Electronic Supporting Information

Photoswitchable NHC-Promoted Ring-Opening Polymerizations

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Materials and Methods. Unless otherwise specified, reagents were purchased from commercial sources and used without further purification. Compound **1o·HPF$_6$** was synthesized according to a literature procedure.[1] Benzyl alcohol (BnOH), *ε*-caprolactone and *δ*-valerolactone were stirred over CaH_2 under an atmosphere of dry N_2 for 18 h, then were distilled under vacuum and degassed by the freeze-pump-thaw method prior to use. Benzene and tetrahydrofuran were dried and degassed using a Vacuum Atmospheres Company solvent purification system. ^{1}H and ^{13}C NMR spectra were recorded using a Varian 400 MHz spectrometer. Chemical shifts δ (in ppm) for ^{1}H NMR are referenced to tetramethylsilane using the residual solvent as an internal standard: $CDCl_3$, 7.24 ppm. The photochemical reactions were performed in 6Q Spectrosil quartz cuvettes (Starna) with 1.0 cm path lengths and 3.0 mL sample solution volumes. The irradiation source for photochemical reactions was a Newport/Oriel 66942 200-500W Hg Arc lamp housing equipped with a 350 W Hg lamp, a Newport 6117 liquid filter, a Newport 71445 electronic safety shutter, and a Newport 71260 filter holder. The source was powered by a Newport 669910 power supply and mounted on a Newport XL48 optical rail with a Newport 13950 shielded cuvette holder placed at a distance of 8 cm from the end of the source. The irradiation wavelength for the photocyclization reactions was obtained using a 313 nm bandpass filter (Andover Corporation). A long-pass edge filter (> 500 nm) (Andover Corporation) was used to introduce visible light. Gas chromatography (GC) was performed on an Agilent 6850 gas chromatograph (HP-1 column, L = 30 m, I.D. = 0.32 mm) equipped with a flame ionization detector (FID). The GC oven temperature was held at 40 °C for 3 min, then increased to 100 °C at 10 °C min^{-1} and finally increased to 250 °C at 20 °C min^{-1}. Durene was used as an internal standard to aid in measuring reaction conversions. Gel permeation chromatography (GPC) was performed using THF as the eluent on a Viscotek GPCmax Solvent/Sample Module, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-3078) thermostatted at 24 °C arranged in series, and a Viscotek VE 3580 refractive index detector. Molecular weight and polydispersity data are reported relative to polystyrene standards in THF.

Ring-opening polymerization of *ε*-caprolactone. Under an atmosphere of N_2 in a glove box, a vial equipped with a magnetic stir bar was charged with 17.4 mg (0.03 mmol) of **1o·HPF$_6$** and 5.0 mL of C_6H_6. A solution of 27 mg (0.15 mmol) of NaHMDS in 5 mL of C_6H_6 was prepared separately, and 1 mL of that solution was added to the vial containing **1o·HPF$_6$**. The mixture was then stirred at room temperature for 20 min before it was filtered through a 0.2 μm PTFE filter into a clean vial. Each of the two quartz cuvettes was then charged with 2.0 mL (0.5 mol%) of the catalyst solution and 2.0 mL of C_6H_6. The cuvettes were then sealed with Teflon-lined septum caps and removed from the glove box. The solution in one cuvette was irradiated with UV light (λ_{irr} = 313 nm) with stirring for 1 h, while the solution in the other cuvette was stirred under ambient light. After 1 h, 0.22 mL (2 mmol) of *ε*-caprolactone was added to each cuvette followed by 2.1 μL of benzyl alcohol (0.02 mmol). The reaction in the cuvette was kept under UV light, while the reaction in the round bottom flask was kept under ambient light throughout the course of the reaction. Aliquots (0.3 mL) were removed after given amounts of time, diluted into 1.0 mL of methanol to quench the reaction and concentrated under reduced pressure. The residue from each aliquot was then redissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy and/or was washed with methanol, redissolved in THF and

analyzed by GPC. For the chain extension experiment described in the main text, a single reaction was set up as described above in a quartz cuvette and after 30 min in ambient light was irradiated with UV light. After 1 h of UV irradiation, a second equivalent of monomer (0.22 mL) was added and the reaction was kept under UV irradiation for a further 3 h prior to irradiation with visible light.

