

Breaking the bottleneck: Stilbene as a model compound for optimizing 6π e⁻ photocyclization efficiency

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1. Materials and Instrumentation

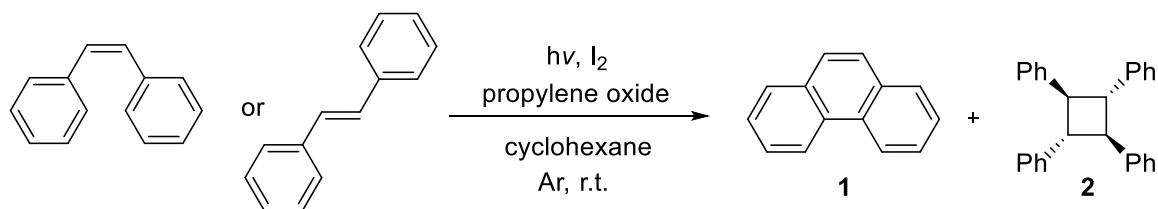
NMR spectra were measured on a Varian NMRS 500-01 (500 MHz) NMR spectrometer. Reported chemical shift values are in reference to an internal TMS standard in CDCl_3 . UV radiation was performed using a 450 W medium-pressure mercury vapor lamp equipped with a quartz water jacket (**Fig. S1**). Solvents and reagents were purchased from Fisher Scientific and TCI Co., Ltd. All solvents and reagents used were reagent grade and were used without additional purification.



Fig. S1 – UV irradiation equipment.

2. Synthetic Procedures

2.1 - Synthesis of phenanthrene – Iodine/Propylene Oxide Route

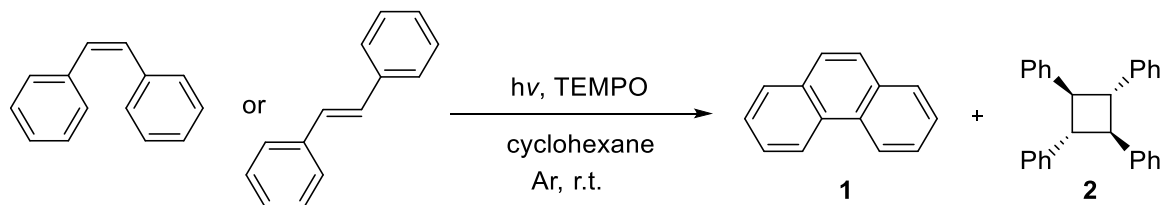


To a 15 mL borosilicate glass vial equipped with a stir bar and septum, 1eq. of (*Z*)- or (*E*)-stilbene, 1eq. of iodine, and 100eq. of propylene oxide (PPO) were added. 10 mL of cyclohexane were added, and the resulting solutions were bubbled with argon for two minutes before being placed in the photoreaction chamber. Care was taken to ensure stilbene samples remained dark before irradiation with a 450 W medium-pressure mercury vapor lamp equipped with a quartz water jacket (**Fig. S1**). After irradiation, cyclohexane and PPO were removed via rotary evaporator. Excess iodine was removed by washing with an aqueous solution of sodium thiosulfate (Na₂S₂O₃).

NMR chemical shifts of 1: ¹H NMR (500 MHz, CDCl₃): δ = 8.70 (d, 2H, ArH), 7.74 (s, 2H, ArH), 7.66 (m, 2H, ArH), 7.60 (m, 2H, ArH)

NMR Chemical Shifts of 2: ¹H NMR (500 MHz, CDCl₃): δ = 7.19-7.06 (m, 15H, ArH), 4.50 (s, 2H, CH), 3.72 (s, 2H, CH)

2.2 - Synthesis of phenanthrene – TEMPO Route¹



To a 15 mL borosilicate glass vial equipped with a stir bar and septum, 1Eq of (*Z*)- or (*E*)-stilbene, and 5 Eq of TEMPO were added. 10mL of cyclohexane were added, and the resulting solutions were bubbled with argon for two minutes before being placed in the photoreaction chamber. Care was taken to ensure stilbene samples remained dark before irradiation with a 450 W medium-pressure mercury vapor lamp equipped with a quartz water jacket (**Fig. S1**). After irradiation, cyclohexane was removed via rotary evaporator. Excess TEMPO was removed by vacuum at 50 °C for 1-2h.

