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Supporting Information

Diselenide-yne chemistry for selenium-containing linear polymer modification

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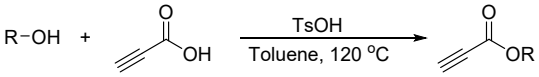
1. Experimental section

1.1 Characterization data for monomers



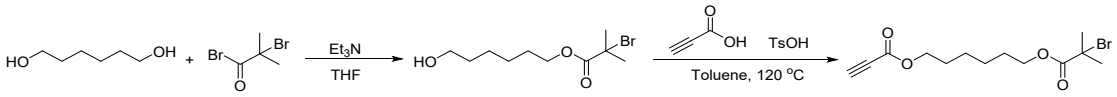
Scheme S1. Synthetic procedure of general monomers.

Characterization data for **2-(2-(2-methoxyethoxy)ethoxy)ethyl propiolate** (Figure S4-5). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 4.33 (t, *J* = 4.5 Hz, 2H), 3.72 (t, *J* = 4.5 Hz, 2H), 3.68-3.59 (m, 6H), 3.57-3.50 (m, 2H), 3.37 (s, 3H), 2.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 152.61, 75.10, 74.53, 71.91, 70.68, 70.59, 68.55, 65.23, 59.03.

Characterization data for **hexyl propiolate** (Figure S6-7). ^{1}H NMR (300 MHz, $CDCl_3$), *δ* (ppm): 4.18 (t, *J* = 7.5 Hz, 2H), 2.87 (s, 1H), 1.74-1.61 (m, 2H), 1.43-1.22 (m, 6H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), *δ* (ppm): 152.82, 74.80, 74.37, 66.48, 31.32, 28.27, 25.41, 22.48, 13.95.

Characterization data for **benzyl propiolate** (Figure S8-9). ^{1}H NMR (300 MHz, $CDCl_3$), *δ* (ppm): δ 7.43-7.30 (m, 5H), 5.23 (s, 2H), 2.89 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), *δ* (ppm): 152.53, 134.52, 128.72, 128.69, 128.57, 75.06, 74.55, 67.92.

1.2 Characterization data for 6-((2-bromo-2-methylpropanoyl)oxy)hexyl propiolate



Scheme S2. Synthetic procedure of 6-((2-bromo-2-methylpropanoyl)oxy)hexyl propiolate.

Characterization data for **6-((2-bromo-2-methylpropanoyl)oxy)hexyl propiolate** (Figure S10-11). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): δ 4.18 (q, J = 6.0 Hz, 4H), 2.88 (s, 1H), 1.92 (s, 6H), 1.76-1.62 (m, 4H), 1.49-1.35 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 171.69, 152.76, 74.73, 74.55, 66.18, 65.84, 55.92, 30.76, 28.20, 25.44, 25.40.

2. Results and Discussion

Table S1 Screening of reaction conditions for selenium-containing brush polymers through SET-LRP. [a]

Entry	$[MMA]_0 : [EGIn]_0 : [Me_6TREN]_0 : [CuBr_2]_0$	$M_{n,SEC}$ [b](g mol^{-1})	$Đ$ [b]
1	50 : 1 : 0.2 : 0.1	20400	1.74
2	50 : 1 : 0.2 : 0.2	12300	1.56
3	50 : 1 : 0.2 : 0.3	9100	2.40

[a] Reaction conditions : $[MMA]_0$ = 8.33 M, polymerized in DMSO at 25 °C using l =1.4 cm, d = 0.5 mm Cu(0)-wire, 4 h. [b] Determined by SEC using polystyrene (PS) as the standard in THF.

Table S2 Grafting of functional monomers through SET-LRP using EGIn as the macroinitiator. [a]

Entry	Monomer	Time (h)	$M_{n,SEC}$ (g mol^{-1})	$Đ$ [b]
1	TEGMA	4	9600	1.77
2	DMAEMA	3	8700	1.76
3	DMAEMA	4	13400	1.92
4	DMAEMA	6	19100	1.85

[a] Reaction conditions: $[M]_0$ = 8.33 M, polymerized in DMSO at 25 °C using l = 1.4 cm, d = 0.5 mm Cu(0)-wire, $[M]_0 : [EGIn]_0 : [Me_6TREN]_0 : [CuBr_2]_0$ = 50 : 1 : 0.2 : 0.2. [b] Determined by SEC using polystyrene (PS) as the standard in THF.

