Electronic Supplementary Information

One-pot synthesis of sterically congested large aromatic hydrocarbons via 1,4-diphenyl-2,3-triphenylyne

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SUPPORTING INFORMATION

CONTENTS

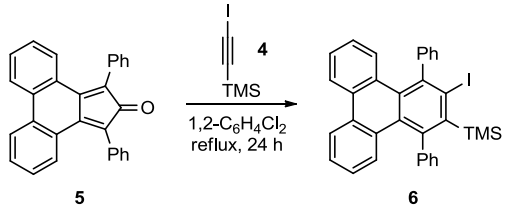
1. Experimental details and spectroscopic data

General methods

All reactions were carried out under argon using oven-dried glassware. Solvents were dried by distillation from a drying agent: THF from Na/benzophenone; CH_3CN from CaH_2. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^1H and ^{13}C NMR spectra were recorded at 250 and 63 MHz (Bruker DPX-250 instrument), 300 and 75 MHz (Varian Mercury-300 instrument) or 500 and 125 MHz (Varian Inova 500), respectively. Low-resolution electron impact mass spectra were determined at 70 eV on a HP-5988A instrument.High-resolution mass spectra (HRMS) were obtained on a Micromass Autospec spectrometer. MALDI-TOF spectra were determined on a Bruker Autoflex instrument.

Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification.

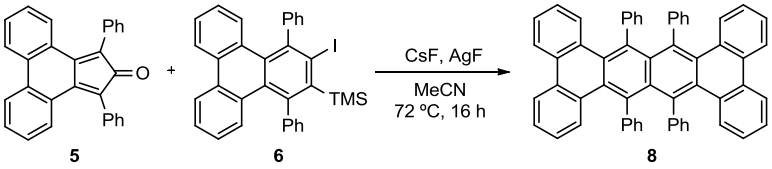
Synthesis of (3-iodo-1,4-diphenyltriphenylen-2-yl)trimethylsilane (6)



Scheme S1

A solution of cyclopentadienone **5** (600 mg, 1.58 mmol)[1] and (iodoethynyl)trimethylsilane (**4**, 352 mg, 1.58 mmol) in 1,2-dichlorobenzene (16 mL) were placed in a round bottom flask and the solution was refluxed for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 4:1 hexane/CH_2Cl_2) to isolate compound **6** (666 mg, 73%) as a white solid. ^1H NMR (250 MHz, $CDCl_3$) δ = 8.35 (dd, *J* = 7.7, 3.2 Hz, 2H), 7.50 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.46-7.29 (m, 12H), 7.24 (m, 1H), 7.05 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 6.94 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 0.16 (s, 9H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.5 (C), 147.2 (C), 145.4 (C), 144.5 (C), 142.5 (C), 132.8 (2CH), 132.6 (2CH), 131.9 (C), 131.7 (C), 130.7 (C), 130.3 (C), 130.2 (CH), 129.9 (C), 129.8 (CH), 129.1 (2CH), 128.9 (2CH), 128.3 (CH), 128.0 (CH), 127.1 (CH), 126.5 (CH), 125.9 (CH), 125.4 (CH), 123.4 (CH), 123.2 (CH), 112.0 (C), 3.5 ($3CH_3$) ppm.

Synthesis of 9,10,19,20-tetraphenyltetrabenzo*[a,c,j,l]*tetracene (8)

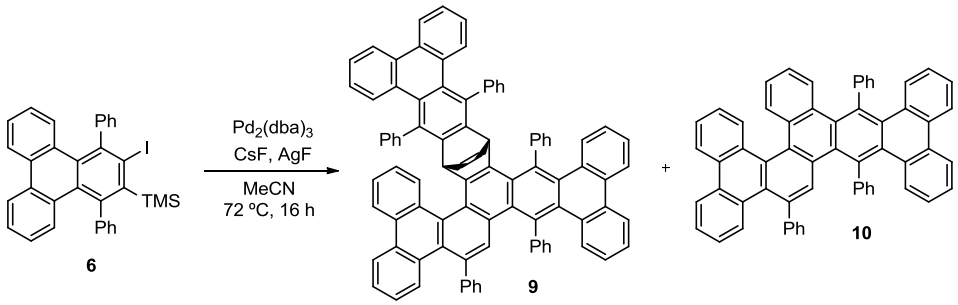


Scheme S2

Finely powdered anhydrous CsF (131 mg, 0.862 mmol) and AgF (65 mg, 0.512 mmol) were added to a solution of iodoarene **6** (100 mg, 0.173 mmol) and cyclopentadienone **5** (100 mg, 0.262 mmol) in CH_3CN (6 mL). The mixture was refluxed under argon for 16 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 4:1 hexane/CH_2Cl_2) to isolate compound **8** (22 mg, 18%) as a greenish solid. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 7.9 Hz, 4H), 7.27 (ddd, *J* = 8.3, 6.5, 1.9 Hz, 4H), 7.01 (m, 8H), 6.96 (m, 4H), 6.82-6.70 (m, 16H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8 (4C), 134.6 (2C), 134.5 (4C), 133.8 (4CH), 133.7 (4CH), 132.5 (4C), 132.0 (4C), 130.2 (4CH), 129.0 (4C), 128.6 (4CH), 128.2 (4CH), 126.8 (8CH), 125.6 (4CH), 123.6 (4CH) ppm. HRMS (MALDI-TOF) for $C_{58}H_{36}$, calculated: 732.28, found 732.29.

[1] Wooi, G. Y.; White, J. M. *Org. Biomol. Chem.*, 2005, **3**, 972.

