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Supporting Information

An Ion-Pairing Approach to Stereoselective Metal-Free Ring-Opening Metathesis Polymerization

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Supporting Information

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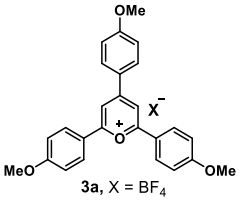
1. General Information

Materials and General Considerations. Dichloromethane and toluene were dried over 3Å molecular sieves prior to use. Tetrahydrofuran (THF) was obtained from an LC Technology solvent purification system. Norbornene (NB) was purchased from Sigma-Aldrich and sublimed prior to use. Enol ethers **2c**–**e** were prepared from the corresponding alcohols followed by isomerization. Pyrilium salts **3a**–**c** were prepared according to literature procedures with modifications. All other reagents and solvents were acquired from commercial sources and used without purification unless otherwise noted. All polymerizations were conducted in standard 2-dram borosilicate glass vials with PTFE-lined screw cap as purchased from Fisher Scientific. Irradiation of photoredox mediated ROMP was done with Norman Lamps MR16-4W blue LEDs (450 nm).

Characterizations. ^{1}H and ^{13}C NMR were recorded on Bruker Avance III 400, 500, or 600 MHz spectrometers. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using protio-solvent (residual) as internal standard ($CDCl_3$, δ_H = 7.26 ppm for ^{1}H NMR, δ_C = 77.16 ppm for ^{13}C NMR). Data are reported as chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, p = pentet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddt = doublet of doublet of triplets), coupling constants (J), and integration. Mass spectrometry data were recorded on a Thermo Q Exactive Plus instrument using electrospray ionization (ESI) with an ion trap detector. Gel permeation chromatography (GPC) was performed using the following setup: an Agilent Technologies Infinity Series II pump, either 2 or 3 inline columns, and Wyatt Technology mini-DAWN light scattering (LS) and Optilab T-rEX refractive index (RI) detectors using THF as the mobile phase with a flow rate of 1 mL/min. The absolute weight-average molecular weights were determined by the dn/dc value of polynorbornene in THF (0.1507 mL/g). Thermogravimetric analysis (TGA) was performed on a TA TGA Q50 under nitrogen from room temperature to 600 °C at 10 °C/min. Differential Scanning Calorimetry (DSC) was performed on a TA DSC Q250 calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min and cooling rate of 5 °C/min.

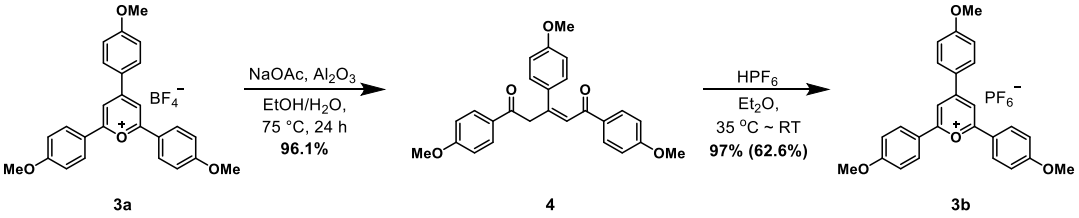
2. Synthesis

2.1. Synthesis of Pyrylium Salts



3a, X = BF_4
3b, X = PF_6
3b, X = BAr^F_4

3a was prepared according to our previous procedure with minor modification.[1] To a flask containing *p*-anisaldehyde (3.0 mL, 25.0 mmol, 1 eq) and *p*-acetylanisole (7.51g, 50.0 mmol, 2 eq) was added BF_3•Et_2O (7.5 mL, 60.8 mmol, 2.4 equiv) dropwise over 5 min. The solution was heated in an oil bath set to 100 °C for 2 h. After cooling down, the reaction mixture was diluted with acetone (100 mL) and water (7.5 mL), and subsequently precipitated into diethyl ether (200 mL). The resulting suspension was filtered to give the crude product as a rust-colored solid. Recrystallization of the solids from hot acetone gave **3a** as an orange powder (2.84 g, 5.84 mmol, 23% yield). Spectral data were consistent with reported values in literature.[2]



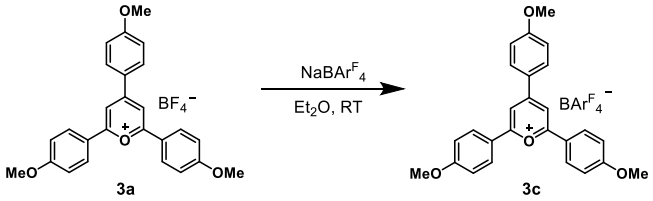
3a **4** **3b**

3b was prepared by conversion of **3a** into its pseudobase (**4**) which was recyclized with the acid corresponding to the desired anion.[3]

Pent-2-ene-1,5-dione (**4**) was prepared according to a literature procedure with minor modification.[4] To a round flak equipped with a condenser was added **3a** (1.46 g, 3.00 mmol, 1 eq) and basic Al_2O_3 (1.53 g. 15.0 mmol, 5 eq). 20 ml of ethanol and an aqueous solution of sodium acetate (1.48 g, 18.0 mmol, 6 eq) in 7.5 mL of water were then added. The above suspension was stirred at 75 °C for 24 h. After cooling down, the precipitate was filtered off and washed with dichloromethane. The filtrate was evaporated to remove ethanol and diluted with dichloromethane and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was washed with saturated brine, and dried over anhydrous Na_2SO_4, which was then passed through a short plug of basic Al_2O_3. The filtrate was concentrated under reduced pressure to give

pure dione **4** as a yellow oil (1.20g, 2.88 mmol, 96% yield). Spectral data were consistent with reported values in literature.[5]

38.6 mg (0.0927 mmol, 1 eq) of **4** was dissolved in hot diethyl ether (8 mL). Then 0.24 mL of hexafluorophosphoric acid solution (~55 wt. % in water, 1.50 mmol, 16.2 eq) was added dropwise at 35 ℃. Orange solids precipitated out. The suspension was cooled down and stirred at room temperature for 10 min. Then the mixture was diluted with diethyl ether (5 mL) and kept in freezer (-15 ℃) for 1 h. The residue was filtered and washed with a small amount of acetone and diethyl ether, giving the crude product with quantitative yield. Recrystallization of the solids from hot acetone yielded **3b** as an orange powder (31.6 mg, 0.0580 mmol, 63% yield). Spectral data were consistent with reported values in literature.[6]

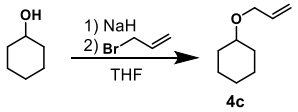


3c was prepared via anion exchange. To a round flask was added **3a** (48.6 mg, 0.100 mmol, 1 eq), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, 88.6 mg, 0.100 mmol, 1 eq) and 30 ml of diethyl ether. The mixture was stirred at room temperature for 20 min with precipitation of sodium tetrafluoroborate salt ($NaBF_4$). After cooling down in an ice bath for 5 min, the reaction mixture was passed through a syringe filter (0.45 μm) to remove insoluble residues. Concentrating the filtrate under reduced pressure gave **3c** as an orange oil. The oil was dissolved in a mixture of dichloromethane and hexane, condensed, and dried under vacuum, resulting in **3c** as orange solids (125 mg, 0.0990 mmol, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.11 – 8.02 (m, 4H), 8.00 – 7.89 (m, 4H), 7.75 – 7.64 (m, 8H), 7.48 (s, 4H), 7.17 – 7.02 (m, 6H), 3.99 – 3.86 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 169.03, 166.70, 166.23, 162.86, 162.41, 162.01, 161.62, 161.22, 134.91, 130.99, 130.09, 129.19, 129.17, 129.14, 129.12, 128.94, 128.92, 128.89, 128.87, 128.66, 127.91, 125.75, 124.32, 123.58, 121.41, 120.52, 117.62, 117.59, 117.55, 116.39, 116.21, 109.92, 56.14. **^{19}F NMR** (377 MHz, $CDCl_3$) δ (ppm): -62.41(s). **MS-ESI** (*m*/*z*): $[M]^+$ calculated for $C_{26}H_{23}O_4$, 399.1591; found, 399.1589 (0.5 ppm). **MS-ESI** (*m*/*z*): $[M]^-$ calculated for $C_{32}H_{12}BF_{24}$, 863.0654; found, 863.0650 (0.5 ppm).

2.2. Synthesis of Enol Ethers

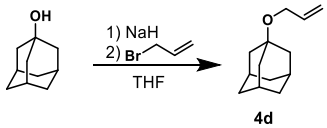
General Procedure A: Synthesis of Allyl Ethers

To a flame dried 250 mL RBF containing NaH (60% dispersion in mineral oil, 50 mmol, 1.3 eq) was added 40 mL of dry THF under nitrogen at 0 °C. Then alcohol (40 mmol, 1 eq) was added dropwise to the cold suspension. The mixture was stirred at 0 °C for 20 min. Then allyl bromide (50 mmol, 1.3 eq) was added dropwise and the mixture was warmed to room temperature. Then the solution was heated to reflux, and stirred for several hours (exact times listed below). The reaction was quenched with 20 mL of saturated aqueous NH_4Cl at 0 °C and diluted with 50 mL of DI water and 50 mL of ethyl acetate. The aqueous layer was extracted 3 times with 20 mL of ethyl acetate. The combined organic layers were washed 3 times with 20 mL of brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting oil was purified by vacuum distillation.



4c

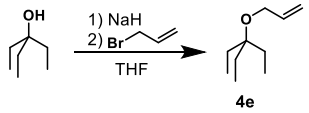
Cyclohexyl (Cy) allyl ether (**4c)** was prepared according to **General Procedure A** using cyclohexanol (4.16 mL, 40.0 mmol, 1 eq), NaH (2.0 g, 50 mmol, 1.3 eq) and allyl bromide (4.4 mL, 50 mmol, 1.3 eq). The reaction was stirred at reflux for 7 h. The product was purified by vacuum distillation (30 – 31 °C, 2 torr) to give **4c** as a colorless liquid (3.50 g, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 5.98 – 5.87 (m, 1H), 5.26 (dq, J = 17.2, 1.7 Hz, 1H), 5.14 (dq, J = 10.3, 1.5 Hz, 1H), 4.00 (dt, J = 5.6, 1.5 Hz, 2H), 3.28 (tt, J = 9.2, 3.8 Hz, 1H), 1.98 – 1.12 (m, 10H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 135.87, 116.36, 77.11, 68.93, 32.43, 25.97, 24.33. **MS-ESI** (m/z): $[M+H]^+$ calculated for $C_9H_{16}O$, 141.1274; found 141.1273 (0.7 ppm).



4d

1-Adamantyl allyl ether (**4d**) was prepared according to **General Procedure A** using1-adamantanol (6.08 g, 40.0 mmol, 1 eq), NaH (2.0 g, 50 mmol, 1.3 eq) and allyl bromide (6.06 g, 4.4 mL, 50.0 mmol, 1.3 eq). The reaction was stirred at reflux for 23 h. The product was purified by vacuum distillation (100 – 101 °C, 2 torr) to give **4d** as a milky wax (3.66 g, 47% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 5.92 (ddt, J = 17.3, 10.7, 5.6 Hz, 1H), 5.26 (dq, J = 17.2, 1.7 Hz, 1H), 5.10 (dq, J = 10.3, 1.5 Hz, 1H), 3.97 (dt, J = 5.6, 1.5 Hz, 2H), 2.14 (q, J = 3.3 Hz, 3H), 1.81 – 1.52 (m, 14H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 136.72, 115.92, 72.58, 61.51, 41.78,

36.64, 30.70. **MS-ESI** (*m*/*z*): $[M+H]^+$ calculated for $C_{13}H_{20}O$, 193.1587; found 193.1586 (0.5 ppm).

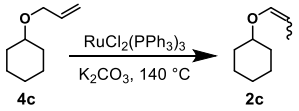


4e

2-Ethyl-3-pentyl (CEt$_3$) allyl ether (**4e**) was prepared according to **General Procedure A** with minor deviations. 3-ethylpentan-3-ol (21.2 mL, 150 mmol, 1 eq), NaH (9.00 g, 300 mmol, 1.5 eq), and allyl bromide (38.9 mL, 450 mmol, 3 eq) were used. The reaction was stirred at reflux for 17 h. After work up, another portion of NaH (3.0 g, 75 mmol, 0.5 eq) was added to the crude product under nitrogen, and the mixture was stirred at room temperature overnight to remove residual alcohol. The product was then distilled directly from the above suspension (55 – 60 °C, 15 torr) to give **4e** as a colorless liquid (7.71 g, 33% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 5.93 (ddt, *J* = 17.2, 10.7, 5.5 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.10 (dq, *J* = 10.3, 1.5 Hz, 1H), 3.78 (dt, *J* = 5.5, 1.5 Hz, 2H), 1.46 (q, *J* = 7.5 Hz, 6H), 0.80 (t, *J* = 7.5 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 136.07, 115.56, 79.23, 61.57, 26.20, 7.53. **MS-ESI** (*m*/*z*): $[M+H]^+$ calculated for $C_{10}H_{20}O$, 157.1587; found 157.1588 (0.6 ppm).

General Procedure B: Isomerization of Ally Ether to form Enol Ether[7]

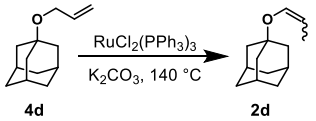
To a flame dried 7 mL scintillation vial was added allyl ether (1 eq), K_2CO_3 (1 mol%), and $RuCl_2(PPh_3)_3$ (0.05 mol%). The vial was flushed with argon and sealed with a PTFE-lined screw on cap. The reaction was stirred at 140 °C for several hours (exact times listed below). Upon complete conversion of allyl to enol ether, as determined by ^{1}H NMR, the reaction was cooled to room temperature, transferred to a RBF, and purified by vacuum distillation.



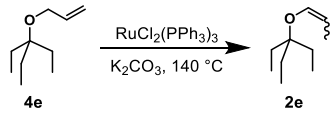
4c **2c**

Enol ether **2c** was prepared according to **General Procedure B** using **4c** (2.00 g, 14.3 mmol, 1 eq,), $RuCl_2(PPh_3)_3$ (6.9 mg, 0.0071 mmol, 0.0005 eq (0.05 mol%)), and K_2CO_3 (19.7 mg, 0.143 mmol, 0.01 eq). The reaction was stirred at 140 °C for 6.33 h. The product was purified by vacuum distillation (30 – 34 °C, 3 torr) to give **2c** as a clear and colorless liquid (1.63 g, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 6.09 (dq, *J* = 12.2, 1.7 Hz, 0.29H, *trans*), 5.99 (dq, *J* = 6.3, 1.7 Hz, 0.69H, *cis*), 4.88 (dq, *J* = 12.3, 6.7 Hz, 0.28H, *trans*), 4.38 (p, *J* = 6.7 Hz, 0.71H, *cis*), 3.62 –

3.53 (m, 1H, *cis/trans*), 1.93 – 1.11 (m, 13H, *cis/trans*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 145.27, 144.31, 101.20, 100.64, 79.03, 78.13, 42.13, 35.72, 32.46, 32.30, 25.75, 25.71, 25.61, 24.27, 23.96, 23.80, 12.66, 9.45. **MS-ESI** (*m*/*z*): $[M+H]^+$ calculated for $C_9H_{16}O$, 141.1274; found 141.1272 (1.4 ppm).



Enol ether **2d** was prepared according to **General Procedure B** using **4d** (2.75 g, 14.3 mmol, 1 eq), $RuCl_2(PPh_3)_3$ (6.9 mg, 0.0071 mmol, 0.0005 eq (0.05 mol%)), and K_2CO_3 (19.7 mg, 0.143 mmol, 0.01 eq). The reaction was stirred at 140 °C for 6.5 h. The product was purified by vacuum distillation (123 °C, 2 torr) to give **2d** as a milky wax (1.73 g, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 6.34 (d, *J* = 12.2 Hz, 0.25H, *trans*), 6.29 (dd, *J* = 6.2, 2.5 Hz, 0.75H, *cis*), 4.98 (dq, *J* = 13.2, 6.8 Hz, 0.25H, *trans*), 4.45 (p, *J* = 6.6 Hz, 0.83H, *cis*), 2.17 (s, 4H, *cis/trans*), 1.80 (dd, *J* = 10.5, 3.0 Hz, 6H, *cis/trans*), 1.70 – 1.52 (m, 10H, *cis/trans*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 139.45, 138.40, 103.27, 102.62, 74.86, 74.84, 42.13, 36.52, 36.48, 30.84, 12.85, 9.55. **MS-ESI** (*m*/*z*): $[M+H]^+$ calculated for $C_{13}H_{20}O$, 193.1587; found 193.1586 (0.5 ppm).



Enol ether **2e** was prepared according to **General Procedure B** using **4e** (2.34 g, 15.0 mmol, 1 eq), $RuCl_2(PPh_3)_3$ (14.4 mg, 0.0150 mmol, 0.001 eq (0.1 mol%)), and K_2CO_3 (41.5 mg, 0.300 mmol, 0.02 eq). The reaction was stirred at 140 °C for 17 h. The product was purified by vacuum distillation (55 – 59 °C, 15 torr) to give **2e** as a colorless liquid (1.73 g, 83% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm): 6.14 (dq, *J* = 12.0, 1.6 Hz, 0.25H, *trans*), 6.09 (dq, *J* = 6.3, 1.7 Hz, 0.77H, *cis*), 4.98 (dq, *J* = 12.0, 6.8 Hz, 0.25H, *trans*), 4.41 (p, *J* = 6.6 Hz, 0.74H, *cis*), 1.59 (dd, *J* = 6.7, 1.7 Hz, 3H, *cis/trans*), 1.57 – 1.47 (m, 8H, *cis/trans*), 0.82 (td, *J* = 7.5, 4.2 Hz, 9H, , *cis/trans*). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm): 139.90, 138.82, 103.46, 102.06, 81.81, 27.28, 12.91, 9.53, 7.64, 7.59. **MS-ESI** (*m*/*z*): $[M+H]^+$ calculated for $C_{13}H_{20}O$,157.1587; found 157.1587 (<0.1 ppm).

2.3. Polymer Synthesis

General Procedure C: Additive Study of MF-ROMP

To a 2-dram glass vial containing a magnetic stir bar and pyrylium **3a** (1.3 mg, 0.00266 mmol, 0.05 eq) were added NB (**1**) (500 mg, 5.31 mmol, 100 eq), phase-transfer catalyst (PTC) (0.0266 mmol, 0.5 eq) and CH_2Cl_2 (2.65 mL, dried over 3Å molecular sieves) under air. The mixture was stirred at room temperature for 1 – 3 min until the pyrylium salt dissolved. Then initiator **2b** (5.9 μL, 0.0531 mmol, 1 eq) was added via micro-syringe. The vial was sealed with PTFE-lined screw cap and irradiated with one blue LED light (450 nm, 4 W) for 1 h at room temperature (~ 22 ℃). Upon completion, a small scoop of hydroquinone (HQ) was added to the reaction mixture and aliquots were taken for analysis to determine monomer conversion and crude molecular weight by ^{1}H NMR spectroscopy and GPC, respectively. Then CH_2Cl_2 and residual norbornene were removed under vacuum, and the left polymer samples were analyzed by ^{1}H NMR spectroscopy to determine the *trans/cis* ratio of the sample. *Trans/cis* ratio was determined as the ratio of the peaks at (δ 2.55 to 2.33 ppm) and (δ 2.85 to 2.70 ppm) and were consistent with the alkene signals from (δ 5.41 to 5.30 ppm) and (δ 5.28 to 5.14 ppm) for each sample. The results are shown in Table S1. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining **3a**. The filtrate was concentrated to approximately 5 mL and precipitated into cold MeOH (80 mL, 3 ℃). The pure polymer was collected by filtration, washed with MeOH, and dried under vacuum to give a white powder.

Table S1. Effect of phase-transfer catalysts additives on MF-ROMP of **1** in CH_2Cl_2.

entry	additive[a]	equivalent[b]	PC	$[1]_0$ (M)[c]	conversion[d] (%)	$M_{n,exp}$[e] (kDa)	$M_{w,exp}$[e] (kDa)	$Đ$[e]	*trans*:*cis*[d]
1	$TBABF_4$	0.5	**3a**	2.0	88	13.0	18.6	1.4	79:21
2	$TBAPF_6$	0.5	**3a**	2.0	87	17.0	26.4	1.6	74:26
3	$NaBAr^F{}_4$	0.5	**3a**	2.0	83	23.3	37.6	1.6	58:42
4	TBACl	0.5	**3a**	2.0	0	--	--	--	--
5	TBABr	0.5	**3a**	2.0	0	--	--	--	--
6	$TBANO_3$	0.5	**3a**	2.0	0	--	--	--	--

[a]TBA = tetrabutylammonium. [b]Relative to enol ether initiator. [c]Initial concentration of **1**. [d]Determined by ^{1}H NMR spectroscopy. [e]Determined by GPC analysis on crude reaction sample using multi-angle light scattering (MALS) and refractive index (RI) detection. Dispersity ($Đ$) = M_w/M_n. All reactions were conducted at room temperature (22 ℃) for 1 h.

General Procedure D: Investigation of Counteranion and Solvent Effect on MF-ROMP

To a 2-dram glass vial containing a magnetic stir bar and pyrylium **3a**–**c** (0.00266 mmol, 0.05 eq) were added NB (**1**) (500 mg, 5.31 mmol, 100 eq) and solvent (2.65 mL, dried over 3Å molecular sieves, solvent mixtures were prepared in volume ratios) under air. The mixture was stirred at room temperature for 1 – 3 min until the pyrylium salt dissolved. Then initiator **2b** (5.9

μL, 0.0531 mmol, 1 eq) was added via micro-syringe. The vial was sealed with a PTFE-lined screw on cap and irradiated with one blue LED light (450 nm, 4 W) for 1 h at room temperature (~ 22 °C). Upon completion, a small scoop of hydroquinone (HQ) was added to the reaction mixture and aliquots were taken for analysis to determine monomer conversion and crude molecular weight by ^{1}H NMR spectroscopy and GPC, respectively. Solvents and residual NB were then removed under vacuum, and the remaining sample was analyzed by ^{1}H NMR spectroscopy to determine the *trans/cis* ratio of the sample. *Trans/cis* ratio was determined as the ratio of the peaks at (δ 2.55 to 2.33 ppm) and (δ 2.85 to 2.70 ppm) and were consistent with the alkene signals from (δ 5.41 to 5.30 ppm) and (δ 5.28 to 5.14 ppm) for each sample. The results are shown in Table 1 and Table S2. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining pyrylium salts. The filtrate was concentrated down to approximately 5 mL and precipitated into cold MeOH (80 mL, 3 °C). The pure polymer was collected by filtration, washed with MeOH, and dried under vacuum to give a white powder.

