Supplementary Information for:

Anthra- and Pentacenequinone Derivatives: Influence of Structure on the Formation of Columnar Liquid Crystal Phases

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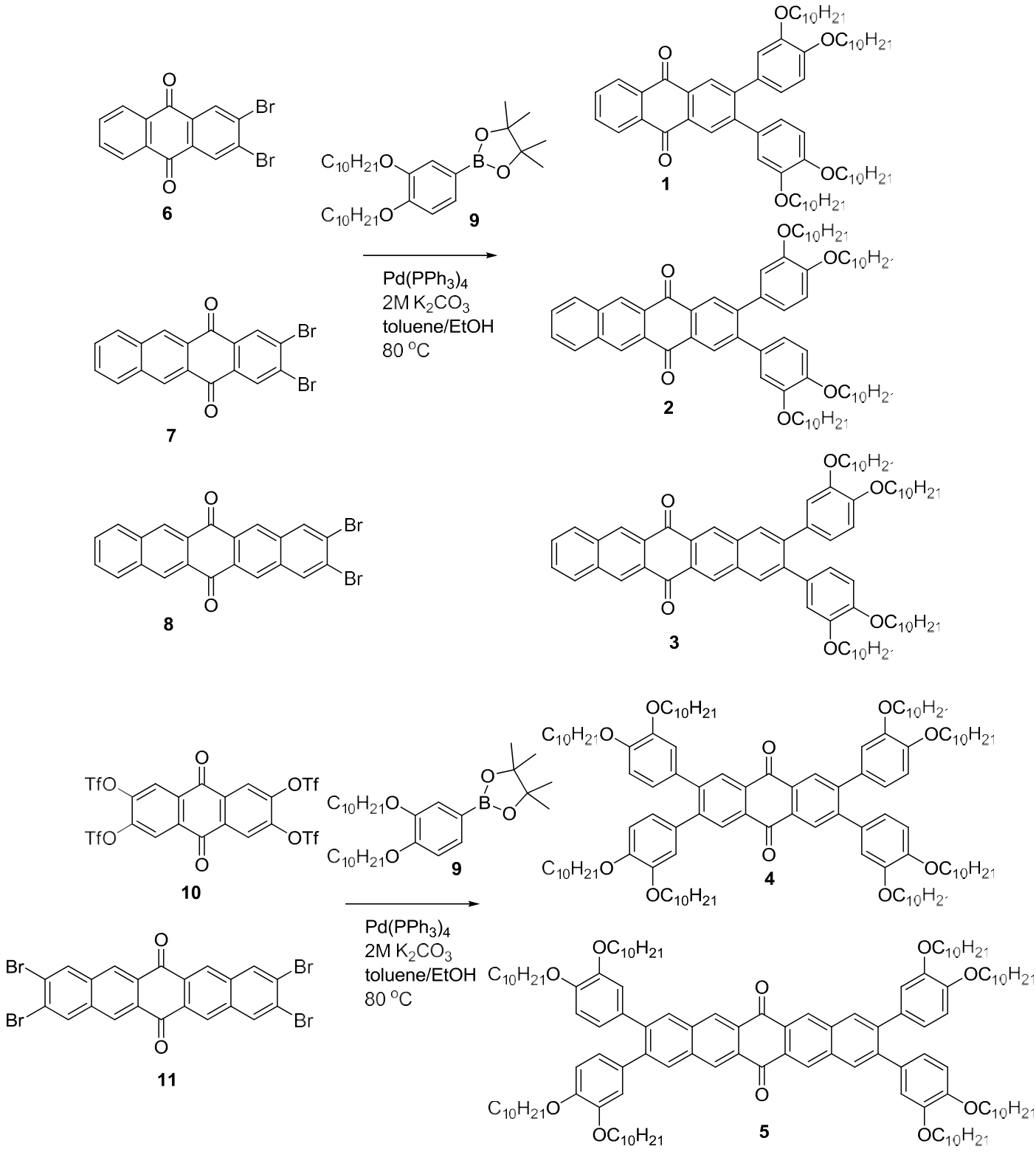
Contents:

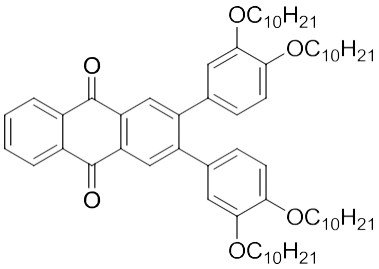
Synthesis


6
9
1
Pd(PPh3)4
2M K2CO3
toluene/EtOH
80 °C
7
2
8
3
10
9
4
Pd(PPh3)4
2M K2CO3
toluene/EtOH
80 °C
11
5

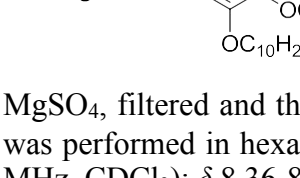
General

^{1}H-NMR and ^{13}C-NMR were recorded using a Varian 300 MHz (^{1}H) Unity Inova NMR or an Agilent Technologies 400 MHz NMR spectrometer, using indicated deuterated solvents purchased from CIL Inc. All chemicals used were purchased from Sigma-Aldrich and were used as received. 2,3-Dibromoanthraquinone (**6**),[1] 2,3-dibromopentacenequinone (**8**),[2] 1- pinacolatoboron-3,4-bis(decyloxy)benzene (**9**),[3] and 2,3,7,8-Tetrahydroxyanthracene-5,10-dione (**10**)[4] were prepared according to literature procedures. Anhydrous and oxygen-free solvents were dispensed from a custom-built solvent purification system which used purification columns packed with activated alumina and supported copper catalyst (Glasscontour, Irvine, CA). Oven or flame-dried glassware was used for all reactions. High resolution mass spectra were recorded at the Centre Régional de Spectrométrie de Masse à l'Université de Montréal using an Agilent LC-MSD TOF spectrometer.

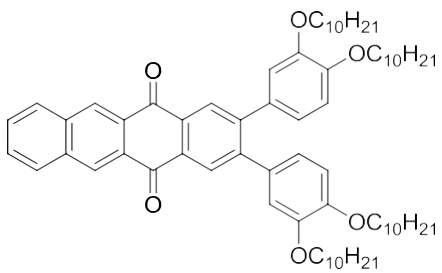
2,3-bis[3,4-bis(decyloxy)phenyl]anthracene-5,10-dione (1). A solution of compound **6** (369 mg, 1.01 mmol), 1-pinacolatoboron-3,4-bis(decyloxy)benzene (1.30 g, 2.52 mmol) in toluene (20 mL) and ethanol (5 mL) was degassed by sparging with N_2 for 10 minutes. $Pd(PPh_3)_4$ (61 mg, 0.052 mmol, 5 mol%) was added, followed by 2M aqueous K_2CO_3 (5 mL). The solution was heated to 80 °C and left it to stir for 4 days under N_2. The reaction mixture was cooled to room temperature and extracted 3 times with CH_2Cl_2. The combined organic extracts were washed with water, then brine, dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. Column chromatography was performed in hexanes/EtOAc (95:5) to give the pure product (0.41 g, 41 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36-8.33 (m, 2H), 8.34 (s, 2H), 7.84-7.81 (m, 2H), 6.83-6.82 (m, 4H), 6.68 (s, 2H), 3.98 (t, J = 6.9 Hz, 4H), 3.72 (t, J = 6.6 Hz, 4H), 1.83-1.79 (m, 4H), 1.69-1.65 (m, 4H), 1.47-1.25 (m, 56H), 0.89-0.86 (m, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 183.3, 149.2, 148.9, 146.4, 134.2, 134.0, 132.7, 132.1, 129.6, 127.4, 122.4, 115.7, 113.5, 69.5, 69.4, 32.2, 29.92, 29.87, 29.85, 29.83, 29.7, 29.65, 29.63, 29.59, 29.54, 29.36, 26.29, 26.24, 22.91, 14.3. HRMS (MALDI) calc'd for C66H96O6+H *m/z* 984.7201, found 984.7207.



2,3-dibromotetracene-5-12-dione (7). 2,3-Dibromonaphthoquinone[1] (0.352 g, 1.11 mmol), *α,α,α′,α′*-tetrabromo-*o*-xylene (0.470 g, 1.11 mmol), and potassium iodide (1.12 g, 6.75 mmol) were combined in an oven-dried flask that was then purged with N_2.Dry DMF (40 mL) was added via cannula and the reaction mixture was heated at 80 °C for three days. The reaction mixture was cooled to room temperature and water (*ca.* 100 mL) was added. The resulting precipitate was collected by suction filtration, washed with water, ethanol, and acetone and then air-dried to yield **7** (0.244 g, 53%) as a light brown solid which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 2H), 8.57 (s, 2H), 8.09-8.05 (m, 2H), 7.9-7.5 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 181.54, 135.47, 133.96, 132.95, 132.45, 130.47, 130.28, 130.13, 129.42.

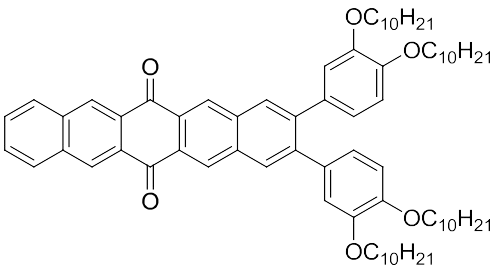


2,3-bis[3,4-bis(decyloxy)phenyl]tetracene-5,12-dione (2). A solution of compound **7** (206 mg, 0.495 mmol), 1-

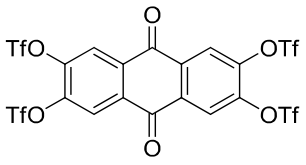


pinacolatoboron-3,4-bis(decyloxy)benzene (553 mg, 1.07 mmol) in toluene (25 mL) and ethanol (7 mL) was degassed by sparging with N_2 for 10 minutes. $Pd(PPh_3)_4$ (58 mg, 0.050 mmol, 10 mol%) was added, followed by 2M aqueous K_2CO_3 (7 mL). The mixture was degassed for a further 10 minutes and then heated at 80 °C for 3 days under N_2. The reaction mixture was cooled to room temperature. The organic phase was separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic extracts were dried using $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (4:1 toluene/DCM) to yield **2** s a yellow solid (308 mg, 60%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (s, 2H), 8.42 (s, 2H), 8.15-8.11 (m, 2H), 7.73-7.70 (m, 2H), 6.86-6.80 (m, 4H), 6.70 (s, 2H), 3.99 (t, *J* = 6.6 Hz, 4H), 3.74 (t, *J* = 6.6 Hz, 4H), 1.82 (m, 4H), 1.68 (m, 4H), 1.50-1.28 (m, 56H), 0.89 (m, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 183.1, 149.1, 148.9, 146.5, 135.4, 133.1, 132.7, 130.35, 130.30, 129.8, 129.7, 129.6, 122.4, 115.7, 113.5, 69.4, 32.2, 29.94, 29.88, 29.86, 29.84, 29.72, 29.66, 26.64, 29.60, 29.55, 29.36, 26.30, 26.26, 22.9, 14.3. HRMS (MALDI) calc'd for $C_{70}H_{98}O_6$+H *m/z* 1035.7436, found 1035.7445.

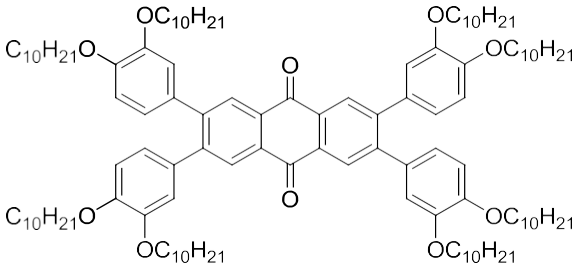
2,3-bis(3,4-bis(dodecyloxy)phenyl)pentacenequinone (3). In a round bottom flask, 2,3-dibromopentacene-6,13-dione[2] (785 mg, 1.68 mmol, 1 eq.), 1-pinacolatoboron-3,4-bis(decyloxy)benzene (2.00 g, 3.87 mmol, 2.3 eq.), toluene (50 mL) and ethanol (15 mL) were combined and degassed for 20 minutes. 2M K_2CO_3 (9 mL) was added to flask and the mixture was degassed further for 15 minutes. $Pd(PPh_3)_4$ (194 mg, 0.168 mmol, 10%) was then added and the solution was heated to 80°C for 2 days under N_2. The solution was cooled to room temperature and water was added to the mixture. The product was extracted with DCM (100 mL) and washed with water (3 x 100 mL). The organic extract was dried with $MgSO_4$ and the solvent evacuated under vacuum. The product was purified via column chromatography (8:2 Hexanes:Ethyl Acetate on silica) and further recrystallized in acetone to yield **3** as a yellow solid (75 mg, 5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 4H), 8.14 (m, 4H), 7.71 (m, 2H), 6.85 (m, 4H), 6.70 (s, 2H), 4.00 (t, *J*=6.6, 4H), 3.74 (t, *J*=6.6, 4H), 1.84 (m, 4H), 1.70 (m, 4H), 1.30 (m, 56H), 0.88 (m, 12 H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ183.0, 148.6, 148.5, 142.9, 135.3, 134.4, 133.1, 131.0, 130.7, 130.1, 129.7, 129.5, 122.1, 115.7, 113.2, 69.2, 31.9, 29.7, 29.65, 29.62, 29.48, 29.42, 29.40, 29.36, 29.33, 29.1, 26.1, 26.0, 22.7, 14.1. HRMS (ASAP) calc'd for $C_{74}H_{100}O_6$+H *m/z* 1085.7598, found 1085.7579.



2,3,6,7-tetrakis(trifluoromethanesulfonyloxy)anthracene-5,10-dione (10). 2,3,6,7-tetrahydroxyanthraquinone[4] (0.13 g, 0.514 mmol) was placed under an N_2 atmosphere. Freshly distilled pyridine was transferred via cannula to reaction flask with vigorous stirring. The solution was cooled to -78 °C. Triflic anhydride (0.87 g, 3.01 mmol) was added. The mixture was then warmed to room temperature overnight and then stirred for 2 days. The solvent was then removed *in vacuo* and the residue was purified by column chromatography in

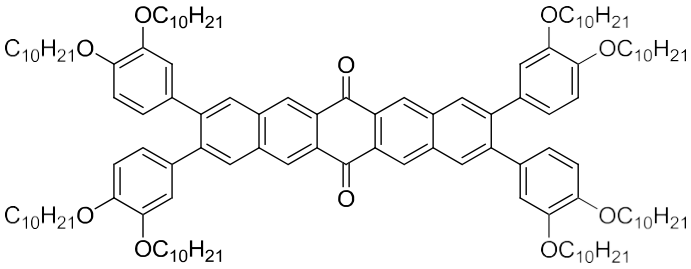


hexanes/EtOAc (90:10) to yield **10** as a white crystalline solid (0.204 g, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.56, 145.18, 133.70, 123.52, 118.75 (q, *J*C-F = 321 Hz). HRMS (APCI) calc'd for $C_{18}H_4O_{14}F_{12}S_4$+H *m/z* 800.8371, found 800.8354.



2,3,6,7-tetrakis[3,4-bis(decyloxy)phenyl]-anthracene-9,10-dione (4): Compound **10** (0.228 g, 0.285 mmol) and 1-pinacolatoboron-3,4-bis(decyloxy)benzene (0.618 g, 0.618 mmol) were added to 8 mL toluene and degassed with N_2 for 15 minutes. $Pd(PPh_3)_4$ (0.029 g, 0.033 mmol) was added, followed by 4 mL of degassed 2M K_3PO_4. The reaction mixture was heated to 80 °C and stirred for 6 days. The mixture was cooled to room temperature and extracted with dichloromethane (40 mL) and washed organic layer with water (40 mL). Performed column chromatography on the crude product with hexanes/dichloromethane (60:40 to 0:100) to yield **4** as a red solid (0.276 g, 55 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 4H), 6.84 (d, *J* = 2.1 Hz, 4H), 6.83 (s, 4H), 6.69 (d, *J* = 2.1 Hz, 4H), 3.99 (t, J = 6.6 Hz, 8H), 3.73 (t, J = 6.6 Hz, 8H), 1.85-1.79 (m, 8H), 1.71-1.64 (m, 8H), 1.51-1.46 (m, 16H), 1.32-1.27 (m, 96H), 0.90-0.87 (m, 24H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 183.2, 149.1, 148.9, 146.3, 132.7, 132.3, 129.5, 122.4, 115.7, 113.5, 69.4, 32.2, 31.11, 29.9, 29.8, 29.70, 29.62, 29.58, 29.53, 29.35, 26.3, 26.2, 22.9, 14.3. HRMS (MALDI) calc'd for $C_{118}H_{184}O_{10}$+H *m/z* 1762.3962, found 1762.3939.

2,3,9,10-tetrakis[3,4-bis(decyloxy)phenyl]-pentacene-6,13-dione (5). Compound **11** (0.590 g, 0.946 mmol) and 1-pinacolatoboron-3,4-bis(decyloxy)benzene (2.42 g, 4.68 mmol) were added to 50 mL toluene and 10 mL ethanol and degassed with N_2 for 15 minutes. $Pd(PPh_3)_4$ (111 mg, 0.096 mmol, 10 mol%) was added, followed by 5 mL of degassed 2M K_3CO_3. The reaction mixture was heated to 80 °C and stirred for 5 days.



