Supporting Information

Direct Laser Writing of Poly(Phenylene Vinylene) on Poly(Barrelene)

Tang Tang,[a] Guillermo Ahumada[a] and Christopher W. Bielawski*[a,b]

[a] Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919 (Republic of Korea)

[b] Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919 (Republic of Korea)

* Correspondence: bielawski@unist.ac.kr; Tel.: +82-52-217-2952

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1. Experimental Details and Data

Materials. Unless otherwise specified, all manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Tungsten hexachloride (WCl_6), (Z)-1,2-bis(phenylsulfonyl)ethylene, and norbornene were purchased from Tokyo Chemical Industry (TCI). n-Butyllithium (n-BuLi) (2.5 M in hexanes) and di-μ-chlorotetraethylene dirhodium(I) ($[Rh(C_2H_4)_2Cl]_2$) were purchased from Sigma-Aldrich. Schrock's catalyst (2,6-diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-t-butoxide)) was purchased from Strem Chemicals. 1,4-Cyclohexadiene, 3-chloroperbenzoic acid (mCPBA), and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) were purchased from TCI. Bromine (Br_2) was purchased from Junsei Chemicals. Dichloromethane, ethoxyethane, toluene, pentane, hexane, and tetrahydrofuran were purchased from Daejung Chemicals. A sodium mercury amalgam was prepared according to literature procedures.[1]

General Methodology. ^1H and ^{13}C NMR spectra were recorded in methylene chloride-d_2 (^1H: 5.32 ppm; ^{13}C: 54.0 ppm) or chloroform-d_1 (^1H: 7.26 ppm; ^{13}C: 77.2 ppm) using Bruker 400 and 100 MHz spectrometers, respectively. Splitting patterns are indicated as follows: br, broad; bd, broad doublet; bt, broad triplet; bm, broad multiplet; s, singlet; d, doublet; t, triplet; m, multiplet. Size exclusion chromatography (SEC) was performed on a Malvern GPCmax system equipped with a refractive index detector. THF was used as the eluent at a flow rate of 0.8 mL min^{-1} at 35 °C. Molecular weights are reported against poly(styrene) standards. Infrared (IR) spectra were recorded on an Agilent Cary-630 FT-IR spectrometer. Melting points were determined with an MPA 100 Optimelt automated melting point system and are uncorrected. Thermogravimetric analyses (TGA) were performed on a Thermal Advantages (TA) Q500 at a heating rate of 10 °C min^{-1} under an atmosphere of nitrogen. Differential scanning calorimetry (DSC) was performed under an atmosphere of nitrogen on a Thermal Advantages Q2000 at a heating or cooling rate of 20 °C min^{-1}. UV-vis spectroscopy data were recorded on an Agilent Cary 100 UV-vis spectrometer outfitted with a Peltier multicell temperature controller. Raman spectrum was acquired with a Horiba LabRAM HR Evolution Raman microscope using laser excitation wavelengths of 532 nm and 633 nm. Direct laser writing was conducted on a laser capture microdissection system using a 355 nm laser with a repetition rate of 100 Hz, a power of 20 mW, and a pulse duration of 1 ns at a moving speed of ~ 350 μm/s.

3,4-Dibromo-7-oxabicyclo[4.1.0]heptane.[2] A solution of Br_2 (42.0 g, 14 mL, 263 mmol) in CH_2Cl_2 (90 mL) was added dropwise to a solution of 1,4-cyclohexadiene (20.0 g, 24 mL, 250 mmol) in CH_2Cl_2 (200 mL) that had been cooled to –10 °C in a bath of ethanol. Note: the reaction mixture turns yellow upon the addition of bromine and the addition was stopped once the color turned to orange. After the addition was complete, the yellow solution was allowed to reach room temperature and then filtered. The solution was concentrated under reduced pressure. The resulting oil (55.6 g, 234 mmol) solidified upon cooling and was subsequently dissolved in CH_2Cl_2 (81 mL). This solution was added to a solution of mCPBA (44.3 g, 257 mmol) in CH_2Cl_2 (300 mL) at room temperature. The mixture was allowed to stir at room temperature for 24 h. A 20% aq. solution of $Na_2S_2O_5$ (300 mL) was added, and the resulting mixture was allowed to stir for 20 min. Upon separation of the layers, the organic layer was washed with a saturated aq. $NaHCO_3$ solution (2 × 200 mL) followed by brine (200 mL). The organic layer was dried with sodium sulfate, filtered, and concentrated under a vacuum to yield the desired product as a white solid (44.6 g, 175 mmol, 70% yield over two steps). The product was carried on to the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.30-4.23 (m, 1H), 4.20-4.13 (m, 1H), 3.24-3.16 (m, 2H), 3.00-2.91 (dd, 1H), 2.90-2.81 (mm, 1H), 2.65-2.57 (dd, 1H), 2.47-2.37 (mm, 1H).

Benzene Oxide (2).[2] DBU (41.5 g, 273 mmol) was added to a solution of 3,4-dibromo-7-oxabicyclo[4.1.0]heptane (15 g, 59 mmol) in Et_2O (150 mL) at room temperature. The mixture was allowed to stir for 24 h, and then a saturated aq. solution of $NaHCO_3$ was added until all of the precipitate was dissolved. Upon separation of the layers, the aqueous layer was extracted with Et_2O (3 × 30 mL). The organic layers were combined and washed with brine. The organic extracts were dried with sodium sulfate, filtered, and concentrated under a vacuum. The yellow liquid (which contained Et_2O) was used immediately to minimize premature decomposition (5.1 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19-6.12 (m, 2H), 5.88-5.81 (m, 2H), 5.02-4.98 (d, 2H).

8-*endo*,9-*endo*-Bis(phenylsulfonyl)-3-oxatricyclo[3.2.2.02,4]-non-6-ene (3). A round bottom flask was charged with freshly prepared benzene oxide (10.00 g, 106.3 mmol), (Z)-1,2-bis(phenylsulfonyl)ethylene (27.3 g, 88.6 mmol), and toluene (200 mL), and then stirred at 80 °C. After 24 h, a precipitate formed, which was subsequently collected, washed with cold benzene (200 mL), and dried under vacuum to afford 27.8 g (78% yield) of the desired product as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-7.91 (m, 4H, Ar), 7.71-7.48 (m, 6H, Ar), 6.13-6.01 (2 H, m), 3.88 (s, 2H), 3.60-3.52 (bs, 2H), 3.17-3.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.47, 134.08, 129.26, 129.11, 126.70, 67.16, 46.32, 37.09. Spectral data were in accord with literature reports.[3]

7r,8r-Bis(phenylsulfonyl)bicyclo[2.2.2]octa-2,5-diene (4). A mixture of WCl_6 (11.8 g, 29.8 mmol) and dry THF (600 mL) was stirred at -78 °C under argon and in the dark. After 40 min, a solution of n-BuLi (23.8 mL of a 2.5 M solution in hexanes) was added and the resulting mixture was slowly warmed to room temperature. The color of the solution changed from deep red to yellow over time. After warming to room temperature, **3** (6.0 g, 14.9 mmol) was added and the resulting mixture was stirred at room temperature for 24 h. During this period, the color changed from yellow to green. The crude reaction mixture was concentrated under reduced pressure, diluted with CH_2Cl_2, and purified through a short column of silica gel using CH_2Cl_2 as the eluent. Removal of the residual solvent afforded 4.4 g of the desired product as white solid in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.90 (d, 4H, Ar), 7.71-7.45 (m, 6H, Ar), 6.75-6.71 (t, 2H), 6.42-6.25 (t, 2H), 4.07-4.00 (m, 2H), 3.74 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.04, 136.97, 134.04, 133.81, 129.17, 129.03, 69.27, 39.92. Spectral data were in accord with literature reports.[3]

Bicyclo[2.2.2]octa-2,5,7-triene (1). A mixture of KH_2PO_4 (3.0 g, 21.7 mmol) and **4** (6 g, 15.5 mmol) in dry methanol (52 mL) was purged with argon. Sodium amalgam (ca. 3 wt.%, 16 : 1 molar ratio of sodium with respect to the substrate) was then added in portions with stirring. The resulting mixture was stirred at room temperature for 2 h. Water was then slowly added, and the mixture was extracted with n-pentane (3 × 100 mL). The combined extracts were concentrated under reduced pressure and purified through a short column of silica gel using pentane as the eluent. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure at 0 °C to afford **1** (0.68 g, 42% yield) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79-6.75 (m, 6H, alkene), 4.87-4.80 (m, 2H, bridgehead). Spectral data were in accord with literature reports.[4]

[Rh(barrelene)Cl]$_2$ (5). A flask was charged with 50.0 mg of barrelene (0.48 mmol) and 5 mL of CH_2Cl_2. In a separate flask, 85.0 mg of $[Rh(C_2H_4)_2Cl]_2$ (0.22 mmol) was dissolved in 10 mL CH_2Cl_2. The CH_2Cl_2 solution containing $[Rh(C_2H_4)_2Cl]_2$ was passed through a 0.1 μm PTFE filter via syringe, and then added to the CH_2Cl_2 solution containing barrelene. The resulting mixture was stirred at room temperature for 12 h, and then concentrated under reduced pressure. Crystals were obtained by slowly evaporating a mixture of CH_2Cl_2 and hexane (1:1 v/v) that was saturated with **5**. The crystals were collected and dried under vacuum to afford the desired complex (96.44 mg, 91% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.41-6.36 (m, 4H, alkene), 4.91-4.83 (m, 4H, bridgehead), 3.67-3.61 (m, 8H, alkenes coordinated to Rh). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 138.35, 54.14, 45.91. HRMS (ACPI): $[M+H]^+$ calcd for $C_{16}H_{16}Rh_2Cl_2$: m/z, 484.8817; Found: 484.8817.

