Supplementry Information for

Oxidative Organophotoredox catalysis: A regioselective synthesis of 2-Nitro substituted Imidazopyridines and 3-substituted Indoles, initiated by visible light

Snehlata Yadav[a], Madhulika Srivastava[a], Pratibha Rai[a], Bhartendu Pati Tripathi[a], Anu Mishra[a]

*Jaya Singh,[b] Jagdamba Singh[a]**

[a]Environmentally Benign Lab, Department of Chemistry, University of Allahabad,211002 India.

[b]L R PG College, Sahibabad, UP, India

E-mail: dr.jdsau@gmail.com; Tel: +91 9415218507

General Information: Reagents were obtained from commercial suppliers, and used without further purification unless otherwise specified by a reference. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method. ^{1}HNMR spectra were recorded on a Bruker AVII 400 spectrometer in $CDCl_3$ using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on the same instrument at100 MHz in $CDCl_3$ and TMS was used as the internal reference. Mass (EI) spectra were recorded on a JEOL D-300 mass spectrometer. Elemental analyses were carried out in a Coleman automatic carbon, hydrogen and nitrogen analyze.

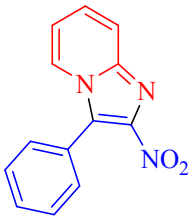
General procedure for the synthesis of 2-nitro substituted imidazopyridines 3 from nitroalkenes 1 and 2-aminopyridines 2

A solution of nitroalkenes (**1**) (1mmol) and 2-aminopyridine (**2**) (1mmol) was taken into round bottom flask in CH_3CN (3ml). The reaction mixture was irradiated with high power green LEDs (2.5w, λ =535nm) in presence of eosin Y (2 mol %) under open atmosphere at room temperature for 5-6 h. After completion of reaction (TLC) water was added and extracted with EtOAc. The

organic layer was dried over anhydrous MgSO4 and filtered. The crude product was obtained by concentrating the resulting solution under reduced pressure and was purified by column chromatography on silica gel using a gradient mixture of EtOAc-Hexane to give the pure product (**3**) in good yield (Table3). All the desired products are known compounds which were characterized by the comparison of their spectra and melting point with those reported in the previous literature[1].

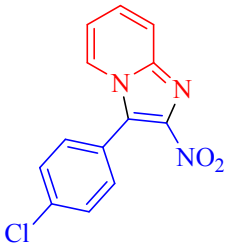
The characterization data of the synthesized 3-aryl substituted imidazopyridines **3** are summarized below with relevant references.

2-Nitro-3-phenylimidazo [1, 2-*a*] pyridine (Table 3, Entry 1)[1]



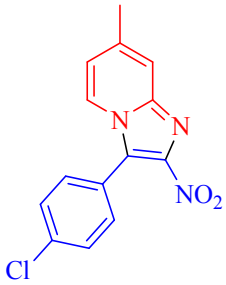
Semisolid; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 8.15 (d, *J* =8.8 Hz, 2H), 7.77-7.73 (m, 1H), 7.52-7.40 (m, 3H), 7.20-7.15 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ 159.3, 149.7, 142.2, 137.5, 135.5, 134.6, 130.0, 129.7, 124.0, 119.4, 112.4; EIMS: 239 $[M]^{+}$ Anal calc for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56 %; Found: C, 64.10; H, 2.85; N, 15.52 %.

3-(4-Chlorophenyl)-2-nitroimidazo [1, 2-*a*] pyridine (Table 3, Entry 2)[1]



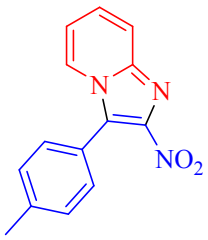
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.8 Hz, 1H), 8.07(d, *J* = 9.2 Hz, 2H), 7.79-7.73 (m, 1H), 7.41 (d, *J* = 9.2 Hz, 2H), 7.22-7.19 (m,2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 148.3, 140.01, 140.5, 139.8, 131.9,130.0, 129.7, 123.4, 117.5, 112.3; EIMS: 273 $[M]^{+}$ Anal calc for $C_{13}H_8ClN_3O_2$:C, 57.05; H,2.95; N, 15.35%; Found: C, 55.10; H, 1.80; N, 14.20%.

3-(4-Chlorophenyl)-7-methyl-2-nitroimidazo [1, 2-*a*] pyridine (Table 3, Entry 3) [1]



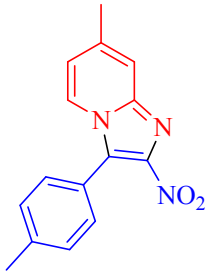
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.39 (d, *J* = 4.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* =8.4 Hz, 2H), 7.04-7.01 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 148.8, 148.6, 140.0, 139.7, 132.3, 130.01, 129.8,123.2, 118.3, 112.4, 21.2; EIMS: 287 $[M]^{+}$ Anal calc for $C_{14}H_{10}ClN_3O_2$: C, 58.45; H, 3.50; N, 14.61; Found: C, 56.32; H, 2.80; N, 13.43%.

