## Tracing and Elucidating Visible-light Mediated Oxidation and C-H Functionalization of Amines Using Mass Spectrometry

Wanpeng Ai,<sup>[a]</sup> Yunpeng Gao,<sup>[a]</sup> Jinjuan Xue,<sup>[a]</sup> Xiaoyun Liu,<sup>[b]</sup> Huwei Liu,<sup>[a]</sup> Jianbo Wang,<sup>[a]</sup> and Yu Bai<sup>\*[a]</sup>

 Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Institute of Analytical Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

[b] Department of Microbiology, School of Basic Medical Sciences, Peking University Health Science Center, Beijing 100191, China

\*Corresponding

author,

Email:

yu.bai@pku.edu.cn

## Table of Contents

S1. Experimental section	3
S2. CID MS/MS spectrum of 2a, 5a, 3a, B and 4a	8
S3. The verification of visible-light photocatalyzed oxidation and C-H functionalization	process
using N-methylaniline	10
S4. The verification of visible-light photocatalyzed oxidation and C-H functionalization	process
using N-ethylaniline	14
S5. Theoretical Analysis	19



Scheme S1 Co-existed reaction pathways in the photoredox catalysis transformation of amine

### **S1.** Experimental section

#### Chemicals and reagents

*N*-methylaniline (98%), *N*-ethylaniline (98%), potassium phosphate tribasic (98.5%) and 1,2,3,4-tetrahydroisoquinoline (97%) were obtained from J&K Scientific Ltd. (Beijing, China). Methanol (HPLC grade), 2-propanol (HPLC grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Methanol-D4 (D,99.8%+.03% TMS) was purchased from the Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Sodium chloride (AR) and ethylene glycol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Iodobenzene (98%) was acquired from Aladdin reagent Co., Ltd (Shanghai, China). Purified Water was obtained from Hangzhou Wahaha Group Co., Ltd. (Zhejiang,China). Copper(I) iodide (AR, ≥99%) and Tris(2,2'-

bipyridine)dichlororuthenium(II) hexahydrate (98%) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Column chromatography silica gel was obtained from Yantai Chemical Industry Research Institute (Shandong, China). Diethyl ether (AR), Petroleum ether (CCER) and Ethyl acetate (AR) were obtained from Beijing Tong Guang Fine Chemicals Company (Beijing, China). Magnesium sulfate (AR) was purchased from Beijing Chemical Works (Beijing, China).

*N*-aryltetrahydroisoquinolines (THIQ) was synthesized according to the literature<sup>[1]</sup>. A typical procedure is described as following: Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were added to a Schlenk tube. The tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (2.00 g, 15 mmol) and Iodobenzene (1.11 mL, 10.0 mmol) were added successively via a syringe at room temperature. The reaction mixture was heated at 85 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added. The aqueous layer was extracted by diethyl ether (2×20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed via rotary evaporation, and the remaining residue was purified via column chromatography (PE/EA, 2%-10%) to give the desired product THIQ. The successful synthesis of THIQ were confirmed by NMR and MS spectrum (Figure S1&Figure S2).



Figure S1. The NMR spectrum of synthesized THIQ



Figure S2. The mass spectrum of synthesized THIQ

#### Apparatus

A frontend coating-removed fused silica capillary (inner I.D.,  $250 \ \mu m$ ) with a tapered tip was assembled as the ESI source, which was concentric and about 8 mm apart from the inlet of MS (Scheme 1& Figure S3). The taper emitter was fabricated by a P-2000 laser pipette puller (Sutter Instrument Co., Novato, CA, USA). A peek tee was used as the holder for the discharge needle and the ESI source with the reaction solution injected continually. Compared with the device of Badu-Tawiah et al<sup>[2]</sup>, a higher energy miniature continuous laser (450 nm, 1 W) was employed as a light source to irradiate the flowing reaction mixture and trigger the photoredox catalysis reaction. The laser focus was 4 mm far from the tapered emitter. The distance between the laser and the capillary was held about 6 cm. The reactants and products were ionized by applying a direct current (DC) voltage of +4 kV. A high resolution Thermo Q Exactive Plus mass spectrometer (San Jose, CA, USA) was employed in this study. The major experimental parameters were as follows: The temperature of the MS inlet capillary: 250 °C, the full MS mass range: 50-750 Da, maximum injection time: 50, microscans: 1, resolution: 70000. All the experiments were conducted in positive ion mode.