The reaction mixture was cooled to room temperature. The organic phase was separated and the aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic extracts were dried using $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography (9:1 hexanes/ethyl acetate) and then recrystallized from hexanes/acetone to yield **5** as a yellow solid (660 mg, 38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.96 (s, 4H), 8.14 (s, 4H), 6.86 (m, 8H), 6.71 (s, 4H), 4.00 (t, J=6.6 Hz, 8H), 3.74 (t, J=6.6 Hz, 8H), 1.84 (m, 8H), 1.70 (m, 8H), 1.3-1.49 (m, 96H), 0.88 (m, 24H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 183.1, 149.0, 148.9, 143.1, 134.6, 133.5, 131.2, 131.1, 129.6, 122.4, 116.3, 113.7, 69.5, 32.2, 29.93, 29.88, 29.85, 29.72, 29.62, 29.62, 29.59, 29.4, 26.32, 26.28, 22.9, 14.3. HRMS (MALDI) calc'd for $C_{126}H_{188}O_{10}$+H *m/z* 1862.4275, found 1862.4193.

Mesophase Characterization

Polarized optical microscopy studies were carried out using an Olympus BX-51 polarized optical microscope equipped with a Linkam LTS 350 heating stage and a digital camera. Differential Scanning Calorimetry (DSC) studies were carried out using a TA Instruments DSC Q200 with a scanning rate of 5 °C/min. DSC phase transitions were reproducible over three heating and cooling cycles, with the exception of the first heating, where melting transitions depended on the initial crystalline from. For the DSC traces shown below, only the second heating/cooling cycle is shown. XRD measurements were run on a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector and GADDS software package. The tube is operated at 40 kV and 40 mA and CuKα1 radiation (=1.54187 Å) with an initial beam diameter of 0.5 mm is used. A modified Instec hot & cold stage HCS 402 operated via controllers STC 200 and LN2-P (for below ambient temperatures) was used for variable temperature XRD measurements. XRD data were obtained both on heating from the crystalline solid (as obtained by recrystallization) and on cooling from the isotropic liquid.

Electrochemical Methods

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudo reference electrode. Experiments were run at a scan rate of 100 mV s−1 in dry and degassed dichloromethane solutions of the analyte (~1 mM) and electrolyte (0.1 M tetrabutylammonium hexafluorophosphate). Cyclic voltammograms were internally referenced against the ferrocene/ferrocenium redox couple (~1 mM internal standard) and corrected for internal cell resistance using the BASi Epsilon software.

Table S1. Summary of Cyclic Voltammetry Data

Compound	E_{ox} onset vs Fc^+/Fc (V)	$E_{1/2\ red1}$ vs Fc^+/Fc (V)	$E_{1/2red2}$ vs Fc^+/Fc (V)
1	0.87	-1.33	-1.71
2	0.80	-1.49	-1.83
3	0.80	-1.49	-1.83
4	0.87	-1.36	-1.78
5	0.81	-1.59	-1.90

References

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2 C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.*, 2005, **7**, 3163.

3 J. A. Paquette, C. J. Yardley, K. M. Psutka, M. A. Cochran, O. Calderon, V. E. Williams and K. E. Maly, *Chem. Commun.*, 2012, **48**, 8210.

4 T. S. Balaban, A. Eichhofer, M. J. Krische and J. M. Lehn, *Helv. Chim. Acta*, 2006, **89**, 333.

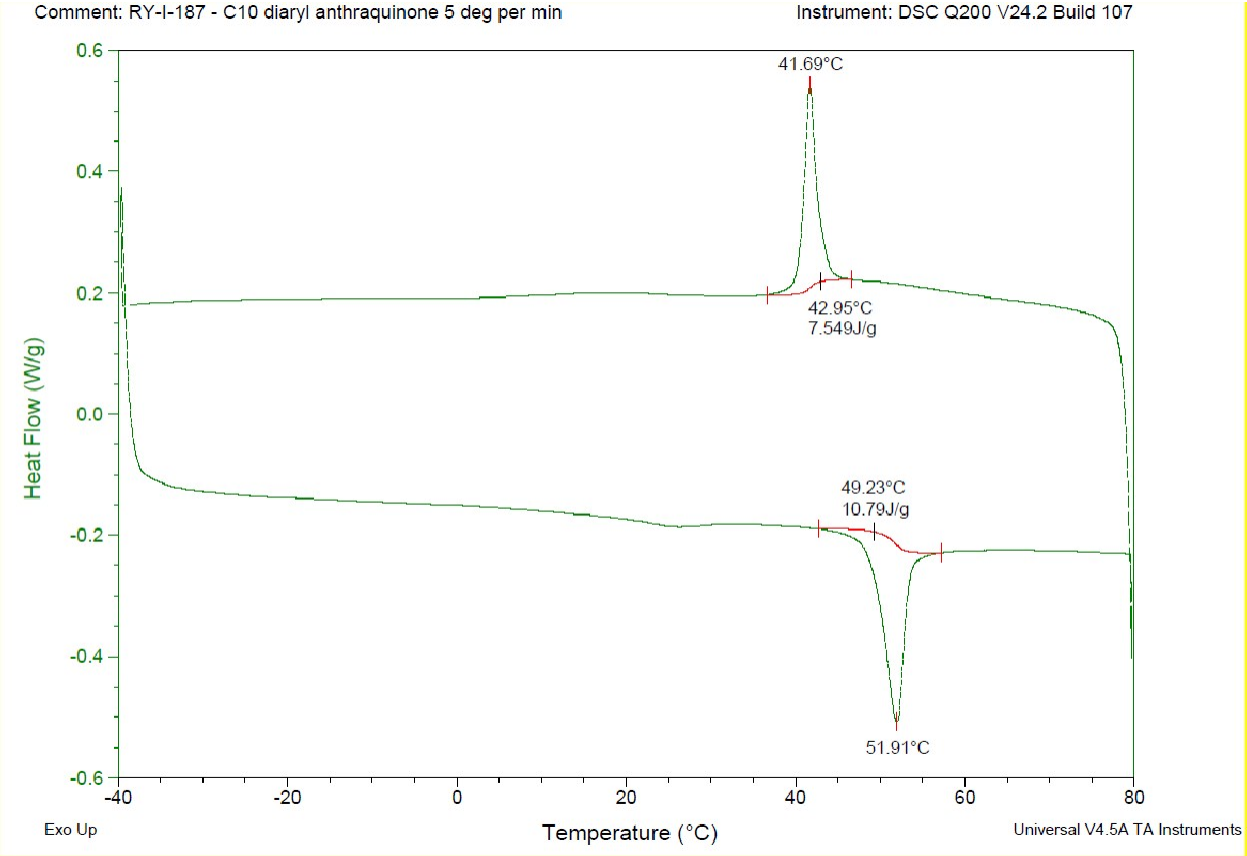
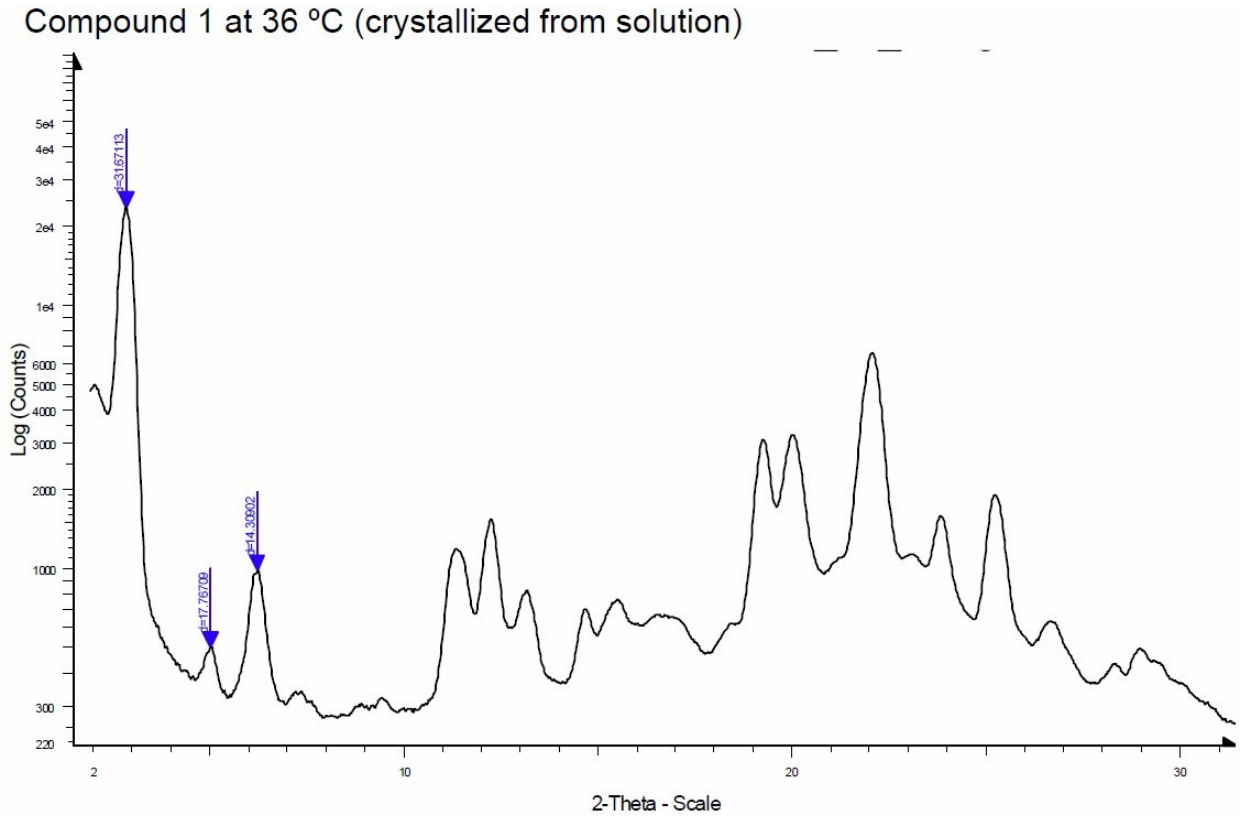
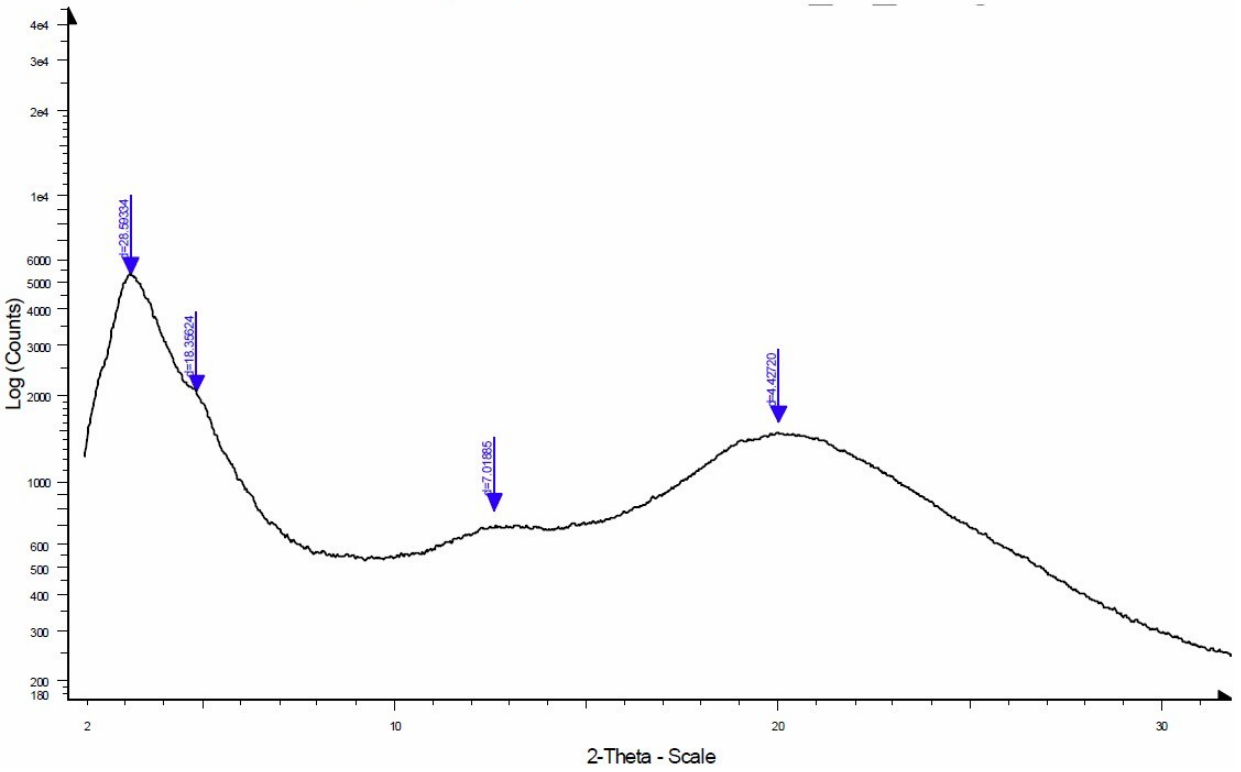


Figure S1. DSC Trace for Compound **1**.

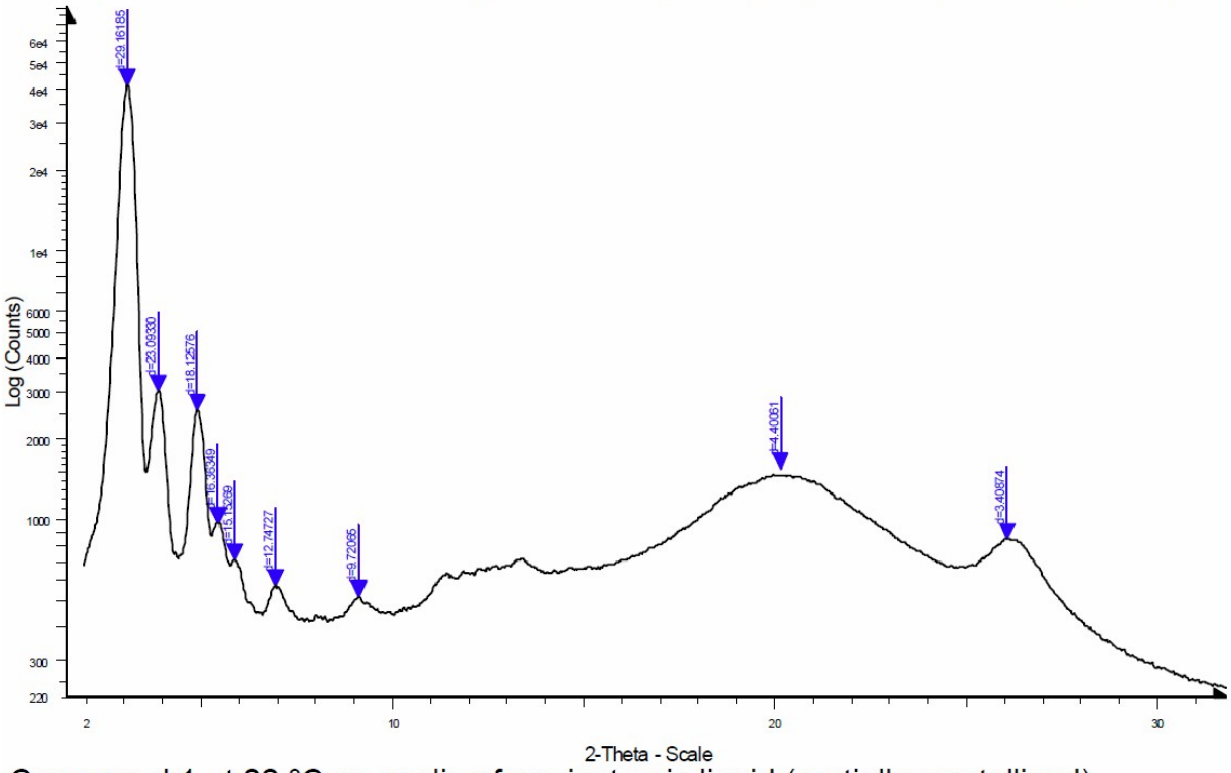
Compound 1 at 36 ºC (crystallized from solution)



