SUPPORTING INFORMATION

Excited-State Dynamics of an Environment-Sensitive Push-Pull Diketopyrrolopyrrole: Major Differences between the Bulk Solution Phase and the Dodecane/Water Interface

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Content

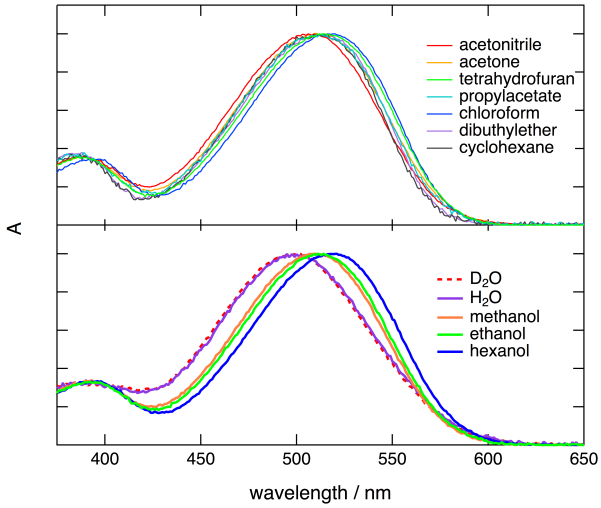


Figure S1: electronic absorption spectrum of **DPP1** in aprotic (top) and protic solvents (bottom).

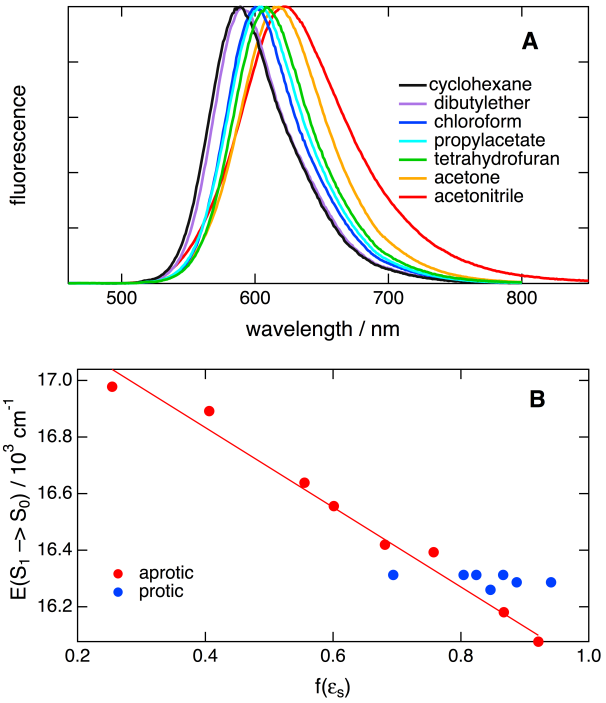


Figure S2: A) fluorescence spectrum of **DPP1** in aprotic solvents; B) solvatochromic plot of the $S_1 \rightarrow S_0$ transition energy of **DPP1** in aprotic and protic solvents and best linear fit of the Onsager equation in aprotic solvents.

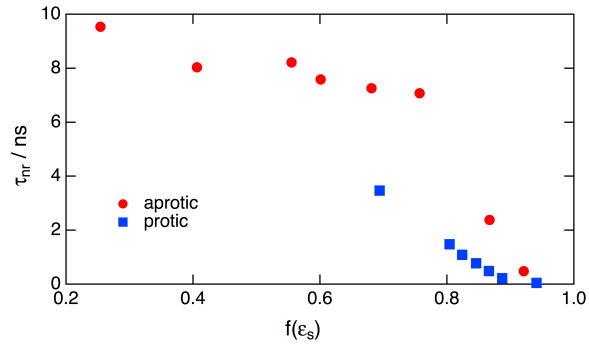


Figure S3: non-radiative time constant of **DPP1** vs. the solvent polarity function.

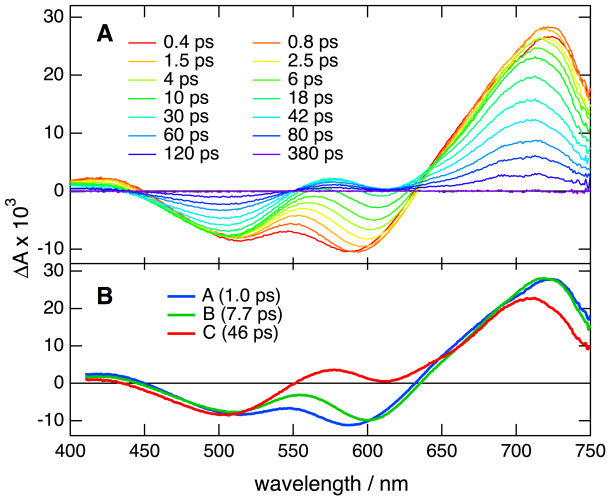


Figure S4: (A) transient absorption spectra recorded at various time delays after 400 nm excitation of **DPP1** in methanol and (B) species-associated difference spectra obtained upon global target analysis assuming a A→B→C→D scheme.

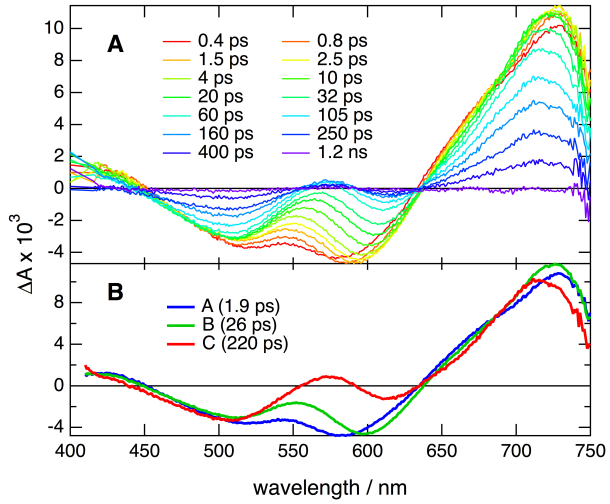


Figure S5: (A) transient absorption spectra recorded at various time delays after 400 nm excitation of **DPP1** in ethanol and (B) species-associated difference spectra obtained upon global target analysis assuming a A→B→C→D scheme.

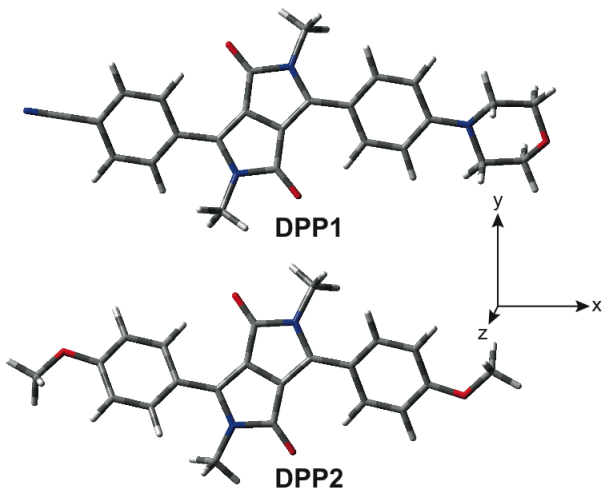


Figure S6: optimized ground-state geometry of **DPP1** and **DPP2** in vacuum computed at the B3LYP/6-31G* level of theory.

Table S1: static hyperpolarizability tensor elements (in atomic units) computed at the B3LYP/6-31G* level of theory (see Figure S6 for the molecular coordinates).

