# Supersized Contorted-Aromatics

# Supporting Information

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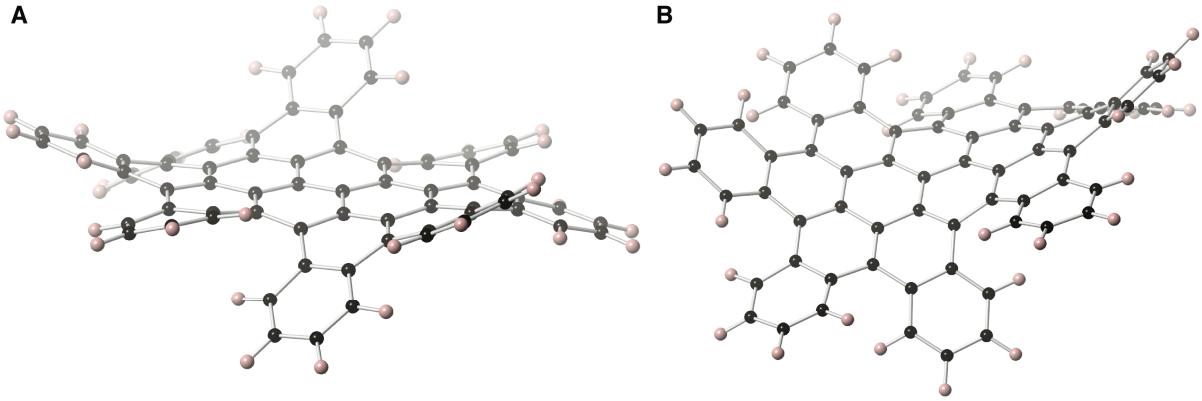



**Figure S1.** Two higher energy confirmations found for the **c-OBCB 1a** using DFT calculations.

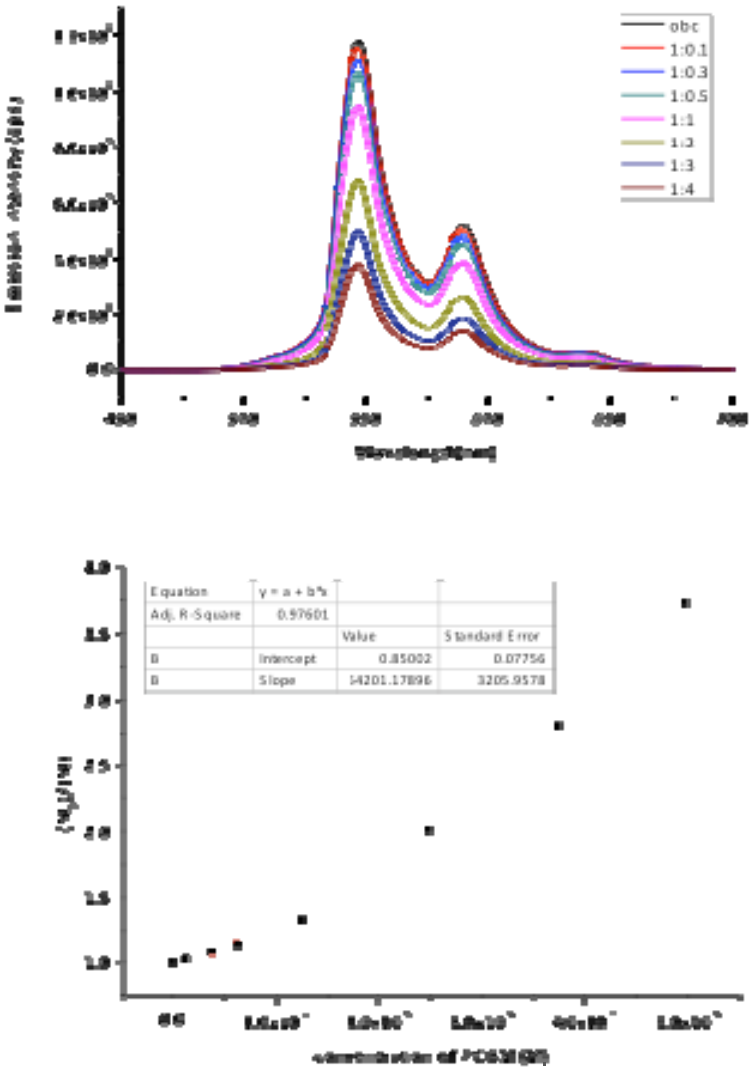



**Figure S2.** Stern-Volmer analysis of the association constant between **c-OBCB 1b** and $PC_{70}BM$.

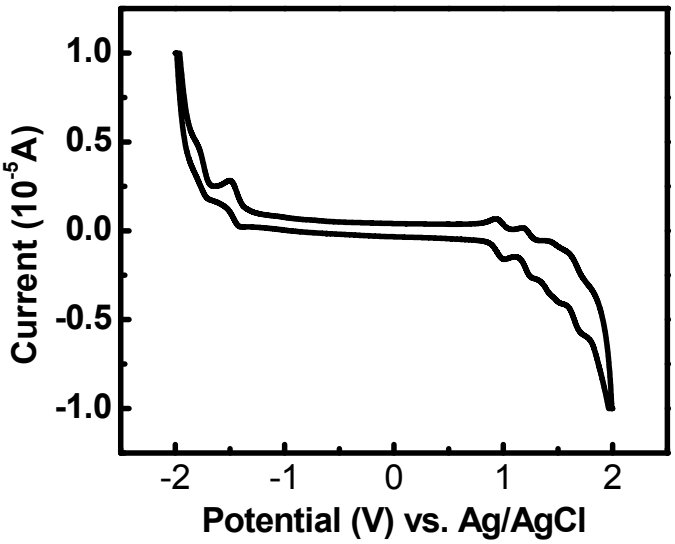



**Figure S3.** Cyclic voltammetry of **c-OBCB 1b** in $CH_2Cl_2$.

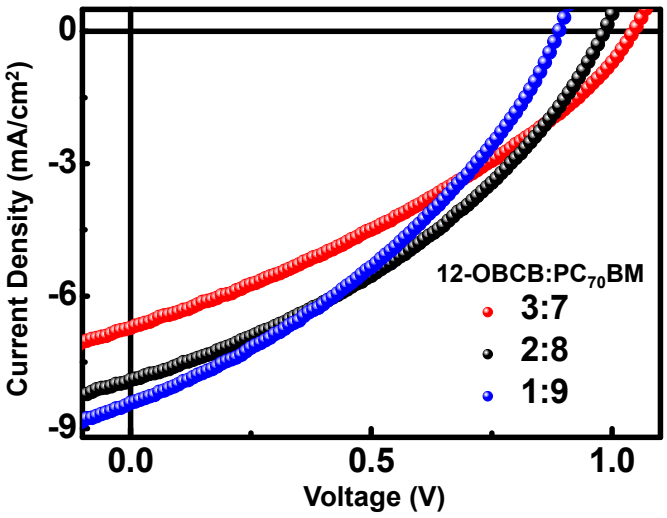
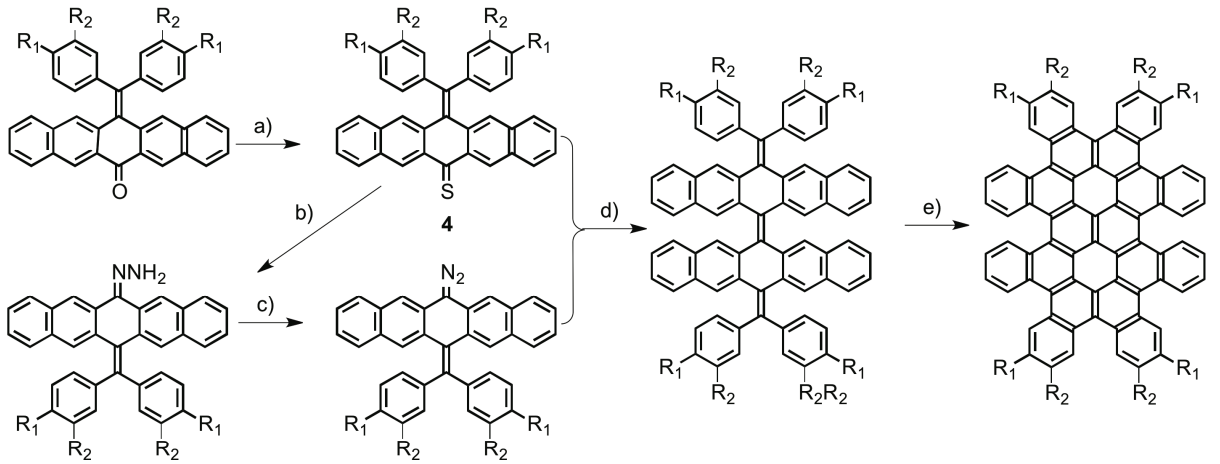



**Figure S4.** Current density-voltage (*J-V*) curves of PEDOT:PSS/**c-OBCB 1b**:**$PC_{70}BM$**/$TiO_x$/Al architecture BHJ solar cells with different weight ratios of the electron donor and acceptor in the active layer

## I. Synthesis

**General.** Reagents employed were either commercially available or prepared according to a known procedure as noted below. Anhydrous and oxygen-free $CH_2Cl_2$, diethyl ether and THF were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Unless otherwise noted, all reactions were run in oven-dried glassware, and monitored by TLC using silica gel 60 $F_{254}$ precoated plates (EM Science) when necessary. Column chromatography was performed on a CombiFlash® Sg100c system using RediSepTM normal phase silica columns (ISCO, Inc., Lincoln, NE). $^1$H NMR (400 MHz), and $^{13}$C NMR (100 MHz) spectra were recorded on Bruker DRX-300 and Bruker DRX-400 spectrometers at room temperature unless otherwise noted. HRMS were recorded on JEOL JMS-HX110A/110A Tandem mass spectrometer. The photochemistry was carried out according to a reported procedure.[1] Thioketone **4a-c** were synthesized according to literature.[2]



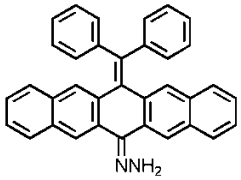

**10a** $R_1 = R_2 = H$
**10b** $R_1 = OC_{12}H_{25}$; $R_2 = H$
**10c** $R_1 = R_2 = OC_{12}H_{25}$

**5a** $R_1 = R_2 = H$
**5b** $R_1 = OC_{12}H_{25}$; $R_2 = H$
**5c** $R_1 = R_2 = OC_{12}H_{25}$

**3a** $R_1 = R_2 = H$
**3b** $R_1 = OC_{12}H_{25}$; $R_2 = H$
**3c** $R_1 = R_2 = OC_{12}H_{25}$

**1a** $R_1 = R_2 = H$
**1b** $R_1 = OC_{12}H_{25}$; $R_2 = H$
**1c** $R_1 = R_2 = OC_{12}H_{25}$

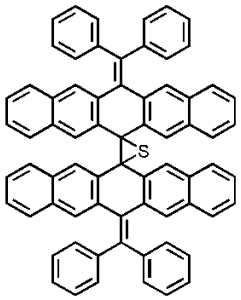
**Scheme S1**. Synthesis of triolefin **3a-c** and **c-OBCB 1a-c**. Key: a) Lawesson's reagent, 80 $^0$C; b) $NH_2NH_2$•$H_2O$; c) HgO or $MnO_2$ or $NiO_2$; d) dichloromethane/absence of light followed by $PPh_3$, xylenes, reflux; e) *hv*, $I_2$, propylene oxide.




**Synthesis of hydrazone 10a**

To 1.5 g of thioketone **4a** in 30 mL of pentanol was added 15 mL of hydrazine monohydrate, the mixture was heated at 120 $^0$C for 12 h. After cooled down to room temperature, the solvent was reduced down to 10 mL. The analytically pure hydrazone **10a** precipitated was collected by filtration.

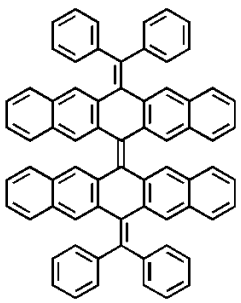
$^1$H NMR of hydrazone **10a** (400 MHz, chloroform-d) δ (ppm): 8.56 (s, 1H), 8.26 (s, 1H), 7.85 - 7.72 (m, 4H), 7.55 – 7.16 (m, 16H), 6.31 (s, 2H).




**Synthesis of thioepoxide**

1.2 g of hydrazone **10a** was dissolved in 200 mL of anhydrous methylenechloride. To this solution, 20 g of $MgSO_4$ was added, followed by 5 g of $MnO_2$. The mixture was kept in the dark and 0.5 mL of saturated NaOH in methanol was added. The reaction mixture was stirred at room temperature for another 30 min and then filtered into 1.0 g of thioketone **4a** in 100 mL of methylenechloride. After stirring at room temperature for an additional 12 h, the solvent was reduced and thioepoxide was purified by column chromatography to yield pure thioepoxide (1.7 g, 79%).