For the anaerobic experience, a similar setup was fabricated referring to Chen's work<sup>[3]</sup> (Figure S4). During the experiments, periodic laser irradiation was employed to monitor the changes of two intermediates. The ultrahigh resolution of MS at 280000 was used for the molecule identification. The temperature of the MS inlet capillary: 275 °C. The other parameters were same as above.



Figure S3 Photograph of the online ESLMS assisted with loser irrediation setup



Figure S4 Photograph of the anaerobic online ESI-WS assisted with laser irradiation setup

## S2. CID MS/MS spectrum of 2a, 5a, 3a, B and 4a



Figure S5 CID MS/MS spectrum of THIQ iminium cation 2a



Figure S6 CID MS/MS spectrum of protonated 1a hydroperoxide (5a)



Figure S7 CID MS/MS spectrum of protonated C-H functionalization product deuterium 3a

Analysis for the substance **B** 



Figure S8 CID MS/MS spectra of ion at m/z 240

When the value of CID energy was set to 10, only two prominent ions at m/z at 240.1016 and 208.1119 were detected in the CID MS/MS spectra (Figure S8a). The protonated C-H functionalization product **3a** at 240.1381 was almost exhausted though it had a bigger signal intensity in the first-order spectrum and the energy was low from the insert picture in Figure S8a. Then the ion at m/z 208.1119 was deduced come prominently from the fragment of the ion at 240.1381, which is self-consistent to the conclusion in Figure S7. When the value of CID energy was set from 10 to 50 (Figure S8b, c, d, e), two remarkable ions at m/z 212.1067 and 222.0911 were detected with the and the signal strength gradually increased, meanwhile, the signal intensity of ion at 240.1014 was diminished. So, it was drawn audaciously a conclusion that two fragment ions at m/z 212.1067 and 222.0911 were come from ion **B**, which was concluded reasonably to the

dehydrogenated 2a hydroperoxide.



Figure S9 CID MS/MS spectrum of protonated oxidation product 4a

# **S3.** The verification of visible-light photocatalyzed oxidation and C-H functionalization process using N-methylaniline

A mixture of *N*-methylaniline **1b** (1 mM) and  $[Ru(II)(bpy)_3]Cl_2$  (5  $\mu$ M) in methanol was injected in the aforementioned apparatus at a flow rate of 10  $\mu$ L/min. The 1.8 min interval time was used to perform the laser turning on/off experiment. When the laser was turned off, only ion of m/z 108.0810 and ion clusters with the prominent peak at m/z 285.0546 were detected in the MS spectrum (Figure S10a), corresponding to the protonated **1b** and Ru(II)(bpy)<sub>3</sub><sup>2+</sup>, respectively. When the laser was switched on, ions at m/z 106.0653 arised in the spectrum, attributing to the iminium cation intermediate **2b** (Figure S10b). Meanwhile, ions at m/z 140.0704 was also detected. CID MS/MS spectrum confirmed the structure of ion at m/z 140.0704 by yielding high resolution fragment ions of m/z 122 and 94 via losses of H<sub>2</sub>O and CO<sub>2</sub>H<sub>2</sub> (Figure S11), which is assigned to be protonated **1b** hydroperoxide. Two new ions at m/z 138.0549 and 172.0599 were detected when laser was on (marked red in Figure S10). As shown in the inset of Figure S10b, two peaks with very close m/a ratio at 138.0549 and m/z 138.0912 were successfully discriminate with our high resolution of 280000 MS. M/z 138.0912 corresponded to the protonated methoxylated product **3b** with the calculated molecule formula of  $C_8H_{12}NO$  with the error of -0.7 ppm. The identification of the ions at m/z 138.0549 was difficult since it is impossible to isolate it from the ions m/z 138.0912 during the CID MS/MS experiment. Therefore, methanol-d4 was employed to react with **1b** to produce distinct m/z product. In the CID MS/MS spectrum, the prominent fragment ions at m/z 111 came from the loss of CO, which demonstrated that the ions at m/z 138.0549 (Figure S12). It suggested that the ion of m/z 138.0549 was **2b** hydroperoxide. In addition, ions at m/z 172.0599 was calculated to the molecular formula of  $C_7H_{10}NO_4$  with the error of -2.9 ppm, which was protonated **1b** dihydroperoxide deduced logically to be the precursor of amide **4b**.