	DPP1	**DPP2**
β_{xxx}	$2.43 \cdot 10^4$	-0.3
β_{xxy}	378	-0.2
β_{xyy}	-530	0.0
β_{yyy}	79	0.1
β_{xxz}	76	400
β_{xyz}	-9.3	136
β_{yyz}	2.3	6.4
β_{xzz}	-178	0.1
β_{yzz}	-4.9	0.1
β_{zzz}	-10	-105

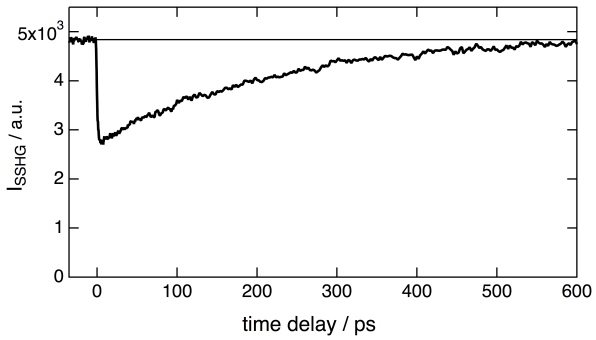


Figure S7: time profile of the unprocessed SSHG intensity at 400 nm at the dodecane/ interfaces after 510 nm excitation of **DPP1**. To obtain the *S* profiles shown in the main text, the square root of the SSHG intensity has first been taken, and the transient change has then been normalized.

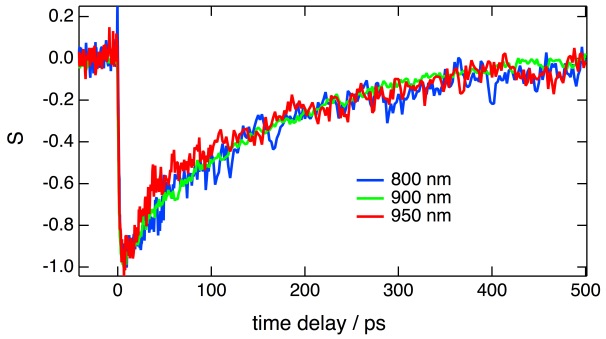


Figure S8: TR-SSHG profiles, *S*(*t*), measured with various probe wavelengths at the dodecane/water upon 510 nm excitation of **DPP1**.

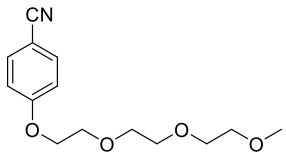
Details on the synthesis

(I) General

All chemicals were used as received unless otherwise noted. All reported ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh). 2-(2-(2-Methoxyethoxy)ethoxy)ethyl *p*-toluenesulfonate,[1] 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane,[2] and 3,6-bis(4-bromophenyl)- 2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**4**)[3] were prepared according to the literature procedures.

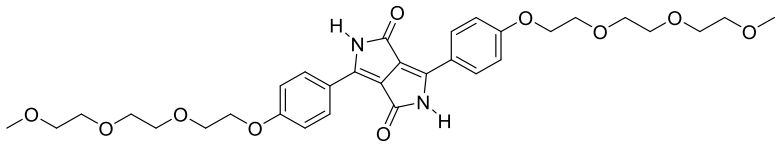
(II) Synthesis

4-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)benzonitrile (1).



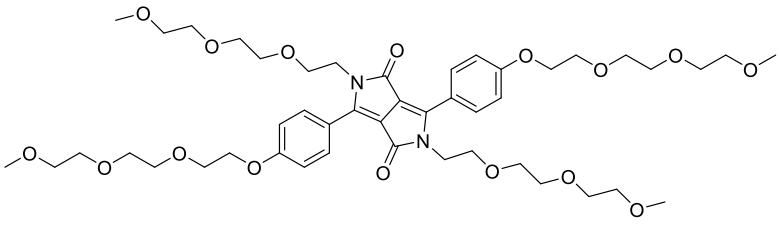
A mixture consisting of *p*-hydroxybenzonitrile (20.7 mmol, 2.47 g), 2-(2-(2-methoxyethoxy)ethoxy)ethyl *p*-toluenesulfonate (18.8 mmol, 6.00 g), powdered potassium carbonate (56.4 mmol, 7.79 g) and 100 ml of DMF was stirred overnight at 90 °C. Then 300 ml of water was added and obtained solution was extracted 5 times with ethyl acetate. Combined organic layers were washed with brine and dried over $MgSO_4$. Solvents were evaporated and the product was purified using column chromatography (silica, hexanes : ethyl acetate 7 : 3 → 3 : 2). 4.72 g (95%) of compound **1** was obtained as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.02 – 6.93 (m, 2H), 4.19 – 4.16 (m, 2H), 3.89 – 3.86 (m, 2H), 3.75 – 3.72 (m, 2H), 3.70 – 3.63 (m, 4H), 3.56 – 3.53 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 134.0, 119.2, 115.3, 104.1, 71.9, 70.9, 70.7, 70.6, 69.4, 67.8, 59.1. HRMS (ESI) calcd for $C_{14}H_{19}NO_4Na$ ($M+Na^+$): 288.1206, found: 288.1216. Elemental analysis calcd (%) for $C_{14}H_{19}NO_4$: C 63.38, H 7.22, N 5.28; found: C 63.36, H 7.07, N 5.35.

3,6-Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (2)



Under an argon atmosphere, in a three-necked flask equipped with a reflux condenser and magnetic stirrer were placed 20 ml of *tert*-amyl alcohol, catalytic amount of iron(III) chloride and sodium (33 mmol, 0.759 g). The mixture was heated under reflux until sodium was completely reacted (about 1 h). The reaction mixture was cooled to 90 °C and nitrile **1** (15.1 mmol, 4.01 g) was added. Then a solution of diisopropyl succinate (6.6 mmol, 1.35 ml) in 5 ml of *tert*-amyl alcohol was added dropwise (30 min). After 16 h of reaction at 90 °C, the mixture was cooled and 50 ml of water and 20 ml of acetic acid were added. Resulting mixture was refluxed for a few minutes and cooled. Solvents were evaporated and the residue was dissolved in hot DMF, then excess of hot water was added and the mixture was cooled down in the refrigerator. Obtained precipitate was filtered off and dried under vacuum. 0.772 g (19%) of product **2** was obtained as dark brown-violet solid. Mp >400 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.13 (br s, 2H), 8.51 – 8.39 (m, 4H), 7.19 – 7.05 (m, 4H), 4.24 – 4.18 (m, 4H), 3.81 – 3.74 (m, 4H), 3.63 – 3.56 (m, 4H), 3.56 – 3.49 (m, 8H), 3.46 – 3.40 (m, 4H), 3.23 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 161.1, 142.9, 129.7, 120.7, 115.0, 109.0, 71.3, 69.9, 69.8, 69.6, 68.8, 67.5, 58.0. HRMS (FD) calcd for $C_{32}H_{40}N_2O_{10}$ (M^+): 612.2683, found: 612.2698. Elemental analysis calcd (%) for $C_{32}H_{40}N_2O_{10}$: C 62.73, H 6.58, N 4.57; found: C 63.01, H 6.45, N 4.73.

