Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of imidazo[1,5-a]pyridines via oxidative amination of C(sp^3)-H bond under air using metal-organic framework Cu-MOF-74 as an efficient heterogeneous catalyst

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Supporting Information

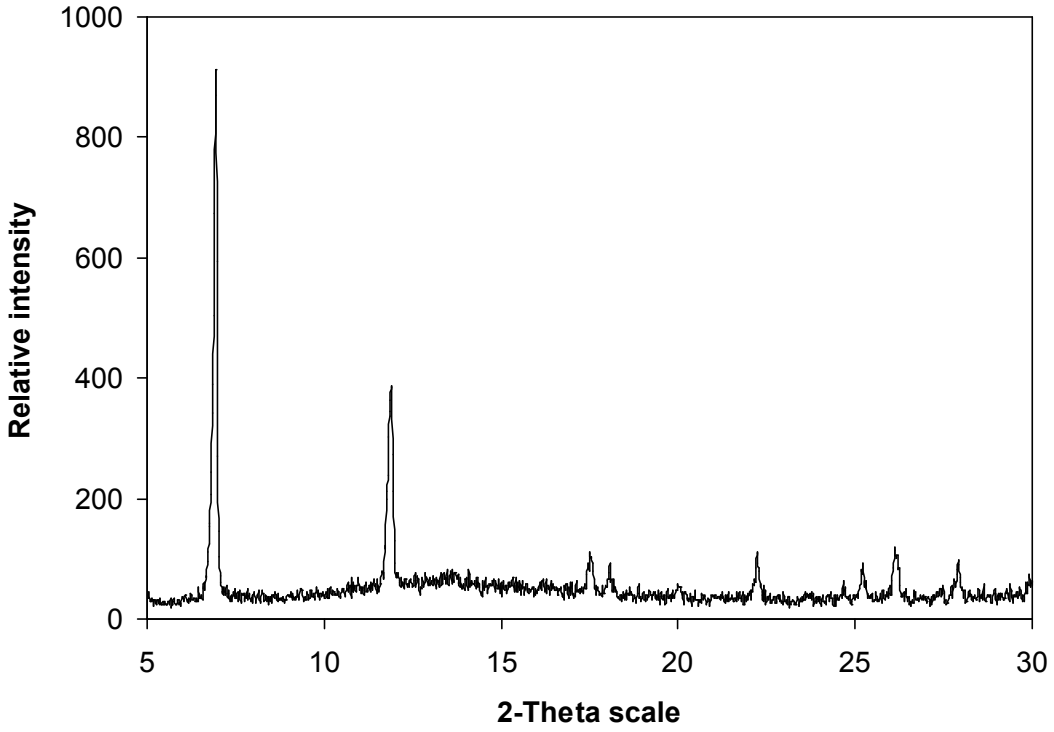

Fig. S1. X-ray powder diffractograms of the Cu-MOF-74.

