Supporting Information

Rare-Earth-Metal Catalyzed Highly Regio- and Stereoselective Polymerization of Terpene-Derived Conjugated Dienes

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Experimental Procedures

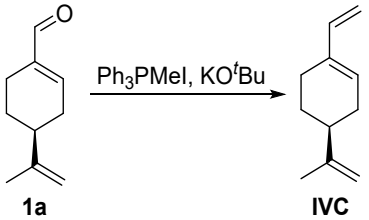
General Considerations

All reactions were conducted under an atmosphere of dry nitrogen, using standard Schlenk line and glovebox (Vigor SG1200/750TS-F) techniques. Solvents and reagents were obtained from commercial sources. THF were distilled from sodium / benzophenone and chlorobenzene was distilled from CaH_2. Commercial reagents, namely perilla aldehyde, α- and β-pinene, potassium *tert*-butoxide and other commercially available reagents were purchased from TCI or Aladdin and used without further purification. ^1H (400 MHz), ^{13}C NMR (100 MHz) and other NMR test measurements were obtained on a JNM-ECZ400S/L 400 MR spectrometer in $CDCl_3$ solution (25 °C). The molecular weight and molecular weight distribution of the polymers were measured by means of gel-permeation chromatography (GPC) on a Waters LC-16 (35 °C). T_g was measured by differential scanning calorimetry (DSC) analyses, which were carried out using a TA Q2000 DSC Instrument under a nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 240 °C, cooling at 20 °C min^{-1} to room temperature, and then recording the second DSC scan from 20 to 240 °C at 10 °C min^{-1}. Thermal gravimetric analyses (TGA) for polymers were done using a thermal analysis instrument (TA Q550, TG instruments) from room temperature to 800 °C under nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Synthesis and analysis of monomers

Synthesis of methyltriphenylphosphonium iodide Triphenylphosphine (78.7 g, 300.0 mmol) was added into a 500 mL three-necked flask and dissolved in toluene (400 mL) under N_2 atmosphere. Iodomethane (22.4 mL, 360.0 mmol) was added to the solution, and the reaction mixture overnight in room temperature. The precipitate was collected by filtration, washed with toluene and ethyl ether, and dried under vacuum for 8 h to give methyltriphenylphosphonium iodide (115.0 g, 283.0 mmol). The product was used for the next reaction without further purification.

Synthesis of IVC

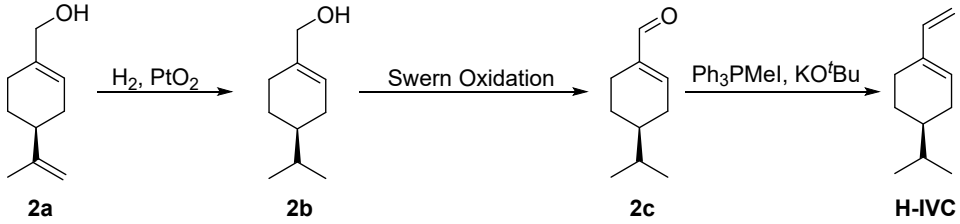


Scheme S1. Synthesis of **IVC**.

In glovebox, potassium *tert*-butoxide (*tert*-BuOK, 14.8 g, 132.0 mmol) were added in portions to a suspension of methyltriphenylphosphonium iodide (48.8 g, 120.0 mmol) in dry THF (100 mL), and the reaction mixture was stirred at room temperature (RT) for 2 h. Perilla aldehyde (15.0 g, 100.0 mmol) was then added dropwise into the above reaction mixture at 0 °C. After stirring overnight at RT, the reaction was quenched by addition of water and further extracted with diethyl ether. The organic solution was dried over $MgSO_4$, and the solvent was subsequently removed. The residue was mixed with a large amount of *n*-hexane to precipitate triphenylphosphine oxide,

and the *n*-hexane solution was concentrated and purified by column chromatography on silica gel to give **IVC** as colorless liquid in a yield of 89.9% (13.3 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.34 (dd, *J* = 17.2, 10.8 Hz, 1H, CH_2=C*H*-C), 5.77 (s, 1H, C=C*H*-CH_2), 5.06 (d, *J* = 17.2 Hz, 1H, CH=CH_2), 4.91 (d, *J* = 10.8 Hz, 1H, CH=CH_2), 4.72 (s, 2H, C=CH_2), 2.19 (t, 5H, C-CH_2-CH_2+CH_2-C*H*-CH_2+CH-CH_2-CH), 1.90 (m, 1H, CH-CH_2-CH_2), 1.74 (s, 3H, C-CH_3), 1.48 (m, 1H, CH-CH_2-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.82 (CH-*C*-CH_3), 139.75 (CH_2=*C*H-C), 135.81 (CH-*C*=CH), 129.23 (C=*C*H-CH_2), 110.18 (CH=*C*H_2), 108.80 (C=*C*H_2), 41.30 (CH_2-*C*H-C), 31.31 (CH-*C*H_2-CH), 27.39 (CH_2-*C*H_2-CH), 24.32 (C-*C*H_2-CH_2), 20.90 (C-*C*H_3).

Synthesis of H-IVC



Scheme S2. Synthesis of **H-IVC**.

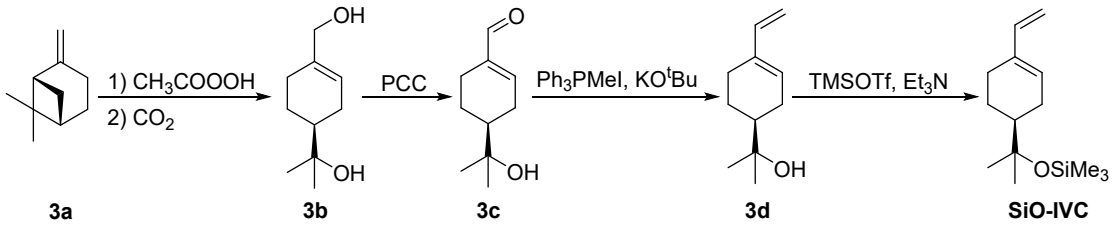
The perillyl alcohol (6.0 g, 39.4 mmol) was dissolved in methanol and treated with catalytic PtO_2 (18.2 mg, 0.079 mmol) under a hydrogen atmosphere (1 atm). The reaction was stirred vigorously for 24 h at room temperature and then filtered through a pad of silica gel. The filtrate was evaporated to give the desired allylic alcohol **2b** in essentially, yield 96.4%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.66 (s, 1H, C=C*H*-CH_2), 3.98 (s, 1H, C-CH_2-OH), 2.06 (m, 2H, CH-CH_2-CH+C-CH_2-CH_2), 1.81 (m, 1H, CH-CH_2-CH), 1.73 (m, 1H, CH_2-C*H*-CH_2), 1.47 (m, 2H, C-CH_2-CH_2+CH-C*H*-CH_3), 1.25 (m, 2H, CH_2-CH_2-CH), 0.89 (dd, *J* = 6.9, 5.0 Hz, 6H, CH-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.46 (CH_2-*C*=CH), 123.61 (CH_2-C=*C*H), 67.44 (C-*C*H_2-OH), 40.22 (CH_2-*C*H-CH), 32.31 (CH-*C*H-CH_3), 28.69 (C=CH-*C*H_2), 26.42 (CH_2-*C*H_2-CH), 26.12 (C-*C*H_2-CH_2), 20.03 (CH-*C*H_3), 19.72 (CH-*C*H_3).

Dry dimethyl sulfoxide (DMSO, 2.9 mL) was added to a cold solution of oxalyl chloride (3.9 mL, 45.6 mmol) in dichloromethane at -78 °C with stirring for 20 min. **2b** (5.86 g, 38.0 mmol) in 5 mL of dichloromethane (DCM) was then added over 1.0 minutes and the mixture was further stirred for 1.0 h with the subsequent addition of triethylamine (4.7 mL). After stirring at -78 °C for another 0.5 h, the reaction mixture was slowly warmed to RT and water was added to quench the reaction. The aqueous layer was extracted with DCM, and the organic phase was collected, dried over anhydrous Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography to obtain the desired product **2c** (4.0 g, 70.3%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.41 (s, 1H, C-C*H*=O), 6.79 (s, 1H, C=C*H*-CH_2), 2.42 (m, 2H, CH-CH_2-CH+C-CH_2-CH_2), 2.03 (m, 2H, CH_2-C*H*-CH_2+CH-CH_2-CH), 1.85 (m, 1H, C-CH_2-CH_2), 1.52 (m, 1H, CH-C*H*-CH_3), 1.36 (m, 1H, CH_2-CH_2-CH), 1.31 (m, 1H, CH_2-CH_2-CH), 0.90 (dd, *J* = 6.9, 2.7 Hz, 6H, CH-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.28 (C-*C*H=O), 151.73 (CH_2-*C*=CH), 140.82 (CH_2-C=*C*H), 39.99 (CH_2-*C*H-CH), 32.09 (CH-*C*H-CH_3), 30.25 (C=CH-*C*H_2), 24.98 (CH_2-*C*H_2-CH), 21.92 (C-*C*H_2-CH_2), 19.87 (CH-*C*H_3), 19.57 (CH-*C*H_3).

H-IVC was synthesized as the procedure for **IVC**. For **2c** (4.0 g, 26.7 mmol), Ph_3PMeI (12.8 g, 32.0 mmol) and *tert*-BuOK (3.9 g, 35.2 mmol) were used, and **H-IVC** was obtained in 86.3% yield as colorless liquid (3.4 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.35 (dd, *J* = 17.2, 10.8 Hz, 1H,

CH_2=C*H*-C), 5.75 (s, 1H, C=C*H*-CH_2), 5.06 (d, *J* = 17.6 Hz, 1H, CH=C*H*$_2$), 4.90 (d, *J* = 10.8 Hz, 1H, CH=C*H*$_2$), 2.29 (m, 1H, CH-C*H*$_2$-CH), 2,11 (m, 2H, CH_2-C*H*-CH_2+CH-C*H*$_2$-CH), 1.87 (m, 2H, C-C*H*$_2$-CH_2), 1.49 (m, 1H, CH-C*H*-CH_3), 1.25 (m, 2H, CH_2-C*H*$_2$-CH), 0.89 (m, 6H, CH-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.91 (CH_2=*C*H-C), 136.05 (CH-*C*=CH), 129.86 (C=*C*H-CH_2), 109.86 (CH=*C*H$_2$), 40.33 (CH_2-*C*H-CH), 32.31 (CH-*C*H-CH_3), 29.54 (C=CH-*C*H$_2$), 25.96 (CH_2-*C*H$_2$-CH), 24.49 (C-*C*H$_2$-CH_2), 20.07 (CH-*C*H$_3$), 19.74 (CH-*C*H$_3$).

Synthesis of SiO-IVC



Scheme S3. Synthesis of **SiO-IVC**.

The epoxidation of (-)-β-pinene (6.1 g, 44.5 mmol) was carried out in dichloromethane by the dropwise addition of 40% peracetic acid (9.3 g, 48.9 mmol) in the presence of sodium carbonate (6.6 g, 62.3 mmol). The temperature of the reaction mixture was kept below 5 °C during the addition and then kept at this temperature for an additional 2 h. The reaction mixture was poured into water and the organic layer was separated, dried by $MgSO_4$ and evaporated to dryness. The residue colorless oil was desired epoxide, which was pure enough for next step without further purification. To an ice-cold saturated aqueous solution of carbon dioxide, the aforementioned crude epoxide was added dropwise under vigorous stirring. After stirring for 2 h at 0 °C, the reaction mixture was extracted with ethyl acetate. The combined organic solution was washed with saturated aqueous ammonium sulphate, dried over $MgSO_4$, and concentrated under vacuum. The residue was then purified by flash chromatography on silica gel to yield pure alcohol **3b** (4.4 g, 58.0%) as colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.63 (s, 1H, C=C*H*-CH_2), 3.94 (s, 2H, C-C*H*$_2$-OH), 2.07 (m, 3H, CH-C*H*$_2$-CH+CH_2-C*H*-C), 1.90 (m, 1H, C-C*H*$_2$-CH_2), 1.80 (m, 1H, C-C*H*$_2$-CH_2), 1.50 (m, 1H, CH_2-C*H*$_2$-CH), 1.23 (m, 1H, CH_2-C*H*$_2$-CH), 1.14 (d, *J* = 5.1 Hz, 6H, CH-C-(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.53 (CH_2-*C*=CH), 122.31 (C=*C*H-CH_2), 72.91 (CH-*C*-OH), 66.90 (C-*C*H$_2$-OH), 45.13 (CH_2-*C*H-C), 27.34 (C=CH-*C*H$_2$), 26.64 (C-*C*H$_3$), 26.61 (C-*C*H$_3$), 26.34 (CH_2-*C*H$_2$-CH), 23.66 (C-*C*H$_2$-CH_2).

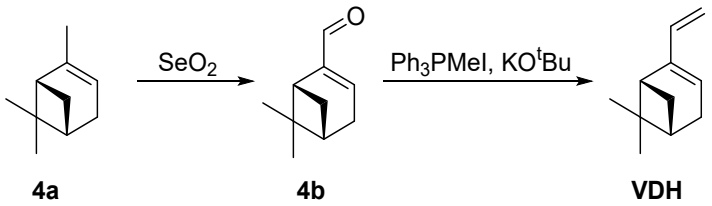
To a magnetically stirred slurry of pyridinium chlorochromate (8.4 g, 38.8 mmol) and sodium acetate (0.6 g, 7.8 mmol) in dichloromethane at 0 °C, **3b** (4.4 g, 25.8 mmol) was added in one portion. The resulting dark reaction mixture was gradually warmed to RT and further stirred for another 2 h. The reaction mixture was filtered through celite and the black residue was further washed with diethyl ether. The combined organic phases were washed successively with 5% aqueous NaOH, 5% aqueous HCl (100 mL), saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed at reduced pressure and the residue was purified through flash chromatographed on silica gel to afford pure aldehyde **3c** (3.0 g, 69.1%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.38 (s, 1H, C-C*H*=O), 6.79 (s, 1H, C=C*H*-CH_2), 2.47 (m, 2H, CH-C*H*$_2$-CH), 2.13 (m, 1H, CH_2-C*H*-C), 1.96 (m, 1H, C-C*H*$_2$-CH_2), 1.58 (m, 1H, C-C*H*$_2$-CH_2), 1.22 (dd, *J* = 7.3, 2.3 Hz, 2H, CH_2-C*H*$_2$-CH), 1.19 (d, *J* = 2.3 Hz, 6H, CH-C-(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.06 (C-*C*H=O), 151.41 (CH_2-*C*=CH), 141.44 (C=*C*H-CH_2), 72.22 (CH-

C-OH), 44.81 (CH_2-*C*H-C), 28.19 (C=CH-*C*H_2), 27.14 (C-*C*H_3), 26.90 (C-*C*H_3), 22.69 (CH_2-*C*H_2-CH), 22.19 (C-*C*H_2-CH_2).

3d was synthesized as the procedure for **IVC**. For **3c** (3.0 g, 19.0 mmol), Ph_3PMeI (8.9 g, 21.8 mmol) and *tert*-BuOK (2.7 g, 24.0 mmol) were used, and **3d** was obtained as colorless liquid (2.52 g, 79.8%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.36 (dd, *J* = 17.5, 10.7 Hz, 1H, CH_2=C*H*-C), 5.75 (s, 1H, C=C*H*-CH_2), 5.06 (d, *J* = 17.5 Hz, 1H, CH=CH_2), 4.91 (d, *J* = 10.7 Hz, 1H, CH=CH_2), 2.36 (d, *J* = 16.8 Hz, 1H, CH-CH_2-CH), 2.23 (d, *J* = 18.3 Hz, 1H, CH-CH_2-CH), 2.16-1.90 (m, 3H, CH_2-C*H*-C+C-CH_2-CH_2), 1.56 (m, 1H, CH_2-CH_2-CH), 1.28 (m, 1H, CH_2-CH_2-CH), 1.20 (d, *J* = 6.3 Hz, 6H, CH-C-(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.64 (CH_2=*C*H-C), 136.04 (CH-*C*=CH), 129.27 (C=*C*H-CH_2), 110.20 (CH=*C*H_2), 72.61 (CH-*C*-OH), 45.26 (CH_2-*C*H-C), 27.47 (C=CH-*C*H_2), 27.43 (C-*C*H_3), 26.43 (C-*C*H_3), 24.76 (CH_2-*C*H_2-CH), 23.50 (C-*C*H_2-CH_2).

