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SUPPORTING INFORMATION

Stoichiometric Imbalance-Promoted Step-Growth Polymerization Based on Self-Accelerating 1,3-Dipolar Cycloaddition Click Reactions

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Experimental

Materials

Benzyl alcohol, 4-carboxybenzaldehyde, hydroquinone, 1-bromohexane, n-butyllithium (2.4 M solution in hexanes) (n-BuLi), p-toluenesulfonyl chloride ($TsNHNH_2$), p-toluenesulfonhydrazide (TsCl), bromoacetyl bromide, bromoacetic acid, p-phenylenediamine, ethyl bromoacetate, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 4-aminobenzoic acid, acetic anhydride, dibenzosuberenone, trifluoroacetic anhydride ($(CF_3COO)_2O$), trimethylsilyl diazomethane ($TMSCH_2N_2$), boron trifluoride etherate (BF_3OEt), triflic anhydride (Tf_2O), ethyldiisopropylamine, bromine (Br_2), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), 4-dimethylaminopyridine (DMAP), trimethylamine (TEA), N-methylhydroxylamine hydrochloride (MeOHNH·HCl), sodium borohydride ($NaBH_4$), sodium nitrite ($NaNO_2$), sodium hydroxide (NaOH), acetic acid, potassium carbonate (K_2CO_3), sodium thiosulfate pentahydrate, potassium tert-butoxide, sodium hydroxide (NaOH), concentrated hydrochloric acid (HCl), sodium acetate, magnesium sulphate ($MgSO_4$), dilute sulfuric acid (dill. H_2SO_4), dilute hydrochloric acid (dill. HCl), deionized water, methanol (MeOH), ethanol (EtOH), acetone, petroleum ether, ethyl acetate, dichloromethane (DCM), chloroform ($CHCl_3$), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP) were purchased as reagent grade from Alfa Aesar, Aldrich, Acros, J&K Chemical, or Beijing Chemical Reagent Co. and used as received unless otherwise noted.

Characterization

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 or on a Bruker Avance 600 spectrometer at room temperature.

High resolution mass spectra (HRMS) were recorded on a Bruker 9.4T Solarix FT-ICR-MS (Bruker, Germany).

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on a Autoflex III MALDI-TOF mass spectrometer equipped with a 355 nm YAG laser. It was operated at an accelerating potential of 20 kV in linear modes. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). Polymer was dissolved in THF with a concentration of 5 g/L. α-Cyano-4-hydroxycinnamic acid (CCA; 23 g/L in THF) was used as the matrix and NaCl (saturated in THF) was used as the cation source. Dithranol (DI; 20 g/L in THF) was used as the matrix and sliver trifluoroacetate (saturated in THF) was used as the cation source.

Fourier transform infrared spectroscopy (FT-IR) was performed on a Thermo Nicolet Avatar-330 Spectrometer at room temperature.

Ultraviolet spectra were recorded on a TU-1901 Ultraviolet Spectrophotometer, in which DMF were used as measurement solvents.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA under nitrogen atmosphere with heating rate of 10 ^{o}C/min.

Differential scanning calorimetry (DSC) was performed on a DSC Q2000 under nitrogen atmosphere with heating rate of 10 ^{o}C/min.

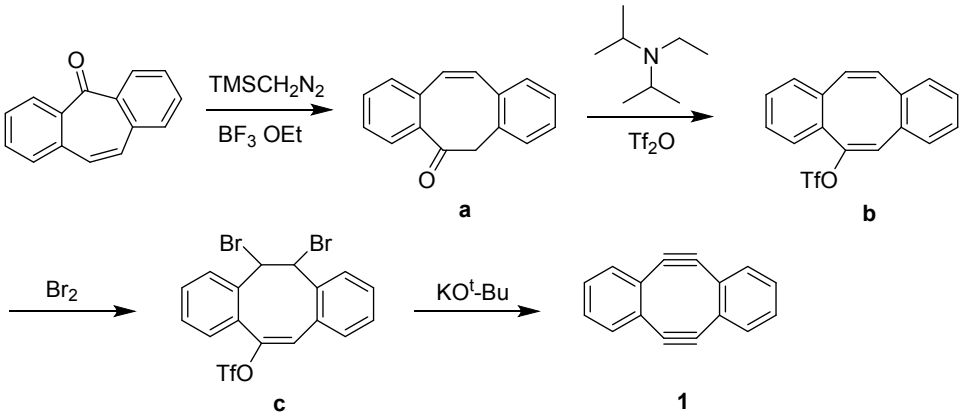
Gel permeation chromatography (GPC) in THF was conducted on a system comprised of a Waters 1515 isocratic HPLC pump, three Agilent Plgel columns (Mixed B, Mixed C, Mixed D), and a Waters 2414 RI detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration.

GPC in DMF was conducted on a system comprised of a Waters 515 HPLC pump, three Agilent mixed columns (Mixed A, Mixed B and Mixed B), and a Waters 2414 RI detector. DMF with 0.01 M LiBr was used as the eluent at a flow rate of 1.00 mL/min. Polystyrene standards were used for the calibration.

GPC in DMF was conducted on a system comprised of a MODEL 12-6 isocratic HPLC pump, two Agilent Plgel columns (Mixed B and Mixed C), a DAWN HELEOSII multiangle laser light scattering (MALLS) detector (Wyatt Technology), and an Optilab T-rEX differential refractometer (Wyatt Technology). DMF with 0.01 M LiBr was used as the eluent at a flow rate of 0.5 mL/min.

Preparation of small molecule compounds

Preparation of compound 1



Compound ***a:***[1] Trimethylsilyl diazomethane (25 ml, 50 mmol) was added dropwise into a DCM (150 mL) solution of dibenzosuberenone (8.25 g, 40 mmol) and boron trifluoride etherate (6.34 ml, 50 mmol) at 0 ^{o}C over a period of 1 hour. After stirring in the dark overnight, the mixture was poured into water (150 mL) and extracted with DCM (3 × 150 ml). The organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with PE/EA (v/v

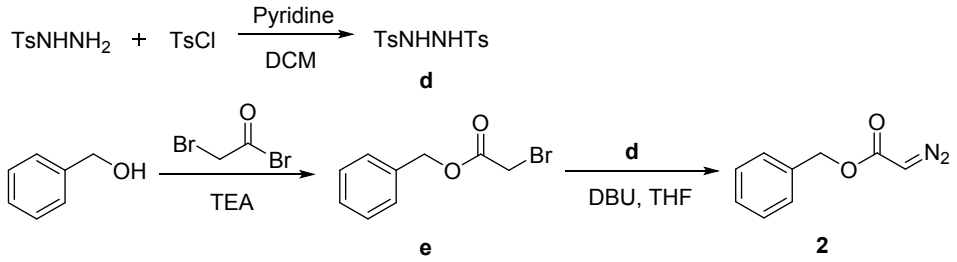
= 22/1) as the eluent to afford the product **a** (5.19 g, 59%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.26 (q, 1H), 7.35 (m, 7H), 7.05 (q, 2H), 4.07 (s, 2H).

*Compound **b**:*[1] Triflic anhydride (10 ml, 59 mmol) was added dropwise into a DCM (100 ml) solution of compound **a** (5.19 g, 23.6 mmol) and ethyldiisopropylamine (10.5 ml, 59 mmol) at 0 °C. After reacting in the dark overnight, the mixture was poured into water (100 mL) and extracted with DCM (3 × 100 ml). The organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with PE/EA (v/v = 30/1) as the eluent to afford the product **b** (6.38 g, 62%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.31 (m, 5H), 7.14 (m, 3H), 6.99 (s, 1H), 6.88 (s, 2H).

*Compound **c**:*[1] Bromine (1.2 ml, 23 mmol) was added dropwise into a DCM (100 ml) solution of compound **b** (6.38 g, 18.1 mmol) at 0 °C. After reacting overnight, a saturated sodium thiosulfate pentahydrate aqueous solution was added into the reaction mixture. After extracting with DCM (3 × 100 ml), the organic phase was collected and dried by $MgSO_4$. The solvent was removed in vacuum and the crude product was used as such for the next step (8.82 g). ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.82 (br, 1H), 7.24 (m, 8H), 6.09 (br, 1H), 5.64 (br, 1H).

*Compound **1**:*[1] Potassium tert-butoxide (11.55 g, 102.6 mmol) was added into a solution of compound **c** (8.82 g, 17.2 mmol) in THF (85 ml) at 0 °C in batches. After stirring in the dark overnight, the mixture was poured into water (100 mL) and extracted with DCM (5 × 100 ml). The organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with PE as the eluent to afford the product **1** (1.6 g). The total yield of the four-step reaction was 20%. ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.93 (q, 4H), 6.74 (q, 4H) (Figure S29A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 132.96, 129.04, 126.90, 109.35 (Figure S29B).

Preparation of compound 2



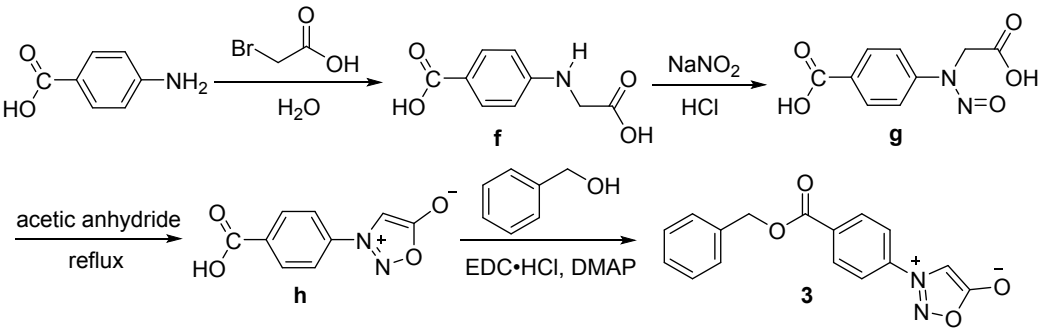
*Compound **d**:*[2] $TsNHNH_2$ (9.31 g, 50 mmol) and TsCl (14.3 g, 75 mmol) were dissolved in DCM (50 ml) followed by the dropwise addition of pyridine (6 ml, 75 mmol). After the reaction was completed, compound **d** precipitated out of the reaction mixture as white solid. The solid product was filtered, dried (13.5 g, 79%) and used as such for the next step. ^{1}H-NMR (DMSO-d_6), δ (ppm): 9.57 (s, 2H), 7.63 (d, 4H), 7.10 (d, 4H), 2.40 (s, 6H) (Figure S30A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 167.05, 135.14, 128.72, 128.64, 128.29, 67.91, 25.94 (Figure S30B). HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2NaO_4S_2$ [M + Na^+] 363.0446, found 363.0444.

*Compound **e**:*[2] A stirred solution of benzyl alcohol (4 ml, 40 mmol) and TEA (16.6 ml, 120 mmol) in DCM (100 ml) was cooled to 0 ^{o}C for 15 minutes followed by the dropwise addition of bromoacetyl bromide (7 ml, 80 mmol). After stirring at 0 ^{o}C for 1 hour, the solvent was removed in vacuum and the crude product was purified by a silica column with PE/EA (v/v = 10/1) as the eluent to afford the compound **e** (4.54 g, 50%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.38 (m, 5H), 5.21 (s, 2H), 3.88 (s, 2H) (Figure S31A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 167.05, 135.87, 128.72, 128.64, 128.29, 67.91, 26.26 (Figure S31B). HRMS (ESI) m/z calculated for $C_9H_9BrNaO_2$ [M + Na^+] 250.9677, found 250.9678.

*Compound **2**:*[2] Compound **e** (4.54 g, 19.8 mmol) and compound **d** (13.5 g, 39.6 mmol) were stirred in THF (50 ml) at 0 ^{o}C followed by the dropwise addition of DBU (9 ml, 59.4 mmol). After stirring for 2 hours, a saturated $NaHCO_3$ aqueous solution was added until pH = 10. After extracting the mixture with EA (3 × 100 ml), the organic phase was collected and dried by $MgSO_4$.

The resultant crude product was purified by a silica column with PE/EA (v/v = 10/1) as the eluent to afford the compound **2** (2.62 g, 75%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.34 (m, 5H), 5.20 (s, 2H), 4.80 (s, 1H) (Figure S32A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 166.65, 135.94, 128.59, 128.32, 128.20, 66.49, 46.29 (Figure S32B). HRMS (ESI) m/z calculated for $C_9H_8N_2NaO_2$ [M + Na^+] 199.0477, found 199.0478.

Preparation of compound 3



*Compound **f**:*[3] A stirred solution of bromoacetic acid (8.38g, 60 mmol) and 4-aminobenzoic acid (8.23g, 60 mmol) was refluxed in water (40 ml) overnight to give the solid crude product. Compound **f** was obtained as white solid after filtration and dried under vacuum (4.78 g, 41%). ^{1}H-NMR (DMSO-d_6), δ (ppm): 7.67 (d, 2H), 6.57 (d, 2H), 3.88 (s, 2H) (Figure S33A). ^{13}C-NMR (DMSO-d_6), δ (ppm): 172.49, 167.92, 152.54, 131.49, 118.19, 111.63, 44.63 (Figure S33B). HRMS (ESI) m/z calculated for $C_9H_8NO_4$ [M - H^+] 194.0457, found 194.0459.

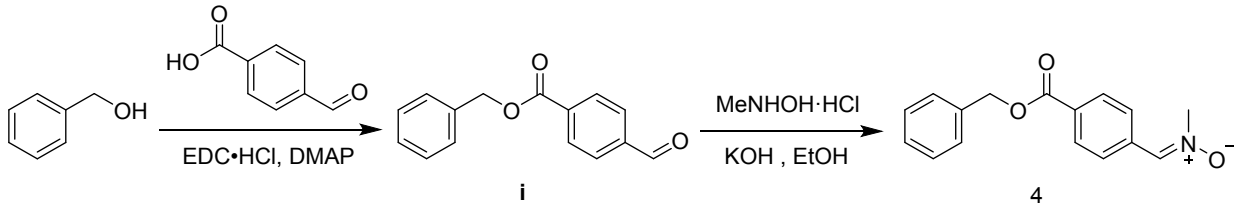
*Compound **g**:*[3] Compound **f** (4.78 g, 24.5 mmol) was dissolved in water (24 ml) at 0 ^{o}C followed by addition of concentrated hydrochloric acid (5 ml). Subsequently, an aqueous solution of $NaNO_2$ (3.4 g, 49 mmol) was added dropwise. The resulting mixture was filtered, washed with water and recrystallized in methanol to give compound **g** (5.2 g, 94%). ^{1}H-NMR (DMSO-d_6), δ (ppm): 13.15 (s, 2H), 8.07 (d, 2H), 7.75 (d, 2H), 4.81 (s, 2H) (Figure S34A). ^{13}C-NMR (DMSO-d_6), δ (ppm):

167.47, 167.05, 144.95, 131.19, 129.86, 119.41, 46.64 (Figure S34B). HRMS (ESI) m/z calculated for $C_9H_7N_2O_4$ [M - H^+] 223.0360, found 223.0360.

*Compound **h**:*[3] The solution of compound **g** (5.2 g, 23.2 mmol) in acetic anhydride (26 ml) was refluxed for three hours to give the solid crude product. It was filtered, washed with water and recrystallized in methanol to give compound **h** (2.91 g, 61%). ^{1}H-NMR (DMSO-d_6), δ (ppm): 13.53 (s, 1H), 8.19 (d, 2H), 8.06 (d, 2H), 7.89 (s, 1H) (Figure S35A). ^{13}C-NMR (DMSO-d_6), δ (ppm): 168.88, 166.40, 137.80, 134.69, 131.49, 122.32, 95.68 (Figure S35B). HRMS (ESI) m/z calculated for $C_9H_5N_2O_4$ [M - H^+] 205.0256, found 205.0255.

*Compound **3**:* Benzyl alcohol (1 ml, 9.7 mmol) and compound **h** (2.91 g, 14.1 mmol) were dissolved in DCM (48 ml), in which EDC·HCl (2.8 g, 14. 6 mmol) and DMAP (237 mg, 1.94 mmol) were sequentially added at room temperature. After stirring for 4 hours, the solvent was removed in vacuum and the solid crude product was purified by a silica column with DCM/EA (v/v = 6/1) as the eluent to afford the compound **3** (2.29 g, 80%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.31 (d, 2H), 7.81 (d, 2H), 7.43 (m, 5H), 6.78 (s, 1H), 5.42 (s, 2H) (Figure S36A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 168.65, 164.41, 137.76, 135.26, 134.01, 131.73, 128.68, 128.43, 121.34 (Figure S36B). HRMS (ESI) m/z calculated for $C_{16}H_{12}N_2NaO_4$ [M + Na^+] 319.0690, found 319.0690.

Preparation of compound 4



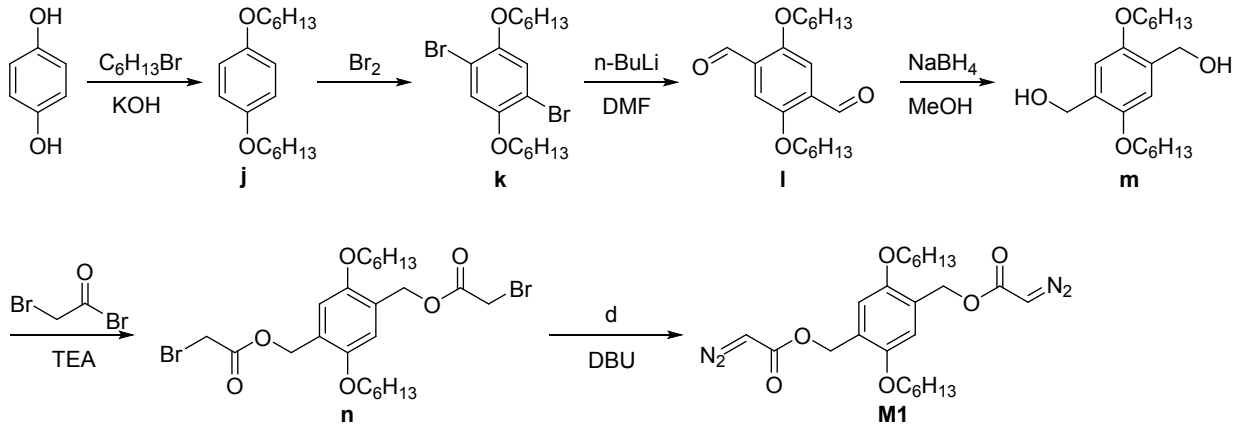
i 4

*Compound **i**:* Benzyl alcohol (2.16 g, 20 mmol) and 4-carboxybenzaldehyde (3.6 g, 24 mmol) were dissolved in 80 ml DCM, in which EDC·HCl (4.56 g, 24 mmol) and DMAP (244 mg, 2

mmol) were sequentially added at 0 °C. After stirring overnight, the solvent was removed in vacuum and the crude product was purified by a silica column with PE/EA (v/v = 10/1) as the eluent to afford the compound **i** (4.69 g, 98%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 10.10 (s, 1H), 8.22 (d, 2H), 7.94 (d, 2H), 7.41 (m, 5H), 5.40 (s, 2H) (Figure S37A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 191.59, 165.41, 139.25, 135.57, 135.12, 130.32, 129.51, 128.70, 128.51, 128.35, 67.32 (Figure S37B). HRMS (ESI) m/z calculated for $C_{15}H_{12}NaO_3$ [M + Na^+] 263.0680, found 263.0679.

*Compound **4**:* MeNHOH·HCl (1.23 g, 14.7mmol) was dissolved in a mixture of EtOH (15 ml) and H_2O (10 ml) followed by the addition of KOH (823 mg, 14.7 mmol). The resulting mixture was stirred at room temperature for 15 minutes. Compound **i** (2.94 g, 12.25 mmol) dissolved in EtOH (10 ml) was subsequently added into the mixture. After stirring for 40 minutes, EtOH was removed in vacuum. The crude mixture was dissolved in H_2O (80 ml) and extracted with EA (3 × 100 ml). The organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with DCM/MeOH (v/v = 20/1) as the eluent to afford the compound **4** (2.05 g, 62%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.25 (d, 2H), 8.09 (d, 2H), 7.40 (m, 6H), 5.37 (s, 2H), 3.91 (s, 3H) (Figure S38A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 165.71, 135.91, 134.43, 134.21, 131.17, 129.84, 128.63, 128.32, 128.23, 128.01 (Figure S38B). HRMS (ESI) m/z calculated for $C_{16}H_{15}NNaO_3$ [M + Na^+] 292.0947, found 292.0944.

Preparation of compound M1



*Compound **j**:*[4] A solution of hydroquinone (11.01g, 100 mmol) and 1-bromohexane (43g, 260 mmol) in DMF (200 ml) was added KOH (14.03g, 250 mmol) and heated to 90 °C. After stirring overnight, the solvent was removed in vacuum. The viscous mixture was added H_2O (100 ml) and extracted with EA (3 × 100 ml). The organic phase was collected and dried by $MgSO_4$. Then the crude product was purified by a silica column with PE/EA (v/v = 24/1) as the eluent to afford the compound **j** (14.13 g, 51%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.82 (s, 4H), 3.90 (t, 4H), 1.73 (m, 4H), 1.47 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H) (Figure S39A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 153.24, 115.42, 68.69, 31.63, 29.39, 25.75, 22.61, 14.02 (Figure S39B). HRMS (ESI) m/z calculated for $C_{18}H_{30}NaO_2$ [M + Na^+] 301.2137, found 301.2138.

*Compound **k**:*[4] Compound **j** (14.13 g, 50.7 mmol) was dissolved in DCM (100 ml) at 0 °C followed by the dropwise addition of bromine (6 ml, 12 mmol). After the reaction was completed, a saturated sodium thiosulfate pentahydrate aqueous solution was added into the resultant mixture. After extracting with DCM (3 × 100 ml), the organic phase was collected and dried by $MgSO_4$. Then the crude product was purified by a silica column with PE as the eluent to afford the compound **k** (20 g, 90%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 7.09 (s, 2H), 3.95 (t, 4H), 1.80 (m, 4H), 1.48 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H) (Figure S40A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 150.14,

118.55, 111.19, 70.36, 31.48, 29.09, 25.61, 22.56, 13.99 (Figure S40B). HRMS (ESI) m/z calculated for $C_{18}H_{28}Br_2NaO_2$ [M + Na^+] 457.0347, found 457.0348.

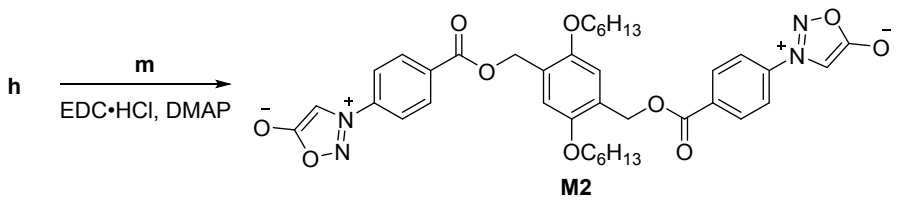
*Compound **l**:*[4] Compound **k** (17.44 g, 40 mmol) was introduced to a two necked flask with dry THF (160 ml) as the solvent. The stirred solution was cooled to -78 ^oC under N_2 atmosphere followed by the dropwise addition of n-butyllithium (2.4 M solution in hexanes) (38 ml, 96 mmol) over a period of 0.5h while maintaining the temperature below -60 ˚C. Stirring was continued at the same temperature for 1 hour followed by the addition of DMF (9.2 ml, 120 mmol). After stirring overnight, the reaction was quenched with H_2O (150 ml) and extracted with EA (3 × 150 ml). The organic phase was collected and dried by $MgSO_4$. Then the crude product was purified by a silica column with PE/EA (v/v = 40/1) as the eluent to afford the compound **l** (6.88 g, 51%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 10.48 (s, 2H), 7.43 (s, 2H), 4.08 (t, 4H), 1.85 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H) (Figure S41A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 189.41, 155.24, 129.32, 111.65, 69.27, 31.46, 29.18, 29.00, 25.67, 22.54, 13.97 (Figure S41B). HRMS (ESI) m/z calculated for $C_{20}H_{30}NaO_4$ [M + Na^+] 357.2036, found 357.2036.

*Compound **m**:* Compound **l** (6.88 g, 20.6 mmol) was suspended in MeOH (70 ml) and cooled down to 0 ˚C. Sodium borohydride (3.1 g, 82 mmol) was slowly added in batches. After stirring for 2 hours, the resulting mixture was acidified to pH = 2-3 with dilute hydrogen chloride. The solid was filtered, washed with water and recrystallized in methanol to give compound **m** (6.3 g, 90%). ^{1}H-NMR (DMSO), δ (ppm): 6.96 (s, 2H), 4.94 (t, 2H), 4.46 (d, 4H), 3.89 (t, 4H), 1.68 (m, 4H), 1.43 (m, 4H), 1.31 (m, 8H), 0.88 (t, 6H) (Figure S42A). ^{13}C-NMR (DMSO-d_6), δ (ppm): 149.50, 129.83, 111.41, 68.66, 58.14, 31.45, 29.34, 25.71, 22.54, 14.34 (Figure S42B). HRMS (ESI) m/z calculated for $C_{20}H_{34}NaO_4$ [M + Na^+] 361.2350, found 361.2349.

*Compound **n**:* A stirred solution of compound **m** (1 g, 2.9 mmol) and TEA (2.4 ml, 17.4 mmol) in DCM (15 ml) was cooled to 0 °C for 15 minutes followed by the dropwise addition of bromoacetyl bromide (1 ml, 11.6 mmol). After stirring at 0 °C for 1 hour, the solvent was removed in vacuum and the crude product was purified by a silica column with PE/EA (v/v = 10/1) as the eluent to afford the compound **n** (840 mg, 50%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.91 (s, 2H), 5.25 (s, 4H), 3.95 (t, 4H), 3.88 (s, 4H), 1.76 (m, 4H), 1.45 (m, 4H), 1.32 (m, 8H), 0.91 (t, 6H) (Figure S43A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 167.02 150.78, 124.57, 113.58, 69.11, 63.26, 31.54, 29.28, 25.85, 25.73, 22.59, 14.01 (Figure S43B). HRMS (ESI) m/z calculated for $C_{24}H_{36}Br_2NaO_6$ [M + Na^+] 601.0772, found 601.0771.

