Supplementary Information

The photocatalytic synthesis and closed-loop recycling of poly(semi-aromatic 1,2-ethanediol)s

Yi-Ming Chen[a], Yu Liu[a], Yong-Ze Chen[a] and Yan-Biao Kang[*a].

[a]Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China.

E-mail: ybkang@ustc.edu.cn

Content

1. General information

All reactions were carried out under atmospheric pressure. Solvents were pre-dried over activated 4 Å molecular sieves and heated to reflux over calcium hydride or Na turnings and iodine crystals (CH_3CN, DCM, NEt_3, THF, DMF, DMSO, MeOH) under nitrogen atmosphere and collected by distillation. Dialdehydes **1a**, **1c**, **1h** and other chemicals without notes in experimental section were purchased from commercial sources. All reactions were performed with SemiLEDs lamps (C35L-U-60), the glass reaction tube was placed 2 cm away from LEDs. Chemical yields refer to pure isolated substances. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Figure S1. General setup for the reaction. 18 W (3 W × 6) blue LED lamps were used as the light source.

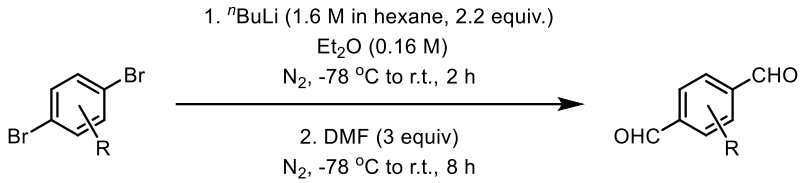
^1H, ^{19}F decoupled, ^{13}C NMR spectra were recorded on a Bruker 400/500 spectrometer; Chemical shifts are reported in δ units relative to $CDCl_3$ [^1H δ = 7.26, ^{13}C δ = 77.16] and d^6-DMSO [^1H δ = 2.50, ^{13}C δ = 39.52]. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). The size exclusion chromatography (SEC) was conducted in DMF at 40 ℃ and a flow rate of 1.0 mL min^{-1} using a Waters 1515 isocratic HPLC pump and Waters 2414 refractive index (RI) detector. The polystyrene standard curve ranging from 2200 to 650000 was used for calibration to achieve the molecular weight (M_n and M_w) and polydispersity index ($Đ$) of the polymers. Thermogravimetric analysis (TGA) parameters were measured by a TA Instruments Q5000IR Thermogravimeter on samples. The obtained polymers were heated from 27 ºC to 800 ℃ at a rate of 10 ℃/min. Differential scanning calorimetry (DSC) parameters were measured by a

TA Instruments Q2000 differential scanning calorimeter (DSC) under a nitrogen atmosphere. The obtained polymers were heated from -50 ºC, 20 ℃ or 25 ºC to 200 ℃ at a rate of 10 ℃/min, staying at 200 ℃ for 5 min to erase thermal history. Then the sample was cooled to the start temperature at a rate of 10 ℃/min, keeping for 5 minutes. Finally, the sample was heated to 200 ℃ at a rate of 10 ℃/min. Uv-Visible spectra were recorded on an UV-3600 spectrometer. (Model: UV-3600; Manufacturer: Shimadzu, Japan). Fluorescence spectra were recorded on a High-Technologies Corporation spectrometer (Model: F-4600; Manufacturer: Hitachi, Japan)

2. General procedures to prepare dialdehydes

General procedure A

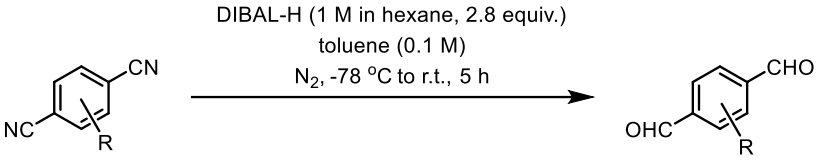
Scheme S1. General procedure A for the preparation of dialdehydes



To a well-stirred suspension of substituted dibromoaromatics (5 mmol) in 30 mL of dry ether under a nitrogen atmosphere at -78 ℃ was added 7 mL (11 mmol) of 1.6 M solution of *n*-butyl lithium in hexane. The resulting suspension was allowed to warm to room temperature and was stirred for 2 h. Then it was added 1.2 mL (15 mmol) of N,N-dimethyl-formamide under a nitrogen atmosphere at -78 ℃. The mixture was allowed to gradually warm to room temperature for 8 h. After addition of 1 M aqueous hydrochloric acid solution, the reaction was extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was crystallized from ethyl acetate or purified by column chromatography to give the appropriate dialdehyde.[1]

General procedure B

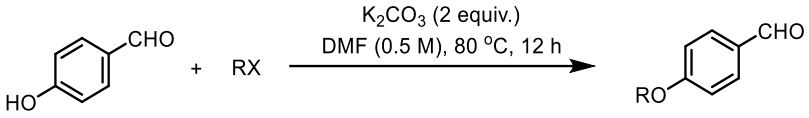
Scheme S2. General procedure B for the preparation of dialdehydes



To a well-stirred suspension of substituted terephthalonitrile (5 mmol) in 50 mL of dry toluene under a nitrogen atmosphere at -78 ℃ was added 14 mL (2.8 mmol) of 1 M diisopropylaluminum hydride (DIBAL-H) in hexane. The resulting suspension was allowed to warm to room temperature and was stirred for 8 h. After addition of 1 M aqueous hydrochloric acid solution, the reaction was extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was crystallized from ethyl acetate or purified by column chromatography to give the appropriate dialdehyde.[2]

General procedure C

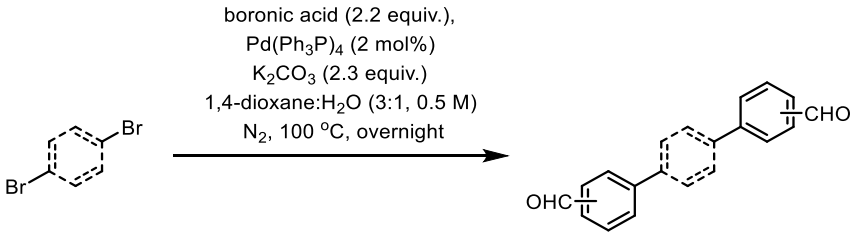
Scheme S3. General procedure C for the preparation of dialdehydes



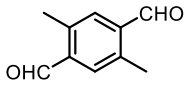
To a 100 mL schlenk tube were added 4-hydroxybenzaldehyde (10 mmol, 1.22 g), corresponding haloalkane/aryl halide and K_2CO_3 (20 mmol, 2.68 g), 20 mL N,N-dimethyl-formamide was added. The mixture was heated up to 80 °C and stirred overnight, washed with water and extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography to give the appropriate dialdehyde.

General procedure D

Scheme S3. General procedure D for the preparation of dialdehydes



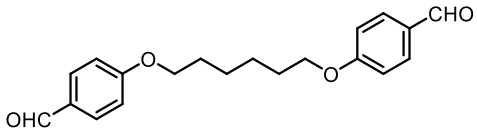
To a 100 mL schlenk tube were added dibromoaromatics (10 mmol), (3 or 4-formylphenyl)boronic acid (22 mmol, 3.30 g), $Pd(Ph_3P)_4$ (0.2 mmol, 0.20 g) and K_2CO_3 (23 mmol, 3.17 g) under nitrogen atmosphere, 20 mL 1,4-dioxane solution of water (1,4-dioxane:H_2O = 3:1) was added. The mixture was heated up to 100 °C and stirred overnight, washed with water and extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was crystallized from ethyl acetate or purified by column chromatography to give the appropriate dialdehyde.



2,5-Dimethylterephthalaldehyde (1b)

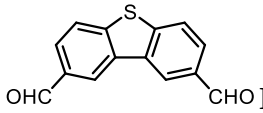
General procedure B. White solid, yield: 68%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.32 (2H, s), 7.68 (2H, s), 2.69 (2H, s), **^{13}C NMR** (125 MHz, $CDCl_3$). δ 192.3, 138.3, 137.0, 134.8, 18.9. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{10}H_{11}O_2^+$ 163.0754, found

163.0755.



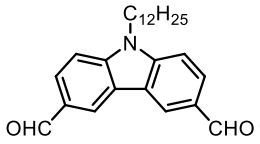
4,4'-(Hexane-1,6-diylbis(oxy))dibenzaldehyde (1c)

General procedure C with 1,6-dibromohexane (0.5 equiv.). White solid, yield: 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.87 (2H, s), 7.82 (2H, d, *J* = 8.0 Hz), 6.98 (2H, d, J = 8.0 Hz), 4.06 (4H, t, *J* = 6.4 Hz), 1.88-1.84 (4H, m), 1.58-1.55 (4H, m). **^{13}C NMR** (100 MHz, $CDCl_3$). δ 190.9, 164.3, 132.1,129.9, 114.8, 68.3, 29.1, 25.9.



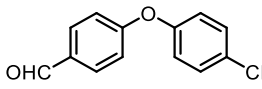
Dibenzo[*b,d*]thiophene-2,8-dicarbaldehyde (1d)

General procedure A. White solid, yield: 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.19 (2H, s), 8.72 (2H, s), 8.03 (4H, s). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.5, 146.3, 135.5, 133.9, 127.8, 124.1, 123.7. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{14}H_9O_2S^+$ 241.0318, found 241.0318.



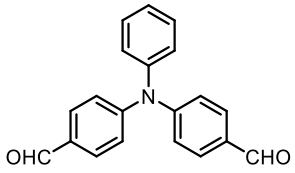
9-Dodecyl-9H-carbazole-3,6-dicarbaldehyde (1e)

General procedure A. White solid, yield: 62%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.11 (2H, s), 8.63 (2H, d, *J* = 1.0 Hz), 8.07 (2H, dd, *J* = 1.0, 8.5 Hz), 7.53 (2H, d, *J* = 8.5 Hz), 4.36 (2H, t, *J* = 7.5 Hz), 1.90 (2H, quint, *J* = 7.5 Hz), 1.40-1.26 (10H, m), 0.86 (3H, t, *J* = 7.0 Hz)**. ^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.6, 144.9, 129.8, 128.0, 124.3, 123.3, 109.9, 43.9, 32.0, 29.7 (2C), 29.6, 29.5, 29.4 (2C), 29.0, 27.3, 22.8, 14.2. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{26}H_{34}NO_2^+$ 392.2584, found 392.2583.



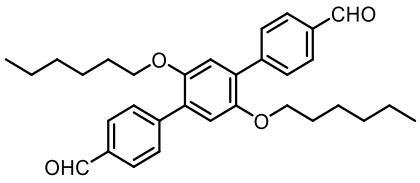
4,4'-Oxydibenzaldehyde (1f)

General procedure C with 4-fluorobenzaldehyde (1 equiv.). White solid, yield: 89%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.98 (2H, s), 7.92 (4H, dt, *J* = 7.6, 1.6 Hz), 7.18 (4H, dt, *J* = 7.6, 1.6 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 161.4, 132.7, 132.4, 119.5. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{14}H_{11}O_3^+$ 227.0703, found 227.0702.



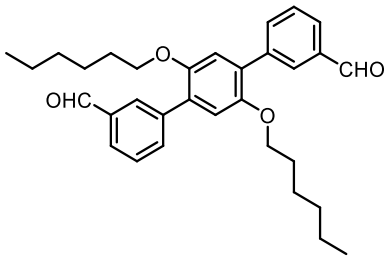
4,4'-(Phenylazanediyl)dibenzaldehyde (1g)

Prepared according to the literature[3]. Light yellow solid, yield: 48%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (2H, s), 7.84 (4H, m), 7.46 (2H, d, *J* = 7.6 Hz), 7.26-7.23 (6H, m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2, 160.4, 132.8, 130.1, 124.5, 123.6, 112.9. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{20}H_{16}NO_2^+$ 302.1176, found 302.1183.



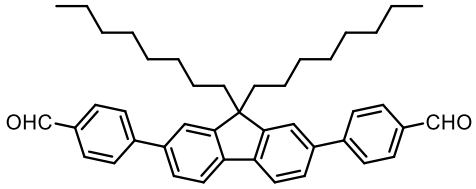
2',5'-Bis(hexyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (1i)

General procedure D. Light green solid, yield: 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.07 (2H, s), 7.95 (4H, d, *J* = 8.0 Hz), 7.77 (4H, t, *J* = 8.4 Hz), 7.00 (2H, s), 3.95 (4H, t, *J* = 6.4 Hz), 1.69 (4H, quint, *J* = 6.4 Hz), 1.39-1.21 (12H, m), 0.85 (6H, t, *J* = 6.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.6, 150.5, 144.7, 135.1, 130.5, 130.3, 129.2, 116.0, 69.8, 31.5, 29.3, 25.9, 22.7, 14.1. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{32}H_{39}O_4^+$ 487.2843, found 487.2841.



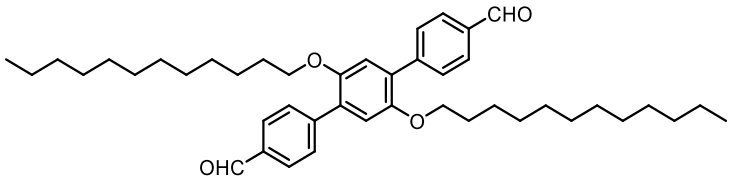
2',5'-Bis(hexyloxy)-[1,1':4',1''-terphenyl]-3,3''-dicarbaldehyde (1j)

General procedure D. White solid, yield: 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.09 (2H, s), 8.12 (2H, s), 7.89 (4H, t, *J* = 8.4 Hz), 7.59 (4H, t, *J* = 8.4 Hz), 7.02 (2H, s), 3.95 (4H, t, *J* = 6.4 Hz), 1.69 (4H, quint, *J* = 6.4 Hz), 1.39-1.24 (12H, m), 0.85 (6H, t, *J* = 6.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.6, 150.4, 139.3, 136.5, 135.8, 131.1, 130.0, 128.8, 128.4, 115.9, 69.7, 31.6, 29.4, 25.9, 22.7, 14.1. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{32}H_{39}O_4^+$ 487.2843, found 487.2841.



4,4'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)dibenzaldehyde (1k)

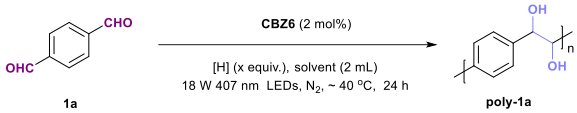
General procedure D. Light green solid, yield: 92%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.09 (2H, s), 8.00 (4H, s), 7.85-7.83 (6H, m), 7.66 (2H, dd, *J* = 1.0, 15.5 Hz), 7.63 (2H, s), 2.09-2.07 (4H, m), 1.17-1.07 (20H, m), 0.78 (6H, t, *J* = 7.0 Hz), 0.71 (4H, brs). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 152.2, 147.7, 141.1, 139.0, 135.2, 130.5, 127.8, 126.7, 121.8, 120.7, 55.6, 40.5, 31.9, 30.1, 29.3, 29.3, 23.9, 22.7. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{43}H_{51}O_2^+$ 599.3884, found 599.3871.



2',5'-Bis(dodecyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (1l)

General procedure D. Light green solid, yield: 86%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.07 (2H, s), 7.94 (4H, d, *J* = 8.0 Hz), 7.77 (4H, d, *J* = 8.0 Hz), 7.01 (2H, s), 3.95 (4H, t, *J* = 6.4 Hz), 1.69 (4H, quint, *J* = 6.8 Hz), 1.35-1.24 (36H, m), 0.88 (6H, t, *J* = 6.8 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 150.5, 144.7, 135.1, 130.3, 129.6, 116.0, 69.7, 32.1, 29.8 (2C), 29.7 (2C), 29.5, 29.4 (2C), 26.2, 22.8, 14.3. **HRMS** (ESI-TOF) m/z:$[M+H]^+$ calcd for $C_{44}H_{63}O_4^+$ 655.4721, found 655.4771.

3. Optimization for polymerization



entry	[H]	x	solvent	conv.(%)	M_n(kDa)	M_w(kDa)	$Đ$	DPn
1	NEt_3	2	acetonitrile	> 95	-	-	-	-
2	NEt_3	2	DMSO	> 95	8.2	46.8	5.71	60
3	NEt_3	2	THF	> 95	6.9	37.4	5.43	51
4[b]	NEt_3	2	DMSO	94	-	-	-	2[c]
5	HCOONa	2	acetonitrile	72	-	-	-	2[c]
6	HCOONa	4	acetonitrile	> 95	-	-	-	2[c]
7	NEt_3	0.5	acetonitrile	> 95	-	-	-	2[c]
8	NEt_3	1	acetonitrile	> 95	-	-	-	20[c]

[a]Conversions of **1a** were determined by ^{1}H NMR. M_n and $Đ$ (polymer dispersity index) were determined by GPC calibrated with PS standards in DMF at 35 ℃. [b]Without **CBZ6**. [c]Determined by ^{1}H NMR, 28 mg 1,3,5-trimethoxybenzene (TMB) was added as internal satndard.

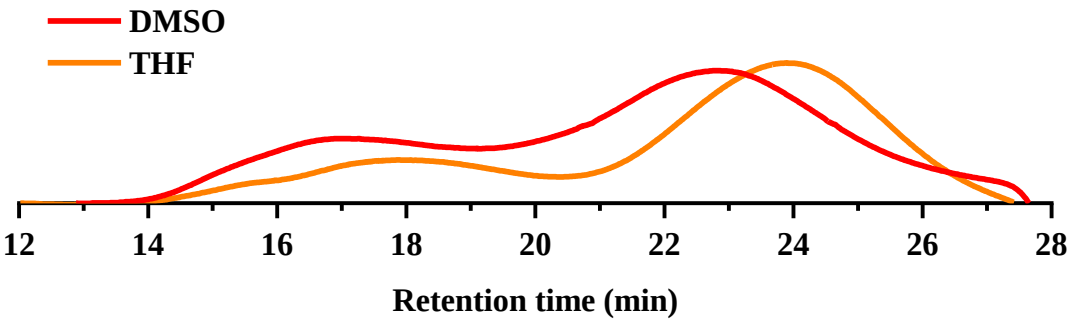


Figure S2. GPC of **poly-1a** prepared from DMSO and THF.

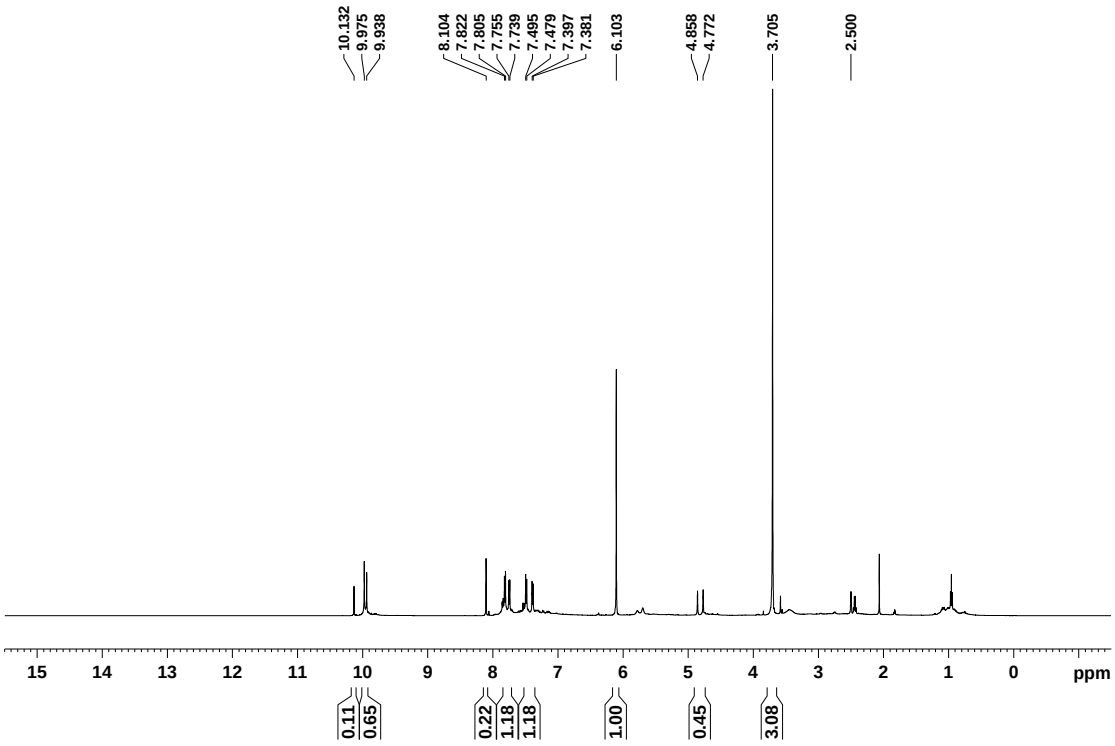


Figure S3. Crude ^{1}H NMR of polymerization when **CBZ6** was absent. 94% (=(2-0.11)/2) of **1a** was consumed and the major product was **2a** (65%).

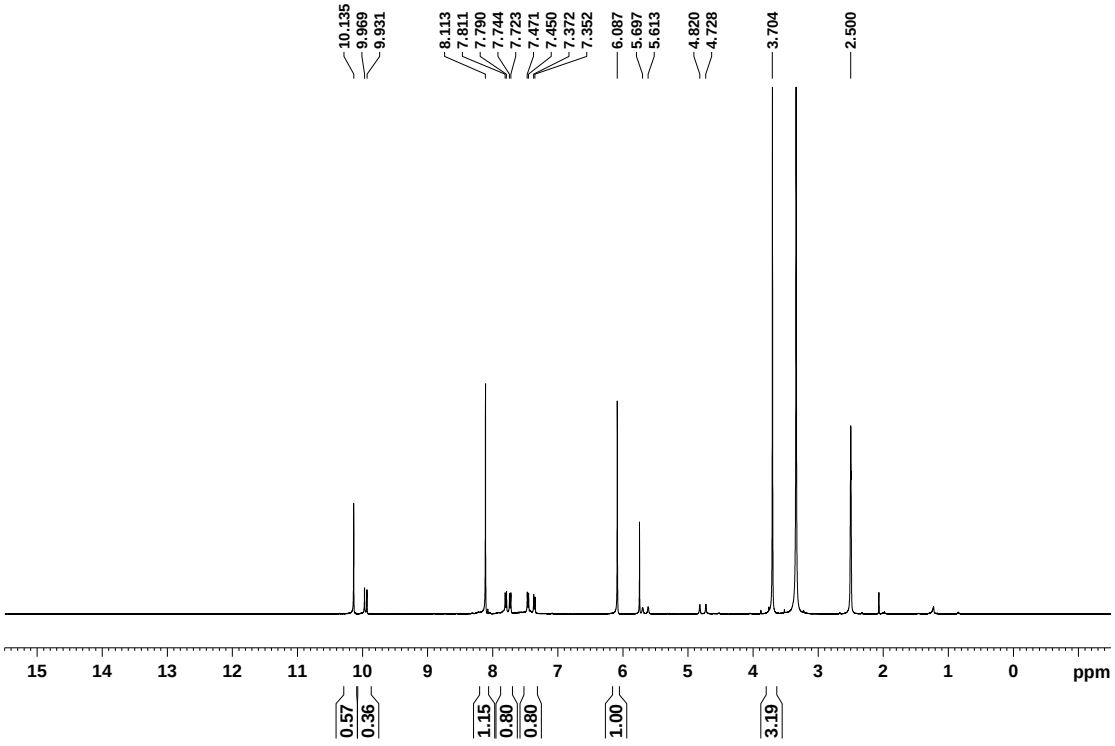


Figure S4. Crude ^{1}H NMR of polymerization when using 2 equiv. HCOONa. 72% (=(2-0.57)/2) of **1a** was consumed and the major product was **2a** (36%).

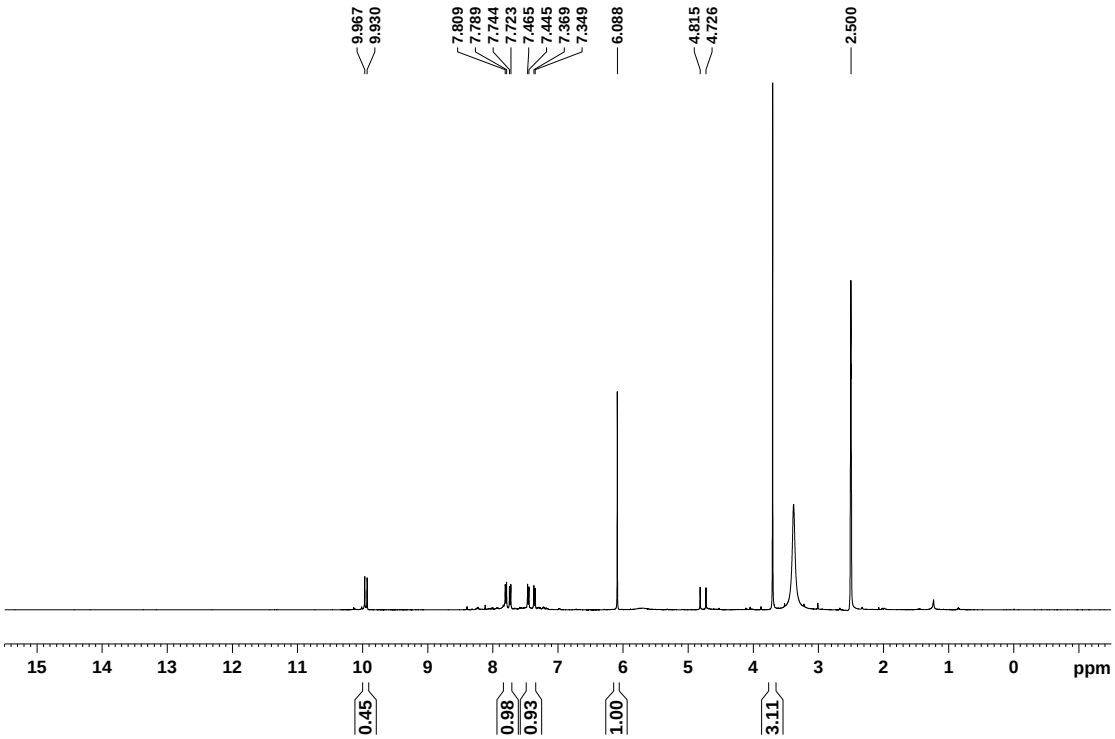


Figure S5. Crude ^{1}H NMR of polymerization when using 4 equiv. HCOONa. All of **1a** was consumed and the product was the mixture of **2a** (45%) and oligomor.

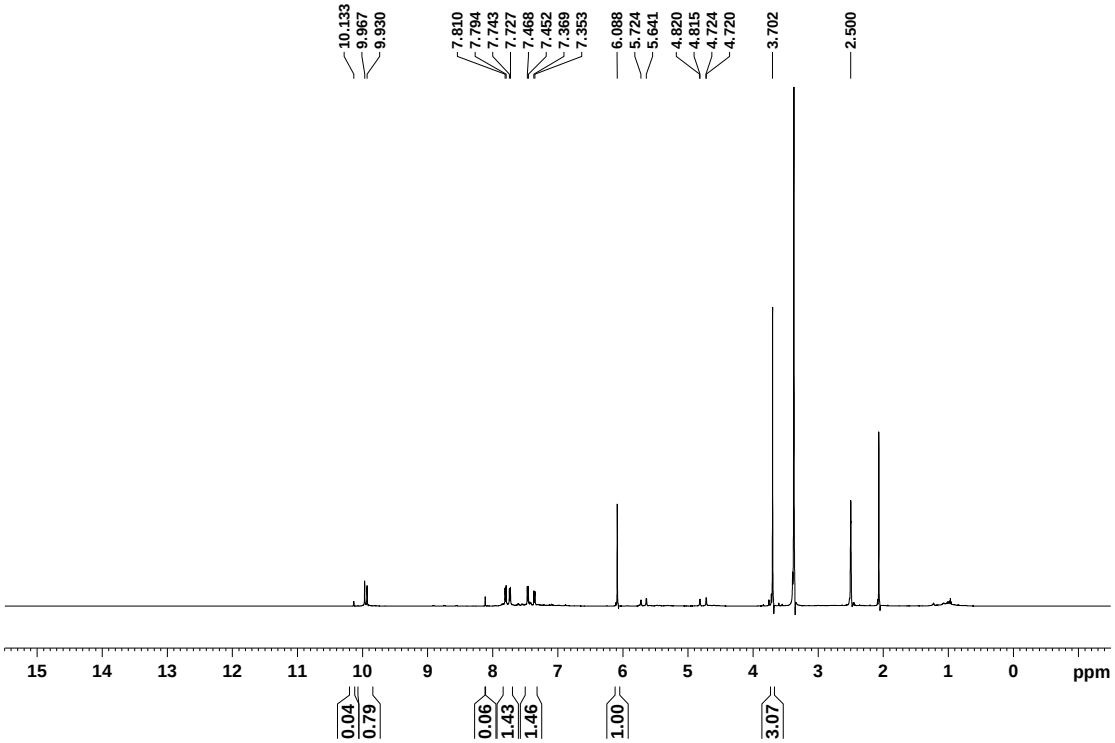


Figure S6. Crude ^{1}H NMR of polymerization when using 0.5 equiv. NEt_3. 98% (=(2-0.04)/2) of **1a** was consumed and the major product was **2a** (79%).

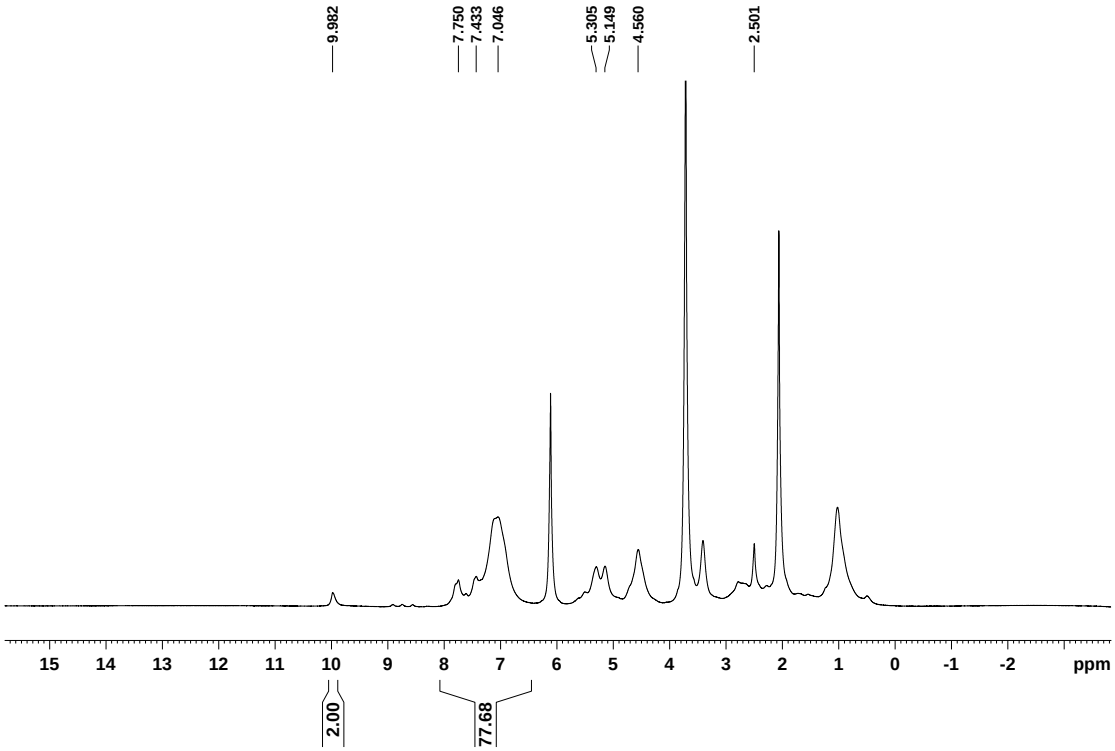
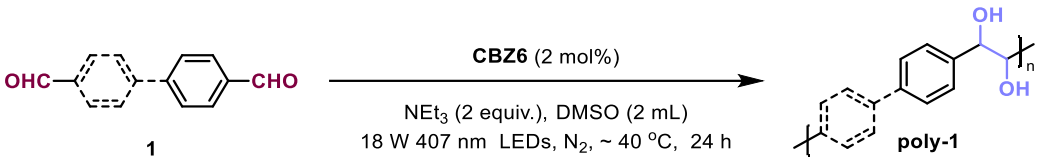


Figure S7. Crude ^{1}H NMR of polymerization when using 1 equiv. NEt_3. All of **1a** and **2a** was consumed. The estimated DP is 19.4 (=77.68/4).

4. General procedure for polymerization

Scheme S3. General procedure for polymerization



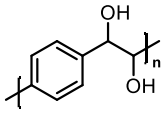
Dialdehydes (0.5 mmol) and **CBZ6** (0.01 mmol, 4.4 mg) were added in an oven-dried 25 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with nitrogen three times. Then NEt_3 (1 mmol, 138 μL) and dry DMSO (2 mL) were added sequentially in the Schlenk tube via syringe under nitrogen atmosphere. Then the tube was placed 2 cm away from LEDs with a fan cooling the reaction, and the reaction was stirred vigorously under the irradiation of light. After 24 h, the tube was removed from the light source.

After reaction, 10 mL water was added into the solution. The mixture was filtered to collect crude product.

If the polymer was soluable in DCM, the crude product was solved in 2 mL DCM. The solution was added dropwise into 20 mL *n*-hexane, additional precipitation procedures were performed twice in methanol to afford the purified product.

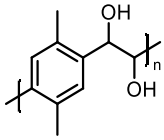
If the polymer was insoluble in DCM but soluable in THF, the crude product was solved in 2 mL THF. The solution was added dropwise into 20 mL MeCN, additional precipitation procedures were performed twice in MeCN to afford the purified product.

If the polymer was insoluble both in DCM and THF, the crude product was washed with DCM twice to afford the purified product.



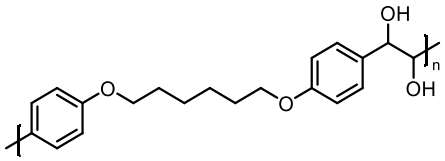
Poly-terephthalaldehyde (poly-1a)

Orange solid (58 mg, 85%). **^{1}H NMR** (500 MHz, *d*^{6}-DMSO) δ 7.14 (4H, brs), 5.27-5.11 (2H, m), 4.51 (2H, brs). **^{13}C NMR** (125 MHz, *d*^{6}-DMSO) δ 141.1, 126.3, 77.6, 77.0. **GPC**: M_n = 75.5 kDa, $Đ$ = 2.44. **TGA**: T_{d5} = 242 °C. **DSC**: -.



