Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A New Synthetic Route to 5,6,11,12-Tetraarylethynyltetracenes

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1. General

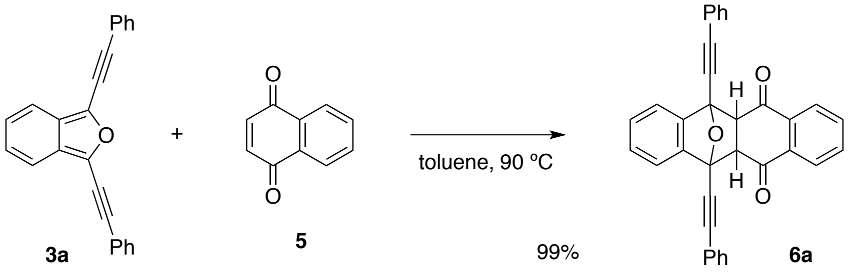
All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon. THF (anhydrous; Wako Pure Chemical Industries, Ltd.) and toluene (anhydrous; Wako Pure Chemical Industries, Ltd.) were used as received.

For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 N (spherical, neutral, 63–210 μm) from Kanto Chemical was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF_{254} (Art 7749).

^{1}H NMR and ^{13}C NMR were measured on a JEOL JNM ECA-300 or a JEOL JNM ECZ-500R spectrometer. Attenuated Total Reflectance Fourier Transformation Infrared (ATR-FTIR) spectra were recorded on a JASCO FT/IR-4200 infrared spectrometer. Photoluminescence spectra were recorded on a JASCO FP-8500 spectrofluorometer. UV-VIS spectra were recorded on a JASCO V-630 spectrophotometer. High resolution mass spectra were obtained with a JEOL The AccuTOF LC-plus JMS-T100LP, a JEOL SpiralTOF JMS-S3000, or a Bruker micrOTOF spectrometer. Melting points (Mp) were measured on a MPA100 OptiMelt Automated Melting Point System from Stanford research systems and are uncorrected.

2. Syntheses of π-extended rubrenes

General Procedure 1



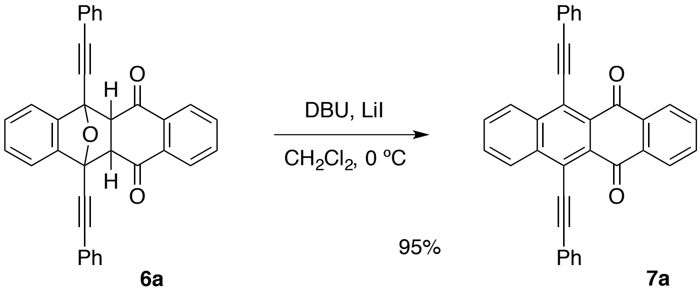
Scheme S1

A mixture of isobenzofuran **3a** (640 mg, 2.01 mmol) and 1,4-naphthoquionone (**5**) (380 mg, 2.40 mmol) in toluene (5.0 mL) was stirred at 90 ºC for 3.5 h. After cooling to room temperature, the precipitates were collected by filtration (ice-cold toluene) to provide cycloadduct **6a** (944 mg, 99%) as a white solid.

mp 127 ºC (dec);
R_f 0.30 (hexane/EtOAc = 8/2);
^{1}H NMR (500 MHz, $CDCl_3$) 4.11 (s, 2H), 6.93–6.98 (m, 2H), 7.13–7.27 (m, 4H), 7.36–7.41 (m, 4H), 7.46–7.50 (m, 2H), 7.64–7.68 (m, 4H), 7.70–7.73 (m, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) 56.3, 81.7, 83.1, 90.7, 120.8, 121.6, 126.4, 128.3, 129.2, 132.3, 134.0, 134.2, 141.4, 191.7;
IR (ATR, cm^{-1}) 3051, 2239, 1676, 1585, 1490, 1443, 1362, 1319, 1275, 1147, 1120, 1063, 974, 913, 881, 804, 749, 686, 631;
HRMS (DART) *m/z* calcd for $C_{34}H_{21}O_3$ $[M+H]^+$: 477.1491; found: 477.1507.

During the course of the NMR measurement, retro Diels–Alder reaction of ***6a*** *partially proceeded.*

General Procedure 2



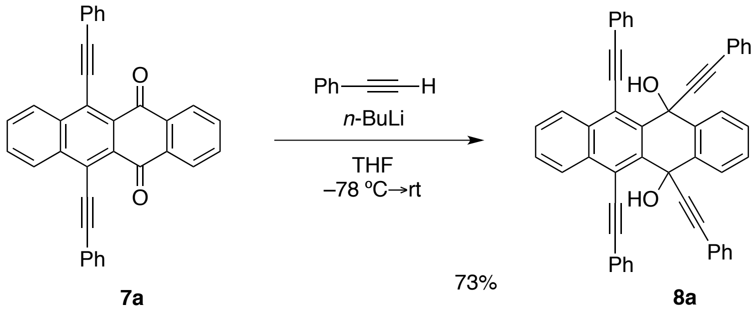
Scheme S2

To a mixture of cycloadduct **6a** (238 mg, 0.499 mmol) in CH_2Cl_2 (20 mL) was sequentially added LiI (134 mg, 1.00 mmol) and DBU (448 μL, 3.00 mmol) at 0 ºC. After stirring for 30 min, the reaction was quenched by addition of 1 M HCl and the products were extracted with CH_2Cl_2 (×3). The combined extracts were washed with brine, and then dried over Na_2SO_4. The crude products were triturated with Et_2O to give tetracenequinone **7a** (217 mg, 95%) as a yellow solid.

mp 205 ºC (dec);
R_f 0.40 (hexane/EtOAc = 8/2);

^{1}H NMR (500 MHz, $CDCl_3$) 7.43–7.50 (m, 6H), 7.78–7.84 (m, 4H), 7.86–7.89 (m, 4H), 8.36–8.40 (m, 2H), 8.86–8.90 (m, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) 88.0, 103.9, 123.0, 123.3, 127.3, 128.57, 128.63, 129.3, 130.1, 131.5, 132.3, 133.8, 134.4, 135.1, 182.2;
IR (ATR, cm^{-1}) 3054, 2360, 2199, 1672, 1591, 1488, 1442, 1373, 1345, 1283, 1254, 1220, 1155, 1025, 981, 917, 771, 723, 687;
HRMS (MALDI, TCNQ matrix) *m/z* calcd for $C_{34}H_{19}O_2$ $[M+H]^+$: 459.1380; found: 459.1398.

General Procedure 3

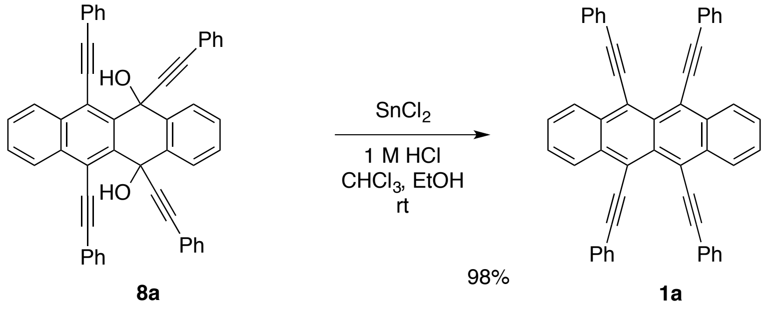


Scheme S3

To a solution of phenylacetylene (264 μL, 2.40 mmol) in THF (5.0 mL) was added *n*-BuLi (1.58 M in hexane, 1.37 mL, 2.16 mmol) at –20 ºC. After stirring for 10 min, tetracenequinone **7a** (90.5 mg, 0.197 mmol) was added at –78 ºC. After gradual warming to room temperature, the mixture was stirred for 12 h. The reaction was quenched by addition of sat. aq. NH_4Cl and the products were extracted with EtOAc (×3). The combined extracts were washed with brine, and then dried over Na_2SO_4. The crude products were triturated with Et_2O to give diol **8a** (94.8 mg, 73%) as a white solid.

mp 198 ºC (dec);
R_f 0.33 (hexane/EtOAc = 8/2);
^{1}H NMR (500 MHz, $CDCl_3$) 5.44 (s, 2H), 7.10–7.23 (m, 6H), 7.25–7.29 (m, 4H), 7.40–7.45 (m, 6H), 7.54–7.58 (m, 2H), 7.69–7.73 (m, 2H), 7.74–7.78 (m, 4H), 8.18–8.23 (m, 2H), 8.64–8.68 (m, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) 67.0, 86.3, 86.9, 93.7, 106.5, 120.3, 122.4, 122.7, 126.7, 128.0, 128.2, 128.7, 128.8, 129.1, 129.4, 131.7, 133.6, 135.0, 137.8;
IR (ATR, cm^{-1}) 3495, 3050, 2360, 1490, 1442, 1348, 1220, 1011, 968, 913, 771, 685;
HRMS (ESI$^+$) *m/z* calcd for $C_{50}H_{30}NaO_2$ $[M+Na]^+$: 685.2138; found: 685.2150.

General Procedure 4

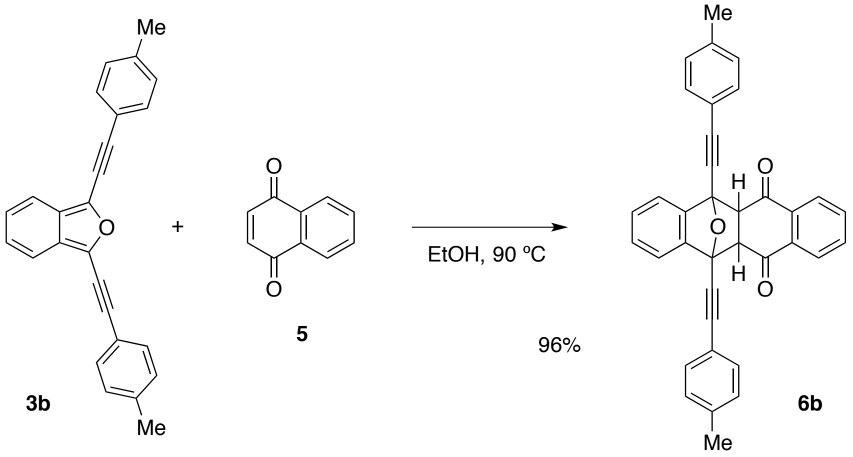


Scheme S4

A mixture of diol **8a** (13.4 mg, 20.2 μmol) and $SnCl_2$ (38 mg, 0.20 mmol) in $CHCl_3$ (0.8 mL)/EtOH (0.2 mL)/1 M HCl (0.2 mL) was stirred at 0 ºC for 2 h, and then stirred at room temperature for 1 h. The mixture was diluted with H_2O and $CHCl_3$. The products were extracted with $CHCl_3$ (×3) and the combined extracts were washed by brine, and dried over Na_2SO_4. Purification by silica-gel column chromatography (hexane/acetone = 9/1) afforded π-extended rubrene **1a** (12.4 mg, 98% yield) as a blue solid.[1]

mp 150 ºC (dec);
R_f 0.53 (hexane/EtOAc = 8/2);
^{1}H NMR (500 MHz, $CDCl_3$) 7.17–7.29 (m, 12H), 7.50–7.57 (m, 8H), 7.62–7.67 (m, 4H), 8.84–8.90 (m, 4H);
^{13}C NMR (125 MHz, $CDCl_3$) 89.5, 108.4, 118.9, 123.9, 127.6, 128.1, 128.3, 131.5, 134.0;
IR (ATR, cm^{-1}) 3033, 2360, 2341, 1541, 1489, 1441, 1406, 1220, 1068, 1025, 914, 772, 686;
HRMS (MALDI, TCNQ matrix) *m/z* calcd for $C_{50}H_{28}$ $[M]^+$: 628.2186; found: 628.2200.

Data of Cycloaddition Products

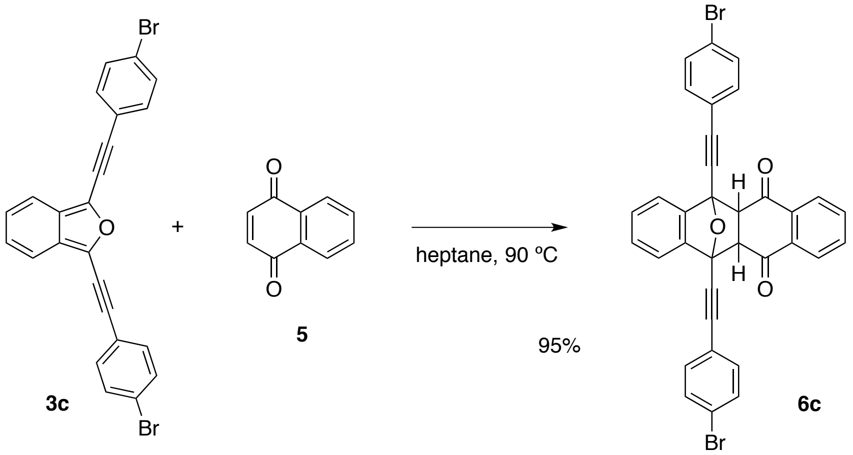


Scheme S5

Following *General Procedure 1*, cycloaddition of isobenzofuran **3b**[2] (133 mg, 0.384 mmol) and 1,4-napthoquinone (**5**) (76.0 mg, 0.481 mmol) in EtOH (1.0 mL) at 90 ºC for 9 h gave adduct **6b** (186 mg, 96%) as a white solid.

R_f 0.28 (hexane/EtOAc = 8/1);
Mp 159 ºC (dec);
^{1}H NMR ($CDCl_3$, 500 MHz) 2.39 (s, 6H), 4.10 (s, 2H), 6.94–6.96 (m, 2H), 7.19 (d, 4H, J = 8.0 Hz), 7.19–7.22 (m, 2H), 7.47–7.50 (m, 2H), 7.55 (d, 4H, J = 8.0 Hz), 7.70–7.73 (m, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) 21.6, 56.4, 81.0, 83.2, 90.9, 118.6, 120.8, 126.4, 128.3, 129.1, 132.2, 133.9, 134.3, 139.5, 141.4, 191.8;
IR (ATR, cm^{-1}) 2915, 2237, 1676, 1585, 1509, 1459, 1362, 1318, 1276, 1119, 1061, 969, 914, 885, 815, 770, 681, 630;
HRMS (DART) *m/z* calcd for $C_{36}H_{25}O_3$ $[M+H]^+$: 505.1804; found: 505.1802.

During the course of the NMR measurement, retro Diels–Alder reaction of ***6b*** *partially proceeded.*

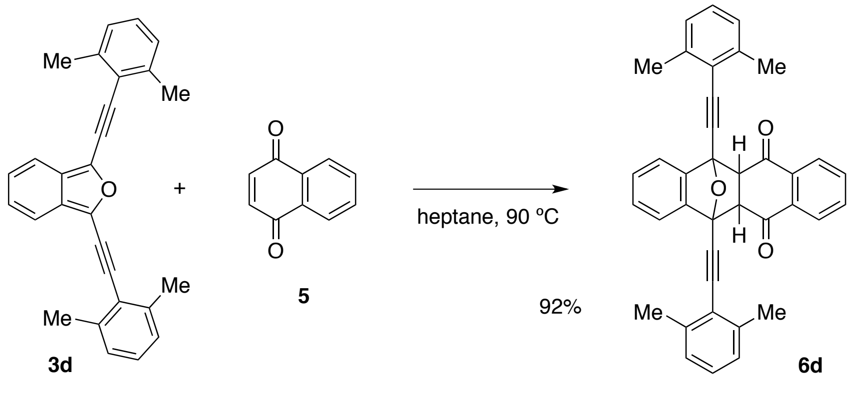


Scheme S6

Following *General Procedure 1*, cycloaddition of isobenzofuran **3c**[2] (194 mg, 0.407 mmol) and 1,4-napthoquinone (**5**) (76.0 mg, 0.481 mmol) in heptane (1.0 mL) at 90 ºC for 6.5 h gave adduct **6c** (244 mg, 95%) as a white solid.

