Electronic Supplementary Information (ESI)

for

Multicomponent Spiropolymerization of Diisocyanides, Alkynes and Carbon Dioxide for Constructing 1,6-Dioxospiro[4,4]nonane-3,8-diene as Structural Units under One-Pot Catalyst-Free Conditions

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1 Experimental

1 Experimental

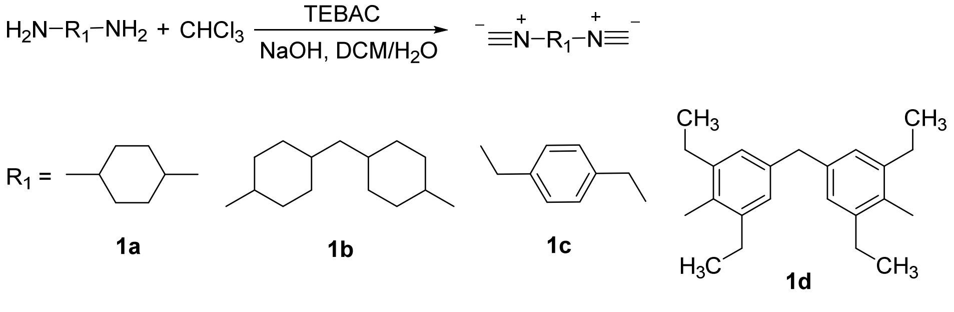
1.1 Materials

Unless stated otherwise, all chemicals were obtained from commercial suppliers and used without further purification. The monomers **1a - d** were synthesized according to the commonly used synthetic routes as shown in Scheme S1. Benzyltriethylammonium chloride and trans-1,4-diaminocyclohexane, 4, 4’ -methylenebis(cyclohexylamine) were bought from Heowns. 1,4-bis(aminomethyl) benzene, 4,4'-methylenebis(2,6-diethylaniline), dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate were bought from Energy Chemical. Chloroform-d was bought from Innochem.

1.2 Equipments

Weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were obtained from gel permeation chromatography (GPC) system equipped with a Waters 1515 isocratic HPLC pump and Waters 2414 refractive index detector. Polystyrene standard was utilized and THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. Fourier transform infrared (FT-IR) spectra were measured on a Bruker (ALPHA) spectrometer. ^{1}H NMR spectra were measured on a Bruker AV 400 spectrometer. Mass spectra were collected by using a Finnigan BIFLEX III mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer STA 8000 at a heating rate of 10 °C min^{-1} under a nitrogen flow. Differential scanning calorimeter (DSC) was measured on a TA DSC Q2000. UV-Vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer.

1.3 Synthesis of monomers 1a ~ d



Scheme S1. The synthetic route to monomers **1a - d**

Monomers **1a - d** were prepared by the same steps. The synthesis procedure of **1b - d** is almost the same with that of **1a**. The detailed method for the synthesis of **1a** was given here as an example.

Trans-1,4-diisocyanocyclohexane (**1a**): To a 500 mL round-bottom flask were added trans-1,4-diaminocyclohexane (8.1200 g, 50 mmol), DCM (20 mL), chloroform (8.044 mL, 100 mmol) and TEBAC (0.2278 g, 1 mmol). A 50% aqueous solution of sodium hydroxide (15 mL) was added. The mixture was heated at 40 °C for 12 hours. The organic layer was combined and washed with DCM and water, and then dried over $MgSO_4$ for an hour. Product **1a** was separated by flash column chromatograph.

1.4 Characterization data of monomers 1a - d

Characterization data of trans-1,4-diisocyanocyclohexane **1a**: White powder of **1a** was obtained in 30.4% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (m, 2H), 2.02-1.99 (d, *J* = 10.4 Hz, 4H), 1.76-1.74 (m, *J* = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.21-156.11 (t, *J* = 4.9 Hz), 49.66-49.55 (t, *J* = 5.6 Hz), 26.86. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_8H_{10}N_2$: 134.0844, Found: 134.0843, error: -0.7 ppm.

Characterization data of 4,4'-methylenebis(cyclohexylisocyano) **1b**: White powder of **1b** was obtained in 34.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (m, 1H), 3.37-3.33 (m, 2H), 2.17-2.14 (d, *J* = 12.0 Hz, 4H), 1.96-1.92 (d, *J* = 12.8 Hz, 2H), 1.76-1.73 (d, *J* = 10.8 Hz, 5H), 1.61-1.50 (m, 9H), 1.36-1.33 (m, 6H), 1.13 (s, 1H), 1.07-1.03 (t, *J* = 7.2 Hz, 1H), 0.92-0.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.94-154.78 (q, *J* = 10.4 Hz), 153.86-153.70 (q, *J* = 10.8 Hz), 52.31-52.14 (q, *J* = 10.8 Hz), 50.66-50.51 (q, *J* = 10.0 Hz), 43.58, 43.42, 43.17, 33.34-33.26 (t, *J* = 4.3 Hz), 33.04, 32.94, 32.73, 30.94, 30.61, 30.59, 27.00. HRMS (ESI, *m/z*) Calcd for $[M+Na]^+$ $C_{15}H_{22}N_2Na$: 230.1681, Found: 230.1671, error: -3.9 ppm.

Characterization data of 1,4-bis(isocyanomethyl)benzene **1c**: White powder of **1c** was obtained in 42.0% yield. ^{1}H ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (s, 4H), 4.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.26-158.16 (t, *J* = 5.1 Hz), 132.75, 121.31, 45.27-45.12 (t, *J* = 7.3 Hz). HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{10}H_8N_2$: 156.0687, Found: 156.0684, error: -1.9 ppm.

Characterization data of 1,1-bis(3-ethyl-4-isocyano-5-ethylphenyl)methane **1d**: White powder of **1d** was obtained in 44.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91 (s, 4H), 3.92 (s, 2H), 2.78-2.72 (q, *J* = 7.6 Hz, 8H), 1.26-1.22 (t, *J* = 7.6 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.92, 141.51, 141.06, 126.82, 41.53, 25.87, 13.97. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{23}H_{26}N_2$: 330.2096, Found: 330.2096, error: 0 ppm.

1.5 Synthetic route to MC

The synthetic route has shown in Scheme 2. To a 30 mL Schlenk tube equipped with a magnetic stir bar were added dimethyl acetylenedicarboxylate **2a** (0.1705 g, 1.2 mmol) and 6 mL toluene. Then, cyclohexyl isocyanide (0.1091 g, 1.0 mmol) was slowly added. The reaction mixture was heated in an oil bath at 80 °C for 12 h under constant stirring under CO_2 atmosphere, cooled to room temperature. The organic layer was combined and washed with DCM and water, and then dried over $MgSO_4$ for an hour. **MC** was separated by flash column chromatograph.

1.6 Characterization data of MC

White powder of **MC** was obtained in 54.0% yield. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.96$ (s, 6H), 3.78 (s, 6H), 3.63 (m, 2H), 1.74-1.71 (m, 4H), 1.62-1.57 (m, 4H), 1.43-1.16 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.44$, 159.68, 150.63, 139.74, 135.87, 111.33, 57.26, 53.36, 53.33, 52.98, 52.95, 33.30, 32.95, 25.59, 24.59, 24.49. HRMS (EI, *m/z*) Calcd for $[M+H]^+$ $C_{27}H_{34}N_2O_{10}$: 546.2213, Found: 546.2222, error: +1.6 ppm.

