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# **Supporting Information**

# **Organophotoredox-catalyzed redox-neutral cascade involving** *N*-(acyloxy)phthalimides and allenamides: Synthesis of indoles

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General Information: Photoredox reactions were performed under an argon atmosphere for all the reaction sets, using pre-dried glassware and standard glass tubes. All the solvents were dried with calcium hydride and freshly distilled under argon. The following starting materials and the reaction components acetyl chloride, benzoyl chloride and propargyl bromide, N-hydroxyphthalimide, aniline and benzoic acid derivatives, oxalyl chloride, phenol derivatives, N,N'-dicyclohexylcarbodiimide (DCC), 4-N,N-dimethylamino-pyridine (DMAP), K<sub>2</sub>CO<sub>3</sub>, DIPEA, Et<sub>3</sub>N, DABCO, KO'Bu, all the photocatalysts and TEMPO, BHT, were obtained from commercial sources and were used without further purification. Other benzoyl chloride and phthalimide ester derivatives were synthesized by the synthetic procedures mentioned below. Yields refer to isolated compounds, estimated to be >95% pure as determined by <sup>1</sup>H NMR and <sup>13</sup>C NMR. All optimized photo-redox reactions were conducted under the photo-irradiation using a 36 W Kessil blue LED (427 nm) lamp. Thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 aluminum sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on Chempure silica gel (60-120 mesh or 100–200 mesh). Nuclear magnetic resonance (NMR) spectroscopy was performed using JEOL 400 MHz and Bruker 500 MHz spectrometers. If not otherwise specified, chemical shifts ( $\delta$ ) are provided in ppm. **HRMS** spectra were recorded using Bruker Maxis Impact mass spectrometer (TOF). The fluorescence experiment was recorded with a "HITACHI f-7000" Scientific Spectrofluorometer. Gas chromatography was performed on SCION 436-GC instrument.

#### **Procedure for the Synthesis of Starting Materials:**

# (A) General Procedure for the Synthesis of N-(prop-2-yn-1-yl)anilines:<sup>1</sup>



To a solution of aniline (20.0 mmol, 1.0 equiv) in DMF (30.0 mL), 3-bromopropyne (2.4 g, 20.0 mmol, 1.0 equiv) and potassium carbonate (4.2 g, 30.0 mmol, 1.5 equiv) were added. Then the mixture was stirred for 12 h at room temperature. The solution was diluted with DCM (20 mL) and washed with aqueous HCl (4 M,  $2 \times 30$  mL), and brine solution (30 mL). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuo. *N*-(prop-2-yn-

1-yl)anilines S1 were further purified by 60-120 mesh silica gel column chromatography using 2% ethyl acetate in hexane as the eluent to obtain 60-80% yield.

#### (B) General Procedure for the Synthesis of Benzoyl Chlorides:<sup>2</sup>



To a suspension of benzoic acid (20 mmol, 1.0 equiv) in DCM (20 mL), oxalyl chloride (5.1 g, 40 mmol, 2.0 equiv) was added dropwise at 0 °C. After that five drop of DMF was added, and stirred at room temperature until the acid was completely consumed (monitored by TLC). The solvent and excess oxalyl chloride were removed by vacuum and the residual benzoyl chloride derivative **S2** was directly used in the following step.

# (C) General Procedure for the Synthesis of *N*-phenyl-*N*-(prop-2-yn-1-yl)benzamide:<sup>3</sup>



The residual benzoyl chloride derivative **S2** or acetyl chloride or tosyl chloride or Boc anhydride (1.2 equiv) was dissolved in DCM (10 mL) and cooled to 0 °C. Then a solution of compound **S1** (1.0 equiv) in DCM was added dropwise, followed by triethylamine (1.2 equiv) in DCM (20 mL). After stirring at room temperature for 24 h (monitored by TLC), the reaction mixture was quenched with  $H_2O$  (20 mL). The organic phase was separated, dried over  $Na_2SO_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to give the compound **S3**.

# (D) General Procedure for the Synthesis of Allenamide:<sup>4</sup>



An oven dried 50 mL flask was equipped with a magnetic stir bar and compounds **S3** (5.0 mmol, 1.0 equiv) in dry THF (10 mL), then KO'Bu (28 mg, 0.25 mmol, 0.05 equiv) was added at 0 °C. The reaction mixture was then allowed to come to the room temperature and stirred for 0.5-1.0 h (monitored by TLC). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to give the allenamide **1a-z** (80-90%).

# (E) General Procedure for the Synthesis of N-(acyloxy)phthalimides:<sup>5</sup>



The *N*-hydroxyphthalimide (1.63 g, 10 mmol, 1.1 equiv), carboxylic acid (12.00 mmol, 1.2 equiv), *N*,*N*'-dicyclohexylcarbodiimide (2.47 g, 12 mmol, 1.2 equiv) and 4-dimethylaminopyridine (0.61 g, 0.50 mmol, 0.05 equiv) were taken in a flask along with a magnetic stirring bar. DCM (15 mL) was added and the orange reaction mixture was stirred for 12 h at room temperature. The white precipitate was filtered off and the solution was concentrated by evaporation. Purification by silica gel column chromatography on using 20% ethyl acetate in hexane to delivered *N*-(acyloxy)phthalimides **2**.

# (F) Optimization Study for the Organo-photoredox Catalyzed Cascade Radical Annulation:

Allenamide **1a/1a-Ac/1a-Boc/1a-Ts** (0.25 mmol, 1.0 equiv), 1,3-dioxoisoindolin-2-yl pivalate (**2a**, 0.75 mmol, 185 mg, 3.0 equiv) and photocatalyst (12.5  $\mu$ mol, 5 mol%)were placed in a pre-dried 15 mL reaction tube. The tube was degassed and purged with argon three times. Solvent (3.0 mL) and base (0.75 mmol, 3.0 equiv) were added and the mixture was irradiated

under light and stirred for 24-36 h under argon atmosphere using a balloon. The reaction mixture was then concentrated under vacuum, and purified by silica gel column chromatography using 2% ethyl acetate in hexane to deliver the annulated product **3aa**.



S. No.	R	Catalyst	Base	Solvent	Yield $(\%)^b$
1	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	74
2	Ac (1a-Ac)	Eosin Y	DIPEA	DCE	45
3	Boc ( <b>1a-Boc</b> )	Eosin Y	DIPEA	DCE	N.D.
4	Ts ( <b>1a-Ts</b> )	Eosin Y	DIPEA	DCE	N.D.
5	Bz ( <b>1a</b> )	Rose Bengal	DIPEA	DCE	30
6	Bz ( <b>1a</b> )	Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	DIPEA	DCE	25
7	Bz ( <b>1a</b> )	Fluorescein	DIPEA	DCE	55
8	Bz ( <b>1a</b> )	Eosin Y	DIPEA	CH <sub>3</sub> CN	72
9	Bz ( <b>1a</b> )	Eosin Y	DIPEA	1,4-Dioxane	60
10	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCM	56
11	Bz ( <b>1a</b> )	Eosin Y	DIPEA	EtOH	N.D.
12	Bz ( <b>1a</b> )	Eosin Y	DABCO	DCE	N.D.
13	Bz ( <b>1a</b> )	Eosin Y	2,6-Lutidine	DCE	N.D.
14	Bz ( <b>1a</b> )	Eosin Y	Et <sub>3</sub> N	DCE	66
15	Bz ( <b>1a</b> )	Eosin Y	$K_2CO_3$	DCE	N.D.
16 <sup><i>c</i></sup>	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	53
$17^{d}$	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	36
$18^{e}$	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	49
19 <sup>f</sup>	Bz ( <b>1a</b> )	-	DIPEA	DCE	N.D.
$20^g$	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	N.D.
21	Bz ( <b>1a</b> )	Eosin Y	-	DCE	N.D.
$22^{h}$	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	N.D.
$23^{i}$	Bz ( <b>1a</b> )	Eosin Y	DIPEA	DCE	53
$24^{j}$	Bz (1a)	Eosin Y	DIPEA	DCE	45

