Supporting Information

for

Efficient electroorganic synthesis of 2,3,6,7,10,11-hexahydroxytriphenylene derivatives

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Characterization data and spectra of synthesized compounds

A. Materials and methods

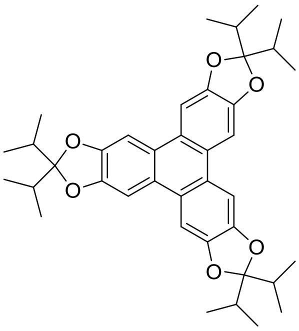
Catechol ketals **1a**–**c** were prepared according to a common protocol, using a Dean–Stark trap [1]. The obtained crude products were purified by distillation in vacuo. Compounds **1d**–**e** were purchased and used without further purification. For CV measurements PC and ACN were desiccated by molecular sieves. Tetrabutylammonium perchlorate ($TBAClO_4$/Fluka) and tetramethylammonium tetrafluoroborate ($TMABF_4$/Acros) were used as purchased. $TBABF_4$ was synthesized from $NaBF_4$ and Bu_4NHSO_3 [2].

Standard cyclic voltammetry was carried out in a conventional three electrode cell using a µ-Autolab Type III potentiostat (Metrohm AG, Herisau, Switzerland). A glassy carbon disc served as working electrode and a glassy carbon rod as counter electrode. As reference an Ag/AgCl electrode (silver wire in saturated LiCl/ethanol solution) was employed.

Melting points were determined with a Melting Point Apparatus B-545 (Büchi, Flawil, Switzerland) and were uncorrected. Microanalysis was performed with a Vario MICRO cube (Elementar-Analysensysteme Hanau, Germany). ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C by using Bruker AC 300, DPX 300 or DPX 400 instruments (Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard or traces of $CHCl_3$ in the corresponding deuterated solvent. Mass spectra were obtained by using a MAT8200, MAT95XL (Finnigan, Bremen, Germany) or MS50 (Kratos, Manchester, England) apparatus employing EI and by using a Quattro LC (Waters-Micromass) or Micro TOF (Bruker) apparatus employing HRMS (positive mode). IR data were obtained by using Alpha Fouriertransform spectrometer (Bruker Optik GmbH, Ettlingen, Germany.

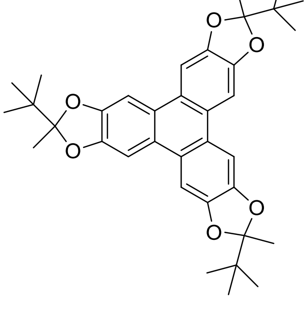
B. Experimental procedures and characterization

2,2,7,7,12,12-Hexa(1-methylethyl)-triphenyleno[2,3-*d*;6,7-*d*';10,11-*d*'']-tris[1,3]dioxole (2a)



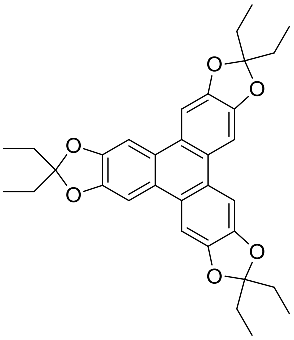
Yield: 1.636 g (2.67 mmol, 80%) of a pale brown solid. Mp >280 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.03 (d, ^3J = 6.8 Hz, 36H), 2.37 (sept, ^3J = 6.8 Hz, 6H), 7.64 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 16.2, 34.5, 99.6, 124.4, 124.8, 149.6; MS (EI, 70 eV) *m*/*z* (%): 612 (100) [M]$^{+\cdot}$, 569 (37), 263 (22); HRMS (EI, 70 eV) for $C_{39}H_{48}O_6$ calc.: 612.3451, found: 612.3451; elem. anal. $C_{39}H_{48}O_6 \cdot 0.5\ H_2O$ (621.79): calc. C 75.33 H 7.94, found: C 75.03 H 7.83.

2,7,12-Tri(1,1-dimethylethyl)-2,7,12-trimethyltriphenyleno[2,3-*d*;6,7-*d*';10,11-*d*'']-tris[1,3]dioxole (2b)



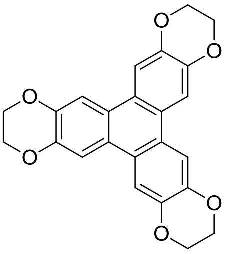
Yield: 1.152 g (2.02 mmol, 61%) of a pale brown solid. Mp: >280 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 1.12 (s, 27H), 1.65 (s, 9H), 7.66 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 20.5, 24.8, 39.8, 100.7, 124.0, 124.5, 148.4; MS (EI, 70 eV) *m*/*z* (%): 570 (100) $[M]^{+\cdot}$, 513 (85), 228 (38); HRMS (EI, 70 eV) for $C_{36}H_{42}O_6$ calc.: 570.2981, found: 570.2980; elem. anal. $C_{36}H_{42}O_6$ (570.72):calc. C 75.76 H 7.42, elem. anal. $C_{36}H_{42}O_6 \cdot 0.5$ MeOH (639.83): calc. C 74.72 H 7.56, found: C 74.62 H 7.28.