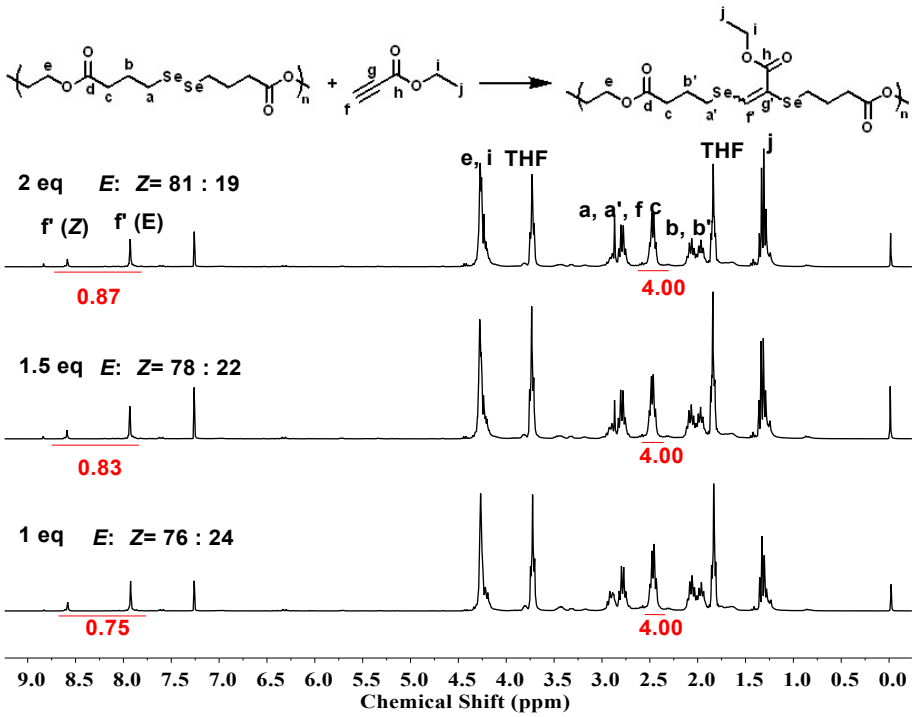


Figure S1. ^{1}H NMR spectra of the reaction mixture of $EGSe_2$ and ethyl propiolate (Table 1, entries 1-3) in $CDCl_3$. Set the integral of c to 4.00, then the degree of functionalization was calculated by the formula (Integral of f')/1.00*100%.

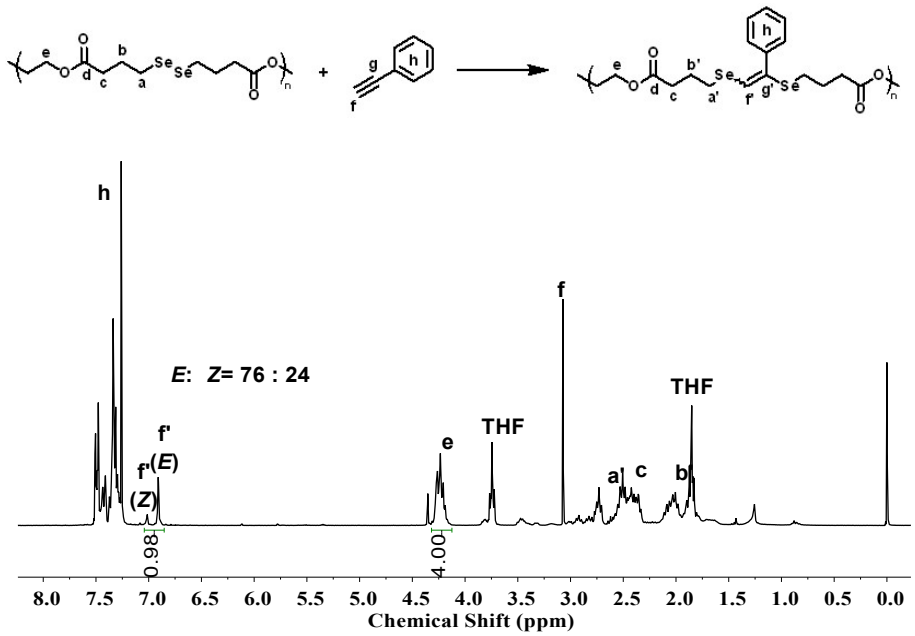


Figure S2. ^{1}H NMR spectrum of the reaction mixture of $EGSe_2$ and phenylacetylene (Table 1, entry 4) in $CDCl_3$. Set the integral of e to 4.00, then the degree of functionalization was calculated by the formula (Integral of f')/1.00*100%.