Ring-opening polymerization of *δ*-valerolactone. Under an atmosphere of N_2 in a glove box, a vial equipped with a magnetic stir bar was charged with 12 mg (0.02 mmol) of **1o·HPF$_6$** and 4.0 mL of C_6H_6. A solution of 17.5 mg (0.095 mmol) of NaHMDS in 5 mL of C_6H_6 was prepared separately, and 1 mL of that solution was added to the vial containing **1o·HPF$_6$**. The catalyst solution was then stirred at room temperature for 20 min before it was filtered through a 0.2 μm PTFE filter into a clean vial. In a separate vial, 402 mg (3 mmol) of the internal standard durene was dissolved in 3.0 mL of C_6H_6. Each of the quartz cuvettes was then charged with 1.0 mL of the durene solution (1 mmol) and either 1.5 mL (0.3 mol%) or 2.0 mL (0.4 mol%) of the catalyst solution. The total volume of the solution in each cuvette was increased to 4.0 mL through the addition of C_6H_6. The cuvettes were then sealed with Teflon-lined septum caps and removed from the glove box. The solution in one cuvette was irradiated with UV light (λ_{irr} = 313 nm) with stirring for 1 h, while the solution in the other cuvette was stirred under ambient light. After 1 h, 0.2 mL (2 mmol) of *δ*-valerolactone was added to each cuvette followed by 0.1 mL (0.024 mmol; 1.2 mol%) or 0.13 mL (0.0032 mmol; 1.6 mol%) of a previously prepared solution of 25 μL of benzyl alcohol in C_6H_6. The reaction in the cuvette was kept under UV light, while the reaction in the round bottom flask was kept under ambient light throughout the course of the reaction. Aliquots (0.1 mL) were removed after given amounts of time, diluted into 1.0 mL of methanol to quench the reaction and precipitate the polymer product. Each aliquot was filtered through a 0.2 μm PTFE filter and analyzed by GC. Alternatively, the methanol precipitate was redissolved in THF and analyzed by GPC. For the photoswitching experiments described in the main text, a single reaction was set up as described above in a quartz cuvette and irradiated with UV or visible light after the indicated periods of time.

Pseudo-First Order Kinetic Analyses for Ring-Opening Polymerization Reactions Catalyzed by NHC Precatalyst 1o·HPF$_6$.

The ring-opening polymerization of δ-valerolactone initiated by benzyl alcohol may be represented as:

$$A + B \longrightarrow P$$

Assuming no side reactions, the δ-valerolactone (A) will always be present in a large excess over the benzyl alcohol (B) quantities. As such, pseudo-first order kinetics may be assumed, and the following rate law applies:

$$\frac{d[P]}{dt} = k[A][B]_0 = k[A]$$

The integrated form of the above equation is as follows:

$$\ln[A] = \ln[A]_0 - kt$$

Rearranging the integrated rate law and substituting the initial concentration of monomer (2.0 M) for $[A]_0$ gives:

$$\ln\left(\frac{[A]}{[A]_0}\right) = \ln\left(\frac{[A]}{2.0}\right) = -kt$$

Thus, plotting $\ln([A]/[A]_0)$ vs. t (s) should give a linear plot where k is equal to the slope of the line. Selected examples are shown in Figures S1 – S4.