What is more, another fragmental ion at m/z 122.0601 was also found in the mass spectrum, corresponding to protonated oxidation product **4b** (Figure S13). Interestingly, oxidation product *N*-phenylformamide was detected with the form of sodium and potassium adduct with the m/z ratio at 144.0418 and 160.0157, respectively (Figure S10b and Figure S14). The information of all identified compounds related to the reaction are listed in Table S1



Figure S10 (a) MS spectrum of *N*-methylaniline and [Ru(II)(bpy)<sub>3</sub>]Cl<sub>2</sub> in methanol when laser was turned off; (b) MS spectrum of *N*-methylaniline and [Ru(II)(bpy)<sub>3</sub>]Cl<sub>2</sub> in methanol when laser was turned on; (c) EIC of the intermediates and products of *N*-methylaniline and [Ru(II)(bpy)<sub>3</sub>]Cl<sub>2</sub> in methanol with laser irradiation.

For further confirmation of the correlation between the product ions and the laser irradiation,

EIC was performed and presented in Figure S10c. One can see that the all the above detected ions

came up along with the periodic laser irradiation in real time.

Table S1. Detected peaks identification of *N*-methylaniline and its related substances



Chemical formula	$C_7H_{10}N^+$	$C_7H_8N^+$	$C_7 H_{10} N O_2^+$	$C_7H_8NO_2^+$
Calculated mass	108.0808	106.0651	140.0706	138.0550
Measured mass	108.081	106.0653	140.0704	138.0549
Error (ppm)	+1.9	+1.9	-1.4	-0.7
	N,HOCH3	Н.Н V- ООН	H-NH=0	
	[ <b>3b</b> +H] <sup>+</sup>	[1b dihydroperoxide+H] <sup>+</sup>	[ <b>4b</b> +H] <sup>+</sup>	
Chemical formula	$C_8H_{12}NO^+$	$C_7 H_{10} N O_4^+$	$C_7H_8NO^+$	
Calculated mass	138.0913	172.0604	122.06	
Measured mass	138.0912	172.0599	122.0601	
Error (ppm)	-0.7	-2.9	+0.8	



Figure S11 CID MS/MS spectrum of 1b hydroperoxide



Figure S12 CID MS/MS spectrum of deuterium 2b hydroperoxide



Figure S13 CID MS/MS spectrum of oxidation product protonated 4b



Figure S14 EIC of sodium and potassium addict peak of oxidation product 4b

# **S4.** The verification of visible-light photocatalyzed oxidation and C-H functionalization process using N-ethylaniline

A mixture of *N*-ethylaniline **1c** (1 mM) and  $[Ru(II)(bpy)_3]Cl_2 (5 \mu M)$  in methanol was injected in the apparatus at a flow rate of 10  $\mu$ L/min with about 1.2 min interval time of turn on-off laser. When the laser was turn off, only protonated **1c** ion of m/z 122.0965, and ion clusters Ru(II)(bpy)<sub>3</sub><sup>2+</sup> were detected in the MS spectrum (Figure S15a).

When the laser was switch on, shown in Figure S15b, ion at m/z 120.0807 was found in the spectrum, attributing to the intermediate **2c** (See Figure S16 for the CID MS/MS spectrum). Furthermore, ion at m/z 154.0858 was found. CID MS/MS spectrum confirmed its structure by

yielding high resolution fragment ions of m/z 136 and 108 via losses of  $H_2O$  and  $CO_2H_2$  (Figure S17), which is judged to the protonated **1c** hydroperoxide.