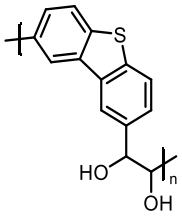
Poly-2,5-dimethylterephthalaldehyde (poly-1b)

Beige solid (56 mg, 68%). **^{1}H NMR** (500 MHz, *d*^{6}-DMSO) δ 7.15-7.03 (4H, m), 5.08-4.77 (4H, m), 2.25-1.76 (6H, m). **GPC**: M_n = 5.4 kDa, $Đ$ = 1.27. **TGA**: T_{d5} = 239 °C. **DSC**: -.



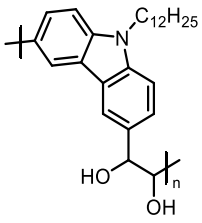
Poly-4,4'-(hexane-1,6-diylbis(oxy))dibenzaldehyde (poly-1c)

White soild (130 mg, 78%). using DIPEA as reductant. **^{1}H NMR** (500 MHz, *d*^{6}-DMSO) δ 7.11-6.94 (4H, *dl* and *meso*), 6.78-6.69 (4H, *dl* and *meso*), 5.21 (*meso*), 5.03 (1H, *dl*), 4.45 (2H, *dl* and *meso*), 3.90-3.86 (4H, m), 1.68 (4H, s), 1.43 (4H, s). **^{13}C NMR** (125 MHz, *d*^{6}-DMSO) δ 157.4, 134.2, 128.4, 128.3, 77.4, 76.6, 67.2, 28.8, 25.4. **GPC**: M_n = 10.4 kDa, $Đ$ = 1.51. **TGA**: T_{d5} = 262 ^{o}C, **DSC**: -.



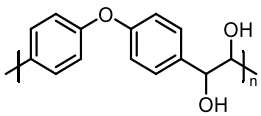
Poly-dibenzo[*b*,*d*]thiophene-2,8-dicarbaldehyde (poly-1d)

Orange solid (61 mg, 50%). **^{1}H NMR** (500 MHz, *d*^{6}-DMSO) δ 7.26, 7.09 (4H, *dl* and *meso*), 6.88-6.76 (4H, m), 5.38-5.22 (2H, *meso* and *dl*), 4.57 (1H, meso), 4.51 (1H, *dl*). **GPC**: M_n = 7.3 kDa. $Đ$ = 5.19. **TGA**: T_{d5} = 262 ^{o}C, **DSC**: -.



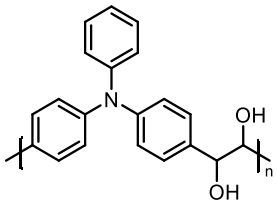
Poly-9-dodecyl-9H-carbazole-3,6-dicarbaldehyde (poly-1e)

Beige solid (118 mg, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (brs), 7.38-7.19 (m), 4.97 (m), 4.26-4.19 (m), 1.83 (s), 1.23-0.87 (s). **GPC**: M_n = 4.9 kDa. $Đ$ = 2.19, **TGA**: T_{d5} = 291 ^{o}C, **DSC**: -.



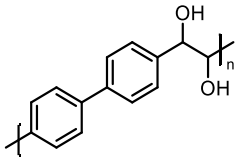
Poly-4,4'-oxydibenzaldehyde (poly-1f)

Beige solid (93 mg, 82%). **^{1}H NMR** (500 MHz, *d*^{6}-DMSO) δ 7.26, 7.09 (4H, *dl* and *meso*), 6.88-6.76 (4H, m), 5.38, 5.22 (2H, *dl* and *meso*), 4.57 (1H, *meso*)., 4.51 (1H, *dl*). **GPC**: M_n = 7.1 kDa. $Đ$ = 1.91. **TGA**: T_{d5} = 289 ^{o}C, **DSC**: T_g = 123 ^{o}C.



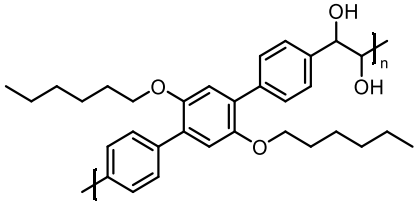
Poly-4,4'-(phenylazanediyl)dibenzaldehyde (poly-1g)

Gray solid (59 mg ,39%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.75 (0.4 terminal H, s), 7.62 (s, terminal aryl H), 7.26-6.97 (m, 13H + terminal aryl H), 4.74-4.60 (2H, m), 1.61 (2H, brs). **GPC**: M_n = 4.9 kDa, $Đ$ = 2.90; **TGA**: T_{d5} = 276 ^{o}C; **DSC**: 161 ^{o}C.



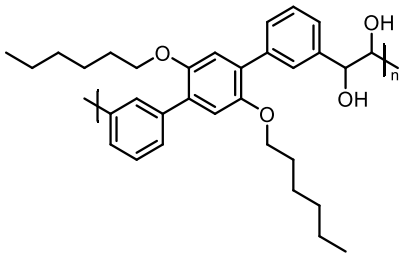
Poly-[1,1'-biphenyl]-4,4'-dicarbaldehyde (poly-1h)

Beige solid (106 mg ,99%). **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.50-7.24 (8H, m), 5.41-5.30 (2H, m), 4.68-4.61 (2H, m). **GPC**: M_n = 5.3 kDa. $Đ$ = 1.25, **TGA**: T_{d5} = 293 ^{o}C, **DSC**: -.



Poly-2',5'-bis(hexyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (poly-1i)

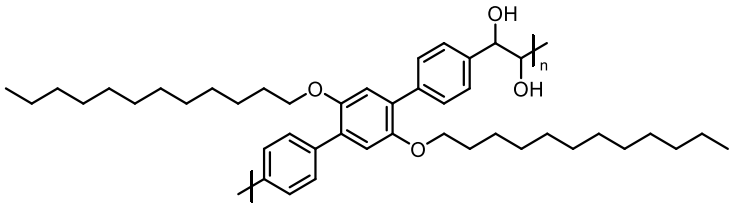
Beige solid (126 mg, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62-7.29 (8H, m), 6.96 (2H, s), 4.87 (2H, s), 3.89 (4H, s), 2.88 (1H, s), 2.21 (1H, s), 1.66 (4H, s), 1.34-1.25 (12H, m), 0.85 (6H, s). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.4, 138.5 (3C), 130.5-129.5, 126.9-126.6, 116.3, 78.7, 78.3, 69.7, 31.5, 29.4, 25.8, 22.7, 14.2. **GPC**: M_n = 8.2 kDa, $Đ$ = 3.32; **TGA**: T_{d5} = 350 ^{o}C, **DSC**: T_g = 107 ^{o}C.



Poly-2',5'-bis(hexyloxy)-[1,1':4',1''-terphenyl]-3,3''-dicarbaldehyde (poly-1j)

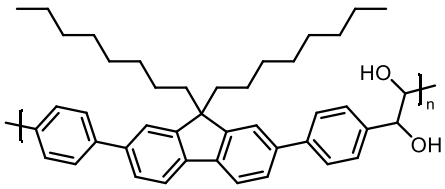
Beige solid (122 mg, 50%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48-6.94 (8H, m), 6.80-

6.70 (2H, m), 4.89-4.79 (2H, m), 3.84-3.76 (4H, m), 2.96 (1H, s), 2.36 (1H, s), 1.58 (4H, s), 1.22-1.11 (12H, m), 0.82 (6H, s). **GPC**: M_n = 7.5 kDa, $Đ$ = 3.80; **TGA**: T_{d5} = 339 ^oC, **DSC**: T_g = 66 ^oC.



Poly-2',5'-bis(dodecyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (poly-1k)

Beige solid (42 mg, 32%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63-7.32 (8H, m), 6.89-6.87 (2H, m), 4.89-4.75 (2H, m), 3.91-3.89 (4H, m), 2.83 (1H, s), 2.16 (1H, s), 1.67 (4H, s), 1.35-1.14 (36H, m), 0.87 (6H, s). **GPC:** M_n = 4.2 kDa, $Đ$ = 1.14. **TGA**: T_{d5} = 306 ^oC. **DSC**: T_g = 35 ^oC.

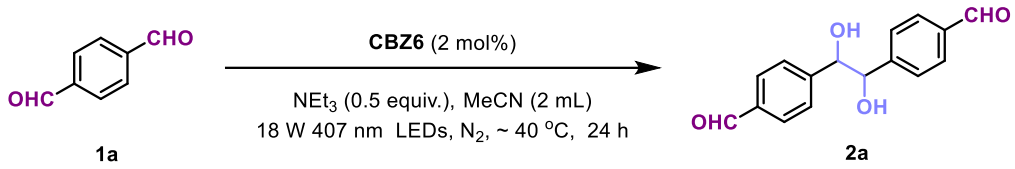


Poly-4,4'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dibenzaldehyde (poly-1l)

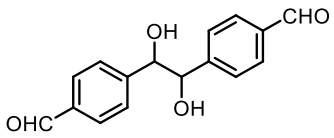
Beige solid (165 mg, 55%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76-7.32 (14H, m), 4.96-4.77 (2H, m), 2.99 (1H, s), 2.32 (1H, s), 2.03 (4H, s), 1.26-1.06 (20H, m), 0.77-0.51 (10H, m). **GPC**: M_n = 7.5 kDa, $Đ$ = 2.58. **TGA**: T_{d5} = 353 ^oC, **DSC**: T_g =137 ^oC.

5. General procedure for dimerization

Scheme S4. General procedure for **2a**



1a (0.5 mmol) and **CBZ6** (0.01 mmol, 4.4 mg) was added in an oven-dried 25 mL Schlenk tube. The reaction tube was placed under vacuum and backfilled with nitrogen three times. Then NEt_3 (0.25 mmol, 35 μL) and dry MeCN (2 mL) were added sequentially in the Schlenk tube via syringe under nitrogen atmosphere. Then the tube was placed 2 cm away from 18 W LEDs with a fan cooling the reaction, and the reaction was stirred vigorously under the irradiation of light. After 24 h, the tube was removed from the light source. The crude product was purified by column chromatography to give the **2a**.

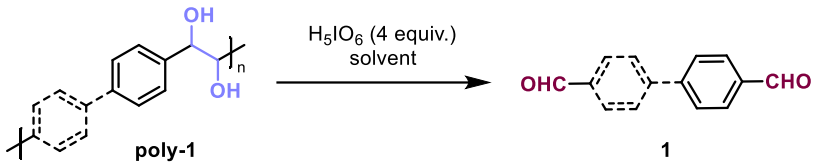


4,4'-(1,2-Dihydroxyethane-1,2-diyl)dibenzaldehyde (2a)[4]

Orange solid (95 mg, 70%), *meso*/*dl* 1:1.8. **^{1}H NMR** of **(*meso*)-** and **(*dl*)-2a** (400 MHz, d^6-DMSO) δ 9.97 (1.8 × 2H, s, *dl*), 9.93 (2H, s, *meso*), 7.80 (1.8 × 4H, d, *J* = 8.0 Hz, *dl*), 7.74 (4H, d, *J* = 8.0 Hz, *meso*), 7.46 (1.8 × 4H, d, *J* = 8.0 Hz, *dl*), 7.36 (4H, d, *J* = 8.0 Hz, *meso*), 5.70 (2H, s, *meso*), 5.62 (1.8 × 2H, s, *dl*), 4.82 (2H, s, meso), 4.72 (1.8 × 2H, s, *dl*). **^{13}C NMR** of **(*meso*)-** and **(*dl*)-2a** (100 MHz, d^6-DMSO) δ 192.9 (*meso* and *dl*), 150.0 (*dl*), 149.2 (*meso*), 135.1 (*dl*), 135.0 (*meso*), 128.7 (*dl*), 128.6 (*meso*), 128.0 (*dl*), 127.7 (*meso*), 76.6 (*meso*), 76.5 (*dl*).

6. General procedure for depolymerization and repolymerization

Scheme S5. General procedure for depolymerization



General procedure for crude ^{1}H NMR yield: **poly-1** (0.1 mmol) and H_5IO_6 (0.4 mmol, 92 mg) were added in a tube. The corresponding solvent was added in the Schlenk tube. The reaction was stirred vigorously. After corresponding hours, TMB or CH_3NO_2 was added into the reaction as internal standard. The yield of **1** was determined by crude ^{1}H NMR.

Note: This reaction is extremely exothermic. H_5IO_6 should be added slowly and portionwise at 0 ^{o}C if the reaction scale is greater than 0.5 mmol.

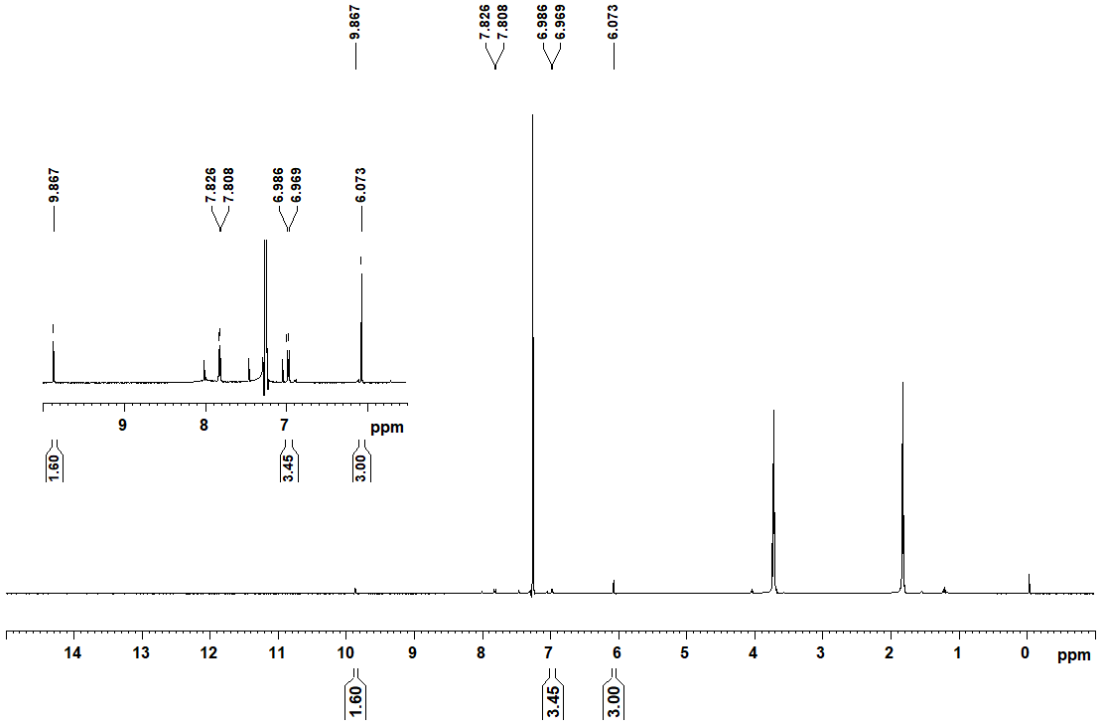
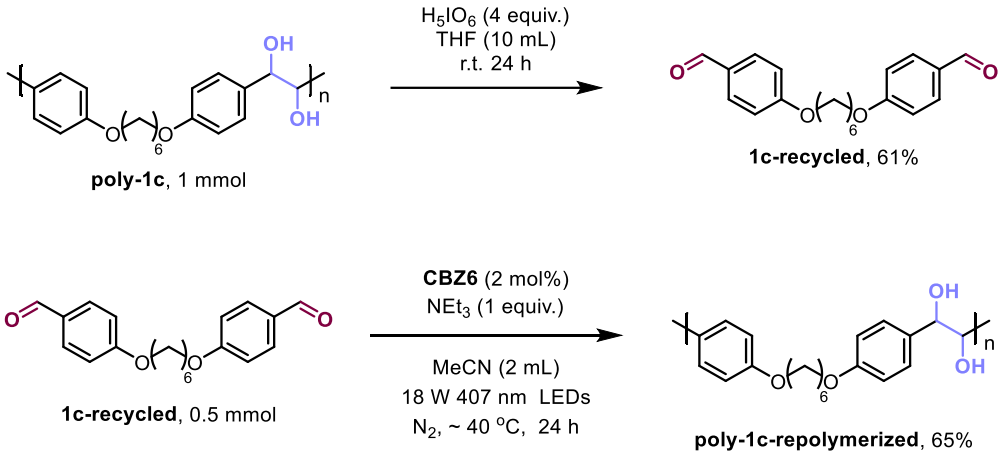


Figure S8. Crude ^{1}H NMR of depolymerization of **poly-1c**. 16.8 mg 1,3,5-trimethoxybenzene (TMB) was added as internal satndard.



General procedure for isolation and repolymerization of **poly-1c**: **poly-1c** (prepared via NEt_3, 326 mg, 0.5 mmol) and H_5IO_6 (4 mmol, 920 mg) were added in a 50 mL round-bottle flask. THF (10 mL) was added in the Schlenk tube. The reaction was stirred vigorously for 24 h. After corresponding hours, the mixture was washed with conc. $Na_2S_2O_3$ solution and extracted with DCM. The oganic phase was purified by column chromatography directly to obtain **1c-recycled** (198 mg, 61%) as a white solid.

1c-recycled (0.5 mmol, 162 mg) was added into an oven-dried 25 mL Schlenk tube. The solvent was vaporized under reduced pressure. The reaction tube was placed under vacuum and backfilled with nitrogen three times. Then NEt_3 (1 mmol, 140 μL) and DMSO (2 mL) were added sequentially in the Schlenk tube via syringe under nitrogen atmosphere. Then the tube was placed 2 cm away from 18 W LEDs with a fan cooling the reaction, and the reaction was stirred vigorously under the irradiation of light. After 24 h, the tube was removed from the light source. The crude product was solved in 2 mL THF. The solution was added dropwise into 20 mL MeCN, additional precipitation procedures were performed twice in MeCN to afford the purified product **poly-1c-repolymerized** (105 mg, 65%) as a white solid.

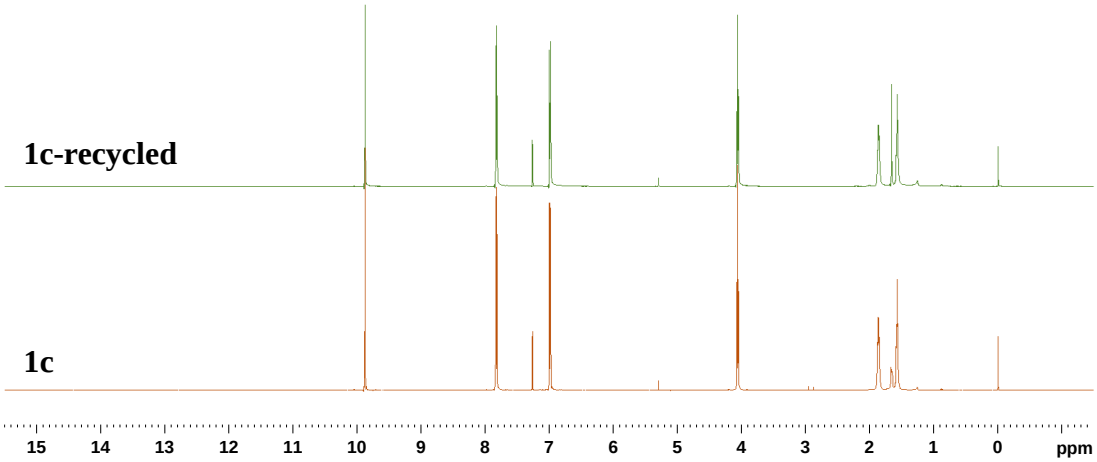


Figure S9. ^{1}H NMR of **1c** and **1c-recycled**.

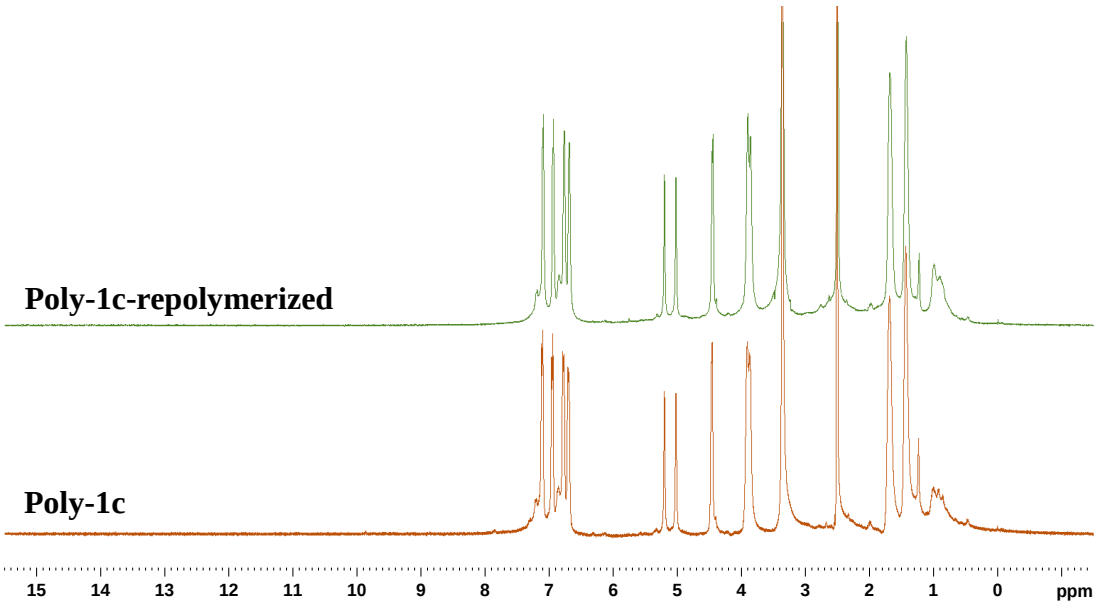


Figure S10. ^{1}H NMR of **poly-1c** and **poly-1c-repolymerized**.

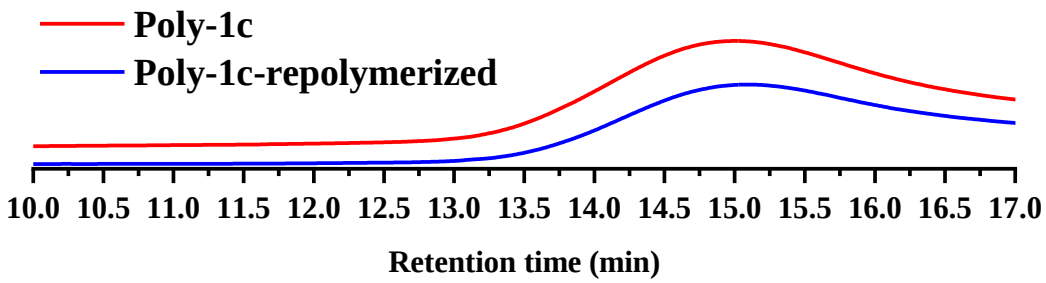


Figure S11. GPC of **poly-1c and poly 1c-repolymerized**. These data were measured by an 1260 Infinity II GPC/SEC, THF as eluent.

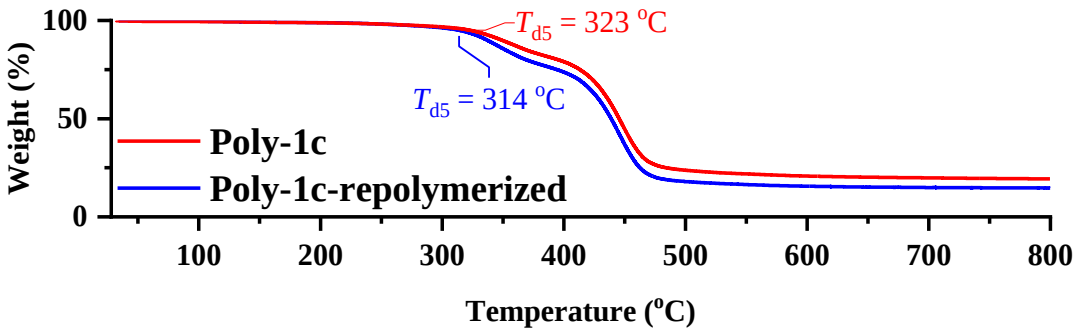


Figure S12. TGA of **poly-1c** and **poly-1c-repolymerized**.

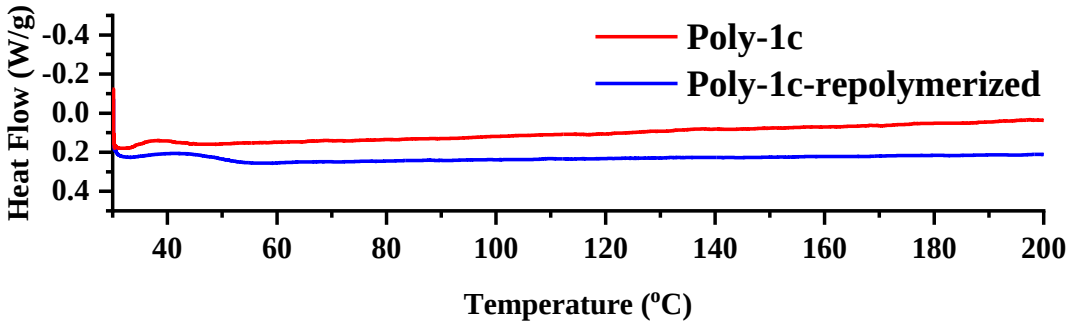


Figure S13. DSC of **poly-1c** and **poly-1c-repolymerized**.

7. Reference

1. H.-P. Shi, J.-X. Dai, X.-F. Zhang, L. Xu, L. Wang, L.-W. Shi, and L. Fang, Experimental and theoretical study of two new pyrazoline derivatives based on dibenzofuran, *Spectrochimica Acta Part A*, 2011, **83**, 242-249.

2. M. J. Strauss, M. Jia, A. M. Evans, I. Castano, R. L. Li, X. Aguilar-Enriquez, E. K. Roesner, J. L. Swartz, A. D. Chavez, A. E. Enciso, J. F. Stoddart, M. Rolandi, and W. R. Dichtel, Diverse Proton-Conducting Nanotubes via a Tandem Macrocyclization and Assembly Strategy, *J. Am. Chem. Soc.* 2021, **143**, 21, 8145-8153.

3. C.-C. Li, W. Yang, W.-Q. Zhou, M.-M. Zhang, R.-Y. Xue, M.-Y. Li, and Z.-Q. Cheng, Branching effect for aggregation-induced emission in fluorophores containing imine and triphenylamine structures, *New J. Chem.*, 2016, **40**, 8837-8845.

4. M. Tomar, C. Bosch, J. Everaert, R. Bhimpuria, A. Thapper, A. Orthaber and K. E. Borbas, Photocatalyst for visible-light-driven Sm(II)-mediated reductions, *Org. Lett.* 2024, **26**, 50, 10752-10756.

8. Solublity of polymers

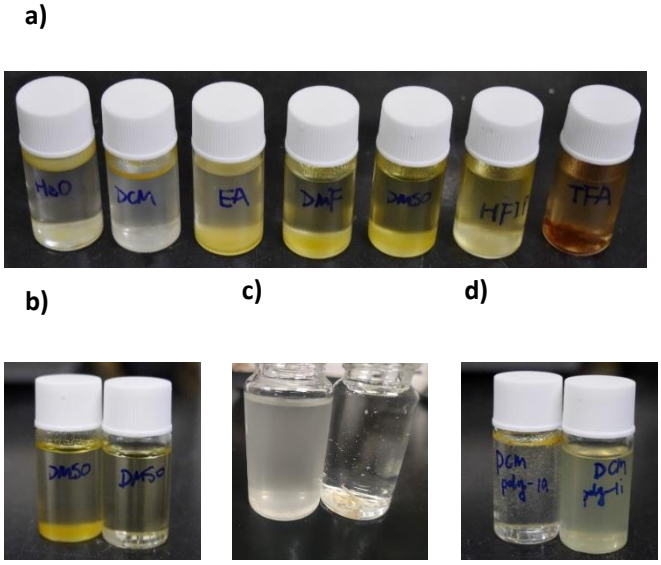


Figure S14. a) **Poly-1a** prepared from acetonitrile in common solutions (water, DCM, EA, DMF, DMSO, HFIP, TFA). b) **Poly-1a** in DMSO (left: prepared from acetonitrile, right: prepared from DMSO). c) **Poly-1a** in 0.1 M HCl (left, pH = 1) and water (right, pH = 7). d) **Poly-1a** (left, prepared from DMSO) and **poly-1i** (right, prepared from DMSO) in DCM.

9. ^{1}H NMR between monomer, dimer, oligomer and polymer

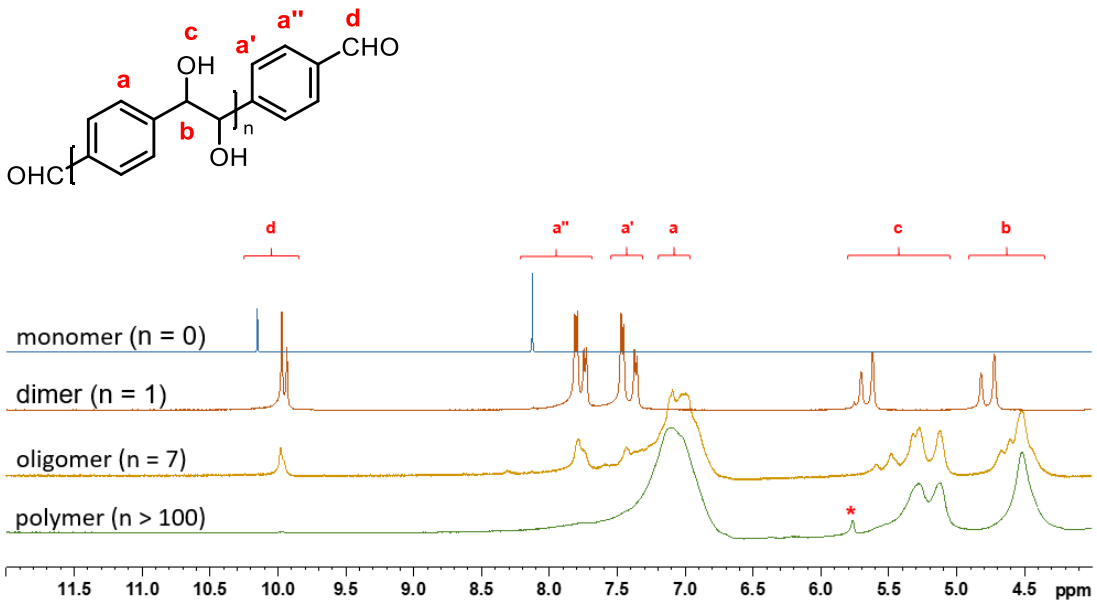


Figure S15. ^{1}H NMR of between monomer, dimer, oligomer and polymer of **1a**. *DCM.

10. FT-IR of between monomer, dimer and polymer

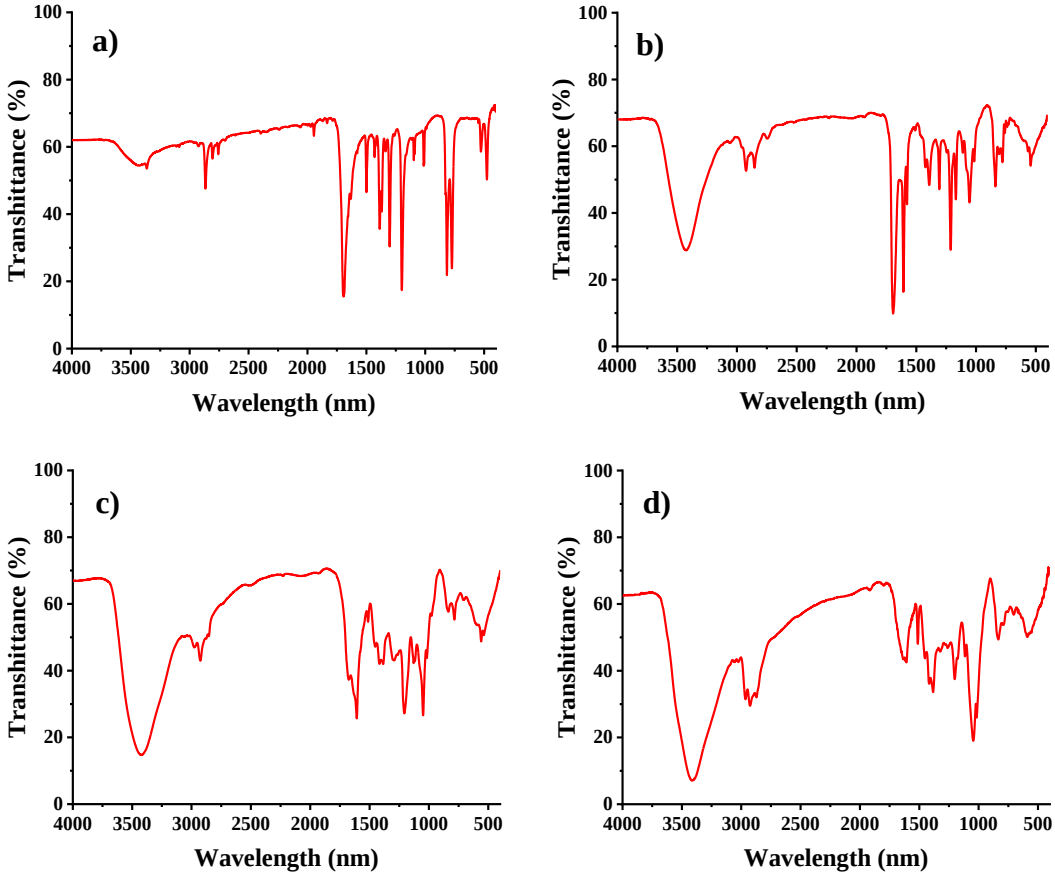


Figure S16. a) FT-IR of **1a**, **b)** FT-IR of **2a**, **c)** FT-IR **poly-1a** (8.2 kDa), **d)** FT-IR **poly-1a** (insoluble, prepared by MeCN).

