Photochemical reactions of a diamidocarbene: cyclopropanation of bromonaphthalene, addition to pyridine, and activation of sp^3 C-H bonds

Tharushi A. Perera,[a,b] William V. Taylor,[a] M. Brenton Gildner,[a] Eric W. Reinheimer,[c] Sho Ito,[d]

Anna Nelson,[a] Shane R. Yost,[a] and Todd W. Hudnall*[a]

[a]Department of Chemistry & Biochemistry, Texas State University, San Marcos, Texas 78666, USA.
[b]Current address: Mercy College, School of Health and Natural Science, 555 Broadway, Dobbs Ferry, NY, 10522.
[c]Rigaku Americas Corporation, 9009 New Trails Dr, The Woodlands, TX 77381, USA
[d]Rigaku Corporation, 3-9-12, Matsubara, Akishima, Tokyo 196-8666, Japan

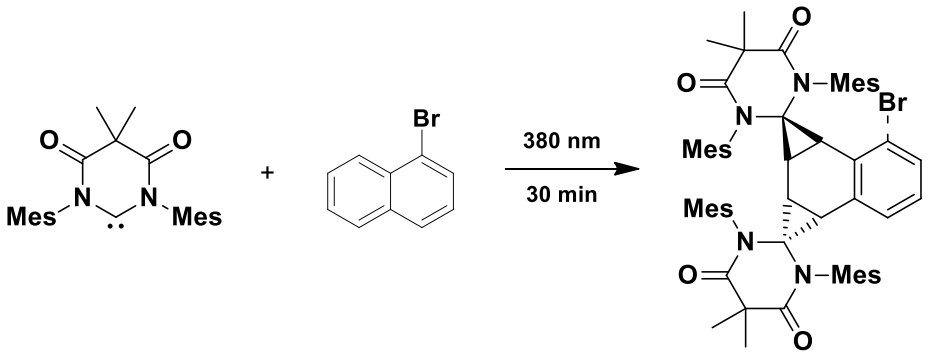
Table of Contents

General Considerations. All procedures were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box unless otherwise noted. The diamidocarbene, DAC (**1**),[1] was synthesized according to literature procedures. Pyridine, cyclohexanes, *n*-pentane, and tetramethylsilane (TMS) were dried over sodium, distilled and degassed. 1-Bromonaphthalene was dried over activated $CaCl_2$, distilled and degassed. All dried and degassed solvents mentioned above were stored over 3 Å molecular sieves in a nitrogen filled glove box, and cyclohexane, *n*-pentane, and TMS were passed over activated silica inside the glove box just prior to use. High resolution mass spectra (HRMS) were obtained in acetonitrile using electrospray-ionization mass spectrometry (ESI-MS) performed in positive-ion mode with a Waters Synapt XS instrument equipped with a Zspray probe. Samples were dissolved in dry benzene and then directly infused using a mixture of benzene and acetonitrile. NMR spectra were recorded on Bruker AscendTM -500 spectrometer at ambient probe temperatures. NMR shifts are given in δ with positive values downfield of TMS (^{1}H: C_6D_6, δ 7.16; $CDCl_3$, δ 7.26; ^{13}C: C_6D_6, δ128.6).

Light Source. Irradiations at 380 nm were conducted using a home-built tube photo reactor, consisting of a short section of 11 cm PVC pipe lined with 36 LED's (superbrightleds.com, RL5-UV031 or RL5-B5515 5mm LEDs) connected in series (Figure S1). A constant current of 50 to 60 mA was applied to power the LED's.[2]

Synthesis of Compounds

Synthesis and Characterization of Compound 2



A 20 mL vial was charged with DAC (0.1 g, 0.27 mmol) and was dissolved with dry bromonaphthalene (1 mL, 7.14 mmol). This solution was syringed into a sealed tube. The sealed tube was removed from the glove box. The tube was then irradiated at 380 nm for 30 minutes. After irradiation, sealed tube was taken back into the glove box and added 10 mL of hexanes and the volatiles were removed under reduced pressure outside of the glove box. Washing of the residual solid with minimal hexanes followed by drying under reduced pressure afforded the desired product as a white solid (0.19g 0.20 mmol, 73% yield). Colorless single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of hexanes vapor into a concentrated benzene solution at room temperature. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.36 (s, 3H), 7.12 – 7.06 (m, 4H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.94 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.46 – 6.42 (m, 1H), 6.31 (d, *J* = 2.1 Hz, 1H), 5.95 (dd, *J* = 18.2, 2.0 Hz, 2H), 2.49 – 2.46 (m, 6H), 2.35 (d, *J* = 13.5 Hz, 6H), 2.23 (d, *J* = 7.0 Hz, 6H), 2.19 (s, 3H), 2.07 (s, 3H), 1.81 – 1.75 (m, 9H), 1.61 (s, 3H), 1.38 (d, *J* = 11.4 Hz, 6H), 0.91 (d, *J* = 12.2 Hz, 6H). ^{13}C NMR (125.75 MHz, $CDCl_3$) δ 172.07, 171.60, 171.44, 171,34, 140.26, 138.61, 138.55, 138.48, 138.22, 137.46, 137.39, 137.16, 137.03, 136.83, 136.82, 65.83, 64.76, 47.29, 46.94, 25.65, 25.07, 24.24, 23.40, 22.28, 21.48, 21.07, 21.00, 20.96, 20.83, 20.73, 20.66, 20.48, 19.81, 19.61, 19.60, 19.47, 16.02, 15.98 Anal. calcd. for $C_{58}H_{63}BrN_4O_4$: C, 72.56; H, 6.61; N, 5.84; Found: C, 72.51; H, 6.66; N, 5.88.

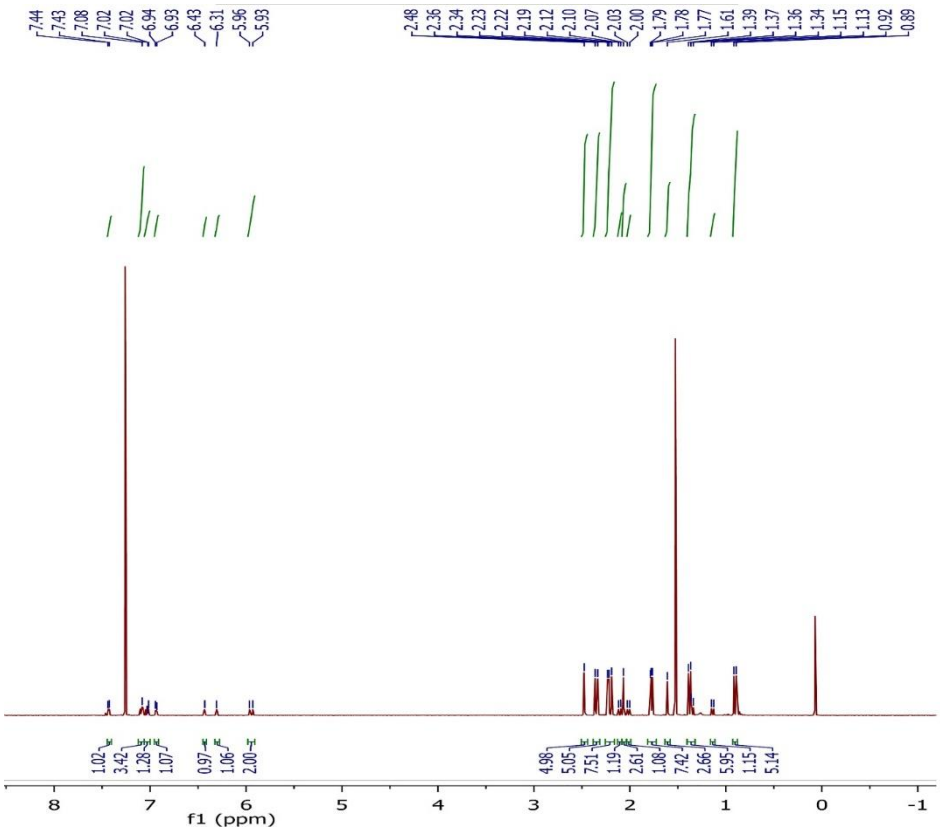


Figure S1. ^{1}H NMR spectrum (full) of **2** in $CDCl_3$ (silicon grease impurity at approximately 0 ppm).

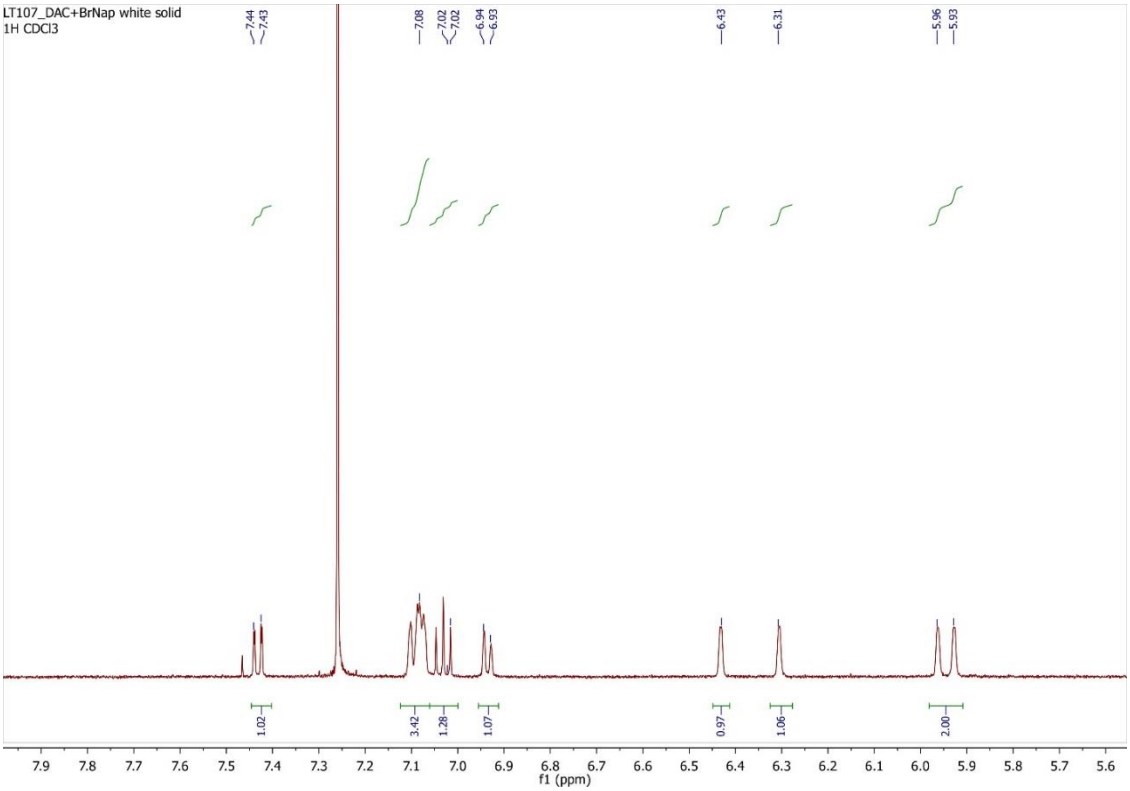


Figure S2. ^{1}H NMR spectrum of **2** in $CDCl_3$ (from 5.6 to 7.9 ppm).

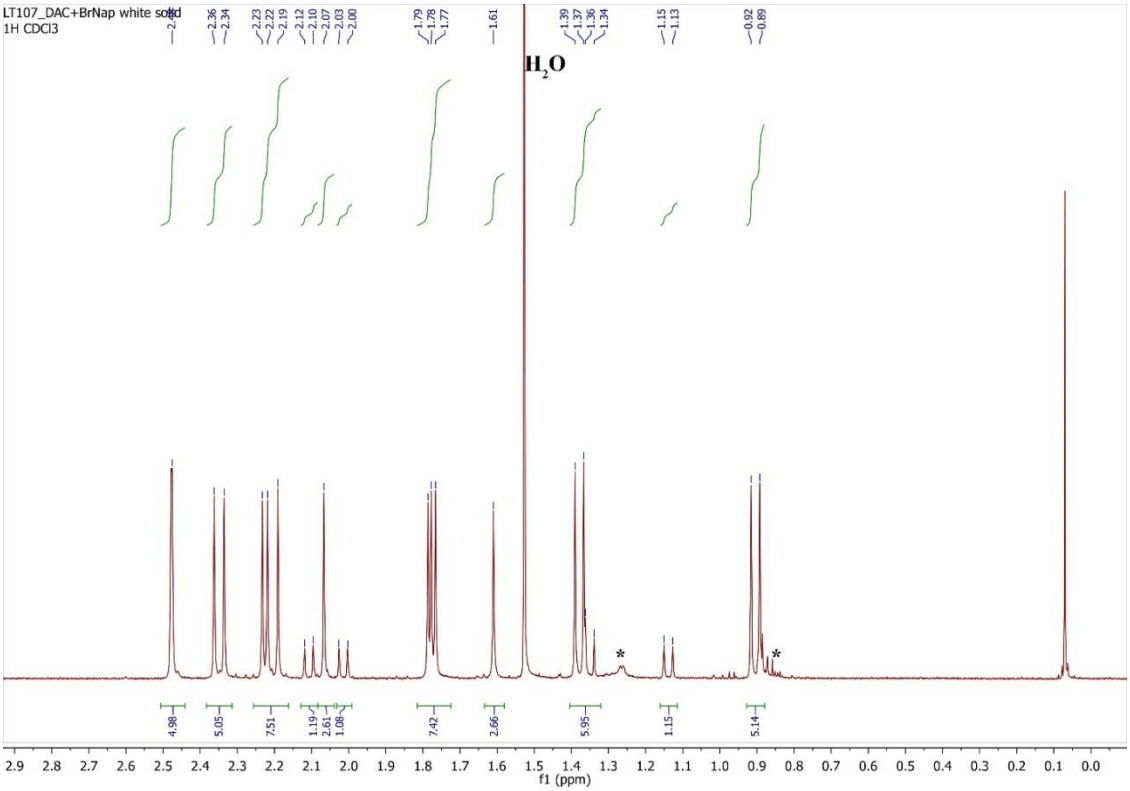


Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$ (from 0 to 2.9 ppm).

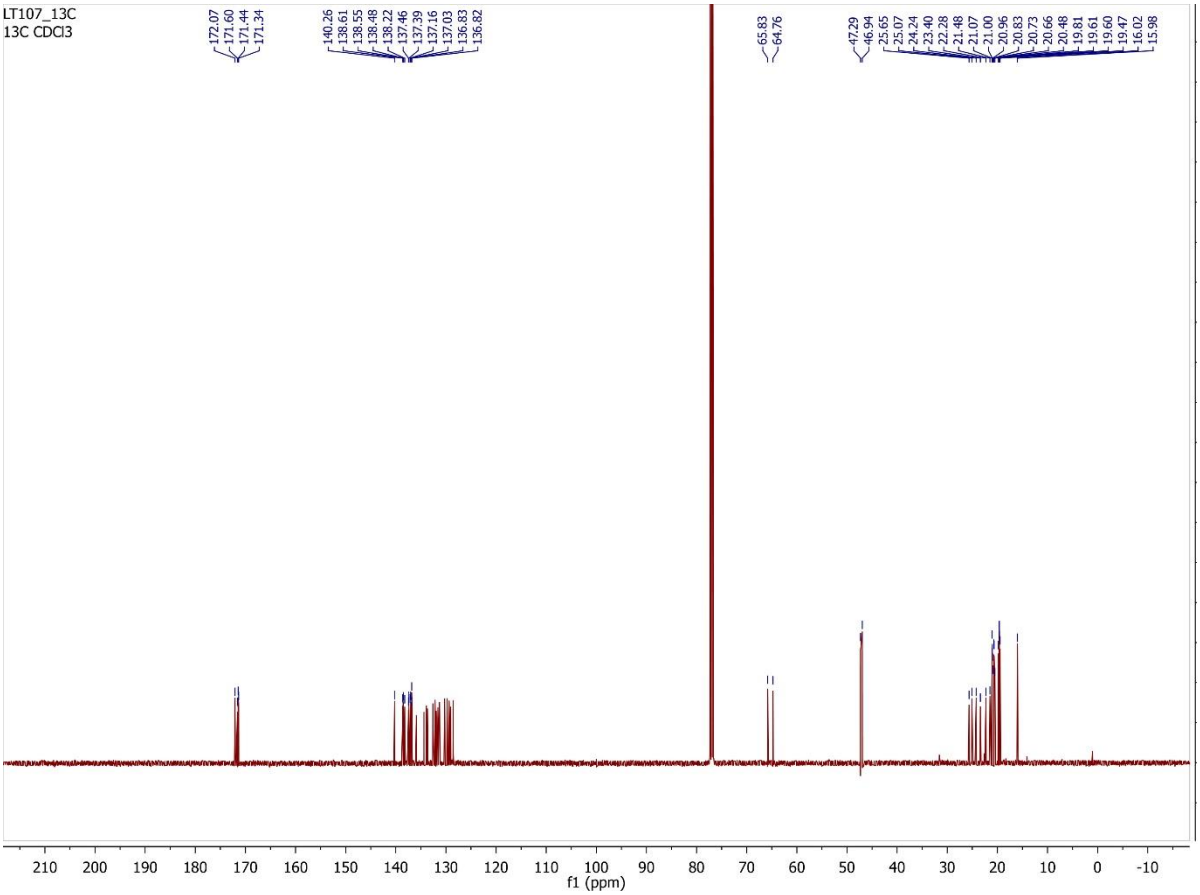


Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$.

