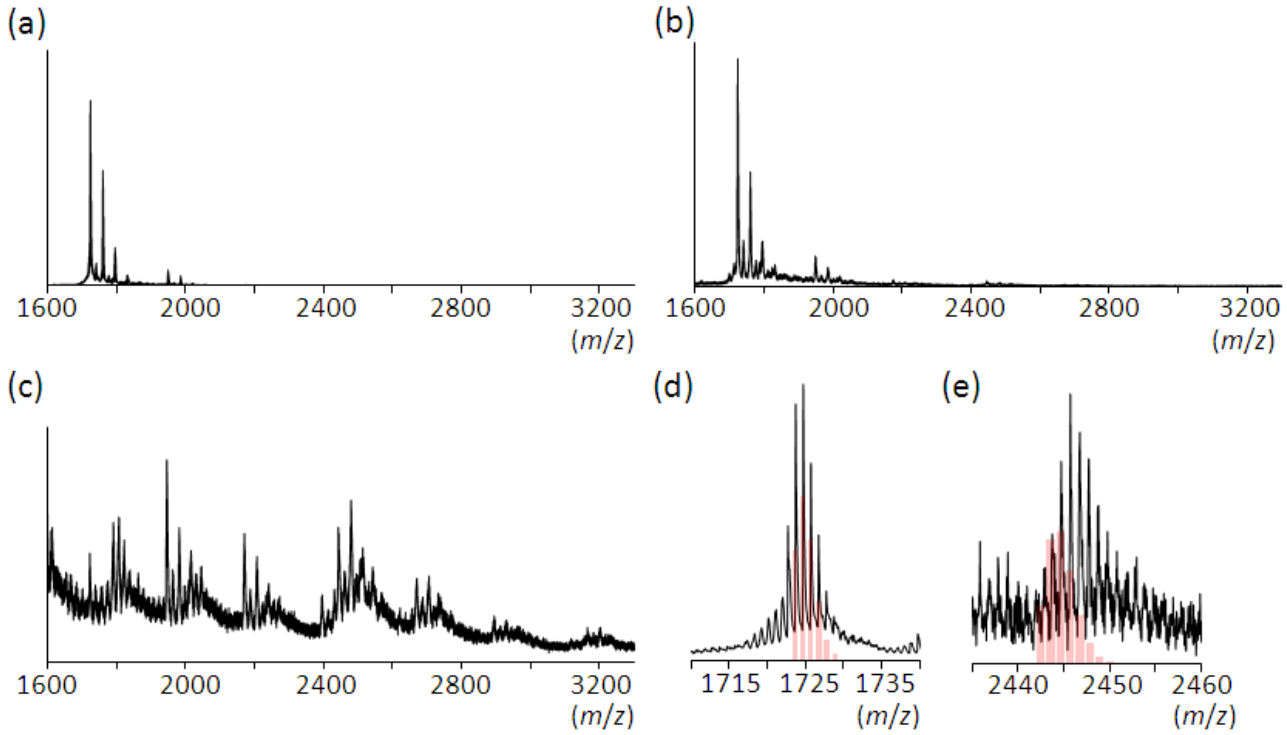


Figure S11. MALDI-TOF mass spectrum measured just after the reductive aromatization of **3b** with C_{60} (matrix: DIT). (a) Positive-ion reflectron mode, (b) positive-ion linear mode, and (c) negative-ion linear mode. Enlarged views of molecular ion peaks of (d) twin nanoring **7b** and (e) 1:1 complex **3b**⊃C_{60} measured by a reflectron positive mode. Pale red bars indicate theoretical distribution of molecular ion peaks.

X-ray crystallographic analyses of 1, 3b, and 3c.

Colorless crystals of **1**, **3b**, and **3c** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2-methanol (for **1** and **3b**) or DMF-Et_2O (for **3c**). The single crystals were scooped from Paratone-N matrix (Hampton Research, USA) and immediately mounted (the mounted position was pre-cooled to -130 °C). The measurements of **1** and **3b** were made on a Rigaku Saturn (Rigaku AFC-10), and the measurement of **3c** was made on a Rigaku VariMax Saturn diffractometer. Data analyses were performed by CrystalClear (Rigaku) and Yadokari-XG 2009.[5] Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods SIR92[6] (for **1**), SHELX97[7] (for **3b** and **3c**) or SIR2004[8] (for **3c**) and subsequent Fourier syntheses (DIRDIF99).[9] Relatively high R and Rw values would be caused by solvent molecules in the crystals. Representative ORTEP drawings are summarized in Figure S12-S14. In the case of **1**, one dichloromethane molecule and several methanol molecules disordered inside of the macrocyclic structure were observed. Therefore, the apparent disordered atoms were given arbitrary carbon or oxygen identities at half-occupancy and refined isotropically. Hydrogen atoms of these solvents were omitted. In the case of **3b**, three dichloromethane molecules and several methanol molecules disordered inside/outside of the macrocyclic structure were observed. These disordered solvents had to be omitted by using SQUEEZE algorithm.[10] In the case of **3c**, four diethyl ether molecules disordered inside/outside of cyclic structure were observed. Two of them have been modeled as having two positions with occupancy factors of 50%.

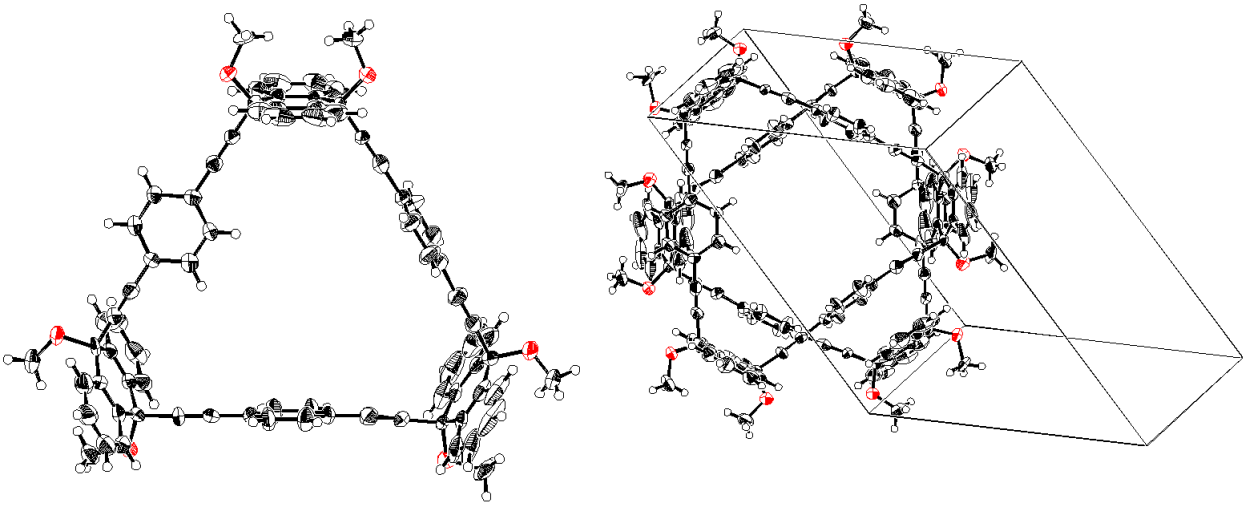


Figure S12. ORTEP drawing of **1**. Solvent molecules were omitted to clarify the structure.

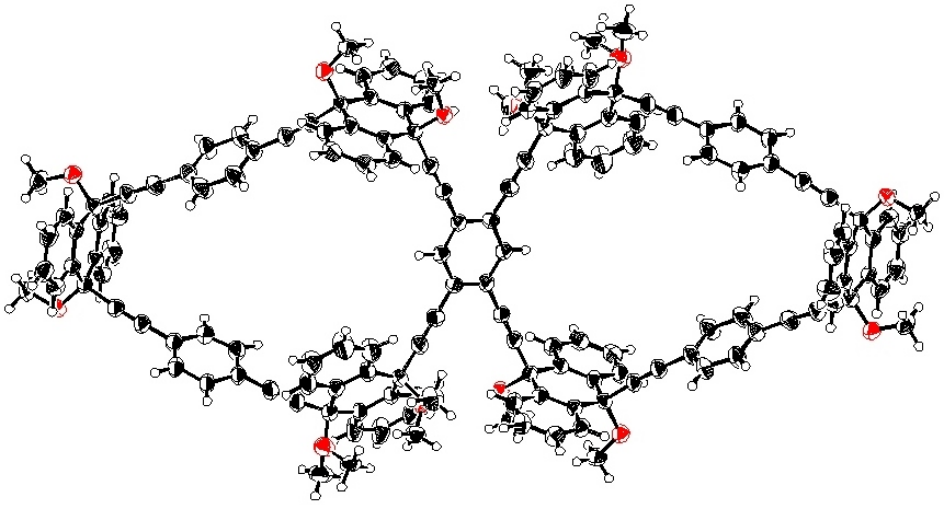


Figure S13. ORTEP drawing of **3b**. Solvent molecules were omitted to clarify the structure.

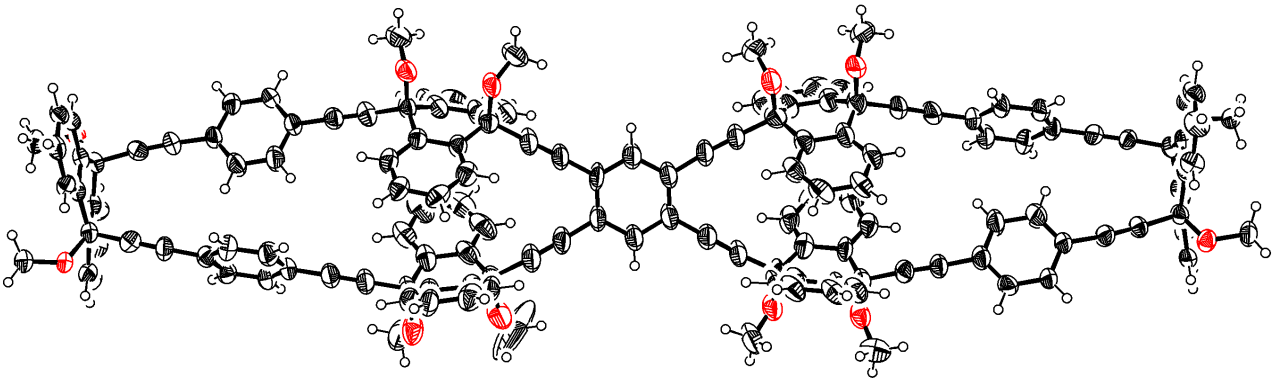


Figure S14. ORTEP drawing of **3c**. Solvent molecules were omitted to clarify the structure.

Table S1. Selected data collection parameters.

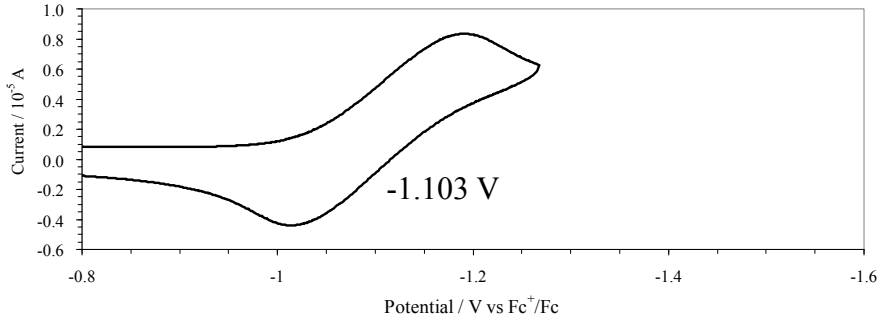
	1	**3b**	**3c**
CCDC No.	932803	932804	932805
Formula	$C_{78}H_{54}O_6 \cdot (CCl_2) \cdot 4(CO)$	$C_{150}H_{102}O_{12}$	$C_{150}H_{102}O_{12} \cdot 3(C_4H_{10}O)$
Crystal system	triclinic	triclinic	triclinic
Lattice parameters	a = 14.595(2) Å	a = 15.079(6) Å	a = 12.1369(5) Å
	b = 17.618(3) Å	b = 16.661(6) Å	b = 15.7383(9) Å
	c = 18.6042(18) Å	c = 17.175(5) Å	c = 34.813(3) Å
	α = 59.083(9)°	α = 69.627(12)°	α = 77.933(6)°
	β = 64.390(14)°	β = 68.110(14)°	β = 85.4972(19)°
	γ = 85.902(17)°	γ = 86.749(16)°	γ = 76.973(6)°
	V = 3630.2(9) Å^3	V = 3740(2) Å^3	V = 6332.0(7) Å^3
Space group	P-1 (#2)	P-1 (#2)	P-1 (#2)
Z value	2	1	2
D_{calc}	1.173 g/cm^3	0.931 g/cm^3	1.216 g/cm^3
F_{000}	1332.00	1098.00	2448.00
2 θ_{max}	54.9°	54.8°	51.0°
μ(MoKα)	1.468 cm^{-1}	0.582 cm^{-1}	0.770 cm^{-1}
No. of Reflections Measured	Total: 29151	Total: 36377	Total: 57913
	Unique: 15922	Unique: 15848	Unique: 23047
	(R_{int} = 0.060)	(R_{int} = 0.037)	(R_{int} = 0.1803)
No. Observations (I>2.00σ(I))	5688	15848	
No. Variables	886	749	
Reflection/Parameter Ratio	6.42	21.16	
Residuals: R(I>2.00s(I))	0.1187	0.1160 (all)	0.1126
Residuals: Rw(I>2.00s(I))	0.1224	0.2554 (all)	0.2627
Goodness of fit indicator	1.104	1.006	1.022
Max shift/error in final cycle	0.000	0.000	0.000
Maximum peak in final diff. map	1.15	0.30	0.79
Minimum peak in final diff. map	-0.39	-0.36	-0.31

Cyclic voltammetry of C_{60}, $\mathbf{2}\supset C_{60}$, $\mathbf{2'}\supset C_{60}$, and $\mathbf{7'}\supset 2C_{60}$.

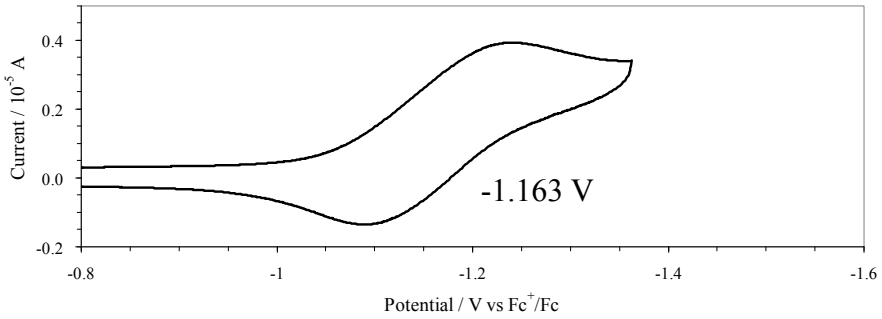
Cyclic voltammograms of C_{60}, $\mathbf{2}\supset C_{60}$, $\mathbf{2'}\supset C_{60}$, and $\mathbf{7'}\supset 2C_{60}$ were measured by cyclic voltammetry (ALS 610C-S, BAS Inc. Japan) in *o*-Dichlorobenzene (Figures S15 and S16).

Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was used as the supporting electrolyte (0.10 M).