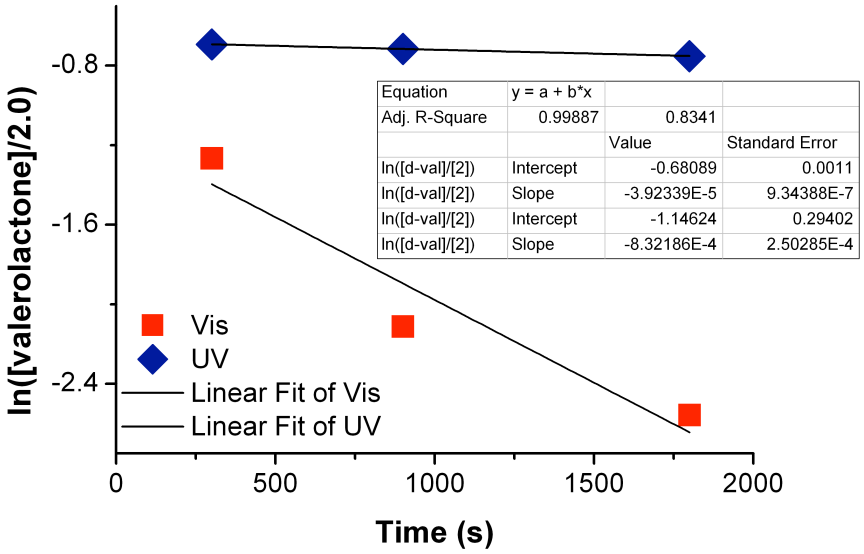


Figure S1. Plot of ln([δ-valerolactone]/2.0) vs. time (s) for the ring opening polymerization of δ-valerolactone catalyzed by **1**. Two reactions were run concurrently with one exposed to UV light (λ_{irr} = 313 nm) for 1 h prior to substrate addition (blue diamonds) and one kept under ambient light (red squares).

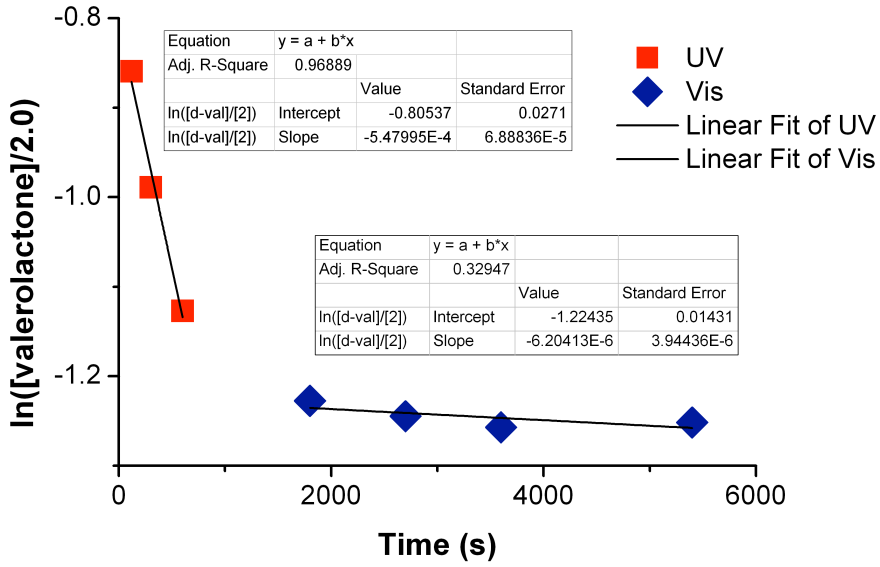


Figure S2. Plot of ln([δ-valerolactone]/2.0) vs. time (s) for the ring opening polymerization of δ-valerolactone catalyzed by **1**. A single reaction was allowed to react under ambient light for 10 min (red squares), then irradiated with UV light (λ_{irr} = 313 nm) for 80 min (blue diamonds).