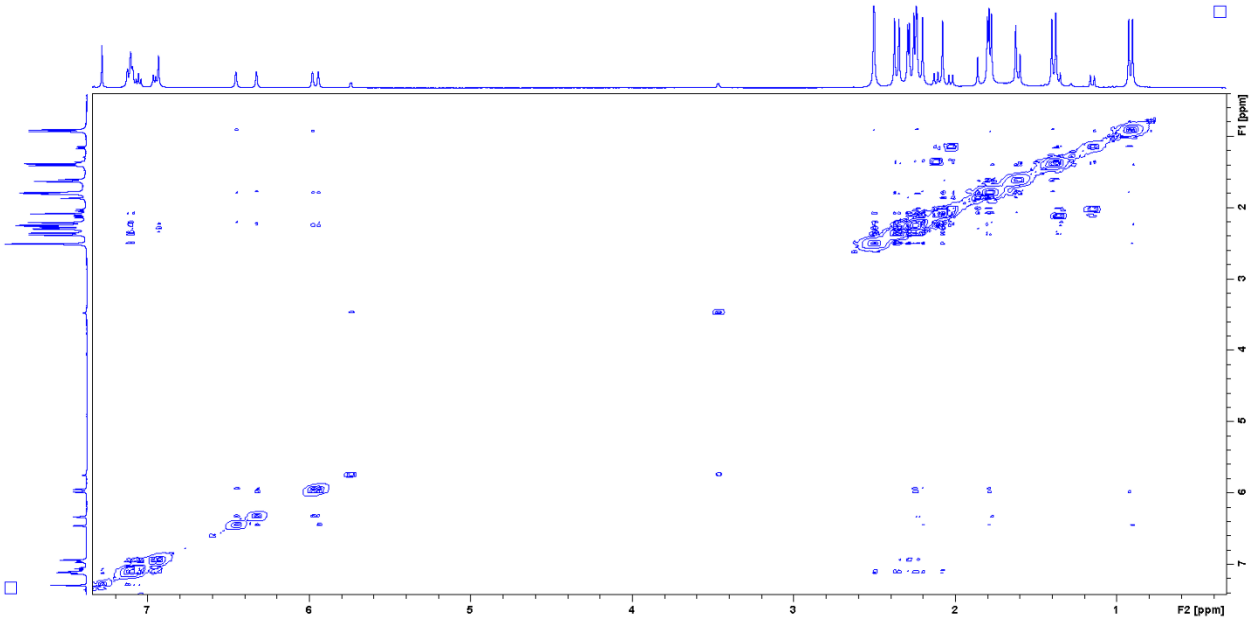


Figure S5. COSY NMR spectrum (full) of **2** in $CDCl_3$.

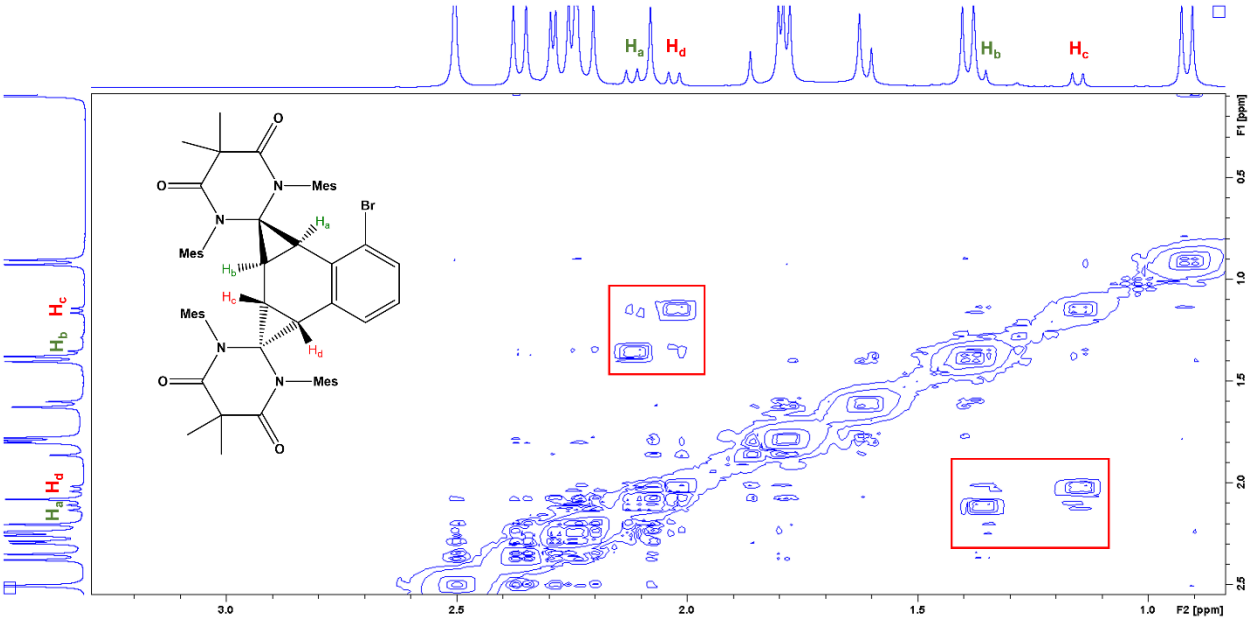


Figure S6. COSY NMR spectrum (aliphatic) of **2** in $CDCl_3$.

Date: 01/04/18

Analysis	Theory	% Found	
C	72.56	72.51	
H	6.61	6.66	
N	5.84	5.88	

M.P./B.P. —

Hydroscopic: Yes Explosive: NO

Molecular Formula: $C_{58}H_{63}BrN_4O_4$

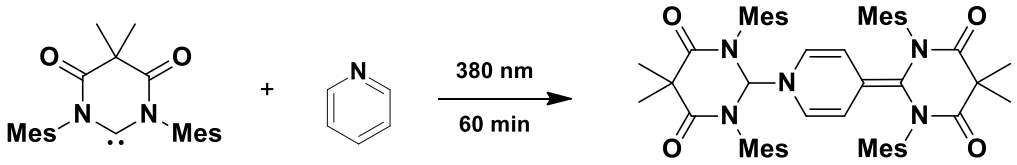
To Be Dried: ☒No ☐Yes at _____°C

ANALYZE for: ☒Single ☐Duplicate

MIDWEST MICROLAB. LLC

Figure S7. Elemental analysis data for compound **2**.

Synthesis and Characterization of 3



A 20 mL vial was charged with DAC (0.1 g, 0.27 mmol) and was dissolved with pyridine (1 mL, 12.4 mmol). This yellow color solution was syringed into a sealed tube. The sealed tube was removed from the glove box. The tube was then irradiated at 380 nm for 1 h. After irradiation, sealed tube was taken back into the glove box and added 5-7 mL of hexanes and the volatiles were removed under reduced pressure outside of the glove box. Washing of the residual solid with minimal hexanes followed by drying under reduced pressure afforded the desired product as a pale-orange solid (0.20 g, 0.24 mmol, 89% yield). pale-orange single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of hexanes vapor into a concentrated benzene solution at room temperature inside the glove box. ^{1}H NMR (500.13 MHz, C_6D_6) δ 6.81 – 6.78 (m, 2H), 6.72 – 6.69 (m, 2H), 6.60 (q, *J* = 0.8 Hz, 2H), 6.58 – 6.56 (m, 2H), 6.03 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.06 (s, 1H), 4.97 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.24 (dd, *J* = 8.4, 2.9 Hz, 1H), 4.16 (dd, *J* = 8.5, 2.1 Hz, 1H), 2.27 (s, 6H), 2.12 (s, 9H), 2.07 (s, 6H), 2.05 (s, 9H), 1.91 (s, 6H), 1.70 (s, 3H), 1.67 (s, 6H), 1.47 (s, 3H). ^{13}C NMR (125.75 MHz, C_6D_6) δ 1.35, 18.71, 19.45, 19.47, 19.89, 20.82, 20.86, 20.88, 20.90, 22.55, 25.44, 26.57, 48.34, 86.12, 105.57, 106.87, 107.75, 125.06, 129.58, 129.90, 129.97, 130.39, 133.28, 134.03, 136.04, 136.54, 136.67, 137.63, 138.04, 138.59, 168.65, 168.68, 170.49. Note for combustion analysis: multiple samples were sent out which all had passing H and N analysis, with reproducible C analysis that was too high. This indicated some issue with the combustion analysis and not any form of inorganic or organic impurity. Anal. calcd. for $C_{53}H_{61}N_5O_4$: C, 76.50; H, 7.39; N, 8.42; Found: C, 77.63; H, 7.19; N, 8.45.

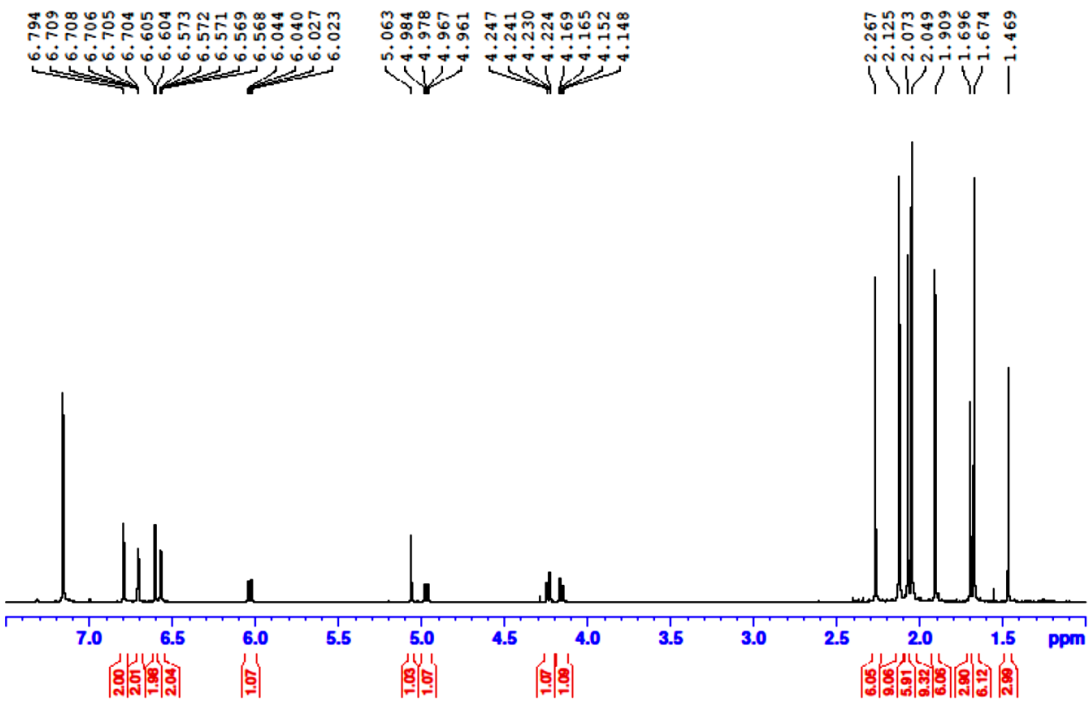


Figure S8. ^{1}H NMR spectrum of **3** in C_6D_6.

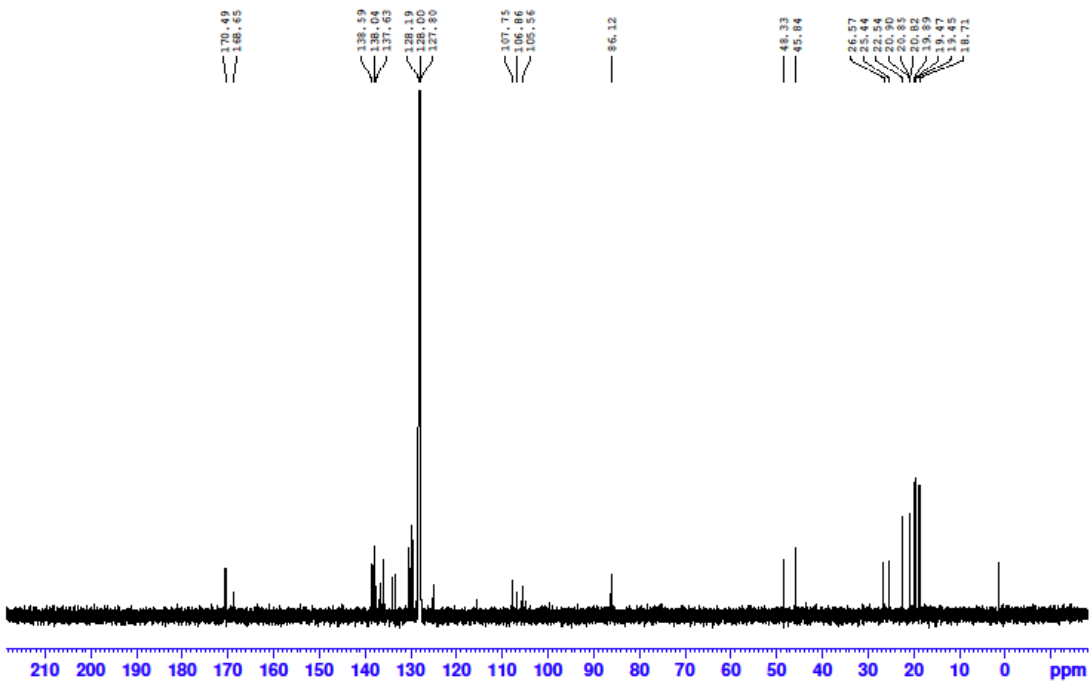


Figure S9. ^{13}C NMR spectrum of **3** in C_6D_6.

Analysis	Theory	% Found		M.P./B.P.	
C	76.00 – 77.00	77.63			
H	6.89 – 7.89	7.19		Hydroscopic:	Explosive:
N	7.92 – 8.92	8.45		$C_{53}H_{61}N_5O_4$ Molecular Formula:	
				To Be Dried: ☒No ☐Yes at _____°C	
				C, H, N ANALYZE for:	☒Single ☐Duplicate

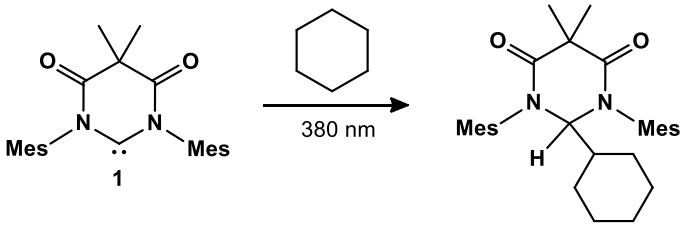
Vial was broken during shipping

* email results to :- Prof. Todd Hudnall
hudnall@txstate.edu

MIDWEST MICROLAB, LLC
7212 N. SHADELAND AVE., SUITE 110
INDIANAPOLIS, IN 46250
PHONE: (317)849-6606
FAX: (317)849-8534

Figure S10. Elemental analysis data for compound **3**.

Synthesis and Characterization of 4



A 50 mL Schlenk tube equipped with a Teflon stopper was charged with DAC (0.10 g, 0.27 mmol) and dry cyclohexane (1 mL) inside of a nitrogen-filled glove box. The tube was then removed from the box, and the resulting suspension was then irradiated at 380 nm for 30 minutes. After irradiation it was noted that the volume of cyclohexane had appeared to decrease and more solid was present in the tube. At that time, all volatiles were removed under reduced pressure. Washing of the residual solid with minimal hexanes followed by drying under reduced pressure afforded the desired product as a white solid (0.09 g, 0.20 mmol, 73% yield). ^{1}H NMR (500 MHz, C_6D_6) δ 6.77 (d, *J* = 2.1 Hz, 2H), 6.70 (d, *J* = 2.1 Hz, 2H), 5.32 (d, *J* = 1.4 Hz, 1H), 2.35 (s, 6H), 2.15 (s, 6H), 2.06 (s, 6H), 1.89 (d, *J* = 2.7 Hz, 3H), 1.82 (s, 3H), 1.66 – 1.58 (m, 1H), 1.46 – 1.38 (m, 2H), 1.35 (dd, *J* = 9.5, 3.4 Hz, 2H), 1.26 (d, *J* = 5.7 Hz, 1H), 0.91 – 0.80 (m, 2H), 0.75 – 0.62 (m, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 1.41, 19.67, 19.79, 20.81, 23.96, 26.35, 26.61, 27.27, 28.89, 43.32, 46.29, 77.67, 130.01, 130.12, 135.08, 136.20, 137.45, 138.47, 171.35. HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{41}N_2O_2$: 461.3163; found: 461.3190.