Synthesis of polyarenes 9 and 10



Scheme S3

Finely powdered anhydrous CsF (131 mg, 0.862 mmol) and AgF (65 mg, 0.512 mmol) were added to a solution of iodoarene **6** (100 mg, 0.173 mmol) and $Pd_2(dba)_3$ (7.9 mg, 8.65 µmol) in CH_3CN (6 mL). The mixture was refluxed under argon for 16 h. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 4:1 hexane/CH_2Cl_2) to isolate compounds **10** (20 mg, 31%) and **9** (18 mg, 28%) as greenish solids. Data for **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 7.7 Hz, 1H), 8.50 (d, *J* = 7.6 Hz, 1H), 8.26 (dd, *J* = 7.9, 3.2 Hz, 2H), 8.19 (m, 2H), 7.97 (m, 1H), 7.75 (s, 1H), 7.70 (m, 2H), 7.67-7.60 (m, 4H), 7.60-7.53 (m, 4H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.40 (m, 2H), 7.37-7.24 (m, 7H), 7.23-7.12 (m, 6H), 7.07 (m, 4H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.92-6.82 (m, 6H), 6.77 (m, 2H), 6.70 (m, 3H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.35 (dd, *J* = 5.5, 1.4 Hz, 1H), 4.96 (dd, *J* = 5.9, 1.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$)[2] δ = 146.13 (C), 145.30 (C), 144.87 (C), 143.78 (C), 143.06 (C), 142.60 (C), 141.82 (C), 141.70 (C), 141.10 (C), 140.60 (CH), 139.08 (CH), 134.60 (C), 133.95 (CH), 133.93 (C), 133.87 (CH), 133.26 (CH), 133.04 (CH), 132.94 (C), 132.77 (C), 132.12 (C), 132.09 (C), 131.98 (C), 131.62 (C), 131.49 (C), 131.28 (CH), 131.23 (C), 131.20 (C), 131.02 (C), 130.89 (CH), 130.75 (C), 130.72 (C), 130.70 (C), 130.56 (CH), 130.25 (CH), 130.23 (CH), 130.18 (C), 130.16 (CH), 130.08 (CH), 129.93 (C), 129.88 (CH), 129.41 (C), 129.37 (CH), 129.31 (C), 128.99 (CH), 128.49 (C), 127.93 (CH), 127.86 (C), 127.59 (C), 127.48 (CH), 126.87 (CH), 126.78 (CH), 126.75 (CH), 126.47 (CH), 126.31 (CH), 126.18 (CH), 125.72 (CH), 125.68 (CH), 125.61 (CH), 125.22 (CH), 125.10 (CH), 125.00 (CH), 124.61 (C), 123.65 (CH), 123.52 (CH), 123.43 (CH), 123.38 (CH), 123.00 (CH), 48.76 (CH), 48.31 (CH) ppm. HRMS (MALDI-TOF) for $C_{90}H_{54}$, calculated: 1134.42, found: 1134.33. Data for **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.48 (dd, *J* = 7.8, 4.7 Hz, 2H), 8.36 (dd, *J* = 7.9, 4.2 Hz, 2H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.70-7.65 (m, 2H), 7.62 (d, *J* = 5.2 Hz, 1H), 7.55 (m, 3H), 7.51-7.42 (m, 6H), 7.39 (m, 4H), 7.33-7.26 (m, 2H), 7.23-7.17 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.03-6.92 (m, 4H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.22 (C), 143.71 (C), 143.22 (C), 136.32 (C), 134.34 (C), 133.90 (CH), 133.86 (CH), 133.74 (CH), 133.67 (CH), 133.51 (C), 132.67 (C), 132.09 (C), 132.08 (C), 131.76 (C), 131.61 (C), 131.49 (C), 131.44 (C), 131.33 (C), 131.30 (CH), 131.19 (CH), 130.95 (C), 130.94 (C), 130.68 (C), 130.61 (CH), 130.36 (CH), 130.32 (C), 130.28 (CH), 130.25 (C), 130.22 (CH), 130.19 (C), 130.17 (C), 130.06 (CH), 129.98 (CH), 129.86 (CH), 129.78 (CH), 129.39 (CH), 128.12 (CH), 127.99 (CH), 127.00 (CH), 126.93 (CH), 126.79 (2CH), 126.63 (CH), 125.70 (CH), 125.57 (2CH), 125.40 (CH), 125.35 (CH), 125.05 (CH), 123.79 (CH), 123.61 (CH), 123.49 (CH), 123.30 (CH) ppm. HRMS (MALDI-TOF) for $C_{60}H_{36}$, calculated: 756.28, found: 756.22.

[2] Due to the large number of aromatic carbons, several signals overlap in the ^{13}C NMR spectrum.

2. X-ray structures [3]

Cambridge Crystallographic Data Centre (CCDC) 876805 and 876806 records contain the supplementary crystallographic data for compounds **8** and **9**, respectively. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk

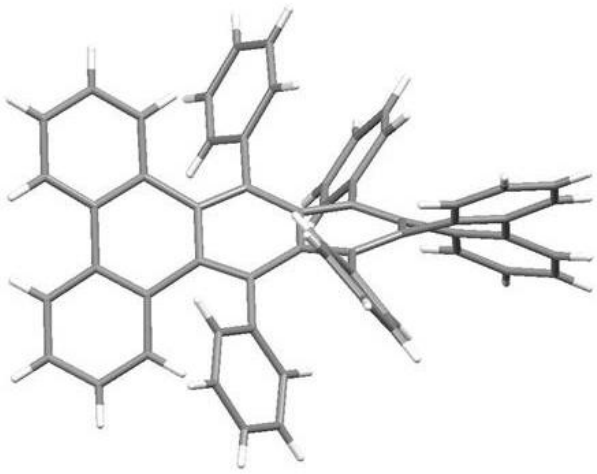


Figure S1

Summary of Data CCDC 876805
Formula: $C_{58}H_{36}$
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space group C2/c

