Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information for

Photocatalytic Synthesis and Closed-Loop Recycling of Conjugated Polyazines

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Contents

1. General Information

All reactions were carried out under atmospheric pressure. Solvents were pre-dried over activated 4Å molecular sieves and heated to reflux over calcium hydride or Mg turnings and iodine crystals (CH_3CN, DCM, Et_3N, THF, DMF, DMSO, DIPA, DIPEA) under nitrogen atmosphere and collected by distillation. Aldehydes and ketones were used with purification as commercially available. Aldehydes, ketones and other chemicals without notes in experimental section were purchased from commercial sources. All reactions were performed with Semi-LED lamps (C35LU-60), the glass reaction tube was placed 1.5 cm away from LEDs. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel or basic aluminum oxide. Chemical yields refer to pure isolated substances. All work-up and purification procedures were carried out with reagent-grade solvents in air.

^1H, ^{19}F decoupled, $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400/500 spectrometer; Chemical shifts are reported in δ units relative to $CDCl_3$ [^1H $\delta = 7.26$, ^{13}C $\delta = 77.16$] and DMSO- d_6 [^1H $\delta = 2.538$, ^{13}C $\delta = 39.52$]. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). Fluorescence Spectrum was recorded on an F-4600 spectrometer.

The size exclusion chromatography (SEC) was conducted in DMF at 40 °C 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 °C at a rate of 10 °C/min, staying at 200 °C for 5 min to erase thermal history. Then the sample was cooled to the starting temperature at a rate of 10 °C/min, keeping for 5 minutes. Finally, the sample was heated to 200 °C at a rate of 20 °C/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 -5 ºC, 20°C or 25 ºC to 200 °C at a rate of 10 °C/min, staying at 200 °C for 5 min to erase thermal history. Then the sample was cooled to the start temperature at a rate of 10 °C/min, keeping for 5 minutes. Finally, the sample was heated to 200 °C at a rate of 10 °C/min.

Synchrotron radiation photoemission spectroscopy (SRPES) measurements: The valence band (VB) positions of HEP-COFs were determined by SRPES measurements, which were conducted at the Photoemission Endstation (BL10B) in the National

Synchrotron Radiation Laboratory in Hefei, China. The secondary electron cutoff was obtained by utilizing an excitation of 100.0 eV. The binding energy (BE) was calibrated and referenced to the E_f of a gold foil. The work function (WF) of samples was determined according to equation $\Phi = h\nu - \Delta E$, where is ΔE the spectrum width, i.e. the energy difference between the secondary electron cutoff and the Fermi level of tested sample. A -15 V bias was applied to the sample to get the secondary electron cutoff, which accelerated all the photoelectrons with higher kinetic energy (KE) to overcome the WF of analyzer.

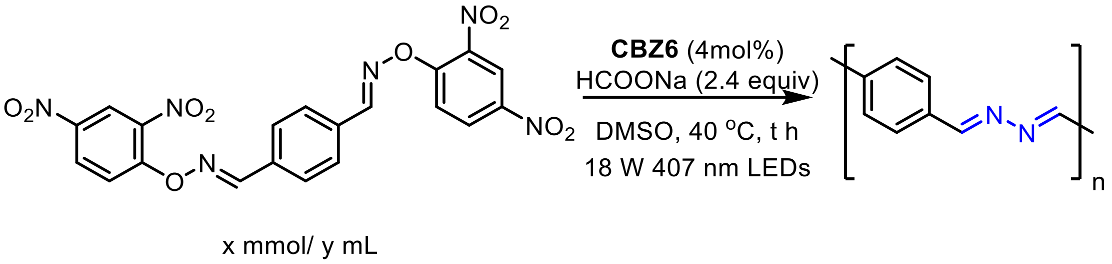
Photocatalytic H_2O_2 production: 50 mg photocatalysts (polymers) and 100 mL aqueous solution containing H_2O_2 (1 mM) were put in a hermetic device composed of a quartz tube. The suspension was well dispersed by ultrasonication for 15 min and O_2 was bubbled into the suspension for 30 min in the dark. Prior to the photocatalytic tests, the suspension was stirred for 30 min in dark to reach the absorption and desorption equilibrium. A 300 W Xe lamp (Perfect Light PLS-SEX 300D) was used as the light source and O_2 was continuously bubbled into the bottle. A cutoff filter (Kenko L-42) was used to achieve visible-light irradiation ($\lambda > 420$ nm, average intensity: 100 mW• cm^{-2}). The concentration of H_2O_2 was determined by UV-vis spectrophotometer. For example, 2 mL liquid was sampled and centrifuged at 14000 rpm and then filtrated with a 0.22 μm filter to further remove the photocatalysts. The sample was mixed with pre-prepared $Ce(SO_4)_2$ solution and the concentrations of H_2O_2 was determined by the UV-vis spectrophotometer. (PS: Determination of H_2O_2 concentration was referring to reference 5)

2. Experimental procedures

2.1 Optimization of Polymerization Conditions

(1*E*,4*E*)-terephthalaldehyde *O*,*O*-di(2,4-dinitrophenyl) dioxime (x mmol, 1.0 equiv), **CBZ6** (4 mol%) and HCOONa (2.4 equiv) were weighed directly into an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (y mL) was added sequentially in the Schlenk tube via syringe. This reaction tube was set in the center of the cylinder (R = 1.5 cm) which is consist of six 407 nm LEDs (3 W) with the cooling of an electric fan. After t h, the tube was removed from the light source. The system was poured into 50 mL water. Brown solid were precipitated, filtered by the Buchner funnel to give the crude product. And then the solid was washed by DCM by three times, dried over vacuum pump to give the pure product.

Table S1. Screening Reaction Conditions for Polymerization[a]

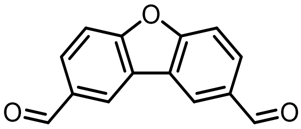


entry	x	y	t	Yield [b] (%)	*M*n (kDa)	PDI (*Đ*)
1	0.50	2.5	18	100	7.2	6.86
2	0.25	2.5	18	100	5.4	3.61
3	0.25	5.0	18	100	4.7	1.66
4	0.25	5.0	36	52	3.1	1.07

[a] Conditions: **CBZ6** (4 mol%), HCOONa (2.4 equiv). [b] Isolated yield.

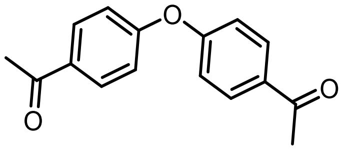
2.2 Synthesis and Characterization of S1

Compounds **S1a**, **S1b**, **S1d** were synthesized according to literature procedures[1-3], **S1c**, **S1e**, **S1f**, **S1g** were synthesized according to the corresponding produres.



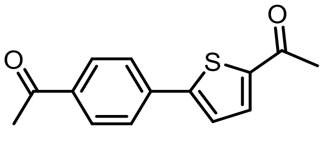
Dibenzo[*b*,*d*]furan-2,8-dicarbaldehyde (S1a)[1]

n-Butyllithium 1.6 M in hexane (9.4 mL, 15 mmol) was added to a solution of 2,8-dibromodibenzo[*b*,*d*]furan (1.62 g, 5 mmol) in dry THF (10 mL) at -78 °C under a nitrogen atmosphere and stirred for 2 h at the same temperature. To the reaction mixture, DMF (1.16 mL, 15 mmol) was added and the solution was stirred for 30 mins. 9.5 mL of 3 M hydrochloric acid was added after the reaction mixture warmed up to room temperature. The organic layer was separated and the aqueous layer was washed with diethyl ether (3 × 15 mL). The extract was dried over Na_2SO_4, filtered, the solvents were removed under vacuum and the solids were recrystallized from petroleum ether to give the pure compound **S1a** as colorless crystals (0.4 g, 36%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 10.15 (s, 2 H), 8.55 (s, 2 H), 8.09 (d, *J* = 6.6 Hz, 2 H), 7.74 (d, *J* = 6.8 Hz, 2 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 191.16, 160.44, 132.77, 130.13, 124.50, 123.62, 112.94.



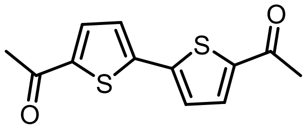
4-Acetylphenyl ether (S1b)[2]

To a stirred mixture of *p*-hydroxyacetophenone (1.36 g, 10 mmol) in dimethyl sulfoxide (5 mL), *p*-fluoroacetophenone (1.38 g, 10 mmol, 1 equiv) and anhydrous K_2CO_3 (2.07 g, 15 mmol, 1.5 equiv) were added and the reaction mixture was refluxed for 2 h. Then the mixture was cooled to room temperature, diluted with water (10 mL), and extracted with ether (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to give a crude product, which on purification by chromatography column with PE: DCM: EA (30:1:1-10:1:1) furnished diketone **S1b** as a white solid (0.94 g, 37%), **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.99 (dd, *J* = 6.8, 1.9 Hz, 4 H), 7.08 (dd, *J* = 6.9, 1.9 Hz, 4 H), 2.60 (s, 6 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 196.81, 160.33, 133.21, 130.87, 118.90, 26.67.



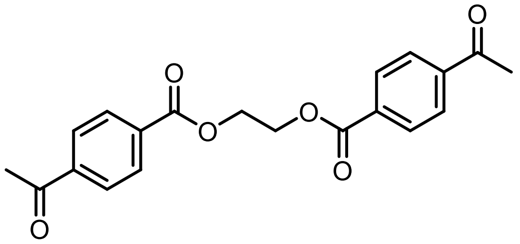
1-(5-(4-Acetylphenyl)thiophen-2-yl)ethan-1-one (S1c)

1-(5-bromothiophen-2-yl)ethan-1-one (5 mmol, 1 equiv), (4-acetylphenyl)boronic acid (12 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.5 mmol, 0.05 equiv) and K_2CO_3 (10 mmol, 1 equiv) were added in DMF (30 mL) and H_2O (5 mL) at room temperature. The resulting mixture was stirred for 12 h at 90 °C. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted with DCM (2 × 20 mL). The collected organic extracts were dried (anhydrous Na_2SO_4), filtered and concentrated under vacuum to give the crude product, and then was purified by flash chromatography to get pure product as a yellow solid (1.09 g, 89 %). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.00 (d, *J* = 8.3 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 3.9 Hz, 1 H), 7.43 (d, *J* = 3.9 Hz, 1 H), 2.63 (s, 3 H), 2.59 (s, 3 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 197.33, 190.72, 150.91, 144.53, 144.53, 137.68, 137.08, 133.50, 129.34, 126.37, 125.37, 26.82, 26.80.



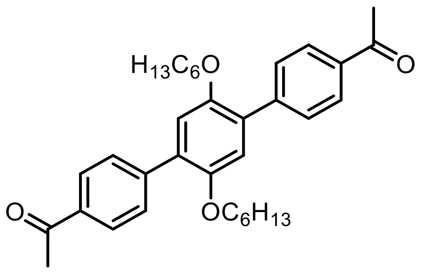
1,1'-([2,2'-Bithiophene]-5,5'-diyl)bis(ethan-1-one) (S1d)[3]

A mixture of 2-acetyl-5-bromothiophene (1.64 g, 8.0 mmol), palladium(II) acetate (90 mg, 0.40 mmol), tetrabutylammonium bromide (1.29 g, 4.0 mmol), and *N,N*-diisopropylethylamine (1.4 mL, 8.0 mmol) in dry toluene (3 mL) was stirred for 4 h at 105 °C under nitrogen atmosphere. After the mixture was cooled to room temperature, water was added. The aqueous phase was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was filtered and washed with *n*-hexane to afford a brown solid (1.63 g), then further washed by DCM for three times to provide compound **S1d** as pale yellow crystals (0.81 g, 81%). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.61 (d, *J* = 3.5 Hz, 2 H), 7.30 (d, *J* = 3.7 Hz, 2 H), 2.57 (s, 6 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 190.55, 144.42, 144.15, 133.33, 126.11, 26.79.



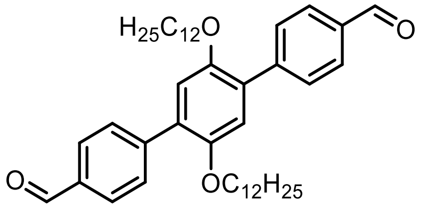
Ethane-1,2-diyl bis(4-acetylbenzoate) (S1e)

To a solution of ethane-1,2-diol (5 mmol, 1.0 equiv), EDCI (11 mmol, 2.2 equiv) and DMAP (3 mmol, 60 mol%) in DCM (20 mL) was added the 4-acetylbenzoic acid (11 mmol, 2.2 equiv). The mixture was stirred at room temperature for 12 h. Then the system was poured into 50 mL 5% aqueous sodium bicarbonate, extracted with DCM by three times and combined the organic layers. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated and purified on silica gel chromatography (EtOAc/petroleum ether as eluent) to give the product as a colorless solid (1.75 g, 99%). m.p. : 133.5-134.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 8.3 Hz, 4 H), 8.01 (d, *J* = 8.2 Hz, 4 H), 4.71 (s, 4 H), 2.64 (s, 6 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz) δ197.63, 165.63, 140.56, 133.55, 130.10, 128.42, 63.15, 27.06. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{20}H_{18}O_6Na^+$ 377.0996 found 377.0992.



1,1'-(2',5'-bis(hexyloxy)-[1,1':4',1''-terphenyl]-4,4''-diyl)bis(ethan-1-one) (S1f)

1,4-dibromo-2,5-bis(hexyloxy)benzene (3 mmol, 1 equiv), (4-acetylphenyl)-boronic acid (6.6 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (0.06 mmol, 0.02 equiv) and K_2CO_3 (9 mmol, 3.0 equiv) were added in DME (9 mL). The resulting mixture was stirred for 12 h at 90 ºC. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted with DCM (2 × 5 mL). The collected organic extracts were dried over with anhydrous Na_2SO_4 and concentrated under vacuum to give the crude product, and then was purified by flash chromatography to get the pure product as a yellow solid (0.84 g, 54 %). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 8.4 Hz, 4 H), 7.71 (d, *J* = 8.4 Hz, 4 H), 7.00 (s, 2 H), 3.94 (t, *J* = 6.4 Hz, 4 H), 2.65 (s, 6 H), 1.72-1.65 (m, 4 H), 1.39-1.30 (m, 4 H), 1.28-1.23 (m, 8 H), 0.86 (t, *J* = 6.8 Hz, 6 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 198.02, 150.45, 143.32, 135.74, 130.42, 129.82, 128.19, 116.00, 69.73, 31.53, 29.35, 26.81, 25.84, 22.69, 14.11. **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ calcd for $C_{34}H_{42}O_4Na^+$ 537.2975 found 537.3012.



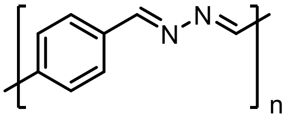
2',5'-bis(dodecyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (S1g)

1,4-dibromo-2,5-bis(dodecyloxy)benzene (3 mmol, 1 equiv), (4-formylphenyl) boronic acid (6.6 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (0.06 mmol, 0.02 equiv) and K_2CO_3 (9 mmol, 3.0 equiv) were added in DME (9 mL) at room temperature. The resulting mixture was stirred for 12 h at 90 ºC. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted with DCM (2 × 20 mL). The collected organic extracts were dried over with anhydrous Na_2SO_4 and concentrated under vacuum to give the crude product, and then was purified by flash chromatography to provide the pure product as a bright yellow solid (1.77 g, 90 %). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 10.07 (s, 2 H), 7.94 (d, *J* = 8.3 Hz, 4 H), 7.77 (d, *J* = 8.2 Hz, 4 H), 7.01 (s, 2 H), 3.94 (t, *J* = 6.4 Hz, 4 H), 1.72-1.66 (m, 4 H), 1.36-1.32 (m, 36 H), 0.88 (t, *J* = 6.8 Hz, 6 H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 192.15, 150.52, 144.74, 135.19, 130.46, 130.30, 129.57, 116.00, 69.77, 32.06, 29.81, 29.71, 29.50, 29.38, 26.20, 22.85, 14.27.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{44}H_{63}O_4^+$ 655.4721 found 655.4771.

2.3. General procedure for polymerization

The substrate (0.25 mmol, 1 equiv), **CBZ6** (4 mol%) and HCOONa (2.4 equiv) were weighed directly into an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (5 mL) was added sequentially in the Schlenk tube via syringe. This reaction tube was set in the center of the cylinder (R = 1.5 cm) which is consist of six 407 nm LEDs (3 W) with the cooling of an electric fan. The reaction mixture was stirred vigorously for 36 h, the tube was removed from the light source. The system was poured into 50 mL water. Brown solid was precipitated, filtered by the Buchner funnel to give the crude product. And then the precipitate was washed by DCM by three times, dried over vacuum pump to give the pure product.



P1 was prepared according to the general procedure using (1*E*,4*E*)-terephthalaldehyde *O*,*O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as a dark brown solid (18 h, 32.5 mg, 100%). **$^{13}C\{^1H\}$ NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^1H NMR** (DMSO-d_6, 500 MHz): δ 8.41-7.75 (m, 4 H), 7.70-7.28 (m, 2 H).

M_n = 4.7 kDa, M_w = 7.8 kDa, $Đ$ = 1.66, DP = 36.

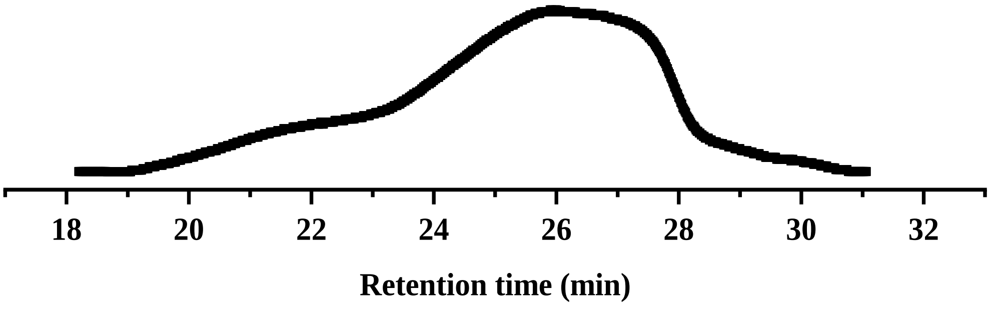


Figure S1. GPC chromatogram for **P1**

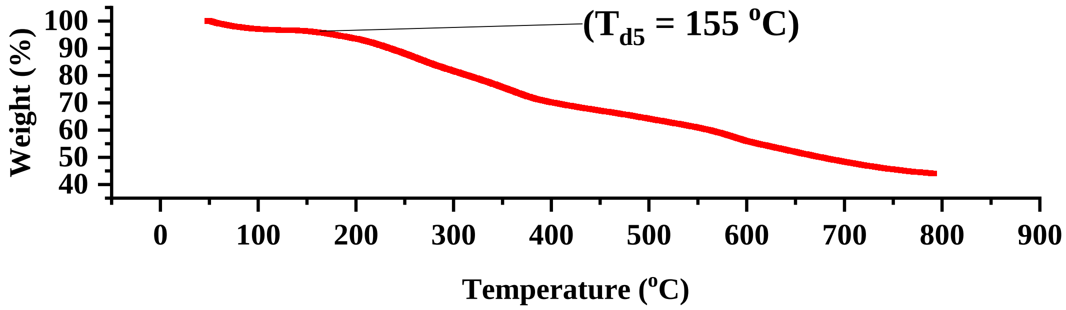


Figure S2. TGA: for **P1**

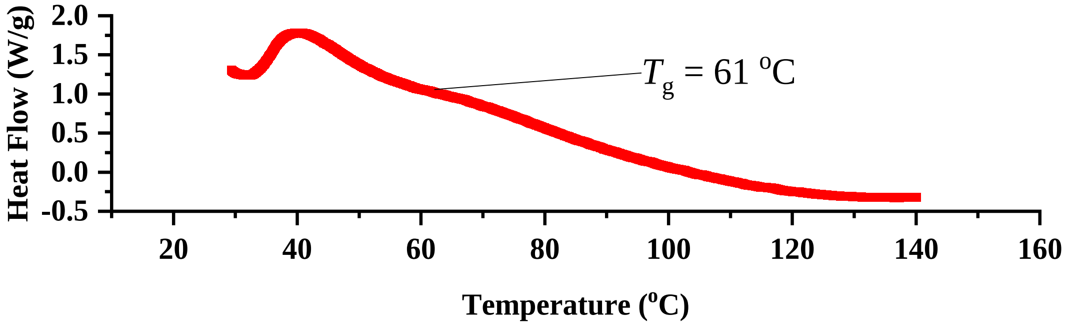
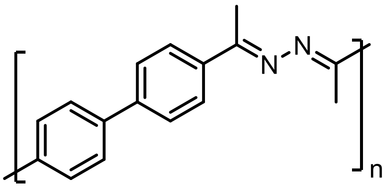


Figure S3. DSC for **P1**



P2 was prepared according to the general procedure using (1*E*,1'*E*)-1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one) *O*,*O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as a dark brown solid (57.4 mg, 98%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 8.12-8.05 (m, 2 H), 7.96-7.86 (m, 2 H), 7.82-7.78 (m, 4 H), 2.58 (s, 3 H), 2.22 (s, 3 H).

M_n = 81.5 kDa, M_w = 320.6 kDa, $Đ$ = 2.29, DP = 348.

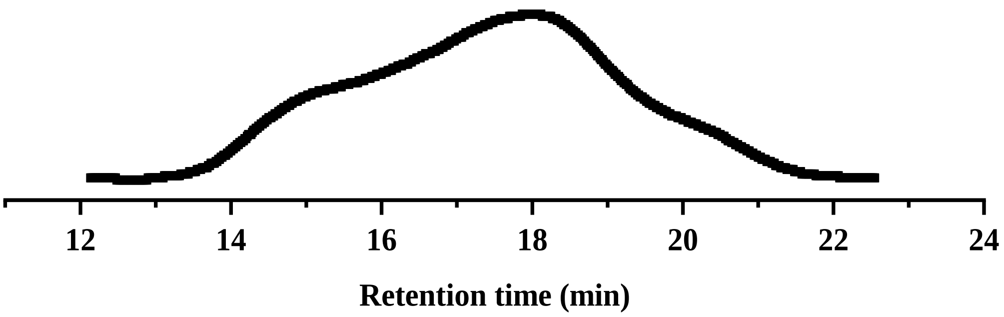


Figure S4. GPC chromatogram for **P2**

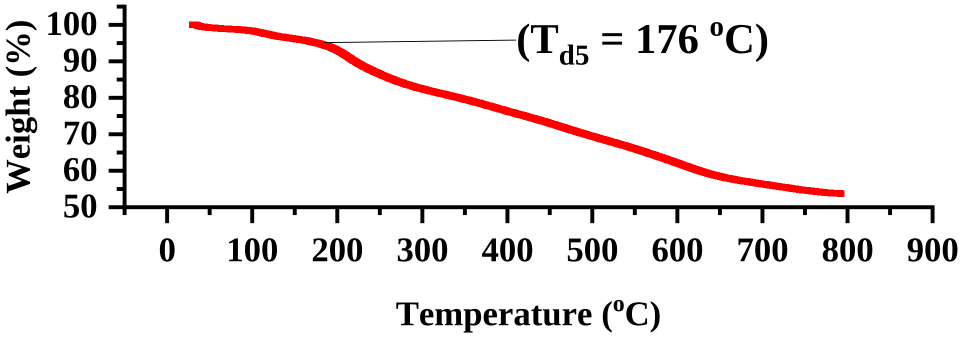


Figure S5. TGA: for **P2**

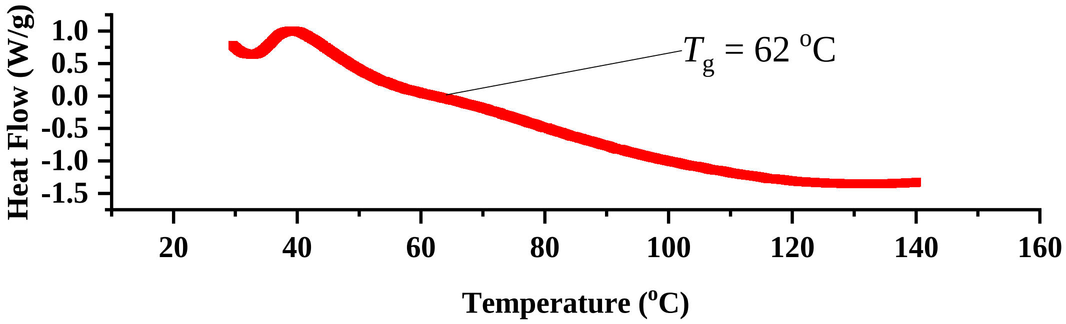
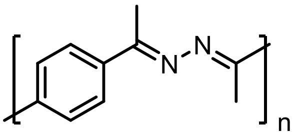


Figure S6. DSC for **P2**



P3 was prepared according to the general procedure using (1*E*, 1'*E*)-1, 1'-(1,4-phenylene)bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (37.5 mg, 95%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.08-8.03 (m, 4 H), 2.64 (s, 3 H), 2.36 (s, 3 H).

M_n = 26.2 kDa, M_w = 55.4 kDa, $Đ$ = 2.83, DP = 350.

