

Supporting Information

Isoacenofuran: Novel Quinoidal Building Block for Efficient Access to High-ordered Polyacene Derivatives

Kei Kitamura,^{1,2} Ryoji Kudo,¹ Haruki Sugiyama,³ Hidehiro Uekusa,³ and Toshiyuki Hamura¹

¹*Department of Applied Chemistry for Environment, School of Science and Technology, Kwansai Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan*

²*Present Address: Faculty of Pharmaceutical Sciences, Tokushima Bunri University, 180 Yamashiro-cho, Tokushima 770-8514, Japan*

³*Department of Chemistry, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo 152-8551, Japan*

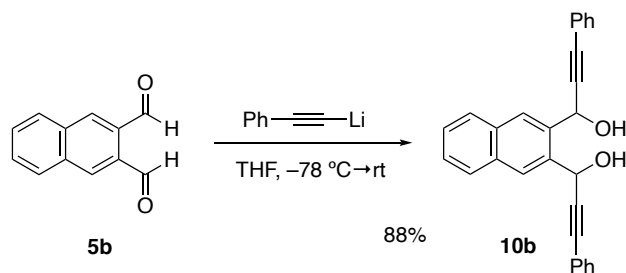
Table of Contents

1. General	S2
2. Synthesis of the Precursor of Isoacenofurans	S3
3. Preparation of 2,3-Anthracenedicarbaldehyde	S6
4. Cycloadditions of Isoacenofuran with Quinones	S8
5. Base-promoted Aromatization of Cycloadducts	S11
6. Synthesis of Substituted Hexacene 21	S14
7. Synthesis of Substituted Hexacene 22	S16
8. X-ray Crystallographic Data	S20
9. UV–Vis–NIR Absorption Spectra	S21
10. Cyclic Voltammograms	S22
11. Time-course ¹ H NMR Analysis	S23
12. HRMS Spectra of Hexacenes	S24
13. ¹ H and ¹³ C NMR Spectra	S25
14. Calculations	S45
15. References	S55

1. General

All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon. THF, toluene, and dichloromethane (super dehydrated; Wako Pure Chemical Industries, Ltd.) were used as received. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F₂₅₄, 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. ¹H NMR and ¹³C NMR were measured on a JEOL JNM ECA-300, a JEOL JNM ECZ-500R, or a Varian 400-MR spectrometer. Attenuated Total Reflectance Fourier Transformation Infrared (ATR-FTIR) spectra were recorded on a JASCO FT/IR-4200 infrared spectrometer. 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. Cyclic voltammetry (CV) were recorded on a ALS/CH Instruments Electrochemical Analyzer Model 620D. Melting points (Mp) were measured on an OptiMelt Automated Melting Point System from Stanford research systems and are uncorrected.

2. Synthesis of the Precursor of Isoacenofurans



To a solution of phenylacetylene (1.39 mL, 12.7 mmol) in THF (2 mL) was added *n*-BuLi (1.64 M in hexane, 7.3 mL, 12 mmol) at -78 °C. After stirring for 5 min, naphthalene-2,3-dicarboxaldehyde (**5b**) (1.00 g, 5.43 mmol) in THF (18 mL) was added, and the mixture was stirred for 30 min. After gradual warming to room temperature for 7 h, the reaction was quenched by sat. aq. NH_4Cl . The products were extracted with EtOAc ($\times 3$), and combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 8/2 \rightarrow 7/3) to give diol **10b** (1.62 g, 88%, dr 65:35) as a pale yellow oil.

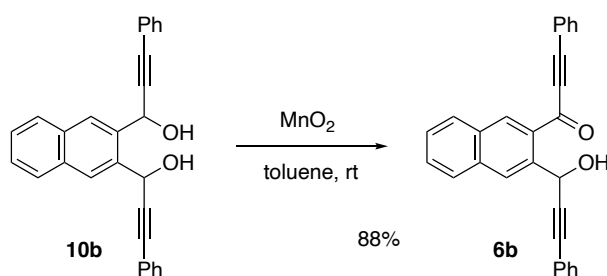
R_f 0.34 (hexane/EtOAc = 7/3);

^1H NMR (CDCl_3 , 300 MHz) 3.26 (s, 0.7H), 3.73 (s, 1.30H), 6.34 (s, 0.70H), 6.49 (s, 1.30H), 7.33–7.37 (m, 6H), 7.52–7.56 (m, 6H), 7.87–7.93 (m, 2H), 8.23 (s, 1.30H), 8.41 (s, 0.70H);

^{13}C NMR (CDCl_3 , 75 MHz) 62.8, 64.4, 87.6, 87.9, 88.0, 122.27, 122.32, 126.9, 127.1, 127.8, 128.0, 128.1, 128.4, 128.7, 128.8, 129.0, 131.79, 131.84, 133.06, 133.10, 135.4, 135.6; *All signals for both diastereomers were listed.*

IR (ATR) 3308, 3056, 3018, 2925, 2229, 1598, 1489, 1442, 1216, 1176, 1017, 954, 895, 752 cm^{-1} ;

HRMS (DART) m/z calcd for $\text{C}_{28}\text{H}_{20}\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 411.1361; found 411.1363.



To a solution of diol **10b** (1.62 g, 4.79 mmol) in toluene (6 mL) was added MnO_2 (600 mg, 6.90 mmol) in several portions at 0 °C, and the reaction was vigorously stirred at room temperature. After stirring for 30 h, the mixture was filtered through Celite[®] pad, and the solvents were evaporated under reduced pressure. The residue was purified by silica gel column chromatography (toluene/EtOAc = 96/4) to give keto-alcohol **6b** (1.41 g, 88%) as a yellow solid.

Mp 94 °C (dec), yellow prism (hexane/CHCl₃);

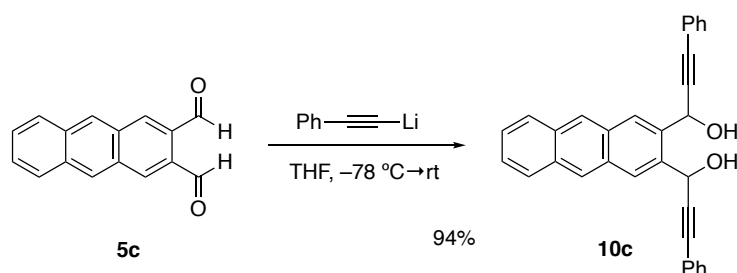
R_f 0.43 (hexane/EtOAc = 7/3);

¹H NMR (CDCl₃, 300 MHz) 5.04 (d, 1H, *J* = 7.7 Hz), 6.15 (d, 1H, *J* = 7.7 Hz), 7.28–7.30 (m, 3H), 7.44–7.54 (m, 5H), 7.61–7.64 (m, 1H), 7.67–7.74 (m, 3H), 7.94 (d, 1H, *J* = 8.0 Hz), 8.03 (d, 1H, *J* = 8.0 Hz), 8.28 (s, 1H), 8.97 (s, 1H);

¹³C NMR (CDCl₃, 75 MHz) 64.4, 86.7, 88.1, 88.3, 94.3, 119.9, 122.7, 127.6, 128.2, 128.3, 128.4, 128.8, 129.2, 129.3, 129.9, 131.1, 131.8, 132.0, 133.1, 133.6, 135.4, 137.3, 137.5, 181.1;

IR (ATR) 3376, 3057, 3032, 2193, 1611, 1572, 1489, 1442, 1301, 1186, 1102, 1025, 957, 897, 752 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₂₈H₁₈O₂Na [M+Na]⁺: 409.1204; found: 409.1193.



To a solution of phenylacetylene (1.0 mL, 9.1 mmol) in THF (25 mL) was added *n*-BuLi (1.57 M in hexane, 5.1 mL, 8.0 mmol) at 0 °C. After stirring for 20 min, 2,3-anthracenedicarboxaldehyde (**5c**) (468 mg, 2.00 mmol) was added at -78 °C and the mixture was stirred at room temperature for 12 h. The reaction was then quenched by addition of sat. aq. NH₄Cl at 0 °C. The products were extracted with EtOAc (×3) and the combined extracts were washed with brine and dried over Na₂SO₄. After concentration, the residue was purified by silica-gel column chromatography (hexane/EtOAc = 9/1 → 7/3) to give diol **10c** (828 mg, 94%, dr 87:13) as yellow oil.

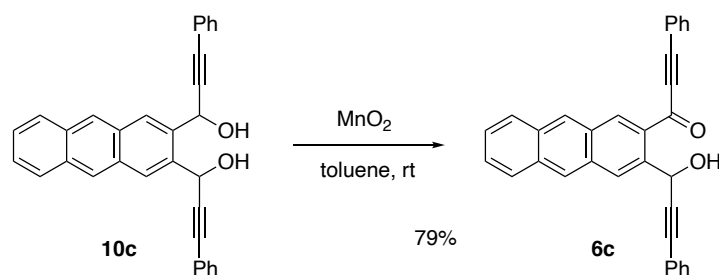
R_f 0.29 (hexane/EtOAc = 7/3);

¹H NMR (CDCl₃, 400 MHz) 3.84 (brs, 2H), 6.36 (s, 0.26H), 6.52 (s, 1.74H), 7.34–7.40 (m, 6H), 7.48–7.53 (m, 2H), 7.54–7.61 (m, 4H), 8.00–8.05 (m, 2H), 8.39 (s, 1.74H), 8.46 (s, 1.74H), 8.50 (s, 0.26H), 8.58 (s, 0.26H);

¹³C NMR (DMSO-*d*₆, 100 MHz) 60.6, 85.4, 90.6, 122.2, 125.8, 126.3, 126.7, 128.1, 128.7, 130.4, 131.45, 131.46, 131.7, 136.9; *Only major diastereomer was recorded for ¹³C NMR.*

IR (ATR) 3274, 2230, 1490, 1444, 1375, 1257, 1175, 1013, 956, 910, 788, 753, 689 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₃₂H₂₂NaO₂ [M+Na]⁺: 461.1512; found: 461.1513.



To a solution of diol **10c** (828 mg, 1.89 mmol) in toluene (19 mL) was added MnO₂ (200 mg, 2.30 mmol) portionwise at 0 °C. The mixture was then vigorously stirred at room temperature for 46 h. After filtration through Celite[®] pad (washed with CH₂Cl₂) and concentration, the residue was purified by silica-gel column chromatography (hexane/EtOAc = 4/1) to give ketol **6c** (653 mg, 79%) as an orange oil.

R_f 0.41 (hexane/acetone = 8/2);

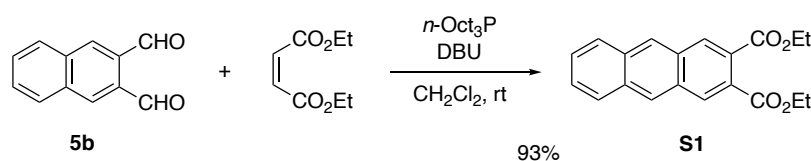
¹H NMR (CDCl₃, 400 MHz) 5.19 (d, 1H, *J* = 8.0 Hz), 6.16 (d, 1H, *J* = 8.0 Hz), 7.28–7.34 (m, 3H), 7.44–7.62 (m, 7H), 7.76 (d, 2H, *J* = 7.6 Hz), 8.05 (t, 2H, *J* = 8.8 Hz), 8.38 (s, 1H), 8.47 (s, 1H), 8.63 (s, 1H), 9.18 (s, 1H);

¹³C NMR (CDCl₃, 100 MHz) 64.6, 86.8, 88.0, 88.4, 94.1, 119.9, 122.8, 126.5, 127.1, 127.4, 128.2, 128.36, 128.39, 128.6, 128.8, 129.3, 129.47, 129.52, 131.1, 131.9, 132.0, 132.5, 133.2, 133.4, 134.1, 135.6, 139.9, 180.8;

IR (ATR) 3391, 3053, 2194, 1614, 1489, 1444, 1317, 1289, 1254, 1195, 1027, 989, 957, 915, 868, 792, 753, 688, 534 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₃₂H₂₀NaO₂ [M+Na]⁺: 459.1356; found: 459.1356.

3. Preparation of 2,3-Anthracenedicarbaldehyde^[1]



To a solution of diethyl maleate (2.1 mL, 13 mmol) in CH_2Cl_2 (20 mL) was added tri-*n*-octylphosphine (6.3 mL, 14 mmol) at 0 °C. After stirring at room temperature for 30 min, 2,3-naphthalenedicarboxaldehyde^[2] (**5b**) (1.83 g, 9.94 mmol) was added at 0 °C and then added DBU (150 μL , 1.00 mmol). After stirring at room temperature for 24 h, the mixture was diluted with H_2O (20 mL). The products were extracted with EtOAc ($\times 3$) and combined organic extracts were washed with brine and dried over Na_2SO_4 . After concentration, the residue was purified by silica-gel column chromatography (hexane/EtOAc = 9/1 \rightarrow 8/2) to give diester **S1** (2.98 g, 93%) as yellow solids.

Mp 91–93 °C;

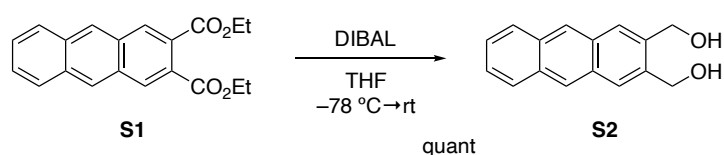
R_f 0.44 (hexane/EtOAc = 8/2);

^1H NMR (CDCl_3 , 400 MHz) 1.43 (t, 6H, $J = 7.2$ Hz), 4.44 (q, 4H, $J = 7.2$ Hz), 7.50–7.55 (m, 2H), 7.98–8.03 (m, 2H), 8.40 (s, 2H), 8.46 (s, 2H);

^{13}C NMR (CDCl_3 , 100 MHz) 14.2, 61.6, 126.7, 127.8, 127.9, 128.3, 130.4, 131.1, 132.9, 167.7;

IR (ATR) 2979, 1729, 1708, 1628, 1467, 1442, 1368, 1288, 1238, 1174, 1131, 1113, 1053, 1019, 960, 933, 880, 863, 776, 743, 662, 583 cm^{-1} ;

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{NaO}_4$ [$\text{M}+\text{Na}$]⁺: 345.1103; found: 345.1101.



To a solution of diester **S1** (650 mg, 2.02 mmol) in THF (20 mL) was added DIBAL (1.0 M in hexane, 10 mL, 10 mmol) at $-78\text{ }^\circ\text{C}$. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 10 min and then stirred for 4 h with gradual warming to room temperature. The reaction was carefully quenched by dropwise addition of MeOH. The products were extracted with EtOAc ($\times 3$) and combined organic extracts were washed with brine and dried over Na_2SO_4 . The volatiles were removed in vacuo to give diol **S2** (481 mg, quant) as white solids.

Mp 256 °C (dec.);

R_f 0.18 (hexane/EtOAc = 5/5);

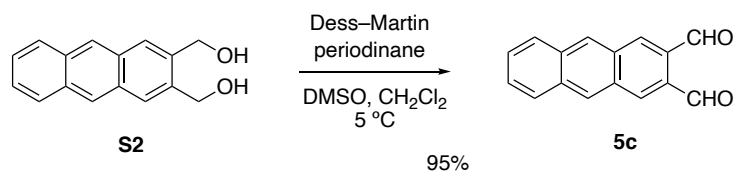
^1H NMR ($\text{DMSO-}d_6$, 400 MHz) 4.76 (d, 4H, $J = 5.2$ Hz), 5.36 (t, 2H, $J = 5.2$ Hz), 7.45–7.50 (m, 2H), 8.03–

8.08 (m, 2H), 8.04 (s, 2H), 8.51 (s, 2H);

^{13}C NMR (DMSO- d_6 , 100 MHz) 60.9, 124.8, 125.3, 125.4, 128.0, 130.6, 131.2, 138.3;

IR (ATR) 3172, 2926, 1462, 1372, 1345, 1225, 1189, 1117, 1034, 1011, 901, 737, 595 cm^{-1} ;

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 261.0891; found: 261.0894.



To a solution of diol **S2** (40.7 mg, 0.171 mmol) in DMSO (1.0 mL) and CH_2Cl_2 (1.0 mL) was added Dess–Martin periodinane (190 mg, 0.448 mmol) at 0 °C. After stirring at 5 °C for 1 h, the reaction was quenched by sequential additions of 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$ and sat. aq. NaHCO_3 . The products were extracted with CH_2Cl_2 ($\times 3$) and combined organic extracts were washed with brine and dried over Na_2SO_4 . After concentration, the residue was purified by silica-gel column chromatography (hexane/EtOAc = 8/2) to give dialdehyde **5c** (37.9 mg, 95%) as yellow solids.

Mp 216–218 °C;

R_f 0.34 (hexane/EtOAc = 8/2);

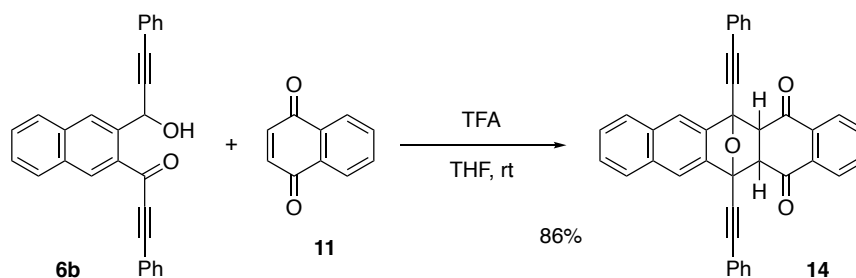
^1H NMR (CDCl_3 , 400 MHz) 7.62–7.68 (m, 2H), 8.07–8.13 (m, 2H), 8.62 (s, 2H), 8.64 (s, 2H), 10.65 (s, 2H);

^{13}C NMR (CDCl_3 , 100 MHz) 127.8, 128.6, 129.5, 130.9, 132.0, 133.8, 136.4, 192.5;

IR (ATR) 2911, 1683, 1612, 1574, 1454, 1403, 1342, 1288, 1172, 1116, 1002, 913, 867, 791, 756, 701, 609, 537 cm^{-1} ;

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{10}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 257.0578; found: 257.0578.

4. Cycloadditions of Isoacenofuran and Quinones



To a mixture of keto-alcohol **6b** (200 mg, 0.518 mmol) and 1,4-naphthoquinone (**11**) (100 mg, 0.632 mmol) in THF (1.7 mL) was added TFA (0.10 mL, 1.3 mmol) at 0 °C, and the mixture was stirred at room temperature for 8 h. The reaction was carefully quenched by an addition of sat. aq. NaHCO₃. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The precipitates were collected by filtration (heptane) to provide cycloadduct **14** (235 mg, 86%, *endo/exo* = 74/26) as a pale brown solid.

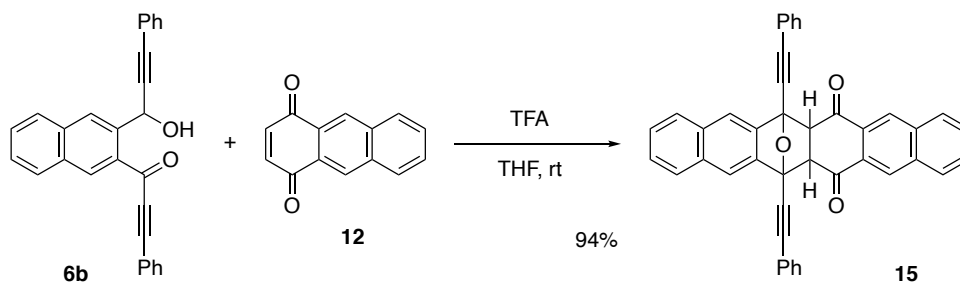
R_f 0.31 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 500 MHz) 3.54 (s, 0.52H), 4.18 (s, 1.48H), 7.21–7.25 (m, 1.48H), 7.36–7.38 (m, 1.48H), 7.39–7.44 (m, 6H), 7.56–7.61 (m, 2H), 7.61 (s, 1.48H), 7.63–7.66 (m, 2.52H), 7.69–7.73 (m, 2.96H), 7.75–7.77 (m, 0.52H), 7.94–7.96 (m, 0.52H), 7.99 (s, 0.52H), 8.04–8.06 (m, 0.52H);

¹³C NMR (CDCl₃, 125 MHz) 56.8, 59.3, 81.8, 83.1, 83.6, 90.8, 118.4, 120.2, 121.4, 121.7, 126.2, 126.6, 126.7, 126.9, 128.2, 128.38, 128.44, 128.6, 129.3, 129.5, 132.4, 132.7, 133.6, 134.1, 134.4, 137.1, 138.8, 192.0, 193.5; *All signals for both diastereomers were listed.*

IR (ATR) 3057, 2921, 2849, 2196, 1670, 1489, 1397, 1348, 1274, 999, 884 cm⁻¹;

HRMS (DART) *m/z* calcd for C₃₈H₂₃O₃ [M+H]⁺: 527.1647; found: 527.1652.



To a mixture of keto-alcohol **6b** (1.00 g, 2.59 mmol) and 1,4-antraquinone (**12**) (590 mg, 2.83 mmol) in THF (6.5 mL) was added TFA (0.50 mL, 6.5 mmol) at 0 °C, and the mixture was stirred for 5 h at room temperature. The reaction was carefully quenched by sat. aq. NaHCO₃. The products were extracted with EtOAc (×3), and combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The precipitates were collected by filtration (heptane) to provide cycloadduct **15** (1.36 g, 94%, *endo/exo* = 93/7) as a pale brown solid.

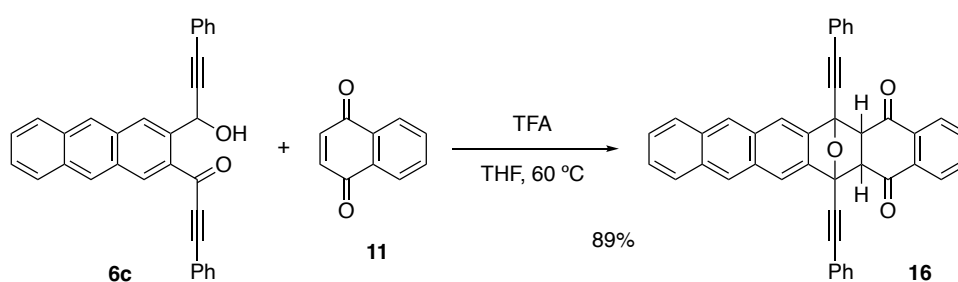
R_f 0.27 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 500 MHz) 3.61 (s, 0.14H), 4.28 (s, 1.86H), 7.19–7.22 (m, 1.86H), 7.40–7.45 (m, 6H), 7.47–7.50 (m, 1.86H), 7.55–7.59 (m, 2H), 7.66 (s, 1.86H), 7.67–7.69 (m, 0.28H), 7.72–7.78 (m, 5.72H), 7.94–7.96 (m, 0.14H), 8.00 (s, 0.14H), 8.05–8.07 (m, 0.14H), 8.21 (s, 1.86H), 8.60 (s, 0.14H);

¹³C NMR (CDCl₃, 125 MHz) 57.0, 82.2, 83.1, 90.6, 120.2, 121.8, 126.4, 128.1, 128.4, 128.6, 129.2, 129.3, 129.6, 130.1, 132.3, 132.6, 134.7, 138.9, 192.0; *Only major diastereomer was recorded for ¹³C NMR.*

IR (ATR) 3051, 2957, 2925, 2243, 1682, 1619, 1491, 1454, 1250, 1193, 1122, 979, 911, 869, 756 cm⁻¹;

HRMS (DART) *m/z* calcd for C₄₂H₂₅O₃ [M+H]⁺: 577.1804; found: 577.1805.



To a mixture of ketol **6c** (259 mg, 0.593 mmol) and 1,4-naphthoquinone (**11**) (102 mg, 0.647 mmol) in THF (2.0 mL) was added TFA (113 μL, 1.48 mmol) at 0 °C. After stirring at 60 °C in oil bath for 10 h, the reaction was quenched by addition of sat. aq. NaHCO₃ and the products were extracted with CH₂Cl₂ (×3). The combined extracts were washed with brine, and then dried over Na₂SO₄. The crude products were triturated with hexane/Et₂O (=4/1) to give cycloadduct **16** (304 mg, 89%, *endo/exo* = 78/22) as a light brown solid.

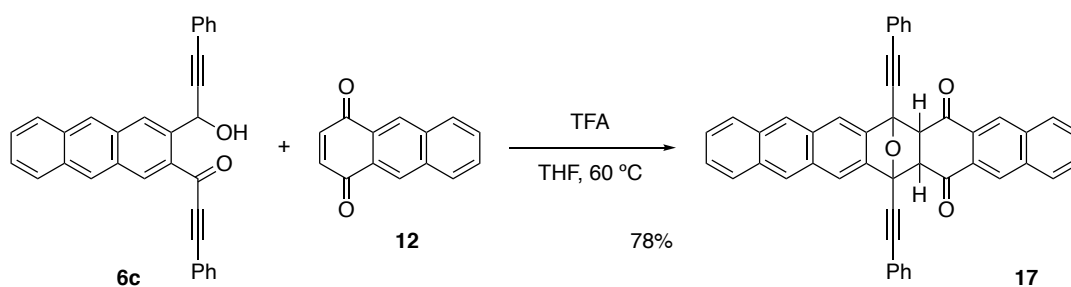
R_f 0.29 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 400 MHz) 3.63 (s, 0.44H), 4.21 (s, 1.56H), 7.12–7.18 (m, 1.56H), 7.40–7.49 (m, 7.56H), 7.50–7.55 (m, 0.44H), 7.60–7.65 (m, 1.56H), 7.65–7.70 (m, 0.44H), 7.71–7.80 (m, 5.56H), 7.89–7.94 (m, 1.56H), 8.02–8.09 (m, 0.88H), 8.11 (s, 0.44H), 8.24 (s, 1.56H), 8.52 (s, 0.44H);

¹³C NMR (CDCl₃, 100 MHz) 56.9, 59.5, 80.0, 81.7, 83.0, 83.6, 90.8, 94.0, 118.4, 120.2, 121.4, 121.6, 125.8, 126.0, 126.2, 126.7, 127.0, 127.4, 128.0, 128.1, 128.4, 128.5, 129.3, 129.5, 130.4, 131.0, 131.8, 132.1, 132.4 (×2), 133.8, 134.0, 134.4, 137.1, 138.3, 141.0, 191.9, 193.4; *All signals for both diastereomers were listed.*

IR (ATR) 3048, 2243, 1679, 1594, 1492, 1443, 1286, 1259, 1134, 1061, 969, 887, 754, 688, 590 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₄₂H₂₅O₃ [M+H]⁺: 577.1804; found: 577.1804.



To a mixture of ketol **6c** (652 mg, 1.49 mmol) and 1,4-anthraquinone (**12**) (330 mg, 1.58 mmol) in THF (4.0 mL) was added TFA (286 μ L, 3.74 mmol) at 0 °C. After stirring at 60 °C in oil bath for 11 h, the reaction was quenched by addition of sat. aq. NaHCO₃ at 0 °C and stirred for 10 min. The precipitates were collected by filtration and sequentially washed with H₂O, EtOH, and Et₂O to give cycloadduct (529 mg, 56.7%, *endo/exo* = 71/29) as off-white solids. Additional products were extracted with EtOAc ($\times 3$) from the mother liquor. The combined extracts were washed with brine, and then dried over Na₂SO₄. After concentration, the residue was purified by silica-gel column chromatography (hexane/acetone = 70/30) to give cycloadduct **17** (195 mg, 20.9%, 78% combined yield) as a yellow solid.