2,2,7,7,12,12-Hexaethyltriphenyleno[2,3-*d*;6,7-*d*';10,11-*d*'']tris[1,3]dioxole (2c)



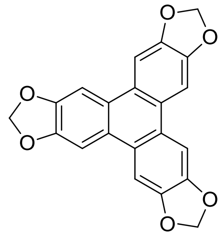
Yield: 1.074 g (2.03 mmol, 61%); Mp >280 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.03 (t, ^3J = 7.4 Hz, 18H), 2.01 (q, ^3J = 7.4 Hz, 12H), 7.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 7.3, 30.9, 100.6, 122.1, 124.5, 148.6; MS (EI, 70 eV) *m*/*z* (%): 528 (100) $[M]^{+\cdot}$, 499 (18), 235 (5); HRMS (EI, 70 eV) for $C_{33}H_{36}O_6$ calc.: 528.2512, found: 528.2501.

2,3,8,9,14,15-Hexahydrotriphenyleno[2,3-*d*;6,7-*d*';10,11-*d*'']tris[1,4]dioxine (2d)



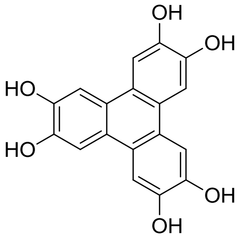
Yield: 0.386 g (0.96 mmol, 29%) of a pale brown solid. Mp >280 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 4.36 (s, 12H); 7.91 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 64.3, 110.3, 123.2, 143.4; MS (EI, 70 eV) *m*/*z* (%): 402 (100) $[M]^{+\cdot}$, 346 (20), 201 (15); spectral data of **2d** match with [3].

Triphenyleno[2,3-*d*;6,7-*d'*;10,11-*d''*]tris[1,3]dioxole (2e)



Yield: 0.466 g (1.29 mmol, 39%) of a brown solid. Totally insoluble, could not be identified by NMR [3]; MS (EI, 70 eV) *m*/*z* (%): 360 (100) $[M]^{+\cdot}$; mp >280 °C; IR (ATR): ν (cm^{-1}) = 1502, 1459 (m) ν(C=C_{aromat}), 1244, 1042 (s) ν(CO); 947 (s) δ(C_{aromat}-H), 851 (s) δ(C_{aromat}-H), 827 (s) δ(C_{aromat}-H); IR data match with [4].

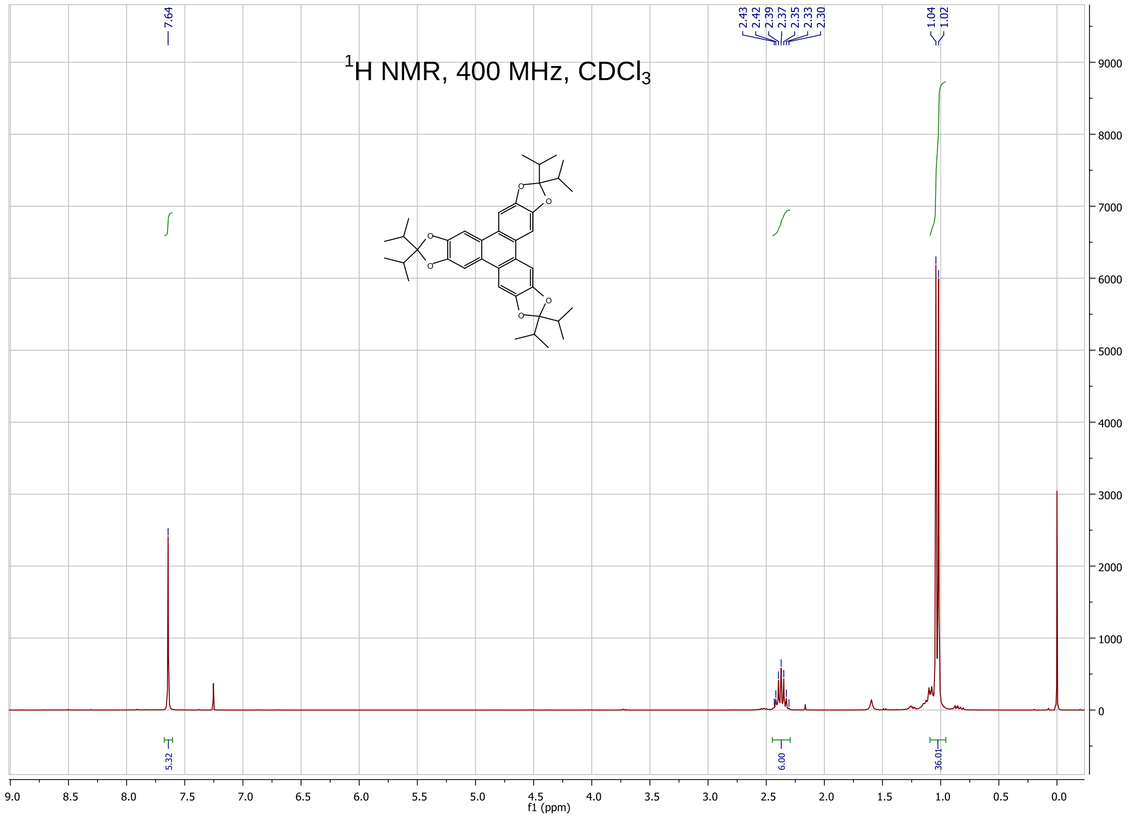
Synthesis of 2,3,6,7,10,11-hexahydroxytriphenylene (3)

