Electronic Supplementary Information for:

Concise, Aromatization-based Approach to an Elaborate C_2-Symmetric Pyrenophane

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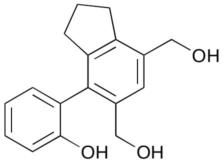
S1. Experimental Procedures and Characterization Data

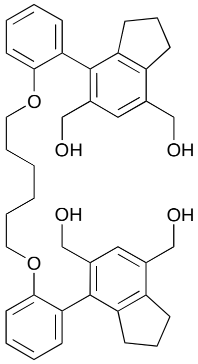
General: Reactions were performed using anhydrous solvents under a balloon containing N_2 unless otherwise indicated. All reactions were performed with oven-dried (120 °C) glassware. THF was distilled immediately prior to use from sodium / benzophenone and DMF was vacuum distilled from CaH_2. Solvents were distilled under reduced pressure using a rotary evaporator. Chromatographic separations were performed using Silicycle silica gel 60, particle size 40-63 mm, unless otherwise mentioned. Thin-layer chromatography (tlc) was performed using commercially precoated plastic-backed POLYGRAM ® SIL G/UV254 silica gel plates, layer thickness 200 mm. Compounds on TLC plates were visualized using a UV lamp (254 and 365 nm). Melting points were obtained using an Optimelt automated melting point system and are uncorrected. Infrared (IR) spectra were recorded using solid samples on a Bruker TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were obtained from $CDCl_3$ or DMSO-d_6 solutions using a Bruker AVANCE (500 MHz) instrument. Chemical shifts are relative to internal standards: TMS (δ_H = 0.00 ppm) and $CDCl_3$ (δ_C = 77.23 ppm), respectively. Low-resolution and high-resolution mass spectroscopic (MS) data were obtained using an Agilent 1100 series LC/MSD instrument and a Waters Micromass® GCT premierTM instrument.

2,3-Dihydro-5,7-bis(hydroxymethyl)-4-(2-hydroxyphenyl)-1*H*-indene (7).



To a 0 °C slurry of $LiAlH_4$ (1.55 g, 40.8 mmol) in THF was added dibenzopyranone **6** (3.00 g, 10.2 mmol) in several portions and the resulting mixture was heated at 70 °C for 5 h. After cooling to 0 °C, water (20 mL) was added carefully over a period of 20 min. The reaction mixture was diluted with aqueous 1.0 M HCl solution (100 mL) and extracted with $CHCl_3$ (3 × 200 mL). The combined organic layers were dried over Na_2SO_4, gravity filtered and the solvent was removed under reduced pressure. The residue was triturated with ether (2 × 15 mL) to afford **7** (2.59 g, 95%) as a colorless solid. R_f = 0.60 (ethyl acetate); mp 148–150 °C; IR (neat) ν 3482 (w), 3265 (m), 3067 (m), 2928 (m), 2361 (w), 1447 (m), 1058 (s) cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 9.23 (br s, 1H), 7.36 (s, 1H); 7.15 (td, J = 7.7, 1.7 Hz, 1H), 6.95 (dd, J = 7.5, 1.7 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 5.06 (t, J = 5.5 Hz, 1H), 4.86 (br s, 1H), 4.49 (d, J = 5.2 Hz, 2H), 4.25 (d, J = 13.5, 1H), 4.17 (d, J = 13.4 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 2.51–2.47 (m, 2H), 1.97–1.89 (m, 2H); ^{13}C NMR (DMSO-d_6, 500 MHz) δ 154.10, 142.36, 138.70, 137.90, 135.79, 131.36, 130.39, 128.10, 125.84, 123.09, 118.70, 115.36, 61.36, 60.74, 31.54, 30.16, 24.25; ESI-(+)-MS *m/z* (%) 294 (19), 293 ($[M + Na]^+$, 100), 253 (7), 223(5), 217 (8).

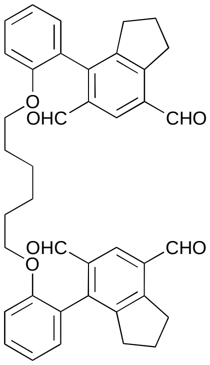
1,6-Bis(2-(2,3-dihydro-5,7-bis(hydroxymethyl)-1*H*-inden-4-yl)phenoxy)hexane (8)



To a suspension of triol **7** (1.00 g, 3.70 mmol) and K_2CO_3 (1.53 g, 11.1 mmol) in DMF (15 mL) was added 1,6-dibromohexane (0.49 g, 2.0 mmol). The resulting mixture was stirred vigorously at 90 °C for 16 h and then cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (50 mL), dried over Na_2SO_4, gravity filtered and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (5% MeOH / $CHCl_3$) to obtain tetraol **8** (0.90 g, 78%) as a colorless solid. R_f = 0.40 (ethyl acetate); mp 131–133 °C; IR (neat) ν 3450–3100 (br, m), 2941 (w), 2860 (w), 2364 (w), 2328 (w), 1444 (s), 1233 (s) cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.36 (s, 1H), 7.32–7.28 (m, 1H), 7.04–7.02 (m, 1H), 7.01 (dd, *J* = 7.4, 1.9 Hz, 1H), 6.97–6.94 (m, 1H), 5.04 (t, *J* = 5.5 Hz, 1H), 4.82 (t, *J* = 5.3 Hz, 1H), 4.47 (d, *J* = 5.5 Hz, 2H), 4.16 (dd, *J* = 14.0, 5.8 Hz, 1H), 4.12 (dd, *J* = 14.0, 5.7 Hz, 1H), 3.87–3.78 (m, 2H), 2.84–2.75 (m, 2H), 2.48–2.36 (m, 2H), 1.93–1.82 (m, 2H), 1.42–1.39 (m, 2H), 1.10–1.07 (m, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 155.33, 142.13, 138.53, 137.73, 135.87, 131.00, 130.40, 128.39, 127.81, 123.11, 120.11, 112.21, 67.29, 61.31, 60.68, 31.51, 30.12, 28.35, 24.78, 24.26; ESI-(+)-MS *m/z* (%) 647 (11), 646 (48), 645 ([M +

Na]$^+$, 100), 569 (9), 551 (7), 359 (8), 305 (7); MALDI-TOF MS cald for $C_{40}H_{46}O_6Na$ 645.3192, found 645.3194.

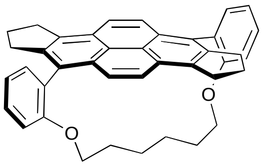
1,6-Bis(2-(5,7-diformyl-2,3-dihydro-1*H*-inden-4-yl)phenoxy)hexane (9)



To a solution of tetraol **8** (0.90 g, 1.5 mmol) in CH_2Cl_2 (45 mL) was added Celite® (2.70 g) in one portion. To this suspension was added PCC (3.74 g, 17.4 mmol) in several portions and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was vacuum filtered through a plug of Celite® and the cake was washed thoroughly with $CHCl_3$ (3 × 50 mL). The filtrate was removed under reduced pressure and the residue was subjected to column chromatography (30% ethyl acetate / hexanes) to afford tetraaldehyde **9** (0.63 g, 72%, *ca*. 1.2:1 mixture of diastereomers by ^{1}H NMR analysis) as a colorless solid. $R_f = 0.30$ (30% ethyl acetate / hexanes); mp 168–171 °C; IR (neat) ν 2944 (w), 2857 (w), 2364 (w), 2329 (w), 1691 (s), 1590 (m), 1241 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.17 (s, 1H), 10.16 (s, 1H), 9.71 (s, 1H), 9.70 (s, 1H), 8.27 (s, 1H), 8.27 (s, 1H), 7.44–7.40 (m, 2H), 7.17–7.15 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.99–6.96 (m, 2H), 3.85–3.82 (m, 4H), 3.45–3.31 (m, 4H), 2.80–2.71 (m, 2H), 2.64–2.54 (m, 2H), 2.18–2.00 (m, 4H), 1.48–1.43 (m, 4H), 1.08–1.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 192.32, 191.70 (191.68), 155.83, 151.74 (151.69), 147.26

