Electronic Supporting Information

Photoswitchable Organocatalysis: Using Light to Modulate the Catalytic Activities of N-Heterocyclic Carbenes

*Bethany M. Neilson and Christopher W. Bielawski**

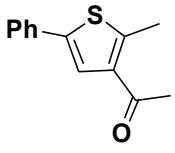
Department of Chemistry & Biochemistry, The University of Texas, Austin, Texas 78712

E-mail: bielawski@cm.utexas.edu

Table of Contents

Materials and Methods. Unless otherwise specified, reagents were purchased from commercial sources and used without further purification. Vinyl acetate, allyl alcohol, ethyl acetate, and 2-aminoethanol were dried over 4Å molecular sieves and bubbled with dry N_2 prior to use. All syntheses were performed under ambient conditions unless specified otherwise. Solvents 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) are referenced to tetramethylsilane using the residual solvent as an internal standard. For ^{1}H NMR: $CDCl_3$, 7.24 ppm; CD_3CN, 1.95 ppm; CD_3OD, 3.30 ppm; DMSO-d_6, 2.50 ppm; C_6D_6, 7.15 ppm. For ^{13}C NMR: $CDCl_3$, 77.0 ppm; DMSO-d_6, 39.5 ppm; CD_3OD, 49.0 ppm; C_6D_6, 128.0 ppm. Quantitative ^{13}C NMR spectra were recorded on a Varian 600 MHz spectrometer using decoupled Nuclear Overhauser Effects with a relaxation delay of 5× the measured T_1 relaxation time. Coupling constants (J) are expressed in hertz (Hz). Melting points were obtained with an Opti-Melt Automated Melting Point System MPA100 apparatus and are uncorrected. Mass spectra (MS, ESI or CI) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as m/z (relative intensity). UV-vis spectra were acquired using a Perkin-Elmer Lambda 35 UV-vis Spectrometer in 6Q Spectrosil quartz cuvettes (Starna) with 1.0 cm path lengths and 3.0 mL sample solution volumes. Beer's law measurements were performed using 10, 20, 30, and 40 μM sample concentrations. The photochemical reactions were performed in the same quartz cuvettes using 4.0 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. Elemental analyses were performed at Midwest Microlab, LLC (Indianapolis, IN). 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). For reactions between allyl alcohol and vinyl acetate, the GC oven temperature was held at 30 °C for 5 min, then increased to 100 °C at 10 °C min^{-1}. For reactions between 2-aminoethanol and ethyl acetate, 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}. The internal standard *n*-octane was used to aid in measuring reaction conversions.

3-acetyl-2-methyl-5-phenylthiophene (2): Compound **2** was prepared according to a modified literature procedure.[1] An oven-dried Schlenk flask equipped with a magnetic stir bar was charged with 3.00 g (17.2 mmol) of 2-methyl-5-phenylthiophene, and the flask was evacuated and refilled with N_2 three times. The reaction flask was kept under static vacuum and 150 mL of dry toluene was added via a cannula. After cooling the reaction vessel to 0 °C in an ice bath, 1.62 mL (17.2 mmol) of acetic anhydride was added via syringe under an atmosphere of N_2. At the same temperature, 2.4 mL (20.5 mmol) of tin(IV) chloride was added dropwise via a N_2 purged syringe. The reaction mixture was stirred for 2 h in the ice bath, and then poured into a mixture of 100 g of ice and 100 mL of 0.5 M HCl. The organic layer was separated and washed with 150 mL of deionized water, then dried over sodium sulfate and concentrated under reduced pressure. Purification of the resulting brown residue by column chromatography on silica gel eluting with a 2:1 v/v mixture of hexanes and dichloromethane



followed by dichloromethane yielded 2.7 g (71% yield) of the desired product as a pale yellow solid. mp 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 2.74 (s, 3H), 7.28 (t, *J* = 7.6, 1H), 7.37 (t, *J* = 7.6, 2H), 7.51 (s, 1H), 7.54 (dd, *J* = 7.6, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 29.7, 124.1, 125.5, 127.6, 128.9, 133.4, 136.8, 139.3, 148.3. HRMS (*m/z*): Calcd. for $C_{13}H_{12}OS$ $[M]^+$, 216.0609; Found, 216.0608. Anal. Calcd. for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; Found: C, 72.21; H, 5.56.

1,2-bis(2'-methyl-5'-phenylthien-3'-yl)-glyoxal monohydrate (3): A three-necked round bottom flask equipped with a reflux condenser, N_2 inlet and magnetic stir bar was charged with 2.67 grams (10.6 mmol) of 2-methyl-3-acetyl-5-phenylthiophene **2**, 1.36 grams (12.3 mmol) of SeO_2, 0.5 mL of deionized water, and 11.5 mL of 1,4-dioxane. The mixture was heated at reflux for 48 h under an atmosphere of nitrogen. The mixture was cooled to room temperature and filtered through Celite, and the filtrate was concentrated under reduced pressure. The resulting orange residue was washed with cold ethyl acetate and 1.35 g of the desired product was collected on a frit by vacuum filtration as a pale yellow powder (44% yield). The product was isolated as a mixture of the glyoxal monohydrate **3** and the corresponding glyoxal compound (85:15 molar ratio). mp 128 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (s, 3H), 2.82 (s, 0.7H), 5.14 (d, *J* = 10.3, 1H), 6.12 (d, *J* = 10, 1H), 7.31 (t, *J* = 7.6, 1.3H), 7.39 (t, *J* = 7.6, 2.5H), 7.54 (dd, *J* = 8, 2.5H), 7.88 (s, 1H), 7.98 (s, 0.18H), 9.53 (s, 0.15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 89.9, 123.9, 125.4, 127.7, 128.7, 131.3, 132.9, 139.9, 153.7, 187.4, 189.9. HRMS (*m/z*): Calcd. for $C_{13}H_{10}O_2S$ $[M-H_2O]^+$, 230.0402; Found, 230.0400.

1,2-bis(2'-methyl-5'-phenylthien-3'-yl)-2-hydroxy-1-ethanone (4): Compound **4** was prepared according to a modified literature procedure.[2a] An oven-dried Schlenk flask with a stir bar was charged with 1.1 g (4.4 mmol) of **3**, 0.9 g (5.2 mmol) of 2-methyl-5-phenylthiophene and 70 mL of dry toluene under an atmosphere of N_2. The reaction mixture was cooled to 0 °C in an ice bath, and 0.6 mL (5.2 mmol) of tin (IV) chloride was added dropwise. The reaction mixture was stirred in the ice bath for 3 h, and then poured into 100 mL of ice water. The mixture was extracted with ethyl acetate (3 × 75 mL) and the combined organic layers were washed with deionized water (2 × 150 mL) and brine (2 × 150 mL). After removing the residual solvent under reduced pressure, the resulting orange residue was washed with cold ethyl acetate to give 1.25 g (70% yield) of the desired product as a beige powder. Spectral data were in agreement with literature values.[2]

1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-ethanedione (5): A round bottom flask with a stir bar was charged with 1.1 g (2.7 mmol) of the α-hydroxy ketone **4** in 50 mL of glacial acetic acid, 98 mg (0.54 mmol) of copper (II) acetate, and 540 mg (6.75 mmol) of NH_4NO_3. The mixture was heated to reflux for 24 h, then cooled to room temperature and poured into 50 mL of ice water. To the mixture was added concentrated ammonium hydroxide until a pH = 7 was observed. The mixture was extracted with ethyl acetate (3 × 50 mL) and the combined organic layers were washed with deionized water (3 × 100 mL), saturated aqueous K_2CO_3 (3 × 100 mL), and brine (2 × 100 mL). The solvent was removed under reduced pressure and the resulting brown residue was passed through a short column of silica gel aided with dichloromethane eluent. The residual solvent was removed under reduced pressure and the resulting orange oil was recrystallized from hot ethyl acetate to yield 0.95 g (65% yield) of the desired product as a beige solid. mp 161 °C

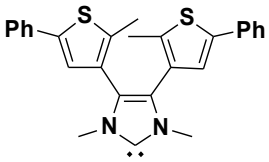
(dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (s, 6H), 7.27 (t, *J* = 7.6, 2H), 7.35 (t, *J* = 8, 4H), 7.47 (s, 2H 7.51 (dd, *J* = 7.2, 4H),). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 124.8, 126.1, 128.3, 129.3, 133.1, 133.3, 141.0, 153.1. HRMS (*m/z*): Calcd. for $C_{24}H_{18}O_2S_2$ $[M]^+$, 402.0749; Found, 402.0748. Anal. Calcd. for $C_{24}H_{18}O_2S_2$: C, 71.61; H, 4.51; Found: C, 70.71; H, 4.56.

1,2-bis-(2'-methyl-5'-phenylthien-3'-yl) imidazole (6): A round bottom flask equipped with a reflux condenser and stir bar was charged with 300 mg (0.74 mmol) of diketone **5**, 50 mL of glacial acetic acid, 0.3 mL of aqueous formaldehyde (37% w/v in H_2O, 3.7 mmol), and 1.2 g (15.5 mmol) of ammonium acetate. The mixture was stirred at 110 °C for 48 h, then cooled to room temperature and poured into 100 mL of ice water. Concentrated ammonium hydroxide was added dropwise until a pH = 7 was observed. The mixture was extracted with ethyl acetate (3 × 50 mL) and the combined organic layers were washed with deionized water (2 × 100 mL), saturated aqueous K_2CO_3 (3 × 100 mL), and brine (1 × 100 mL). After washing the resulting residue with cold ethyl acetate, 120 mg (39% yield) of the desired product was collected via filtration as a beige solid. mp 190 °C (dec). ^{1}H NMR (400 MHz, CD_3OD): δ 2.11 (s, 6H), 7.22 (t, *J* = 6.8, 2H), 7.24 (s, 2H), 7.32 (t, *J* = 7.6, 4H), 7.52 (d, *J* = 7.2, 4H), 7.82 (s, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 14.1, 125.7, 126.2, 128.4, 129.9, 132.2, 135.5, 136.4, 137.1, 141.7. HRMS (*m/z*): Calcd. for $C_{25}H_{21}N_2S_2$ $[M+H]^+$, 413.1141; Found, 413.1142. Anal. Calcd. for $C_{25}H_{20}N_2S_2$: C, 72.78; H, 4.89; N, 6.79; Found: C, 72.41; H, 4.89; N, 6.72.

1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazolium Iodide (7): A 40 mL vial with a stir bar was charged with 100 mg (0.24 mmol) of imidazole **6**, 123 mg (0.89 mmol) of K_2CO_3, 10 mL of CH_3CN and 75 μL of iodomethane (1.2 mmol), sealed with a Teflon-lined cap, and heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature and filtered through Celite. After the filtrate was concentrated under reduced pressure, the residue was taken up into dichloromethane. The remaining K_2CO_3 was removed by a second filtration through Celite and the dichloromethane was removed from the filtrate under reduced pressure. The residue was triturated in diethyl ether and 113 mg (82% yield) of the desired product was isolated by filtration as a pale yellow powder. mp 206 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 6H), 3.94 (s, 6H), 7.14 (s, 2H), 7.29 (t, *J* = 7.4, 2H), 7.36 (t, *J* = 7.6, 4H), 7.50 (d, *J* = 7.2, 4H), 10.43 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 35.1, 121.9, 123.1, 125.5, 128.1, 129.0, 132.9, 138.2, 141.8, 142.9. HRMS (*m/z*): Calcd. for $C_{27}H_{25}N_2S_2$ $[M+1-I]^+$, 441.14537; Found, 441.1454. Anal. Calcd. for $C_{27}H_{25}IN_2S_2$: C, 57.04; H, 4.43; N, 4.93; Found: C, 57.73; H, 4.73; N, 4.54.

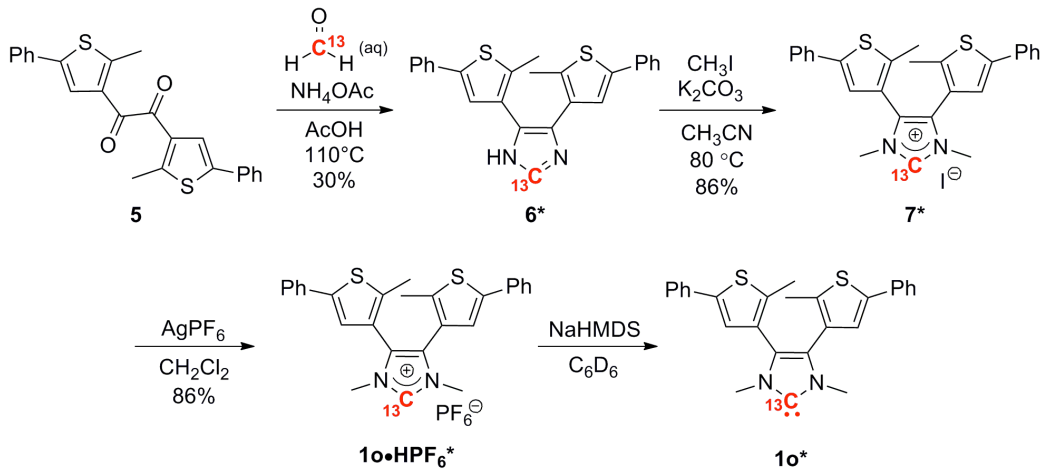
1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazolium Hexafluorophosphate (1o·HPF$_6$): A 20 mL vial equipped with a stir bar was charged with 100 mg (0.18 mmol) of **7** dissolved in 10 mL of dichloromethane. To the vial was added 45.5 mg (0.18 mmol) of silver hexafluorophosphate dissolved in 2 mL of dichloromethane. A white precipitate formed immediately, and the reaction was stirred at room temperature for a further 15 min. The mixture was then filtered through a 0.2 μm PTFE filter and the filtrate was concentrated and dried under reduced pressure to yield 75 mg (73% yield) of the desired product as a pale yellow powder. mp 221 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 6H), 3.81 (s, 6H), 7.11 (s, 2H), 7.29 (t, *J* = 7.6, 2H), 7.37 (t, *J* = 7.6, 4H), 7.50 (d, *J* = 7.6, 4H), 8.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 34.5, 122.0, 123.2, 125.6, 128.1, 128.2, 129.1, 133.1, 137.7, 142.0, 142.8. UV/Vis (C_6H_6): λ_{abs} = 293 nm (ε = 24894 dm^3 mol^{-1}).