<sup>*a*</sup>Reaction conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), catalyst (5 mol%), base (3 equiv) and solvent (3.0 mL) under argon atmosphere using Blue LEDs (427 nm) for 36 h. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Using 2 mol% Eosin Y. <sup>*d*</sup>Using 1.5 equiv DIPEA. <sup>*e*</sup>Reaction was carried out for 24 h. <sup>*f*</sup>In the absence of photocatalyst. <sup>*s*</sup>In the absence of light. <sup>*h*</sup>Air atmosphere. N.D. = Not detected. <sup>*i*</sup>Using Blue LEDs (440 nm). <sup>*j*</sup>UsingWhite CFL.

# General Procedure for the Organo-photoredox Catalyzed Cascade Radical Annulation Involving Allenamides 1 and *N*-(acyloxy)phthalimides 2 (GP):



Allenamides derivative 1(0.25 mmol, 1.0 equiv), *N*-(acyloxy)phthalimide derivative 2 (0.75 mmol, 3.0 equiv) and Eosin Y (9 mg, 12.5 µmol, 5 mol%)were placed in a pre-dried 15 mL reaction tube. The tube was degassed and purged with argon three times. DCE (3.0 mL) and DIPEA (97 mg, 0.75 mmol, 3.0 equiv) were added, and the mixture was irradiated using 36 W Kessil blue LED (427 nm) lamp and stirred for 36 h under argon atmosphere using a balloon. After completion, the reaction mixture was concentrated under vacuum, and purified by silica gel column chromatography using 1-3% ethyl acetate in hexane to deliver the annulated product **3**.

# Scheme S1: Scale Up Experiment and Post-Synthetic Modification



# Gram Scale Synthesis of 3aa:



*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (1.18 gm, 5 mmol, 1.0 equiv), 1,3dioxoisoindolin-2-yl pivalate **2a** (3.7 g, 15 mmol, 3.0 equiv) and Eosin Y (173 mg, 62.5  $\mu$ mol, 5 mol%)were placed in a pre-dried 100 mL two neck round bottom flask. The flask was degassed and purged with argon three times. DCE (50.0 mL) and DIPEA (1.95 g, 15 mmol, 3.0 equiv) were added, and the mixture was irradiated using a 36 W Kessil blue LED (427 nm) lamp and stirred for 36 h under argon atmosphere using a balloon. After completion, the reaction mixture was concentrated under vacuum and purified by silica gel column chromatography using 2% ethyl acetate in hexane to deliver the annulated product **3aa** (0.89 g, 61%).

#### **Product derivatizations:**

## 1) Synthesis of 3-neopentyl-1*H*-indole (S4):



An oven-dried 10 mL flask was equipped with a magnetic stir bar and a solution of indole derivative **3aa** (145 mg, 0.5 mmol, 1.0 equiv) in MeCN (2 mL), water (1.0 mL) andNaOH (30 mg, 1.5 mmol, 3.0 equiv) were added. The reaction mixture was then heated to 80 °C for 1.0 h (monitored by TLC). At ambient temperature EtOAc (10 ml) was added. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to deliver compound **S4** (89 mg, 95%).

# 2) Synthesis of (2,5-dibromo-3-neopentyl-1*H*-indol-1-yl)(phenyl) methanone (S5):



An oven-dried 10 mL flask was equipped with a magnetic stir bar and a solution of indole derivative **3aa** (145 mg, 0.5 mmol, 1.0 equiv) in methanol (3.0 mL), NBS (178 mg, 1.0 mmol, 2.0 equiv) were added. The reaction mixture was then stirred at room temperature for 1.0 h (monitored by TLC). After completion, the solvent was evaporated and the residue was dissolved in H<sub>2</sub>O (10 mL) and EtOAc (10 ml). The organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to deliver the compound **S5** (142 mg, 63%).

## **Report of NMR Spectra:**

(3-neopentyl-1H-indol-1-yl)(phenyl)methanone (3aa): GP was followed using



eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3aa** (54 mg, 74%); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, *J* = 7.7

Hz, 1H), 7.74 (t, J = 4.2 Hz, 2H), 7.64 – 7.50 (m, 4H), 7.34 (m, 2H), 7.05 (s, 1H), 2.56 (s, 2H), 0.96 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 136.2, 135.1, 132.5, 131.9, 129.3, 128.7, 125.9, 124.8, 123.7, 120.1, 119.9, 116.4, 38.7, 32.2, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>21</sub>NONa [M + Na ]<sup>+</sup> 314.1521; found 314.1516.



## 1-(3-neopentyl-1H-indol-1-yl)ethan-1-one (3aa-Ac):

**GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a-Ac** (43 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3aa-Ac** (26 mg, 45%); <sup>1</sup>**H NMR** (400

MHz, CDCl<sub>3</sub>)  $\delta$  8.42 (d, *J* = 6.1 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.38 – 7.25 (m, 2H), 7.16 (s, 1H), 2.63 (s, 3H), 2.59 (s, 2H), 0.99 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 135.7, 132.2, 125.0, 123.7, 123.4, 120.7, 119.9, 116.5, 38.8, 32.1, 29.9, 24.2. **HRMS-ESI** (m/z): calcd for C<sub>15</sub>H<sub>19</sub>NONa [M + Na]<sup>+</sup> 252.1364; found 252.1363.

### (5-methyl-3-neopentyl-1H-indol-1-



yl)(phenyl)methanone (3ba): GP was followed using eosin
Y (9.0 mg, 5.0 mol%), N-(propa-1,2-dien-1-yl)-N-(p-tolyl)benzamide 1b (62 mg, 0.25 mmol), and 1,3-dioxoisoindolin2-yl pivalate 2a (185 mg, 0.75 mmol). After 36 h, purification by

column chromatography using 1% ethyl acetate in hexanes yielded **3ba** (53 mg, 70%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.36 (s, 1H), 7.19 (d, J = 8.3 Hz, 1H), 7.02 (s, 1H), 2.55 (s, 2H), 2.50 (s, 3H), 0.98 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 135.2, 134.4, 133.2, 132.7, 131.7, 129.2, 128.6, 126.0, 126.0, 119.9, 119.8, 116.0, 38.6, 32.1, 29.9, 21.7. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 328.1677; found 328.1663.



(5-ethyl-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (3ca): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-ethylphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1c** (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by

column chromatography using 1% ethyl acetate in hexanes yielded **3ca** (57 mg, 72%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.38 (s, 1H), 7.22 (d, J = 8.3 Hz, 7.03 (s, 1H), 2.79 (q, *J* = 7.5 Hz, 2H), 2.56 (s, 2H), 1.31 (t, *J* = 7.5 Hz, 3H), 0.98 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 139.9, 135.2, 134.5, 132.7, 131.7, 129.2, 128.6, 126.0, 125.0, 120.1, 118.6, 116.1, 38.7, 32.1, 29.9, 29.2, 16.4. **HRMS-ESI** (m/z): calcd for C<sub>22</sub>H<sub>25</sub>NONa [M + Na]<sup>+</sup> 342.1834; found 342.1836.