ROMP of 1 in CH_2Cl_2. Barrelene (113.0 mg, 1.09 mmol) and CH_2Cl_2 (5.35 mL) were added to an air-free reaction flask (10 mL) at room temperature under a positive flow of nitrogen. A solution of Schrock's catalyst in anhydrous CH_2Cl_2 (e.g., 4.4 mg of catalyst in 0.1

mL of solvent) was added to the solution of barrelene, and the resulting mixture was gently stirred for 1 h at room temperature. The formation of a semi-crystalline solid was observed over the course of the polymerization. The reaction was then quenched upon the addition of methanol, and the resulting mixture was poured into cold methanol. The precipitated solids were collected and dried under vacuum (83% yield). The product was found to be insoluble in common organic solvents (e.g., THF, CH_2Cl_2, $CHCl_3$, toluene, DMF and DMSO).

ROMP of 1 in pentane. Barrelene (113 mg, 1.09 mmol) and pentane (5.35 mL) were added to an air-free reaction flask (10 mL) at room temperature under a positive flow of nitrogen. A solution of Schrock's catalyst was dissolved in anhydrous pentane (e.g., 4.4 mg of catalyst in 0.1 mL of pentane) was injected, and the mixture was gently stirred for 3 h at room temperature. During the polymerization reaction, a flocculent solid was observed to form. After 3 h, the reaction was then quenched via treatment with methanol and the resulting mixture was poured into cold methanol. The precipitate that formed was collected, washed with pentane, and dried under vacuum (85 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71-5.49 (bm, 4H, HC=CH in the 1,4-cyclohexadienyl unit), 5.37-5.28 (br, 2H, *trans* exocyclic HC=CH), 5.19-5.06 (br, 2H, *cis* exocyclic HC=CH), 3.80-3.65 (br, 2H, allylic near a *cis* exocyclic HC=CH), 3.38-3.25 (br, 2H, allylic near a *trans* exocyclic HC=CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.83, 132.41,127.68, 39.39, 34.70.

Copolymerization of norbornene and barrelene. Norbornene (1.08 g, 11.54 mmol), barrelene (0.20 g, 1.92 mmol), and CH_2Cl_2 (33.0 mL) were added to an air-free reaction flask (100 mL) at room temperature under a positive flow of nitrogen. A solution of Schrock's catalyst was dissolved in anhydrous CH_2Cl_2 (e.g., 34.29 mg of catalyst in 0.6 mL of solvent) was injected, and the mixture was gently stirred for 2 h at room temperature. The polymerization was then quenched upon the addition of methanol, and the resulting mixture was poured into cold methanol to induce precipitation. The precipitated solids were collected and dried under vacuum (1.16 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71-5.49 (bm, 4H, HC=CH in the 1,4-cyclohexadienyl unit), 5.37-5.28 (br, 2H, *trans* exocyclic HC=CH in the barrelene repeat unit), 5.19-5.06 (br, 2H, *cis* exocyclic HC=CH in the barrelene repeat unit), 3.80-3.65 (br, 2H, allylic near a *cis* exocyclic HC=CH in the barrelene repeat unit), 3.38-3.25 (br, 2H, allylic near a *trans* exocyclic HC=CH in the barrelene repeat unit), 5.42-5.27 (br, 2H, *trans* HC=CH in the norbornene repeat unit), 5.28-5.09 (br, 2H, *cis* HC=CH in the norbornene repeat unit), 2.89-2.67 (br, 2H, allylic near a *cis* HC=CH in the norbornene repeat unit), 2.50-2.34 (br, 2H, allylic near a *trans* HC=CH in the norbornene repeat unit), 1.95-1.68 (bm, 3H, cyclopentyl), 1.24–1.44 (bm, 2H, cyclopentyl), 1.11-0.93 ppm (bm, 1H, cyclopentyl).

Table S1. Summary of various polymerization reactions.

Run	$[\mathbf{6}]_0 : [\mathbf{1}]_0$	Time	Yield (%)	M_n ($\times 10^{-3}$ Da)	$Đ$	**6** : **1** in copolymer
1[a]	norbornene (**6**)	20 min	96	47.9	1.27	-
2[b]	6	2 h	91	48.1	1.39	6.3
3[b]	15	2 h	89	46.4	1.43	15.7

[a] Polymerization was carried out at room temperature in CH_2Cl_2; [norbornene (**6**)]$_0$ = 0.4 M. $[\mathbf{6}]_0/[\text{cat.}]_0 = 300$. [b] Polymerizations were carried out at room temperature in CH_2Cl_2; $[\mathbf{6}+\mathbf{1}]_0 = 0.4$ M. $[\mathbf{6}+\mathbf{1}]_0/[\text{cat.}]_0 = 300$.

2. Single Crystal X-ray Diffraction Data

Single metallic light-yellow prism-shaped crystals were obtained by slow evaporation of a mixture of CH_2Cl_2 and hexane (1:1 v/v) that was saturated with **5**. X-ray intensity data were collected at 123 K on a Rigaku XtaLAB P200 diffractometer equipped with a Pilatus 200K detector using ω scans and Cu Kα radiation (λ = 1.54187 Å). The images were interpreted and integrated with the program CrystalClear–SM Expert (version 2.1 b45, 2015) from Rigaku.[5] After indexation of the X-ray diffraction pattern, the unit cell was refined based on 1023 reflections (13% of the total of 7893 reflections that were measured). Data reduction, scaling and numerical absorption corrections using the ABSCOR program[6] were performed. The final completeness was 93.60% to θ_{max} = 68.283°. Using Olex2,[7] the structure was solved with the ShelXT[8] program using Direct Methods and refined with the ShelXL[9] refinement package using full-matrix least-squares minimization on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined in the riding mode. CCDC-1585233 contains additional crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/. Crystallographic data: $C_{16}H_{16}Cl_2Rh_2$; M = 485.01 g•mol^{-1}; monoclinic; space group $P2_1/c$ (No. 14); a = 10.747(3) Å, b = 11.263(3) Å, c = 12.692(4) Å; β = 102.758(12)°, $\alpha = \gamma$ = 90°; V = 1498.4(7) Å^3; T = 123 K; Z = 4; Z' = 1; $\rho_{calcd.}$ = 1.197 g cm^{-3}; μ(Cu Kα) = 20.964 mm^{-1}; $F(000)$ = 0.944; crystal size 0.20 × 0.06 × 0.05 mm^3; 7893 reflections measured (7.266° ≤ θ ≤ 68.283°), 2574 unique reflections (R_{int} = 0.0392) which were used in all calculations. The final R_1 was 0.0330 ($I > 2\sigma(I)$) and wR_2 was 0.0812 (all data).

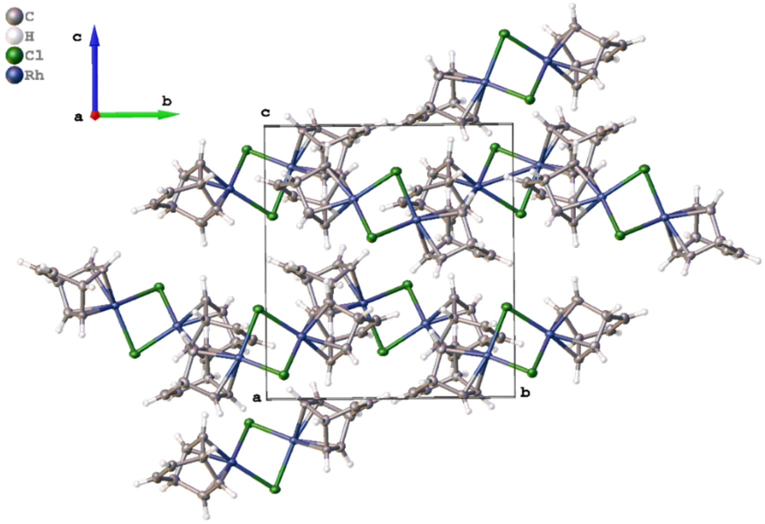

Figure S1. Packing arrangement observed in the crystal structure of **5**.