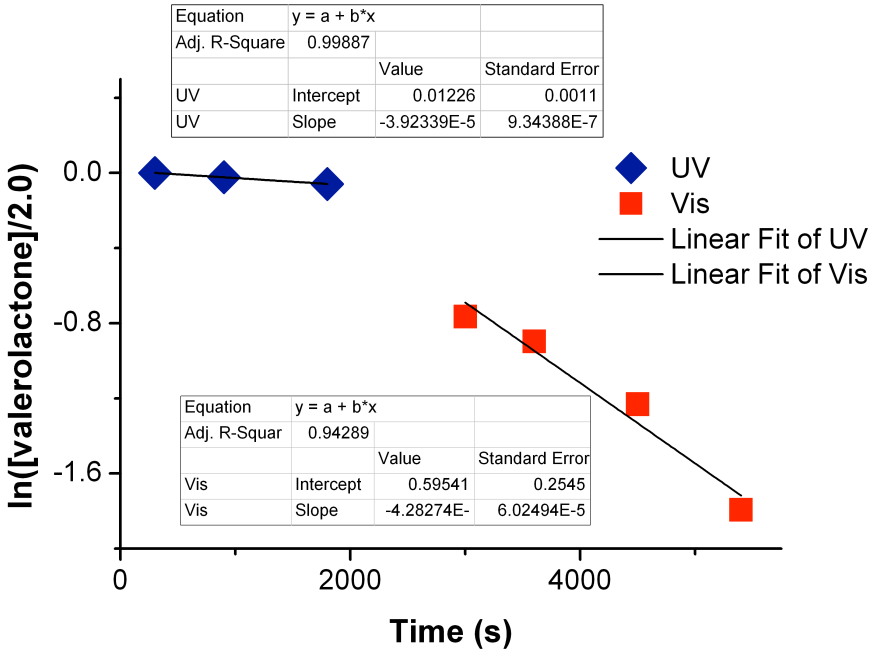


Figure S3. Plot of ln([δ-valerolactone]/2.0) vs. time (s) for the ring opening polymerization of δ-valerolactone catalyzed by **1**. A single reaction was exposed to UV irradiation (λ_{irr} = 313 nm) for 1 h prior to substrate addition and was kept under UV irradiation for a further 30 min (blue diamonds). The reaction was subsequently exposed to visible irradiation ((λ_{irr} > 500 nm) for a further 1 h (red squares).

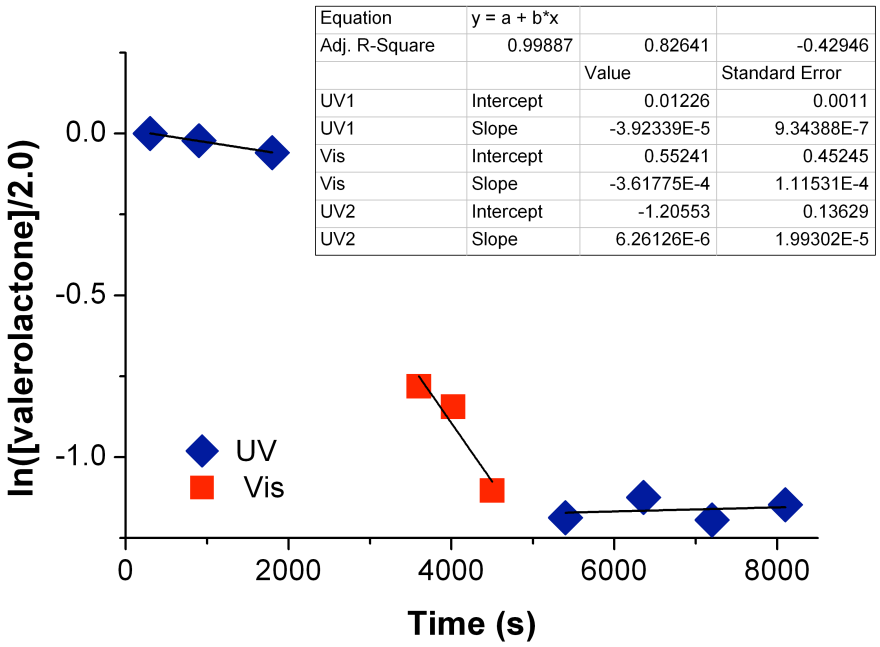


Figure S4. Plot of ln([δ-valerolactone]/2.0) vs. time (s) for the ring opening polymerization of δ-valerolactone catalyzed by **1**. A single reaction was exposed to UV irradiation (λ_{irr} = 313 nm) for 1 h prior to substrate addition and was kept under UV irradiation for a further 30 min (blue diamonds). The reaction was then exposed to visible irradiation (λ_{irr} > 500 nm) for 1 h (red squares), followed by subsequent UV irradiation for a further 1.25 h.