HRMS (*m/z*): Calcd. for $C_{27}H_{25}N_2S_2$ $[M+1\text{-}PF_6]^+$, 441.14537; Found, 441.1455. Anal. Calcd. for $C_{27}H_{25}F_6N_2PS_2$: C, 55.28; H, 4.30; N, 4.78; Found: C, 55.33; H, 4.34; N, 4.44.



1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazolylidene (1o): Under an atmosphere of N_2 in a glove box, a 8 mL vial equipped with a stir bar was charged with 11.0 mg (0.02 mmol) of **1o·HPF$_6$**. In a separate 8 mL vial, 6 mg (0.033 mmol) of NaHMDS was dissolved in 2 mL of C_6D_6, and 1 mL of the base solution was added to the vial containing **1o·HPF$_6$**. The mixture was stirred at room temperature for 30 min and then transferred to an NMR tube or reaction vessel. The free NHC **1o** was not isolated, but was characterized in situ. ^{1}H NMR (400 MHz, C_6D_6): δ 1.83 (s, 6H), 3.55 (s, 6H), 6.99 (m, 4H), 7.08 (t, J = 7.6, 4H), 7.45 (d, J = 7.6, 4H). ^{13}C NMR (100 MHz, C_6D_6) δ 13.6, 33.9, 122.6, 123.7, 125.8, 129.3, 133.7, 142.1, 142.9, 201.9. UV/Vis (C_6H_6): λ_{abs} = 291 nm.

Synthesis of ^{13}C labeled NHC 1o*. The ^{13}C labeled NHC **1o*** was synthesized using an analogous route to that employed for **1o** with the exception that ^{13}C-enriched formaldehyde solution was used in the formylative cyclization of **5** to give the labeled imidazole **6***. Subsequent alkylation, anion metathesis, and in situ deprotonation yielded **1o***.



1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-2-^{13}C-imidazole (6*): ^{1}H NMR (400 MHz, CD_3OD): δ 2.13 (s, 6H), 7.23 (t, J = 7.6, 2H), 7.25 (s, 2H), 7.33 (t, J = 8, 4H), 7.53 (d, J = 8, 4H), 7.82 (d, J = 207, 1H). ^{13}C NMR (100 MHz, CD_3OD): δ 136.4.

1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethyl-2-^{13}C-imidazolium iodide (7*): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 6H), 3.95 (s, 6H), 7.17 (s, 2H), 7.27 (t, J = 7.6, 2H), 7.35 (t, J = 8, 4H), 7.50 (d, J = 7.2, 4H), 10.39 (d, J = 220, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1.

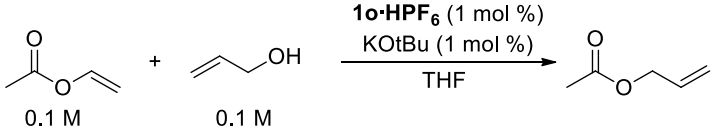
1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethyl-2-^{13}C-imidazolium hexafluoro-phosphate (1o·HPF$_6$*): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 6H), 3.81 (s, 6H), 7.13 (s, 2H), 7.29 (t, J = 8, 2H), 7.37 (t, J = 8, 4H), 7.50 (d, J = 8, 4H), 8.86 (d, J = 220, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6. HRMS (*m/z*): Calcd. for $C_{27}H_{25}N_2S_2$ $[M+1\text{-}PF_6]^+$, 442.14872; Found, 442.14850.

1,2-bis-(2'-methyl-5'-phenylthien-3'-yl)-1,3-dimethylimidazol-2-^{13}C-ylidene (1o*): ^{1}H NMR (400 MHz, C_6D_6): δ 1.81 (s, 6H), 3.63 (s, 6H), 6.94 (s, 2H), 7.01 (t, J = 8, 2H), 7.08 (t,

J = 8, 4H), 7.45 (d, J = 4, 4H). ^{13}C NMR (100 MHz, C_6D_6): δ 13.8, 37.0, 124.5, 125.8, 127.1, 129.2, 134.2, 138.9, 141.7, 150.9, 201.9.

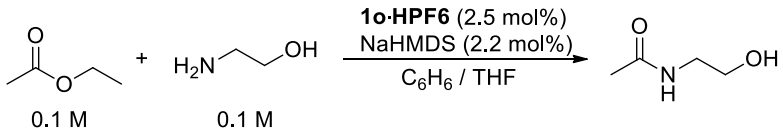
Photochemical Experiments with 1o*. Under an inert N_2 atmosphere in a glove box, 2 mg (0.012 mmol) of NaHMDS in 1 mL of C_6D_6 was added to a 5.8 mg (0.01 mmol) sample of **1o·HPF$_6$*** in an 8 mL vial. The solution was allowed to stir at room temperature for 1 h, then transferred to an NMR tube and analyzed by ^{13}C NMR spectroscopy. Under an inert atmosphere, the solution was then diluted further with 3 mL of C_6D_6 and transferred to a quartz cuvette ([**1o***] = 1 × 10^{-3} M). The cuvette was then either removed from the glove box and irradiated directly (λ_{irr} = 313 nm) for 1 h, or 2-aminoethanol and/or ethyl acetate were added in stoichiometric (0.01 mmol) or superstoichiometric (0.4 mmol) quantities along with 0.1 mL of THF under inert atmosphere prior to irradiation (λ_{irr} = 313 nm). The UV-treated solution was concentrated under reduced pressure to a volume of approximately 1 mL prior to ^{13}C NMR analysis. Subsequent visible light irradiation was carried out directly in the NMR tube using the concentrated sample at approximately [**1***] = 4.0 × 10^{-3} M and the irradiated sample was analyzed again by ^{13}C NMR spectroscopy.

Transesterification of Vinyl Acetate and Allyl Alcohol:



Under an atmosphere of N_2 in a glove box, a vial equipped with a magnetic stir bar was charged with 5.8 mg (0.01 mmol) of **1o·HPF$_6$**, 2 mg (0.01 mmol) of KOtBu, and 10 mL of THF. The solution was stirred at room temperature for 30 min, after which a 4 mL portion was transferred to a quartz cuvette equipped with a stir bar and a second 4 mL portion was transferred to a 10 mL round bottom flask equipped with a stir bar. The cuvette was then sealed with a Teflon-lined septum cap, and the round bottom flask was sealed with a rubber septum secured with a copper wire. The two reaction vessels were removed from the glove box and the solution in the quartz cuvette was irradiated with UV light (λ_{irr} = 313 nm) with stirring for 1 h, while the solution in the round bottom flask was stirred under ambient light. After 1 h, 65 μL (0.4 mmol) of *n*-octane (internal standard) was added to each vessel via a N_2 purged syringe, followed by 37 μL (0.4 mmol) of vinyl acetate and 27 μL (0.4 mmol) of allyl alcohol. The reaction in the cuvette was kept under UV irradiation and the reaction in the round bottom flask was kept under ambient light throughout the course of the reaction. Aliquots were removed after given amounts of time, diluted with wet methanol to quench the reaction and analyzed by GC. 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 amounts of time.

Amidation of Ethyl Acetate with 2-Aminoethanol:



Under an atmosphere of N_2 in a glove box, a vial equipped with a magnetic stir bar was charged with 11 mg (0.02 mmol) of **1o·HPF$_6$**. A solution of 16 mg (0.02 mmol) of NaHMDS in 10 mL of THF was prepared, and 2 mL of that solution was added to the vial containing **1o·HPF$_6$**. The catalyst solution was diluted with 6 mL of benzene and then stirred at room

temperature for 15 min. A 4 mL portion of the catalyst solution was transferred to a quartz cuvette equipped with a stir bar and a second 4 mL portion was transferred to a 10 mL round bottom flask with a stir bar. The cuvette was then sealed with a Teflon-lined septum cap, and the round bottom flask was sealed with a rubber septum secured with a copper wire. The two reaction vessels were removed from the glove box and the solution in the quartz cuvette was irradiated with UV light (λ_{irr} = 313 nm) with stirring for 1 h, while the solution in the round bottom flask was stirred under ambient light. After 1 h, 63 µL (0.4 mmol) of *n*-octane (internal standard) was added to each vessel via a N_2 purged syringe, followed by 33.5 µL (0.4 mmol) of ethyl acetate and 24 µL (0.4 mmol) of 2-aminoethanol. The reaction in the cuvette was kept under UV light for the first 2 h, while the reaction in the round bottom flask was kept under ambient light throughout the course of the reaction. Aliquots were removed after given amounts of time, diluted into wet methanol to quench the reaction and analyzed by GC. 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 amounts of time.

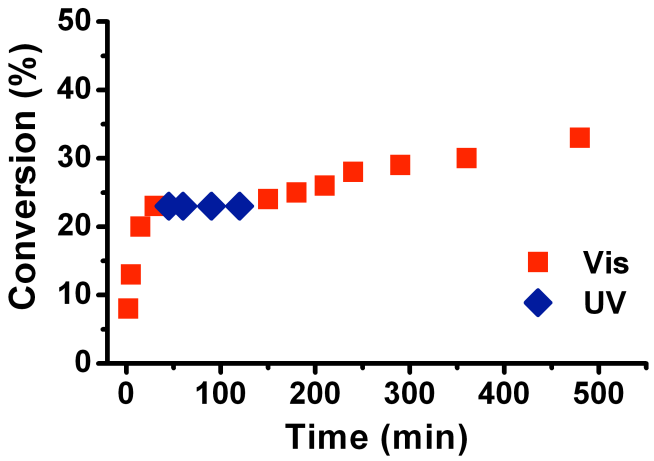


Figure S1. Plot of reaction conversion versus time for the condensation of ethyl acetate and 2-aminoethanol catalyzed by **1** (prepared in situ from **1·HPF$_6$** and 0.9 equiv. of NaHMDS) in 3:1 C_6H_6 : THF (v/v). The reaction was monitored over time by GC using *n*-octane as an internal standard. A single reaction was set up, allowed to react under ambient light for 30 min (■), then exposed to UV light (◆) (λ_{irr} = 313 nm) for 30 min and finally kept in the dark for 1 h prior to exposure to visible light (λ_{irr} > 500 nm) (■).

2nd Order Kinetic Analyses:

The condensation reactions between allyl alcohol and vinyl acetate or between ethyl acetate and aminoethanol may be represented as:

$$A + B \longrightarrow P$$

Assuming no side reactions, the two reactants will always be present in equimolar quantities. As such, the above equation may be simplified to:

$$2A \longrightarrow P$$

The above equation may be expressed as the following rate law:

$$\frac{d[P]}{dt} = k[A]^2$$

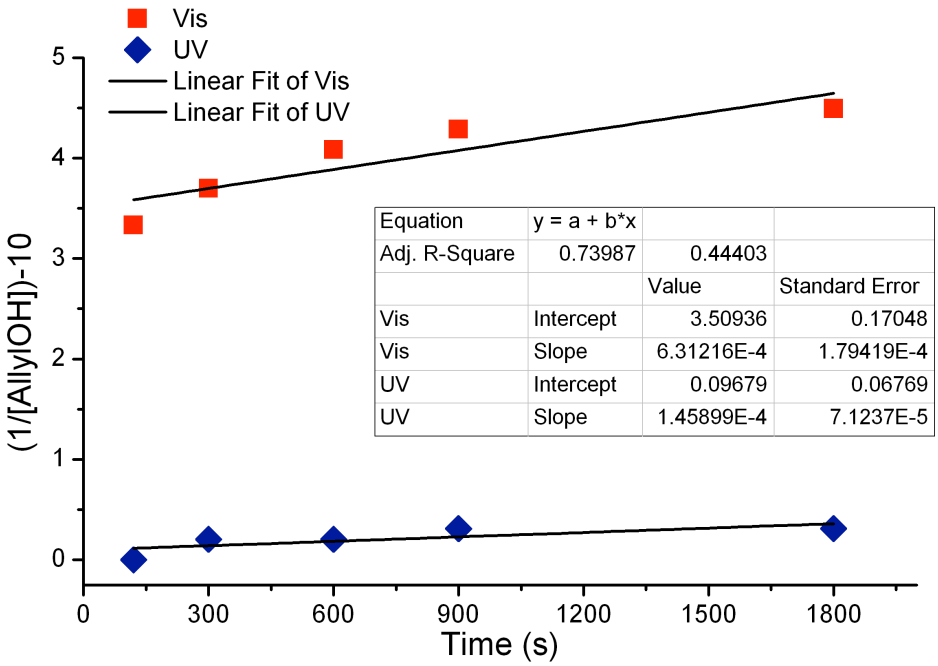
The integrated form of the above equation is as follows:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Rearranging the integrated rate law and substituting the initial concentration of 0.1 M for $[A]_0$ gives:

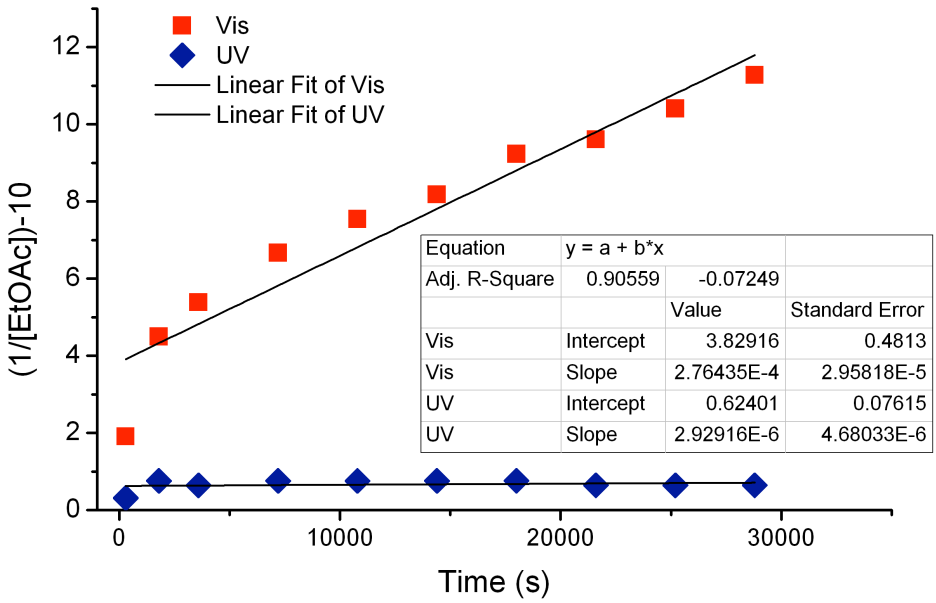
$$\frac{1}{[A]} - 10 = kt$$

Thus, plotting (1/[A]-10) (M) vs. *t* (s) should give a linear plot where *k* is equal to the slope of the line, as shown below in Figures S2 – S4 for selected examples. Each reported rate constant (k_{vis}, k_{UV}, k) was obtained from the average of at least three separate experiments.



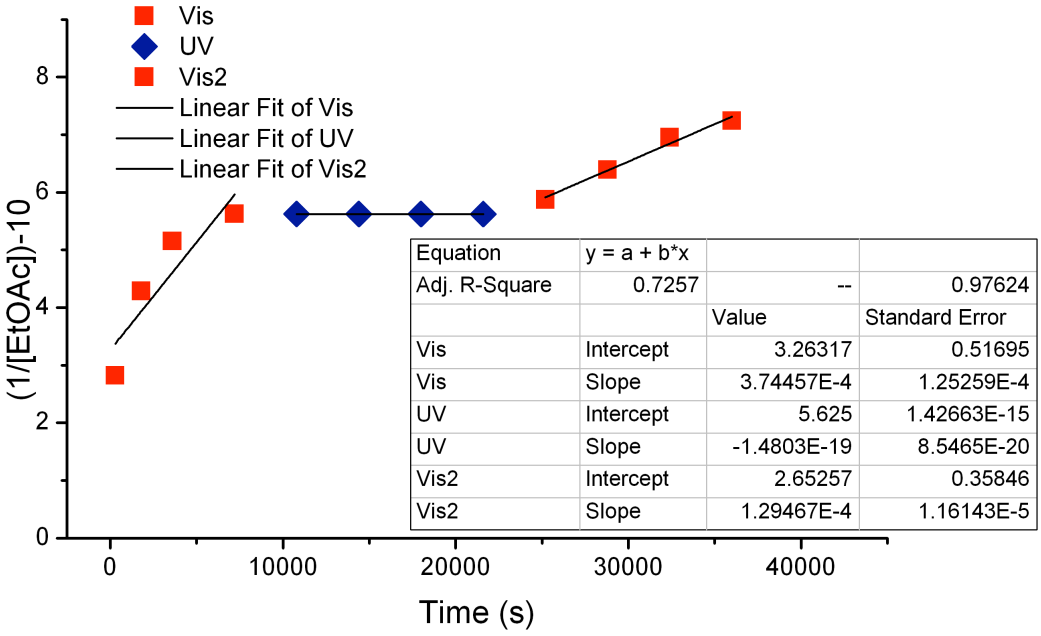
Equation	y = a + b*x		
Adj. R-Square	0.73987	0.44403	
		Value	Standard Error
Vis	Intercept	3.50936	0.17048
Vis	Slope	6.31216E-4	1.79419E-4
UV	Intercept	0.09679	0.06769
UV	Slope	1.45899E-4	7.1237E-5

Figure S2. Plot of (1/[allyl alcohol])-10 (M) vs. time (s) for the NHC catalyzed reaction between allyl alcohol and vinyl acetate. Two reactions were run concurrently with one exposed to UV light (λ_{irr} = 313 nm) for 1 h prior to substrate addition (♦) and one kept under ambient light (■).



Equation	y = a + b*x		
Adj. R-Square	0.90559	-0.07249	
		Value	Standard Error
Vis	Intercept	3.82916	0.4813
Vis	Slope	2.76435E-4	2.95818E-5
UV	Intercept	0.62401	0.07615
UV	Slope	2.92916E-6	4.68033E-6

Figure S3. Plot of (1/[ethyl acetate])-10 (M) vs. time (s) for the NHC catalyzed reaction between 2-aminoethanol and ethyl acetate. Two reactions were run concurrently with one exposed to UV light (λ_{irr} = 313 nm) for 1 h prior to substrate addition (♦) and one kept under ambient light (■).



Equation	y = a + b*x		
Adj. R-Square	0.7257	--	0.97624
		Value	Standard Error
Vis	Intercept	3.26317	0.51695
Vis	Slope	3.74457E-4	1.25259E-4
UV	Intercept	5.625	1.42663E-15
UV	Slope	-1.4803E-19	8.5465E-20
Vis2	Intercept	2.65257	0.35846
Vis2	Slope	1.29467E-4	1.16143E-5

Figure S4. Plot of (1/[ethyl acetate])-10 (M) vs. time (s) for the NHC catalyzed reaction between 2-aminoethanol and ethyl acetate. A single reaction was allowed to react under ambient light for 3 h (■), then irradiated with UV light (λ_{irr} = 313 nm) for 1 h and kept in the dark for a further 3 h (♦) prior to exposure to visible light (■) (λ_{irr} > 500 nm).

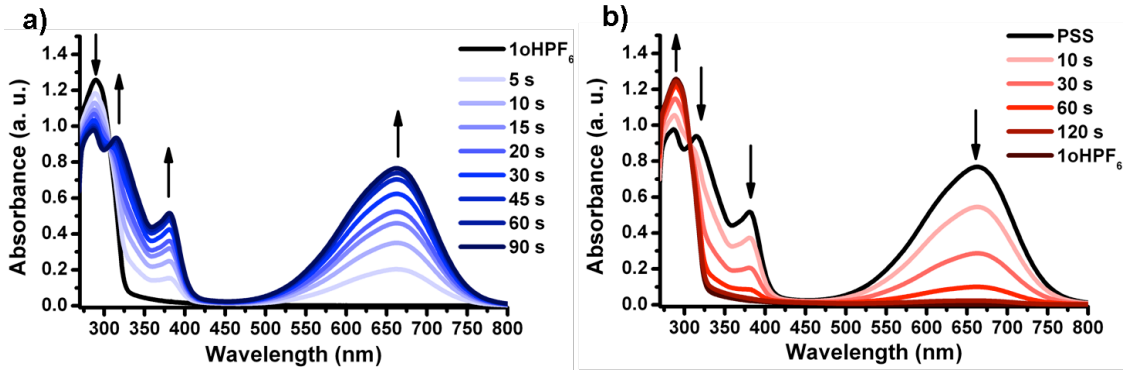


Figure S5. (a) UV-vis spectral changes of **1o·HPF$_6$** in acetonitrile ([**1o·HPF$_6$**]$_0$ = 4 × 10^{-5} M) upon UV irradiation (λ_{irr} = 313 nm) for 0, 5, 10, 15, 20, 30, 45, 60, and 90 s (indicated). (b) UV-vis spectra of **1o·HPF$_6$** in acetonitrile ([**1o·HPF$_6$**]$_0$ = 4 × 10^{-5} M), the photostationary state (PSS) reached after UV irradiation of **1o·HPF$_6$** for 90 s, and the spectral changes of the PSS upon visible irradiation (λ_{irr} > 500 nm) for 10, 30, 60, and 120 s (indicated). The arrows indicate the evolution of the spectral changes over time.

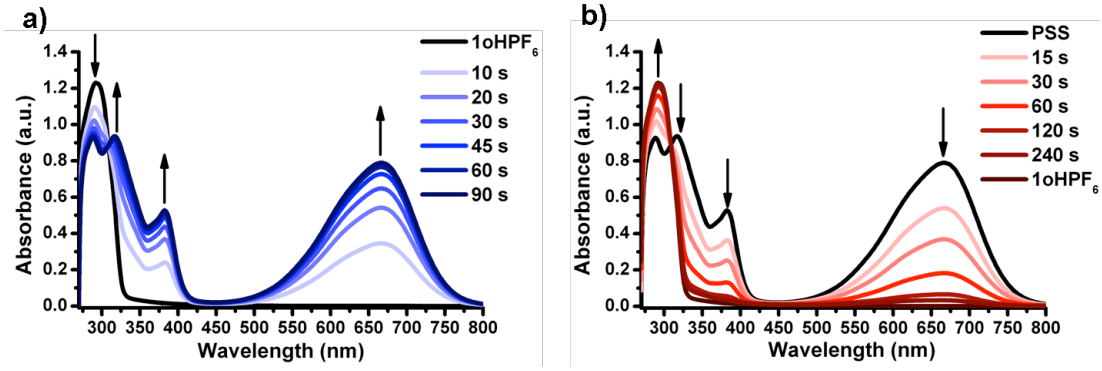


Figure S6. (a) UV-vis spectral changes of **1o·HPF$_6$** in THF ([**1o·HPF$_6$**]$_0$ = 4 × 10^{-5} M) upon UV irradiation (λ_{irr} = 313 nm) for 0, 10, 20, 30, 45, 60, and 90 s (indicated). (b) UV-vis spectra of **1o·HPF$_6$** in THF ([**1o·HPF$_6$**]$_0$ = 4 × 10^{-5} M), the photostationary state (PSS) reached after UV irradiation of **1o·HPF$_6$** for 90 s, and spectral changes of the PSS upon visible irradiation (λ_{irr} > 500 nm) for 15, 30, 60, 120, and 240 s (indicated). The arrows indicate the evolution of the spectral changes over time.

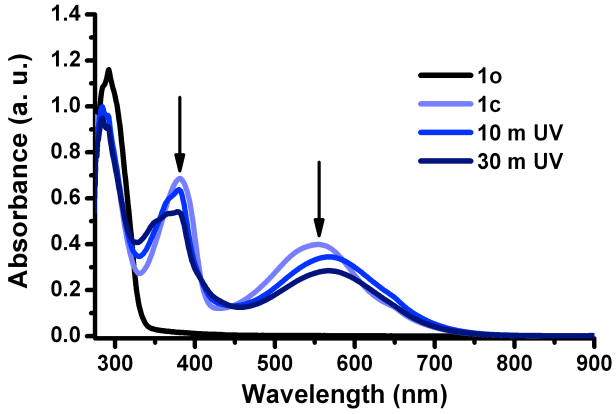


Figure S7. UV-vis spectra of **1o**, **1c**, and the spectral changes of **1c** upon prolonged UV irradiation (λ_{irr} = 313 nm) in benzene ([**1o**]$_0$ = 4 × 10^{-5} M). The spectra were recorded after irradiation for 0 (**1o**), 2 (**1c**), 10 and 30 min (indicated).