R$_f$ 0.29 (hexane/acetone = 8/2);
Mp 148 ºC (dec);
^{1}H NMR (CDCl$_3$, 500 MHz) 4.10 (s, 2H), 6.95–6.98 (m, 2H), 7.19–7.21 (m, 2H), 7.49–7.55 (m, 10H), 7.71–7.74 (m, 2H);
^{13}C NMR (CDCl$_3$, 125 MHz) 56.1, 82.8, 83.1, 89.6, 120.5, 120.8, 123.8, 126.5, 128.4, 131.7, 131.8, 133.7, 134.1, 141.1, 191.6;
IR (ATR, cm^{-1}) 3076, 2245, 1678, 1586, 1486, 1457, 1394, 1362, 1319, 1280, 1261, 1154, 1121, 1069, 1010, 968, 924, 822, 767, 726, 626;
HRMS (DART) *m/z* calcd for $C_{34}H_{19}Br_2O_3$ $[M+H]^+$: 634.9684; found: 634.9638.

During the course of the NMR measurement, retro Diels–Alder reaction of ***6c*** *partially proceeded.*



Scheme S7

Following *General Procedure 1*, cycloaddition of isobenzofuran **3d**[2] (150 mg, 0.400 mmol) and 1,4-napthoquinone (**5**) (76.0 mg, 0.481 mmol) in heptane (1.0 mL) at 90 ºC for 8 h gave adduct **6d** (195 mg, 92%) as an off-white solid.

R$_f$ 0.40 (hexane/EtOAc = 8/2);

Mp 119 ºC (dec);

^{1}H NMR ($CDCl_3$, 500 MHz) 2.62 (s, 12H), 4.14 (s, 2H), 6.94–6.97 (m, 2H), 7.11 (d, 4H, J = 8.0 Hz), 7.19 (dd, 2H, J = 8.0, 8.0 Hz), 7.19–7.22 (m, 2H), 7.46–7.49 (m, 2H), 7.69–7.72 (m, 2H);

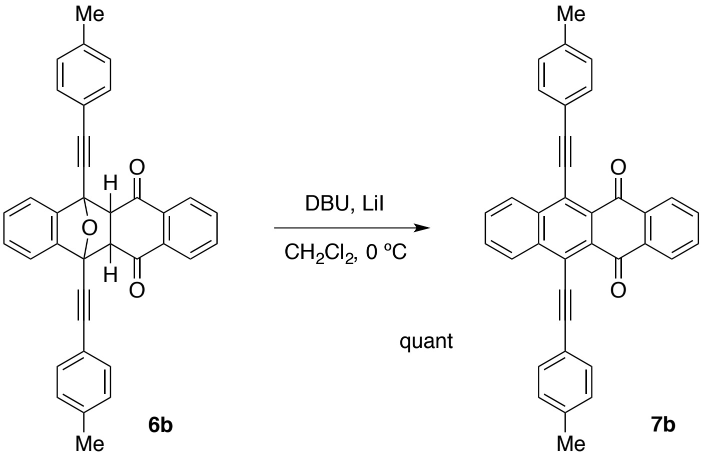
^{13}C NMR ($CDCl_3$, 125 MHz) 21.3, 56.7, 83.5, 88.6, 89.9, 120.7, 121.5, 126.4, 126.8, 128.3, 128.7, 133.9, 134.3, 141.4, 141.6, 191.7;

IR (ATR, cm^{-1}) 2944, 2228, 1680, 1591, 1464, 1285, 1256, 1125, 1062, 974, 929, 889, 744, 629;

HRMS (DART) *m/z* calcd for $C_{38}H_{29}O_3$ $[M+H]^+$: 533.2117; found: 533.2116.

During the course of the NMR measurement, retro Diels–Alder reaction of ***6d*** *partially proceeded.*

Data of Tetracenequinones



Scheme S8

Following *General Procedure 2*, cycloadduct **6b** (101 mg, 0.200 mmol) in CH_2Cl_2 was charged with LiI (54.0 mg, 0.403 mmol) and DBU (179 µL, 1.20 mmol) to give tetracenequinone **7b** (97.3 mg, quant) as a yellow solid.

R$_f$ 0.48 (hexane/EtOAc = 8/2);

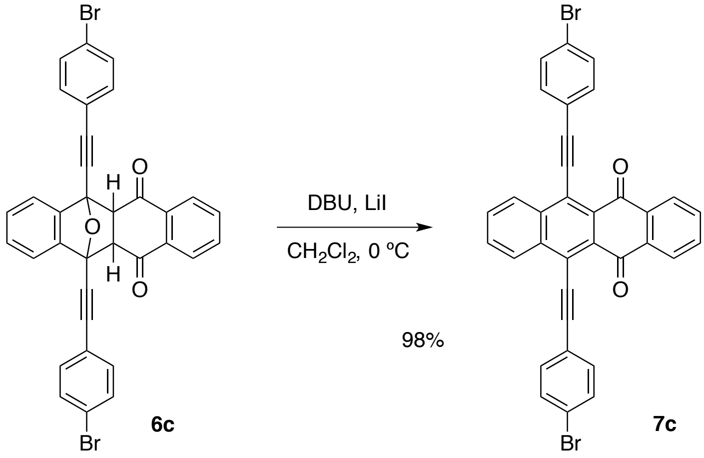
Mp 212 ºC (dec);

^{1}H NMR ($CDCl_3$, 500 MHz) 2.44 (s, 6H), 7.28 (d, 4H, J = 8.0 Hz), 7.77 (d, 4H, J = 8.0 Hz), 7.77–7.84 (m, 4H), 8.36–8.40 (m, 2H), 8.86–8.90 (m, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) 21.7, 87.6, 104.2, 120.2, 123.0, 127.2, 128.7, 129.4, 130.0, 131.4, 132.3, 133.7, 134.4, 135.1, 139.7, 182.3;

IR (ATR, cm^{-1}) 2911, 2197, 1669, 1590, 1506, 1375, 1344, 1289, 1252, 1159, 1060, 980, 818, 769, 722;

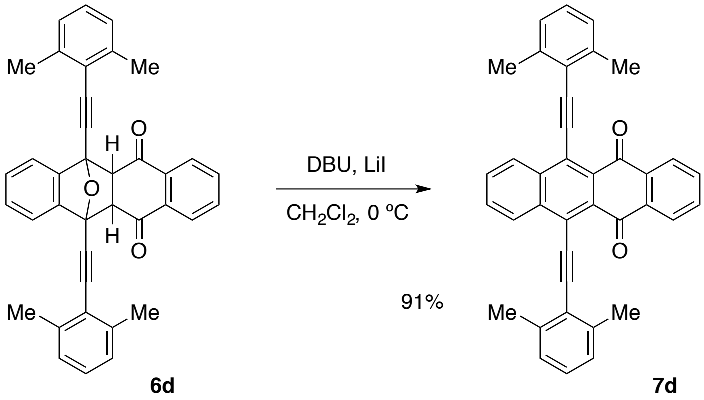
HRMS (MALDI, TCNQ matrix) *m/z* calcd for $C_{36}H_{23}O_2$ $[M+H]^+$: 487.1693; found: 487.1689.



Scheme S9

Following *General Procedure 2*, cycloadduct **6c** (177 mg, 0.279 mmol) in CH_2Cl_2 (11 mL) was charged with LiI (83.6 mg, 0.625 mmol) and DBU (261 μL, 1.75 mmol) to give tetracenequinone **7c** (169 mg, 98%) as a yellow solid.

R_f 0.44 (hexane/acetone = 8/2);
Mp 176 °C (dec);
^{1}H NMR ($CDCl_3$, 500 MHz) 7.60 (d, 4H, J = 8.0 Hz), 7.71 (d, 4H, J = 8.0 Hz), 7.76–7.81 (m, 4H), 8.32–8.85 (m, 2H), 8.75–8.79 (m, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) 89.0, 102.6, 122.2, 122.7, 123.8, 127.3, 128.5, 130.2, 131.6, 131.9, 133.7, 133.9, 134.3, 134.9, 182.1;
IR (ATR, cm^{-1}) 3065, 2203, 1673, 1592, 1484, 1377, 1348, 1290, 1257, 1155, 1068, 1010, 983, 822, 764, 718;
HRMS (MALDI, TCNQ matrix) *m/z* calcd for $C_{34}H_{17}O_2Br_2$ $[M+H]^+$: 614.9590; found: 614.9595.



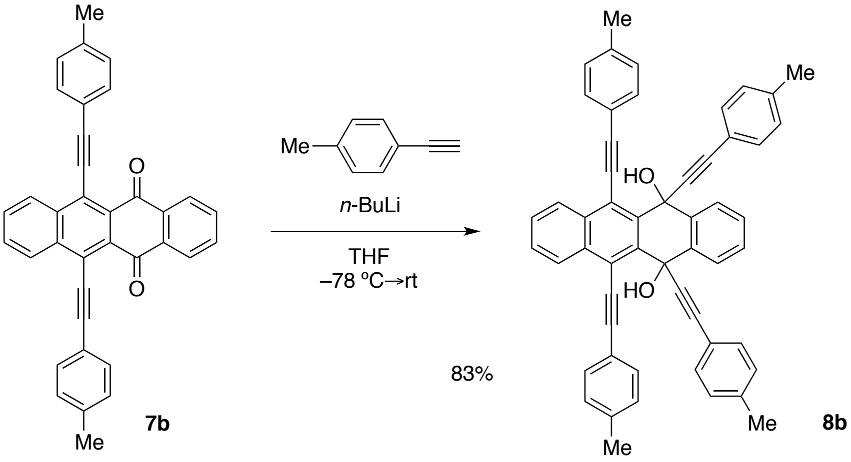
Scheme S10

Following *General Procedure 2*, cycloadduct **6d** (100 mg, 0.188 mmol) in CH_2Cl_2 (7.5 mL) was charged with LiI (50.3 mg, 0.376 mmol) and DBU (168 μL, 1.13 mmol) to give tetracenequinone **7d** (88.7 mg, 91%) as a yellow solid.

R_f 0.43 (hexane/EtOAc = 9/1);
Mp 228 °C (dec);

^{1}H NMR (CDCl$_3$, 500 MHz) 2.79 (s, 12H), 7.13–7.18 (m, 4H), 7.20–7.24 (m, 2H), 7.76–7.81 (m, 4H), 8.31–8.35 (m, 2H), 8.98–9.02 (m, 2H);
^{13}C NMR (CDCl$_3$, 125 MHz) 21.7, 95.4, 101.9, 123.1, 123.3, 127.1 (×2), 128.8 (×2), 129.9, 131.4, 133.7, 134.5, 135.3, 141.4, 182.3;
IR (ATR, cm^{-1}) 2921, 2166, 1679, 1594, 1468, 1376, 1346, 1260, 1162, 1054, 985, 760, 721;
HRMS (MALDI, TCNQ matrix) *m/z* calcd for $C_{38}H_{27}O_2$ [M+H]$^+$: 515.2006; found: 515.2019.

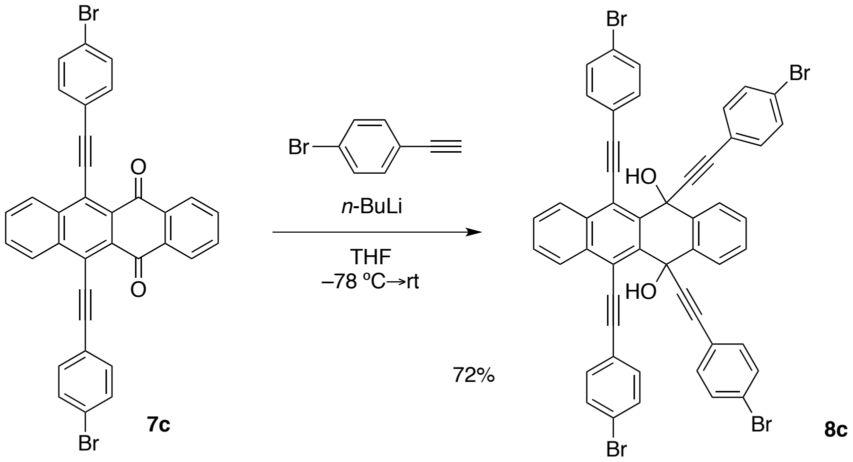
Data of Diols



Scheme S11

Following *General Procedure 3*, tetracenequinone **7b** (51.0 mg, 0.105 mmol) in THF (2.5 mL) was reacted with the lithium acetylide generated from 4-ethynyltoluene (76 µL, 0.60 mmol) and *n*-BuLi (1.60 M in hexane, 0.31 mL, 0.50 mmol) to give diol **8b** (62.3 mg, 83%, *dr* 80:20) as a white solid.

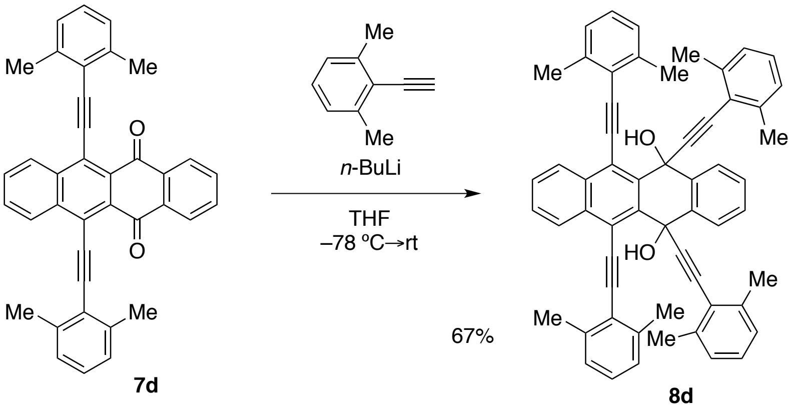
R$_f$ 0.38 (hexane/EtOAc = 8/2);
Mp 224 ºC (dec);
^{1}H NMR (CDCl$_3$, 500 MHz) 2.24 (s, 1.2H), 2.26 (s, 4.8H), 2.42 (s, 6H), 5.49 (s, 1.6H), 5.82 (s, 0.4H), 6.91 (d, 0.8H, J = 8.0 Hz), 6.96 (d, 3.2H, J = 7.5 Hz), 7.13 (d, 0.8H, J = 8.0 Hz), 7.16 (d, 3.2H, J = 8.0 Hz), 7.23 (d, 4H, J = 7.5 Hz), 7.53–7.56 (m, 2H), 7.65 (d, 4H, J = 8.0 Hz), 7.67–7.70 (m, 2H), 8.16–8.21 (m, 2H), 8.63–8.66 (m, 2H);
^{13}C NMR (CDCl$_3$, 125 MHz) 21.4, 21.7, 66.4*, 67.0, 85.8*, 86.2*, 86.3, 86.4, 92.1*, 93.2, 106.6*, 106.7, 119.3*, 119.4, 119.64*, 119.69*, 119.74, 120.2, 126.6*, 126.7, 127.8*, 127.9*, 128.0, 128.7*, 128.8, 128.9*, 129.0, 129.4, 131.56, 131.63*, 133.5, 134.9*, 135.0, 137.7, 138.06*, 138.16*, 138.22, 139.67, 139.73*;
The signals marked with an asterisk (*) were assigned to the minor diastereomer.
IR (ATR, cm^{-1}) 3507, 3025, 2207, 1508, 1340, 1285, 1193, 1124, 1032, 997, 965, 811, 762, 684;
HRMS (ESI$^+$) *m/z* calcd for $C_{54}H_{38}NaO_2$ [M+Na]$^+$: 741.2764; found: 741.2765.