3. NMR Spectra

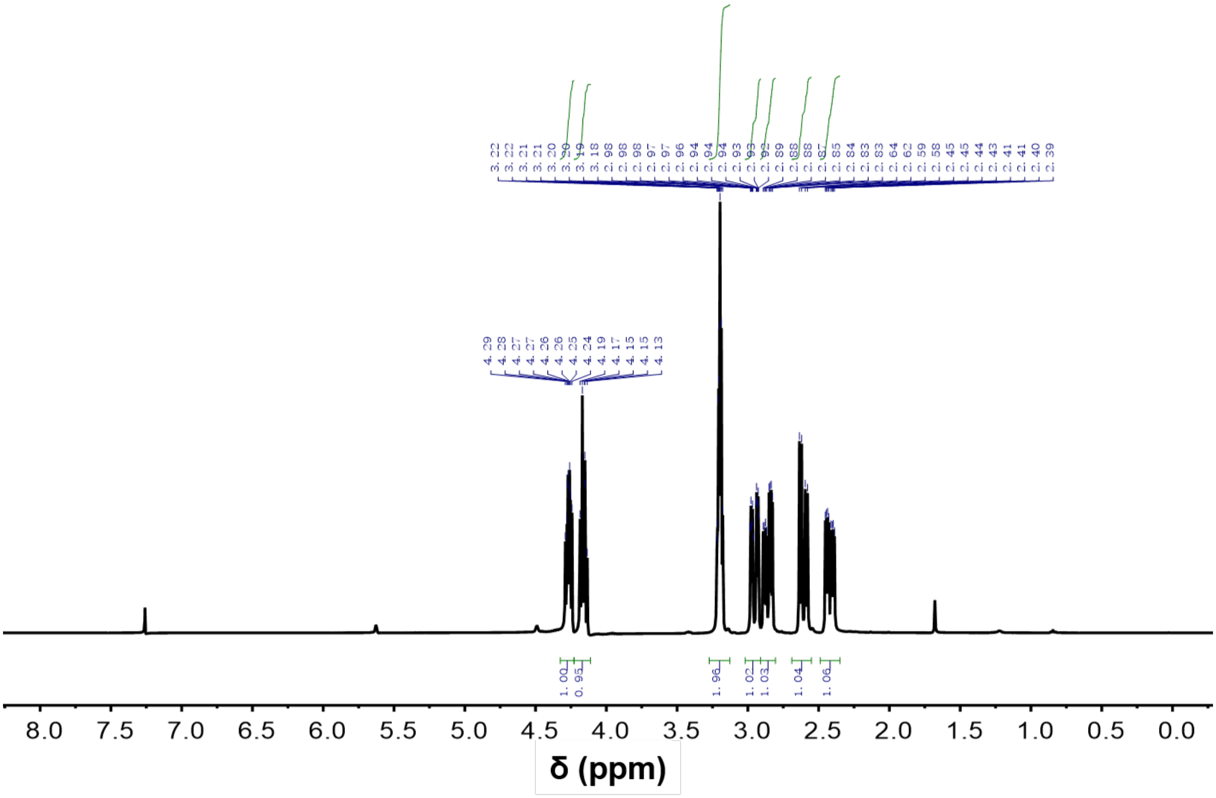

Figure S2. ^{1}H NMR spectrum of 3,4-dibromo-7-oxabicyclo[4.1.0]heptane in $CDCl_3$.

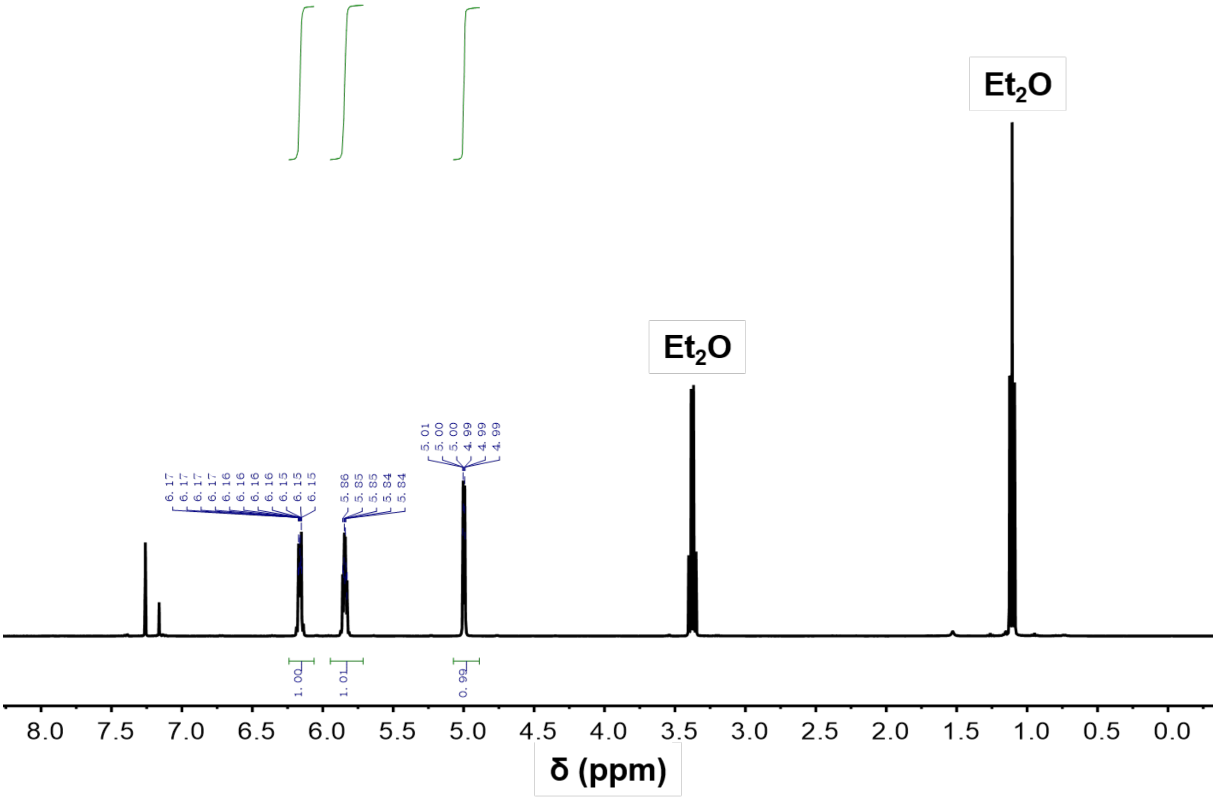

Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$.

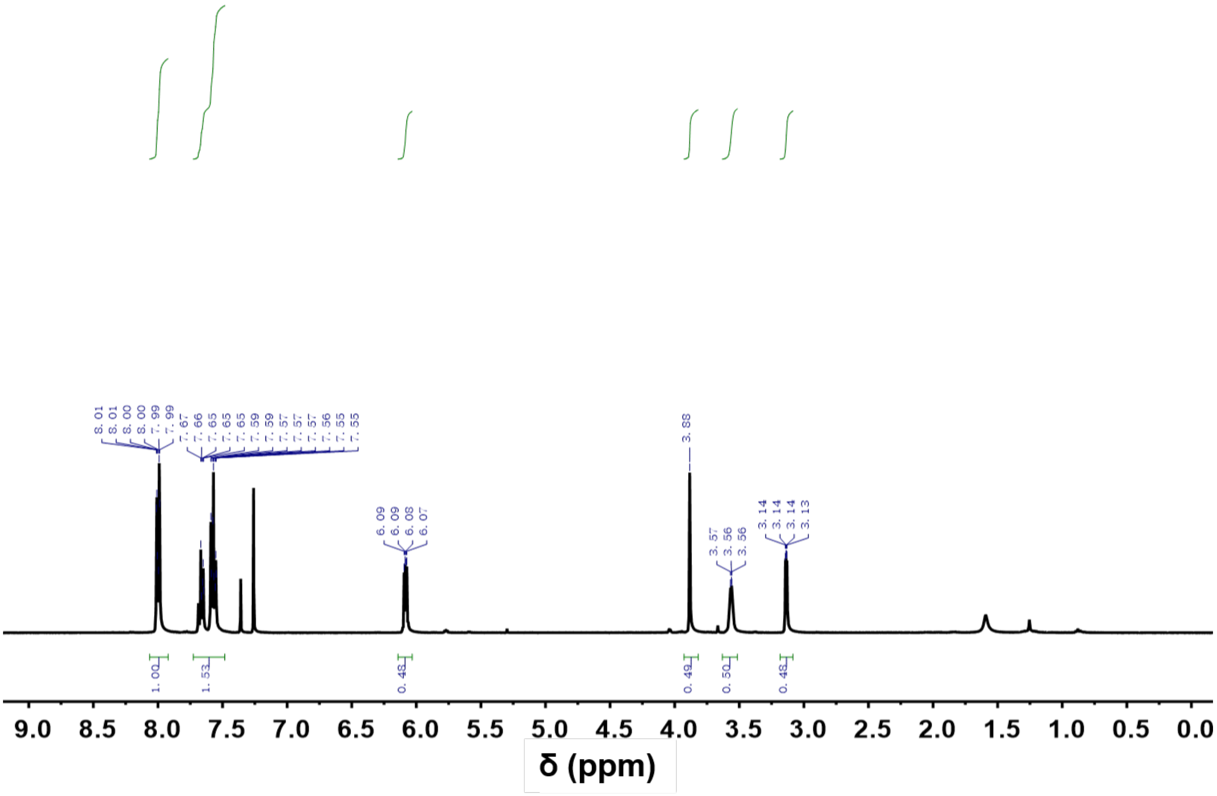

Figure S4. ^{1}H NMR spectrum of **3** in $CDCl_3$.

