Supporting Information

Visible light-induced photoredox catalyzed C-N coupling of amides with alcohols

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General Remarks
All chemicals were reagent grade, obtained from Merck and further they were used without purification.

General experimental Procedure
In a tube furnished with a magnetic stirrer bar, benzamide (1 mmol), benzyl alcohol (1 mmol), 0.5 equivalent of KOH and eosin Y (2 mol%) were added to 3 mL of EtOH. The resulting mixture was stirred at room temperature for 6-10 h, under green LED irradiation to give the intermediate I (without isolation), further which was reduced by 0.5 equivalent of NaBH₄ to give the desired product (3a-m). To obtain the pure product 3a-m, the crude product was purified by silica gel chromatography (100-200 mesh silica gel; EtOAc/Hexane). All of the products were identified by their spectral data and chemical analysis.

Supporting Information Summary
General experimental, general method for the synthesis of N-alkylated compounds, and characterization information of products. Melting points were determined by open glass capillary method and are uncorrected. All chemicals used were reagent grade and were used as received. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE DPX (400 MHz and 100 MHz) FT spectrometer in CDCl₃ using TMS as an internal reference (chemical shift in δ ppm).

N-benzylbenzamide (3a)
White solid, 96% yield. mp: 180-181 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.79 (d, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 2H), 7.37-7.35 (m = 4H), 7.32-7.28 (m, 1H), 6.44 (s, 1H), 4.65 (d, $J = 5.7$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.4, 138.2, 134.3, 131.5, 128.7, 128.5, 127.9, 127.6, 126.9, 44.1.

$N$-(4-methylbenzyl)benzamide (3b)

White solid, 95% yield. mp: 196-197 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.78 (d, $J = 7.3$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 4.3$ Hz, 2H), 7.16 (d, $J = 4.3$ Hz, 2H), 6.39 (s, 1H), 4.60 (d, $J = 5.7$ Hz, 2H), 2.34 (s, 3H). C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.2, 159.2, 134.5, 131.5, 130.2, 129.3, 128.6, 126.9, 114.2, 55.3, 43.7

$N$-(3-bromobenzyl)benzamide (3c)

White solid, 97% yield. m.p: 241-242 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.83 – 7.74 (m, 2H), 7.57 – 7.47 (m, 2H), 7.47 – 7.39 (m, 3H), 7.32 – 7.26 (m, 1H), 7.21 (t, $J = 7.7$ Hz, 1H), 6.55 (s, 1H), 4.61 (d, $J = 5.8$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.5, 140.7, 134.2, 131.9, 130.9, 130.8, 128.8, 127.1, 126.6, 122.9, 43.6.

$N$-(2-bromobenzyl)benzamide (3d)

White solid, 82% yield. m.p: 241-242 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.84 – 7.74 (m, 2H), 7.57 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.54 – 7.39 (m, 4H), 7.29 (td, $J = 7.5$, 1.3 Hz, 1H), 7.16 (td, $J = 7.7$, 1.8 Hz, 1H), 6.69 (s, 1H), 4.71 (d, $J = 6.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.4, 137.4, 134.4, 133.0, 131.8, 130.8, 129.4, 128.7, 127.9, 127.1, 124.0, 44.5.
**N-(3,5-dimethylbenzyl)benzamide (3e)**

![Chemical structure of 3e]

White solid, 98% yield. m.p: 228-229 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.84 – 7.77 (m, 2H), 7.53 – 7.46 (m, 1H), 7.42 (ddt, $J = 8.3, 6.5, 1.3$ Hz, 2H), 6.97 (d, $J = 1.6$ Hz, 2H), 6.94 (s, 1H), 6.51 (s, 1H), 4.56 (d, $J = 5.6$ Hz, 2H), 2.31 (d, $J = 0.8$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.4, 138.5, 138.2, 134.6, 131.6, 129.3, 128.7, 127.1, 125.9, 44.2, 21.4.