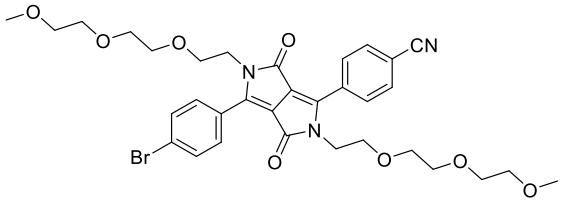
3,6-Bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (3)



A mixture of diketopyrrolopyrrole **2** (0.51 mmol, 312 mg), tetrabutylammonium bisulfate (TBAHS, 0.025 mmol, 8.5 mg), powdered potassium carbonate (5.6 mmol, 774 mg) and 10 ml of DMF was heated to 120 °C under an argon atmosphere. Then a solution of 1-chloro-2-(2-(2-methoxyethoxy)ethoxy)ethane (5.1 mmol, 932 mg) in 3

ml of DMF was added dropwise by a syringe (30 min). The reaction mixture was stirred for 20 h at 120 °C, cooled and diluted with 50 ml of water. Resulting mixture was extracted 5 times with chloroform, organic layers were combined, washed with water and dried over $MgSO_4$. Solvents were evaporated and the product was purified using column chromatography (silica, dichloromethane : acetone 2 : 1 → 1 : 1). 241 mg (52%) of the dye **3** was obtained as orange fluorescent amorphous solid. Mp >400 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 4H), 7.06 – 7.01 (m, 4H), 4.22 – 4.18 (m, 4H), 3.95 (t, J = 5.7 Hz, 4H), 3.91 – 3.88 (m, 4H), 3.79 – 3.74 (m, 8H), 3.72 – 3.69 (m, 4H), 3.69 – 3.65 (m, 4H), 3.60 – 3.55 (m, 16H), 3.51 – 3.48 (m, 4H), 3.39 (s, 6H), 3.34 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 161.1, 148.2, 131.3, 120.7, 114.8, 108.7, 72.0, 71.9, 70.9, 70.7, 70.6 (3 signals), 70.5, 69.6, 68.9, 67.6, 59.1, 59.0, 42.2. HRMS (ESI) calcd for $C_{46}H_{68}N_2O_{16}Na$ ($M+Na^+$): 927.4461, found: 927.4490.

3-(4-Bromophenyl)-6-(4-cyanophenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (5)

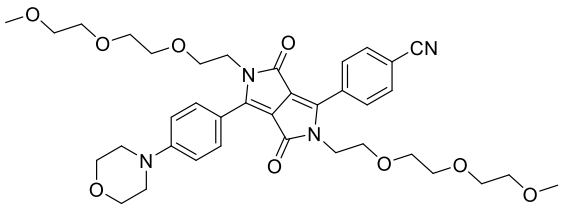


3,6-Bis(4-bromophenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (**4**, 1.40 mmol, 1.03 g), copper(I) cyanide (1.51 mmol, 135 mg) and 10 ml of DMF were stirred under argon at 160 °C in a tightly closed Schlenck vessel. After 16 h the reaction mixture was cooled down and a solution of 1.68 g of $FeCl_3 \cdot 6H_2O$ in 2.8 ml of concentrated hydrochloric acid and 0.7 ml of water was added. Resulting mixture was stirred for 20 min at 90 °C, cooled down, diluted with water and extracted with 5 portions of dichloromethane. Organic layers were combined, washed twice with water and dried over Na_2SO_4. Solvents were removed under reduced pressure and the product was purified by silica-gel chromatography (silica, dichloromethane : acetone 9 : 1 → 3 : 1) and recrystallized from ethanol. Product **5** (381 mg, 40%) was obtained as red fibrous crystals. Mp >400 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.97 – 7.94 (m, 2H), 7.84 – 7.80 (m, 2H), 7.70 – 7.66 (m, 2H), 3.93 – 3.87 (m, 4H), 3.80 – 3.74 (m, 4H), 3.60 –

3.54 (m, 12H), 3.53 – 3.49 (m, 4H), 3.37 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 162.6, 149.7, 146.6, 132.5, 132.2, 132.1, 131.1, 130.1, 126.5, 126.3, 118.3, 114.1, 110.9, 109.7, 71.9 (2 signals), 70.6 (4 signals), 70.5 (2 signals), 68.9, 68.8, 59.1, 42.8, 42.5. HRMS (ESI) calcd for $C_{33}H_{38}N_3O_8Na$ ($M+Na^+$): 706.1733, found: 706.1740. Elemental analysis calcd (%) for $C_{33}H_{38}N_3O_8$: C 57.90, H 5.60, N 6.14; found: C 58.20, H 5.64, N 6.25.

Besides the desired product **5**, starting material **4** (236 mg, 23%) and dicyanated dye (226 mg, 26%) were also separated by column chromatography.

3-(4-Cyanophenyl)-2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-6-(4-(morpholin-4-yl)phenyl)-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (6)