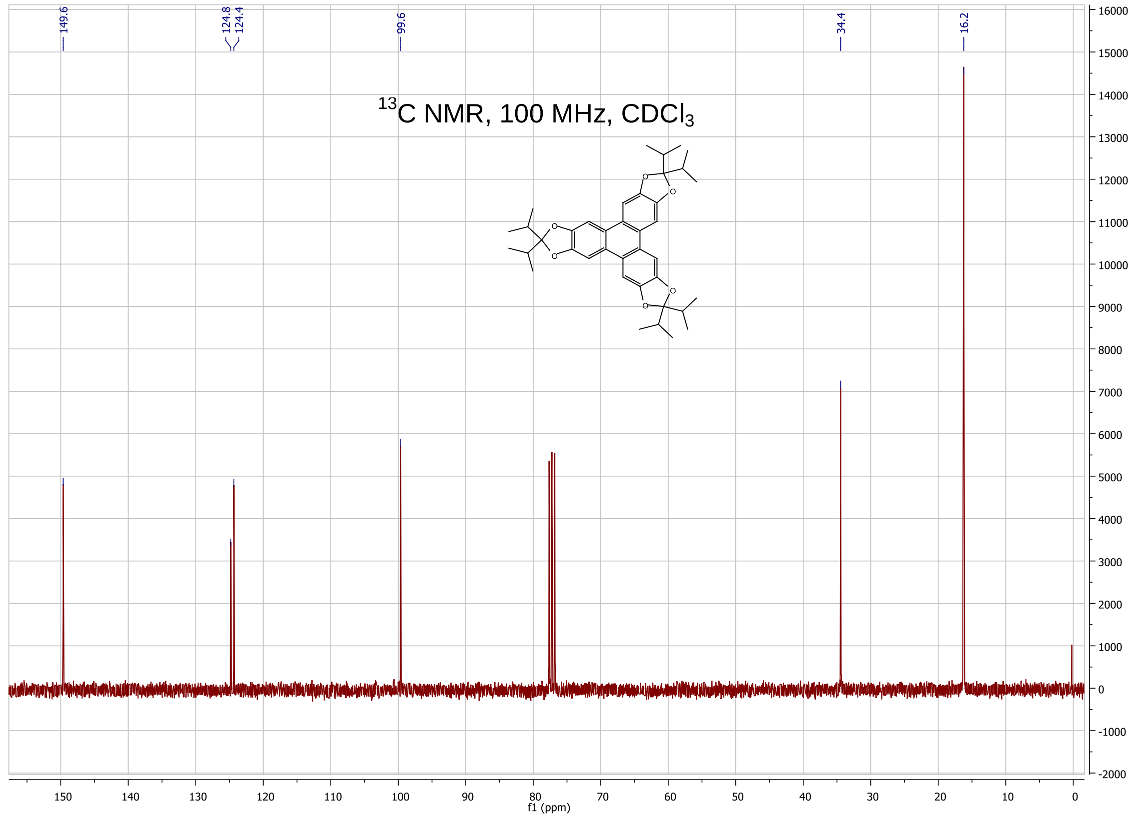


Compound **2b** (0.119 g, 0.21 mmol) was suspended in 33% HBr in acetic acid (15 mL) and heated to reflux for 24 h. The mixture was allowed to come to ambient temperature. The precipitate formed was filtered off, washed with water (10 mL) and vacuum-dried to yield a grey solid (0.065 g, 0.20 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.61 (s, 6H), 9.28 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 107.8, 121.8, 145.2; MS (ESI, 10 eV): 347 $[M + Na]^{+}$, 325 $[M + H]^{+}$; IR (ATR): 3320 (br) ν(OH), 1442 (s) δ(OH), 1138 (s) ν(CO); spectral data match with [4].