2 FT-IR spectra of spiropolymers

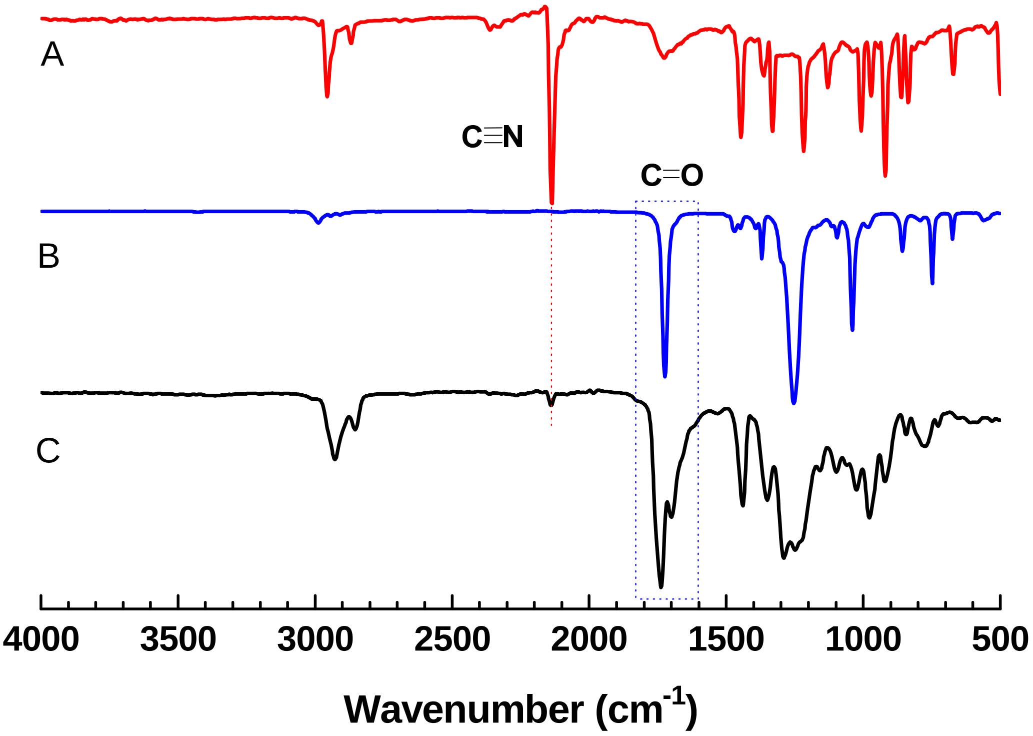


Figure S1. FT-IR spectra of (A) **1a**, (B) **2b**, and (C) **P1a2b**.

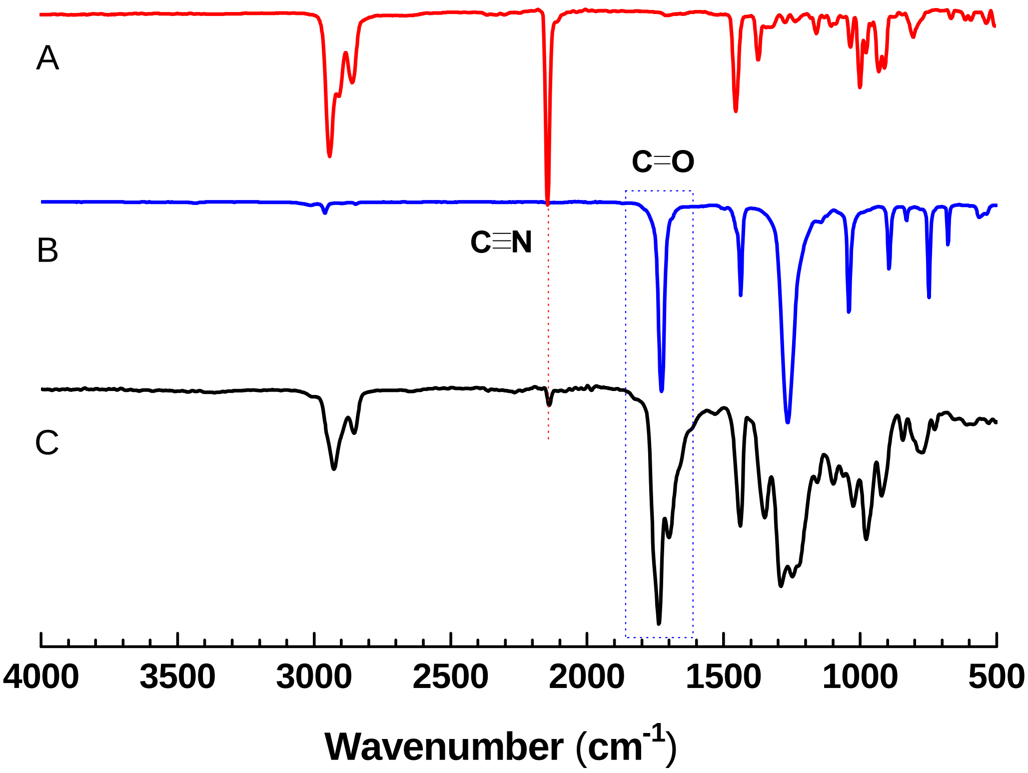


Figure S2. FT-IR spectra of (A) **1b**, (B) **2a**, and (C) **P1b2a**.

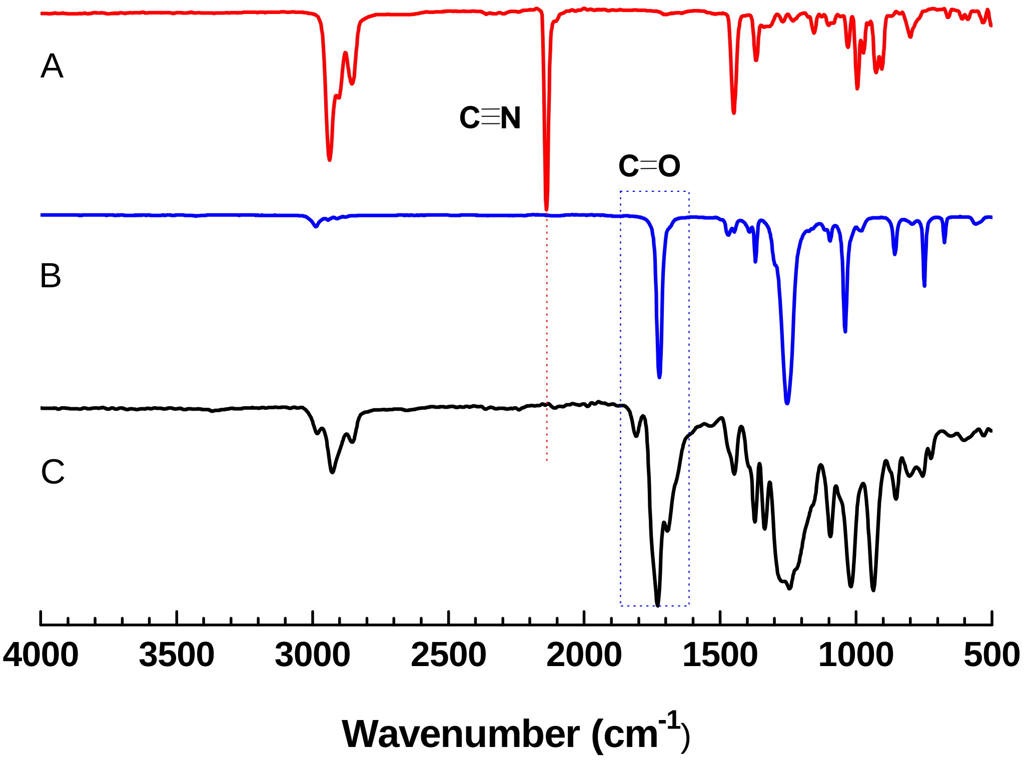


Figure S3. FT-IR spectra of (A) **1b**, (B) **2b**, and (C) **P1b2b**.

