Electronic Supplementary Information

Large phenyl-substituted acenes by cycloaddition reactions of the 2,6-naphthodiyne synthon

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SUPPORTING INFORMATION

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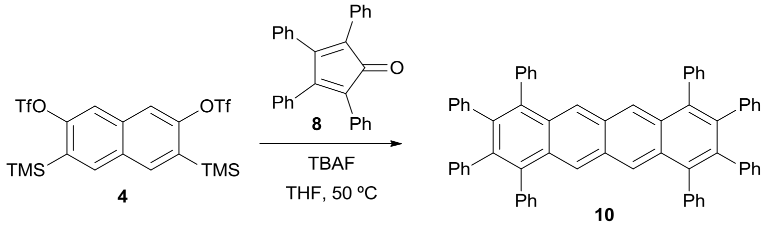
1. Experimental details and spectroscopic data

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. 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. The naphthodiyne precursor **4**,[1] and dienones **11**[2] and **12**[3] were prepared following a published procedures. However, bistriflate **4** is commercially available (ABCR GmbH).

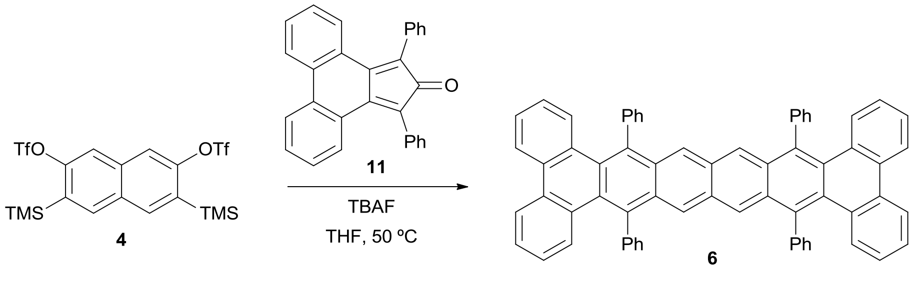
Synthesis of tetracene 10



Scheme S1

A solution of tetrabutylammonium fluoride (TBAF, 0.62 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone **8** (237 mg, 0.612 mmol) and naphthodiyne precursor **4** (160 mg, 0.281 mmol) in THF (5.6 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 5:2 hexane/CH_2Cl_2) to isolate tetracene **10** (54 mg, 23%) as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.29 (s, 4H), 7.31–7.23 (m, 16H), 7.21 (d, J = 6.6 Hz, 4H), 6.87–6.80 (m, 20H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.91 (4C), 139.92 (4C), 138.85 (4C), 138.30 (4C), 131.73 (8CH), 131.52 (8CH), 131.39 (4C), 130.21 (2C), 127.93 (8CH), 126.86 (4CH), 126.79 (4CH), 126.76 (8CH), 125.52 (4CH) ppm. MS (MALDI-TOF) for $C_{66}H_{44}$, calculated: 836.34, found 836.41.

Synthesis of hexacene 6



Scheme S2

A solution of tetrabutylammonium fluoride (TBAF, 0.39 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone **11** (147 mg, 0.387 mmol) and naphthodiyne precursor **4** (100 mg, 0.176 mmol) in THF (3.6 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 3:1 hexane/toluene, under N_2) to isolate hexacene **6** (22 mg, 15%) as a violet solid. ^1H NMR (500 MHz, C_6D_6) δ = 8.95 (s, 4H), 8.00 (d, J = 7.7 Hz, 4H), 7.60 (d, J = 8.2 Hz, 4H), 7.51 (dd, J = 6.4, 3.0 Hz, 8H),

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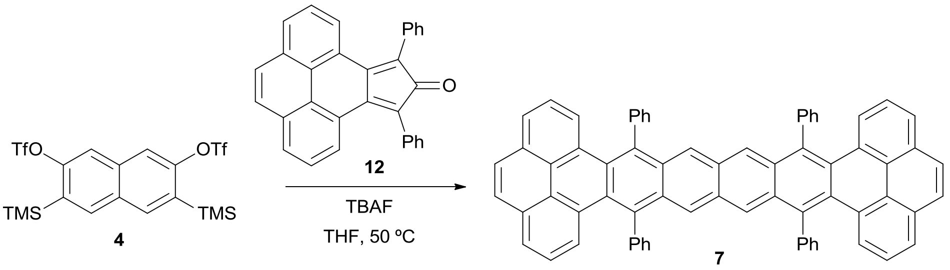
[1] C. Kitamura, Y. Abe, T. Ohara, A. Yoneda, T. Kawase, T. Kobayashi, H. Naito, T. Komatsu, *Chem.−Eur. J.* 2010, **16**, 890.
[2] G. Y. Wooi, J. M. White, *Org. Biomol. Chem.*, 2005, **3**, 972.
[3] R. A. Pascal, Jr., W. D. McMillan, V. D. Engen, R. G. Eason, *J. Am. Chem. Soc.* 1987, **109**, 4660.

7.09 (t, *J* = 7.1 Hz, 4H), 6.85 (t, *J* = 8.1 Hz, 4H) ppm. ^{13}C NMR (125 MHz, C_6D_6) δ = 142.48 (4C), 136.17 (4C), 133.66 (8CH), 132.97 (4C), 132.45 (4C), 132.00 (4CH), 131.11 (2C), 130.26 (4C), 129.72 (8CH), 128.37 (4CH), 127.93 (4CH), 127.18 (4CH), 126.76 (4CH), 124.27 (4CH) ppm. MS (MALDI-TOF) for $C_{66}H_{40}$, calculated: 832.31, found 832.28.

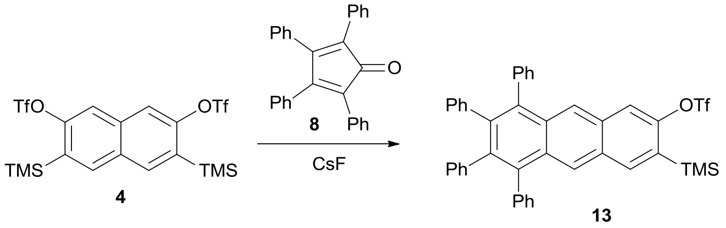
Synthesis of octacene 7



Scheme S3

A solution of tetrabutylammonium fluoride (TBAF, 0.56 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone **12** (228 mg, 0.561 mmol) and naphthodiyne precursor **4** (145 mg, 0.255 mmol) in THF (6.5 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 3:1 hexane/toluene, under N_2) to isolate octacene **7** (40 mg, 18%) as a violet solid. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ = 8.52 (s, 4H), 7.74 (s, 4H), 7.69 (d, *J* = 7.5 Hz, 4H), 7.62–7.37 (m, 24H), 7.17 (t, *J* = 7.8 Hz, 4H) ppm. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ = 142.15 (4C), 136.46 (4C), 132.91 (8CH), 131.56 (4C), 131.01 (4C), 130.90 (4C), 130.18 (2C), 129.53 (8CH), 129.48 (4CH), 129.22 (4C), 128.09 (4CH), 126.96 (4CH), 126.60 (4C), 126.49 (4CH), 126.40 (4CH), 125.26 (4CH) ppm. MS (MALDI-TOF) for $C_{70}H_{40}$, calculated: 880.31, found 880.23.