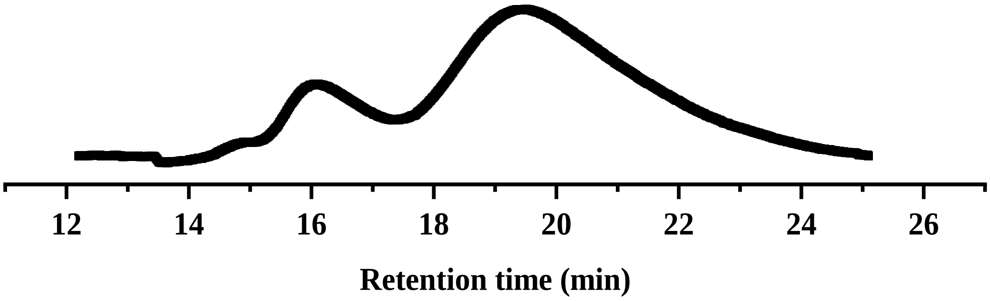


Figure S7. GPC chromatogram for **P3**

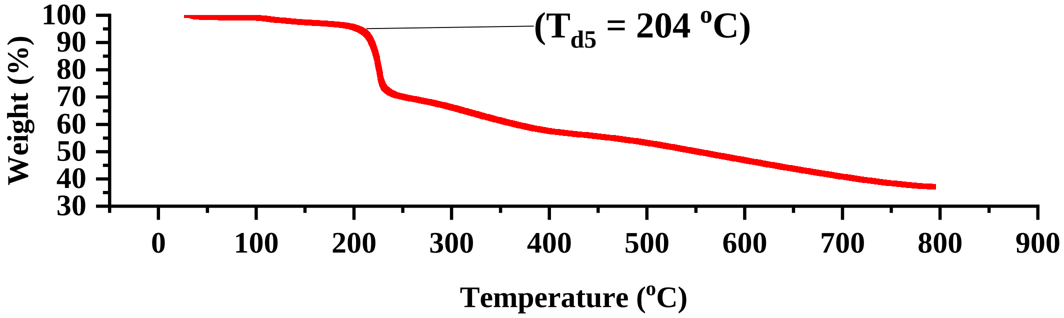


Figure S8. TGA: for **P3**

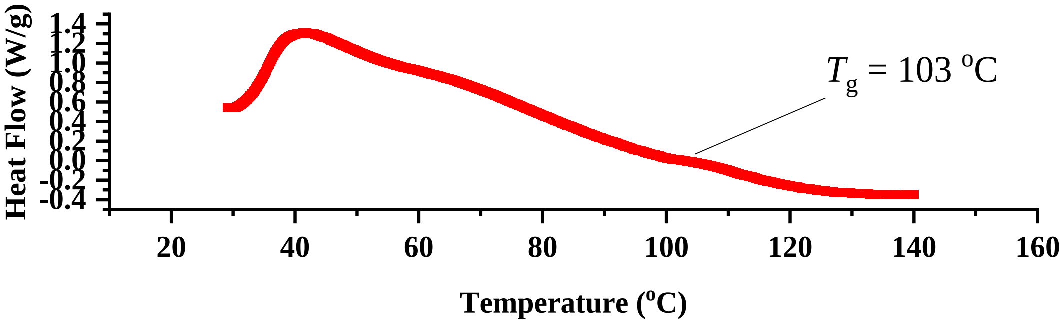
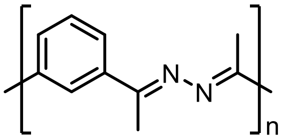


Figure S9. DSC for **P3**



P4 was prepared according to the general procedure using (1*E*, 1'*E*)-1,1'-(1,3-phenylene)bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (31.1 mg, 66%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-d_6, 500 MHz):

δ 8.67-7.07 (m, 4 H), 2.58 (s, 3 H), 2.38 (s, 3 H).
M_n = 56.7 kDa, $Đ$ = 2.88, DP = 327.

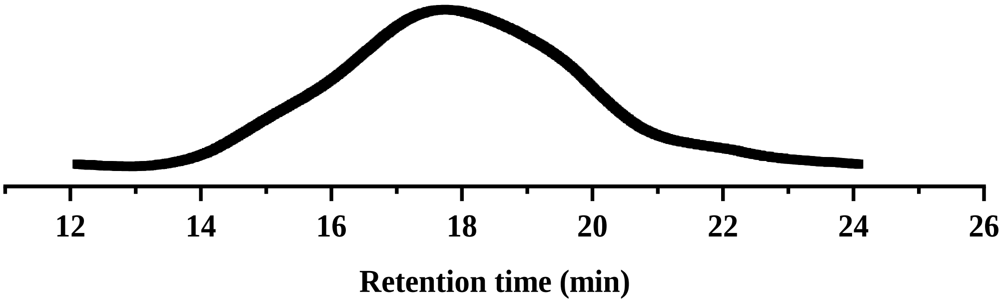


Figure S10. GPC chromatogram for **P4**

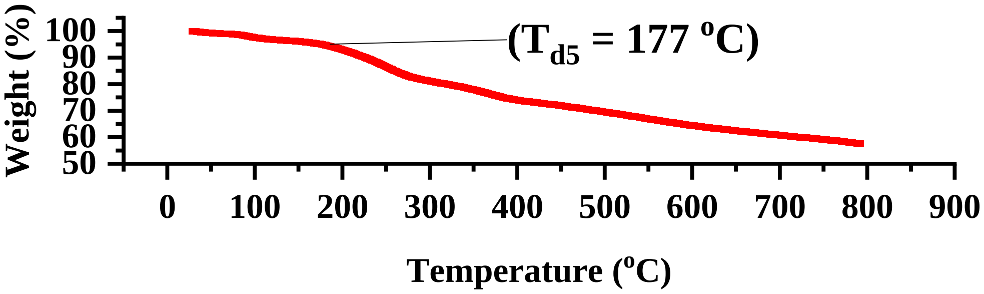


Figure S11. TGA: for **P4**

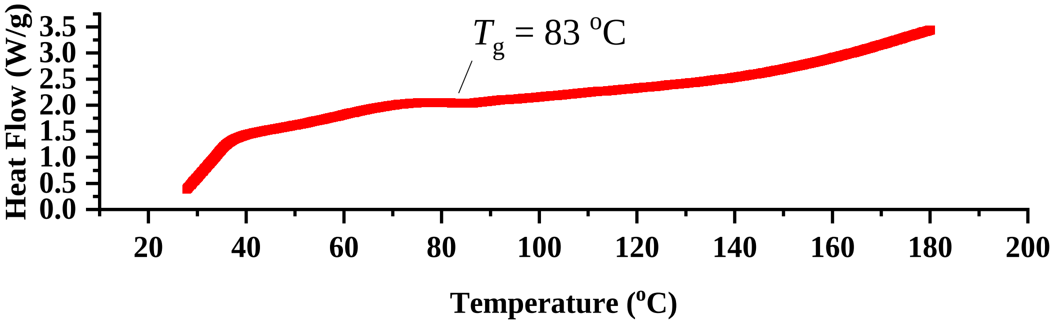
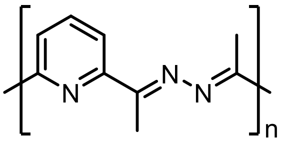


Figure S12. DSC for **P4**



P5 was prepared according to the general procedure using (1*E*, 1'*E*)-1,1'-(pyridine-2,6-diyl)bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (26.9 mg, 68%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. ^{1}**H NMR** (DMSO-d_6, 500 MHz): δ 8.33-7.47 (m, 3 H), 2.43 (s, 6 H).

M_n = 30.7 kDa, $Đ$ = 3.26, DP = 193.

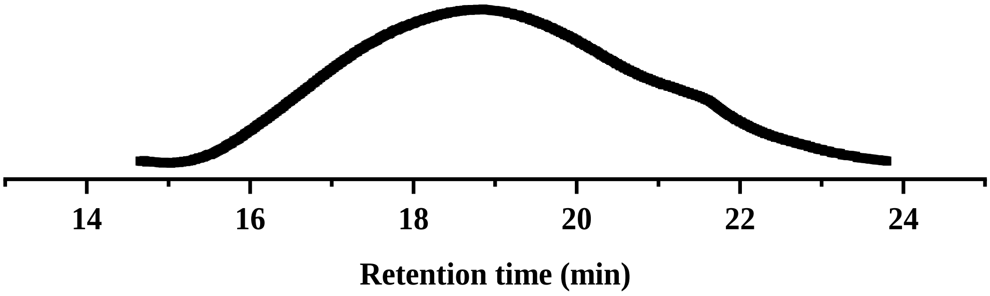


Figure S13. GPC chromatogram for **P5**

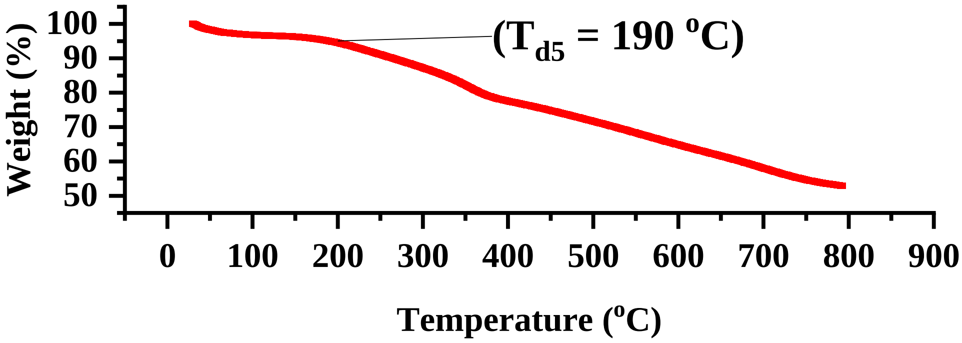


Figure S14. TGA: for **P5**

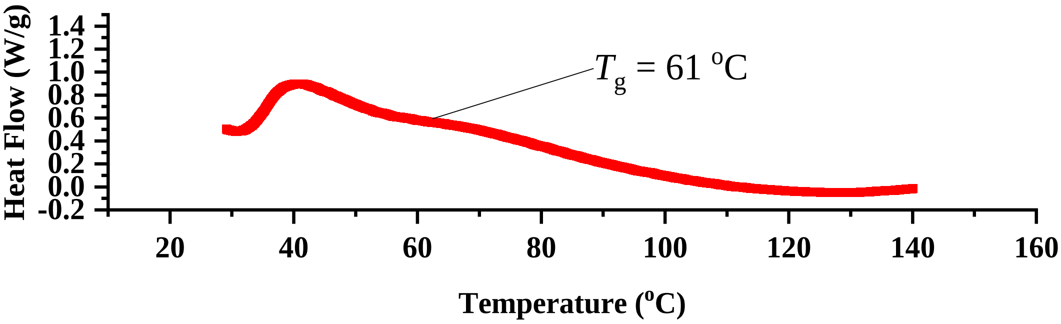
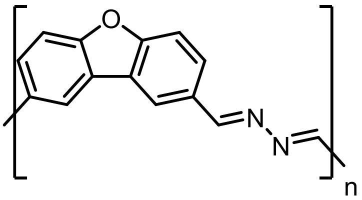


Figure S15. DSC for **P5**



P6 was prepared according to the general procedure using (1*E*, 1'*E*)-

dibenzo[*b*,*d*]furan-2,8-dicarbaldehyde *O*,*O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (19.3 mg, 35%). **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.84 (s, 2 H), 8.12 (d, J = 8.5 Hz, 3 H), 8.05 (d, J = 8.5 Hz, 3 H). **^{13}C{^{1}H} NMR** (DMSO-d_6, 125 MHz): δ 157.96, 132.75, 127.14, 118.82, 113.73, 106.73.
M_n = 2.3 kDa, $Đ$ = 1.00, DP = 10.

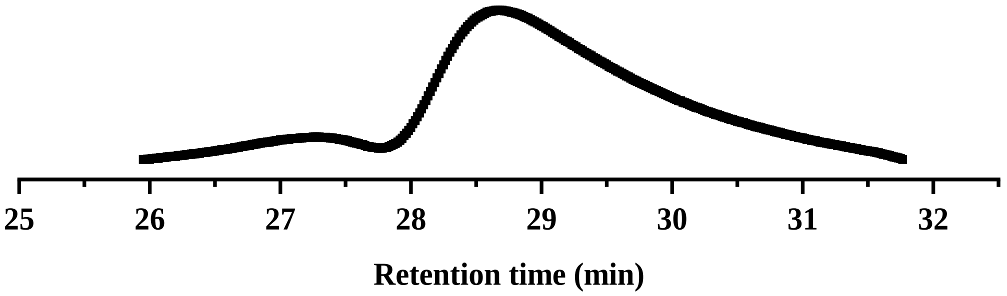


Figure S16. GPC chromatogram for **P6**

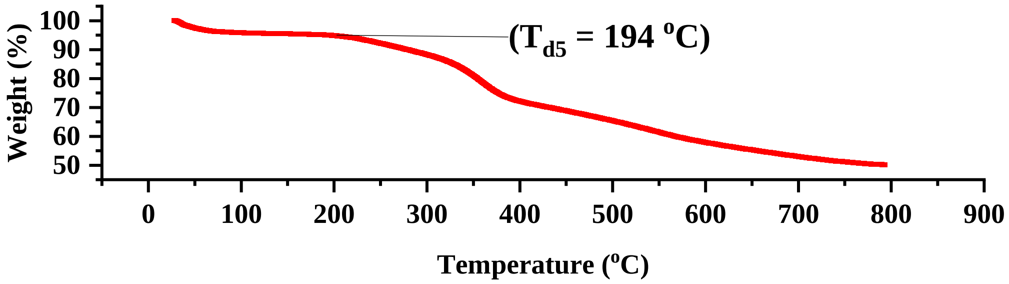


Figure S17. TGA: for **P6**

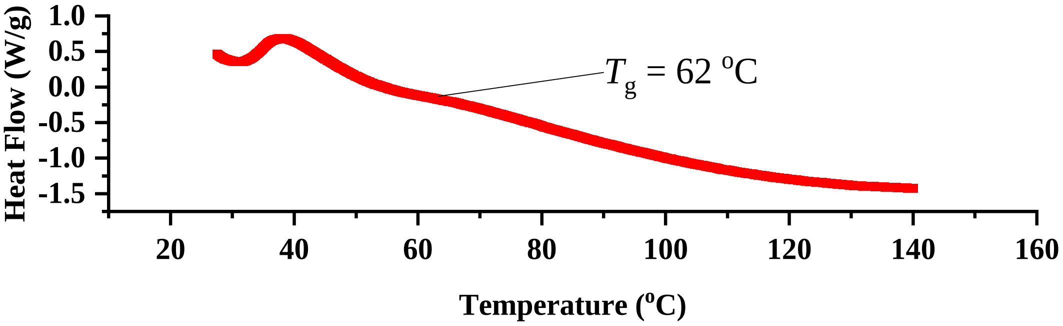
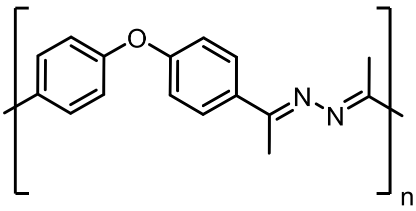


Figure S18. DSC for **P6**



P7 was prepared according to the general procedure using (1*E*, 1'*E*)-1,1'-(oxybis(4,1-phenylene))bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (28.9 mg, 46%). **$^{13}C\{^1H\}$ NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^1H NMR** (DMSO-d_6, 500 MHz): δ 8.08-7.46 (m, 4 H), 7.23-7.11 (m, 4 H), 2.61-2.58 (m, 3 H), 2.34-2.01 (m, 3 H).

M_n = 10.5 kDa, $Đ$ = 7.26, DP = 42.

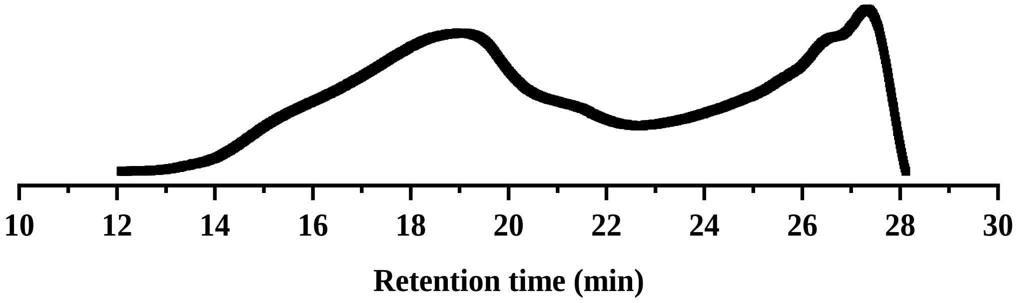


Figure S19. GPC chromatogram for **P7**

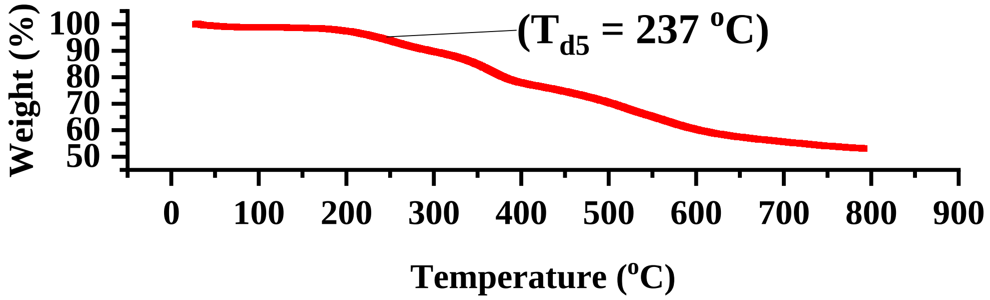


Figure S20. TGA: for **P7**

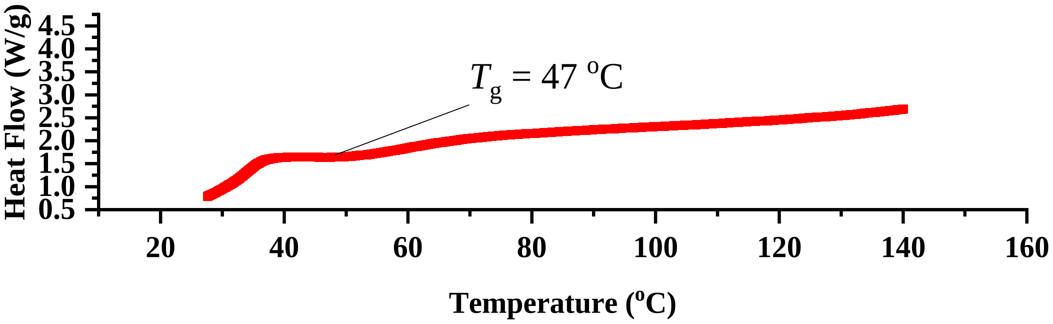
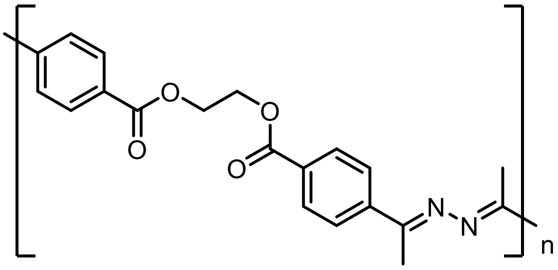


Figure S21. DSC for **P7**



P8 was prepared according to the general procedure using Ethane-1,2-diyl bis(4-((*E*)-1-((2,4-dinitrophenoxy)imino)ethyl)benzoate) as substrate and was obtained as dark brown solid (20.3 mg, 23%). ^{13}**C{**^{1}**H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. ^{1}**H NMR** (DMSO-d_6, 500 MHz): δ 8.07-7.64 (m, 4 H), 4.69 (s, 2 H), 2.40-2.03 (m, 3 H).

M_n = 93 kDa, $Đ$ = 2.19, DP = 266.

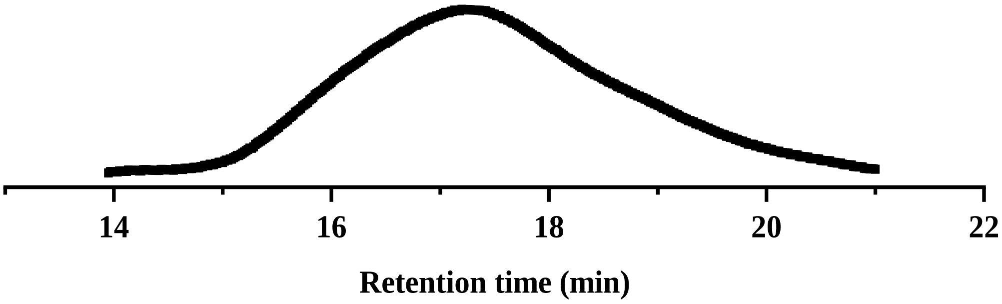


Figure S22. GPC chromatogram for **P8**

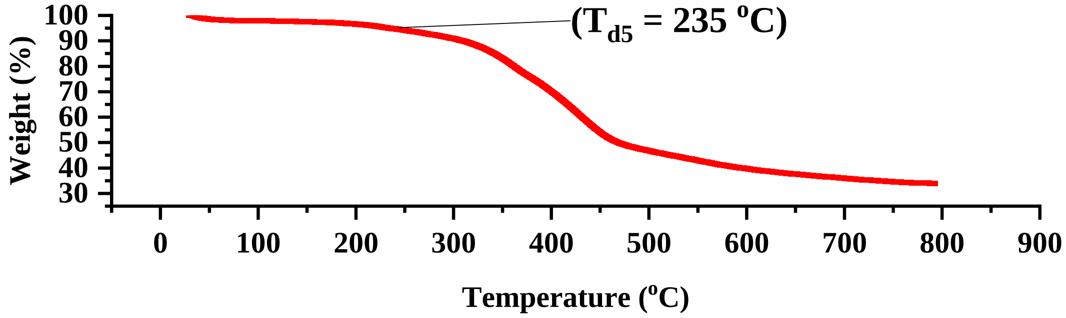


Figure S23. TGA: for **P8**

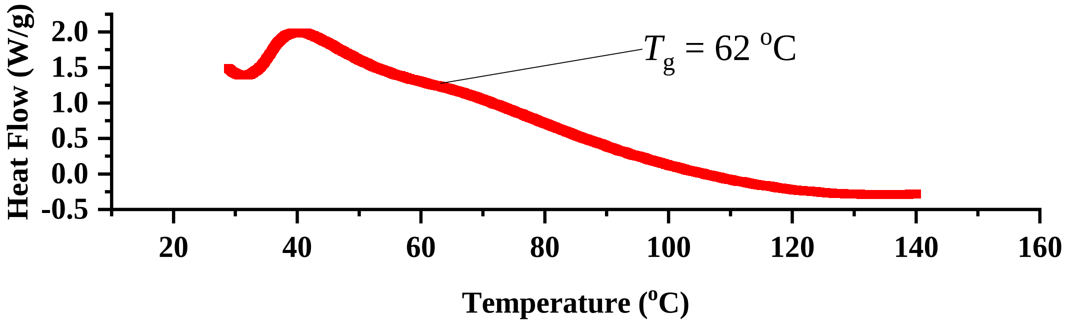
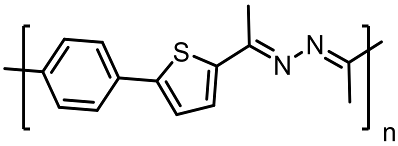


Figure S24. DSC for **P8**



P9 was prepared according to the general procedure using (*E*)-1-(5-(4-((*E*)-1-((2,4-dinitrophenoxy)imino)ethyl)phenyl)thiophen-2-yl)ethan-1-one *O*-(2,4-dinitrophenyl) oxime as substrate and was obtained as dark brown solid (61.3 mg, 100%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.01-7.77 (m, 6 H), 2.59 (s, 3 H), 2.06-2.00 (m, 3 H). Elem. anal. Calcd. for $(C_{14}H_{12}N_2S)_n$ $(240.07)_n$: C, 69.98%; H, 5.04%; N, 11.67%; S, 13.32%. Found: C, 62.68%; H, 3.77%; N, 9.12%; S, 8.20%.
M_n = 9.7 kDa, $Đ$ = 6.10, DP = 40.