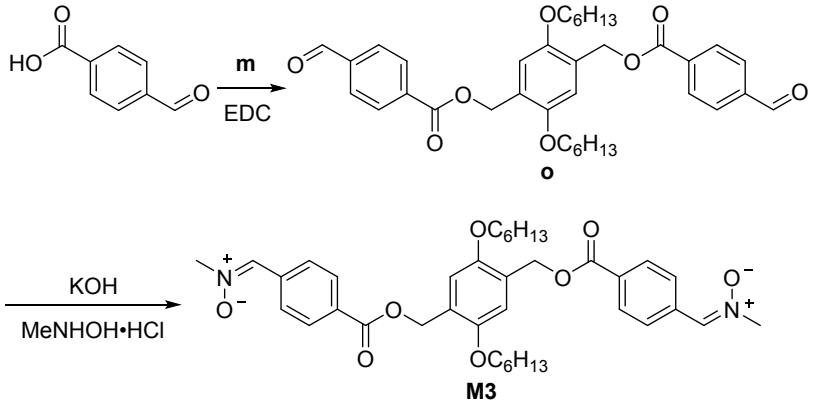
M1: Compound **d** (1.36 g, 4 mmol) and compound **n** (580.35 mg, 1 mmol) were stirred in THF (5 ml) at 0 °C followed by the dropwise addition of DBU (0.9 ml, 6 mmol). After stirring for 2 hours, a saturated $NaHCO_3$ aqueous solution was added until pH = 10. After extracting the mixture with EA (3 × 50 ml), the organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with PE/EA (v/v = 10/1) as the eluent to afford the **M1** (500 mg, 86%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.87 (s, 2H), 5.23 (s, 4H), 4.79 (s, 1H), 3.93 (t, 4H), 1.75 (m, 4H), 1.45 (m, 4H), 1.34 (m, 4H), 0.90 (t, 6H) (Figure S44A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 166.69, 150.85, 125.22, 113.75, 69.14, 61.93, 46.26, 31.59, 29.35, 25.76, 22.62, 14.02 (Figure S44B). HRMS (ESI) m/z calculated for $C_{24}H_{34}N_4NaO_6$ [M + Na^+] 497.2375, found 497.2371.

Preparation of compound M2



***M2**:* Compound **h** (732 mg, 3.55 mmol) and compound **m** (400 mg, 1.2 mmol) were dissolved in 7 ml DCM, in which EDC·HCl (681 mg, 3.55 mmol) and DMAP (58.6 mg, 0.48 mmol) were sequentially added at room temperature. After stirring overnight, the solvent was removed in vacuum and the solid crude product was purified by a silica column with DCM/EA (v/v = 6/1) as the eluent to afford **M2** (687 mg, 80%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.30 (d, 4H), 7.80 (d, 4H), 7.00 (s, 2H), 6.76 (s, 2H), 5.46 (s, 4H), 3.98 (t, 4H), 1.76 (m, 4H), 1.41 (m, 4H), 1.28 (m, 8H), 0.87 (t, 6H) (Figure S45A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 168.73, 164.50, 151.17, 137.70, 134.15, 131.67,124.94, 121.30, 93.81, 69.10, 63.19, 31.52, 29.33, 25.78, 22.56, 14.01 (Figure S45B). HRMS (ESI) m/z calculated for $C_{38}H_{42}N_4NaO_{10}$ [M + Na^+] 737.2783, found 737.2793.

Preparation of compound M3

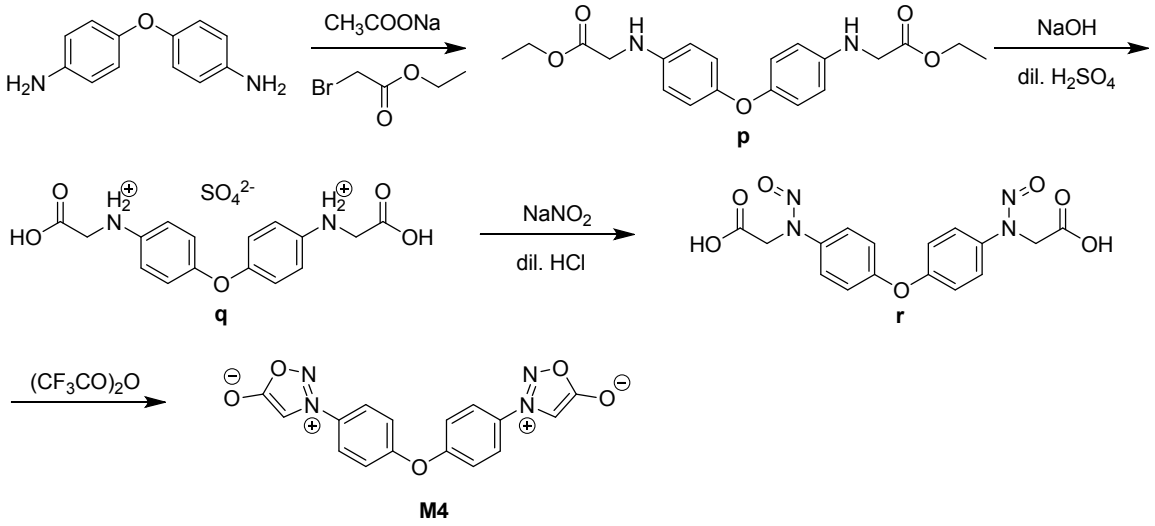


*Compound **o**:* Compound **m** (1.8 g, 5.3 mmol) and 4-carboxybenzaldehyde (2.38 g, 15.9 mmol) were dissolved in 30 ml DCM, in which EDC·HCl (3 g, 15.9 mmol) and DMAP (259 mg, 2.1 mmol) were sequentially added at 0 ^{o}C. After stirring overnight, the solvent was removed in vacuum and the crude product was purified by a silica column with PE/EA (v/v = 6/1) as the eluent to afford the compound **o** (2.43 g, 76%). ^{1}H-NMR ($CDCl_3$), δ (ppm): 10.10 (s, 2H), 8.21 (d, 4H), 7.94 (d, 4H), 7.00 (s, 2H), 5.43 (s, 4H), 3.97 (t, 4H), 1.75 (m, 4H), 1.42 (m, 4H), 1.27 (m, 8H), 0.86 (t, 6H) (Figure S46A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 191.59, 165.47, 151.13, 139.19, 135.34,

130.28, 129.50, 125.11, 114.20, 69.12, 62.86, 31.52, 29.33, 25.76, 22.54, 13.98 (Figure S46B). HRMS (ESI) m/z calculated for $C_{36}H_{42}NaO_8$ [M + Na^+] 625.2773, found 625.2772.

***M3**:* MeNHOH·HCl (0.74 g, 8.8 mmol) was dissolved in a mixture of EtOH (34 ml) and H_2O (6 ml) followed by the addition of KOH (493 mg, 8.8 mmol). The resulting mixture was stirred at room temperature for 15 minutes. Compound **l** (2.43g, 4 mmol) was added into the mixture subsequently. After stirring for 1 hour, EtOH was removed in vacuum. The crude mixture was added H_2O (50 ml) and extracted with EA (3 × 50 ml). The organic phase was collected and dried by $MgSO_4$. The resultant crude product was purified by a silica column with DCM/MeOH (v/v = 20/1) as the eluent to afford **M3** (2.18 g, 83%). ^{1}H-NMR (CDCl3), δ (ppm): 8.25 (d, 4H), 8.09 (d, 4H), 7.44 (s, 2H), 6.99 (s, 2H), 5.41 (s, 4H), 3.96 (t, 4H), 3.92 (s, 6H), 1.74 (m, 4H), 1.42 (m, 4H), 1.27 (m, 8H), 0.85 (t, 6H) (Figure S47A). ^{13}C-NMR ($CDCl_3$), δ (ppm): 165.75, 151.00, 134.36, 134.23, 131.35, 129.76, 127.97, 125.26, 113.96, 69.15, 62.38, 54.79, 31.50, 29.32, 25.73, 22.51, 13.98 (Figure S47B). HRMS (ESI) m/z calculated for $C_{38}H_{48}N_2NaO_8$ [M + Na^+] 683.3305, found 683.3303.

Preparation of compound M4



*Compound **p**:*[5] p-Phenylenediamine (10 g, 50 mmol), ethyl bromoacetate (12.2 ml, 110 mmol), and CH_3COONa (18.7 g, 229 mmol) were dissolved in CH_3CH_2OH (65 ml) in a 150 ml flask equipped with a water condenser. After degassing, the mixture was stirred at 75 ^oC for 4 hours under a nitrogen atmosphere. It was then exposed to air and slowly added H_2O until the solution became clear. After cooling down to 0 ^oC in the fridge for a few hours, the pure product precipitated out of the solution. The crystals were filtered and dried in vacuum (8.67 g, 47%). ^{1}H-NMR (DMSO-d_6), δ (ppm): 6.72 (d, 4H), 6.51 (d, 4H), 5.75 (t, 2H), 4.12 (q, 4H), 3.83 (d, 4H), 1.19 (t, 6H) (Figure S48A). ^{13}C-NMR (DMSO-d_6), δ (ppm): 171.81, 149.29, 144.34, 119.46, 113.54, 60.67, 45.76, 14.57 (Figure S48B). HRMS (ESI) m/z calculated for $C_{20}H_{24}N_2NaO_5$ [M + Na^+] 395.1580, found 395.1577.

*Compound **q**:*[5] Compound **p** (8.67 g, 23.3 mmol) was dissolved in a mixture of CH_3CH_2OH (10 ml) and H_2O (90 ml). NaOH (3.66 g, 91.5 mmol) was added slowly into the solution. Then the mixture was refluxed at 100 ^oC for 2 hours. When the yellow-brown transparent solution was cooled down to room temperature, dilute H_2SO_4 aqueous solution was added dropwise until the grey solid precipitated out of the solution. It was collected by filtration, washed with water and dried in vacuum (7.07 g, 96%).

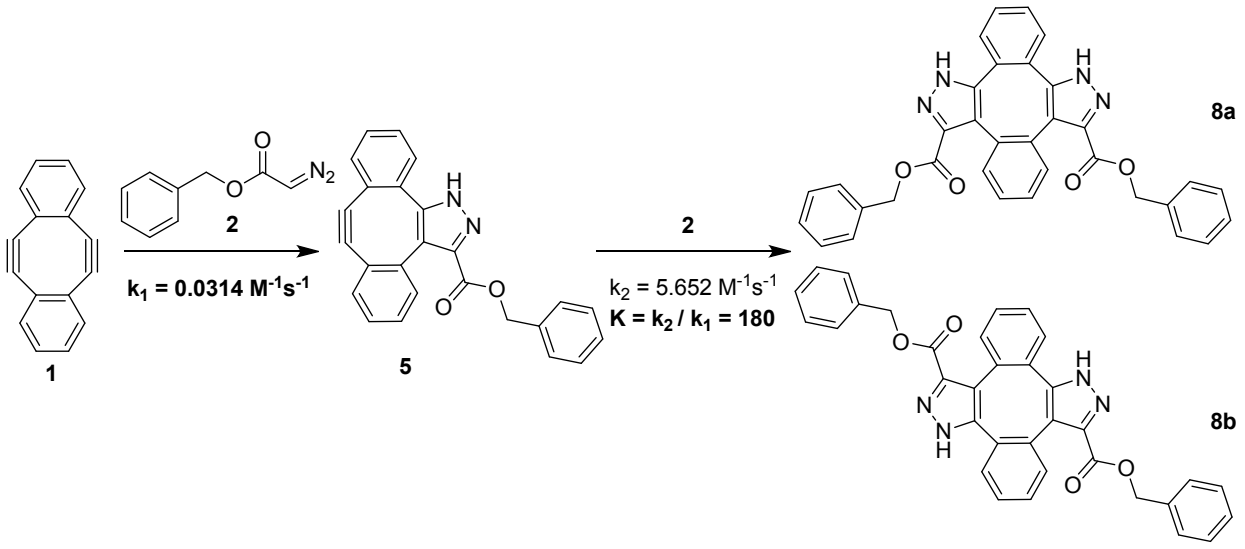
*Compound **r**:*[5] Compound **q** (7.07 g, 22.4 mmol) was stirred in glacial acetic acid (48 ml) with the temperature maintained at 0-5 ^oC. Sodium nitrite (7.73 g, 112 mmol) in 100 ml H_2O was added dropwise into the glacial acetic acid in half an hour. After stirring for additional 1 hour, it was added concentrated HCl dropwise until the pH = 1 to produce the precipitation of brown solid. The solid was collected by filtration, washed with water and dried in vacuum (8.14 g, 95%). ^{1}H-NMR (DMSO-d_6), δ (ppm): 13.15 (s, 2H), 7.68 (d, 4H), 7.24 (d, 4H), 4.75 (s, 4H) (Figure S49A). ^{13}C-

NMR (DMSO-d_6), δ (ppm): 167.59, 156.25, 137.65, 122.69, 120.02, 47.74 (Figure S49B). HRMS (ESI) m/z calculated for $C_{16}H_{13}N_4O_7$ [M - H^+] 373.0790, found 373.0790.

M4:[5] Compound **r** (8.14 g, 21.2 mmol) was dissolved in the DCM (42 ml) and stirred under a nitrogen atmosphere at 0 °C. $(CF_3COO)_2O$ (27 ml, 191 mmol) was added dropwise into the solution. After the complete addition, the flask was refluxed at 45 °C for 2 hours. When the reaction finished, the mixture was poured into ice water to give the brown solid compound. The crude product was collected by filtration and recrystallized in DMF. After recrystallization overnight, the yellow solid precipitated out of the solution was filtered, washed with water and CH_3CH_2OH and dried in vacuum to give **M4** (6 g, 84%). ^{1}H-NMR (DMSO-d_6)), δ (ppm): 8.04 (d, 4H), 7.80 (s, 2H), 7.44 (d, 4H) (Figure S50A). ^{13}C-NMR (DMSO-d_6), δ (ppm): 171.81, 149.29, 144.34, 119.46, 113.54, 60.67, 45.76, 14.57 (Figure S50B). HRMS (ESI) m/z calculated for $C_{16}H_{10}N_4NaO_5$ [M + Na^+] 361.0545, found 361.0543.

Evaluating self-accelerating property of 1,3-dipolar cycloaddition reactions between DIBOD and varied 1,3-dipoles

Evaluation of self-accelerating double strain-promoted diazo-alkyne click reaction



Estimation of rate constant ratio ($K = k_2/k_1$) of double strain-promoted diazo-alkyne click reaction.

As shown in above scheme, the model reaction of double strain-promoted click reaction between DIBOD (**1**) and diazo compound (**2**) was used to estimate the rate constant ratio K (k_2/k_1), in which compound **5** was the presumed mono-cycloaddition intermediate and compound **8** was the bis-cycloaddition products of cis-bis-cycloadduct (**8a**) and trans-bis-cycloadduct (**8b**). To perform this, DIBOD (38.4 mg, 0.192 mmol) and compound **2** (42.3 mg) were separately dissolved in 3 mL DMSO-d6. After the locking and shimming processes by a sample of purified **8** in DMSO-d6, the above DIBOD DMSO-d6 solution (0.4 mL) and compound **2** DMSO-d6 solution (0.4 mL) were mixed in one NMR test tube and characterized by Bruker Avance 600 spectrometer right away. The reaction process was then monitored by successive ^{1}H-NMR characterization with a designed reaction time interval. The exact initial molar ratio of DIBOD and compound **2** ($[\mathbf{1}]_0/[\mathbf{2}]_0$) reacted in the NMR test tube was determined by ^{1}H-NMR characterization as 1/1.25, which was used for the following K (k_2/k_1) calculation.

Based on the time-dependent consumption of DIBOD from ^{1}H-NMR characterization, the rate constant ratio K (k_2/k_1) could be determined by the following equation (1) according to the theory of the reported work.[6-8]

$$\tau = \int_{1}^{1/\beta} \frac{dw}{\left(\frac{2}{S} - 2\right)w + \frac{1}{K-1}\left(2K - 1 - w^{1-K}\right)} \qquad (1)$$

In this equation, the variables of β, K, S, and τ are defined as following. For the given variables, the right side of equation (1) was numerically calculated by the computation program of MathCAD.

$$\beta = \frac{[1]}{[1]_0}, K = \frac{k_2}{k_1}, S = 2\frac{[1]_0}{[2]_0}, \tau = k_1[1]_0 t$$

The value of β was calculated from ^{1}H-NMR characterization of the reaction mixture exemplified in Figure S1C using the following equation (2). Figure S2A shows the relationship between the resultant β values and the corresponding reaction times (t).

$$\beta = \frac{[1]}{[1]_0} = \frac{Area_a}{Area_a + Area_b + Area_c + Area_d} \qquad (2)$$

By virtue of the array of β values from Figure S2A, the corresponding τ values could be calculated for the array of t based on equation (1) by assuming a certain K value. With the definition of $\tau = k_1[1]_0 t$, the calculated τ values could be plotted against t for a series of assumed K values (Figure S2B), in which the corresponding correlation coefficients (R^2) were obtained from the fitting of the linear equations by virtue of the least square method. Subsequently, by plotting the R^2 values against K, the maximum R^2 could be estimated at K = 180 from the resultant curve in Figure S2C. This indicated that the second cycloaddition reaction was 180 times faster than the first cycloaddition reaction for the used model reaction.

Calculation of k_1.

For the above model reaction scheme, the reaction rate was given by equation (3).

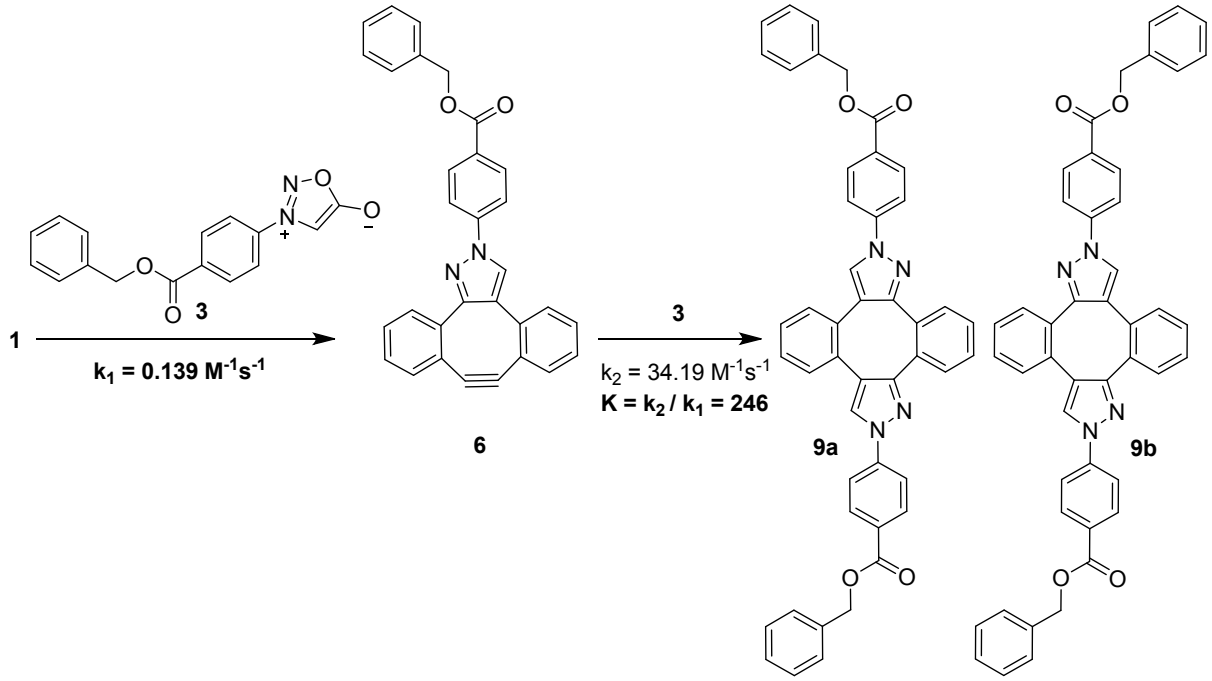
$$-\frac{d[1]}{dt} = k_1\beta[1]_0([2]_0 - 2(1-\beta)[1]_0) \qquad (3)$$

With $[1]_0$ = 0.032 M and $[2]_0$ = 0.04 M, equation (3) could be solved to give equation (4).

$$t = \frac{1}{0.02368k_1}\ln\frac{\beta}{0.064k_1\beta - 0.02368k_1} + c \qquad (4)$$

Subsequently, the equation (4) was used to fit the plot of the reaction time (t) and β values in Figure S2D. This produced the corresponding k_1 value of $(3.14 \pm 2.42) \times 10^{-2}$ M^{-1} s^{-1}.

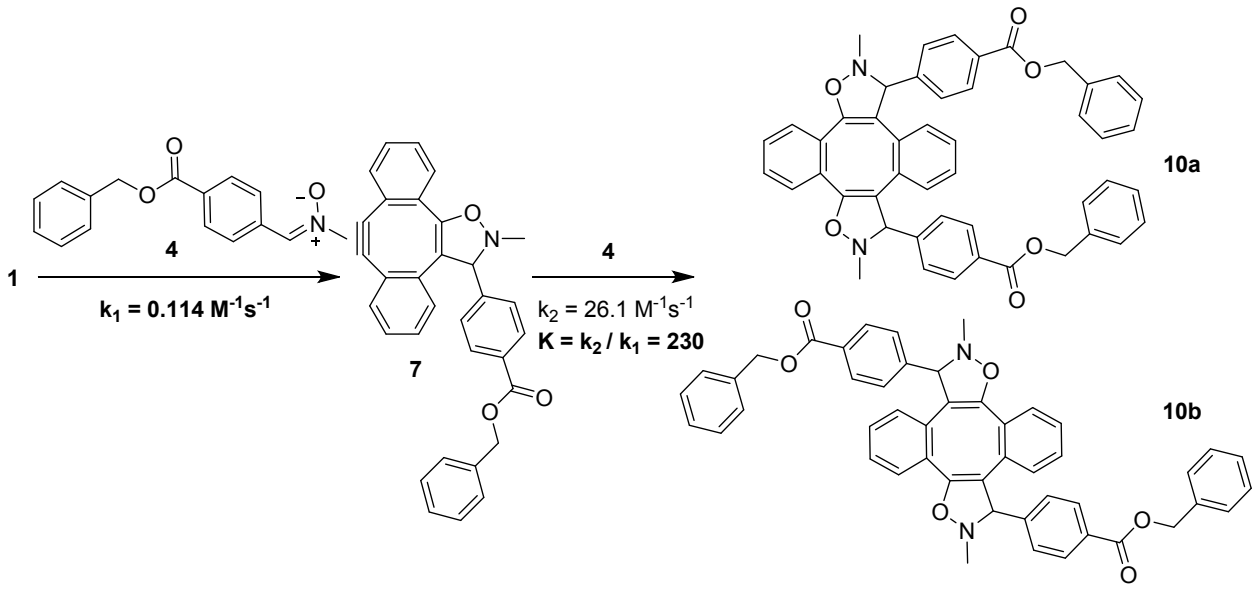
Evaluation of self-accelerating double strain-promoted sydnone-alkyne click reaction



The same estimation process was used for the evaluation of self-accelerating double strain-promoted sydnone-alkyne click reaction. By plotting the R^2 values against K, the maximum R^2 could be estimated at K = 246 from the resultant scatter plot in Figure S4C. This indicated that the second cycloaddition reaction was 246 times faster than the first cycloaddition reaction for the

used model reaction. The corresponding k_1 value of $(1.39 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1} can be abtained from Figure S4D.

Evaluation of self-accelerating double strain-promoted nitrone-alkyne click reaction



The same estimation process was applied for the evaluation of self-accelerating double strain-promoted nitrone-alkyne click reaction. By plotting the R^2 values against K, the maximum R^2 could be estimated at K = 230 from the resultant scatter plot in Figure S6C. This indicated that the second cycloaddition reaction was 230 times faster than the first cycloaddition reaction for the used model reaction. The corresponding k_1 value of $(1.14 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1} can be abtained from Figure S6D.

Preparation of Poly 1, 2, 3, and 4.

The polymerization was performed in an Agilent injection vial (2 ml or 4 ml) under ambient conditions. The solvent was added by a microliter syringe (100 ul).

The same preparation process was applied for preparing **Poly 1** and **2**. A representative

procedure for **Poly 1** was demonstrated as follows. DIBOD (22 mg, 0.11 mmol) was added into a solution of **M1** (47.5 mg, 0.1 mmol) in DMF (0.2 mL) to start the step-growth polymerization.

A representative procedure for **Poly 3** was demonstrated as follows. DIBOD (22 mg, 0.11 mmol) was added into a solution of **M3** (66.1 mg, 0.1 mmol) in $CHCl_3$ (0.2 mL) to start the step-growth polymerization.

A representative procedure for **Poly 4** was demonstrated as follows. DIBOD (22 mg, 0.11 mmol) was added into a solution of **M4** (33.8 mg, 0.1 mmol) in NMP (0.2 mL) to start the step-growth polymerization.

Manipulating the molecular weight of Poly 1 with mono-diazo compound

A representative procedure (molar ratio = 10%): DIBOD (22 mg, 0.11 mmol) was added into a solution of **M1** (47.5 mg, 0.1 mmol) and compound **2** (1.76 mg, 10^{-2} mmol) in DMF (0.2 mL) to start the step-growth polymerization.

