

Supporting Information

Synthesis and Characterization of Thermally Cured Polytriazole Polymers Incorporating Main or Side Chain Benzoxazine Crosslinking Moieties

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Materials

The following reagents and solvents were purchased from commercial suppliers and used as received unless otherwise noted: *p*-Xylylene dichloride (Sigma-Aldrich, 98%), sodium azide (Sigma-Aldrich, $\geq 99\%$), bisphenol A (Sigma-Aldrich, 97%), tetrabutylammonium bromide (99%, Sigma-Aldrich), propargyl bromide (80 wt.% solution in toluene, ACROS), 3,5-dihydroxybenzoic acid (Alfa-Aesar, 98%), propargylamine (ACROS, 99%), 18-crown-6 (ACROS, 99%), 1,2-diaminoethane (TEDIA, 99%), paraformaldehyde (Alfa-Aesar, 97%), phenol (Sigma-Aldrich, 99%), potassium carbonate (Sigma-Aldrich, 99%), sodium hydroxide (Sigma-Aldrich, $\geq 97\%$), potassium hydroxide (Sigma-Aldrich, $\geq 97\%$), sulfuric acid (Scharlau, 98%), anhydrous magnesium sulfate (99%, Sigma-Aldrich), *N,N*-Dimethylformamide (DMF) (TEDIA, 99.8%), toluene (TEDIA, 99.5%), tetrahydrofuran (THF) (TEDIA, 99.8%), benzene (Sigma-Aldrich, 99.8%), ethanol (TEDIA, $\geq 99.5\%$), methanol (TEDIA, $\geq 99.5\%$), acetone (TEDIA, $\geq 99.5\%$), chloroform (TEDIA, $\geq 99.8\%$), ethyl acetate (EA) (TEDIA, $\geq 99.5\%$), dioxane (TEDIA, $\geq 99.0\%$), *n*-hexane (TEDIA, $\geq 95.0\%$), and glacial acetic acid (TEDIA, $\geq 99.7\%$). The deionized (DI) water used in all reactions, solution preparations, and polymer isolations was purified to a resistance of 18 M Ω (Milli-Q Reagent Water System, Millipore Corporation). Silica particles (diameter: 3 μm) were obtained from Polysciences, Inc. (USA). Copper(I) iodide ($\geq 97\%$, Riedel-de Haën) was washed with glacial acetic acid to remove any soluble oxidized species and then it was filtered, washed with ethanol, and dried.

Synthesis of Monomers

1,4-BIS(AZIDOMETHYL)BENZENE (BAB). *p*-Xylylene dichloride (8.8g, 50 mmol), sodium azide (9.75g, 150 mmol), DMF (100 mL), and benzene (100 mL) were added into a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was slowly heated to 80 °C and then maintained at that temperature for 12 h and then poured into a beaker containing deionized water (200 mL). The organic layer was separated and the aqueous layer extracted three times with benzene. The combined organic phases were dried overnight (MgSO₄) and then the benzene was evaporated to yield a light-yellow solid. [Scheme 1 (a)]

Yield: 83%; mp = 27-29 °C; ¹H NMR (DMSO-d₆), ppm: δ = 4.44 (a), 7.38 (b) [Figure S1 (a)].
¹³C NMR (CDCl₃), ppm: δ = 54.03 (1), 129.58 (2), 136.20 (3) [Figure S1 (b)].

4,4'-(PROPANE-2,2-DIYL)BIS((PROP-2-YNYLOXY)BENZENE) (PBPB). Bisphenol A (11.4 g, 50 mmol), sodium hydroxide (6 g, 150 mmol), deionized water, and tetrabutylammonium bromide

(1.6 g, 5 mmol) were placed in a three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen gas inlet tube, after which the reagents were heated to 80 °C. Propargyl bromide (14.87 g, 125 mmol) was added dropwise over 3 h and then the mixture was maintained at 80 °C for 10 h. The reaction product was washed several times with deionized water to remove tetrabutylammonium bromide and the salt formed in the reaction. The product was obtained through recrystallization with ethyl alcohol. [Scheme 1 (b)]

Yield: 89%; mp = 78 °C; ¹H NMR (CDCl₃), ppm: δ = 1.67 (a), 2.54 (b), 4.68 (c), 6.91 (d), 7.19 (e) [Figure S2 (a)]; ¹³C NMR (CDCl₃), ppm: δ = 31.36 (1), 42.16 (2), 56.10 (3), 75.59 (4), 79.07 (5), 114.61 (6), 128.20 (7), 144.20 (8), 155.69 (9) [Figure S2 (b)].

METHYL 3,5-DIHYDROXYBENZOATE (1). 3,5-dihydroxybenzoic acid (10 g, 65 mmol), sulfuric acid (1 ml) and methanol (125 ml) were placed in a three-necked round bottom flask equipped with a magnetic stirrer. The reaction mixture was heated to 90 °C under nitrogen for 24 hours and then the solvent was evaporated to dryness, and the crude product was washed several times with deionized water until the pH was in the range 6-7. The product was obtained through recrystallized in methanol to give the white crystals. [Scheme 1 (c)]

Yield: 92%; mp = 168 °C; ¹H NMR (DMSO-d₆), ppm: δ = 3.76 (a), 6.42 (b), 6.80 (c), 9.63 (d) [Figure S3 (a)]; ¹³C NMR (DMSO-d₆), ppm: δ = 52.88 (1), 107.89 (2), 132.20 (3), 159.39 (4), 166.91 (5) [Figure S3 (b)].

METHYL 3,5-BIS(PROP-2-YNYLOXY)BENZOATE (2). To a stirred solution of methyl 3,5-dihydroxybenzoate (16.8 g, 100 mmol) and propargyl bromide (29.7 g, 220 mmol) in acetone (300 ml) were added potassium carbonate (15.1 g, 109 mmol) and 18-crown-6 (0.1 g, 0.4 mmol). The reaction mixture was heated at reflux under nitrogen for 24 hours, filtered and evaporated to dryness. The crude material was then crystallized in methanol to give the ester as pale yellow crystals. [Scheme 1 (c)]

Yield: 82.6%; mp = 110 °C; ¹H NMR (DMSO-d₆), ppm: δ = 3.59 (a), 3.84 (b), 4.84 (c), 6.87 (d), 7.15 (e) [Figure S4 (a)]; ¹³C NMR (DMSO-d₆), ppm: δ = 53.38 (1), 56.64 (2), 79.32 (3), 79.69 (4), 107.89 (5), 109.14 (6), 132.20 (7), 159.02 (8), 166.54 (9) [Figure S4 (b)].

N-AMINOETHYL 3,5-BIS(PROPARGYLOXYL)BENZAMIDE (3). A solution of methyl 3,5-bis(prop-2-ynyloxy)benzoate (6.25 g, 25.6 mmol) in 30 mL of methanol was added dropwise into a stirred solution of 1,2-diaminoethane (73.9 g, 1.23 mol) in 120 mL of methanol at 0 °C. After the addition was completed (within ~ 1 h), the mixture was allowed to warm to room temperature and was then stirred for 96 h. The solvent was removed under reduced pressure using a rotary evaporator at a temperature below 40 °C. Subsequently, the excess 1,2-diaminoethane was removed using an azeotropic mixture of toluene and methanol (9:1 v/v).

After drying in a vacuum oven for 24 h, the compound 3 was obtained as yellowish oil. [Scheme 1 (c)]

Yield: 92%; ^1H NMR (CDCl_3), ppm: $\delta = 2.02$ (a), 2.47 (b), 2.83 (c), 3.38 (d), 4.61 (e), 6.63 (f), 6.96 (g, h) [Figure S5 (a)]; ^{13}C NMR (CDCl_3), ppm: $\delta = 41.04$ (1), 42.39 (2), 56.06 (3), 76.03 (4), 78.04 (5), 105.03 (6), 106.69 (7), 136.70 (8), 158.68 (9), 167.02 (10) [Figure S5 (b)].

Table S1 Characterization of neat PTA, PTA-SBz and PTA-MBz polymers

Polymer	Theoretical content (mol%) ^a			Measured content (mol%) ^b		
	x	y	z	x	y	z
PTA	50	0	50	48.2	0	51.8
PTA-SBz-2	50	10	40	49.2	8.8	42.0
PTA-SBz-4	50	20	30	49.8	19.5	30.7
PTA-SBz-6	50	30	20	48.8	29.2	22.0
PTA-SBz-8	50	40	10	51.4	37.6	11.0
PTA-SBz-10	50	50	0	48.0	52.0	0
PTA-MBz-10	50	50	0	48.4	51.6	0

^a Determined from the initial feed ratio of monomers.