3d (2.52 g, 15.2 mmol) and triethylamine (15.3 g, 151.6 mmol) was dissolved in dichloromethane at 0 °C, and trimethylsilyl trifluoromethanesulphonate (6.74 g, 30.0 mmol) was subsequently added. The reaction mixture was stirred at 0 °C for 1 h and quenched by addition of aqueous $NaHCO_3$. The organic solution was washed by saturated aqueous $NaHCO_3$ (2 × 50 mL) and dried over $MgSO_4$. The solvent was removed at reduced pressure and the residue was purified through flash chromatographed on neutral alumina to afford **SiO-IVC** as colorless liquid in a yield of 85.5% (3.1 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.38 (dd, *J* = 17.4, 10.5 Hz, 1H, CH_2=C*H*-C), 5.76 (s, 1H, C=C*H*-CH_2), 5.06 (d, *J* = 17.4 Hz, 1H, CH=CH_2), 4.90 (d, *J* = 10.5 Hz, 1H, CH=CH_2), 2.35 (d, *J* = 16.9 Hz, 1H, CH-CH_2-CH), 2.23 (d, *J* = 18.8 Hz, 1H, CH-CH_2-CH), 2.06 (m, 1H, CH_2-C*H*-C), 1.94 (m, 2H, C-CH_2-CH_2), 1.51 (m, 1H, CH_2-CH_2-CH), 1.26 (m, 1H, CH_2-CH_2-CH), 1.20 (d, *J* = 5.5 Hz, 6H, CH-C-(CH_3)$_2$), 0.11 (s, 1H, O-Si(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 139.80 (CH_2=*C*H-C), 136.00 (CH-*C*=CH), 129.88 (C=*C*H-CH_2), 109.91 (CH=*C*H_2), 75.62 (CH-*C*-O), 46.07 (CH_2-*C*H-C), 27.66 (C=CH-*C*H_2), 27.50 (C-*C*H_3), 27.22 (C-*C*H_3), 24.87 (CH_2-*C*H_2-CH), 23.49 (C-*C*H_2-CH_2), 2.67 (O-Si(*C*H_3)$_3$).

Synthesis of VDH



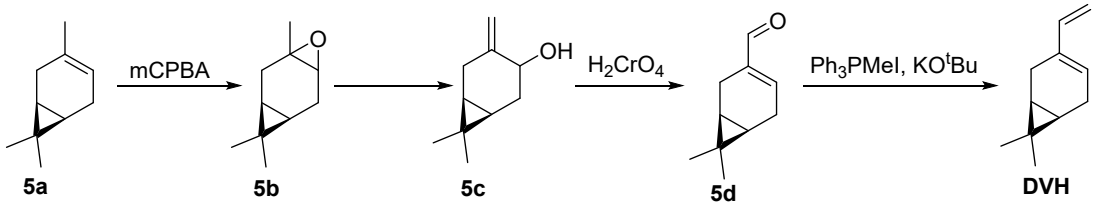
Scheme S4. Synthesis of **VDH**.

A solution of SeO_2 (34.9 g, 315.0 mmol) in anhydrous EtOH (350 mL) was refluxed for 30 min, and α-pinene (40.9 g, 300.0 mmol) in EtOH (60 mL) was added dropwise at 70.0 °C. After stirring for 5 h, the reaction mixture was cooled to RT and filtrated to remove the residual selenium. The mixture was extract with ethyl ether (100 mL × 3), and the combined organic solution was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was distilled in a reduced pressure to provide **4b** as colorless oil in 52.5% yield (23.6 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.36 (dd, *J* = 17.6, 10.7 Hz, 1H, CH_2=C*H*-C), 5.55 (s, 1H, C=C*H*-CH_2), 5.05 (d, *J* = 17.4 Hz, 1H, CH=CH_2), 4.88 (d, *J* = 11.0 Hz, 1H, CH=CH_2), 2.56 (m, 1H, C-C*H*-C), 2.39 (m, 3H, C-C*H*-CH_2+CH-CH_2-CH), 2.12 (s, 1H, CH-CH_2-CH), 1.33 (s, 3H, C-CH_3), 1.14 (d, *J* = 8.7 Hz, 1H, CH-CH_2-CH), 0.80 (s, 3H, C-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.62 (C-*C*H=O), 152.36

(CH-*C*=CH), 148.31 (C=*C*H-CH_2), 42.33 (CH_2-*C*H-C), 39.98 (C-*C*H-C), 38.28 (CH-*C*-CH_3), 34.11 (CH-*C*H_2-CH), 32.98 (C=CH-*C*H_2), 24.63 (C-*C*H_3), 22.72 (C-*C*H_3).

VDH was synthesized as the procedure for **IVC**. For **4b** (15.0 g, 100.0 mmol), Ph_3PMeI (48.8 g, 120.0 mmol) and *tert*-BuOK (14.8 g, 132.0 mmol) were used, and **VDH** was obtained in a yield of 84.3% as colorless liquid (12.5 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.37 (dd, *J* = 17.2, 10.8 Hz, 1H, CH_2=C*H*-C), 5.55 (s, 1H, C=C*H*-CH_2), 5.05 (d, *J* = 17.2 Hz, 1H, CH=CH_2), 4.88 (d, *J* = 10.8 Hz, 1H, CH=CH_2), 2.36 (m, 5H, C-C*H*-C+C-C*H*-CH_2+CH-CH_2-CH+CH-CH_2-CH), 1.33 (s, 3H, C-CH_3), 1.15 (s, 1H, CH-CH_2-CH), 0.79 (s, 3H, C-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.89 (CH_2=*C*H-C), 137.95 (CH-*C*=CH), 124.63 (C=*C*H-CH_2), 109.70 (CH=*C*H_2), 41.15 (CH_2-*C*H-C), 40.41 (C-*C*H-C), 37.84 (CH-*C*-CH_3), 32.01 (CH-*C*H_2-CH), 31.38 (C=CH-*C*H_2), 26.49 (C-*C*H_3), 20.88 (C-*C*H_3).

Synthesis of DVH



Scheme S5. Synthesis of **DVH**.

The compound **5d** was synthesized according to previous reports.[1] (+)-3-carene (68.0 g, 500.0 mmol) was epoxidized with *m*-chloroperbenzoic acid (109.0 g of 85.0% purity, 540.0 mmol), and **5b** was obtained as colorless oil after distillation (60.0 g, 85.0%). Then, *n*-Butyllithium (120.0 mL of 2.5 M in hexanes, 300.0 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (51.0 mL, 300.0 mmol) in toluene at 0 °C. After 15 min, a solution of diethylaluminum chloride (302.0 mL of 1.0 M in hexane, 302.0 mmol) was introduced, and the resulting white suspension was stirred for another 30 min. A solution of **5b** (22.3 g, 150.0 mmol) was added to the above mixture. After stirring at 0 °C for 30 min, ice-cold 10% hydrochloric acid was cautiously added to quench the reaction. The resulting mixture was extracted with Et_2O (100 mL × 5), and the combined organic solution were dried over anhydrous Na_2SO_4, evaporated to afford **5c** (22.0 g, 98.0%) as an oily solid. A solution of **5c** (10.0 g, 66.0 mmol) in DCM was treated with 2 M aqueous chromic acid (66.0 mL, 131.0 mmol) at 60 °C, and the reaction mixture was stirred for 2 h. After routine workup, **5d** was obtained in a yield of 70.0% (7.7 g). Finally, **DVH** was synthesized as the procedure for **IVC**. For **5d** (7.7 g, 51.0 mmol), Ph_3PMeI (25.0 g, 62.0 mmol) and *tert*-BuOK (7.7 g, 68.0 mmol) were used and **DVH** was obtained in a yield of 82.3% as colorless liquid (6.2 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.31 (dd, *J* = 17.2, 10.8 Hz, 1H, CH_2=C*H*-C), 5.61 (s, 1H, C=C*H*-CH_2), 5.09 (d, *J* = 17.6 Hz, 1H, CH=CH_2), 4.85 (d, *J* = 10.8 Hz, 1H, CH=CH_2), 2.47 (m, 2H, C=CH-CH_2), 2.20 (m, 2H, C-CH_2-CH), 1.05 (s, 3H, C-CH_3), 0.80 (m, 1H, CH_2-C*H*-C), 0.75 (s, 3H, C-CH_3), 0.69 (m, 1H, CH_2-C*H*-C). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.03 (CH_2=*C*H-C), 133.63 (CH-*C*=CH), 128.60 (C=*C*H-CH_2), 109.30 (CH=*C*H_2), 28.41 (C=CH-*C*H_2), 21.45 (C-*C*H_2-CH), 18.75 (CH_2-*C*H-C), 17.88 (C-*C*H_3), 17.32 (C-*C*H_3), 17.04 (CH-CH_2-*C*H), 13.42 (CH-*C*-CH_3).

Polymerization of monomers

In the glovebox, a chlorobenzene solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (10.0 μmol) was added to a chlorobenzene solution (1 mL) of rare-earth metal complex (10.0 μmol). Then, 5 equivalents of TIBA (0.5 mL, 50.0 μmol, 1.0 M in toluene) was added to **IVC** (150 mg, 1.0 mmol) solution and further stirring for 5 minutes. The monomer mixture was subsequently added to the catalyst solution with vigorously stirring to start the polymerization for a desired time. The viscous solution was moved out of glovebox and poured into a large quantity (60.0 mL) of methanol with butylated hydroxytoluene (BHT) to precipitate the polymer, which was dried under vacuum at 60 °C to a constant weight.

Table S1. Polymerization of **IVC** by complex **1**.[a]

Entry	[**IVC**]/[**1**]	*t* / h	Con. / %	3,4-Selectivity[b] / %	M_n[e]	M_w / M_n[e]
1[b]	100	3	98	>99	20.6	2.02
2[c]	100	2	86	>99	18.2	1.93
3	50	0.5	58	>99	3.90	2.09
4	50	1	98	>99	7.01	2.01
5	100	5min	10	>99	1.10	2.01
6	100	25min	44	>99	5.70	2.01
7	100	35min	61	>99	8.83	1.98
8	100	45min	80	>99	11.4	2.01

[a]Conditions: [**IVC**]:[**1**]:$[Ph_3C][B(C_6F_5)_4]$:[TIBA] = 100:1:1:5, [Cat.] = 10 μmol, [**IVC**] = 1 g / 15 mL in chlorobenzene at 25 °C. [b]Without TIBA. [c]In toluene. [d]Measured by ^{1}H NMR spectroscopy in $CDCl_3$. [e]Determined by gel permeation chromatography (GPC) in THF at 35 °C against a polystyrene standard. In the unit of 10^4 g mol^{-1}.

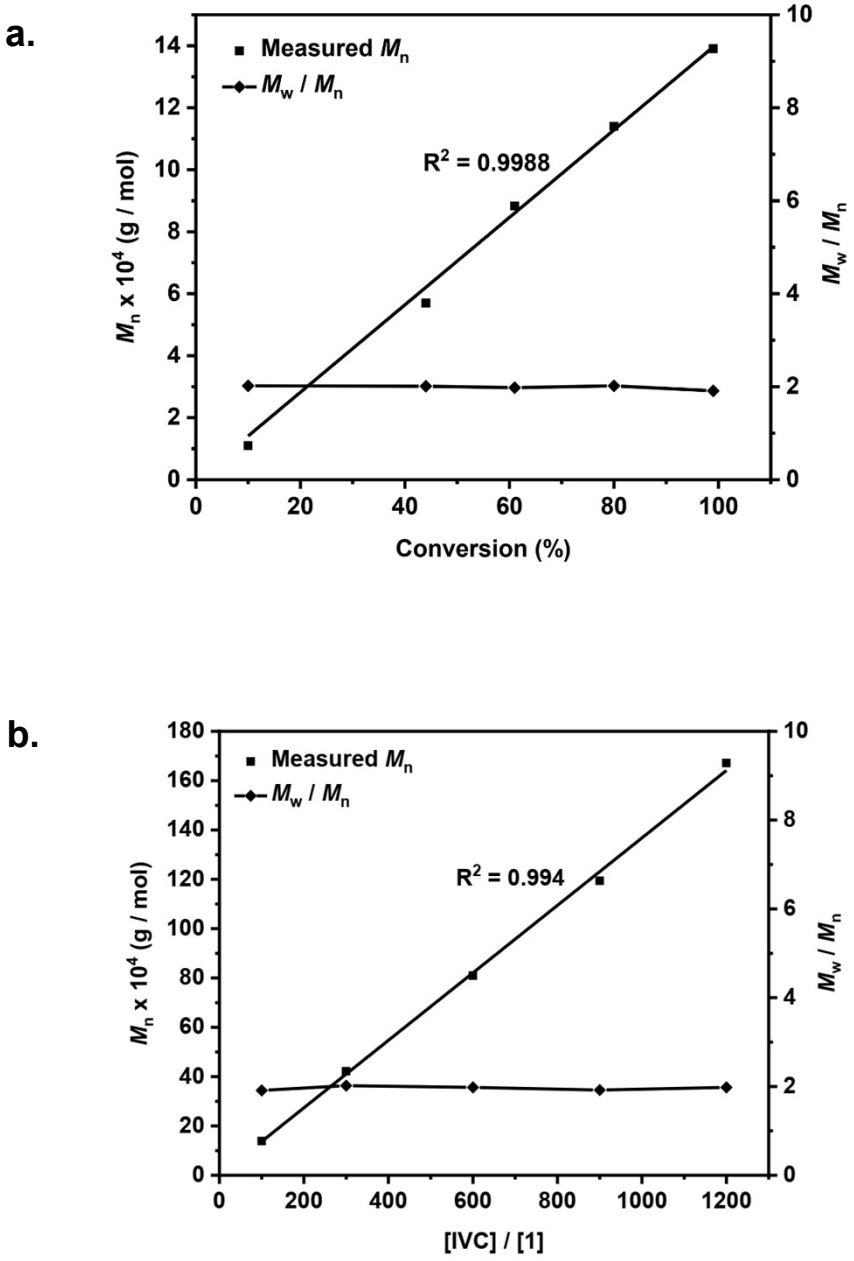


Figure S1. Polymerization of **IVC** with complex **1**/[$(Ph_3C)(B(C_6F_5)_4)$] as a precursor: molecular weight *vs* conversion (a) and molecular weight *vs* [**IVC**]/[**1**] (b).

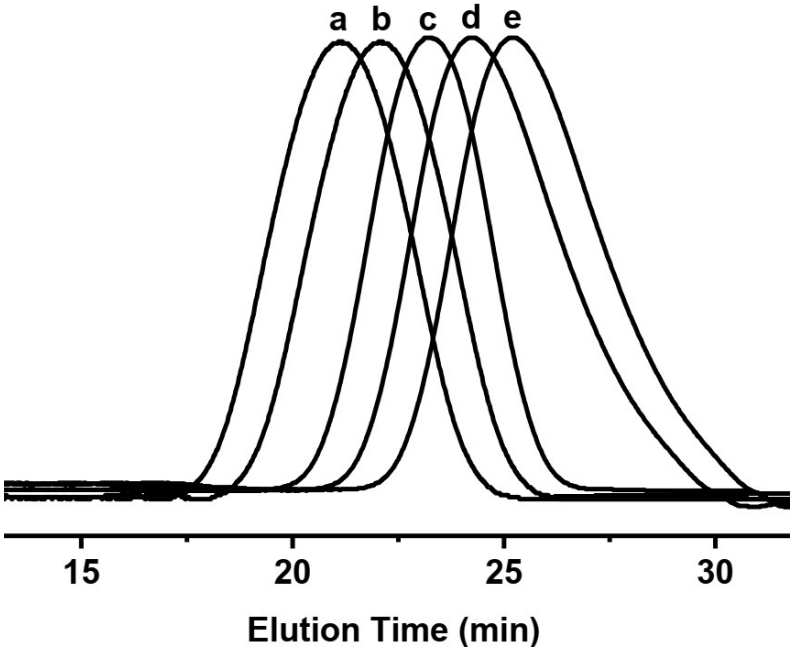


Figure S2. GPC curves of different monomer conversion. [**IVC**]/[**1**] = 100, conversion: 99% (a), 80% (b), 61% (c), 44% (d), and 10% (e) in Table S1.