Similarly, two new peaks of ions were detected in m/z 152.0702, 186.0757 (marked red in Figure S15b). As for the CID MS/MS spectrum of ion of m/z 152.0702, a similar difficulty was proposed for isolating it with the almost same ion of m/z 152.1067, though they can be differentiated in the high resolution first-order spectrum. The latter was calculated to the ion formula of  $C_9H_{14}NO$ with the error of -2.0 ppm, corresponding to the protonated C-H functionalization product 3c. To identify the ion of m/z 152.0702, methanol-d4 was employed to react with the 1c to produce distinct m/z product. The prominent fragment of 124 by means of loss of CO in CID MS/MS spectrum explained the structure of ion at m/z 152.0702 (Figure S18), corresponding to the **2c** hydroperoxide. The other detected ion of m/z 186.0757 was calculated to the ion formula of C<sub>8</sub>H<sub>12</sub>NO<sub>4</sub> with the error of -2.1 ppm, which was protonated 1c dihydroperoxide assigned logically in the precursor of amide 4c. What is more, another product ion at m/z 136.0754 was also found in the spectrum, corresponding to protonated oxidation product 4c (see Figure S19 for the CID MS/MS spectrum). Interestingly, oxidation product 4c was also detected of the sodium and potassium addict peak at m/z 158.0571 and 174.0312(see EIC in Figure S20). The error between calculated mass and measured mass for all the detected substances above were listed in Table S2. EIC was performed and presented in Figure S15c. One can see that the all the above detected ions came up along with the periodic laser irradiation in real time.



Figure S15 (a) MS spectrum of *N*-ethylaniline and  $[Ru(II)(bpy)_3]Cl_2$  in methanol with the laser tuning off. (b) MS spectrum of *N*-ethylaniline and  $[Ru(II)(bpy)_3]Cl_2$  in methanol with the laser tuning on (c) EIC of the intermediates and products of *N*-ethylaniline and  $[Ru(II)(bpy)_3]Cl_2$  in methanol with laser irradiation.

Table S2. Detected peaks identification of N-ethylaniline and its related substances						
	$\begin{array}{c} \begin{array}{c} H \\ H $					
	$[1c+H]^+$ 2c $[1c hydroperoxide+H]^+$ 2c hydroperoxide					
Chemical formula	$C_8H_{12}N^+$	$C_8H_{10}N^+$	$C_8H_{12}NO_2{}^+$	$C_8H_{10}NO_2^+$		

Calculated mass	122.0964	120.0808	154.0863	152.0706
Measured mass	122.0965	120.0807	154.0858	152.0702
Error (ppm)	+0.8	-0.8	-3.2	-2.6
	N, HOCH3	H.H.OOH N.Y.OOH	H,HO	
		[1c dihydroperoxide+H] <sup>+</sup>	$[4c+H]^+$	
	[ <b>3c</b> +H] <sup>+</sup>	[1c dihydroperoxide+H]+	[ <b>4c</b> +H] <sup>+</sup>	
Chemical formula	[ <b>3c</b> +H] <sup>+</sup> C <sub>9</sub> H <sub>14</sub> NO <sup>+</sup>	$[1c dihydroperoxide+H]^+$ $C_8H_{12}NO_4^+$	$[4c+H]^+$ $C_8H_{10}NO^+$	
Chemical formula Calculated mass	[ <b>3c</b> +H] <sup>+</sup> C <sub>9</sub> H <sub>14</sub> NO <sup>+</sup> 152.1070	[1c dihydroperoxide+H] <sup>+</sup> C <sub>8</sub> H <sub>12</sub> NO <sub>4</sub> <sup>+</sup> 186.0761	[ <b>4c</b> +H] <sup>+</sup> C <sub>8</sub> H <sub>10</sub> NO <sup>+</sup> 136.0757	
Chemical formula Calculated mass Measured mass	[ <b>3c</b> +H] <sup>+</sup> C <sub>9</sub> H <sub>14</sub> NO <sup>+</sup> 152.1070 152.1067	[ <b>1c</b> dihydroperoxide+H] <sup>+</sup> C <sub>8</sub> H <sub>12</sub> NO <sub>4</sub> <sup>+</sup> 186.0761 186.0757	[ <b>4c</b> +H] <sup>+</sup> C <sub>8</sub> H <sub>10</sub> NO <sup>+</sup> 136.0757 136.0754	







