Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

1,3-Dipolar and Diels-Alder Cycloaddition Reactions on Polyester Backbone Possessing Internal Electron-Deficient Alkyne Moieties

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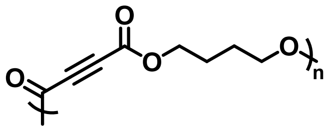
EXPERIMENTAL

Synthesis of Polyester, P1 Using ADCA and 1,4-Butanediol



ADCA (2.00 g, 17.5 mmol, 1 equiv) was dissolved in 40 mL of benzene and stirred under nitrogen. 1,4-Butanediol (1.58 g, 17.5 mmol, 1 equiv) and PTSA (0.33 g, 1.75 mmol, 0.1 equiv) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 °C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 ^{o}C. ^{1}H NMR ($CDCl_3$, δ) 4.30 (bs, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$), 1.82 (bs, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$); ^{13}C NMR ($CDCl_3$, δ) 151.6, 74.7, 66.0, 30.8, 25.0.

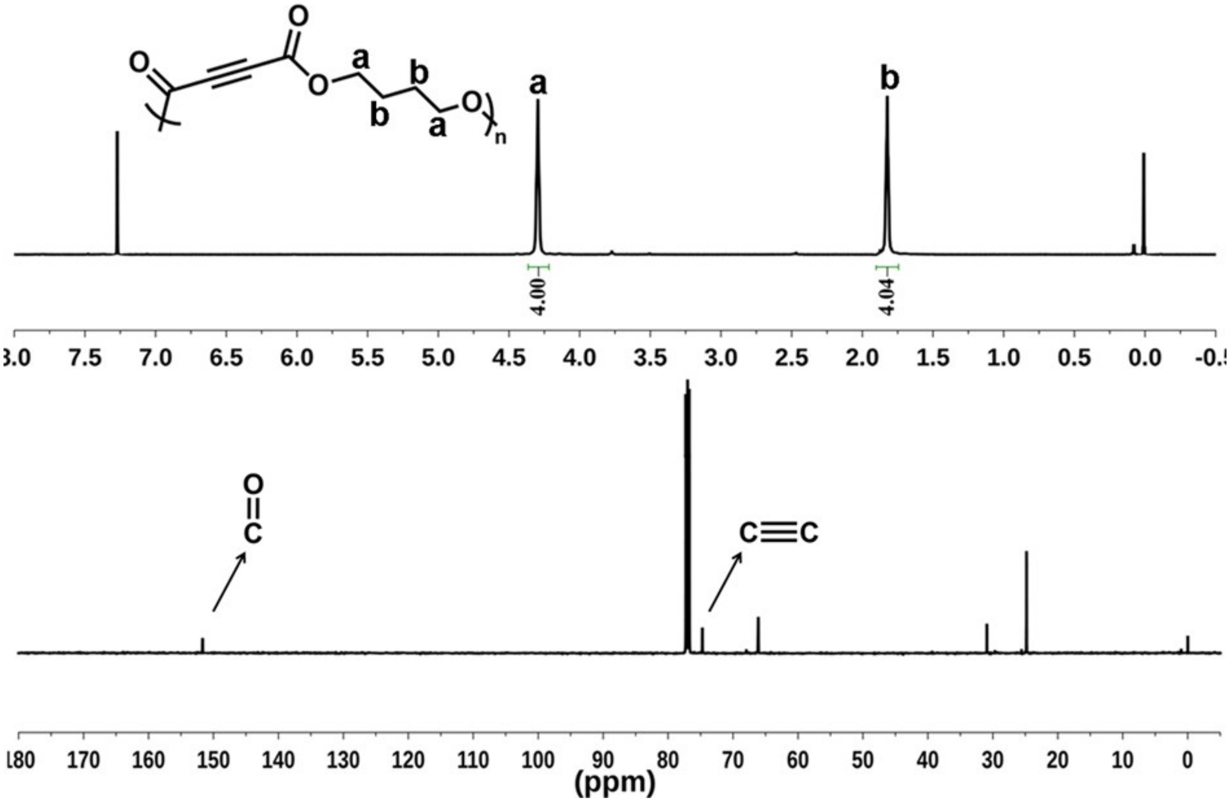
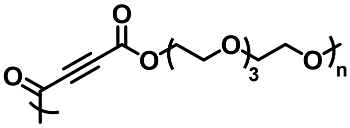


Figure S1. ^{1}H (up) and ^{13}C NMR (down) spectra of **P1** in $CDCl_3$ (500 and 125 MHz, respectively).

Synthesis of Polyester, P2 Using ADCA and Tetraethylene Glycol



ADCA (1.0 g, 8.8 mmol, 1 equiv) was dissolved in 20 mL of benzene and stirred under nitrogen and tetraethylene glycol (1.51 mL, 8.80 mmol, 1 equiv) and PTSA (0.17 g, 0.90 mmol, 0.1 equiv) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 °C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 °C. ^{1}H NMR ($CDCl_3$, δ) 4.40 (m, 4H, $C{=}OOC\mathit{H}_2CH_2O$), 3.75 (m, 4H, $C{=}OOCH_2C\mathit{H}_2O$), 3.67 (s, 8H, $OC\mathit{H}_2C\mathit{H}_2O$); ^{13}C NMR ($CDCl_3$, δ) 151.7, 74.9, 70.6, 68.4, 65.8.