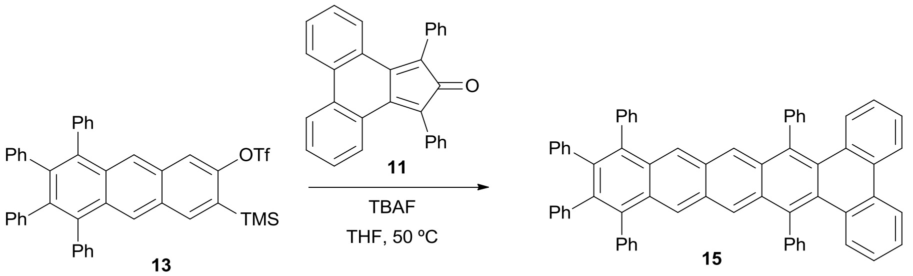
Synthesis of tetraphenylanthracyne precursor 13



Scheme S4

Finely powdered anhydrous CsF (55 mg, 0.359 mmol) was added over a solution of cyclopentadienone **8** (126 mg, 0.329 mmol) and naphthodiyne precursor **4** (170 mg, 0.299 mmol) in CH_3CN/CH_2Cl_2 (2:1, 9.0 mL). The mixture was heated at 50 ºC under argon for 16 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; 3:1 hexane/CH_2Cl_2) to isolate triflate **13** (84 mg, 40%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.27 (s, 1H), 8.22 (s, 1H), 8.04 (s, 1H), 7.82 (s, 1H), 7.39–7.21 (m, 10H), 7.01–6.78 (m, 10H), 0.43 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.40 (C), 140.49 (2C), 139.91 (C), 139.59 (C), 139.52 (C), 139.44 (C), 139.03 (CH), 138.59 (C), 138.27 (C), 132.14 (C), 131.73 (C), 131.62 (CH), 131.57 (CH), 131.36 (CH), 129.65 (C), 128.06 (CH), 128.01 (CH), 127.03 (CH), 126.95 (CH), 126.88 (CH), 126.82 (CH), 126.42 (CH), 125.74 (CH), 116.24 (CH), -0.45 ($3CH_3$) ppm. MS (MALDI-TOF) for $C_{44}H_{31}F_3O_3SSi$, calculated: 702.19, found 702.23.

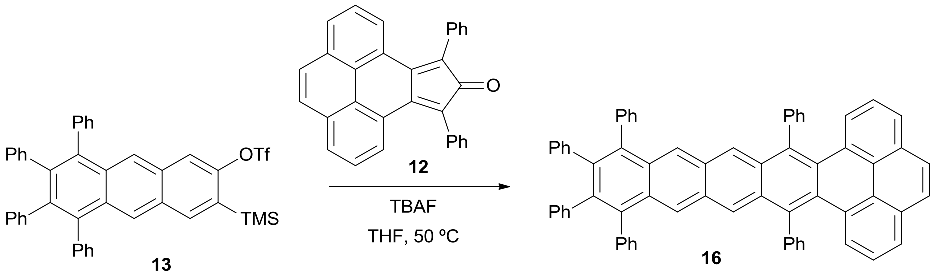
Synthesis of pentacene 15



Scheme S5

A solution of tetrabutylammonium fluoride (TBAF, 0.040 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone **11** (10 mg, 0.026 mmol) and triflate **13** (16 mg, 0.023 mmol) in THF (2.0 mL). The mixture was stirred at r.t. under argon for 16 h. Then, the solvent was evaporated under reduced pressure, the residue was redissolved in THF (5 mL) and MeOH (10 mL) was added. The solid was filtered and washed with MeOH (3 x 15 mL) to obtain pentacene **15** (8.1 mg, 42%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.54 (s,2H), 8.32 (s, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.56 (m, 12H), 7.28 (m, 12H), 6.85 (m, 12H) ppm. MS (MALDI-TOF) for $C_{66}H_{42}$, calculated: 834.33, found 834.19.

Synthesis of hexacene 16



Scheme S6

A solution of tetrabutylammonium fluoride (TBAF, 0.106 mL, 1.0 M in THF) was added dropwise over a solution of cyclopentadienone **12** (32 mg, 0.078 mmol) and triflate **13** (50 mg, 0.071 mmol) in THF (3.0 mL). The mixture was stirred at r.t. under argon for 16 h. Then, MeOH (10 mL) was added and the solid was filtered and washed with MeOH (3 x 15 mL) to obtain hexacene **16** (23 mg, 40%) as a pink solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (s, 2H), 8.33 (s, 2H), 7.79 (s, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.54 (m, 12H), 7.26 (m, 12H), 6.84 (m, 10H) ppm. MS (MALDI-TOF) for $C_{68}H_{42}$, calculated: 858.33, found 858.21.

2. Absorption and emission spectra

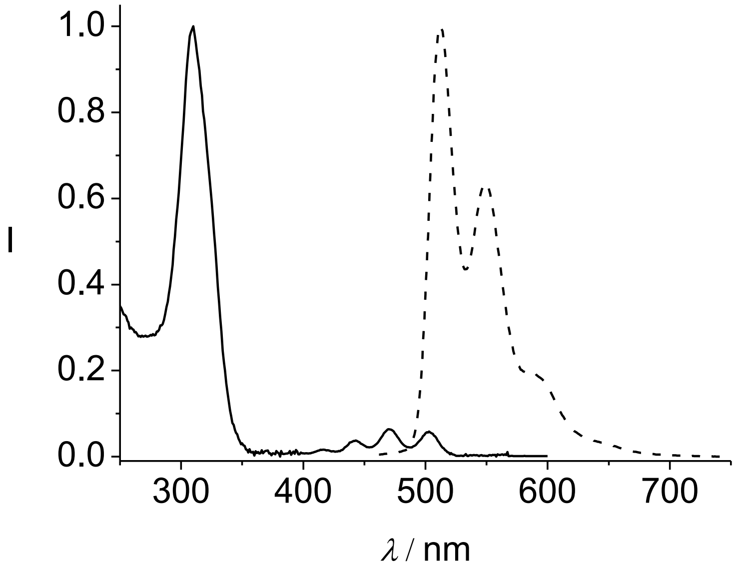


Figure S1. Absorption (solid line) and emission (dashed line) spectra of **10** in CH_2Cl_2.