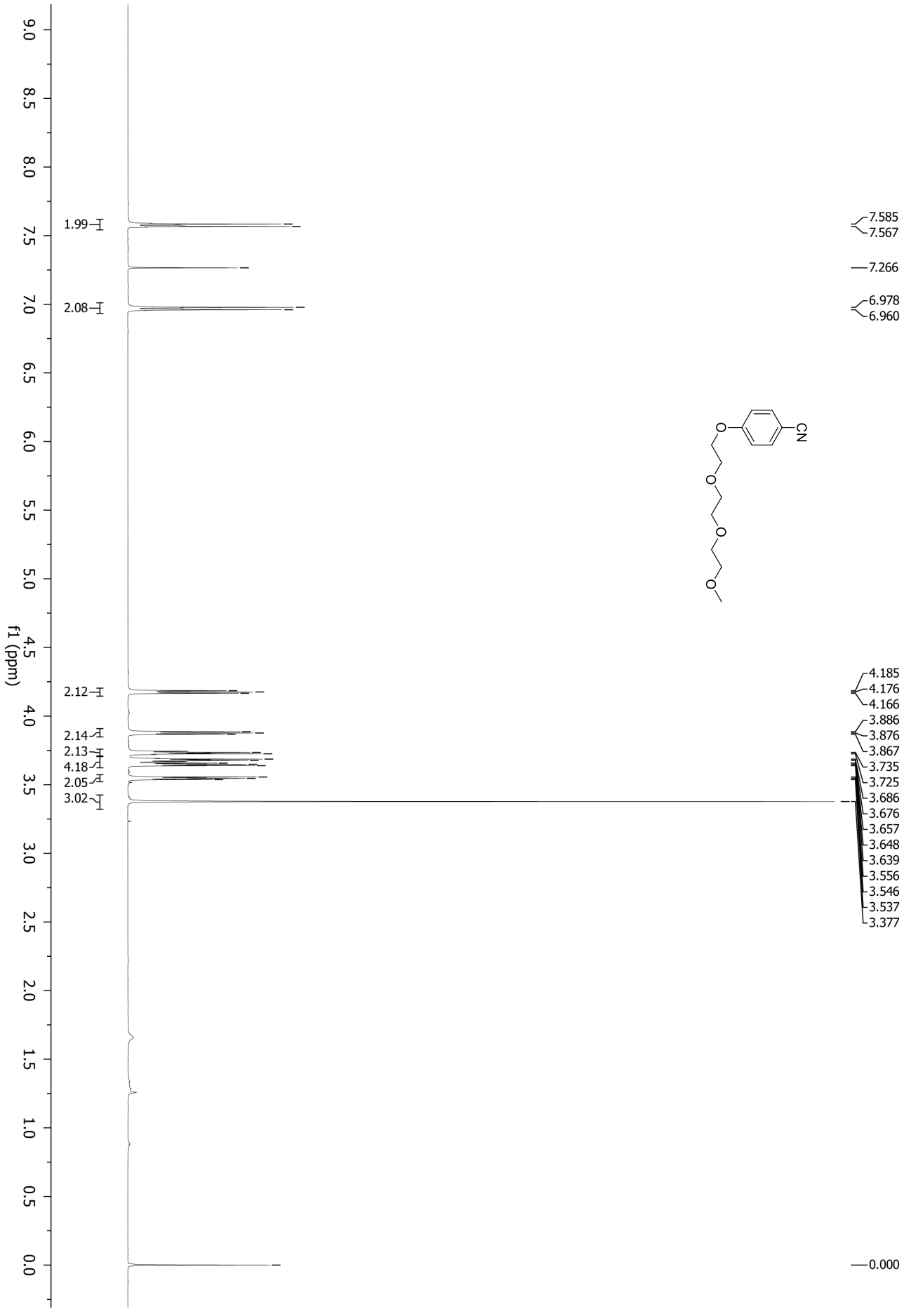


In a 20 ml Schlenck flask containing a magnetic stirring bar were placed: dye **5** (0.15 mmol, 103 mg), palladium(II) acetate (0.005 mmol, 1.1 mg), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 0.015 mmol, 6.2 mg) and caesium carbonate (0.45 mmol, 147 mg). The vessel was evacuated and backfilled with argon (3 times). Under a positive pressure of argon 4 ml of anhydrous toluene and morpholine (0.23 mmol, 20 μl) were added. The flask was again carefully evacuated and backfilled with argon three-times, the vessel was tightly closed and the reaction mixture was stirred for 16 h at 120 °C (above the boiling point). After the mixture was cooled, water and dichloromethane were added, layers were separated. The aqueous layer was extracted with dichloromethane 5 times. Combined organic layers were washed twice with water and dried over Na_2SO_4. Solvents were evaporated and the product was purified by the column chromatography (silica, dichloromethane : acetone 6 : 1) and recrystallized from acetone. Dye **6** (72 mg, 69%) was obtained as a dark red powder. Mp >400 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 8.11 – 8.06 (m, 2H), 7.82 – 7.77 (m, 2H), 7.01 – 6.95 (m, 2H), 3.99 (t, J = 5.7 Hz, 2H), 3.91 (t, J = 5.2 Hz, 2H), 3.89 – 3.85 (m, 4H), 3.82 – 3.76 (m, 4H), 3.63 – 3.54 (m, 12H), 3.53 – 3.47 (m, 4H), 3.37 (s, 3H), 3.36 – 3.33 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 162.5, 153.2, 151.6, 143.8, 132.5, 132.4, 131.4,

130.0, 118.5, 117.6, 113.9, 113.5, 111.2, 108.0, 71.9, 70.6 (3 signals), 70.5, 69.0, 68.9, 66.9, 59.1, 59.0, 47.5, 42.7, 42.5. HRMS (ESI) calcd for $C_{37}H_{46}N_4O_9Na$ ($M+Na^+$): 713.3162, found: 713.3157. Elemental analysis calcd (%) for $C_{37}H_{46}N_4O_9$: C 64.33, H 6.71, N 8.11; found: C 64.11, H 6.72, N 7.93.