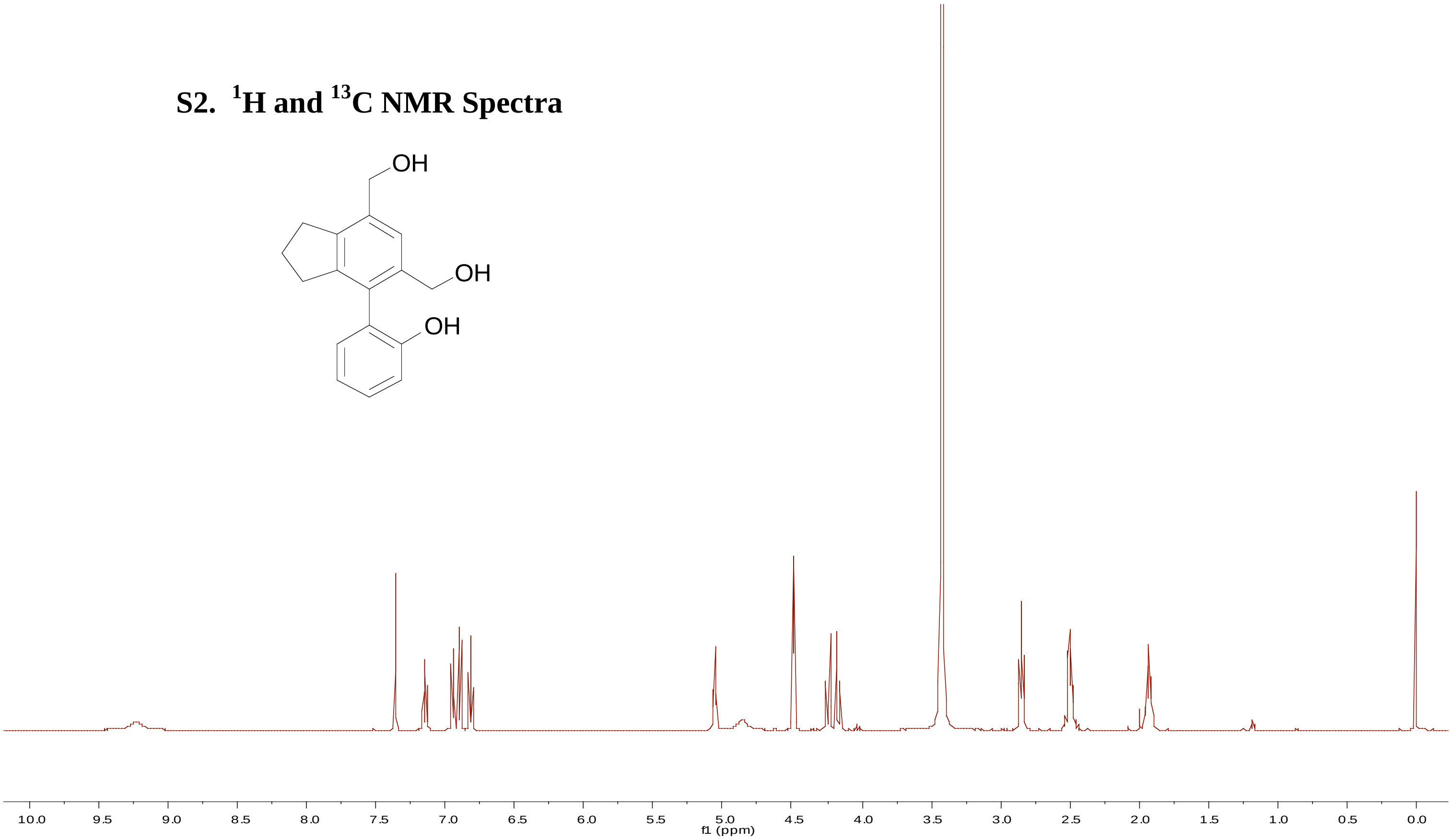
(147.23), 143.41, 133.36, 131.43, 130.75, 130.32, 129.82 (129.78), 124.42, 120.69, 111.94, 68.00 (67.96), 33.10, 31.27, 28.75, 25.41 (25.36), 24.91 (24.88); APCI-(+)-MS *m/z* (%) 617 (11), 616 (43), 615 ($[M + H]^+$, 100). HRMS [(EI-(+)] calcd for $C_{40}H_{38}O_6$ 614.2668, found 614.2670.

