

Supporting Information

Seven-Membered Ring-Forming Cyclopolymerization of 1,8-Nonadiyne Derivatives Using Grubbs Catalysts: Rational Design of Monomers and Insights into the Mechanism for Olefin Metathesis Polymerizations

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General experimental

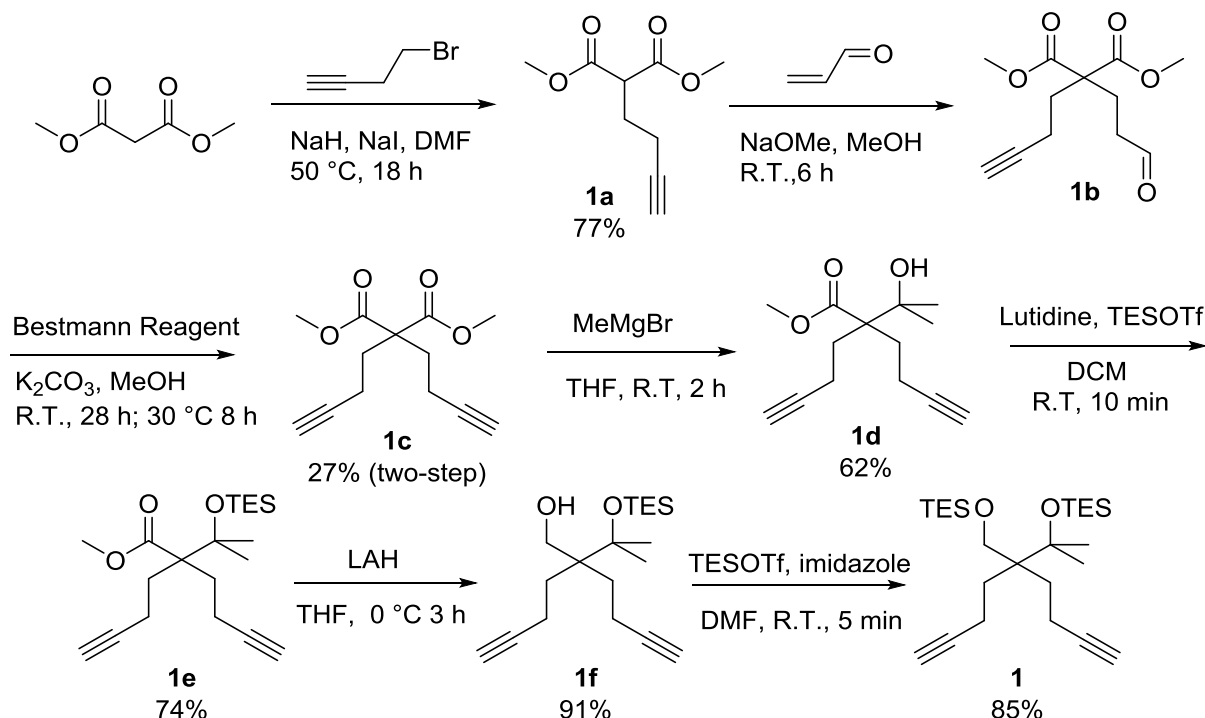
All reagents which are commercially available were used without further purification. Solvents for monomer synthesis were commercially obtained. Solvents for monomer synthesis were also commercially obtained. For polymerization, THF was distilled from sodium and benzophenone and degassed 10 minutes before using on polymerization. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm).

^1H -NMR and ^{13}C -NMR were recorded by Varian/Oxford As-500 (500 MHz for ^1H and 125 MHz for ^{13}C), Bruker DRX-300 (300 MHz for ^1H , 75 MHz for ^{13}C) and Agilent 400-MR (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometers. High temperature ^{13}C NMR were recorded by Bruker (400 MHz for ^1H and 100 MHz for ^{13}C or 600 MHz for ^1H and 150 MHz for ^{13}C) spectrometers in the National Instrumentation Center for Environmental Management (NICEM) at SNU. UV-vis spectra were measured by Jasco Inc. UV/vis-Spectrometer V-550 and V-650.

CHCl_3 Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with Waters system (515 HPLC pump and 2410 refractive index detector), and Shodex GPC LF-804 column eluted CHCl_3 (HPLC grade, J. T. Baker). Samples in 0.001-0.003 wt% chloroform or THF were filtered with a 0.45- μm PTFE filter before injection. Flow rate was 1.0 mL/min and temperature of column was maintained at 35 $^\circ\text{C}$. Infrared spectroscopy (IR) analyses were performed by JASCO FT/IR-600 plus spectrometer. High resolution mass spectroscopy (HRMS) analyses were performed by the ultra-high resolution ESI Q-TOF mass spectrometer (Bruker, Germany) in the Sogang Centre for Research Facilities.

Cyclic voltammetry (CV) measurements were carried out on a CHI 660 Electrochemical Analyzer (CH Instruments, Inc., Texas, USA). Cyclic voltammetry (CV) measurement was carried out at the room temperature on a CHI 660 Electrochemical Analyzer (CH Instruments, Inc., Texas, USA) using an degassed acetonitrile solution of tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6 , 0.1 M). Polymer solution was prepared by dissolving the polymer in dichloromethane (20 mg/ml). Cyclic voltammogram was recorded using the glassy carbon working electrode and a reference electrode of Ag/Ag^+ (0.1 M AgNO_3 in acetonitrile) with a platinum wire counter electrode at a scan rate of 50 mV/s. The absolute energy level was obtained using ferrocene/ferrocenium as an internal standard. The oxidation potential of ferrocene was regarded as - 4.8 eV.

Experimental procedure for monomer synthesis



Scheme S1. Synthesis of Carbon Monomer 1

1a: Di-methyl malonate (1 g, 7.57 mmol) is added to the Ar-purged flask in DMF (12 ml). Solution was cooled to $0\text{ }^\circ\text{C}$ and sodium hydride (60% in mineral oil, 3.56 mmol, 0.14 mg) was added. After stirring for 15 min at room temperature, 1-bromo-4-butyne (0.47 g, 3.56 mmol) and NaI (0.53 g, 3.56 mmol) were added to the reaction mixture. After stirring for 18 h at $50\text{ }^\circ\text{C}$, cool down the solution to rt. The mixture was quenched by aqueous NH_4Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with MgSO_4 and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel ($\text{EtOAc}:\text{Hexane}=1:10$) to afford the compound **1a** (0.50 mg, 2.74 mmol, 77 %). ^1H NMR (500 MHz, CDCl_3) δ 3.75 (s, 6H, OCH_3), 3.62 (t, $J = 7.4\text{ Hz}$, 1H, COCHCO), 2.41 – 2.26 (m, 2H, CH_2C), 2.19 – 2.09 (m, 2H, CHCH_2), 2.00 (t, $J = 1.5\text{ Hz}$, 1H, CCH); ^{13}C NMR (125 MHz, CDCl_3) δ 169.55, 82.44, 69.91, 52.78, 50.33, 27.70, 16.69; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_9\text{H}_{12}\text{O}_4$, 207. 0634, found, 207. 0628.

1b: Acrolein (0.15 g, 2.74 mmol) was added to the **1a** solution in MeOH then, NaOMe (29.6 mg, 0.55 mmol) was added to the mixture. After stirring for 6 h, evaporate the solution to remove MeOH . Product was extracted with diethyl ether and the organic layer was washed with Brine. The organic layer was dried with MgSO_4 and concentrated to give a yellow colored liquid. Without further purification, it was used for the next step.

1c: K_2CO_3 (0.76 g, 5.48 mmol) and Bestmann reagent (0.8 ml, 3.29 mmol) were added to the **1b** (0.66 g, 2.74 mmol) solution in MeOH (39 ml). After stirring for 12 h, the reaction was quenched by aqueous NaHCO_3 solution. Product was extracted with diethyl ether and organic layer was washed with brine. The organic layer was dried with MgSO_4 and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel ($\text{EtOAc}:\text{Hexane}=1:5$) to afford the compound **1c** (0.17 g,

0.74 mmol, two-step: 27%). ^1H NMR (500 MHz, CDCl_3) δ 3.71 (s, 6H, OCH_3), 2.21 – 2.05 (m, 8H, CHCH_2CH_2), 1.95 (t, $J = 2.2$ Hz, 2H, CCH); ^{13}C NMR (125 MHz, CDCl_3) δ 171.02, 82.93, 69.08, 56.58, 52.69, 31.74, 14.11; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$, 259.0947, found, 259.0942.

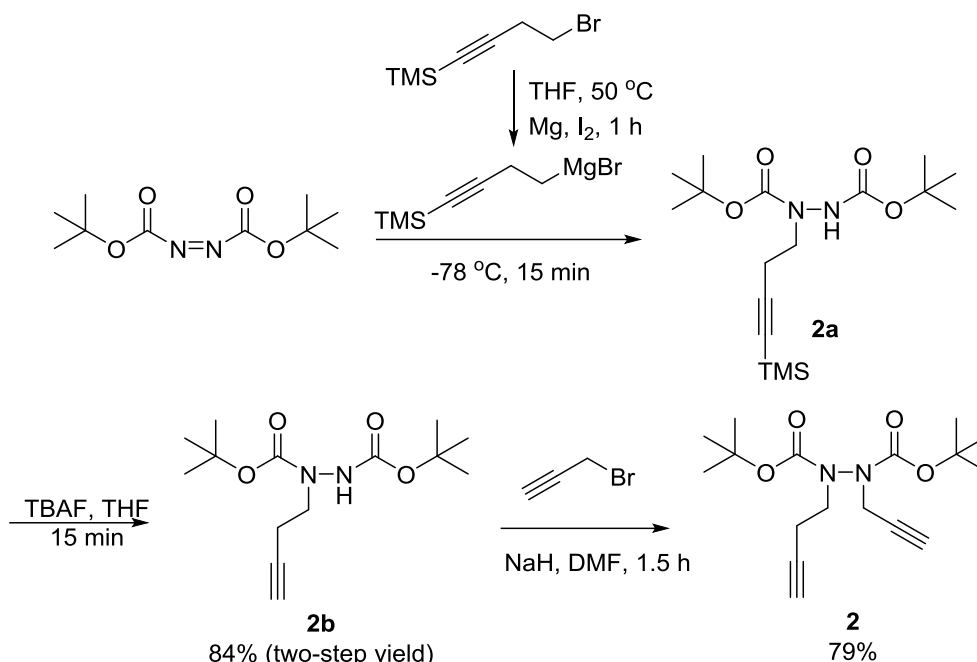
1d-1f and **1** were synthesised by slightly modifying our previously reported monomer synthetic method¹. Strong base, 2,6- lutidine (instead of imidazole) and better leaving group, triflate (OTf) (instead of chloride (Cl)) were used, otherwise other conditions were same.

1d: ^1H NMR (500 MHz, CDCl_3) δ 3.70 (s, 3H, OCH_3), 2.99 (s, 1H, OH), 2.35 – 2.22 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}$), 2.15 – 2.01 (m, 2H, CCH_2CH_2), 2.01 – 1.78 (m, 4H, $\text{CCH}_2\text{CH}_2+\text{CCH}$), 1.21 (s, 6H, $\text{C}(\text{CH}_3)_2$); ^{13}C NMR (125 MHz, CDCl_3) δ 175.83, 84.21, 74.56, 68.78, 55.86, 52.04, 52.00, 31.62, 26.79, 15.40; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$, 259.1310, found, 259.1307.

1e: ^1H NMR (500 MHz, CDCl_3) δ 3.68 – 3.63 (s, 3H, OCH_3), 2.38 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 2.23 – 2.13 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 2.09 – 1.93 (m, 6H, $\text{CH}_2\text{CH}_2\text{C}+\text{CCH}$), 1.30 (s, 6H, $\text{C}(\text{CH}_3)_2$), 0.99 – 0.91 (t, $J = 10$ Hz, 9H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.65 – 0.56 (dd, $J = 15, 5$ Hz, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 174.73, 84.87, 77.84, 68.34, 57.23, 51.69, 30.80, 27.73, 15.07, 7.20, 6.87; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{Si}$, 373.2175, found, 373.2166.

1f: ^1H NMR (500 MHz, CDCl_3) δ 3.59 (d, $J = 5.0$ Hz, 2H, CH_2OH), 3.53 (t, $J = 5.2$ Hz, 1H, OH), 2.39 – 2.28 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 2.27 – 2.17 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 1.98 – 1.94 (t, $J = 2.2$ Hz, 2H, CCH), 1.79 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 1.61 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 1.30 (s, 6H, $\text{C}(\text{CH}_3)_2$), 0.97 (t, $J = 10$ Hz, 9H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.65 (dd, $J = 15, 5$ Hz, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 85.00, 81.77, 68.47, 65.57, 45.91, 31.07, 26.66, 14.56, 7.11, 6.85; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_2\text{Si}$, 345.2226, found, 345.2222.

1: ^1H NMR (500 MHz, CDCl_3) δ 3.53 (s, 2H, OCH_2), 2.39 – 2.22 (m, 4H, $\text{CH}_2\text{CH}_2\text{C}$), 1.92 ((t, $J = 2.2$ Hz, 2H, CCH), 1.81 – 1.70 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 1.65 (m, 2H, $\text{CH}_2\text{CH}_2\text{C}$), 1.24 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.00 – 0.92 (t, $J = 10$ Hz, 9H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.64 – 0.54 (dd, $J = 15, 5$ Hz, 6H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 86.01, 78.86, 67.71, 65.72, 46.97, 31.47, 27.41, 14.62, 7.31, 7.01, 4.40; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{25}\text{H}_{48}\text{O}_2\text{Si}_2$, 459.3093, found, 459.3085.

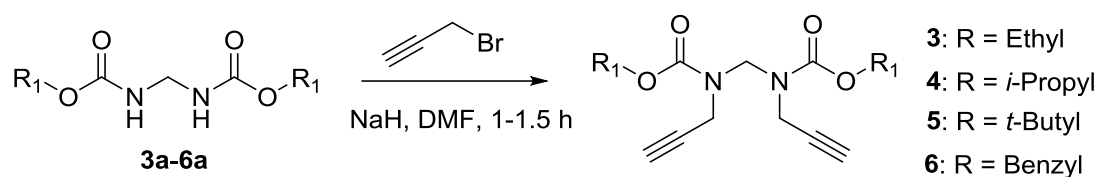


Scheme S2. Synthesis of Hydrazine Monomer 2

2a: In-situ generated TMS-protected butynyl magnesium bromide from (4-bromo-1-butyne-1-yl)trimethylsilane (1.07 g, 5.21 mmol) was added to the di-tert-butyl azodicarboxylate (1g, 4.34 mmol) solution in THF at -78 °C by cannula transfer. After stirring for 15 min, the reaction mixture was allowed to warm to rt. After the reaction mixture was quenched by water, the product was extracted with DCM and the organic layer was washed with brine. The organic layer was dried with MgSO₄ and concentrated. Without further purification, it was used for the next step.

2b: Tetrabutylammonium fluoride in 1.0 M THF solution (6.51 ml 6.51 mmol) was added to the **2a** (1.55g, 4.34 mmol) solution in THF (14 ml). After stirring for 15 min, reaction was quenched with water. The product was extracted with ethyl acetate and was washed with brine. The organic layer was dried with MgSO₄ and concentrated. The product was purified by column chromatography (EtOAc:Hexane=1:3) to afford the product **2b** (1.04g, 3.65 mmol, 84% yield). ¹H NMR (500 MHz, CDCl₃) δ 6.41 (s, 0.5H, NH), 6.13 (s, 0.5H, NH), 3.65 (s, 2H, NCH₂), 2.50 (br m, 2H, CH₂C), 1.95 (s, 1H, CCH), 1.49 (s, 18H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 155.08, 81.43, 69.73, 49.60, 48.67, 28.33, 28.06, 17.84; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₄H₂₄N₂O₄, 307.1634, found, 307.1630.

2: 2b (1.04g, 3.65 mmol) was dissolved in DMF (18 ml). NaH (60% in mineral oil, 0.15 g, 3.65 mmol) was added to the solution. After stirring for 15 min at 0 °C, propargyl bromide (80wt% in toluene, 0.6 ml, 4.02 mmol) was added to the solution. The reaction was warm to rt and stirred for 1.5 h. The reaction was quenched with water and the product was extracted with diethyl ether. The organic layer was washed with brine, dried with MgSO₄ and concentrated. The product was purified with by column chromatography (EtOAc:Hexane=1:5) to afford the product **2** (0.93g, 2.88 mmol, 79%). ¹H NMR (500 MHz, CDCl₃) δ 4.64 – 4.27 (m, 1.5H, NCH₂C), 4.00 – 3.85 (m, 0.5H, NCH₂C), 3.75 – 3.47 (m, 2H, NCH₂CH₂), 2.62 – 2.46 (m, 2H, NCH₂CH₂), 2.25 (t, *J* = 2.5 Hz, 1H, CCH), 1.94 (t, *J* = 2.6 Hz, 1H, CCH), 1.51 – 1.37 (m, 18H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 154.14, 82.00, 81.68, 81.52, 78.45, 77.42, 77.16, 76.91, 73.04, 69.60, 50.71, 49.32, 39.50, 39.35, 28.27, 28.24, 28.14, 18.42, 18.01; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₇H₂₆N₂O₄, 345.1791, found, 345.1789.



Scheme S3. Synthesis of Aminoal Monomers 3-6.

3a-6a were prepared according to the literature and their spectroscopic data were reported in the same literature except **5a**.²

5a: ¹H NMR (500 MHz, CDCl₃) δ 5.69 (br s, 2H, NHCH₂NH), 4.37 (br s, 2H, NHCH₂NH), 1.39 (m, 18H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 156.17, 79.85, 47.51, 28.42; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₁H₂₂N₂O₄, 269.1478, found, 269.1473.