Figures

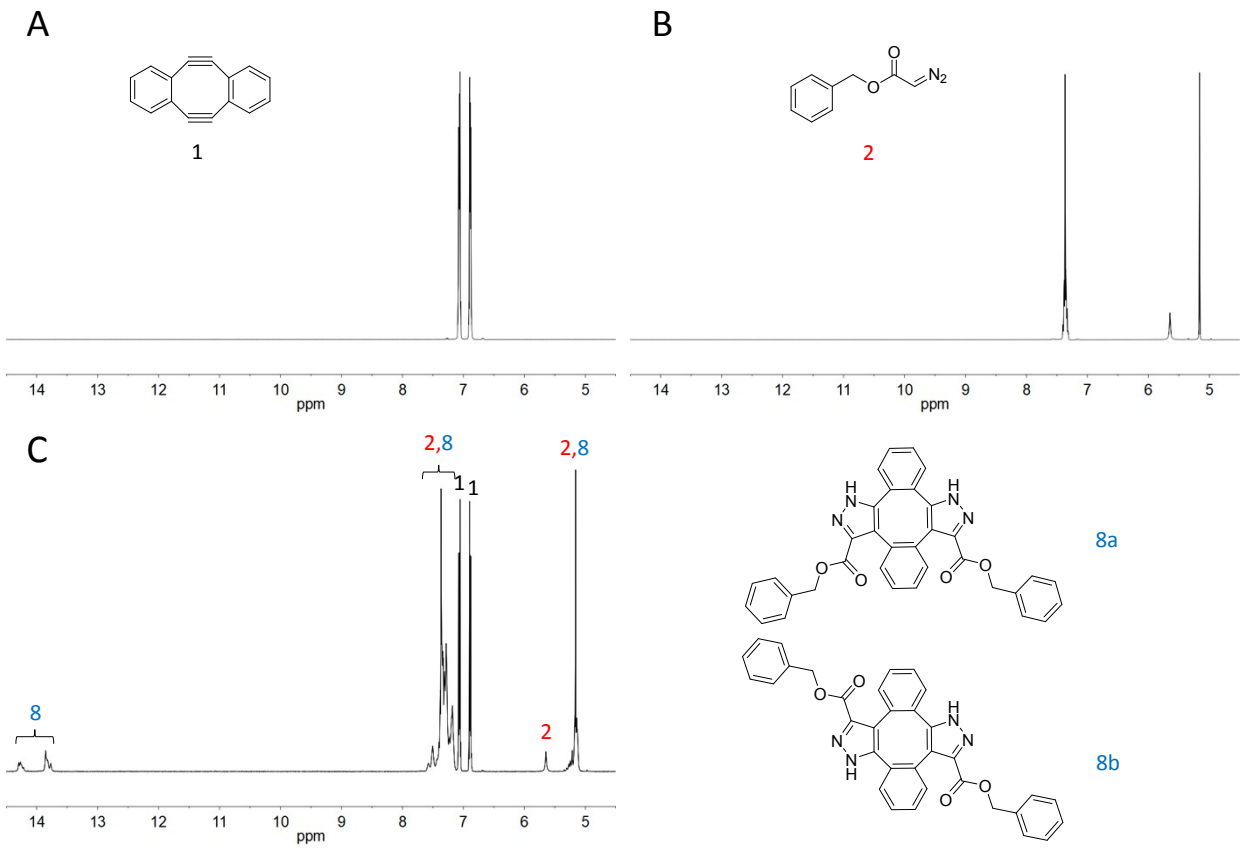


Figure S1. ^{1}H-NMR spectra of DIBOD (A), diazo compound (B), and the reaction mixture at 20 min (C) in DMSO-d_6.

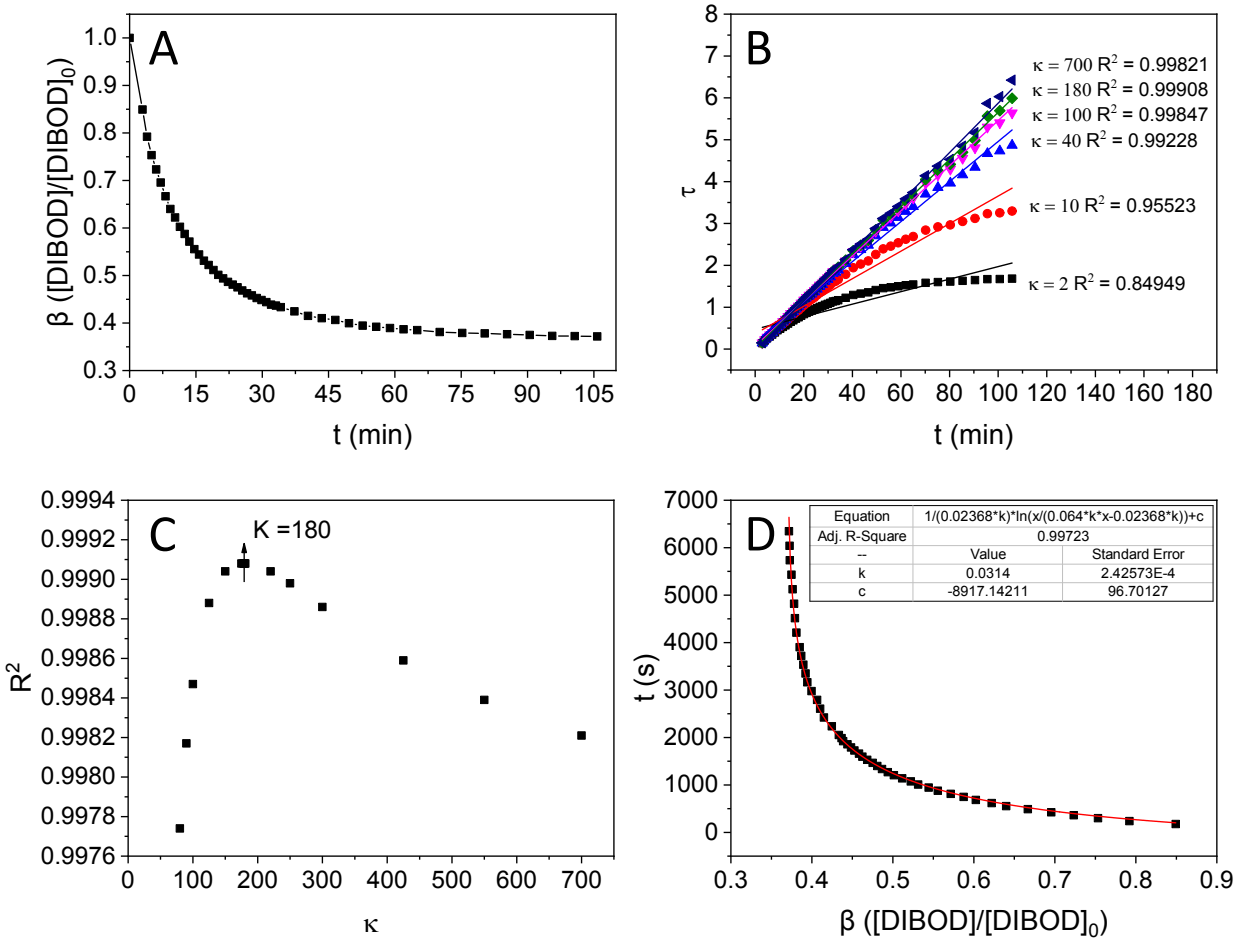


Figure S2. (A) Relationship between β ($[1]/[1]_0$) and reaction time (t) calculated from ^{1}H-NMR characterization of the reaction mixture. (B) Relationship between τ and reaction time (t) for the given K. (C) Relationship between correlation coefficient R^2 and K (k_2/k_1). (D) Relationship between reaction time (t) and β ($[1]/[1]_0$) calculated from ^{1}H-NMR characterization of the reaction mixture, in which the red nonlinear fitting curve produced the k_1 value of $(3.14 \pm 2.42) \times 10^{-2}$ M^{-1} s^{-1}.

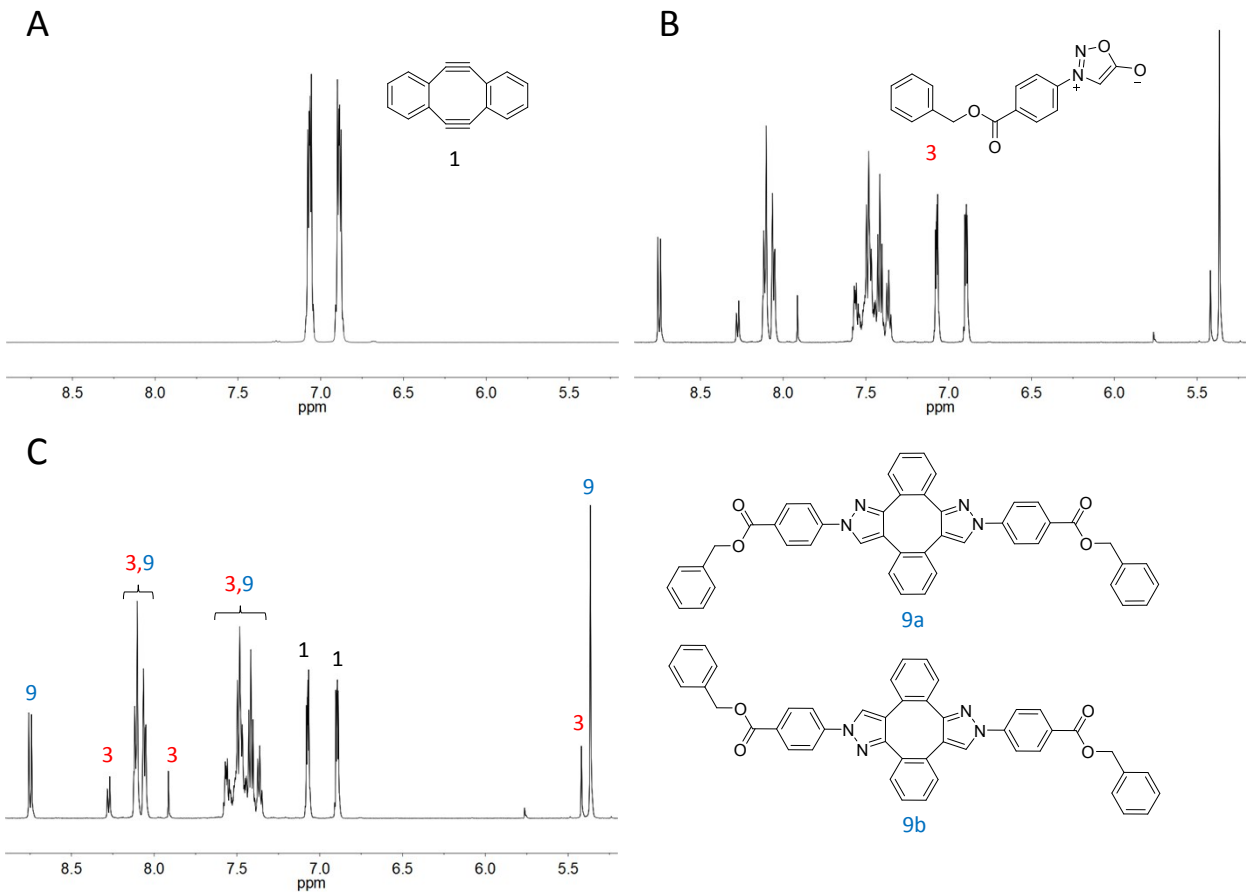


Figure S3. ^{1}H-NMR spectra of DIBOD (A), sydnone compound (B), and the reaction mixture at 20 min (C) in DMSO-d_6.

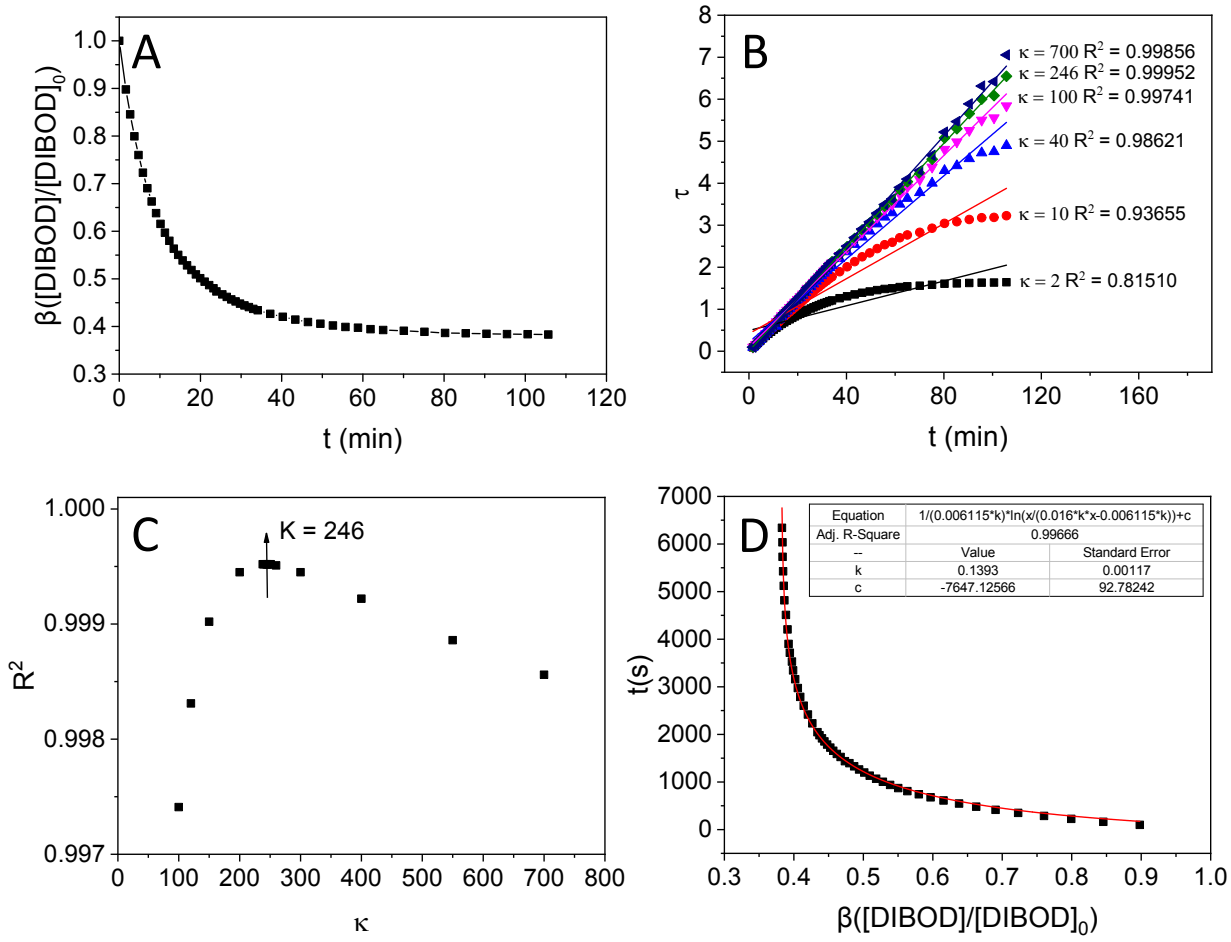


Figure S4. (A) Relationship between β ($[1]/[1]_0$) and reaction time (t) calculated from ^{1}H-NMR characterization of the reaction mixture. (B) Relationship between τ and reaction time (t) for the given K. (C) Relationship between correlation coefficient R^2 and K (k_2/k_1). (D) Relationship between reaction time (t) and β ($[1]/[1]_0$) calculated from ^{1}H-NMR characterization of the reaction mixture, in which the red nonlinear fitting curve produced the k_1 value of $(1.39 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1}.

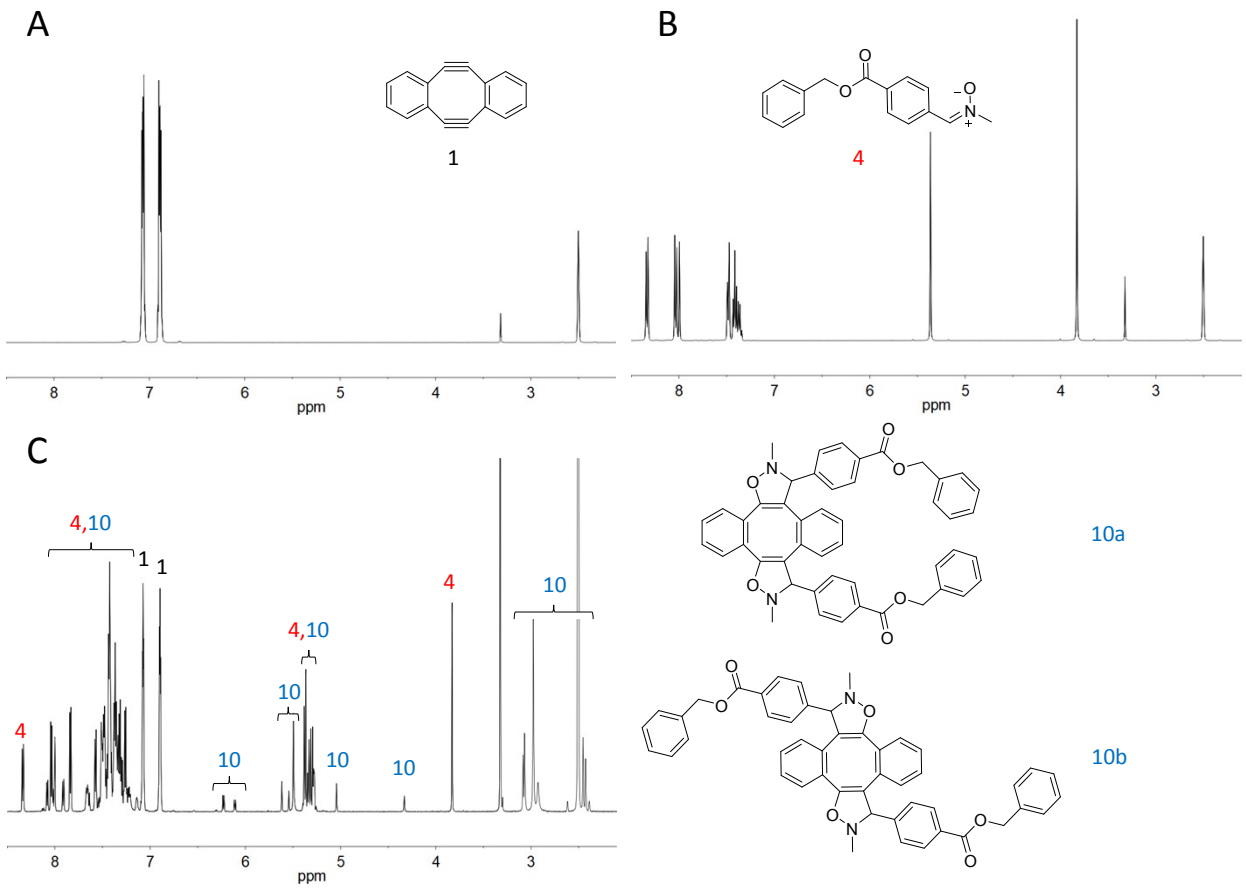


Figure S5. ^{1}H-NMR spectra of DIBOD (A), nitrone compound (B), and the reaction mixture at 20 min (C) in DMSO-d_6.

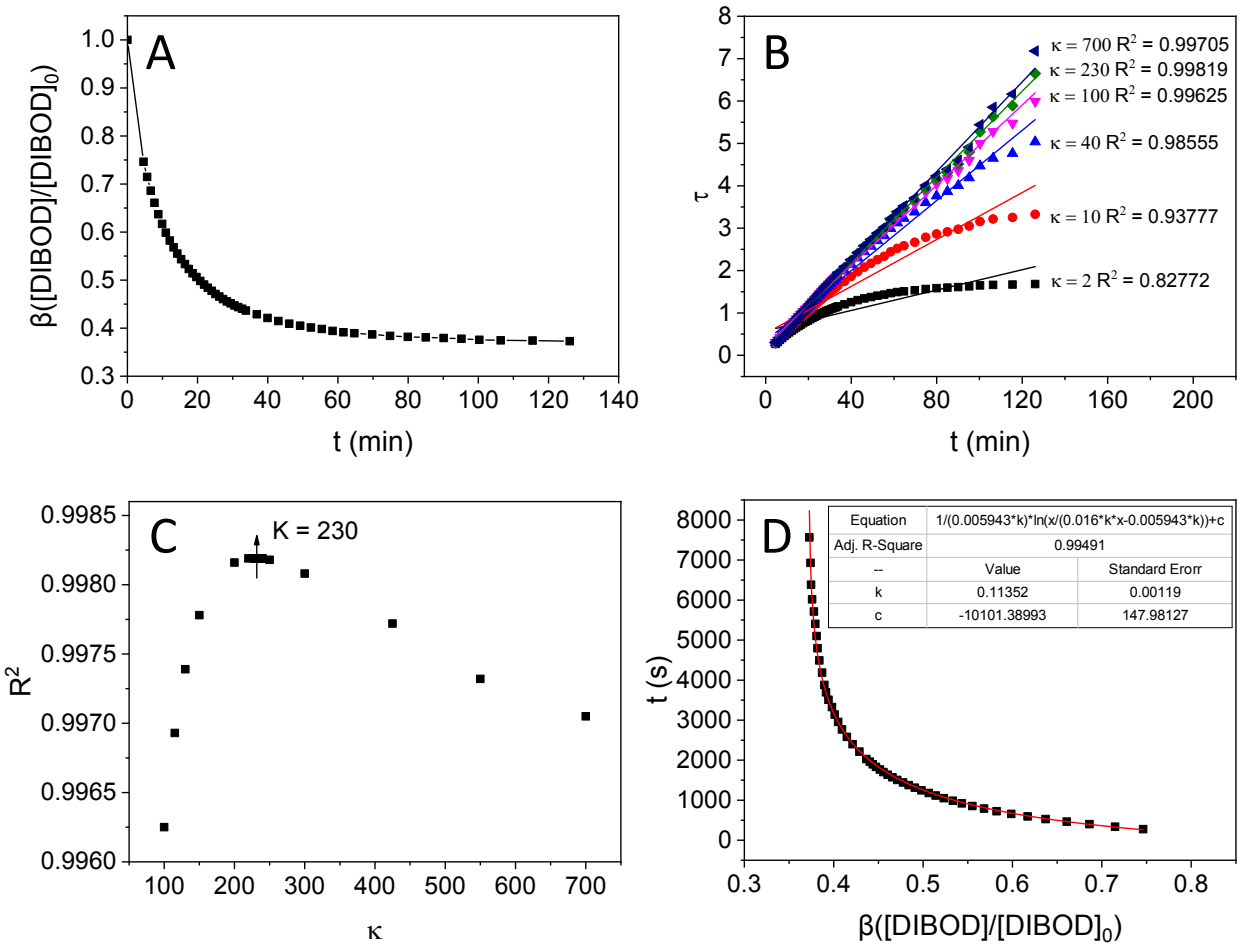


Figure S6. (A) Relationship between β ($[1]/[1]_0$) and reaction time (t) calculated from ^{1}H-NMR characterization of the reaction mixture. (B) Relationship between τ and reaction time (t) for the given K. (C) Relationship between correlation coefficient R^2 and K (k_2/k_1). (D) Relationship between reaction time (t) and β ($[1]/[1]_0$) calculated from ^{1}H-NMR characterization of the reaction mixture, in which the red nonlinear fitting curve produced the k_1 value of $(1.14 \pm 0.01) \times 10^{-1}$ M^{-1} s^{-1}.

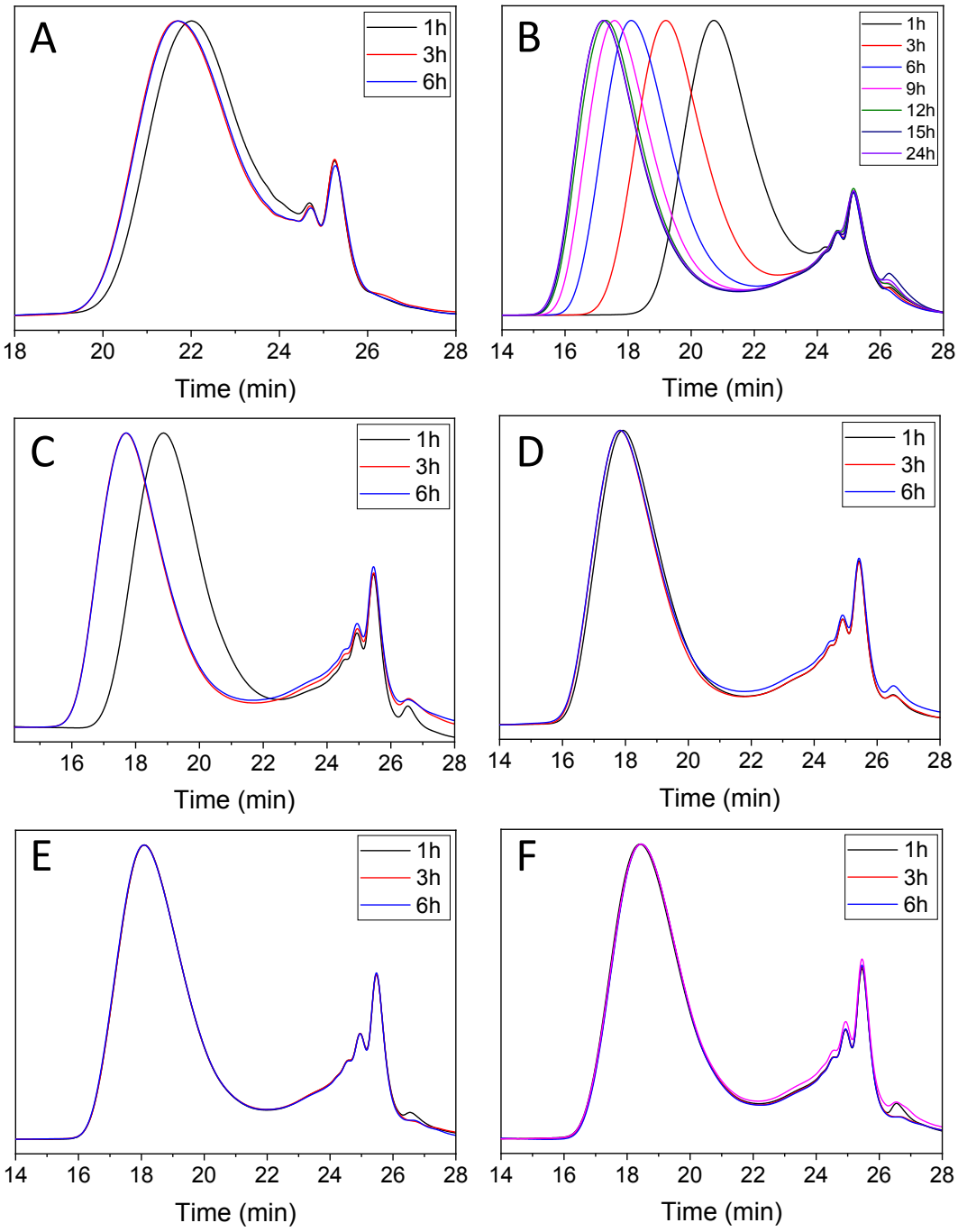


Figure S7. GPC curves of raw **Poly 1** prepared from a constant $[M1]_0$ of 0.2 M and varied S ($[DIBOD]_0/[\mathbf{M1}]_0$) values of 0.91 (A), 1.0 (B), 1.1 (C), 1.2 (D), 1.5 (E), and 2.0 (F) at different reaction time. The polymerizations were all performed at room temperature in DMF. THF was used as eluent and polystyrene standards were used for calibration.