R_f 0.25 (hexane/EtOAc = 8/2);

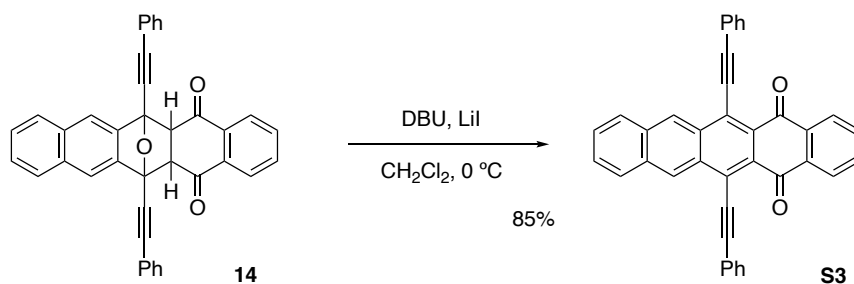
¹H NMR (CDCl₃, 500 MHz) 3.71 (s, 0.58H), 4.30 (s, 1.42H), 7.31–7.35 (m, 1.42H), 7.35–7.39 (m, 1.42H), 7.42–7.47 (m, 6H), 7.51–7.55 (m, 0.58H), 7.65–7.71 (m, 3.16H), 7.74–7.77 (m, 2.84H), 7.78–7.82 (m, 1.42H), 7.80 (s, 1.42H), 8.02–8.09 (m, 1.16H), 8.13 (s, 0.58H), 8.15 (s, 1.42H), 8.22 (s, 1.42H), 8.53 (s, 0.58H), 8.62 (s, 0.58H);

¹³C NMR (CDCl₃, 125 MHz) 57.1, 59.9, 80.2, 82.1, 83.1, 83.9, 90.7, 93.9, 118.4, 120.3, 121.5, 121.8, 125.6, 126.0, 127.0, 127.4, 127.9, 128.1, 128.4, 128.5, 128.7, 128.9, 129.0, 129.3, 129.5, 129.6, 129.9, 130.0, 130.2, 130.5, 131.0, 131.7, 132.1, 132.4, 132.9, 134.6, 135.4, 138.5, 140.1, 141.1, 191.9, 193.6; *All signals for both diastereomers were listed.*

IR (ATR) 3052, 2242, 1682, 1620, 1491, 1442, 1390, 1327, 1288, 1247, 1191, 1053, 982, 888, 755, 688 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₄₆H₂₆NaO₃ [M+Na]⁺: 649.1780; found: 649.1781.

5. Base-promoted Aromatization of Cycloadducts



To a solution of cycloadduct **14** (200 mg, 0.380 mmol) in CH_2Cl_2 (9.5 mL) was sequentially added LiI (102 mg, 0.762 mmol) and DBU (0.34 mL, 2.3 mmol) at 0 °C. After stirring for 90 min at this temperature, the reaction was quenched by an addition of 2 M HCl and the products were extracted with CH_2Cl_2 ($\times 3$). The combined extracts were washed with brine, and then dried over Na_2SO_4 . After concentration, the crude products were triturated with Et_2O to give pentacenequinone **S3** (164 mg, 85%) as an orange solid.

Mp 154 °C (dec);

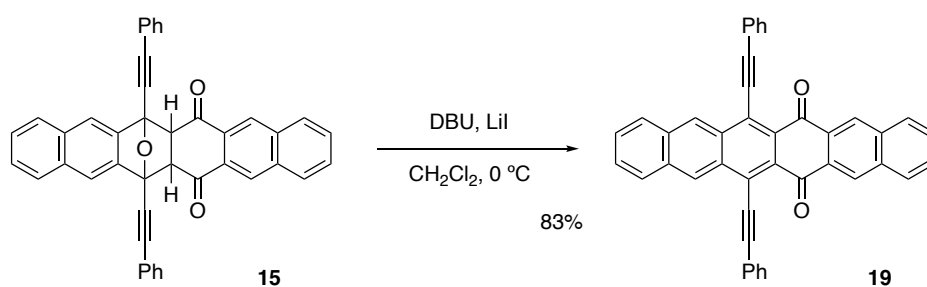
R_f 0.36 (hexane/EtOAc = 8/2);

^1H NMR (CDCl_3 , 500 MHz) 7.47–7.54 (m, 6H), 7.65–7.67 (m, 2H), 7.81–7.82 (m, 2H), 7.95–7.97 (m, 4H), 8.18–8.20 (m, 2H), 8.41–8.43 (m, 2H), 9.46 (s, 2H);

^{13}C NMR (CDCl_3 , 125 MHz, 50 °C) 88.8, 104.7, 123.6, 124.1, 127.4, 127.9, 128.7, 129.0, 129.1, 129.3, 131.0, 131.5, 132.5, 133.7, 133.8, 134.9, 182.1;

IR (ATR) 3055, 2923, 2853, 2175, 1669, 1593, 1488, 1396, 1345, 1273, 995, 913, 884 cm^{-1} ;

HRMS (MALDI, DCTB matrix) m/z calcd for $\text{C}_{38}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 509.1536; found: 509.1521.



To a solution of cycloadduct **15** (1.45 g, 2.51 mmol) in CH_2Cl_2 (100 mL) was sequentially added LiI (669 mg, 5.00 mmol) and DBU (2.24 mL, 15.0 mmol) at 0 °C. After stirring for 30 min at this temperature, the reaction was quenched by an addition of 2 M HCl and stirred for 30 min. The precipitates were collected by filtration and sequentially washed with H_2O , EtOH, and hexane to give heptacenequinone **19** (1.16 g, 83%) as a red solid.

Mp 144 °C (dec);

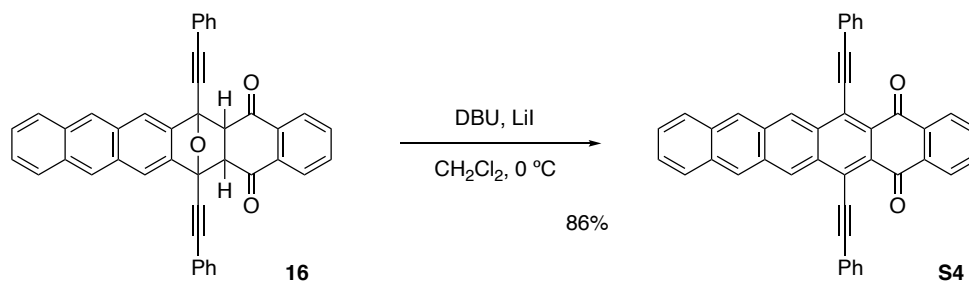
R_f 0.36 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 500 MHz, 50 °C) 7.46–7.53 (m, 6H), 7.63–7.65 (m, 2H), 7.67–7.69 (m, 2H), 7.97 (d, 4H, J = 8.0 Hz), 8.10–8.12 (m, 2H), 8.16–8.18 (m, 2H), 8.95 (s, 2H), 9.46 (s, 2H);

¹³C NMR (CDCl₃, 125 MHz, 50 °C) 89.0, 104.8, 123.7, 124.1, 127.8, 128.7, 129.03, 129.04, 129.1, 129.3, 129.4, 130.0, 131.1, 131.5, 131.8, 132.5, 133.8, 135.4, 182.1;

IR (ATR) 3051, 2187, 1672, 1619, 1489, 1456, 1394, 1344, 1266, 1183, 1026, 888, 754 cm⁻¹;

HRMS (MALDI, TCNQ matrix) *m/z* calcd for C₄₂H₂₃O₂ [M+H]⁺: 559.1693; found: 559.1710.



To a solution of cycloadduct **16** (229 mg, 0.397 mmol) in CH₂Cl₂ (16 mL) was sequentially added LiI (107 mg, 0.799 mmol) and DBU (360 μL, 2.41 mmol) at 0 °C. After stirring for 1 h, the reaction was quenched by addition of 2 M HCl and stirred for 30 min. The products were extracted with CHCl₃ (×3) and combined organic extracts were washed with brine and dried over Na₂SO₄. After concentration, the residue was triturated with Et₂O. The precipitates were sequentially washed with Et₂O, EtOH, and hexane to give hexacenequinone **S4** (192 mg, 86%) as a dark brown solid.

Mp >300 °C;

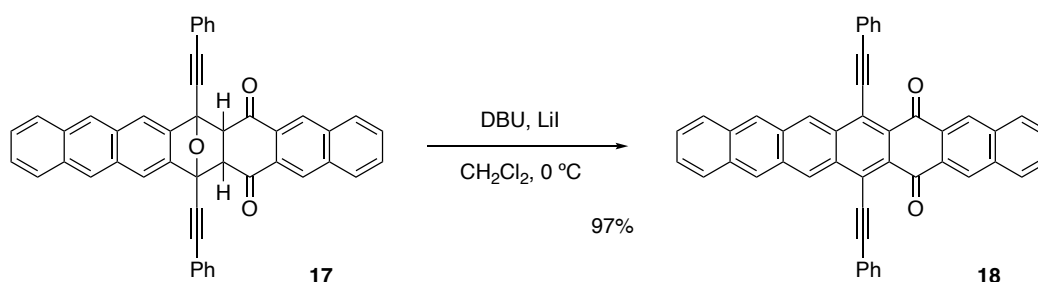
R_f 0.50 (hexane/acetone = 7/3);

¹H NMR (C₂D₂Cl₄, 500 MHz, 50 °C) 7.52–7.61 (m, 8H), 7.83–7.87 (m, 2H), 8.00–8.04 (m, 4H), 8.07–8.11 (m, 2H), 8.39–8.43 (m, 2H), 8.82 (s, 2H), 9.63 (s, 2H);

¹³C NMR (C₂D₂Cl₄, 125 MHz, 50 °C) 89.0, 104.9, 123.5, 124.4, 126.7, 127.4, 127.9, 128.5, 128.8, 129.6, 130.1, 130.2, 130.7, 131.2, 132.6, 133.1, 133.9, 134.8, 181.9;

IR (ATR) 2930, 2188, 1648, 1593, 1489, 1443, 1396, 1349, 1280, 1107, 1001, 898, 758, 721, 687, 567 cm⁻¹;

HRMS (MALDI, TCNQ matrix) *m/z* calcd for C₄₂H₂₃O₂ [M+H]⁺: 559.1693; found: 559.1687.



To a solution of cycloadduct **17** (506 mg, 0.807 mmol) in CH₂Cl₂ (32 mL) was sequentially added LiI (214 mg, 1.60 mmol) and DBU (720 μL, 4.82 mmol) at 0 °C. After stirring for 30 min, the reaction was quenched by addition of 2 M HCl and stirred for 30 min. The precipitates were collected by filtration and sequentially washed with H₂O, EtOH, and hexane to give heptacenequinone **18** (475 mg, 97%) as a dark-red solid.

Mp >300 °C

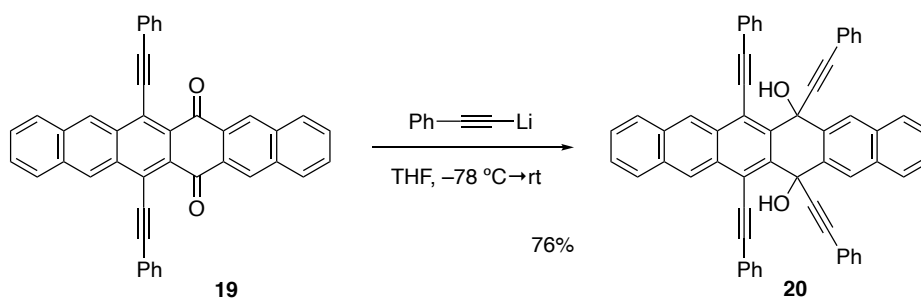
¹H NMR (C₂D₂Cl₄, 500 MHz, 100 °C) 7.51–7.61 (m, 8H) 7.70–7.75 (m, 2H), 8.02–8.06 (m, 4H), 8.09–8.14 (m, 2H), 8.14–8.19 (m, 2H), 8.88 (s, 2H), 8.99 (s, 2H), 9.75 (s, 2H);

¹³C NMR could not be obtained due to the poor solubility in common organic solvents.

IR (ATR) 3048, 2190, 1668, 1617, 1590, 1487, 1455, 1390, 1345, 1274, 1247, 1172, 1061, 1026, 900, 752, 686 cm⁻¹;

HRMS (MALDI, DCTB matrix) *m/z* calcd for C₄₆H₂₅O₂ [M+H]⁺: 609.1849; found: 609.1850.

6. Synthesis of Substituted Hexacene 21



To a solution of phenylacetylene (1.32 mL, 12.0 mmol) in THF (50 mL) was added *n*-BuLi (1.57 M in hexane, 6.4 mL, 10 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 10 min, hexacenequinone **19** (558 mg, 0.999 mmol) was added at $-78\text{ }^{\circ}\text{C}$. After gradual warming to room temperature, the mixture was continued to stir for 15 h. The reaction was quenched by an addition of sat. aq. NH_4Cl and the products were extracted with EtOAc ($\times 3$). The combined extracts were washed with brine, and then dried over Na_2SO_4 . After concentration, the crude products were triturated with Et_2O to give diol **20** (576 mg, 76%, single diastereomer) as an orange solid.

Mp $133\text{ }^{\circ}\text{C}$ (dec);

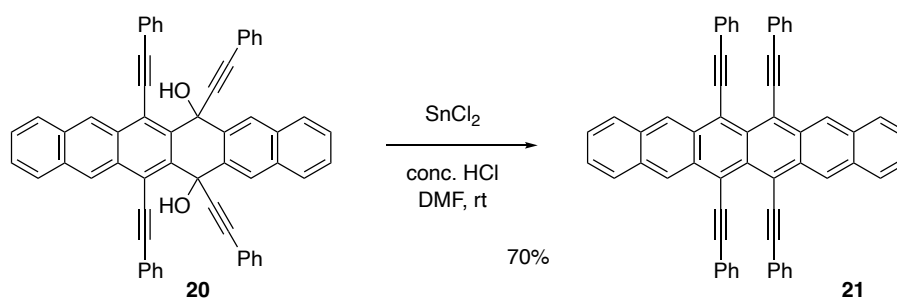
R_f 0.38 (hexane/acetone = 7/3);

^1H NMR (CDCl_3 , 500 MHz) 5.69 (s, 2H), 7.14–7.20 (m, 6H), 7.27–7.29 (m, 4H), 7.48–7.59 (m, 10H), 7.86–7.89 (m, 4H), 8.01–8.04 (m, 2H), 8.14–8.17 (m, 2H), 8.82 (s, 2H), 9.26 (s, 2H);

^{13}C NMR (CDCl_3 , 125 MHz) 67.5, 86.4, 87.3, 94.3, 107.4, 120.6, 122.5, 122.7, 125.9, 126.5, 126.8, 128.0, 128.18, 128.22, 128.6, 128.8, 129.5, 130.8, 131.7, 131.8, 132.1, 132.9, 133.4, 133.7, 138.0;

IR (ATR) 3364, 3053, 2925, 2860, 2193, 1596, 1489, 1442, 998, 888, 746 cm^{-1} ;

HRMS (APCI) m/z calcd for $\text{C}_{58}\text{H}_{35}\text{O}_2$ $[\text{M}+\text{H}]^+$: 763.2632; found: 763.2633.



Note: All operations in this section were conducted against light and oxygen. All solvents for reactions and filtrations were degassed. During reaction, the glassware was shielded with aluminum foils.

A solution of diol **20** (29.8 mg, 39.1 μmol) in DMF (2.0 mL) was degassed by argon bubbling for 5 min. To this mixture was sequentially added SnCl_2 (30.0 mg, 0.158 mmol) and one drop of concentrated HCl at $0\text{ }^{\circ}\text{C}$ and then degassed by argon bubbling for 5 min. After stirring at room temperature for 2 h, the mixture was

diluted with deionized H₂O (20 mL) and stirred for 10 min. The precipitated were collected by filtration and sequentially washed with H₂O, EtOH, ice-cold Et₂O, and pentane to afford hexacene **21** (20.0 mg, 70% yield) as a light green solid.

Mp >300 °C (dec);

¹H NMR (C₂D₂Cl₄, 500 MHz) 7.24–7.33 (m, 12H), 7.43–7.47 (m, 4H), 7.60–7.65 (m, 8H), 8.03–8.07 (m, 4H), 9.38 (s, 4H);

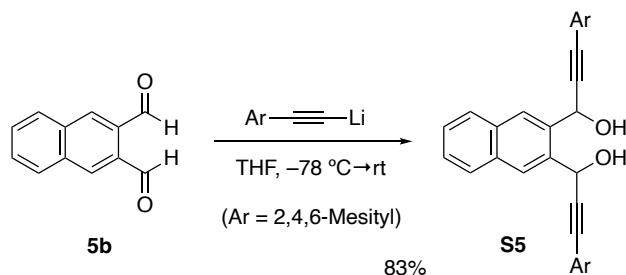
¹³C NMR could not be obtained due to the instability of **21** in solutions.

IR (ATR) 3051, 2922, 2187, 1596, 1490, 1441, 1069, 750, 687 cm⁻¹;

UV–Vis (CHCl₃) λ_{max} nm (log ε) 340 (4.87), 845 (3.90);

HRMS (MALDI, DCTB matrix, AgTFA) *m/z* calcd for C₅₈H₃₂ [M]⁺: 728.2499; found: 728.2481.

7. Synthesis of Substituted Hexacene 22



To a solution of 2-ethynyl-1,3,5-trimethylbenzene (375 mg, 2.60 mmol) in THF was added *n*-BuLi (1.64 M in hexane, 1.46 mL, 2.39 mmol) at 0 °C. After stirring for 20 min, 2,3-naphthalenedicarboxaldehyde (**5b**) (192 mg, 1.04 mmol) was added at -78 °C and the mixture was stirred at room temperature for 12 h. The reaction was then quenched by addition of sat. aq. NH₄Cl at 0 °C. The products were extracted with EtOAc (×3) and the combined extracts were washed with brine and dried over Na₂SO₄. After concentration, the residue was washed with Et₂O to give diol **S5** (405 mg, 83%, dr 77:23) as a white solid.

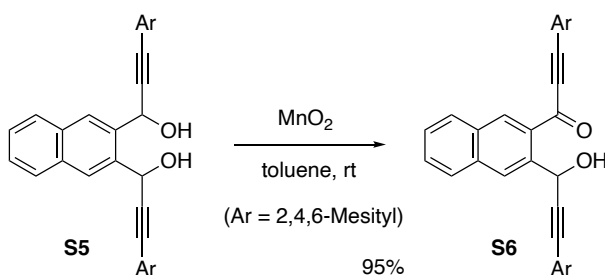
R_f 0.23 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 500 MHz) 2.29 (s, 1.38H), 2.30 (s, 4.62H), 2.45 (s, 2.76H), 2.48 (s, 9.24H), 3.31 (d, 1.54H, *J* = 4.6 Hz), 3.80 (d, 0.46H, *J* = 6.9 Hz), 6.44 (d, 1.54H, *J* = 4.6 Hz), 6.63 (d, 0.46H, *J* = 6.9 Hz), 6.88 (s, 0.92H), 6.90 (s, 3.08H), 7.51–7.55 (m, 2H), 7.84–7.89 (m, 2H), 8.28 (s, 0.46H), 8.52 (s, 1.54H);

¹³C NMR (CDCl₃, 125 MHz) 21.1, 21.2, 21.3, 63.0, 64.8, 85.6, 85.8, 95.0, 95.4, 119.1, 126.9, 127.0, 127.70, 127.74, 127.9, 128.0, 129.0, 133.1, 135.8, 136.0, 138.3, 140.5; *All signals for both diastereomers were listed.*

IR (ATR) 3265, 2916, 2227, 1609, 1434, 1276, 1247, 1174, 851, 749, 598 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₃₄H₃₂NaO₂ [M+Na]⁺: 495.2295; found: 495.2285.



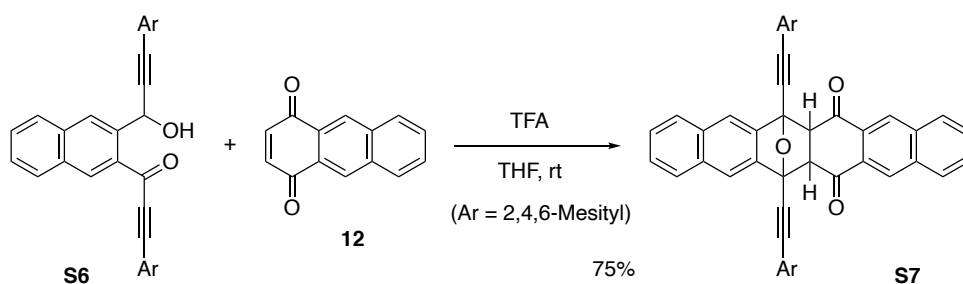
To a solution of diol **S5** (473 mg, 1.00 mmol) in toluene (10 mL) was added MnO₂ (104 mg, 1.20 mmol) portionwise at 0 °C. The mixture was then vigorously stirred at room temperature for 46 h. After filtration through Celite[®] pad (washed with CH₂Cl₂), the solvents were removed *in vacuo* to give ketol **S6** (447 mg, 95%) as a white solid.

Mp 155 °C (dec.);

R_f 0.44 (hexane/EtOAc = 8/2);

¹H NMR (CDCl₃, 500 MHz) 2.25 (s, 3H), 2.34 (s, 3H), 2.42 (s, 6H), 2.57 (s, 6H), 5.39 (d, 1H, *J* = 8.6 Hz),

6.19 (d, 1H, $J = 8.6$ Hz), 6.82 (s, 2H), 6.96 (s, 2H), 7.58–7.62 (m, 1H), 7.65–7.69 (m, 1H), 7.91 (d, 1H, $J = 8.0$ Hz), 7.96 (d, 1H, $J = 8.0$ Hz), 8.29 (s, 1H), 9.07 (s, 1H);
 ^{13}C NMR (CDCl_3 , 125 MHz) 21.1, 21.3, 21.6, 65.0, 84.2, 93.2, 95.9, 96.2, 116.7, 119.5, 127.46, 127.52, 128.1, 128.2, 129.1, 129.2, 129.8, 131.8, 134.0, 135.3, 137.6, 137.7, 137.8, 140.5, 141.4, 143.0, 181.1;
 IR (ATR) 3448, 2912, 2183, 1606, 1459, 1402, 1286, 1187, 1103, 1018, 989, 898, 847, 749, 659, 573 cm^{-1} ;
 HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{30}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 493.2138; found: 493.2144.



To a mixture of ketol **S6** (238 mg, 0.499 mmol) and 1,4-anthraquinone (**12**) (237 mg, 1.14 mmol) in THF (10 mL) was added TFA (182 μL , 2.38 mmol) at 0 $^\circ\text{C}$. After stirring at room temperature for 24 h, the reaction was quenched by addition of sat. aq. NaHCO_3 and the products were extracted with EtOAc ($\times 3$). The combined extracts were washed with brine, and then dried over Na_2SO_4 . The crude products were triturated with hexane/toluene (=1/1) to give cycloadduct **S7** (474 mg, 75%, *endo/exo* = 83/17) as a yellow solid.

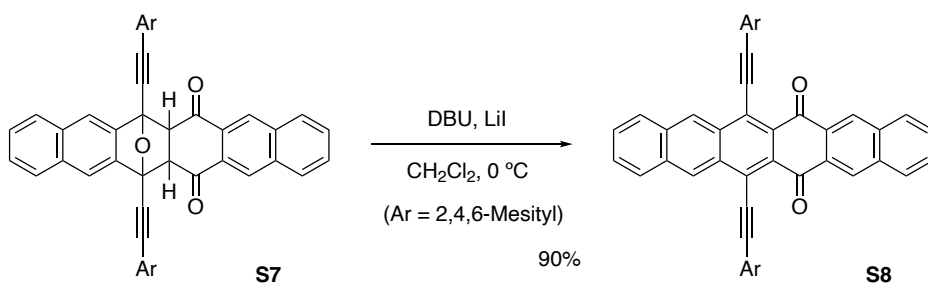
R_f 0.46 (hexane/EtOAc = 8/2);

^1H NMR (CDCl_3 , 500 MHz) 2.32 (s, 1.02H), 2.33 (s, 4.98H), 2.56 (s, 2.04H), 2.64 (s, 9.96H), 3.62 (s, 0.34H), 4.28 (s, 1.66H), 6.93 (s, 0.68H), 6.95 (s, 3.32H), 7.15–7.19 (m, 1.66H), 7.42–7.46 (m, 1.66H), 7.52–7.58 (m, 2H), 7.63 (s, 1.66H), 7.64–7.68 (m, 0.34H), 7.69–7.73 (m, 1.66H), 7.92–7.96 (m, 0.34H), 8.01 (s, 0.34H), 8.02–8.06 (m, 0.34H), 8.17 (s, 1.66H), 8.57 (s, 0.34H);

^{13}C NMR (CDCl_3 , 125 MHz) 21.2, 21.4, 57.4, 59.5, 83.4, 84.4, 87.5, 88.7, 89.6, 91.4, 118.2, 118.4, 118.6, 120.0, 126.3, 126.8, 127.67, 127.71, 128.1, 128.4, 128.5, 128.6, 129.0, 129.3, 129.5, 129.8, 130.2, 132.6, 132.9, 133.2, 134.6, 135.3, 138.8, 139.1, 139.5, 140.0, 141.3, 142.6, 192.0, 193.7; *All signals for both diastereomers were listed.*

IR (ATR) 2917, 2227, 1684, 1669, 1619, 1455, 1396, 1335, 1280, 1246, 1193, 1113, 1045, 986, 913, 876, 846, 773, 691, 578 cm^{-1} ;

HRMS (ESI) m/z calcd for $\text{C}_{48}\text{H}_{36}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 683.2557; found: 683.2568.



To a solution of cycloadduct **S7** (263 mg, 0.398 mmol) in CH_2Cl_2 (10 mL) was sequentially added LiI (107 mg, 0.799 mmol) and DBU (360 μL , 2.41 mmol) at 0 $^\circ\text{C}$. After stirring for 30 min, the reaction was quenched by addition of 2 M HCl and stirred for 30 min. The precipitates were collected by filtration and sequentially washed with H_2O , EtOH, and Et_2O to give hexacenequinone (139.3 mg, 54.4%) as a red solid. The mother liquor was concentrated and the residue was triturated with Et_2O to give quinone **S8** (90.6 mg, 35.4%, 90% combined yield).

Mp 260 $^\circ\text{C}$ (dec.)

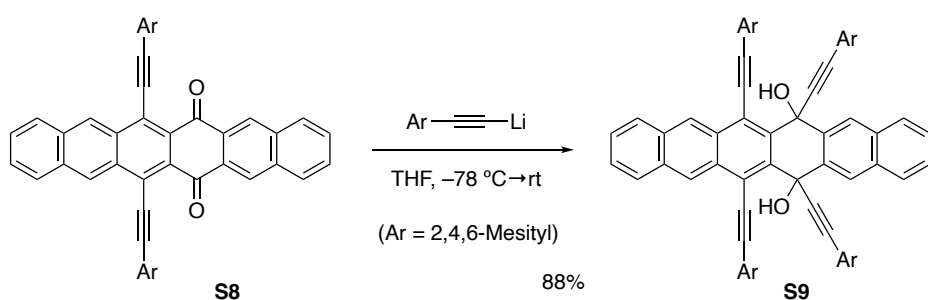
R_f 0.20 (hexane/ $\text{CH}_2\text{Cl}_2 = 1/1$);

^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 500 MHz) 2.38 (s, 6H), 2.86 (s, 12H), 7.05 (s, 4H), 7.61–7.65 (m, 2H), 7.67–7.71 (m, 2H), 8.06–8.10 (m, 2H), 8.11–8.15 (m, 2H), 8.85 (s, 2H), 9.59 (s, 2H);

^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 125 MHz) 21.5, 21.8, 95.7, 103.1, 120.2, 124.1, 127.9, 128.1, 128.5, 128.9, 129.1, 129.2, 129.8, 130.9, 131.2, 131.4, 133.4, 135.0, 139.4, 141.5, 182.1;

IR (ATR) 2913, 2159, 1677, 1621, 1514, 1457, 1394, 1342, 1271, 1184, 1027, 950, 883, 842, 760, 730, 649 cm^{-1} ;

HRMS (MALDI, DCTB matrix) m/z calcd for $\text{C}_{48}\text{H}_{34}\text{O}_2$ $[\text{M}]^+$: 642.2553; found: 642.2567.



To a solution of 2-ethynyl-1,3,5-trimethylbenzene (346 mg, 2.40 mmol) in THF (10 mL) was added *n*-BuLi (1.64 M in hexane, 1.22 mL, 2.00 mmol) at 0 $^\circ\text{C}$. After stirring for 20 min, hexacenequinone **S8** (130 mg, 0.202 mmol) was added at $-78\text{ }^\circ\text{C}$. 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 ($\times 3$). 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 **S9** (178 mg, 88%, dr 70:30) as an orange solid.