Table S2. Polymerization results and GPC Data for MF-ROMP of **1** in different solvents.

entry	solvents[a]	E_T^N	PC	time (min)	conversion[b] (%)	$M_{n,exp}$[c] (kDa)	$M_{w,exp}$[c] (kDa)	$Đ$[c]	*trans*:*cis*[b]
1	Acetone/Tol =1	--	**3c**	60	12	4.83	7.39	1.5	84:16
2	CH_3CN/Tol = 1/2	--	**3c**	40	74	11.3	20.1	1.8	82:18
3	CH_2Cl_2	0.309	**3c**	60	77	15.6	22.5	1.4	56:44
4	CH_2Cl_2/Tol = 1	--	**3c**	20	47	9.35	11.5	1.2	54:46
5	Et_2O/Tol = 1	--	**3c**	60	10	2.33	3.26	1.4	64:36
6	Tol	0.099	**3c**	60	21	2.11	2.70	1.3	55:45
7	CH_3CN/Tol = 1/2	--	**3a**	40	69	8.09	10.8	1.3	83:17
8	CH_3CN/Tol = 1/2	--	**3b**	40	60	6.69	7.62	1.1	82:18

[a]Tol = toluene. [b]Determined by ^{1}H NMR spectroscopy. [c]Determined by GPC analysis on crude reaction sample using multi-angle light scattering (MALS) and refractive index (RI) detection. Dispersity ($Đ$) = M_w/M_n. All reactions were conducted at room temperature (22 ℃).

Table S3. Polarity, dielectric constant and donor number of solvents screened in MF-ROMP.

solvent	$E_T^{N_a}$	ε[b]	DN[c]
ACN	0.460	37.5	14.1
acetone	0.355	20.7	17.0
DCM	0.309	8.93	1.0
Et_2O	0.117	4.33	19.2
Tol	0.099	2.38	0.1

[a]Normalized solvent polarity value based on the negatively solvatochromic pyridinium A-phenolate betaine dye.[8] [b]Dielectric constant. [c]Gutmann's Donor Number of slovents.[9]

General Procedure E: MF-ROMP of 1 at -78 °C

To a 2-dram glass vial containing a magnetic stir bar and pyrylium **3a** or **3c** (0.00181 mmol, 0.05 eq) were added NB (**1**) (170 mg, 1.81 mmol, 50 eq), and solvent (3.61 mL of CH_2Cl_2 or toluene dried over 3Å molecular sieves) under air. The mixture was stirred at room temperature for 1 – 3 min until the pyrylium salt dissolved. Then initiator **2a**, **2b,** or **2e** was added. **2a** and **2b** (4.0 μL, 0.0361 mmol, 1 eq) were added via micro-syringe, while **2e** (5.6 mg, 0.0361 mmol, 1 eq) was added gravimetrically. The vial was sealed with a PTFE-lined screw on cap, allowed to thermally equilibrate in the cooling bath for 5 min, and then irradiated with two blue LED lights (450 nm, 4 W) for 1 h at -76 ℃ (as shown in Figure S1a). Upon completion, the reaction mixture was warmed up to room temperature. A small scoop of hydroquinone (HQ) was added, and aliquots were taken for analysis to determine monomer conversion and crude molecular weight by ^{1}H NMR spectroscopy and GPC, respectively. Solvent and residual NB were removed under vacuum, and the remaining sample was analyzed by ^{1}H NMR spectroscopy to determine the *trans/cis* ratio of the sample. *Trans/cis* ratio was determined as the ratio of the peaks at (δ 2.55 to 2.33 ppm) and (δ 2.85 to 2.70 ppm) and was consistent with the alkene signals from (δ 5.41 to 5.30 ppm) and (δ 5.28 to 5.14 ppm) for each sample. The results are shown in Table 1. The polymer sample was then diluted with CH_2Cl_2 and passed through basic alumina to remove any remaining pyrylium salts. The filtrate was concentrated down to approximately 5 mL and precipitated into cold MeOH (80 mL, -12 ℃). The pure polymer was collected by filtration, washed with MeOH, and dried under vacuum to give a white powder. *Trans/cis* ratio was further confirmed by ^{1}H NMR and quantitative ^{13}C NMR of the pure polymer sample.

General Procedure F: Charton Study

Pyrilium **3a** (1.5 mg, 0.0030 mmol, 5 mol% relative to initiator), NB (**1)** (564 mg, 6.00 mmol, 100 eq), and initiator (0.060 mmol, 1 eq) were added to a 2-dram borosilicate glass vial gravimetrically. 3 mL of CH_2Cl_2 dried over 3Å molecular sieves were added to the vial. 15 μL of 1,2-dicholoethane (DCE) were added as an internal standard. An aliquot was taken and diluted with $CDCl_3$ for analysis by ^{1}H NMR spectroscopy to determine the initial NB to DCE ratio. The reaction solution was separated equally into three 2-dram borosilicate glass vials for parallel reactions. After being sealed with a PTFE-lined screw on cap, each sample was clamped in a mineral oil bath at 25 or 50 °C, or an ethanol bath at -30 °C and allowed to thermally equilibrate for 10 min. The sample was then irradiated with two blue LEDs (as shown in Figure S1a–b) with

magnetic stirring, until approximately 40% conversion was achieved. A small scoop of hydroquinone (HQ) was added to the reaction mixture, and an aliquot was taken and diluted with $CDCl_3$ for analysis by ^1H NMR spectroscopy to determine monomer conversion. Conversion was calculated as the consumption of NB (δ 6.06 to 5.94 ppm) relative to DCE (δ 3.78 to 3.69 ppm). A second aliquot was taken and diluted with tetrahydrofuran (THF) for analysis of the crude molecular weight by GPC. CH_2Cl_2 and residual norbornene were removed *in vacuum*, and the residue was analyzed by ^1H NMR spectroscopy in $CDCl_3$ to determine the *trans/cis* ratio of the sample. *Trans/cis* ratio was determined as the ratio of the peaks at (δ 2.51 to 2.30 ppm) and (δ 2.83 to 2.70 ppm) and was consistent with the alkene signals from (δ 5.41 to 5.25 ppm) and (δ 5.25 to 5.14 ppm) for each sample (Table S4). *Trans/cis* ratio was further confirmed by quantitative ^{13}C NMR of the pure polymer sample. Charton plots were generated at each temperature (Figure 1c and Figure S2).

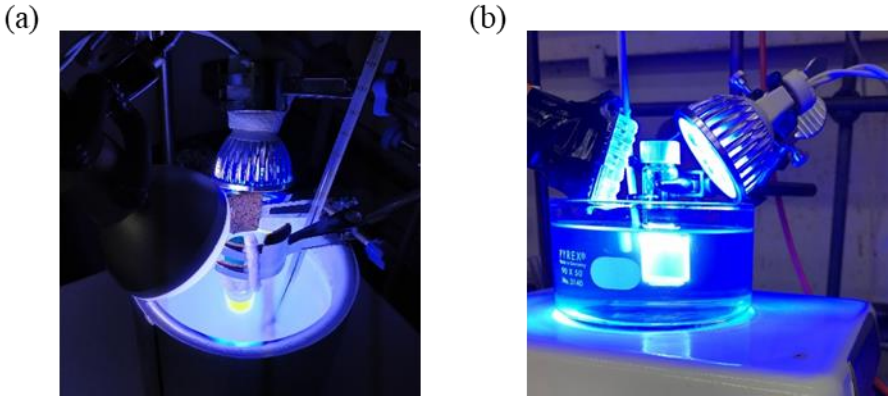
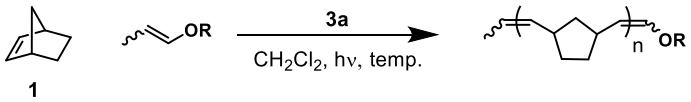


Figure S1. Setup for MF-ROMP at (a) -76, (b) 25, and 50 °C.

Table S4. Summarized *trans/cis* ratio of MF-ROMP of **1** using **3a** as the photocatalyst, CH_2Cl_2 as the solvent and **2a-e** as initiators as investigated at -30, 25, and 50 °C.



1

R	***ν***	***trans/cis***		
		-30 °C	**25 °C**	**50 °C**
Me	0.52	2.4	2.29 ± 0.02	2.5
Et	0.56	3.7	3.15 ± 0.02	3.5
Cy	0.87	6.1	4.9 ± 0.1	5.0
1-Ad	1.33	11.1	7.0 ± 0.4	6.5
CEt_3	2.38	18.7	11.2 ± 0.5	7.3

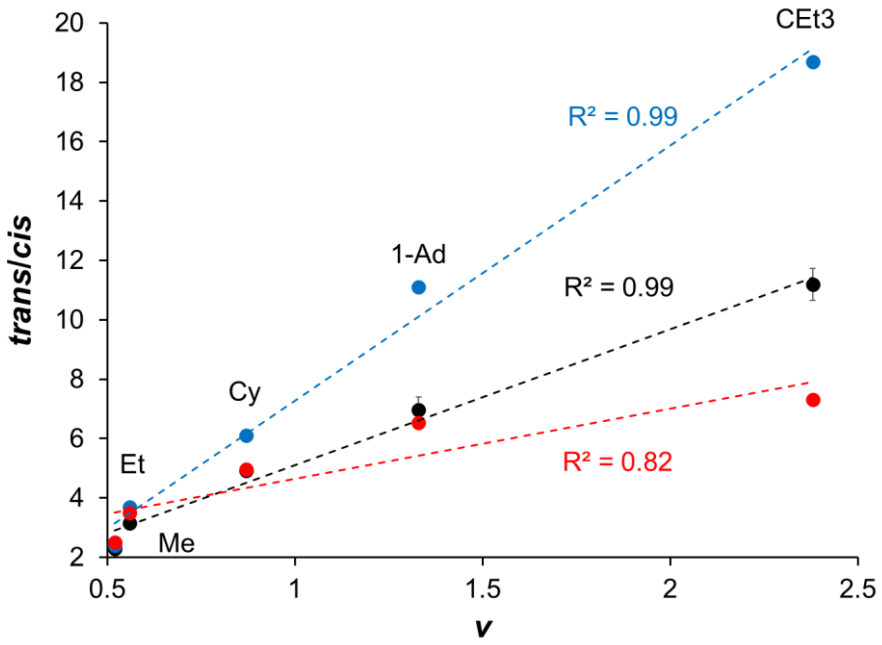


Figure S2. Linear correlation of *trans*/*cis* ratio vs. Charton parameter (ν) at -30 (**blue**), 25 (**black**), and 50 °C (**red**), slope = 8.60, 4.59 and 2.36, respectively. Points at 25 °C are the average of three runs. Error bars represent the standard deviation of the three runs.

General Procedure G: Monitoring *trans/cis* ratio versus time

Pyrilium **3a** (0.5 mg, 0.0010 mmol, 5 mol% relative to initiator), NB (**1)** (188 mg, 2.00 mmol, 100 eq), and initiator (0.020 mmol, 1 eq) were added to a 2-dram borosilicate glass vial gravimetrically. 1 mL of CH_2Cl_2 dried over 3Å molecular sieves were added to the vial. 5 µL of 1,2-dicholoethane (DCE) were added as an internal standard. An aliquot was taken and diluted with $CDCl_3$ for analysis by ^{1}H NMR spectroscopy to determine the initial NB to DCE ratio. The vial was placed into a 25 ℃ oil bath, and magnetically stirred at 650 rpm. After thermally equilibrating for 10 min, the reaction was irradiated with 2 blue LED lights as described in general procedure F. Aliquots were taken at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 45, and 60 min, diluted with $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. A plot of *trans/cis* ratio as a function of time for initiators **2a**–**2e** is shown in Figure S3.

Variations in *trans/cis* ratio are observed early in the reaction due to inaccurate integration of the ^{1}H NMR spectrum, which is attributed to the low monomer conversions, as well as the overlap of monomer signals with polymer signals.

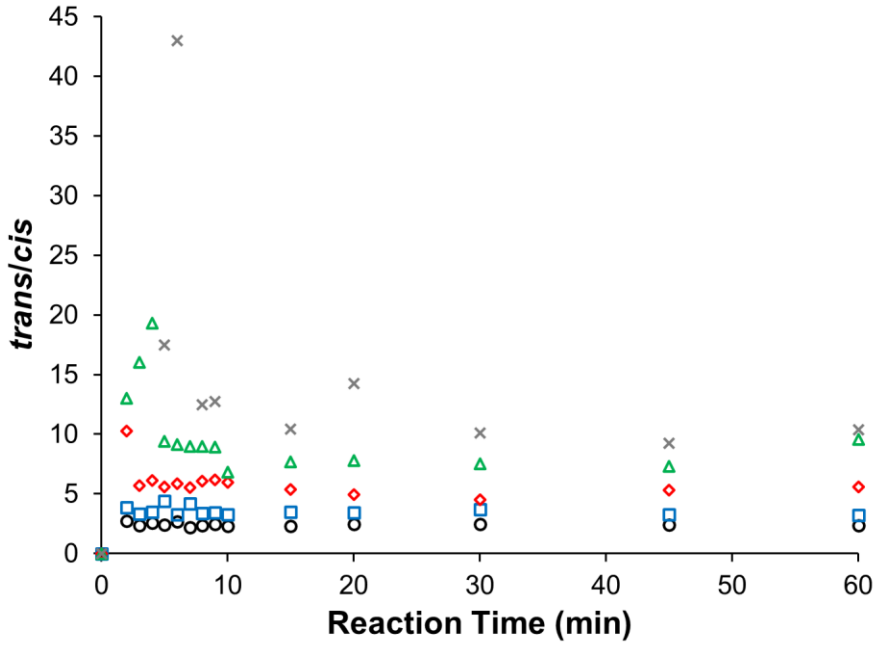


Figure S3. Alkene *trans/cis* ratio as a function of time with initiators **2a** (**black** circles), **2b** (**blue** squares), **2c** (**red** diamonds), **2d** (**green** triangles), and **2e** (**gray** x).

3. Thermogravimetric Analysis (TGA)

TGA was performed on a TA TGA Q50 under nitrogen from room temperature to 600 °C at a heating rate of 10 °C/min. The decomposition temperature (T_d) of each sample was determined by the onset of the weight loss from TGA thermograms.

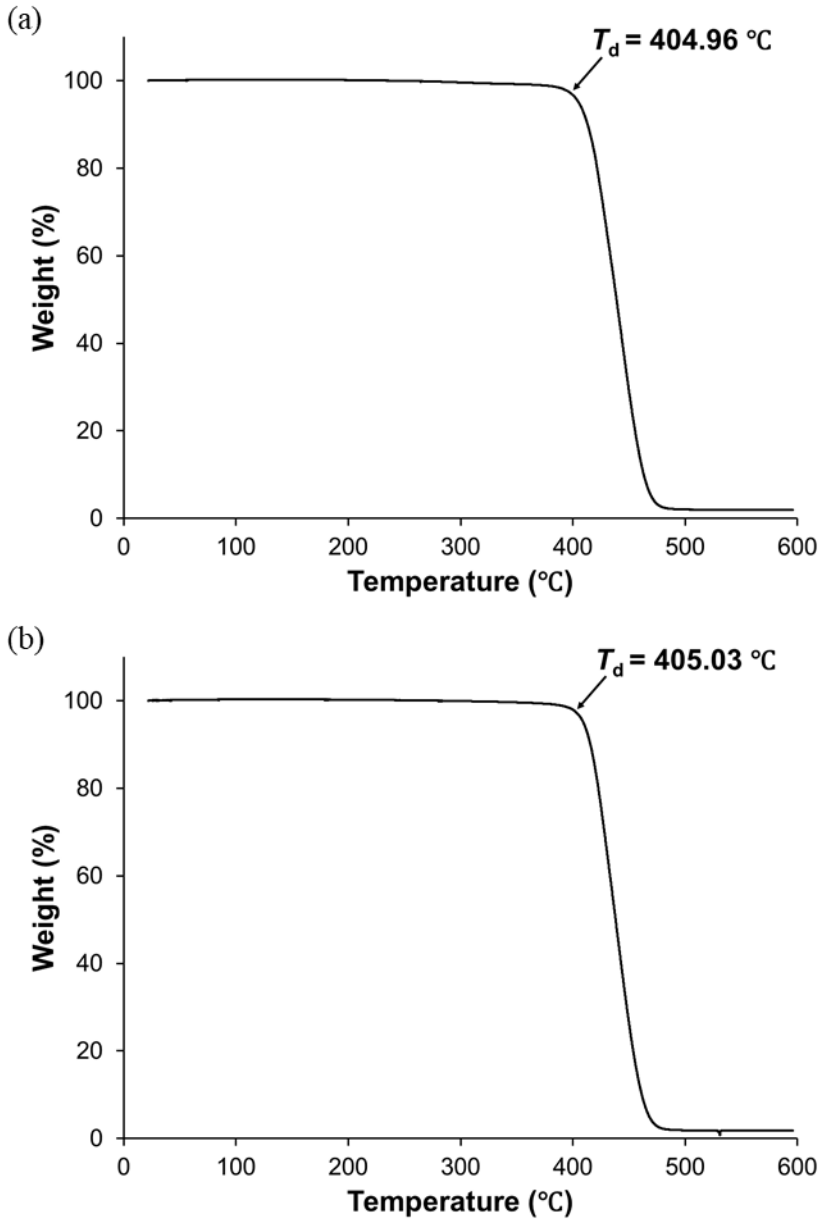


Figure S4. Representative TGA thermograms of PNB with (a) > 98% *trans* content (Table 1, entry 13), and (b) 65% *cis* content (Table 1, entry 6).

4. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed on a TA DSC Q250 calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min and cooling rate of 5 °C/min. Heat flow normalized by mass of the sample (W/g) from first cooling and the second heating were recorded and reported. The glass transition temperature (T_g) of each sample was determined by the midpoint of DSC curve during the second heating cycle. The melting (T_m) and crystallization (T_c) temperature were reported as the peak temperature. Representative DSC thermograms of PNB with > 98% *trans* content (solid black line, Table 1, entry 13), and 75% *cis* content (dashed gray line, Table 1, entry 7) are shown in Figure 1d in the main text.

5. Mechanism Study by Quantum Chemical Calculations

5.1. Proposed Reaction Mechanism

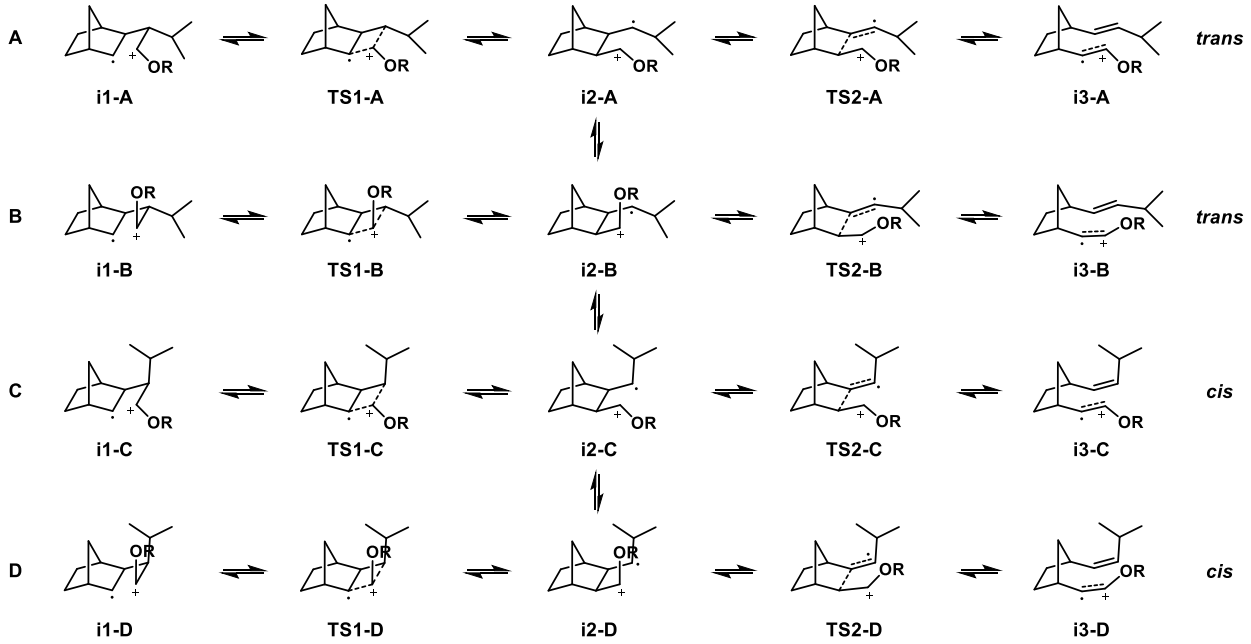


Figure S5. Proposed reaction path from **i1** to **i3**.

5.2. Calculated Reaction Progress

All quantum chemical calculations were carried out using the Q-Chem 5.0 software package[10] at the B3LYP level of theory[11] using a spin unrestricted formalism and the 6-31G* basis set[12] for optimization and frequency calculations. The structures without counterions were modeled as cationic doublets. Double-Ended Growing String Method (GSM) was used to identify transition states and minimum-energy reaction paths from optimized reactant and product structures.[13],[14] SMD solvation corrections[15] were performed for all transition states and stable intermediates at B3LYP/6-31G* with CH_2Cl_2 and toluene as the solvents. Reported energies are Gibbs free energies with enthalpy and entropy corrections in the solvent phase. All geometries were confirmed to have the appropriate number of imaginary frequencies.

Quantum chemical calculations of the model with R = Et were performed at the B3LYP/6-31G* level, simulating the isomerization of **i2** and subsequent ring-opening to **i3**. An isopropyl group was used instead in place of the polymer to simplify the calculation. Counteranion binding around the active chain end was neglected at this stage. SMD solvation corrections were performed using CH_2Cl_2 and toluene.