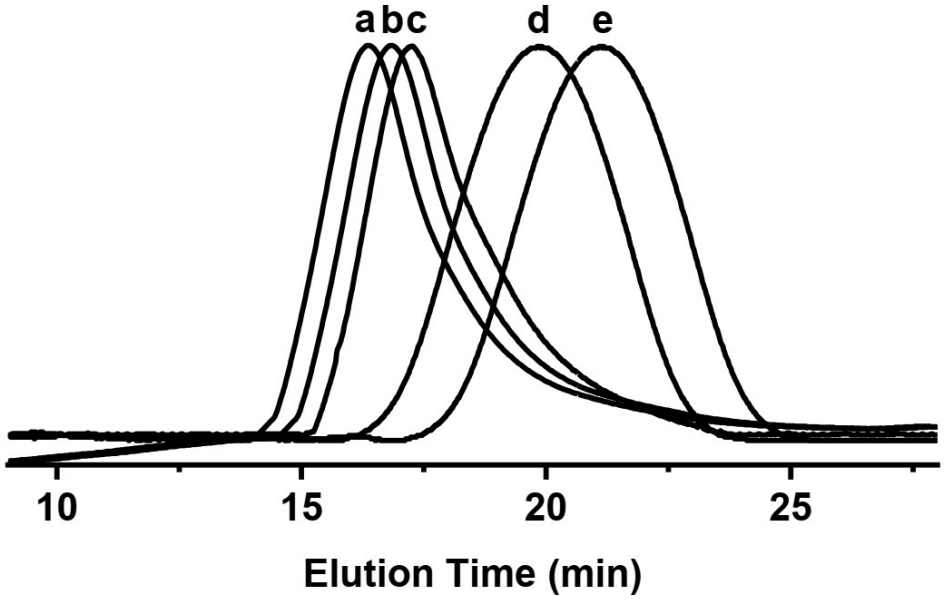


Figure S3. GPC curves of different monomer feeds catalyzed by complex **1**. [**IVC**]/[**1**]: 1200 (a), 900 (b), 600 (c), 300 (d), and 100 (e) in Table 2.

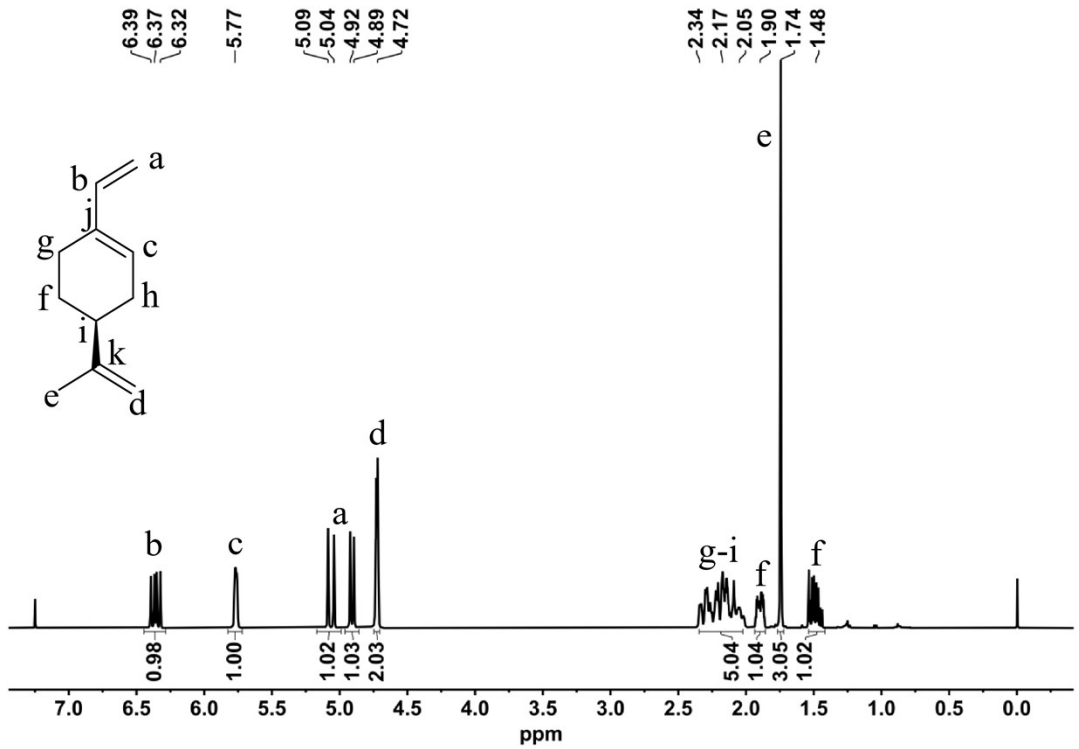


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **IVC**.

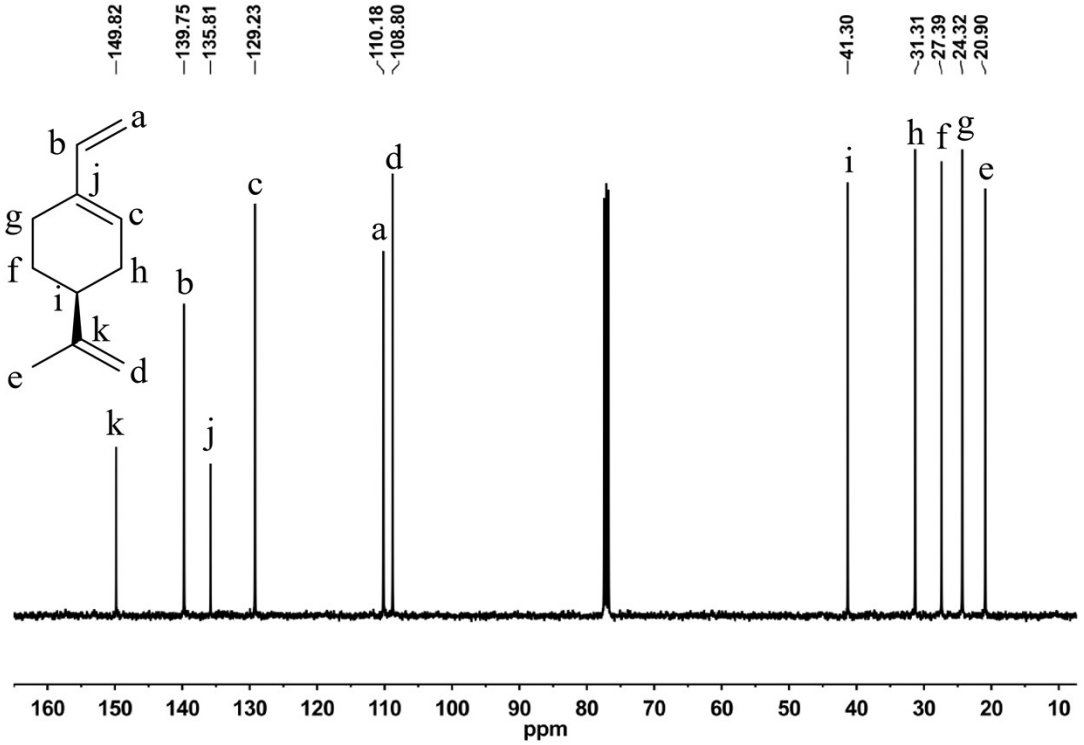


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **IVC**.

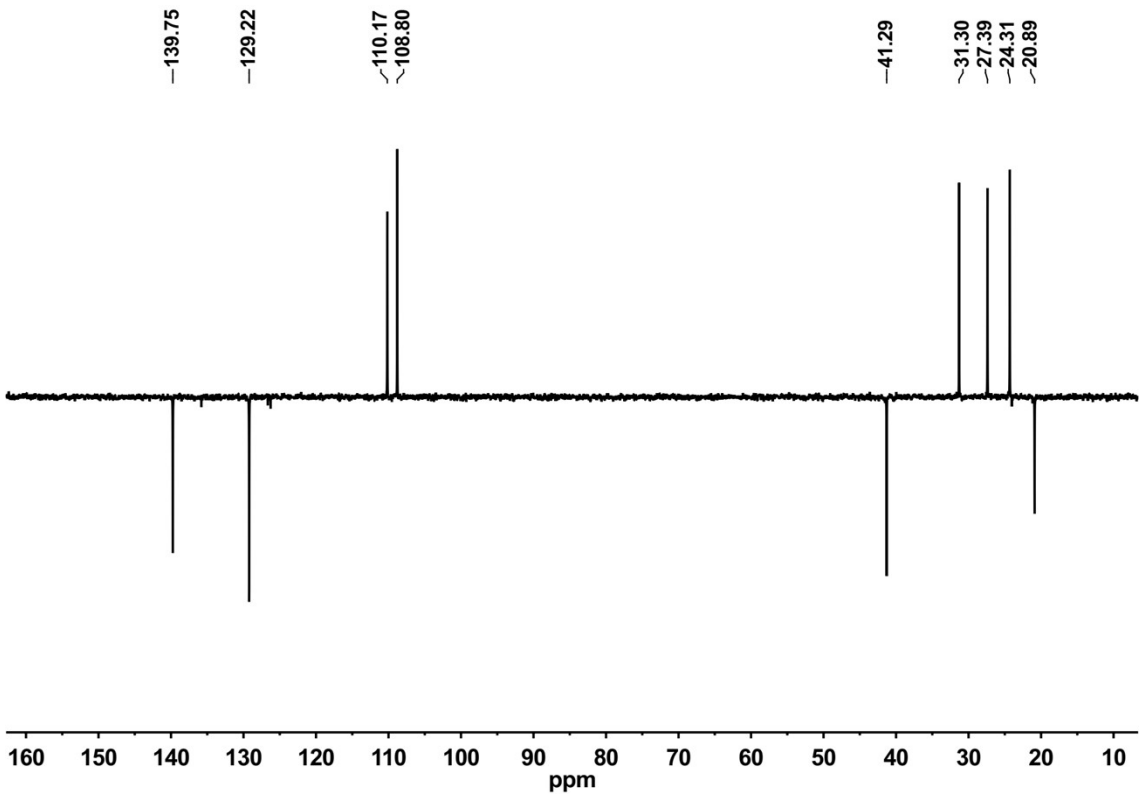


Figure S6. DEPT^{135} spectrum (100 MHz, $CDCl_3$, 25 °C) of **IVC**.

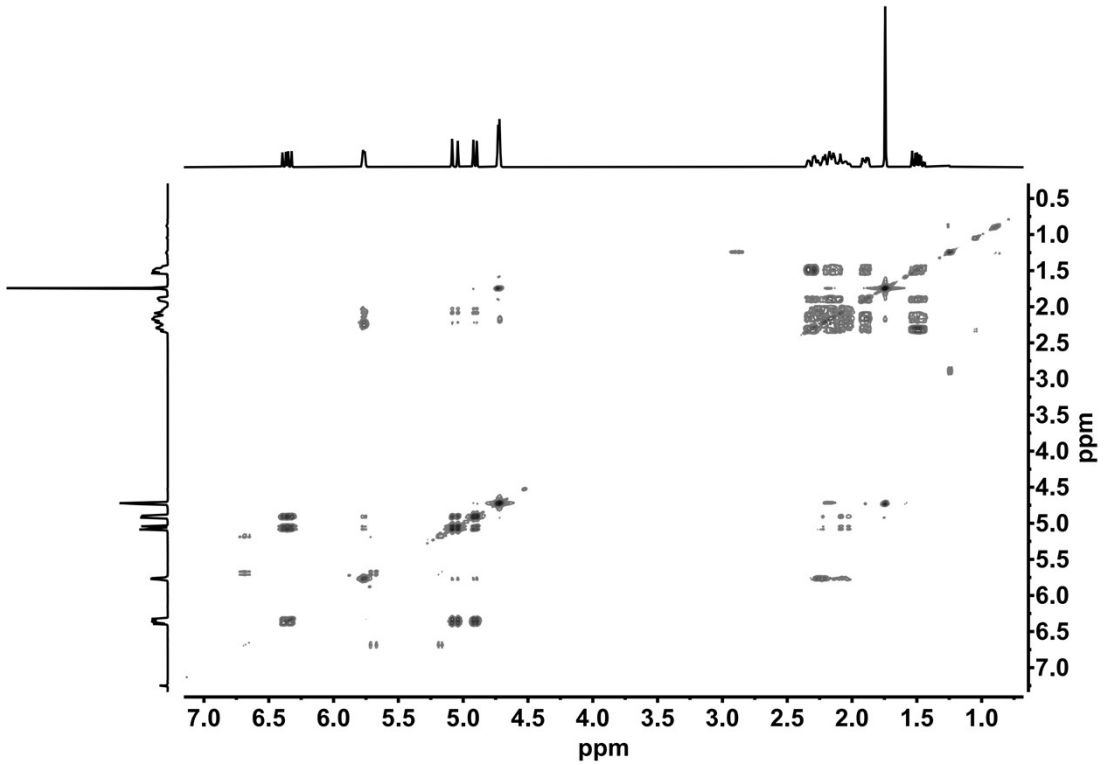


Figure S7. ^{1}H-^{1}H COSY spectrum of **IVC**.

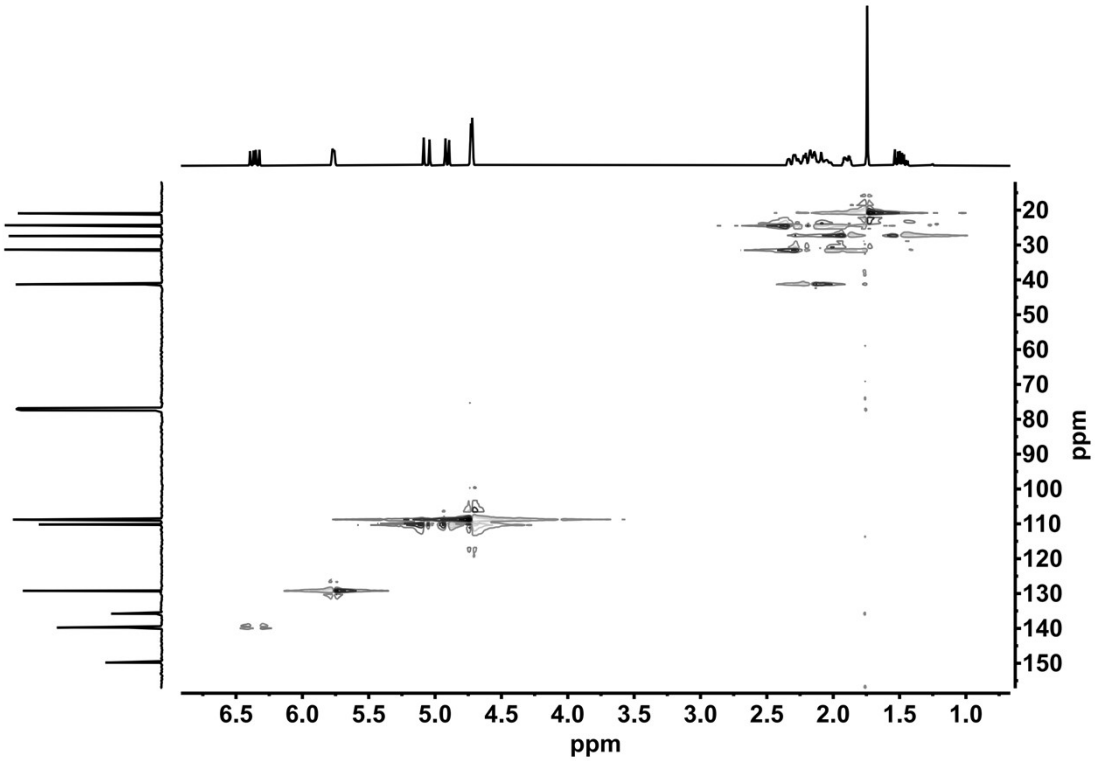


Figure S8. ^{1}H-^{13}C HSQC spectrum of **IVC**.