**N-((6-methylpyridin-3-yl)methyl)benzamide (3f)**

![Chemical structure of 3f]

White solid, 90% yield. m.p: 258-259 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.50 (d, $J = 2.3$ Hz, 1H), 7.82 – 7.75 (m, 2H), 7.64 (dd, $J = 8.0, 2.3$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 (ddt, $J = 8.2, 6.6, 1.3$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 1H), 6.49 (s, 1H), 4.63 (d, $J = 5.8$ Hz, 2H), 2.56 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.7, 157.7, 148.5, 136.5, 134.2, 131.8, 131.2, 128.8, 127.1, 123.4, 41.3, 24.1.

**N-(thiophen-3-ylmethyl)benzamide (3g)**

![Chemical structure of 3g]

White solid, 97% yield. m.p: 236-237 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.82 – 7.73 (m, 2H), 7.52 – 7.45 (m, 1H), 7.45 – 7.36 (m, 2H), 7.30 (dd, $J = 5.0, 2.9$ Hz, 1H), 7.19 (qd, $J = 3.0, 2.0, 1.3$ Hz, 1H), 7.07 (dd, $J = 4.9, 1.4$ Hz, 1H), 6.60 (s, 1H), 4.62 (d, $J = 5.4$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.4, 139.1, 134.4, 131.7, 128.7, 127.5, 127.08, 127.07, 126.59, 126.57, 122.6, 77.5, 77.2, 76.8, 39.4.

**N-(furan-3-ylmethyl)benzamide (3h)**

![Chemical structure of 3h]

Brown solid, 63% yield. m.p: 151-153 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.80 – 7.75 (m, 2H), 7.54 – 7.47 (m, 1H), 7.47 – 7.39 (m, 4H), 6.43 (dd, $J = 1.9, 0.9$ Hz, 1H), 6.24 (s, 1H), 4.50 (dd, $J = 5.6, 0.9$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.5, 143.8, 140.5, 134.5, 131.7, 128.8, 127.0, 122.3, 110.5,
35.2.

4-methyl-N-(3-phenylpropyl)benzamide (3i)

Yellow solid, 72% yield. m.p: 240-242 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.63 – 7.52 (m, 2H), 7.33 – 7.27 (m, 3H), 7.25 – 7.16 (m, 5H), 6.06 (s, 1H), 3.50 (td, $J$ = 7.1, 5.8 Hz, 2H), 2.73 (t, $J$ = 7.5 Hz, 2H), 2.38 (s, 4H), 2.03 – 1.88 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.5, 141.8, 141.7, 132.0, 129.3, 128.7, 128.5, 126.9, 126.2, 39.9, 33.7, 31.3, 21.6.

N-(4-fluorobenzyl)benzamide (3j)

White solid, 96% yield. m.p: 196-198 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.08 – 8.04 (s, 1H), 7.9 – 7.8 (d, 2H), 7.79-7.50 (t, 1H), 7.49-7.41 (dd, $J$ = 5.6 Hz, 2H), 7.40-7.35 (d, $J$ = 5.6 Hz, 2H), 7.28-7.27 (d, $J$ = 5.6 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 134.65 131.71, 128.68, 127.91, 40.50-39.25.

N-benzyl-4-methoxybenzamide (3k)

White solid, 97% yield. m.p: 226-228 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.03 (s, 1H), 7.0-6.98 (d, 2H), 6.06-6.04 (d, 2H), 2.98 (s, $J$ = 5.6 Hz, 2H), 2.09 (s, $J$ = 5.6 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 161.65, 128.93, 112.9, 77.25-76.74, 54.77, 39.9-38.9.