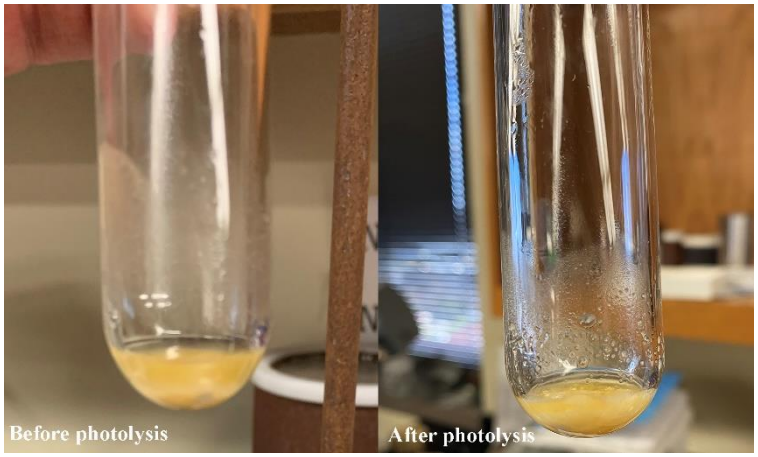


Figure S11. Before (left) and after (right) photolysis of DAC **1** in cyclohexane.

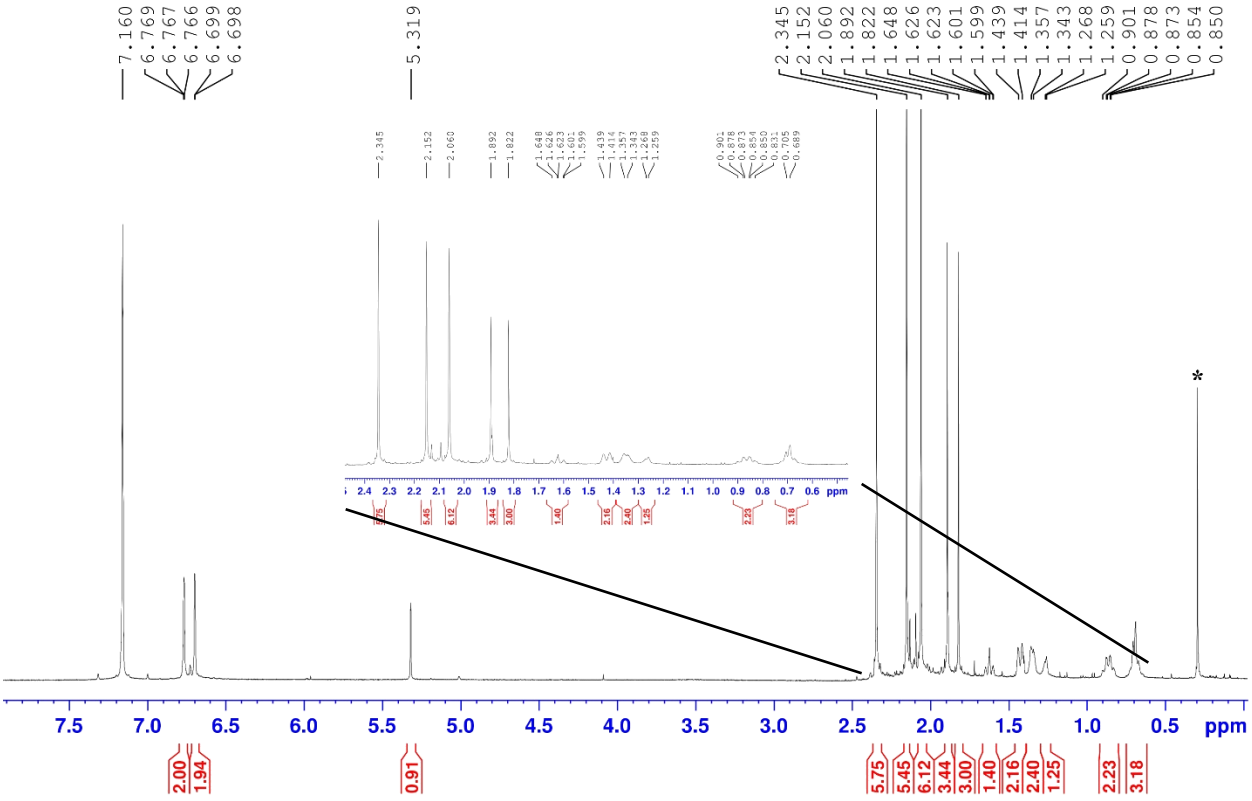


Figure S12. ^{1}H NMR spectrum of **4** in C_6D_6 (* denotes silicon grease impurity).

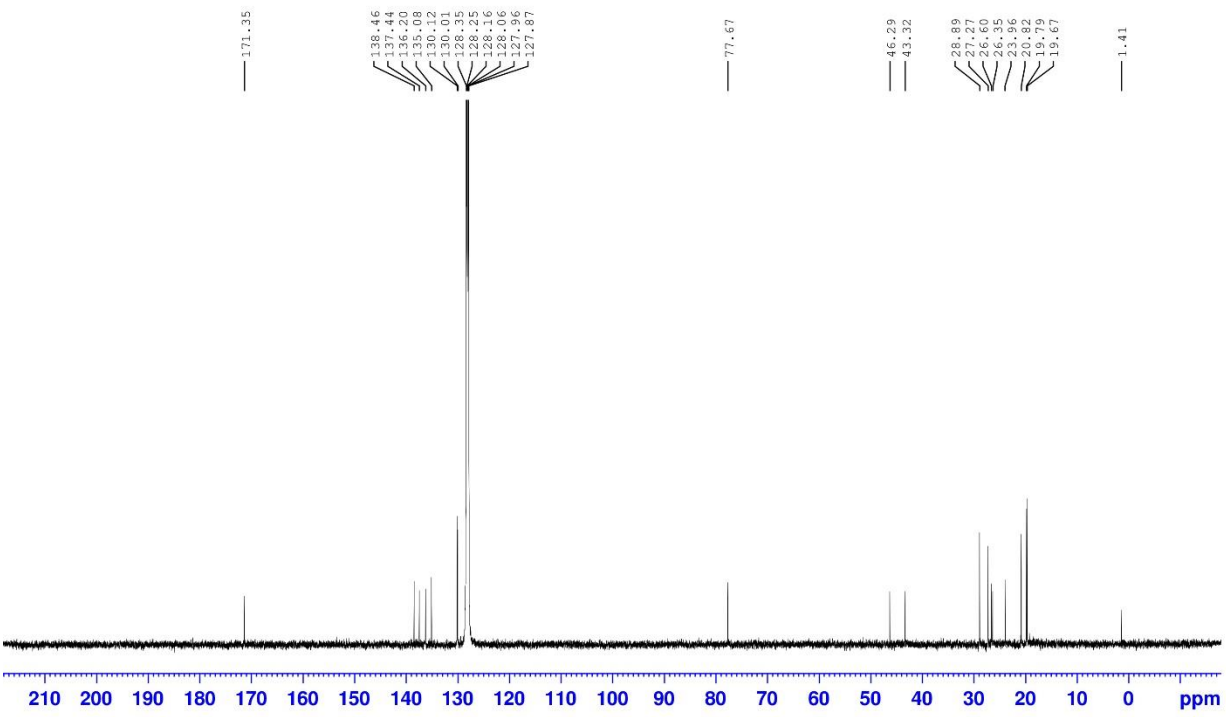


Figure S13. ^{13}C NMR spectrum of **4** in C_6D_6 (* denotes silicon grease impurity).

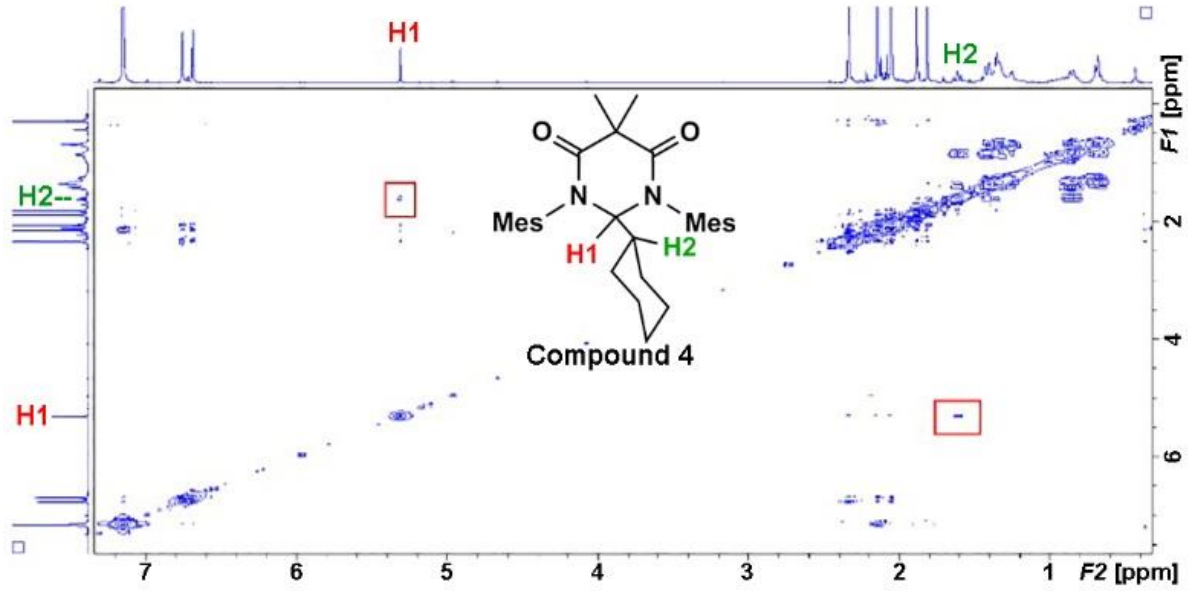


Figure S14. COSY NMR spectrum of **4** in C_6D_6.

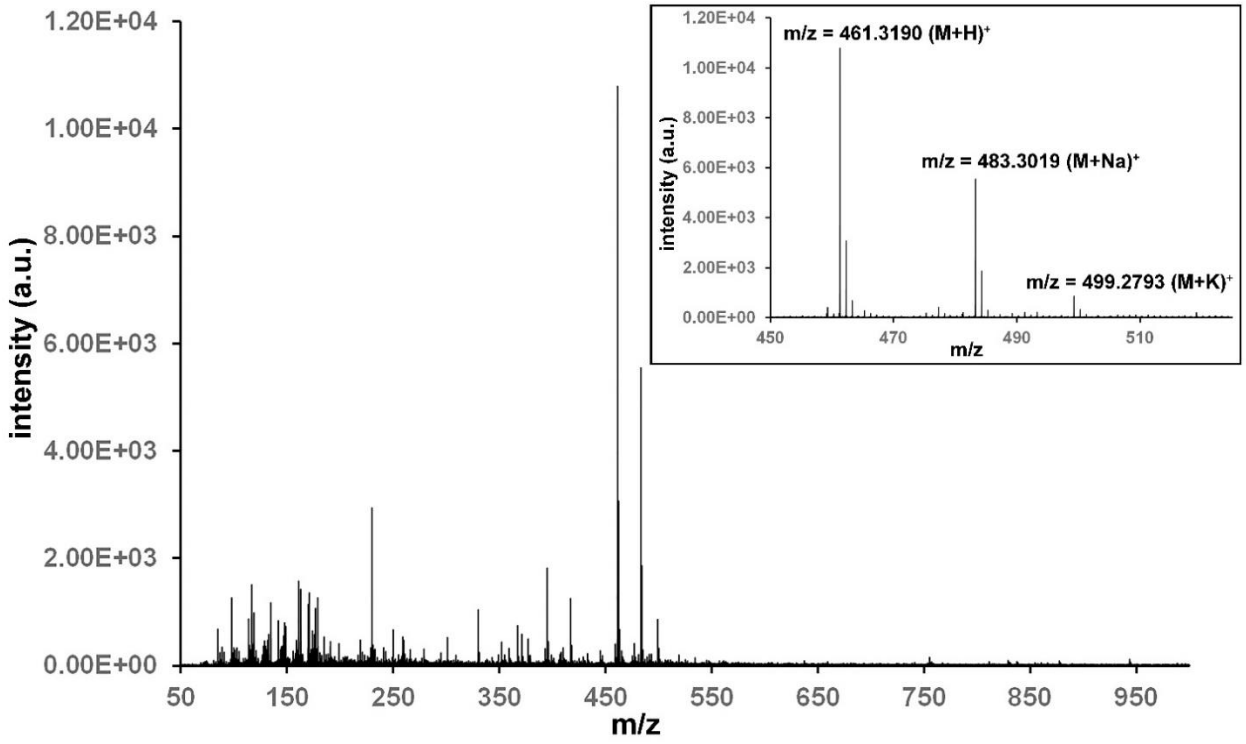
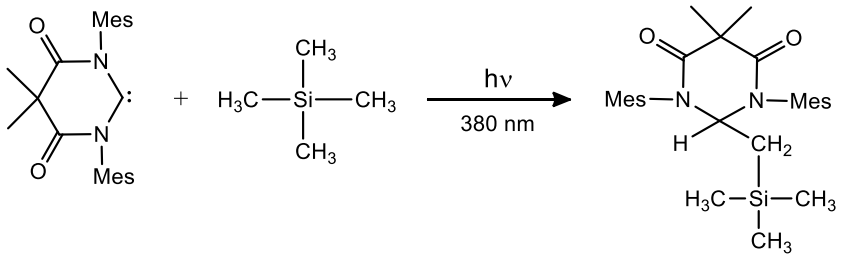


Figure S15. HRMS (ESI) of **4** in CH_3CN.

Synthesis and Characterization of 5



A Schlenk tube was charged with DAC (0.05 g, 0.13 mmol) and dry tetramethylsilane (1 mL) was added. The mixture was irradiated at 380 nm for four days. Volatiles were removed under reduced pressure to yield the crude product as an off-white solid (0.047 mg, 0.10 mmol, 76 % yield, 75 % purity based on ^{1}H NMR) which was then brought into a glovebox. The solid was dissolved in pentane, filtered through a Celite plug, and placed in the freezer overnight to precipitate out the impurity. The pentane solution was filtered, and the solvent removed *in vacuo* to yield an off-white solid. This process was repeated twice more until no further solid precipitated from the cold pentane solution. The final product was isolated after the third precipitation attempt as an off-white

solid (0.025 g, 0.053 mmol, 41 % yield, 85 % purity by ^{1}H NMR). ^{1}H NMR (500 MHz, C_6D_6) δ 6.74 – 6.70 (d, *J = 19.7* Hz, 4H), 5.32 (t, *J = 4.7* Hz, 1H), 2.26 (s, 6H), 2.17 (s, 6H), 2.06 (s, 6H), 1.87 (s, 3H), 1.83 (s, 3H), 1.32 – 1.31 (d, *J = 4.6* Hz, 2H), -0.64 (s, 9H). ^{13}C NMR (500 MHz, C_6D_6) δ 170.08, 137.98, 137.85, 135.66, 134.76, 130.18, 130.11, 70.37, 64.19, 46.54, 40.80, 36.13, 30.57, 24.86, 20.76, 19.69, 18.87, -1.83. HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{41}N_2O_2Si_1$: 465.2932; found: 465.2935.

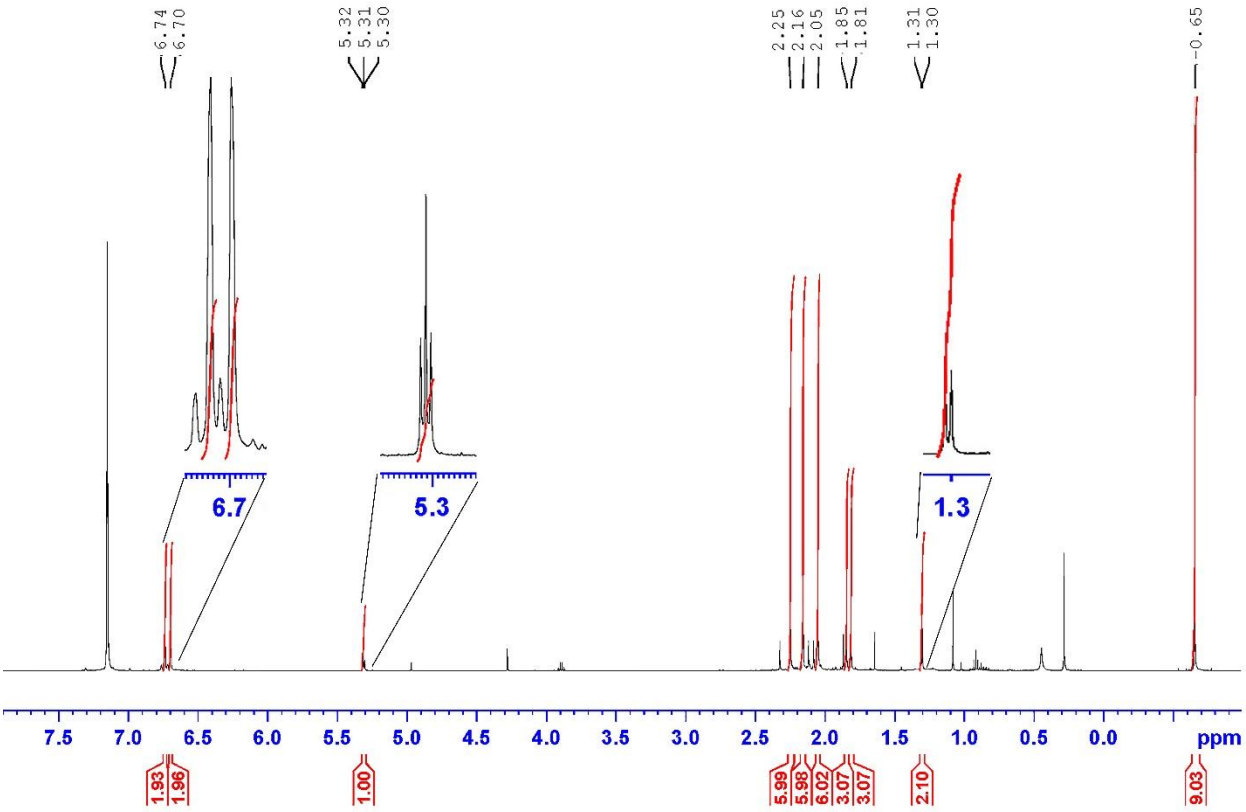


Figure S16. ^{1}H NMR spectrum of **5** in C_6D_6 (minor impurities are present).