Scheme S12

Following *General Procedure 3*, tetracenequinone **7c** (28.1 mg, 0.0456 mmol) in THF (1.3 mL) was reacted with the lithium acetylide generated from *p*-bromophenylacetylene (61.2 mg, 0.338 mmol) and *n*-BuLi (1.60 M in hexane, 0.17 mL, 0.27 mmol) to give diol **8c** (32.2 mg, 72%, *dr* >99:1) as a white solid.

R_f 0.28 (hexane/acetone = 8/2);
Mp 173 ºC (dec);
^{1}H NMR ($C_2D_2Cl_4$, 500 MHz) 5.21 (s, 2H), 7.16 (d, 4H, J = 8.0 Hz), 7.36 (d, 4H, J = 8.0 Hz), 7.58–7.64 (m, 10H), 7.78–7.81 (m, 2H), 8.17–8.21 (m, 2H), 8.62–8.65 (m, 2H);
^{13}C NMR ($C_2D_2Cl_4$, 125 MHz) 66.9, 85.4, 87.8, 94.5, 105.8, 120.3, 121.1, 121.4, 122.9, 124.2, 126.7, 128.89, 128.90, 129.6, 131.6, 132.2, 133.0, 133.2, 133.5, 134.7, 137.4;
IR (ATR, cm^{-1}) 3510, 2924, 2853, 2204, 1715, 1486, 1362, 1259, 1227, 1071, 1010, 968, 820, 763;
HRMS (ESI$^+$) *m/z* calcd for $C_{50}H_{26}Br_4NaO_2$ $[M+Na]^+$: 996.8533; found: 996.8559.



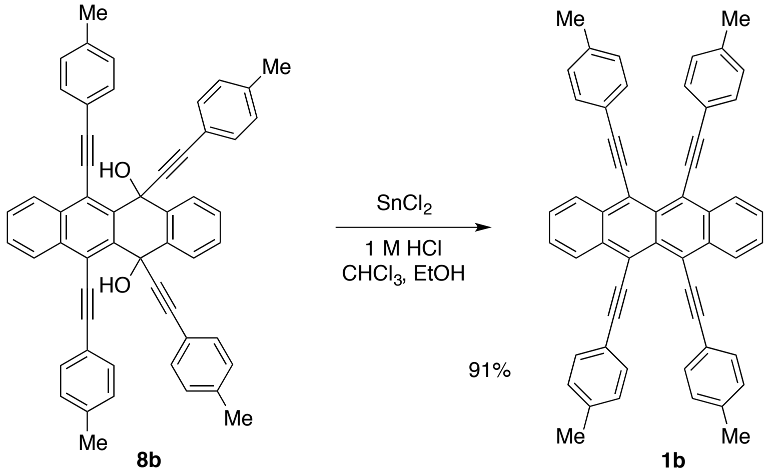
Scheme S13

Following *General Procedure 3*, tetracenequinone **7d** (49.1 mg, 0.0954 mmol) in THF (4.0 mL) was reacted with the lithium acetylide generated from 2,6-dimethylphenylacetylene (75.9 mg, 0.583 mmol) and *n*-BuLi (1.60 M in hexane, 0.30 mL, 0.48 mmol) to give diol **8d** (49.8 mg, 67%, *dr* 96:4) as a white solid.

R_f 0.33 (hexane/EtOAc = 9/1);
Mp 170 ºC (dec);

^{1}H NMR (CDCl$_3$, 500 MHz) 1.95 (s, 11.52H), 2.11 (s, 0.48H), 2.63 (s, 12H), 5.71 (s, 0.08H), 6.07 (s, 1.92H), 6.74 (d, 3.84H, J = 7.5 Hz), 6.84 (d, 0.16H, J = 7.5 Hz), 6.90 (dd, 1.92H, J = 8.0, 7.5 Hz), 6.97 (dd, 0.08H, J = 7.8, 7.7 Hz), 7.12 (d, 4H, J = 7.5 Hz), 7.22 (dd, 2H, J = 7.5, 7.5 Hz), 7.50–7.54 (m, 2H), 7.67–7.70 (m, 2H), 8.15–8.18 (m, 2H), 8.77–8.80 (m, 2H);
^{13}C NMR (CDCl$_3$, 125 MHz) 20.5, 21.8, 66.5, 84.5, 94.1, 101.0, 104.9, 119.7, 122.1, 122.2, 126.2, 126.7, 127.2, 127.3, 127.7, 127.9, 128.7, 129.0, 133.7, 135.1, 138.2, 140.5, 140.9;
IR (ATR, cm^{-1}) 3512, 2916, 2169, 1468, 1373, 1353, 1233, 1166, 1093, 1025, 907, 756, 729, 678;
HRMS (ESI) calcd for $C_{58}H_{46}NaO_2$ [M+Na]$^+$: 797.3390; found: 797.3389.

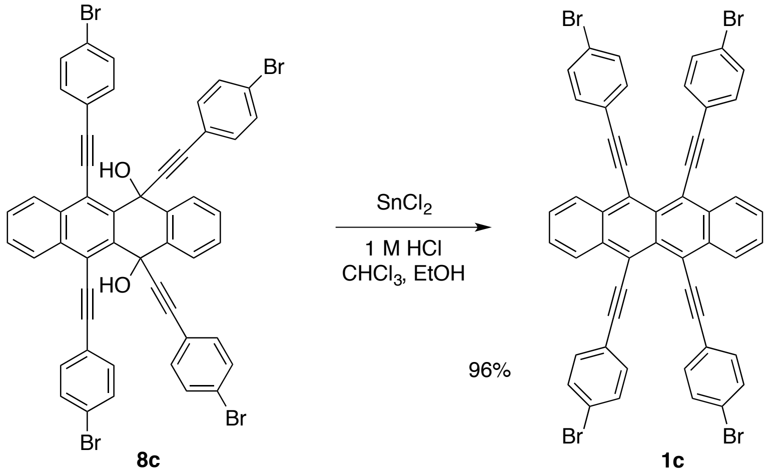
Data of π-Extended Rubrenes



Scheme S14

Following *General Procedure 4*, diol **8b** (14.0 mg, 19.5 µmol) was treated with SnCl$_2$ (38.0 mg, 0.200 mmol) to afford π-extended rubrene **1b** (12.1 mg, 91%) as a deep-blue solid.

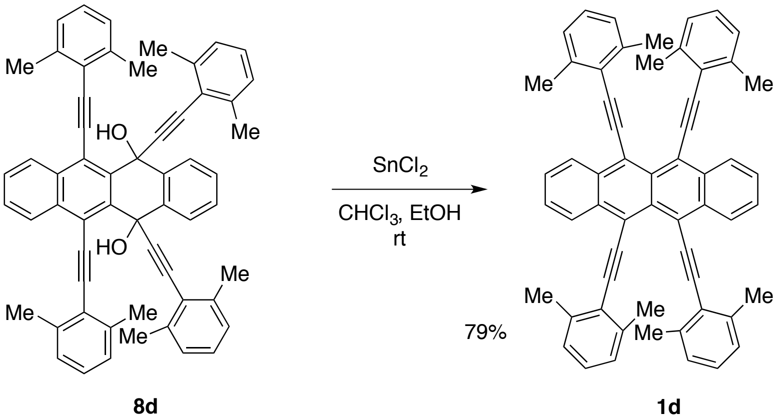
The spectroscopic data was identical with our previous report.[1]



Scheme S15

Following *General Procedure 4*, diol **8c** (82.6 mg, 0.0844 mmol) was treated with SnCl$_2$ (202 mg, 1.07 mmol) to afford π-extended rubrene **1c** (76.4 mg, 96%) as a deep-blue solid.

R_f 0.39 (hexane/EtOAc = 9/1);
Mp 170 ºC (dec);
^{1}H NMR ($CDCl_3$, 300 MHz) 7.36–7.40 (m, 16H), 7.63–7.69 (m, 4H), 8.77–8.83 (m, 4H);
^{13}C NMR ($CDCl_3$, 125 MHz) 90.4, 107.2, 118.7, 122.6, 122.8, 127.4, 127.9, 131.5, 132.7, 132.8, 133.9;
IR (ATR, cm^{-1}) 3065, 2923, 2177, 1584, 1486, 1391, 1259, 1174, 1070, 1011, 876, 818, 752, 677;
HRMS (MALDI, DCTB matrix) *m/z* calcd for $C_{50}H_{24}Br_4$ $[M]^+$: 939.8606; found: 939.8610.



8d **1d**

Scheme S16

Following *General Procedure 4*, diol **8d** (21.5 mg, 27.7 µmol) was treated with $SnCl_2$ (52.6 mg, 0.277 mmol) to afford π-extended rubrene **1d** (16.1 mg, 79%) as a deep-blue solid.

The spectroscopic data was identical with our previous report. [1]

3. [2+4] Cycloaddition and Cycloreversion Monitored by ^{1}H-NMR

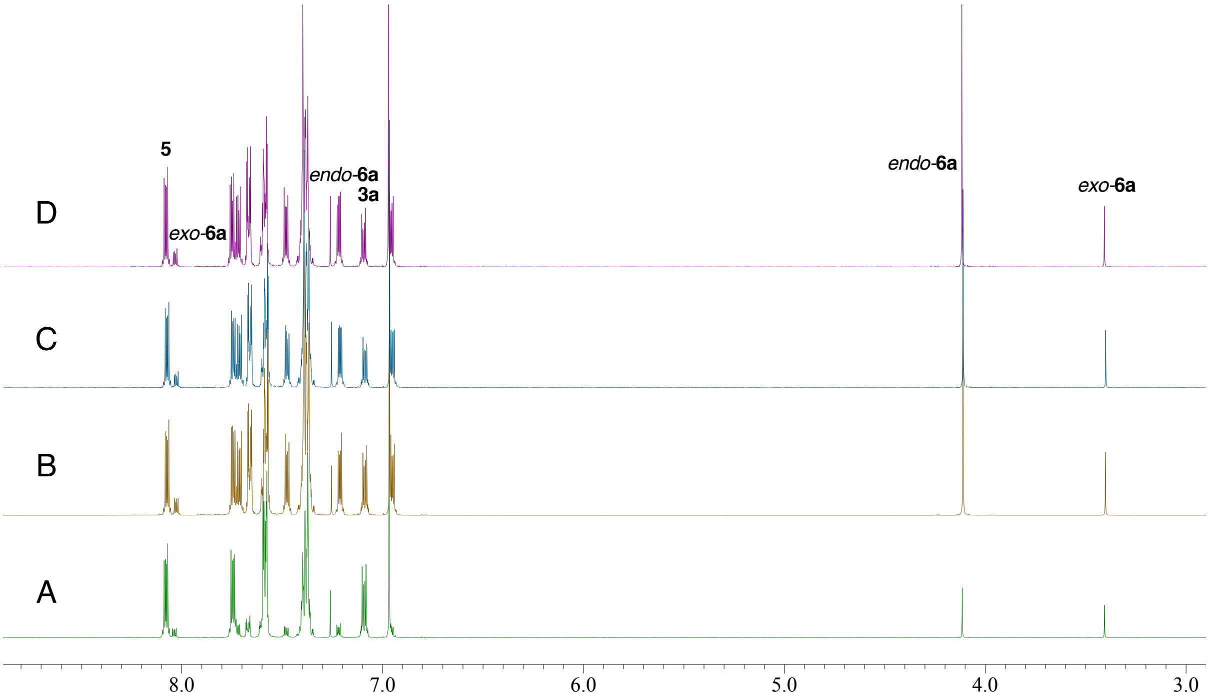


Figure S1. [4+2]-cycloaddition of isobenzofuran **3a** with 1,4-naphthoquinone (**5**) monitored by ^{1}H NMR (A: 5 min, B: 2 h, C: 7 h, D: 15 h).

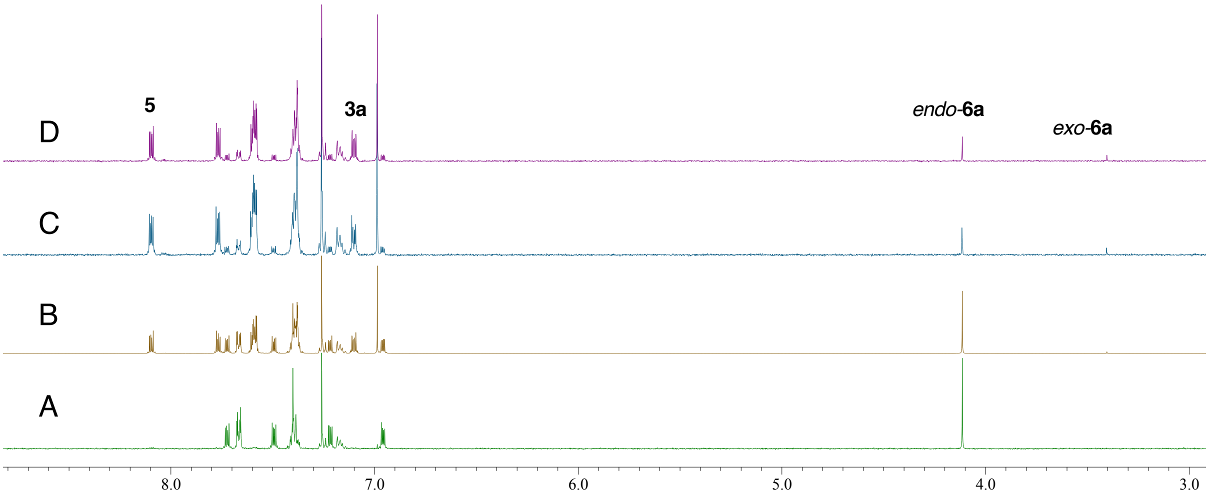


Figure S2. Cycloreversion of cycloadduct **6a** monitored by ^{1}H NMR (A: 5 min, B: 2 h, C: 7 h, D: 15 h).

4. UV-Vis and Fluorescence Spectra

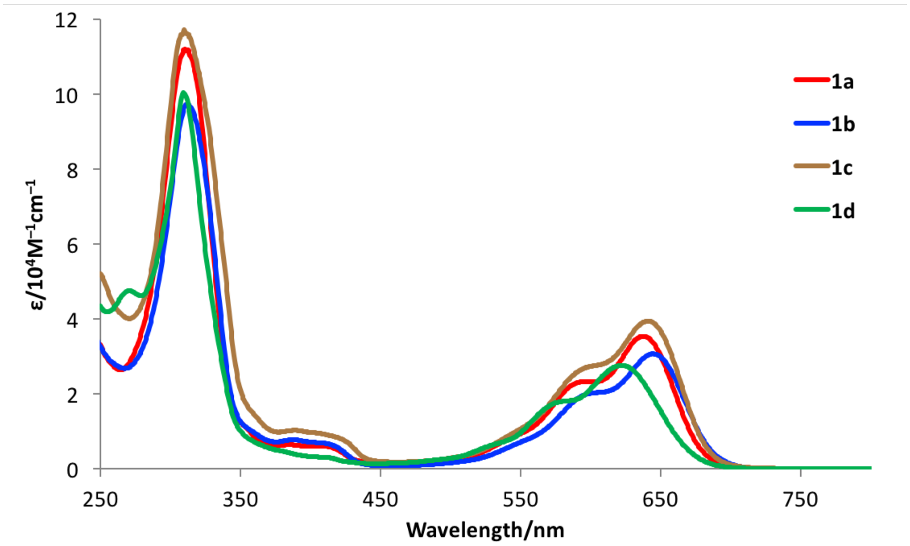


Figure S3. UV-Vis spectra of π-extended rubrenes measured in $CHCl_3$ (2.0×10^{-5} M).

