Supporting Information

Imide-Yne Click Polymerization: A New and Versatile Tool for the Toolbox of X-Yne Click Polymerization

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1. Materials

Propiolic acid (95%), ethylene glycol (99.8%), 1,4-cyclohexanedimethanol (mixture of cis and trans, 99%), bis(2-hydroxyethyl)disulfide (technical grade), 1,6-hexanediol (99%), p-toluenesulfonic acid monohydrate (p-TsOH, 98%), 1,1,1-tris(hydroxymethyl)ethane (98%), carbon tetrachloride (CCl_4, 99%), sodium sulfate (Na_2SO_4), 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99%), benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA, 98%), 4,4′-oxydiphthalic anhydride (ODPA, 97%), urea (98%), 1,6-hexanedithiol (HDT, 97%), 4,4'-thiobisbenzenethiol (98%), piperazine (99%), maleimide (99%), methyl propiolate (99%), dimethyl acetylenedicarboxylate (DMAD, 99%), cis-1,2,3,6-tetrahydrophthalimide (96%), 1-propanethiol (99%), triethylamine (TEA, 99.5%), 1,4-diazabicyclo[2.2.2] octane (DABCO, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 4-(dimethylamino)pyridine (DMAP, 99%), benzene (99%), chloroform ($CHCl_3$, 99.8%, amylene stabilized), dichloromethane (DCM, 99%), ethanol (99%), tetrahydrofuran (THF, 99%) were all purchased from Aldrich and used as received. Dimethyl sulfoxide (DMSO, 99.9%, Aldrich), *N*,*N*-dimethylacetamide (DMAc, 99.8%, Aldrich), *N*,*N*-dimethylformamide (DMF, 99.8%, Aldrich), *N*-methyl-2-pyrrolidone (NMP, 99.5%, Aldrich) were anhydrous and high-performance liquid chromatography (HPLC) quality and used without further purification. Methanol and hexane were of reagent grade and used as received. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from TCI.

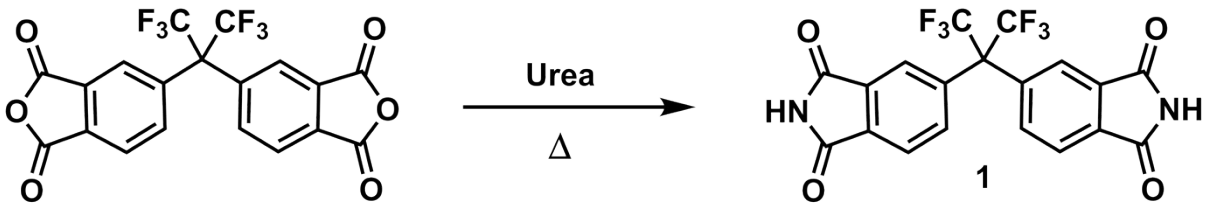
2. Instrumentation

^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{19}F NMR (470 MHz) and ^{31}P NMR (202 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$ and d_6-DMSO. Gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (model 1100) with a pump, refractive index and UV detectors, and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2) (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges of the columns were 2000−4 000 000, 50−100 000, 500−30 000, and 500−20 000 g/mol, respectively. THF was used as an eluent at a flow rate of 0.3 mL/min at 30 °C, and 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used as an internal standard. The weight-average molecular weights (M_w) and dispersities ($Đ$) of the polymers were calculated based on linear polystyrene (PS) standards (Polymer Laboratories). Thermogravimetric analyses (TGA) of the synthesized polymers were performed by using a PerkinElmer thermogravimetric analyzer (Pyris 1 TGA model). Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere on the TA Q1000 DSC apparatus. Synthesized polymers and were heated to 250 °C with a heating rate of 10 °C/min. After holding for 2 min at this temperature, samples were cooled to 25 °C with a cooling rate of 10 °C/min, followed by keeping at this temperature for 2 min. Finally, they were reheated to 250 °C with a heating rate of 10 °C/min. Data from the second heating cycle were reported. Mass spectra were obtained using a Thermo Fisher Scientific LC-HRMS spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Cary 630 FT-IR (Agilent Technologies) instrument in the 4000-400 cm^{-1} range.

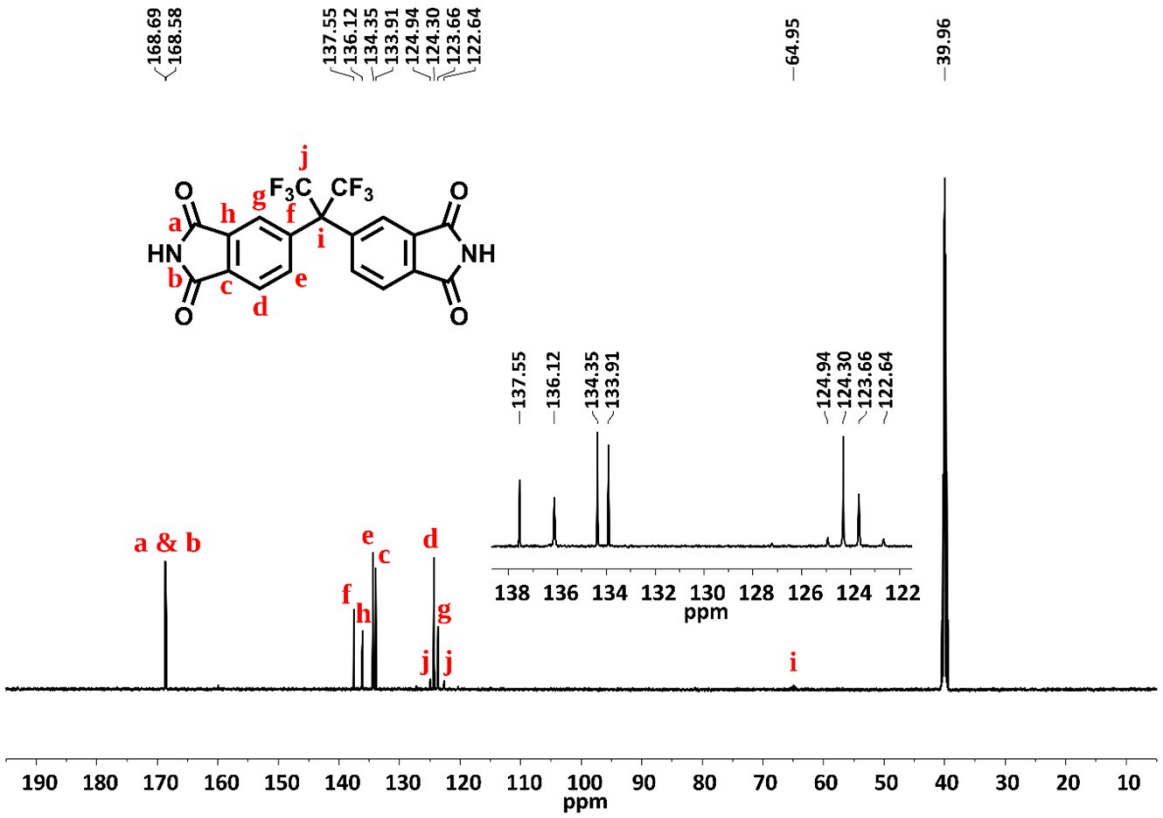
3. Experimental and Characterization Data (NMR, GPC, DSC, TGA, FT-IR, HRMS)

3.1. Synthesis of bisimide monomers from commercially available dianhydrides (1-3)

3.1.1. Synthesis of 5,5'-(perfluoropropane-2,2-diyl)bis(isoindoline-1,3-dione) (1)



To a 250 mL round bottom flask were added 6FDA (8.88 g, 0.02 mol) and urea (7.20 g, 0.12 mol). The flask was heated to 150 °C in a heating mantle for 5 to 10 minutes. The flask was kept in the heating mantle until gas release was no longer observed. Then, the flask was allowed to cool to room temperature. Solid residue was washed with hot ethanol and filtered with a sintered glass filter. The washing procedure was repeated two times. The resultant product was dried overnight in a vacuum oven at 40 °C and obtained as a white solid (yield: 6.81 g, 77%). ^{1}H NMR (d_6-DMSO, δ): 11.62 (s, 2H, N*H*), 7.98-7.64 (m, 6H, Ar*H*). ^{13}C NMR (d_6-DMSO, δ): 168.69, 168.58, 137.55, 136.12, 134.35, 133.91, 124.94, 124.30, 123.66, 122.64, 64.95. ^{19}F NMR (d_6-DMSO, δ): -62.98. ESI-MS, m/z $C_{19}H_8F_6N_2O_4$ calculated: 442.039; found: 443.062 $[M+H]^+$.



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igure S1. ^{13}C NMR spectrum of **1** in d_6-DMSO (125 MHz).

Figure S2. ^{19}F NMR spectrum of **1** in d_6-DMSO (470 MHz).

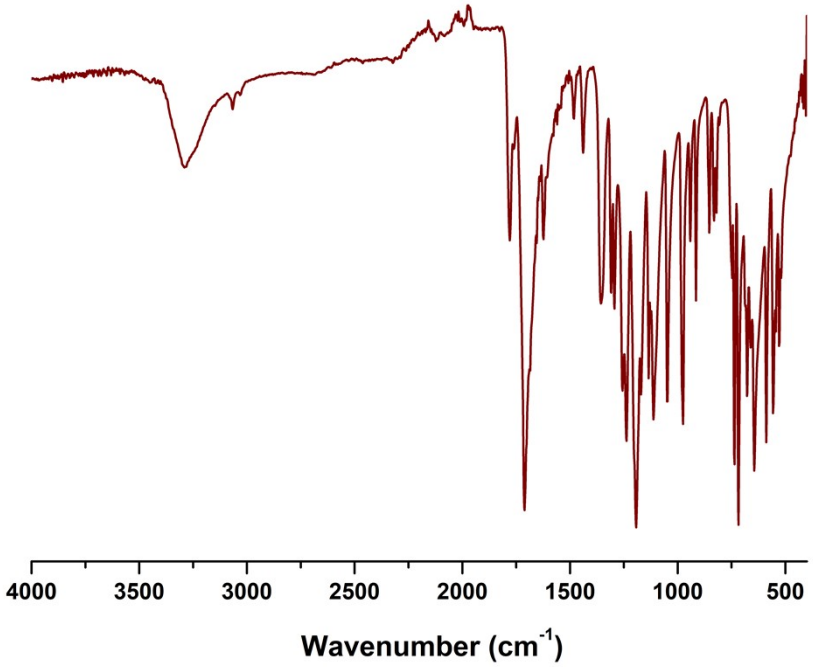
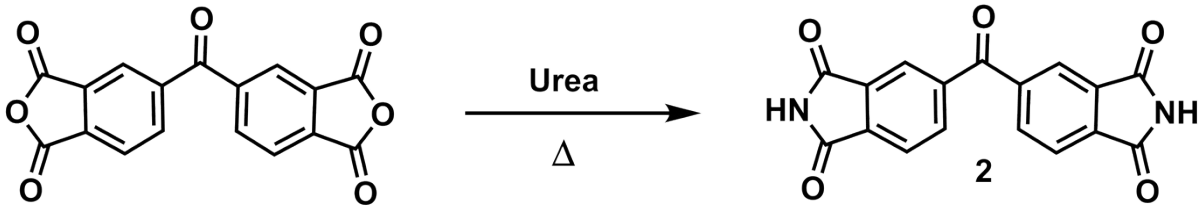


Figure S3. FT-IR spectrum of **1**.

3.1.2. Synthesis of 5,5'-carbonylbis(isoindoline-1,3-dione) (2)



To a 250 mL round bottom flask were added BTDA (6.44 g, 0.02 mol) and urea (7.20 g, 0.12 mol). The flask was heated to 150 °C in a heating mantle for 5 to 10 minutes. The flask was kept in the heating mantle until gas release was no longer observed. Then the flask was allowed to cool to room temperature. Solid residue was washed with hot ethanol and filtered with a sintered glass filter. The washing procedure was repeated two times. The resultant product was dried in a vacuum oven at 40 °C overnight and obtained as a white solid (yield: 4.67 g, 73%).

^{1}H NMR (d_6-DMSO, δ): 11.62 (s, 2H, N*H*) 8.15-7.98 (m, 6H, Ar*H*). ^{13}C NMR (d_6-DMSO, δ): 193.91, 168.83, 168.82, 141.77, 136.21, 135.98, 133.36, 123.95, 123.83.

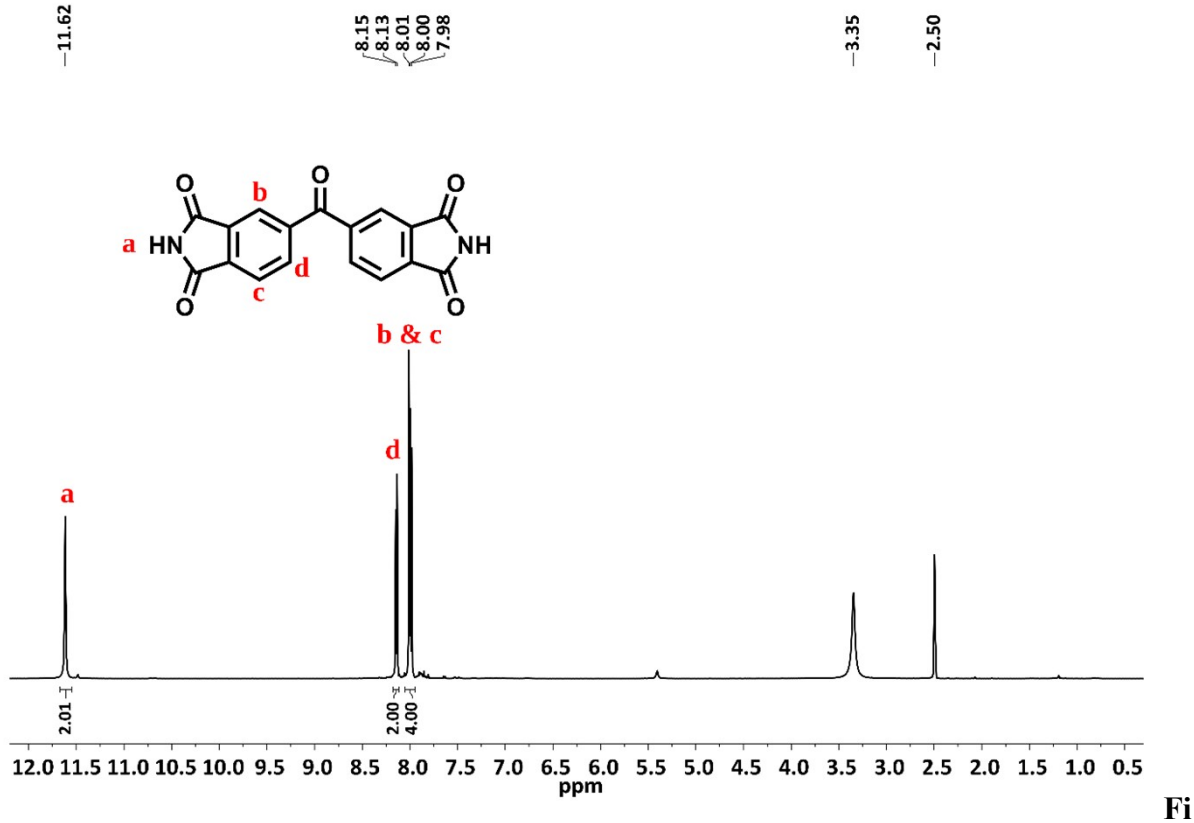
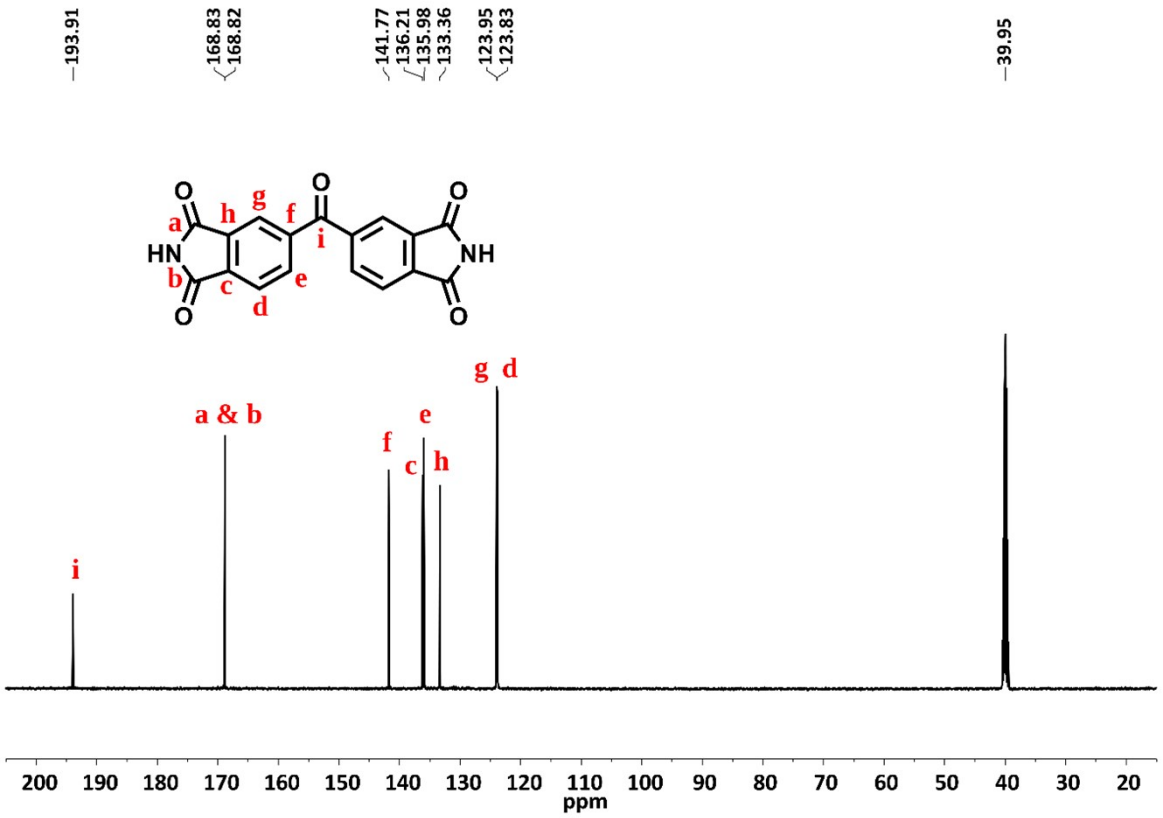


Figure S4. ^{1}H NMR spectrum of **2** in d_6-DMSO (500 MHz).



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igure S5. ^{13}C NMR spectrum of **2** in d_6-DMSO (125 MHz).

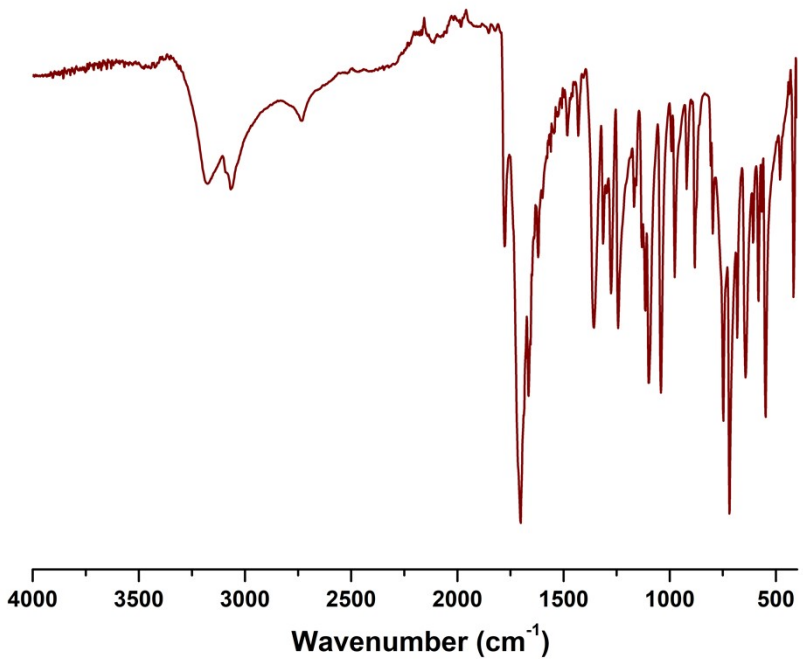
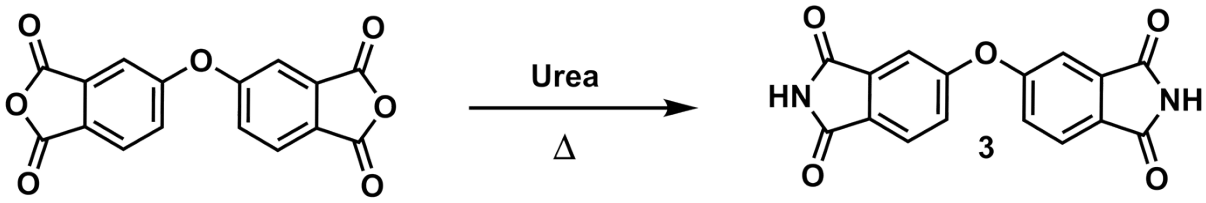


Figure S6. FT-IR spectrum of **2**.

3.1.3. Synthesis of 5,5'-oxybis(isoindoline-1,3-dione) (3)



To a 250 mL round bottom flask were added ODPA (6.20 g, 0.02 mol) and urea (7.20 g, 0.12 mol). The flask was heated to 150 °C in a heating mantle for 5 to 10 minutes. The flask was kept in the heating mantle until gas release was no longer observed. Then the flask was allowed to cool to room temperature. Solid residue was washed with hot ethanol and filtered with a sintered glass filter. The washing procedure was repeated two times. The resultant product was dried in a vacuum oven at 40 °C overnight and obtained as a white solid (yield: 4.25 g, 69%). ^{1}H NMR (d_6-DMSO, δ): 11.37 (s, 2H, N*H*), 7.88-7.43 (m, 6H, Ar*H*). ^{13}C NMR (d_6-DMSO, δ): 168.89, 168.66, 160.99, 135.9, 128.62, 125.92, 124.91, 113.71.

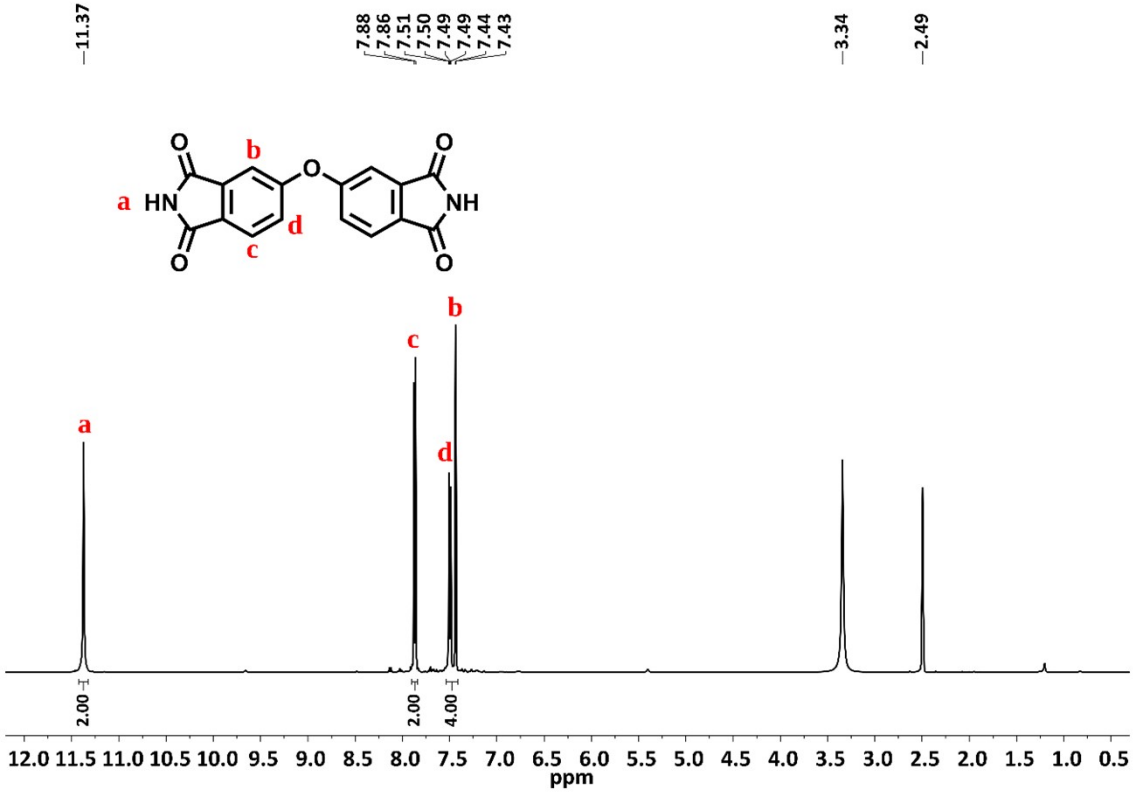


Figure S7. ^{1}H NMR spectrum of **3** in d_6-DMSO (500 MHz).

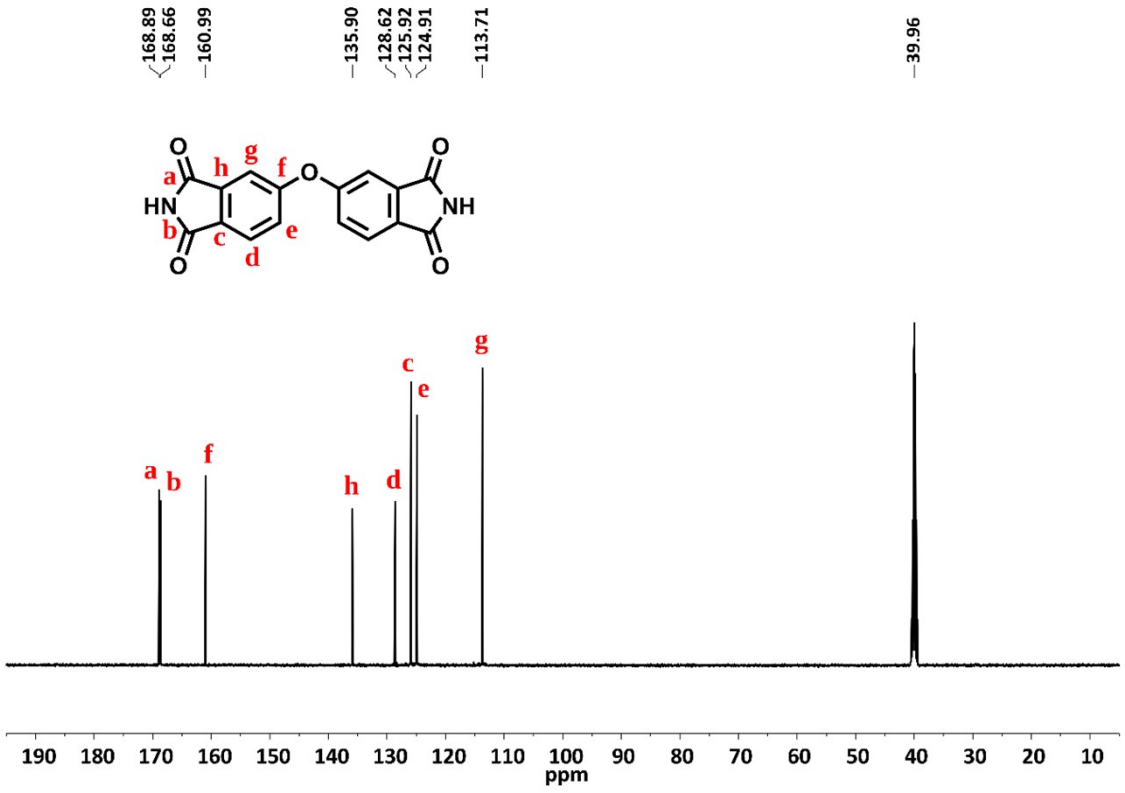


Figure S8. ^{13}C NMR spectrum of **3** in d_6-DMSO (125 MHz).

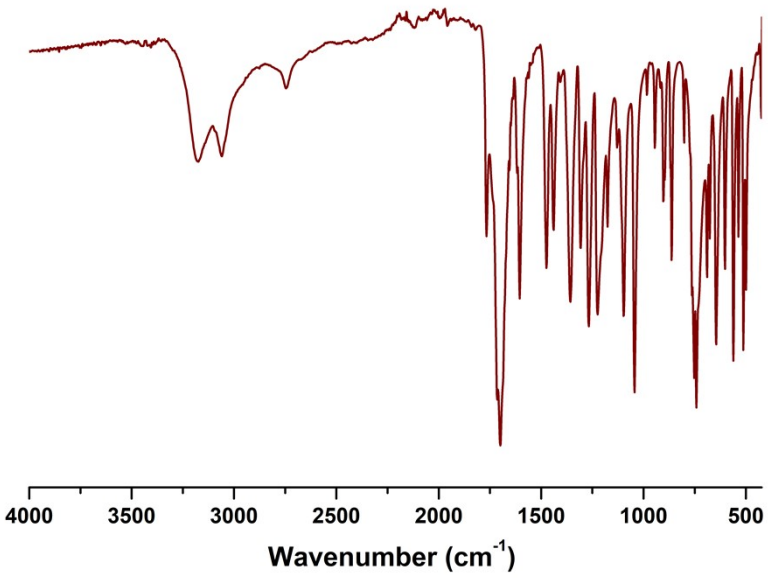
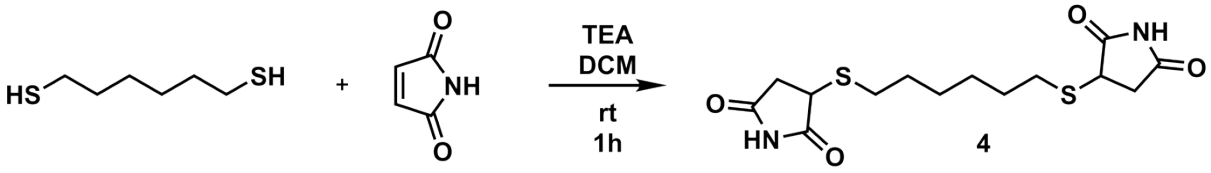


Figure S9. FT-IR spectrum of **3**.

3.2. Synthesis of bisimide monomers from maleimide (4-6)

3.2.1. Synthesis of 3,3'-(hexane-1,6-diylbis(sulfanediyl))bis(pyrrolidine-2,5-dione) (4)



To a 50 mL round bottom flask equipped with a magnetic stir bar was added maleimide (1.5 g, 15.45 mmol) and dissolved in 30 mL of DCM. Upon dissolution of maleimide, HDT (945 μL, 6.18 mmol) and TEA (215 μL, 1.545 mmol) were added to the flask, respectively, and the mixture was allowed to stir at room temperature for 1 hour. As the reaction progressed, the reaction medium turned into a suspension containing a solid precipitate. After the specified time, the solids were filtered with a sintered glass filter and washed with DCM. The resultant product was dried in a vacuum oven at 40 °C overnight, yielding a white solid product (yield: 1.80 g, 85%). ^{1}H NMR (d_6-DMSO, δ): 11.30 (s, 2H, N*H*), 3.87 (t, 2H, SC*H*), 3.12 (m, 2H, C=OCH_2), 2.71-2.66 (m, 4H, SCH_2), 2.44-2.40 (m, 2H, C=OCH_2), 1.54 (br, 4H, SCH_2CH_2), 1.34 (br, 4H, $SCH_2CH_2CH_2$). ^{13}C NMR (d_6-DMSO, δ): 178.66, 177.08, 40.93, 37.70, 30.79, 28.86, 28.12. ESI-MS, m/z $C_{14}H_{20}N_2O_4S_2$ calculated: 344.086; found: 345.093 $[M+H]^+$.

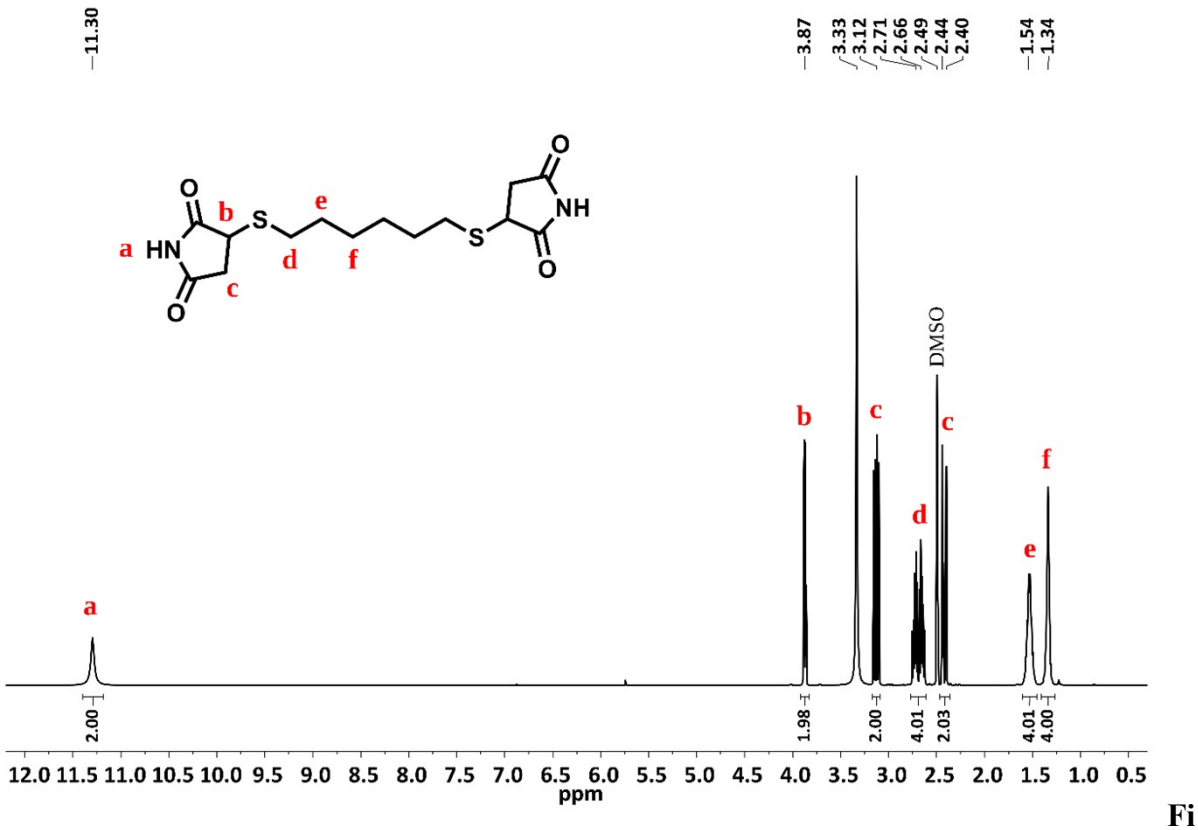


Figure S10. ^{1}H NMR spectrum of **4** in d_6-DMSO (500 MHz).

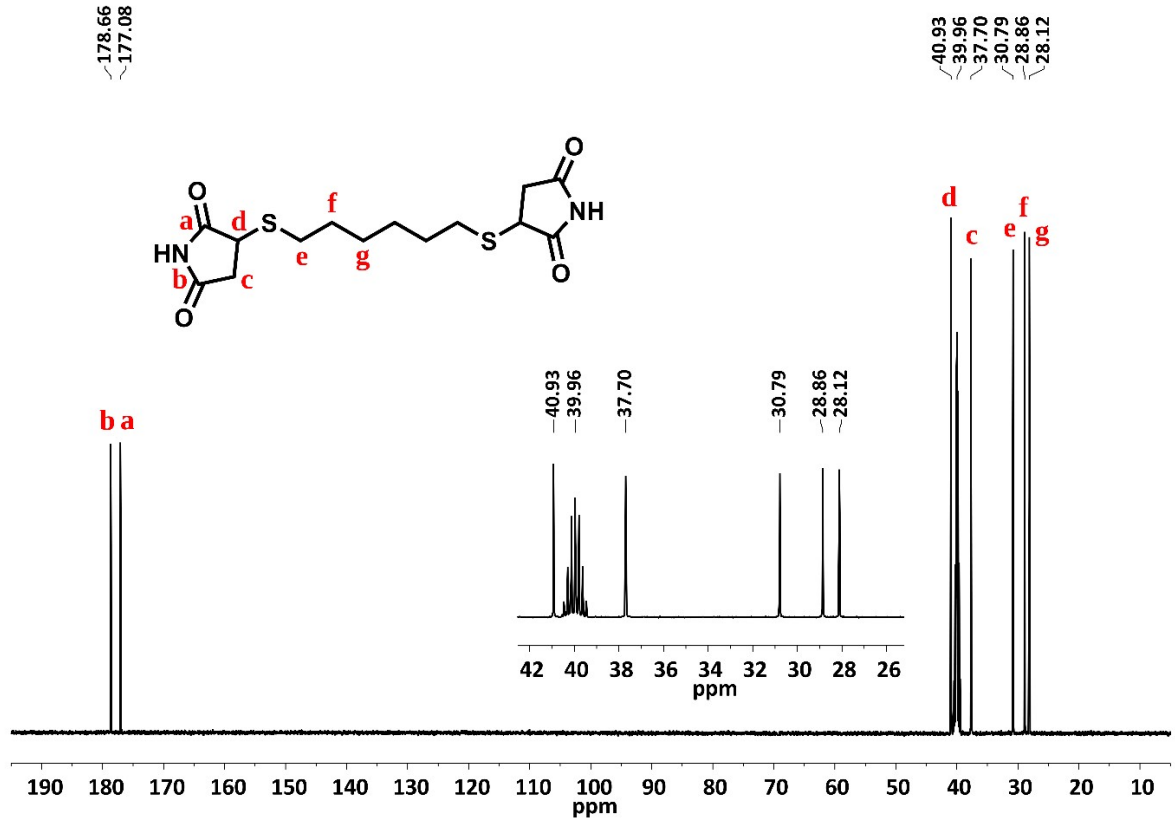


Figure S11. ^{13}C NMR spectrum of **4** in d_6-DMSO (125 MHz).

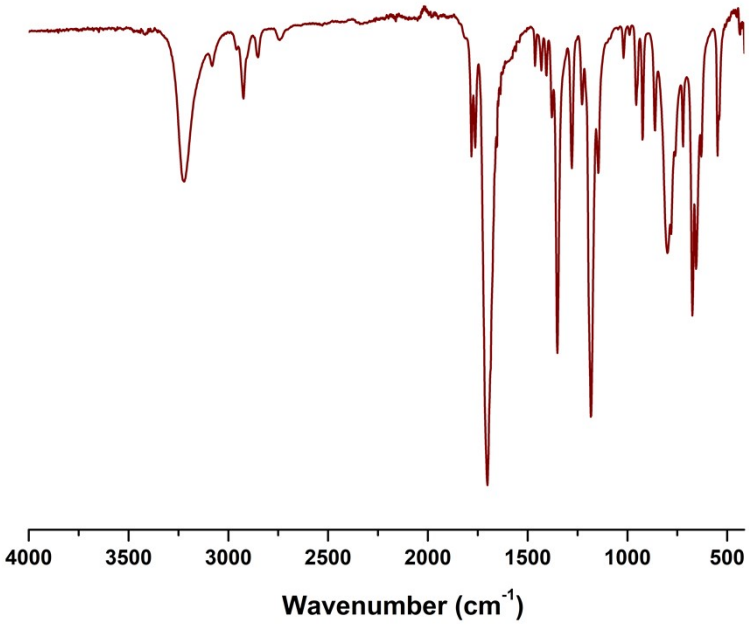
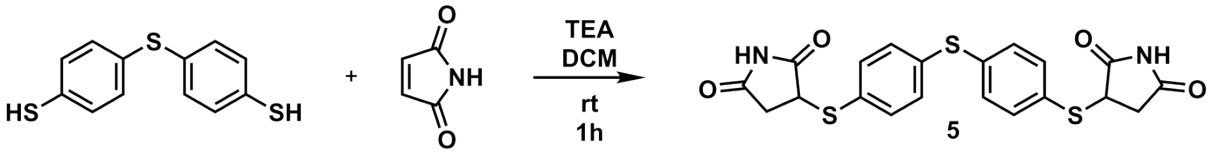


Figure S12. FT-IR spectrum of **4**.

3.2.2. Synthesis of 3,3'-((thiobis(4,1-phenylene))bis(sulfanediyl))bis(pyrrolidine-2,5-dione) (5)



To a 50 mL round bottom flask equipped with a magnetic stir bar was added maleimide (1 g, 10.3 mmol) and dissolved in 20 mL of DCM. Upon dissolution of maleimide, 4,4'-thiobisbenzenethiol (1.03 g, 4.12 mmol) and TEA (143.5 µL, 1.03 mmol) were added to the flask, respectively, and the mixture was allowed to stir at room temperature for 1 hour. As the reaction progressed, the reaction medium turned into a suspension containing a solid precipitate. After the specified time, the solids were filtered with a sintered glass filter and washed with DCM. The resultant product was dried in a vacuum oven at 40 °C overnight, yielding a white

solid product (yield: 1.65 g, 90%). ^{1}H NMR (d_6-DMSO, δ): 11.40 (s, 2H, N*H*), 7.46 (d, 4H, SCC*H*), 7.30 (d, 4H, CHSCCC*H*), 4.42 (t, 2H, C=OC*H*), 3.19 (m, 2H, C=OCH_2), 2.57 (m, 2H, C=OCH_2). ^{13}C NMR (d_6-DMSO, δ): 177.50, 176.65, 134.50, 132.89, 132.87, 132.60, 132.59, 131.68, 44.68, 37.66. ESI-MS, m/z $C_{20}H_{16}N_2O_4S_3$ calculated: 444.027; found: 445.034 $[M+H]^+$.

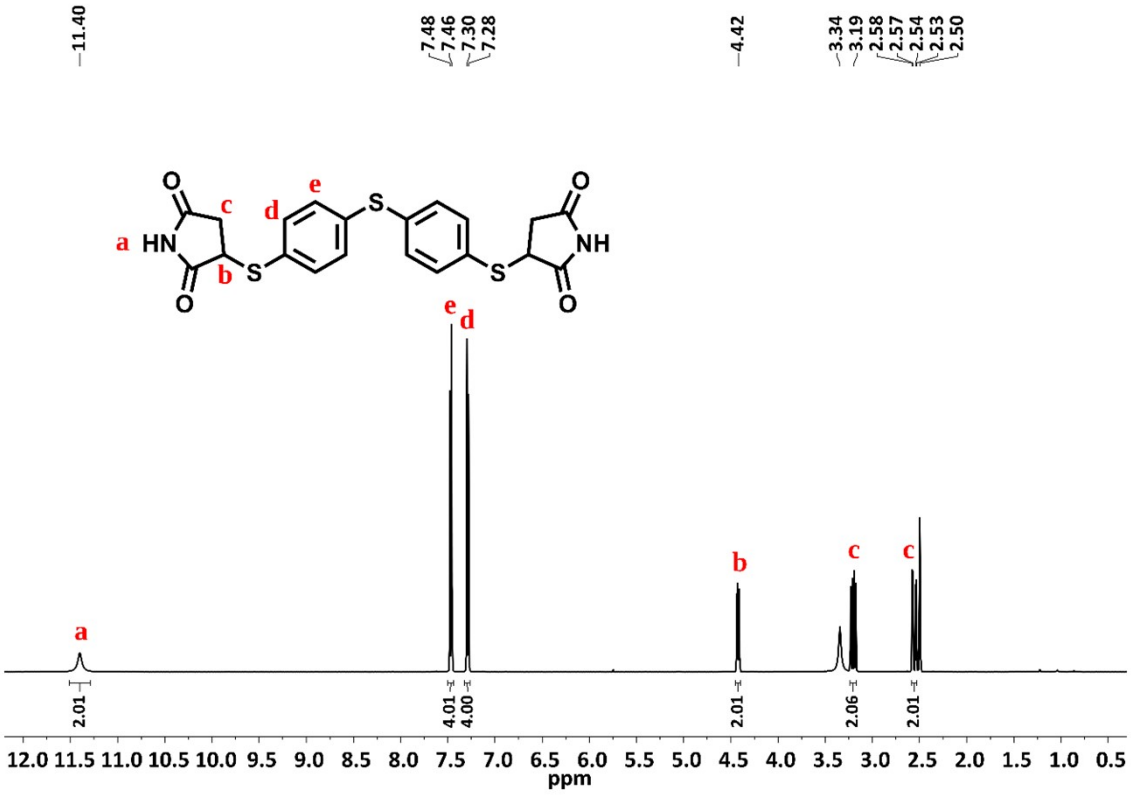


Figure S13. ^{1}H NMR spectrum of **5** in d_6-DMSO (500 MHz).

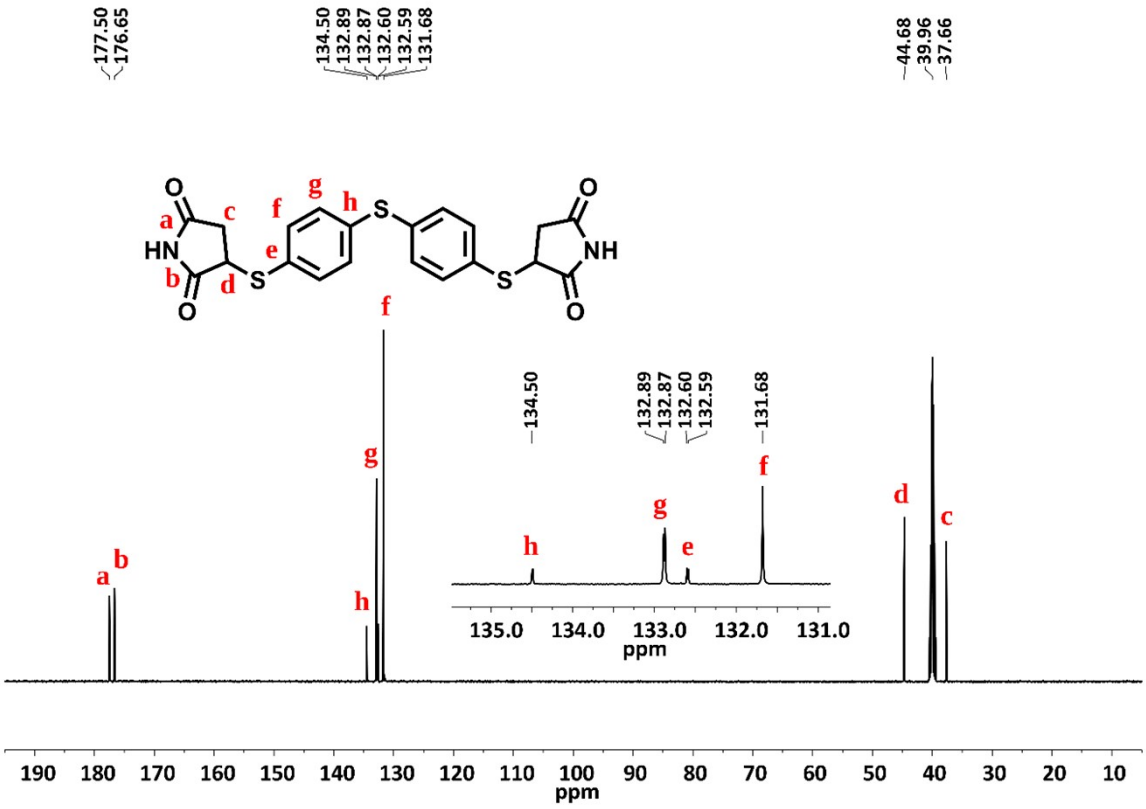


Figure S14. ^{13}C NMR spectrum of **5** in d_6-DMSO (125 MHz).