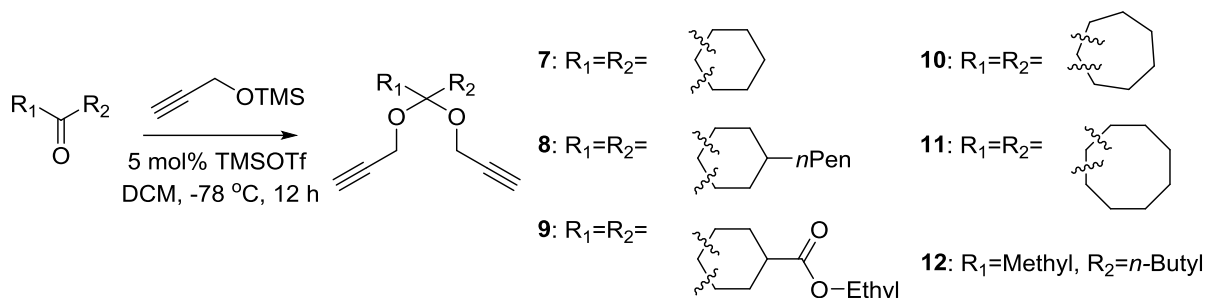
3-6: Aminoal compound (**3a-6a**, 3.00 mmol) was dissolved in the DMF (7.5 ml). Propargyl bromide (80wt% in toluene, 1.12 ml, 7.5 mmol) was first added to the aminoal solution then, NaH (60% in mineral oil, 0.26 g, 6.6 mmol) was added. After stirring for 1.5 h, the reaction was quenched with water and the product was extracted with diethyl ether. The organic layer was washed with brine and dried with MgSO₄. The organic layer was concentrated and the product was purified by column chromatography (EtOAc:Hexane=1:10 → EtOAc:Hexane=1:3) to afford the product. In the ¹H and ¹³C NMR spectra, we observed broad and multiple signals due to rotational isomers.

3: 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 4.97 (br s, 2H, NCH₂N), 4.10 (dd, *J* = 14.2, 7.0 Hz, 4H, OCH₂CH₃), 4.00 (br s, 4H, NCH₂C), 2.13 (br s, 2H, CCH), 1.19 (br s, *J* = 4.8 Hz, 6H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 156.09, 155.76, 155.17, 79.38, 79.04, 71.28, 71.04, 62.05, 58.23, 57.45, 56.71, 35.67, 35.01, 14.40; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₃H₁₈N₂O₄, 289.1165, found, 289.1157.

4: 68% yield. ¹H NMR 500 MHz, CDCl₃) δ 5.04 (br s, 2H, CH(CH₃)₂), 4.96 (br s, 2H, NCH₂N), 4.04 (br s, 4H, NCH₂C), 2.17 (br s, 2H, CCH), 1.26 (br s, 12H, CH(CH₃)₂); ¹³C NMR (125 MHz, CDCl₃) δ 156.01, 155.64, 154.96, 79.73, 79.44, 70.99, 69.95, 58.29, 57.27, 56.38, 35.85, 34.87, 22.14; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₅H₂₂N₂O₄, 317.1478, found, 317.1473.

5: 65% yield. ¹H NMR (500 MHz, CDCl₃) δ 4.93 (br s, 2H, NCH₂N), 4.00 (br s, 4H, NCH₂C), 2.12 (br s, 2H, CCH), 1.53 – 1.35 (br s, 18H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 155.37, 154.93, 154.30, 81.48, 81.00, 79.70, 70.76, 57.18, 36.18, 35.23, 34.17, 28.31; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₇H₂₆N₂O₄, 345.1791, found, 345.1784.

6: 75% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.24 (br m, 10H, Ph), 5.20 – 5.10 (m, 4H, PhCH₂O), 5.09 (br s, 2H, NCH₂N), 4.14 (br s, 2H, NCH₂C), 4.01 (d, *J* = 30.1 Hz, 2H, NCH₂C), 2.15 (s, 2H, CCH); ¹³C NMR (125 MHz, CDCl₃) δ 155.97, 155.61, 154.98, 136.09, 135.70, 128.39, 128.02, 127.70, 79.23, 71.66, 71.36, 67.98, 67.62, 58.74, 57.79, 57.01, 35.94, 35.20; HR-MS (ESI) [M+Na]⁺ calcd. for C₂₃H₂₂N₂O₄, 413.1478, found, 413.1470.



Scheme S4. Synthesis of Aminoal Monomers 7-12.

7-12 were synthesized by the same method in the literature.³ We used 2.5 equiv (propargyloxy)trimethylsilane and the product was purified by column chromatography (EtOAc:Hexane=1:50).

7: 88% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.13 (d, J = 2.5 Hz, 4H, OCH_2), 2.38 (t, J = 2.5 Hz, 2H, CCH), 1.70 – 1.65 (m, 4H, CH_2CCH_2), 1.53 (dt, J = 11.9, 6.1 Hz, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.38 (dt, J = 11.5, 5.9 Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (125 MHz, CDCl_3) δ 102.13, 80.72, 73.43, 48.66, 33.50, 25.40, 22.89; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$, 215.1048, found, 215.1043.

8: 89% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.15 (dd, J = 32.6, 2.4 Hz, 4H, OCH_2), 2.39 (dd, J = 5.4, 2.5 Hz, 2H, CCH), 1.97 (d, J = 12.5 Hz, 2H, CyHex), 1.63 (dd, J = 9.1, 3.9 Hz, 2H, CyHex), 1.45 (td, J = 13.3, 3.7 Hz, 2H, $\text{CCH}_2(\text{CH}_2)_3\text{CH}_3$), 1.34 – 1.10 (m, 11H, $\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$ +CyHex), 0.87 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 102.43, 80.89, 80.65, 73.46, 48.86, 48.78, 36.69, 36.25, 33.00, 32.26, 29.20, 26.97, 22.79, 14.22; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{26}\text{O}_2$, 285.1831, found, 285.1826.

9: 85% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.08 (t, J = 6.2 Hz, 2H, OCH_2CH_3), 4.07 – 4.00 (m, 4H, OCH_2C), 2.33 (t, J = 2.1 Hz, 2H, CCH), 2.24 (tt, J = 10.5, 3.9 Hz, 1H, CH_2CHCH_2), 1.91 (d, J = 13.4 Hz, 2H, CyHex), 1.83 – 1.75 (m, 2H, CyHex), 1.67 (td, J = 13.9, 3.4 Hz, 2H, CyHex), 1.51 – 1.41 (m, 2H, CyHex), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.04, 101.38, 80.56, 80.31, 73.69, 73.65, 60.41, 48.91, 48.82, 41.69, 32.12, 25.17, 14.31; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_4$, 287.1260, found, 287.1254.

10: 72% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.11 (d, J = 2.5 Hz, 4H, OCH_2C), 2.37 (t, J = 2.5 Hz, 2H, CCH), 1.89 – 1.80 (m, 4H, CyHep), 1.58 – 1.47 (m, 8H, CyHep); ^{13}C NMR (125 MHz, CDCl_3) δ 106.57, 80.75, 73.36, 49.05, 36.70, 29.25, 21.83; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$, 229.1205, found, 229.1198.

11: 65% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.12 – 4.08 (m, 4H, OCH_2C), 2.39 – 2.35 (m, 2H, CCH), 1.81 (s, 4H, CyOct), 1.54 (s, 10H, CyOct); ^{13}C NMR (125 MHz, CDCl_3) δ 105.97, 80.74, 73.38, 48.94, 31.11, 28.13, 24.66, 21.60; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$, 243.1361, found, 243.1354.

12: 65% yield. ^1H NMR (500 MHz, CDCl_3) δ 4.16 – 4.07 (m, 4H, OCH_2), 2.37 (t, J = 2.5 Hz, 2H, CCH), 1.65 – 1.59 (m, 2H, CCH_2CH_2), 1.37 – 1.24 (m, 7H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89 (m, 3H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 103.69, 80.60, 73.44, 49.23, 49.21, 36.92, 26.39, 22.93, 21.87, 14.06; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_2$, 217.1205, found, 217.1198.

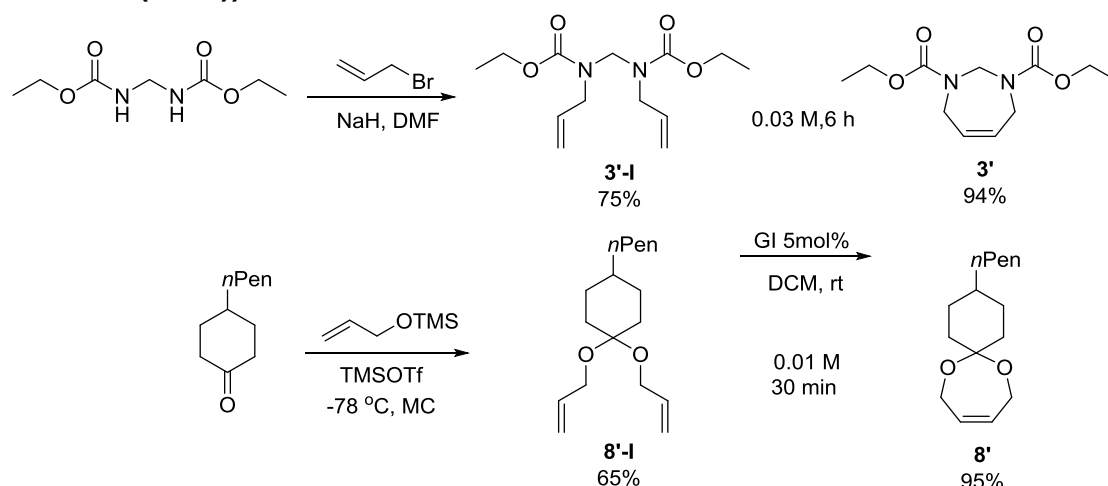
13 were prepared by the same method for the synthesis of aminoal monomer **3** except the equivalent of propargyl bromide (0.9 eq. to **3a**) and NaH (1.0 eq. to **3a**). 42% yield. ^1H NMR (400 MHz, CDCl_3) δ 5.76

(s, 0.5H, NH), 5.48 (s, 0.5H, NH), 4.77 (s, 2H, NCH₂C), 4.20 (m, 6H, NCH₂N+OCH₂), 2.24 (s, 1H, CCH), 1.29 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 157.05, 156.65, 156.03, 155.43, 79.53, 71.37, 62.14, 61.24, 53.90, 53.18, 36.77, 29.73, 29.40, 14.61; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₀H₁₆N₂O₄, 251.1008, found, 251.1003.

14-16 were prepared according to the literature and their spectroscopic data were reported in the same literature except **14**.^{4,5}

14: ¹H NMR (500 MHz, CDCl₃) δ 4.08 (s, 4H, OCH₂), 2.38 (d, *J* = 2.7 Hz, 4H, CH₂CCH), 2.26 (tt, *J* = 8.8, 5.4 Hz, 2H, CH₂CHCH₂), 2.01 (t, *J* = 2.6 Hz, 2H, CCH), 1.64 – 1.53 (m, 4H, , CHCH₂CH₃), 1.53 – 1.38 (m, 4H, CHCH₂CH₂), 1.30 – 1.14 (m, 8H, C₂H₄CH₃), 0.85 (td, *J* = 7.4, 4.2 Hz, 12H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 175.83, 78.77, 71.75, 64.64, 47.47, 40.10, 31.82, 29.64, 25.56, 22.70, 22.17, 13.98, 11.89; HR-MS (ESI) [M+Na]⁺ calcd. for C₂₅H₄₀O₄, 427.2825, found, 427.2813.

Experimental procedure for synthesis of model compounds (Ring-Closing Metathesis (RCM))



Scheme S5. Synthesis of Model Compounds 3' and 8'

Procedure for **3'-I** and **8'-I** synthesis is identical as mentioned above but propargyl was changed to allyl reagent.

3'-I: ¹H NMR (400 MHz, CDCl₃) δ 5.72 (s, 2H, CH₂CHCH₂), 5.10 (br m, 4H, CH₂CHCH₂), 4.83 (s, 2H, NCH₂N), 4.09 (br m, 4H, OCH₂), 3.82 (br m, 4H, NCH₂CH), 1.27 – 1.12 (m, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 156.54, 155.61, 128.77, 128.71, 128.08, 61.85, 60.05, 59.82, 44.30, 43.94, 43.88, 14.75, 14.71.; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₃H₂₂N₂O₄, 293.1478, found, 293.1472.

8'-I: ¹H NMR (500 MHz, CDCl₃) δ 5.90 (dtt, *J* = 22.0, 10.9, 5.5 Hz, 2H, CH₂CHCH₂), 5.26 (ddd, *J* = 17.1, 14.0, 1.7 Hz, 2H, CH₂CHCH₂), 5.15 – 5.05 (m, 2H, CH₂CHCH₂), 3.93 (dd, *J* = 41.2, 5.5 Hz, 4H, OCH₂), 1.99 (d, *J* = 12.4 Hz, 2H, CyHex), 1.65 – 1.56 (m, 2H, CyHex), 1.39 (td, *J* = 13.3, 3.8 Hz, 2H, CyHex), 1.33 – 1.07 (m, 11H, C₄H₈CH₃+CyHex), 0.86 (t, *J* = 7.1 Hz, 3H, CH₃); ¹³C NMR (125 MHz, CDCl₃) δ 135.57, 135.38, 115.90, 115.77, 100.80, 61.28, 61.06, 36.87, 36.39, 33.26, 32.26, 29.35, 26.97, 22.75, 14.15; HR-MS (ESI) [M+Na]⁺ calcd. for C₁₇H₃₀O₂, 289.2144, found, 289.2144.

Substrates **3'-I** and **8'-I** (0.5 mmol) were dissolved in DCM (degassed for 15 min with Ar), respectively. Grubbs catalyst 1st generation (GI, 0.025 mmol) was added to the solution. The reaction mixture was stirred and monitored by TLC. After complete consumption of the substrate, the reaction was quenched

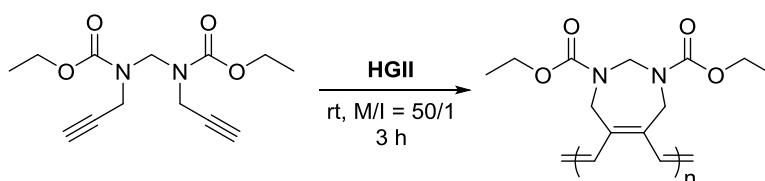
by EVE. After solvent evaporation, the product was purified by column (EtOAc:Hexane=1:5 for **3'** and EtOAc:Hexane=1:50 for **8'**) to afford the each product.

3': ^1H NMR (400 MHz, CDCl_3) δ 5.75 – 5.63 (m, 2H, CHCH), 5.07 (t, J = 18.5 Hz, 2H, NCH_2N), 4.14 (dq, J = 14.2, 7.0 Hz, 4H, OCH_2), 3.93 (dd, J = 34.3, 10.5 Hz, 4H, NCH_2CH), 1.24 (dd, J = 15.1, 7.5 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 156.54, 156.26, 155.61, 155.45, 128.77, 128.71, 128.08, 61.85, 60.05, 59.82, 44.30, 43.94, 43.88, 14.75, 14.71; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_4$, 265.1165, found, 265.1161.

8': ^1H NMR (500 MHz, CDCl_3) δ 5.67 – 5.61 (m, 2H, CHCH), 4.28 – 4.17 (m, 4H, OCH_2), 2.08 (dd, J = 14.4, 2.5 Hz, 2H, CyHex), 1.66 – 1.58 (m, 2H, CyHex), 1.37 (td, J = 13.3, 4.0 Hz, 2H, CyHex), 1.31 – 1.07 (m, 11H, $\text{C}_4\text{H}_8\text{CH}_3$ +CyHex), 0.86 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 129.81, 129.78, 102.30, 60.94, 60.70, 36.98, 36.38, 32.28, 32.20, 29.55, 27.00, 22.78, 14.19; HR-MS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_2$, 261.1831, found, 261.1826.

General procedure for polymerization

A 4-mL sized screw-cap vial with septum was flame dried and charged with monomer and a magnetic bar. The vial was purged with argon three times, and degassed anhydrous THF was added. After the Ar-purged **HGII** in another 4-mL vial was dissolved in THF, the solution was rapidly injected to the monomer solution at rt under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and concentrated by evaporation. The polymer was purified by precipitation in hexane (aminal polymers) or methanol (acetal polymers) at rt. Obtained polymer was filtered and dried in vacuo. Remaining small amount of crude mixture (<10%) was used for calculating the monomer conversion by ^1H NMR.



Conc. (M)	Conv. (%)
0.03	67
0.06	60
0.12	59
0.6	26

Table S1. Screening Concentrations

¹H and ¹³C NMR characterization of polymers

Poly(**3**): ¹H NMR (300 MHz, CDCl₃) δ 7.78 – 6.00 (m, 2H), 5.09 (s, 2H), 4.41 (s, 4H), 4.08 (s, 4H), 1.22 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 156.12, 155.00, 141.54, 136.22, 125.46, 61.79, 60.61, 45.41, 14.68.

Poly(**4**): ¹H NMR (500 MHz, CDCl₃) δ 7.78 – 6.64 (m, 2H), 5.10 (s, 2H), 4.87 (s, 2H), 4.34 (d, *J* = 80.8 Hz, 4H), 1.17 (d, *J* = 50.6 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 155.40, 154.61, 136.41, 125.64, 69.28, 60.24, 44.85, 22.27.

Poly(**5**): ¹H NMR (500 MHz, CDCl₃) δ 7.68 – 6.17 (m, 2H), 4.99 (s, 2H), 4.29 (s, 4H), 1.63 – 1.10 (m, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 155.68, 154.16, 135.49, 127.02, 124.86, 80.38, 60.19, 58.88, 44.99, 28.47.

Poly(**6**): ¹H NMR (500 MHz, CDCl₃) δ 7.77 – 6.41 (m, 12H), 5.01 (s, 6H), 4.70 – 3.78 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 156.16, 154.65, 141.64, 136.57, 128.60, 127.93, 125.90, 123.25, 60.30, 45.49.

