**Supporting Information** 

# Organic Photoredox Catalyzed Dealkylation/Acylation of Tertiary Amines to Access Amides

Chen Liu, <sup>a†</sup> Han-Nan Chen, <sup>a†</sup> Teng-Fei Xiao, <sup>a</sup> Xiu-Qin Hu, <sup>a\*</sup> Peng-Fei Xu, <sup>a,b</sup> Guo-Qiang Xu <sup>a\*</sup>

<sup>[a]</sup> State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P.R. China, E-mail: gqxu@lzu.edu.cn;
<sup>[b]</sup> State Key Laboratory of Veterinary Etiological Biology, College of Veterinary Medicine, Lanzhou University, Lanzhou 730000 (P.R. China).

## This PDF file includes

Materials and Methods Figures S1 to S12 Tables S1 to S2 NMR Spectra References

## **Table of Contents**

Gene	eral Information	3
Expe	erimental Procedures	3
1.	Synthesis of photocatalyst	3
2.	Optimization of reaction conditions	
3.	General procedure and characterization data	9
4.	Mechanistic Investigations	26
5.	Determination of the Quantum Yield	
6.	NMR spectra of products	33
Refe	erences	87

# **General Information**

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a VARIAN Mercury plus 300 BB (300 MHz) or Bruker AVANCE III HD 400 (400 MHz), AVANCE NEO 600 (600 MHz). The spectra were recorded in CDCl<sub>3</sub> as solvent at room temperature, <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl<sub>3</sub>:  $\delta_{\rm H} = 7.26$  ppm,  $\delta_{\rm C} = 77.00$  ppm). Data for <sup>1</sup>H NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for <sup>13</sup>C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

# **Experimental Procedures**

## 1. Synthesis of photocatalyst

**MANI** and **Cz-NI** were prepared according to your previous reports,<sup>1</sup> and **Cz-NI-Ph** was synthesized according to the following procedure:



4-Bromo-1,8-naphthalic anhydride (3.0 g, 10.83 mmol) was dissolved in distilled ethanol (150 mL). Aniline (1.20 mL, 12.99 mmol) was added to the solution, and then

the solution was refluxed overnight under nitrogen. The solution was cooled and the precipitate was filtered with no further purification. The product was an ivory powder (2.8 g, yield 74%).

To a two-necked flask under nitrogen were added compounds 6-Bromo-2-phenyl-1Hbenzo[de]isoquinoline-1,3(2H)-dione (1 mmol), carbazole (1.2 mmol), Pd(OAc)<sub>2</sub> (0.020 mmol), tri-tert-butyl phosphine (0.04 mmol), and sodium tert-butoxide (1.5 mmol). Toluene (10 ml) was then added to the flask via a syringe. The resulting mixture was stirred for 12 h at 120 °C. After cooling, to the mixture was added water (3 ml) and then ethyl acetate (20 ml). The organic layer was separated from the aqueous layer, washed with water and brine solution, and dried over anhydrous magnesium sulfate. Evaporated to afford the crude product which was purified by column chromatography on silica gel (n-Hexane/ethyl acetate = 20:1-10:1) to afford yellow powder. Yield (232) mg, 53%). Mp = 217–219 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (d, J = 7.7 Hz, 1H), 8.71 (dd, J = 7.2, 1.1 Hz, 1H), 8.27 – 8.17 (m, 2H), 7.95 (d, J = 7.7 Hz, 1H), 7.86 (dd, J = 8.5, 1.1 Hz, 1H), 7.65 (dd, J = 8.5, 7.3 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.54 – 7.48 (m, 1H), 7.42 - 7.32 (m, 6H), 7.08 - 7.02 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.10, 163.69, 141.71, 140.66, 135.21, 132.40, 131.97, 130.49, 130.08, 129.46, 129.19, 128.85, 128.60, 127.71, 127.42, 126.39, 123.81, 123.55, 122.82, 120.78, 120.61, 109.96.



**Figure S1**. Cyclic voltammograms measurements were performed with the three-electrode CHI660D potentio station by using a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel as reference electrode. The voltammograms were taken in a degassed MeCN solution ( $[n-Bu_4NBF_4] = 0.1 \text{ M}$ , [Cz-NI-Ph] = 1 mM. The scan rate was 0.1 V/s.



**Figure S2**. UV-vis spectrum of **Cz-NI-Ph** at different concentrations in toluene with a path length of 1cm.



Figure S3. Beer-Lambert law of Cz-NI-Ph at the maximum wavelength of absorption.



**Figure S4**. Excitation and emission spectra of **Cz-NI-Ph** in toluene  $(3 \times 10^{-4} \text{ M})$ .



Figure S5. Transient emission decay profiles of Cz-NI-Ph (3×10<sup>-4</sup> M).



<sup>13</sup>C NMR of Cz-NI-Ph in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## 2. Optimization of reaction conditions

Table S1: Condition optimization of aromatic amine with acyl chloride.<sup>[a]</sup>