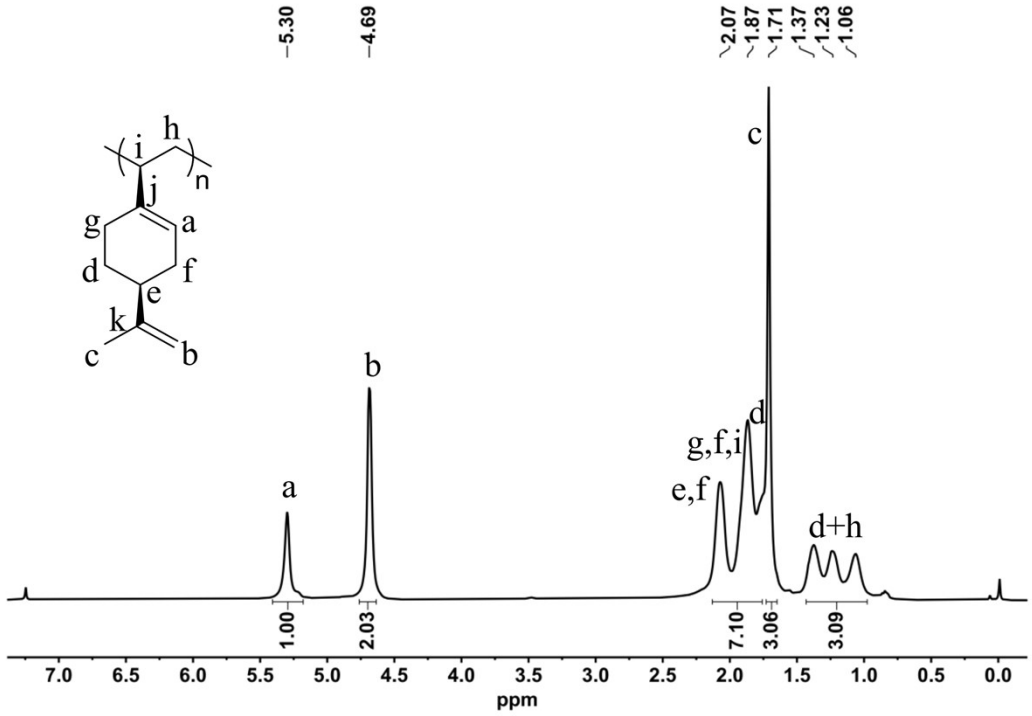


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of PIVC (Entry 2 in Table 1).

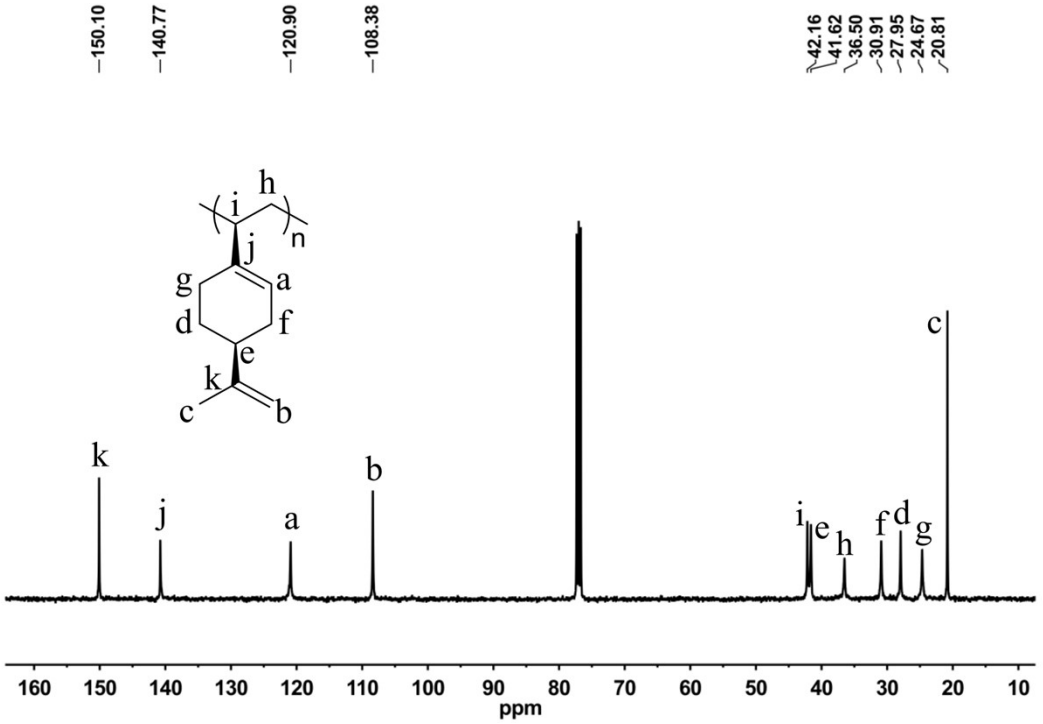


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of PIVC (Entry 2 in Table 1).

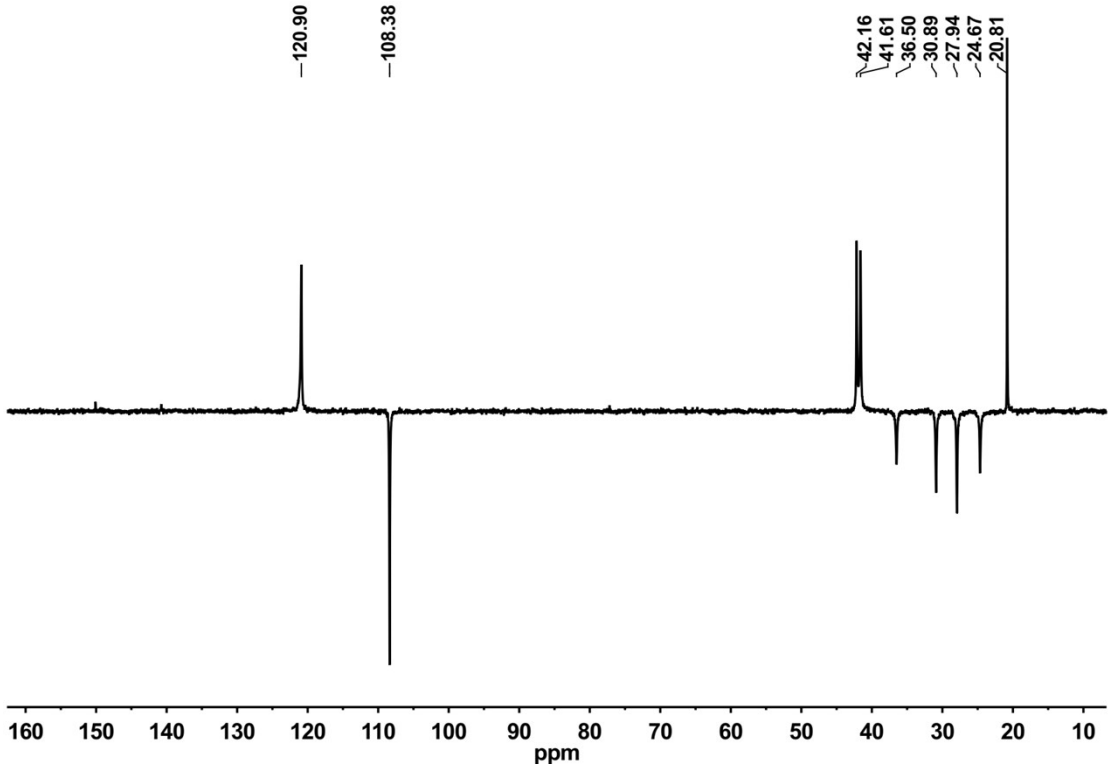


Figure S11. DEPT^{135} spectrum (100 MHz, $CDCl_3$, 25 °C) of PIVC (Entry 2 in Table 1).

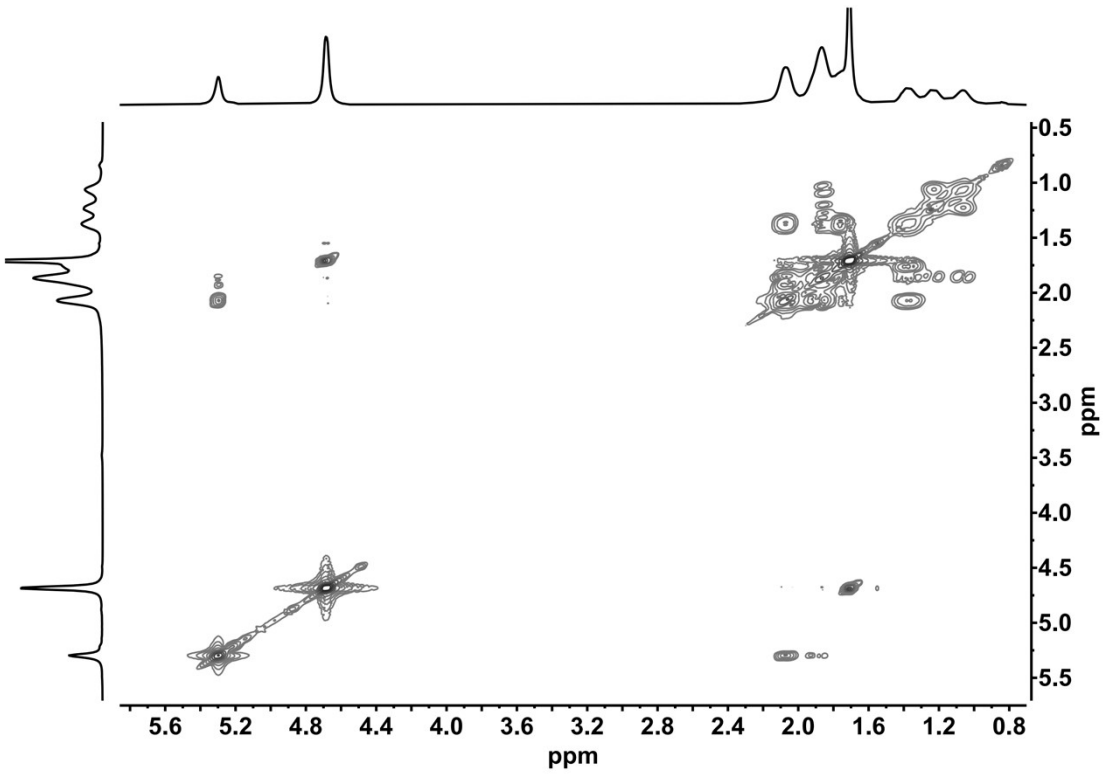


Figure S12. ^{1}H-^{1}H COSY spectrum of PIVC (Entry 2 in Table 1).

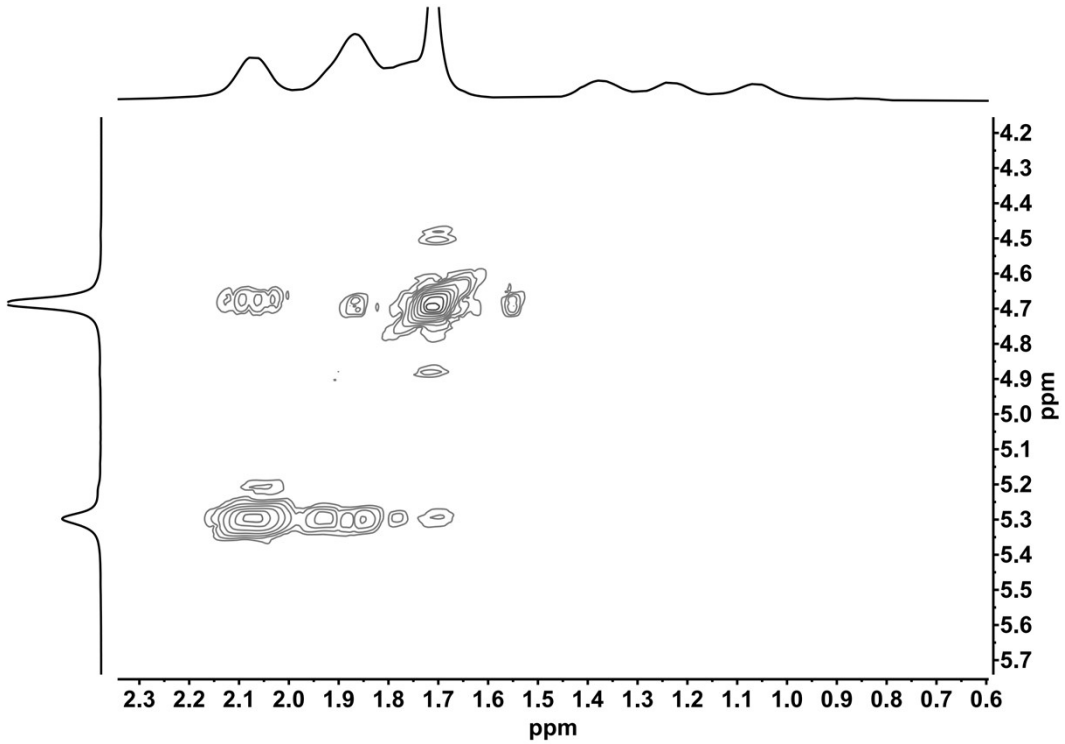


Figure S13. Part of ^{1}H-^{1}H COSY spectrum of PIVC (Entry 2 in Table 1).

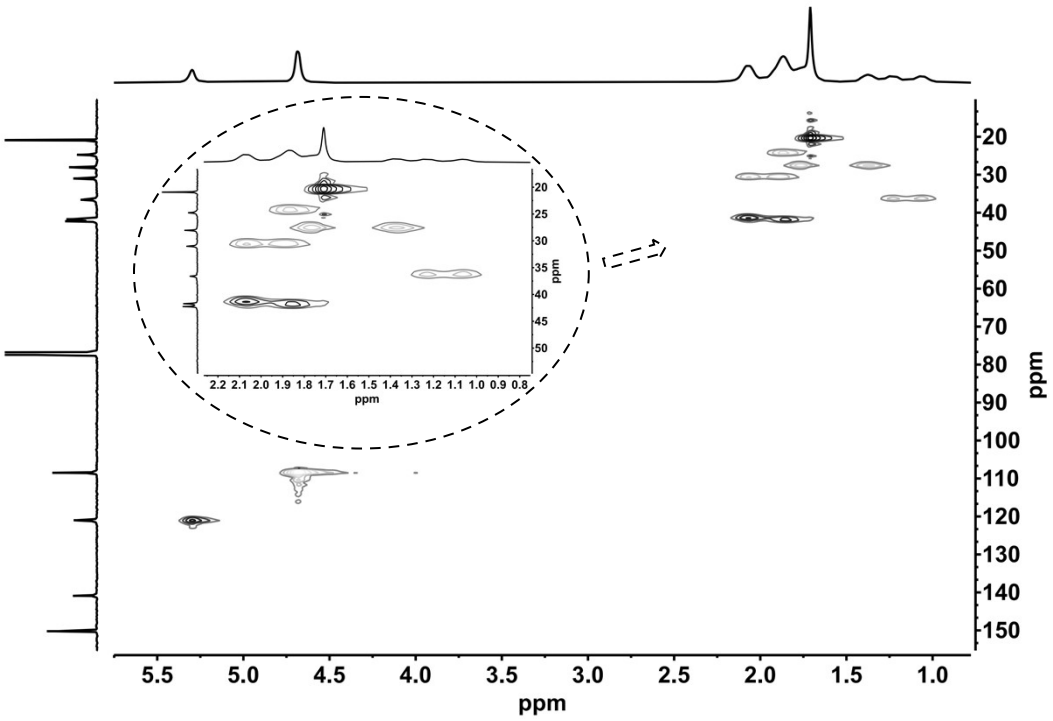


Figure S14. ^{1}H-^{13}C HSQC spectrum of PIVC (Entry 2 in Table 1).