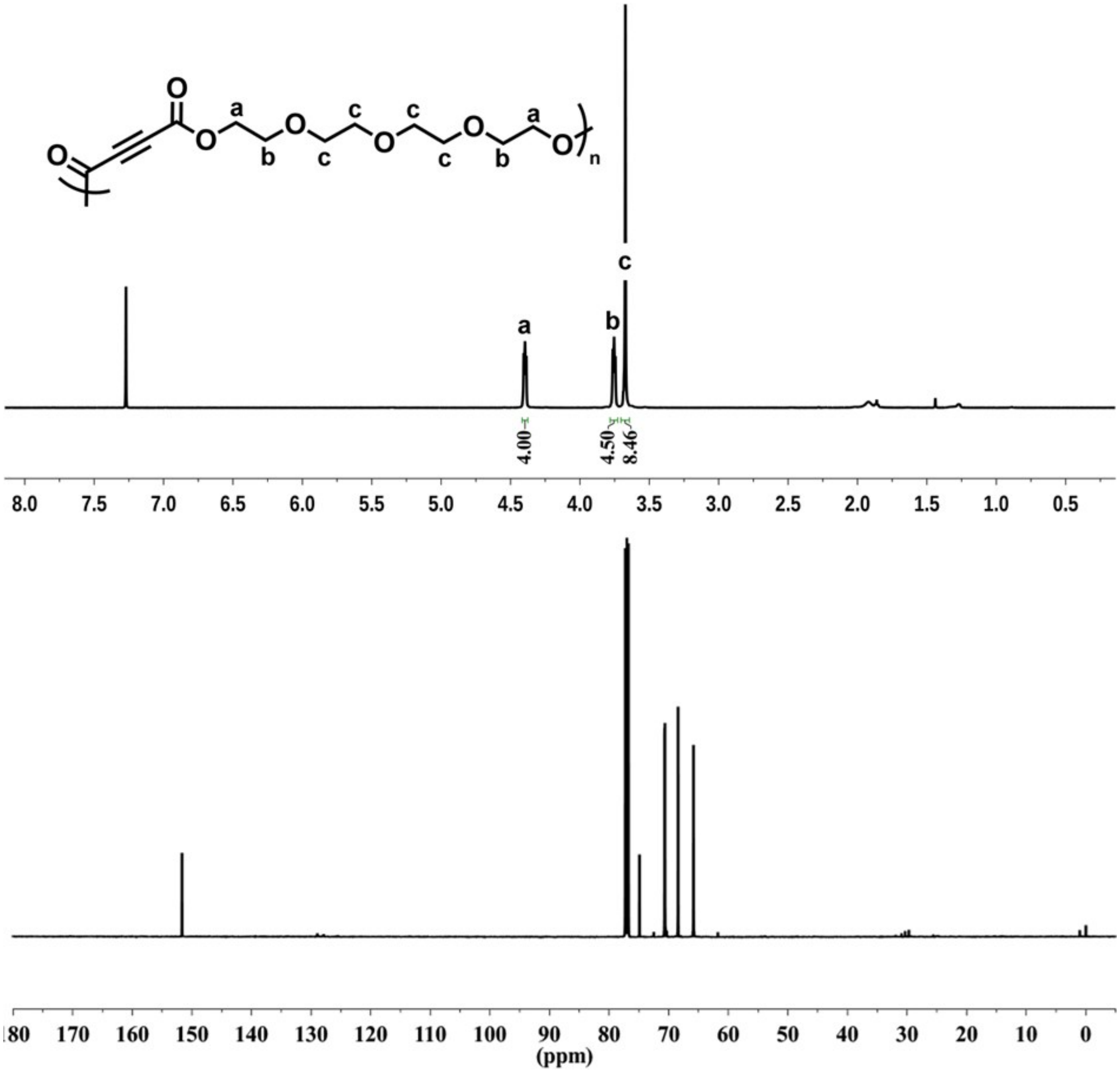
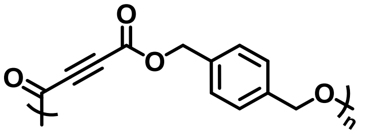


Figure S2. ^{1}H (up) and ^{13}C NMR (down) spectra of **P2** in $CDCl_3$ (500 and 125 MHz, respectively).

Synthesis of Polyester, P3 Using ADCA and 1,4-Benzenedimethanol



ADCA (0.50 g, 4.4 mmol, 1 equiv) was dissolved in 20 mL of benzene and stirred under nitrogen. 1,4-Benzenedimethanol (0.60 g, 4.4 mmol, 1 equiv) and PTSA (0.08 g, 0.4 mmol, 0.1 equiv) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100°C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 °C. ^{1}H NMR ($CDCl_3$, δ) 7.38 (bs, 4H, Ar*H*), 5.25 (bs, 4H, C=OOC*H*$_2$Ph), 4.57 (s, 4H, C=OOC*H*$_2$Ph); ^{13}C NMR ($CDCl_3$, δ) 151.2, 134.7, 129.2, 128.9, 128.0, 126.2, 74.8, 71.6, 68.3, 41.6

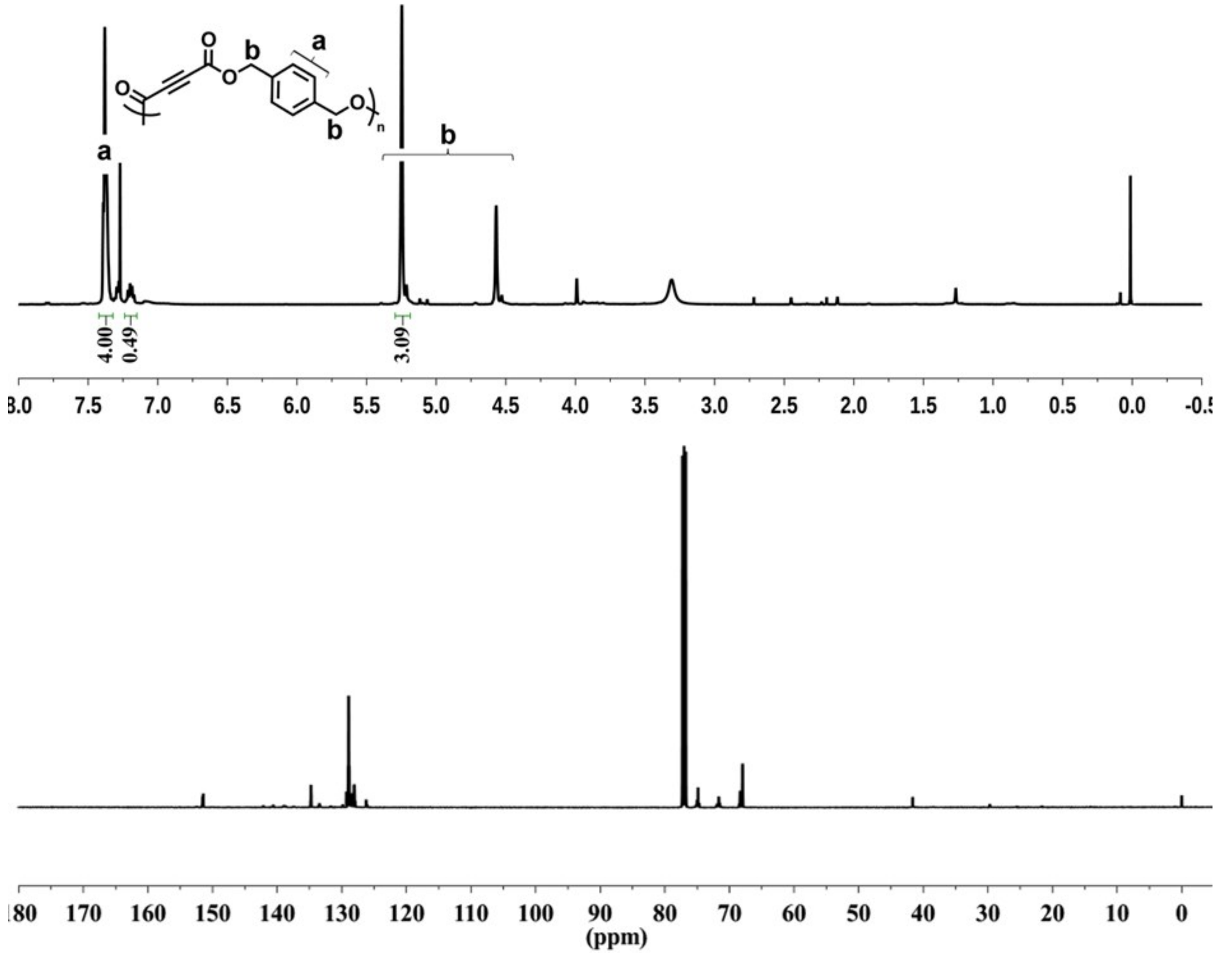
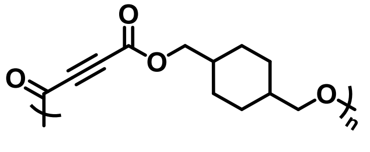


Figure S3. ^{1}H (up) and ^{13}C NMR (down) spectra of **P3** in $CDCl_3$ (500 and 125 MHz, respectively).

