Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Protonation of Silylenol Ether via Excited State Proton Transfer Catalysis

Anjan Das, Tanmay Banerjee, Kenneth Hanson*
Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, 32306, United States

Contents

Materials

2-Phenylcyclohexanone, 2-(3-Methoxyphenyl)cyclohexanone, 2-Bromocyclohexanone, 2-Methylcyclohexanone, 2-Benzylcyclohexanone, 2-Methyl-1-Indanone, lithium diisopropylamide (LDA), Trimethylsilylchloride, Triethylsilylchloride, Trisopropylsilylchloride, Triphenylsilylchloride, 2-napthol, 7-bromo-2-napthol, 2,6-Di-*tert*-butyl-4-methylphenol, *N*-Hydroxysuccinimide, Bis[2-(4,6-difluorophenyl)pyridinato-C^2,*N*](picolinato)iridium(III) and triphenylmethane were used as received from Sigma-Aldrich. 4-nitro-2-napthol[1] and the substrates were prepared according to a published literature procedure.[2-4]

Instrumentation

Absorption spectroscopy. The UV-visible spectra were recorded using an Agilent 8453 UV-Visible photo diode array spectrophotometer with a standard 1 cm x 1 cm cuvette.

Light Source. A ThorLabs M365L2- UV (366 nm, fwhm = 7.5 nm) mounted LED was used as the light source for UV ereactions and was controlled by ThorLabs LEDD1B T-Cube series LED driver. For the sensitized reactions a 445 nm laser from Aixiz (PGL-V-H-447) was used. The light intensity was measured using an Ophir power meter (Vega 7Z01560) and sensor (3A-FS 7Z02628).

^{1}H NMR. Proton nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm) relative to residual toluene peaks (7.09 (m), 7.00 (s), 6.98 (m), 2.09 (m) ppm).

Reaction set-up

All solutions for the photocatalytic reaction were prepared in 0.6 mL toluene-d_8 with NMR tubes (Norell® Select Series™ 5 mm glass NMR tubes medium wall, NORS5500MW7) as the reaction vessels. The samples were directly irradiated with the LED as shown in Figure S1.

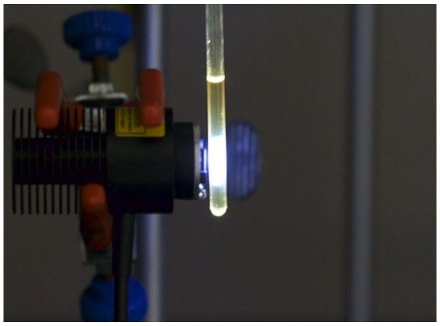


Figure S1. Photo of the photoreaction setup with a NMR tube directly irradiated with the 366 nm LED.

Calculation of reaction yields

Reaction yields were calculated using ^{1}H-NMR with triphenylmethane as the internal reference. Triphenylmethane and the substrate have been used in equimolar amounts. An example spectrum can be seen in Figure S6. The product yield (96 % in Figure S6) can be calculated by integration of the product 2-phenylcyclohexanone proton signal at 3.16 ppm (marked in blue) with the triphenylmethane proton signal at 5.4 ppm (marked in red) integrated to 1.

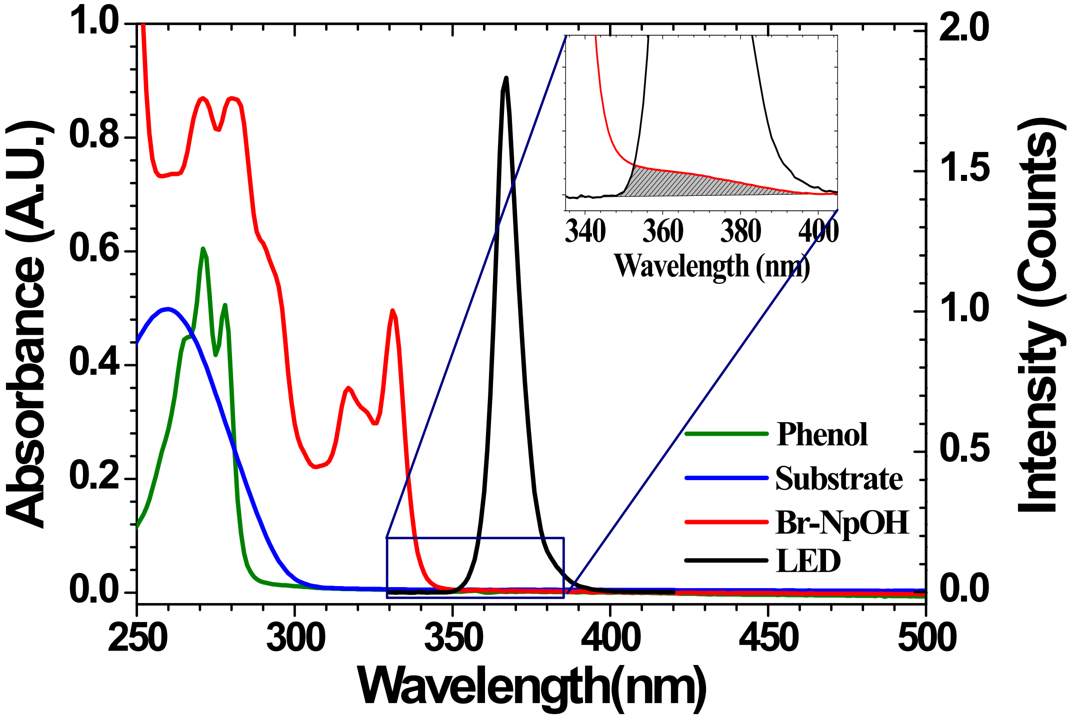


Figure S2. Absorption spectra of phenol, substrate and Br-NpOH in CH_2Cl_2 as well as the LED emission spectrum. Inset: a zoomed in spectrum emphasizing the spectral overlap between absorption spectrum of Br-NpOH and the LED emission spectrum.