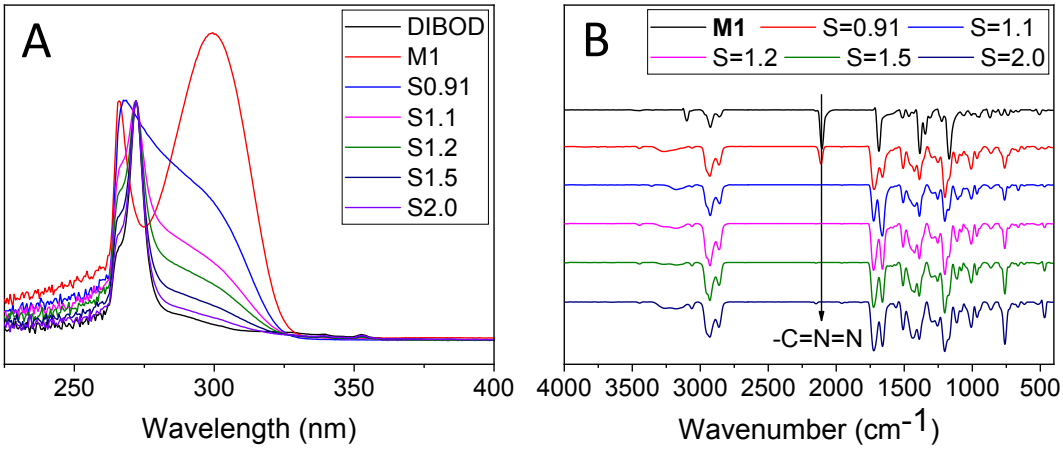


Figure S8. (A) UV-Vis spectra of DIBOD (black), **M1** (red), and raw **Poly 1** prepared from $[\mathbf{M1}]_0$ = 0.2 M and varied S ($[DIBOD]_0/[\mathbf{M1}]_0$) values of 0.91 (blue), 1.1 (magenta), 1.2 (olive), 1.5 (navy), and 2.0 (violet) in 3 h, where DMF was used as the measurement solvent. (B) FT-IR spectra of **M1** (black) and raw **Poly 1** prepared from $[\mathbf{M1}]_0$ = 0.2 M and varied S ($[DIBOD]_0/[\mathbf{M1}]_0$) values of 0.91 (red), 1.1 (blue), 1.2 (magenta), 1.5 (olive), and 2.0 (navy) in 3 h.

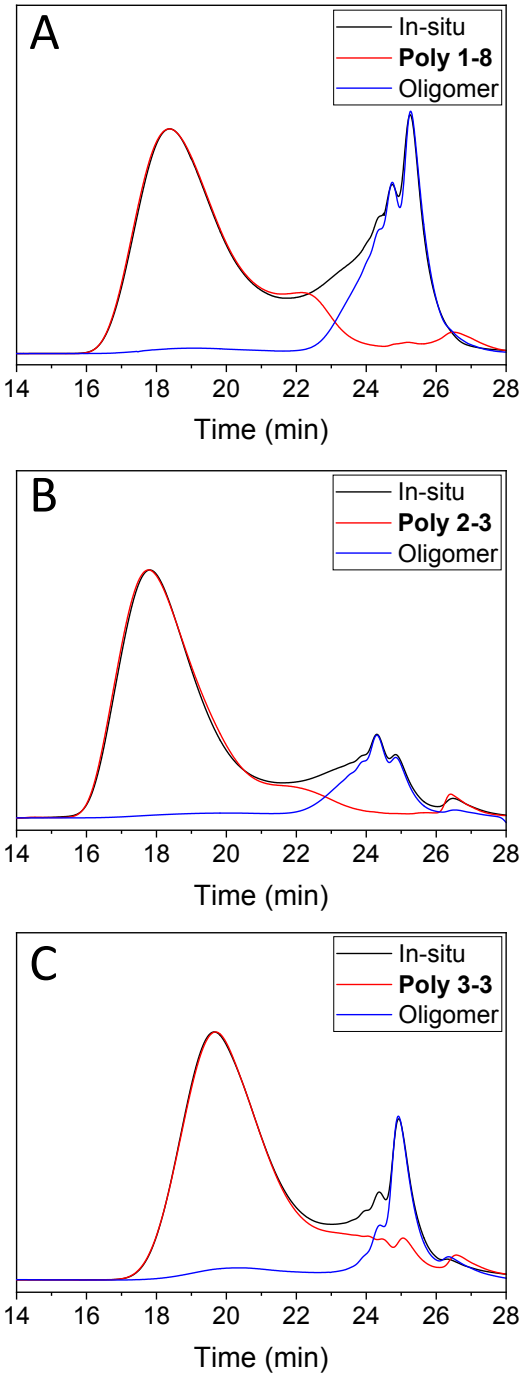


Figure S9. (A) GPC curves of raw **Poly 1-8** (black) and the corresponding high molecular weight **Poly 1-8** (red) and low molecular weight **Poly 1-8** oligomers (blue) separated from precipitation. (B) GPC curves of raw **Poly 2-3** (black) and the corresponding high molecular weight **Poly 2-3** (red) and low molecular weight **Poly 2-3** oligomers (blue) separated from precipitation. (C) GPC

curves of raw **Poly 3-3** (black) and the corresponding high molecular weight **Poly 3-3** (red) and low molecular weight **Poly 3-3** oligomers (blue) separated from precipitation. All the polymers were obtained from S = 1.1 and $[M1]_0$ = 0.1 M.

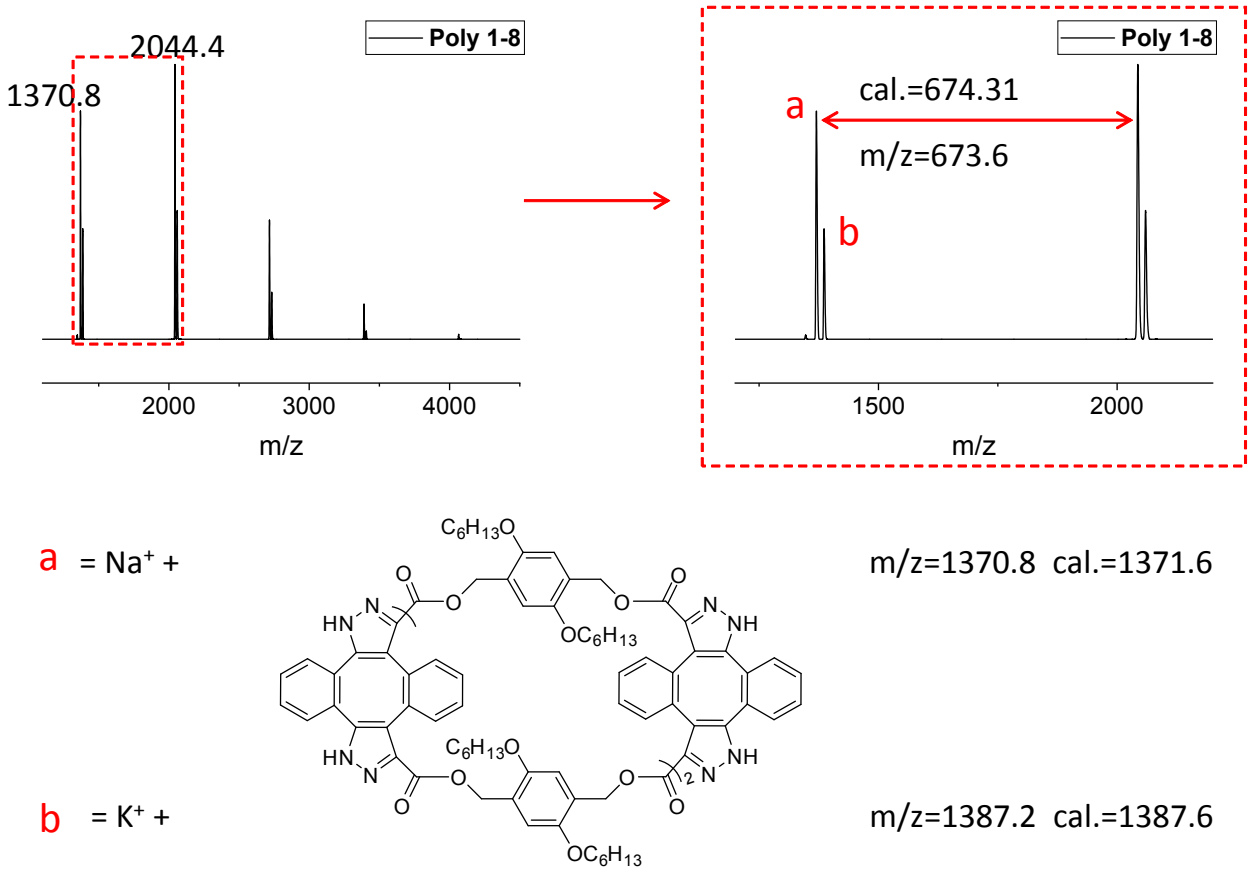


Figure S10. MALDI-TOF MS of low molecular weight **Poly 1-8** oligomers. One of the isomers was used to demonstrate the molecular structures.

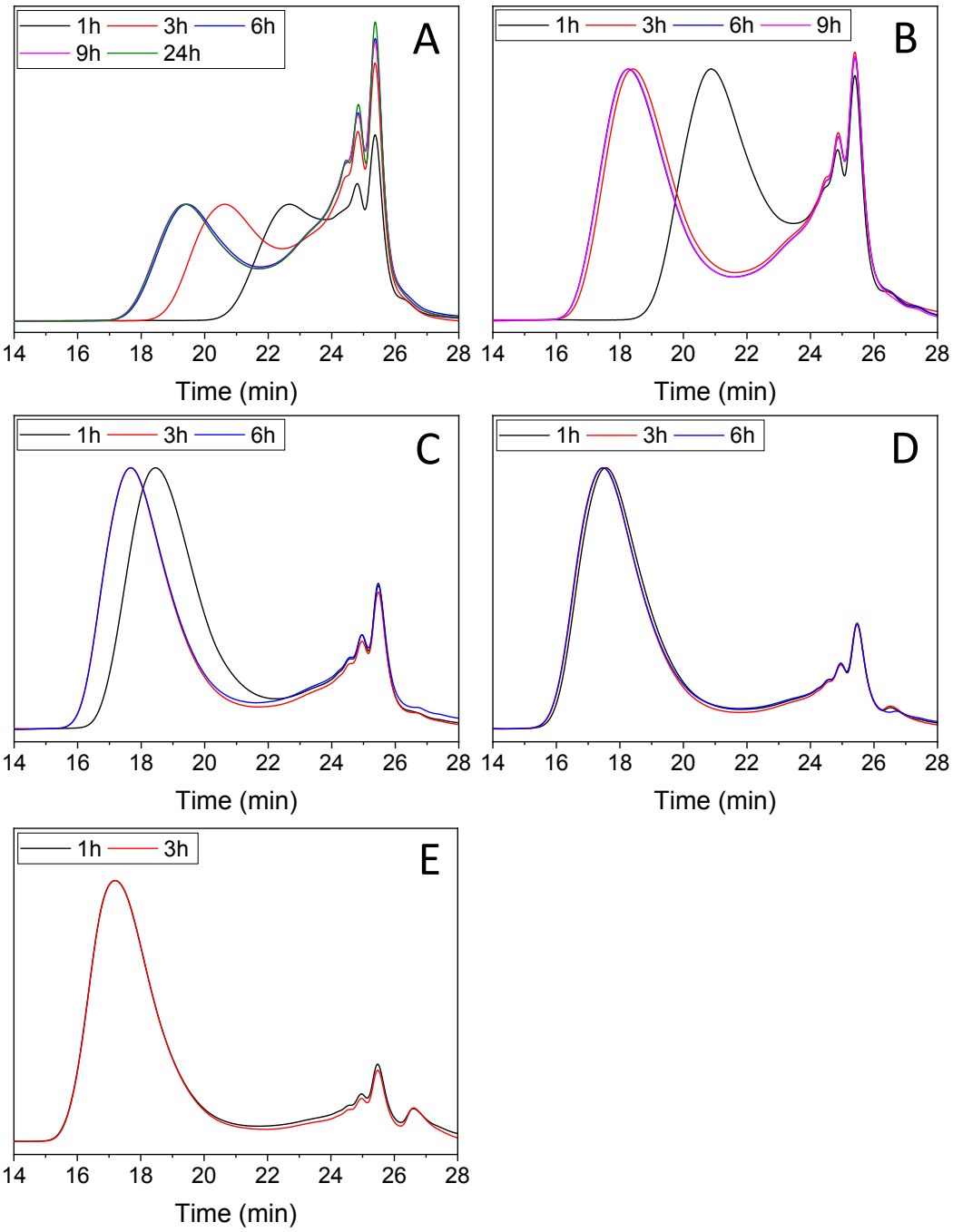


Figure S11. GPC curves of raw **Poly 1** prepared from a constant S ($[DIBOD]_0/[\mathbf{M1}]_0$) of 1.1 and different $[\mathbf{M1}]_0$ of 0.05 M (A), 0.1 M (B), 0.2 M (C), 0.3 M (D), and 0.5 M (E) at varied reaction time. THF was used as eluent and polystyrene standards were used for calibration.

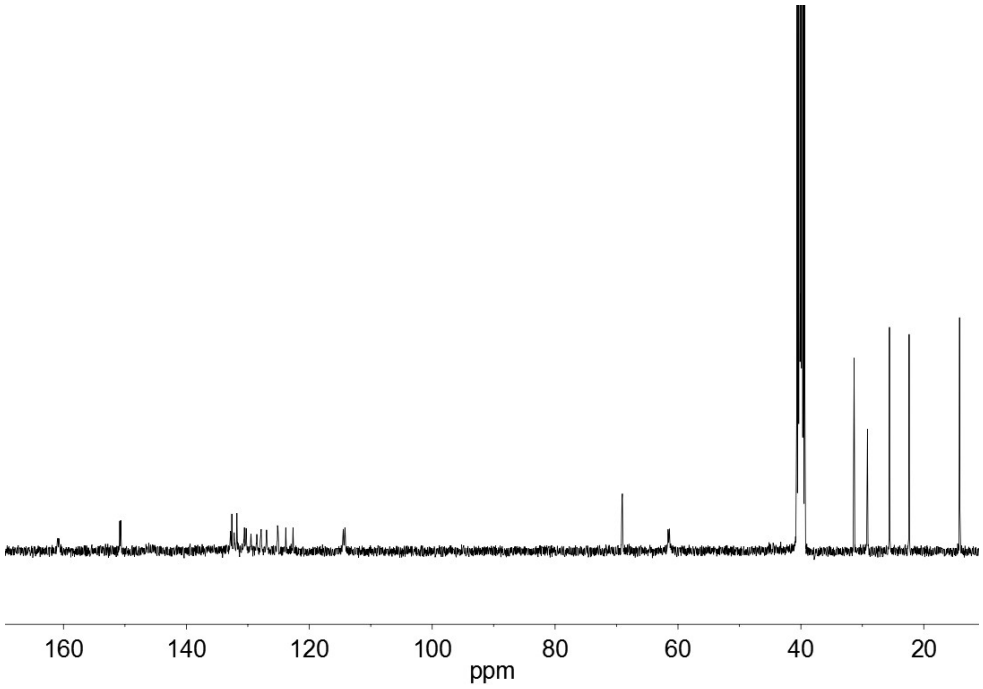


Figure S12. ^{13}C-NMR spectrum of the precipitated **Poly 1-10** in DMSO-d_6.

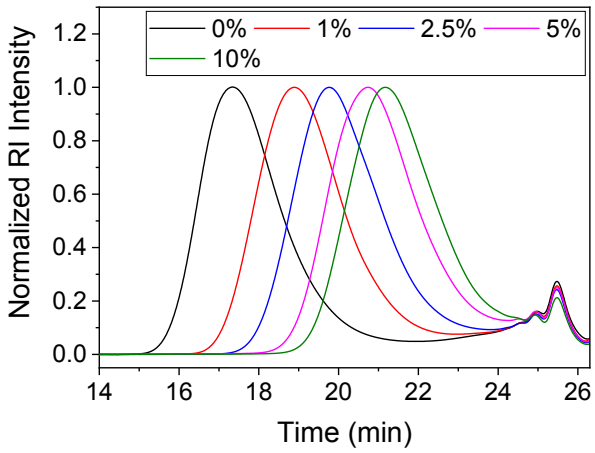


Figure S13. GPC curves of raw **Poly 1** prepared from $[\mathbf{M1}]_0$ = 0.5 M, S ($[\text{DIBOD}]_0/[\mathbf{M1}]_0$) =1.1, and varied [*mono*-diazo compound **2**]$_0$/$[\mathbf{M1}]_0$ = 0% (black), 1% (red), 2.5% (blue), 5% (magenta), and 10% (olive) in 3 h. THF was used as the eluent and polystyrene standards were used for the calibration.

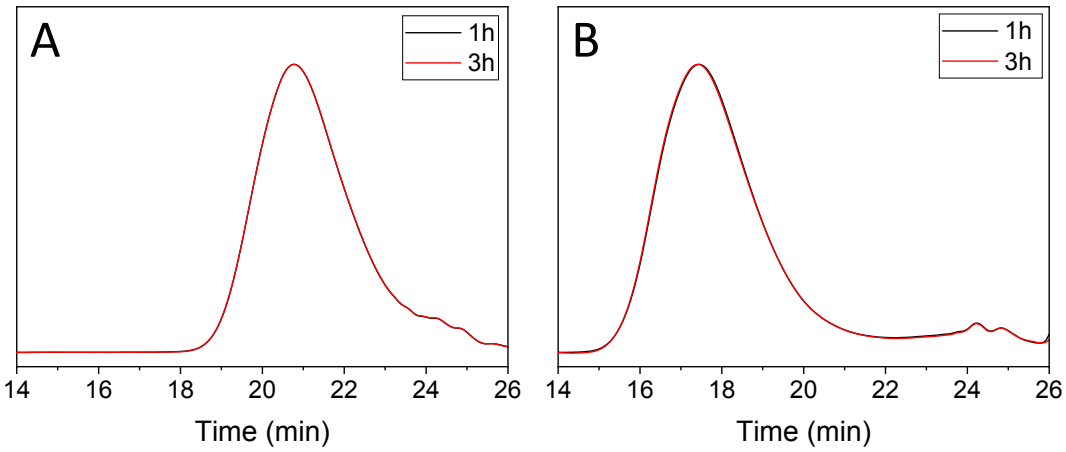


Figure S14. GPC curves of raw **Poly 2** prepared from a constant $[\mathbf{M2}]_0$ of 0.5 M and different S ($[DIBOD]_0/[\mathbf{M2}]_0$) values of 0.91 (A) and 1.1 (B) with 1 h (black) and 3 h (red) reaction time. THF was used as the eluent and polystyrene standards were used for the calibration.

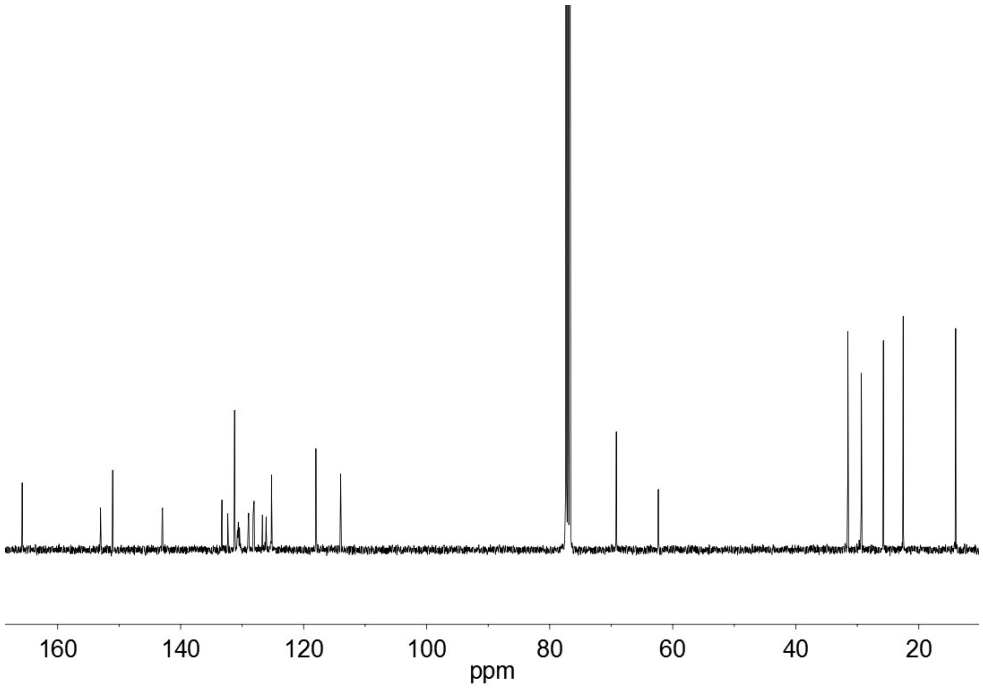


Figure S15. ^{13}C-NMR spectrum of the precipitated **Poly 2-2** in $CDCl_3$.

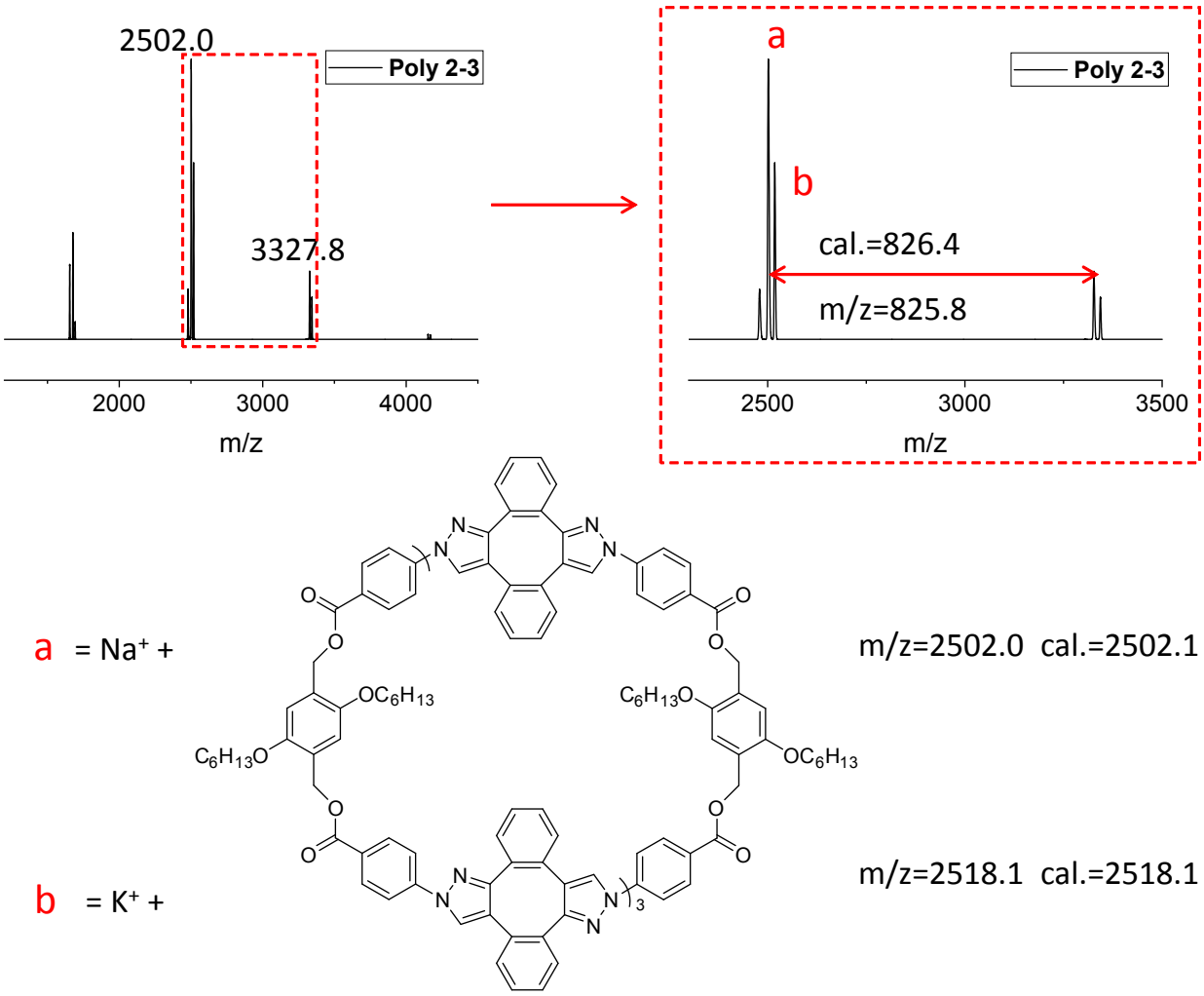


Figure S16. MALDI-TOF MS of low molecular weight **Poly 2-3** oligomers. One of the isomers was used to demonstrate the molecular structures.

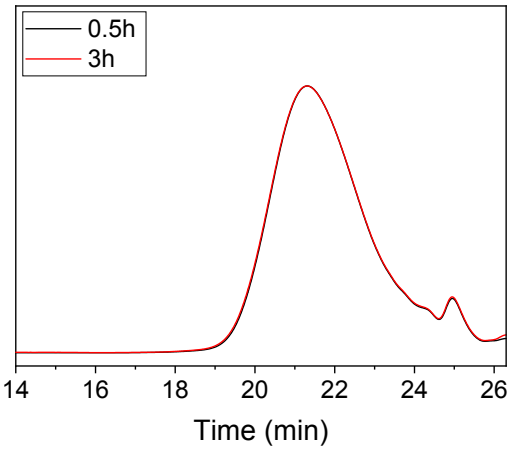


Figure S17. GPC curves of raw **Poly 3-1** prepared from $[\mathbf{M3}]_0$ = 0.5 M and S ($[DIBOD]_0/[\mathbf{M3}]_0$) = 0.91 in 0.5 h (black) and 3 h (red). THF was used as the eluent and polystyrene standards were used for the calibration.

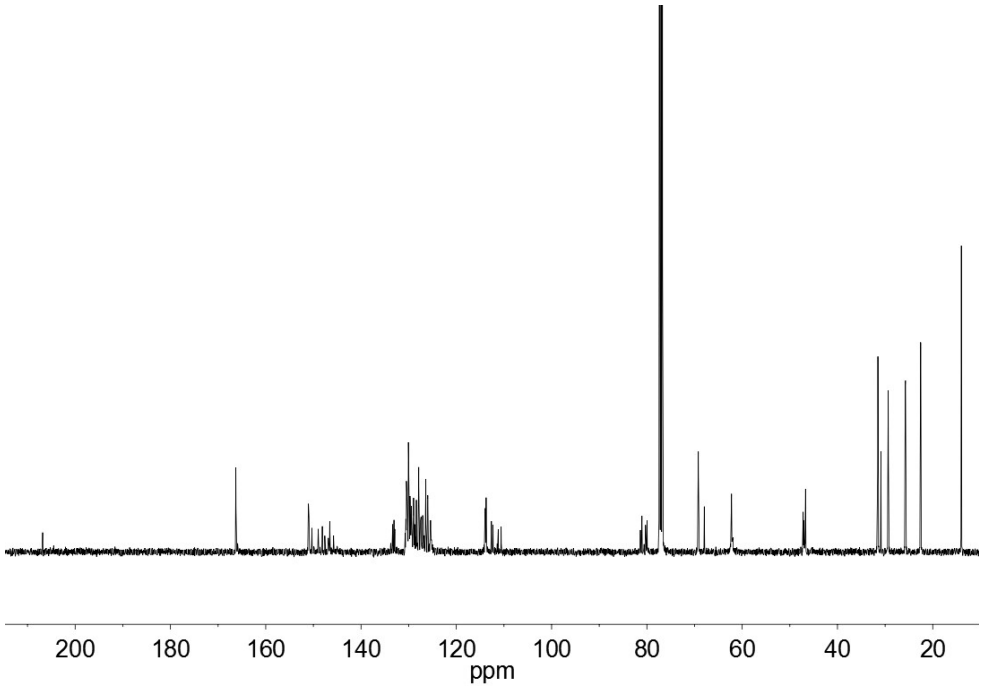


Figure S18. ^{13}C-NMR spectrum of the precipitated **Poly 3-2** in $CDCl_3$.

