Metal-Free Photoredox Catalyzed Direct α-Oxygenation of *N*,*N*-dibenzylanilines to Imides Under Visible Light

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<u>S.No</u>	Table of contents	Pages
1	General considerations	S1
2	Characterization data for the products	S3-S9
3	References	S 9
4	¹ H, ¹³ C NMR and HRMS spectra of compounds	S10 – S33

1. General considerations:

The ¹H and ¹³C NMR spectra were recorded in CDCl₃ on Bruker spectrometers 300 MHz NMR spectrometer with TMS as an internal standard. Mass spectra were recorded on Xevo G2S Q-TOF spectrometer. The light source for photochemical reactions was Kessil 456nm Blue LED (model number: KSPR160L-456-EU). Different wave lengths containing LEDs such as 370nm, 390nm, 467nm and 527nm were purchased from Kessil and used. Reaction tubes made of borosilicate glass were used as reaction vessels. The distance between the light source and the reaction vessel was 8 cm. TLC was performed on using Merck pre-coated TLC plates (Merck 60 F254) and detected under UV light. Column chromatographic separation was carried out with silica gel (100-200 mesh). Reagents and solvents were purified as per standard procedures and used.



Figure S1: Reaction setup with Kessil PR160L-456nm Blue LED

2. Characterization data for the products



N-benzoyl-N-phenylbenzamide 2a¹.

2a (81 mg) was obtained from **1a** (98 mg) following general procedure B; White solid; 75% yield (eluent: EtOAc/Hexanes= 1:9);¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.11 (d, *J*= 7.2 Hz, 2H), 7.71 (t, *J*= 4.2 Hz, 2H), 7.58 (t, *J*= 7.5 Hz, 1H), 7.47-7.38 (m, 4H), 7.35-7.28 (m, 4H), 7.26 (d, *J*= 7.5 Hz, 1H), 7.19-7.16 (m, 1H).¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.4, 140.2, 135.0, 132.1, 129.4, 129.2, 128.4, 127.8, 127.5.



N-benzoyl-*N*-(p-tolyl)benzamide 2b.

2b (68 mg) was obtained from **1b** (107 mg) following general procedure B; White solid; 60% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.71 (t, *J*= 7.2 Hz, 4H), 7.43-7.38 (m, 2H), 7.33-7.24 (dd, *J*= 7.5 Hz, 11.4 Hz, 4H), 7.13 (d, *J*= 8.2 Hz, 2H), 7.05 (d, *J*= 8.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.5, 137.6, 135.2, 132.1, 130.2, 129.3, 128.4, 127.7, 21.0; HRMS: (M+H)⁺ calculated for C₂₁H₁₇NO₂: 316.1338, found: 316.1327.



N-benzoyl-*N*-(4-(tert-butyl)phenyl)benzamide 2c.

2c (86 mg) was obtained from **1c** (113 mg) following general procedure B; White solid; 70% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.73 (d, *J*= 7.5 Hz, 4H), 7.40 (t,

J= 7.2 Hz, 2H), 7.30 (t, J= 7.8 Hz, 4H), 7.19 (d, J= 8.1 Hz, 2H), 7.10 (d, J= 8.4 Hz, 2H). 2.87 (t, J= 6.9 Hz, 1H), 1.21 (d, J= 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.5, 148.4, 137.8, 135.3, 132.1, 129.3, 128.4, 127.6, 127.5, 33.7, 23.8; HRMS: (M+H)⁺ calculated for C₂₃H₂₁NO₂: 344.1650, found: 344.1638.



N-benzoyl-*N*-(4-fluorophenyl)benzamide 2d.

2d (86 mg) was obtained from **1d** (104 mg) following general procedure B; White solid; 75% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.71 (d, *J*= 7.2 Hz, 4H), 7.41 (t, *J*= 7.5 Hz, 2H), 7.31 (t, *J*= 7.8 Hz, 4H), 7.18- 7.14 (m, 2H), 7.03 (t, *J*= 7.2 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.2, 163.3, 160.0, 134.8, 132.3, 129.6, 129.5, 129.5, 129.2, 128.5, 128.4, 116.6, 116.3; HRMS: (M+H)⁺ calculated for C₂₀H₁₄FNO₂: 320.1081, found: 320.1077.



N-benzoyl-*N*-(4-chlorophenyl)benzamide 2e.

2e (102 mg) was obtained from **1e** (110 mg) following general procedure B; White solid; 85% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.10 (d, *J*= 7.2 Hz, 1H), 7.71 (d, *J*= 7.2 Hz, 3H), 7.48-7.29 (m, 8H), 7.11 (d, *J*= 8.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.1, 138.7, 134.7, 133.6, 132.4, 130.1, 129.6, 129.0, 128.4; HRMS: (M+H)⁺ calculated for C₂₀H₁₄ClNO₂: 336.0791, found: 336.0785.