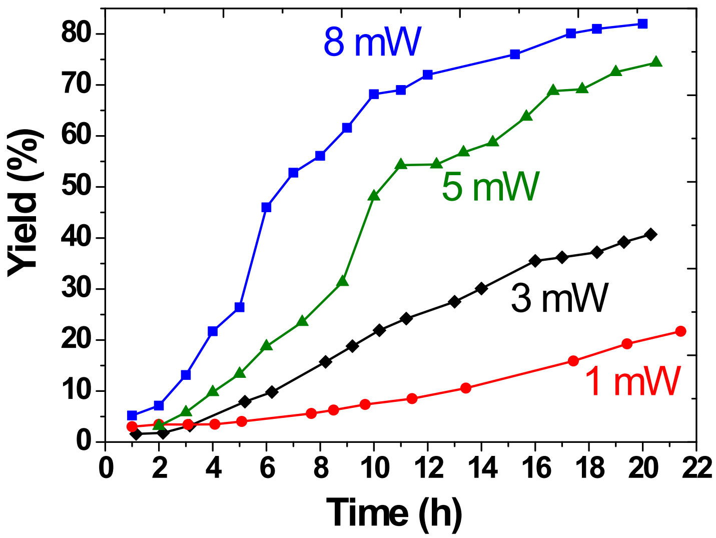


Figure S3. Light intensity dependence on the generation of 2-phenylcyclohexanone. (2.5 M substrate, 5 M PhOH and 0.025 M Br-NpOH in toluene-d_8)

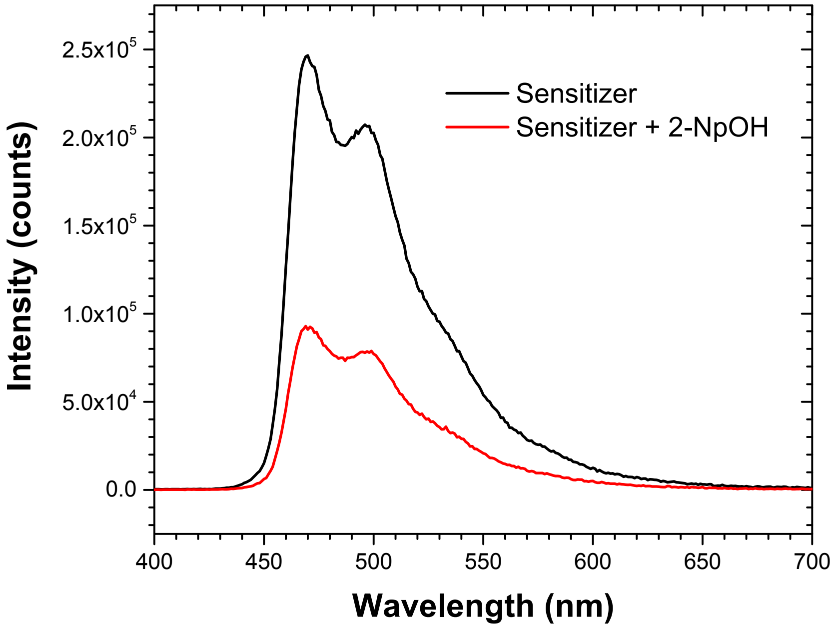


Figure S4. Emission spectra of bis(4,6-difluorophenyl-pyridine)(picolinate)iridium(III) without and with 25 equivalents of 2-napthol.

Table S1. Reaction conditions for the sensitized protonation of 1-phenyl-2-(trimethylsiloxy)cyclohexene in toluene-d_8.[a]

Entry	SENS (M)	Dye (M)	Sacrificial acid (M)	Yield (%)[b]
1	**1** (0.05)	2-NpOH (1)	-	35
2	**1** (0.05)	2-NpOH (1)	NHS (5)	72
3	**1** (0.1)	2-NpOH (1)	NHS (5)	73
4	**1** (0.025)	2-NpOH (1)	NHS (5)	74
5	**1** (0.025)	2-NpOH (0.5)	NHS (5)	38
6	**1** (0.025)	2-NpOH (1)	Phenol (5)	0
7	**1** (0.025)	2-NpOH (1)	BHT (5)	35
8	**1** (0.025)	-	NHS (5)	0

[a]All the reactions were carried out with 2 (M) of the substrate and the reaction mixtures were N_2 deaerated for 30 min before excitation with 445 nm light. [b] Calculated by using ^{1}HNMR using internal reference after 20 h.

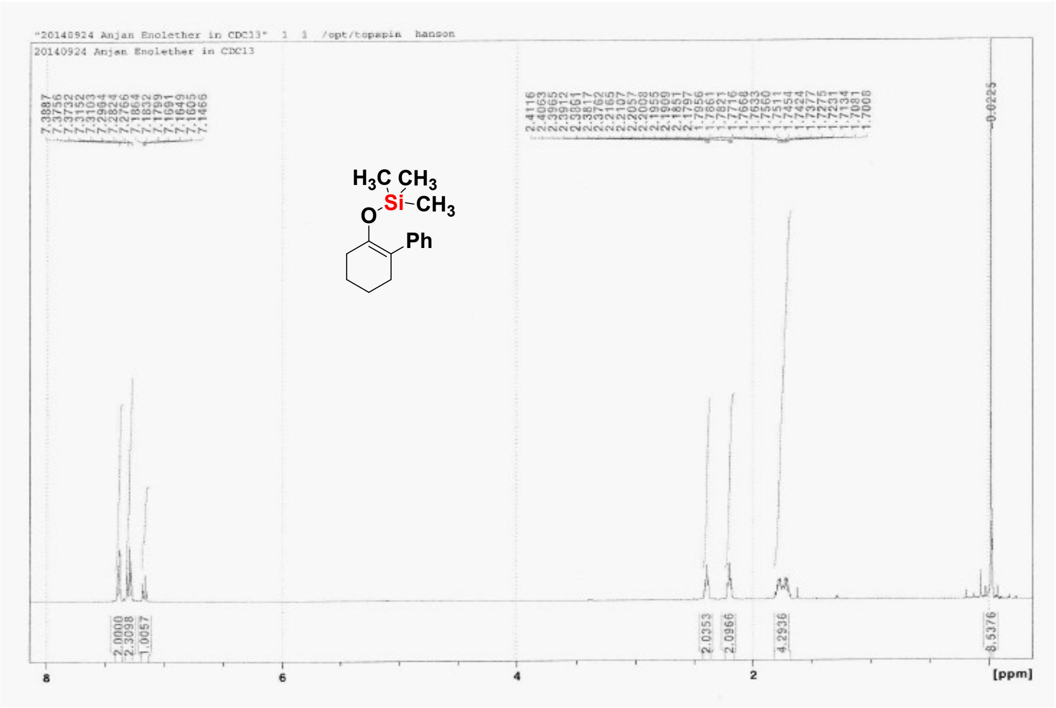


Figure S5. ^{1}H-NMR spectra of 1-phenyl-2-(trimethylsiloxy)cyclohexene.