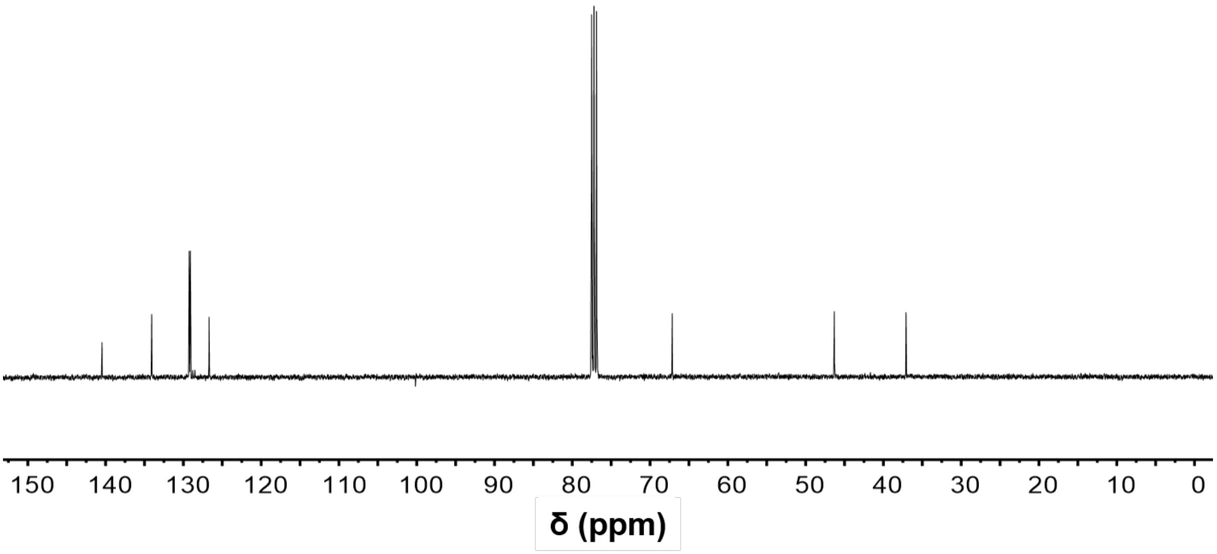

Figure S5. ^{13}C NMR spectrum of **3** in $CDCl_3$.

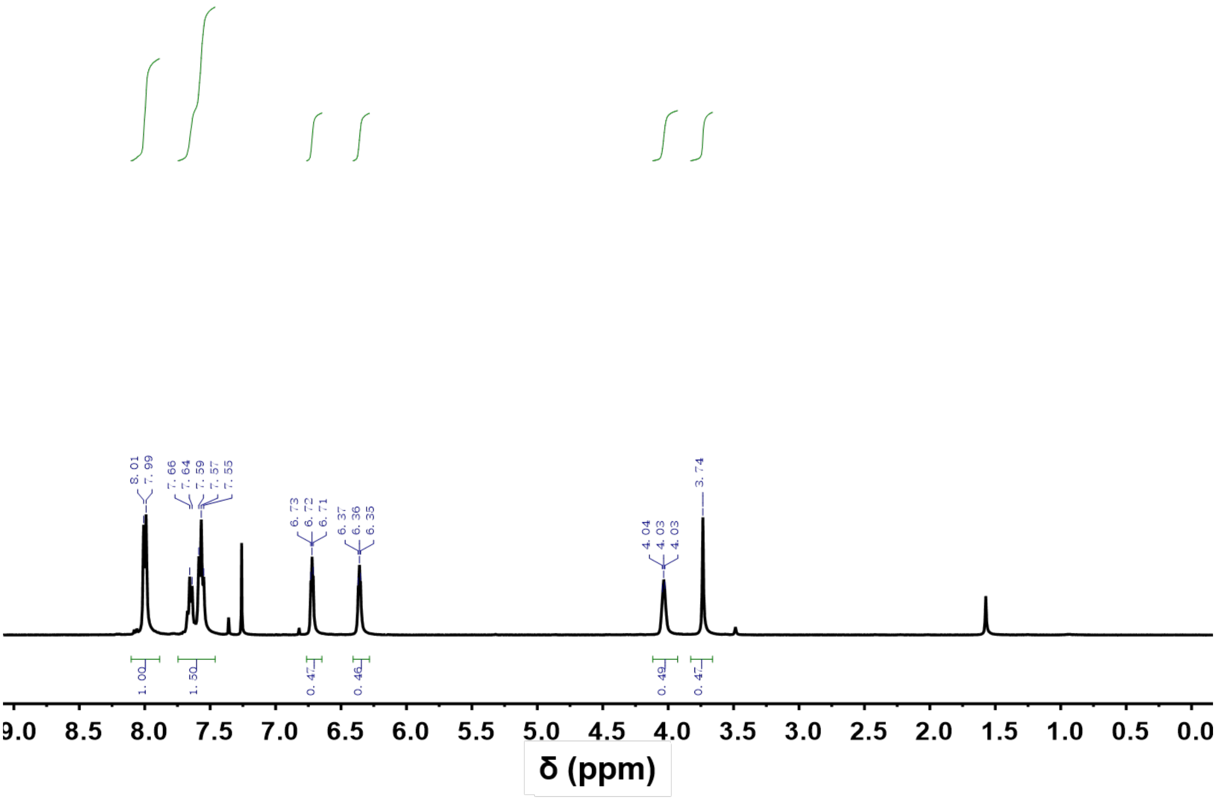

Figure S6. ^{1}H NMR spectrum of **4** in CDCl$_3$.

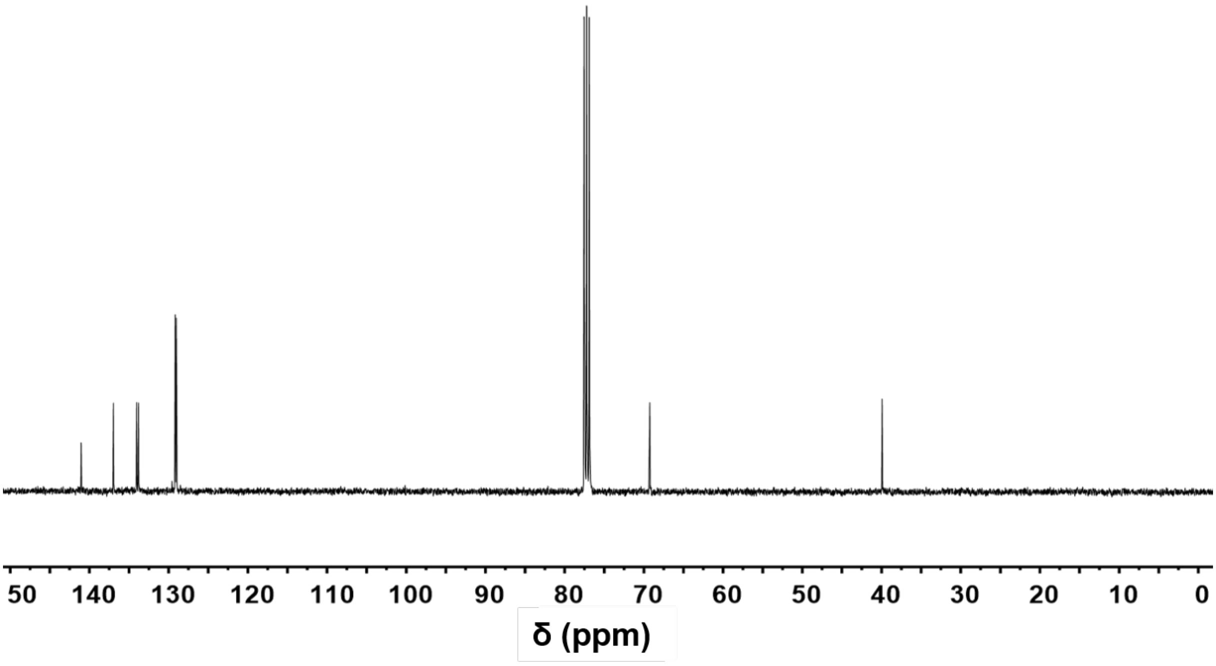

Figure S7. ^{13}C NMR spectrum of **4** in CDCl$_3$.