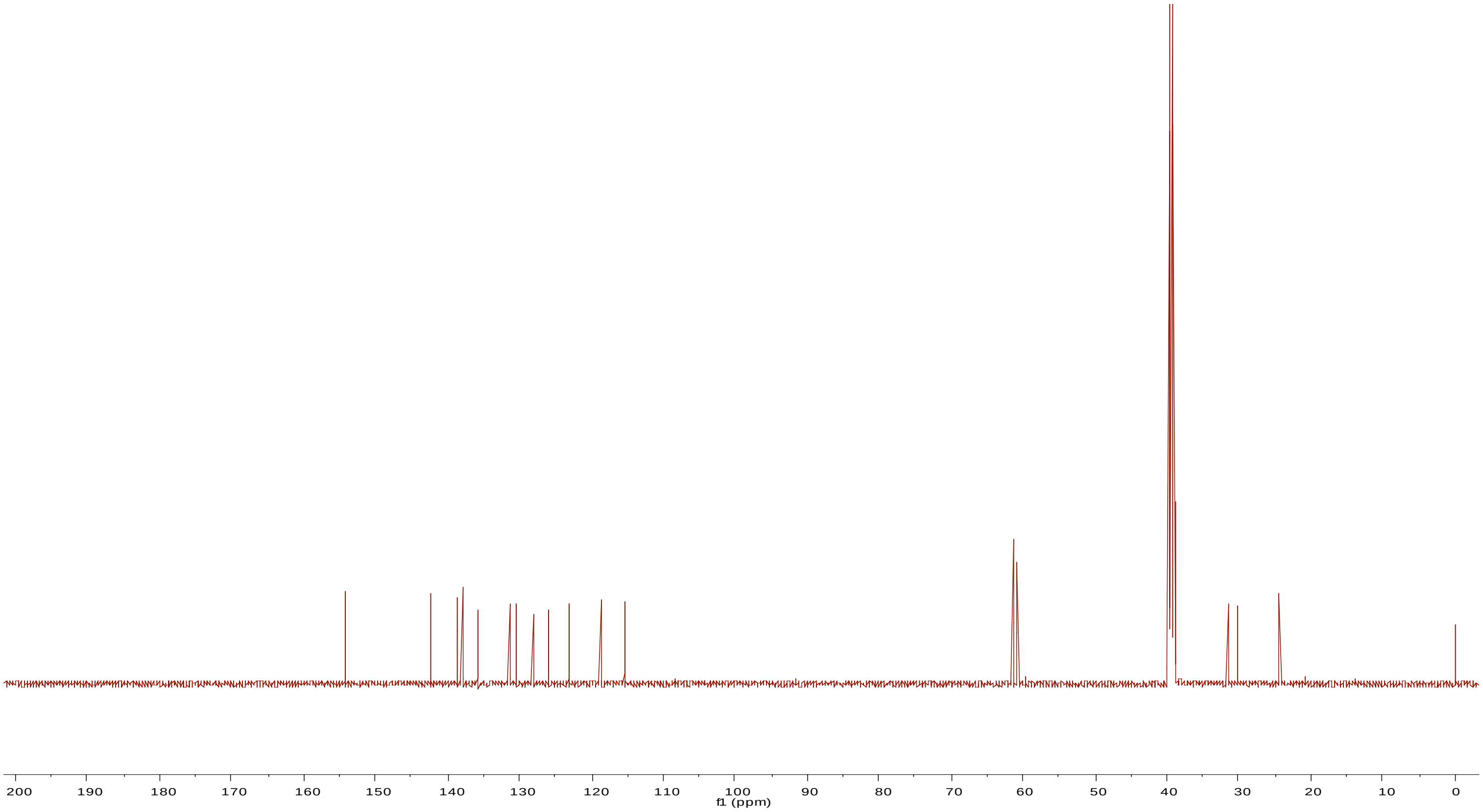
Pyrenophane 11

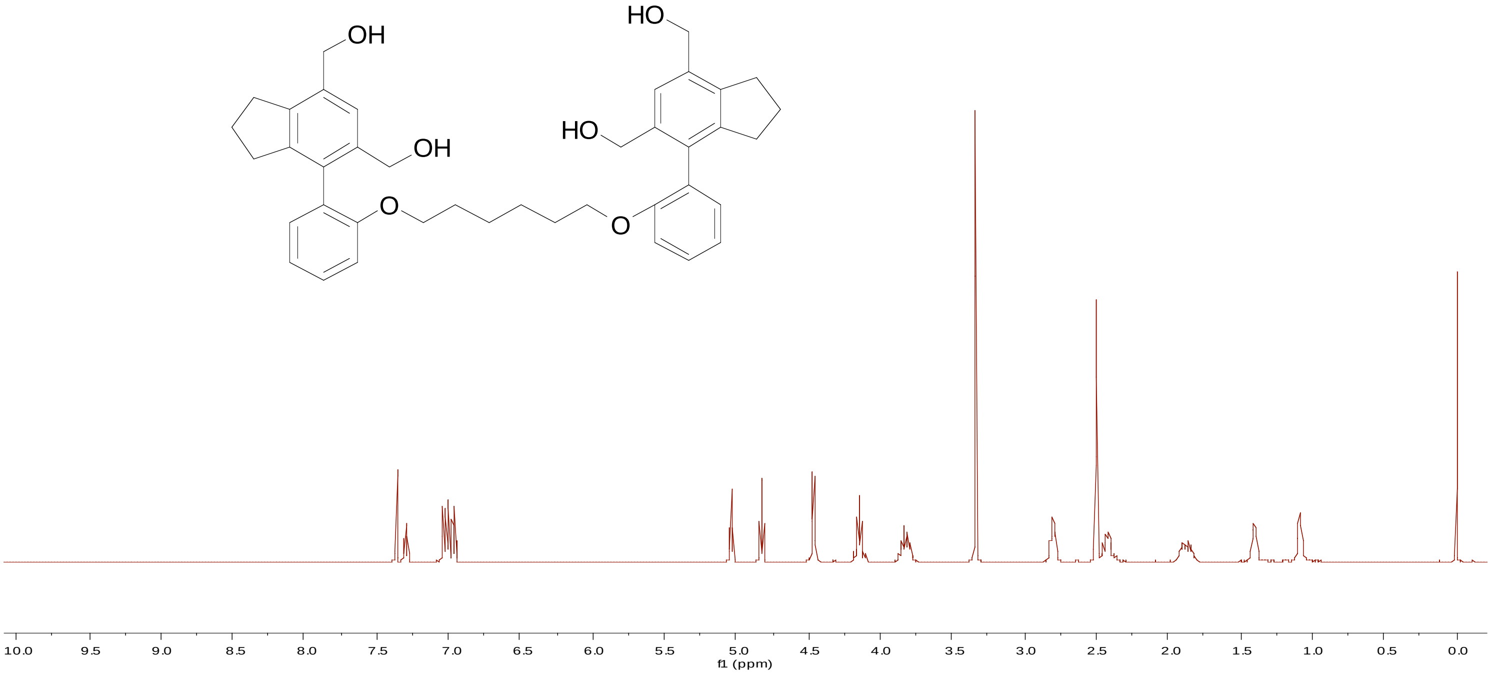


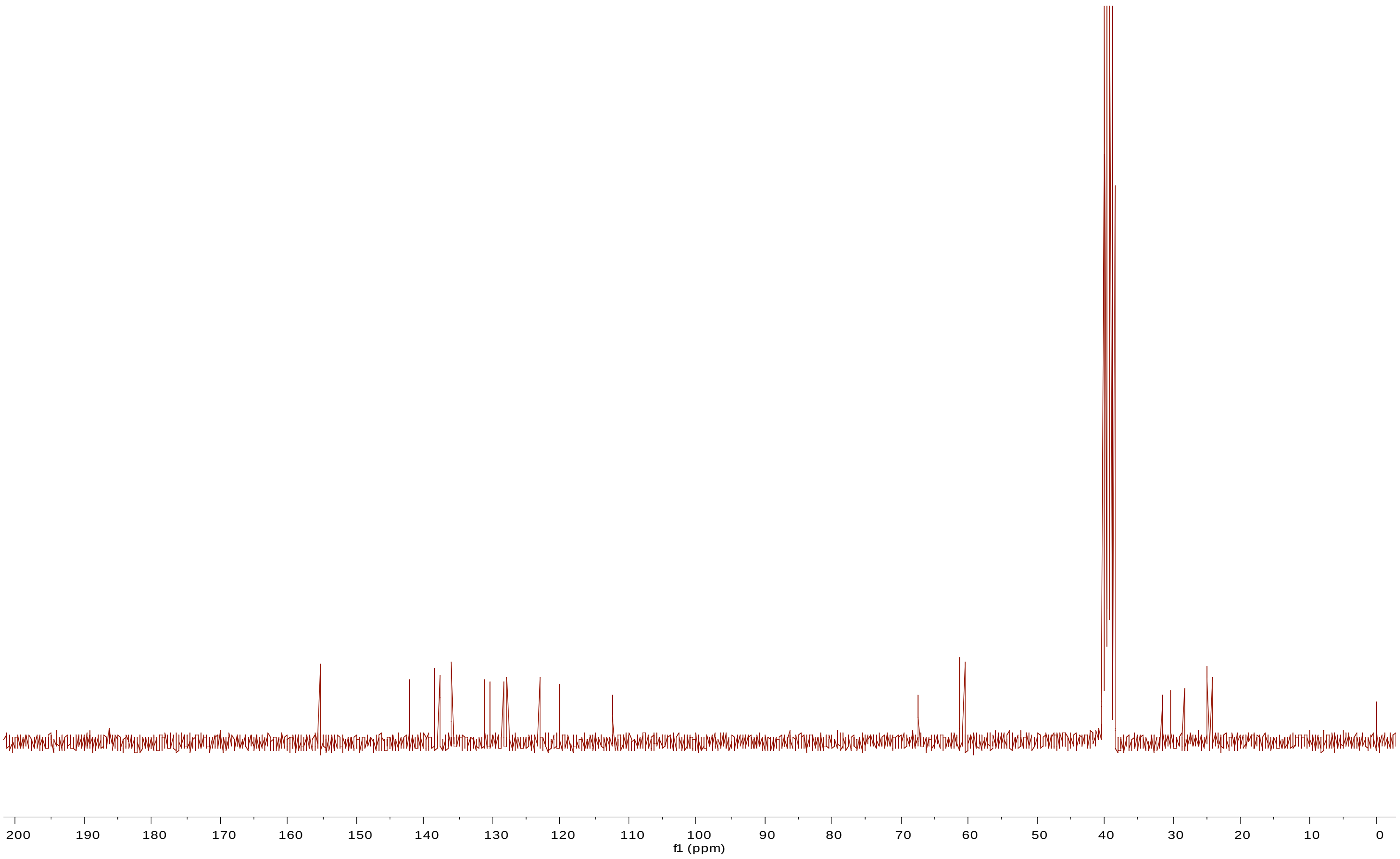
To a 0 °C suspension of Zn (<10 micron, 1.06 g, 17.1 mmol) in THF (35 mL) was added $TiCl_4$ (1.0 M in CH_2Cl_2, 13.0 mL, 13 mmol) over a period of 15 min and the resulting mixture was heated at 70 °C for 1 h. Pyridine (0.13 mL, 1.67 mmol) was added to the hot reaction mixture and heating was continued for 15 min. A solution of tetraaldehyde **9** (0.50 g, 0.81 mmol) in THF (30 mL, boiling was required for complete dissolution of **9**) was added over a period of 30 min and heating was continued for 24 h. The reaction mixture was cooled to room temperature and 10% aqueous NaOH solution (20 mL) was added. The precipitate that formed was removed by vacuum filtered through a plug of Celite®, which was then washed with $CHCl_3$ (3 × 35 mL). The filtrate was washed with H_2O (2 × 50 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was subjected to column chromatography using neutral Al_2O_3 (5–10% ethyl acetate / hexanes) and the product was triturated with diethyl ether (2 × 1 mL) to give pyrenophane **11** (53 mg, 12 %) as an off-white solid. $R_f = 0.50$ (10% ethyl acetate / hexanes); mp 185-188 °C; ^1H NMR (CD_2Cl_2, 500 MHz) δ 7.89 (d, $J = 9.2$ Hz, 1H), 7.73 (d, $J = 6.8$ Hz, 1H), 7.69 (d, $J = 9.2$ Hz, 1H), 7.42 (t, $J = 8.3$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.55 (t, *J* = 7.4 Hz, 2H), 3.32-3.26 (m, 2H), 3.20-3.16 (m, 1H), 2.85-2.79 (m, 1H), 2.35-2.24 (m, 2H), 0.38-0.33 (m, 1H), 0.17-0.11 (m, 1H), −0.35 - –0.43 (m, 1H), −0.47 - –0.55 (m, 1H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 158.48, 141.83, 138.73, 130.91, 129.87, 129.39, 126.21, 125.10, 123.18, 122.09, 116.96, 70.96, 33.71, 32.40, 30.66, 26.03, 25.62; APCI-(+)-MS *m/z* (%) 551 (10), 550 (43), 549 ($[M + H]^+$, 100), 547 (4); HRMS [(EI-(+)] calcd for $C_{40}H_{36}O_2$ 548.2715, found 548.2718.