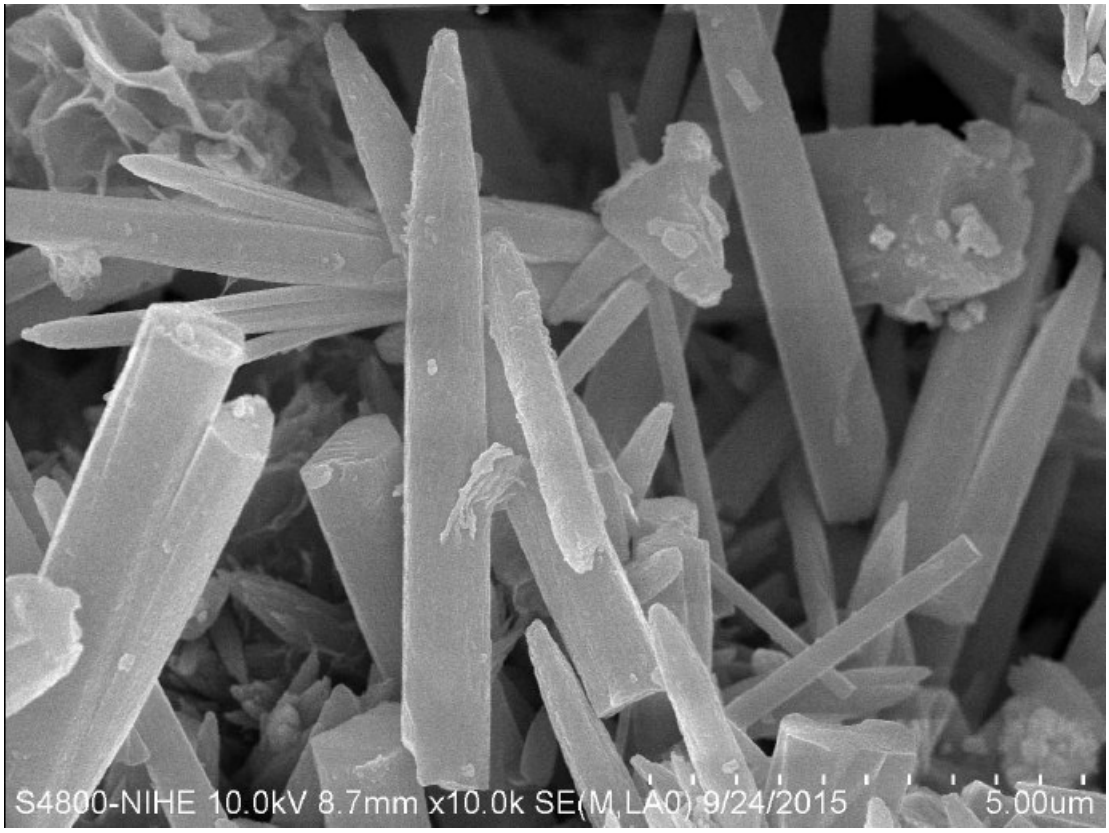

Fig. S2. SEM micrograph of the Cu-MOF-74.