NMR chemical shifts of 1: ¹H NMR (500 MHz, CDCl₃): δ = 8.70 (d, 2H, ArH), 7.74 (s, 2H, ArH), 7.66 (m, 2H, ArH), 7.60 (m, 2H, ArH)

NMR Chemical Shifts of 2: ¹H NMR (500 MHz, CDCl₃): δ = 7.19-7.06 (m, 15H, ArH), 4.50 (s, 2H, CH), 3.72 (s, 2H, CH)

3. Calculations

Calculation of Yields - Calculations of yields were performed by tracking the singlet 2H peaks from (Z)- and (E)-stilbene and phenanthrene as shown in Figs. S2-S5. Tetraphenylcyclobutane (TPCB) formation was tracked via its characteristic two singlets corresponding to its 4 center protons.

P = NMR Integration of the phenanthrene 2H Peak

C = NMR Integration of the (Z)-stilbene 2H Peak

T = NMR Integration of the (E)-stilbene 2H Peak

CB = Sum of both TPCB singlet peak integrations

$$Y_{\text{phenanthrene}} = \frac{P}{P + C + T + \left(\frac{CB}{2}\right)} \quad \text{S1}$$

The sum of the integral of the TPCB peaks was divided by two in order to directly compare the 2H peaks of the stilbenes and phenanthrene to the 4H peaks of TPCB.

Calculation of Phenanthrene Concentration (mmol/L) – Phenanthrene concentration was calculated by multiplying the previously calculated percent yield of phenanthrene by the initial stilbene concentration.

C_s = Initial Stilbene Concentration (mmol/L)

$$C_{\text{phenanthrene}} = Y_{\text{phenanthrene}} \times C_{\text{stilbene}}|_{t=0} \quad \text{S2}$$