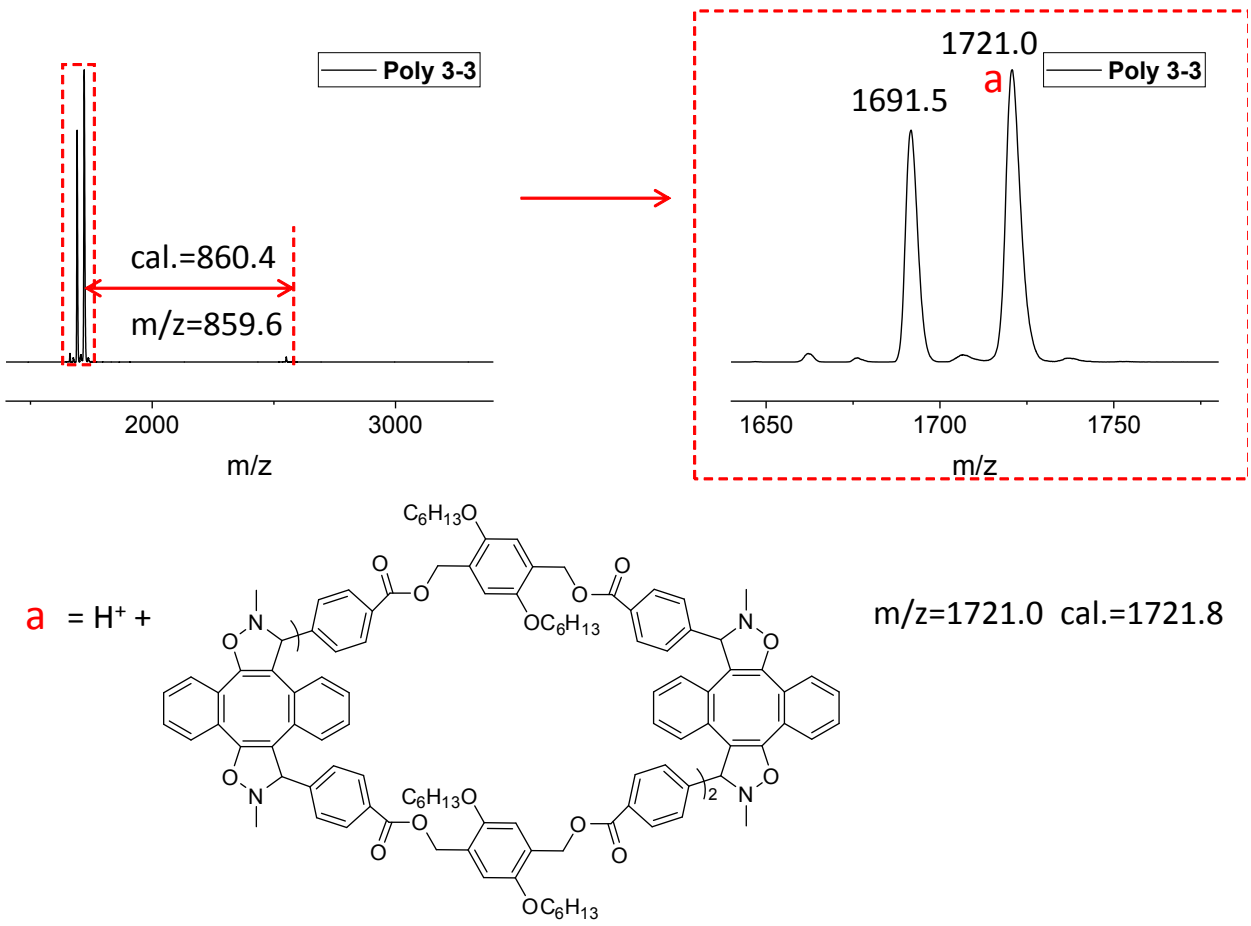


Figure S19. MALDI-TOF MS of low molecular weight **Poly 3-3** oligomers. One of the isomers was used to demonstrate the molecular structures.

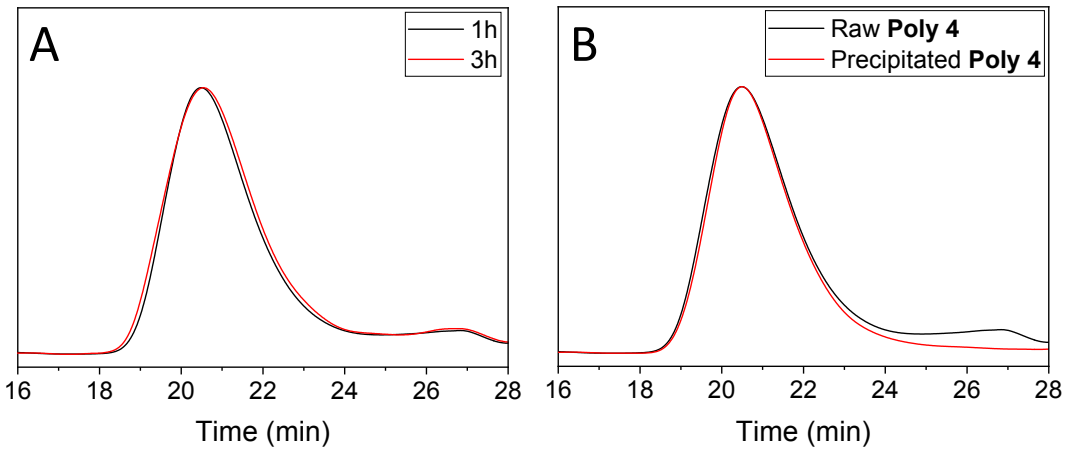


Figure S20. (A) GPC curves of the raw **Poly 4** prepared from $[\mathbf{M4}]_0$ = 0.5 M and S ($[DIBOD]_0/[\mathbf{M4}]_0$) = 1.1 in 1 h (black) and 3 h (red). (B) GPC curves of the raw **Poly 4** (black curve) and precipitated **Poly 4** (red curve). DMF was used as the eluent and polystyrene standards were used for the calibration.

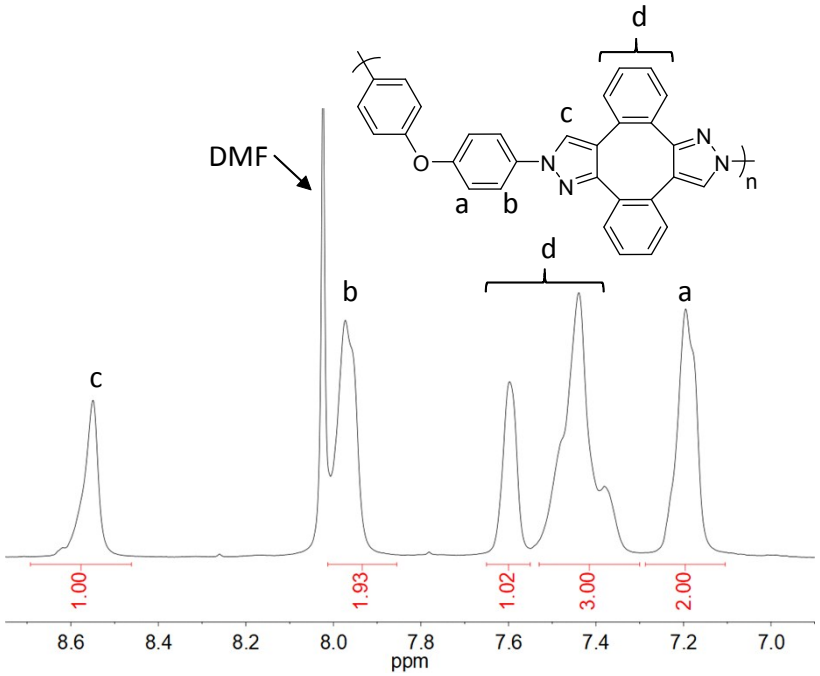


Figure S21. ^{1}H-NMR spectra of the precipitated **Poly 4** in DMF-d_7.

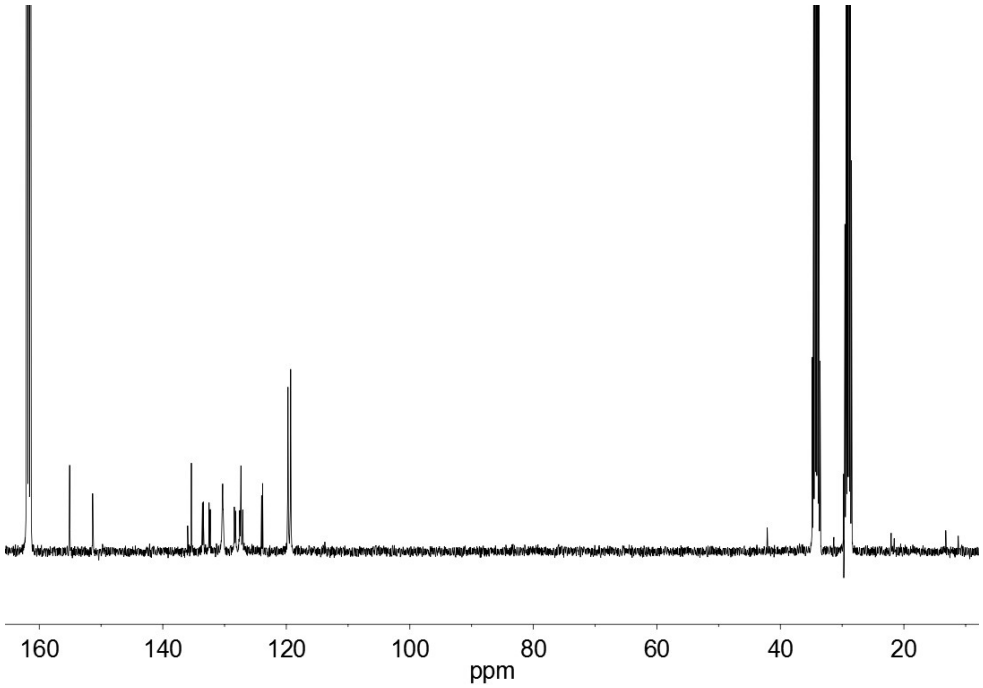


Figure S22. ^{13}C-NMR spectrum of the precipitated **Poly 4** in DMF-d_7.

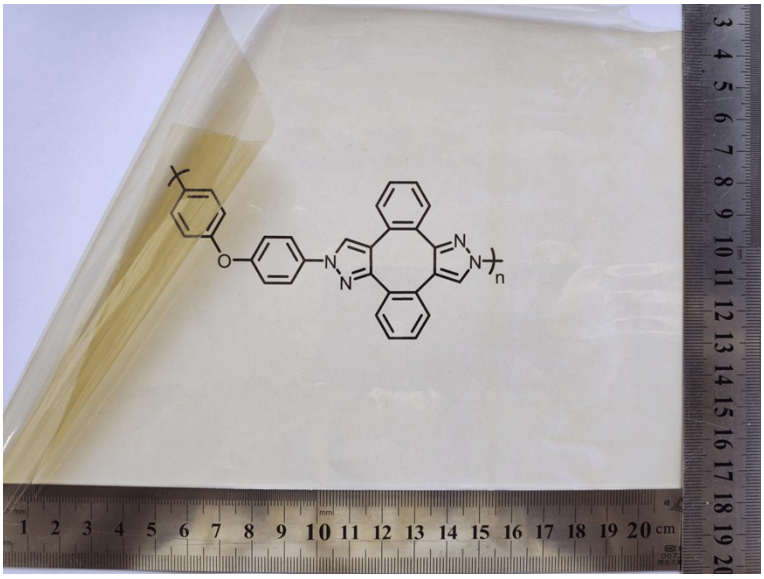


Figure S23. The photograph of thin film of precipitated **Poly 4**.

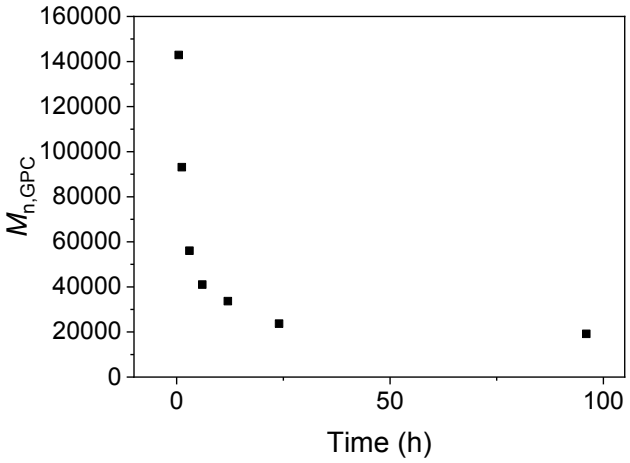


Figure S24. The relationship of $M_{n,GPC}$ of degraded **Poly 3-2** and degradation time.

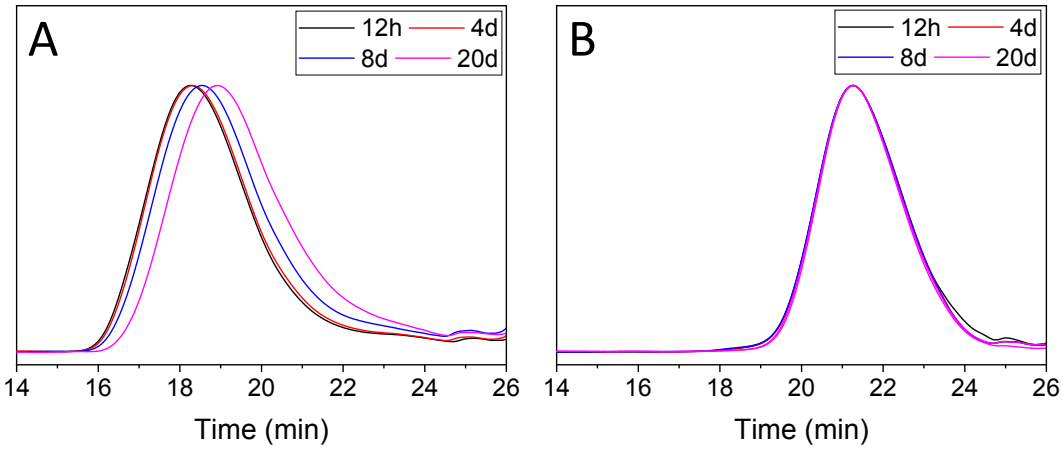


Figure S25. (A) GPC curves of the freshly precipitated **Poly 3-2** stored at room temperature for 12 h (black), 4 d (red), 8 d (blue), and 20 d (magenta). (B) GPC curves of the freshly precipitated **Poly 3-1** stored at room temperature for 12 h (black), 4 d (red), 8 d (blue), and 20 d (magenta). THF was used as the eluent and polystyrene standards were used for the calibration.

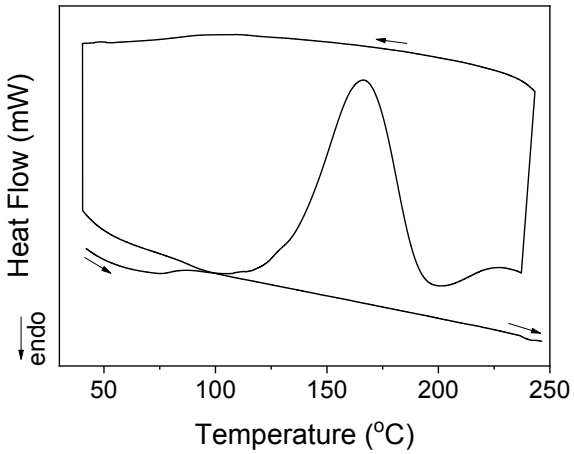


Figure S26. The DSC curve of the freshly precipitated **Poly 3-2**, which was recorded with a heating rate of 10 ˚C/min under N_2.

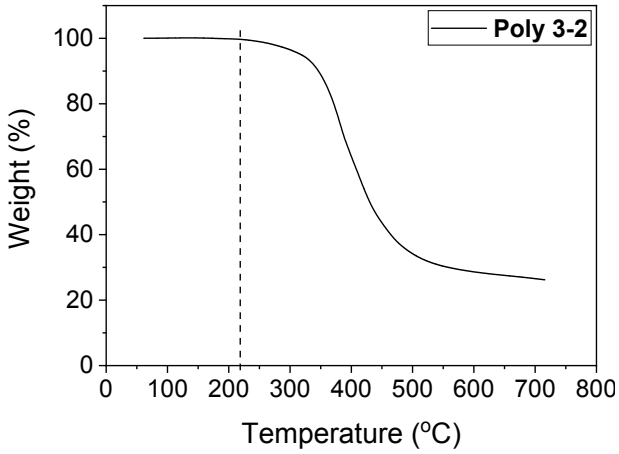


Figure S27. TGA curve of the freshly precipitated **Poly 3-2**, which was recorded with a heating rate of 10 ˚C/min under N_2.

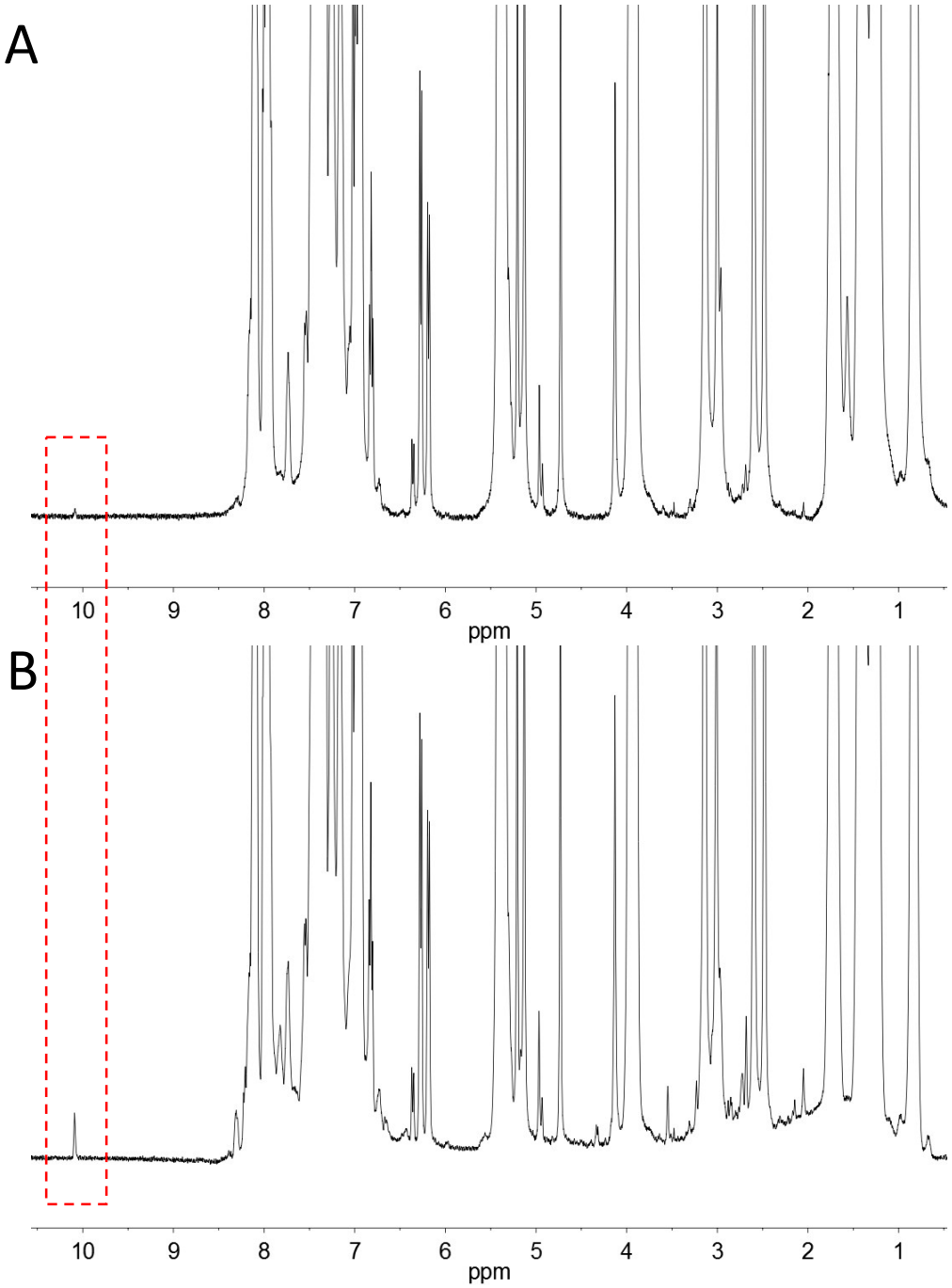


Figure S28. ^{1}H-NMR spectra of the freshly precipitated **Poly 3-2** in $CDCl_3$ (A) and the precipitated **Poly 3-2** storing in $CDCl_3$ at room temperature after 4 days (B).

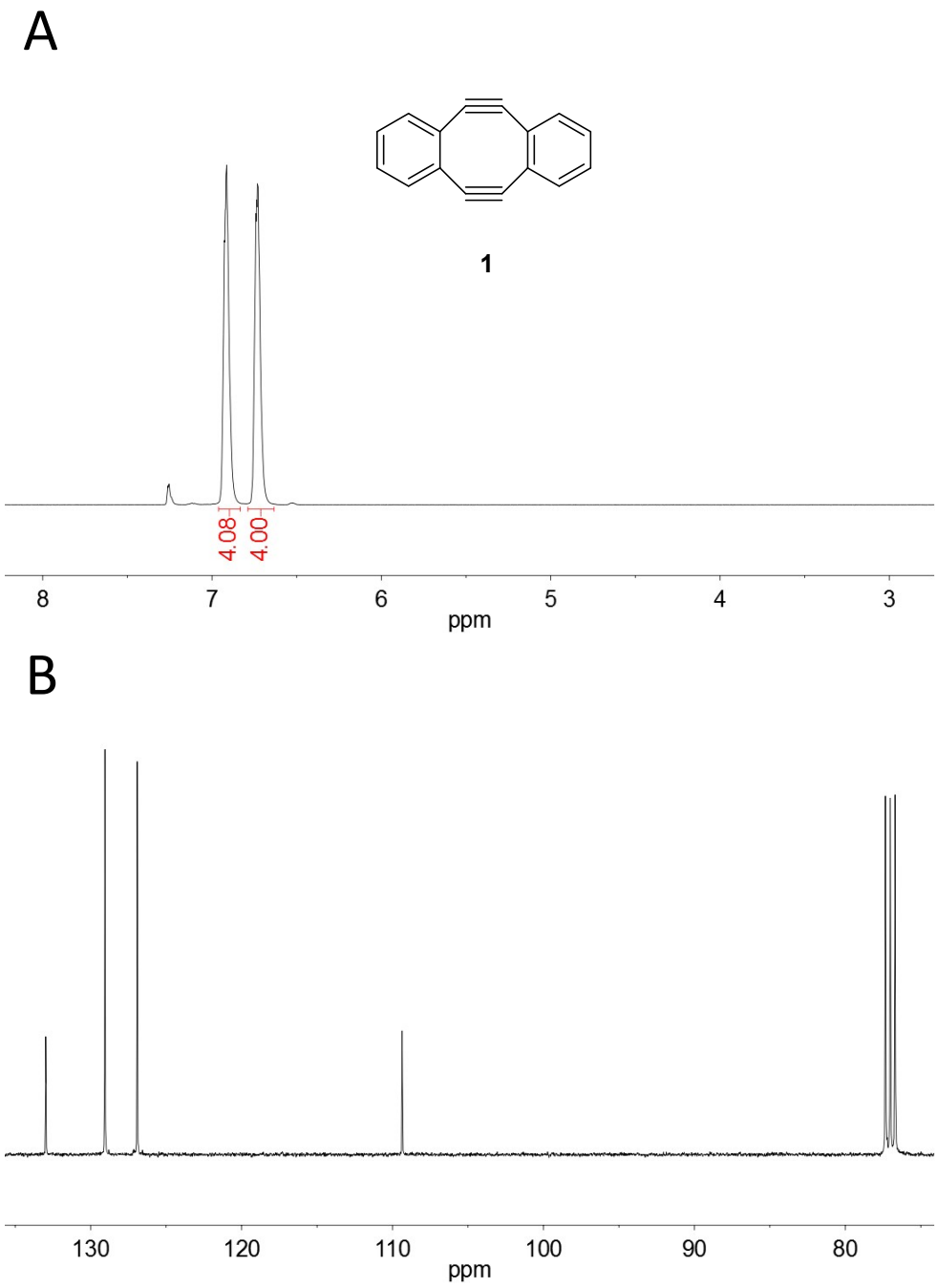


Figure S29. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **1** in $CDCl_3$.