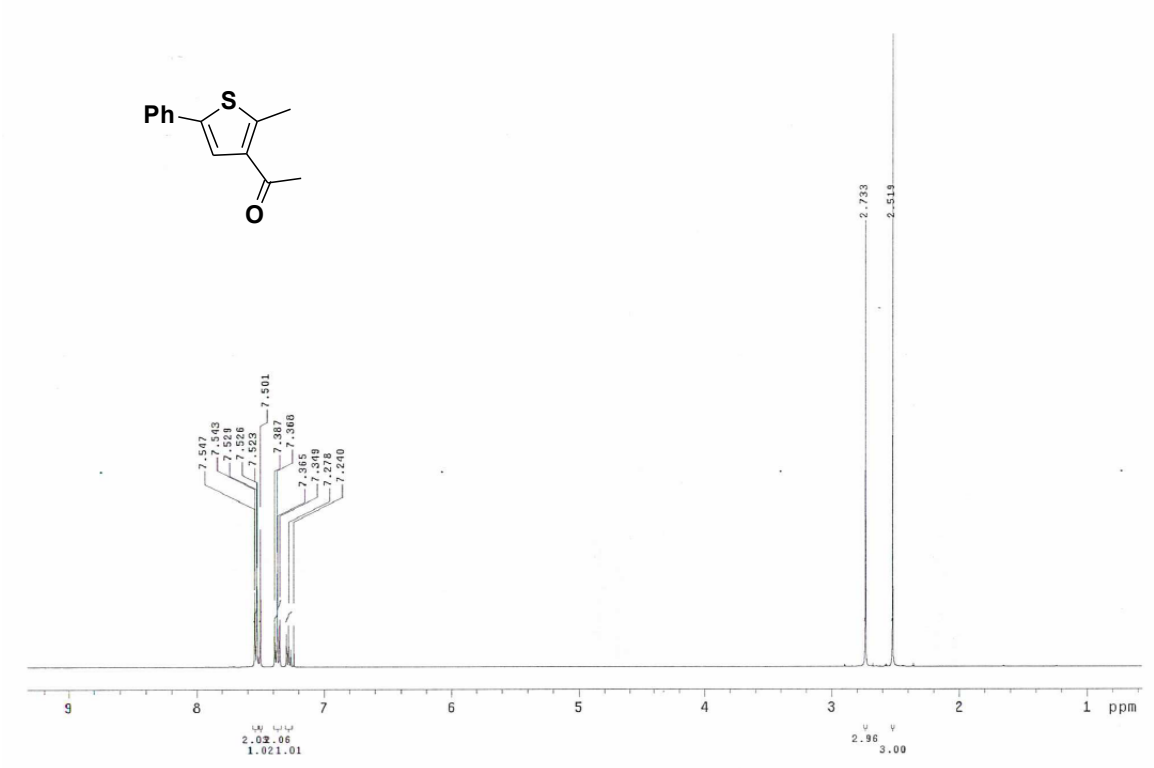


Figure S8. ^{1}H NMR spectrum of **2** ($CDCl_3$).

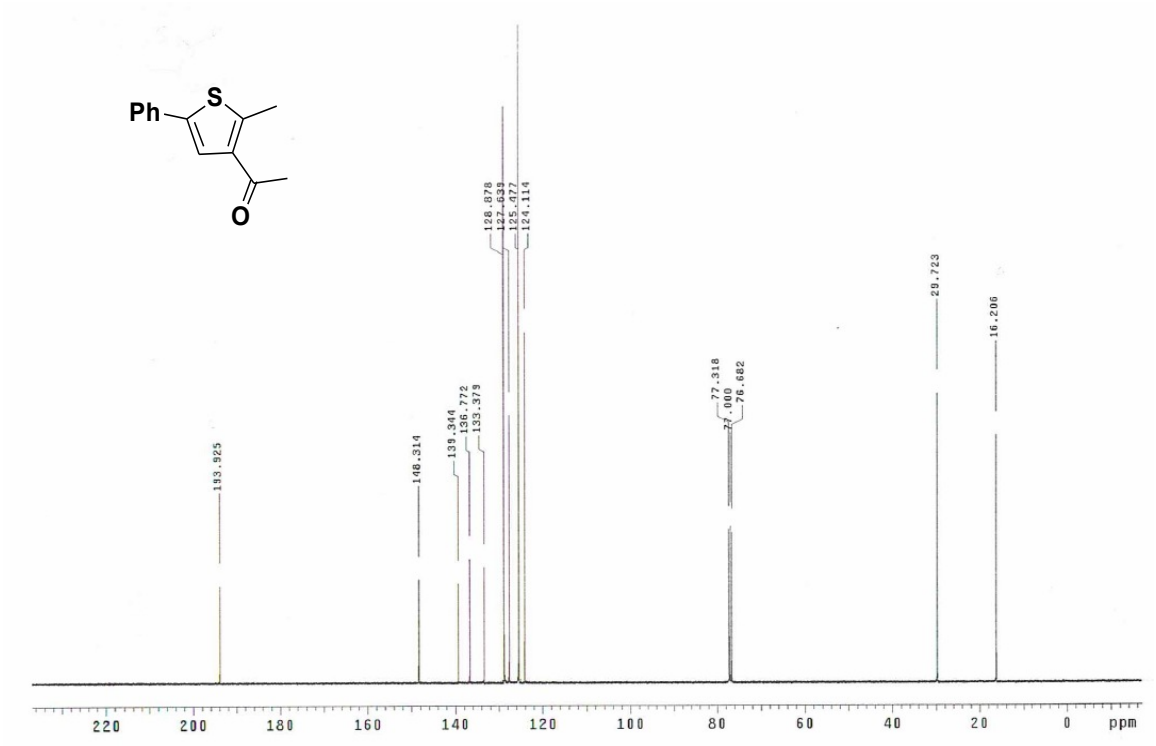


Figure S9. ^{13}C NMR spectrum of **2** ($CDCl_3$).

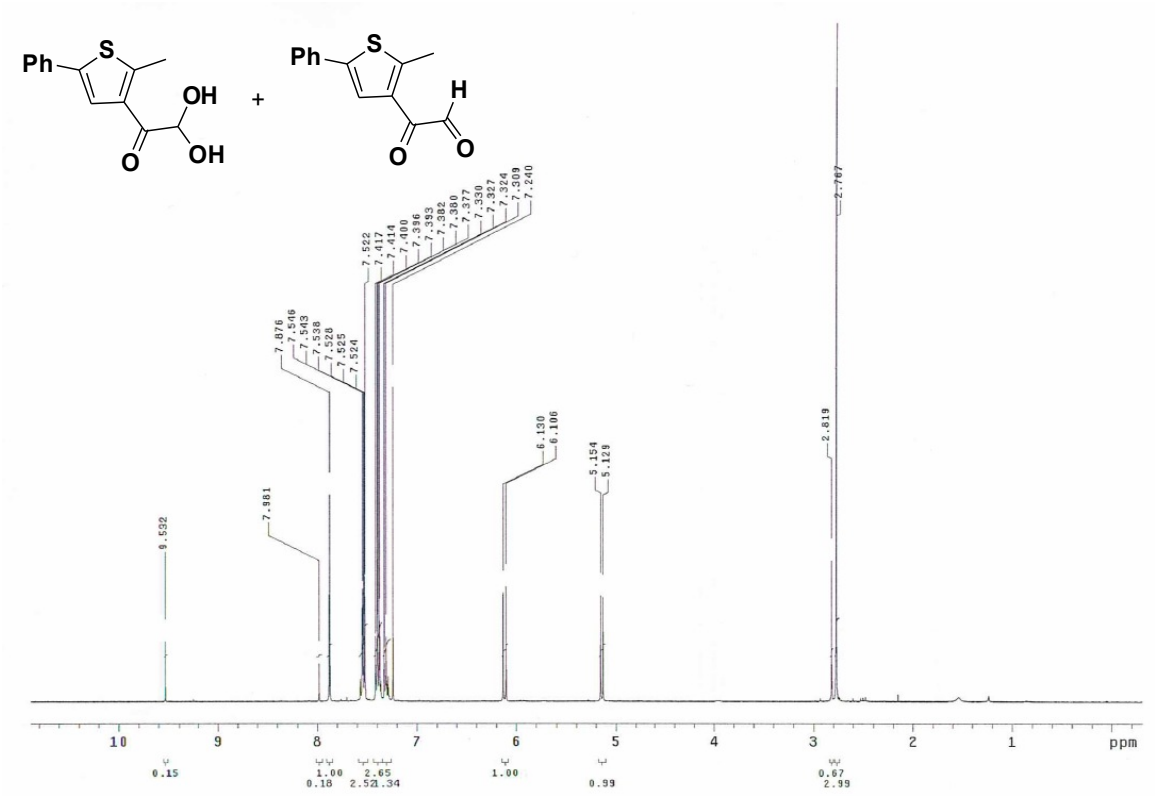


Figure S10. ^{1}H NMR spectrum of **3** ($CDCl_3$).

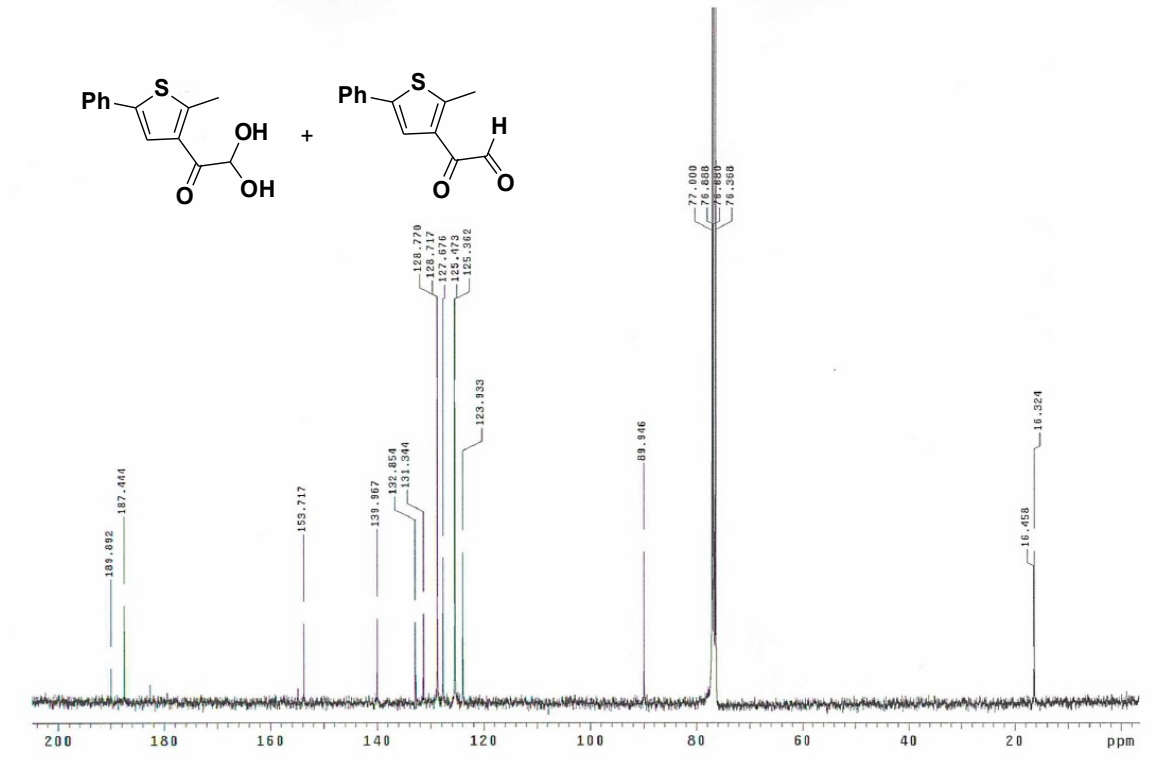


Figure S11. ^{13}C NMR spectrum of **3** ($CDCl_3$).

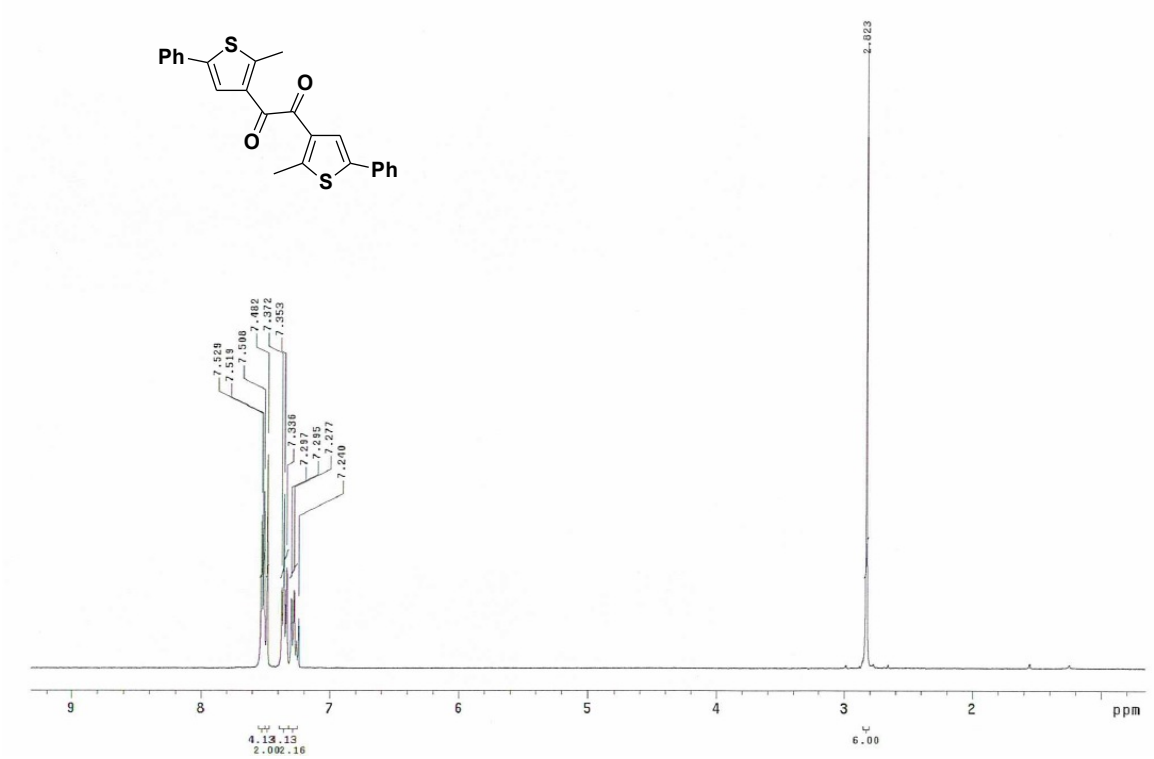


Figure S12. ^{1}H NMR spectrum of **5** ($CDCl_3$).