5. NMR Data

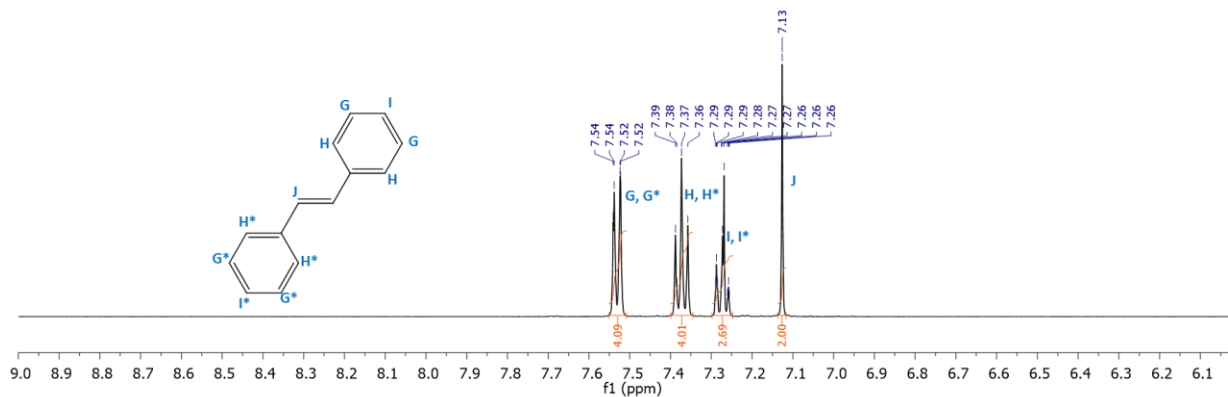


Fig. S2 – ¹H NMR Spectrum (500MHz, CDCl₃) – Pure (E)-stilbene

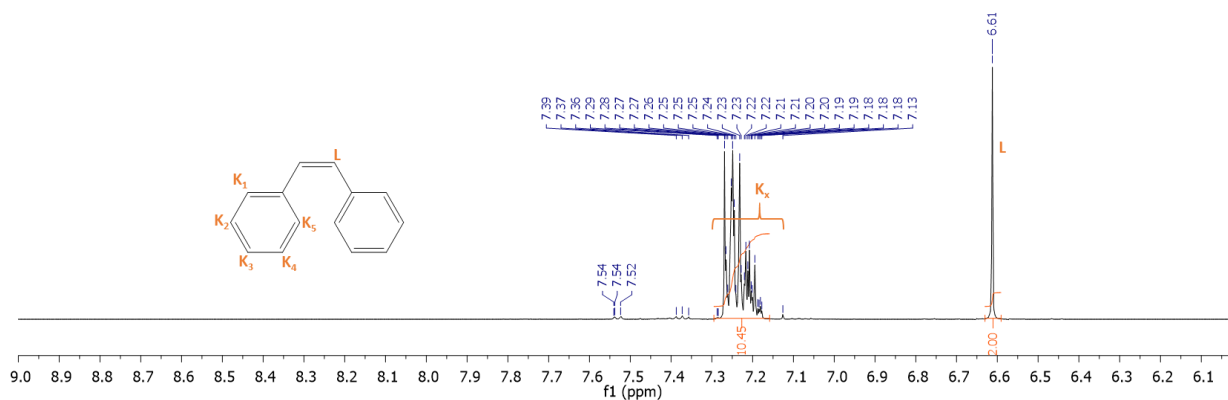
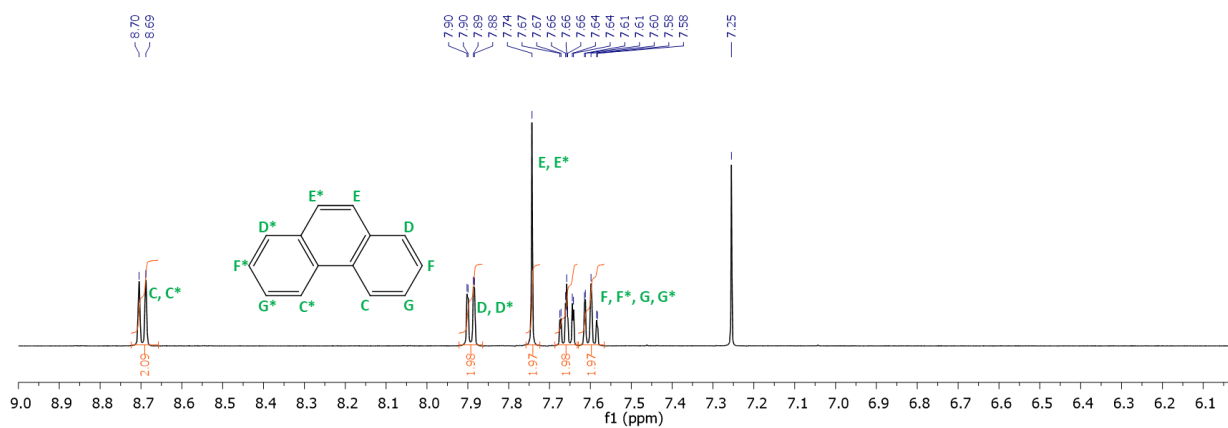


Fig. S3 – ¹H NMR Spectrum (500 MHz, CDCl₃) – Pure (97%) (Z)-stilbene



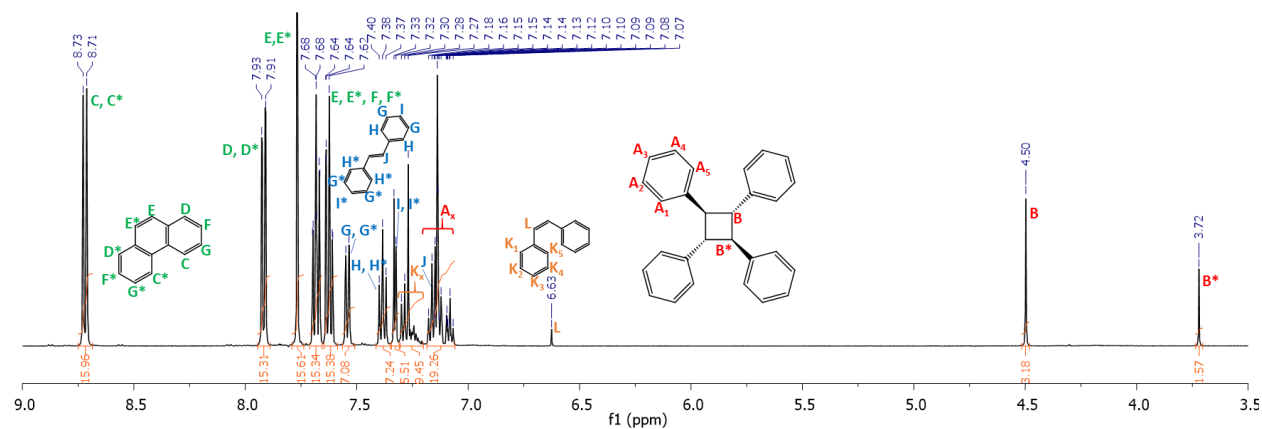


Fig. S5 – ¹H NMR Spectrum (500 MHz, CDCl₃) – tetraphenylcyclobutane shown here after a 16 hr, 10 mM reaction with iodine/PPO.