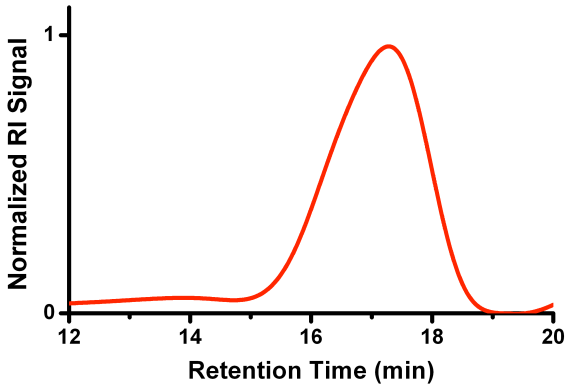


Figure S5. Gel permeation chromatogram of poly(ε-caprolactone) formed from the ROP of ε-caprolactone catalyzed by **1o**. Conditions: (ε-caprolactone]$_0$ = 2.0 M; [BnOH]$_0$/[**1o**]$_0$ = 2; [δ-valerolactone]$_0$/[**1o**] = 200; 25 °C; 1 h. M_n = 15,900 Da; PDI = 1.15. $M_{n(theor)}$ = 11,400 Da.

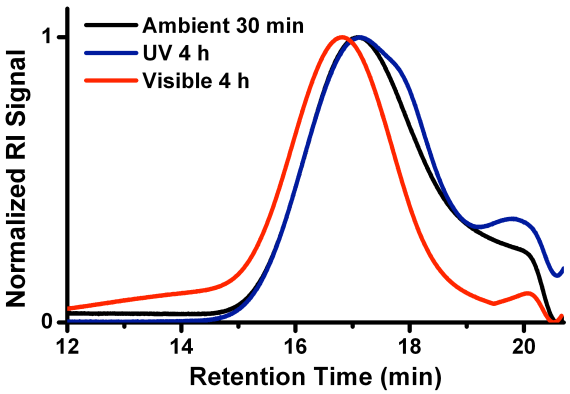


Figure S6. Crude gel permeation chromatograms of aliquots removed from the photo-gated ROP of ε-caprolactone catalyzed by **1o**. A solution of ε-caprolactone (2 mmol), 0.5 mol% **1o**, and 1.0 mol% BnOH in benzene (4.0 mL) was allowed to react in ambient light for 30 min (black line). The reaction vessel was then irradiated with UV light for 1 h, after which a second equivalent of ε-caprolactone (2 mmol) was added. The reaction vessel was kept under UV irradiation for a further 3 h (blue line), prior to exposure to visible light for a further 4 h (red line). Ambient 30 min: M_n = 12,500 Da; PDI = 1.57; $M_{n(theor)}$ = 11,400 Da. UV 4 h: M_n = 12,200 Da; PDI = 1.78; $M_{n(theor)}$ = 11,400 Da. Visible 4 h: M_n = 19,000 Da; PDI = 1.31; $M_{n(theor)}$ = 16,000 Da.

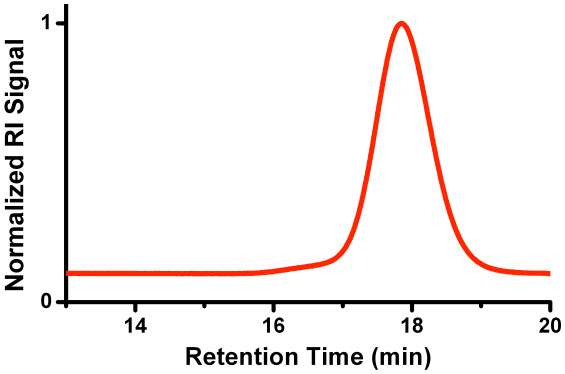


Figure S7. Gel permeation chromatogram of poly(δ-valerolactone) formed from the ROP of δ-valerolactone catalyzed by **1o**. Conditions: $[\delta\text{-valerolactone}]_0$ = 0.5 M; $[BnOH]_0/[\mathbf{1o}]_0$ = 4; $[\delta\text{-valerolactone}]_0/[\mathbf{1o}]$ = 250; 25 °C; 30 min. M_n = 7,400 Da; PDI = 1.16. $M_{n(theor)}$ = 5,900 Da.