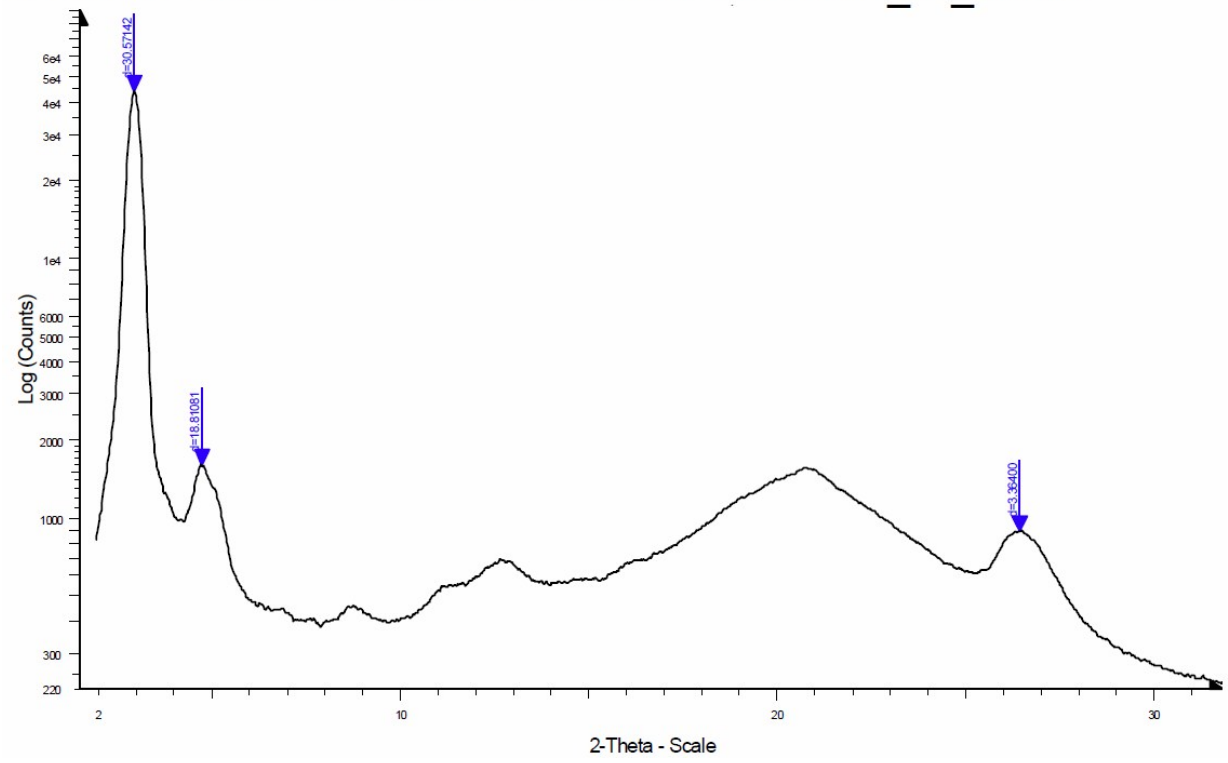
Compound 1 at 58 ºC (isotropic liquid)



Compound 1 at 40 ºC on cooling from isotropic liquid (monotropic mesophase)



Compound 1 at 22 ºC on cooling from isotropic liquid (partially crystallized)



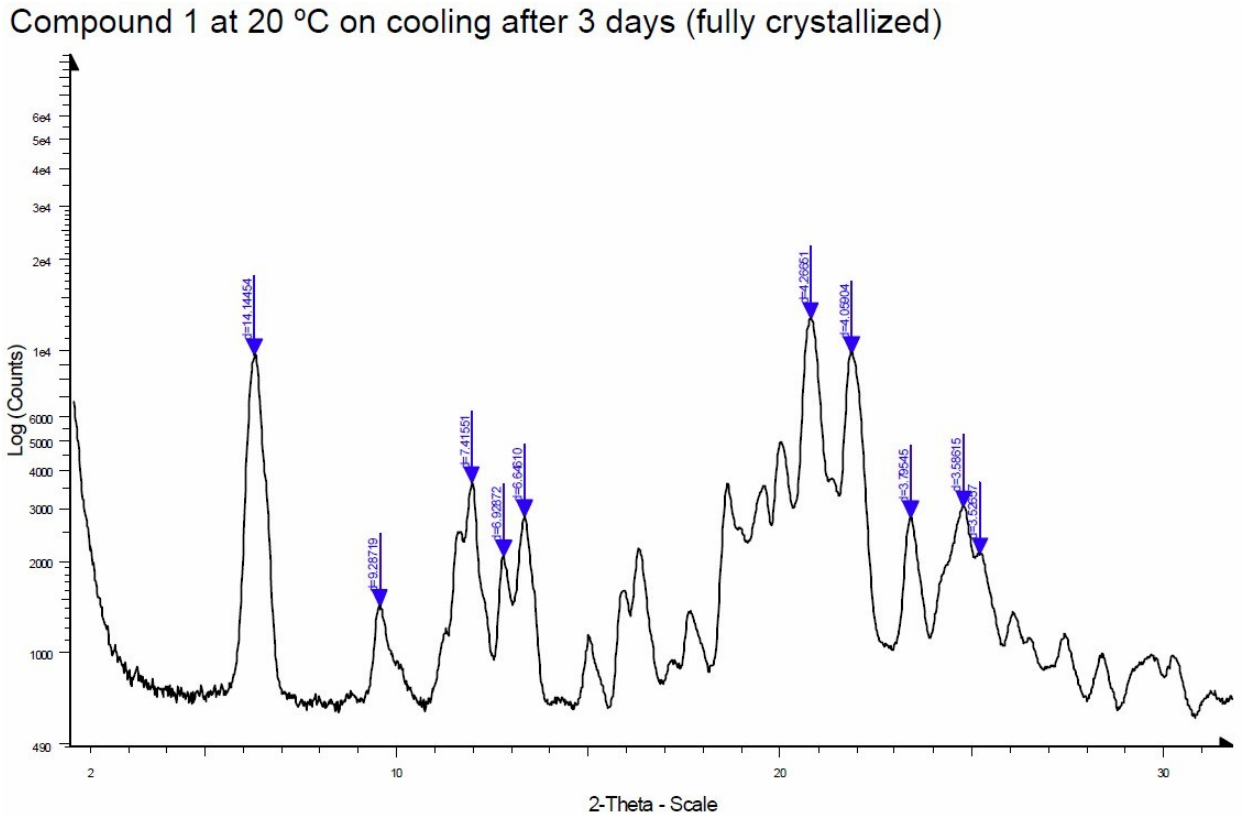


Figure S2. Representative XRD data (Intensity vs. 2θ) for **1** at different temperatures on heating and cooling.

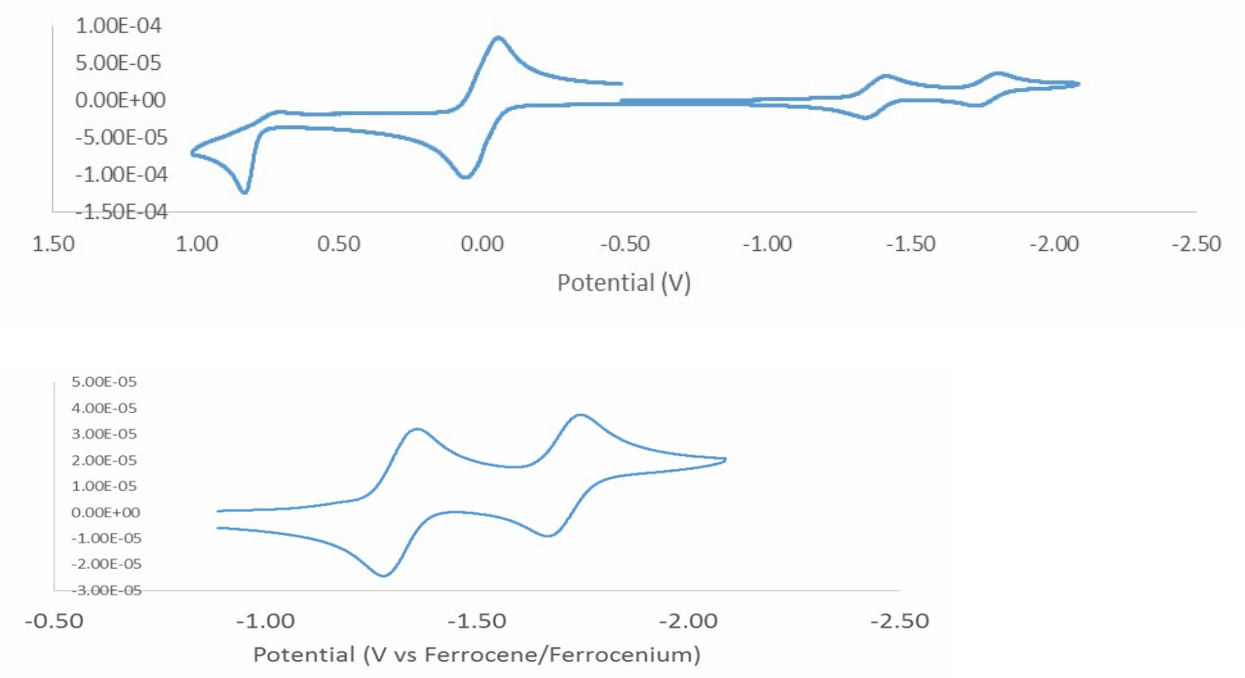


Figure S3. Representative CV traces of **1** in CH_2Cl_2 at 250 mV/s.

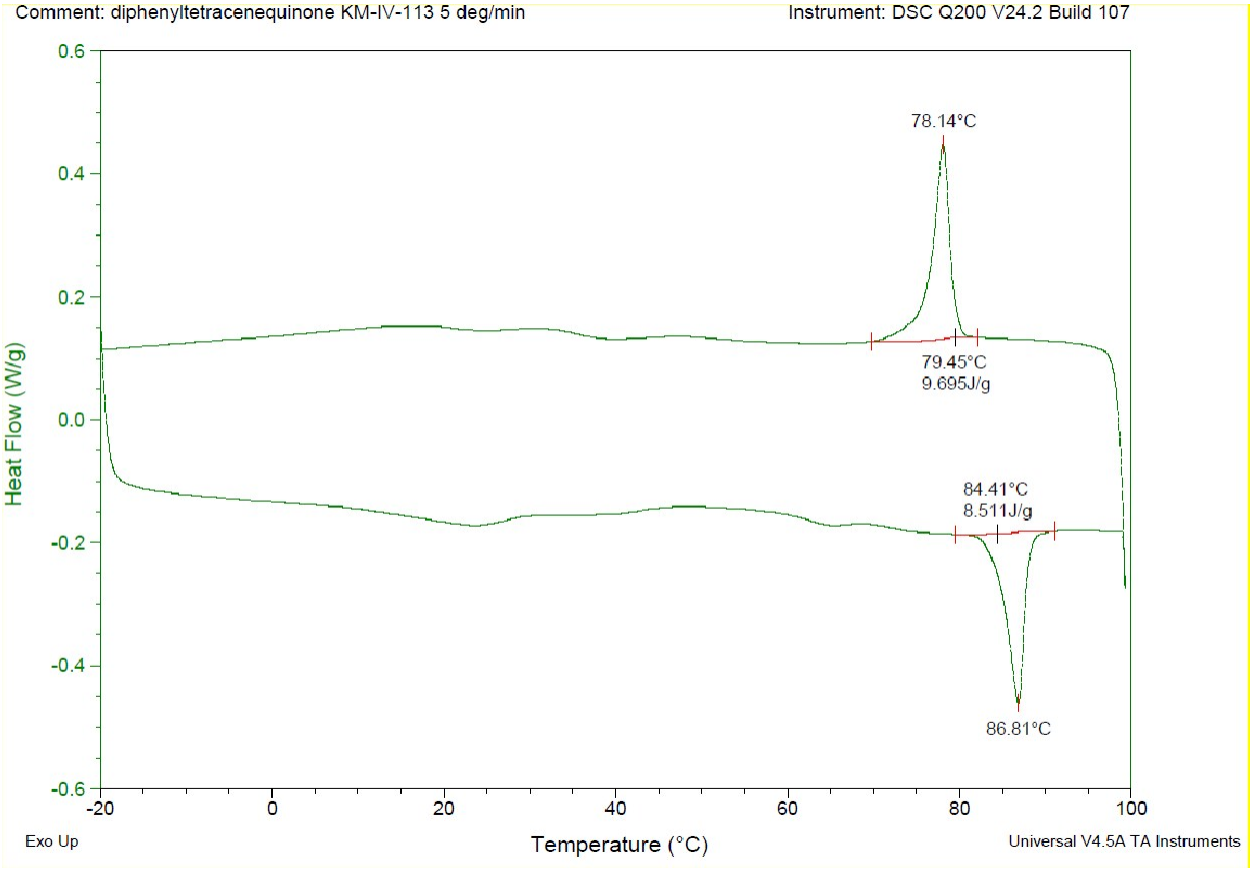
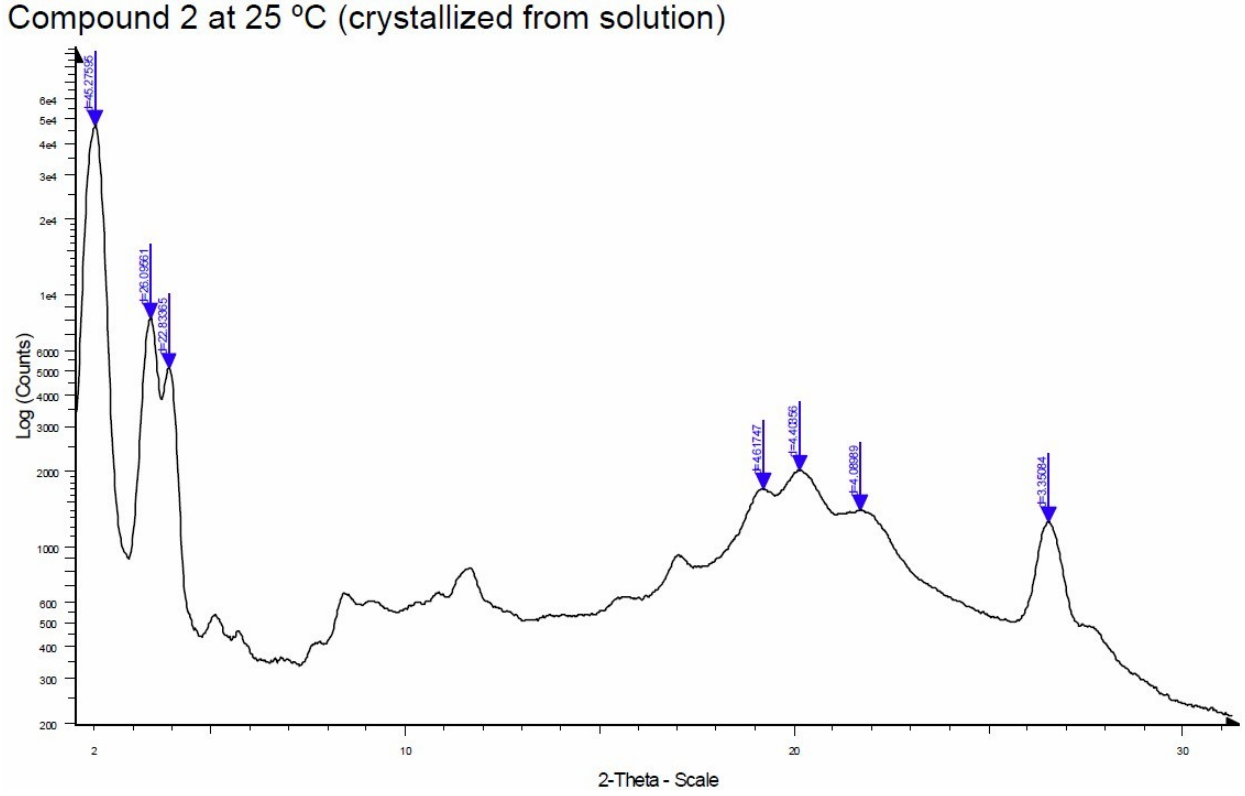
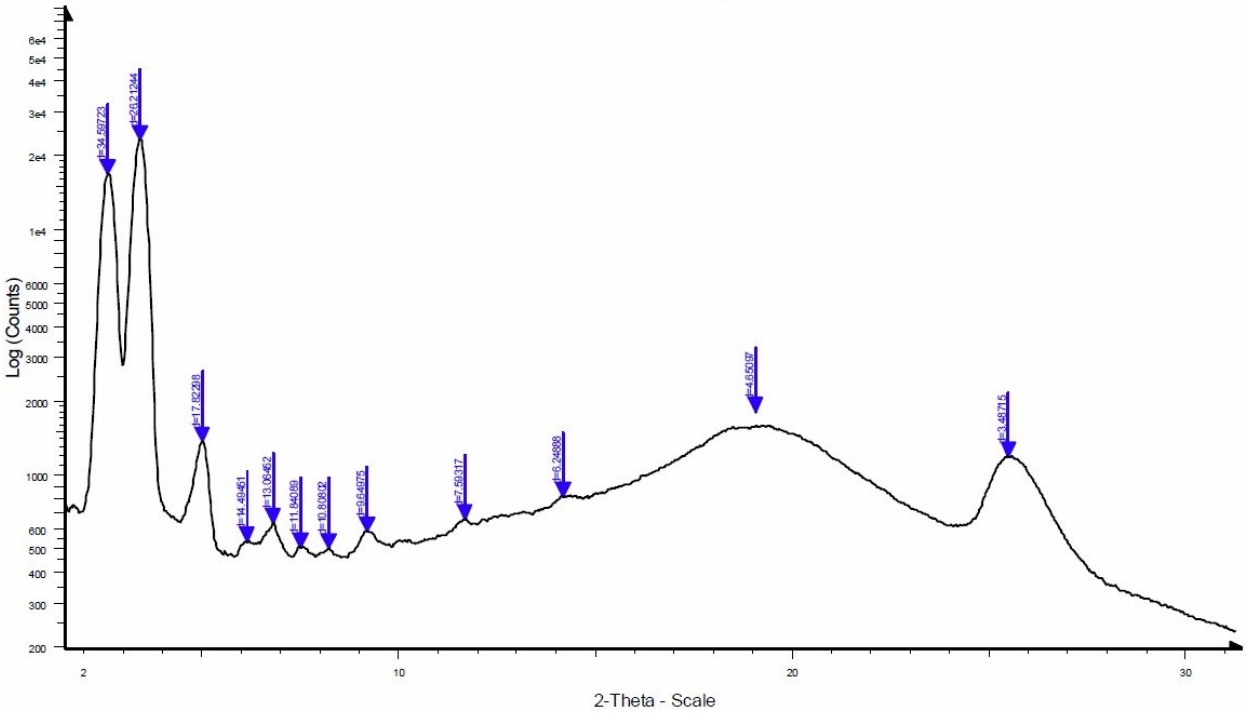


Figure S4. DSC Trace for Compound **2**.