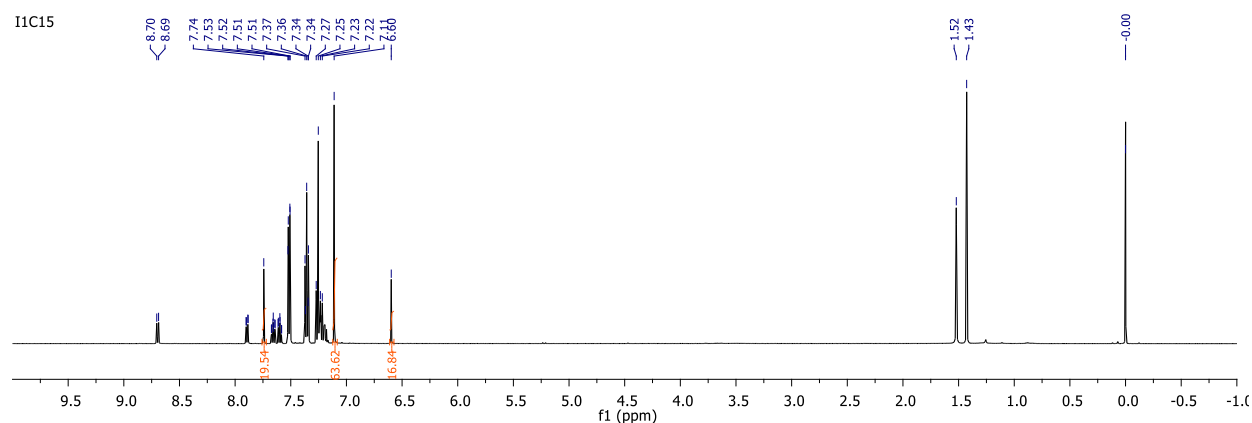


Fig. S6 – ¹H NMR Spectrum (500 MHz, CDCl₃) – 1 mM (Z)-stilbene, iodine, 15 min reaction time

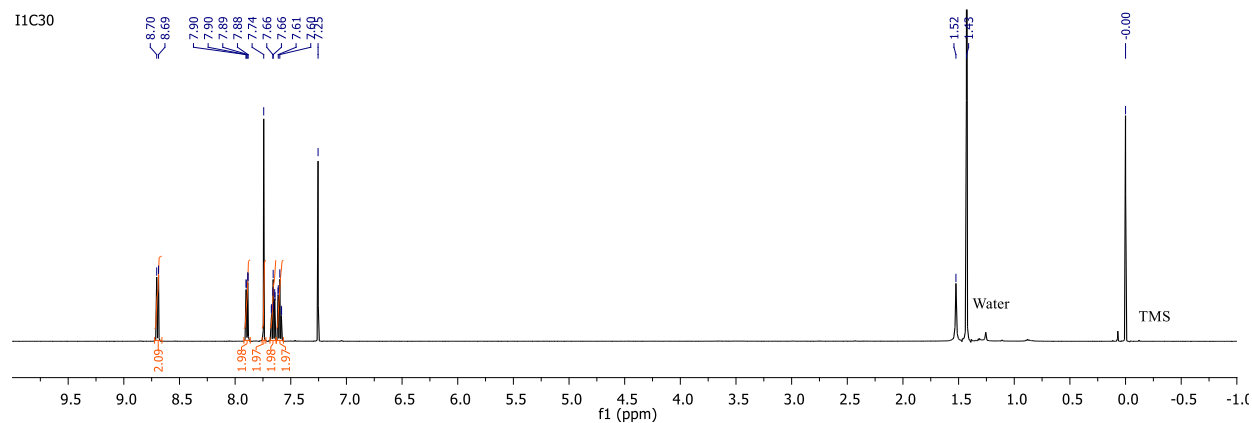


Fig. S7 – ¹H NMR Spectrum (500 MHz, CDCl₃) – 1 mM (Z)-stilbene, iodine, 30 min reaction time