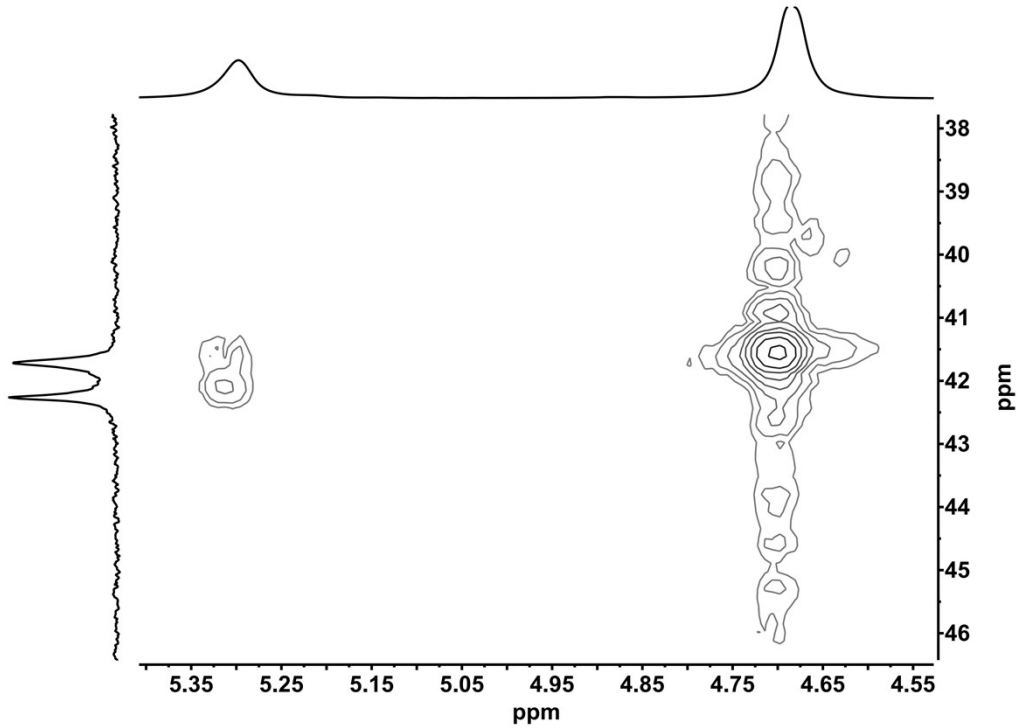


Figure S15. Part of ^{1}H-^{13}C HMBC spectrum of PIVC (Entry 2 in Table 1).

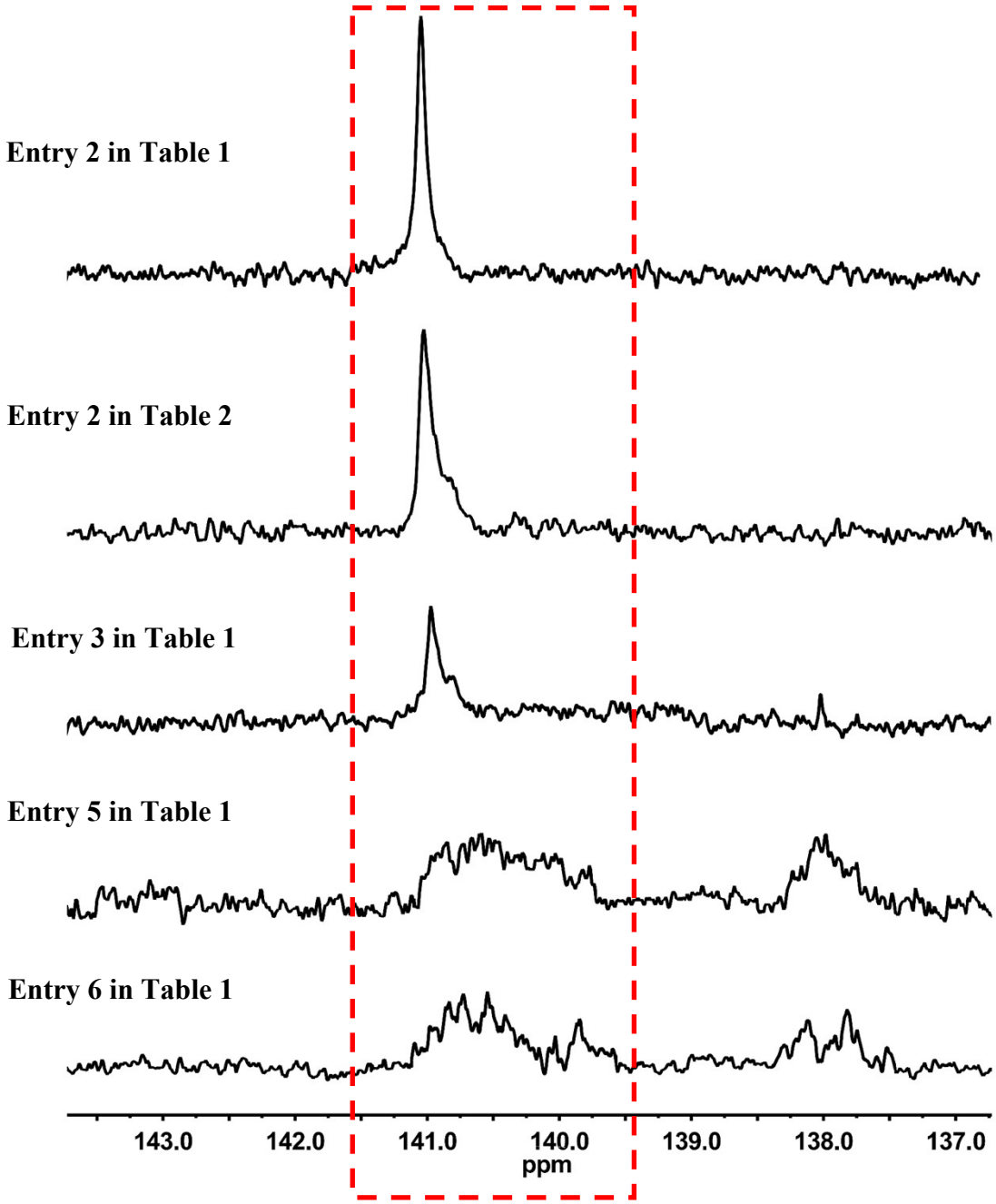


Figure S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of PIVC in Table 1 and Table 2.

NOTE: The signal of the carbon atom in the side chain $C(CH_2\text{-})=CH\text{-}$ at δ 139.75 ppm, which is directly bonded to the polymeric chain, is diagnostic for the isotacticity of the polymer. As the 3,4-isotactic polyisoprene (*J. Am. Chem. Soc.* **2005**, *127*, 14562-14563), the peaks in the red frame of Figure S16 were probably assigned to the polymeric sequence with *mm* triad, and the leftmost peak at δ 139.75 ppm was belonged to *mmmm* sequence.

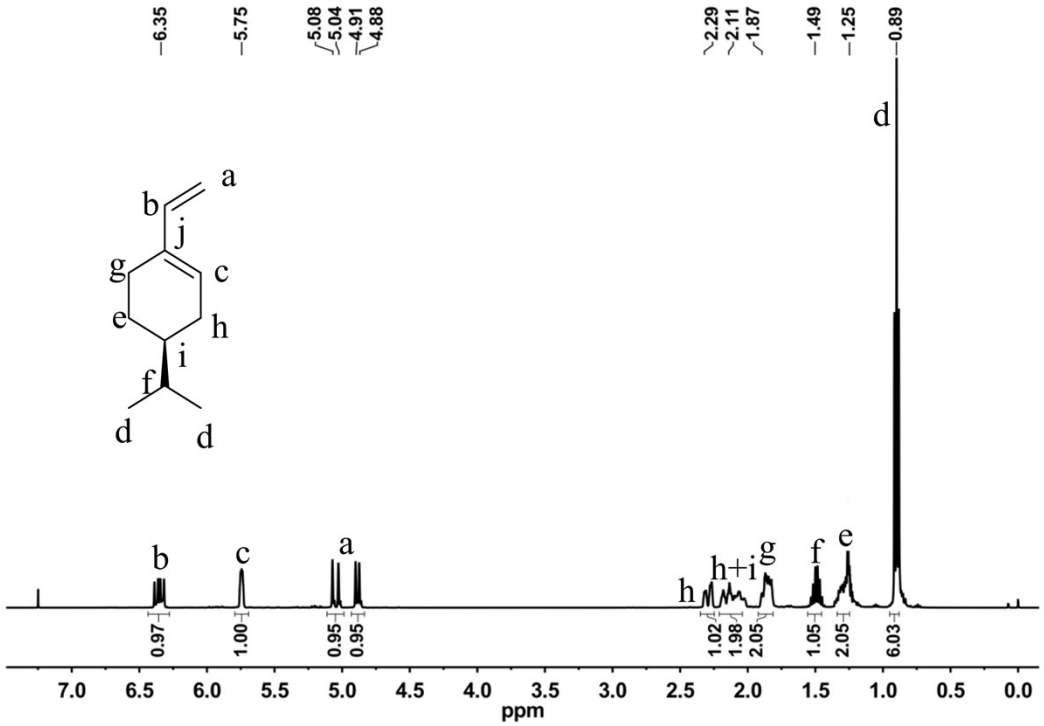


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **H-IVC**.

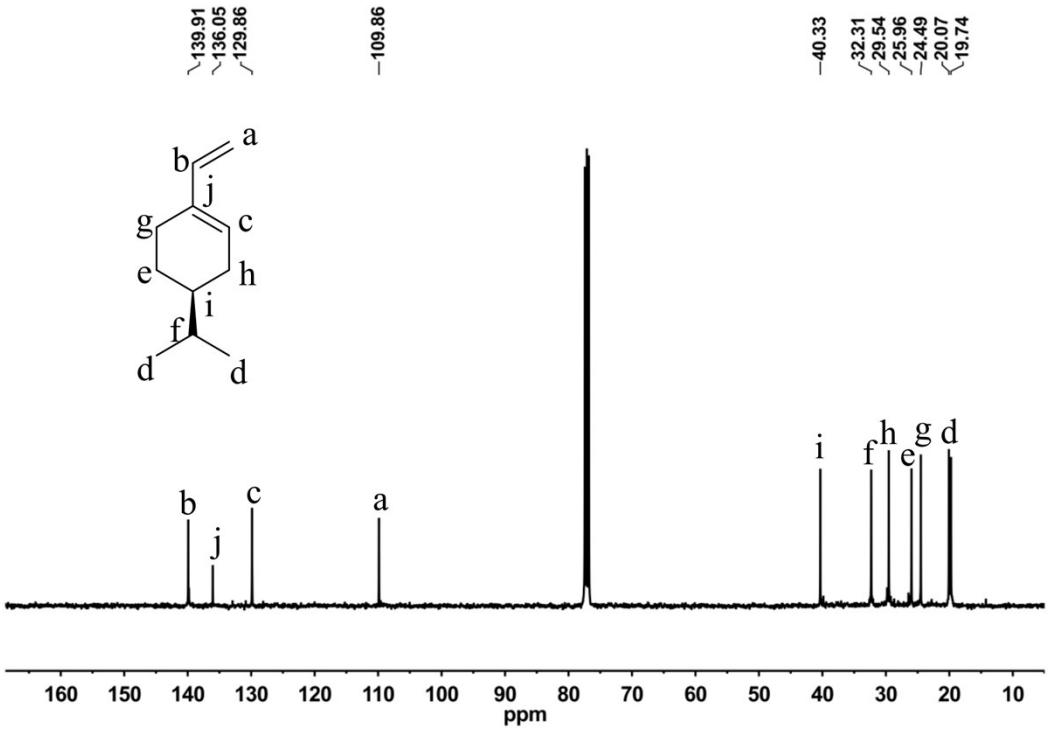


Figure S18. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **H-IVC**.

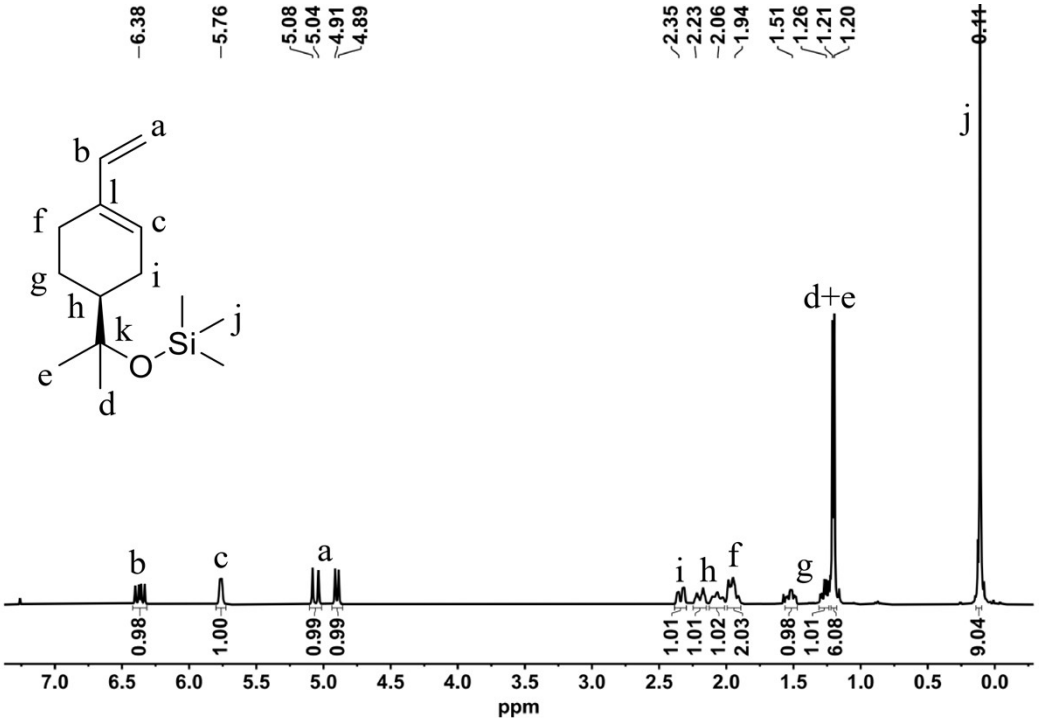


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **SiO-IVC**.

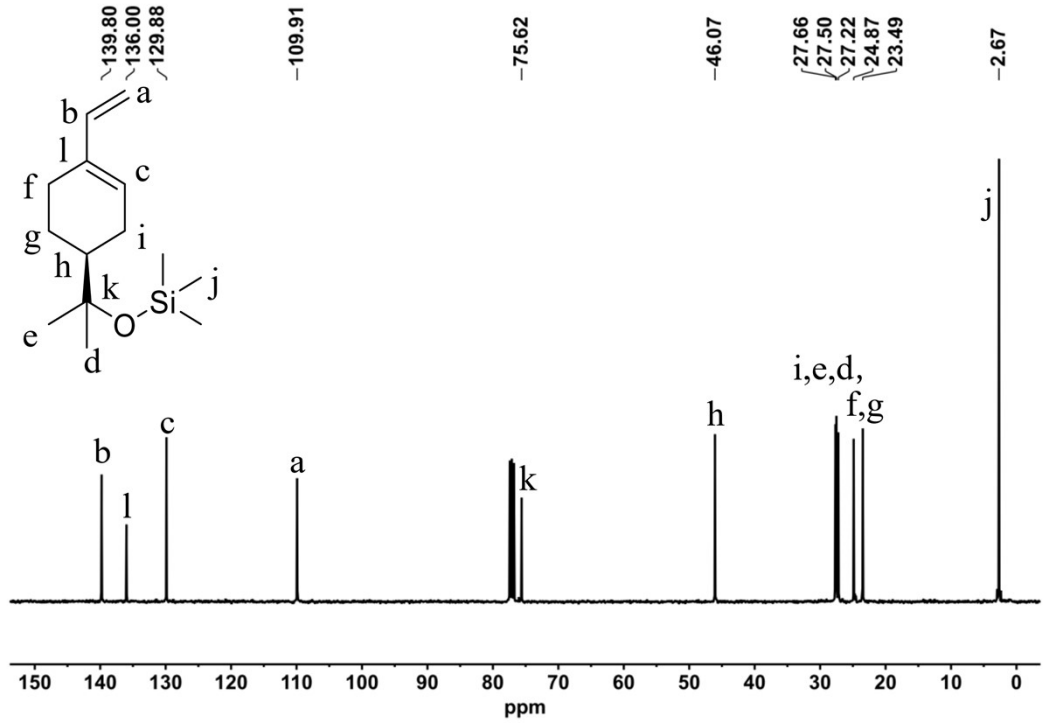


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **SiO-IVC**.