(5-isopropyl-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (3da): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-isopropylphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1d** (69 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by

column chromatography using 1% ethyl acetate in hexanes yielded **3da** (55 mg, 66%); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, J = 8.5 Hz, 1H), 7.72 (dd, J = 8.2, 1.4 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.52 (ddd, J = 6.8, 4.6, 1.2 Hz, 2H), 7.40 (d, J = 1.6 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.02 (s, 1H), 3.05 (dt, J = 13.8, 6.9 Hz, 1H), 2.56 (s, 2H), 1.33 (d, J = 6.8 Hz, 6H), 0.97 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.3, 144.6, 135.2, 134.6, 132.6, 131.7, 129.2, 128.6, 126.0, 123.6, 120.2, 117.2, 116.1, 38.7, 34.4, 32.2, 29.9, 24.6. **HRMS-ESI** (m/z): calcd for C<sub>23</sub>H<sub>27</sub>NONa [M + Na]<sup>+</sup> 356.1990; found 356.1979.



(5-methoxy-3-neopentyl-1H-indol-1yl)(phenyl)methanone (3ea): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide 1e (66 mg, 0.25 mmol), and 1,3dioxoisoindolin-2-yl pivalate 2a (185 mg, 0.75 mmol). After 36

h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3da** (57 mg, 71%); <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 8.9 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.58 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.56 – 7.48 (m, 2H), 6.99 (dt, *J* = 9.0, 2.8 Hz, 3H), 3.89 (s, 3H), 2.52 (s, 2H), 0.96 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 156.7, 135.1, 133.6, 131.7, 130.9, 129.2, 128.6, 126.7, 123.1, 120.0, 117.2, 112.7, 103.2, 55.9, 38.7, 32.2, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 344.1626; found 344.1618.



# (5-fluoro-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (3fa): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-fluorophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1f** (63 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36

h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3fa** (46 mg, 60%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 6.1 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 13.3 Hz, 2H), 2.52 (s, 2H), 0.96 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 159.9 (d, *J* = 240.3 Hz), 134.7, 133.7 (d, *J* = 9.4 Hz), 132.5, 131.9, 129.2, 128.7, 127.4, 119.8 (d, *J* = 4.0 Hz), 117.5 (d, *J* = 9.1 Hz), 112.4 (d, *J* = 24.8 Hz), 105.6 (d, *J* = 23.8 Hz), 38.6, 32.1, 29.8. <sup>19</sup>**F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -118.7. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NFONa [M + Na]<sup>+</sup> 332.1427; found 332.1430.

# (5-chloro-3-neopentyl-1H-indol-1-



**yl)(phenyl)methanone (3ga): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-chlorophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1g** (67 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded

**3ga** (51 mg, 63%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 3H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.07 (s, 1H), 2.52 (s, 2H), 0.96 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 134.6, 134.5, 133.8, 132.1, 129.4, 129.3, 128.7, 127.1, 124.9, 119.6, 119.4, 117.4, 38.6, 32.1, 29.8 **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NClONa [M + Na]<sup>+</sup> 348.1131; found 348.1119.



(5-bromo-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (3ha): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-bromophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1h** (78 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl

acetate in hexanes yielded **3ha** (64 mg, 70%); <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.69 (s, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 8.7 Hz, 1H), 7.05 (s, 1H), 2.51 (s, 2H), 0.95 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 134.9, 134.6, 134.3, 132.1, 129.3, 128.8, 127.6, 127.0, 122.7, 119.4, 117.8, 117.1, 38.6, 32.1, 29.8. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NBrONa [M + Na]<sup>+</sup> 392.0626; found 392.0624.



(3-neopentyl-5-(trifluoromethyl)-1H-indol-1yl)(phenyl)methanone (3ia): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(propa-1,2-dien-1-yl)-*N*-(4-(trifluoromethyl)phenyl)benzamide 1i (76 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate 2a (185 mg, 0.75 mmol). After

36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3ia** (48 mg, 54%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.37 (dt, *J* = 22.5, 7.4 Hz, 2H), 6.94 (s, 1H), 2.57 (s, 2H), 0.97 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ 167.05, 138.45, 136.10, 133.50

(q, J = 32.8 Hz), 132.56, 129.48, 125.81 (q, J = 3.7 Hz), 125.20 (q, J = 32.8 Hz), 124.15, 123.71 (q, J = 272.6 Hz), 121.1, 120.1, 116.5, 38.6, 32.1, 29.9.<sup>19</sup>**F NMR** (471 MHz, CDCl<sub>3</sub>)  $\delta$  -63.0. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>20</sub>NF<sub>3</sub>ONa [M + Na]<sup>+</sup> 382.1395; found 382.1351.



(4-methyl-3-neopentyl-1H-indol-1yl)(phenyl)methanone & (6-methyl-3-neopentyl-1H-indol-1-

yl)(phenyl)methanone (3ja + 3j'a):

GP was followed using eosin Y (9.0 mg, 5.0

mol%), *N*-(propa-1,2-dien-1-yl)-*N*-(m-tolyl)benzamide **1j** (62 mg, 0.25 mmol), and 1,3dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded (**3ja+3j'a**) (43 mg, 57%).

For **3ja:** <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 6.8 Hz, 1H), 7.12 – 7.05 (m, 2H), 2.81 (s, 2H), 2.75 (s, 3H), 1.00 (s, 9H).

For **3j'a:** <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 6.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 2.57 (s, 1H), 2.54 (s, 2H), 1.00 (s, 9H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 168.4, 136.6, 136.5, 135.2, 135.2, 134.9, 131.8, 131.7, 131.0, 130.3, 130.3, 129.3, 129.2, 128.6, 126.5, 126.4, 125.4, 125.1, 124.6, 120.3, 120.1, 119.5, 116.7, 114.3, 39.1, 38.7, 32.2, 32.1, 29.9, 29.7, 22.0, 21.2. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 328.1677; found 328.1666.



(4-chloro-3-neopentyl-1H-indol-1-yl)(phenyl)methanone & (6chloro-3-neopentyl-1H-indol-1yl)(phenyl)methanone (3ka + 3k'a): GP was followed using eosin

Y (9.0 mg, 5.0 mol%), *N*-(3-chlorophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1k** (67 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification

by column chromatography using 1% ethyl acetate in hexanes yielded (**3ka+3k'a**) (48 mg, 59%).

For **3ka** : <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.22 (m, 2H), 7.08 (s, 1H), 2.94 (s, 2H), 0.97 (s, 9H).

For **3k'a** : <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.47 (s, 1H), 7.74 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.22 (m, 2H), 7.04 (s, 1H), 2.53 (s, 2H), 0.95 (s, 9H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.4, 137.7, 136.5, 134.6, 132.2, 132.1, 130.9, 130.8, 129.6, 129.4, 129.3, 128.7, 128.5, 128.4, 127.5, 126.7, 126.4, 125.7, 125.3, 124.2, 120.6, 119.8, 119.5, 116.7, 115.1, 38.6, 37.8, 32.1, 29.8, 29.5. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>ClNONa [M + Na]<sup>+</sup> 348.1131; found 348.1123.