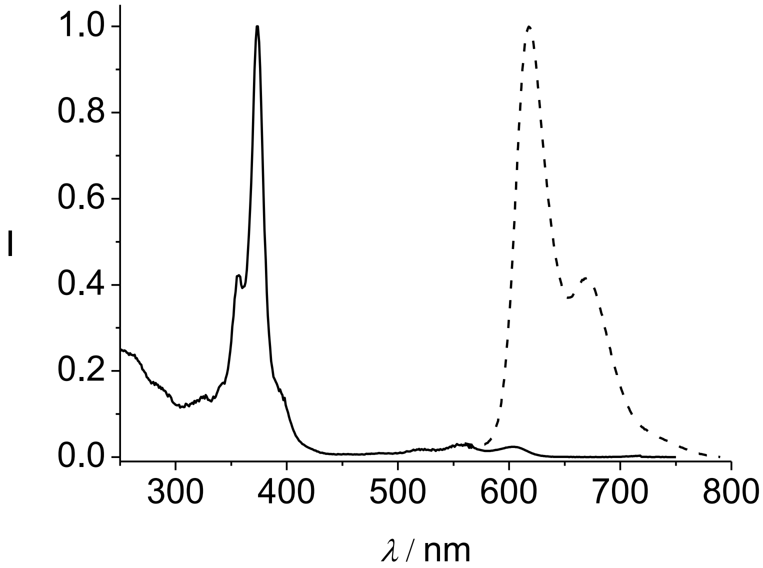


Figure S2. Absorption (solid line) and emission (dashed line) spectra of **6** in CH_2Cl_2.

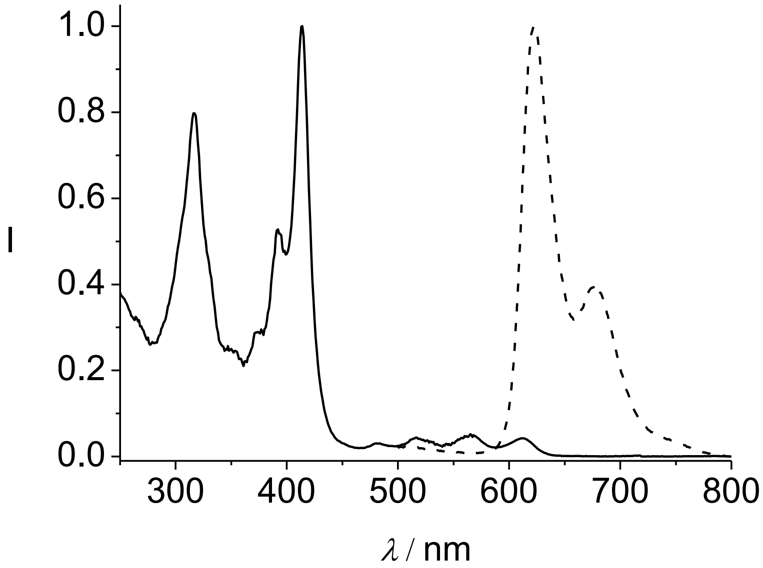


Figure S3. Absorption (solid line) and emission (dashed line) spectra of **7** in CH_2Cl_2.

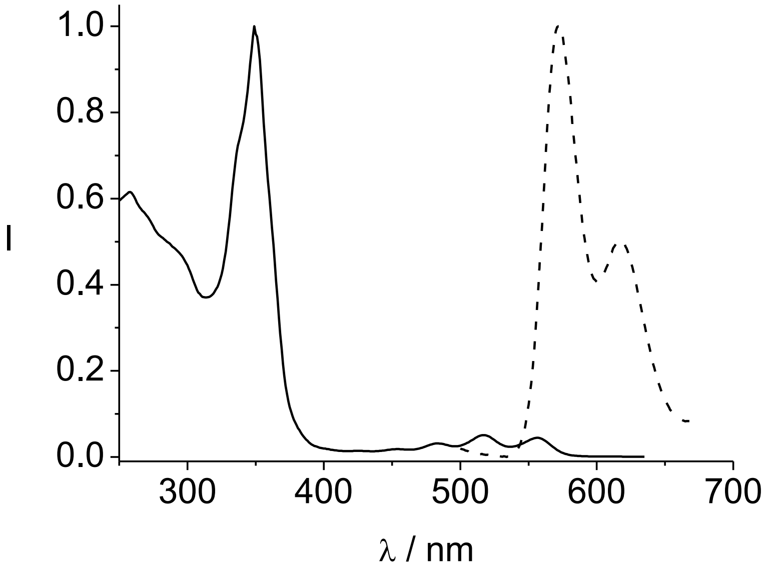


Figure S4. Absorption (solid line) and emission (dashed line) spectra of **15** in CH_2Cl_2.

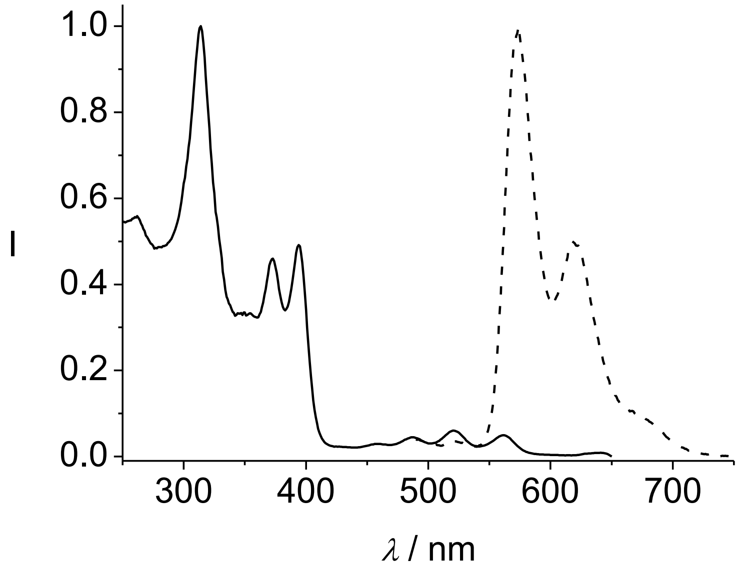


Figure S5. Absorption (solid line) and emission (dashed line) spectra of **16** in CH_2Cl_2.

