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Supporting Information

NEW 3p-2SPIRO LADDER TYPE PHENYLENE MATERIALS: SYNTHESIS, PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS IN OLEDS

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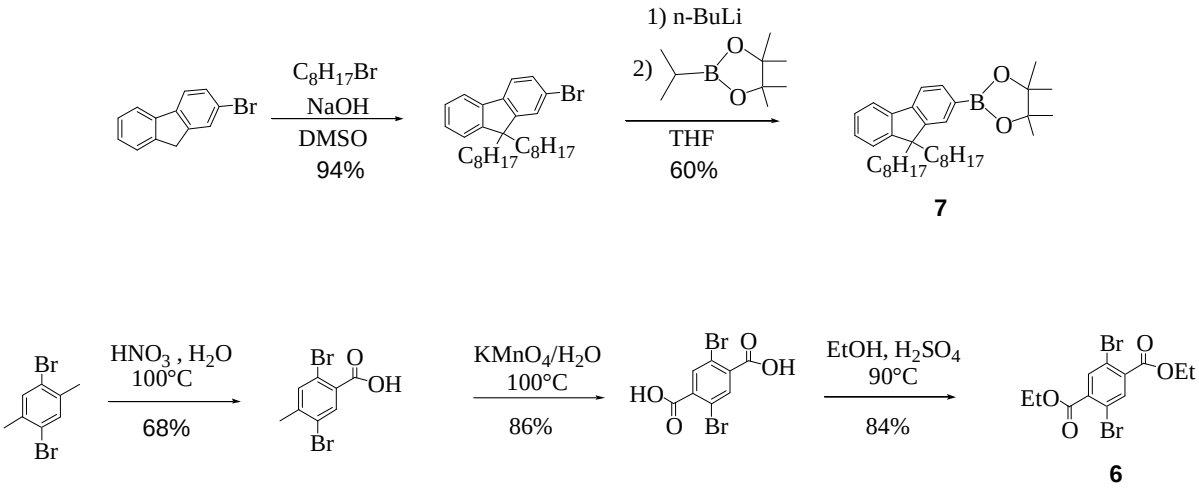
Table of contents

Syntheses

9,9-dioctylfluorene-2-boronate ester **7** has been prepared according to literature procedures starting from commercially available 2-bromofluorene.[1-3] Di-ester **6** was prepared according to a modified Tour procedure[4] starting from 1,4-dibromo-2,5-dimethylbenzene in a two-step oxidation reaction followed by an esterification.[1]



Scheme 1. Synthesis of **6** and **7**.

2,5-dibromo-4-methylbenzoic acid. 1,4-dibromo-2,5-dimethylbenzene (13.2 g, 50.0 mmol) was added to a solution of water (55 mL) and nitric acid (65%, 45 mL). The mixture was stirred for 6 days under reflux. Sublimated 2,5-dibromo-4-xylene was regularly reintroduced into the flask. After cooling, the white precipitate was filtered to give the title compound (6.1 g, 42%). Water (100 mL) was added to the filtrate. The nitric acid was neutralized by sodium carbonate (6.0 g). The filtrate was then carefully acidified by a solution of hydrochloric acid 37 % until pH=1 and extracted with diethyl ether (3×100 mL). The organic layers were dried ($MgSO_4$) and evaporated in *vacuo* to give the *title compound* (3.8 g, 26 %) as a colourless solid. M.p. 189 °C (ethanol) (lit.;[4] m.p. 193-195 (hexane/ether)); ^{1}H NMR (300 MHz; [D6] DMSO) δ=13.58 (br s, 1H; exch D_2O, OH), 7.92 (s, 1H; ArH), 7.72 (s, 1H; ArH), 2.35 ppm (s, 3H; Me); ^{13}C NMR (75 MHz; [D6] DMSO) d = 165.6 (C), 142.6 (C), 135.8 (C), 133.8 (C), 132.1 (C), 122.9 (CH), 119.2 (CH), 21.9 ppm (Me) ; IR (KBr) n = 3100-2535 (OH), 1678 (C=O), 1586, 1474, 1428, 1375, 1340, 1300, 1256, 1142, 1056 cm^{-1}; elemental analysis calcd (%) for $C_8H_6O_2\,^{79}Br_2$: C, 32.69; H, 2.06; found C, 32.59; H, 2.06.

2,5-dibromoterephthalic acid. Potassium permanganate (8.69 g, 55.0 mmol) was added to a mixture of 2,5-dibromo-4-methylbenzoic acid (6.62 g, 19.5 mmol) and water (50 mL). The mixture was stirred under reflux for 6 days. Then the mixture was filtered on celite. The filtrate was acidified until discolouration. The precipitate was filtered to give the *title compound* (5.70 g, 86%) as a colourless solid. M.p. 296 °C (ethanol) (lit.;[4] m.p. 308-316); ^{1}H NMR (300 MHz; DMSO d6) d=8.00 ppm (s, 2H; ArH), (no OH signal observed); ^{13}C NMR (75 MHz; [D6] DMSO) d = 165.5 (C), 137.0 (C), 134.9 (C), 118.8 ppm (CH); IR (KBr) n = 3095, 3000- 2520 (OH), 1701 (C=O), 1472, 1397, 1295, 1247, 1136, 1057 cm^{-1}; HRMS (EI): *m/z* calcd for $C_8H_4O_4\,^{79}Br_2$: 321.84763 [M]+•; found: 321.8484.

[1] As also observed by Tour and coworkers, the direct oxidation of the two methyl groups of 1,4-dibromo-2,5-dimethylbenzene led to very low yield of the corresponding di-carboxilic acid (<5%).

Diethyl 2,5-di-bromoterephthalate 6. Concentrated sulfuric acid (6.67 g, 3 mL, 68.0 mmol, 98%) was added to a mixture of 2,5-dibromoterephthalic acid (5.50 g, 17.0 mmol) and ethanol (150 mL). The mixture was stirred under reflux for 3 days. The solvent was then evaporated in *vacuo* and the residue was purified by column chromatography on silica gel eluting with dichloromethane to give the *title compound* (5.72 g, 84%) as a colourless solid. M.p. 121 °C (methanol); ^{1}H NMR (300 MHz; $CDCl_3$) d=8.01 (s, 2H; ArH), 4.40 (q, J= 7.2 Hz, 4H; CH_2), 1.40 ppm (t, J= 7.2 Hz, 6H; Me); ^{13}C NMR (75 MHz; $CDCl_3$) d=164.1 (C), 136.4 (C), 135.7 (C), 120.0 (CH), 62.3 (CH_2), 14.1 ppm (Me); IR (KBr) n = 3095, 3037, 2980, 2933, 2868, 1723 (C=O), 1686, 1474, 1369, 1286, 1244, 1131, 1058, 1015 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{12}H_{12}O_4{}^{79}Br_2$: 377.9124 [M]+•; found: 377.9124.

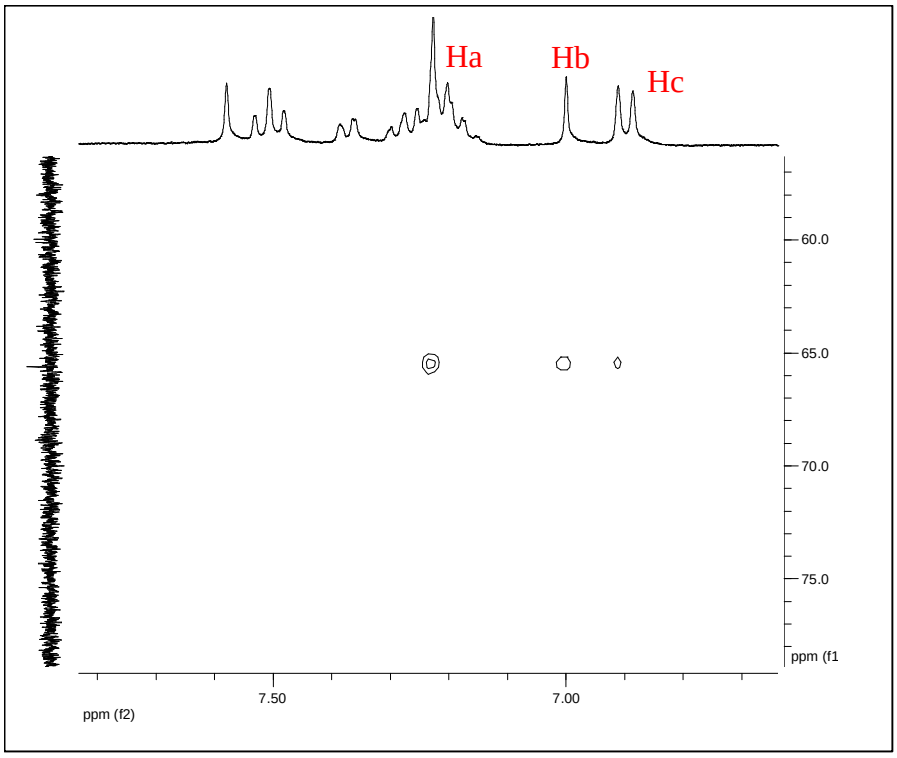


Figure 1. Portion of the HMBC spectrum (CD_2Cl_2) of **2**

X-Ray

8:

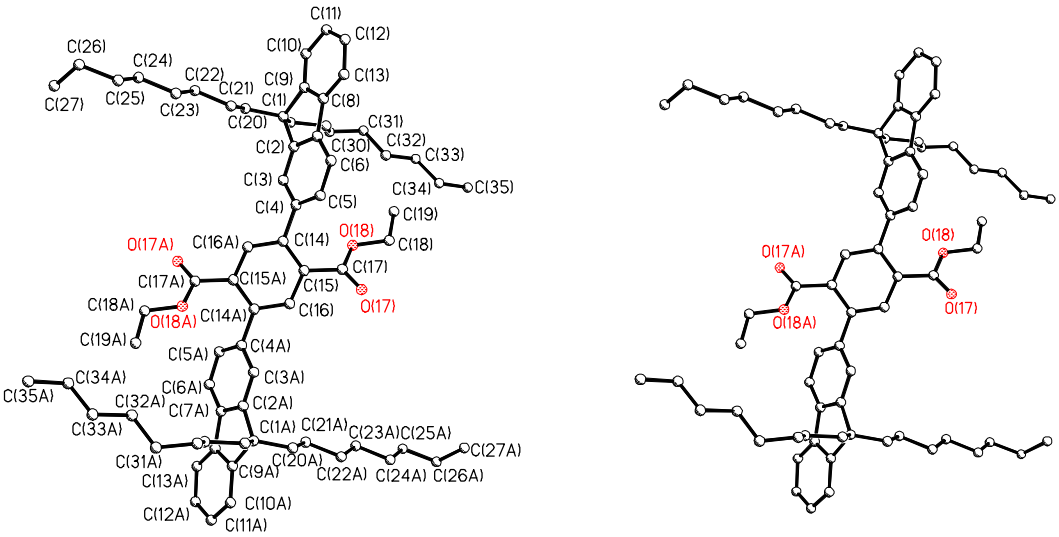


Figure 2. Molecular structure of **8** from single crystal X-Ray diffraction data (hydrogen atoms have been omitted for clarity).

2:

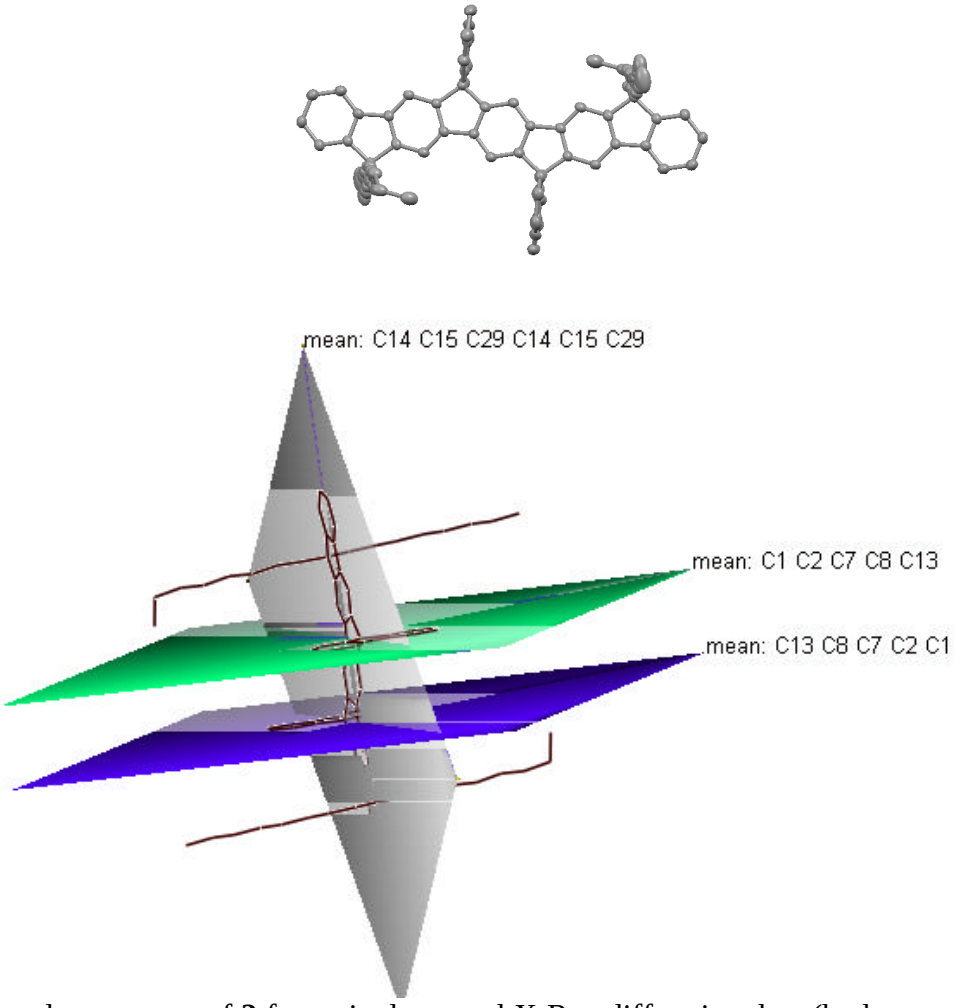


Figure 3. Molecular structure of **2** from single crystal X-Ray diffraction data (hydrogen atoms have been omitted for clarity).
The angle between the plane C14/ C15/C29/C14/ C15/C29 (grey) and the planes C1/C2/C7/C8/C13/ (green) is **86.2°**.