N	Me + CI	base (1.0 eq.), solven N <sub>2</sub> , 25 °C, White LE	: ; ) <b></b> t (0.05M) iD, 6 h	N N
ll-1a	ll-2a			ll-3aa
entry	photocatalyst	solvent	base	yield(%)
1	Cz-NI-Ph	DCM	KOAc	33
2	Cz-NI-Ph	DCE	KOAc	64
3	Cz-NI-Ph	EA	KOAc	84
4	Cz-NI-Ph	CHCl <sub>3</sub>	KOAc	56
5	Cz-NI-Ph	Toluene	KOAc	75
6	Cz-NI-Ph	1,4-Dioxane	KOAc	39
7	Cz-NI-Ph	n-Hexane	KOAc	23
8	Cz-NI-Ph	EA	K <sub>2</sub> CO <sub>3</sub>	82
9	Cz-NI-Ph	EA	$\mathrm{KH}_2\mathrm{PO}_4$	69
10	Cz-NI-Ph	EA	K <sub>2</sub> HPO <sub>4</sub>	89
11	Cz-NI-Ph	EA	NaOAC	78
12	Cz-NI-Ph	EA	PhCO <sub>2</sub> K	58
13	Cz-NI-Ph	EA	KHCO3	99
14	Cz-NI-Ph	EA	CsOAc	18
15	MANI	EA	KHCO <sub>3</sub>	16
16	Cz-NI	EA	KHCO <sub>3</sub>	84
17	4CzIPN	EA	KHCO <sub>3</sub>	92
18	Eosin Y	EA	KHCO <sub>3</sub>	60
19	Acr-Mes <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	EA	KHCO3	31
20	<i>fac</i> -Ir(ppy) <sub>3</sub>	EA	KHCO <sub>3</sub>	61
21	$Ir(ppy)_2$ (dtbbpy)PF <sub>6</sub>	EA	KHCO <sub>3</sub>	83
22	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	EA	KHCO <sub>3</sub>	16
23	Ir(dFCF3ppy)2(dtbpy)PF6	EA	KHCO3	84
24 <sup>b</sup>	Ph-Cz-NI	EA	KHCO <sub>3</sub>	0
25°	Ph-Cz-NI	EA	KHCO <sub>3</sub>	16
26		EA	KHCO <sub>3</sub>	11
27	Ph-Cz-NI	EA		85

<sup>*a*</sup>Reaction conditions: **II-1a** (0.1 mmol), **II-2a** (0.11 mmol), photocatalyst (1 mol %), base (1.0 equiv., 0.1 mmol), PFNB (0.5 equiv., 0.05 mmol), white LEDs, at 25 °C under nitrogen atmosphere for 6 h. Yields determined by <sup>1</sup>H NMR using toluene as standard. <sup>*b*</sup>no light. <sup>*c*</sup>no PFNB, FNB: Pentafluoronitrobenzene.

	Et <sub>3</sub> N + ( II-1b	CI II-2a	Condition B : Cz-NI-Ph (1 mol %); PFNB (0.5 eq.)	
			base, EA (0.05M), H <sub>2</sub> O (10 eq.) N <sub>2</sub> , 25 °C, White LED,  6 h	II-3ba
entry	7		base(equiv)	yield(%)
1			KHCO <sub>3</sub> (1.0)	32
2			KOAc (1.0)	trace
3			K <sub>2</sub> CO <sub>3</sub> (1.0)	15
4			KH <sub>2</sub> PO <sub>4</sub> (1.0)	trace
5			K <sub>2</sub> HPO <sub>4</sub> (1.0)	11
6			K <sub>3</sub> PO <sub>4</sub> (1.0)	36
7			CS <sub>2</sub> CO <sub>3</sub> (1.0)	54
8			K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O (1.0)	69
9			K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O (0.5)	47
10			K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O (2.0)	45
11			K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O (3.0)	23
12 <sup>b</sup>			K <sub>3</sub> PO <sub>4</sub> (1.0)	81
13 <sup>b</sup>			K <sub>3</sub> PO <sub>4</sub> (1.2)	83
14 <sup>b</sup>			K <sub>3</sub> PO <sub>4</sub> (1.5)	86

Table S2: Condition optimization of aliphatic amine with acyl chloride.<sup>[a]</sup>

<sup>*a*</sup>Reaction conditions: **II-1b** (0.1 mmol), **II-2a** (0.15 mmol), Cz-NI-Ph (1 mol %), base (1.0-1.5 equiv.), PFNB (0.5 equiv., 0.05 mmol), white LEDs, at 25 °C under nitrogen atmosphere for 6 h. isolated yield. PFNB: Pentafluoronitrobenzene. <sup>*b*</sup> addition of H<sub>2</sub>O (10 equiv., 1 mmol)

## 3. General procedure and characterization data



**General catalysis procedure A:** A dried 10 mL reaction tube was charged with **Cz-NI-Ph** (0.44 mg, 0.001 mmol, 1 mol%) and KHCO<sub>3</sub> (10.0 mg, 0.1 mmol, 1.0 equiv.) were weighed into an oven-dried 8 mL quartz cuvette with a magnetic stirring bar, and then EA (0.05 M, 2 mL) was added. The aniline **1** (0.1 mmol, 1.0 equiv.) and PFNB

(6.5  $\mu$ L, 0.05 mmol, 0.5 equiv.) were added into the mixture *via* microsyringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the benzoyl chloride **2** (0.11 mmol, 1.1 equiv.) was added into the mixture *via* micro-syringe. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 °C for 6 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to give the corresponding product.

**General catalysis procedure B:** A dried 10 mL reaction tube was charged with **Cz-NI-Ph** (0.44 mg, 0.001 mmol, 1 mol%) and  $K_3PO_4$  (31.8 mg, 0.15 mmol, 1.5 equiv.) were weighed into an oven-dried 8 mL quartz cuvette with a magnetic stirring bar, and then EA (0.05 M, 2 mL) and H<sub>2</sub>O (18 µL, 10 equiv.) was added. The amine **1** (0.1 mmol, 1.0 equiv.) and PFNB (6.5 µL, 0.05 mmol, 0.5 equiv.) were added into the mixture *via* microsyringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the acyl chloride **2** (0.15 mmol, 1.5 equiv.) was added into the mixture *via* micro-syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the acyl chloride **2** (0.15 mmol, 1.5 equiv.) was placed beside a white LED light. The reaction was stirred at 25 °C for 6 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to give the corresponding product.

*N*-methyl-*N*-phenylbenzamide (3aa).



Compound **3aa** was obtained as a yellow oil in 99% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.28 (d, J = 7.2 Hz, 2H), 7.25-7.20 (m, 3H), 7.19 – 7.08 (m, 3H), 7.07 – 6.99 (m, 2H), 3.50 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.69, 144.93, 135.94, 129.58, 129.14, 128.71, 127.72, 126.92, 126.48, 77.25, 38.40. HRMS (ESI): [M + Na]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>NONa], 234.0889; found, 234.0889.