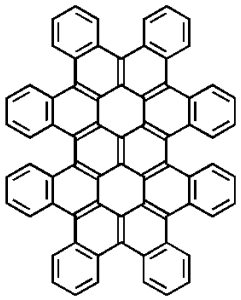
$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 8.25 (s, 2H), 8.09 (s, 2H), 7.86 - 7.84 (d, 4H), 7.72 – 7.63 (m, 10H), 7.46 – 7.35 (m, 10H), 7.35—7.20 (m, 10H), 7.12 – 7.08 (t, 2H), 6.69 – 6.66 (d, 4H).



**Synthesis of triolefin 3a**

1.7 g (1.854 mmol, 1.0 eq.) of thioepoxide and 0.6 g (2.23 mmol, 1.2 eq.) of $PPh_3$ in 60 mL of xylenes was heated to reflux for 12 h. After cooled down to room temperature, the solvent was reduced under vacuum. And triolefin precipitates **3a** were collected by filtration, washed with methanol and hexanes, and recrystalized in toluene to yield pure **3a**. (1.5 g, 89% yield).

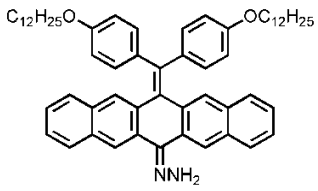
$^1$H NMR of triolefin **3a** (400 MHz, chloroform-d) δ (ppm): 7.78 (s, 4H), 7.75 (d, 4H), 7.70 (d, 8H), 7.51 - 7.42 (m, 12H), 7.33 – 7.30 (d, 4H), 7.26 – 7.15 (m, 8H), 7.09 (s, 4H).



**Synthesis of c-OBCB 1a**

The photolysis setup has been previously described.[1] A mixture of compound **3a** (150 mg, 0.17 mmol), iodine (260 mg, 1.02 mmol), and propylene oxide (20 mL) in 350 mL of anhydrous benzene was irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is reduced to 15 mL under reduced pressure and a yellow powder precipitates. Compound **1a** is isolated by vacuum filtration and washed with 100 mL of 20% $CH_2Cl_2$ in hexanes to yield 100 mg of **1a** (83% yield).

$^1$H NMR **c-OBCB 1a** (400 MHz, toluene-$d_8$) δ (ppm): 9.55 (d, 4H), 9.42 (d, 4H), 9.31 (d, 4H), 9.09 (d, 4H), 8.00 – 7.92 (m, 8H), 7.78 (t, 4H), 7.57 (t, 4H).



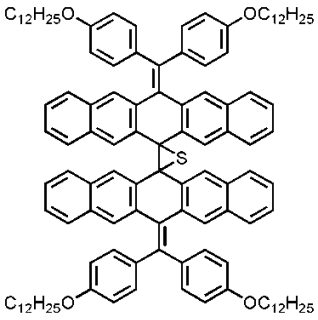

**Synthesis of hydrazone 10b**

To 2.0 g of thioketone **4b** in 30 mL of pentanol was added 15 mL of hydrazine monohydrate, the mixture was heated at 120 $^0$C for 12 h.

After cooled down to room temperature, the solvent was evaporated under vacuum. The analytically pure hydrazone **10b** was used without further purification.

$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 8.70 (s, 2H), 7.94 (t, 2H), 7.69 (s, 2H), 7.42 (d, 2H), 7.41 (d, 2H), 7.40 (t, 2H), 7.16 (d, 4H), 6.76 (d, 4H), 6.30 (s, 2H), 3.86 (m, 4H), 1.71 (m, 4H), 1.58 – 1.35 (m, 36H), 0.97 – 0.94 (m, 6H).

HRMS (FAB+) cald. for $C_{59}H_{72}N_2O_2$: 840.5594; found: 840.43.



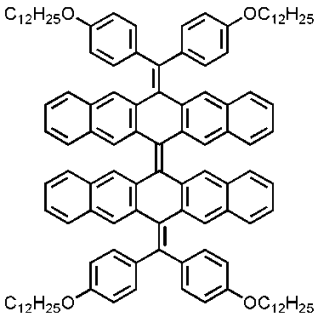

**Synthesis of thioepoxide**

1.5 g of hydrazone **10b** was dissolved in 200 mL of anhydrous methylenechloride. To this solution, 20 g of $MgSO_4$ was added, followed by 5 g of $MnO_2$. The mixture was kept in the dark and 0.5 mL of saturated NaOH in methanol was added. The reaction mixture was stirred at room temperature for another 30 min. This solution of diazo compound **5b** generated in situ was then filtered into 1.4 g of thioketone **4b** in 100 mL of methylene chloride. After stirring at room temperature for an additional 12 h, the solvent was evaporated and thioepoxide was purified by column chromatography with 1:4 (v:v) methylene chloride and hexanes ($R_f$ = 0.2) to yield pure thioepoxide (2.1 g, 73% yield).

$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 8.23 (s, 1H), 8.13 (s, 1H), 7.80 (s, 2H), 7.80 (s, 2H), 7.74 (s, 2H), 7.72 (d, 2H), 7.68 (d, 4H), 7.64 (d, 4H), 7.58 (d, 2H), 7.52 (d, 2H), 7.46 (d, 2H), 7.39 (d, 1H), 7.32 (d, 2H), 7.30 (d, 2H), 7.24 (d, 2H), 7.08 (m, 1H), 7.02 (d, 4H), 6.96 (d, 2H), 6.82 (d, 2H), 6.71 (d, 1H), 6.64 (s, 1H), 4.06 (m, 4H), 4.05 - 4.03 (m, 2H), 3.98 (s, 2H), 1.88 – 1.79 (m, 8H), 1.58 – 1.35 (m, 72H), 0.97 – 0.94 (m, 12H).

$^{13}$C NMR (100 MHz, chloroform-d) δ (ppm): 158.3, 137.7, 136.1, 135.4, 132.3, 131.6, 131.4, 131.1, 130.4, 128.2, 128.1, 128.0, 127.2, 126.1, 126.0, 115.2, 114.8, 68.5, 32.4, 29.9, 26.6, 23.2, 14.6.

HRMS (FAB+) cald. for $C_{118}H_{140}O_4S$: 1654.4368, found: 1654.22.



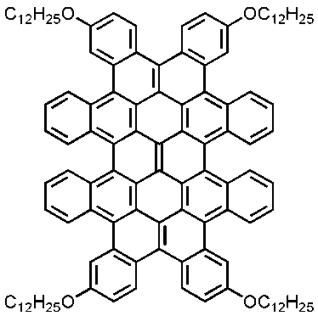

**Synthesis of triolefin 3b**

2.1 g (1.29 mmol, 1.0 eq.) of thioepoxide synthesized above and 0.42 g (1.55 mmol, 1.2 eq.) of $PPh_3$ in 40 mL of xylenes was heated to reflux for 12 h. After cooled down to room temperature, the solvent was reduced under vacuum. And triolefin **3b** was purified by column chromatography using 3:7 (v:v) methylene chloride and hexanes ($R_f$ = 0.2) as the eluent to give 1.7 g of product in 81% yield.

$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 7.83 (s, 4H), 7.78 (s, 4H), 7.70 (d, 8H), 7.61 (d, 4H), 7.35-7.32 (dd, 8H), 7.29 – 7.24 (dd, 4H), 7.04 (d, 8H), 4.08 (t, 8H), 1.93 – 1.86 (m, 8H), 1.61 – 1.53 (m, 8H), 1.38 (s, 64H), 1.08 – 0.99 (m, 12H).

$^{13}$C-NMR (100 MHz, chloroform-d) δ (ppm): 158.5, 137.5, 136.0, 135.8, 135.1, 134.0, 132.3, 131.6, 128.2, 127.9, 127.6, 127.2, 126.1, 125.8, 123.5, 117.8, 117.4, 68.5, 32.4, 29.9, 26.6, 23.2, 14.6.

HRMS (FAB+) Cald. for $C_{118}H_{140}O_4$: 1622.3718, found: 1622.20.




**Synthesis of *c*-OBCB 1b**

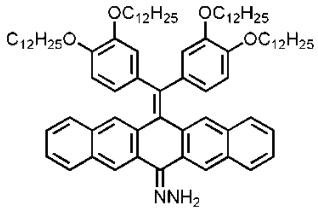
The photolysis setup has been previously described[1]. A mixture of compound **3b** (551 mg, 0.34 mmol), iodine (520 mg, 2.04 mmol), and

propylene oxide (20 mL) in 350 mL of anhydrous benzene was irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is evaporated under vacuum. Compound **1b** is purified by column chromatography using 1:4 (v:v) methylene chloride and hexanes as the eluent to give 440 mg of product in 80% yield.

$^{1}$H NMR (400 MHz, chloroform-d) δ (ppm): 9.28 (d, 4H), 9.11 (d, 4H), 9.04 (d, 4H), 8.82 (d, 4H), 7.69 (t, 4H), 7.52 (t, 4H), 7.35 (dd, 4H), 4.28 - 4.24 (t, 4H), 4.19 - 4.15 (t, 4H), 1.92 – 1.85 (m, 8H), 1.57 – 1.52 (m, 8H), 1.28 (s, 64H), 0.90 – 0.87 (t, 12H).

$^{13}$C-NMR (100 MHz, chloroform-d) δ (ppm): 158.3, 131.8, 131.7, 131.4, 130.8, 129.0, 128.6, 127.5, 126.6, 125.5, 125.3, 125.0, 124.2, 124.1, 122.3, 121.5, 119.8, 117.0, 111.2, 68.8, 32.4, 30.1, 26.6, 23.1, 14.6.

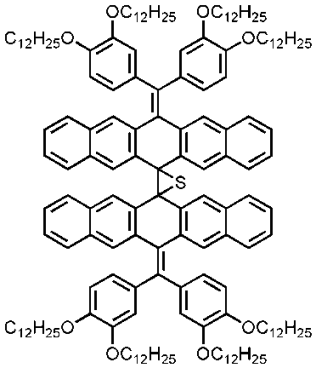
HRMS (FAB+) cald. for $C_{118}H_{128}O_4$: 1610.2765, found: 1610.15.




**Synthesis of hydrazone 10c**

To 2.5 g of thioketone **4c** in 30 mL of pentanol was added 15 mL of hydrazine monohydrate, the mixture was heated at 120 $^{0}$C for 12 h. After cooled down to room temperature, the solvent was evaporated under vacuum. The analytically pure hydrazone **10c** was used without further purification.

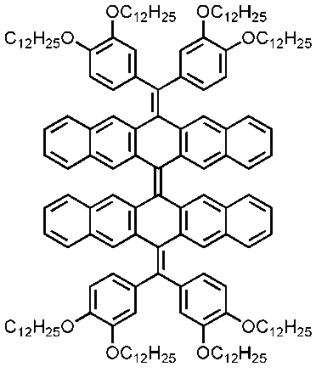
$^{1}$H NMR (400 MHz, chloroform-d) δ (ppm): 8.55 (s, 1H), 8.27 (s, 1H), 7.84 – 7.82 (m, 3H), 7.64 (s, 1H), 7.52 – 7.29 (m, 6H), 6.92 – 6.84 (m, 4H), 6.78 – 6.76 (t, 2H), 6.30 (s, 2H), 3.92 (m, 4H), 3.82 – 3.73 (m, 4H), 1.80 (m, 4H), 1.62 (m, 4H), 1.35 (m, 72H), 0.90 – 0.87 (t, 12H).



**Synthesis of thioepoxide**

2.0 g of hydrazone **10c** was dissolved in 200 mL of anhydrous methylenechloride. To this solution, 20 g of $MgSO_4$ was added, followed by 5 g of $MnO_2$. The mixture was kept in the dark and 0.5 mL of saturated NaOH in methanol was added. The reaction mixture was stirred at room temperature for another 30 min then filtered into 1.8 g of thioketone **4c** in 100 mL of methylenechloride. After stirring at room temperature for an additional 12 h, the solvent was reduced and thioepoxide was purified by column chromatography to yield pure thioepoxide (3.0 g, 79% yield).

$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 8.21 (s, 2H), 8.17 (s, 2H), 7.73 – 7.65 (t, 2H), 7.61 – 7.58 (d, 4H), 7.46 – 7.15 (m, 14H), 7.04 – 6.87 (m, 6H), 6.57 (d, 6H), 4.06 – 3.73 (m, 16H), 1.80 (m, 16H), 1.30 (m, 144H), 0.90 (m, 24H).

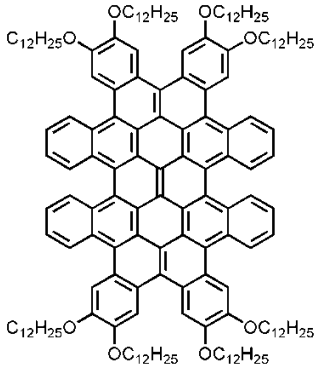


**Synthesis of triolefin 3c**

3.0 g (1.85 mmol, 1.0 eq.) of thioepoxide and 0.60 g (2.22 mmol, 1.2 eq.) of $PPh_3$ in 40 mL of xylenes was heated to reflux for 12 h. After cooled down to room temperature, the solvent was reduced under vacuum. And triolefin **3c** was purified by column chromatography (2.4 g, 80% yield).