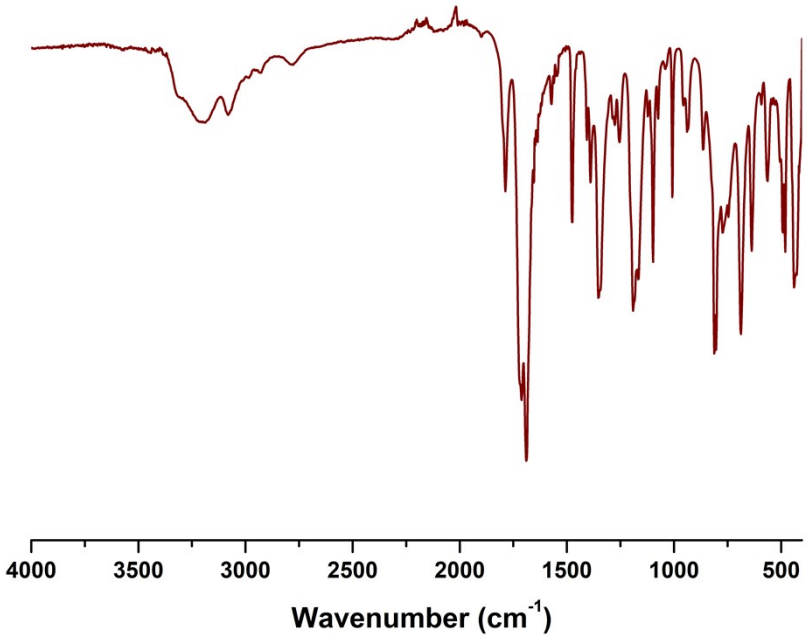
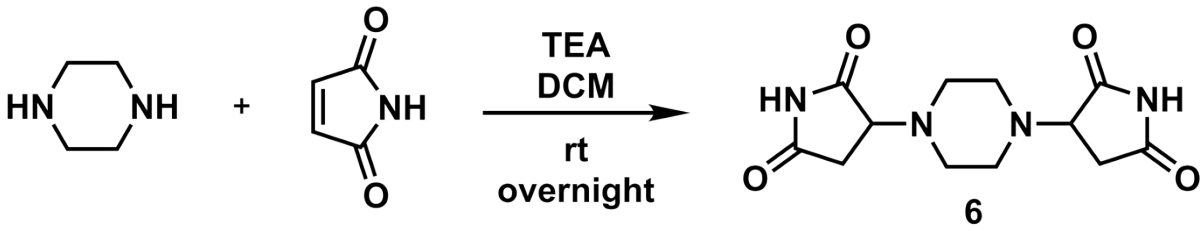


Figure S15. FT-IR spectrum of **5**.

3.2.3. Synthesis of 3,3'-(piperazine-1,4-diyl)bis(pyrrolidine-2,5-dione) (6)



To a 50 mL round bottom flask equipped with a magnetic stir bar was added maleimide (1 g, 10.3 mmol) and dissolved in 15 mL of DCM. After that, TEA (143.5 µL, 1.03 mmol) was added to the flask. Piperazine (355 mg, 4.12 mmol) was weighed and dissolved with 5 mL of DCM and added via a dropping funnel slowly and the solution was allowed to stir at room temperature overnight. As the reaction progressed, the reaction medium turned into a suspension containing a solid precipitate. After the specified time, the solids were filtered with a sintered glass filter and washed with DCM and methanol. The resultant product was dried in a vacuum oven at 40 °C overnight, yielding a white solid product (yield: 845 mg, 73%). ^{1}H NMR (d_6-DMSO, δ): 10.88 (br, 2H, N*H*), 3.80 (t, 2H, NC*H*), 2.73 (br, 6H, C=OCH_2 & NCH_2), 2.57-2.54 (br, 2H, C=OCH_2), 2.39 (br, 4H, NCH_2). ^{13}C NMR (d_6-DMSO, δ): 178.45, 177.21, 64.07, 63.55, 48.81, 32.68. ESI-MS, m/z $C_{12}H_{16}N_4O_4$ calculated: 280.117; found: 281.124 $[M+H]^+$.

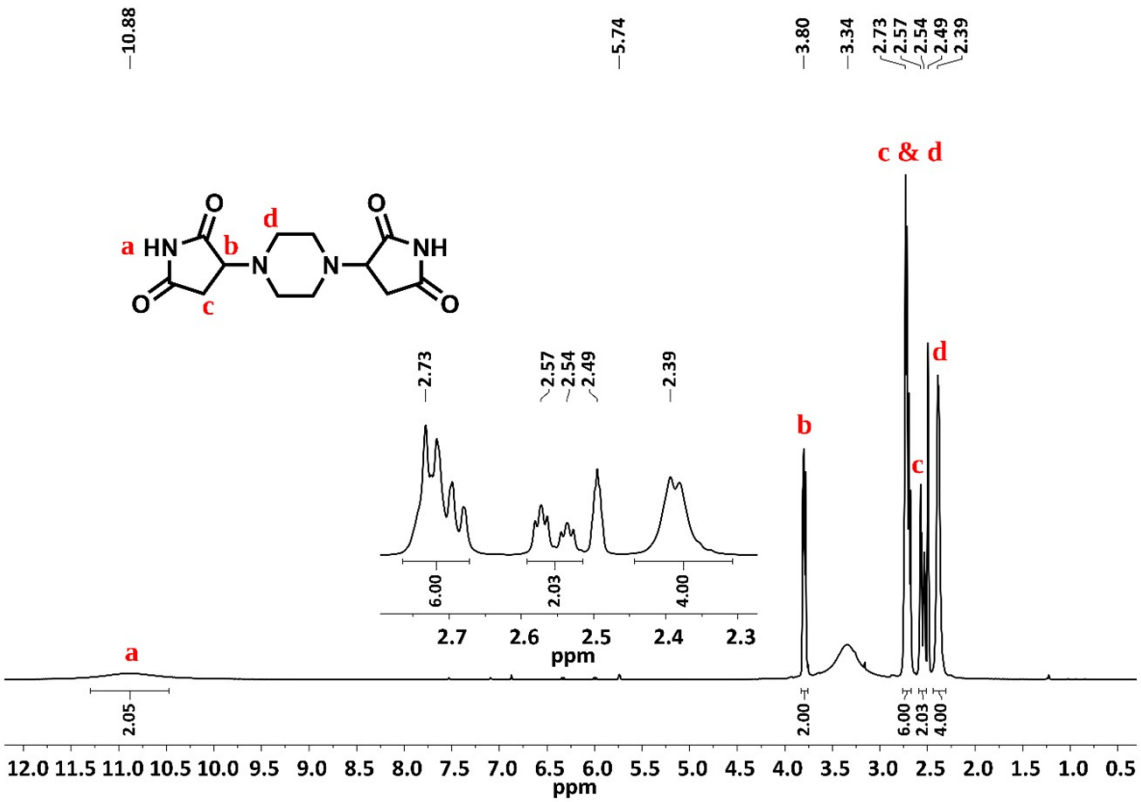


Figure S16. ^{1}H NMR spectrum of **6** in d_6-DMSO (500 MHz).

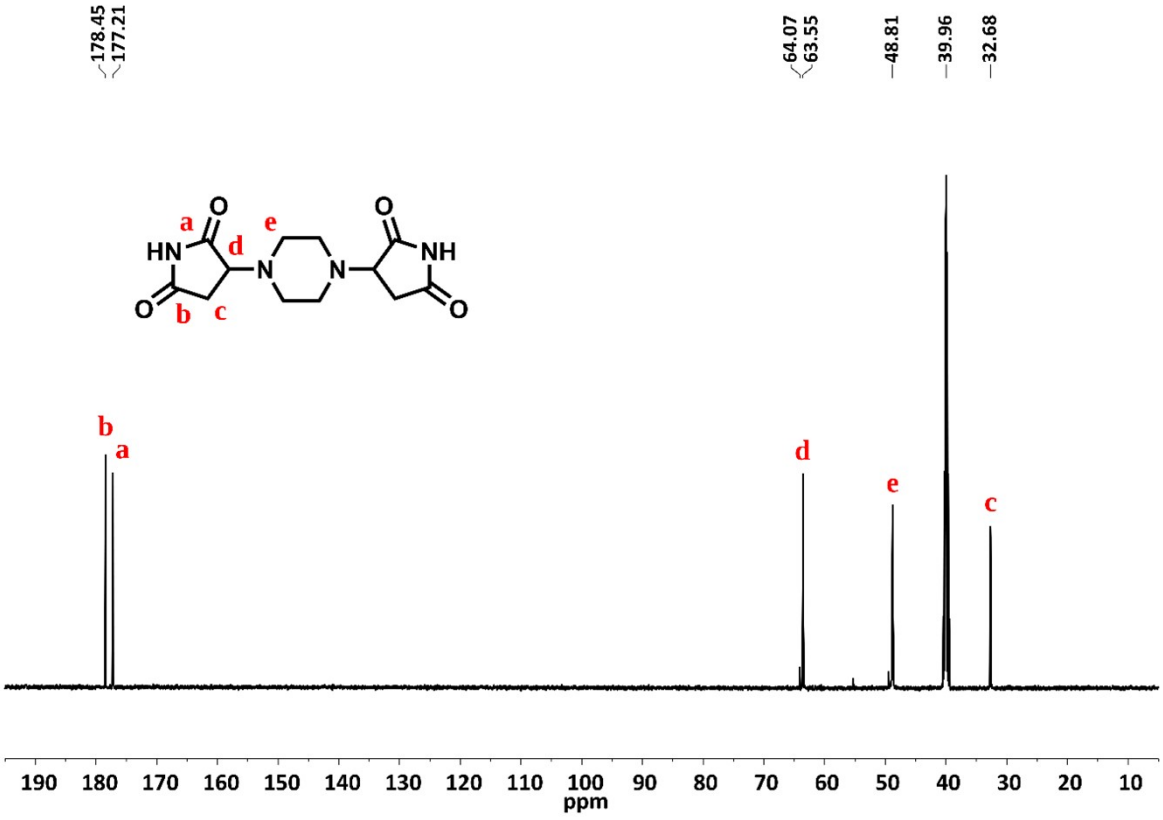


Figure S17. ^{13}C NMR spectrum of **6** in d_6-DMSO (125 MHz).

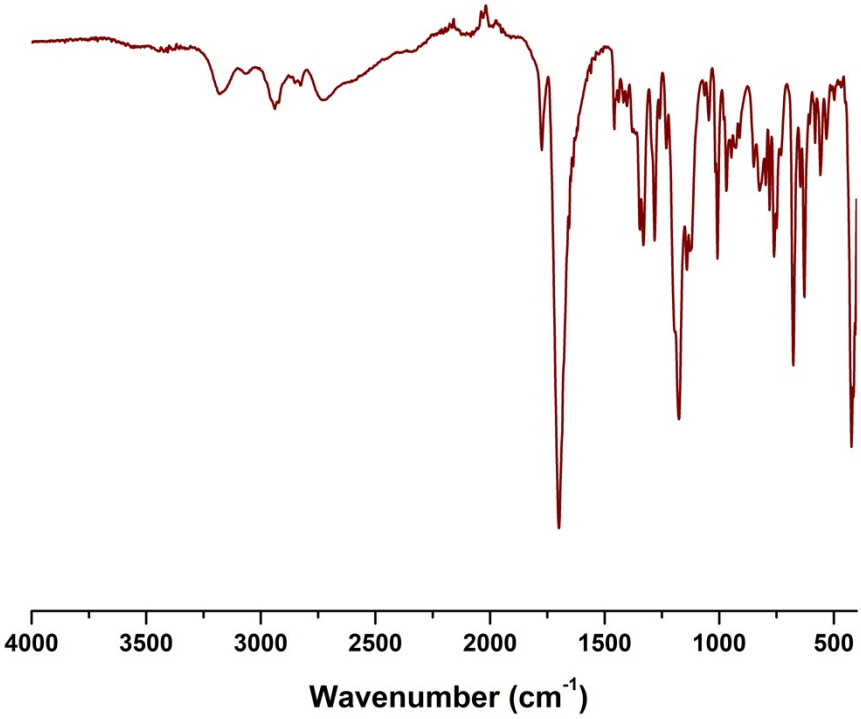
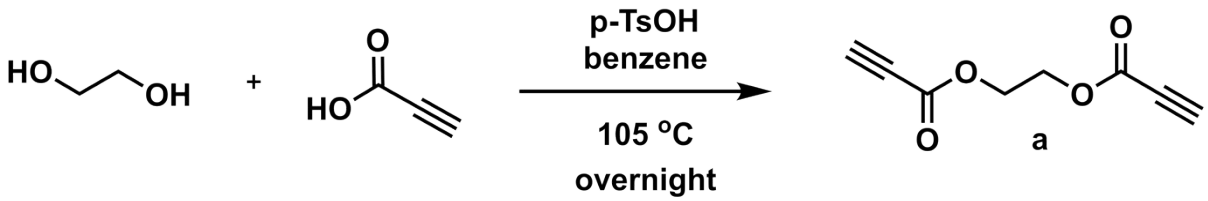


Figure S18. FT-IR spectrum of **6**.

3.3. Synthesis of dipropiolate monomers (a-e)

3.3.1. Synthesis of ethane-1,2-diyl dipropiolate (a)



To a 50 mL round bottom flask equipped with a magnetic stir bar were added ethylene glycol (1.5 g, 24.2 mmol) and 30 mL of benzene. Propiolic acid (7.5 mL, 121 mmol) and p-TsOH (460.3 mg, 2.42 mmol) were then added to the flask, respectively, and the mixture was allowed to stir under a reflux system equipped with a Dean-Stark apparatus at 105 °C overnight. After the specified time, reaction mixture was concentrated under reduced pressure and dissolved with 60 mL of DCM. The solution was extracted with 60 mL of distilled water three times. The

organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatography on silica gel using hexane: ethyl acetate (5:1, v/v) as eluent (yield: 3.5 g, 87%). ^{1}H NMR ($CDCl_3$, δ): 4.43 (s, 4H, C=OOC*H*$_2$), 2.96 (s, 2H, C≡C*H*). ^{13}C NMR ($CDCl_3$, δ): 152.23, 75.79, 74.09, 63.09. ESI-MS, m/z $C_8H_6O_4$ calculated: 166.027; found: 167.034 $[M+H]^+$.

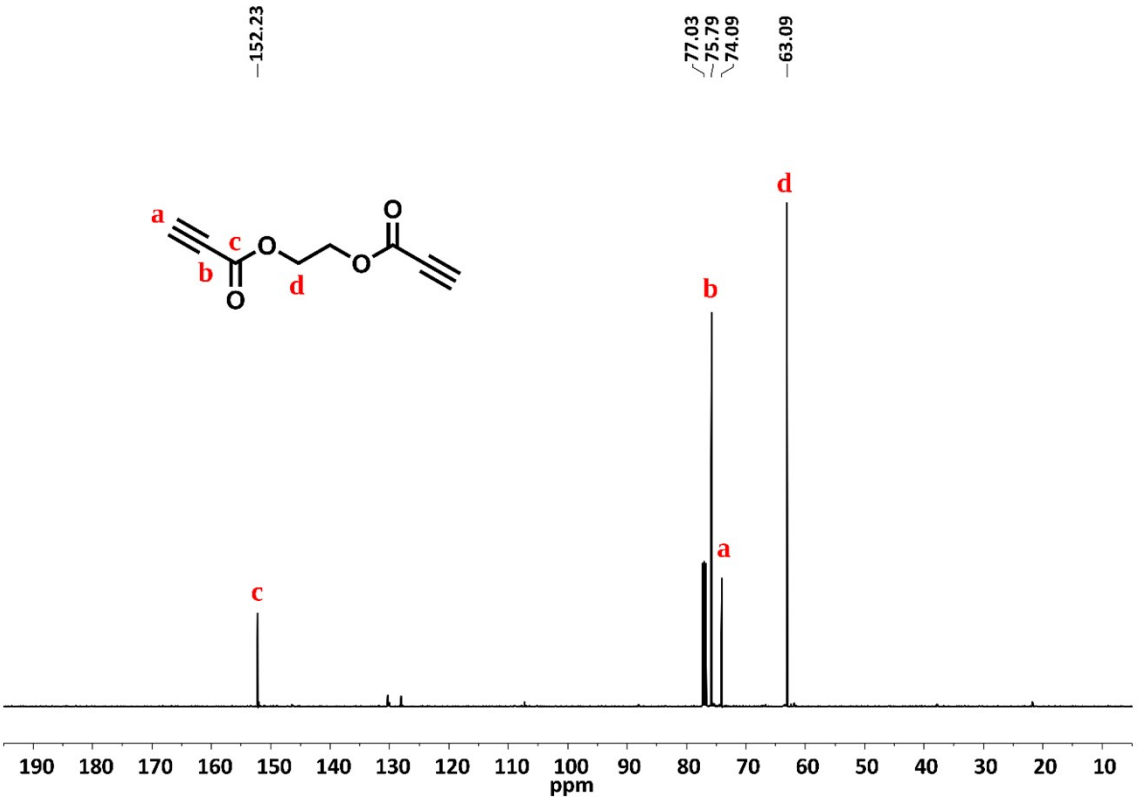


Figure S19. ^{13}C NMR spectrum of **a** in $CDCl_3$ (125 MHz).

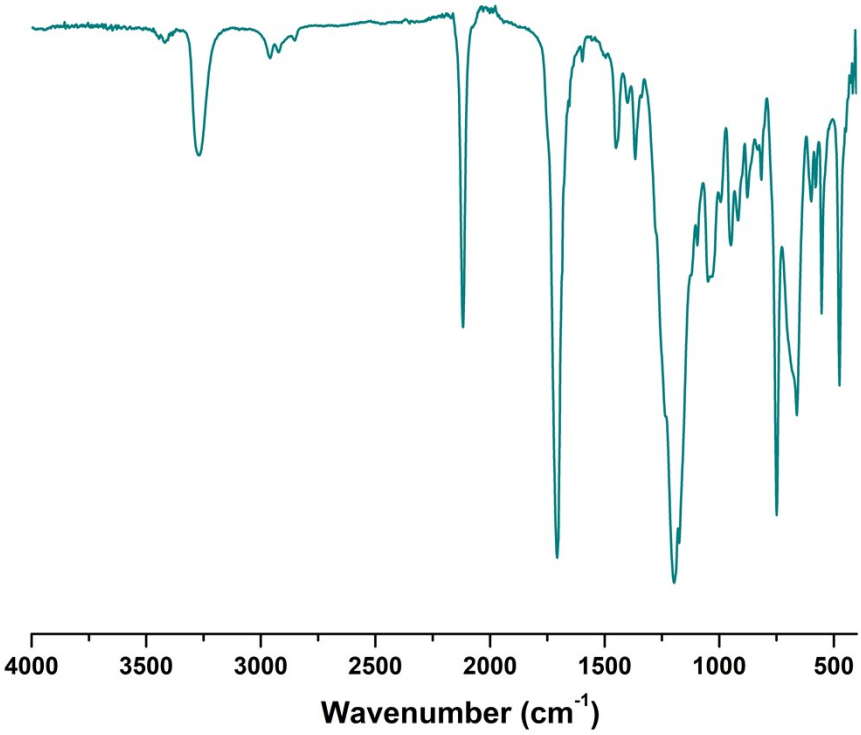
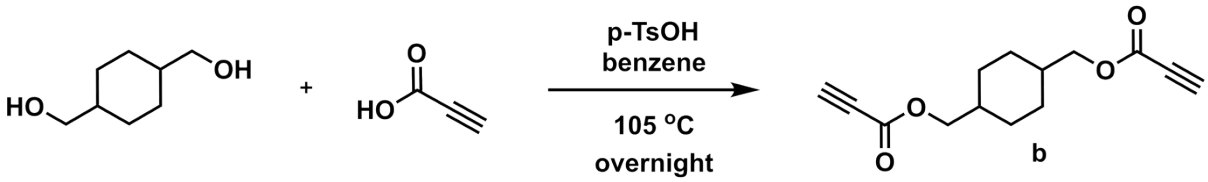


Figure S20. FT-IR spectrum of **a**.

3.3.2. Synthesis of cyclohexane-1,4-diylbis(methylene) dipropiolate (b)



To a 50 mL of round bottom flask equipped with a magnetic stir bar, were added 1,4-cyclohexanedimethanol (1.35 g, 9.36 mmol) and 30 mL of benzene. Propiolic acid (2.9 mL, 46.8 mmol) and p-TsOH (178.05 mg, 0.936 mmol) were then added to the flask, respectively, and the mixture was allowed to stir under a reflux system equipped with a Dean-Stark apparatus at 105 °C overnight. After the specified time, reaction mixture was concentrated under reduced pressure and dissolved with 60 mL of DCM. The solution was extracted with 60 mL of distilled

water three times. The organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness to give compound **b** as a light brown solid (yield: 2 g, 86%). ^{1}H NMR ($CDCl_3$, δ): 4.13-4.02 (d, 4H, OC*H*$_2$), 2.90 (s, 2H, C≡C*H*), 1.86-1.04 (m, 10H, OCH$_2$C*H* & OCH$_2$CHC*H*$_2$). ^{13}C NMR ($CDCl_3$, δ): 152.77, 74.65, 70.91, 68.83, 36.67, 34.13, 28.53, 25.06. ESI-MS, m/z $C_{14}H_{16}O_4$ calculated: 248.105; found: 271.094 $[M+Na]^+$.

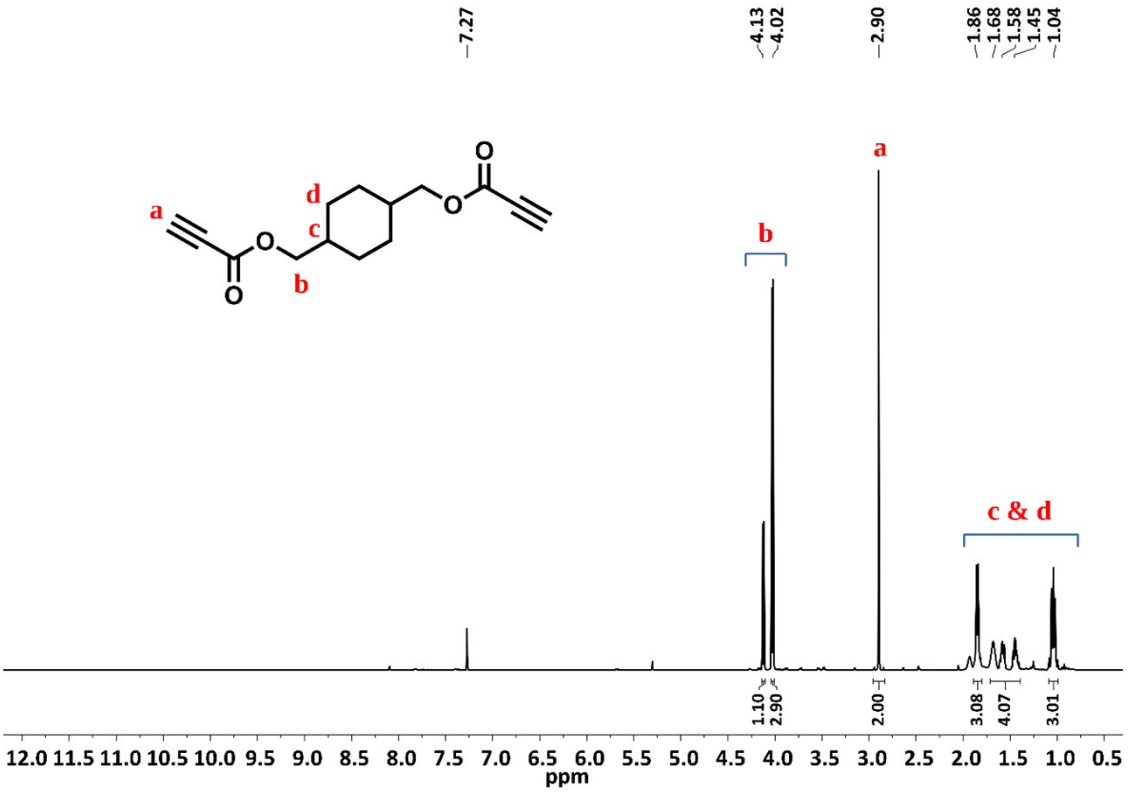


Figure S21. ^{1}H NMR spectrum of **b** in $CDCl_3$ (500 MHz).

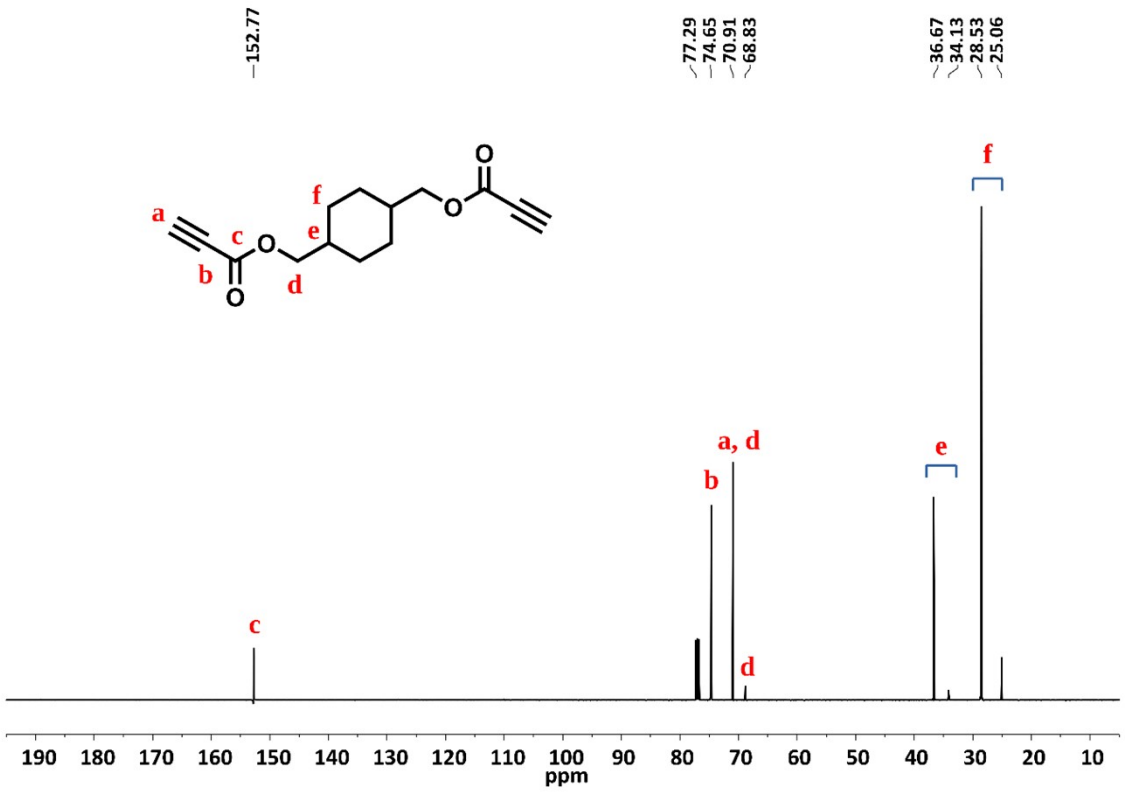


Figure S22. ^{13}C NMR spectrum of **b** in $CDCl_3$ (125 MHz).

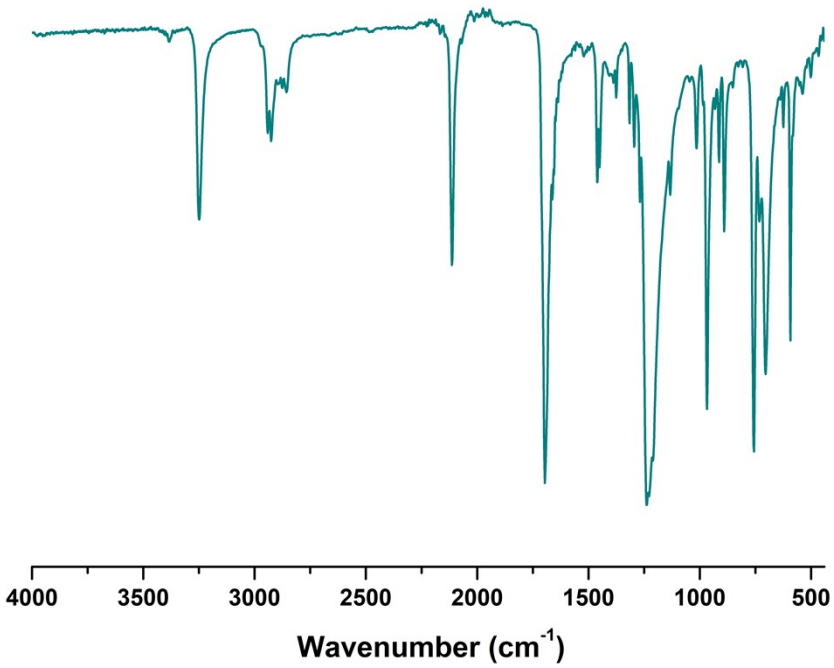
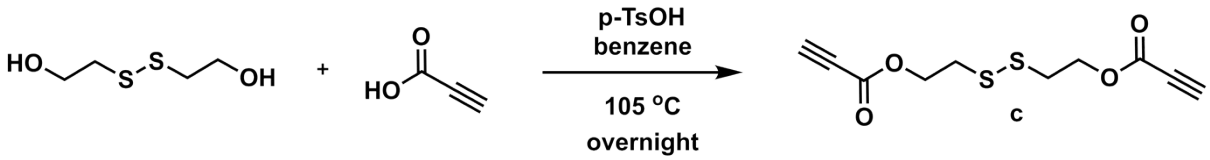
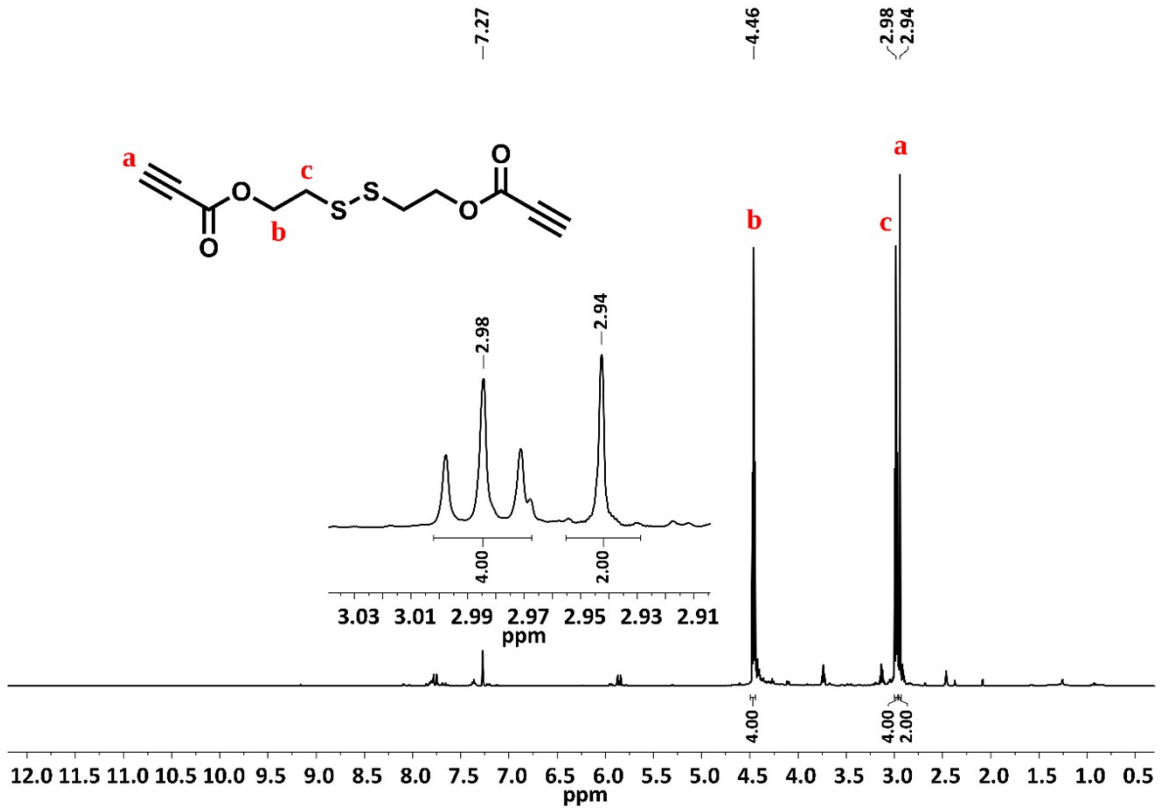


Figure S23. FT-IR spectrum of **b**.

3.3.3. Synthesis of disulfanediylbis(ethane-2,1-diyl) dipropiolate (c)



To a 50 mL round bottom flask equipped with a magnetic stir bar were added bis(2-hydroxyethyl) disulfide (1.06 g, 6.87 mmol) and 30 mL of benzene. Propiolic acid (2.11 mL, 34.35 mmol) and p-TsOH (130.7 mg, 0.687 mmol) were then added to the flask, respectively, and the mixture was allowed to stir under a reflux system equipped with a Dean-Stark apparatus at 105 °C overnight. After the specified time, reaction mixture was concentrated under reduced pressure and dissolved with 60 mL of DCM. The solution was extracted with 60 mL of distilled water three times. The organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness to give compound **c** as a viscous black liquid (yield: 1.42 g, 80%). ^{1}H NMR ($CDCl_3$, δ): 4.46 (t, 4H, OC*H*$_2$), 2.98 (t, 4H, SC*H*$_2$), 2.94 (s, 2H, C≡C*H*). ^{13}C NMR ($CDCl_3$, δ): 152.32, 75.88, 75.44, 74.29, 63.88, 36.70. ESI-MS, m/z $C_{10}H_{10}O_4S_2$ calculated: 258.002; found: 276.036 $[M+NH_4]^+$.



F

igure S24. ^{1}H NMR spectrum of **c** in $CDCl_3$ (500 MHz).

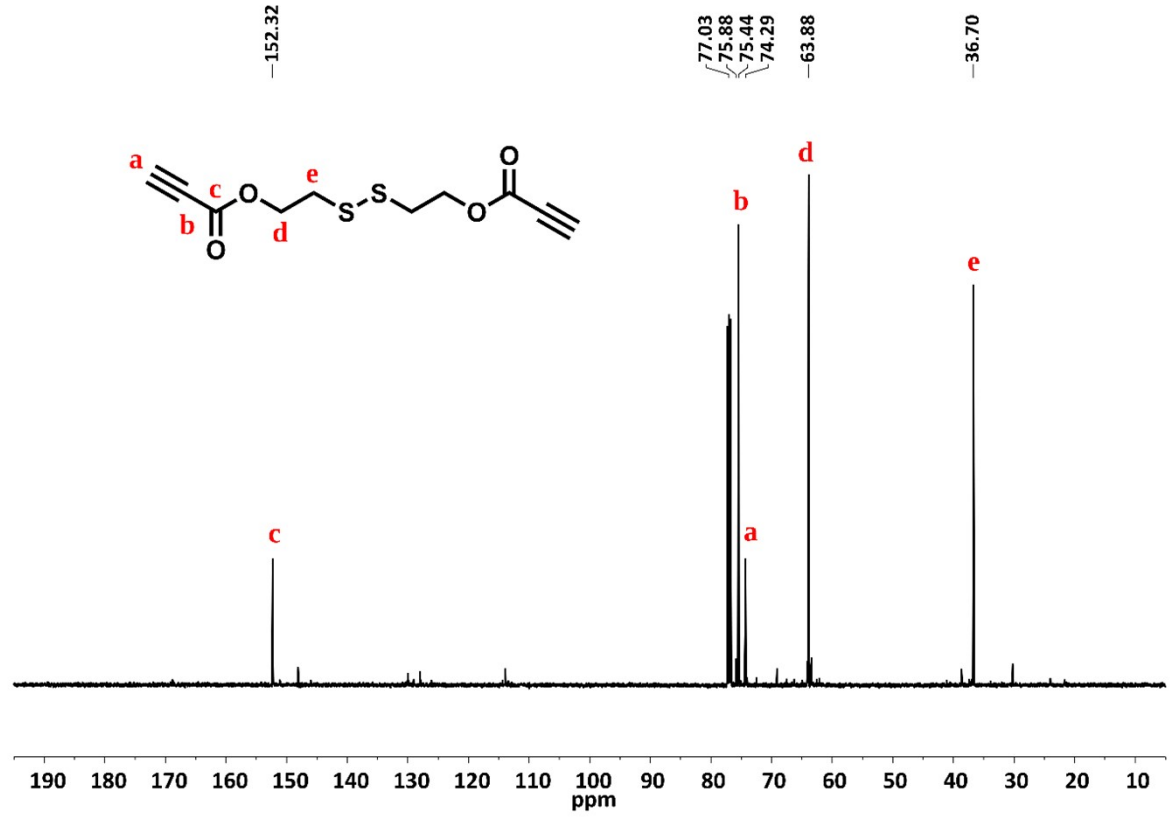


Figure S25. ^{13}C NMR spectrum of **c** in $CDCl_3$ (125 MHz).

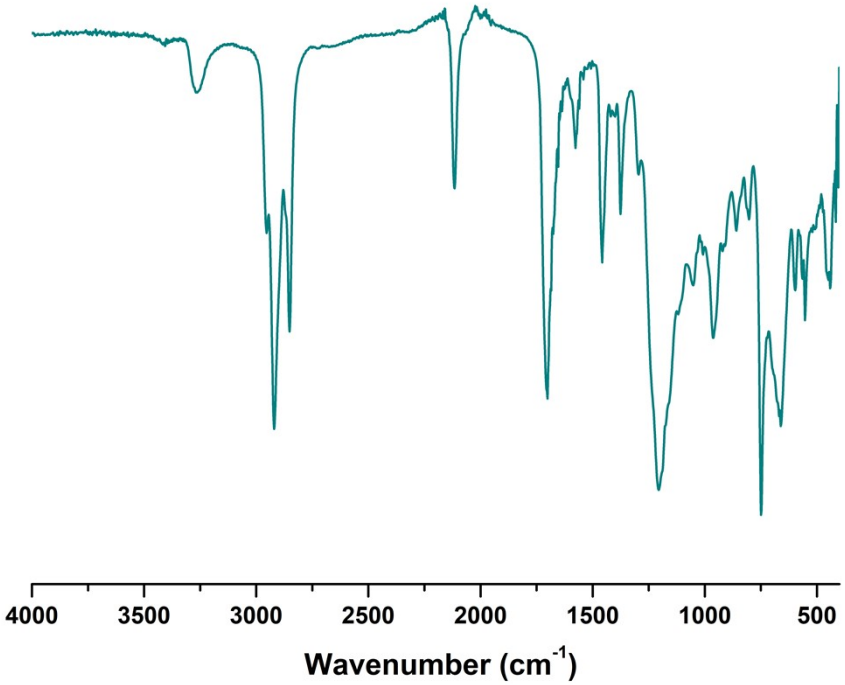
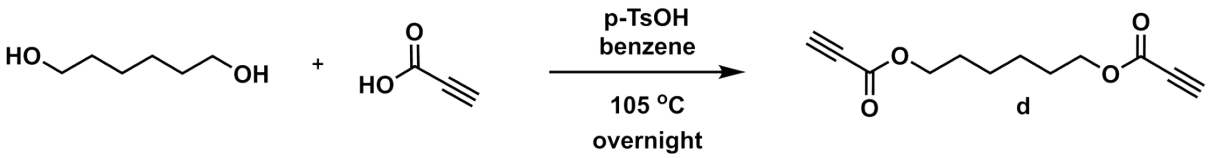


Figure S26. FT-IR spectrum of **c**.

3.3.4. Synthesis of hexane-1,6-diyl dipropiolate (d)



To a 50 mL of round bottom flask equipped with a magnetic stir bar, were added 1,6-hexanediol (2.55 g, 21.6 mmol) and 40 mL of benzene. Propiolic acid (6.695 mL, 108 mmol) and p-TsOH (410.8 mg, 2.16 mmol) were then added to the flask, respectively, and the mixture was allowed to stir under a reflux system equipped with a Dean-Stark apparatus at 105 °C overnight. After the specified time, reaction mixture was concentrated under reduced pressure and dissolved with 60 mL of DCM. The solution was extracted with 60 mL of distilled water three times. The organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness to give

compound **d** as a light-brown solid (yield: 4.32 g, 90%). ^{1}H NMR ($CDCl_3$, δ): 4.19 (t, 4H, OC*H*$_2$), 2.89 (s, 2H, CC≡*H*), 1.70 (m, 4H, OCH$_2$C*H*$_2$), 1.42 (m, 4H, OCH$_2$CH$_2$C*H*$_2$). ^{13}C NMR ($CDCl_3$, δ): 152.75, 74.69, 74.60, 66.14, 28.15, 25.38. ESI-MS, m/z $C_{12}H_{14}O_4$ calculated: 222.089; found: 245.078 $[M+Na]^+$.

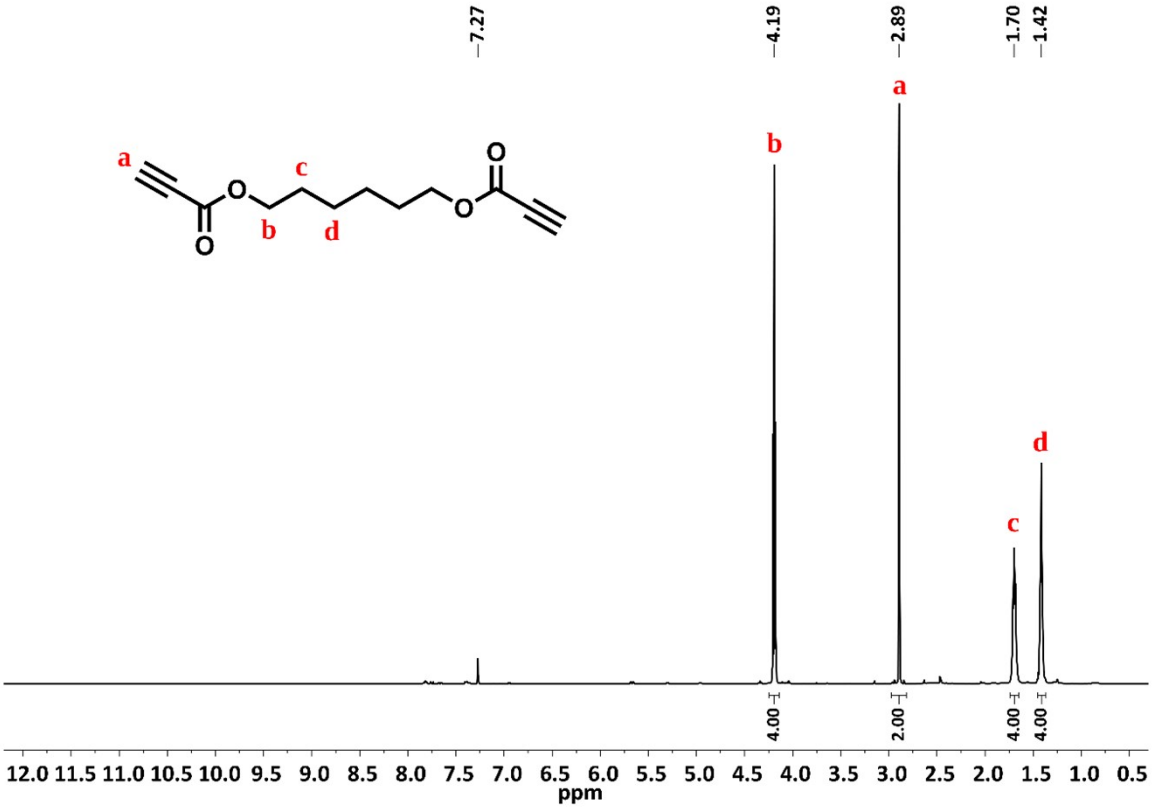


Figure S27. ^{1}H NMR spectrum of **d** in $CDCl_3$ (500 MHz).

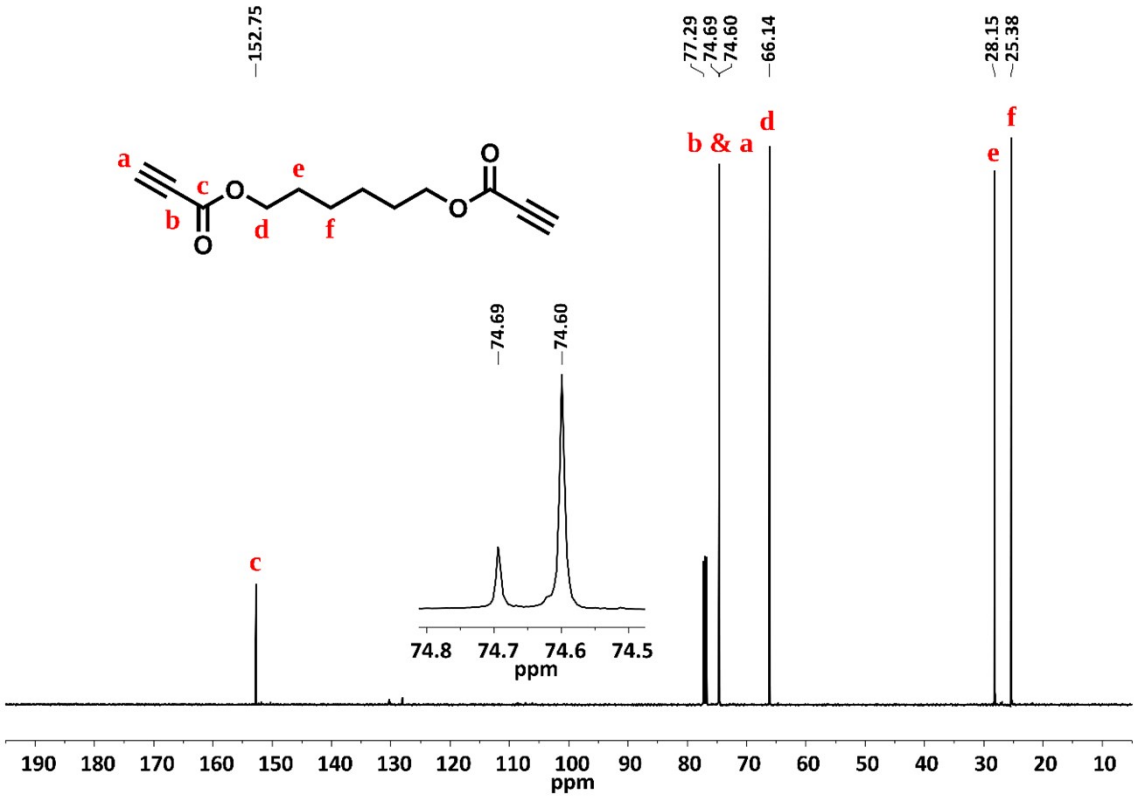


Figure S28. ^{13}C NMR spectrum of **d** in $CDCl_3$ (125 MHz).

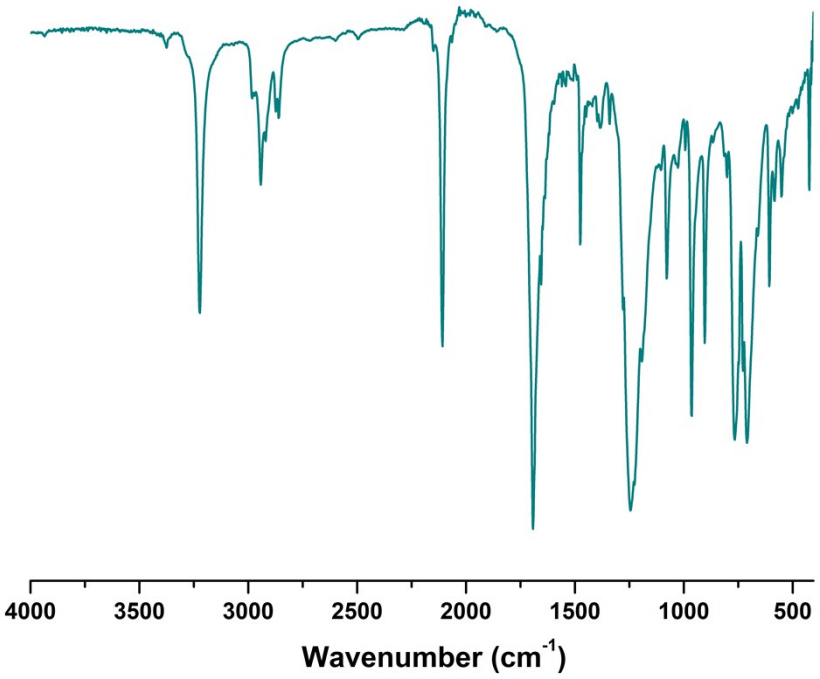
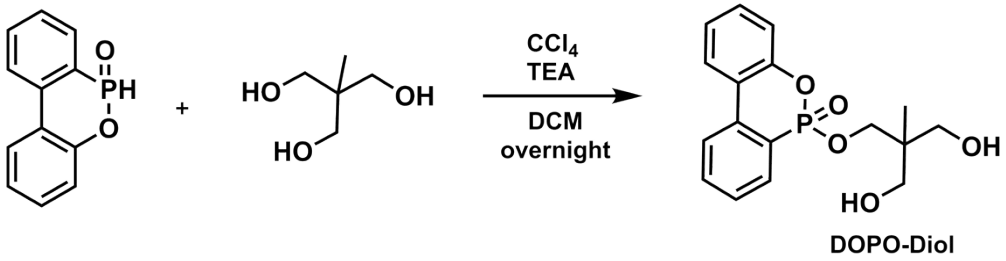


Figure S29. FT-IR spectrum of **d**.