(III) Literature

1. Ouchi, M.; Inoue, Y.; Liu, Y.; Nagamune, S.; Nakamura, S.; Wada, K.; Hakushi, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1260–1262.
2. Gudipati, V.; Curran, D. P.; Wilcox, C. S. *J. Org. Chem.* **2006**, *71*, 3599-3607.
3. Nowak-Król, A.; Grzybowski, M.; Romiszewski, J.; Drobizhev, M.; Wicks, G.; Chotkowski, M.; Rebane, A.; Górecka, E.; Gryko, D. T. *Chem. Commun.* **2013**, *49*, 8368–8370.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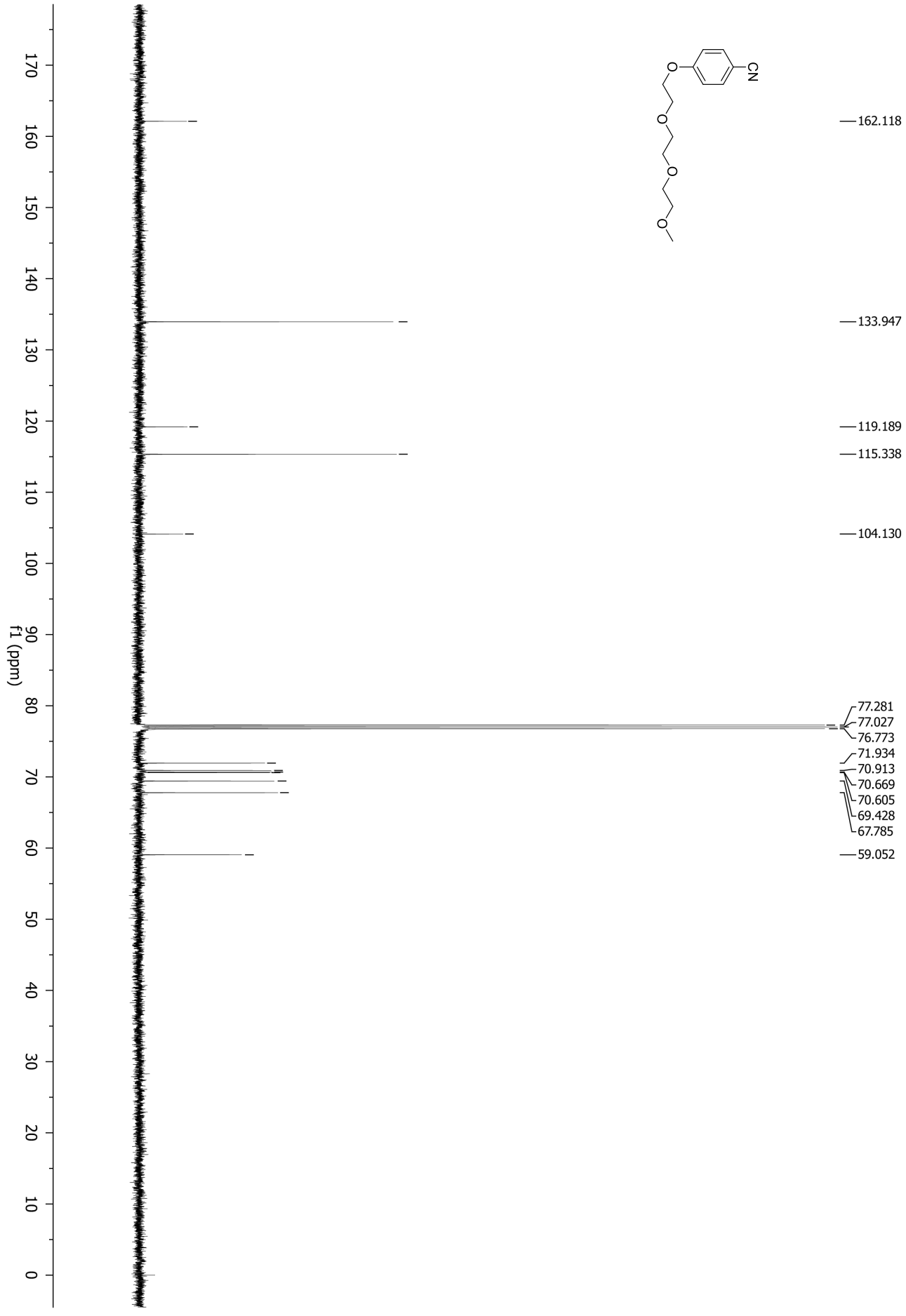
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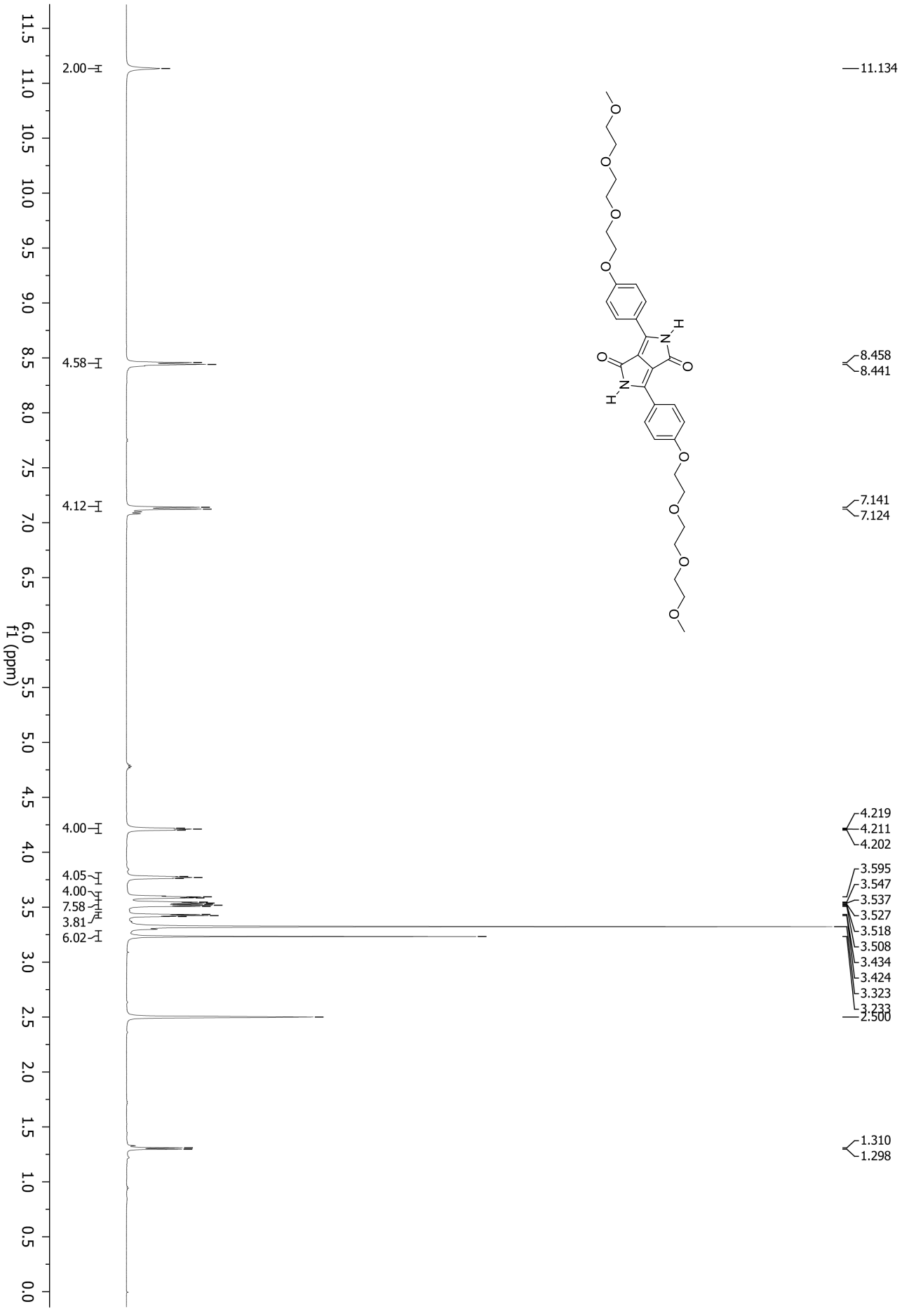
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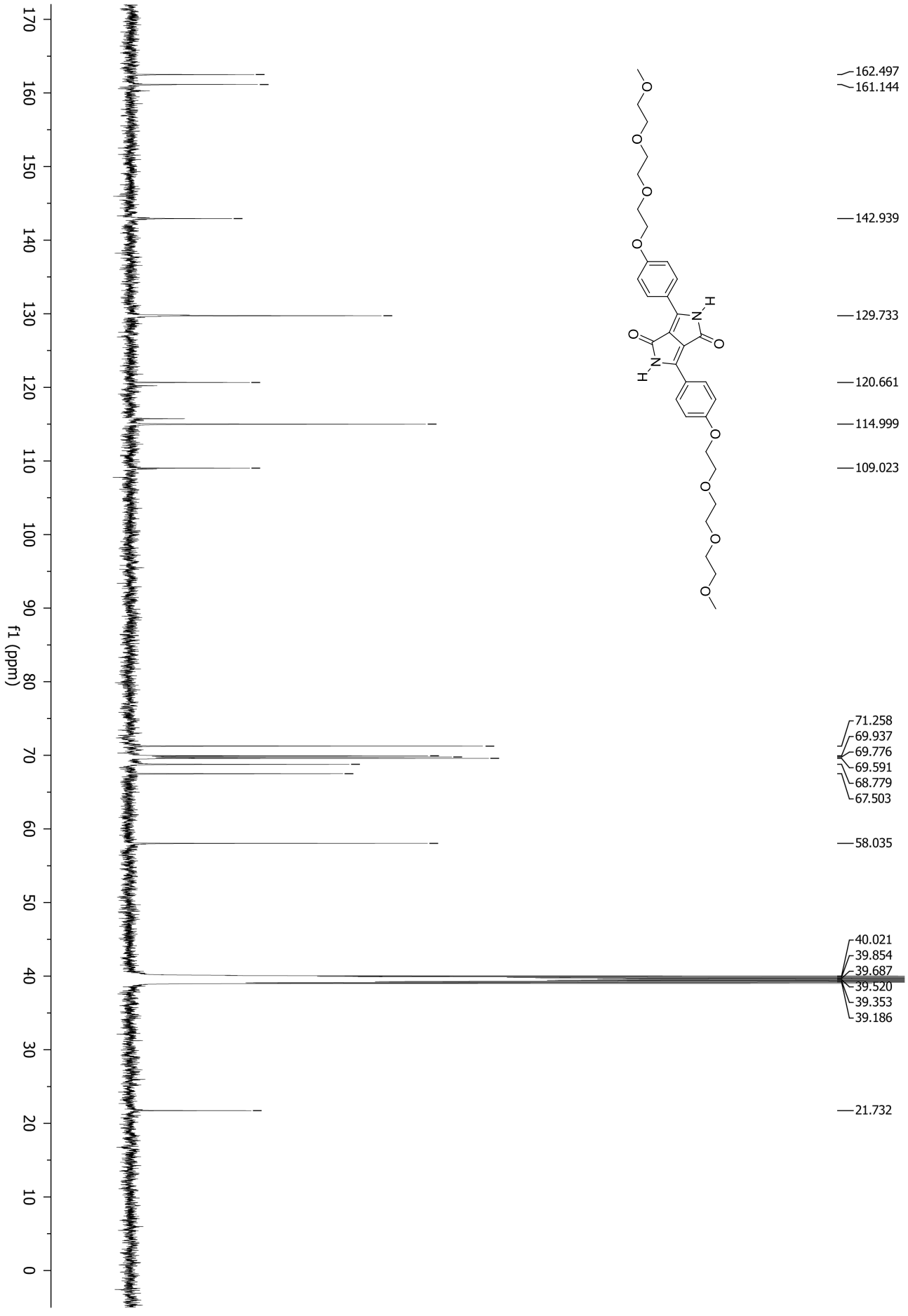
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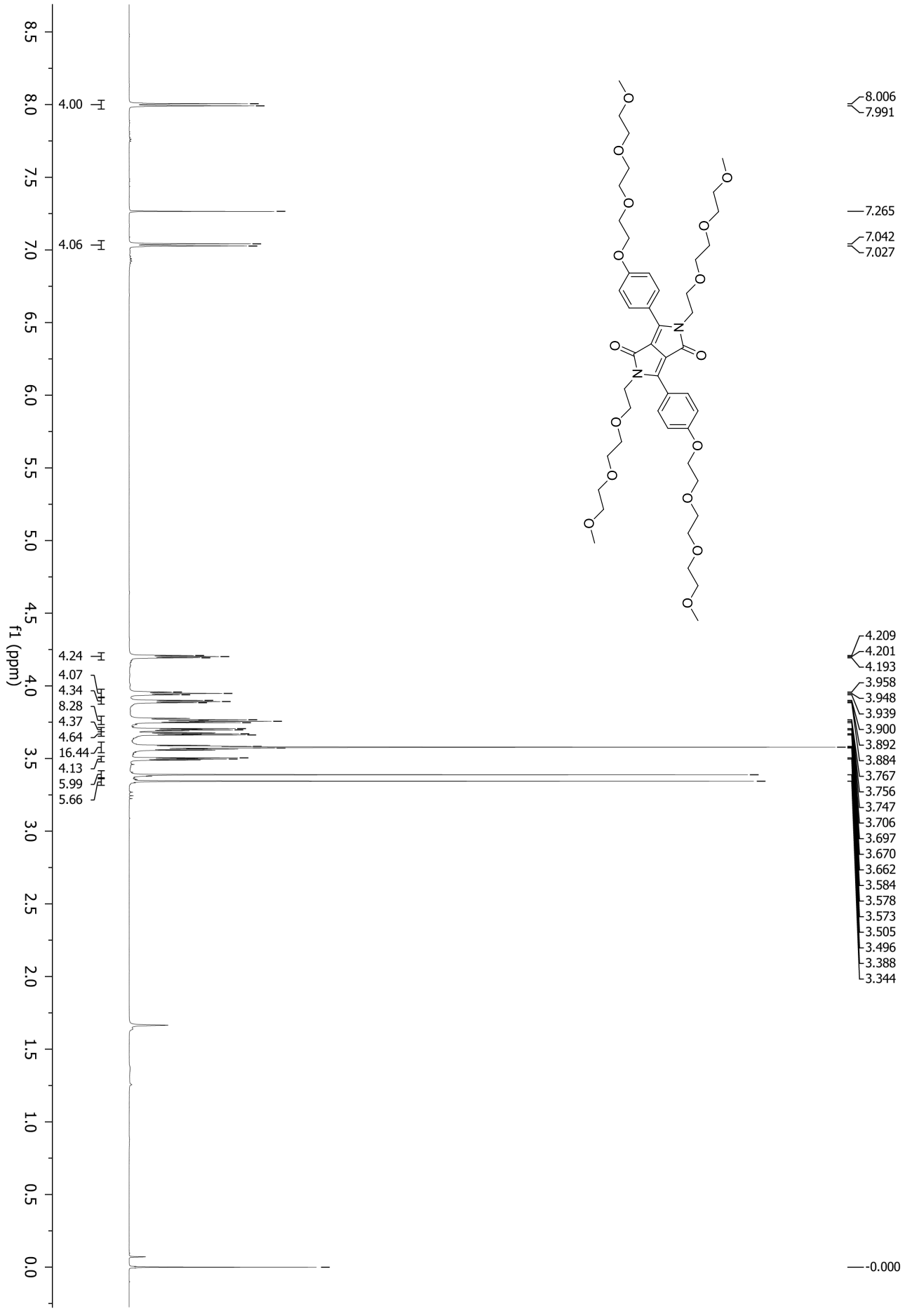