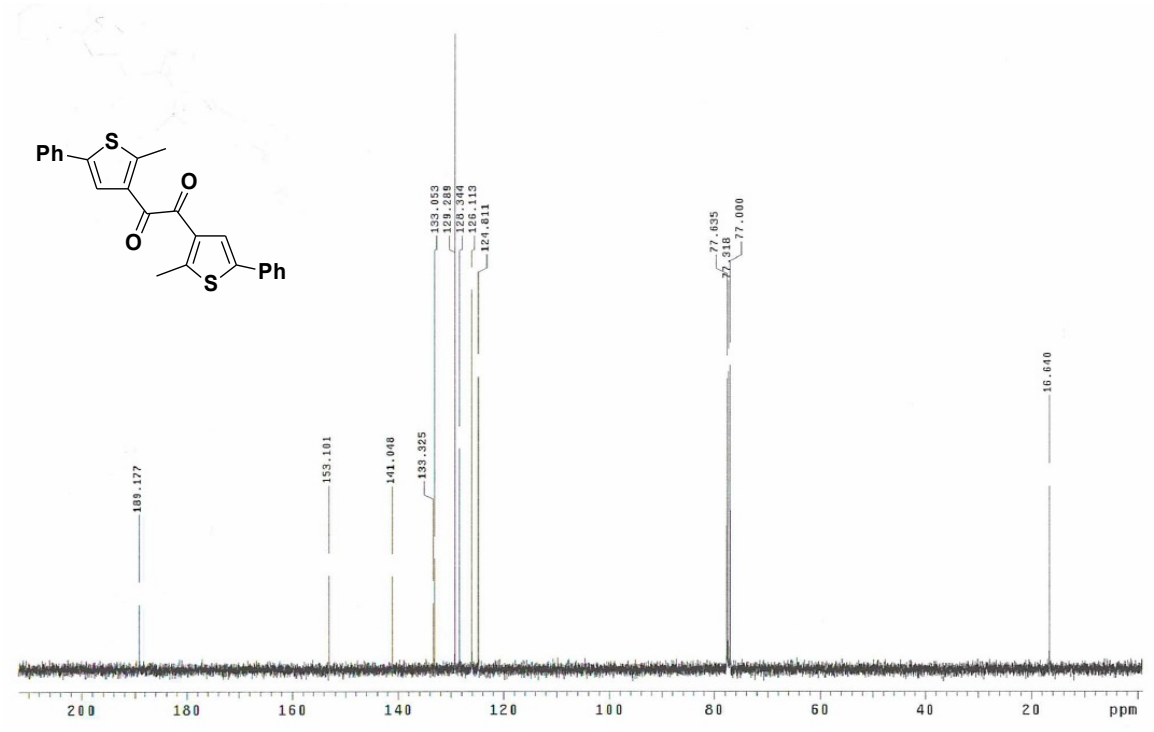


Figure S13. ^{13}C NMR spectrum of **5** ($CDCl_3$).

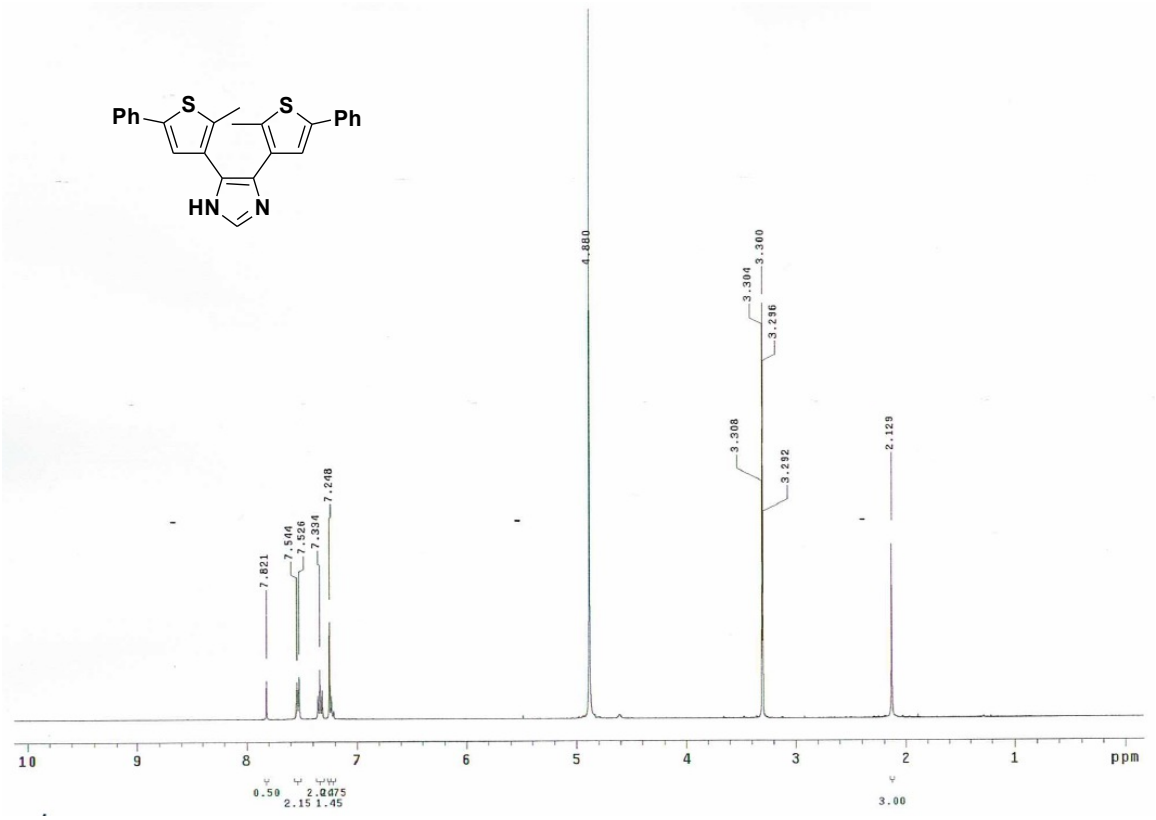


Figure S14. ^{1}H NMR spectrum of **6** (CD_3OD).

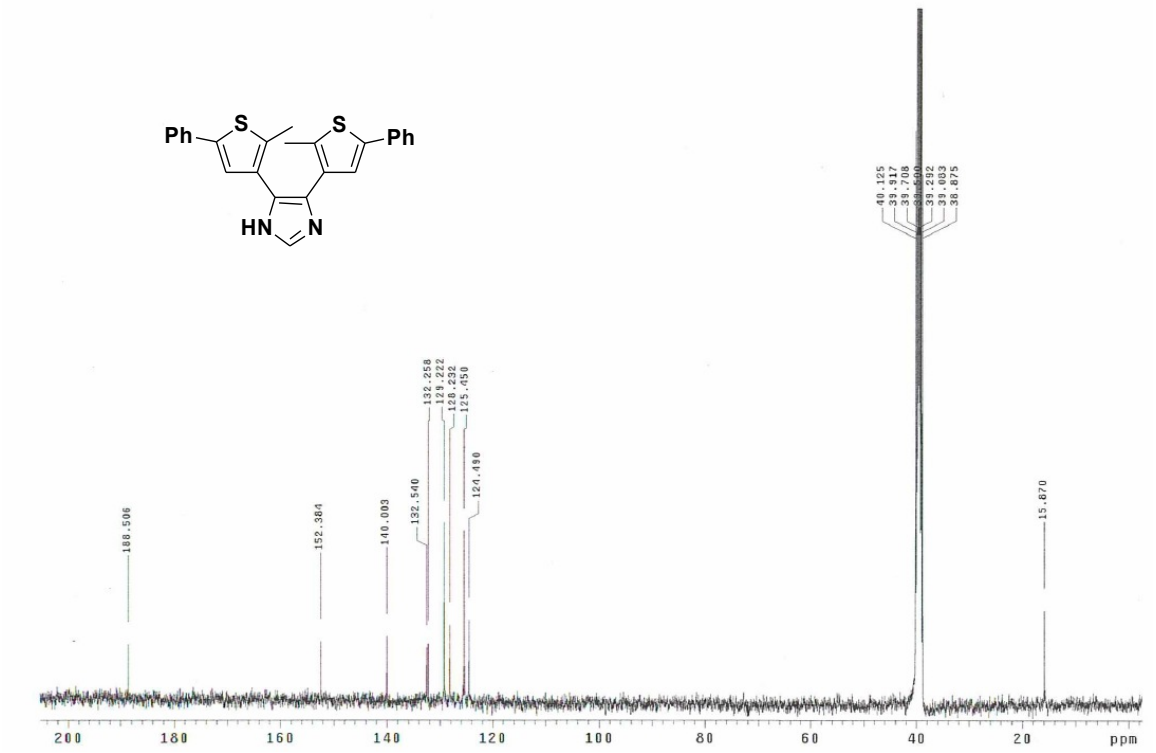


Figure S15. ^{13}C NMR spectrum of **6** ($(CD_3)_2SO$).

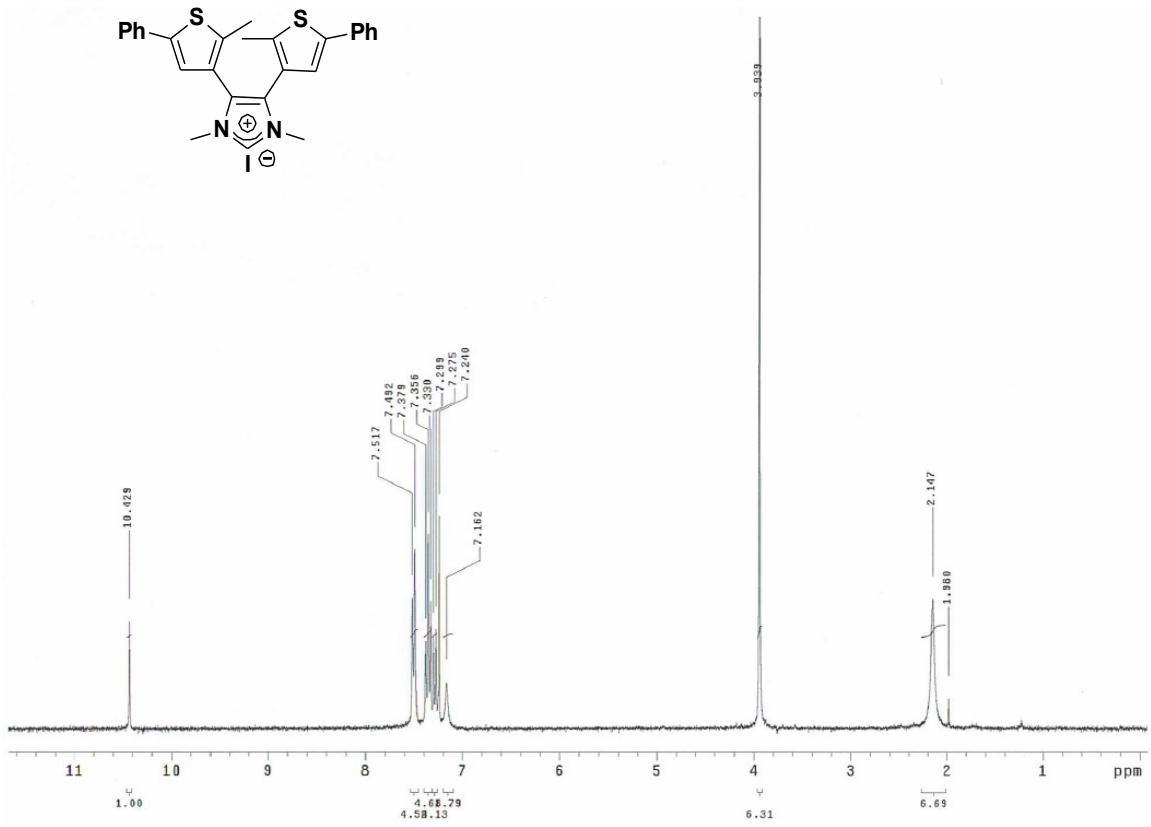


Figure S16. ^{1}H NMR spectrum of **7** ($CDCl_3$).