Compound 2 at 25 ºC (crystallized from solution)



Compound 2 at 72 ºC on cooling from isotropic liquid (metastable mesophase)



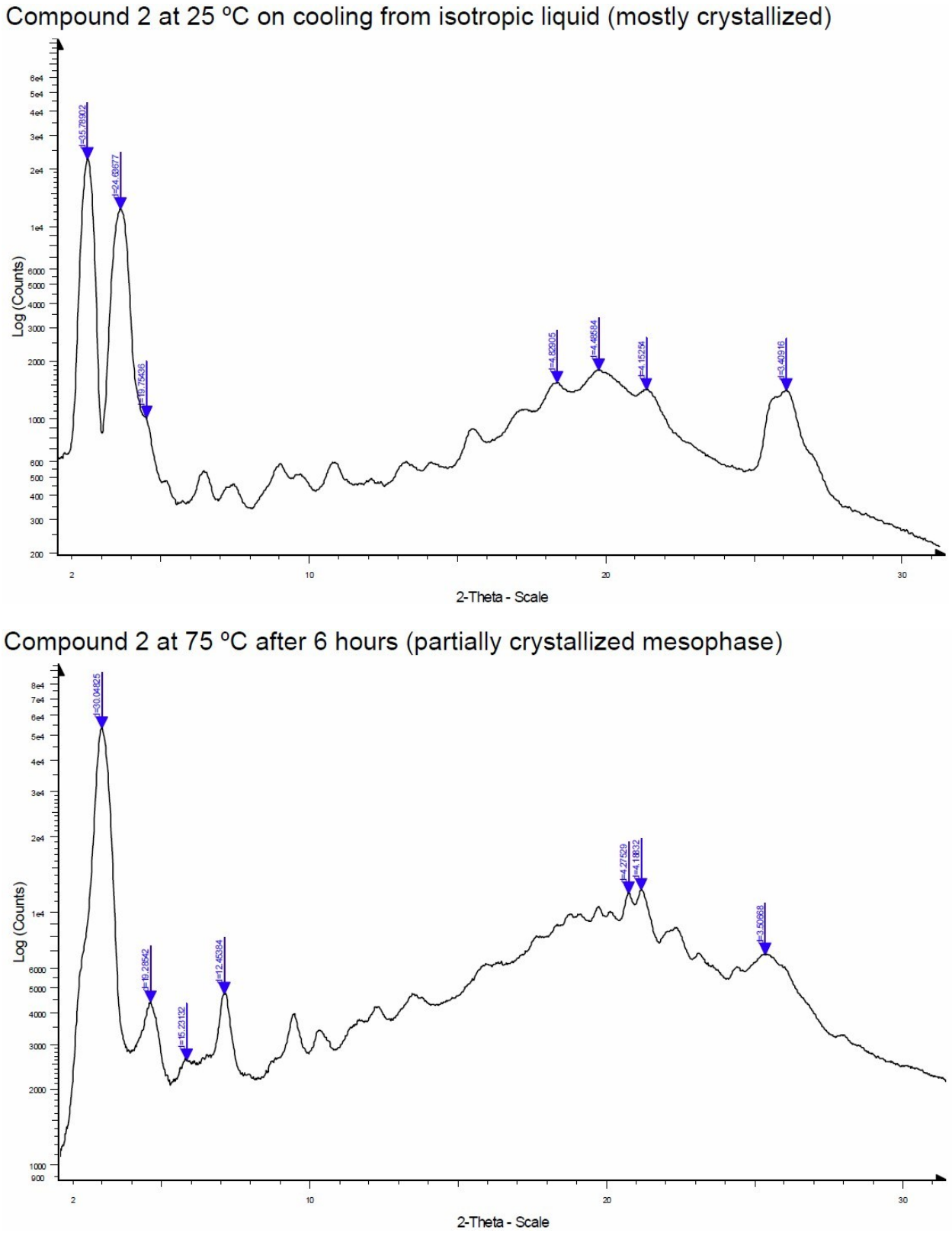
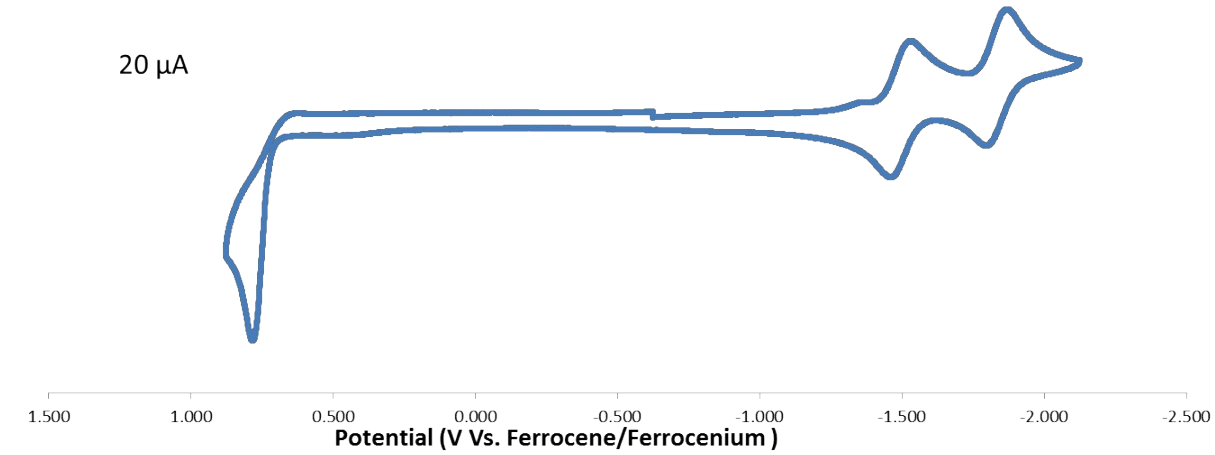


Figure S5. Representative XRD data (Intensity vs. 2θ) for **2** at different temperatures on heating and cooling.



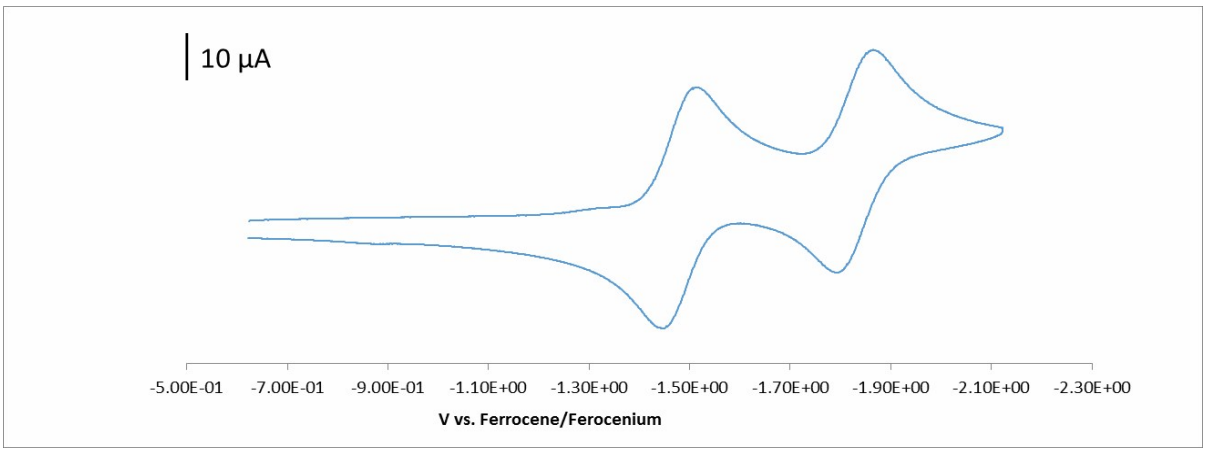


Figure S6. Representative CV traces of **2** in CH_2Cl_2 at 250 mV/s

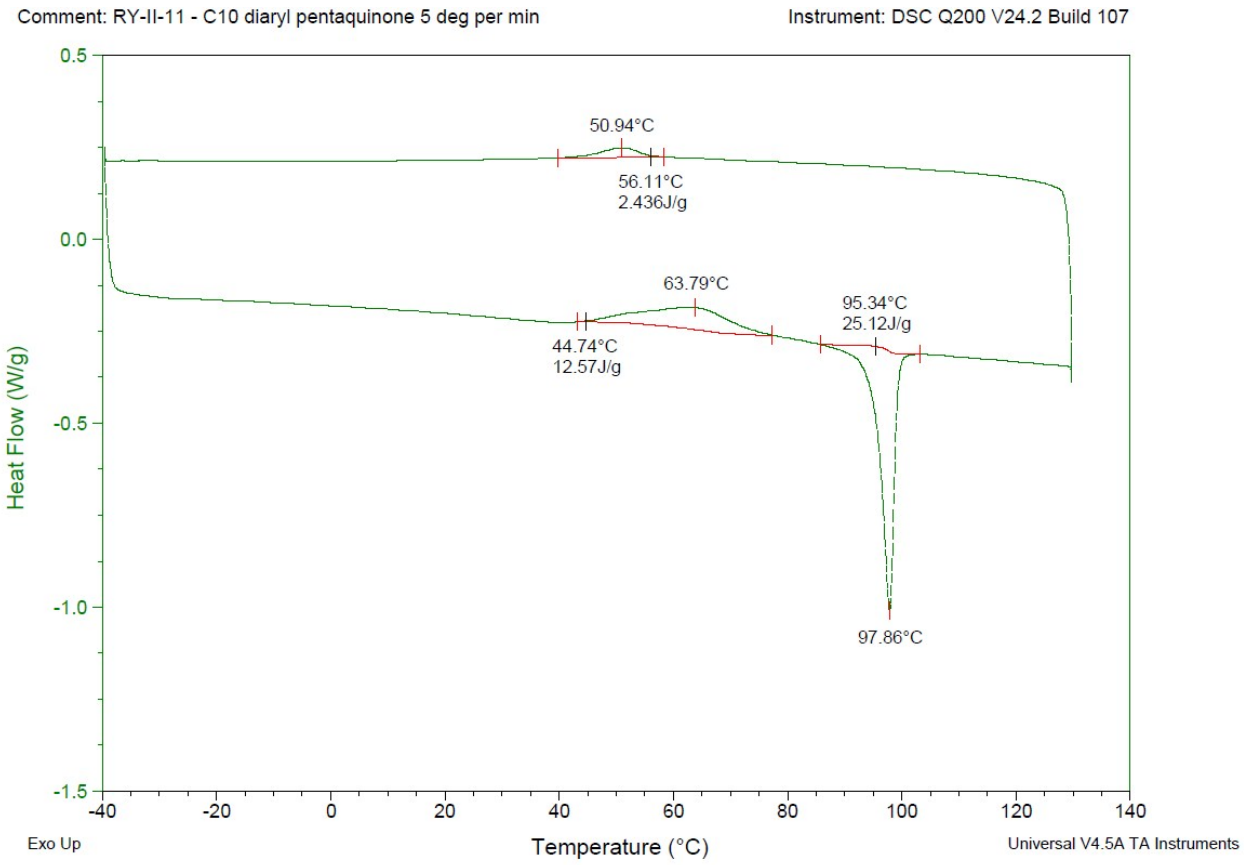


Figure S7. DSC Trace for Compound **3**.