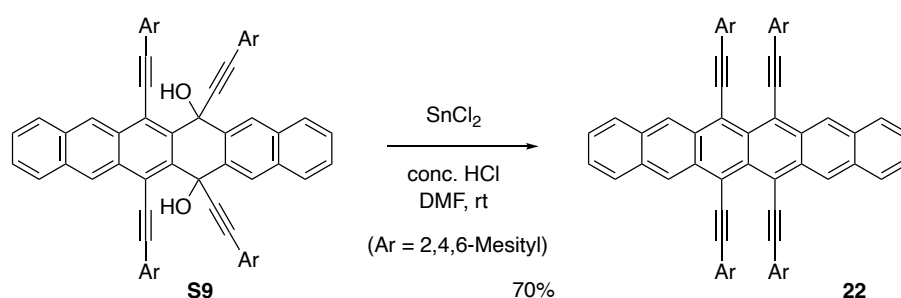
R_f 0.58 (hexane/EtOAc = 4/1);

¹H NMR (CDCl₃, 500 MHz) 1.83 (s, 8.40H), 2.07 (s, 6H), 2.14 (s, 3.60H), 2.37 (s, 6H), 2.73 (s, 8.40H), 2.75 (s, 3.60H), 6.00 (s, 0.60H), 6.44 (s, 2.80H), 6.46 (s, 1.20H), 6.64 (s, 1.40H), 7.00 (s, 4H), 7.45–7.58 (m, 4H), 7.91–8.10 (m, 4H), 8.76 (s, 1.40H), 8.80 (s, 0.60H), 9.40 (s, 1.40H), 9.43 (s, 0.60H);

¹³C NMR (CDCl₃, 125 MHz) 20.3, 20.7, 21.2, 21.5, 21.9, 22.0, 67.2, 68.0, 85.2, 85.9, 94.0, 94.4, 100.2, 102.2, 105.9, 106.6, 119.1, 119.4, 119.47, 119.53, 120.7, 125.85, 125.90, 126.0, 126.2, 126.4, 126.6, 126.9, 127.3, 128.0, 128.21, 128.24, 128.38, 128.42, 131.1, 131.2, 132.6, 132.7, 133.5, 133.6, 134.06, 134.09, 137.4, 137.7, 137.9, 139.0, 139.4, 140.3, 140.5, 140.86, 140.90; *All signals for both diastereomers were listed.*

IR (ATR) 3492, 2915, 2172, 1609, 1478, 1359, 1220, 1172, 1093, 1030, 890, 849, 772, 741, 656 cm⁻¹;

HRMS (ESI) *m/z* calcd for C₇₀H₅₈NaO₂ [M+Na]⁺: 953.4329; found: 953.4324.



Note: All operations in this section were conducted against light and oxygen. All solvents for reactions and filtrations were degassed. During reaction, the glassware was shielded with aluminum foils.

A solution of diol **S9** (40.9 mg, 43.9 μmol) in DMF (2.5 mL) was degassed by argon bubbling for 5 min. To this mixture was sequentially added SnCl₂ (38 mg, 0.20 mmol) and one drop of concentrated HCl at 0 °C and then degassed by argon bubbling for 5 min. After stirring at room temperature for 2 h, the mixture was diluted with deionized H₂O (20 mL) and stirred for 10 min. The precipitated were collected by filtration and sequentially washed with H₂O, EtOH, ice-cold Et₂O, and pentane to afford hexacene **22** (27.5 mg, 70% yield) as a dark brown solid. Single crystals of **22** suitable for X-ray crystallographic analysis were obtained by recrystallization from a solution of CHCl₃ diffused with MeOH.

Mp >300 °C (dec.);

¹H NMR (C₂D₂Cl₄, 500 MHz) 2.23 (s, 12H), 2.58 (s, 24H), 6.73 (s, 8H), 7.38–7.42 (m, 4H), 7.92–7.96 (m, 4H), 9.44 (s, 4H);

¹³C NMR (C₂D₂Cl₄, 125 MHz) 21.3, 21.4, 97.6, 108.7, 118.5, 120.8, 126.4, 126.6, 127.4, 128.5, 129.8, 131.4, 132.7, 137.9, 139.8;

IR (ATR) 2912, 2164, 1608, 1479, 1394, 1373, 1298, 1270, 1184, 1135, 1032, 948, 873, 853, 738, 657 cm⁻¹;

UV–Vis (CHCl₃) λ_{max} nm (log ε) 342 (5.11), 853 (4.18);

HRMS (MALDI, DCTB matrix) *m/z* calcd for C₇₀H₅₆ [M]⁺: 896.4377; found: 896.4388.

8. X-ray Crystallographic Data

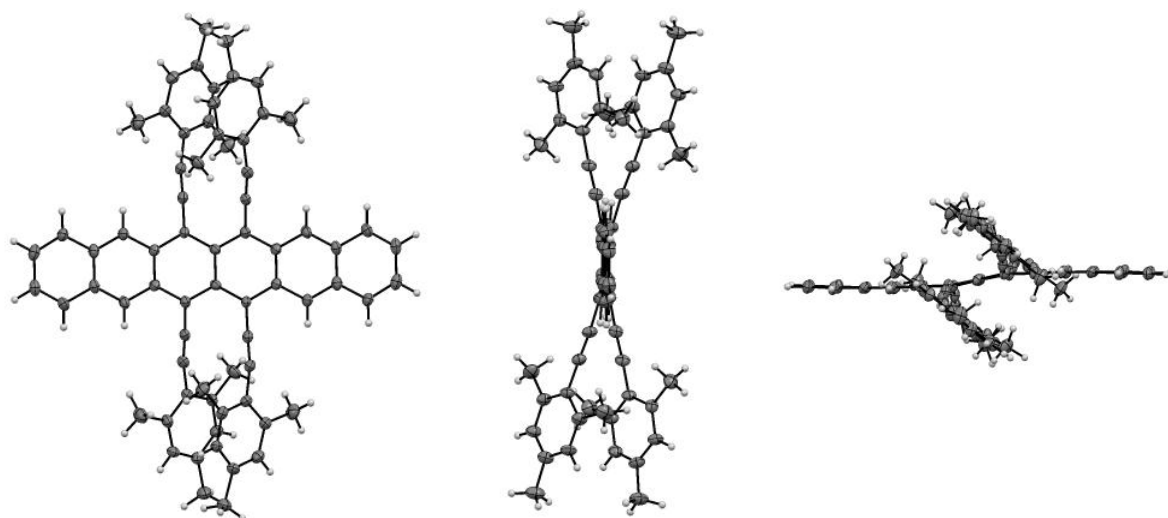


Figure S1. ORTEP drawings of hexacene **22** at the 50% probability level (CCDC 1991642).

$C_{70}H_{56}$, MW = 897.14, $0.180 \times 0.028 \times 0.028$ mm, Monoclinic, space group $P 2_1/n$, $Z = 2$, $T = 93(2)$ K, $a = 8.80384(16)\text{\AA}$, $b = 9.18711(17)\text{\AA}$, $c = 30.3074(6)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 96.5951(10)^\circ$, $\gamma = 90^\circ$, $V = 2435.10(8)\text{\AA}^3$, $\lambda(\text{Cu K}\alpha) = 1.54186\text{\AA}$, $\mu = 0.520\text{ mm}^{-1}$. Intensity data were collected on a Rigaku R-Axis RAPID II. The structure was solved by direct methods (*SHELXT 2014/4*) and refined by the full-matrix least-squares on F^2 (*SHELXL-2018/1*). A total of 52552 reflections were measured and 52552 were independent. Final $R_1 = 0.0887$, $wR_2 = 0.2264$ (24533 refs; $I > 2\sigma(I)$), and GOF = 0.994 (for all data, $R_1 = 0.1527$, $wR_2 = 0.2787$).

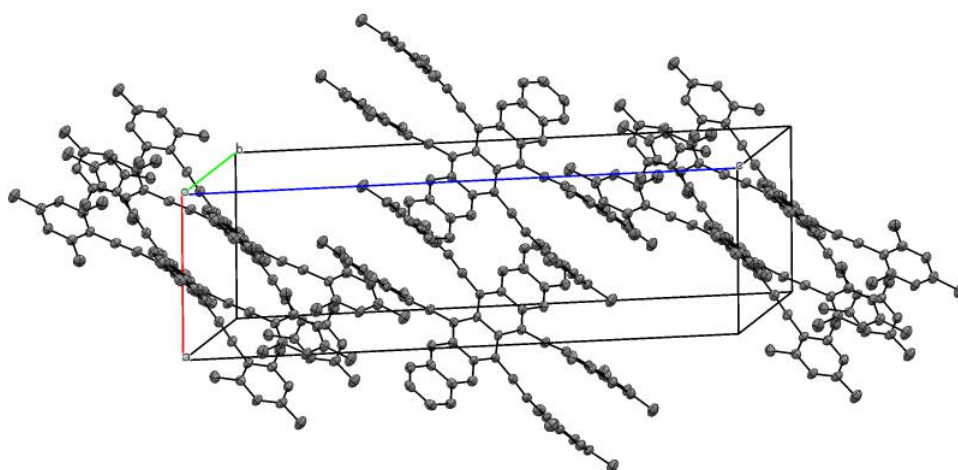


Figure S2. Packing structure of hexacene **22** at the 50% probability level (CCDC 1991642, all hydrogen atoms are omitted for clarity).

9. UV-Vis-NIR Absorption Spectra

The spectra were recorded in degassed spectrochemical-grade chloroform (2×10^{-5} M) using quartz cells with 1 cm path length. The solutions of hexacenes **21** and **22** were prepared in the dark and the initial spectrum were obtained. The solution was then exposed to room light and the spectra were acquired at several intervals.

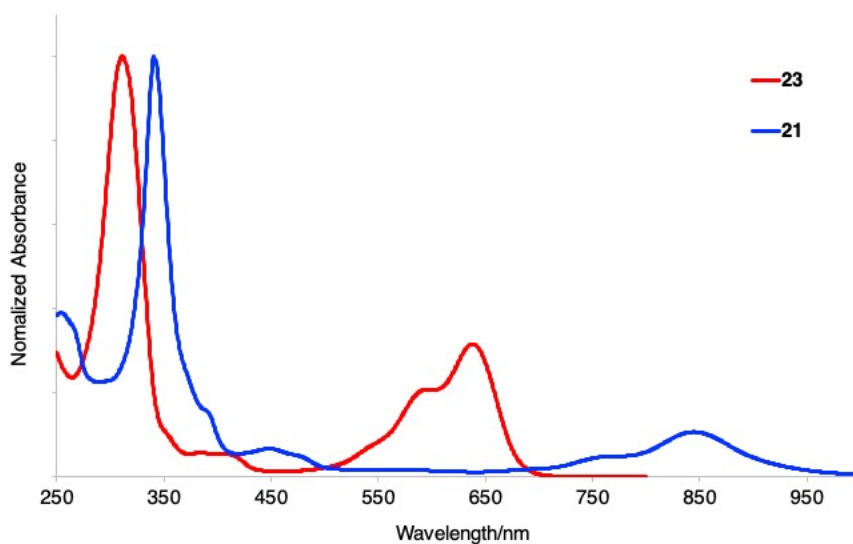


Figure S3. UV-vis-NIR absorption spectra of tetracene **23** and hexacene **21** in CHCl_3 (2×10^{-5} M).

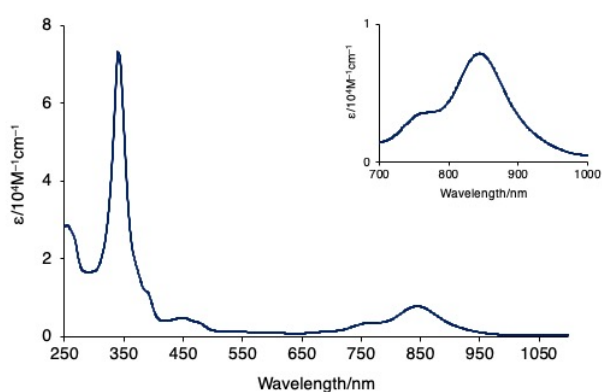


Figure S4. Absorption spectrum of hexacene **21**.

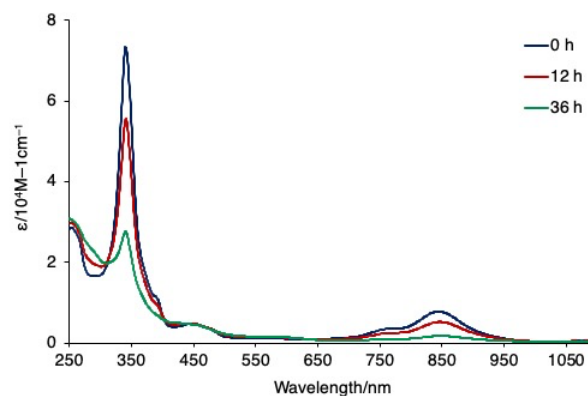


Figure S5. Absorption spectra of hexacene **21**.

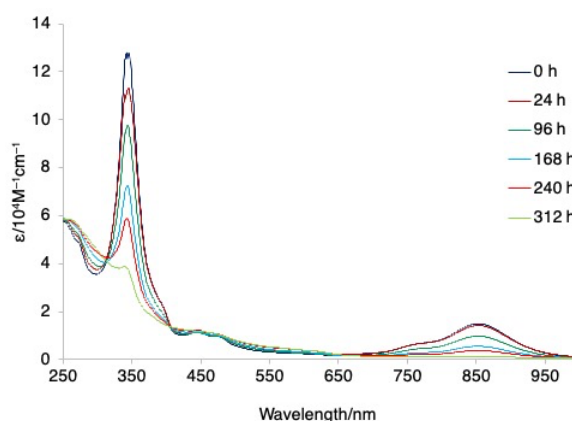
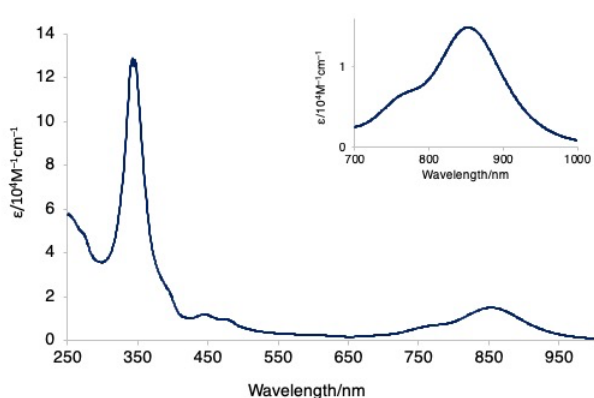
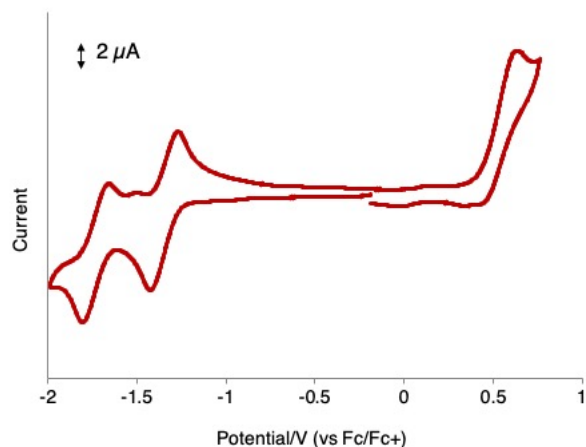
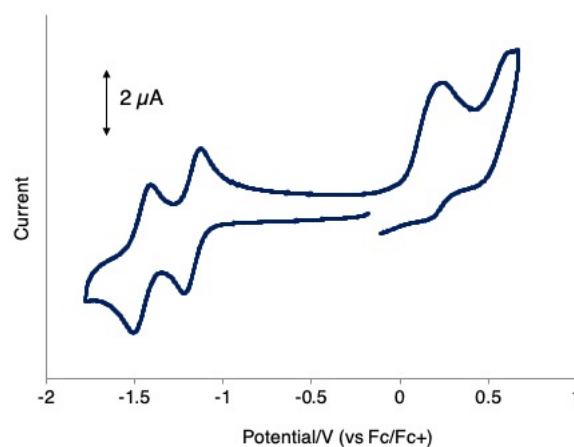


Figure S6. Absorption spectrum of hexacene **22**.**Figure S7.** Absorption spectra of hexacene **22**.

10. Cyclic Voltammograms

The measurements were carried out in degassed THF (1.0 mM) with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte at room temperature. A glassy carbon was used as working electrode, platinum wire was used as counter electrode, and Ag/AgNO₃ was used as reference electrode. The scan rate is 100 mV/s. The potential was calibrated against the ferrocene/ferrocenium couple (Fc/Fc⁺).

**Figure S8.** Cyclic voltammograms of **23** (red).**Figure S9.** Cyclic voltammograms of **22** (blue).**Table S1.** Electrochemically derived HOMO and LUMO energy

compound	E_1^{red} (V)	E_2^{red} (V)	E^{ox} (V)	E_g^{elect} (V)	E_g^{opt} (V) ^[1]	HOMO (eV) ^[2]	LUMO (eV) ^[3]
23	-1.33	-1.37	+0.60	1.93	1.81	-5.40	-3.47
22	-1.18	-1.46	+0.21	1.39	1.31	-5.01	-3.62

[1] Estimated from the onset of the UV/Vis absorption spectrum by using $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$. [2] $E_{\text{HOMO}} = -(4.8 + E^{\text{ox}})$ eV. [3] $E_{\text{LUMO}} = -(4.8 + E_1^{\text{red}})$ eV.

11. Time-course ^1H NMR Analysis

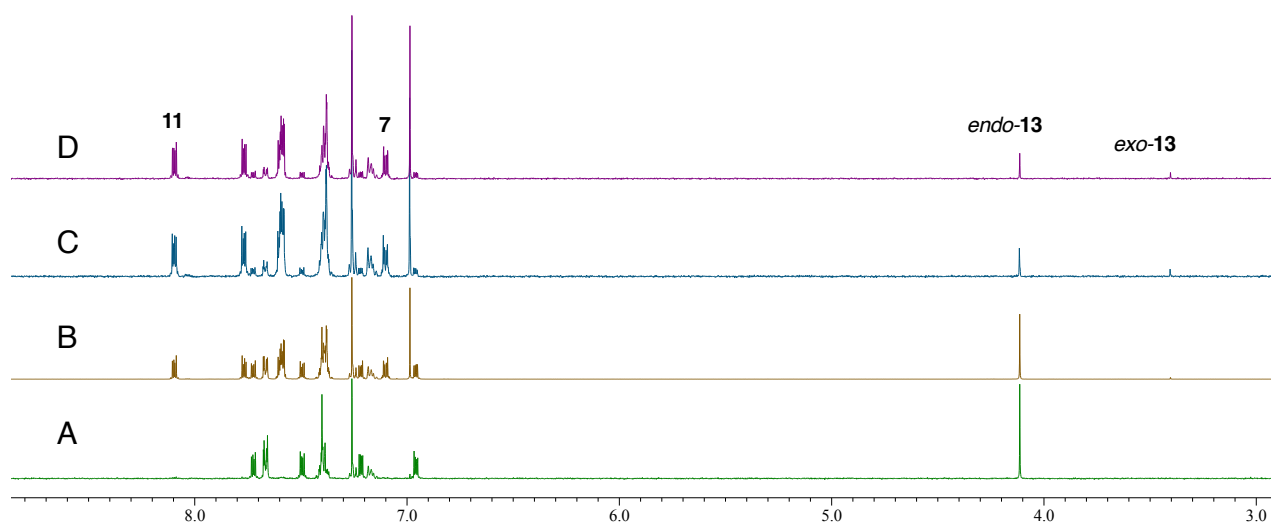


Figure S10. Cycloreversion of cycloadduct **13-endo** monitored by ^1H NMR at room temperature (A: 5 min, B: 2 h, C: 7 h, D: 15 h).

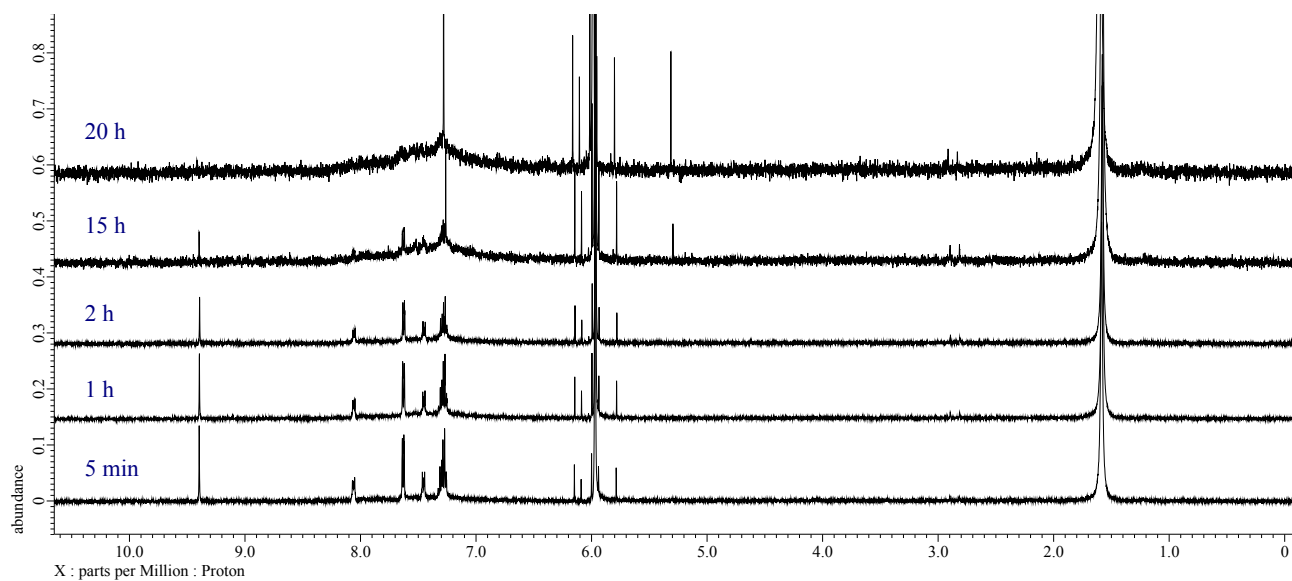


Figure S11. Stability study of hexacene **21** monitored by ^1H NMR in CDCl_3 under ambient conditions.

12. HRMS Spectra of Hexacenes

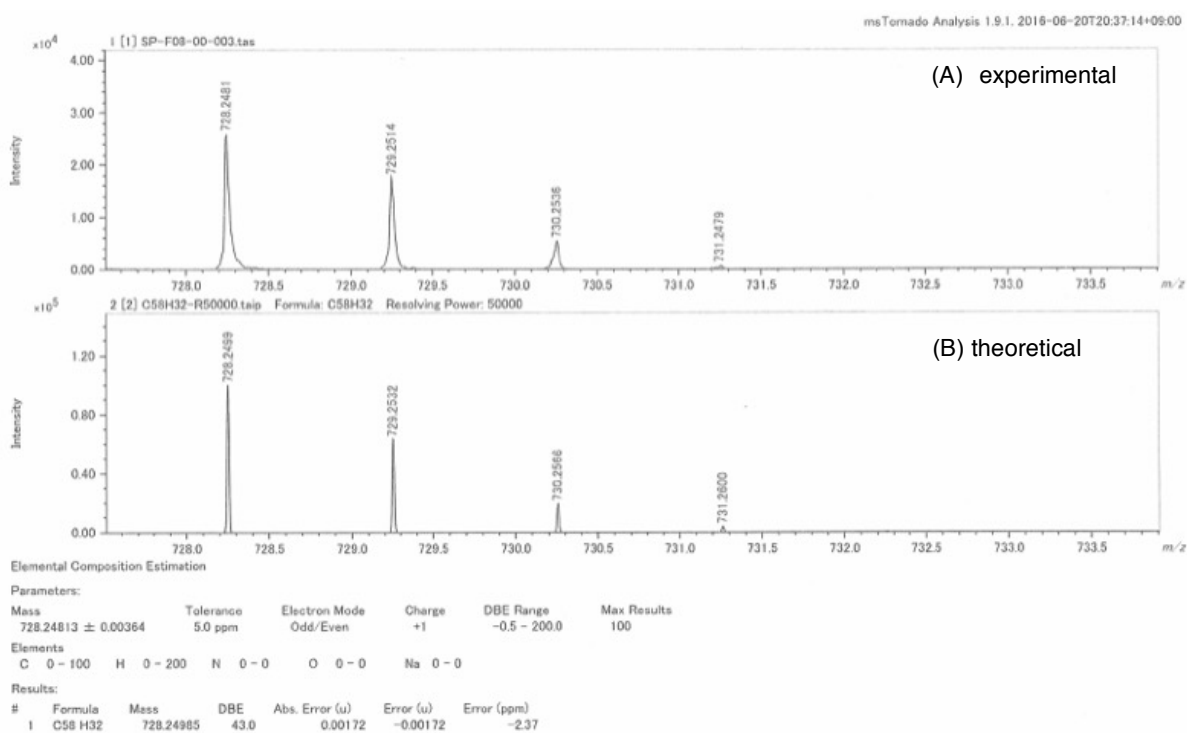


Figure S12. MALDI-TOF HRMS spectra of hexacene 21.