Synthesis of Polyester, P4 Using ADCA and 1,4-Cyclohexanedimethanol



ADCA (1.0 g, 8.8 mmol, 1 equiv) was dissolved in 20 mL of benzene and stirred under nitrogen and 1,4-cyclohexanedimethanol (1.26 g, 8.80 mmol, 1equiv) and PTSA (0.17 g, 0.90 mmol, 0.1 equiv) were added to the solution in that order. The mixture was gradually heated in a round bottomed flask, with a Dean-Stark apparatus attached, in an oil bath set to 100 °C and stirred overnight. After that time, solvent was removed under reduced pressure, THF was added to the residue and finally precipitated in methanol. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 °C. ^{1}H NMR ($CDCl_3$, δ) 4.16 (m, 4H, C*H*$_2$CH), 4.08 (m, 4H, C*H*$_2$CH), 2.1-1.0 (m, aliphatic protons of cyclohexane); ^{13}C NMR ($CDCl_3$, δ) 151.9, 74.8, 71.5, 69.4, 36.6, 34.1, 28.4, 25.0.

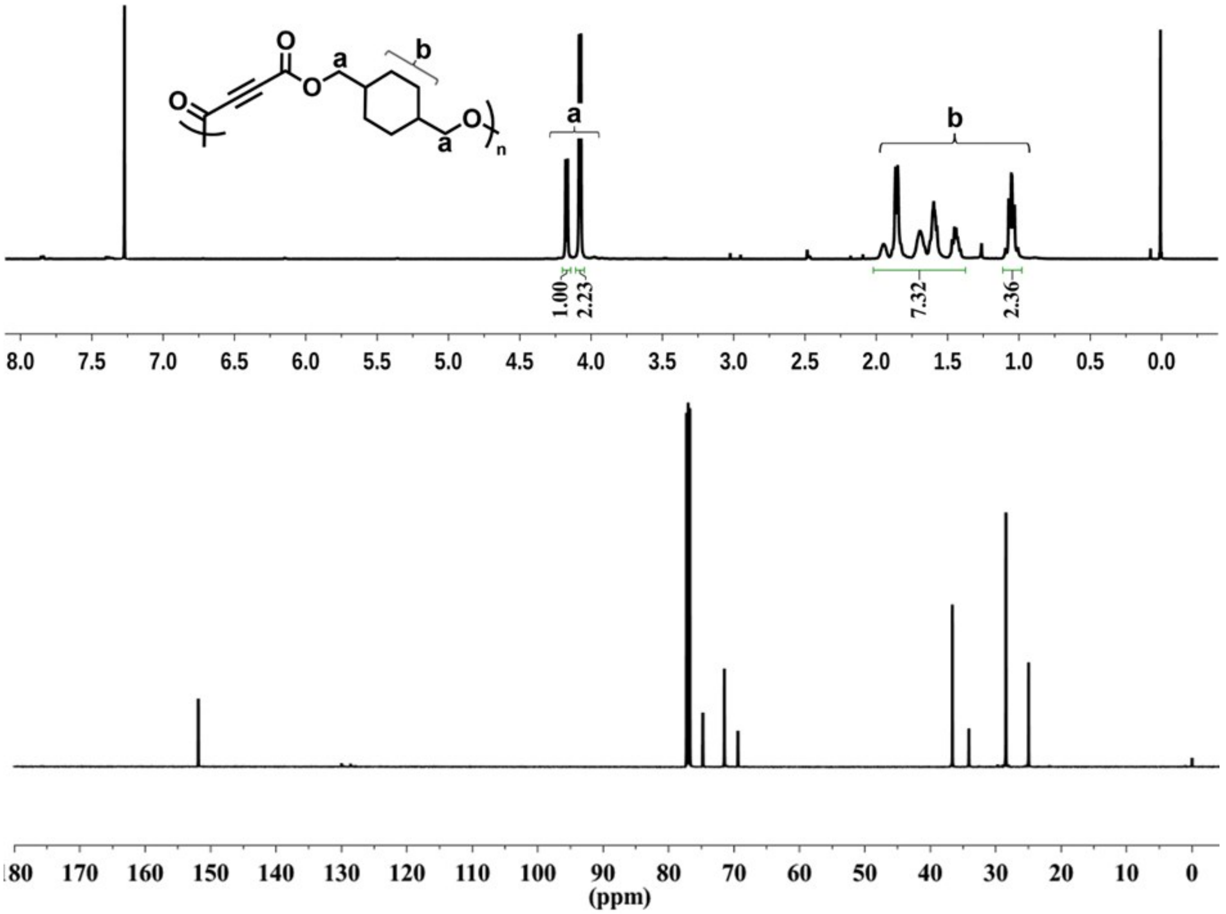
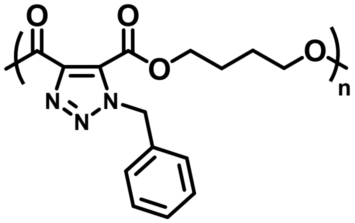


Figure S4. ^{1}H (up) and ^{13}C NMR (down) spectra of **P4** in $CDCl_3$ (500 and 125 MHz, respectively).

1,3-DIPOLAR CYCLOADDITION REACTIONS

1,3-Dipolar Cycloaddition Reaction Between P1 and Benzyl Azide (P5)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of 1,4-dioxane and transferred to a 10 mL of Schlenk tube. Next benzyl azide (0.16 g, 1.2 mmol per alkyne, 2 equiv) was added to the solution and the reaction mixture was degassed by two FPT cycles, left in vacuum. The tube was then placed in a thermostated oil bath and stirred at 40 °C for 16 h. After that time, the polymer solution was precipitated in 40 mL methanol and the solvent was removed by decantation. The residual polymer was dissolved in THF and consequently precipitated in methanol. The purified polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.12 g, 67 %, $M_{\mathrm{n,GPC}}$ = 6400 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.73, relative to PS standards). ^{1}H NMR (CDCl$_3$, δ) 7.3-7.1 (m, ArH), 5.78 (bs, 2H, CH_2Ph), 4.30 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 1.80 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR (CDCl$_3$, δ) 160.0, 158.4, 140.1, 134.0, 128.9, 127.9, 68.0, 66.2, 65.0, 53.9, 25.1, 24.9, 24.6.