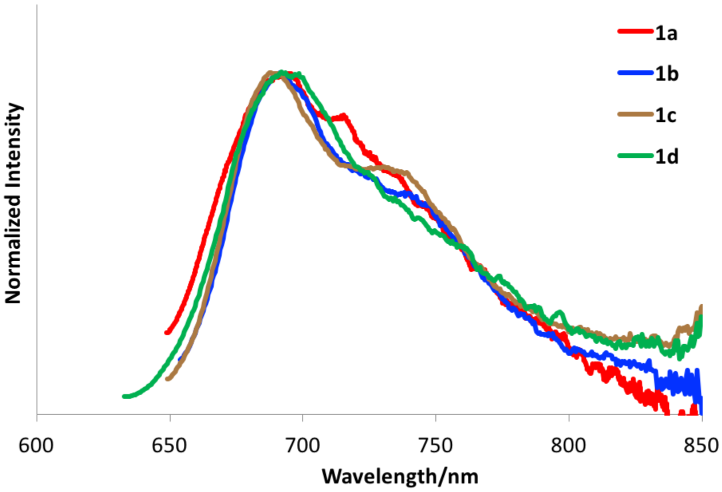


Figure S4. Fluorescence spectra of π-extended rubrenes measured in $CHCl_3$ (2.0×10^{-5} M).

	λ_{abs}/nm	λ_{em}/nm[1]	Φ[2]	Stokes shift/cm^{-1}
1a	640	693	0.057	1200
1b	645	692	0.066	1050
1c	641	688	0.095	1070
1d	623	693	0.054	1620

[1] Excited at the longest absorption maxima (*c* 2.0×10^{-5} M). [2] Absolute Photoluminescence quantum yields were recorded on a JASCO FP-8500 spectrofluorometer with an integrating sphere.

5. Confocal microscopy

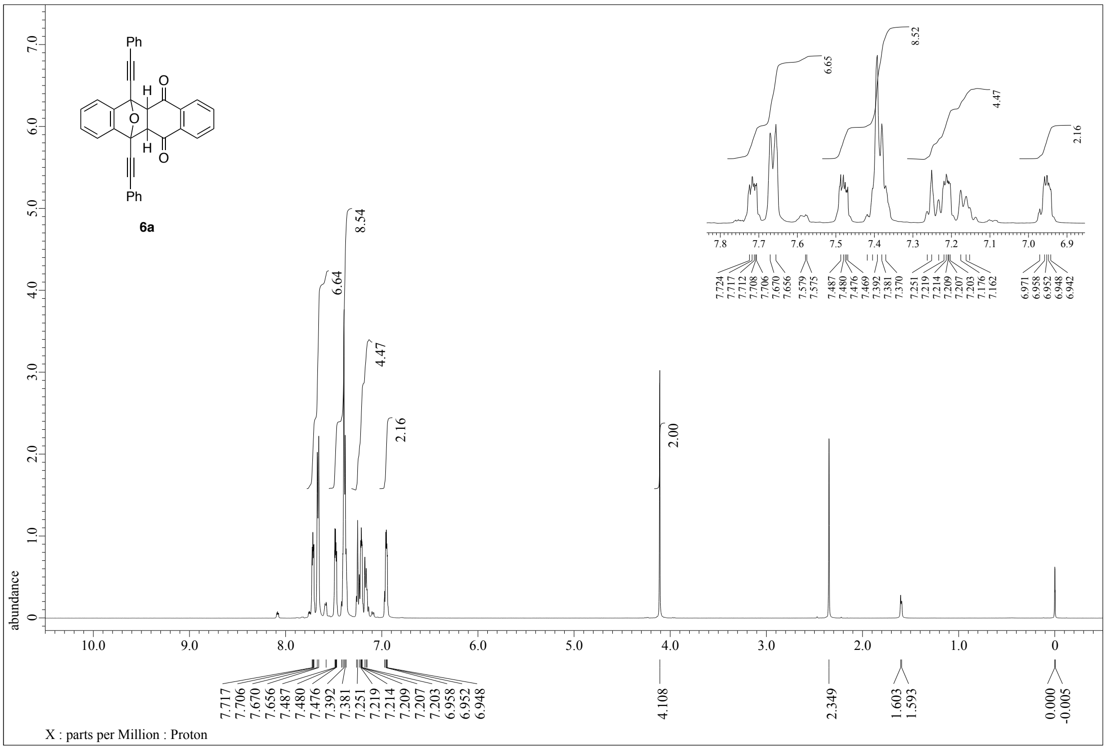
HeLaS3 cells were seeded and incubated in a 96-well plate for 24 h at 37°C before imaging experiment. The culture medium was removed and washed with 100 μL fresh medium. The medium was then replaced by 100 μL fresh medium containing 100 μM of π-extended rubrene **1a**, and incubated for 30 min at 37°C. The cells were washed with PBS (pH = 7.4) for three times, and fixed with 4% paraformaldehyde solution in PBS for 10 min at rt. The cells were analyzed by fluorescent microscope (Keyence BZ-X710, Japan) with excitation wavelength at a range of 590-650 nm and with emission wavelength at a range of 663-738 nm.

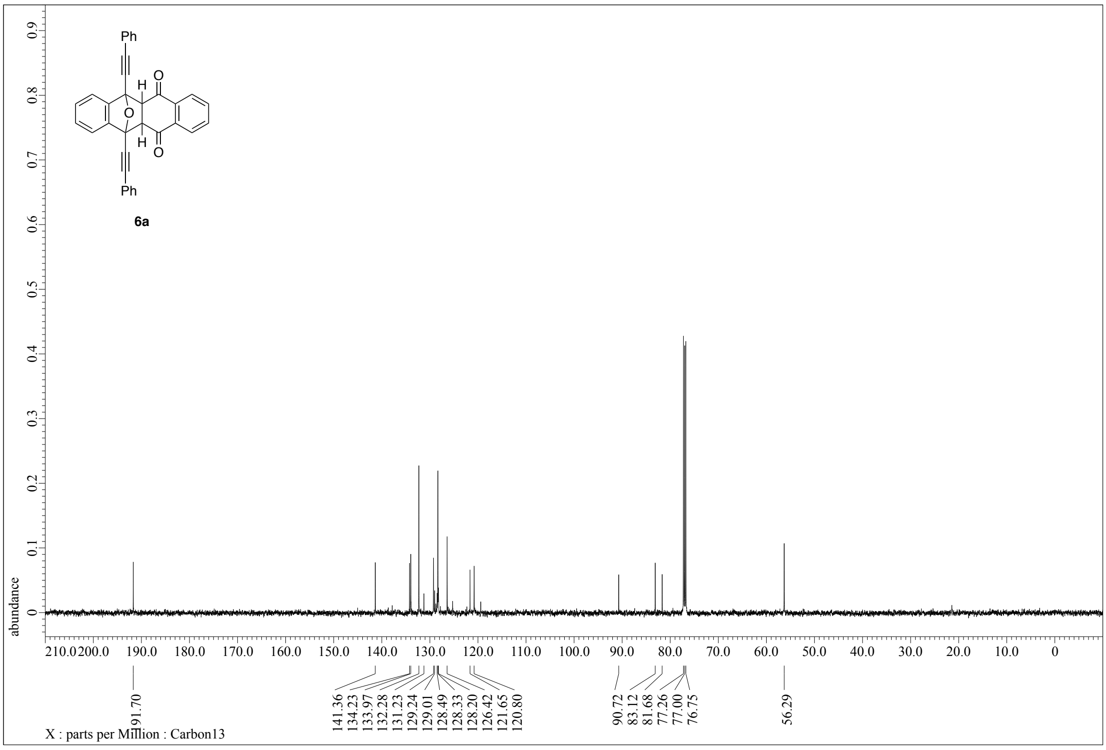
6. Reference

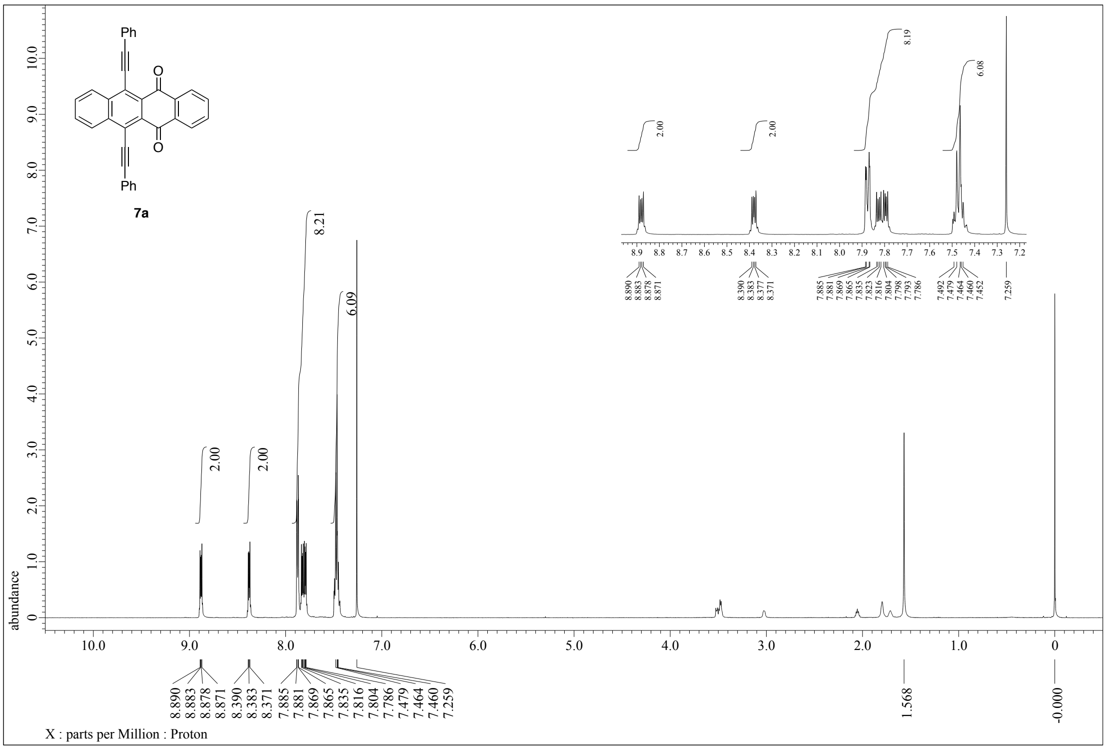
[1] K. Kitamura, K. Asahina, Y. Nagai, H. Sugiyama, H. Uekusa, T. Hamura, *Chem. Eur. J.* **2018**, *24*, 14034.

[2] R. Kudo, K. Kitamura, T. Hamura, *Chem. Lett.* **2017**, *46*, 25.