Poly(**8**): ¹H NMR (500 MHz, CDCl₃) δ 6.61 (br m, 2H), 4.78 – 4.17 (m, 4H), 2.08 (br s, 2H), 1.58 (br s, 2H), 1.48 – 1.03 (br m, 14H), 0.87 (br m, 3H); ¹³C NMR (125 MHz, , CDCl₃) δ 136.26, 124.98, 102.22, 61.41, 36.99, 36.38, 32.31, 32.02, 29.53, 27.04, 22.83, 14.25.

Poly(**9**): ¹H NMR (500 MHz, CDCl₃) δ 6.73 – 5.91 (br m, 2H), 4.73 – 4.34 (m, 4H), 4.14 (br s, 2H), 2.35 (s, 1H), 2.11 (s, 2H), 1.98 – 1.64 (m, 4H), 1.53 (s, 2H), 1.24 (br s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 175.20, 136.12, 125.25, 101.20, 61.45, 60.40, 42.06, 31.14, 25.53, 14.38.

Poly(**10**): ¹H NMR (500 MHz, CDCl₃) δ 6.76 – 5.94 (br m, 2H), 4.68 – 3.98 (br m, 4H), 1.93 (br s, 4H), 1.57 (br s, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 136.19, 125.06, 106.19, 61.77, 35.52, 29.15, 22.38.

Poly(**11**): ¹H NMR (500 MHz, CDCl₃) δ 6.68 – 5.91 (br m, 2H), 4.65 – 4.01 (br m, 4H), 1.92 (br s, 4H), 1.57 (br s, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 136.16, 125.09, 105.55, 61.47, 30.66, 28.23, 25.09, 22.01.

Poly(**12**): ¹H NMR (500 MHz, CDCl₃) δ 6.74 – 5.71 (br m, 2H), 4.64 – 3.91 (br m, 4H), 1.81 – 1.53 (br s, 2H), 1.37 (br m, 7H), 0.91 (br m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.16, 124.95, 103.57, 61.73, 36.07, 26.72, 23.11, 21.12, 14.18.

Procedures for mechanistic experiments

① 1:1 reaction of **13** and **GIII**

GIII (8.7 mg, 0.011 mmol) and hexamethyldisilane (internal standard, 10 μ l) were dissolved in THF- d_8 (0.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^1H NMR spectrum. **13** (3 mg, 0.011 mmol) THF- d_8 (60 μ l) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The reaction was monitored by ^1H NMR. After 300 min of the mixing, ethyl vinyl ether (EVE, 0.1 ml) was added to the reaction mixture to quench the reaction and mixed by shaking NMR tube for 10 sec. Fischer carbene was measured by the same method as mentioned above.

② Reaction kinetics

Monomer (0.05 mmol) and hexamethyldisilane (50 μ l) were dissolved in THF- d_8 (4.5 ml). Initial monomer was measured by integral ratio of monomer to hexamethyldisilane in ^1H NMR spectrum. **HGII** (3.1 mg, 0.005 mmol) THF- d_8 (50 μ l) solution was added to the monomer solution and mixed by shaking NMR tube for 10 sec. The reaction was monitored by ^1H NMR for 5 min.

③ Carbene decay

GIII (8.0 mg, 0.01 mmol) and hexamethyldisilane (50 μ l) were dissolved in THF- d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^1H NMR spectrum. Monomer (0.1 mmol) THF- d_8 (50 μ l) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was monitored by ^1H NMR for 15 min.

④ PyCl addition

Catalyst (0.01 mmol) and hexamethyldisilane (50 μ l) were dissolved in THF- d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^1H NMR spectrum. Monomer (0.1 mmol) THF- d_8 (50 μ l) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. 3-Chloropyridine (9.5 μ l, 0.1 mmol) was added to the reaction mixture and mixed by shaking NMR tube for 10 sec. The propagating carbene was monitored by ^1H NMR.

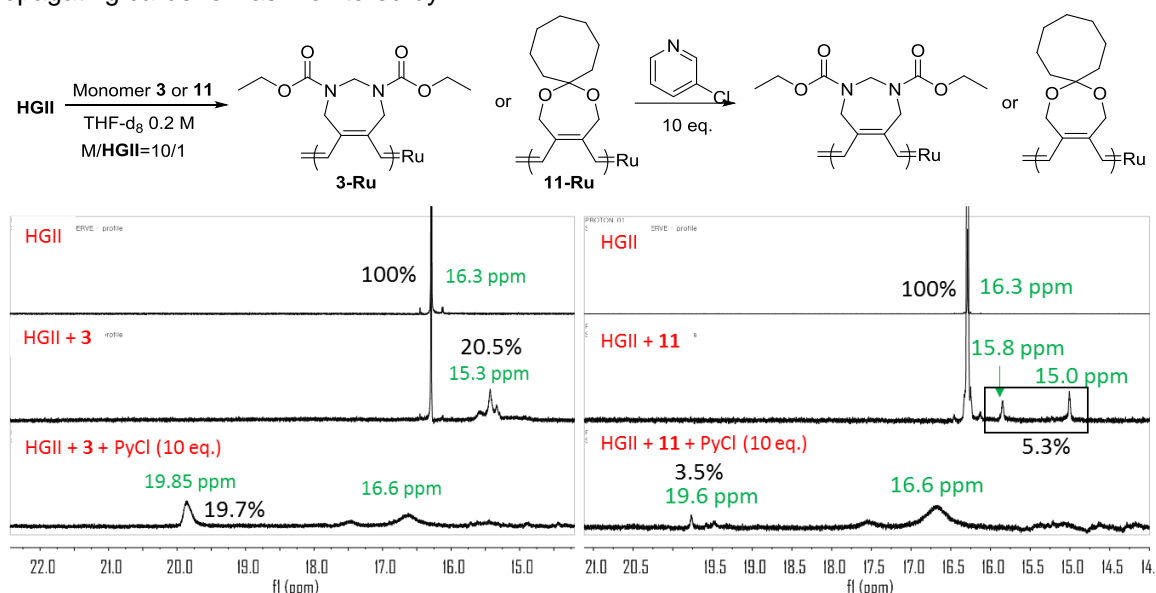


Figure S1. NMR Spectra of Propagating Carbene upon Addition of PyCl

In the experiment with **HGII**, broad signal at 16.6 ppm was observed when PyCl was added (Figure S1). To confirm if this signal comes from the **HGII**, we observed the mixture of **HGII** and PyCl by ^1H NMR. Complete shift (from 16.3 ppm to 16.6 ppm) was observed.

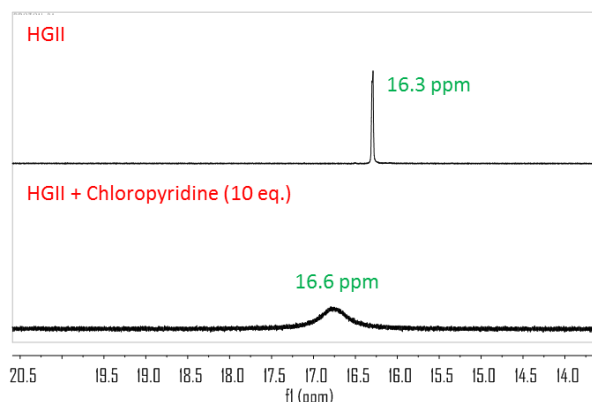


Figure S2. NMR Spectra of HGII and the mixture of HGII and PyCl

⑤ Dynamic equilibrium

GIII (8.0 mg, 0.01 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of **GIII** to hexamethyldisilane in ^1H NMR spectrum. A minimal **7** (19.23 mg, 0.1 mmol) THF-d_8 (50 μl) solution was added to the **GIII** solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. ^1H NMR was taken whenever 1 equiv. PyCl was added to the solution.

⑥ Hydride observation

HGII (6.13 mg, 0.005 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^1H NMR spectrum. Monomer (0.1 mmol) THF-d_8 (50 μl) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene was measured by the same method. The propagating carbene and hydride were monitored for 15 min by ^1H NMR.

⑦ Addition of 2,6-dichloro-1,4-benzoquinone

HGII (6.13 mg, 0.005 mmol), 2,6-dichloro-1,4-benzoquinone (3.54 mg, 0.02 mmol) and hexamethyldisilane (50 μl) were dissolved in THF-d_8 (4.5 ml). Initial benzylidene was measured by integral ratio of catalyst to hexamethyldisilane in ^1H NMR spectrum. Acetal **11** (22.03 mg, 0.1 mmol) THF-d_8 (50 μl) solution was added to the catalyst solution and mixed by shaking NMR tube for 10 sec. The propagating carbene and hydride were monitored for 15 min by ^1H NMR.

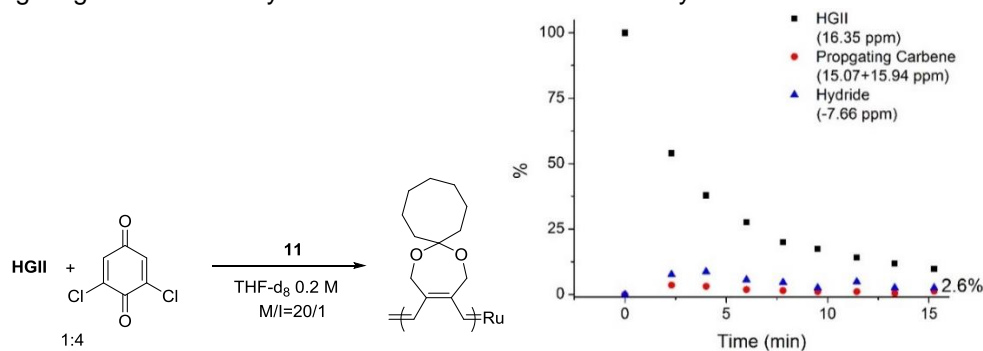


Figure S3. Plot of Hydride and Propagating Carbene over Time

Figure S4. IR spectrum

Polymerization was carried out by the same procedure for general polymerization. After 10 min, 20 μ l of the reaction mixture was taken by a micro-syringe and loaded on the plate then IR spectrum was obtained.

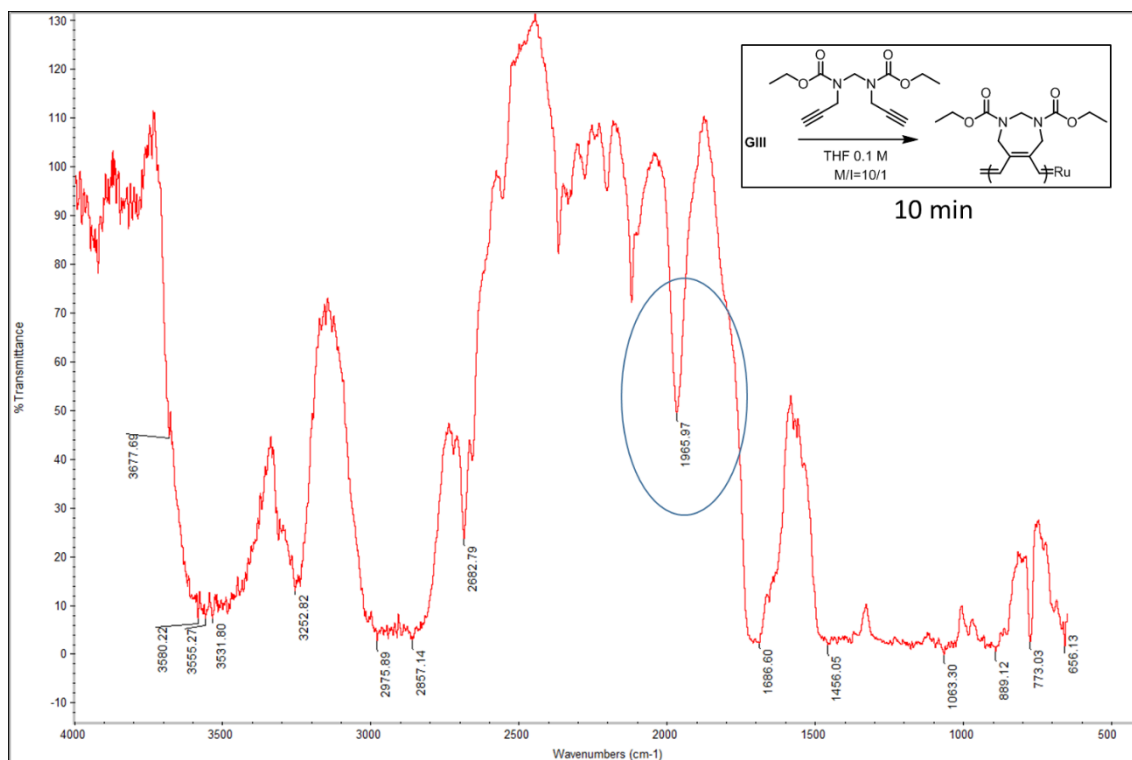


Figure S5. SEC traces of homopolymers obtained from controlled polymerization (in Table 2)

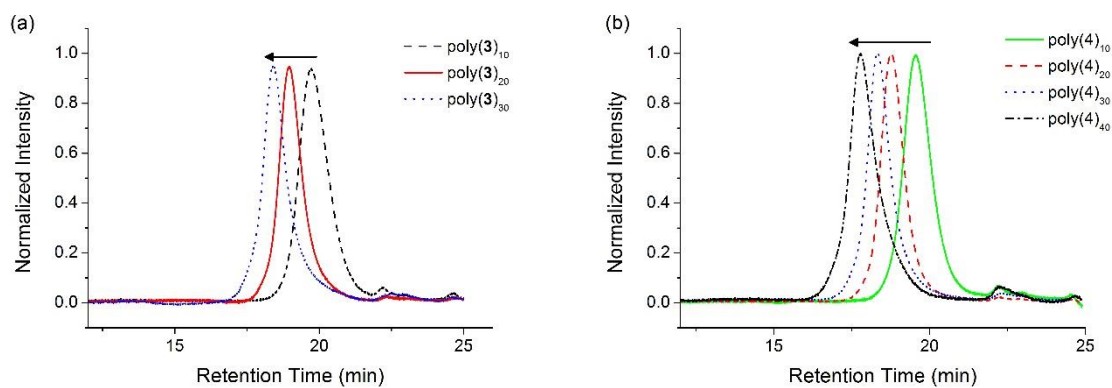
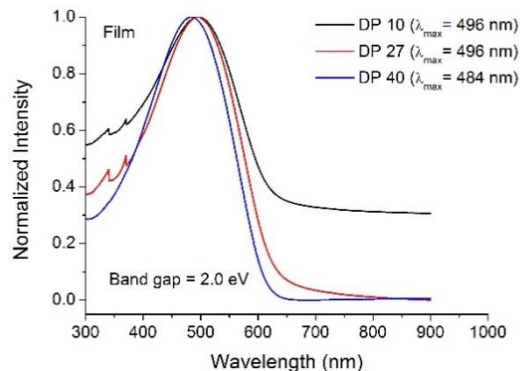
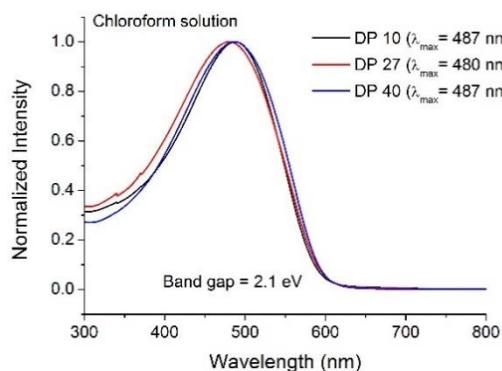
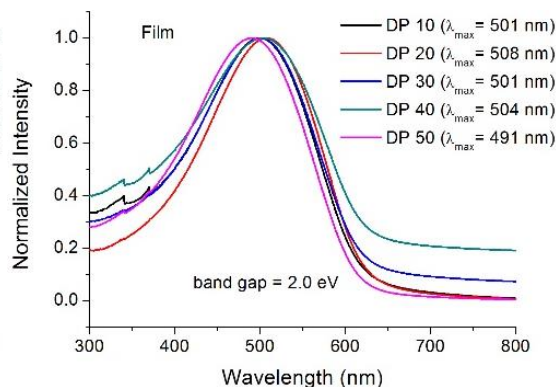
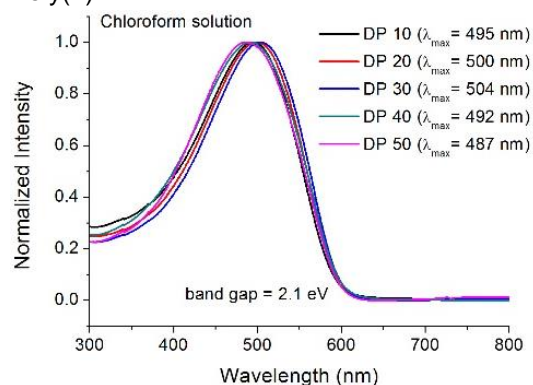


Figure S6. UV/vis absorption spectra

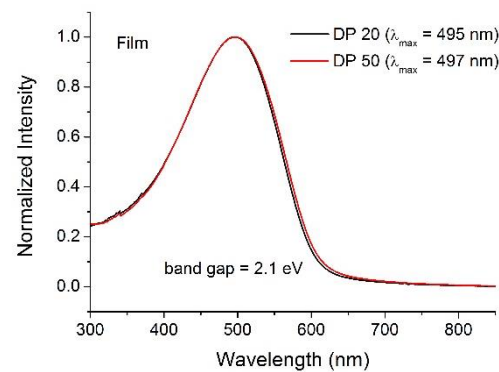
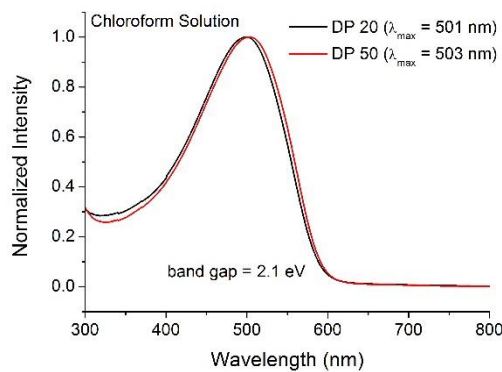
Poly(3)