3.3.5. Synthesis of 2-methyl-2-(((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) oxy)methyl)propane-1,3-diyl dipropiolate (DOPO-Dipropiolate) (e)

3.3.5.1. Synthesis of 6-(3-hydroxy-2-(hydroxymethyl)-methylpropoxy)dibenzo[c,e] [1,2]oxaphosphinine 6-oxide (DOPO-Diol)



DOPO-Diol

To a 250 mL round bottom flask equipped with a magnetic stir bar was added 1,1,1-tris(hydroxymethyl)ethane (6.67 g, 55.5 mmol) and partially dissolved in 60 mL of DCM. Then, TEA (19.34 mL, 138.75 mmol) and DOPO (6.00 g, 27.76 mmol) were added to the flask, respectively. Upon complete dissolution of DOPO, the mixture was cooled to 0 °C in an ice bath. After that, CCl_4 (5.35 mL, 55.5 mmol) was added to the reaction medium dropwise, then the flask was removed from the ice bath and allowed to stir overnight at room temperature. After the specified time, solid fragments were filtered and the mixture was diluted with 40 mL of DCM and extracted with 100 mL of distilled water three times. The organic layers were dried over Na_2SO_4, filtered, and evaporated to dryness to give DOPO-Diol as a viscous brown liquid (yield: 5.85 g, 63%). ^{1}H NMR ($CDCl_3$, δ) 7.96-7.26 (m, 8H, Ar-*H*), 4.43 (t, 1H, P=OOCH_2), 4.08 (t, 1H, P=OOCH_2), 3.62-3.57 (m, 4H, CCH_2OH), 3.27 (br, 2H, -O*H*), 0.72 (s, 3H, CCH_3). ^{13}C NMR ($CDCl_3$, δ) 149.62, 137.07, 133.84, 130.66, 130.12, 128.47, 128.34 125.29, 124.97, 124.15, 122.48, 122.23, 120.78, 120.18, 68.63, 67.56, 67.17, 41.35, 15.65. ^{31}P NMR ($CDCl_3$, δ) 13.27, 11.66. ESI-MS, m/z $C_{17}H_{19}O_5P$ calculated: 334.097; found: 335.104 $[M+H]^+$.

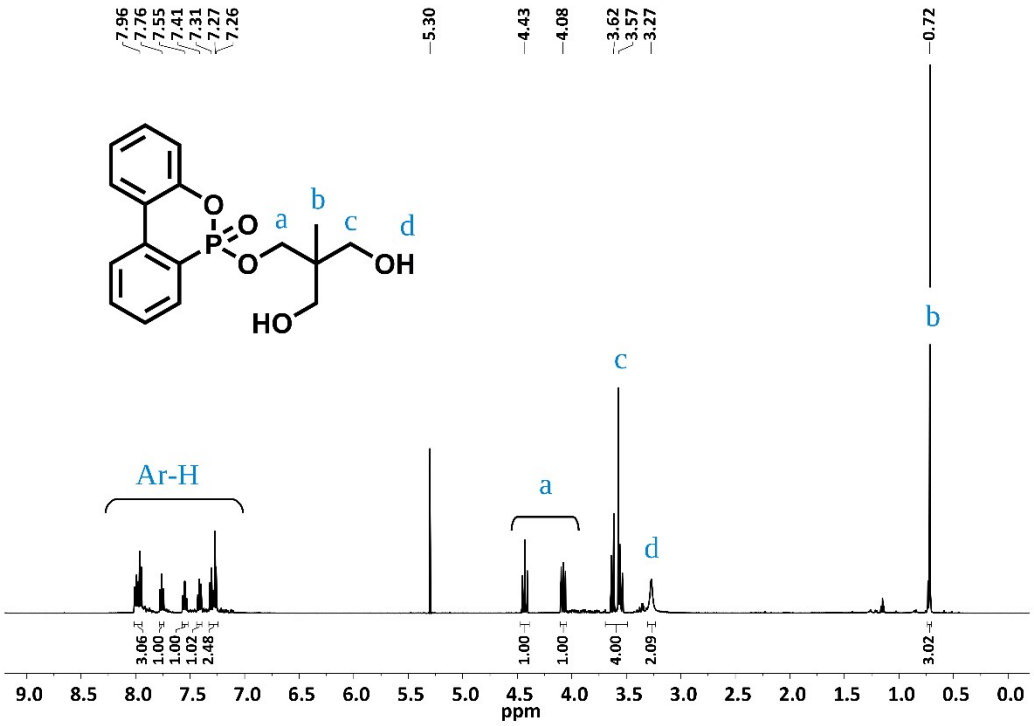


Figure S30. ^{1}H NMR spectrum of **DOPO-Diol** in $CDCl_3$ (500 MHz).

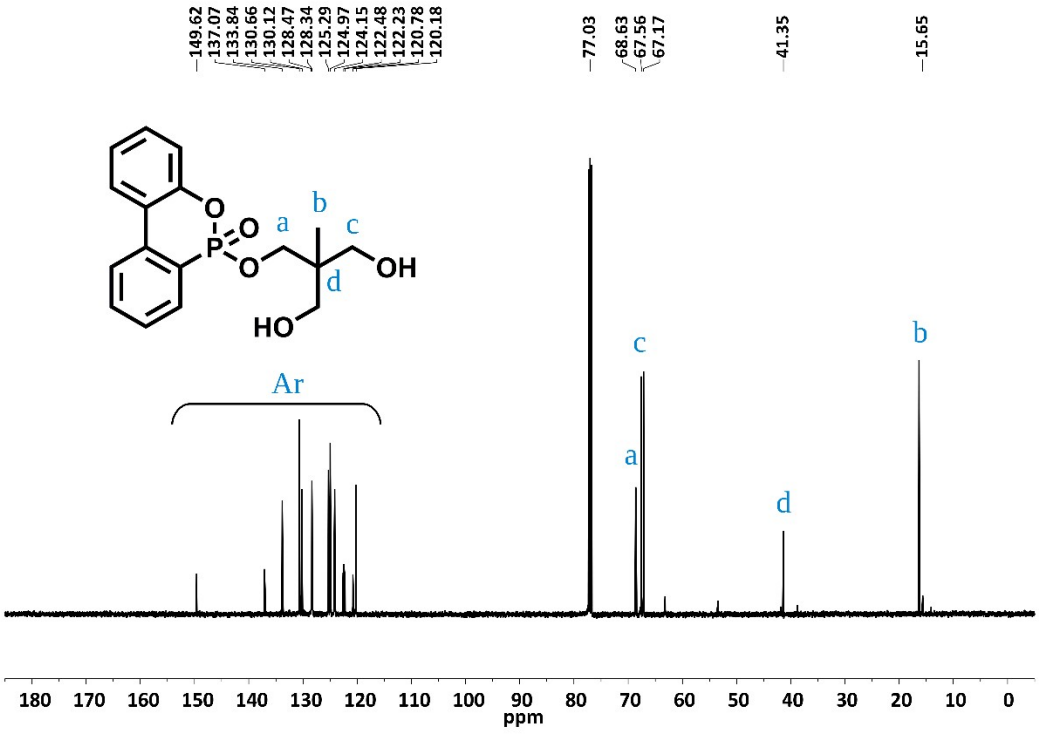


Figure S31. ^{13}C NMR spectrum of **DOPO-Diol** in $CDCl_3$ (125 MHz).

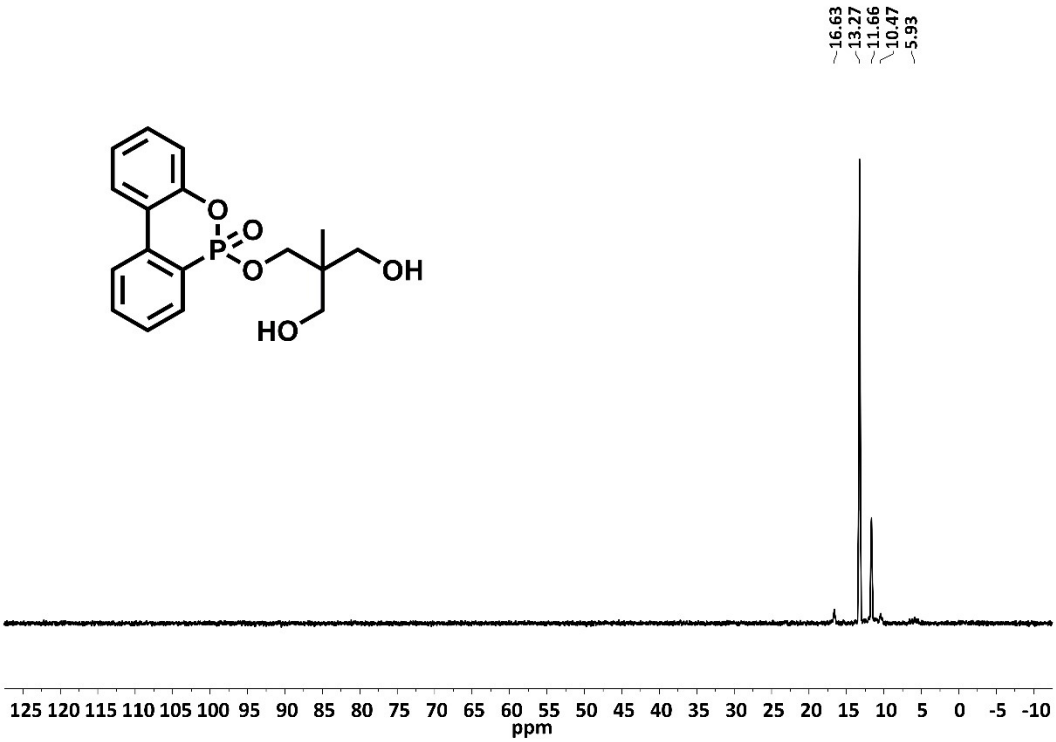


Figure S32. ^{31}P NMR spectrum of **DOPO-Diol** in $CDCl_3$ (202 MHz).

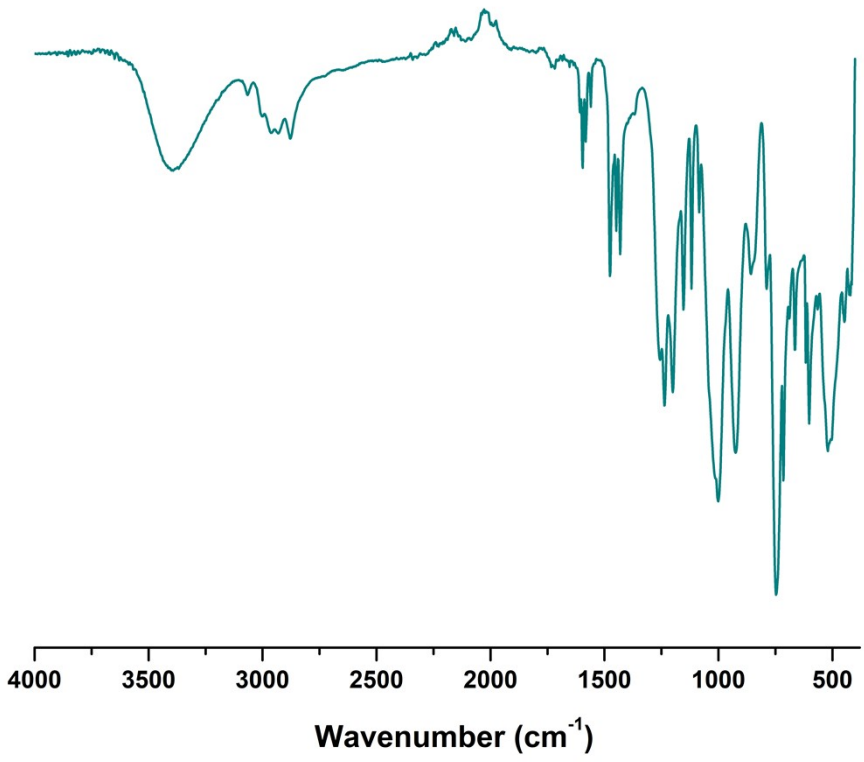
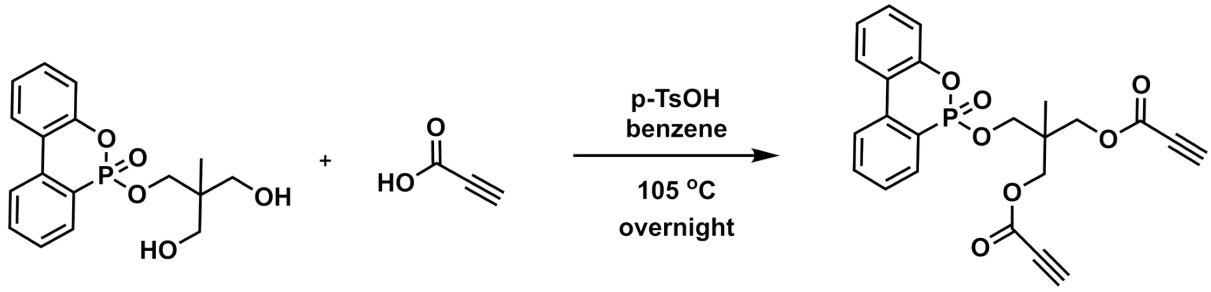


Figure S33. FT-IR spectrum of **DOPO-Diol**.

3.3.5.2. Synthesis of 2-methyl-2-(((6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) oxy)methyl)propane-1,3-diyl dipropiolate (DOPO-Dipropiolate) (e)



DOPO-Dipropiolate (e)

To a 100 mL round bottom flask equipped with a magnetic stir bar were added DOPO-Diol (3.50 g, 10.47 mmol) and 30 mL of benzene. Propiolic acid (2.6 mL, 41.88 mmol) and p-TsOH (0.2 g, 1.05 mmol) were then added to the flask, respectively, and the mixture was allowed to stir under a reflux system equipped with a Dean-Stark apparatus at 105 °C overnight. After the specified time, the reaction mixture was concentrated under reduced pressure, and the crude product was dissolved in 100 mL of DCM and extracted with 100 mL of distilled water three times. The organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness to give compound **e** (DOPO-Dipropiolate) as a viscous brown liquid (yield: 4.3 g, 93%). ^{1}H NMR ($CDCl_3$, δ) 7.95-7.27 (m, 8H, Ar-*H*), 4.10 (s, 2H, P=OOCH_2), 3.94 (m, 4H, C=OOCH_2), 2.92 (s, 2H, C≡C*H*), 0.93 (s, 3H, CCH_3). ^{13}C NMR ($CDCl_3$, δ): 152.07, 149.69, 137.13, 133.80, 130.72, 130.25, 128.47, 124.97, 124.15, 122.50, 122.24, 120.79, 120.12, 77.02, 75.59, 74.08, 66.92, 66.54, 38.98, 16.34. ^{31}P NMR ($CDCl_3$, δ) 10.64, 5.84. ESI-MS, m/z $C_{23}H_{19}O_7P$ calculated: 438.087; found: 439.093 $[M+H]^+$.

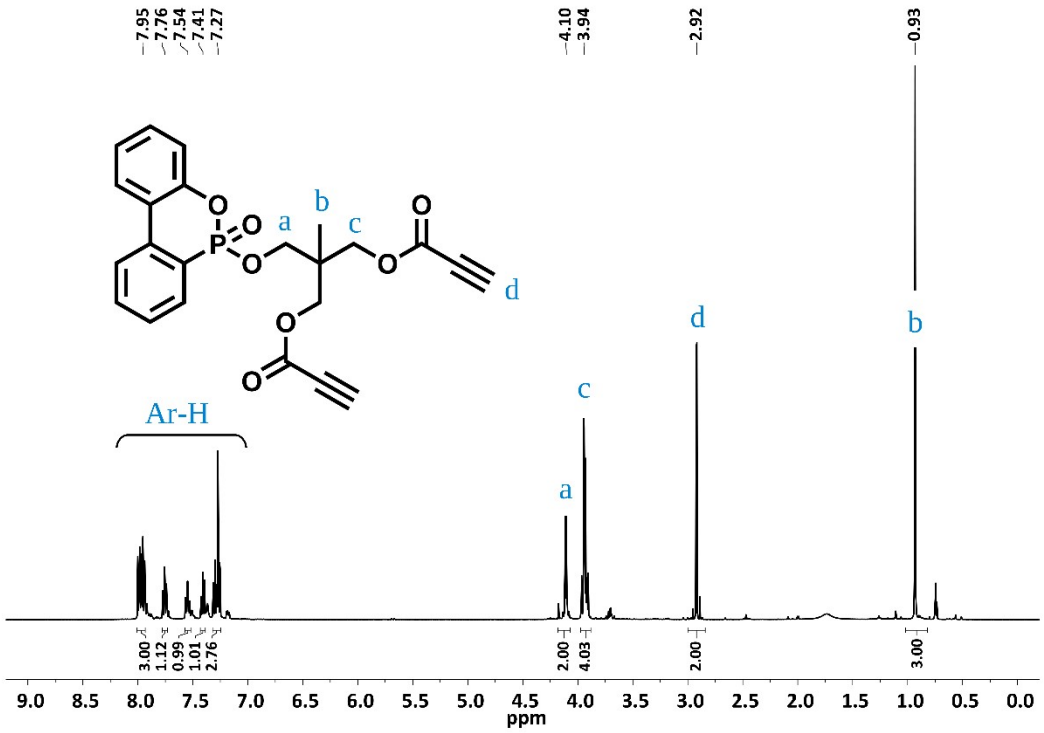


Figure S34. ^{1}H NMR spectrum of **DOPO-Dipropiolate (e)** in $CDCl_3$ (500 MHz).

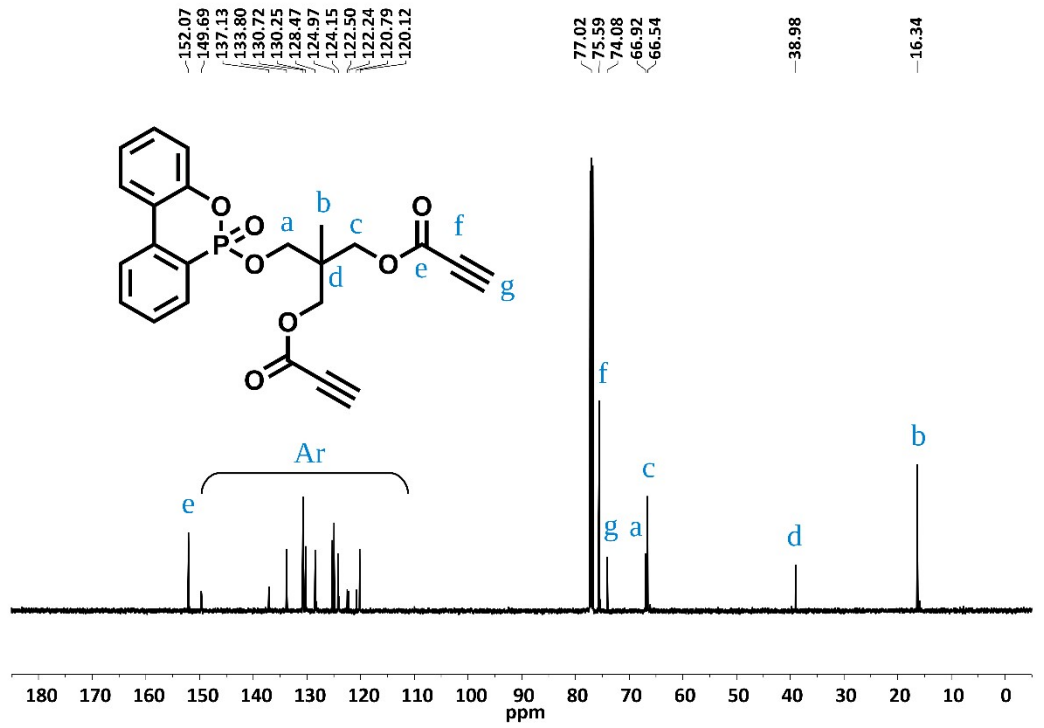


Figure S35. ^{13}C NMR spectrum of **DOPO-Dipropiolate (e)** in $CDCl_3$ (125 MHz).

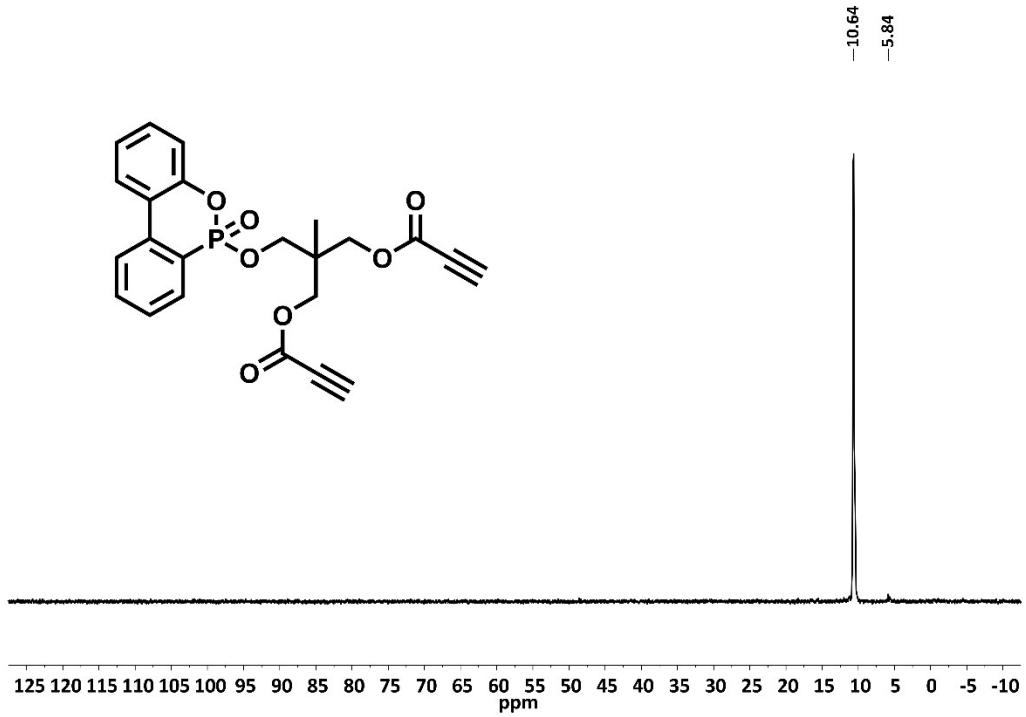


Figure S36. ^{31}P NMR spectrum of **DOPO-Dipropiolate (e)** in $CDCl_3$ (202 MHz).

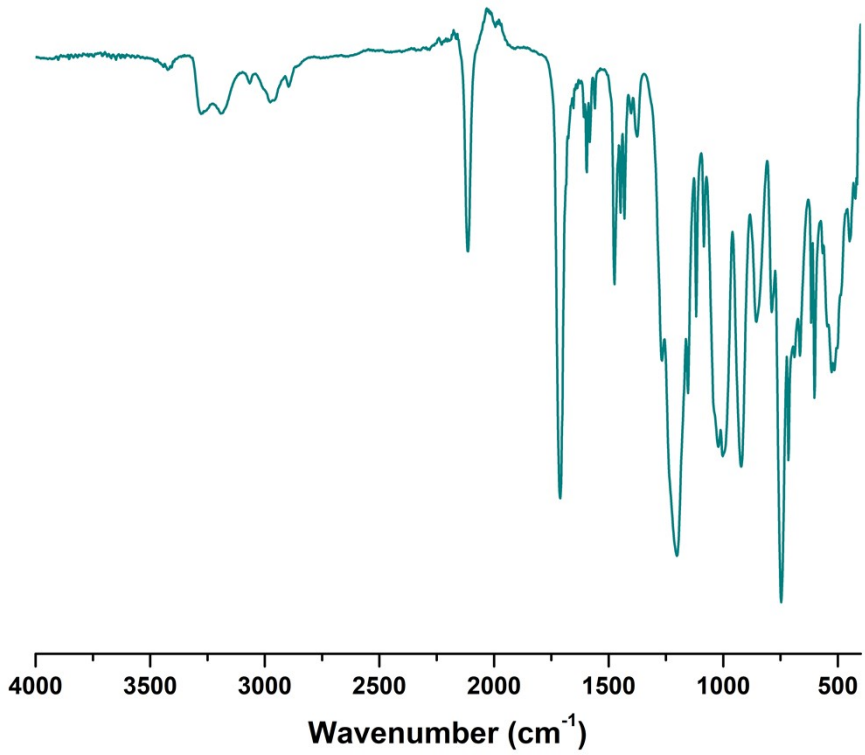
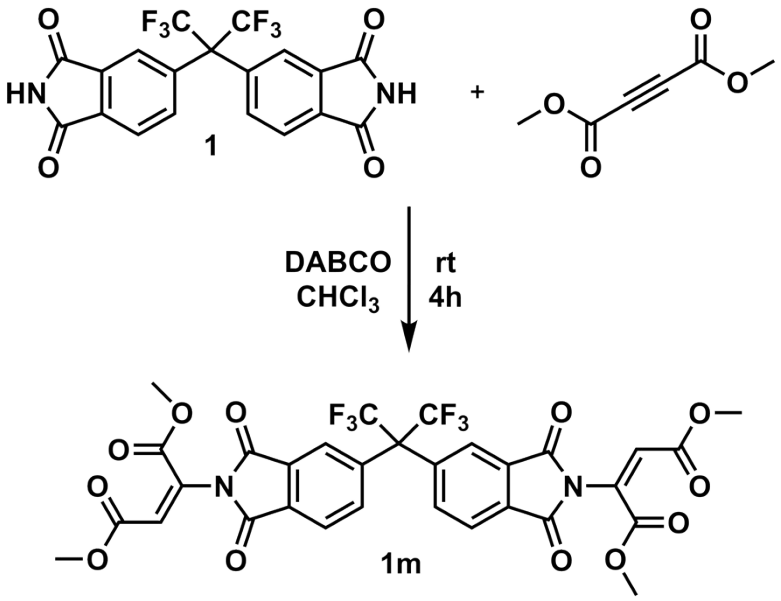


Figure S37. FT-IR spectrum of **DOPO-Dipropiolate (e)**.

3.4. Synthesis of imide-yne monomers from dimethyl acetylenedicarboxylate (1m, 2m, 3m)

3.4.1. Synthesis of tetramethyl 2,2'-((perfluoropropane-2,2-diyl)bis(1,3-dioxoisoindoline-5,2-diyl))dimaleate (1m)



To a 10 mL round bottom flask equipped with a magnetic stir bar was added compound **1** (774 mg, 1.75 mmol) and suspended in 7 mL of $CHCl_3$. DMAD (648.7 μL, 5.25 mmol) and DABCO (49 mg, 0.44 mmol) were added to the reaction medium, respectively, and the mixture was allowed to stir at room temperature for 4 hours. After the specified time, the solution was diluted with 30 mL of DCM and extracted with 30 mL of acidified water three times. The organic layers were collected and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. After that, the solution was precipitated into hexane and filtered. The dissolution-precipitation ($CHCl_3$-hexane) procedure was repeated two times. The resultant product (**1m**) was dried in a vacuum oven at 40 °C overnight and obtained as an off-white solid (yield: 1.1 g, 86%). ^{1}H NMR ($CDCl_3$, δ): 8.01-7.77 (m, 6H, Ar-*H*), 7.22-6.72 (s, 2H, NC=C*H*), 3.91-3.76 (m, 12H, OCH_3). ^{13}C NMR ($CDCl_3$, δ): 164.31, 163.04, 162.01, 139.22, 136.33, 132.93, 131.44, 129.19, 125.41, 124.44, 119.60, 65.20, 53.60, 52.57. ^{19}F NMR ($CDCl_3$, δ): -63.19. ESI-MS, m/z $C_{31}H_{20}F_6N_2O_{12}$ calculated: 726.092; found: 744.125 $[M+NH_4]^+$.

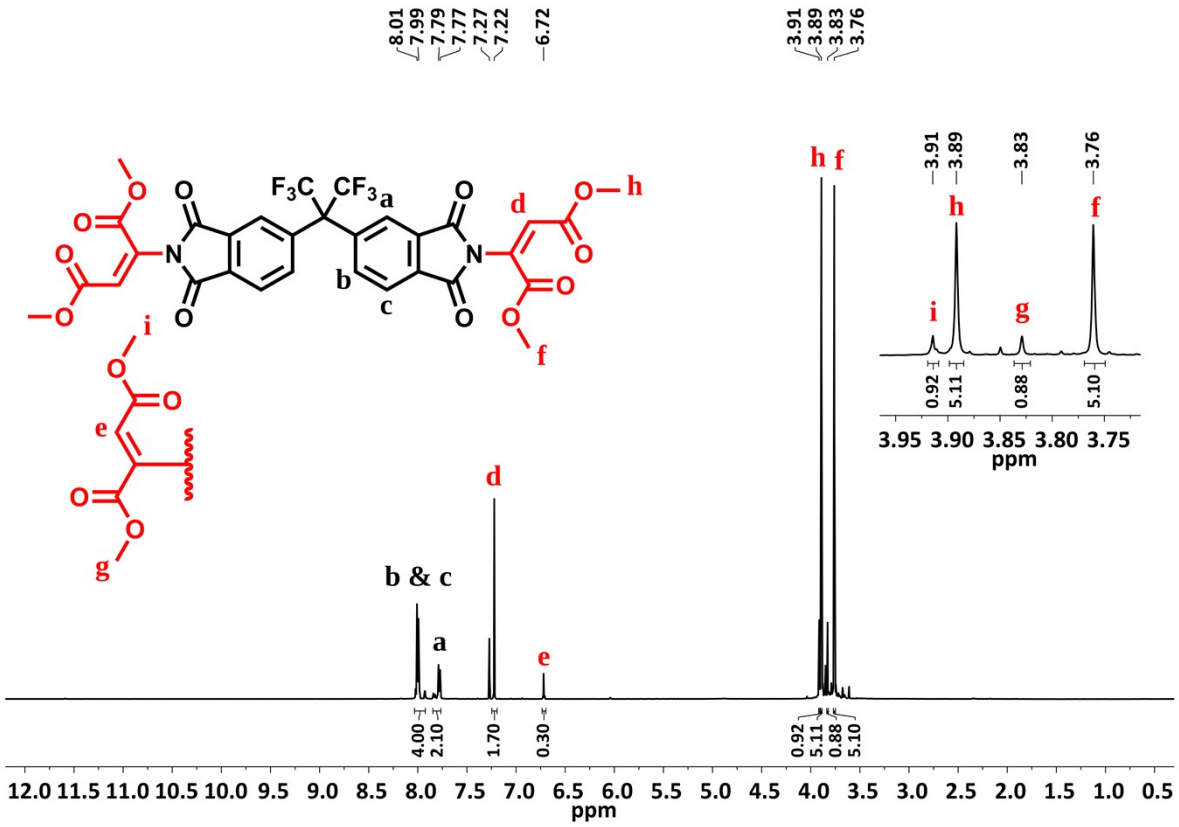


Figure S38. ^{1}H NMR spectrum of **1m** in $CDCl_3$ (500 MHz).

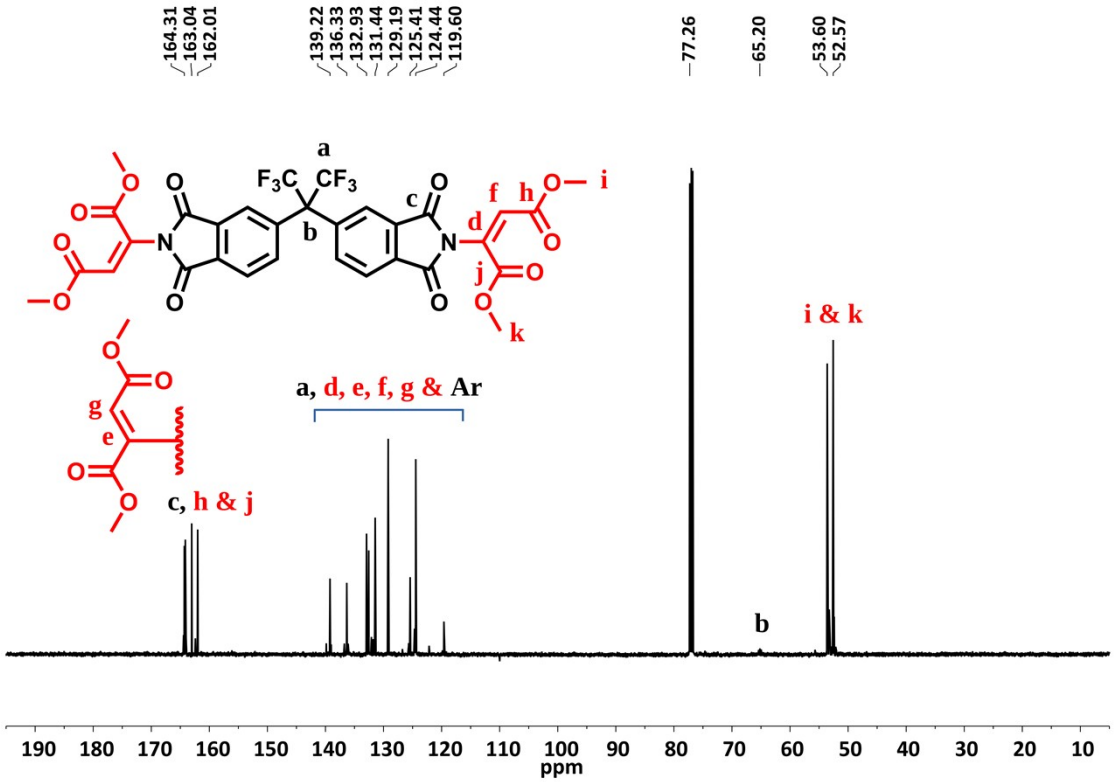


Figure S39. ^{13}C NMR spectrum of **1m** in $CDCl_3$ (125 MHz).

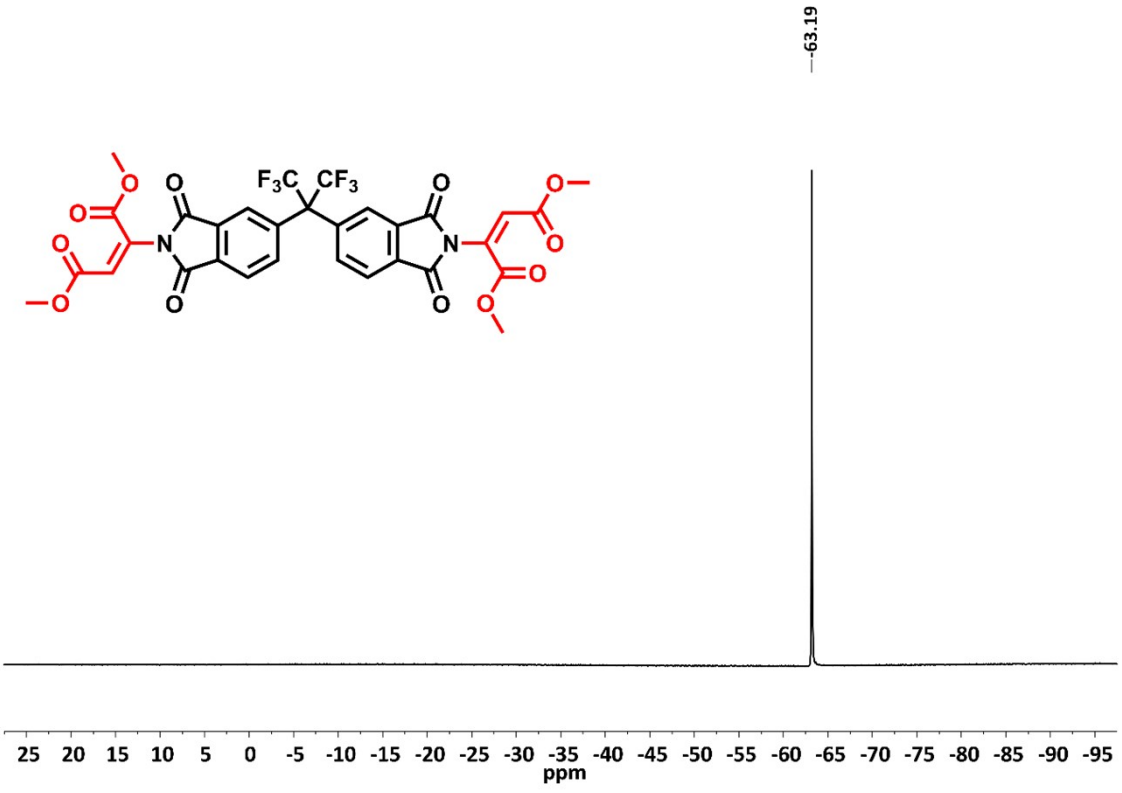


Figure S40. ^{19}F NMR spectrum of **1m** in $CDCl_3$ (470 MHz).

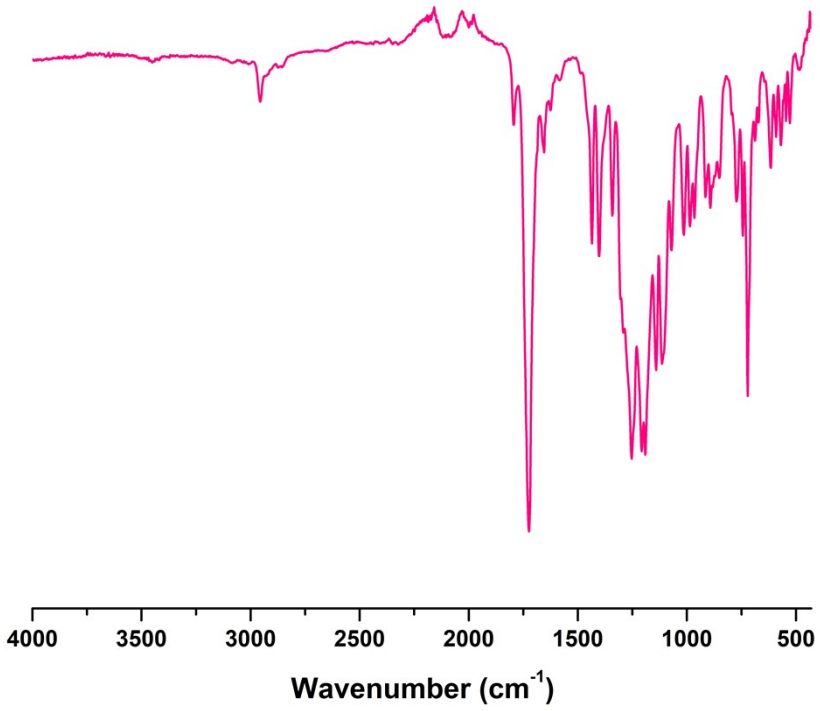
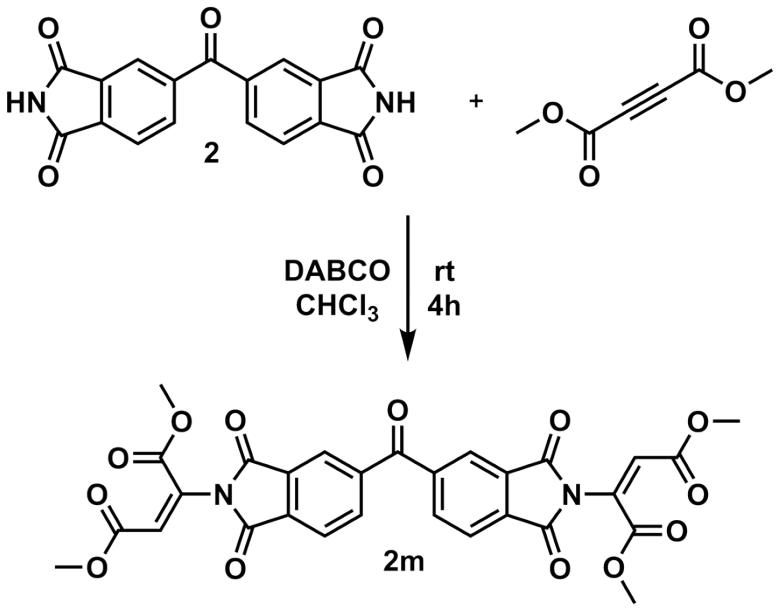


Figure S41. FT-IR spectrum of **1m.**

3.4.2. Synthesis of tetramethyl 2,2'-(carbonylbis(1,3-dioxoisoindoline-5,2-diyl))dimaleate (2m)



To a 10 mL round bottom flask equipped with a magnetic stir bar was added compound **2** (400 mg, 1.25 mmol) and suspended in 5 mL of $CHCl_3$. DMAD (463.4 μL, 3.75 mmol) and DABCO (35 mg, 0.31 mmol) were added to the reaction medium, respectively, and the mixture was allowed to stir at room temperature for 4 hours. After the specified time, the solution was diluted with 30 mL of DCM and extracted with 30 mL of acidified water three times. The organic layers were collected and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. After that, the solution was precipitated into hexane and filtered. The dissolution-precipitation ($CHCl_3$-hexane) procedure was repeated two times. The resultant product (**2m**) was dried in a vacuum oven at 40 °C overnight and obtained as a pale brown solid (yield: 483.6 mg, 64%). ^{1}H NMR ($CDCl_3$, δ): 8.29-8.11 (m, 6H, Ar-*H*), 7.23-6.75 (s, 2H, NC=C*H*), 3.92-3.75 (m, 12H, OCH_3). ^{13}C NMR ($CDCl_3$, δ): 192.57, 164.36, 163.20, 162.00, 141.87, 135.88, 135.28, 132.51, 131.47, 129.26, 125.05, 124.64, 119.39, 53.63, 52.59. ESI-MS, m/z $C_{29}H_{20}N_2O_{13}$ calculated: 604.097; found: 622.129 $[M+NH_4]^+$.

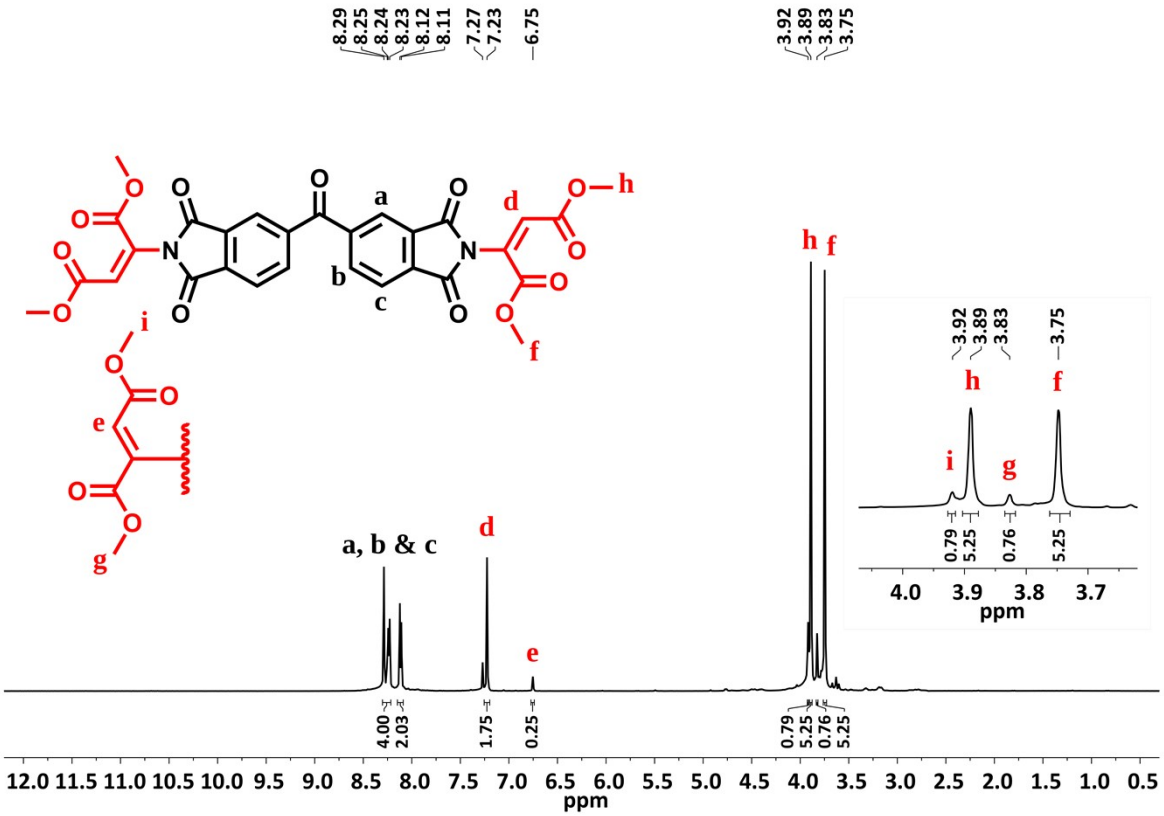


Figure S42. ^{1}H NMR spectrum of **2m** in $CDCl_3$ (500 MHz).

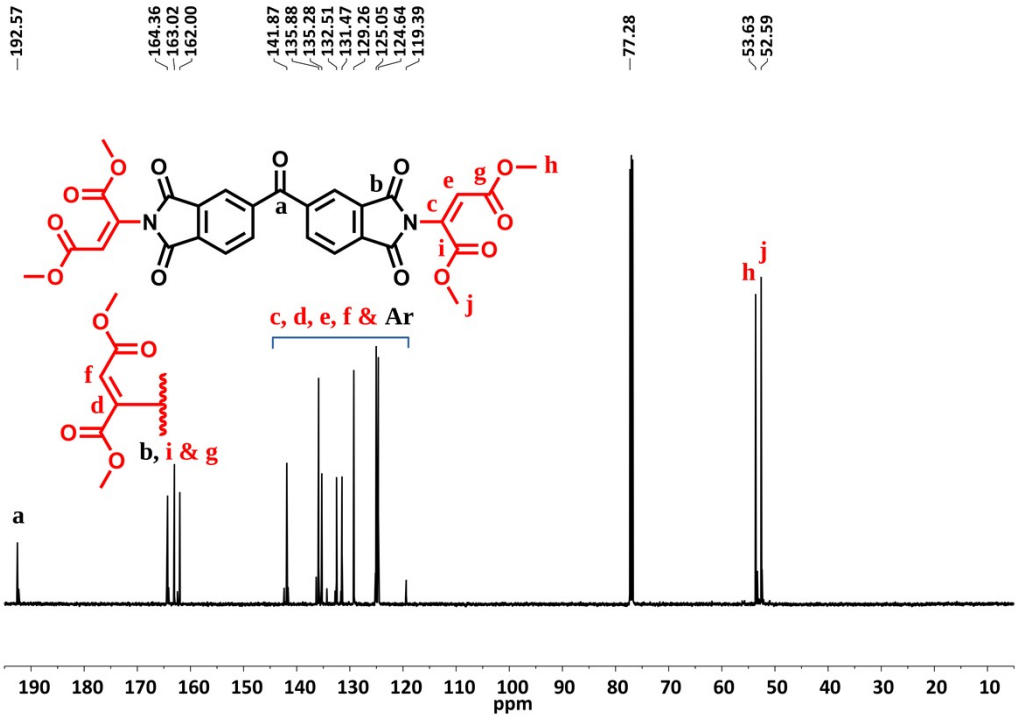


Figure S43. ^{13}C NMR spectrum of **2m** in $CDCl_3$ (125 MHz).