## *N*,4-Dimethyl-*N*-phenylbenzamide (3ba).



Compound **3ba** was obtained as a brown liquid in 99% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.19 (m, 2H), 7.15 (t, *J* = 7.4 Hz 1H), 7.12 – 7.04 (m, 2H), 6.94 (d, J = 8.1 Hz, 2H), 6.87 – 6.81 (m, 2H), 3.40 (s, 3H), 2.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.67, 141.31, 135.27, 135.05, 128.72, 128.43, 127.66, 126.66, 125.65, 37.46, 19.91. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1225.

#### *N*-(4-Chlorophenyl)-*N*-methylbenzamide (3ca).



Compound **3ca** was obtained as a brown oil in 98% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.23 (m, 3H), 7.23 – 7.15 (m, 4H), 7.01 – 6.93 (m, 2H), 3.47 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.62, 143.50, 135.57, 132.09, 129.86, 129.33, 128.65, 128.07, 127.94, 38.38. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>ClNO], 246.0680; found, 246.0678.

#### N-(4-Bromophenyl)-N-methylbenzamide (3da).



Compound **3da** was obtained as a yellow oil in 97% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, J = 8.0 Hz, 2H), 7.28(d, J = 8.1 Hz, 3H), 7.22 – 7.20 (m, 2H), 6.91 (d, J = 8.2 Hz, 2H), 3.47 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.57, 144.02, 135.52, 132.31, 129.90, 128.68, 128.40, 127.97, 119.94, 38.35. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>BrNO], 290.0175; found, 290.0172.

#### *N*-(4-cyanophenyl)-*N*-methylbenzamide (3ea).



Compound **3ea** was obtained as a yellow oil in 43% yield;<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53 – 7.50 (m, 2H), 7.34 – 7.28 (m, 3H), 7.25 – 7.21 (m, 2H), 7.15 – 7.13 (m, 2H), 3.48 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.60, 148.89, 135.04, 133.05, 130.45, 128.71, 128.20, 126.93, 118.16, 109.66, 38.04. HRMS (ESI): [M + H]+ calcd for [C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O], 237.1022; found, 237.1025.

N-methyl-N-(m-tolyl)benzamide (3fa).



Compound **3fa** was obtained as a brown solid (mp 92°C-96°C) in 93% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 6.80 (d, *J* = 7.8, 1H), 3.48 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.68, 144.83, 139.13, 136.04, 129.54, 128.85, 128.67, 127.68, 127.39, 127.26, 124.07, 38.44, 21.24. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1225.

## *N*-(3-bromophenyl)-*N*-methylbenzamide (3ga).



Compound **3ga** was obtained as a yellow oil in 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.26 (m, 5H), 7.22 – 7.19 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 1H), 6.93 – 6.93 (m, 1H), 3.48 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.59, 146.23, 135.45, 130.26, 129.97, 129.70, 129.55, 128.64, 127.96, 125.76, 122.44, 38.37. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>BrNO], 290.0175; found, 290.0172.

N-methyl-N-(o-tolyl)benzamide (3ha).



Compound **3ha** was obtained as a yellow oil in 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.26 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.14 – 7.02 (m, 6H), 3.38 (s, 3H), 2.21

(s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.80, 143.52, 135.89, 134.77, 131.30, 129.62, 128.64, 128.27, 127.71, 127.54, 126.96, 37.52, 17.76. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1224.

*N*-(2-bromophenyl)-*N*-methylbenzamide (3ia).



Compound **3ia** was obtained as a yellow solid (mp 92°C-96°C) in 37% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.16 – 7.12 (m, 3H), 7.10 – 7.05 (m, 2H), 3.39 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  171.01, 143.71, 135.70, 133.73, 130.70, 129.79, 129.01, 128.42, 128.08, 127.66, 122.76, 37.12. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>BrNO], 290.0175; found, 290.0173.

#### N-mesityl-N-methylbenzamide (3ja).



Compound **3ja** was obtained as a yellow oil in 83% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.28 (m, 2H), 7.24 – 7.21 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.78 (s, 2H), 3.29 (s, 3H), 2.21 (s, 3H), 2.16 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.60, 139.72, 137.46, 135.84, 134.89, 129.76, 129.50, 128.53, 127.79, 127.44, 36.35, 20.88, 17.98. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>17</sub>H<sub>20</sub>NO], 254.1539; found, 2254.1537.

N-Ethyl-N-phenylbenzamide (3ka).



Compound **3ka** was obtained as a sticky yellow liquid in 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 7.16 – 7.13 (m, 3H), 7.04 – 7.01 (m, 2H), 3.99 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.19, 143.26, 136.35, 129.43, 129.08, 128.66, 127.94, 127.68, 126.62, 45.37, 12.96. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1225.

#### N-phenyl-N-propylbenzamide (3la)



Compound **3la** was obtained as a yellow oil in 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.26 (m, 2H), 7.23 – 7.19 (m, 3H), 7.16 – 7.11 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 2H), 3.90 – 3.87 (m, 2H), 1.70 – 1.60 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.39, 143.52, 136.45, 129.37, 129.06, 128.62, 127.85, 127.67, 126.55, 51.97, 20.94, 11.36. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>18</sub>NO], 240.1383; found, 240.1380.

*N*-(6-oxohexyl)-*N*-phenylbenzamide (3ma).



Compound **3ma** was obtained as a sticky yellow liquid in 67% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.75 (t, J = 1.7 Hz, 1H), 7.27 – 7.19 (m, 5H), 7.16 – 7.12 (m, 3H) 7.02 – 7.00 (m, 2H), 3.93 ((t, J = 7.6 Hz, 2H), 2.45 – 2.41 (m, 2H), 1.67 – 1.63 (m, 4H), 1.43 – 1.35 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  202.55, 170.39, 143.39, 136.25, 129.47, 129.14, 128.65, 127.80, 127.69, 126.66, 50.05, 43.73, 27.39, 26.39, 21.74. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>19</sub>H<sub>22</sub>NO<sub>2</sub>], 296.1645; found, 296.1645.