$^1$H NMR (400 MHz, chloroform-d) δ (ppm): 7.77 (s, 4H), 7.69 (s, 4H), 7.48 (d, 4H), 7.28 – 7.19 (m, 16H), 7.14 – 7.10 (t, 4H), 6.93 (d, 4H), 4.03 – 3.98 (m, 8H), 3.96 – 3.92 (m, 4H), 3.92 – 3.86 (m, 4H), 1.86 – 1.79 (m, 8H), 1.73 – 1.69 (m, 8H), 1.53 – 1.45 (m, 8H), 1.32 – 1.20 (s, 136H), 0.90 – 0.85 (m, 24H).

$^{13}$C-NMR (100 MHz, chloroform-d) δ (ppm): 149.3, 149.0, 140.5, 137.5, 136.0, 135.8, 135.7, 134.0, 132.3, 131.6, 128.2, 127.9, 127.3, 127.2, 126.1, 125.8, 123.5, 117.5, 117.4, 70.1, 32.4, 30.0, 26.6, 22.8, 14.6.

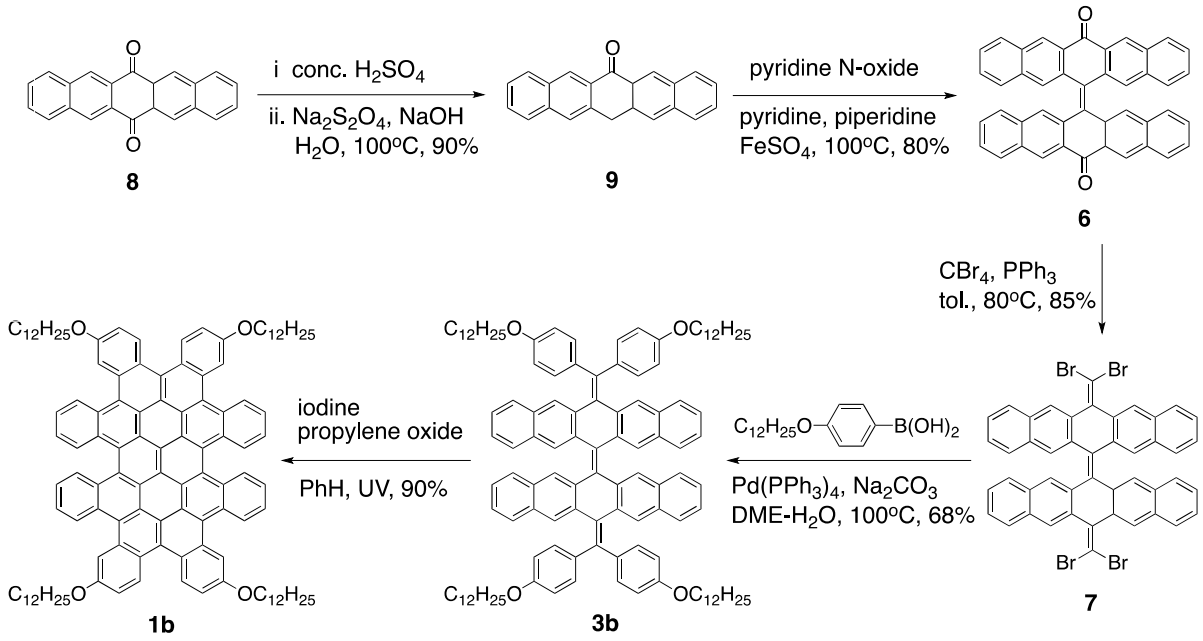



**Synthesis of c-OBCB 1c**

The photolysis setup has been previously described.[1] A mixture of compound 3c (800 mg, 0.4934 mmol), iodine (754 mg, 2.96 mmol), and propylene oxide (20 mL) in 350 mL of anhydrous benzene was irradiated with UV light (Hanovia 450 W high-pressure quartz Hg-vapor lamp) in an immersion well. Argon was bubbled through the reaction vessel during the photolysis. To maintain a constant temperature, the whole apparatus is submerged in a large bath of circulating water. After 12 hours of irradiation, the solvent is evaporated under vacuum. Compound **1c** is purified by column chromatography (650 mg, 82% yield).

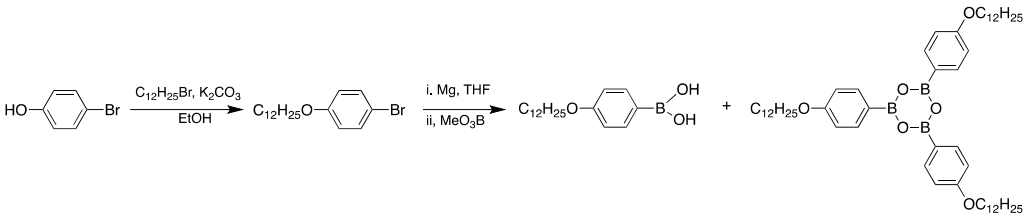
$^{1}$H NMR (400 MHz, chloroform-d) δ (ppm): 9.39 (d, 4H), 9.21 (d, 4H), 9.02 (s, 4H), 8.98 (s, 4H), 7.81 – 7.76 (t, 4H), 7.61 – 7.57 (t, 4H), 4.60 – 4.37 (m, 16H), 2.15 – 2.12 (m, 16H), 1.75 – 1.22 (m, 144H), 0.92 (s, 24H).

$^{13}$C-NMR (100 MHz, chloroform-d) δ (ppm): 149.2, 131.9, 131.0, 129.0, 128.6, 126.4, 125.9, 125.7, 125.6, 125.4, 124.0, 123.6, 121.4, 121.2, 121.0, 112.3, 111.2, 69.9, 32.4, 30.1, 26.7, 23.1, 14.5.




**Scheme S2.** Speedy synthesis of **c-OBCB 1b**.

**Synthesis of (4-(dodecyloxy)phenyl)boronic acid**



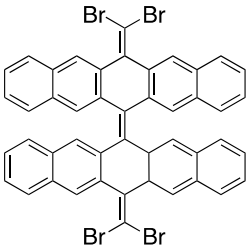

(4-(dodecyloxy)phenyl)boronic acid was prepared according to literature procedure by Cammidge, et al.[3] Boroxine derived from boronic acid exists in the product after purification, which is also reported by Pérez, et al[4],. The mixture of boronic acid and boroxine was used in the Suzuki coupling.

**Synthesis of starting materials (9) and (6)**

The synthesis of 13,13a-dihydropentacen-6(5a*H*)-one (**9**) was adapted from German literature protocol by Clar et al. [5] Compound **6** was synthesized according to a literature protocol reported by Chen et al. [6] The authors claimed the product contained a small amount of pentacenequinone. However, they mislabeled the 8.97 ppm peak, which belongs to pentacenequione, as a peak in

compound **6** in the reported $^{1}$H NMR. $^{1}$H NMR (400MHz, $CDCl_3$), δ (ppm): 8.76 (s, 4H), 7.99 (d, J=8.4 Hz, 4H), 7.56 (s, 4H), 7.46 (m, 4H), 7.30 (m, 4H), 7.11 (d, J=7.9 Hz, 4H).

**Synthesis of 13,13'-bis(dibromomethylene)-13,13a-dihydro-5a*H*,13'*H*-6,6'-bipentacenylidene**

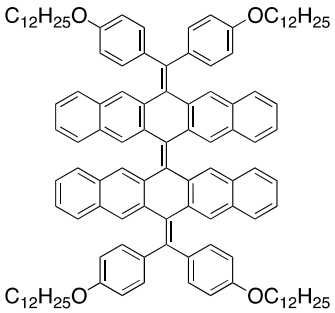



**7**

**(7)**

An oven-dried 250 mL two-necked round bottom flask with a condenser were charged with tetrabromomethane (1.66 g, 4 mmol) and triphenylphosphine (2.63 g, 10 mmol), and 50 mL of anhydrous toluene. The mixture was stirred at room temperature for 5 minutes before adding compound **6**. The reaction mixture was stirred under nitrogen at 80 $^{0}$C overnight. After cooling down, the reaction mixture was filtered under vacuum. The green solid was collected, dissolved in DCM, and MeOH was added to form yellow precipitate, which was then collected by Millipore to give the titled compound with 85% yield. $^{1}$H NMR (400 MHz, Methylene Chloride-d2) δ (ppm): 8.43 (s, 4H), 7.90 (d, *J* = 8.2 Hz, 4H), 7.63 (s, 4H), 7.48 -7.26 (m, 12H). Compound **7** was not soluble enough to obtain a $^{13}$C-NMR spectrum. Molecular Mass (Ion mode:FAB): cald for $C_{46}H_{26}Br_4$ 893.9, found [M+2H] 896.3.

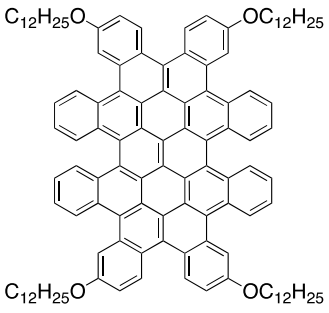
**Synsthesis of triolefin 3b**




**3b**

To a 100 mL heavy-walled round bottom flask with a screw thread cap were charged with compound **7** (180 mg, 0.2 mmol), (4-(dodecyloxy)phenyl)boronic acid (612 mg, 2 mmol), sodium carbonate (636 mg, 6 mmol), 15 mL of dimethoxyethane and 5 mL of water, the solution was bubbled for 20 minutes before adding catalyst $Pd(PPh_3)_4$ (46 mg, 0.04 mmol). The reaction mixture was stirred at 100 $^0$C for 24 hours with the cap closed. The solution was allowed to cool down, extracted with ether and the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by chromatography (1:4 DCM:Hexanes). $^1$H NMR and $^{13}$C NMR are identical as reported in the above synthesis.

**Synthesis of c-OBCB 1b**




**1b**

The photolysis setup has been previously described [1](Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *Journal of Organic Chemistry* **1991**, *56*, 3769). $^1$H NMR and $^{13}$C NMR are identical as reported in the methods above. $^1$H-NMR depends on the concentration.

$^1$H NMR of 0.001 M **c-OBCB 1b** (400 MHz, chloroform-d) δ (ppm): 9.43 – 9.36 (m, 4H), 9.28 (d, $J$ = 9.1 Hz, 4H), 9.16 – 9.09 (m, 4H), 8.96 (d, $J$ = 2.6 Hz, 4H), 7.75 (ddd, $J$ = 8.2, 6.8, 1.3 Hz, 4H),

7.59 – 7.50 (m, 8H), 4.46 (dt, *J* = 9.0, 6.5 Hz, 4H), 4.36 (dt, *J* = 8.9, 6.4 Hz, 4H), 2.04 (p, *J* = 6.5 Hz, 8H), 1.67 (p, *J* = 7.2 Hz, 8H), 1.33 – 1.23 (m, 64H), 0.93 – 0.85 (m, 12H).

$^{1}$H NMR of 0.02 M **c-OBCB 1b** (400 MHz, chloroform-d) δ (ppm): 9.32 (d, *J* = 8.3 Hz, 4H), 9.12 (d, *J* = 8.7 Hz, 8H), 8.86 (d, *J* = 2.7 Hz, 4H), 7.71 (t, *J* = 7.6 Hz, 4H), 7.53 (t, *J* = 7.6 Hz, 4H), 7.42 (dd, *J* = 9.0, 2.5 Hz, 4H), 4.39 – 4.17 (m, 8H), 1.93 (dt, *J* = 13.0, 6.4 Hz, 8H), 1.48 – 1.27 (m, 72H), 0.90 (t, *J* = 6.6 Hz, 12H).

## II. Theoretical methods of DFT calculations:

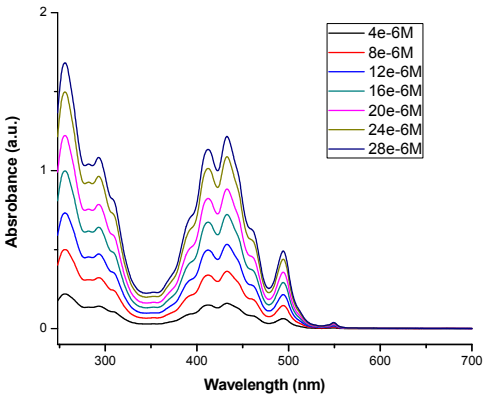
The DFT calculations were done with Jaguar (versions 5.0, 6.0 and 6.5) [Schrodinger, L.L.C., Portland, OR, 1991-2005.] Except where specified, complete geometric relaxation was performed. Thermochemistry calculations were performed with hybrid functional of Becke, B3LYP.[7] Selected calculations for **c-OBCB 1a** was done using the generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof. [8] These lead to the same conclusions concerning structure and orbital distributions described in the text. The surface DFT calculations were performed with the PBE functional using ABINIT. The ABINIT code is a common project of the Université Catholique de Louvain, C. I., and other contributors. URL: http://www.abinit.org.[9]

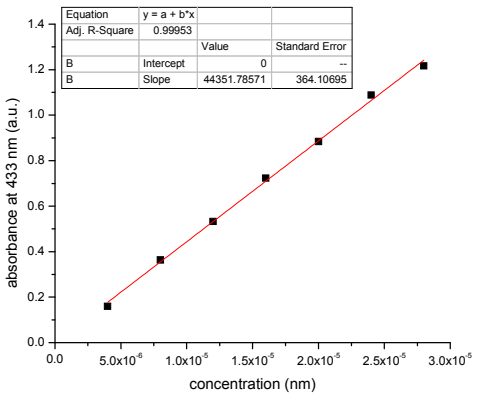
## III. X-ray diffraction.