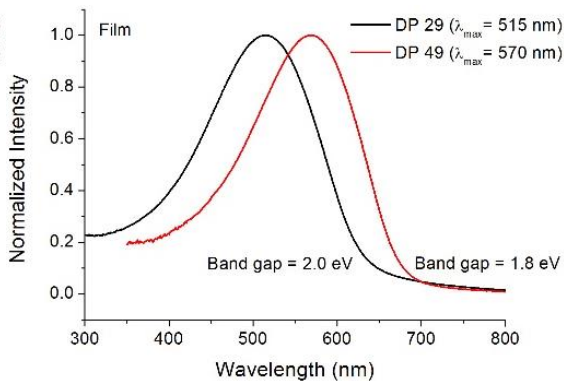
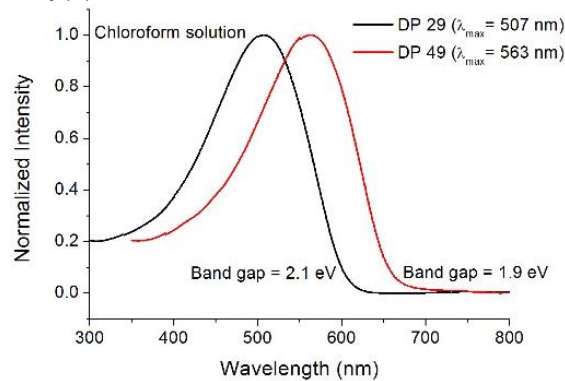
Poly(4)



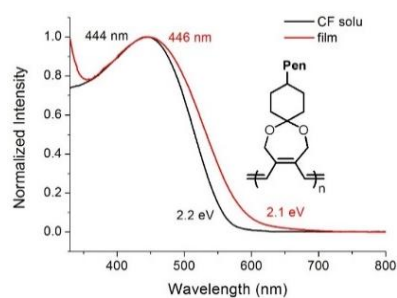
Poly(5)



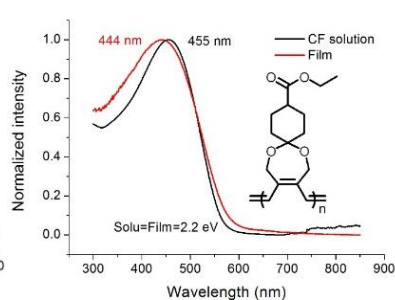
Poly(6)



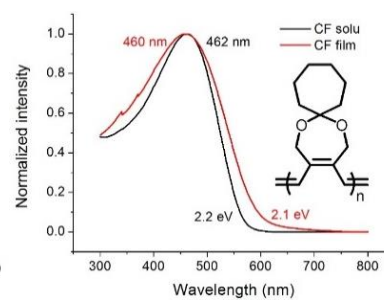
Poly(8)



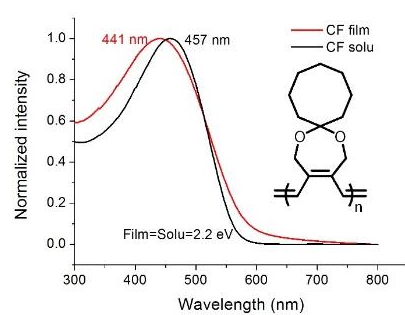
Poly(9)



Poly(10)



Poly(11)



Poly(12)

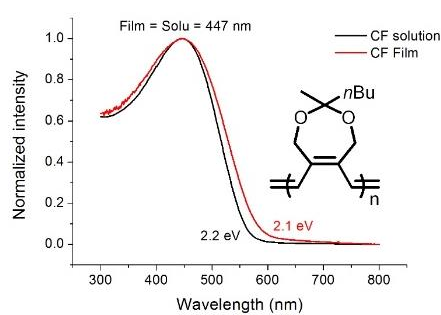


Figure S7. Cyclic voltammograms

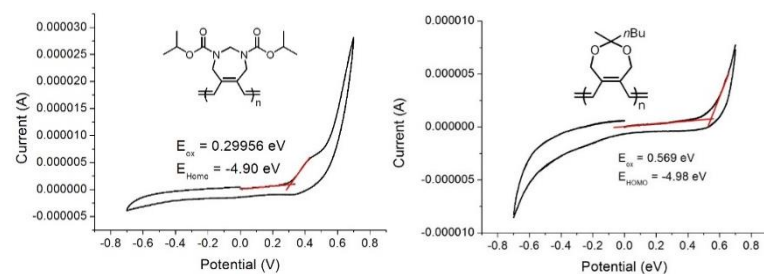
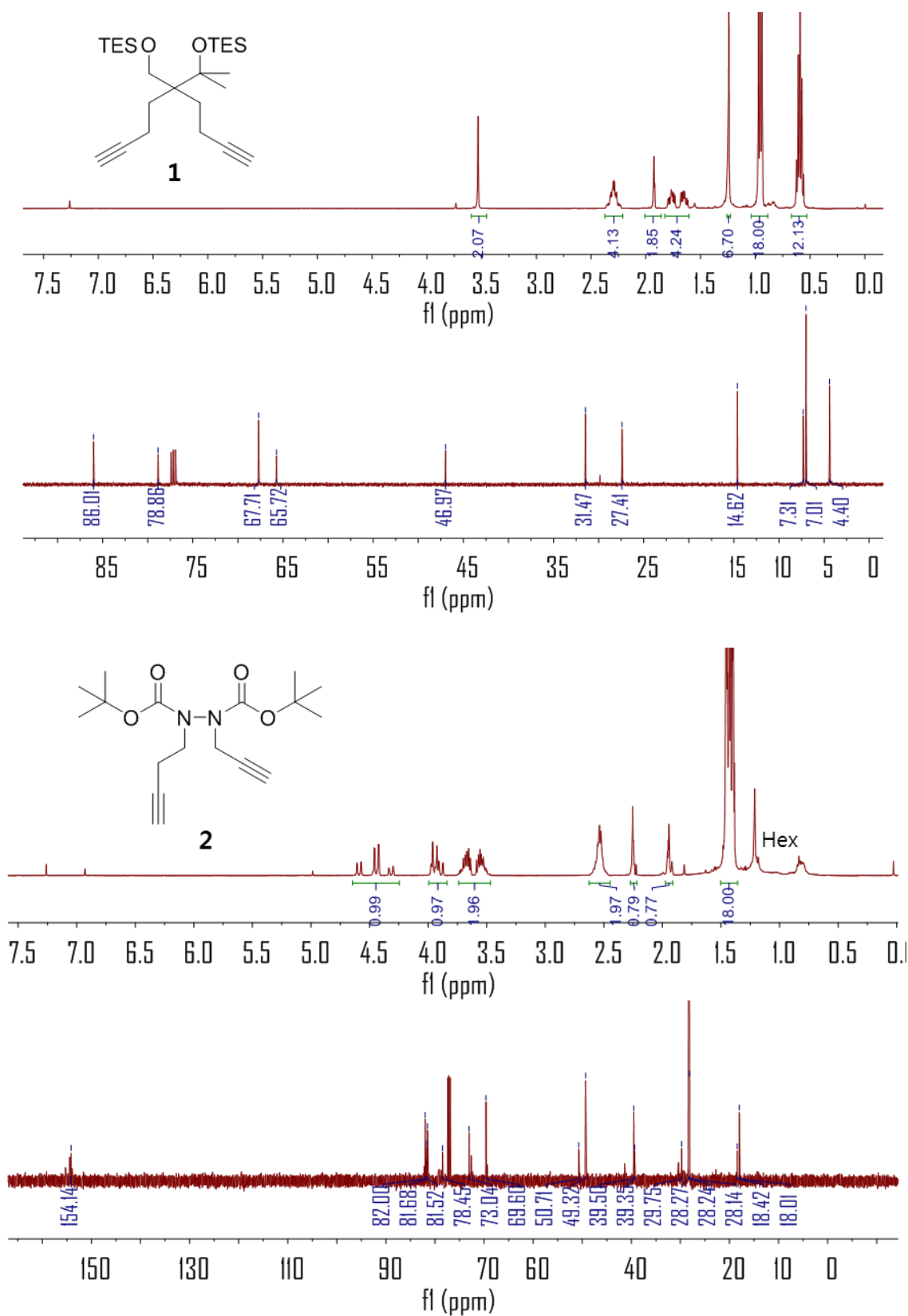
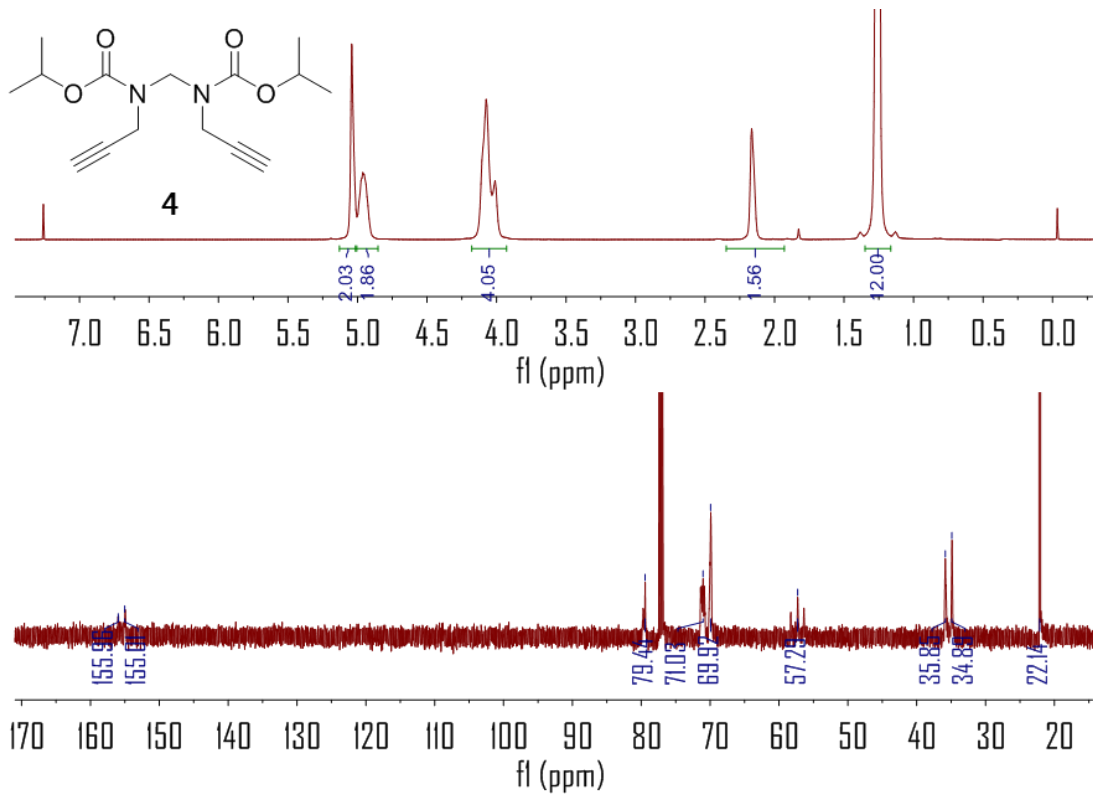
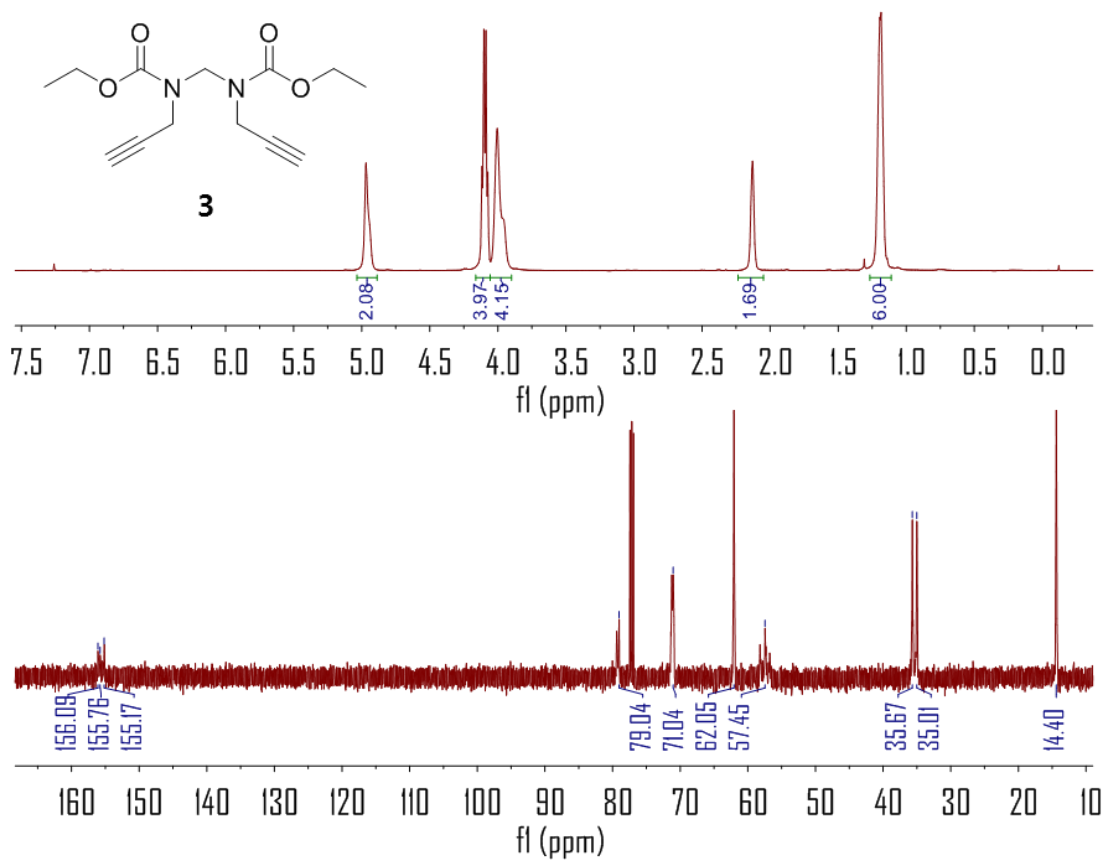
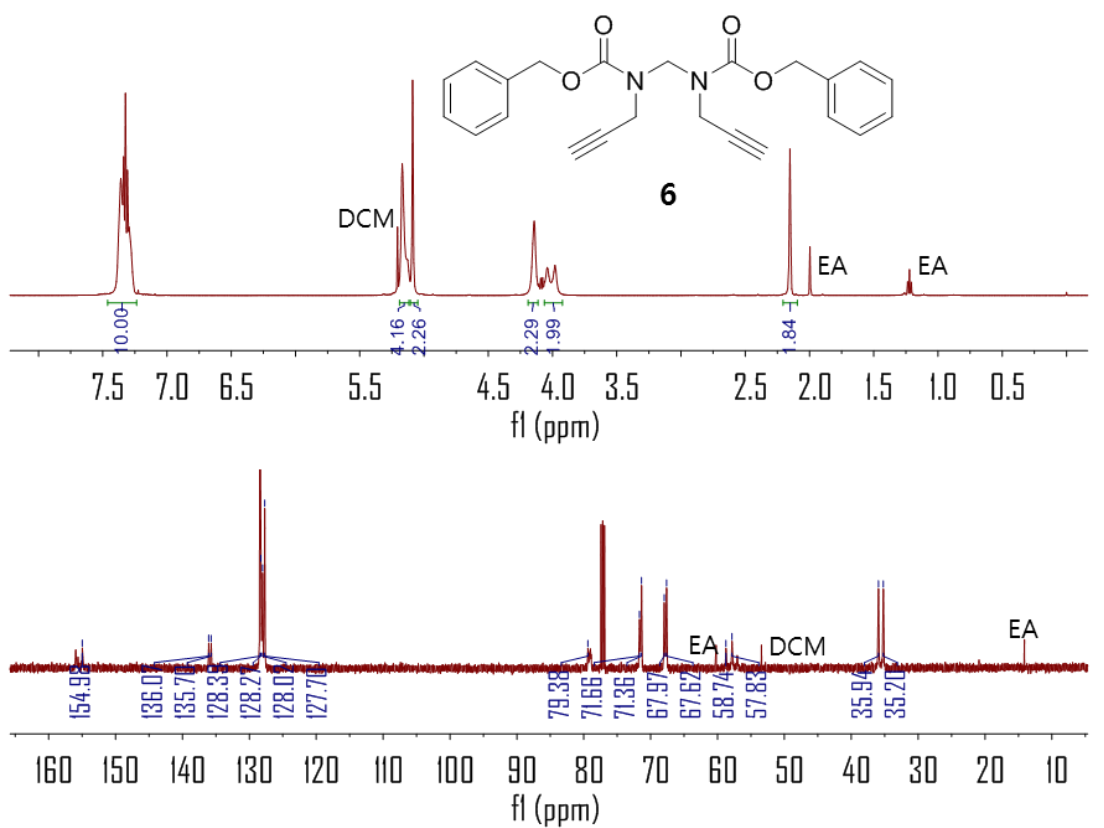
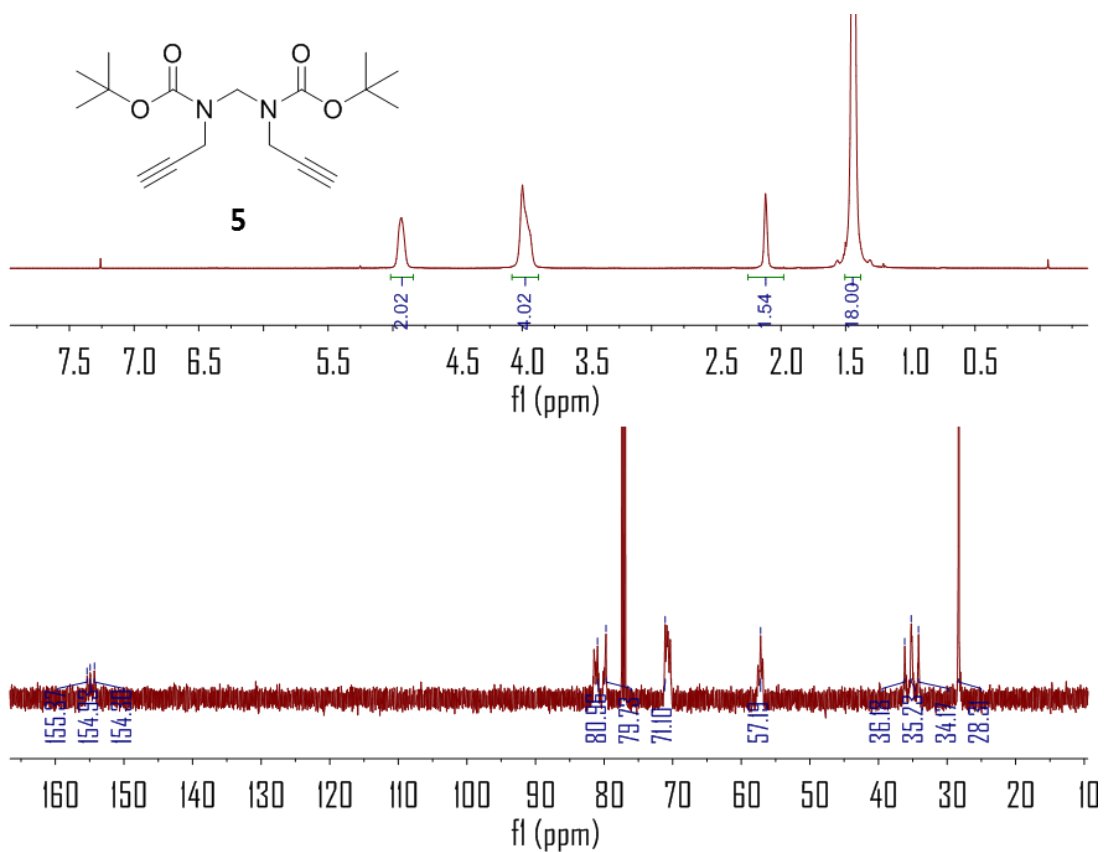
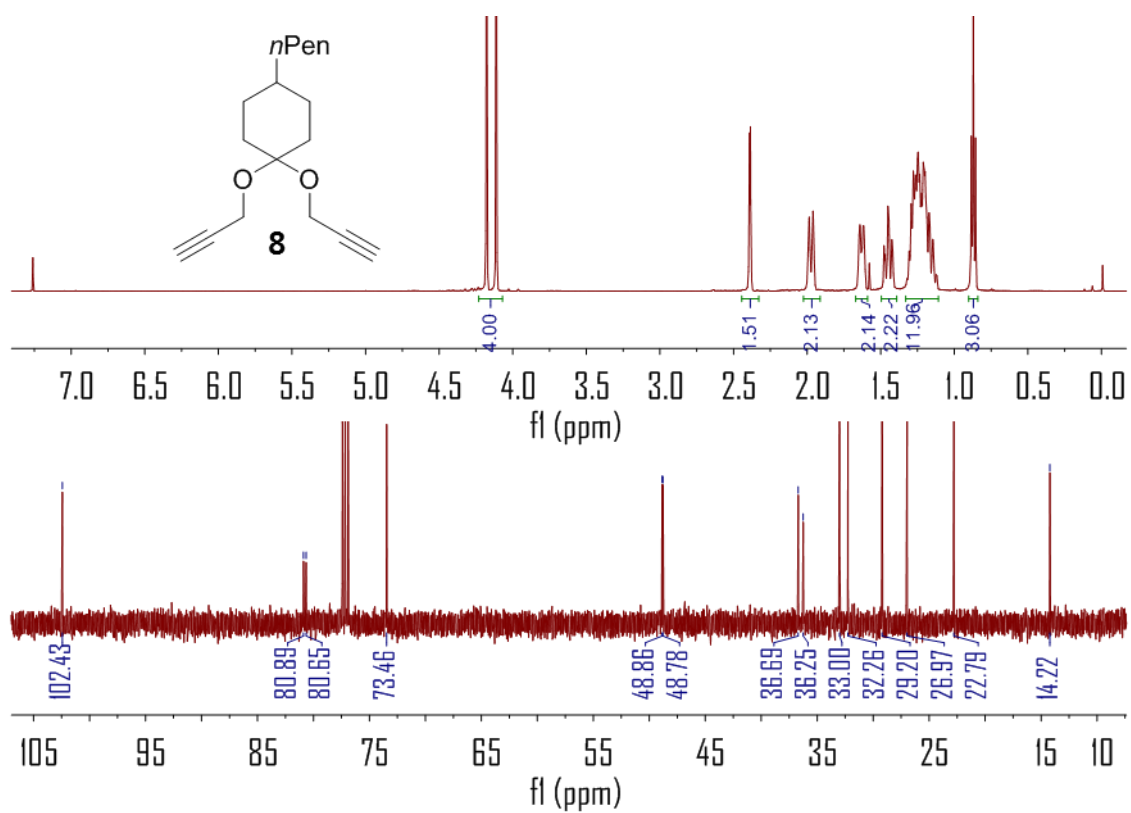
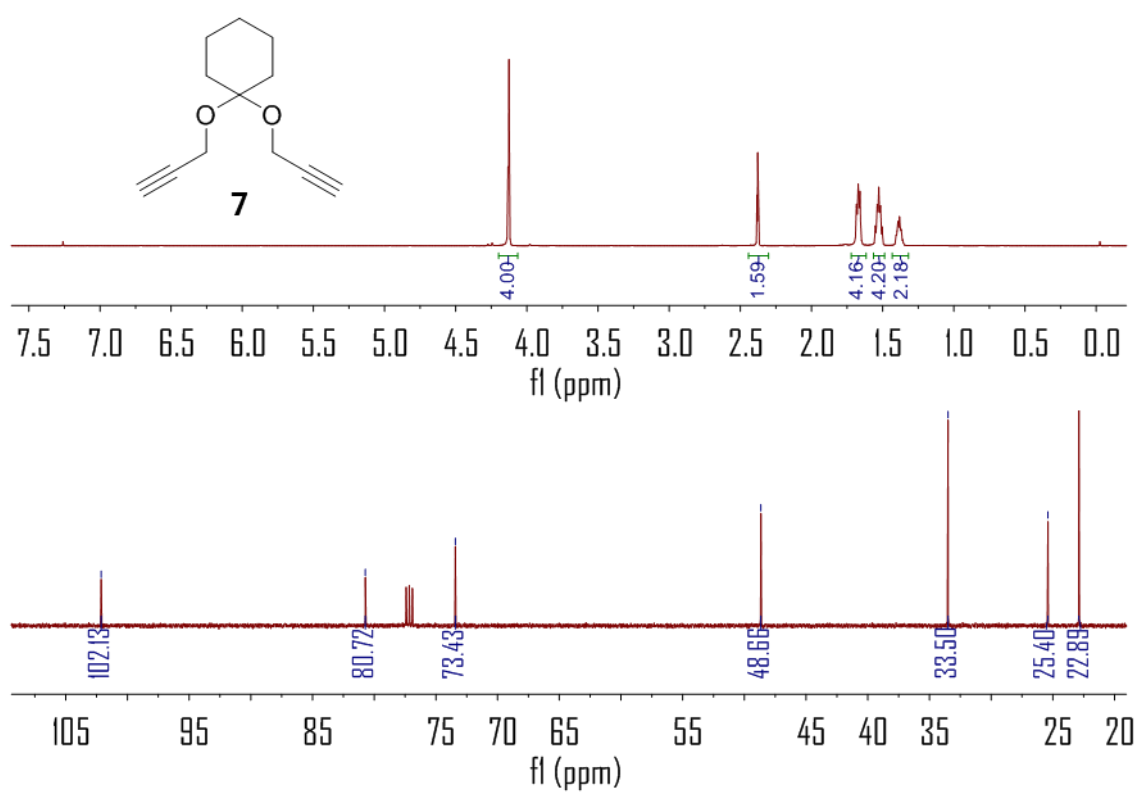