## 8-benzoyl-8-azabicyclo[3.2.1]octan-3-one (3na).



Compound **3na** was obtained as a colourless oil in 68% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 – 7.53 (m, 2H), 7.50 – 7.48 (m, 1H), 7.46-7.44 (m, 2H), 5.07 (s, 1H), 4.41 (s, 1H), 2.95 (s, 1H), 2.53 – 2.50 (m, 2H),,2.34 (s, 1H), 2.17 (s, 2H), 1.77 (d, J = 8.3 Hz, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  207.51, 168.95, 135.56, 130.61, 128.68, 127.13, 55.99, 51.47, 49.73,48.83,29.64, 28.86. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub>], 230.1176; found, 230.1174.

#### *N*-butyl-*N*-phenylbenzamide (3pa).



Compound **3pa** was obtained as a yellow oil in 37% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.25 (m, 2H), 7.25 – 7.09 (m, 6H), 7.06 – 6.99 (m, 2H), 3.96 – 3.88 (m, 2H), 1.67 – 1.55 (m, 2H), 1.41 – 1.32 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.35, 143.54, 136.43, 129.37, 129.06, 128.63, 127.85, 127.66, 126.55, 50.26, 29.83, 20.21, 13.86. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>17</sub>H<sub>20</sub>NO], 254.1539; found, 254.1538.

*N*-isopropyl-*N*-phenylbenzamide (3qa).



Compound **3qa** was obtained as a yellow oil in 67% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.16 (m, 5H), 7.13-7.09 (m, 3H), 7.01 (d, *J* = 7Hz, 2H), 5.09 (s, 1H), 1.20 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.72, 139.59,137.28, 130.65, 128.91, 128.61, 128.10, 127.58, 127.36, 47.72,21.12. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>18</sub>NO], 240.1383; found, 240.1381.

#### *N*-benzyl-*N*-phenylbenzamide (3ra).



Compound **3ra** was obtained as a black solid (mp 76°C-80°C) in 45% yield.<sup>1</sup>NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.19 (m, 8H), 7.16 – 7.05 (m, 5H), 6.89 (d, *J* = 7.2 Hz, 2H), 5.13 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.59, 143.55, 137.58, 136.00, 129.66, 129.00, 128.78, 128.49, 128.41, 127.75, 127.73, 127.38, 126.68, 53.88. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>20</sub>H<sub>17</sub>NONa], 310.1202; found, 310.1200.

## *N*,4-Dimethyl-*N*-phenylbenzamide (3ab).



Compound **3ab** was obtained as a yellow oil in 99% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.27 – 7.17 (m, 4H), 7.16 – 7.11 (m, 1H), 7.05 – 7.05 (m, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.49 (s, 3H), 2.25 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.72, 145.20, 139.80, 132.93, 129.14, 128.90, 128.38, 126.88, 126.35, 38.50, 21.33. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1228.

#### 4-(tert-butyl)-N-methyl-N-phenylbenzamide (3ac).



Compound **3ac** was obtained as a sticky yellow liquid in 75% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.20 (m, 4H), 7.18 – 7.13 (m, 3H), 7.06 – 7.04 (m, 2H), 3.49 (s, 3H), 1.23 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.64, 152.92, 145.18, 132.82, 129.11, 128.69, 126.85, 126.34, 124.63, 38.57, 34.68, 31.10. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>18</sub>H<sub>22</sub>NO], 268.1696; found, 268.1696.

#### 4-Methoxy-N-methyl-N-phenylbenzamide (3ad).



Compound **3ad** was obtained as a sticky yellow liquid in 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.22 (m, 4H), 7.16 – 7.12 (m, 1H), 7.05 – 7.03 (m, 2H), 6.68 – 6.64 (m, 2H), 3.74 (s, 3H), 3.48 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.28, 160.59, 145.46, 130.90, 129.19, 127.96, 126.85, 126.28, 112.97,55.18, 38.62. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub>], 242.1176; found, 242.1175.

#### 4-Fluoro-N-methyl-N-phenylbenzamide (3ae).



Compound **3ae** was obtained as a yellow oil in 97% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.22 (m, 4H), 7.18 – 7.14 (m, 1H), 7.04 – 7.02 (m, 2H), 6.87 – 6.81 (m, 2H), 3.49 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.58, 164.44,161.95,144.87, 131.52 (d,  $J_{C-F}$ = 3.5 Hz), 131.08 (d,  $J_{C-F}$ = 8.7 Hz), 129.30, 126.78 (d,  $J_{C-F}$ = 8.7 Hz), 114.81 (d,  $J_{C-F}$ = 21.6 Hz), 38.51. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -110.10.HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>FNO], 230.0976; found, 230.0977.

### 4-Chloro-N-methyl-N-phenylbenzamide (3af).



Compound **3af** was obtained as a yellow solid (mp 86°C- 90°C) in 97% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 – 7.22 (m, 4H), 7.19 – 7.12 (m, 3H), 7.03 – 7.01 (m, 2H), 3.49 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.49, 144.65, 135.69, 134.28, 130.25, 129.36, 128.02, 126.88, 126.79, 38.48. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>ClNO], 246.0680; found, 246.0682.

4-Bromo-N-methyl-N-phenylbenzamide (3ag).



Compound **3ag** was obtained as a yellow solid(mp 60-66 °C) in 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.22 (m, 4H), 7.19 – 7.15 (m, 3H), 7.03 – 7.01 (m, 2H), 3.49 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.54, 144.63, 134.75, 130.98, 130.45, 129.38, 126.88, 126.81, 124.12, 77.24, 38.48. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>13</sub>BrNO], 290.0175; found, 290.0180.

#### 4-Cyano-N-methyl-N-phenylbenzamide (3ah).



Compound **3ah** was obtained as a sticky yellow liquid in 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 7.01 (d, J = 7.5 Hz, 2H), 3.51 (s, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.66, 143.92, 140.32, 131.64, 129.53, 129.21, 127.28, 126.93, 118.14, 113.18, 38.34. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O], 237.1022; found, 237.1025.