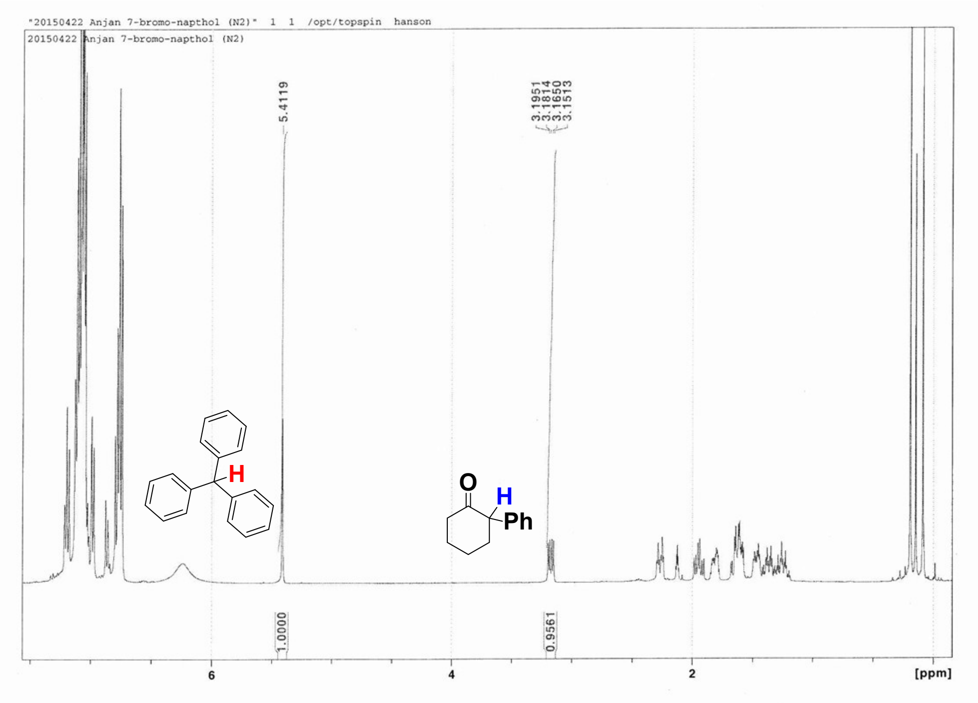


Figure S6. Example of reaction yield measurements using ^{1}H-NMR spectra with triphenylmethane as the internal reference.

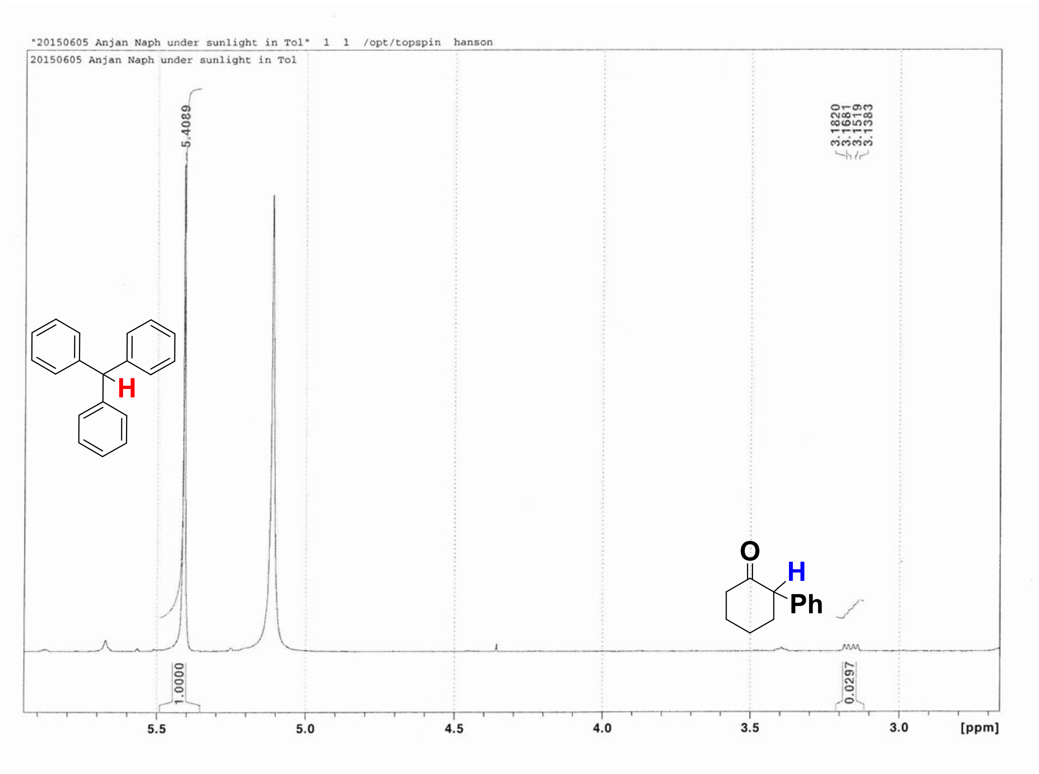


Figure S7. ^{1}H-NMR spectra of the reaction mixture after 3 days in a window with exposure to ambient sunlight (Tallahassee, Florida; June 3-5).