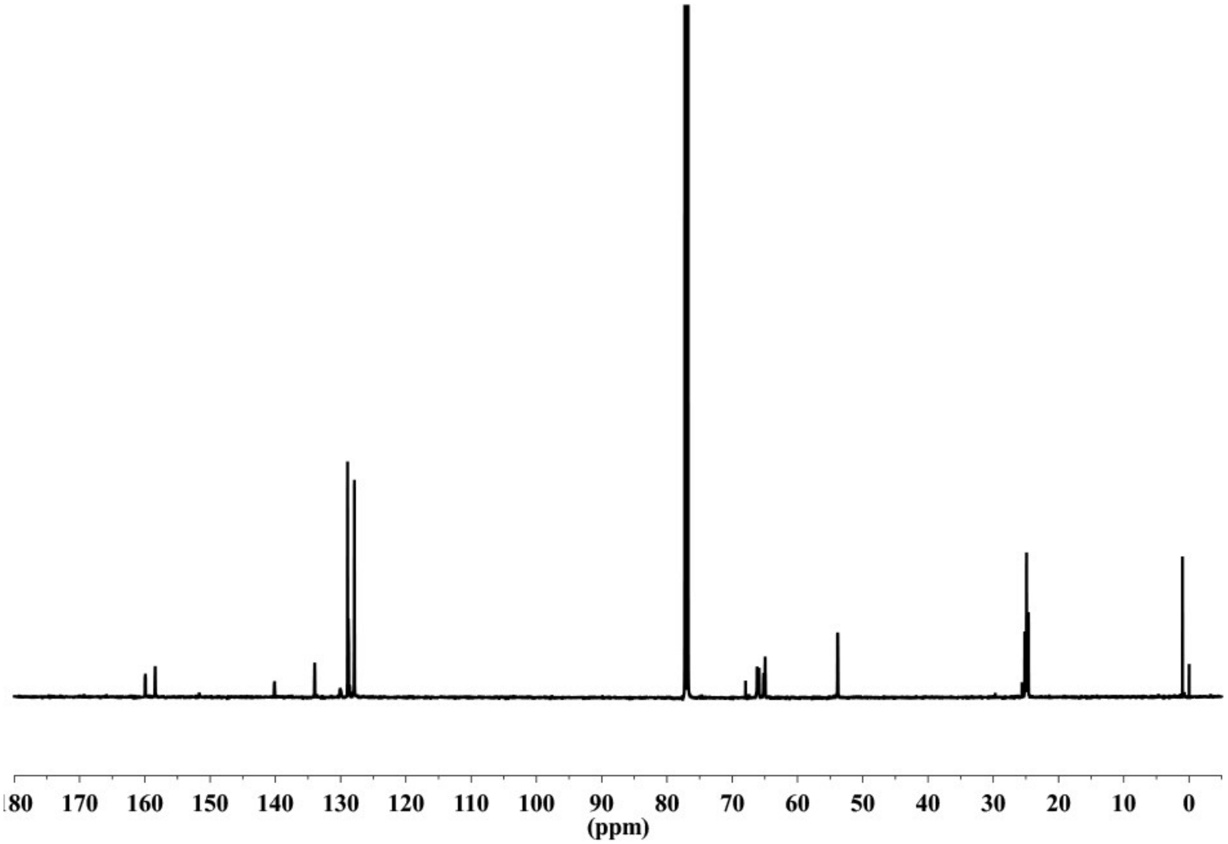
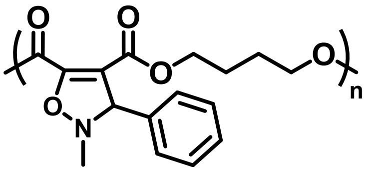


Figure S5. ^{13}C NMR spectrum of **P5** in $CDCl_3$ (125 MHz).

Dipolar Cycloaddition Reaction Between P1 and *N*-Methyl Phenyl Nitrone (P6)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of 1,4-dioxane and transferred to a round bottomed flask. Next, *N*-methyl phenyl nitrone (0.16 g, 1.2 mmol, 2 equiv per alkyne) was added to the solution and stirred at room temperature for 16 h under nitrogen. After that time, the polymer solution was precipitated in 40 mL methanol and the solvent was removed by decantation. The residual polymer was dissolved in THF and consequently precipitated in diethyl ether. The purified polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.10 g, 56 %,

$M_{n,GPC}$ = 6150 g/mol, M_w/M_n = 1.98, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.36, (m, Ar*H*), 5.02 (m, 2H, C*H*(Ph)), 4.30 (m, 4H, C=OOC*H*$_2$CH$_2$CH$_2$C*H*$_2$OC=O), 3.00 (m, 3H, C*H*$_3$), 1.80 (m, 4H, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 162.0, 158.9, 151.6, 139.3, 134.5, 129.7, 129.0, 128.7, 128.5, 127.4, 109.3, 68.0, 66.0, 63.8, 47.3, 29.7, 25.6, 24.9

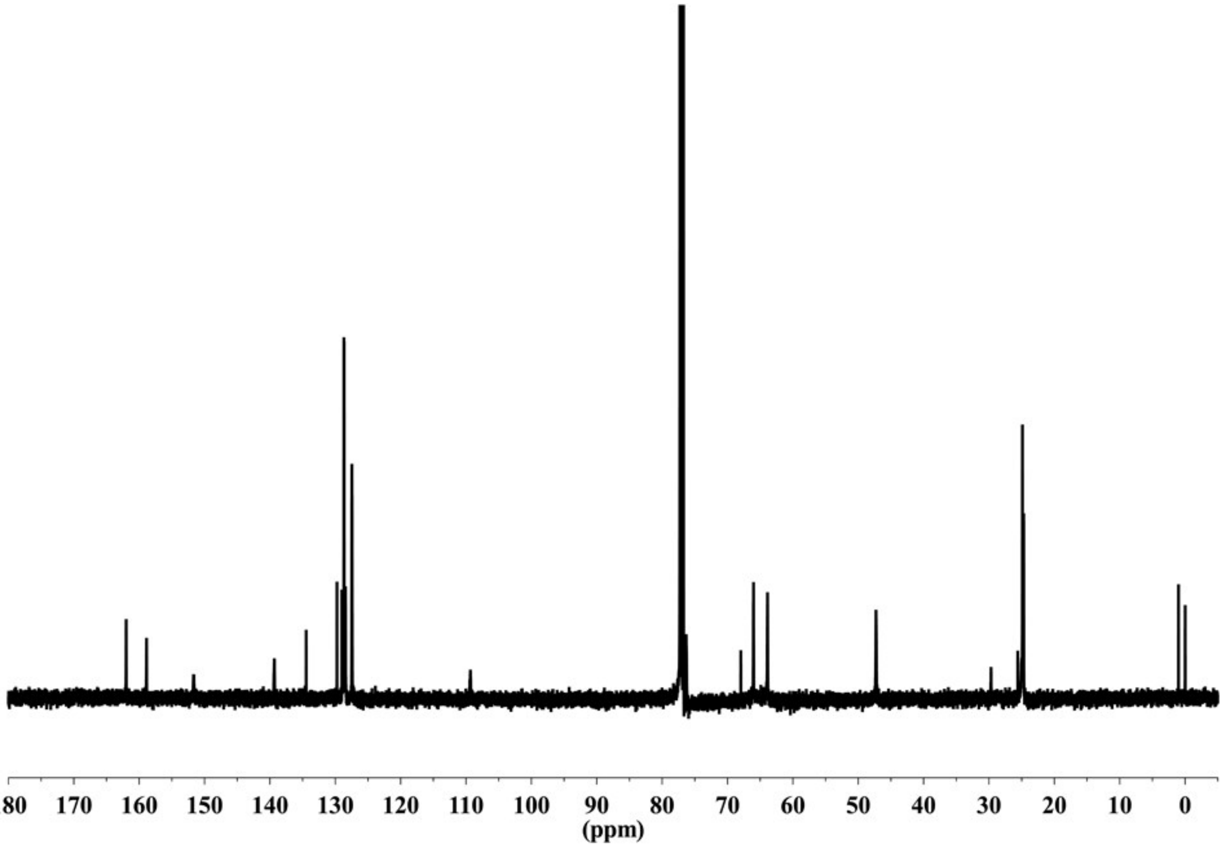
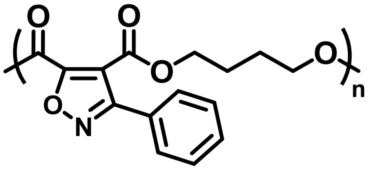


Figure S6. ^{13}C NMR spectrum of **P6** in $CDCl_3$ (125 MHz).