N-methyl-N-phenyl-4-(trifluoromethyl)benzamide (3ai).



Compound **3ai** was obtained as a yellow oil in 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.39 (m, 4H), 7.25 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 7.04 – 7.02 (m, 2H),

3.51 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.19, 144.23, 139.44, 131.48, 129.43, 129.00, 127.05, 126.92, 125.01, 124.79 (q,  $J_{C-F}$ = 8.7 Hz), 38.40. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.94.HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>NO], 280.0944; found, 280.0944.

N-methyl-N-phenyl-4-(trifluoromethoxy)benzamide (3aj).



Compound **3aj** was obtained as a yellow oil in 93% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.30 (m, 2H), 7.34 – 7.21 (m, 2H), 7.21 – 7.13 (m, 1H), 7.01 (m, 4H), 3.50 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.23, 149.84, 144.57, 134.35, 130.57, 129.36, 126.87 (d,  $J_{C-F} = 1.8$  Hz), 121.54, 119.87, 118.98, 38.49. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -57.78.HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub>], 296.0893; found, 296.0895.

#### *N*,3-dimethyl-*N*-phenylbenzamide (3ak).



Compound **3ak** was obtained as a yellow oil in 84% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 – 7.19 (m, 3H), 7.14 – 7.12 (m, 1H), 7.03 (d, *J* = 7.5, Hz, 3H), 7.01 – 6.98 (m, 2H), 3.49 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.87, 145.00, 137.54, 135.85, 130.32, 129.44, 129.09, 127.44, 126.89, 126.43, 125.76, 38.40, 21.22. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1227.

3-methoxy-N-methyl-N-phenylbenzamide (3al).



Compound **3al** was obtained as a yellow oil in 87% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.21 (m, 2H), 7.16 – 7.12 (m, 1H), 7.07 – 7.03 (m, 3H), 6.87 – 6.83 (m, 2H), 6.79 – 6.77 (m, 1H), 3.65 (s, 3H), 3.50 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.41, 158.92, 144.94, 137.09, 129.17, 128.76, 126.81, 126.54, 121.23, 116.08, 113.68, 55.19, 38.42. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub>], 242.1176; found, 242.1177.

## N,2-dimethyl-N-phenylbenzamide (3am).



Compound **3am** was obtained as a sticky yellow liquid in 89% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 7.06 –7.03 (m, 3H), 6.87 – 6.83 (m, 2H), 6.78 – 6.76 m, 1H), 3.65 (s, 3H), 3.49 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.40, 158.93, 144.95, 137.10, 129.17, 128.76, 126.82, 126.54, 121.24, 116.08, 113.69, 55.19, 38.42. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>NO], 226.1226; found, 226.1227.

## *N*,3,5-trimethyl-*N*-phenylbenzamide (3an).



Compound **3an** was obtained as a sticky yellow liquid in 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.21 (m, 2H), 7.15 – 7.11 (m, 1H), 7.05 – 7.03 (m, 2H), 6.89 – 6.85 (m, 3H), 3.48 (s, 3H), 2.15 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.04, 145.04, 137.20, 135.78, 131.18, 129.02, 126.84, 126.50, 126.37, 38.39, 21.08. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>18</sub>NO], 240.1383; found, 240.1384.

## 3,5-dimethoxy-N-methyl-N-phenylbenzamide (3ao).



Compound **3ao** was obtained as a yellow oil in 99% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (t, J = 7.5 Hz, 2H), 7.17 – 7.14 (m, 1H), 7.06 (d, J = 7.8 Hz, 2H), 6.44 (d, J = 2.2 Hz, 2H), 6.32 (t, J = 1.7 Hz, 1H), 3.61 (d, J = 0.9 Hz, 6H), 3.49 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.22, 160.04, 144.94, 137.58, 129.20, 126.70, 126.59, 106.78, 102.52, 55.31, 38.41. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>18</sub>NO<sub>3</sub>], 272.1281; found, 272.1281.

N-methyl-N-phenylacetamide (3ap).



Compound **3ap** was obtained as a yellow solid (mp 86°C- 92°C ) in 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 2H), 3.27 (s, 3H), 1.87 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.62, 144.62, 129.75, 127.73, 127.09, 37.17, 22.41. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>9</sub>H<sub>11</sub>NONa], 172.0733; found, 172.0732.

*N*-methyl-*N*-phenylpropionamide (3aq).



Compound **3aq** was obtained as a brown oil in 82% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.40 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.17 (m, 2H), 3.27 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  174.00, 144.27, 129.74, 127.70, 127.31, 37.32, 27.52, 9.73. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>10</sub>H<sub>13</sub>NONa], 186.0889; found, 186.0887.

N-methyl-N-phenylacrylamide (3ar).



Compound **3ar** was obtained as a yellow oil in 34% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.40 (m, 2H), 7.35 – 7.32 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.38 – 6.35 (m, 1H), 6.08 (dd, *J* = 16.3, 10.4 Hz, 1H), 5.51 (d, *J* = 10.3, 1H), 3.36 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  165.75, 143.45, 129.60, 128.52, 127.61, 127.38, 127.30, 37.42. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>10</sub>H<sub>12</sub>NO], 162.0913; found, 162.0912.

N-Methyl-N-phenylfuran-2-carboxamide (3as).



Compound **3as** was obtained as a sticky yellow liquid in 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.34 (m, 3H), 7.33 (d, *J* = 1.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.22 (dd,

J = 3.5, 1.7 Hz, 1H), 5.86 (d, J = 3.4 Hz, 1H), 3.46 (s, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.42, 147.08, 144.24, 144.18, 129.60, 127.83, 127.40, 116.31, 110.90, 38.47. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>12</sub>NO<sub>2</sub>], 202.0863; found, 202.0863.

N-Methyl-N-phenylthiophene-2-carboxamide (II-3at).