Thermogravimetric analysis

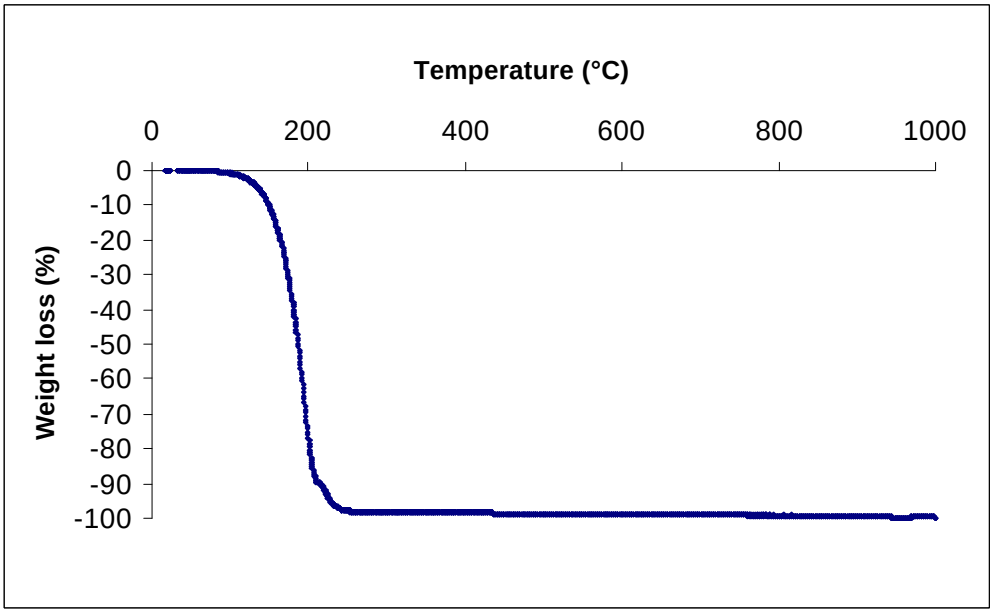


Figure 4. 9-Fluorenone (*Td*=135°C)

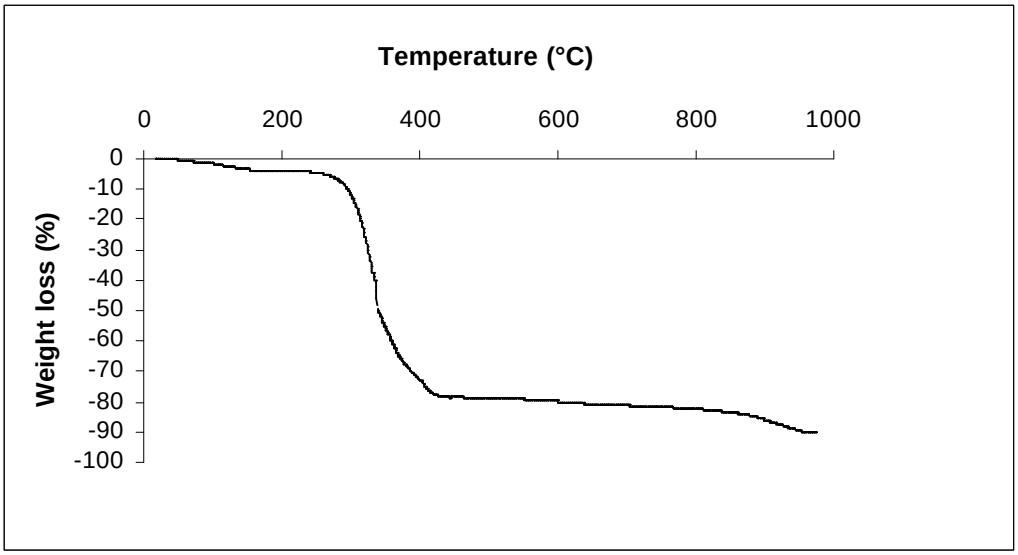


Figure 5. Indeno[1,2-b]fluorene-6,12-dione **3** (*Td*=265°C)

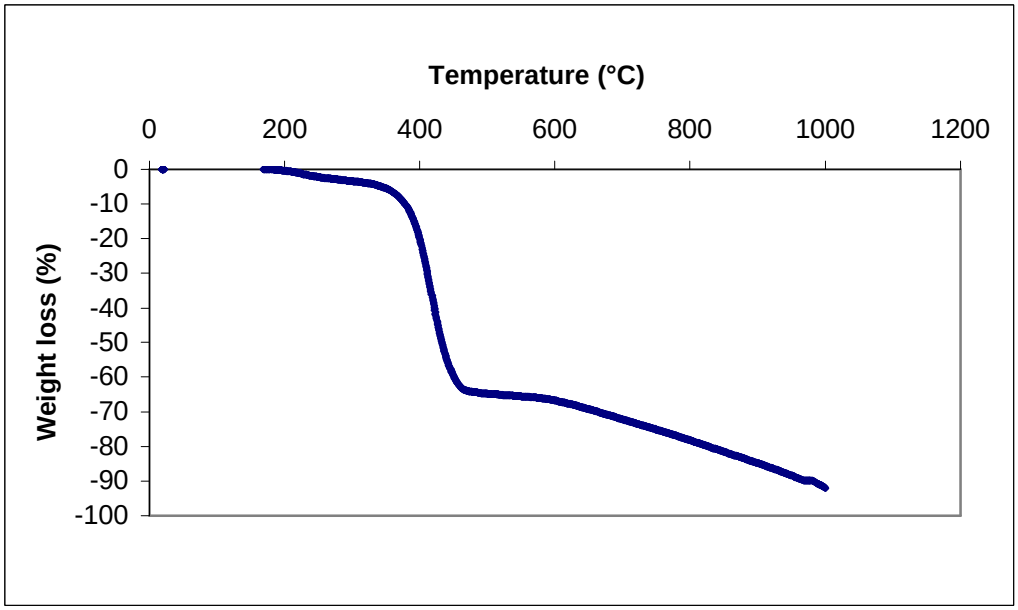


Figure 6. Mono ketone **13** (*Td*=345°C)

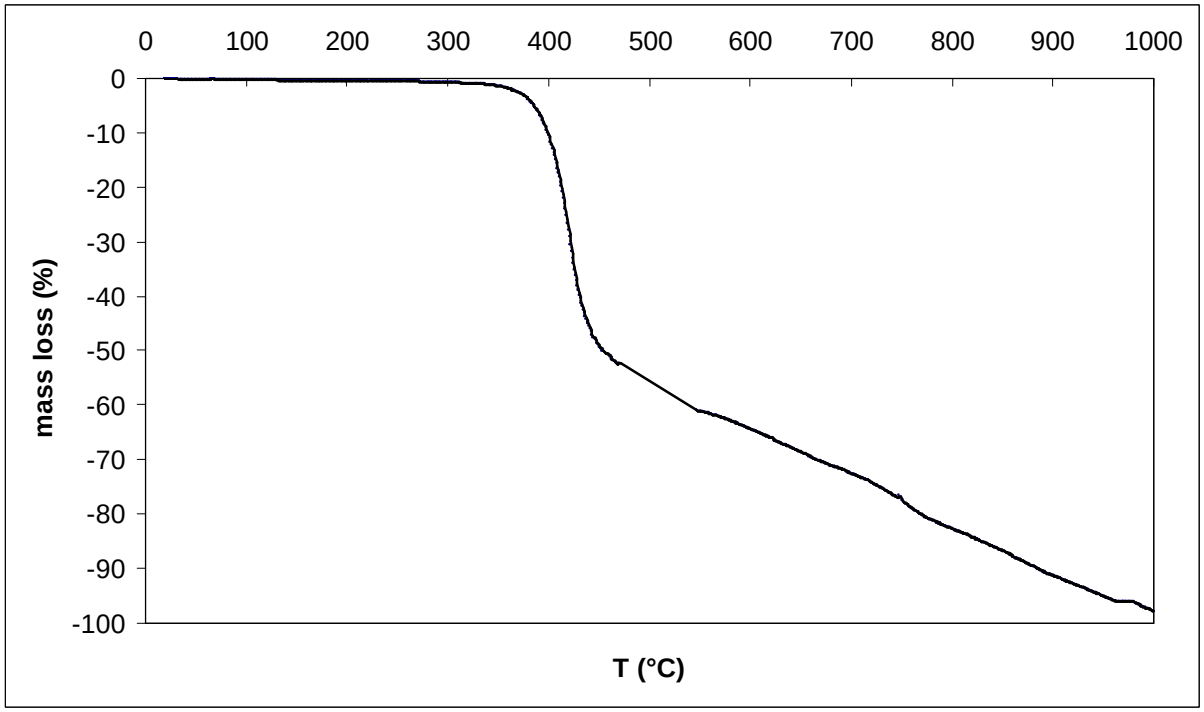


Figure 7. Diketone **10** (*Td*=385°C)

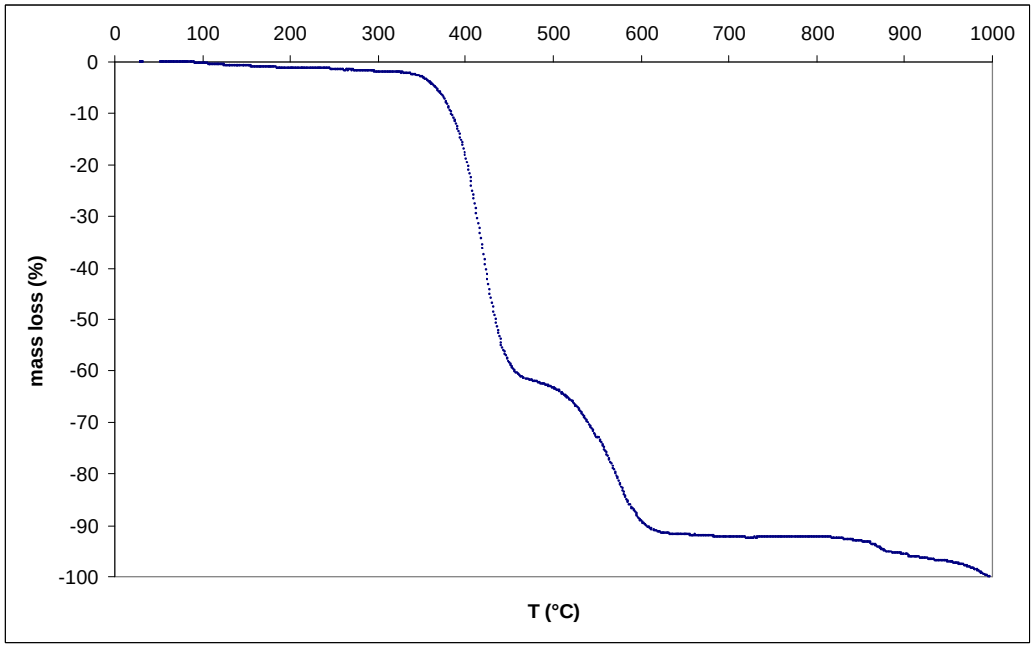


Figure 8. Dispiro **2** (*Td*=365°C)

Electrochemistry

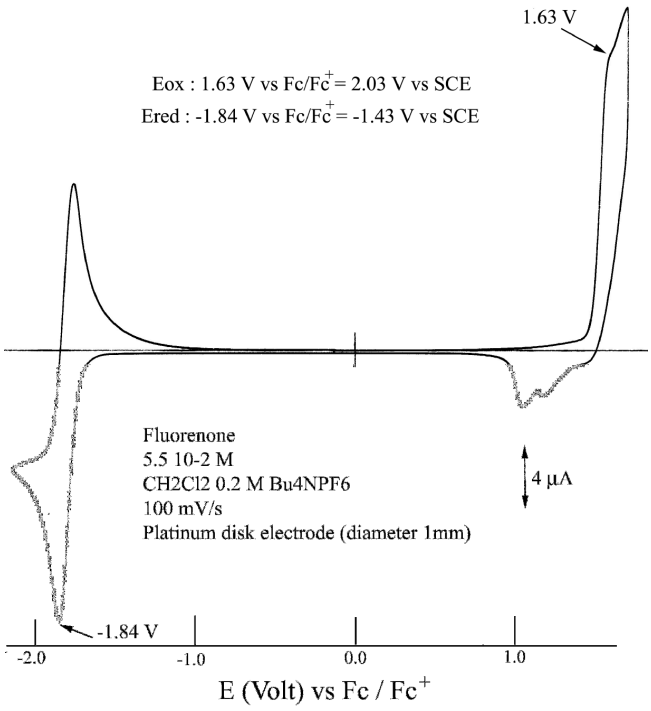


Figure 9. 9-Fluorenone

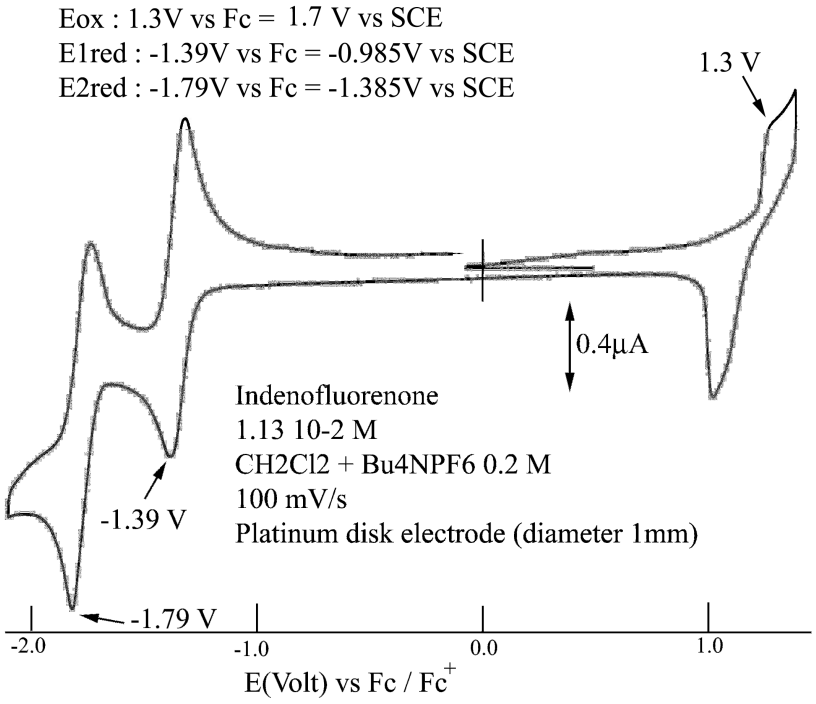


Figure 10. Indeno[1,2-*b*]fluorene-6,12-dione **3**

Microscopy

Comparative studies by microscopy of the thin films qualities depending of the deposition process: Spin coating *vs.* evaporation (×20).