2-Nitro-3-*p*-tolylimidazo [1, 2-*a*] pyridine (Table 3, Entry 4) [1]



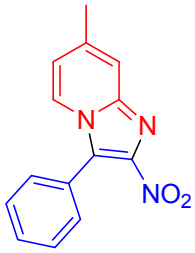
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61-8.59 (m, 1H), 8.15-8.13 (m, 2H), 7.86-7.83 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29-7.24 (m, 2H), 2.32(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 158.4, 149.1, 143.2, 137.1, 130.8,129.7, 128.6, 128.1, 122.5, 117.2, 112.4, 21.1; EIMS: 253$[M]^{+}$; Anal calc for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59%; Found: C, 66.38; H, 4.40; N, 16.57%.

7-Methyl-2-nitro-3-*p*-tolylimidazo [1, 2-*a*] pyridine (Table 3, Entry 5) [1]



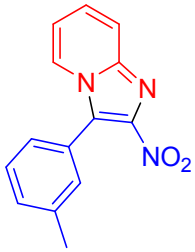
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35(d, *J* = 4.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz,2H), 7.00-6.97 (m, 2H), 2.34 (s, 3H), 2.31(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 158.5, 149.1, 144.3, 139.2, 132.3, 129.8, 129.5,129.1, 124.1, 117.4, 112.5, 21.2, 20.8; EIMS: 267 $[M]^{+}$; Anal calc for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72%; Found: C, 65.32; H, 3.80; N, 14.67%.

7-Methyl-2-nitro-3-phenylimidazo [1, 2-*a*] pyridine (Table 3, Entry 8)[1]



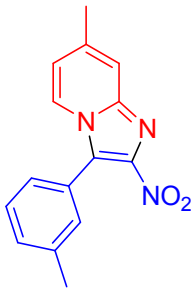
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 5.2Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.51-7.49 (m, 1H), 7.46-7.43 (m, 2H), 7.01-6.97 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ158.4, 148.6, 148.1, 142.1, 134.6, 135.3, 129.2, 129.6, 124.2, 117.9, 112.5, 21.1; EIMS: 253 $[M]^+$; Anal calc for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59%; Found: C, 64.49; H, 3.22; N, 14.50%.

2-Nitro-3-*m*-tolylimidazo [1, 2-*a*] pyridine (Table 3, Entry 10) [1]



Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.4 Hz, 1H), 7.95-7.92 (m, 2H), 7.75-7.73 (m, 1H), 7.29-7.23 (m, 2H), 7.20-7.16 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 149.1, 140.4, 138.8,138.2, 134.1, 133.4, 128.9, 128.8, 126.0, 122.7, 118.1, 111.4, 21.2; EIMS: 253 $[M]^+$; Anal calc for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59%; Found: C, 64.21; H, 3.67; N, 15.01%.

7-Methyl-2-nitro-3-*m*-tolylimidazo [1, 2-*a*] pyridine (Table 3, Entry 11) [1]



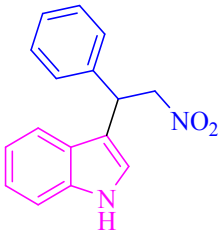
Semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 4.8 Hz, 1H), 7.94-7.91 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H) 7.02-6.99 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 148.9, 148.4, 142.8, 139.2, 134.4, 134.1, 129.5,129.3, 126.2, 124.1, 117.6, 112.6, 21.1,

21.3; EIMS: 267 $[M]^+$, Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72%; Found: C, 65.43; H, 3.57; N, 14.59%.

General procedure for the synthesis of 3-substituted indoles 5 from nitroalkenes 1 and Indoles 4

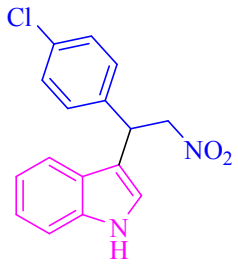
A solution of nitroalkenes (**1**) (1mmol) and indole (**4**) (1mmol) was taken into round bottom flask in EtOH (3ml). The reaction mixture was irradiated with high power green LEDs (2.5w λ =535nm) under open atmosphere at room temperature for 2-3 h. After completion of reaction (TLC) water was added and extracted with EtOAc. The organic layer was dried over anhydrous MgSO4 and filtered. The crude product was obtained by concentrating the resulting solution under reduced pressure and was purified by column chromatography on silica gel using a gradient mixture of EtOAc-Hexane to give the pure product (**5**) in excellent yield (table5). All the desired product are known compounds which were characterized by the comparison of their spectra and melting point with those reported in the previous literature.[2, 3, 4, 5, 6, 7]