11. UV/vis and fluorescence of the polymers

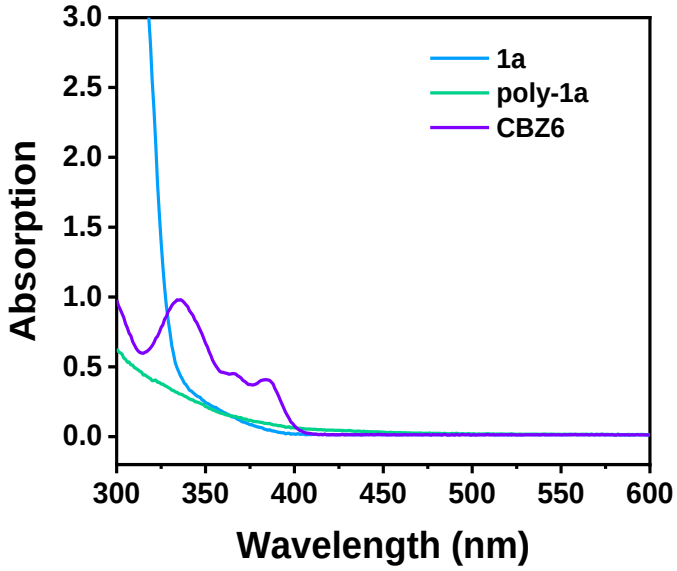


Figure S17. UV-vis spetra of **1a** (2 mM), **poly-1a** (2 mM) and **CBZ6 (**0.04 mM**)** in DMSO. **CBZ6** was completely removed in polymer.

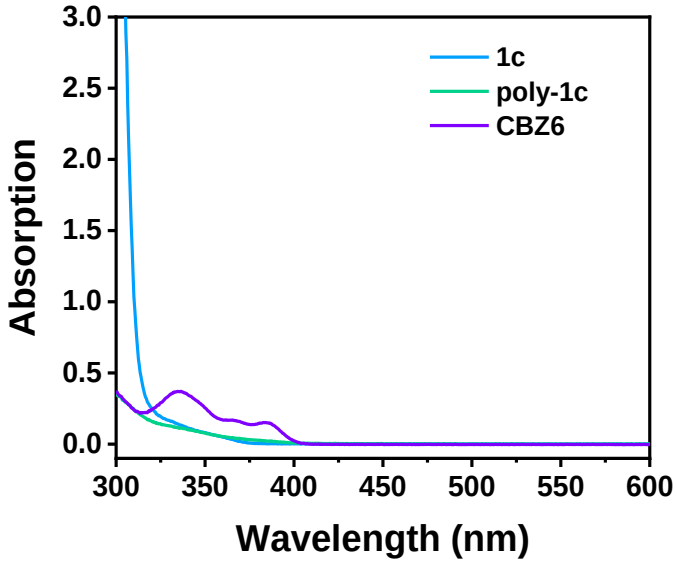


Figure S18. UV-vis spetra of **1c** (0.5 mM), **poly-1c** (0.5 mM) and **CBZ6 (**0.01 mM**)** in DMSO. **CBZ6** was completely removed in polymer.

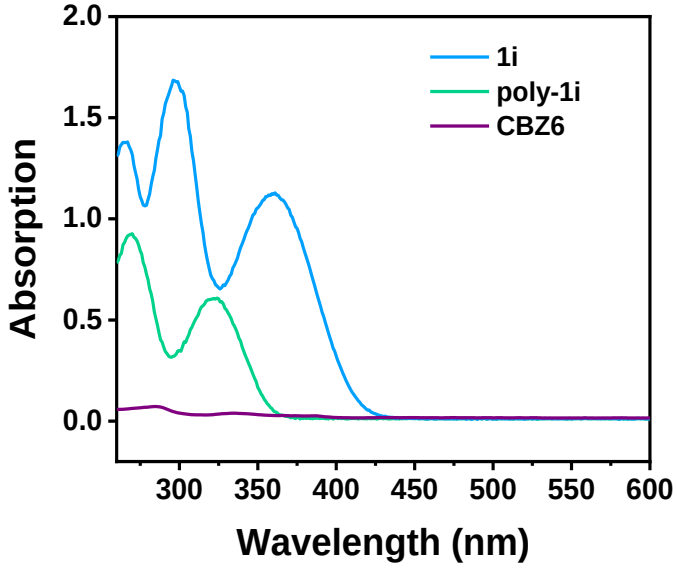


Figure S19. UV-vis spetra of **1i** (0.05 mM) and **poly-1i** (0.05 mM) and **CBZ6 (**0.001 mM**)** in DMSO.

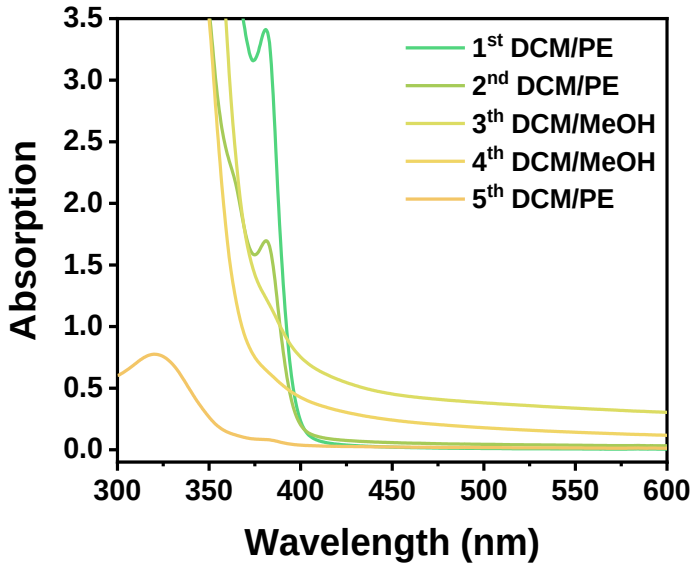


Figure S20. UV-vis spetra of the filtrate after precipitation dissolution procedure of **poly-1i** using good solvent/nonsolvent. **poly-1i** is slightly soluble in MeOH.

12. GPC, TGA and DSC data of the polymers

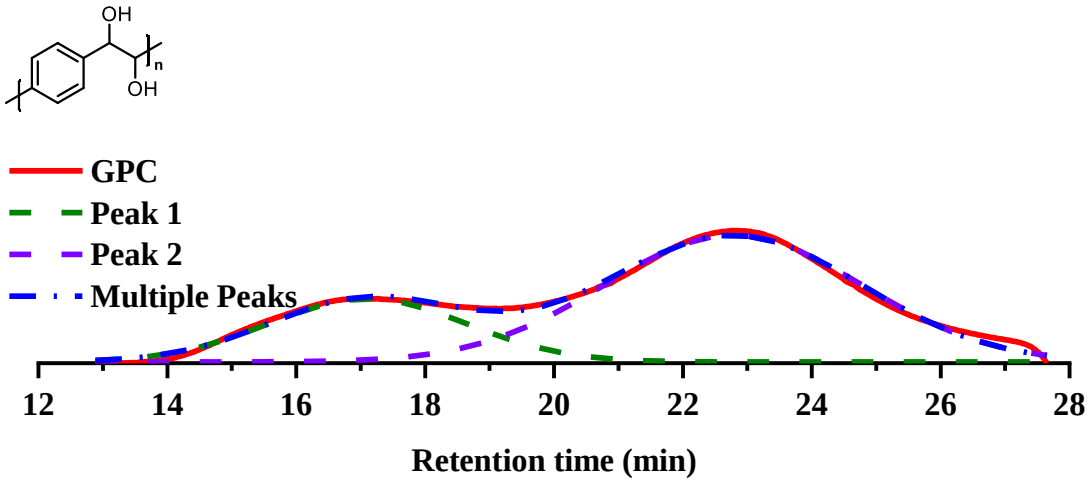


Figure S21. GPC of **poly-1a (From DMSO)**.

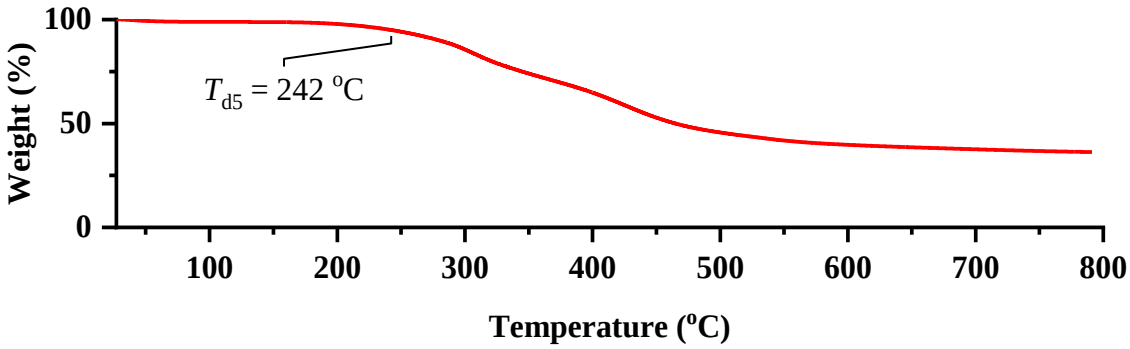


Figure S22. TGA of **poly-1a**.

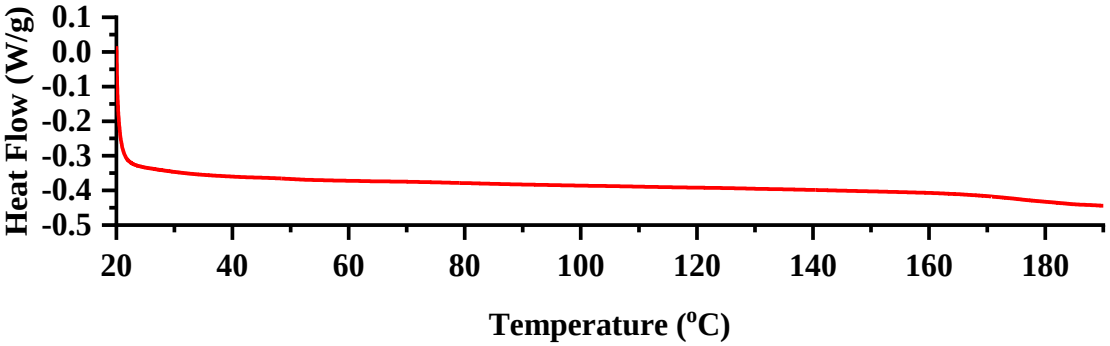


Figure S23. DSC of **poly-1a**.

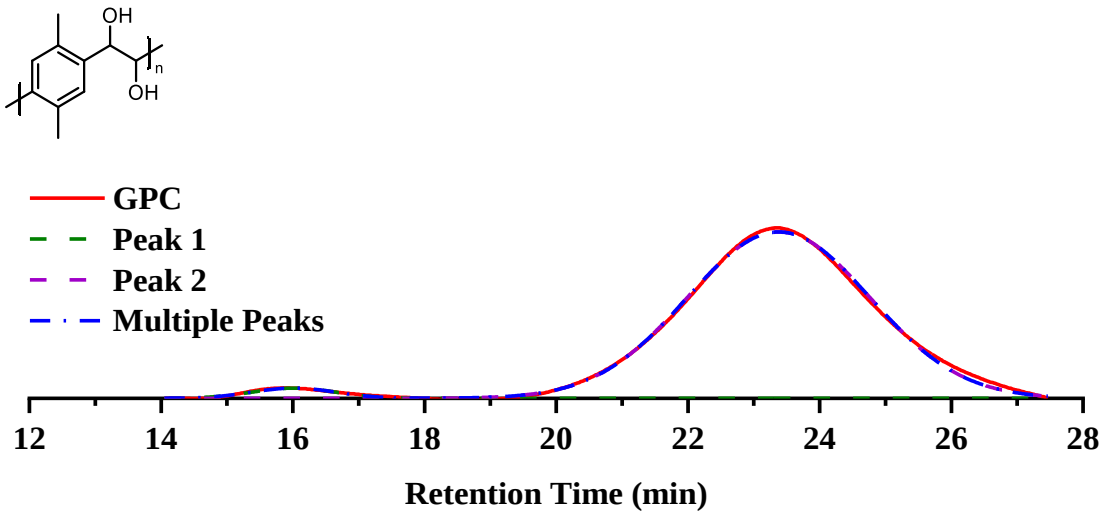


Figure S24. GPC of **poly-1b**.

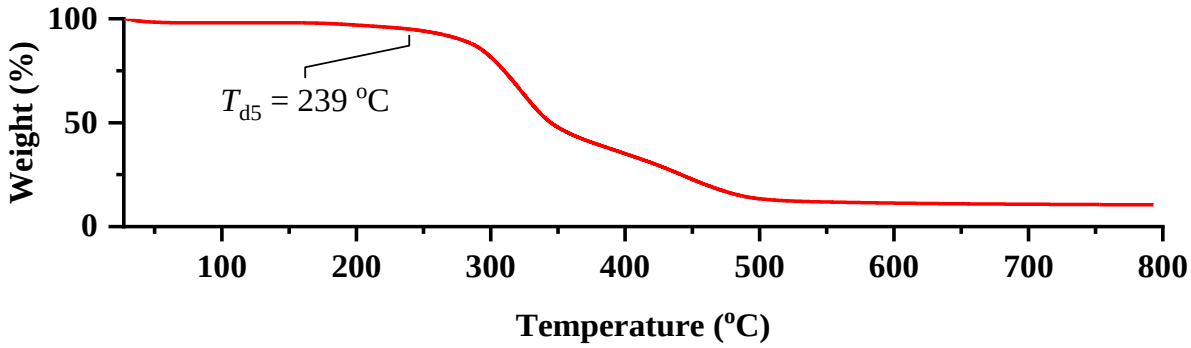


Figure S25. TGA of **poly-1b**.

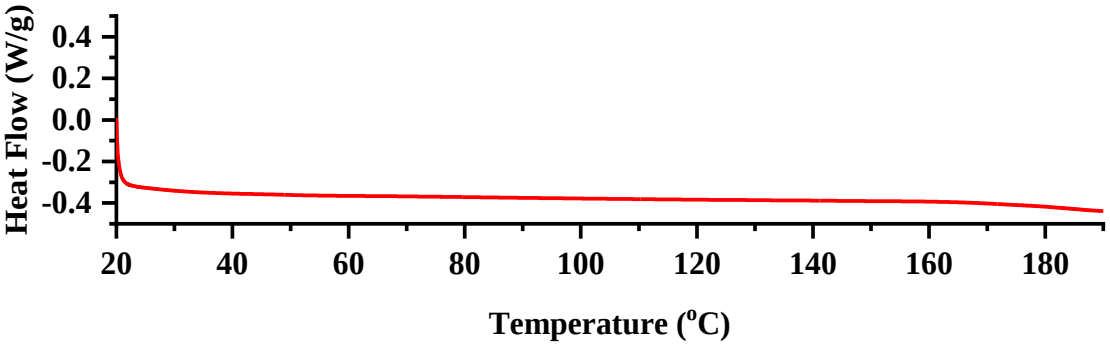


Figure S26. DSC of **poly-1b**.

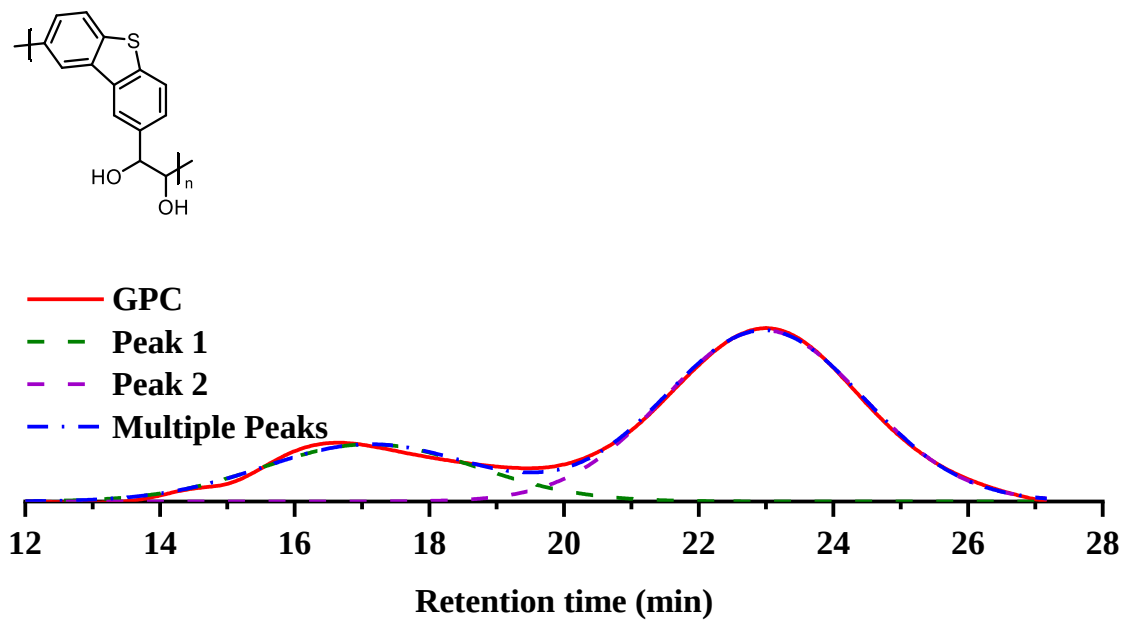


Figure S27. GPC of **poly-1d**.

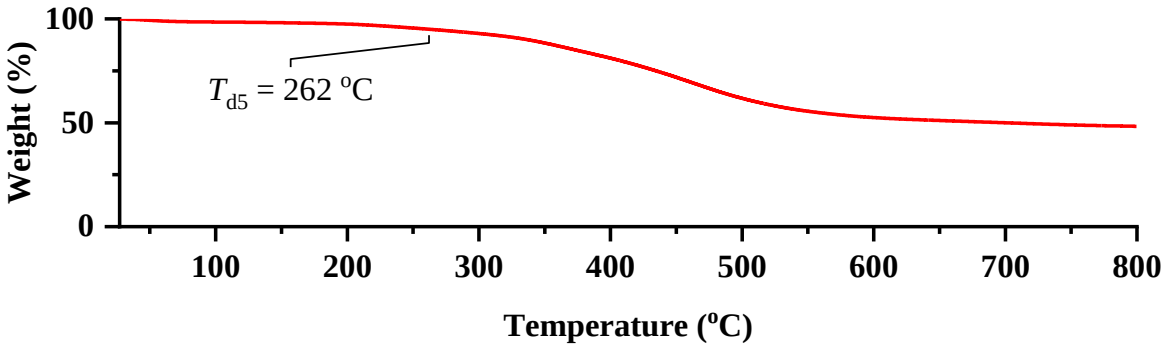


Figure S28. TGA of **poly-1d**.

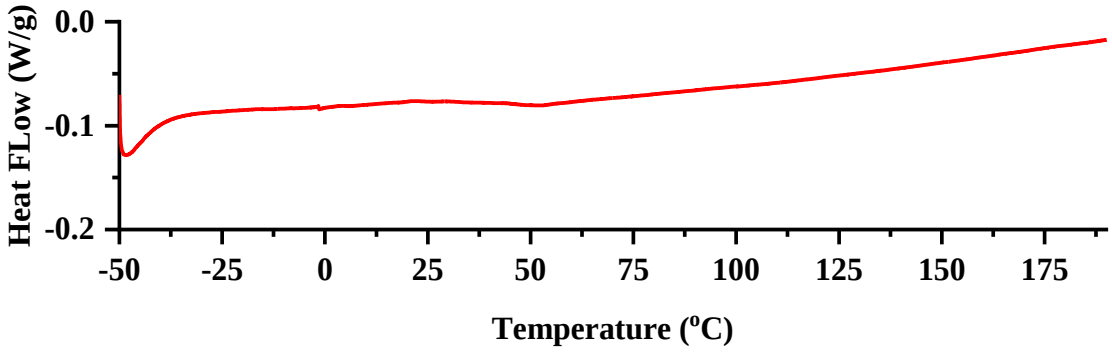


Figure S29. DSC of **poly-1d**.

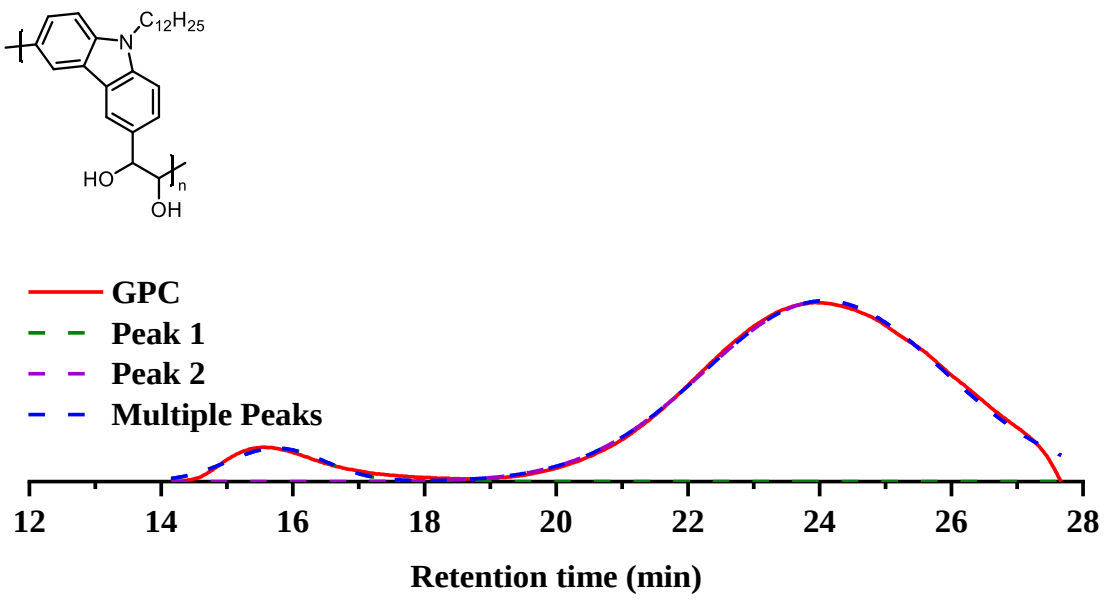


Figure S30. GPC of **poly-1e**.

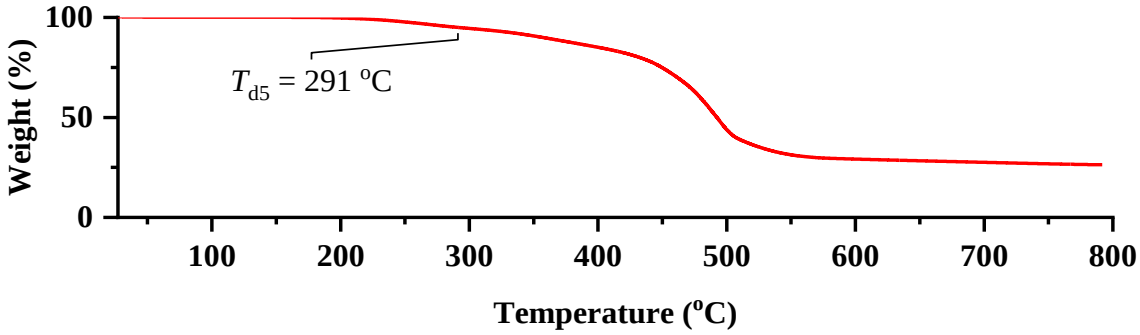


Figure S31. TGA of **poly-1e**.

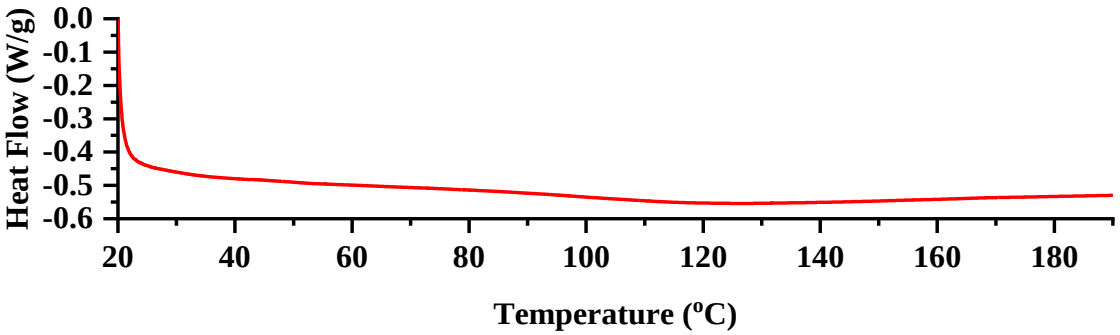


Figure S32. DSC of **poly-1e**.

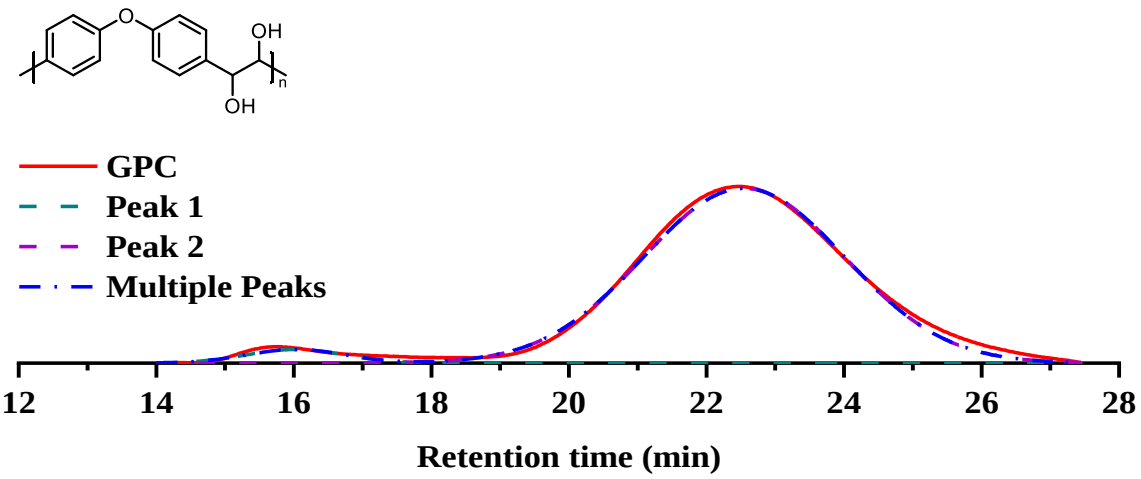


Figure S33. GPC of **poly-1f**.

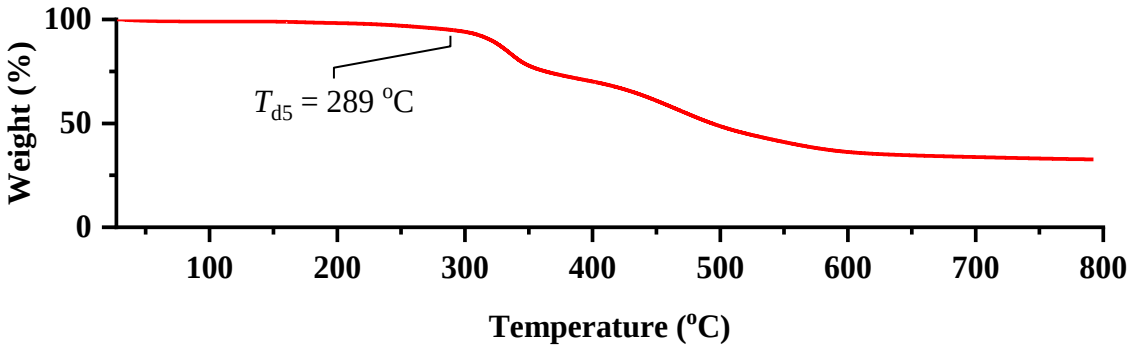


Figure S34. TGA of **poly-1f**.

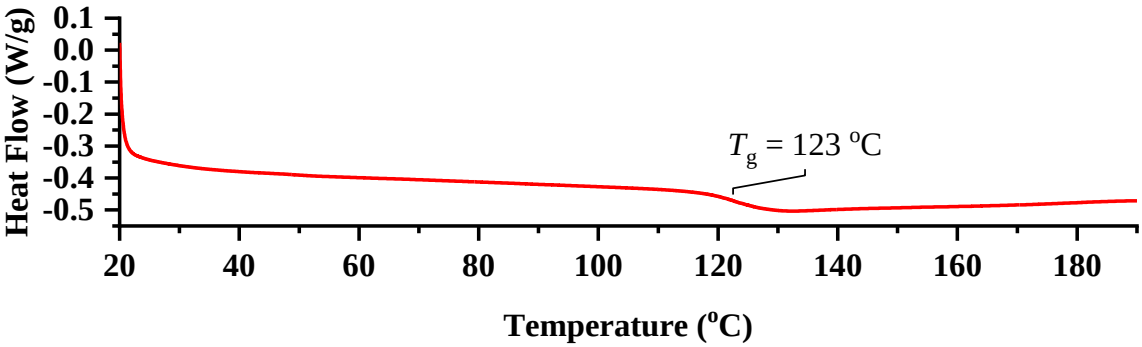


Figure S35. DSC of **poly-1f**

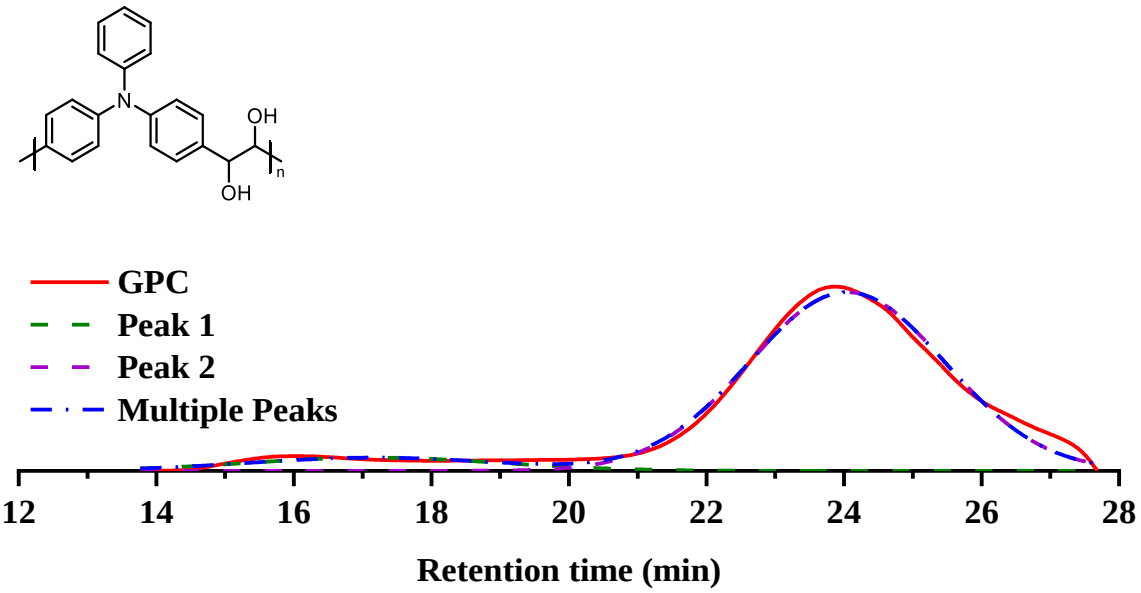


Figure S36. GPC of **poly-1g**.

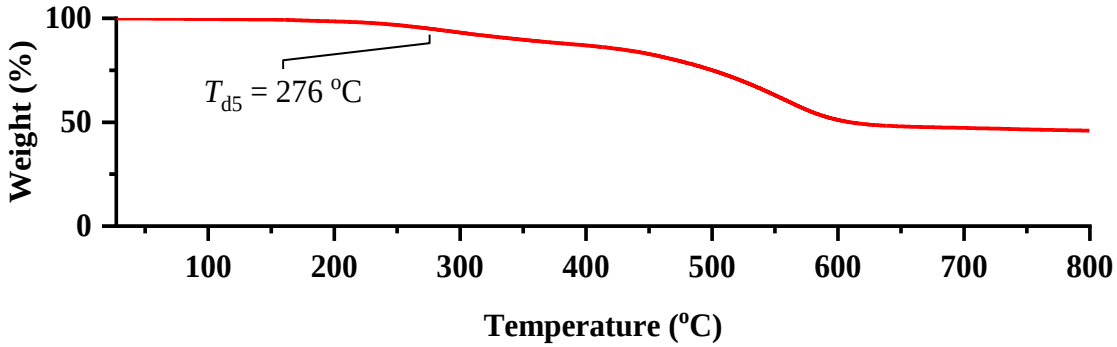


Figure S37. TGA of **poly-1g**.

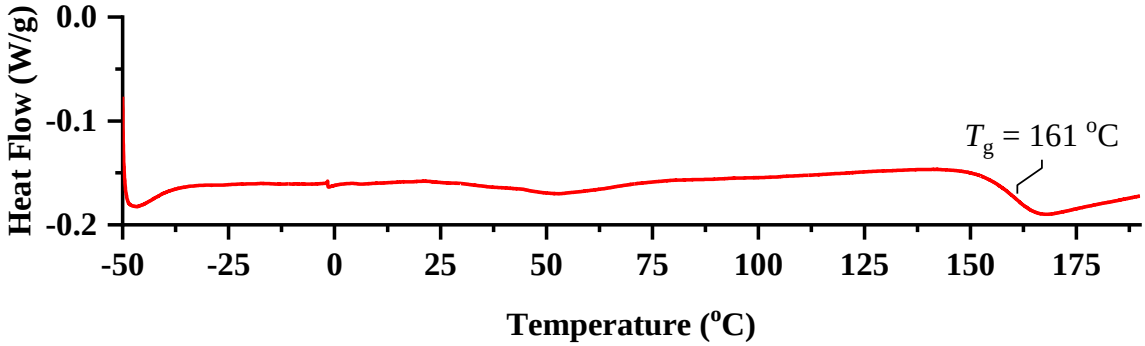


Figure S38. DSC of **poly-1g**.