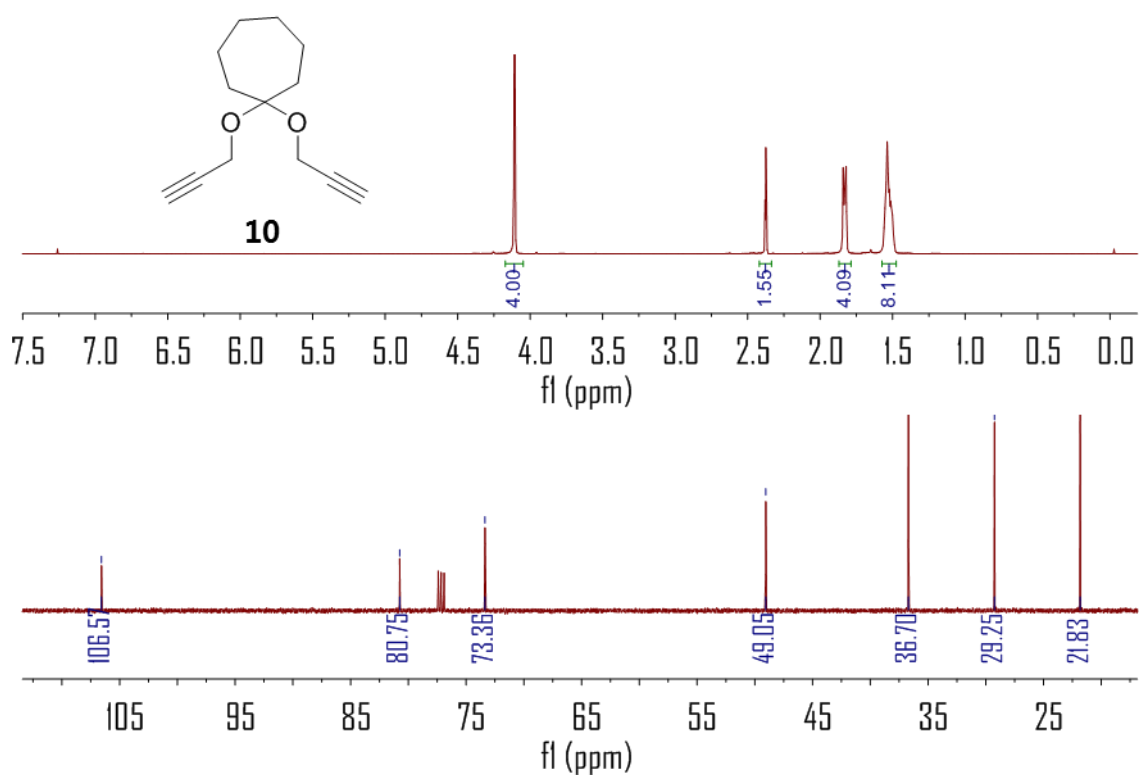
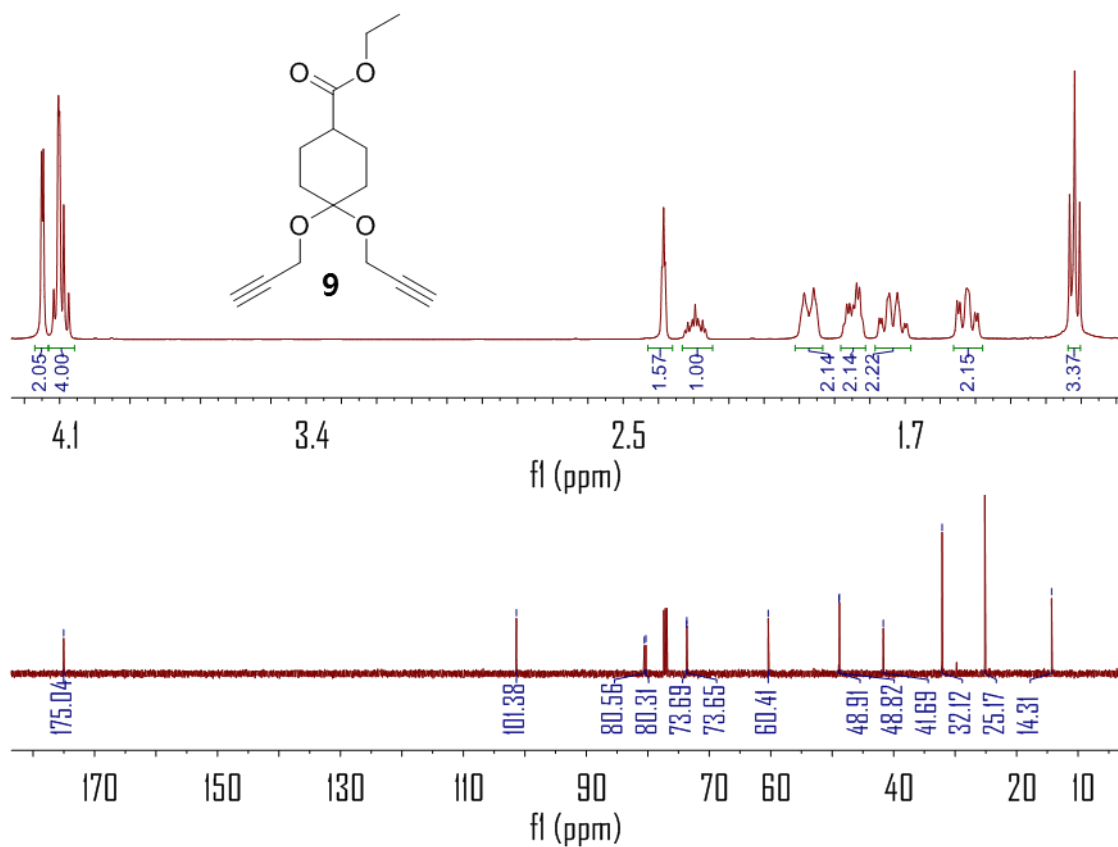
Figure S8. ^1H and ^{13}C NMR spectra of monomers in CDCl_3

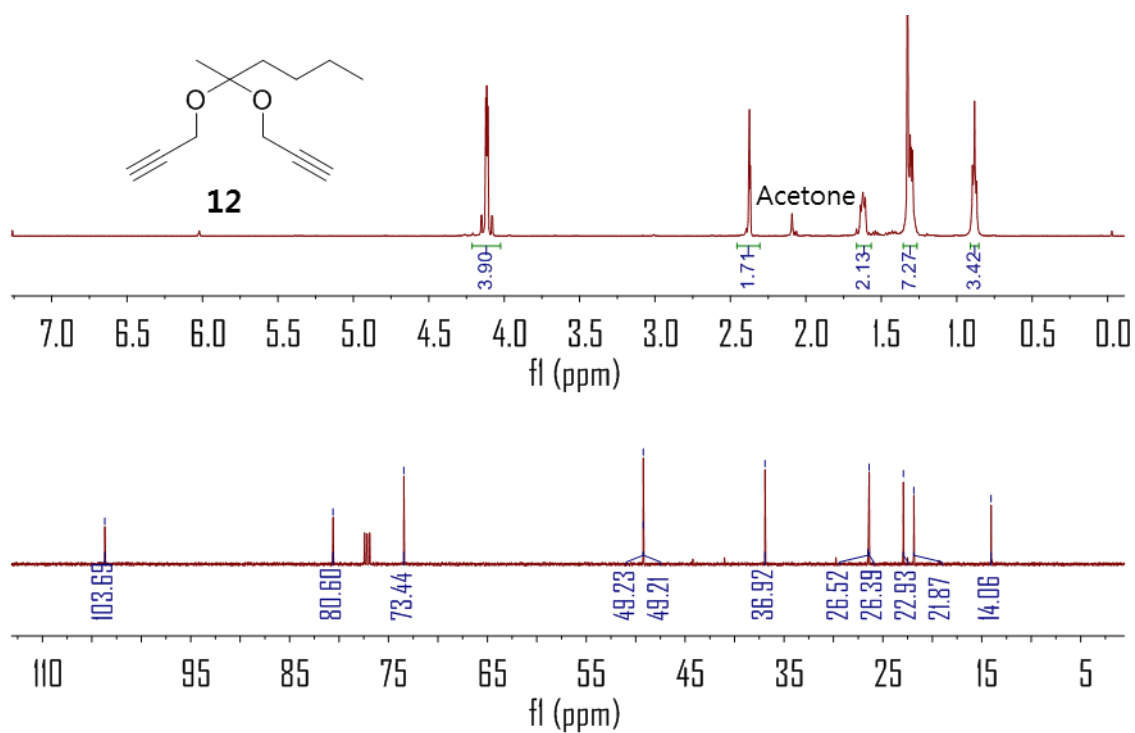
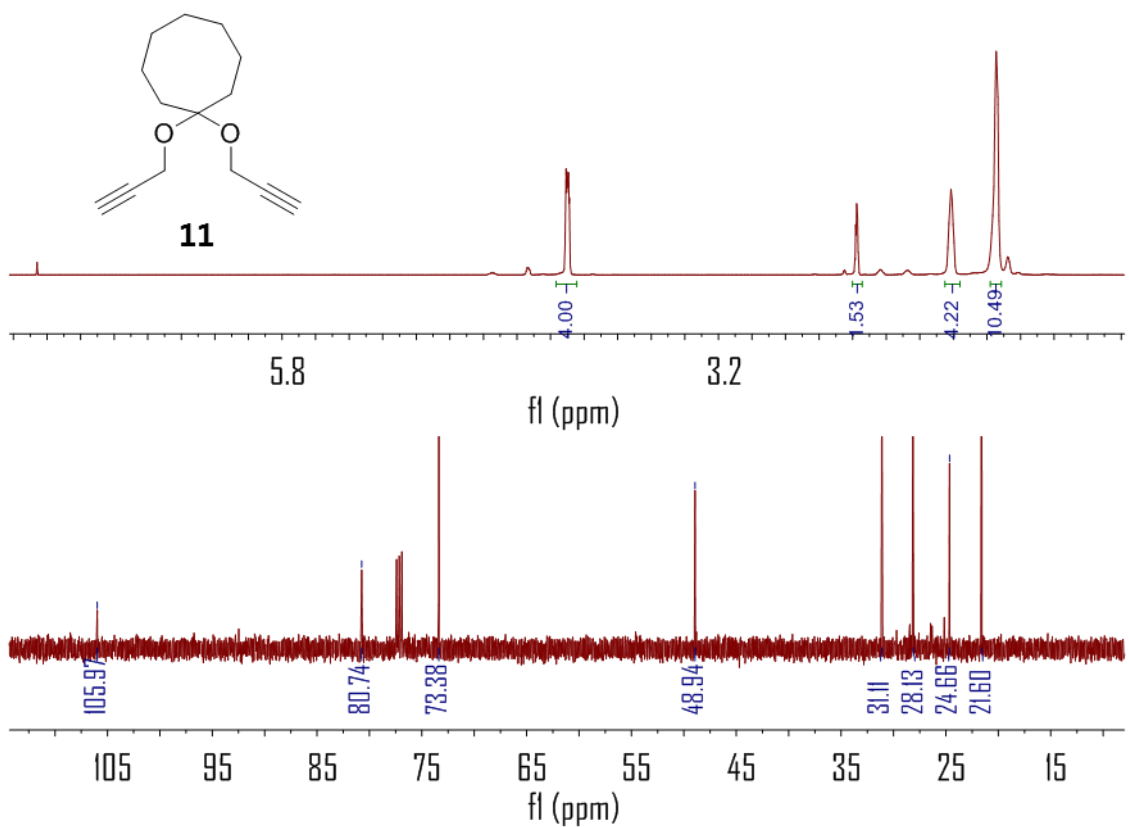