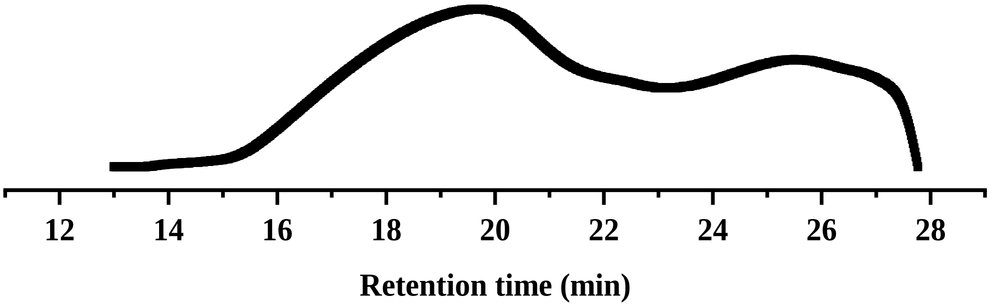


Figure S25. GPC chromatogram for **P9**

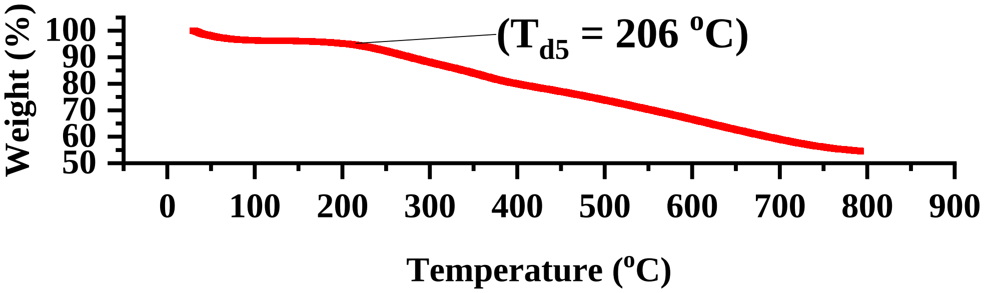


Figure S26. TGA: for **P9**

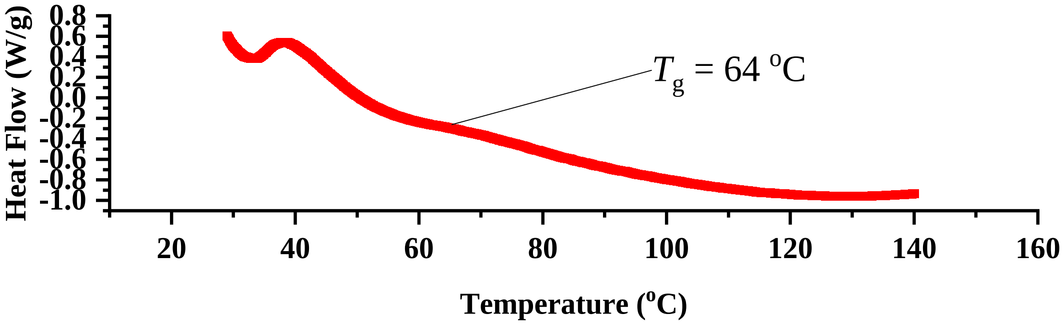
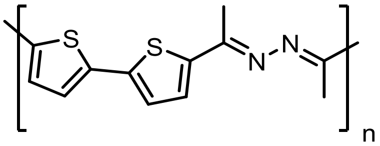


Figure S27. DSC for **P9**



P10 was prepared according to the general procedure using (1*E*, 1'*E*)-1,1'-([2,2'-bithiophene]-5,5'-diyl)bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as dark brown solid (44.3 mg, 64%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-*d*$_6$, 500 MHz): δ 7.97-7.76 (m, 2 H), 7.67-7.45 (m, 2 H), 2.58 (s, 3 H), 2.46-

2.30 (m, 3 H).

M_n = 64.8 kDa, $Đ$ = 2.66, DP = 280.

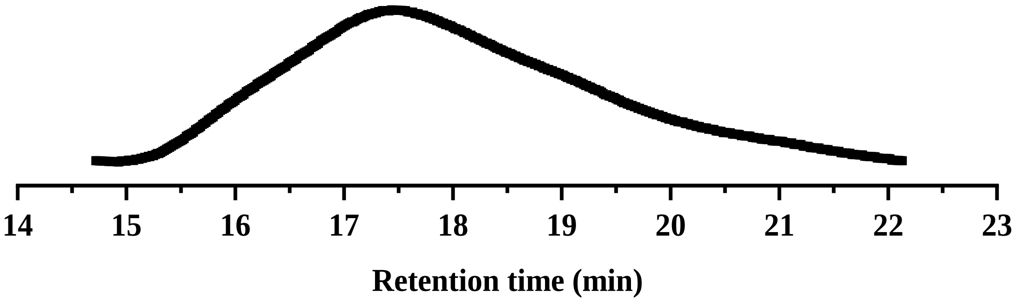


Figure S28. GPC chromatogram for **P10**

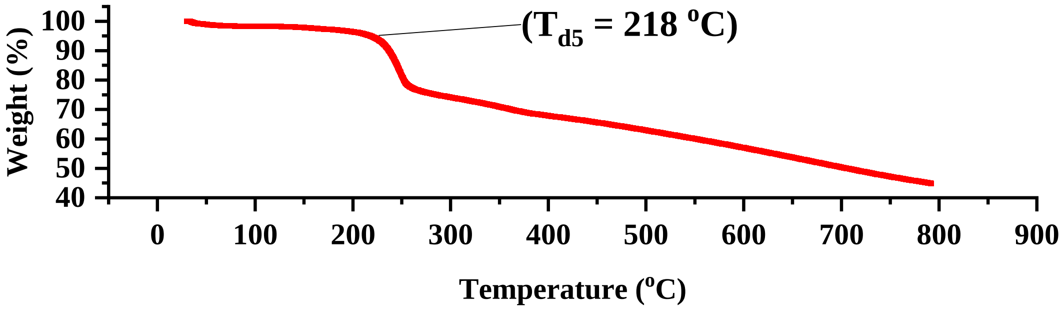


Figure S29. TGA: for **P10**

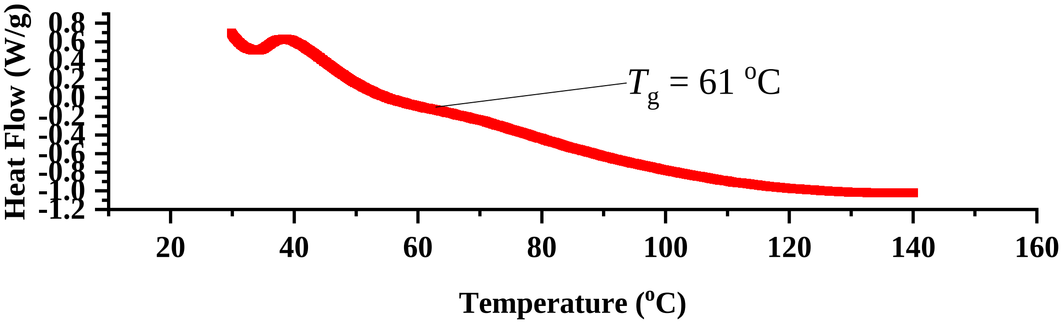
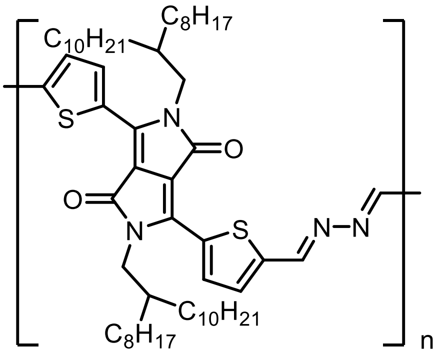


Figure S30. DSC for **P10**



P11 was prepared according to the general procedure using (1*E*, 1'*E*)-5, 5'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[*3*,*4*-*c*]pyrrole-1,4-diyl)bis(thiophene-2-carbaldehyde) *O*, *O*-di(2,4-dinitrophenyl) dioxime (0.15 mmol) as substrate and was obtained as dark brown solid (120 mg, 88%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals.**^{1}H NMR** ($CDCl_3$, 500 MHz)[4] : δ 7.74-7.65 (m, 2 H), 7.57-7.52 (m, 2 H), 7.47–7.45 (m, 1 H), 7.39-7.38 (m, 1 H), 3.53 (d, J = 5.4 Hz, 4 H), 2.21 (t, J = 7.0 Hz, 2 H), 1.25 (s, 64 H), 0.88 (t, J = 6.0 Hz, 12 H).

M_n = 59.8 kDa, $Đ$ = 2.99, DP = 66.

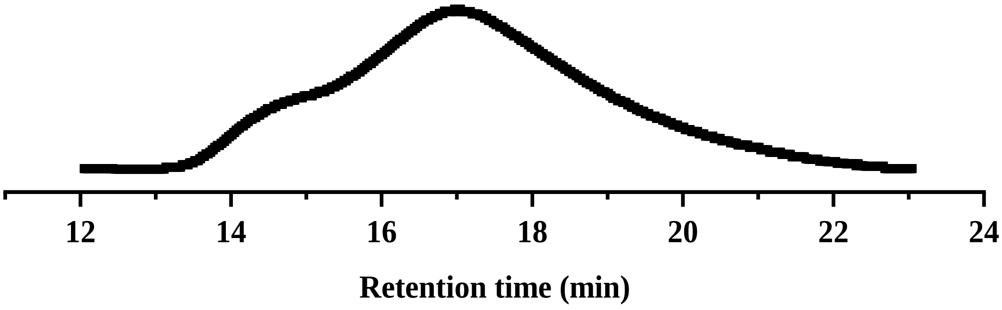


Figure S31. GPC chromatogram for **P11**

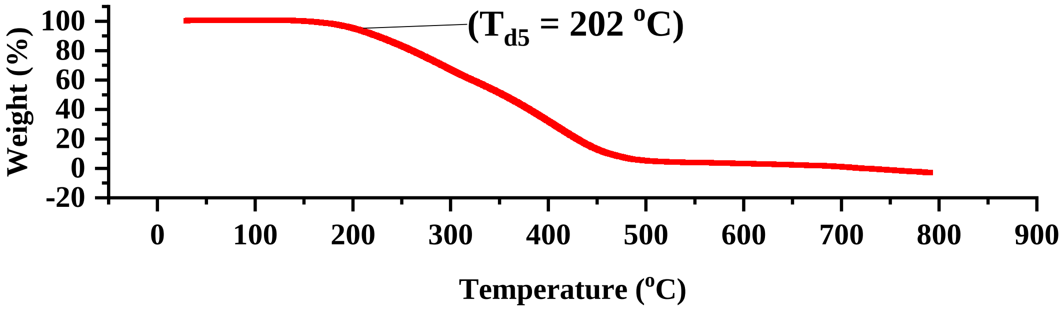


Figure S32. TGA: for **P11**

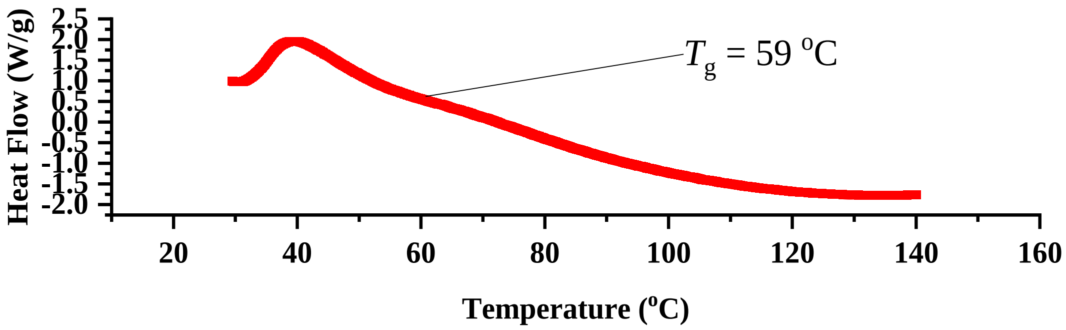
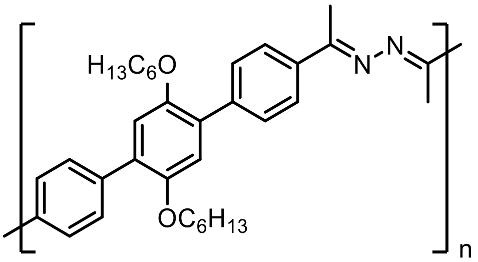


Figure S33. DSC for **P11**



P12 was prepared according to the general procedure using (1*E*,1'*E*)-1,1'-(2'-(hexa-1,3,5-triyn-1-yloxy)-5'-(hexyloxy)-[1,1':4',1''-terphenyl]-4,4''-diyl)bis(ethan-1-one) *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as brown solid (128 mg, quant). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 8.01-8.00 (m, 2 H), 7.80-7.62 (m, 4 H), 7.46-7.35 (m, 4 H), 7.11-7.09 (m, 2 H), 3.99 (s, 4 H), 2.62 (s, 2 H), 1.61 (s, 4 H), 1.31-1.23 (m, 16 H), 0.85-0.81 (m, 6 H).

M_n = 5.3 kDa, $Đ$ = 4.45, DP = 10.

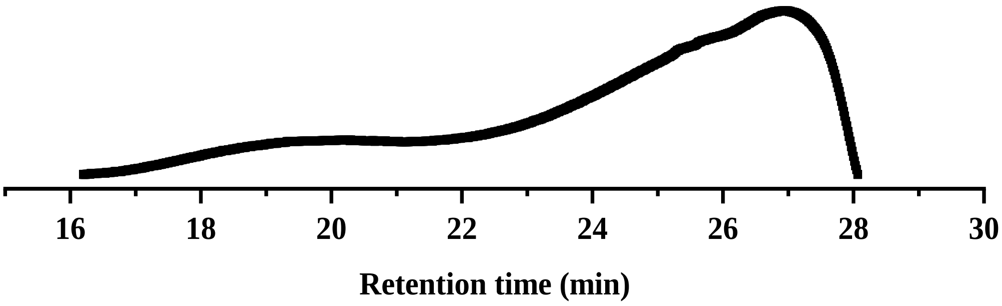


Figure S34. GPC chromatogram for **P12**

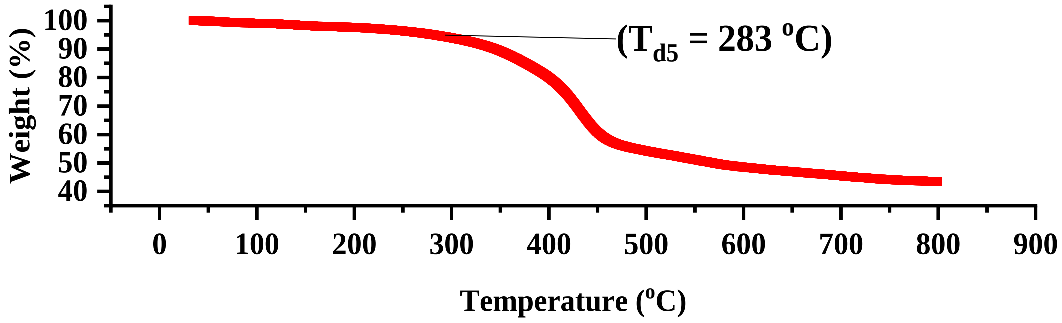


Figure S35. TGA: for **P12**

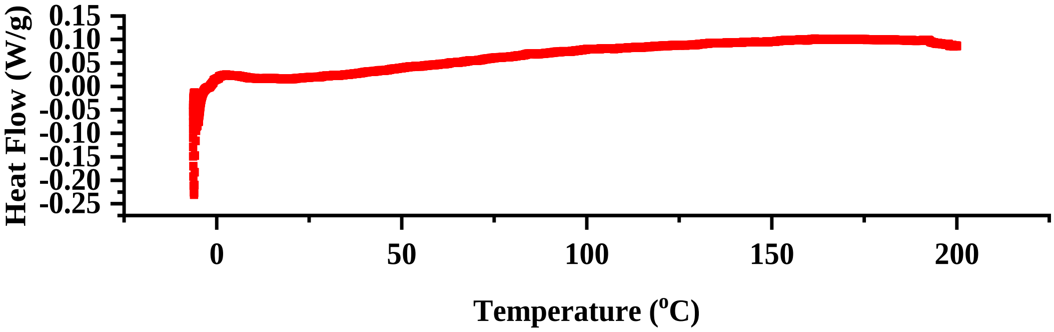
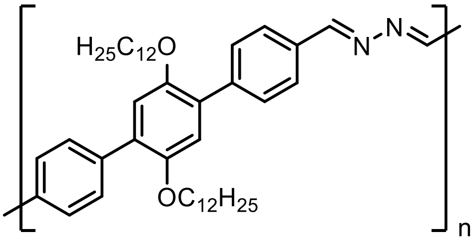


Figure S36. DSC for **P12**



P13 was prepared according to the general procedure using (1*E*,1'*E*)-2'-(dodeca-1,3,5,7,9,11-hexayn-1-yloxy)-5'-(dodecyloxy)-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde *O*, *O*-di(2,4-dinitrophenyl) dioxime as substrate and was obtained as brown solid (106.3 mg, 64%). **^{13}C{^{1}H} NMR** spectrum could not be analyzed because of the weak intensity of the signals. **^{1}H NMR** (CDCl$_3$, 500 MHz): δ 7.72-7.70 (m, 10 H), 6.94 (s, 2 H), 3.93 (t, J = 6.4 Hz, 4 H), 1.70-1.65 (m, 4 H), 1.33-1.25 (m, 36 H), 0.88 (t, J = 6.5 Hz, 6 H).

M_n = 3.2 kDa, $Đ$ = 1.09, DP = 5.

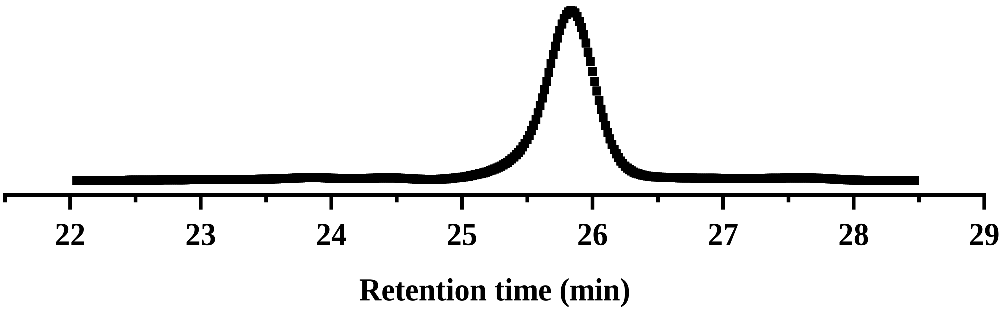


Figure S37. GPC chromatogram for **P13**

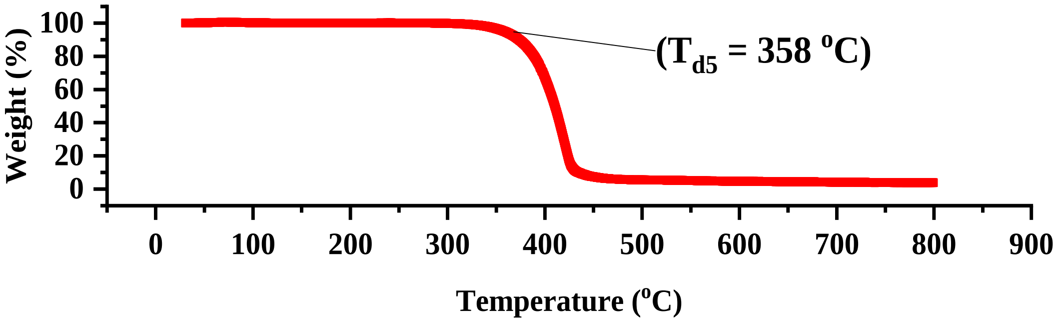


Figure S38. TGA: for **P13**

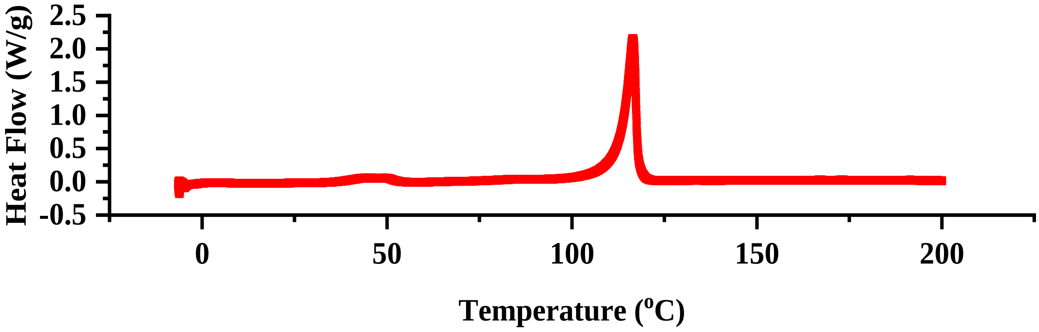
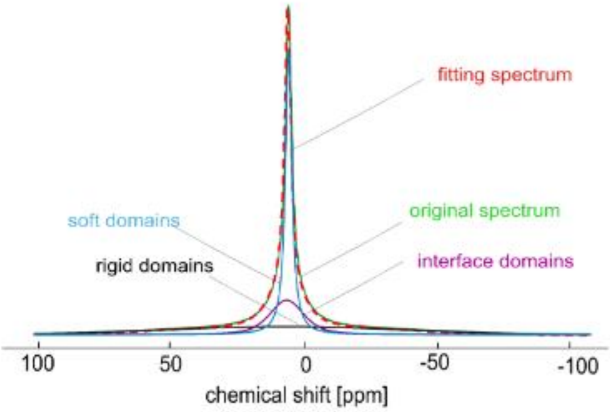


Figure S39. DSC for **P13**

According to referee's suggestion, we make some explanations to the discrepancies in the ^{1}HNMR spectra of the polymers. Actually, most solvents do not ingress into the crystalline regions of a polymer, and mass transfer or diffusion occurs only in the continuous amorphous phase between the crystallites. There, the solvent affects the segmental chain mobility and can trigger changes in the morphology of semi-crystalline polymers. (*Eur. Polym. J.*, **2016**, *80*, 48-57). Usually, the speed of the transverse magnetization decay is described by the relaxation time, and the decays could be analyzed by fitting them with the sum of two exponential functions:

$$A(t) = A^{\mathrm{rigid}} \exp\left(-t/T_{2\mathrm{eff}}^{\mathrm{rigid}}\right) + A^{\mathrm{soft}} \exp\left(-t/T_{2\mathrm{eff}}^{\mathrm{soft}}\right).$$

Besides, the relaxation times T2eff are related to the chain mobilities in each fraction. The relative fractions of the relaxation components $A^{i}/(A^{\mathrm{rigid}} + A^{\mathrm{soft}})$ represent the relative numbers of hydrogen atoms (molar fractions) of polymers with different molecular mobility. The ^{1}H wide-line NMR spectra of the polymer samples were decomposed into three components corresponding to the rigid, the soft and the interface domains (Fig as followed).



The line shapes of the rigid and soft components were taken to be Gaussian and Lorentzian functions, respectively, while a combination of both functions was used for the line shape of the interface domains (*Magn. Reson. Chem.*, **2002**, *40*, 70-76).

In all, the chain mobilities in each fraction of polymers cause changes in the corresponding relaxation times. And the relaxation time affects the line width and signal intensity of the nuclear magnetic resonance spectrum, which leading to the discrepancies in the ^{1}HNMR spectra of the polymers. Besides, for example (**P12)**, compared with broad and weak peaks of the aromatic component (the rigid domains), the long alkyl side chains (the soft domains) showed higher signal intensity and sharper peaks. For **P13**, A lower degree of polymerization might further lead to another increase in the chain mobilities.

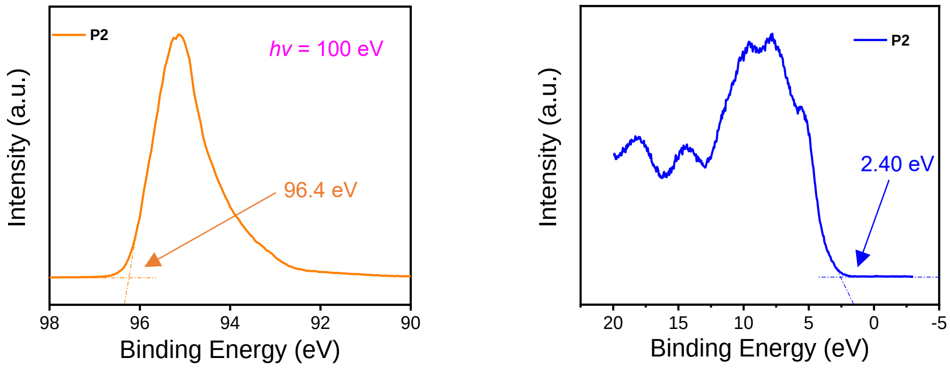


Figure S40. (a) Secondary electron cut-off and (b) valence band spectra of **P2** measured by SRPES.

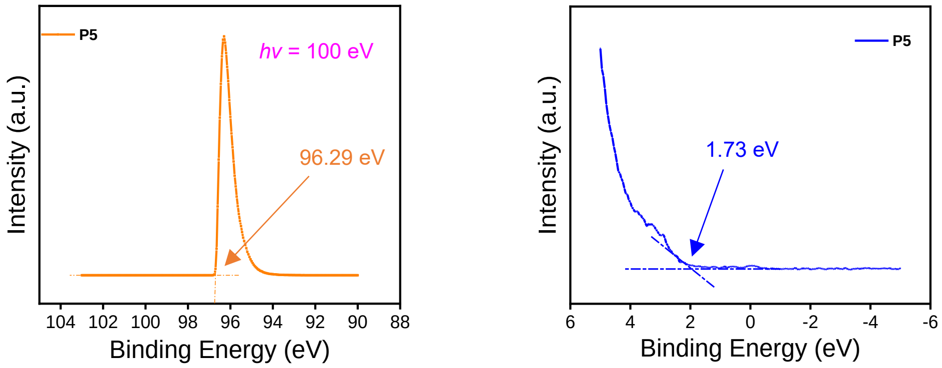


Figure S41. (a) Secondary electron cut-off and (b) valence band spectra of **P5** measured by SRPES.