Compound **II-3at** was obtained as a brown solid (mp 68°C- 72°C ) in 99% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.35 (m, 3H), 7.29 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.27 – 7.23 (m, 2H), 6.77 (dd, J = 5.0, 3.8 Hz, 1H), 6.72 (dd, J = 3.8, 1.2 Hz, 1H), 3.45 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.74, 144.28, 138.17, 132.09, 130.48, 129.78, 128.14, 128.06, 126.63, 39.06.HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>12</sub>NOS], 218.0634; found, 2218.0636.

*N*-methyl-*N*-(naphthalen-2-yl)benzamide (3au).



Compound **3au** was obtained as a sticky yellow liquid in 99% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (s, 1H), 7.71 (t, *J* = 6.1 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.32 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.12 – 7.07 (m, 3H), 3.55 (s, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.61, 144.95, 133.56, 133.28, 132.42, 129.41, 129.23, 128.62, 127.57, 127.24, 127.11, 126.92, 126.52, 126.30, 125.50, 38.57. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>18</sub>H<sub>16</sub>NO], 262.1226; found, 262.1227.

#### N, N-diethylbenzamide (4ba).



Compound **4ba** was obtained as a yellow oil in 83% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.37–7.35 (m, 5H), 3.55 (s, 2H), 3.25 (s, 2H), 1.24 (s, 3H), 1.10 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  171.05, 137.09, 128.86, 128.17, 126.04, 43.06, 49.00, 14.00, 12.70. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>16</sub>NO], 178.1226; found, 178.1227.

N, N-diethyl-p-methylbenzamide (4bb).



Compound **4bb** was obtained as a colorless oil in 79% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.53 (s, 2H), 3.27 (s, 2H), 2.37 (s, 3H), 1.25 – 1.12 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.50, 139.07, 134.40, 128.98, 126.36, 43.30, 39.29, 21.34. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>18</sub>NO], 192.1383; found, 192.1383.

N,N-diethyl-4-fluorobenzamide (4bc).



Compound **4bc** was obtained as a yellow oil in 73% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.37 (m, 2H), 7.09 – 7.07 (m, 2H), 3.54 (s, 2H), 3.26 (s, 2H), 1.23 (s, 3H), 1.13 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.40, 162.57 (d,  $J_{C-F} = 97.2$  Hz), 133.31(d,  $J_{C-F} = 3.3$  Hz), 128.52 (d,  $J_{C-F} = 8.4$  Hz), 115.47 (d,  $J_{C-F} = 21.5$  Hz), 43.41, 39.40, 14.20, 12.88. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -111.39.HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>15</sub>FNO], 197.1132; found, 197.1133.

4-chloro-N,N-diethylbenzamide (4bd).



Compound **4bd** was obtained as a yellow oil in 64% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ 7.37 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 3.54 (s, 2H), 3.24 (s, 2H), 1.27 – 1.22 (m, 3H), 1.11 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.21, 135.64, 135.14, 128.69, 127.85, 43.32, 39.39, 14.23, 12.86. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>15</sub>ClNO], 212.0837; found, 212.0838.

4-bromo-N, N-diethylbenzamide (4be).



Compound **4be** was obtained as a yellow oil in 78% yield.<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

δ 7.53 (d, J = 8.3 Hz, 2H), 7.27 – 7.25 (m, 2H), 3.53 (s, 2H), 3.24 (s, 2H), 1.27 – 1.23 (m, 3H), 1.11 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.21, 136.11, 131.63, 128.06, 123.32, 43.29, 39.38, 14.20, 12.87. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>15</sub>BrNO], 256.0332; found, 256.0333.

4-cyano-N, N-diethylbenzamide (4bf).



Compound **4bf** was obtained as a yellow oil in 52% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 3.56 (d, J = 6.3 Hz, 2H), 3.21 (d, J = 6.4 Hz, 2H), 1.26 (s, 3H), 1.12 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.20, 141.59, 132.40, 127.07, 118.18, 113.07, 43.25, 39.48, 14.20, 12.84. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>15</sub>N<sub>2</sub>O], 203.1179; found, 203.1180.

#### N, N-diethyl-m-methylbenzamide (4bg).



Compound **4bg** was obtained as a yellow liquid in 66% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.25 (m, 1H), 7.20 – 7.13 (m, 3H), 3.54 (s, 2H), 3.25 (s, 2H), 2.36 (s, 3H), 1.28 – 1.22 (m, 3H), 1.11 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.49, 138.22, 137.29, 129.76, 128.21, 126.93, 123.16, 43.28, 39.19, 21.36, 14.19, 12.92. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>18</sub>NO], 192.1383; found, 192.1385.

#### N, N-diethyl-o-methylbenzamide (4bh).



Compound **4bh** was obtained as a yellow oil in 64% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 – 7.15 (m, 4H), 3.74 (s, 1H), 3.44 (s, 1H), 3.12 (q, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.85, 137.17, 133.83, 130.27, 128.50, 125.77, 125.43, 42.58, 38.65, 18.79, 13.99, 12.88. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>18</sub>NO], 192.1383; found, 192.1385. N,N-diethyl-3,5-dimethylbenzamide (4bi).



Compound **4bi** was obtained as a yellow liquid in 76% yield.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.01 (s, 1H), 6.96 (s, 2H), 3.53 (s, 2H), 3.25 (s, 2H), 2.32 (s, 6H), 1.23 (s, 3H), 1.10 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.67, 138.02, 137.29, 130.57, 123.85, 43.21, 39.06, 21.28, 14.23, 12.95. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>20</sub>NO], 206.1539; found, 206.1541.

#### N, N-diethyl-1-naphthylamide (4bj).



Compound **4bj** was obtained as a yellow oil in 87% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 – 7.84 (m, 4H), 7.54 – 7.49 (m, 2H), 7.47 (dd, J = 8.4, 1.4 Hz, 1H), 3.60 (s, 2H), 3.30 (s, 2H), 1.28 – 1.26 (m, 3H), 1.13 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.33, 134.64, 133.41, 132.80, 128.32, 128.28, 127.80, 126.78, 126.60, 125.76, 123.95, 43.41, 39.34, 21.28, 14.29, 13.03. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>18</sub>NO], 228.1383; found, 228.1383.