N-benzoyl-*N*-(3-chlorophenyl)benzamide 2f.

2f (111 mg) was obtained from **1f** (110 mg) following general procedure B; White solid; 92% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.72 (d, *J*= 7.2 Hz, 4H), 7.44-7.39 (m, 3H), 7.31 (t, *J*= 7.8 Hz, 4H), 7.27- 7.23 (m, 2H), 7.08-7.05 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.1, 141.4, 135.1, 134.8, 132.5, 130.3, 129.3, 128.6, 128.1, 127.9, 126.2; HRMS: (M+H)⁺ calculated for C₂₀H₁₄ClNO₂: 336.0791, found: 336.0783.



N-benzoyl-*N*-(2-bromophenyl)benzamide 2g.

2g (102 mg) was obtained from **1g** (126 mg) following general procedure B; White solid; 75% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.80 (d, *J*= 7.2 Hz, 4H), 7.66 (d, *J*= 7.5 Hz, 1H), 7.41 (t, *J*= 7.2 Hz, 2H), 7.32 (t, *J*= 7.2 Hz, 4H), 7.22 (t, *J*= 5.7 Hz, 1H), 7.13-7.10 (dd, *J*= 2.7 Hz, 2.4 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 172.6, 139.5, 134.7, 133.8, 132.3, 130.8, 129.5, 129.1, 128.5, 128.4, 122.6; HRMS: (M+H)⁺ calculated for C₂₀H₁₄BrNO₂: 380.0286, found: 336.0258.



N-benzoyl-N-(4-bromophenyl)benzamide 2h.

2h (95 mg) was obtained from **1h** (126 mg) following general procedure B; White solid; 70% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.86 (d, *J*= 7.8 Hz, 3H), 7.77 (s, 1H), 7.55-7.53 (t, *J*= 8.7 Hz 5H), 7.50 (d, *J*= 5.7 Hz, 4H), 7.46 (d, *J*= 1.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.0, 139.2, 134.7, 132.6, 132.4, 129.3, 129.2, 128.5, 121.4.



N-benzoyl-*N*-(4-cyanophenyl)benzamide 2i.

2i (45 mg) was obtained from **1i** (107 mg) following general procedure B; White solid; 39% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.01 (d, *J*= 7.2 Hz, 4H), 7.63-7.53 (dd, *J*= 7.5 Hz, 8.1 Hz, 2H), 7.37 (t, *J*= 7.2 Hz, 3H), 7.27-7.19 (m, 5H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 172.8, 144.3, 134.3, 133.2, 132.8, 129.3, 128.7, 128.2, 117.8, 111.2.



N-(4-acetylphenyl)-*N*-benzoylbenzamide 2j.

2j (55 mg) was obtained from **1j** (113 mg) following general procedure B; White solid; 45% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.83 (d, *J*= 8.4 Hz, 2H), 7.63 (d, *J*= 7.2 Hz, 4H), 7.34 (t, *J*= 6.6 Hz, 2H), 7.23 (d, *J*= 7.8 Hz, 3H), 7.20 (d, *J*= 8.1 Hz, 2H), 7.16 (d, *J*= 6.9 Hz, 1H), 2.49 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 196.6, 173.0, 144.4, 135.9, 134.6, 132.6, 129.5, 129.3, 128.6 127.6, 26.3.



N-benzoyl-*N*-(3-nitrophenyl)benzamide 2k.

2k (37 mg) was obtained from **1k** (114 mg) following general procedure B; White solid; 30% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.15 (d, *J*= 5.1 Hz, 2H), 7.72-7.70 (t, *J*= 7.2 Hz, 3H), 7.54-7.52 (m, 1H), 7.47-7.42 (t, *J*= 7.5 Hz, 2H), 7.35 (d, *J*= 7.8 Hz, 3H), 7.32-

7.30 (t, *J*= 1.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃):δ_C 172.9, 148.9, 134.4, 133.7, 132.8, 130.1, 129.3, 128.7, 127.0, 122.9, 122.3.



N-benzoyl-N-(4-nitrophenyl)benzamide 2l.

21 (37 mg) was obtained from **11** (114 mg) following general procedure B; White solid; 30% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.24 (d, *J*= 9 Hz, 1H), 8.14 (d, *J*= 7.5 Hz, 3H), 7.74 (d, *J*= 7.2 Hz, 2H), 7.62 (d, *J*= 7.5 Hz, 1H), 7.49 (t, *J*= 7.5Hz, 4H) 7.39-7.27 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 172.8, 145.8, 133.6, 132.9, 130.2, 129.3, 128.7, 128.4, 124.8.