The X-ray diffraction measurements were performed on an Inel CPS 120 diffractometer using Ni filtered Cu K□ X-rays using a solid sample holder. The instrument was calibrated using a $Y_2O_3$/Silver Behenate mixture.

## VI. UV-vis spectroscopy.

General Procedure and Instrumentation: Absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer. Stock solutions of **c-OBCB 1b** were prepared with anhydrous chloroform as solvent. A 1-cm quartz cuvette was charged with appropriate volume of blank chloroform and a background spectrum was recorded. The cuvette was charged with appropriate amount of stock solution of **c-OBCB 1b** in chloroform and an absorption spectrum was recorded. The experiment was repeated to record spectra of seven different concentrations of **c-OBCB 1b** (as listed in the graph below). Linear regression of the absorption at peak 433 nm vs. concentration was used to calculate the extinction coefficient according Beer-Lambert law A=εlc, where ε is the extinction coefficient, l is the cuvette width that equals 1cm and c is the molar concentration of the sample. The extinction coefficient of the whole spectrum was proportionate to the value at 433 nm.




**V. Fluorescence spectroscopy.**

Solution photoluminescence spectra were taken with a Jobin Yvon Fluorolog-3 Spectrofluorometer (Model FL-TAU3) from solution of **c-OBCB 1b**. The samples were excited at the wavelength of maximum absorption (433 nm), and the integration time was 2 s. The samples were made from a stock solution of **c-OBCB 1b** and a stock solution of $PC_{70}BM$. The final concentration of **c-OBCB 1b** was kept constant to be 1 $x10^{-3}$ M, and 0, 0.1, 0.3, 0.5. 1, 2, 3, 4 molar

equivalents of $PC_{70}BM$ were added to make eight samples. According to Stern-Volmer analysis, the emission intensity at 549 nm was plotted with respect to the concentration of $PC_{70}BM$ and the linear regression gives an association constant of ~5 $x10^4$ $M^{-1}$.

## VI. Cyclic Voltammetry

General Procedure and Data Analysis: Cyclic voltammetry (CV) was performed using a CHI600c potentiostat interfaced to a PC using the Chi600c electrochemical analyzer software package. The cell was a standard three-electrode setup using a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum counter electrode**.** All electrodes were purchased from Bioanalytical Systems, Inc. Measurements were carried out under argon in anhydrous dichloromethane solution with a tetrabutylammonium hexafluorophosphate as supporting electrolyte (0.1 M). All potentials were measured as the midpoint peak oxidation potential with respect to the Fc+/Fc redox couple. The scan rate in was 0.01 V/s. Calculated from the curve Figure S3, the HOMO, LUMO and band gap of **c-OBCB 1b** are -5.4 ev, -3.0 ev and 2.4 ev, respectively, by using ferrocene as the standard reference.

## References

(1) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *Journal of Organic Chemistry* **1991**, *56*, 3769.

(2) Xiao, S.; Myers, M.; Miao, Q.; Sanaur, S.; Pang, K.; Steigerwald, M. L.; Nuckolls, C. *Angewandte Chemie, International Edition* **2005**, *44*, 7390.

(3) Cammidge A. N.; Gopee, H, *J. Porphyrins Phthalocyanines* 2009; **13:** 236–246.

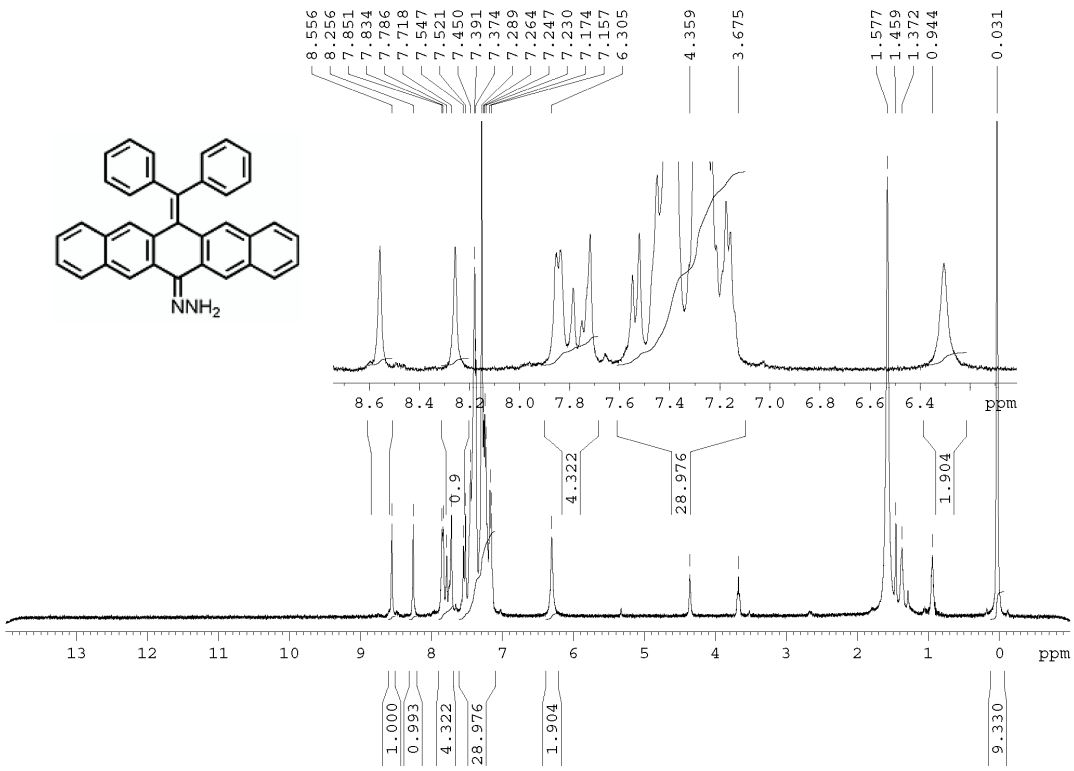
(4) Romero, C.; Peña, D.; Pérez D.; Guitián, E.; *Chemistry A European Journal* **2006,** 12, 5677 – 5684.

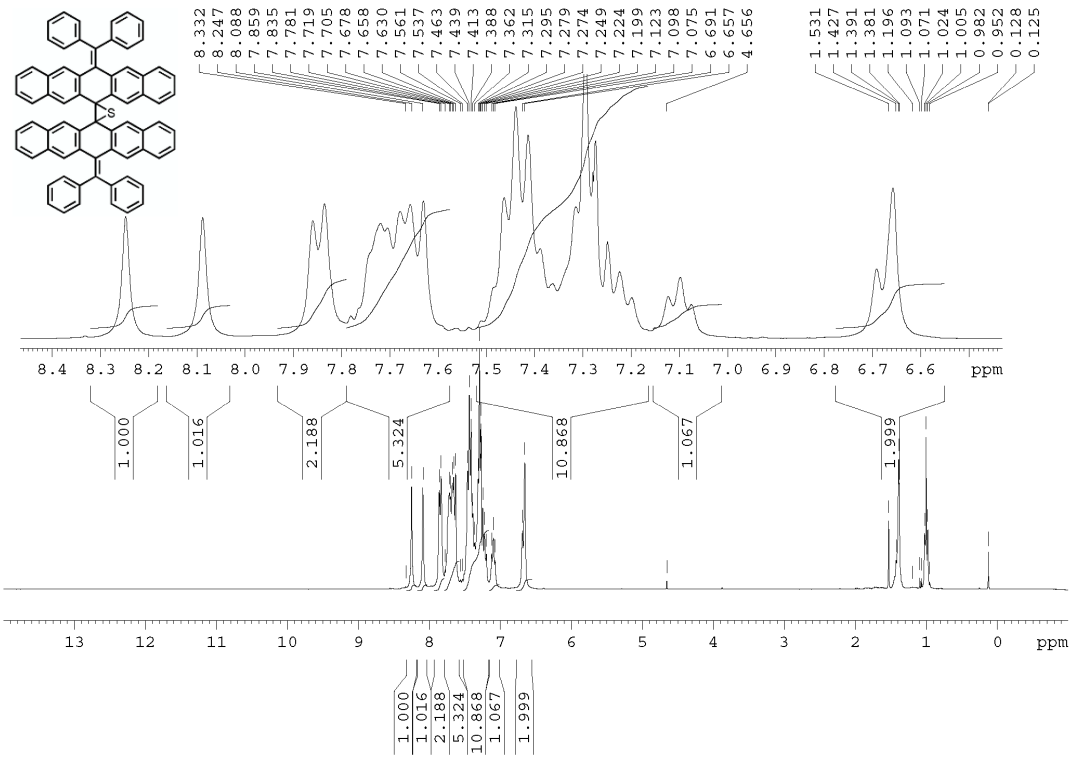
(5) Clar, E.; *Chemische Berichte*, **1949,** 82, 495-514.

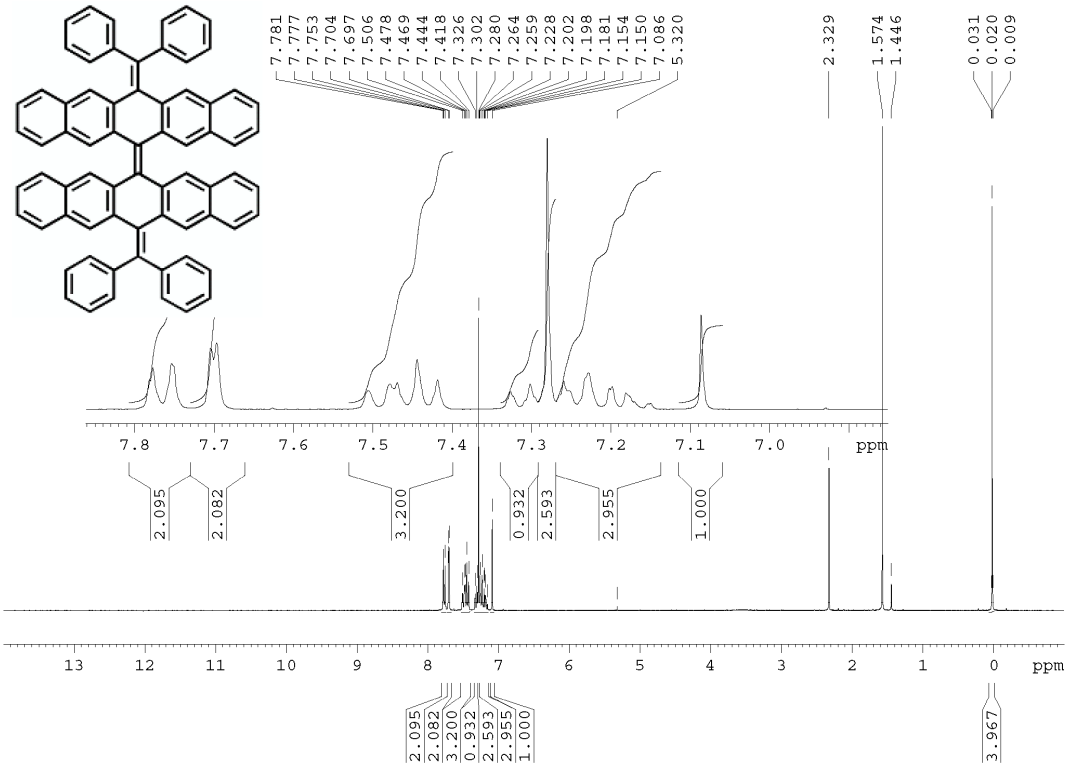
(6) Zhang, X.; Jiang, X.; Luo, J.; Chi, C.; Chen, H.; Wu, J.; *Chemistry A European Journal* **2010,** 16, 464-468