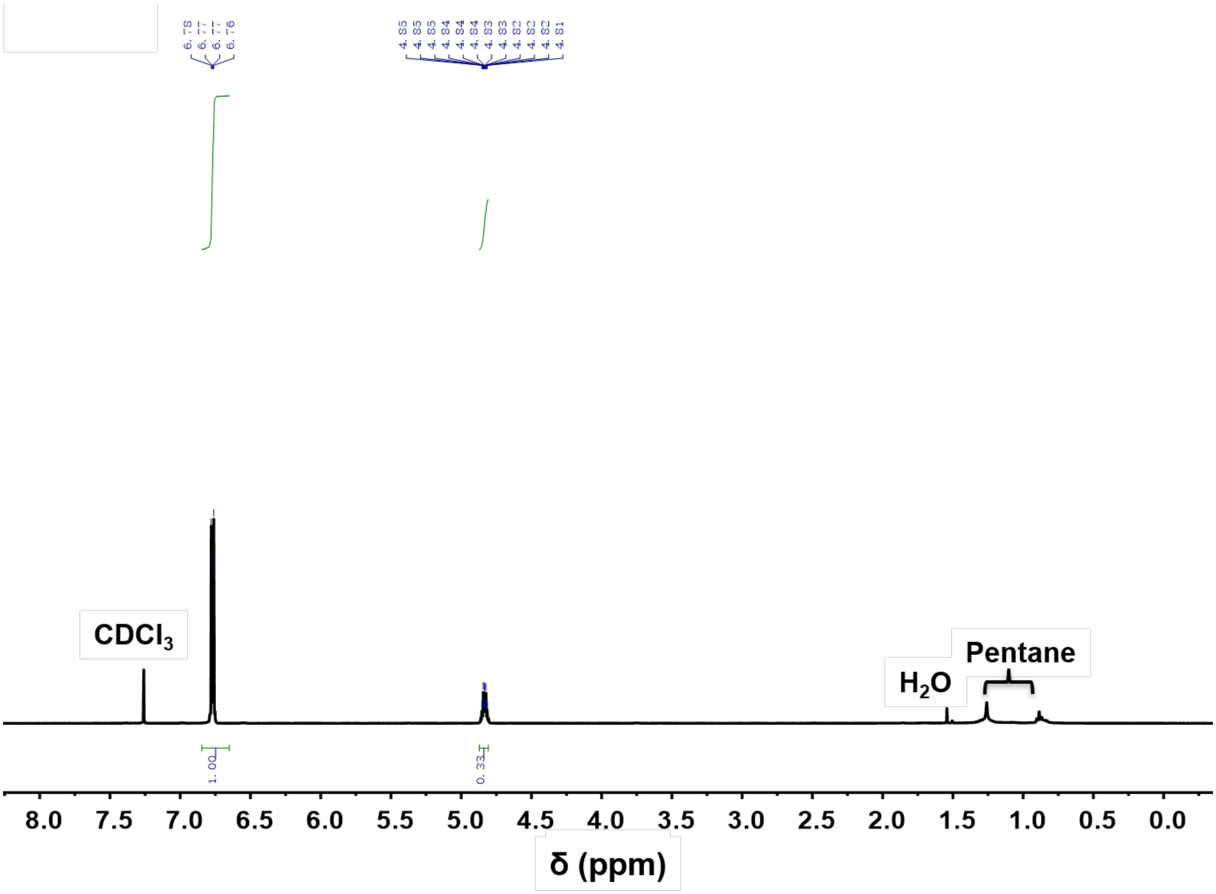

Figure S8. ^{1}H NMR spectrum of **1** in CDCl$_3$.

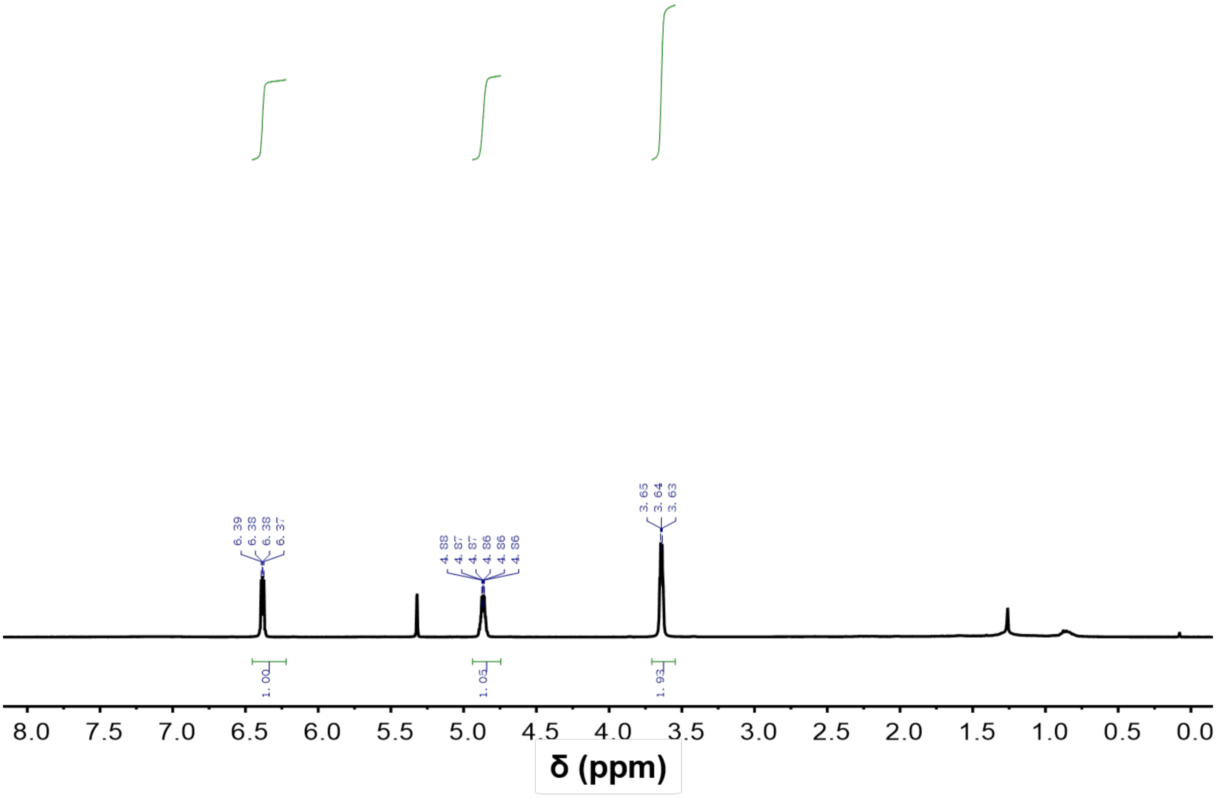

Figure S9. ^{1}H NMR spectrum of **5** in CD$_2$Cl$_2$.

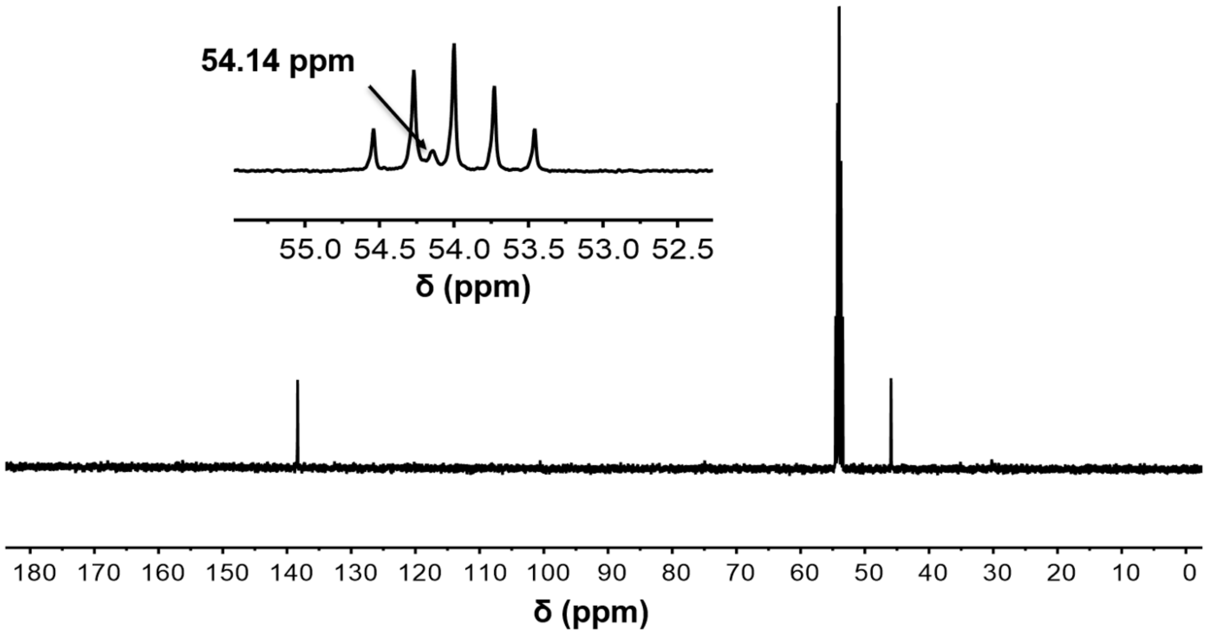

Figure S10. ^{13}C NMR spectrum of **5** in CD_2Cl_2.