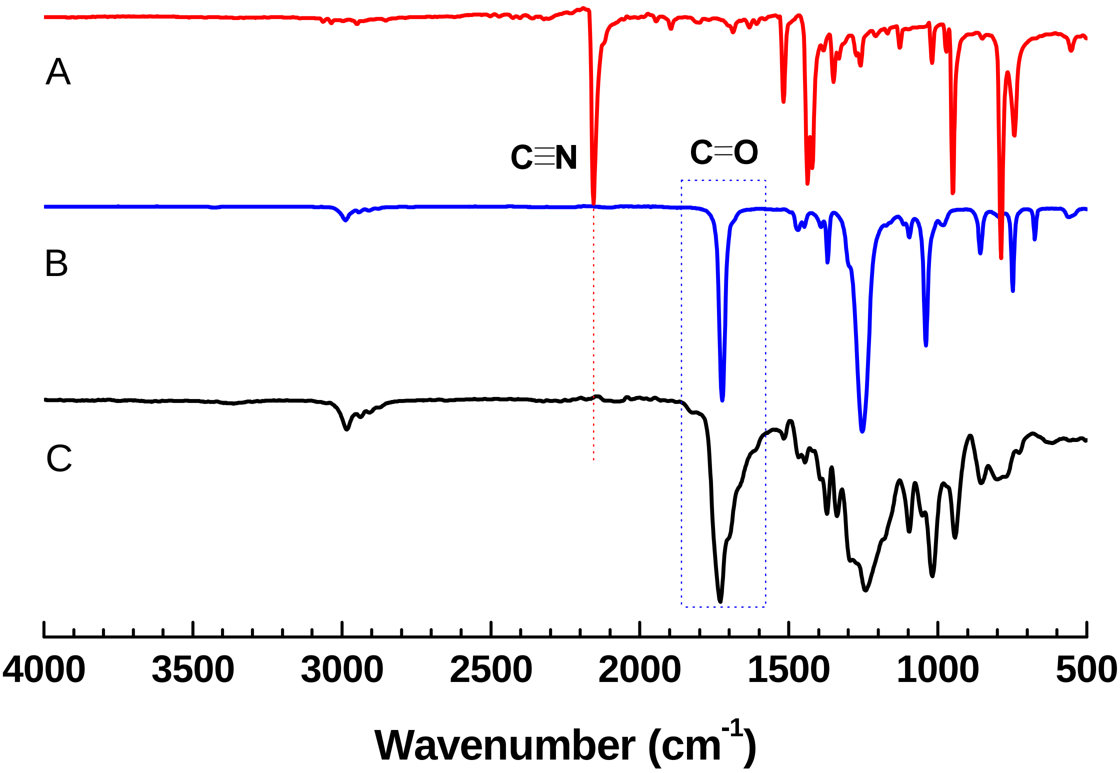


Figure S4. FT-IR spectra of (A) **1c**, (B) **2b**, and (C) **P1c2b**.

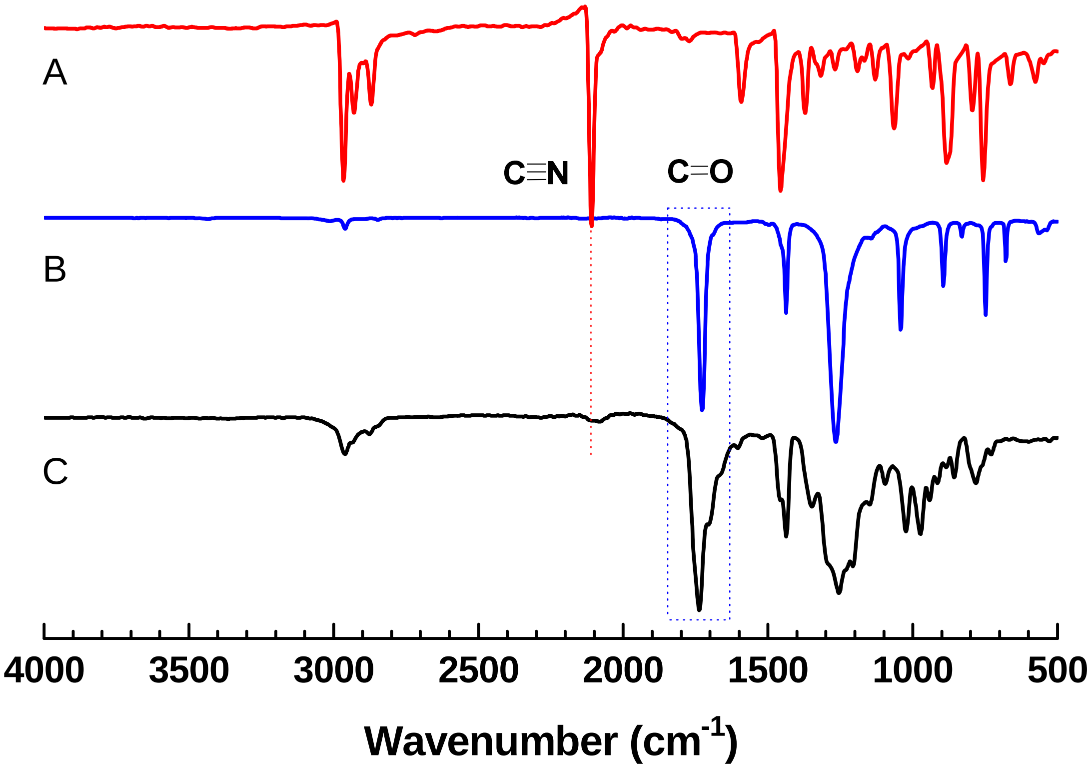


Figure S5. FT-IR spectra of (A) **1d**, (B) **2a**, and (C) **P1d2a**.

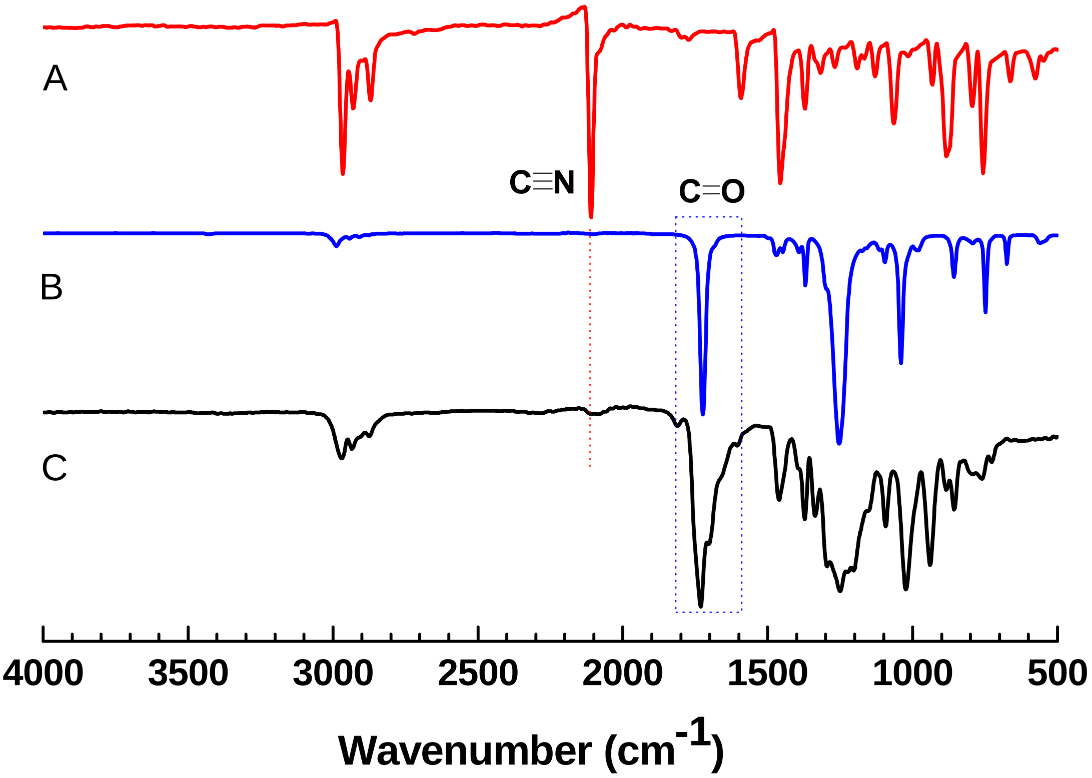


Figure S6. FT-IR spectra of (A) **1d**, (B) **2b**, and (C) **P1d2b**.