Dipolar Cycloaddition Reaction Between P1 and Benzonitrile Oxide (P7)



Benzonitrile oxide was *in situ* prepared and then reacted with **P1**. Briefly, benzaldehyde oxime (0.145 g, 1.20 mmol, 2 equiv per alkyne), *N*-chlorosuccinimide (0.16 g, 1.2 mmol, 2 equiv) and triethylamine (167 µL, 1.2 mmol, 2 equiv) were added in a 50 mL flask. The mixture was dissolved in 30 mL CH_2Cl_2 and stirred at 0 °C for 4 h under nitrogen. After the specified time, **P1** (0.1 g, 0.6 mmol of alkyne, 1 equiv) was added to the solution and stirred at room temperature for 16 h. After that time, the solvent was removed under reduced pressure yielding yellow polymerization mixture. The residual polymer was dissolved in THF and subsequently precipitated in 40 mL methanol. The dissolution-precipitation procedure was repeated with diethyl ether. The purified polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield =0.08 g, 47 %, $M_{n,GPC}$ = 6650 g/mol, M_w/M_n = 1.72, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.65 (bs, Ar*H*), 7.48 (bs, Ar*H*), 4.34 (m, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$), 1.71 (m, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$); ^{13}C NMR ($CDCl_3$, δ) 161.1, 159.4, 155.9, 130.7, 128.9, 128.1, 127.0, 116.3, 66.1, 65.5, 25.0, 24.8.

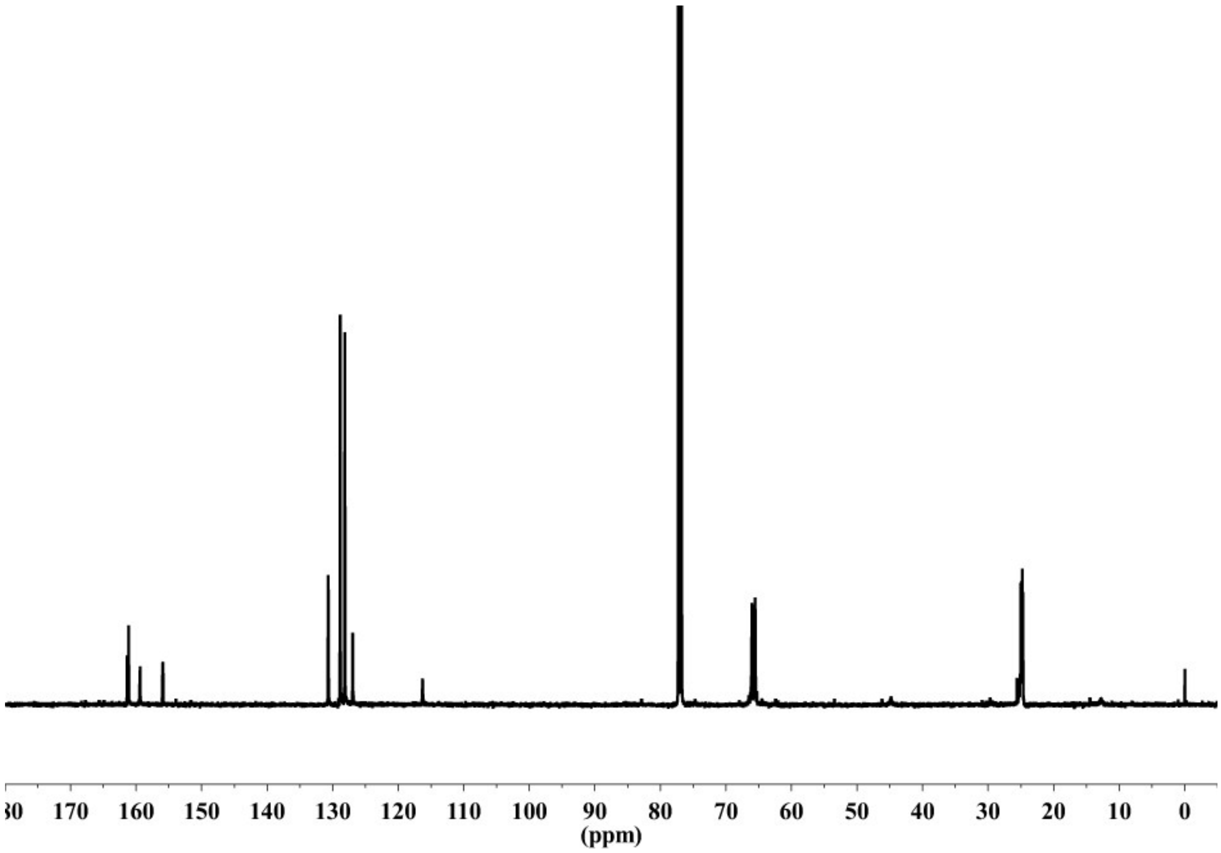
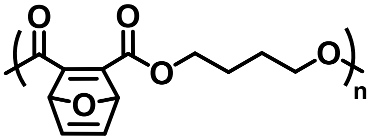


Figure S7. ^{13}C NMR spectrum of **P7** in $CDCl_3$ (125 MHz).

DIELS-ALDER CYCLOADDITION REACTIONS

Diels-Alder Cycloaddition Reaction Between P1 and Furan (P8)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of 1,4-dioxane and transferred to a 10 mL of Schlenk tube. Next furan (86.6 µL, 1.20 mmol per alkyne, 2 equiv) was added to the solution and the reaction mixture was degassed by two FPT cycles, left in vacuum and stirred for 16 h at 100 °C. After the specified time, solution was precipitated in methanol and residual solvent was removed by decantation. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.10 g, 71 %, $M_{n,GPC}$ = 6200 g/mol, M_w/M_n = 1.68, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.23 (s, 2H, C*H*=C*H*), 5.68 (s, 2H, C*H*O, bridge-head protons), 4.25 (bs, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 1.80 (bs, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 162.6, 153.1, 151.7, 143.2, 851, 73.2, 66.3, 65.9, 64.8, 29.7, 25.1.