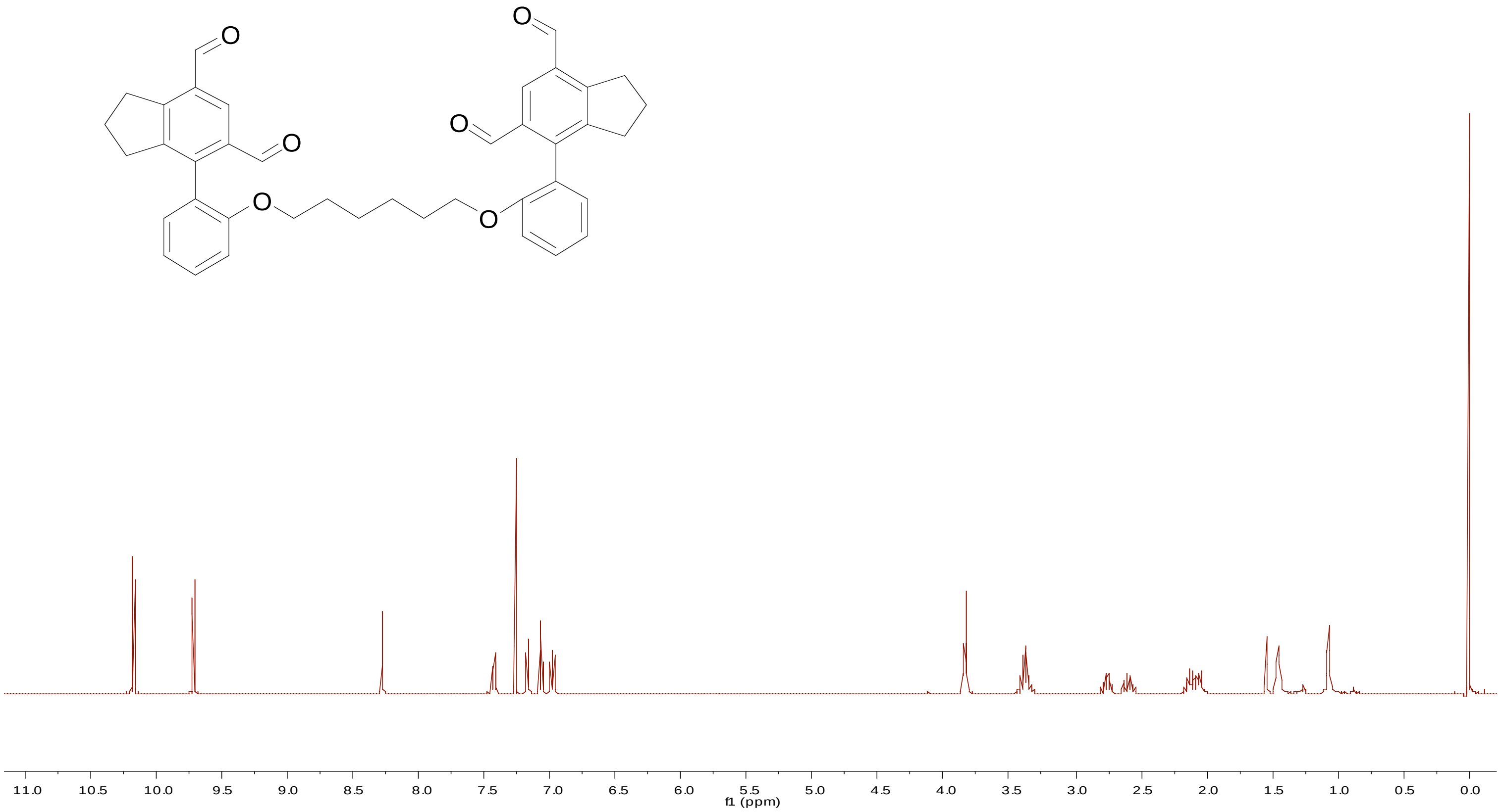
S2. ^{1}H and ^{13}C NMR Spectra






OH
OH
HO
HO
O
O
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)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
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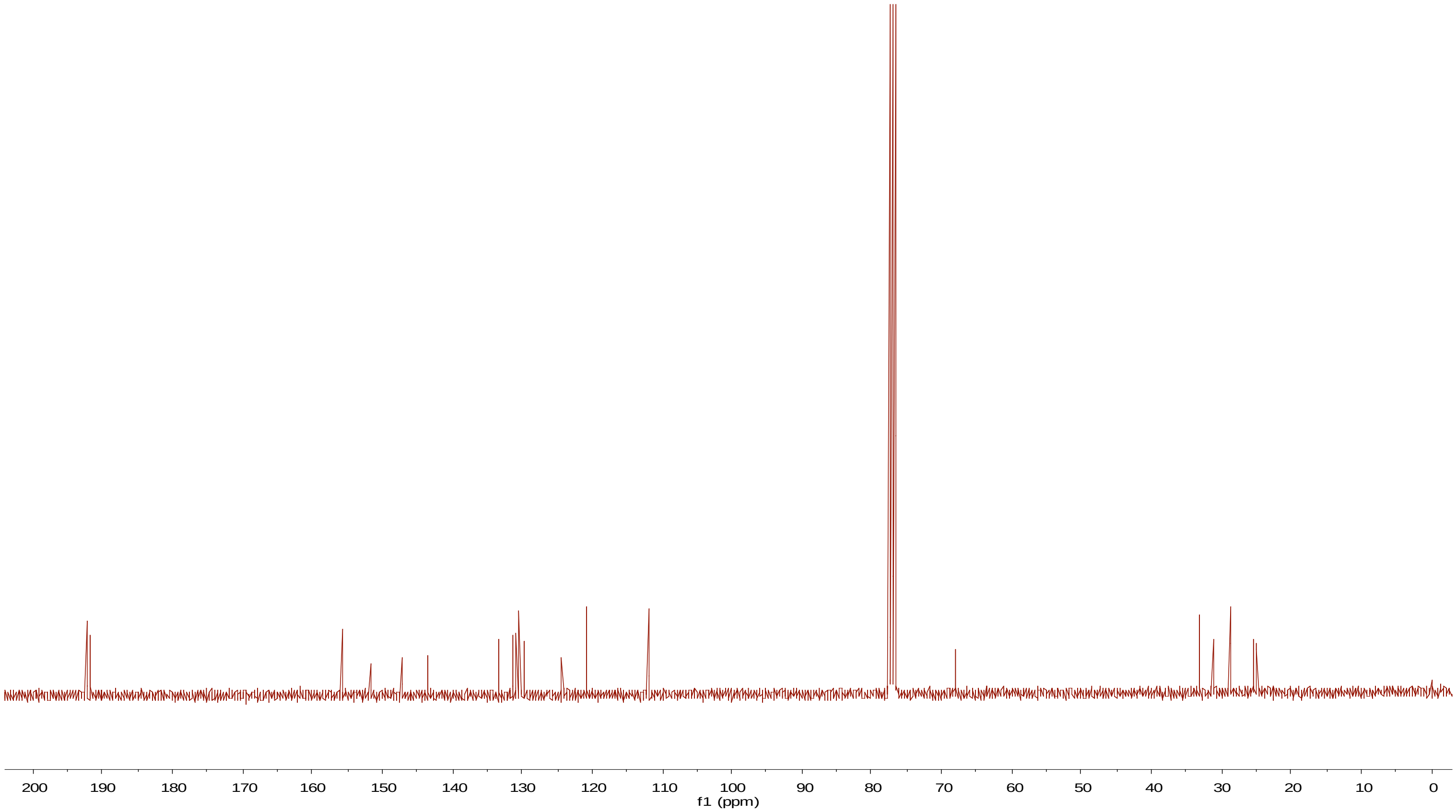