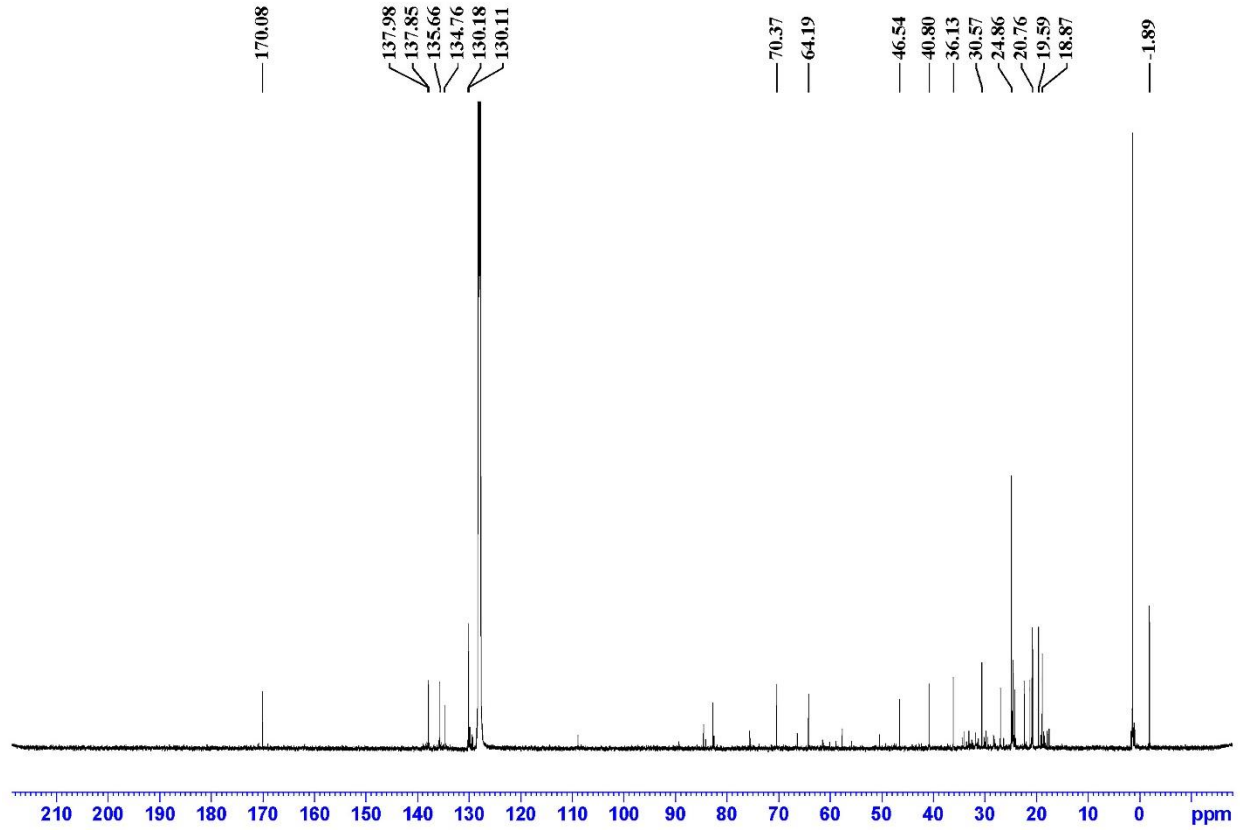


Figure S17. ^{13}C NMR spectrum of **5** in C_6D_6 (peaks corresponding to impurities are not denoted).

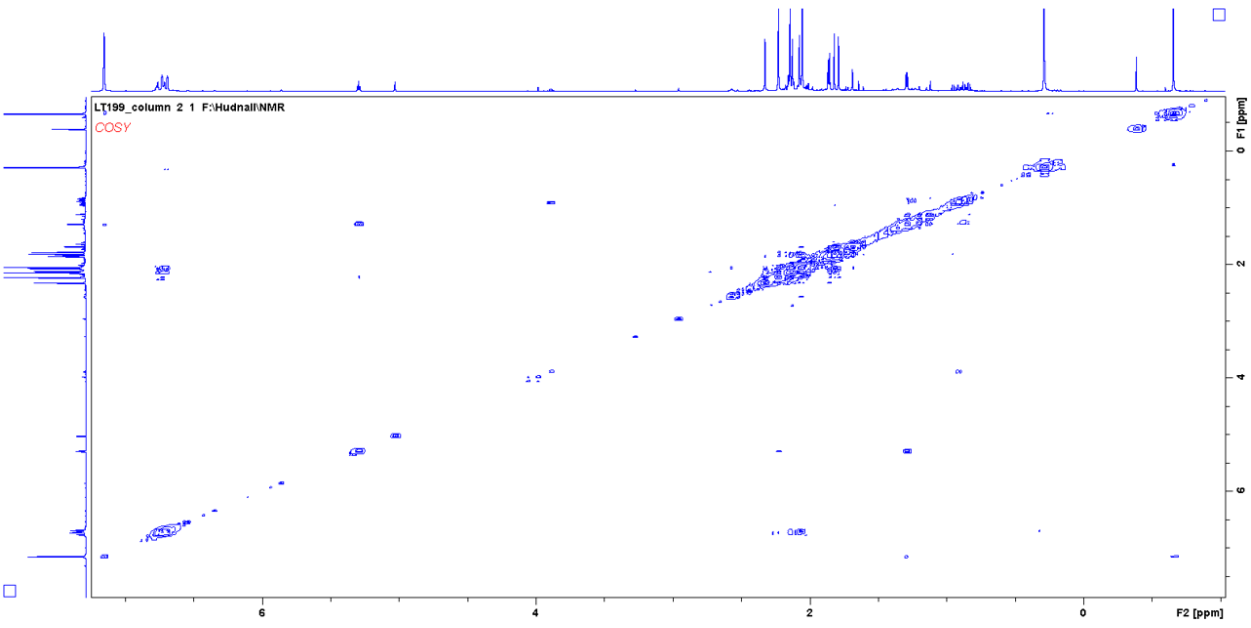


Figure S18. Full COSY NMR spectrum of **5** in C_6D_6.

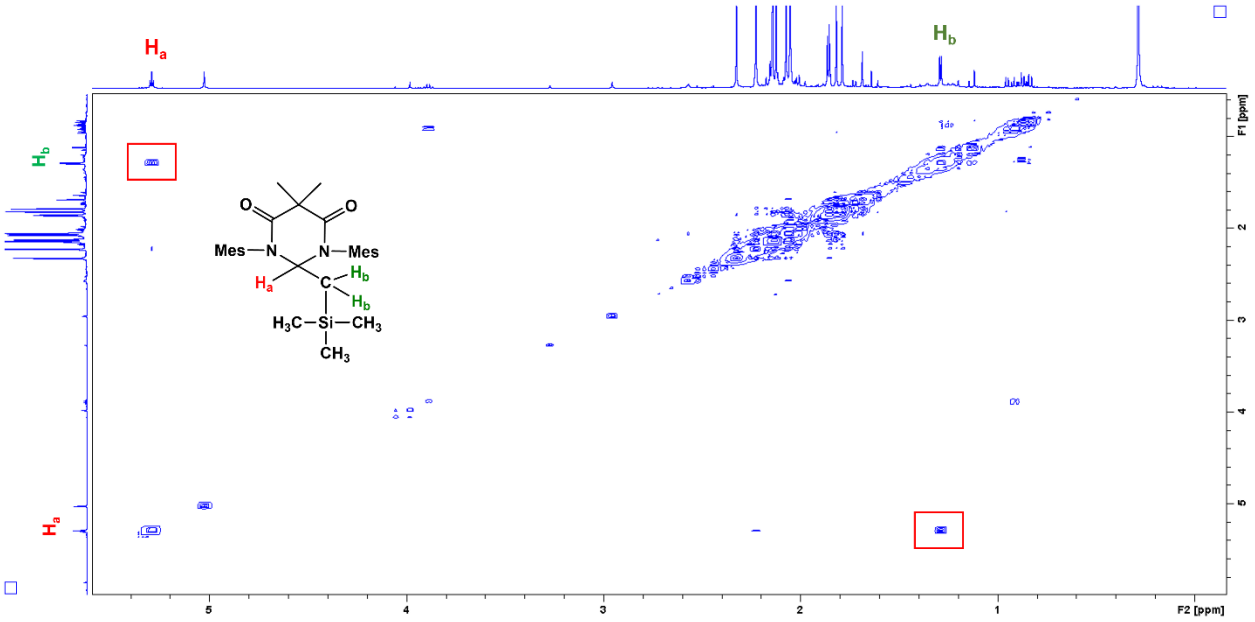


Figure S19. COSY NMR spectrum (0 to 5.6 ppm) of **5** in C_6D_6.

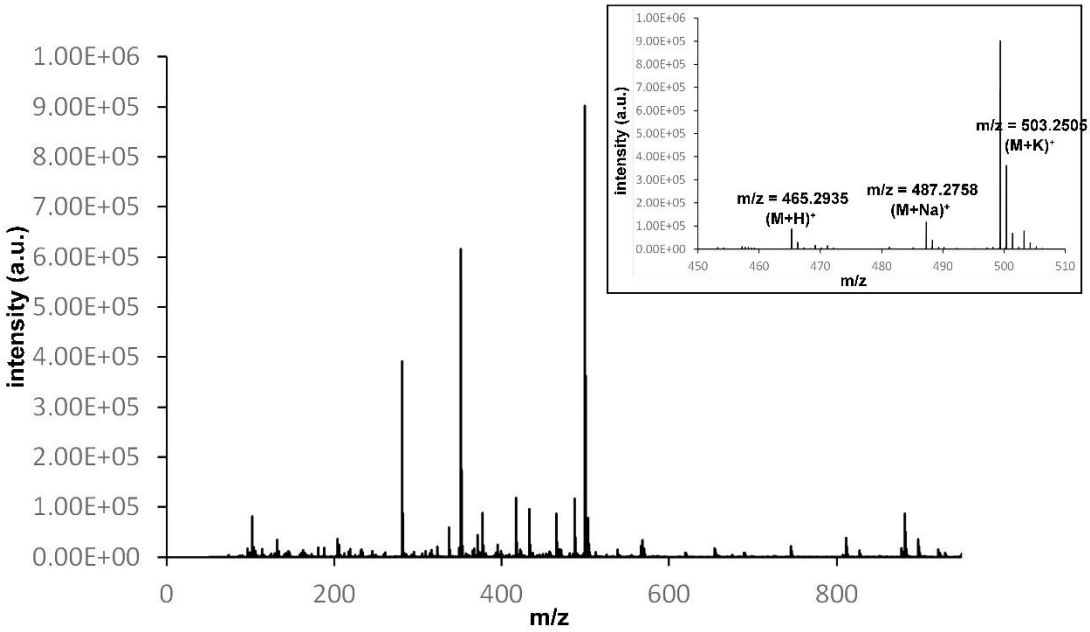
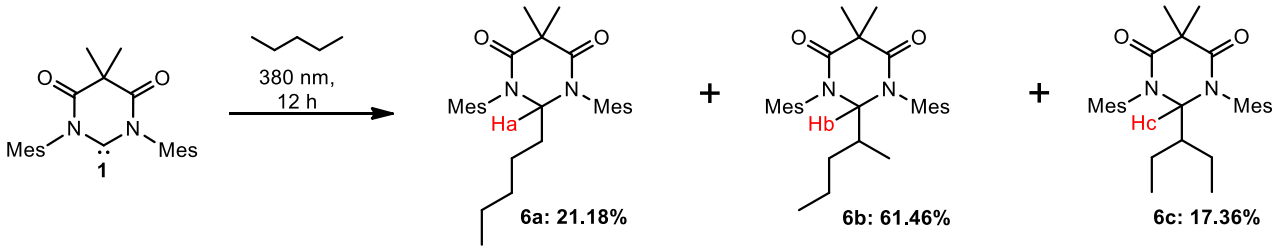


Figure S20. HRMS (ESI) of **5** in CH_3CN, several unknown species are also present due to 85% purity of compound **5**.

Synthesis and Characterization of 6a-c



Chemical Formula: $C_{29}H_{40}N_2O_2$, m/z = 449.3168 (M+H) and 471.2988 (M+Na)

A 50 mL Schlenk tube equipped with a Teflon stopper was charged with DAC (0.150 g, 0.40 mmol) and dry *n*-pentane (1 mL) inside of a nitrogen-filled glove box. The tube was then removed from the box, and the resulting suspension was then irradiated at 380 nm for 12 hours. After irradiation it was noted that the volume of pentane appeared to decrease and the majority of the solid had dissolved to give a yellowish solution and a white insoluble material. The yellow supernatant solution was separated by filtration and all volatiles removed in vacuo to give the isomeric mixture of compounds **6a**, **6b** and **6c** (0.156 g, 87.3% yield). Based on ^{1}H NMR and DFT studies, the ratio of 6a:6b:6c was determined to be 1.22:3.54:1.00. For the ^{1}H NMR, the mixture was treated as a single product for integration purposes to show that all protons add up the approximately 40 (molecular formula for compounds **6**: $C_{29}H_{40}N_2O_2$). ^{1}H NMR (500 MHz, C_6D_6) δ 6.66-6.75 (4 singlets at 6.66, 6.70, 6.72, and 6.75, 4H, MesC-*H*), the following three peaks were all integrated as a single signal (for a total of 1H) in the NMR shown below: 5.57 (d, *J* = 1.45 Hz, 1H, *Hc* from compound **6c**), 5.40 (d, *J* = 1.65 Hz, 1H, *Hb* from compound **6b**), 5.37 (t, *J* = 6.2 Hz, 1H, *Ha* from compound **6a**), the entire aliphatic region was integrated as a single signal for a total of ~36H with selected peaks listed here: 2.32 (s), 2.30 (s), 2.15 (s), 2.14 (s), 2.07 (s), 2.06 (s), 1.92 (s) 1.91 (s), 1.87 (s), 1.81 (s), 1.20 (s), 0.77 (d, *J* = 10.0 Hz), 0.48 (t, J = 5.0 Hz), 0.45 (t, J = 5.0 Hz). HRMS (ESI): $[M+H]^+$ calcd. for $C_{29}H_{41}N_2O_2$: 449.3168; found: 449.3166, and $[M+Na]^+$calcd. for $C_{29}H_{40}N_2O_2Na$: 471.2988; found: 471.2987.

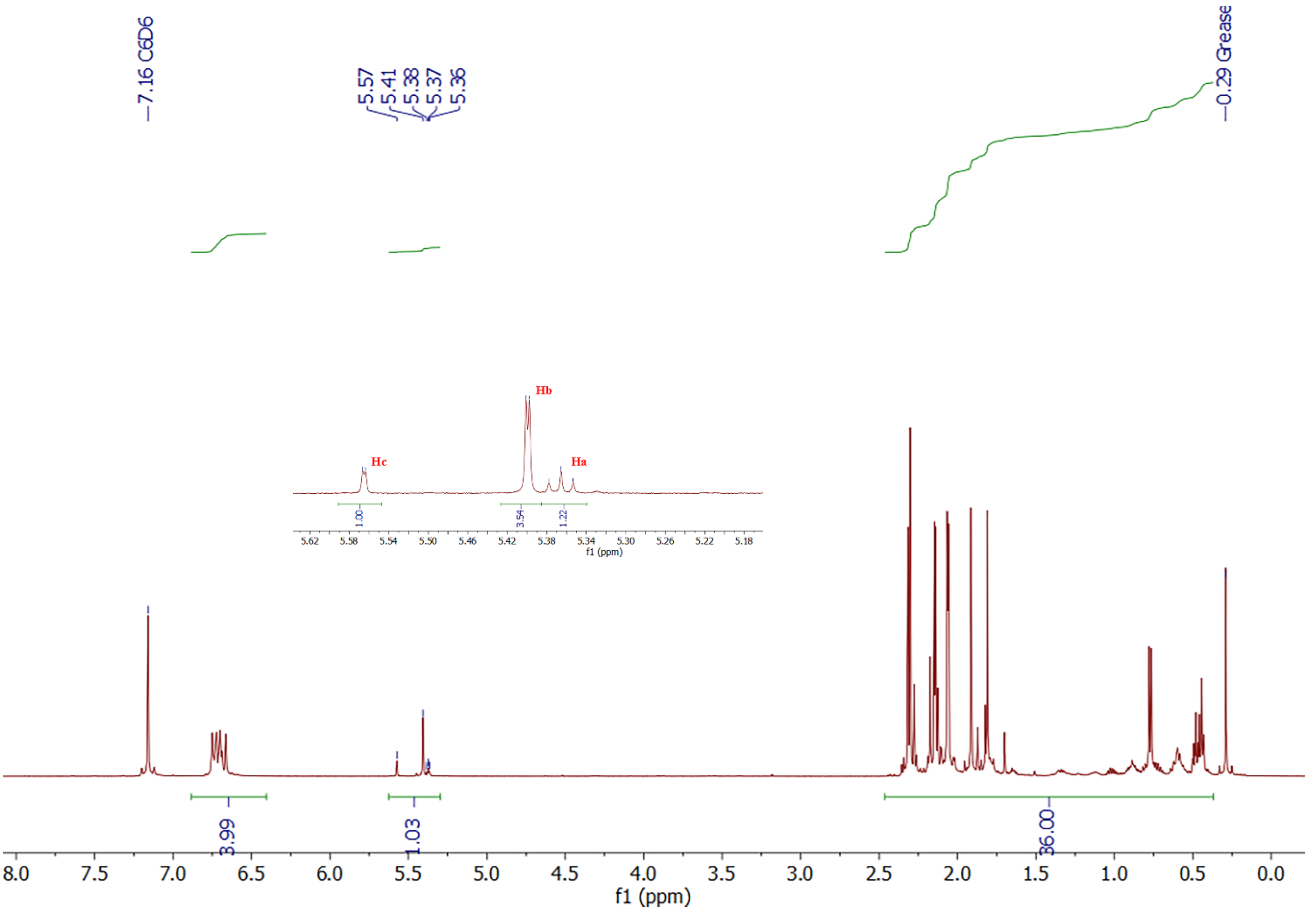


Figure S21. ^{1}H NMR spectrum of isomeric mixture of **6** in C_6D_6.