3 ^{1}H NMR spectra of spiropolymers

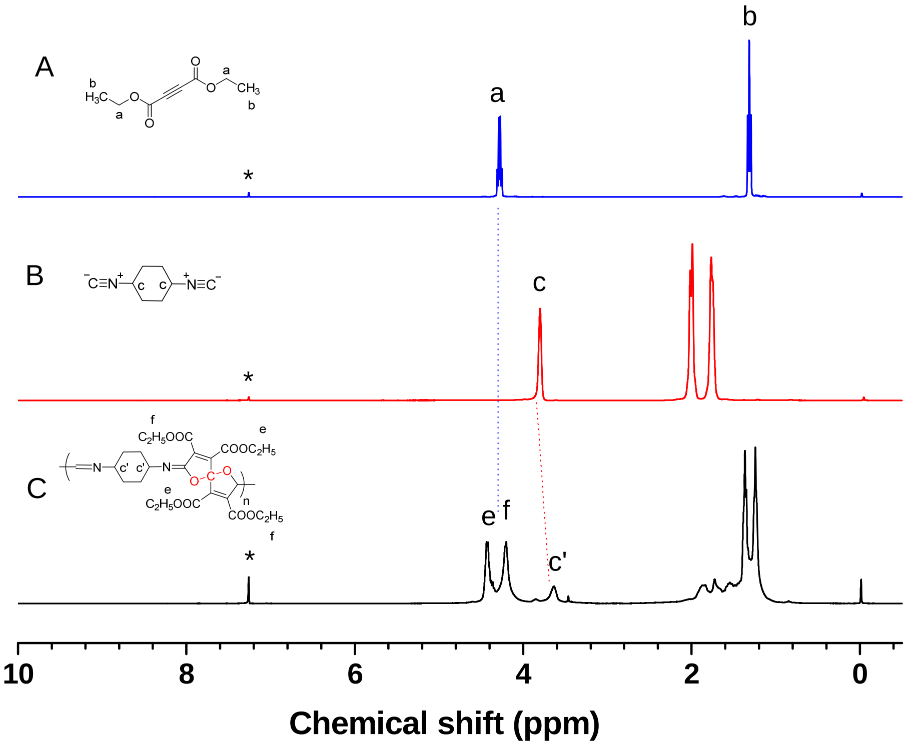


Figure S7. ^{1}H NMR spectra of (A) **1a**, (B) **2b**, and (C) **P1a2b** in $CDCl_3$. The solvent peaks are marked with asterisks.

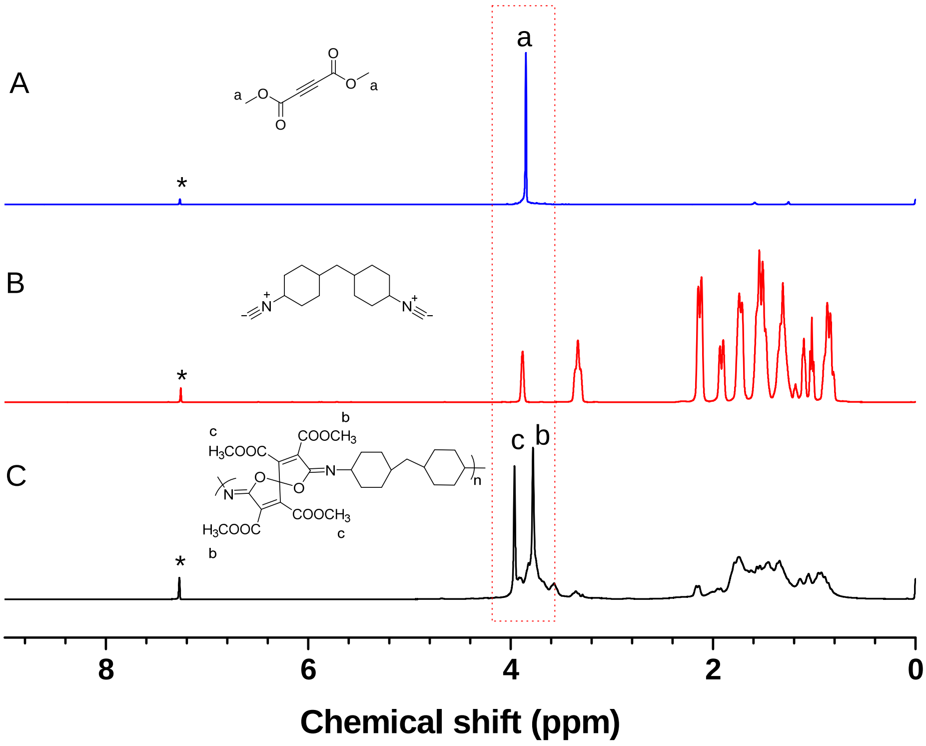


Figure S8. ^{1}H NMR spectra of (A) **1b**, (B) **2a**, and (C) **P1b2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

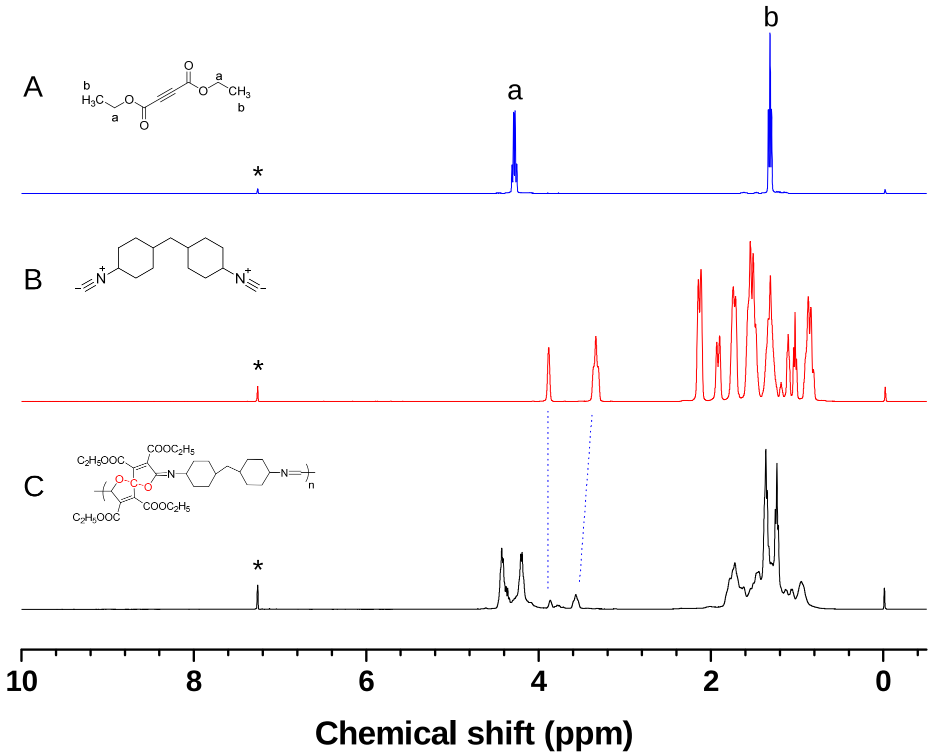


Figure S9. ^{1}H NMR spectra of (A) **1b**, (B) **2b**, and (C) **P1b2b** in $CDCl_3$. The solvent peaks are marked with asterisks.