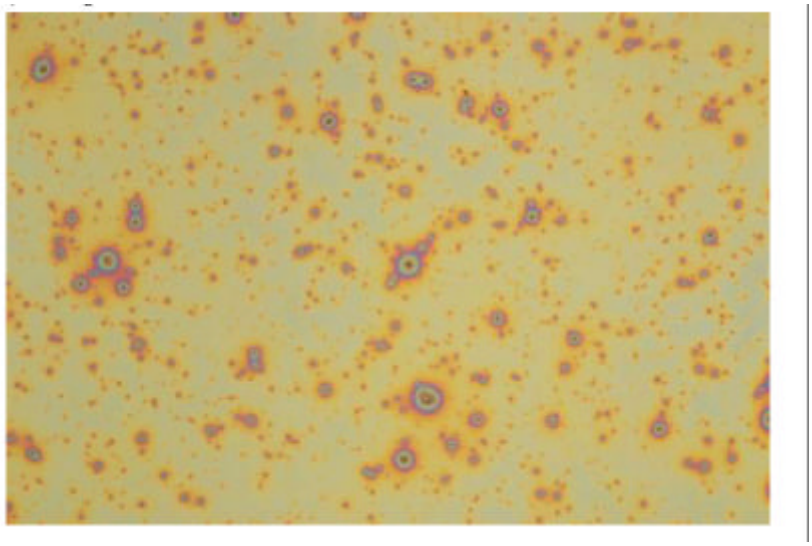


Figure 11. Image of a thin film deposited by spin coating.

Figure 12. Image of a thin film deposited by evaporation process.

REFERENCES

[1] Sonntag, M.; Kreger, K.; Hanft, D.; Strohriegl, P.; Setayesh, S.; de Leeuw, D. *Chem. Mater.* **2005**, *17*, 3031-3039.

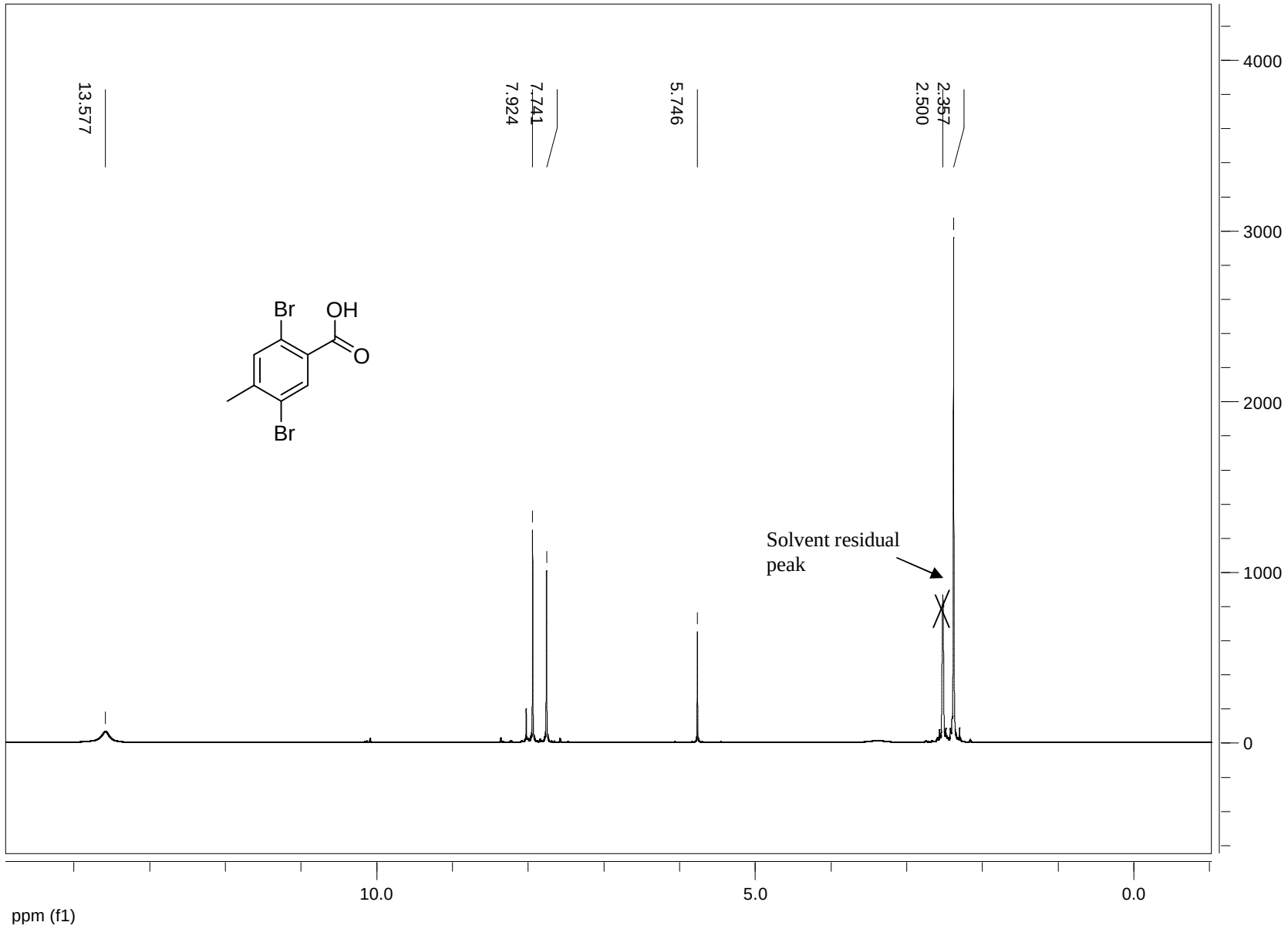
[2] Belletête, M.; Beaupré, S.; Bouchard, J.; Blondin, P.; Leclerc, M.; Durocher, G. *J. Phys. Chem. B* **2000**, *104*, 9118-9125.

[3] Li, T.; Yamamoto, T.; Lan, H.-L.; Kido, J. *Polym. Adv. Technol.* **2004**, *15*, 266-269.

[4] Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723-11736.

Copy of ^{1}H and ^{13}C NMR spectra

2,5-dibromo-4-methylbenzoic acid (d6-DMSO)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Br
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3000
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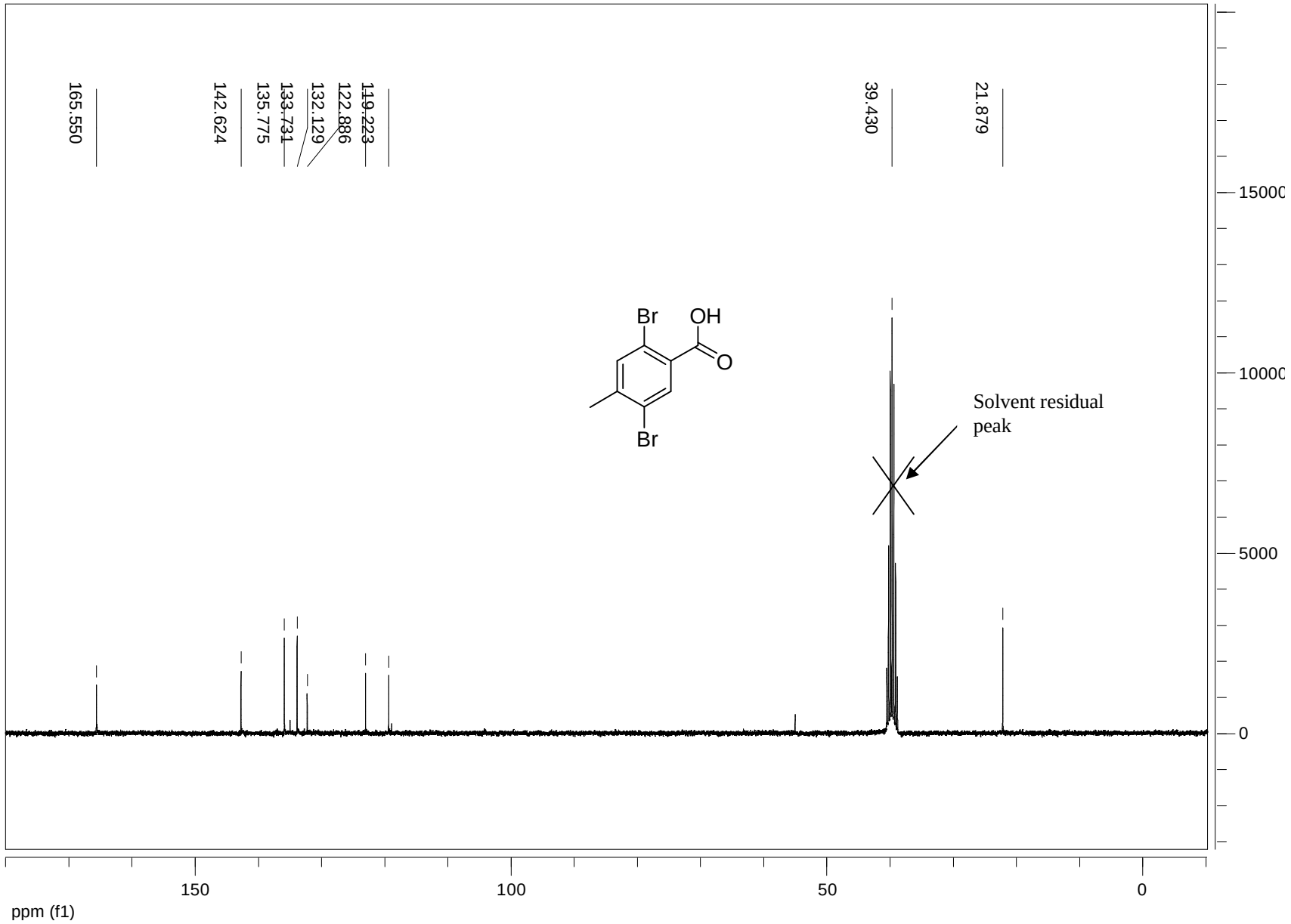
1000
0
10.0
5.0
0.0
ppm (f1)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132.129
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O
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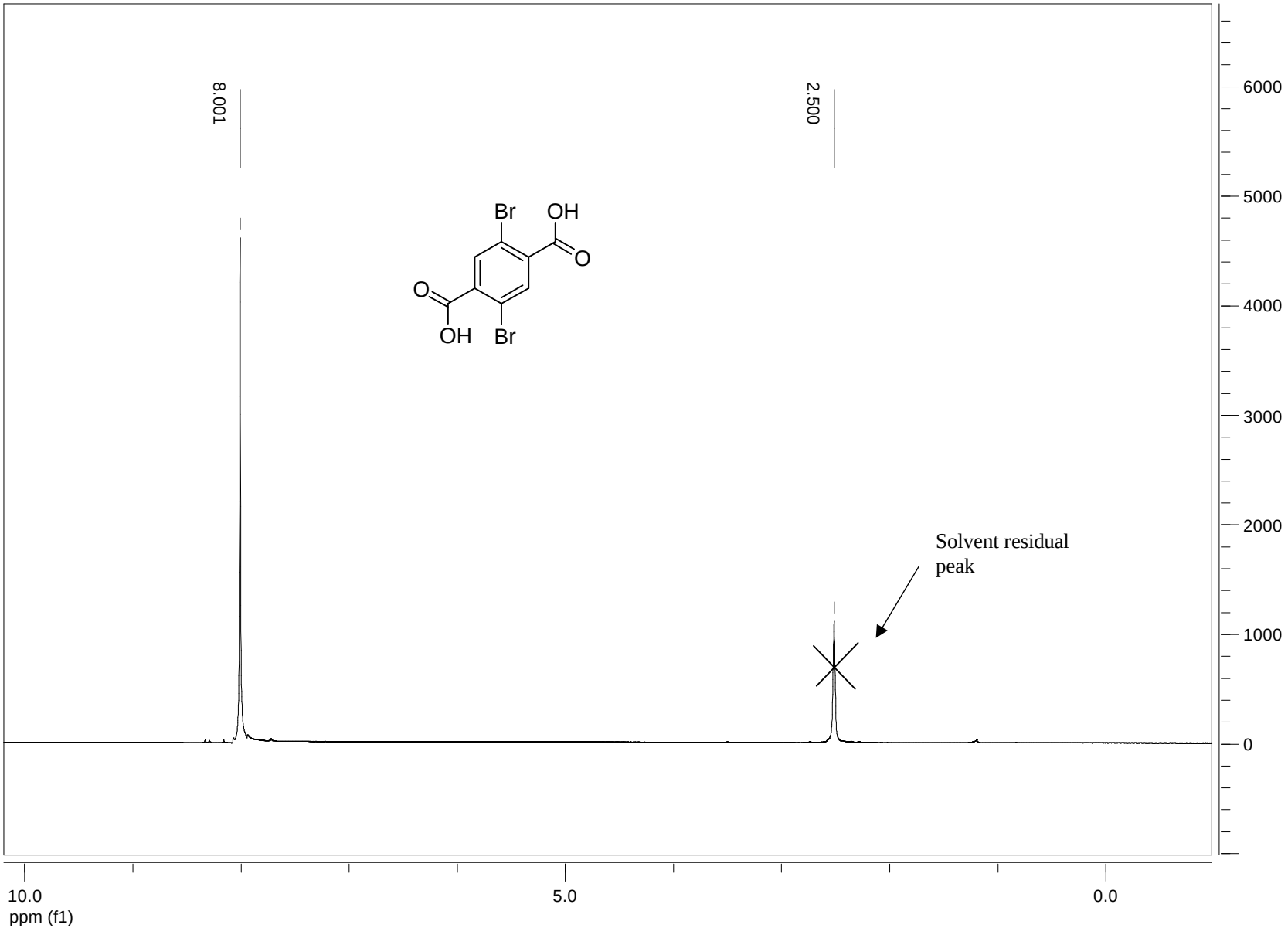
0
ppm (f1)