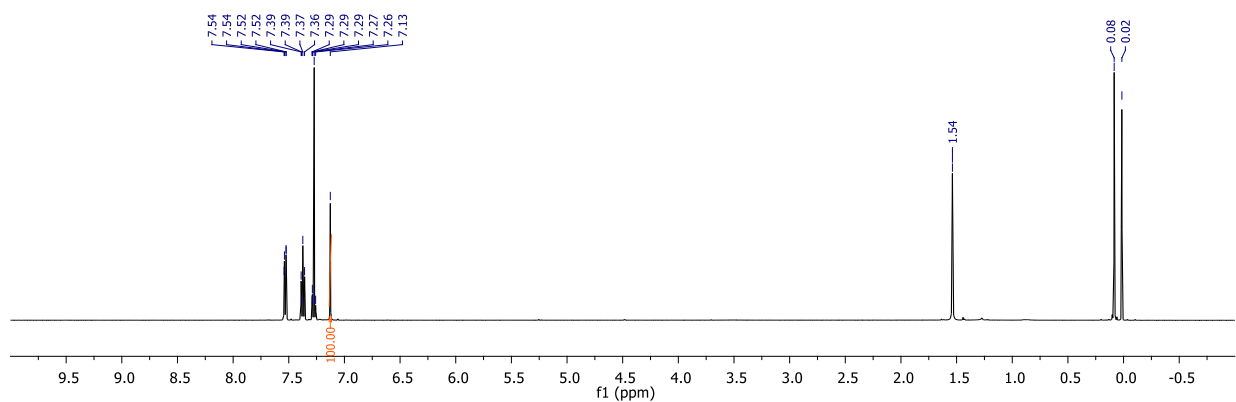


Fig. S8 – ¹H NMR Spectrum (500 MHz, CDCl₃) –20 mM (*E*)-stilbene, iodine, 15 min reaction time

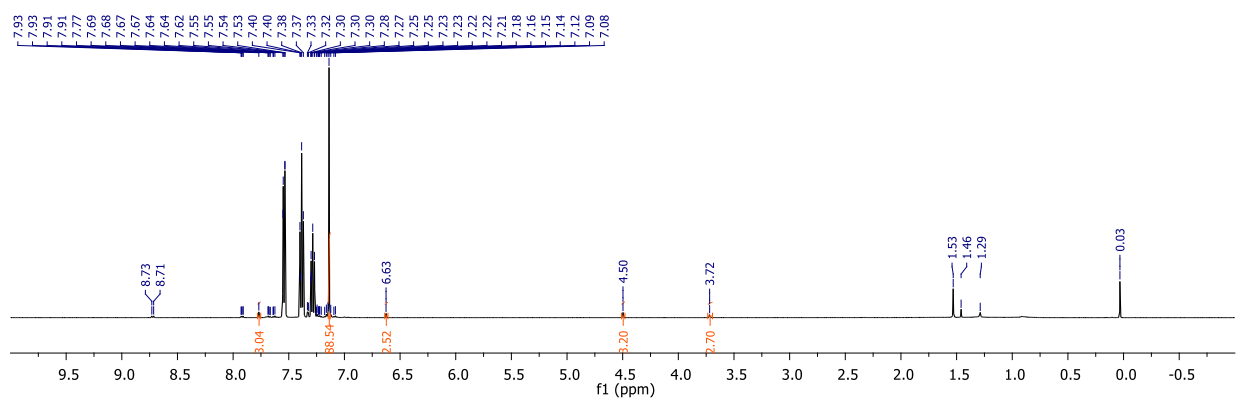


Fig. S9 – ¹H NMR Spectrum (500 MHz, CDCl₃) –20 mM (*E*)-stilbene, iodine, 2 hr reaction time