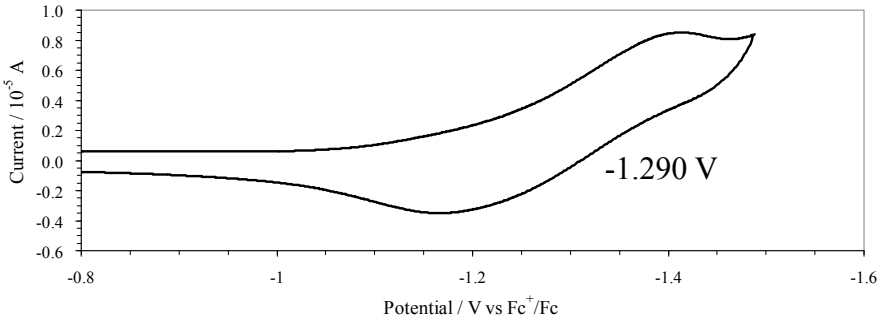
(a) C_{60}



(b) $\mathbf{2}\supset C_{60}$



(c) $\mathbf{2'}\supset C_{60}$



(d) $\mathbf{7'}\supset 2C_{60}$

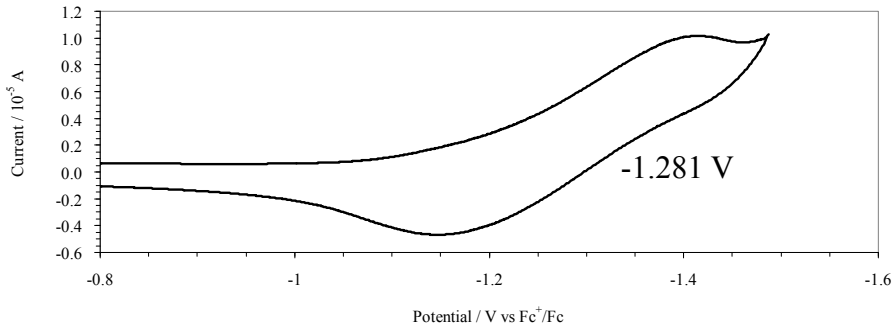


Figure S15. Cyclic voltammogram of (a) C_{60} (1 mM), (b) $\mathbf{2}\supset C_{60}$ (1.9 mM), (c) $\mathbf{2'}\supset C_{60}$ (1.8 mM), and (d) $\mathbf{7'}\supset 2C_{60}$ (1.3 mM) in *o*-dichlorobenzene. Scan rate = 50 mV/s.

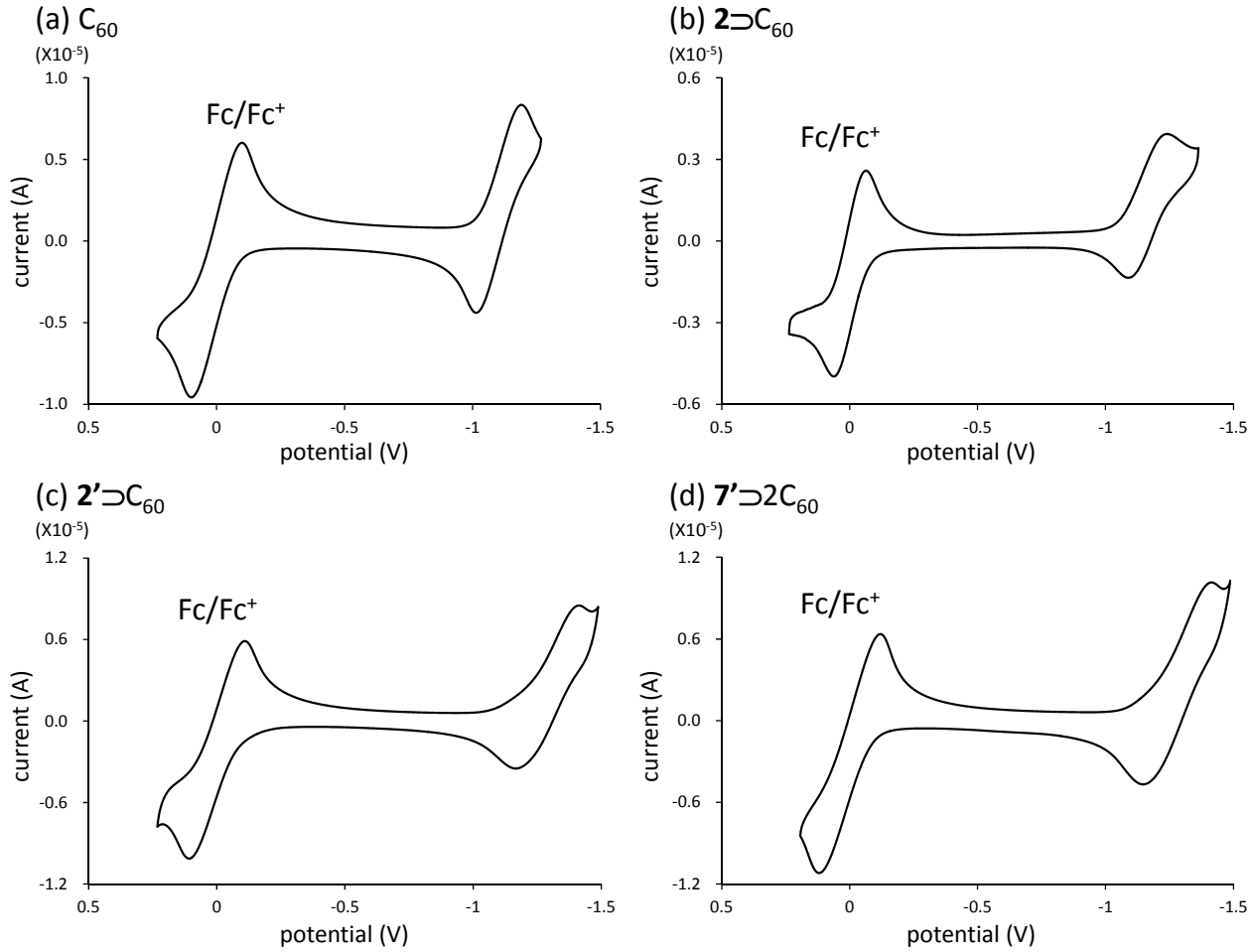


Figure S16. Cyclic voltammogram of (a) C_{60} (1 mM), (b) **2**⊃C_{60} (1.9 mM), (c) **2′**⊃C_{60} (1.8 mM), and (d) **7′**⊃2C_{60} (1.3 mM) with ferrocene (1 mM) in *o*-dichlorobenzene. Scan rate = 50 mV/s.

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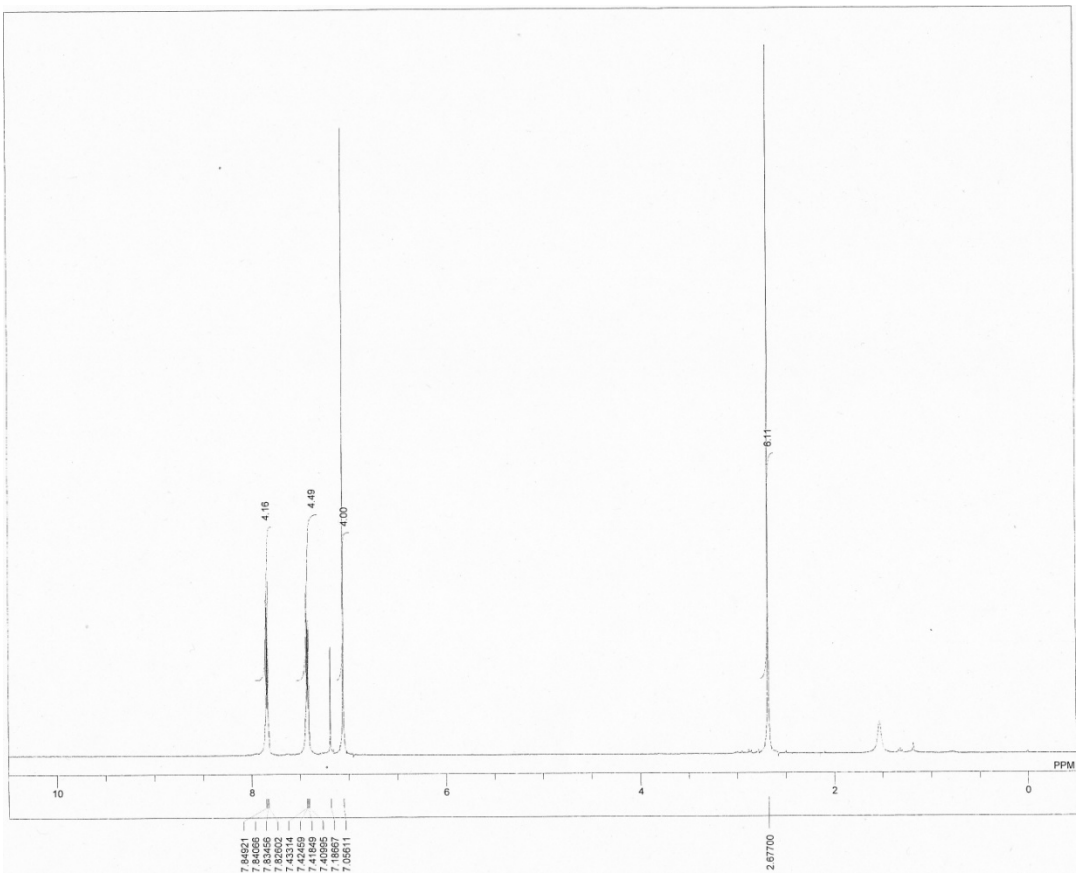
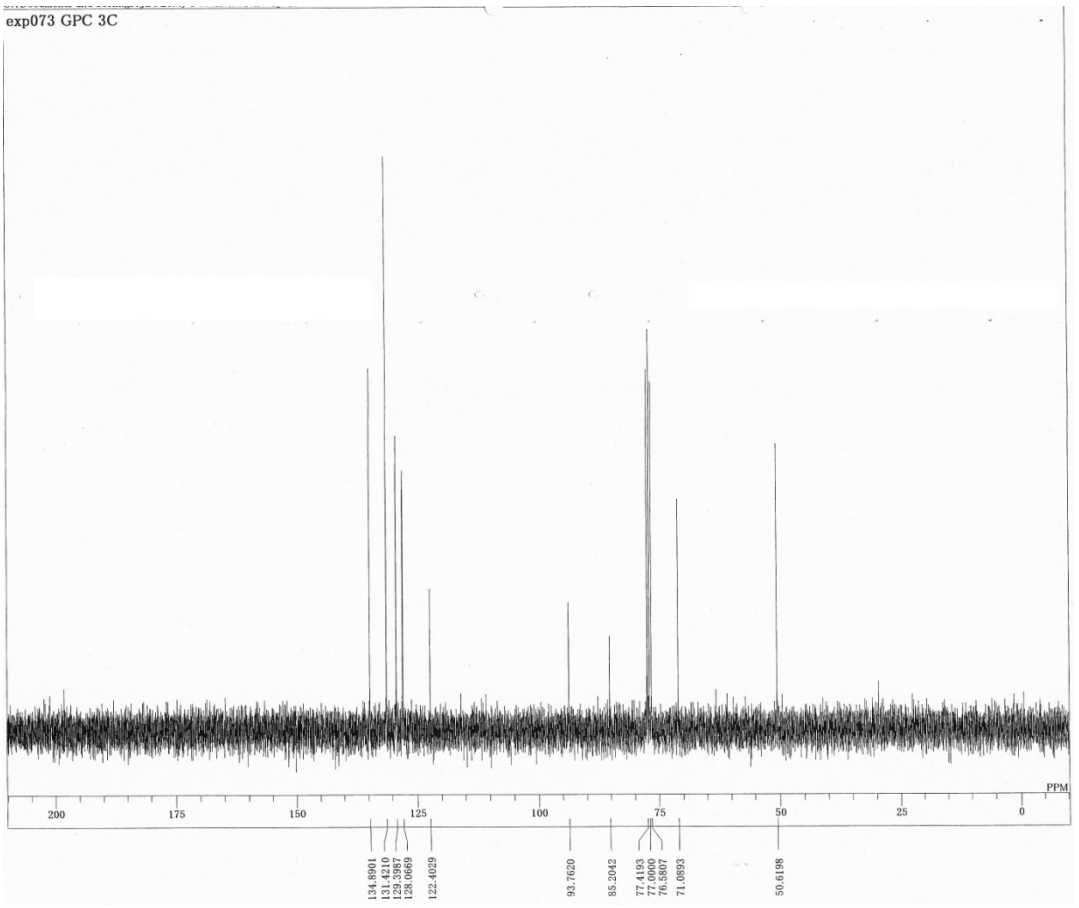
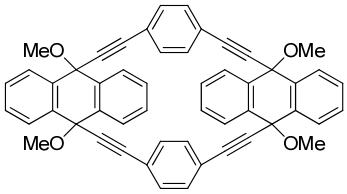
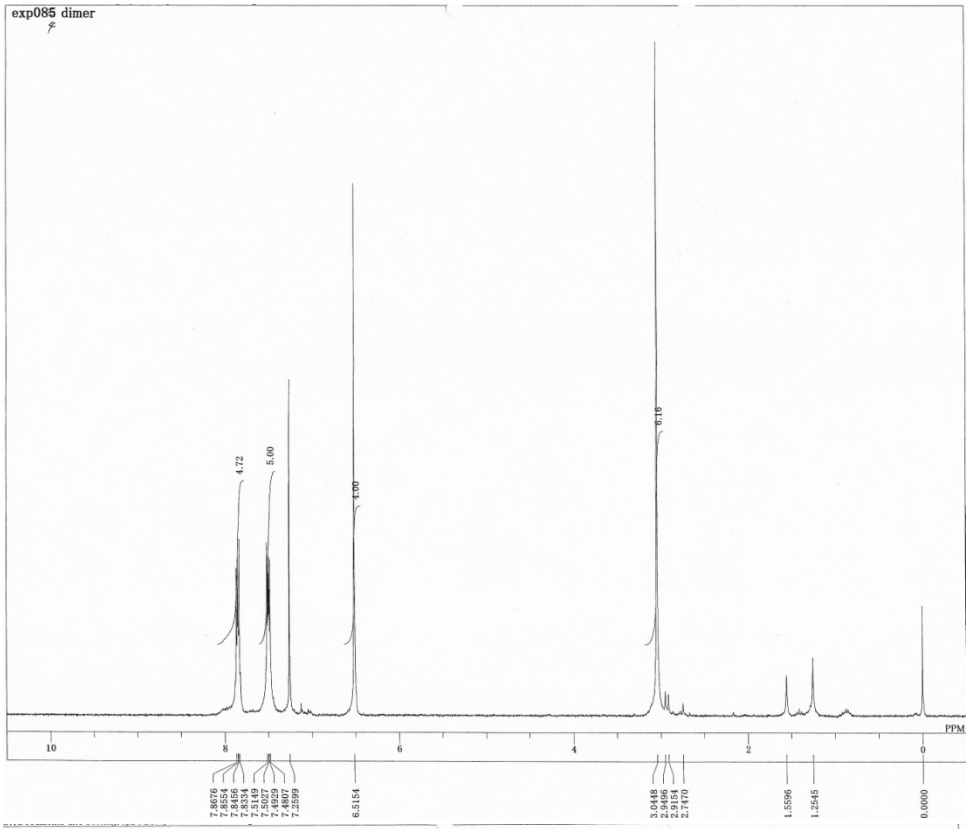
^{1}H NMR and ^{13}C NMR of 1.