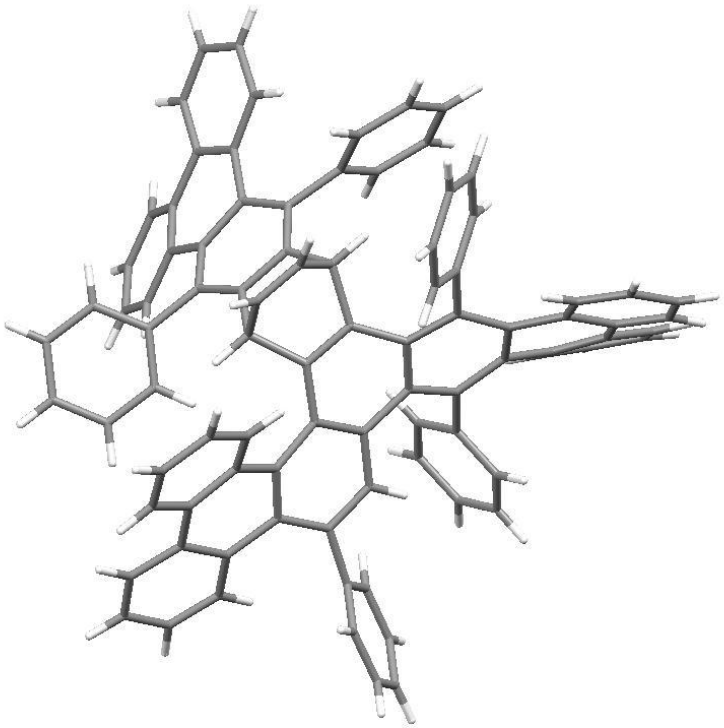
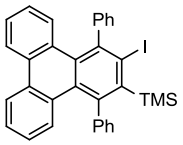


Figure S2

Summary of Data CCDC 876806
Formula: $C_{90}H_{54}$
Unit cell parameters: a 16.4992(4) b 17.0089(3) c 27.7954(6)
alpha 94.7510(10) beta 92.7850(10) gamma 118.860(5)
space group P-1

[3] Technical support from *Unidade de Raios X, Edificio CACTUS, Universidade de Santiago de Compostela*, is gratefully acknowledged.