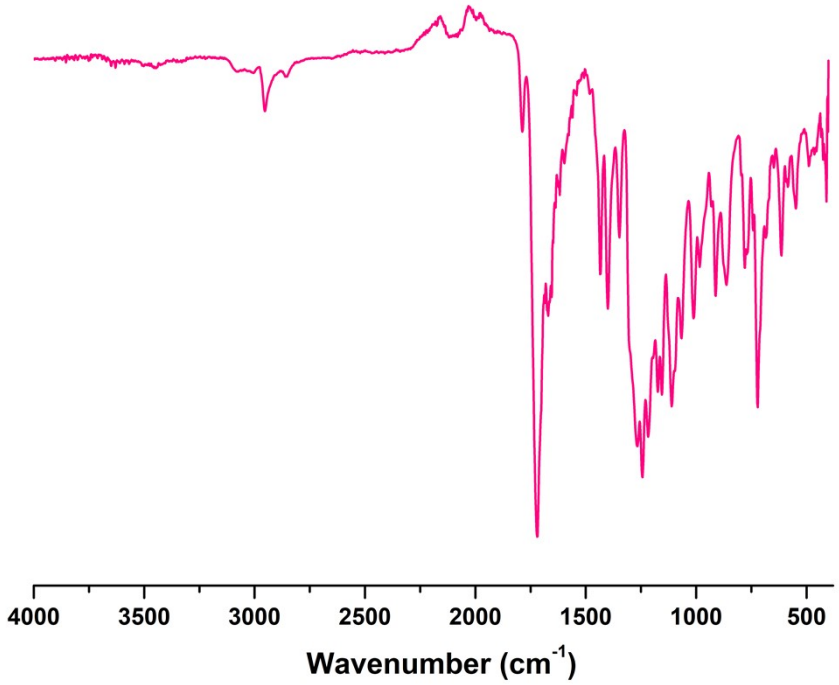
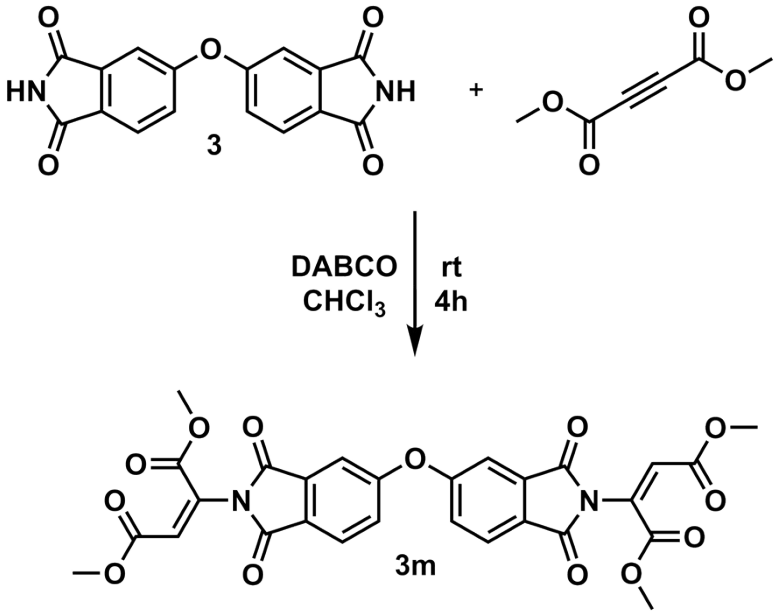


Figure S44. FT-IR spectrum of **2m.**

3.4.3. Synthesis of tetramethyl 2,2'-(oxybis(1,3-dioxoisoindoline-5,2-diyl))dimaleate (3m)



To a 10 mL round bottom flask equipped with a magnetic stir bar was added compound **3** (665 mg, 2.15 mmol) and suspended in 8.6 mL of $CHCl_3$. DMAD (797 µL, 6.45 mmol) and DABCO (60 mg, 0.54 mmol) were added to the reaction medium, respectively, and the mixture was allowed to stir at room temperature for 4 hours. After the specified time, the solution was diluted with 30 mL of DCM and extracted with 30 mL of acidified water three times. The organic layers were collected and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. After that, the solution was precipitated into hexane and filtered. The dissolution-precipitation ($CHCl_3$-hexane) procedure was repeated two times. The resultant product (**3m**) was dried in a vacuum oven at 40 °C overnight and obtained as a pale brown solid (yield: 802.5 mg, 63%). ^{1}H NMR ($CDCl_3$, δ): 7.99-7.45 (m, 6H, Ar-*H*), 7.18-6.72 (s, 2H, NC=C*H*), 3.91-3.74 (m, 12H, OCH_3). ^{13}C NMR ($CDCl_3$, δ): 164.49, 163.09, 162.18, 161.12, 134.86, 131.55, 128.84, 127.66, 126.56, 124.91, 118.12, 114.36, 53.53, 52.49. ESI-MS, m/z $C_{28}H_{20}N_2O_{13}$ calculated: 592.097; found: 610.129 $[M+NH_4]^+$.

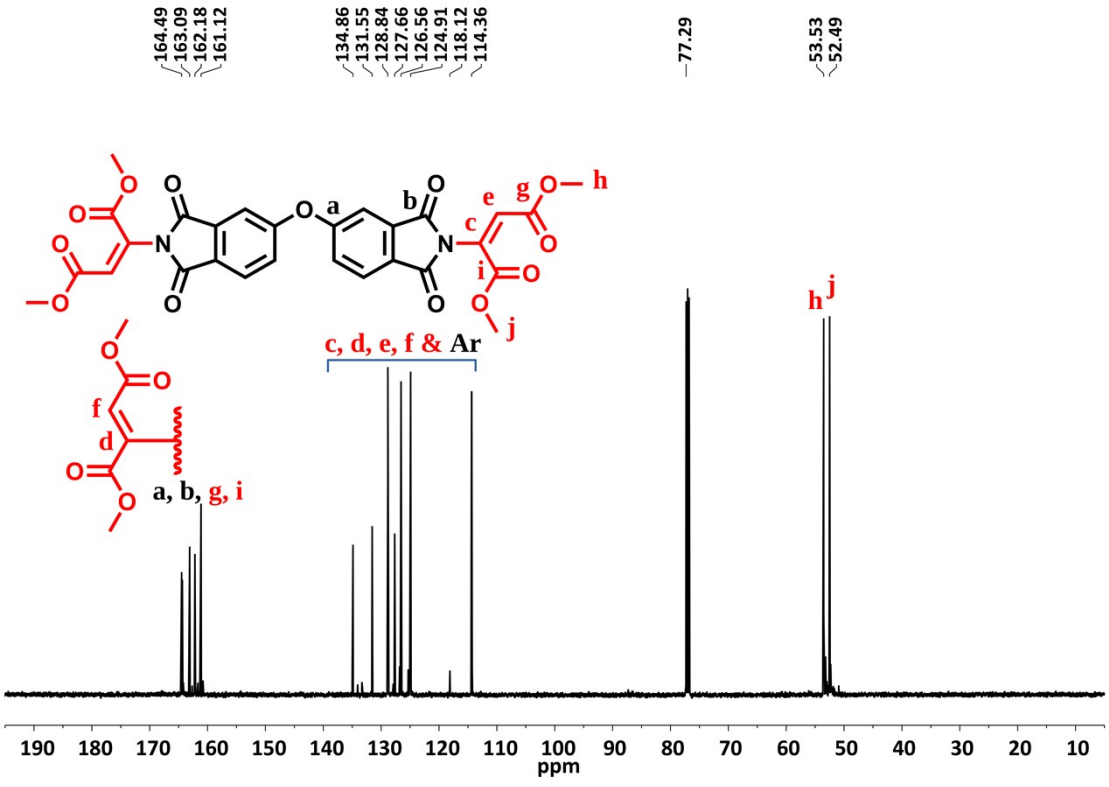


Figure S45. ^{13}C NMR spectrum of **3m** in $CDCl_3$ (125 MHz).

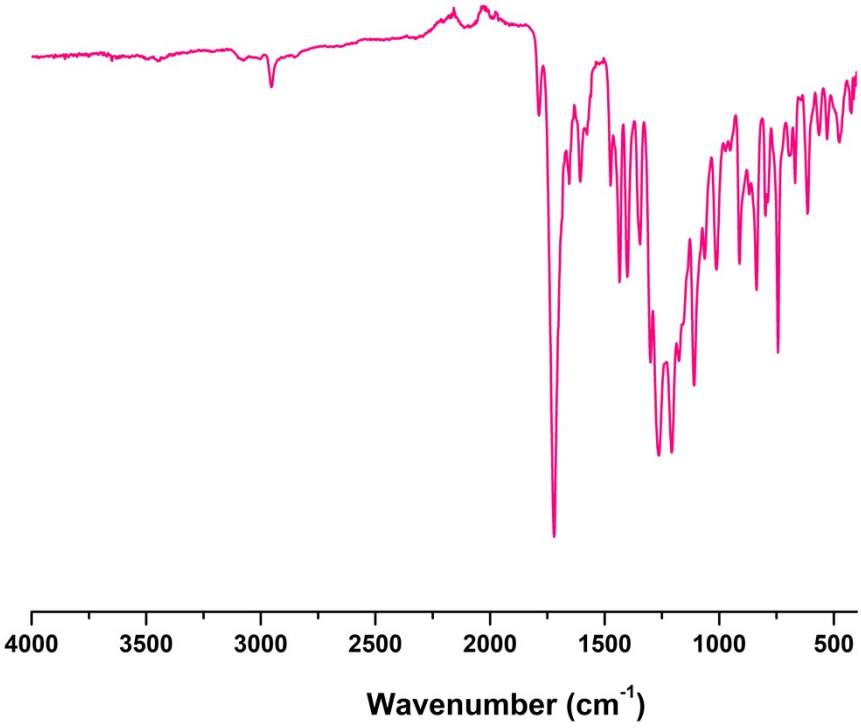
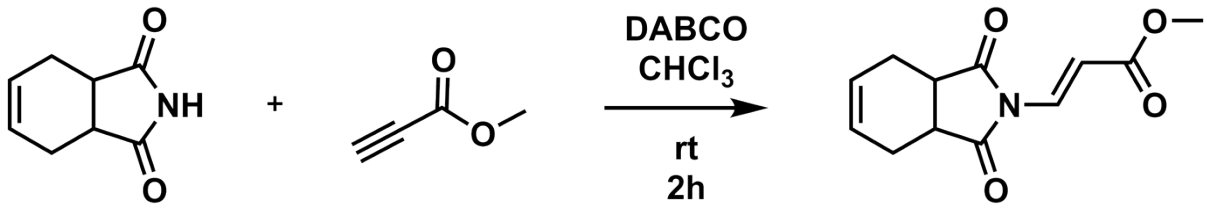


Figure S46. FT-IR spectrum of **3m.**

3.5. Imide-yne Model Reactions

3.5.1. Synthesis of methyl (E)-3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)acrylate (Model-1)



To a 25 mL round bottom flask equipped with a magnetic stir bar was added cis-1,2,3,6-tetrahydrophthalimide (303 mg, 2 mmol) and dissolved in 8 mL of $CHCl_3$. Methyl propiolate (213.5 µL, 2.4 mmol) and DABCO (22.4 mg, 0.2 mmol) were added to the reaction medium, respectively. After the addition of DABCO, an exothermic reaction occurred and the color of

the solution turned pale yellow. The mixture was allowed to stir at room temperature for 2 hours. After the specified time, the solution was diluted with 20 mL of DCM and extracted two times with 30 mL of distilled water and 30 mL of acidified water. Organic layers were dried over Na_2SO_4, filtered, and dried under reduced pressure to give a white viscous product (yield: 420 mg, 89%). ^{1}H NMR ($CDCl_3$, δ): 7.68-5.65 (m, 2H, NC*H* & NCH=C*H*), 5.91 (q, 2H, C=OCHCH$_2$C*H*), 3.77 (m, 3H, OCH_3), 3.18 (q, 2H, C=OC*H*), 2.62-2.30 (m, 4H, C=OCHCH_2). ^{13}C NMR ($CDCl_3$, δ): 177.56, 177.01, 167.21, 166.41, 157.35, 146.23, 130.98, 127.71, 126.75, 121.24, 117.44, 110.48, 103.94, 51.78, 39.25, 38.75, 23.54. ESI-MS, m/z $C_{12}H_{13}NO_4$ calculated: 235.084; found: 236.091 $[M+H]^+$.

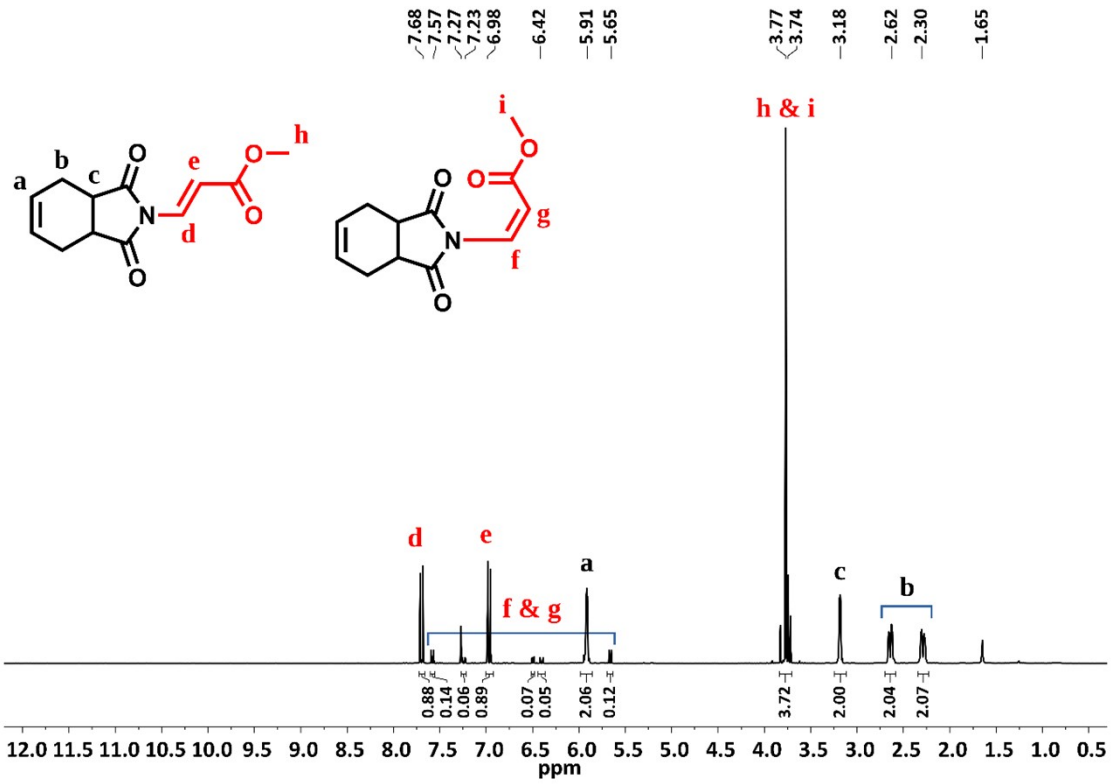


Figure S47. ^{1}H NMR spectrum of **Model-1** in $CDCl_3$ (500 MHz).

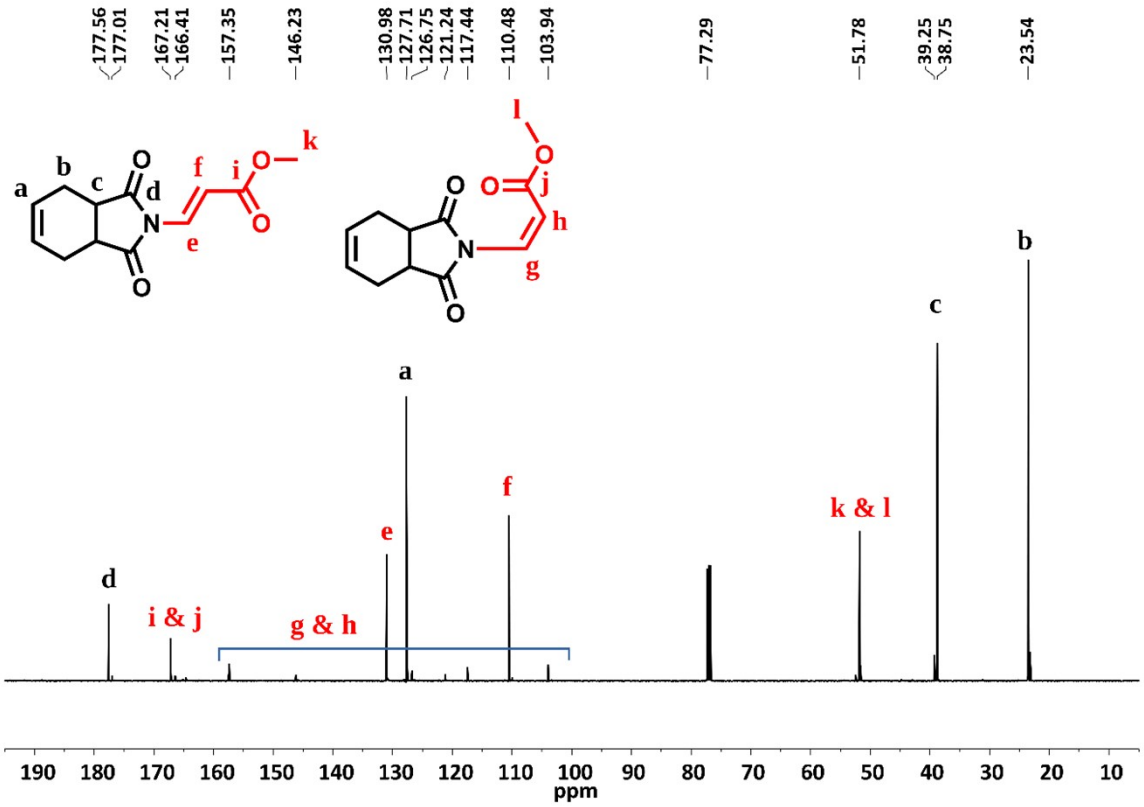


Figure S48. ^{13}C NMR spectrum of **Model-1** in $CDCl_3$ (125 MHz).

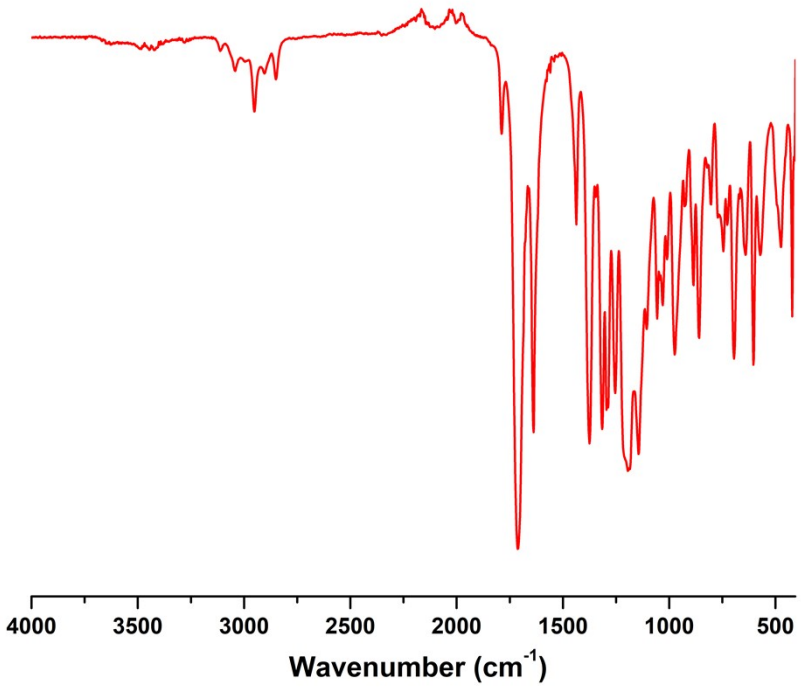
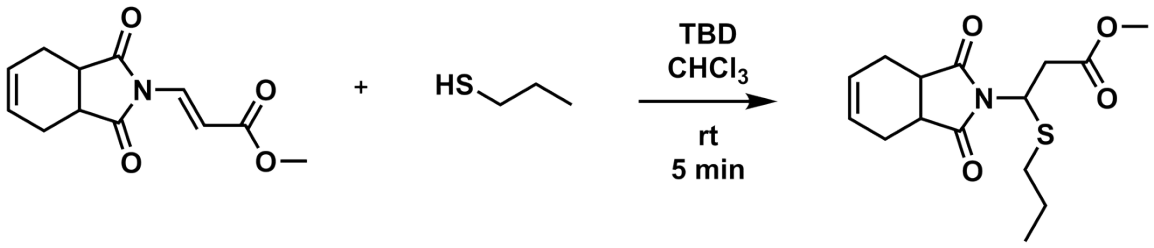


Figure S49. FT-IR spectrum of **Model-1.**

3.5.2. Further Modification: Synthesis of methyl 3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)-3-(propylthio)propanoate (Modified Model-1)



To a 10 mL round bottom flask equipped with a magnetic stir bar was added methyl (E)-3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)acrylate (470.5 mg, 2 mmol) and dissolved in 2 mL of $CHCl_3$. 1-propanethiol (544 μL, 6 mmol) and TBD (69.6 mg, 0.5 mmol) were added to the reaction medium respectively. Upon the addition of TBD, the color of the solution turned yellow. The mixture was allowed to stir at room temperature for 5 minutes. After the specified time, the solution was diluted with 20 mL of DCM and extracted two times with 20 mL of acidified water. Organic layers were dried over Na_2SO_4, filtered, and dried under reduced pressure to give a yellow viscous product (yield: 257 mg, 82%). ^{1}H NMR ($CDCl_3$, δ): 5.89 (q, 2H, C=OCHCH_2C*H*), 5.48 (t, 1H, NC*H*), 3.64 (s, 3H, OCH_3), 3.31-3.00 (m, 2H, NCHCH_2), 3.06 (m, 2H, C=OC*H*), 2.59-2.21 (m, 4H, C=OCHCH_2), 2.55-2.46 (m, 2H, SCH_2), 1.58 (m, 2H, SCH$_2$CH_2), 0.93 (t, 3H, SCH$_2$CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, δ): 179.10, 169.90, 127.80, 127.56, 51.92, 51.42, 38.83, 36.97, 34.17, 23.53, 22.72, 13.33. ESI-MS, m/z $C_{15}H_{21}NO_4S$ calculated: 311.119; found: 312.126 $[M+H]^+$.

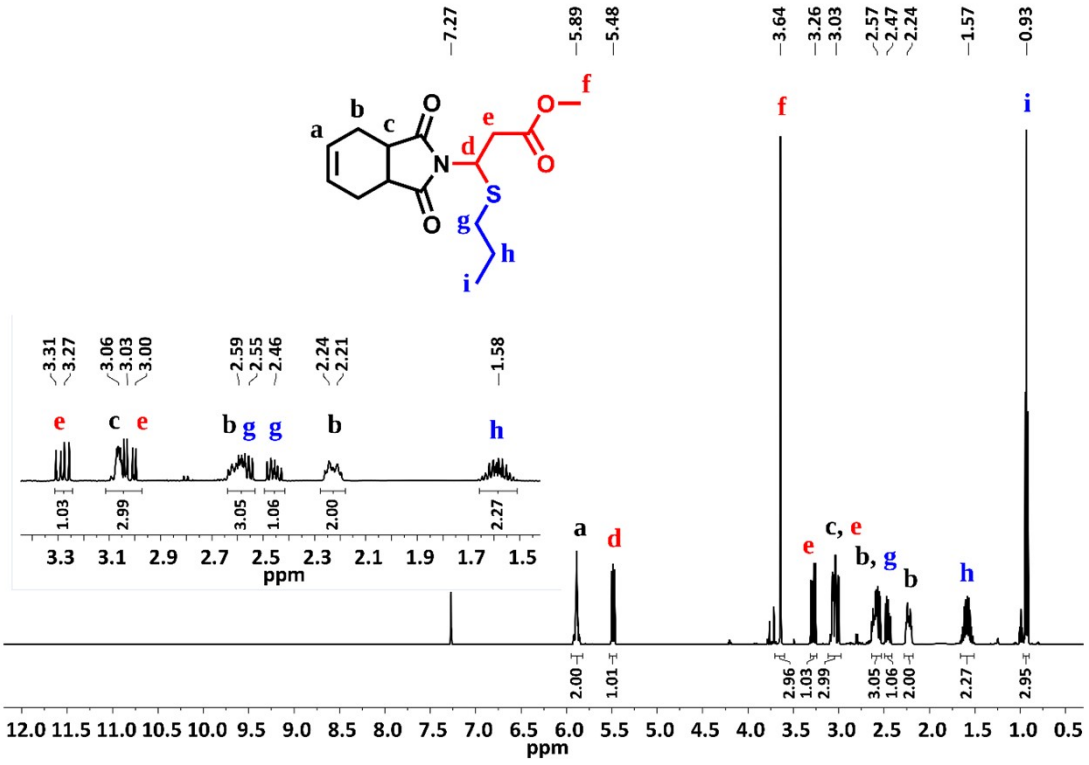


Figure S50. ^{1}H NMR spectrum of **modified Model-1** in $CDCl_3$ (500 MHz).

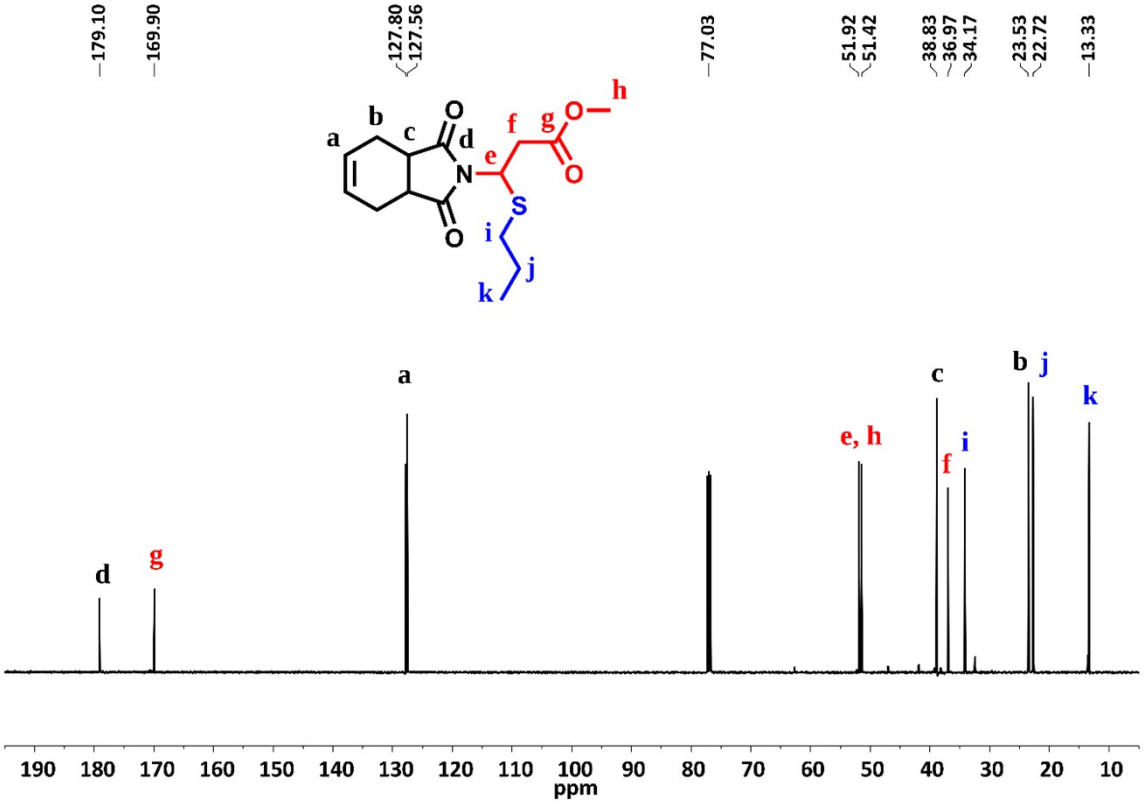


Figure S51. ^{13}C NMR spectrum of **modified Model-1** in $CDCl_3$ (125 MHz).

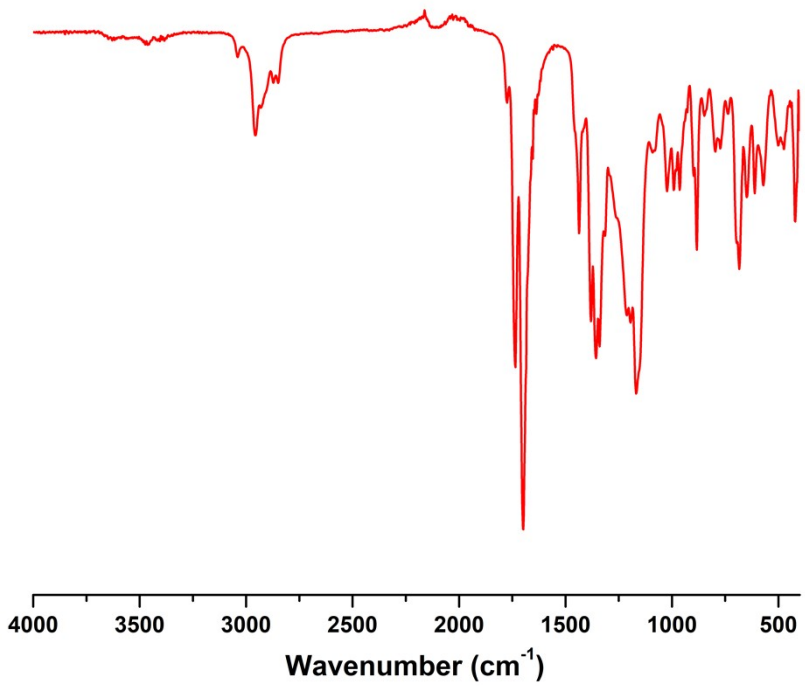
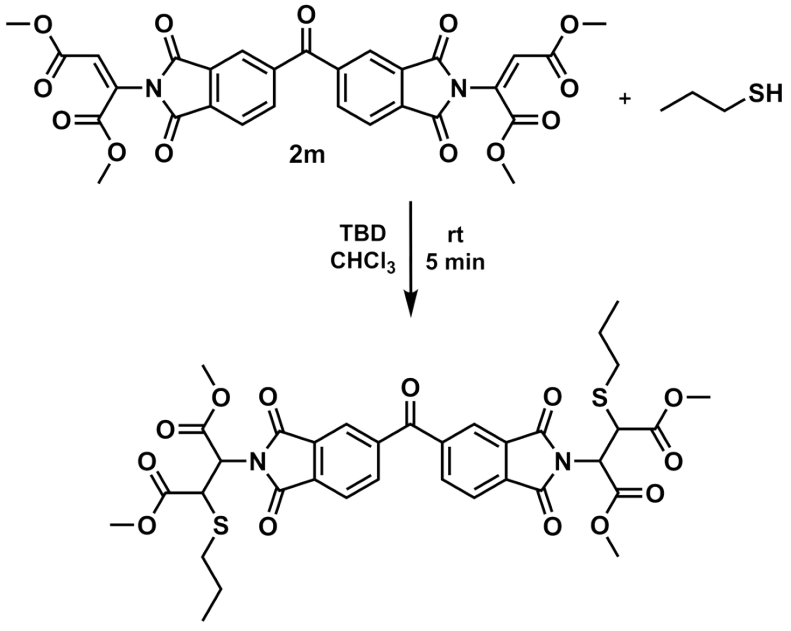


Figure S52. FT-IR spectrum of **modified Model-1.**

3.5.3. Model reaction for thiol-ene polymerization of imide-yne monomer: Synthesis of Tetramethyl 3,3'-(carbonylbis(1,3-dioxoisoindoline-5,2-diyl))bis(2-(propylthio)succinate) (Model-2)



To a 10 mL round bottom flask with a magnetic stir bar was added **2m** (754.8 mg, 1 mmol) and dissolved in 2 mL of $CHCl_3$. 1-propanethiol (272 µL, 3 mmol) and TBD (34.8 mg, 0.25 mmol) were then added to the reaction medium, respectively. The mixture was allowed to stir at room temperature for 5 minutes. Upon the addition of TBD, an exothermic reaction occured and the pale yellow solution turned to dark brown instantly. After the specified time, the solution was diluted with 20 mL of DCM and extracted with acidified water twice. The organic layers were collected and dried over Na_2SO_4, filtered, and evaporated to dryness to give the **Model-2** compound as a yellow solid (yield: 666 mg, 88%). ^{1}H NMR ($CDCl_3$, δ): 8.24-8.10 (m, 6H, Ar-*H*), 5.43 (d, 2H, NC*H*), 4.27 (m, 2H, SC*H*), 3.86 (s, 6H, NCHC=OOCH_3), 3.75 (s, 6H, SCHC=OOCH_3), 2.54 (m, 4H, SCH_2), 1.45 (m, 4H, SCH$_2$CH_2), 0.86 (t, 6H, SCH$_2$CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, δ): 192.68, 170.51, 168.01, 165.91, 141.81, 135.77, 134.92, 132.07, 124.39, 53.39, 52.79, 51.44, 45.04, 32.51, 22.19, 13.25.

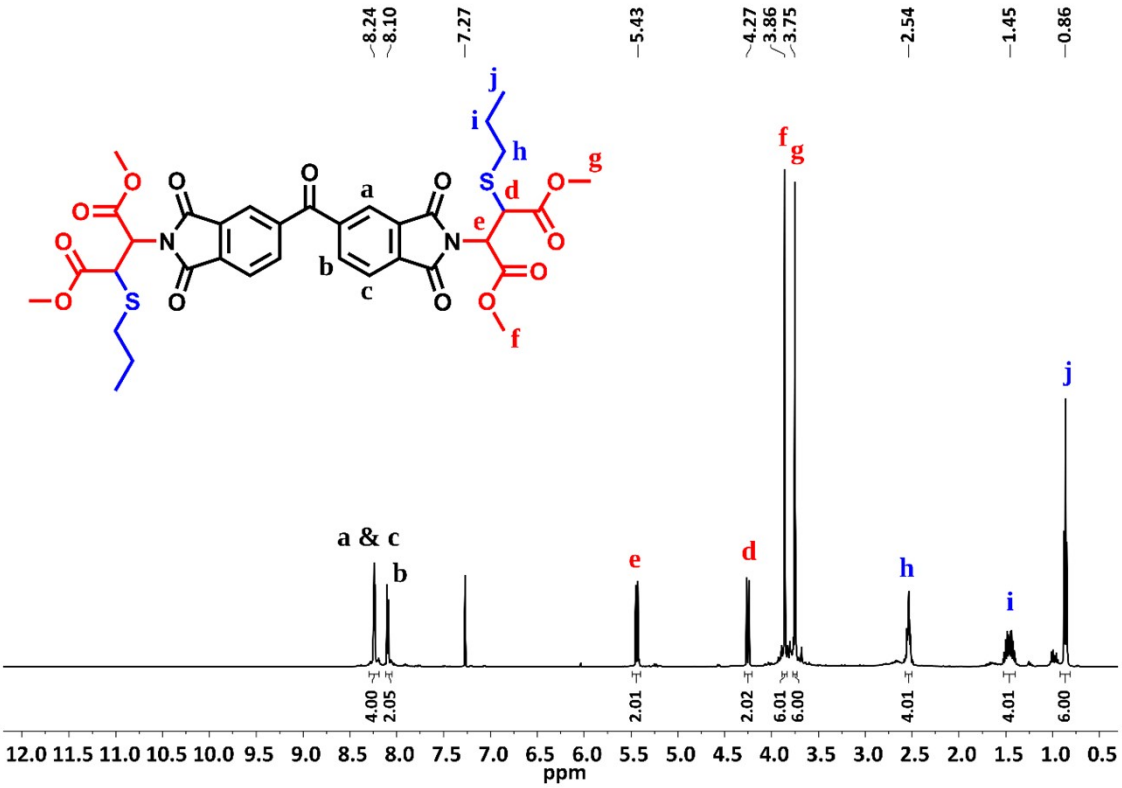


Figure S53. ^{1}H NMR spectrum of **Model-2** in $CDCl_3$ (500 MHz).

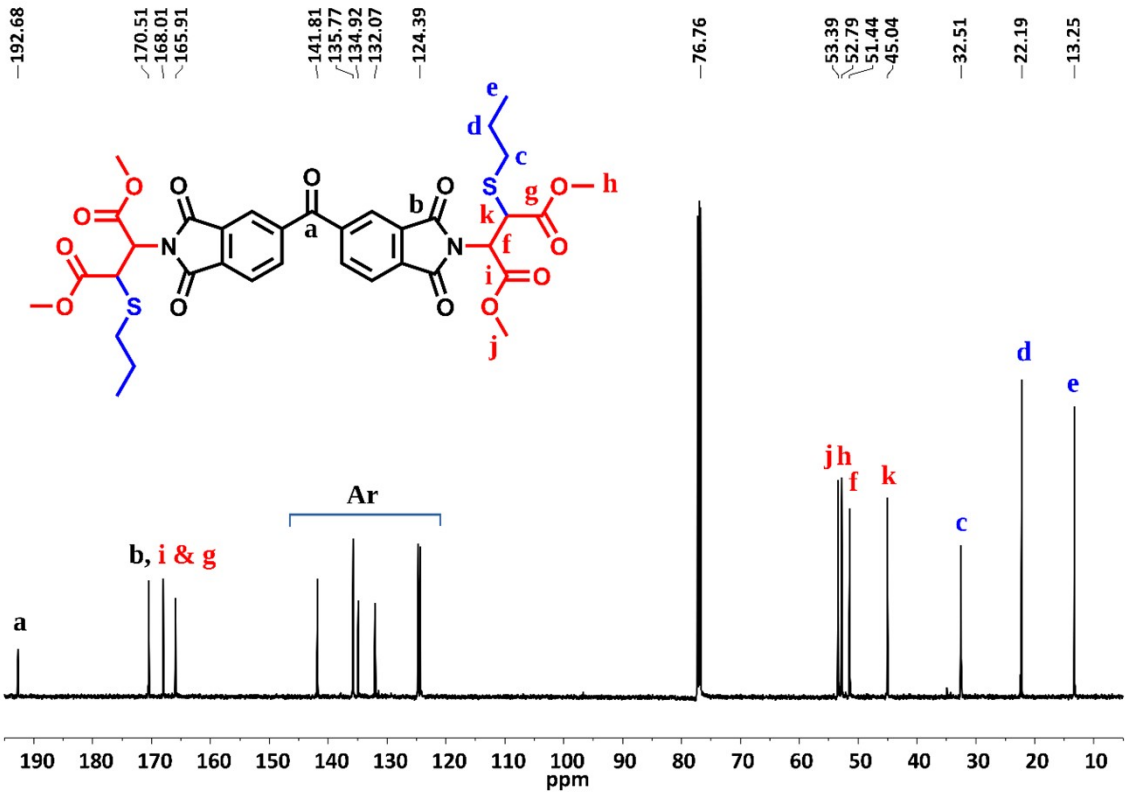
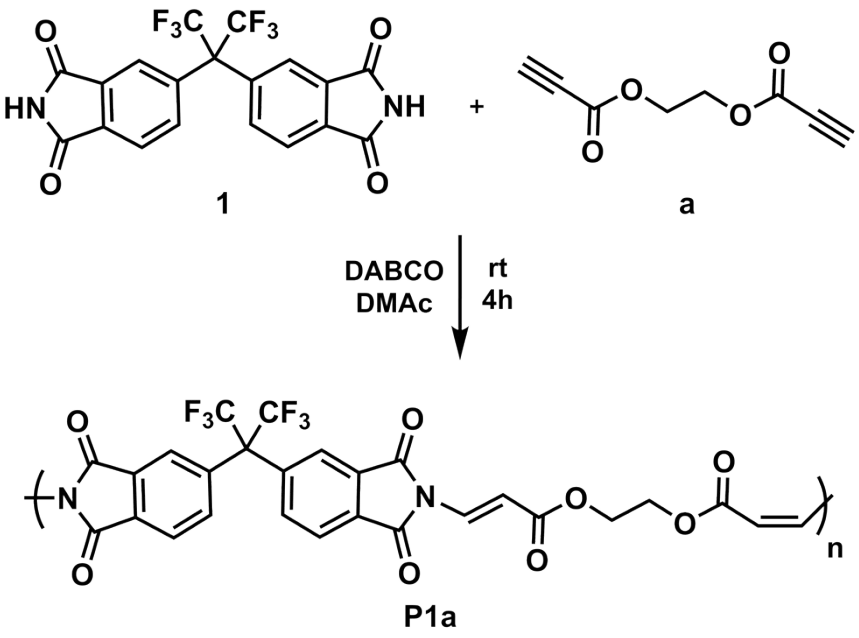


Figure S54. ^{13}C NMR spectrum of **Model-2** in $CDCl_3$ (125 MHz).

3.6. Imide-Yne Click Polymerization for Poly(Imide Esters)s

3.6.1. Synthesis of P1a



General procedure for imide-yne click polymerization was followed: Compound **a** (50 mg, 0.3 mmol), compound **1** (132.7 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol), and DMAc (1.2 mL) were used. The resultant polymer **P1a** was obtained as a pale-yellow powder (yield: 164 mg, 90%). ^{1}H NMR (d_6-DMSO, δ): 8.16-5.53 (br, 10H, Ar-*H* & NC*H* & NCH=C*H*), 4.43 (br, 4H, C=OOCH_2). ^{13}C NMR (d_6-DMSO, δ): 168.18, 166.11, 164.47, 137.96, 136.55, 133.95, 132.26, 131.53, 124.95, 124.20, 122.04, 119.76, 106.71, 100.38, 64.36, 62.39. ^{19}F NMR (d_6-DMSO, δ): -62.95.

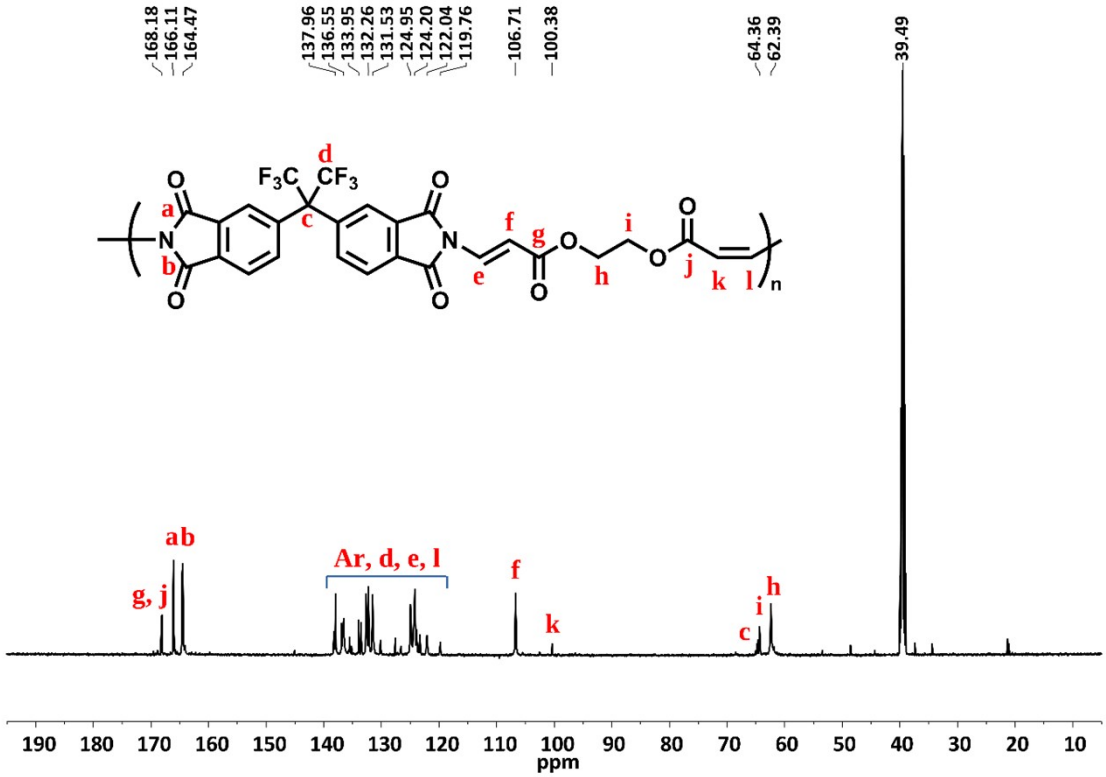


Figure S55. ^{13}C NMR spectrum of **P1a** in d_6-DMSO (125 MHz).

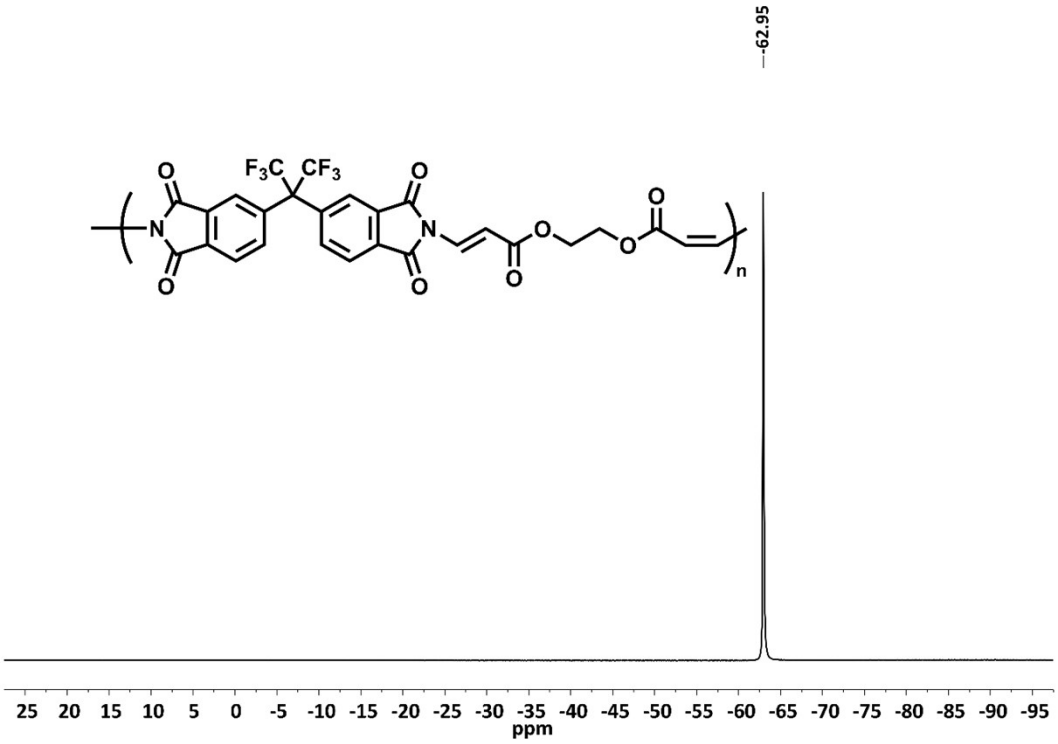


Figure S56. ^{19}F NMR spectrum of **P1a** in d_6-DMSO (470 MHz).

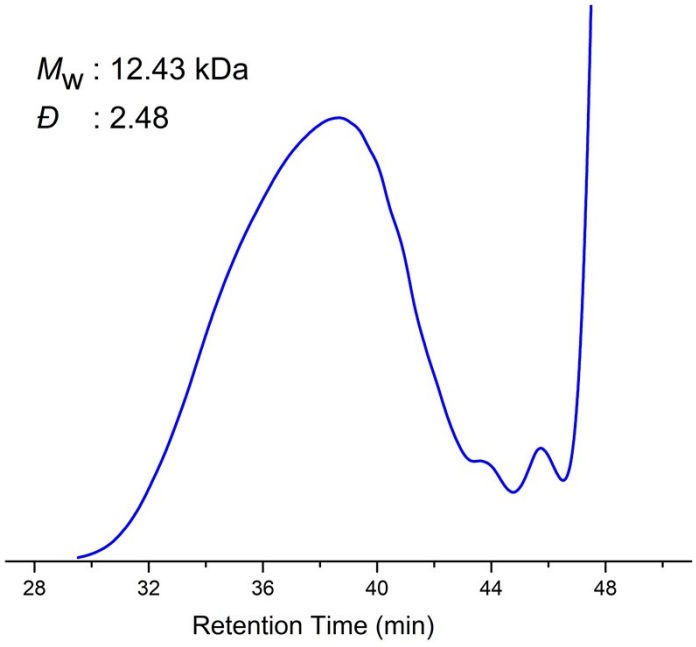


Figure S57. GPC trace of **P1a**.