3. Voltammograms

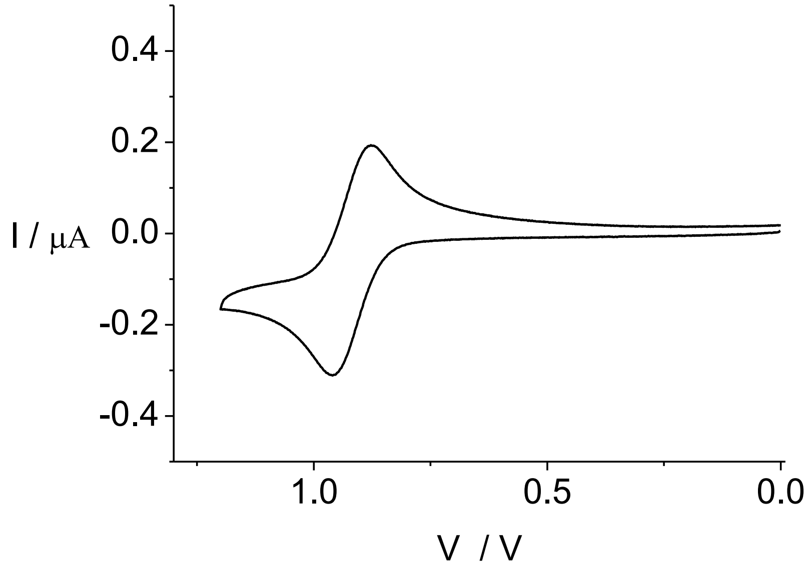


Figure S6. Cyclic voltammogram of **10** in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode.

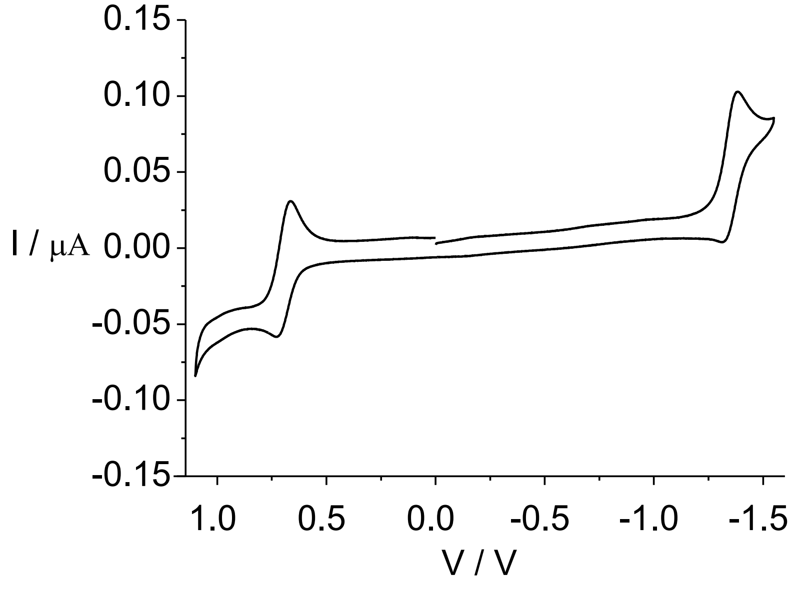


Figure S7. Cyclic voltammogram of **6** in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode.

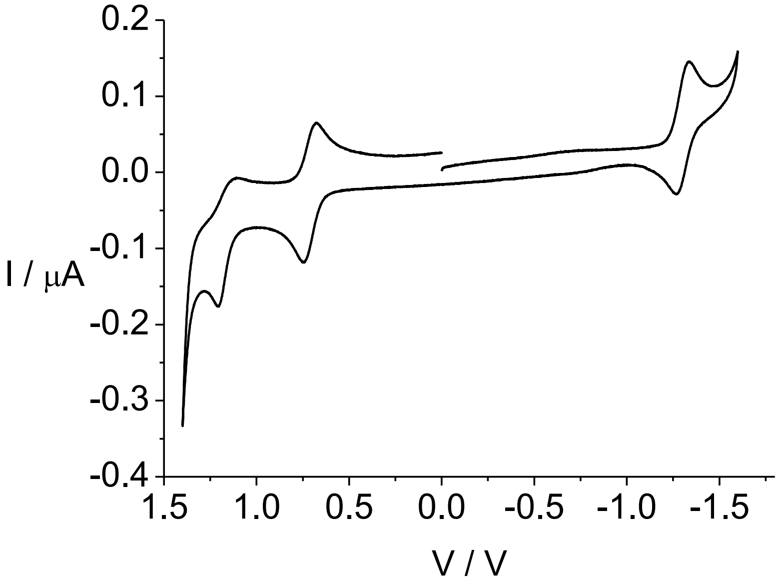


Figure S8. Cyclic voltammogram of **7** in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode.

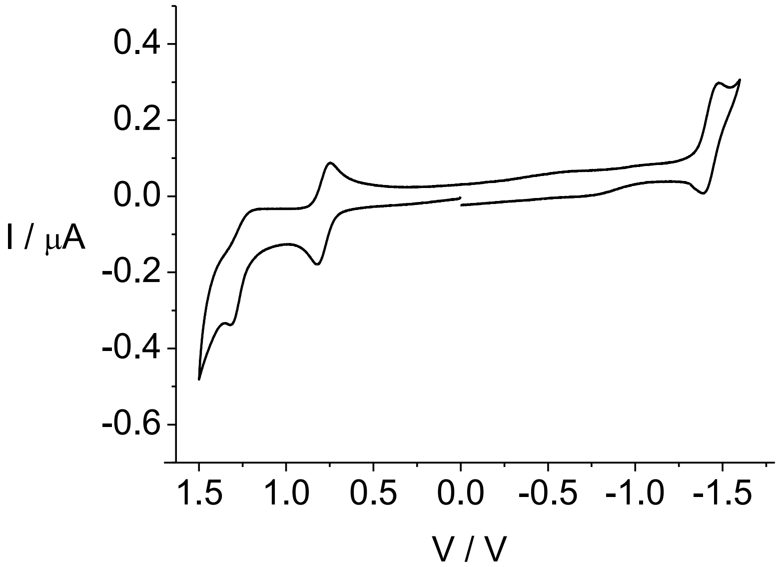


Figure S9. Cyclic voltammogram of **15** in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode.