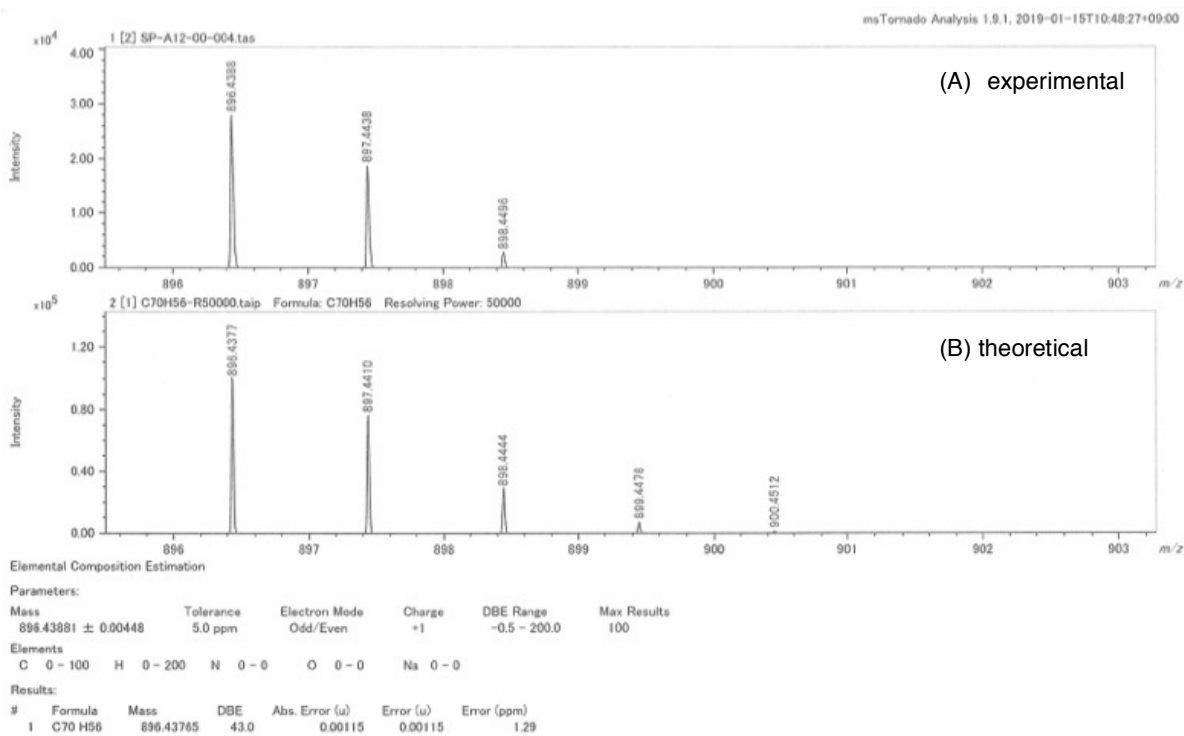
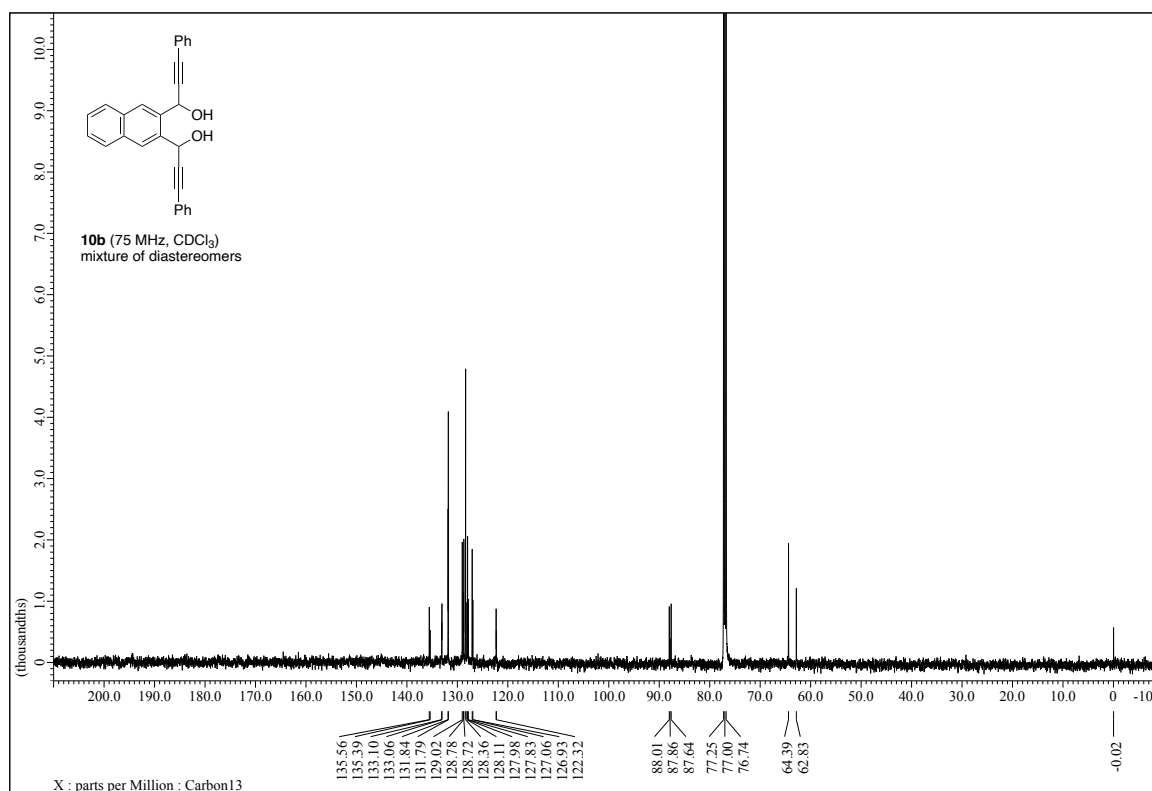
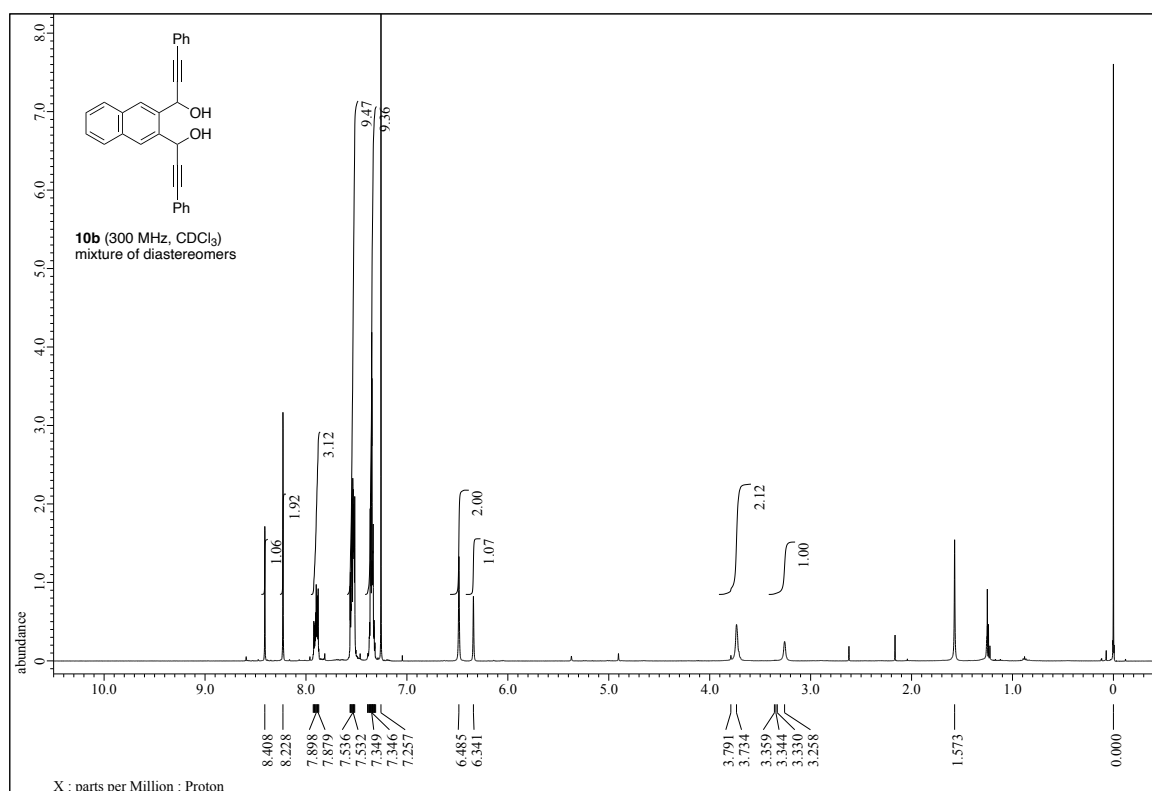
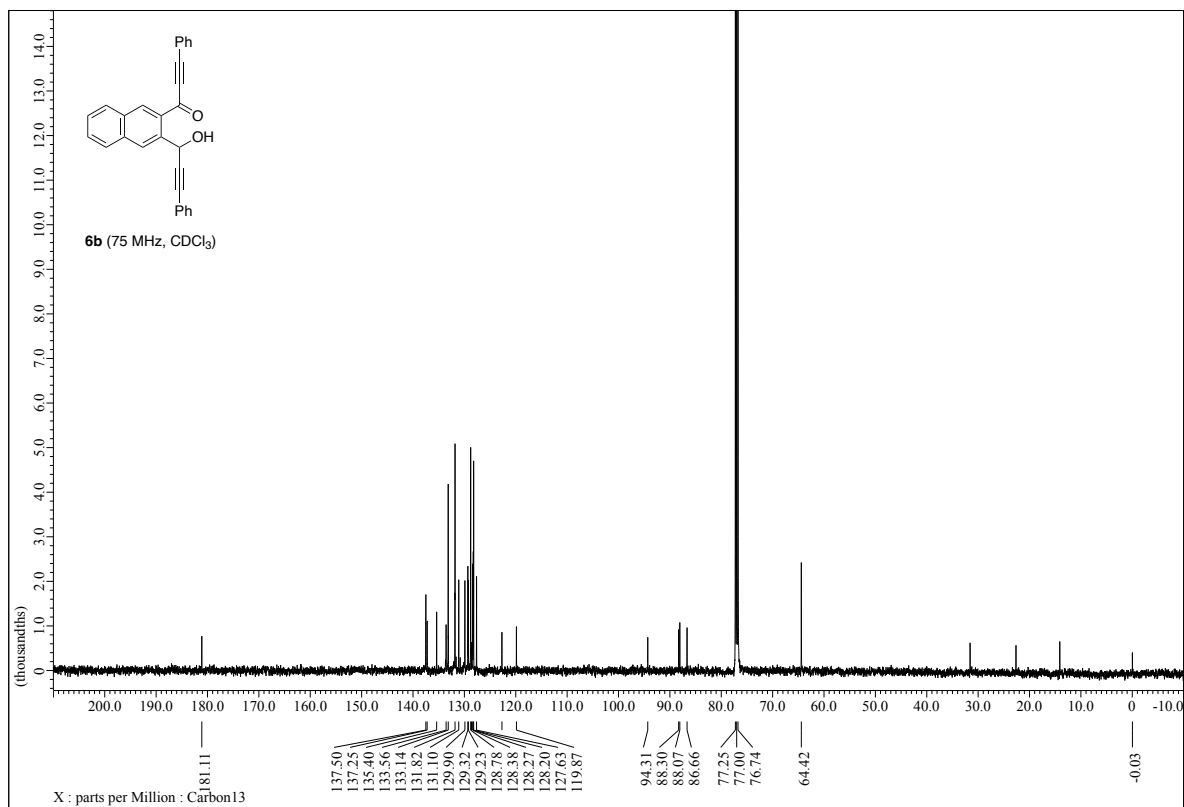
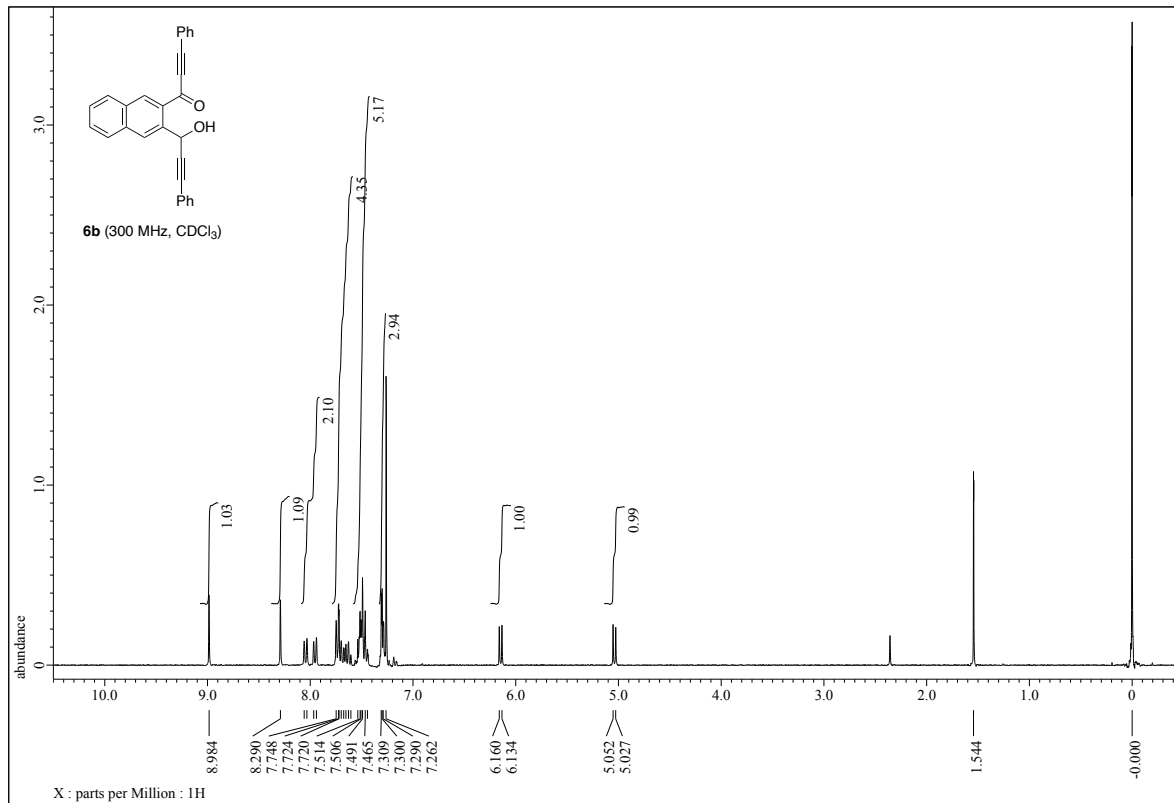
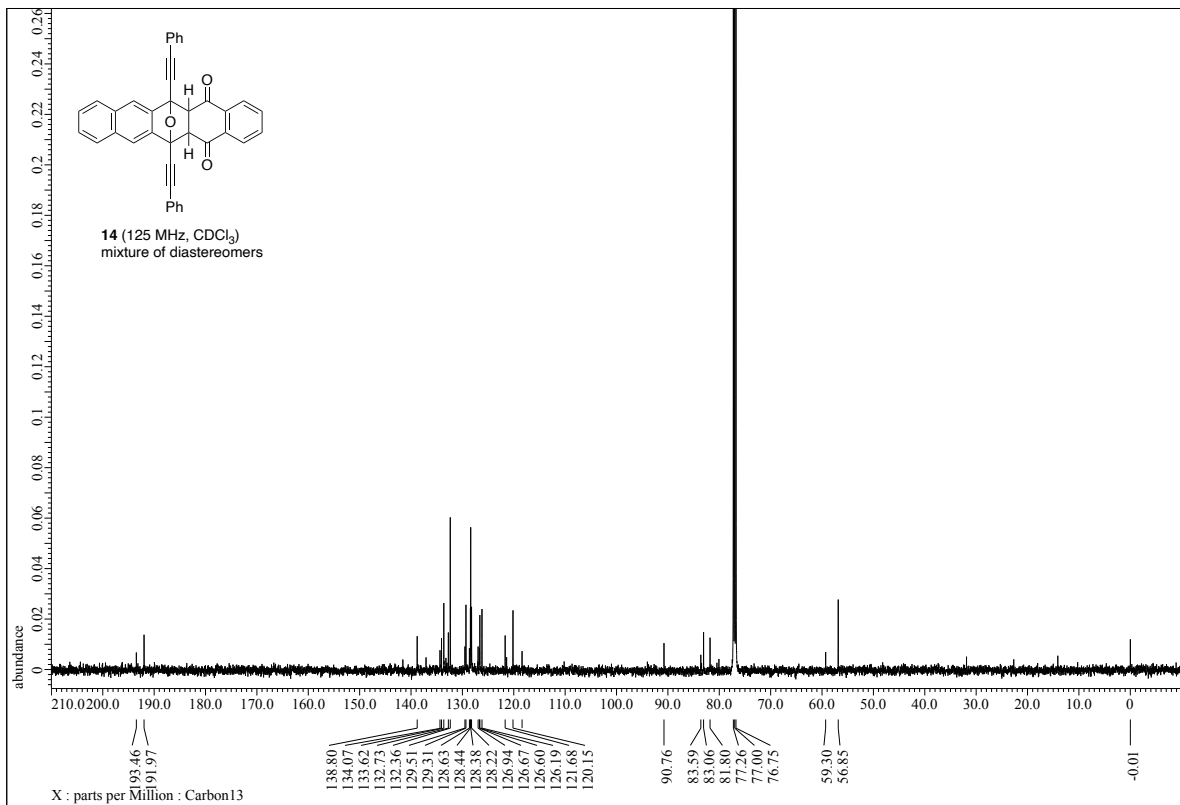
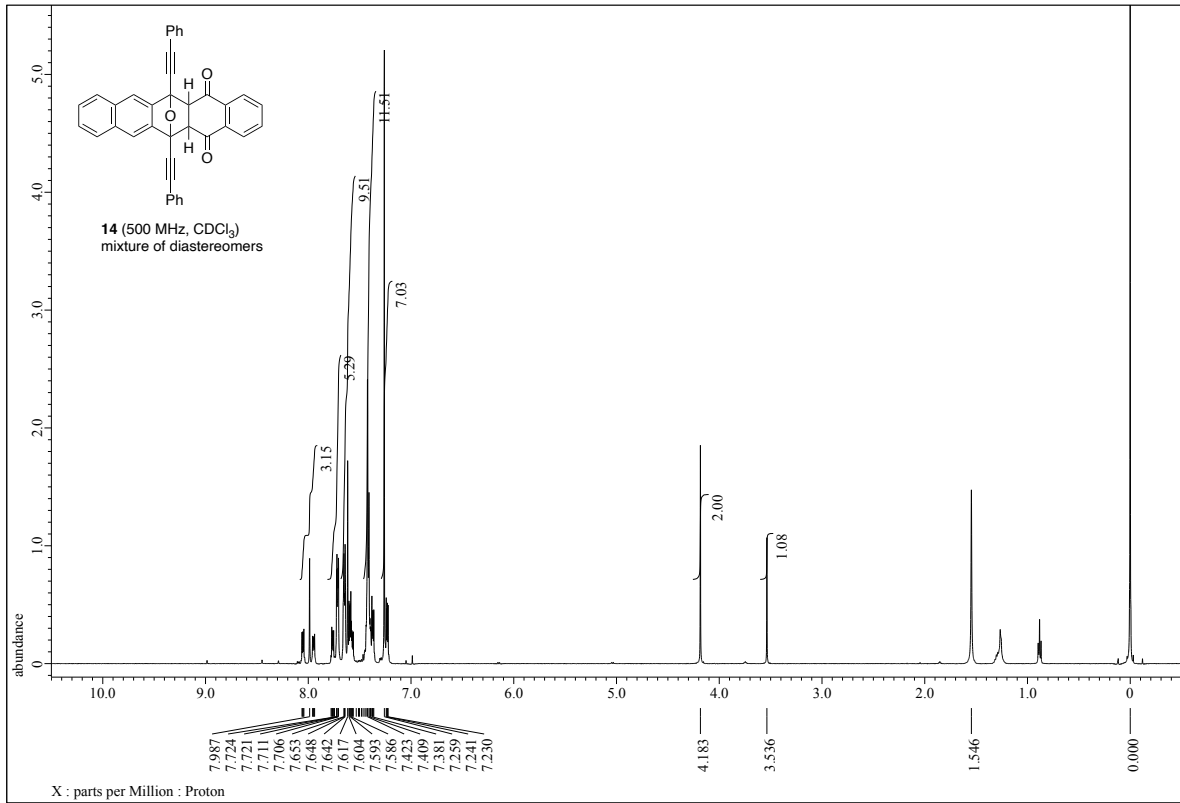


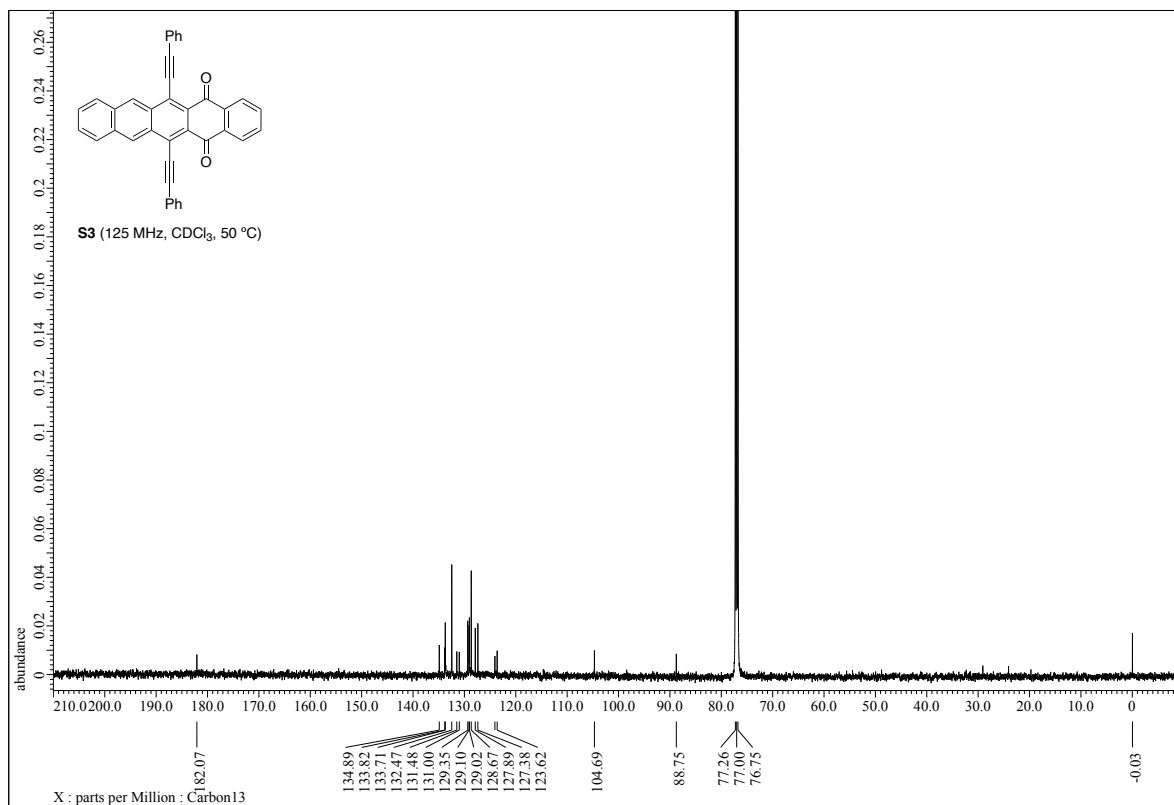
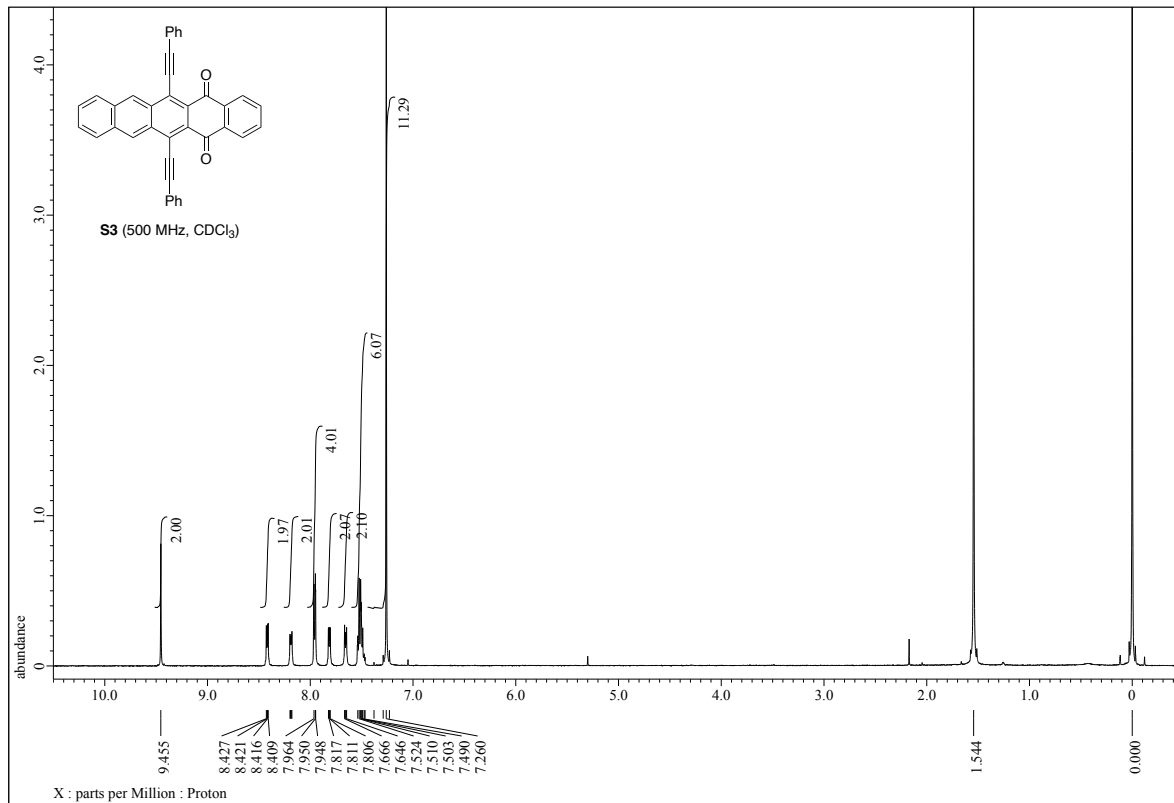
Figure S13. MALDI-TOF HRMS spectra of hexacene 22.

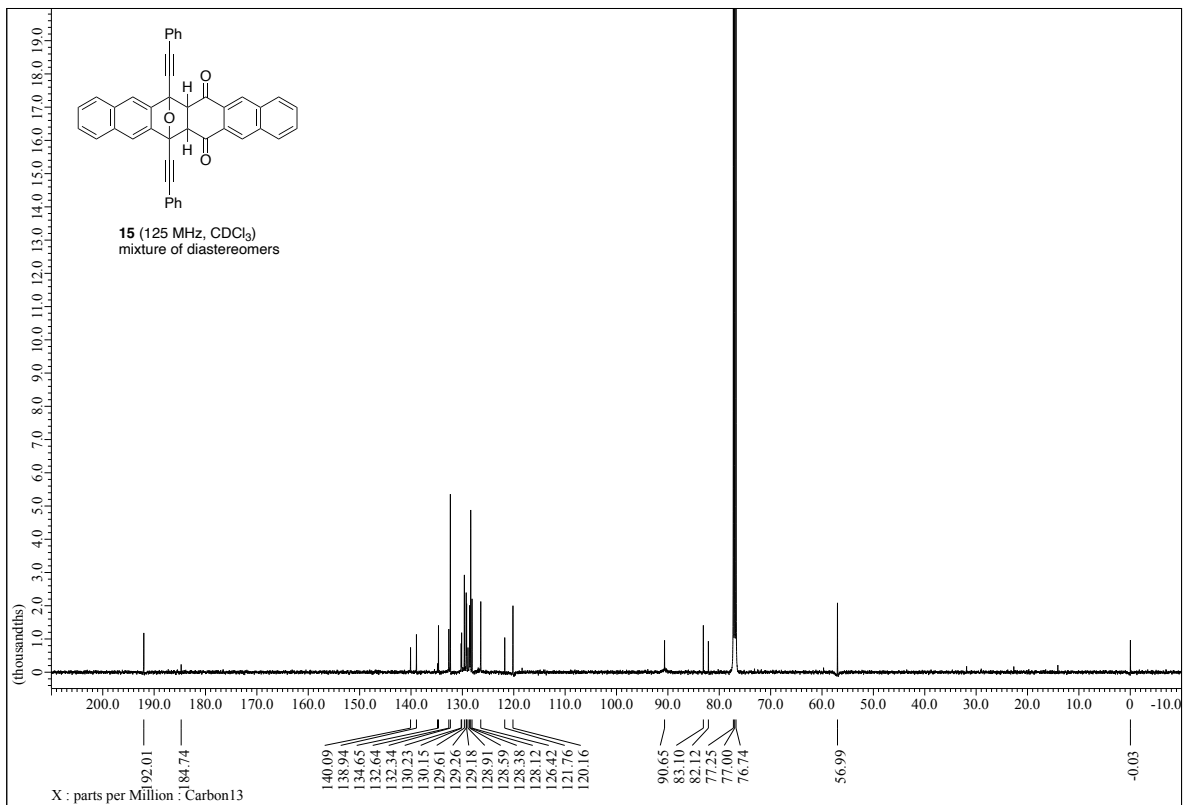
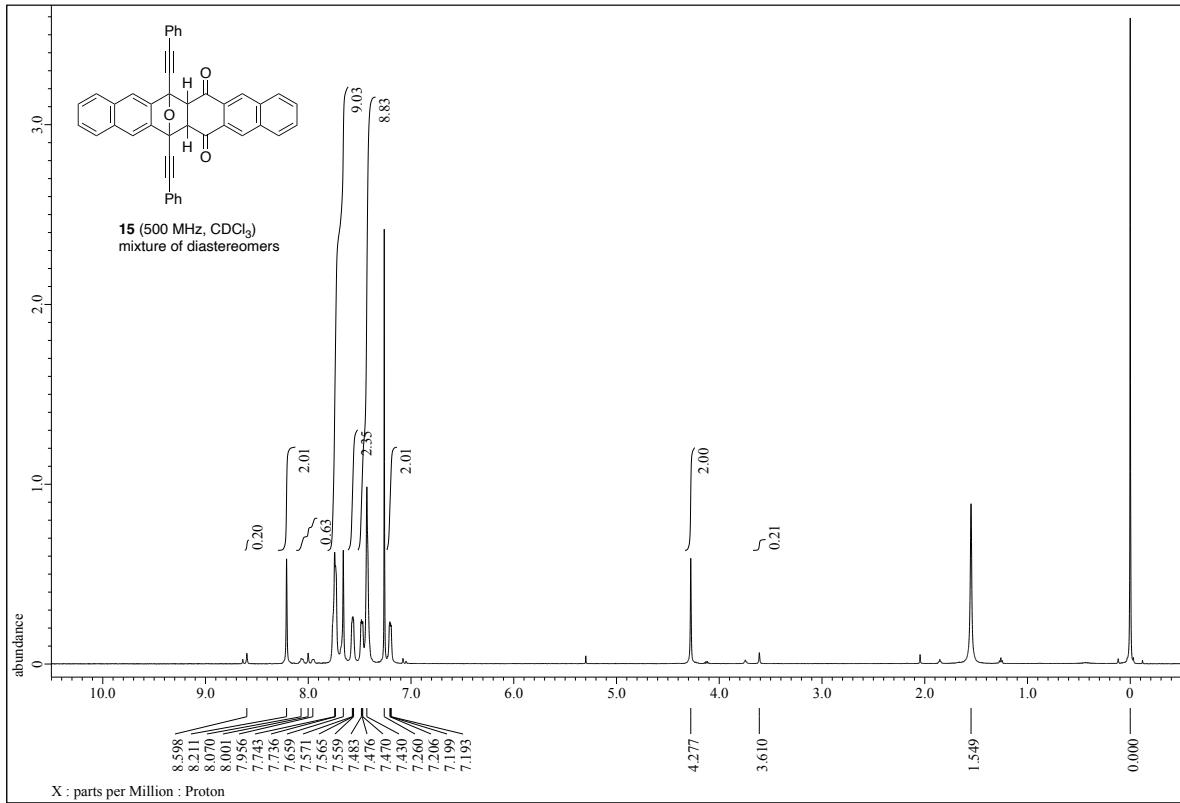
13. ¹H and ¹³C NMR spectra