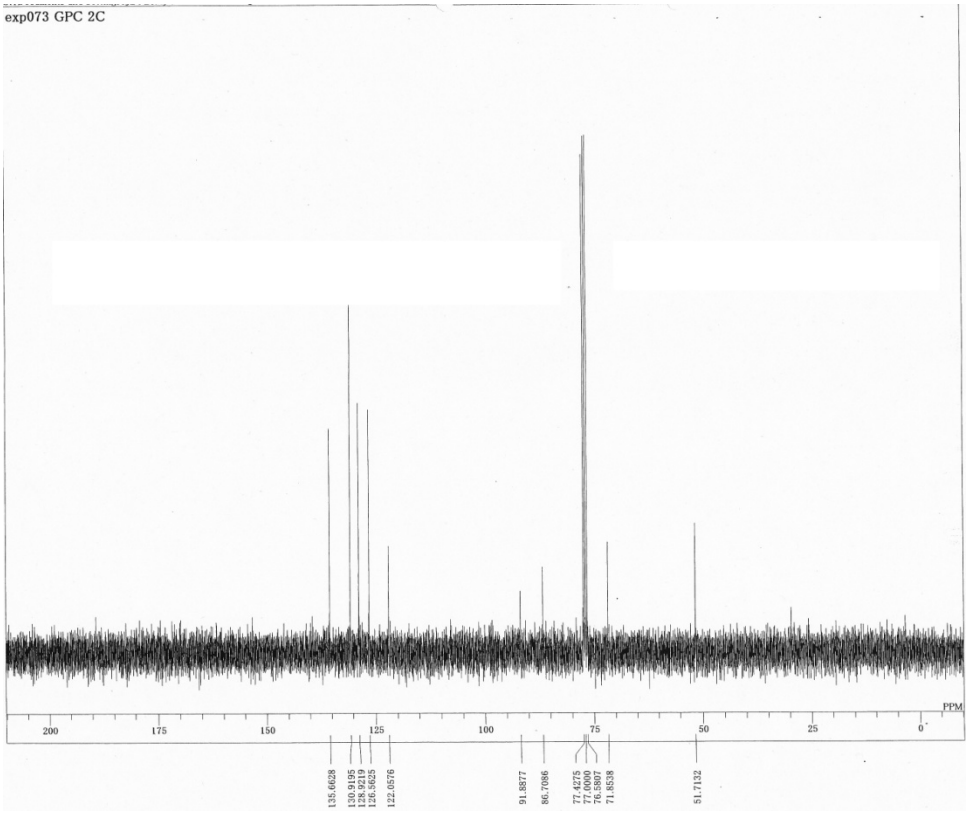




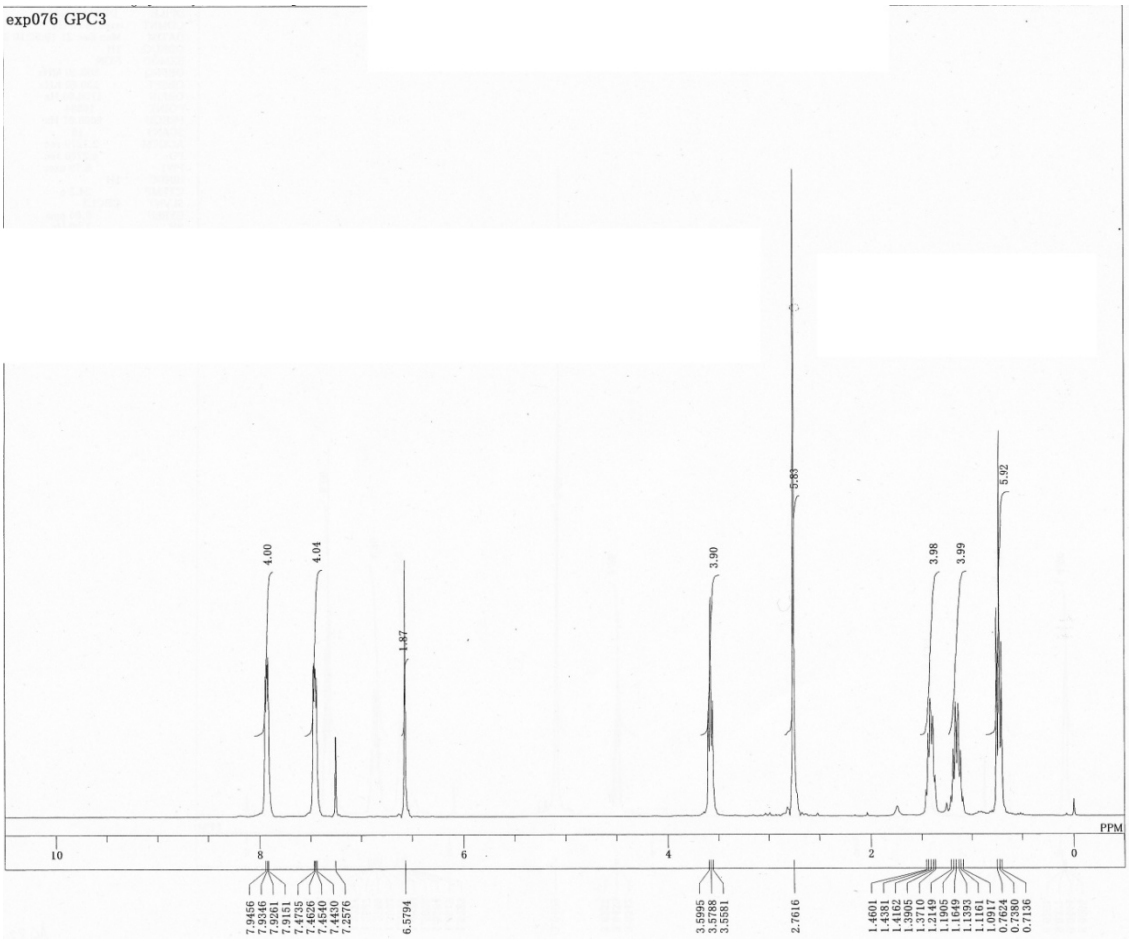
^{1}H NMR and ^{13}C NMR of cyclodimer.

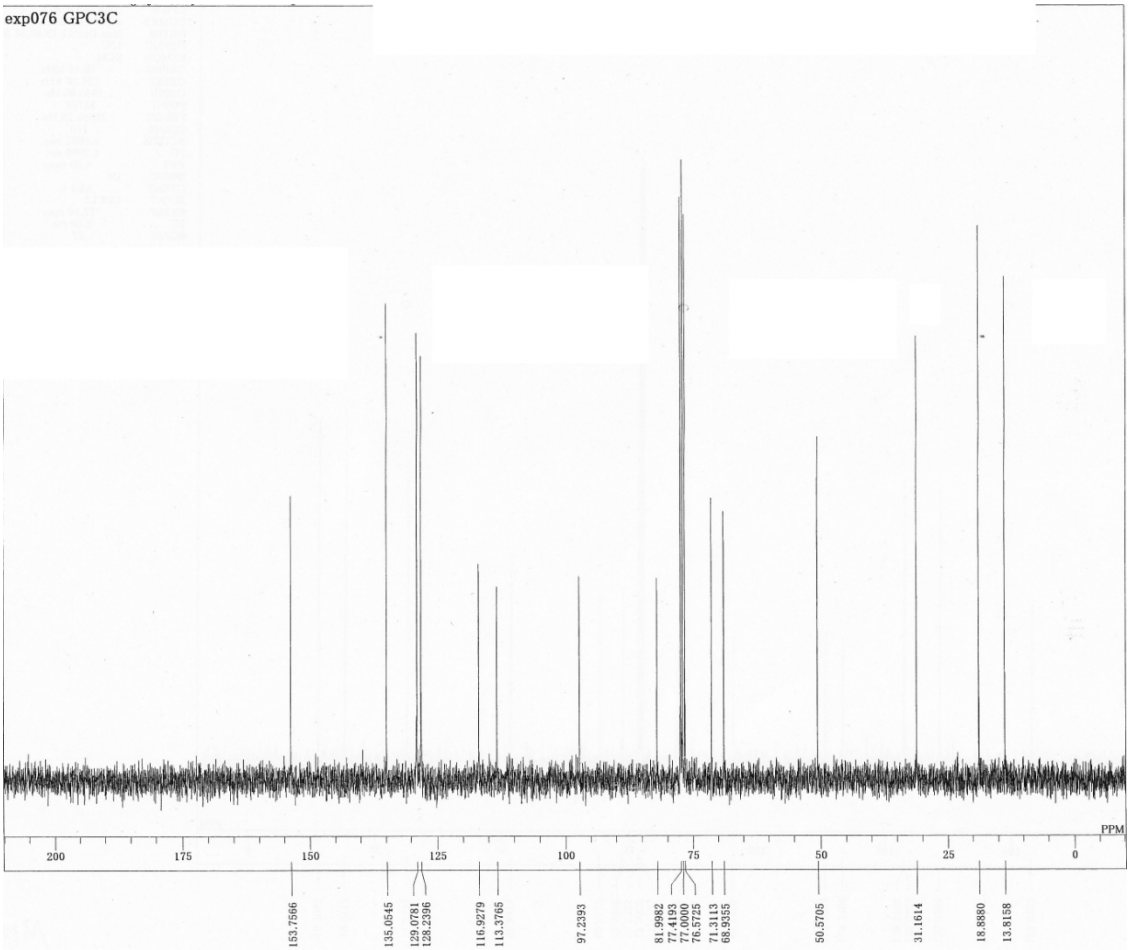




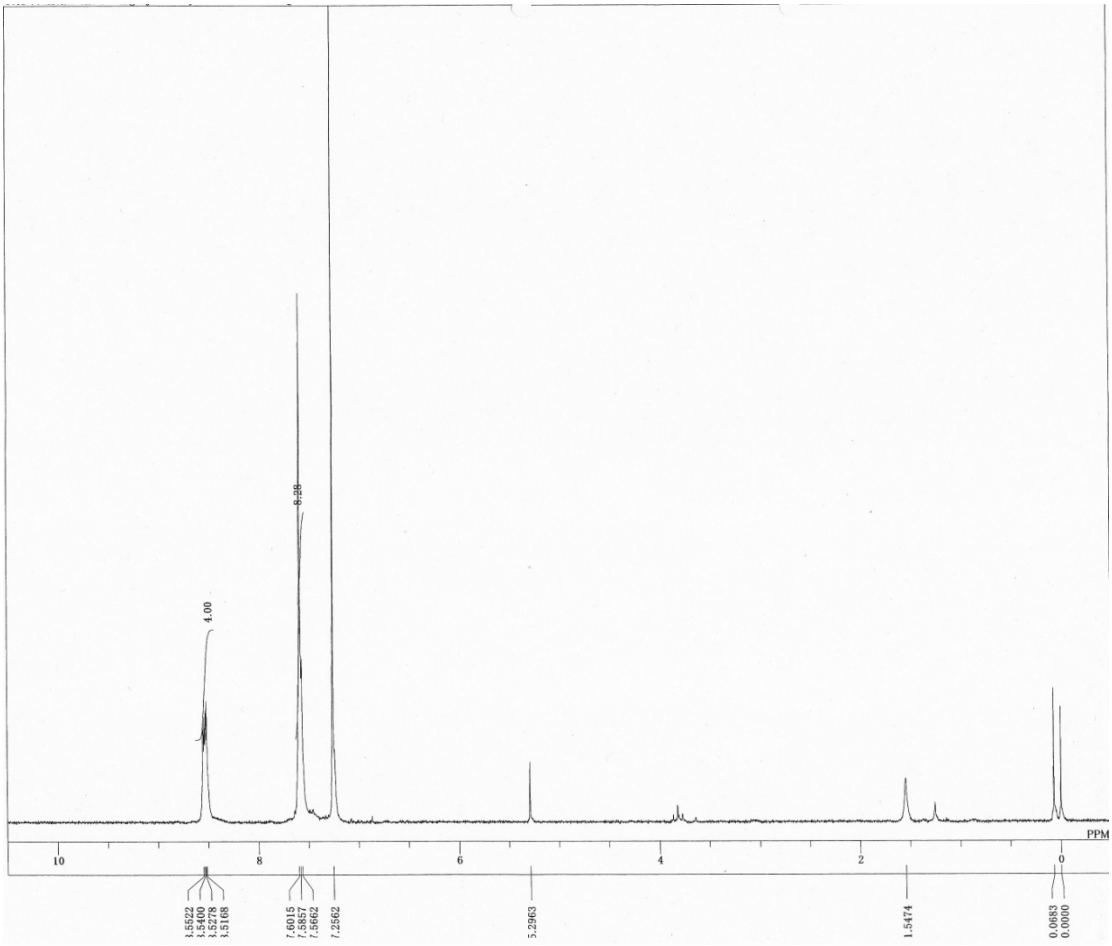


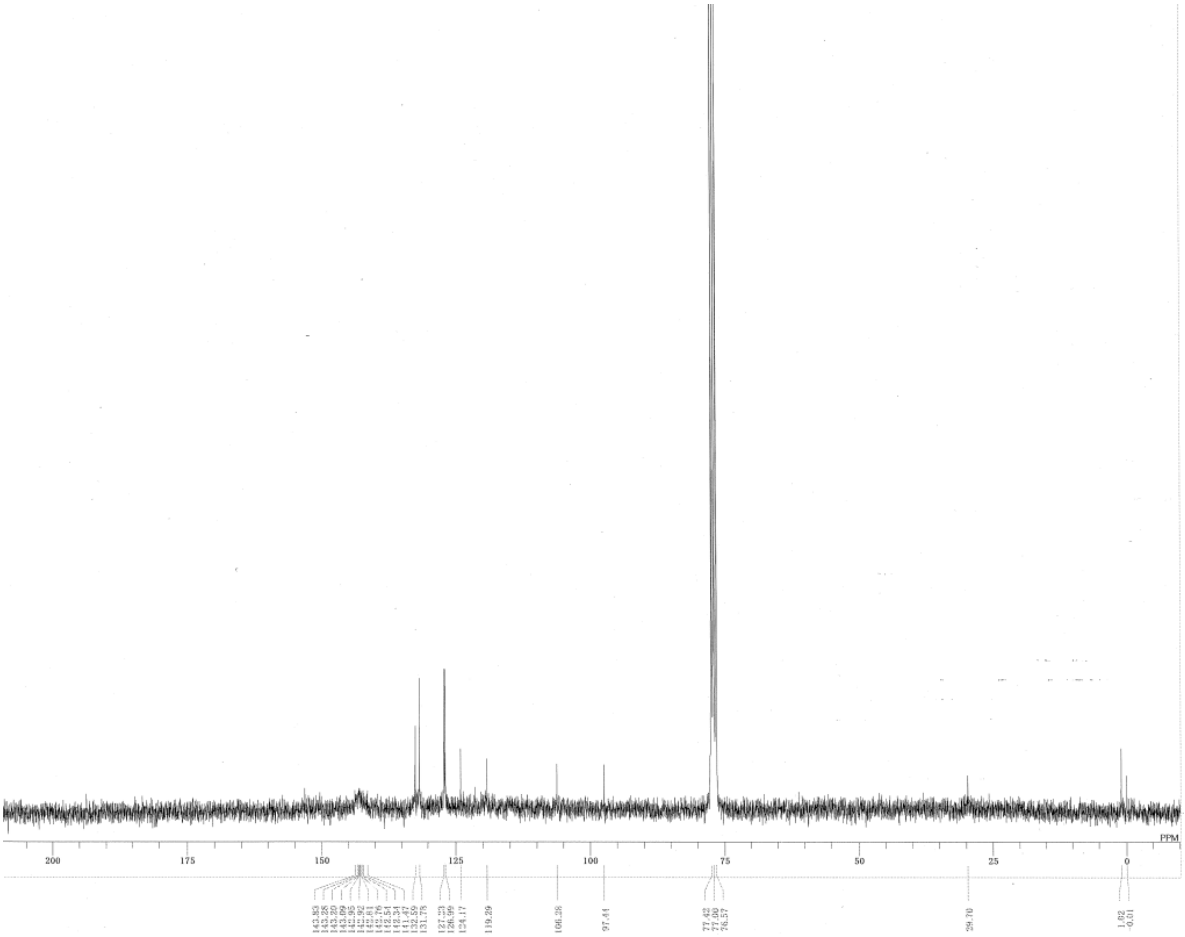
^{1}H NMR and ^{13}C NMR of 1′.