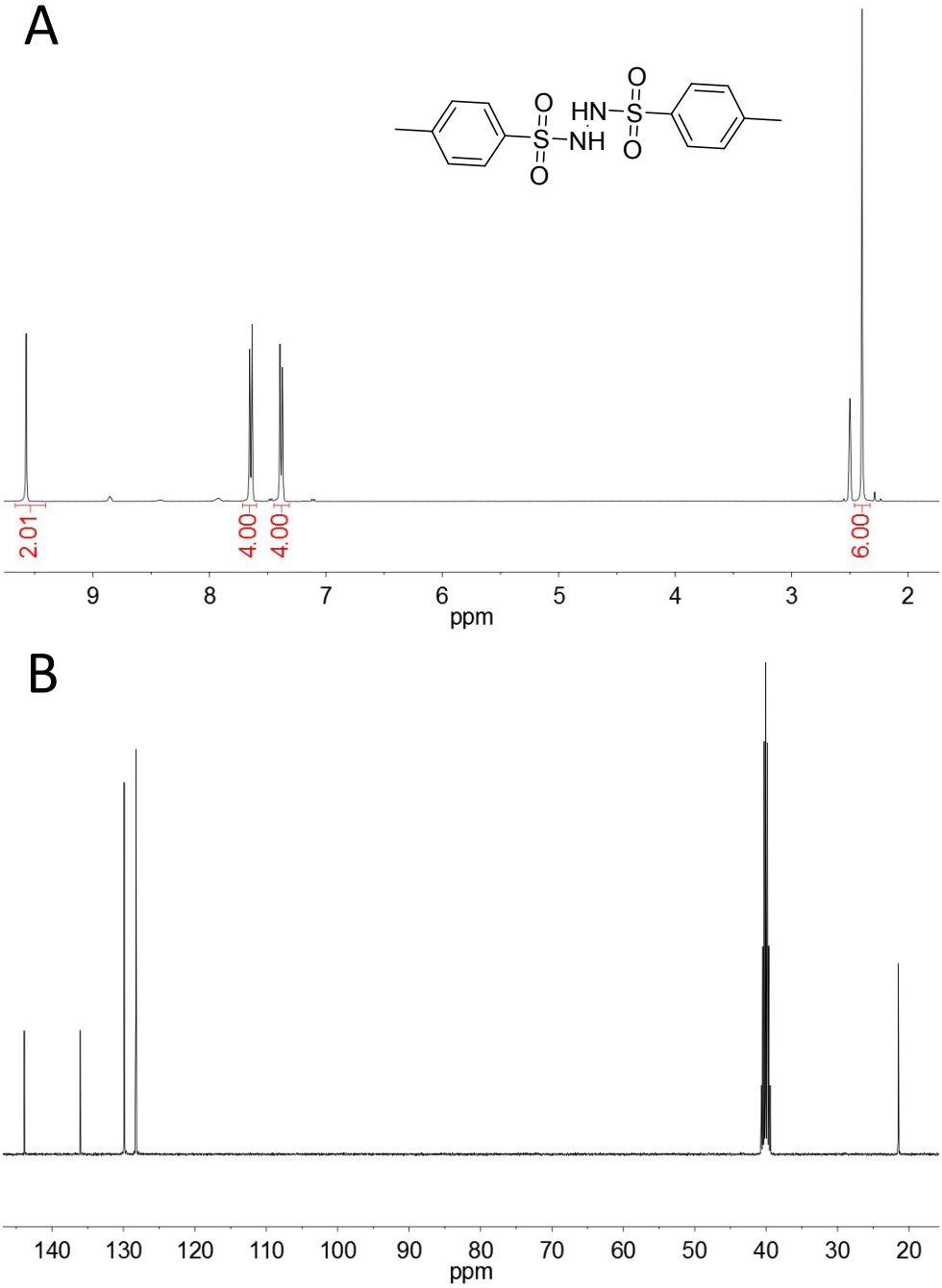


Figure S30. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **d** in DMSO-d_6.

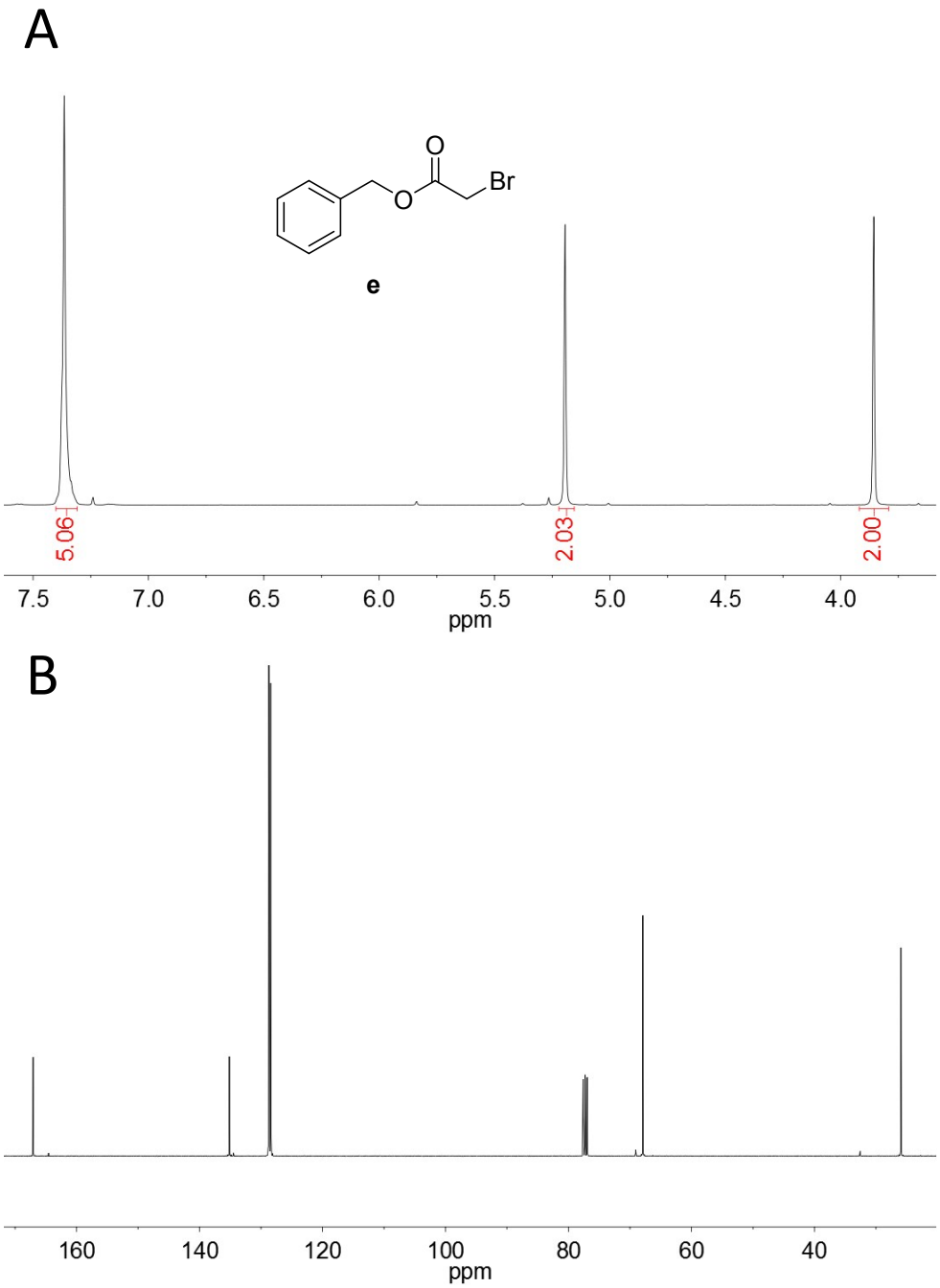


Figure S31. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **e** in $CDCl_3$.

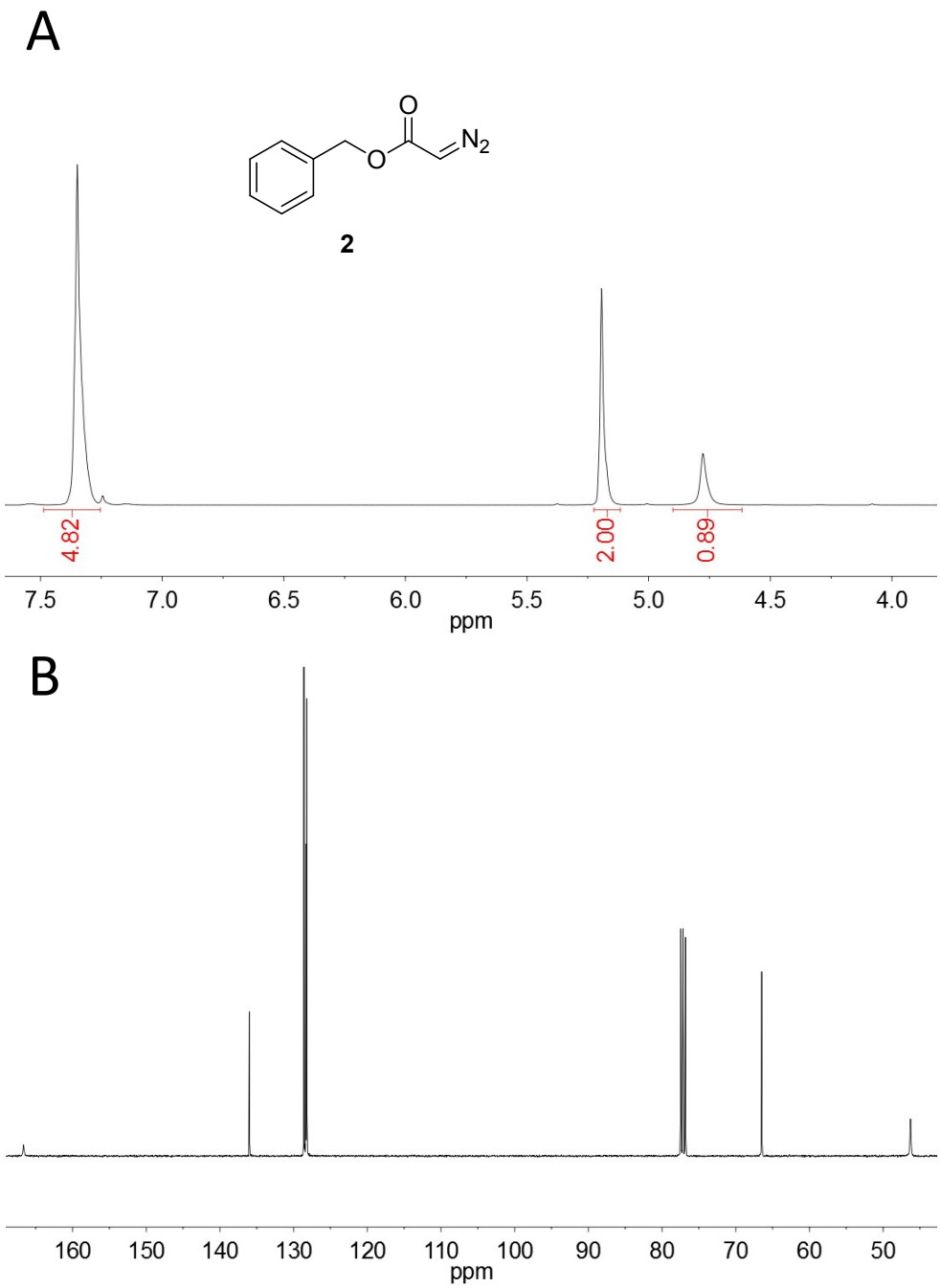


Figure S32. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **2** in $CDCl_3$.

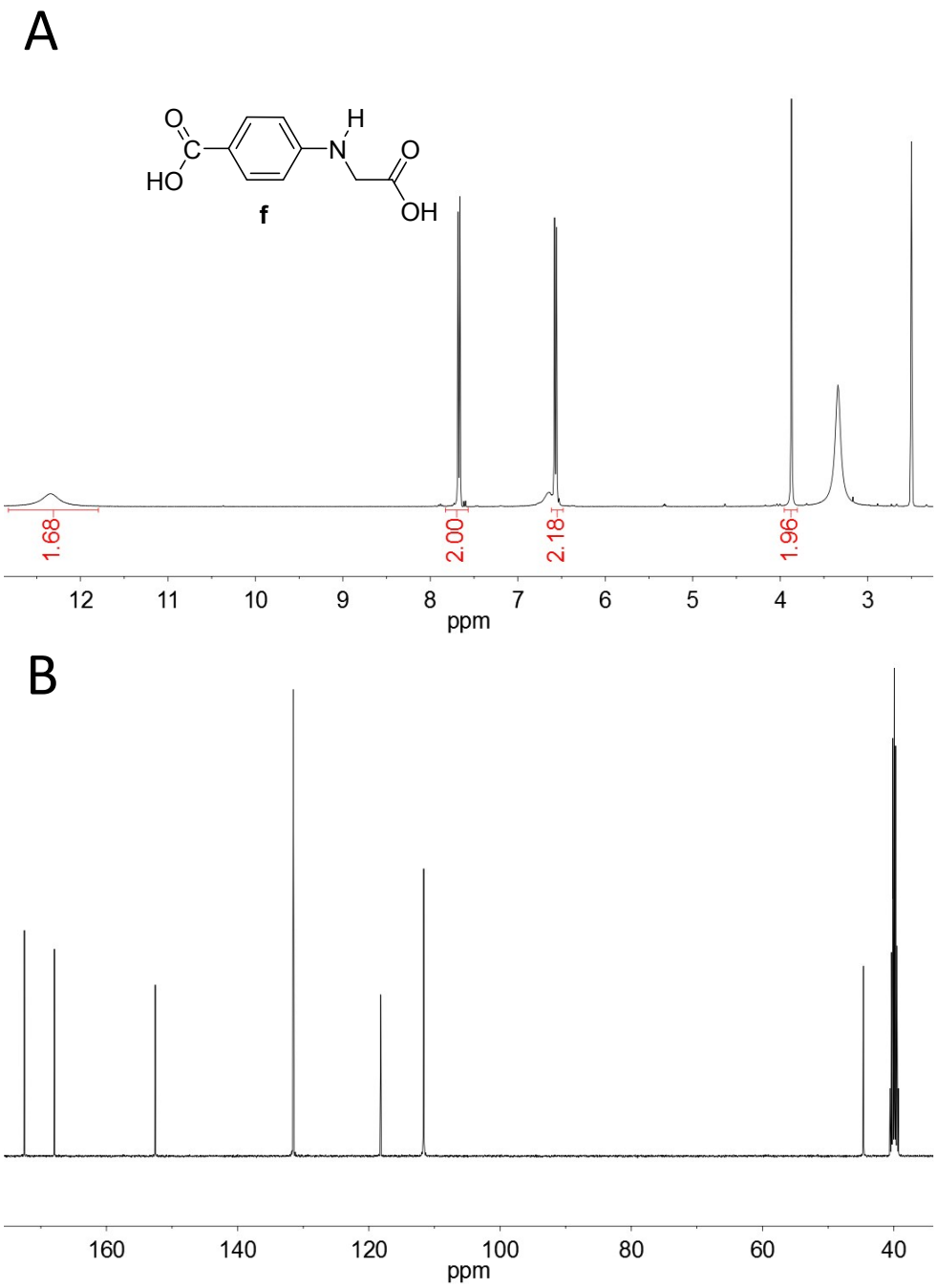


Figure S33. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **f** in DMSO-d_6.

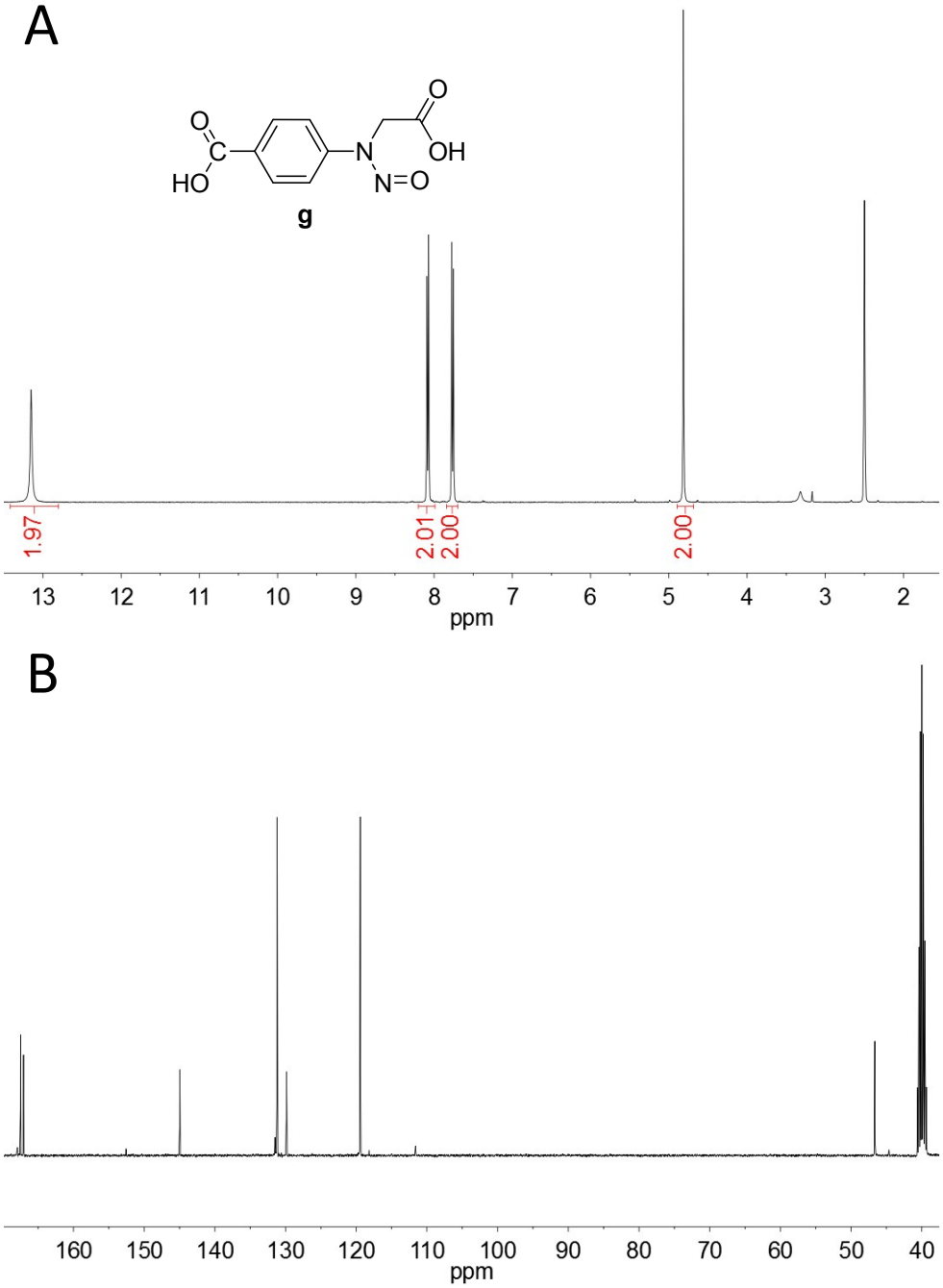


Figure S34. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **g** in DMSO-d_6.

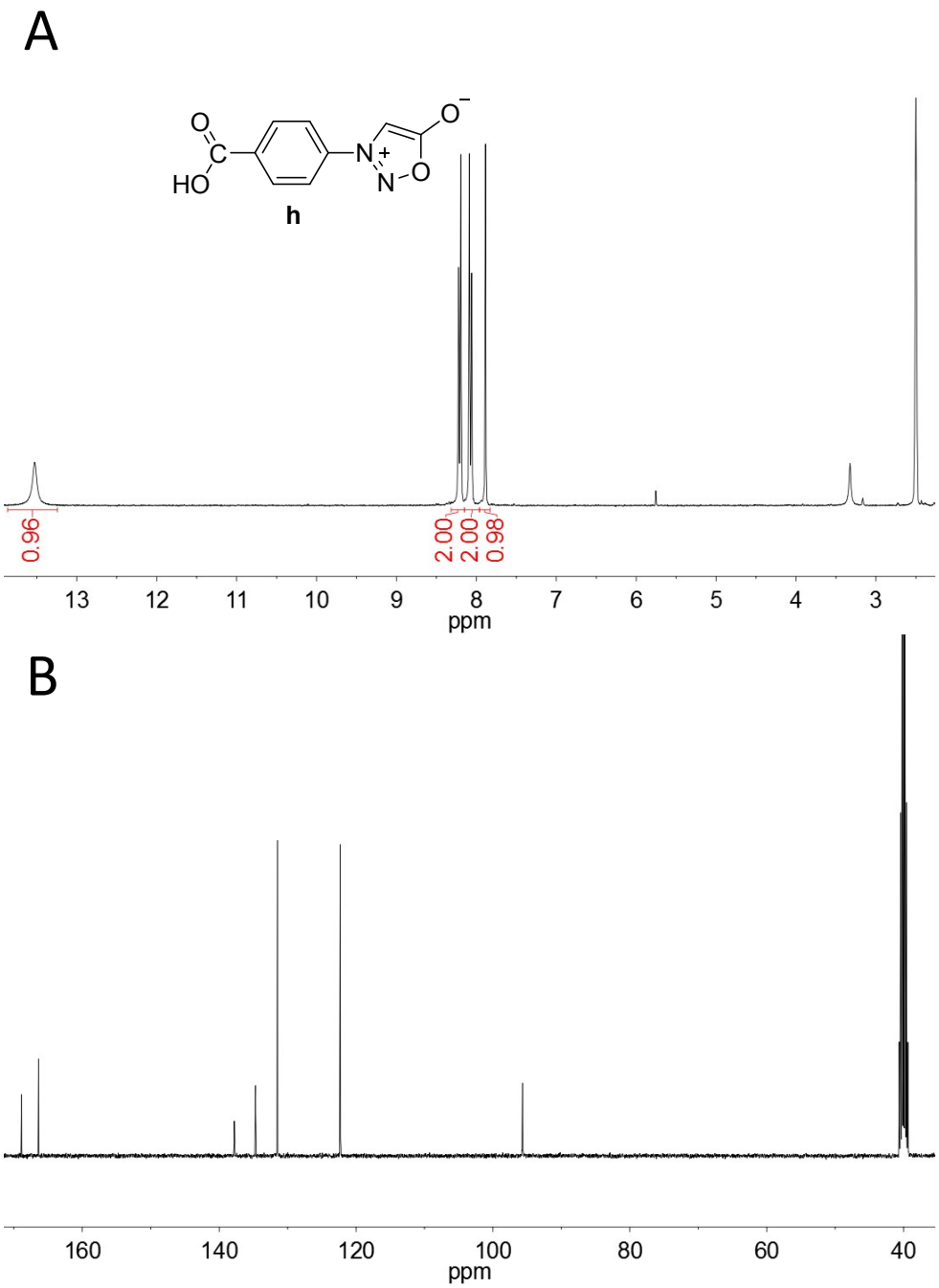


Figure S35. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **h** in DMSO-d_6.

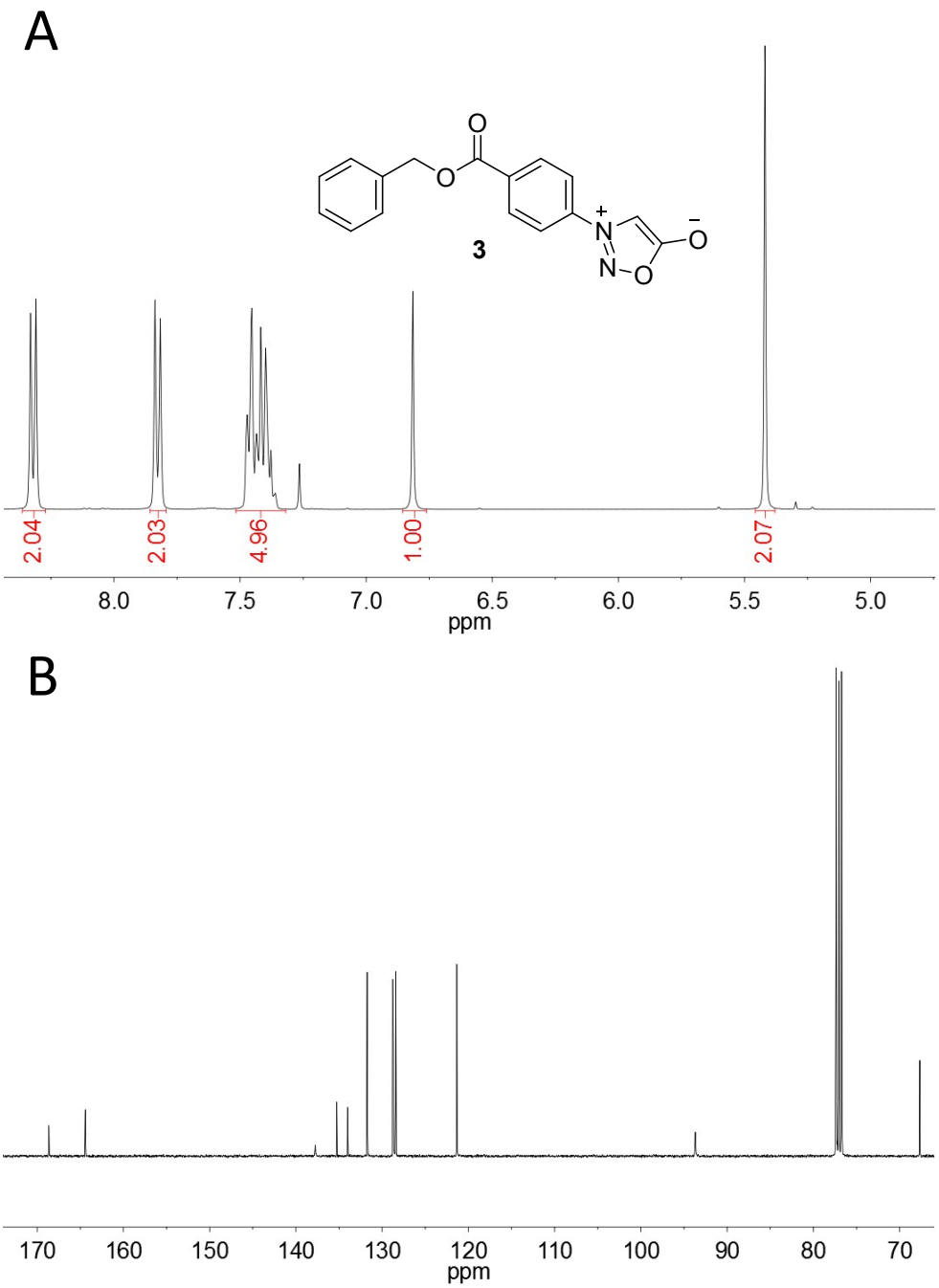


Figure S36. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **3** in $CDCl_3$.