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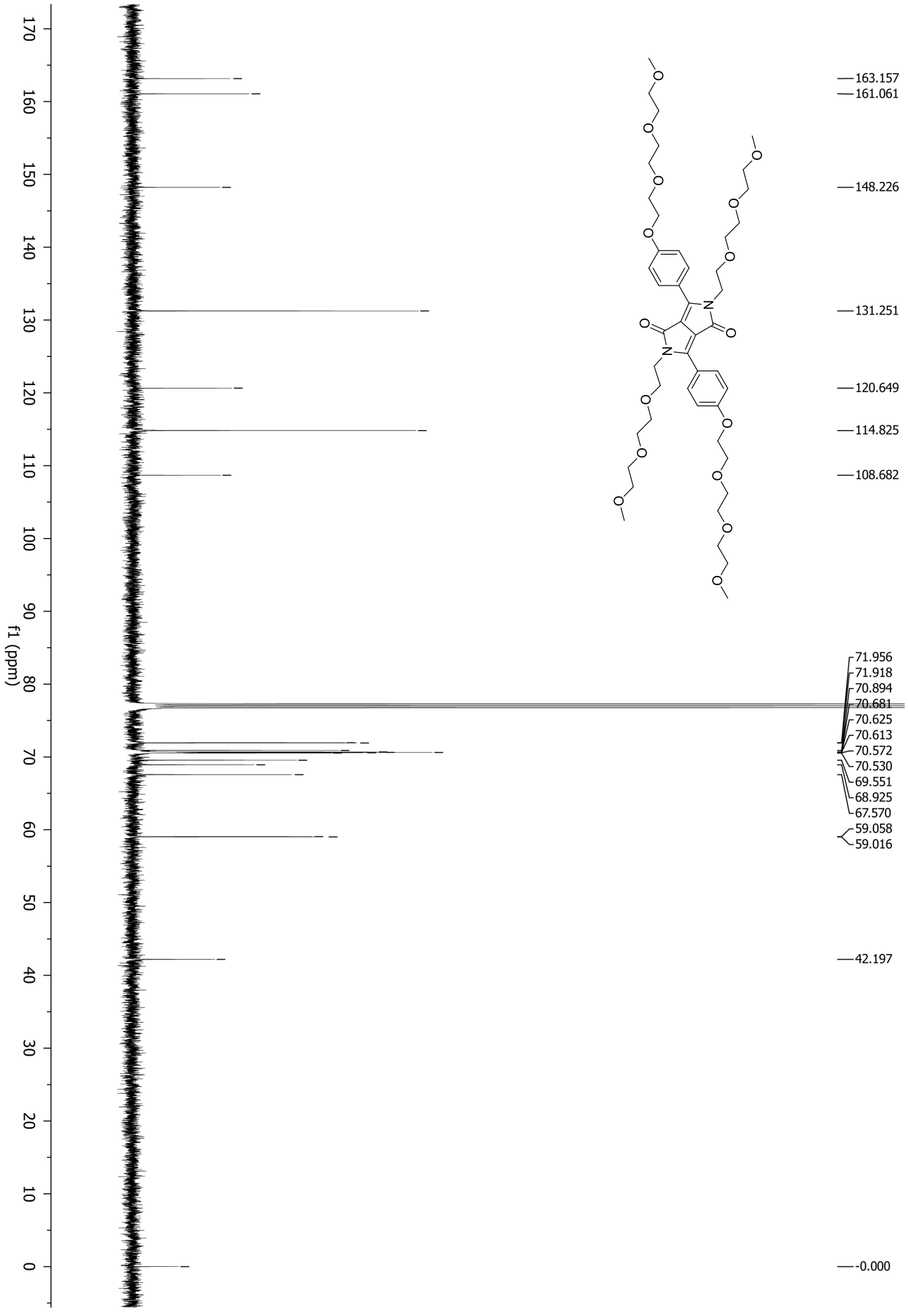
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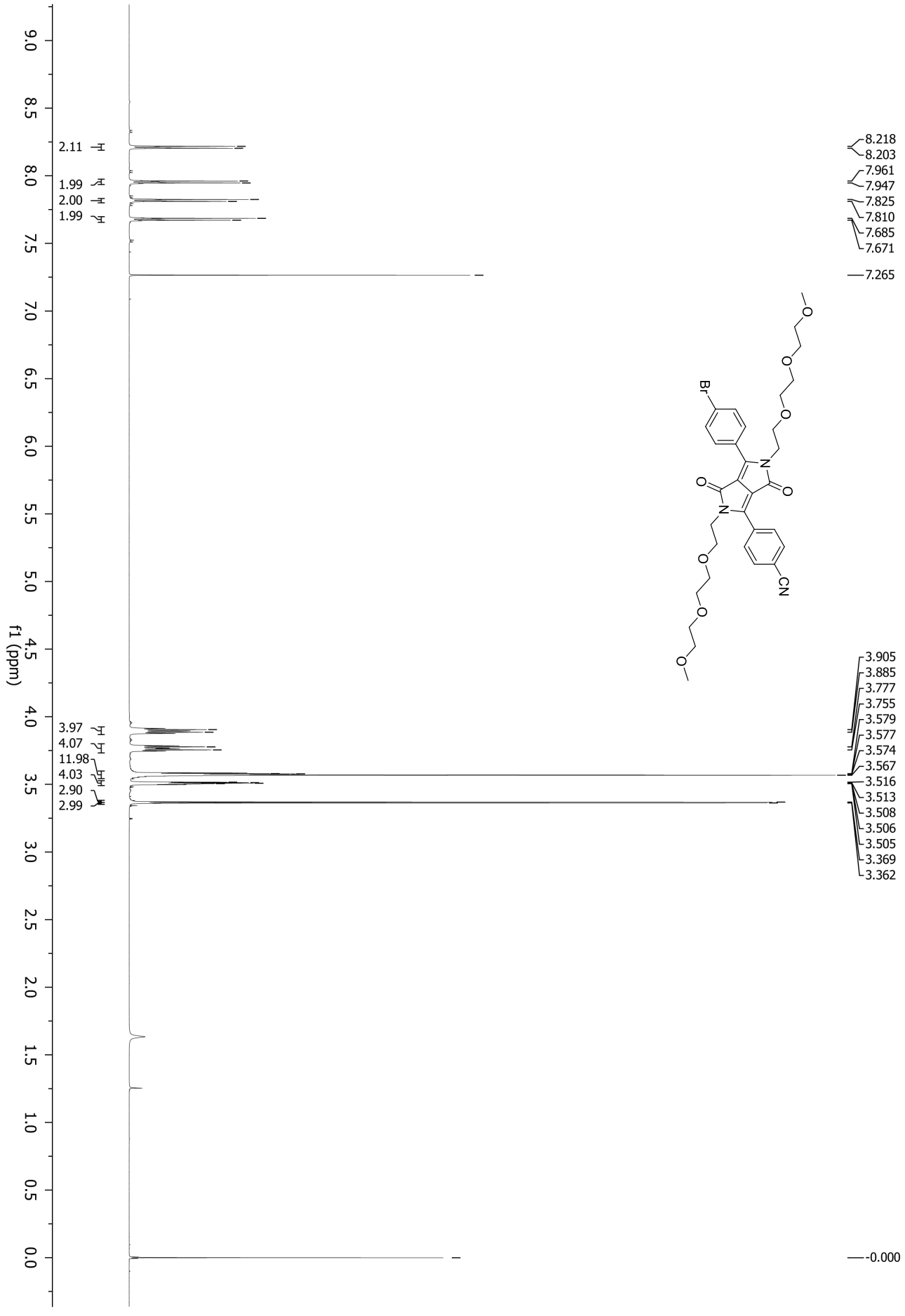
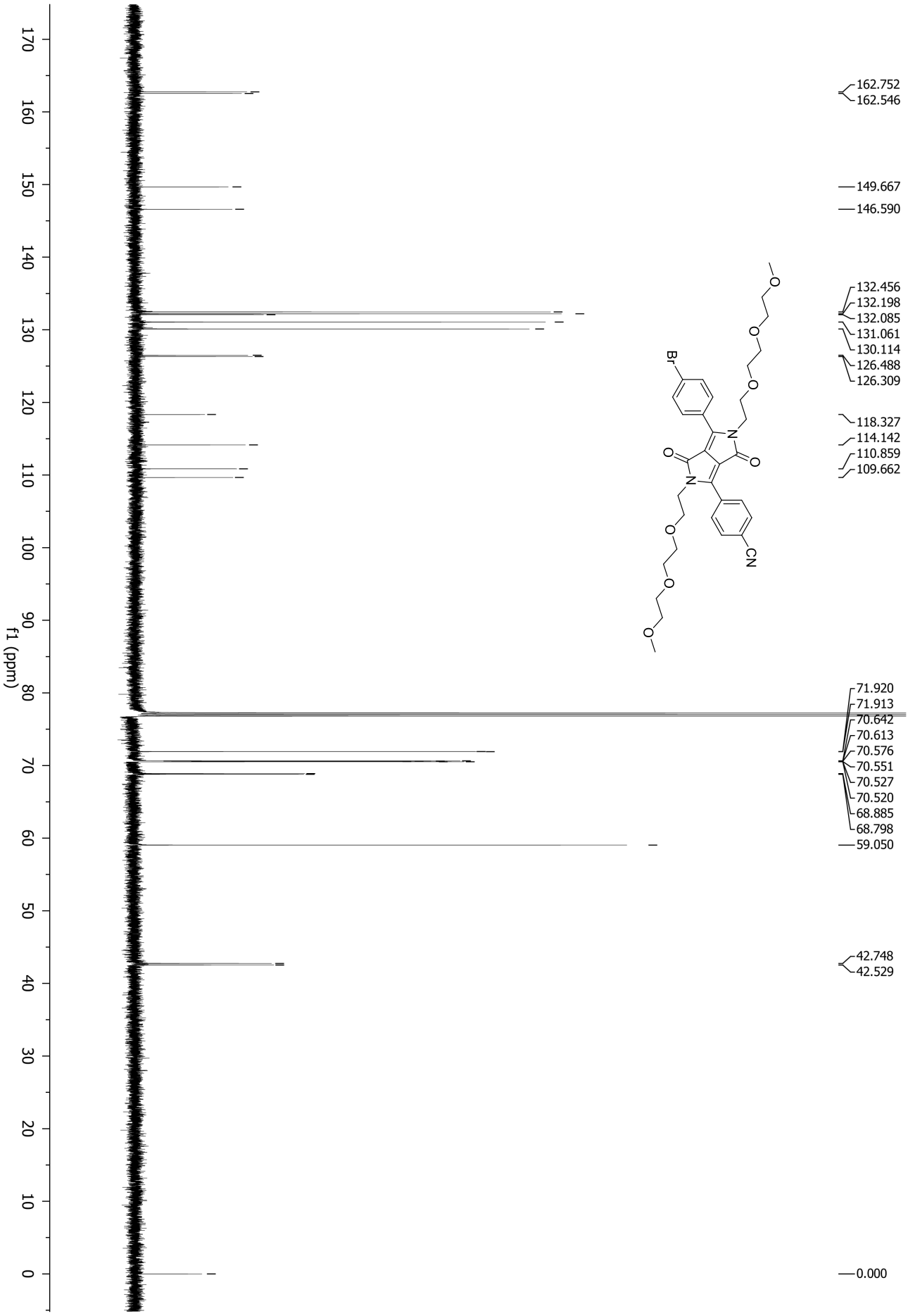
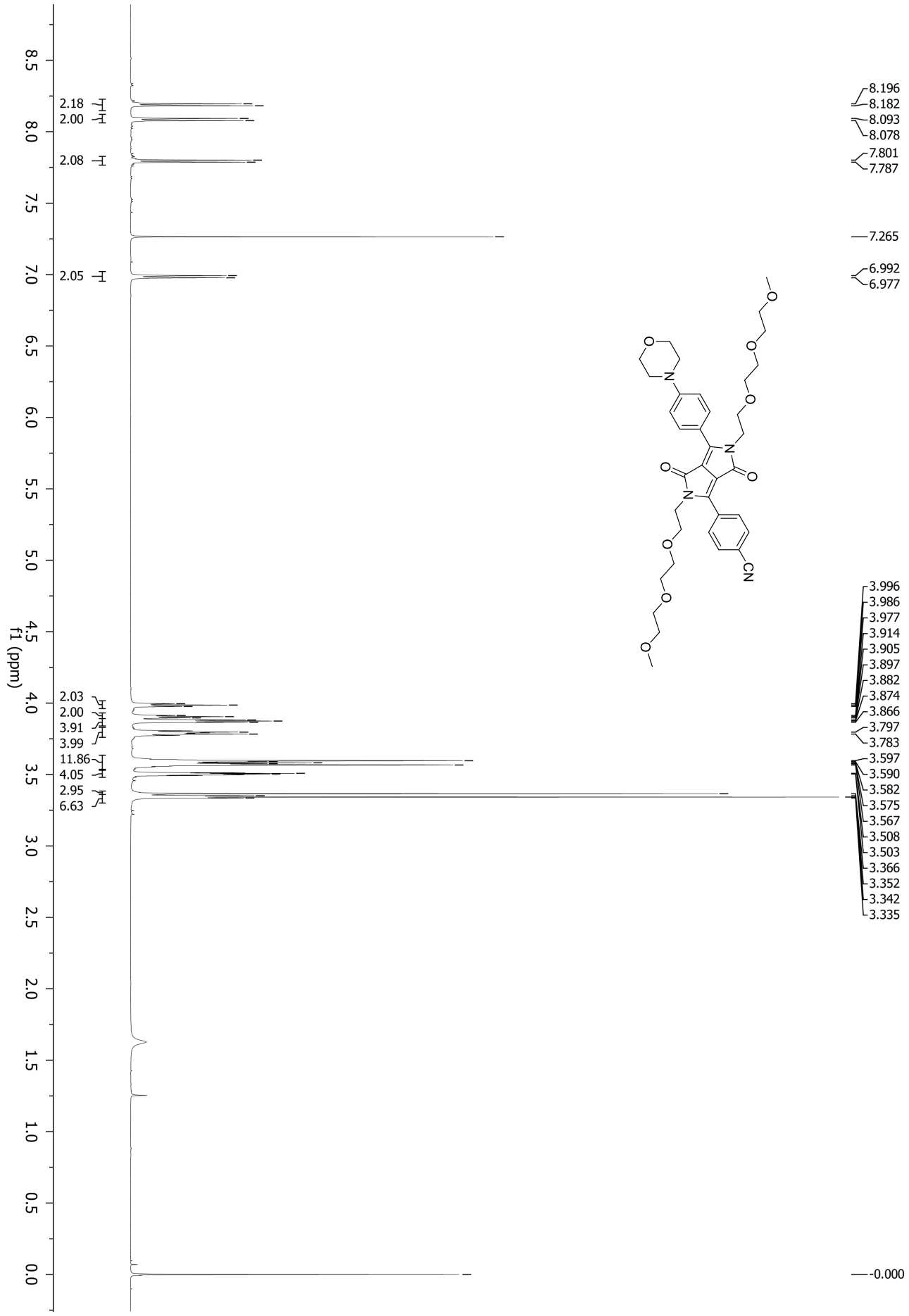
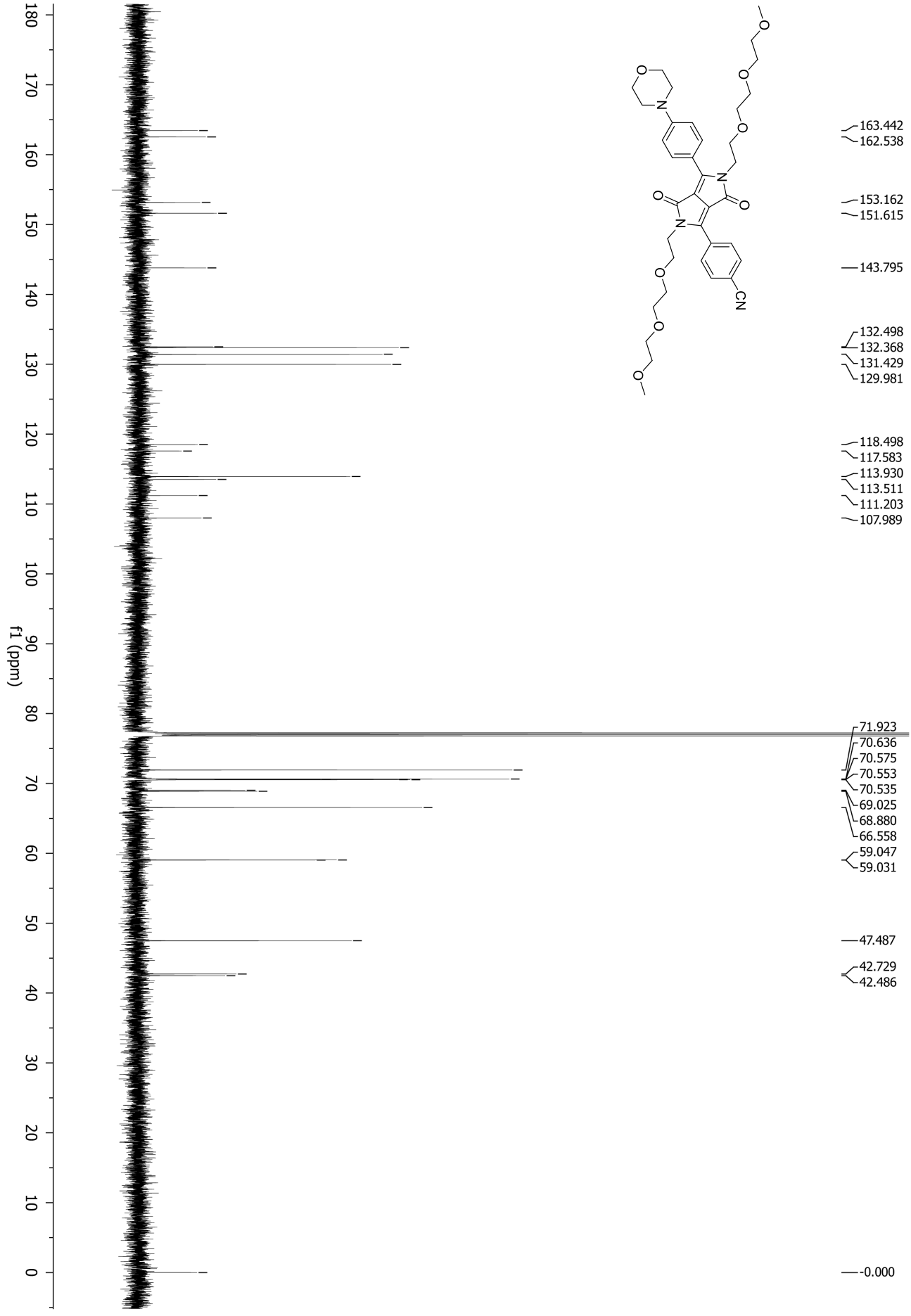
114.825
108.682
71.956
71.918
70.894
70.681
70.625
70.613
70.572
70.530
69.551
68.925
67.570
59.058
59.016
42.197
-0.000