(3-neopentyl-4-(trifluoromethyl)-1H-indol-1-yl)(phenyl)methanone & (3-neopentyl-6-

(trifluoromethyl)-1H-indol-1-

yl)(phenyl)methanone (3la + 3l'a):

**GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(propa-1,2-dien-1-yl)-*N*-(3-(trifluoromethyl)phenyl)benzamide **11** (77 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 3% ethyl acetate in hexanes yielded (**3la**+**3la**) (44 mg, 49%).

For **3la:** <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.71 – 7.61 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 2.76 (s, 2H), 0.94 (s, 9H).

For **3la:** <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 7.80 – 7.71 (m, 2H), 7.71 – 7.61 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 2.58 (s, 2H), 0.96 (s, 9H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.3, 168.3, 137.1, 135.2, 134.7, 134.2, 134.2, 132.3, 132.2, 129.3, 129.2, 128.7, 128.7, 128.1, 126.7 (q, *J* = 32.1 Hz), 124.7 (q, *J* = 272.1 Hz), 124.3 (q, *J* = 272.1 Hz), 123.6, 122.1 (q, *J* = 7.0 Hz), 121.8 (q, *J* = 32.1 Hz), 120.3 (q, *J* = 4.0 Hz), 120.3, 120.1 120.0, 119.6, 118.4, 113.8, 113.0, 38.4, 37.3, 37.3, 37.2 (q, *J* = 3.0 Hz), 37.2, 32.0, 29.6, 29.6.

<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -55.5, -60.9. HRMS-ESI (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NF<sub>3</sub>ONa [M + Na]<sup>+</sup> 382.1395; found 382.1395.



(4,5-dimethyl-3-neopentyl-1Hindol-1-yl)(phenyl)methanone & (5,6-dimethyl-3-neopentyl-1Hindol-1-yl)(phenyl)methanone (3ma +3m'a): GP was followed using

eosin Y (9.0 mg, 5.0 mol%), *N*-(3,4-dimethylphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1m** (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 3% ethyl acetate in hexanes yielded (**3ma** + **3m'a**) (44 mg, 55%).

For **3ma:** <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.62 – 7.55 (m, 1H), 7.54 – 7.48 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.97 (s, 1H), 2.80 (s, 2H), 2.59 (s, 3H), 2.38 (s, 3H), 0.95 (s, 9H).

For **3m'a:** <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.21 (s, 1H), 7.76 – 7.69 (m, 2H), 7.62 – 7.55 (m, 1H), 7.54 – 7.48 (m, 2H), 7.30 (s, 1H), 6.92 (s, 1H), 2.50 (s, 2H), 2.51 (s, 3H), 2.40 (s, 3H), 0.95 (s, 9H).

<sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 168.3, 135.5, 135.3, 135.3, 133.8, 132.5, 132.4, 131.7, 131.6, 130.7, 130.4, 129.2, 129.2, 129.2, 128.6, 127.1, 127.0, 125.2, 120.3, 120.2, 120.0, 117.0, 113.6, 39.7, 38.7, 32.3, 32.1, 29.9, 29.8, 20.6, 20.4, 20.3, 16.7. **HRMS-ESI** (m/z): calcd for C<sub>22</sub>H<sub>25</sub>NONa [M + Na]<sup>+</sup> 342.1834; found 342.1823.



## (4-methoxy-3-neopentyl-1H-indol-1-

yl)(phenyl)methanone (3na): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(3-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide 1n (66 mg, 0.25 mmol), and 1,3dioxoisoindolin-2-yl pivalate 2a (185 mg, 0.75 mmol). After 36

h, purification by column chromatography using 3% ethyl acetate in hexanes yielded **3na** (50 mg, 63%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 2.76 (s, 2H), 0.89 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.6, 154.5, 137.7, 135.2, 131.8, 129.3, 128.6, 125.6, 124.8, 121.6, 120.1, 109.4, 104.8, 55.0,

39.0, 32.2, 29.5. **HRMS-ESI** (m/z): calcd for  $C_{21}H_{23}NO_2H [M + H]^+$  322.1807; found 322.1804.



(7-methyl-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (30a): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(propa-1,2-dien-1-yl)-*N*-(*o*tolyl)benzamide **10** (62 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by

column chromatography using 1% ethyl acetate in hexanes yielded **30a** (46 mg, 60%); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (dd, J = 8.3, 1.2 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.54 (dd, J =10.7, 4.5 Hz, 2H), 7.44 (d, J = 7.7 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 6.96 (s, 1H), 2.55 (s, 2H), 2.48 (s, 3H), 0.94 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 135.9, 134.5, 133.7, 133.0, 130.5, 128.8, 127.5, 127.4, 126.1, 123.7, 119.1, 117.7, 38.7, 32.1, 29.9, 21.8. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 328.1677; found 328.1688.



#### (3-neopentyl-1H-indol-1-yl)(p-tolyl)methanone

(3pa): GP was followed using eosin Y (9.0 mg, 5.0 mol%), 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide 1p (62 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate 2a (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded 3pa

(55 mg, 72%); <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.08 (s, 1H), 2.56 (s, 2H), 2.47 (s, 3H), 0.96 (s, 9H). <sup>13</sup>**C** NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 142.5, 136.2, 132.5, 132.2, 129.5, 129.3, 126.1, 124.7, 123.5, 119.9, 119.8, 116.3, 38.7, 32.2, 29.9, 21.8. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NOH [M + H]<sup>+</sup> 306.1858; found 306.1858.



(4-(tert-butyl)phenyl)(3-neopentyl-1H-indol-1yl)methanone (3qa): GP was followed using eosin Y (9.0 mg, 5.0 mol%), 4-(tert-butyl)-*N*-phenyl-*N*-(propa-1,2-dien-1yl)benzamide 1q (73 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate 2a (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes

yielded **3qa** (59 mg, 68%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.41 (d, J = 8.0 Hz, 1H), 7.71 (d, J

= 7.8 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.9 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.12 (s, 1H), 2.58 (s, 2H), 1.40 (s, 9H), 0.98 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 155.6, 136.2, 132.4, 132.1, 129.4, 126.2, 125.6, 124.7, 123.5, 119.9, 119.8, 116.4, 38.7, 35.2, 32.2, 31.3, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>24</sub>H<sub>29</sub>NONa [M + Na]<sup>+</sup> 370.2147; found 370.2141.



# (4-methoxyphenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3ra): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 4-methoxy-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1r** (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes

yielded **3ra** (53 mg, 66%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.32 (dt, *J* = 23.4, 7.3 Hz, 2H), 7.11 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 3.91 (s, 3H), 2.58 (s, 2H), 0.97 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 162.7, 136.3, 132.4, 131.7, 127.1, 126.2, 124.5, 123.4, 119.9, 119.6, 116.2, 114.0, 55.6, 38.7, 32.2, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NOH [M + H]<sup>+</sup> 322.1807; found 322.1804



## (4-iodophenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3sa): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 4-iodo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1t** (90 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes

yielded **3ta** (67 mg, 64%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.35 (dt, *J* = 21.6, 6.9 Hz, 2H), 7.00 (s, 1H), 2.56 (s, 2H), 0.97 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 137.9, 136.1, 134.5, 132.5, 130.7, 125.5, 124.9, 123.9, 120.6, 120.0, 116.4, 99.0, 38.7, 32.1, 29.9 **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NIONa [M + Na] + 340.0487; found 340.0462.



# (4-bromophenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3ta): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 4-bromo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1s** (78 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes

yielded **3sa** (60 mg, 65%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.00 (s, 1H), 2.57 (s, 2H), 0.97 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 136.1, 133.8, 132.5, 132.0, 130.8, 126.7, 125.5, 124.9, 123.9, 120.6, 120.0, 116.3, 38.7, 32.1, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>21</sub>NBrOH [M + H]<sup>+</sup> 370.0807; found 370.0800.