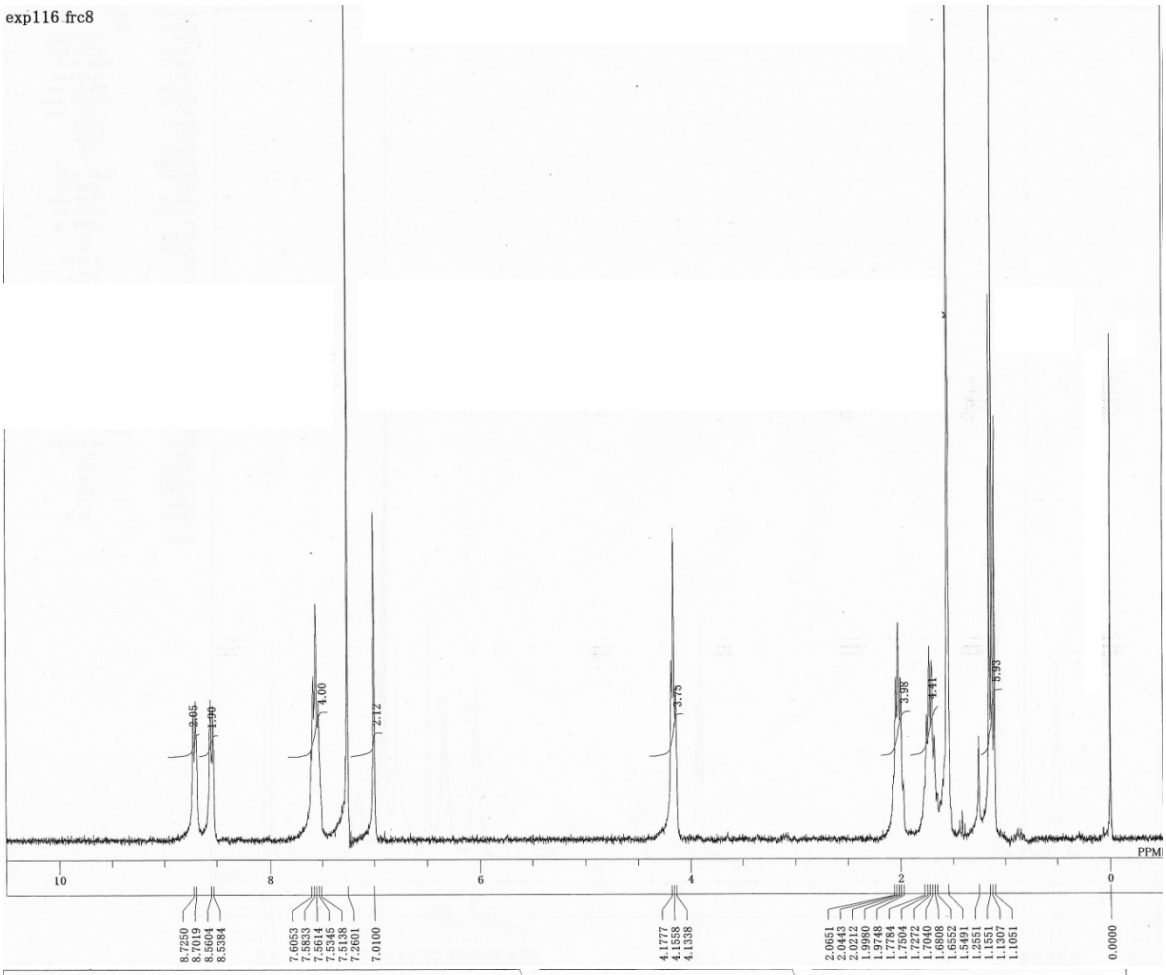


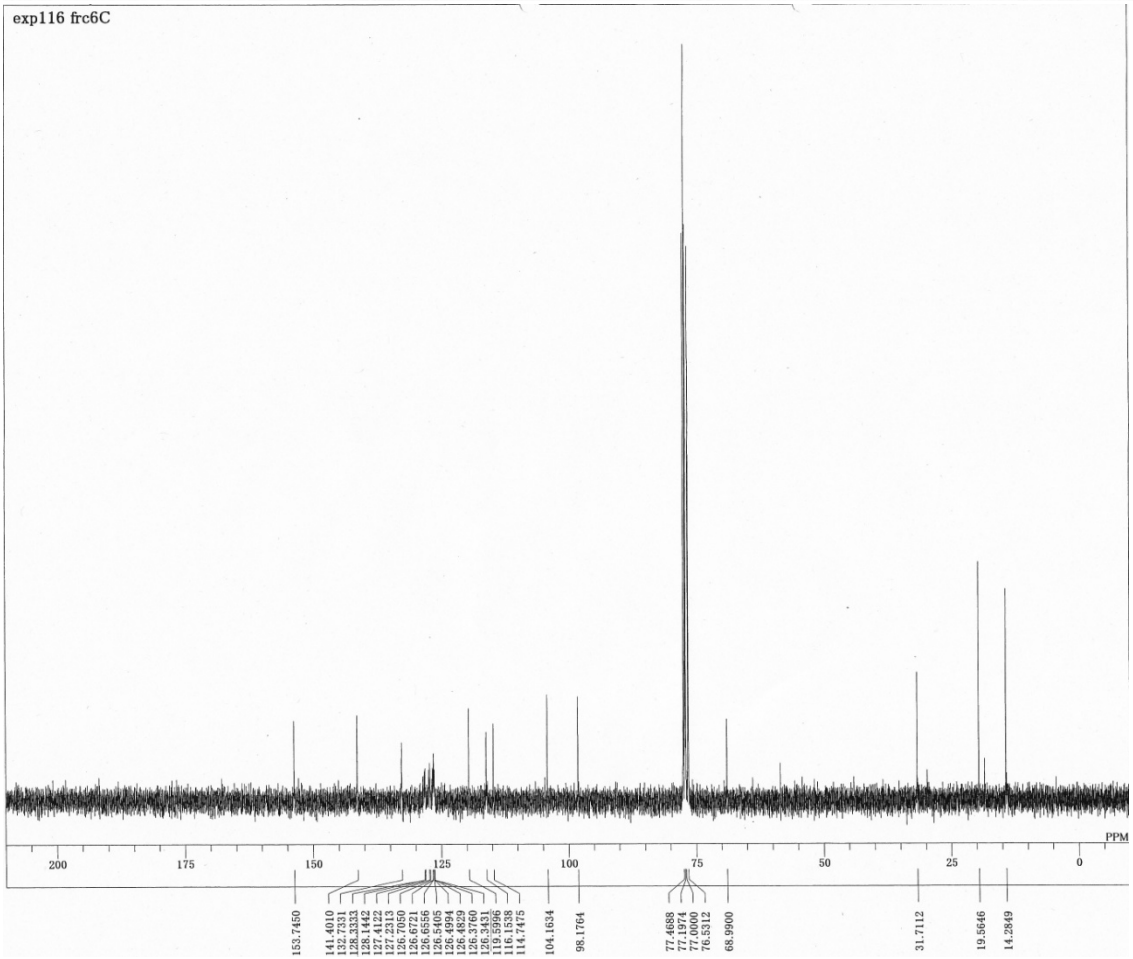
^{1}H NMR and ^{13}C NMR of 2⊃C_{60}.



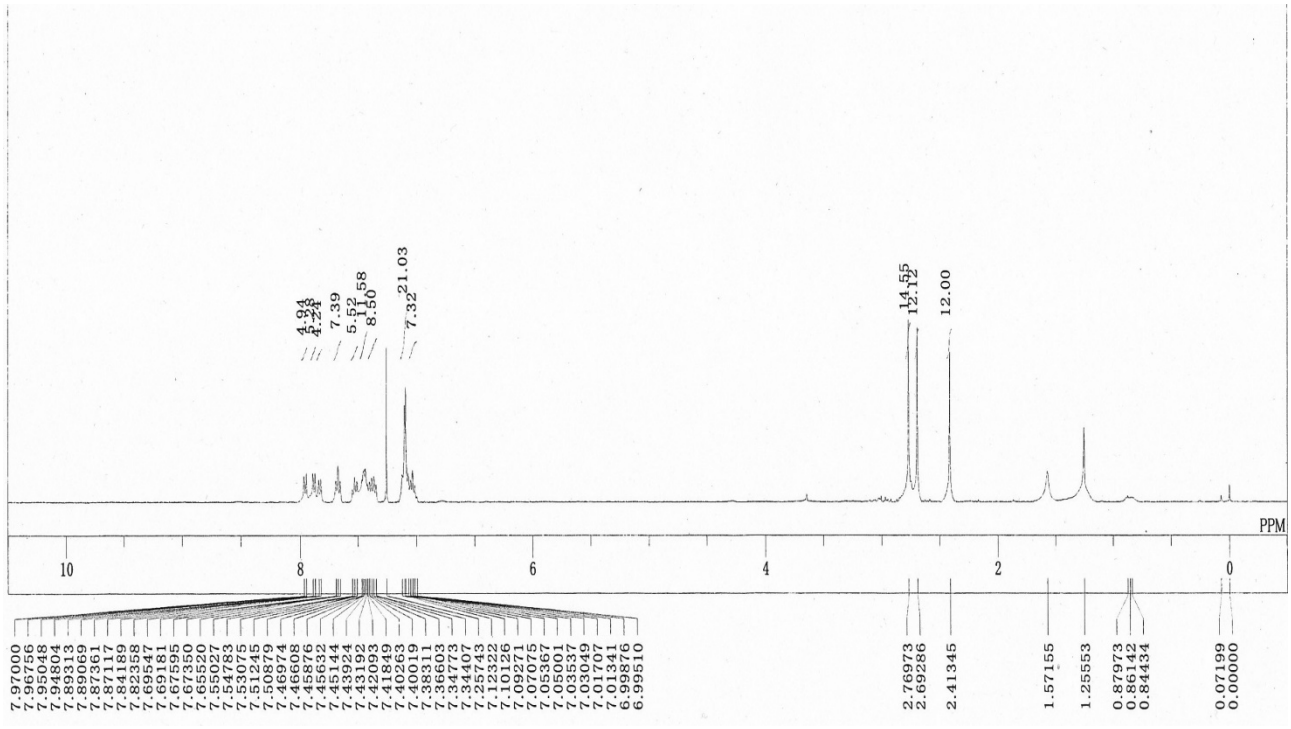


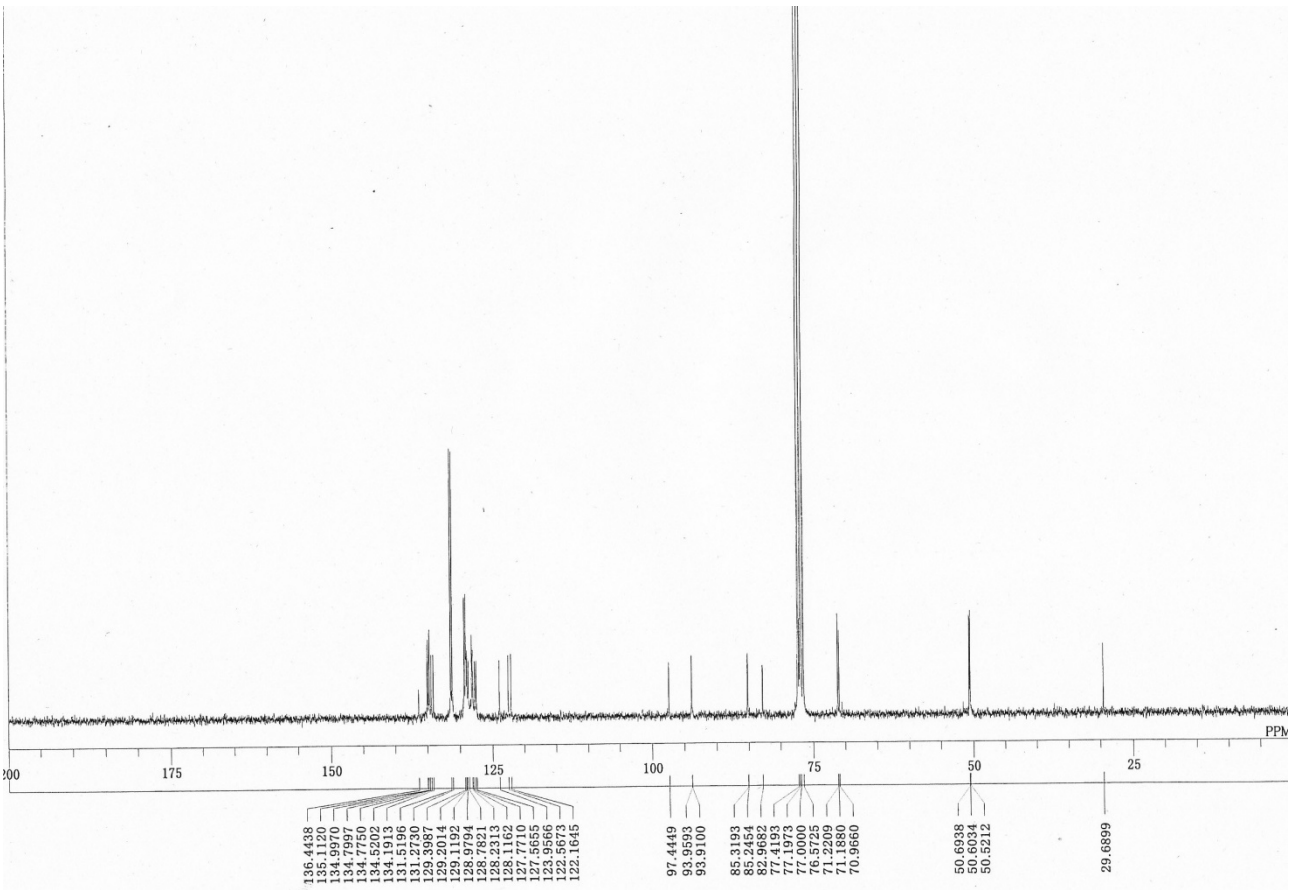
^{1}H NMR and ^{13}C NMR of 2′⊃C_{60}.



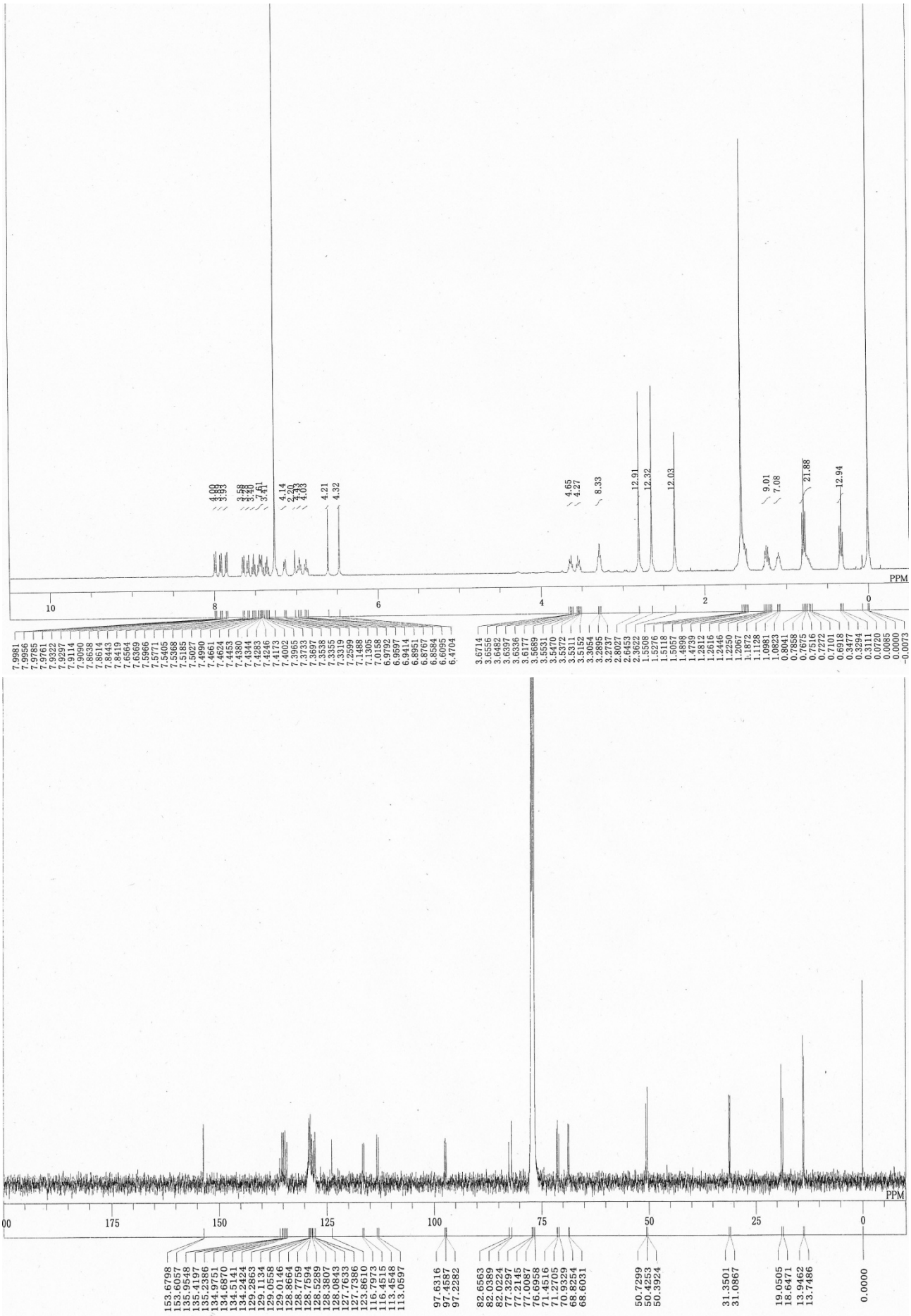


^{1}H NMR and ^{13}C NMR of 3a.