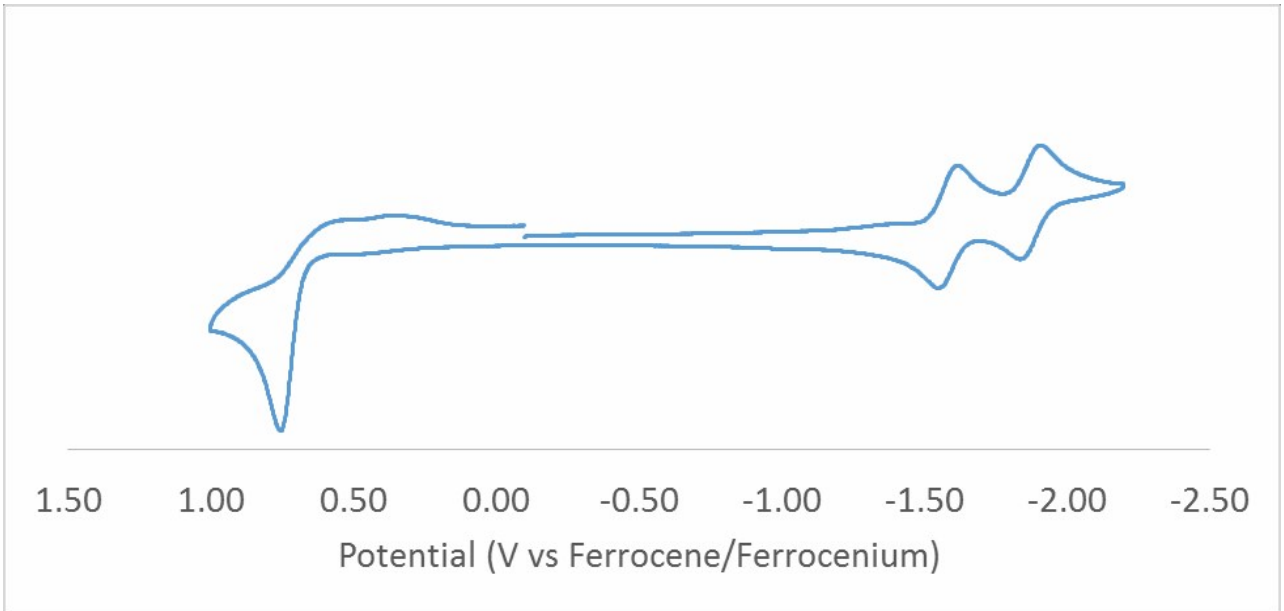


Figure S8. Representative CV trace of **3** in CH_2Cl_2 at 250 mV/s

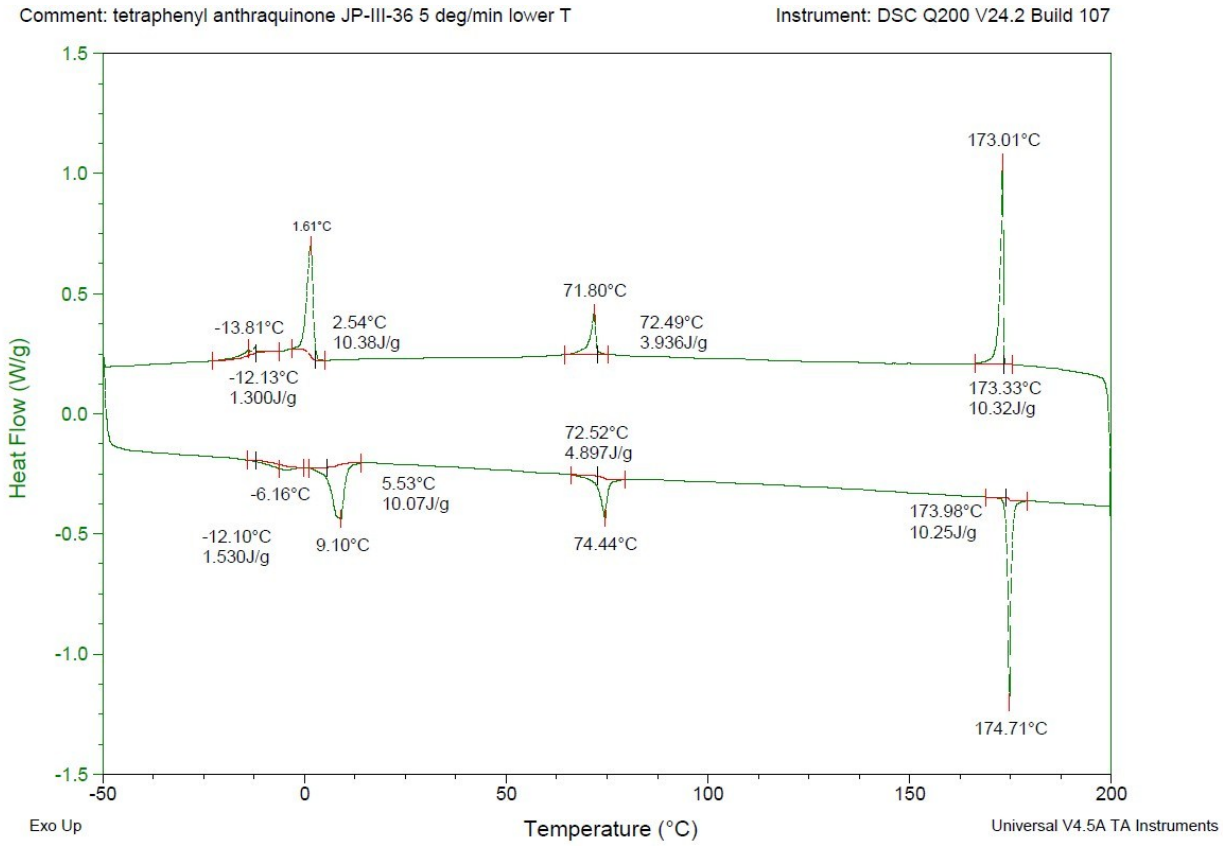
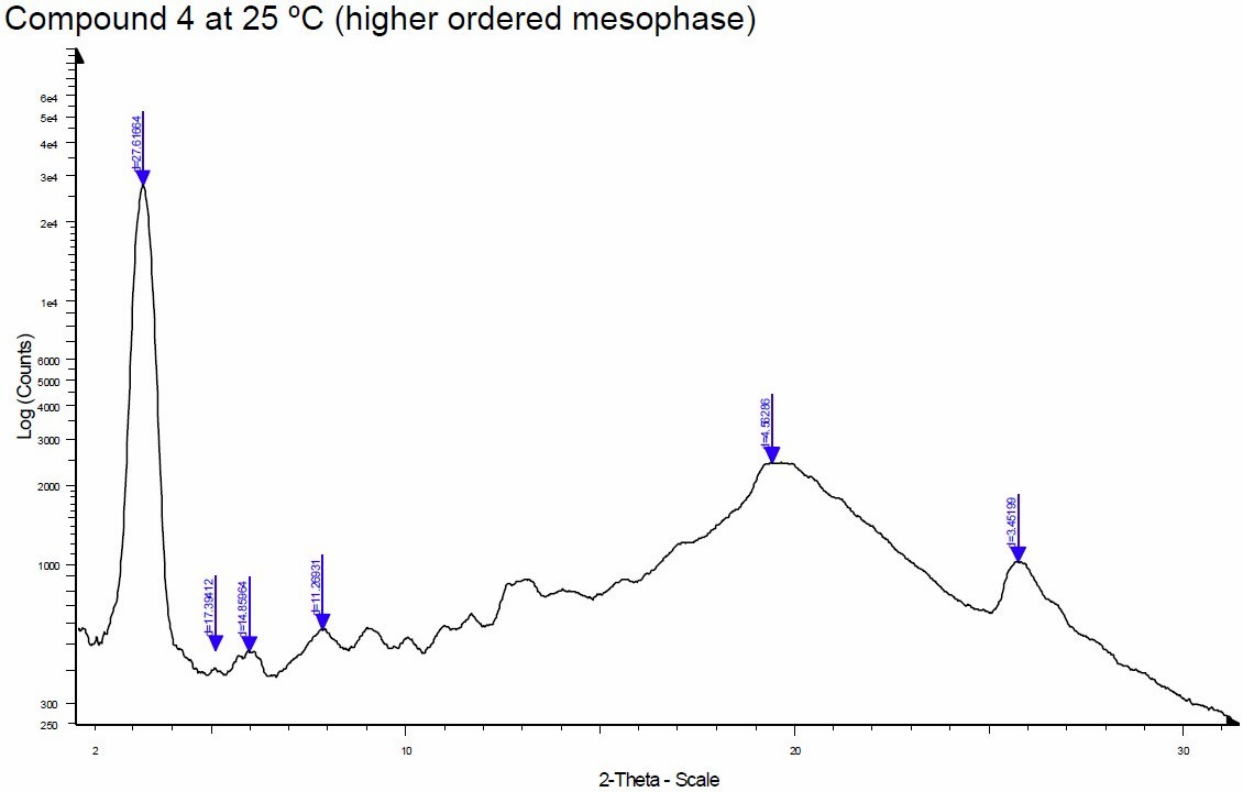
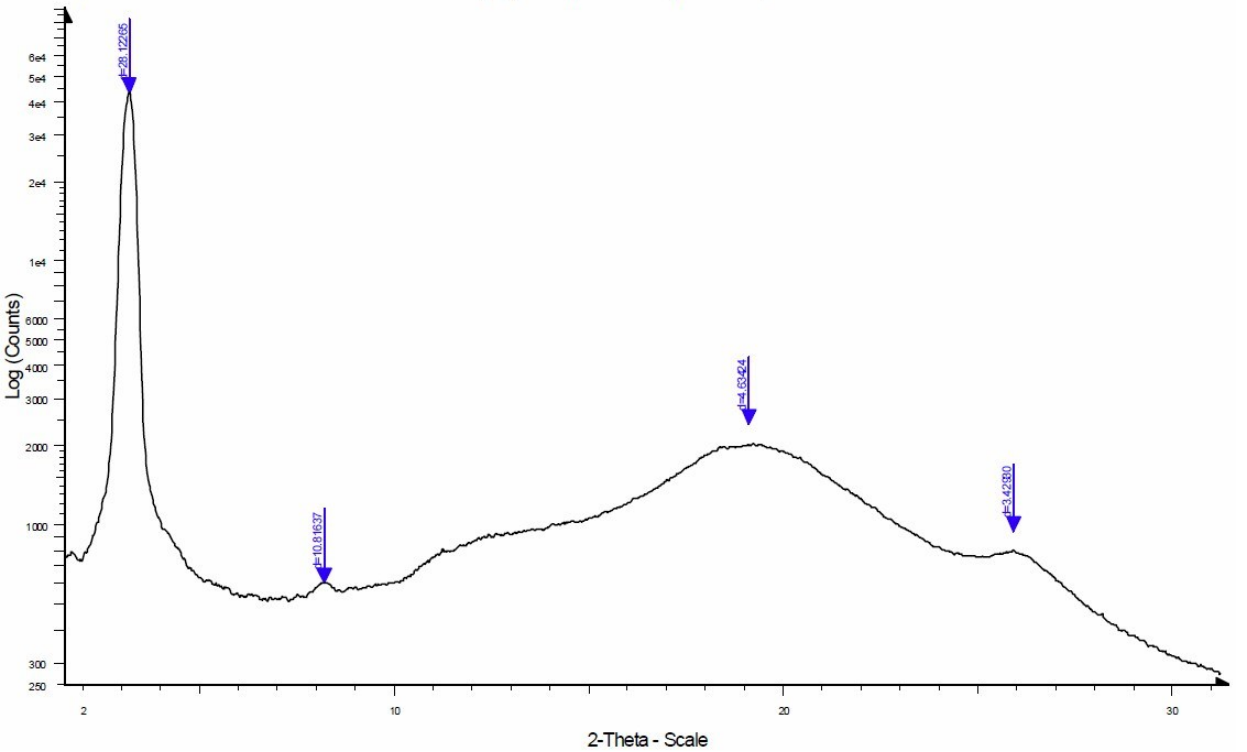


Figure S9. DSC Trace for Compound **4**.

Compound 4 at 25 ºC (higher ordered mesophase)



Compound 4 at 90 ºC on heating (Col_h mesophase)



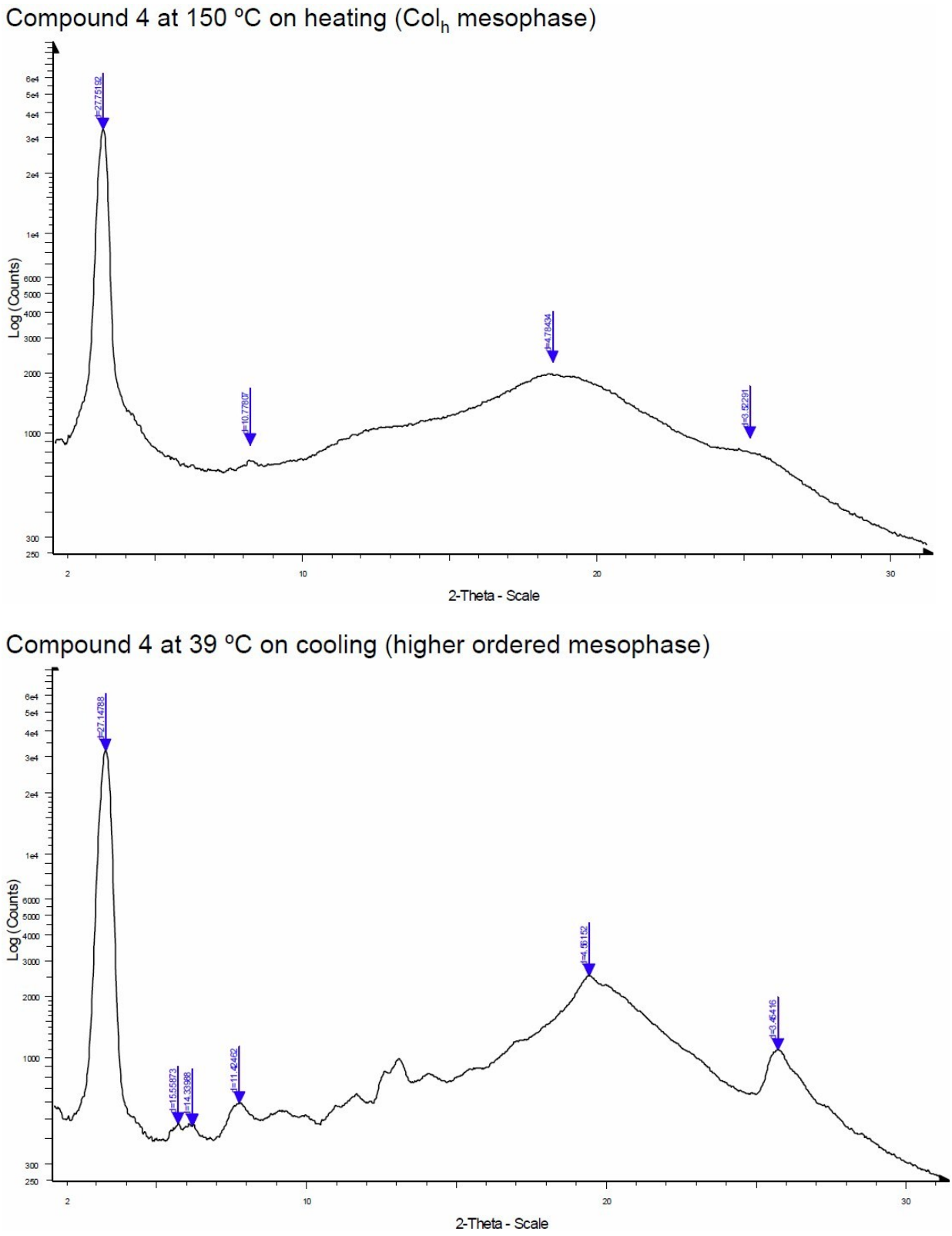


Figure S10. Representative XRD data (Intensity vs. 2θ) for **4** at different temperatures on heating and cooling.

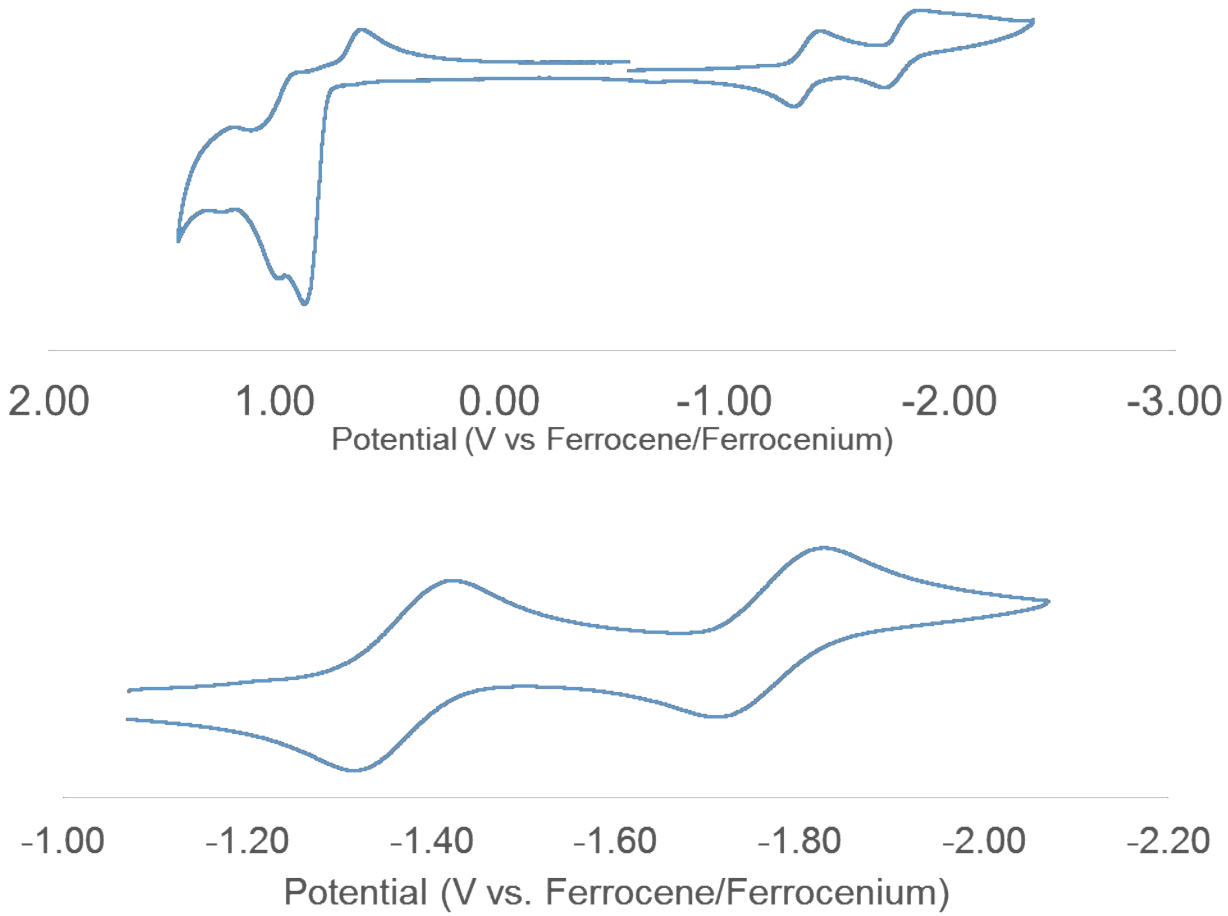


Figure S11. Representative CV traces of **4** in CH_2Cl_2 at 250 mV/s

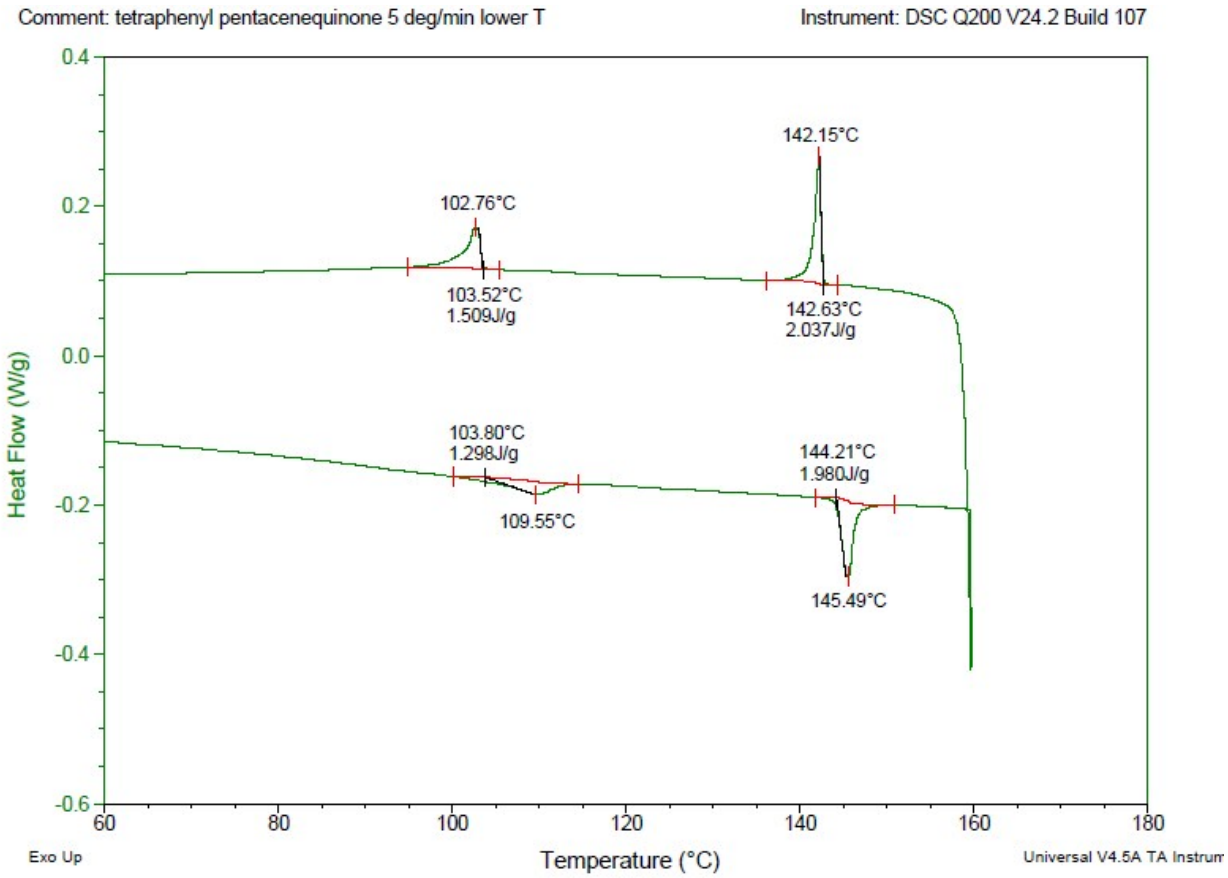


Figure S12. DSC Trace for Compound **5**.