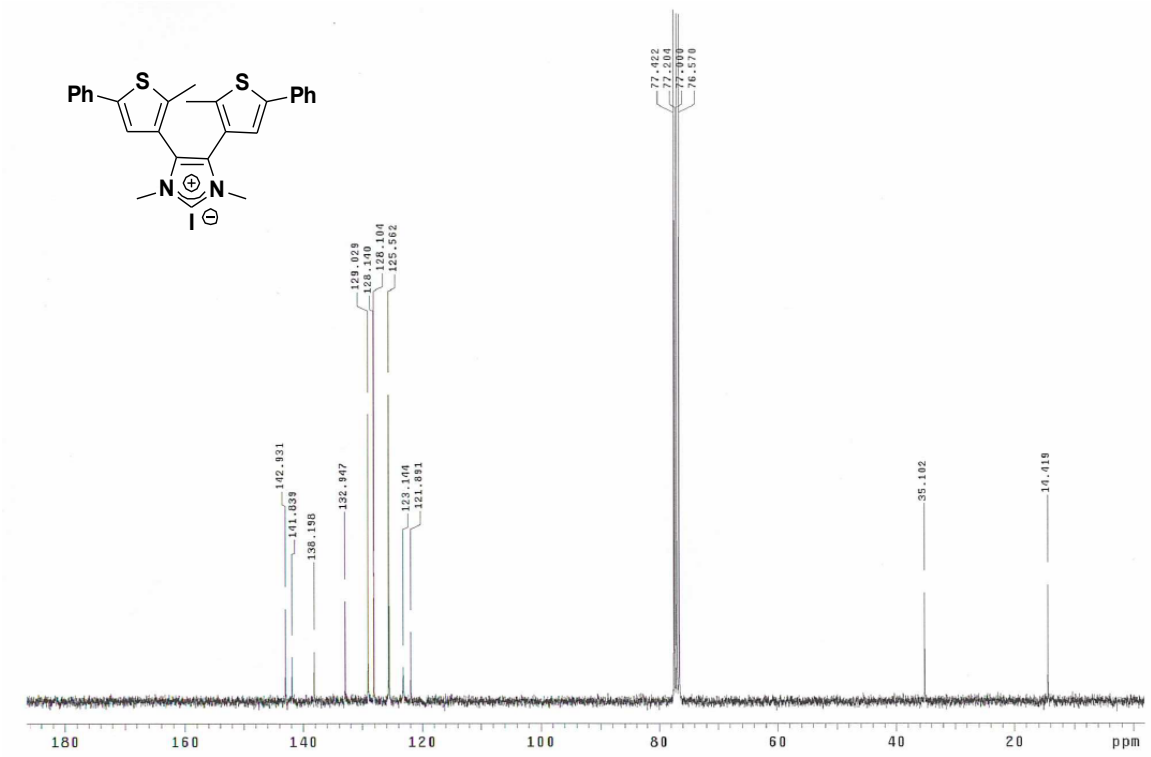


Figure S17. ^{13}C NMR spectrum of **7** ($CDCl_3$).

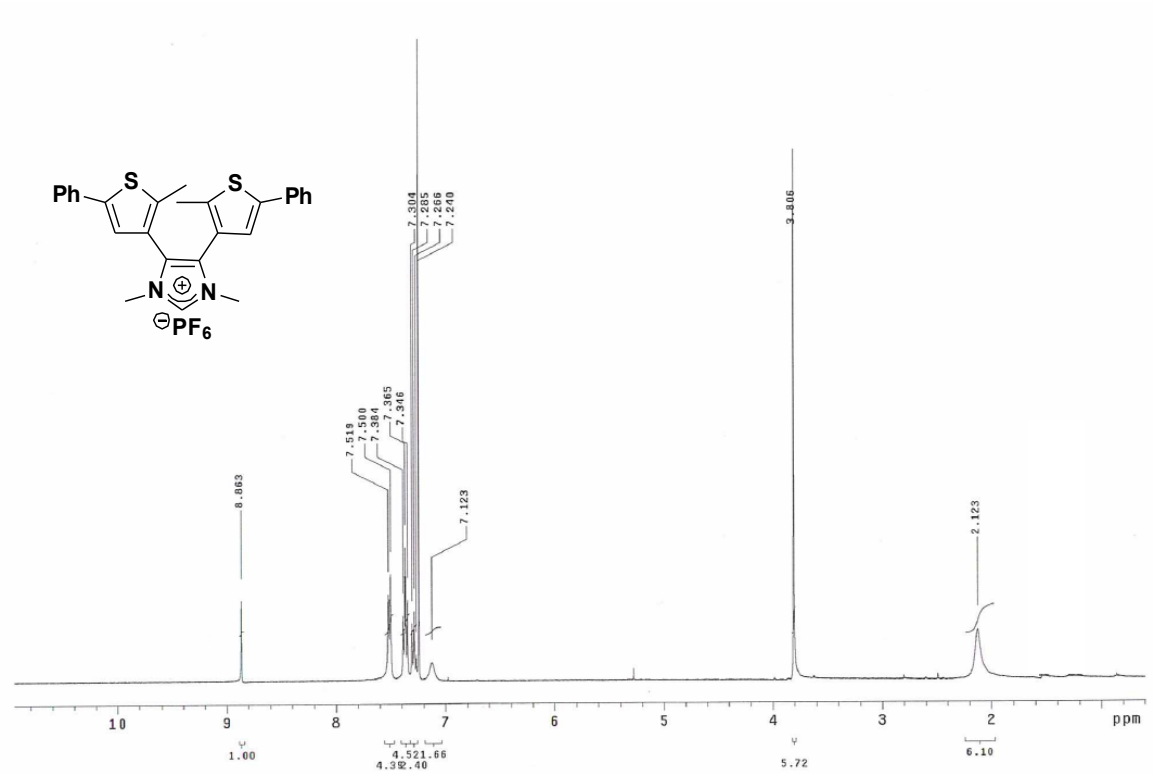


Figure S18. ^{1}H NMR spectrum of **1o•HPF$_6$** ($CDCl_3$).

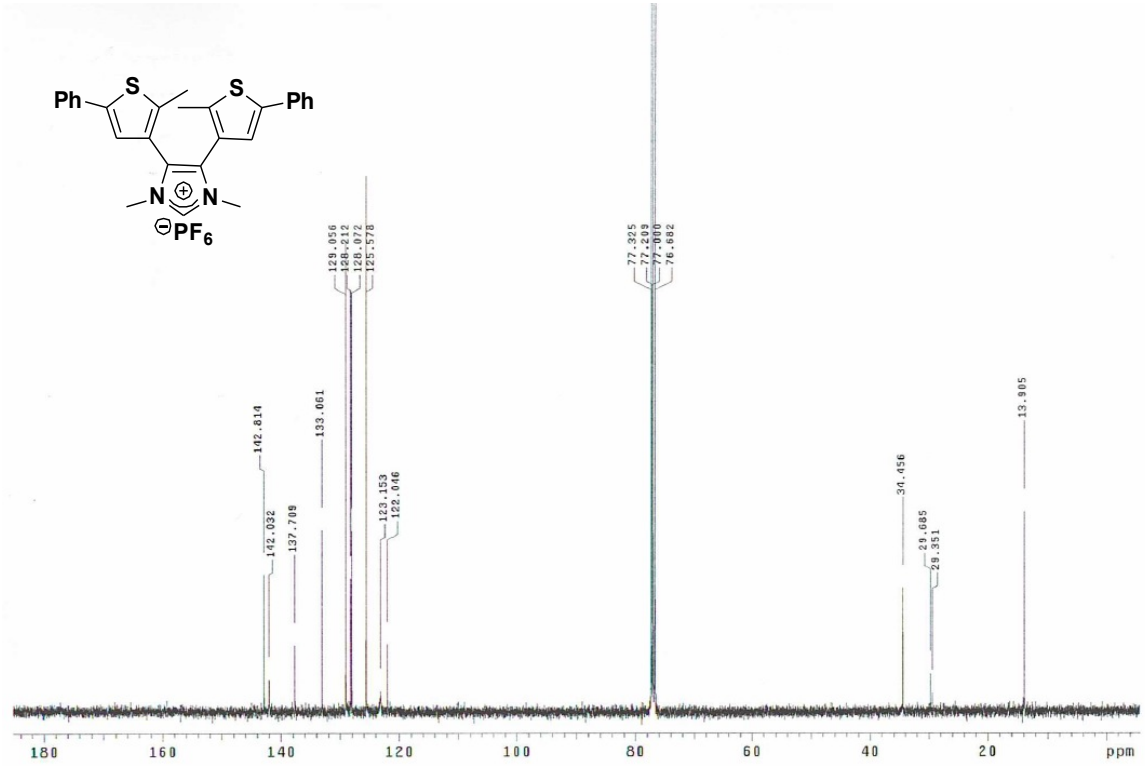


Figure S19. ^{13}C NMR spectrum of **1o•HPF$_6$** ($CDCl_3$).

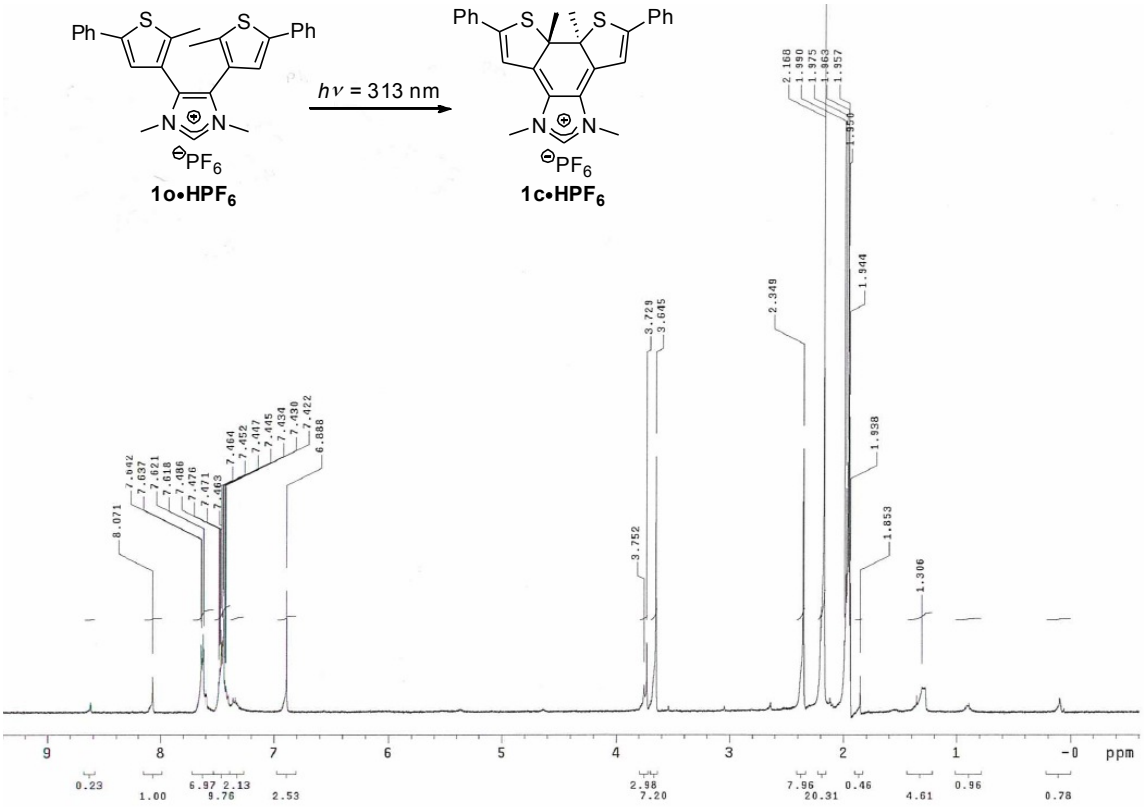


Figure S20. ^{1}H NMR spectrum of the mixture of **1o•HPF$_6$** and **1c•HPF$_6$** obtained after the irradiation of **1o•HPF$_6$** ([**1o•HPF$_6$**]$_0$ = 1 × 10^{-3} M) for 45 min (λ_{irr} = 313 nm) (CD_3CN).

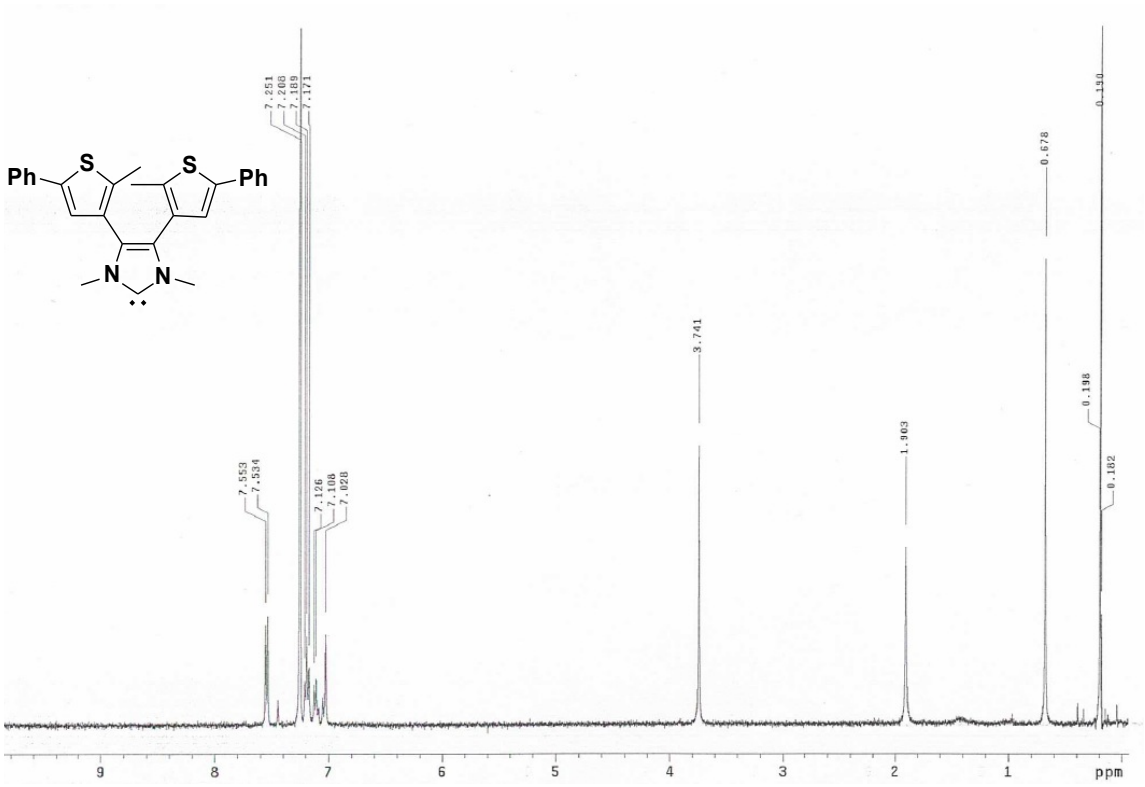


Figure S21. ^{1}H NMR spectrum of **1o** (C_6D_6).