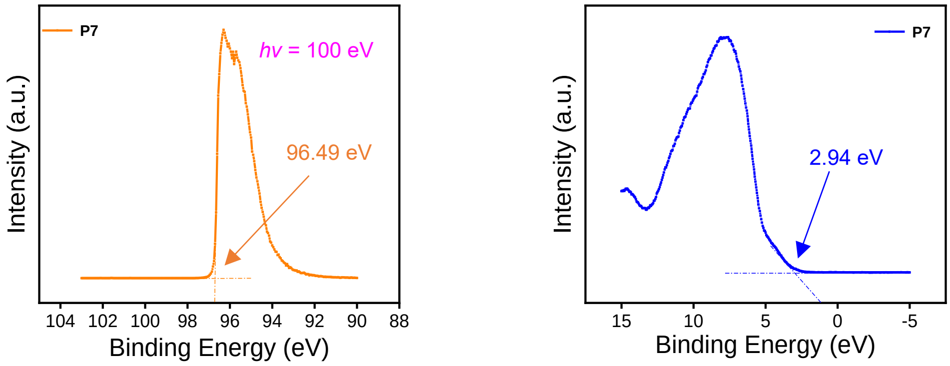


Figure S42. (a) Secondary electron cut-off and (b) valence band spectra of **P7** measured by SRPES.

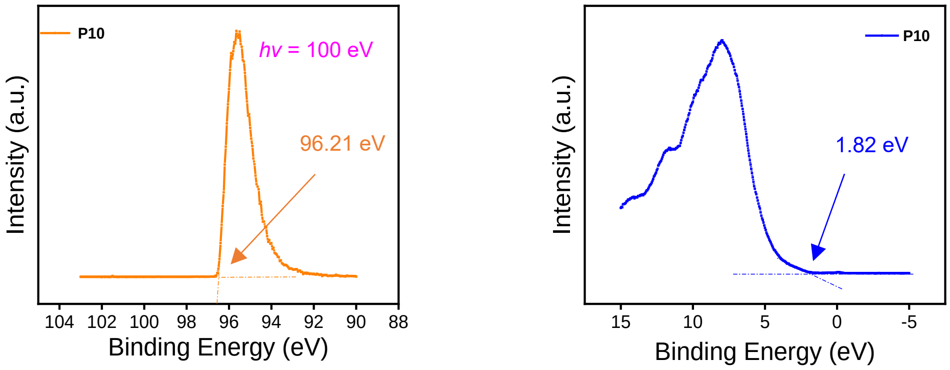


Figure S43. (a) Secondary electron cut-off and (b) valence band spectra of **P10** measured by SRPES.

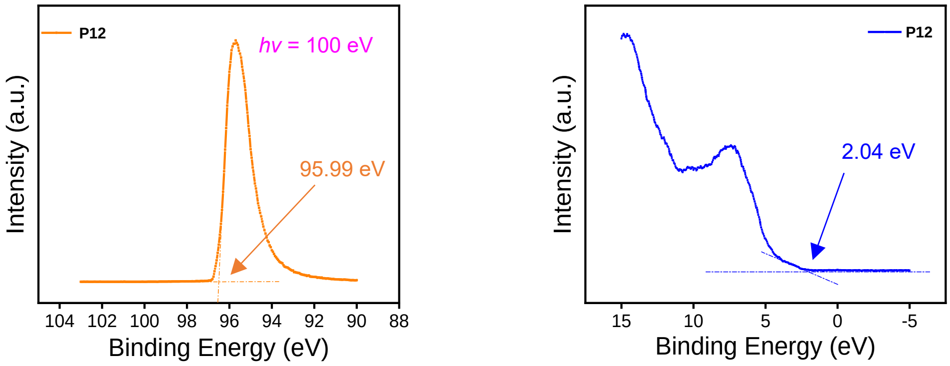


Figure S44. (a) Secondary electron cut-off and (b) valence band spectra of **P12** measured by SRPES.

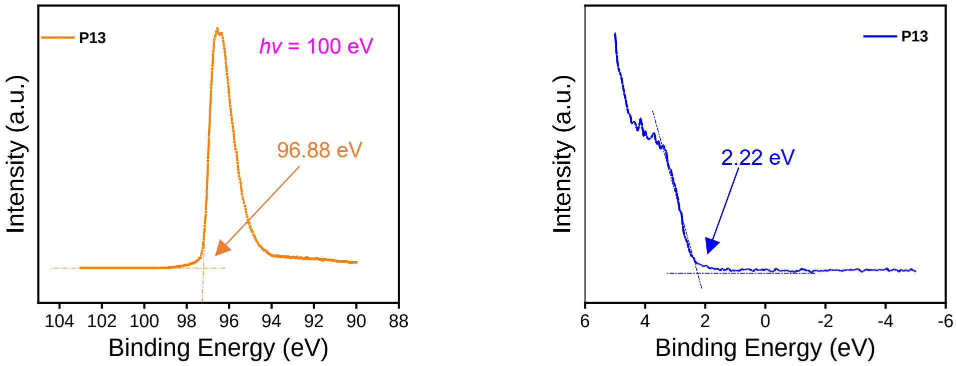
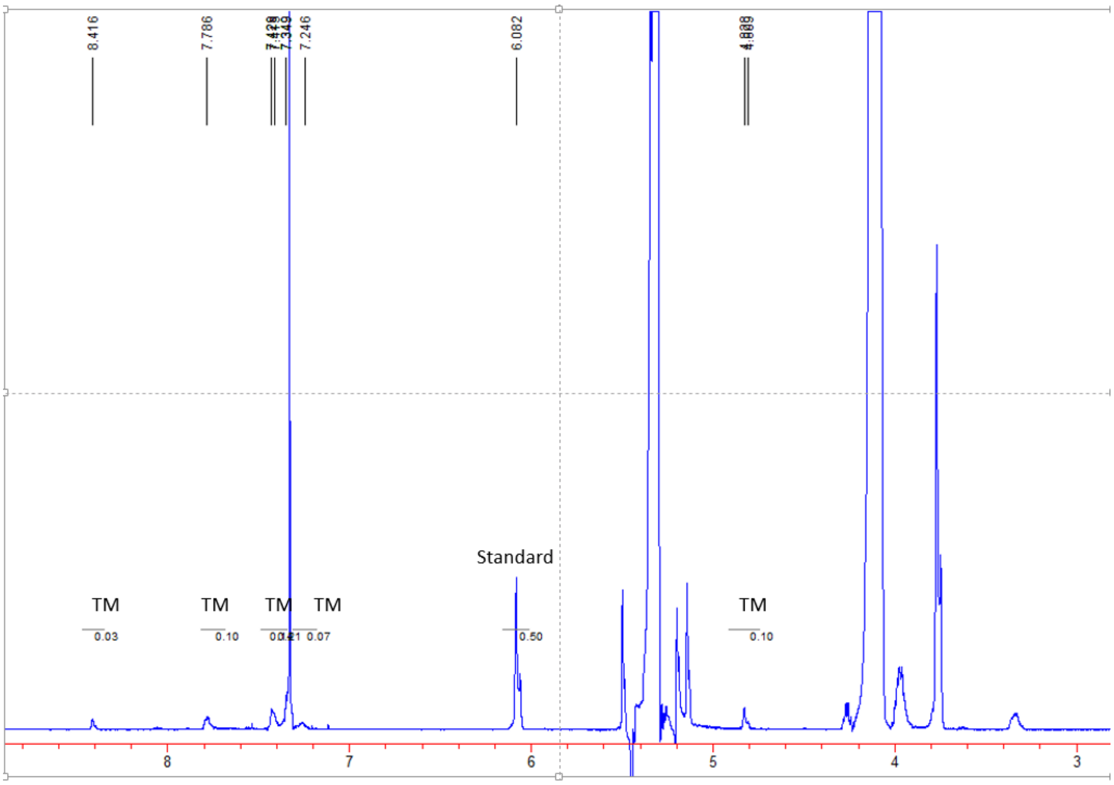


Figure S45. (a) Secondary electron cut-off and (b) valence band spectra of **P13** measured by SRPES.

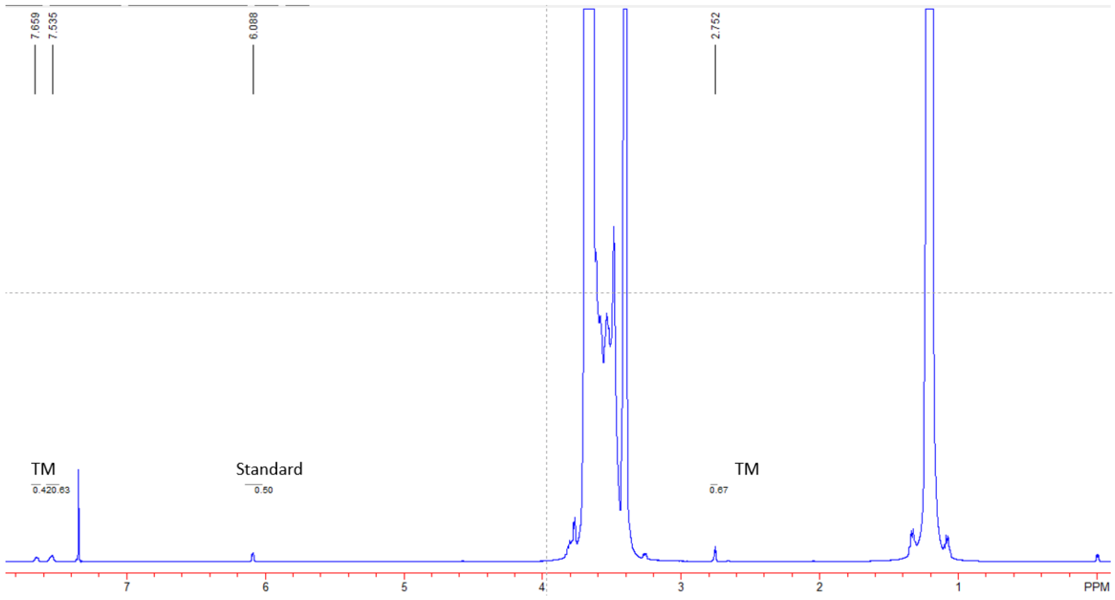
2.4 Benzylamine oxidation experiments

Benzylamine (0.1 mmol, 11 μL), MeCN (1.0 mL), **P2** (5 mg) and Tetrabutylammonium bromide (5 mol%, 3.22 mg) were added to an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar, dried *in vacuo* and charged with oxygen for three times. The reaction was initiated with a 407 nm LED (9 W) for 2 h. The quantity of products was detected by **^{1}H NMR** technology with 1,3,5-trimethoxybenzene as an internal standard.



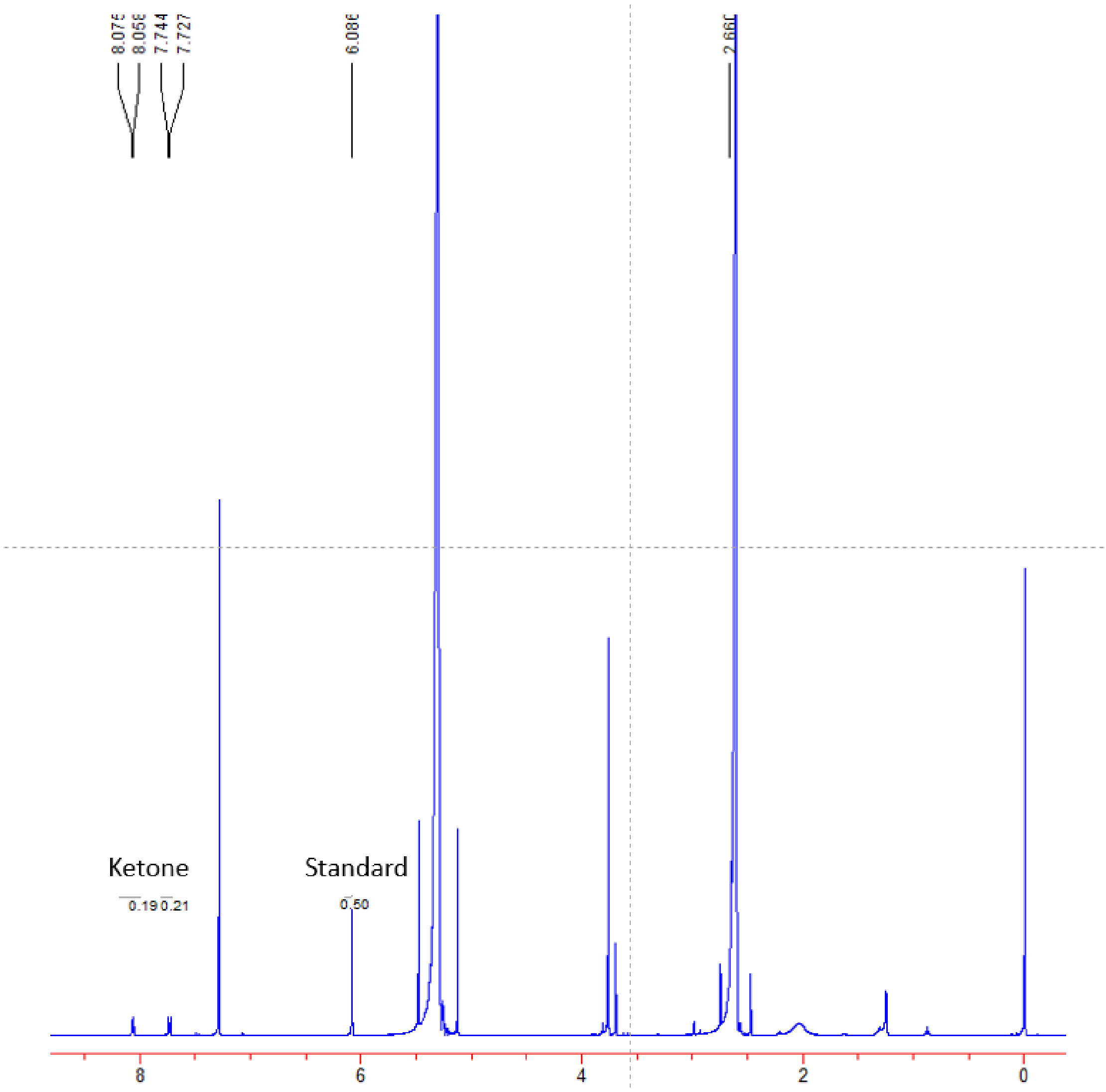
2.5 Thioanisole oxidation experiments

Thioanisole (0.2 mmoL, 24 μL), a mixture of 1.0 mL MeOH to water (v/v=1:1), **P2** (5 mg) and Tetrabutylammonium bromide (5 mol%, 3.22 mg) were added to an oven-dried 25 mL Schlenk tube equipped with a magnetic stirring bar, then dried *in vacuo* and charged with oxygen for three times. The reaction was initiated with a 407 nm LED (9 W) for 1 h. The quantity of products was detected by ^{1}**H NMR** technology with 1,3,5-trimethoxybenzene as an internal standard.

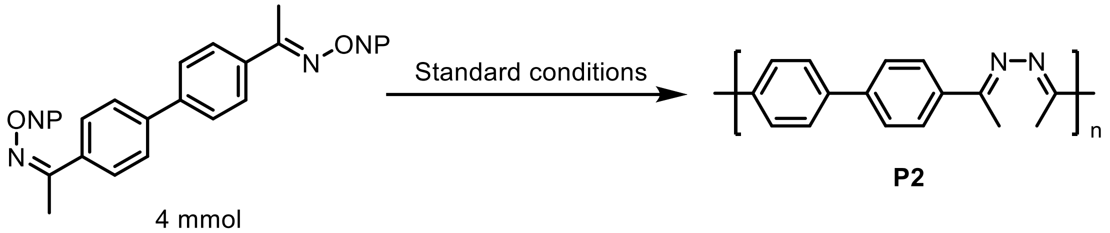


2.6 Degradation of P2

P2 (0.10 mmol, 1.0 equiv) and ion-exchange resin (NCK-9) ($C_{\text{hydrogen ion}}$ ≥4.7 mmol/g) (170 mg, 8.0 equiv) were weighed into a flask of 25 mL, then added a mixture of 0.5 mL DMSO to water (v/v=1:1), the reaction system was heated to 90 °C for 24 h. After the reaction mixture was cooled into the room temperature, 5.0 mL H_2O was added and DCM (3 × 3 mL) extracted the mixture. The organic phase was combined and concentrated for the quantification of ketone. The yield of the corresponding ketone was determined by **^{1}H NMR** using 1,3,5-trimethoxybenzene as an internal standard. The hydrazine was quantified by iodimetry using iodine standard solution [GBW(E)081614 ($C_{(1/2\ \mathrm{I2})}$ = 0.1005 mol/L)]. The 50% yield for hydrazine was determined based on three runs of the reactions.



2.7 Gram-scale reaction of P2



(1*E*,1'*E*)-1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one) *O*,*O*-di(2,4-dinitrophenyl) dioxime as substrate (4.0 mmol, 1 equiv), **CBZ6** (4 mol%) and HCOONa (2.4 equiv) were weighed directly into an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, dried *in vacuo* and charged with nitrogen for three times. Dry DMSO (20 mL) was added sequentially in the Schlenk tube via syringe. Then the tube was placed 1.5 cm away from LEDs (3 W × 6), and the reaction mixture was stirred vigorously under the irradiation. After 36 h, the tube was removed from the light source. The system was poured into 100 mL water. Brown solid were precipitated, filtered by the Buchner funnel to give the crude product. And then the solid was washed by DCM by three times, dried over vacuum pump to give the pure product. (0.998 g, quant) and **CBZ6** recycled in 99% yield (69 mg).

3. References

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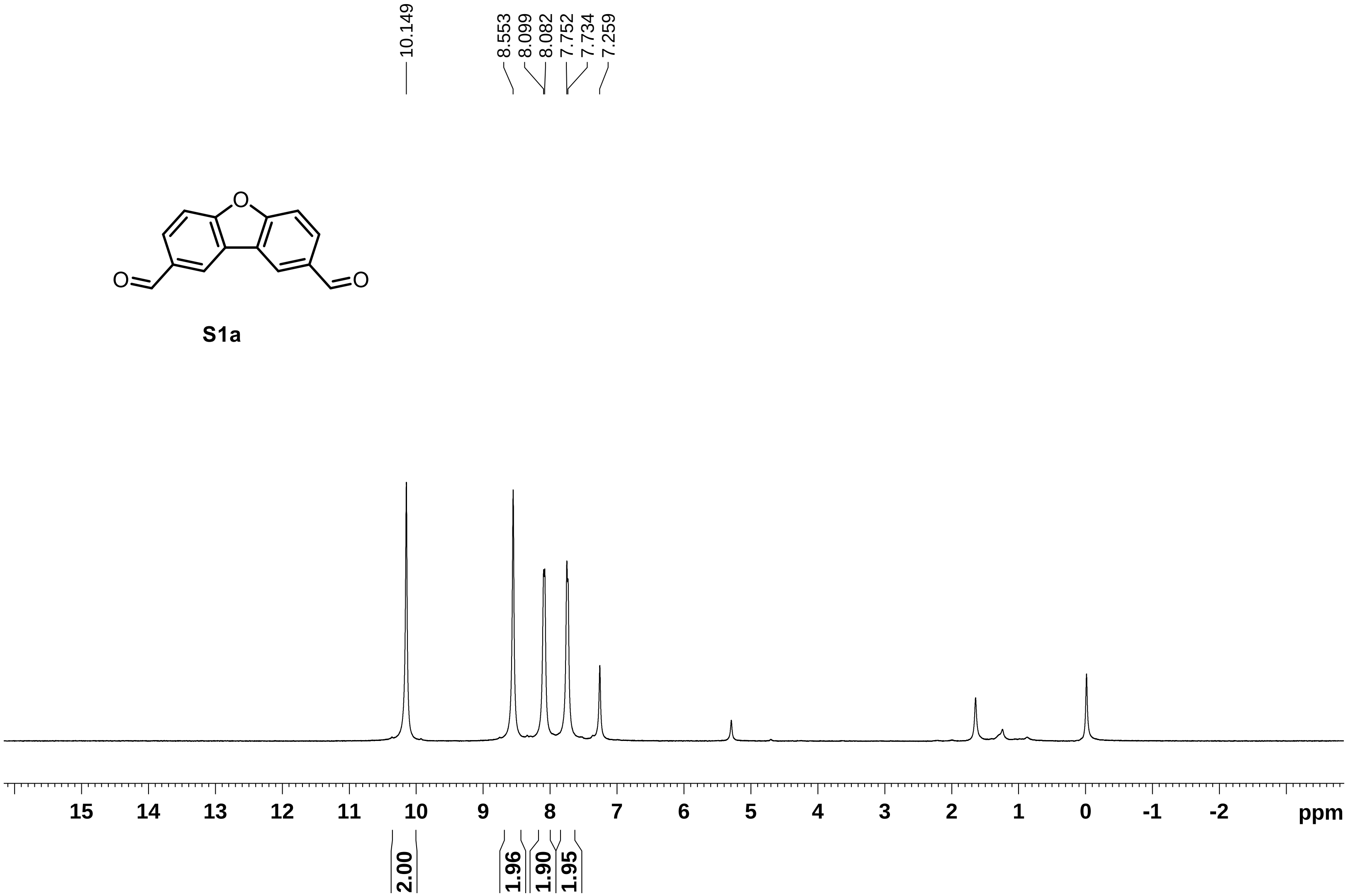
4. NMR Spectra



S1a

Figure S46. ^{1}H NMR spectrum of **S1a** ($CDCl_3$, 400 M).

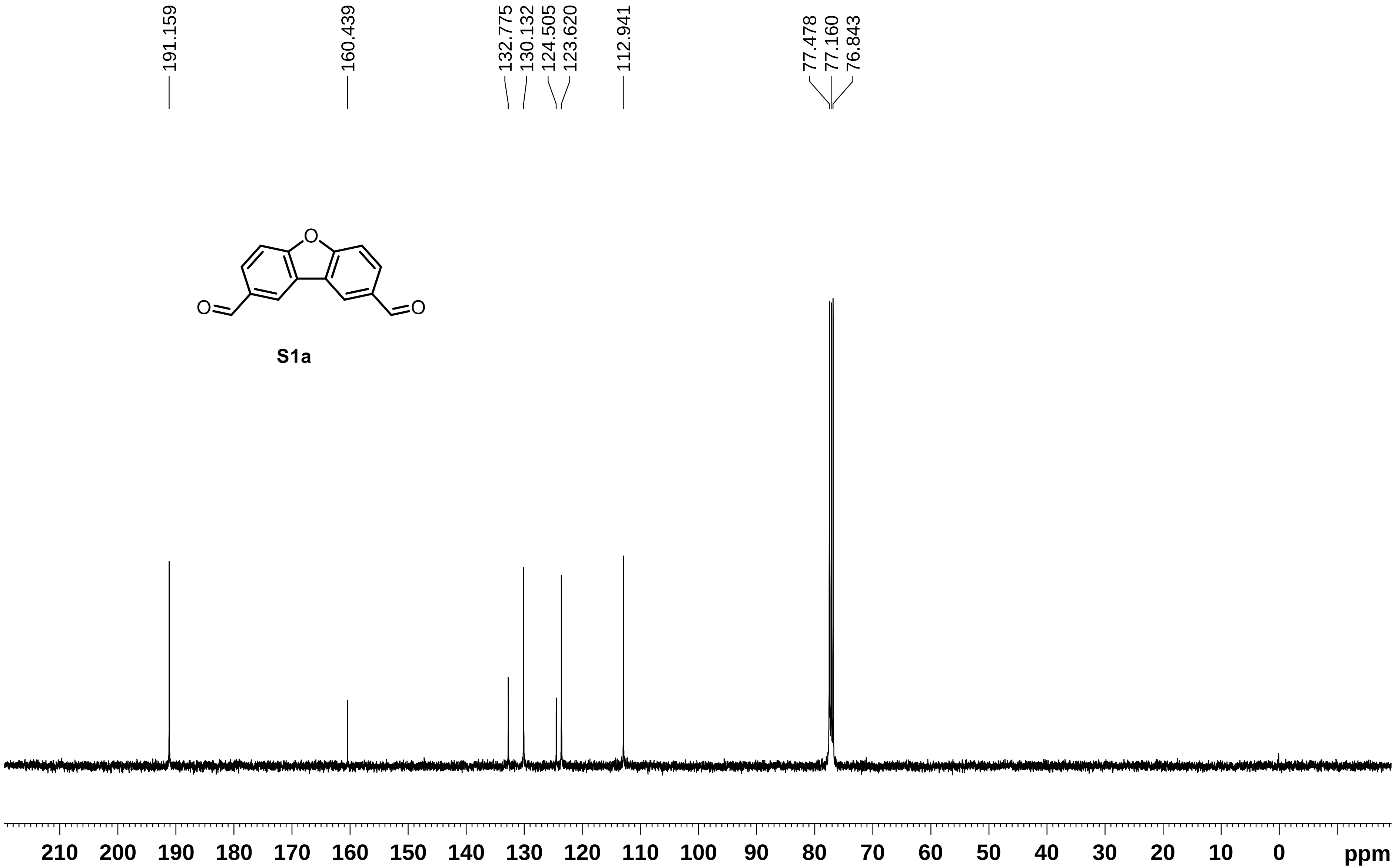


Figure S47. $^{13}C\{^1H\}$ NMR spectrum of **S1a** ($CDCl_3$, 100 M).