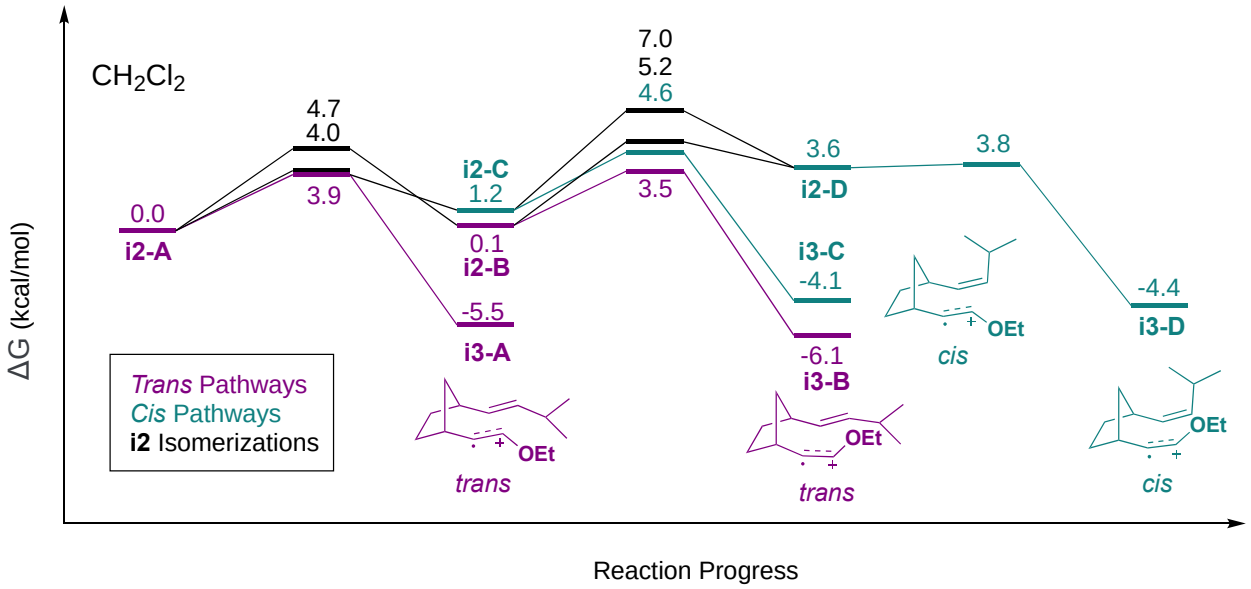


Figure S6. Calculated reaction progress describing the isomerization of **i2** and subsequent ring-opening to **i3** for the model with R = Et in CH_2Cl_2.

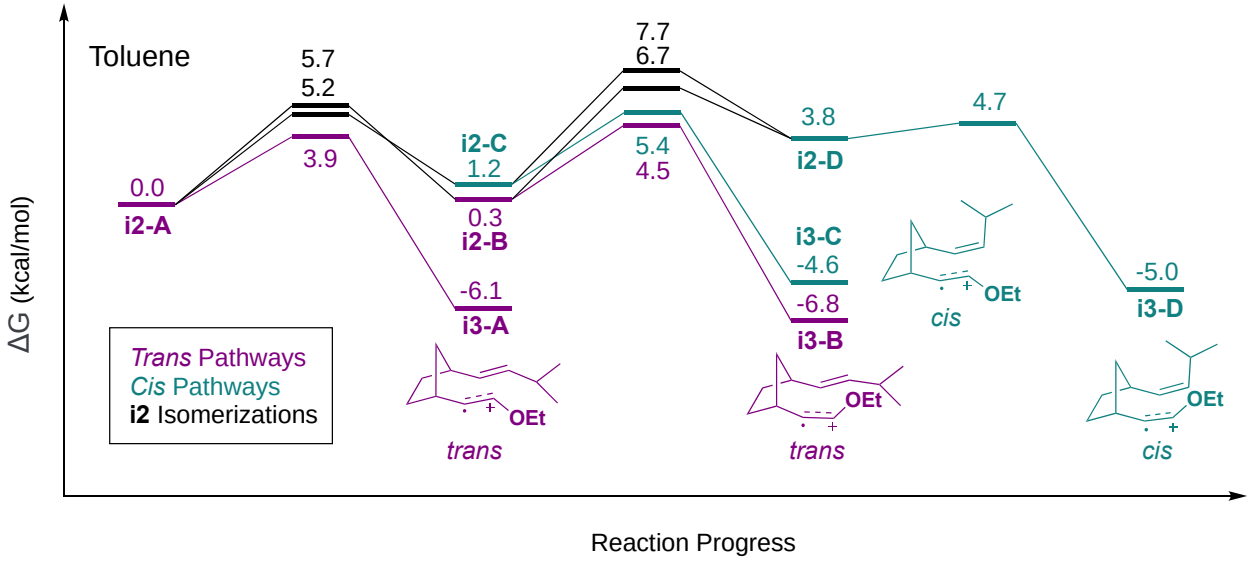


Figure S7. Calculated reaction progress describing the isomerization of **i2** and subsequent ring-opening to **i3** for the model with R = Et in toluene.

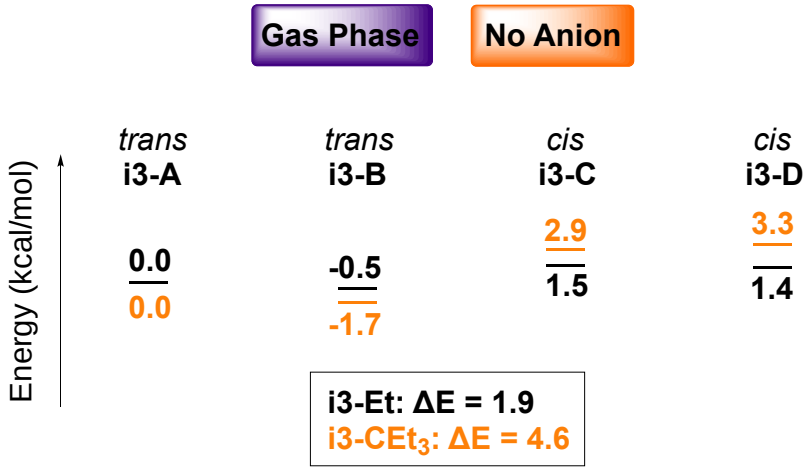
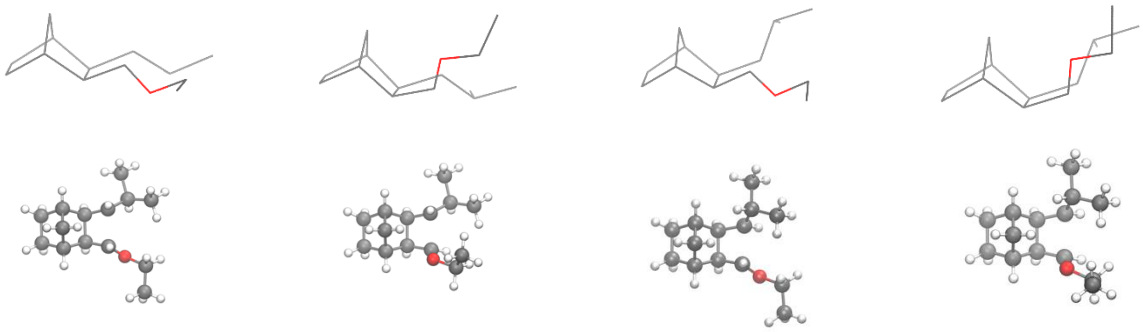


Figure S8. Calculated energies of **i3** with R = Et (black) and R = CEt_3 (orange) in gas phase without a coordinated anion. The ΔE reported for each data set corresponds to the difference in energy between the lowest energy *trans* structure and the lowest energy *cis* structure.

Table S5. Calculated Gibbs free energies of **i3** with R = Me, Et, Cy, and CEt_3 in gas phase without a coordinated anion. The ΔE reported for each data set corresponds to the difference in energy between the lowest energy *trans* structure (**i3-A** or **i3-B**) and the lowest energy *cis* structure (**i3-C** or **i3-D**).

	i3-A	**i3-B**	**i3-C**	**i3-D**	**Δ E**
R = Me	0.0	-0.7	1.1	1.4	1.8
R = Et	0.0	-0.5	1.5	1.4	1.9
R = Cy	0.0	-1.3	1.0	1.1	2.3
R = CEt_3	0.0	-1.7	2.9	3.3	4.6

5.3. Representative 3D Structures



i2-A-Et **i2-B-Et** **i2-C-Et** **i2-D-Et**

Figure S9. Optimized 3D structures of selected intermediates.

5.4. Optimized Cartesian Coordinates of Selected Structures – B3LYP/6-31G*

i2-A-Et
39

C -2.095931 3.540669 0.841397
C -0.517583 3.428603 0.792304
C -2.550897 2.470027 -0.190041
H -2.511491 3.399620 1.842405
C -2.271553 1.091666 0.458874
C -0.711648 0.977425 0.403253
H -2.750733 0.302706 -0.127943
H -2.667541 1.022180 1.476935
C -0.282221 2.310760 -0.255768
H -0.397660 0.132078 -0.215850
H -0.260931 0.837858 1.391238
C -1.435131 2.543985 -1.256324
H -3.578666 2.606033 -0.538216
H -1.382647 3.495950 -1.798947
H -1.515619 1.746524 -2.001192
H 0.729813 2.306073 -0.668884
C -0.164988 4.835225 0.386137
H -0.096278 3.191267 1.774106
C 0.502765 5.791000 1.321615
C 0.474982 7.244315 0.829247
H 0.966451 7.341024 -0.146070
H 1.005016 7.893167 1.532718
H -0.545413 7.627937 0.732761
C 1.974537 5.305950 1.494438
H -0.008159 5.017892 -0.679598
H 2.478649 5.970369 2.203726
H 2.518912 5.346558 0.545029
H 2.029908 4.286155 1.885724
C -2.312108 4.965895 0.410366
H 0.020951 5.719623 2.307059
O -2.817812 5.796456 1.274860
H -2.421486 5.223617 -0.646277
C -3.319205 7.111926 0.834966
C -4.834136 7.107698 0.880666
H -2.925211 7.310761 -0.166556
H -2.886382 7.819768 1.543707
H -5.254922 6.394914 0.164569
H -5.196936 8.107710 0.620284
H -5.195593 6.863067 1.883242
*****

i2-B-Et
39

C -2.028748 3.467154 1.177803
C -0.468295 3.414764 0.890174
C -2.636706 2.670615 0.003092
H -2.288850 3.054384 2.160563
C -2.305743 1.181599 0.275491
C -0.764706 1.101465 0.009253
H -2.861872 0.545357 -0.418952
H -2.578915 0.868380 1.288523
C -0.401408 2.550326 -0.400089
H -0.537387 0.412302 -0.809270
H -0.198247 0.762020 0.882467
C -1.671338 2.985579 -1.160991
H -3.695395 2.878048 -0.167261
H -1.681160 4.031130 -1.483284
H -1.863742 2.363121 -2.040351
H 0.548023 2.645172 -0.934501
C -0.210963 4.890049 0.729805
H 0.103809 2.996453 1.723309
C 0.653093 5.659229 1.680349
C 0.457765 7.178917 1.592375
H 0.670600 7.545401 0.581124
H 1.137380 7.690219 2.280365
H -0.561972 7.480976 1.857492
C 2.128533 5.275129 1.356334
H -0.285330 5.292870 -0.282323
H 2.786730 5.793251 2.061276
H 2.405868 5.581700 0.342328
H 2.301975 4.199713 1.456185
C -2.236983 4.962792 1.216916
H 0.451878 5.317014 2.705544
O -3.001847 5.526459 0.323708
H -2.112474 5.496149 2.164239
C -3.428896 6.928067 0.468879
C -2.990468 7.721201 -0.744634
H -3.018578 7.318481 1.405600
H -4.517063 6.869871 0.548978
H -1.900284 7.779102 -0.816204
H -3.379998 8.740962 -0.658313
H -3.387724 7.282100 -1.663957
*****

i2-C-Et
39

C -1.641830 3.484482 0.666469
C -0.382137 3.235151 -0.262279
C -2.518666 2.227949 0.403781
H -1.396227 3.654292 1.717537
C -1.778989 1.027823 1.049406
C -0.568913 0.792352 0.084522
H -2.441983 0.158337 1.081246
H -1.470992 1.235135 2.079128

C -0.738023 1.909736 -0.976069
H -0.628944 -0.190478 -0.391516
H 0.397167 0.845285 0.596247
C -2.276223 1.969141 -1.099123
H -3.557030 2.347993 0.725375
H -2.650757 2.754928 -1.764263
H -2.708464 1.021127 -1.432969
H -0.182672 1.730610 -1.900151
C -0.402317 4.547236 -1.011555
H 0.542646 3.151898 0.321440
C -0.442724 4.709718 -2.498746
C 1.029171 4.529509 -2.987398
H 1.674888 5.321463 -2.593982
H 1.042719 4.589047 -4.080853
H 1.445579 3.561724 -2.693650
C -0.991705 6.071815 -2.949287
H 0.089069 5.366376 -0.480262
H -0.905422 6.170479 -4.035372
H -0.430904 6.897059 -2.494463
H -2.050861 6.191073 -2.694522
C -2.185182 4.753257 0.060036
H -1.036447 3.906322 -2.949139
O -2.215612 5.822422 0.806270
H -2.880327 4.716346 -0.783226
C -2.925623 7.032512 0.359838
C -3.955639 7.405815 1.406714
H -3.371760 6.829180 -0.618719
H -2.149394 7.794178 0.255078
H -4.728301 6.636739 1.497240
H -4.436323 8.343490 1.108925
H -3.485480 7.556908 2.382291

*****

i2-D-Et

39

C -2.113027 3.586909 0.942224
C -0.536292 3.635392 0.761914
C -2.559151 2.541869-0.104534
H -2.412587 3.326169 1.965445
C -2.087438 1.163324 0.424838
C -0.537432 1.211340 0.210873
H -2.546398 0.361837-0.160870
H -2.368423 0.999576 1.470381
C -0.306170 2.623258-0.386901
H -0.212107 0.447659-0.501465
H 0.024376 1.049582 1.136573
C -1.569154 2.783077-1.262786
H -3.622546 2.596955-0.347922
H -1.679896 3.758384-1.744200
H -1.636607 2.011711-2.036156
H 0.656758 2.734875-0.891748
C -0.329398 5.111227 0.507442
H -0.012404 3.340099 1.679039
C 0.317509 5.713121-0.695382
C 1.855851 5.627377-0.437323
H 2.146694 6.244296 0.419276
H 2.375149 6.006012-1.324051
H 2.191223 4.601817-0.258636
C -0.094832 7.172203-0.946566
H -0.235311 5.715825 1.413088
H 0.509727 7.600908-1.751319
H 0.054872 7.790041-0.053134
H -1.144114 7.247487-1.248850
C -2.509024 5.021724 0.693712
H 0.099447 5.111863-1.583793
O -3.233080 5.324043-0.342262
H -2.533744 5.727802 1.527537
C -3.894731 6.647154-0.399619
C -4.337526 6.890579-1.823747
H -3.177808 7.392633-0.043269
H -4.738199 6.588724 0.294335
H -3.483503 6.949108-2.504909
H -4.877403 7.841897-1.867877
H -5.010774 6.099324-2.164994

*****

i3-A-Et

39

C -2.561620 3.904930 -0.318559
C 0.187936 3.713311 0.430480
C -2.396909 2.429689 -0.488707
H -2.520872 4.350913 0.671523
C -2.376340 1.680076 0.869084
C -0.871730 1.551906 1.258586
H -2.830472 0.692924 0.746354
H -2.966572 2.202124 1.628551
C -0.081940 2.260668 0.129208
H -0.582945 0.498542 1.310751
H -0.654958 1.985593 2.239397
C -0.999170 2.084148 -1.100332
H -3.182985 2.060384 -1.161678
H -0.728229 2.712213 -1.953571
H -1.002194 1.040530 -1.434090
H 0.881963 1.764305 -0.057264
C 0.709938 4.616525 -0.443548
H 0.037616 4.041318 1.460550
C 1.116828 6.017816 -0.101183
C 0.440637 7.044352 -1.032094
H 0.704584 6.858702 -2.080593
H 0.772801 8.056498 -0.779310
H -0.649403 7.011269 -0.933618
C 2.657118 6.137586 -0.191511
H 0.919275 4.299268 -1.468087
H 2.964378 7.153959 0.076487
H 3.009620 5.936760 -1.209934
H 3.154707 5.438953 0.487883
C -2.924628 4.736872 -1.364443
H 0.814853 6.227554 0.933402
O -3.137493 6.012457 -1.157760
H -3.069019 4.357604 -2.377957
C -3.528832 6.874170 -2.282681
C -4.426751 7.970423 -1.751147
H -4.024300 6.250706 -3.033609
H -2.595332 7.268502 -2.696100
H -5.349145 7.559318 -1.331456
H -4.691323 8.641006 -2.575007
H -3.915828 8.557057 -0.982572

*****

3i-B-Et

39

C -2.474446 3.878938 -0.274473
C 0.232162 3.626901 0.431728
C -2.346104 2.413975 -0.532777
H -2.480127 4.246945 0.747372
C -2.329245 1.589401 0.780143
C -0.823907 1.430818 1.156863
H -2.788601 0.612738 0.604243
H -2.914072 2.070263 1.570809
C -0.035653 2.190199 0.058124
H -0.541116 0.374590 1.153637
H -0.598652 1.813272 2.156962
C -0.960298 2.079591 -1.171709
H -3.145179 2.109329 -1.221173
H -0.696639 2.738931 -2.002056
H -0.976971 1.051063 -1.548405
H 0.930092 1.704717 -0.147284
C 0.679971 4.598240 -0.412574
H 0.140155 3.885003 1.488273
C 1.082978 5.982815 -0.004635
C 0.378418 7.054197 -0.859814
H 0.604041 6.922385 -1.924996
H 0.716107 8.053756 -0.568680
H -0.709554 7.017541 -0.730277
C 2.621103 6.119132 -0.131451
H 0.830643 4.352962 -1.466160
H 2.928130 7.124259 0.175910
H 2.947307 5.968468 -1.167063
H 3.140743 5.393072 0.500775
C -2.762271 4.826618 -1.244756
H 0.811690 6.133273 1.048378
O -2.860756 4.493037 -2.507481
H -2.927379 5.872850 -0.984623
C -3.293778 5.496612 -3.486190
C -4.764170 5.302643 -3.807118
H -2.656042 5.316796 -4.353522
H -3.078302 6.489485 -3.077669
H -4.952712 4.293649 -4.184341
H -5.055054 6.018612 -4.582975

H -5.391686 5.477717 -2.927416

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i3-C-Et

39

C -2.804035 3.666961 -0.246537
C -0.110886 3.813321 0.374515
C -2.440575 2.234015 -0.482728
H -2.954115 4.032703 0.766323
C -2.213073 1.449591 0.838966
C -0.669667 1.449609 1.069663
H -2.589528 0.428486 0.735091
H -2.763150 1.899658 1.671456
C -0.090626 2.363899 -0.036428
H -0.269380 0.437972 0.956845
H -0.394056 1.790738 2.071981
C -1.069941 2.114796 -1.213046
H -3.224387 1.775886 -1.104277
H -0.951219 2.818647 -2.041587
H -0.949001 1.098300 -1.603876
H 0.926483 2.072051 -0.326621
C 0.487290 4.851792 -0.277060
H -0.579048 4.043058 1.331025
C 1.344107 4.797816 -1.505358
C 2.791573 5.197542 -1.129219
H 2.826033 6.215146 -0.723676
H 3.427509 5.165695 -2.019924
H 3.213384 4.518347 -0.382115
C 0.793897 5.738176 -2.598704
H 0.385532 5.843784 0.167398
H 1.439674 5.706056 -3.482110
H 0.762196 6.776094 -2.245662
H -0.216999 5.449467 -2.910637
C -3.130483 4.539333 -1.272359
H 1.362719 3.775943 -1.901244
O -3.530939 5.755233 -1.005682
H -3.085594 4.239933 -2.321294
C -3.932913 6.653854 -2.093074
C -3.069845 7.899282 -2.057016
H -4.984059 6.876923 -1.894249
H -3.852502 6.110241 -3.040198
H -3.150015 8.403416 -1.089845
H -3.414782 8.590770 -2.832896
H -2.019402 7.661938 -2.251211

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i3-D-Et

39

C -2.675317 3.768995 -0.244600
C -0.016380 3.759903 0.436361
C -2.395348 2.333354 -0.549157
H -2.773525 4.087731 0.789013
C -2.251194 1.474196 0.736583
C -0.719157 1.404265 1.027225
H -2.658695 0.474577 0.562202
H -2.818741 1.897923 1.571496
C -0.059000 2.326729 -0.025435
H -0.354612 0.381114 0.898261
H -0.469767 1.702900 2.049936
C -1.007471 2.173983 -1.241366
H -3.178942 1.962886 -1.224965
H -0.838484 2.899909 -2.038952
H -0.924075 1.166728 -1.664595
H 0.953162 1.994424 -0.290984
C 0.614978 4.799881 -0.187451
H -0.455856 3.971498 1.410438
C 1.449201 4.758498 -1.430562
C 2.912133 5.113439 -1.070213
H 2.981375 6.122059 -0.647223
H 3.530752 5.081470 -1.973063
H 3.329533 4.409027 -0.344220
C 0.902062 5.741619 -2.488660
H 0.560370 5.777390 0.295809
H 1.533888 5.716805 -3.382388
H 0.899929 6.769882 -2.108198
H -0.119507 5.483760 -2.790058
C -2.984827 4.739290 -1.184870
H 1.436008 3.747316 -1.852745
O -3.004216 4.464099 -2.465925
H -3.229550 5.759319 -0.884689
C -3.470787 5.485040 -3.411992
C -4.934981 5.257878 -3.739513
H -2.828466 5.351970 -4.284000
H -3.283969 6.470282 -2.972172
H -5.094484 4.254764 -4.144855
H -5.246644 5.986645 -4.495124
H -5.567708 5.390321 -2.855990