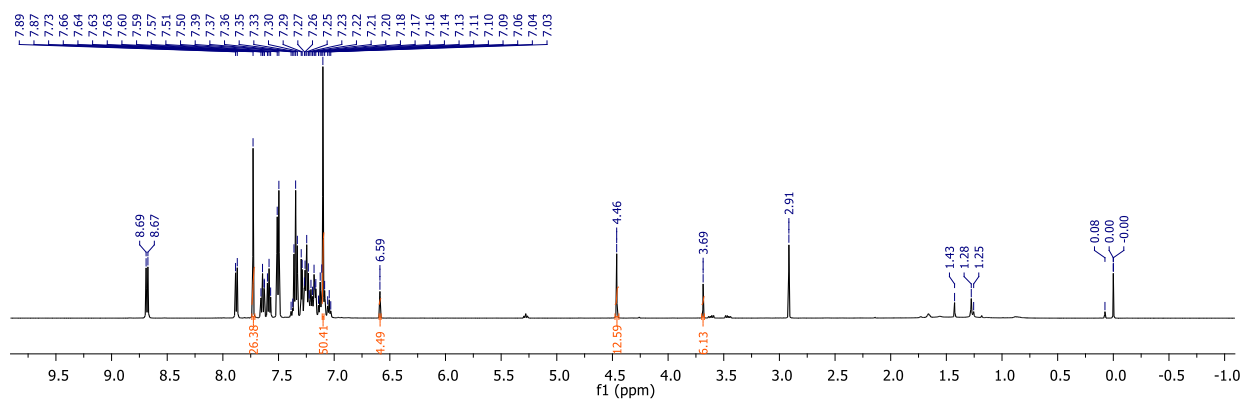


Fig. S10 – ¹H NMR Spectrum (500 MHz, CDCl₃) – 20 mM (*E*)-stilbene, iodine, 16 hr reaction time

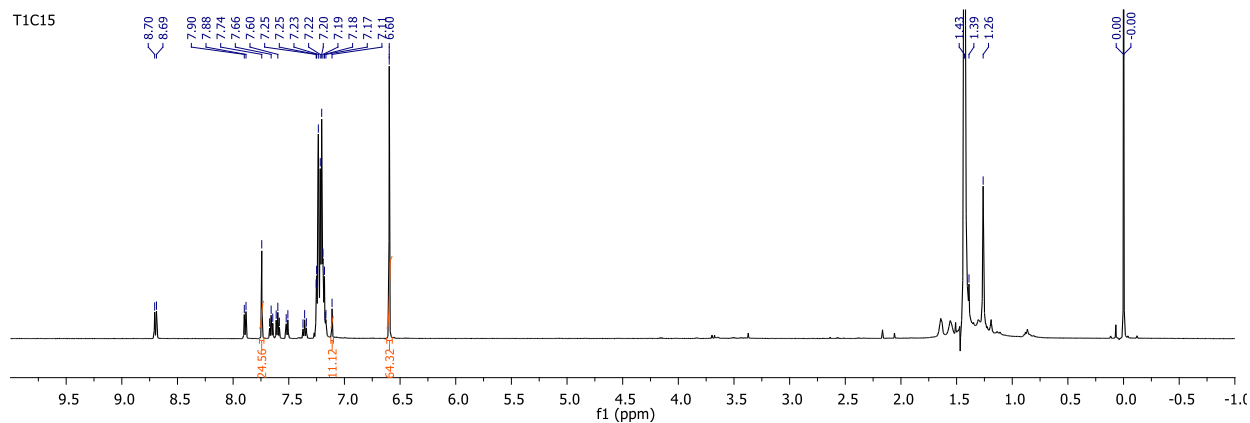


Fig. S11 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 1 mM (Z)-stilbene, TEMPO, 15 min reaction time

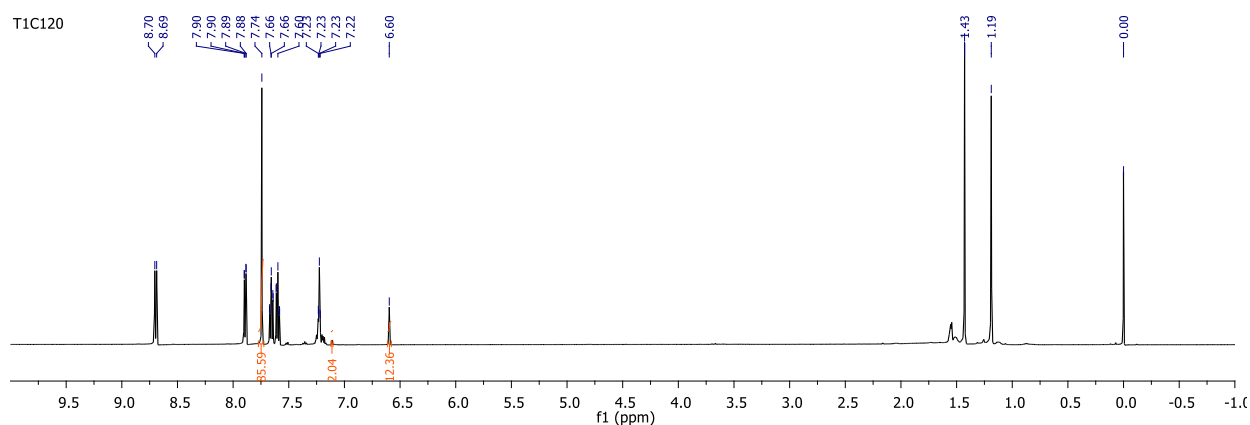


Fig. S12 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 1 mM (Z)-stilbene, TEMPO, 2 hr reaction time