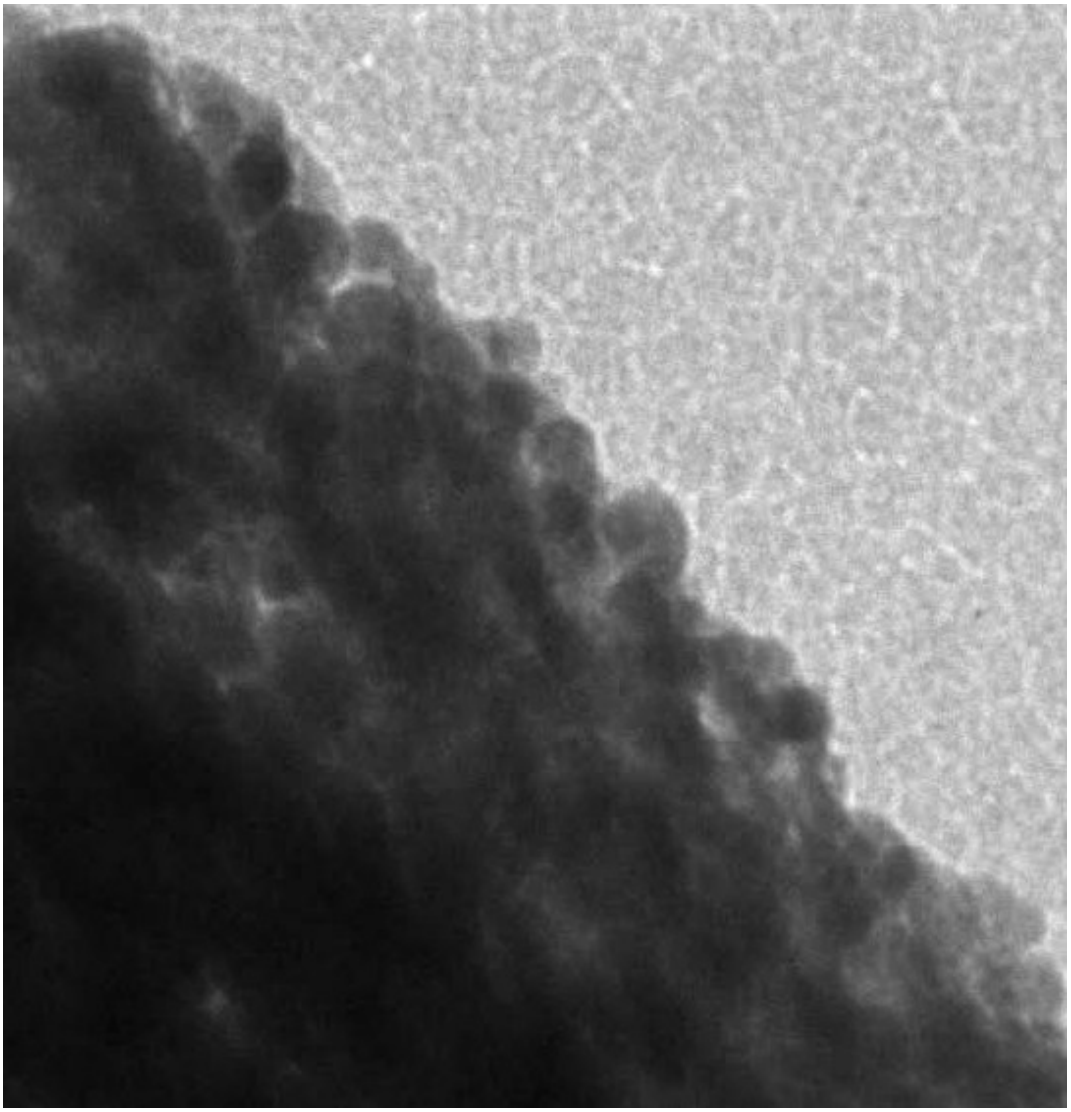

Fig. S3. TEM micrograph of the Cu-MOF-74.

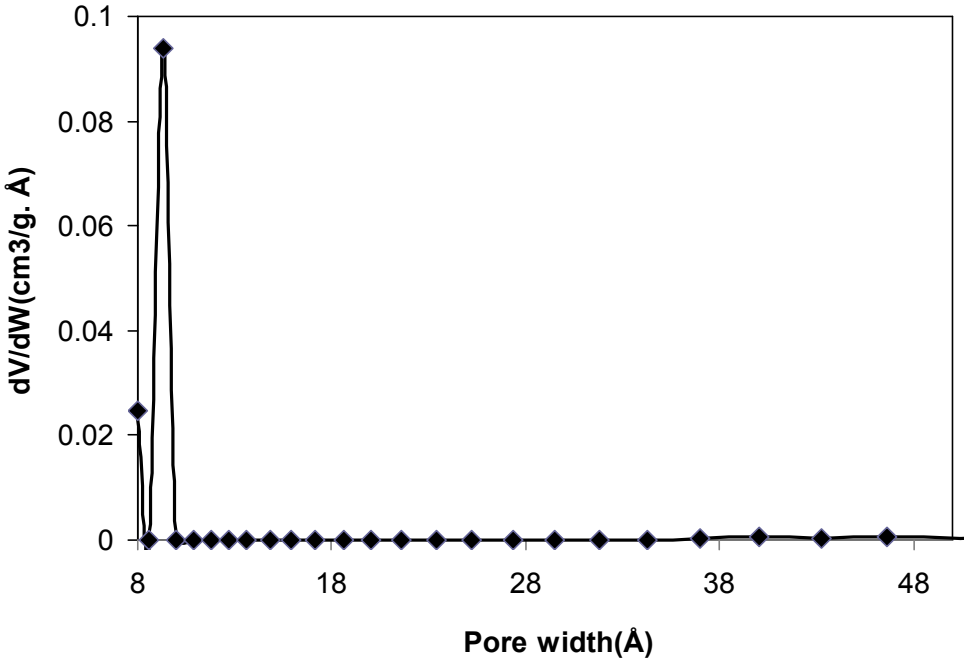

Fig. S4. Pore size distribution of the Cu-MOF-74.