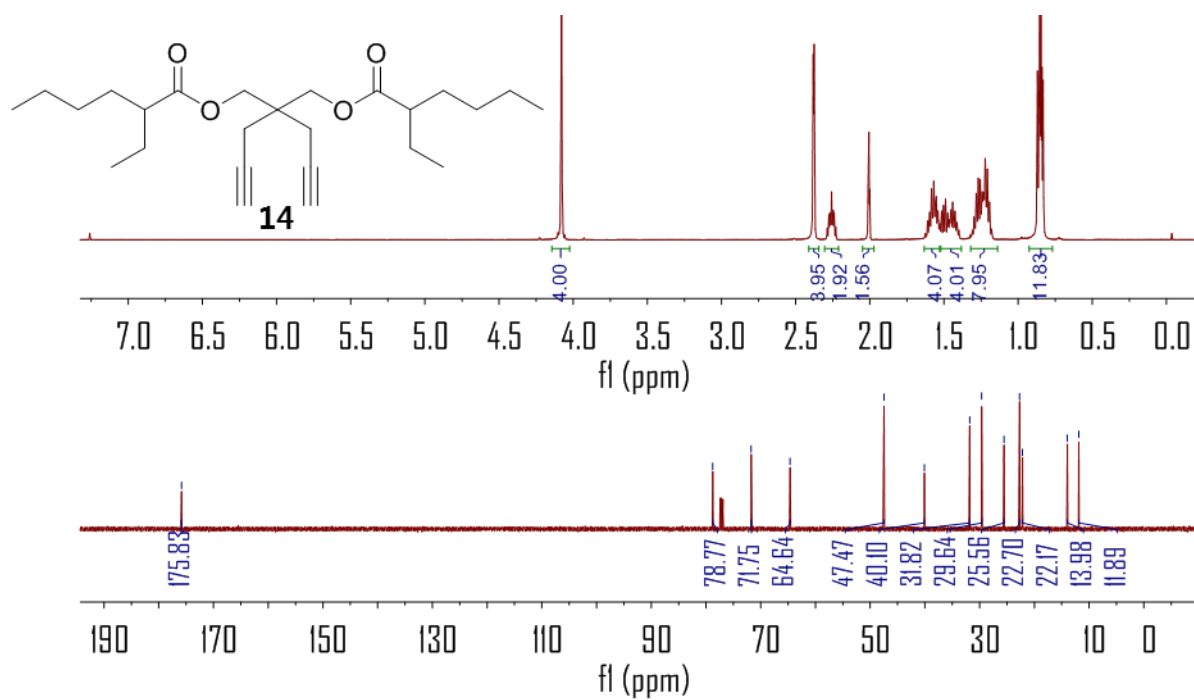
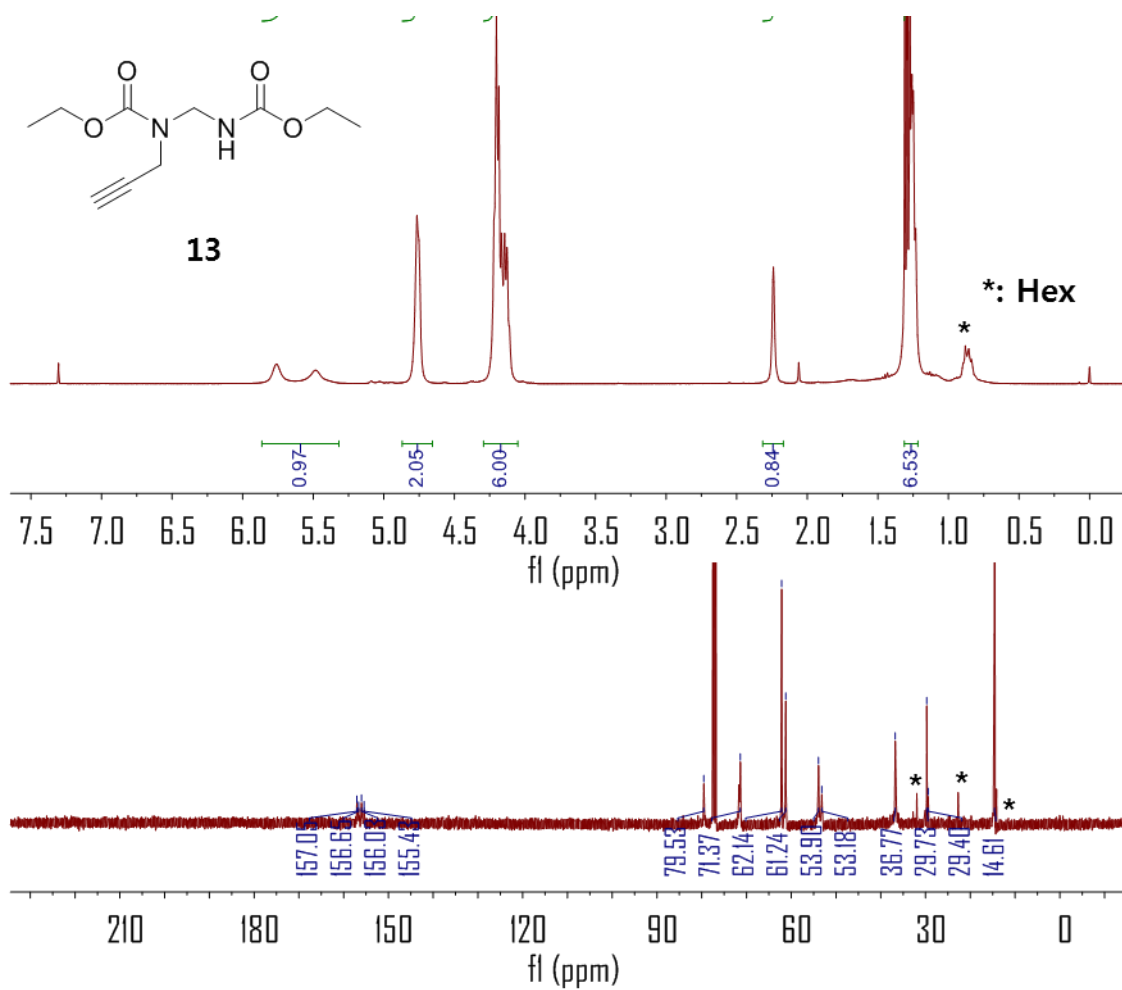
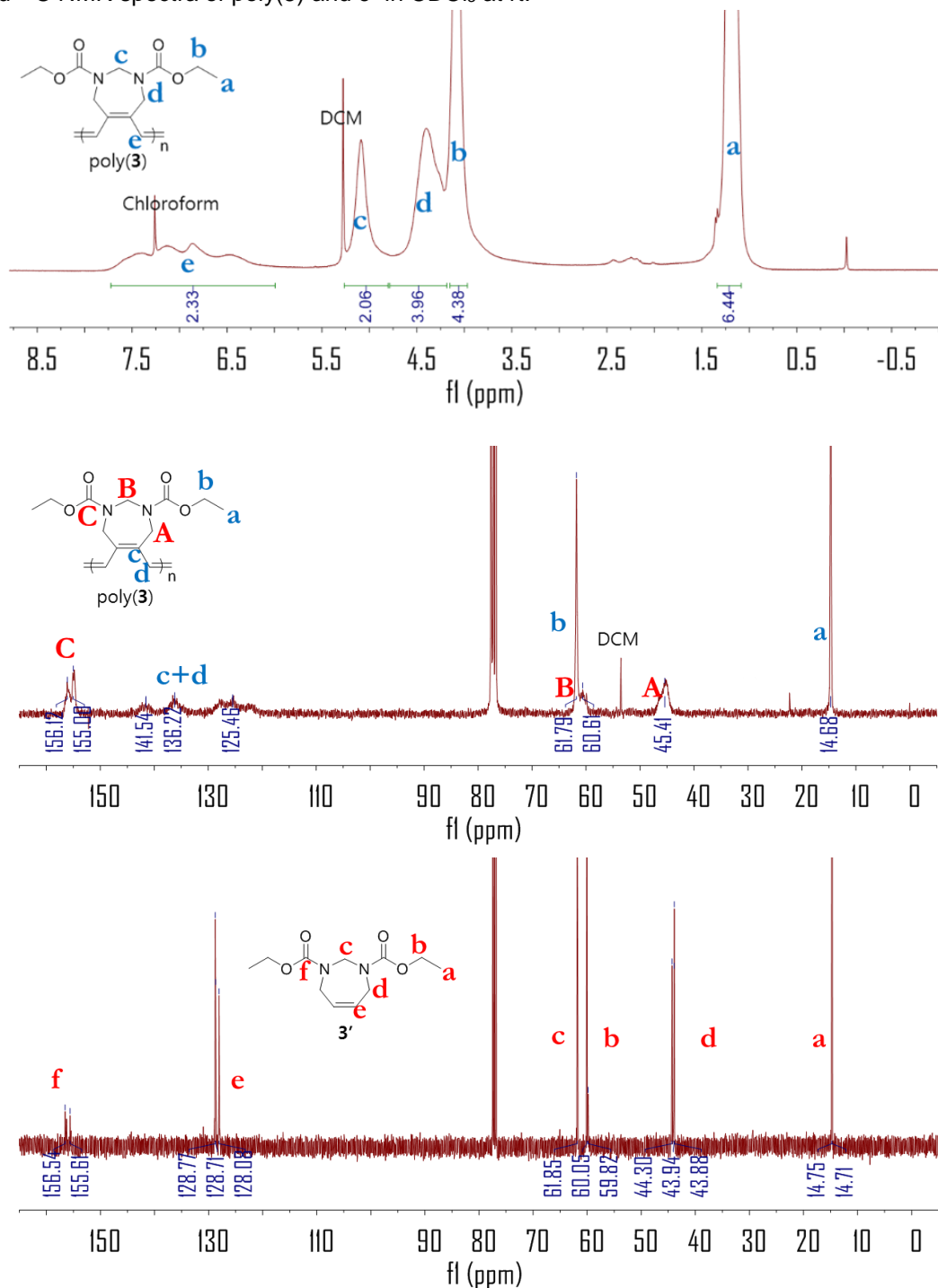


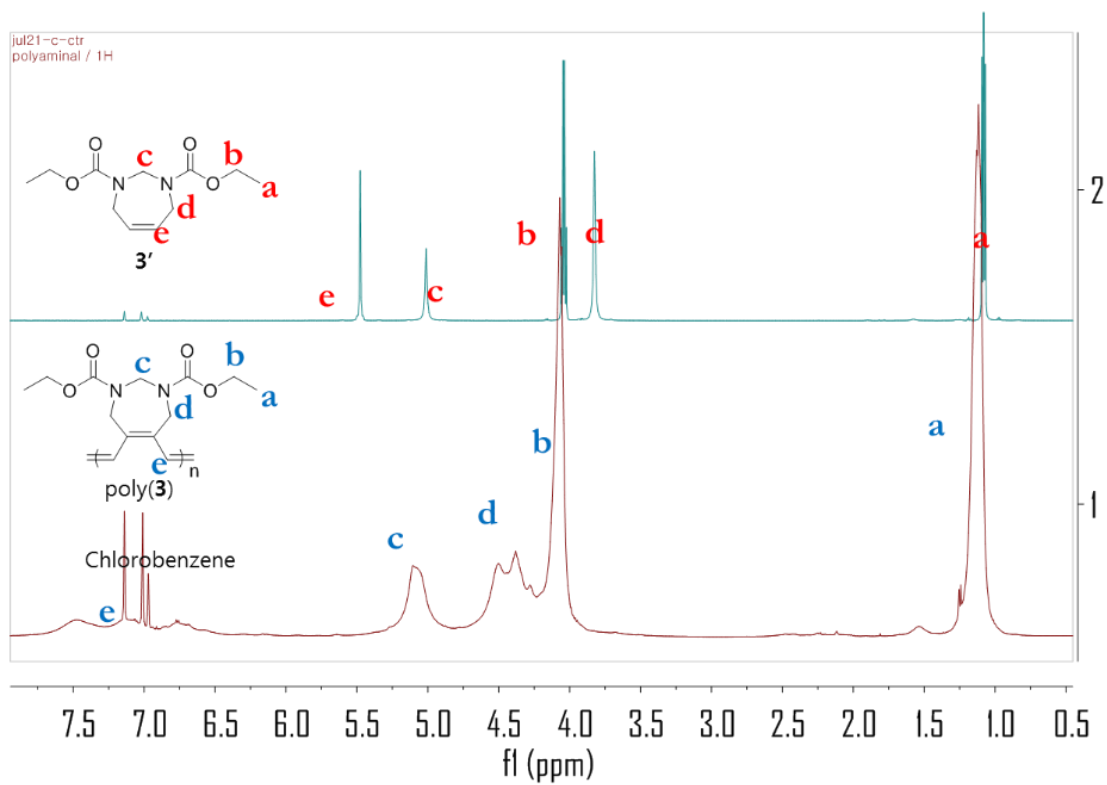
Figure S9. ^1H and ^{13}C NMR spectra of polymers

Broad signals in ^1H NMR and multiple signals in ^{13}C NMR spectra of amination polymers are due to rotamers thus, we took NMR at high temperature (exact temperature is stated in each NMR spectrum).

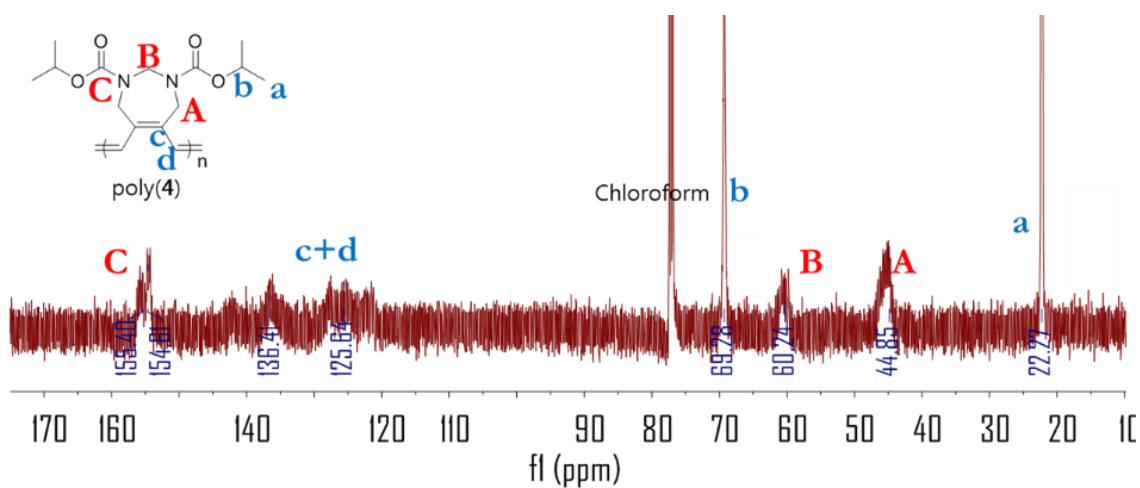
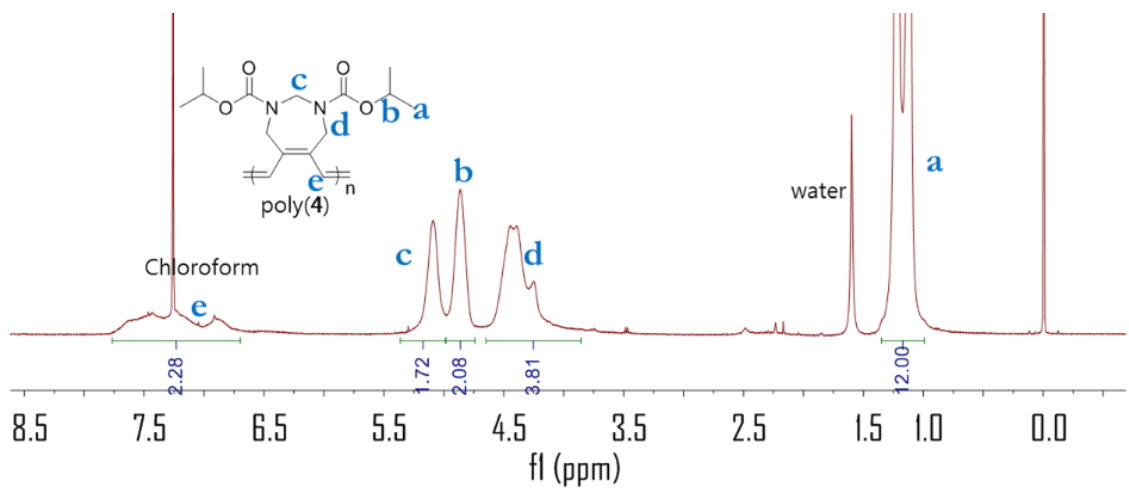
^1H and ^{13}C NMR spectra of poly(**3**) and **3'** in CDCl_3 at rt.