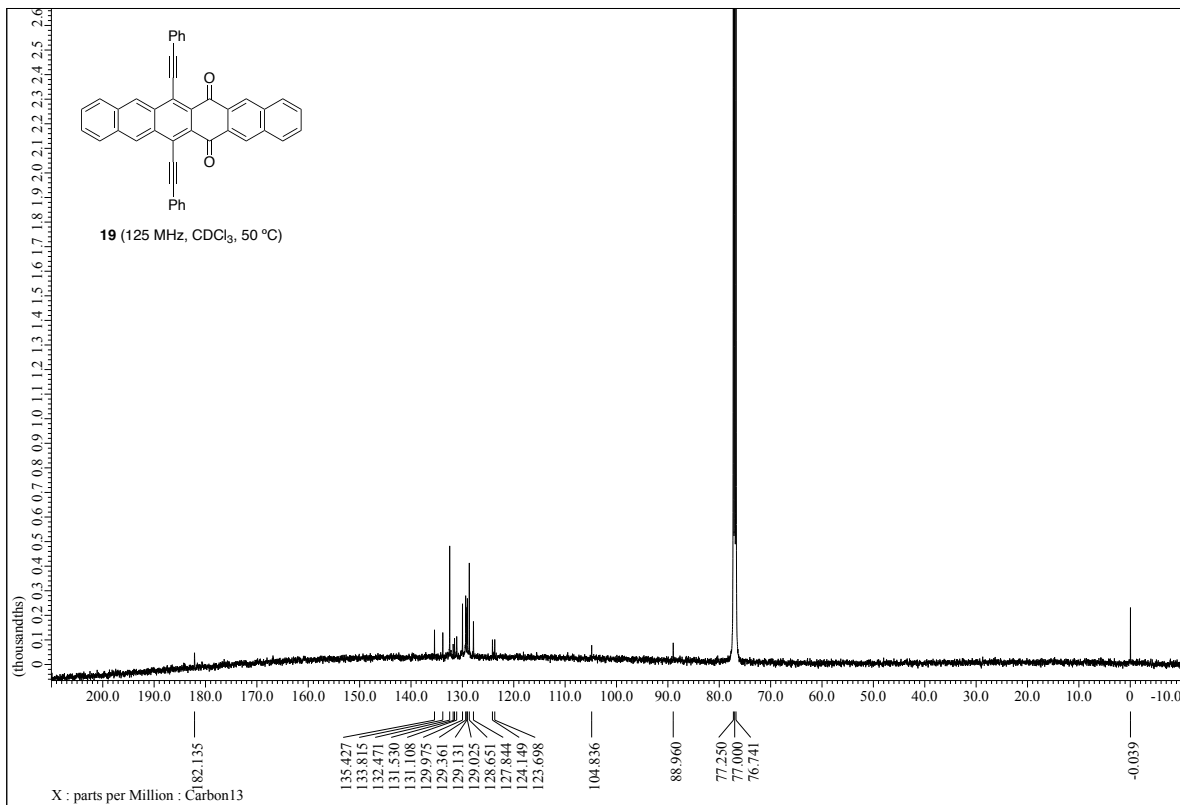
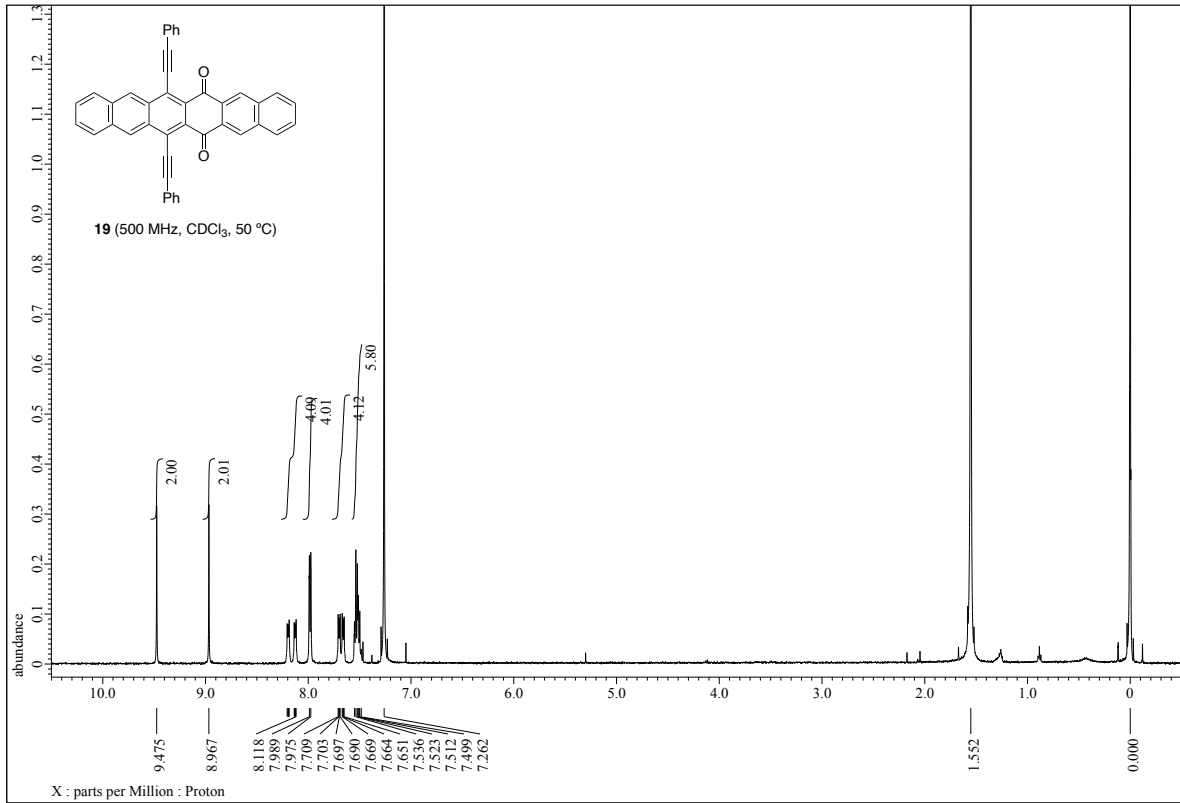


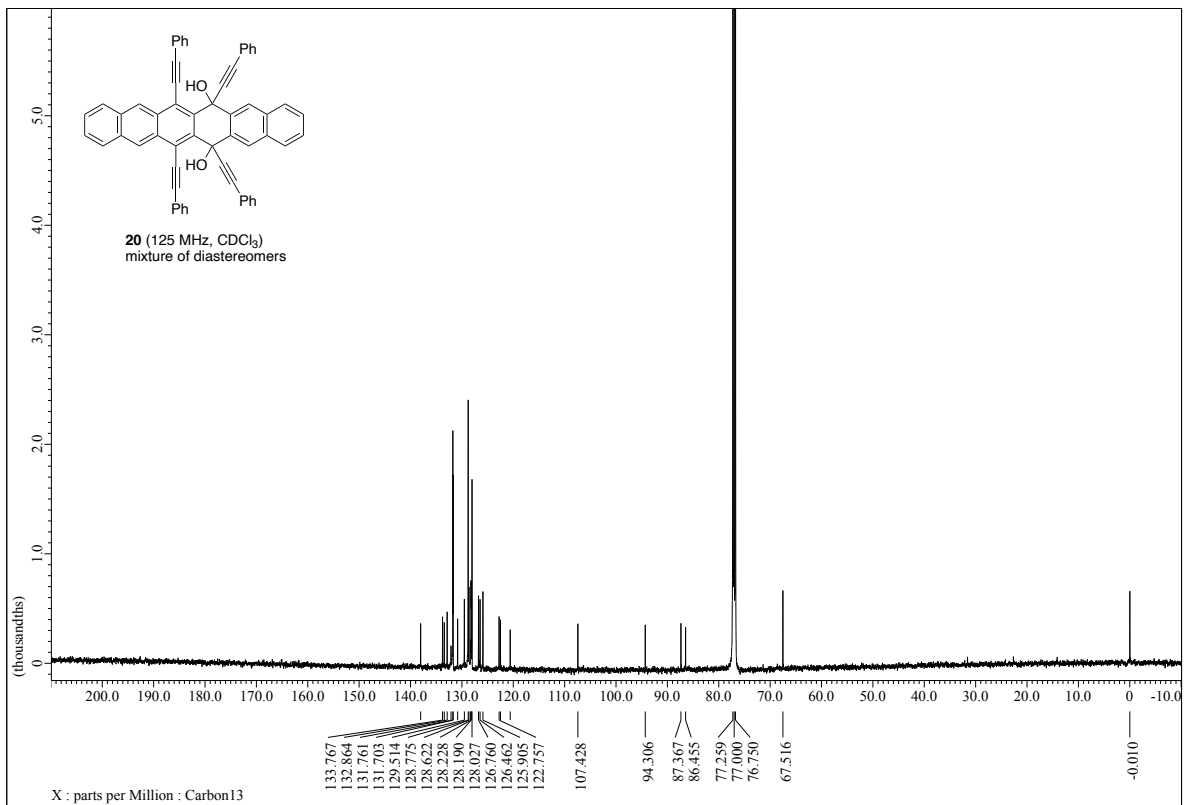
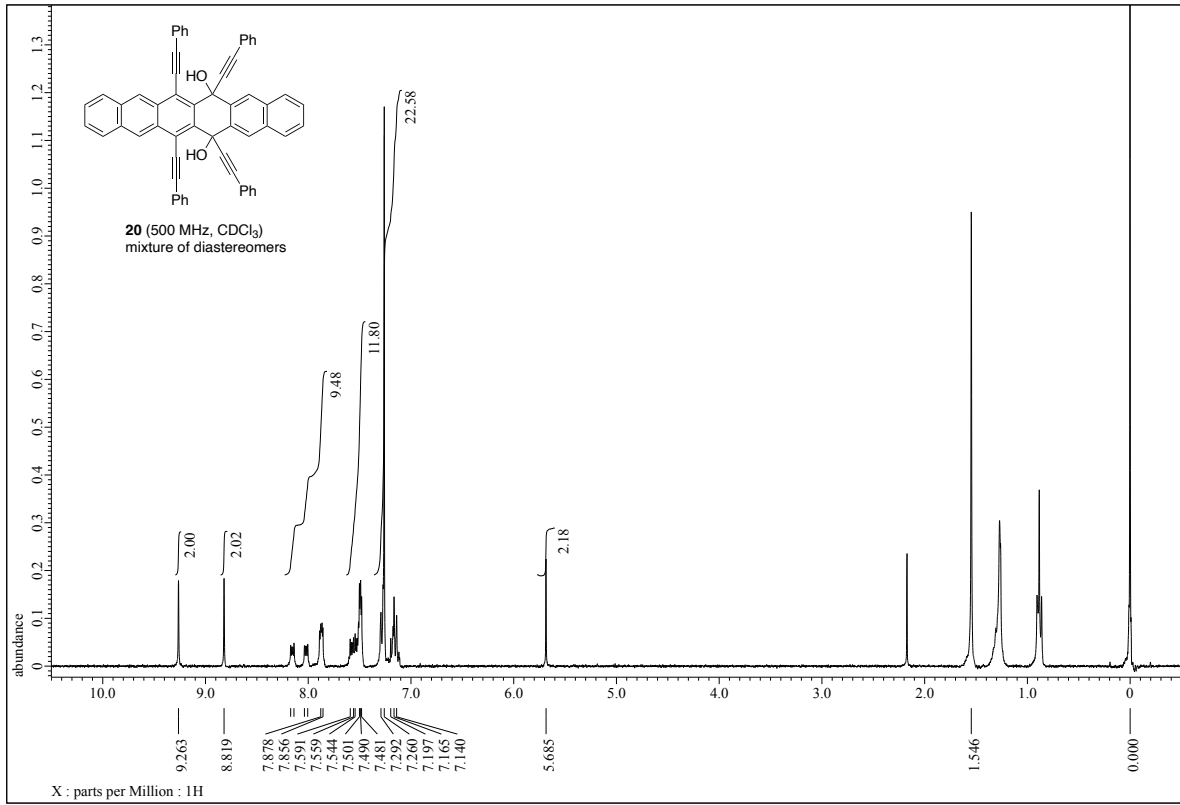


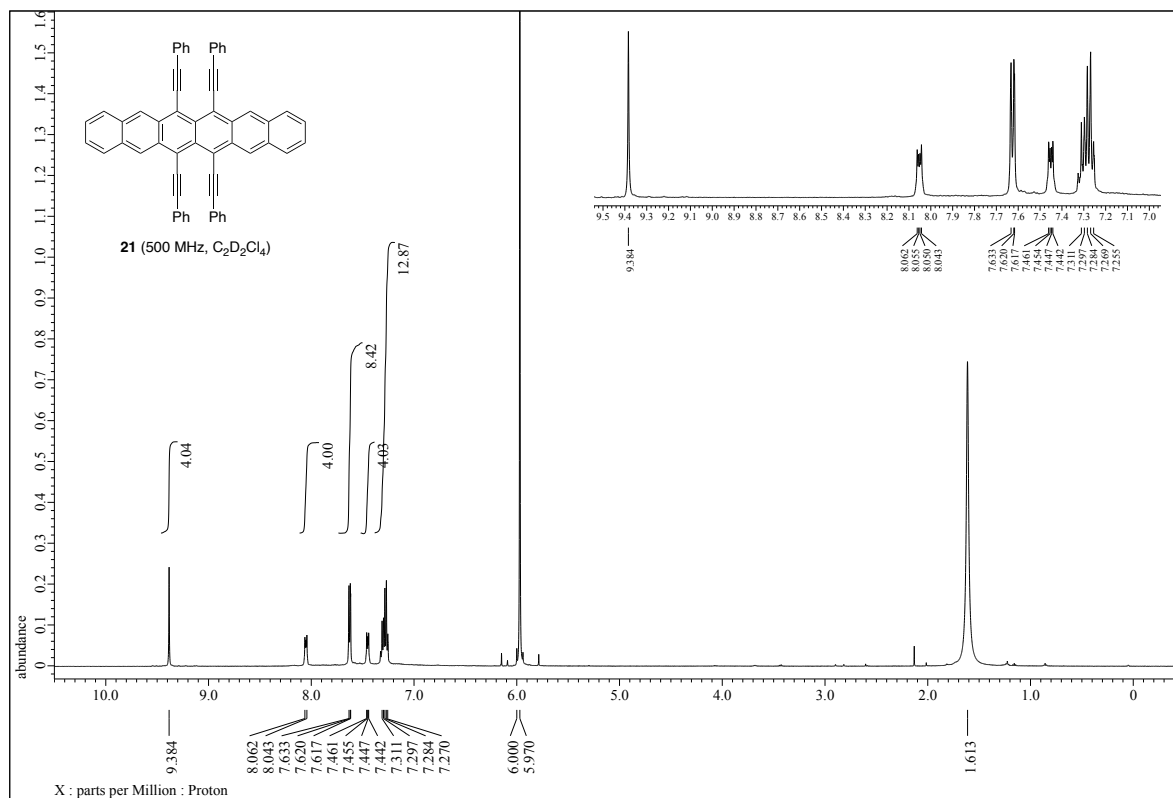


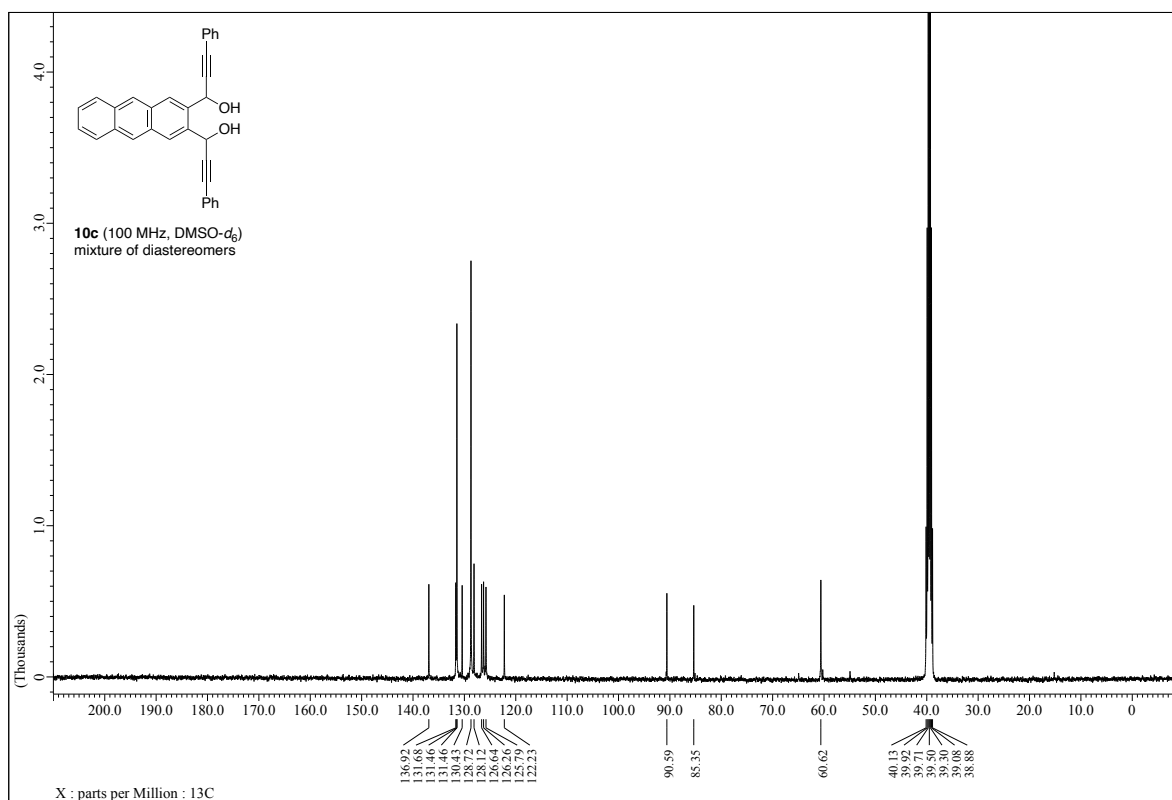
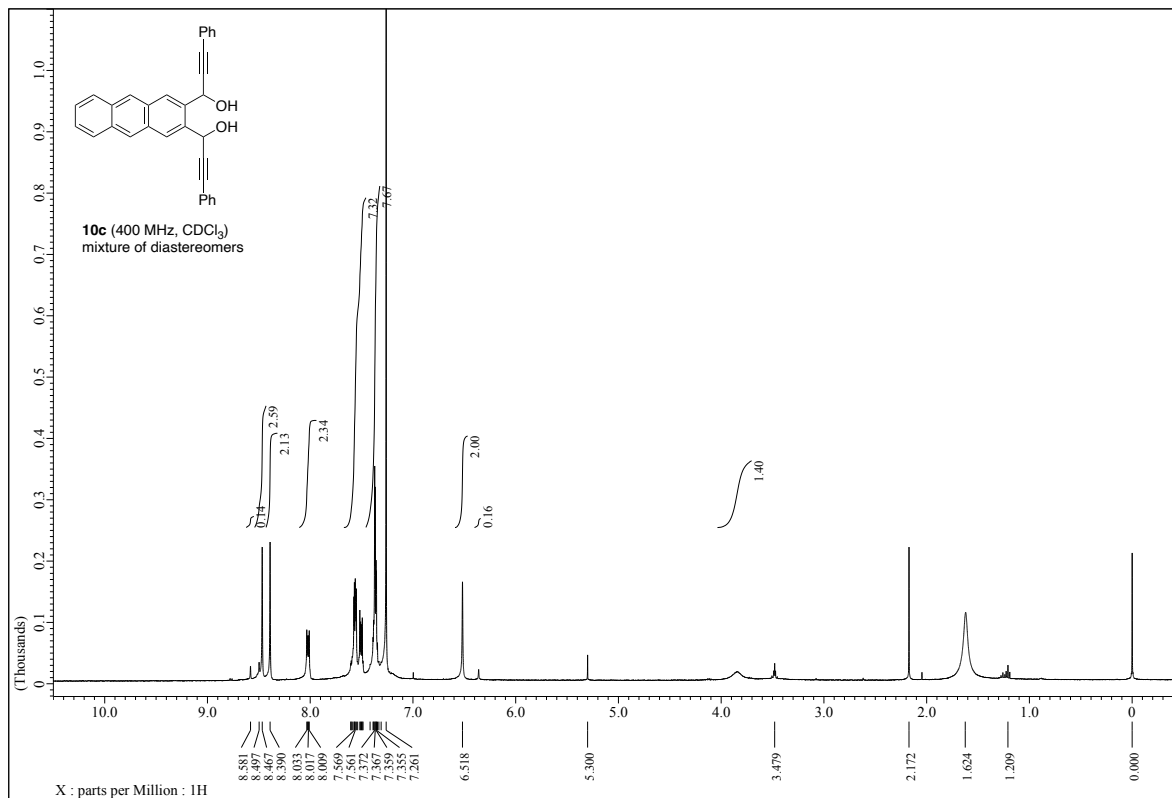


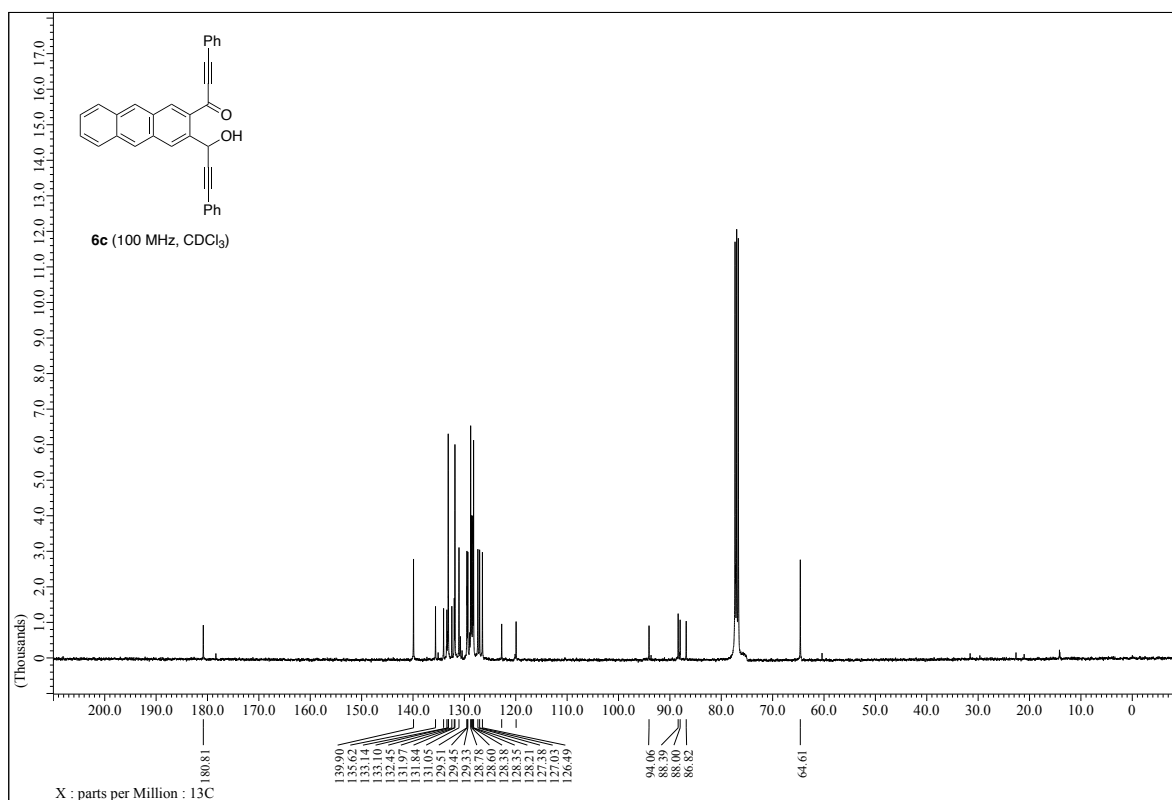
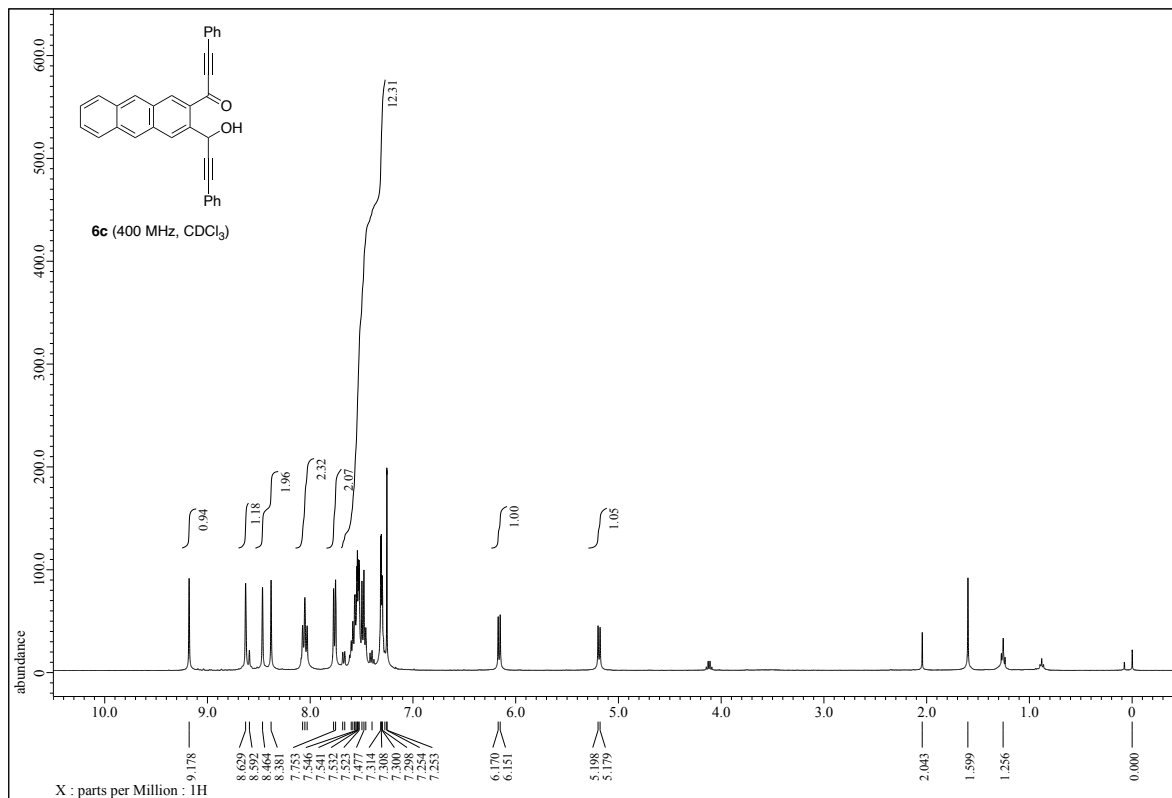