7. ^{1}H and ^{13}C NMR Spectra



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8.19
6.08
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8.390 8.383 8.377 8.371
7.885 7.881 7.869 7.865 7.835 7.823 7.816 7.804 7.798 7.793 7.786
7.492 7.479 7.464 7.460 7.452
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8.890 8.883 8.878 8.871 8.390 8.383 8.371 7.885 7.881 7.869 7.865 7.835 7.816 7.804 7.786 7.479 7.464 7.460 7.259
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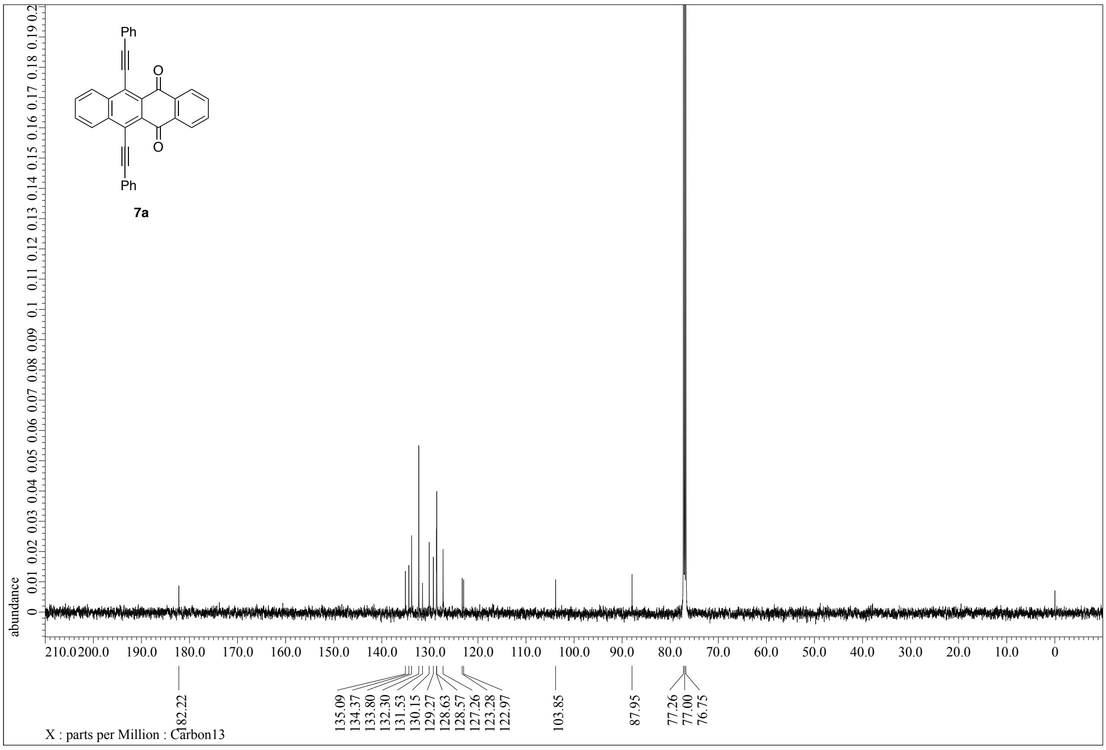
X : parts per Million : Proton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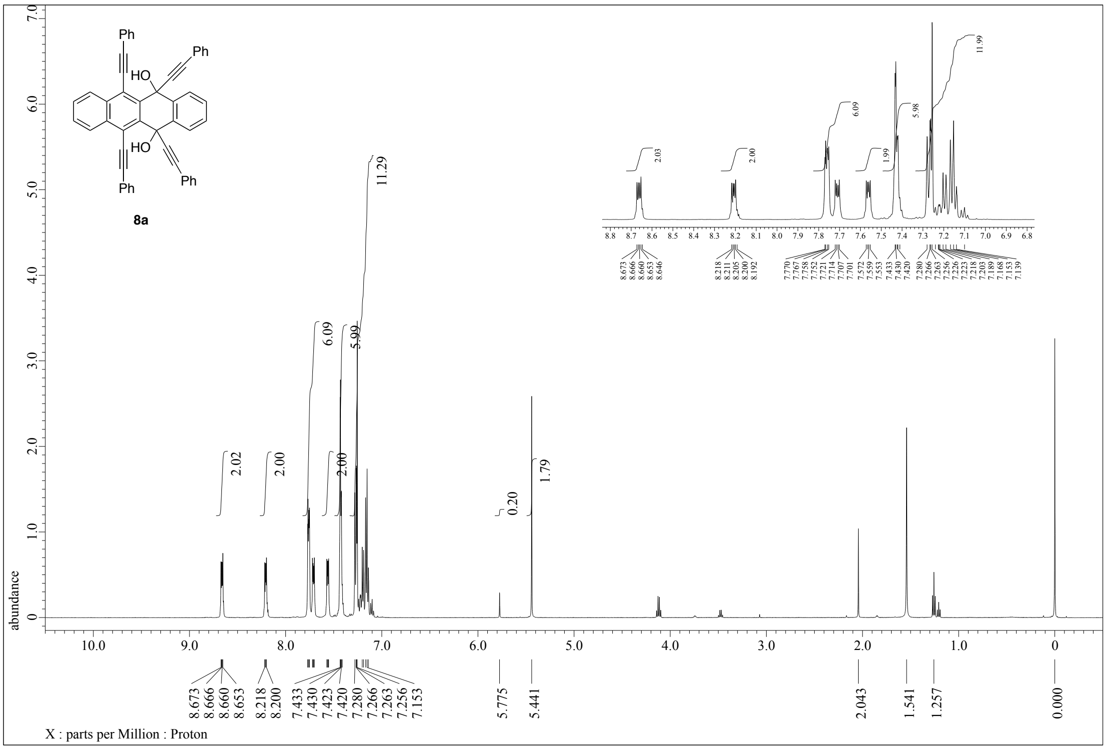
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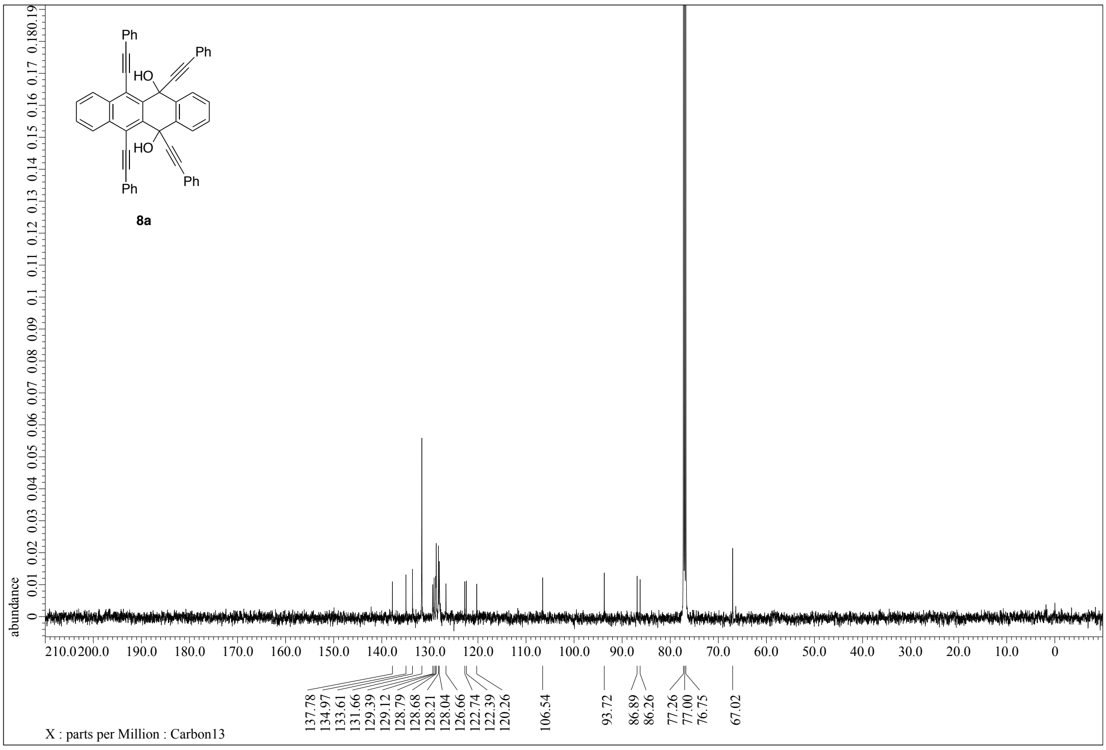
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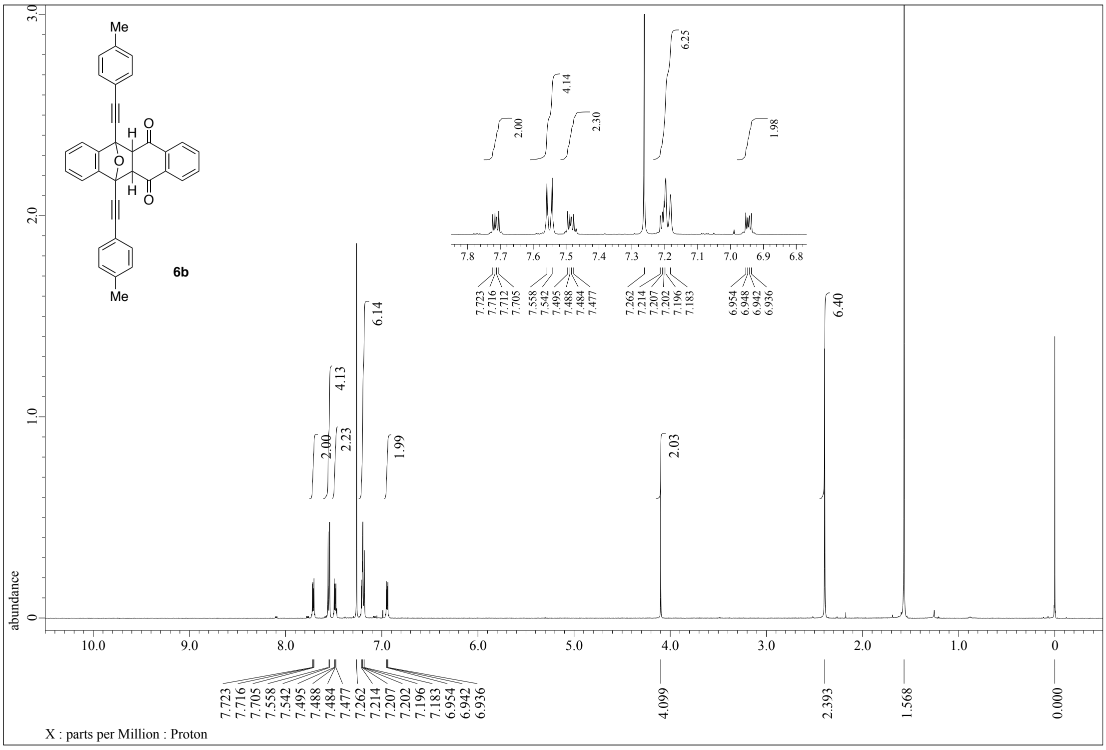
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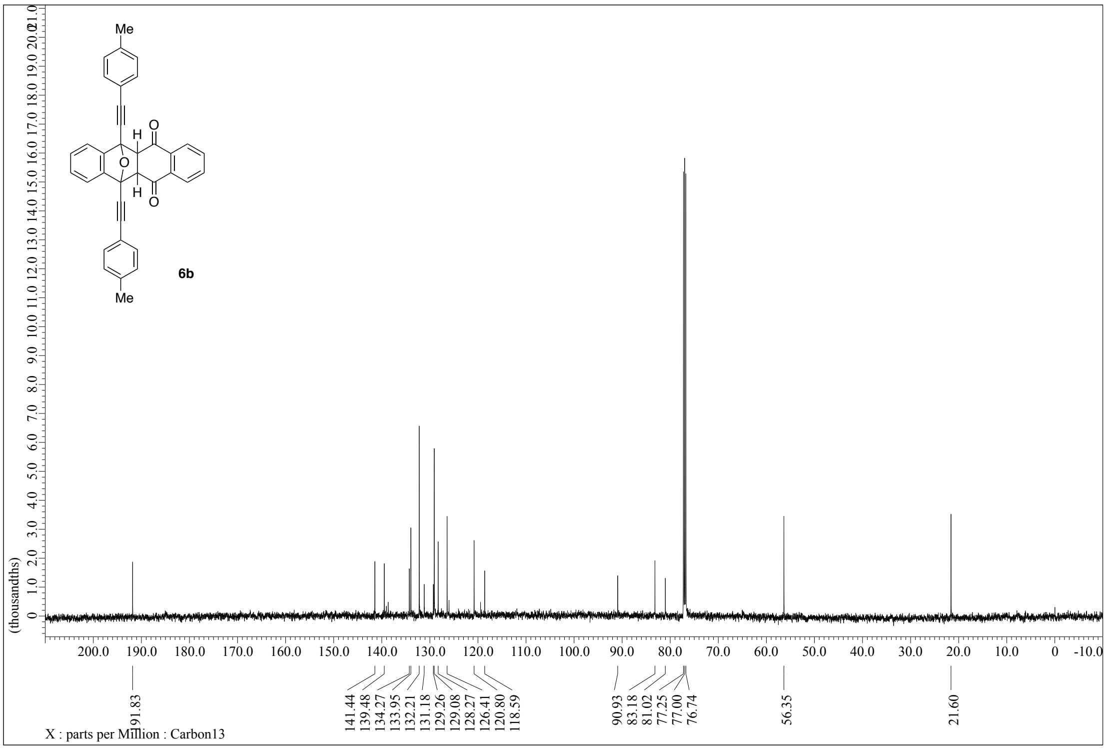
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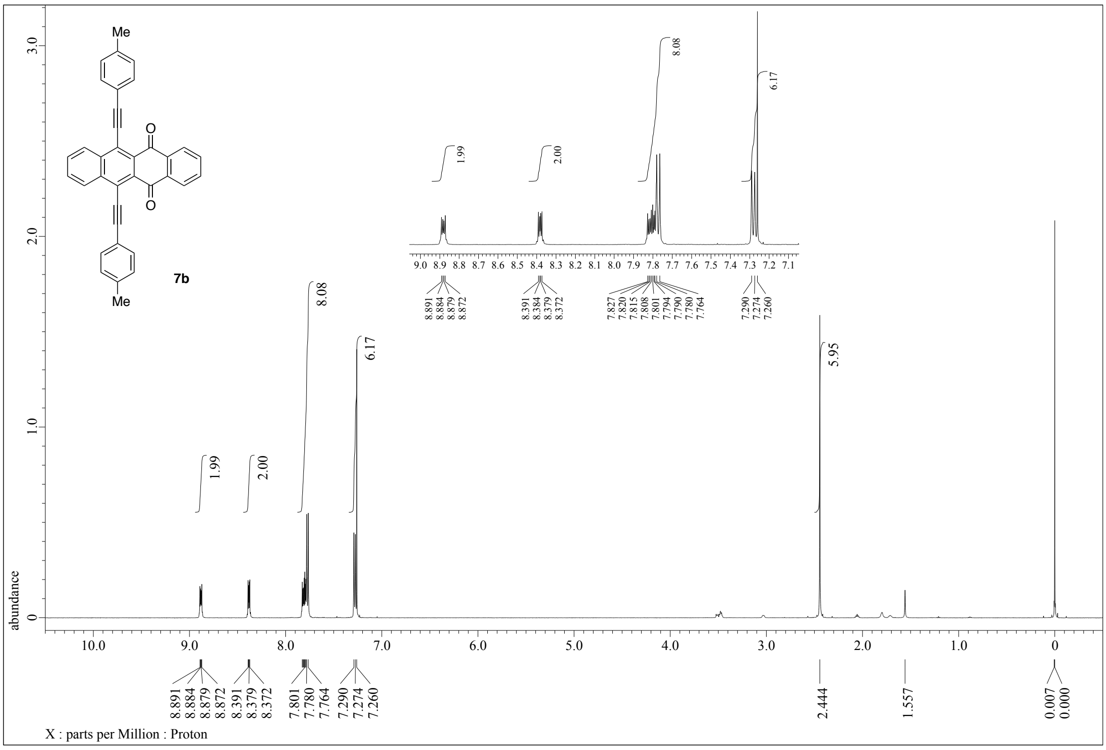
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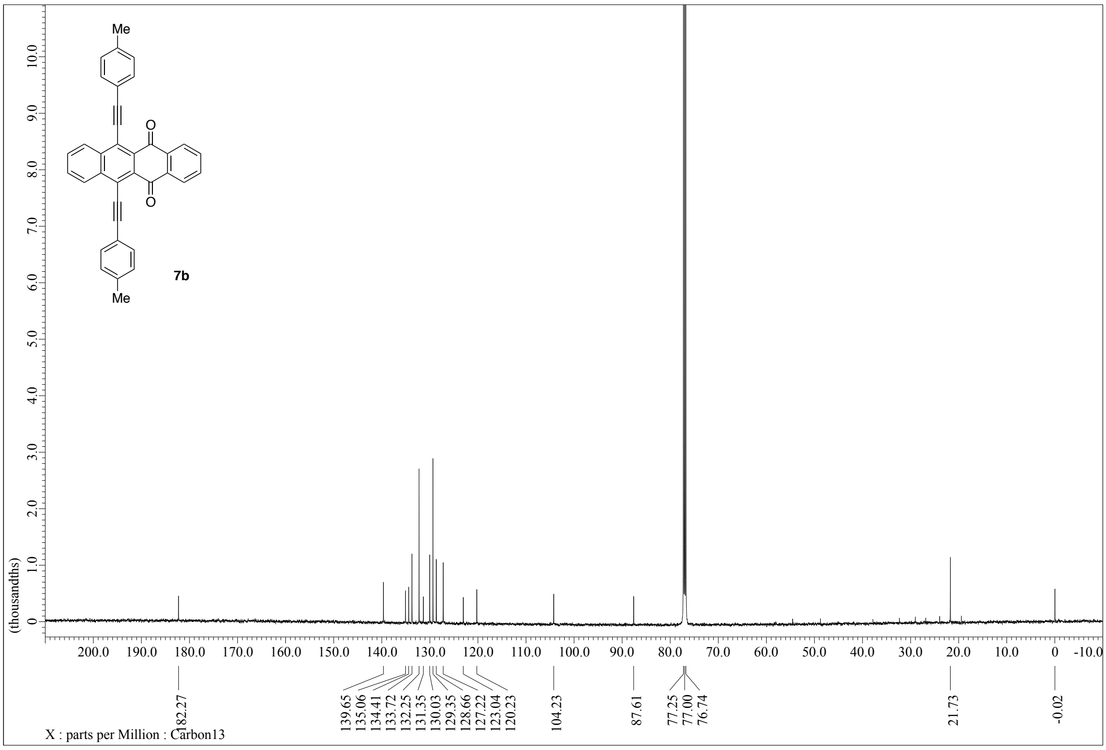
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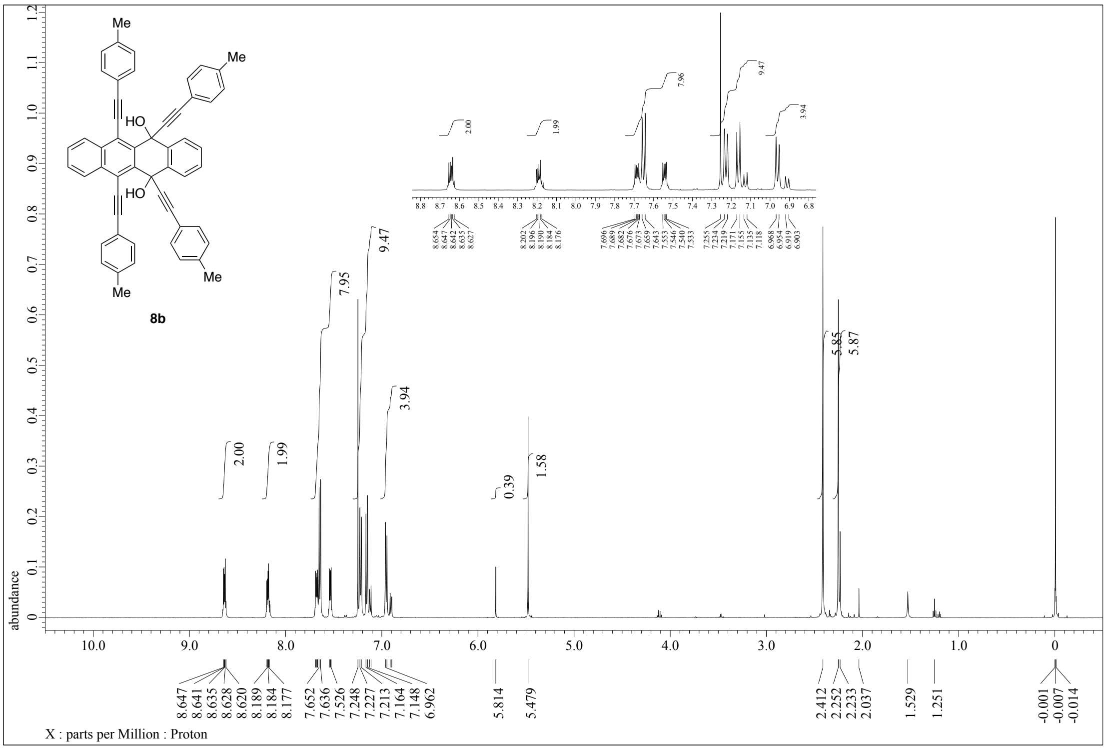