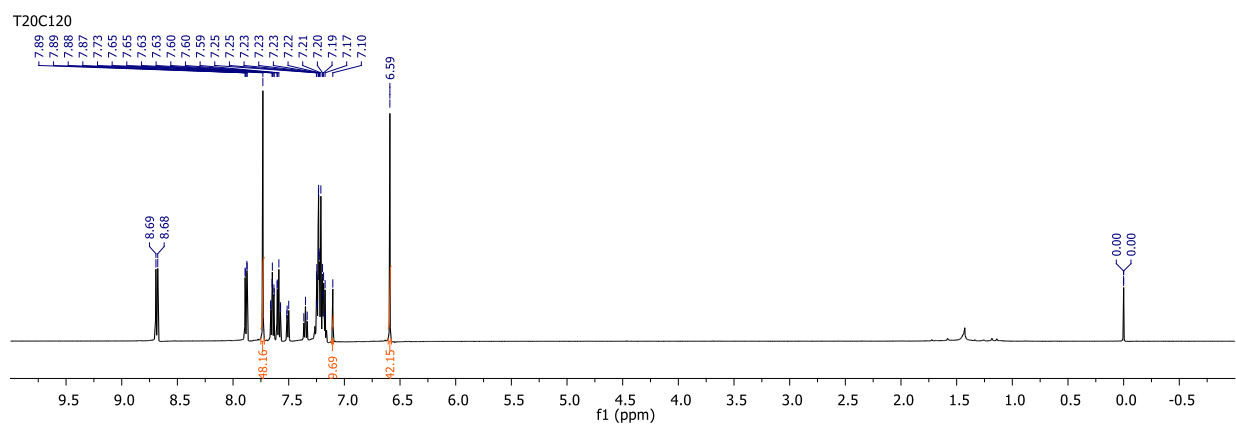


Fig. S14 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 20 mM (Z)-Stilbene, TEMPO, 2 hr reaction time

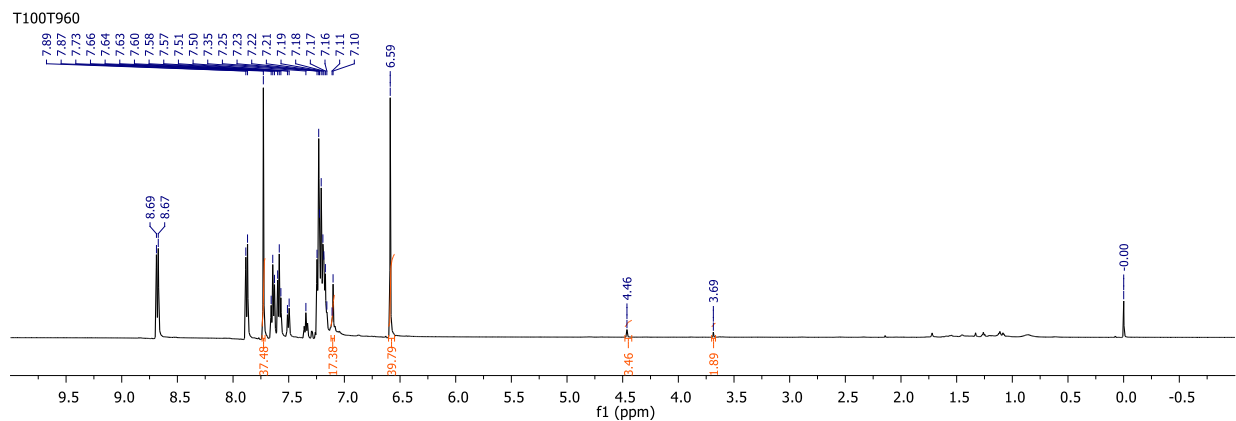


Fig. S15 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 100 mM (*E*)-stilbene, TEMPO, 16 hr reaction time