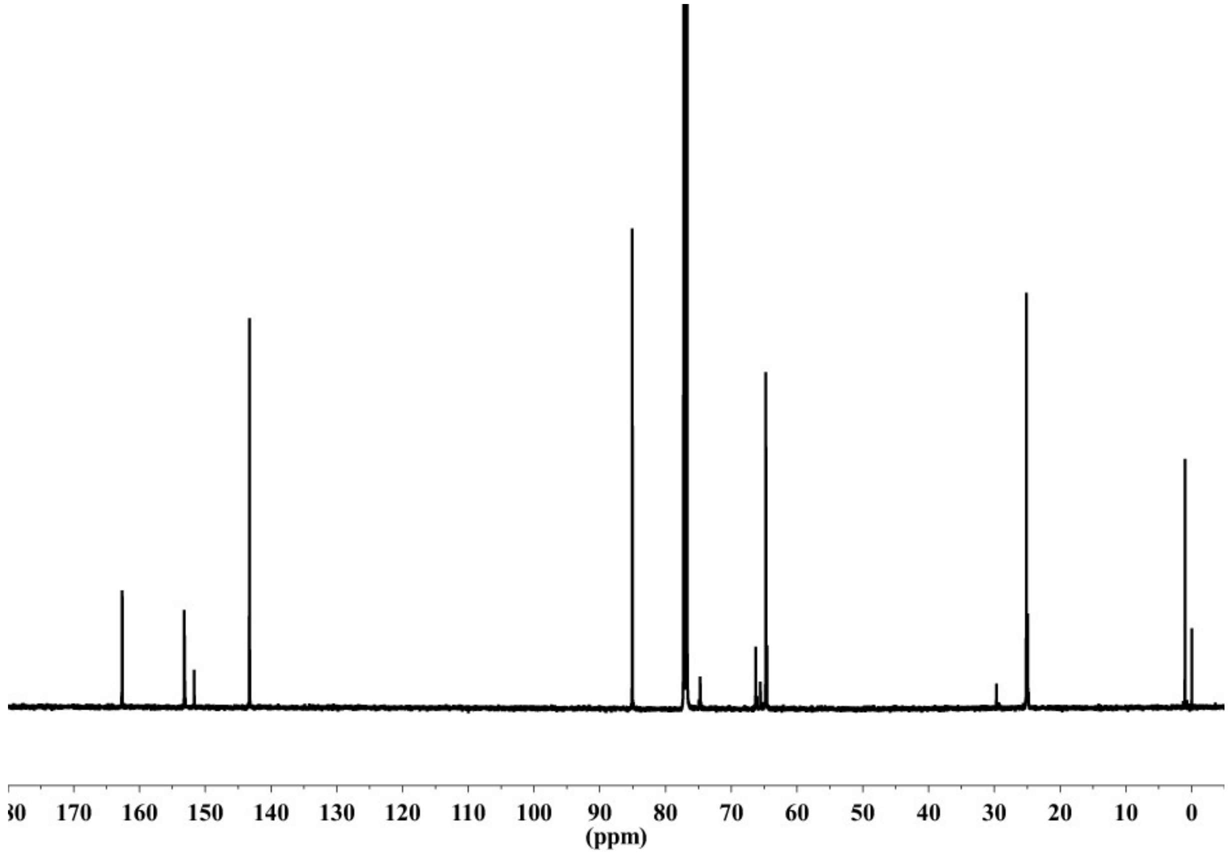
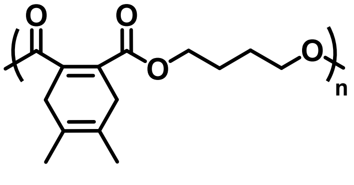


Figure S8. ^{13}C NMR spectrum of **P8** in $CDCl_3$ (125 MHz).

Diels-Alder Cycloaddition Reaction Between P1 and 2,3-Dimethyl-1,3-Butadiene (P9)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of 1,4-dioxane and transferred to a 10 mL of Schlenk tube. Next 2,3-Dimethyl-1,3-Butadiene (134.7 µL, 1.2 mmol per alkyne, 2 equiv) was added to the solution and the reaction mixture was degassed by two FPT cycles, left in vacuum and stirred for 16 h at 80 °C. After the specified time, solution was precipitated in methanol and residual solvent was removed by decantation. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.08 g, 54 %, $M_{n,GPC}$ = 6700 g/mol, M_w/M_n = 1.75, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.20 (bs, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 2.91 (bs, 4H, C=CCH_2C=C), 1.76 (bs, 6H, CH_3), 1.67 (bs, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 167.9, 132.8, 130.0, 121.5, 64.5, 34.2, 25.2, 19.7, 18.0.

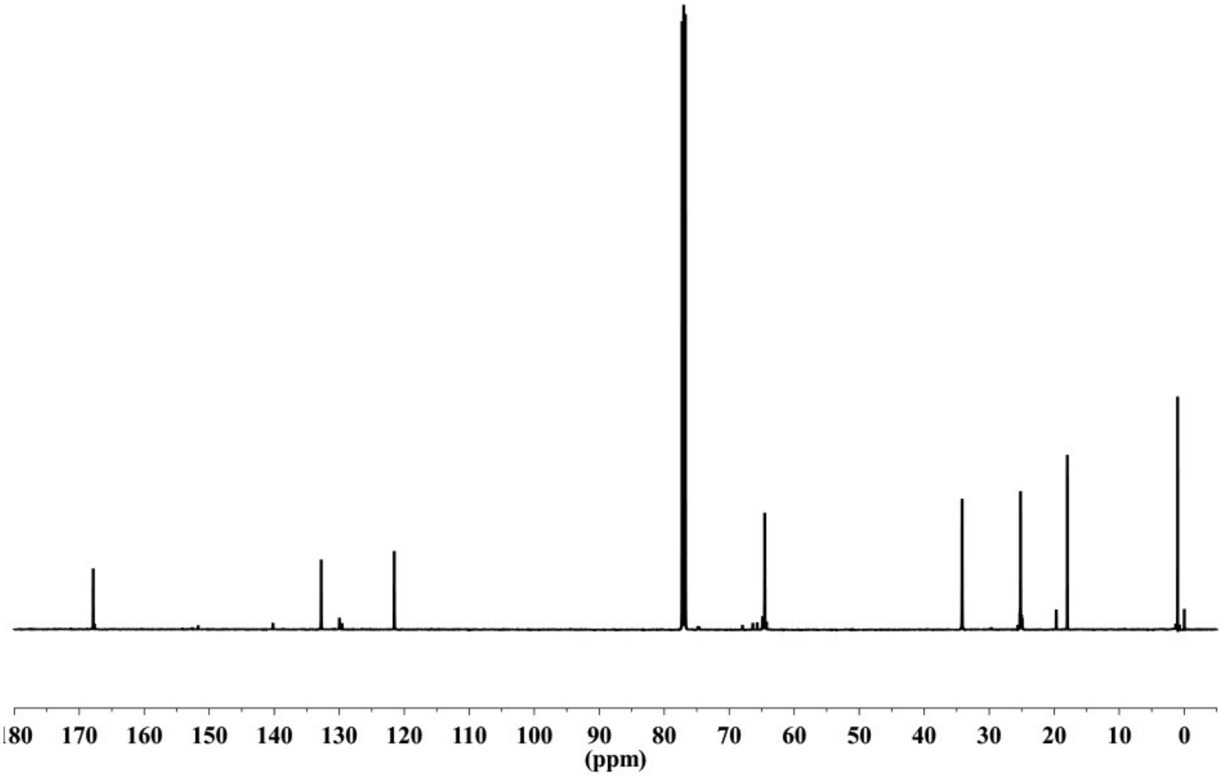
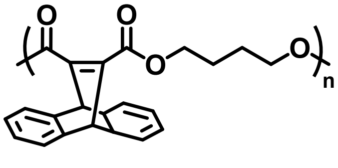


Figure S9. ^{13}C NMR spectrum of **P9** in $CDCl_3$ (125 MHz).