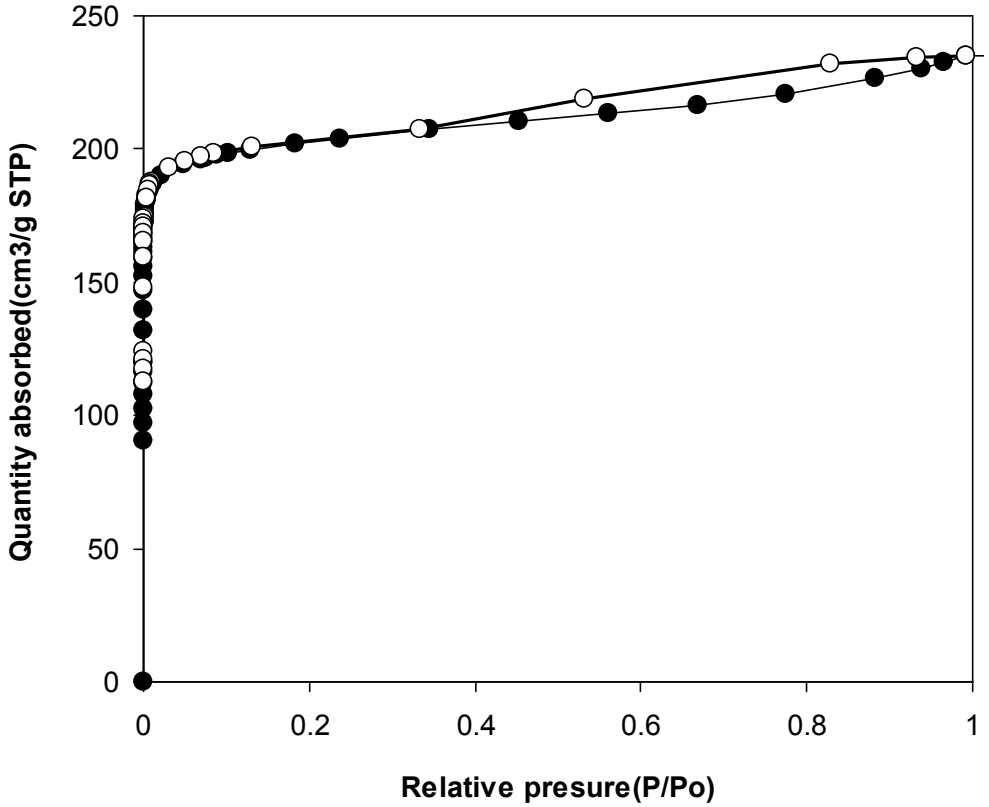

Fig. S5. Nitrogen adsorption/desorption isotherm of the Cu-MOF-74. Adsorption data are shown as closed circles and desorption data as open circles.

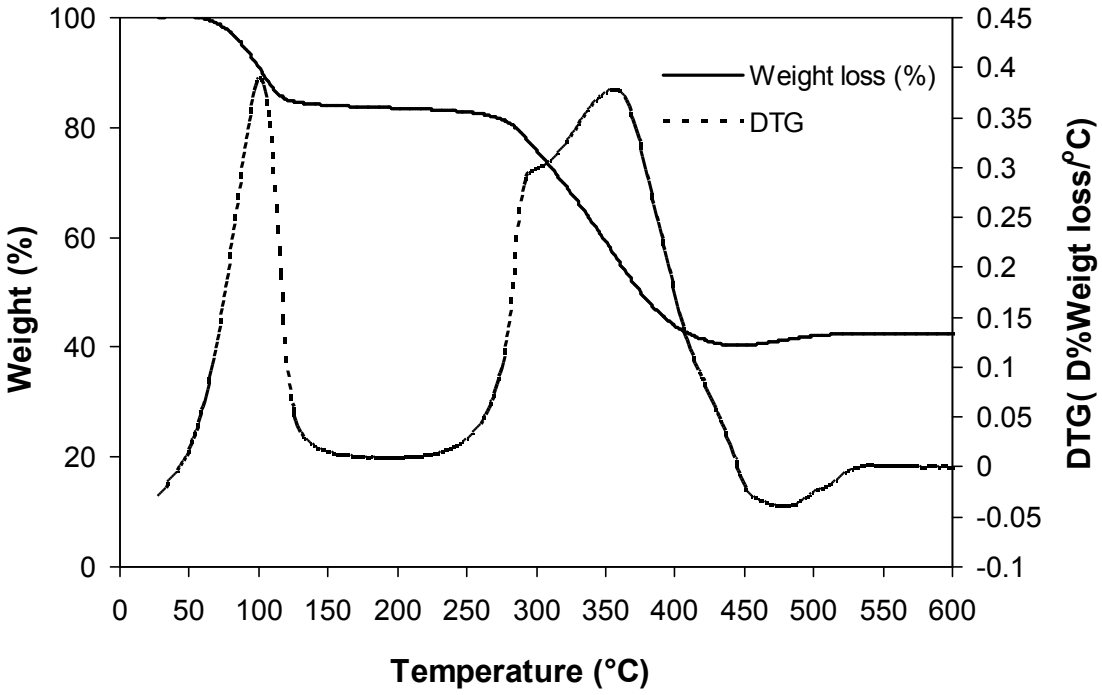

Fig. S6. TGA analysis of the Cu-MOF-74.