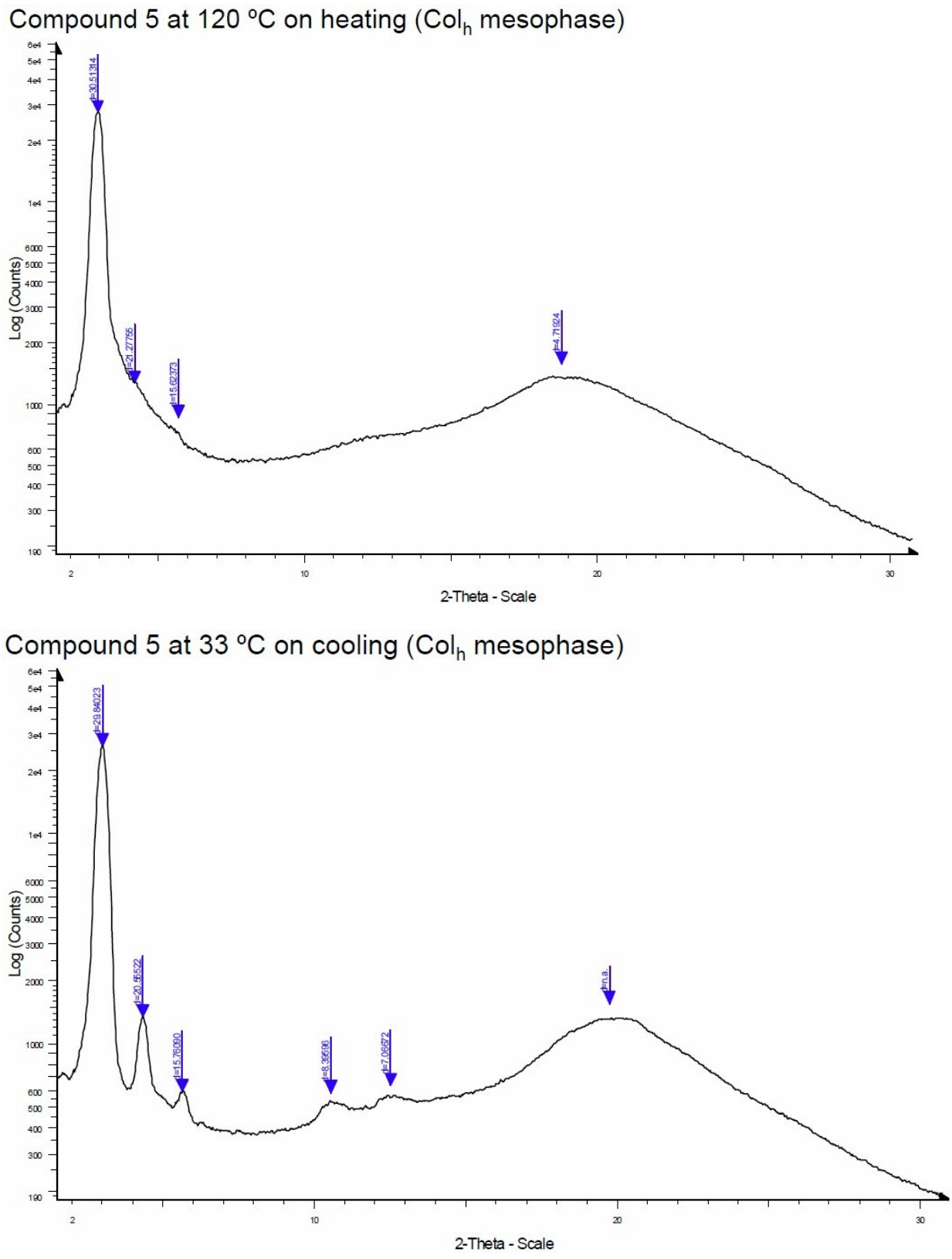


Figure S13. Representative XRD data (Intensity vs. 2θ) for **5** at different temperatures on heating and cooling.

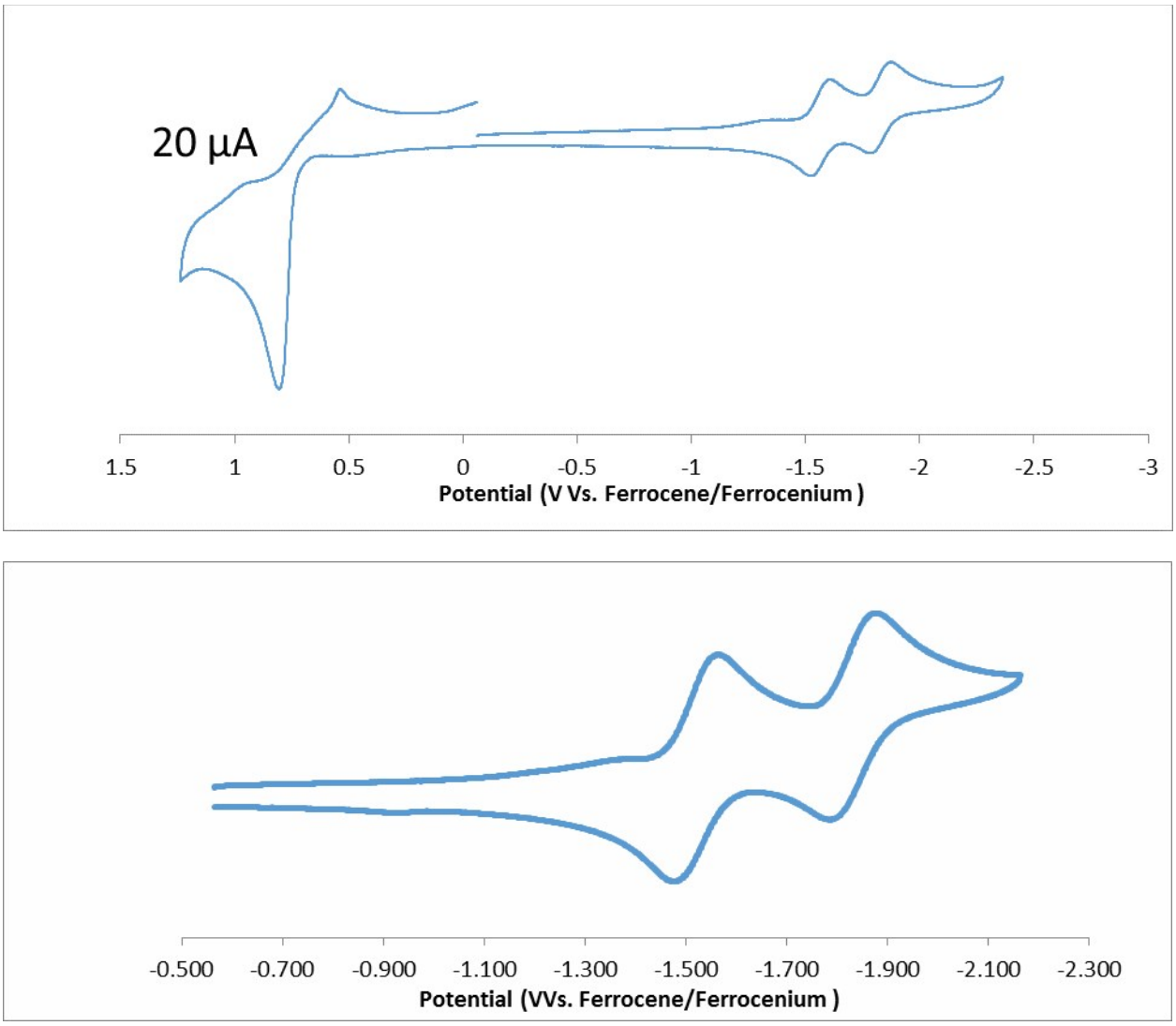
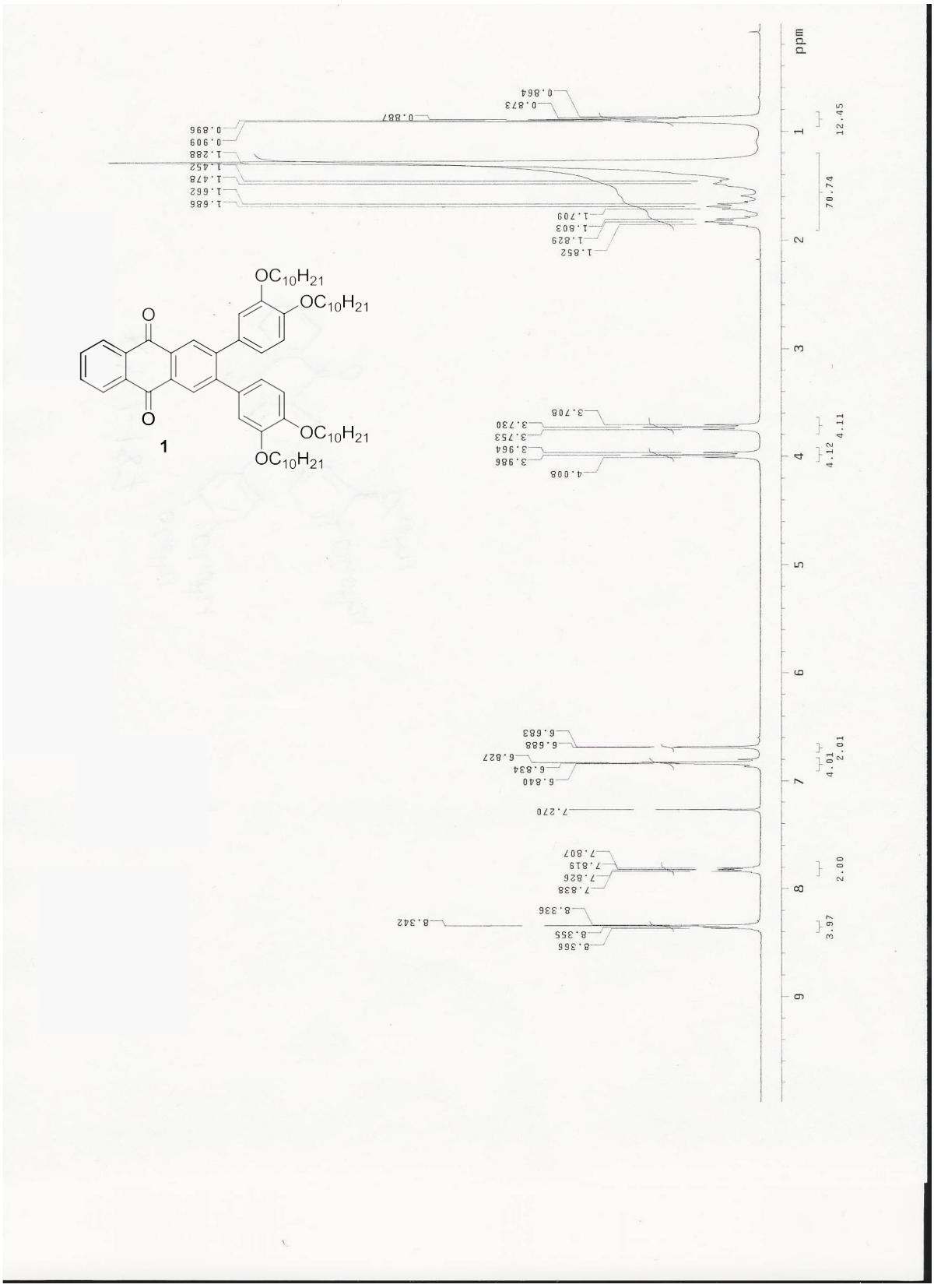
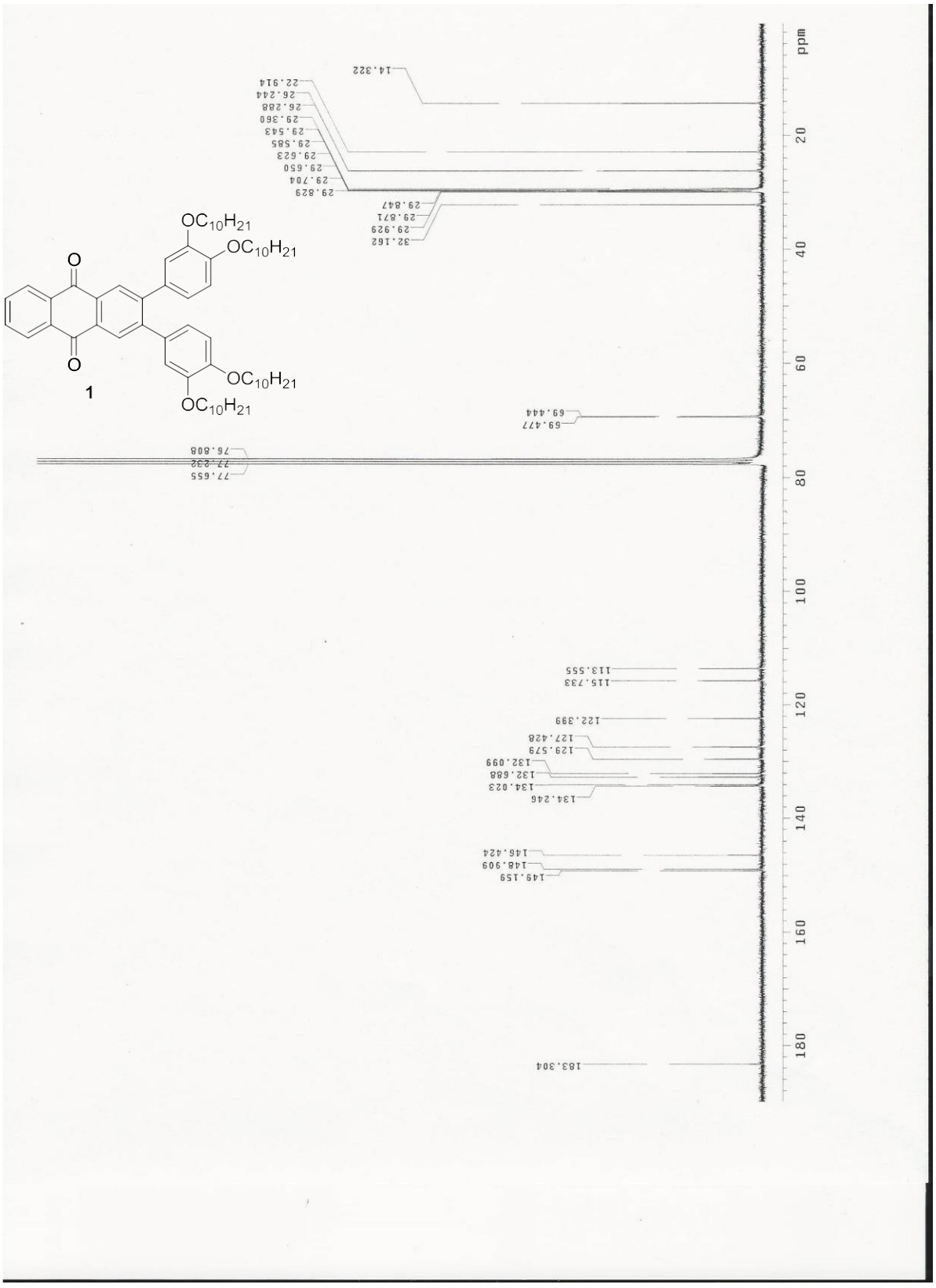
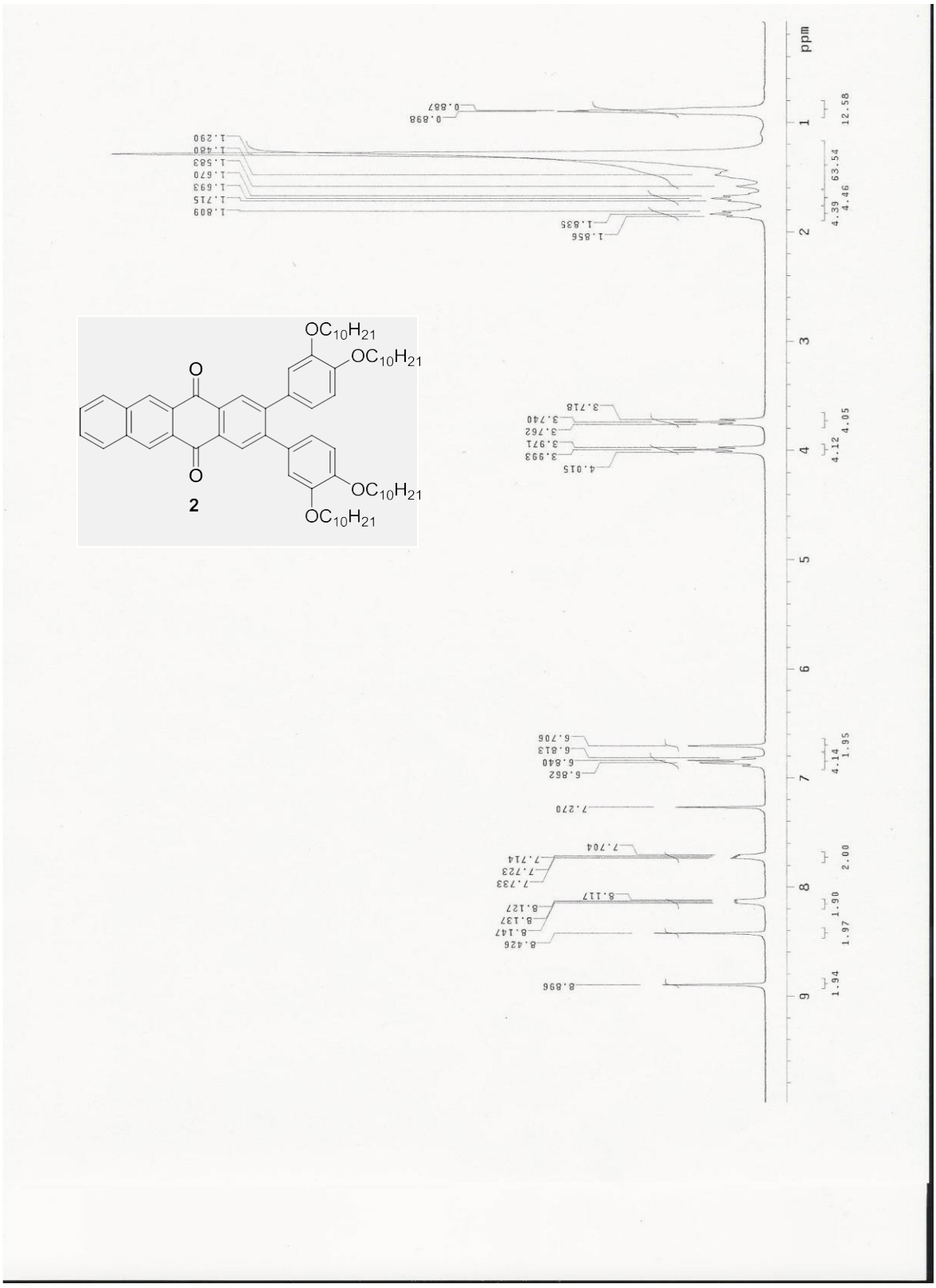