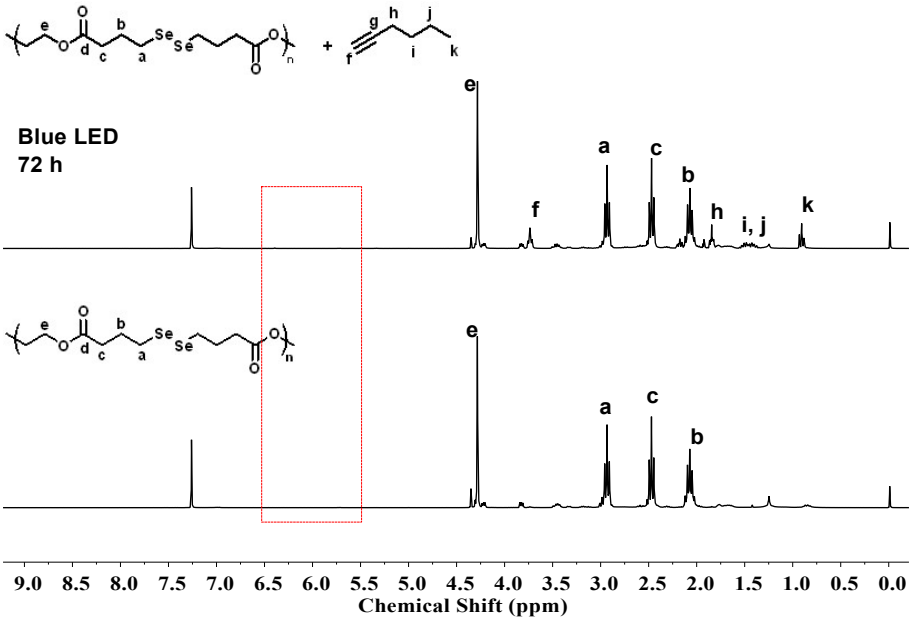


Figure S3. ^{1}H NMR spectra of $EGSe_2$ and the reaction mixture of $EGSe_2$ and 1-hexyne (Table 1, entry 5) in $CDCl_3$. As shown in the spectra, the signal peak of the double bond was not observed at 6.5-5.5 ppm, thus the reaction did not happen even in 72 hours under the Blue LED irradiation.

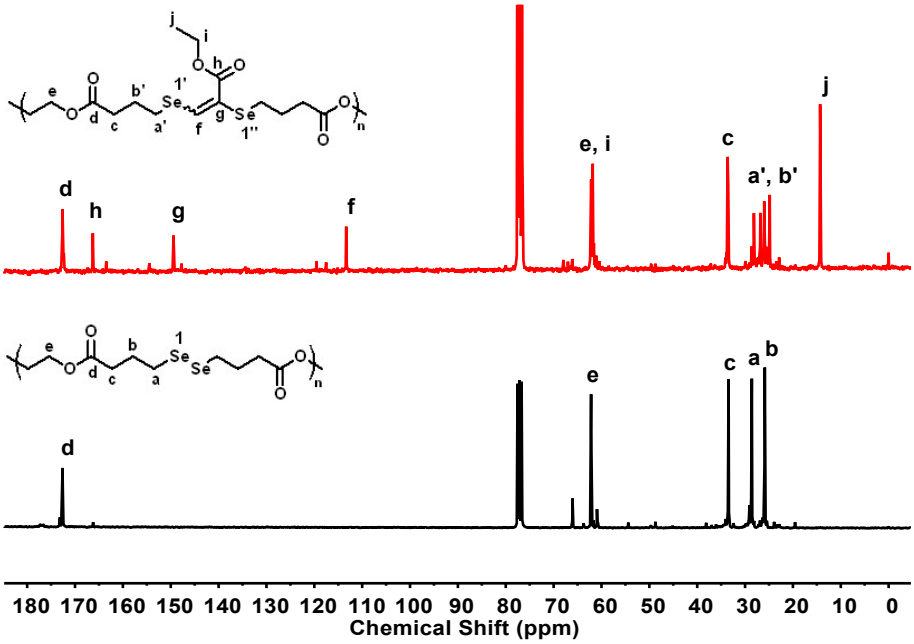


Figure S4. ^{13}C NMR spectra of $EGSe_2$ and $EGSe_2$-Et in $CDCl_3$.