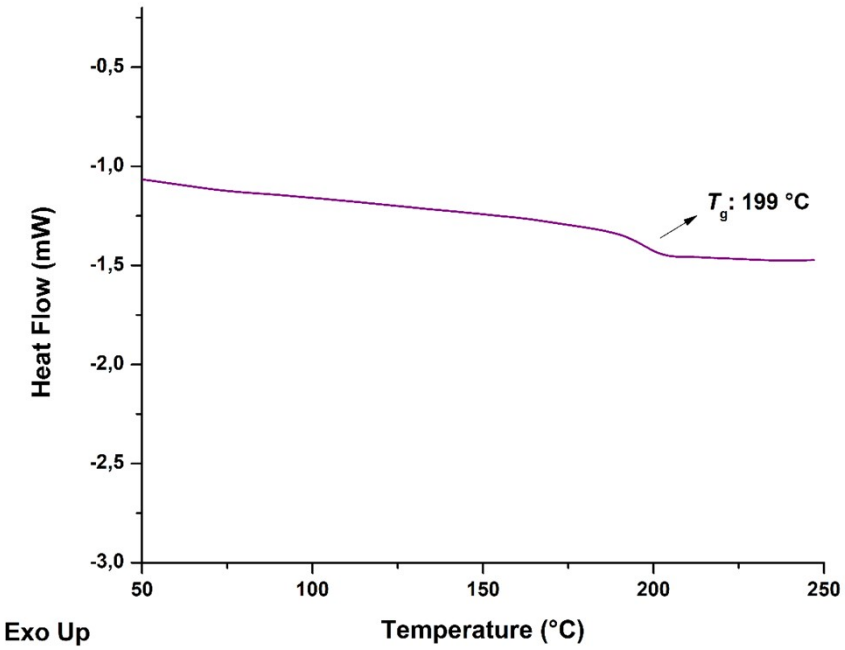


Figure S58. DSC spectrum of **P1a**.

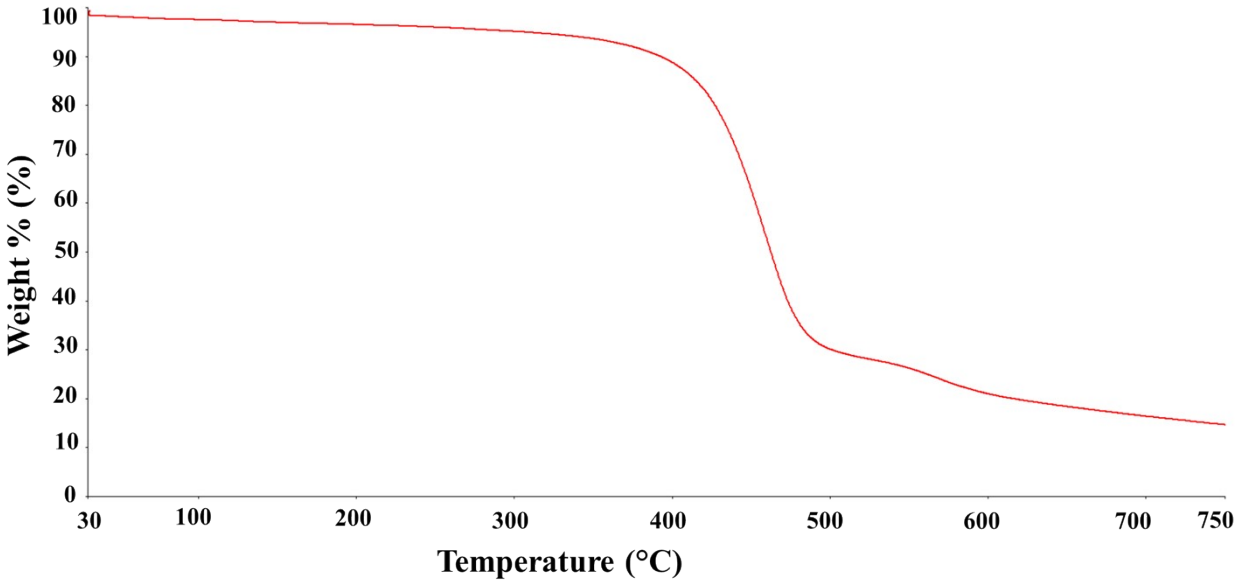


Figure S59. TGA thermogram of **P1a**.

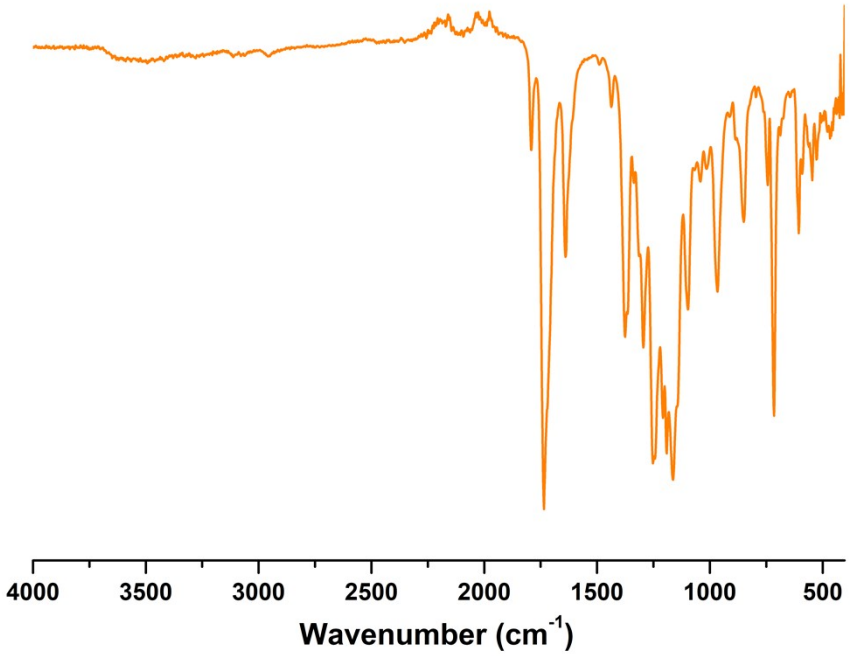
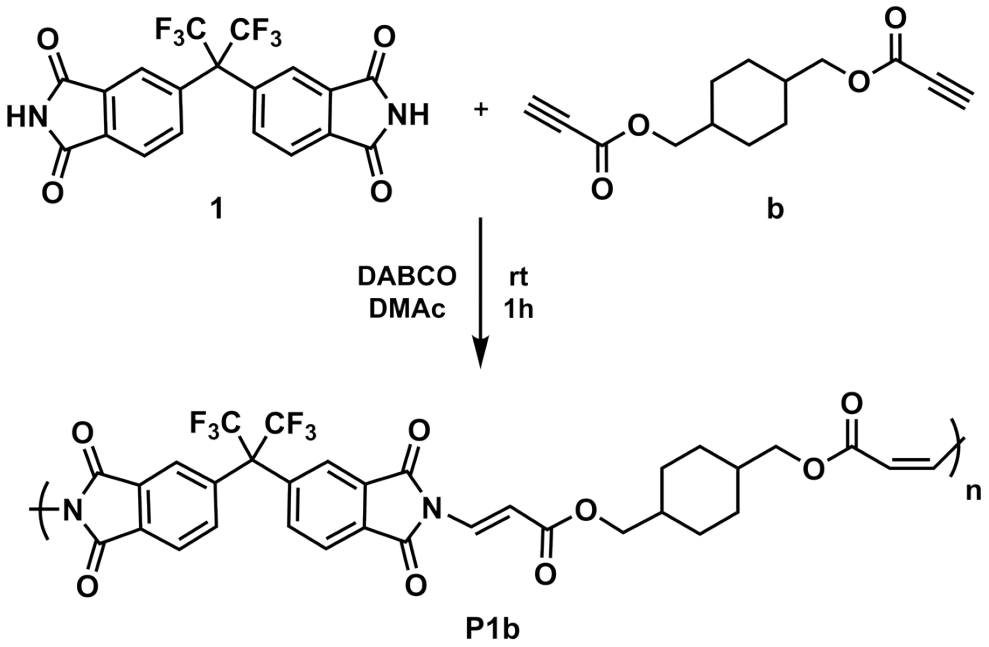


Figure S60. FT-IR spectrum of **P1a.**

3.6.2. Synthesis of P1b



General procedure for imide-yne click polymerization was followed: Compound **b** (74.5 mg, 0.3 mmol), Compound **1** (132.7 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. Polymerization proceeded for 1 hour at room temperature. The resultant polymer **P1b** was obtained as a pale-yellow powder (yield: 170.2 mg, 82%). ^{1}H NMR (d_6-DMSO, δ): 8.17-5.63 (br, 10H, Ar-*H* & NC*H* & NCH=C*H*), 3.97 (br, 4H, C=OOCH_2), 1.61-1.01 (br, 10H, C=OOCH$_2$C*H* & C=OOCH$_2$CHCH_2). ^{13}C NMR (d_6-DMSO, δ): 168.65, 166.71, 164.97, 138.29, 136.91, 133.97, 132.76, 131.59, 125.40, 124.55, 122.49, 120.18, 107.51, 103.25, 70.93, 69.41, 65.03, 37.07, 28.71, 25.19. ^{19}F NMR (d_6-DMSO, δ): -62.90.

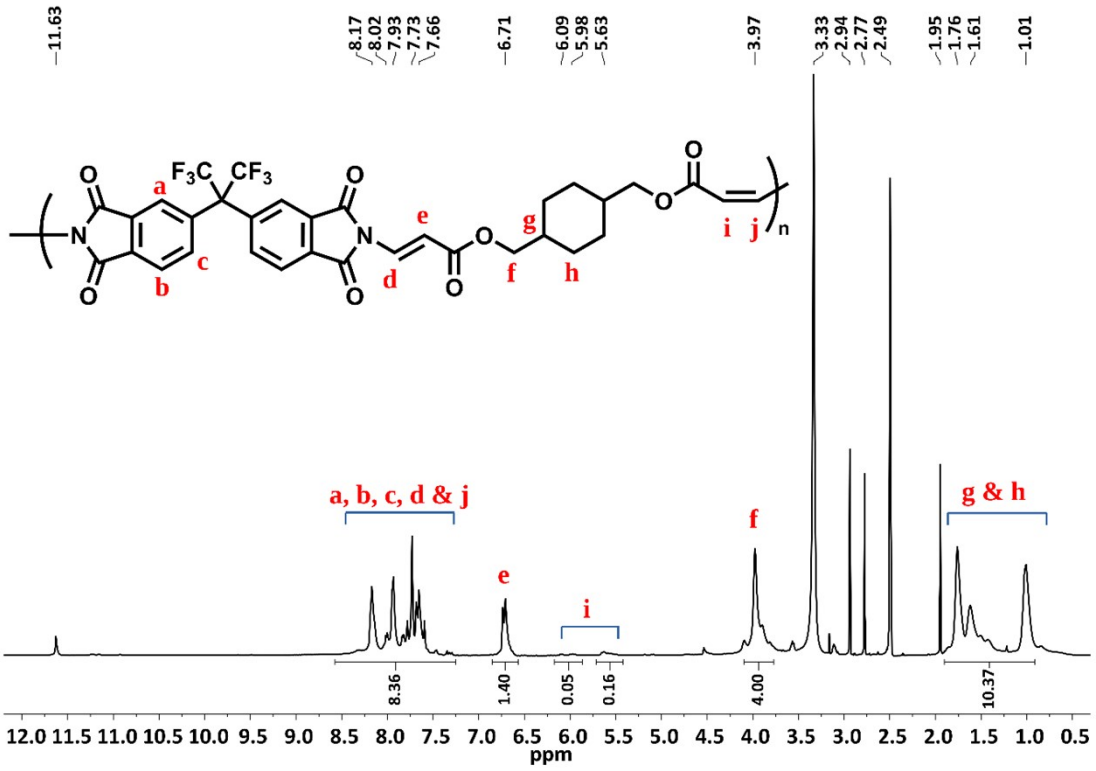


Figure S61. ^{1}H NMR spectrum of **P1b** in d_6-DMSO (500 MHz).

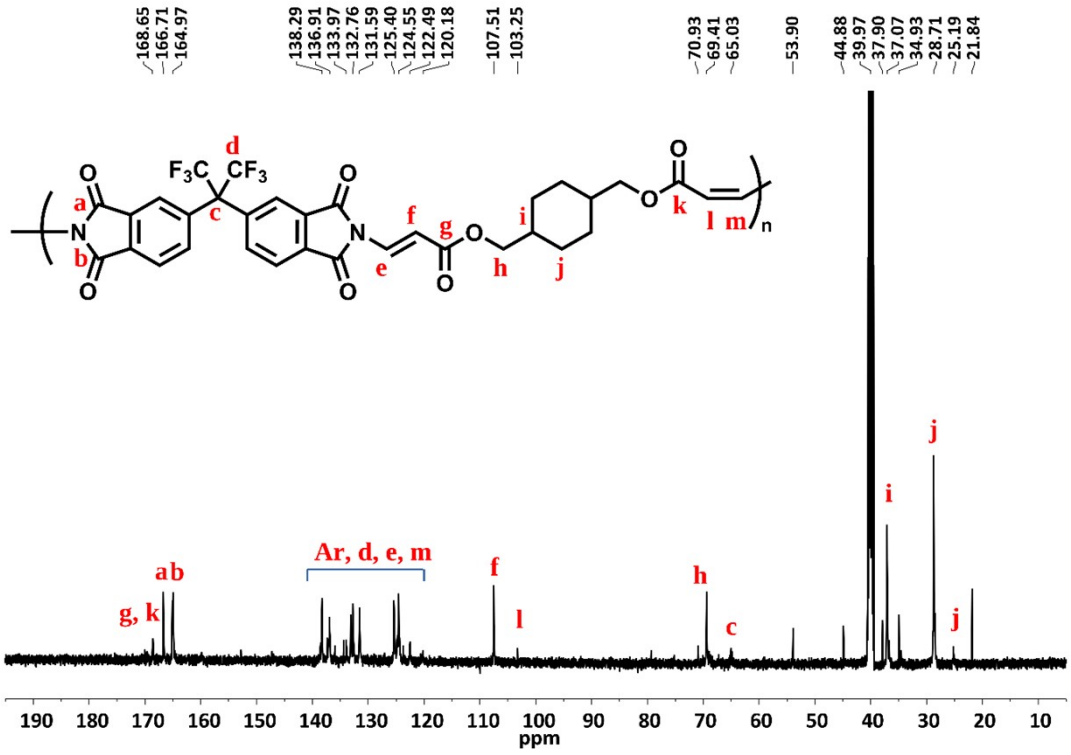


Figure S62. ^{13}C NMR spectrum of **P1b** in d_6-DMSO (125 MHz).

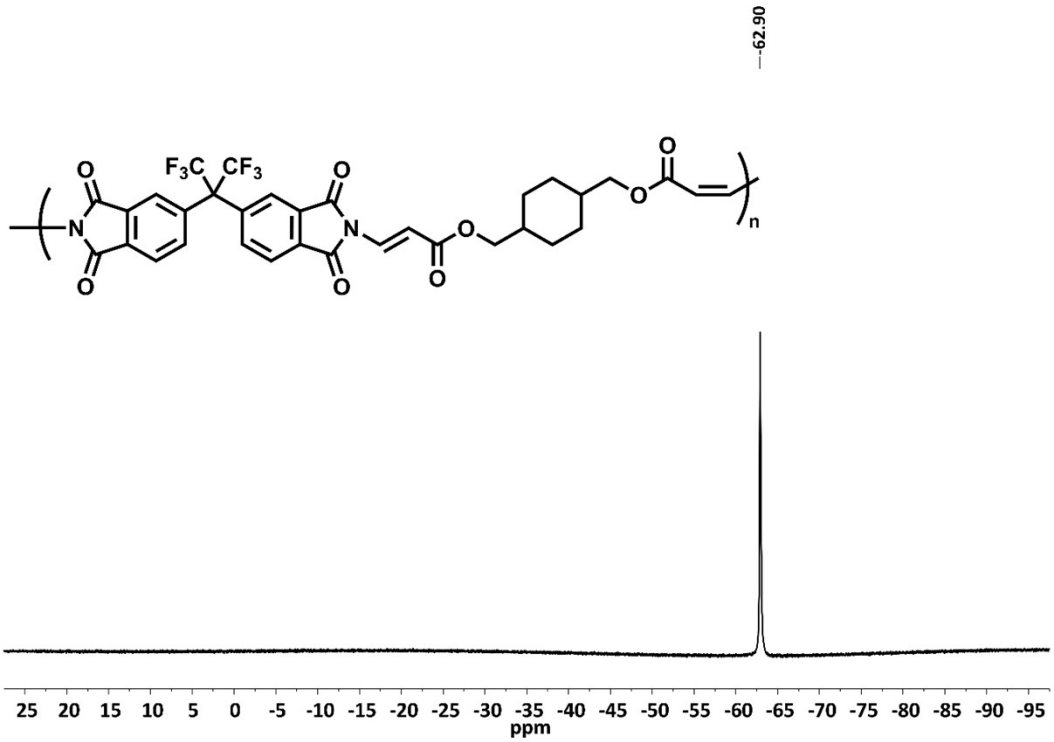


Figure S63. ^{19}F NMR spectrum of **P1b** in d_6-DMSO (470 MHz).

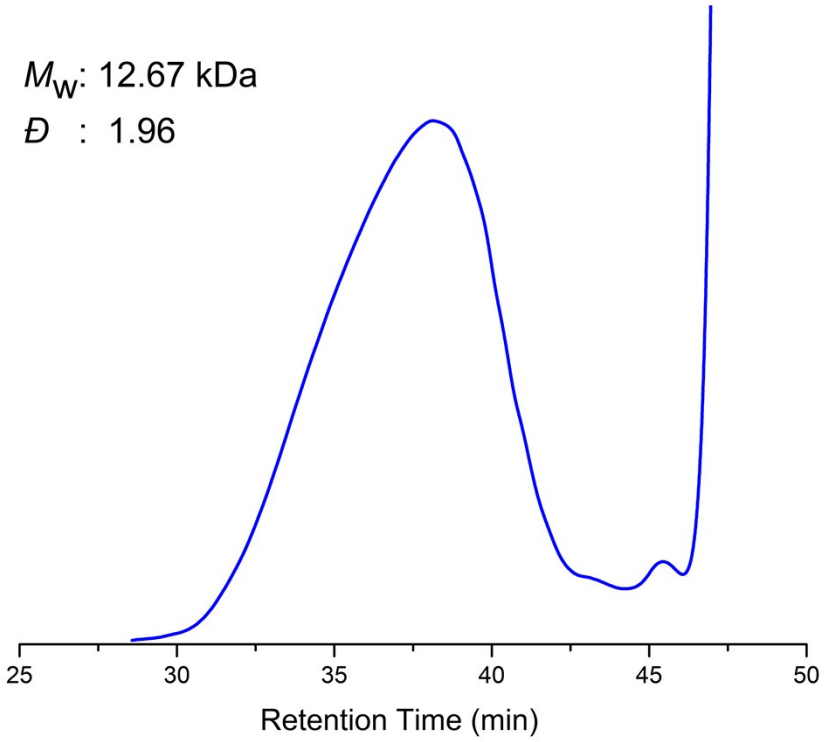


Figure S64. GPC trace of **P1b**.

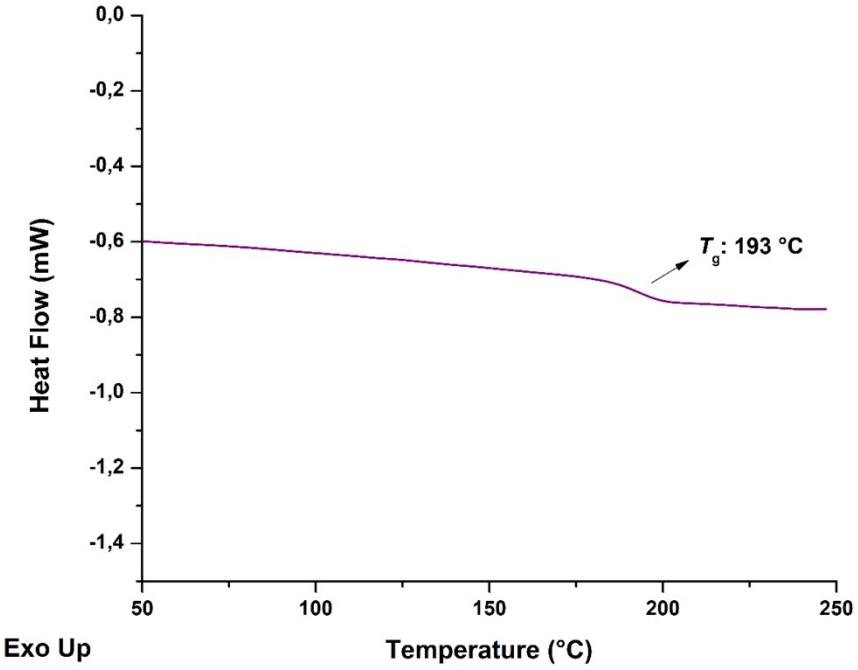


Figure S65. DSC spectrum of **P1b**.

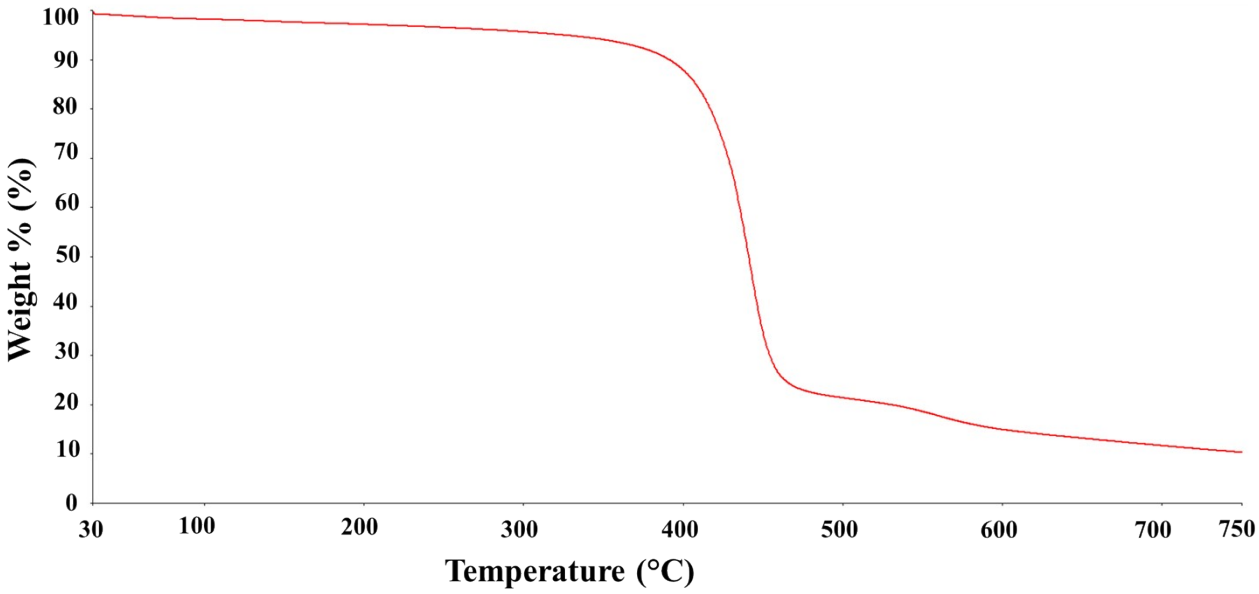


Figure S66. TGA thermogram of **P1b**.

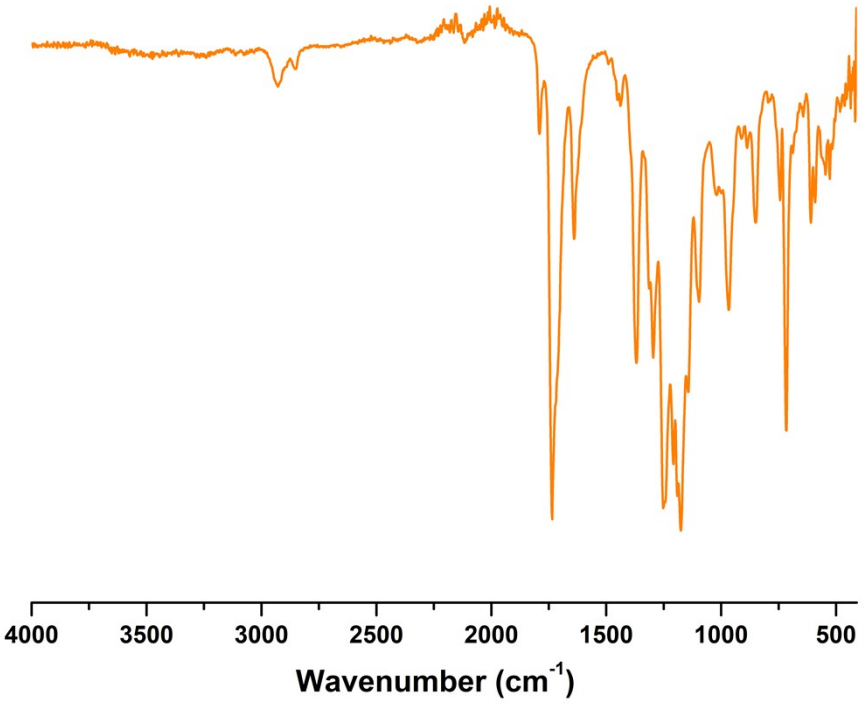
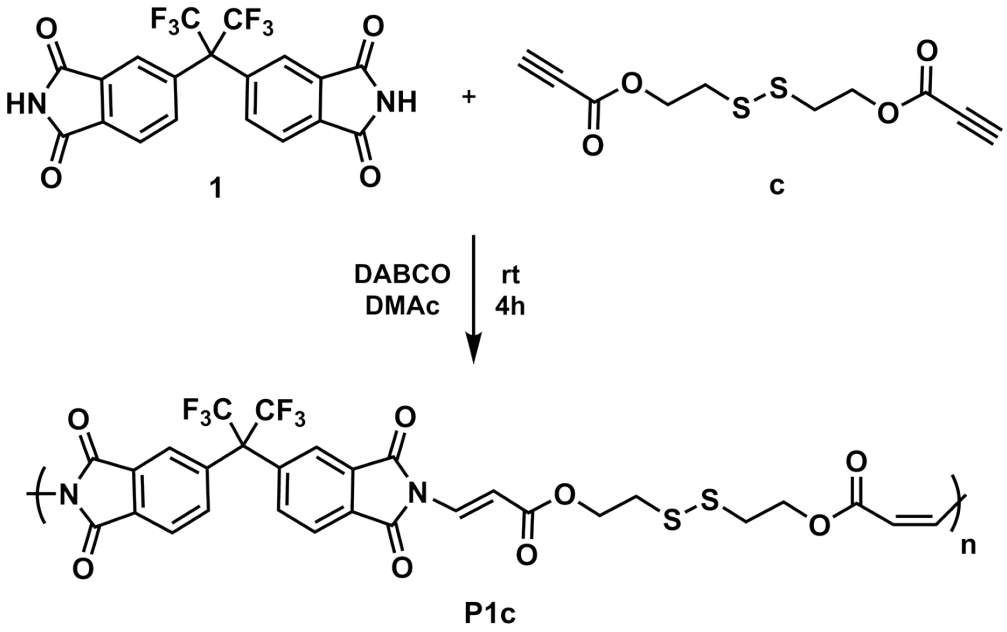


Figure S67. FT-IR spectrum of **P1b.**

3.6.3. Synthesis of P1c



General procedure for imide-yne click polymerization was followed: Compound **c** (77.5 mg, 0.3 mmol), compound **1** (132.7 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P1c** was obtained as a milky brown powder (yield: 151.4 mg, 72%). ^{1}H NMR (d_6-DMSO, δ): 8.17-5.56 (br, 10H, Ar-*H* & NC*H* & NCH=C*H*), 4.41 (br, 4H, C=OOCH_2), 3.08 (br, 4H, SCH_2). ^{13}C NMR (d_6-DMSO, δ): 168.65, 166.48, 164.93, 138.57, 138.30, 136.94, 135.95, 134.41, 133.12, 131.97, 125.41, 124.58, 123.70, 122.46, 107.12, 103.01, 65.02, 62.59, 36.86. ^{19}F NMR (d_6-DMSO, δ): -62.90.

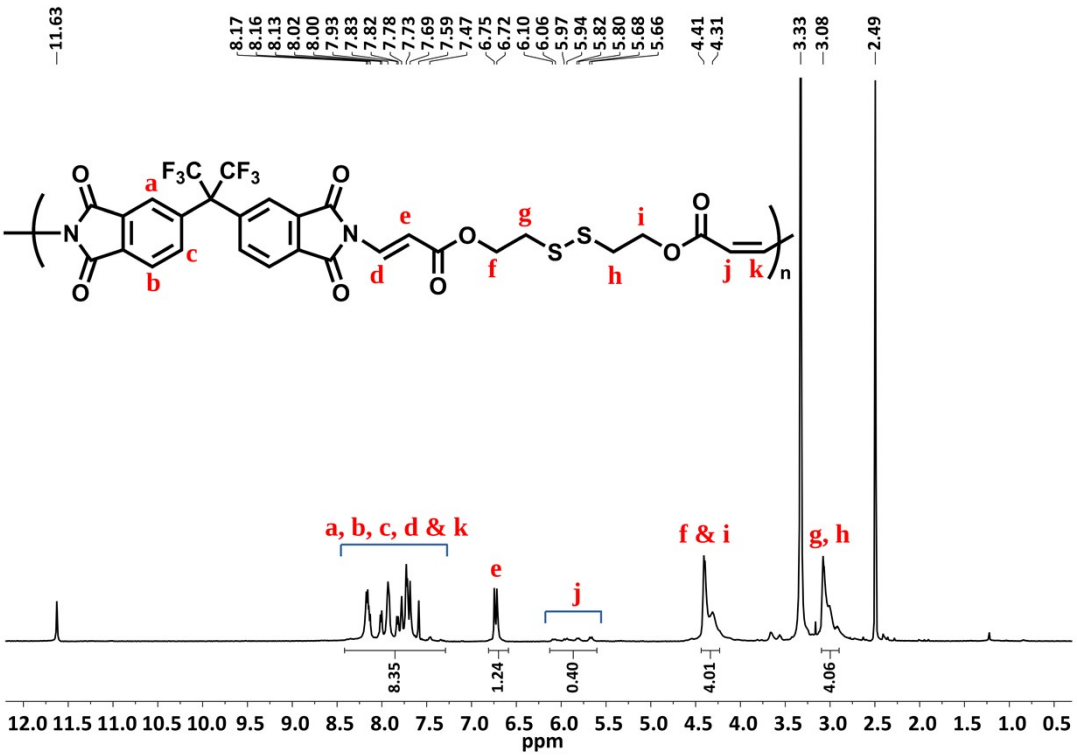


Figure S68. ^{1}H NMR spectrum of **P1c** in d_6-DMSO (500 MHz).

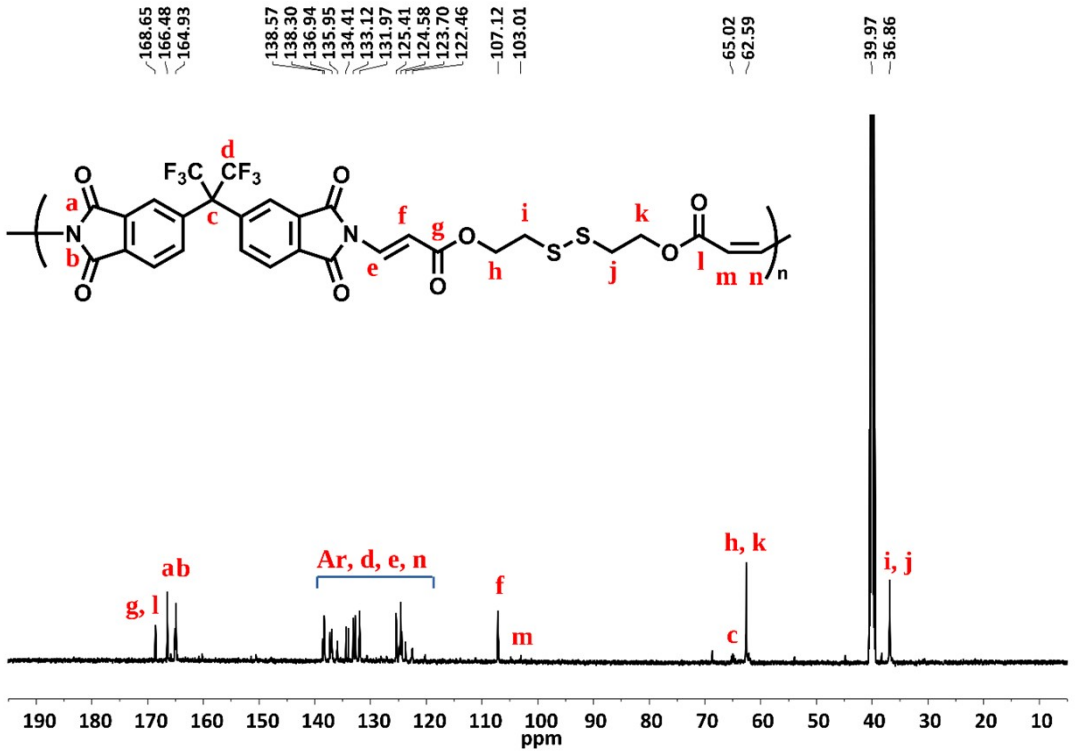


Figure S69. ^{13}C NMR spectrum of **P1c** in d_6-DMSO (125 MHz).

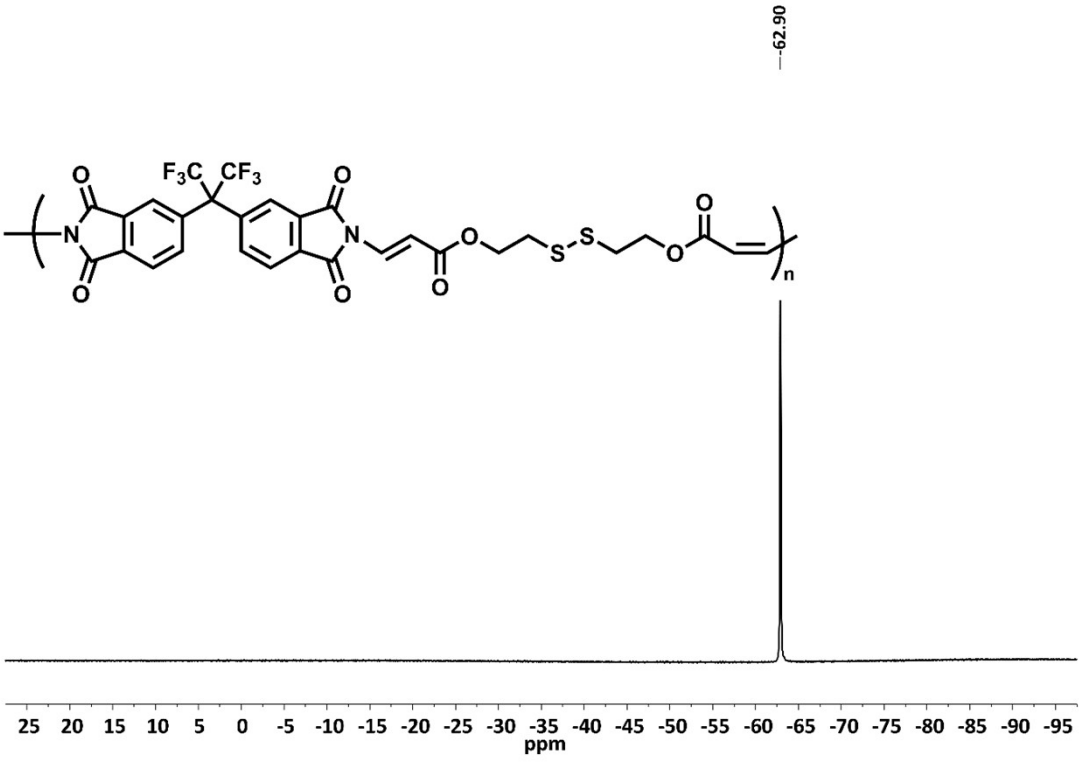


Figure S70. ^{19}F NMR spectrum of **P1c** in d_6-DMSO (470 MHz).

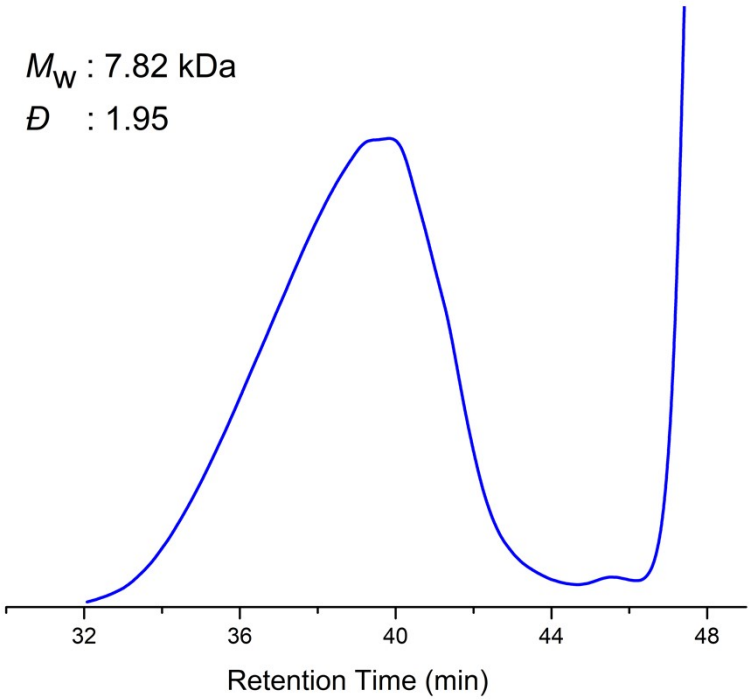


Figure S71. GPC trace of **P1c**.

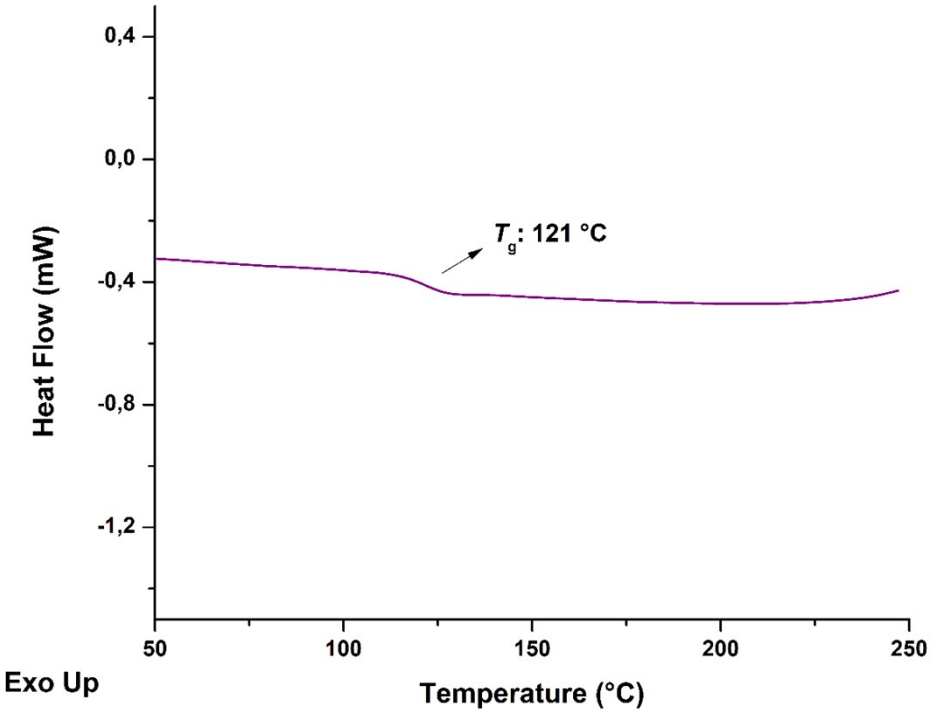


Figure S72. DSC spectrum of **P1c**.

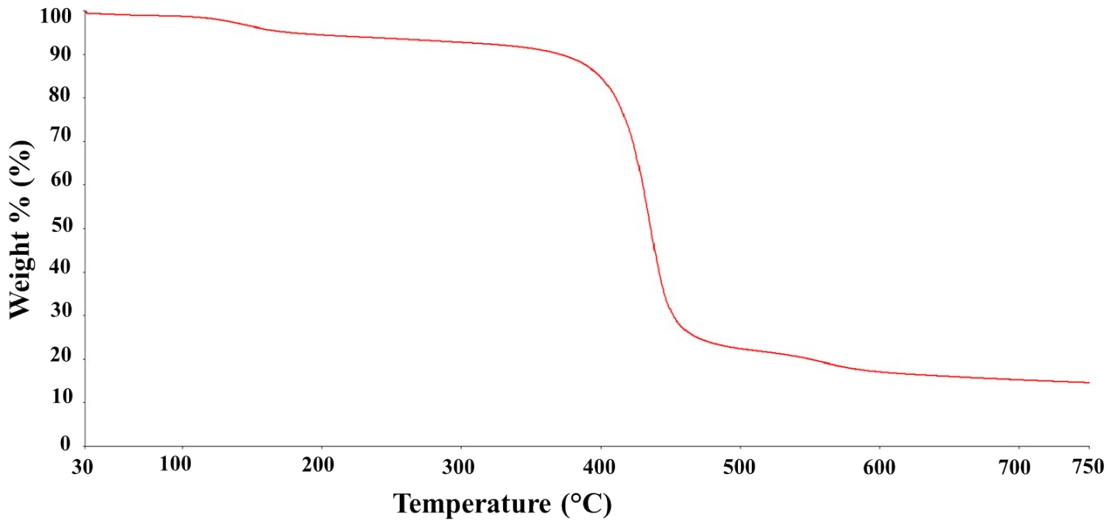


Figure S73. TGA thermogram of **P1c**.

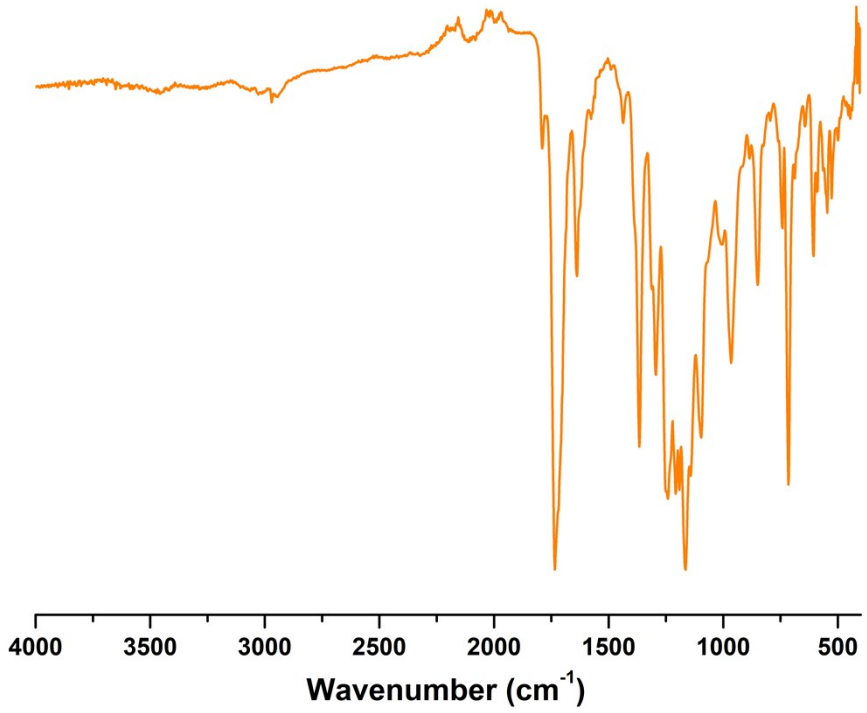
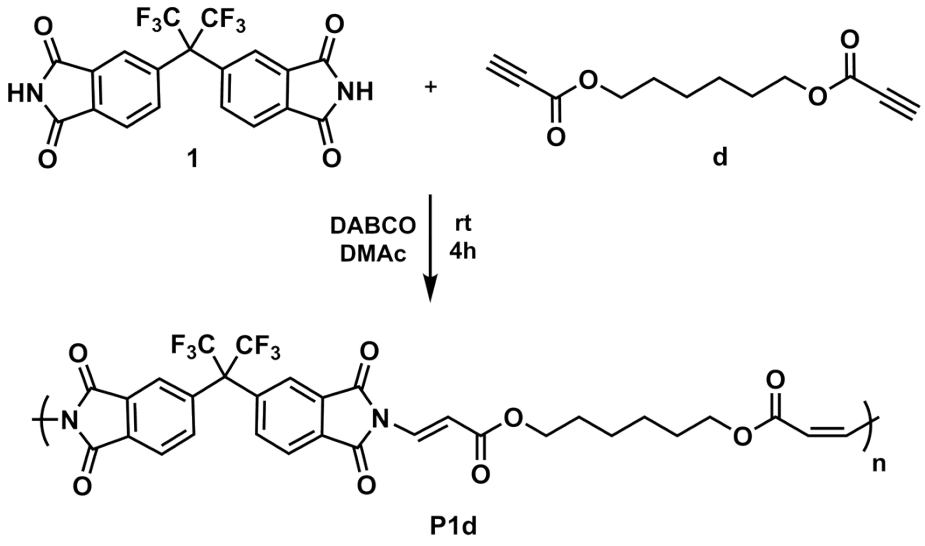


Figure S74. FT-IR spectrum of **P1c.**

3.6.4. Synthesis of P1d



General procedure for imide-yne click polymerization was followed: Compound **d** (66.8 mg, 0.3 mmol), compound **1** (132.7 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P1d** was obtained as a pale-yellow powder (yield: 171.5 mg, 84%). ^{1}H NMR (d_6-DMSO, δ): 8.14-5.60 (br, 10H, Ar-*H* & NC*H* & NCH=C*H*), 4.13 (br, 4H, C=OOCH_2), 1.63 (br, 4H, C=OOCH$_2$CH_2), 1.36 (br, 4H, C=OOCH$_2$CH$_2$CH_2). ^{13}C NMR (d_6-DMSO, δ): 168.53, 166.66, 164.88, 142.27, 138.33, 136.92, 134.39, 132.65, 131.42, 125.36, 124.59, 122.54, 122.44, 120.18, 107.63, 103.26, 64.63, 28.46, 25.52. ^{19}F NMR (d_6-DMSO, δ): -62.92.