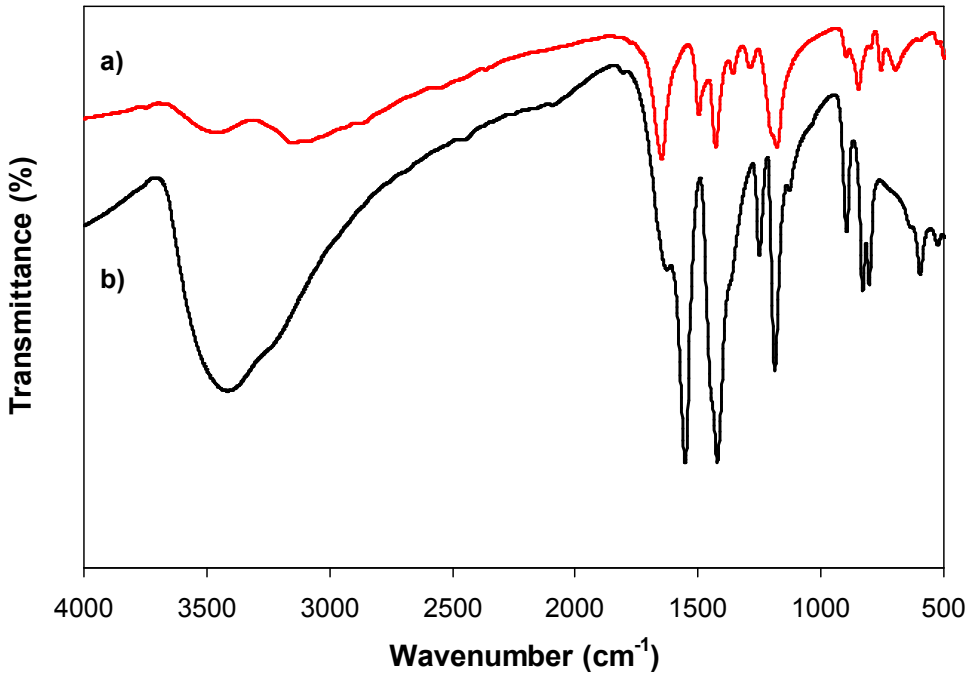

Fig. S7. FT-IR spectra of terephthalic acid (a), and the Cu-MOF-74 (b).