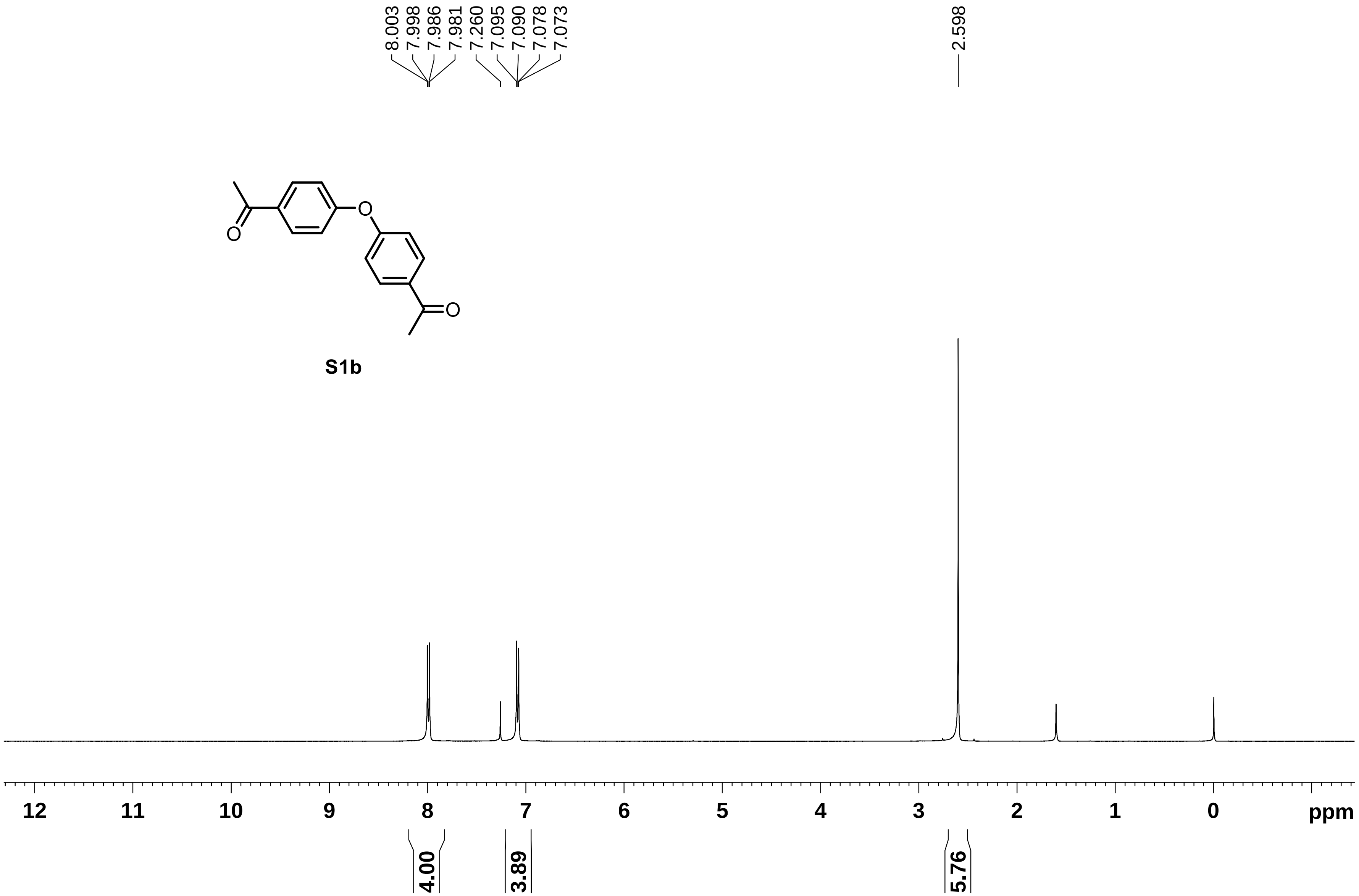


Figure S48. ^{1}H NMR spectra of **S1b** ($CDCl_3$, 400M).

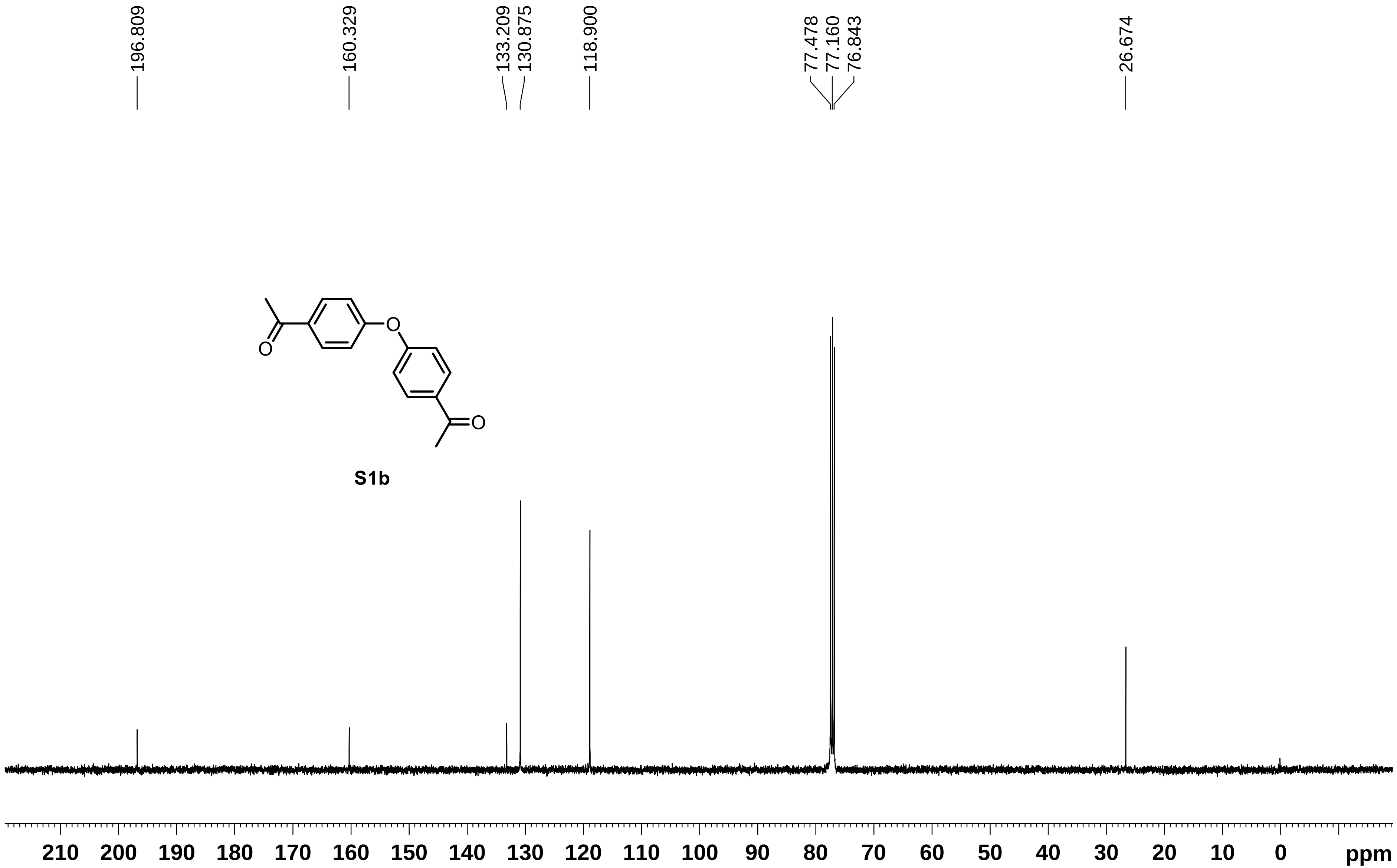


Figure S49. $^{13}C\{^1H\}$ NMR spectra of **S1b** ($CDCl_3$, 100M).

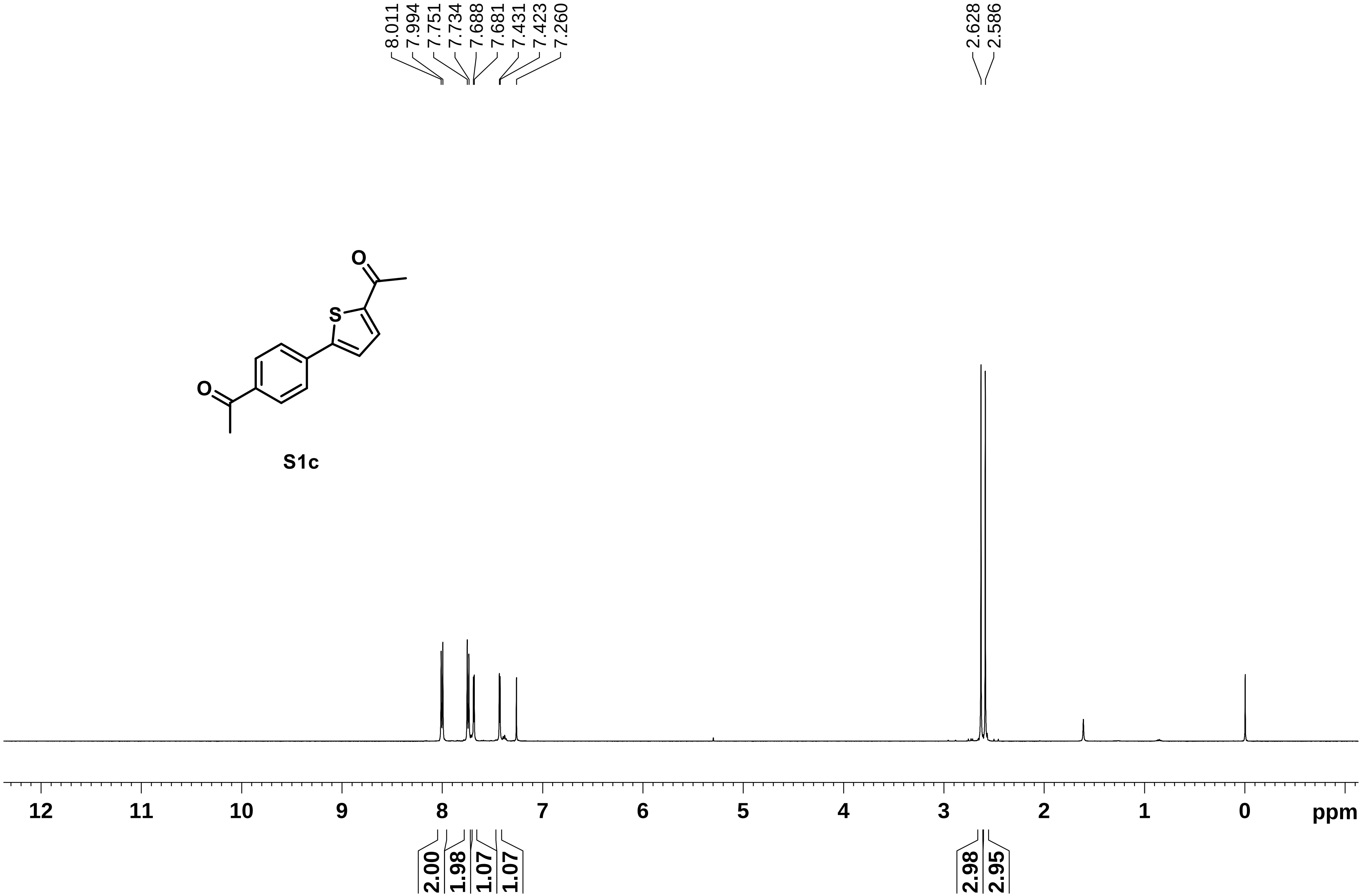


Figure S50. ^{1}H NMR spectra of **S1c** ($CDCl_3$, 500M).

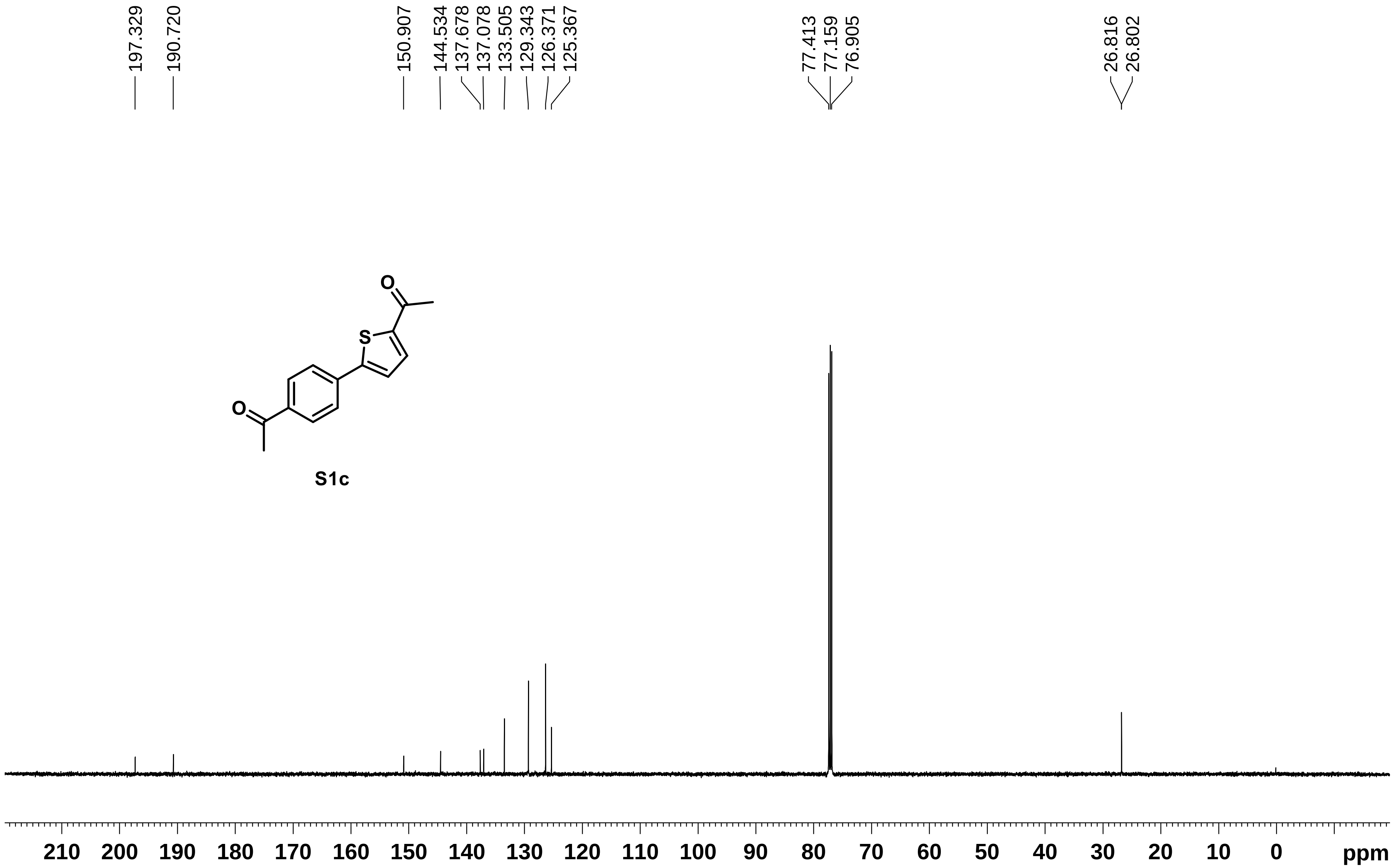


Figure S51. ^{13}C{^{1}H} NMR spectra of **S1c** (CDCl$_3$, 125M).

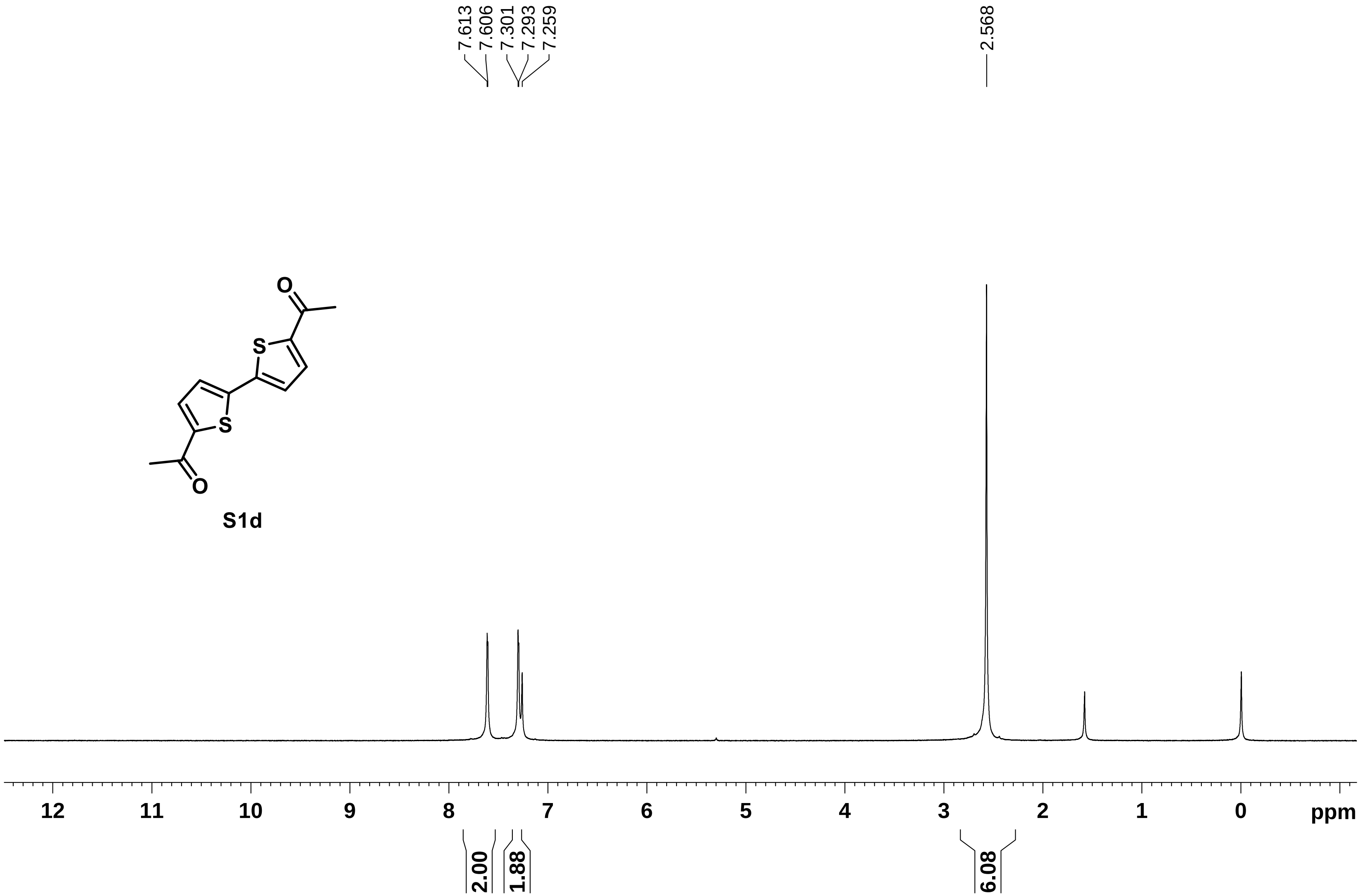


Figure S52. ^{1}H NMR spectra of **S1d** ($CDCl_3$, 500M).

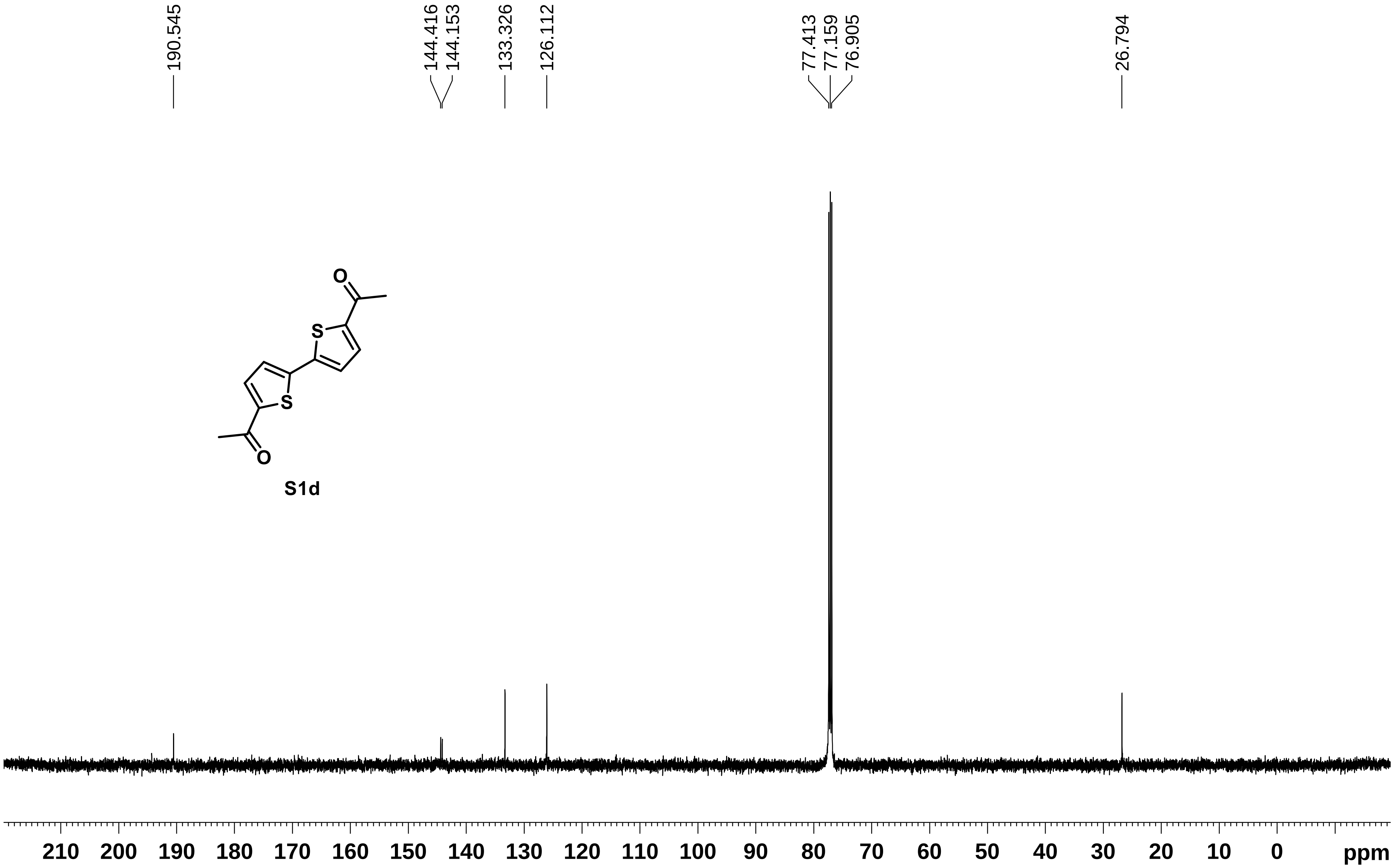


Figure S53. $^{13}C\{^1H\}$ NMR spectra of **S1d** ($CDCl_3$, 125M).