O
O

11.0
10.5
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)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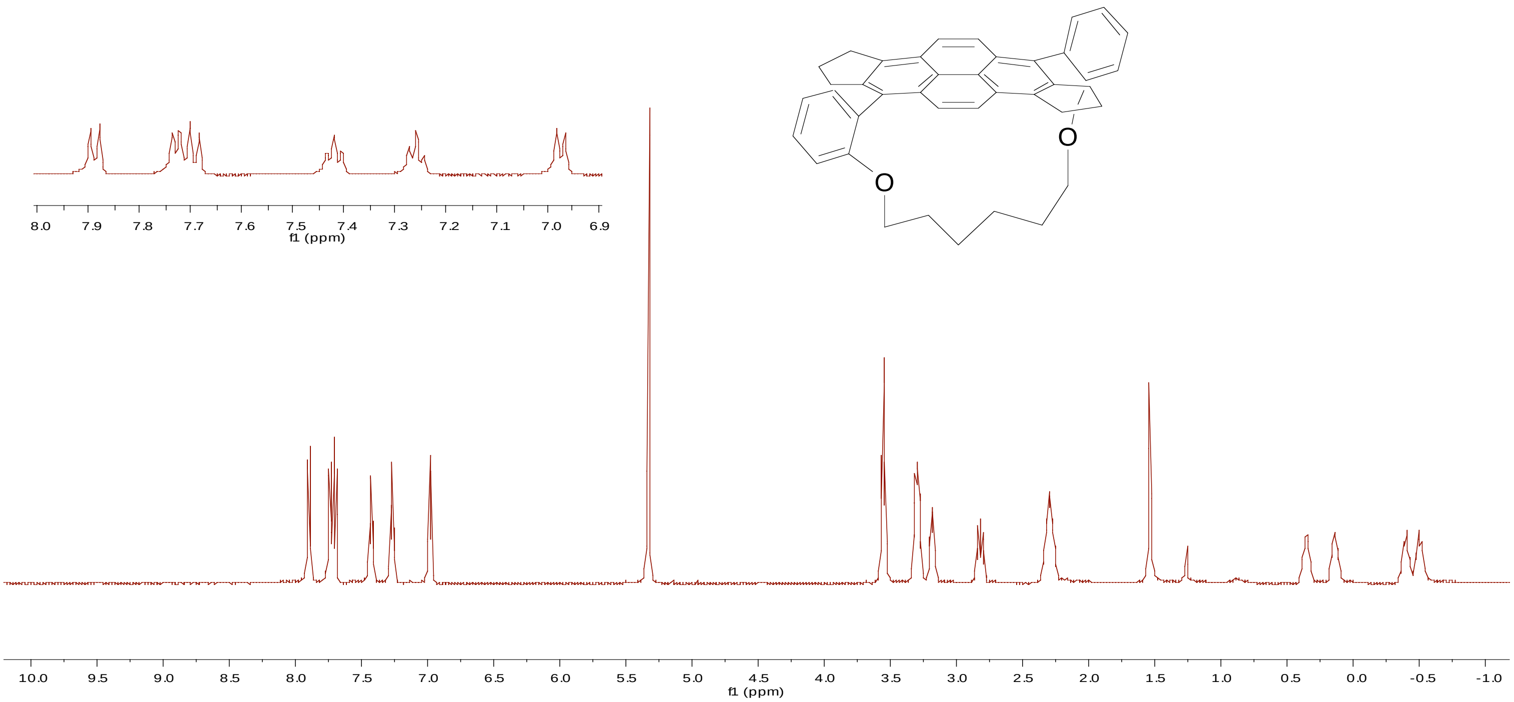
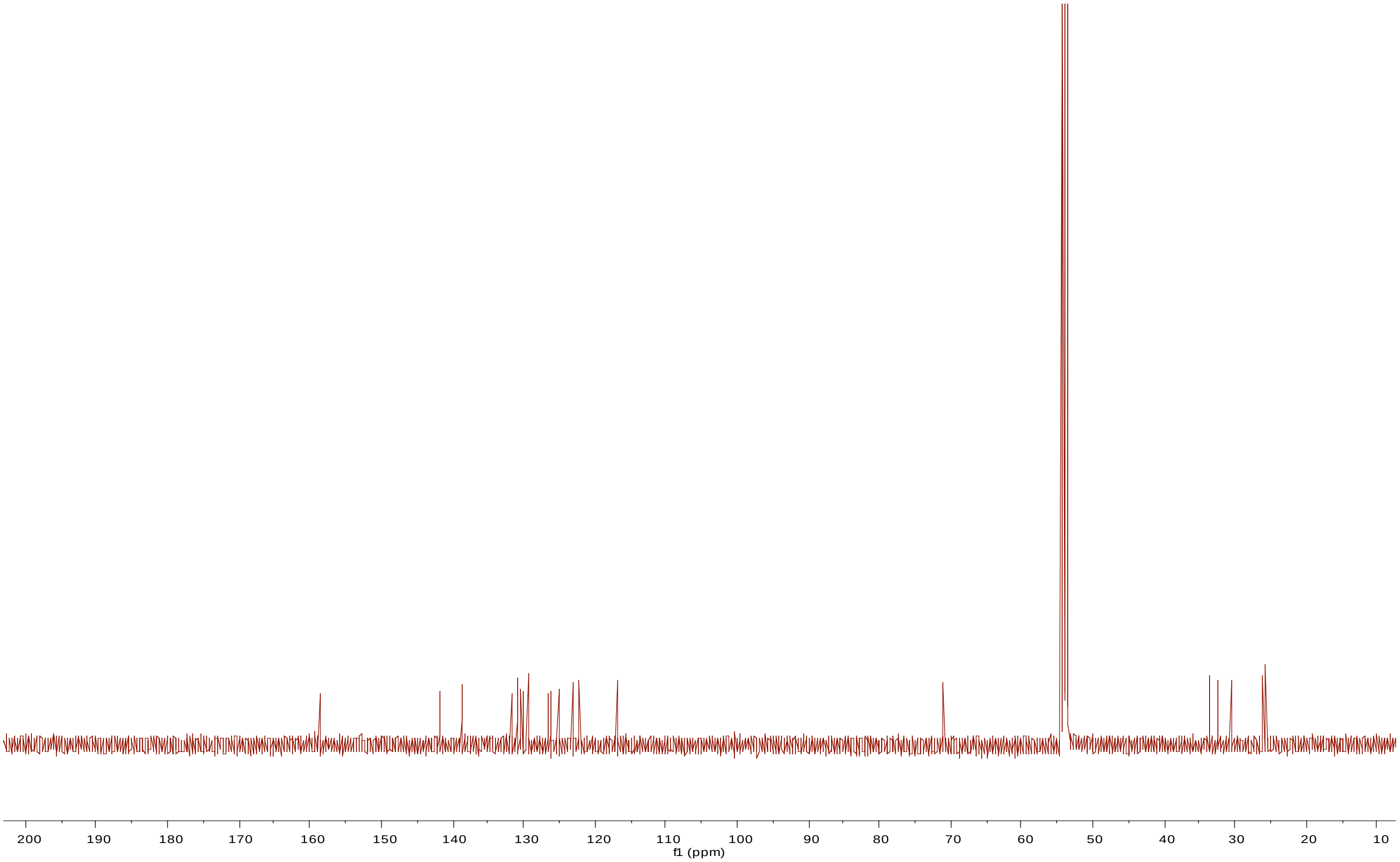
20
10
0
f1 (ppm)