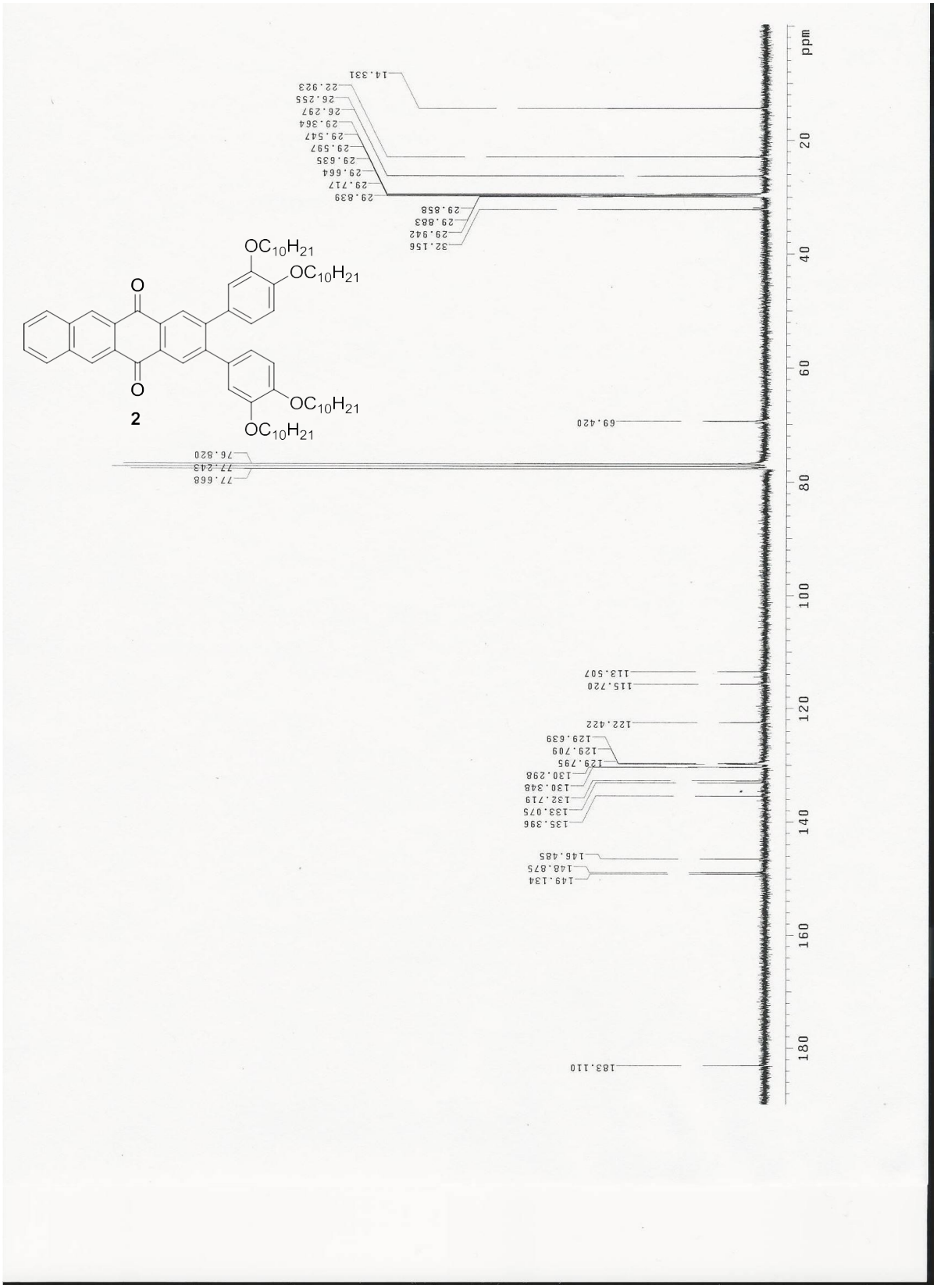
Figure S14. Representative CV traces of **5** in CH_2Cl_2 at 250 mV/s

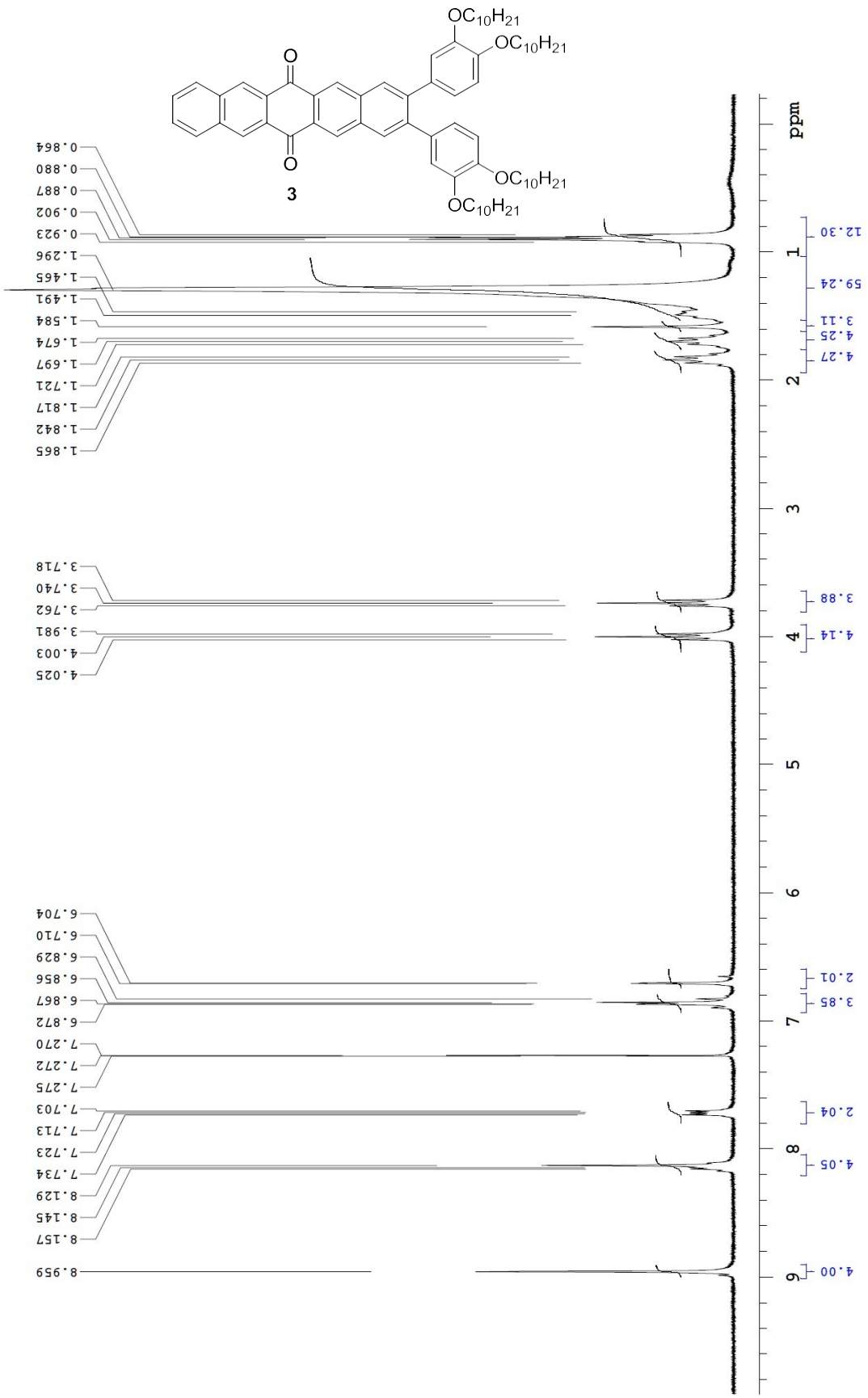
^{1}H and ^{13}C NMR Spectra

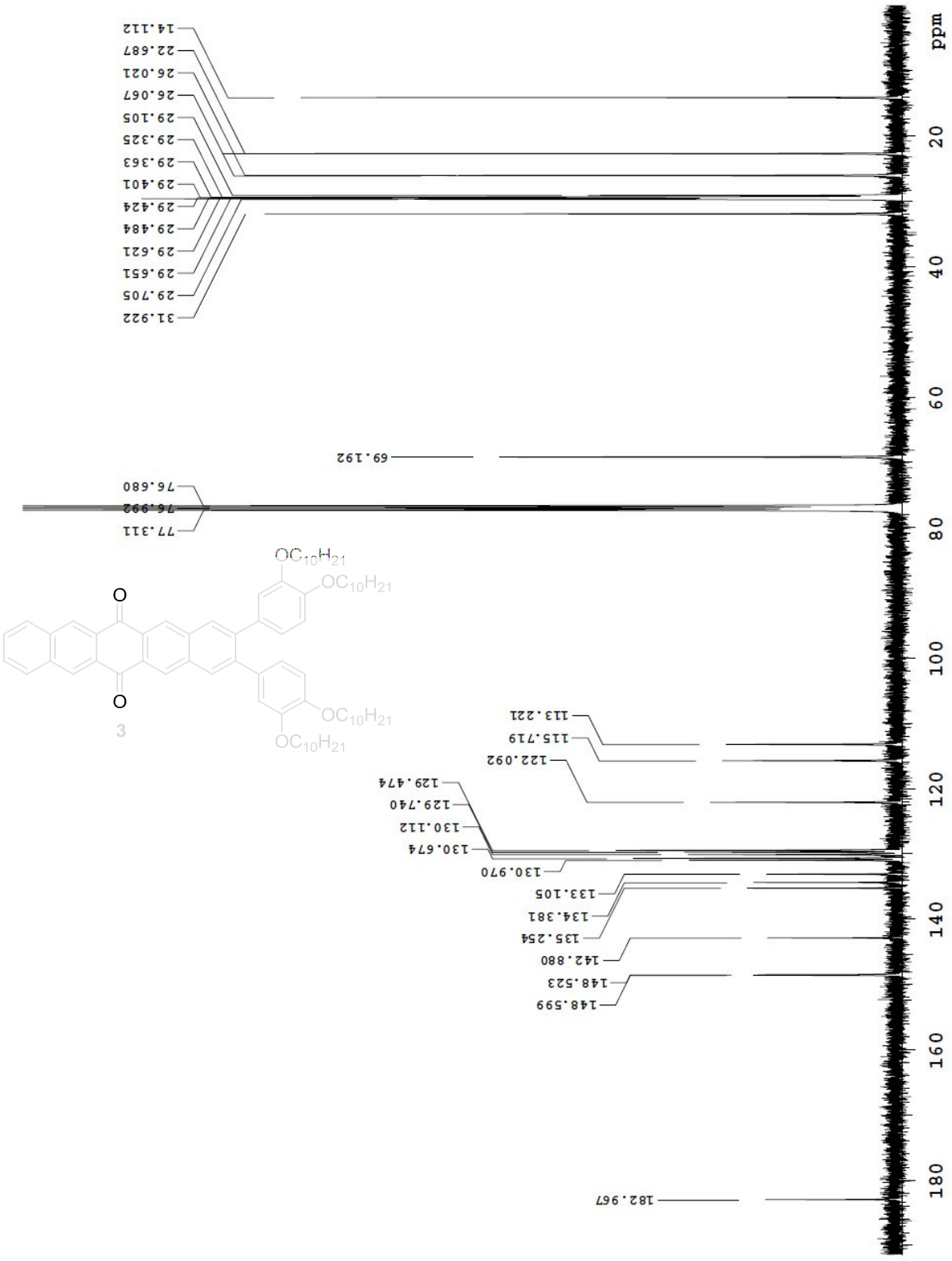


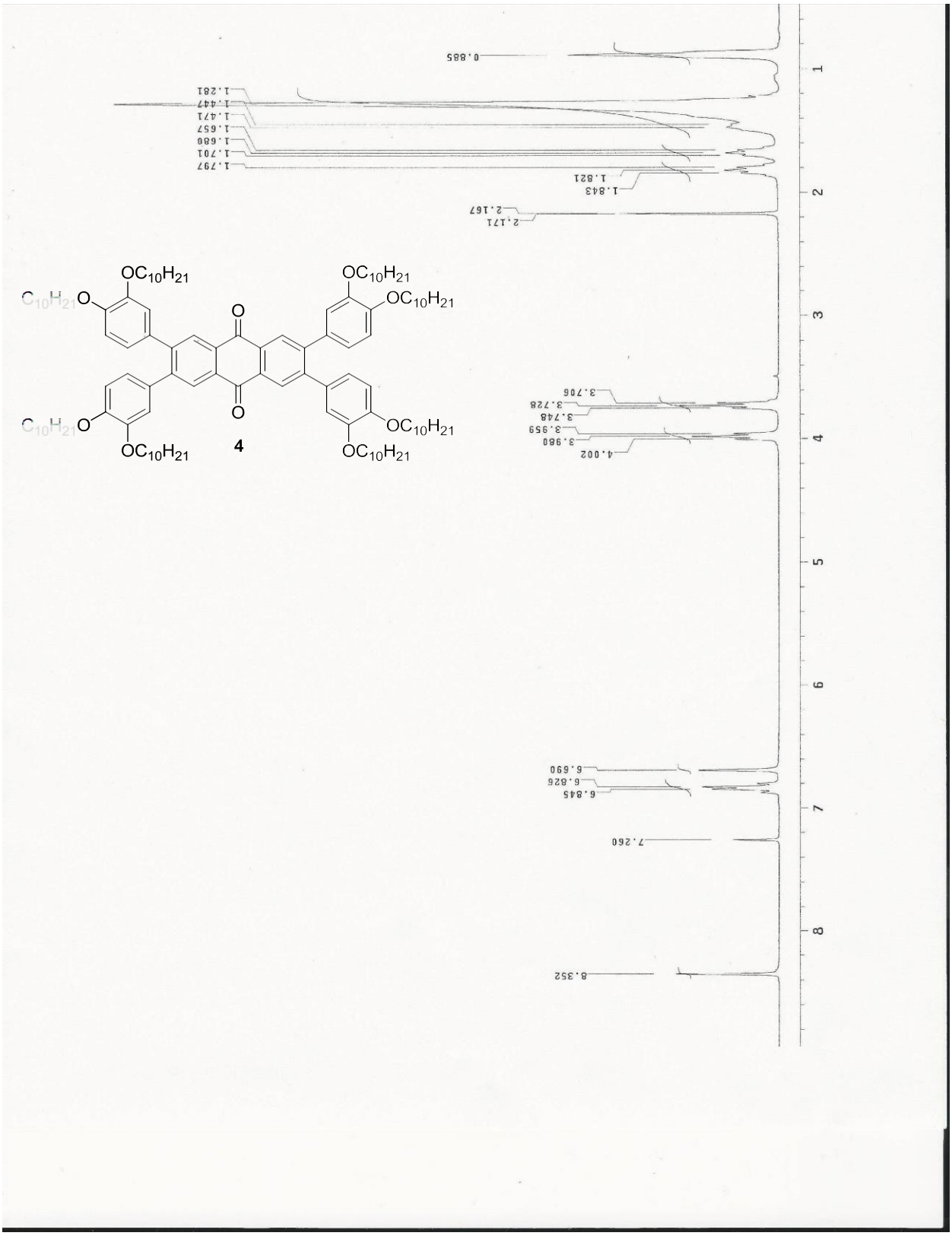

OC10H21
OC10H21
OC10H21
OC10H21
O
O
1
14.322
22.914
26.244
26.288
29.360
29.543
29.585
29.623
29.650
29.704
29.829
29.847
29.871
29.929
32.162
69.444
69.477
76.808
77.232
77.655
113.555
115.733
122.399
127.428
129.579
132.099
132.688
134.023
134.246
146.424
148.909
149.159
183.304
ppm
20
40
60
80
100
120
140
160
180

