Supplementary Information

Acid Catalyzed Silica Supported One Pot Benzoylation Route to Synthesize 2-(Substituted phenyl) [4, 5-b]pyridines under Ambient Conditions

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General procedure for synthesis of 2-(substituted phenyl) [4, 5-b]pyridines (3b-j)

To the mixture of benzoic acid (2 mmol) and 2-amino-3-hydroxypyridine (0.11 g, 1 mmol), add $\text{HClO}_4\cdot\text{SiO}_2$ nanoparticles (5 mol%) using 3 mL methanol as a solvent under stirring at room temperature. Progress of the reaction was continuously monitored by TLC (n-hexane and ethyl acetate in 2:1). After the completion of process as marked by TLC the solid was recovered by rotatory evaporator. The beauty of the process lies in the easy recovery of the catalyst by adding excess of chloroform. The product was recrystallised from acetonitrile and then washed with dichloromethane (2 x 5 mL).

Characterization data of compounds 3b-j

2-(2-Chlorophenyl)oxazolo[4,5-b]pyridine (3b). Off white solid; m.p. 98-103 °C; IR (KBr, cm^{-1}) 3061, 1670, 1627, 1579, 1540, 1258, 1050, 1030, 756; ^1H NMR (400 MHz, DMSO) δ 6.543-6.577 (t, 1H), 7.091-7.110 (d, 1H), 7.334-7.557 (m, 4H), 7.723-7.740 (d, 1H); ^{13}C NMR (100 MHz, DMSO) δ 118.6, 120.8, 125.8, 128.3, 129.1, 130.5, 132.5, 142.2, 148.4, 154.3, 159.2; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: 231.029; Anal. Calcd for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{O}$: C, 62.49; H, 3.06; N, 12.15. Found: C, 62.42; H, 3.08; N, 12.17.

2-(2-Methoxyphenyl)oxazolo[4,5-b]pyridine (3c). Off white solid; m.p. 110-112 °C; IR (KBr, cm^{-1}) 3050, 2962, 2845, 1680, 1596, 1518, 1490, 1244, 1085, 760; ^1H NMR (400 MHz, DMSO) δ 3.798-3.808 (s, 3H), 6.483-6.514 (t, 1H), 7.357-7.562 (m, 4H), 7.686-7.702 (d, 1H), 7.951-7.976 (d, 1H); ^{13}C NMR (100 MHz, DMSO) δ 62.2, 111.6, 115.2, 118.9, 121.2, 123.2, 129.4, 142.6, 148.5, 154.8, 157.3, 159.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: 227.077; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.05; H, 4.50; N, 12.35.

2-(3-Methoxyphenyl)oxazolo[4,5-b]pyridine (3d). White solid; m.p. 115-118 °C; IR (KBr, cm^{-1}) 3038, 2958, 2855, 1684, 1590, 1517, 1497, 1260, 1082, 755; ^1H NMR (400 MHz, DMSO) δ 3.837-3.845 (s, 3H), 6.591-6.614 (d, 1H), 7.159-7.182 (t, 1H), 7.286-7.358 (m, 3H), 7.561-7.582 (d, 1H), 7.902-7.918 (d, 1H); ^{13}C NMR (100 MHz, DMSO) δ 62.2, 111.3, 114.5, 118.8, 119.2, 127.1, 130.7, 142.8, 148.1, 154.8, 161.5, 167.8; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: 227.074; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.01; H, 4.48; N, 12.38.

2-(3-Chlorophenyl)oxazolo[4,5-b]pyridine (3e). White solid; m.p. 148-151 °C; IR (KBr, cm^{-1}): 3045, 1684, 1591, 1517, 1492, 1263, 1082, 1055, 772; ^1H NMR (400 MHz, DMSO) δ 6.652-6.683 (t, 1H), 7.112-7.134 (d, 1H), 7.357-7.368 (s, 2H), 7.561-7.642 (m, 3H); ^{13}C NMR (100 MHz, DMSO) δ 118.6, 119.4, 125.1, 127.8, 128.2, 129.1, 134.5, 142.4, 148.7, 154.5, 167.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: 231.024; Anal. Calcd for $\text{C}_{12}\text{H}_7\text{ClN}_2\text{O}$: C, 62.49; H, 3.06; N, 12.15. Found: C, 62.45; H, 3.10; N, 12.14.