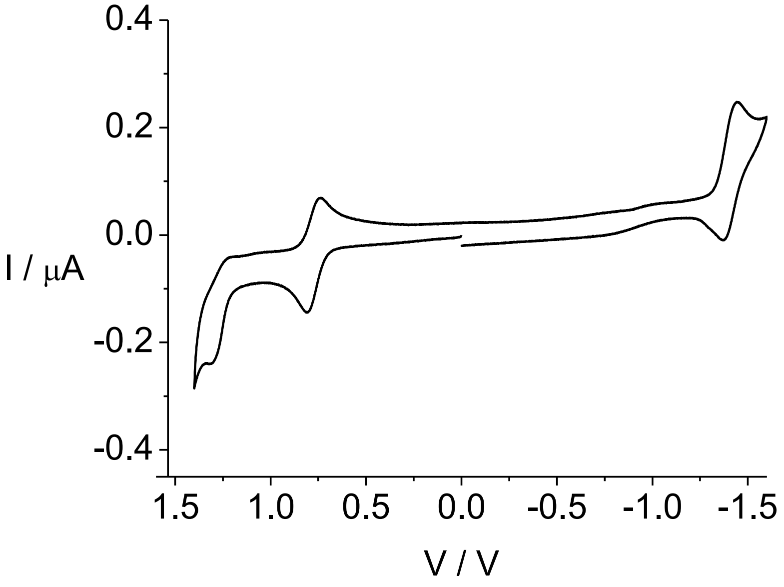
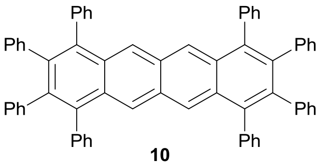


Figure S10. Cyclic voltammogram of **16** in CH_2Cl_2/0.1 M Bu_4NPF_6 using AgCl/Ag as reference electrode

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



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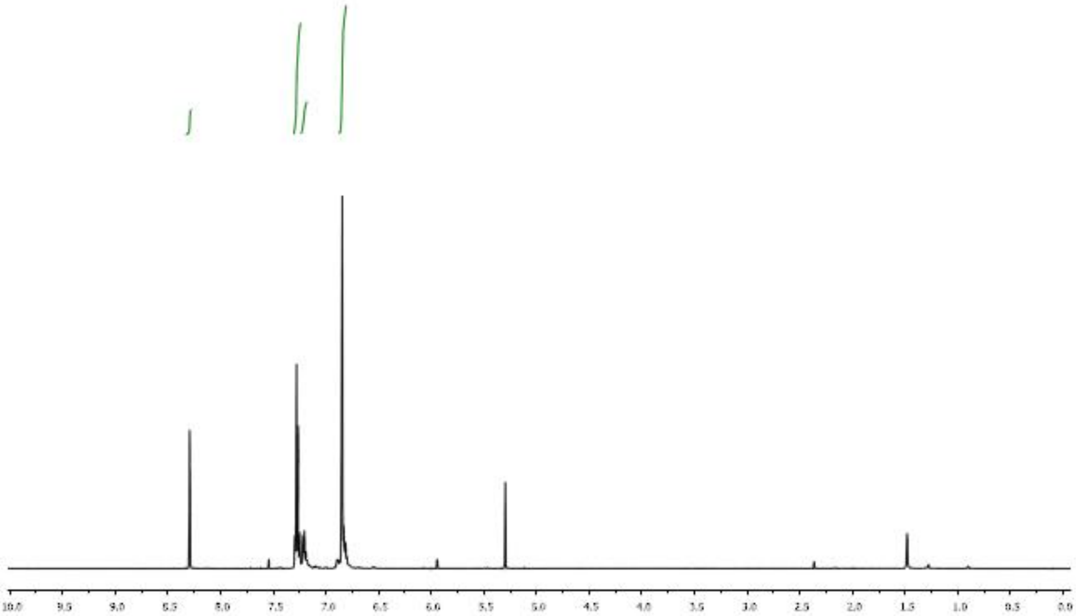