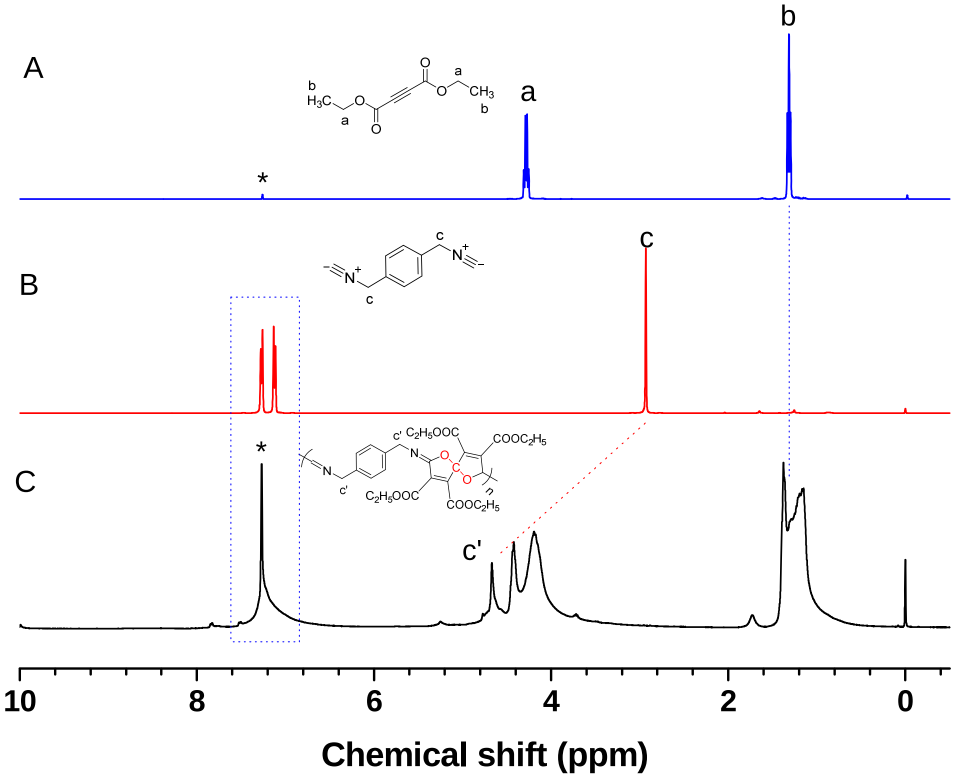


Figure S10. ^{1}H NMR spectra of (A) **1c**, (B) **2b**, and (C) **P1c2b** in $CDCl_3$. The solvent peaks are marked with asterisks.

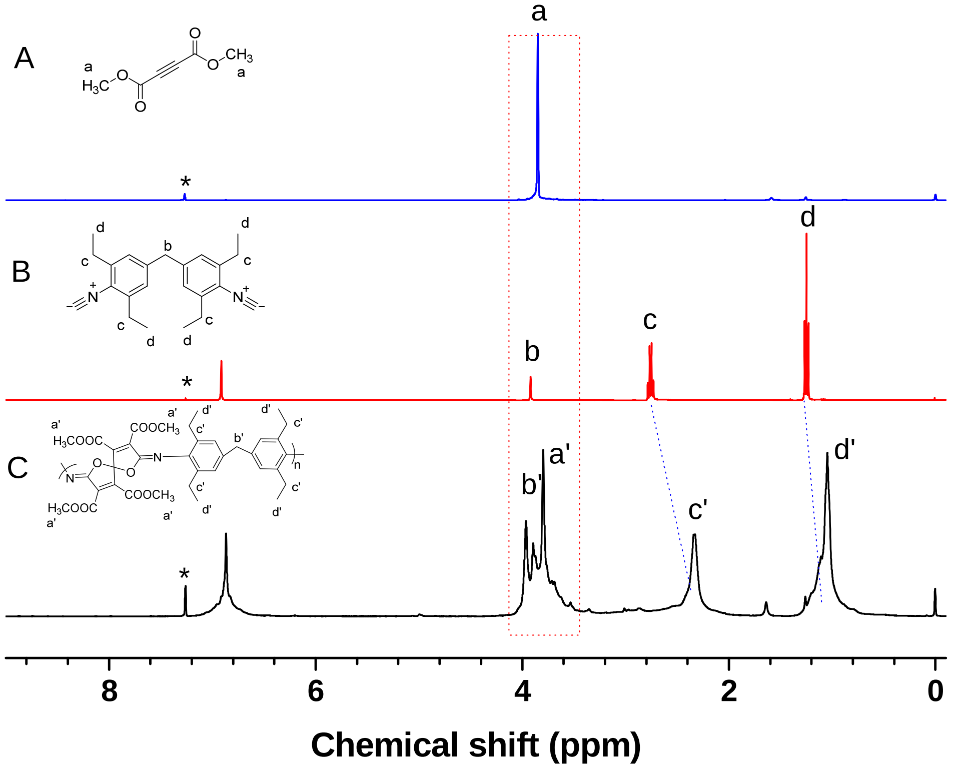


Figure S11. ^{1}H NMR spectra of (A) **1d**, (B) **2a**, and (C) **P1d2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

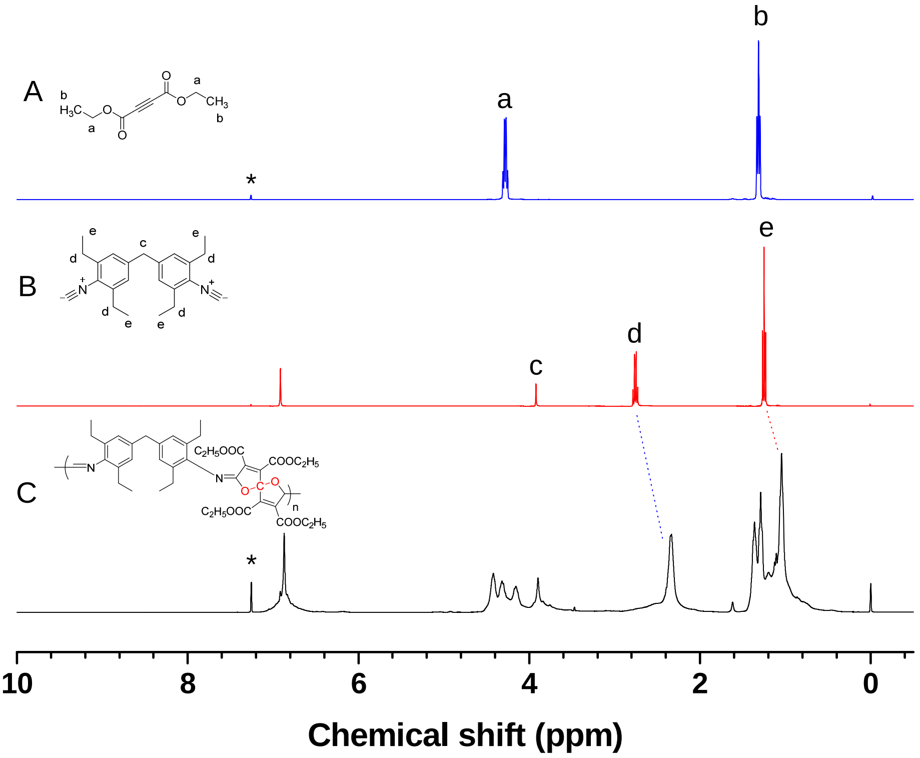


Figure S12. ^{1}H NMR spectra of (A) **1d**, (B) **2b**, and (C) **P1d2b** in CDCl3. The solvent peaks are marked with asterisks.