3. ^{1}H and ^{13}C NMR spectra



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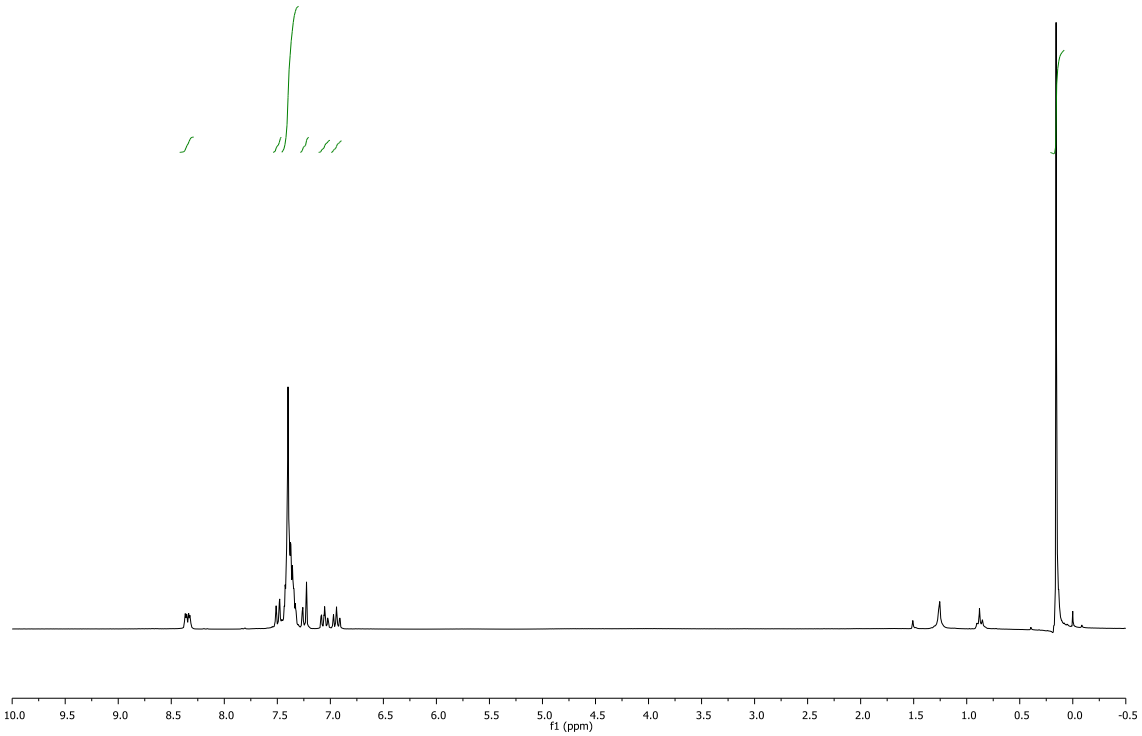