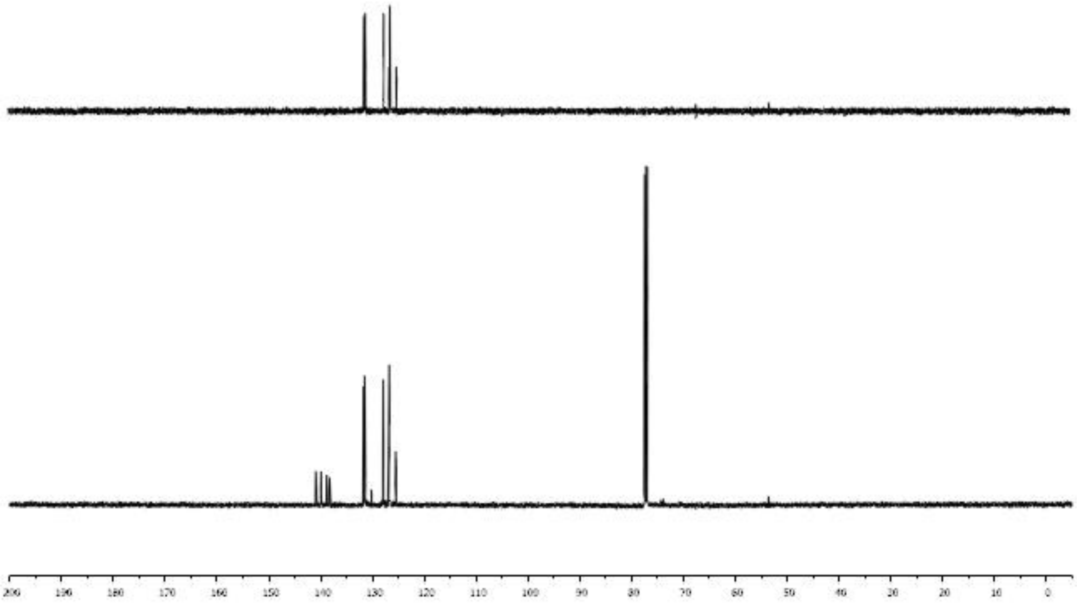

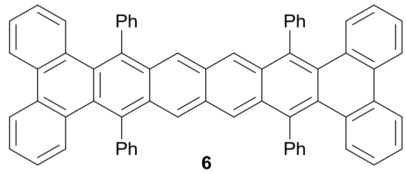
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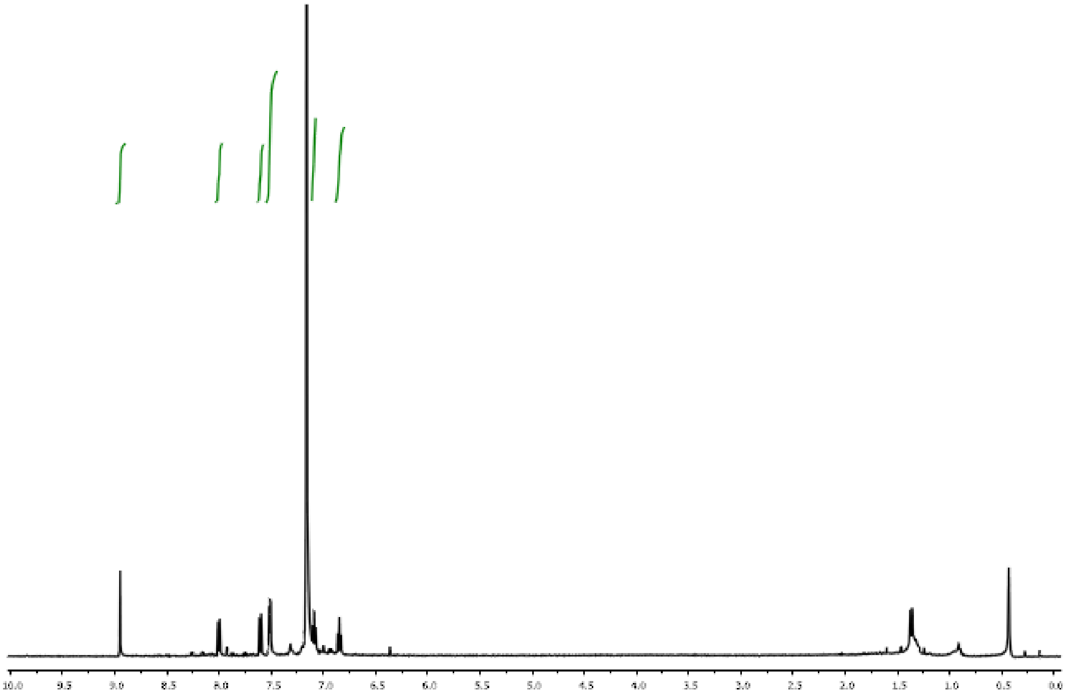
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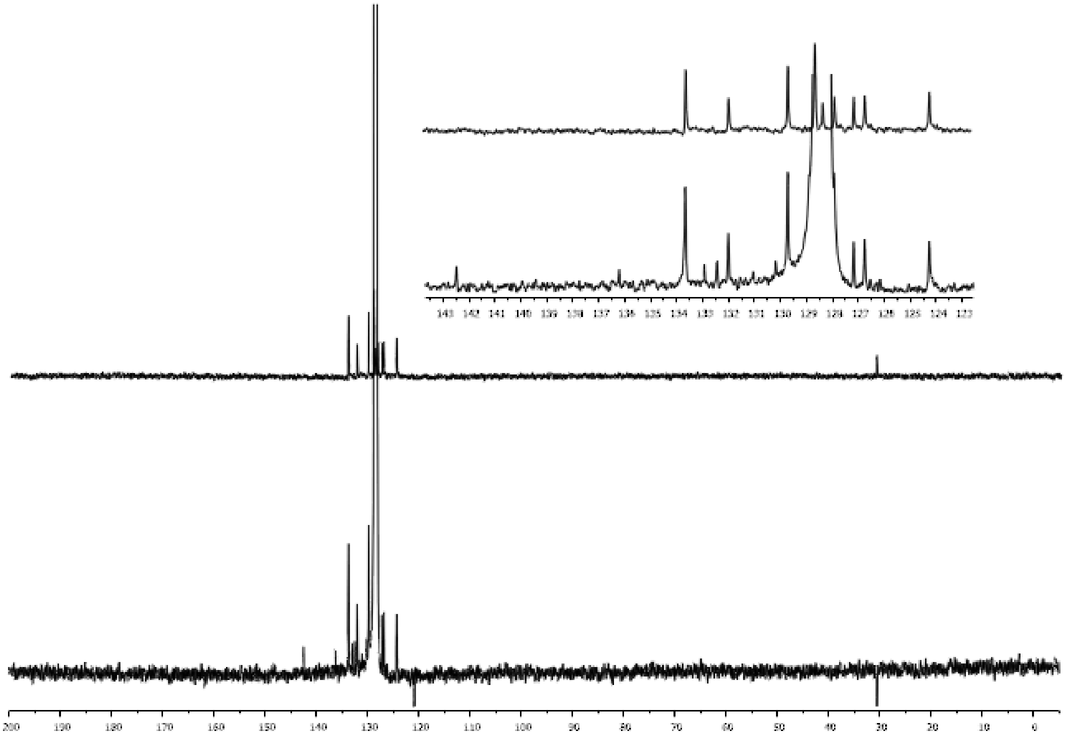
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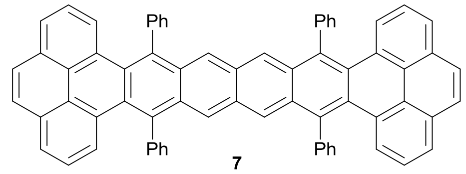
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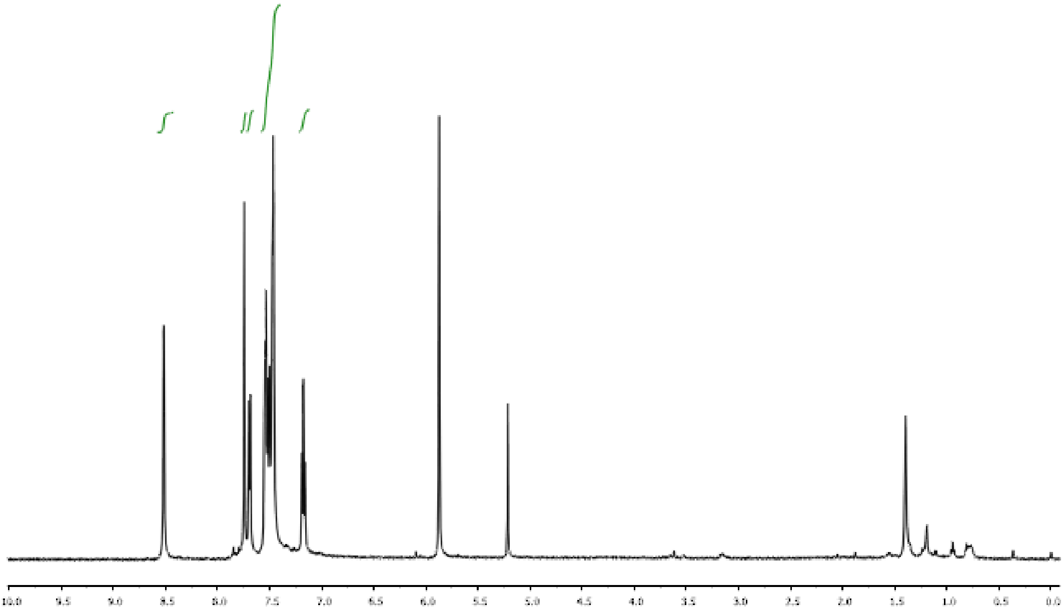