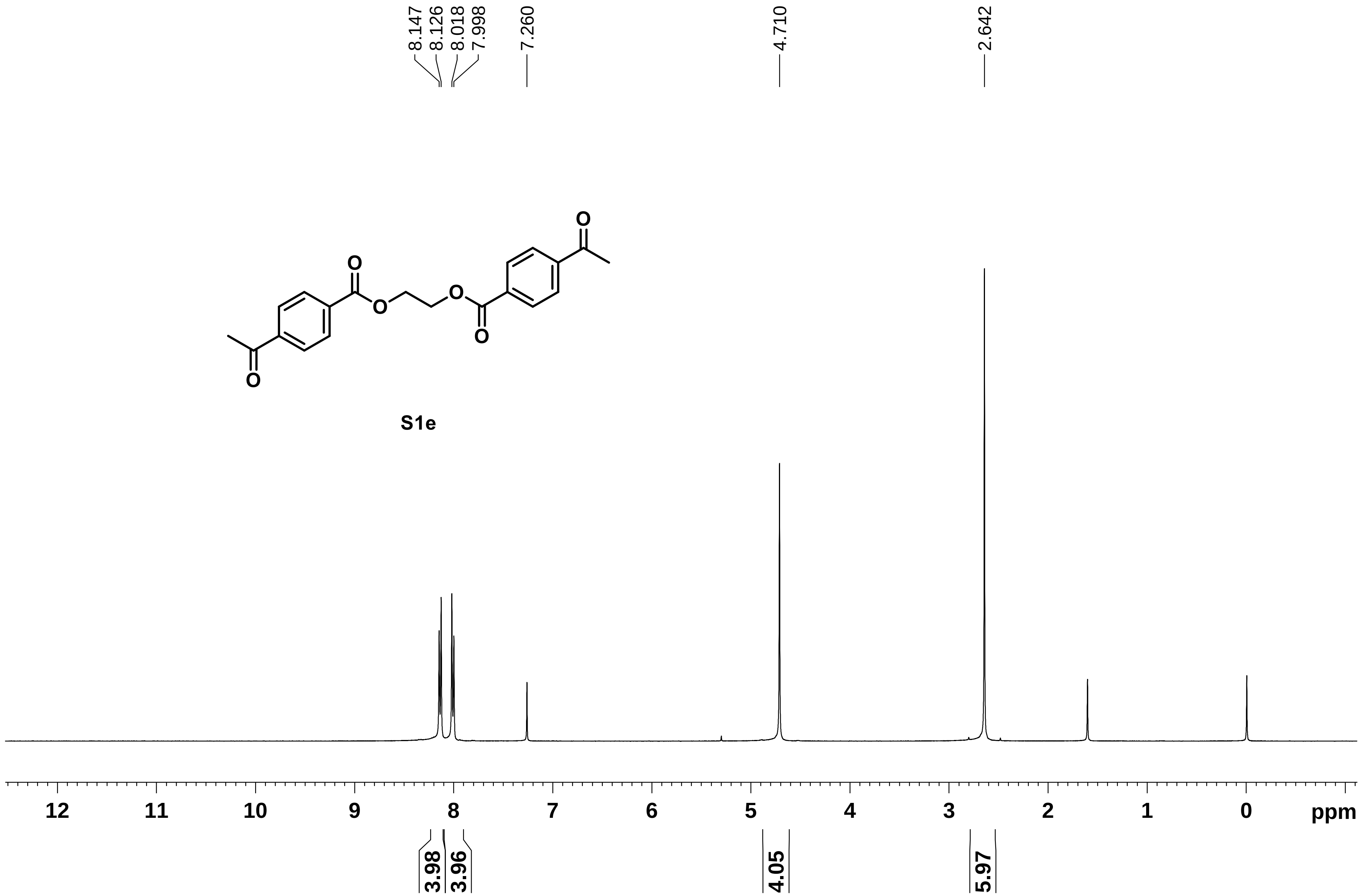


Figure S54. ^{1}H NMR spectra of **S1e** (CDCl$_3$, 400M).

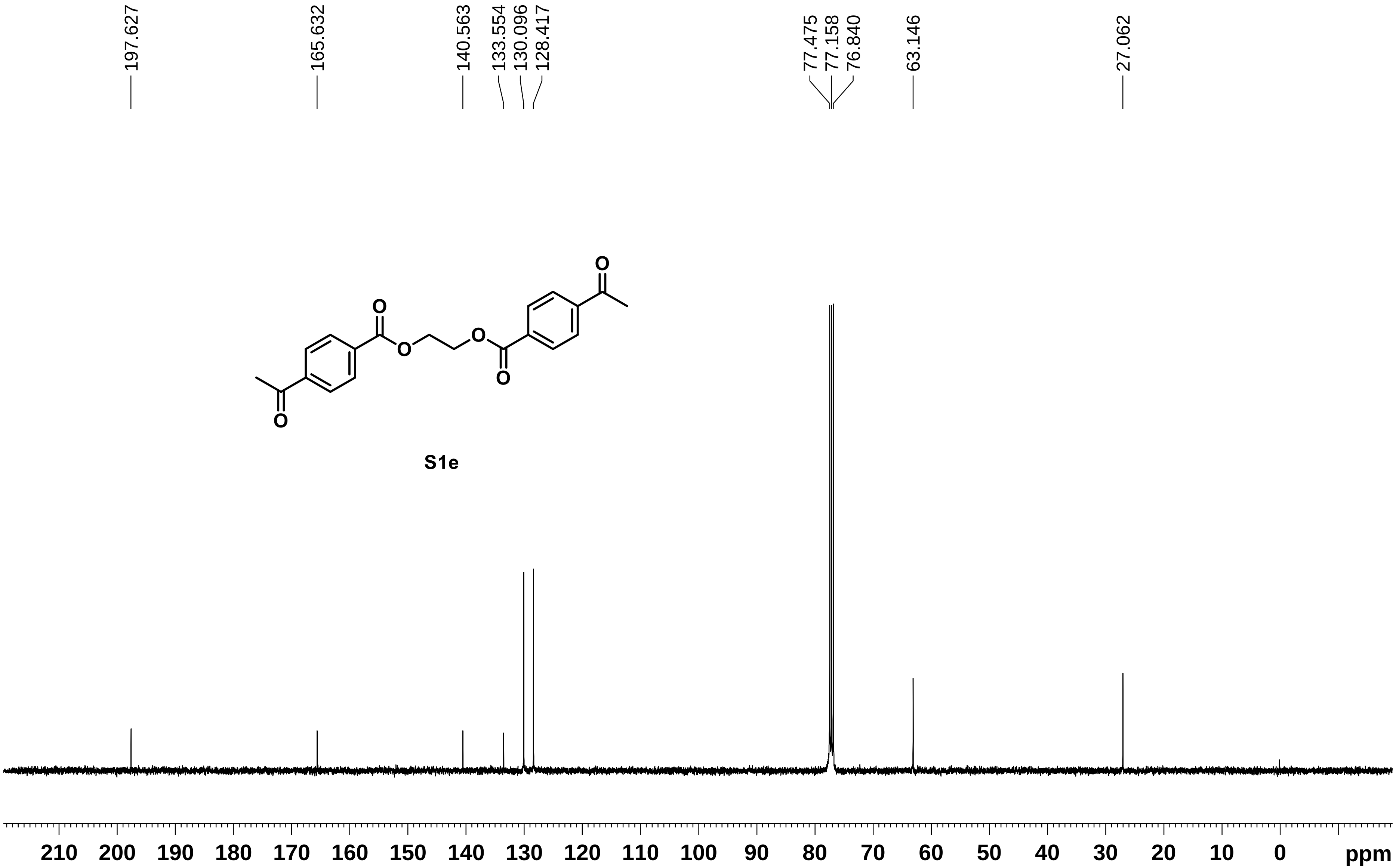


Figure S55. $^{13}C\{^1H\}$ NMR spectra of **S1e** ($CDCl_3$, 100M).

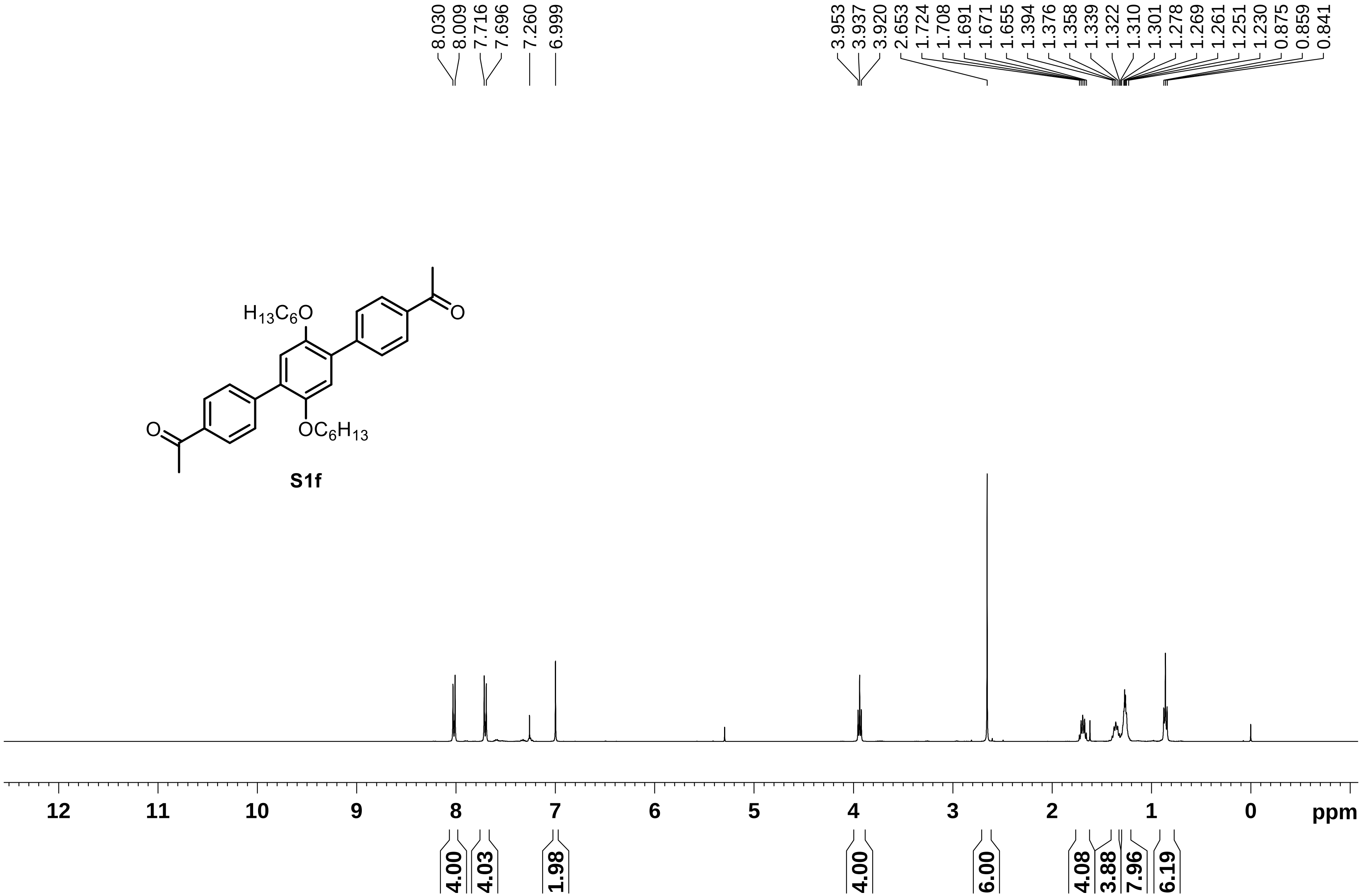


Figure S56. ^{1}H NMR spectra of **S1f** (CDCl$_3$, 400M).

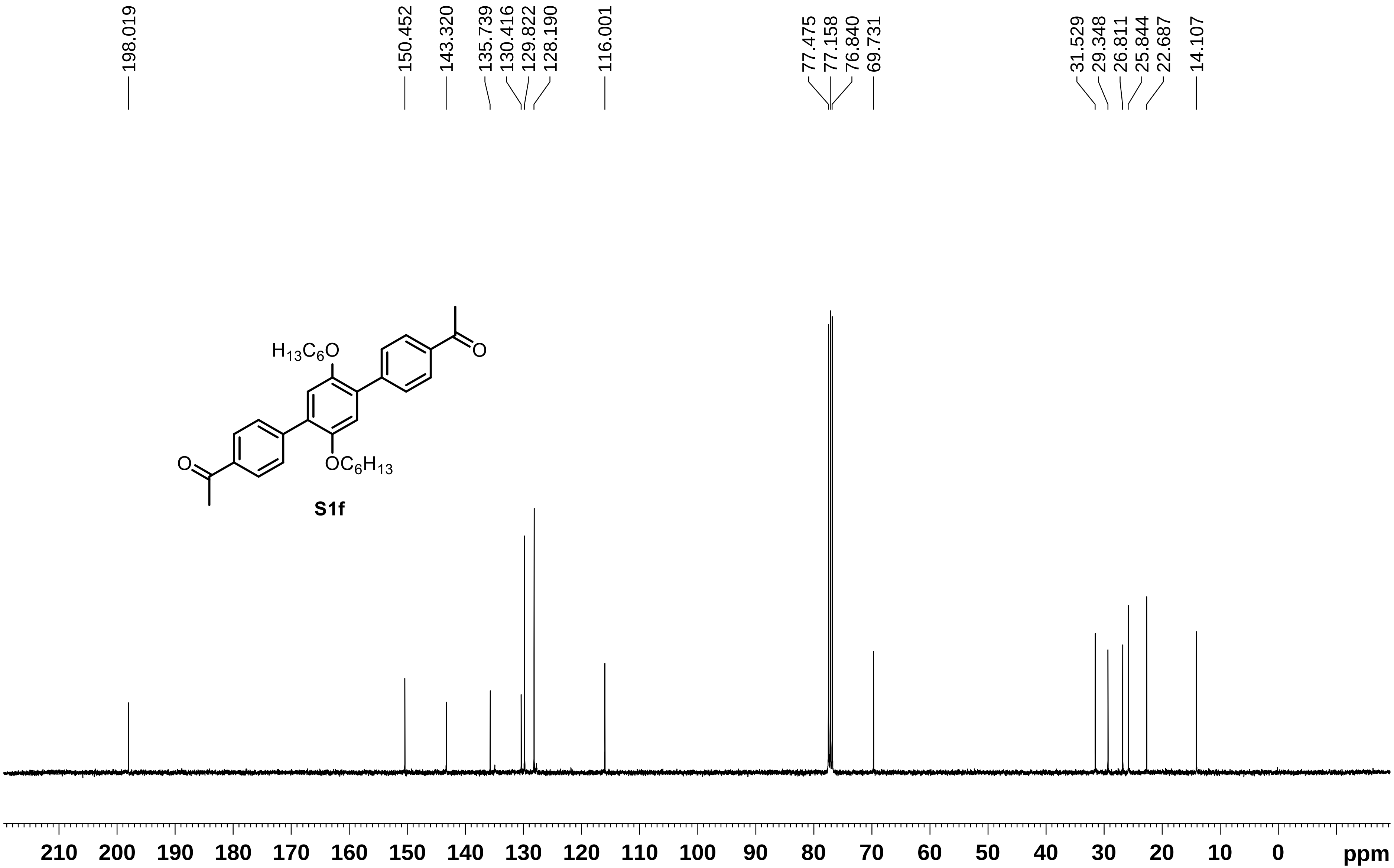


Figure S57. ^{13}C{^{1}H} NMR spectra of **S1f** ($CDCl_3$, 100M).

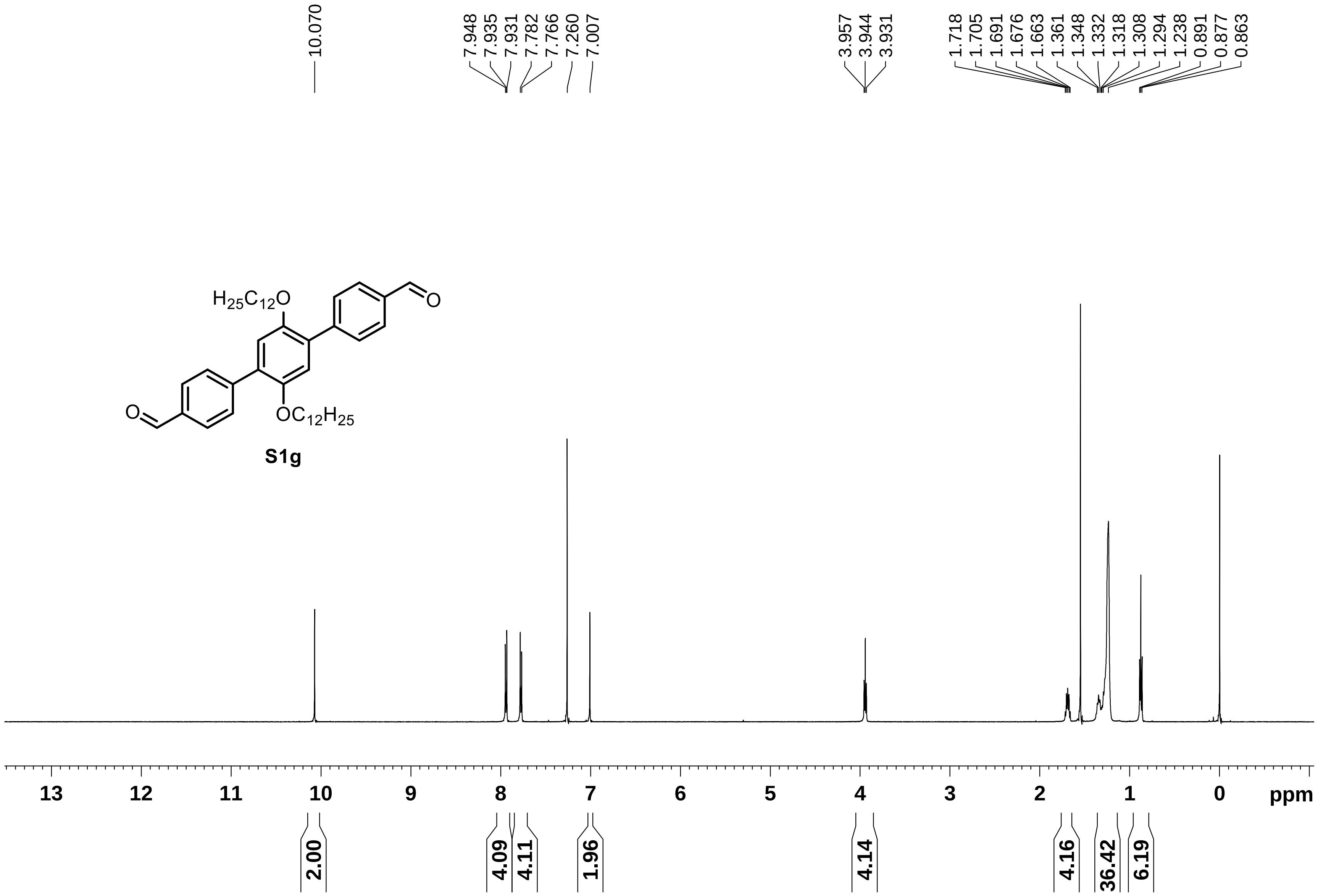


Figure S58. ^{1}H NMR spectra of **S1g** (CDCl$_3$, 500M).

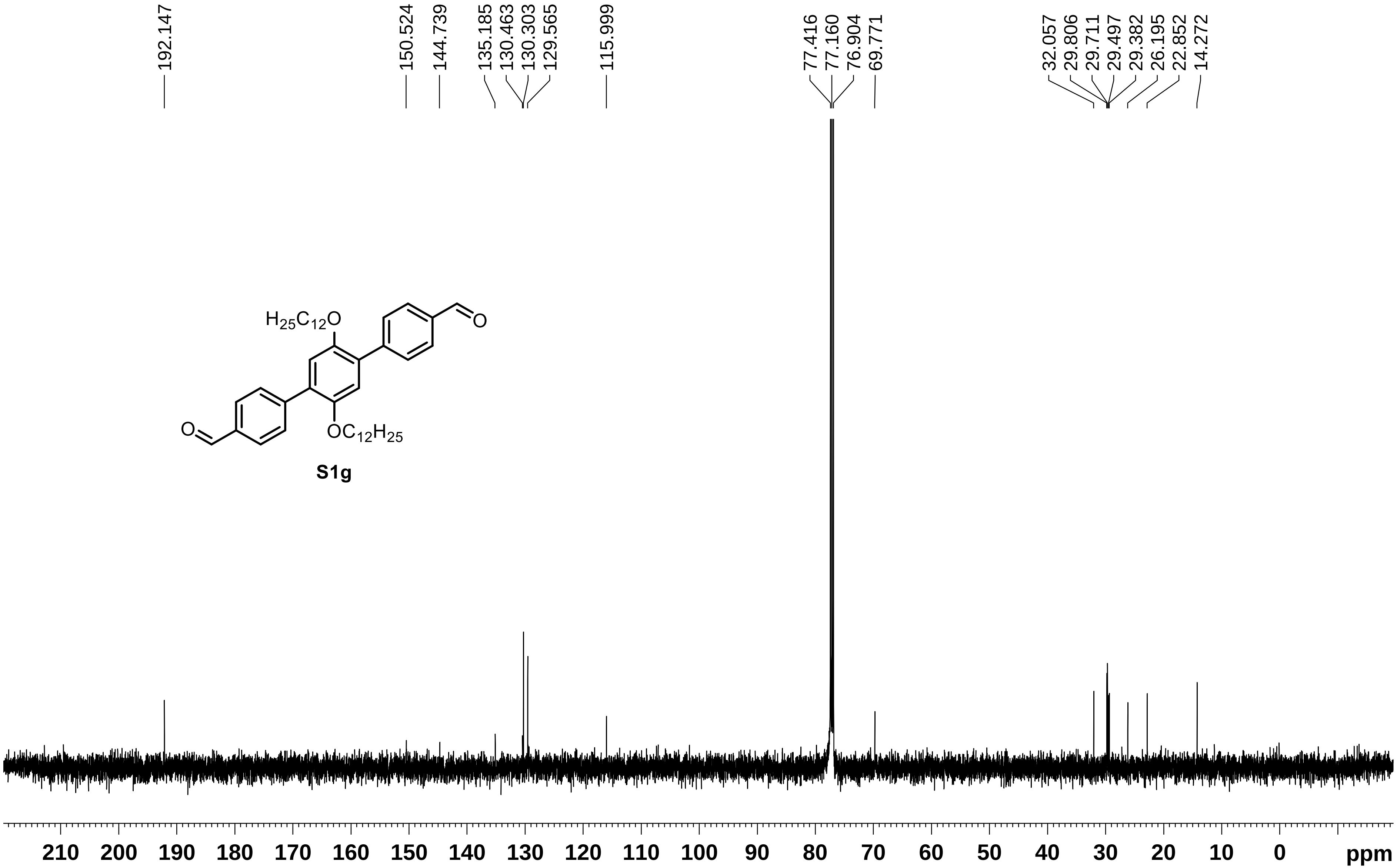


Figure S59. $^{13}C\{^1H\}$ NMR spectra of **S1g** ($CDCl_3$, 125M).

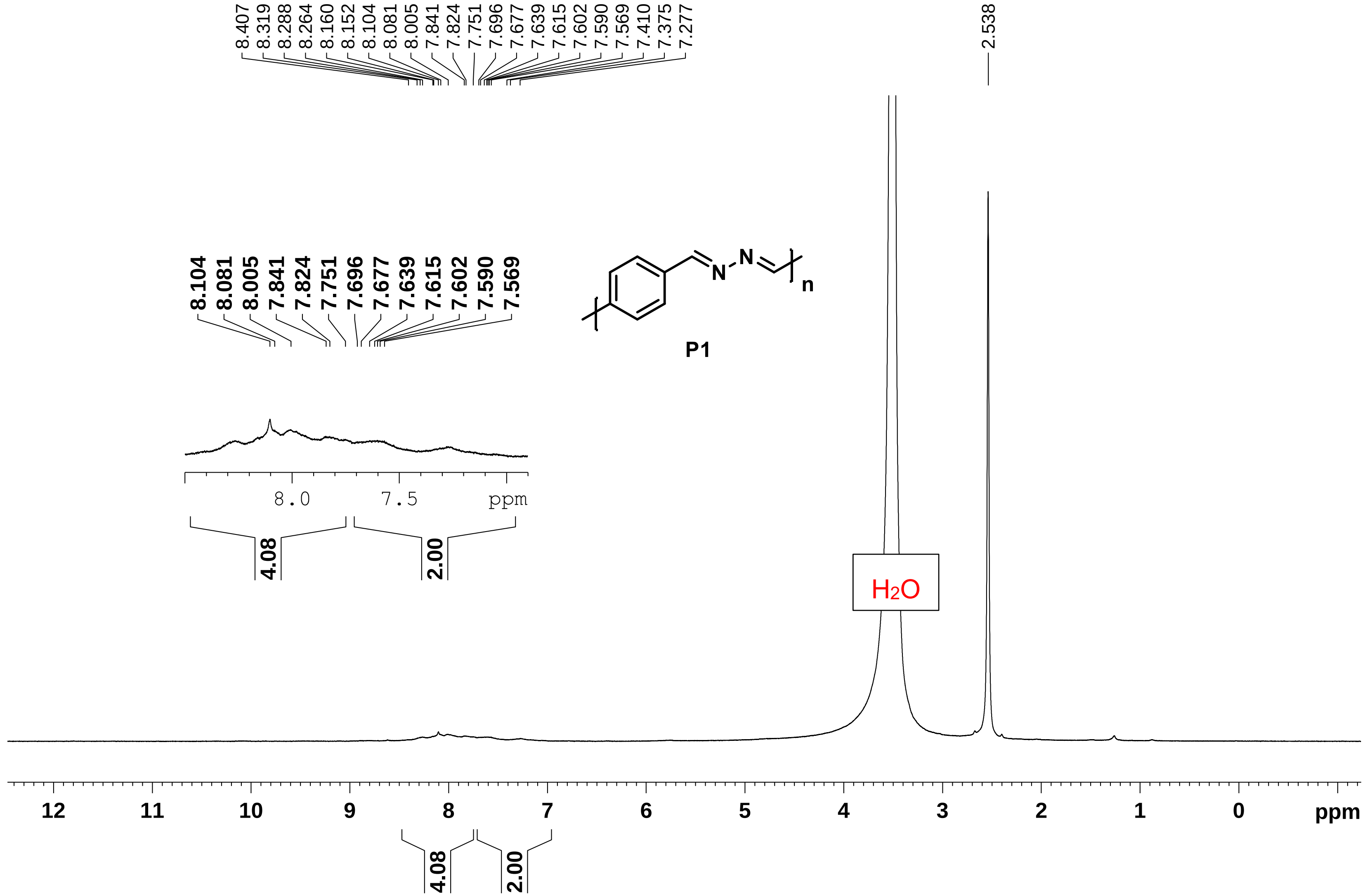


Figure S60. ^{1}H NMR spectra of **P1** (DMSO-*d*$_6$, 500M).