2-methyl-*N*-(2-methylbenzoyl)-*N*-phenylbenzamide 4a².

4a (78 mg) was obtained from **3a** (108 mg) following general procedure B; White solid; 66% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.39 (d, *J*= 7.2 Hz, 2H), 7.28 (d, *J*= 7.2 Hz, 2H), 7.19 (d, *J*= 8.1 Hz, 3H), 7.09 (d, *J*= 7.2 Hz, 2H), 7.02-6.95 (dd, *J*= 7.2 Hz, 7.5 Hz, 4H), 2.30 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 173.2, 139.5, 137.7, 136.1, 131.1, 130.6, 129.3, 127.9, 127.7, 127.6, 125.3, 19.8.



4-methyl-*N*-(4-methylbenzoyl)-*N*-phenylbenzamide 4b².

4b (65 mg) was obtained from **3b** (108 mg) following general procedure B; White solid; 55% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.52 (d, *J*= 8.1 Hz, 2H), 7.44 (d,

J= 7.2 Hz, 2H), 7.23 (d, J= 9.9 Hz, 1H), 7.18 (d, J= 8.1 Hz, 3H), 7.15-7.03 (m, 5H), 2.35 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 172.9, 137.8, 135.8, 132.5, 131.2, 130.8, 129.4, 127.5, 125.3, 19.7.



4-fluoro-*N*-(4-fluorobenzoyl)-*N*-phenylbenzamide 4c².

4c (80 mg) was obtained from 3c (111 mg) following general procedure B; White solid; 66% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃):δ_H 7.76-7.75 (t, *J*= 5.4 Hz, 4H), 7.38-733 (t, *J*= 6.6 Hz, 2H), 7.29-7.25 (t, *J*= 7.2 Hz, 2H), 7.16 (d, *J*= 7.5 Hz, 2H), 7.04 (t, *J*= 8.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ_{C} 172.1, 166.8, 163.4, 140.1, 131.9, 131.8, 130.8, 129.6, 129.1, 127.8, 127.7, 115.9, 115.6.



3-chloro-*N*-(3-chlorobenzoyl)-*N*-phenylbenzamide 4d².

4d (93 mg) was obtained from **3f** (123 mg) following general procedure B; White solid; 70% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.69 (s, 2H), 7.56 (d, *J*= 7.8 Hz, 2H), 7.42-7.34 (dd, *J*= 8.1 Hz, 7.5 Hz, 4H), 7.31-7.23 (m, 3H), 7.15 (d, *J*= 7.2 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 171.7, 139.4, 136.3, 134.8, 132.3, 129.7, 129.7, 129.3, 128.1, 127.8, 127.0.



4-chloro-*N*-(4-chlorobenzoyl)-*N*-phenylbenzamide 4e².

4e (90 mg) was obtained from 3g (123 mg) following general procedure B; White solid; 68% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 8.06 (d, *J*= 7.8 Hz, 2H), 7.69 (d, *J*= 7.5 Hz, 3H), 7.48 (d, *J*= 7.5 Hz, 2H), 7.35 (d, *J*= 8.1 Hz, 4H), 7.17 (d, *J*= 6.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 172.2, 138.9, 133.0, 131.6, 130.7, 129.7, 128.9, 128.9, 127.8.



N-benzoyl-2-methyl-*N*-phenylbenzamide 4f.

4f (60 mg) was obtained from **3c** (103 mg) following general procedure B; White solid; 53% yield (eluent: EtOAc/Hexanes= 1:9); ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 7.70 (d, *J*= 7.2 Hz, 2H), 7.53 (d, *J*= 7.5 Hz, 1H), 7.44-7.32 (m, 4H), 7.29- 7.22 (m, 5H), 7.14 (t, *J*= 6.3 Hz, 2H), 2.50 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 171.6, 171.3, 138.0, 136.1, 133.9, 133.5, 130.3, 129.4, 128.8, 127.5, 127.3, 126.5, 126.0, 125.8, 123.6, 18.0.

3. References

1. A. Ben-Haida, P. Hodge and H. M. Colquhoun, *Macromolecules*, 2005, 38, 722-729.

2. A. A. Kadam, T. L. Metz, Y. Qian and L. M. Stanley, ACS Catal., 2019, 9, 5651-5656.



4. ¹H , ¹³C NMR and HRMS spectra of products





HRMS spectrum of compound 2b





HRMS Spectrum of compound 2c





HRMS Spectrum of compound 2d





HRMS Spectrum of compound 2e





Channel name: Low energy : Time 0.2880 +/- 0.0657 minutes

Item name: MSR-4A-336

HRMS Spectrum of compound 2f





HRMS Spectrum of compound 2g







S25



S26















S33