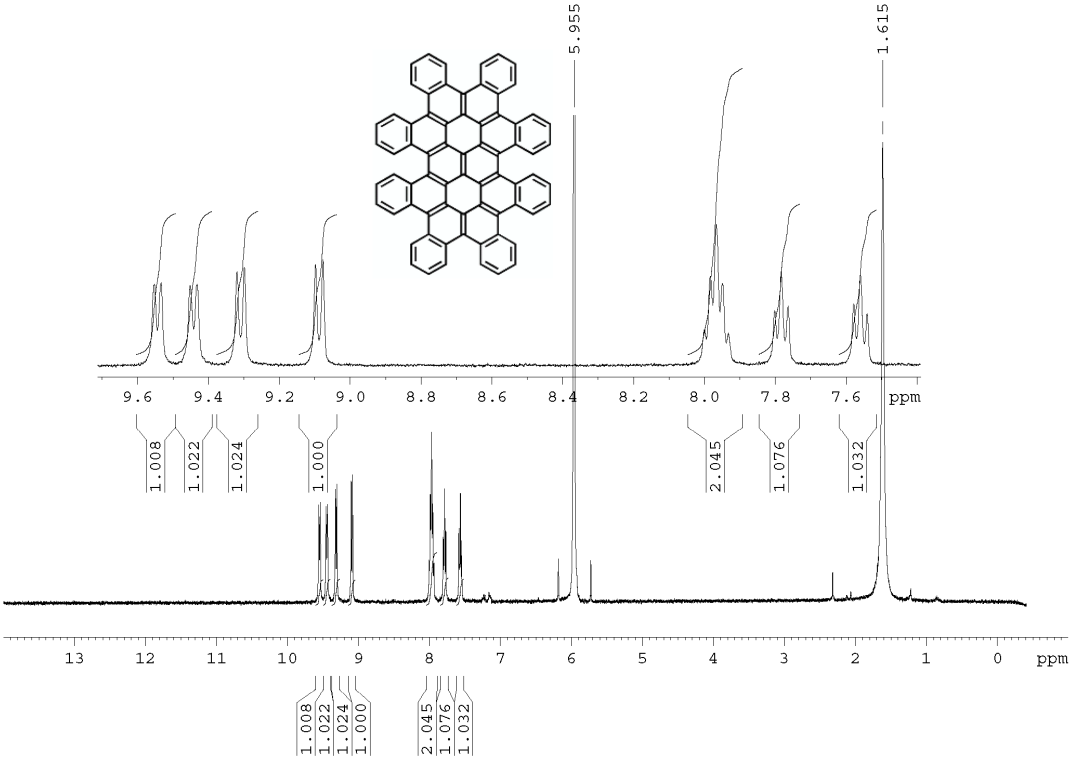
(7) Becke, A. D. *Journal of Chemical Physics* **1993**, *98*, 5648.
(8) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865.
(9) Gonze, X. *computational Materials Science* **2002**, *25*, 478.

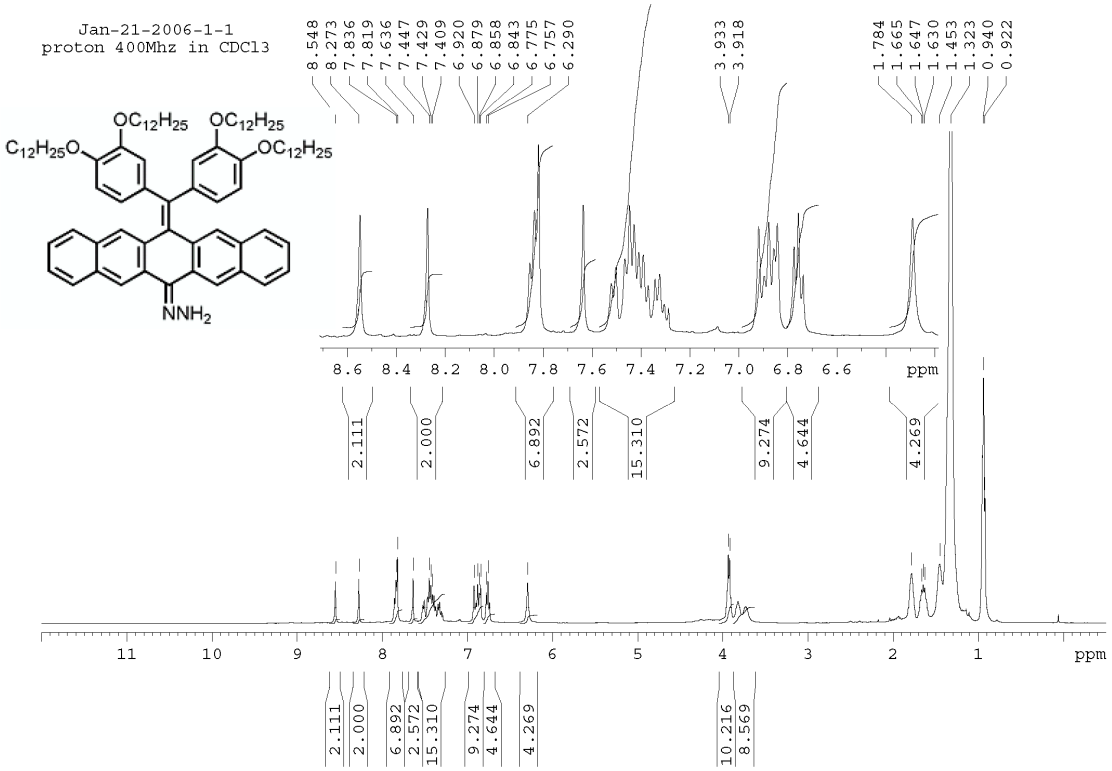
Spectra for OBCs Synthesized through Barton-Kellogg olefination


8.556
8.256
7.851
7.834
7.786
7.718
7.547
7.521
7.450
7.391
7.374
7.289
7.264
7.247
7.230
7.174
7.157
6.305
4.359
3.675
1.577
1.459
1.372
0.944
0.031
NNH2
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 ppm
0.9
4.322
28.976
1.904
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
0.993
4.322
28.976
1.904
9.330


8.332
8.247
8.088
7.859
7.835
7.781
7.719
7.705
7.678
7.658
7.630
7.561
7.537
7.463
7.439
7.413
7.388
7.362
7.315
7.295
7.279
7.274
7.249
7.224
7.199
7.123
7.098
7.075
6.691
6.657
4.656
1.531
1.427
1.391
1.381
1.196
1.093
1.071
1.024
1.005
0.982
0.952
0.128
0.125
S
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 ppm
1.000
1.016
2.188
5.324
10.868
1.067
1.999
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.000
1.016
2.188
5.324
10.868
1.067
1.999


7.781
7.777
7.753
7.704
7.697
7.506
7.478
7.469
7.444
7.418
7.326
7.302
7.280
7.264
7.259
7.228
7.202
7.198
7.181
7.154
7.150
7.086
5.320
2.329
1.574
1.446
0.031
0.020
0.009
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
2.095
2.082
3.200
0.932
2.593
2.955
1.000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.095
2.082
3.200
0.932
2.593
2.955
1.000
3.967




Jan-21-2006-1-1
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OC12H25
OC12H25
C12H25O
OC12H25
NNH2
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8.273
7.836
7.819
7.636
7.447
7.429
7.409
6.920
6.879
6.858
6.843
6.775
6.757
6.290
3.933
3.918
1.784
1.665
1.647
1.630
1.453
1.323
0.940
0.922
ppm
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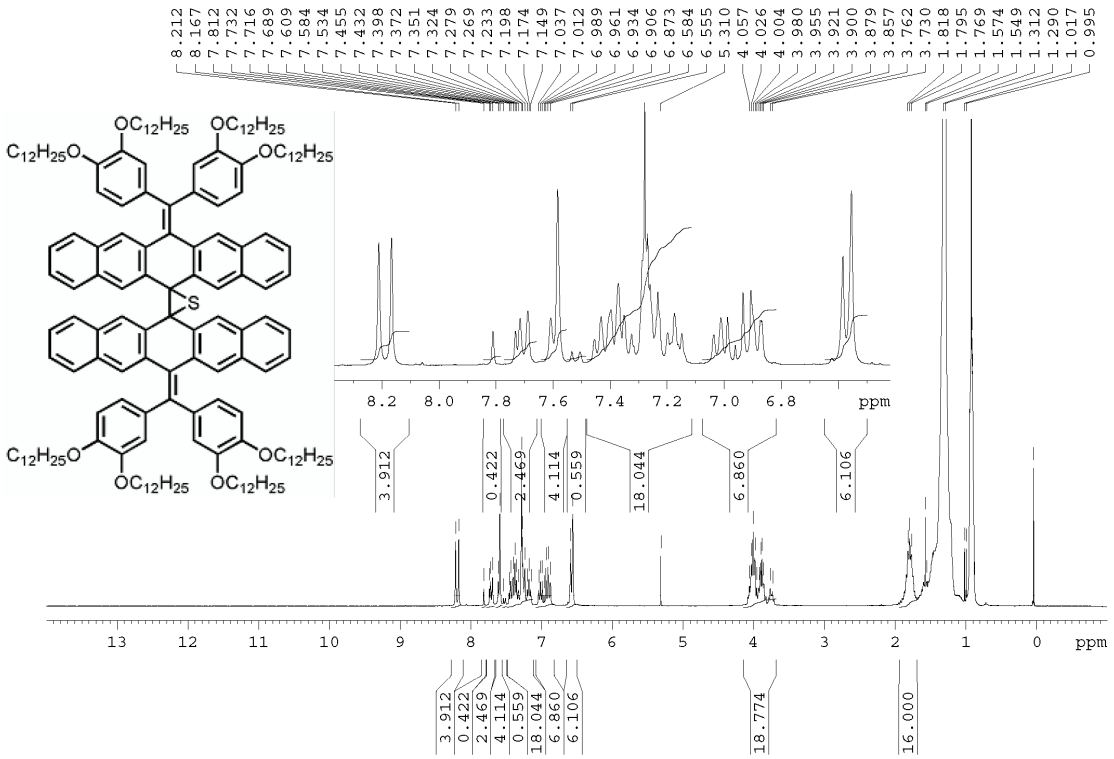
2.000
6.892
2.572
15.310
9.274
4.644
4.269
10.216
8.569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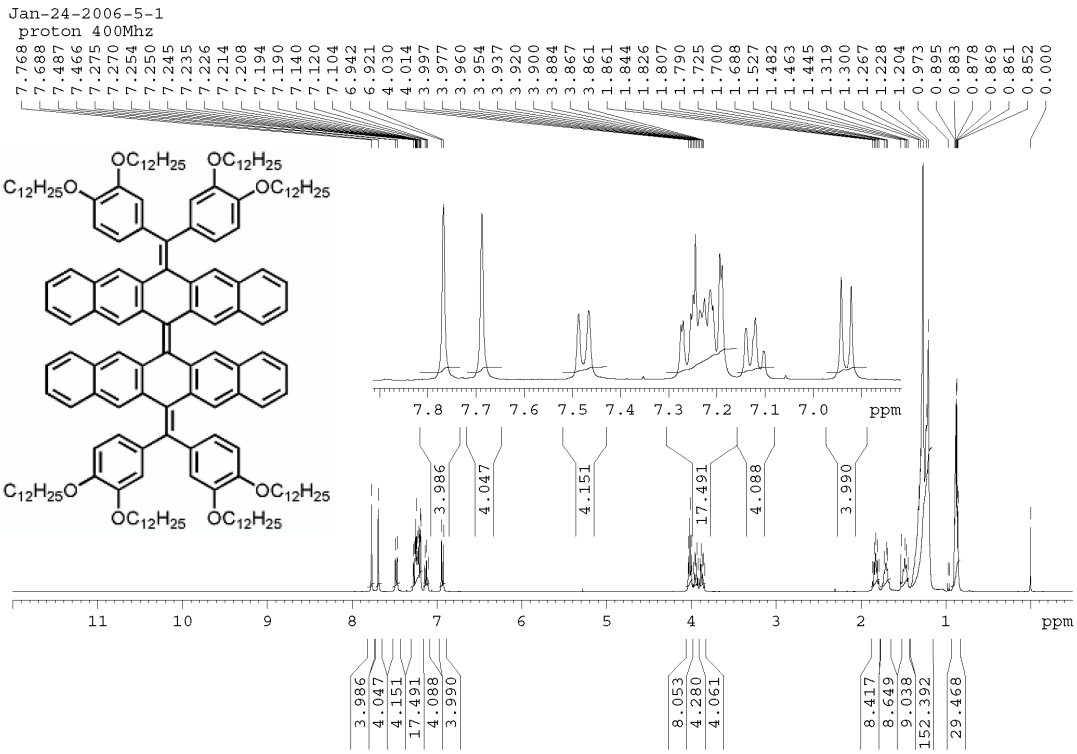
8.167
7.812
7.732
7.716
7.689
7.609
7.584
7.534
7.455
7.432
7.398
7.372
7.351
7.324
7.279
7.269
7.233
7.198
7.174
7.149
7.037
7.012
6.989
6.961
6.934
6.906
6.873
6.584
6.555
5.310
4.057
4.026
4.004
3.980
3.955
3.921
3.900
3.879
3.857
3.762
3.730
1.818
1.795
1.769
1.574
1.549
1.312
1.290
1.017
0.995
OC12H25
C12H25O
S
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
3.912
0.422
2.469
4.114
0.559
18.044
6.860
6.106
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.912
0.422
2.469
4.114
0.559
18.044
6.860
6.106
18.774
16.000