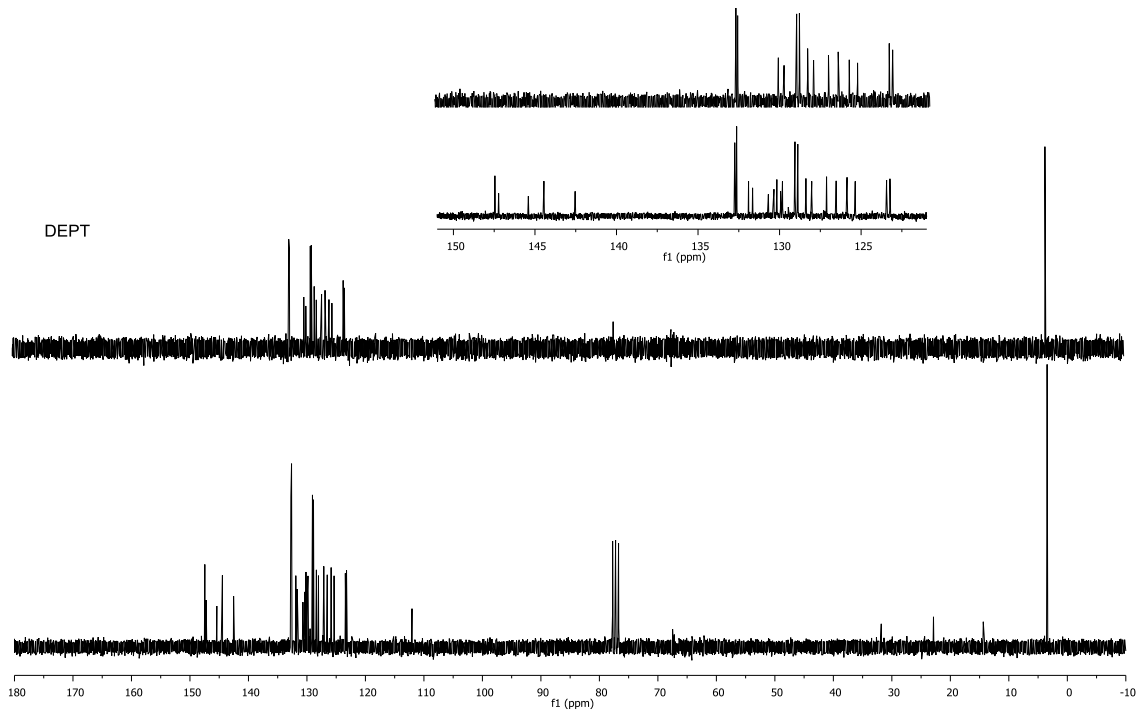
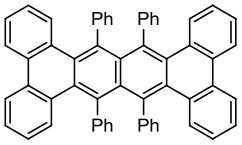
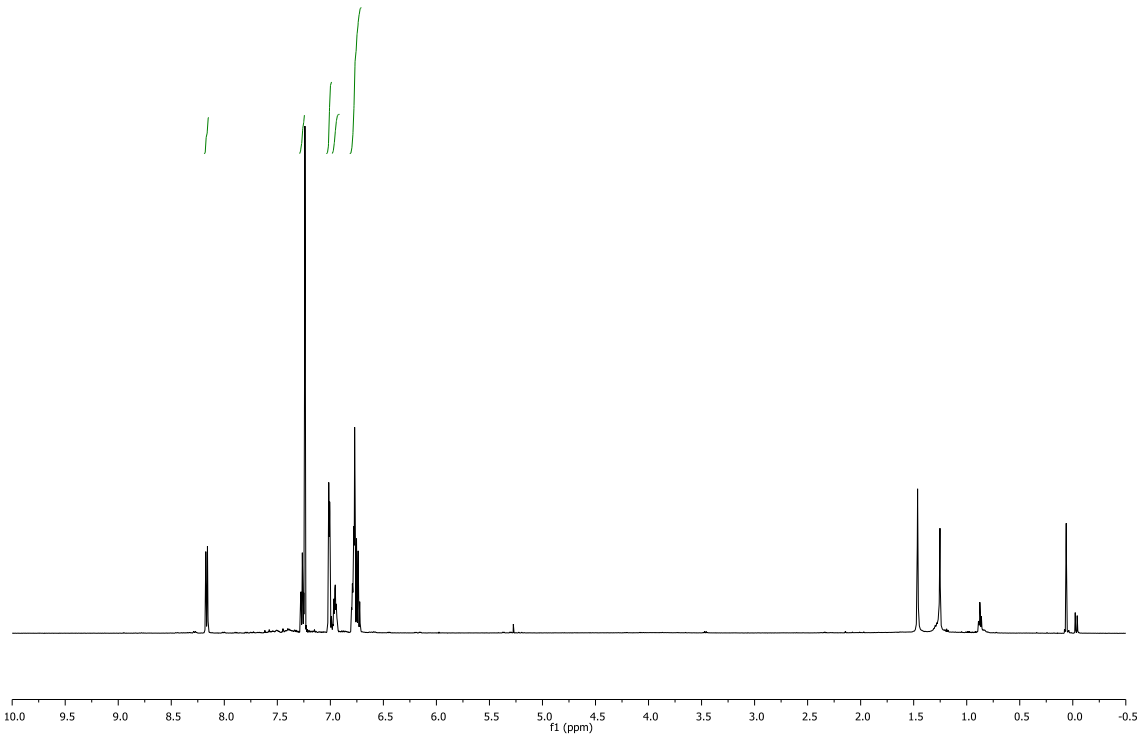
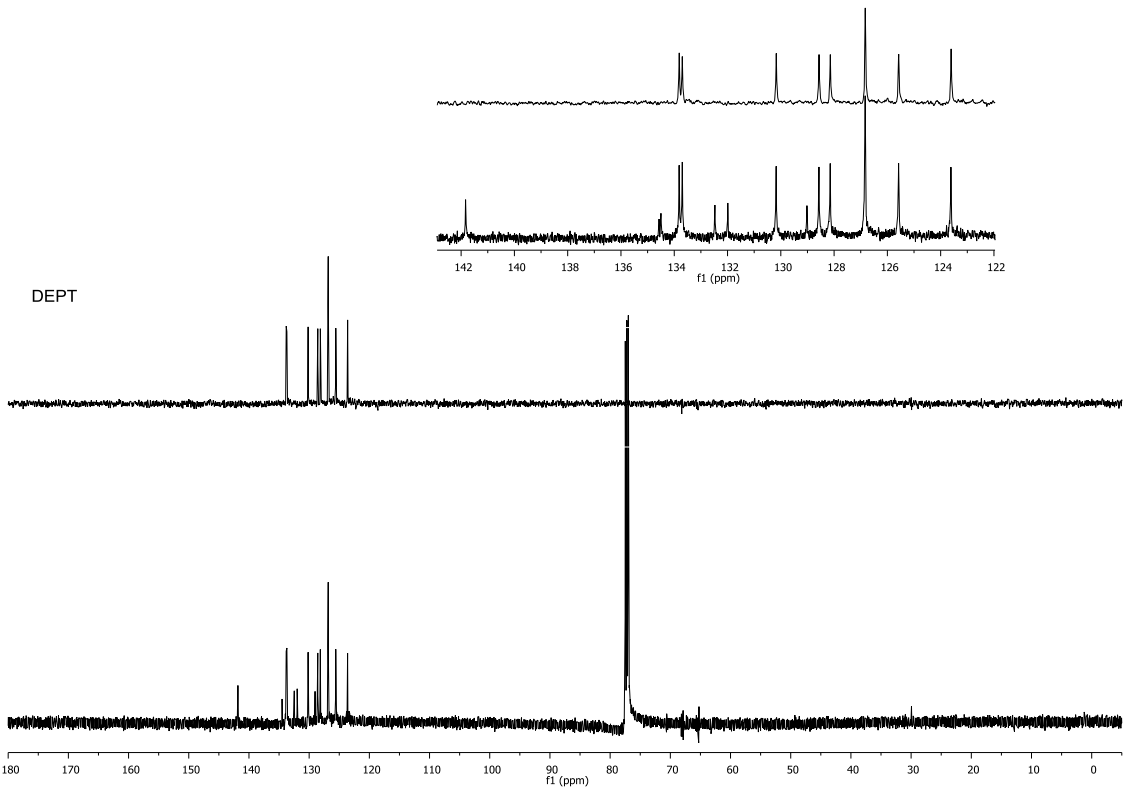