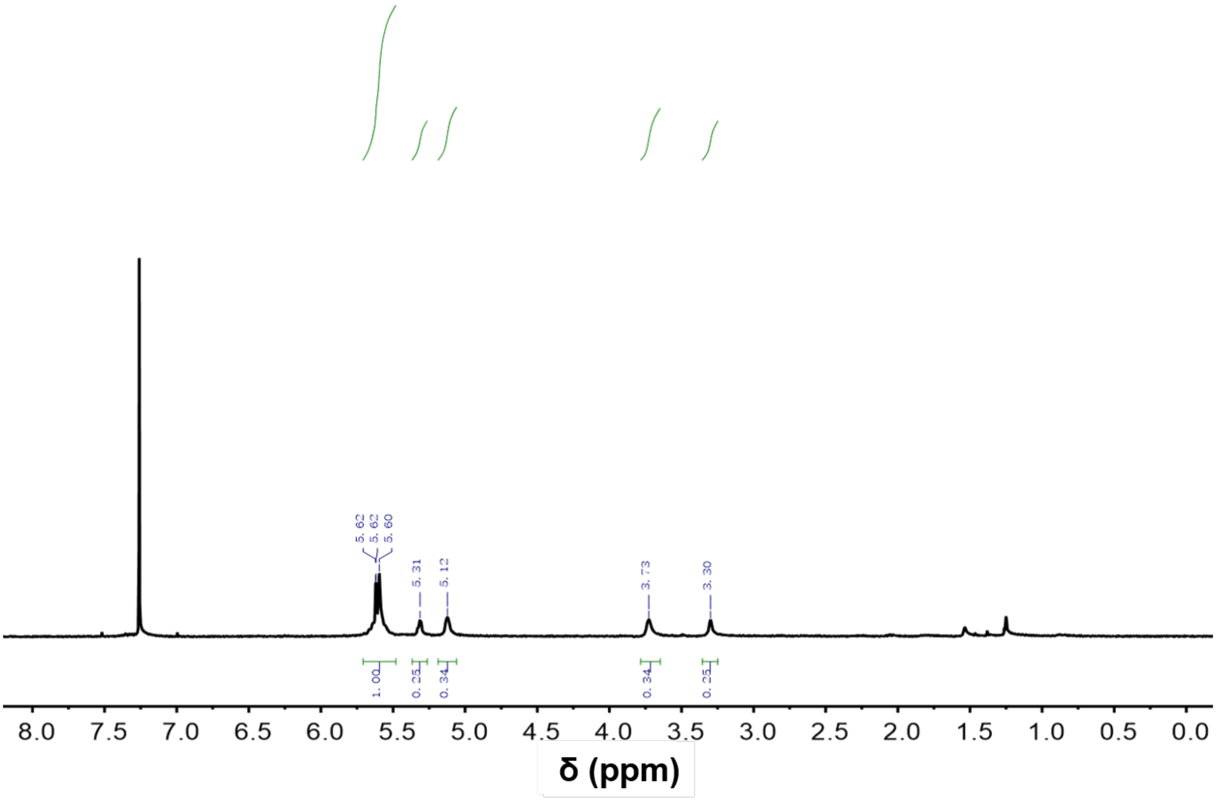

Figure S11. ^{1}H NMR spectrum of poly(barrelene) (as synthesized in pentane) in $CDCl_3$.

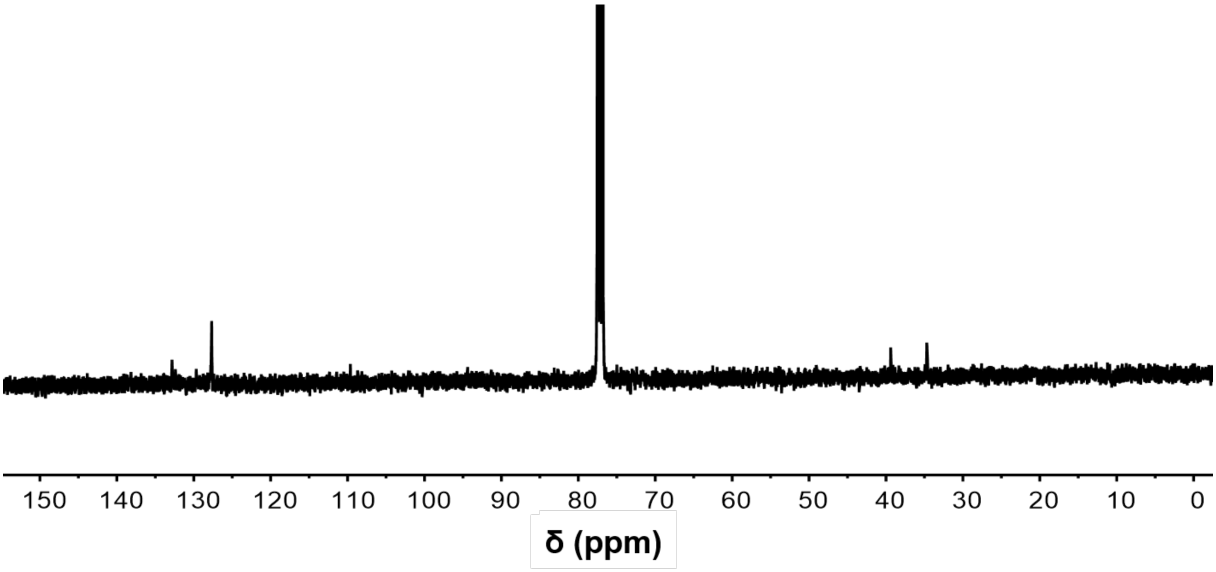

Figure S12. ^{13}C NMR spectrum of poly(barrelene) (as synthesized in pentane) in $CDCl_3$.

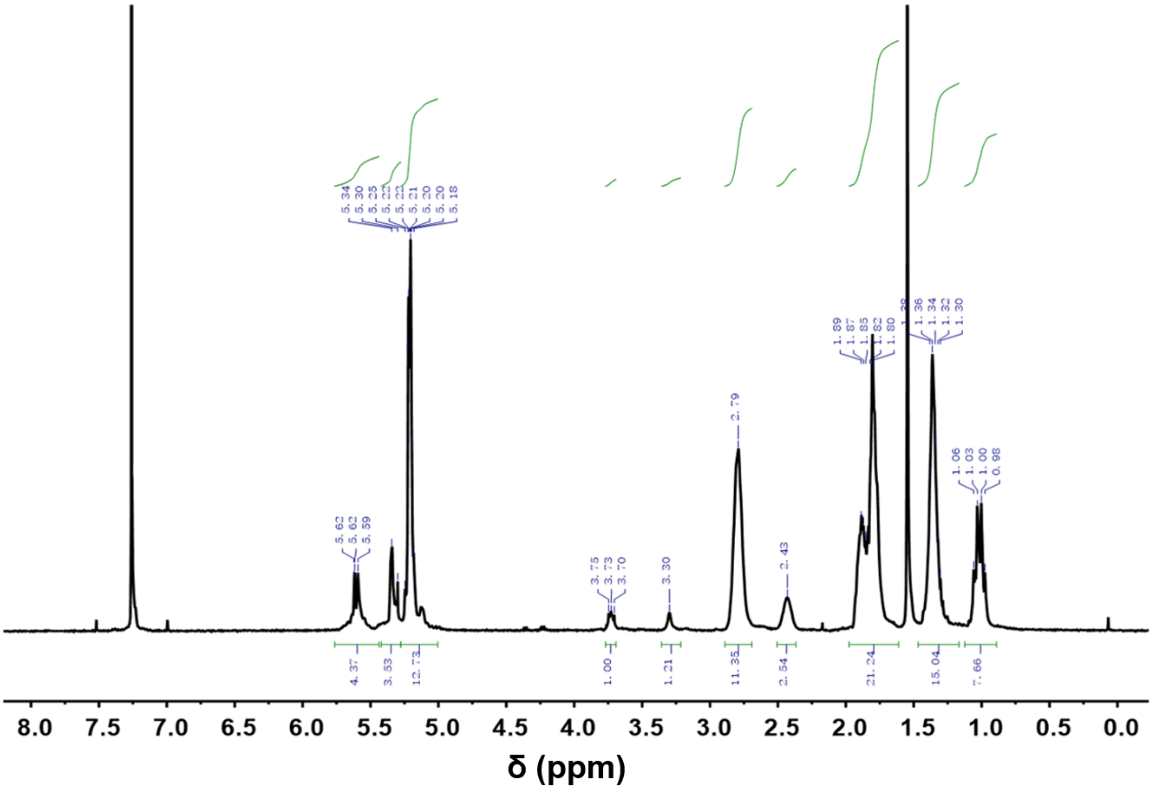

Figure S13. ^{1}H NMR spectrum of copolymer **7** (**6** : **1** = 6.3) in $CDCl_3$.