Jan-24-2006-5-1
proton 400Mhz
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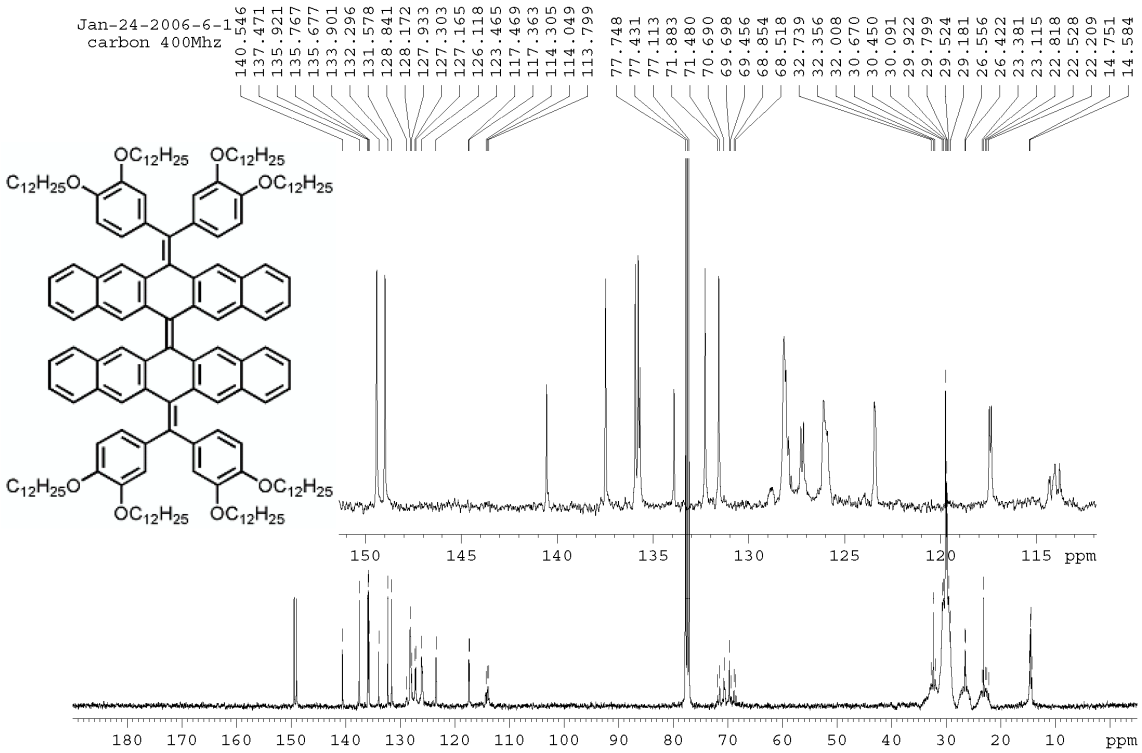
7.688
7.487
7.466
7.275
7.270
7.254
7.250
7.245
7.235
7.226
7.214
7.208
7.194
7.190
7.140
7.120
7.104
6.942
6.921
4.030
4.014
3.997
3.977
3.960
3.954
3.937
3.920
3.900
3.884
3.867
3.861
1.861
1.844
1.826
1.807
1.790
1.725
1.700
1.688
1.527
1.482
1.463
1.445
1.319
1.300
1.267
1.228
1.204
0.973
0.895
0.883
0.878
0.869
0.861
0.852
0.000
OC12H25
C12H25O
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
3.986
4.047
4.151
17.491
4.088
3.990
11 10 9 8 7 6 5 4 3 2 1 ppm
3.986
4.047
4.151
17.491
4.088
3.990
8.053
4.280
4.061
8.417
8.649
9.038
152.392
29.468


Jan-24-2006-6-1
carbon 400Mhz
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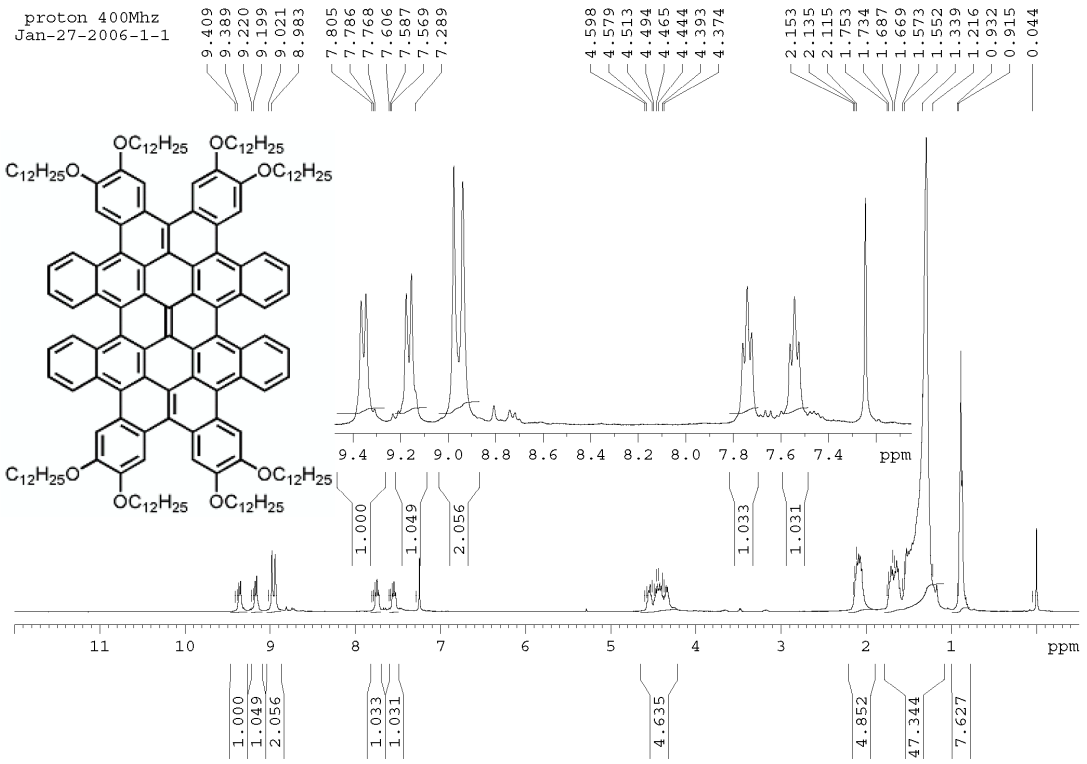
137.471
135.921
135.767
135.677
133.901
132.296
131.578
128.841
128.172
127.933
127.303
127.165
126.118
123.465
117.469
117.363
114.305
114.049
113.799
77.748
77.431
77.113
71.883
71.480
70.690
69.698
69.456
68.854
68.518
32.739
32.356
32.008
30.670
30.450
30.091
29.922
29.799
29.524
29.181
26.556
26.422
23.381
23.115
22.818
22.528
22.209
14.751
14.584
OC12H25
C12H25O
150
145
140
135
130
125
120
115 ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


proton 400Mhz
Jan-27-2006-1-1
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9.389
9.220
9.199
9.021
8.983
7.805
7.786
7.768
7.606
7.587
7.569
7.289
4.598
4.579
4.513
4.494
4.465
4.444
4.393
4.374
2.153
2.135
2.115
1.753
1.734
1.687
1.669
1.573
1.552
1.339
1.216
0.932
0.915
0.044
OC12H25
C12H25O
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 ppm
1.000
1.049
2.056
1.033
1.031
11 10 9 8 7 6 5 4 3 2 1 ppm
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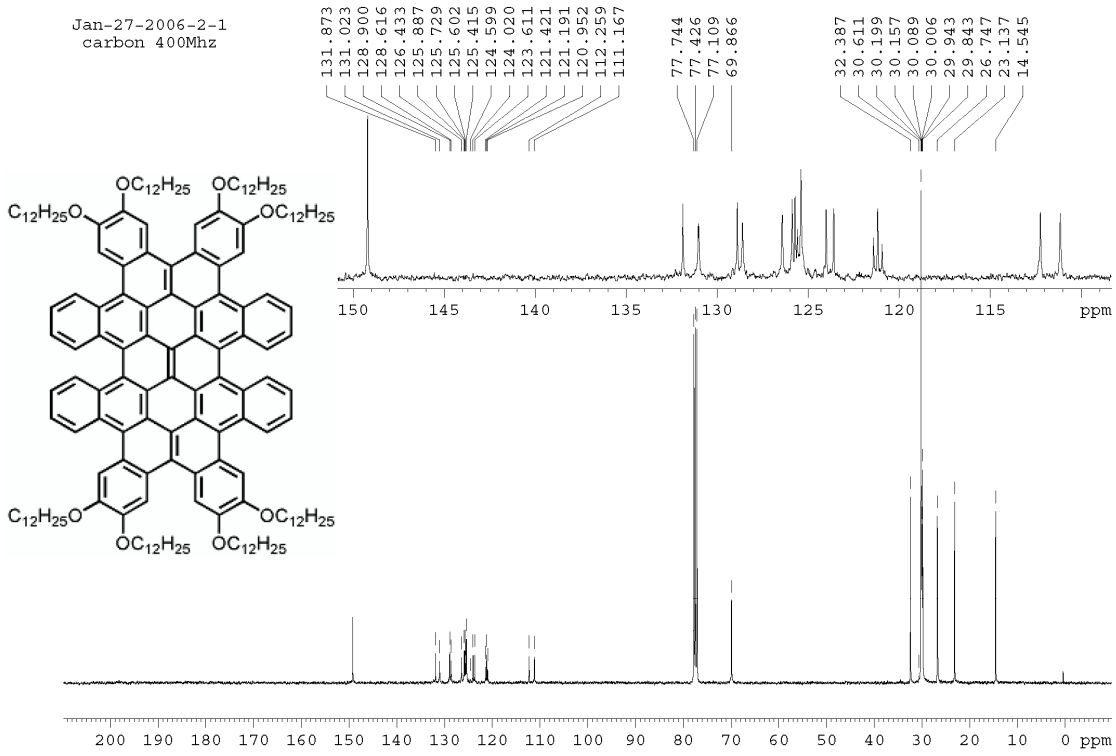
1.049
2.056
1.033
1.031
4.635
4.852
47.344
7.627


Jan-27-2006-2-1
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128.616
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125.887
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125.602
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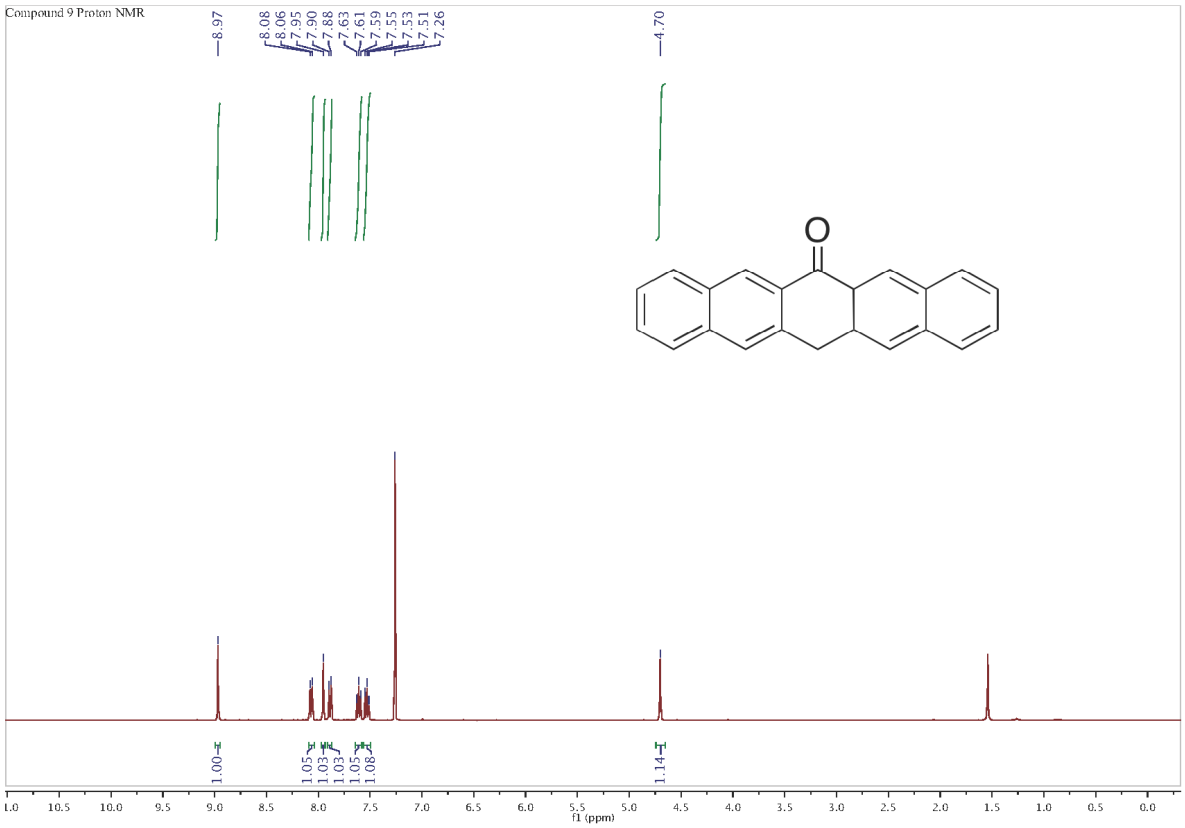
124.599
124.020
123.611
121.421
121.191
120.952
112.259
111.167
77.744
77.426
77.109
69.866
32.387
30.611
30.199
30.157
30.089
30.006
29.943
29.843
26.747
23.137
14.545
OC12H25
C12H25O
150 145 140 135 130 125 120 115 ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Spectra for OBCs Synthesized through Ramirez olefination/Suzuki coupling sequence