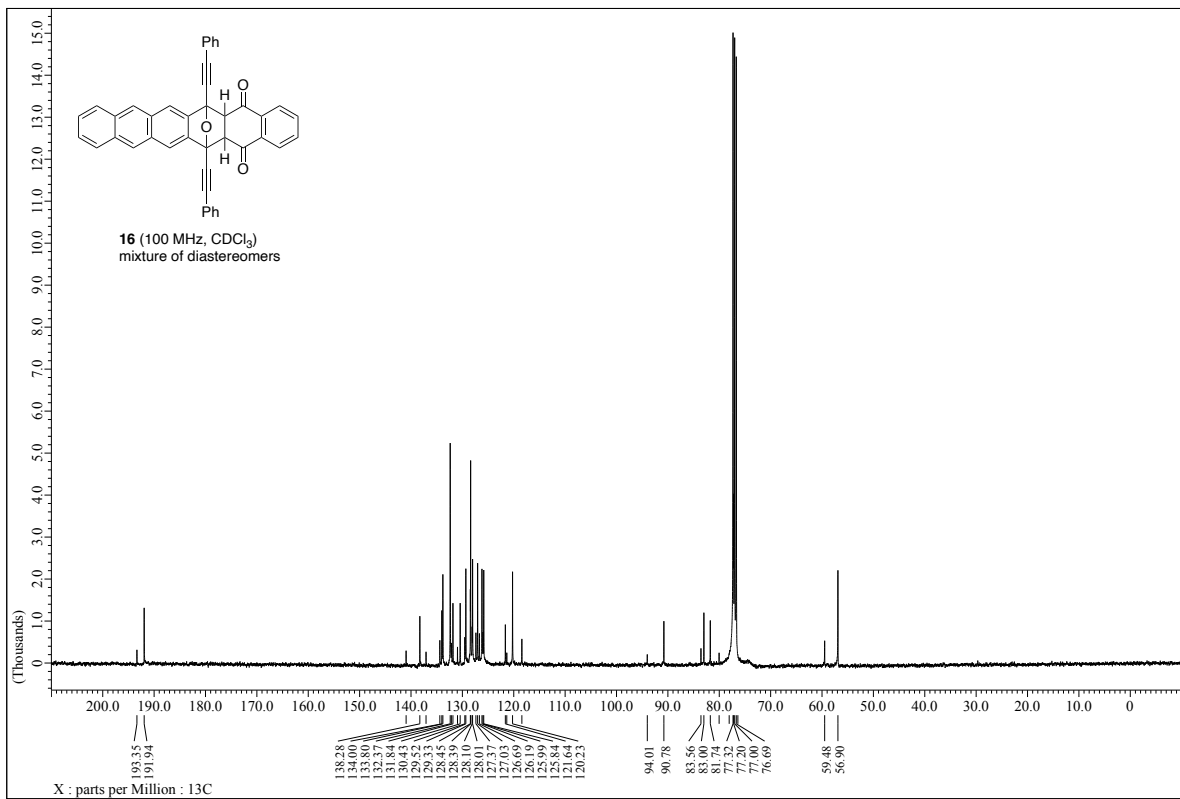
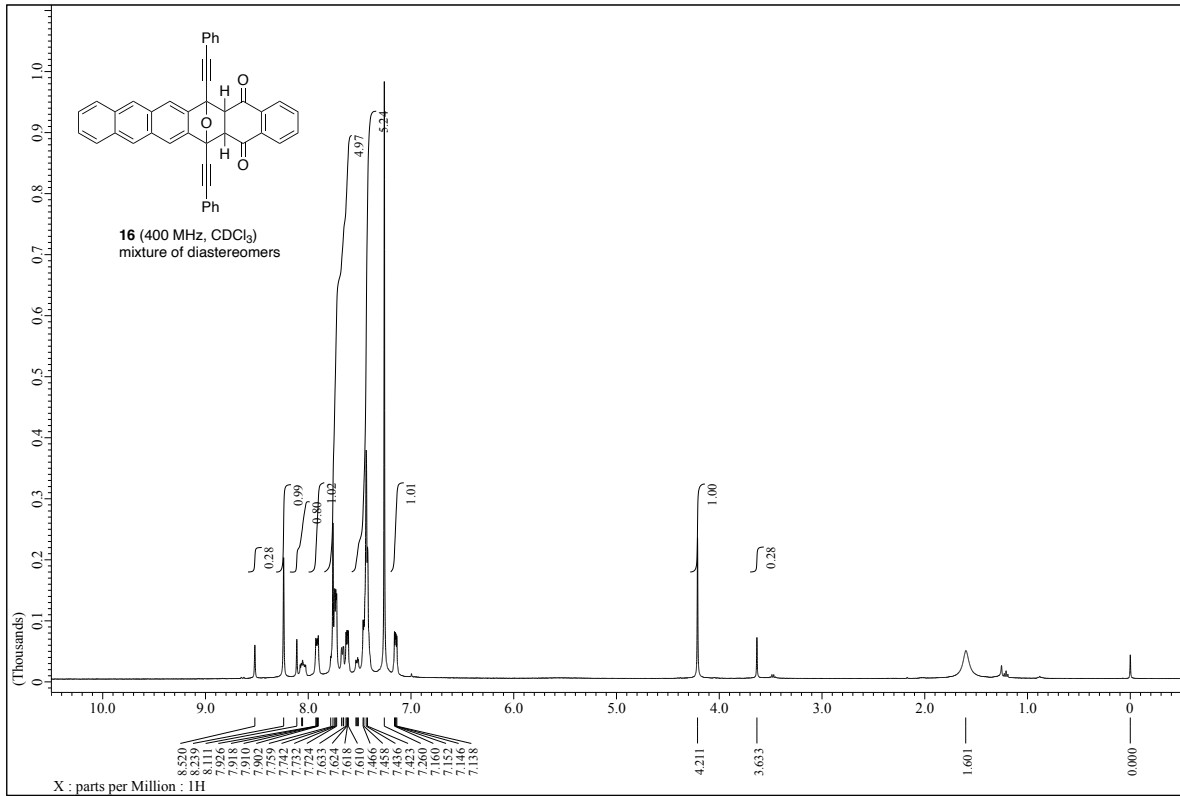


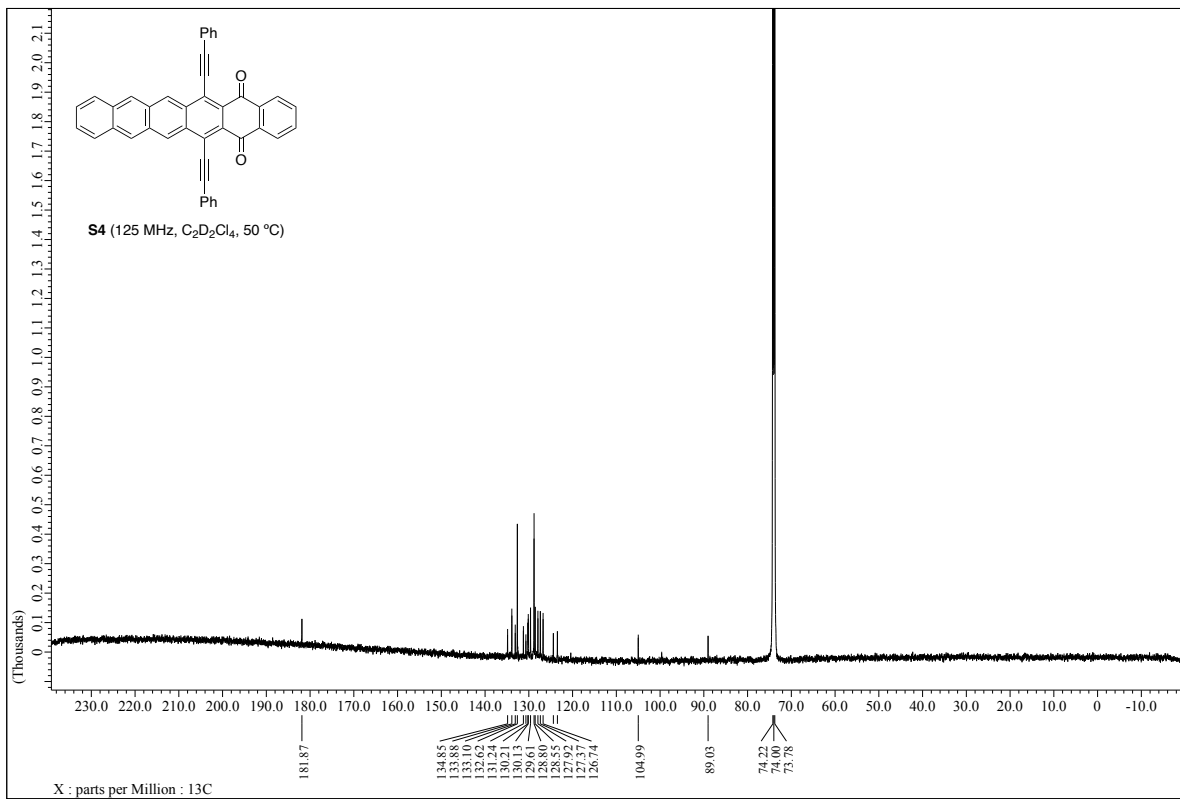
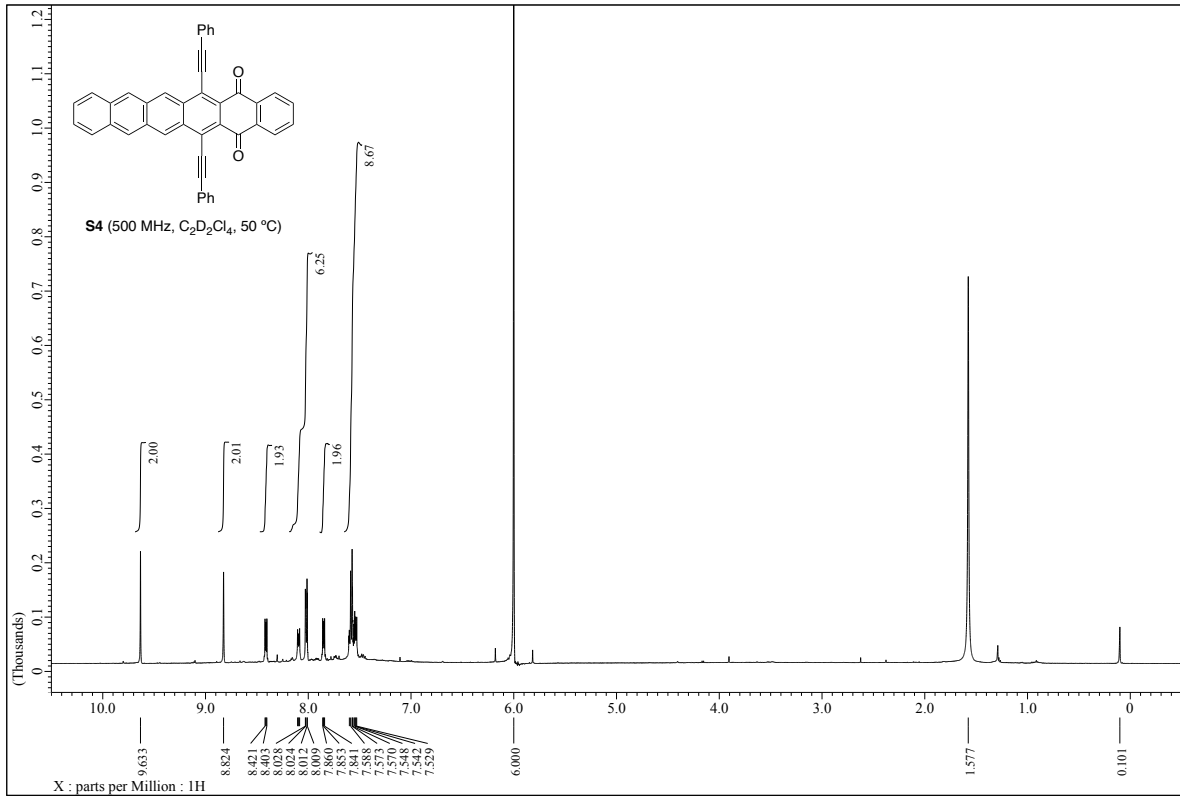


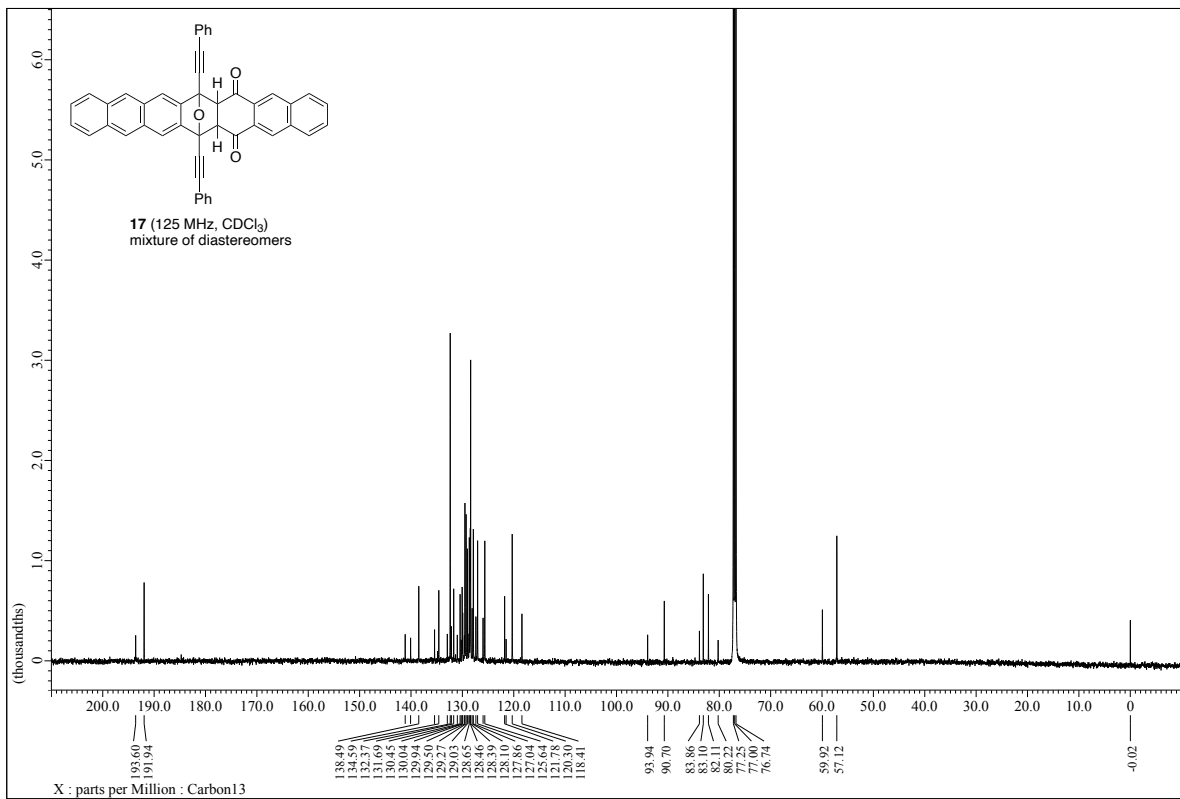
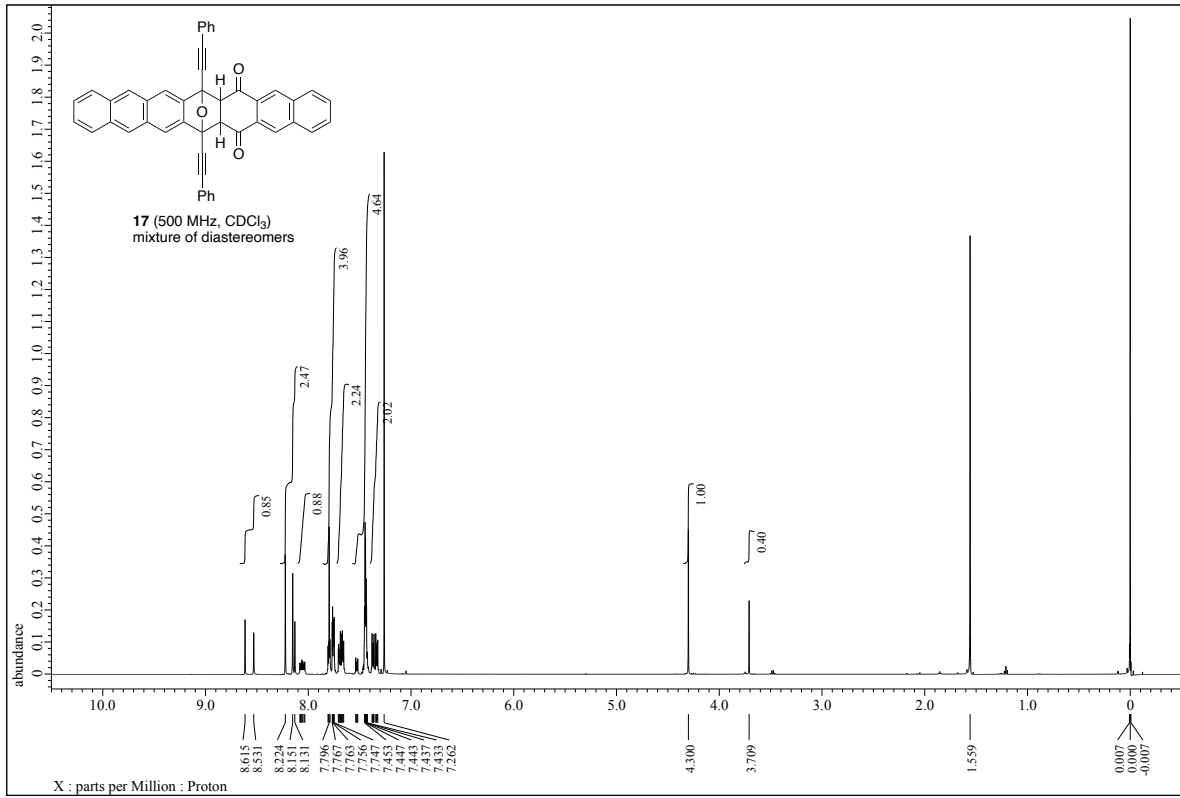


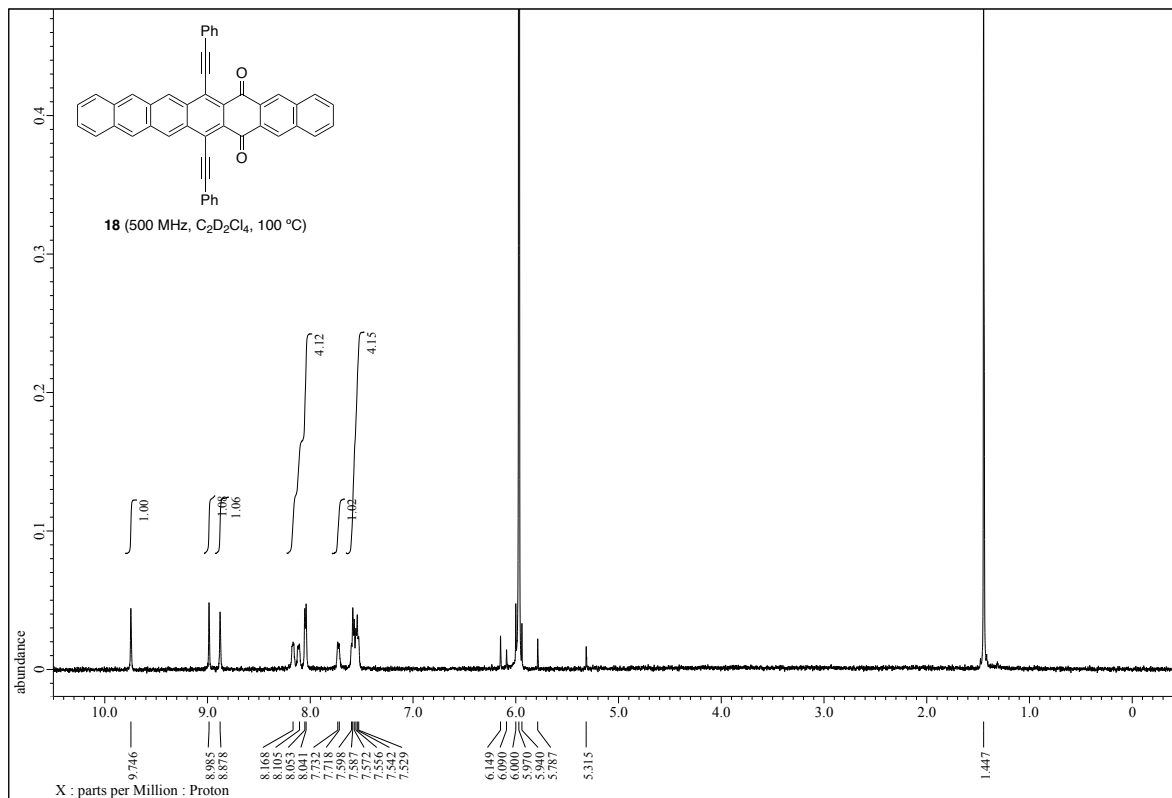


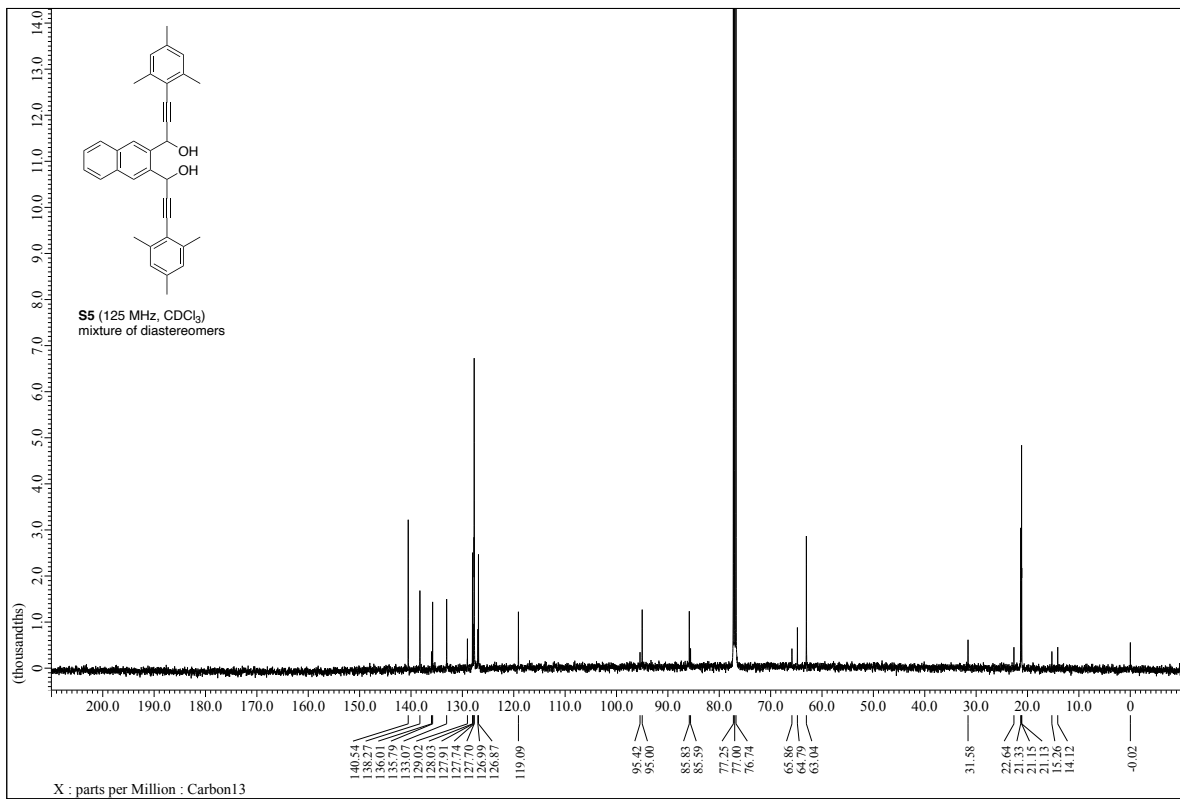
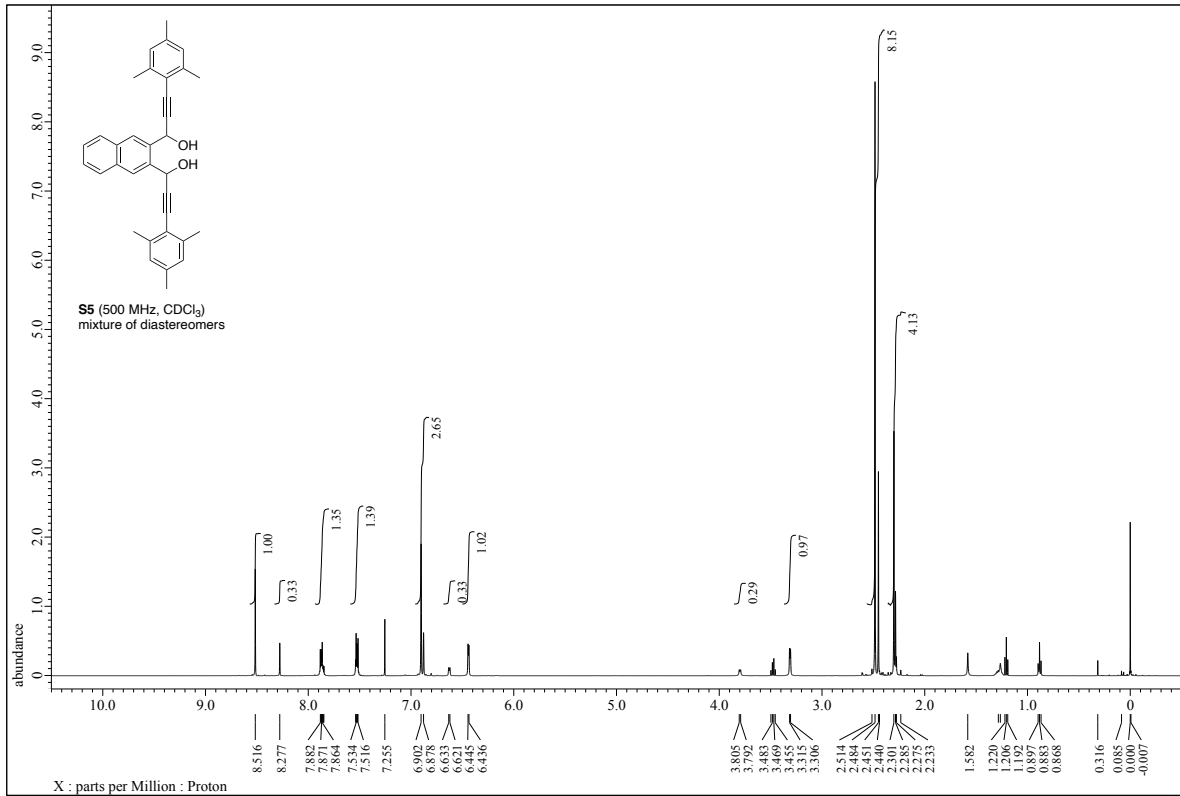