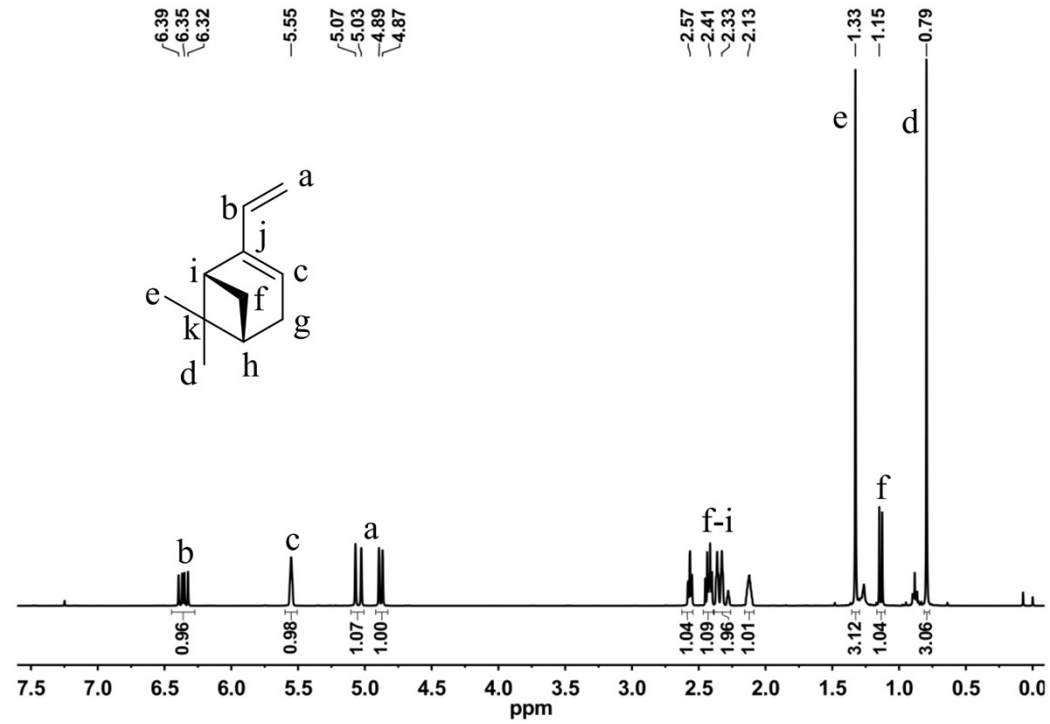


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **VDH**.

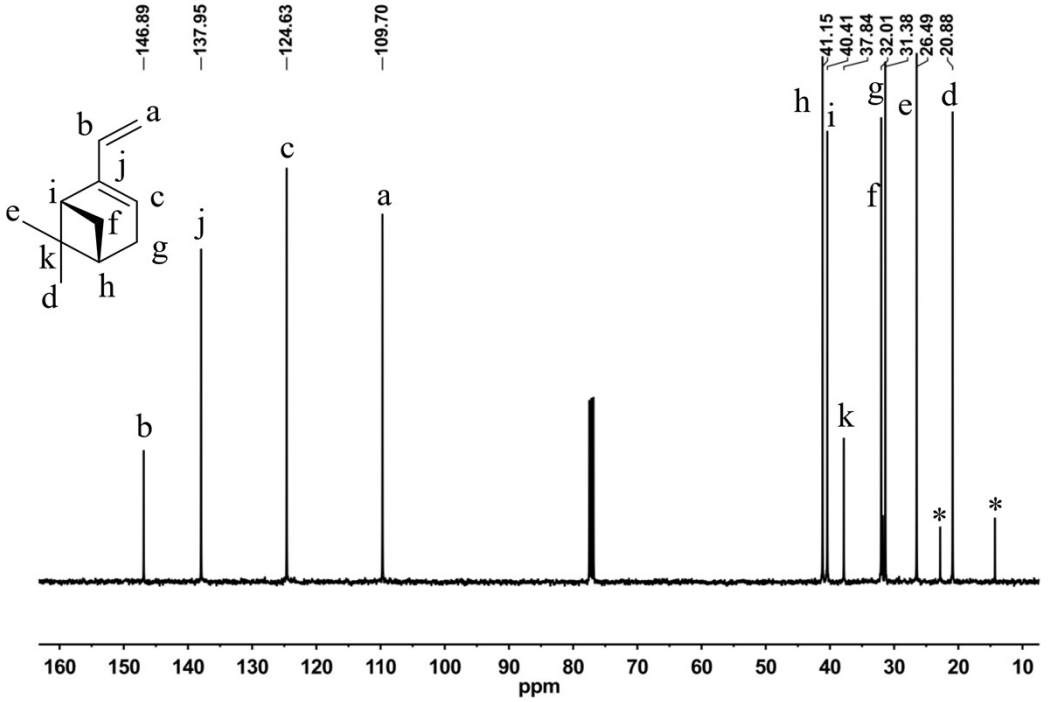


Figure S22. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **VDH**.

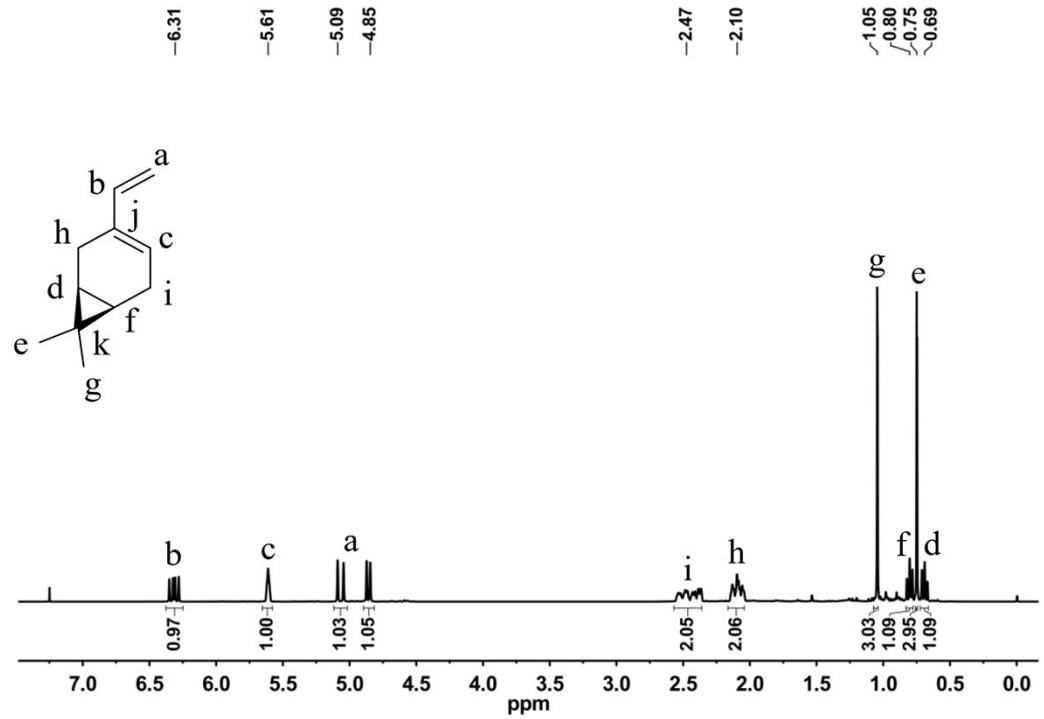


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of **DVH**.

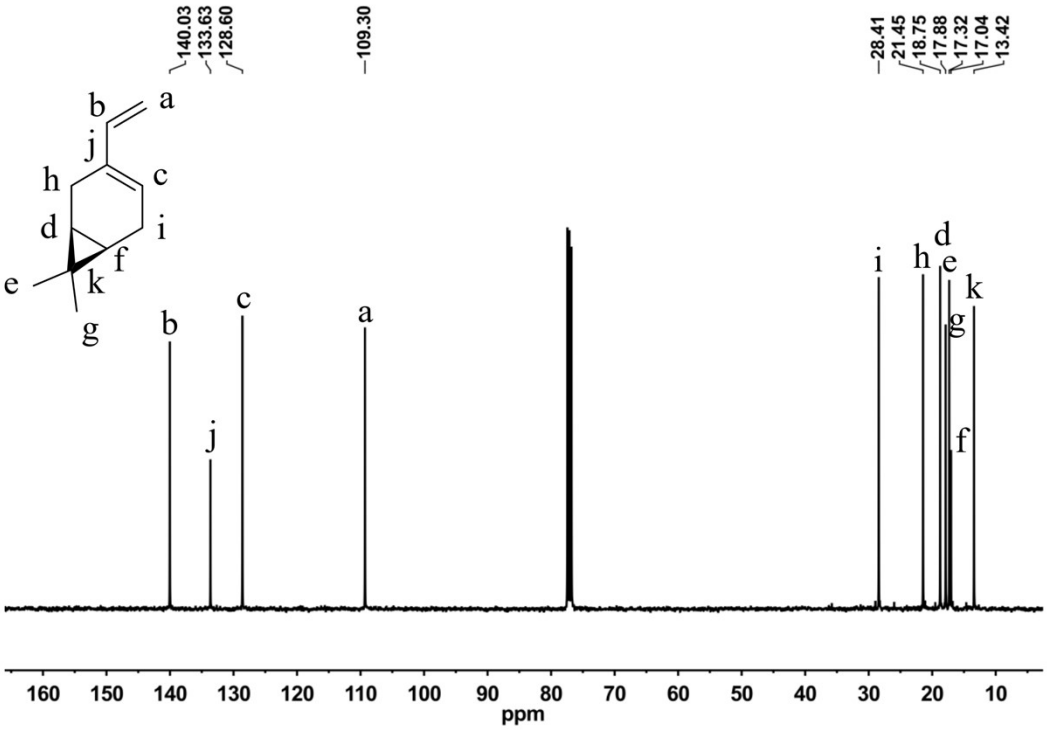


Figure S24. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of **DVH**.

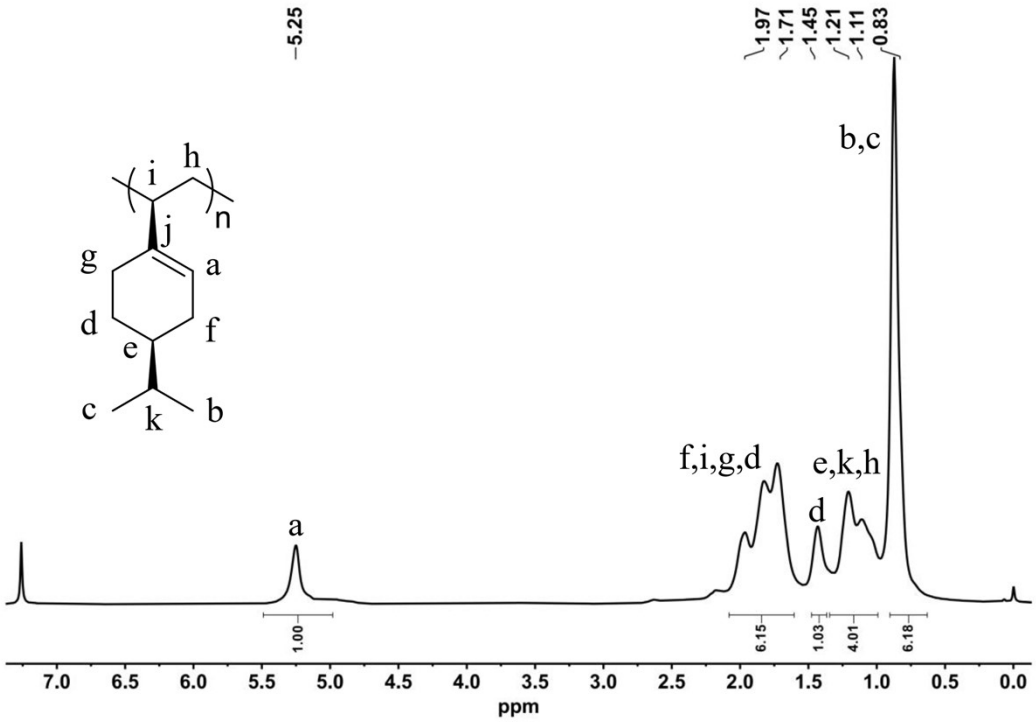


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of P(H-IVC) (Entry 1 in Table 3).

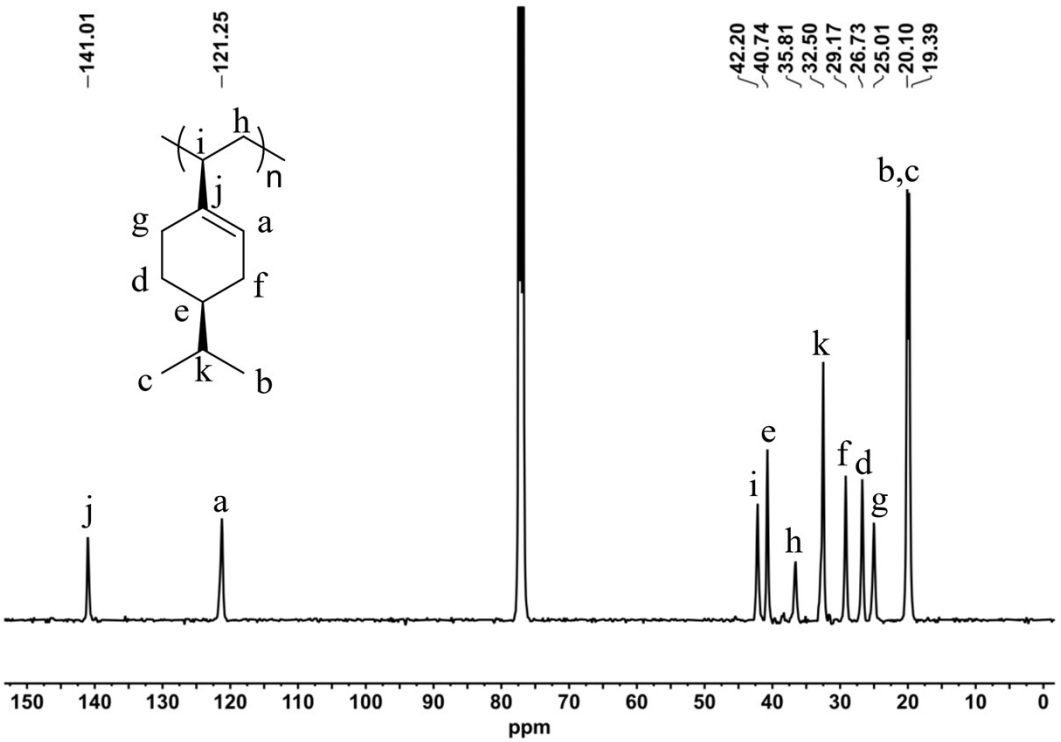


Figure S26. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of P(H-IVC) (Entry 1 in Table 3).