f1 (ppm)
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
2.11
1.99
2.00
1.99
3.97
4.07
11.98
4.03
2.90
2.99
8.218
8.203
7.961
7.947
7.825
7.810
7.685
7.671
7.265
3.905
3.885
3.777
3.755
3.579
3.577
3.574
3.567
3.516
3.513
3.508
3.506
3.505
3.369
3.362
-0.000
Br
CN
O
N


f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
162.752
162.546
149.667
146.590
132.456
132.198
132.085
131.061
130.114
126.488
126.309
118.327
114.142
110.859
109.662
71.920
71.913
70.642
70.613
70.576
70.551
70.527
70.520
68.885
68.798
59.050
42.748
42.529
0.000
Br
CN


f1 (ppm)
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
2.18
2.00
2.08
2.05
2.03
2.00
3.91
3.99
11.86
4.05
2.95
6.63
8.196
8.182
8.093
8.078
7.801
7.787
7.265
6.992
6.977
3.996
3.986
3.977
3.914
3.905
3.897
3.882
3.874
3.866
3.797
3.783
3.597
3.590
3.582
3.575
3.567
3.508
3.503
3.366
3.352
3.342
3.335
-0.000
O
N
O
O
N
O
O
O
O
O
O
O
N
CN


f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
163.442
162.538
153.162
151.615
143.795
132.498
132.368
131.429
129.981
118.498
117.583
113.930
113.511
111.203
107.989
71.923
70.636
70.575
70.553
70.535
69.025
68.880
66.558
59.047
59.031
47.487
42.729
42.486
-0.000