Assignment of ^{1}H NMR spectrum of 6a-6c using DFT methods

As described in the main text, the signals corresponding to Hb and Hc (for compounds **6b** and **6c**, respectively) were assigned using DFT methods (see computational chemistry section for more detail.) The calculated data and the experimental data are provided in Table S1 below. The calculated NMR shifts were all within 0.1 ppm of the experimental chemical shifts in the ^{1}H NMR spectrum. Optimization of **6b** and **6c** showed that the dihedral angle between the Hb or Hc and their vicinal protons were 78.29° and 80.02°, respectively. When inputted into the Karplus equation, small coupling constants of 1.22 and 1.16 Hz for Hb and Hc, respectively were calculated. These values were in good agreement with the experimental coupling constants of 1.65 and 1.45 Hz for **6b** and **6c**, respectively.

Table S1. Selected experimental and calculated ^{1}H NMR data (C_6D_6) for compounds **6a-c**.

Proton	Exp. Chemical Shift (ppm)	Calc. Chemical Shift (ppm)	Delta of exp. vs. calc. chemical shift (ppm)	Exp. $^{3}J_{H-H}$ (Hz)	Calc. $^{3}J_{H-H}$ (Hz)	Delta of exp. vs. calc. $^{3}J_{H-H}$ (Hz)	Calc. Dihedral Angle (°)
Ha	5.366	5.276	0.090	6.2	6.14	0.06	166/79
Hb	5.399	5.301	0.098	1.65	1.22	0.43	78.29
Hc	5.565	5.459	0.106	1.45	1.16	0.29	80.02

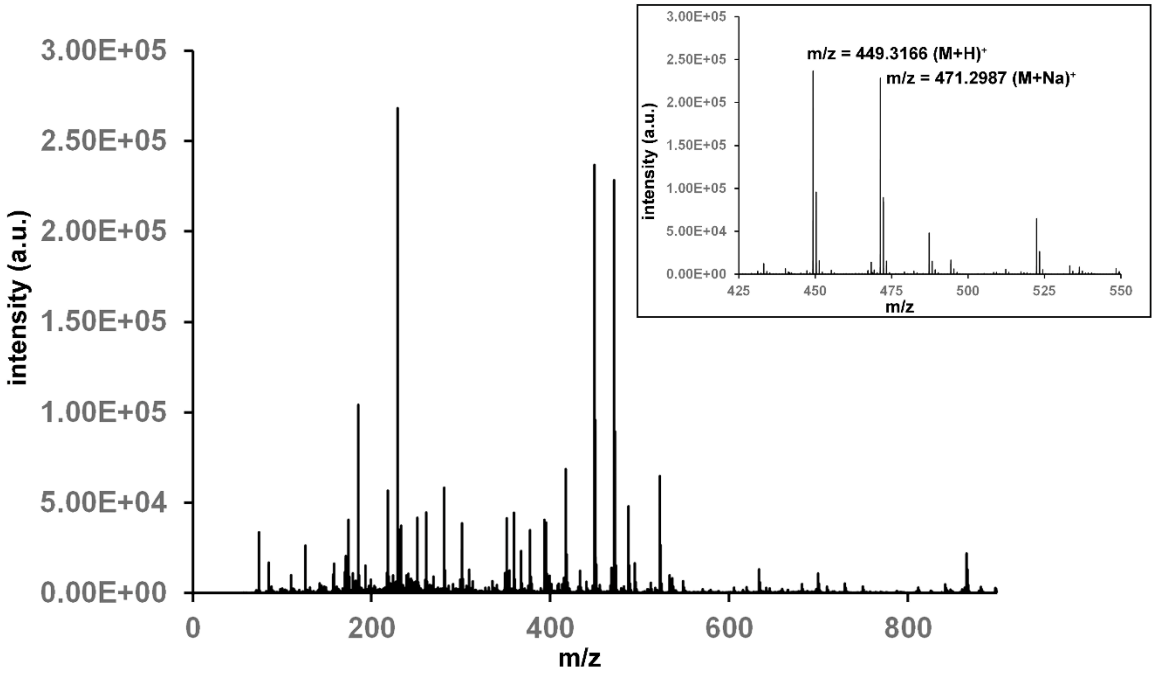


Figure S22. HRMS (ESI) of **6** in CH_3CN, small peaks corresponding to [M+K]+ and [M+DMFH]+ are also observed at m/z = 487.2770 and 522.2059, respectively.

Crystallography:

Single Crystal X-ray Diffraction:

General Considerations: A small colorless block-like crystal of **2** with dimensions 0.19 x 0.15 x 0.10 mm^3 and a small yellow plate-like crystal of **3** with dimensions 0.12 x 0.06 x 0.03 mm^3 were secured to Mitegen micromounts using Paratone oil and mounted on a dual-source Rigaku Oxford Diffraction (ROD) Synergy-S X-ray diffractometer. Reflection data were collected at 100 K using microfocused Cu $K_{\alpha 1}$ radiation (= 1.54184 Å) and a Pilatus P200K Hybrid Photon Counting (HPC) detector for **2** and a HyPix-6000HE HPC detector for **3**. For the crystalline samples, data collection strategies to ensure completeness and desired redundancy were determined using CrysAlis^{Pro} [1,2]. Data processing for all samples was done using CrysAlis^{Pro} and included a numerical absorption correction on **2** a multi-scan absorption correction on **3** applied using the SCALE3 ABSPACK scaling algorithm [3]. Both structures were solved via intrinsic phasing methods using ShelXT [4] and refined with ShelXL [5] within the Olex2 graphical user interface [6]. Space groups were unambiguously verified by PLATON [7]. The final structural refinement included anisotropic temperature factors on all constituent non-hydrogen atoms. Hydrogen atoms for **3** were located in the difference map and freely-refined while within **2** they were attached via the riding model at calculated positions using suitable HFIX commands. Within the structural model for **2**, qualitative indicators suggesting disorder within the bromonaphthalene were observed. The occupancy ratios for the two bromonaphthalene configurations were set to 50:50 with respect to one another after being split and the commands SIMU, RIGU, and EADP used to attain reasonable bond distances and thermal parameters. Additionally, for **2**, a solvent mask was applied to regions of electron density presumed to be interstitial CH_2Cl_2 solvent molecules whose disorder could not be satisfactorily modeled. Key details of the crystal and structure refinement data are summarized in Table S2. Further crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **2** and **3** were assigned as 2201799 and 2201797, respectively.

Single Crystal Electron Diffraction:

General Considerations: To ensure collection of complete data, data collections on multiple crystalline, nanometer size grains of compound **4** were completed at room temperature using a Synergy-ED electron diffractometer equipped with a HyPix-ED detector optimized for operation in the electron diffraction experimental setup and a 200kV electron source at a wavelength of 0.025 Å. Data collection strategies for the individual grains and the merging of their respective datasets to achieve complete, redundant data were completed using CrysAlis^{Pro}.[3] Data processing was done using CrysAlis^{Pro3} and included multi-scan absorption corrections applied using the SCALE3 ABSPACK scaling algorithm.[4] All structures were solved via intrinsic phasing methods using ShelXT[5] and refined with ShelXL[6] within the Olex2 graphical user interface.[7] Space groups were unambiguously verified by PLATON.[8] The final structural refinement included anisotropic temperature factors on all constituent non-hydrogen atoms. Hydrogen atoms were attached via the riding model at calculated positions using suitable HFIX commands. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF file which was deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **4** was assigned as 2201798.

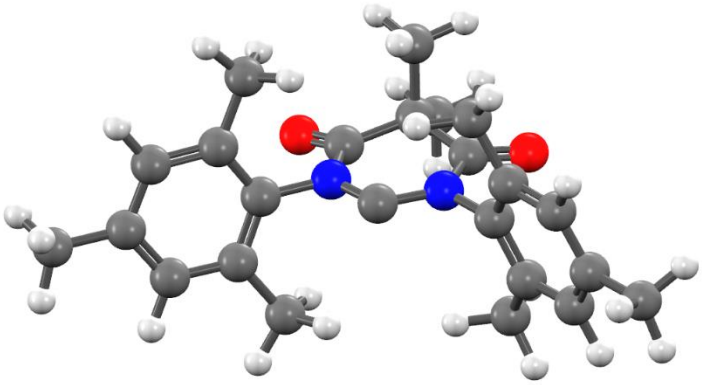
Table S2. Crystal Data, Data Collection and Structure Refinement for **2**, **3**, and **4.**

Compound	**2**	**3**	**4**
CCDC code	2201799	2201797	2201798
Formula	$C_{58}H_{63}BrN_4O_4$	$C_{53}H_{61}N_5O_4$	$C_{30}H_{40}N_2O_2$
Formula weight	960.03	832.06	460.66
Temp.	100(2)	100(2)	293(2)
Space group	*I2/a*	*P2₁/c*	*P2₁/n*
a, Å	14.89710(10)	13.6441(2)	9.56(13)
b, Å	23.3372(2)	13.8612(2)	19.48(12)
c, Å	33.3618(3)	25.1810(5)	15.5(3)
α, deg	90.00	90.00	90.00
β, deg	92.4690(10)	103.1817(19)	94.1(2)
γ, deg	90.00	90.00	90.00
volume, Å^3	11587.68(16)	4636.84(14)	2879(67)
Z	8	4	4
Density (calculated), mg/m^3	1.101	1.192	1.063
μ, mm^{-1}	1.309	0.594	0.000
Scan	*ω* scan	*ω* scan	*Continuous Rotation*
***θ* range for data collection, deg**	5.841-66.600	6.287-66.589	0.099-0.749
Reflections measured	31898	27365	22427
Independent observed reflns.	10182	8177	3387
Independent reflns. [*I*>2σ]	9552	6821	2054
Data/restraints/parameters	10182/114/707	8177/0/803	3387/0/316
R_{int}	0.0311	0.0513	0.0988
Final *R* Indices [*I*>2σ]	R_1 = 0.0518,	R_1 = 0.0431,	R_1 = 0.1648,
	*wR*2 = 0.1375	*wR*2 = 0.1147	*wR*2 = 0.3778
***R* Indices (all data)**	R_1 = 0.0541	R_1 = 0.0527,	R_1 = 0.2325,
	*wR*2 = 0.1389	*wR*2 = 0.1206	*wR*2 = 0.4085
Goodness-of-fit on *F²*	1.068	1.054	2.063

DFT Calculations:

Probable thermal (singlet) and photochemical (triplet) intermediates for the formation of compound **3** starting from pyridine and singlet DAC **1** (**1**^{S}) which have been defined as the zero-point energy were calculated using the Q-Chem 5-package[9] with the wB97x-D functional and 6-31G*/cc-pvtz basis sets for the optimization/energy calculations, respecitively.[10, 11] All calculations were performed with unrestricted = true and there was minimal spin contamination observed in the triplet states (S^2 ~ 2.07). Optimized structures and GAIO-SCF (benzene) NMR calculations for compounds **6a-6c** were performed using Gaussian09[12] with the B3LYP[13] functional and 6-31G+g[14] basis set for all atoms.

Optimized geometry and Z-matrix (X,Y,Z coordinates) for 1^{S}:

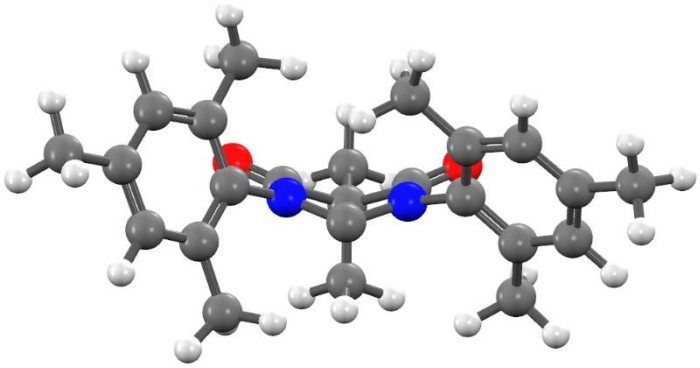


Z-Matrix For 1S			
	X	Y	Z
C	-7.9253	-0.76542	0.39898
C	-6.58645	-0.94575	-0.25533
C	-6.49139	-0.95019	-1.64544
H	-7.39238	-0.81275	-2.23369
C	-5.2546	-1.09734	-2.29138
C	-5.28772	-0.99124	-3.79845
C	-4.06283	-1.27301	-1.51697
N	-2.77424	-1.40718	-2.14558
C	-4.17748	-1.27091	-0.09062
C	-3.01882	-1.48396	0.85698
C	-5.43249	-1.10107	0.51126
H	-5.50983	-1.10183	1.59293
C	3.59414	2.75012	0.09457
C	2.56201	1.86967	-0.54771

C	1.40878	2.43683	-1.08863
H	1.28142	3.51314	-1.048
C	0.42003	1.64211	-1.68727
C	-0.76229	2.37432	-2.27493
C	0.58391	0.22532	-1.74214
N	-0.44418	-0.61064	-2.29973
C	1.76635	-0.34594	-1.17701
C	2.0352	-1.83037	-1.09158
C	2.73664	0.48653	-0.60053
H	3.62709	0.04612	-0.16569
C	-1.75658	-0.47302	-1.70045
C	-0.17497	-1.49918	-3.30246
C	-2.53853	-2.35087	-3.10754
C	-1.20855	-2.47682	-3.82267
C	-0.66679	-3.90705	-3.61236
C	-1.4322	-2.22164	-5.32691
O	-3.42331	-3.14565	-3.4067
O	0.94059	-1.51981	-3.80922
H	-7.84525	-0.7732	1.50699
H	-8.60594	-1.5864	0.09063
H	-8.36354	0.20658	0.0883
H	-4.29444	-0.99126	-4.2793
H	-5.75849	-0.02748	-4.08582
H	-5.89464	-1.82158	-4.21874
H	-2.05921	-1.72634	0.36947
H	-3.24266	-2.34816	1.51715
H	-2.88224	-0.58002	1.48823
H	4.45175	2.16079	0.48369
H	3.13608	3.29946	0.94434
H	3.97766	3.48152	-0.64698
H	-1.47464	1.7264	-2.81599
H	-0.39866	3.11697	-3.01629
H	-1.3072	2.9114	-1.46982
H	1.21109	-2.46604	-1.45728
H	2.18516	-2.11327	-0.02827
H	2.95728	-2.07721	-1.65944
H	-0.5055	-4.1065	-2.5306
H	0.3001	-4.04941	-4.14234
H	-1.37833	-4.66558	-4.00467
H	-1.82035	-1.19274	-5.49114
H	-2.16599	-2.94292	-5.74803

H	-0.48382	-2.33252	-5.89594

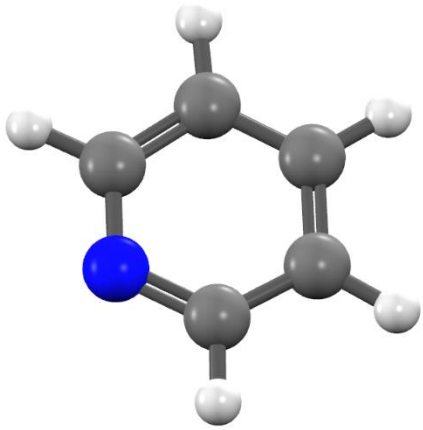
Optimized geometry and Z-matrix (X,Y,Z coordinates) for 1^T:



Z-Matrix for 1T			
	X	Y	Z
C	-7.56386	-0.76325	0.79268
C	-6.29552	-0.94165	-0.01095
C	-6.34219	-0.96697	-1.40809
H	-7.30249	-0.85613	-1.91317
C	-5.19107	-1.12358	-2.17982
C	-5.26702	-1.15145	-3.68713
C	-3.96719	-1.26801	-1.51083
N	-2.75691	-1.4029	-2.28259
C	-3.87931	-1.25403	-0.11452
C	-2.55417	-1.44456	0.583622
C	-5.05777	-1.08499	0.61684
H	-5.00449	-1.07439	1.705676
C	3.25283	2.740385	0.352383
C	2.283159	1.838277	-0.37709
C	1.516179	2.335286	-1.43625
H	1.628047	3.378164	-1.73514
C	0.616936	1.527894	-2.13003
C	-0.18144	2.078237	-3.28984
C	0.486032	0.188584	-1.73098
N	-0.47193	-0.64059	-2.4208
C	1.241449	-0.34986	-0.68329
C	1.140793	-1.80314	-0.28902
C	2.135381	0.498892	-0.02099
H	2.730695	0.094104	0.797891

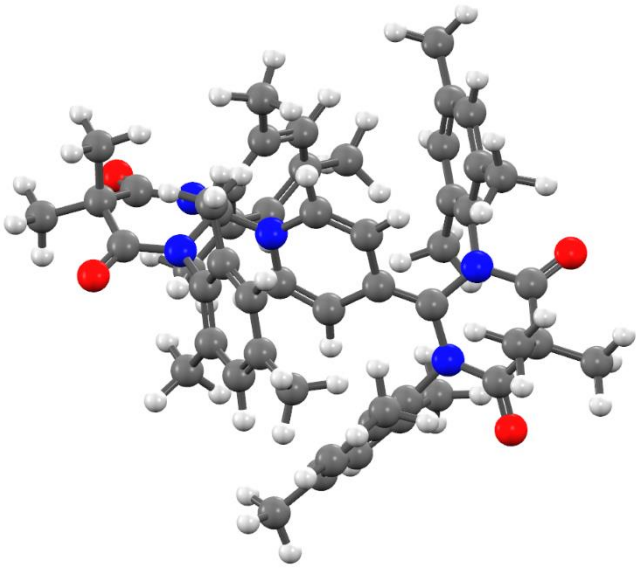
C	-1.82859	-0.37801	-2.31722
C	-0.07626	-1.70328	-3.2306
C	-2.48805	-2.5403	-3.04137
C	-1.23936	-2.42354	-3.93473
C	-0.78821	-3.82048	-4.36219
C	-1.62744	-1.5777	-5.17446
O	-3.20695	-3.52239	-3.01442
O	1.091386	-2.01992	-3.36225
H	-7.35842	-0.77409	1.868862
H	-8.282	-1.56461	0.577106
H	-8.05262	0.189424	0.551228
H	-4.51255	-0.49288	-4.13666
H	-6.25471	-0.82542	-4.03076
H	-5.08811	-2.16837	-4.05877
H	-2.09124	-2.39214	0.278103
H	-2.68837	-1.46661	1.670565
H	-1.8466	-0.63846	0.344857
H	3.768483	2.2037	1.156449
H	2.734399	3.599754	0.796599
H	4.014077	3.134652	-0.33298
H	-0.07719	1.43914	-4.17638
H	0.163122	3.085007	-3.54965
H	-1.25232	2.1353	-3.05455
H	0.112581	-2.17323	-0.36902
H	1.481489	-1.94935	0.742104
H	1.76017	-2.41605	-0.95492
H	-0.52301	-4.42925	-3.49096
H	0.091643	-3.74196	-5.00762
H	-1.59977	-4.32368	-4.89638
H	-1.93633	-0.5619	-4.89651
H	-2.45461	-2.06309	-5.70672
H	-0.76732	-1.50959	-5.85147

Optimized geometry and Z-matrix (X,Y,Z coordinates) for pyridine:



Z-Matrix for pyridine			
	X	Y	Z
N	-2.98595	-0.02825	-0.20355
C	-3.96807	-0.78514	-0.83446
H	-4.78812	-0.28771	-1.36206
C	-3.90806	-2.17433	-0.79473
H	-4.68095	-2.76995	-1.2911
C	-2.86605	-2.80688	-0.12427
H	-2.81892	-3.90007	-0.09305
C	-1.8841	-2.04996	0.50665
H	-1.06429	-2.5477	1.03436
C	-1.94403	-0.66071	0.46697
H	-1.17132	-0.06506	0.96334

Optimized geometry and Z-matrix (X,Y,Z coordinates) for compound 3:



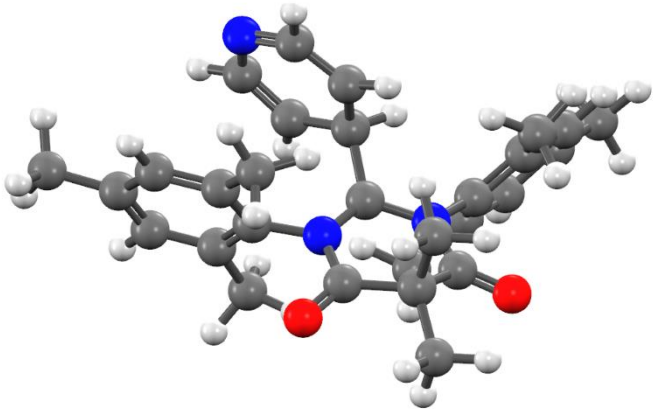
Z-Matrix for 3			
	X	Y	Z
C	-8.12785	-0.74895	0.94941
C	-6.72641	-0.83362	0.42092
C	-6.38452	-0.12805	-0.73536
H	-7.13435	0.47668	-1.23343
C	-5.08815	-0.19447	-1.2598
C	-4.7924	0.60182	-2.50616
C	-4.10607	-0.98448	-0.60797
N	-2.79114	-1.08778	-1.16926
C	-4.45351	-1.7045	0.56189
C	-3.47805	-2.59993	1.28002
C	-5.76017	-1.61663	1.0641
H	-6.02811	-2.17297	1.95401
C	4.14516	2.80019	0.14307
C	2.97204	1.9236	-0.18521
C	1.7633	2.49642	-0.58684
H	1.68371	3.57324	-0.66365
C	0.65952	1.70051	-0.92205
C	-0.57462	2.42077	-1.40845
C	0.76193	0.28289	-0.84391
N	-0.35328	-0.54855	-1.22967
C	1.99779	-0.29425	-0.42714
C	2.2071	-1.78096	-0.27695
C	3.08066	0.53418	-0.10523

H	4.01673	0.08895	0.21212
C	-1.63727	-0.47149	-0.54911
C	-0.20016	-1.32072	-2.35138
C	-2.65529	-1.87536	-2.28142
C	-1.32878	-2.11518	-2.96675
C	-0.98028	-3.61487	-2.88333
C	-1.47242	-1.69316	-4.44603
O	-3.63909	-2.44326	-2.74589
O	0.88731	-1.36197	-2.91871
H	-8.25788	-1.36106	1.86678
H	-8.83788	-1.11773	0.17871
H	-8.37277	0.30646	1.19175
H	-3.73906	0.52022	-2.83951
H	-4.99487	1.67648	-2.3145
H	-5.44487	0.25361	-3.33445
H	-2.48916	-2.65471	0.78567
H	-3.88385	-3.63253	1.32124
H	-3.32283	-2.22699	2.31064
H	5.03739	2.20366	0.42784
H	3.8941	3.46484	0.99168
H	4.40684	3.4188	-0.74154
H	-1.38987	1.74922	-1.73199
H	-0.31119	3.03982	-2.2923
H	-0.96093	3.08549	-0.60716
H	1.2994	-2.37724	-0.49043
H	2.49923	-2.00396	0.77136
H	3.02017	-2.11583	-0.95457
H	-0.87766	-3.92695	-1.82057
H	-0.0222	-3.8318	-3.40365
H	-1.77212	-4.23651	-3.35427
H	-1.72025	-0.61186	-4.51995
H	-2.27539	-2.273	-4.95073
H	-0.5305	-1.87639	-5.00749
N	-1.60855	1.09626	3.36734
C	-0.61368	0.19924	2.86176
H	0.20065	-0.14166	3.49584
C	-0.6707	-0.26716	1.61039
H	0.09634	-0.97607	1.3268
C	-1.7403	0.11479	0.66832
C	-2.65894	0.94313	1.1819
H	-3.48898	1.28196	0.57294

C	-2.58282	1.4544	2.58851
H	-3.35628	2.12501	2.94077
H	-5.26799	-0.02091	3.28654
C	-3.84568	-4.61583	5.13901
C	-3.51296	-3.15737	5.25675
C	-2.31088	-2.76573	5.85032
H	-1.63679	-3.52545	6.23018
C	-1.97795	-1.40952	5.9869
C	-0.70031	-1.0928	6.71988
C	-2.86466	-0.41539	5.49101
N	-2.55635	0.98349	5.60143
C	-4.09497	-0.82104	4.90239
C	-5.11263	0.1567	4.36954
C	-4.40047	-2.18376	4.79361
H	-5.3379	-2.48579	4.34133
C	2.02842	6.00646	1.23174
C	1.15644	5.19547	2.14786
C	1.72546	4.26897	3.024
H	2.80193	4.14424	3.03007
C	0.93584	3.53461	3.92602
C	1.68363	2.64876	4.88746
C	-0.47856	3.71645	3.93471
N	-1.3435	3.01368	4.852
C	-1.04739	4.66026	3.0242
C	-2.52851	4.94212	2.92587
C	-0.22401	5.38103	2.15196
H	-0.66815	6.10055	1.47297
C	-1.48155	1.5464	4.76379
C	-2.0019	3.75886	5.79617
C	-3.23777	1.7111	6.53603
C	-2.98186	3.1734	6.78104
C	-4.31935	3.9338	6.65318
C	-2.41746	3.34404	8.20716
O	-4.07124	1.15526	7.24469
O	-1.78009	4.96311	5.87748
H	-4.83188	-4.77358	4.65234
H	-3.87853	-5.07308	6.15053
H	-3.06986	-5.1282	4.53252
H	-0.55626	-0.01611	6.91773
H	0.16936	-1.4907	6.15637
H	-0.7305	-1.57414	7.72056

H	-4.81777	1.2144	4.49271
H	-6.07747	0.01479	4.89993
H	1.43118	6.71056	0.61381
H	2.59431	5.34697	0.54826
H	2.74756	6.59969	1.83476
H	1.063	2.23998	5.6985
H	2.45735	3.25269	5.4071
H	2.18608	1.8276	4.33318
H	-3.15167	4.33573	3.6057
H	-2.87687	4.73009	1.89324
H	-2.71814	6.0121	3.1563
H	-4.73887	3.81754	5.6307
H	-4.18113	5.01805	6.85652
H	-5.06492	3.55293	7.38463
H	-1.45383	2.79645	8.30699
H	-3.12269	2.94501	8.96807
H	-2.23393	4.41485	8.44111
H	-0.55243	1.10816	5.13204

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate A^{S1}:

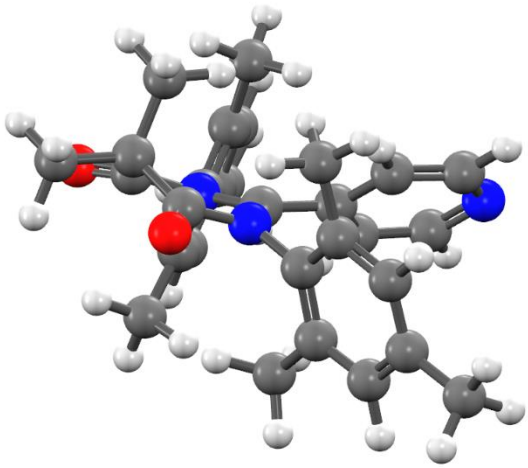


Z-Matrix for AS1			
	X	**Y**	**Z**
C	-7.93766	-1.03635	0.52877
C	-6.56195	-1.13806	-0.0617
C	-6.26568	-0.45179	-1.24297
H	-7.03483	0.1447	-1.72063
C	-4.99	-0.52704	-1.81715
C	-4.7452	0.22966	-3.09743

C	-3.98401	-1.30411	-1.19095
N	-2.68215	-1.39089	-1.77828
C	-4.28933	-2.01552	-0.00416
C	-3.28661	-2.89765	0.69148
C	-5.57385	-1.91846	0.55004
H	-5.80444	-2.46005	1.46027
C	4.07008	2.77459	-0.39946
C	2.93476	1.88381	-0.81104
C	1.87492	2.41277	-1.55277
H	1.88886	3.46165	-1.82711
C	0.80041	1.60569	-1.951
C	-0.29054	2.24686	-2.77005
C	0.78241	0.23196	-1.59169
N	-0.31152	-0.60826	-1.98732
C	1.86133	-0.30311	-0.83969
C	1.91045	-1.74291	-0.39439
C	2.92357	0.52964	-0.46062
H	3.74276	0.11862	0.11841
C	-1.64922	-0.42032	-1.40368
C	-0.08378	-1.54129	-2.96201
C	-2.47789	-2.3231	-2.75412
C	-1.15615	-2.48154	-3.47445
C	-0.66586	-3.93179	-3.27886
C	-1.37876	-2.20298	-4.9754
O	-3.39623	-3.0701	-3.07612
O	1.03064	-1.62559	-3.4681
H	-8.02842	-1.63122	1.46236
H	-8.68531	-1.41287	-0.20088
H	-8.16414	0.02459	0.76566
H	-3.70942	0.12003	-3.47618
H	-4.93533	1.31088	-2.9343
H	-5.43619	-0.14232	-3.88318
H	-2.30382	-2.91785	0.17883
H	-3.67229	-3.93789	0.7278
H	-3.13307	-2.54198	1.73187
H	4.83637	2.21994	0.18292
H	3.68386	3.60326	0.23078
H	4.55643	3.20074	-1.30203
H	-1.08483	1.53824	-3.07407
H	0.14639	2.66979	-3.69894
H	-0.76087	3.06616	-2.1866

H	1.01955	-2.32726	-0.69527
H	1.96876	-1.78336	0.71379
H	2.81029	-2.23434	-0.82064
H	-0.50272	-4.144	-2.19979
H	0.28989	-4.10601	-3.81921
H	-1.40819	-4.66021	-3.67151
H	-1.73251	-1.15899	-5.12485
H	-2.13894	-2.89264	-5.40201
H	-0.43789	-2.33798	-5.55155
N	-3.11086	1.40364	2.18594
C	-2.21835	0.29595	2.2889
H	-2.0305	-0.15337	3.25839
C	-1.62938	-0.20422	1.18801
H	-0.96242	-1.05711	1.27237
C	-1.86184	0.42939	-0.13754
C	-2.83298	1.36482	-0.20337
H	-3.1785	1.74155	-1.16124
C	-3.41925	1.91618	1.04166
H	-4.13162	2.73213	0.9898
H	-0.99512	1.05905	-0.19189

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate B^{S1}:

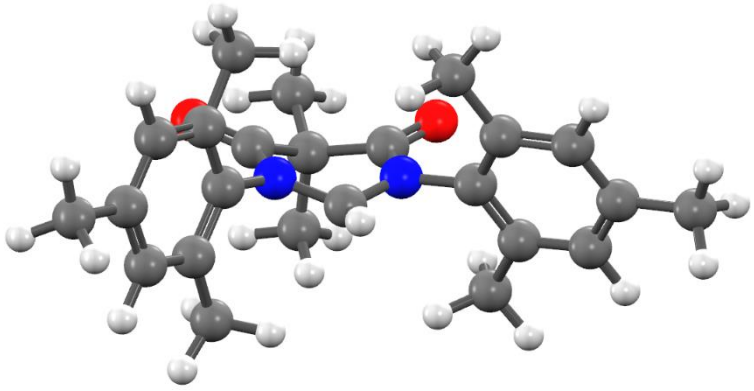


Z-Matrix for BS1			
	X	**Y**	**Z**
C	-7.93766	-1.03635	0.52877
C	-6.56195	-1.13806	-0.0617
C	-6.26568	-0.45179	-1.24297

H	-7.03483	0.1447	-1.72063
C	-4.99	-0.52704	-1.81715
C	-4.7452	0.22966	-3.09743
C	-3.98401	-1.30411	-1.19095
N	-2.68215	-1.39089	-1.77828
C	-4.28933	-2.01552	-0.00416
C	-3.28661	-2.89765	0.69148
C	-5.57385	-1.91846	0.55004
H	-5.80444	-2.46005	1.46027
C	4.07008	2.77459	-0.39946
C	2.93476	1.88381	-0.81104
C	1.87492	2.41277	-1.55277
H	1.88886	3.46165	-1.82711
C	0.80041	1.60569	-1.951
C	-0.29054	2.24686	-2.77005
C	0.78241	0.23196	-1.59169
N	-0.31152	-0.60826	-1.98732
C	1.86133	-0.30311	-0.83969
C	1.91045	-1.74291	-0.39439
C	2.92357	0.52964	-0.46062
H	3.74276	0.11862	0.11841
C	-1.64922	-0.42032	-1.40368
C	-0.08378	-1.54129	-2.96201
C	-2.47789	-2.3231	-2.75412
C	-1.15615	-2.48154	-3.47445
C	-0.66586	-3.93179	-3.27886
C	-1.37876	-2.20298	-4.9754
O	-3.39623	-3.0701	-3.07612
O	1.03064	-1.62559	-3.4681
H	-8.02842	-1.63122	1.46236
H	-8.68531	-1.41287	-0.20088
H	-8.16414	0.02459	0.76566
H	-3.70942	0.12003	-3.47618
H	-4.93533	1.31088	-2.9343
H	-5.43619	-0.14232	-3.88318
H	-2.30382	-2.91785	0.17883
H	-3.67229	-3.93789	0.7278
H	-3.13307	-2.54198	1.73187
H	4.83637	2.21994	0.18292
H	3.68386	3.60326	0.23078
H	4.55643	3.20074	-1.30203