# 4-(3-neopentyl-1H-indole-1-carbonyl)benzonitrile

(**3ua**): GP was followed using eosin Y (9.0 mg, 5.0 mol%), 4cyano-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1u** (65 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded **3ua** (43 mg, 55%); <sup>1</sup>H

**NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 7.9 Hz, 1H), 7.82 (s, 4H), 7.59 (d, J = 7.6 Hz, 1H), 7.36 (dt, J = 18.6, 7.1 Hz, 2H), 6.89 (s, 1H), 2.56 (s, 2H), 0.96 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 138.9, 135.9, 132.5, 129.5, 125.2, 124.8, 124.2, 121.3, 120.1, 117.8, 116.4, 115.3, 38.5, 32.0, 29.8. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>ONa [M + Na]<sup>+</sup> 339.1473; found 339.1436.



## (3-neopentyl-1H-indol-1-yl)(o-tolyl)methanone

(**3va**): **GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 2methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1v** (62 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded **3va** (50 mg, 66%); <sup>1</sup>**H** 

**NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.34 (s, 4H), 6.80 (s, 1H), 2.53 (s, 2H), 2.35 (s, 3H), 0.94 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.9, 135.8, 135.7, 135.5, 132.8, 130.9, 130.5, 127.5, 126.0, 125.2, 124.8, 123.8, 120.7, 120.0, 116.4,

38.6, 32.1, 29.9, 19.4. **HRMS-ESI** (m/z): calcd for  $C_{21}H_{23}NONa [M + Na]^+$  328.1677; found 328.1639.



# (2-methoxyphenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3wa): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 2-methoxy-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1w** (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes

yielded **3wa** (43 mg, 54%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 (s, 1H), 7.52 (dd, J = 19.8, 7.9 Hz, 2H), 7.46 (d, J = 7.4 Hz, 1H), 7.32 (dt, J = 14.7, 7.1 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.82 (s, 1H), 3.77 (s, 3H), 2.52 (s, 2H), 0.94 (s, 9H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.1, 156.4, 135.7, 132.7, 132.2, 129.3, 125.8, 125.2, 124.7, 123.6, 120.9, 120.1, 119.8, 116.5, 111.4, 106.6, 55.7, 38.6, 32.0, 29.8. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>2</sub>Na [M + Na]<sup>+</sup> 344.1627; found 344.1603.

## (2-fluorophenyl)(3-neopentyl-1H-indol-1-yl)methanone (3xa): GP was followed



using eosin Y (9.0 mg, 5.0 mol%), 2-fluoro-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1x** (63 mg, 0.25 mmol), and 1,3dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3xa** (47 mg, 61%); <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (s, 1H), 7.77 – 7.54 (m, 3H), 7.51 – 7.34

(m, 3H), 7.28 (dd, J = 16.1, 7.0 Hz, 1H), 6.91 (s, 1H), 2.59 (s, 2H), 1.00 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.2, 159.1 (d, J = 251.9 Hz), 135.8, 133.1 (d, J = 8.1 Hz), 132.8, 130.2 (d, J = 2.7 Hz), 125.1, 125.0, 124.8 (d, J = 3.6 Hz), 124.1, 123.8 (d, J = 16.0 Hz), 121.1, 120.0, 116.6, 116.5 (d, J = 4.5 Hz), 38.6, 32.1, 29.8. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -112.7. HRMS-ESI (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NFOH [M + H]<sup>+</sup> 310.1607; found 310.1609.



# (2-bromophenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3ya): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), 2-bromo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1y** (78 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes

yielded **3xa** (54 mg, 59%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 2H), 7.44 – 7.30 (m, 3H), 6.65 (s, 1H), 2.52 (s, 2H), 0.94 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 137.5, 135.6, 133.3, 132.9, 131.7, 128.9, 127.8, 125.1, 124.9, 124.1, 121.4, 120.0, 119.8, 116.5, 38.6, 32.1, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NBrONa [M + Na]<sup>+</sup> 392.0626; found 392.0647.



(3-iodophenyl)(3-neopentyl-1H-indol-1-

**yl)methanone (3za):GP**was followed using eosin Y (9.0 mg, 5.0 mol%), 3-iodo-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1z** (90 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl pivalate **2a** (185 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes

yielded **3za** (62 mg, 60%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 7.9 Hz, 1H), 8.10 (s, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.60 (s, 1H), 7.36 (dt, J = 21.6, 7.1 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.00 (s, 1H), 2.58 (s, 2H), 0.98 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.6, 140.7, 138.0, 136.9, 136.1, 132.5, 130.3, 128.2, 125.5, 125.0, 123.9, 120.7, 120.0, 116.4, 94.1, 38.6, 32.1, 29.9. **HRMS-ESI** (m/z): calcd for C<sub>20</sub>H<sub>20</sub>NIONa [M + Na] + 340.0487; found 340.0482.



(3-((1-methylcyclohexyl)methyl)-1H-indol-1yl)(phenyl)methanone (3ab): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1yl)benzamide 1a (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl 1-methylcyclohexane-1-carboxylate 2b (215 mg, 0.75 mmol). After 36 h, purification by column chromatography

using 1% ethyl acetate in hexanes yielded **3ab** (48 mg, 58%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 6.9 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.54 (q, *J* = 7.4 Hz, 2H), 7.34 (dt, *J* = 19.9, 7.2 Hz, 2H), 7.05 (s, 1H), 2.58 (s, 2H), 1.46 (dd, *J* = 50.8, 10.4 Hz, 5H), 1.35 – 1.14 (m, 5H), 0.91 (s, 3H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.5, 136.2, 135.1, 132.8, 131.8, 129.3, 128.7, 126.0, 124.7, 123.7, 120.0, 119.4, 116.4, 37.9, 34.5, 33.6, 26.5, 26.4, 22.3. **HRMS-ESI** (m/z): calcd for C<sub>23</sub>H<sub>25</sub>NONa [M + Na] <sup>+</sup> 354.1834; found 354.1814.



(5-methoxy-3-((1-methylcyclohexyl)methyl)-1Hindol-1-yl)(phenyl)methanone (3eb): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide 1e (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl 1-methylcyclohexane-1-carboxylate 2b (215 mg, 0.75 mmol). After 36 h, purification by column

chromatography using 2% ethyl acetate in hexanes yielded **3eb** (60 mg, 67%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d, *J* = 12.8 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 (dt, *J* = 8.4, 4.0 Hz, 2H), 7.06 – 6.93 (m, 3H), 3.89 (s, 3H), 2.54 (s, 2H), 1.56 – 1.37 (m, 4H), 1.36 – 1.18 (m, 4H), 0.91 (s, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  205.1, 168.1, 156.5, 135.8, 135.1, 131.7, 129.2, 128.6, 126.8, 119.3, 117.1, 112.6, 103.3, 55.9, 37.9, 34.5, 33.6, 26.5, 26.3, 22.2. **HRMS-ESI** (m/z): calcd for C<sub>24</sub>H<sub>27</sub>NO<sub>2</sub>NH [M + H]<sup>+</sup> 362.2120; found 362.2116.