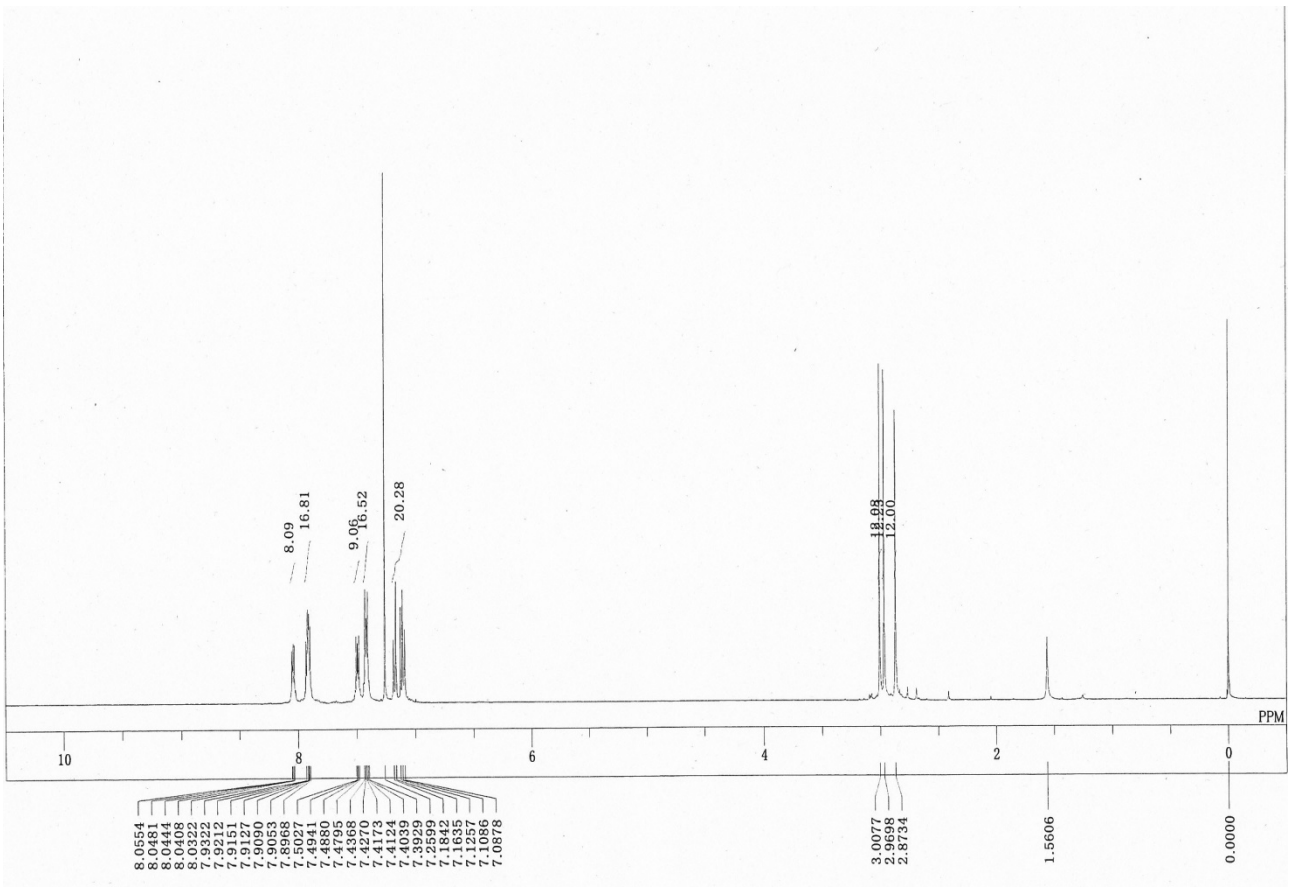


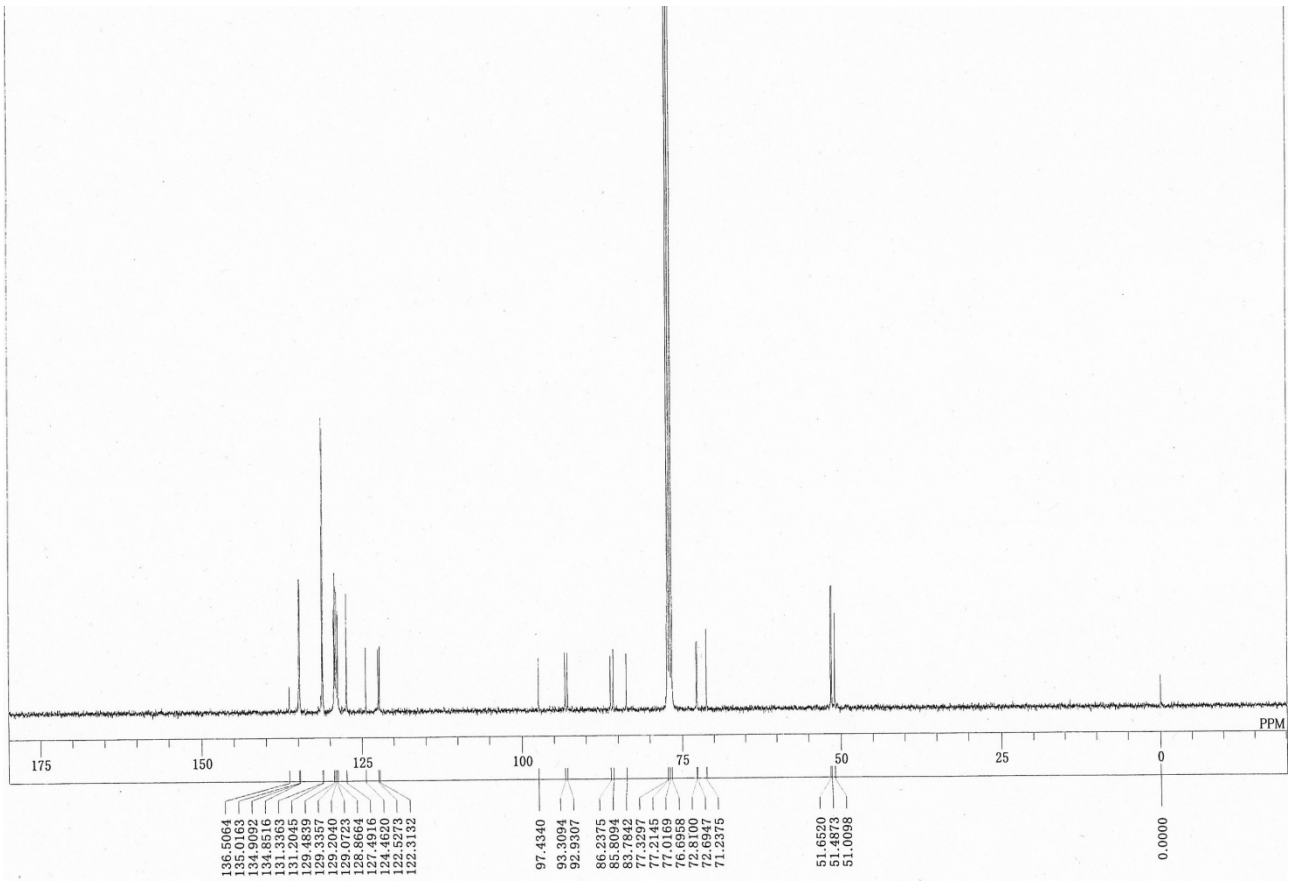


^{1}H NMR and ^{13}C NMR of 3a′.

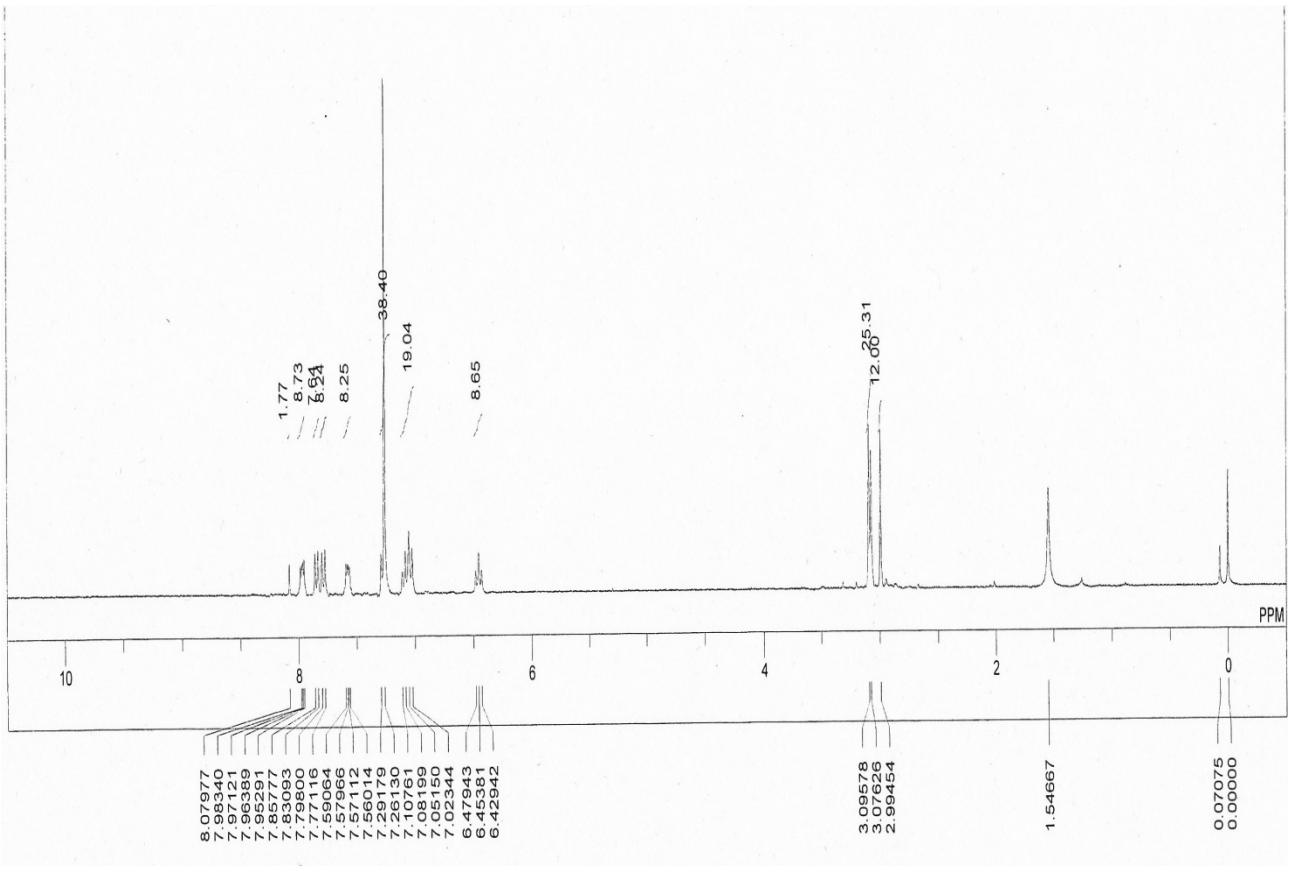


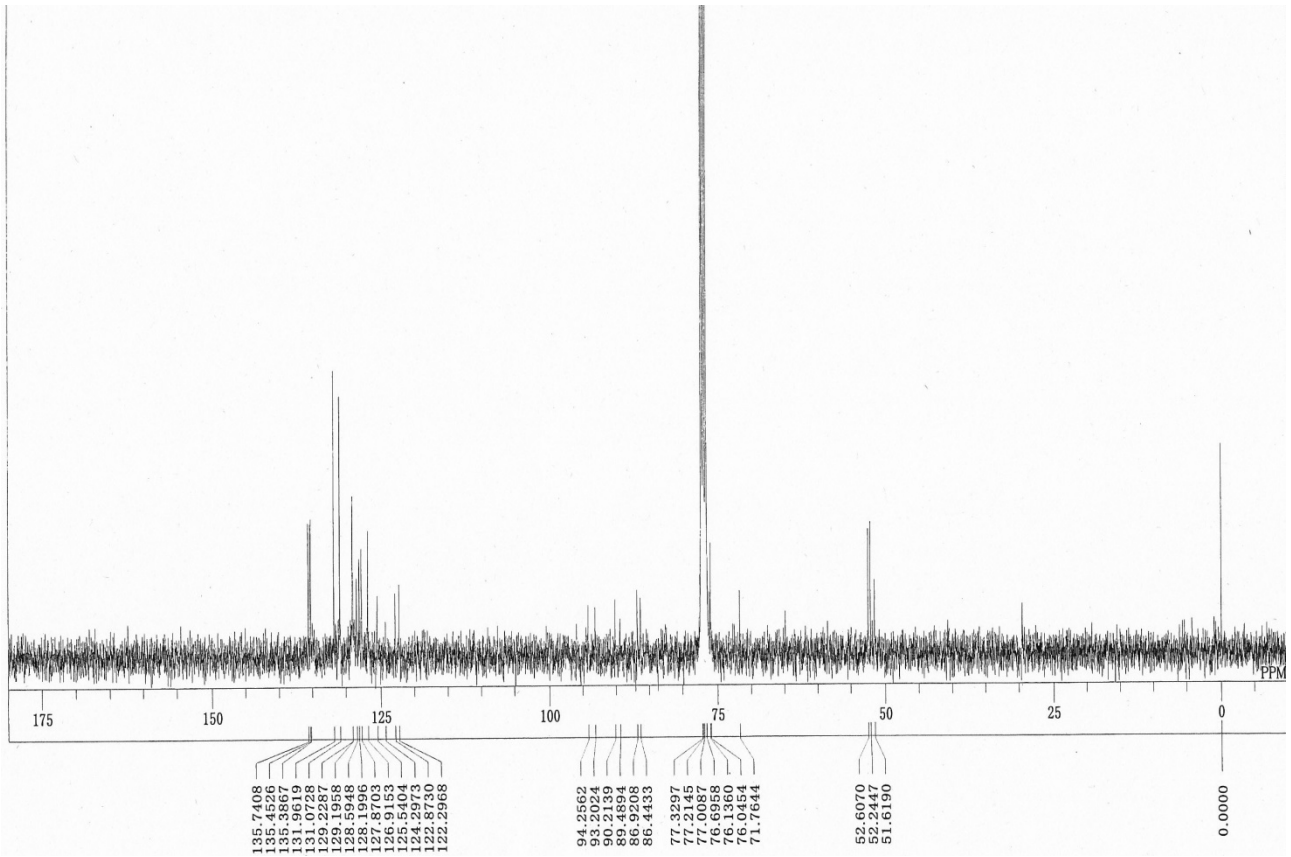
^{1}H NMR and ^{13}C NMR of 3b.