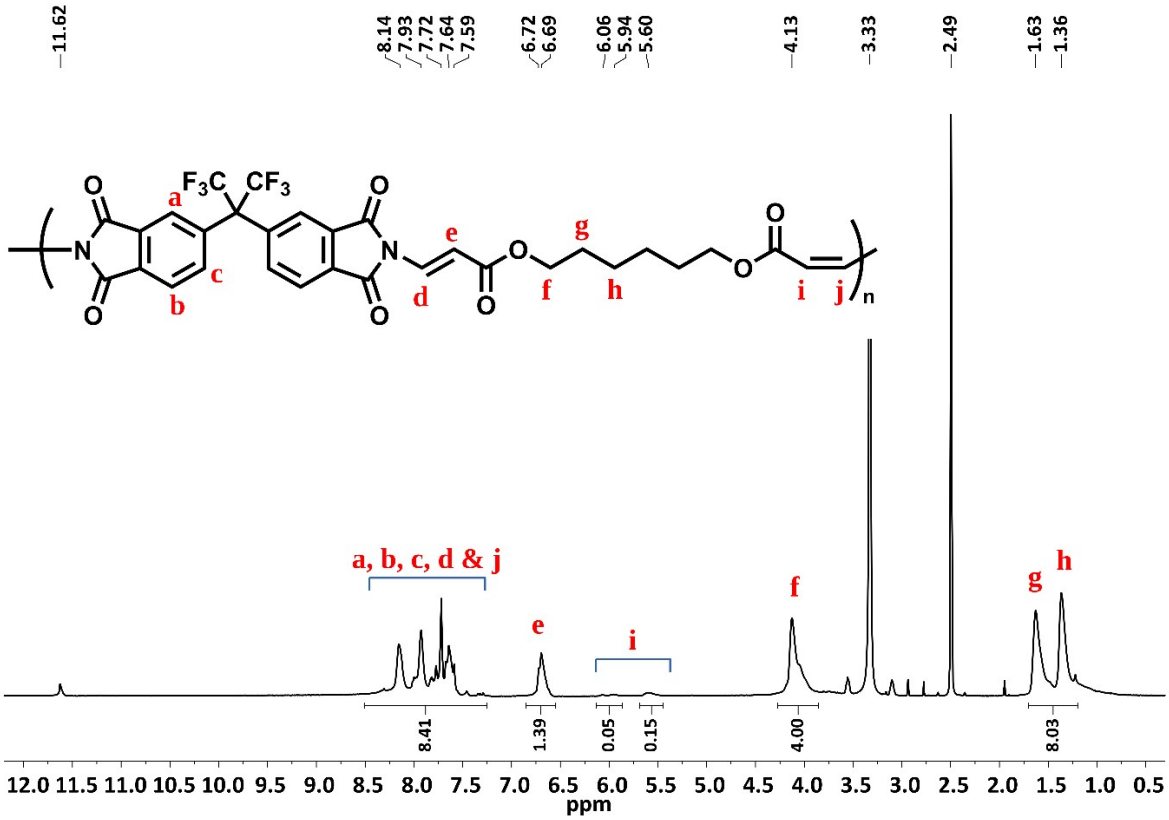


Figure S75. ^{1}H NMR spectrum of **P1d** in d_6-DMSO (500 MHz).

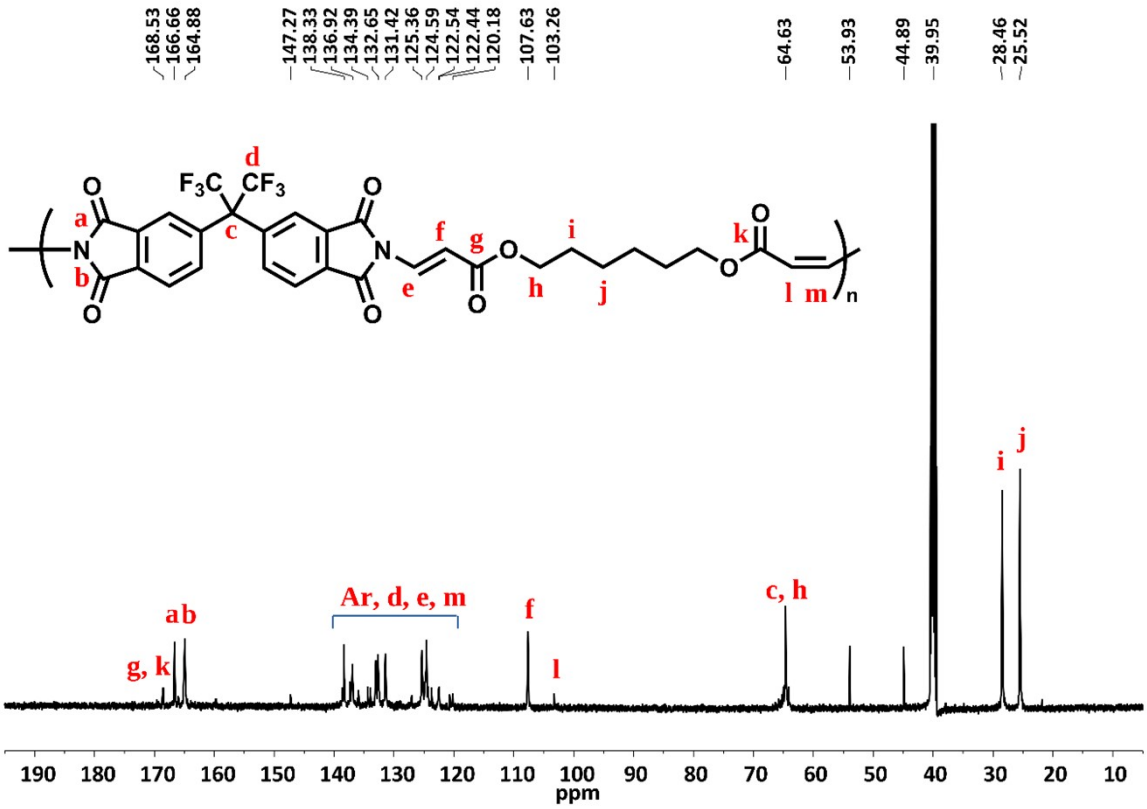


Figure S76. ^{13}C NMR spectrum of **P1d** in d_6-DMSO (125 MHz).

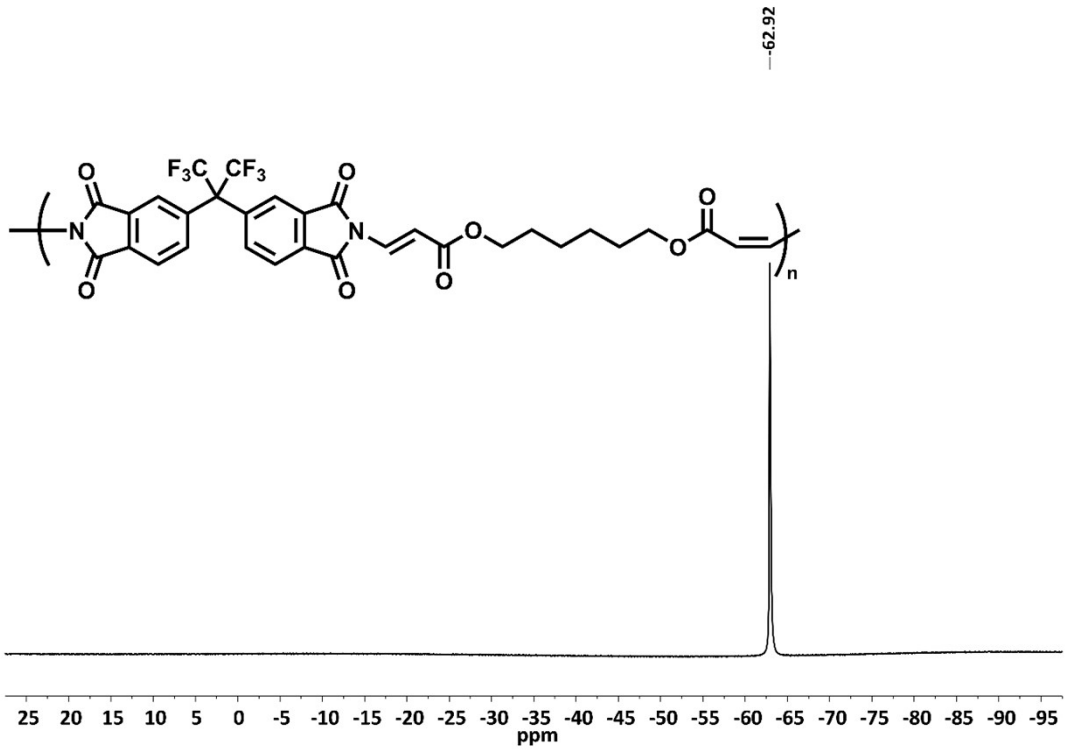


Figure S77. ^{19}F NMR spectrum of **P1d** in d_6-DMSO (470 MHz).

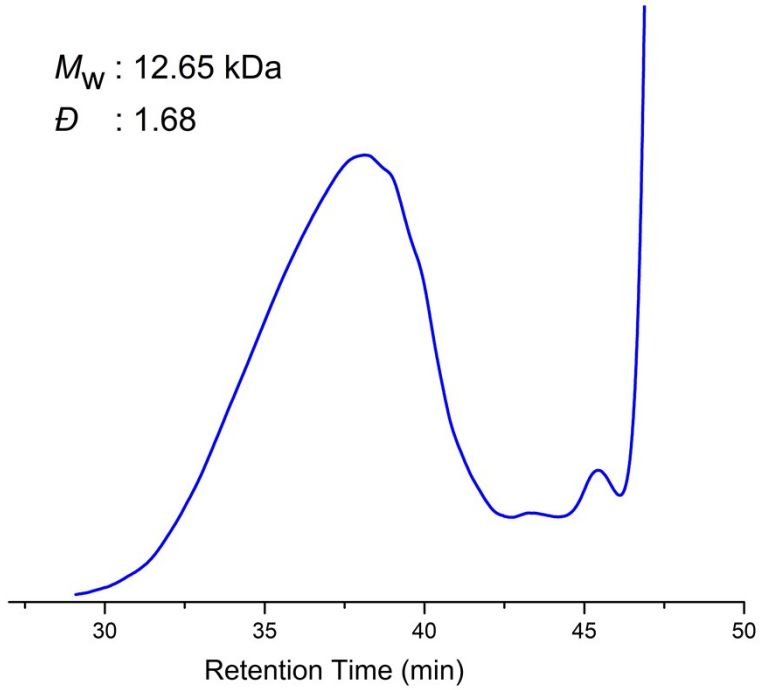


Figure S78. GPC trace of **P1d**.

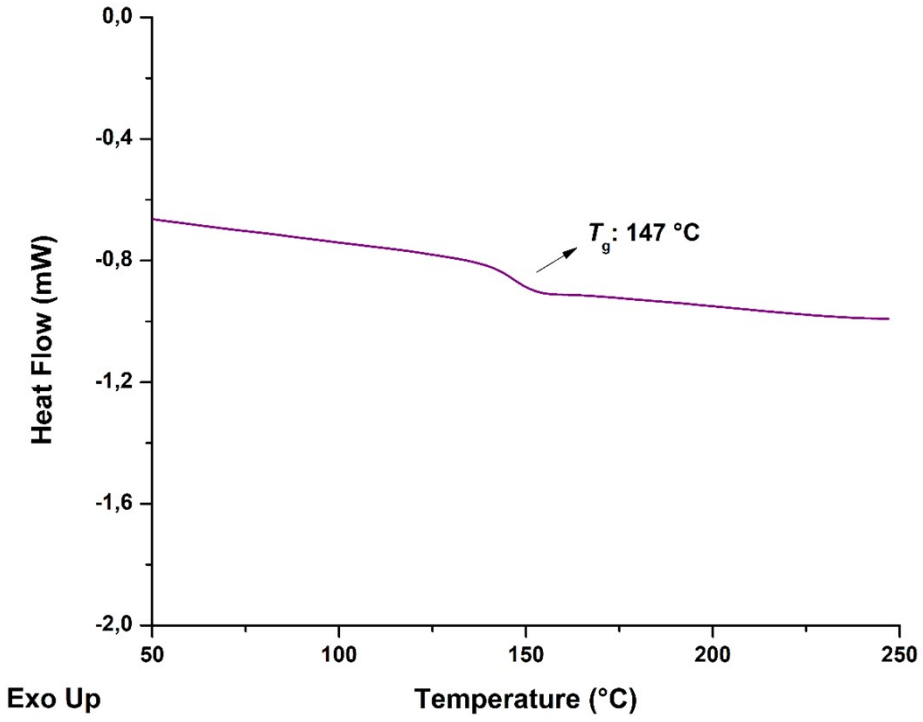


Figure S79. DSC spectrum of **P1d**.

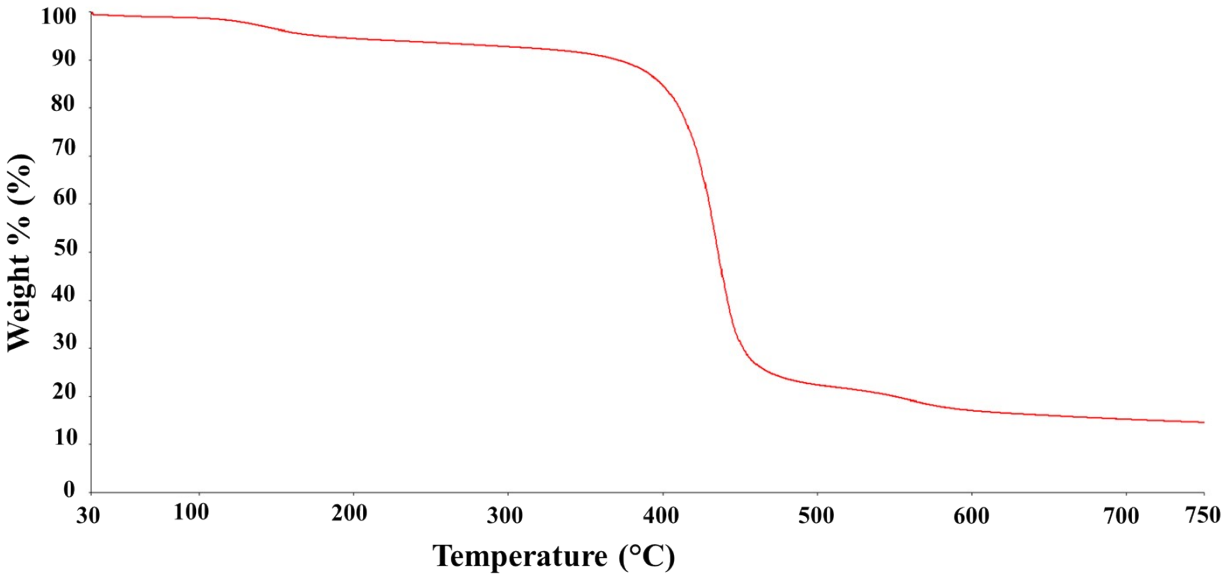


Figure S80. TGA thermogram of **P1d**.

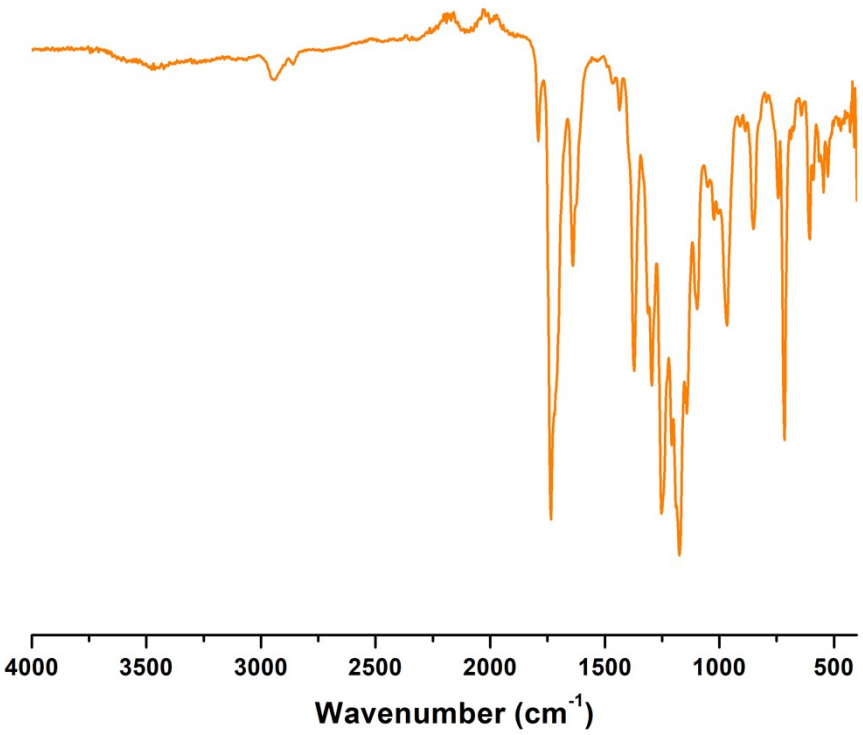
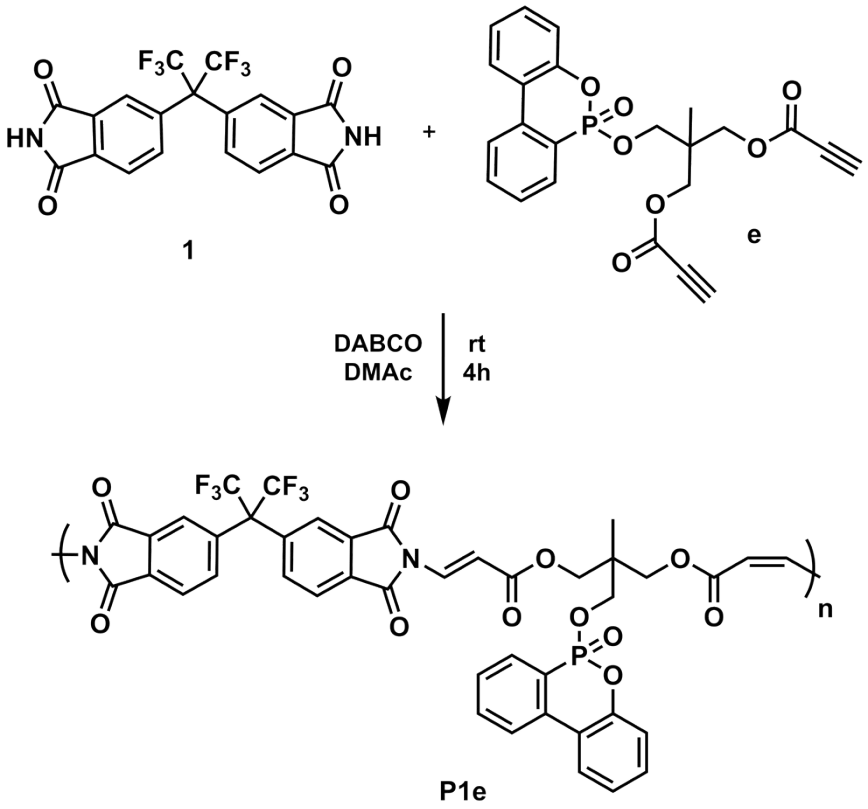


Figure S81. FT-IR spectrum of **P1d**.

3.6.5. Synthesis of P1e



General procedure for imide-yne click polymerization was followed: Compound **e** (131.5 mg, 0.3 mmol), compound **1** (132.7 mg, 0.3 mmol), DABCO (3.4, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P1e** was obtained as an off-white powder (yield: 211.5 mg, 80%). ^{1}H NMR (d_6-DMSO, δ): 8.18-5.52 (br, 18H, Ar-*H* & NC*H* & NCH=C*H*), 4.13-3.95 (br, 6H, C=OOCH_2 & P=OOCH_2), 0.84 (br, 3H, CCH_3). ^{13}C NMR (d_6-DMSO, δ): 168.54, 166.35, 164.92, 149.68, 138.33, 137.32, 136.72, 133.12, 131.78, 131.37, 130.24, 125.56, 122.49, 120.23, 107.07, 102.83, 67.75, 65.61, 64.83, 16.48. ^{19}F NMR (d_6-DMSO, δ): -62.90. ^{31}P NMR (d_6-DMSO, δ): 9.82.

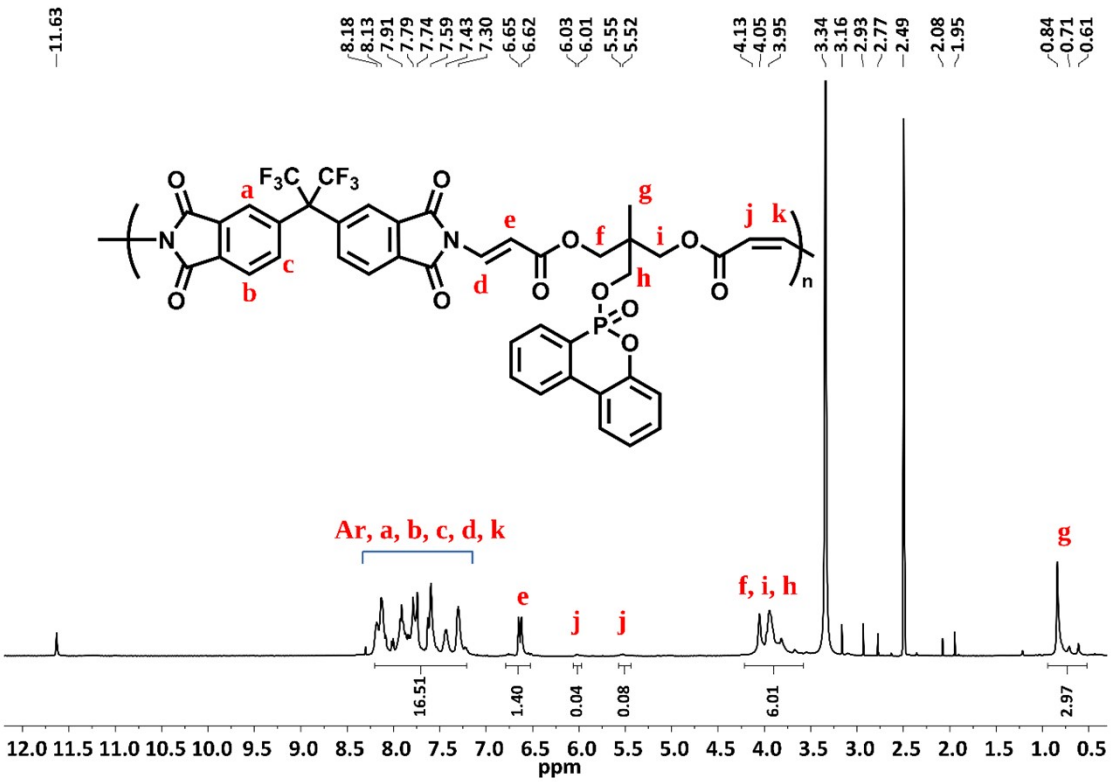


Figure S82. ^{1}H NMR spectrum of **P1e** in d_6-DMSO (500 MHz).

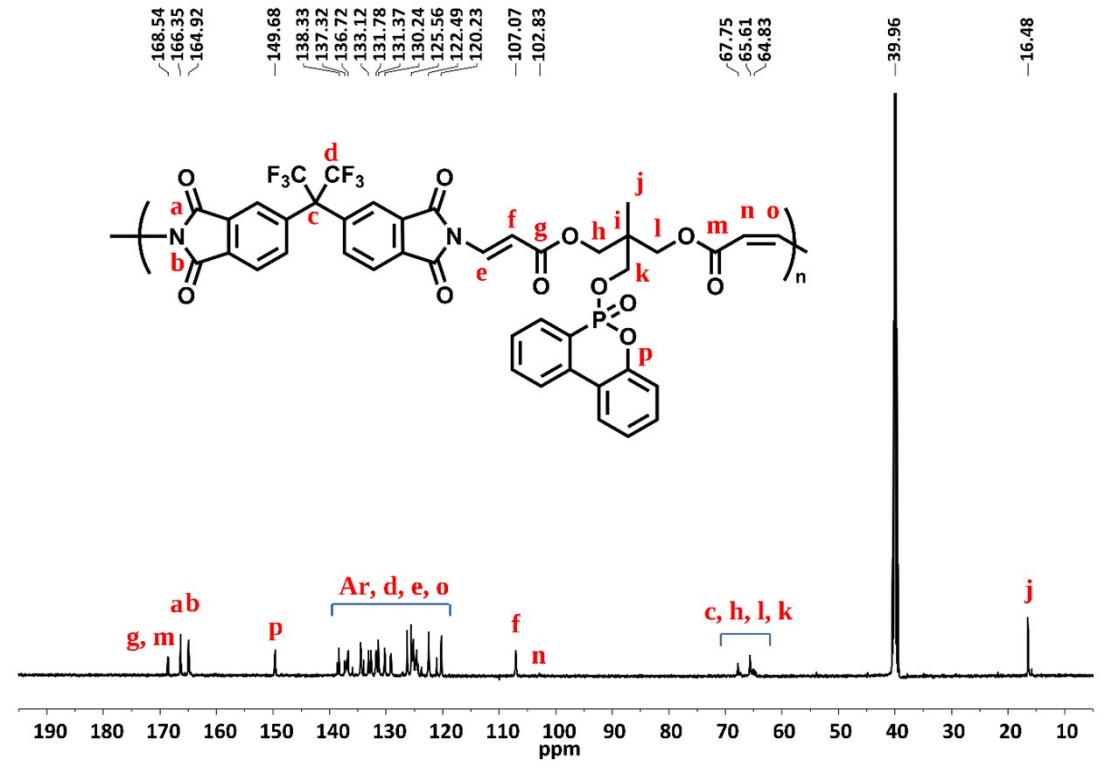


Figure S83. ^{13}C NMR spectrum of **P1e** in d_6-DMSO (125 MHz).

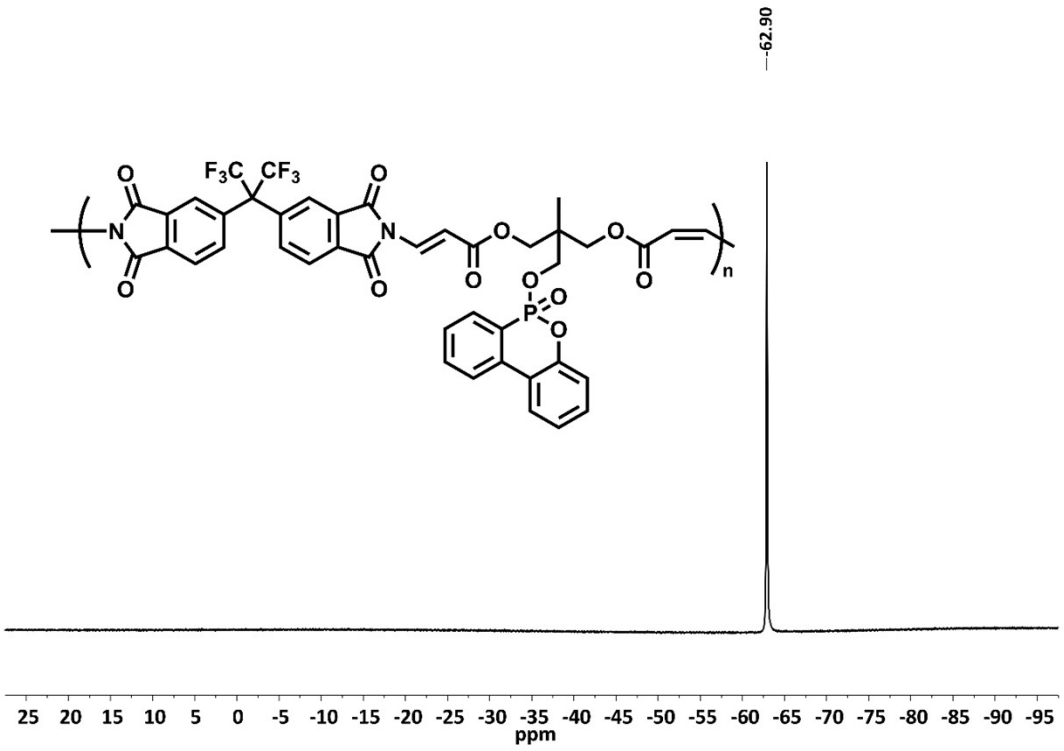


Figure S84. ^{19}F NMR spectrum of **P1e** in d_6-DMSO (470 MHz).

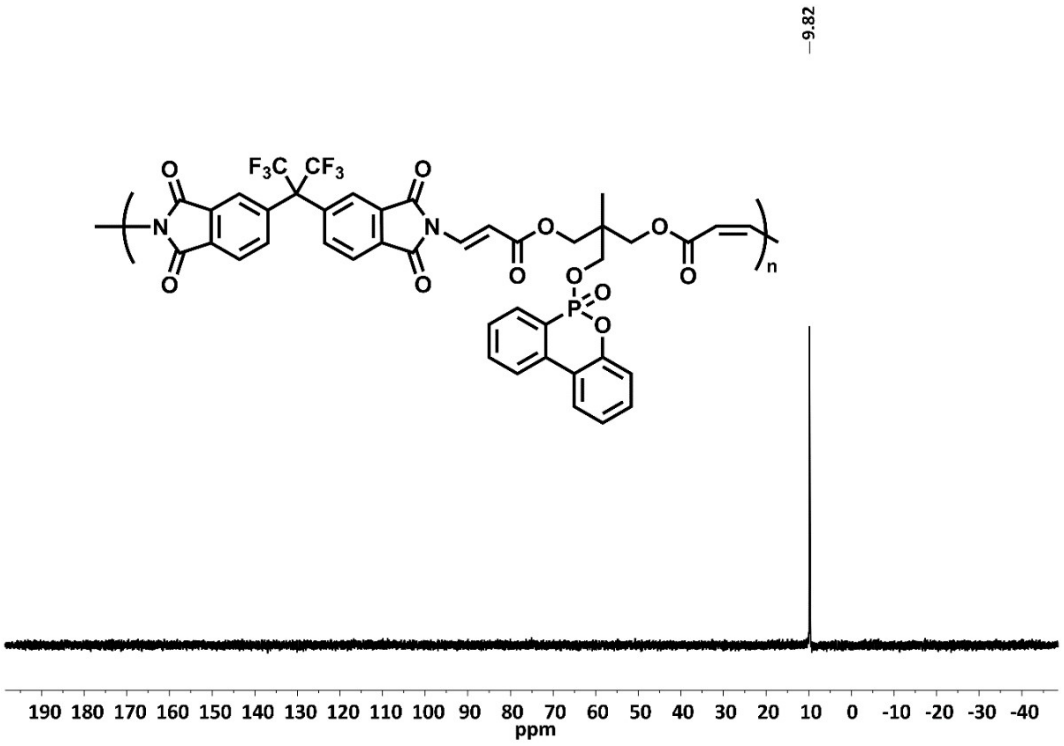


Figure S85. ^{31}P NMR spectrum of **P1e** in d_6-DMSO (202 MHz).

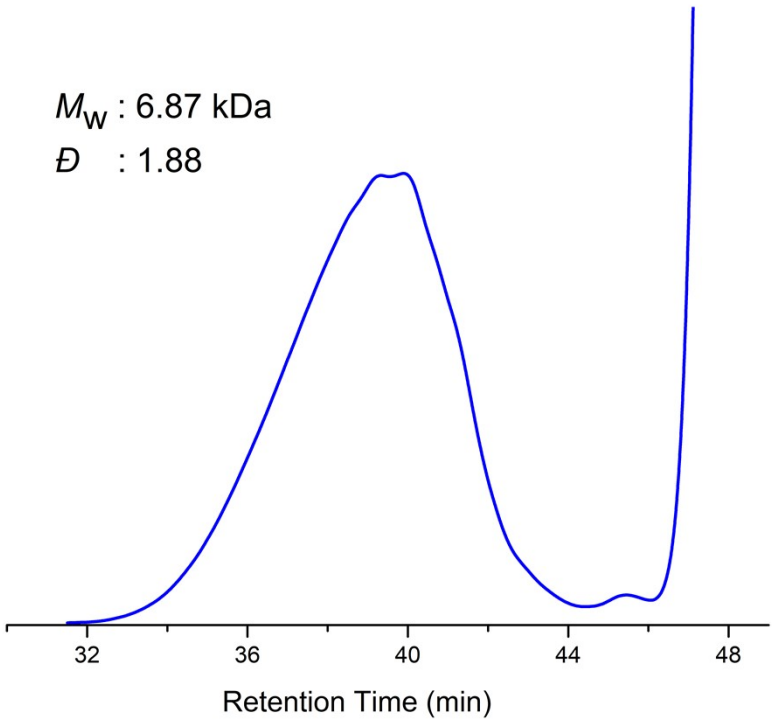


Figure S86. GPC trace of **P1e**.

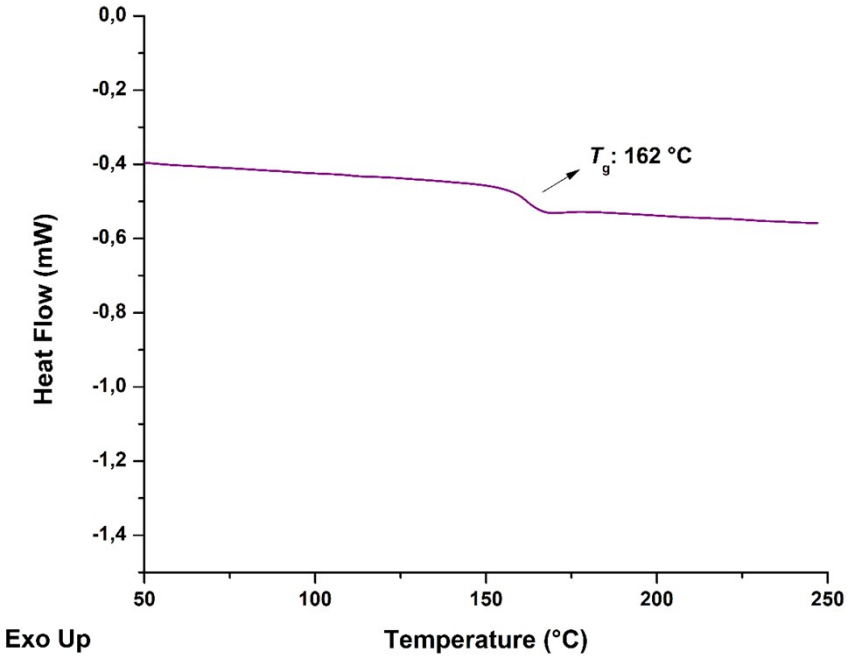


Figure S87. DSC spectrum of **P1e**.

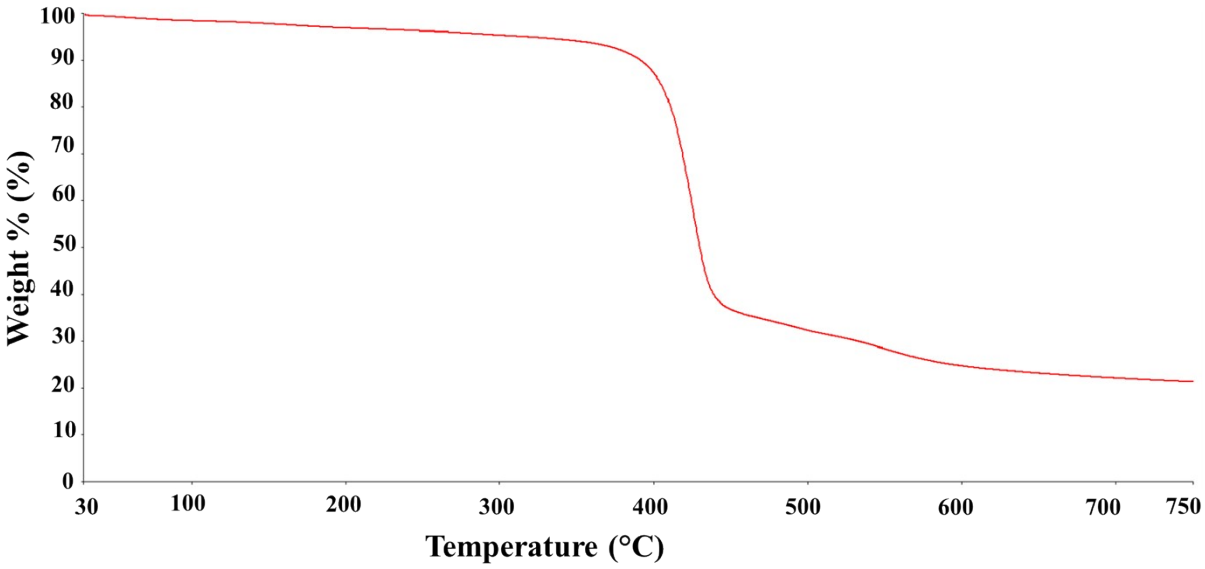


Figure S88. TGA thermogram of **P1e**.

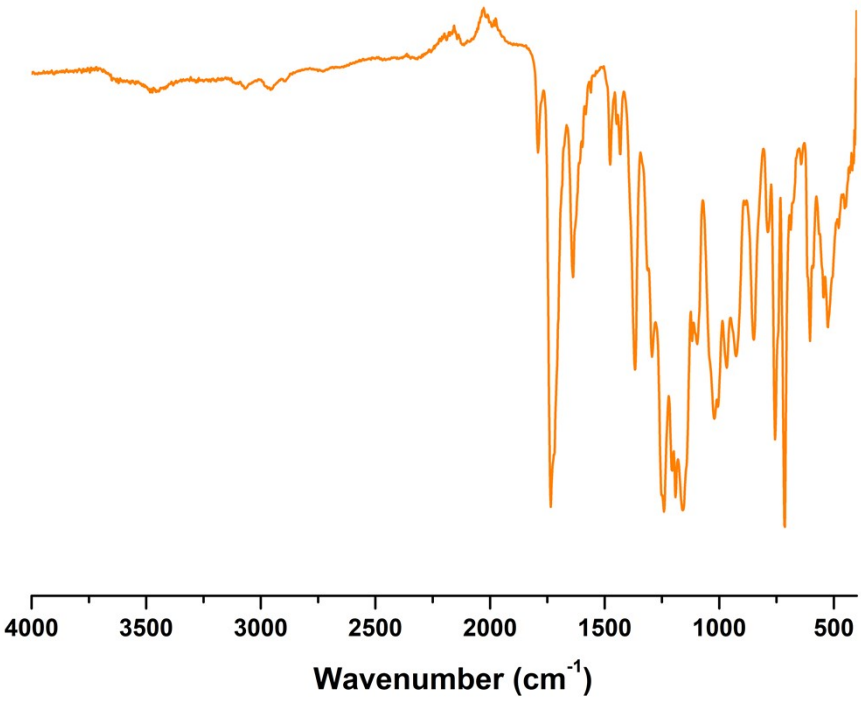
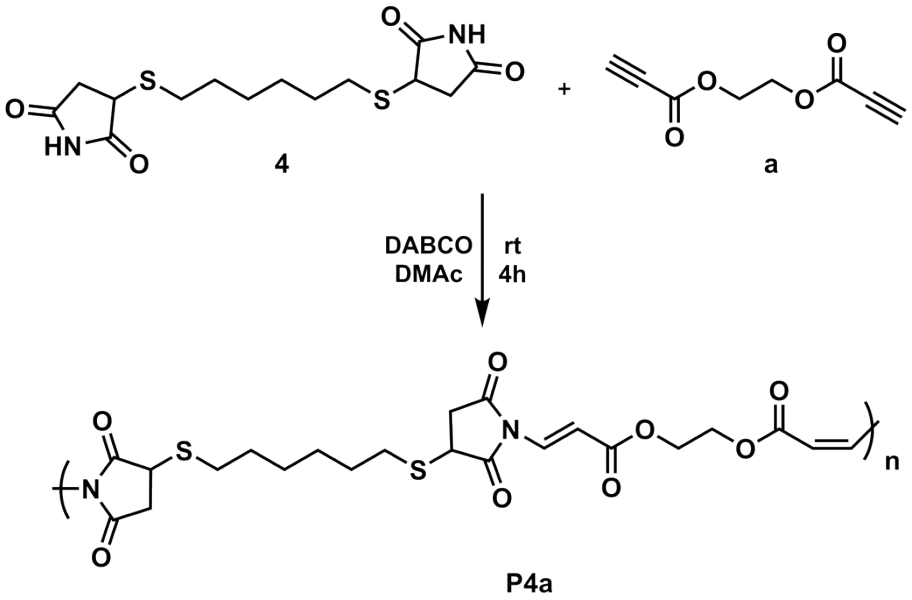


Figure S89. FT-IR spectrum of **P1e.**

3.6.6. Synthesis of P4a



General procedure for imide-yne click polymerization was followed: Compound **a** (50 mg, 0.3 mmol), compound **4** (103.35 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P4a** was obtained as a burgundy solid (yield: 95 mg, 62%). ^{1}H NMR (d_6-DMSO, δ): 7.78-6.05 (m, 4H, NC*H* & NCH=C*H*), 4.40 (br, 4H, C=OOCH_2), 4.05-3.85 (m, 2H, SC*H*), 3.29-2.40 (m, 8H, SCHCH_2 & SCH_2), 1.54 (m, 4H, SCH_2CH_2CH_2), 1.35 (s, 4H, $SCH_2CH_2CH_2$CH_2). ^{13}C NMR (d_6-DMSO, δ): 178.64, 177.05, 175.30, 173.63, 166.40, 132.09, 130.62, 128.06, 117.39, 108.75, 62.82, 40.93, 37.70, 36.07, 31.18, 30.80, 28.86, 28.06.

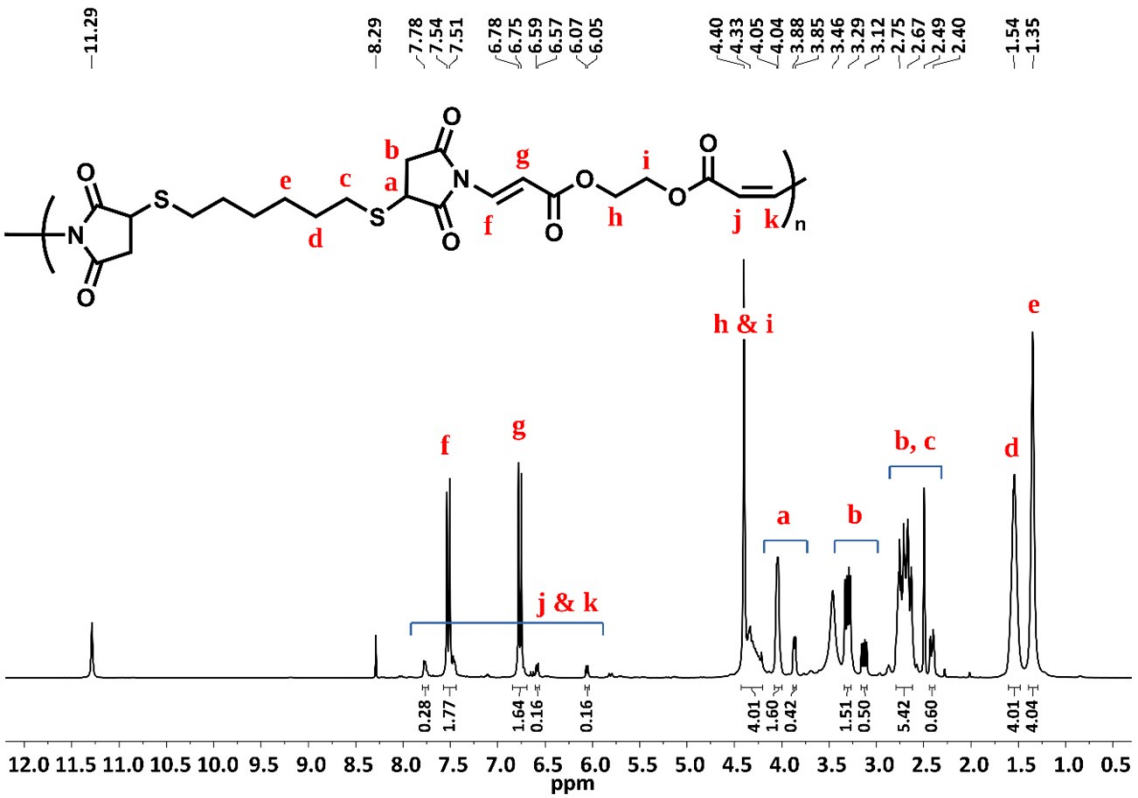


Figure S90. ^{1}H NMR spectrum of **P4a** in d_6-DMSO (500 MHz).

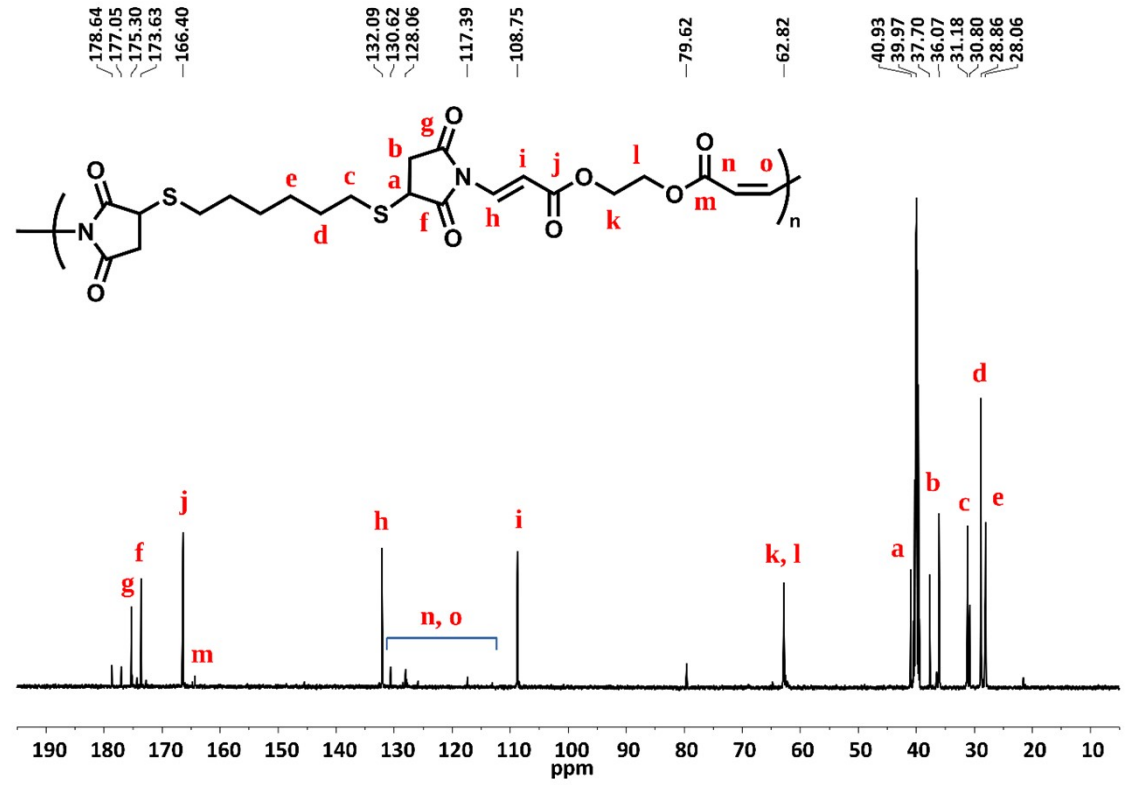


Figure S91. ^{13}C NMR spectrum of **P4a** in d_6-DMSO (125 MHz).

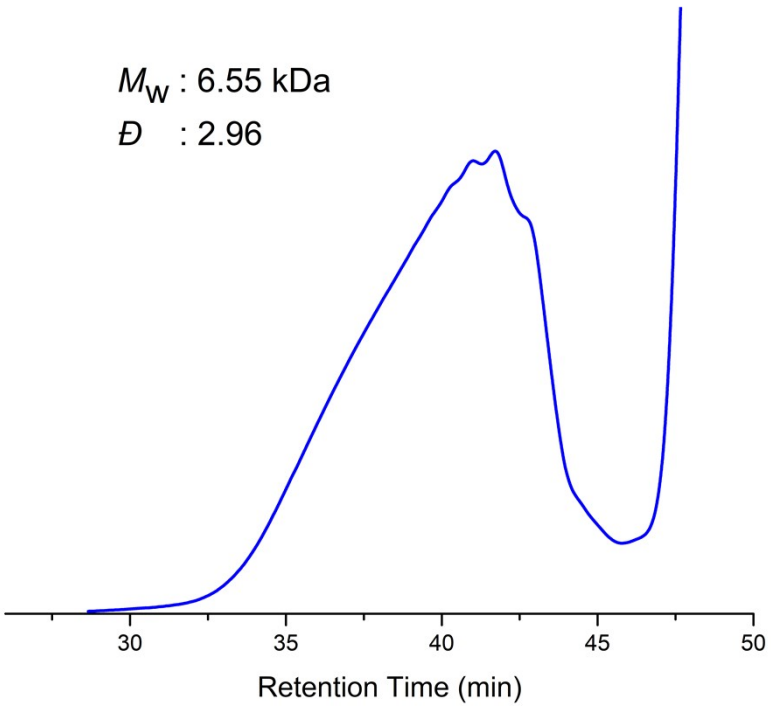


Figure S92. GPC spectra of **P4a**.