(3-(2,2-dimethylbutyl)-1H-indol-1-

**yl)(phenyl)methanone (3ac):** GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl 2,2-dimethylbutanoate **2c** (196 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate

in hexanes yielded **3ac** (53 mg, 70%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.60 (dd, *J* = 14.4, 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.34 (dt, *J* = 22.0, 7.3 Hz, 2H), 7.05 (s, 1H), 2.56 (s, 2H), 1.33 (q, *J* = 7.2 Hz, 2H), 1.00 – 0.85 (m, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 136.1, 135.1, 132.7, 131.8, 129.3, 128.7, 125.9, 124.7, 123.7, 119.9, 119.9, 116.4, 36.8, 34.8, 34.6, 26.7, 8.7. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 328.1677; found 328.1664.



(5-chloro-3-(2,2-dimethylbutyl)-1H-indol-1yl)(phenyl)methanone (3gc):GPwas followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-chlorophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide 1g (67 mg, 0.25 mmol), and 1,3dioxoisoindolin-2-yl 2,2-dimethylbutanoate 2c (196 mg, 0.75

mmol). After 36 h, purification by column chromatography

using 3% ethyl acetate in hexanes yielded **3gc** (48 mg, 57%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.31 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 9.7 Hz, 3H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.07 (s, 1H), 2.51 (s, 2H), 1.32 (q, *J* = 7.3 Hz, 2H), 0.88 (s, 9H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 134.6, 134.5, 134.0, 132.1, 129.4, 129.3, 128.7, 127.1, 124.9, 119.6, 119.2, 117.4, 36.7, 34.7, 34.6, 26.6, 8.7. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>22</sub>ClNONa [M + Na]<sup>+</sup> 362.1288; found 362.1269.

# (3-(((1s,3R,5S)-adamantan-1-yl)methyl)-5-methoxy-1H-indol-1-yl)(phenyl)



**methanone (3ed):** GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1e** (66 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl (1r,3R,5S)-adamantane-1-carboxylate **2d** (244 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded **3ed** (64 mg, 64%);

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 (d, *J* = 8.9 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 3.3 Hz, 1H), 6.97 (s, 2H), 3.90 (s, 3H), 2.38 (s, 2H), 1.93 (s, 3H), 1.66 (d, *J* = 12.6 Hz, 4H), 1.59 – 1.46 (m, 8H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 156.6, 135.1, 133.9, 131.7, 129.2, 128.7, 126.8, 123.1, 118.6, 117.2, 112.5, 103.5, 55.9, 42.8, 39.5, 37.0, 33.9, 28.8. **HRMS-ESI** (m/z): calcd for C<sub>27</sub>H<sub>30</sub>NO<sub>2</sub>H [M + H]<sup>+</sup> 400.2277; found 400.2266.



(3-butyl-1H-indol-1-yl)(phenyl)methanone (3ae): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl butyrate **2e** (175 mg, 0.75 mmol). After 36 h, purification by column chromatography using 3% ethyl acetate in hexanes yielded **3ae** (32 mg, 46%); <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.49 (m, 4H),

7.38 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.05 (s, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.76 – 1.61 (m, 2H), 1.46 – 1.36 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 136.6, 135.6, 135.1, 133.0, 130.7, 129.2, 128.7, 125.1, 123.9, 123.7, 123.1, 119.2, 116.7, 31.4, 24.8, 22.8, 14.0. **HRMS-ESI** (m/z): calcd for C<sub>19</sub>H<sub>19</sub>NONa [M + Na]<sup>+</sup> 300.1364; found 300.1341.



**yl)(phenyl)methanone (3he): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-(4-bromophenyl)-*N*-(propa-1,2-dien-1-yl)benzamide **1h** (78 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl butyrate **2e** (175 mg, 0.75 mmol). After 36

(5-bromo-3-butyl-1H-indol-1-

h, purification by column chromatography using 2% ethyl acetate in hexanes yielded **3ha** (51 mg, 58%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 5.5 Hz, 1H), 7.74 – 7.66 (m, 3H), 7.61 (t, J = 7.6 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.46 (d, J = 5.5 Hz, 1H), 7.06 (s, 1H), 2.62 (t, J = 6.6 Hz, 2H), 1.62 (p, J = 8.2 Hz, 2H), 1.39 (q, J = 7.6 Hz, 2H), 0.97 – 0.86 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 135.3, 134.6, 133.2, 132.0, 129.2, 128.8, 127.9, 125.0, 122.3, 122.0, 118.1, 117.1, 31.4, 24.6, 22.7, 14.0. HRMS-ESI (m/z): calcd for C<sub>19</sub>H<sub>18</sub>NBrONa [M + H]<sup>+</sup> 378.0469; found 378.0453.



# (3-phenethyl-1H-indol-1-yl)(phenyl)methanone

(**3af**): **GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl 3-phenylpropanoate **2f** (221 mg, 0.75 mmol). After 36 h, purification by column chromatography using 1% ethyl acetate in hexanes yielded **3af** 

(49 mg, 60%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 3H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 3H), 7.05 (s, 1H), 2.71 (t, *J* = 7.5 Hz, 4H), 2.01 (p, *J* = 7.5 Hz, 2H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.5, 142.1, 136.6, 135.1, 131.8, 131.3, 129.2, 128.7, 128.6, 128.5, 126.0, 125.2, 124.1, 123.8, 122.5, 119.1, 116.7, 35.8, 30.8, 24.6. **HRMS-ESI** (m/z): calcd for C<sub>21</sub>H<sub>23</sub>NONa [M + H]<sup>+</sup> 362.1521; found 362.1515.



# (3-decyl-1H-indol-1-yl)(phenyl)methanone (3ag):

**GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl decanoate **2g** (238 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl acetate in hexanes yielded **3ag** (43 mg, 48%); <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.57 (ddd, *J* = 22.6, 14.6, 7.2 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.05 (s, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.65 (dd, *J* = 14.8, 7.3 Hz, 2H), 1.40 – 1.34 (m, 2H), 1.26 (s, 12H), 0.88 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 136.6, 135.2, 131.8, 131.4, 129.2, 128.7, 125.0, 123.9, 123.7, 123.1, 119.2, 116.7, 32.0, 29.7, 29.7, 29.6, 29.5, 29.3, 29.2, 25.1, 22.8, 14.2. **HRMS-ESI** (m/z): calcd for C<sub>25</sub>H<sub>31</sub>NONa [M + Na]<sup>+</sup> 384.2303; found 384.2281.



(Z)-(3-(heptadec-8-en-1-yl)-1H-indol-1yl)(phenyl)methanone (3ah): GP was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide 1a (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl oleate 2h (320 mg, 0.75 mmol). After 36 h, purification by column

chromatography using 2% ethyl acetate in hexanes yielded **3ah** (51 mg, 45%); <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.3 Hz, 2H), 7.56 (ddd, J = 29.6, 14.8, 7.4 Hz, 4H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.05 (s, 1H), 5.34 (s, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.01 (s, 2H), 1.65 (dd, J = 14.9, 7.4 Hz, 2H), 1.26 (s, 22H), 0.88 (s, 3H). <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 136.6, 135.1, 131.7, 131.4, 130.1, 129.9, 129.2, 128.6, 125.2, 123.9, 123.7, 123.1, 119.2, 116.7, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 27.4, 25.1, 22.8, 14.3. **HRMS-ESI** (m/z): calcd for C<sub>33</sub>H<sub>45</sub>NONa [M + Na]<sup>+</sup> 494.3393; found 494.3400.