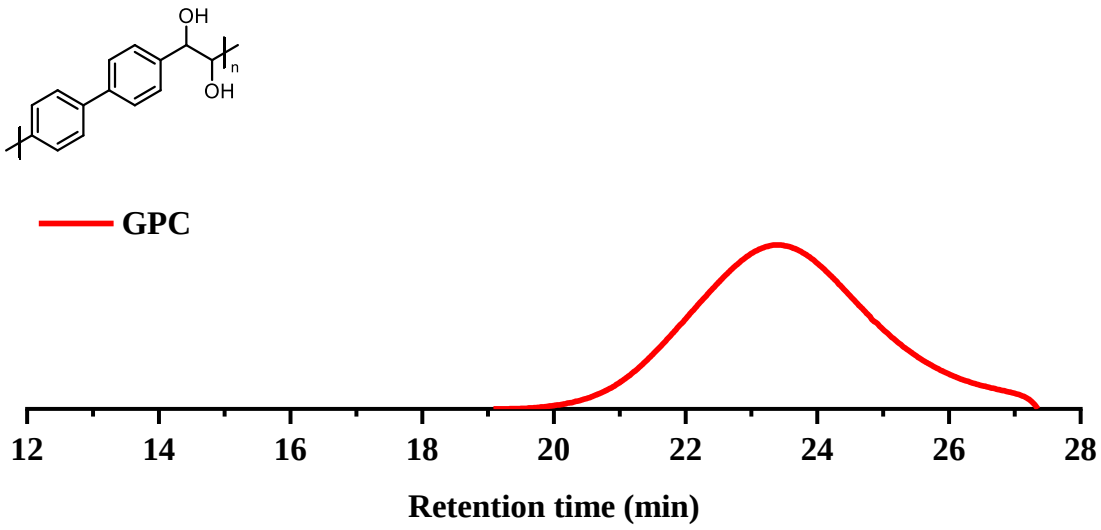


Figure S39. GPC of **poly-1h**.

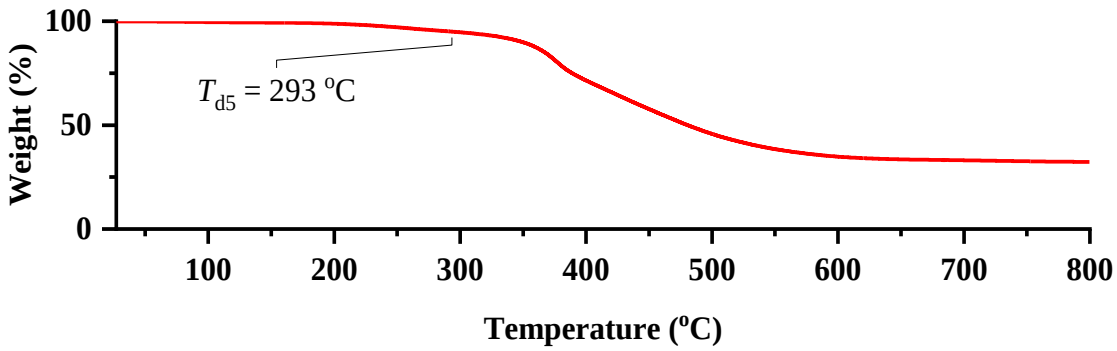


Figure S40. TGA of **poly-1h**.

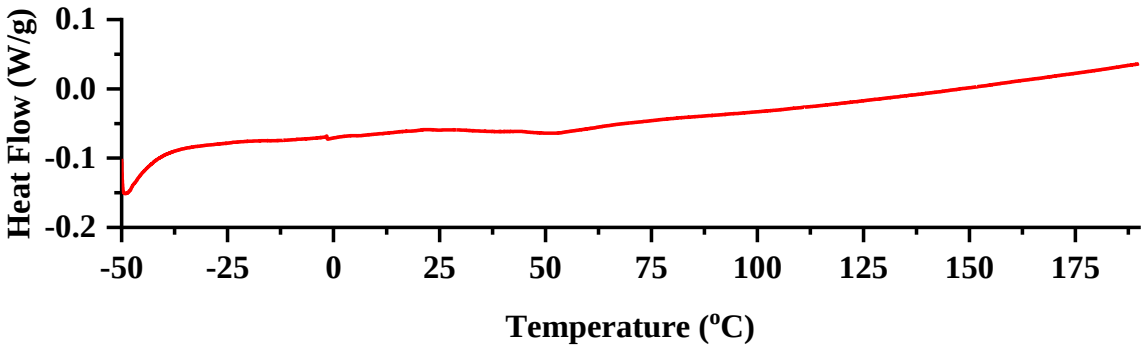


Figure S41. DSC of **poly-1h**.

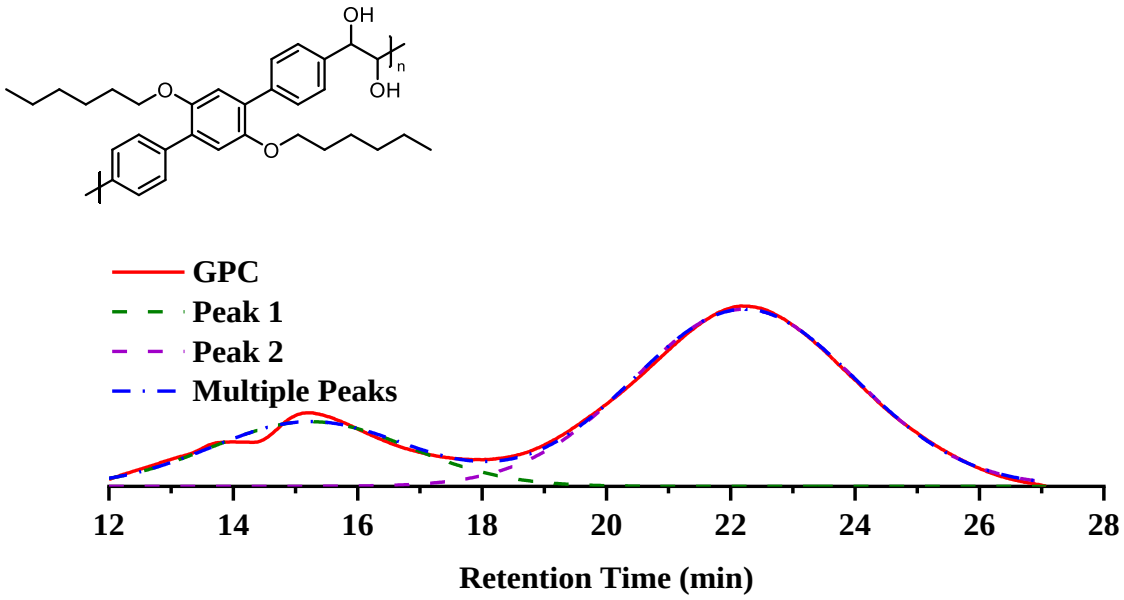


Figure S42. GPC of **poly-1i**.

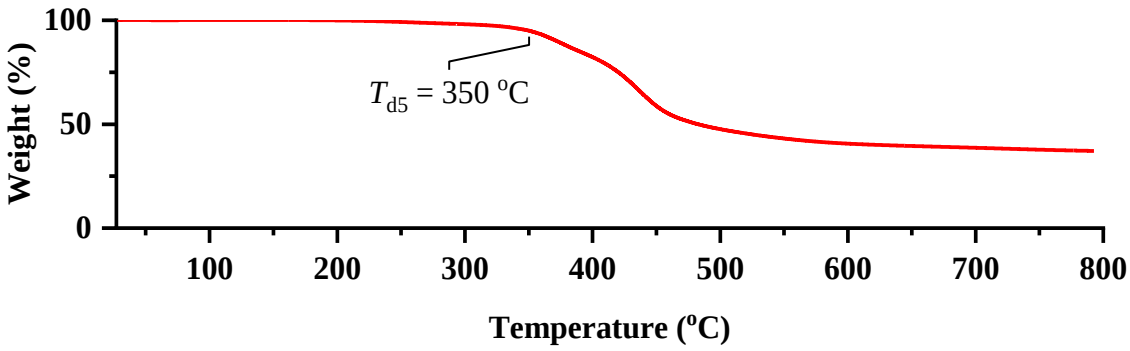


Figure S43. GPC of **poly-1i**.

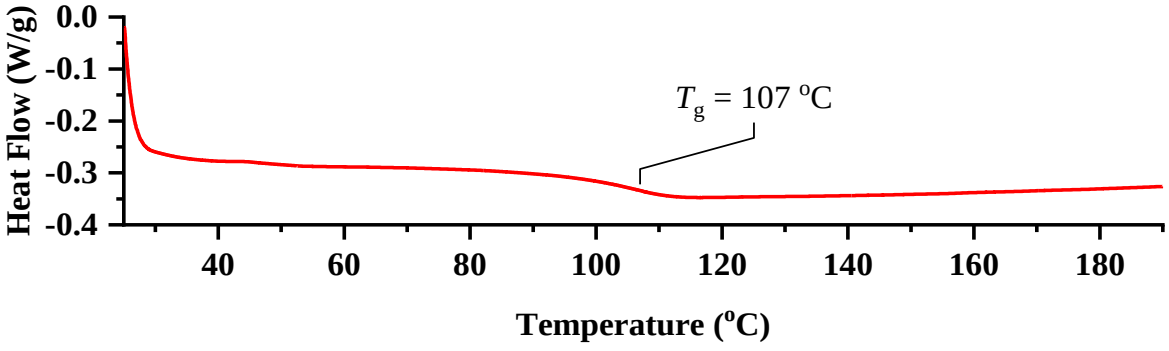


Figure S44. DSC of **poly-1i**.

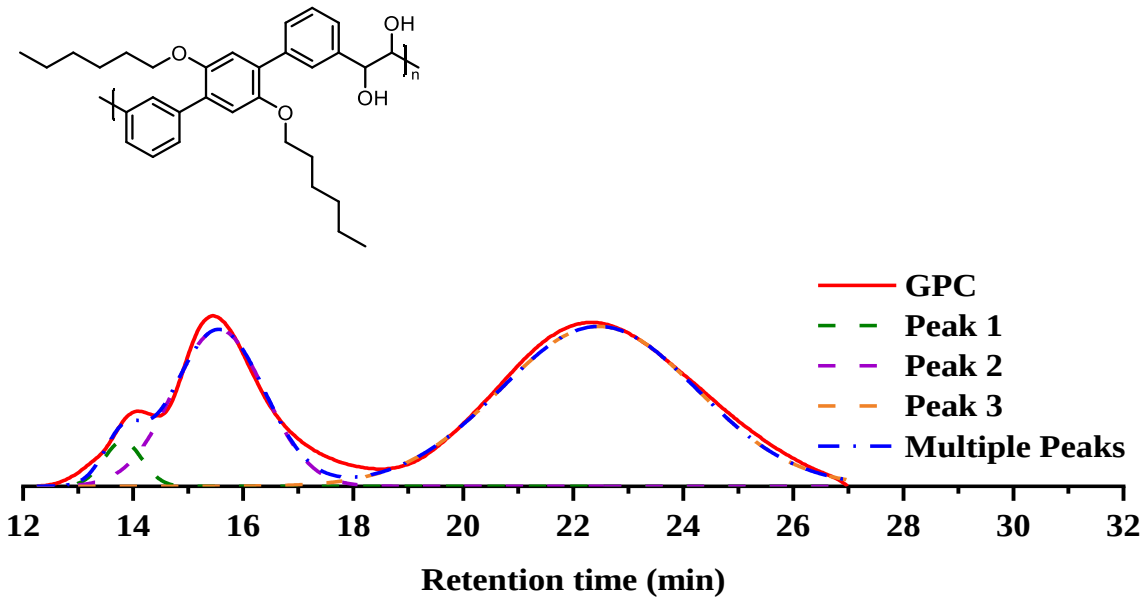


Figure S45. GPC of **poly-1j**.

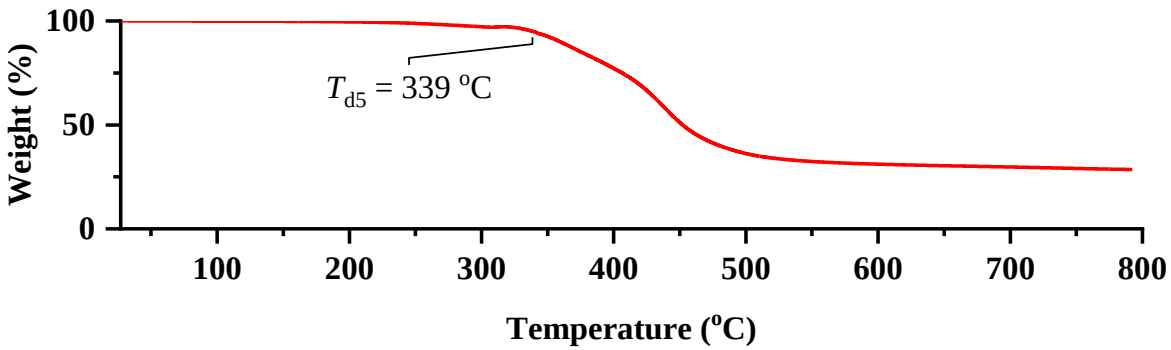


Figure S46. TGA of **poly-1j**.

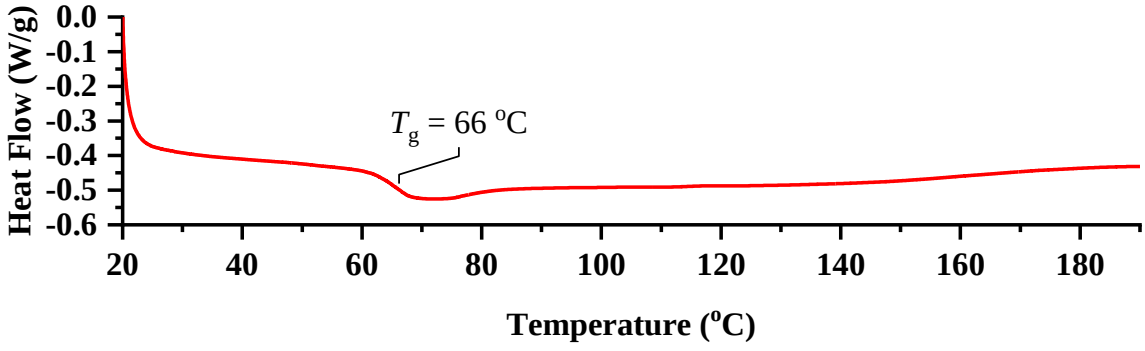


Figure S47. DSC of **poly-1j**.

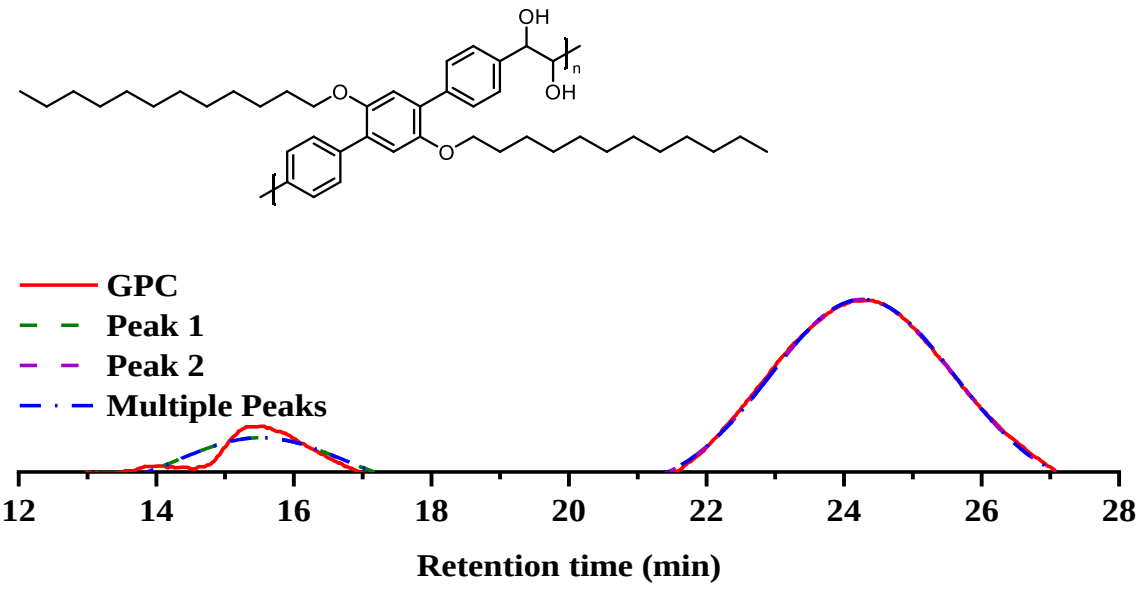


Figure S48. GPC of **poly-1k**.

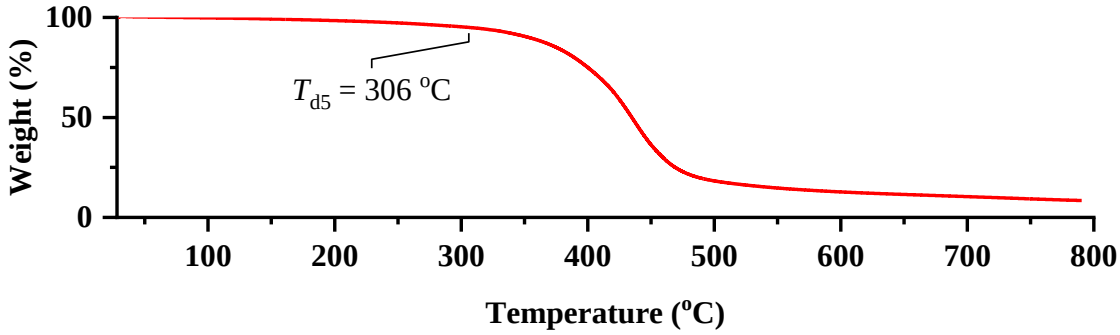


Figure S49. TGA of **poly-1k.**

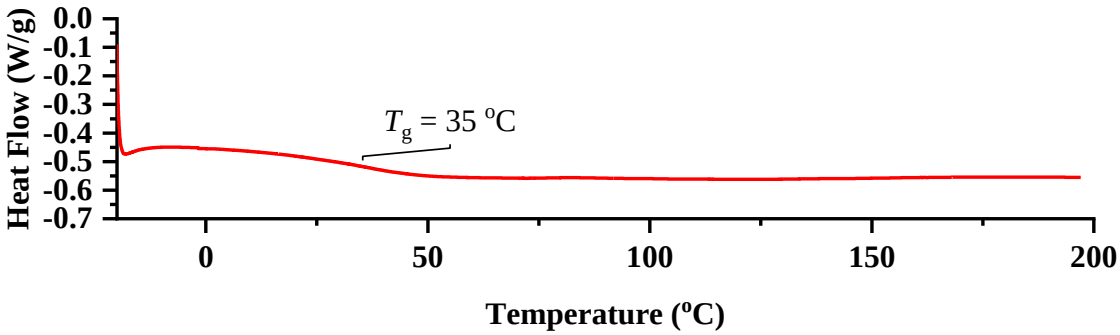


Figure S50. DSC of **poly-1k.**

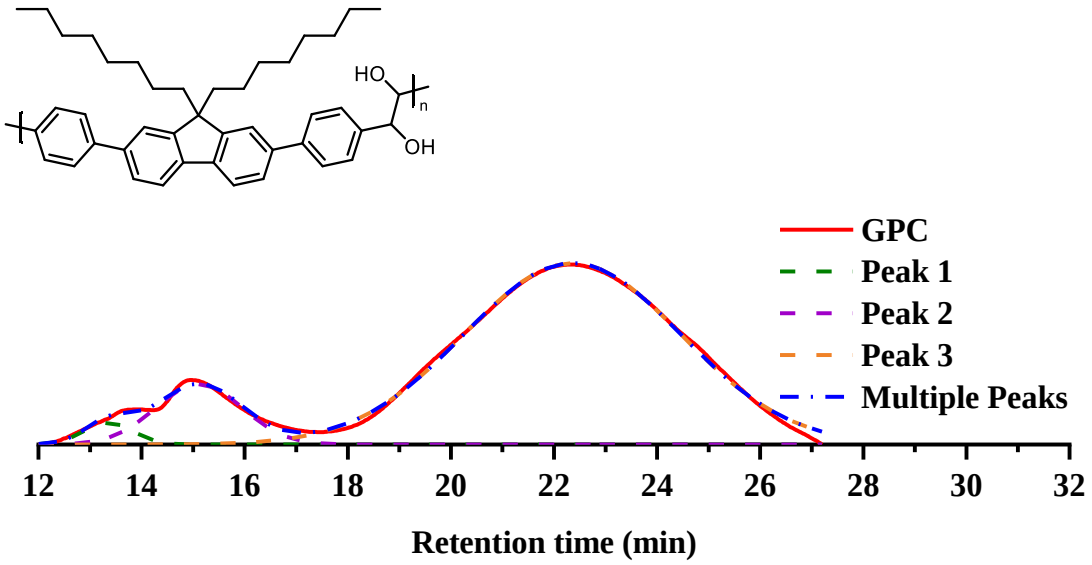


Figure S51. GPC of **poly-1l**.

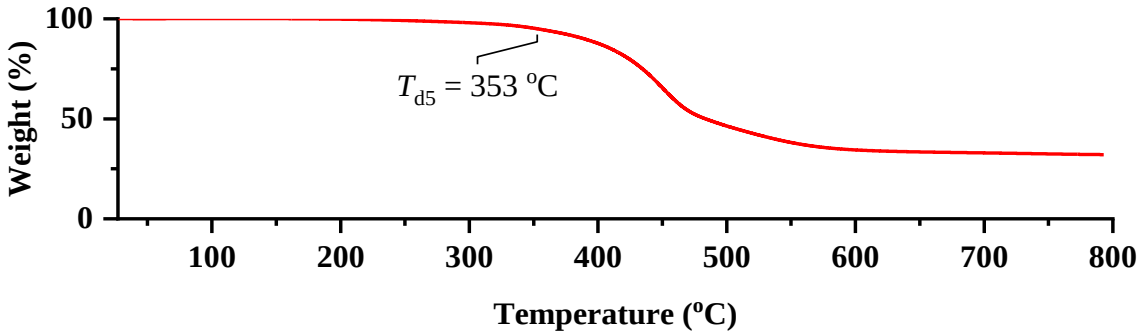


Figure S52. TGA of **poly-1l**.

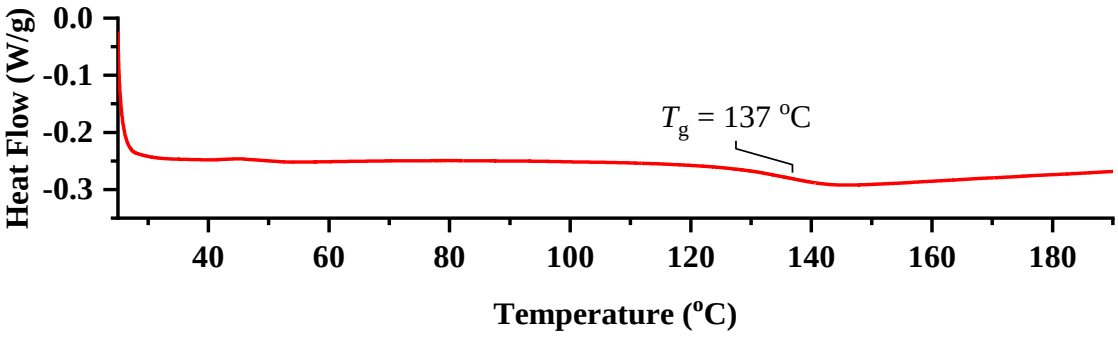


Figure S53. DSC of **poly-1l**.

13. NMR spectra

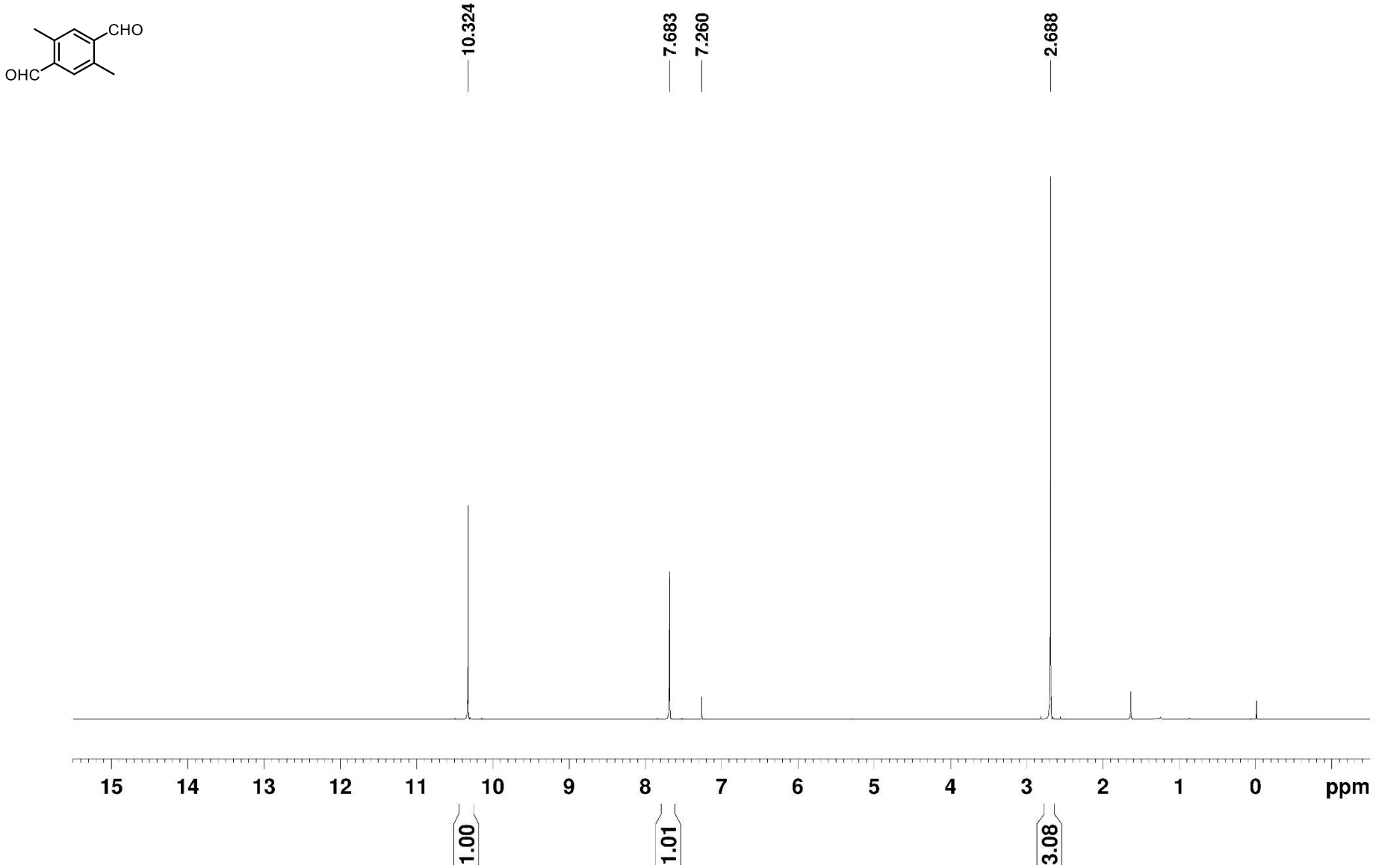


Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) of **1b**.

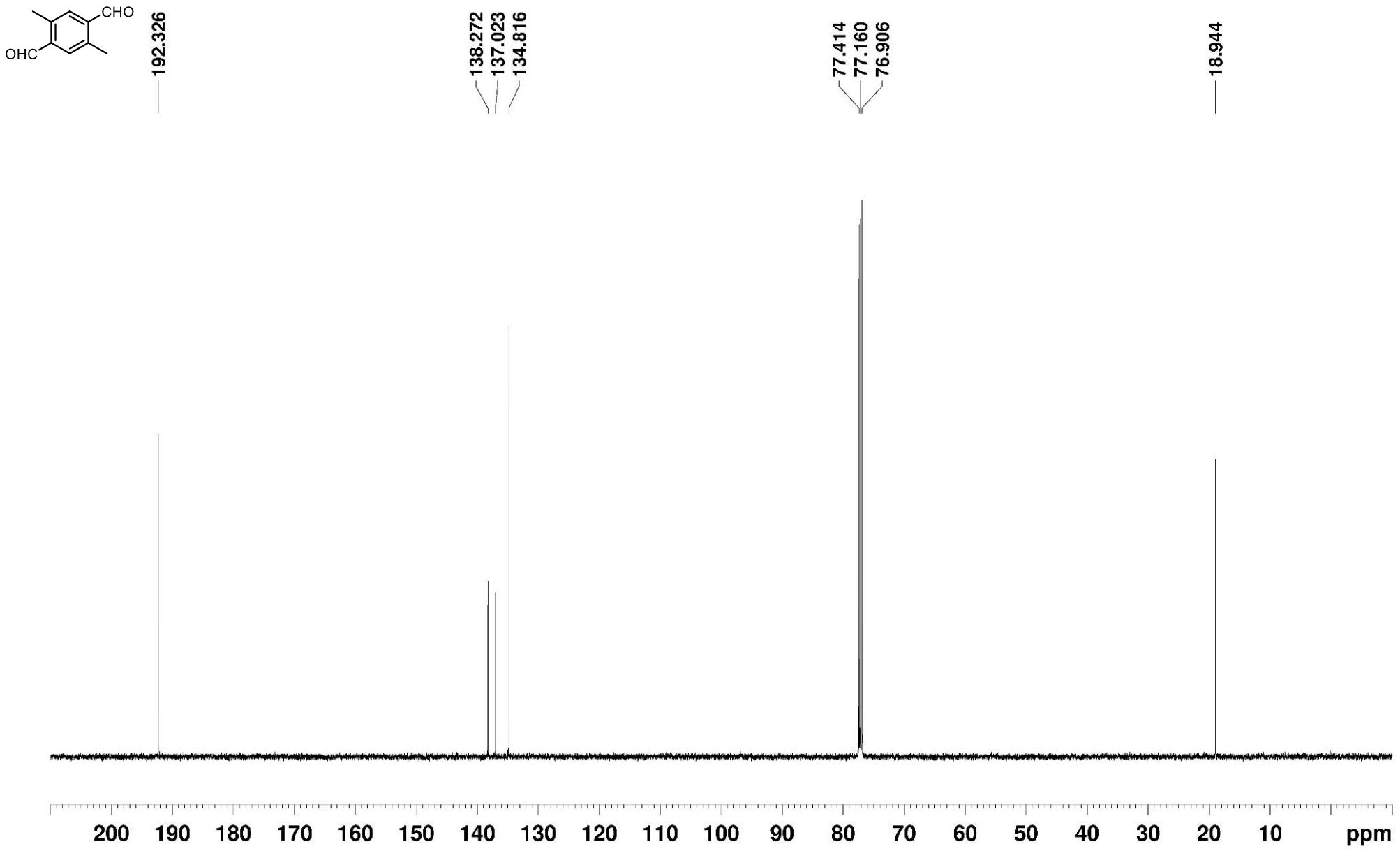


Figure S55. ^{13}C NMR (125 MHz, $CDCl_3$) of **1b**.

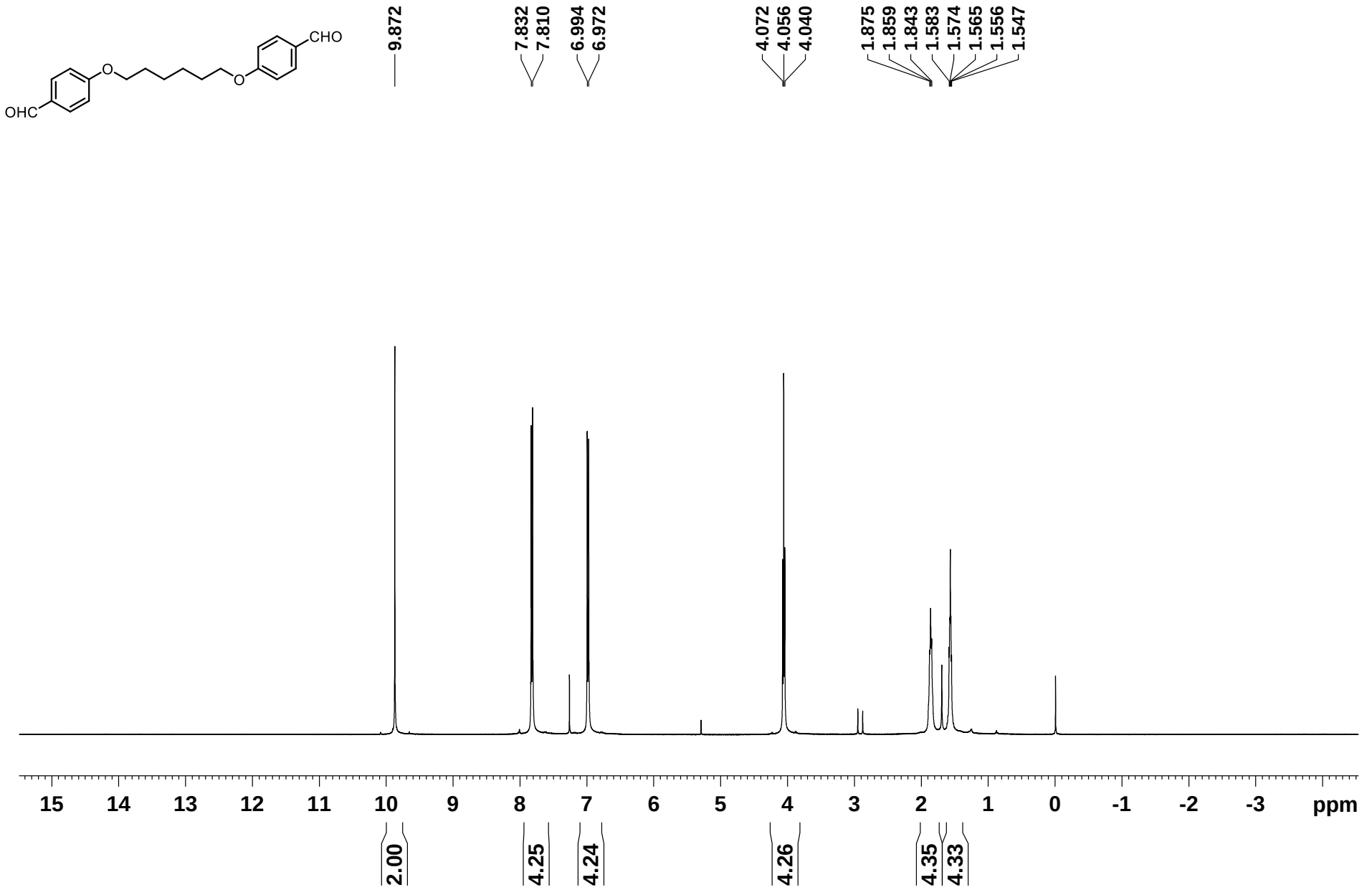


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) of **1c**.