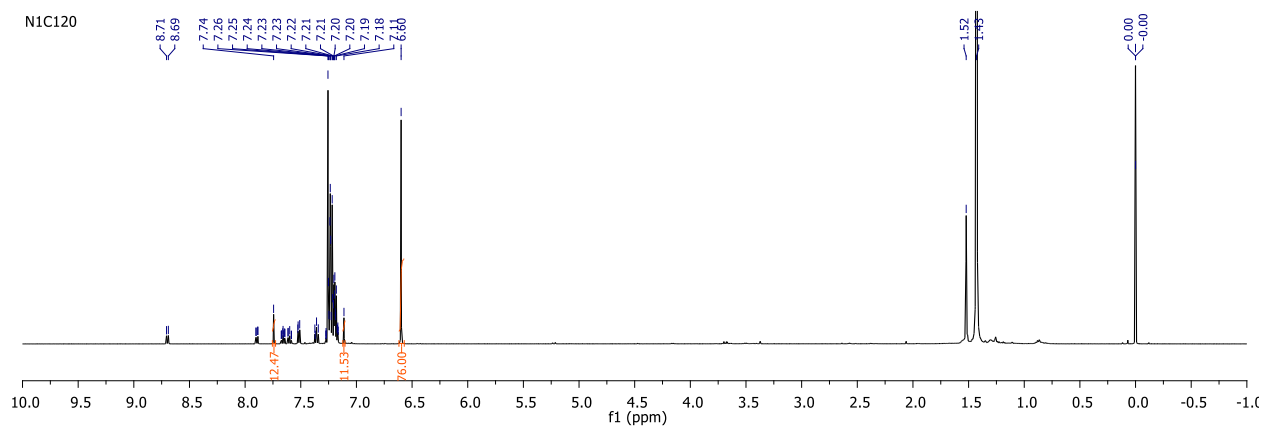


Fig. S17 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 1 mM (*Z*)-stilbene, no oxidizing agent, 2 hr reaction time

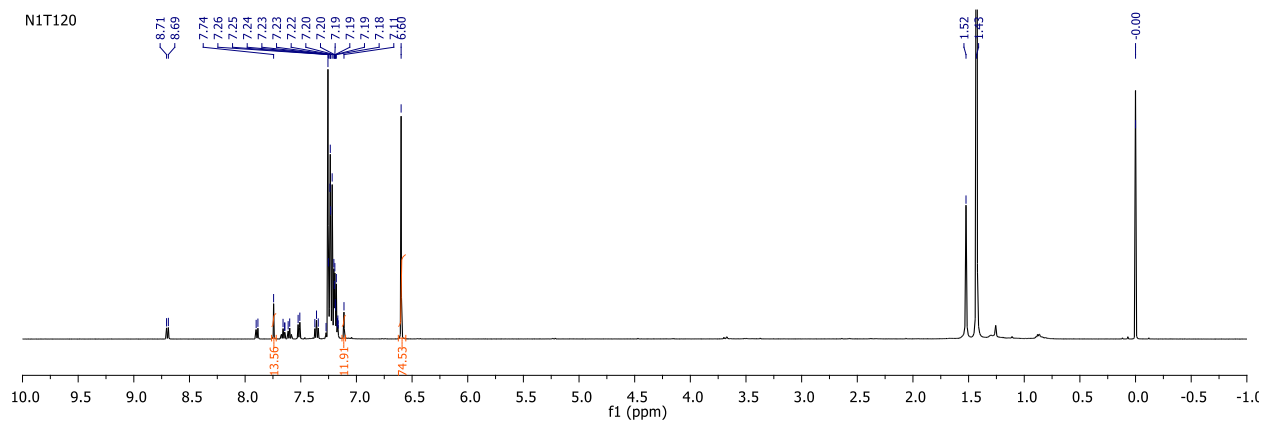


Fig. S18 – ^1H NMR Spectrum (500 MHz, CDCl_3) – 1 mM (*E*)-stilbene, no oxidizing agent, 2 hr reaction time

6. References

- (1) Matsushima, T.; Kobayashi, S.; Watanabe, S. Air-Driven Potassium Iodide-Mediated Oxidative Photocyclization of Stilbene Derivatives. *J. Org. Chem.* **2016**, *81* (17), 7799–7806. <https://doi.org/10.1021/acs.joc.6b01450>.