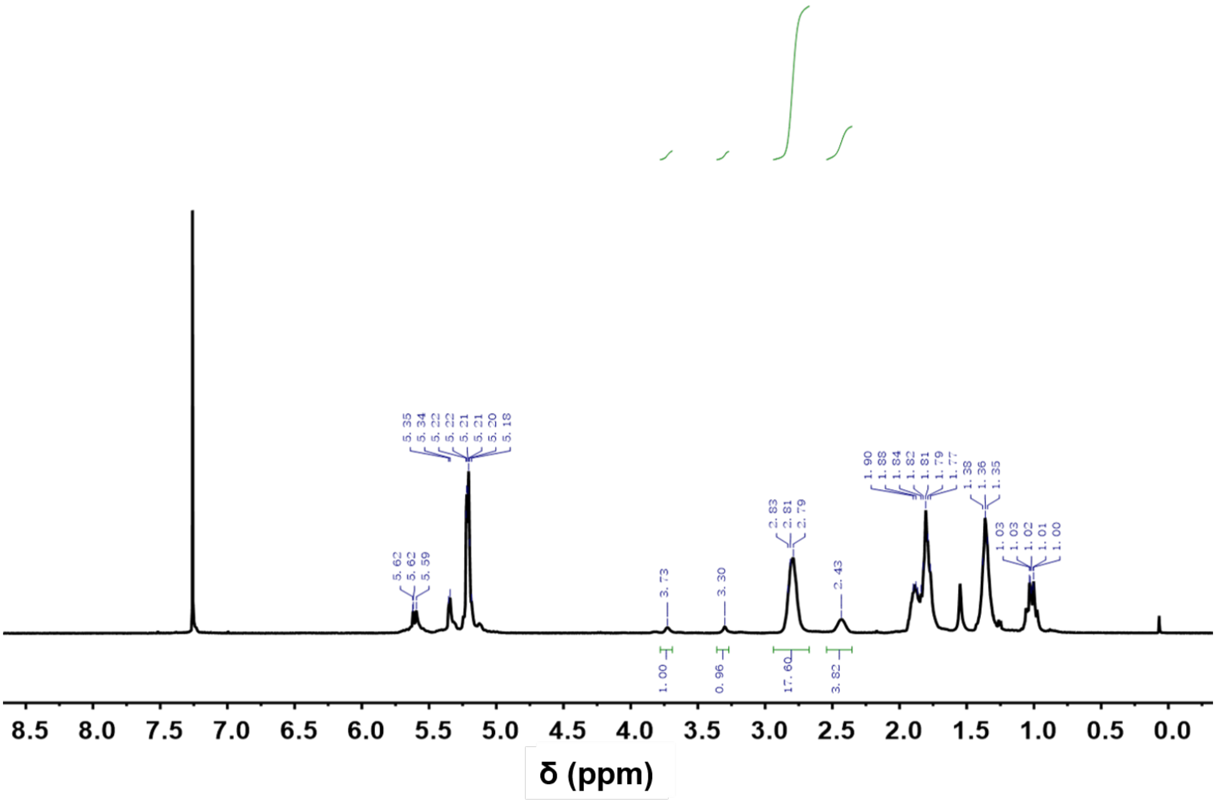

Figure S14. ^{1}H NMR spectrum of copolymer **7** in $CDCl_3$ after being exposed to aerated CH_2Cl_2 for three (3) weeks. The ratio of **6** : **1** in the copolymer increased from 6.3 to 10.9.

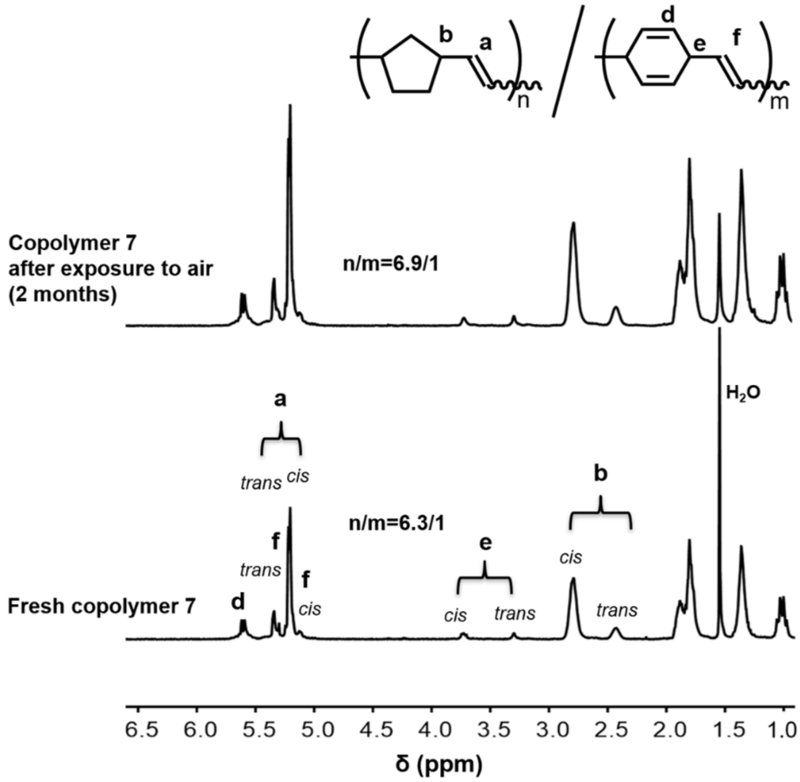

Figure S15. ^{1}H NMR spectrum of copolymer **7** (**6** : **1** = 6.3) in $CDCl_3$ (bottom) and ^{1}H NMR spectrum of the same copolymer after being exposed to air for two (2) months in the solid-state in $CDCl_3$ (top).

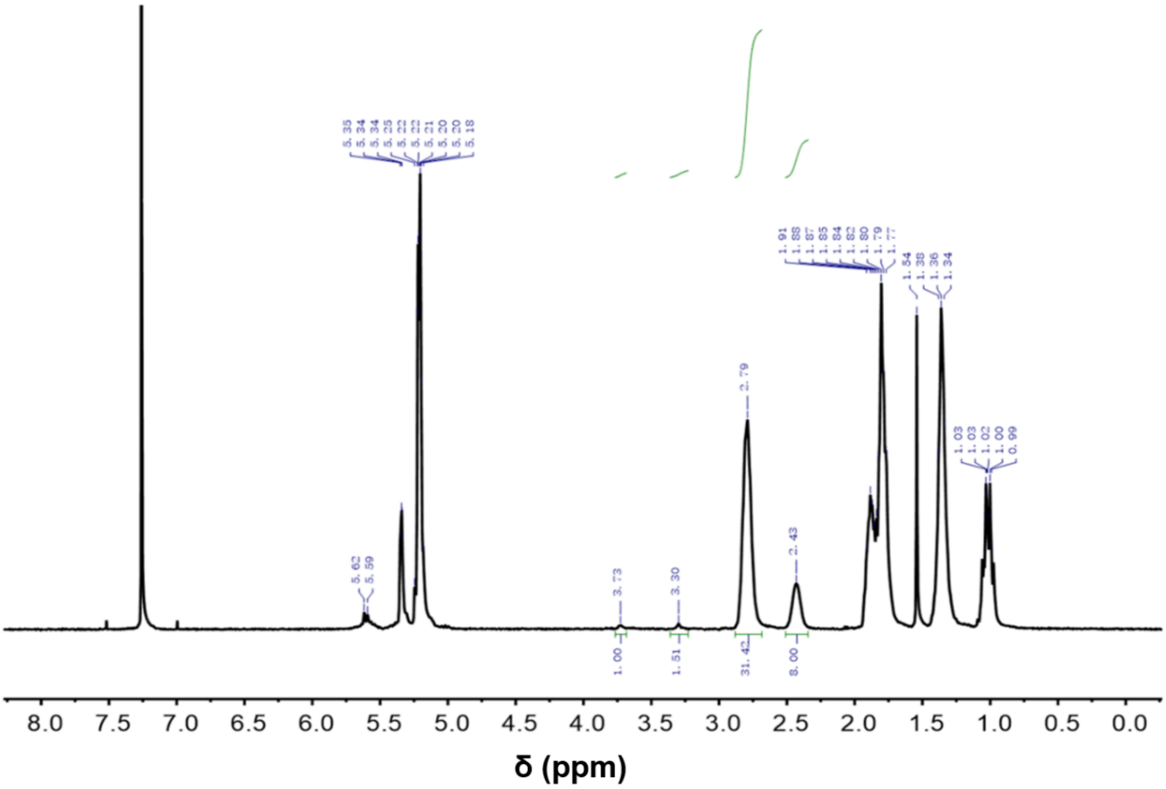

Figure S16. ^{1}H NMR spectrum of copolymer **7** (**6** : **1** = 15.7) in $CDCl_3$.