Figure S17 CID MS/MS spectrum of protonated 1c hydroperoxide



Figure S18 CID MS/MS spectrum of 2c hydroperoxide



Figure S19 CID MS/MS spectrum of protonated oxidation product 4c



Figure S20 EIC of sodium and potassium addict peak of oxidation product 4 c

### **S5.** Theoretical Analysis

Calculation was carried out to investigate the possibility of formation of the **6a**, **7a** intermediates in the two-path dehydrogenation pathway. Density functional theory (DFT) within the Gaussian 09<sup>[4]</sup> program and the Becke-3-Lee-Yang-Parr exchange-correlation functional (B3LYP)<sup>[5]</sup> were used in this work. The 6-31+g(d) basis set was employed for all elements. The structures of intermediates **2a**, **5a**, **6a**, **7a**, and **4a**, as shown in Figure S21 were fully optimized. We also applied the single-point Solvation Model Based on Density (SMD) calculation<sup>[6]</sup> for all molecules to model the methanol solvent environment.



Figure S21 Optimized structures of (a) 2a, (b) 5a, (c) 6a, (d) 7a, and (e) 4a.

The frequency analysis of the optimized structure was carried out at 298 K and 1 atm pressure, which were our experimental conditions, to obtain the Gibbs free energy (G). All Gibbs free energies in our calculations are listed in Table S3.

Table S3 The free energy of solution	$(G_{\rm sol})$ of each molecule/ion based	on the B3LYP/ 6-31+g(d) level calculation
--------------------------------------	--	---

at	t 298 K and 1 atm pressure				
_	G <sub>sol</sub> (Hartree)				
	<b>2a</b> -634.454230				
	5a	-785.554680			
	6a	-784.799223			
	7a	-935.906645			

<b>4</b> a	-709.269714
$^{3}O_{2}$	-150.343737
OOH-	-151.094704
$H_2O$	-76.434261
$^{1}O_{2}$	-150.283205
5a+.	-785.360768

Actually, the process from **5a** to **6a** has two possible paths, namely **5a** produce **6a** through **5a**<sup>+,</sup> similar to the first-step dehydrogenation, as well as **5a** produce **6a** directly with proton coupled charge transfer process. However, from the theoretical calculation, we can get the  $\Delta E_{(sol)}$  (**5a**<sup>+,+</sup>/**5a**) was 5.28 V (see Eq S1), which is bigger than the  $\Delta E(Ru^{2+*}/Ru^+)$  (~0.77 V)<sup>[7]</sup>. so maybe the process from **5a** to **6a** through **5a**<sup>+,+</sup> was impossible. We proposed that **5a** directly produce **6a** by reacting with <sup>1</sup>O<sub>2</sub> produced from the <sup>3</sup>O<sub>2</sub> under the situation of visible light catalysis, which means the process from **5a** to **6a** was proton coupled charge transfer (PCET) process<sup>[8]</sup>.

Eq S1:  $5a \xrightarrow{Ru^{2^{+*}/Ru^{+}}} 5a^{+\cdot}$  $\Delta E = \frac{\Delta G}{nF} = \frac{(-785.360768 - (-785.554680)) \times 2625.5 * 1000}{1 \times 96485} V = 5.28 V$ 

Then, the changes of Gibbs free energy for equations S2-S6 (Figure 2) are list below:

Eq S2: 
$$2a + OOH^- \rightarrow 5a$$

 $(-785.554680 - (-634.454230 - 151.094704)) \times 27.2 = -0.156291 \text{ eV}$ 

Eq S3:  $5a + {}^{3}O_{2} \rightarrow 5a + {}^{1}O_{2}$  (via Ru<sup>2+\*</sup>  $\rightarrow$  Ru<sup>+</sup> under visible light)

 $((-785.554680 - 150.283205) - (-785.554680 - 150.343737)) \times 27.2 = 1.646470 \text{ eV}$ 

Eq S4:  $5a + {}^{1}O_{2} \rightarrow 6a + OOH^{-}$ 

 $((-784.799223 - 151.094704) - (-785.554680 - 150.283205)) \times 27.2 = -1.524342 \text{ eV}$ 