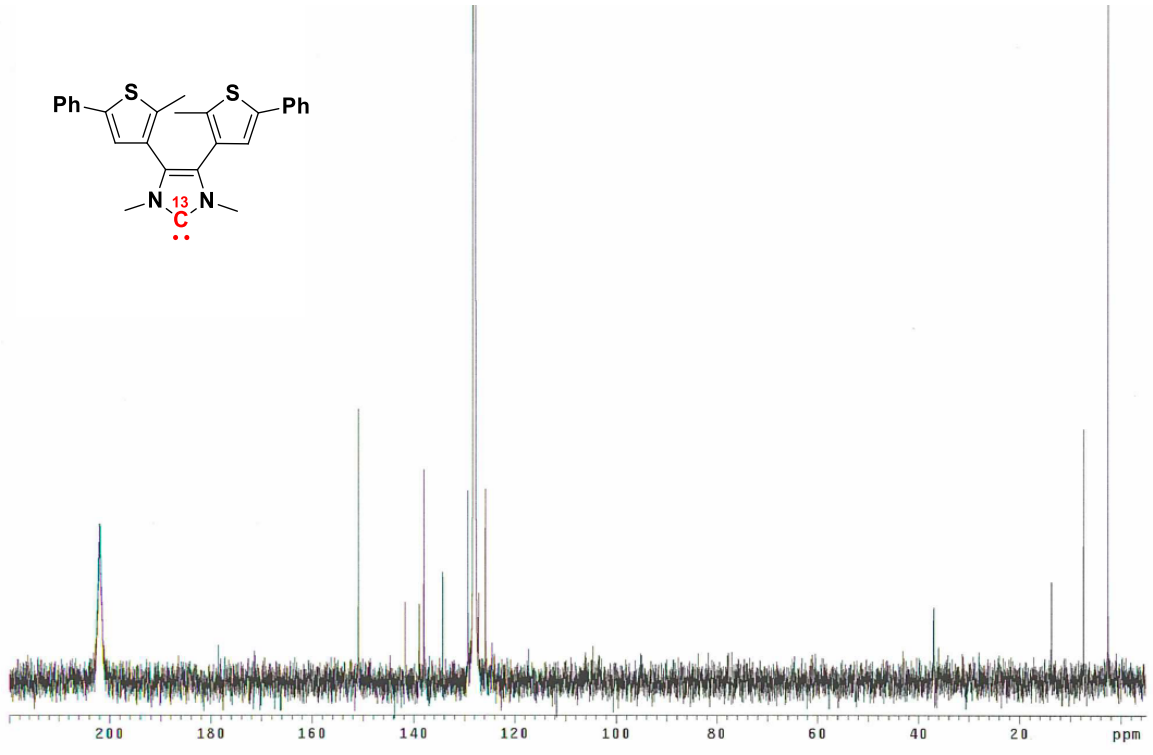


Figure S22. ^{13}C NMR spectrum of **1o*** (C_6D_6).

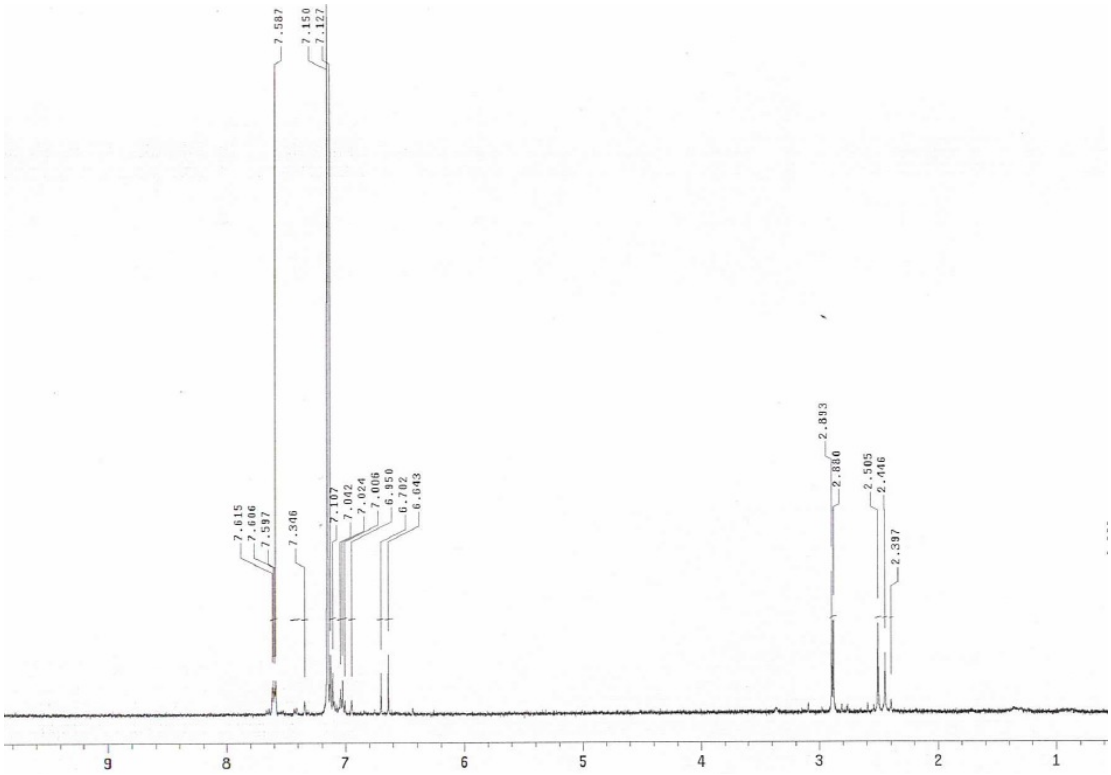


Figure S23. ^{1}H NMR spectrum of the mixture of **1o** and **1c** obtained after the irradiation of **1o** ($[\mathbf{1o}]_0 = 1 \times 10^{-3}$ M) for 1 h in C_6D_6 (λ_{irr} = 313 nm).

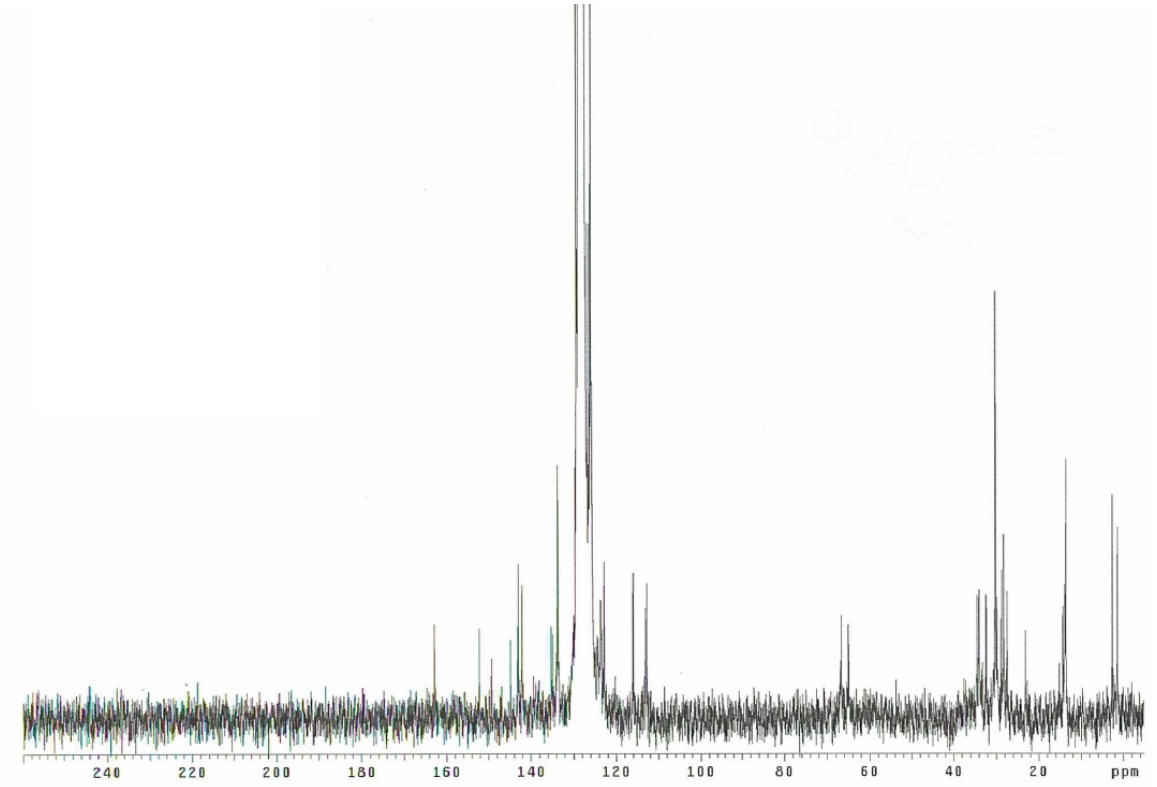


Figure S24. ^{13}C NMR spectrum of the mixture of **1o** and **1c** obtained after the irradiation of **1o** ($[\mathbf{1o}]_0 = 1 \times 10^{-3}$ M) for 1 h in C_6D_6 (λ_{irr} = 313 nm).

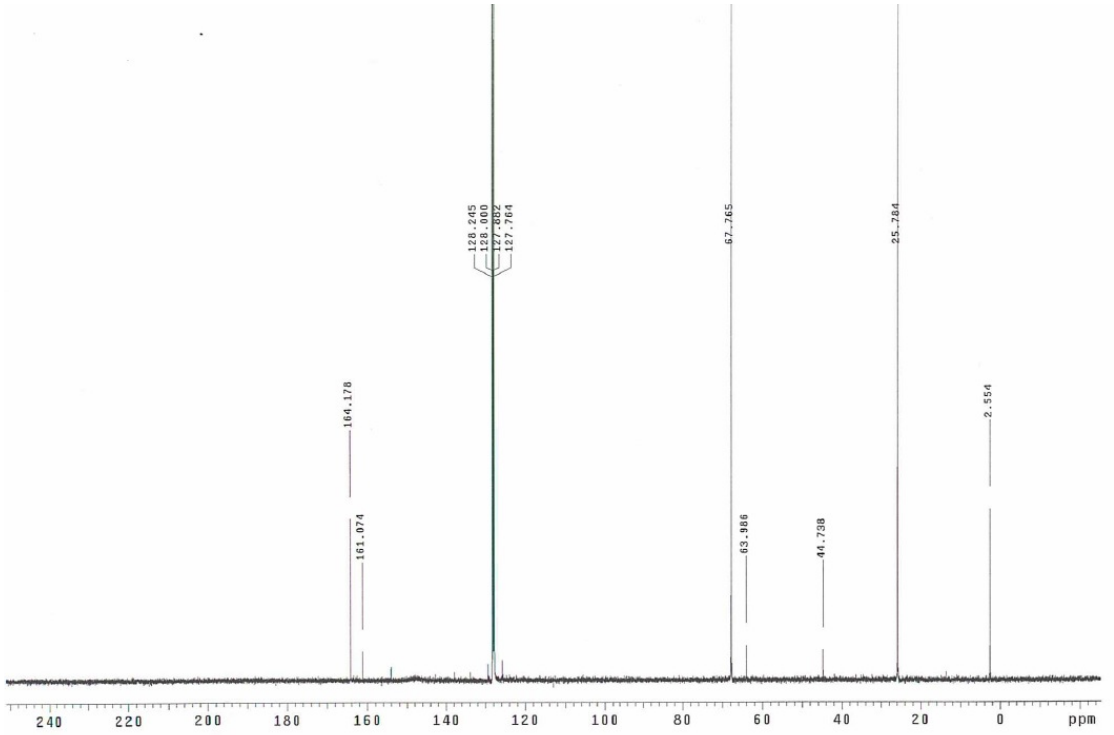


Figure S25. ^{13}C NMR spectrum of the adduct obtained after the addition of one equivalent of 2-aminoethanol to **1o*** (2.5% v/v THF in C_6D_6).