3-(2-Nitro-1-phenylethyl)-1H-indole (Table 5, Entry 1) [2, 5, 7, 3, 4]



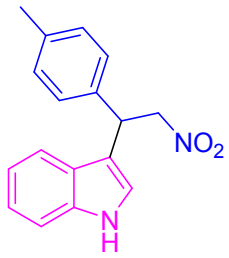
Semisolid; ^{1}HNMR ($CDCl_3$, 400MHz): δ 8.10 (s, 1H), 7.45 (d, J= 8.0 Hz, 1H), 7.35-7.27 (m, 5H), 7.26 (s, 1H), 7.23-7.16 (m, 1H), 7.10- 7.00 (m, 2H), 5.24- 5.16 (m, 1H), 5.13-5.01 (m, 1H), 4.97-4.90 (m, 1H); ^{13}C NMR ($CDCl_3$,100MHz): 137.45, 136.55, 136.15, 129.0, 129.76, 127.65, 126.10, 122.65, 122.10, 120.01, 119.10, 114.65, 112.01, 80.10, 41.50; EIMS: 266 $[M]^+$, Anal. Calcd. for $C_{16}H_{14}O_3N_2$: C, 72.16; H, 5.30; N, 10.52; found: C: 68.16; H, 4.98; N, 8.89.

3-(1-(4-Chlorophenyl)-2-nitroethyl)-1H-indole (Table 5, Entry 2) [2, 5, 4]



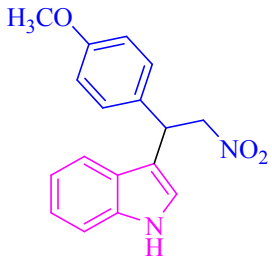
Semisolid; ^{1}H NMR($CDCl_3$, 400MHz): δ 8.13 (s, 1H), 7.45-7.36 (m, 3H), 7.35-7.16 (m, 4H), 7.13- 7.05 (m, 1H), 7.04- 6.97(m, 1H), 5.90- 5.01 (m, 1H), 5.29- 5.11 (m, 1H), 4.97-4.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): 137.91, 136.57, 133.51, 129.24, 126.05, 123.09, 121.55, 120.23, 118.84, 118.35, 114.02, 111.54, 79.35, 41.10; EIMS: 300 $[M]^+$; 302 $[M+2]^+$; [Anal. Calcd. for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31; found: C, 62.21; H, 3.95; N, 8.34.

3-[1-(4-Methylphenyl)-2-nitroethyl]-1H-indole *(*Table 5, Entry 3*)* [2, 4, 5, 6,]



Semisolid; ^{1}H NMR ($CDCl_3$, 400MHz): δ8.05 (s, 1H), 7.47 (d, J=8.0 Hz,1H), 7.35 (d, J = 8.0Hz, 1H), 7.26-7.07 (m, 5H), 7.03-6.99 (m, 2H), 5.21-5.12 (m, 1H), 5.02–5.11 (m, 1H), 4.97-4.84 (m, 1H), 2.32 (s,1H); ^{13}CNMR($CDCl_3$,100MHz): 137.25, 136.55,136.15, 129.62, 127.35, 126.32122.62, 121.55, 120.12, 119.01, 114.65, 111.35, 79.98, 41.42, 20.91; (EIMS): 280 $[M]^+$; Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; found: C, 68.03; H, 4.90; N, 8.75.

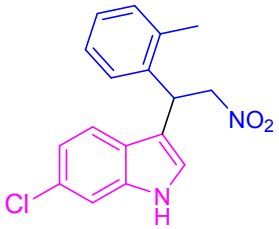
3-(1-(4-Methoxyphenyl)-2-nitroethyl)-1H-indole *(*Table 5, Entry 4*)*. [2, 4, 5,]



Whitish solid; M. P.: 150-151; ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.06 (s, 1H), 7.45 (d, 2H), 7.35 (d, 1H), 7.27- 7.20 (m, 3H), 7.10-7.03 (m, 1H), 7.02 (s,1H), 6.85 (d, 2H), 5.16- 5.09 (m,1H), 5.07–

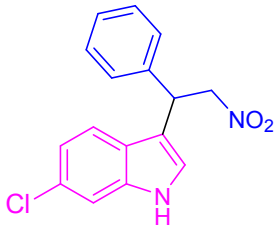
5.01(m,1H), 4.92- 4.83 (m, 1H), 3.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 100MHz): 160.01, 139.41, 136.59, 131.28, 128.89, 126.12, 122.75, 121.51, 120.01, 119.18, 114.32, 111.43, 79.92, 55.31, 40.89; EIMS: 296 $[M]^+$; Anal. Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45; found: C, 67.12; H, 5.01; N, 8.90.