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i3-A-Et-BF_4

44

C -2.635185 3.633613 0.507148
C 0.084688 3.127933 0.738882
C -2.566619 2.505918-0.479930
H -2.524808 3.446198 1.575228
C -2.454182 1.125460 0.219970
C -0.925652 0.841788 0.338718
H -2.948509 0.365761-0.394632
H -2.934295 1.137785 1.199728
C -0.222961 2.073161-0.294067
H -0.656879-0.066966-0.209944
H -0.630416 0.711817 1.381821
C -1.257450 2.580595-1.321753
H -3.435681 2.567310-1.150948
H -1.043894 3.581970-1.708894
H -1.328624 1.892057-2.172839
H 0.710970 1.794239-0.805118
C 0.509164 4.396681 0.471241
H 0.005251 2.830073 1.783198
C 0.892663 5.387697 1.532434
C 0.304891 6.780864 1.247241
H 0.632152 7.165968 0.271693
H 0.632838 7.492187 2.013362
H -0.788728 6.754441 1.263347
C 2.434895 5.458795 1.629823
H 0.649143 4.714844-0.566188
H 2.724859 6.177892 2.404656
H 2.883288 5.783961 0.682185
H 2.860437 4.485252 1.893144
C -3.050222 4.889397 0.114680
H 0.493380 5.026863 2.485495
O -3.196813 5.860561 0.995912
H -3.291975 5.128147-0.924079
C -3.800349 7.109839 0.577385
C -5.259295 7.146893 1.002109
H -3.681216 7.219523-0.507235
H -3.214380 7.884186 1.077375
H -5.839684 6.370953 0.492199
H -5.687965 8.122463 0.748557
H -5.347885 6.996132 2.081548
F -1.778704 2.632772 5.240854
F -2.796433 2.288940 3.196056
B -1.601015 2.657993 3.878464
F -0.568473 1.775919 3.471508
F -1.258570 3.967805 3.434088

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i3-B-Et-BF_4

44

C -2.903209 3.418531 1.179863
C 0.489884 3.471335 0.457528
C -2.600132 2.691760-0.068253
H -2.274537 3.294638 2.055952
C -1.855924 1.342913 0.176120
C -0.552468 1.408237-0.650047
H -2.483534 0.489173-0.099092
H -1.626121 1.229746 1.241726
C -0.210699 2.914299-0.755239
H -0.728831 1.009414-1.657435
H 0.255575 0.821226-0.202602
C -1.604607 3.551086-0.972233
H -3.526358 2.558069-0.638266
H -1.630486 4.612048-0.722438
H -1.923139 3.422809-2.013166
H 0.415563 3.106775-1.635892
C 1.651784 4.131809 0.428424
H -0.009774 3.371943 1.420839
C 2.336378 4.740239 1.627085

C 2.420236 6.272876 1.487088
H 2.929141 6.556977 0.555963
H 2.990458 6.700857 2.320854
H 1.422728 6.720290 1.496975
C 3.733816 4.123862 1.824494
H 2.164022 4.266207-0.529258
H 4.227724 4.555473 2.703352
H 4.375427 4.316760 0.954413
H 3.676673 3.038065 1.963878
C -3.872884 4.421869 1.320169
H 1.726718 4.521196 2.513486
O -4.670795 4.709170 0.333681
H -3.972513 4.972951 2.253596
C -5.615783 5.821252 0.526277
C -4.906644 7.163533 0.524345
H -6.151050 5.634377 1.463236
H -6.306997 5.705981-0.309683
H -4.234791 7.259463 1.380113
H -5.666221 7.951787 0.576789
H -4.328253 7.296466-0.394024
F -0.709691 7.177064 2.577134
F -1.182044 4.959872 3.009593
F -2.858481 6.528763 3.149708
B -1.652861 6.182877 2.495799
F -2.006282 5.966958 1.104156

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i3-C-Et-BF_4

44

C -2.527561 3.207299 0.956314
C -0.175170 3.191449-0.531172
C -2.644652 1.866194 0.296287
H -2.145895 3.286434 1.972288
C -1.695874 0.817996 0.950643
C -0.445283 0.744009 0.022749
H -2.193959-0.154649 1.007703
H -1.435425 1.104817 1.973334
C -0.656619 1.853698-1.035250
H -0.393239-0.233184-0.469092
H 0.489984 0.880710 0.573230
C -2.198457 1.869158-1.186239
H -3.696278 1.547726 0.379537
H -2.571358 2.718228-1.766337
H -2.544632 0.951340-1.677374
H -0.177401 1.607131-1.990543
C -0.021995 4.327016-1.270486
H 0.165112 3.264304 0.501618
C -0.212165 4.489919-2.751992
C 1.152813 4.790336-3.410765
H 1.589300 5.709348-3.002593
H 1.032130 4.921450-4.492487
H 1.864694 3.976690-3.238938
C -1.211280 5.624826-3.057581
H 0.311244 5.206925-0.721325
H -1.296145 5.779807-4.139232
H -0.882422 6.567235-2.604440
H -2.213121 5.397775-2.673817
C -2.954343 4.408017 0.412446
H -0.601966 3.560420-3.186495
O -3.050309 5.455015 1.180245
H -3.240326 4.522385-0.634098
C -3.142092 6.787563 0.600586
C -3.877359 7.673094 1.584102
H -3.652968 6.714636-0.368059
H -2.102475 7.093459 0.467973
H -4.910011 7.340957 1.731803
H -3.893109 8.699694 1.203238
H -3.360535 7.670389 2.547656
F 1.105892 4.511121 1.836140
F -0.907292 4.808775 2.895911
F 0.766163 6.368948 3.160864
B 0.182500 5.475994 2.289673
F -0.307264 6.179034 1.132127

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i3-D-Et-BF_4

44

C -1.676893 4.275474 1.233258
C 0.784966 3.745167-0.505782
C -2.081966 3.130339 0.376474
H -0.925807 4.165873 2.007851
C -1.390241 1.794513 0.779512
C -0.352413 1.483241-0.337522
H -2.128231 0.991805 0.867803
H -0.916854 1.885779 1.762578
C -0.207124 2.794023-1.146007
H -0.732421 0.692950-0.994299
H 0.603872 1.133754 0.064611
C -1.650935 3.343837-1.113787
H -3.177377 3.062100 0.421305
H -1.739255 4.383012-1.439365
H -2.297709 2.731654-1.754868
H 0.092311 2.589281-2.181258
C 1.309808 4.854388-1.050958
H 1.112795 3.483136 0.500692
C 1.063042 5.414948-2.429196
C 2.381345 5.462791-3.226893
H 3.118784 6.100717-2.723745
H 2.214247 5.872567-4.230037
H 2.819095 4.464498-3.332518
C 0.433935 6.819291-2.338708
H 2.017223 5.428125-0.448304
H 0.265972 7.234187-3.339457
H 1.092720 7.509123-1.796637
H -0.527330 6.792748-1.813252
C -2.299234 5.535255 1.224198
H 0.362495 4.763075-2.966433
O -3.274130 5.784238 0.401158
H -1.947115 6.334678 1.868852
C -3.976372 7.068075 0.584787
C -3.434581 8.097161-0.388995
H -3.858386 7.355179 1.631434
H -5.019448 6.818888 0.382360
H -2.384849 8.328597-0.178717
H -4.009297 9.023882-0.285521
H -3.521210 7.751728-1.424193
F -3.523990 5.082459 3.148442
B -2.758898 5.890802 4.080040
F -1.433240 5.429064 4.023832
F -3.303532 5.810633 5.330357
F -2.795751 7.215845 3.564420

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i3-A-Et-$BAr^F{}_4$

108

C -3.036977 3.596882 0.276794
C -0.195775 2.971495 0.986057
C -2.744393 2.623462-0.824595
H -3.173135 3.240569 1.294191
C -2.841499 1.159674-0.340890
C -1.457385 0.855621 0.299226
H -3.017673 0.512064-1.206411
H -3.670631 1.008406 0.353414
C -0.508684 2.014433-0.136508
H -1.073628-0.111749-0.034287
H -1.526109 0.800188 1.389730
C -1.260711 2.701268-1.298496
H -3.409016 2.832148-1.674824
H -0.921130 3.721140-1.499494
H -1.157887 2.120957-2.223027
H 0.448140 1.612347-0.496820
C 0.426120 4.169296 0.846365
H -0.404181 2.628926 1.998905
C 0.883899 5.045464 1.974162
C 0.353230 6.483529 1.820338
H 0.666786 6.918195 0.862572
H 0.742915 7.119664 2.622377
H -0.738928 6.503007 1.877560
C 2.429033 5.028670 2.029251
H 0.693490 4.514357-0.155700
H 2.778837 5.630829 2.875073
H 2.862762 5.447267 1.112503
H 2.802402 4.008143 2.149002
C -3.238891 4.935736 0.053017
H 0.502161 4.633514 2.915056
O -3.566617 5.745401 1.043554
H -3.159095 5.374280-0.943703
C -3.718193 7.163691 0.760708
C -4.296077 7.823203 1.995880

H -4.373067 7.272483-0.112028
H -2.726117 7.558891 0.513505
H -5.278535 7.406405 2.234718
H -4.407132 8.896918 1.812668
H -3.639044 7.678520 2.856731
F 3.515832-0.336916 1.830752
F 5.054604 2.158438 5.892513
H 4.094815 1.356715 3.854489
F 2.590451 1.551543 1.300678
C 2.393037 0.390927 1.997879
C 3.100044 1.182877 4.248772
C 3.841433 2.074696 6.484119
F 3.496823 3.328052 6.865680
F 1.389552-0.259806 1.362067
C 2.088723 0.657693 3.443481
C 2.801475 1.473326 5.577658
F 3.994599 1.354568 7.616381
F -2.080545 4.644576 3.225826
C 0.814392 0.414911 3.966011
C 1.520375 1.237585 6.086283
C -2.499823 5.154137 4.419629
F -1.945269 6.389699 4.523616
H 0.064397-0.011318 3.309522
C 0.486183 0.689831 5.305964
H 1.324576 1.497311 7.124025
F -3.834352 5.350871 4.301691
H -1.653095 2.616538 4.294975
C -2.148461 4.257438 5.566601
C -1.758827 2.942623 5.324183
F 2.410211-2.322968 8.862824
F -0.960399-3.396697 2.302662
C -2.275257 4.729663 6.877064
H 1.037296-1.197002 7.109077
B -1.019093 0.494735 5.963122
C -1.509277 2.019479 6.357451
H -2.569988 5.753244 7.078841
C 0.103272-1.284454 7.654392
H -0.857880-1.987694 4.654258
C -2.010991 3.847835 7.918530
C -1.769935-1.480948 4.348968
C -2.069057-0.214107 4.894539
C -1.643765 2.517843 7.660573
F 1.306787-4.120935 8.347523
C 1.256417-2.988612 9.089855
C -2.189552-3.450516 2.868926
C -1.007212-0.515516 7.258110
F -0.865973 4.347562 9.924279
C -2.598881-2.110022 3.417835
F -5.026675 1.516057 2.287780
C -3.293615 0.346168 4.491748
C 0.051696-2.153899 8.746263
F -2.618556 5.551227 9.458260
C -2.089968 4.310640 9.348750
F -3.045407-3.900275 1.922948
H -1.464089 1.861615 8.507234
C -3.785152-1.505636 3.000718
F 1.256979-3.37078210.387108
C -4.126754-0.272427 3.554140
H -3.611208 1.295865 4.908717
F -2.128883-4.390944 3.836215
C -5.356404 0.455484 3.096026
H -4.427582-1.988754 2.275434
C -2.187461-0.700041 8.009776
F -6.190089-0.320916 2.375329
C -1.122268-2.294185 9.488405
F -2.848216 3.48179710.099354
H -3.086263-0.155903 7.730657
C -2.244512-1.557360 9.108231
F -6.058919 0.978663 4.119595
H -1.162451-2.96069910.341227
F -3.756048-0.50646910.591000
C -3.521938-1.645770 9.898403
F -3.503783-2.65822910.792987
F -4.594364-1.835159 9.095185

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i3-B-Et-BAr$^{F}_{4}$
108

C -3.039723 5.771576 -4.270684
C -0.171585 5.389213 -4.605503
C -3.096512 5.174554 -5.638668
H -2.657010 5.181522 -3.445641
C -2.931358 3.636350 -5.603784
C -1.394544 3.382977 -5.611803
H -3.396219 3.209948 -6.498926
H -3.429592 3.184125 -4.742938
C -0.724638 4.764661 -5.865363
H -1.123816 2.675399 -6.400433
H -1.046093 2.942395 -4.673236
C -1.859786 5.614523 -6.481893
H -4.017967 5.499475 -6.136681
H -1.680291 6.692218 -6.443137
H -2.027464 5.331088 -7.528237
H 0.101485 4.670196 -6.582201
C 0.347806 6.637003 -4.518911
H -0.132983 4.762132 -3.714426
C 0.990380 7.228189 -3.297704
C 0.398291 8.611797 -2.969528
H 0.534906 9.306807 -3.807922
H 0.894742 9.043476 -2.093528
H -0.671210 8.539054 -2.746550
C 2.518296 7.323370 -3.513675
H 0.357337 7.267482 -5.411749
H 3.000318 7.736023 -2.620181
H 2.756069 7.981071 -4.358962
H 2.947944 6.338620 -3.714873
C -3.484233 7.023692 -3.932726
H 0.801029 6.561201 -2.447555
O -4.029016 7.829010 -4.836541
H -3.425071 7.387713 -2.908614
C -4.456105 9.149503 -4.414342
C -3.40203210.185748 -4.767445
H -4.667041 9.126890 -3.339373
H -5.390944 9.325598 -4.951670
H -2.46946910.003854 -4.223204
H -3.76682111.183171 -4.499342
H -3.19091510.172905 -5.840936
F 1.936625-2.251156 -4.813971
F 3.798005 2.305852 -5.055686
H 2.541392 0.061497 -4.899616
F 0.221281-2.554363 -3.506208
C 1.485631-2.073621 -3.551775
C 2.117737 0.330292 -3.939238
C 2.696908 2.714401 -4.393157
F 1.793364 3.083070 -5.349255
F 2.230682-2.862595 -2.745855
C 1.540177-0.632657 -3.121293
C 2.142267 1.653927 -3.488636
F 3.021518 3.845771 -3.722463
F -3.739522 0.948409 -3.203002
C 1.013463-0.285427 -1.869339
C 1.606712 1.990484 -2.246141
C -4.250973 1.690299 -2.191542
F -5.151695 2.541258 -2.749096
H 0.573074-1.072849 -1.264847
C 1.039528 1.029857 -1.383278
H 1.643731 3.029794 -1.931921
F -4.939953 0.849910 -1.395229
H -1.934140 0.686837 -1.304090
C -3.166453 2.428283 -1.454524
C -2.017988 1.742232 -1.055897
F 5.407057 3.121239 -0.068294
F 1.786570-3.809435 1.476479
C -3.310438 3.788310 -1.177184
H 3.217788 1.946478 -0.159480
B 0.373460 1.497352 0.047866
C -0.966721 2.367686 -0.355995
H -4.206447 4.319463 -1.473448
C 2.812488 2.428313 0.723713
H 1.988774-0.626573 0.926757
C -2.270714 4.441510 -0.517689
C 0.991536-0.733675 1.343708
C -0.000364 0.220420 1.020189
C -1.125400 3.743061 -0.116531
F 5.784533 2.058722 1.788225
C 5.161421 3.137223 1.260875
C 1.803316-2.847048 2.428235
C 1.431708 2.348136 0.984680
F -1.679205 6.583953 -1.338431
C 0.736667-1.812437 2.187096
F -3.849129-1.126949 2.188446

C -1.248963 0.047451 1.642050
C 3.686159 3.127052 1.560165
F -3.604751 6.404377 -0.351453
C -2.336100 5.926067 -0.322177
F 1.639391-3.469773 3.617436
H -0.343981 4.290523 0.400685
C -0.521488-1.968598 2.776385
F 5.771369 4.231959 1.771692
C -1.509174-1.026252 2.498478
H -2.047862 0.757401 1.451843
F 3.042129-2.308983 2.418541
C -2.873216-1.129190 3.126040
H -0.720755-2.797720 3.443907
C 0.987587 2.970610 2.172728
F -3.022968-2.252268 3.860038
C 3.211201 3.768796 2.703768
F -1.768228 6.339333 0.820765
H -0.057335 2.892457 2.457753
C 1.849864 3.683078 3.004112
F -3.122427-0.078115 3.942136
H 3.886773 4.314683 3.351873
F 0.977484 5.694360 3.890524
C 1.312049 4.417719 4.202326
F 2.221327 4.486233 5.200053
F 0.202272 3.834803 4.702996

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i3-C-Et-BAr$^{F}_{4}$

108

C -2.774091 -0.244615 -3.718004
C -0.762848 -0.781659 -5.738265
C -3.377976 -1.369859 -4.496548
H -2.078867 -0.448259 -2.908096
C -2.696072 -2.742360 -4.215861
C -1.837046 -3.056164 -5.473687
H -3.452467 -3.514235 -4.050243
H -2.089950 -2.706448 -3.308032
C -1.799891 -1.735765 -6.274178
H -2.316023 -3.832003 -6.080788
H -0.839566 -3.414033 -5.213382
C -3.226931 -1.180696 -6.034162
H -4.448887 -1.399613 -4.241236
H -3.352440 -0.147926 -6.372043
H -3.966415 -1.801826 -6.553221
H -1.638931 -1.904613 -7.346069
C -0.310954 0.345727 -6.348929
H -0.280626 -1.060499 -4.803420
C -0.665764 0.853348 -7.717653
C 0.612421 0.896999 -8.585776
H 1.360636 1.566270 -8.144513
H 0.375969 1.270734 -9.588398
H 1.063368 -0.095708 -8.685344
C -1.317000 2.251460 -7.651832
H 0.439762 0.930749 -5.819012
H -1.551462 2.601893 -8.663173
H -0.650148 2.979081 -7.180519
H -2.248076 2.229112 -7.073443
C -3.189534 1.070937 -3.854503
H -1.377745 0.166408 -8.191425
O -2.772277 1.986222 -3.023011
H -3.889011 1.378843 -4.633137
C -3.262317 3.362039 -3.186180
C -4.617734 3.530129 -2.525189
H -3.279594 3.579382 -4.257792
H -2.492748 3.965822 -2.710468
H -5.379494 2.894654 -2.990574
H -4.931522 4.573345 -2.640148
H -4.566221 3.307253 -1.457896
F 5.133215 4.607468 3.235794
F 2.843086 1.334235 5.833634
H 3.938765 2.837558 4.307528
F 4.073770 5.205287 1.429663
C 4.695495 4.164657 2.036119
C 3.507919 2.420793 3.405975
C 2.331280 0.663241 4.777948
F 0.994462 0.565410 4.974764
F 5.789774 3.887656 1.288577
C 3.786844 2.973345 2.159238
C 2.652594 1.320528 3.464530
F 2.817636 -0.599559 4.831929
F -2.119142 3.855264 1.974207
C 3.226485 2.433566 0.994566
C 2.091536 0.796821 2.298637
C -2.589773 3.305238 0.841396
F -3.943635 3.261881 0.942891
H 3.473021 2.901634 0.045900
C 2.363861 1.327023 1.022141
H 1.414009 -0.049127 2.389381
F -2.313069 4.190843 -0.161642
H -0.018836 2.774559 0.400056
C -1.993400 1.958689 0.550501
C -0.618447 1.871111 0.317590
F 4.159111 -3.540265 2.121390
F 6.006435 2.061518 -2.852045
C -2.796943 0.820455 0.497816
H 3.529438 -1.058120 1.110029
B 1.649303 0.654523 -0.303246
C 0.018644 0.660909 -0.016957
H -3.859441 0.878745 0.700587
C 3.128646 -1.552427 0.230581
H 4.077883 0.917254 -1.666477
C -2.191536 -0.398069 0.196369
C 3.319880 1.500435 -2.181903
C 2.004587 1.517104 -1.670021
C -0.815696 -0.470563 -0.059933
F 5.747711 -2.769802 0.860689
C 4.596110 -3.480008 0.843051
C 5.098937 2.084631 -3.849158
C 2.193997 -0.879922 -0.572330
F -2.392783 -2.750474 0.432373
C 3.691858 2.203360 -3.328337
F -0.151291 4.752195 -3.464600
C 1.084462 2.281839 -2.399483
C 3.572047 -2.848553 -0.061676
F -4.176647 -1.551933 0.793651
C -3.041052 -1.629404 0.070142
F 5.423319 3.109263 -4.672255
H -0.386487 -1.443323 -0.278482
C 2.754518 2.965138 -4.028959
F 4.910884 -4.739961 0.465496
C 1.447947 2.995337 -3.550859
H 0.050145 2.331073 -2.072671
F 5.269377 0.943437 -4.560450
C 0.395287 3.793982 -4.251524
H 3.040795 3.520530 -4.913606
C 1.735554 -1.593727 -1.694819
F 0.834045 4.398126 -5.375790
C 3.079978 -3.539089 -1.165137
F -3.439969 -1.827699 -1.231783
H 1.032056 -1.113768 -2.371631
C 2.149075 -2.895647 -1.981613
F -0.661406 3.000298 -4.635056
H 3.414947 -4.544746 -1.385453
F 0.230630 -3.926574 -2.914903
C 1.537217 -3.606523 -3.148313
F 2.167416 -4.751380 -3.466988
F 1.519912 -2.831273 -4.270750

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i3-D-Et-BAr$^{F}_{4}$

108

C 0.920526 3.802452 2.825583
C 1.626790 3.060667 0.317104
C-0.147807 2.772361 2.660311
H 1.945632 3.486260 2.981879
C 0.406475 1.328867 2.771991
C 0.763740 0.902276 1.313066
H-0.363602 0.674157 3.190692
H 1.268250 1.275438 3.442113
C 0.437195 2.134323 0.427154
H 0.154438 0.047434 1.003593
H 1.811001 0.601016 1.219331
C-0.714013 2.810058 1.209835
H-0.944767 2.985635 3.383902
H-0.959006 3.818265 0.869909
H-1.622835 2.198336 1.160515
H 0.099844 1.841366-0.575878
C 1.717892 4.203660-0.418072
H 2.535836 2.742584 0.823159
C 0.699092 4.793620-1.349633