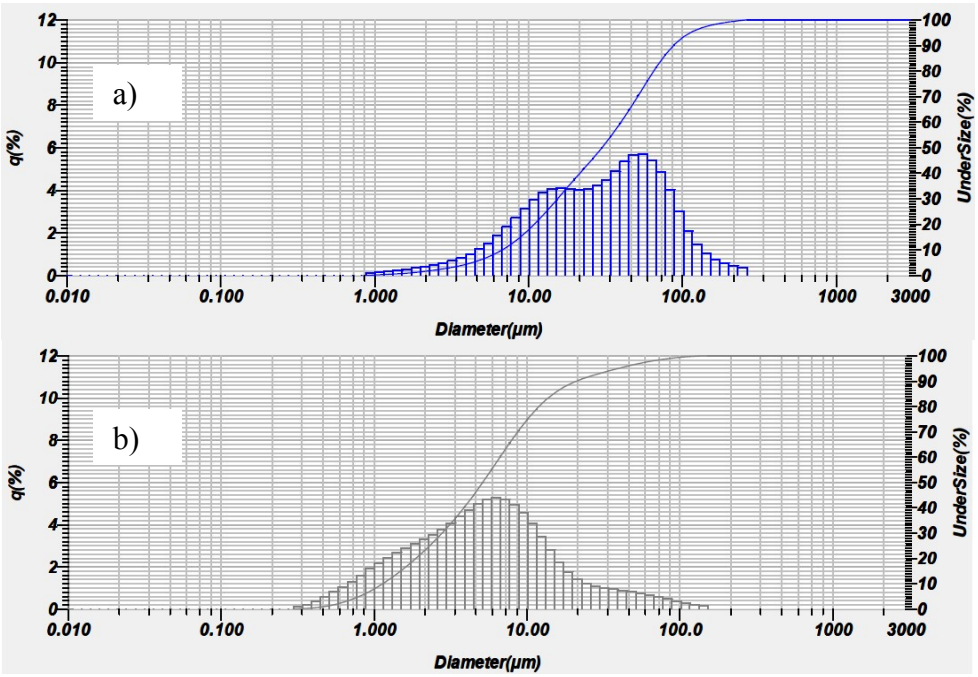

Fig. S8. Particles size distribution of non-grinded (a) and grinded (b) Cu MOF-74

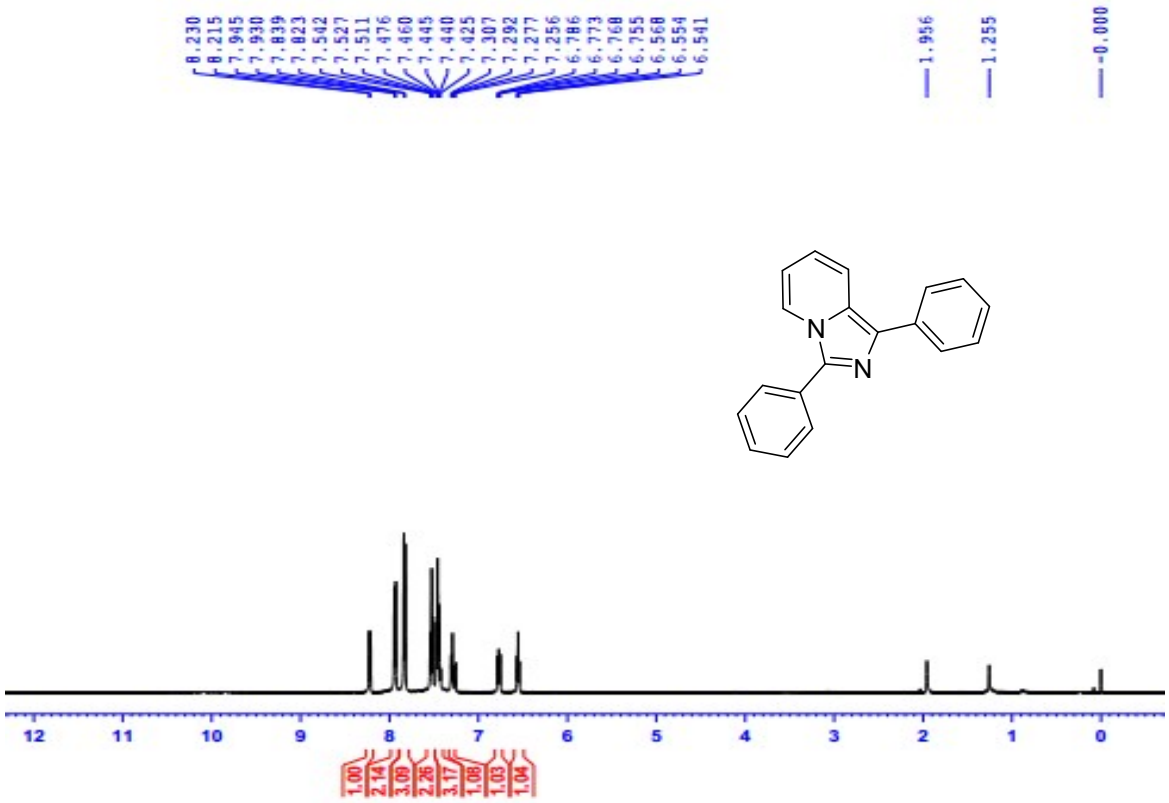

Fig. S9. [1]H-NMR spectra of 1,3-diphenylimidazo[1,5-a]pyridine.