#### (3-(cyclohexylmethyl)-1H-indol-1-

**yl)(phenyl)methanone (3ai): GP** was followed using eosin Y (9.0 mg, 5.0 mol%), *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide **1a** (59 mg, 0.25 mmol), and 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate **2i** (205 mg, 0.75 mmol). After 36 h, purification by column chromatography using 2% ethyl

acetate in hexanes yielded **3ai** (42 mg, 53%); <sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.57 (dq, J = 20.6, 7.3 Hz, 4H), 7.37 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.04 (s, 1H), 2.54 (d, J = 6.9 Hz, 2H), 1.81 – 1.56 (m, 6H), 1.22 – 1.13 (m, 3H), 0.96 (q, J = 11.5 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 136.6, 135.1, 131.8, 131.7, 129.2, 128.7, 125.0, 124.7, 123.7, 121.4, 119.4, 116.6, 38.1, 33.7, 33.0, 26.6, 26.4. HRMS-ESI (m/z): calcd for C<sub>22</sub>H<sub>23</sub>NONa [M + Na]<sup>+</sup> 340.1677; found 340.1612.



**3-neopentyl-1H-indole (S4):** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 2.56 (s, 2H), 0.88 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 136.0, 129.0, 123.2, 121.6, 119.8, 119.2, 114.4, 111.0, 39.2, 32.3, 29.8. **HRMS-**

**ESI** (m/z): calcd for  $C_{13}H_{18}NH [M + H]^+$  188.1439; found 188.1426.



## (2,7-dibromo-3-neopentyl-1H-indol-1-

**yl)(phenyl)methanone (S5):** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.69 (m, 3H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 2.63 (s, 2H), 1.04 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.7, 138.0, 134.6,

133.7, 130.5, 128.9, 128.9, 126.1, 121.8, 121.1, 117.9, 116.6, 112.0, 38.6, 34.3, 30.5. **HRMS-ESI** (m/z): calcd for  $C_{20}H_{19}NBr_2ONa$  [M + Na]<sup>+</sup> 469.9731; found 469.9798.

# **Procedure for the Control Experiments (Scheme 2):**



- (a) *N*-phenyl-*N*-(prop-2-yn-1-yl)benzamide (4, 59 mg, 0.25 mmol, 1.0 equiv), 1,3-dioxoisoindolin-2-yl pivalate (2a, 0.75 mmol, 185 mg, 3.0 equiv) and Eosin Y (9 mg, 12.5 μmol, 5 mol%) were placed in a pre-dried 15 mL reaction tube. The tube was degassed and purged with argon three times. DCE (3.0 mL) and DIPEA (97 mg, 0.75 mmol, 3.0 equiv) was added, and the mixture was irradiated under 36 W 427 nm Kessil blue LED lamp and stirred for 36 h under argon atmosphere using a balloon. After 36 h, the crude reaction mixture was analyzed by gas chromatography, where the product 3aa was not detected.
- (b) N-phenyl-N-(propa-1,2-dien-1-yl)benzamide (1a, 59 mg, 0.25 mmol, 1.0 equiv), 1,3-dioxoisoindolin-2-yl pivalate (2a, 0.75 mmol, 185 mg, 3.0 equiv) and Eosin Y (9 mg, 12.5 μmol, 5 mol%) and TEMPO (117 mg, 0.75 mmol, 3.0 equiv) were placed in a predried 15 mL reaction tube. The tube was degassed and purged with argon three times. DCE (3.0 mL) and DIPEA (97 mg, 0.75 mmol, 3.0 equiv) was added, and the mixture was irradiated under 36 W 427 nm Kessil blue LED lamp and stirred for 36 h under argon atmosphere using a balloon. After 36 h, the crude reaction mixture was analyzed by gas chromatography, where the product 3aa was not detected.
- (c) *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide (1a, 59 mg, 0.25 mmol, 1.0 equiv), 1,3-dioxoisoindolin-2-yl pivalate (2a, 0.75 mmol, 185 mg, 3.0 equiv) and Eosin Y (9 mg, 12.5 μmol, 5 mol%) and and BHT (165 mg, 0.75 mmol, 3.0 equiv) were placed in a pre-dried 15 mL reaction tube. The tube was degassed and purged with argon three

times. DCE (3.0 mL) and DIPEA (97 mg, 0.75 mmol, 3.0 equiv) was added, and the mixture was irradiated under 36 W 427 nm Kessil blue LED lamp and stirred for 36 h under argon atmosphere using a balloon. The reaction mixture was then concentrated under vacuum, and purified by silica gel column chromatography using 2% ethyl acetate in hexane to deliver an inseparable mixture of **3aa** and adduct **7** (56%, **3aa**:**5** = 2:1). Formation of **5** was confirmed by comparing the <sup>1</sup>H and <sup>13</sup>C chemical shifts with literature report.<sup>6</sup>

# Light- dark experiment:



*N*-phenyl-*N*-(propa-1,2-dien-1-yl) benzamide **1a** (118 mg, 0.5 mmol, 1.0 equiv), 1,3dioxoisoindolin-2-yl pivalate **2a** (370 mg, 1.5 mmol, 3.0 equiv) and eosin Y (18 mg, 25.0  $\mu$ mol, 5 mol%) were placed in a pre-dried 15 mL glass tube. The flask was degassed and purged with argon three times. DCE (6.0 mL) and DIPEA (194 mg, 1.5 mmol, 3.0 equiv) were added, and the mixture was irradiated using a 36 W Kessil blue LED (427 nm) lamp and the reaction was placed in light and dark in every alternative 2 hour. After every time interval of 2 hour the reaction aliquot was taken out 1 ml by a syringe and quenched with water, organic part taken in DCM and NMR was carried out. The yield was determined using 1,1,2,2-tetrachloroethane as NMR standard.

Entry	Time (h)	Light source	Yield (%)
1	2	on	18
2	4	off	18
3	6	on	27
4	8	off	27
5	10	on	34
6	12	off	34



#### **Determination of Quantum Yield:**

#### (A) Determination of light intensity of the Blue LED:

The photon flux was determined by using standard ferrioxalate actinometry.<sup>7</sup> A 0.15 M solution of ferrioxalate was made by mixing 737 mg of potassium ferrioxalate hydrate in 10 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. A buffered solution of phenanthroline was made by mixing 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 kept in the dark. To determine the photon flux, 1.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 60.0 seconds at  $\lambda = 427$  nm placing 8 cm away from 36 W Kessil blue LED lamp. After irradiation, 0.175 mL of the phenanthroline solution was added to the cuvette. The solution was then kept for 1 h to permit the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was determined at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was determined. Conversion was calculated using eq. 1

$$mol \ Fe^{2+} = \frac{V.\Delta A}{\varepsilon. l} \quad \dots \dots \dots 1$$

Where V is the total volume (0.001175 L) of the solution after addition of the phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.000 cm), and  $\epsilon$  is the molar absorptivity at 510 nm (11,100 L mol<sup>-1</sup> cm<sup>-1</sup>).

$$mol \ Fe^{2+} = \frac{0.001175 \text{ L. } (0.401 - 0.136)}{1 \ cm \ . \ 11100 \ \text{L.cm}^{-1} \text{.mol}^{-1}}$$
$$= 2.8052 \times 10^{-8} \text{ mol}$$

The photon flux can be calculated using eq 2.

$$photon flux = \frac{mol Fe^{2+}}{\Phi \cdot t \cdot f} \dots \dots 2$$

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at  $\lambda$  = 427 nm), t is the time (60 s), and f is the fraction of light absorbed at  $\lambda$  = 427 nm, f = 1.000  $-10^{-A}$ .