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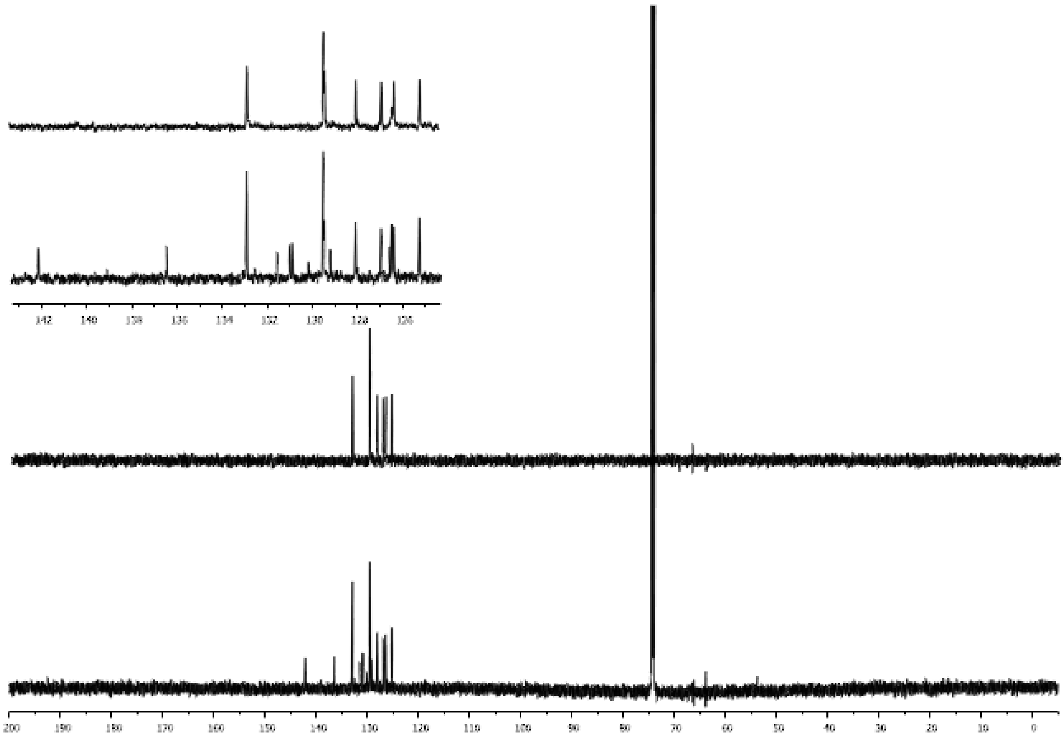
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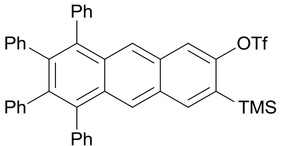
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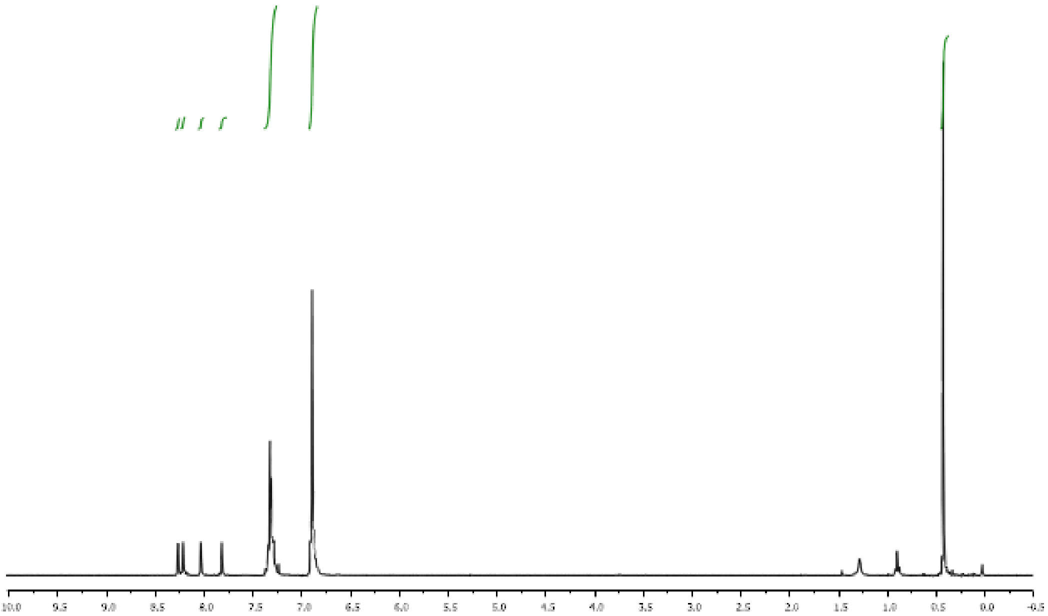
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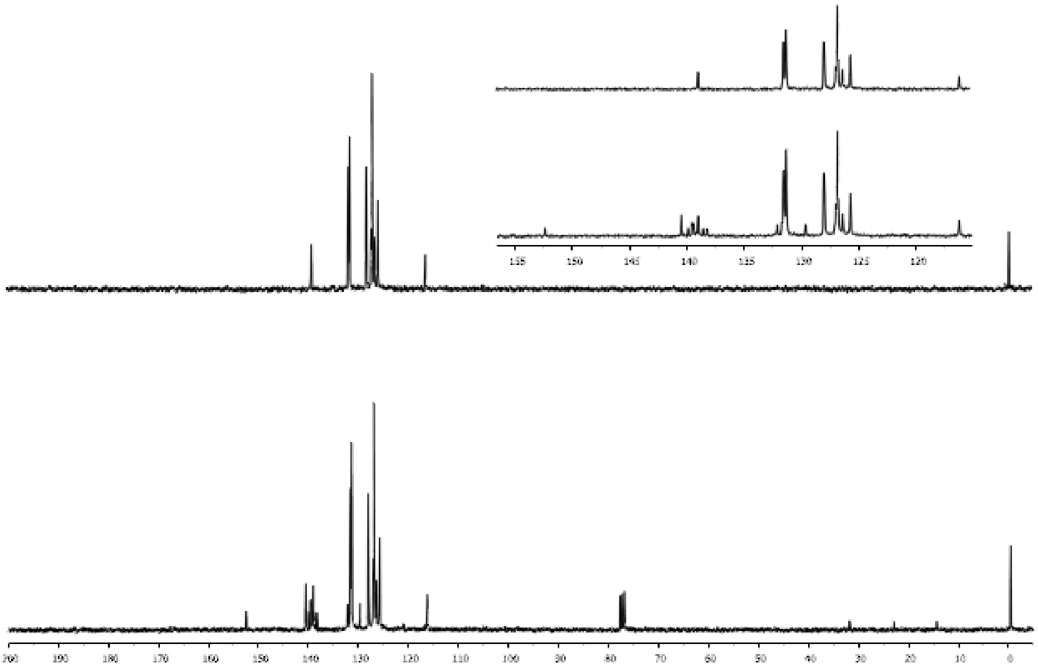