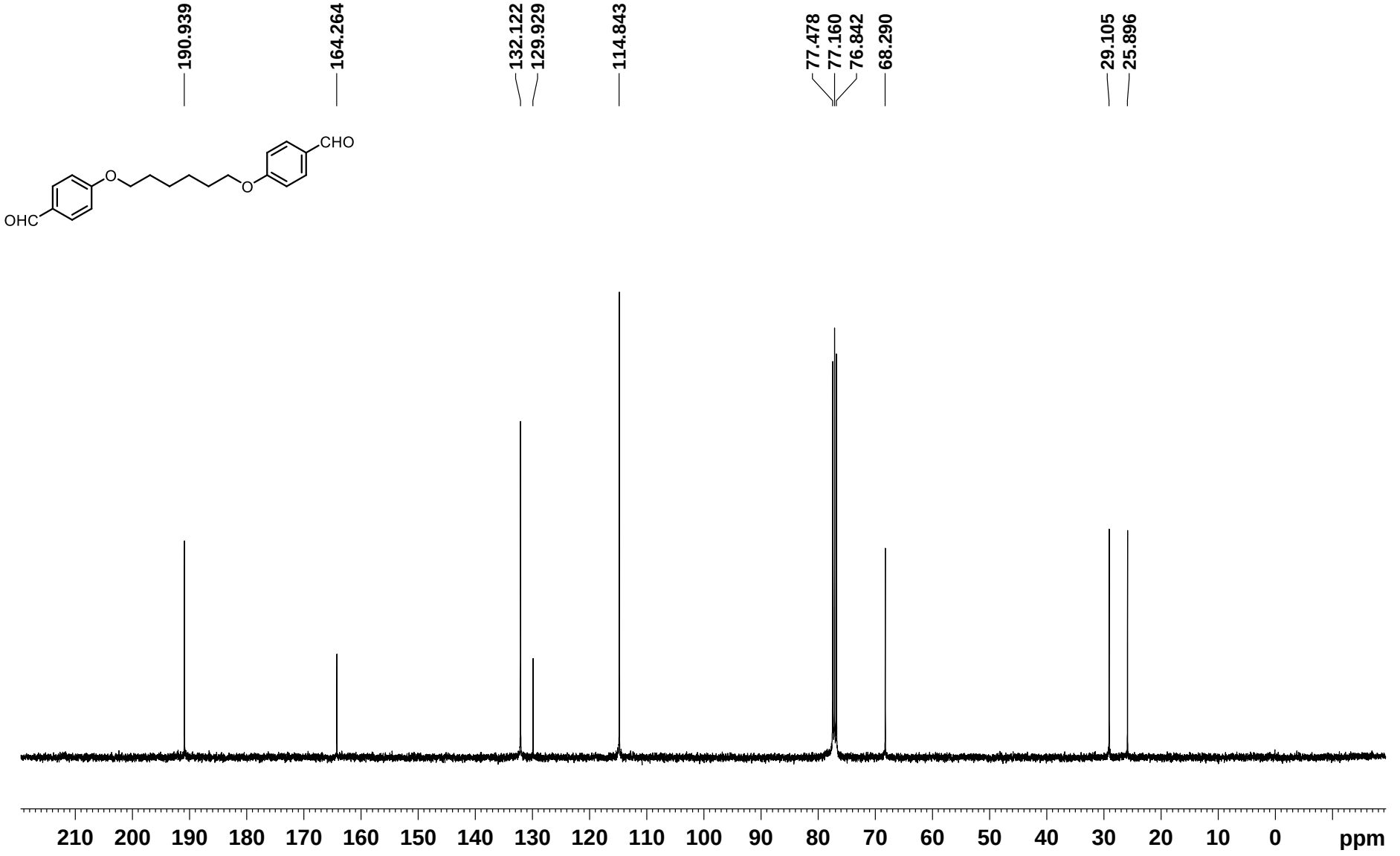


Figure S57. ^{13}C NMR (100 MHz, $CDCl_3$) of **1c**.

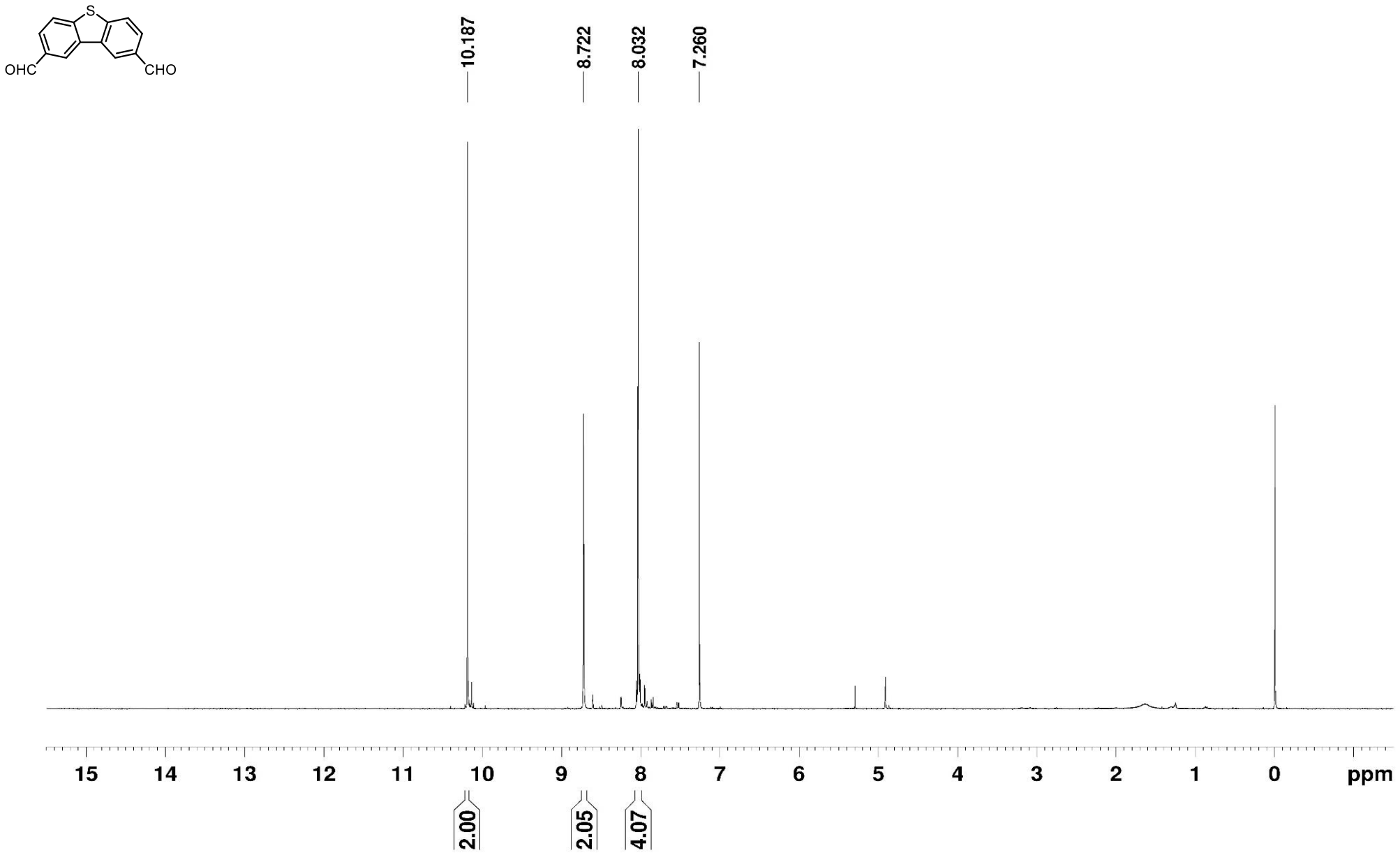


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) of **1d**.

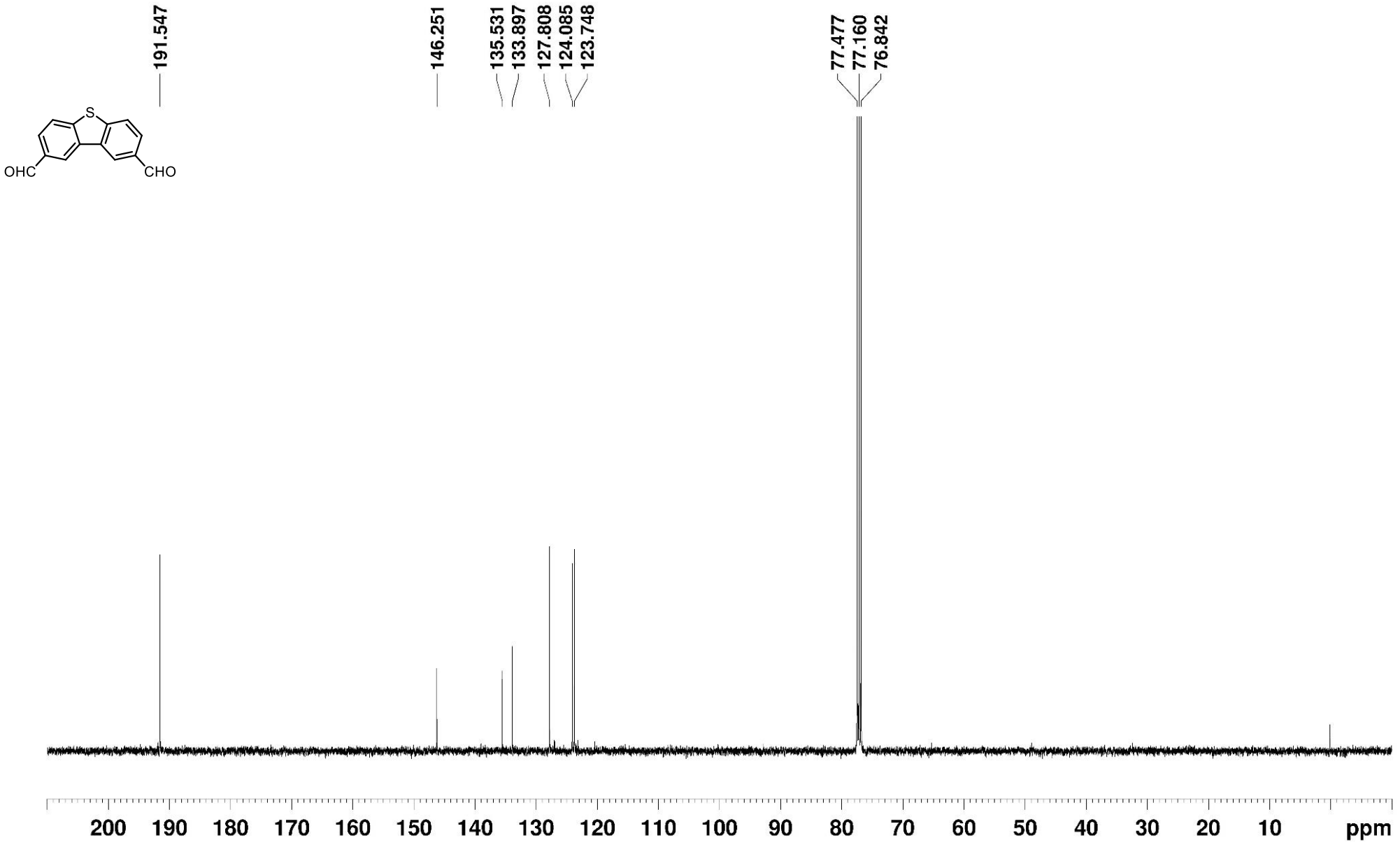


Figure S59. ^{13}C NMR (100 MHz, $CDCl_3$) of **1d**.

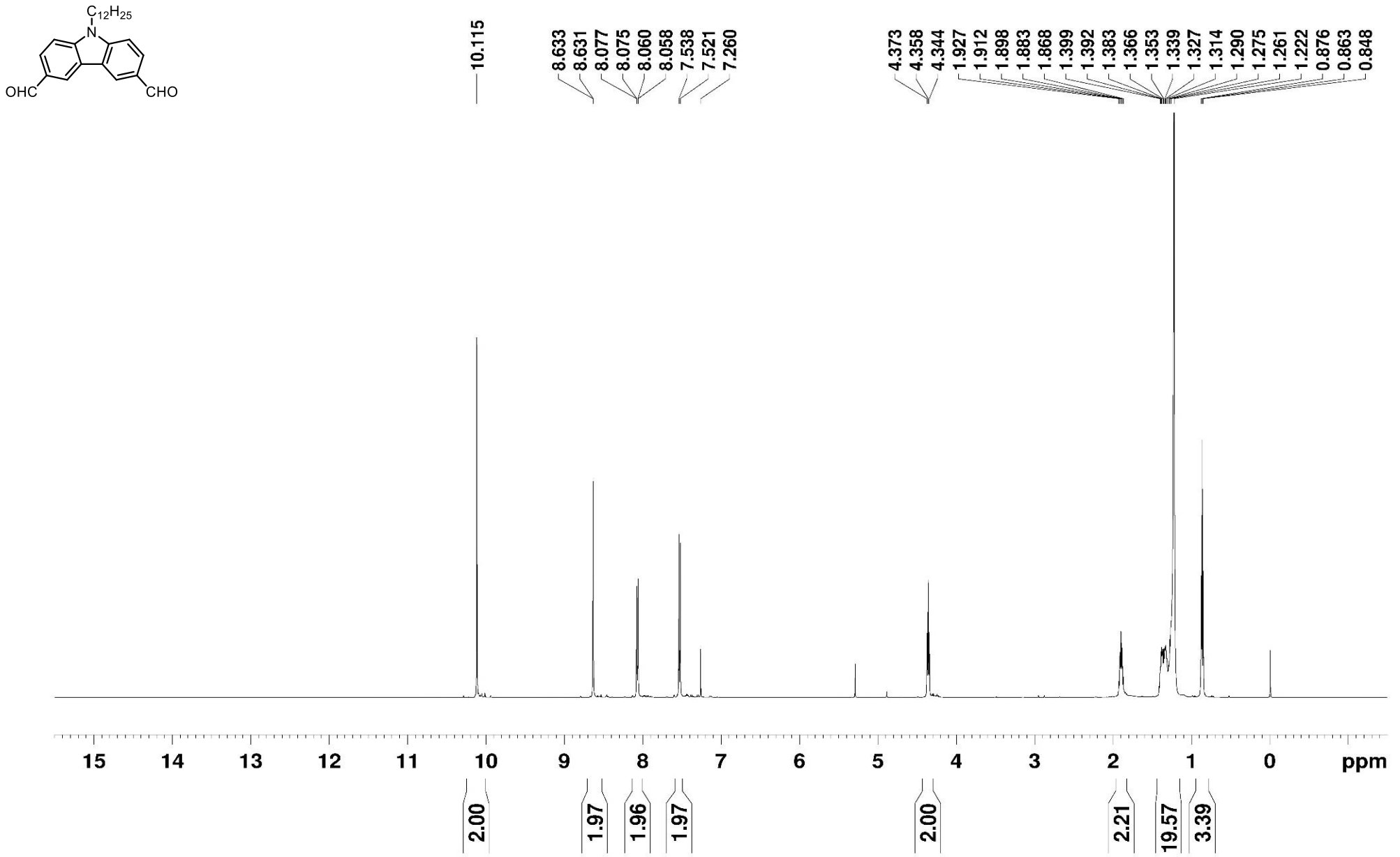


Figure S60. ^{1}H NMR (500 MHz, $CDCl_3$) of **1e**.

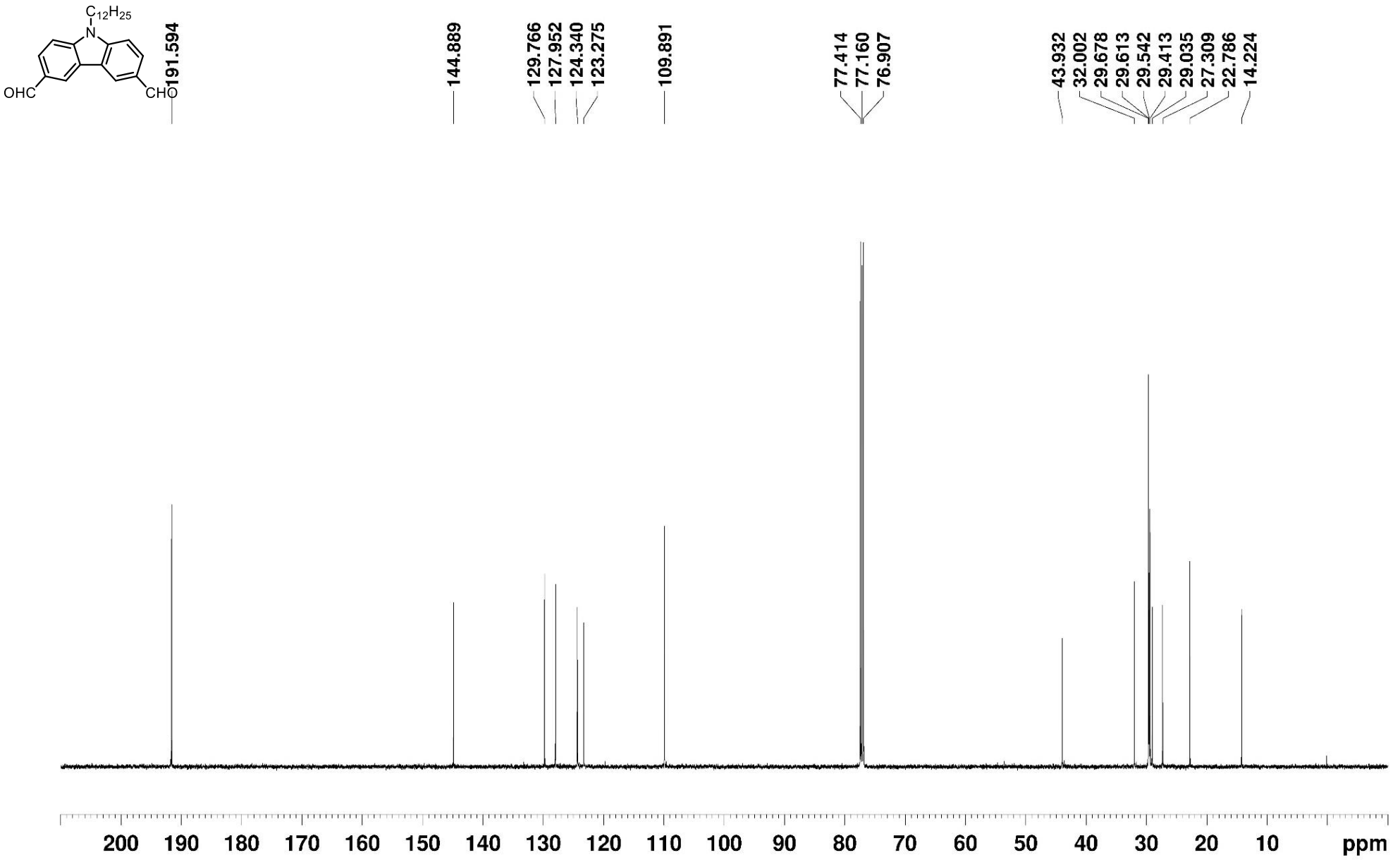


Figure S61. ^{13}C NMR (125 MHz, $CDCl_3$) of **1e**.

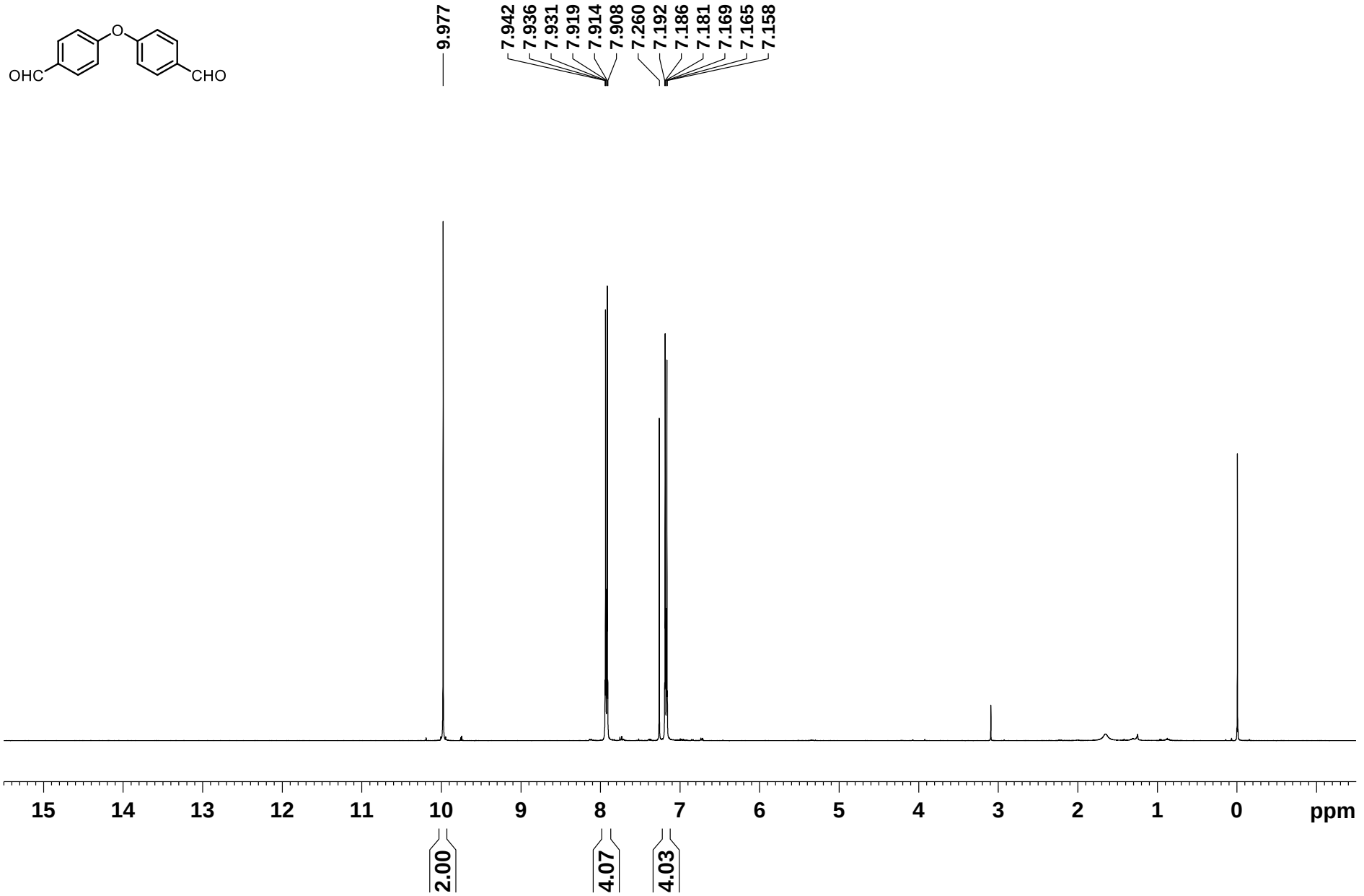


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of **1f**.

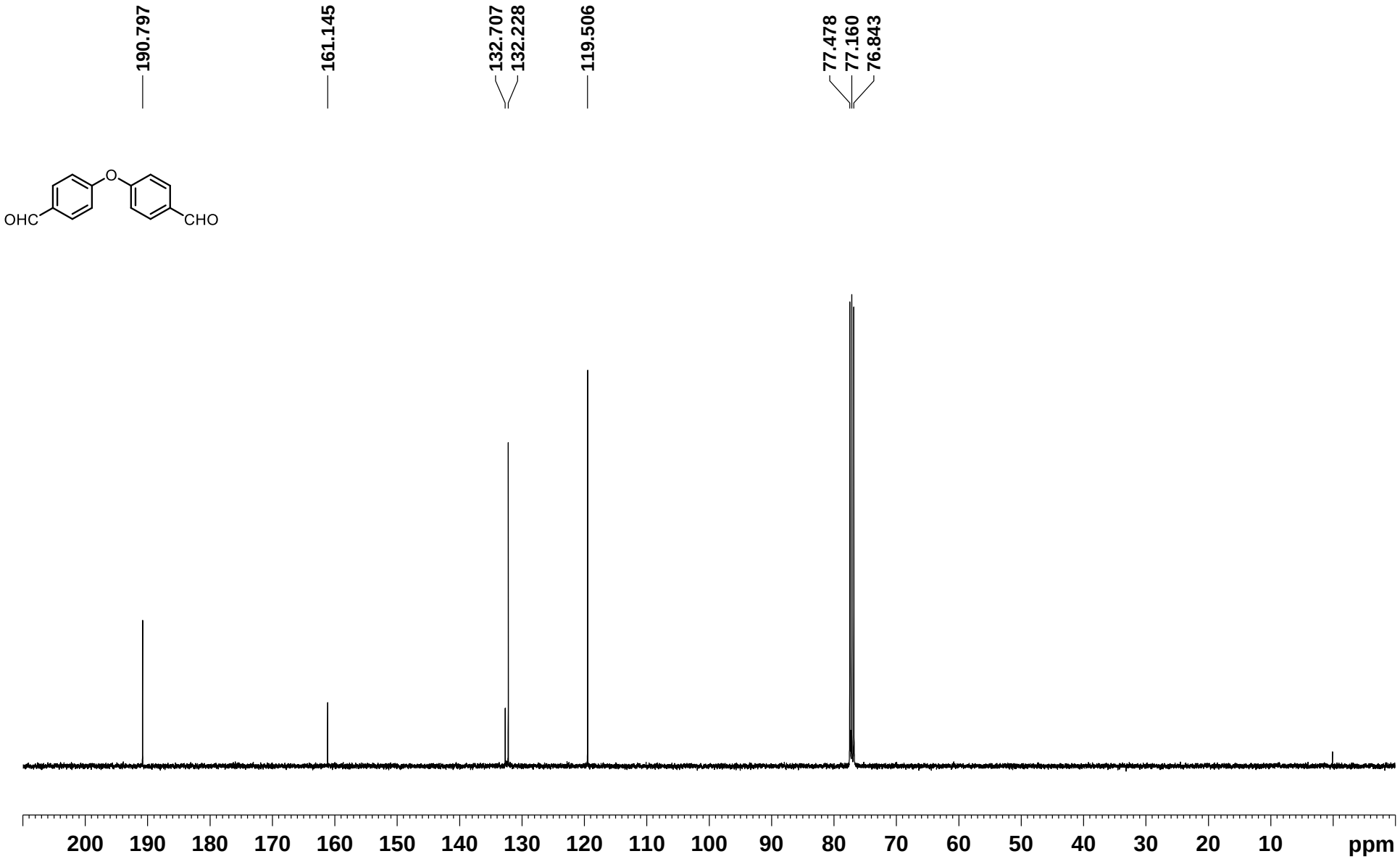


Figure S63. ^{13}C NMR (100 MHz, $CDCl_3$) of **1f**.

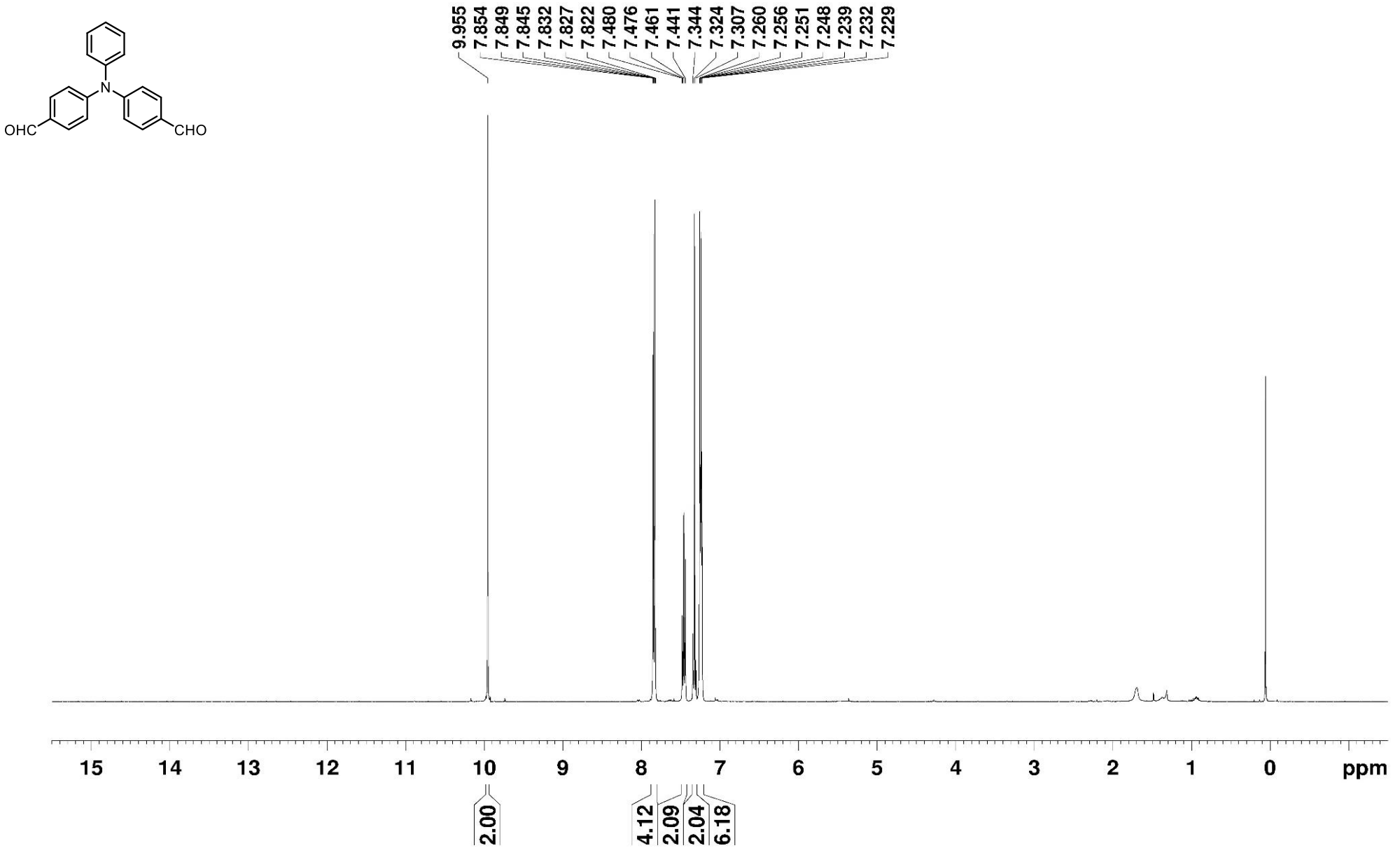


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of **1g**.

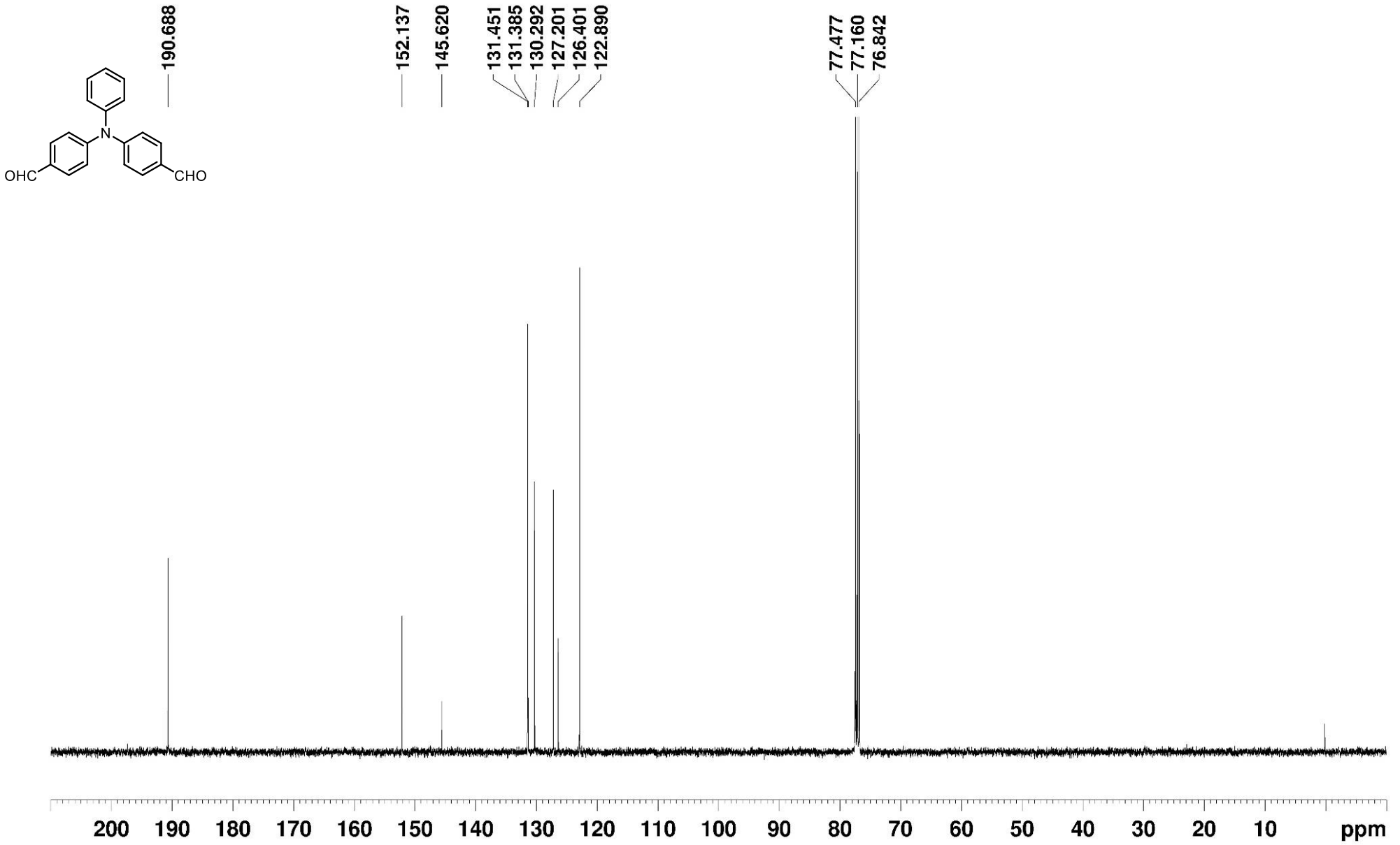


Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) of **1g**.