Calculated  $f = 1.000 - 10^{-A} = 1.000 - 10^{-0.401} = 0.6028$ .

Photon flux = 
$$\frac{2.8052 \times 10^{-8} \text{ mol}}{1.01 \times 608 \times 0.6028} = 7.679 \times 10^{-10} \text{ Einstein s}^{-1}$$

## **(B) Quantum Yield Calculation:**



*N*-phenyl-*N*-(propa-1,2-dien-1-yl) benzamide **1a** (118 mg, 0.5 mmol, 1.0 equiv), 1,3dioxoisoindolin-2-yl pivalate **2a** (370 mg, 1.5 mmol, 3.0 equiv) and Eosin Y (18 mg, 25.0  $\mu$ mol, 5 mol%) were placed in a pre-dried 15 mL glass tube. The flask was degassed and purged with argon three times. DCE (6.0 mL) and DIPEA (194 mg, 1.5 mmol, 3.0 equiv) were added, and the mixture was irradiated using a 36 W Kessil blue LED (427 nm) lamp and after irradiation for 2 h, yield of the product was determined by NMR using 1,1,2,2-tetrachloroethane as standard. The product revealed 18% yield (9.0 × 10<sup>-5</sup> mol).

The quantum yield was calculated as follows:

$$\phi = \frac{mol \ product}{flux. \ t. \ f}$$

Where, flux is the photon flux determined by ferrioxalate actinometry  $(7.679 \times 10^{-10}$  Einstein/s), t is the time (7200 s), and f (> 0.999) is the fraction of light absorbed by eosin Y at 427 nm under the reaction condition mentioned above.

$$\Phi = \frac{9 \times 10^{-5}}{7.679 \times 10^{-10} \times 7200 \times 1}$$
$$= 16.28$$

## Luminescence quenching Experiments:

#### (A) Preparation of the Stock Solution:

A 1 mM solution of the Eosin Y catalyst was prepared in a sample vial by dissolving 2.59 mg of the catalyst in 4 mL of MeCN (spectroscopic grade, purchased from Spectrochem). The freshly prepared solution was used for the spectroscopic measurement. The required amount was taken using a micropipette from the mother solution as an aliquot and it was diluted further by dissolving in 1 mL of MeCN in the cuvette. Similarly, 4 mL 0.3 M solution of diisopropyl ethyl amine (DIPEA), phthalimido ester (**2a**), and *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide (**1a**) were prepared by dissolving the requisite amount of each substrate in MeCN. Freshly prepared solutions were used for the quenching experiment.

#### **(B)** Quenching studies:

Fluorescence emission spectra of the photocatalyst in presence of different reactions components (1a, 2a, and DIPEA) were recorded and analyzed in detail to estimate the light emission properties of the pure catalyst system and their distractions by external interference from the substrates. Emission intensities of Eosin Y were recorded with a "HITACHI f-7000" Scientific Spectrofluorometer using a 10.0 mm quartz cuvette. The catalyst exhibits an absorption maxima at 510 nm (confirmed from literature). Hence, the sample solution of Eosin Y with a proper concentration of 1 mM in MeCN was excited (degassed for 15 mins before recording the spectra) with a wavelength of 450 nm, and the emission maxima were found to be observed at 539 nm. The individual substrates 1a and 2a were silent to show any emission feature in that region. To study the quenching behavior of Eosin Y, different concentration of 2a was added to the catalyst solution and the emission spectra were measured following the aforementioned procedure. The quenching effect of the redox-active phthalimide ester was quite significant on the photocatalyst; the intensity of the emission maxima decreased gradually upon increasing the concentration of 2a. Some sets of solutions with different concentrations of the ester were used; the experiment was repeated and finally, the Stern-Volmer plot was

depicted. DIPEA was found to be much less effective to impose a quenching effect on the emission intensities of the catalyst even with a high concentration of that. On the other hand, no significant change in the emission maxima of Eosin Y was observed when *N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzamide (**1a**) was used as the quencher. The corresponding Stern-Volmer plot was drawn for all the cases.

#### (C) Luminescence Spectra:



Luminescence spectra of Eosin Y (1 mM) as a function of concentration of Phthalimido ester (0.3 M) in MeCN with Excitation at 450 nm



Luminescence spectra of Eosin Y (1 mM) as a function of concentration of Substrate (0.3 M) in MeCN with Excitation at 450 nm





# General Procedure for Cyclic Voltammetry (CV):

Cyclic voltammetry was performed in a three-electrode cell (beaker type cell) at room temperature. The working electrode was a gold electrode and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 5 mL of CH<sub>3</sub>CN containing 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> (194 mg) were poured into the electrochemical cell in all experiments. The scan rate was 0.1 V/s. Reduction peaks were noticed at -1.33 V for dioxoisoindolin-2-yl pivalate (**2a**) and -1.17 V for eosin Y. The oxidation peaks were noticed at + 0.87 V for DIPEA and +1.73 V for *N*-phenyl-*N*-(propa-1,2-dien-1-yl) benzamide (**1a**). The redox potential values suggested that eosin Y oxidized first and the reaction proceeded through an oxidative quenching pathway.







# NMR spectra:










SI-39









f1 (ppm) ( 



0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 f1 (ppm)





f1 (ppm) ( 



f1 (ppm) 



0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 fl (ppm)







f1 (ppm) ( 



0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 f1 (ppm)



f1 (ppm) ( 





SI-53



110 100 f1 (ppm) ( 



SI-55







SI-58











0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 f1 (ppm)



f1 (ppm) l. 



# 8.37 8.37 8.36 8.36 8.36 8.36 8.35 8.35 7.74 7.75 <li

#### 2.58 11.50 11.51 11.55 11.55 11.45 11.45 11.45 11.45 11.45 11.45 11.46 11.44 11.32 11.33 11.45 11.33 11.133 11.33







SI-66

















## 8.38 8.36 8.36 8.36 8.36 8.36 8.36 8.36 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.73 7.73 7.73 7.73 7.73 7.73 7.73 7.73 7.73 7.74 7.74 7.75 7.73 7.75 7.73 7.74 7.75 7.73 7.74 7.75 7.74 7.74 7.75 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.75 7.74 7.74 7.75 7.74 7.74 7.74 7.74 7.75 7.74 7.74 7.75 7.75 7.74 7.74 7.74 7.75 7.75 7.74 7.75 7.74 7.74 7.75 7.74 7.74 7.74 7.75 7.74 7.75 7.74 7.75 7.74 7.75 7.75 7.74 7.75 7.75 7.74 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.75 <li

#### 







### $\begin{array}{c} 2.63\\ 2.62\\ 2.62\\ 1.66\\ 1.66\\ 1.65\\ 1.64\\ 1.61\\ 1.33\\$






SI-73









## $\begin{array}{c} 2.55\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 2.53\\ 1.75\\ 1.75\\ 1.63\\$

## 8.38 8.36 8.36 8.36 8.36 8.36 8.36 7.75 7.60 7.76 7.60 7.75 7.60 7.75 7.60 7.75 7.60 7.75 7.60 7.73 7.60 7.73 7.60 7.73 7.60 7.74 7.75 7.74 7.74 7.75 7.75 7.75 7.75 7.75 7.75 7.75 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.75 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.75 7.74 7.74 7.74 7.75 7.74 7.75 7.74 7.74 7.74 7.74 7.75 7.74 7.75 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.74 7.75 7.74 7.74 7.74 7.74 7.74 7.74 <li







110 100 f1 (ppm) ( 









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