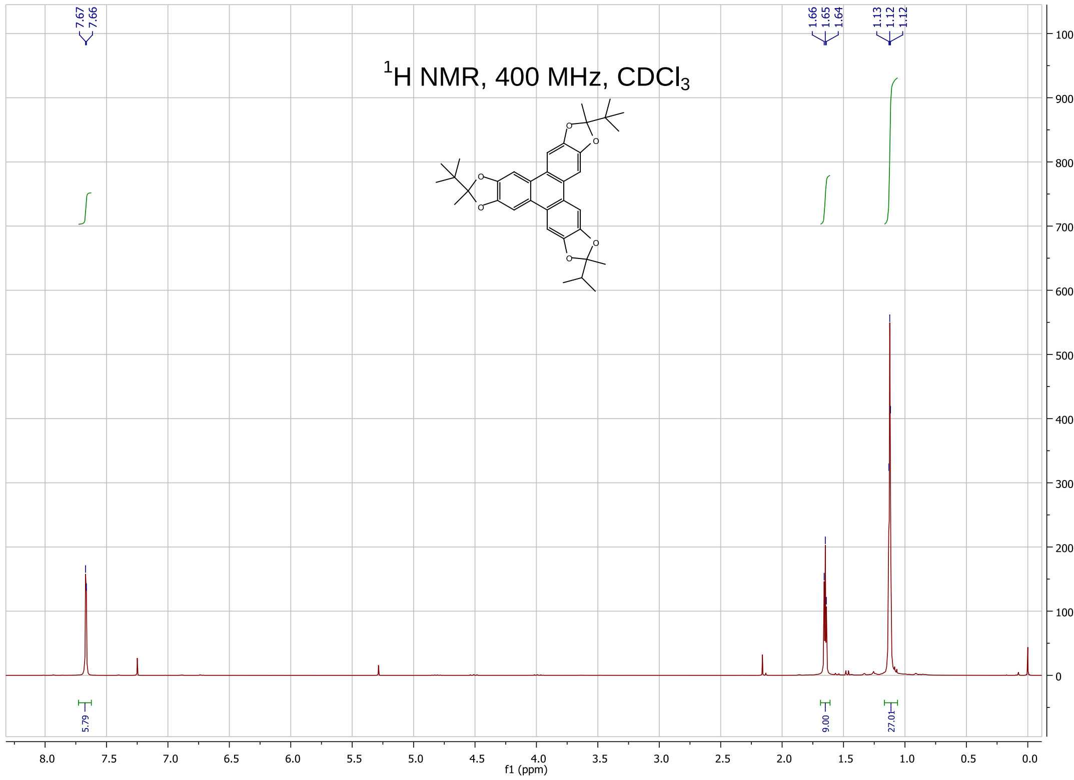
C. ^{1}H and ^{13}C NMR spectra

Compound **2a**:

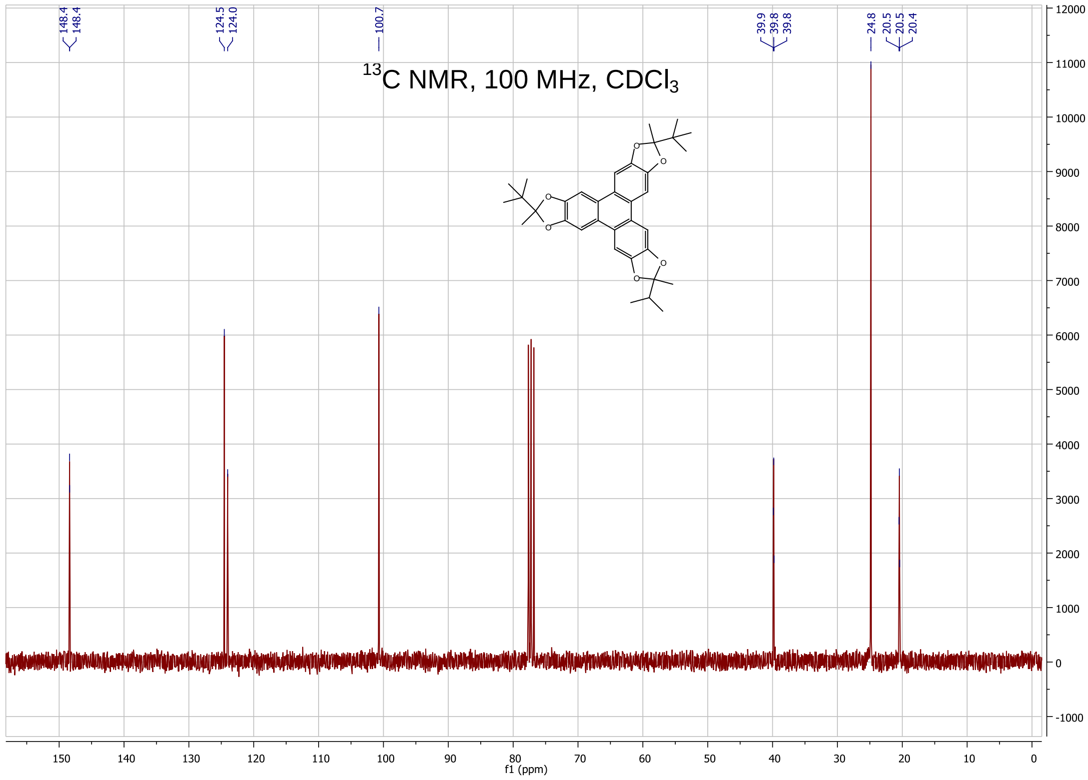




Compound **2b**:

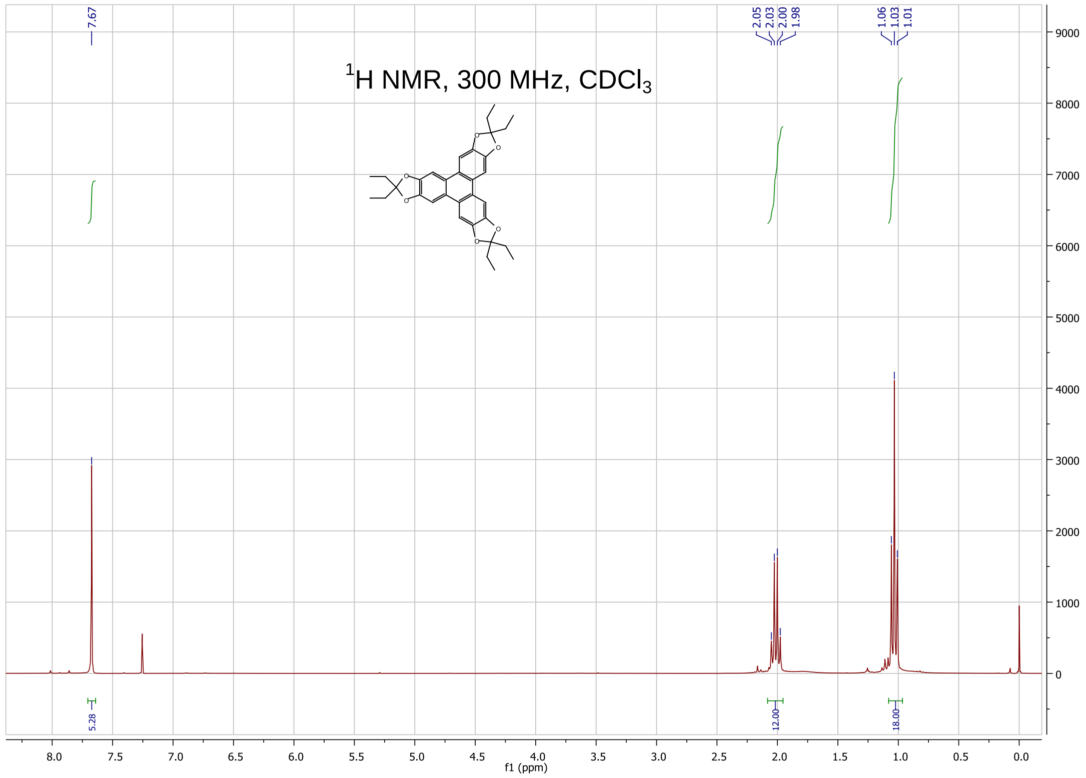


1H NMR, 400 MHz, CDCl3
7.67
7.66
1.66
1.65
1.64
1.13
1.12
1.12
5.79
9.00
27.01
f1 (ppm)