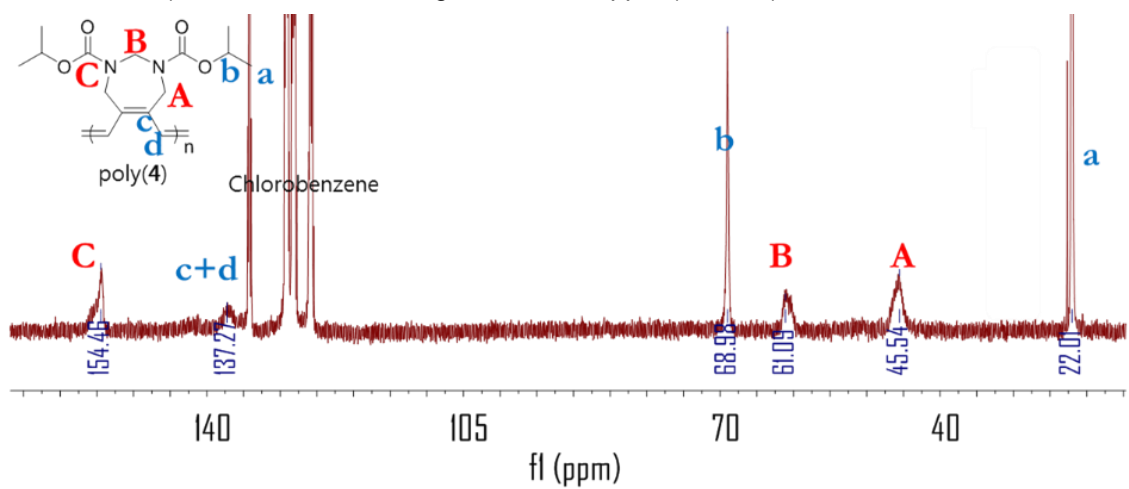
^1H NMR spectra of **3'** and poly(**3**) in chlorobenzene- d_5 at 90 °C.



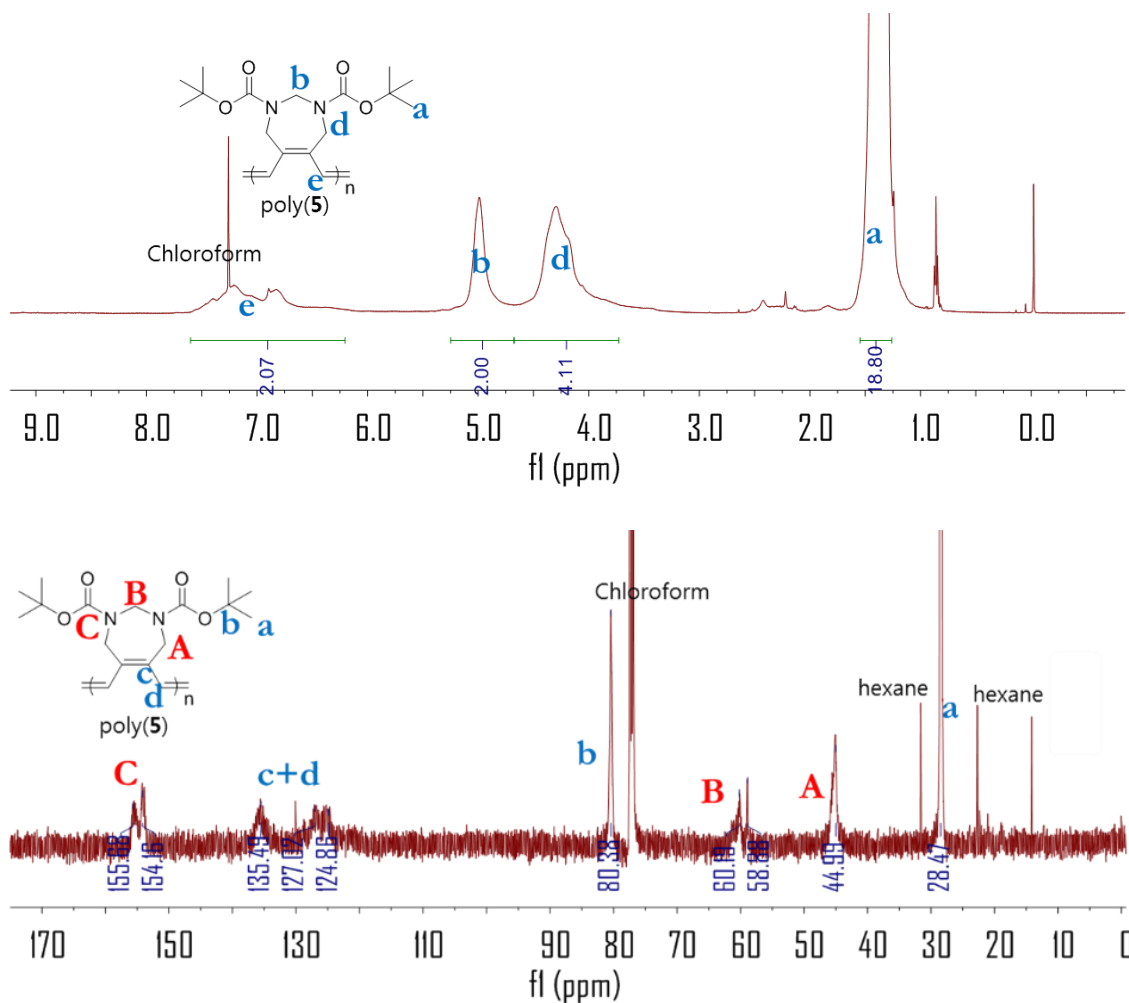
^1H and ^{13}C NMR spectra of poly(**4**) in CDCl_3 at rt.



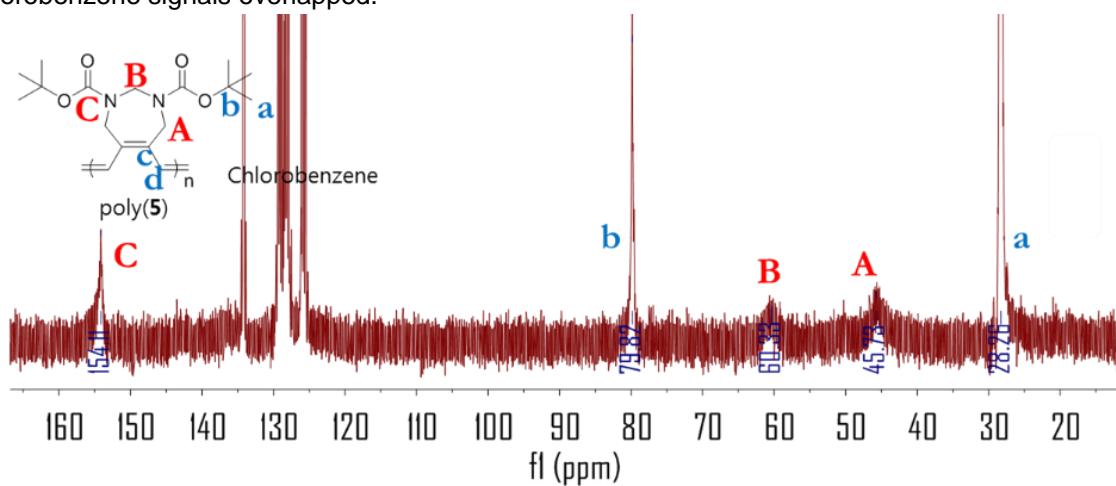
^{13}C NMR spectrum of poly(**4**) in chlorobenzene- d_5 at 70 °C. Multiple signals near 155 ppm (in chloroform- d at rt) coalesced into one signal at 154.46 ppm (at 70 °C).



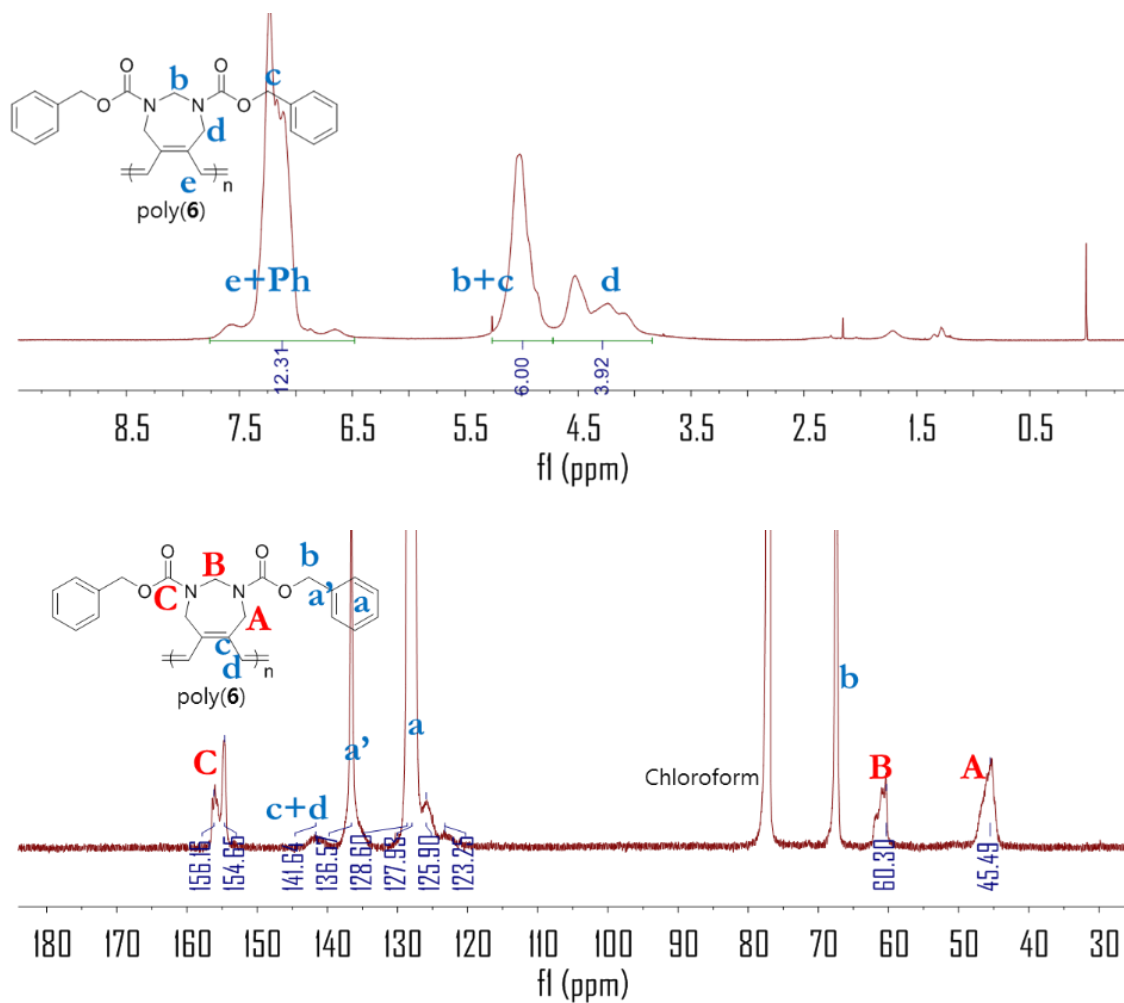
^1H and ^{13}C NMR spectra of poly(**5**) in CDCl_3 at rt.



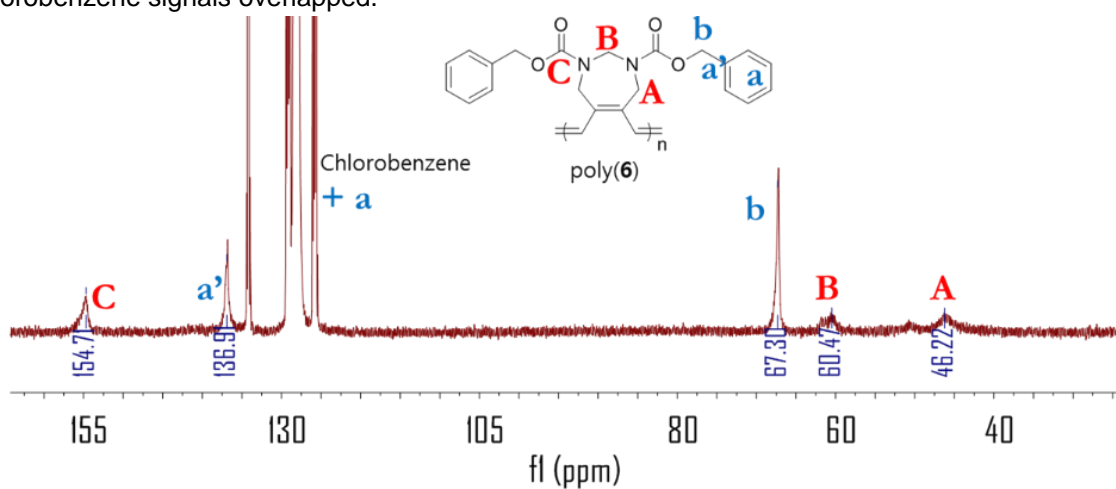
^{13}C NMR spectrum of poly(**5**) in chlorobenzene- d_5 at 80 °C. Multiple signals near 155 ppm (in chloroform- d at rt) coalesced into one signal at 154.11 ppm (at 80 °C). Olefinic carbon and chlorobenzene signals overlapped.



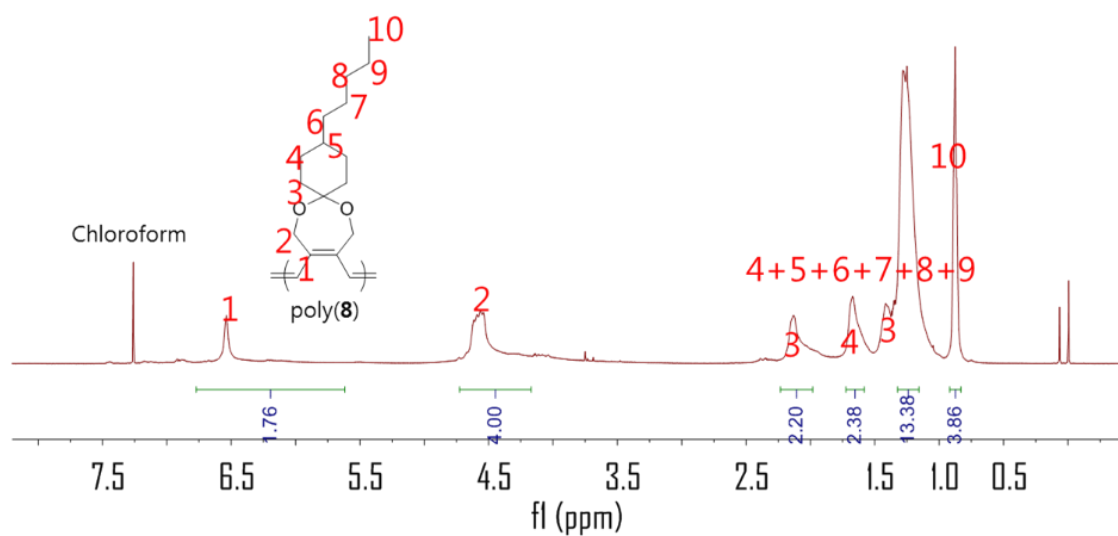
^1H and ^{13}C NMR spectra of poly(**6**) in CDCl_3 at rt.



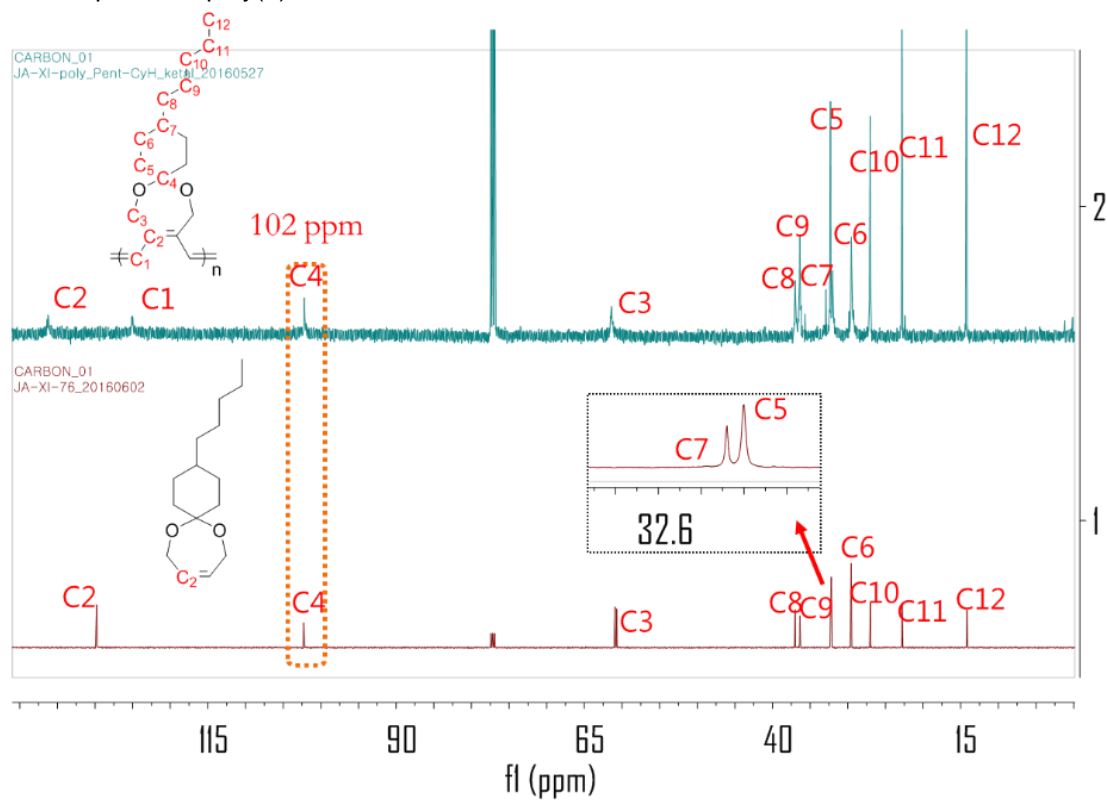
^{13}C NMR spectrum of poly(**6**) in chlorobenzene- d_5 at 70 $^\circ\text{C}$. Multiple signals near 155 ppm (in chloroform- d at rt) coalesced into one signal at 154.71 ppm (at 70 $^\circ\text{C}$). Olefinic carbon and chlorobenzene signals overlapped.