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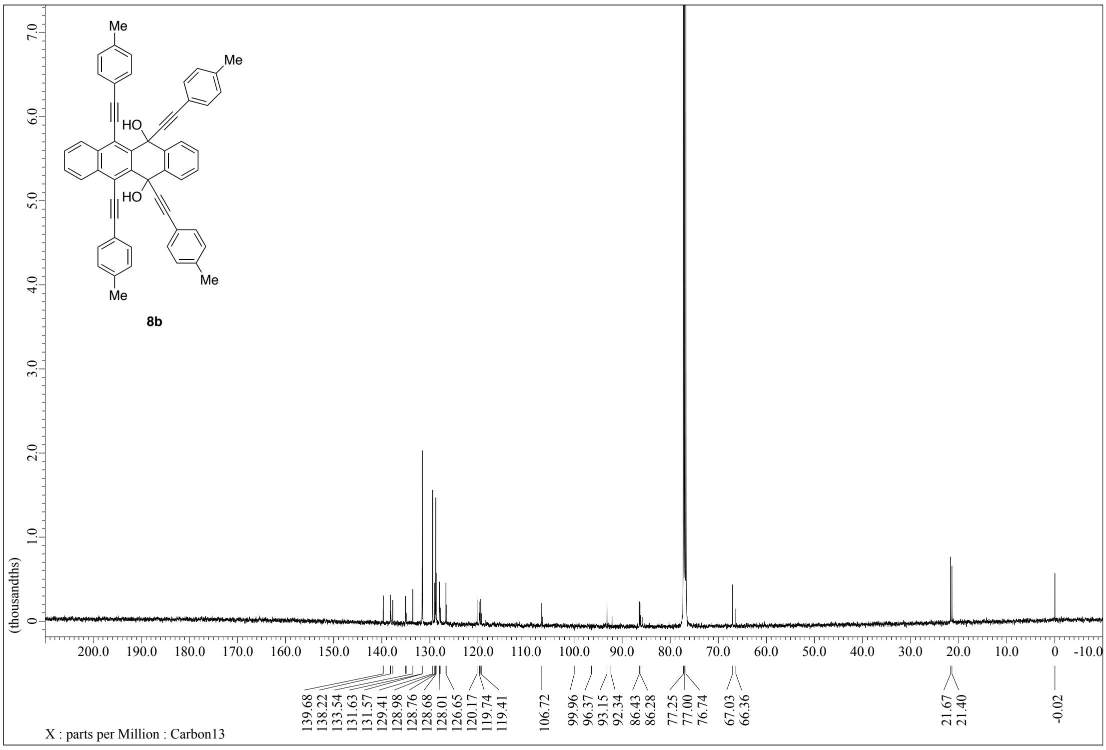