C 1.327092 4.943085-2.752189
H 2.196968 5.609385-2.716227
H 0.599006 5.373221-3.448672
H 1.654162 3.977352-3.151213
C 0.212194 6.166320-0.834914
H 2.657025 4.753770-0.355330
H-0.478266 6.615144-1.557525
H 1.053332 6.853834-0.697360
H-0.314510 6.071547 0.120822
C 0.684088 5.166086 2.947168
H-0.165658 4.122697-1.421435
O-0.537335 5.633160 2.900036
H 1.500283 5.872690 3.097222
C-0.757163 7.066711 3.145394
C-2.214039 7.256975 3.499916
H-0.471660 7.593820 2.231876
H-0.100698 7.372270 3.961573
H-2.869591 6.905380 2.697614
H-2.396814 8.325028 3.655806
H-2.452730 6.725734 4.424431
F 8.69741511.098779 5.908851
F 6.662061 9.90176010.242450
H 7.60700410.347402 8.014198
F 8.270444 9.884582 4.150375
C 8.467862 9.833525 5.487668
C 7.027459 9.574548 7.522890
C 5.614048 9.361009 9.580459
F 4.63273010.296871 9.574736
F 9.615862 9.142614 5.685398
C 7.307554 9.202541 6.207085
C 5.985635 8.933565 8.187249
F 5.156427 8.32669310.321714
F 5.364427 8.212760 0.063020
C 6.554858 8.210408 5.578084
C 5.242688 7.932780 7.549596
C 4.245080 7.519227 0.339254
F 3.317304 7.884068-0.586856
H 6.788046 7.964463 4.545500
C 5.504951 7.534505 6.230100
H 4.443213 7.455987 8.107553
F 4.530095 6.210108 0.105853
H 5.056374 6.248467 2.554790
C 3.757844 7.743658 1.743507
C 4.314934 7.003215 2.795887
F 4.764344 3.781633 9.894514
F 9.873762 4.474742 4.232688
C 2.791081 8.713785 1.991686
H 4.995992 4.816999 7.685195
B 4.633028 6.400622 5.415401
C 3.949314 7.205966 4.138680
H 2.342556 9.273626 1.179099
C 3.931856 4.905374 7.486624
H 7.442864 5.695649 5.803679
C 2.406765 8.940363 3.316035
C 6.928376 4.965211 5.187372
C 5.571775 5.152250 4.877372
C 2.992853 8.220736 4.360172
F 3.693088 2.087250 9.053822
C 3.558177 3.376920 9.449489
C 9.112921 3.734014 5.072111
C 3.501884 5.687587 6.391953
F 1.84587111.226088 3.670429
C 7.648696 3.850313 4.739699
F 4.948916 2.485290 1.445880
C 4.982925 4.140314 4.099279
C 3.042291 4.242526 8.330259
F 0.398850 9.987466 2.625224
C 1.353885 9.976351 3.600623
F 9.552916 2.457582 4.980759
H 2.696240 8.452817 5.378907
C 7.041410 2.876262 3.951379
F 2.712528 3.37047810.505737
C 5.691479 3.032728 3.633179
H 3.926244 4.218452 3.859617
F 9.380751 4.164831 6.323313
C 5.008836 2.047704 2.735109
H 7.599289 2.013698 3.607633
C 2.115305 5.743486 6.205347
F 5.602240 0.842510 2.711622
C 1.662992 4.314026 8.110618
F 0.705062 9.729970 4.764306
H 1.710483 6.348830 5.402072
C 1.208764 5.069379 7.036708
F 3.703037 1.840312 3.099102
H 0.969760 3.802628 8.768074
F-0.645690 6.378839 6.342548
C-0.252255 5.128353 6.711016
F-1.043403 4.741418 7.725509
F-0.563934 4.326070 5.645264

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TS2-A-Et

39

C -2.307309 3.517058 0.749694
C -0.575646 3.544223 0.727301
C -2.602506 2.384825 -0.281288
H -2.611614 3.300698 1.775724
C -2.283572 1.044586 0.420308
C -0.722948 1.027709 0.452375
H -2.686193 0.213369 -0.165596
H -2.732449 0.981781 1.416818
C -0.333505 2.354927 -0.237294
H -0.324925 0.180127 -0.113008
H -0.321519 0.953093 1.468154
C -1.444892 2.518931 -1.289550
H -3.613863 2.432968 -0.696717
H -1.411391 3.481216 -1.815137
H -1.452864 1.726168 -2.044223
H 0.689964 2.367407 -0.621017
C 0.076009 4.816638 0.343312
H -0.339799 3.305011 1.768931
C 0.728754 5.730662 1.339892
C 0.722198 7.192607 0.861148
H 1.264234 7.298417 -0.086329
H 1.207237 7.843797 1.594977
H -0.297433 7.566745 0.704902
C 2.179070 5.264711 1.627658
H 0.316980 4.965591 -0.709935
H 2.644969 5.917189 2.374667
H 2.785751 5.304230 0.715819
H 2.204956 4.238795 2.010284
C -2.779025 4.809778 0.347311
H 0.172588 5.669481 2.288653
O -3.147607 5.681406 1.195970
H -2.789934 5.097748 -0.709443
C -3.594891 7.037796 0.766427
C -5.088699 7.154815 0.972999
H -3.284212 7.170282 -0.274082
H -3.023209 7.705115 1.412405
H -5.641741 6.469298 0.323566
H -5.391610 8.177798 0.724755
H -5.360633 6.963360 2.014719

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TS2-B-Et

39

C -2.202224 3.466946 1.115532
C -0.508444 3.559975 0.822642
C -2.692638 2.586639 -0.052960
H -2.298346 3.010100 2.107008
C -2.260819 1.136056 0.270640
C -0.719499 1.159262 0.014045
H -2.770366 0.433611 -0.394607
H -2.517172 0.848134 1.295780
C -0.450362 2.620128 -0.415122
H -0.446231 0.480162 -0.799034
H -0.133247 0.863412 0.889774
C -1.729980 2.966318 -1.199627
H -3.760422 2.699268 -0.255902
H -1.793529 4.014114 -1.508784
H -1.868861 2.337358 -2.084013
H 0.493643 2.756754 -0.949676
C 0.071550 4.906726 0.609731
H -0.071568 3.103997 1.716210
C 0.932518 5.595780 1.630125
C 0.766108 7.126290 1.571393
H 1.036977 7.511960 0.580959
H 1.411728 7.617719 2.306445
H -0.266846 7.431836 1.781177
C 2.419295 5.204014 1.442345

H 0.090657 5.293688 -0.409949
H 3.036666 5.684547 2.209383
H 2.787190 5.522808 0.460585
H 2.561050 4.120971 1.522836
C -2.703978 4.810915 1.220872
H 0.632037 5.251363 2.632438
O -3.320058 5.384288 0.270457
H -2.526562 5.395909 2.130203
C -3.777706 6.799841 0.371202
C -3.129372 7.598948 -0.736658
H -3.524174 7.155752 1.374263
H -4.861201 6.724289 0.262380
H -2.044162 7.649690 -0.612132
H -3.526697 8.618931 -0.702282
H -3.364352 7.175905 -1.717142

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TS2-C-Et

39

C -1.908105 3.463745 0.740268
C -0.497056 3.385333 -0.261077
C -2.610717 2.129512 0.361654
H -1.568973 3.542349 1.774877
C -1.794145 0.986647 1.012321
C -0.529026 0.891560 0.103165
H -2.373882 0.059870 0.999932
H -1.552852 1.200410 2.058089
C -0.747806 2.017366 -0.934768
H -0.476932 -0.077843 -0.400908
H 0.404740 1.014556 0.660774
C -2.274522 1.972276 -1.134564
H -3.671617 2.110220 0.625885
H -2.655217 2.779725 -1.771546
H -2.629282 1.021782 -1.544475
H -0.149848 1.896527 -1.840437
C -0.241959 4.568579 -1.123862
H 0.280067 3.330784 0.511057
C -0.229355 4.602909 -2.626030
C 1.210334 4.386348 -3.161332
H 1.875628 5.187255 -2.819623
H 1.211682 4.389118 -4.257316
H 1.630221 3.433001 -2.824184
C -0.791904 5.938531 -3.150588
H 0.180863 5.440143 -0.620841
H -0.740463 5.976770 -4.243477
H -0.215362 6.786465 -2.761302
H -1.841695 6.079770 -2.862761
C -2.639019 4.640709 0.363177
H -0.852505 3.789936 -3.020229
O -2.539063 5.723080 1.020339
H -3.282270 4.642925 -0.523317
C -3.243321 6.965787 0.593590
C -4.110216 7.445719 1.735373
H -3.805828 6.730358 -0.314304
H -2.430626 7.654952 0.358818
H -4.910359 6.734943 1.960975
H -4.568737 8.396169 1.442365
H -3.515369 7.617755 2.636691

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TS2-D-Et

39

C -2.228639 3.855452 0.485691
C -0.564075 3.879621 0.194437
C -2.616733 2.424742 -0.002613
H -2.679340 4.630417 -0.139297
C -2.030590 1.324162 0.912907
C -0.506802 1.338852 0.567903
H -2.489489 0.363834 0.661014
H -2.228123 1.479174 1.979559
C -0.395399 2.478016 -0.465901
H -0.203812 0.395005 0.105349
H 0.131759 1.474628 1.444657
C -1.711349 2.319788 -1.249773
H -3.691935 2.336585 -0.178907
H -1.885451 3.116113 -1.981451
H -1.805119 1.353564 -1.755114
H 0.521809 2.449378 -1.062087
C 0.345899 4.229567 1.320885
H -0.480548 4.654042 -0.574326
C 1.216970 5.457327 1.285281
C 2.444072 5.304879 2.195828
H 2.144905 5.217187 3.248005
H 3.100675 6.176165 2.108382
H 3.028002 4.415578 1.935835
C 0.435195 6.747403 1.634567
H 0.547183 3.478234 2.081091
H 1.085537 7.622895 1.535897
H 0.080016 6.717244 2.673228
H -0.428596 6.900652 0.976806
C -2.445103 4.184524 1.870186
H 1.573153 5.581304 0.248957
O -2.873497 5.331967 2.206039
H -2.221947 3.475290 2.672124
C -3.001022 5.706236 3.653924
C -3.814296 6.974788 3.725457
H -1.976447 5.831938 4.009872
H -3.477508 4.859285 4.153455
H -3.322203 7.790857 3.189679
H -3.910776 7.264100 4.777095
H -4.818109 6.827929 3.317952

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i2A-i2B-TS-Et

39

C -2.011767 3.833168 0.966379
C -0.430348 3.639976 0.831276
C -2.582763 2.897401 -0.197486
H -2.422893 3.473325 1.920121
C -2.408736 1.441760 0.292327
C -0.864757 1.221647 0.205610
H -2.950168 0.771268 -0.382982
H -2.814978 1.284017 1.296098
C -0.340421 2.582409 -0.312147
H -0.621332 0.425093 -0.503683
H -0.419657 0.946049 1.166545
C -1.475619 3.020910 -1.259276
H -3.603158 3.160723 -0.485471
H -1.352309 4.030367 -1.668353
H -1.629502 2.327321 -2.092181
H 0.660090 2.534696 -0.746982
C 0.349929 4.884357 0.526927
H -0.073945 3.221362 1.780278
C 1.190343 5.583042 1.557804
C 1.436861 7.056212 1.190648
H 1.961883 7.137115 0.231369
H 2.054516 7.547762 1.949200
H 0.499546 7.620969 1.108431
C 2.539799 4.841747 1.752117
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i2A-i2C-TS-Et

39

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*****

i2B-i2D-TS-Et

39

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i2C-i2D-TS-Et

39

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7. NMR Spectra and GPC Traces

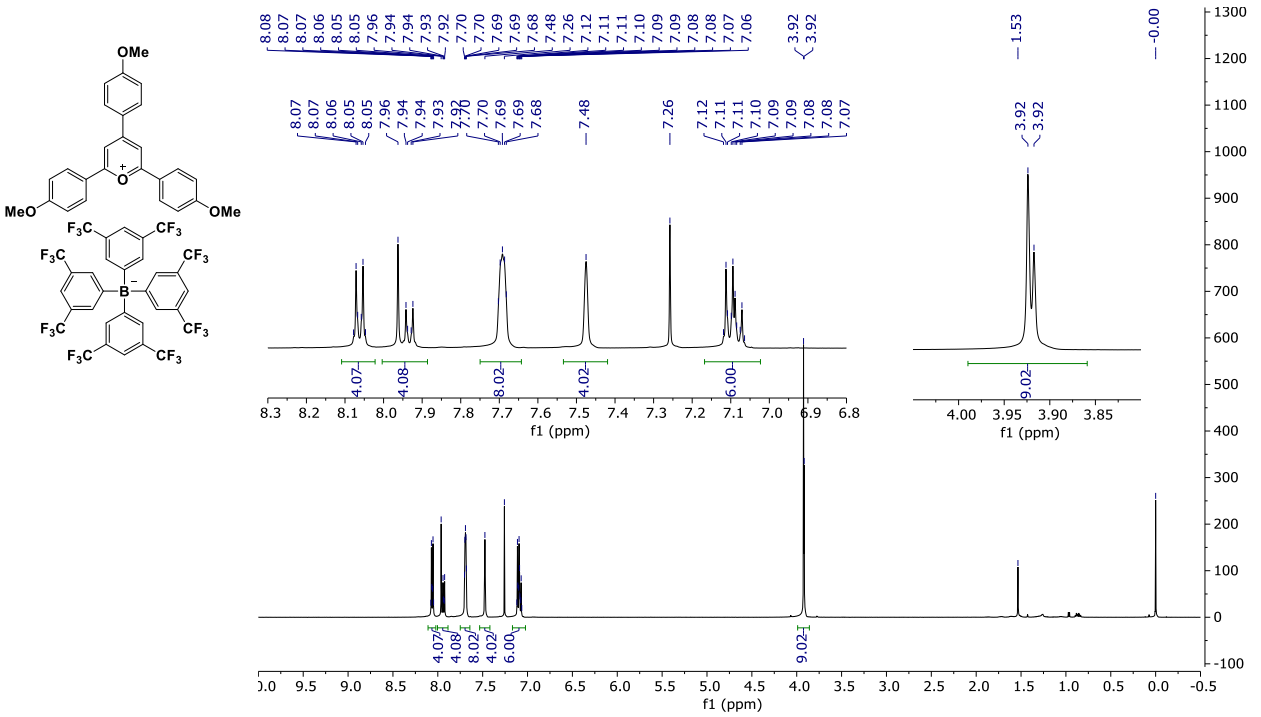

Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3c**.

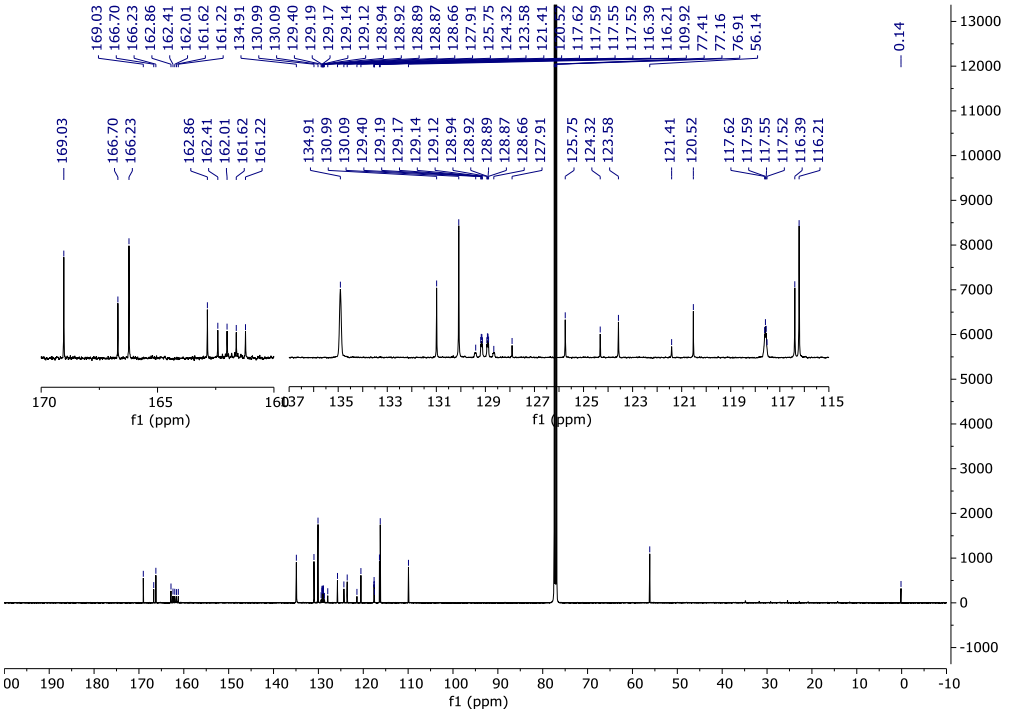

Figure S11. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **3c**.

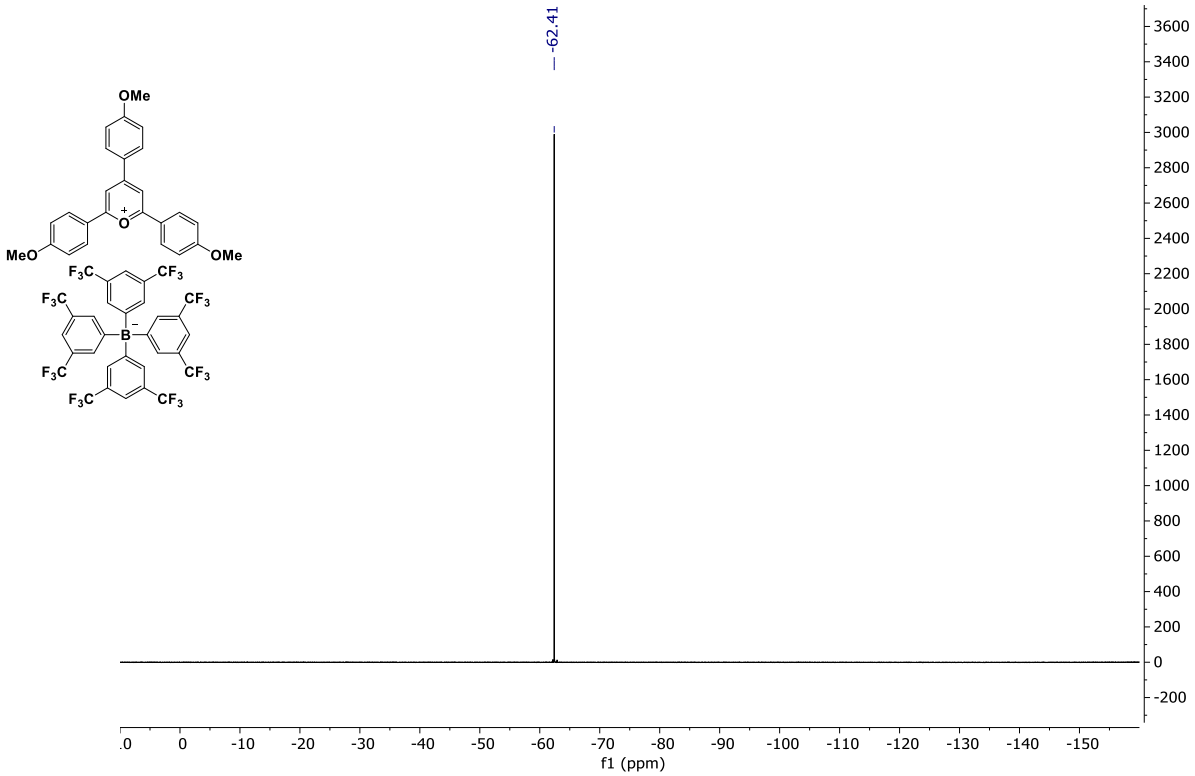

Figure S12. ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of **3c**.

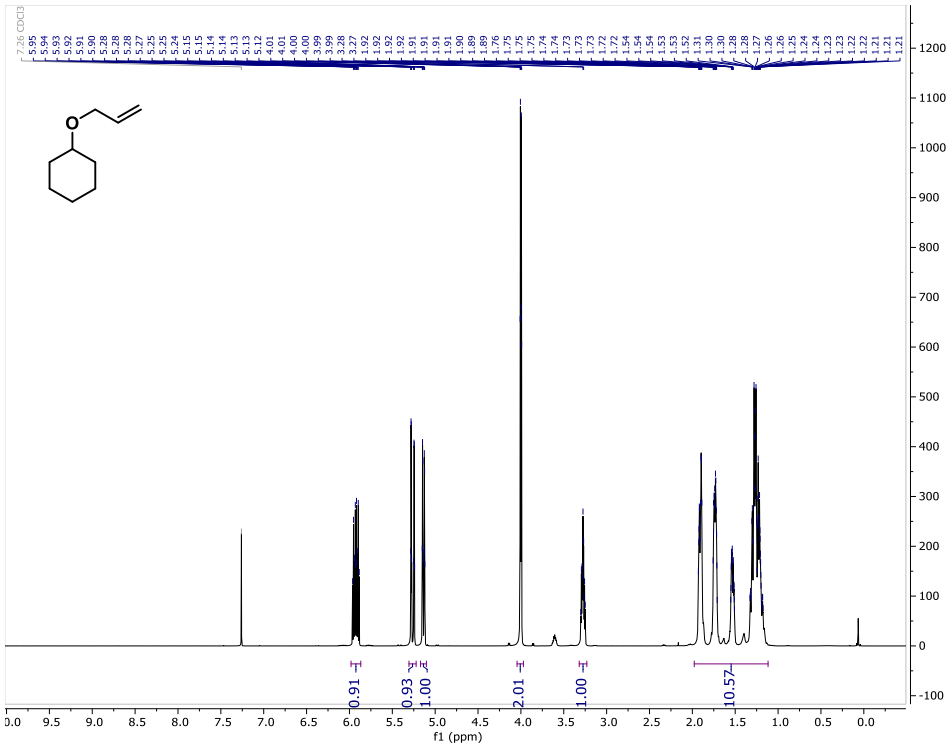

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4c**.