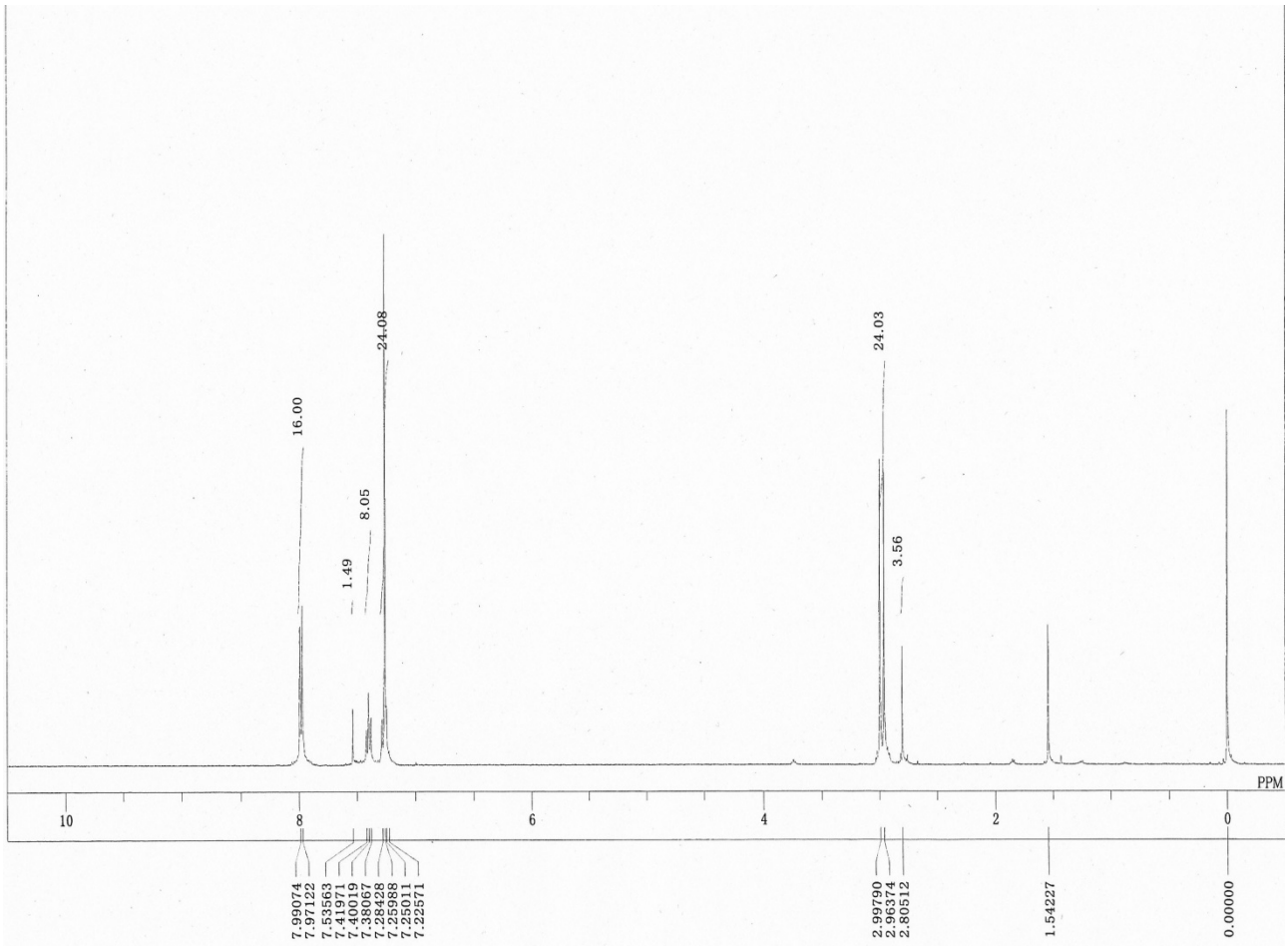


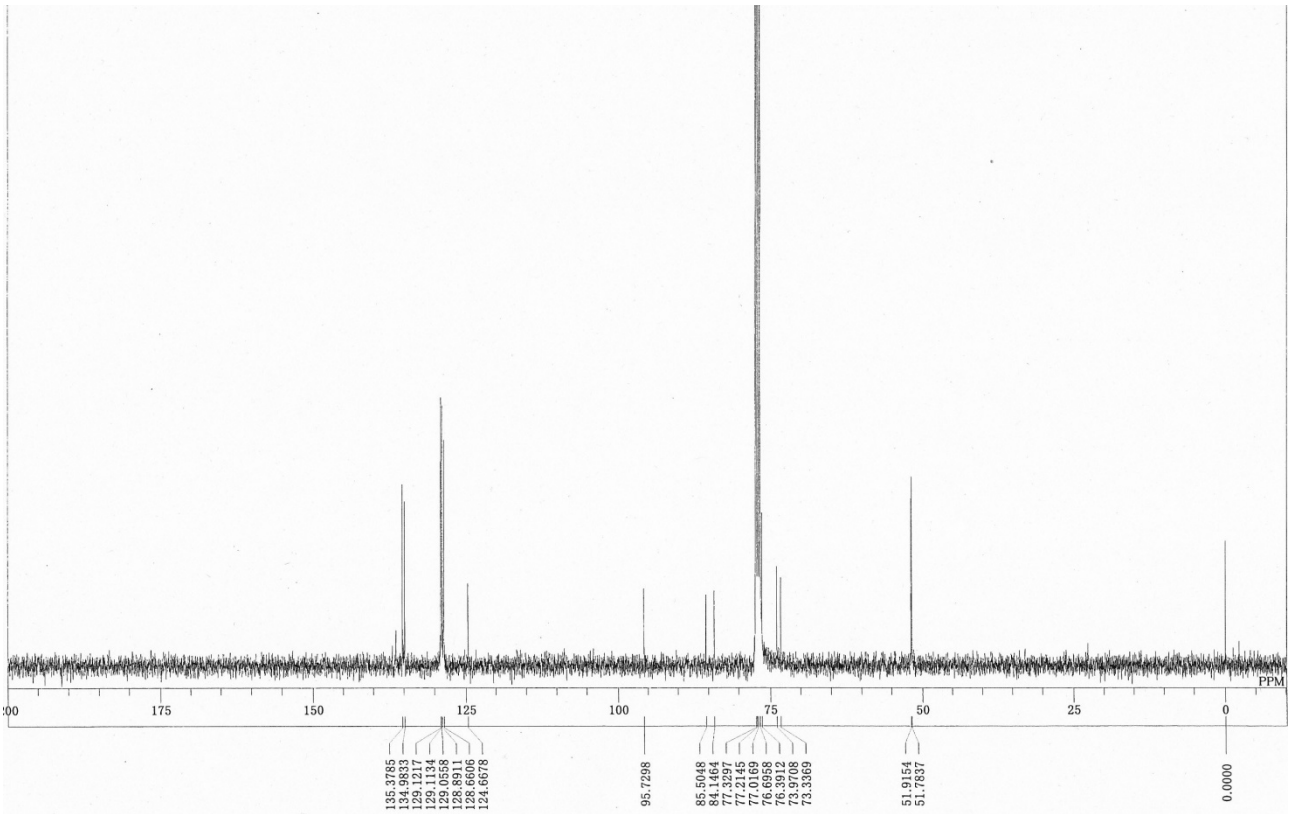
^{1}H NMR and ^{13}C NMR of 3c.



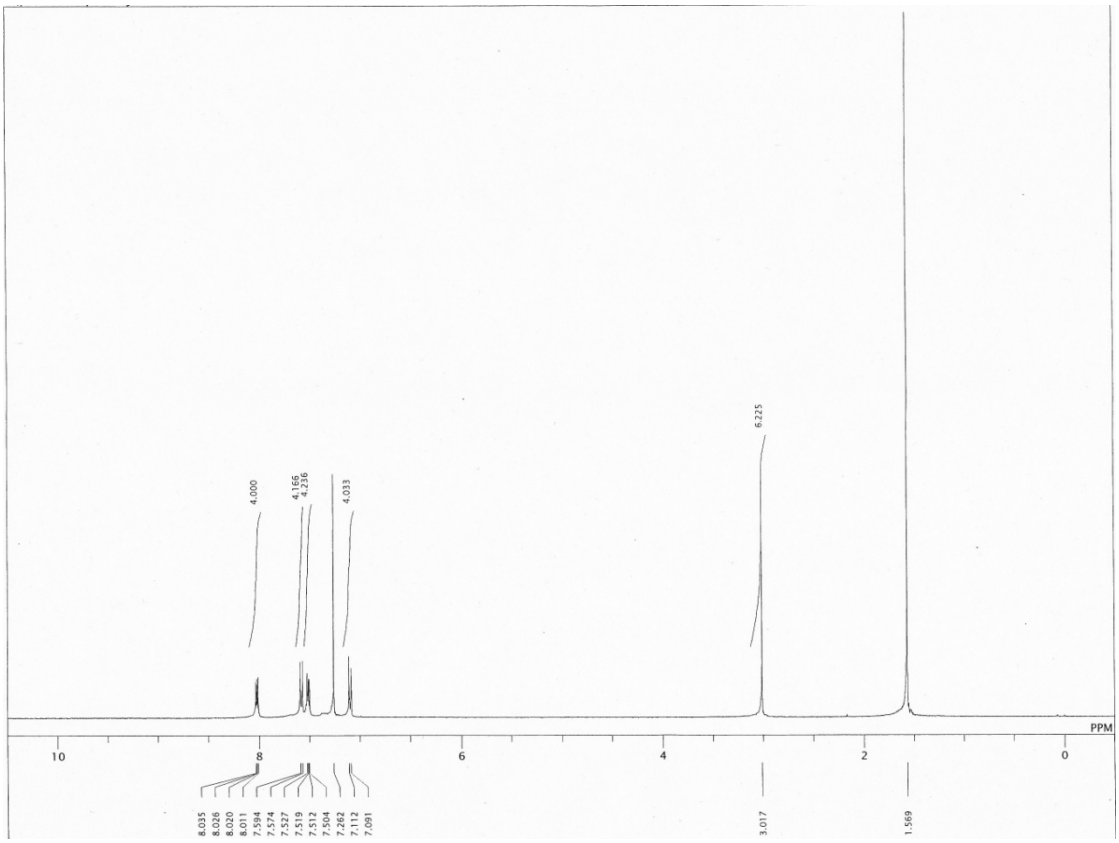


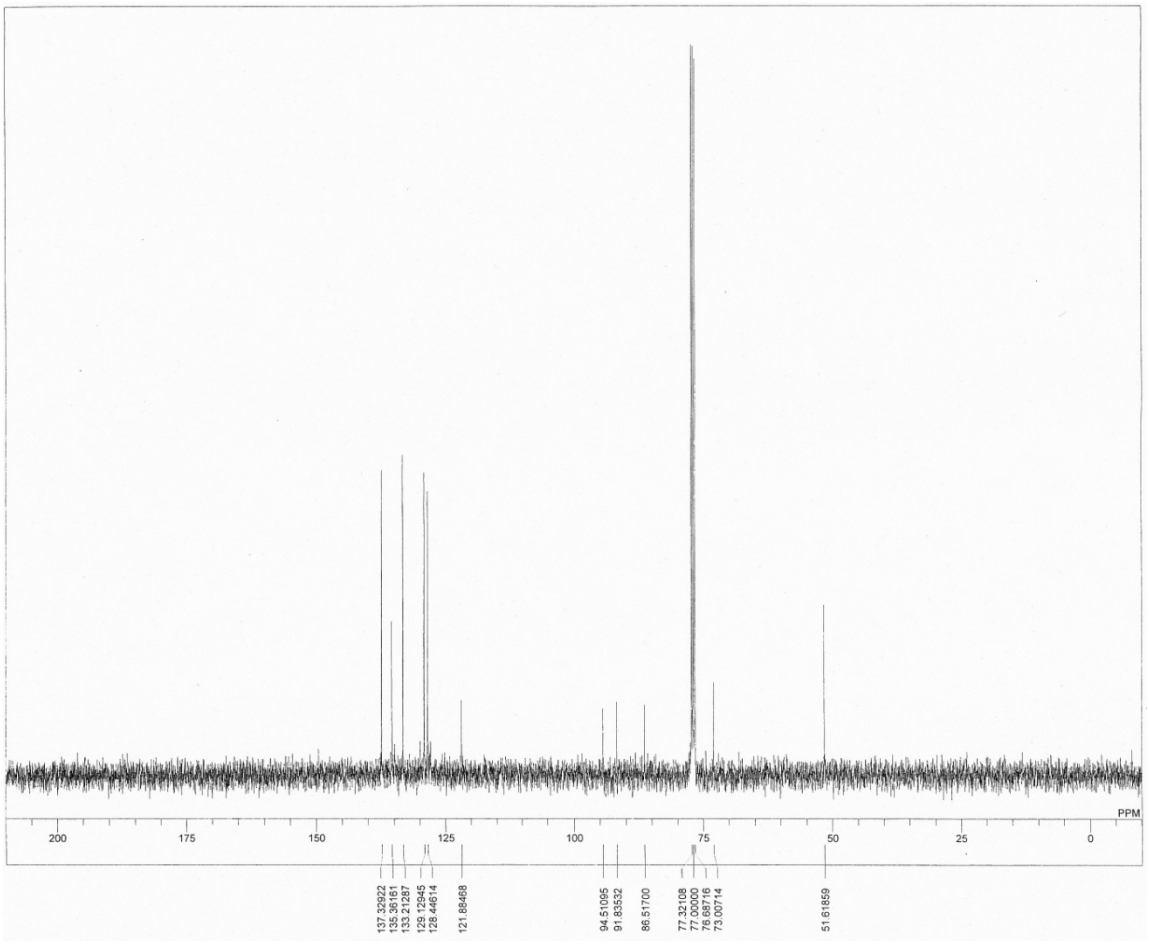
^{1}H NMR and ^{13}C NMR of 4.