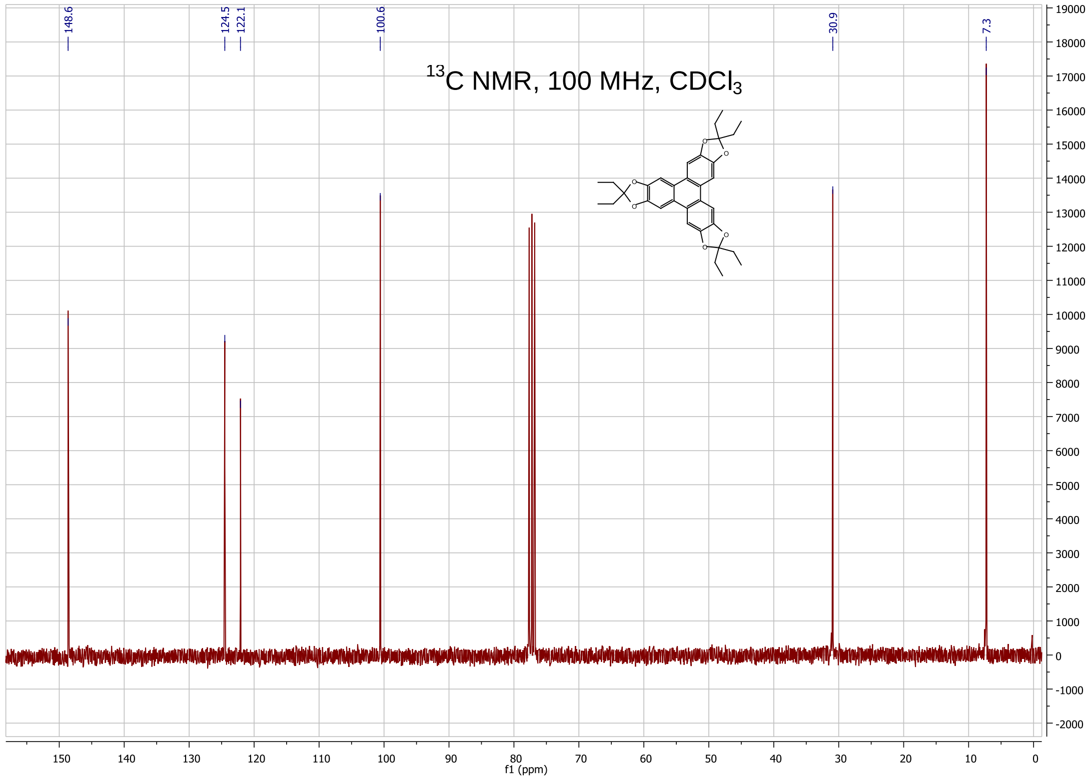


13C NMR, 100 MHz, CDCl3
148.4
148.4
124.5
124.0
100.7
39.9
39.8
39.8
24.8
20.5
20.5
20.4
f1 (ppm)

Compound **2c**:

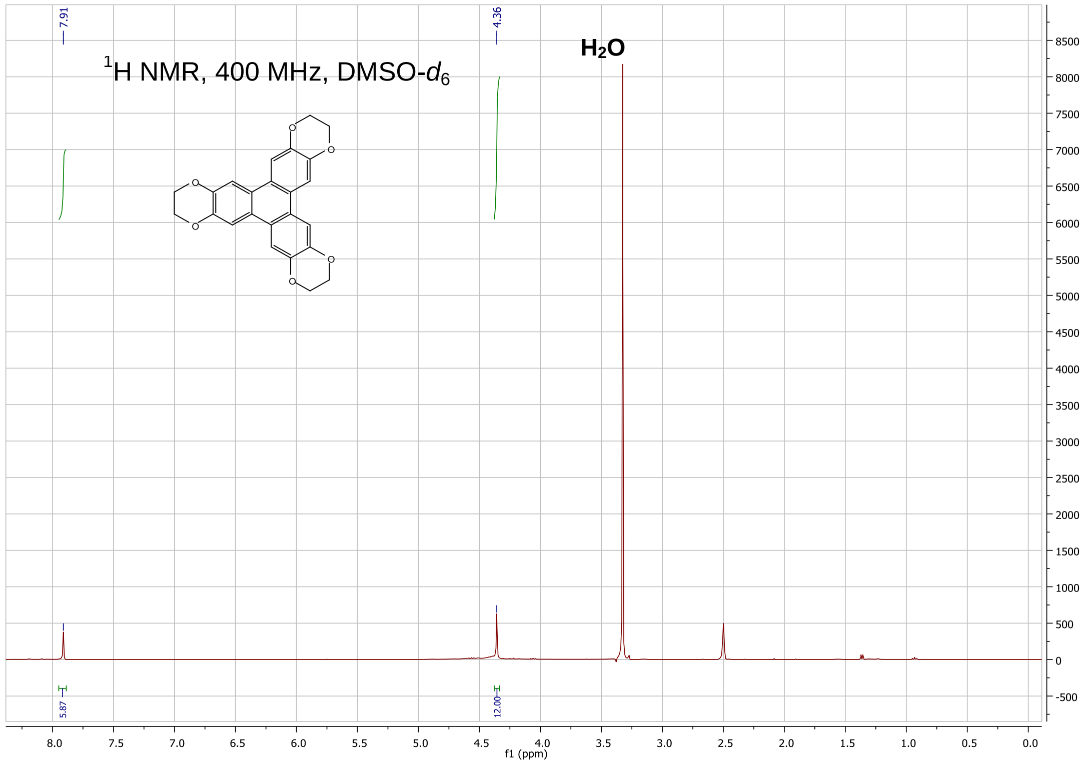


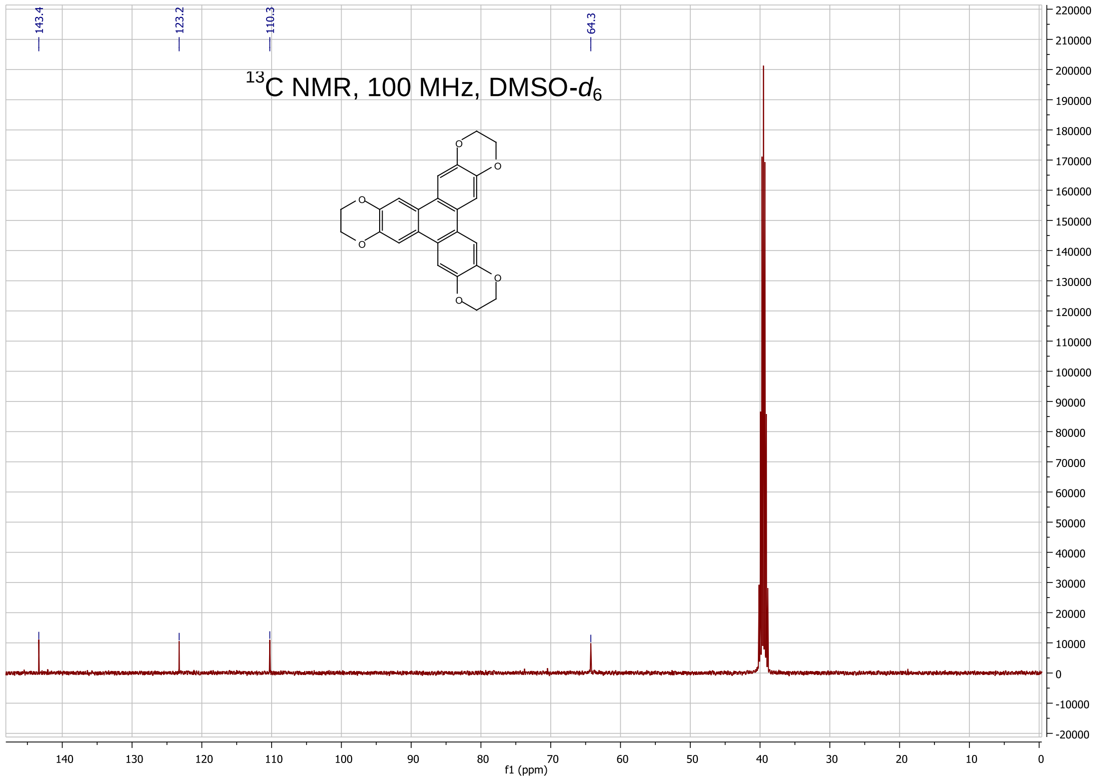
^{1}H NMR, 300 MHz, CDCl$_3$
7.67
2.05
2.03
2.00
1.98
1.06
1.03
1.01
5.28
12.00
18.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0



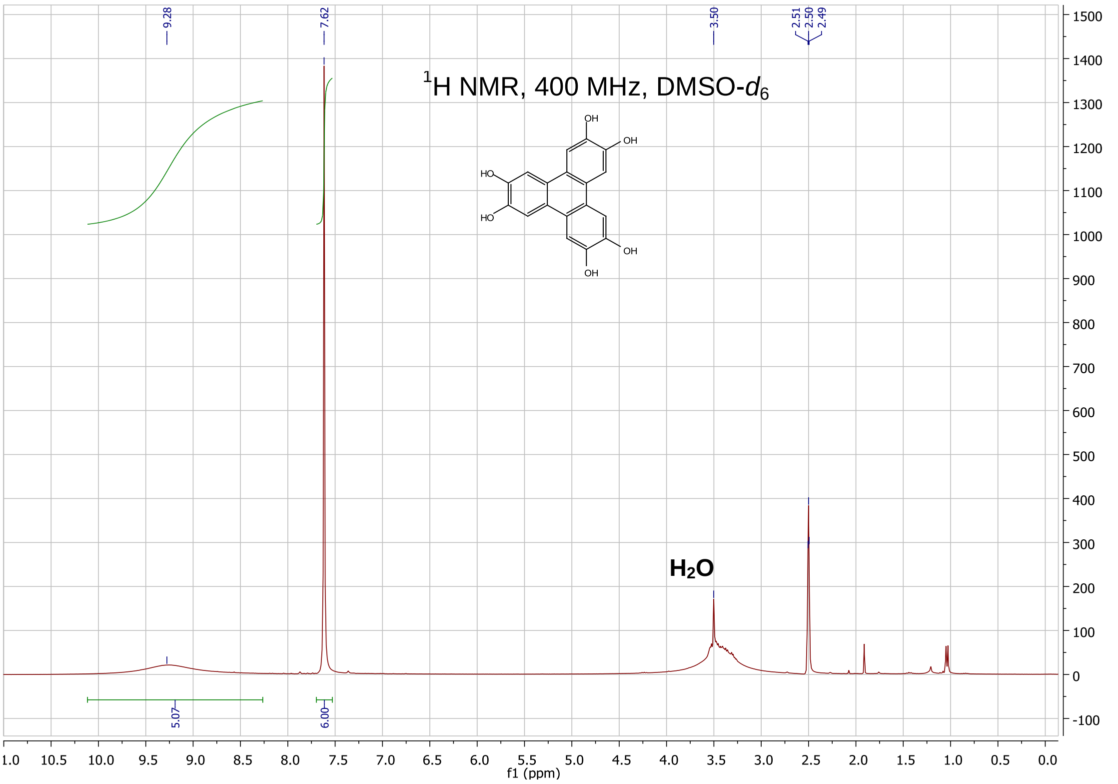
^{13}C NMR, 100 MHz, CDCl$_3$
148.6
124.5
122.1
100.6
30.9
7.3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000