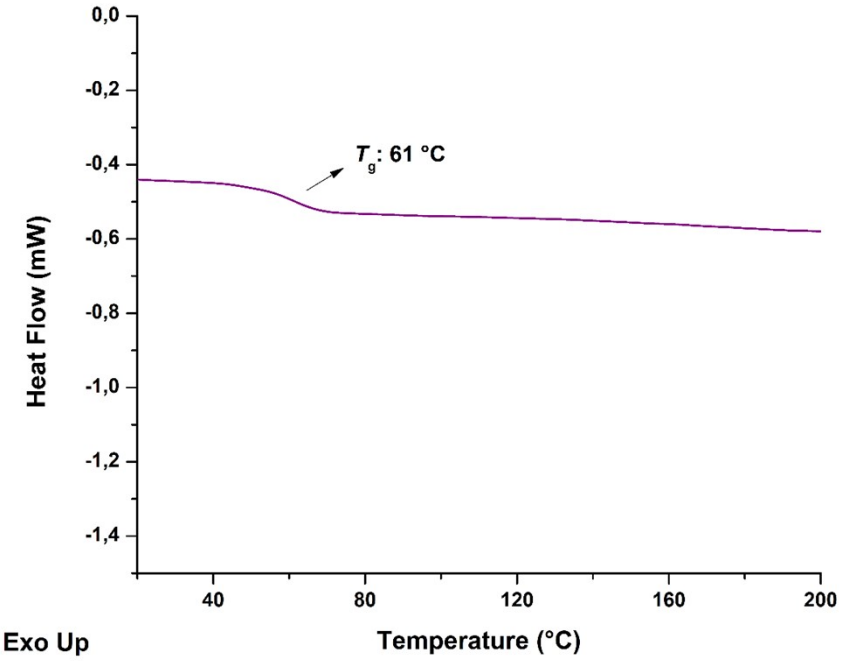


Figure S93. DSC spectrum of **P4a**.

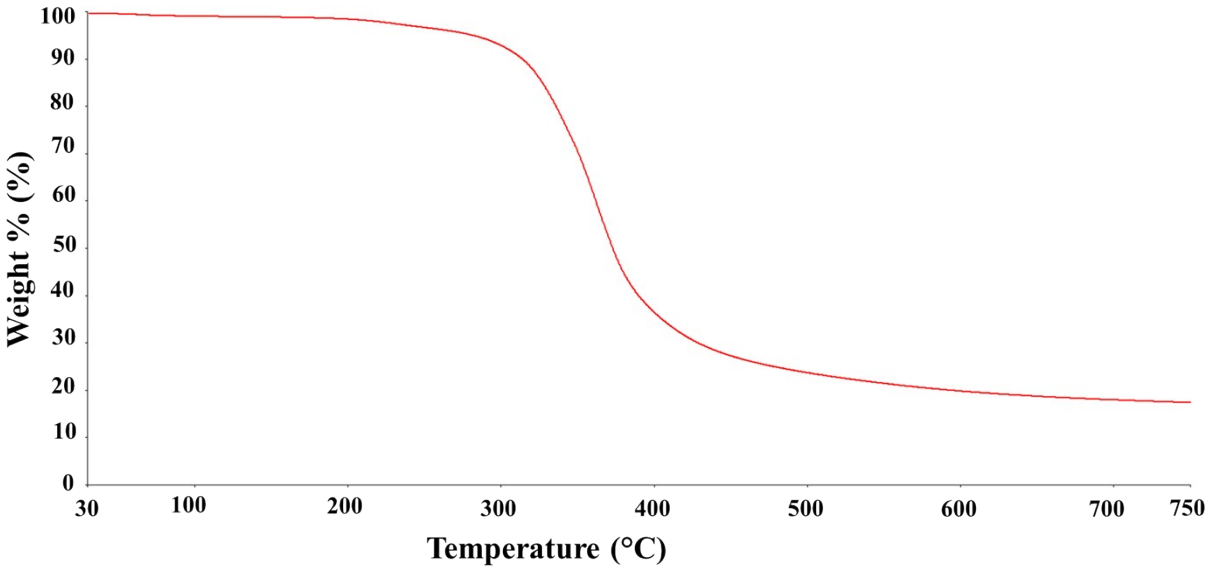


Figure S94. TGA thermogram of **P4a**

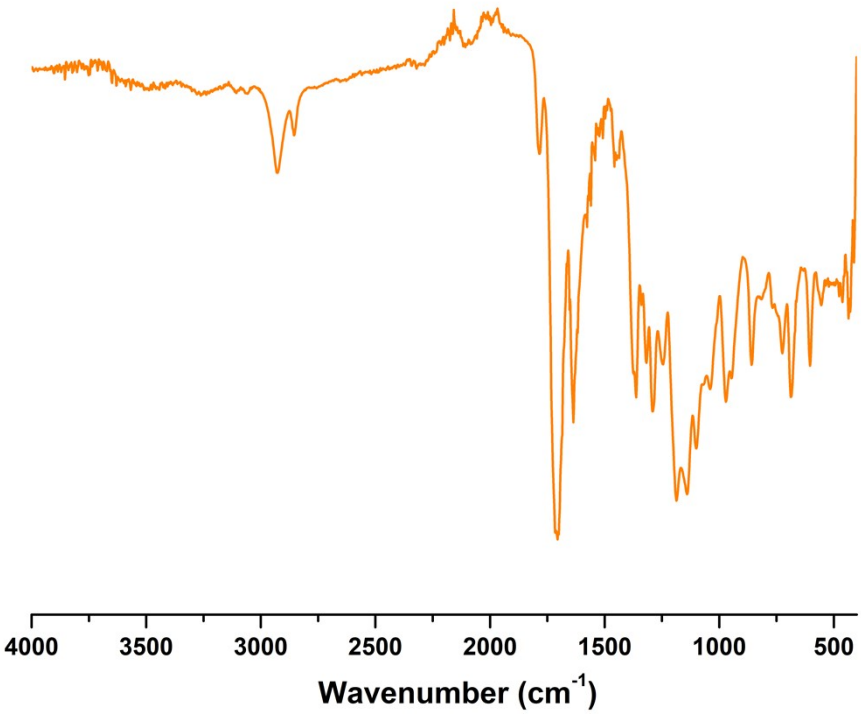


Figure S95. FT-IR spectrum of **P4a**.

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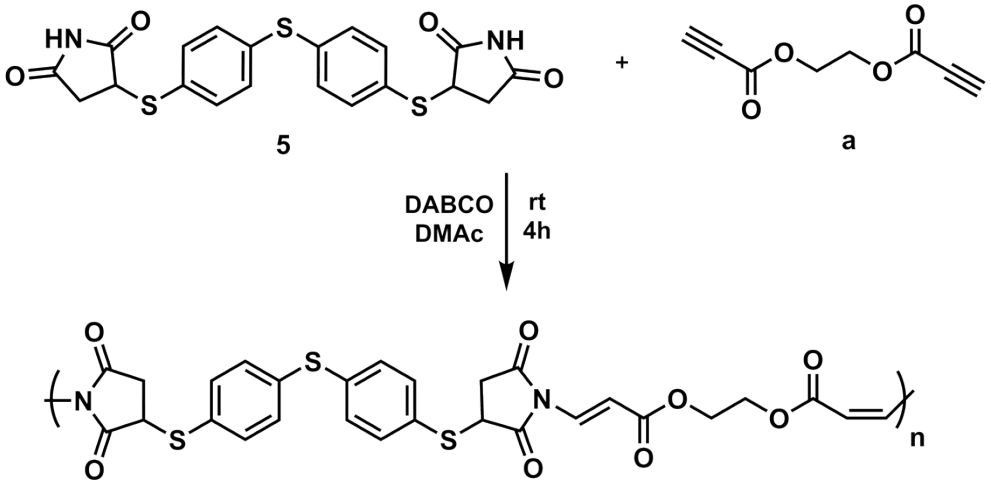
3.6.7. Synthesis of P5a



General procedure for imide-yne click polymerization was followed: Compound **a** (50 mg, 0.3 mmol), compound **5** (133.35 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P5a** was obtained as a purple solid (yield: 128 mg, 70%). ^{1}H NMR (d_6-DMSO, δ): 7.85-5.67 (m, 4H, C=ONC*H* & OC=OC*H*), 7.48-7.32 (m, 8H, Ar-H), 4.44-4.07 (br, 6H, CSC*H* & C=OOCH_2), 3.70-3.24 (br, 4H, SCHCH_2). ^{13}C NMR (d_6-DMSO, δ): 177.46, 176.60, 173.60, 171.99, 166.37, 165.87, 164.41, 147.52, 137.56, 133.78, 132.83, 132.62, 131.15, 129.82, 129.77, 115.40, 62.53, 44.55, 37.69.

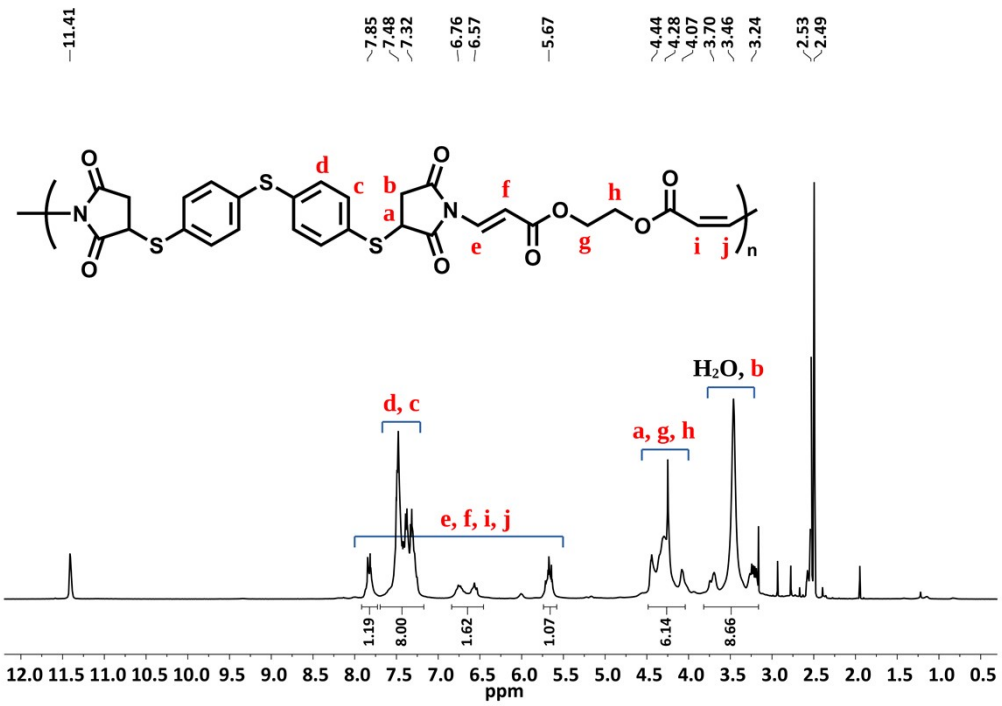


Figure S96. ^{1}H NMR spectrum of **P5a** in d_6-DMSO (500 MHz).

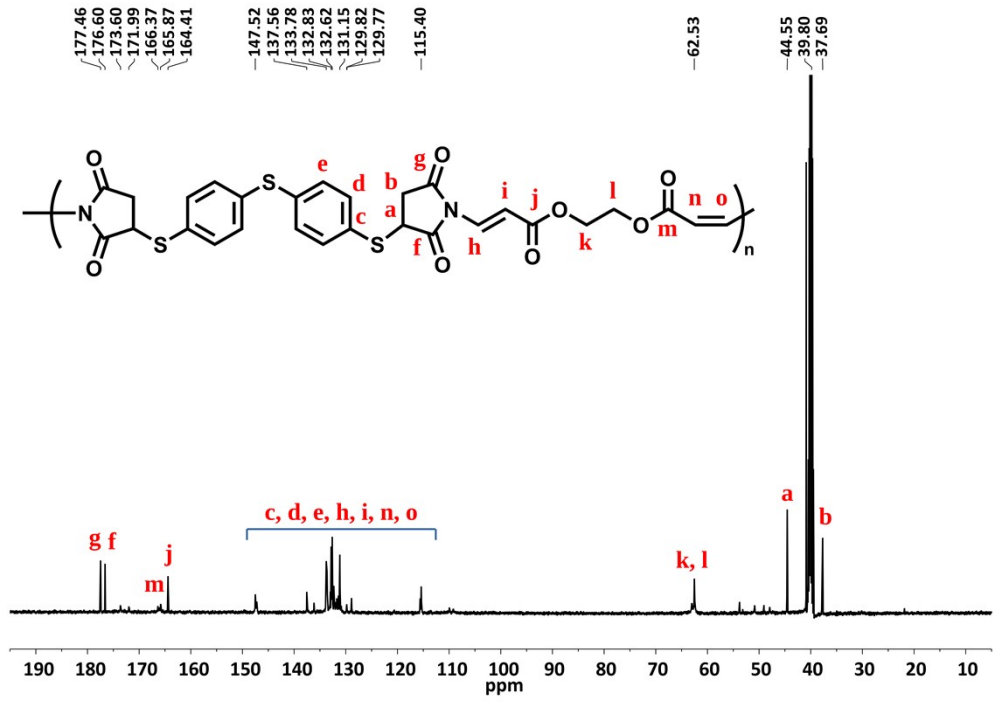


Figure S97. ^{13}C NMR spectrum of **P5a** in d_6-DMSO (125 MHz).

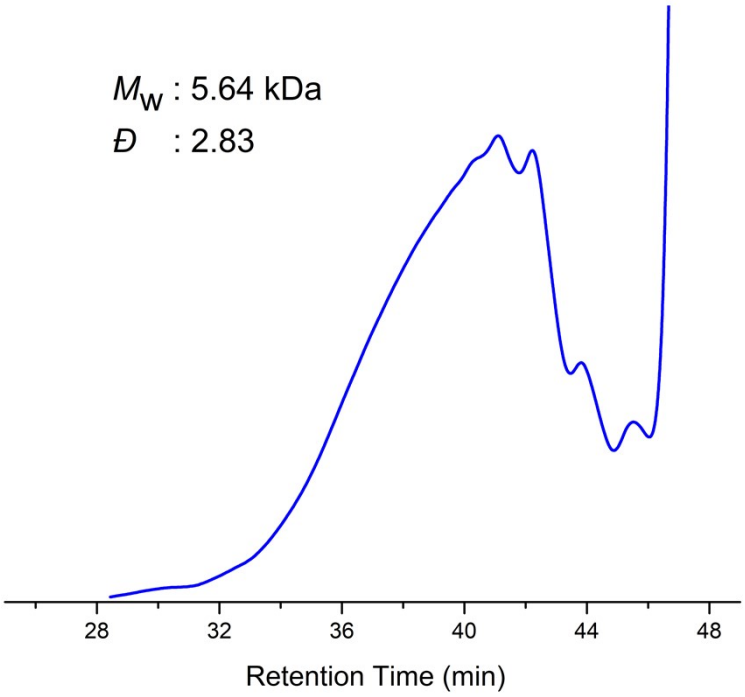


Figure S98. GPC trace of **P5a**.

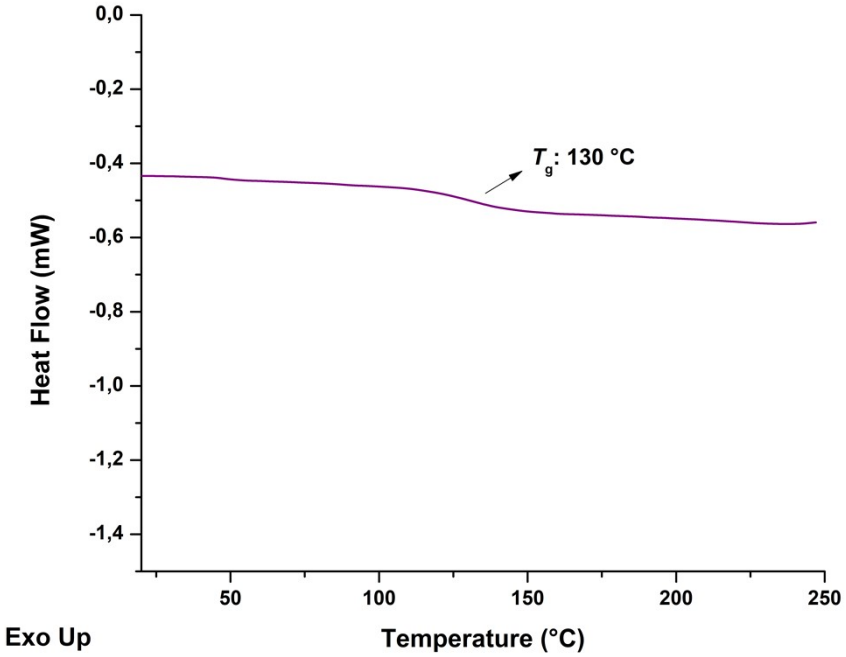


Figure S99. DSC spectrum of **P5a**.

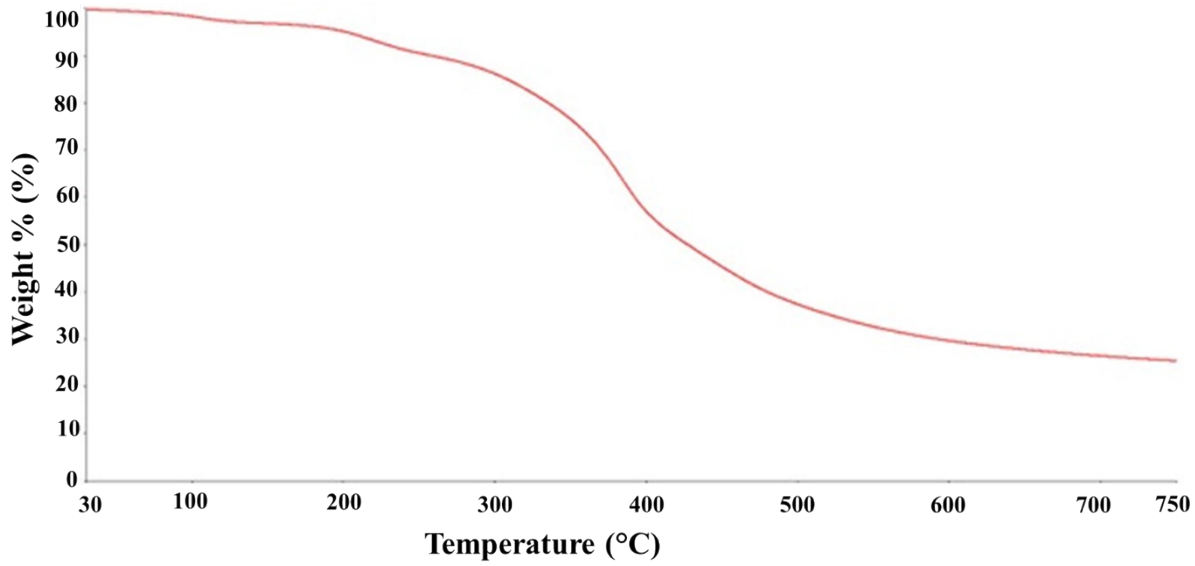


Figure S100. TGA thermogram of **P5a**.

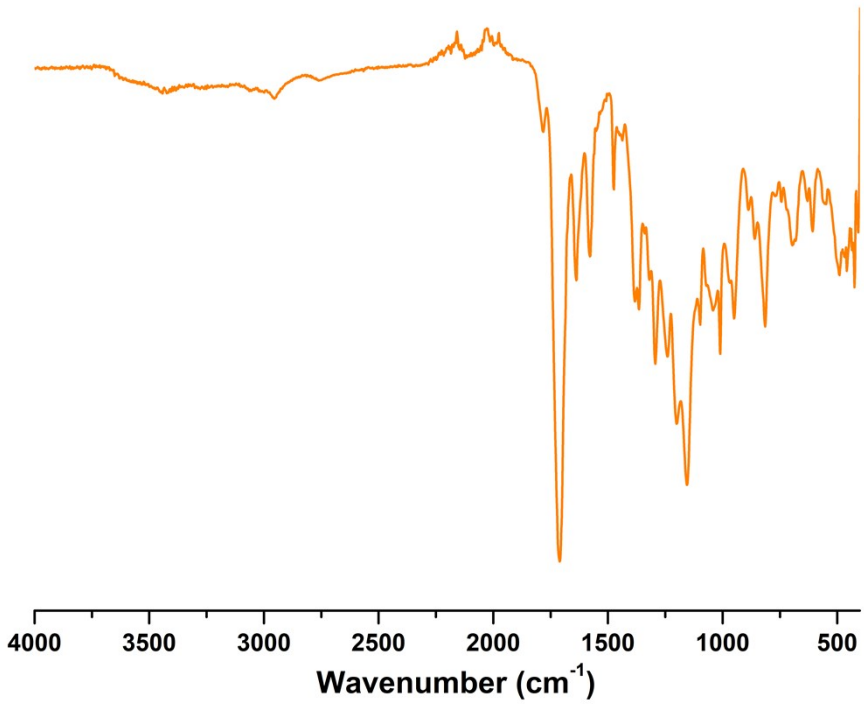
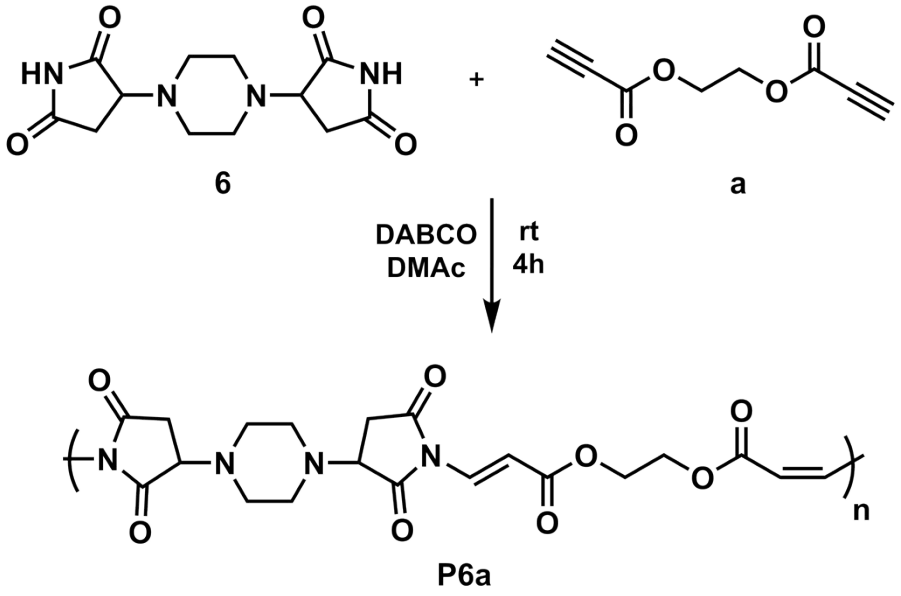


Figure S101. FT-IR spectrum of **P5a**.

3.6.8. Synthesis of P6a



General procedure for imide-yne click polymerization was followed: Compound **a** (50 mg, 0.3 mmol), compound **6** (suspended in the reaction medium, 84.1 mg, 0.3 mmol), DABCO (3.4 mg, 0.03 mmol) and DMAc (1.2 mL) were used. The resultant polymer **P6a** was obtained as a brown solid (yield: 126 mg, 94%). ^{1}H NMR (d_6-DMSO, δ): 7.52 (d, 2H, C=ONC*H*), 6.77 (d, 2H, C=OCCHC*H*), 4.39 (br, 4H, C=OOCH_2), 4.00 (t, 2H, NC=OC*H*), 2.91-2.81 (m, 8H, C=OCH_2 & NCH_2), 2.43 (br, 4H, NCH_2). ^{13}C NMR (d_6-DMSO, δ): 178.44, 177.20, 174.98, 173.87, 166.48, 131.76, 108.68, 63.52, 62.78, 62.04, 48.92, 32.66, 31.38.

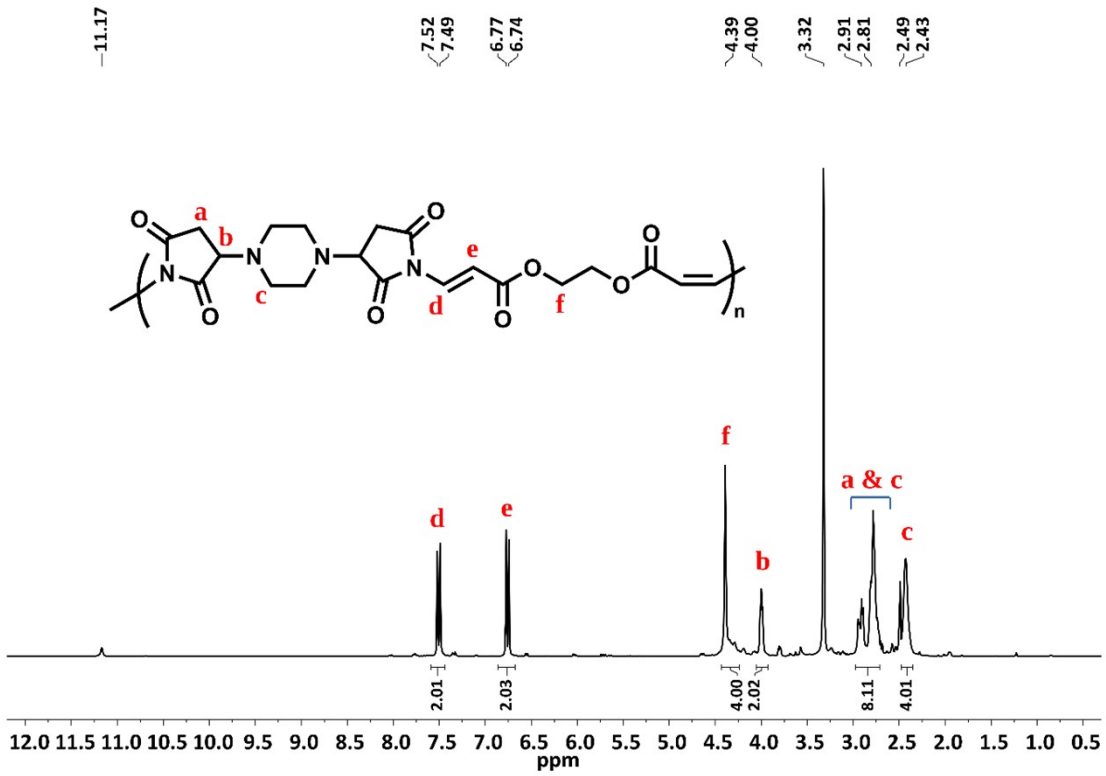


Figure S102. ^{1}H NMR spectrum of **P6a** in d_6-DMSO (500 MHz).

Figure S103. ^{13}C NMR spectrum of **P6a** in d_6-DMSO (125 MHz).

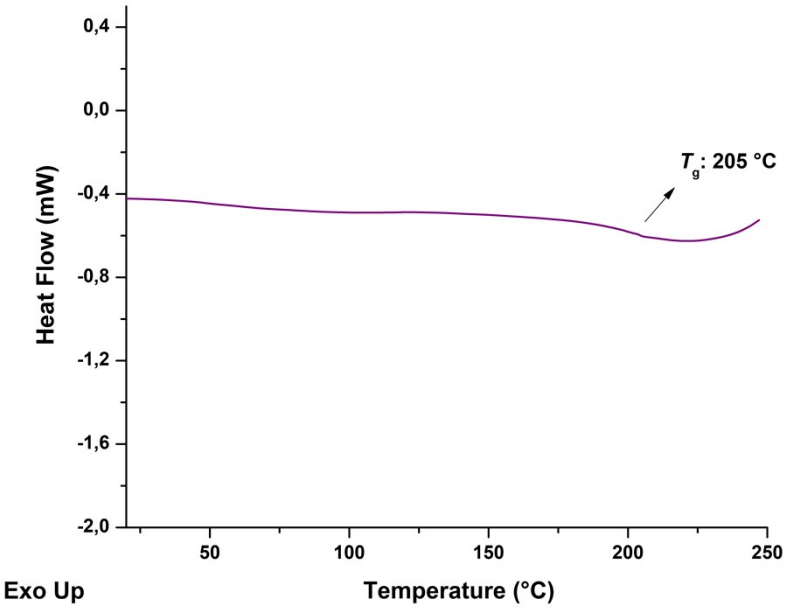


Figure S104. DSC spectrum of **P6a**.

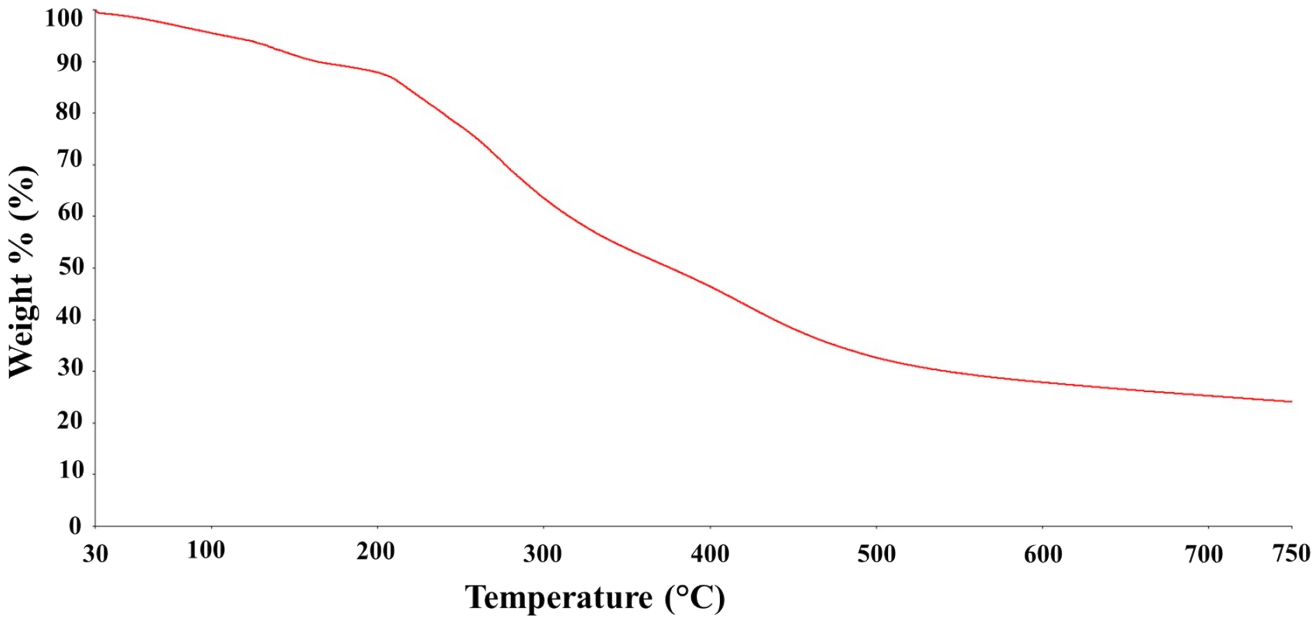


Figure S105. TGA thermogram of **P6a**.

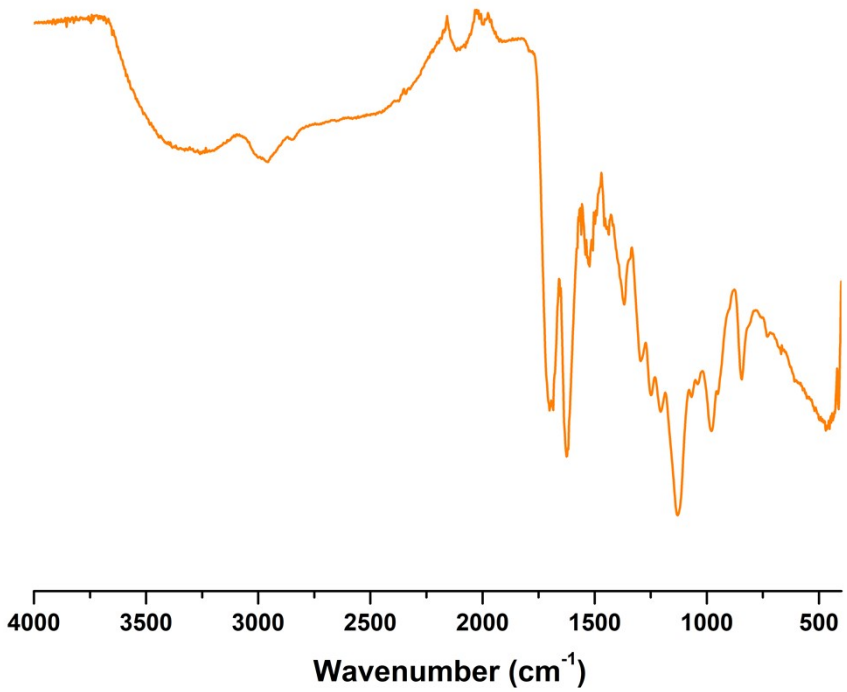
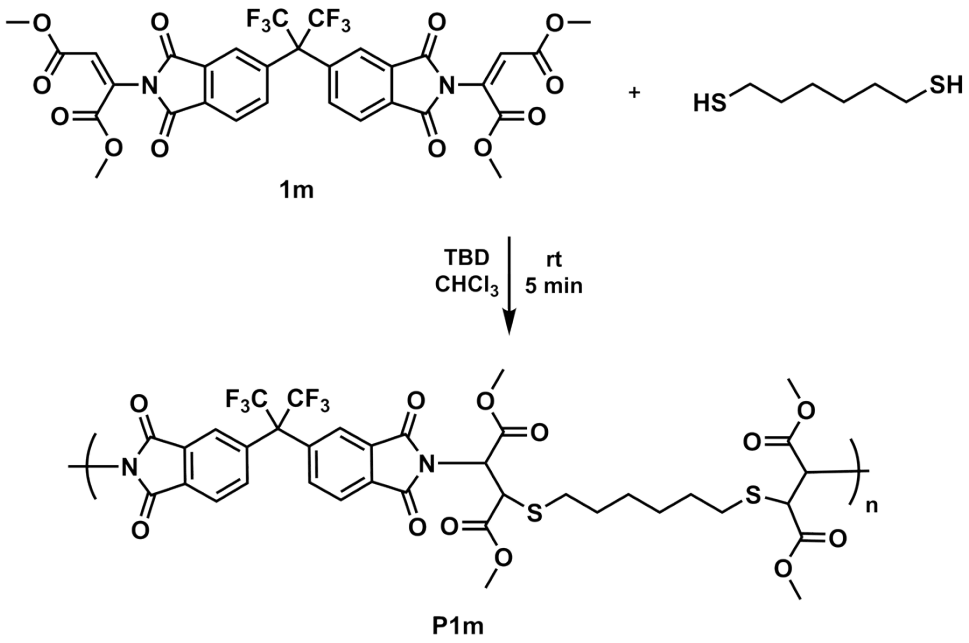


Figure S106. FT-IR spectrum of **P6a**.

3.7. Nucleophilic Thiol-ene Polymerization of Imide-yne monomers

3.7.1. Synthesis of P1m



General procedure for thiol-ene polymerization of imide-yne monomers was followed: Compound **1m** (876.8 mg, 1 mmol), HDT (152.9 μL, 1 mmol), TBD (34.8 mg, 0.25 mmol) and $CHCl_3$ (1 mL) were used. The resultant polymer **P1m** was obtained as a pale yellow solid. (yield: 721 mg, 81%). ^{1}H NMR ($CDCl_3$, δ): 7.98-7.83 (m, 6H, Ar-*H*), 5.40-5.19 (m, 2H, NC*H*), 4.54-4.23 (m, 2H, SC*H*), 3.84 (br, 6H, NCHC=OOCH_3), 3.74 (br, 6H, SCHC=OOCH_3), 2.52 (m, 4H, SCH_2), 1.37-1.21 (br, 8H, SCH$_2$CH_2 & SCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, δ): 170.38, 167.98, 165.97, 139.07, 136.16, 132.50, 132.10, 125.22, 124.24, 65.17, 53.39, 52.78, 51.38, 45.00, 33.66, 30.21, 28.58, 28.09, 27.67, 24.42. ^{19}F NMR ($CDCl_3$, δ): -63.18.

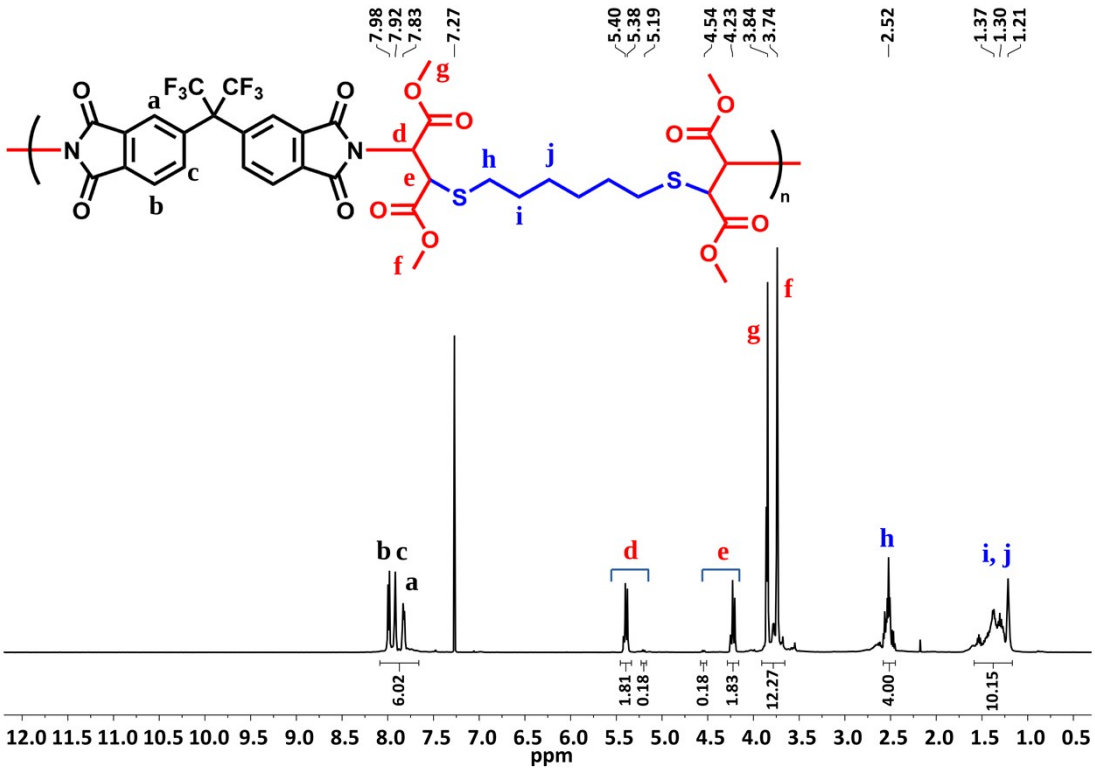


Figure S107. ^{1}H NMR spectrum of **P1m** in $CDCl_3$ (500 MHz).

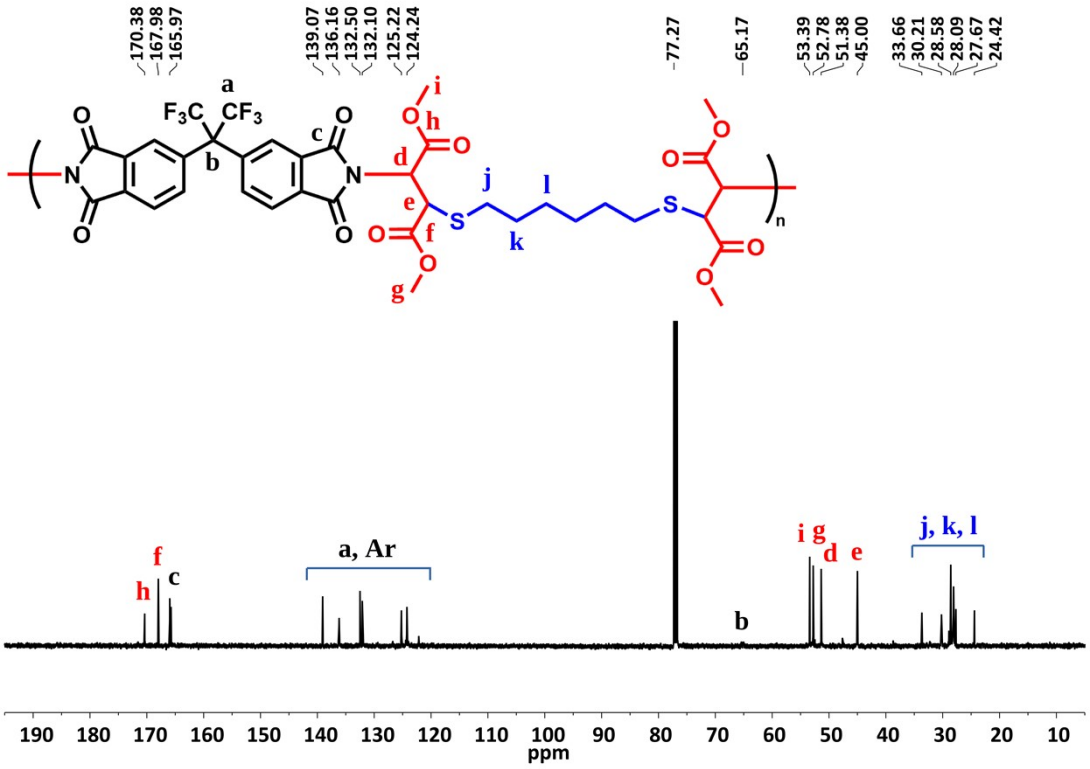


Figure S108. ^{13}C NMR spectrum of **P1m** in $CDCl_3$ (125 MHz).

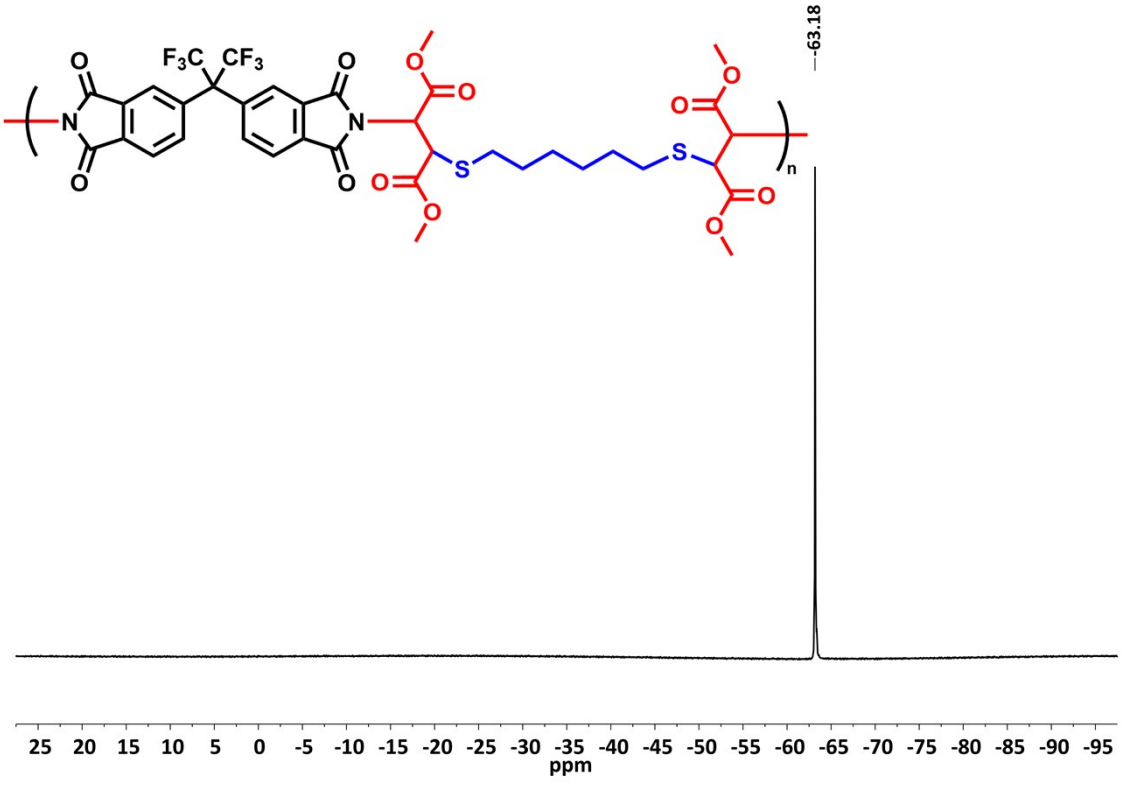


Figure S109. ^{19}F NMR spectrum of **P1m** in $CDCl_3$ (470 MHz).

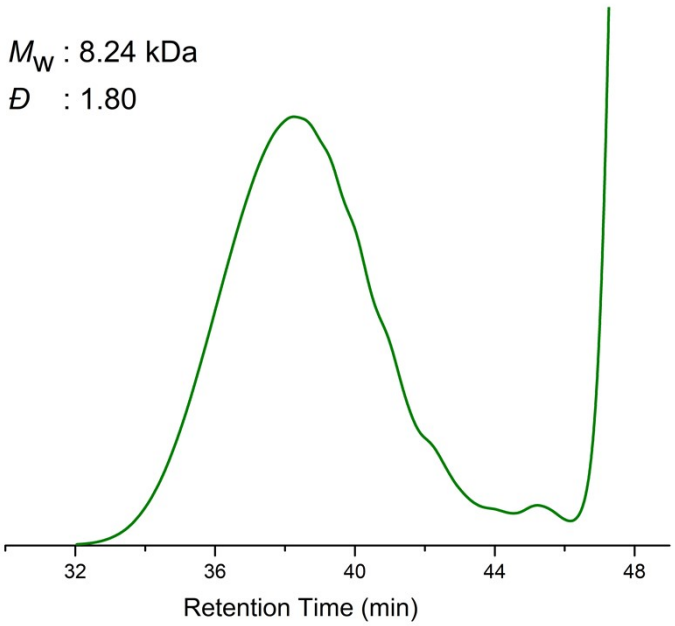


Figure S110. GPC trace of **P1m**.

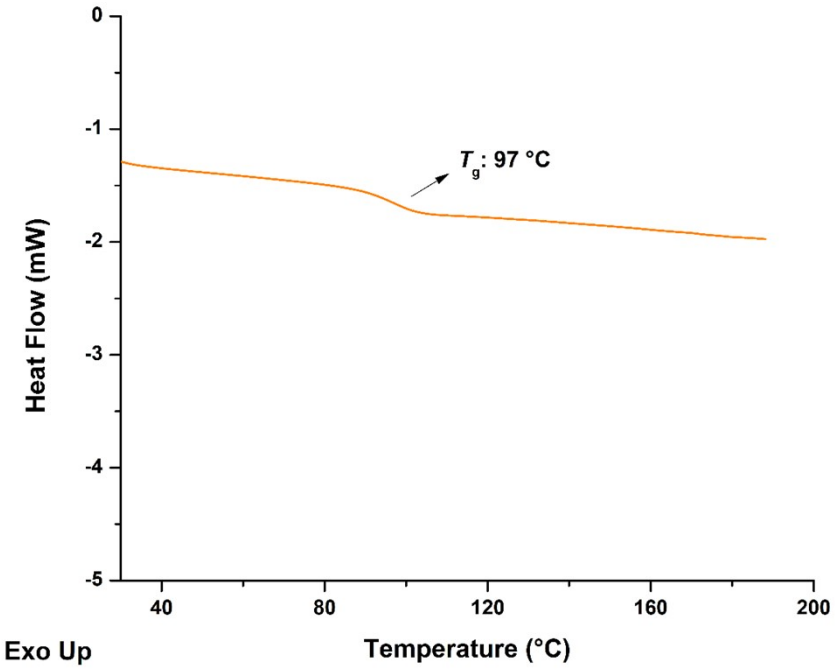


Figure S111. DSC spectrum of **P1m**.