Ph
Ph
Ph
Ph

8


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 -0.5
f1 (ppm)


142 140 138 136 134 132 130 128 126 124 122
f1 (ppm)
DEPT
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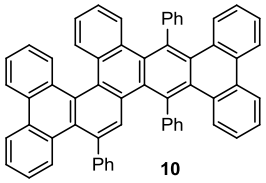
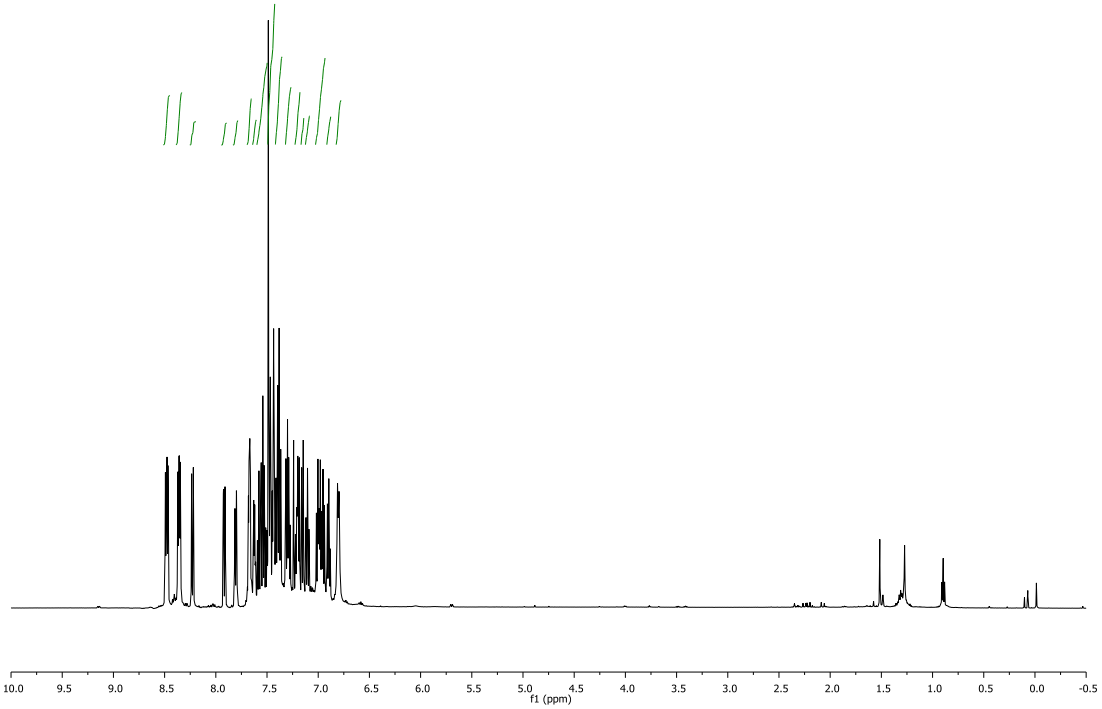
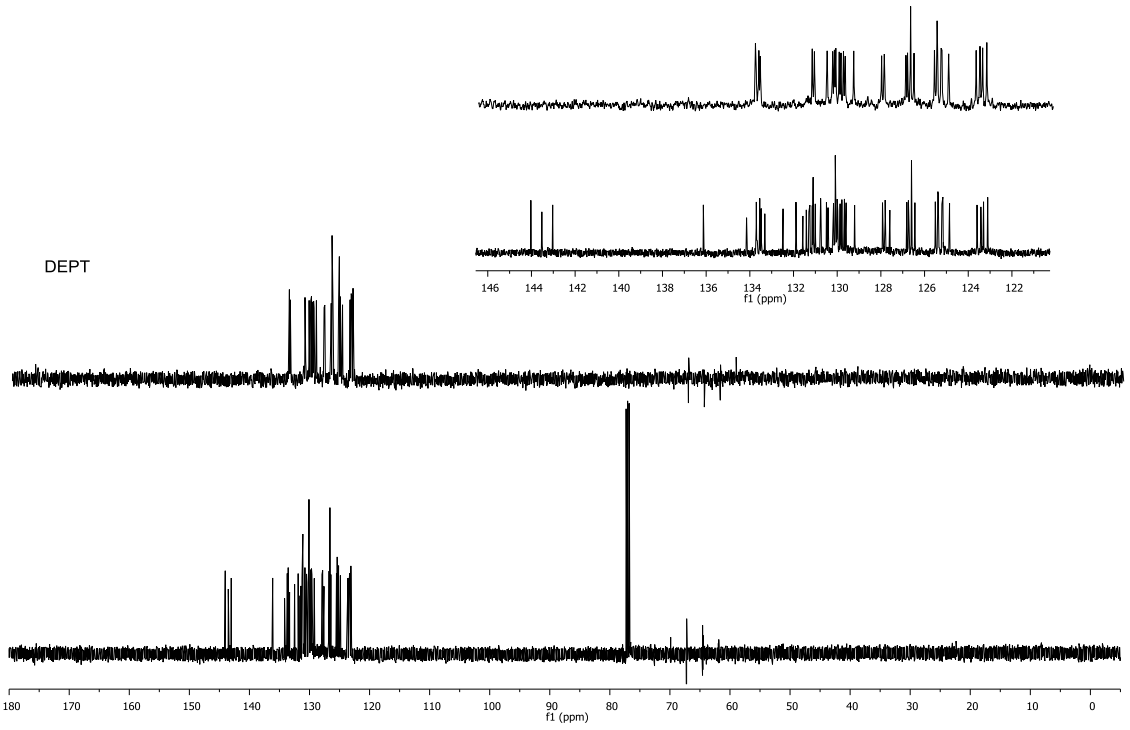
f1 (ppm)


Ph
Ph
Ph

10


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 -0.5
f1 (ppm)


DEPT
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f1 (ppm)
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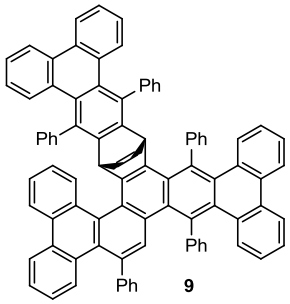
f1 (ppm)



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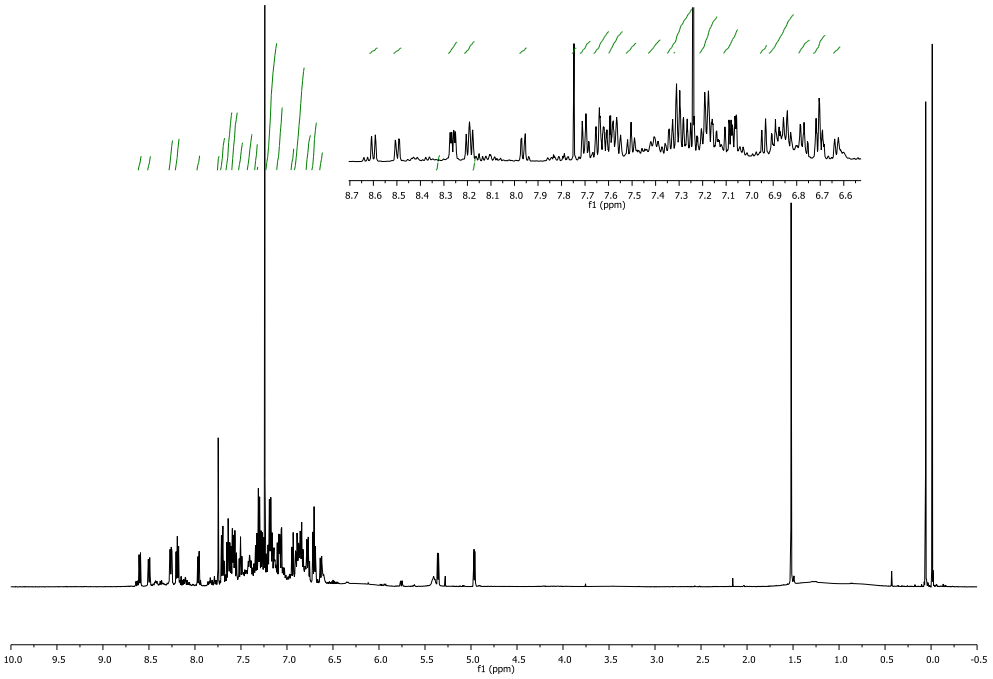