H	-1.08483	1.53824	-3.07407
H	0.14639	2.66979	-3.69894
H	-0.76087	3.06616	-2.1866
H	1.01955	-2.32726	-0.69527
H	1.96876	-1.78336	0.71379
H	2.81029	-2.23434	-0.82064
H	-0.50272	-4.144	-2.19979
H	0.28989	-4.10601	-3.81921
H	-1.40819	-4.66021	-3.67151
H	-1.73251	-1.15899	-5.12485
H	-2.13894	-2.89264	-5.40201
H	-0.43789	-2.33798	-5.55155
N	-3.11086	1.40364	2.18594
C	-2.21835	0.29595	2.2889
H	-2.0305	-0.15337	3.25839
C	-1.62938	-0.20422	1.18801
H	-0.96242	-1.05711	1.27237
C	-1.86184	0.42939	-0.13754
C	-2.83298	1.36482	-0.20337
H	-3.1785	1.74155	-1.16124
C	-3.41925	1.91618	1.04166
H	-4.13162	2.73213	0.9898

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate B^{S2}:

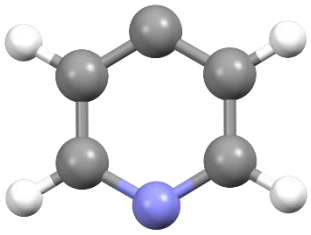


Z-Matrix for BS2			
	X	**Y**	**Z**
C	-7.97981	-0.87162	0.37949
C	-6.62708	-1.01485	-0.25497
C	-6.49055	-0.85525	-1.63392

H	-7.36729	-0.61976	-2.22744
C	-5.24019	-0.97336	-2.25806
C	-5.20541	-0.7128	-3.74485
C	-4.08443	-1.27783	-1.47797
N	-2.79046	-1.39933	-2.09112
C	-4.23505	-1.4415	-0.06926
C	-3.09989	-1.80559	0.85733
C	-5.50096	-1.30289	0.51827
H	-5.60903	-1.43302	1.58928
C	3.67249	2.83382	-0.09263
C	2.61523	1.92561	-0.64963
C	1.46986	2.47198	-1.22984
H	1.36481	3.55033	-1.27816
C	0.46334	1.65147	-1.7596
C	-0.70888	2.34897	-2.40517
C	0.60167	0.23457	-1.70217
N	-0.42897	-0.6215	-2.21842
C	1.77171	-0.31569	-1.09953
C	2.00396	-1.7969	-0.92135
C	2.76082	0.53815	-0.59045
H	3.64541	0.11401	-0.12858
C	-1.74827	-0.50264	-1.62841
C	-0.16497	-1.51519	-3.21785
C	-2.56027	-2.32368	-3.07183
C	-1.21336	-2.47145	-3.75797
C	-0.70771	-3.9135	-3.5442
C	-1.40145	-2.20292	-5.26496
O	-3.46117	-3.0826	-3.41135
O	0.95501	-1.55175	-3.71541
H	-7.93527	-1.02074	1.47939
H	-8.67445	-1.62484	-0.04825
H	-8.37923	0.14524	0.18057
H	-4.19089	-0.72906	-4.1818
H	-5.61357	0.29982	-3.94778
H	-5.83341	-1.46276	-4.27091
H	-2.1385	-1.99014	0.34542
H	-3.35145	-2.74671	1.39037
H	-2.95547	-0.99825	1.6062
H	4.5215	2.26042	0.33691
H	3.23612	3.46527	0.70987
H	4.06451	3.48943	-0.89831

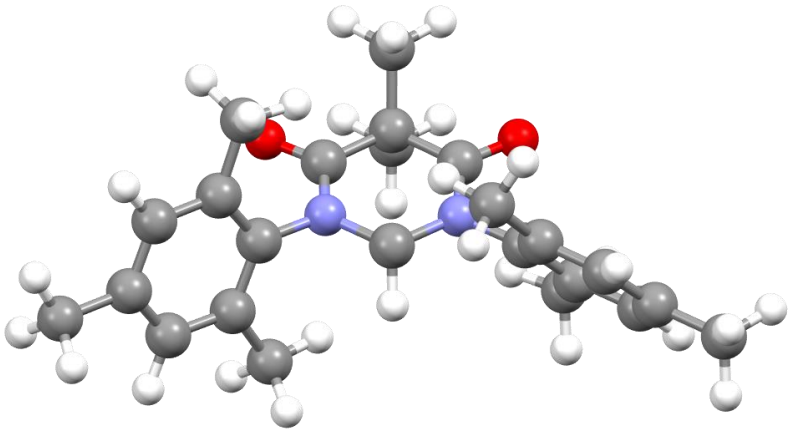
H	-1.43645	1.66363	-2.87652
H	-0.3377	3.01448	-3.21306
H	-1.23932	2.96562	-1.64913
H	1.16364	-2.42878	-1.2604
H	2.14219	-2.01757	0.15822
H	2.9213	-2.10052	-1.46865
H	-0.57143	-4.11931	-2.46004
H	0.26597	-4.07485	-4.05579
H	-1.42867	-4.6544	-3.95263
H	-1.76359	-1.16468	-5.43018
H	-2.14166	-2.90549	-5.7057
H	-0.44455	-2.33125	-5.81581
H	-1.94563	0.23261	-0.81671

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate A^{T1}:



Z-Matrix for AT1			
	X	**Y**	**Z**
N	-2.98595	-0.02825	-0.20355
C	-3.96807	-0.78514	-0.83446
H	-4.78812	-0.28771	-1.36206
C	-3.90806	-2.17433	-0.79473
H	-4.68095	-2.76995	-1.2911
C	-2.86605	-2.80688	-0.12427
C	-1.8841	-2.04996	0.50665
H	-1.06429	-2.5477	1.03436
C	-1.94403	-0.66071	0.46697
H	-1.17132	-0.06506	0.96334

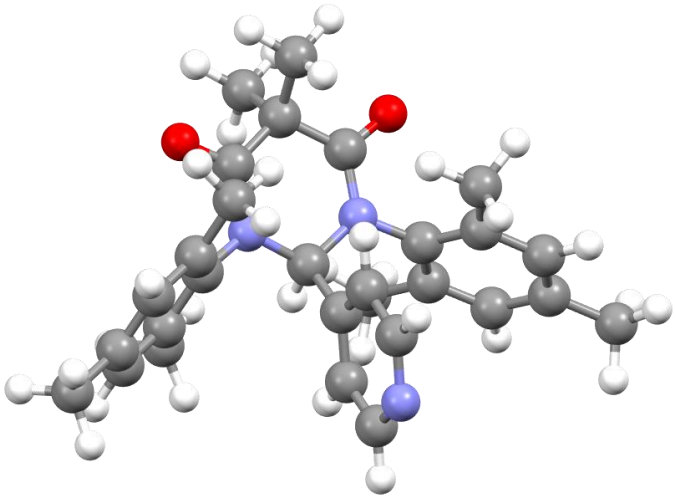
Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate A^{T1}:



Z-Matrix for AT2			
	X	Y	Z
C	-7.94897	-1.03128	0.4597
C	-6.60093	-1.12782	-0.19329
C	-6.4823	-0.91062	-1.56594
H	-7.36884	-0.66462	-2.1404
C	-5.23751	-0.98404	-2.2071
C	-5.2218	-0.66099	-3.68203
C	-4.06873	-1.30234	-1.45219
N	-2.78084	-1.37673	-2.08484
C	-4.19979	-1.52139	-0.04981
C	-3.04611	-1.89744	0.84825
C	-5.46142	-1.42759	0.55623
H	-5.5553	-1.60071	1.62245
C	3.68843	2.79667	-0.07671
C	2.61424	1.9142	-0.64224
C	1.58731	2.4764	-1.40457
H	1.58508	3.5457	-1.58504
C	0.57149	1.67777	-1.94985
C	-0.46405	2.3659	-2.80207
C	0.57615	0.277	-1.71356
N	-0.4633	-0.55661	-2.23568
C	1.62432	-0.29138	-0.94093
C	1.70201	-1.76378	-0.62411
C	2.62999	0.5342	-0.41868
H	3.42528	0.09627	0.1738
C	-1.76313	-0.46351	-1.58778
C	-0.19032	-1.42176	-3.25558

C	-2.55499	-2.26458	-3.10078
C	-1.22253	-2.37809	-3.80955
C	-0.69434	-3.81808	-3.63729
C	-1.43119	-2.07361	-5.30665
O	-3.45209	-3.0245	-3.44998
O	0.93151	-1.43649	-3.74988
H	-7.89083	-1.22391	1.55211
H	-8.63668	-1.77711	0.00838
H	-8.36576	-0.01353	0.30578
H	-4.21157	-0.64379	-4.12902
H	-5.64587	0.3535	-3.83787
H	-5.84444	-1.39689	-4.23348
H	-2.08714	-2.03997	0.31869
H	-3.27201	-2.86392	1.34645
H	-2.90946	-1.11743	1.62682
H	4.43606	2.21343	0.50201
H	3.23362	3.55091	0.5995
H	4.21529	3.31966	-0.90239
H	-1.18187	1.66798	-3.27323
H	0.04324	2.89994	-3.63303
H	-1.02372	3.10417	-2.18972
H	0.85644	-2.34886	-1.03277
H	1.69558	-1.90491	0.47715
H	2.64485	-2.18272	-1.03503
H	-0.54223	-4.04924	-2.56028
H	0.27518	-3.9534	-4.16397
H	-1.40998	-4.55873	-4.05551
H	-1.81024	-1.03698	-5.44125
H	-2.16593	-2.7758	-5.75703
H	-0.47838	-2.17371	-5.8703
H	-2.15491	0.57169	-1.64081

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate B^{T1}:

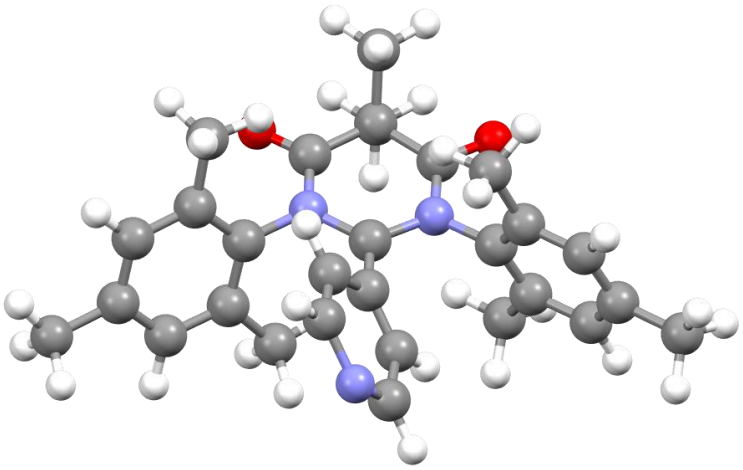


Z-Matrix for BT1			
	X	Y	Z
C	-8.01096	-0.97086	0.46176
C	-6.64655	-1.08174	-0.15346
C	-6.31582	-0.29594	-1.26081
H	-7.0578	0.3804	-1.67003
C	-5.04822	-0.38167	-1.85746
C	-4.80581	0.45768	-3.08395
C	-4.07912	-1.27	-1.32164
N	-2.75703	-1.35596	-1.88003
C	-4.43053	-2.08482	-0.2084
C	-3.48539	-3.07918	0.41801
C	-5.70462	-1.97431	0.36212
H	-5.96145	-2.59147	1.21598
C	3.7844	2.99054	-0.26371
C	2.69257	2.0831	-0.75166
C	1.7028	2.57543	-1.60442
H	1.74455	3.6141	-1.91279
C	0.67462	1.74628	-2.08395
C	-0.289	2.3693	-3.05778
C	0.62329	0.38152	-1.68091
N	-0.43757	-0.50419	-2.10103
C	1.64685	-0.11141	-0.81165
C	1.70327	-1.53005	-0.29304
C	2.66109	0.74431	-0.36658
H	3.42891	0.36072	0.29662
C	-1.81838	-0.24346	-1.64464

C	-0.10663	-1.58434	-2.87502
C	-2.4479	-2.45042	-2.63678
C	-1.09774	-2.64921	-3.27707
C	-0.5461	-4.0213	-2.83081
C	-1.26249	-2.62671	-4.81002
O	-3.30486	-3.30473	-2.83944
O	1.04491	-1.70448	-3.28086
H	-8.12633	-1.65522	1.32963
H	-8.78285	-1.23108	-0.29257
H	-8.17899	0.06888	0.81256
H	-3.82938	0.26389	-3.56445
H	-4.8846	1.53455	-2.82726
H	-5.57519	0.21179	-3.84667
H	-2.5038	-3.13207	-0.0864
H	-3.93244	-4.09423	0.3747
H	-3.31245	-2.80958	1.48166
H	4.49669	2.45505	0.40064
H	3.34281	3.83384	0.30715
H	4.35159	3.39159	-1.12961
H	-0.97618	1.64618	-3.52609
H	0.28552	2.80936	-3.90033
H	-0.86445	3.17654	-2.55734
H	0.86993	-2.1707	-0.62694
H	1.67379	-1.51868	0.81715
H	2.65032	-2.00876	-0.62003
H	-0.42572	-4.0547	-1.72647
H	0.44168	-4.22513	-3.29854
H	-1.23075	-4.84336	-3.13289
H	-1.66103	-1.64143	-5.13883
H	-1.96696	-3.41711	-5.1482
H	-0.28933	-2.79602	-5.31953
N	-1.90428	1.04944	2.46213
C	-1.41198	-0.18434	2.17526
H	-1.0517	-0.81517	2.97584
C	-1.3705	-0.63668	0.85311
H	-0.97561	-1.61665	0.64261
C	-1.8378	0.18867	-0.17872
C	-2.33858	1.46289	0.15546
H	-2.71129	2.13639	-0.6072
C	-2.36465	1.87454	1.48718
H	-2.75211	2.852	1.74398

H	-2.20737	0.6233	-2.19246

Optimized geometry and Z-matrix (X,Y,Z coordinates) for intermediate C^{T1}:

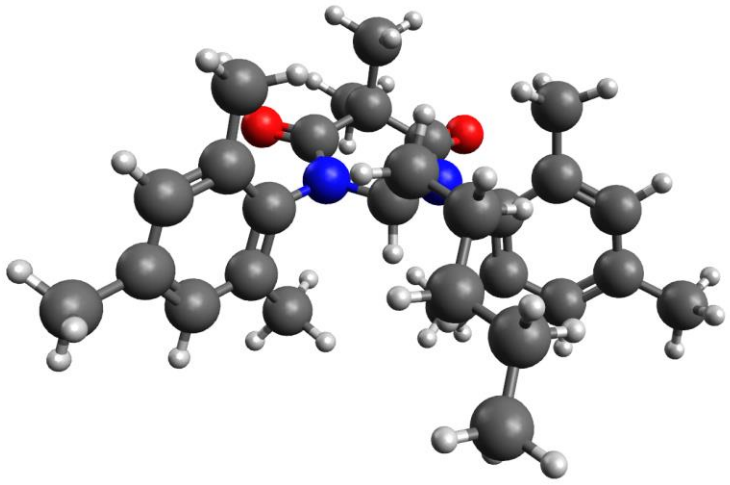


Z-Matrix for CT1			
	X	Y	Z
C	-8.03636	-0.95667	0.38868
C	-6.65667	-1.08477	-0.18705
C	-6.31761	-0.36741	-1.33924
H	-7.05675	0.27509	-1.8043
C	-5.03482	-0.46562	-1.89563
C	-4.73139	0.3424	-3.13086
C	-4.06695	-1.29503	-1.27768
N	-2.74641	-1.39746	-1.82303
C	-4.41271	-2.0289	-0.11677
C	-3.4403	-2.95027	0.57352
C	-5.70409	-1.91496	0.41542
H	-5.96573	-2.47764	1.3042
C	3.82714	2.91637	-0.27856
C	2.75798	1.94166	-0.67702
C	1.63526	2.39851	-1.36899
H	1.55632	3.45121	-1.61793
C	0.61787	1.51677	-1.75543
C	-0.53169	2.0973	-2.54223
C	0.72054	0.13491	-1.43348
N	-0.32974	-0.7716	-1.82013
C	1.87064	-0.32841	-0.73822
C	2.05989	-1.76919	-0.33732