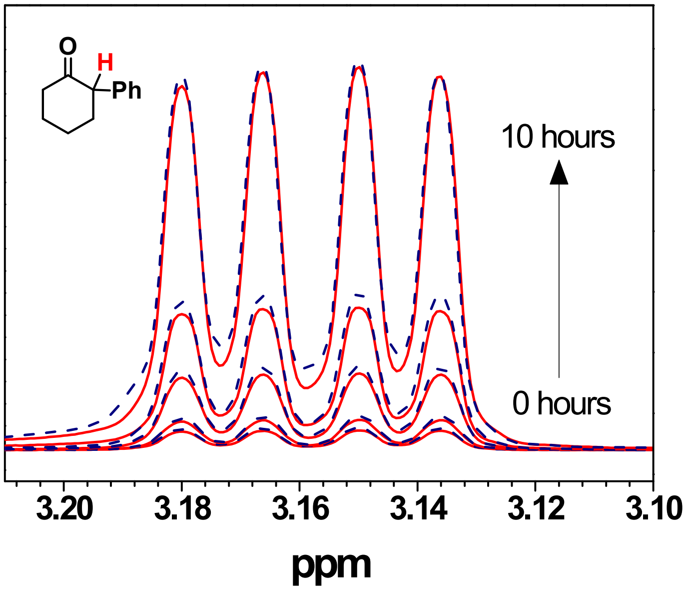
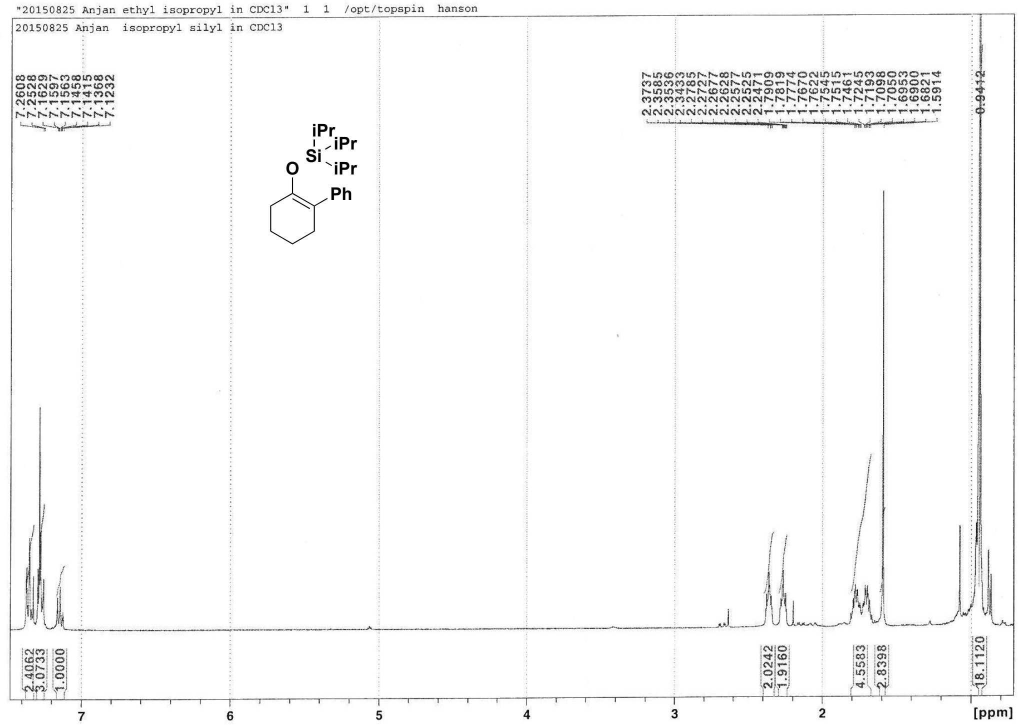
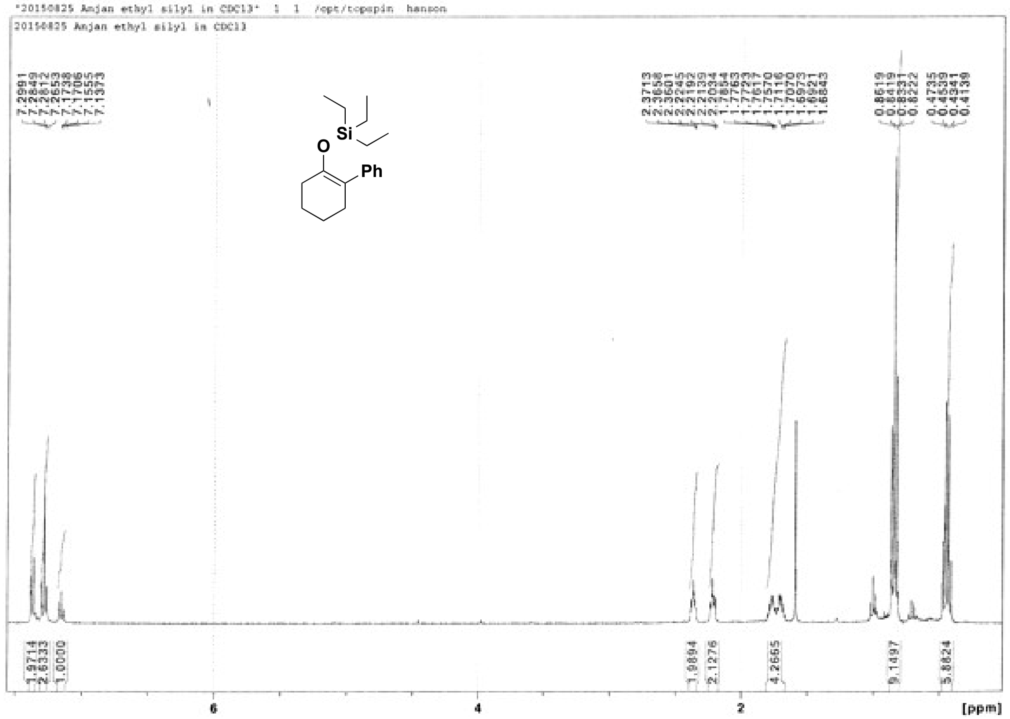
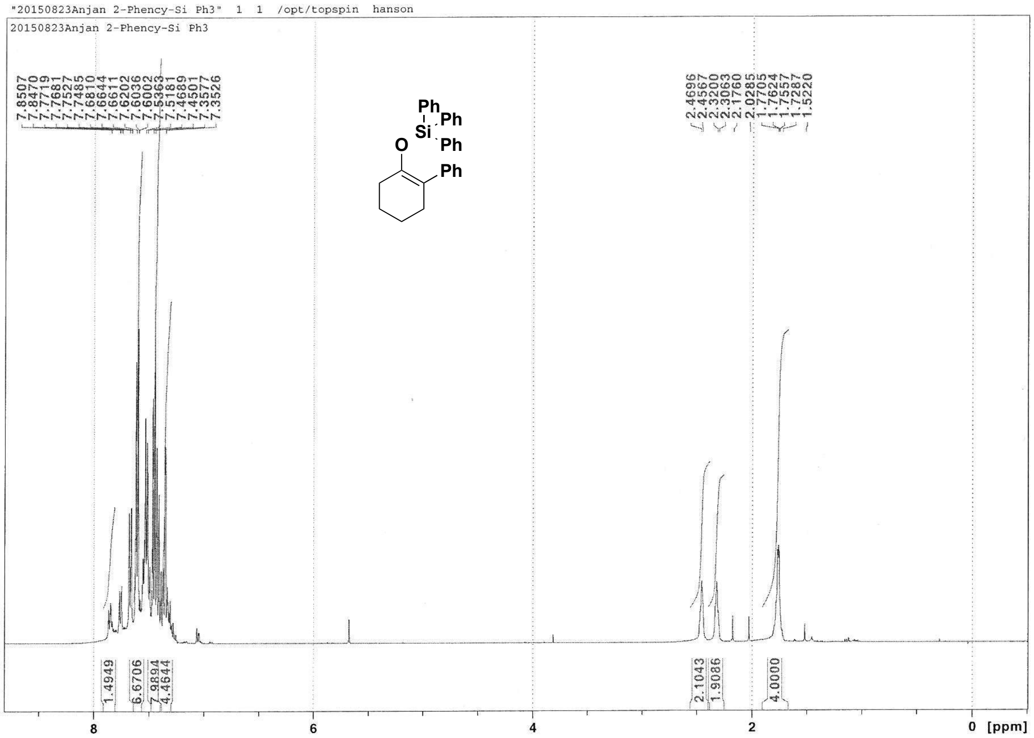


Figure S8. ^{1}H-NMR spectrum showing the characteristic 2-phenylcyclohexanone multiplet (**H** in the inset molecule) during the light modulation experiment over the first 10 hour period (light on for 1 hour then off for 1 hour). The solid red lines correspond to product after 1 hour of irradiation time. The blue dashed line corresponds to the product after being in the dark for 1 hour.