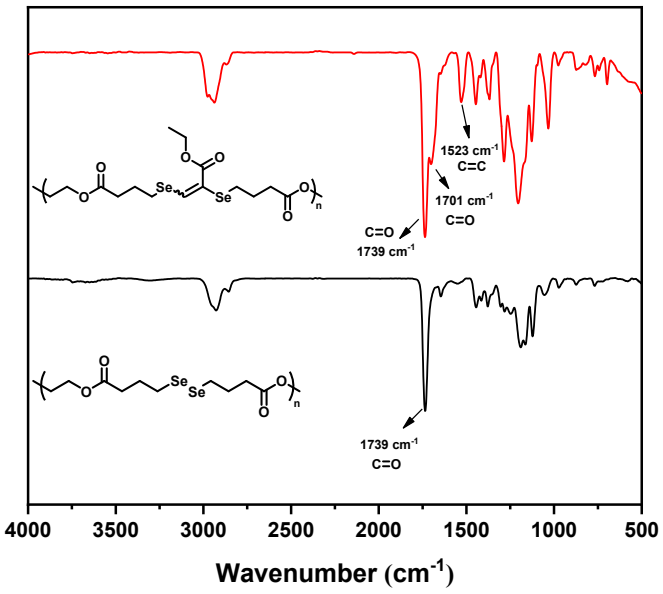


Figure S5. FT-IR spectra of $EGSe_2$ and $EGSe_2$-Et.

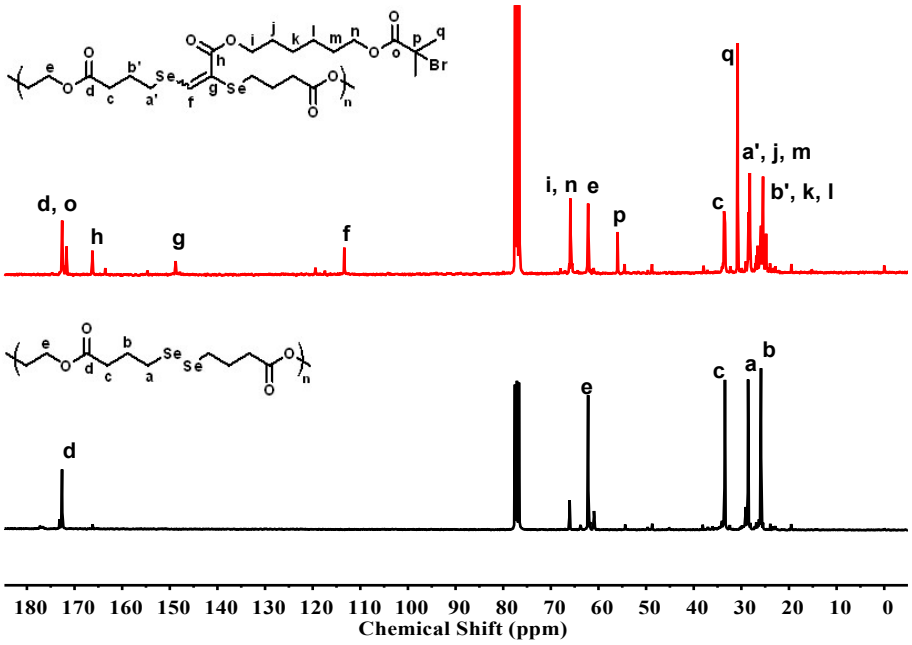


Figure S6. ^{13}C NMR spectra of $EGSe_2$ and EGIn in $CDCl_3$.