^b Calculated from the integral areas of the characteristic peaks in ¹H NMR spectra.

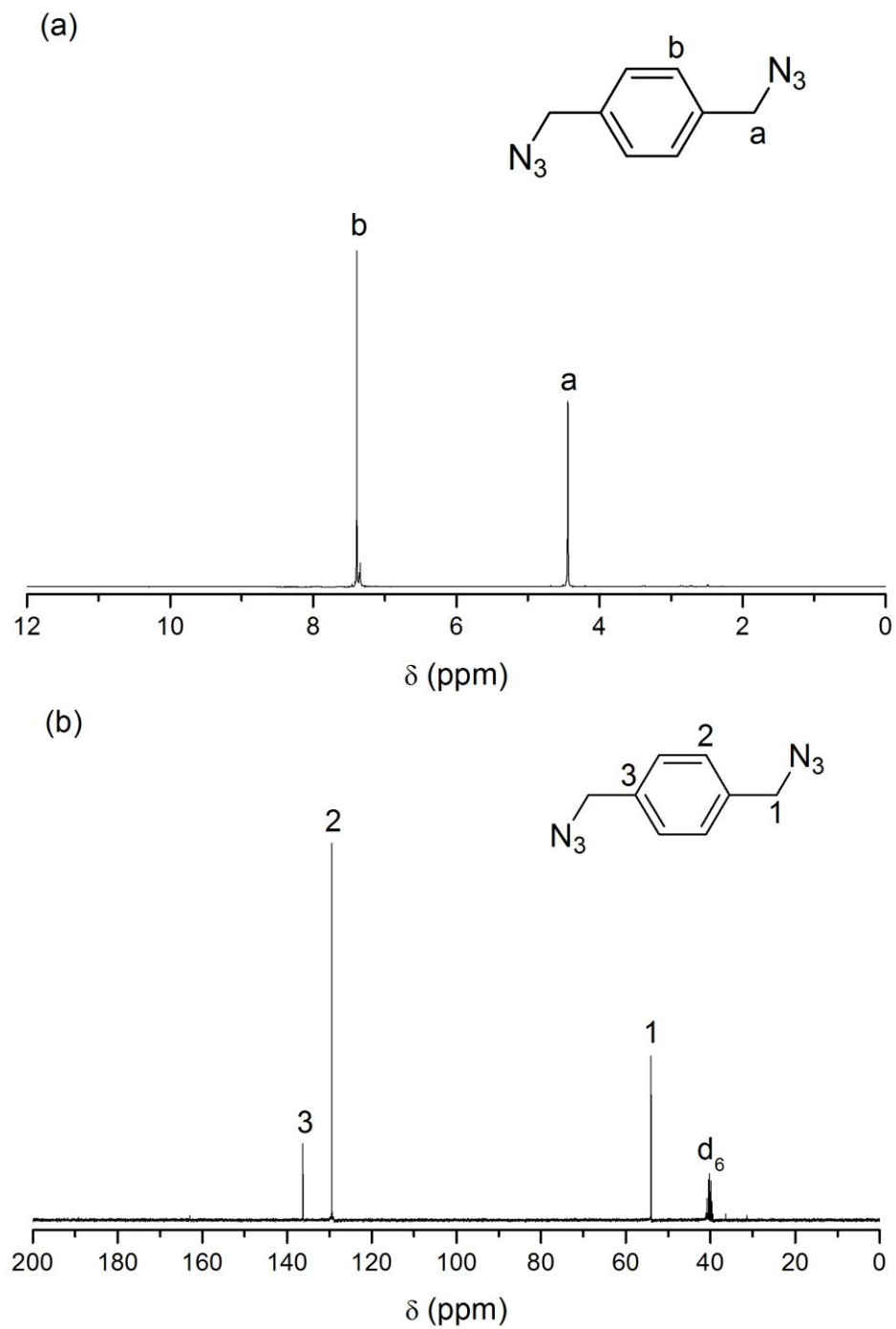


Figure S1. (a) ^1H and (b) ^{13}C NMR spectra of **1,4-Bis(azidomethyl)benzene (BAB)**