6-chloro-3-(1-(2-methylphenyl)-2-nitroethyl)-1H-indole (Table 5, Entry 7) [3]



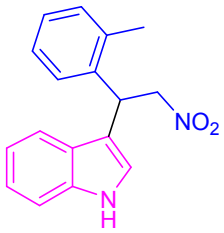
Brownish solid; M. P.: 154-156 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ11.19 (s, 1H), 7.41-7.39 (m, 2H), 7.40-7.33 (m, 2H), 7.17-7.09 (m, 3H), 6.98-6.95 (m, 1H), 5.30-5.28 (t, 1H), 5.24- 5.20 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6): 137.9, 136.9, 136.1, 131.2, 127.9, 127.4, 125.9, 125.5, 125.0, 120.0, 119.5, 119.0, 114.0, 110.9, 79.2, 37.1, 19.5; EIMS: 314$[M]^+$; Anal. Calcd. for $C_{17}H_{15}ClN_2O_2$: C,64.87; H, 4.80; N, 8.90; found: C, 62.25; H, 4.32; N, 7.56.

6-chloro-3-(2-nitro-1-phenylethyl)-1H-indole (Table 5, Entry 8) [3]



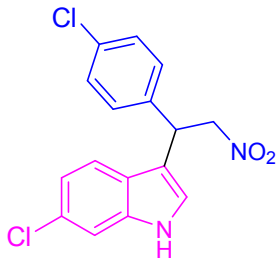
Pinkish liquid**;** ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.30 (s, 1H), 7.27-7.26 (m, 7H), 7.00-6.96 (t, 2H), 5.13-5.09 (t, 1H), 5.01-4.96 (dd, 1H), 4.86-4.91 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 138.3, 136.7, 128.8, 128.0, 123.9, 122.2, 121.1, 120.9, 120.4, 120.0**,** 114.1, 110.9, 79.0, 41.5; EIMS: 300$[M]^+$; Anal. calcd for $C_{16}H_{13}ClN_2O_2$ C,63.90; H, 4.36; N, 9.31; found: C, 61.34; H, 4.78; N, 8.85.

3-(2-nitro-1-o-tolylethyl)-1H-indole (Table 5, Entry 9) [3]



Brownish solid; M. P.: 143-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ8.09 (s, 1H), 7.54-7.53 (d, 1H), 7.42-7.40 (d, 1H), 7.35-7.30 (t, 1H), 7.28-7.21 (m, 4H), 7.20-7.16 (m, 1H), 6.95 (s, 1H), 5.53-5.49 (t, 1H), 5.13-5.06 (dd), 5.00- 4.94 (dd), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.5, 137.0, 131.2, 127.6, 126.6, 126.4, 122.6, 122.3, 122.0, 120.3, 120.0, 119.3, 114.9, 111.5, 79.0, 37.9, 19.6; EIMS: 280[M]$^{+}$; Anal. calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; found: C, 70.32; H, 5.01; N, 9.01.

6-chloro-3-(1-(4-chlorophenyl)-2-nitroethyl)-1H-indole (Table 5, Entry 10)[3]



Light Brownish solid; M.P.: 137-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.30-7.20 (m, 6H), 7.03-7.00 (m, 2H), 5.10-5.06 (t, 1H), 5.02-4.97 (dd, 1H), 4.89-4.84 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.6, 137.0, 133.5, 129.2, 129.0, 128.8, 124.5, 122.1, 121.0, 119.8, 114.1, 111.5, 79.2, 41.0; EIMS: 334[M]$^{+}$; Anal. calcd for $C_{16}H_{12}Cl_2N_2O_2$: C, 57.33; H, 3.61; N, 8.36; found: C, 55.12; H, 3.01; N, 7.98.

References:

1. K. Monir, A. K. Bagdi, M. Ghosh, and A. Hajra, *Org. Lett*., 2014, **16**, 4630.
2. A. M. A. Al Majid, M. S. Islam, A. Barakat, M. H. M. Al-Agamy and Mu. Naushad**,** *Scientific World Journal,* 2014, **15**, 649197; http://dx.doi.org/10.1155/2014/649197.
3. M. Jeganathan, K. Kanagaraj, A. Dhakshinamoorthya, and K. Pitchumani, *Tetrahedron Lett.*, 2014, **55**, 2061.
4. A. Mane, T. Lohar and R. Salunkhe, *Tetrahedron Letters,* 2016, **57**, 2341.
5. T. Kitanosono, M. Miyo and S. Kobayashi, *Tetrahedron,* 2015, **71**, 7739.

6. P. M. Habib, V. Kavala, C.-W. Kuo, M. J. Raihan and C.-F. Yao, *Tetrahedron,* 2010, **66**, 7050.
7. N. T. Tran, S. O. Wilson and A. K. Franz, *Org. Lett*., 2012, **14**, 186.