4. DSC and TGA Data

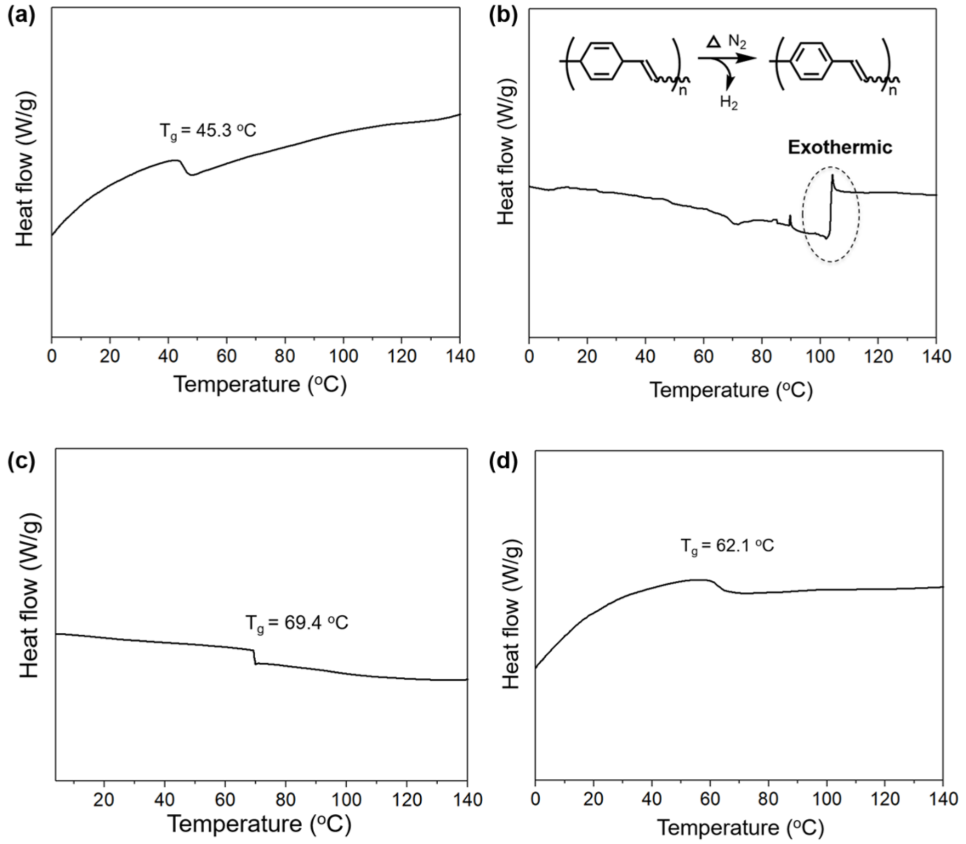

Figure S17. DSC data recorded for (a) poly(norbornene), (b) copolymer **7** (**6** : **1** = 6.3), (c) copolymer **7** (**6** : **1** = 6.3) after treatment with DDQ, and (d) copolymer **7** (**6** : **1** = 15.7) after treatment with DDQ. Data were recorded under an atmosphere of nitrogen at a rate of 20 °C/min.

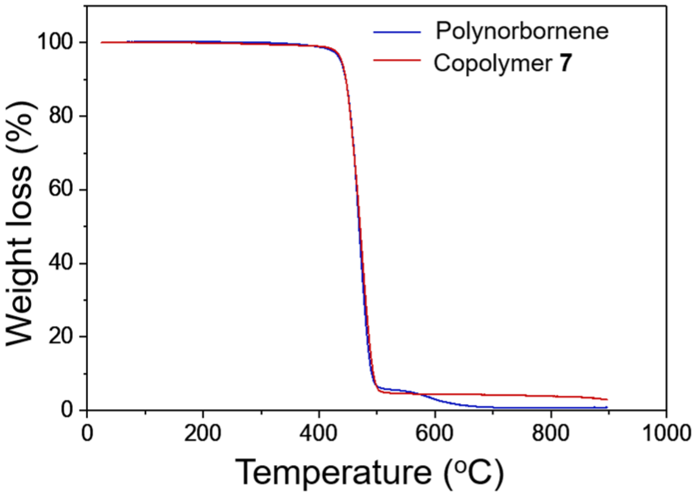

Figure S18. TGA data recorded for (*blue*) poly(norbornene) and (*red*) copolymer **7** (**6** : **1** = 6.3). Data were recorded under an atmosphere of nitrogen at a rate of 10 °C/min.

5. SEC Data

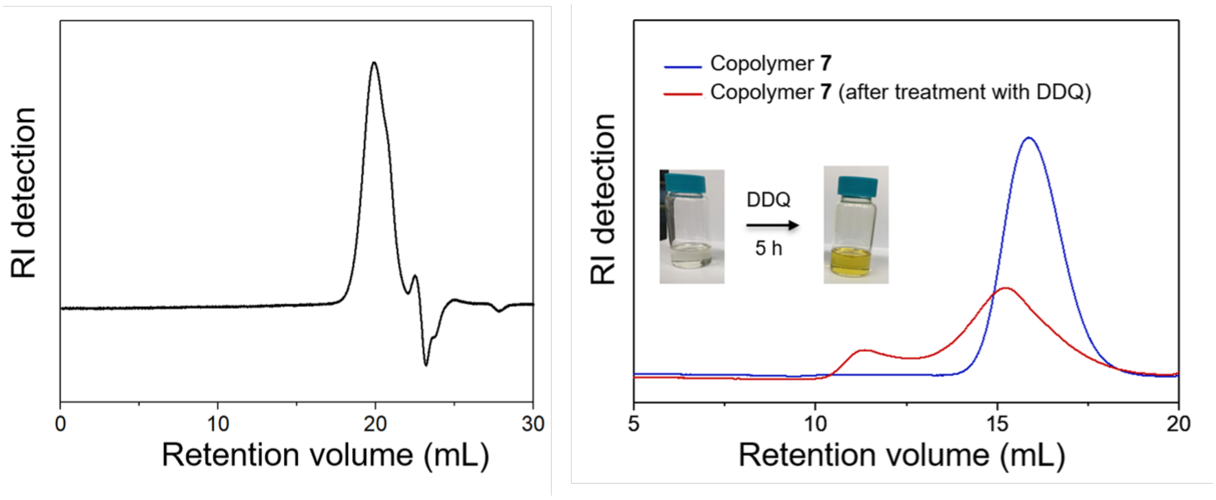

Figure S19. SEC data recorded for (*left*) poly(**1**) that was synthesized in pentane and (*right*) copolymer **7** (**6** : **1** = 15.7) before and after treatment with DDQ (*indicated*).

6. Raman Spectra

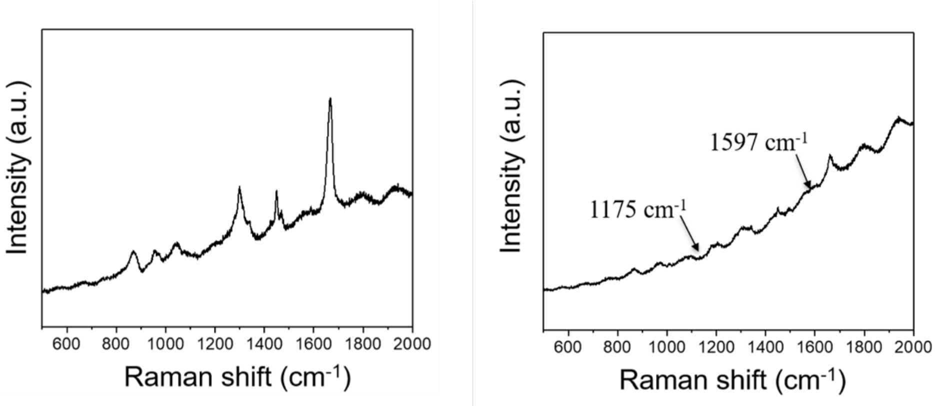

Figure S20. Raman data recorded for films of (*left*) poly(norbornene) and (*right*) copolymer **7** (**6** : **1** = 6.3) after exposure to air for two months.

7. DLW Data

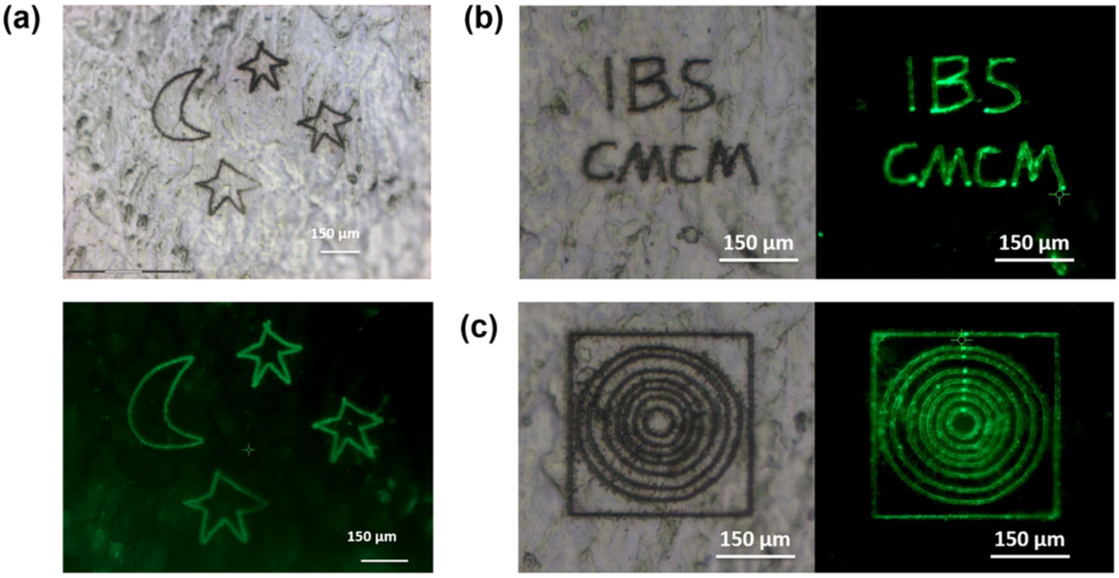

Figure S21. (a) Examples of patterns that were written on copolymer **7** (**6** : **1** = 6.3). Photographs were taken under visible light (*top*) and UV-light (λ_{ex} = 488 nm; *bottom*). (b, c) Examples of patterns that were written on copolymer **7** (**6** : **1** = 15.7). Photographs were taken under visible light (*left*) and UV-light (λ_{ex} = 488 nm; *right*).

8. References

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