O
O
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
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
-1.0
f1 (ppm)


200
190
180
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120
110
100
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80
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60
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40
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20
10
f1 (ppm)

S3. Details of the Resolution of 11

Requestor:	Graham Bodwell	Sample ID:	C2-SYM
Amount received:	20 mg	Quote #:	

Analysis Summary:

The following SFC separation yielded 9 mg of peak-1 (chemical purity >99%, ee >99%) and 10 mg of peak-2 (chemical purity >99%, ee >99%). Chromatograms are included in this report.

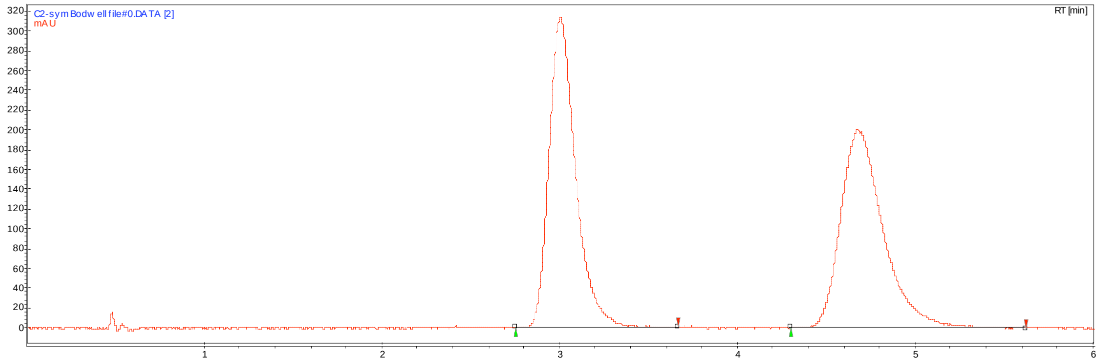
Preparative Method:

OD-H (2 x 20 cm)
40% ethanol(0.1% DEA)/CO_2, 100 bar
60 mL/min, 254 nm.
inj vol.: 5 mL, 0.75 mg/mL 1:1:1 ethanol:DCM:DMSO

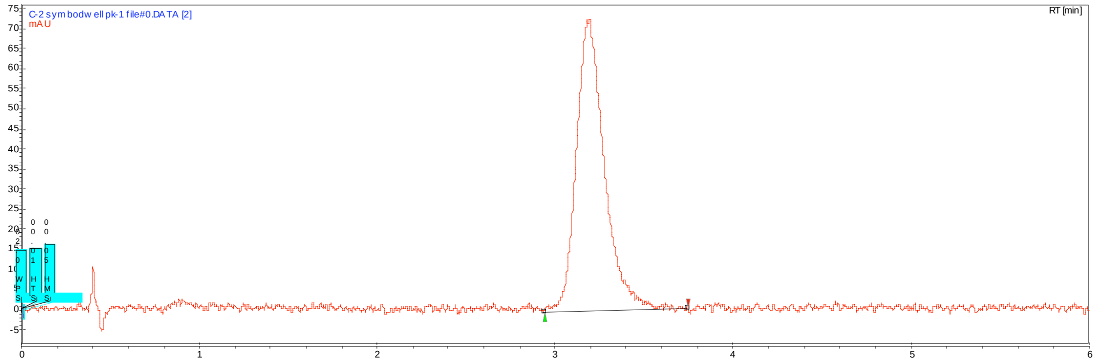
Analytical Method:

OD-H (15 x 0.46 cm)
40% methanol(0.1% DEA)/CO_2, 100 bar
3 mL/min, 220 and 254 nm

Sample: C2-SYM

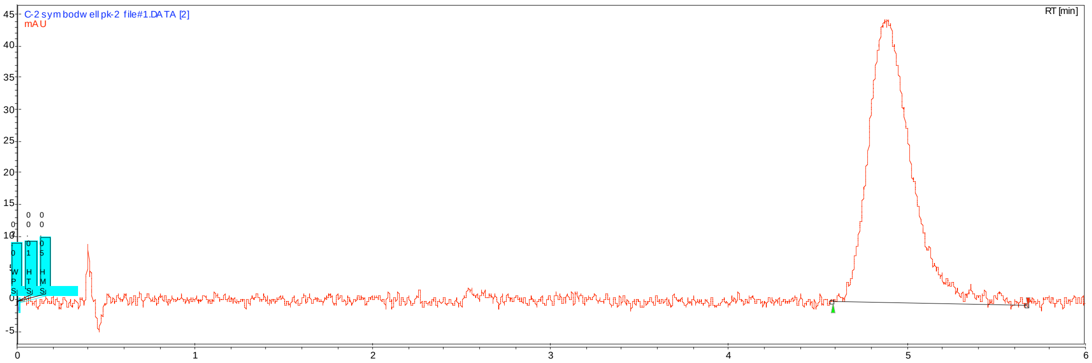


Sample: C2-SYM peak-1



Index	Time (min)	Area (%)
Peak-1	3.19	100.00
Peak-2		
Total		100.00

Sample: C2-SYM peak-2



Index	Time (min)	Area (%)
Peak-1		
Peak-2	4.88	100.00
Total		100.00

S4. Supplementary Crystallographic Information for 11

Single Crystal X-ray Diffraction Studies. A crystal of **11** was mounted on a low temperature diffraction loop and measured on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods[S4-1] and expanded using Fourier techniques.[S4-2] Neutral atom scattering factors were taken from Cromer and Waber.[S4-3] Anomalous dispersion effects were included in Fcalc;[S4-4] the values for Δf' and Δf" were those of Creagh and McAuley.[S4-5] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S4-6] All calculations and visualizations were performed using CrystalStructure[S4-7,S4-8] and Mercury[S4-9] crystallographic software packages, except for refinement, which was performed using SHELXL-97.[S4-1] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced in calculated positions and refined on a riding model. Crystallographic details are summarized in Table S4-1.