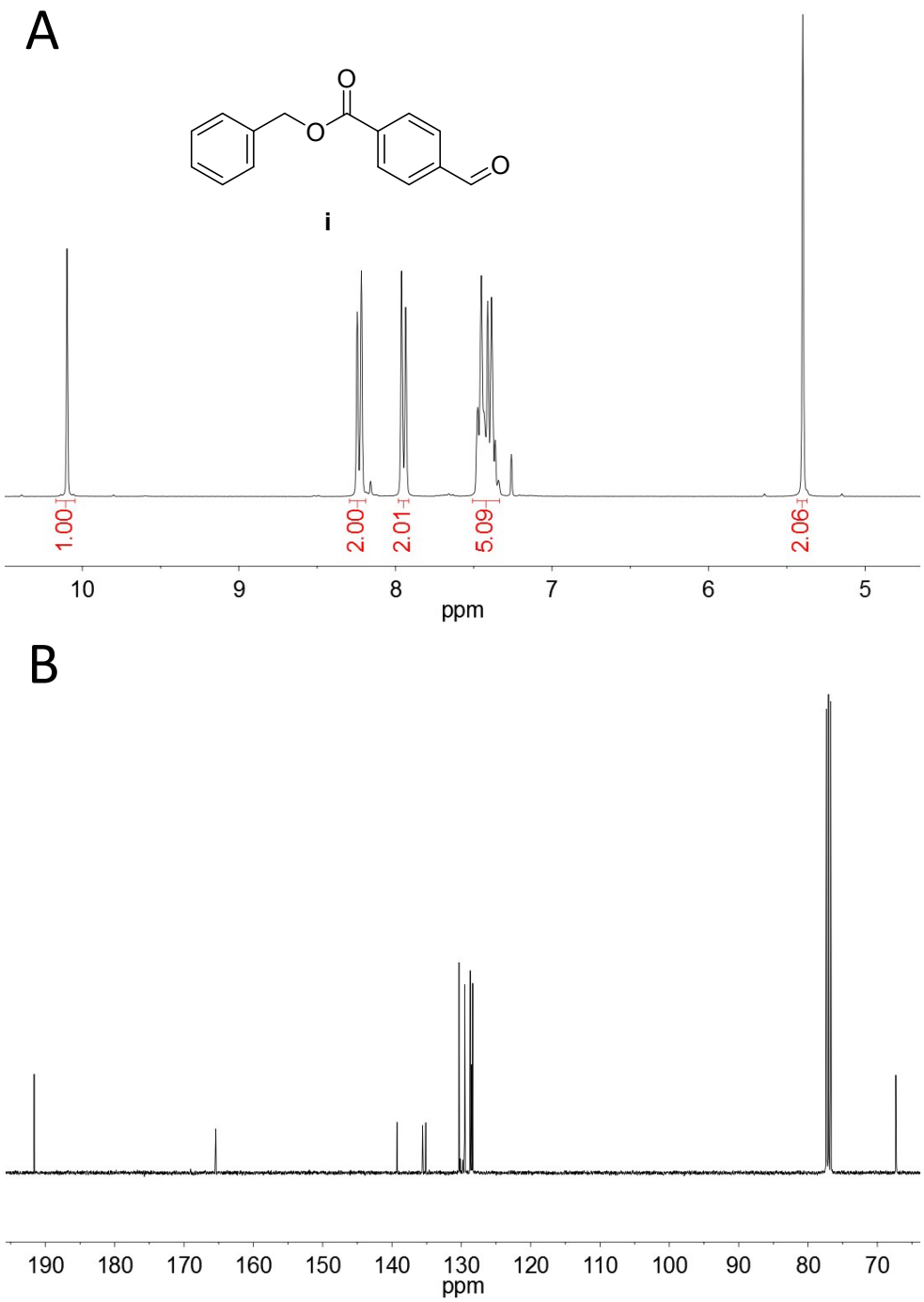


Figure S37. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **i** in $CDCl_3$.

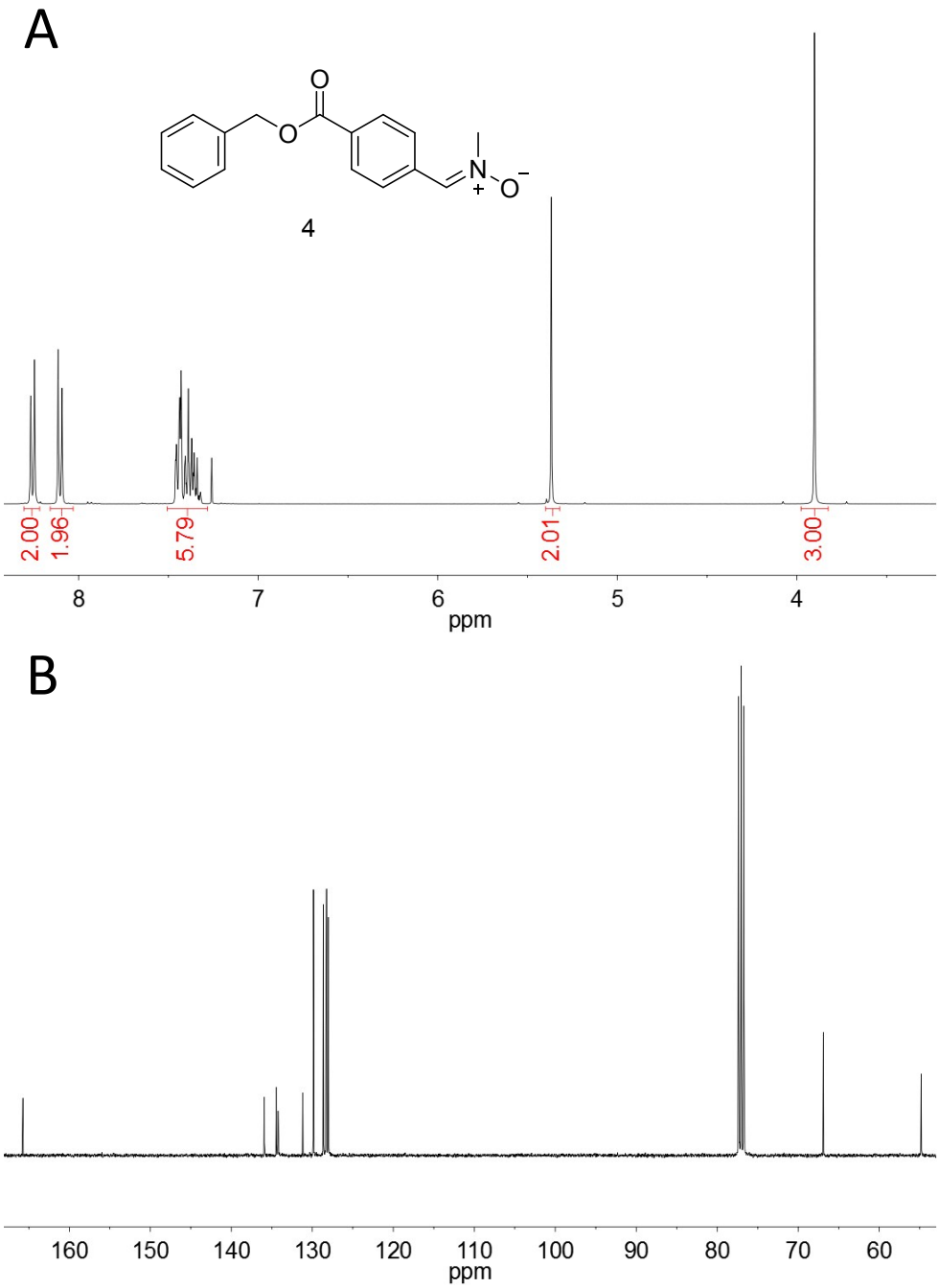


Figure S38. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **4** in $CDCl_3$.

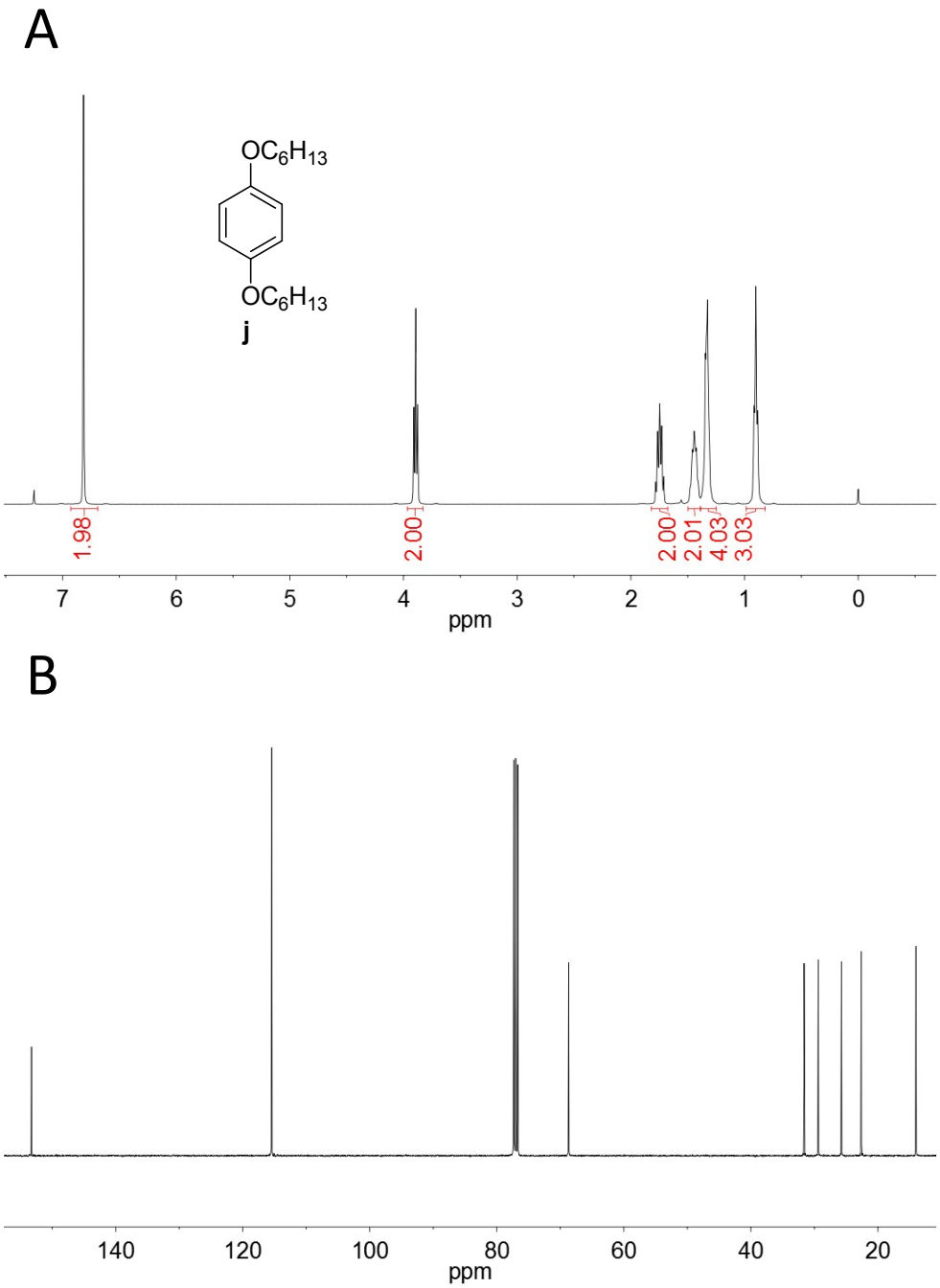


Figure S39. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **j** in $CDCl_3$.

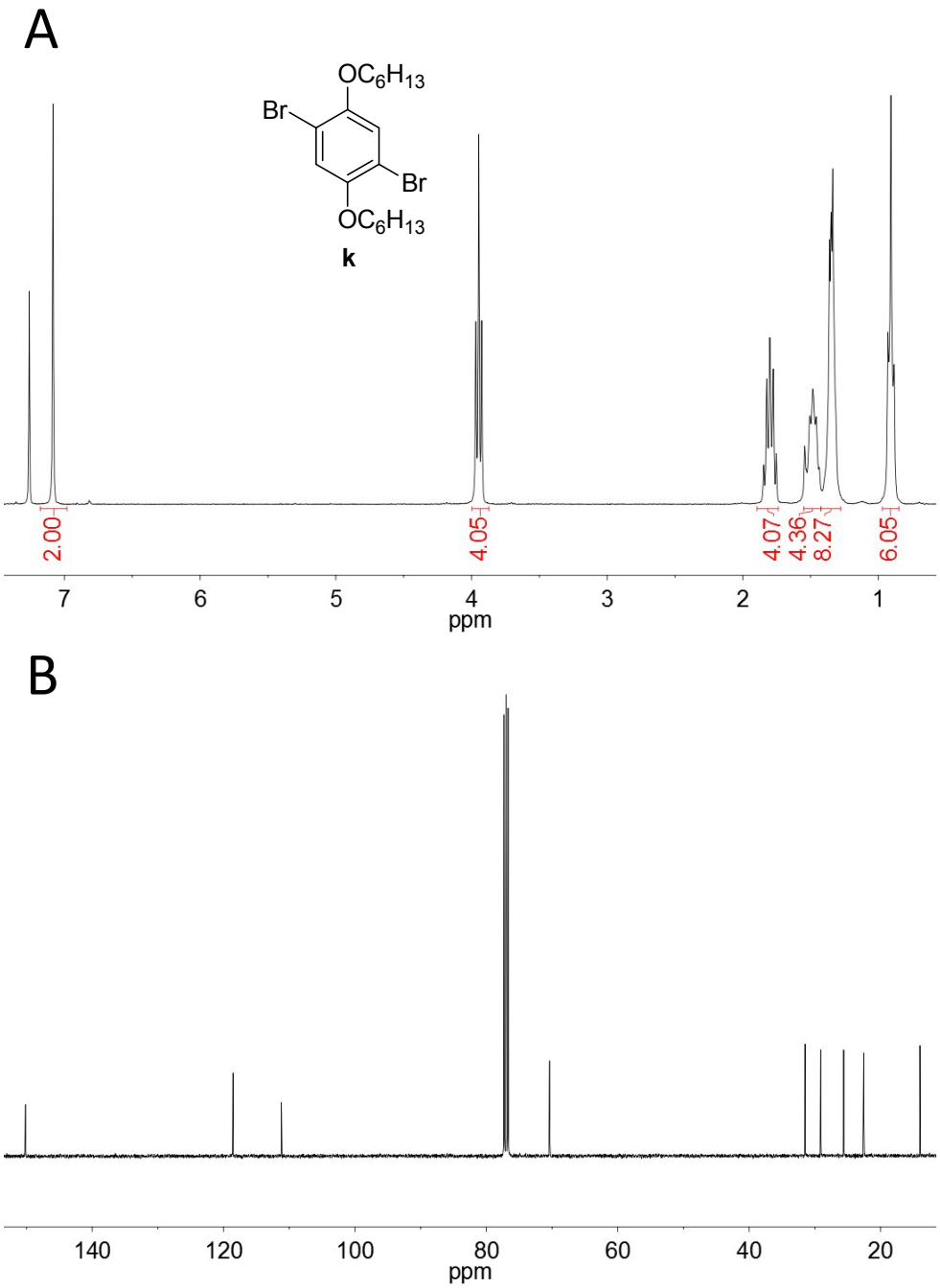


Figure S40. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **k** in $CDCl_3$.

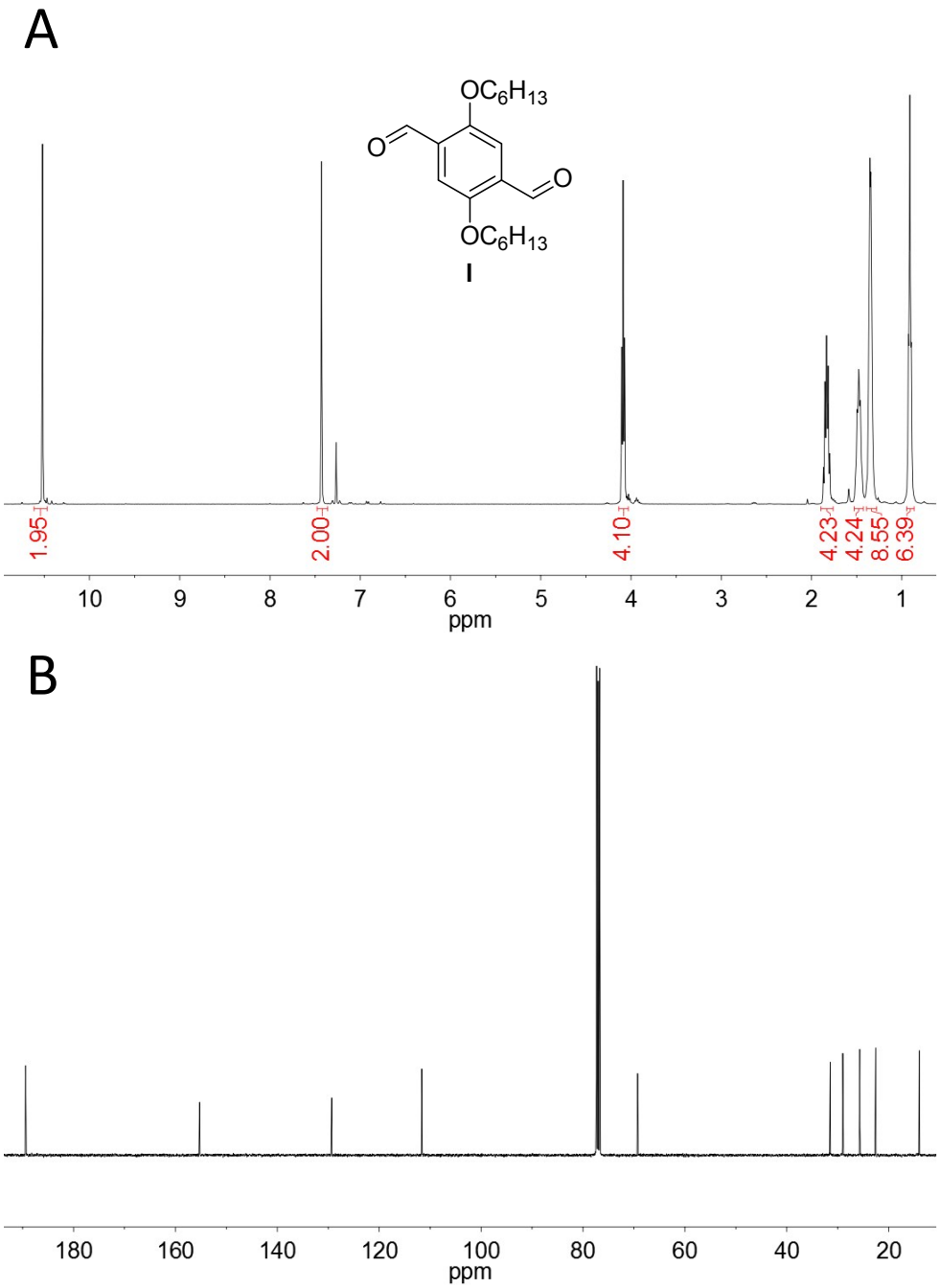


Figure S41. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **I** in $CDCl_3$.

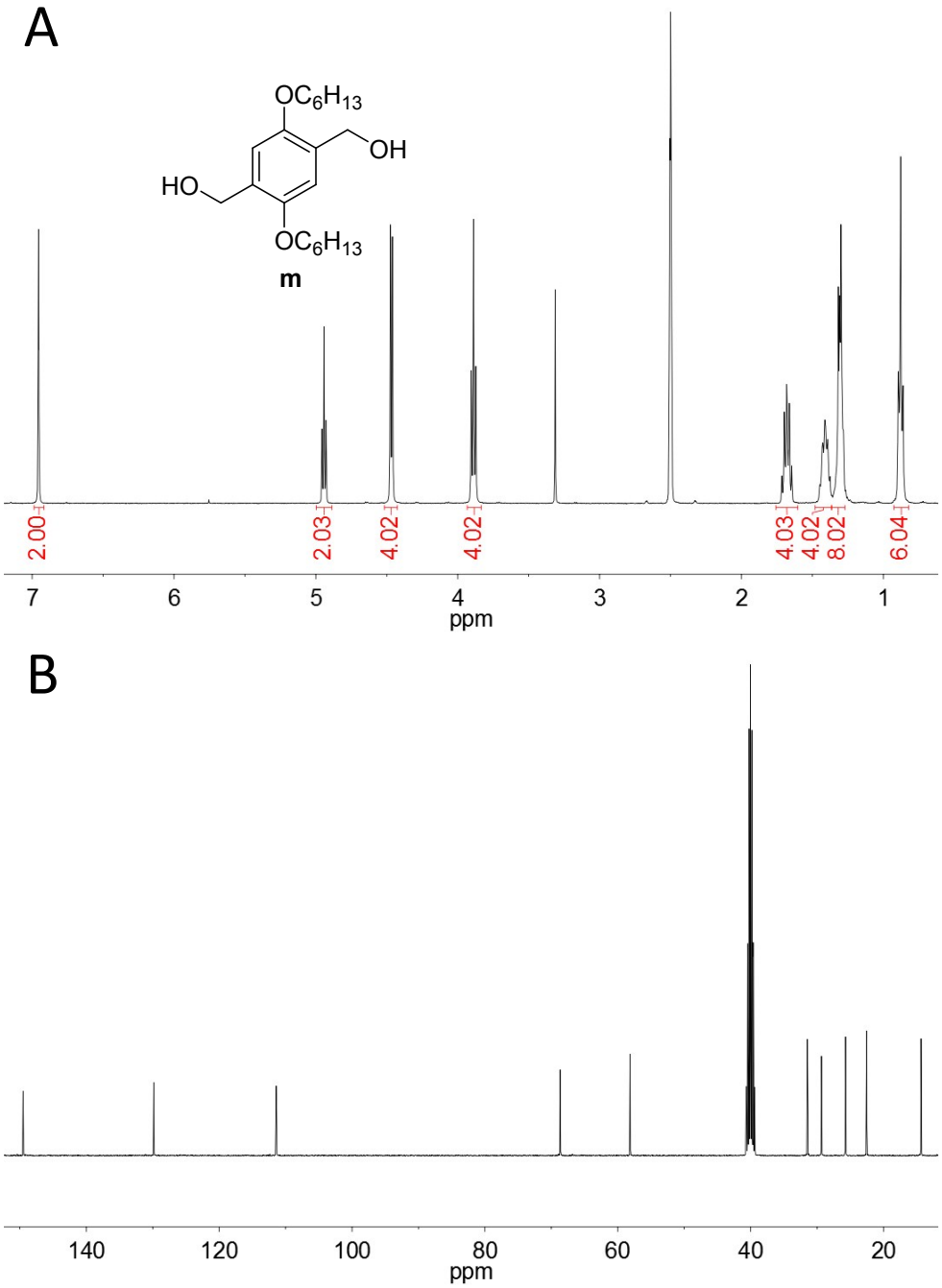


Figure S42. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **m** in DMSO-d_6.

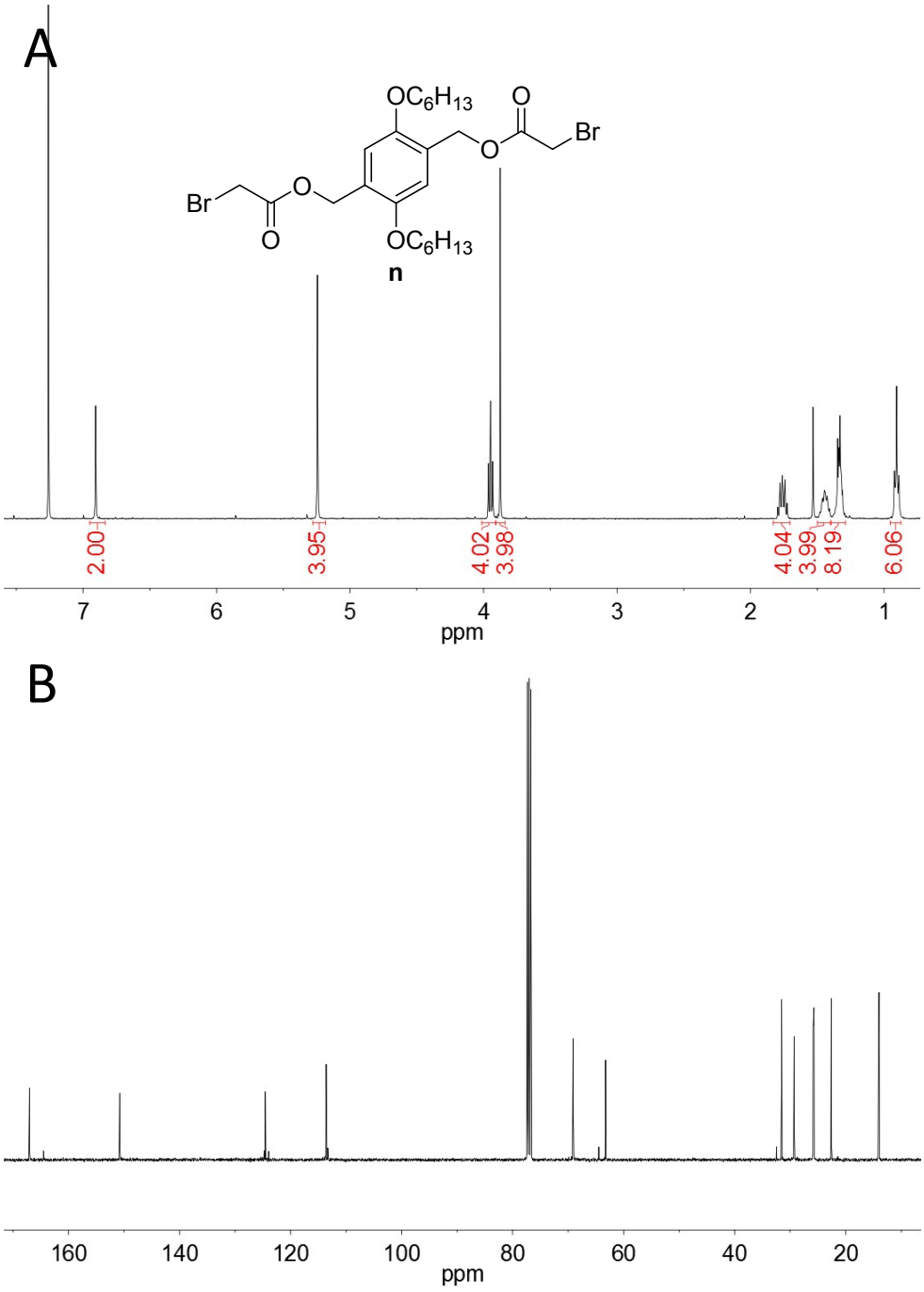


Figure S43. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **n** in $CDCl_3$.