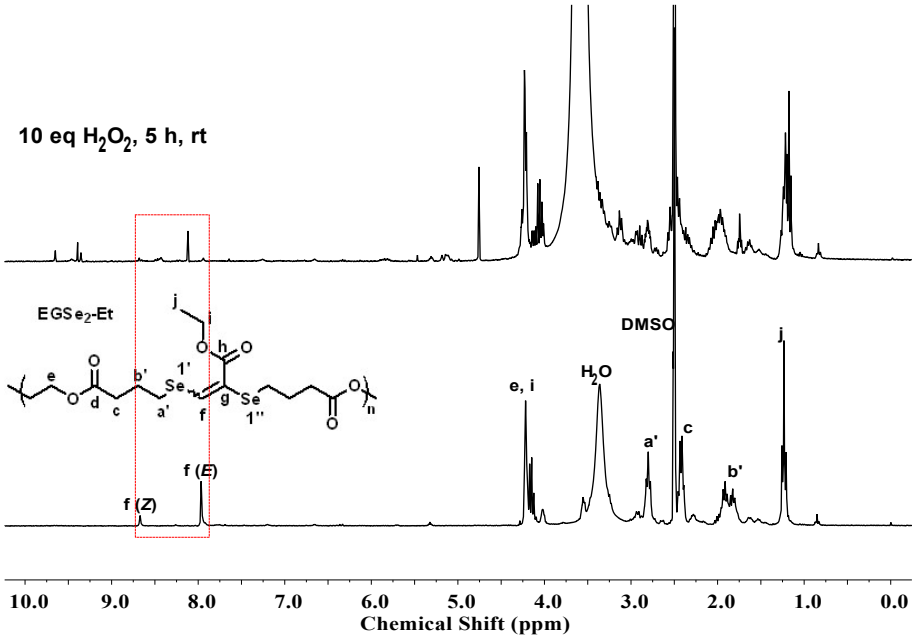


Figure S7. ^{1}H NMR spectra of $EGSe_2$-Et before and after oxidization with 10 eq H_2O_2 in DMSO-d_6. $EGSe_2$-Et (9.2 mg) dissolved in DMSO-d_6 (1 mL) was mixed with 30% H_2O_2 (20 μL) at room temperature. After incubation for 5 h, the solution was evaluated by ^{1}H NMR.

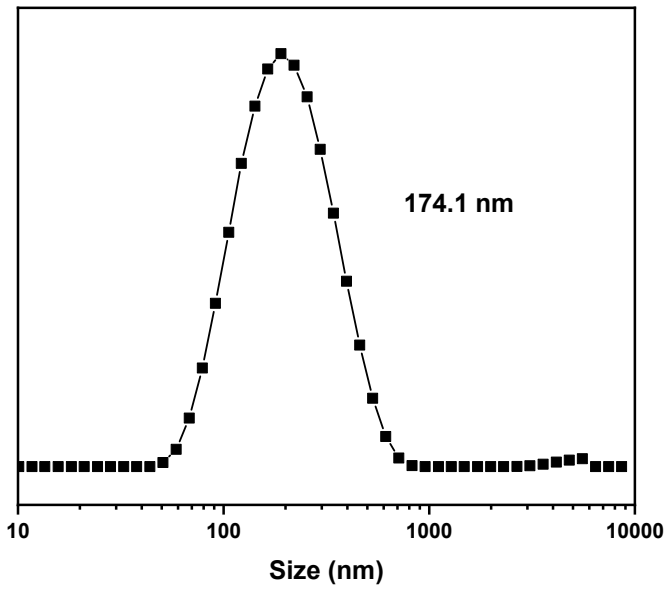


Fig S8. Particle size of polyplexes at a polymer/pDNA weight ratio = 3. Sample: EGIn-*g*-PDMAEMA, M_n = 8700 g mol^{-1}, $Đ$ = 1.76.