Diels-Alder Cycloaddition Reaction Between P1 and Anthracene (P10)



P1 (0.10 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of 1,4-dioxane and transferred to a 10 mL of Schlenk tube. Next anthracene (0.21 g, 1.2 mmol per alkyne, 2 equiv) and 2 mL of DMF were added to the solution. The reaction mixture was degassed by two FPT cycles, left in vacuum and stirred for 16 h at 120 °C. After the specified time, solution was precipitated in methanol and residual solvent was removed by decantation. The dissolution–precipitation (THF-methanol) procedure was repeated two times. The recovered polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.13 g, 63 %, $M_{n,GPC}$ = 5750 g/mol, M_w/M_n = 1.44, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.37 (bs, 2H, Ar*H*), 7.00 (bs, 2H, Ar*H*), 5.46 (bs, 2H, C*H*, bridge protons), 4.16 (bs, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$), 1.70 (bs, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$); ^{13}C NMR ($CDCl_3$, δ) 165.3, 151.7, 146.9, 143.7, 125.4, 123.8, 74.9, 66.3, 65.6, 64.8, 64.6, 52.5, 25.0, 24.9.

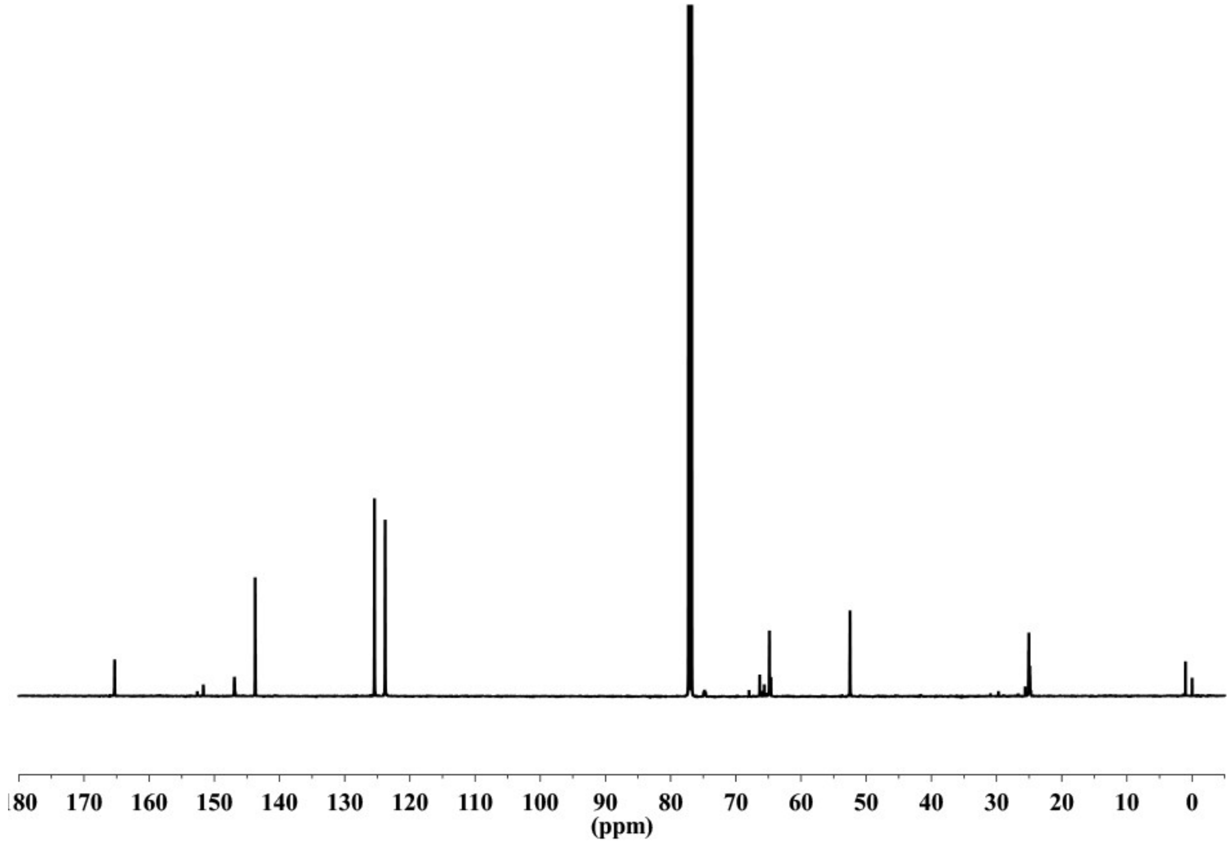


Figure S10. ^{13}C NMR spectrum of **P10** in $CDCl_3$ (125 MHz).

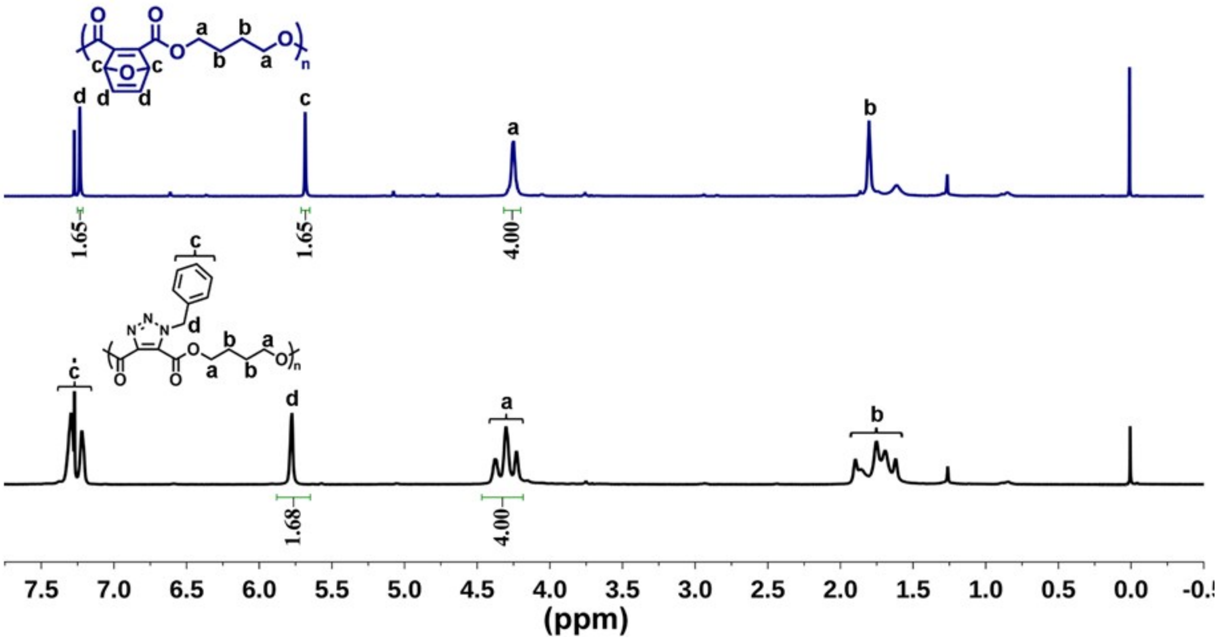


Figure S11. ^{1}H NMR spectra of **P8** (up) and **P11** (down) after sequential 1,3-dipolar cycloaddition/retro-Diels-Alder reaction in $CDCl_3$ (500 MHz).