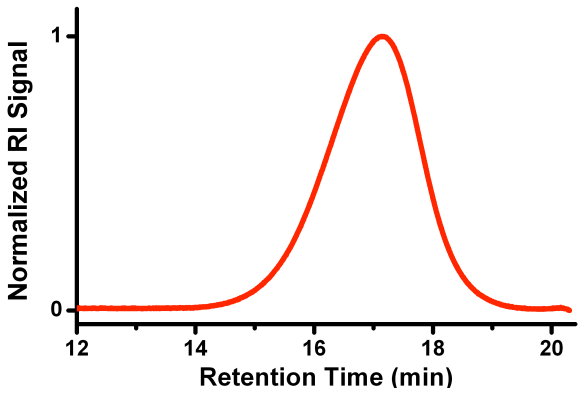
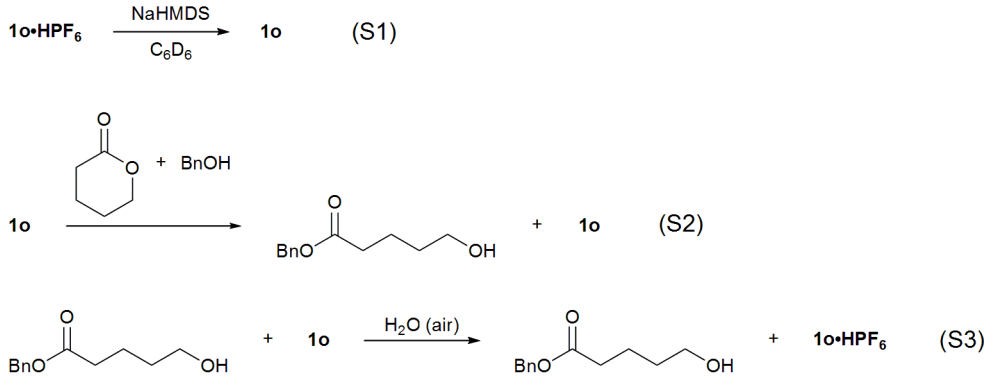


Figure S8. Gel permeation chromatogram of the polymer formed upon the addition of an equimolar mixture of ε-caprolactone (1 mmol) and δ-valerolactone (1 mmol) to a solution of **1o** (0.01 mmol) and benzyl alcohol (0.04 mmol) in benzene (4.0 mL). M_n = 14,300 Da; PDI = 1.59. $M_{n(theor)}$ = 11,300 Da.

Summary of Stoichiometric Reactions.



Under an atmosphere of N_2 in a glove box, a vial equipped with a magnetic stir bar was charged with 5.9 mg (0.01 mmol) of **1o·HPF$_6$**. A solution of 9.2 mg (0.05 mmol) of NaHMDS in 5 mL of C_6D_6 was prepared separately, and 1 mL of that solution was added to the vial containing **1o·HPF$_6$**. The reaction mixture was stirred at room temperature for 20 min prior to ^{1}H NMR analysis (Eq. S1). Subsequently, 1 μL of δ-valerolactone (0.01 mmol) and 1 μL of benzyl alcohol (0.01 mmol) were added to the solution of **1o**, and the resulting solution was analyzed by ^{1}H NMR spectroscopy (Eq. S2). The solution was then removed from the glove box and exposed to air (Eq. S3), and the C_6D_6 was then evaporated under reduced pressure. The resulting residue was taken up into $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The spectrum recorded in $CDCl_3$ was consistent with that reported[2] for benzyl 5-hydroxypentanoate and the regeneration of **1o·HPF$_6$**.[1] Unreacted δ-valerolactone and benzyl alcohol were also observed; see Figures S9-S11. Treatment of **1o** with δ-valerolactone resulted in no reaction, as evidenced by ^{1}H NMR spectroscopy, although the subsequent addition of benzyl alcohol resulted in formation of benzyl 5-hydroxypentanoate. Likewise, **1o** did not react with benzyl alcohol; however, the subsequent addition of δ-valerolactone afforded the ester product.