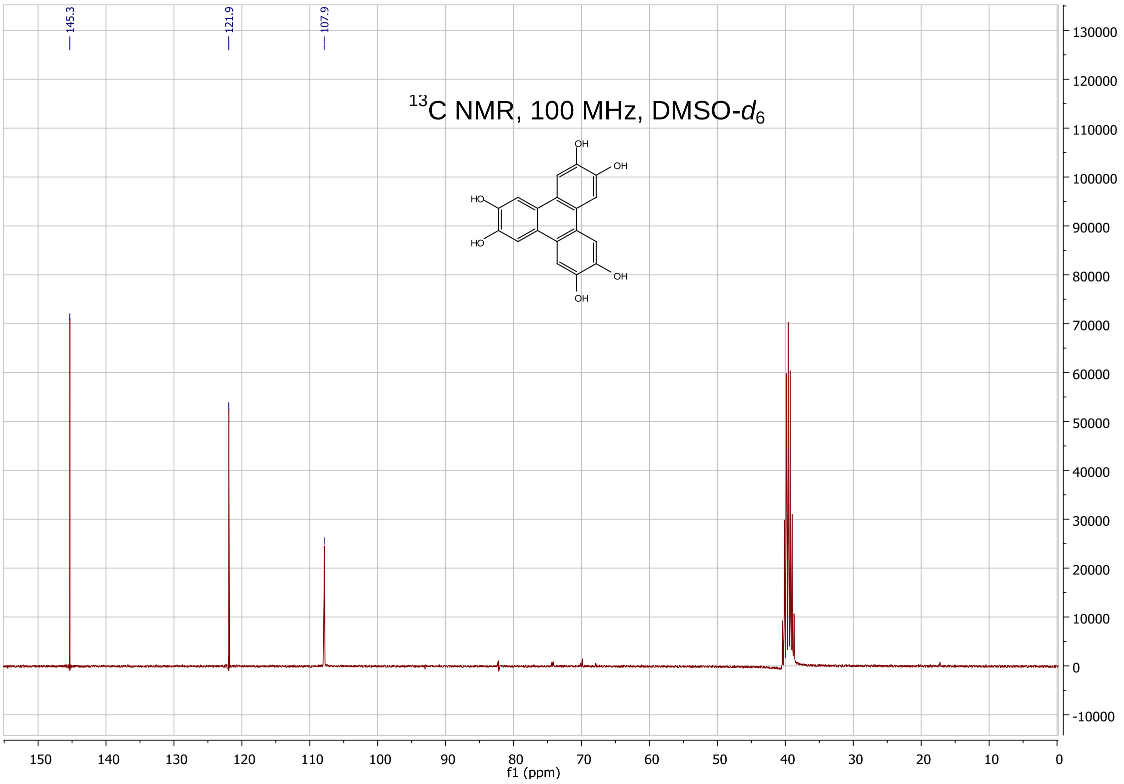
Compound **2d**:


7.91
4.36
H2O
1H NMR, 400 MHz, DMSO-d6
O
O
O
O
O
O
5.87
12.00
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)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


143.4
123.2
110.3
64.3
13C NMR, 100 MHz, DMSO-d6
O
O
O
O
O
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000

Compound **3**:


^{1}H NMR, 400 MHz, DMSO-d_6


^{13}C NMR, 100 MHz, DMSO-d_6

D. References

1. Boshta, N. M.; Bomkamp, M.; Waldvogel, S. R. *Tetrahedron* **2009,** *65,* 3773–3779. doi:10.1016/j.tet.2009.02.053
2. House, O.; Feng, E.; Peet, N. P. *J. Org. Chem.* **1971,** *36,* 2371–2375. doi:10.1021/jo00815a038
3. Chapuzet, J.-M.; Simonet, J. *Tetrahedron* **1991,** *47,* 791–798. doi:10.1016/S0040-4020(01)87068-X
4. Voisin, E.; Williams, V. E. *Macromolecules* **2008,** *41,* 2994–2997. doi:10.1021/ma800320j