2,5-dibromoterephthalic acid (d6-DMSO)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OH
O
O
OH
Br
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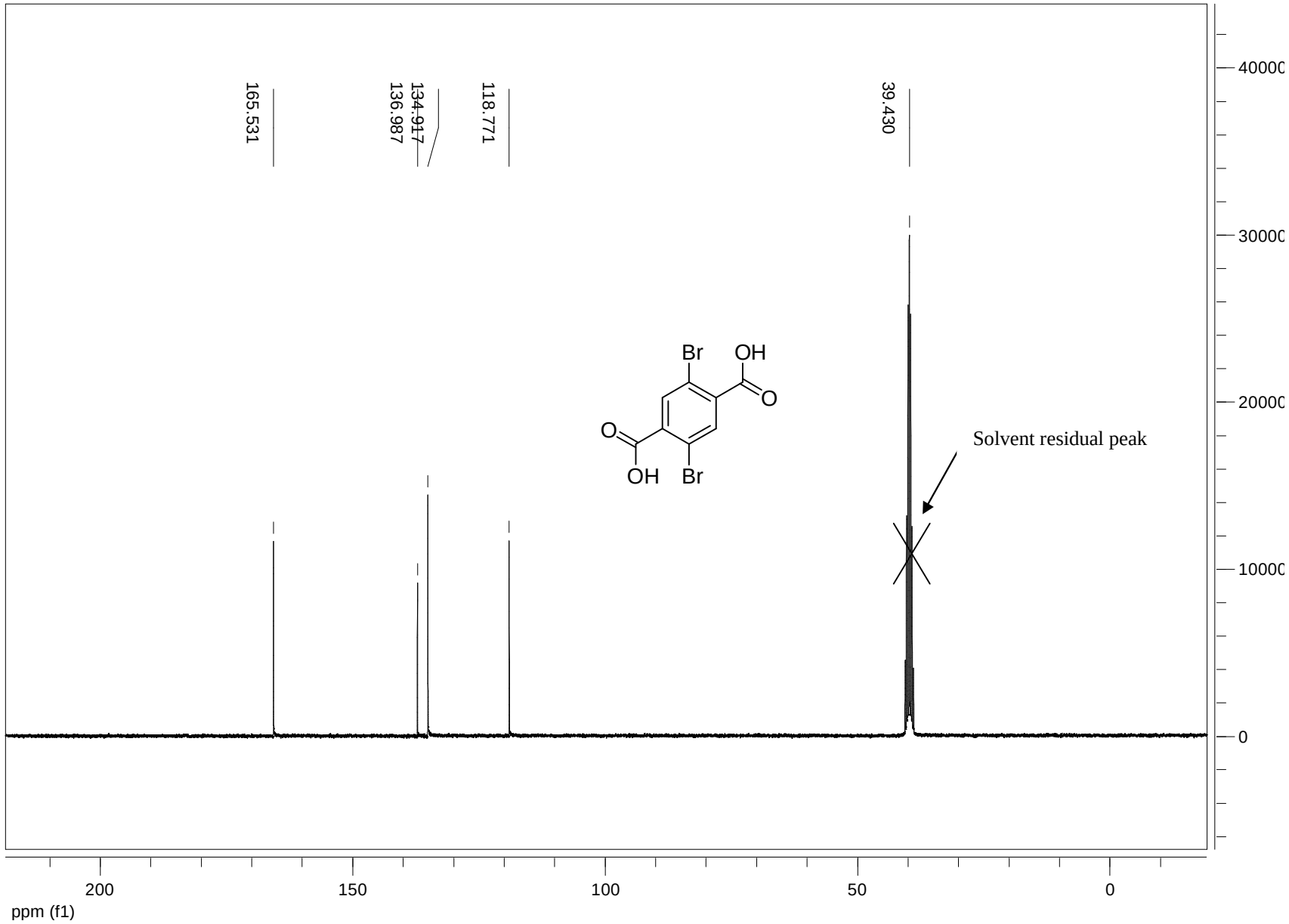
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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134.917
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OH
O
O
OH
Br
Solvent residual peak
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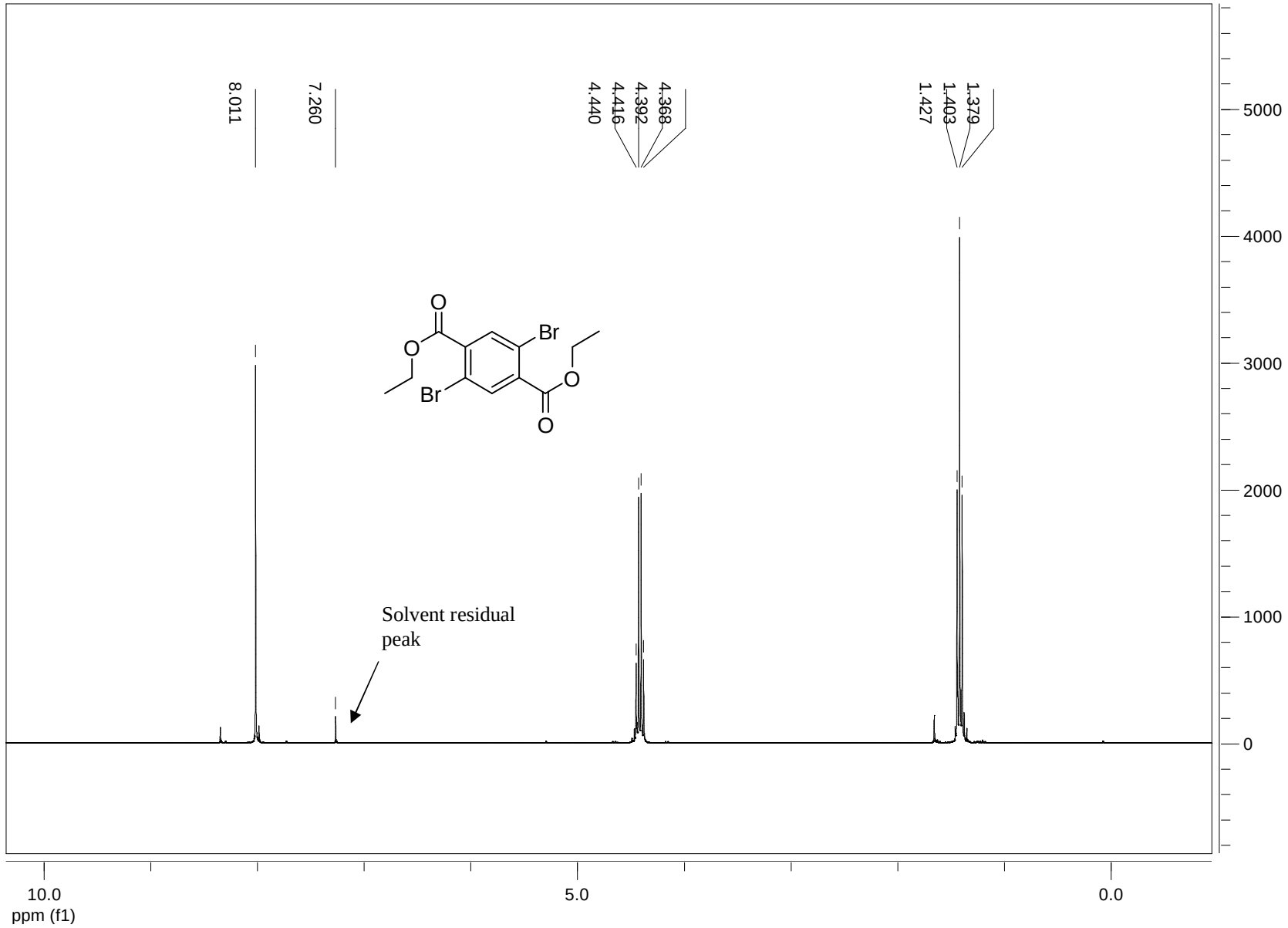
20000
10000
0
200
150
100
50
0
ppm (f1)

Diethyl 2,5-dibromoterephthalate 6 ($CDCl_3$)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4.440
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4.392
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1.403
1.379
O
O
Br
Br
O
O
Solvent residual peak
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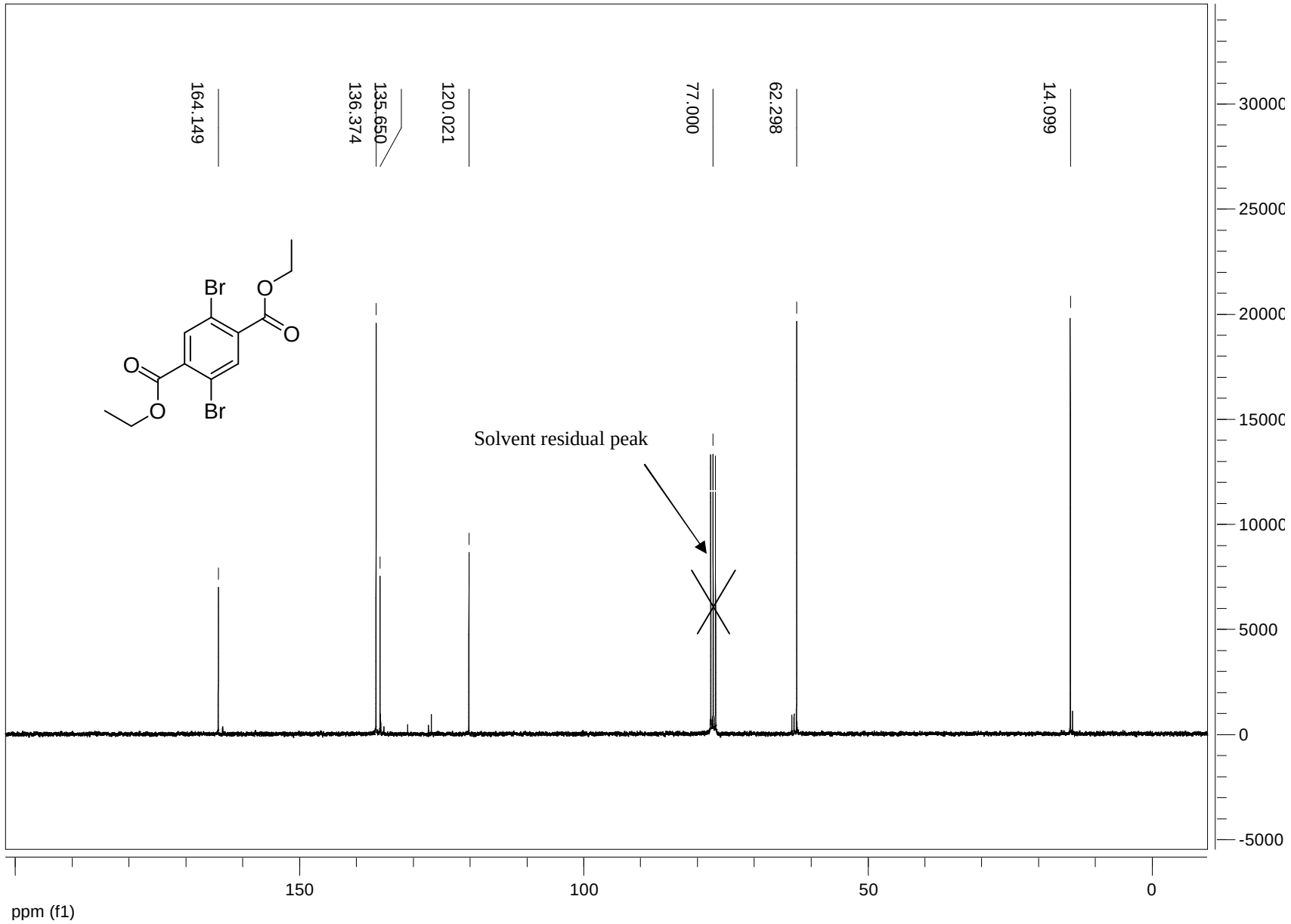
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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77.000
62.298
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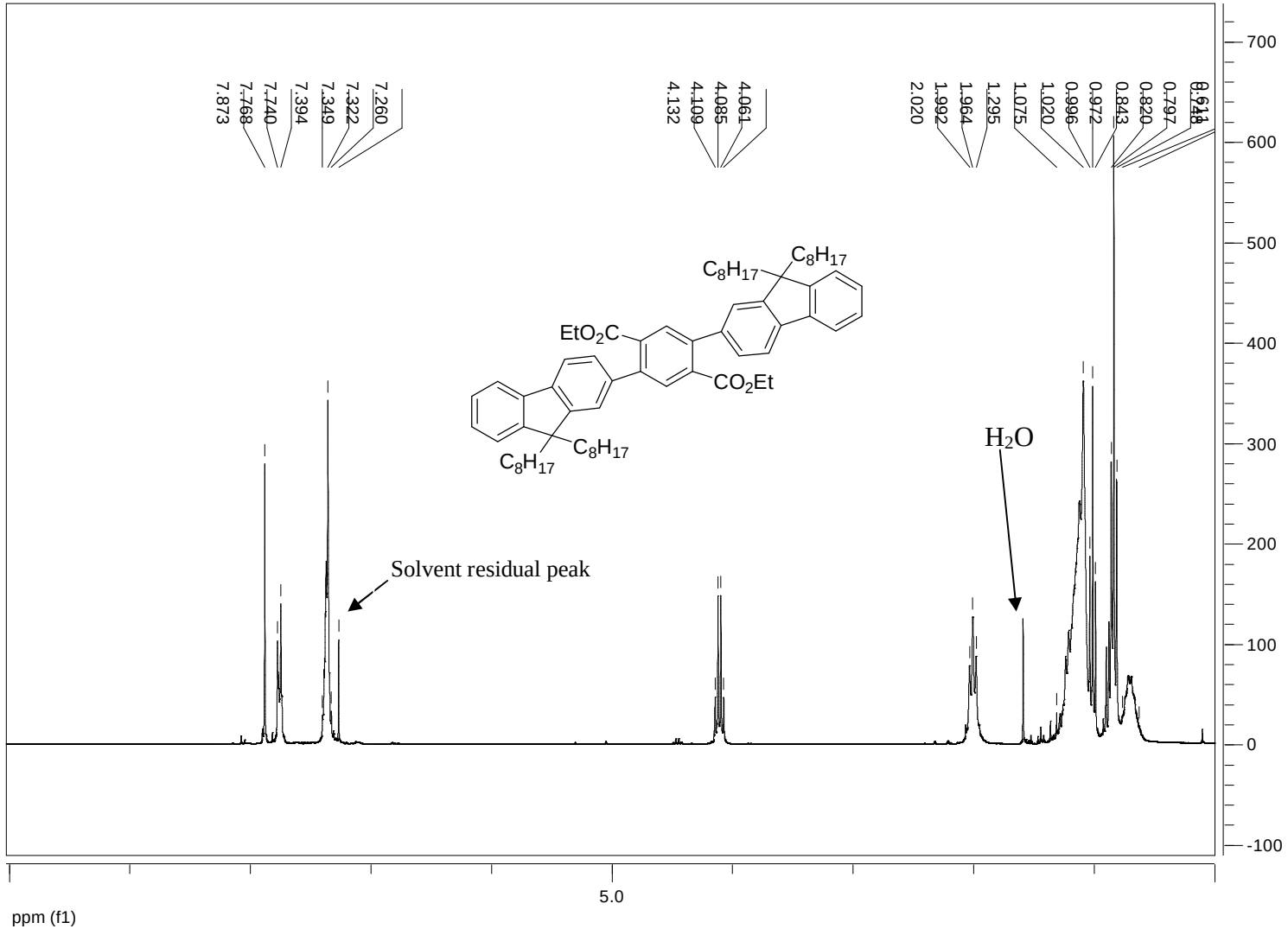
Br
O
O
O
O
Br
Solvent residual peak
30000
25000
20000
15000
10000
5000
0
-5000
150
100
50
0
ppm (f1)