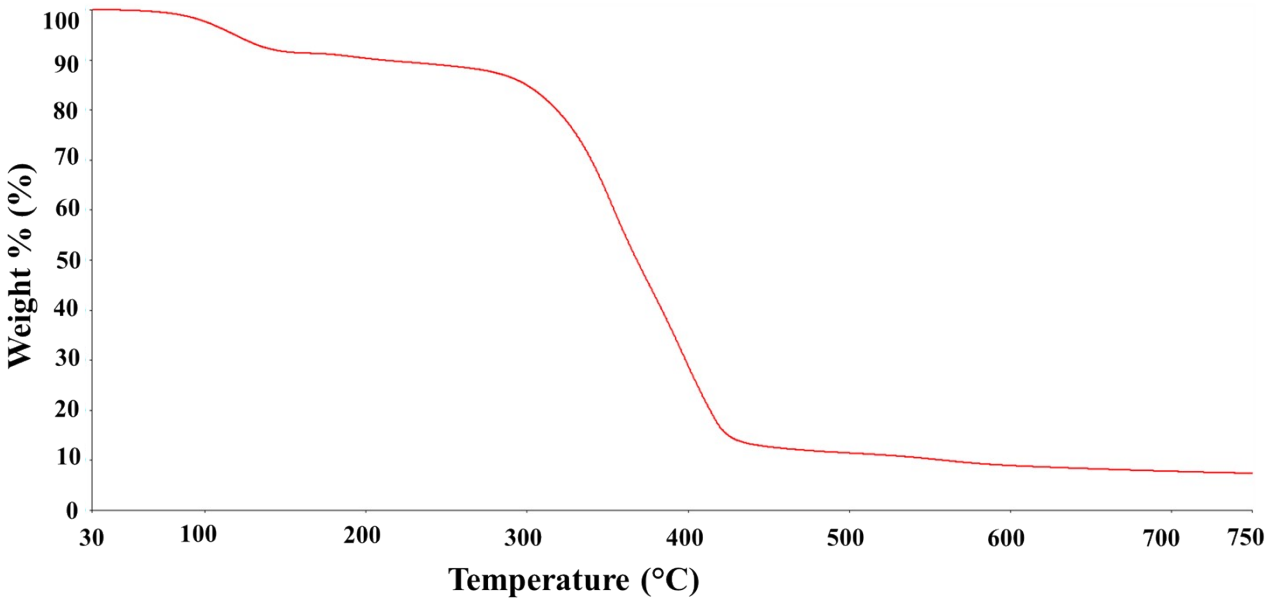


Figure S112. TGA thermogram of **P1m**.

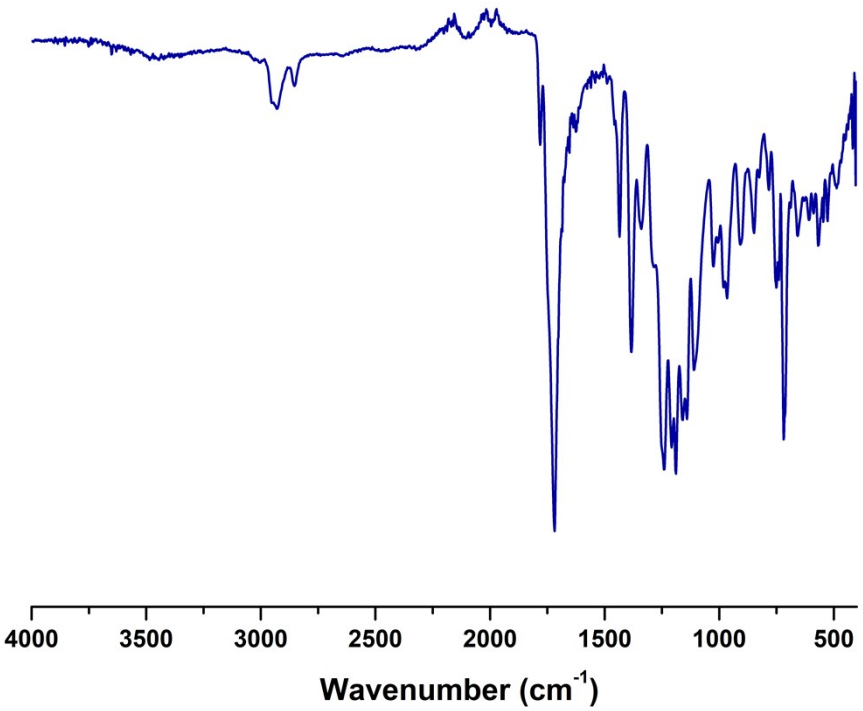
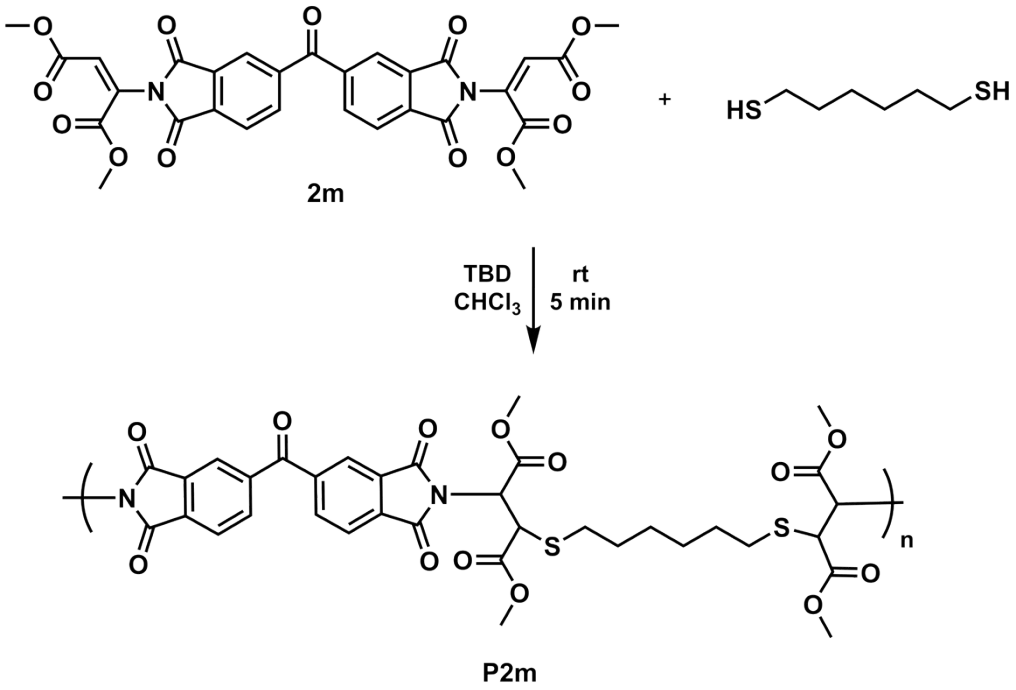


Figure S113. FT-IR spectrum of **P1m**.

3.7.2. Synthesis of P2m



General procedure for thiol-ene polymerization of imide-yne monomers was followed: Compound **2m** (754.8 mg, 1 mmol), HDT (152.9 μL, 1 mmol), TBD (34.8 mg, 0.25 mmol) and $CHCl_3$ (1 mL) were used. The resultant polymer **P2m** was obtained as a pale yellow solid. (yield: 664 mg, 88%). ^{1}H NMR ($CDCl_3$, δ): 8.24-8.10 (m, 6H, Ar-*H*), 5.40-5.19 (m, 2H, NC*H*), 4.54-4.22 (m, 2H, SC*H*), 3.84 (br, 6H, NCHC=OOCH_3), 3.74 (br, 6H, SCHC=OOCH_3), 2.50 (m, 4H, SCH_2), 1.33-1.18 (br, 8H, SCH_2CH_2 & $SCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, δ): 192.65, 170.39, 167.99, 165.92, 141.86, 135.91, 134.82, 132.00, 124.78, 124.43, 53.43, 52.84, 51.34, 45.00, 33.71, 30.22, 28.02, 24.44.

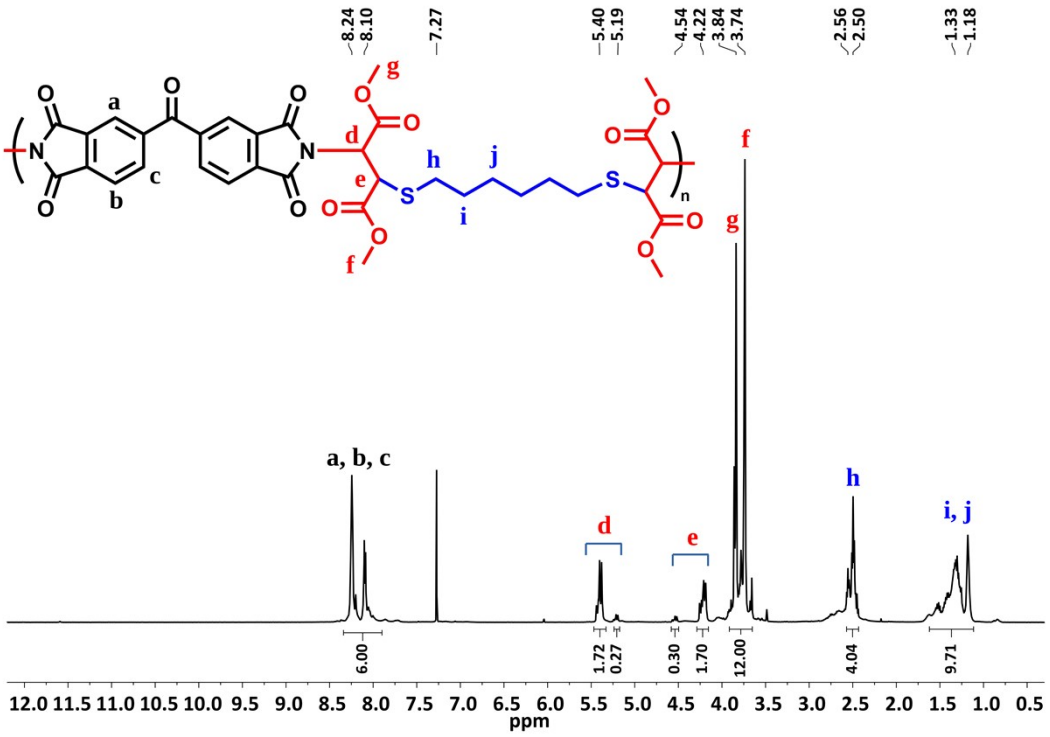


Figure S114. ^{1}H NMR spectrum of **P2m** in $CDCl_3$ (500 MHz).

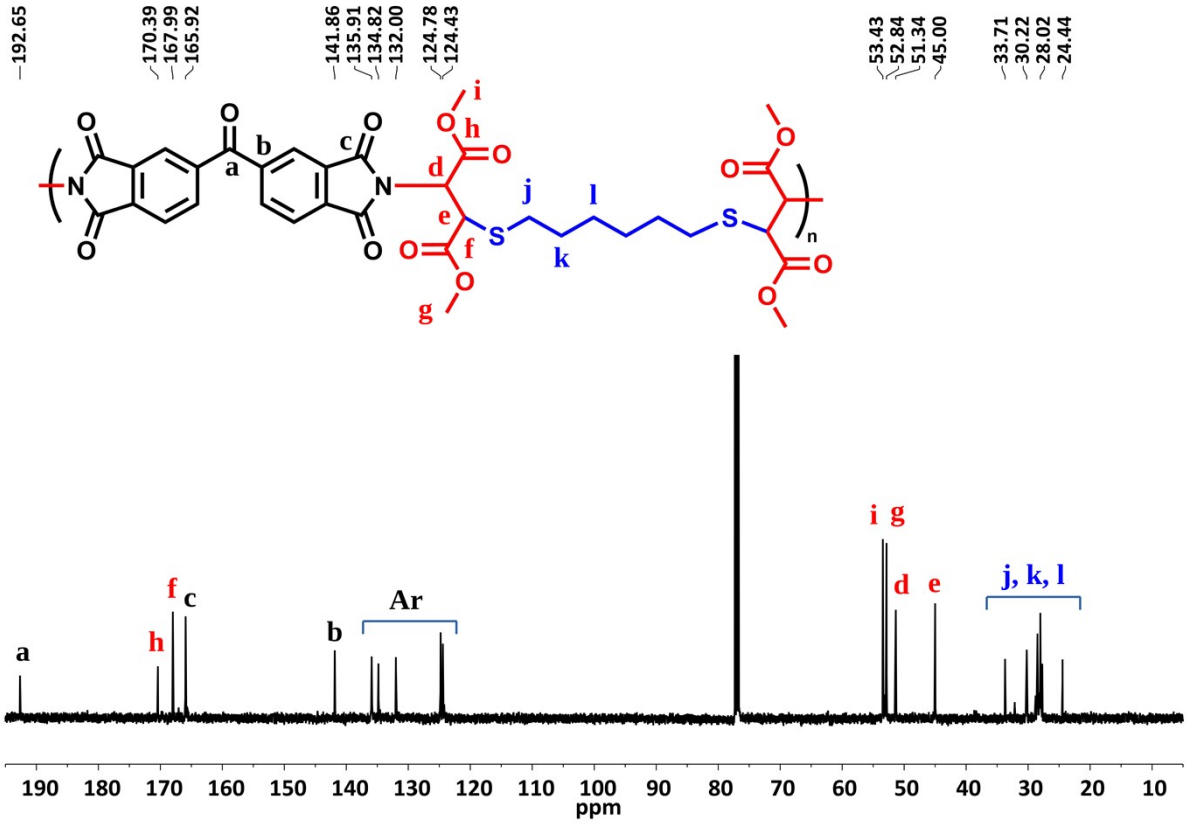


Figure S115. ^{13}C NMR spectrum of **P2m** in $CDCl_3$ (125 MHz).

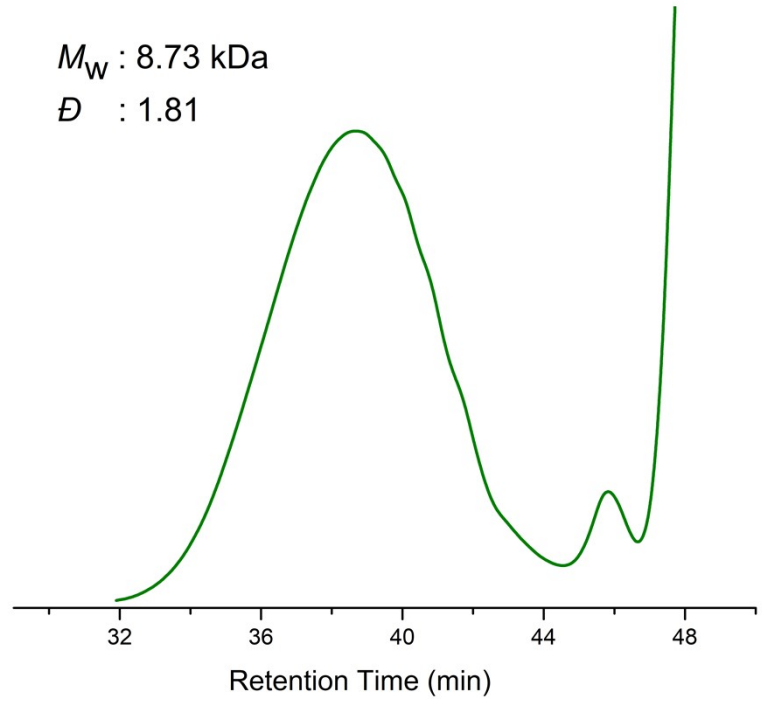


Figure S116. GPC trace of **P2m**.

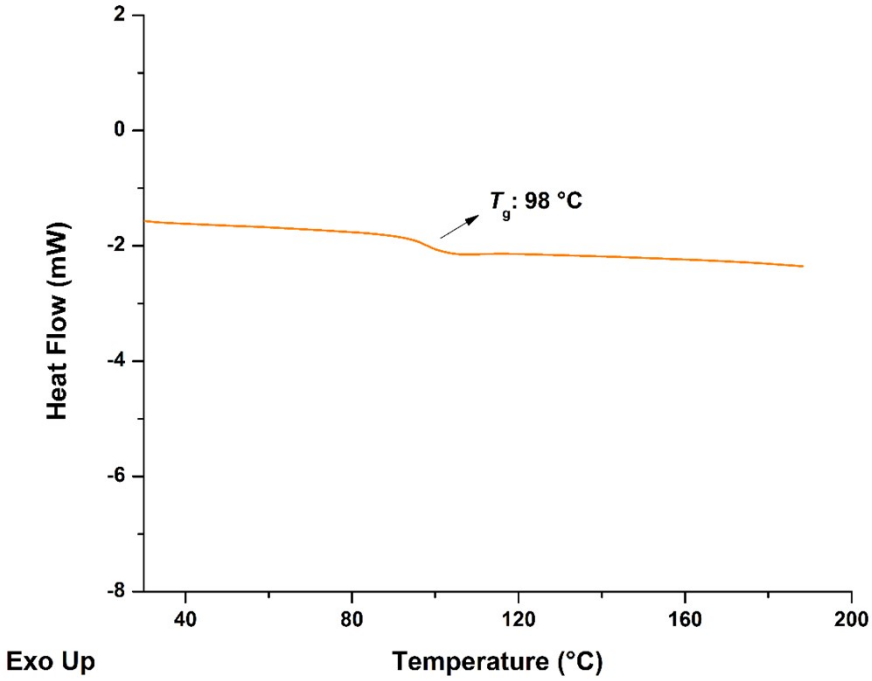


Figure S117. DSC spectrum of **P2m**.

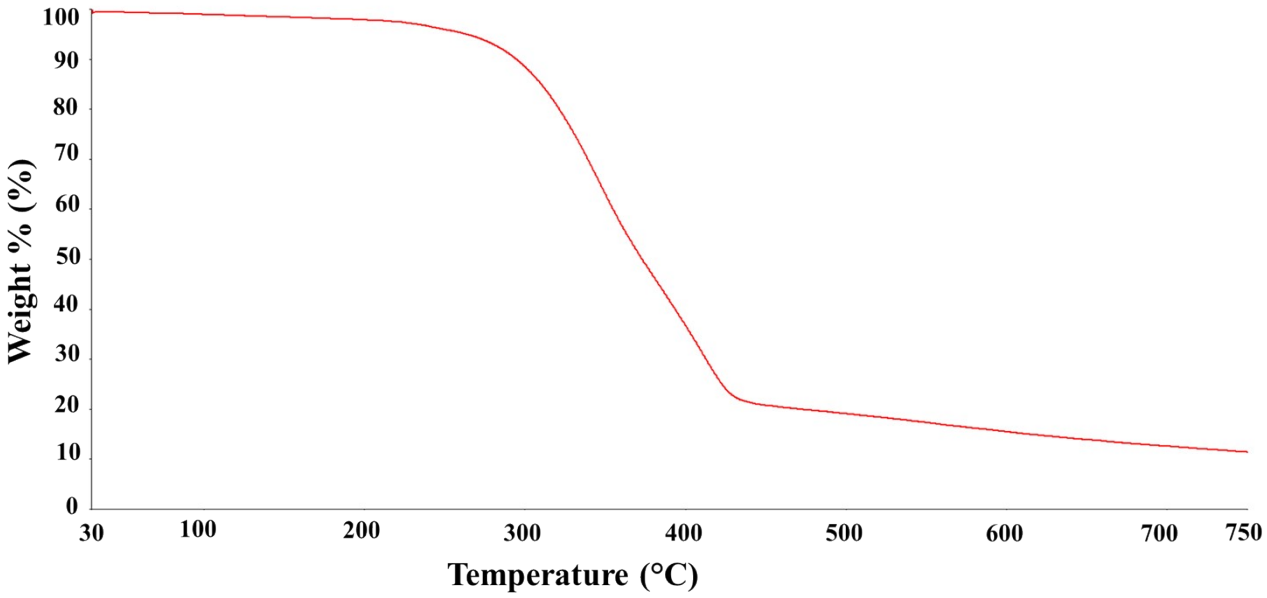


Figure S118. TGA thermogram of **P2m**.

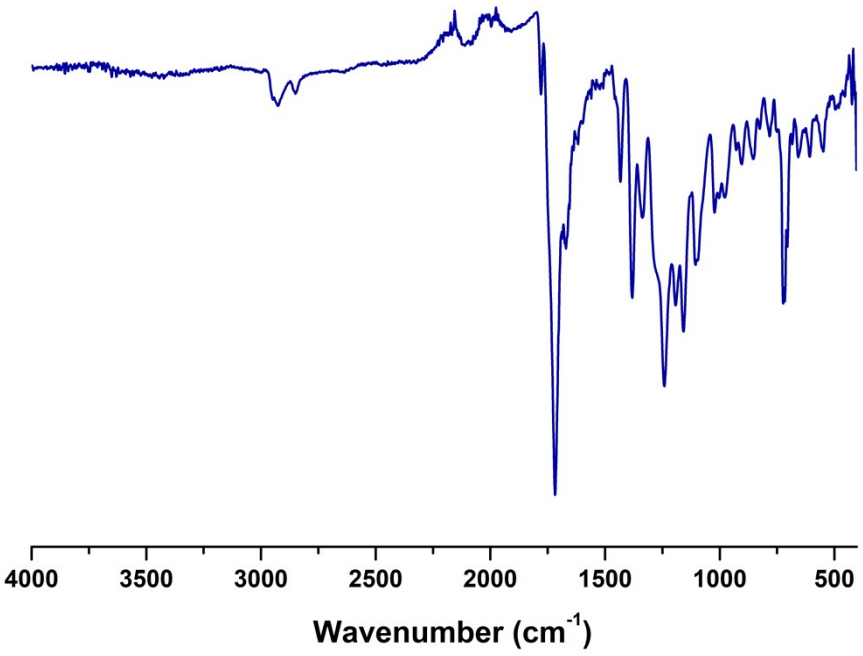
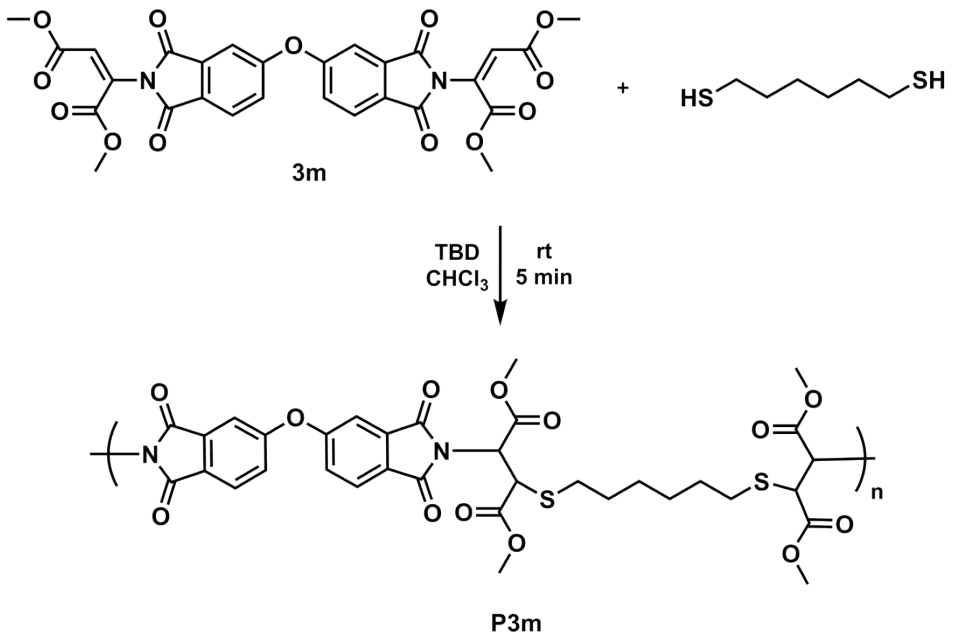


Figure S119. FT-IR spectrum of **P2m**.

3.7.3. Synthesis of P3m



General procedure for thiol-ene polymerization of imide-yne monomers was followed: Compound **3m** (742.8 mg, 1 mmol), HDT (152.9 μL, 1 mmol), TBD (34.8 mg, 0.25 mmol) and $CHCl_3$ (1 mL) were used. The resultant polymer **P3m** was obtained as a pale yellow foamy solid (yield: 632 mg, 85%). ^{1}H NMR ($CDCl_3$, δ): 7.95-7.46 (m, 6H, Ar-*H*), 5.36-5.18 (m, 2H, NC*H*), 4.51-4.21 (m, 2H, SC*H*), 3.83 (br, 6H, NCHC=OOCH_3), 3.73 (br, 6H, SCHC=OOCH_3), 2.50 (m, 4H, SCH_2), 1.30-1.18 (br, 8H, SCH_2CH_2 & $SCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, δ): 170.49, 168.21, 166.04, 161.11, 134.39, 127.13, 126.32, 124.88, 114.16, 53.32, 52.76, 51.22, 45.11, 33.72, 30.23, 28.54, 28.03, 24.43.

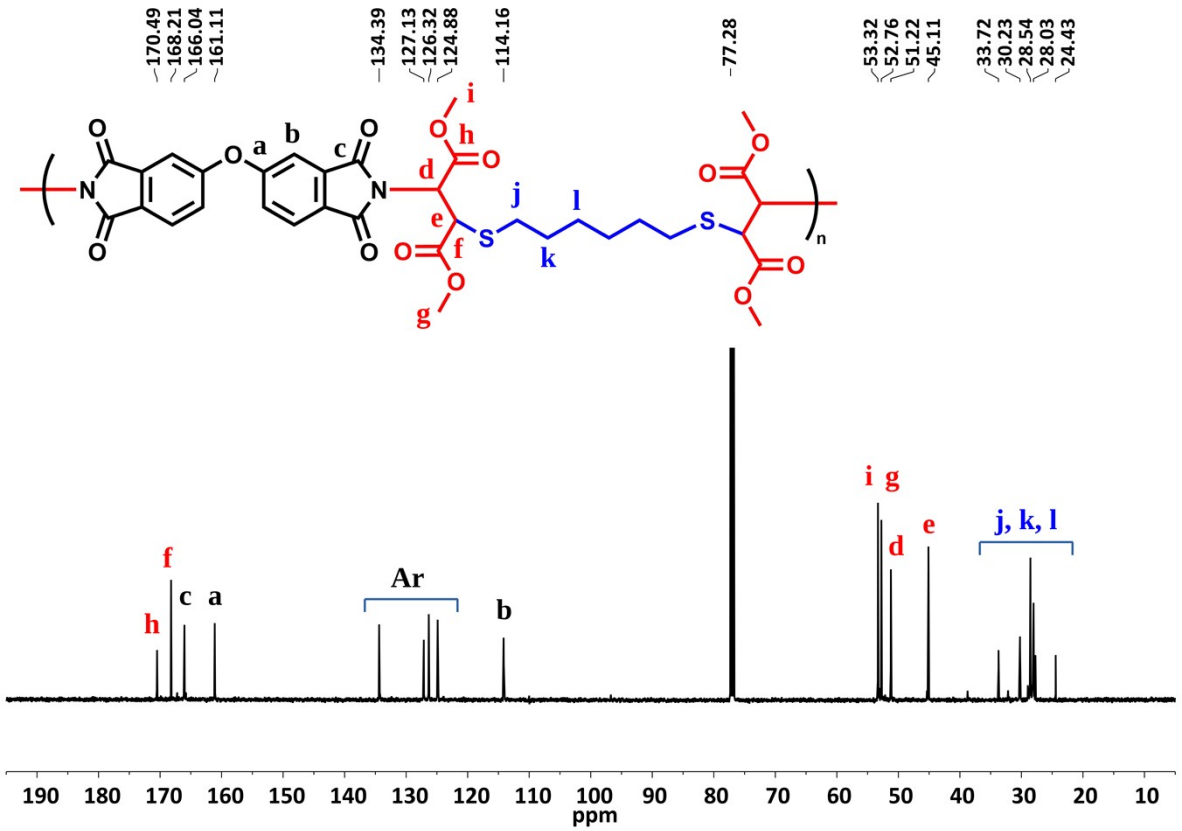


Figure S120. ^{13}C NMR spectrum of **P3m** in $CDCl_3$ (125 MHz).

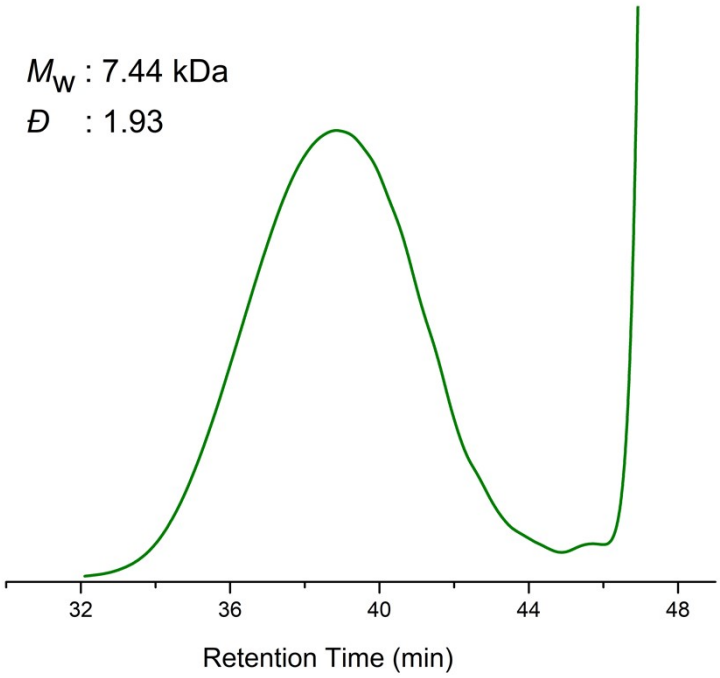


Figure S121. GPC trace of **P3m**.

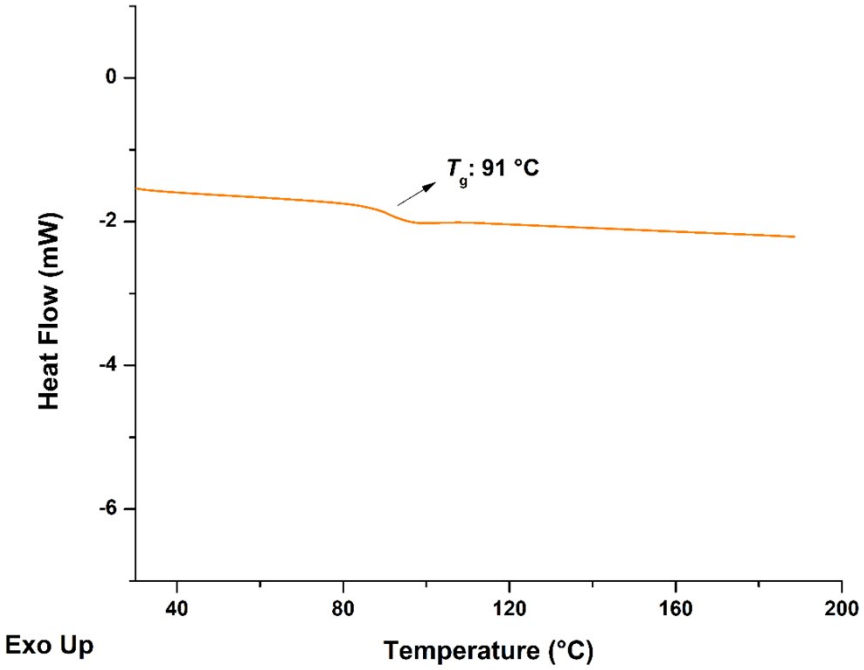


Figure S122. DSC spectrum of **P3m**.

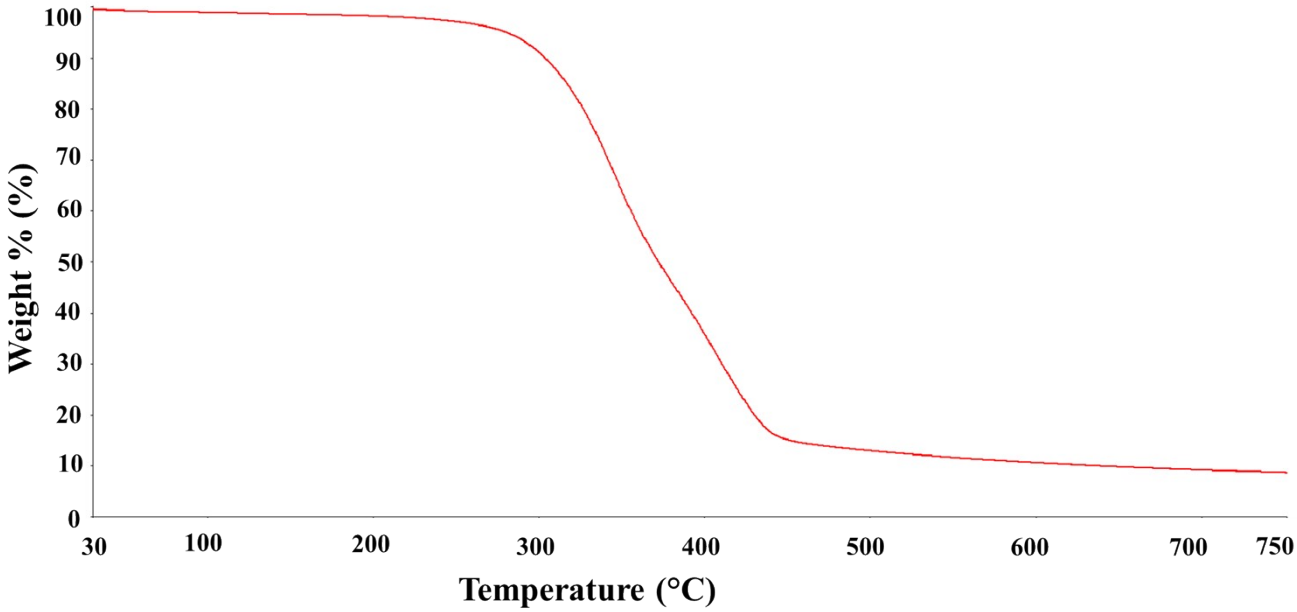


Figure S123. TGA thermogram of **P3m**.

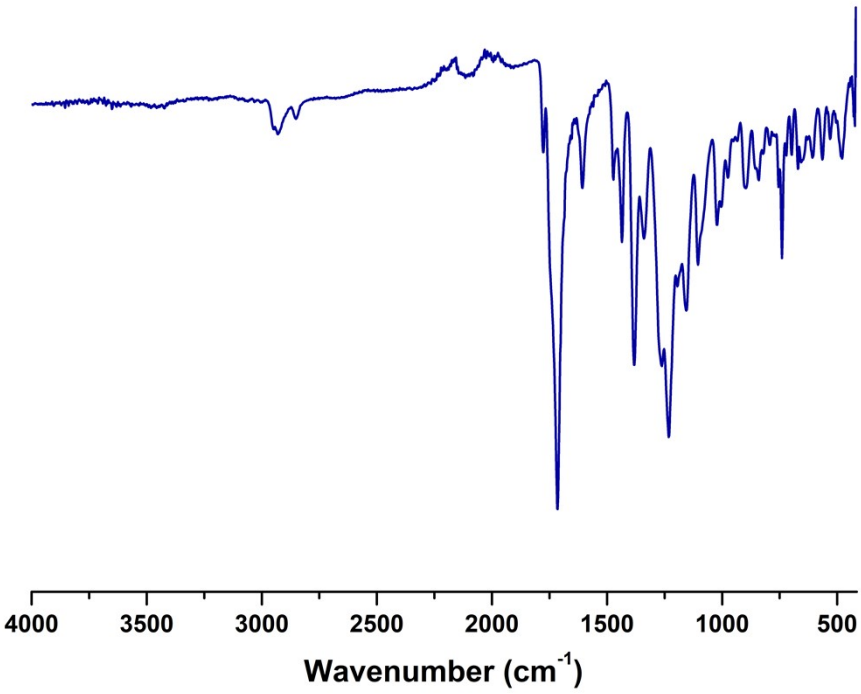
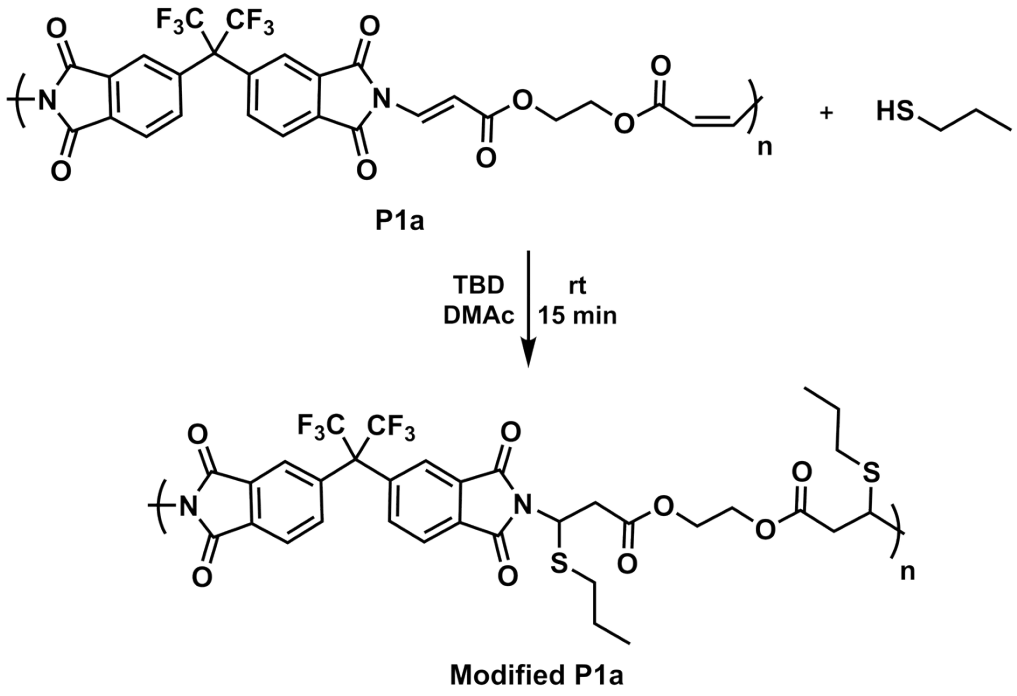


Figure S124. FT-IR spectrum of **P3m**.

3.8. Post-polymerization modification of P1a with 1-propanethiol



To a 10 mL round bottom flask equipped with a magnetic stir bar was added **P1a** (182.5 mg, 0.3 mmol) and dissolved in 0.6 mL of DMAc. Then, 1-propanethiol (81.6 μL, 0.9 mmol) and TBD (10.4 mg, 0.075 mmol) were added to the reaction medium, respectively. Upon the addition of TBD, the pale yellow solution turned to dark brown instantly. The flask was allowed to stir at room temperature for 15 minutes. The solution was diluted with 1 mL of $CHCl_3$ and precipitated into acidified methanol and filtered. The dissolution-precipitation procedure ($CHCl_3$-acidified methanol) was repeated two times. The resultant polymer was obtained as a pale-yellow powder and dried in a vacuum oven at 40 °C for 24 hours (yield: 223.5 mg, 89%). ^{1}H NMR (d_6-DMSO, δ): 8.04-7.70 (m, 6H, Ar-*H*), 5.56 (t, 2H, C=ONC*H*), 4.18 (br, 4H, C=OOCH_2), 3.34 (t, 4H, SCH_2), 3.13-2.57 (m, 4H, C=ONCHCH_2), 1.52 (br, 4H, SCH_2CH_2), 0.85 (t, 6H, $SCH_2CH_2CH_3$). ^{13}C NMR (d_6-DMSO, δ): 169.47, 166.19, 137.90, 136.59, 132.81, 132.42, 124.68, 124.06, 64.96, 62.78, 50.88, 49.04, 37.79, 33.58, 22.59, 13.44.

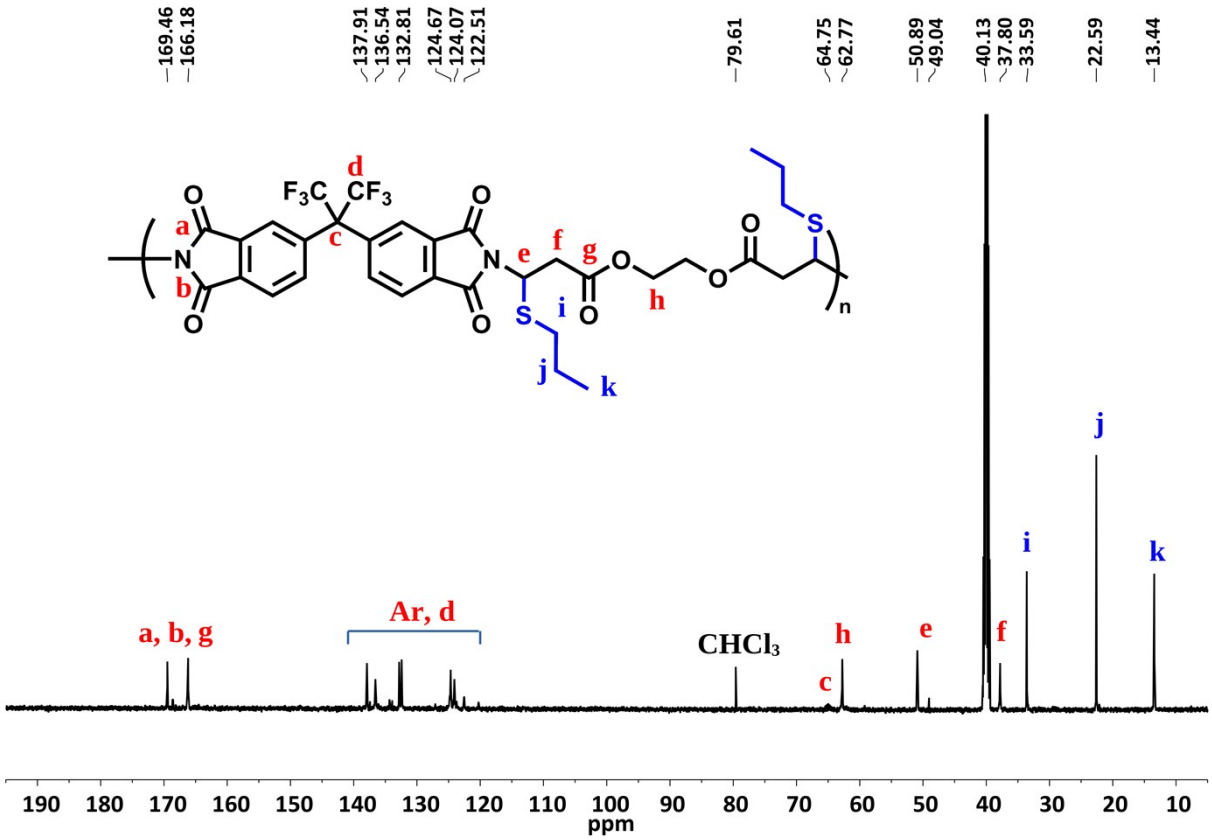


Figure S125. ^{13}C NMR spectrum of **modified P1a** in d_6-DMSO (125 MHz).

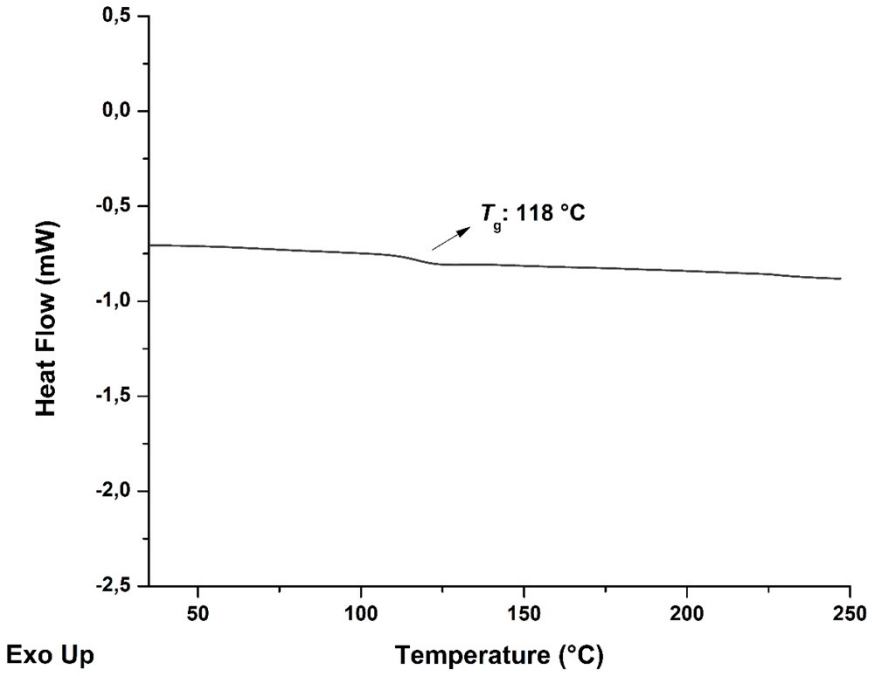


Figure S126. DSC spectrum of **modified P1a**.

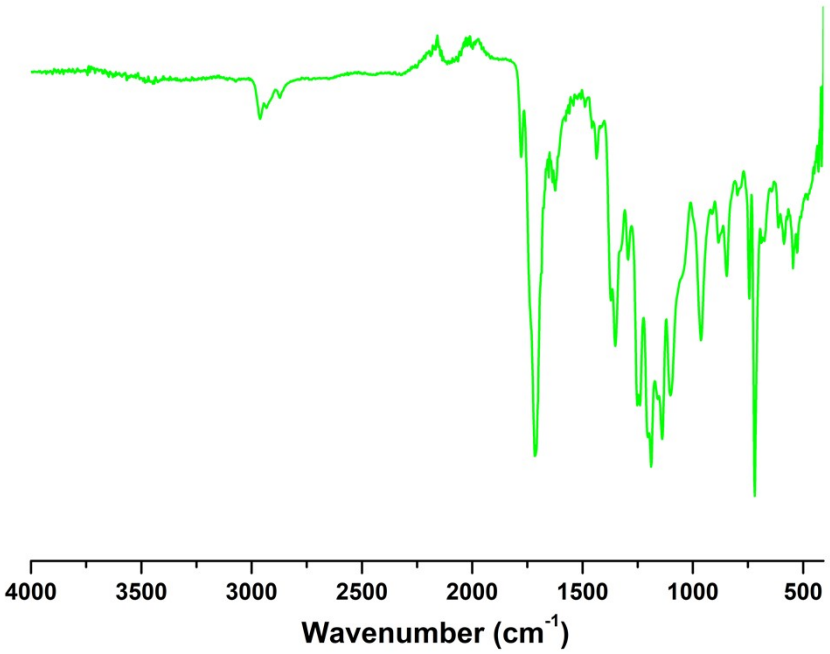


Figure S127. FT-IR spectrum of **modified P1a**.

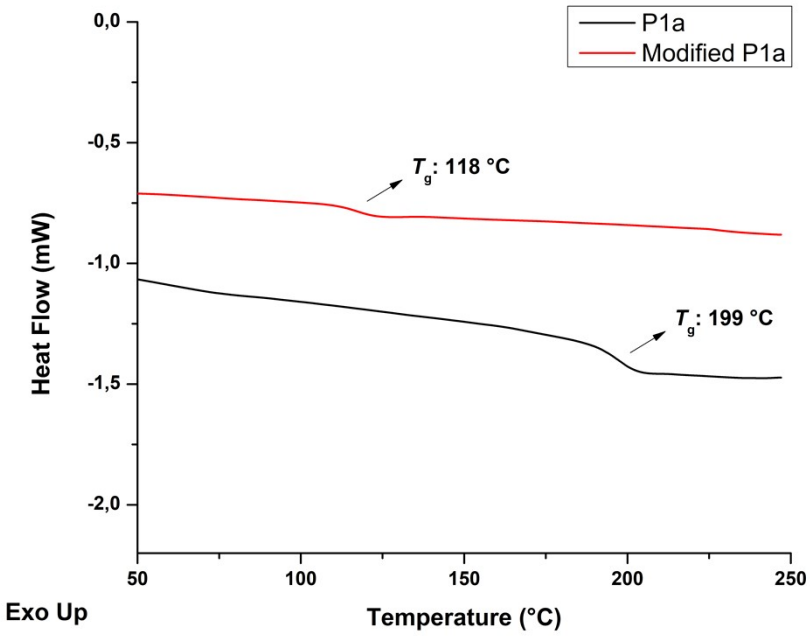


Figure S128. Overlaid DSC spectra of **P1a** and **modified P1a**.