Pyrenophane **11** crystallized in the triclinic space group $P\bar{1}$ with Z = 2. Figure S4-1 shows the asymmetric unit, while the alternate view in Figure S2 highlights the numerous intramolecular (methylene)C–H···π interactions (3.30 – 3.51 Å; Table S4-2). Note that the longer (methylene)C–H···π interactions are considered insignificant due to the small Donor – Hydrogen … Acceptor (D – H ··· A) bond angles (these deviate significantly from linearity).[S4-S10] The torsion angle for C8-C26-C18-C16 is 175.1° while the bend angle between the planes defined by C7-C8-C26 and C17-C18-C16 is 17.4°. The twist in the pyrene system can be assessed based on the torsion angles through the middle of the pyrene system (C6-C7-C26-C27-C28-C16-C17-C29; Table S4-3); each angle would measure 180° in a planar system, however, here, the five angles range from

160.0 – 174.1°. Further intermolecular π···π interactions (3.47 Å; Figure S4-3) are present between adjacent molecules in the packed unit cell, as calculated from closest mean plane contacts.

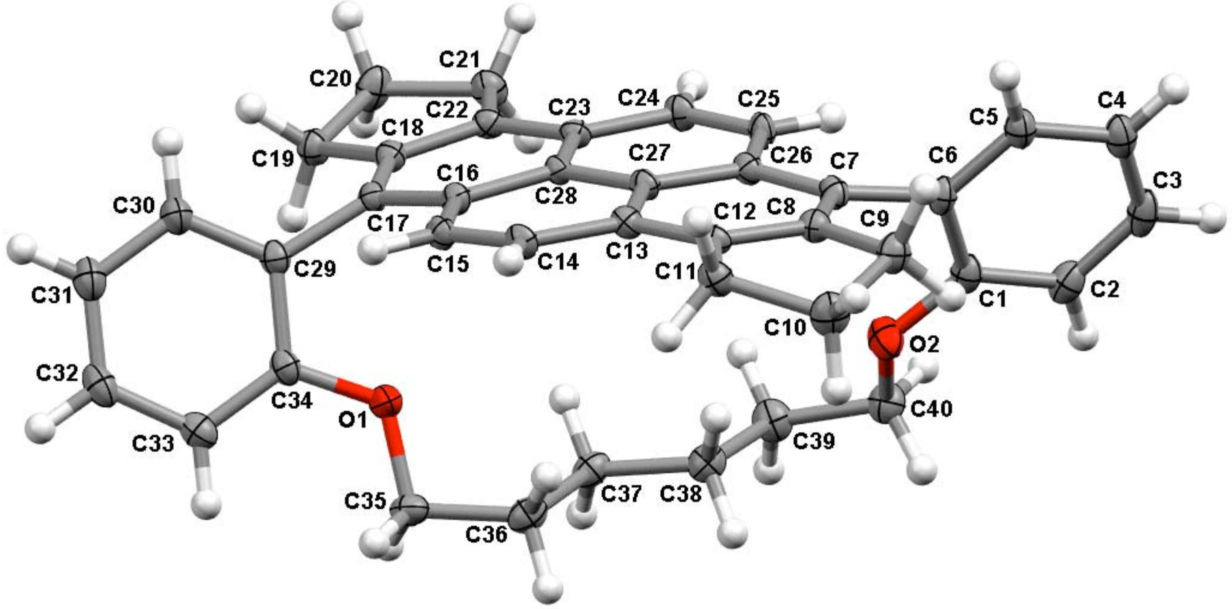


Figure S4-1: Asymmetric unit for **11** with 30% probability ellipsoids; H-atom labels omitted for clarity.

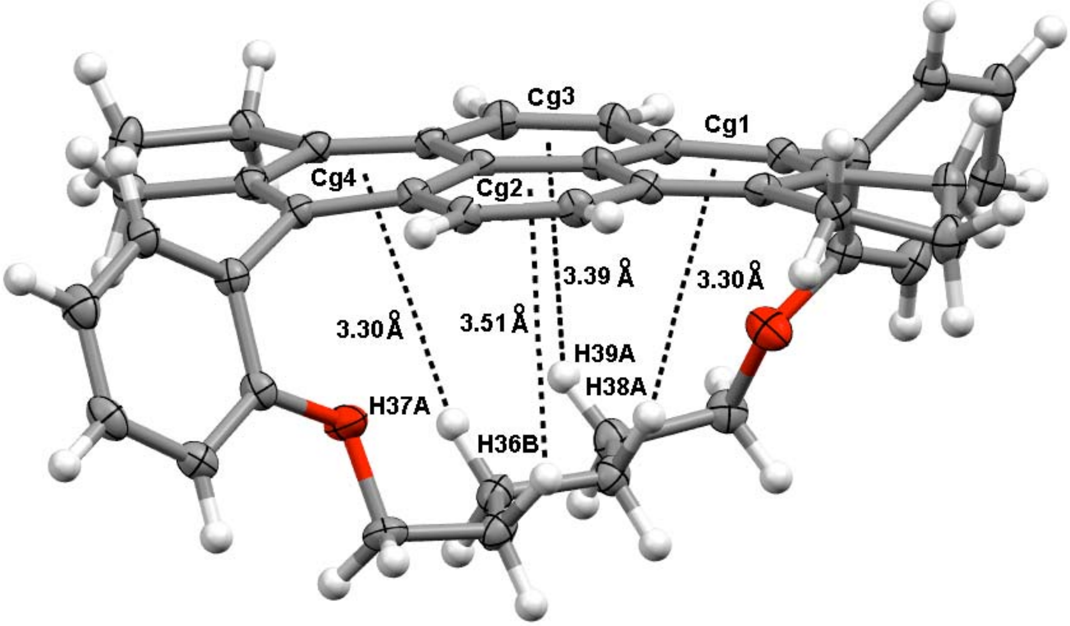


Figure S4-2: Alternate view of the asymmetric unit of **11**, with (sp^3)C–H to π contacts indicated by dashed lines.

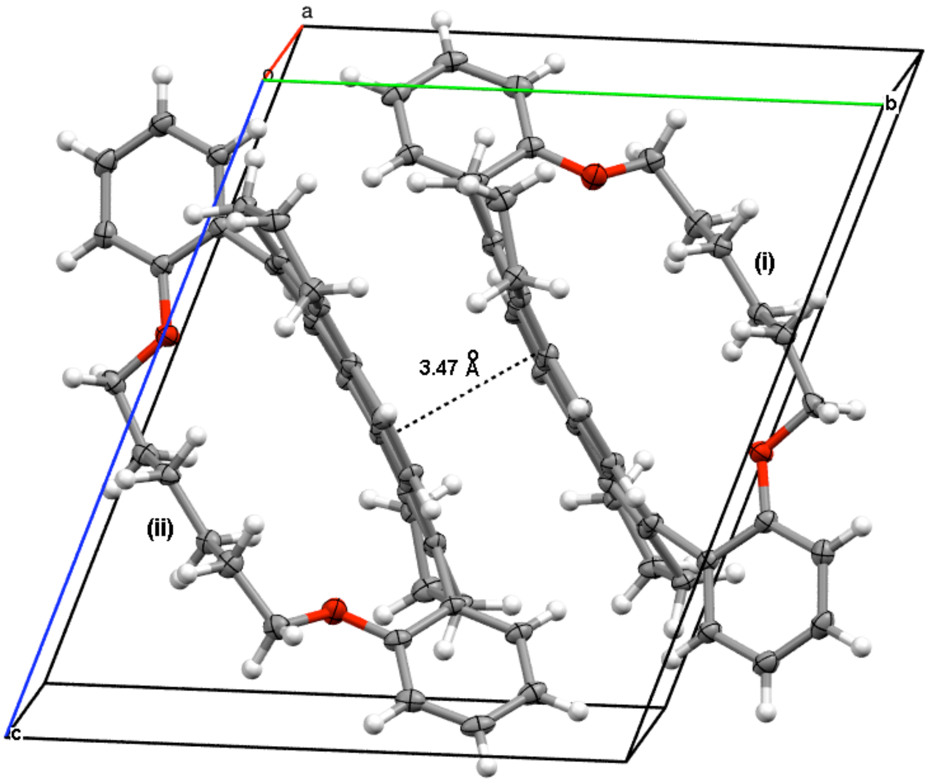


Figure S4-3: Packed unit cell for **11**. Separation between the planes formed by the atoms C13, C16, C23, C26, C27 and C28, and their symmetry equivalent, inversion related, counterparts generated by the operation (ii) 1-x, 1-y, 1-z indicated by a dashed line.