N-(naphthalen-2-ylmethyl)benzamide (3l)

White solid, 97% yield. m.p: 256-258 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.89 – 7.74 (m, 6H), 7.56 – 7.39 (m, 6H), 6.51 (s, 1H), 4.81 (d, $J$ = 5.6 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.5, 135.7, 134.5, 133.5, 133.0, 131.7, 128.8, 128.8, 127.9, 127.8, 127.1, 126.7, 126.5, 126.2, 126.1, 44.4.
**N-butylhexanamide (3m)**

Colourless oil, 35% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.79\) (br s, 1H), 3.20 (q, \(J = 6.8\) Hz, 2H), 2.12 (t, \(J = 7.6\) Hz, 2H), 1.62-1.55 (m, 2H), 1.48-1.40 (m, 2H), 1.33-1.21 (m, 6H), 0.90-0.83 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 173.14, 39.09, 36.73, 31.65, 31.40, 25.46, 22.31, 19.98, 13.83, 13.64\).
$^1$H and $^{13}$C NMR spectra of compounds

**Figure S1a:** $^1$H NMR (400 MHz, CDCl$_3$) of $N$-benzylbenzamide (3a)

**Figure S1b:** $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-benzylbenzamide (3a)
Figure S2a: $^1$H NMR (400 MHz, CDCl$_3$) of $N$-(4-methylbenzyl)benzamide (3b)

Figure S2b: $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-(4-methylbenzyl)benzamide (3b)
Figure S3a: $^1$H NMR (400 MHz, CDCl$_3$) of N-(3-bromobenzyl)benzamide (3c)

Figure S3b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-(3-bromobenzyl)benzamide (3c)
Figure S4a: $^1$H NMR (400 MHz, CDCl$_3$) of N-(2-bromobenzyl)benzamide (3d)

Figure S4b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-(2-bromobenzyl)benzamide (3d)
Figure S5a: $^1$H NMR (400 MHz, CDCl$_3$) of N-(3,5-dimethylbenzyl)benzamide (3e)

Figure S5b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-(3,5-dimethylbenzyl)benzamide (3e)
Figure S6a: $^1$H NMR (400 MHz, CDCl$_3$) of $N$-((6-methylpyridin-3-yl)methyl)benzamide (3f)

Figure S6b: $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-((6-methylpyridin-3-yl)methyl)benzamide (3f)
Figure S7a: $^1$H NMR (400 MHz, CDCl$_3$) of $N$-(thiophen-3-ylmethyl)benzamide (3g)

Figure S7b: $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-(thiophen-3-ylmethyl)benzamide (3g)
**Figure S8a:** $^1$H NMR (400 MHz, CDCl$_3$) of $N$-(furan-3-ylmethyl)benzamide (3h)

**Figure S8b:** $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-(furan-3-ylmethyl)benzamide (3h)
Figure S9a: $^1$H NMR (400 MHz, CDCl$_3$) of 4-methyl-N-(3-phenylpropyl)benzamide (3i)

Figure S9b: $^{13}$C NMR (100 MHz, CDCl$_3$) of 4-methyl-N-(3-phenylpropyl)benzamide (3i)
Figure S10a: $^1$H NMR (400 MHz, CDCl$_3$) of N-(4-fluorobenzyl)benzamide (3j)

Figure S10b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-(4-fluorobenzyl)benzamide (3j)
Figure S11a: $^1$H NMR (400 MHz, CDCl$_3$) of N-benzyl-4-methoxybenzamide (3k)

Figure S11b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-benzyl-4-methoxybenzamide (3k)
Figure S12a: $^1$H NMR (400 MHz, CDCl$_3$) of N-(naphthalen-2-ylmethyl)benzamide (3l)

Figure S12b: $^{13}$C NMR (100 MHz, CDCl$_3$) of N-(naphthalen-2-ylmethyl)benzamide (3l)
Figure S13a: $^1$H NMR (400 MHz, CDCl$_3$) of $N$-butylhexanamide (3m)

Figure S13b: $^{13}$C NMR (100 MHz, CDCl$_3$) of $N$-butylhexanamide (3m)