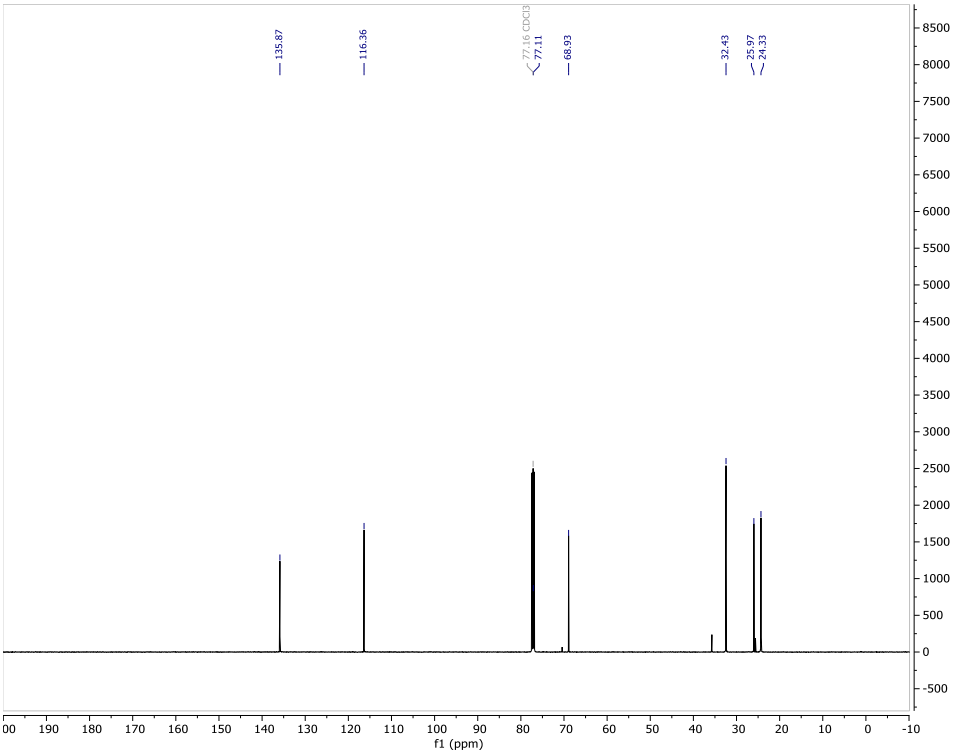

Figure S14. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **4c**.

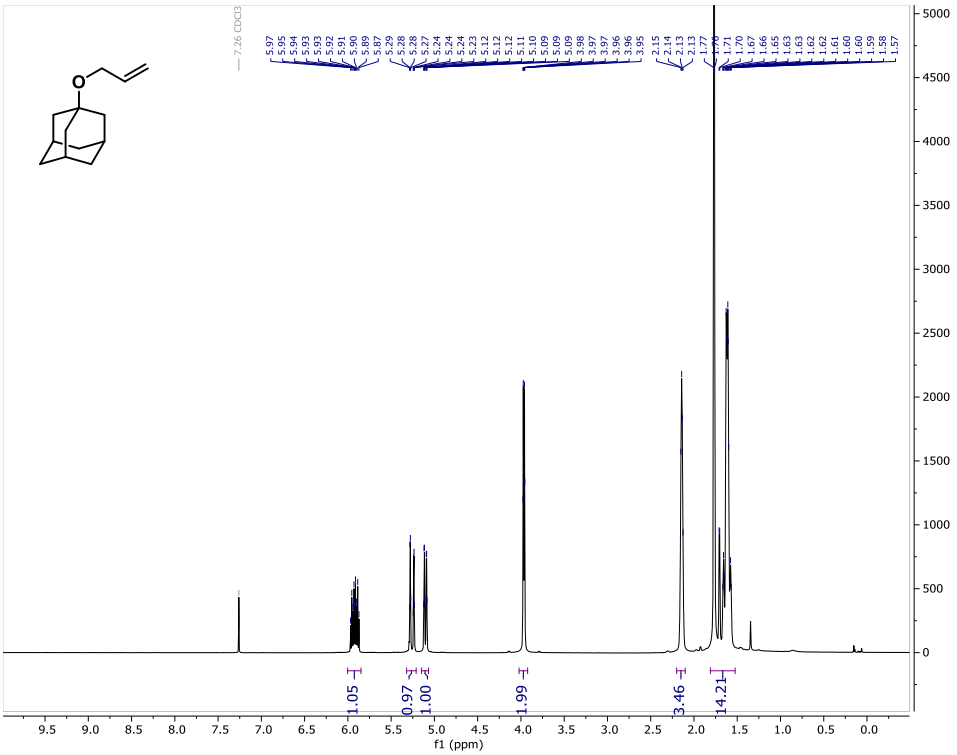

Figure S15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4d**.

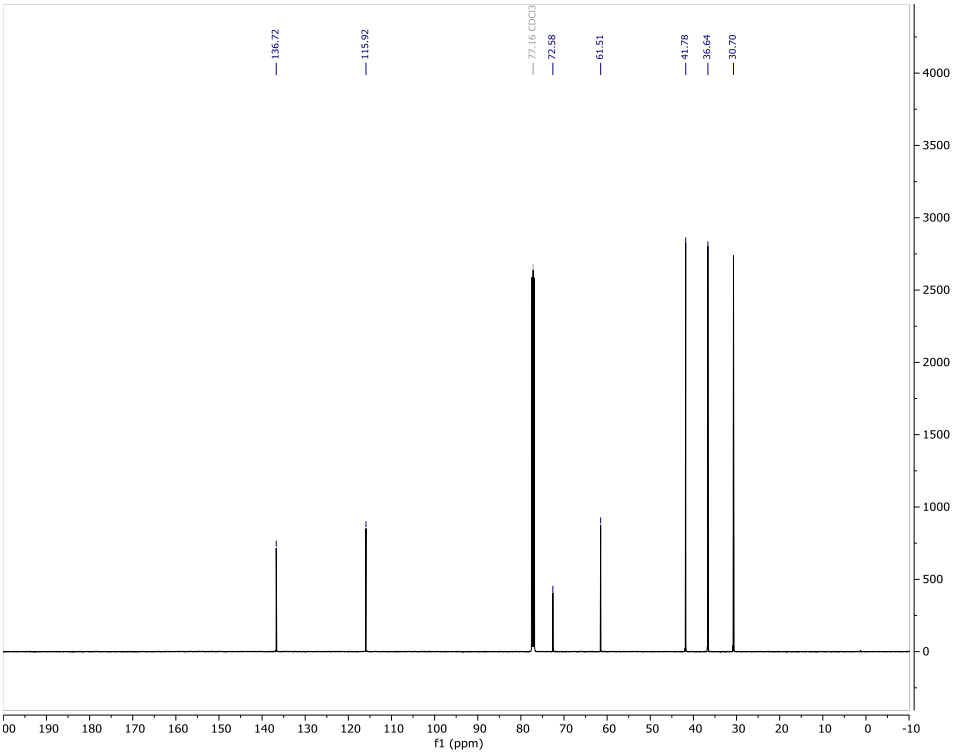

Figure S16. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **4d**.

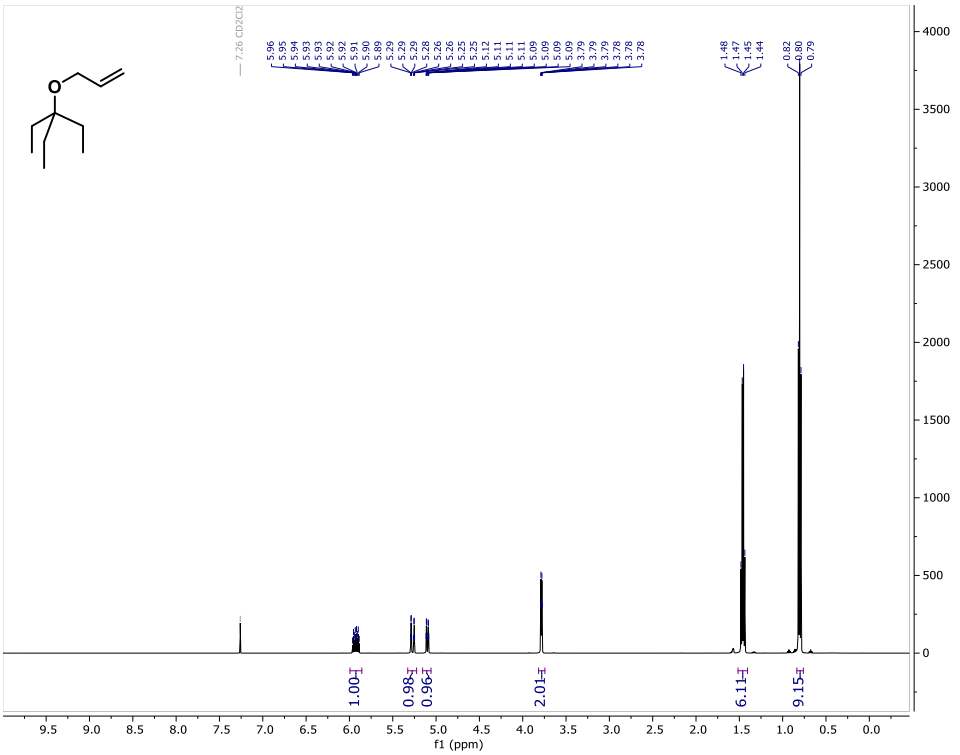

Figure S17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **4e**.

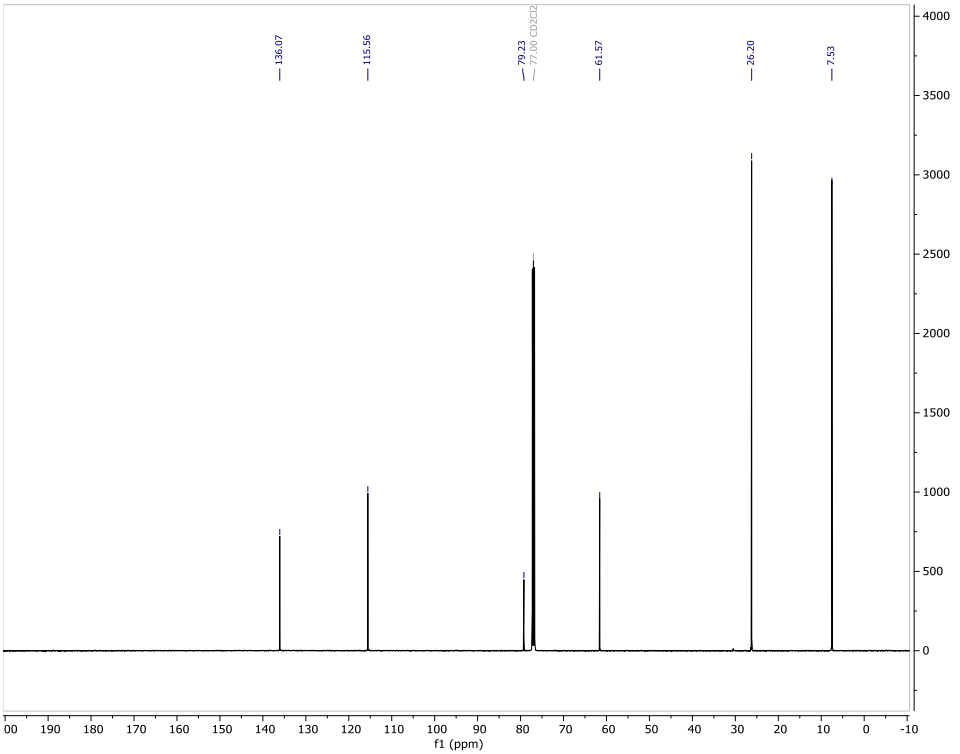

Figure S18. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **4e**.

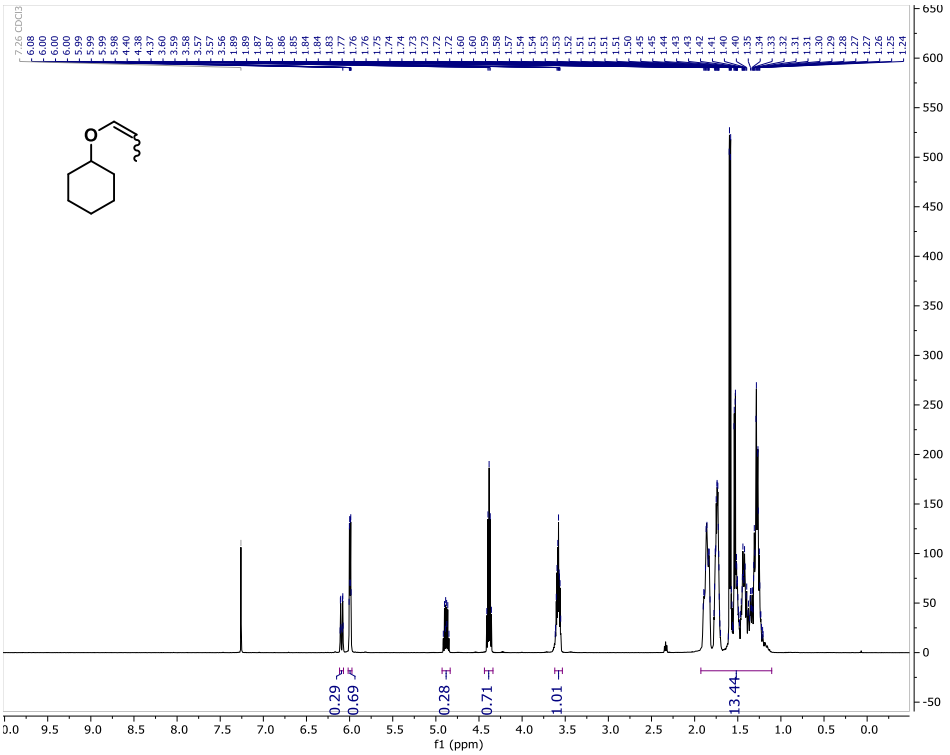

Figure S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2c**.

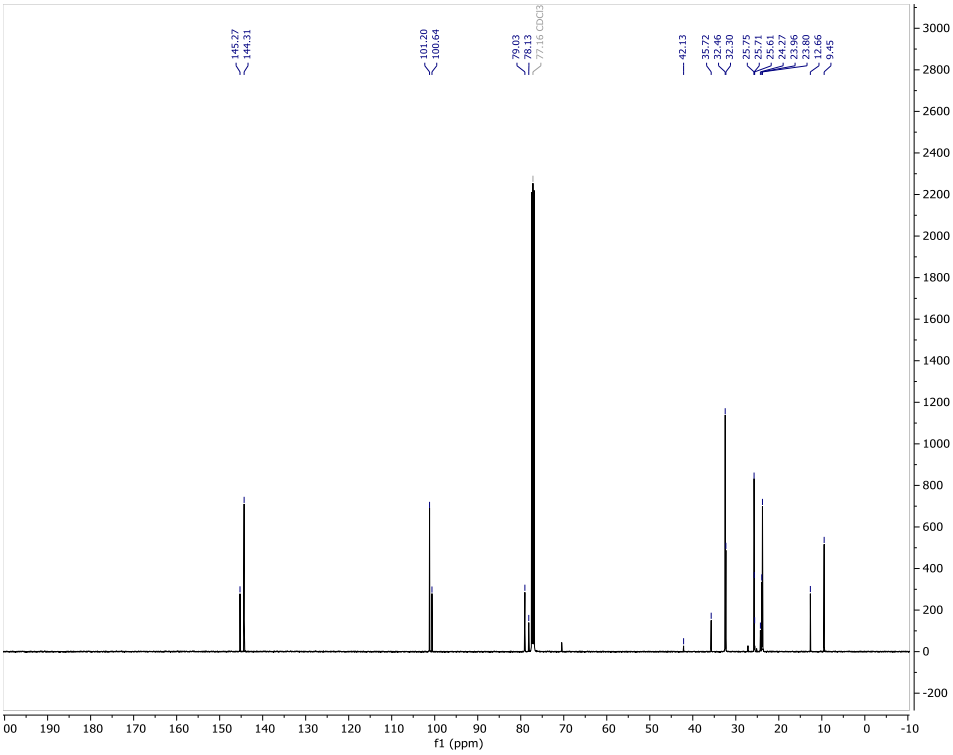

Figure S20. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2c**.

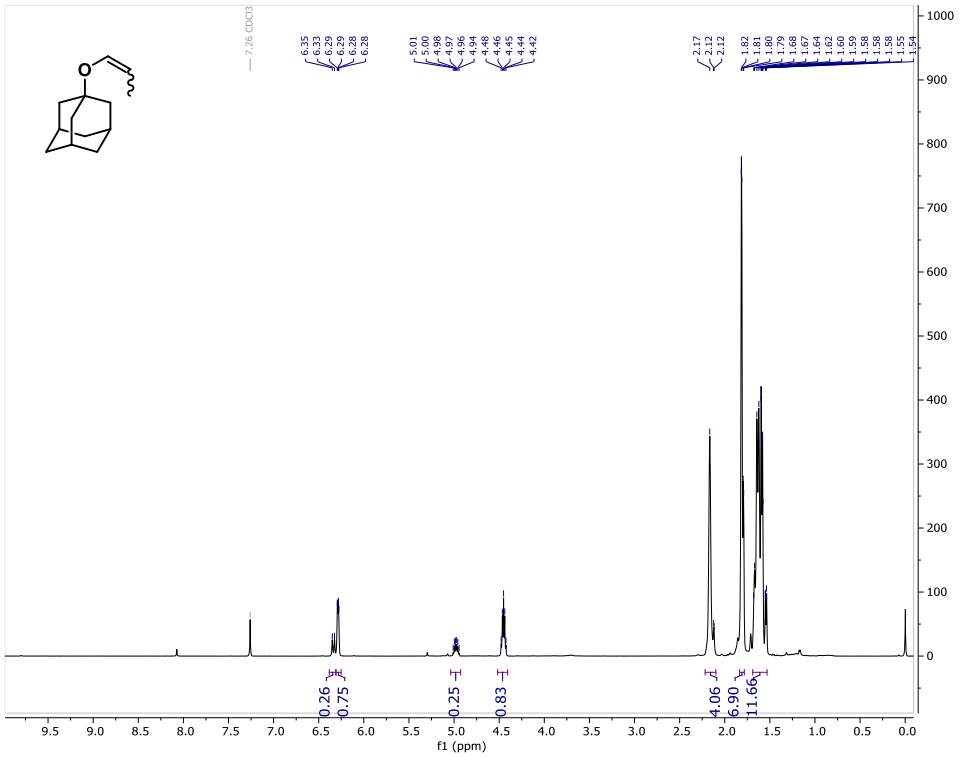

Figure S21. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2d**.

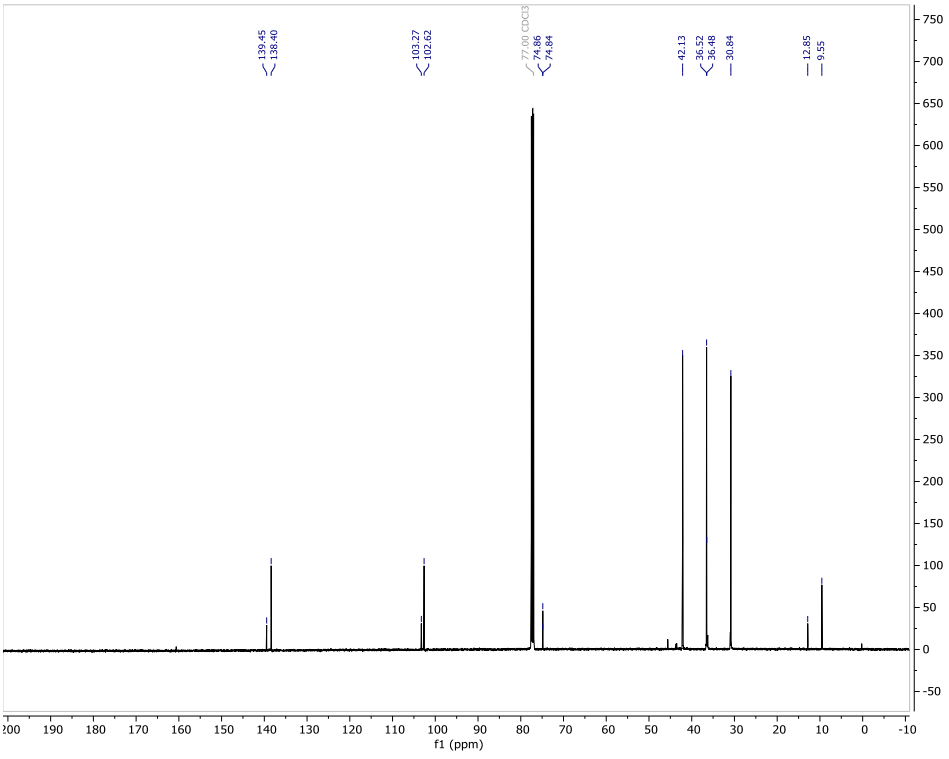

Figure S22. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2d**.

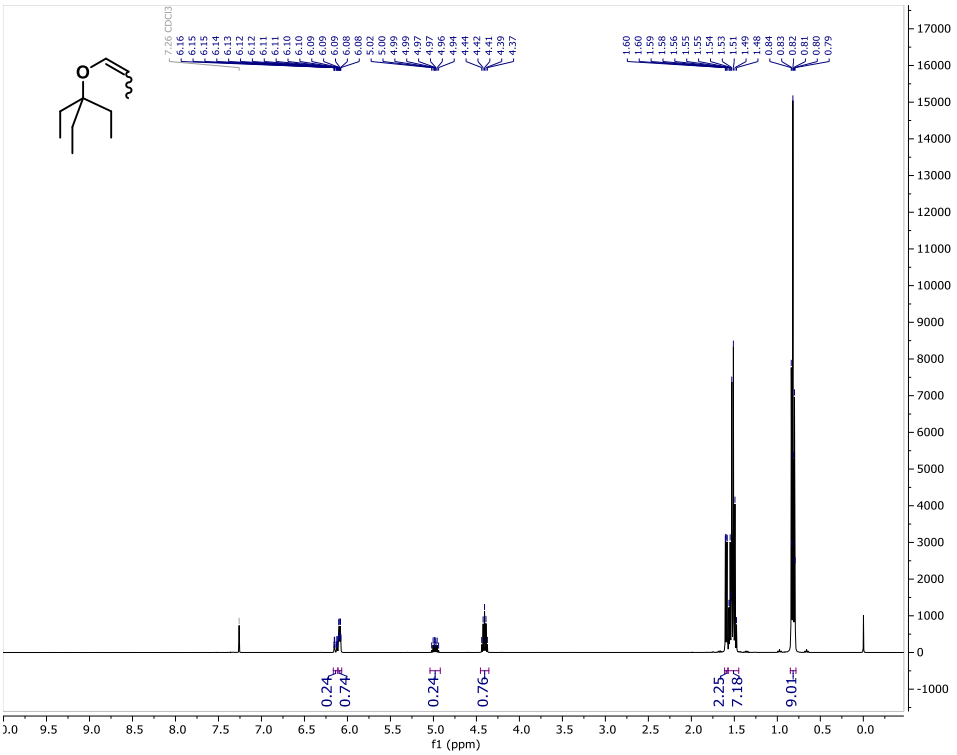

Figure S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2e**.