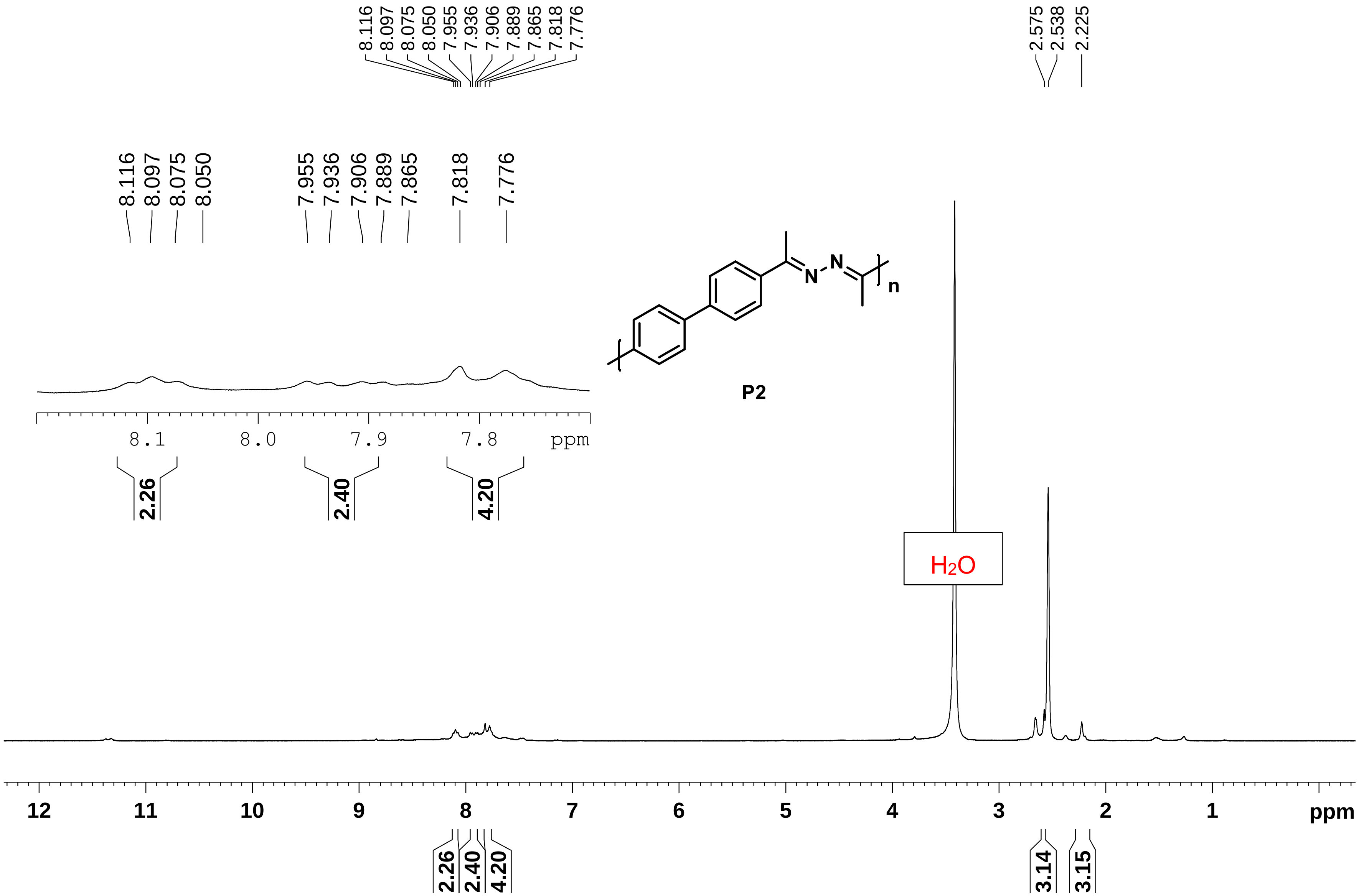


Figure S61. ^{1}H NMR spectra of **P2** (DMSO-d_6, 400M).

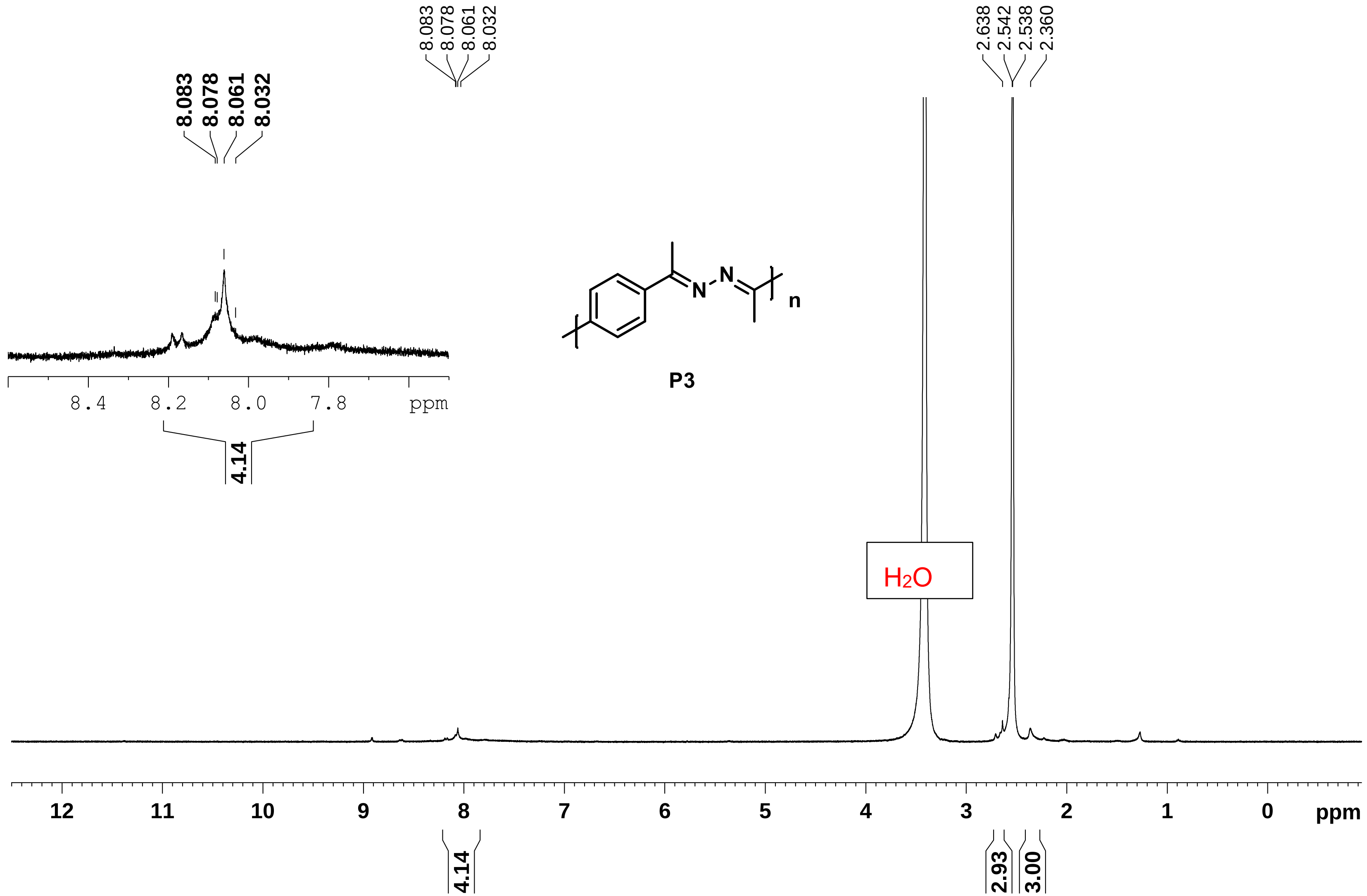


Figure S62. ^{1}H NMR spectra of **P3** (DMSO-d_6, 500M).

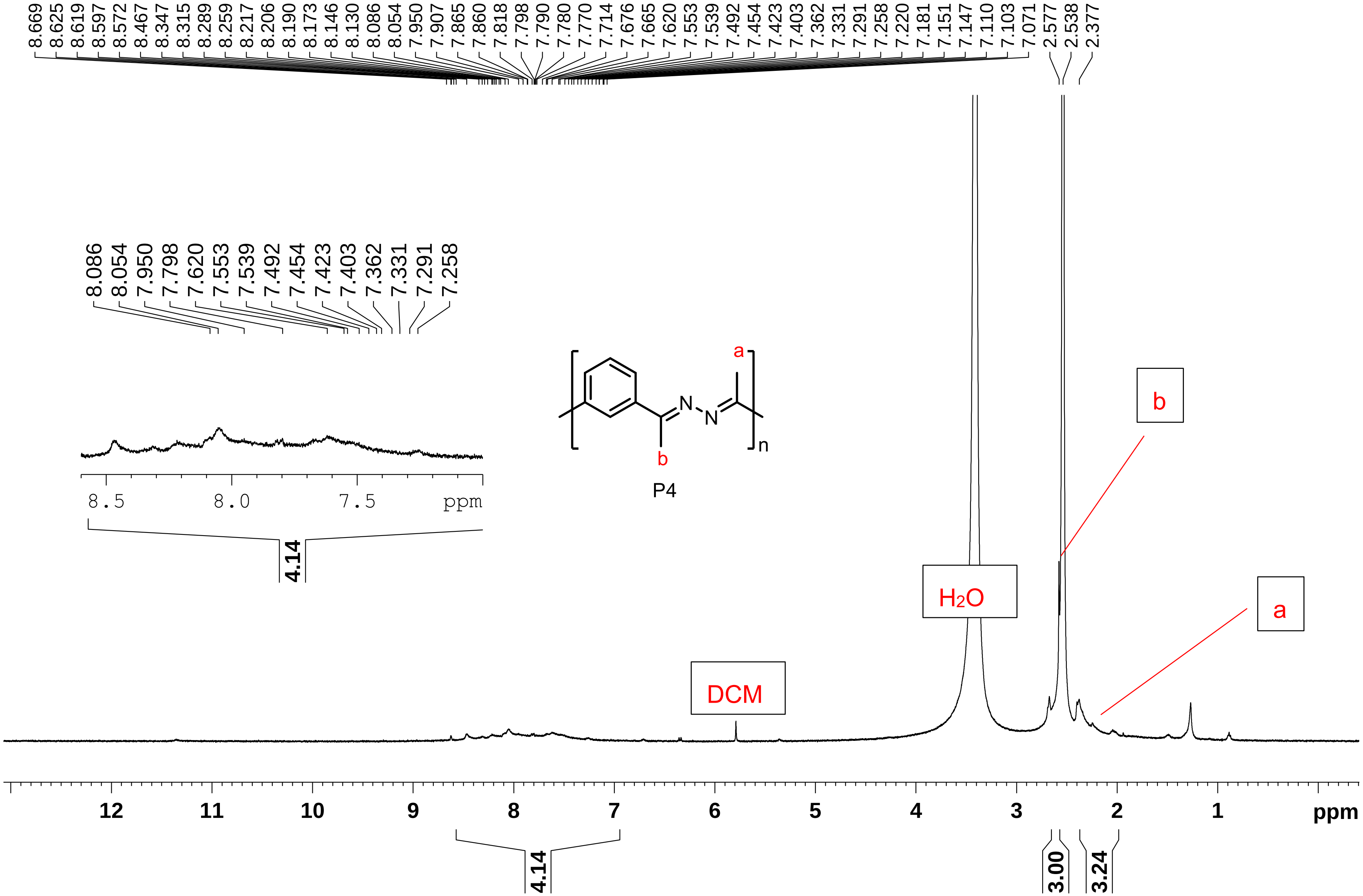


Figure S63. ^{1}H NMR spectra of **P4** (DMSO-d_6, 500 M).

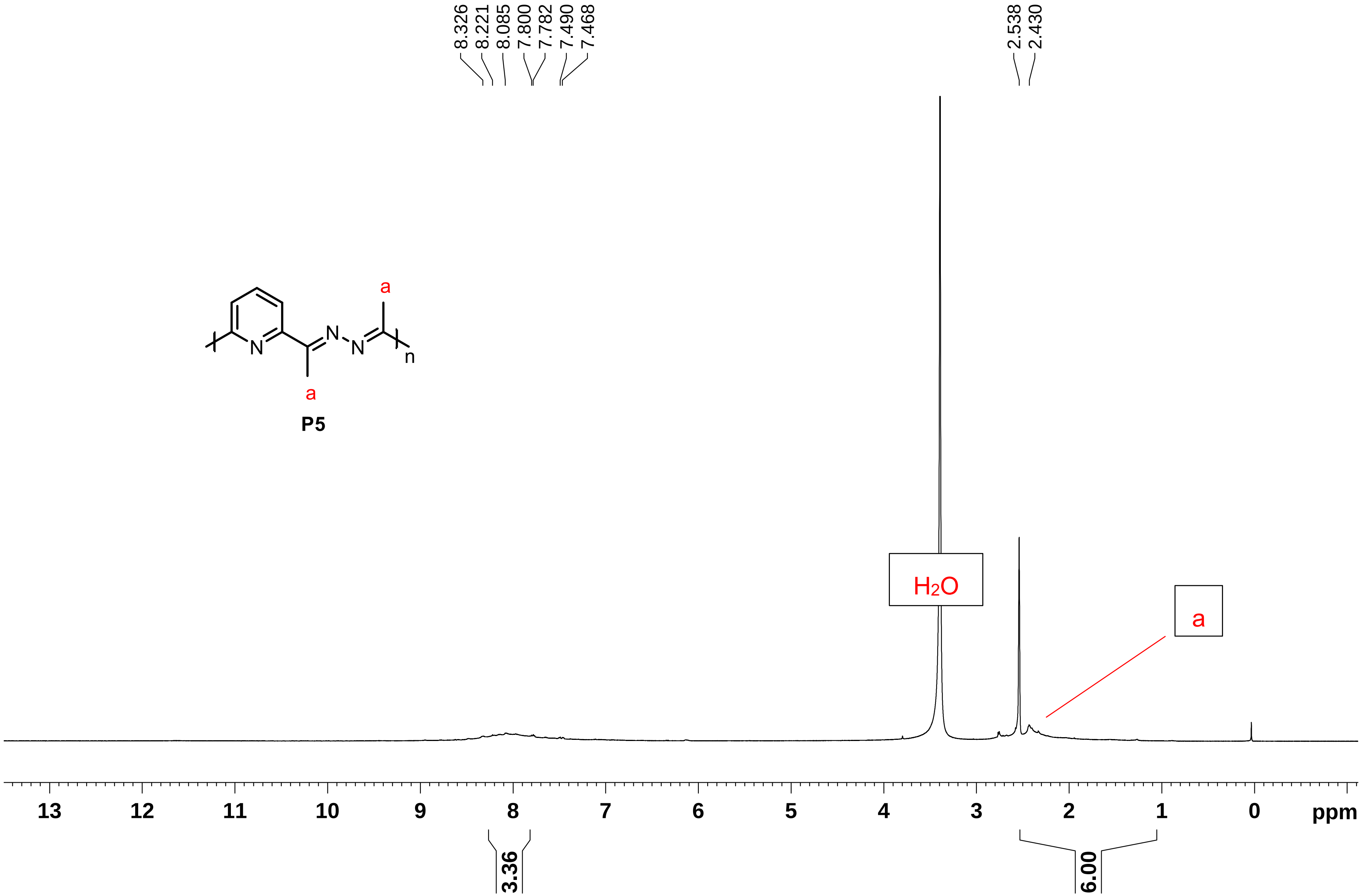


Figure S64. ^{1}H NMR spectra of **P5** (DMSO-d_6, 500M).

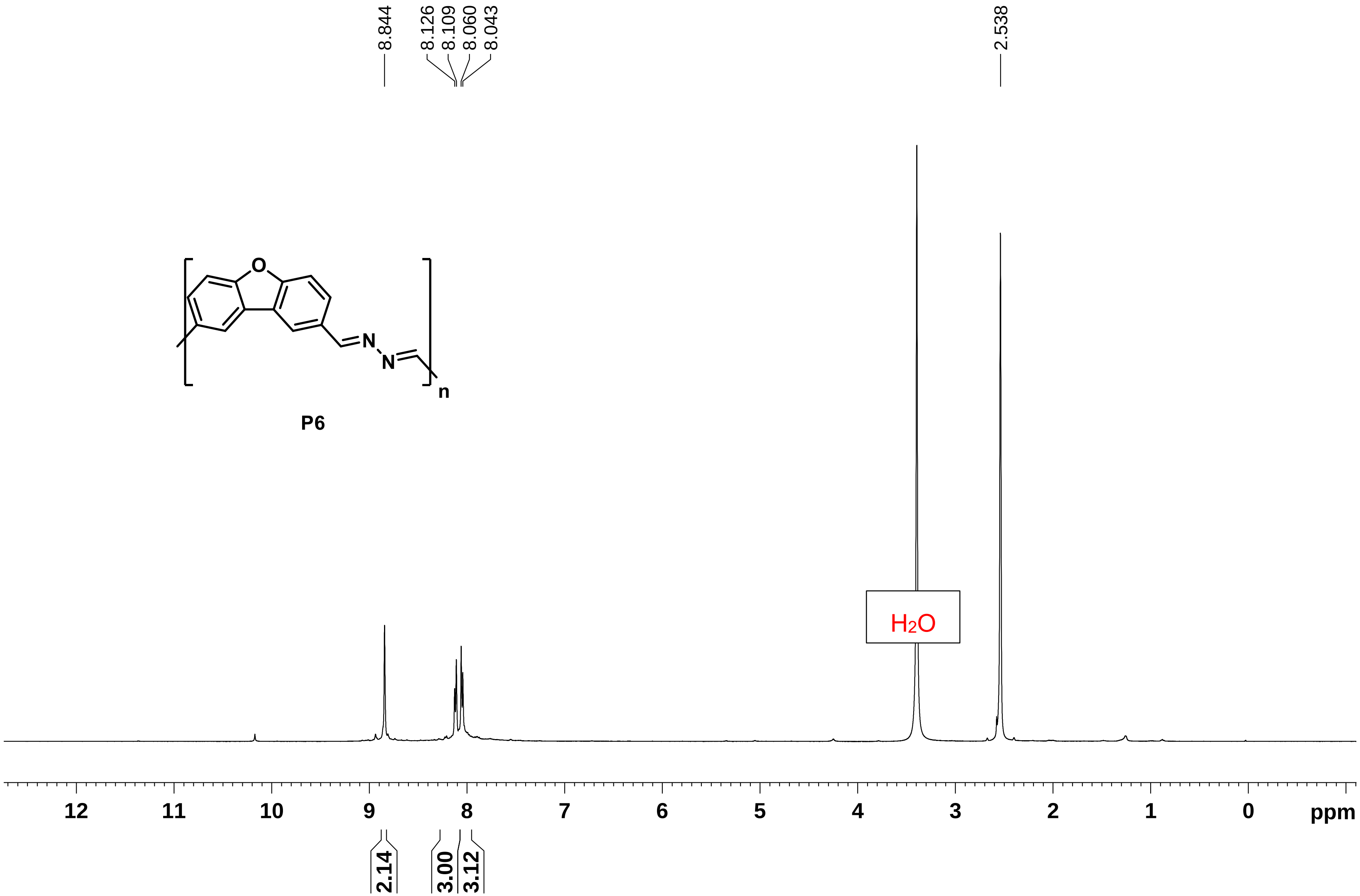


Figure S65. ^{1}H NMR spectra of **P6** (DMSO-d_6, 500M).

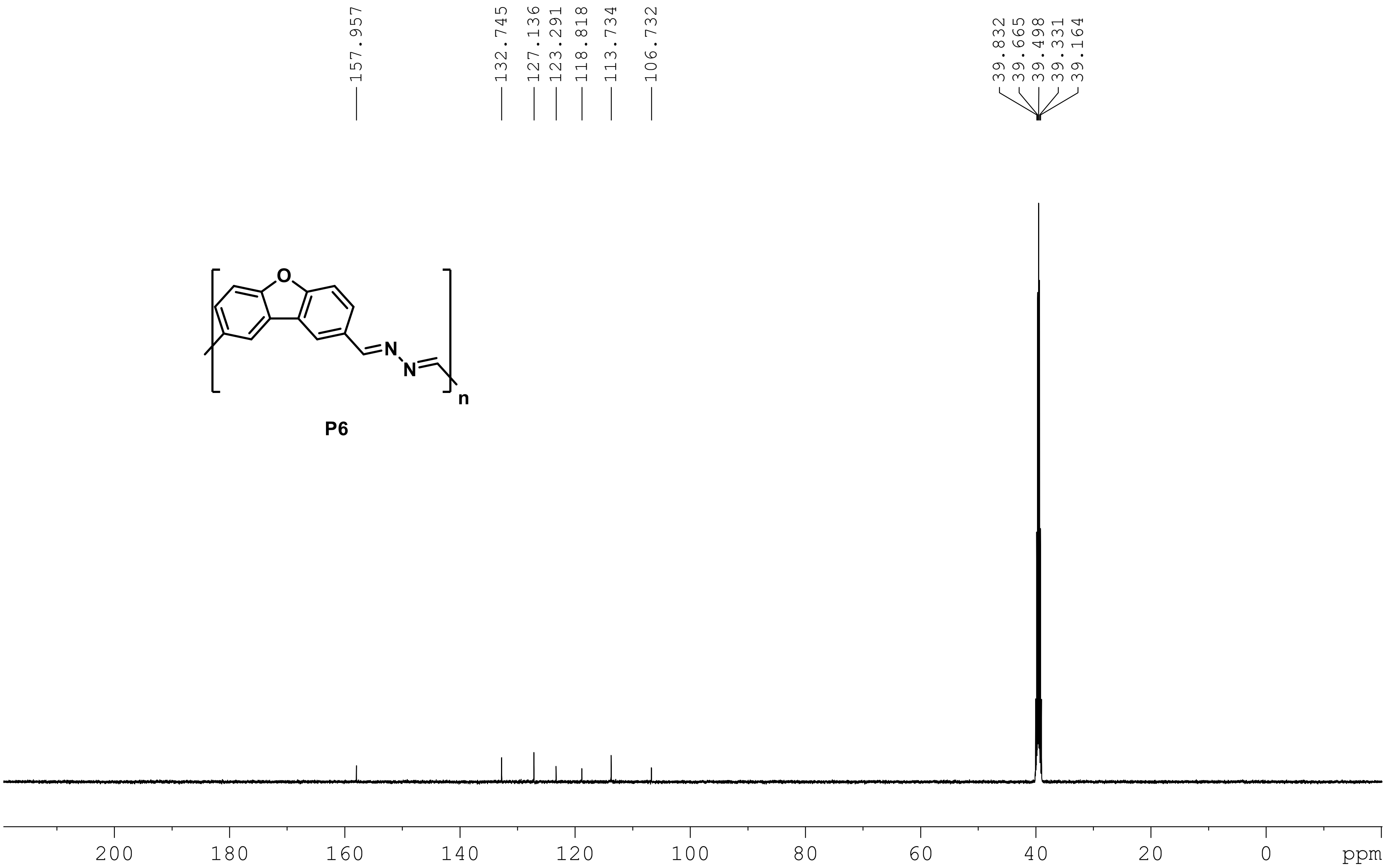


Figure S66. $^{13}C\{^{1}H\}$ NMR spectra of **P6** (DMSO-d_6, 125 M).