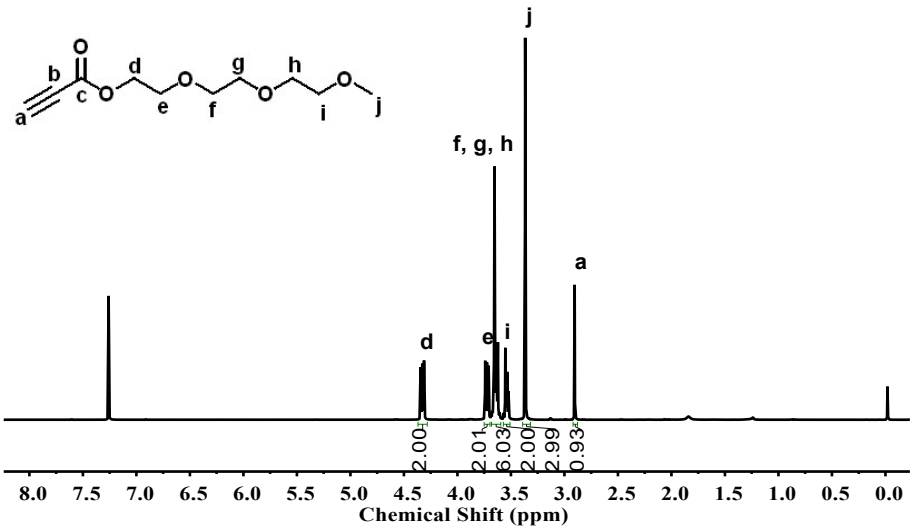


Figure S9. ^{1}H NMR spectrum of 2-(2-(2-methoxyethoxy)ethoxy)ethyl propiolate in $CDCl_3$.

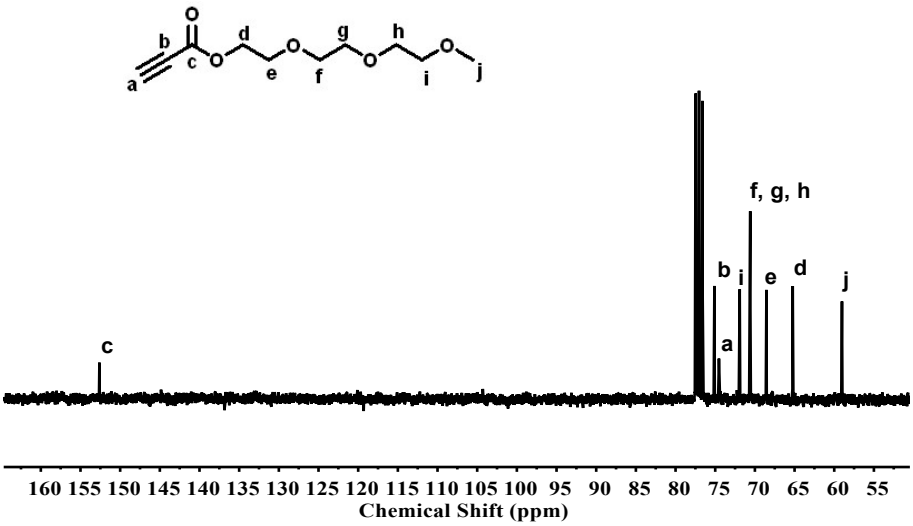


Figure S10. ^{13}C NMR spectrum of 2-(2-(2-methoxyethoxy)ethoxy)ethyl propiolate in $CDCl_3$.

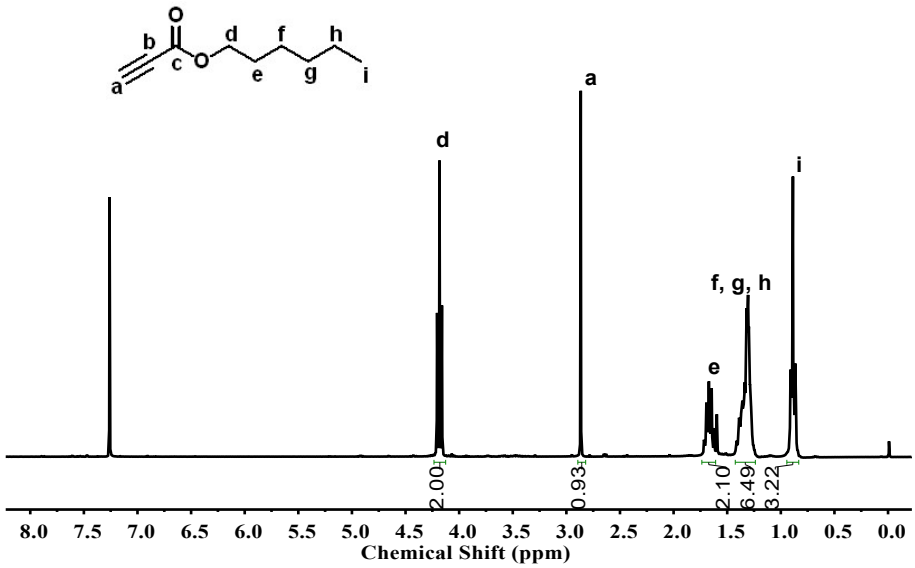


Figure S11. ^{1}H NMR spectrum of hexyl propiolate in $CDCl_3$.