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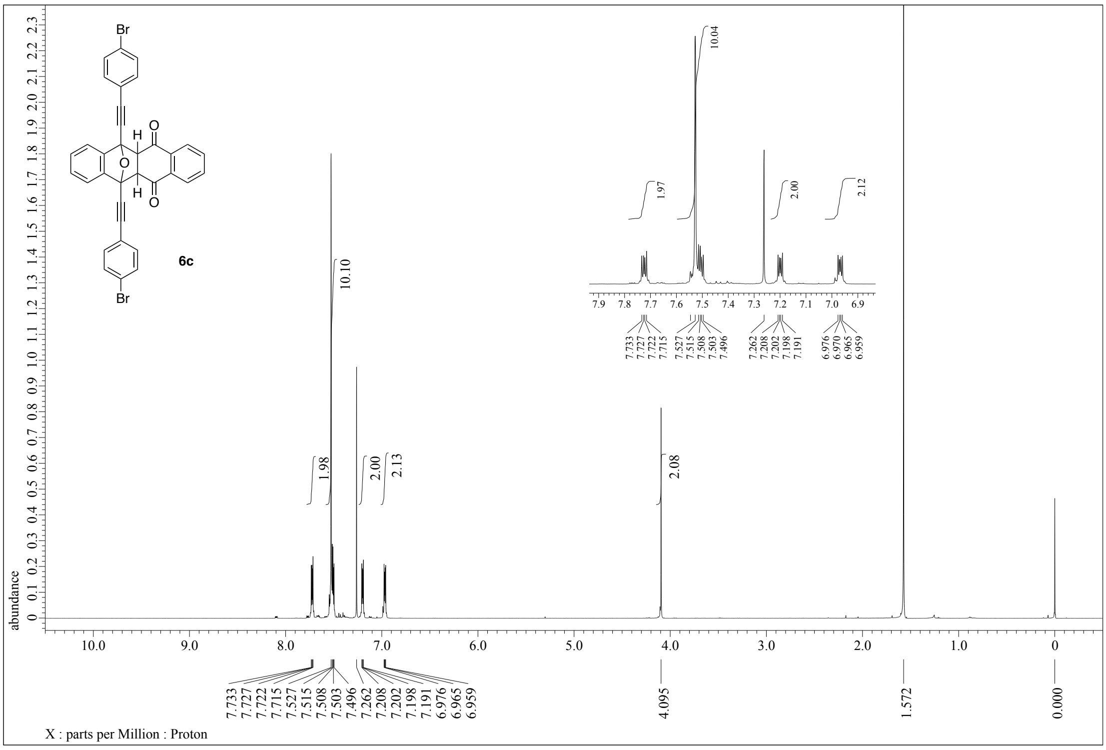
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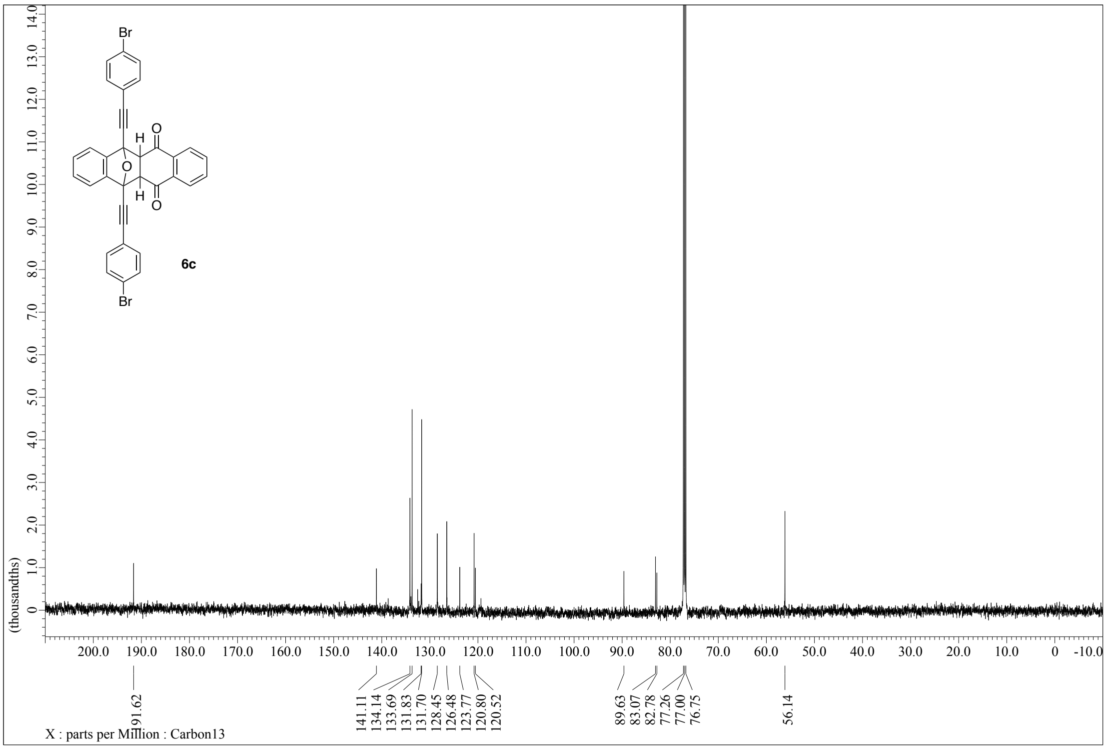
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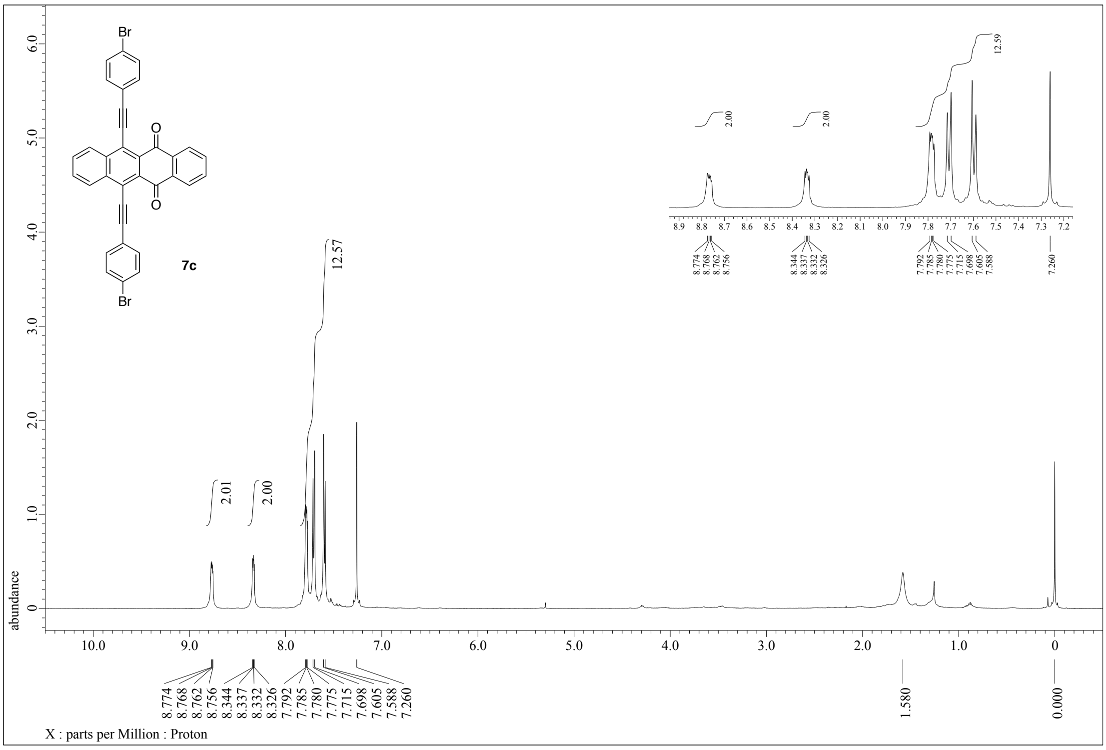
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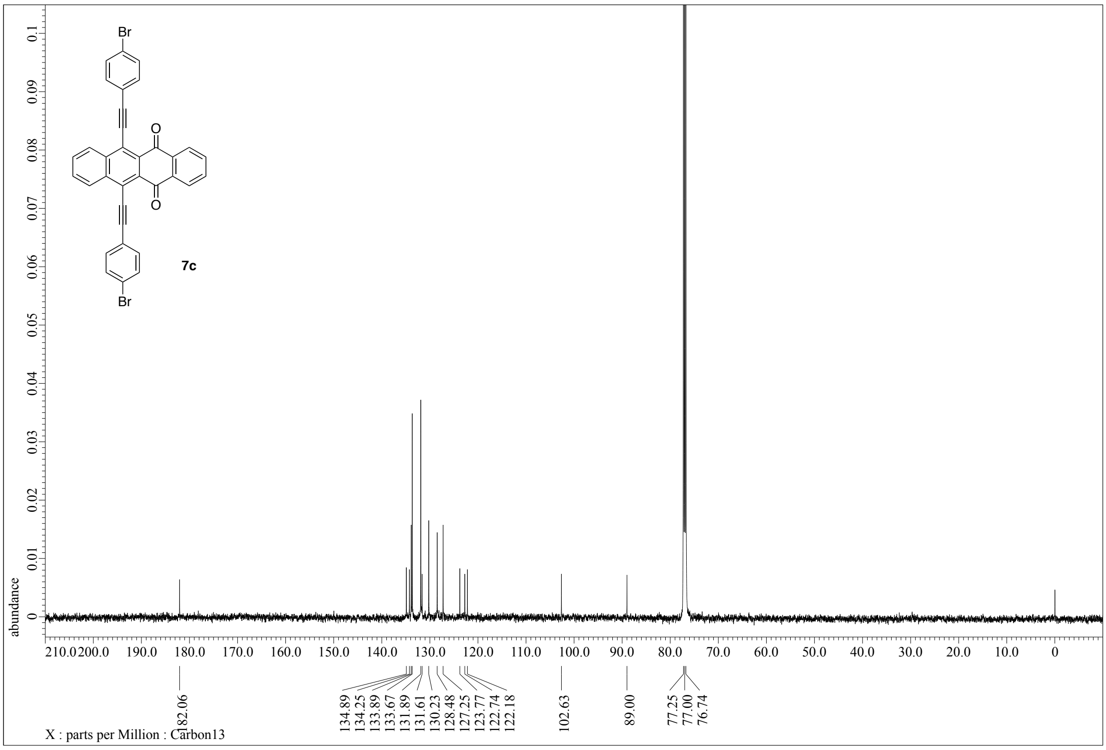
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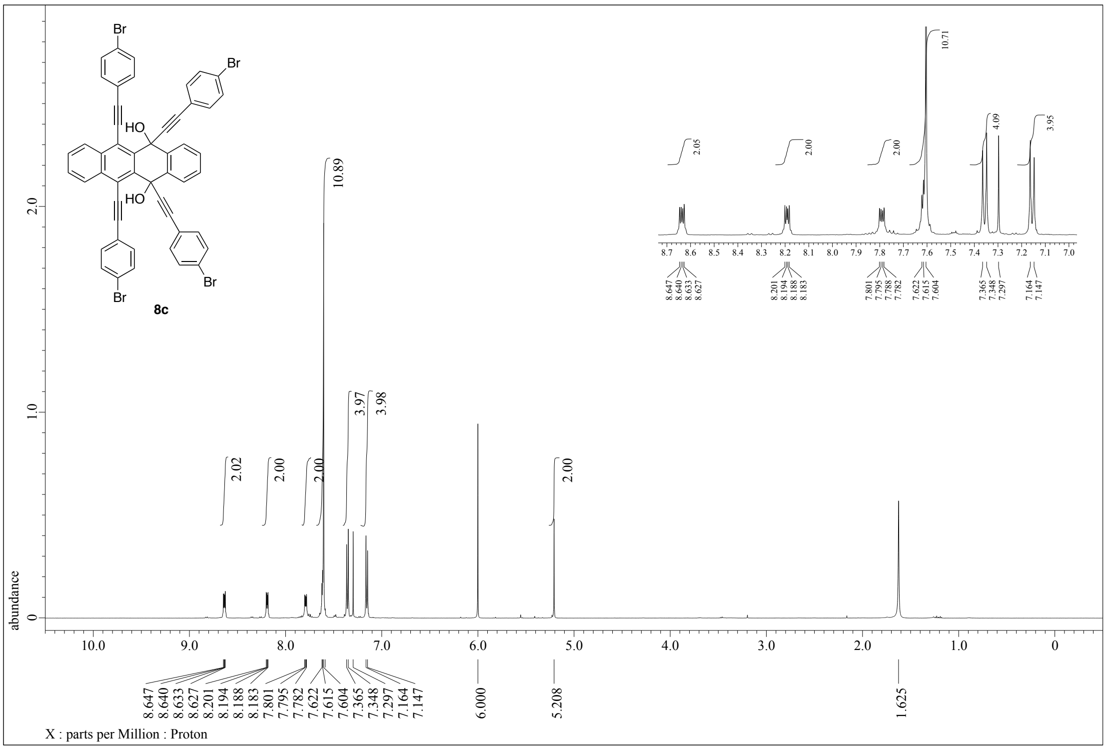
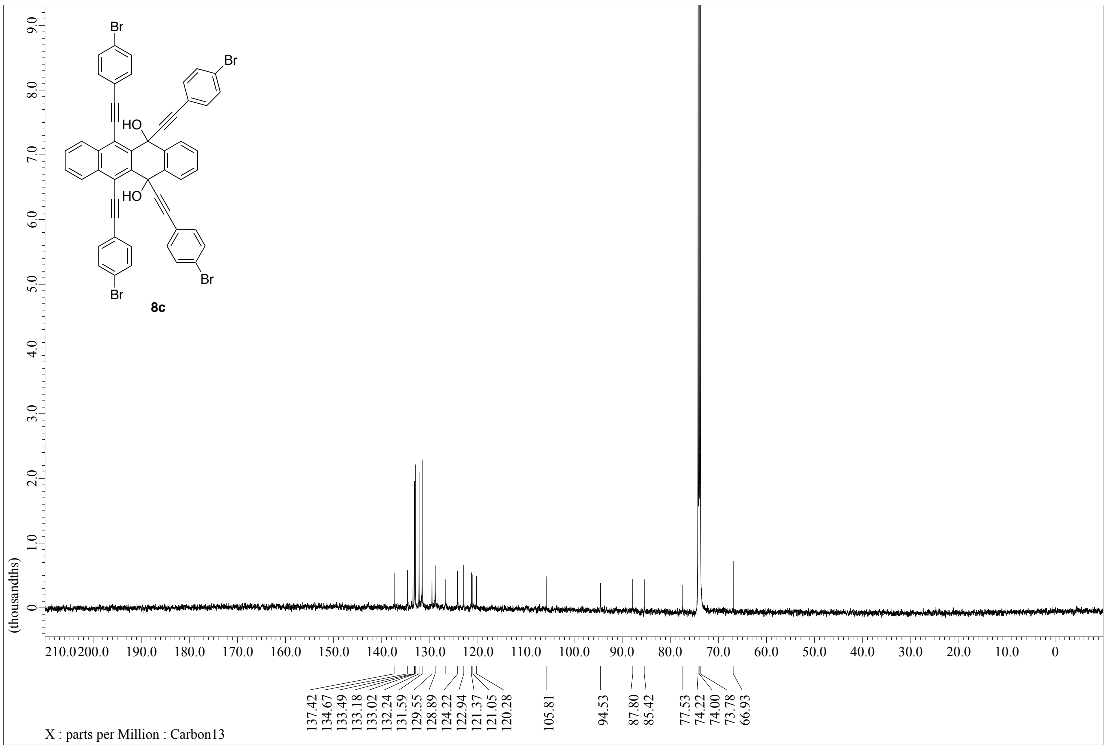
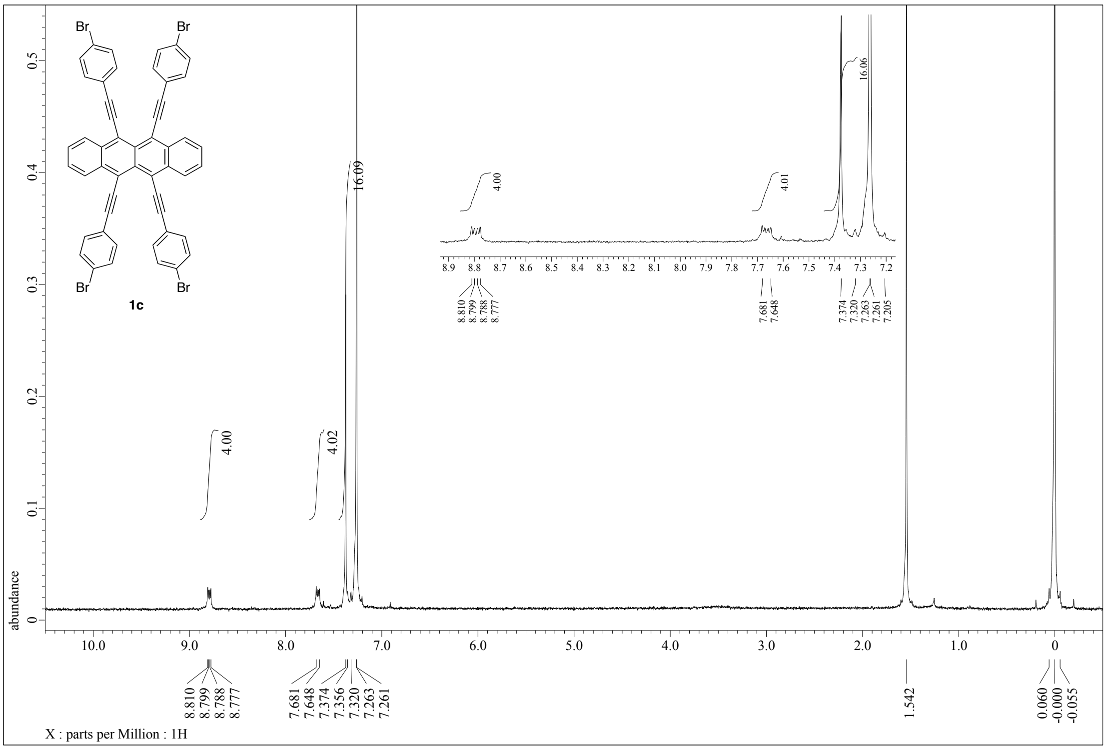
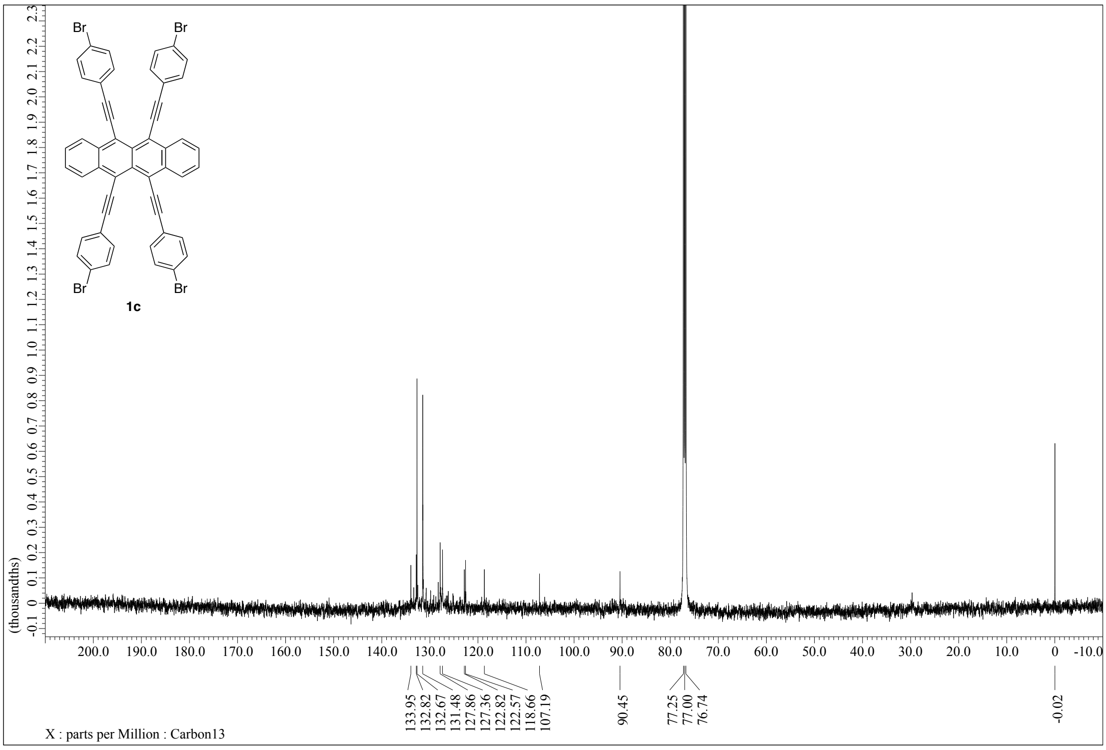
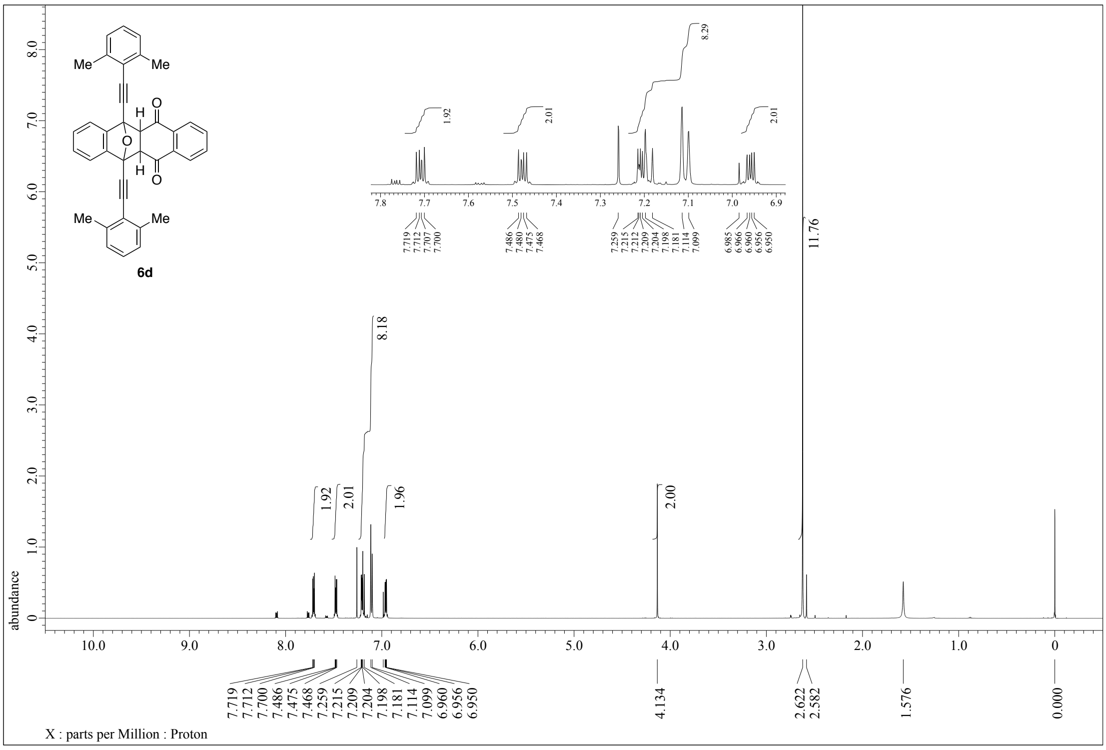
0.01
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
182.06
134.89 134.25 133.89 133.67 131.89 131.61 130.23 128.48 127.25 123.77 122.74 122.18
102.63
89.00
77.25 77.00 76.74
X : parts per Million : Carbon13

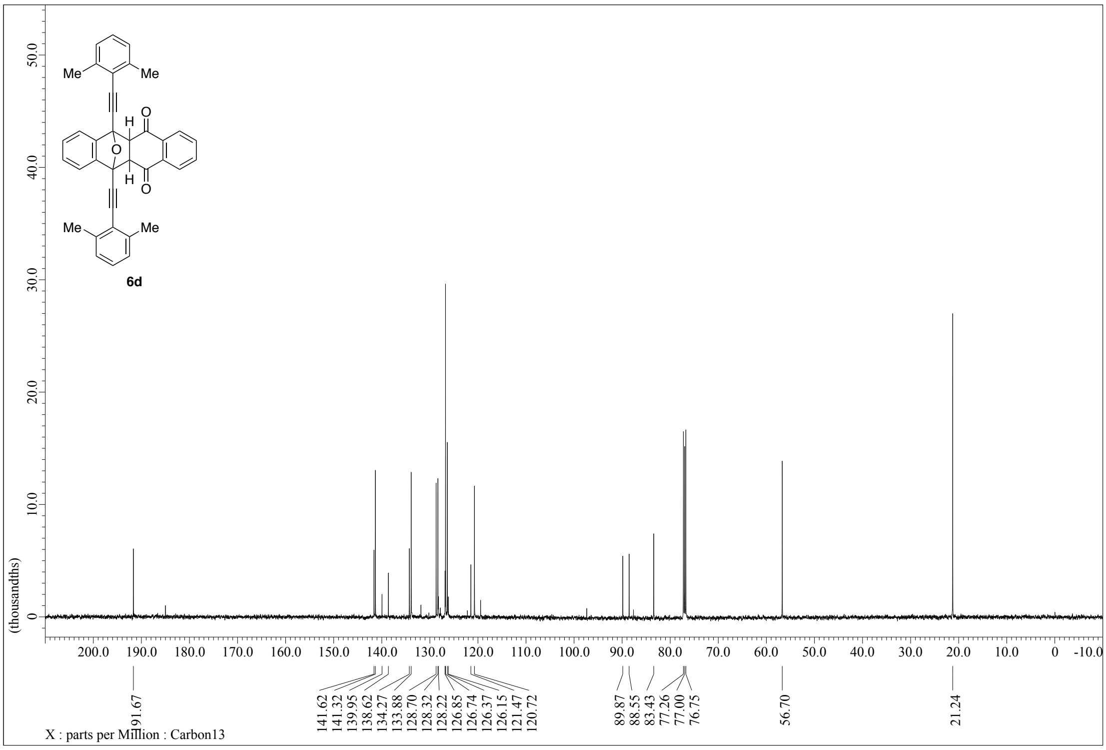

Br
Br
HO
HO
Br
Br
8c
10.89
3.97
3.98
2.02
2.00
2.00
2.00
10.71
2.05
2.00
2.00
4.09
3.95
8.647
8.640
8.633
8.627
8.201
8.194
8.188
8.183
7.801
7.795
7.788
7.782
7.622
7.615
7.604
7.365
7.348
7.297
7.164
7.147
6.000
5.208
1.625
abundance
0
1.0
2.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