2-(3-Bromophenyl)oxazolo[4,5-b]pyridine (3f). Pale yellow solid; m.p. 156-160 °C; IR (KBr, cm^{-1}): 3047, 1693, 1595, 1522, 1486, 1225, 1062, 965, 755; ^1H NMR (400 MHz, DMSO) δ 6.582-6.617 (t, 1H), 7.082-7.196 (m, 3H), 7.385-7.402 (d, 1H), 7.581-7.607 (d, 2H); ^{13}C NMR (100 MHz, DMSO) δ 118.8, 119.9, 122.7, 126.3, 128.3, 131.6, 133.8, 142.4, 148.3, 154.3, 167.3; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: 231.029; Anal. Calcd for $\text{C}_{12}\text{H}_7\text{BrN}_2\text{O}$: C, 52.39; H, 2.56; N, 10.18. Found: C, 52.42; H, 2.58; N, 10.20.

2-(4-Methylphenyl)oxazolo[4,5-b]pyridine (3g). Off white solid; m.p. 138-140 °C; IR (KBr, cm^{-1}): 3043, 2974, 2857, 1689, 1597, 1508, 1493, 1267, 1078, 759; ^1H NMR (400 MHz, DMSO) δ 2.238-6.245 (s, 3H), 7.213-7.335 (m, 4H), 7.874-7.895 (d, 3H); ^{13}C NMR (100 MHz, DMSO) δ 29.3, 118.7, 119.7, 126.3, 127.5, 131.4, 142.5, 148.8, 154.3, 167.5; MS (ESI) m/z $[\text{M}+\text{H}]^+$: 211.085; Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.25; H, 4.83; N, 4.77.

2-(4-Methoxyphenyl)oxazolo[4,5-b]pyridine (3h). White solid; m.p. 178-180 °C; IR (KBr, cm⁻¹): 3047, 2968, 2850, 1691, 1588, 1503, 1492, 1267, 1060, 750; ¹H NMR (400 MHz, DMSO) δ 3.857-3.862 (s, 3H), 6.613-6.645 (t, 1H), 7.053-7.075 (d, 2H), 7.306-7.324 (d, 1H), 7.831-7.842 (d, 1H), 7.952-7.978 (d, 2H); ¹³C NMR (100 MHz, DMSO) δ 63.2, 114.5, 115.7, 118.6, 119.2, 122.3, 142.8, 148.1, 154.5, 160.5, 167.6; HRMS (ESI) *m/z* [M+H]⁺: 227.082; Anal. Calcd for C₁₃H₁₀N₂O₂: C, 69.02; H, 4.46; N, 12.38. Found: C, 68.99; H, 4.51; N, 12.35.

2-(4-Chlorophenyl)oxazolo[4,5-b]pyridine (3i). Off white solid; m.p. 165-168 °C; IR (KBr, cm⁻¹): 3057, 1689, 1585, 1519, 1488, 1270, 1090, 1056, 768; ¹H NMR (400 MHz, DMSO) δ 6.679-6.714 (t, 1H), 7.223-7.244 (d, 1H), 7.387-7.412 (d, 2H), 7.581-7.605 (d, 2H), 7.861-7.887 (d, 1H); ¹³C NMR (100 MHz, DMSO) δ 118.3, 119.9, 128.1, 129.7, 134.3, 142.1, 148.5, 154.6, 167.9; HRMS (ESI) *m/z* [M+H]⁺: 231.030; Anal. Calcd for C₁₂H₇ClN₂O: C, 62.49; H, 3.06; N, 12.15. Found: C, 62.48; H, 3.11; N, 12.17.

2-(4-(Trifluoromethyl)phenyl)oxazolo[4,5-b]pyridine (3j). White solid; m.p. 162-164 °C; IR (KBr, cm⁻¹): 3055, 1693, 1596, 1509, 1490, 1265, 1150, 1082, 776; ¹H NMR (400 MHz, DMSO) δ 6.718-6.754 (t, 1H), 7.154-7.178 (d, 1H), 7.369-7.404 (d, 2H), 7.881-7.902 (d, 1H), 7.962-7.986 (d, 2H); ¹³C NMR (100 MHz, DMSO) δ 118.1, 119.6, 124.7, 125.5, 127.7, 131.9, 133.5, 142.4, 148.8, 154.6, 167.6; HRMS (ESI) *m/z* [M+H]⁺: 265.059; Anal. Calcd for C₁₃H₇F₃N₂O: C, 59.10; H, 2.67; N, 10.60. Found: C, 59.09; H, 2.69; N, 10.55.