Compound 9 Proton NMR
8.97
8.08
8.06
7.95
7.90
7.88
7.63
7.61
7.59
7.55
7.53
7.51
7.26
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O
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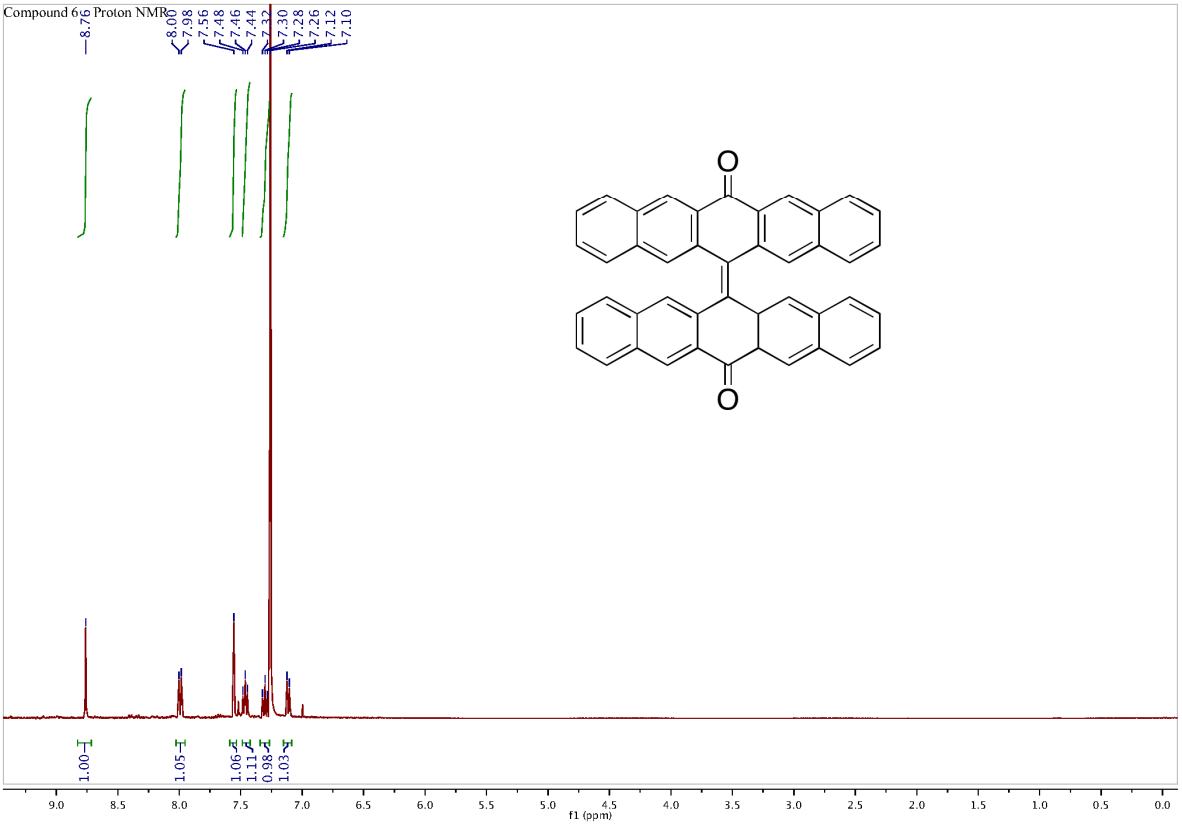
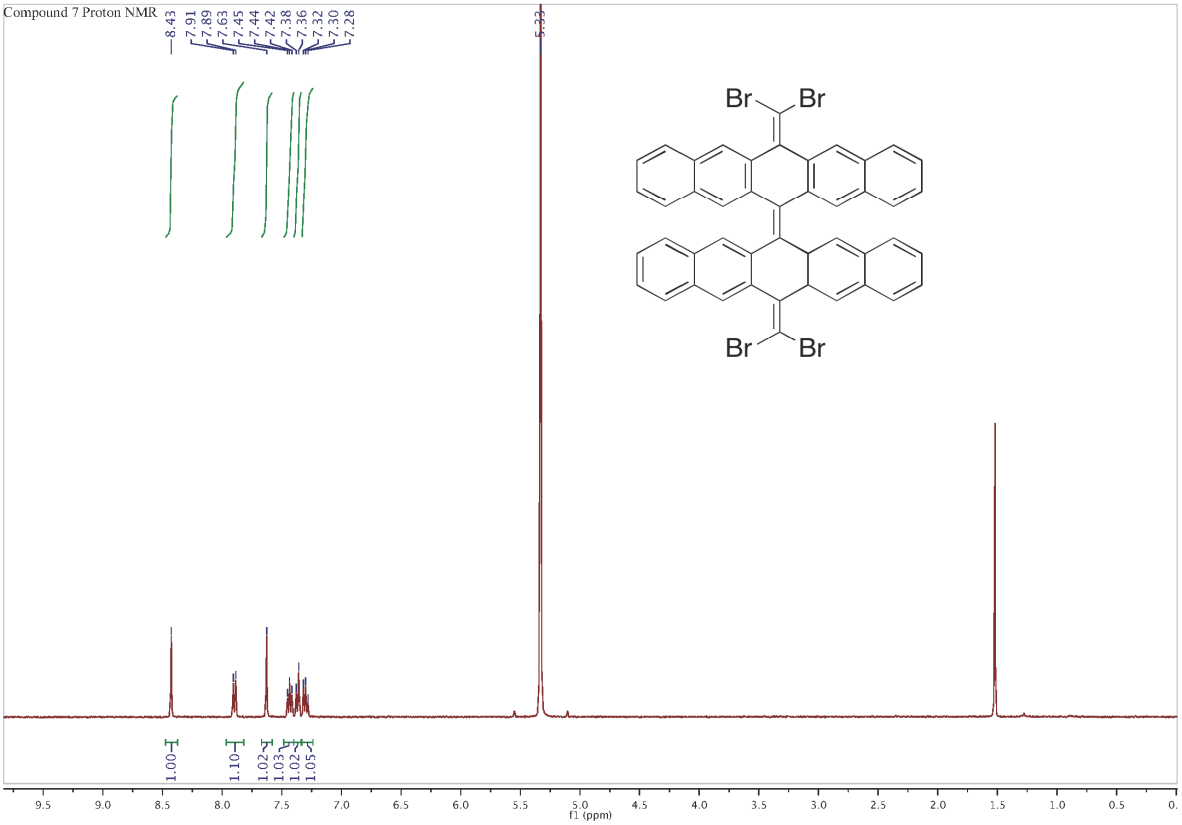
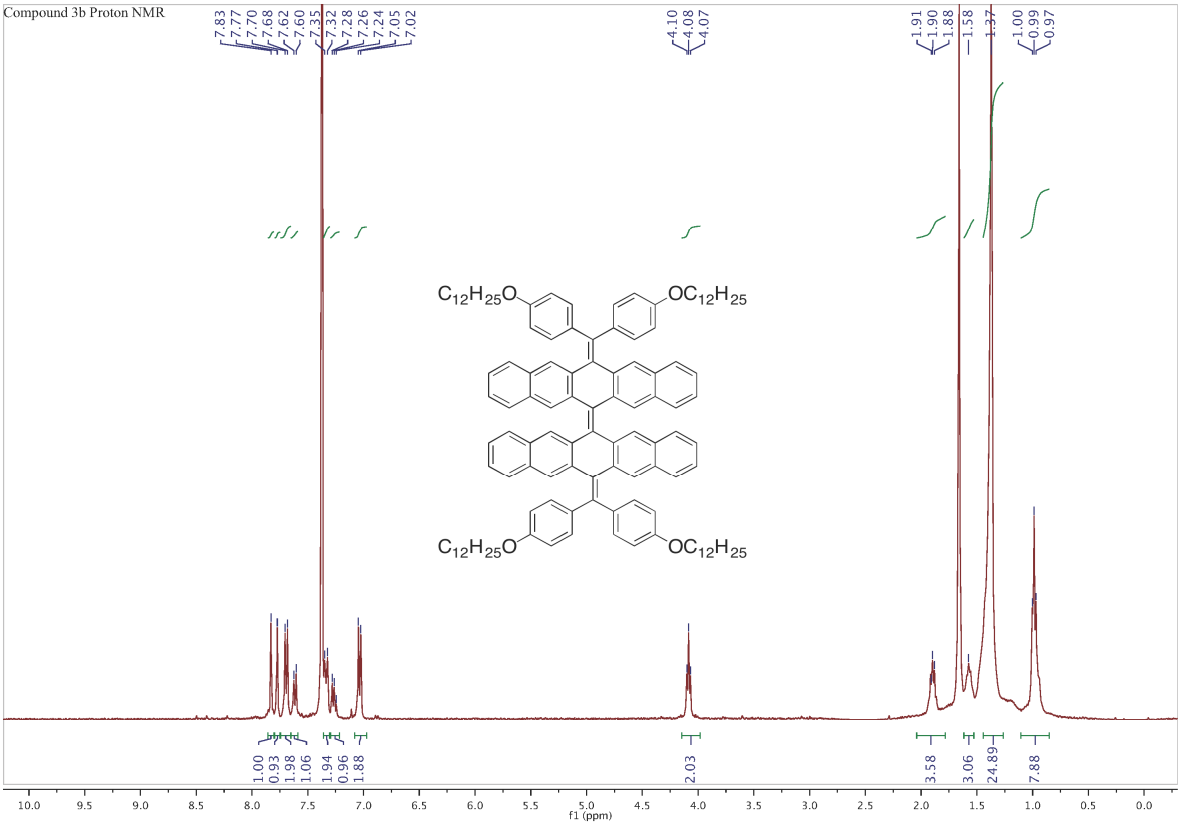
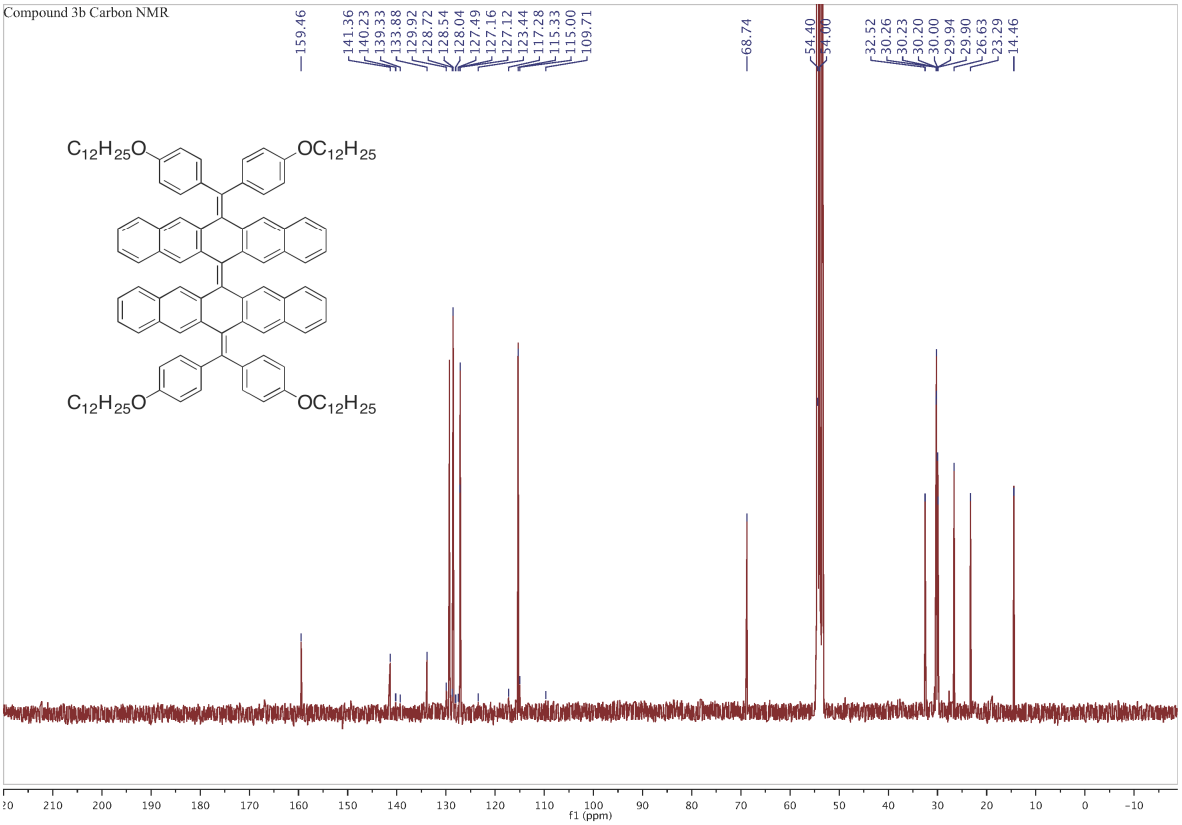
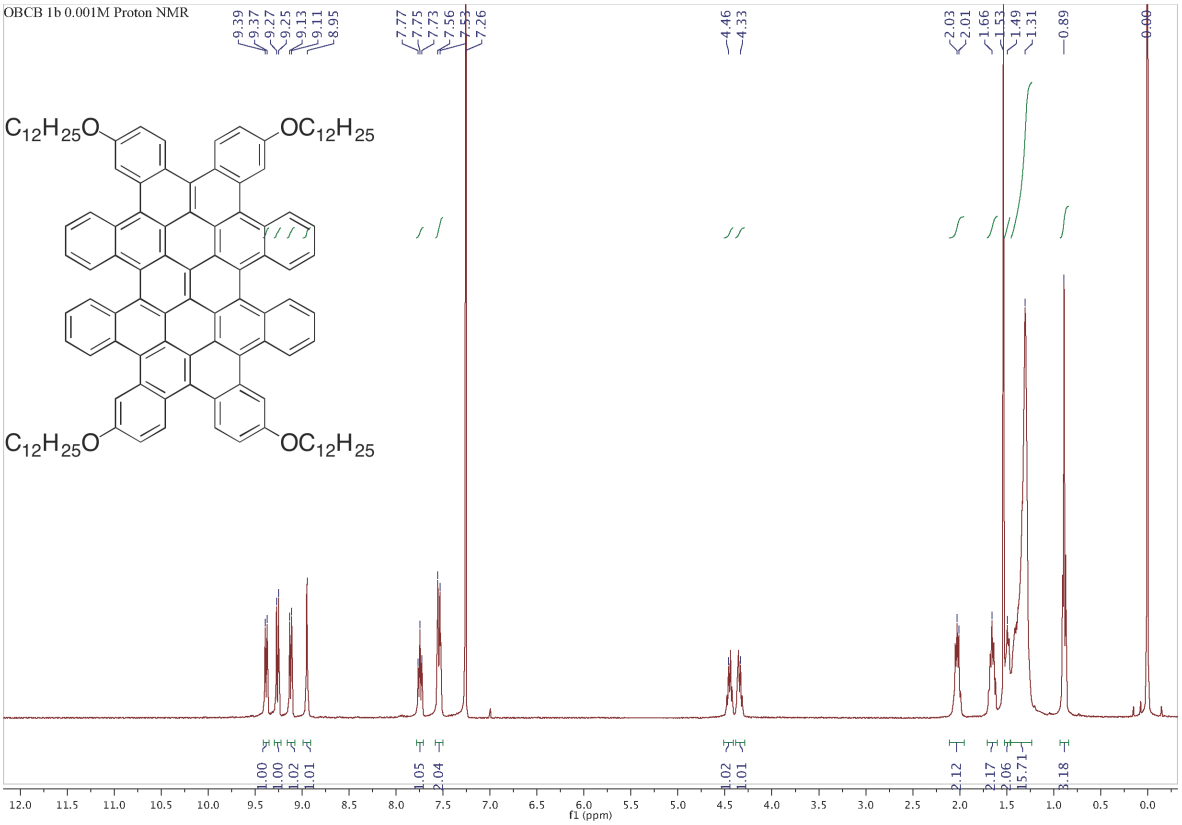
1.05
1.03
1.03
1.05
1.08
1.14
f1 (ppm)