^{1}H-NMR Spectra of Substrates and Products:



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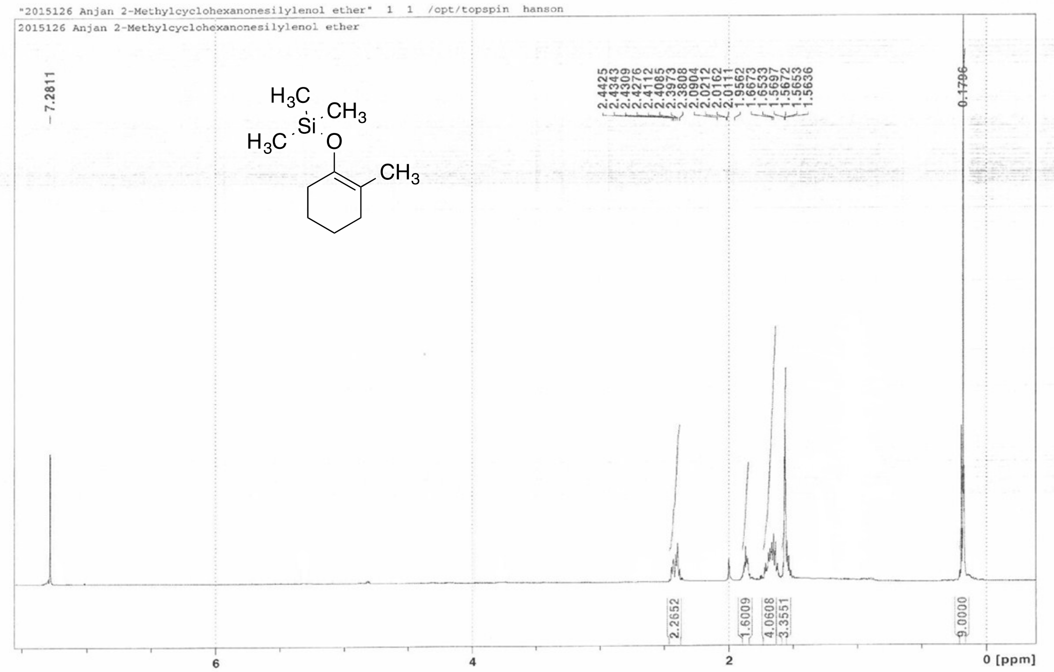
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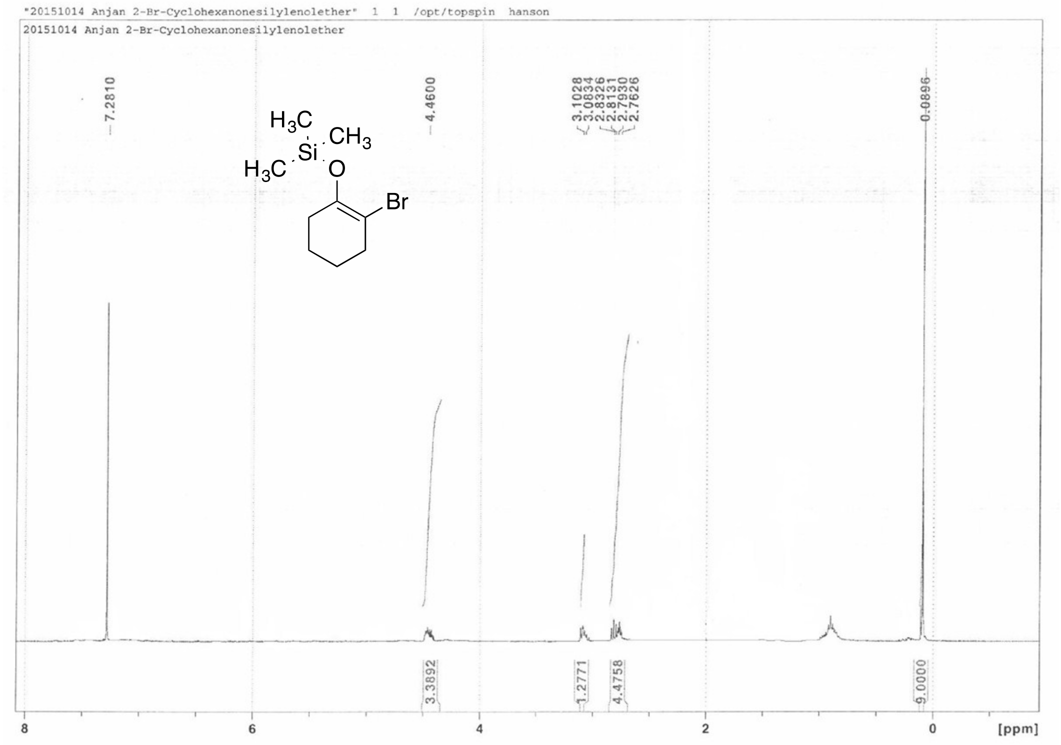
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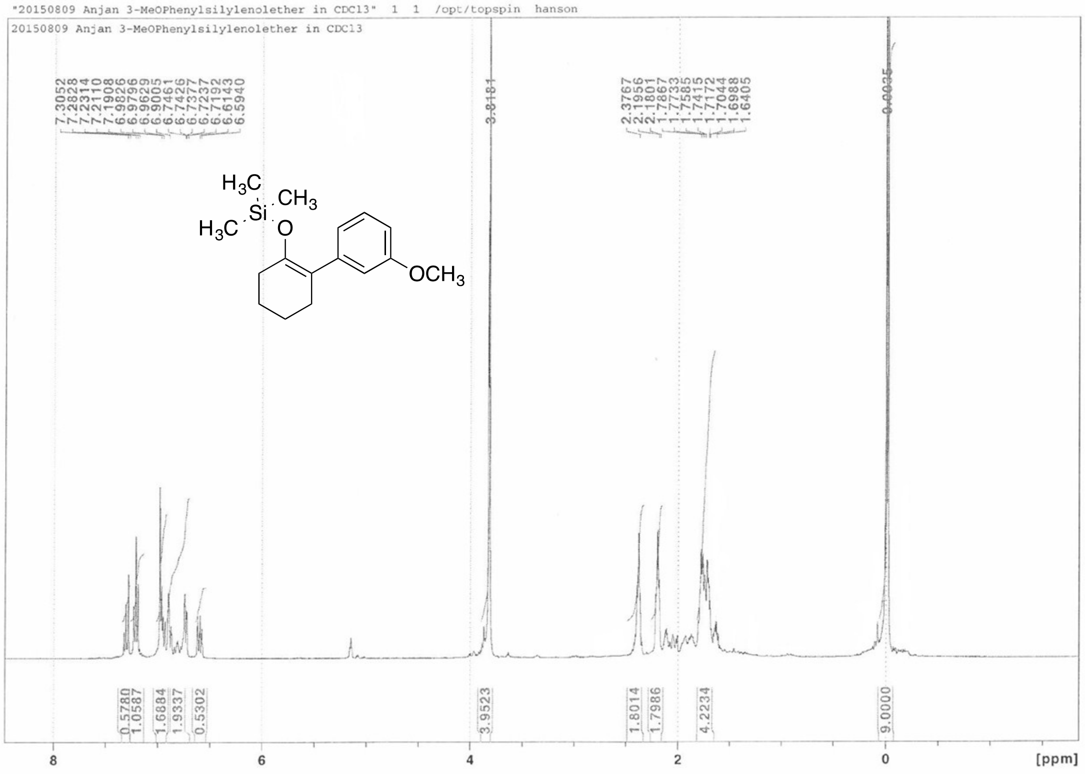