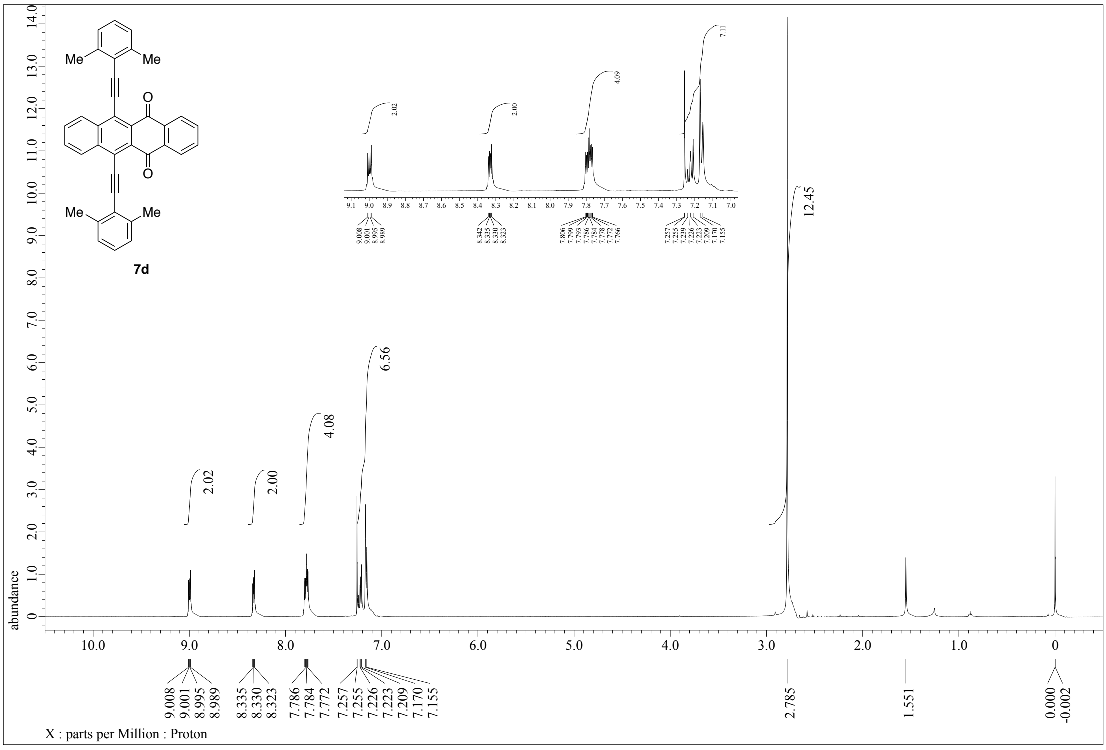

Br
Br
HO
HO
Br
Br
8c
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
210.0200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.42
134.67
133.49
133.18
133.02
132.24
131.59
129.55
128.89
124.22
122.94
121.37
121.05
120.28
105.81
94.53
87.80
85.42
77.53
74.22
74.00
73.78
66.93
X : parts per Million : Carbon13

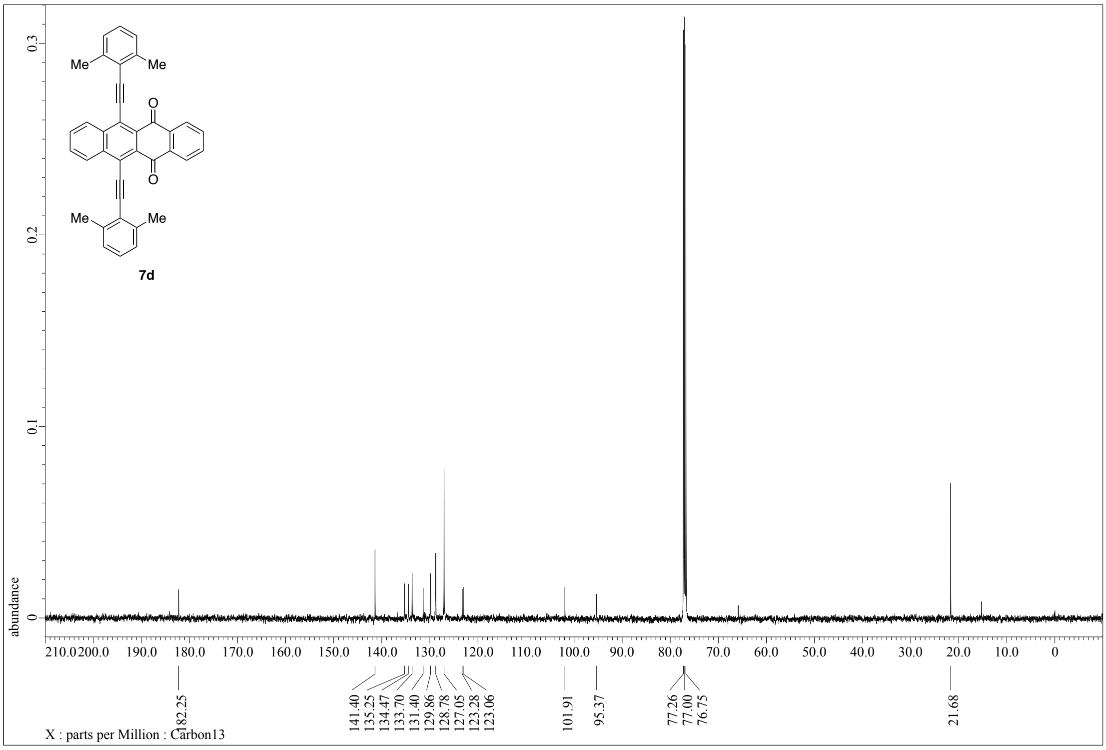

Br
Br
Br
Br
1c
abundance
0
0.1
0.2
0.3
0.4
0.5
4.00
4.02
16.09
4.00
4.01
16.06
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
8.810
8.799
8.788
8.777
7.681
7.648
7.374
7.320
7.263
7.261
7.205
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
8.810
8.799
8.788
8.777
7.681
7.648
7.374
7.356
7.320
7.263
7.261
1.542
0.060
-0.000
-0.055
X : parts per Million : 1H

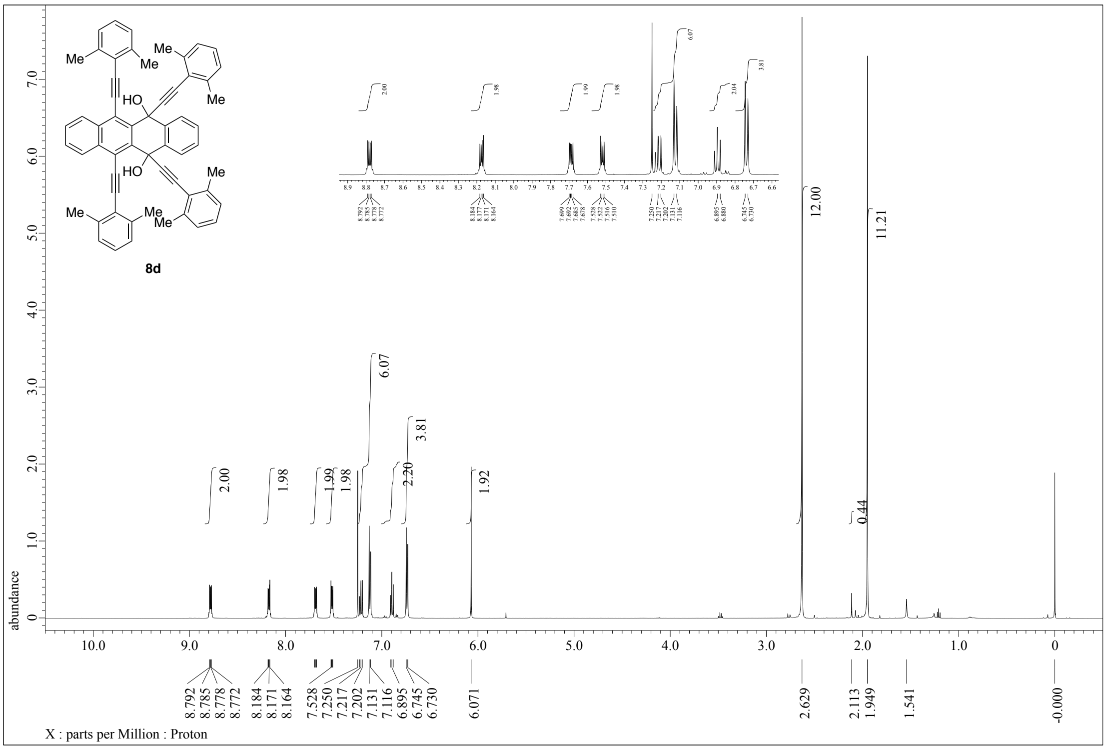

Br
Br
Br
Br
1c
(thousandths)
-0.1 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
133.95
132.82
132.67
131.48
127.86
127.36
122.82
122.57
118.66
107.19
90.45
77.25
77.00
76.74
-0.02
X : parts per Million : Carbon13

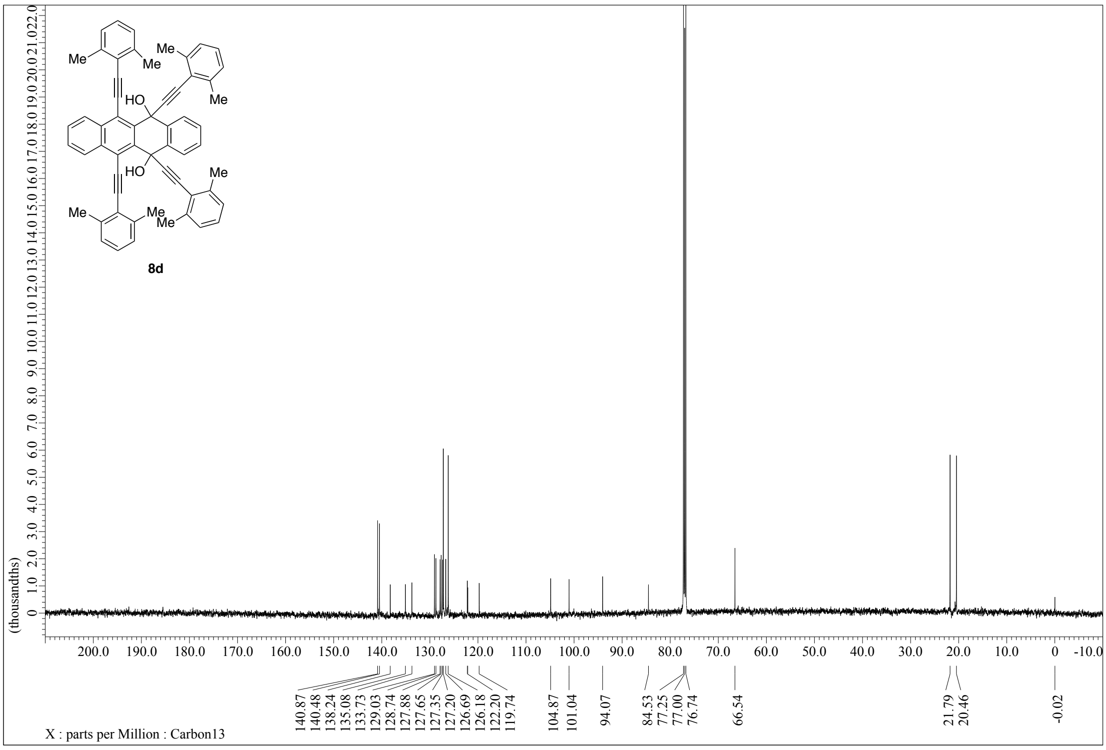

Me
Me
H
O
O
H
O
Me
Me
6d
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
1.92
2.01
8.29
2.01
7.719 7.712 7.707 7.700
7.486 7.480 7.475 7.468
7.259 7.215 7.212 7.209 7.204 7.198 7.181 7.114 7.099
6.985 6.966 6.960 6.956 6.950
11.76
8.18
1.92
2.01
1.96
2.00
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.719 7.712 7.700 7.486 7.475 7.468 7.259 7.215 7.209 7.204 7.198 7.181 7.114 7.099 6.960 6.956 6.950
4.134
2.622 2.582
1.576
0.000
X : parts per Million : Proton


Me
Me
H
O
O
H
O
Me
Me
6d
(thousandths)
0
10.0
20.0
30.0
40.0
50.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
191.67
141.62 141.32 139.95 138.62 134.27 133.88 128.70 128.32 128.22 126.85 126.74 126.37 126.15 121.47 120.72
89.87 88.55 83.43 77.26 77.00 76.75
56.70
21.24
X : parts per Million : Carbon13


7d
Me
Me
Me
Me
O
O
abundance
2.02
2.00
4.08
6.56
12.45
9.008
9.001
8.995
8.989
8.335
8.330
8.323
7.786
7.784
7.772
7.257
7.255
7.226
7.223
7.209
7.170
7.155
2.785
1.551
0.000
-0.002
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


7d
Me
Me
Me
Me
O
O
abundance
0.3
0.2
0.1
0
182.25
141.40
135.25
134.47
133.70
131.40
129.86
128.78
127.05
123.28
123.06
101.91
95.37
77.26
77.00
76.75
21.68
X : parts per Million : Carbon13


Me
Me
Me
Me
HO
HO
Me
Me
Me
Me
8d
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
2.00
1.98
1.99
1.98
6.07
2.04
3.81
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
8.792
8.785
8.778
8.772
8.184
8.177
8.171
8.164
7.699
7.692
7.685
7.678
7.528
7.522
7.516
7.510
7.250
7.217
7.202
7.131
7.116
6.895
6.880
6.745
6.730
2.00
1.98
1.99
1.98
6.07
2.20
3.81
1.92
12.00
0.44
11.21
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.792
8.785
8.778
8.772
8.184
8.171
8.164
7.528
7.250
7.217
7.202
7.131
7.116
6.895
6.745
6.730
6.071
2.629
2.113
1.949
1.541
-0.000
X : parts per Million : Proton


Me
Me
Me
Me
HO
HO
Me
Me
Me
Me
8d
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
140.87
140.48
138.24
135.08
133.73
129.03
128.74
127.88
127.65
127.35
127.20
126.69
126.18
122.20
119.74
104.87
101.04
94.07
84.53
77.25
77.00
76.74
66.54
21.79
20.46
-0.02
X : parts per Million : Carbon13