4 ^{13}C NMR spectra of spiropolymers

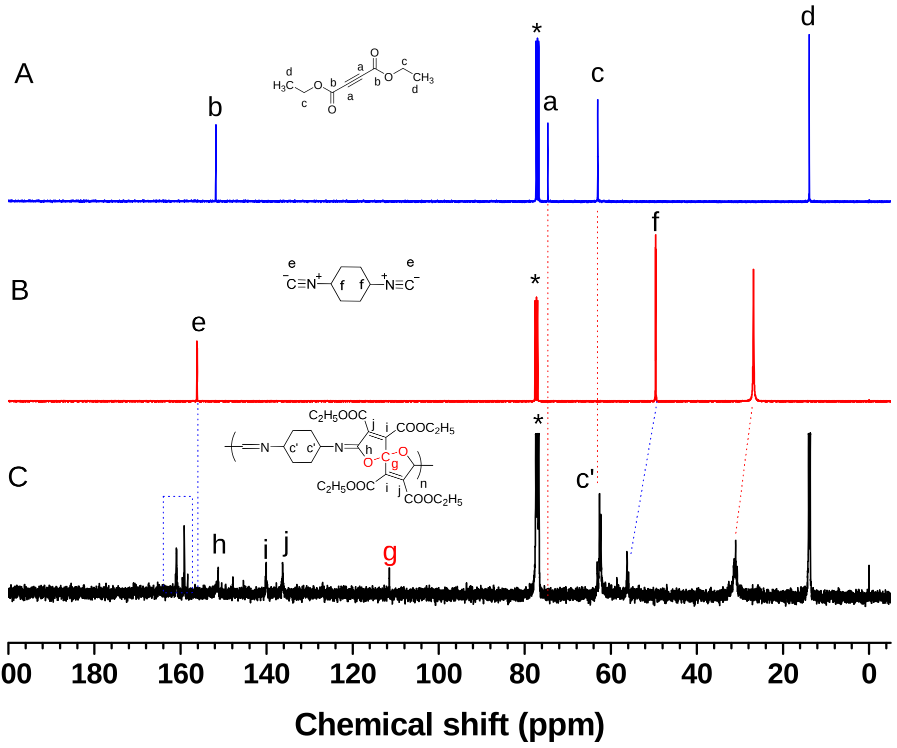


Figure S13. ^{13}C NMR spectra of (A) **1a**, (B) **2b**, and (C) **P1a2b** in CDCl3. The solvent peaks are marked with asterisks.

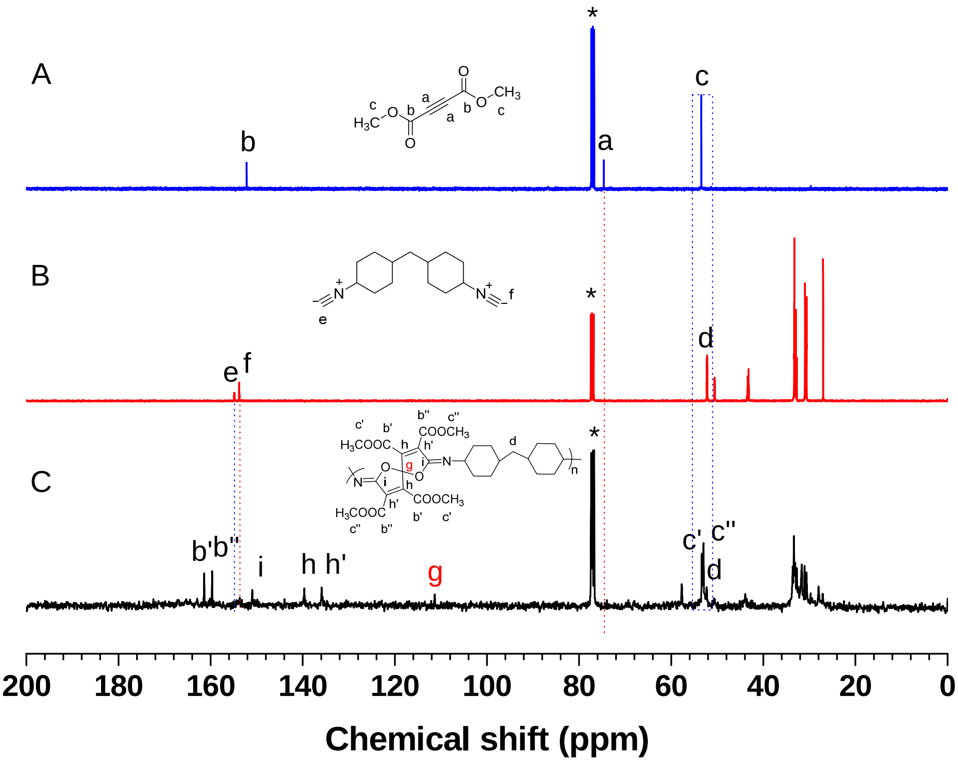


Figure S14. ^{13}C NMR spectra of (A) **1b**, (B) **2a**, and (C) **P1b2a** in CDCl$_3$. The solvent peaks are marked with asterisks.

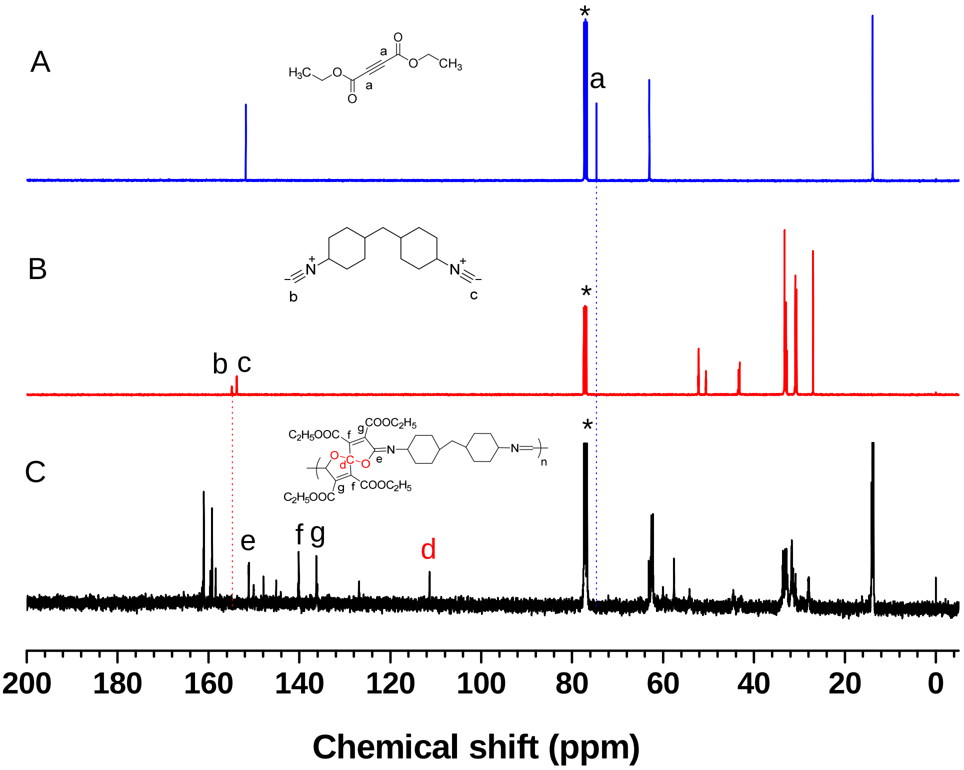


Figure S15. ^{13}C NMR spectra of (A) **1b**, (B) **2b**, and (C) **P1b2b** in CDCl$_3$. The solvent peaks are marked with asterisks.