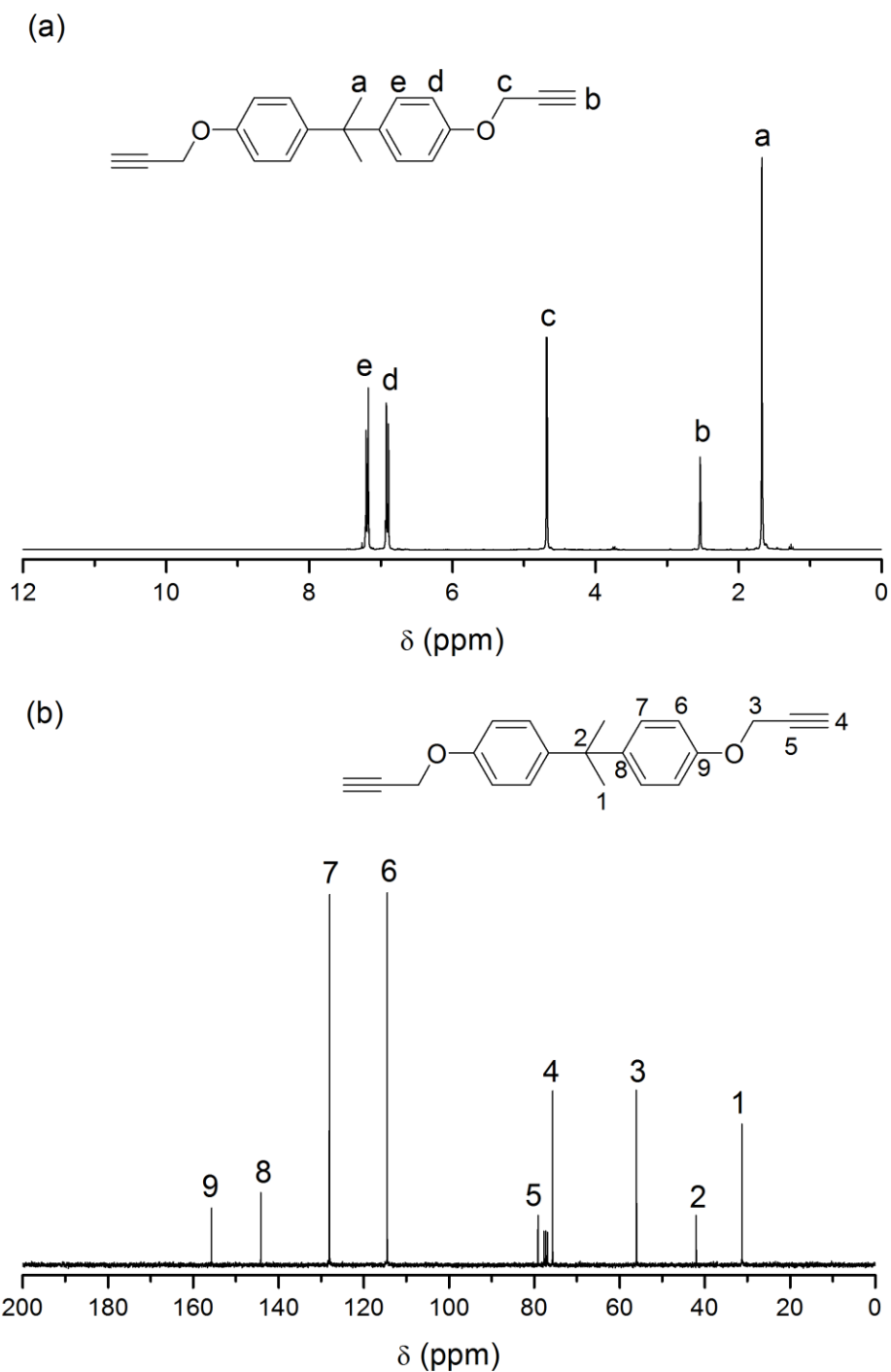
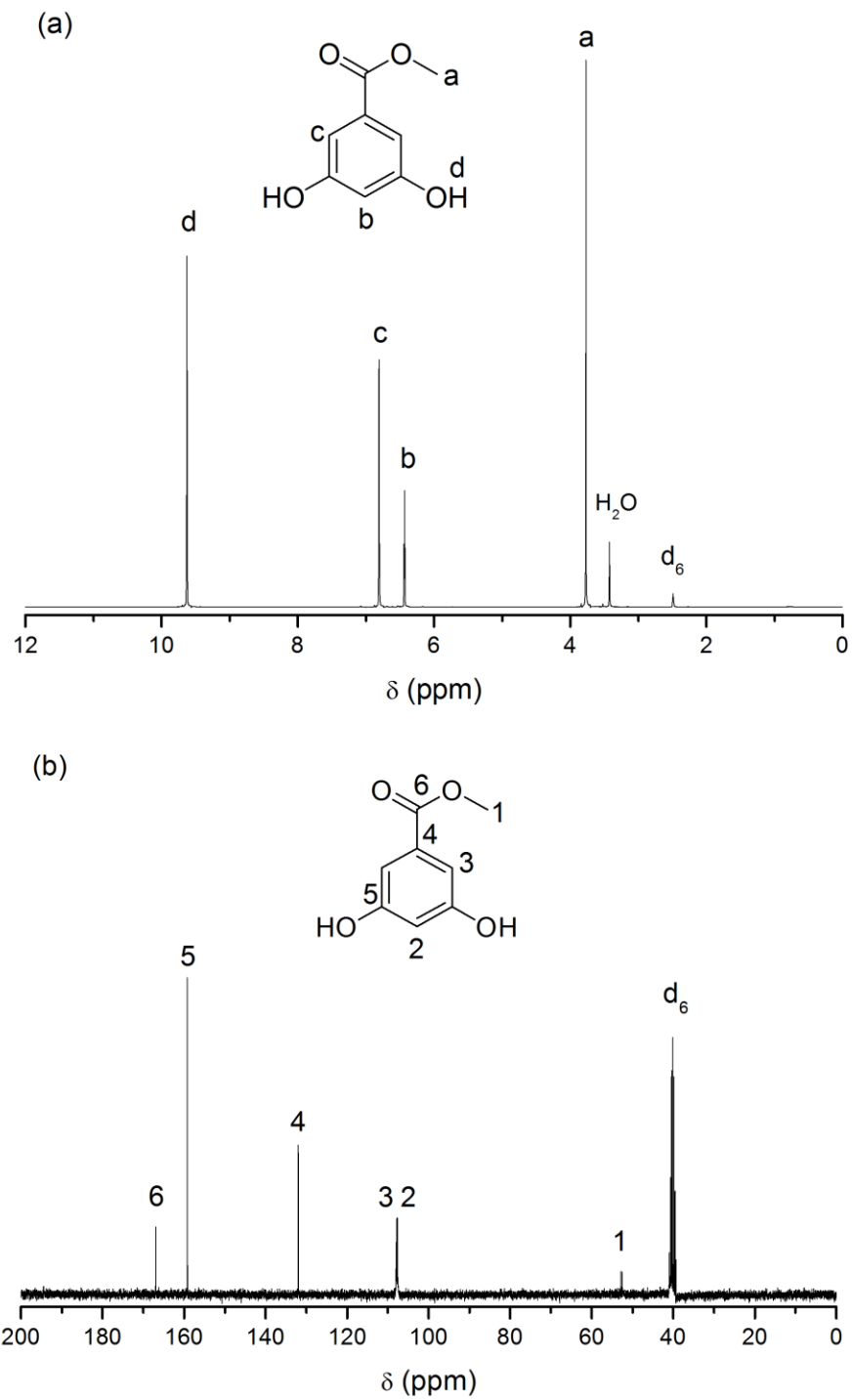
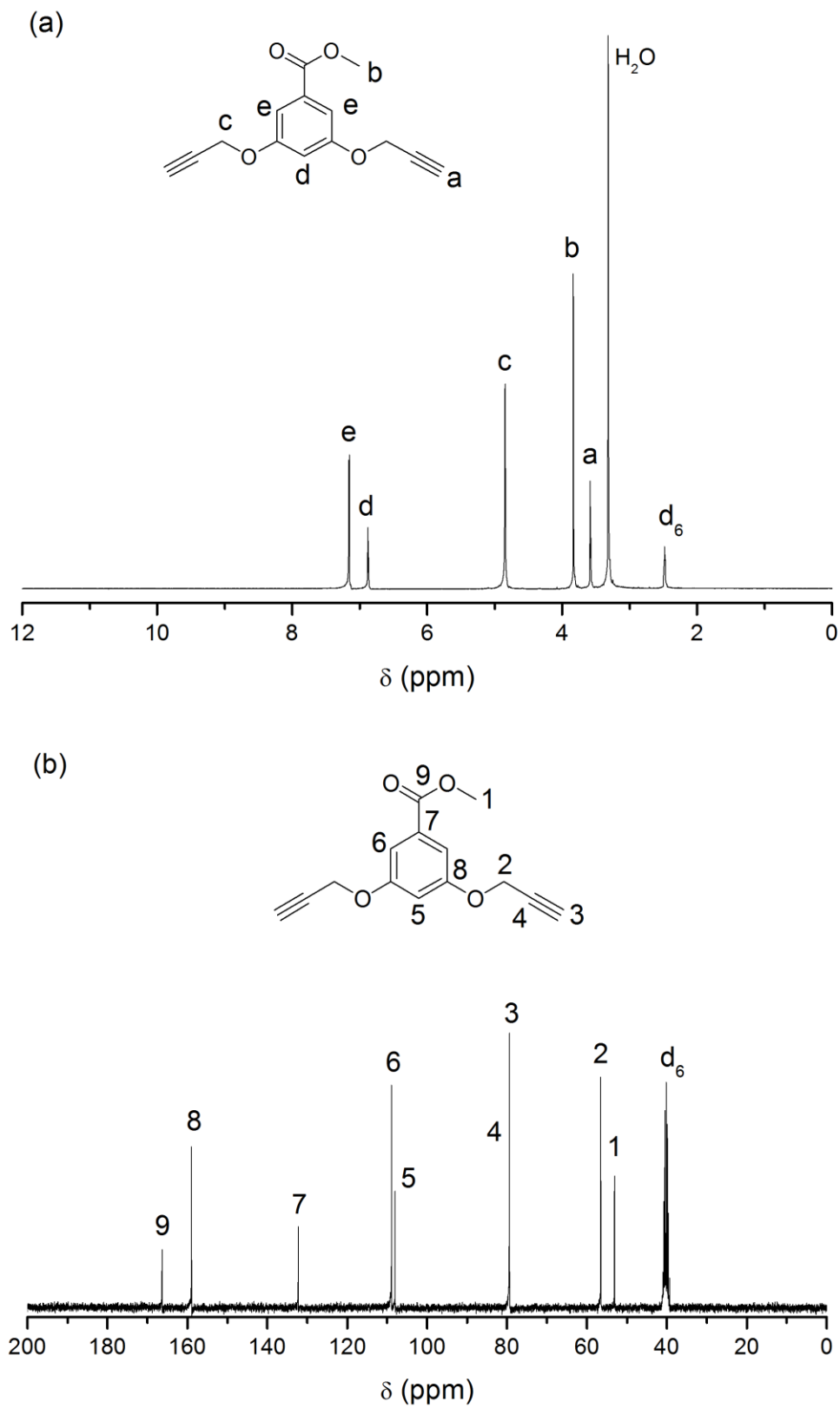
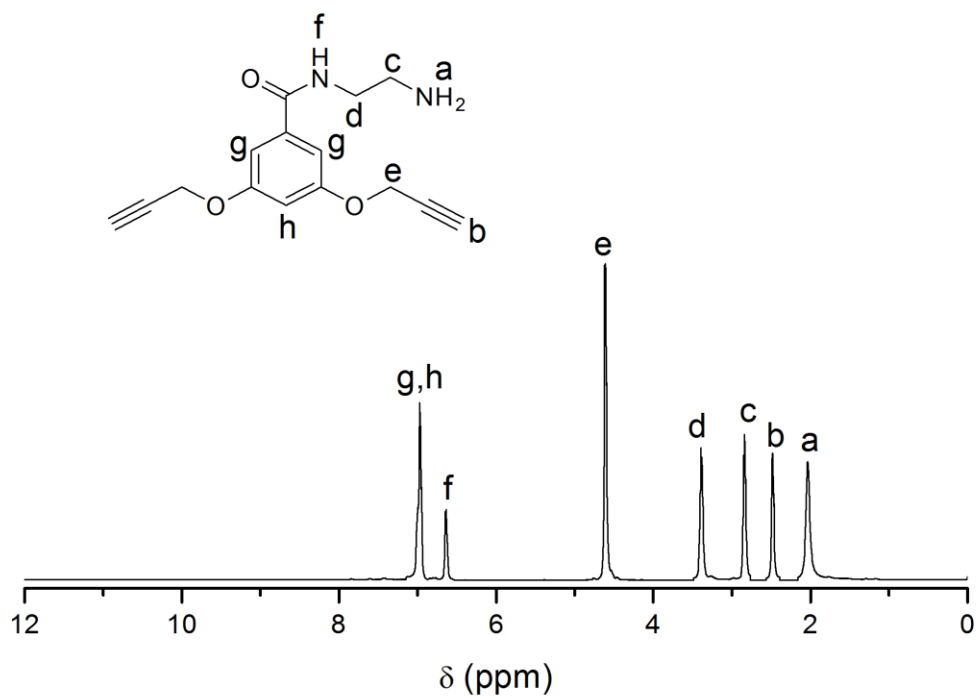