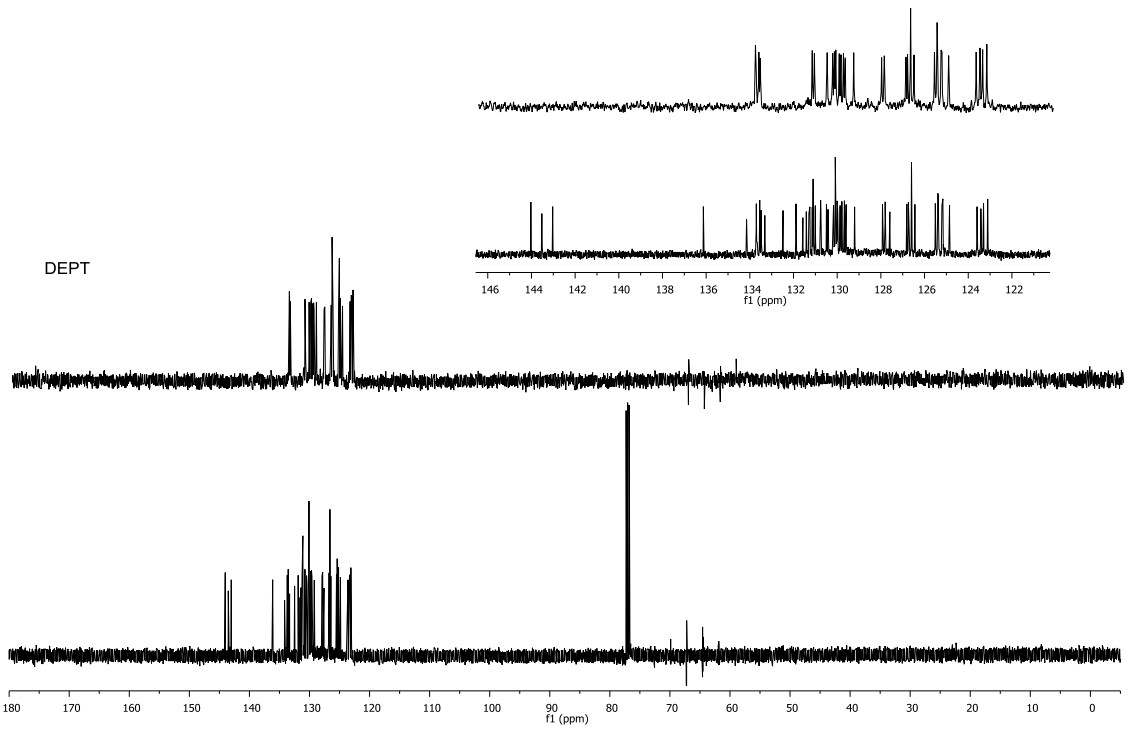

4. Absorption-Emission spectra

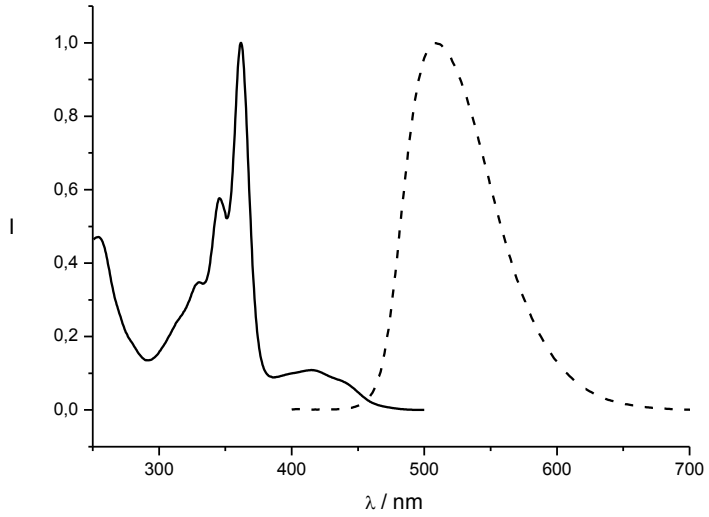

Figure S3. Absorption (solid line) and emission (dashed line) spectra of **8** in CH_2Cl_2.

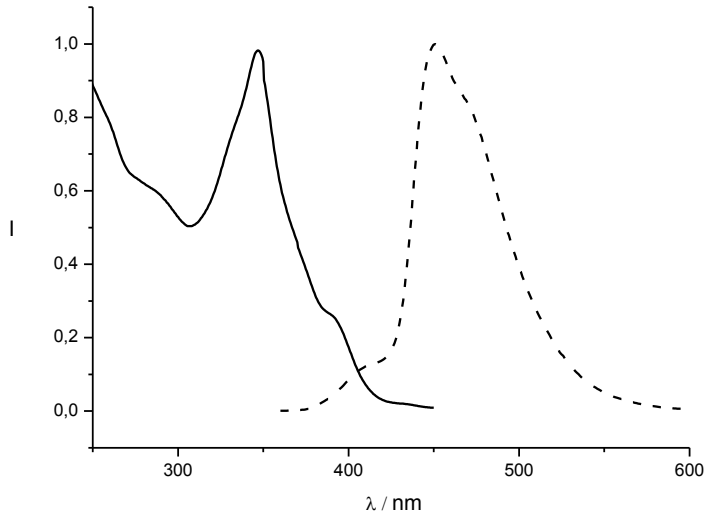

Figure S4. Absorption (solid line) and emission (dashed line) spectra of **10** in CH_2Cl_2.