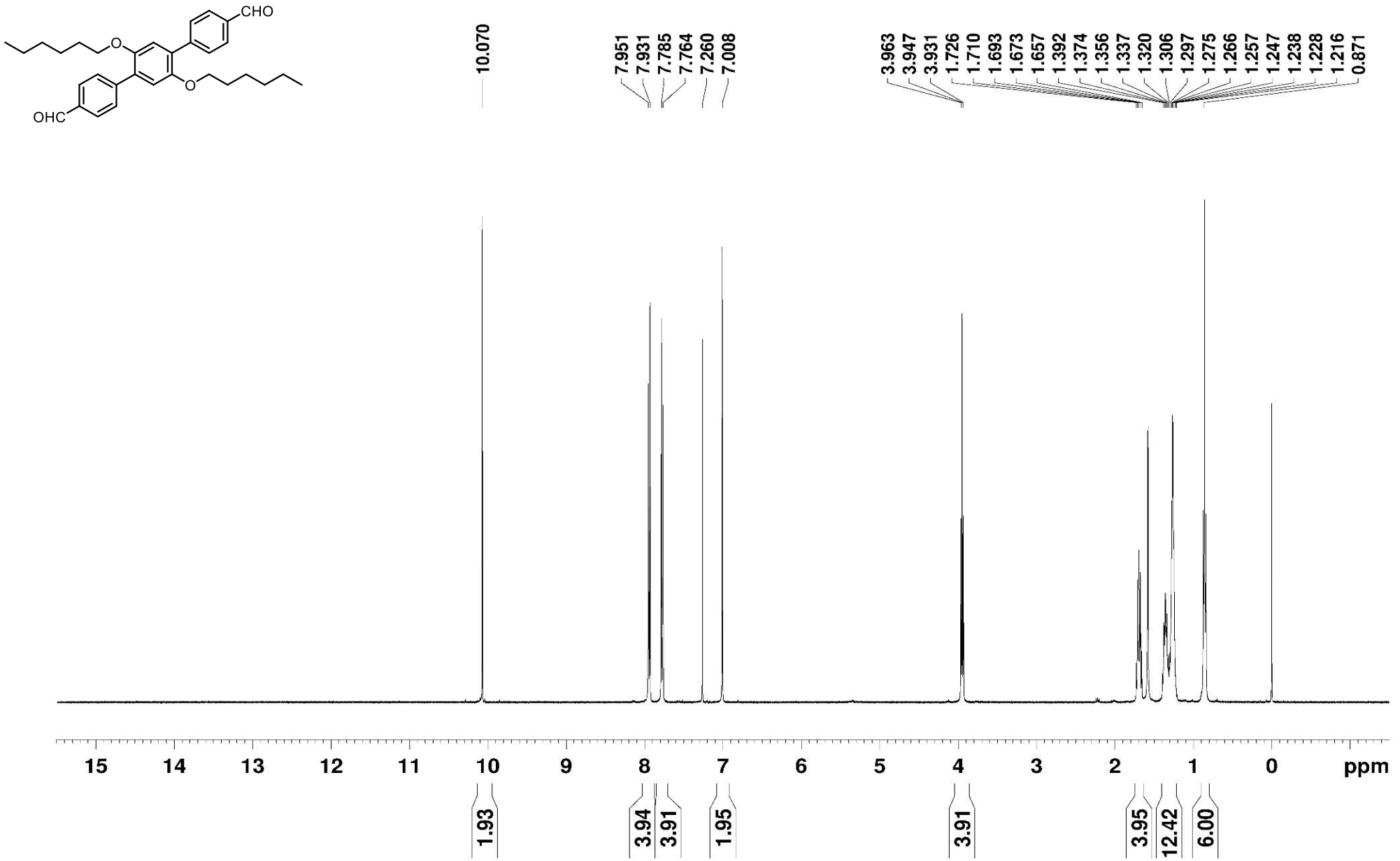


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of **1i**.

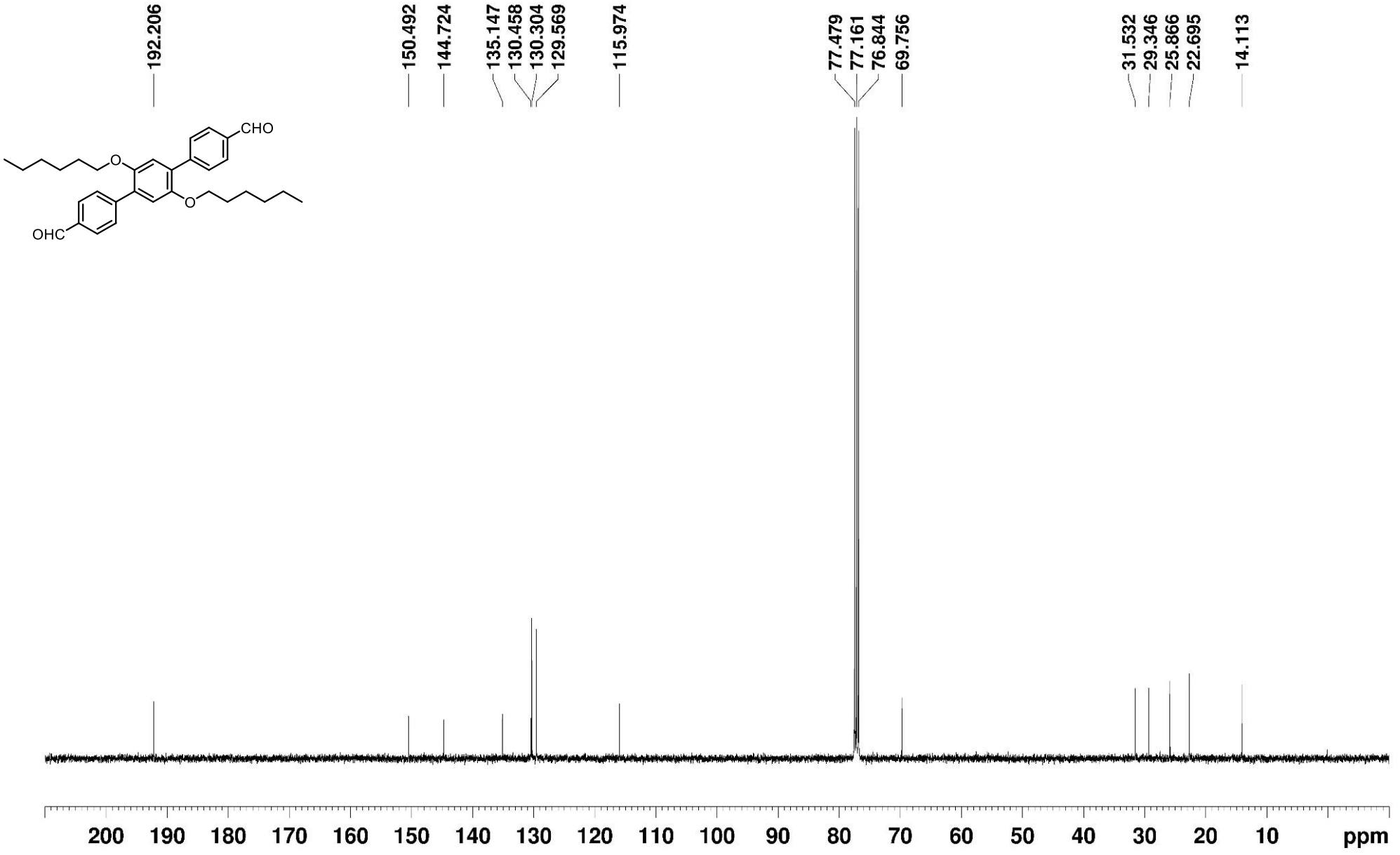


Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) of **1i**.

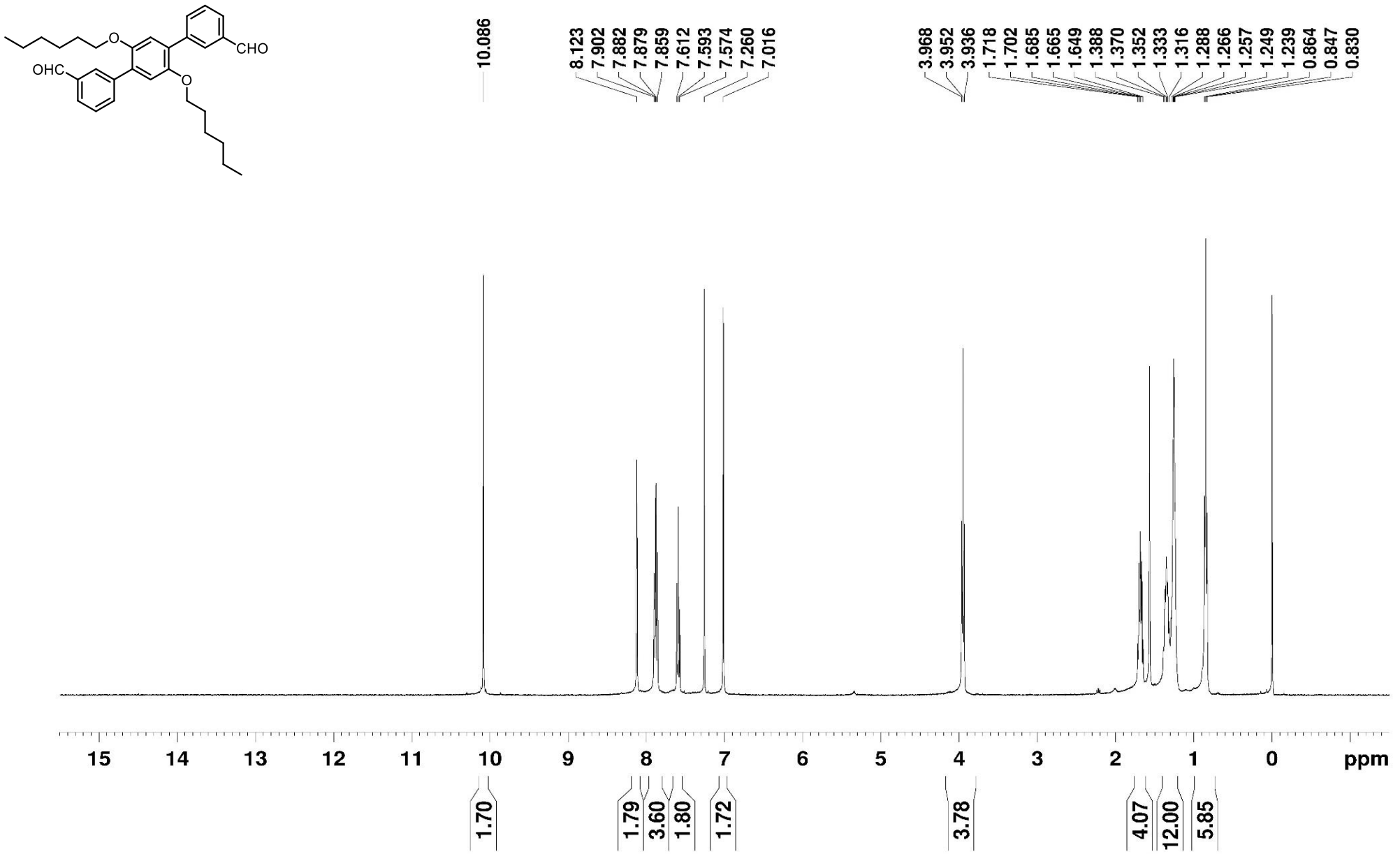


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of **1j**.

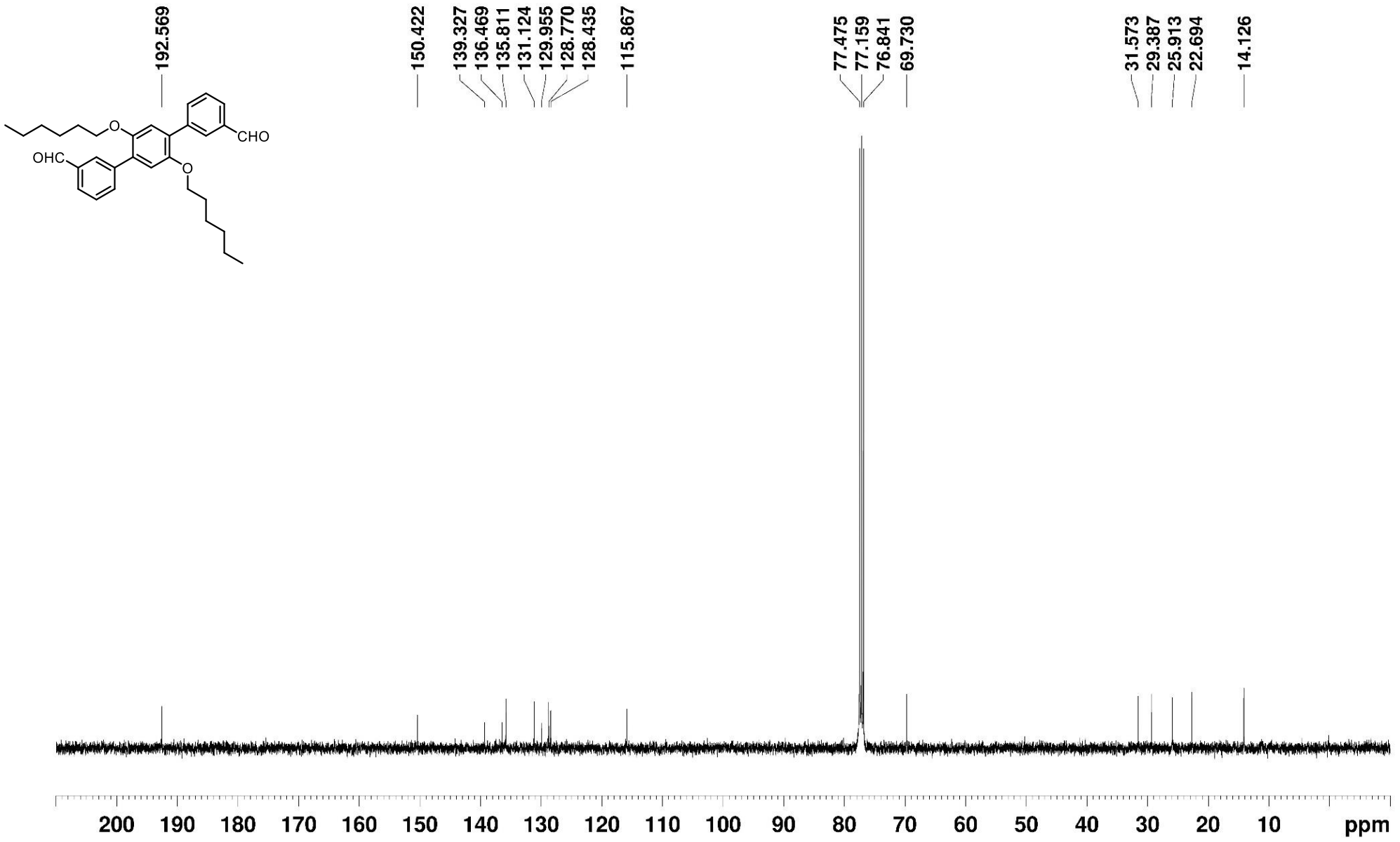


Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) of **1j**.

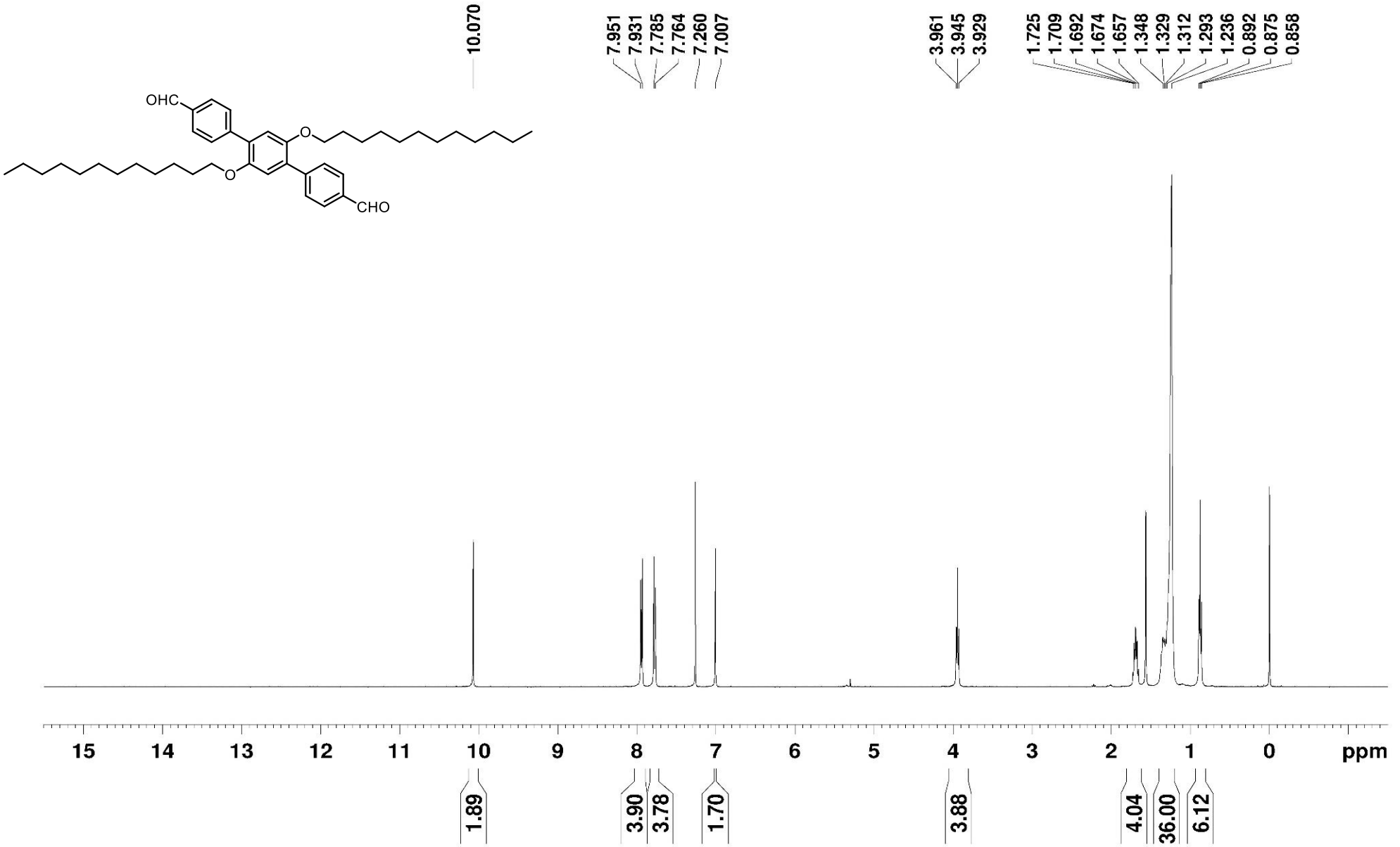


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of **1k**.

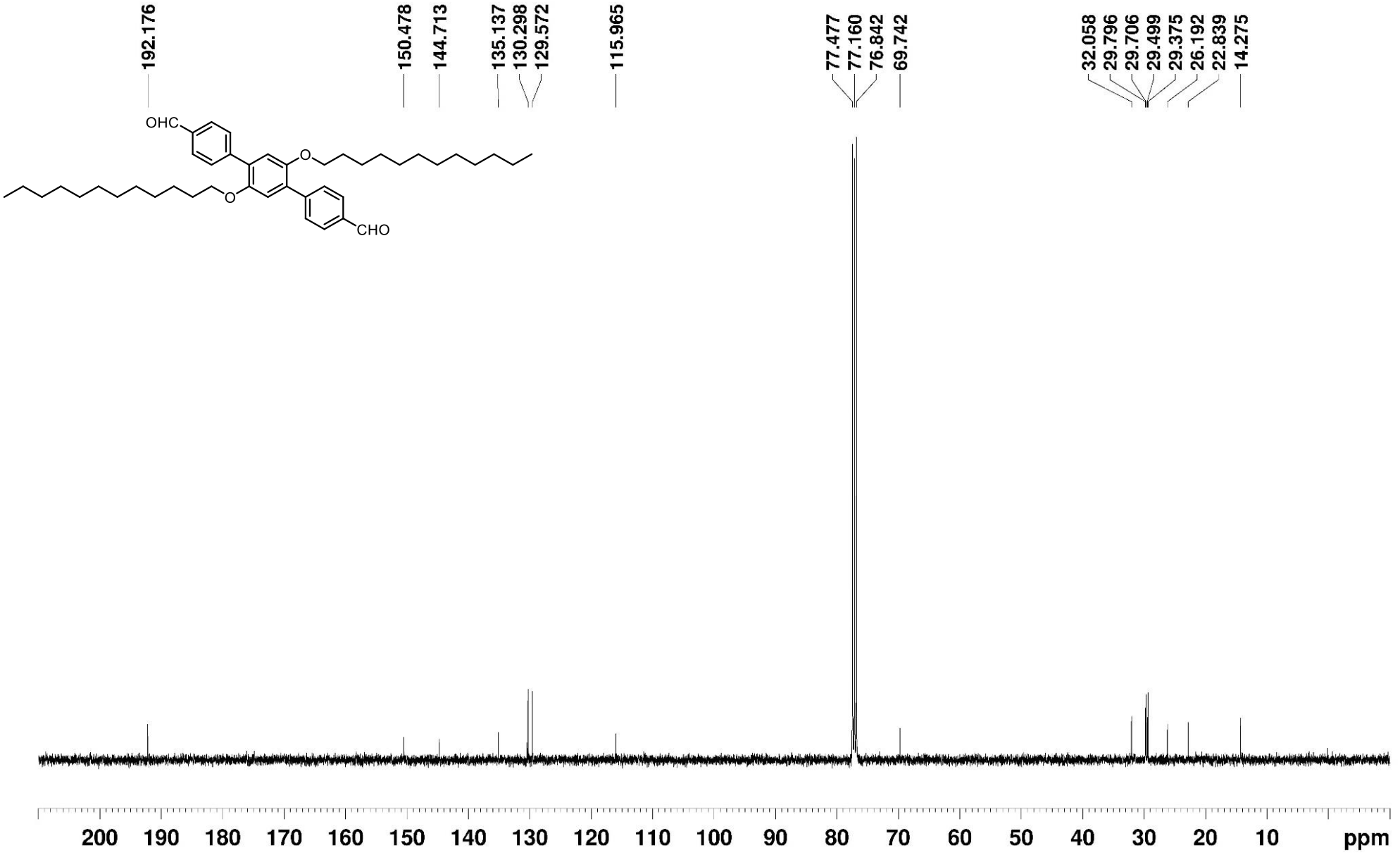


Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) of **1k**.

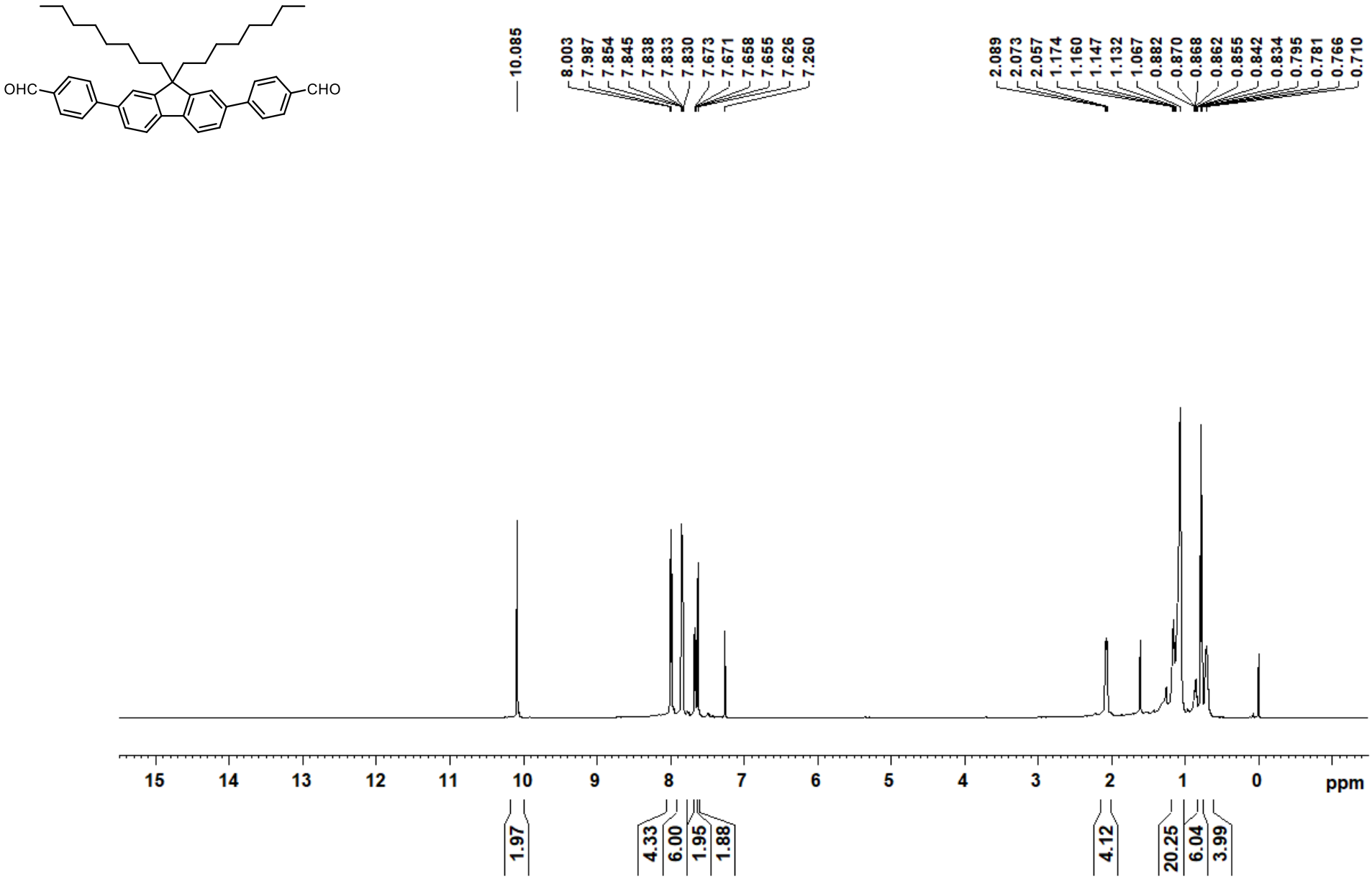


Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) of **1l**.

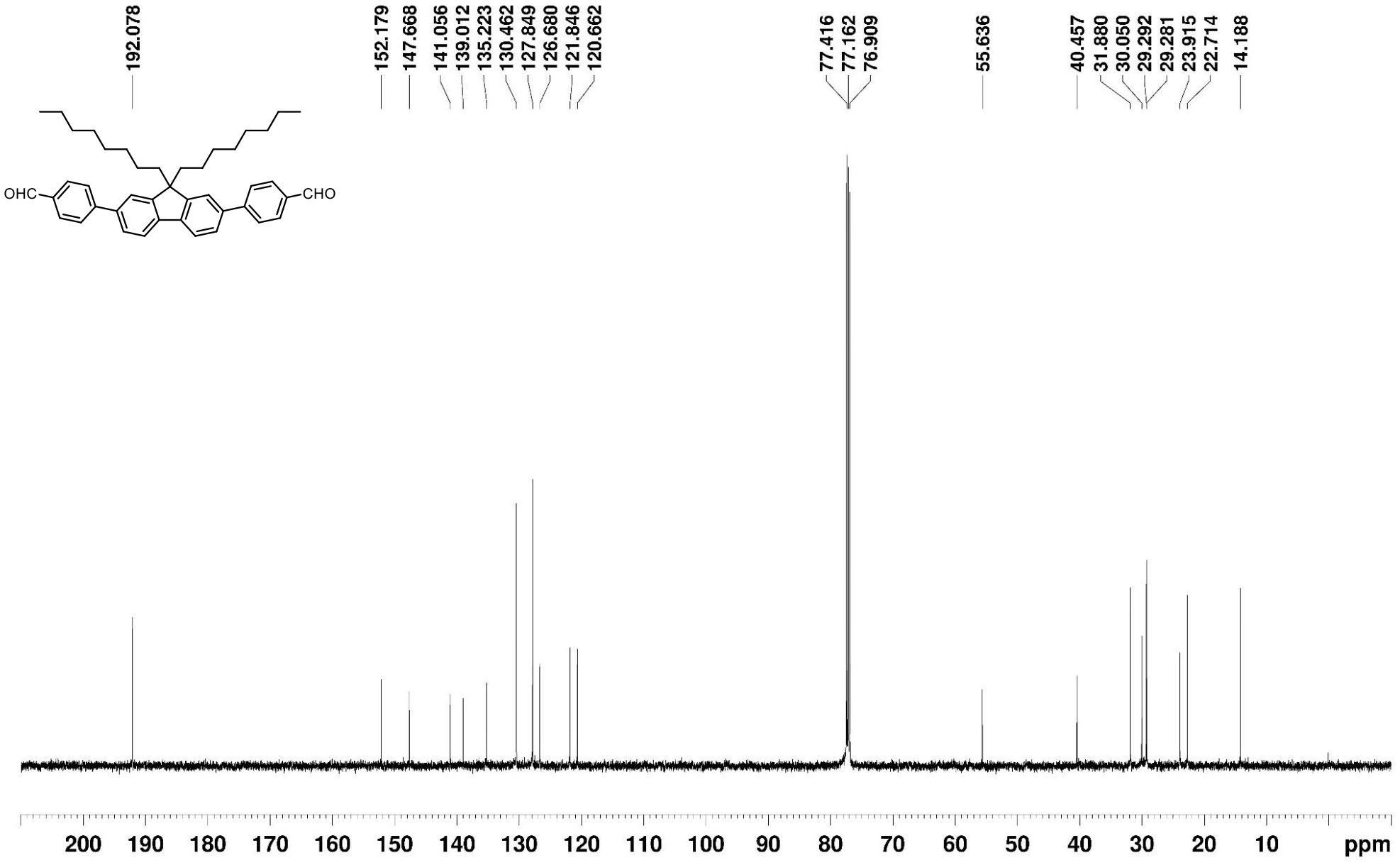


Figure S73. ^{13}C NMR (125 MHz, $CDCl_3$) of **1l**.

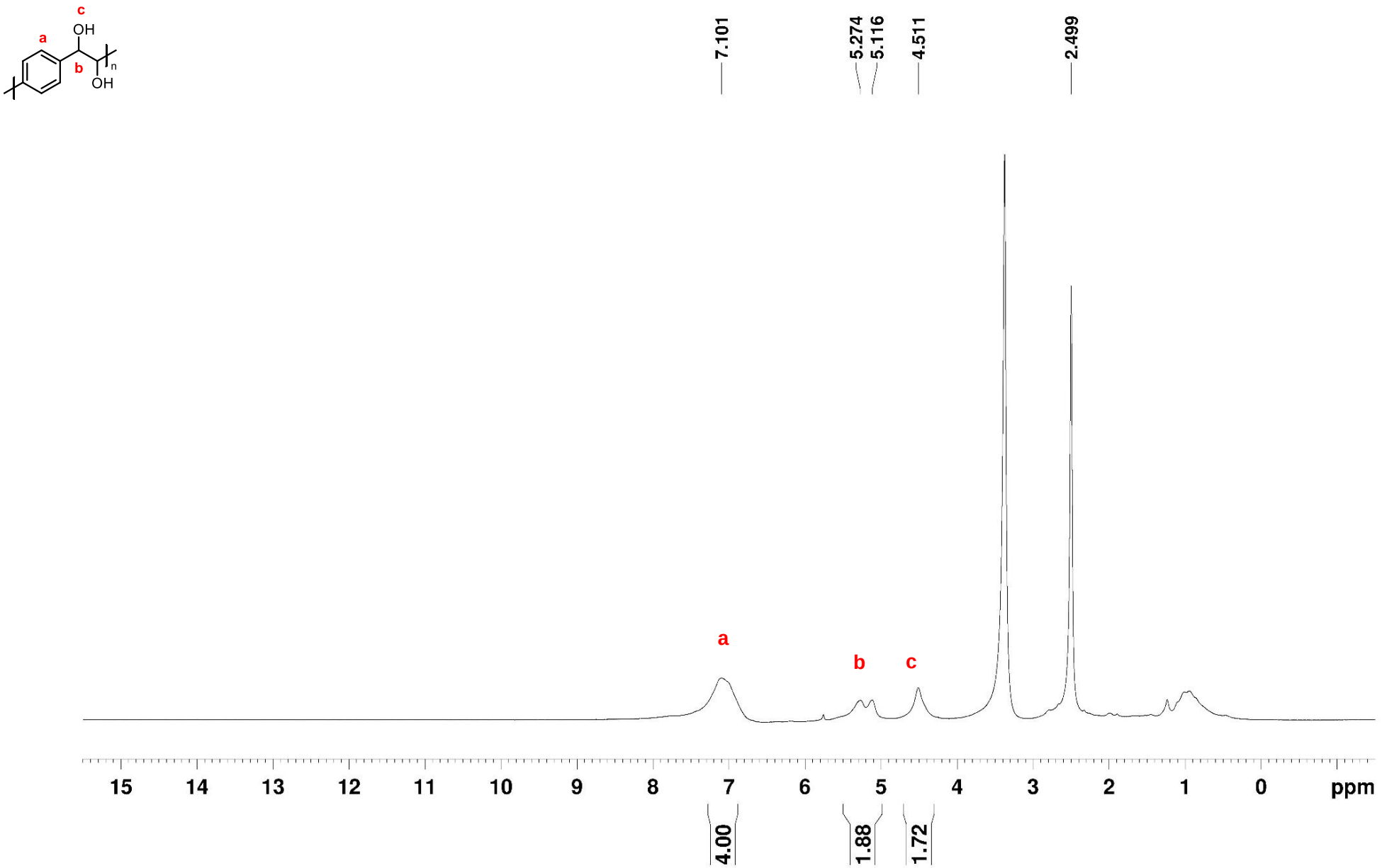


Figure S74. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1a**.