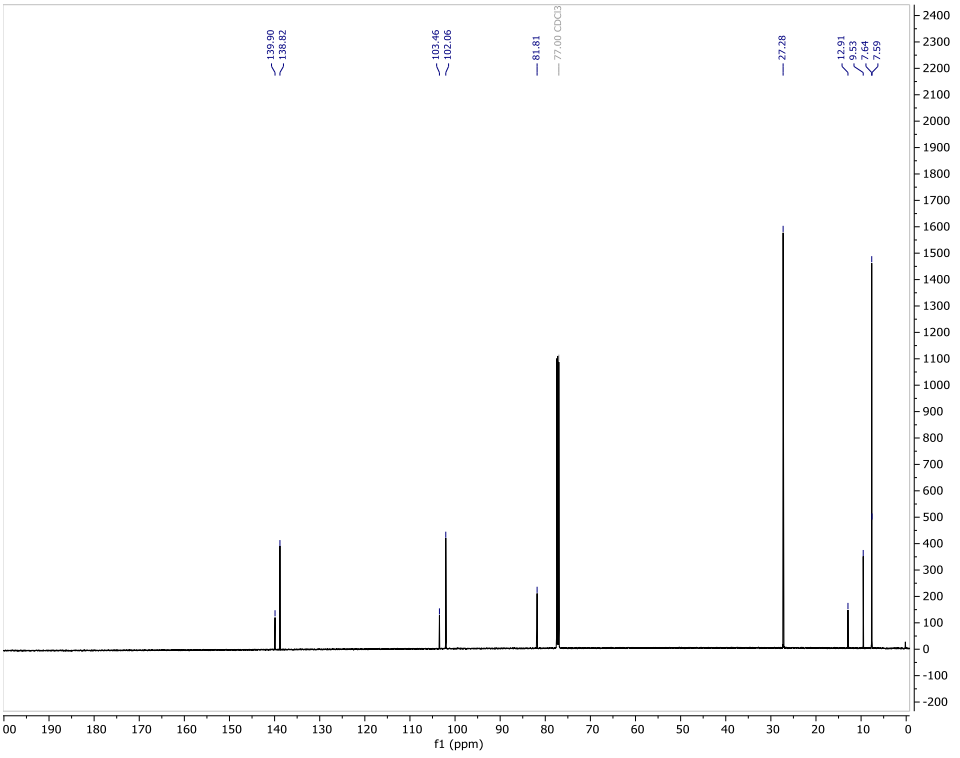

Figure S24. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of **2e**.

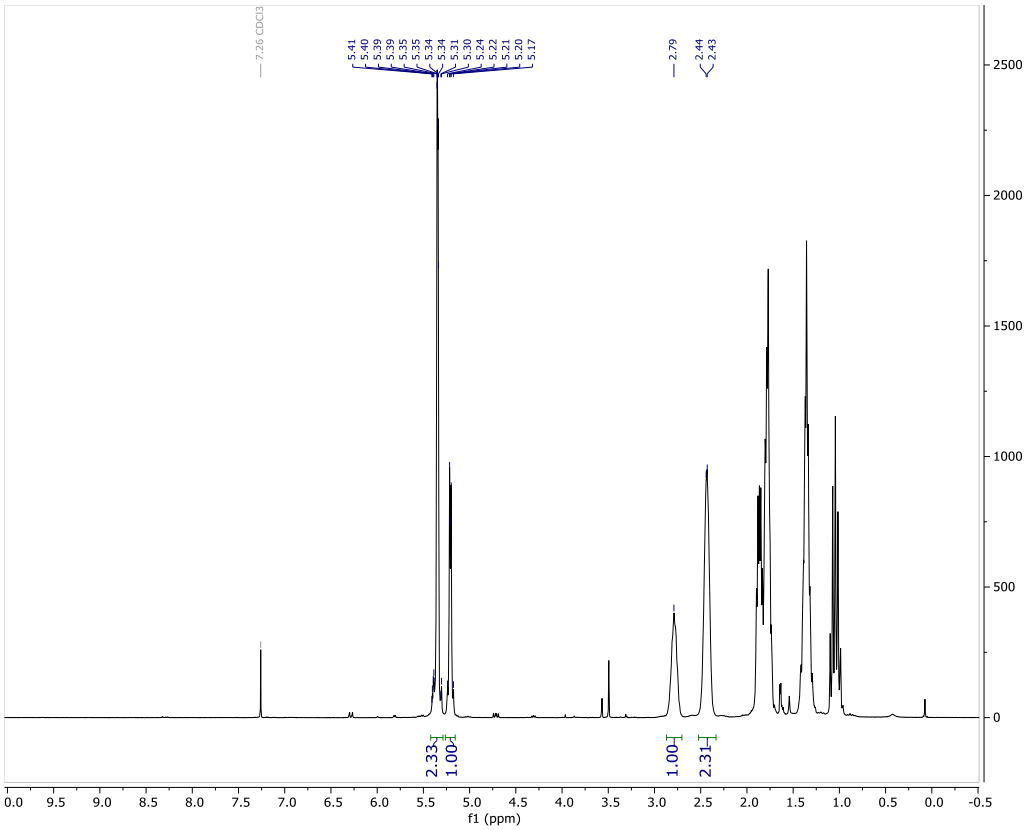

Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 70% *trans* content prepared with **2a** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 8).

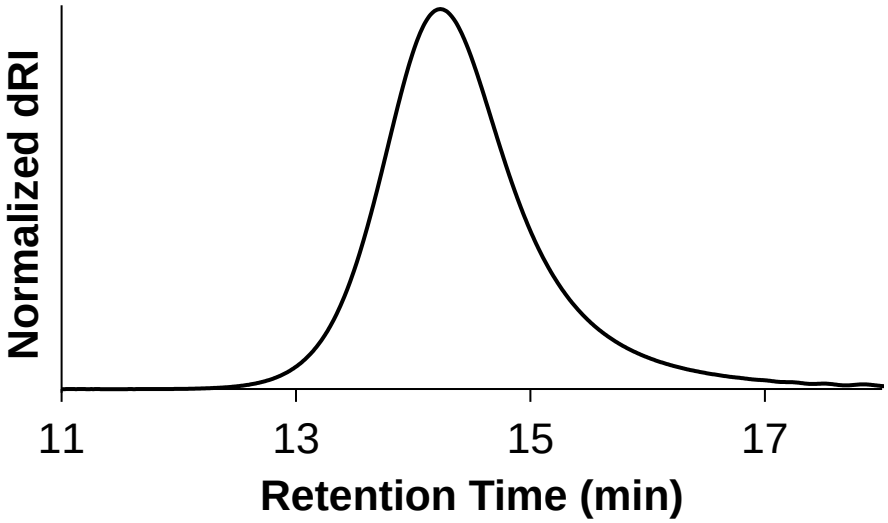

Figure S26. GPC trace of PNB with 70% *trans* content prepared with **2a** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 8).

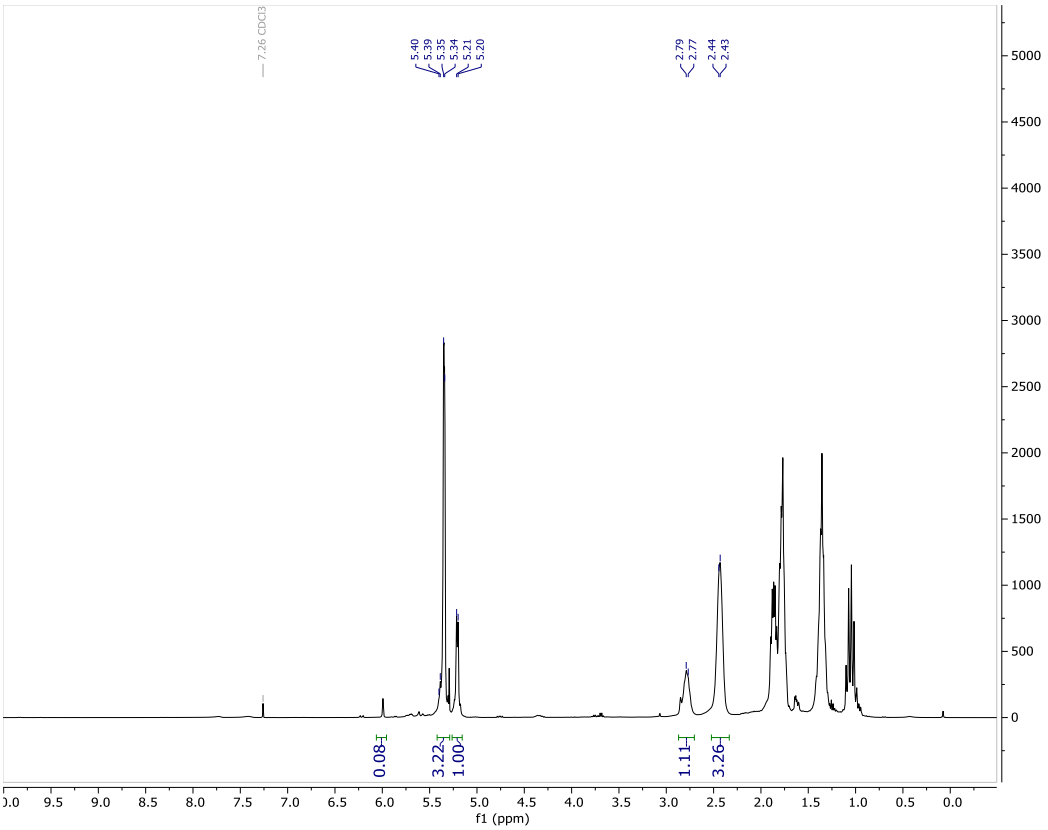

Figure S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 76% *trans* content prepared with **2b** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 9).

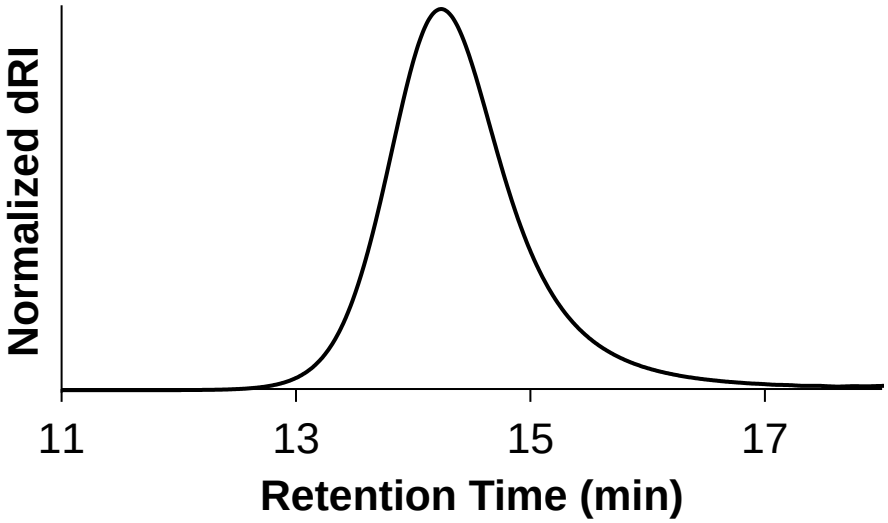

Figure S28. GPC trace of PNB with 76% *trans* content prepared with **2b** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 9).

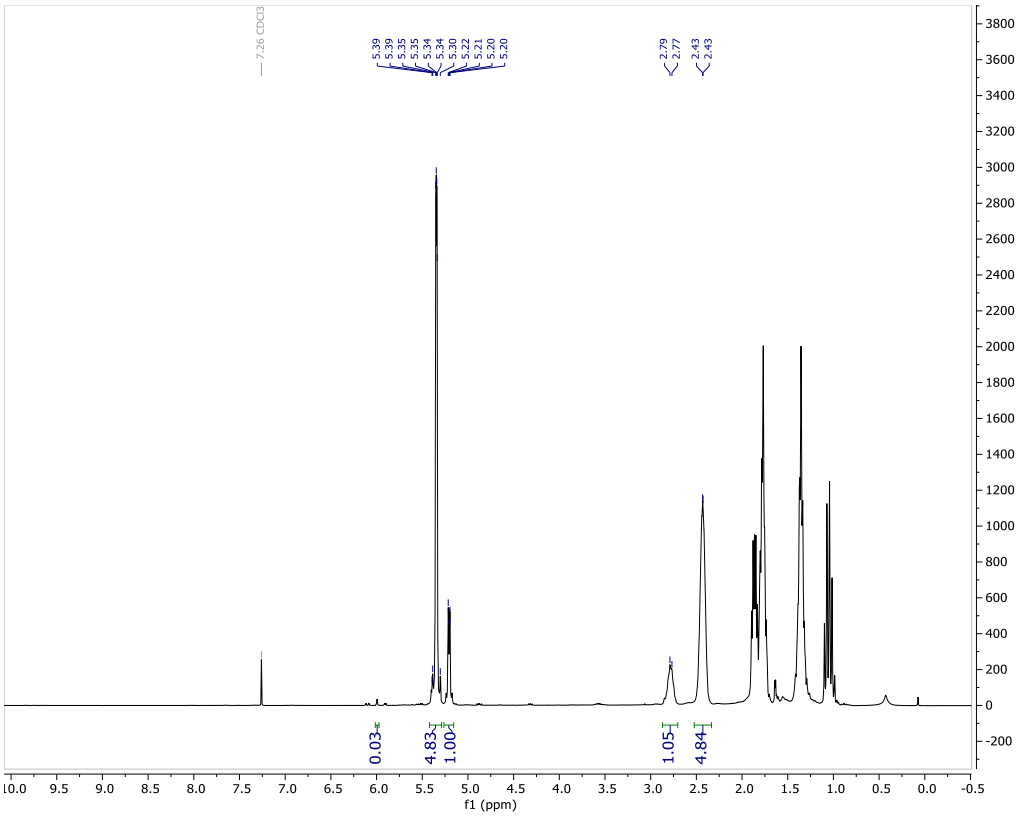

Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 83% *trans* content prepared with **2c** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 10).

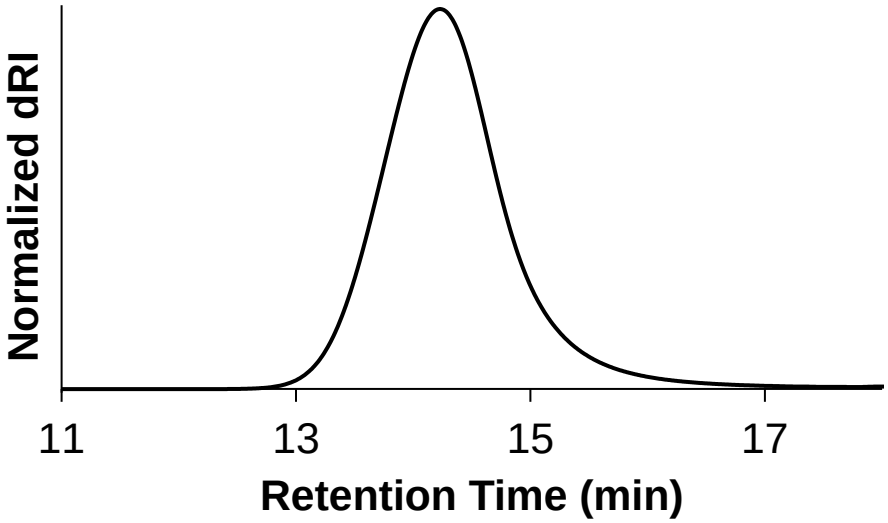

Figure S30. GPC trace of PNB with 83% *trans* content prepared with **2c** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 10).

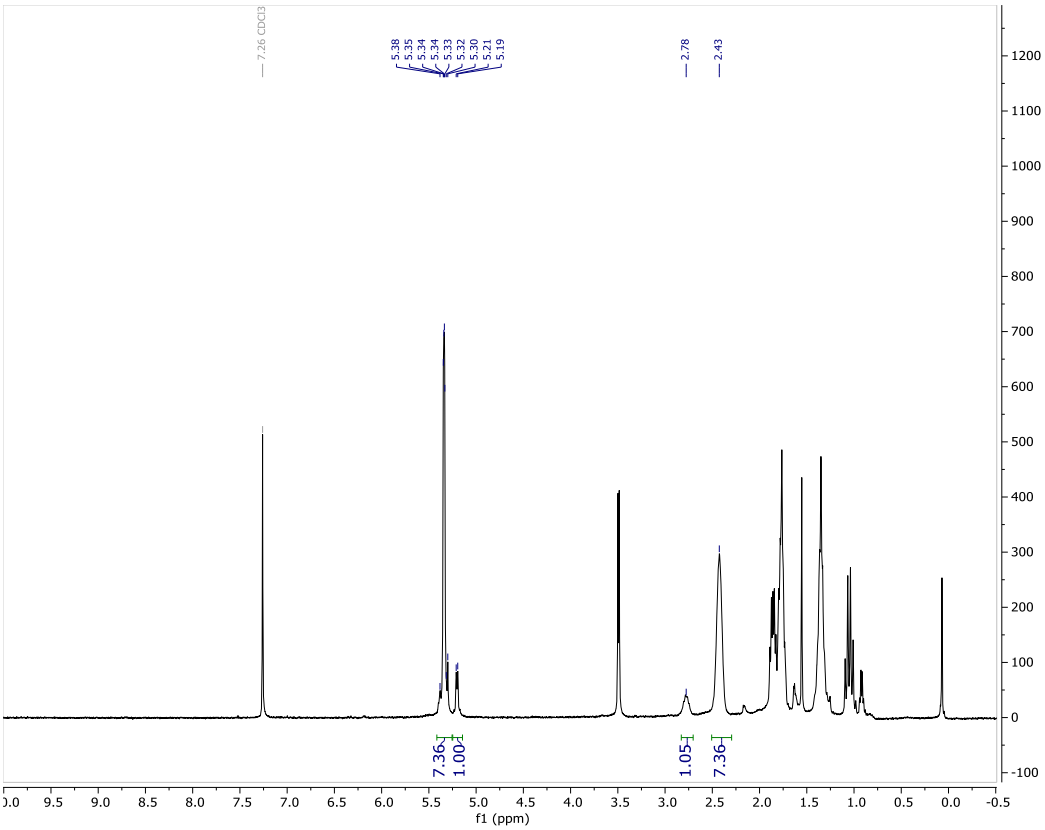

Figure S31. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 88% *trans* content prepared with **2d** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 11).

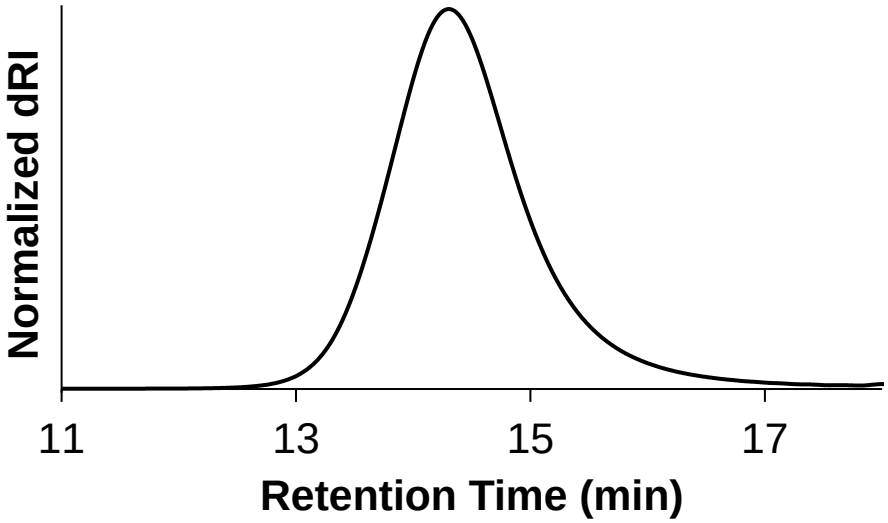

Figure S32. GPC trace of PNB with 88% *trans* content prepared with **2d** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 11).

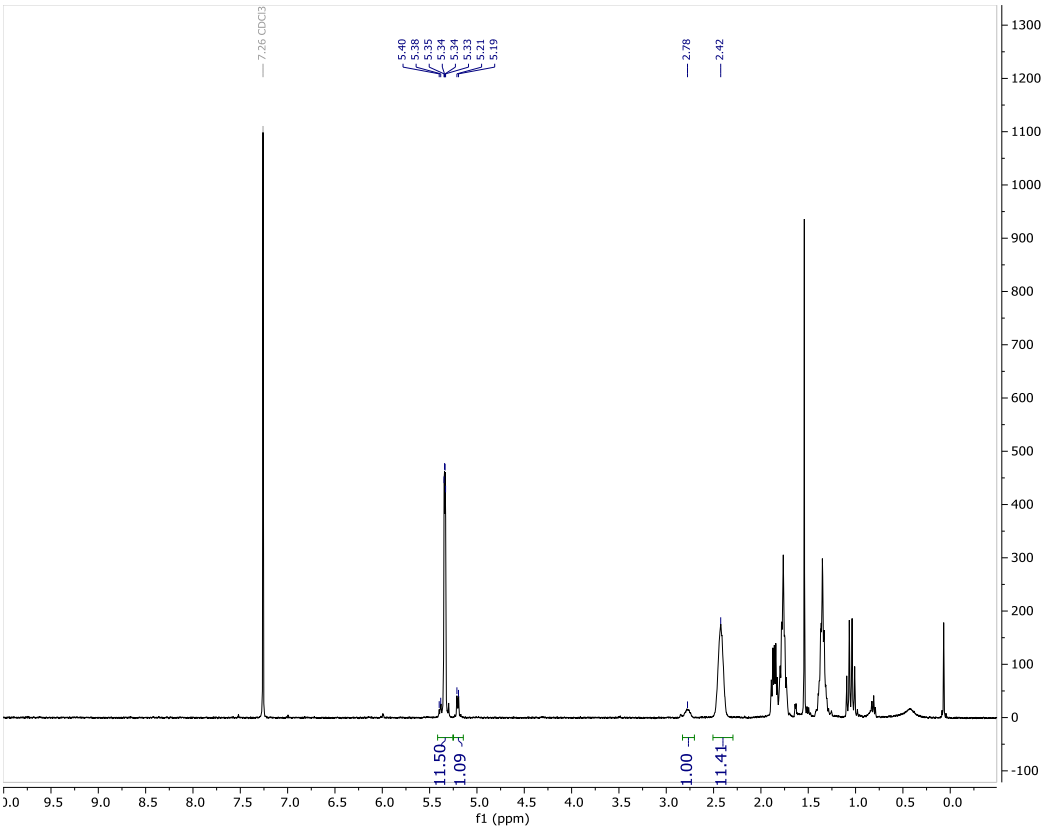

Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 92% *trans* content prepared with **2e** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 12).