## N,N-diethylthiophene-2-carboxamide (4bk).



Compound **4bk** was obtained as a yellow liquid in 86% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 (dd, J = 5.0, 1.2 Hz, 1H), 7.32 (dd, J = 3.7, 1.1 Hz, 1H), 7.03 (dd, J = 5.0, 3.6 Hz, 1H), 3.54 (q, J = 7.1 Hz, 4H), 1.25 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  163.82, 138.33, 128.22, 127.96, 126.69, 41.83, 13.55. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>9</sub>H<sub>14</sub>NOS], 184.0791; found, 184.0790.

N,N-dibutylbenzamide (4bl).



Compound **4bl** was obtained as a yellow oil in 85% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.36 (m, 3H), 7.36 – 7.32 (m, 2H), 3.49 (s, 2H), 3.18 (s, 2H), 1.64 (s, 2H), 1.48 (s, 2H), 1.44-1.34 (m, 2H), 1.20-1.08 (m, 2H), 0.98 (s, 3H), 0.78 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.5, 137.0, 128.8, 128.1, 126.2, 48.5, 44.2, 30.5, 29.4, 20.1, 19.5, 13.7, 13.4. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>24</sub>NO], 234.1852; found, 234.1850.

N,N-diisopropylbenzamide (4bm).



Compound **4bm** was obtained as a yellow oil in 26% yield. H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 3.86 (m, 1H), 3.51 (m, 1H), 1.54 (m, 6H), 1.14 (m, 6H). <sup>113</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.1, 138.9, 128.6, 128.4, 125.6, 51.0, 45.8, 20.7. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>20</sub>NO], 206.1539; found, 206.1538.

N-ethyl-N-isopropylbenzamide (4bn).



Compound **4bn** was obtained as a yellow oil in 19% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.36 (m, 3H), 7.36 – 7.32 (m, 2H), 4.13-3.73 (m, 1H), 3.54-3.30 (m, 2H), 1.33-1.27 (m, 3H), 1.20-1.10 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.1, 137.6, 128.8, 128.4, 126.0, 50.2, 35.2, 21.1, 14.8. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>18</sub>NO], 192.1383; found, 192.1381.

2-(N-ethylbenzamido)ethyl [1,1'-bi(cyclohexane)]-1-carboxylate (4bo).



Compound **4bo** was obtained as a yellow oil in 31% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.31 (m, 5H), 4.59-3.93 (m, 2H), 3.92-3.58 (m, 2H), 3.58-3.10(m, 2H), 2.23-1.90 (m, 2H), 1.82-1.51 (m, 8H), 1.40-0.8 (m, 14H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  176.0, 171.9, 136.4, 129.3, 128.3, 126.2, 61.6, 50.8, 46.7, 44.7, 43.3, 31.3, 27.7, 26.9, 26.4, 25.8, 23.7, 14.0. HRMS (ESI): [M + H]<sup>+</sup> calcd for [C<sub>24</sub>H<sub>36</sub>NO<sub>3</sub>], 386.2690; found, 386.2692.

## 4. Mechanistic Investigations

#### **4.1 Luminescence Quenching Experiments**

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared prior to each set of experiments. Luminescence quenching experiments were run with CHCl<sub>3</sub> as the solvent. The solutions were irradiated at 410 nm and the luminescence was measured from 440 nm to 700 nm (emission maximum is at 530 nm). The concentration of Ph-Cz-NI stock solution was 0.3 mM in EA. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I0/I against concentration is done in Origin.



Figure S6. Fluorescence quenching data with Ph-Cz-NI and N, N-dimethylaniline (1a).



**Figure S7.** Stern-Volmer plot of Ph-Cz-NI and variable *N*, *N*-dimethylaniline (**1a**) (the intensity data was collected at 530 nm).



Figure S8. Fluorescence quenching data with Ph-Cz-NI and PFNB.



**Figure S9.** Stern-Volmer plot of Ph-Cz-NI and variable PFNB (the intensity data was collected at 530 nm).



Figure S10. Fluorescence quenching data with Ph-Cz-NI and benzoyl chloride (2a).



Figure S11. Stern-Volmer plot of Ph-Cz-NI and variable PhCOCl (2a) (the intensity data was collected at 530 nm).



Figure S12. Stern-Volmer quenching experiments of Cz-NI-Ph with different components (the intensity data was collected at 530 nm).

## 5. Determination of the Quantum Yield

#### 1) Determination of the light intensity at 436 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.<sup>2-4</sup> A 0.15 M solution of ferrioxalate was prepared by dissolving 1.84 g of potassium ferrioxalate hydrate in 25 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. A buffered solution of phenanthroline was prepared by dissolving 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at  $\lambda = 420$  nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

mol Fe<sup>2+</sup> = 
$$\frac{V \cdot \Delta A}{l \cdot \varepsilon}$$
 (eq.1)

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and  $\varepsilon$  is the molar absorptivity at 510 nm (11,100 L mol<sup>-1</sup> cm<sup>-1</sup>).

The photon flux can be calculated using eq 2.

photon flux = 
$$\frac{\text{mol Fe}^{2+}}{\phi \cdot t \cdot f}$$
 (eq.2)

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (1.01 at  $\lambda$ =436 nm),<sup>5</sup> t is the time (90.0 s), and *f* is the fraction of light absorbed at  $\lambda$  = 436nm by the ferrioxalate actinometer. This value is calculated using eq. 3, where A436 nm is the absorbance of the ferrioxalate solution at 436 nm.

$$f = 1 - 10^{-A_{436nm}}$$
 (eq.3)

Sample calculation:

$$\operatorname{mol}\operatorname{Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{0.00235 \, L \cdot 1.244}{1.0 \, cm \cdot 11,100 \, L \cdot mol^{-1} \cdot cm^{-1}} = 2.63 \, \times \, 10^{-7} \, mol$$

An absorption spectrum gave an A(436 nm) value of > 3, indicating that the fraction of absorbed light (f) is about 1.0.