C	2.87202	0.58211	-0.36847
H	3.74282	0.22742	0.17069
C	-1.65586	-0.63856	-1.26083
C	-0.07622	-1.67762	-2.81281
C	-2.526	-2.31776	-2.80815
C	-1.15096	-2.5779	-3.39576
C	-0.76017	-4.0441	-3.12245
C	-1.2254	-2.33098	-4.91745
O	-3.46421	-2.9861	-3.23042
O	1.05324	-1.76168	-3.28271
H	-8.16167	-1.58478	1.29635
H	-8.78703	-1.27519	-0.36469
H	-8.22655	0.10138	0.66706
H	-3.6894	0.21236	-3.48615
H	-4.8822	1.42132	-2.91385
H	-5.41665	0.04221	-3.95047
H	-2.44985	-2.98893	0.07784
H	-3.85239	-3.98175	0.57903
H	-3.28801	-2.61584	1.62078
H	4.65643	2.41636	0.26508
H	3.39303	3.69518	0.38359
H	4.24453	3.40356	-1.185
H	-1.27243	1.34388	-2.8693
H	-0.13835	2.57703	-3.46361
H	-1.05429	2.8649	-1.93403
H	1.20968	-2.41826	-0.62302
H	2.1636	-1.83193	0.76676
H	2.98175	-2.16982	-0.80815
H	-0.70581	-4.22984	-2.02716
H	0.23095	-4.28208	-3.566
H	-1.50462	-4.7445	-3.5589
H	-1.50555	-1.27529	-5.12561
H	-1.98075	-2.99428	-5.39226
H	-0.24763	-2.53728	-5.40426
N	-2.08111	1.64902	2.19153
C	-1.11578	0.6084	2.1028
H	-0.47952	0.39021	2.95426
C	-0.99939	-0.10916	0.97259
H	-0.26733	-0.9089	0.95115
C	-1.86474	0.15366	-0.19653
C	-2.7628	1.12724	-0.05326

H	-3.427	1.39002	-0.86518
C	-2.86316	1.91114	1.20155
H	-3.59205	2.70955	1.28607

Optimized geometry and Z-matrix (X,Y,Z coordinates) for 6a:

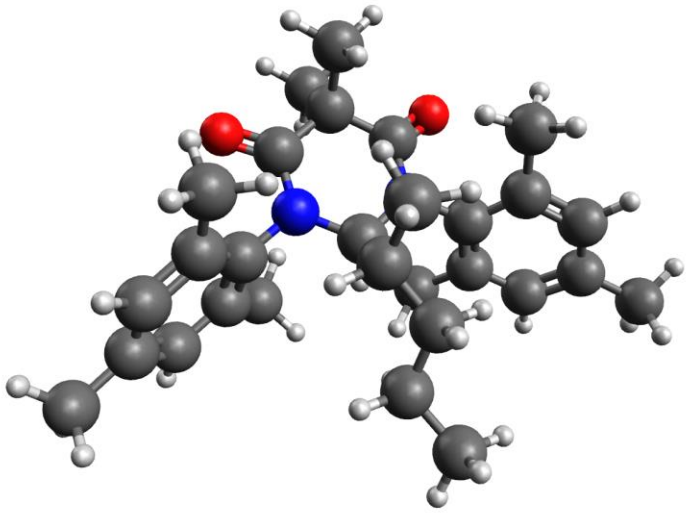


Z-Matrix for **6a**			
	X	Y	Z
C	-0.99224	-2.47904	0.411817
N	-0.01373	-2.97069	1.406545
C	1.1877	-2.36567	1.704673
C	1.530221	-1.04377	1.014773
C	0.797071	-0.82186	-0.30931
N	-0.37895	-1.50273	-0.52257
O	1.235483	-0.03103	-1.14033
O	1.957292	-2.85472	2.527201
C	1.141441	0.113416	1.977899
H	0.06828	0.126391	2.197905
H	1.686141	0.000239	2.92057
H	1.41297	1.071723	1.524121
C	3.050351	-0.99554	0.757048
H	3.586923	-1.11237	1.700734
H	3.363426	-1.80183	0.084789
H	3.312525	-0.0435	0.291057
C	-1.13303	-1.18309	-1.72075
C	-1.16275	-2.09498	-2.79046
C	-1.8052	0.056985	-1.81822

C	-1.93496	-1.78587	-3.91956
C	-2.56163	0.316704	-2.96467
C	-2.6549	-0.59543	-4.02287
H	-1.95163	-2.49305	-4.74727
H	-3.08156	1.270427	-3.03849
C	-0.32694	-4.19527	2.122823
C	-0.69915	-4.13253	3.484869
C	-0.20462	-5.43536	1.474057
C	-1.01765	-5.32154	4.14435
C	-0.54196	-6.60139	2.179039
C	-0.9619	-6.5687	3.507944
H	-1.30853	-5.27324	5.192443
H	-0.44765	-7.56065	1.672816
C	-0.71968	-2.83579	4.257596
H	0.303322	-2.48097	4.428201
H	-1.25716	-2.04199	3.729919
H	-1.19923	-2.97591	5.231487
C	0.315155	-5.56841	0.062358
H	-0.49723	-5.5872	-0.67509
H	0.986761	-4.74808	-0.20308
H	0.868859	-6.50654	-0.04939
C	-1.32692	-7.83291	4.251831
H	-0.76108	-7.92267	5.187309
H	-2.39242	-7.84544	4.516346
H	-1.12354	-8.72435	3.649303
C	-3.50191	-0.29113	-5.23718
H	-3.2535	-0.95263	-6.07396
H	-4.57027	-0.42232	-5.01834
H	-3.36491	0.743849	-5.57189
C	-0.36201	-3.37537	-2.78924
H	0.531649	-3.29523	-2.16542
H	-0.95106	-4.22642	-2.42446
H	-0.04232	-3.62217	-3.80713
C	-1.68052	1.133935	-0.76698
H	-1.74404	0.740848	0.251516
H	-0.70977	1.635398	-0.85909
H	-2.46715	1.885519	-0.8889
H	-1.26861	-3.34412	-0.19857
C	-2.28886	-1.895	1.03246
H	-2.00708	-1.19154	1.824844
H	-2.77121	-1.30533	0.246359

C	-3.34488	-2.88955	1.554899
H	-2.94178	-3.51437	2.357237
H	-4.14577	-2.28802	2.009238
C	-3.96829	-3.78676	0.473987
H	-4.32943	-3.1627	-0.3577
H	-3.20493	-4.45464	0.049397
C	-5.12665	-4.64465	1.002941
H	-5.9009	-3.98605	1.423079
H	-4.76572	-5.26419	1.836225
C	-5.7508	-5.54439	-0.0702
H	-6.57598	-6.14008	0.33828
H	-6.14875	-4.95083	-0.90348
H	-5.01027	-6.24129	-0.4837

Optimized geometry and Z-matrix (X,Y,Z coordinates) for 6b:

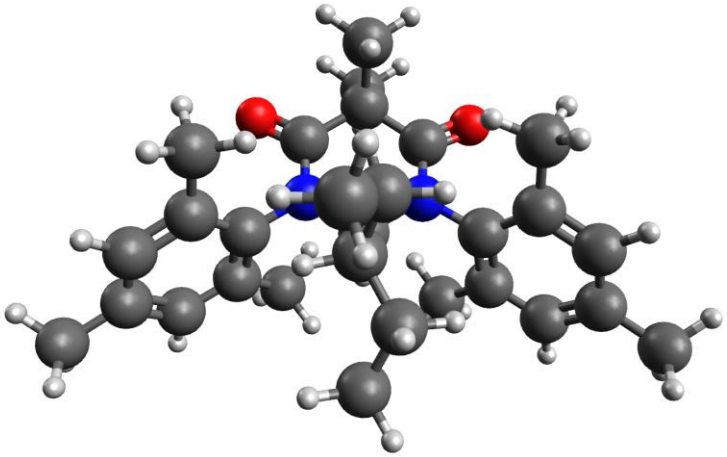


Z-Matrix for **6b**			
	X	Y	Z
C	-1.05193	-2.49019	0.665486
N	0.040442	-3.01175	1.52225
C	1.356576	-2.59842	1.496254
C	1.743155	-1.3734	0.669275
C	0.700025	-0.92935	-0.3546
N	-0.55443	-1.49206	-0.31732
O	0.99644	-0.09385	-1.20577

O	2.212763	-3.185	2.153275
C	2.023459	-0.19494	1.639153
H	1.135842	0.082957	2.218368
H	2.816049	-0.47985	2.337238
H	2.345872	0.677601	1.063497
C	3.045425	-1.70561	-0.10015
H	3.822587	-1.99731	0.609368
H	2.893165	-2.53465	-0.80111
H	3.36479	-0.83041	-0.66973
C	-1.45824	-1.14516	-1.40345
C	-1.63987	-2.05134	-2.46374
C	-2.10325	0.111685	-1.41891
C	-2.54243	-1.72195	-3.48581
C	-2.99273	0.391813	-2.46016
C	-3.24339	-0.51622	-3.49607
H	-2.67865	-2.42522	-4.30577
H	-3.49185	1.359295	-2.46995
C	-0.25098	-4.17585	2.343832
C	-0.22099	-4.07391	3.752515
C	-0.513	-5.4178	1.731769
C	-0.60325	-5.18686	4.509744
C	-0.88618	-6.50306	2.535809
C	-0.96778	-6.40412	3.925936
H	-0.59254	-5.10108	5.595367
H	-1.09306	-7.45849	2.056159
C	0.301401	-2.86493	4.492689
H	0.28383	-1.95437	3.895784
H	-0.27001	-2.68952	5.411515
H	1.347717	-3.03942	4.771115
C	-0.34655	-5.65259	0.247868
H	-1.29525	-5.57079	-0.29787
H	0.361118	-4.95004	-0.19906
H	0.033576	-6.6646	0.072054
C	-1.40962	-7.57462	4.77378
H	-0.81499	-7.65217	5.691313
H	-2.46058	-7.47022	5.075806
H	-1.31701	-8.52065	4.229485
C	-4.23138	-0.1891	-4.59207
H	-4.10298	-0.84926	-5.45643
H	-5.26569	-0.30281	-4.24019
H	-4.11892	0.845516	-4.93689

C	-0.86806	-3.34565	-2.57506
H	0.094061	-3.29498	-2.05861
H	-1.426	-4.19456	-2.16072
H	-0.67034	-3.57667	-3.62711
C	-1.81342	1.18401	-0.39671
H	-1.86347	0.81383	0.630073
H	-0.80412	1.583521	-0.55048
H	-2.52674	2.008755	-0.4928
H	-1.40783	-3.33507	0.070178
C	-2.30278	-1.93096	1.427274
H	-2.82546	-1.34786	0.66092
C	-3.31664	-3.00813	1.884102
H	-2.83596	-3.73216	2.551525
H	-4.06975	-2.48976	2.496229
C	-4.05593	-3.7476	0.758189
H	-4.53453	-3.0137	0.094134
H	-3.34723	-4.30672	0.132478
C	-5.1141	-4.7205	1.293622
H	-5.8687	-4.19402	1.892058
H	-4.65842	-5.48687	1.933136
H	-5.63553	-5.23282	0.476143
C	-1.97413	-0.98359	2.590501
H	-1.78548	-1.53644	3.513679
H	-1.10205	-0.35346	2.388311
H	-2.82473	-0.31772	2.778535

Optimized geometry and Z-matrix (X,Y,Z coordinates) for 6c:



Z-Matrix for **6c**			
	X	Y	Z
C	-1.07307	-2.51002	0.700117
N	0.022186	-3.04455	1.547947
C	1.344629	-2.65255	1.504922
C	1.740536	-1.43366	0.674198
C	0.696358	-0.98289	-0.34474
N	-0.5693	-1.5192	-0.28705
O	0.998311	-0.16049	-1.20657
O	2.199327	-3.25326	2.151113
C	2.03235	-0.25493	1.640813
H	1.147525	0.031831	2.220098
H	2.823436	-0.54484	2.338641
H	2.361633	0.61341	1.062615
C	3.037395	-1.77797	-0.09812
H	3.81487	-2.07332	0.609476
H	2.876248	-2.60802	-0.79583
H	3.361279	-0.90708	-0.67172
C	-1.48489	-1.13999	-1.35075
C	-1.73907	-2.0409	-2.40117
C	-2.07175	0.144107	-1.35418
C	-2.65853	-1.67579	-3.39493
C	-2.98354	0.459467	-2.36607
C	-3.30788	-0.44059	-3.3876
H	-2.85092	-2.37469	-4.20736
H	-3.43984	1.448077	-2.36423
C	-0.27028	-4.21022	2.367526

C	-0.22483	-4.11485	3.775885
C	-0.54486	-5.44852	1.752819
C	-0.60987	-5.22795	4.532163
C	-0.91839	-6.53415	2.555428
C	-0.98937	-6.4395	3.946771
H	-0.588	-5.14703	5.617957
H	-1.13574	-7.48633	2.073884
C	0.32079	-2.9161	4.516214
H	0.30933	-2.00243	3.923842
H	-0.23851	-2.73725	5.441823
H	1.367442	-3.10648	4.78289
C	-0.39498	-5.67789	0.266293
H	-1.34979	-5.59402	-0.26813
H	0.307907	-4.97437	-0.18666
H	-0.01715	-6.68942	0.082777
C	-1.43782	-7.60926	4.792078
H	-0.88639	-7.65542	5.738023
H	-2.50499	-7.53105	5.040936
H	-1.29295	-8.56058	4.268545
C	-4.31981	-0.07847	-4.45029
H	-4.20938	-0.70876	-5.33922
H	-5.34606	-0.20765	-4.0803
H	-4.217	0.967417	-4.7619
C	-1.02386	-3.36552	-2.53277
H	-0.0491	-3.35404	-2.03833
H	-1.60566	-4.19299	-2.10771
H	-0.85981	-3.60108	-3.58964
C	-1.6892	1.210969	-0.35821
H	-1.51894	0.809847	0.64287
H	-0.75443	1.689923	-0.67337
H	-2.46525	1.980685	-0.2935
H	-1.43919	-3.35225	0.107455
C	-2.32189	-1.951	1.472848
H	-2.83816	-1.33778	0.724013
C	-3.33336	-3.05363	1.877689
H	-2.83916	-3.825	2.476858
H	-4.07542	-2.59008	2.539694
C	-4.08943	-3.70153	0.709182
H	-4.6266	-2.94974	0.117563
H	-3.42666	-4.24465	0.025334
C	-1.98343	-1.03437	2.664757

H	-1.77426	-1.65085	3.544144
H	-1.06291	-0.47515	2.454192
H	-4.82565	-4.42356	1.082132
C	-3.09589	-0.03544	3.017992
H	-2.79304	0.596858	3.861259
H	-3.32979	0.624375	2.174154
H	-4.02375	-0.54142	3.308789

References

[1] T. W. Hudnall, J. P. Moerdyk, C. W. Bielawski, *Chem. Commun.* **2010**, *46*, 4288-4290.

[2] T. A. Perera, E. W. Reinheimer, T. W. Hudnall, *J. Am. Chem. Soc.* **2017**, *139*, 14807–14814.

[3] 171.41.103 ed., Rigaku Oxford Diffraction, **2021**.

[4] Rigaku Oxford Diffraction, **2017**.

[5] G. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3-8.

[6] G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3-8.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

[8] A. Spek, *Acta Crystallogr. D* **2009**, *65*, 148-155.

[9] E. Epifanovsky, A. T. B. Gilbert, X. Feng, J. Lee, Y. Mao, N. Mardirossian, P. Pokhilko, A. F. White, M. P. Coons, A. L. Dempwolff, Z. Gan, D. Hait, P. R. Horn, L. D. Jacobson, I. Kaliman, J. Kussmann, A. W. Lange, K. U. Lao, D. S. Levine, J. Liu, S. C. McKenzie, A. F. Morrison, K. D. Nanda, F. Plasser, D. R. Rehn, M. L. Vidal, Z.-Q. You, Y. Zhu, B. Alam, B. J. Albrecht, A. Aldossary, E. Alguire, J. H. Andersen, V. Athavale, D. Barton, K. Begam, A. Behn, N. Bellonzi, Y. A. Bernard, E. J. Berquist, H. G. A. Burton, A. Carreras, K. Carter-Fenk, R. Chakraborty, A. D. Chien, K. D. Closser, V. Cofer-Shabica, S. Dasgupta, M. d. Wergifosse, J. Deng, M. Diedenhofen, H. Do, S. Ehlert, P.-T. Fang, S. Fatehi, Q. Feng, T. Friedhoff, J. Gayvert, Q. Ge, G. Gidofalvi, M. Goldey, J. Gomes, C. E. González-Espinoza, S. Gulania, A. O. Gunina, M. W. D. Hanson-Heine, P. H. P. Harbach, A. Hauser, M. F. Herbst, M. H. Vera, M. Hodecker, Z. C. Holden, S. Houck, X. Huang, K. Hui, B. C. Huynh, M. Ivanov, Á. Jász, H. Ji, H. Jiang, B. Kaduk, S. Kähler, K. Khistyaev, J. Kim, G. Kis, P. Klunzinger, Z. Koczor-Benda, J. H. Koh, D. Kosenkov, L. Koulias, T. Kowalczyk, C. M. Krauter, K. Kue, A. Kunitsa, T. Kus, I. Ladjánszki, A. Landau, K. V. Lawler, D. Lefrancois, S. Lehtola, et al., *J. Chem. Phys.* **2021**, *155*, 084801.

[10] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

[11] T. H. D. Jr., *J. Chem. Phys.* **1989**, *90*, 1007-1023.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,

T. Vreven, J. Montgomery, J. A. , J. E. Perelta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, in *GAUSSIAN 09 (Revision C.01)*, Gaussian, Inc, Wallingford, CT, **2010**.

[13] (a)A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; (b)C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B, PRB* **1988**, *37*, 785-789.

[14] W. J. Hehre, R. Ditchfield, J. A. Pople, *Journal of Chemical Physics* **1972**, *56*, 2257-2261.