Eq S5:  $6a + OOH^- \rightarrow 7a$ 

 $(-935.906645 - (-784.799223 - 151.094704)) \times 27.2 = -0.345930 \text{ eV}$ 

Eq S6:  $7a \rightarrow 4a + H_2O + {}^3O_2$ 

 $(-709.269714 - 76.434261 - 150.343737 (-784.799223 - 151.094704)) \times 27.2 = -3.837022 \text{ eV}$ 

The total Gibbs energy difference of Eqs S2-S6 is:

- 0.156291 + 1.646470 - 1.524342 - 0.345930 - 3.837022 = -4.217115 eV

The total outcome of Eqs S2-S6 is:

 $2a + \mathrm{OOH}^{\text{-}} \rightarrow 4a + \mathrm{H}_2\mathrm{O}$ 

The change of Gibbs free energy is consistent with the sum of all  $\Delta$ Gs of equations S2-S6:

 $((-709.269714 - 76.434261) - (-634.454230 - 151.094704)) \times 27.2 = -4.217115 \text{ eV}$ 

The Cartesian coordinates of all optimized ge	cometries are listed below (in Å):

2a			
С	-3.88439051	-1.23579608	0.00026300
С	-2.51158951	-1.23579608	0.00026300
С	-1.78965151	-0.01067508	0.00026300
С	-2.50752151	1.21319092	0.00063300
С	-3.92893751	1.18381792	0.00078700
С	-4.60044251	-0.01415708	0.00049700
Н	-4.44512151	-2.18214208	0.00018300
Н	-1.94680051	-2.18011808	0.00003500
С	-1.78477151	2.43791692	0.00074800
Н	-4.47617851	2.13827392	0.00086900
Н	-5.70007951	-0.04052408	0.00059900
Н	-2.34922751	3.38245792	0.00100800
С	0.30410149	1.21609292	0.00001600
Н	0.92149088	1.20516916	-0.87383239
Н	0.92204661	1.20506378	0.87347017
С	-0.36792451	0.01886792	0.00000000
Н	-0.03393578	-0.50103783	0.87352707
Н	-0.03439126	-0.50091271	-0.87377553
Ν	-0.41191051	2.43798492	0.00047500
С	-0.41160123	3.40153743	-1.10969006
С	0.79682330	3.85849588	-1.63634987
С	-1.61935928	3.85890432	-1.63664752
С	0.79739458	4.77312966	-2.68928219
Н	1.74882558	3.49831156	-1.22017599
С	-1.61896116	4.77306531	-2.69055426

Н	-2.57187808	3.49871777	-1.22179501
С	-0.41086561	5.23031997	-3.21682448
Н	1.74984792	5.13383327	-3.10403761
Н	-2.57137919	5.13319001	-3.10610729
Н	-0.41016520	5.95143099	-4.04706225
5.0			
Sa C	-4 44079700	-0 17490500	-0 58838900
C	-3.54992000	-1.21452700	-0.32041700
C	-2.17425300	-0.97294900	-0.21272300
C	-1.69726600	0.33842900	-0.37993700
С	-2.59692300	1.38356300	-0.64588600
С	-3.96223300	1.13095800	-0.75369600
Н	-5.50563900	-0.37975900	-0.66480700
Н	-3.92411700	-2.22802700	-0.18980200
С	-0.25351100	0.62865000	-0.26269500
Н	-2.21448200	2.39571200	-0.75044200
Н	-4.65161600	1.94501800	-0.96116400
Н	0.13017900	1.44366600	-0.86785900
С	0.11808700	-1.59179400	0.64204700
Н	0.88146800	-2.37125600	0.58600200
Н	-0.02953300	-1.31689900	1.69296000
С	-1.18817100	-2.09495100	0.02534200
Н	-1.62654100	-2.85646500	0.68177300
Н	-0.96715900	-2.59009700	-0.93199900
Ν	0.60794700	-0.42925500	-0.12288900
С	2.01396200	-0.20199800	-0.22022700
С	2.87688700	-0.54376300	0.82923100
С	2.54525000	0.35124400	-1.39492200
С	4.25228300	-0.33445100	0.70097200
Н	2.47461300	-0.94325200	1.75462400
С	3.91773600	0.57236400	-1.50990000
Н	1.88347400	0.58884000	-2.22360000
С	4.77954700	0.22680800	-0.46418900
Н	4.90982600	-0.59713500	1.52575900
Н	4.31538100	0.99981600	-2.42689900
Н	5.84932500	0.39263000	-0.55799300
0	-0.16294700	1.72521300	1.28628700
0	-0.82616700	1.03322200	2.36087700
Н	-1.71196200	1.43844300	2.34868400
6a			
С	4.50084600	0.11152500	-0.48174900
С	3.59379400	1.16808600	-0.40792000