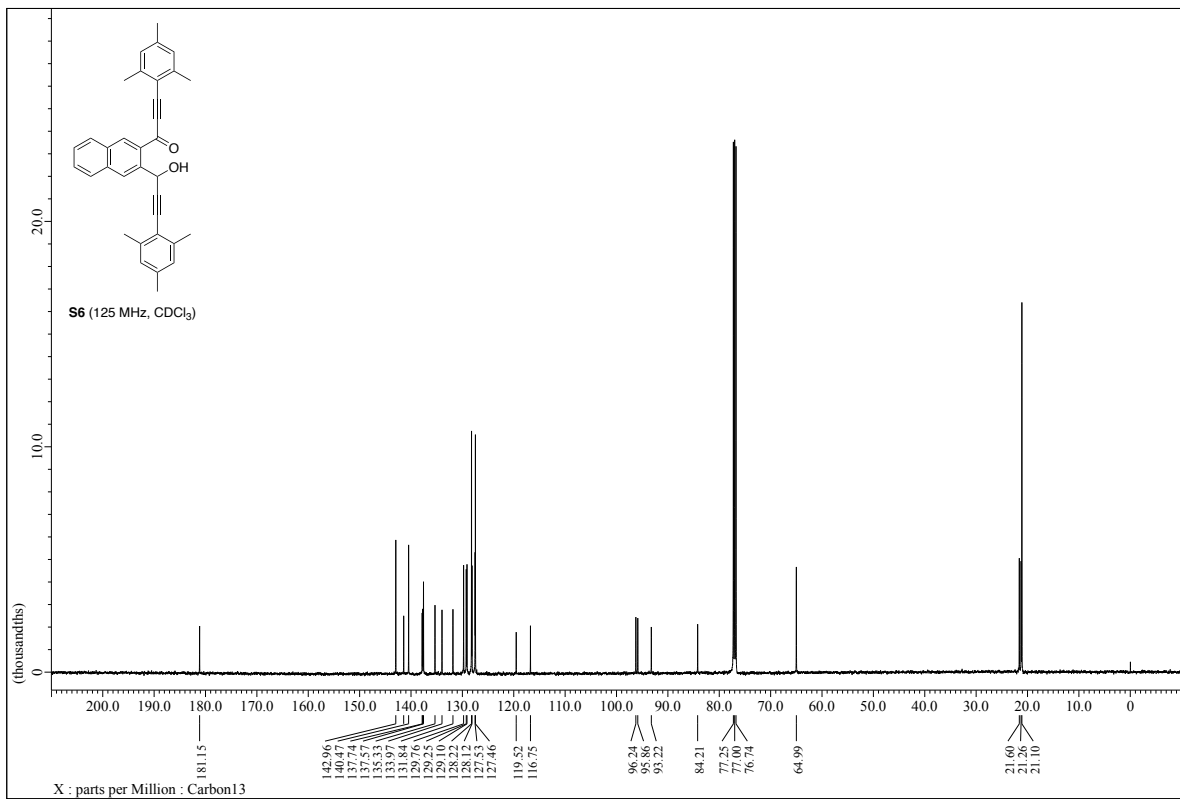
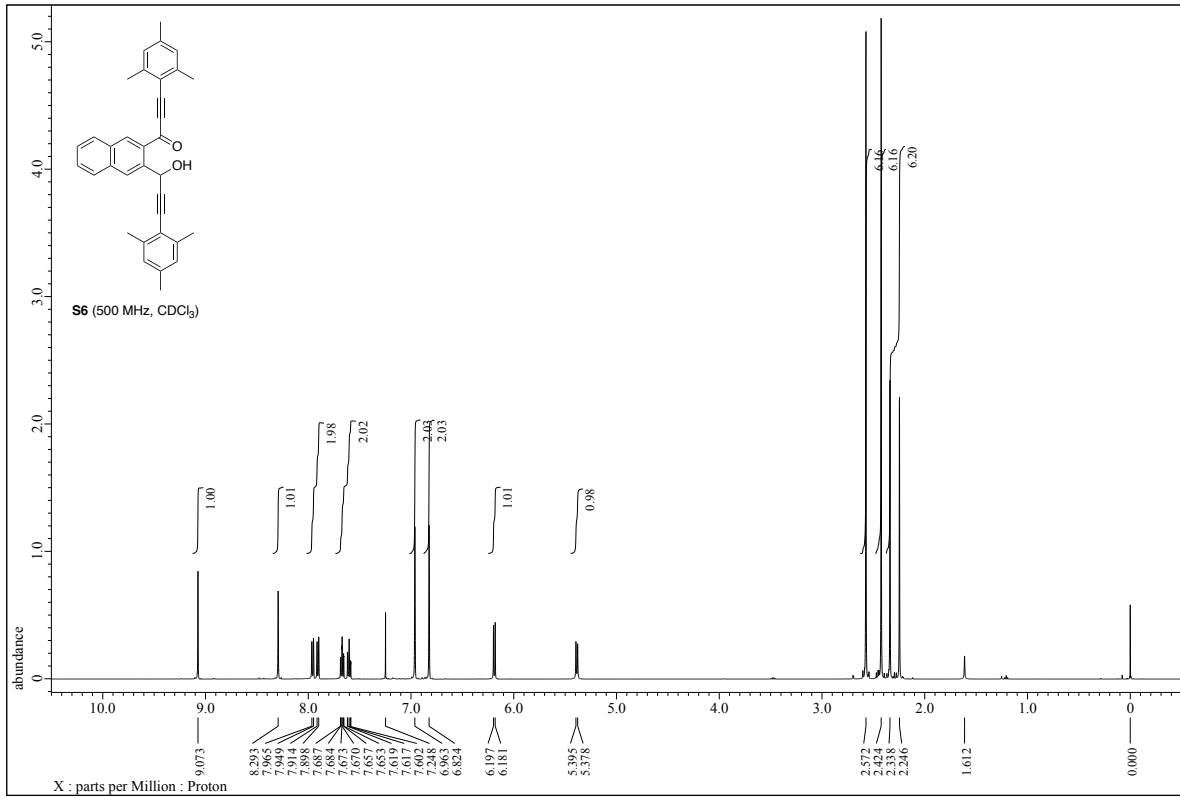


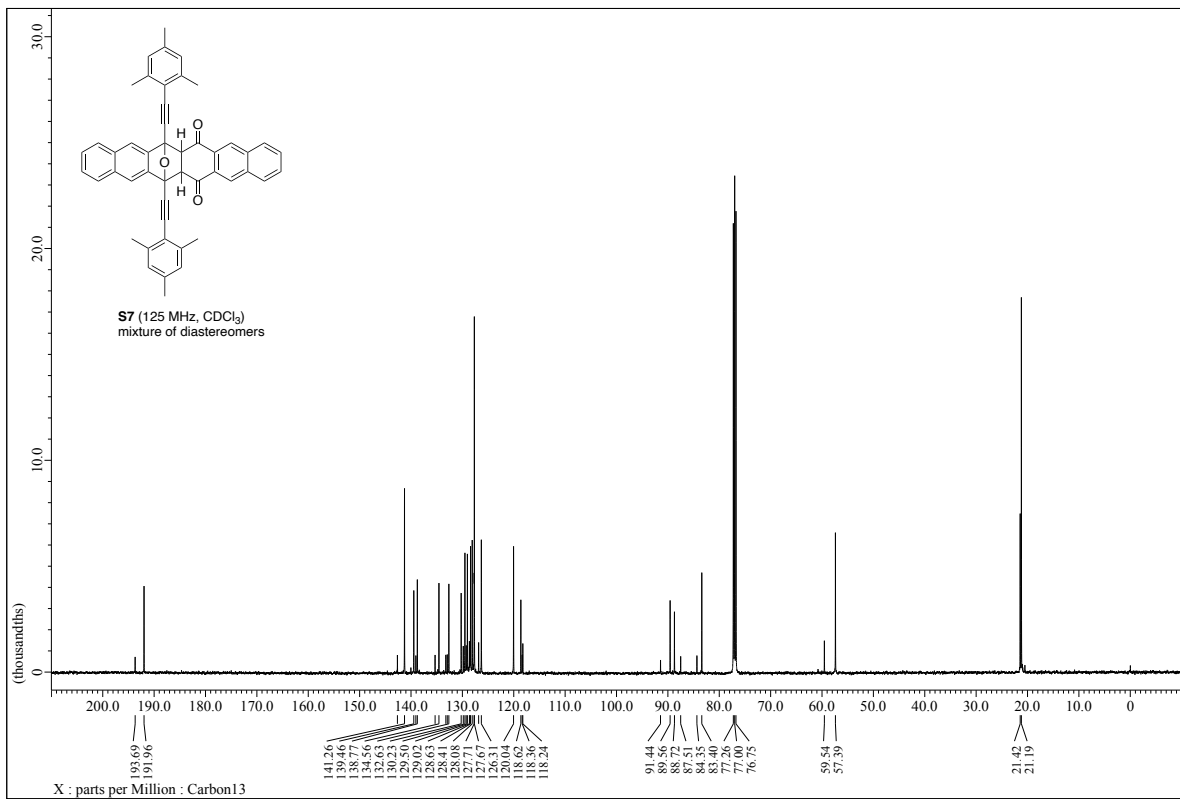
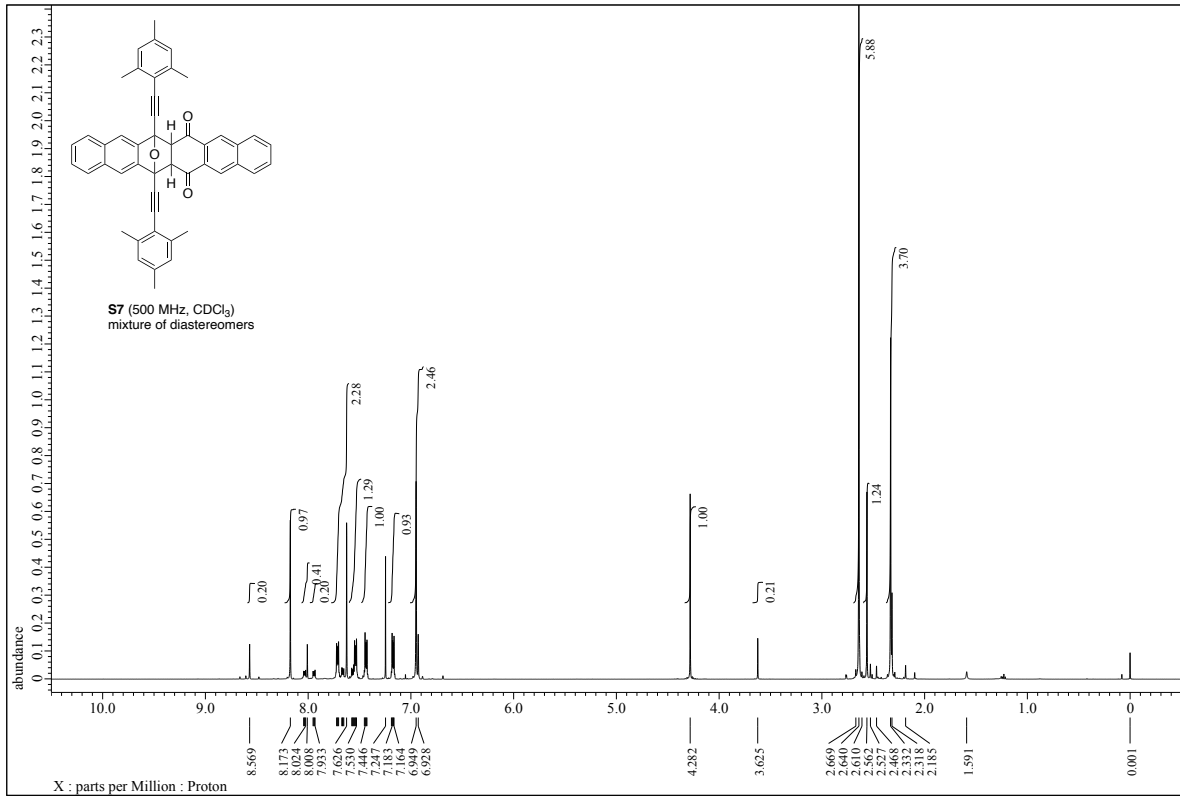


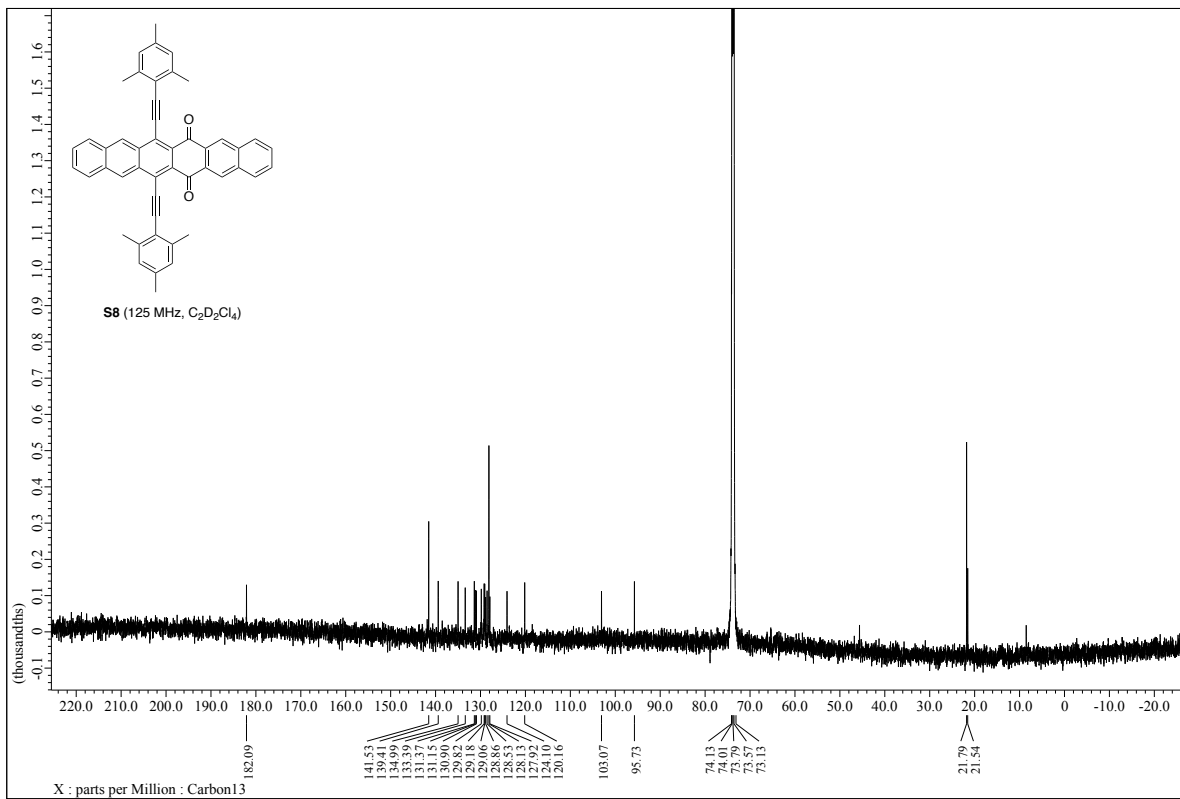
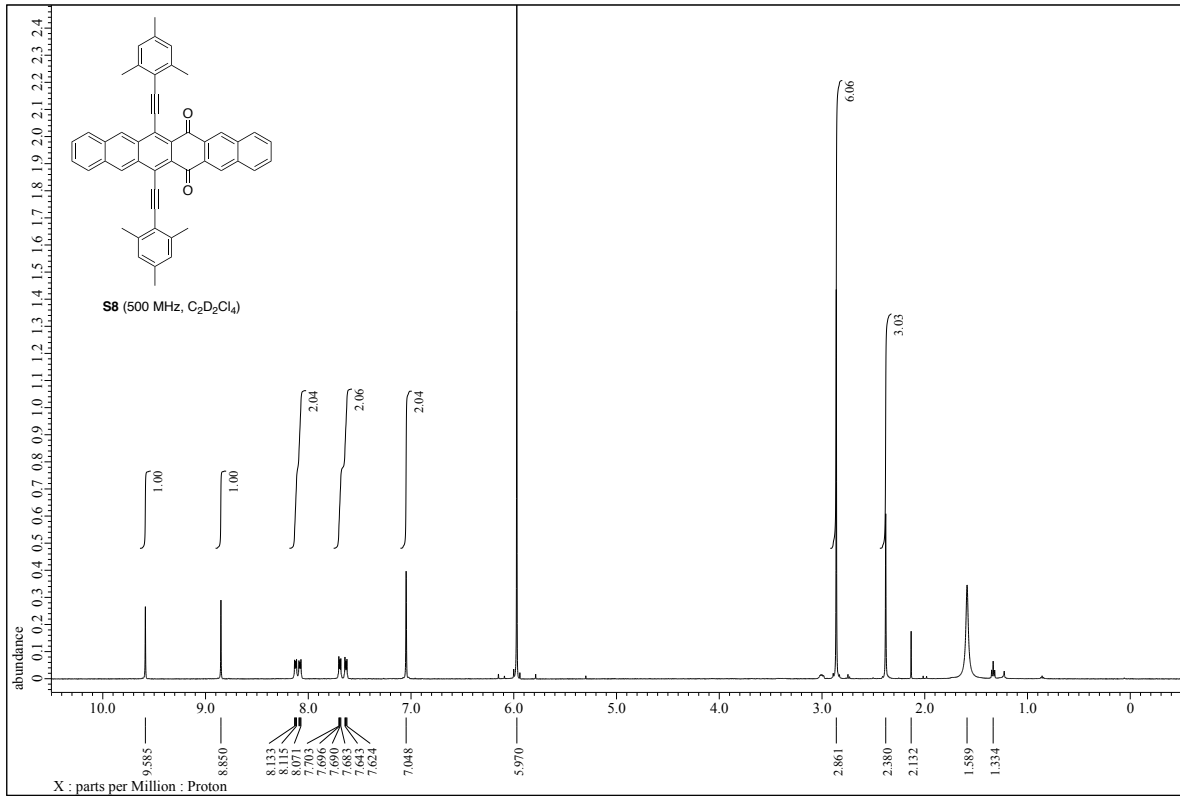


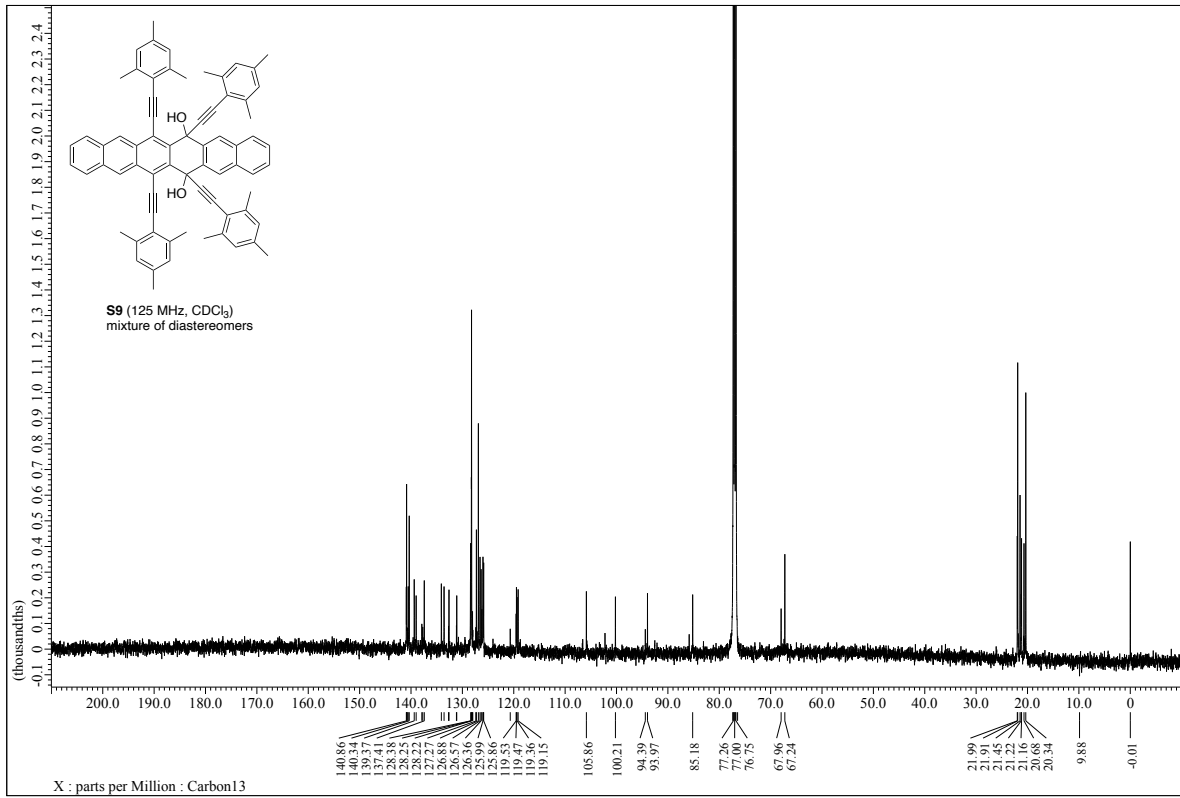
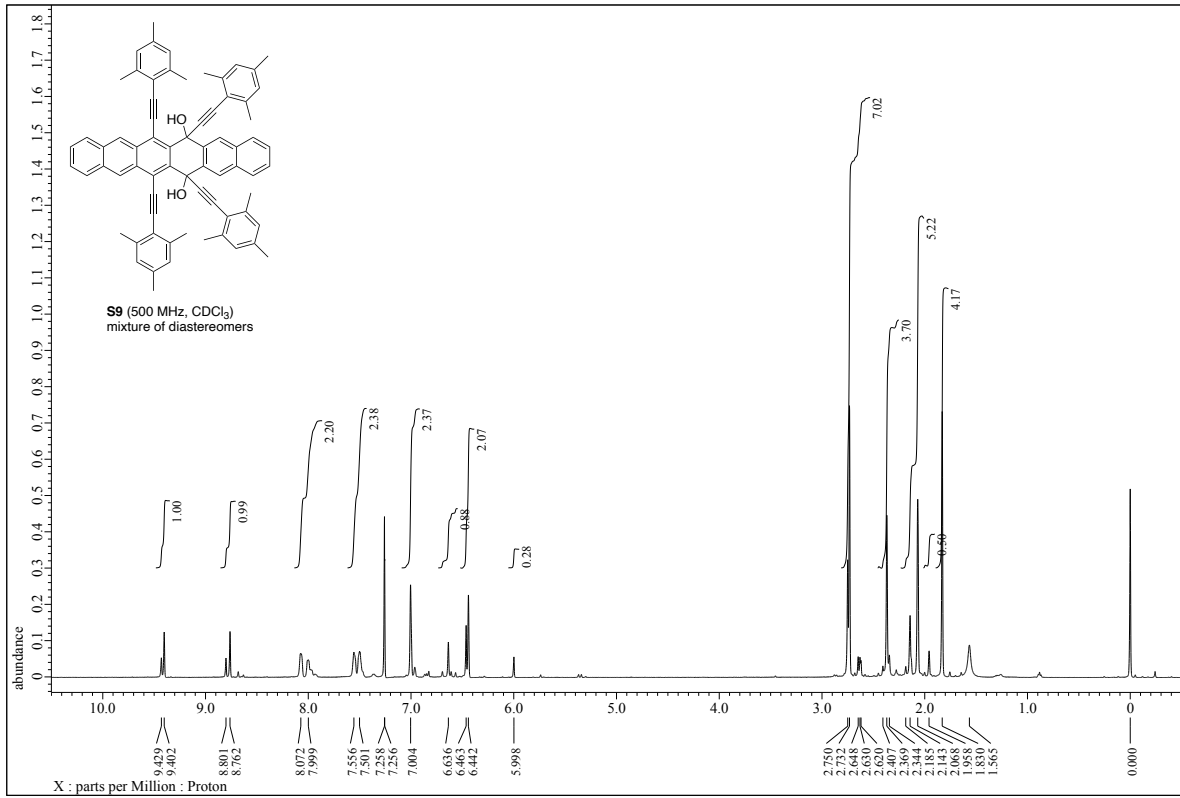


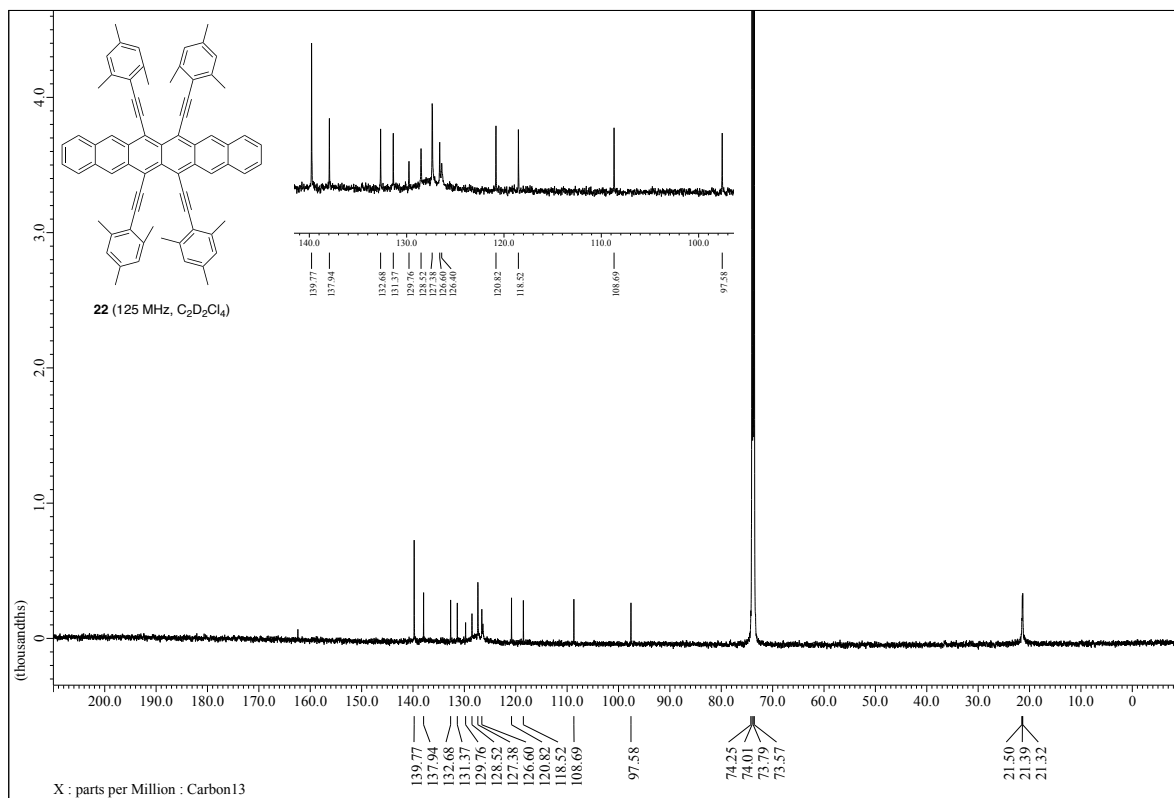
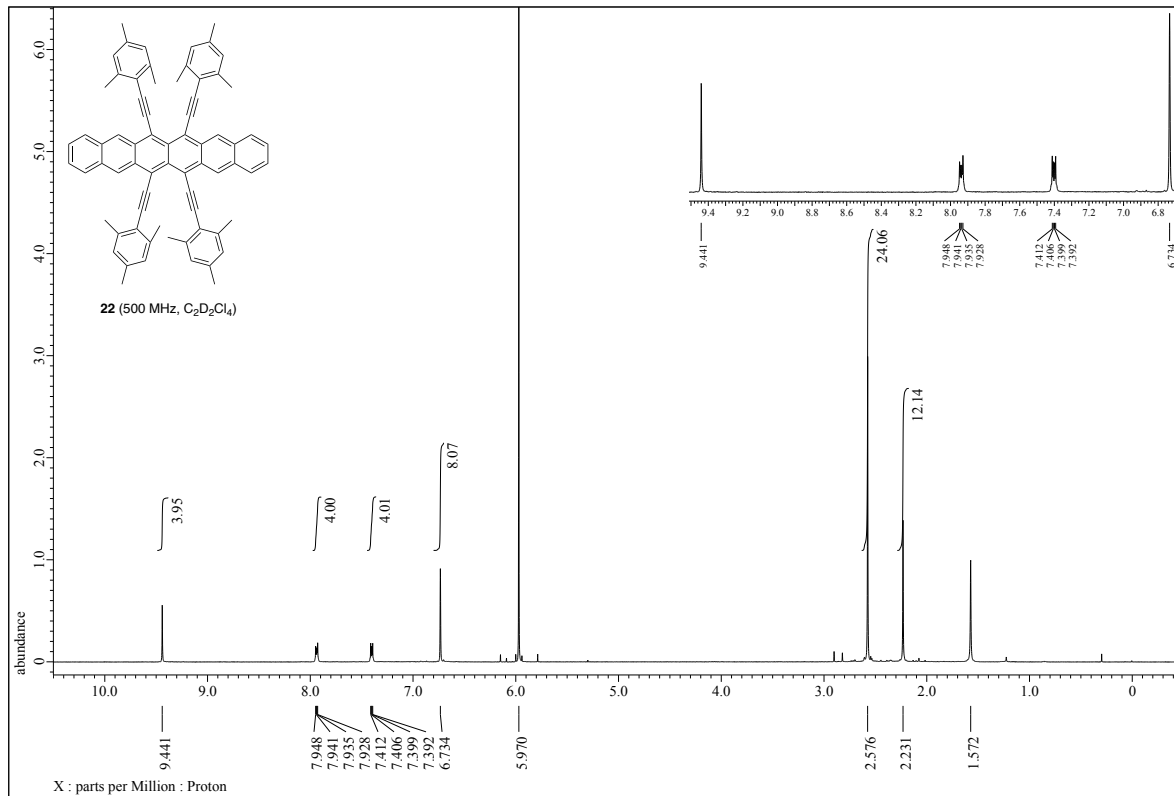












14. Calculations

DFT calculations were performed with the Gaussian 09 program^[3] and Spartan 16 program^[4]. Geometry optimizations were carried out at the RB3LYP level of density functional theory with the 6-31G(d) basis set for compounds **7**, **8**, **9**, **13**, **14**, **16**, and **15**. For hexacene **22**, the optimization was performed at the RB3LYP level of density functional theory with the 6-311G(d,p) basis set.