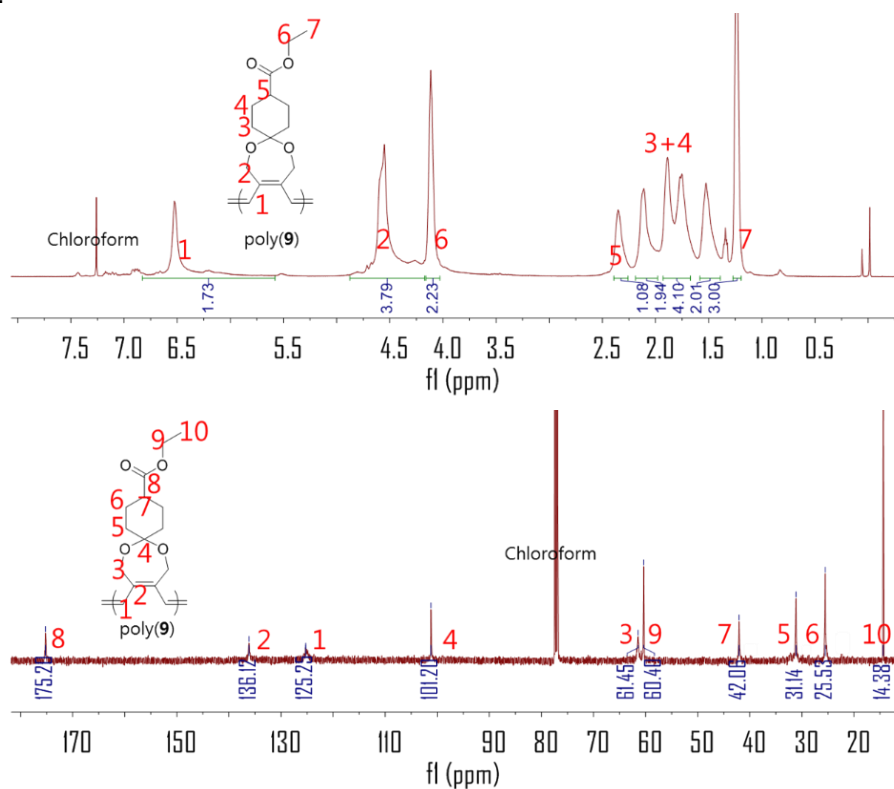
^1H NMR spectra of poly(**8**) in CDCl_3 at rt.



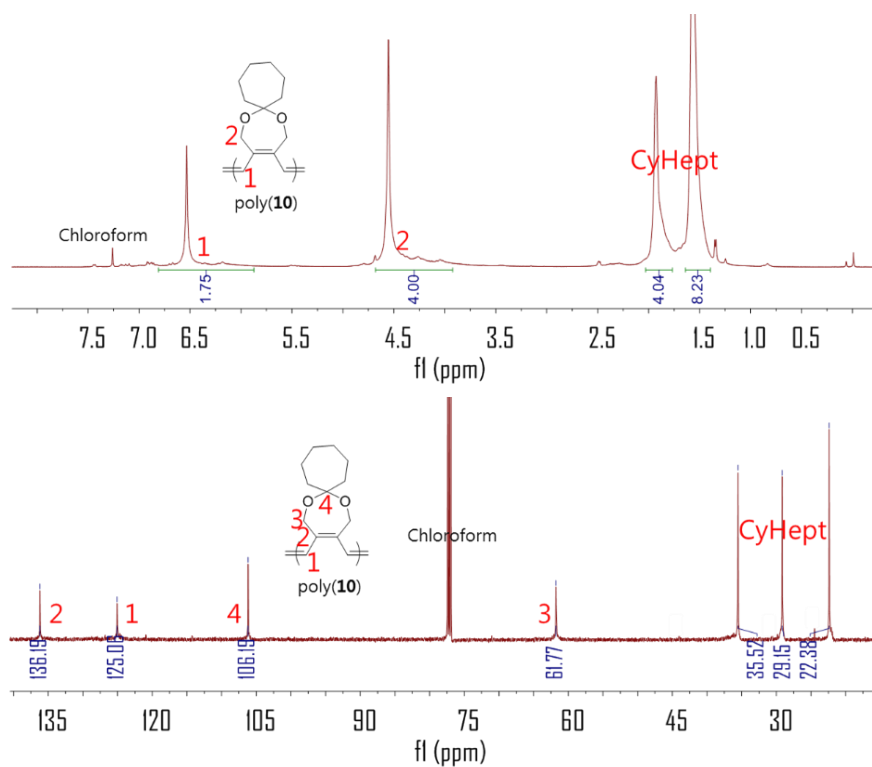
^{13}C NMR spectra of poly(**8**) and **8'** in CDCl_3 at rt.



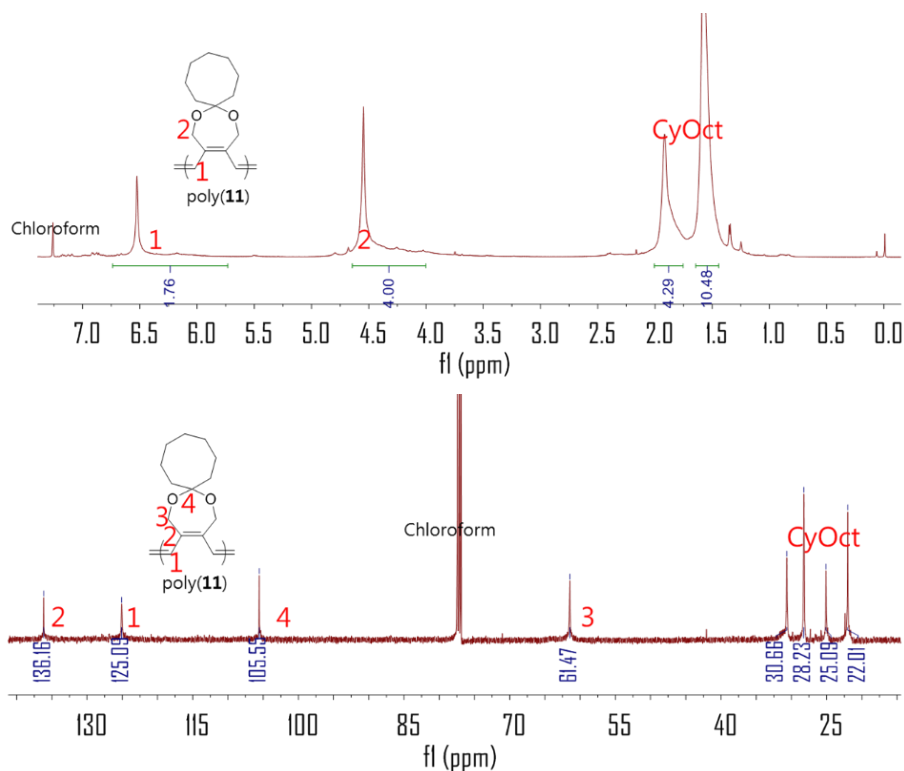
^1H and ^{13}C NMR spectra of poly(**9**) in CDCl_3 at rt. Single quaternary carbon signal was observed at 101.20 ppm.



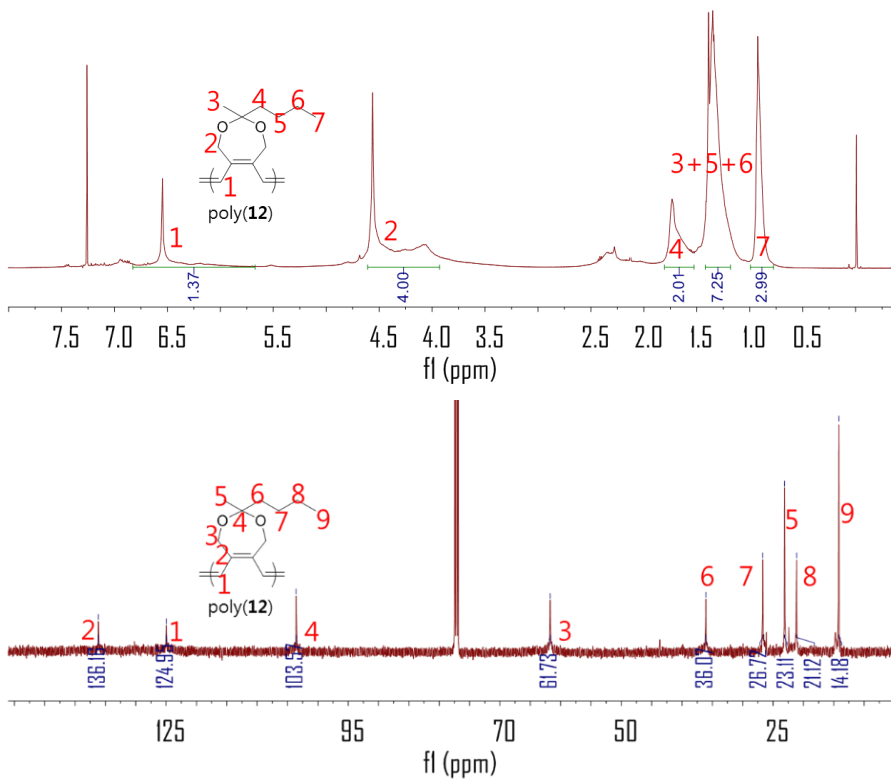
^1H and ^{13}C NMR spectra of poly(**10**) in CDCl_3 at rt. Single quaternary carbon signal was observed at 106.19 ppm.



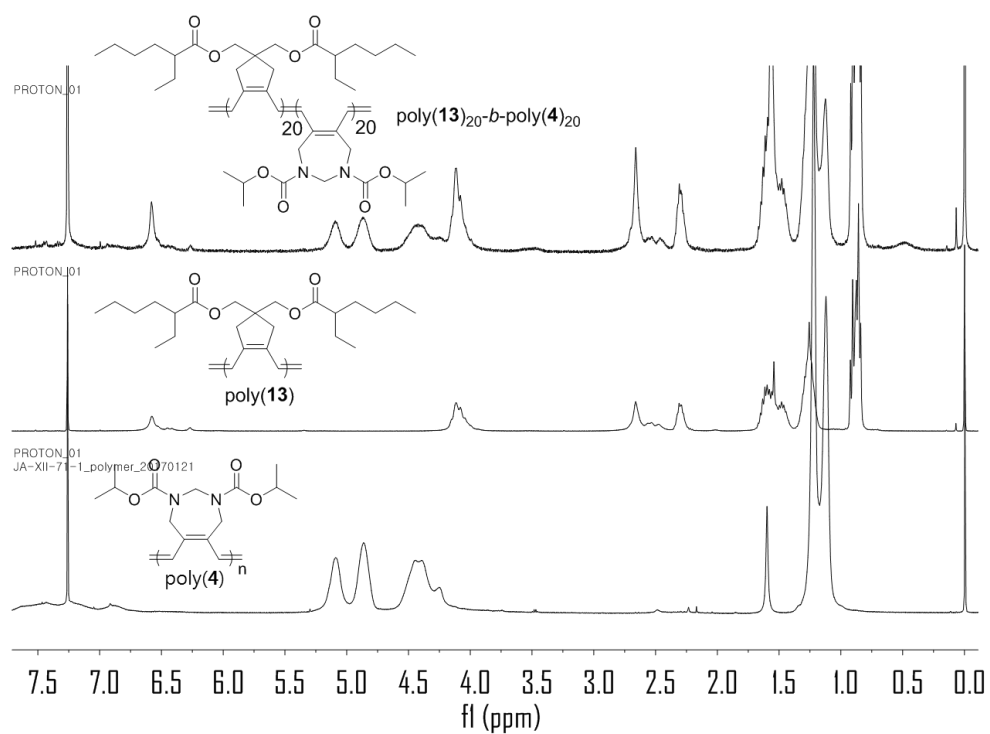
^1H and ^{13}C NMR spectra of poly(**11**) in CDCl_3 at rt. Single quaternary carbon signal was observed at 105.55 ppm.



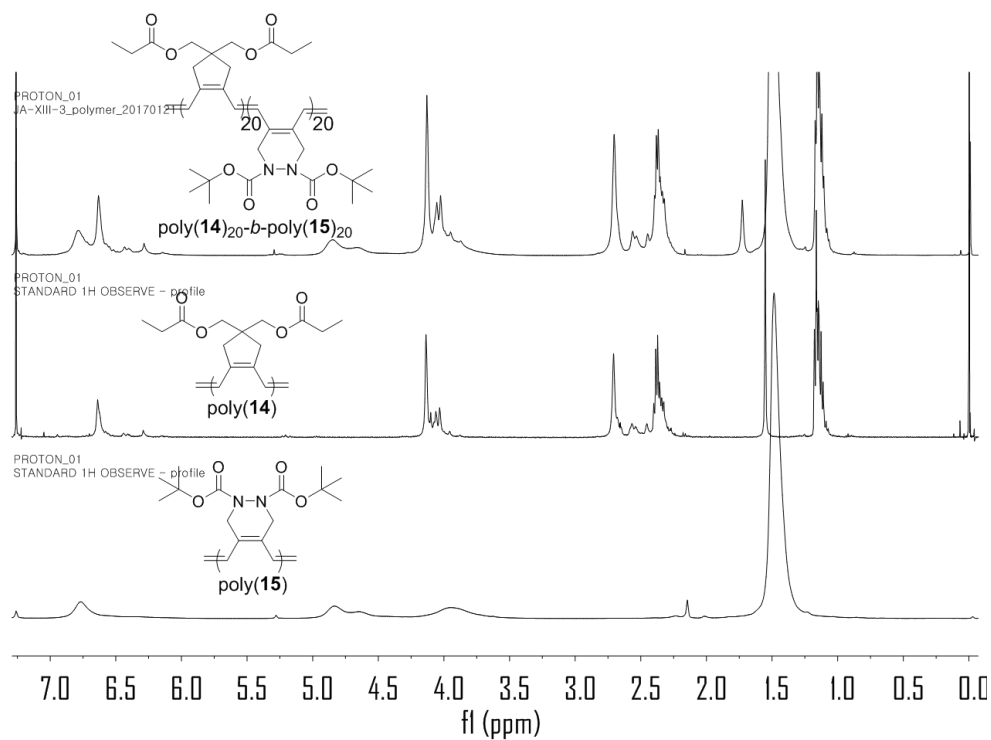
^1H and ^{13}C NMR spectra of poly(**12**) in CDCl_3 at rt. Single quaternary carbon signal was observed at 103.57 ppm.



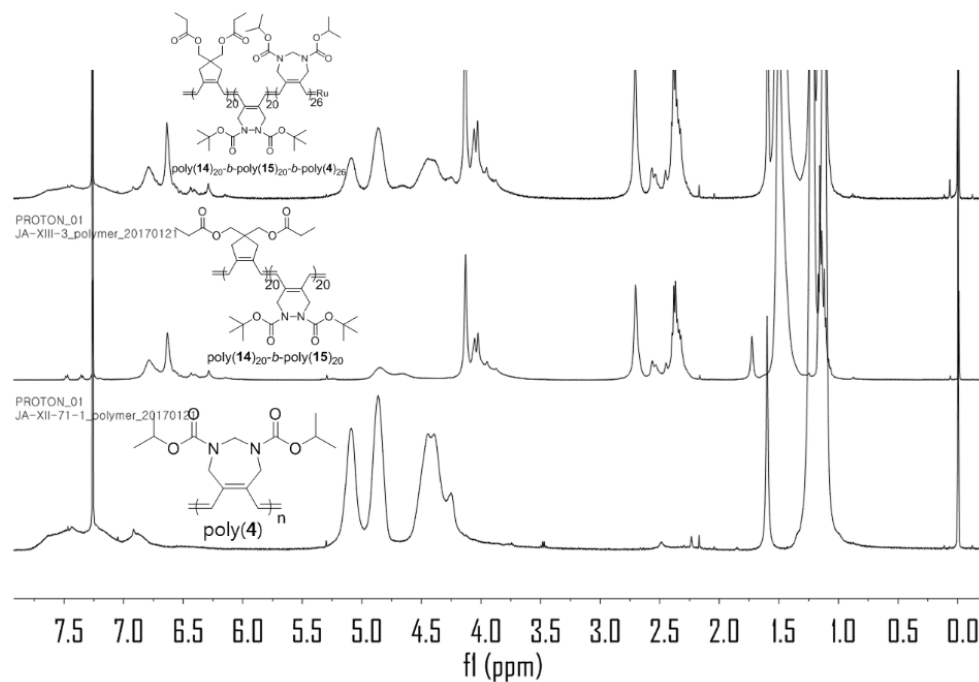
^1H NMR spectra of poly(**13**)₂₀-*b*-poly(**4**)₂₀, poly(**13**) and poly(**4**) in CDCl_3 at rt.



^1H NMR spectra of poly(**14**)₂₀-*b*-poly(**15**)₂₀, poly(**14**) and poly(**15**) in CDCl_3 at rt.



^1H NMR spectra of poly(**14**)₂₀-*b*-poly(**15**)₂₀-*b*-poly(**4**)₂₆, poly(**14**)₂₀-*b*-poly(**15**)₂₀ and poly(**4**).



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