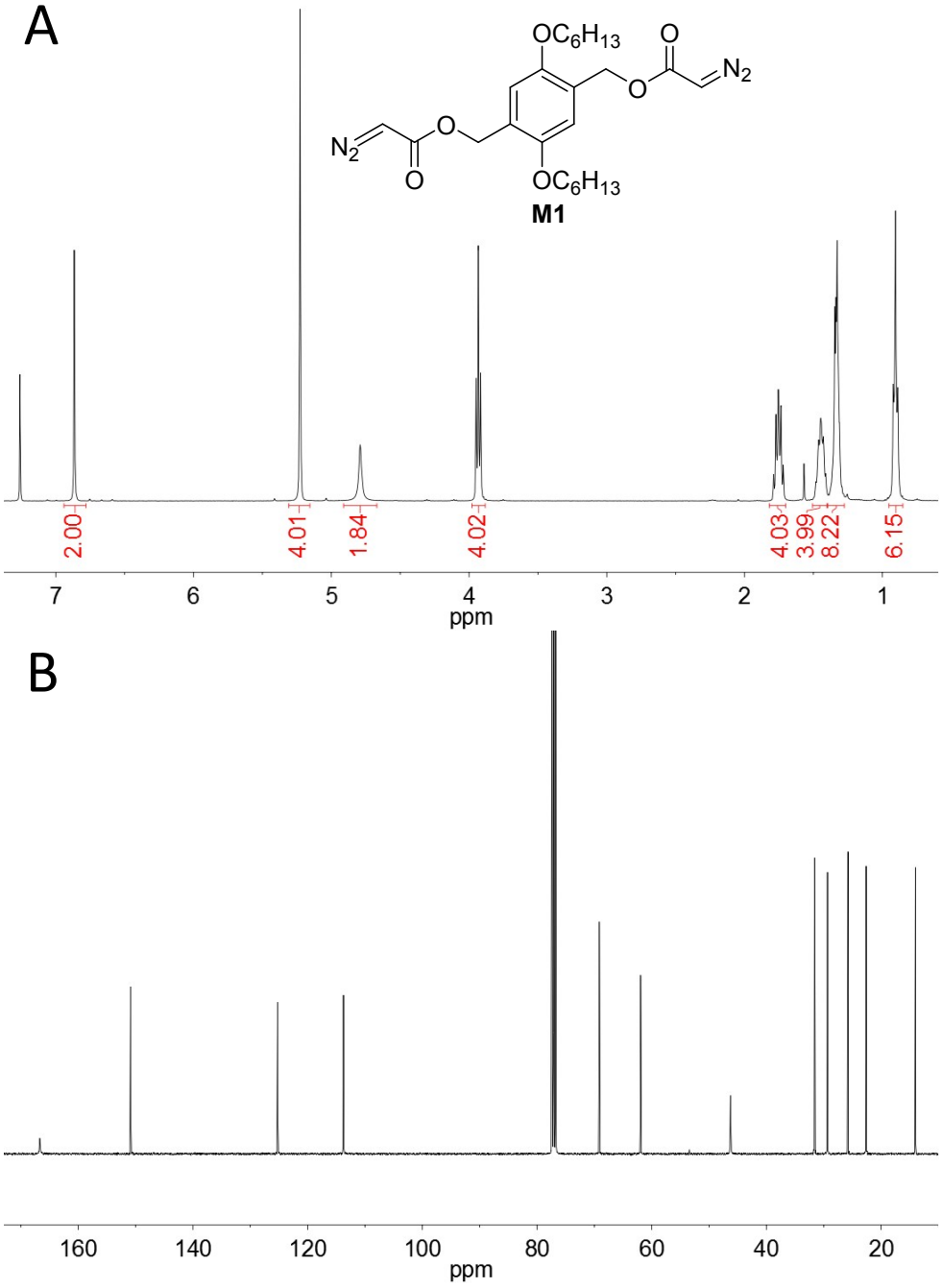


Figure S44. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **M1** in $CDCl_3$.

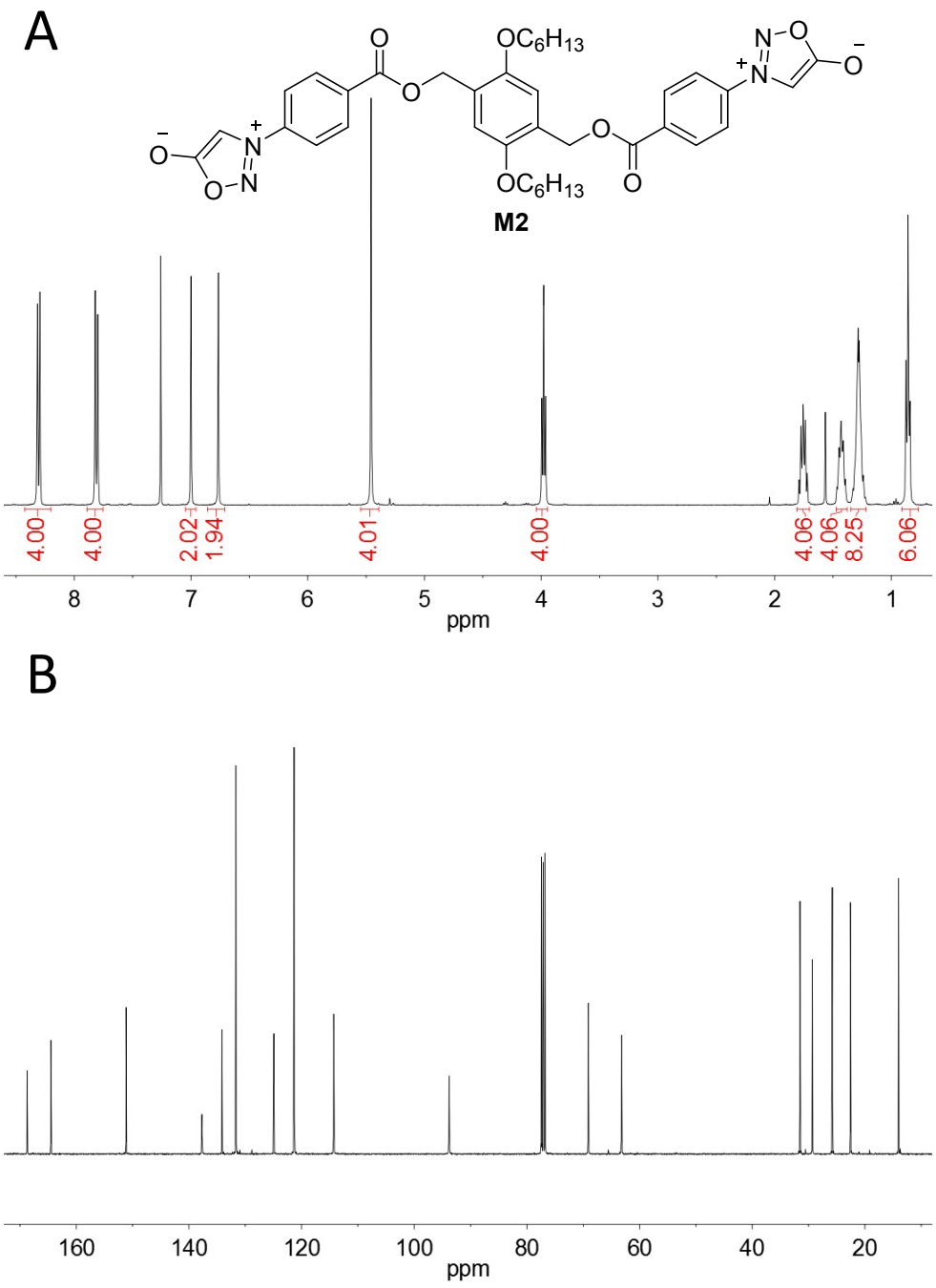


Figure S45. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **M2** in $CDCl_3$.

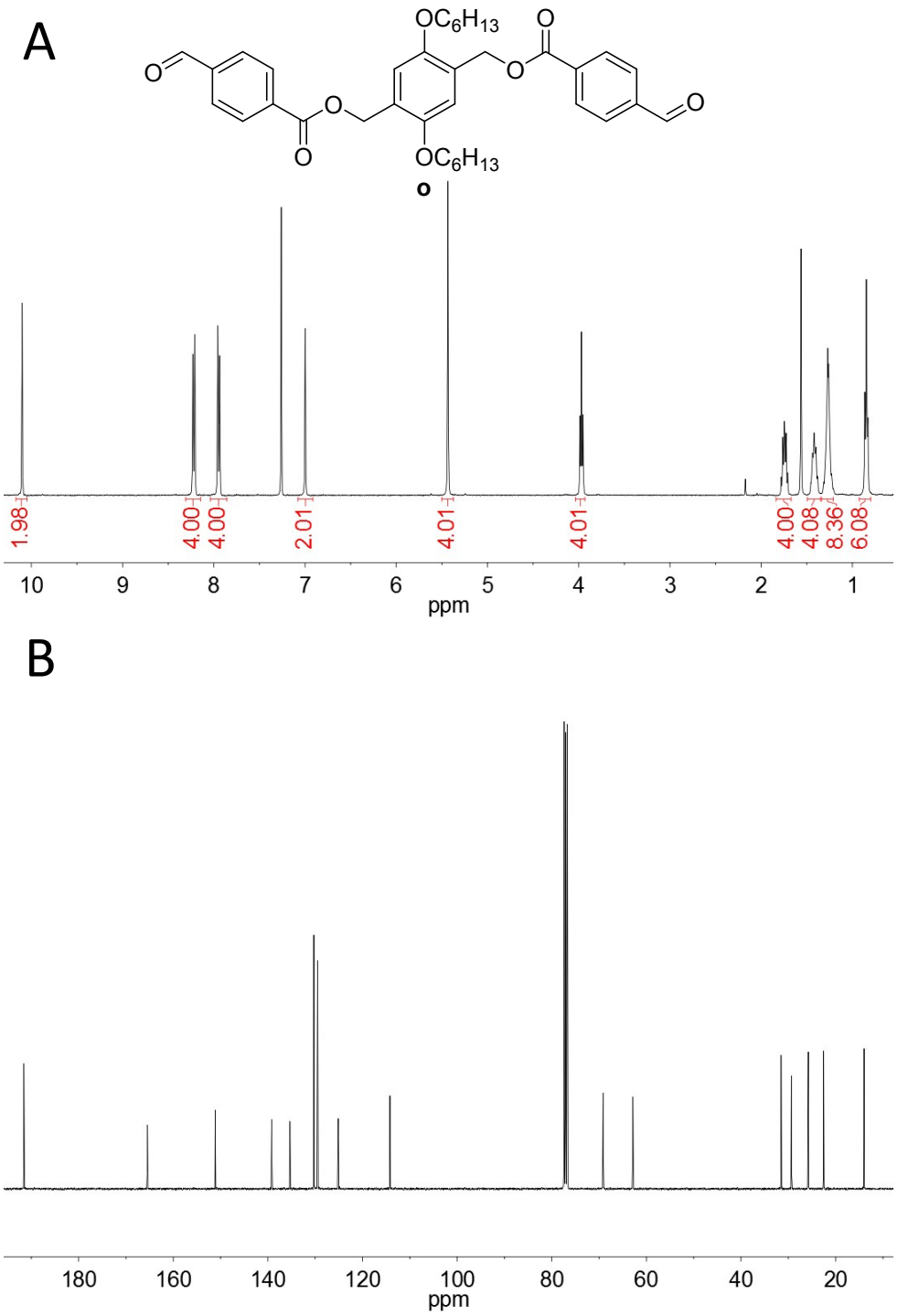


Figure S46. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **o** in $CDCl_3$.

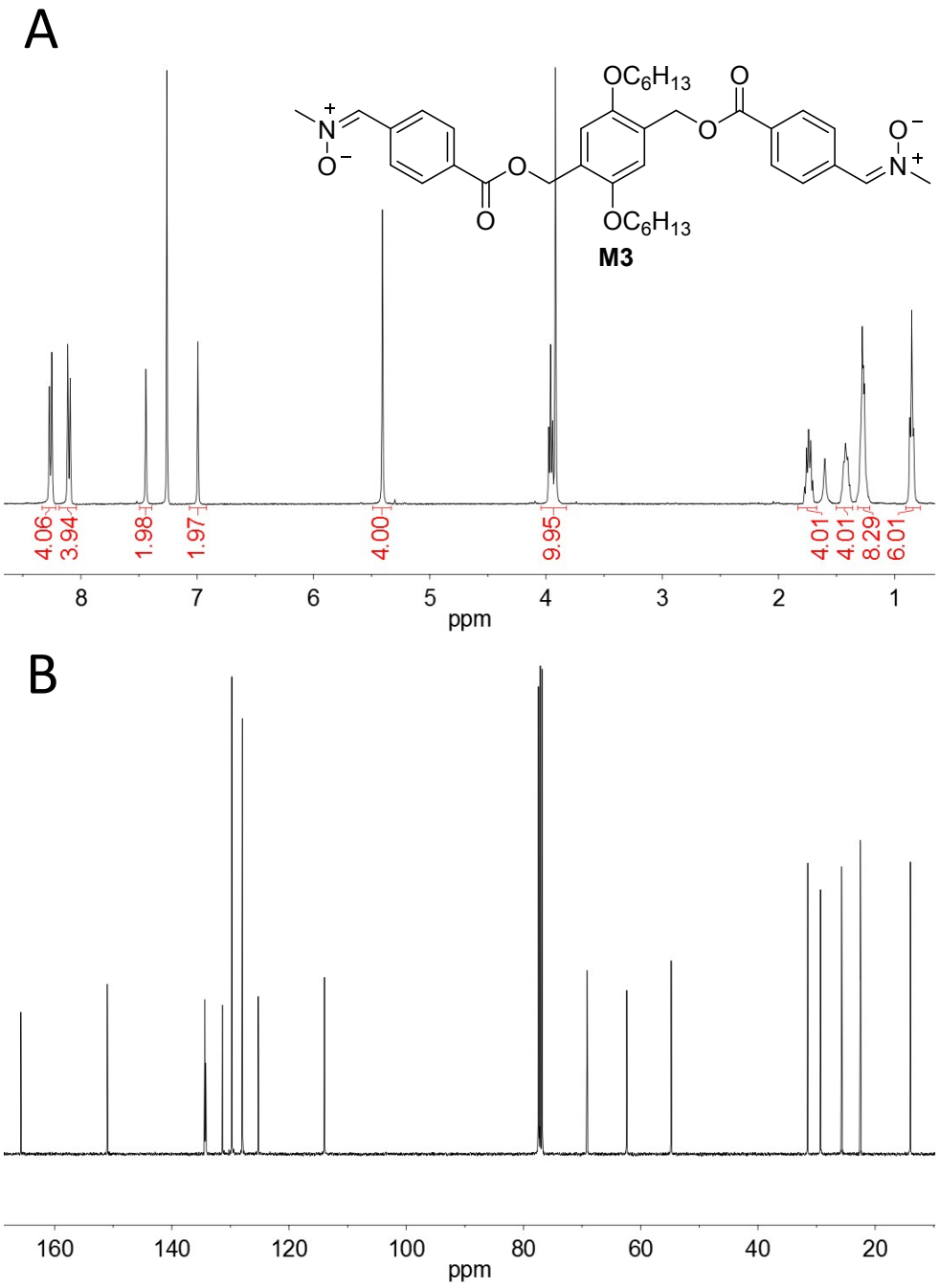


Figure S47. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **M3** in $CDCl_3$.

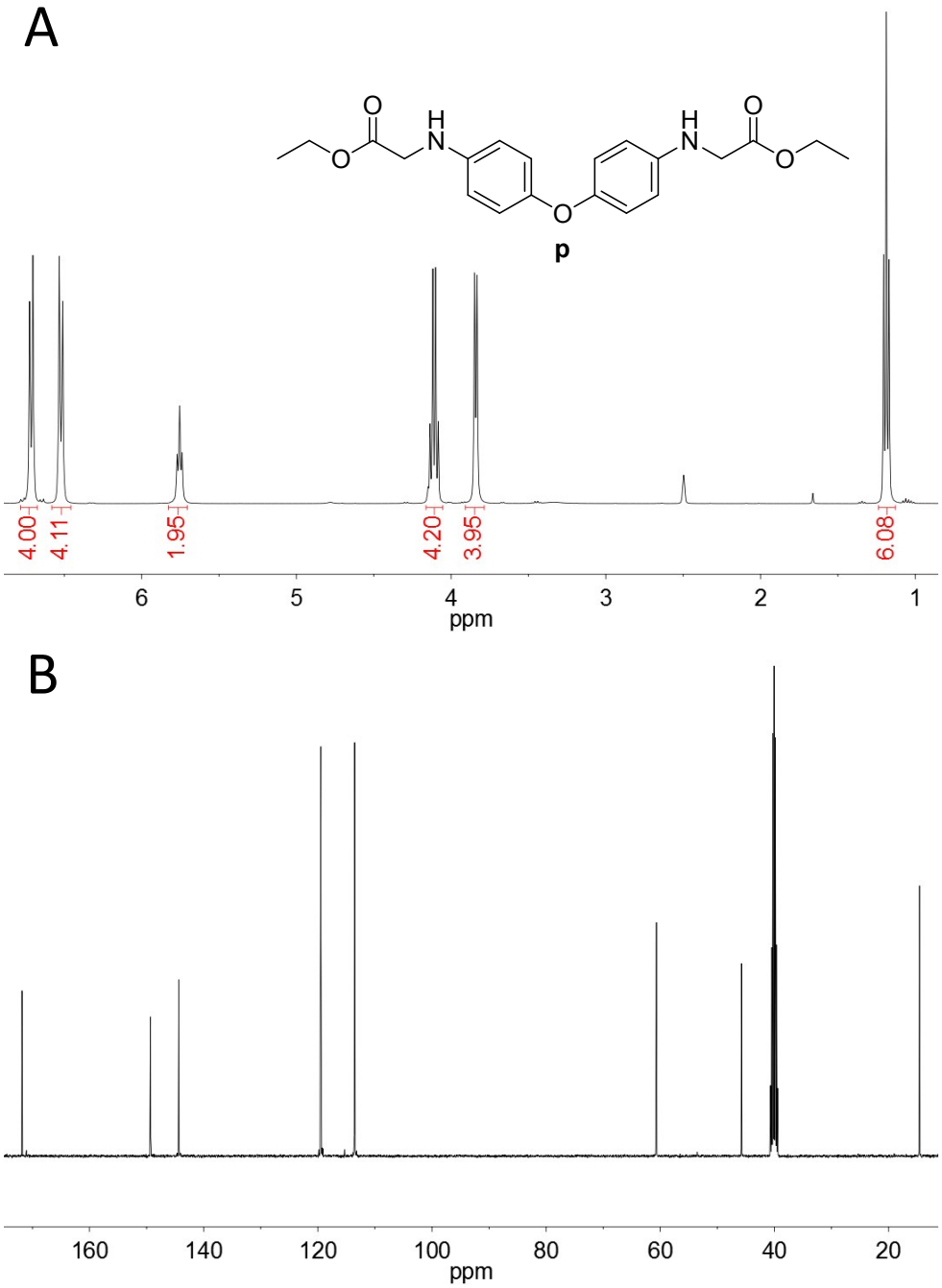


Figure S48. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **p** in DMSO-d_6.

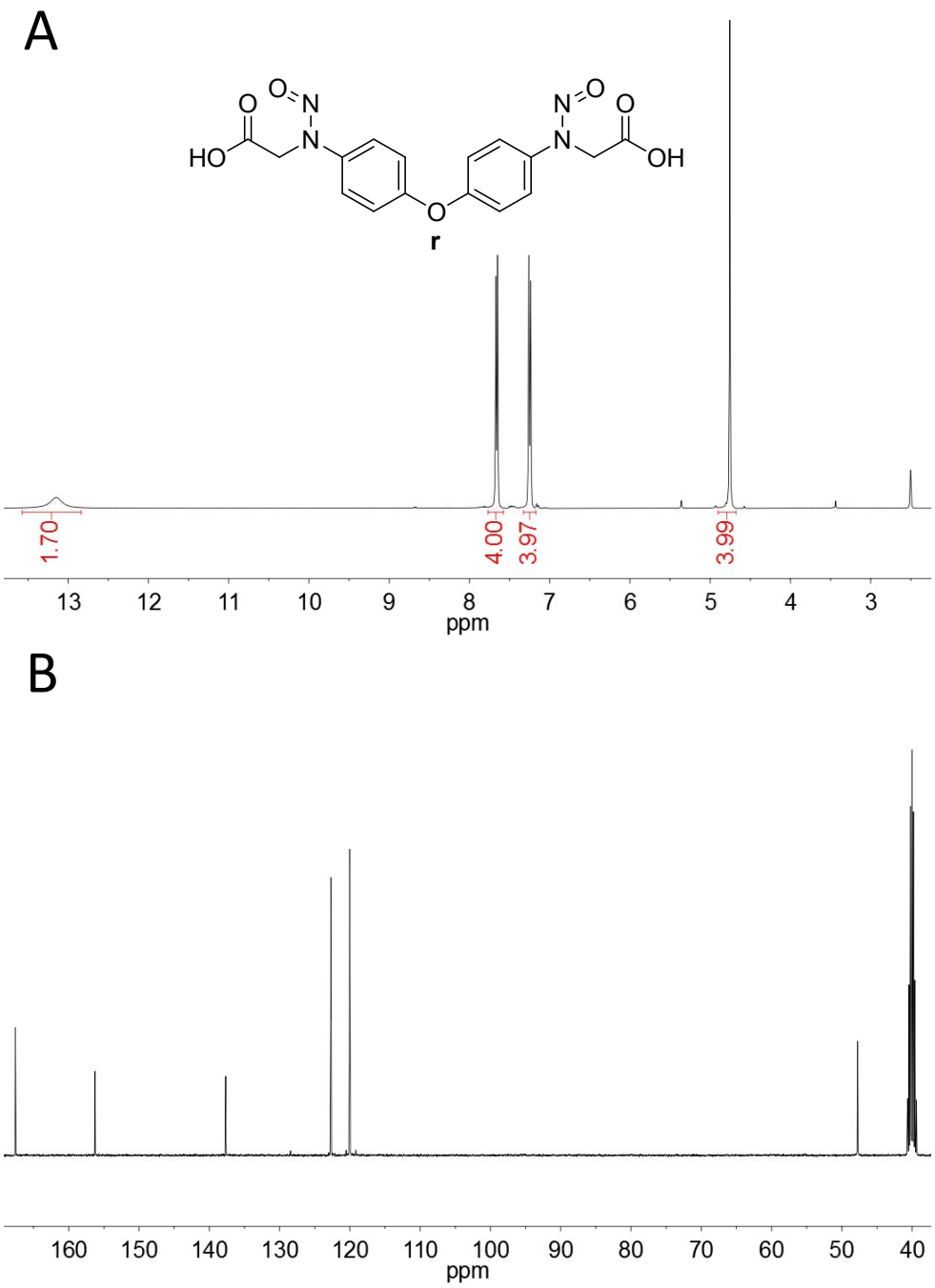


Figure S49. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **r** in DMSO-d_6.

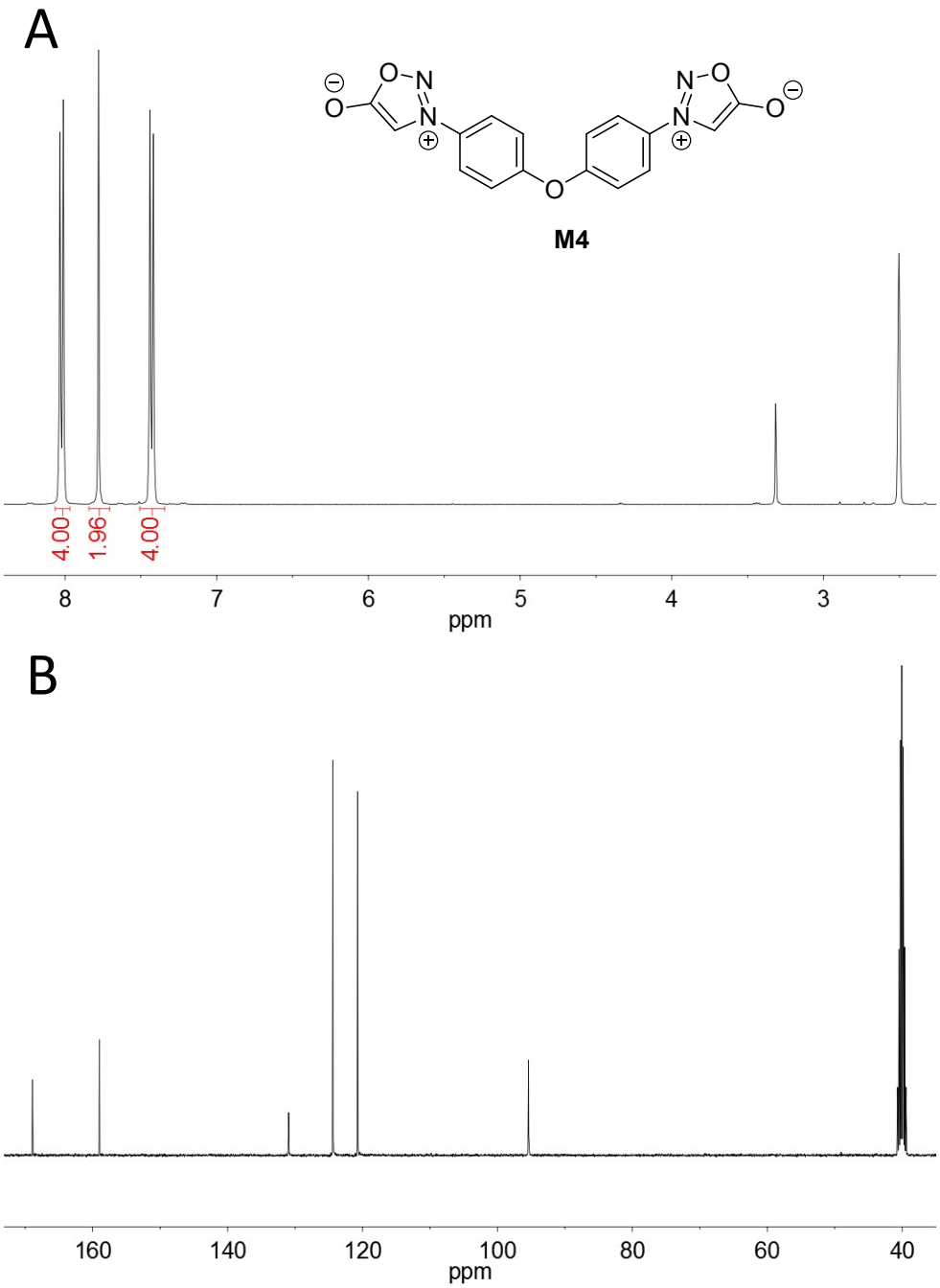


Figure S50. ^{1}H-NMR (A) and ^{13}C-NMR (B) spectra of compound **M4** in DMSO-d_6.

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