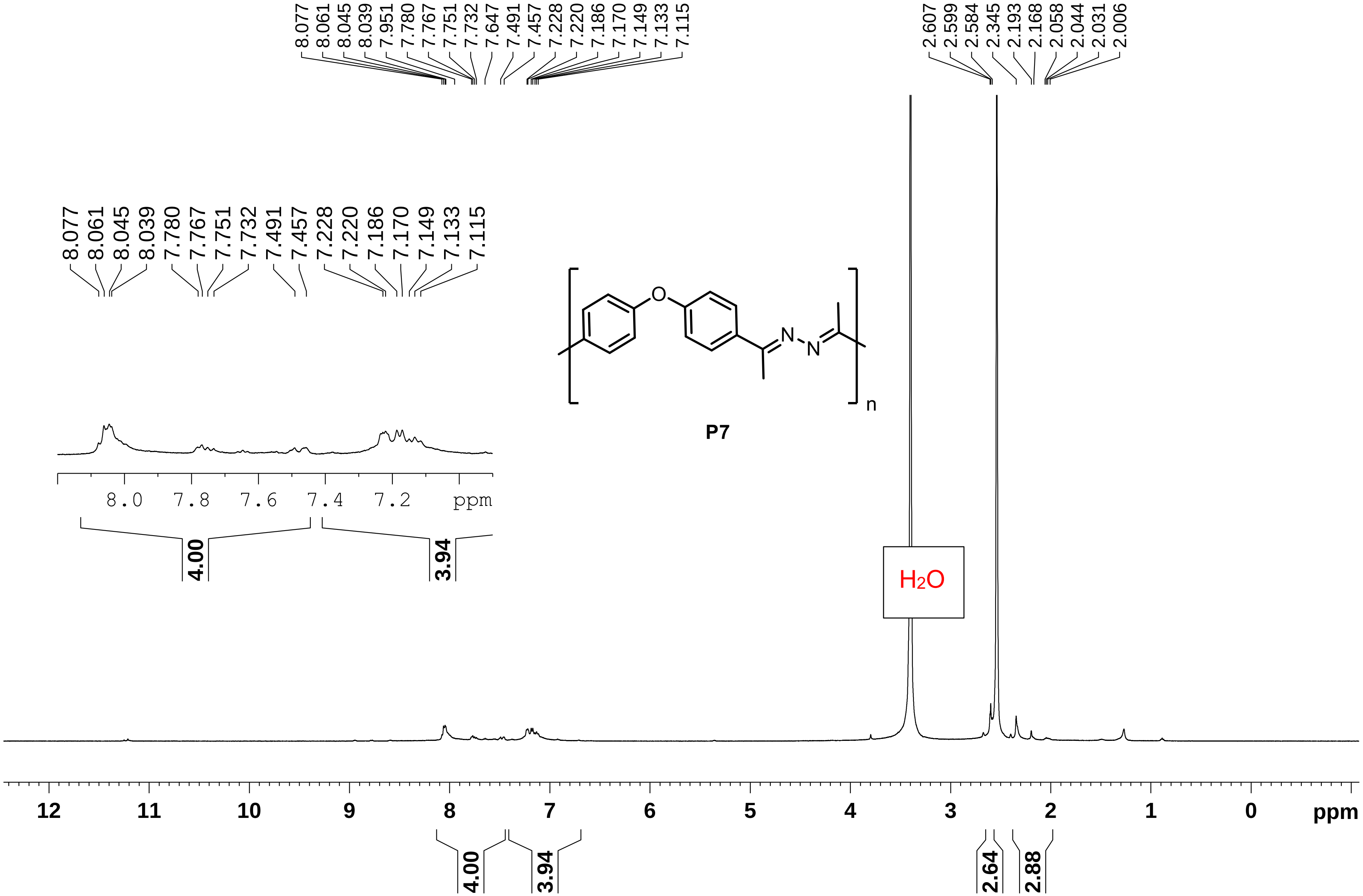


Figure S67. ^{1}H NMR spectra of **P7** (DMSO-d_6, 500 M).

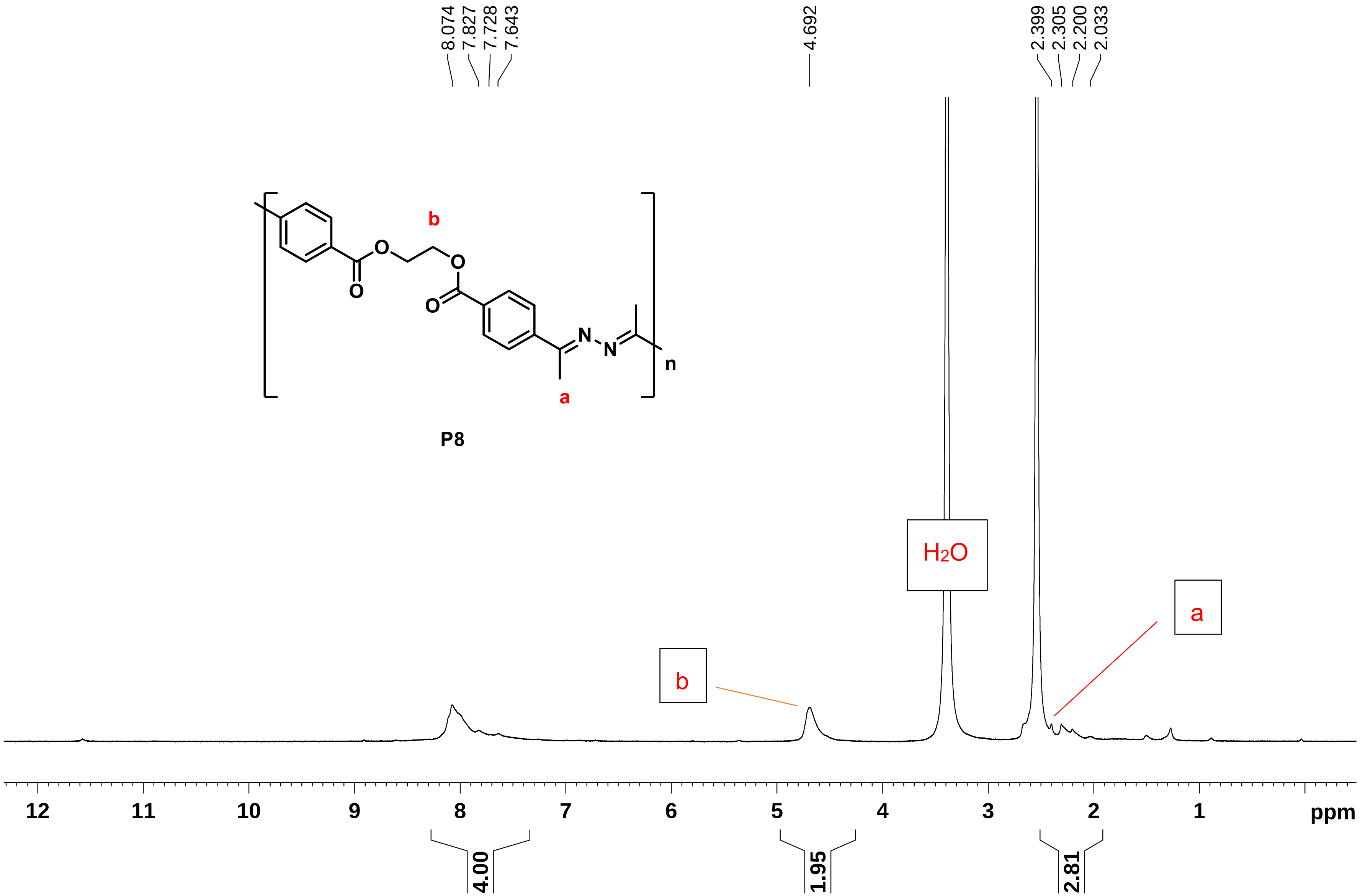


Figure S68. ^{1}H NMR spectra of **P8** (DMSO-d_6, 500M).

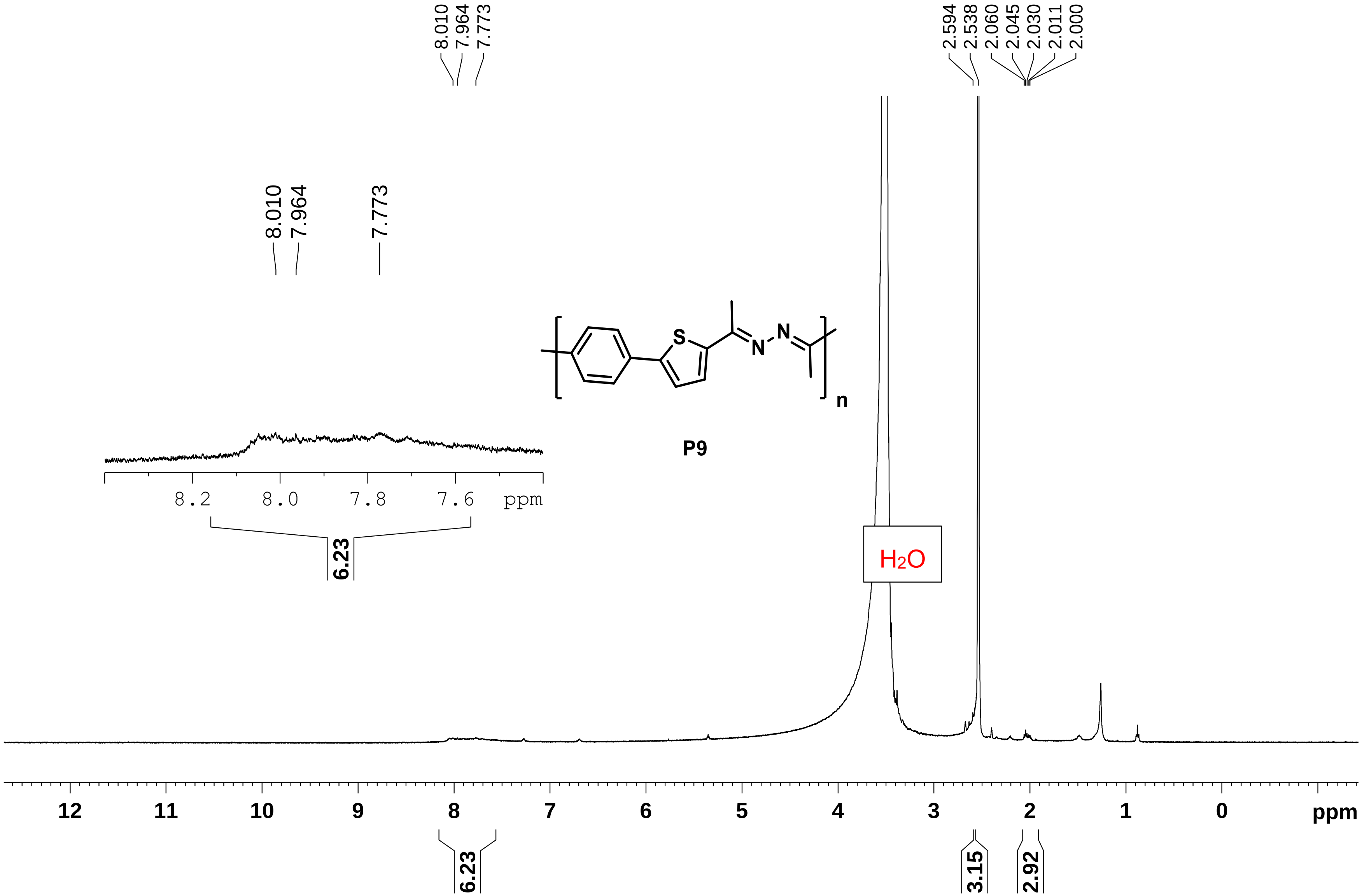


Figure S69. ^{1}H NMR spectra of **P9** (DMSO-d_6, 500M).

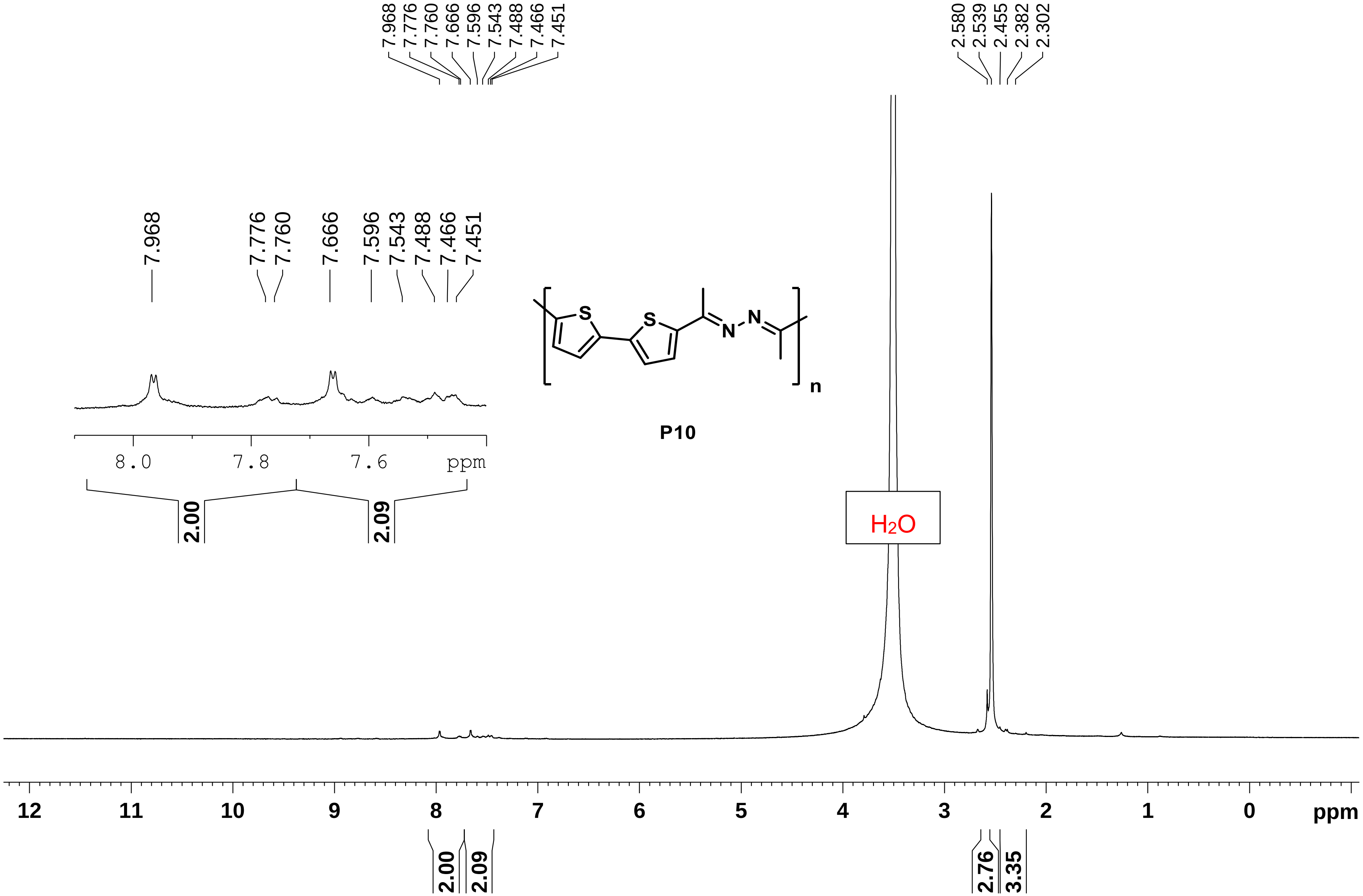


Figure S70. ^{1}H NMR spectra of **P10** (DMSO-*d*$_6$, 500M).

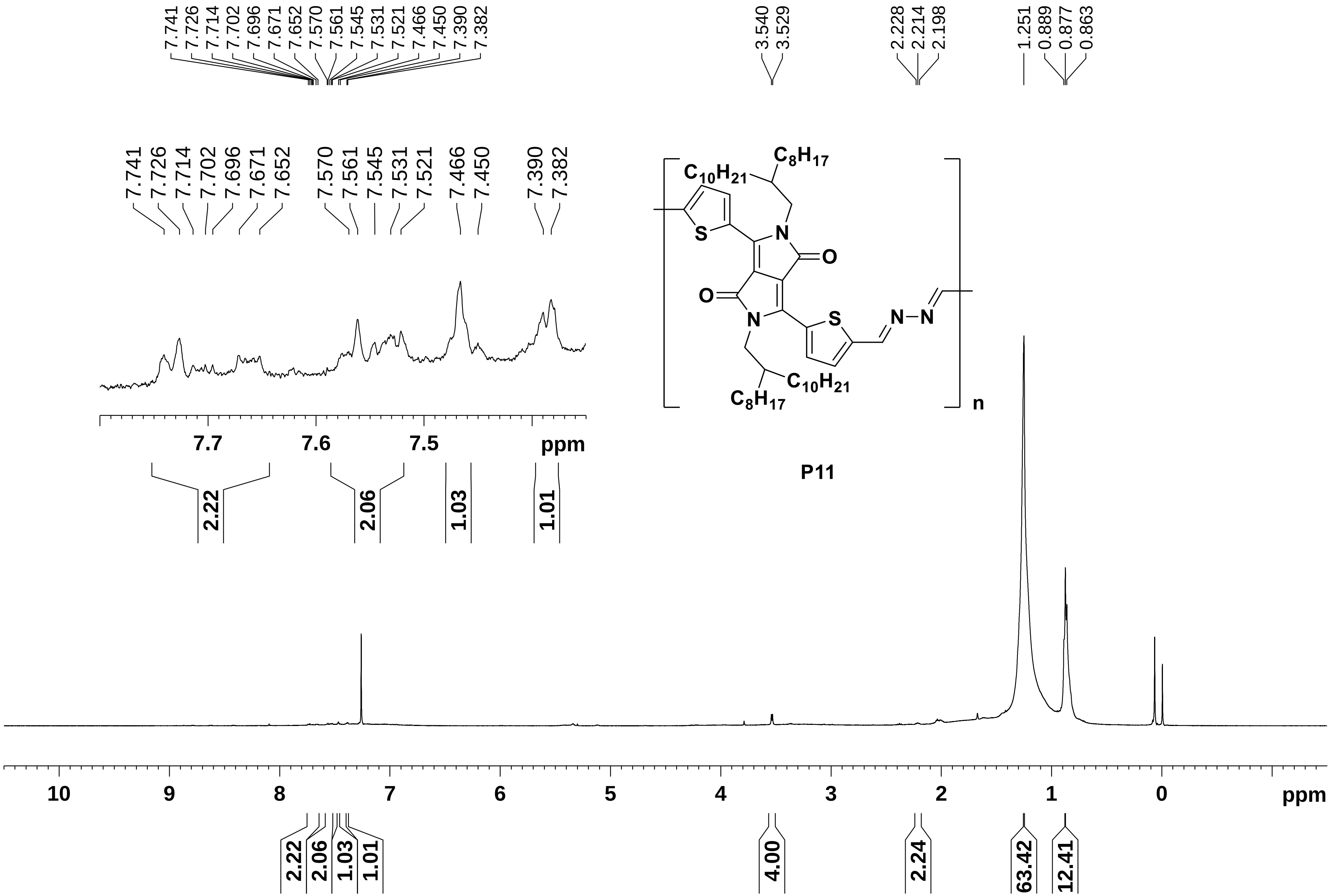


Figure S71. ^{1}H NMR spectra of **P11** (CDCl$_3$, 500M).

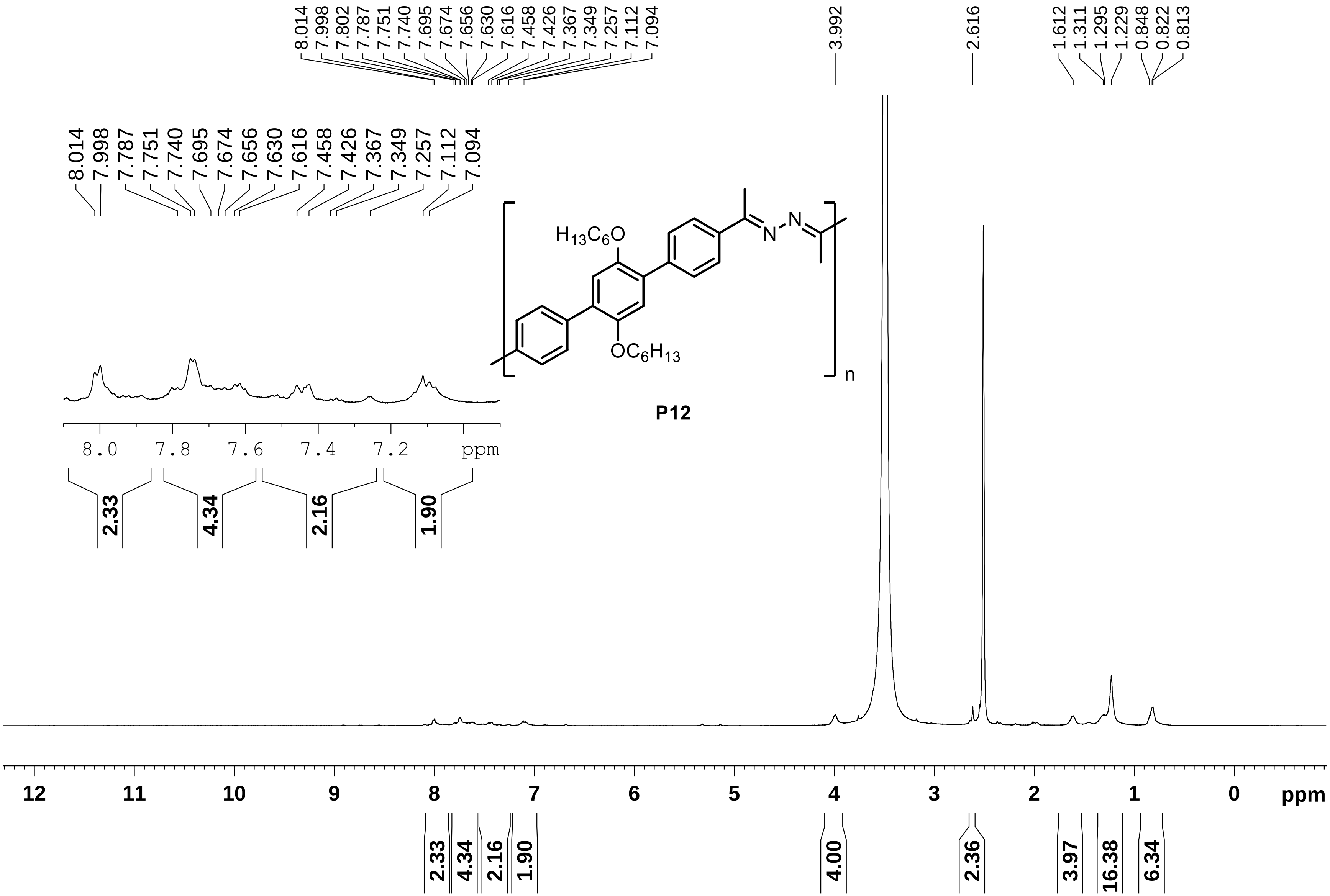


Figure S72. ^{1}H NMR spectra of **P12** (DMSO-d_6, 500M).

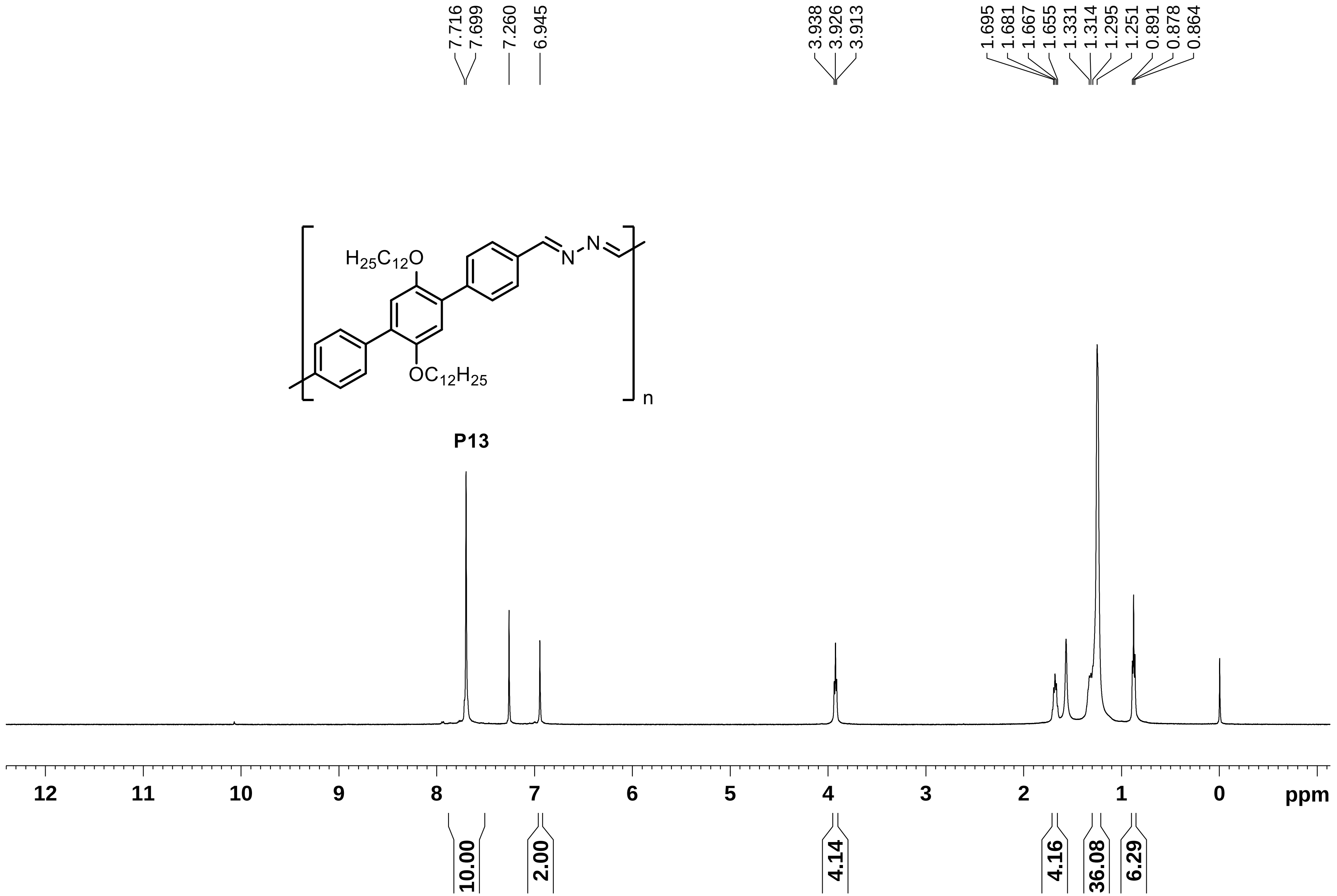


Figure S73. ^{1}H NMR spectra of **P13** ($CDCl_3$, 500M).