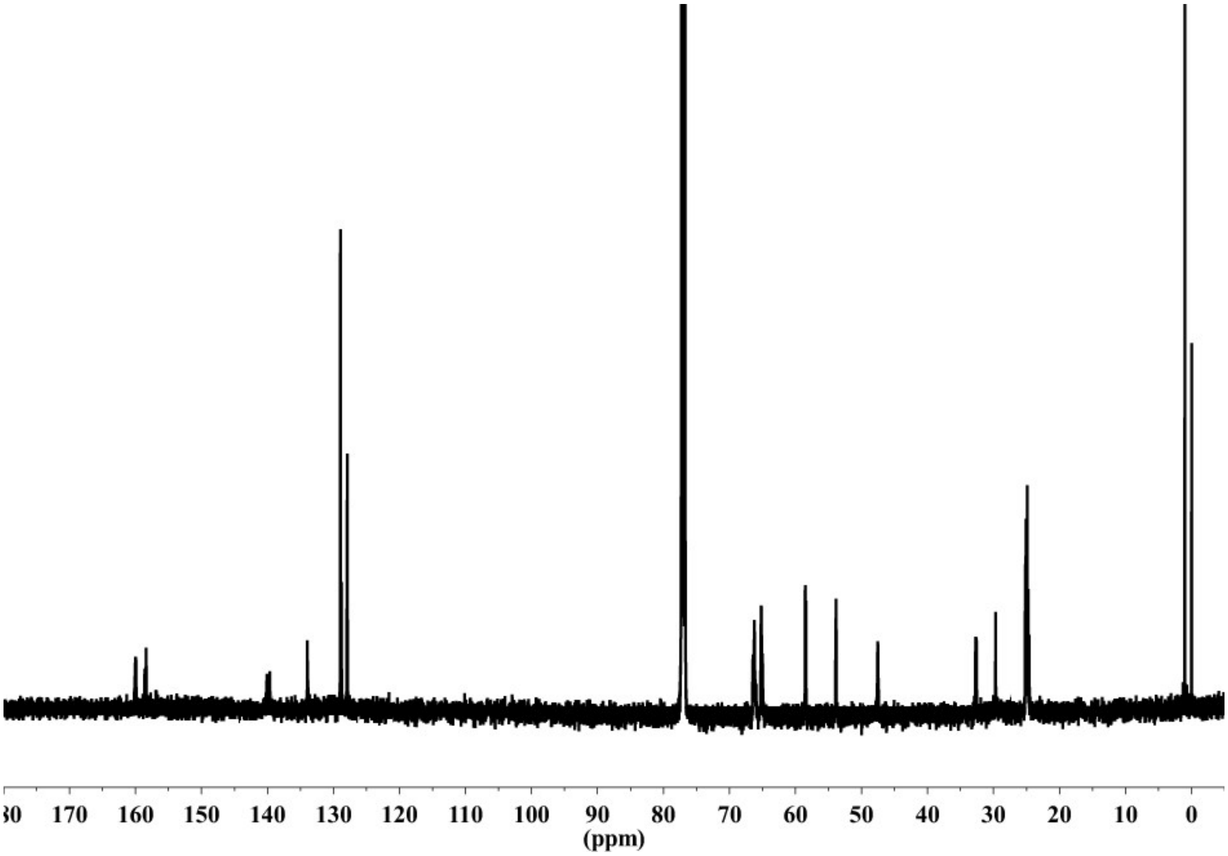


Figure S12. ^{13}C NMR spectrum of **P12** in $CDCl_3$ (125 MHz).

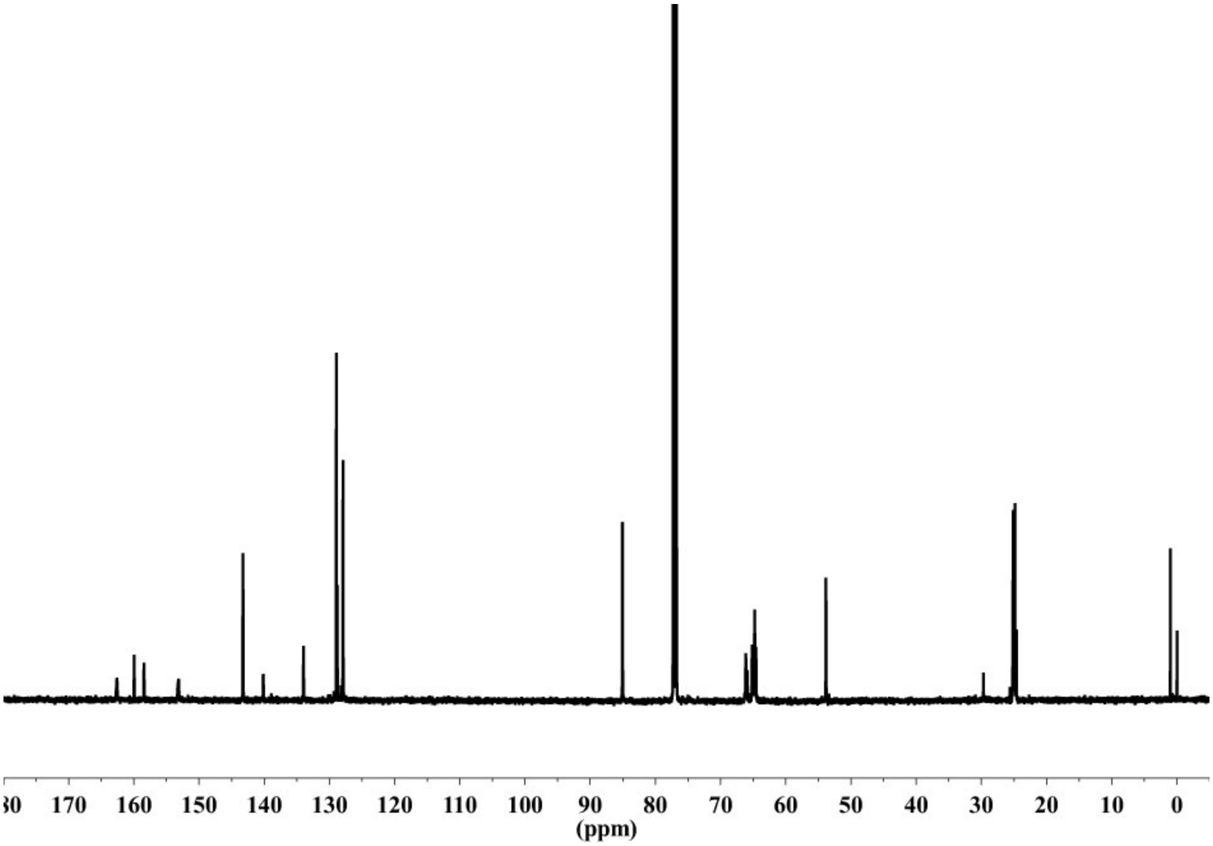


Figure S13. ^{13}C NMR spectrum of **P14** in $CDCl_3$ (125 MHz).