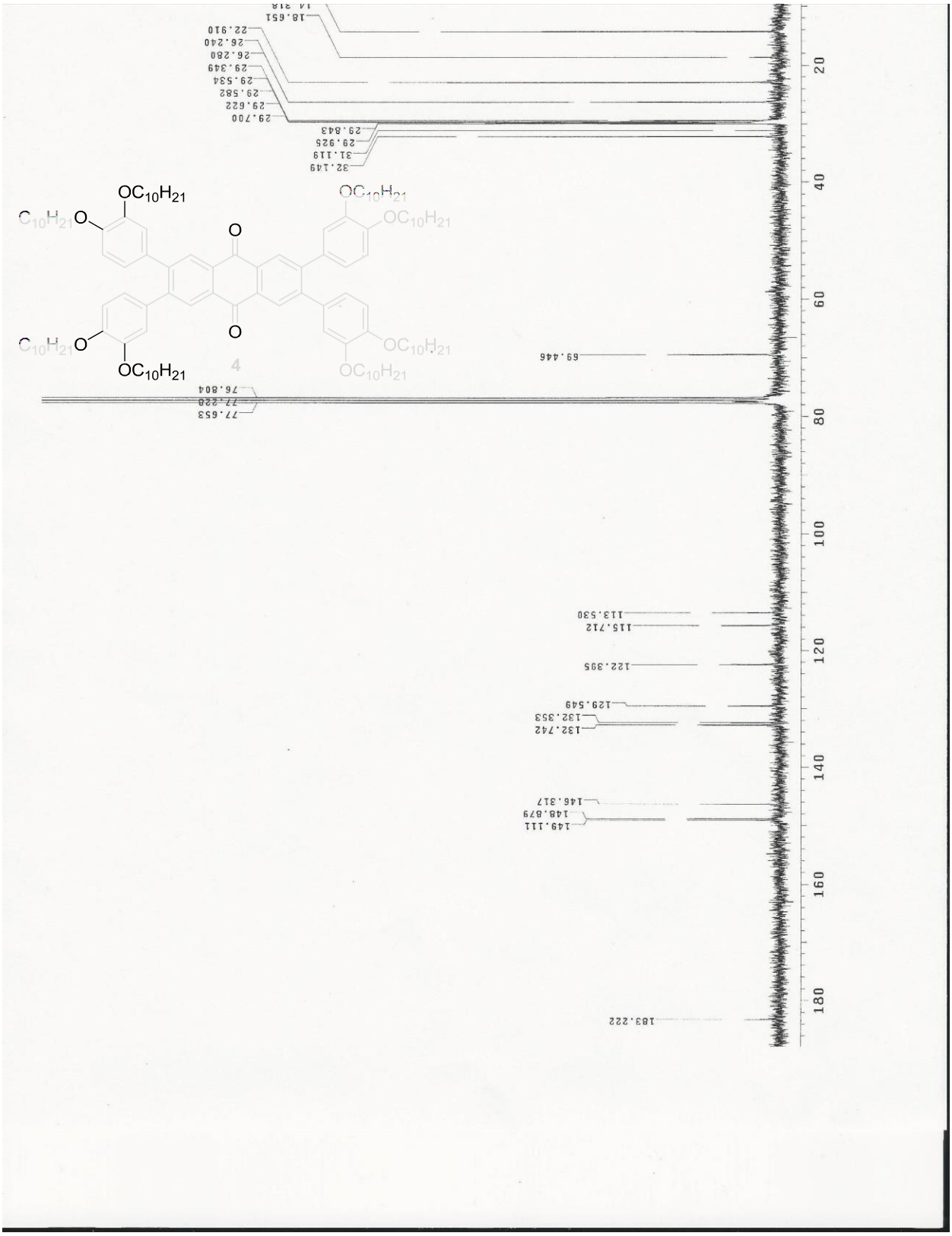

OC10H21
OC10H21
O
O
OC10H21
OC10H21
2
ppm
0.887
0.898
1.290
1.480
1.583
1.670
1.693
1.715
1.809
1.835
1.856
3.718
3.740
3.762
3.971
3.993
4.015
6.706
6.813
6.840
6.862
7.270
7.704
7.714
7.723
7.733
8.117
8.127
8.137
8.147
8.426
8.896
12.58
63.54
4.39
4.46
4.05
4.12
1.95
4.14
2.00
1.90
1.97
1.94

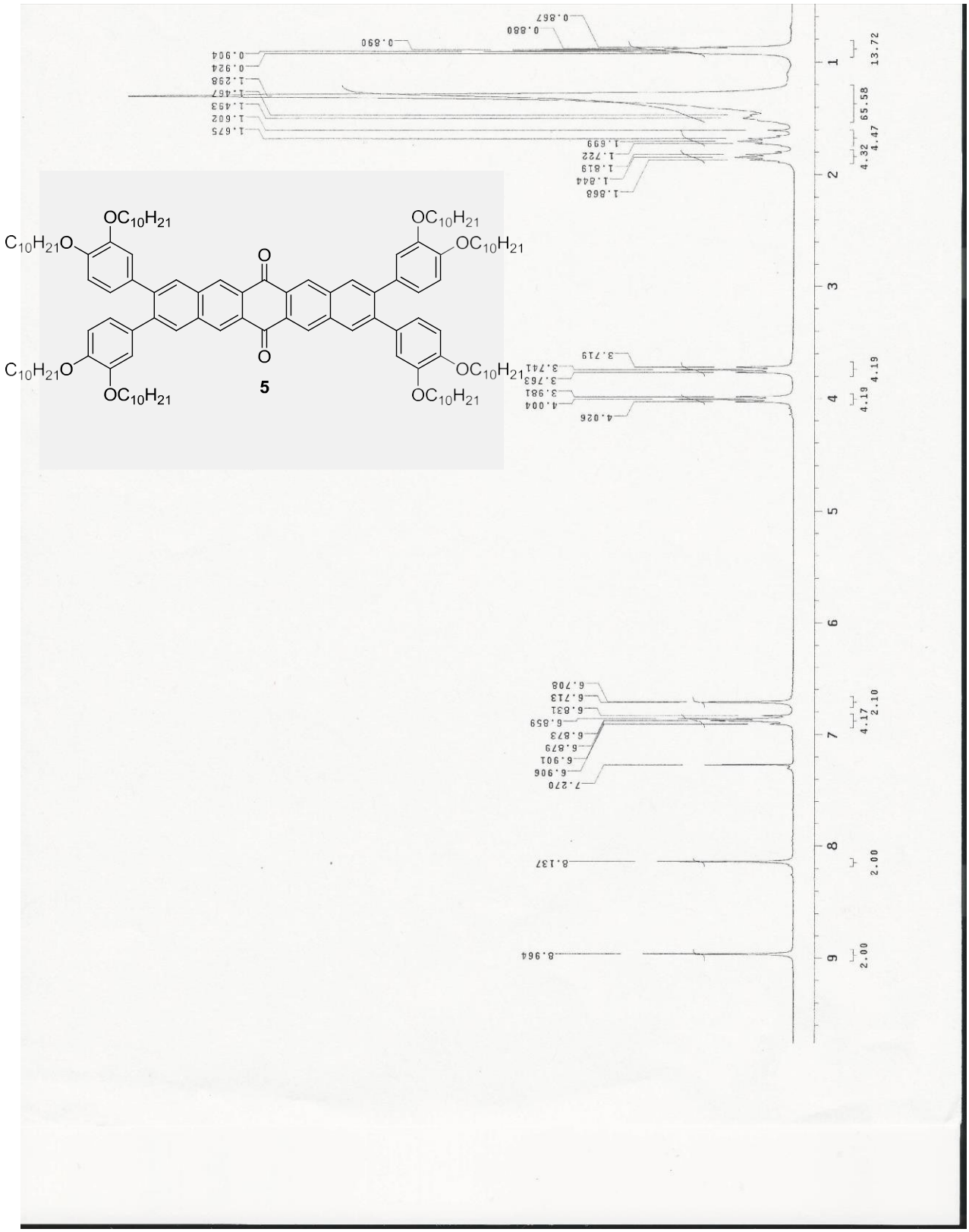

OC10H21
OC10H21
OC10H21
OC10H21
O
O
2
14.331
22.923
26.255
26.297
29.364
29.547
29.597
29.635
29.664
29.717
29.839
29.858
29.883
29.942
32.156
69.420
76.820
77.243
77.668
113.507
115.720
122.422
129.639
129.709
129.795
130.298
130.348
132.719
133.075
135.396
146.485
148.875
149.134
183.110
ppm
20
40
60
80
100
120
140
160
180

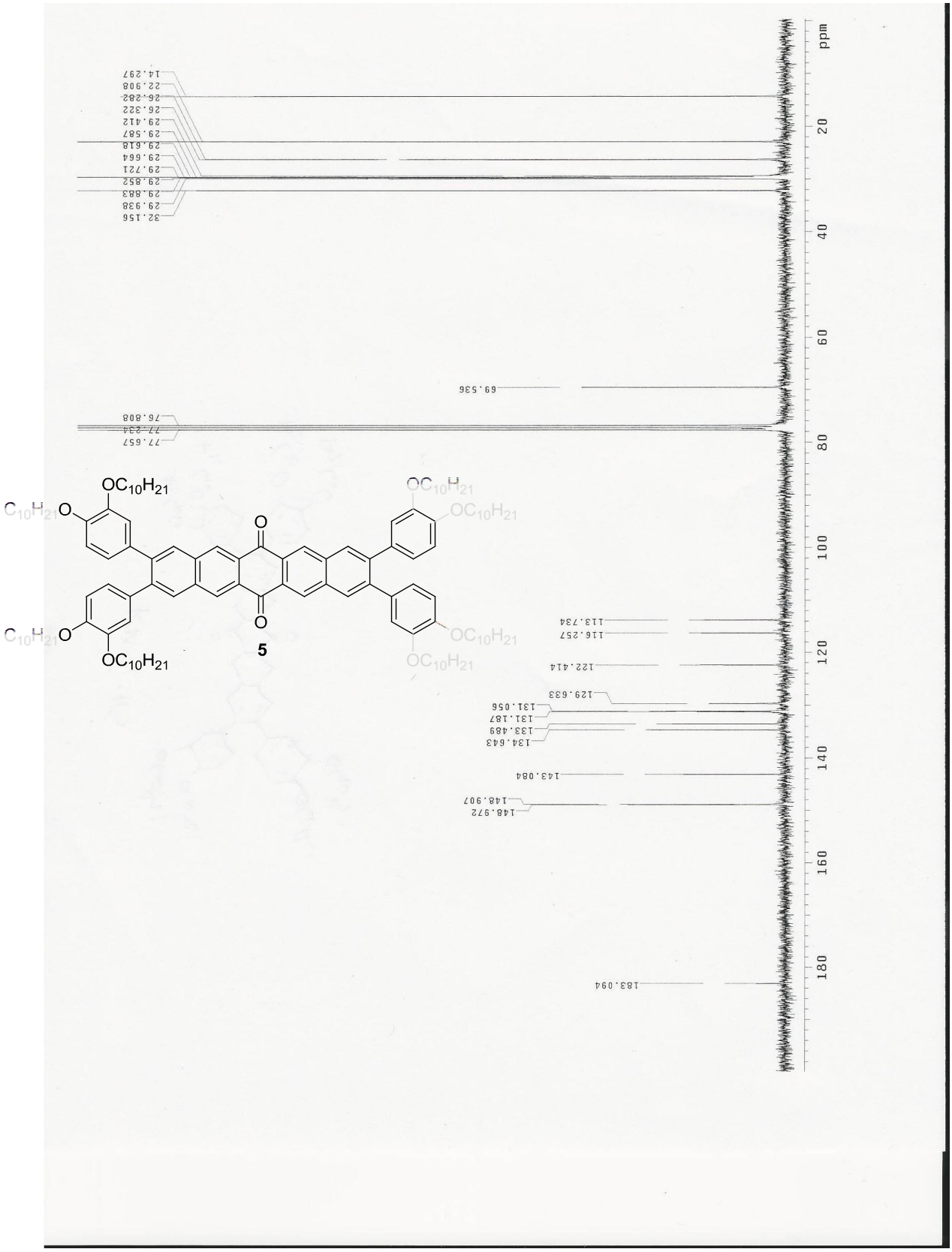

OC10H21
OC10H21
O
O
OC10H21
OC10H21
3
0.864
0.880
0.887
0.902
0.923
1.296
1.465
1.491
1.584
1.674
1.697
1.721
1.817
1.842
1.865
3.718
3.740
3.762
3.981
4.003
4.025
6.704
6.710
6.829
6.856
6.867
6.872
7.270
7.272
7.275
7.703
7.713
7.723
7.734
8.129
8.145
8.157
8.959
ppm
1
2
3
4
5
6
7
8
9
12.30
59.24
3.11
4.25
4.27
3.88
4.14
2.01
3.85
2.04
4.05
4.00


14.112
22.687
26.021
26.067
29.105
29.325
29.363
29.401
29.424
29.484
29.621
29.651
29.705
31.922
69.192
76.680
76.992
77.311
113.221
115.719
122.092
129.474
129.740
130.112
130.674
130.970
133.105
134.381
135.254
142.880
148.523
148.599
182.967
ppm
20
40
60
80
100
120
140
160
180
O
O
OC10H21
OC10H21
OC10H21
OC10H21
3


0.885
1.281
1.447
1.471
1.657
1.680
1.701
1.797
1.821
1.843
2.167
2.171
3.706
3.728
3.748
3.959
3.980
4.002
6.690
6.826
6.845
7.260
8.352
1
2
3
4
5
6
7
8
OC10H21
O
4


OC10H21
O
4
183.222
149.111
148.879
146.317
132.742
132.353
129.549
122.395
115.712
113.530
69.446
77.653
77.220
76.804
32.149
31.119
29.925
29.843
29.700
29.622
29.582
29.534
29.349
26.280
26.240
22.910
18.651
20
40
60
80
100
120
140
160
180


OC10H21
C10H21O
O
O
OC10H21
OC10H21
OC10H21
C10H21O
OC10H21
OC10H21
5
0.867
0.880
0.890
0.904
0.924
1.298
1.467
1.493
1.602
1.675
1.699
1.722
1.819
1.844
1.868
3.719
3.741
3.763
3.981
4.004
4.026
6.708
6.713
6.831
6.859
6.873
6.879
6.901
6.906
7.270
8.137
8.964
13.72
65.58
4.47
4.32
4.19
4.19
2.10
4.17
2.00
2.00


14.297
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26.282
26.322
29.412
29.587
29.618
29.664
29.721
29.852
29.883
29.938
32.156
69.536
76.808
77.234
77.657
113.734
116.257
122.414
129.633
131.056
131.187
133.489
134.643
143.084
148.907
148.972
183.094
ppm
20
40
60
80
100
120
140
160
180
OC10H21
O
5