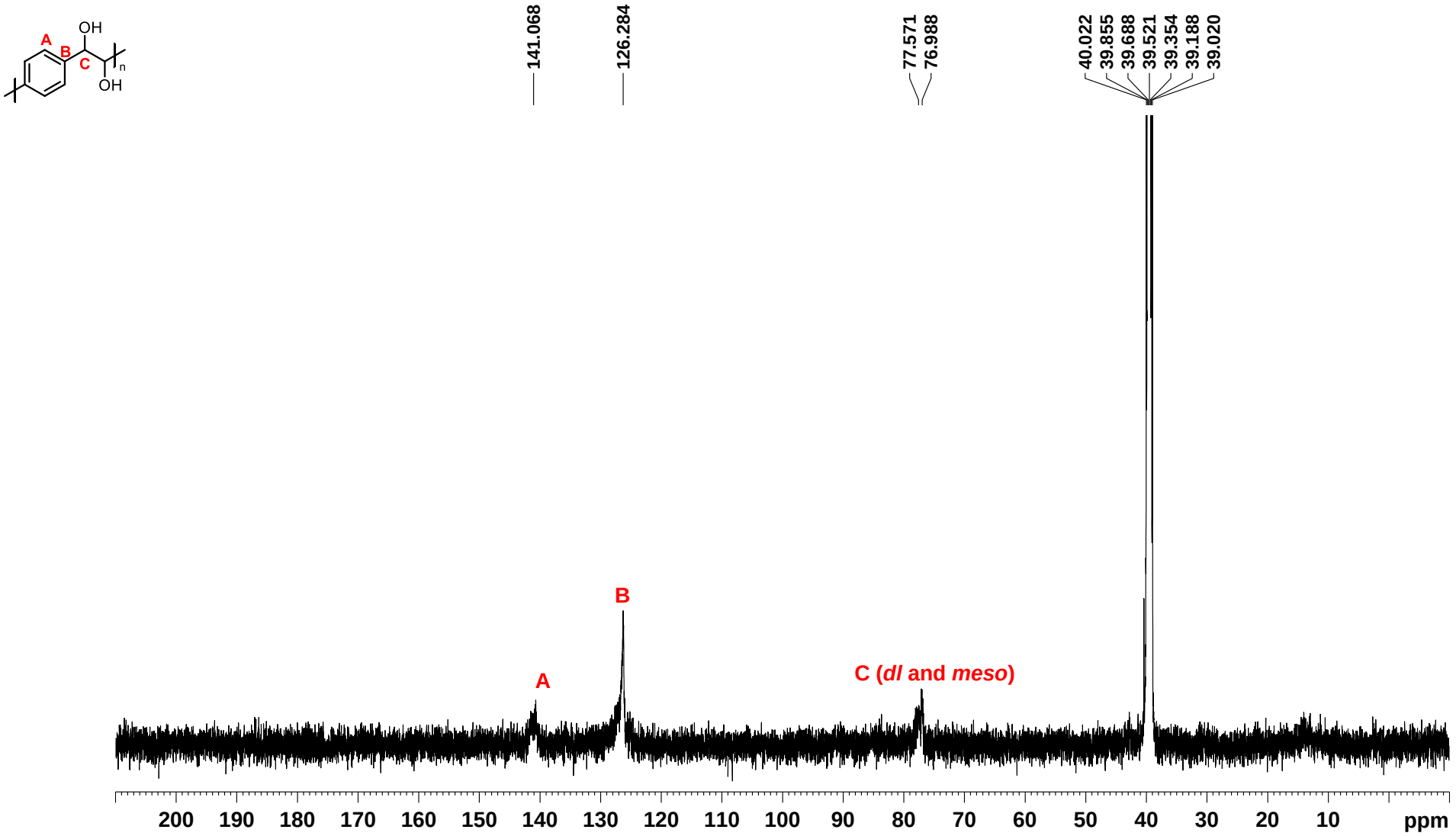


Figure S75. ^{13}C NMR (125 MHz, d^6-DMSO) of **poly-1a**.

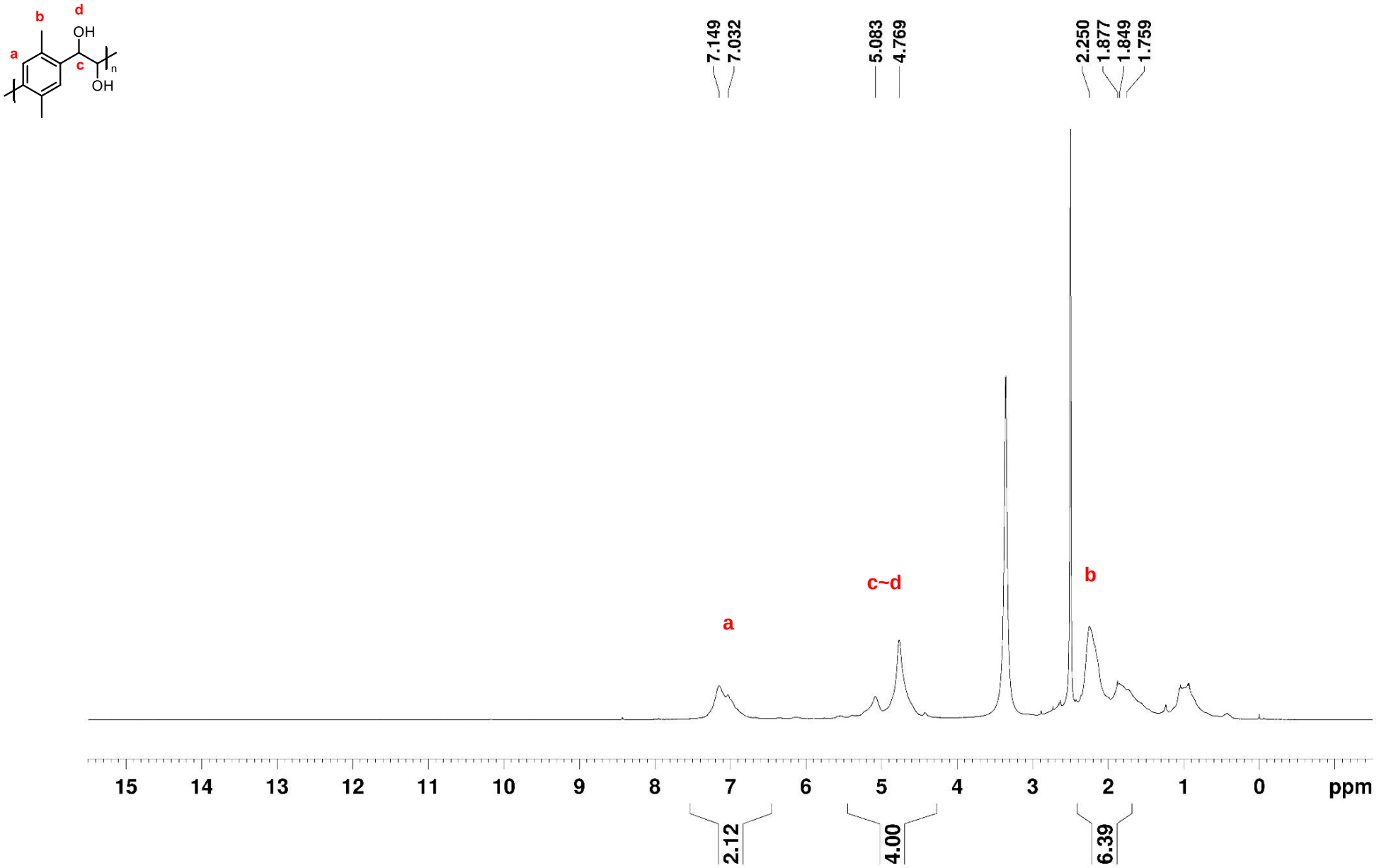


Figure S76. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1b**.

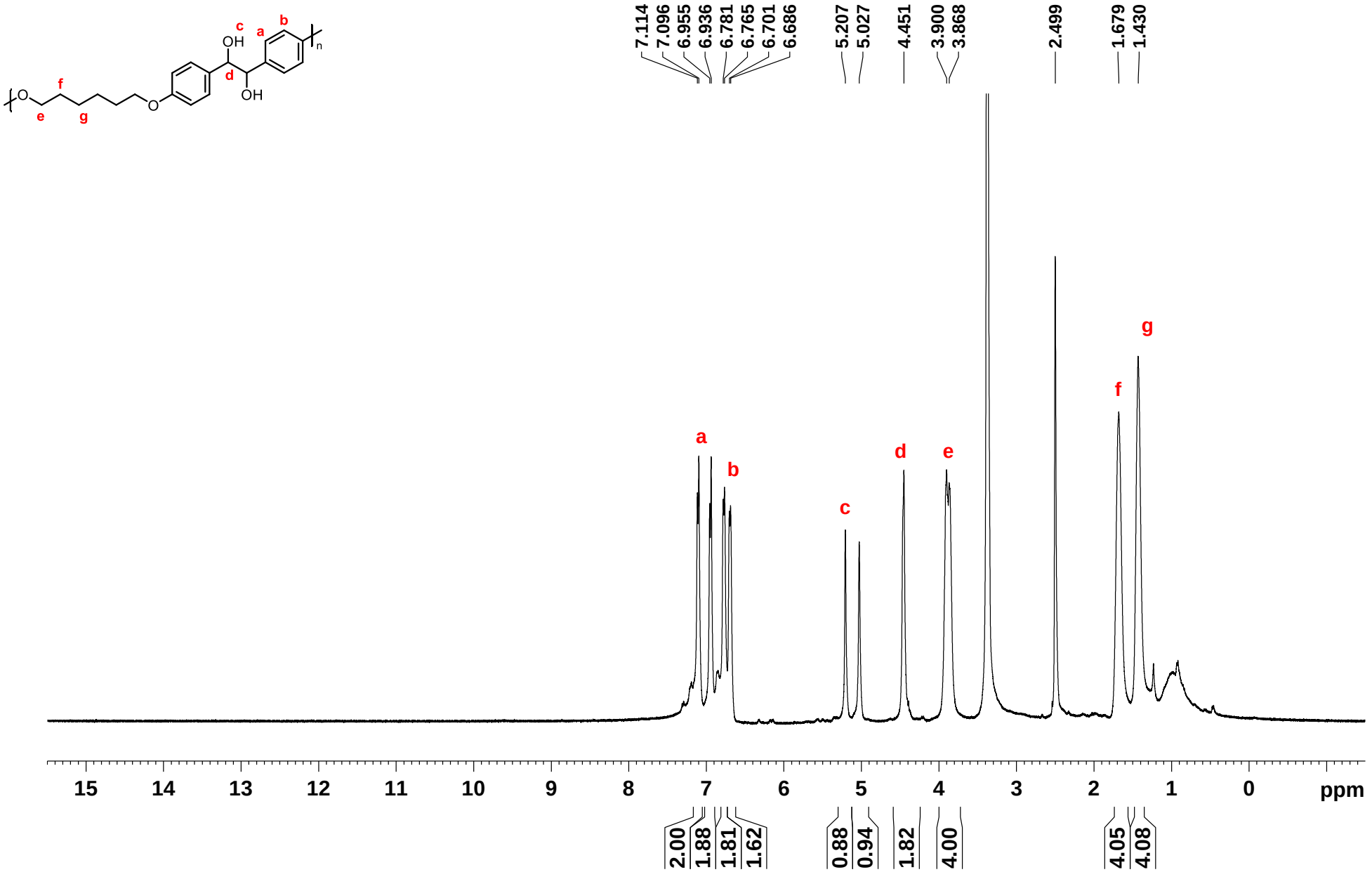


Figure S77. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1c**.

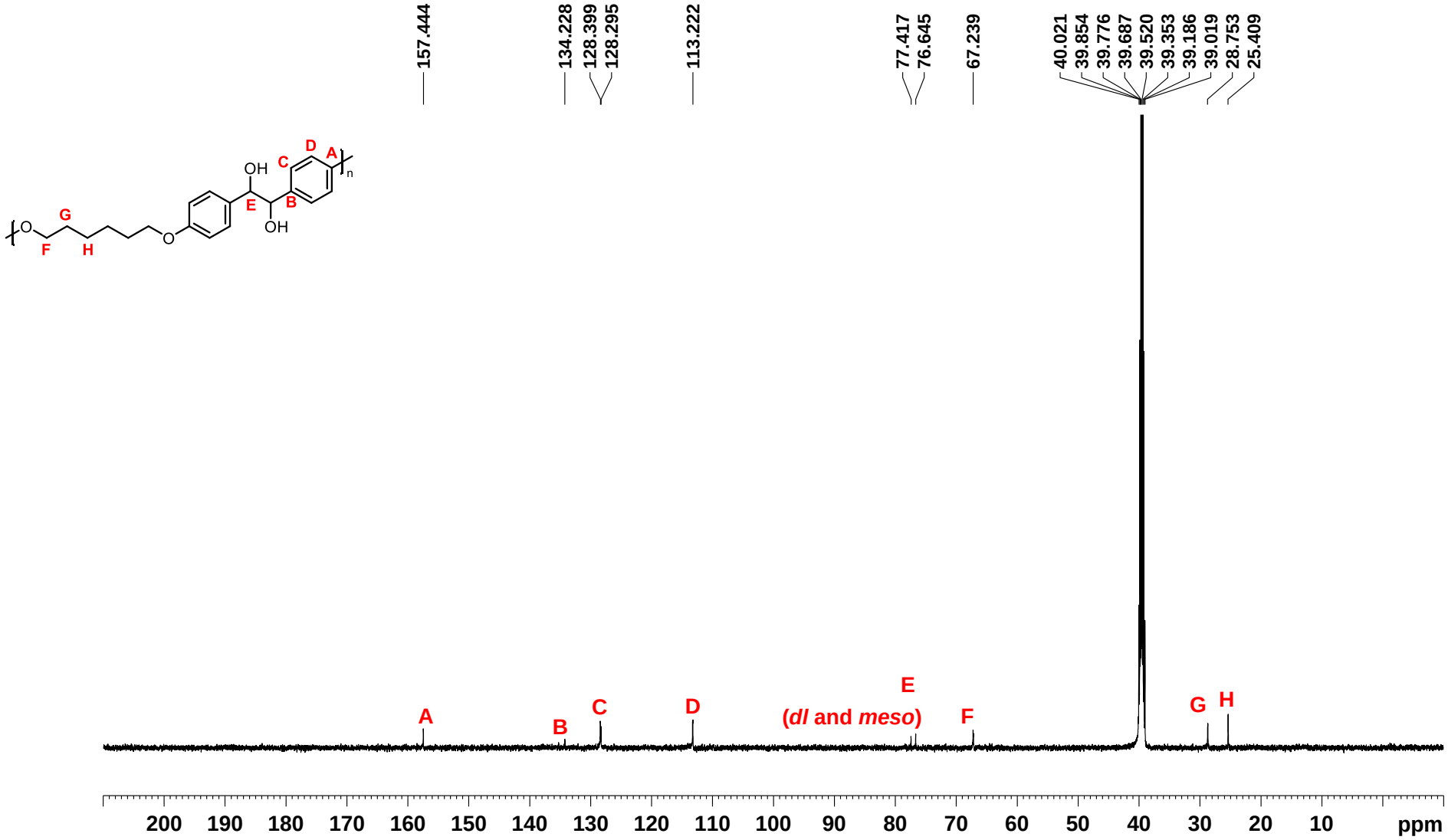


Figure S78. ^{13}C NMR (125 MHz, d^6-DMSO) of **poly-1c**.

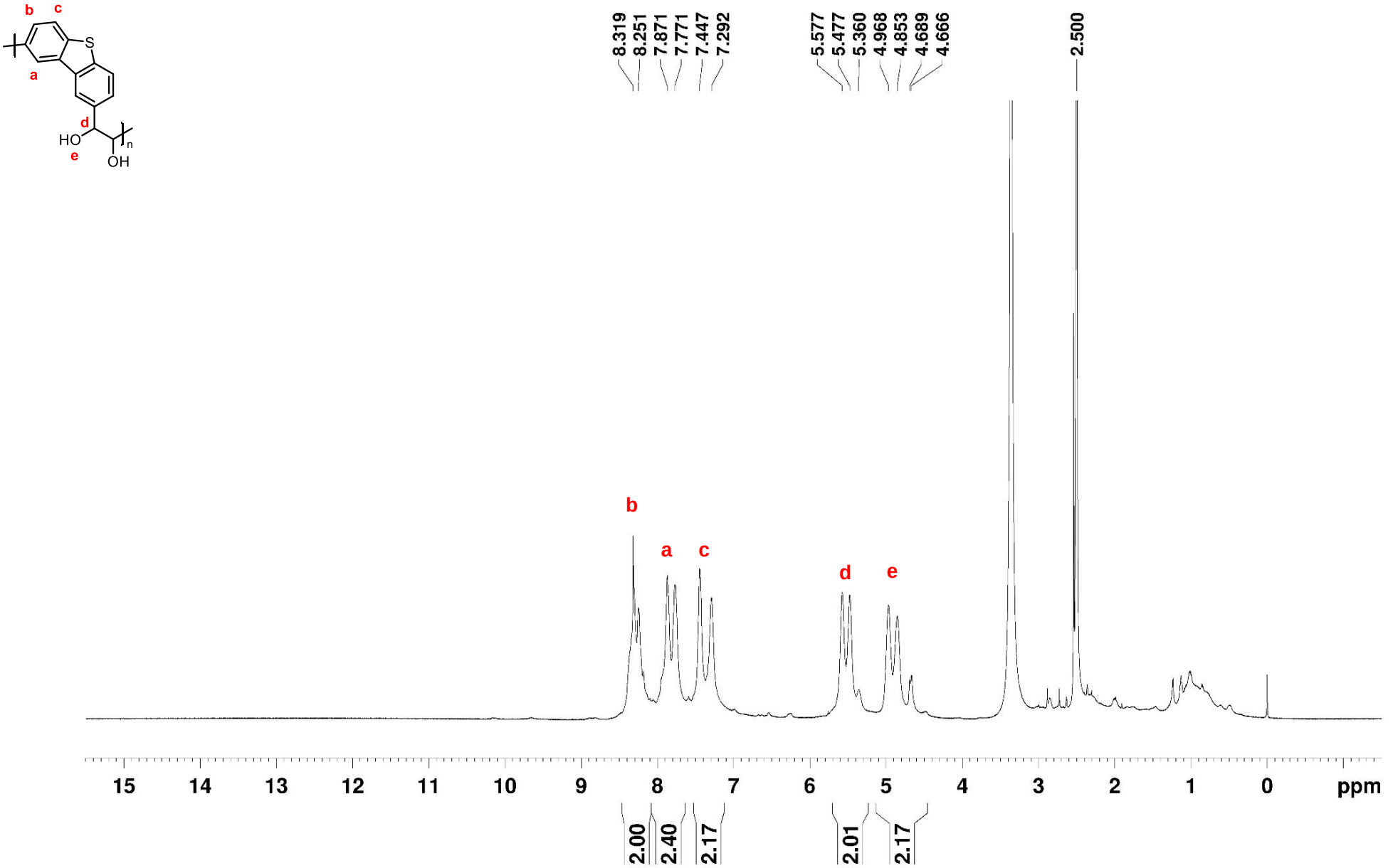


Figure S79. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1d**.

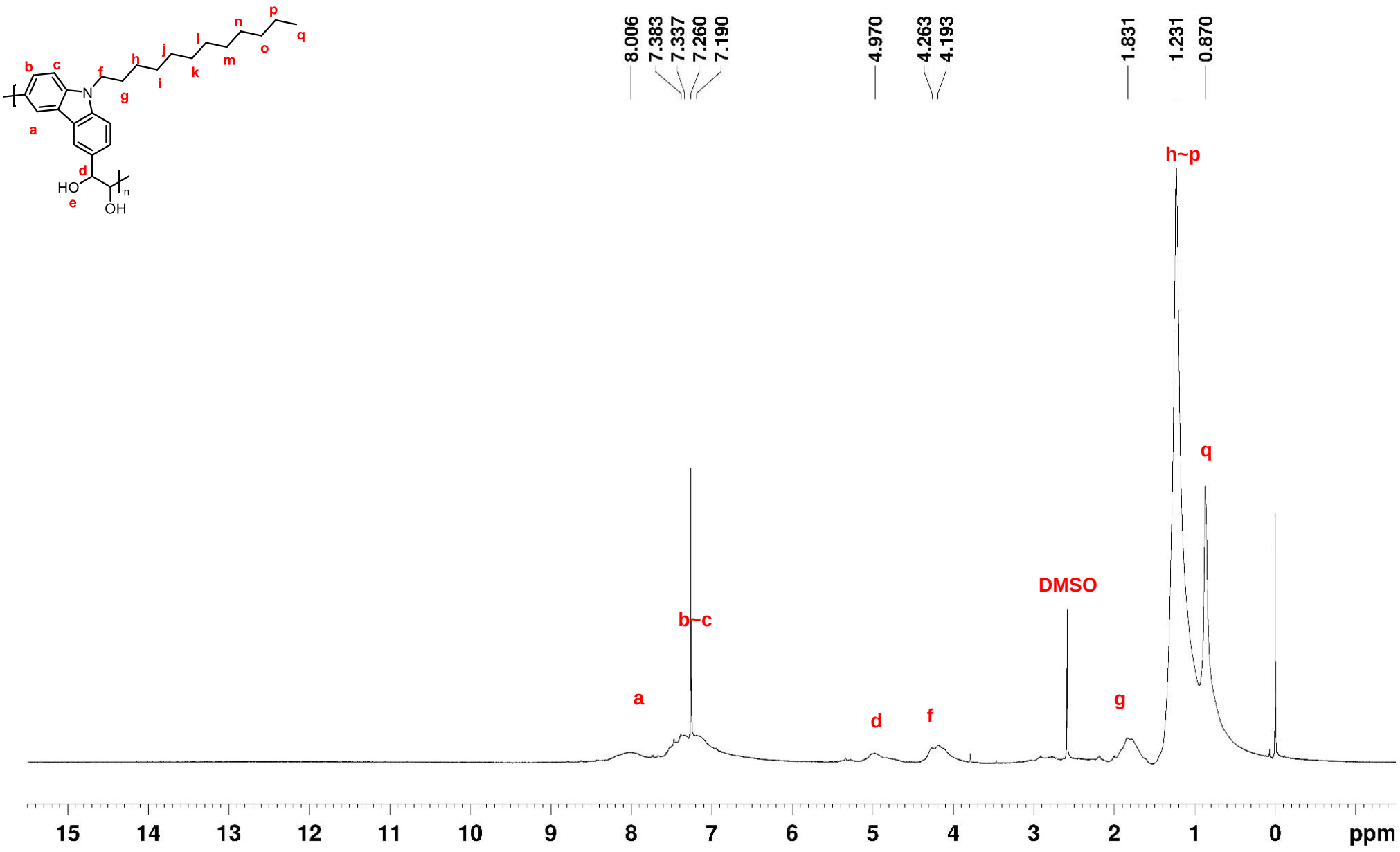


Figure S80. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1e**.

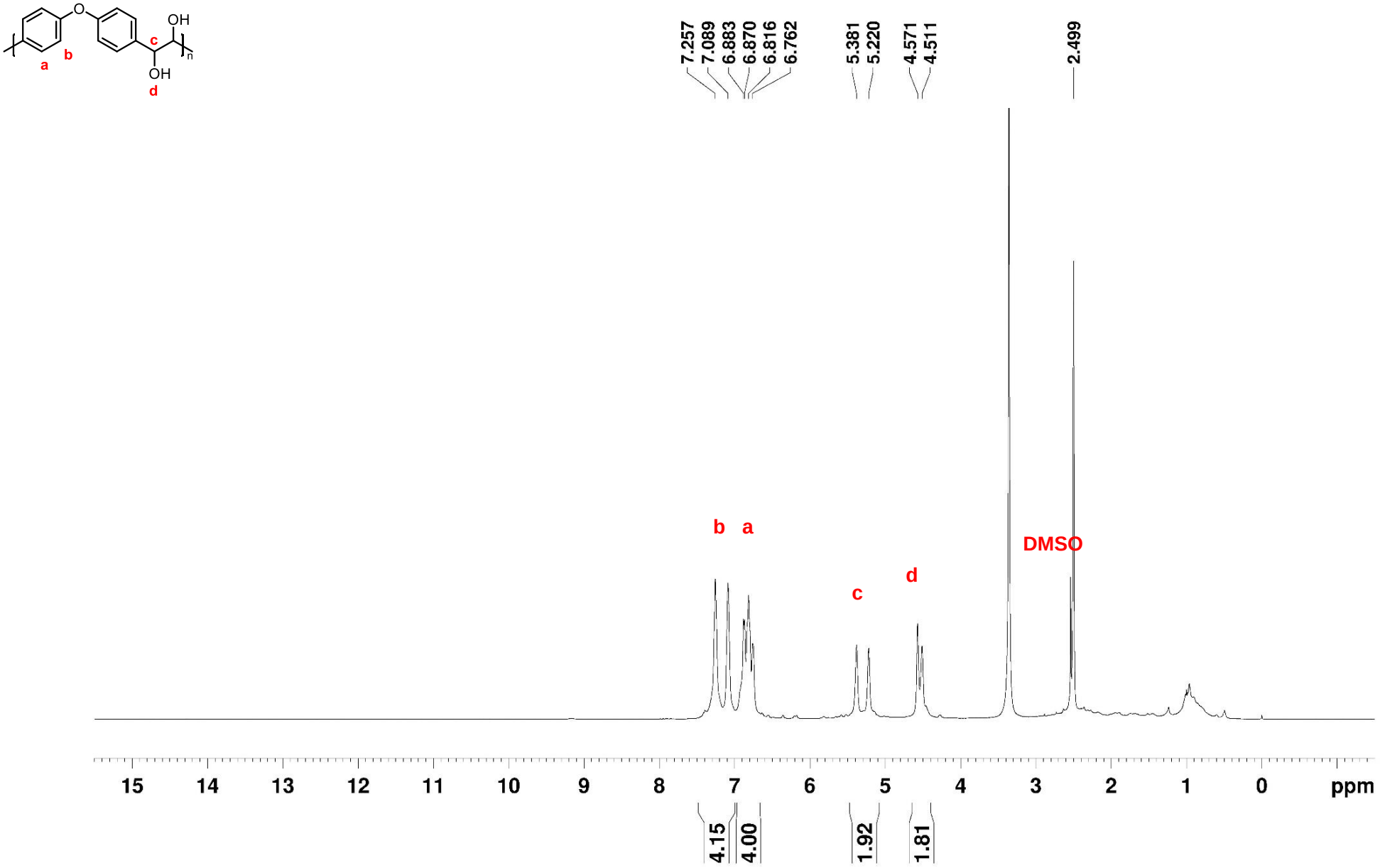


Figure S81. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1f.**

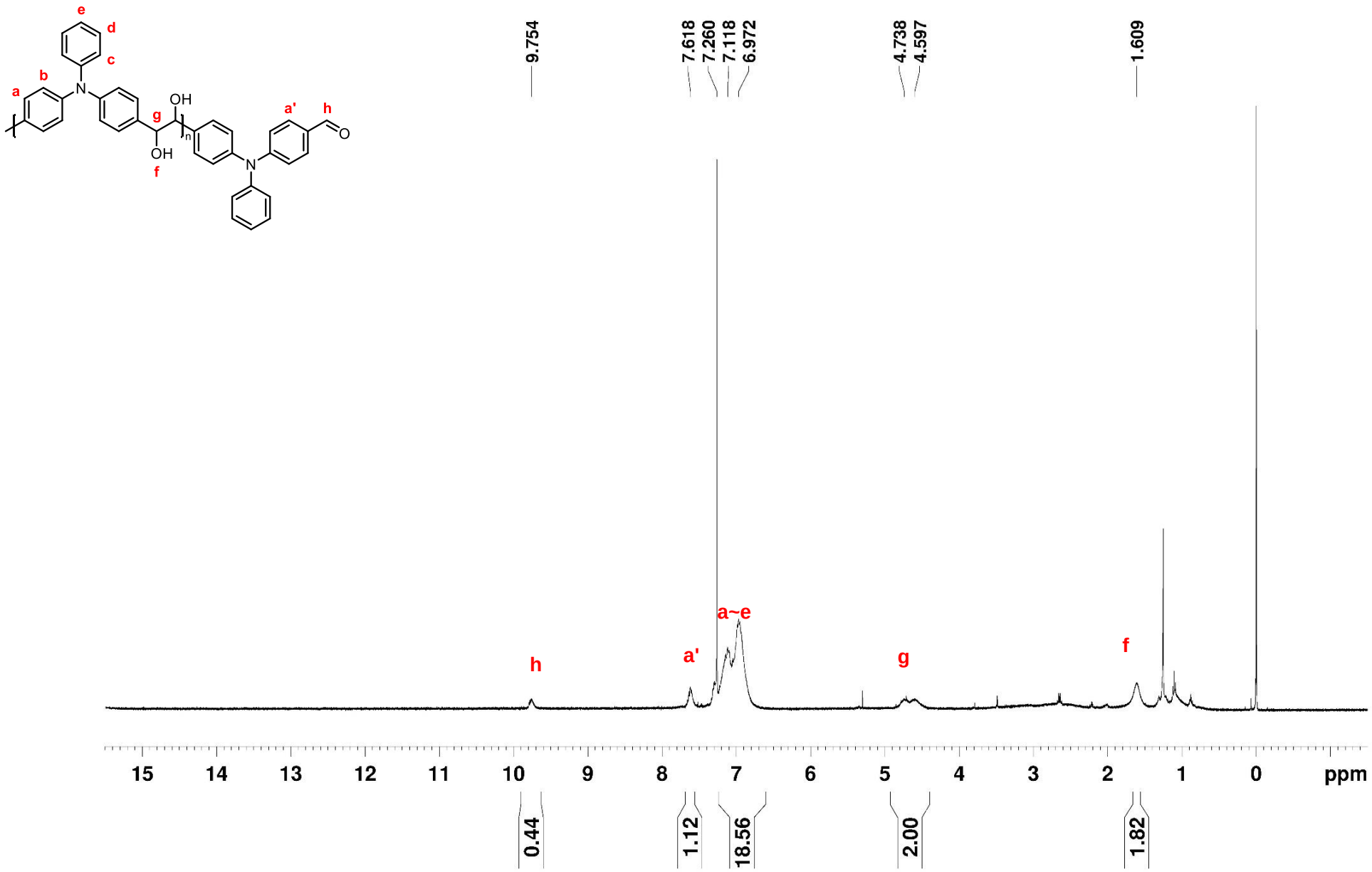


Figure S82. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1g**.

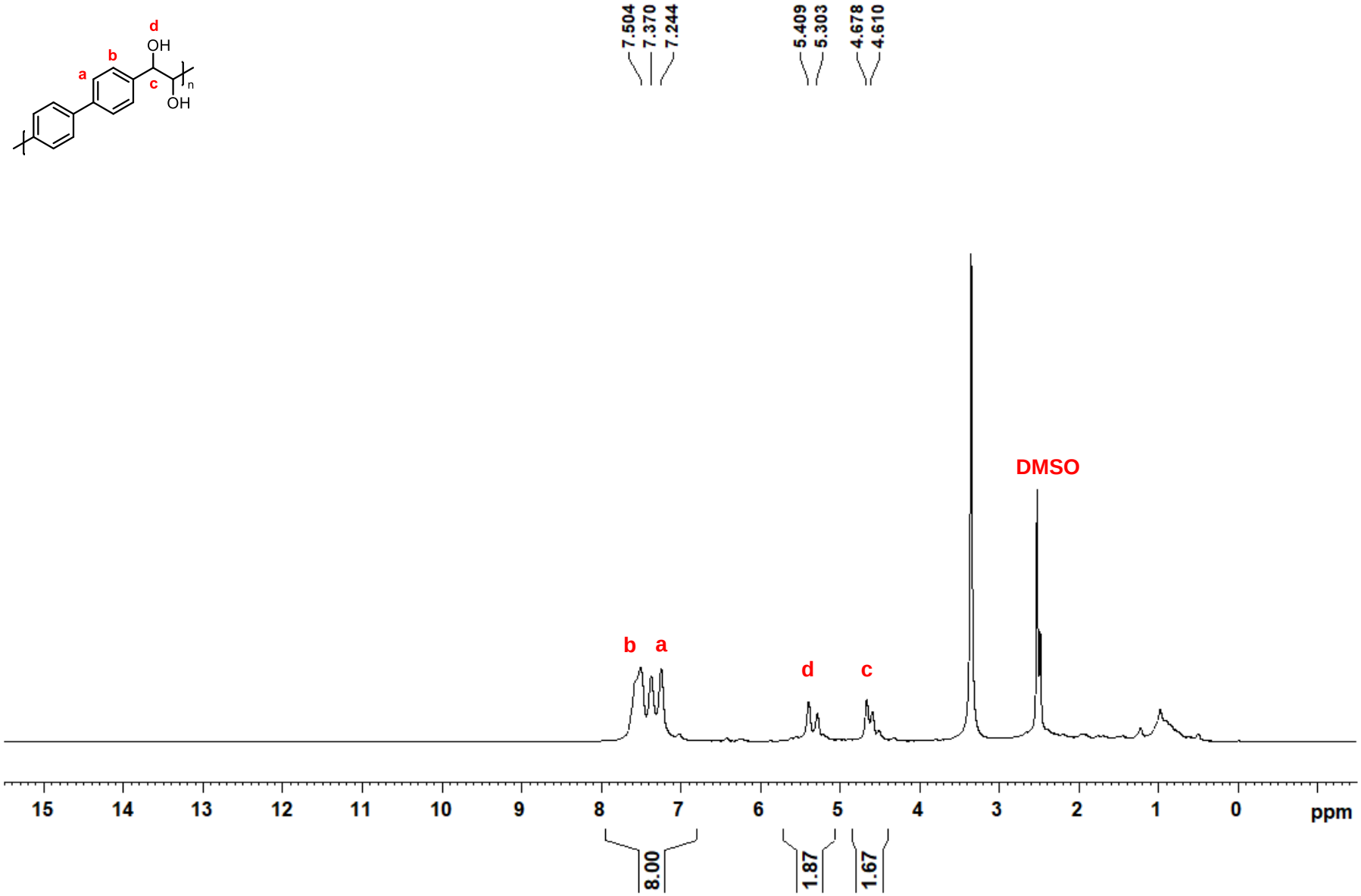


Figure S83. ^{1}H NMR (500 MHz, d^{6}-DMSO) of **poly-1h**.