Diethyl 2,5-bis(9, 9-dioctyl-9*H*-fluoren-2-yl)terephtalate 8 ($CDCl_3$)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1.964
1.295
1.075
1.020
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0.972
0.843
0.820
0.797
0.611
0.748
700
600
500
400
300
200
100
0
-100
C_8H_{17}
C_8H_{17}
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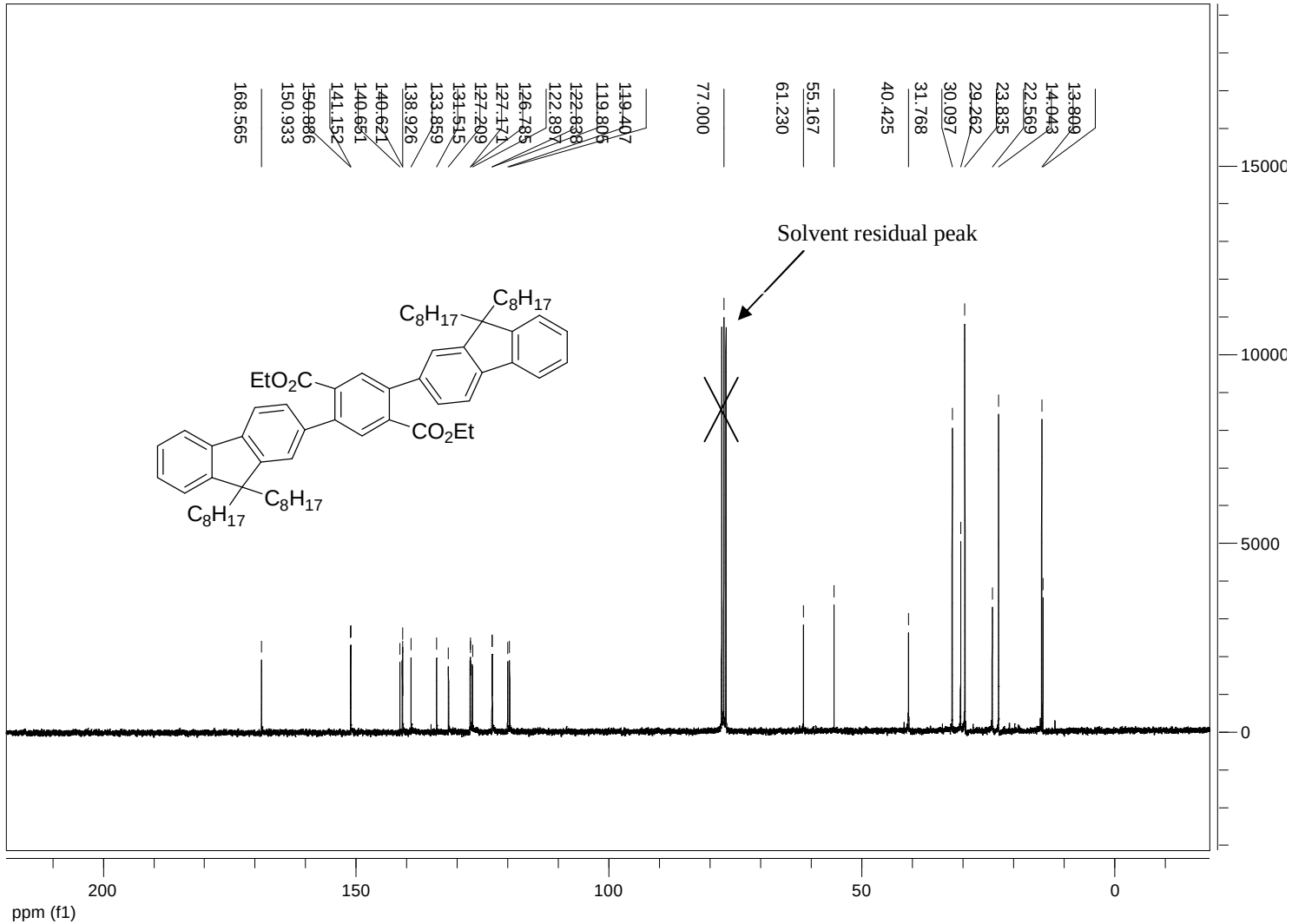
ppm (f1)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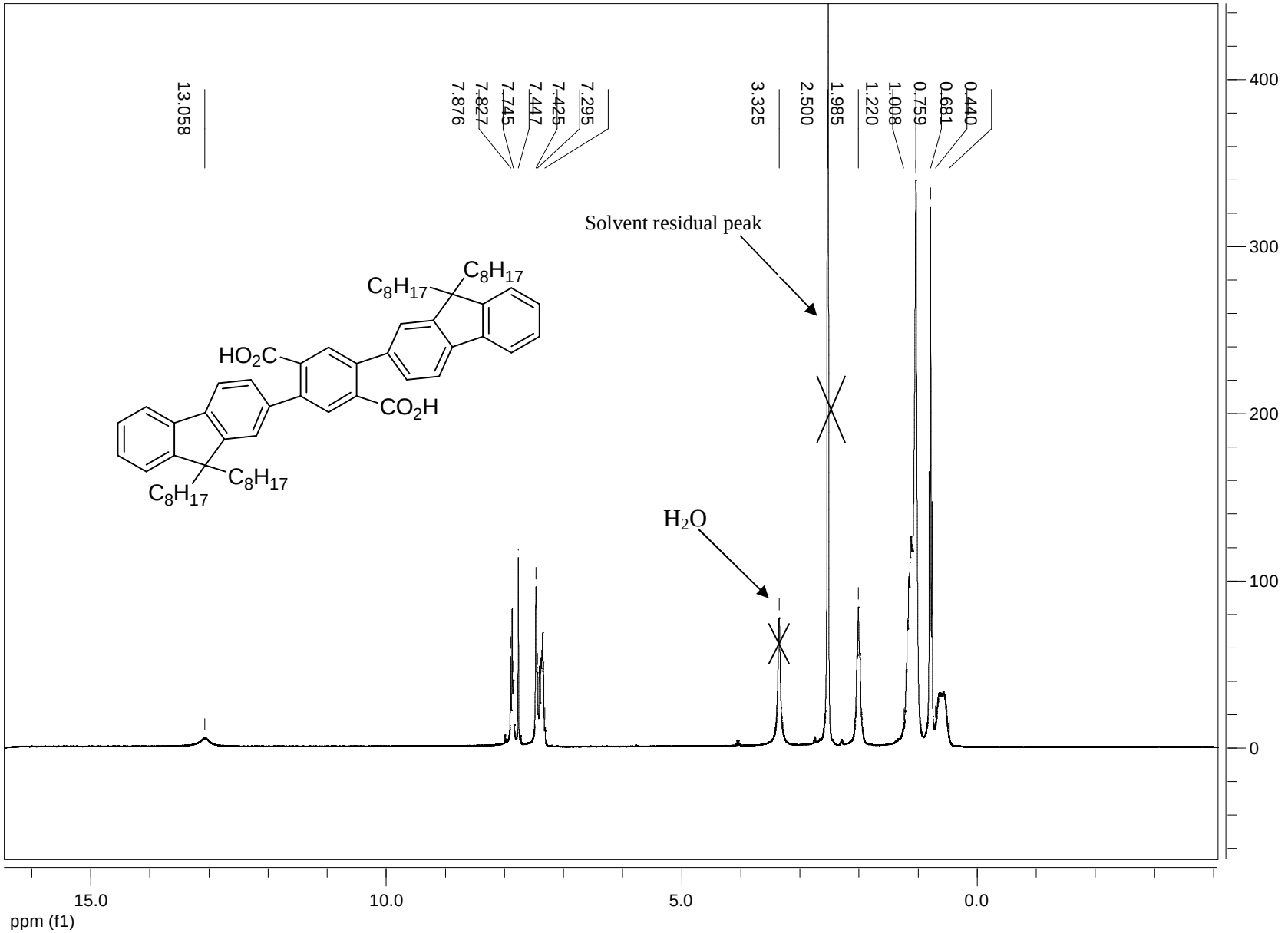
122.897
122.838
119.805
119.407
77.000
61.230
55.167
40.425
31.768
30.097
29.262
23.835
22.569
14.043
13.809
Solvent residual peak
C_8H_{17}
C_8H_{17}
C_8H_{17}
C_8H_{17}
EtO_2C
CO_2Et
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