 $f = 1 - 10^{-A_{436nm}} \approx 1.0$ 

Figure S5. The absorption spectrum of the ferrioxalate actinometer

photon flux =  $\frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} = \frac{2.63 \times 10^{-7} \text{ mol}}{1.01 \cdot 90.0 \text{ s} \cdot 1.0} = 2.89 \times 10^{-9} \text{ einstein} \cdot \text{s}^{-1}$ 

#### 2) Determination of the reaction quantum yield at 436 nm



**Cz-NI-Ph** (0.44 mg, 0.001 mmol, 1 mol%) and KHCO<sub>3</sub> (10.0 mg, 0.1 mmol, 1.0 equiv.) were weighed into an oven-dried 8 mL quartz cuvette with a magnetic stirring bar, and then EA (0.05 M, 2 mL) was added. The N,N-dimethylaniline **1a** (12.6  $\mu$ l, 0.1

mmol, 1.0 equiv.) and PFNB (6.5  $\mu$ L, 0.05 mmol, 0.5 equiv.) were added into the mixture *via* microsyringe. The reaction mixture was degassed by three cycles of freezepump-thaw. After the mixture was thoroughly degassed, the benzoyl chloride **2a** (12.8  $\mu$ l, 15.5 mg, 0.11 mmol, 1.1 equiv.) was added into the mixture *via* micro-syringe. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by blue light ( $\lambda = 436$  nm) for 10 minutes (600 s). After irradiation, the yield of the product **3aa** was determined by <sup>1</sup>H NMR based on a 1,3,5-trimethoxybenzene standard and the final yield was 6.06% (6.06 · 10<sup>-6</sup> mol).

The reaction quantum yield ( $\Phi$ ) was determined using eq. 4, where the photon flux is 2.89 × 10<sup>-9</sup> E's<sup>-1</sup> (determined by actinometry as described above), t is the reaction time (1800 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq. 3. An absorption spectrum of the reaction mixture gave an absorbance value of about 2 at 436 nm, indicating that essentially all the incident light (f > 0.999) is absorbed by the photocatalyst.

$$f = 1 - 10^{-A_{436nm}} = 1 - 10^{-2} = 0.99$$

$$\Phi = \frac{\text{mol of product formed}}{\text{photon flux} \cdot t \cdot f} = \frac{6.06 \times 10^{-6}}{2.89 \times 10^{-9} \times 6008 \times 0.99} = 3.5 \quad (\text{eq.4})$$

The reaction quantum yield ( $\Phi$ ) was thus determined to be 3.5.

# 6. NMR spectra of products

<sup>1</sup>H NMR of **3aa** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



## <sup>13</sup>C NMR of **3aa** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ba** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of 3ca in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3ca** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3da** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)




<sup>13</sup>C NMR of **3ea** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3fa** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3fa** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ga** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3ha** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



## <sup>13</sup>C NMR of **3ha** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ia** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





# <sup>13</sup>C NMR of **3ja** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3ka** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of 3ka in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3la** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ma** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3na** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3na** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3pa** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3qa** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



## <sup>13</sup>C NMR of **3qa** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ra** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ab** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ac** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ad** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)







<sup>13</sup>C NMR of **3ae** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR of **3af** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





 $^1\mathrm{H}$  NMR of 3ag in CDCl3 (400 MHz, CDCl3)



<sup>13</sup>C NMR of **3ag** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3ah** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3ah** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3ai** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





<sup>19</sup>F NMR of **3ai** in CDCl<sub>3</sub> (376 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3aj** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR of **3ak** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR of **3al** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3al** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3am** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3am** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR of **3an** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **3an** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **3ao** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **3ao** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **3ap** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)

7.5 502 502 502

6.5

6.0

5.5

5.0

4.5 4.0



3.5

8

3.0

2.5

2.0

89

1.5

1.0

0.5

0.0 ppm

# <sup>13</sup>C NMR of **3ap** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **3aq** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)





## <sup>13</sup>C NMR of **3aq** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3ar** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)







<sup>1</sup>H NMR of **3as** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



## <sup>13</sup>C NMR of **3as** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **3at** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of **3at** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3au** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



## <sup>13</sup>C NMR of **3au** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of 4ba in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4ba** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **4bb** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)


<sup>13</sup>C NMR of **4bb** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **4bc** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4bc** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>19</sup>F NMR of **4bc** in CDCl<sub>3</sub> (376 MHz, CDCl<sub>3</sub>)



#### <sup>1</sup>H NMR of **4bd** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4bd** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



#### <sup>1</sup>H NMR of **4be** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4be** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



#### <sup>1</sup>H NMR of **4bf** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4bf** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



#### <sup>1</sup>H NMR of **4bg** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4bg** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **4bh** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of **4bh** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR of **4bi** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





#### <sup>13</sup>C NMR of **4bj** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **4bk** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of **4bk** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of **4bl** in CDCl<sub>3</sub> (600 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of **4bl** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)





# <sup>1</sup>H NMR of **4bm** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of **4bm** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)







<sup>13</sup>C NMR of **4bn** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **4bo** in CDCl<sub>3</sub> (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **4bo** in CDCl<sub>3</sub> (101 MHz, CDCl<sub>3</sub>)



# References

- 1. M.-J. Yi, H.-X. Zhang, T.-F. Xiao, J.-H. Zhang, Z.-T. Feng, L.-P. Wei, G.-Q. Xu and P.-F. Xu, *ACS Catal.*, 2021, **11**, 3466-3472.
- 2. Cismesiaa, M. A. and P. Yoon, T. P. Chem. Sci. 2015, 6, 6019–6019.
- 3. Hatchard, C. G.; Parker, C. A. Proc. Roy. Soc. (London) 1956, A235, 518-536.
- (a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Pure Appl. Chem. 2004, 76, 2105–2146. (b) Monalti, M. et. al. Chemical Actinometry. Handbook of Photochemistry, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, 2006, 601–616.