Copies of IR, ^1H NMR and HRMS

Figure S1

G-2

Figure S2

Chemical structure of **3b** is shown in the top right corner of the spectrum.

The ¹H NMR spectrum (CDCl₃) shows the following peaks (ppm) and integrations:

- 7.800, 7.795, 7.785, 7.780, 7.775, 7.770, 7.765, 7.760, 7.755, 7.750, 7.745, 7.740, 7.735, 7.730, 7.725, 7.720, 7.715, 7.710, 7.705, 7.700, 7.695, 7.690, 7.685, 7.680, 7.675, 7.670, 7.665, 7.660, 7.655, 7.650, 7.645, 7.640, 7.635, 7.630, 7.625, 7.620, 7.615, 7.610, 7.605, 7.600, 7.595, 7.590, 7.585, 7.580, 7.575, 7.570, 7.565, 7.560, 7.555, 7.550, 7.545, 7.540, 7.535, 7.530, 7.525, 7.520, 7.515, 7.510, 7.505, 7.500, 7.495, 7.490, 7.485, 7.480, 7.475, 7.470, 7.465, 7.460, 7.455, 7.450, 7.445, 7.440, 7.435, 7.430, 7.425, 7.420, 7.415, 7.410, 7.405, 7.400, 7.395, 7.390, 7.385, 7.380, 7.375, 7.370, 7.365, 7.360, 7.355, 7.350, 7.345, 7.340, 7.335, 7.330, 7.325, 7.320, 7.315, 7.310, 7.305, 7.300, 7.295, 7.290, 7.285, 7.280, 7.275, 7.270, 7.265, 7.260, 7.255, 7.250, 7.245, 7.240, 7.235, 7.230, 7.225, 7.220, 7.215, 7.210, 7.205, 7.200, 7.195, 7.190, 7.185, 7.180, 7.175, 7.170, 7.165, 7.160, 7.155, 7.150, 7.145, 7.140, 7.135, 7.130, 7.125, 7.120, 7.115, 7.110, 7.105, 7.100, 7.095, 7.090, 7.085, 7.080, 7.075, 7.070, 7.065, 7.060, 7.055, 7.050, 7.045, 7.040, 7.035, 7.030, 7.025, 7.020, 7.015, 7.010, 7.005, 7.000, 6.995, 6.990, 6.985, 6.980, 6.975, 6.970, 6.965, 6.960, 6.955, 6.950, 6.945, 6.940, 6.935, 6.930, 6.925, 6.920, 6.915, 6.910, 6.905, 6.900, 6.895, 6.890, 6.885, 6.880, 6.875, 6.870, 6.865, 6.860, 6.855, 6.850, 6.845, 6.840, 6.835, 6.830, 6.825, 6.820, 6.815, 6.810, 6.805, 6.800, 6.795, 6.790, 6.785, 6.780, 6.775, 6.770, 6.765, 6.760, 6.755, 6.750, 6.745, 6.740, 6.735, 6.730, 6.725, 6.720, 6.715, 6.710, 6.705, 6.700, 6.695, 6.690, 6.685, 6.680, 6.675, 6.670, 6.665, 6.660, 6.655, 6.650, 6.645, 6.640, 6.635, 6.630, 6.625, 6.620, 6.615, 6.610, 6.605, 6.600, 6.595, 6.590, 6.585, 6.580, 6.575, 6.570, 6.565, 6.560, 6.555, 6.550, 6.545, 6.540, 6.535, 6.530, 6.525, 6.520, 6.515, 6.510, 6.505, 6.500, 6.495, 6.490, 6.485, 6.480, 6.475, 6.470, 6.465, 6.460, 6.455, 6.450, 6.445, 6.440, 6.435, 6.430, 6.425, 6.420, 6.415, 6.410, 6.405, 6.400, 6.395, 6.390, 6.385, 6.380, 6.375, 6.370, 6.365, 6.360, 6.355, 6.350, 6.345, 6.340, 6.335, 6.330, 6.325, 6.320, 6.315, 6.310, 6.305, 6.300, 6.295, 6.290, 6.285, 6.280, 6.275, 6.270, 6.265, 6.260, 6.255, 6.250, 6.245, 6.240, 6.235, 6.230, 6.225, 6.220, 6.215, 6.210, 6.205, 6.200, 6.195, 6.190, 6.185, 6.180, 6.175, 6.170, 6.165, 6.160, 6.155, 6.150, 6.145, 6.140, 6.135, 6.130, 6.125, 6.120, 6.115, 6.110, 6.105, 6.100, 6.095, 6.090, 6.085, 6.080, 6.075, 6.070, 6.065, 6.060, 6.055, 6.050, 6.045, 6.040, 6.035, 6.030, 6.025, 6.020, 6.015, 6.010, 6.005, 6.000, 5.995, 5.990, 5.985, 5.980, 5.975, 5.970, 5.965, 5.960, 5.955, 5.950, 5.945, 5.940, 5.935, 5.930, 5.925, 5.920, 5.915, 5.910, 5.905, 5.900, 5.895, 5.890, 5.885, 5.880, 5.875, 5.870, 5.865, 5.860, 5.855, 5.850, 5.845, 5.840, 5.835, 5.830, 5.825, 5.820, 5.815, 5.810, 5.805, 5.800, 5.795, 5.790, 5.785, 5.780, 5.775, 5.770, 5.765, 5.760, 5.755, 5.750, 5.745, 5.740, 5.735, 5.730, 5.725, 5.720, 5.715, 5.710, 5.705, 5.700, 5.695, 5.690, 5.685, 5.680, 5.675, 5.670, 5.665, 5.660, 5.655, 5.650, 5.645, 5.640, 5.635, 5.630, 5.625, 5.620, 5.615, 5.610, 5.605, 5.600, 5.595, 5.590, 5.585, 5.580, 5.575, 5.570, 5.565, 5.560, 5.555, 5.550, 5.545, 5.540, 5.535, 5.530, 5.525, 5.520, 5.515, 5.510, 5.505, 5.500, 5.495, 5.490, 5.485, 5.480, 5.475, 5.470, 5.465, 5.460, 5.455, 5.450, 5.445, 5.440, 5.435, 5.430, 5.425, 5.420, 5.415, 5.410, 5.405, 5.400, 5.395, 5.390, 5.385, 5.380, 5.375, 5.370, 5.365, 5.360, 5.355, 5.350, 5.345, 5.340, 5.335, 5.330, 5.325, 5.320, 5.315, 5.310, 5.305, 5.300, 5.295, 5.290, 5.285, 5.280, 5.275, 5.270, 5.265, 5.260, 5.255, 5.250, 5.245, 5.240, 5.235, 5.230, 5.225, 5.220, 5.215, 5.210, 5.205, 5.200, 5.195, 5.190, 5.185, 5.180, 5.175, 5.170, 5.165, 5.160, 5.155, 5.150, 5.145, 5.140, 5.135, 5.130, 5.125, 5.120, 5.115, 5.110, 5.105, 5.100, 5.095, 5.090, 5.085, 5.080, 5.075, 5.070, 5.065, 5.060, 5.055, 5.050, 5.045, 5.040, 5.035, 5.030, 5.025,

BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

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Current Data Parameters
NAME          Feb18-2015
EXPNO         80
PROCNO        1
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F2 - Acquisition Parameters
Date_      20150218
Time_      13.35
INSTRUM    spect
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PULPROG    zg30
TD         65536
SOLVENT    DMSO
NS         8
DS         2
SWH         12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7263477 sec
RG         144
BW         41.600 usec
DE         6.00 usec
TE         296.3 K
D1         1.00000000 sec
TDO        1

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===== CHANNEL f1 =====
NUC1                1H
F1                  10.90 usec
FL1                 -3.00 dB
SP01               400.1324710 MHz
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F2 - Processing parameters	
SI	32768
SP	400.1299901 MHz
WIN	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

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Figure S3

WATERS, Q-TOF MICROMASS (LC-MS)

GAGANDEEP G-1 71 (0.796) Cm (1:81)

SAIF/CIL,PANJAB UNIVERSITY,CHANDIGARH

TOF MS ES+
2.76e4

Figure S4

WATERS, Q-TOF MICROMASS (LC-MS)
GAGANDEEP G-1 71 (0.796) Cm (1:81)

SAIF /CIL,PANJAB UNIVERSITY,CHANDIGARH
TOF MS ES+
421

Figure S5

WATERS, Q-TOF MICROMASS (LC-MS)
GAGANDEEP G-1 71 (0.796) Cm (1:81)

SAIF/CIL,PANJAB UNIVERSITY,CHANDIGARH

TOF MS ES+
2.76e4

Figure S6