2,5-bis(9,9-dioctyl-9*H*-fluoren-2-yl)terephtalic acid 9 (d6-DMSO)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7.827
7.745
7.447
7.425
7.295
3.325
2.500
1.985
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1.008
0.759
0.681
0.440
Solvent residual peak
H2O
HO2C
CO2H
C8H17
C8H17
C8H17
C8H17
400
300
200
100
0
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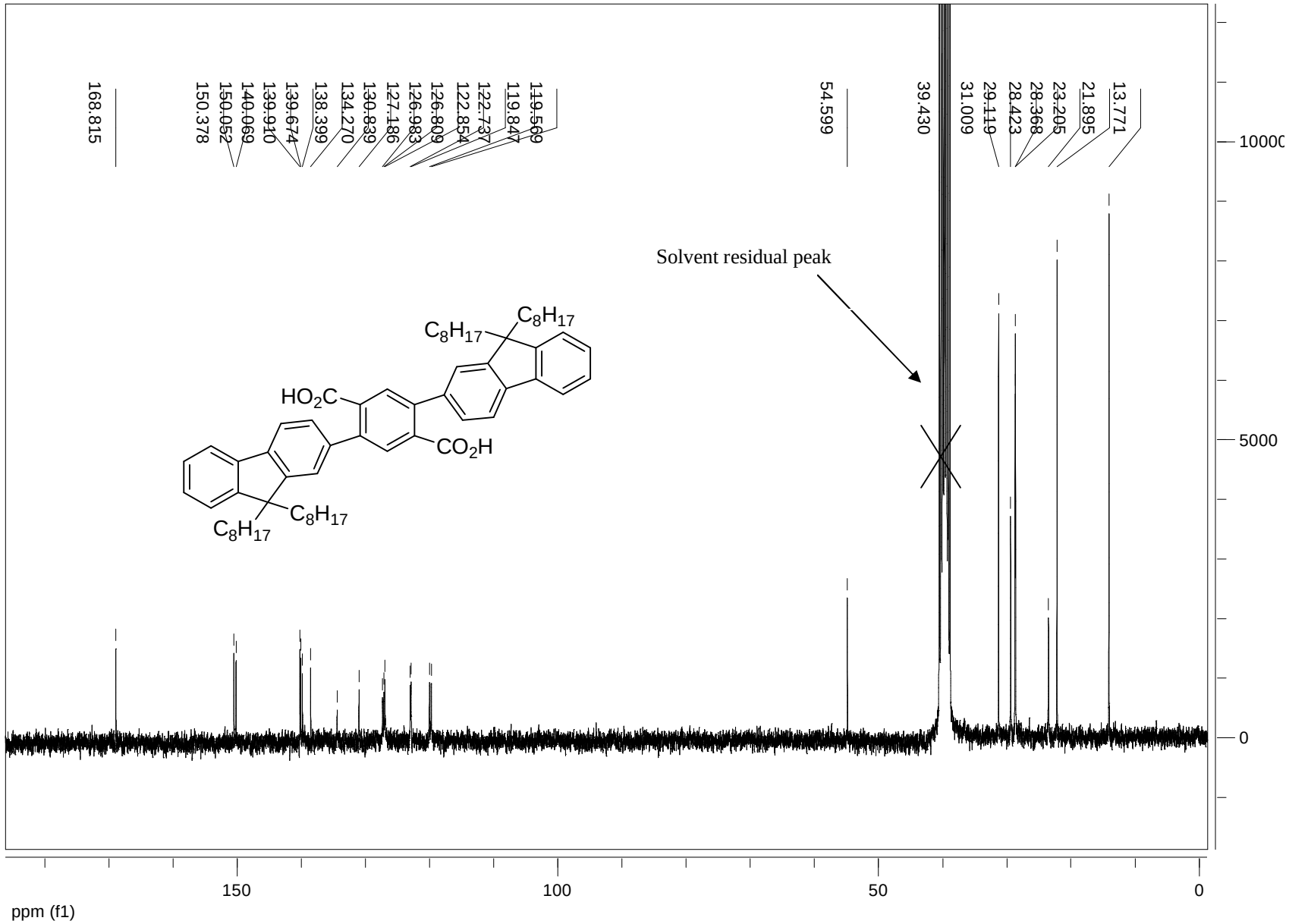
0.0
ppm (f1)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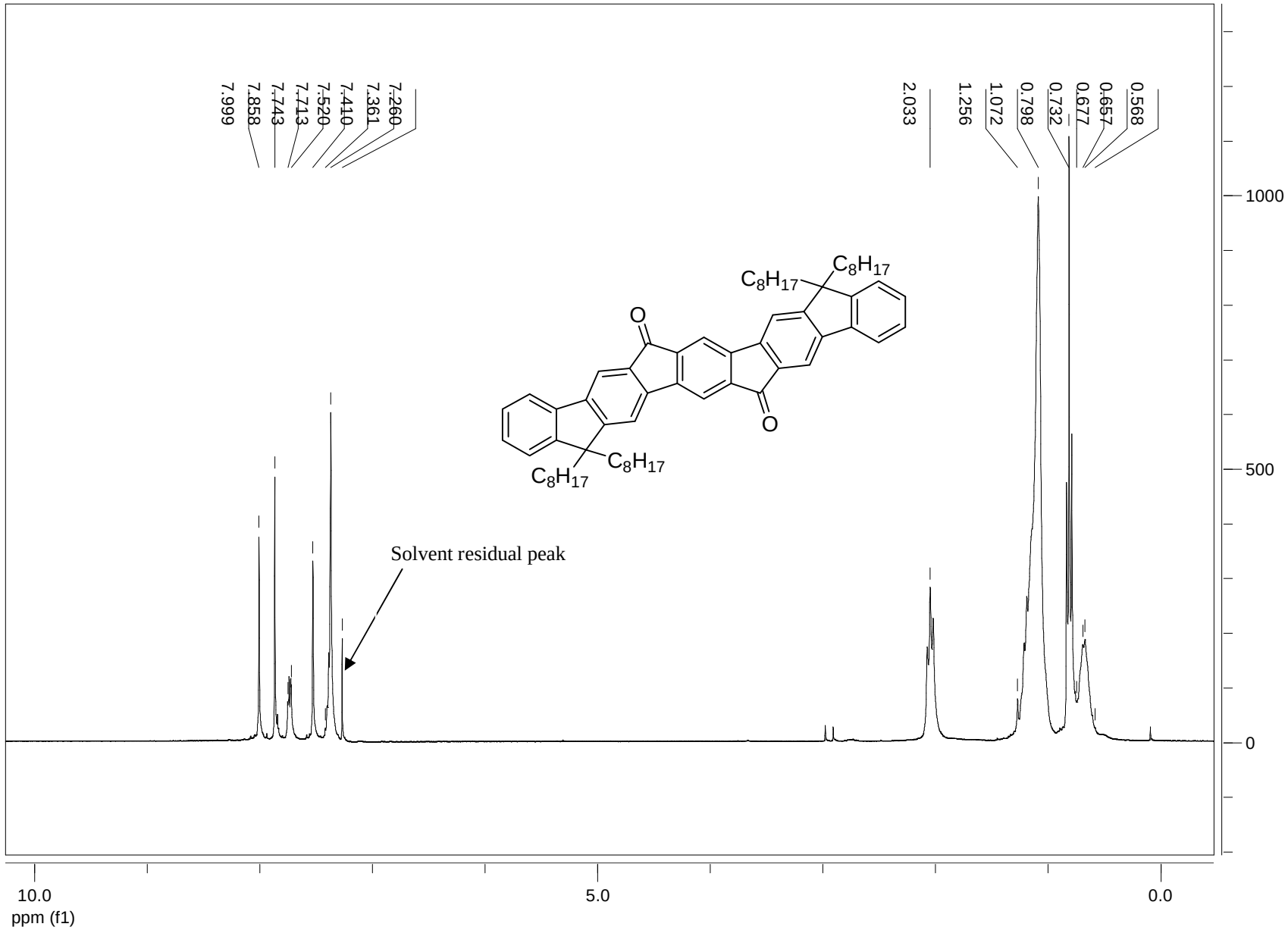
122.854
122.737
119.847
119.569
54.599
39.430
31.009
29.119
28.423
28.368
23.205
21.895
13.771
Solvent residual peak
HO2C
CO2H
C8H17
C8H17
C8H17
C8H17
10000
5000
0
150
100
50
0
ppm (f1)

9,9,18,18-tetraoctyl-9, 18-dihydrobenzo[5,6]-*s*- indaceno[1,2-*b*]indeno[2,1-*h*]fluorene-6,15-dione

10 ($CDCl_3$)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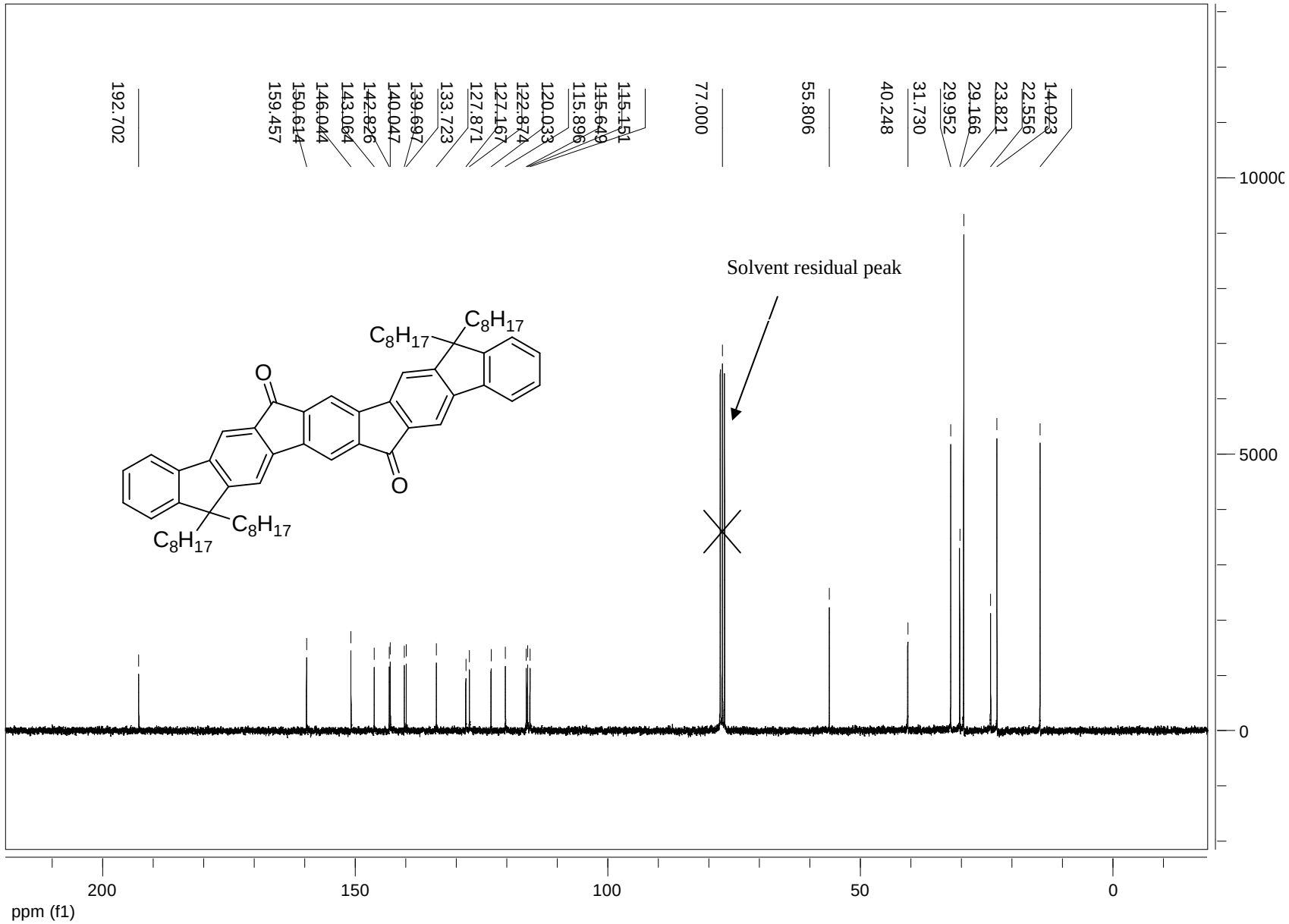
7.520
7.410
7.361
7.260
2.033
1.256
1.072
0.798
0.732
0.677
0.657
0.568
C8H17
C8H17
C8H17
C8H17
O
O
Solvent residual peak
1000
500
0
10.0
5.0
0.0
ppm (f1)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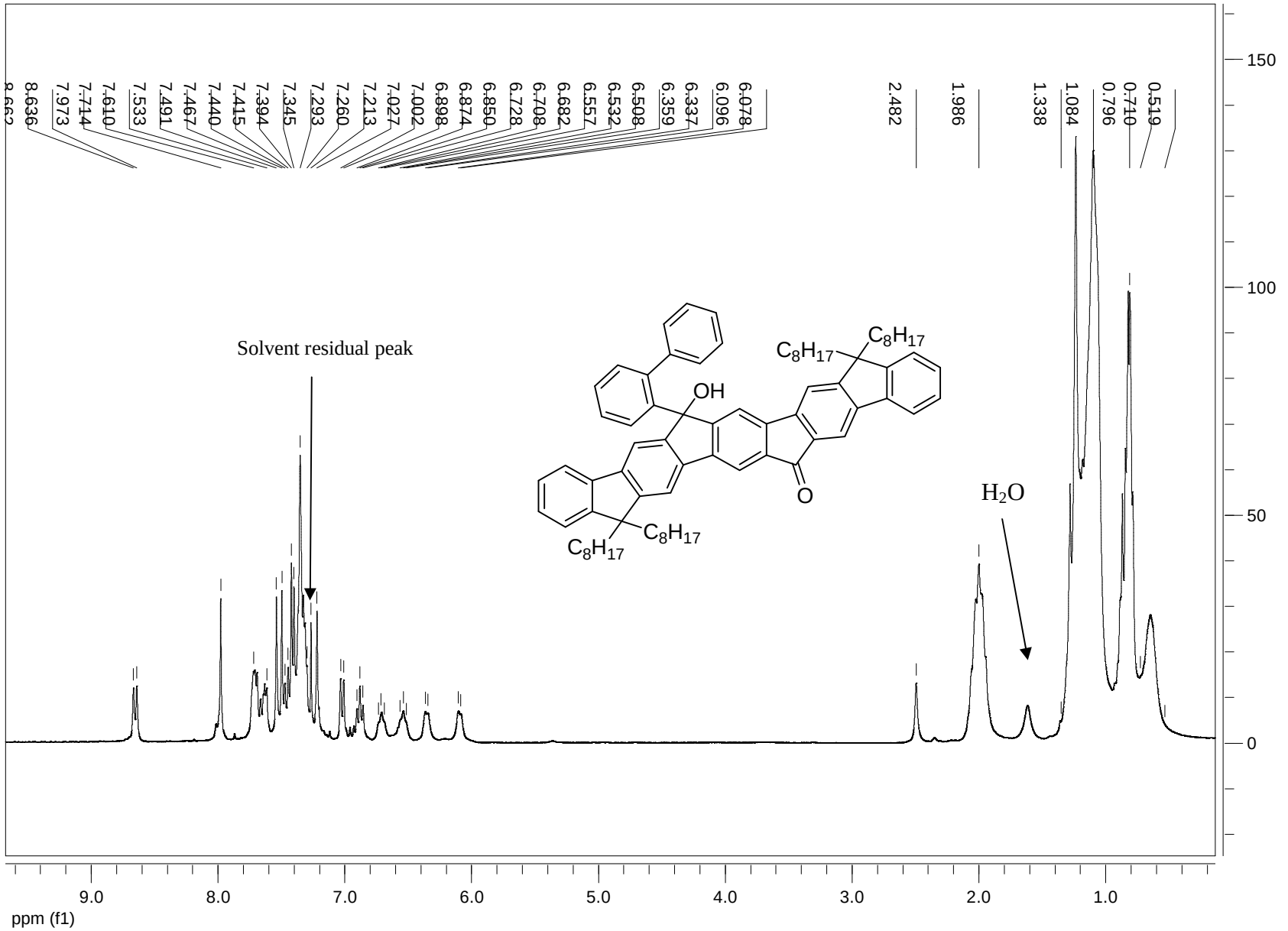
115.896
115.649
115.151
77.000
55.806
40.248
31.730
29.952
29.166
23.821
22.556
14.023
Solvent residual peak
C8H17
C8H17
C8H17
C8H17
O
O
10000
5000
0
200
150
100
50
0
ppm (f1)