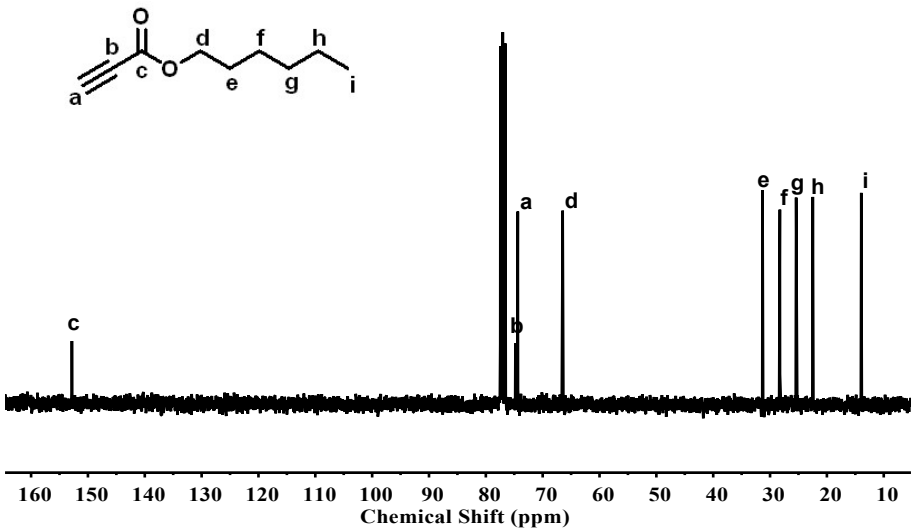


Figure S12. ^{13}C NMR spectrum of hexyl propiolate in $CDCl_3$.

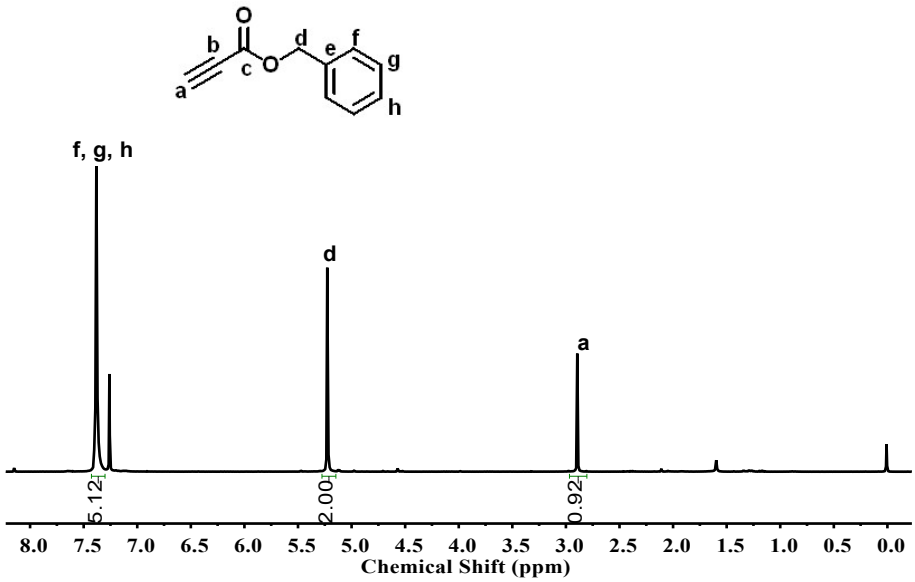


Figure S13. ^{1}H NMR spectrum of benzyl propiolate in $CDCl_3$.