5. Voltammograms of hydrocarbons 8 and 10

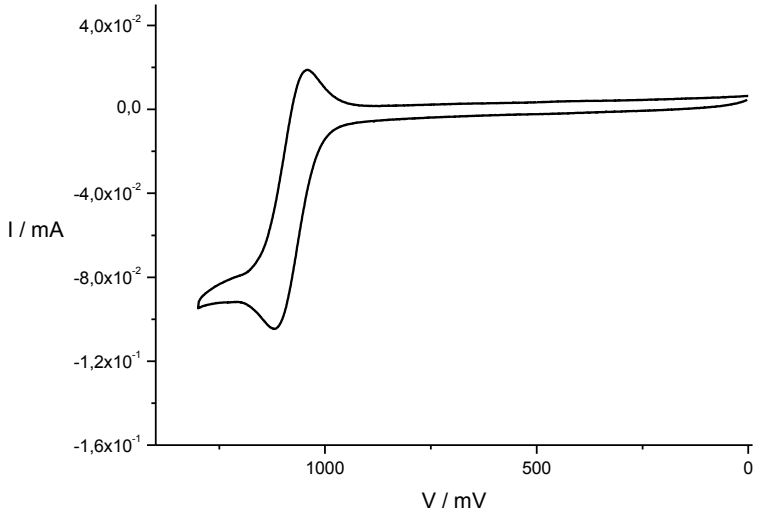

Figure S5. Cyclic voltammogram of hydrocarbon **8** in CH_2Cl_2 (0.1 mM).

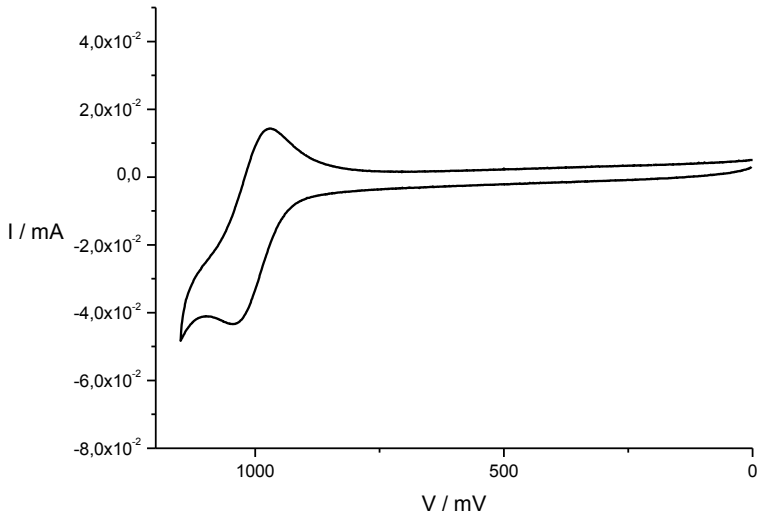

Figure S6. Cyclic voltammogram of hydrocarbon **10** in CH_2Cl_2 (0.1 mM).

6. Chromatogram of compound 8 by chiral-HPLC

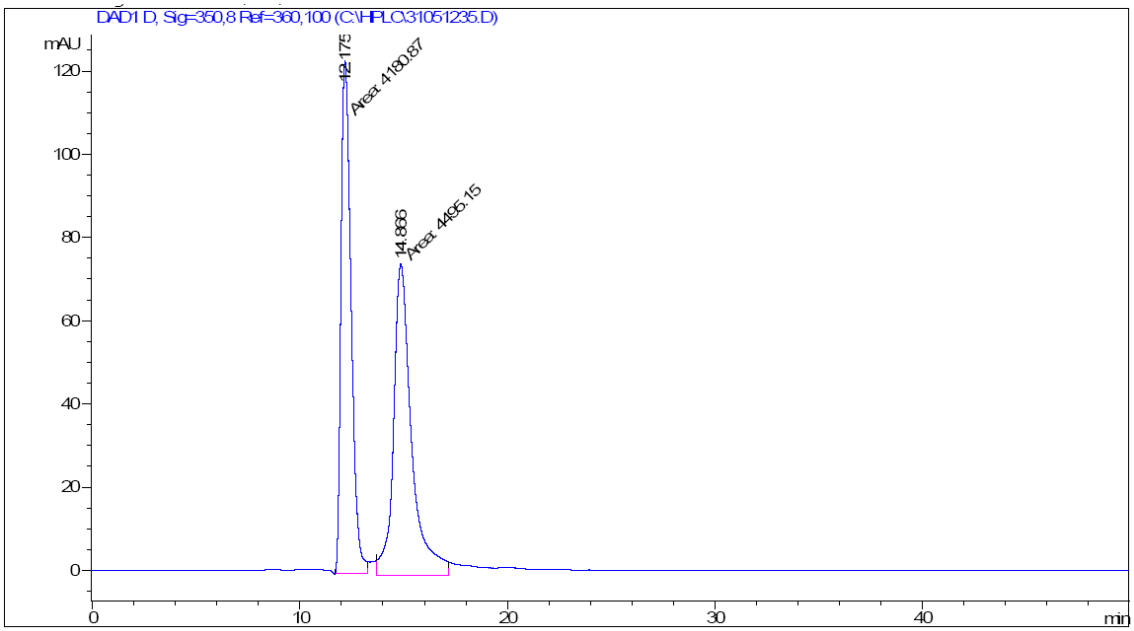

Figure S7. Chromatogram of hydrocarbon **8** by chiral HPLC (hexane, Chiralpac IA, 20ºC).