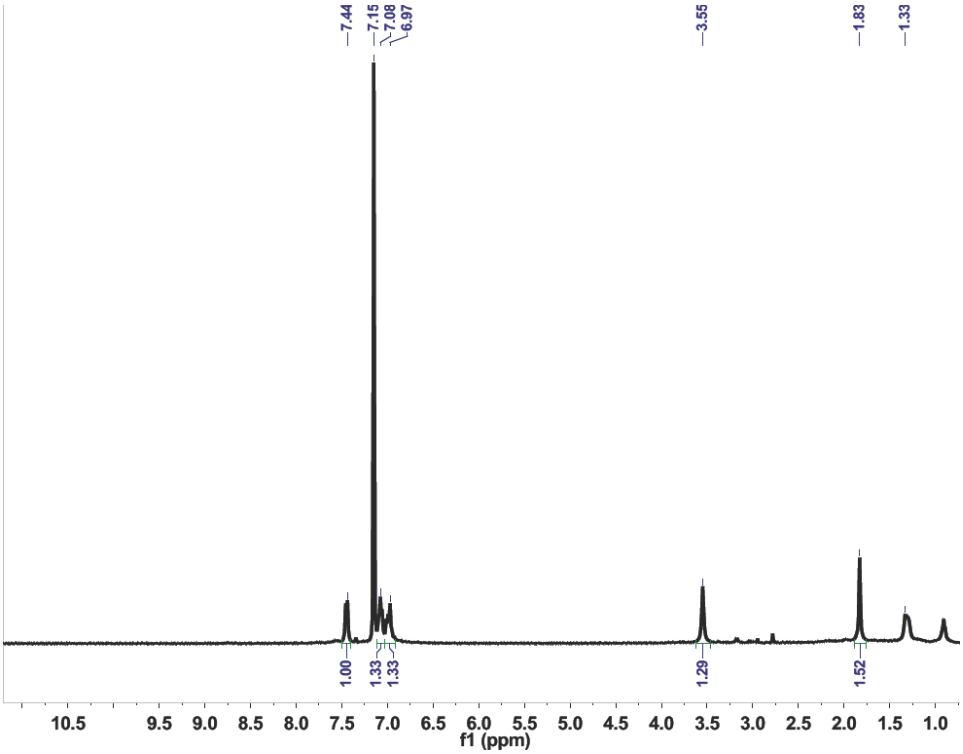


Figure S9. Crude ^{1}H NMR spectrum of **1o** formed upon treating **1o·HPF$_6$** with NaHMDS in C_6D_6.