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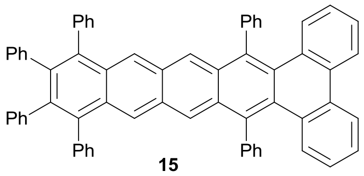
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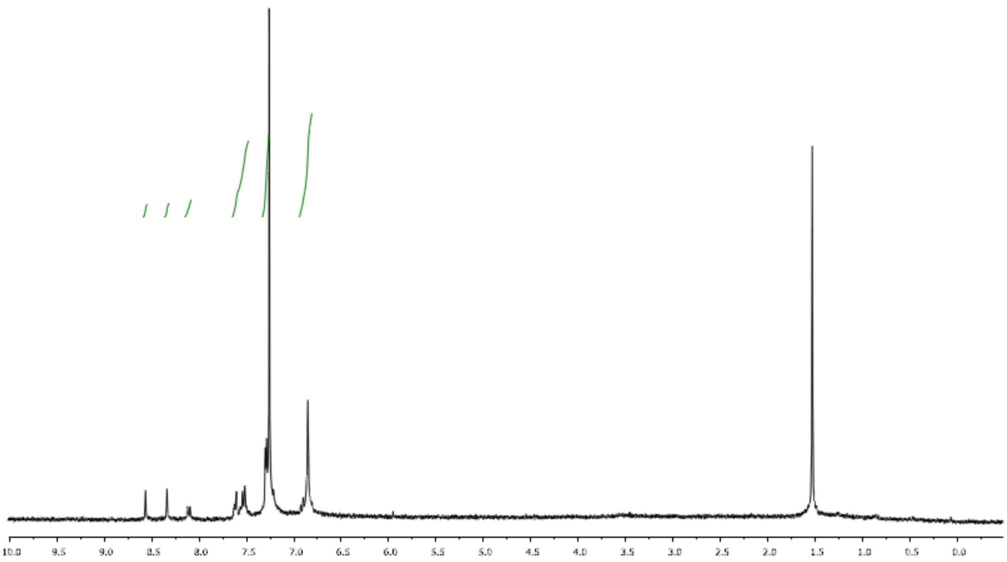
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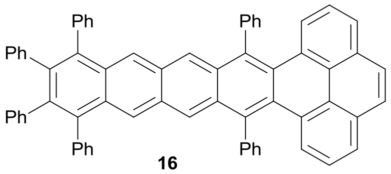
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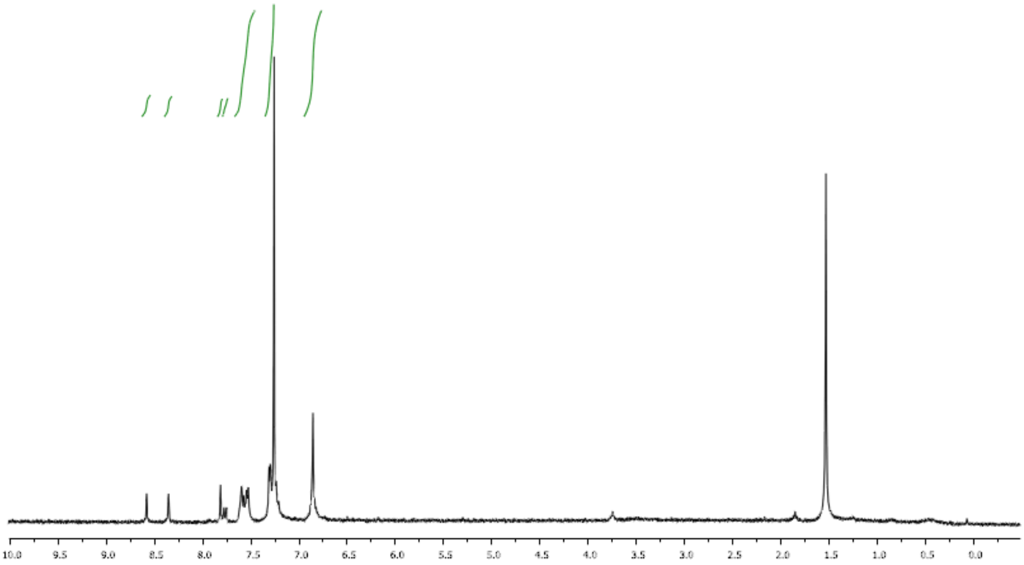
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