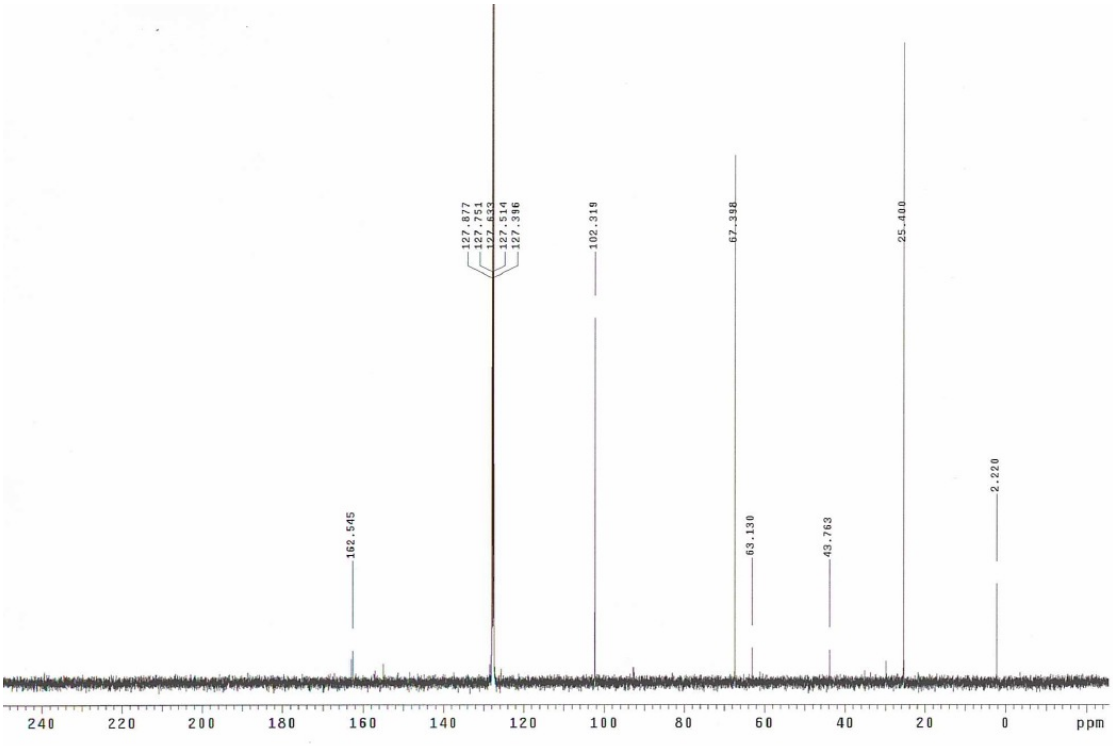


Figure S26. ^{13}C NMR spectrum of the adduct obtained after the addition of one equivalent of 2-aminoethanol to **1o*** and subsequent irradiation ([**1o***]$_0$ = 1 × 10^{-3} M) for 1 h (λ_{irr} = 313 nm) (2.5% v/v THF in C_6D_6).

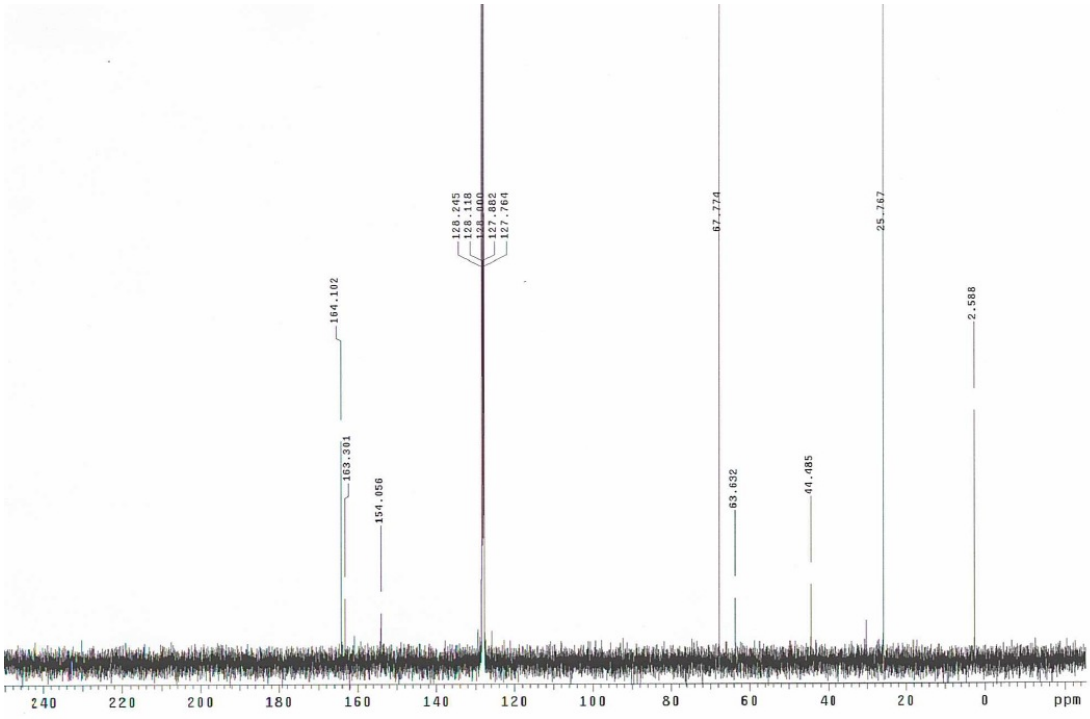


Figure S27. ^{13}C NMR spectrum of the cycloreverted adduct of **1o*** in the presence of 1.0 equivalent of 2-aminoethanol obtained after UV irradiation ([**1o***]$_0$ = 1 × 10^{-3} M) for 1 h (λ_{irr} = 313 nm) followed by visible light irradiation for 2 h (λ_{irr} > 500 nm) (2.5% v/v THF in C_6D_6).

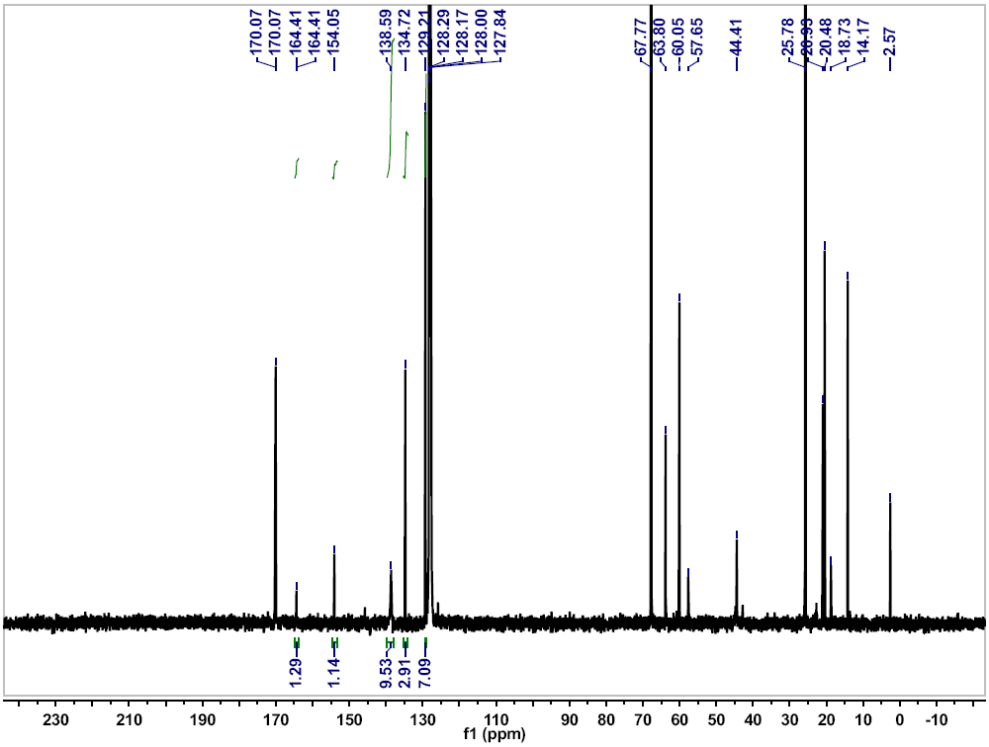


Figure S28. Quantitative ^{13}C NMR spectrum of the adduct obtained after the addition of 2-aminoethanol (0.4 mmol) and ethyl acetate (0.4 mmol) to **1o*** ([**1o***]$_0$ = 0.01 mmol) with *p*-xylene (0.08 mmol) added as an internal standard (2% v/v THF in C_6D_6).

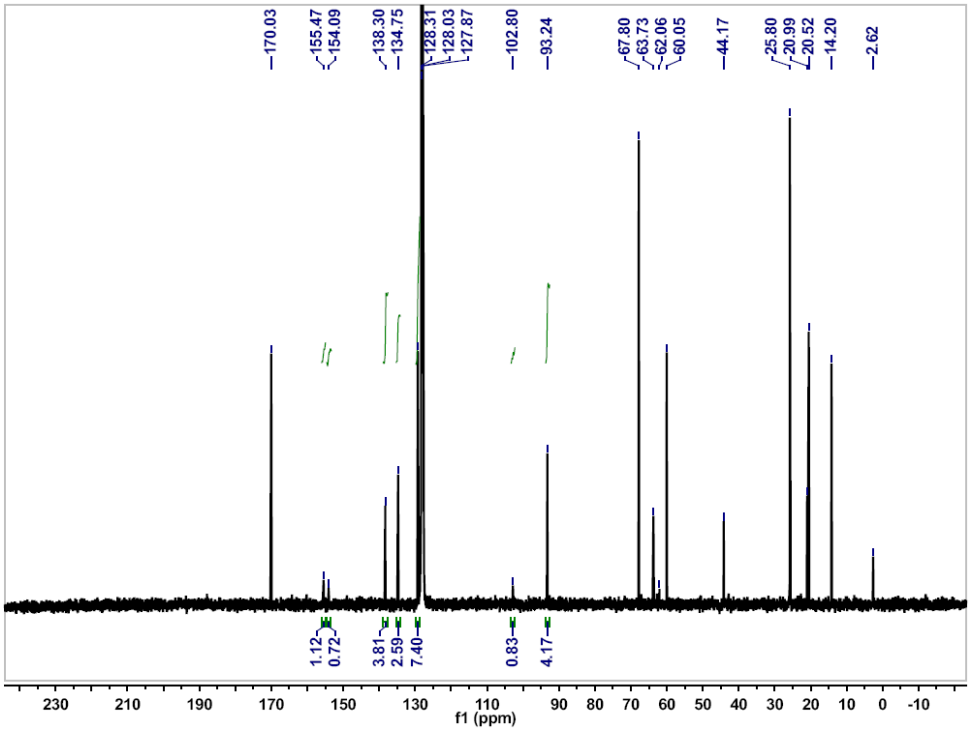


Figure S29. Quantitative ^{13}C NMR spectrum of the adduct obtained after the addition of 2-aminoethanol (0.4 mmol) and ethyl acetate (0.4 mmol) to **1o*** ([**1o***]$_0$ = 0.01 mmol) and subsequent irradiation ([**1o***] = 1×10^{-3} M) for 1 h (λ_{irr} = 313 nm) with *p*-xylene (0.08 mmol) added as an internal standard (2% v/v THF in C_6D_6).

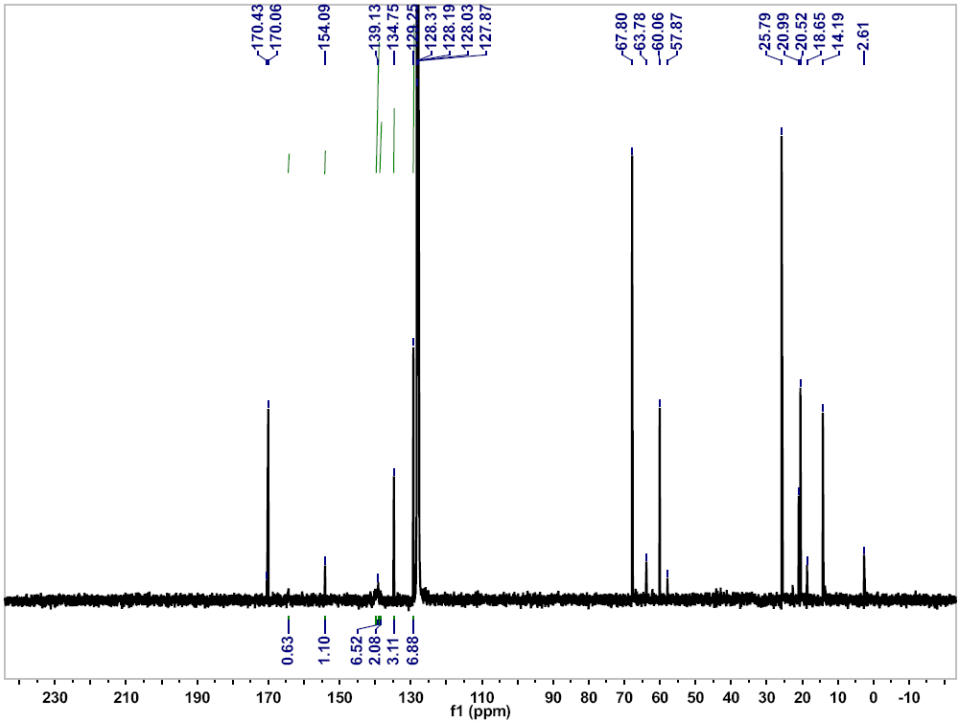


Figure S30. Quantitative ^{13}C NMR spectrum of the cycloreverted adduct of **1o*** in the presence of 2-aminoethanol (0.4 mmol) and ethyl acetate (0.4 mmol) obtained after UV irradiation of **1o*** ($[\mathbf{1o^*}]_0 = 1 \times 10^{-3}$ M) for 1 h (λ_{irr} = 313 nm) followed by visible light irradiation for 2 h (λ_{irr} > 500 nm) with *p*-xylene (0.08 mmol) as an internal standard (2% v/v THF : C_6D_6).

References

(1) Iwamoto, O.; Sugiyama, H.; Hara, T. Fulgimide Derivatives. U. S. Patent 5,359,085, October 25, 1994.

(2) Lemieux, V.; Spantulescu, M. D.; Baldridge, K. K.; Branda, N. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 5034.