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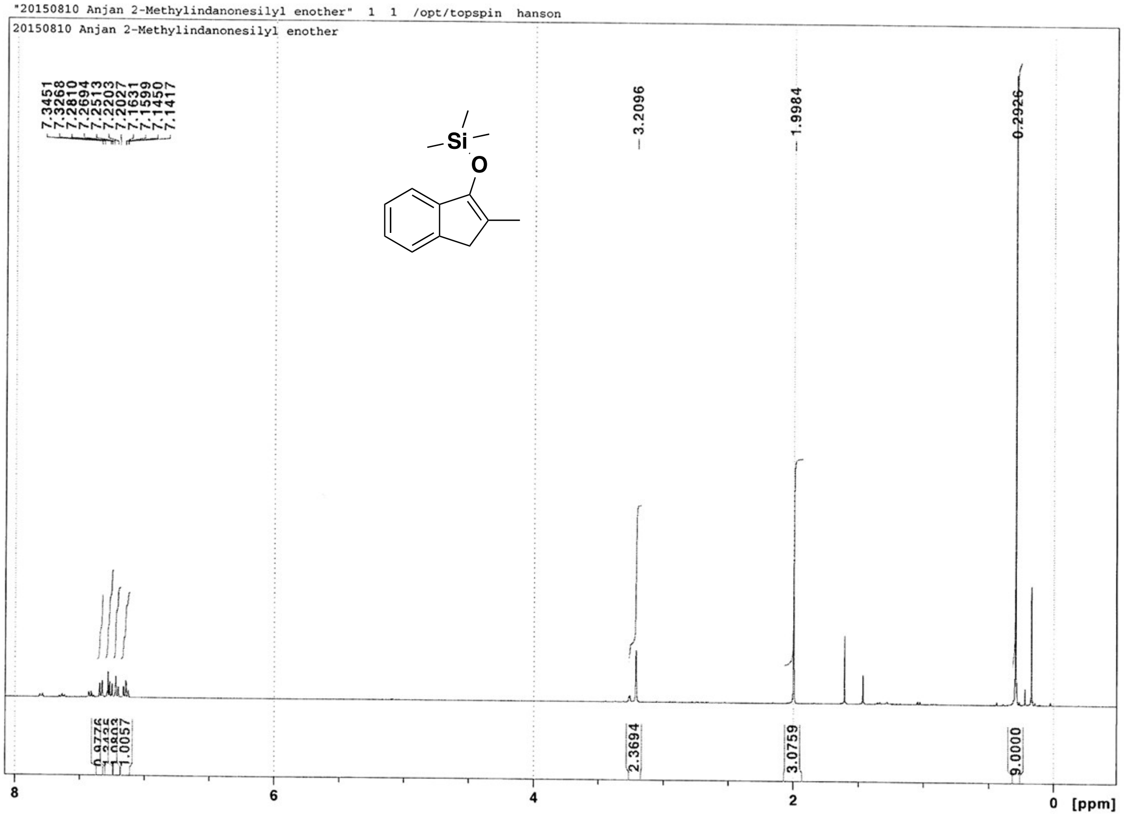
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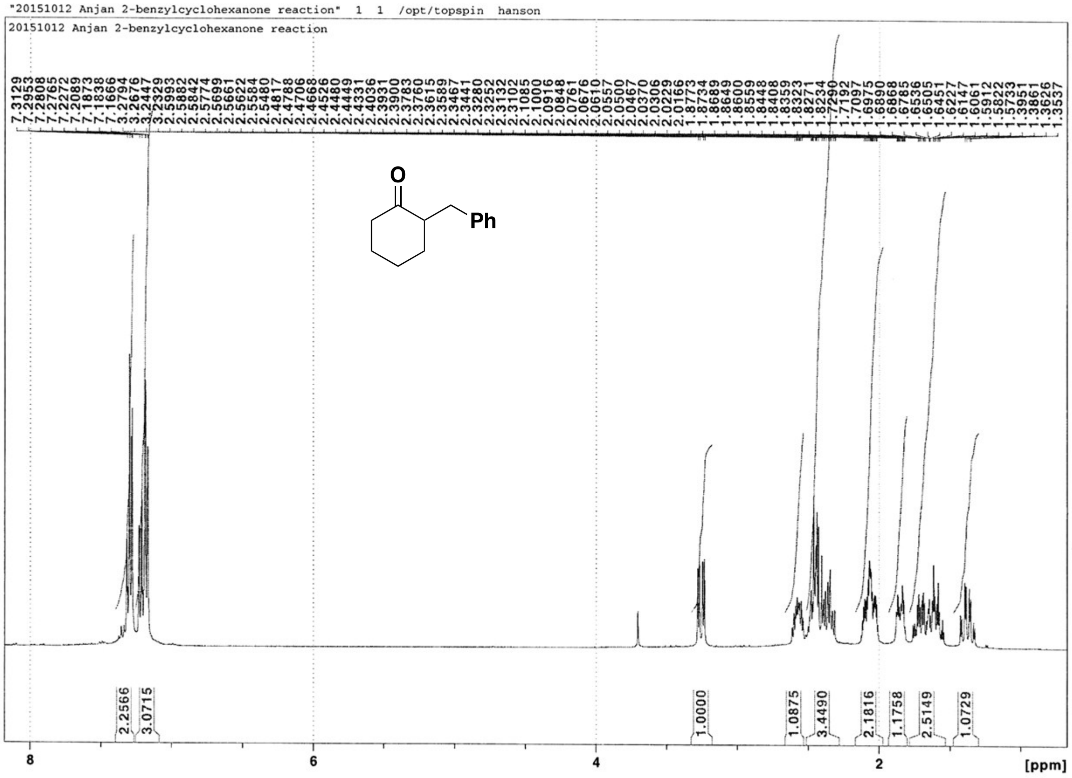
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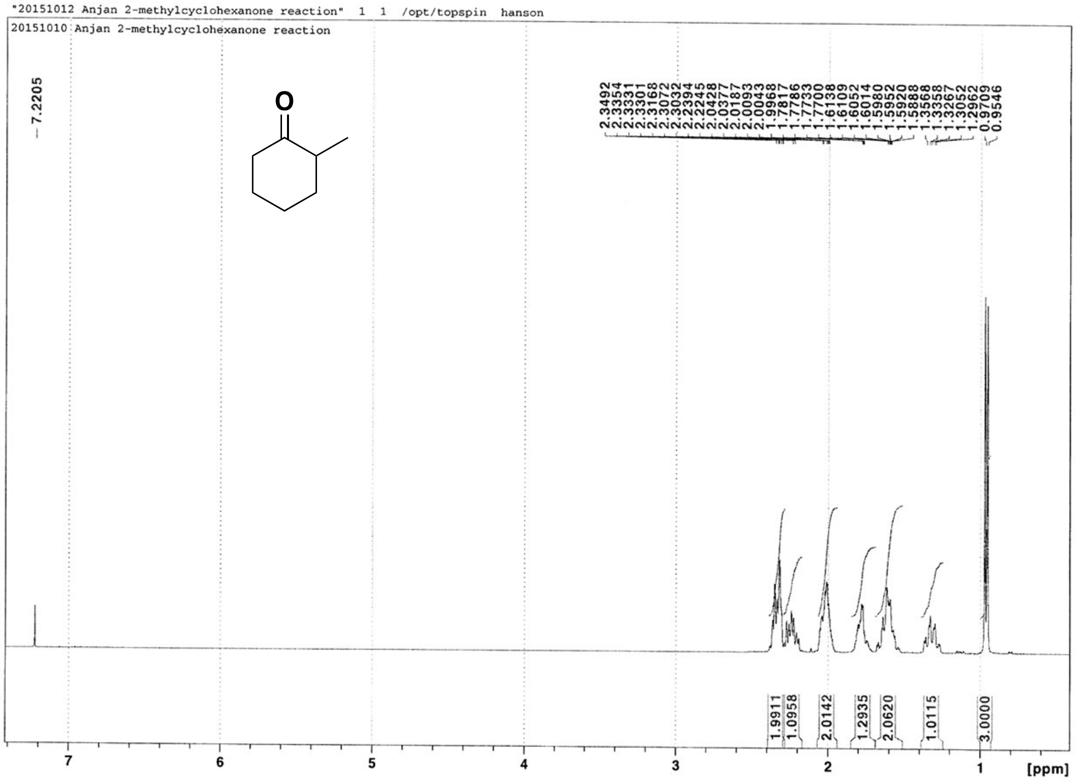