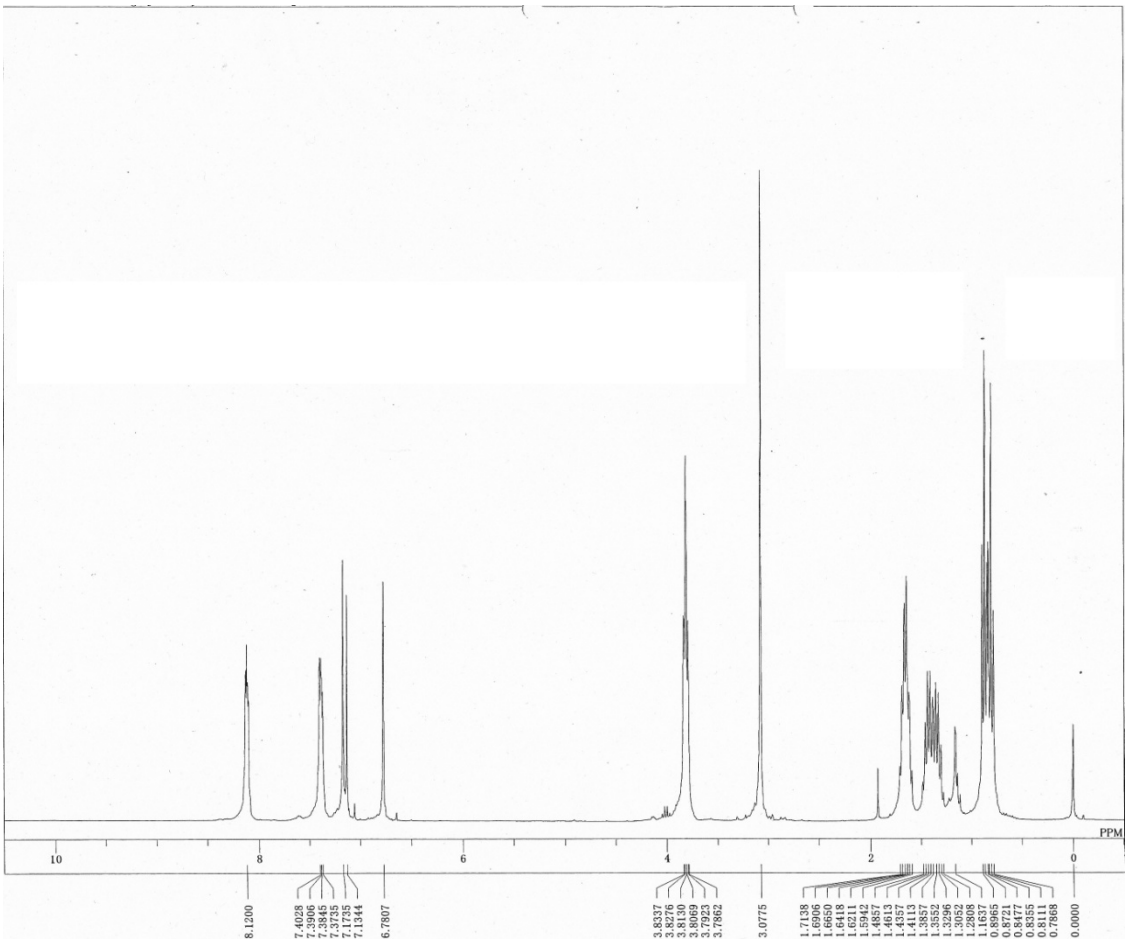


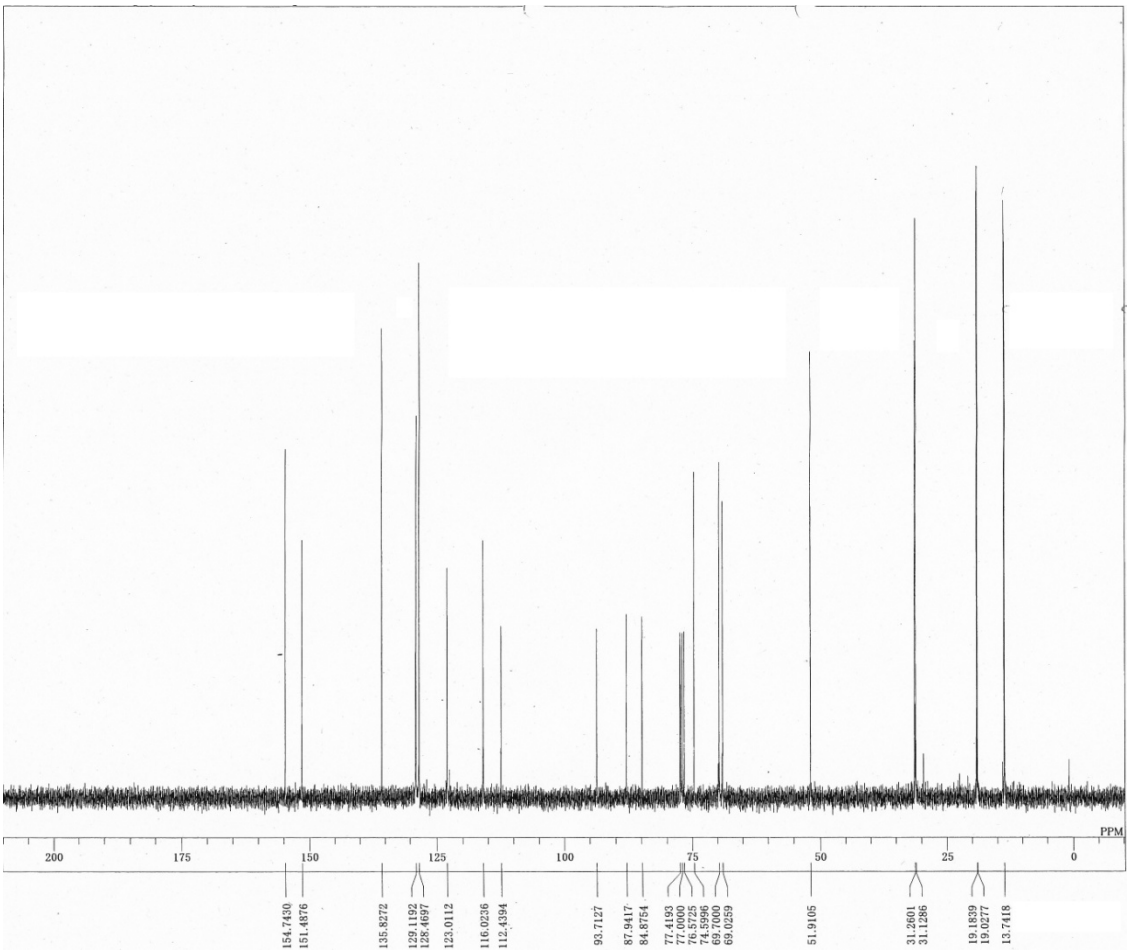
^{1}H NMR and ^{13}C NMR of 5a.



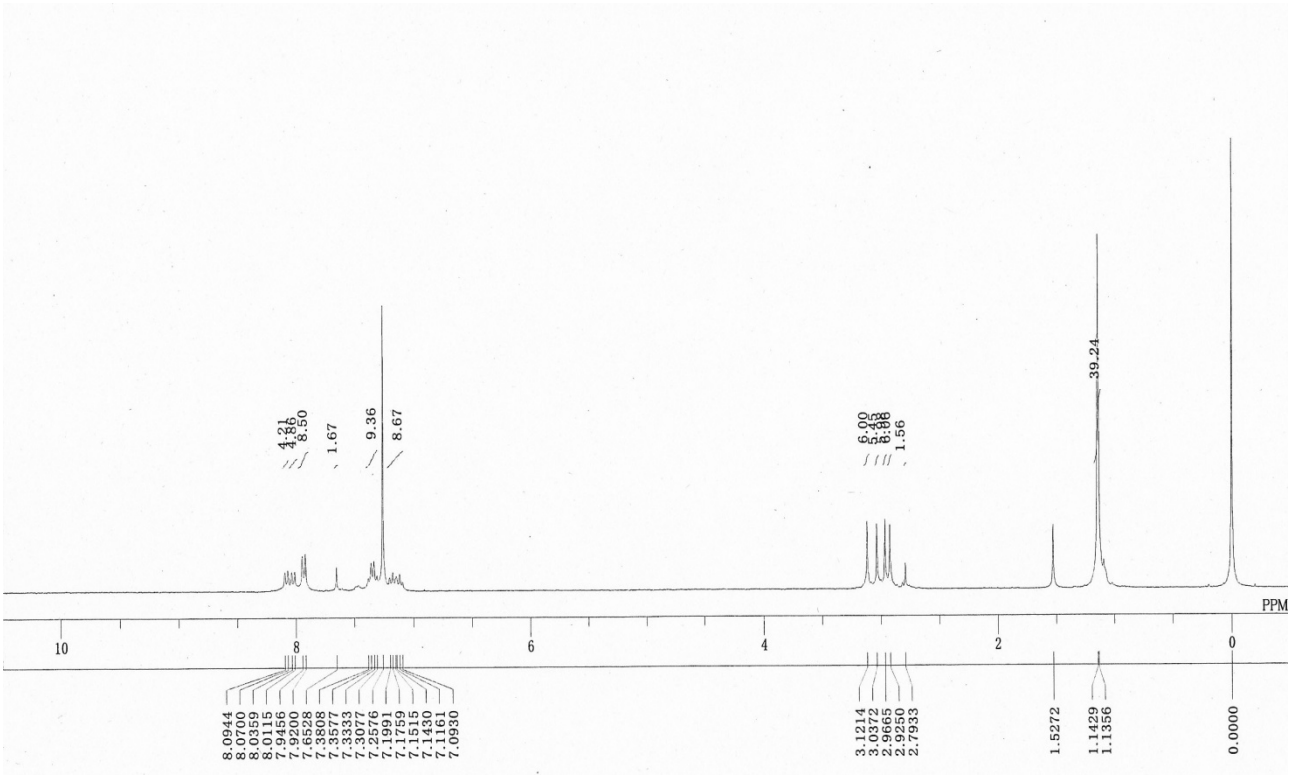


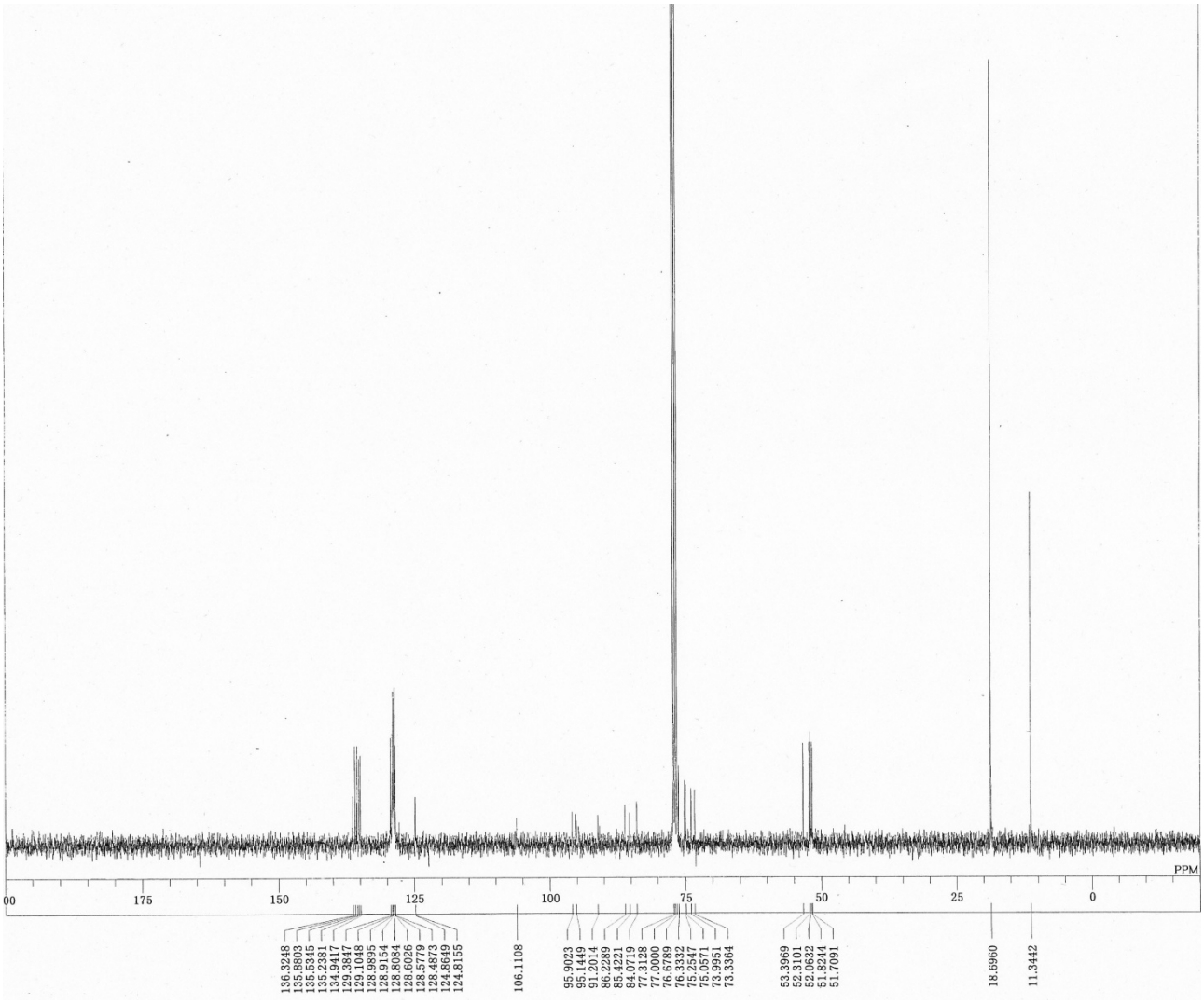
^{1}H NMR and ^{13}C NMR of 5b.