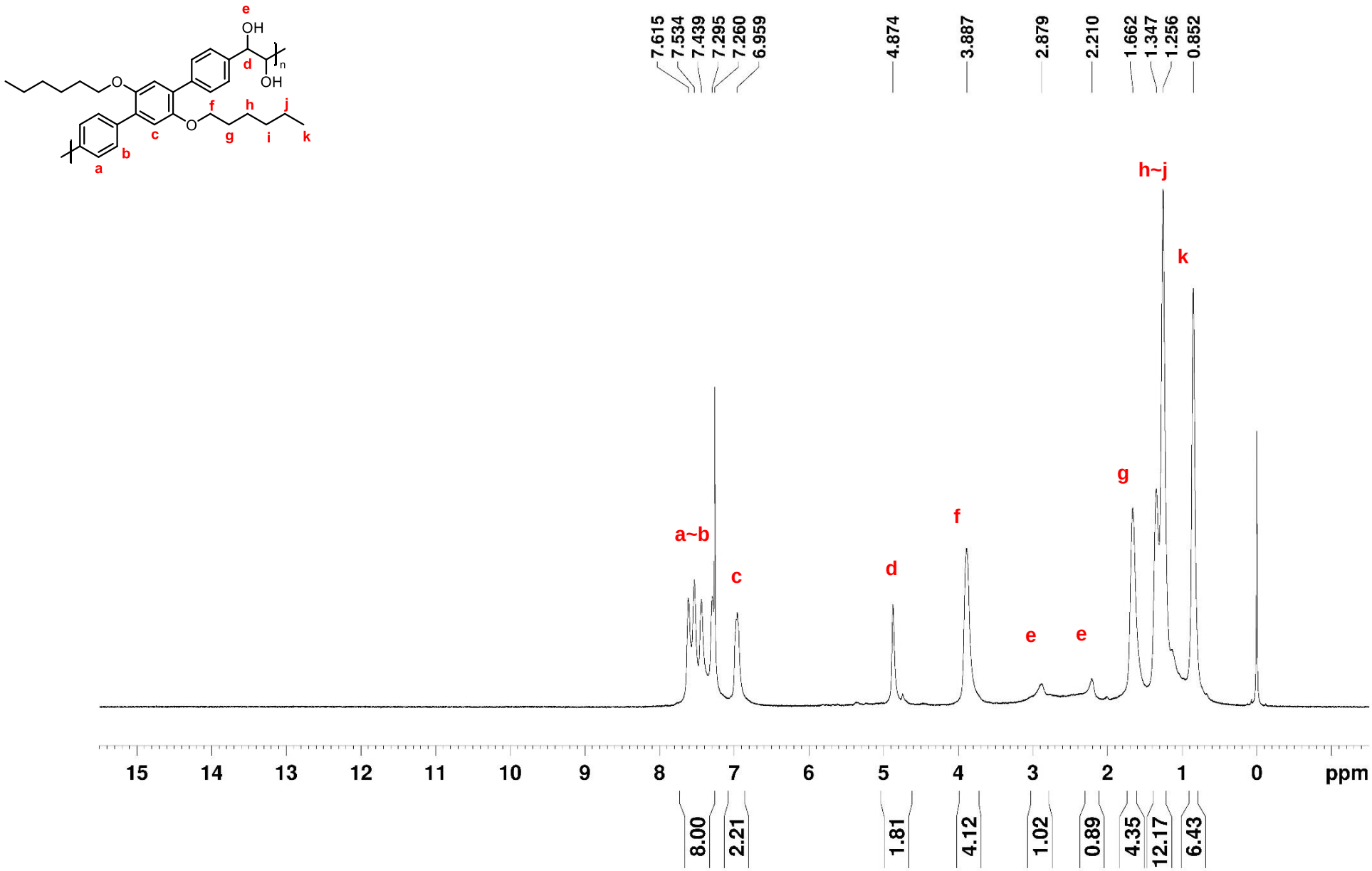


Figure S84. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1i**.

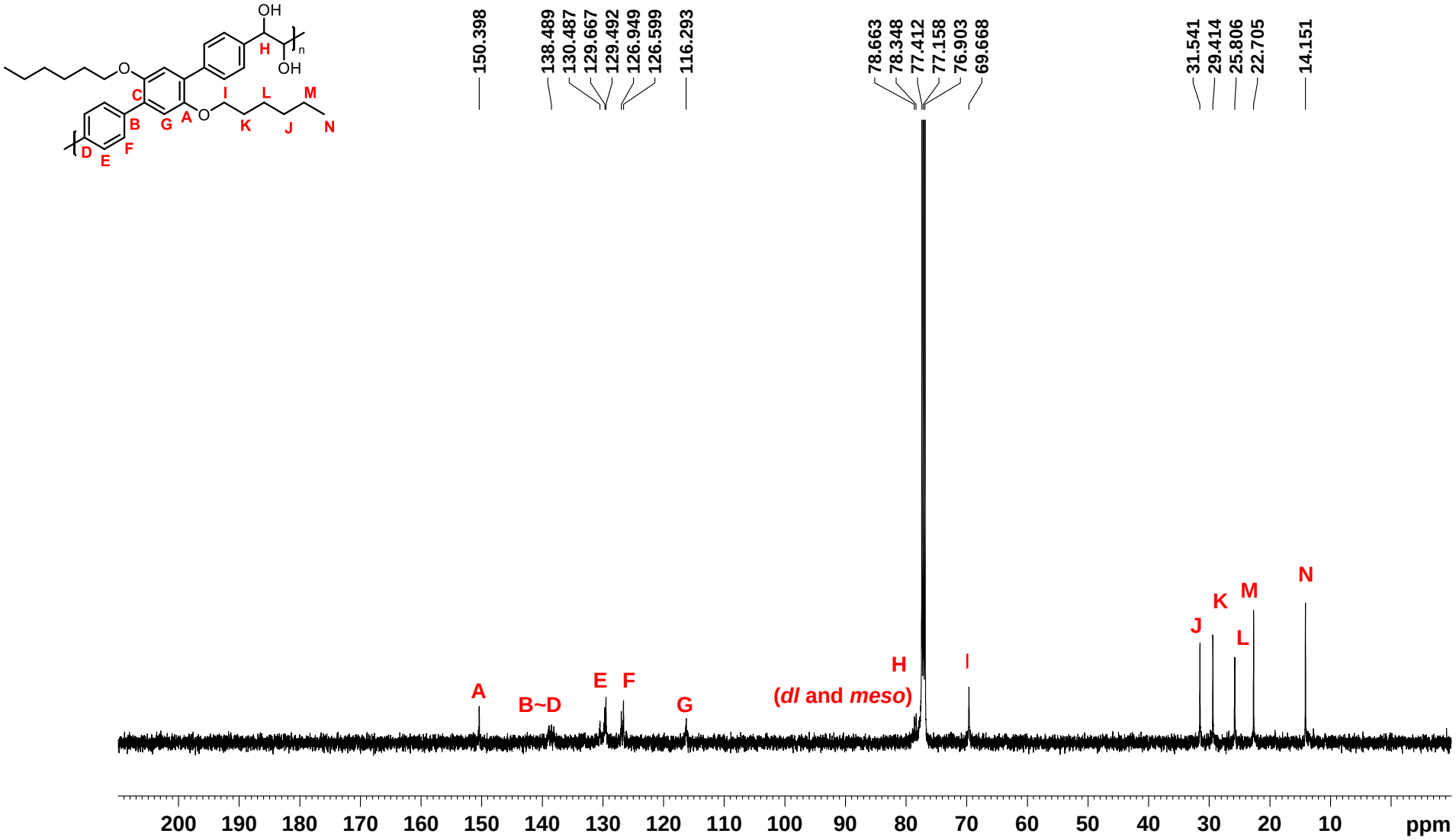


Figure S85. ^{13}C NMR (125 MHz, $CDCl_3$) of **poly-1i**.

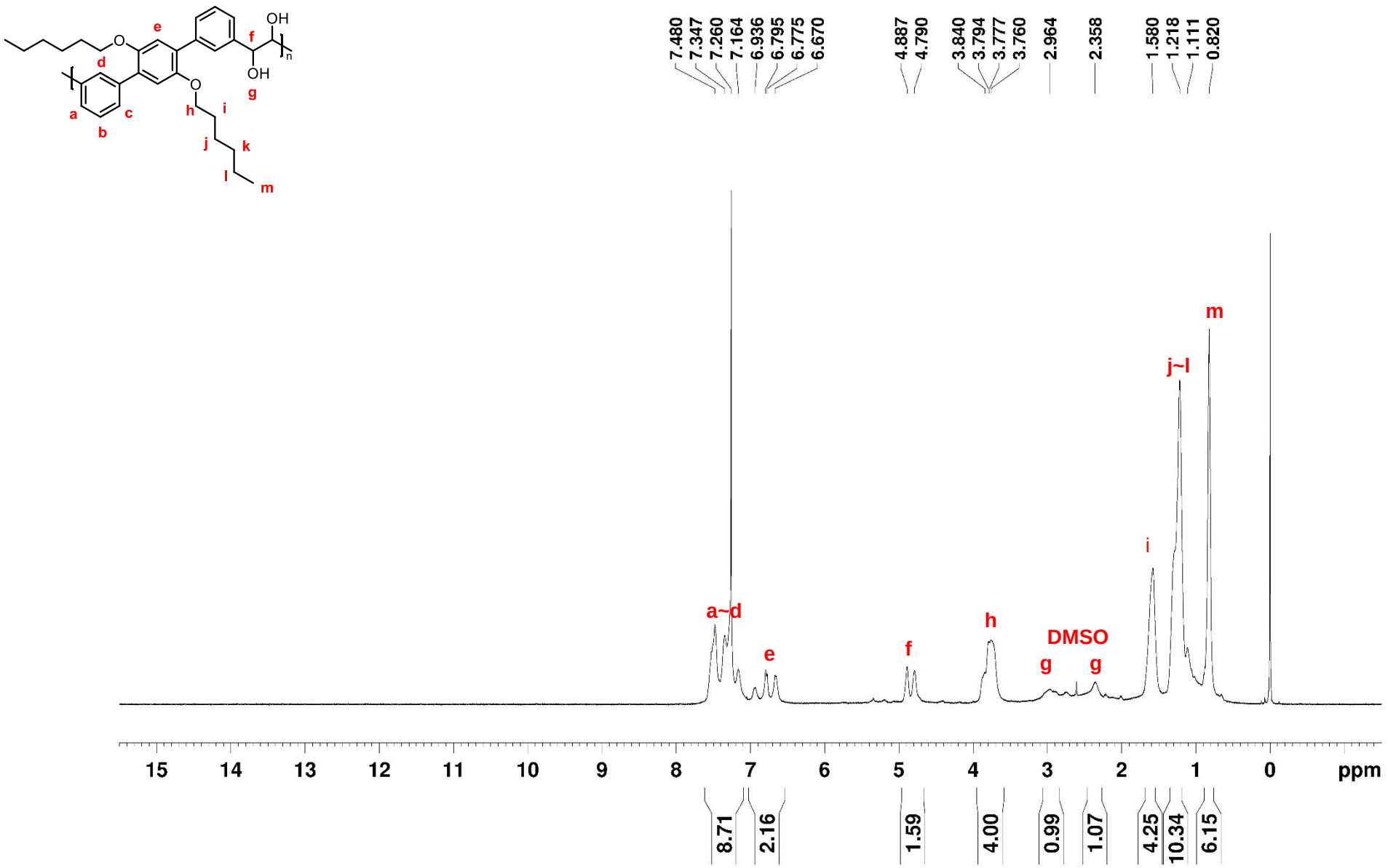


Figure S86. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1j**.

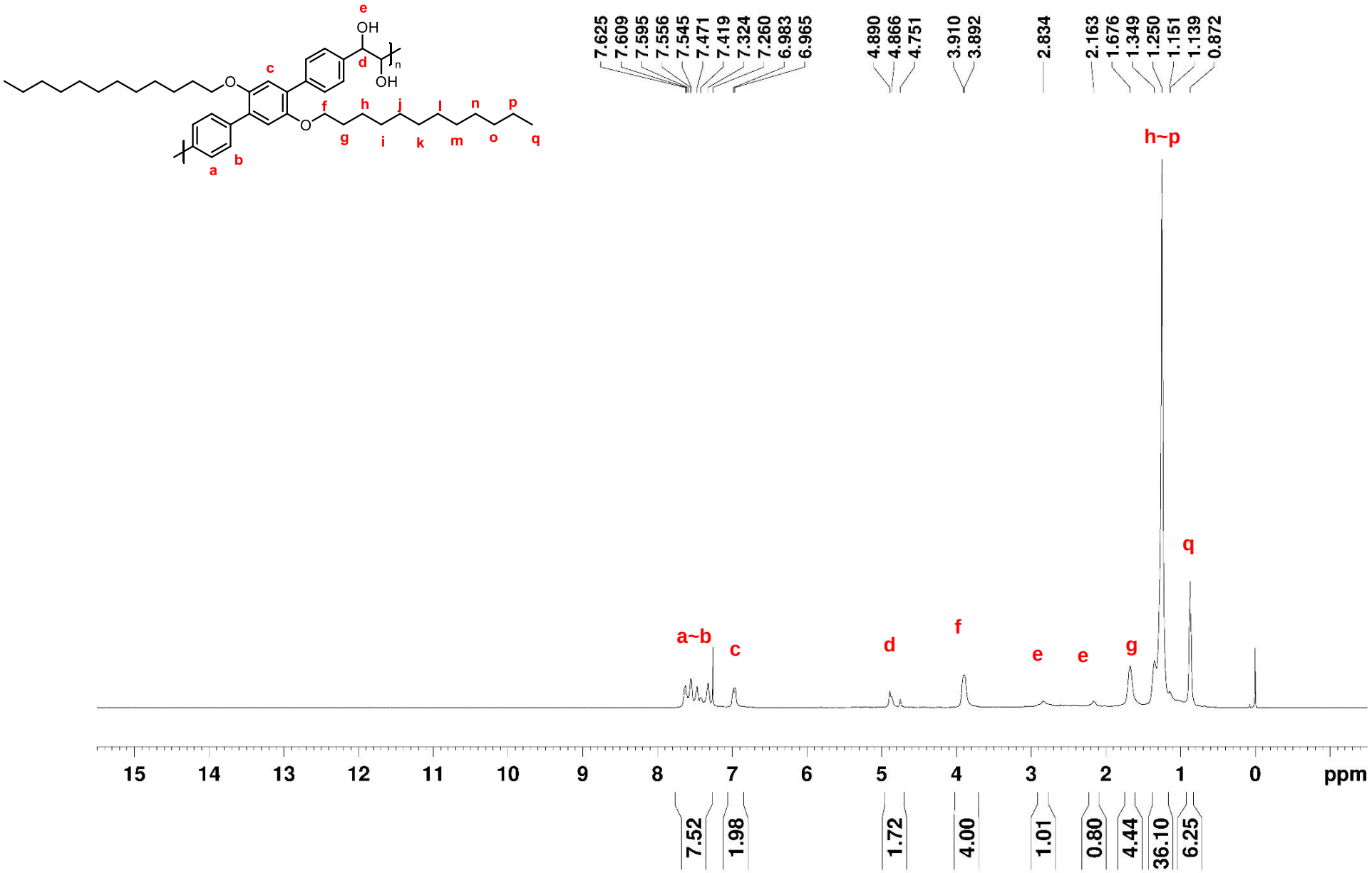


Figure S87. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1k**.

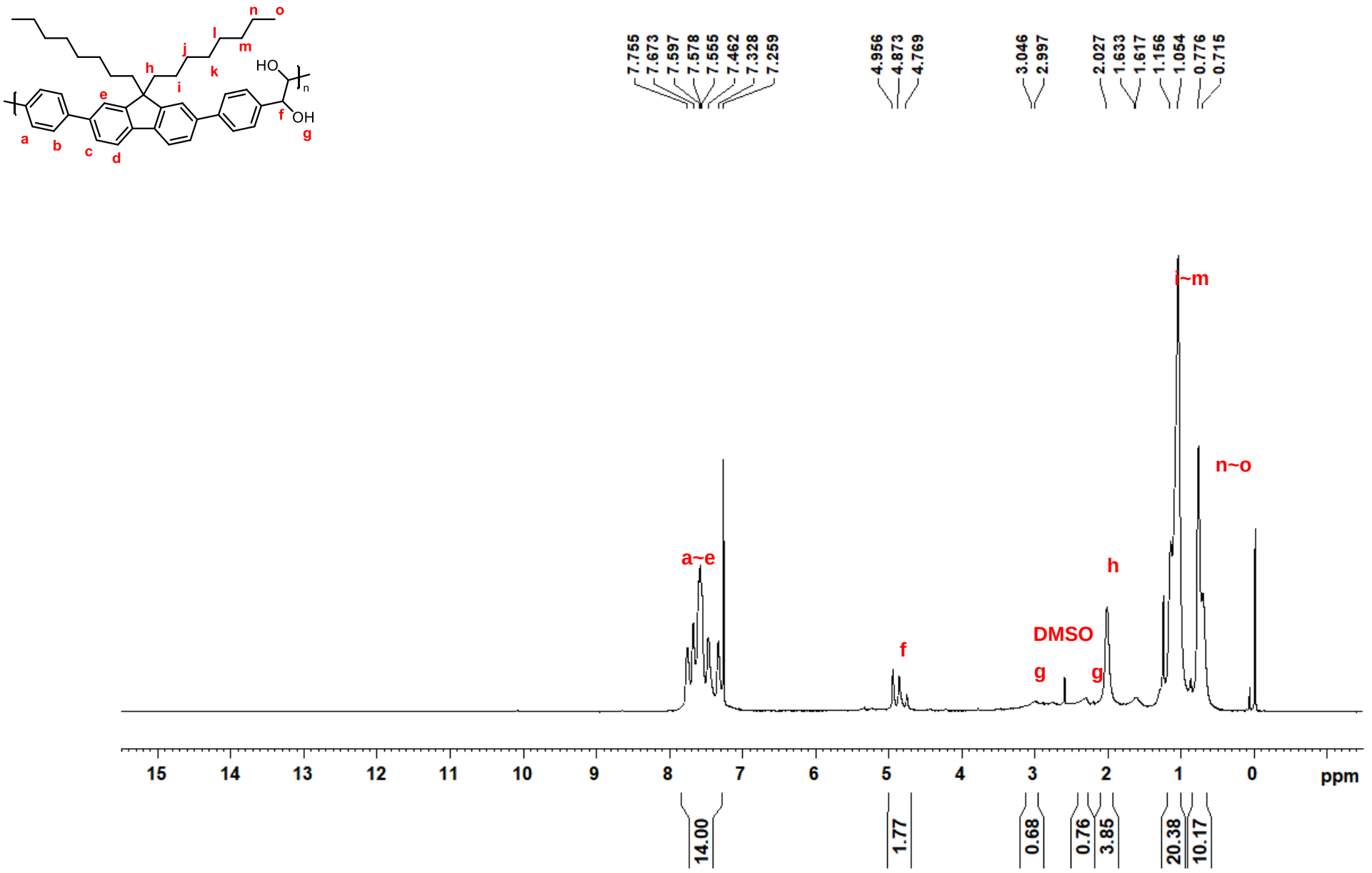


Figure S88. ^{1}H NMR (500 MHz, $CDCl_3$) of **poly-1l**.

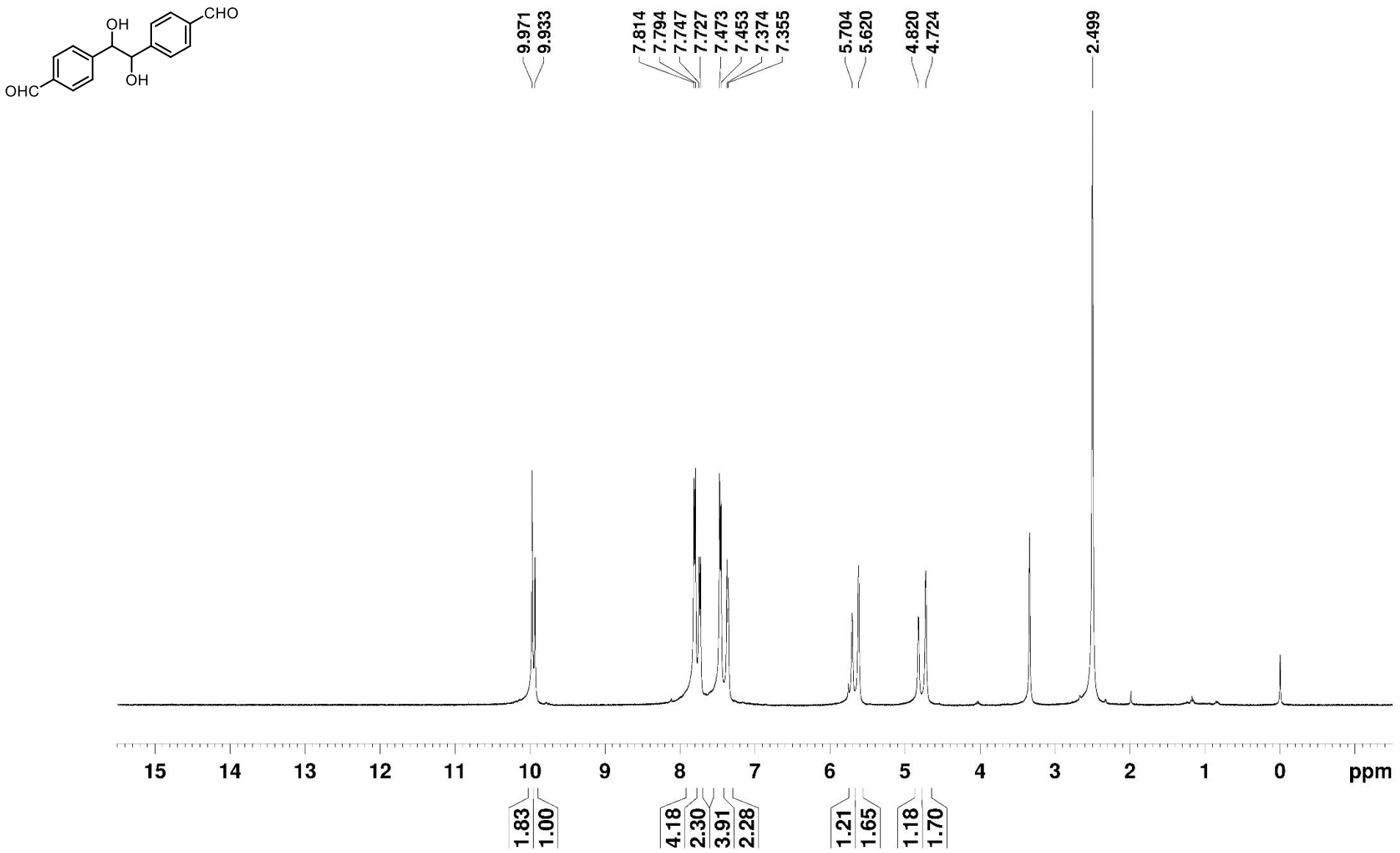


Figure S89. ^{1}H NMR (400 MHz, d^{6}-DMSO) of **2a**.

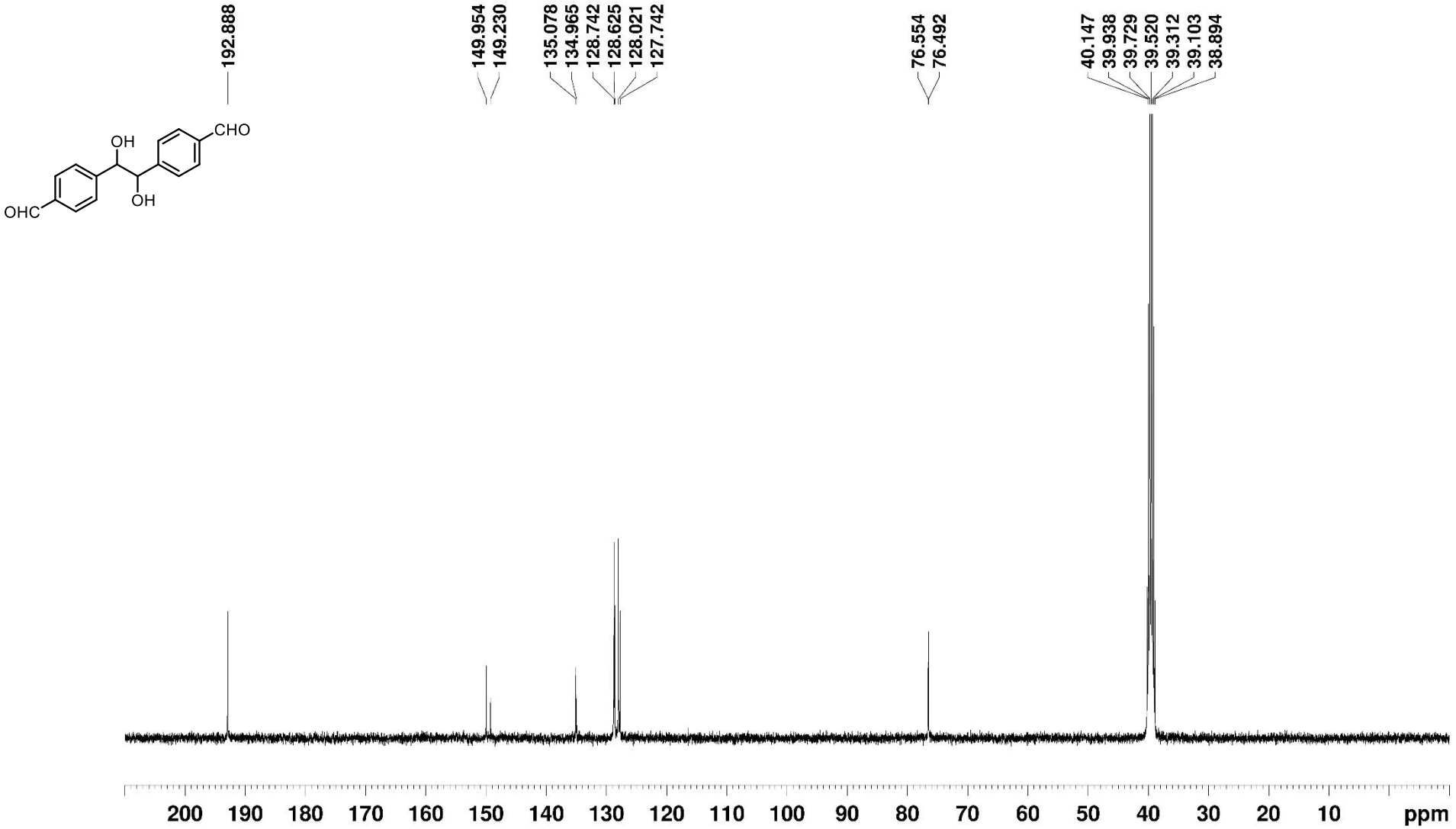


Figure S90. ^{13}C NMR (100 MHz, d^6-DMSO) of **2a**.

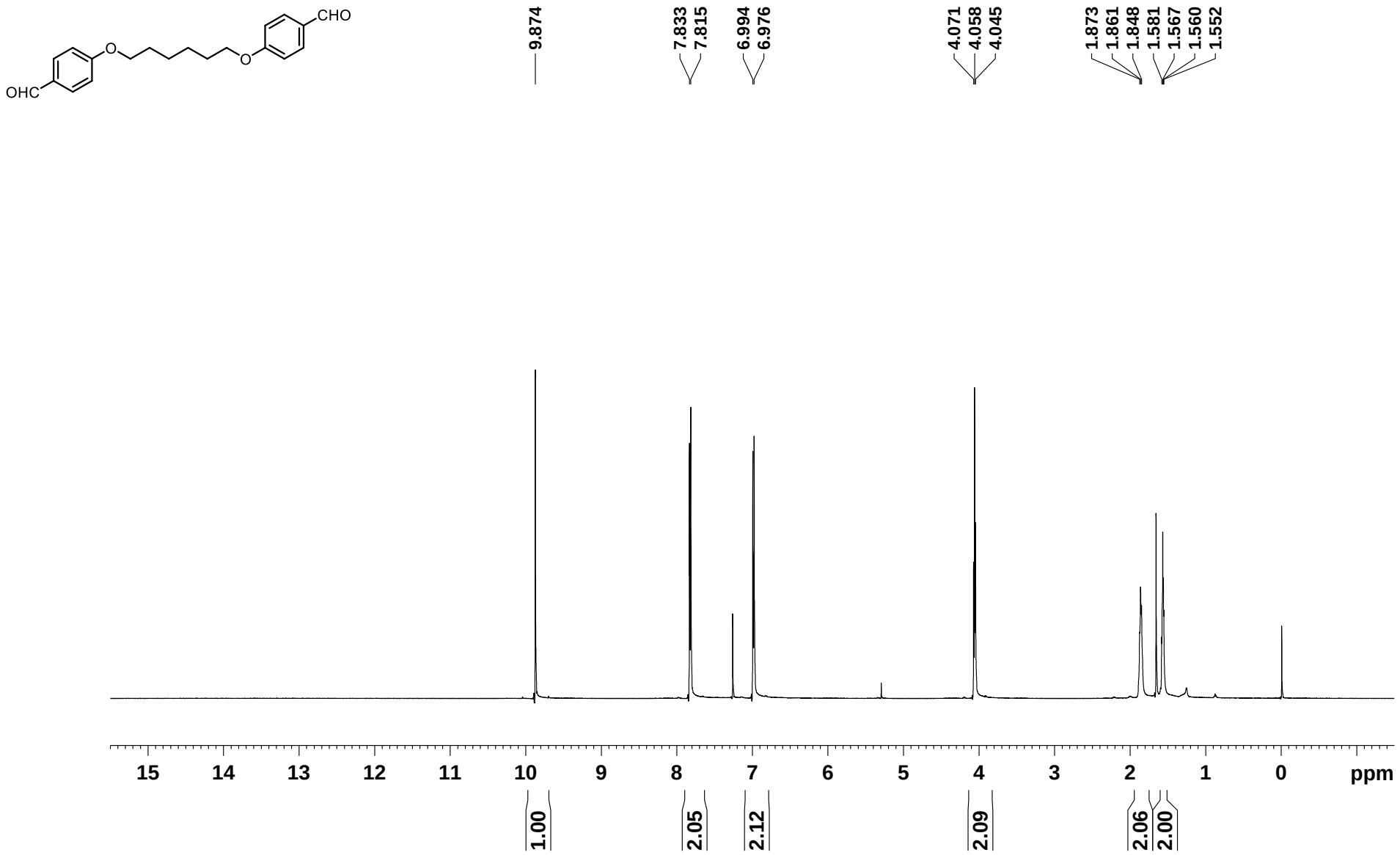


Figure S91. ^{1}H NMR (500 MHz, $CDCl_3$) of **1c-recycled**.

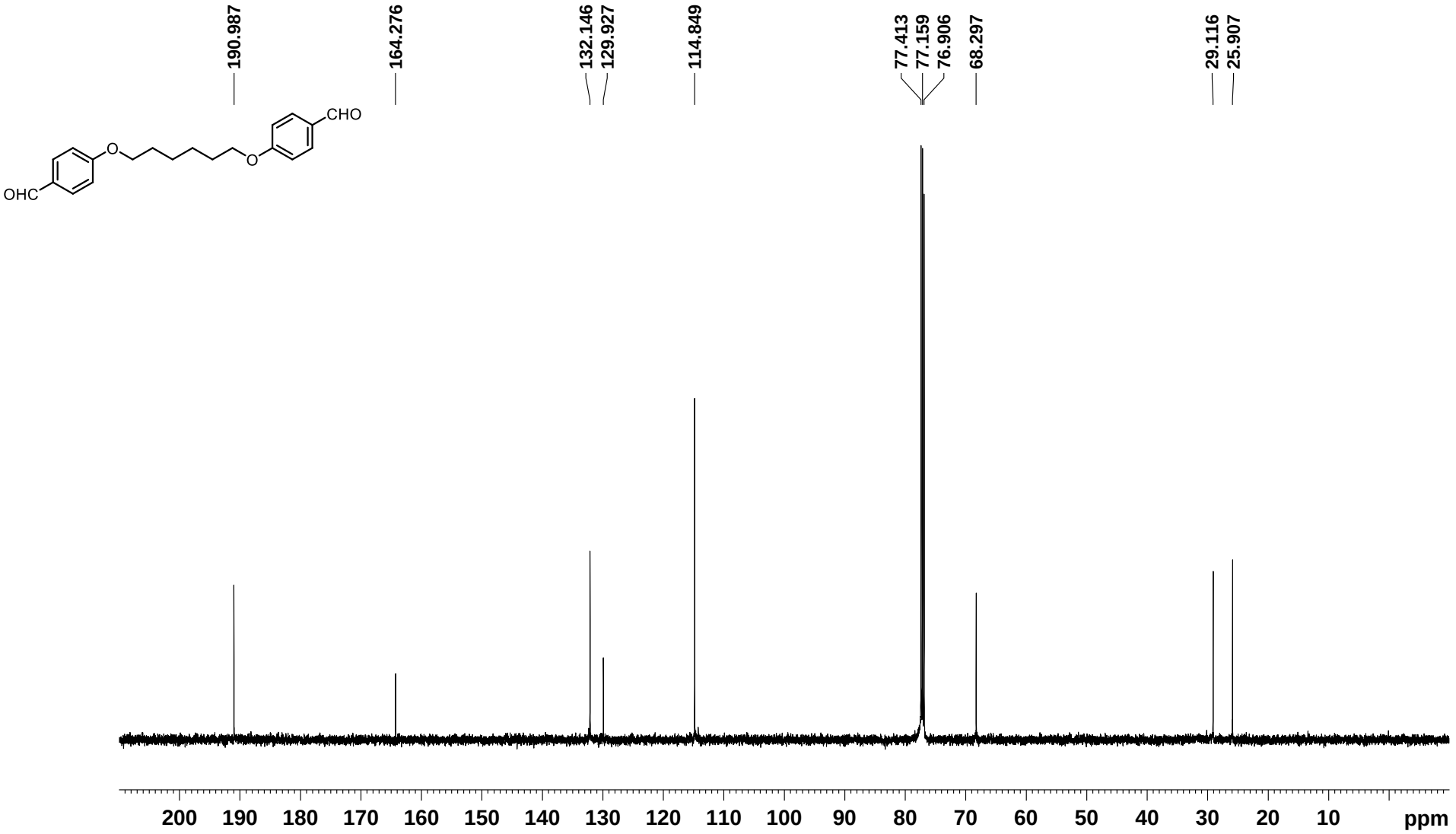


Figure S92. ^{13}C NMR (125 MHz, $CDCl_3$) of **1c-recycled**.