С	2.21561600	0.93375200	-0.28962700
С	1.75409500	-0.38985900	-0.24503400
С	2.66894900	-1.45113700	-0.31683600
С	4.03649400	-1.20773600	-0.43633400
Н	5.56506900	0.31436600	-0.57171100
Н	3.95542800	2.19417300	-0.43791600
С	0.27848000	-0.72006300	-0.10907800
Н	2.29900000	-2.47330900	-0.27603500
Н	4.73471900	-2.03860300	-0.49501800
С	-0.08729000	1.66386100	0.42645000
Н	-0.83653500	2.44107400	0.25511000
Н	0.04540600	1.55008300	1.51159400
С	1.22849600	2.07705500	-0.23379300
Н	1.66271100	2.92641300	0.30887900
Н	1.01864100	2.42483900	-1.25582200
Ν	-0.57516900	0.42918800	-0.19962900
С	-1.97823500	0.19197000	-0.23902200
С	-2.85274900	0.76956500	0.69454500
С	-2.52089000	-0.61328300	-1.25672100
С	-4.23125600	0.55324200	0.60612400
Н	-2.45898500	1.37190300	1.50695100
С	-3.89397100	-0.84034000	-1.32899300
Н	-1.86531500	-1.04525200	-2.00812000
С	-4.76163400	-0.25503300	-0.40020100
Н	-4.88847300	1.01024400	1.34211200
Н	-4.28963400	-1.46377700	-2.12723300
Н	-5.83279900	-0.42648600	-0.46331200
0	0.04448900	-1.55565300	1.06775800
0	0.44375100	-0.82798000	2.26388700
Н	1.31921200	-1.22154200	2.43758400
7a			
С	4.50084600	0.11152500	-0.48174900
С	3.59379400	1.16808600	-0.40792000
С	2.21561600	0.93375200	-0.28962700
С	1.75409500	-0.38985900	-0.24503400
С	2.66894900	-1.45113700	-0.31683600
С	4.03649400	-1.20773600	-0.43633400
Н	5.56506900	0.31436600	-0.57171100
Н	3.95542800	2.19417300	-0.43791600
С	0.27848000	-0.72006300	-0.10907800
Н	2.29900000	-2.47330900	-0.27603500
Н	4.73471900	-2.03860300	-0.49501800
С	-0.08729000	1.66386100	0.42645000