15-biphenyl-2-yl-15-hydroxy-9,9,18,18-tetraoctyl-15,18-dihydrobenzo[5,6]-*s*-indaceno[1,2-*b*]indeno[2,1-*h*]fluoren-6(9*H*)-one 12 ($CDCl_3$)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7.260
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7.027
7.002
6.898
6.874
6.850
6.728
6.708
6.682
6.557
6.532
6.508
6.359
6.337
6.096
6.078
2.482
1.986
1.338
1.084
0.796
0.710
0.519
Solvent residual peak
OH
C8H17
C8H17
C8H17
C8H17
O
H2O
150
100
50
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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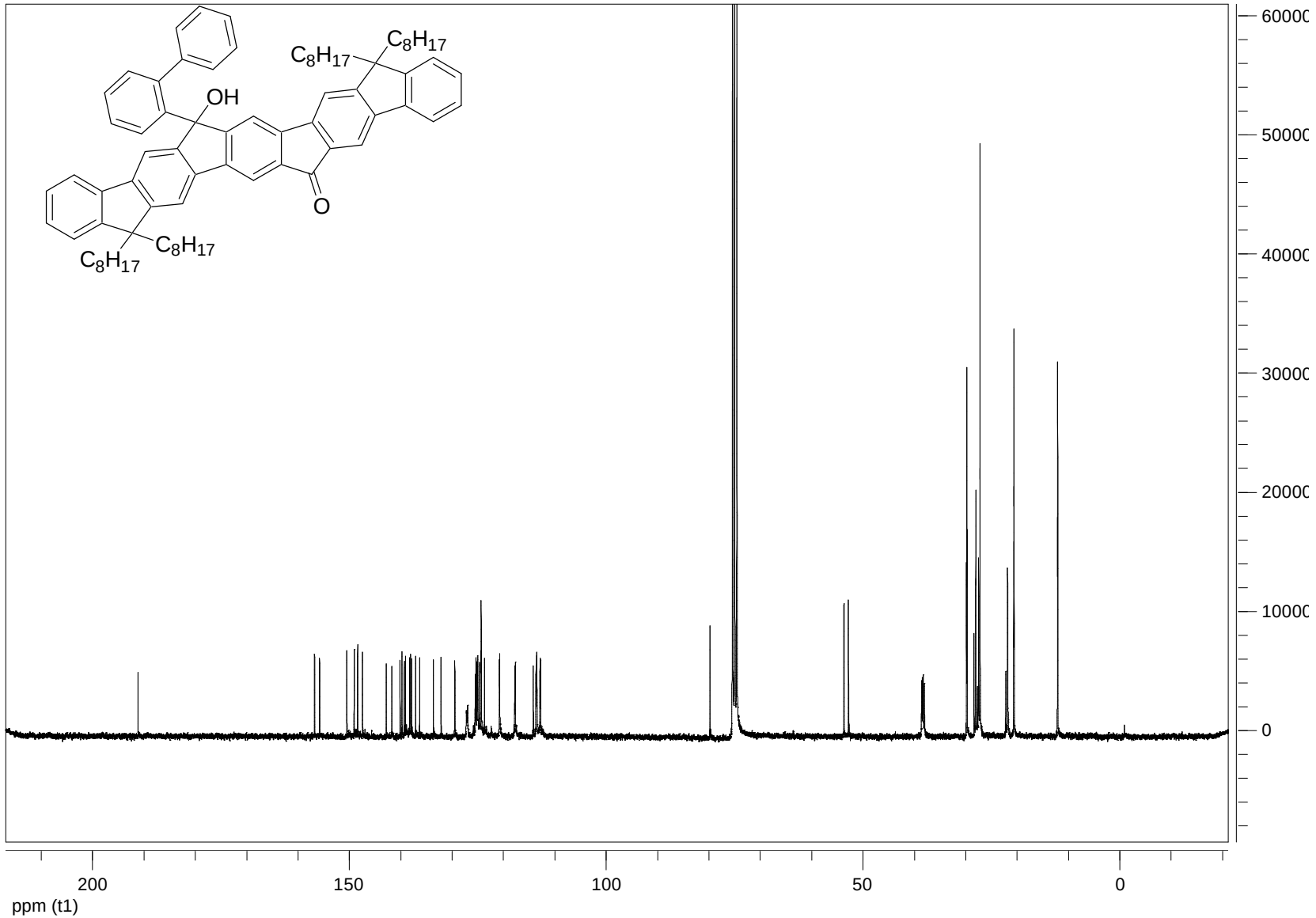
1.0
ppm (f1)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C_8H_{17}
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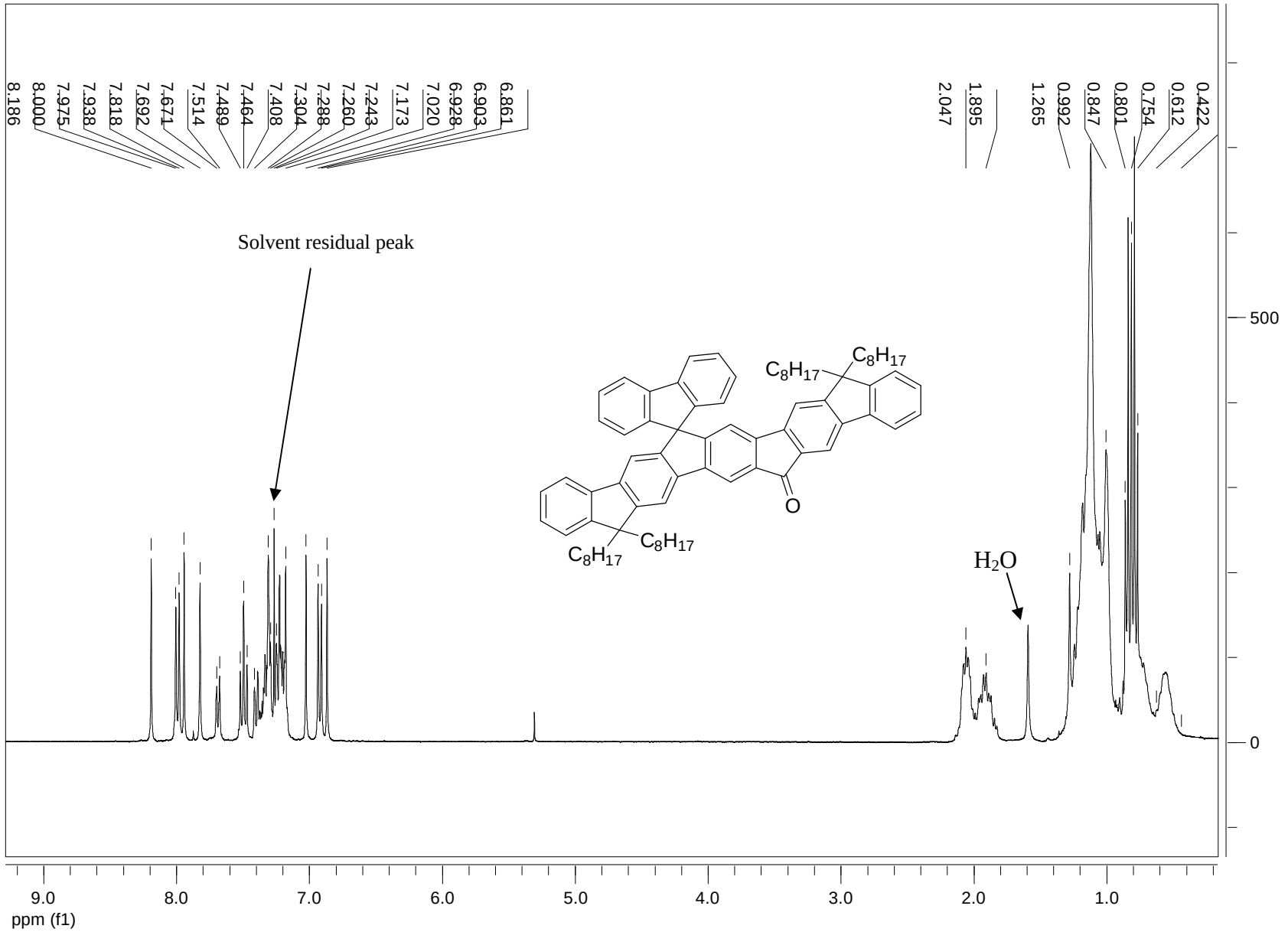
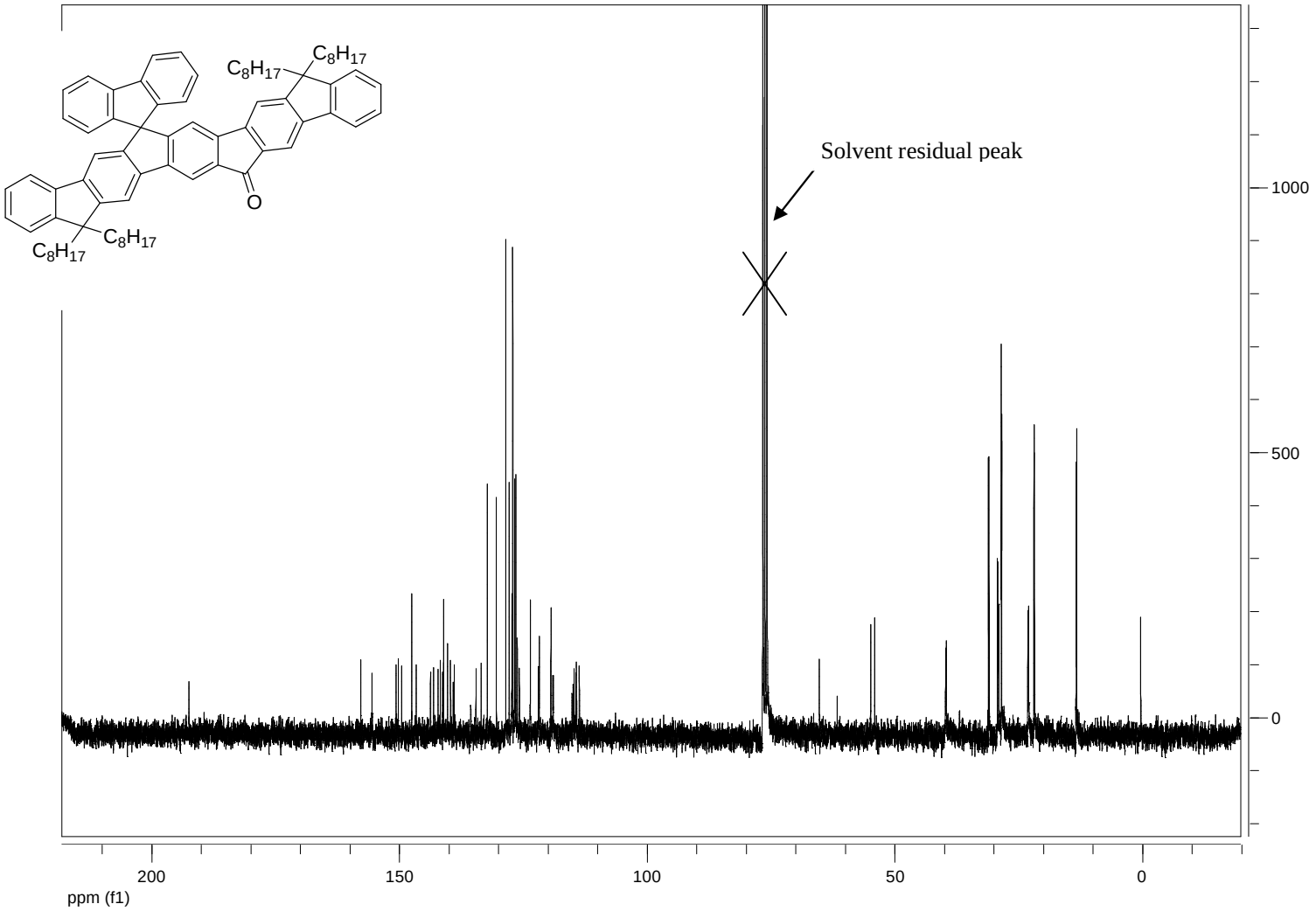
C_8H_{17}
O
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

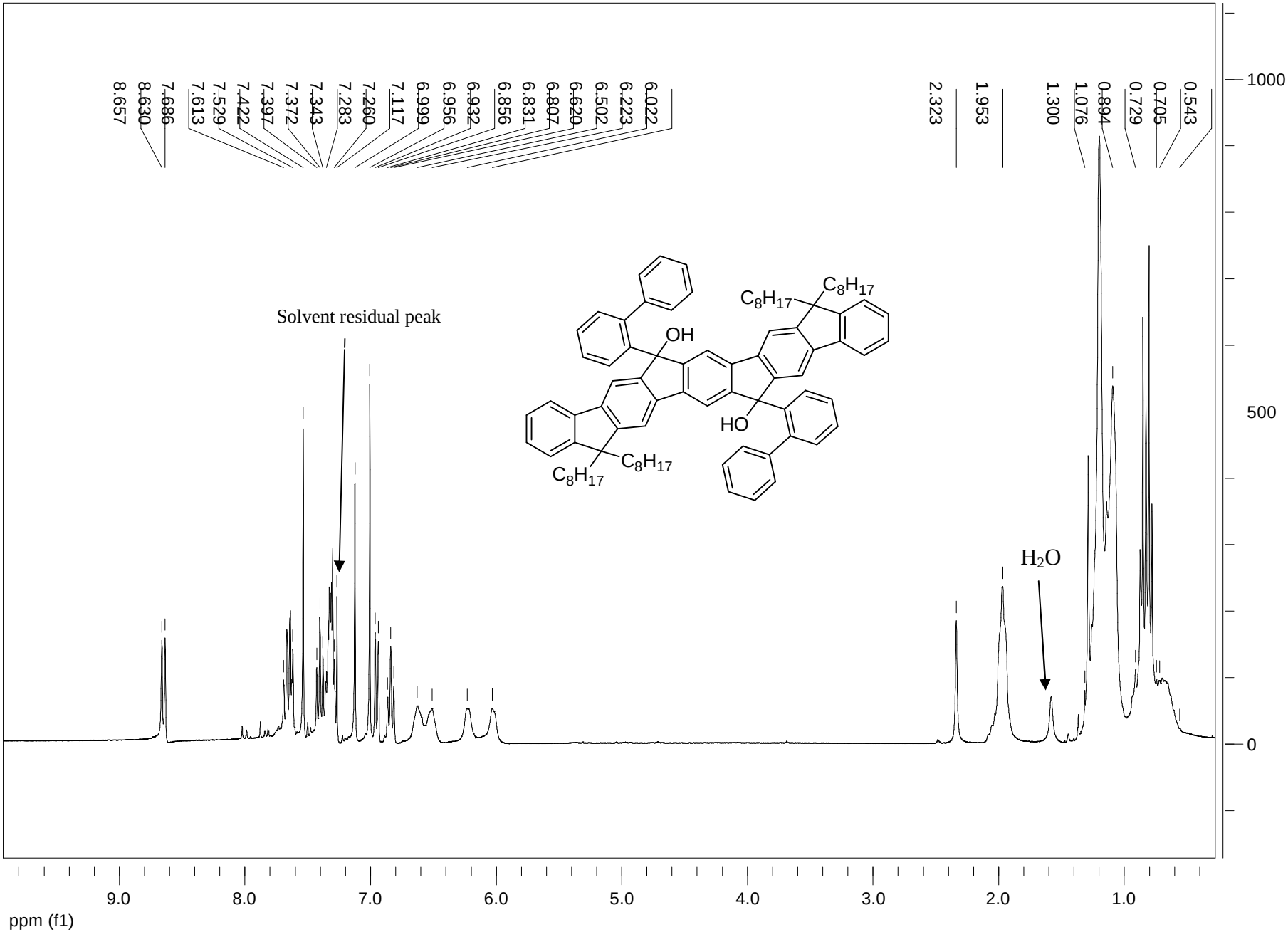
9,9,18,18-tetraoctyl-9,18-dihydro-15*H*-spiro[benzo[5,6]-s-indaceno[1,2-*b*]indeno[2,1-*h*]fluorene-6,9'-fluoren]-15-one 13 ($CDCl_3$)