Table S4-1 Summary of X-ray Data

Compound reference	**11**
Chemical formula	$C_{40}H_{36}O_2$
Formula Mass	548.69
Crystal system	Triclinic
a/Å	9.395(5)
b/Å	12.771(6)
c/Å	13.799(7)
α/°	104.045(8)
β/°	107.143(4)
γ/°	106.279(6)
Unit cell volume/Å^3	1419.9(12)
Temperature/K	153(2)
Space group	$P\overline{1}$
No. of formula units per unit cell, Z	2
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.077
No. of reflections measured	13837
No. of independent reflections	5859
R_{int}	0.0590
Final R_1 values ($I > 2\sigma(I)$)	0.0884
Final $wR(F^2)$ values (all data)	0.1924
Goodness of fit on F^2	1.150

$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, I > 2\sigma(I)$
$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2}$, all data

Table S4-2: Intramolecular (methylene)C-H…π interactions for **11**

D – H ··· A	**D – H**	**H ··· A**	**D – H ··· A**
C38 – H38A ... Cg1	0.99 Å	3.30 Å	159.8°
C36 – H36B ... Cg2	0.99 Å	3.51 Å	128.1°
C39 – H39A ... Cg3	0.99 Å	3.39 Å	128.5°
C37 – H37A ... Cg4	0.99 Å	3.30 Å	157.6°

For Table S4-2:
Cg1 is the centroid of C7, C8, C12, C13, C26, C27
Cg2 is the centroid of C13-C15, C27, C28
Cg3 is the centroid of C23-C28
Cg4 is the centroid of C16-C18, C22, C23, C28

Table S4-3: Torsion angles through the middle of the pyrene system (°)

C6 – C7 – C26 – C27	168.5(2)
C7 – C26 – C27 – C28	–174.1(2)
C26 – C27 – C28 – C16	172.0(2)
C17 – C16 – C28 – C27	–171.5(2)
C28 – C16 – C17 – C29	160.1(2)

References for Section S4:

S4-1. SHELX97: G.M. Sheldrick, *Acta Cryst*. 2008, **A64**, 112.

S4-2. DIRDIF99: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

S4-3. D.T. Cromer, J.T. Waber, "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

S4-4. J.A. Ibers, W.C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

S4-5. D. C. Creagh, W.J. McAuley, "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

S4-6. D. C. Creagh, J.H. Hubbell, "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

S4-7. CrystalStructure 3.7.0: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2005). 9009 New Trails Dr. The Woodlands TX 77381 USA.

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S5. Experimental Details of the Absorption and Emission Spectra and Beer's Law Plot

Sample Preparation. Samples were dissolved 2.5 mL of $CHCl_3$ (Fisher, Spectral grade) in a 1.0 cm path-length screw-top quartz cuvettes received from Starna. UV-Vis and fluorescence spectra of solvent were routinely recorded prior to addition of the sample to ensure that the solvent did not contain absorbing or emitting impurities. Extinction coefficients were determined by gravimetric methods with typical concentrations of between 10^{-5} to 10^{-6} M.

Electronic Spectra. UV-vis spectra were obtained using an Agilent 8453A Diode Array UV-visible spectrophotometer. Manipulation of the UV-visible spectroscopic data were conducted using ChemStation software provided by Agilent or by exporting the data and utilizing Microcal Origin 8.0 analysis software.

Luminescence measurements were performed using a Photon Technology International (PTI) Quantamaster 6000 photon counting spectrofluorometer equipped with a 75 W Ushio Xenon arc lamp as the excitation source. The emitted light was collected 90° to the excitation beam and detected by a Hammamatsu R-928 photomultiplier tube (PMT) housed in Products for Research water-cooled PMT housing. Emission spectra were corrected for instrument response and light loss using correction factors supplied by manufacturer. Excitation spectra were corrected in real time using correction factors supplied by the manufacturers.

Emission quantum yields were measured on optically dilute (Abs < 0.2 with λ_{exc} = 350 nm, 1 atm N_2) $CHCl_3$ solutions at 295 ± 3 K by relative actinometry using a standard quinine bisulfate in 0.1 M aqueous sulfuric acid (Φ_{std} = 0.52 at λ_{exc} = 350 nm). Quantum yields were determined using:

$$\phi_{em} = \phi_{std}\left(\frac{A_{std}}{A_{un}}\right)\left(\frac{I_{un}}{I_{std}}\right)\left(\frac{n_{un}}{n_{std}}\right)^2 \qquad [S5\text{-}1]$$

Where *A* is a solution absorbance, *I* the emission intensity, *n* the refraction index of the solvent and the subscripts *un* and *std* refer to the unknown and standard, respectively.

Time Resolved Emission Measurements. Lifetimes were obtained using PTI LaserStrobe TM-3 fluorescence lifetime spectrofluorometer. Sample excitation was afforded by a PTI GL-3300 nitrogen laser coupled to the high-resolution PTI GL-302 dye laser. Instrument response functions (IRF) were obtained using a scattering solution (milk or coffee powder in H_2O). The extraction of lifetimes from experimental data was performed using by curve fitting procedures based on Marquardt minimization algorithm provided by PTI or the data was exported and data analysis was accomplished using Microcal Origin 8.0 software.

Beer's Law Plot

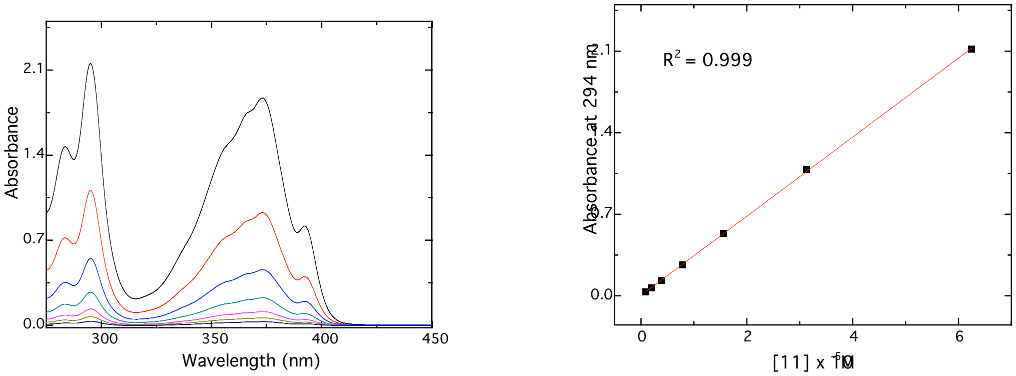

Fig. S5-1. Absorption spectral data obtained as a function of **[11]** (left) and a plot of absorbance as a function of [**11**] (right). The red line is the result of a linear least squares analysis of the data according to the equation $A = \varepsilon[\mathbf{11}]$ at $\lambda = 294$ nm; the slope = 3.33 x 10^4 $M^{-1}cm^{-1}$ with an intercept of 0.002, $R^2 = 0.999$. Experiment performed in $CHCl_3$ at 298 ± 3 K.