Figure S2. (a) ^1H and (b) ^{13}C NMR spectra of 4,4'-(propane-2,2-diyl)bis(prop-2-ynoxy)benzene (PBPB)





(a)



(a)

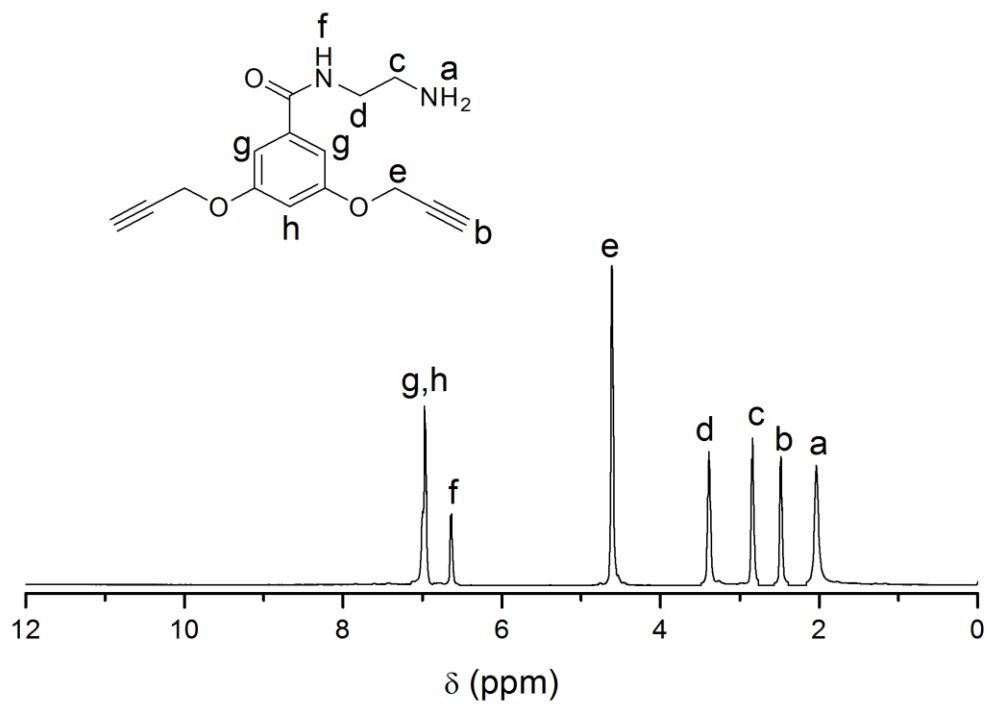


Figure S5. (a) ¹H and (b) ¹³C NMR spectra of N-Aminoethyl 3,5-Bis(propargyloxy)benzamide (3)