Н	-0.83653500	2.44107400	0.25511000
Н	0.04540600	1.55008300	1.51159400
С	1.22849600	2.07705500	-0.23379300
Н	1.66271100	2.92641300	0.30887900
Н	1.01864100	2.42483900	-1.25582200
Ν	-0.57516900	0.42918800	-0.19962900
С	-1.97823500	0.19197000	-0.23902200
С	-2.85274900	0.76956500	0.69454500
С	-2.52089000	-0.61328300	-1.25672100
С	-4.23125600	0.55324200	0.60612400
Н	-2.45898500	1.37190300	1.50695100
С	-3.89397100	-0.84034000	-1.32899300
Н	-1.86531500	-1.04525200	-2.00812000
С	-4.76163400	-0.25503300	-0.40020100
Н	-4.88847300	1.01024400	1.34211200
Н	-4.28963400	-1.46377700	-2.12723300
Н	-5.83279900	-0.42648600	-0.46331200
0	0.04448900	-1.55565300	1.06775800
0	0.44375100	-0.82798000	2.26388700
Н	1.31921200	-1.22154200	2.43758400
0	-0.10143606	-1.67134278	-1.10689090
0	0.32513069	-2.87063739	-0.75741523
Н	0.08150527	-3.50704111	-1.43360822
<b>4</b> a			
С	4.50084600	0.11152500	-0.48174900
С	3.59379400	1.16808600	-0.40792000
С	2.21561600	0.93375200	-0.28962700
С	1.75409500	-0.38985900	-0.24503400
С	2.66894900	-1.45113700	-0.31683600
С	4.03649400	-1.20773600	-0.43633400
Н	5.56506900	0.31436600	-0.57171100
Н	3.95542800	2.19417300	-0.43791600
С	0.27848000	-0.72006300	-0.10907800
Н	2.29900000	-2.47330900	-0.27603500
Н	4.73471900	-2.03860300	-0.49501800
С	-0.08729000	1.66386100	0.42645000
Н	-0.83653500	2.44107400	0.25511000
Н	0.04540600	1.55008300	1.51159400
С	1.22849600	2.07705500	-0.23379300
Н	1.66271100	2.92641300	0.30887900
Н	1.01864100	2.42483900	-1.25582200
Ν	-0.57516900	0.42918800	-0.19962900
С	-1.97823500	0.19197000	-0.23902200

С	-2.85274900	0.76956500	0.69454500
С	-2.52089000	-0.61328300	-1.25672100
С	-4.23125600	0.55324200	0.60612400
Н	-2.45898500	1.37190300	1.50695100
С	-3.89397100	-0.84034000	-1.32899300
Н	-1.86531500	-1.04525200	-2.00812000
С	-4.76163400	-0.25503300	-0.40020100
Н	-4.88847300	1.01024400	1.34211200
Н	-4.28963400	-1.46377700	-2.12723300
Н	-5.83279900	-0.42648600	-0.46331200
0	0.04448900	-1.55565300	1.06775800
H <sub>2</sub> O			
0	-1.83899212	0.60377358	-0.04815571
Н	-0.87899212	0.60377358	-0.04815571
Н	-2.15944671	1.50870941	-0.04815571
OOH-			
0	-3.29235093	1.11284557	0.48773962
0	-1.97235093	1.11282931	0.48773962
Н	-1.65190384	1.14440842	1.39212694
$O_2$			
0	-1.83899212	0.60377358	-0.04815571
0	-0.51899212	0.60377358	-0.04815571

- [1] Zhang, T. et al. Bifunctional organic sponge photocatalyst for efficient cross-dehydrogenative coupling of tertiary amines to ketones. Chem. Commun. 53, 12536-12539, doi:10.1039/C7CC06997A (2017).
- [2] Chen, S., Wan, Q. & Badu-Tawiah, A. K. Picomole-Scale Real-Time Photoreaction Screening: Discovery of the Visible-Light-Promoted Dehydrogenation of Tetrahydroquinolines under Ambient Conditions. Angew. Chem. Int. Ed. 55, 9345-9349, doi:10.1002/anie.201603530 (2016).
- [3] Cai, Y. et al. Detection of Fleeting Amine Radical Cations and Elucidation of Chain Processes in Visible-Light-Mediated [3 + 2] Annulation by Online Mass Spectrometric Techniques. J. Am. Chem. Soc. 139, 12259-12266, doi:10.1021/jacs.7b06319 (2017).
- [4] Frisch, M.; et al. Gaussian 09, revision A. 01; Gaussian, Inc., Wallingford, CT. 2009.
- [5] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (7) (1993) 5648e5652.
- [6] Marenich, A. V.; et al. J. Phys. Chem. B 2009, 113, 6378-6396.
- [7] a) D. Staveness, I. Bosque, C. R. Stephenson, Acc. Chem. Res. 2016, 49, 2295-2306; b) L. Marzo, S. K. Pagire,
  O. Reiser, B. König, Angew. Chem. Int. Ed. 2018, 57, 10034-10072.
- [8] L. J. Rono, H. G. Yayla, D. Y. Wang, M. F. Armstrong, R. R. Knowles, J. Am. Chem. Soc. 2013, 135, 17735-17738.