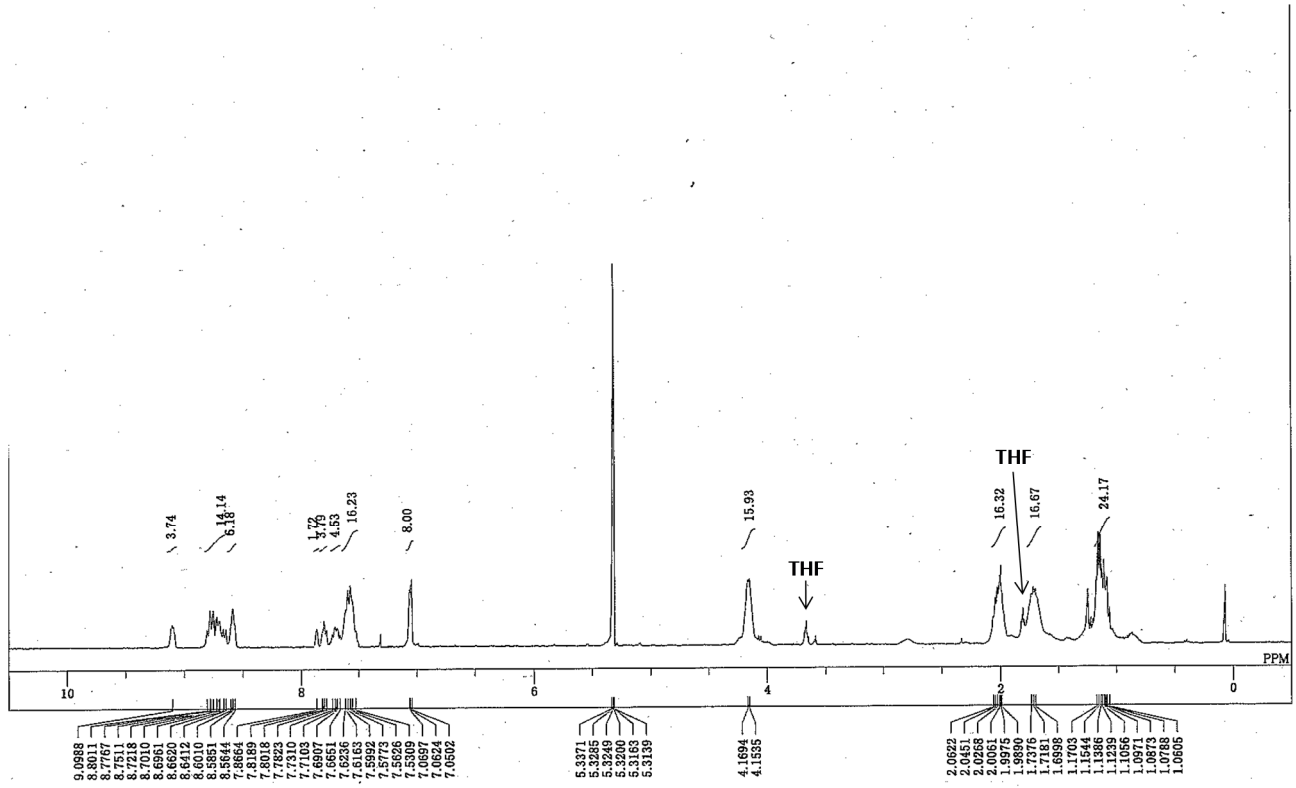


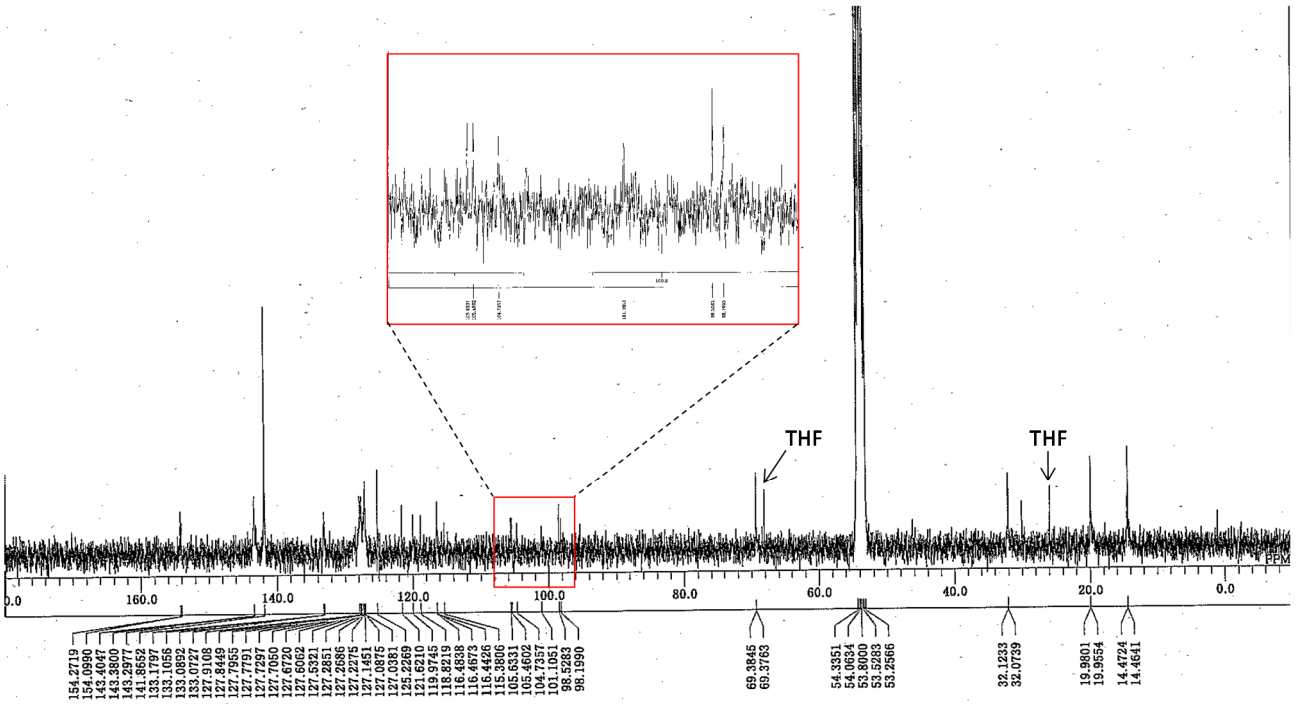
^{1}H NMR and ^{13}C NMR of 6.



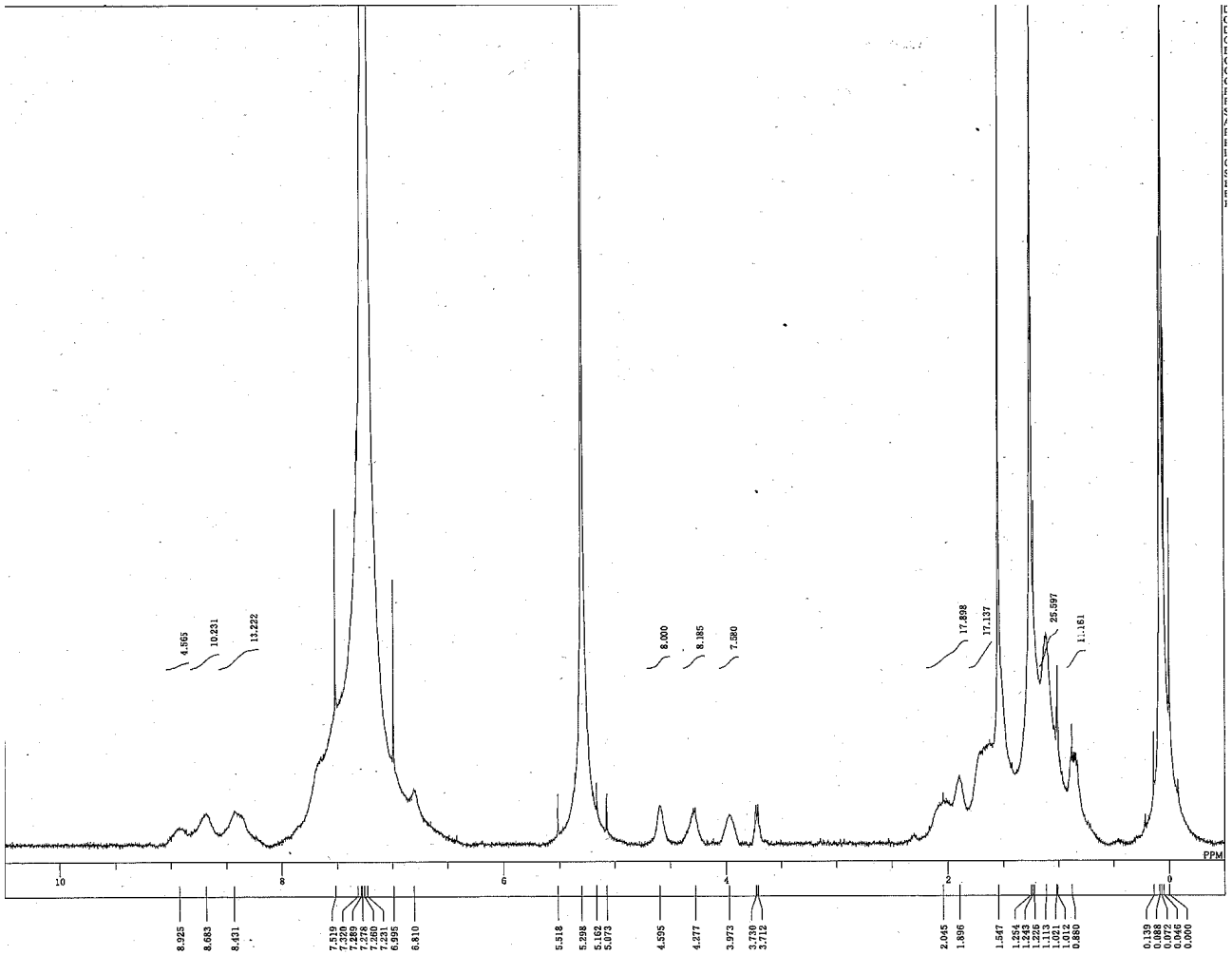


^{1}H NMR and ^{13}C NMR of 7′⊃2C$_{60}$ (in CD_2Cl_2).

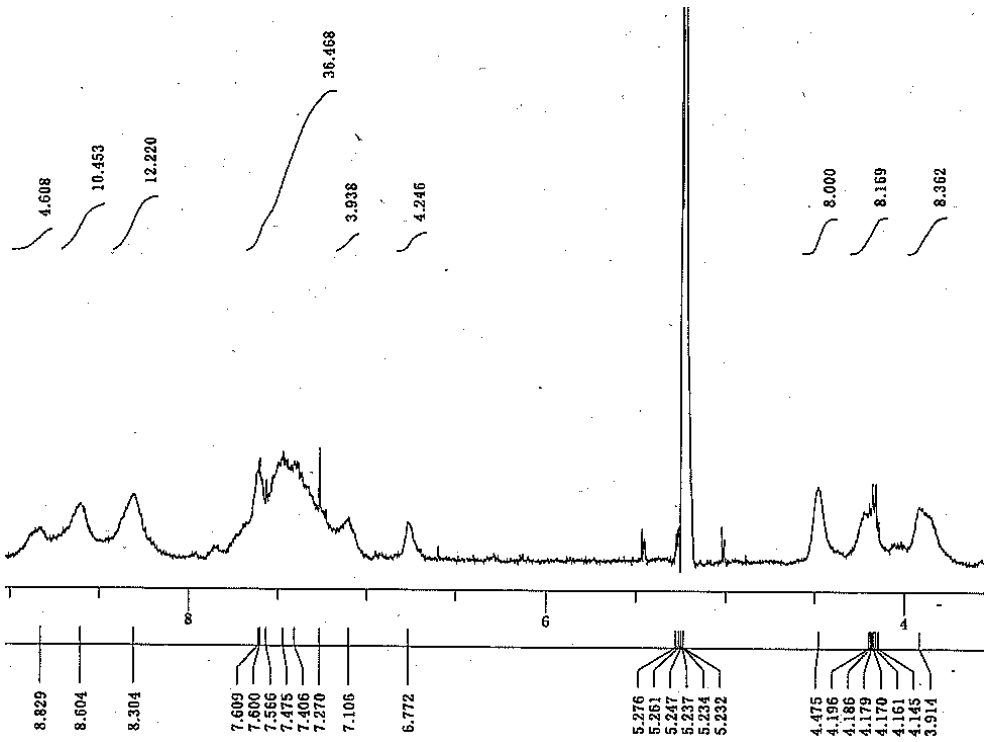




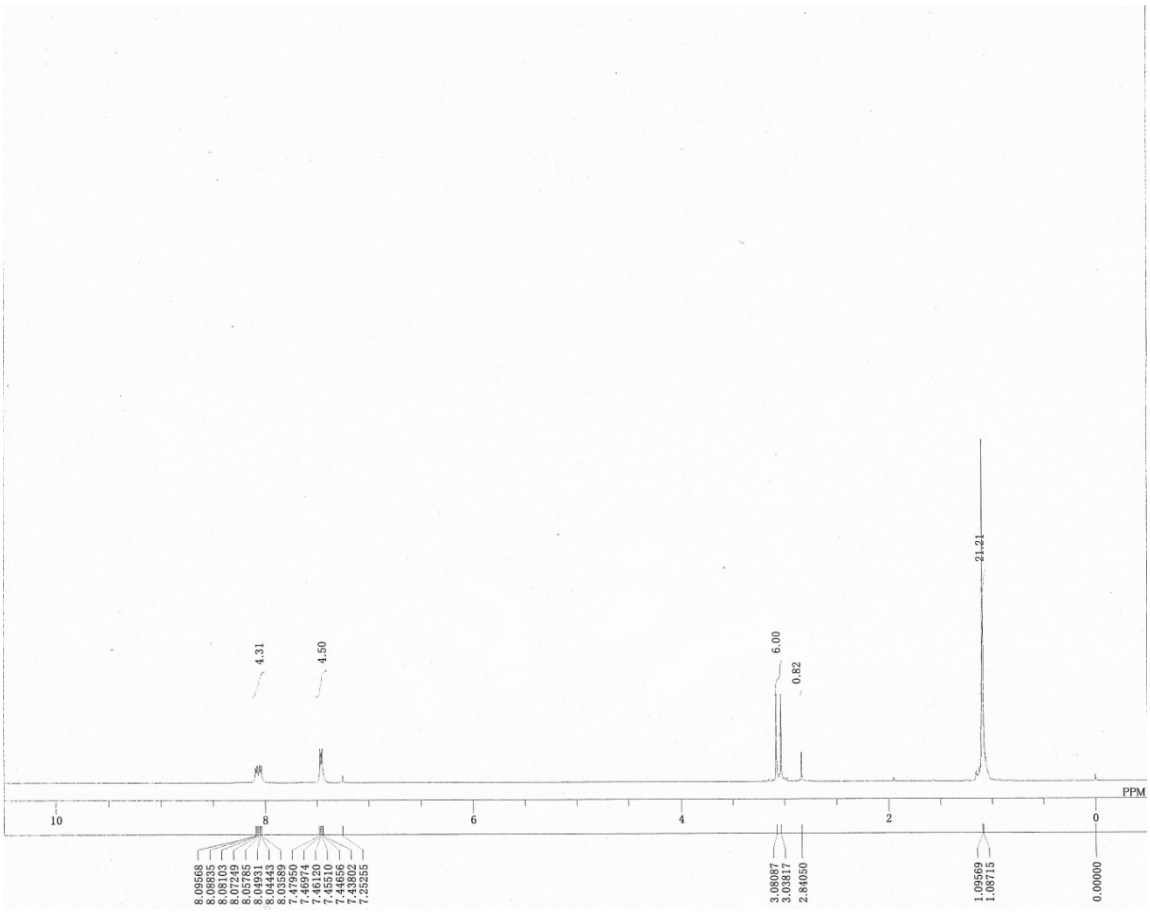
^{1}H NMR of 7′⊃2mC_{60} (in $CDCl_3$ with small amounts of CH_2Cl_2).

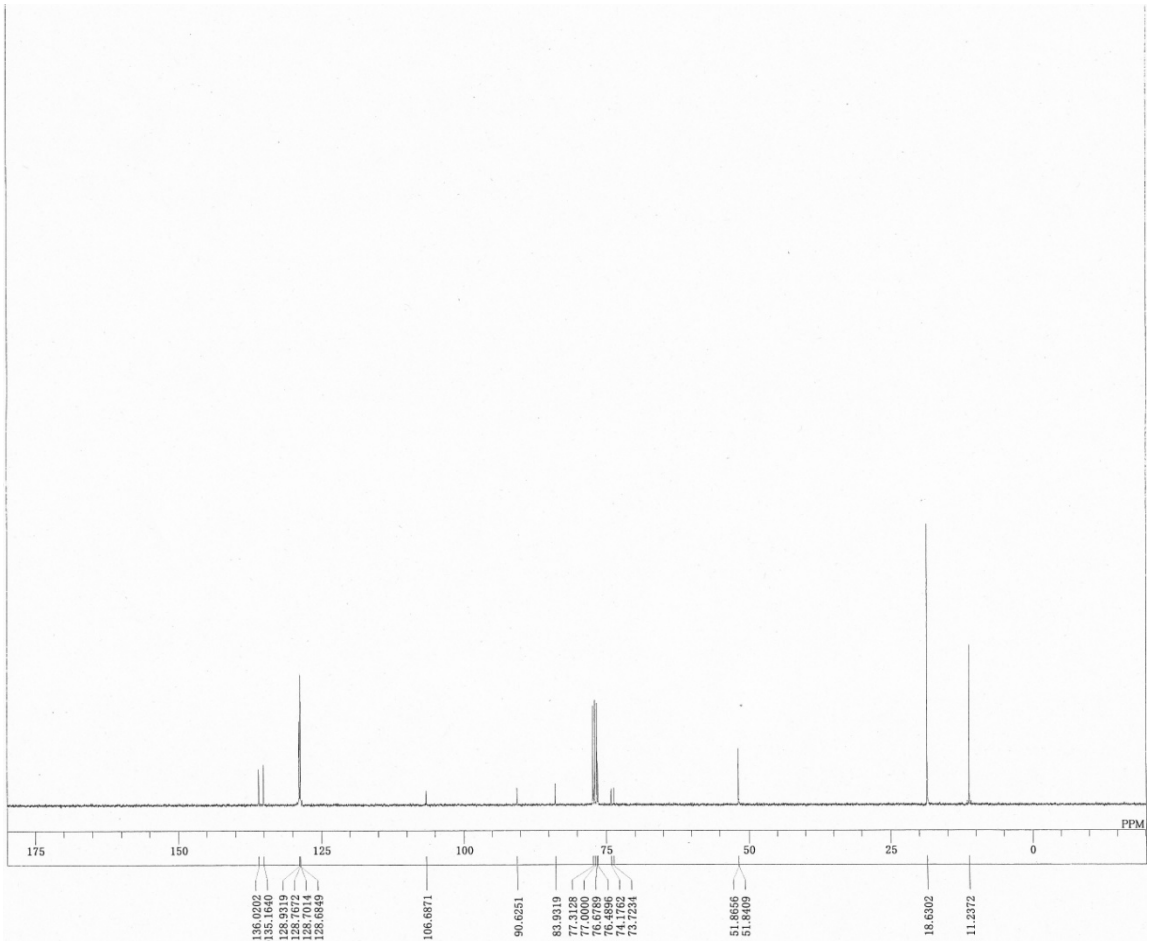


^{1}H NMR of 7′⊃2mC_{60} (in CD_2Cl_2)



^{1}H NMR and ^{13}C NMR of 8a.





^{1}H NMR and ^{13}C NMR of 8b.