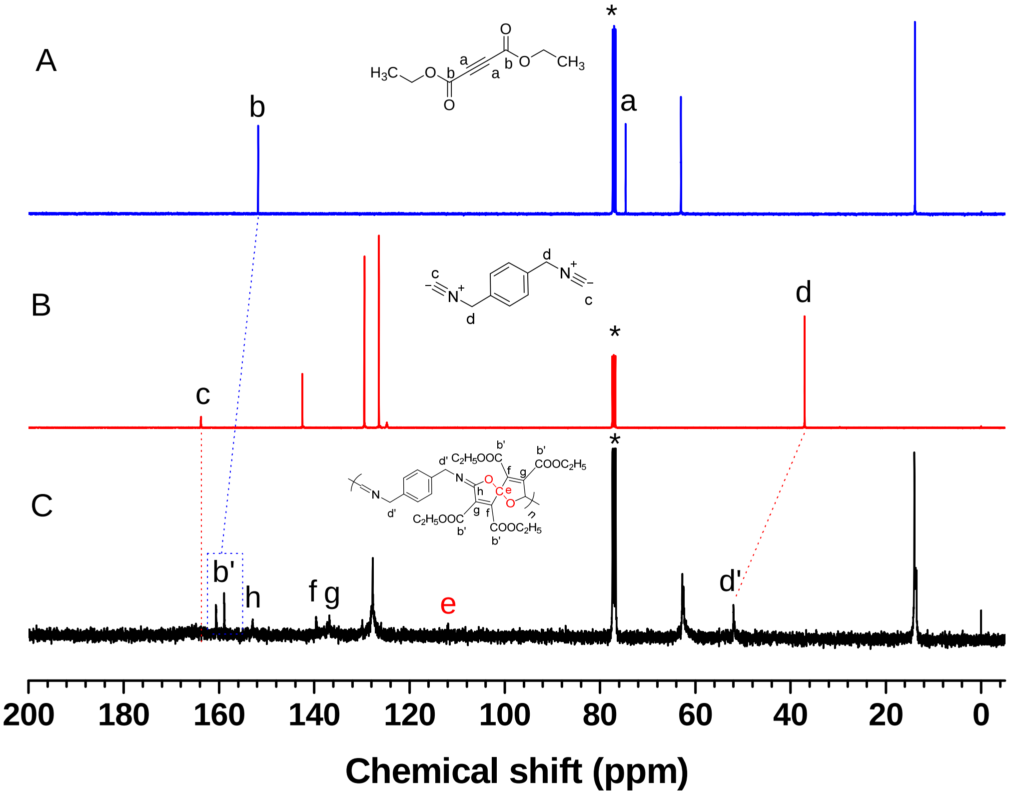


Figure S16. ^{13}C NMR spectra of (A) **1c**, (B) **2b**, and (C) **P1c2b** in CDCl$_3$. The solvent peaks are marked with asterisks.

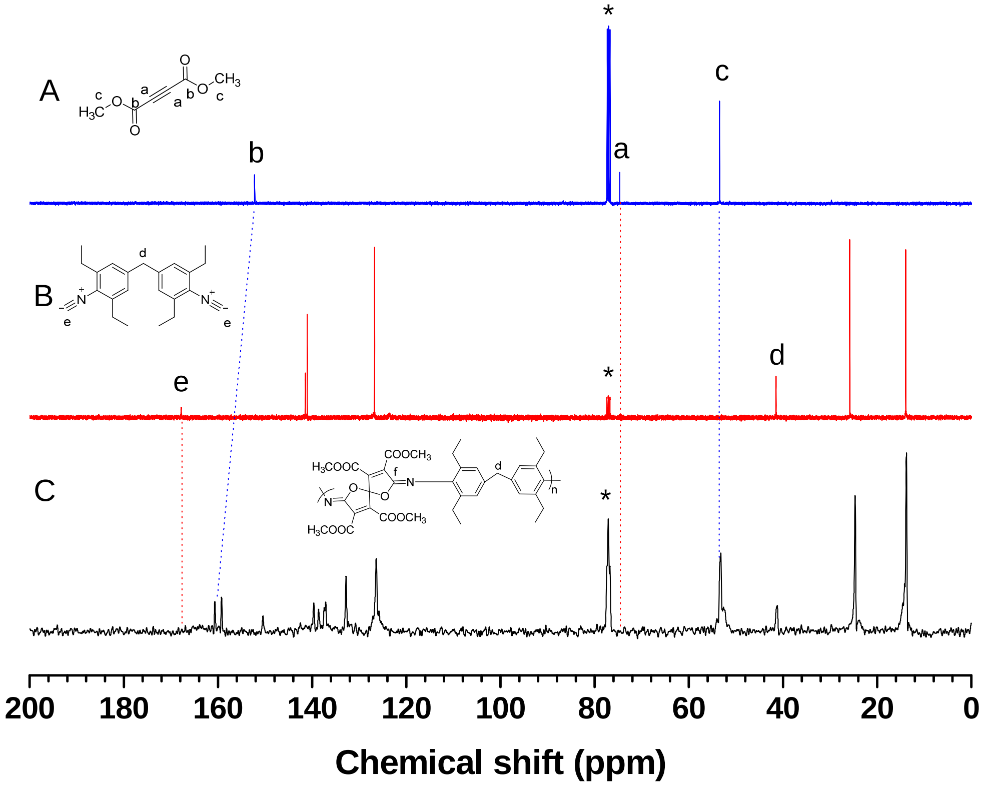


Figure S17. ^{13}C NMR spectra of (A) **1d**, (B) **2a**, and (C) **P1d2a** in CDCl$_3$. The solvent peaks are marked with asterisks.

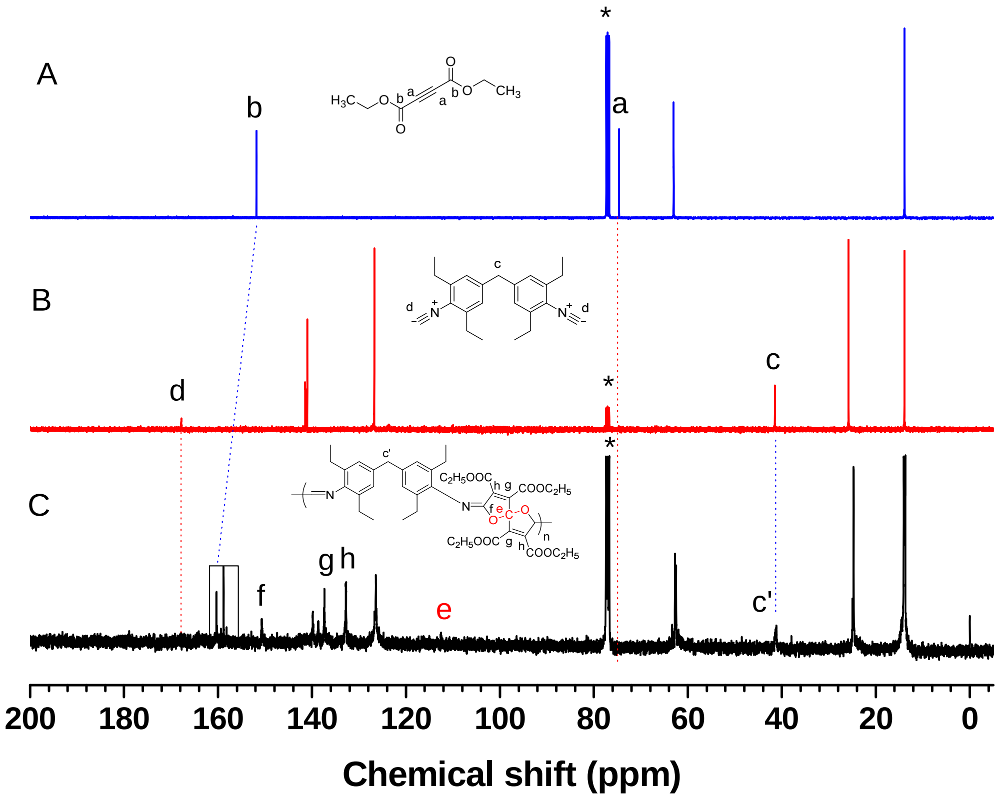


Figure S18. ^{13}C NMR spectra of (A) **1d**, (B) **2b**, and (C) **P1d2b** in $CDCl_3$. The solvent peaks are marked with asterisks.