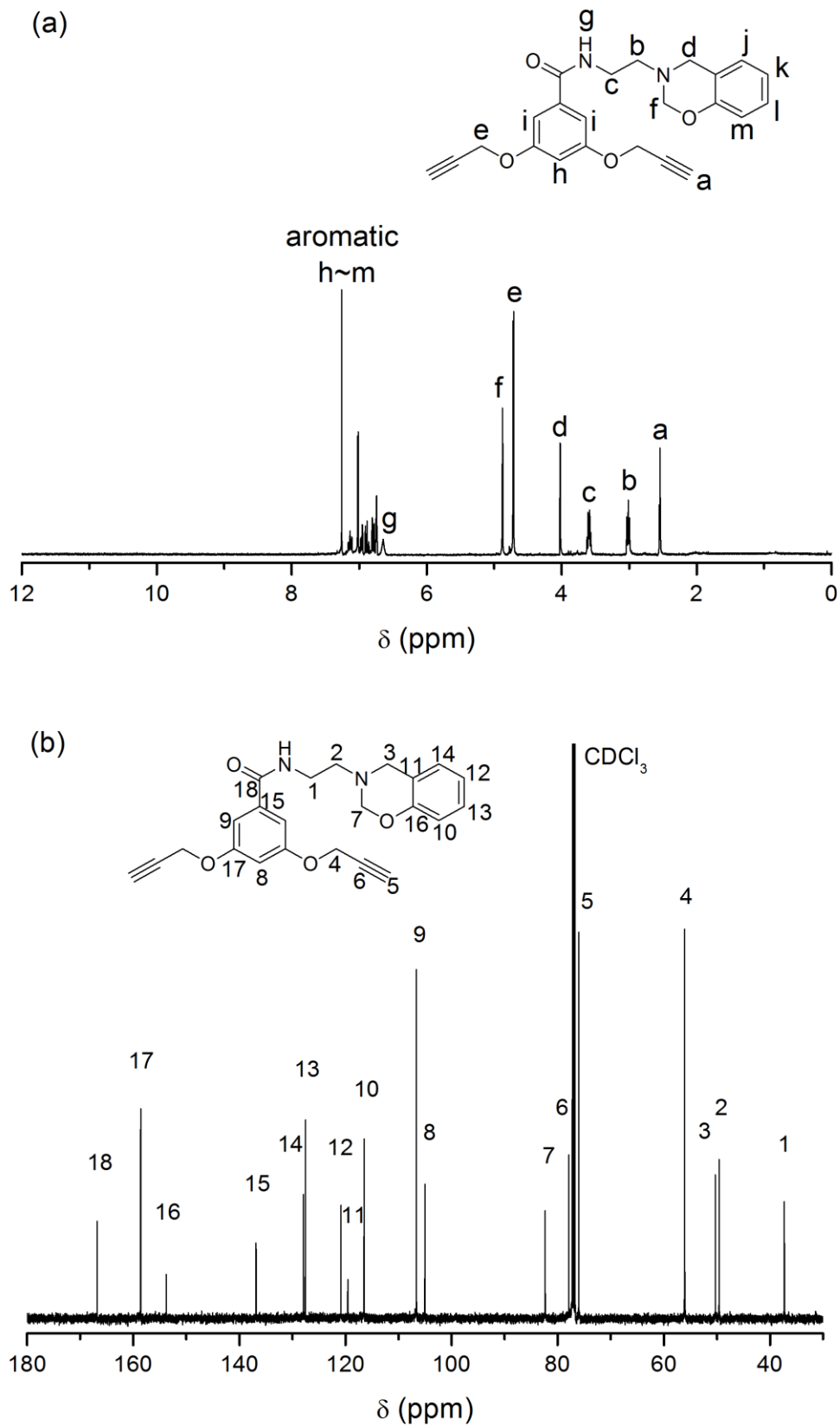
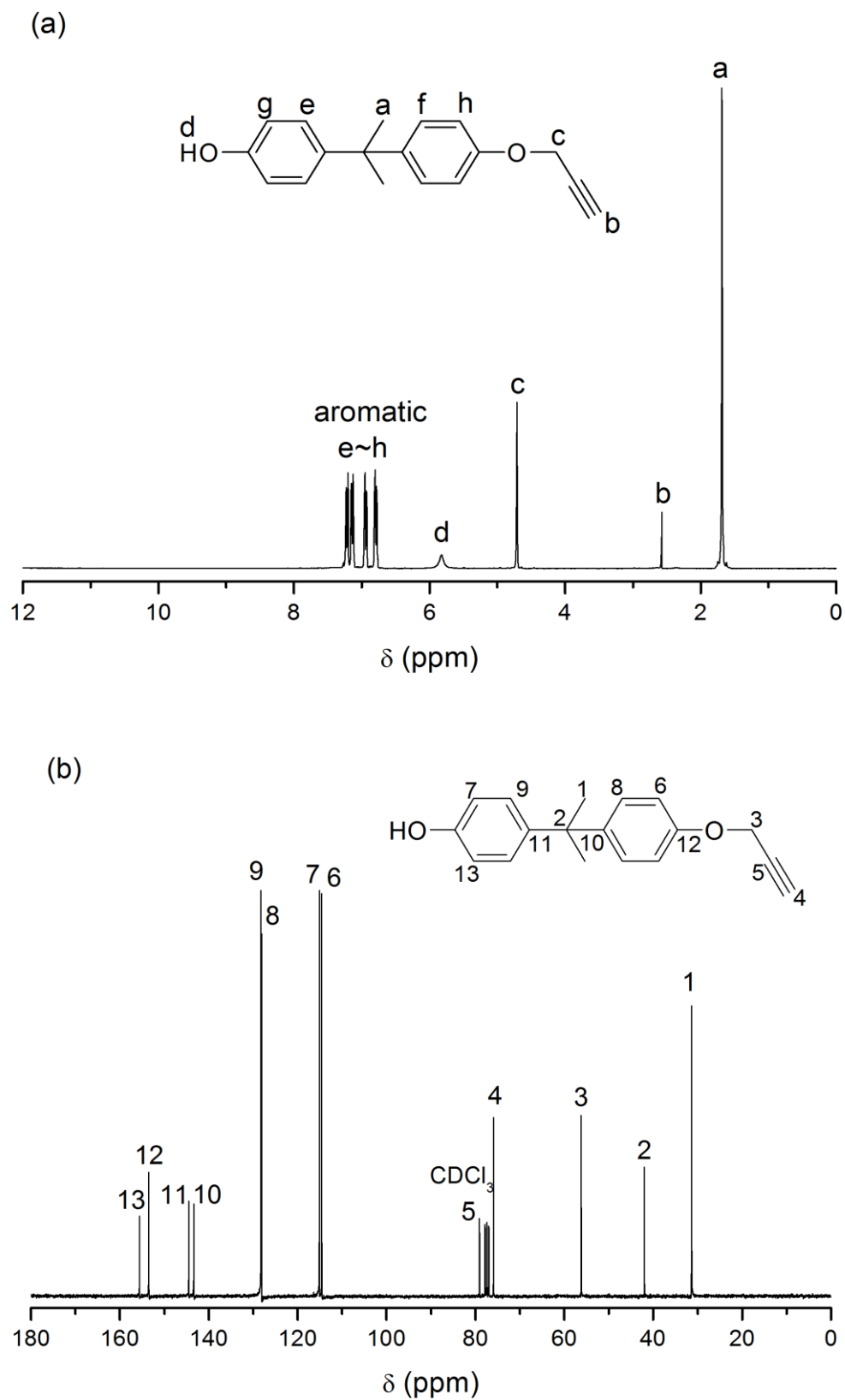
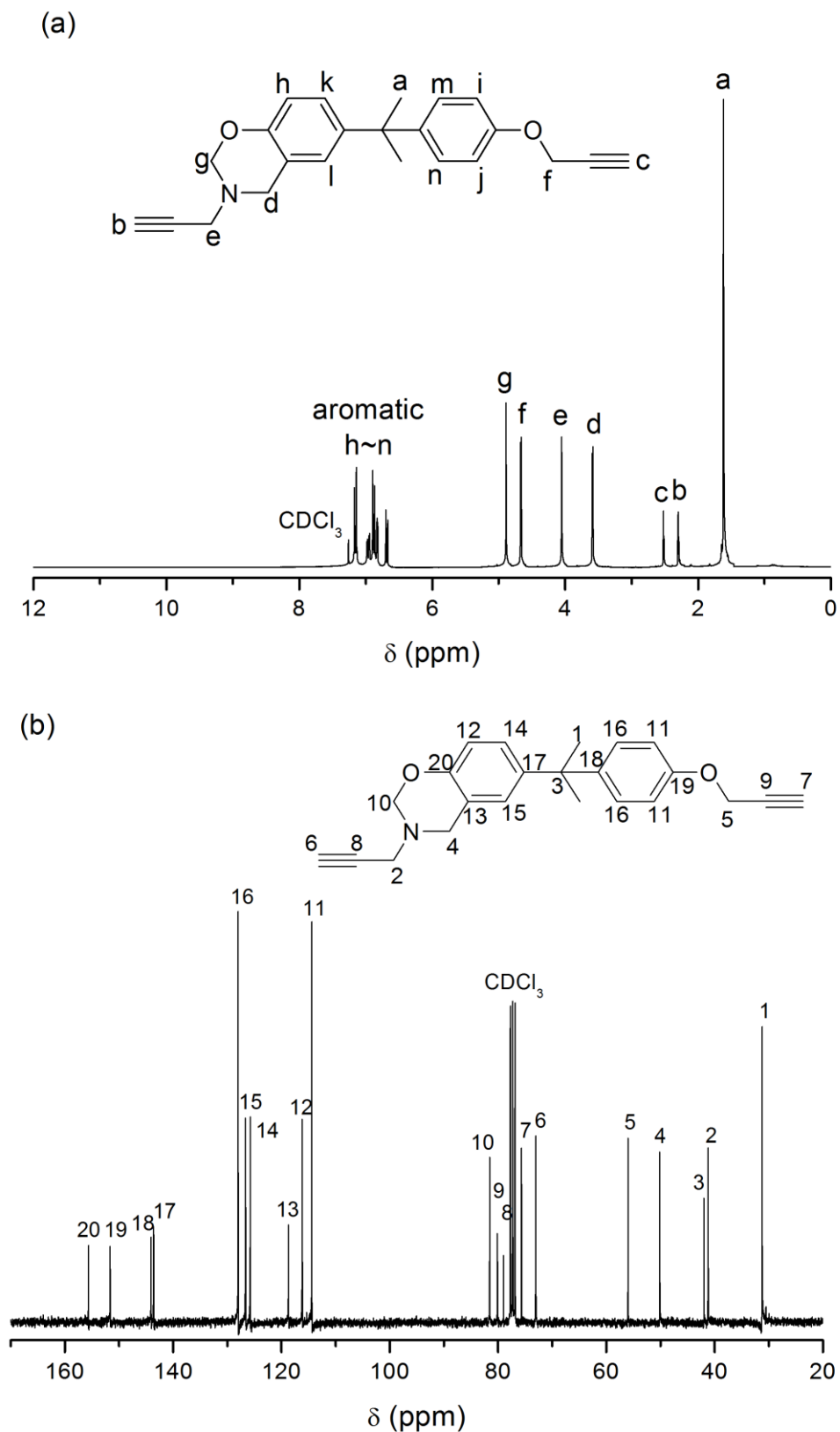


Figure S6. (a) ^1H and (b) ^{13}C NMR spectra of **N-(2-(2H-benzo[e][1,3]oxazin-3(4H)-yl)ethyl)-3,5-bis(prop-2-ynyloxy)benzamide (SBz, 4)**