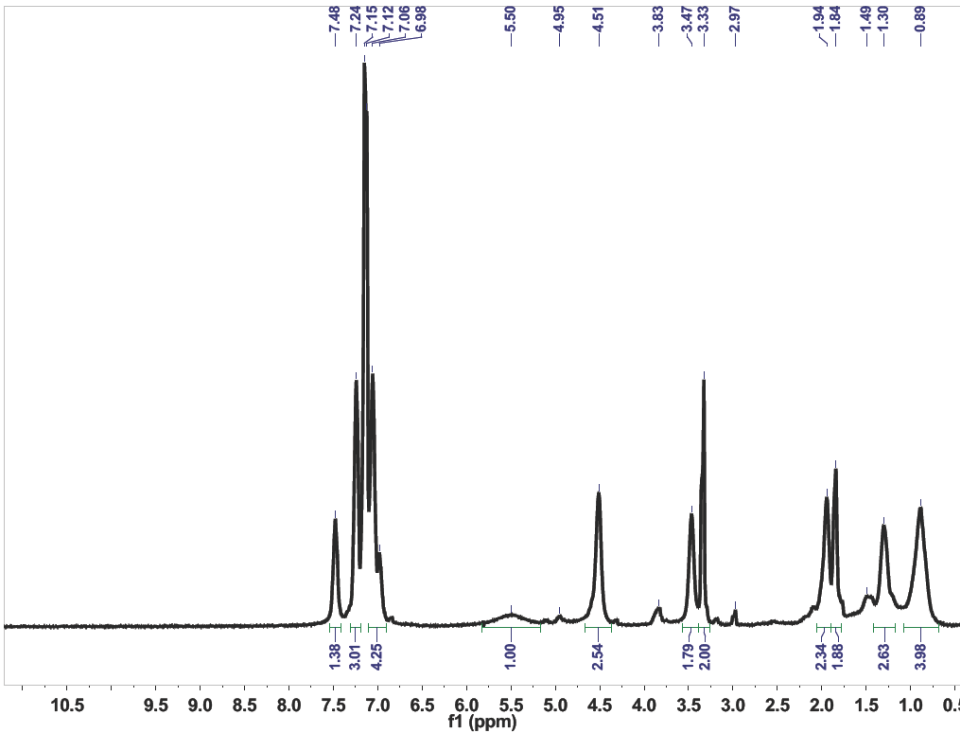


Figure S10. Crude ^{1}H NMR spectrum recorded in C_6D_6 of the reaction mixture obtained after treating **1o** with equimolar quantities of δ-valerolactone and benzyl alcohol.

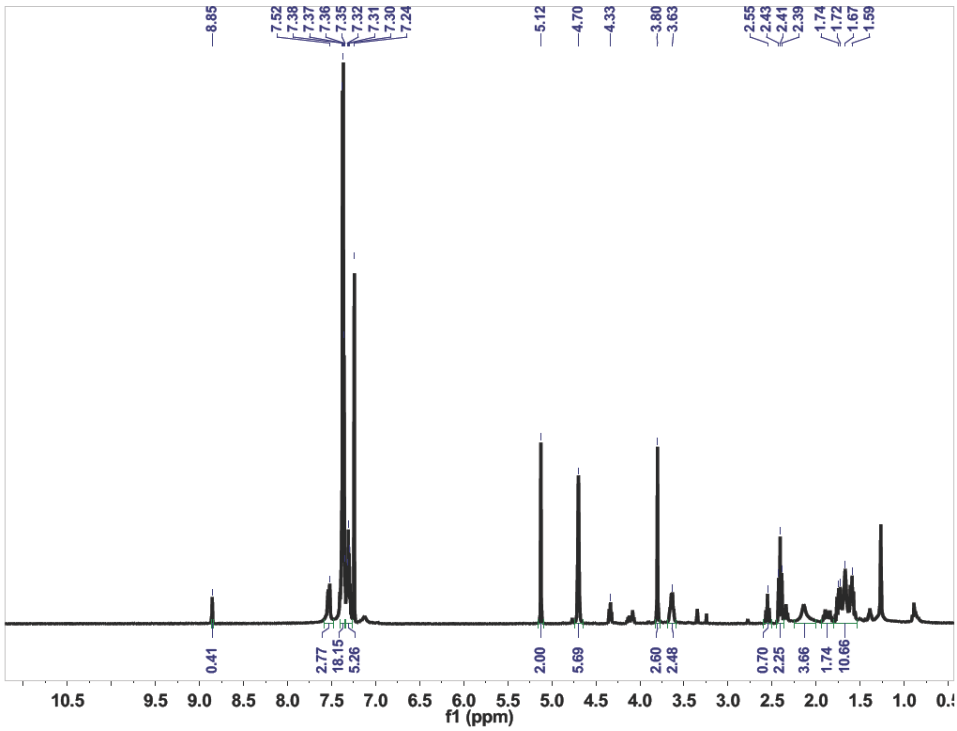


Figure S11. Crude ^{1}H NMR spectrum recorded in $CDCl_3$ of the reaction mixture obtained after treating a C_6D_6 solution of **1o** with equimolar quantities of δ-valerolactone and benzyl alcohol. The spectrum was used to facilitate a comparison to literature spectra.[2]

References

(1) B. M. Neilson and C. W. Bielawski, *J. Am. Chem. Soc.*, 2012, **134**, 12693.

(2) M. A. Christiansen and M. B. Andrus, *Tetrahedron Lett.*, 2012, **53**, 4805.