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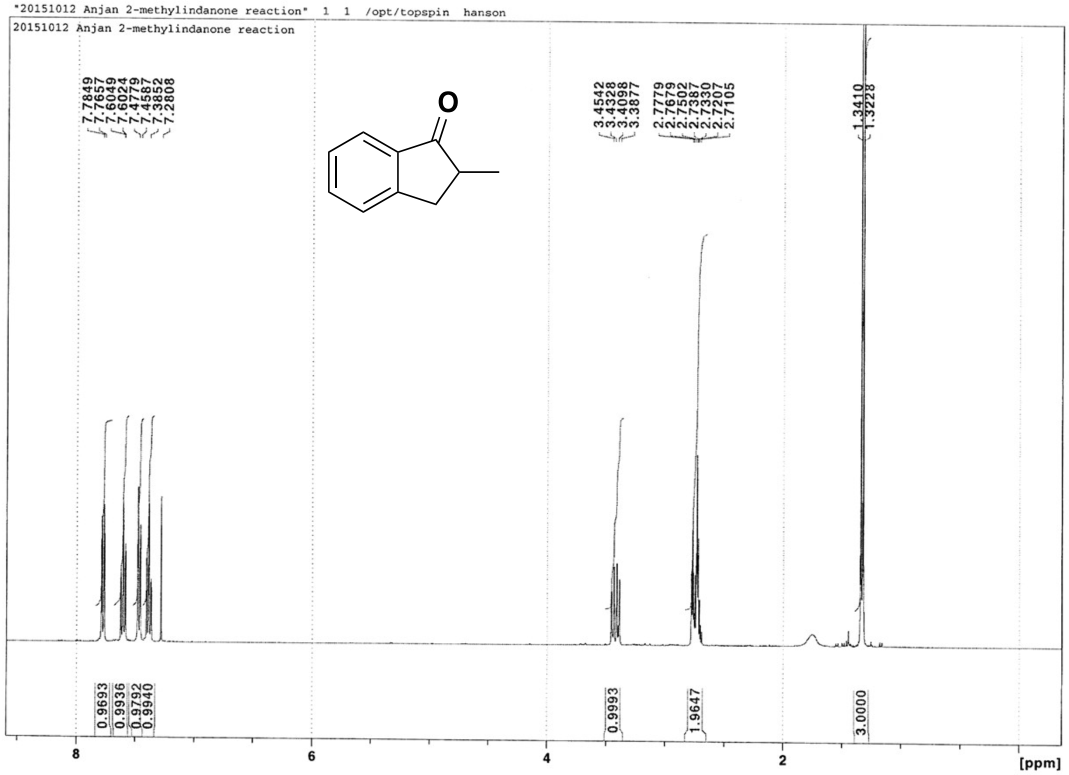
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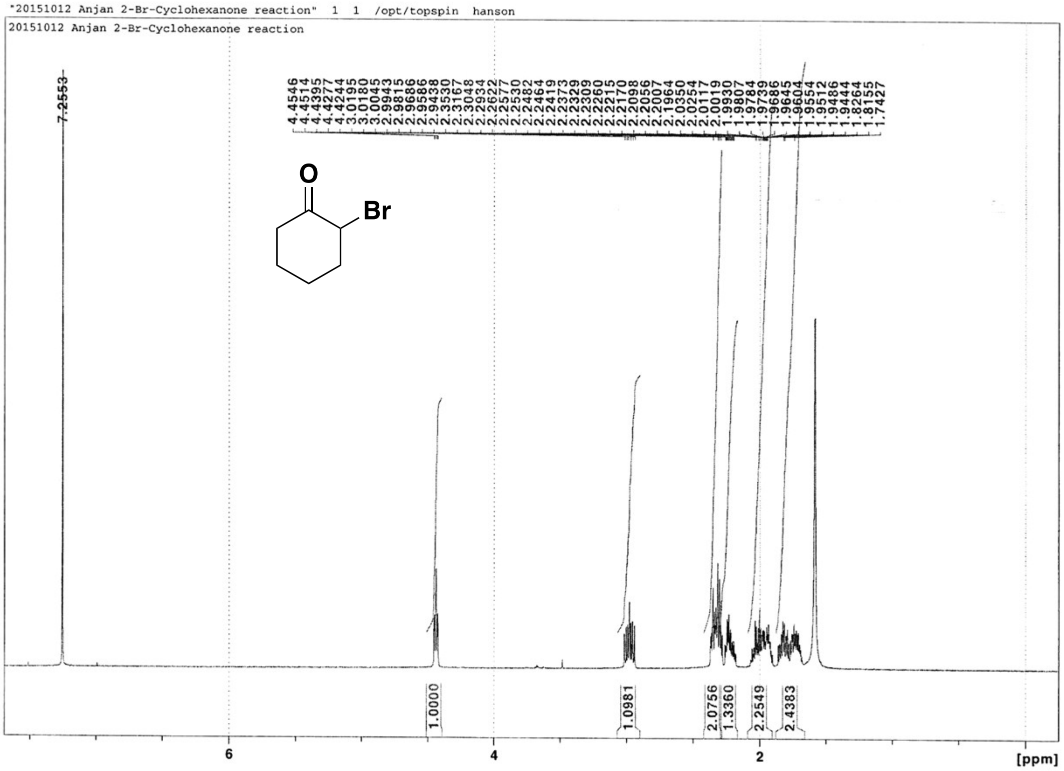
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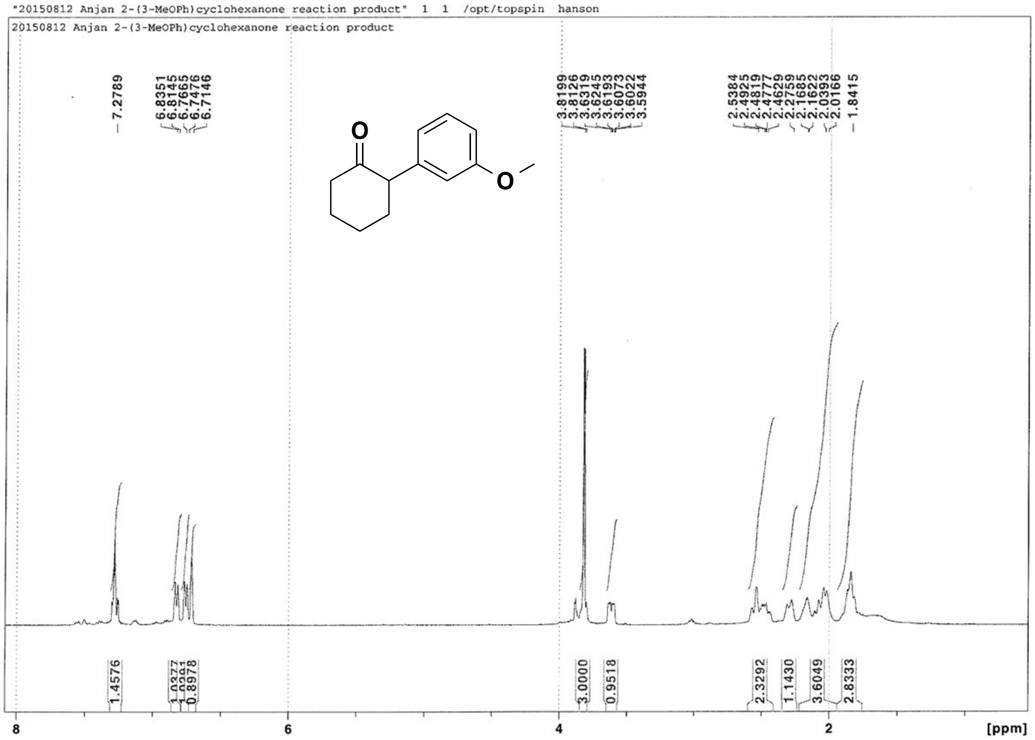
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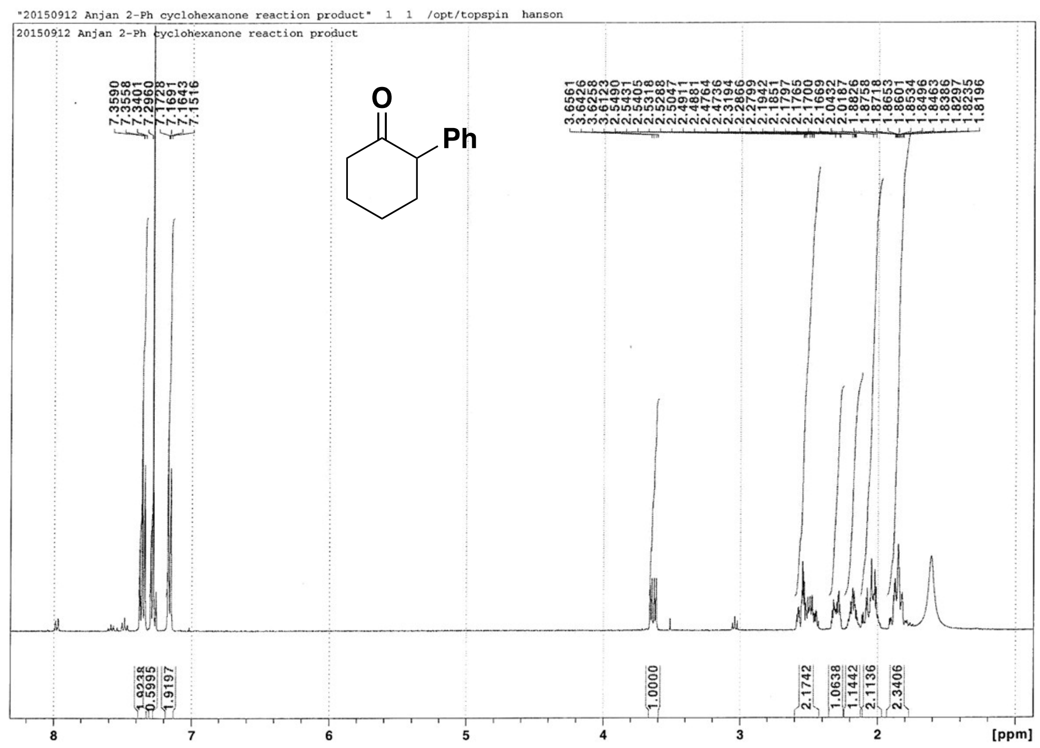

References

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2. C. H. Cheon, T. Imahorib and H. Yamamoto, *Chem. Commun*., 2010, **46**, 6980–6982.

3. C. H. Cheon, O. Kanno and F. D. Toste, *J. Am. Chem. Soc.*, 2011, **133**, 12875-12879.

4. C.H. Cheon and H. Yamamoto, *J. Am. Chem. Soc.*, 2008,**130**, 9246-9247.