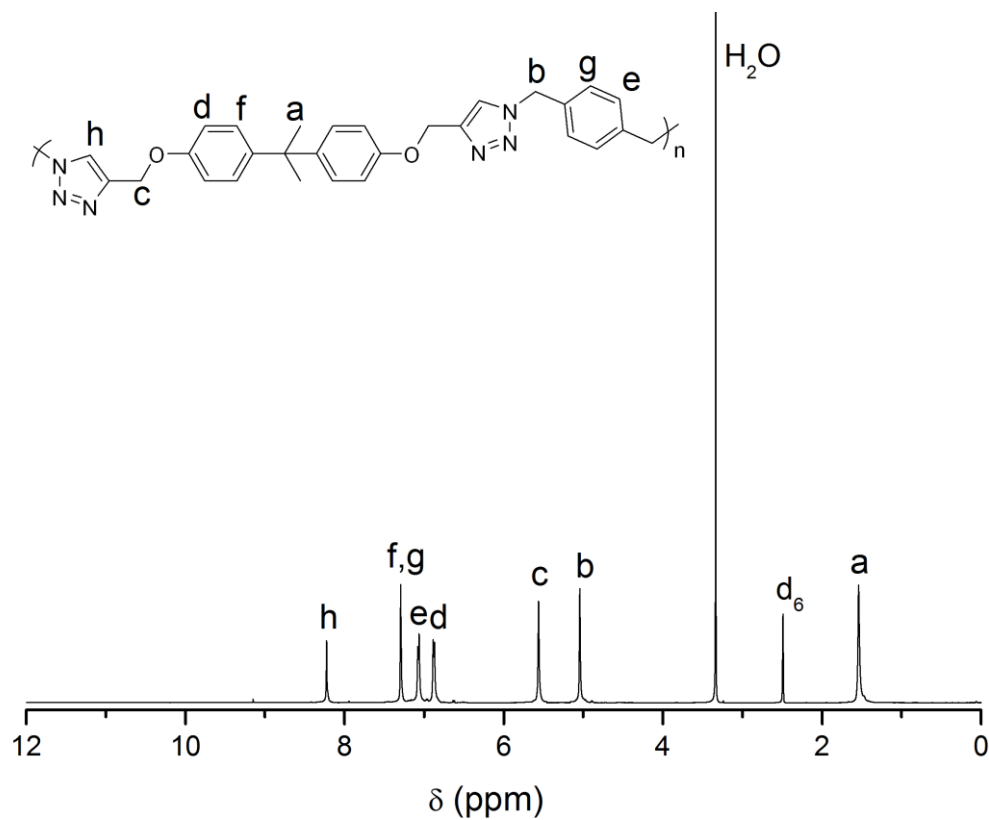


Figure S9. ¹H NMR spectrum of **polytriazole (PTA)**

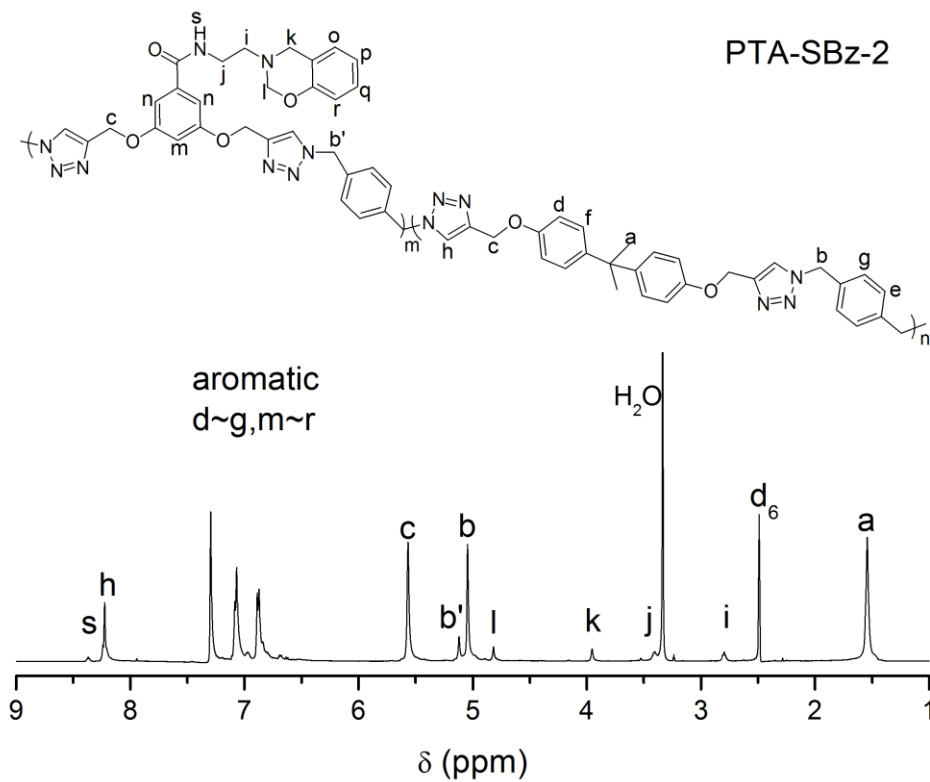


Figure S10. ¹H NMR spectrum of **PTA-SBz-2**

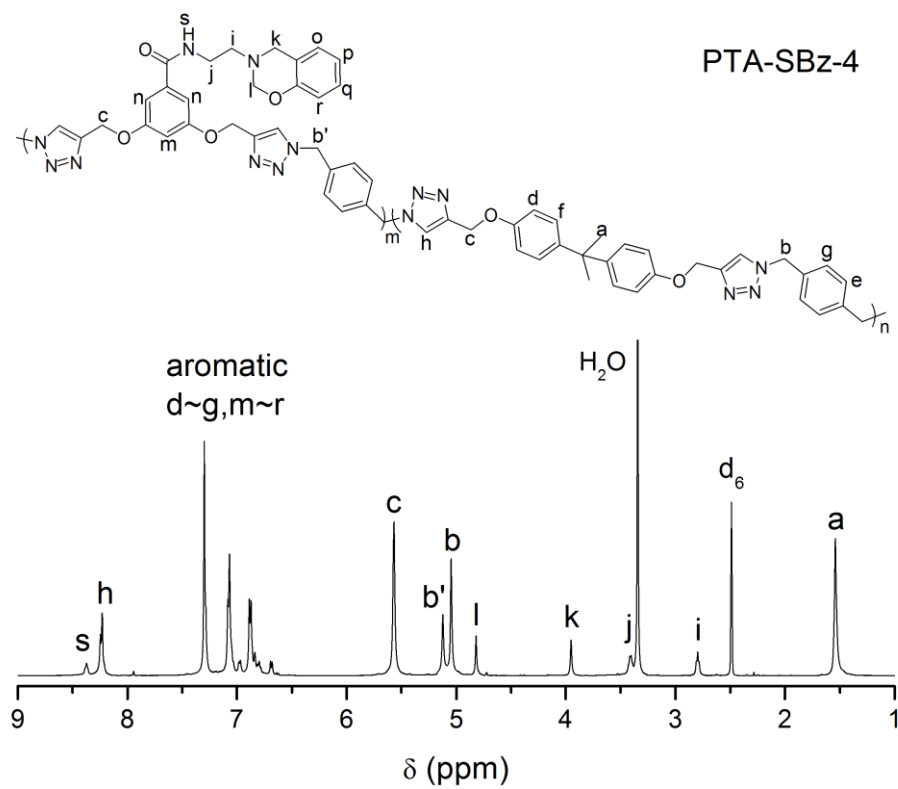


Figure S11. ¹H NMR spectrum of **PTA-SBz-4**