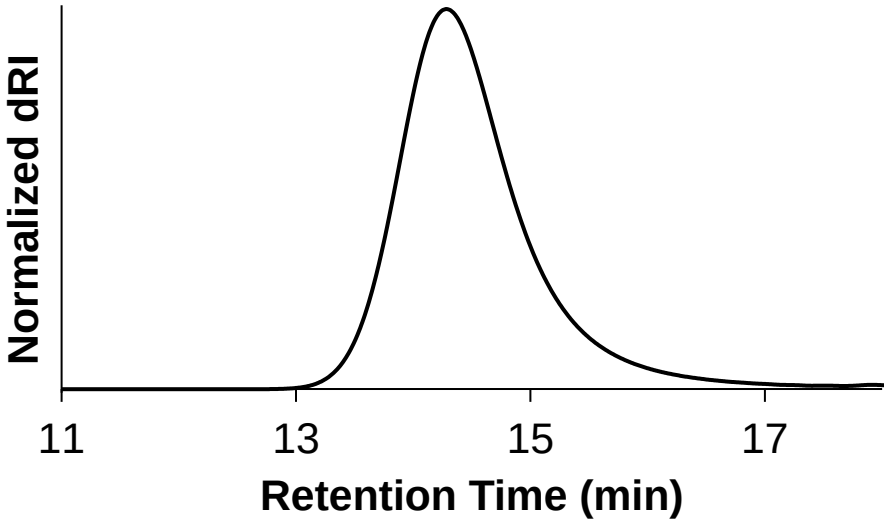

Figure S34. GPC trace of PNB with 92% *trans* content prepared with **2e** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at 25 ℃ (Table 1, entry 12).

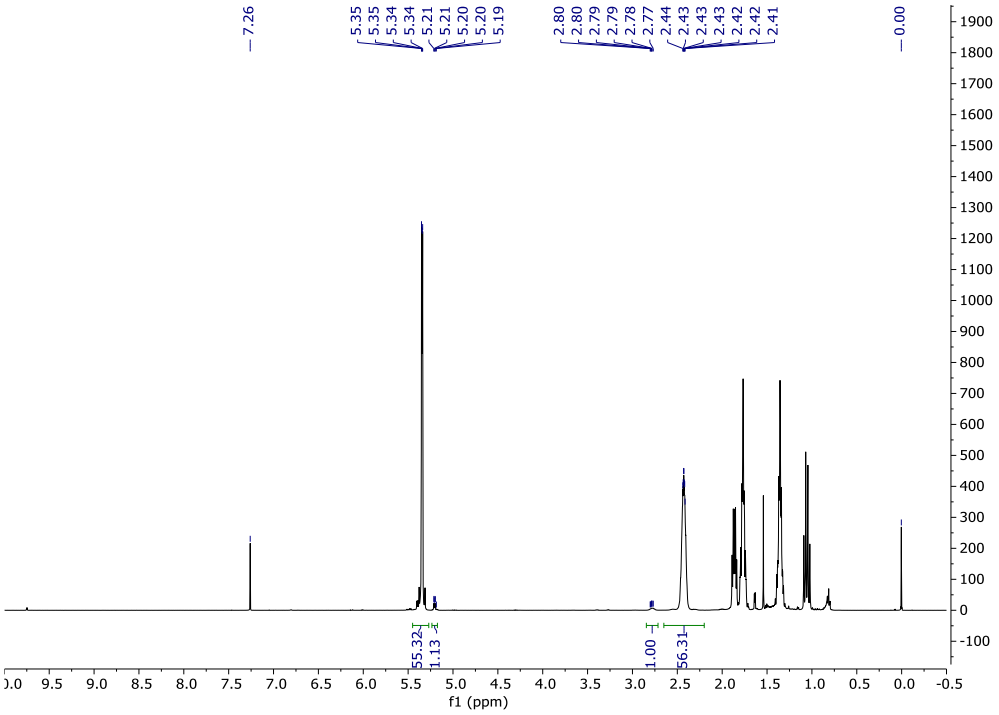

Figure S35. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with > 98% *trans* content prepared with **2e** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at -76 ℃ (Table 1, entry 13).

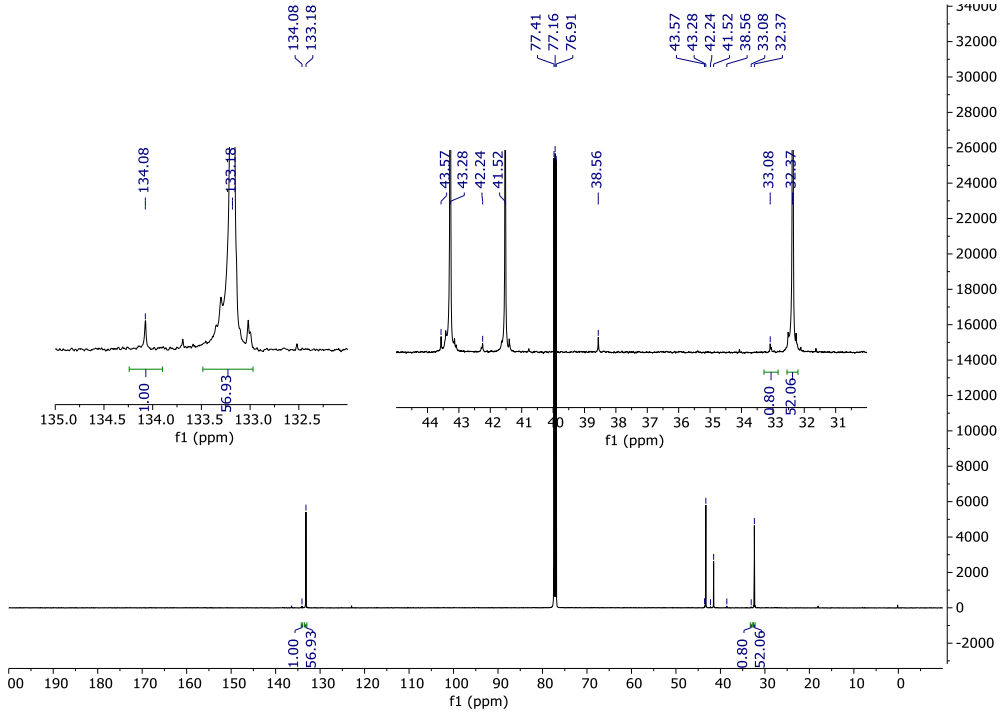

Figure S36. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) of PNB with > 98% *trans* content prepared with **2e** as initiator, **3a** as photocatalyst, CH_2Cl_2 as the solvent at -76 ℃ (Table 1, entry 13).

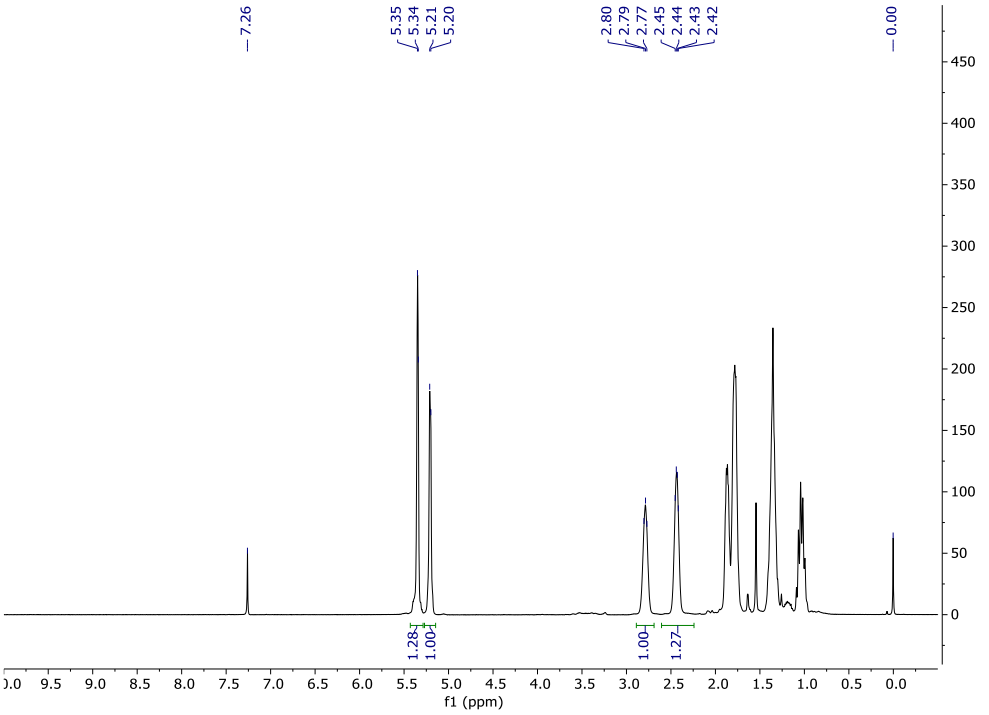

Figure S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 56% *trans* content prepared with **2b** as initiator, **3c** as photocatalyst, CH_2Cl_2 as the solvent at -76 ℃ (Table 1, entry 4).

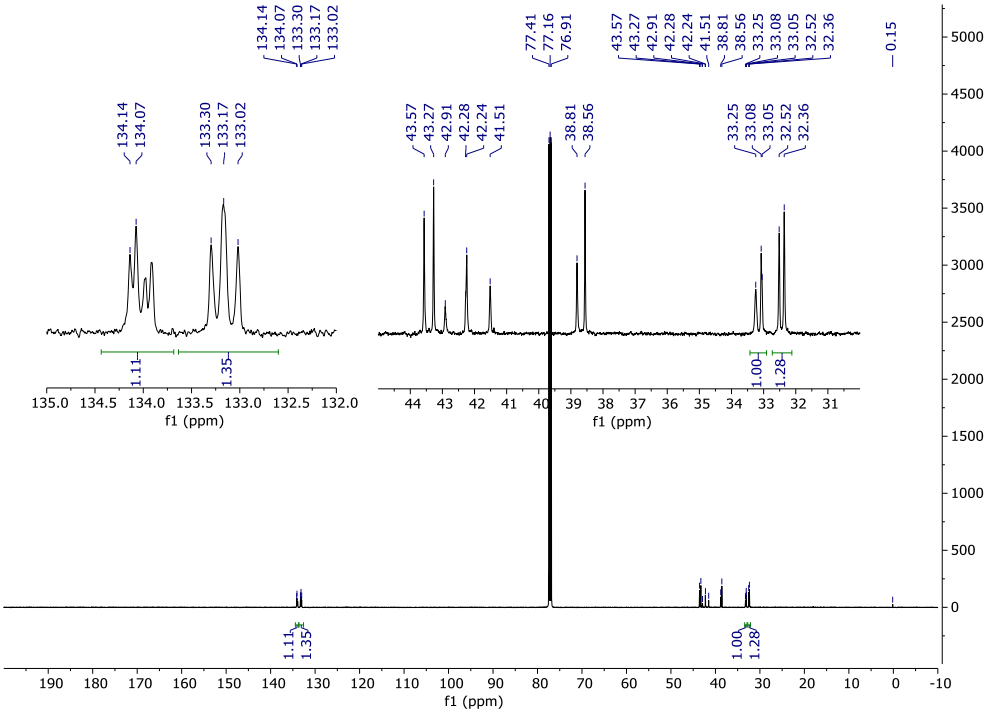

Figure S38. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) of PNB with 56% *trans* content prepared with **2b** as initiator, **3c** as photocatalyst, CH_2Cl_2 as the solvent at -76 ℃ (Table 1, entry 4).

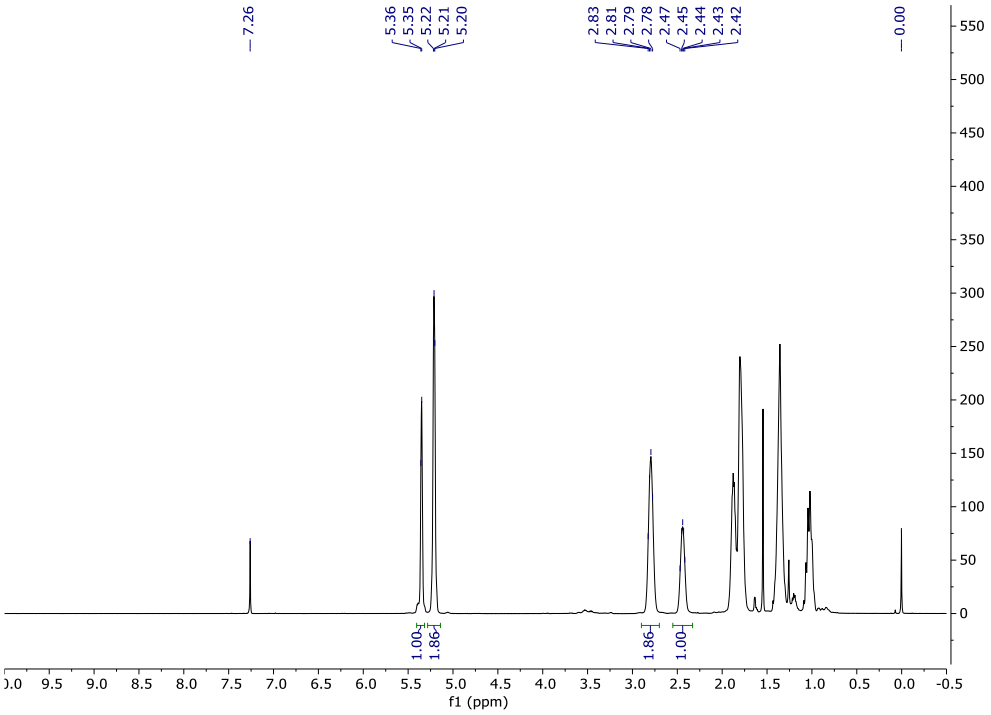

Figure S39. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 65% *cis* content prepared with **2b** as initiator, **3c** as photocatalyst, toluene as the solvent at -76 ℃ (Table 1, entry 6).

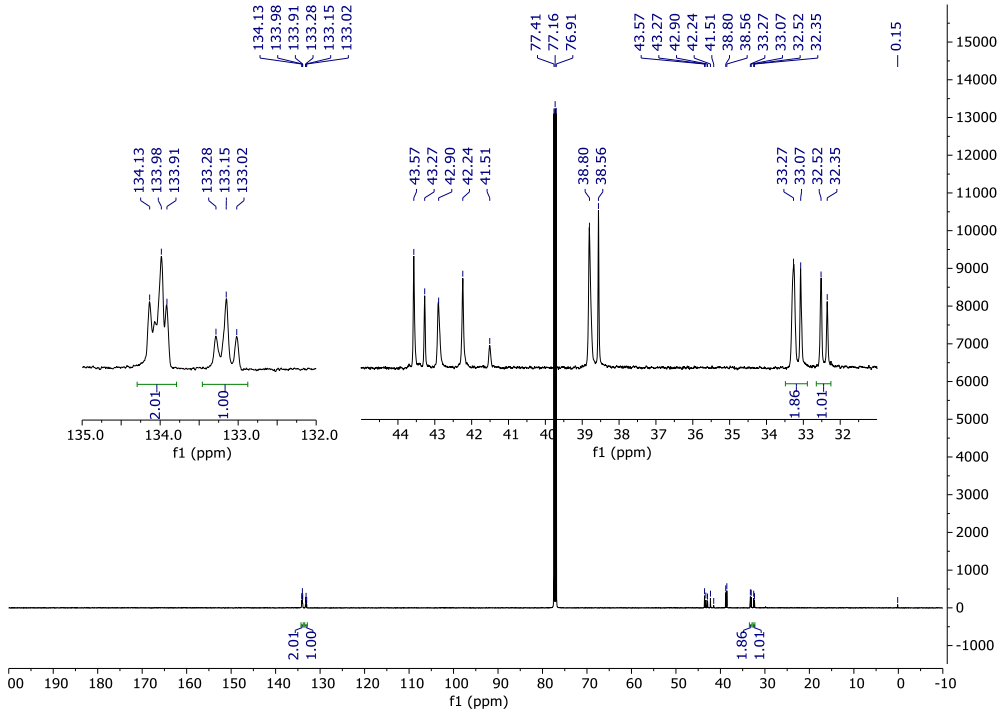

Figure S40. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) of PNB with 65% *cis* content prepared with **2b** as initiator, **3c** as photocatalyst, toluene as the solvent at -76 ℃ (Table 1, entry 6).

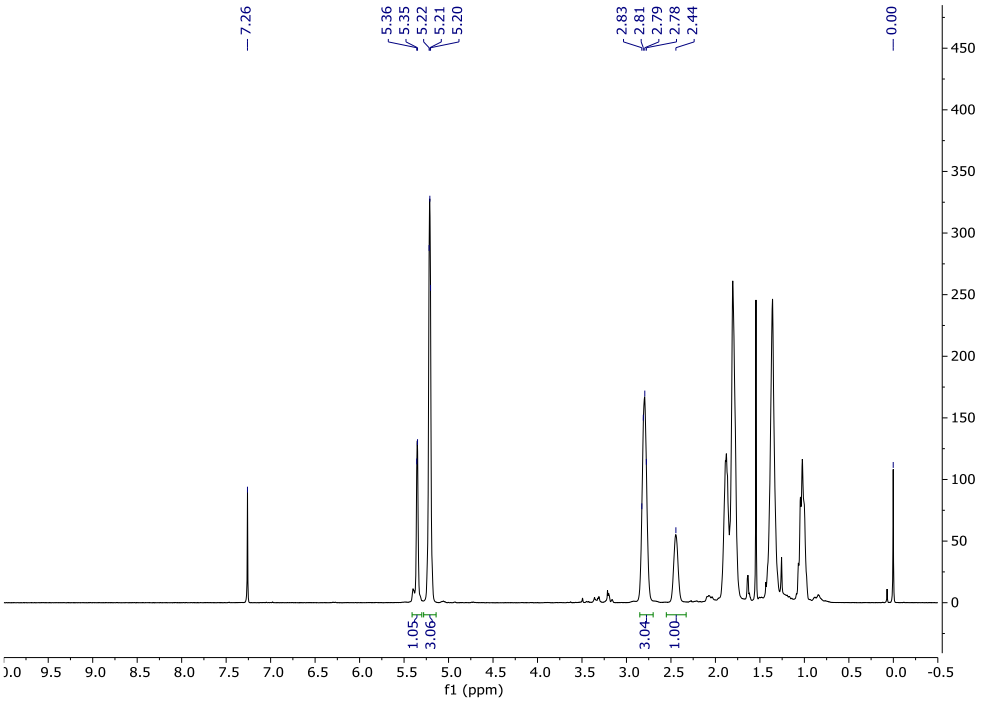

Figure S41. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PNB with 75% *cis* content prepared with **2a** as initiator, **3c** as photocatalyst, toluene as the solvent at -76 ℃ (Table 1, entry 7).

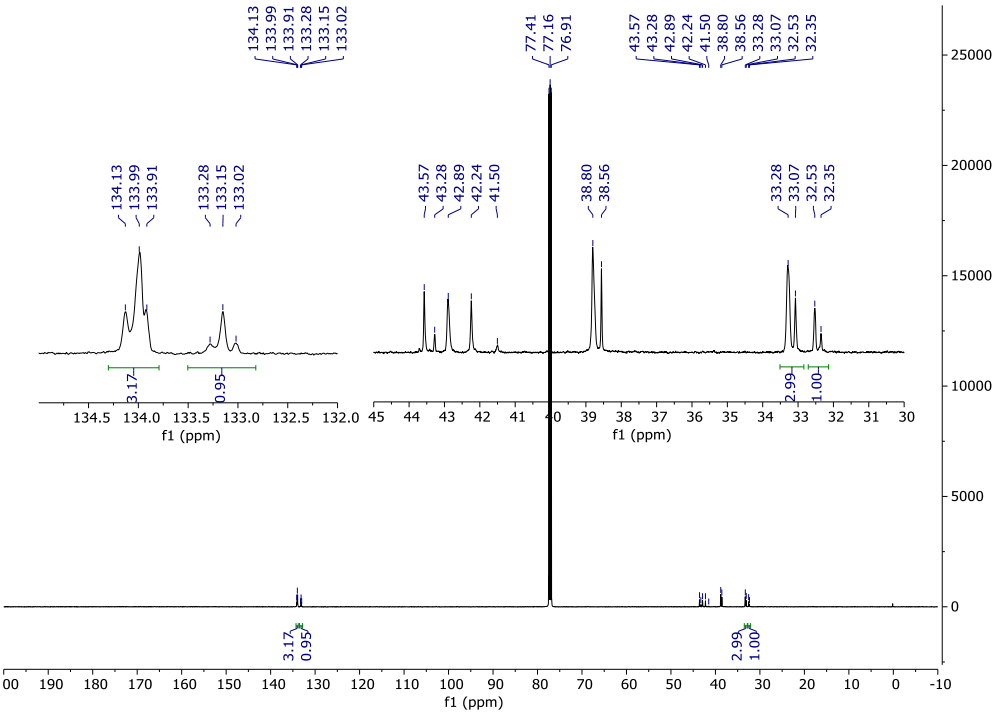

Figure S42. Quantitative ^{13}C NMR (126 MHz, $CDCl_3$) of PNB with 75% *cis* content prepared with **2a** as initiator, **3c** as photocatalyst, toluene as the solvent at -76 ℃ (Table 1, entry 7).