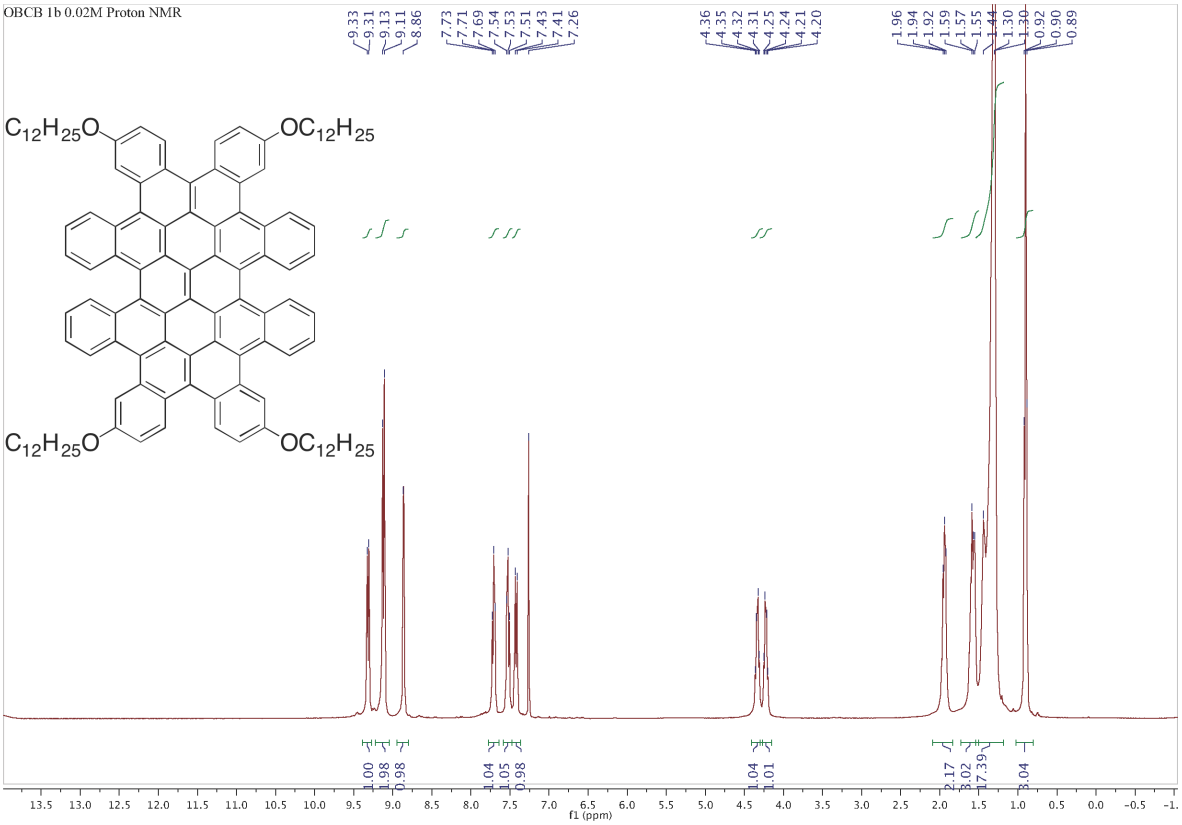

Compound 6 Proton NMR
8.76
8.00
7.98
7.56
7.48
7.46
7.44
7.32
7.30
7.28
7.26
7.12
7.10
O
O
1.00
1.05
1.06
1.11
0.98
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

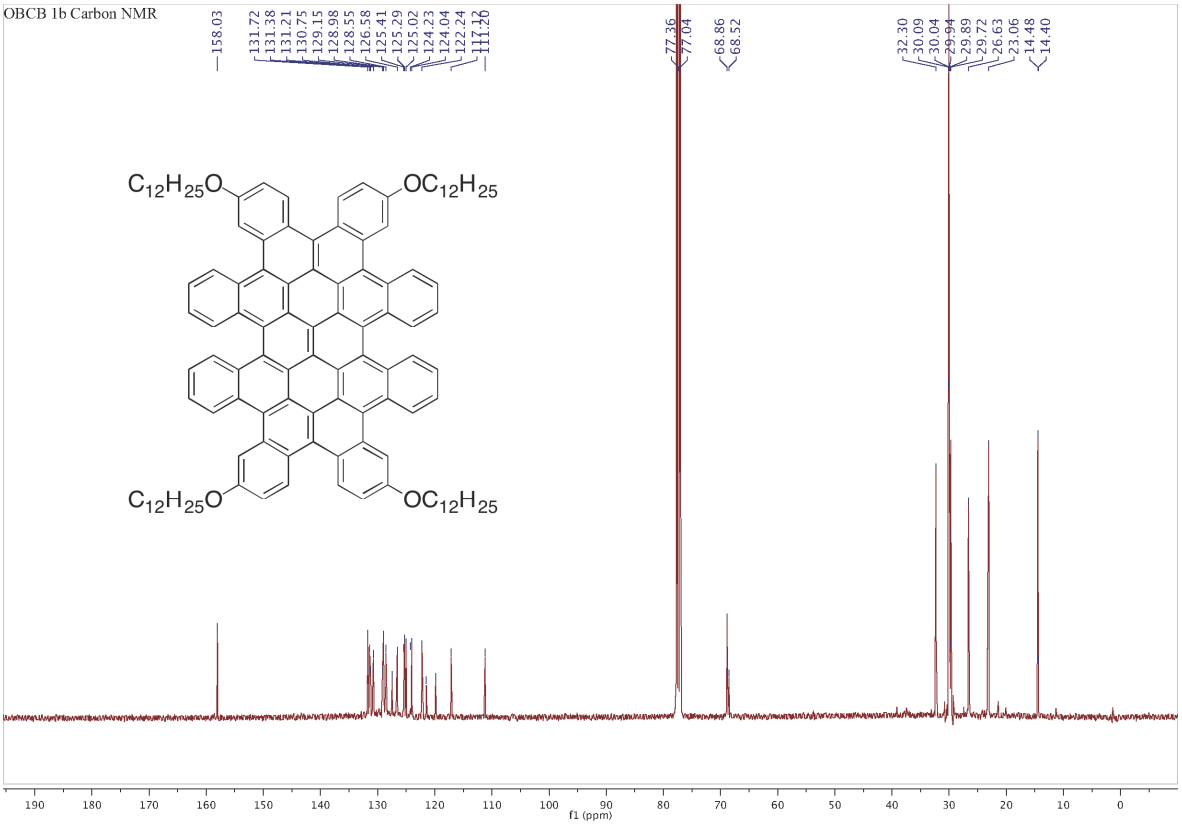

Compound 7 Proton NMR
8.43
7.91
7.89
7.63
7.45
7.44
7.42
7.38
7.36
7.32
7.30
7.28
5.33
Br
Br
Br
Br
1.00
1.10
1.02
1.03
1.02
1.05
f1 (ppm)


Compound 3b Proton NMR
7.83
7.77
7.70
7.68
7.62
7.60
7.35
7.32
7.28
7.26
7.24
7.05
7.02
4.10
4.08
4.07
1.91
1.90
1.88
1.58
1.37
1.00
0.99
0.97
C12H25O
OC12H25
C12H25O
OC12H25
1.00
0.93
1.98
1.06
1.94
0.96
1.88
2.03
3.58
3.06
24.89
7.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Compound 3b Carbon NMR
159.46
141.36
140.23
139.33
133.88
129.92
128.72
128.54
128.04
127.49
127.16
127.12
123.44
117.28
115.33
115.00
109.71
68.74
54.40
54.00
32.52
30.26
30.23
30.20
30.00
29.94
29.90
26.63
23.29
14.46
C12H25O
OC12H25
C12H25O
OC12H25
f1 (ppm)


OBCB 1b 0.001M Proton NMR
9.39
9.37
9.27
9.25
9.13
9.11
8.95
7.77
7.75
7.73
7.56
7.53
7.26
4.46
4.33
2.03
2.01
1.66
1.53
1.49
1.31
0.89
0.00
C12H25O
OC12H25
C12H25O
OC12H25
1.00
1.00
1.02
1.01
1.05
2.04
1.02
1.01
2.12
2.17
2.06
15.71
3.18
f1 (ppm)


OBCB 1b 0.02M Proton NMR
$C_{12}H_{25}O$
$OC_{12}H_{25}$
$C_{12}H_{25}O$
$OC_{12}H_{25}$
f1 (ppm)


OBCB 1b Carbon NMR
158.03
131.72
131.38
131.21
130.75
129.15
128.98
128.55
126.58
125.41
125.29
125.02
124.23
124.04
122.24
77.36
77.04
68.86
68.52
32.30
30.09
30.04
29.94
29.89
29.72
26.63
23.06
14.48
14.40
C12H25O
OC12H25
C12H25O
OC12H25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)