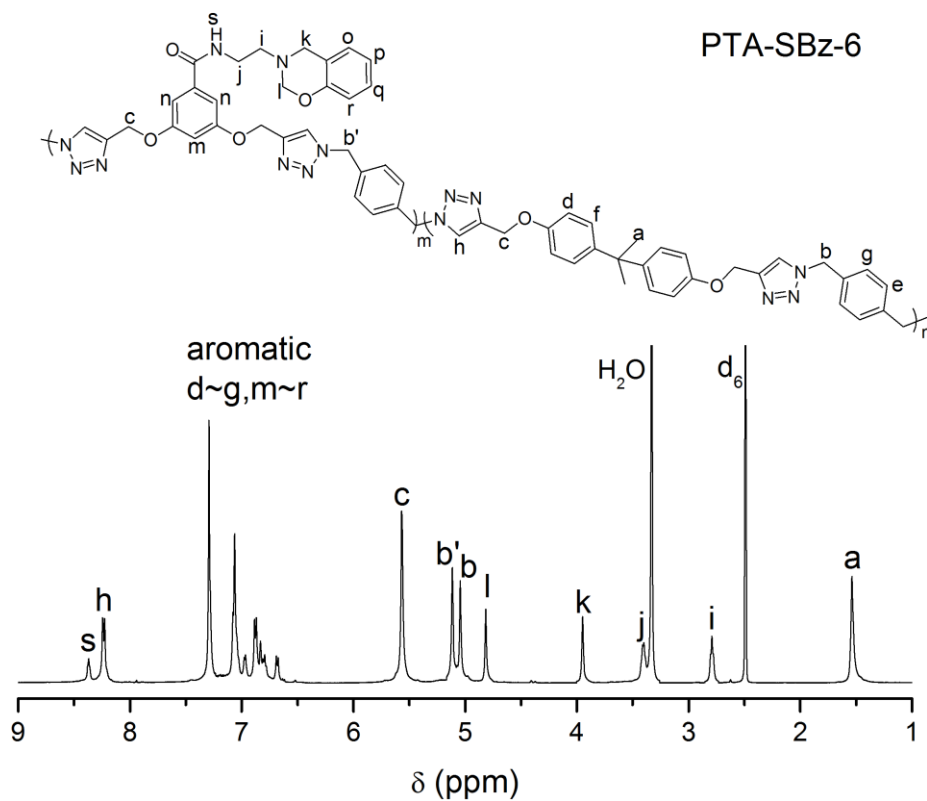


Figure S12. ¹H NMR spectrum of **PTA-SBz-6**

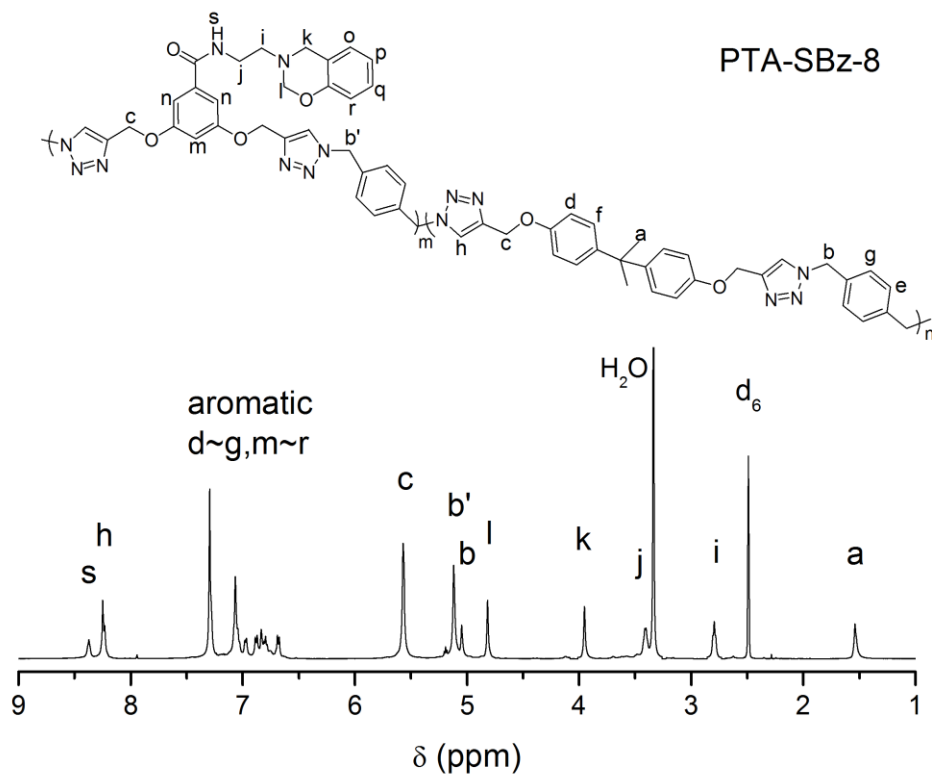


Figure S13. ^1H NMR spectrum of PTA-SBz-8

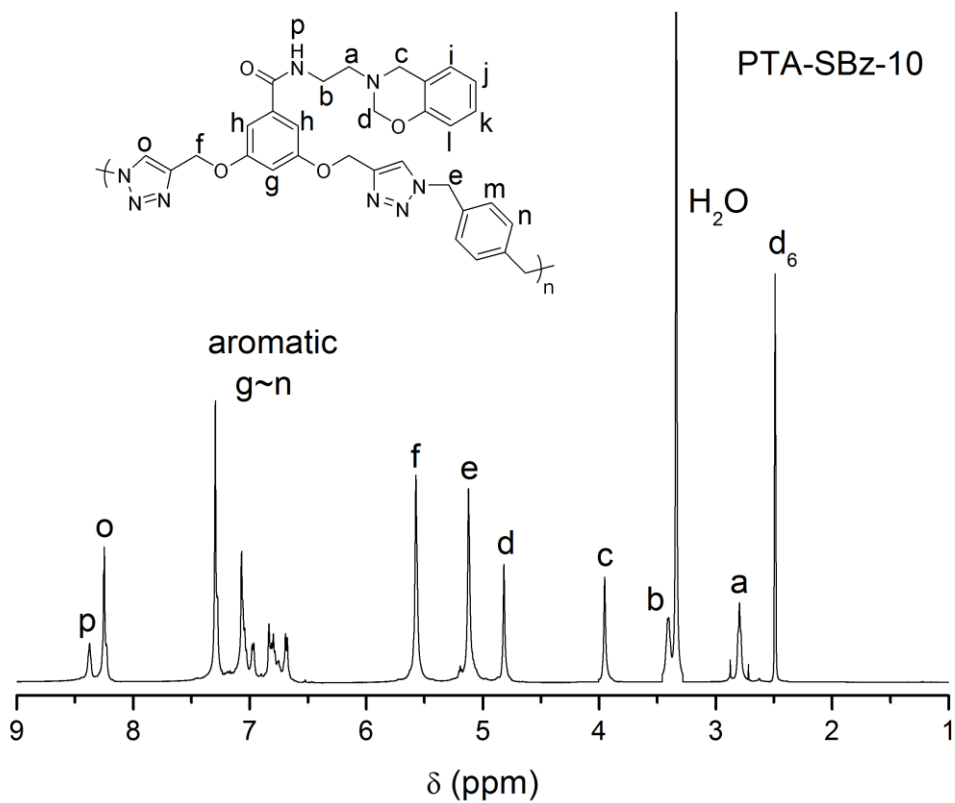


Figure S14. ^1H NMR spectrum of PTA-SBz-10

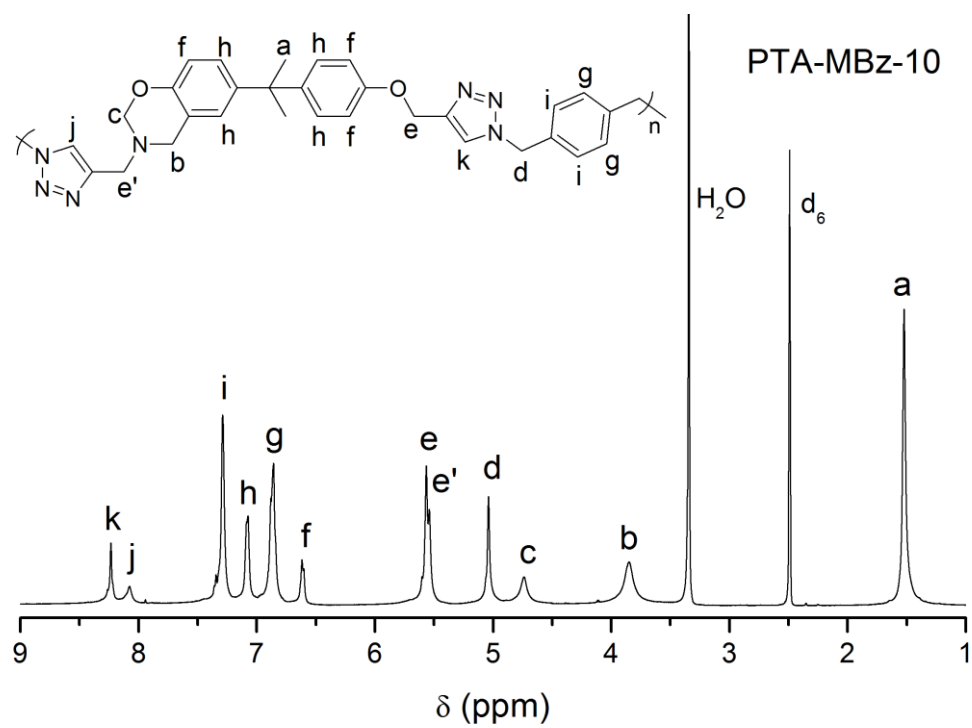