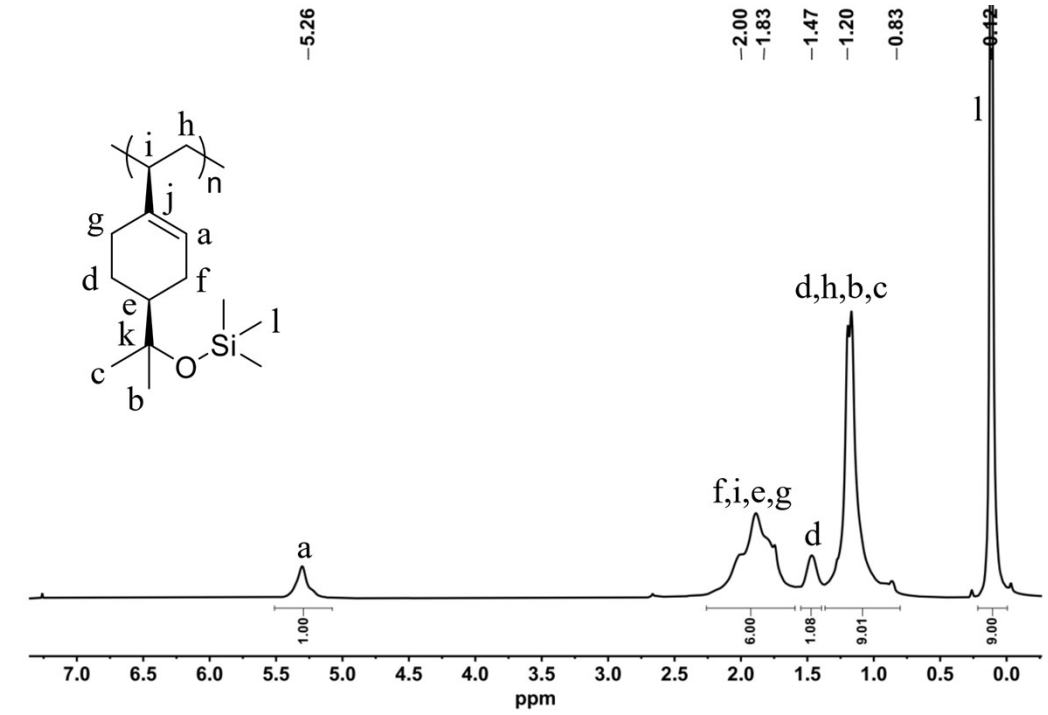


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of P(SiO-IVC) (Entry 2 in Table 3).

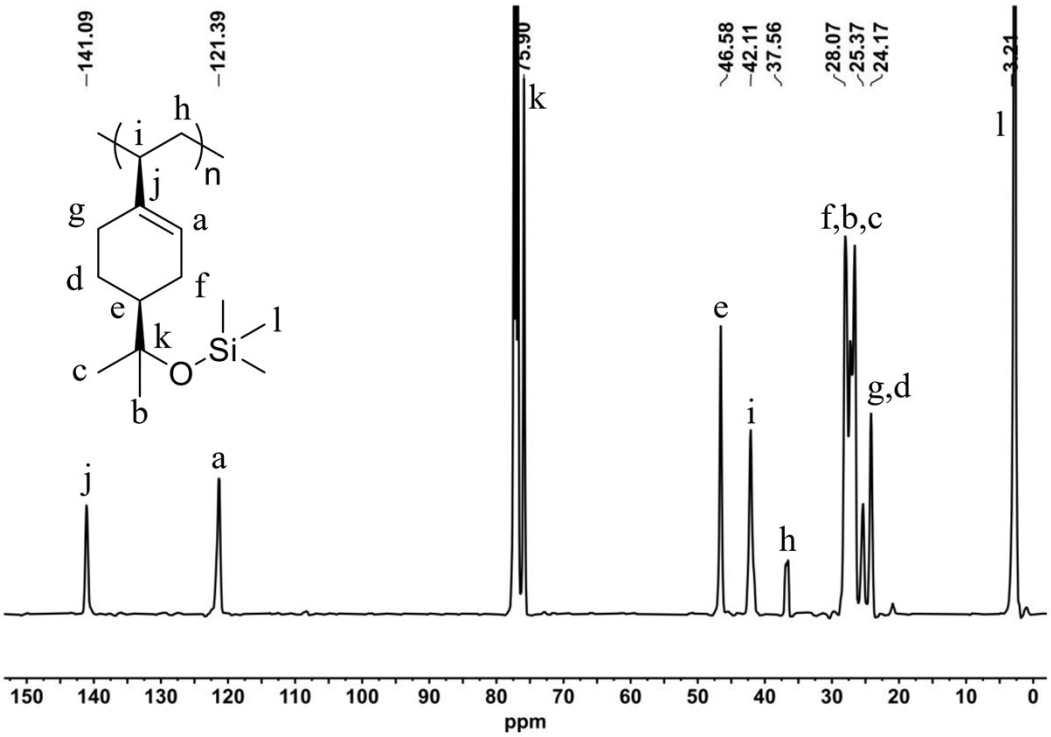


Figure S28. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of P(SiO-IVC) (Entry 2 in Table 3).

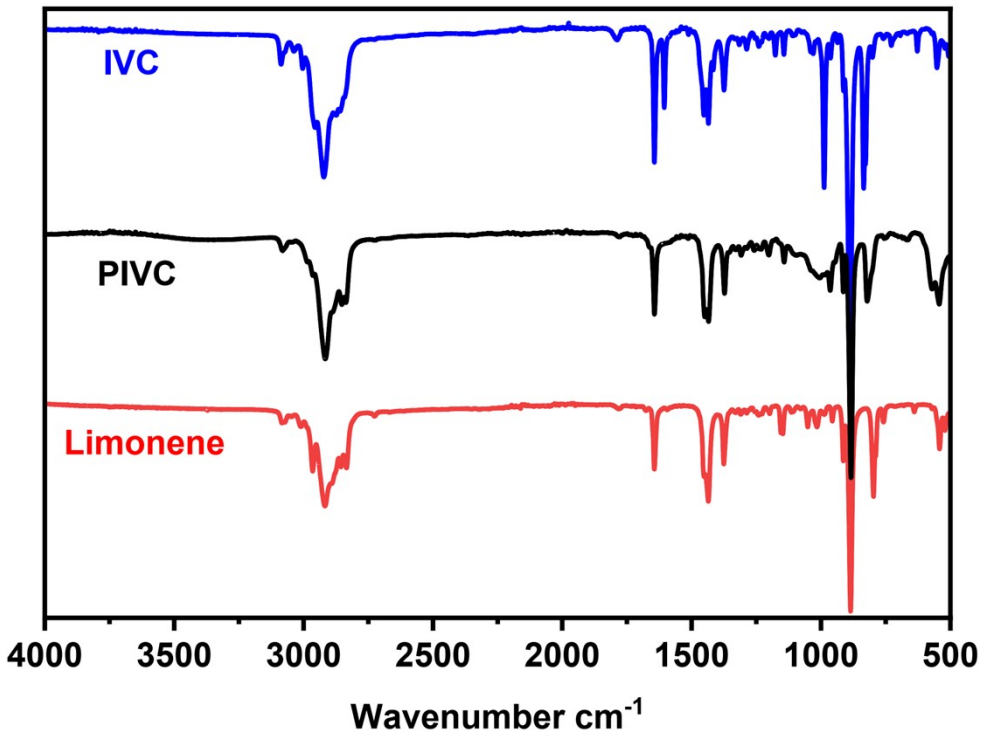


Figure S29. FTIR spectrum of **IVC**, PIVC and (-)-limonene.

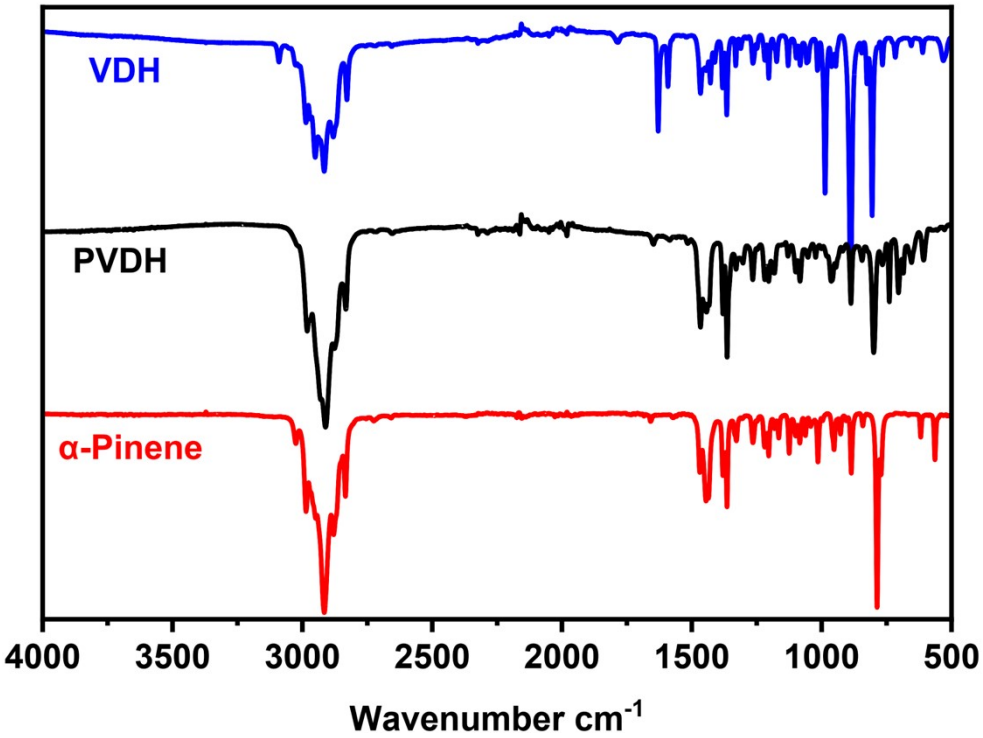


Figure S30. FTIR spectrum of **VDH**, PVDH and (-)-α-Pinene.

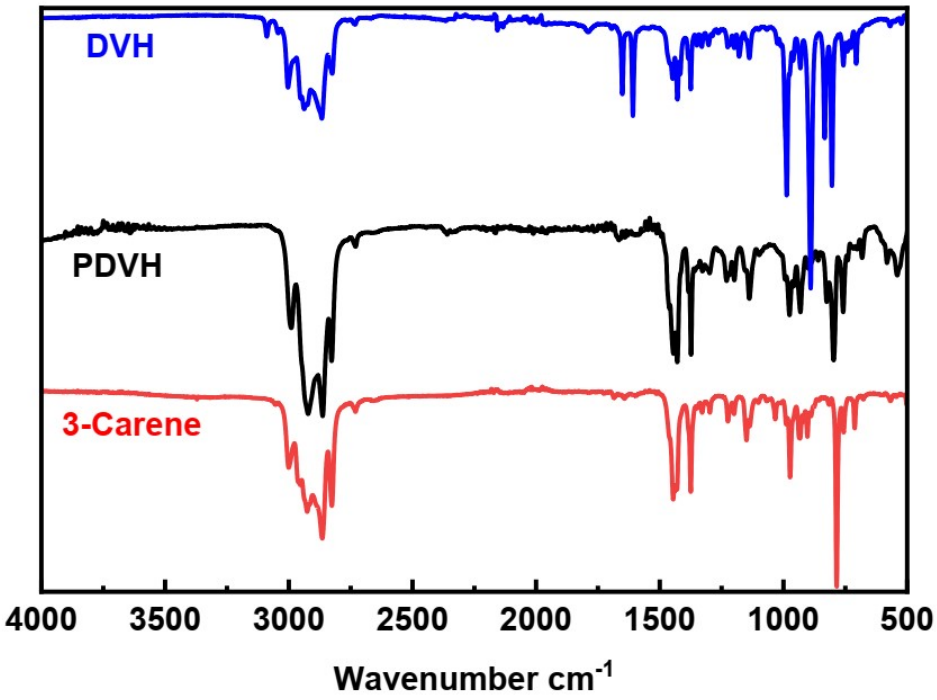


Figure S31. FTIR spectrum of **DVH**, PDVH and (+)-3-Carene.

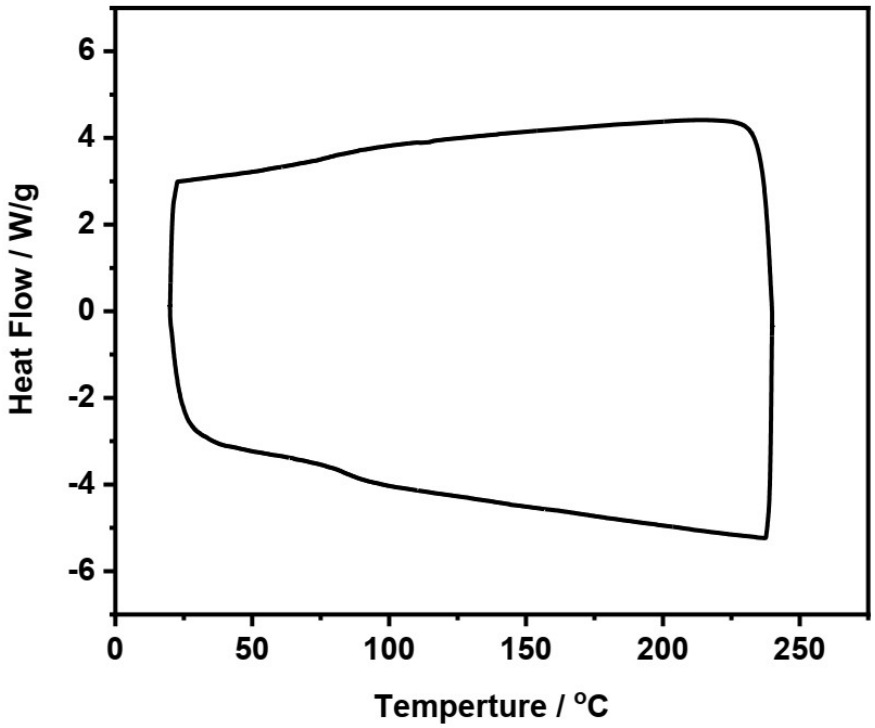


Figure S32. DSC thermograms of PIVC, and the T_g was 86.8 °C.

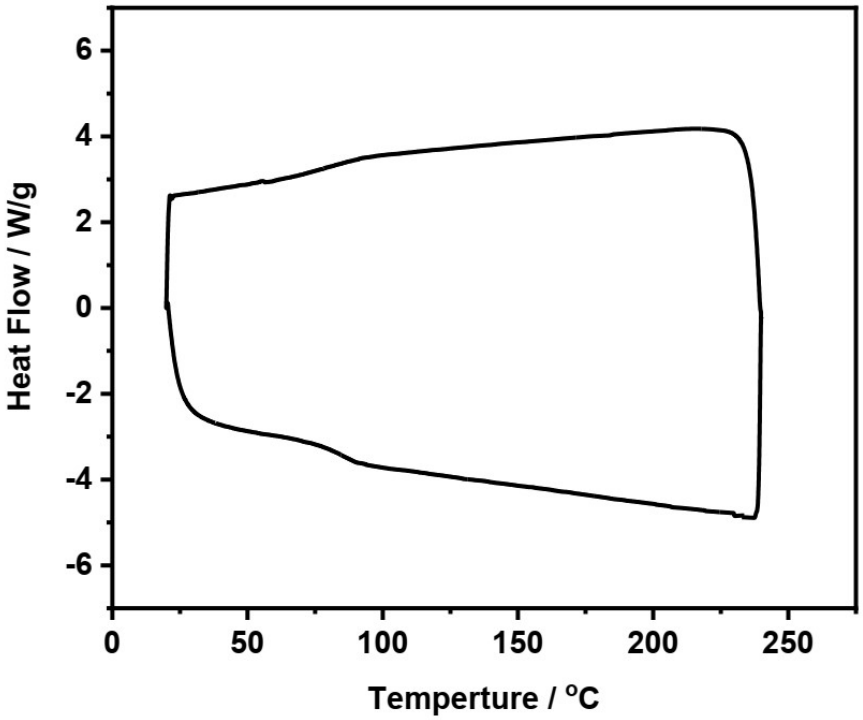


Figure S33. DSC thermograms of P(H-IVC), and the T_g was 84.6 °C.