Table S2. Cartesian coordinates (Å) of the optimized structure for isoacnofuran **7**.

Atom	X	Y	Z
C	0.00002200	0.71575400	-4.41717600
C	-0.00002200	-0.71575400	-4.41717600
C	-0.00004000	-1.43440900	-3.24678100
C	-0.00001500	-0.71864500	-2.02139000
C	0.00001500	0.71864500	-2.02139000
C	0.00004000	1.43440900	-3.24678100
C	-0.00002400	-1.11554800	-0.68009900
O	0.00000000	0.00000000	0.11373200
C	0.00002400	1.11554800	-0.68009900
C	0.00002200	2.37071900	-0.07213700
C	-0.00002200	-2.37071900	-0.07213700
C	0.00002200	3.48118400	0.43313900
C	-0.00002200	-3.48118400	0.43313900
C	-0.00000200	-4.76679900	1.03564200
C	0.00003700	-5.93379000	0.24274700
C	0.00005400	-7.18956900	0.84200600
C	0.00003400	-7.30822500	2.23441100
C	-0.00000400	-6.15805200	3.02834500
C	-0.00002200	-4.89689900	2.44075600
C	0.00000200	4.76679900	1.03564200
C	0.00002200	4.89689900	2.44075600
C	0.00000400	6.15805200	3.02834500
C	-0.00003400	7.30822500	2.23441100
C	-0.00005400	7.18956900	0.84200600
C	-0.00003700	5.93379000	0.24274700
H	0.00004000	1.23801000	-5.36987600
H	-0.00004000	-1.23801000	-5.36987600
H	-0.00007000	-2.52026200	-3.24695000
H	0.00007000	2.52026200	-3.24695000
H	0.00005400	-5.83937600	-0.83879100
H	0.00008300	-8.08047500	0.21979900
H	0.00004800	-8.29082800	2.69788800
H	-0.00001900	-6.24447300	4.11155000
H	-0.00005200	-4.00164900	3.05467200
H	0.00005200	4.00164900	3.05467200
H	0.00001900	6.24447300	4.11155000
H	-0.00004800	8.29082800	2.69788800
H	-0.00008300	8.08047500	0.21979900
H	-0.00005400	5.83937600	-0.83879100

Table S3. Cartesian coordinates (Å) of the optimized structure for isoacnofuran **8**.

Atom	X	Y	Z
C	-0.73042400	-3.56896400	-0.00001100
C	0.72927400	-3.56927300	0.00001100
C	1.43335600	-2.36401300	0.00001800
C	0.72198100	-1.15702900	0.00000300
C	-0.72210800	-1.15672300	-0.00000400
C	-1.43399500	-2.36340500	-0.00001800
C	-1.40933300	-4.83294100	-0.00002500
C	-0.71650400	-6.01048400	-0.00001300
C	0.71431900	-6.01078800	0.00001400
C	1.40764700	-4.83353800	0.00002500
C	1.11801900	0.19314200	0.00000500
O	0.00038800	0.97953400	-0.00000100
C	-1.11757600	0.19361500	-0.00000600
C	-2.36892900	0.80246500	0.00000400
C	2.36963100	0.80145900	-0.00000500
C	-3.48055900	1.30758500	-0.00000500
C	3.48142200	1.30622400	0.00000400
C	-4.76512500	1.90972400	-0.00000100
C	-4.89547900	3.31528400	-0.00011800
C	-6.15649600	3.90277200	-0.00012400
C	-7.30693200	3.10903300	-0.00001100
C	-7.18827900	1.71651900	0.00011100
C	-5.93280000	1.11702500	0.00011700
C	4.76585600	1.90864500	0.00000100
C	5.93370000	1.11619500	-0.00011700
C	7.18905000	1.71595700	-0.00010900
C	7.30740800	3.10849600	0.00001300
C	6.15680300	3.90199000	0.00012500
C	4.89591200	3.31423300	0.00011800
H	2.51991900	-2.36490900	0.00003000
H	-2.52055900	-2.36384100	-0.00003100
H	-2.49670400	-4.83103200	-0.00004600
H	-1.24917300	-6.95749200	-0.00002500
H	1.24658700	-6.95802200	0.00002600
H	2.49501900	-4.83209000	0.00004600
H	-4.00025200	3.92923200	-0.00021100
H	-6.24278400	4.98599800	-0.00021600
H	-8.28946800	3.57261200	-0.00001700
H	-8.07926800	1.09441200	0.00019900
H	-5.83865200	0.03546300	0.00021200
H	5.83978100	0.03461200	-0.00021200
H	8.08017200	1.09403900	-0.00019600
H	8.28984500	3.57228400	0.00002000
H	6.24286100	4.98523500	0.00021700
H	4.00055400	3.92799100	0.00021000

Table S4. Cartesian coordinates (Å) of the optimized structure for isoacenoferan **9**.

Atom	X	Y	Z
C	-0.73255000	-2.61858600	-0.00006400
C	0.73255900	-2.61858300	0.00006000
C	1.43608600	-1.40222800	0.00011100
C	0.72430500	-0.20355700	0.00003800
C	-0.72430500	-0.20356000	-0.00004900
C	-1.43608200	-1.40223400	-0.00011800

C	-1.40704700	-3.86384900	-0.00012600
C	-0.72764100	-5.07398700	-0.00006500
C	0.72766000	-5.07398300	0.00006500
C	1.40706200	-3.86384300	0.00012400
C	1.11891100	1.15126200	0.00007000
O	-0.00000400	1.93355900	-0.00001100
C	-1.11891600	1.15125700	-0.00008700
C	-2.36848800	1.76050000	-0.00007700
C	2.36848200	1.76050800	0.00005700
C	-3.48081400	2.26531200	-0.00006600
C	3.48080800	2.26531900	0.00004900
C	-1.41106900	-6.33725400	-0.00012500
C	-0.71687000	-7.51268900	-0.00006300
C	0.71689900	-7.51268600	0.00006400
C	1.41109300	-6.33724800	0.00012500
C	-4.76465500	2.86766200	-0.00000100
C	-4.89473200	4.27349500	0.00023900
C	-6.15550300	4.86129900	0.00029400
C	-7.30631400	4.06800000	0.00011000
C	-7.18806600	2.67538900	-0.00013800
C	-5.93292400	2.07540300	-0.00019700
C	4.76464500	2.86767700	-0.00000100
C	5.93291700	2.07542400	0.00024500
C	7.18805700	2.67541600	0.00020100
C	7.30629800	4.06802800	-0.00008100
C	6.15548300	4.86132100	-0.00031600
C	4.89471500	4.27351100	-0.00027500
H	2.52252100	-1.40237500	0.00019000
H	-2.52251600	-1.40238500	-0.00019800
H	-2.49509100	-3.86453800	-0.00022000
H	2.49510500	-3.86452800	0.00021700
H	-2.49849200	-6.33507700	-0.00022000
H	-1.24751400	-8.46087400	-0.00011000
H	1.24754700	-8.46086900	0.00011100
H	2.49851600	-6.33506600	0.00022000
H	-3.99933700	4.88719800	0.00038000
H	-6.24140600	5.94456100	0.00048500
H	-8.28867800	4.53192300	0.00015100
H	-8.07928200	2.05359600	-0.00029000
H	-5.83923200	0.99380000	-0.00038700
H	5.83923100	0.99382100	0.00046200
H	8.07927600	2.05362700	0.00039200
H	8.28866000	4.53195600	-0.00011100
H	6.24138100	5.94458400	-0.00053300
H	3.99931700	4.88720900	-0.00045400

Table S5. Cartesian coordinates (Å) of the optimized structure for naphthoquinone **11**.

Atom	X	Y	Z
C	-0.26001200	-0.70453200	0.00000000
C	-0.26001200	0.70453200	0.00000000
C	1.02469300	1.46280500	0.00000000
C	2.28138800	0.67178500	0.00000000
C	2.28138800	-0.67178500	0.00000000
C	1.02469300	-1.46280500	0.00000000
O	1.06155000	-2.68795900	0.00000000

O	1.06155000	2.68795900	0.00000000
C	-1.47270400	-1.40017800	0.00000000
C	-2.67756900	-0.69961500	0.00000000
C	-2.67756900	0.69961500	0.00000000
C	-1.47270400	1.40017800	0.00000000
H	3.19898000	1.25385700	0.00000000
H	3.19898000	-1.25385700	0.00000000
H	-1.44742100	-2.48517800	0.00000000
H	-3.61873600	-1.24235400	0.00000000
H	-3.61873600	1.24235400	0.00000000
H	-1.44742100	2.48517800	0.00000000

Table S6. Cartesian coordinates (Å) of the optimized structure for cycloadduct **13**.

Atom	X	Y	Z
C	0.55040100	1.19798000	-0.77441300
C	0.55040100	1.19798000	0.77441300
C	1.87517700	1.02530900	1.49727400
C	3.10272500	0.72457000	0.70479600
C	3.10272500	0.72457000	-0.70479600
C	1.87517700	1.02530900	-1.49727400
C	4.29270900	0.45852900	1.39706800
C	5.46524000	0.18831200	0.70063100
C	5.46524000	0.18831200	-0.70063100
C	4.29270900	0.45852900	-1.39706800
C	-0.48480500	0.02140500	-1.09452900
C	0.17955600	-1.29430300	-0.69841100
C	0.17955600	-1.29430300	0.69841100
C	-0.48480500	0.02140500	1.09452900
C	0.74734300	-2.33111100	-1.42135500
C	1.30598100	-3.39602200	-0.69893600
C	1.30598100	-3.39602200	0.69893600
C	0.74734300	-2.33111100	1.42135500
C	-1.11749300	0.09265600	-2.39210400
C	-1.11749300	0.09265600	2.39210400
C	-1.59021000	0.14333300	-3.50663500
C	-1.59021000	0.14333300	3.50663500
O	1.91769600	1.12808300	-2.71500800
O	1.91769600	1.12808300	2.71500800
H	0.09419600	2.11424200	-1.15778800
H	0.09419600	2.11424200	1.15778800
O	-1.41546000	0.21285400	0.00000000
C	-2.12154100	0.22840500	-4.82929500
C	-1.35963800	0.82261000	-5.85383500
C	-1.87075200	0.90582600	-7.14636200
C	-3.14260200	0.40429500	-7.43470600
C	-3.90444600	-0.18499800	-6.42281100
C	-3.40091600	-0.27648300	-5.12759300
C	-2.12154100	0.22840500	4.82929500
C	-1.35963800	0.82261000	5.85383500
C	-1.87075200	0.90582600	7.14636200
C	-3.14260200	0.40429500	7.43470600
C	-3.90444600	-0.18499800	6.42281100
C	-3.40091600	-0.27648300	5.12759300
H	4.26782100	0.47314100	2.48163100
H	6.38300700	-0.01972500	1.24383200
H	6.38300700	-0.01972500	-1.24383200

H	4.26782100	0.47314100	-2.48163100
H	0.74494900	-2.32604700	-2.50751400
H	1.73905100	-4.23644100	-1.23450700
H	1.73905100	-4.23644100	1.23450700
H	0.74494900	-2.32604700	2.50751400
H	-0.37294000	1.20964300	-5.61852400
H	-1.27547100	1.36493600	-7.93098600
H	-3.53869900	0.47260600	-8.44426500
H	-4.89407900	-0.57573000	-6.64351100
H	-3.98793500	-0.73458200	-4.33757600
H	-0.37294000	1.20964300	5.61852400
H	-1.27547100	1.36493600	7.93098600
H	-3.53869900	0.47260600	8.44426500
H	-4.89407900	-0.57573000	6.64351100
H	-3.98793500	-0.73458200	4.33757600

Table S7. Cartesian coordinates (Å) of the optimized structure for cycloadduct **14**.

Atom	X	Y	Z
C	-0.21935900	1.70206300	-0.77472600
C	-0.21935900	1.70206300	0.77472600
C	1.09254800	1.95843900	1.49695300
C	2.35340500	2.04528100	0.70493000
C	2.35340500	2.04528100	-0.70493000
C	1.09254800	1.95843900	-1.49695300
C	3.56782100	2.15495500	1.39712300
C	4.76694200	2.25398300	0.70060400
C	4.76694200	2.25398300	-0.70060400
C	3.56782100	2.15495500	-1.39712300
C	-0.82399700	0.25901300	-1.09624400
C	0.22462400	-0.77851100	-0.70861900
C	0.22462400	-0.77851100	0.70861900
C	-0.82399700	0.25901300	1.09624400
C	1.06713900	-1.57905300	-1.42707800
C	1.95459300	-2.44540600	-0.71901300
C	1.95459300	-2.44540600	0.71901300
C	1.06713900	-1.57905300	1.42707800
C	-1.44748200	0.12984400	-2.39369700
C	-1.44748200	0.12984400	2.39369700
C	-1.90807300	0.03712600	-3.51056300
C	-1.90807300	0.03712600	3.51056300
O	1.09881100	2.08160700	-2.71345100
O	1.09881100	2.08160700	2.71345100
H	-0.94267400	2.42615400	-1.15821400
H	-0.94267400	2.42615400	1.15821400
O	-1.76595400	0.13506900	0.00000000
C	2.84080900	-3.31928700	-1.40140800
C	3.69038800	-4.15288500	-0.70735500
C	3.69038800	-4.15288500	0.70735500
C	2.84080900	-3.31928700	1.40140800
C	-2.43116300	-0.03459000	-4.83729800
C	-1.88615600	0.78065300	-5.84815900
C	-2.38859300	0.71572500	-7.14504600
C	-3.43767800	-0.15486800	-7.45130900
C	-3.98386300	-0.96535500	-6.45309700
C	-3.48600400	-0.91080500	-5.15355500

C	-2.43116300	-0.03459000	4.83729800
C	-1.88615600	0.78065300	5.84815900
C	-2.38859300	0.71572500	7.14504600
C	-3.43767800	-0.15486800	7.45130900
C	-3.98386300	-0.96535500	6.45309700
C	-3.48600400	-0.91080500	5.15355500
H	3.53987400	2.16171000	2.48168400
H	5.70452400	2.33443600	1.24377600
H	5.70452400	2.33443600	-1.24377600
H	3.53987400	2.16171000	-2.48168400
H	1.06220200	-1.57794700	-2.51403000
H	1.06220200	-1.57794700	2.51403000
H	2.83753100	-3.31868200	-2.48879600
H	4.36377400	-4.81432700	-1.24568300
H	4.36377400	-4.81432700	1.24568300
H	2.83753100	-3.31868200	2.48879600
H	-1.07195800	1.45409700	-5.59852700
H	-1.96148700	1.34761100	-7.91904800
H	-3.82829200	-0.20150100	-8.46423300
H	-4.79988900	-1.64339500	-6.68785300
H	-3.90567500	-1.53922700	-4.37411000
H	-1.07195800	1.45409700	5.59852700
H	-1.96148700	1.34761100	7.91904800
H	-3.82829200	-0.20150100	8.46423300
H	-4.79988900	-1.64339500	6.68785300
H	-3.90567500	-1.53922700	4.37411000

Table S8. Cartesian coordinates (Å) of the optimized structure for cycloadduct **16**.

Atom	X	Y	Z
C	-0.77478600	-1.66291700	1.57368100
C	0.77492200	-1.66284300	1.57371400
C	1.49678800	-0.65358400	2.45095900
C	0.70491700	0.39915700	3.15039600
C	-0.70504000	0.39909200	3.15036500
C	-1.49678300	-0.65372200	2.45089300
C	1.39700700	1.40011700	3.84678200
C	0.70043800	2.39337700	4.52585500
C	-0.70080600	2.39331200	4.52582400
C	-1.39725300	1.39998700	3.84672100
C	-1.09698000	-1.46559200	0.02292400
C	-0.71326700	-0.03927000	-0.35500800
C	0.71332000	-0.03919800	-0.35497500
C	1.09716200	-1.46548100	0.02297200
C	-1.43193000	1.07976800	-0.63919700
C	-0.72537300	2.28891800	-0.96111900
C	0.72521600	2.28899200	-0.96108600
C	1.43188200	1.07991500	-0.63913000
C	-2.39431900	-1.94265300	-0.39913100
C	2.39457000	-1.94240600	-0.39902400
C	-3.51161500	-2.29516900	-0.70818000
C	3.51191200	-2.29481100	-0.70803300
O	-2.71281400	-0.71243800	2.56428700
O	2.71281900	-0.71218400	2.56440100
H	-1.15852600	-2.65101500	1.83999400
H	1.15874500	-2.65090600	1.84004000

O	0.00014100	-2.21780100	-0.55787100
C	-1.40265500	3.46960400	-1.28264800
C	-0.72187900	4.65288100	-1.60239300
C	0.72151000	4.65295500	-1.60236000
C	1.40239200	3.46974700	-1.28258400
C	-1.40724500	5.86321500	-1.93021800
C	-0.71295500	7.00375700	-2.23947500
C	0.71237600	7.00383000	-2.23944200
C	1.40676800	5.86335900	-1.93015400
C	-4.83813600	-2.71272700	-1.03221100
C	-5.84028300	-2.68809500	-0.04302700
C	-7.13703400	-3.09021900	-0.35178800
C	-7.45166400	-3.52370000	-1.64230100
C	-6.46208800	-3.55203800	-2.62799000
C	-5.16283900	-3.14835200	-2.33042600
C	4.83841600	-2.71236400	-1.03213500
C	5.84061200	-2.68772500	-0.04300100
C	7.13735200	-3.08983600	-0.35182900
C	7.45192200	-3.52331000	-1.64236000
C	6.46229700	-3.55165300	-2.62799900
C	5.16305800	-3.14798000	-2.33036800
H	2.48156100	1.37251200	3.83855200
H	1.24358400	3.16879600	5.05902000
H	-1.24404700	3.16868000	5.05896700
H	-2.48180400	1.37228200	3.83844400
H	-2.51878400	1.07333800	-0.64221000
H	2.51873700	1.07359600	-0.64209400
H	-2.49076600	3.46915000	-1.28458100
H	2.49050400	3.46940400	-1.28446700
H	-2.49471600	5.86023700	-1.93017500
H	-1.24673400	7.91707600	-2.48782700
H	1.24607200	7.91720300	-2.48777000
H	2.49423900	5.86049200	-1.93006000
H	-5.58447200	-2.34968900	0.95635900
H	-7.90435700	-3.06690000	0.41725800
H	-8.46442400	-3.83843700	-1.87900100
H	-6.70343600	-3.88873200	-3.63253900
H	-4.39008100	-3.16694400	-3.09270200
H	5.58484800	-2.34932300	0.95639800
H	7.90471400	-3.06651200	0.41717900
H	8.46467300	-3.83803700	-1.87911100
H	6.70359800	-3.88834000	-3.63256200
H	4.39026400	-3.16657500	-3.09260600

Table S9. Cartesian coordinates (Å) of the optimized structure for hexacene **22**.

Atom	X	Y	Z
C C0	-4.9214894	0.0224614	-0.7005590
C C1	-4.9095150	-0.3113934	0.7077614
C C2	-3.6924373	-0.4265875	1.3631631
C C3	-2.4620852	-0.2219820	0.7050064
C C4	-2.4725643	0.0659766	-0.7116891
C C5	-3.7154549	0.2024313	-1.3623461
C C6	-1.2260349	-0.2477897	1.4094093
C C7	-0.0001896	-0.0000048	0.7218271
C C8	-0.0001872	-0.0000008	-0.7337166

C C9	-1.2411591	0.1682640	-1.4201597
C C10	1.2257261	0.2477802	1.4093518
C C11	2.4618706	0.2219881	0.7049684
C C12	2.4723534	-0.0659867	-0.7116385
C C13	1.2408582	-0.1682632	-1.4200954
C C14	3.6924265	0.4266214	1.3630320
C C15	4.9097116	0.3114233	0.7077273
C C16	4.9216883	-0.0224816	-0.7004958
C C17	3.7154505	-0.2024607	-1.3621951
C C18	-6.1856905	0.1487719	-1.3633735
C C19	-7.3527856	-0.0396572	-0.6851287
C C20	-7.3408443	-0.3692292	0.7071950
C C21	-6.1619534	-0.5002778	1.3783549
C C22	6.1622792	0.5003267	1.3782612
C C23	7.3412559	0.3692627	0.7071828
C C24	7.3531990	0.0396342	-0.6850722
C C25	6.1860211	-0.1488103	-1.3632425
C C26	1.2871508	-0.5549160	-2.7823194
C C27	1.2434999	0.6397506	2.7726792
C C28	-1.2436985	-0.6397741	2.7727360
C C29	1.4227920	-1.0120416	-3.8992743
C C30	1.3472108	1.1038608	3.8893907
C C31	-1.3473326	-1.1038912	3.8894539
C C32	1.5078405	-1.5807029	-5.1998183
C C33	-1.3933527	-1.6737453	5.1935782
C C34	1.3932831	1.6737154	5.1935119
C C35	-1.9151297	-0.9394638	6.2825322
C C36	-1.9356761	-1.5327498	7.5443234
C C37	-1.4558780	-2.8237829	7.7640057
C C38	-0.9501382	-3.5352673	6.6723996
C C39	-0.9090554	-2.9911840	5.3922467
C C40	0.9090148	2.9911647	5.3921884
C C41	0.9501527	3.5352553	6.6723345
C C42	1.4559182	2.8237675	7.7639269
C C43	1.9356872	1.5327243	7.5442362
C C44	1.9150754	0.9394261	6.2824526
C C45	-1.2873466	0.5549258	-2.7823858
C C46	-1.4229214	1.0120424	-3.8993544
C C47	-1.5078992	1.5806942	-5.1999078
C C48	-2.3677351	1.0211190	-6.1760514
C C49	-2.4281239	1.6085294	-7.4354719
C C50	-1.6680578	2.7345381	-7.7649300
C C51	-0.8245677	3.2684543	-6.7900263
C C52	-0.7270087	2.7186661	-5.5131633
C C53	2.3676883	-1.0211012	-6.1759350
C C54	2.4281160	-1.6084966	-7.4353616
C C55	1.6680594	-2.7345001	-7.7648594
C C56	0.8245503	-3.2684357	-6.7899848
C C57	0.7269950	-2.7186982	-5.5130982
C C58	-1.7722612	3.3605491	-9.1339738
C C59	1.7722871	-3.3604778	-9.1339160
C C60	0.1810419	3.3375350	-4.4814922
C C61	3.1865710	0.2054706	-5.8646752
C C62	-1.4678169	-3.4369768	9.1430322
C C63	1.4679102	3.4369665	9.1429507
C C64	-2.4120364	0.4709516	6.0964335
C C65	2.4119474	-0.4710024	6.0963595

C	C66	-3.1866462	-0.2054392	-5.8648162
C	C67	-0.1811277	-3.3375546	-4.4814809
C	C68	-0.3745556	-3.7961940	4.2351001
C	C69	0.3744803	3.7961730	4.2350565
H	H1	-3.6797810	-0.6615722	2.4197241
H	H2	-3.7222263	0.4429419	-2.4174691
H	H3	3.6797509	0.6616592	2.4195961
H	H4	3.7222121	-0.4430229	-2.4173219
H	H5	-6.1939864	0.3995324	-2.4188231
H	H6	-8.3031415	0.0602834	-1.1974984
H	H7	-8.2822992	-0.5143581	1.2251598
H	H8	-6.1504927	-0.7494621	2.4341053
H	H9	6.1507501	0.7495608	2.4340081
H	H10	8.2826867	0.5144217	1.2251716
H	H11	8.3035343	-0.0603414	-1.1974619
H	H12	6.1942589	-0.3996241	-2.4186886
H	H13	-2.3393520	-0.9680323	8.3793202
H	H14	-0.5847450	-4.5472082	6.8216518
H	H15	0.5847820	4.5472032	6.8215935
H	H16	2.3393867	0.9680062	8.3792214
H	H17	-3.0842871	1.1727291	-8.1833686
H	H18	-0.2273689	4.1436715	-7.0279866
H	H19	3.0842904	-1.1726773	-8.1832376
H	H20	0.2273332	-4.1436293	-7.0279854
H	H21	-2.7278138	3.8818270	-9.2569132
H	H22	-0.9748380	4.0876054	-9.3000881
H	H23	-1.7120455	2.6052830	-9.9227149
H	H24	0.9748754	-4.0875399	-9.3000600
H	H25	1.7120742	-2.6051930	-9.9226390
H	H26	2.7278470	-3.8817432	-9.2568538
H	H27	0.8954117	2.6083693	-4.0899719
H	H28	0.7369067	4.1755052	-4.9057906
H	H29	-0.3910821	3.7050400	-3.6241112
H	H30	3.8000794	0.4923124	-6.7204340
H	H31	2.5432227	1.0514894	-5.6061347
H	H32	3.8496803	0.0385378	-5.0107615
H	H33	-1.8175861	-4.4727018	9.1152981
H	H34	-0.4621284	-3.4472404	9.5776739
H	H35	-2.1154240	-2.8788436	9.8223500
H	H36	2.1155254	2.8788231	9.8222522
H	H37	1.8176986	4.4726848	9.1152020
H	H38	0.4622342	3.4472513	9.5776210
H	H39	-2.9588858	0.8109239	6.9779523
H	H40	-1.5751335	1.1577169	5.9330344
H	H41	-3.0685618	0.5550386	5.2268612
H	H42	3.0685531	-0.5550833	5.2268491
H	H43	2.9586879	-0.8110218	6.9779284
H	H44	1.5750408	-1.1577392	5.9328538
H	H45	-2.5433116	-1.0514736	-5.6062957
H	H46	-3.8497479	-0.0385125	-5.0108948
H	H47	-3.8001672	-0.4922470	-6.7205770
H	H48	-0.8958832	-2.6085104	-4.0904516
H	H49	-0.7364961	-4.1759269	-4.9056337
H	H50	0.3908635	-3.7045490	-3.6237893
H	H51	-1.1360486	-3.9247781	3.4601671
H	H52	0.4740155	-3.2973820	3.7580866
H	H53	-0.0502002	-4.7846928	4.5649889

H	H54	0.0501366	4.7846728	4.5649529
H	H55	1.1359481	3.9247521	3.4600984
H	H56	-0.4741091	3.2973628	3.7580727

15. References

- [1] C.-H. Lin, K.-H. Lin, B. Pal, L.-D. Tsou, *Chem. Commun.* **2009**, 803.
- [2] a) C. F. Wilcox, Jr., K. A. Weber, *J. Org. Chem.* **1986**, *51*, 1088; b) O. Farooq, *Synthesis* **1994**, 1035; c) Y. E. Türkmen, T. J. Montavon, S. A. Kozmin, V. H. Rawal, *J. Am. Chem. Soc.* **2012**, *134*, 9062.
- [3] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- [4] Spartan '16, Wavefunction, Inc., Irvine, CA; Y. Shao et al., *Mol. Phys.* **2015**, *113*, 184.