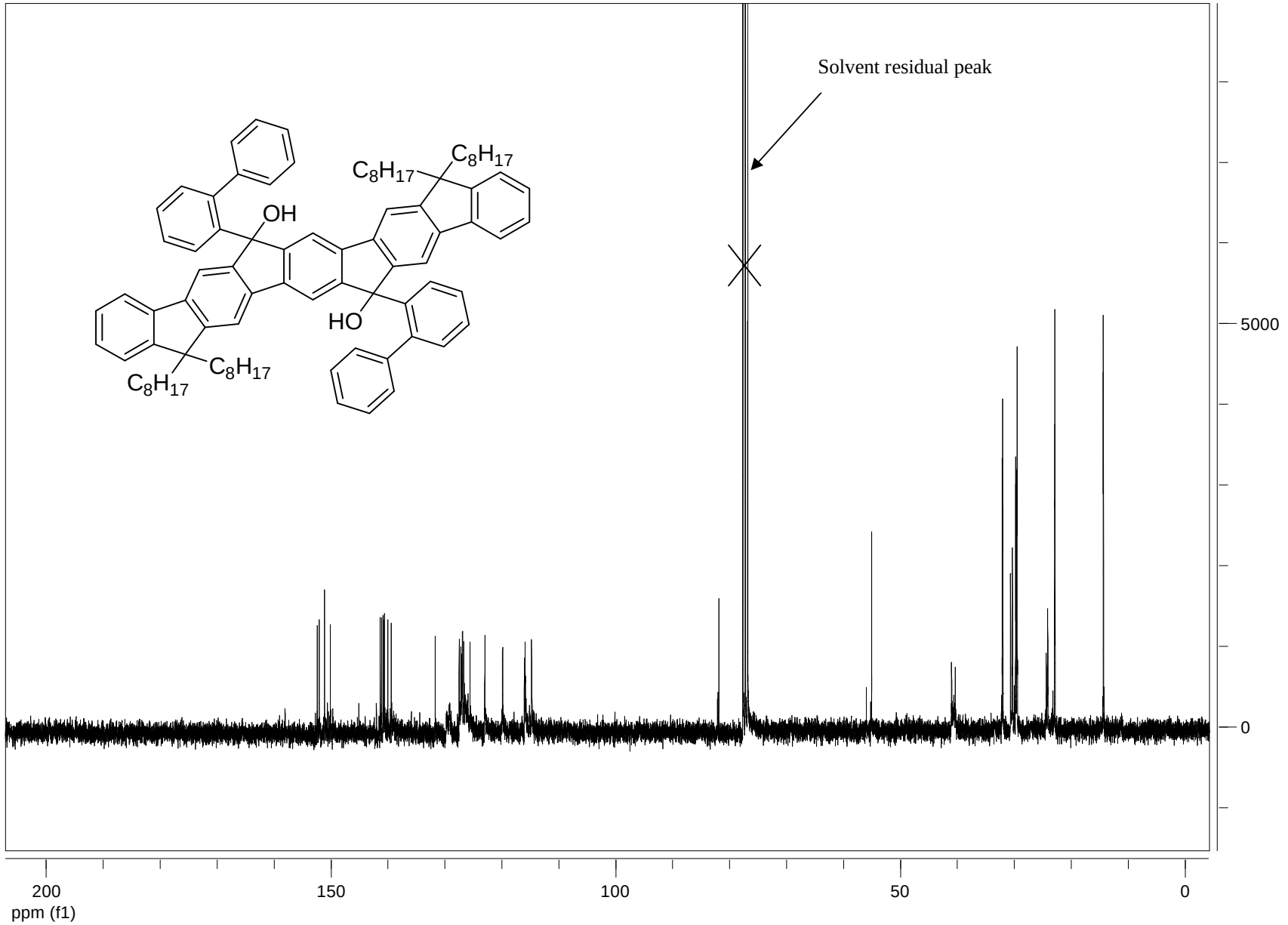

8.186
8.000
7.975
7.938
7.818
7.692
7.671
7.514
7.489
7.464
7.408
7.304
7.288
7.260
7.243
7.173
7.020
6.928
6.903
6.861
2.047
1.895
1.265
0.992
0.847
0.801
0.754
0.612
0.422
Solvent residual peak
H2O
C8H17
C8H17
C8H17
C8H17
O
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


C8H17
C8H17
C8H17
C8H17
O
Solvent residual peak
1000
500
0
200
150
100
50
0
ppm (f1)

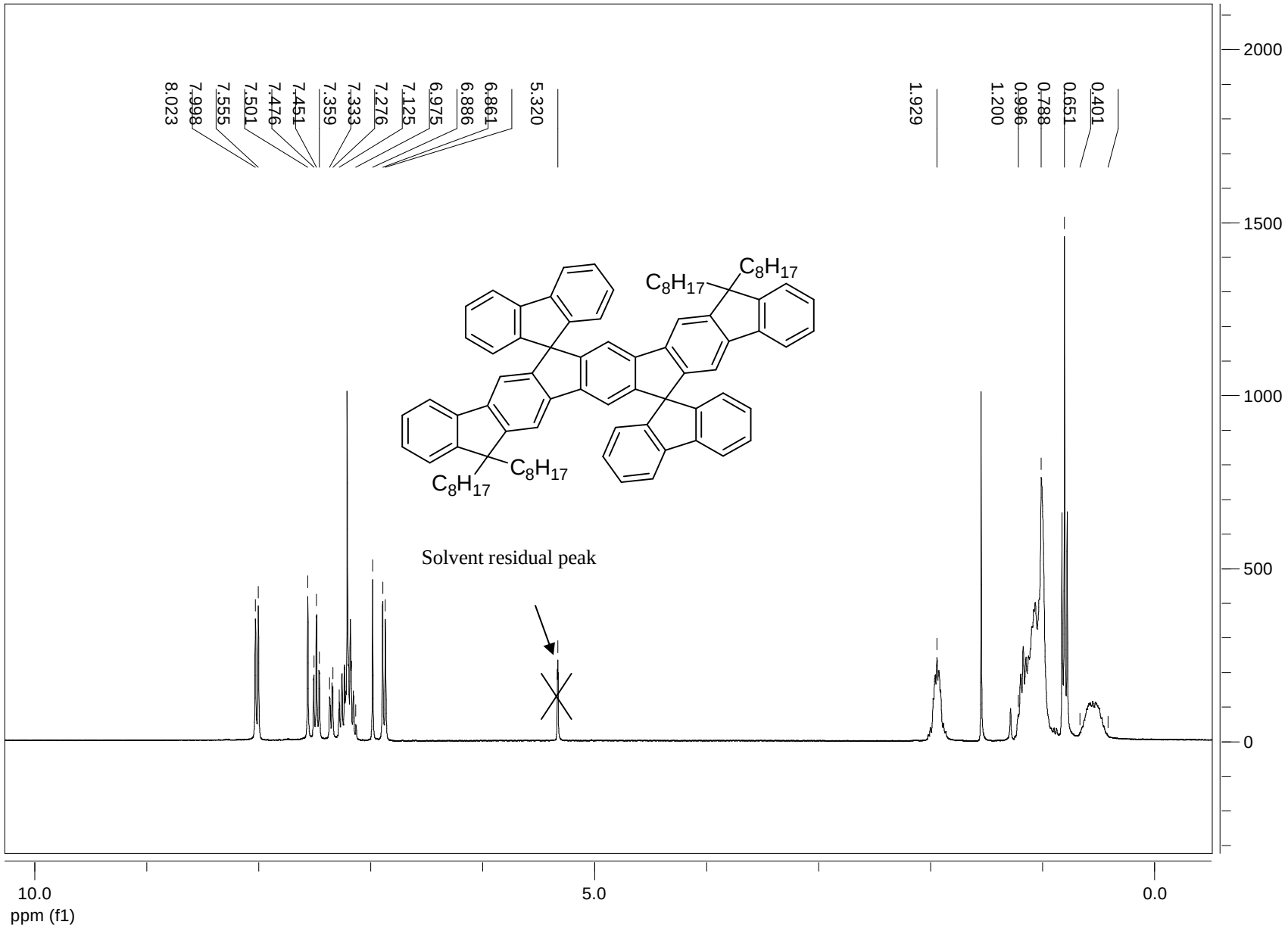
6,15-dibiphenyl-2-yl-9,9,18,18-tetraoctyl-6,9,15,18-tetrahydrobenzo[5,6]-*s*-indaceno[1,2-*b*]indeno[2,1-*h*]fluorene-6,15-diol

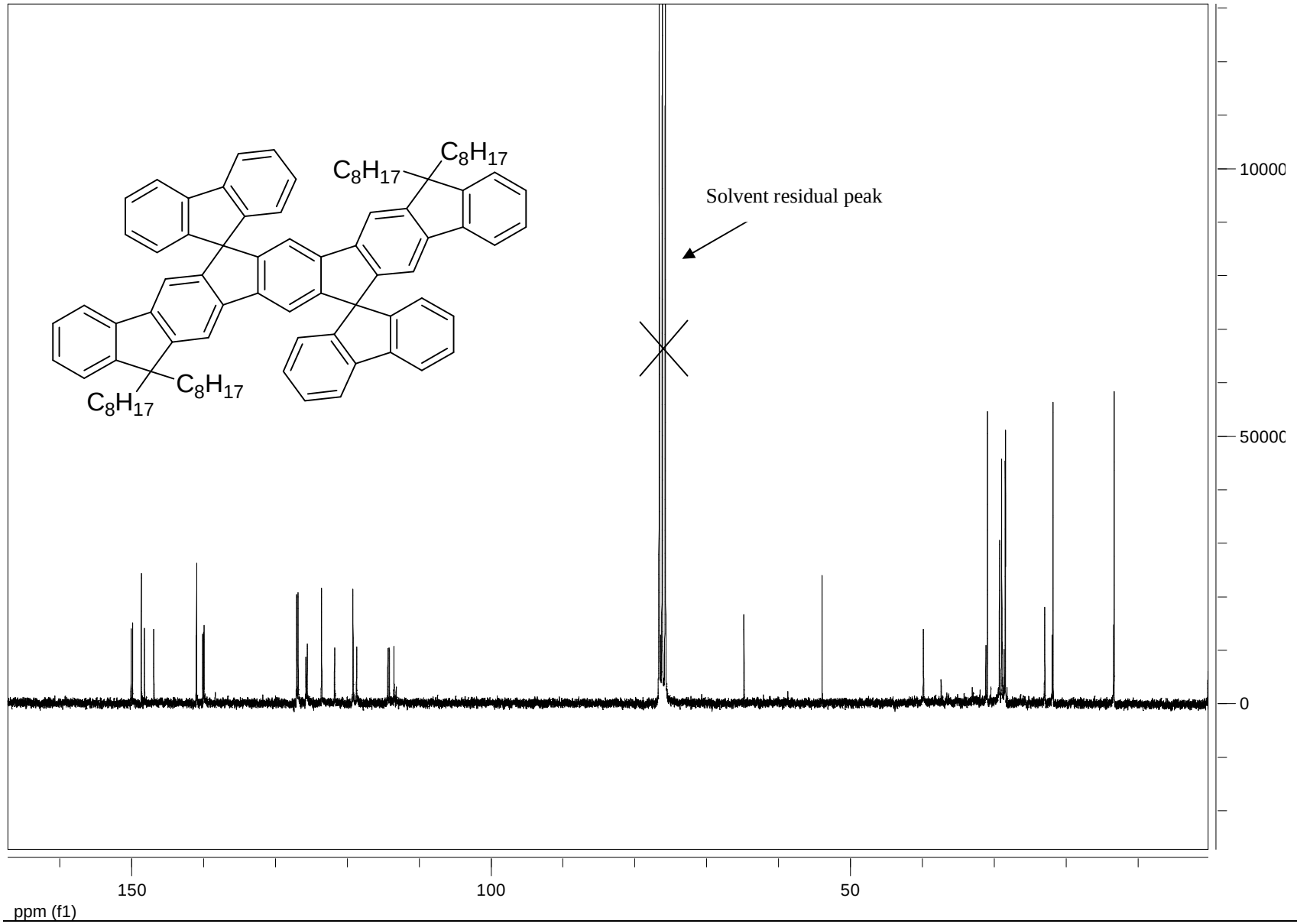
11 ($CDCl_3$)


8.657
8.630
7.686
7.613
7.529
7.422
7.397
7.372
7.343
7.283
7.260
7.117
6.999
6.956
6.932
6.856
6.831
6.807
6.620
6.502
6.223
6.022
2.323
1.953
1.300
1.076
0.894
0.729
0.705
0.543
Solvent residual peak
OH
HO
C8H17
C8H17
C8H17
C8H17
H2O
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


Solvent residual peak
OH
HO
C_8H_{17}
C_8H_{17}
C_8H_{17}
C_8H_{17}
5000
0
200
150
100
50
0
ppm (f1)

9',9',18',18'-tetraoctyl-9',18'-dihydrodispiro[fluorene-9,6'-benzo[5,6]-*s*-indaceno[1,2-*b*]indeno[2,1-*h*]fluorene-15',9''-fluorene] 2 (^{1}H: CD_2Cl_2; ^{13}C: $CDCl_3$)


8.023
7.998
7.555
7.501
7.476
7.451
7.359
7.333
7.276
7.125
6.975
6.886
6.861
5.320
1.929
1.200
0.996
0.788
0.651
0.401
C8H17
C8H17
C8H17
C8H17
Solvent residual peak
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (f1)


C_8H_{17}
C_8H_{17}
C_8H_{17}
C_8H_{17}
Solvent residual peak
10000
50000
0
150
100
50
ppm (f1)