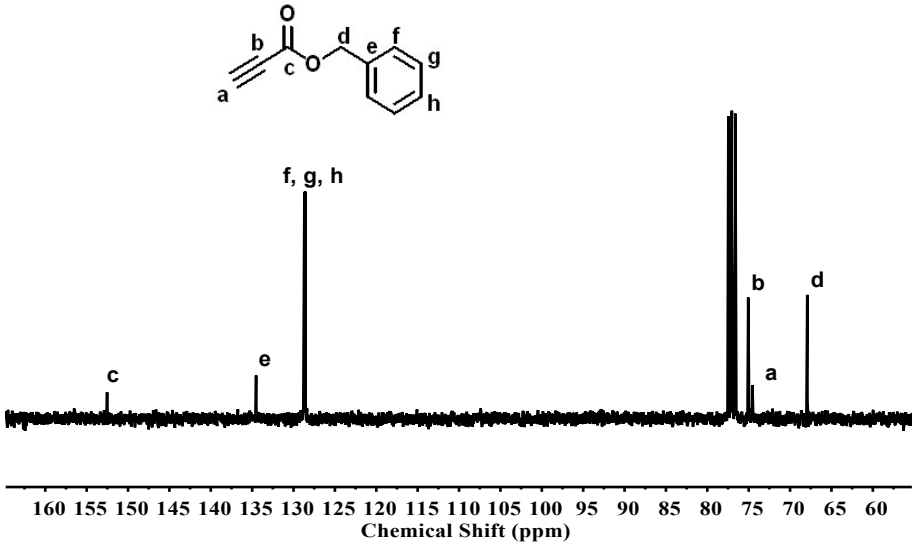


Figure S14. ^{13}C NMR spectrum of benzyl propiolate in $CDCl_3$.

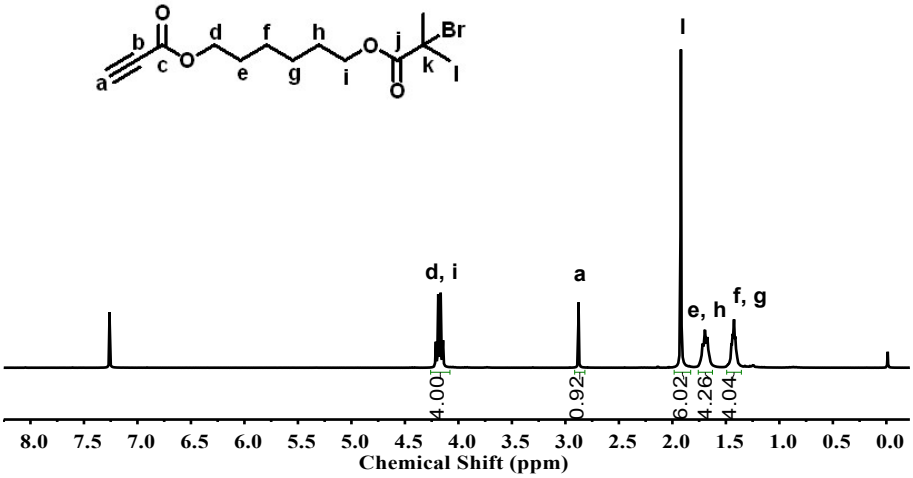


Figure S15. ^{1}H NMR spectrum of 6-((2-bromo-2-methylpropanoyl)oxy)hexyl propiolate in $CDCl_3$.

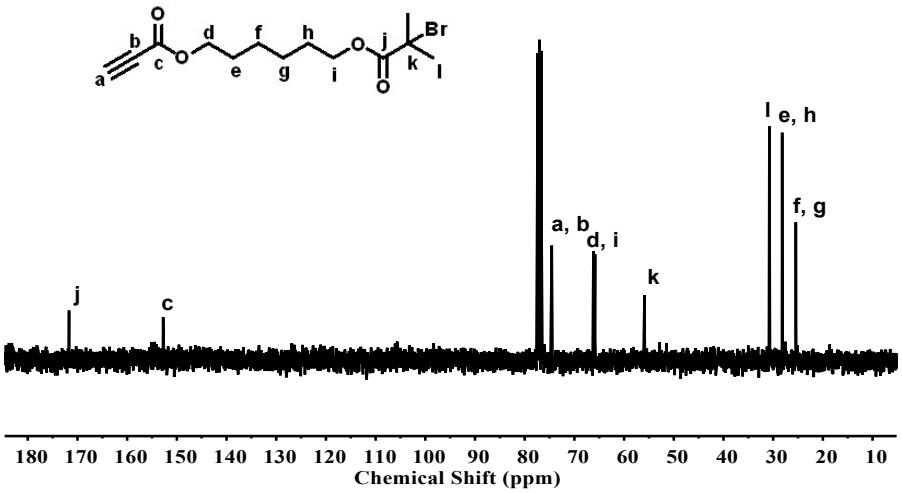


Figure S16. ^{13}C NMR spectrum of 6-((2-bromo-2-methylpropanoyl)oxy)hexyl propiolate in $CDCl_3$.