Figure S15. ¹H NMR spectrum of **PTA-MBz-10**

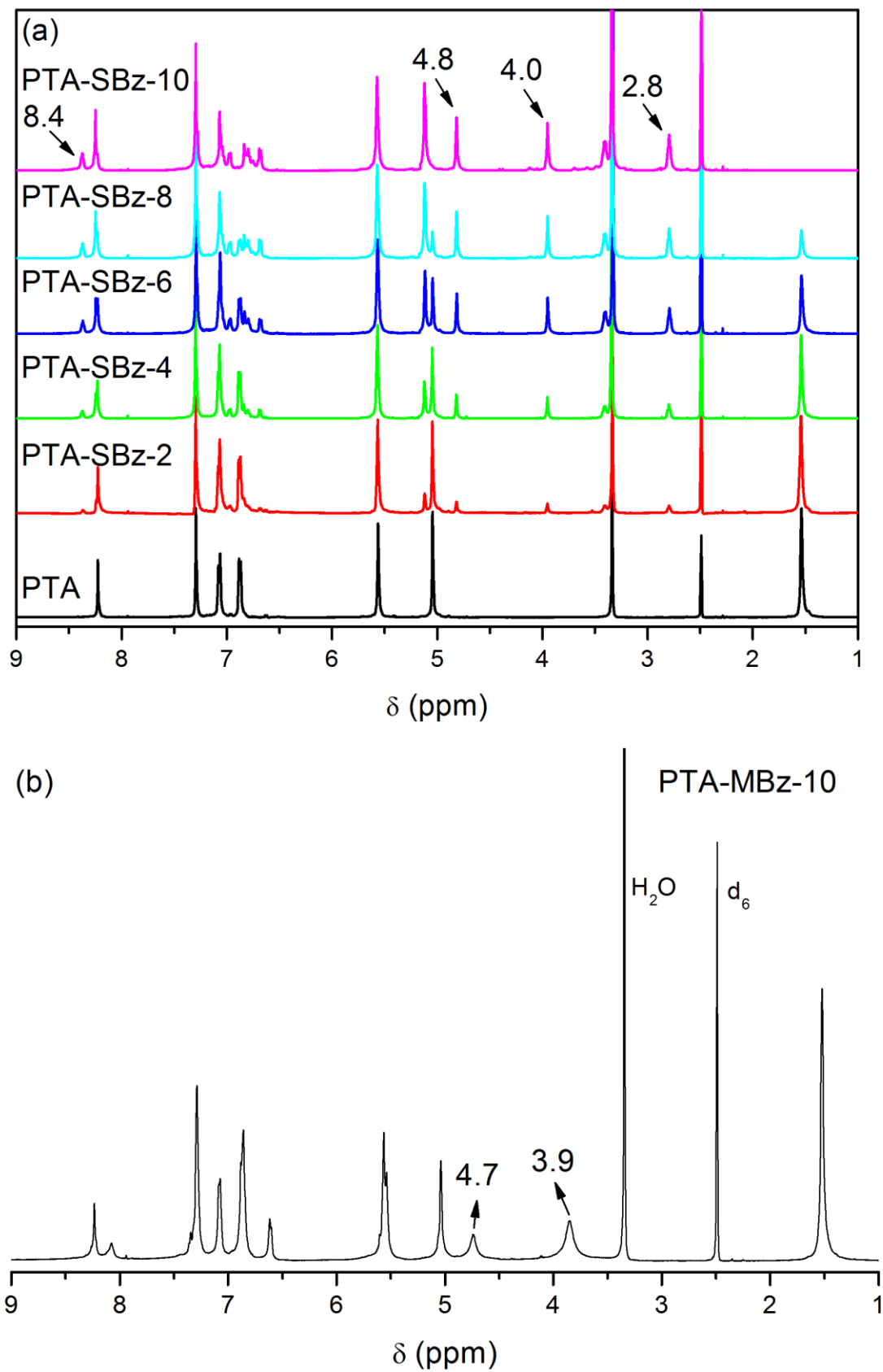


Figure S16. ^1H NMR spectra of (a) PTA, PTA-SBz and (b) PTA-MBz

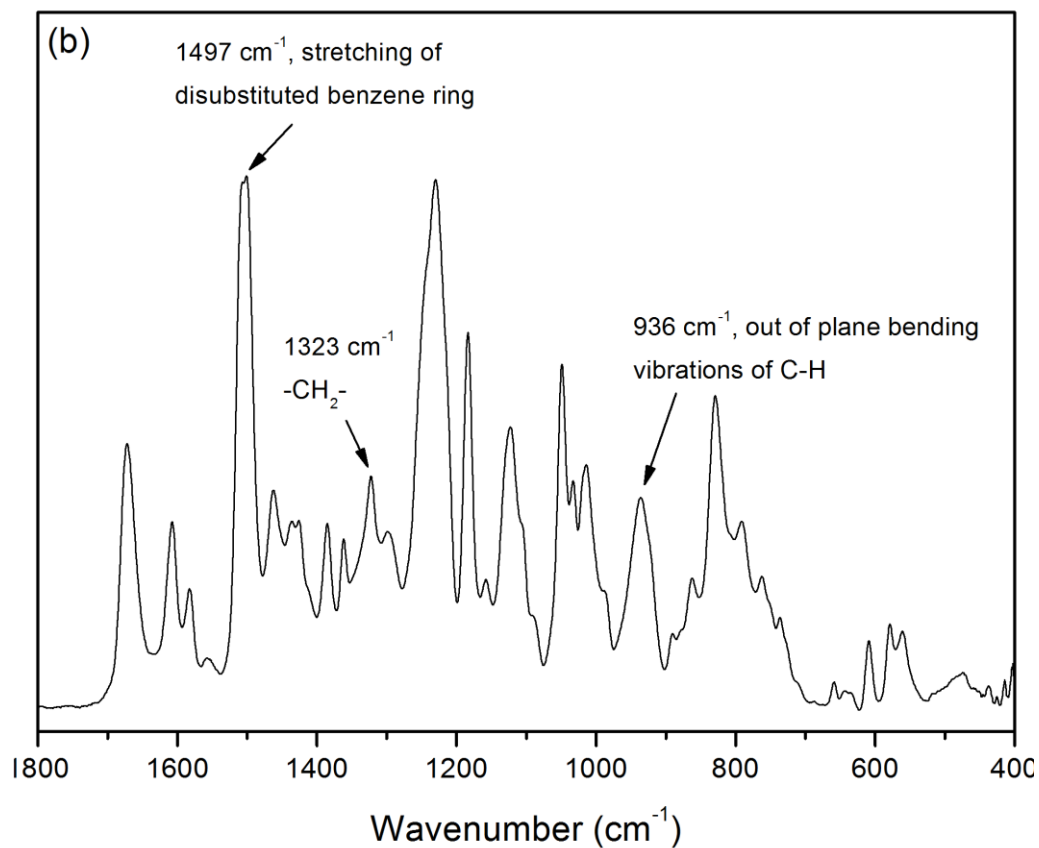
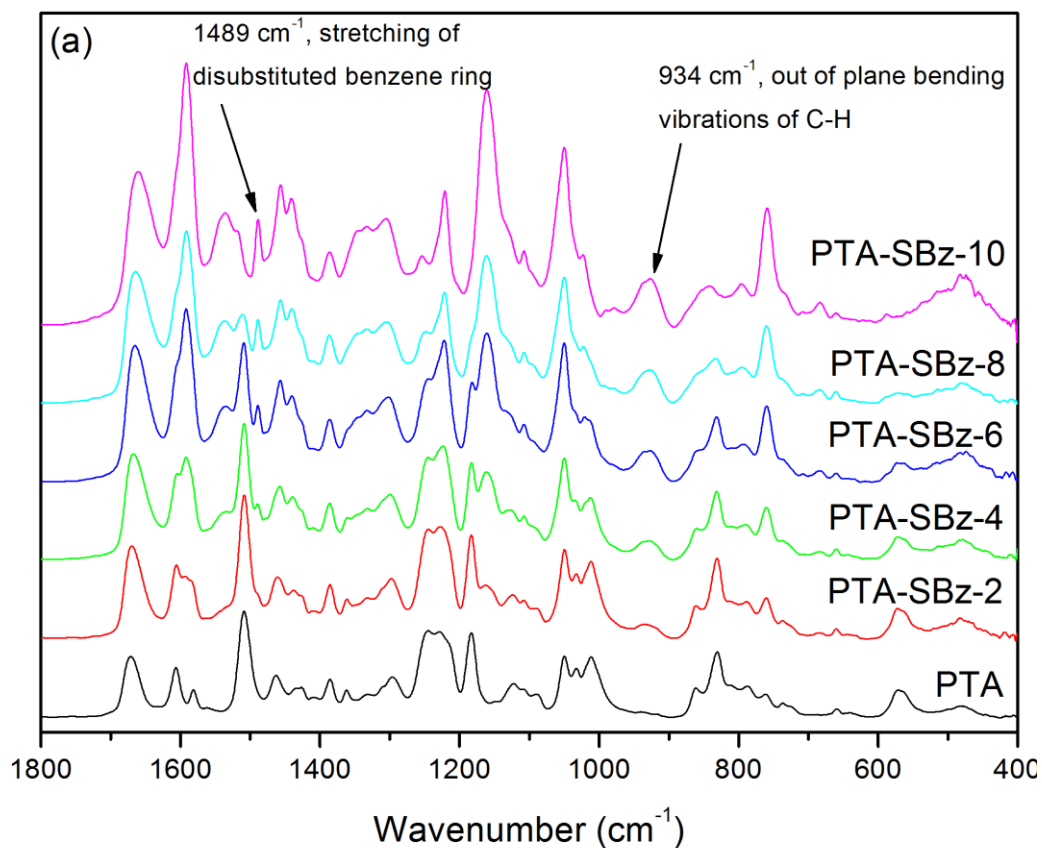


Figure S17. IR spectra of (a) PTA, PTA-SBz and (b) PTA-MBz