5 The DSC results of spiropolymers

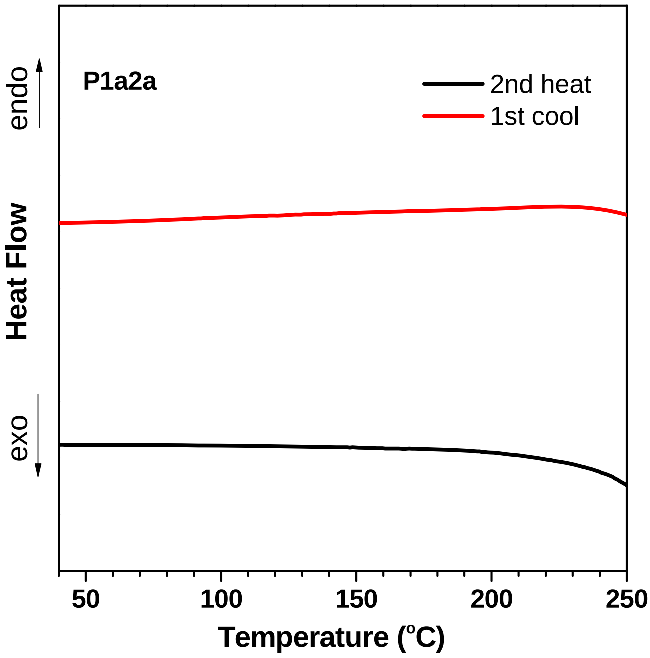


Figure S19. DSC curve of **P1a2a**. The measurement was performed under N_2 at the heating rate of 10 °C/min.

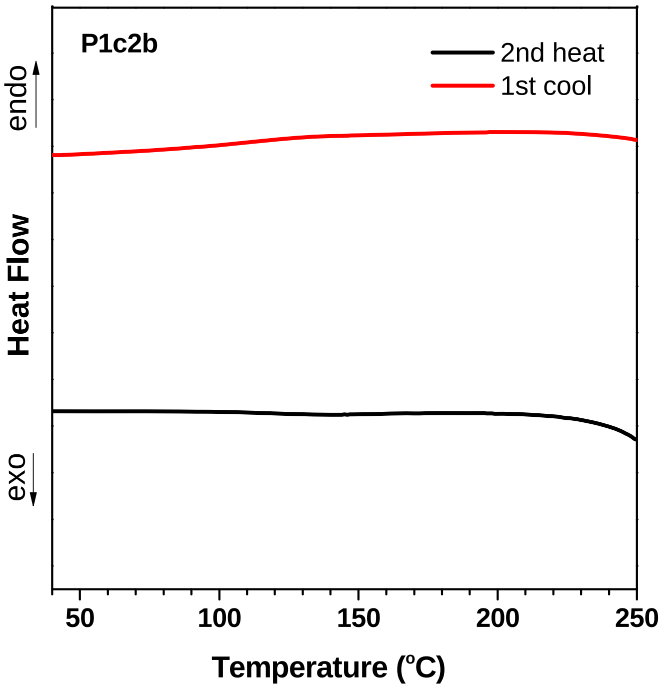


Figure S20. DSC curve of **P1c2b**. The measurement was performed under N_2 at the heating rate of 10 °C/min.

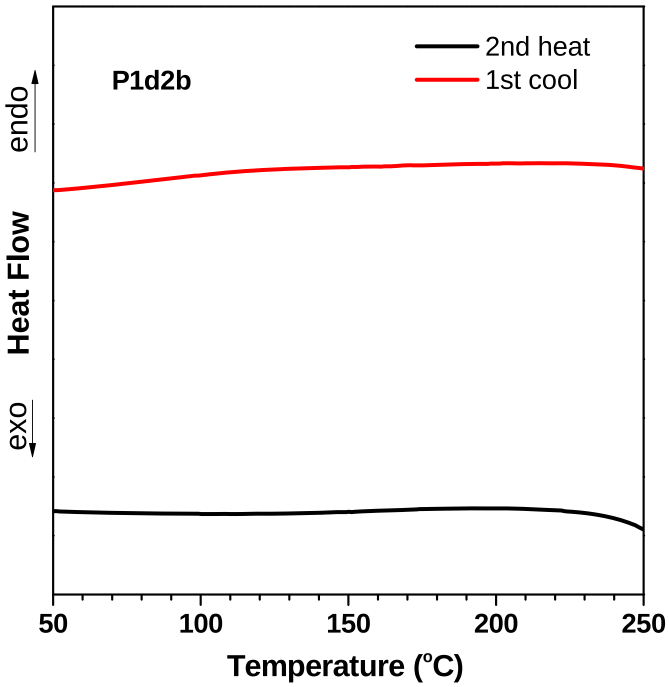


Figure S21. DSC curve of **P1d2b**. The measurement was performed under N_2 at the heating rate of 10 °C/min.

6 Normalized UV−vis absorption spectra of spiropolymers

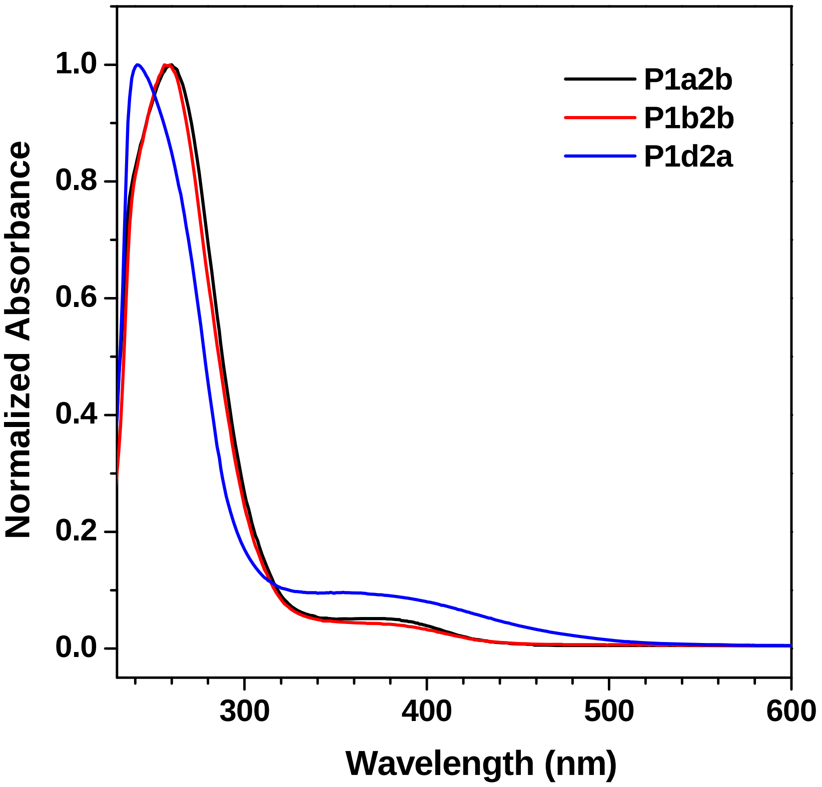


Figure S22. Normalized UV−vis absorption spectra of **P1a2b**, **P1b2b**, and **P1d2a** in THF (10 μmol/L of the repeating structure unit as a reference).