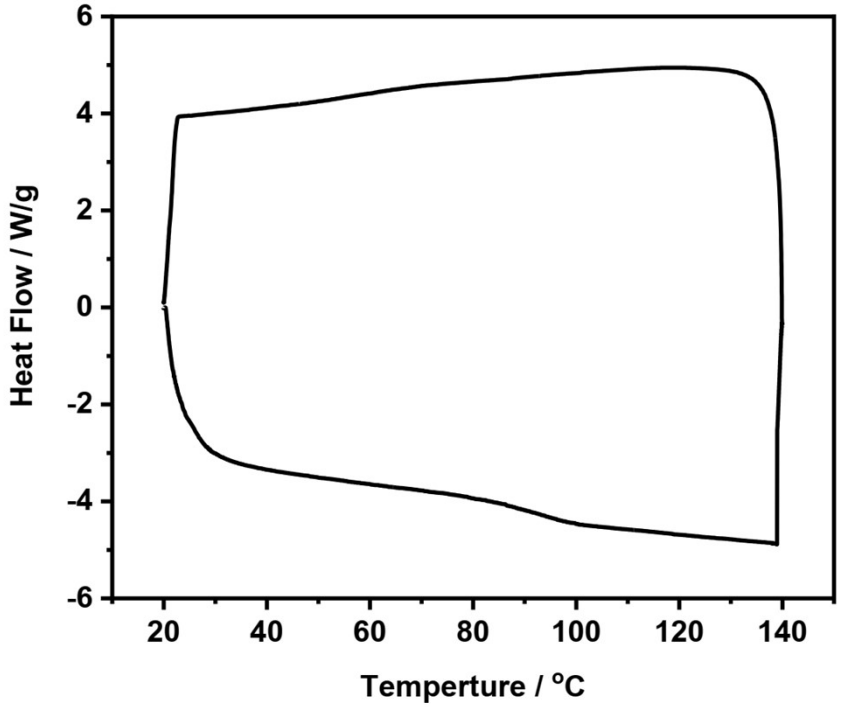


Figure S34. DSC thermograms of P(SiO-IVC), and the T_g was 93.1 °C.

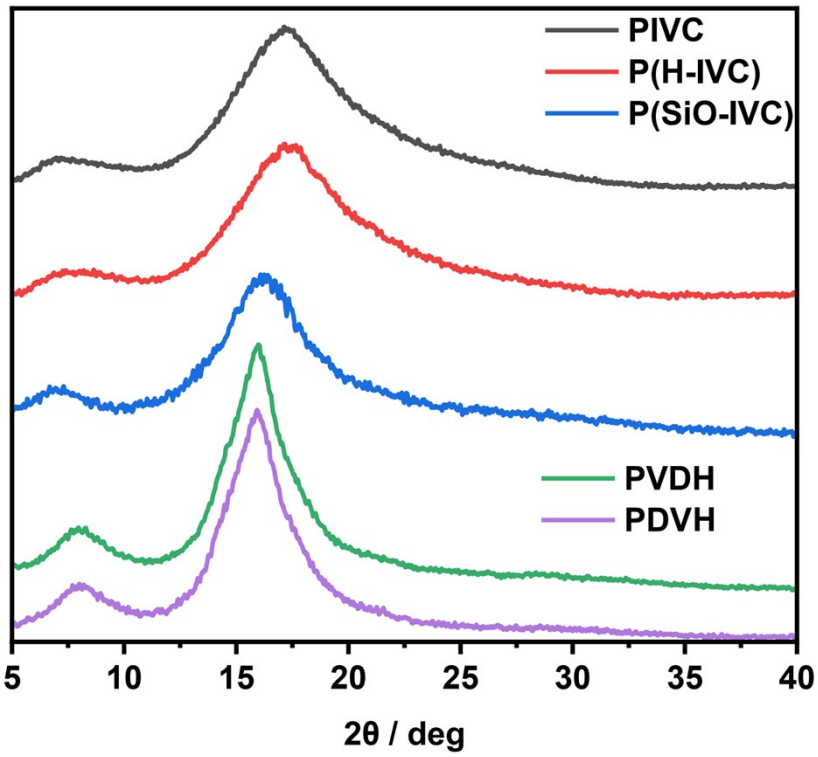
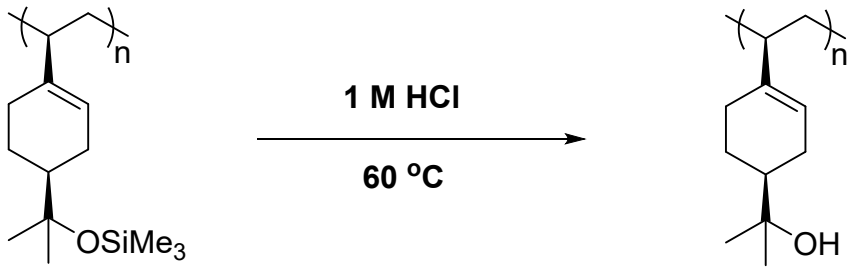


Figure S35. WAXD spectrum of polymers which catalyzed by complex **1**.

Table S2 the summary of temperatures of 5% weight loss for the samples

Samples	The temperature of 5% weight loss
PIVC	326.9
PVDH	320.7
PDVH	323.1
P(H-IVC)	357.5
P(SiO-IVC)	214.3

Hydrolysis of P(SiO-IVC).



P(SiO-IVC)

M_n = 14.5 x 10^4 g mol^{-1}, M_w/M_n = 2.41
> 99% 3,4-, > 99% *mmmm*
T_g = 82.1 °C

Scheme S6. The hydrolysis reaction of P(SiO-IVC) by dilute acid.

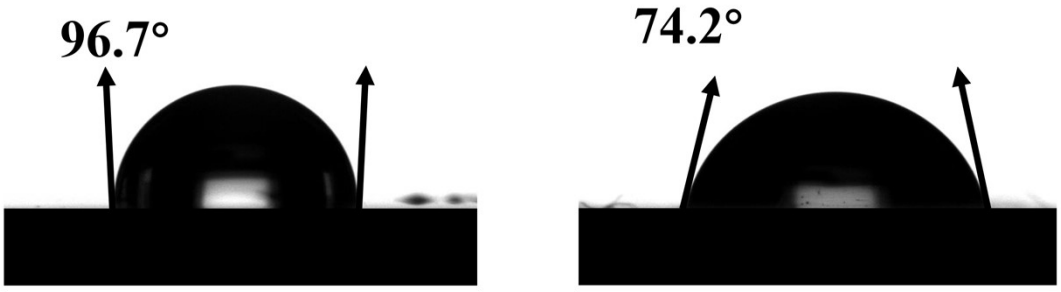


Figure S36. The contact angles of the P(SiO-IVC) (left) and the hydrolysate of P(HO-IVC) (right).

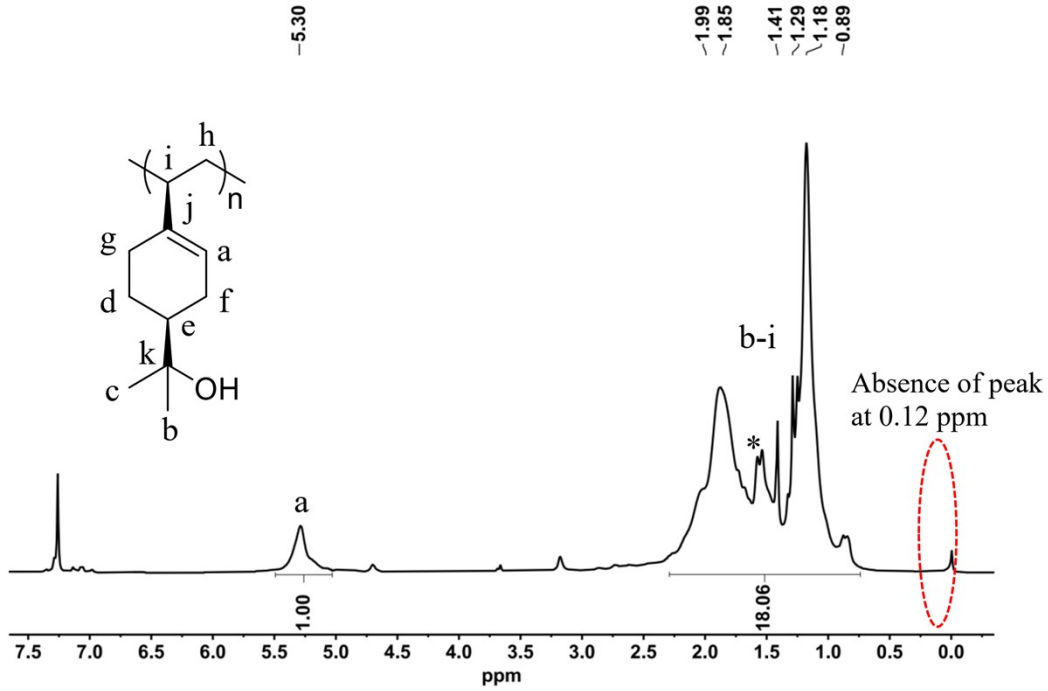


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of P(HO-IVC) (* was water in $CDCl_3$).

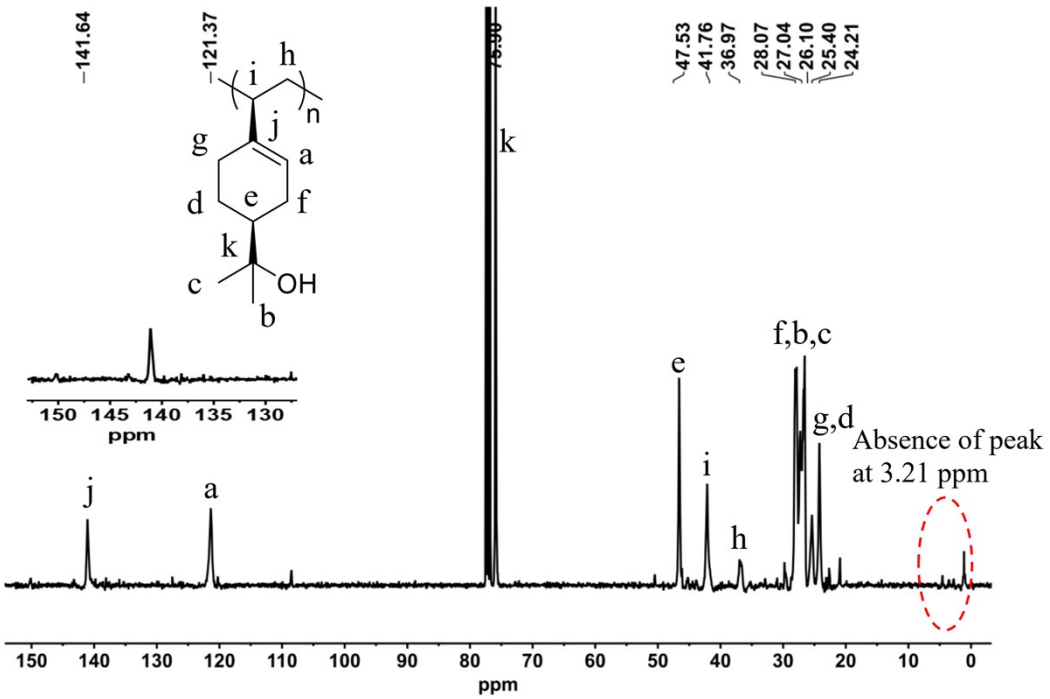
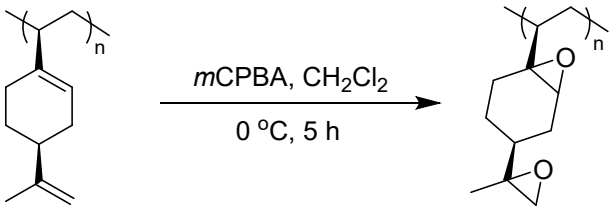


Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25 °C) of P(HO-IVC).



Scheme S7. The epoxidized reaction of PIVC by *m*CPBA

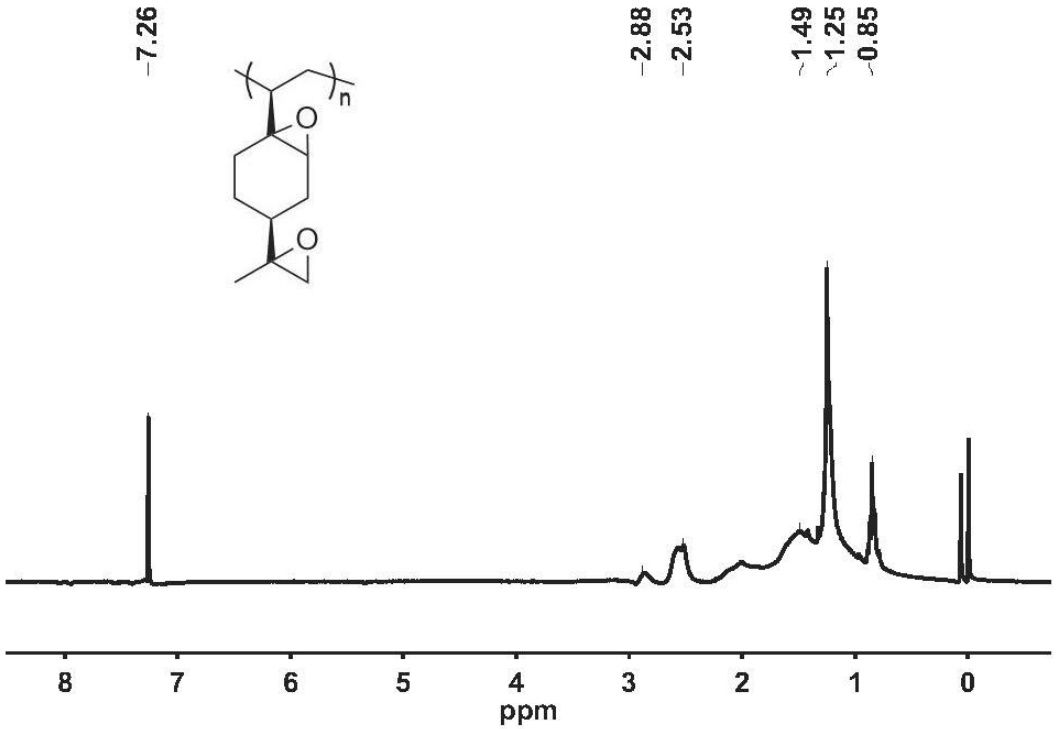


Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of epoxidized PIVC

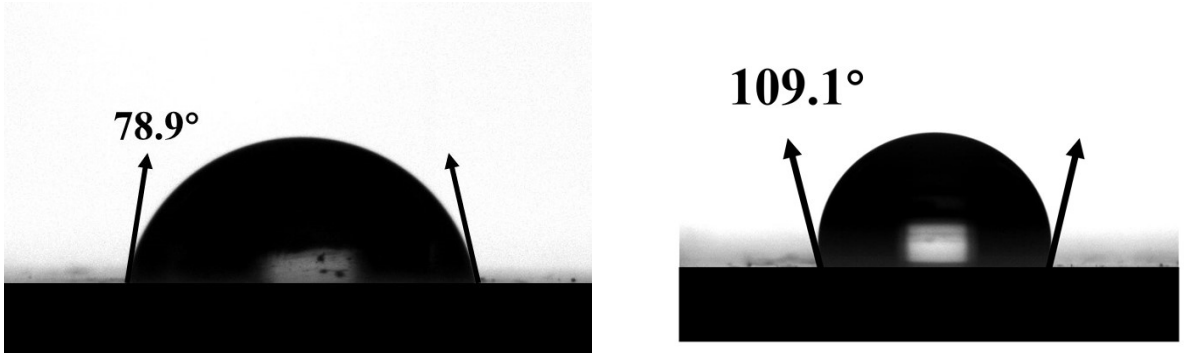


Figure S40. The contact angles of the epoxidized PIVC in Scheme S7 (left) and PIVC (right).

References

[1] Paquette, L. A.; Ross, R. J.; Shi. Y.-J. Regioselective Routes to Nucleophilic Optically Active 2- and 3-Carene Systems. *J. Org. Chem.* **1990**, *55*, 1589-1598.