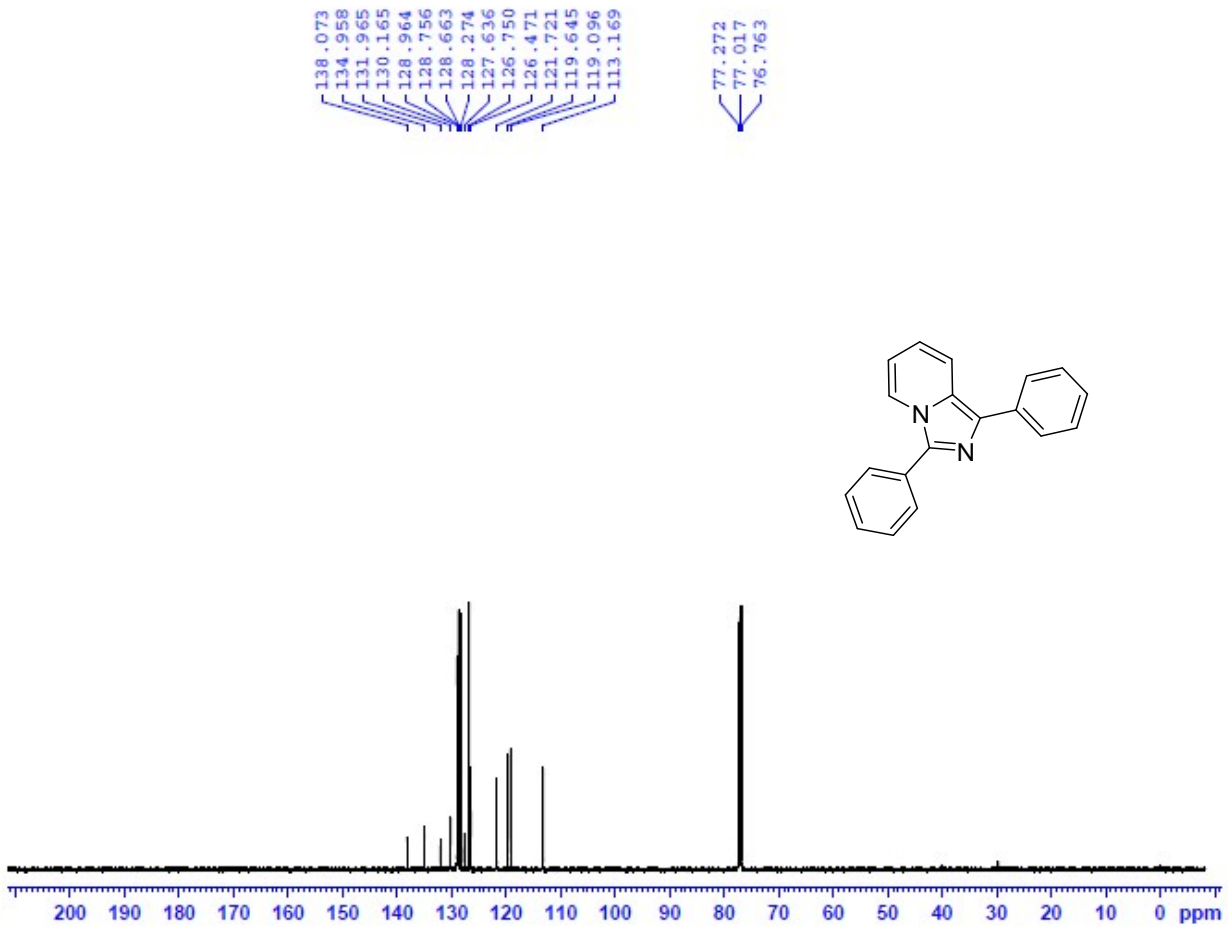

Fig. S10. ^{13}C-NMR spectra of 1,3-diphenylimidazo[1,5-a]pyridine.

Characterization data for 1,3-diphenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:8): yellow solid, 70% yield. This compound is known [1]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J*=7.5 Hz, 1H), 7.95 (s, 1H), 7.93 (s, 1H), 7.84-7.82 (m, 3H), 7.54-7.42 (m, 5H), 7.31-7.26 (m, 1H), 6.79-6.75 (m, 1H), 6.55 (t, *J*=6.8 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.07, 134.96, 131.96, 130.16, 130.0, 128.96, 128.76, 128.66, 128.27, 127.64, 126.75, 126.47, 121.72, 119.10, 113.17 .

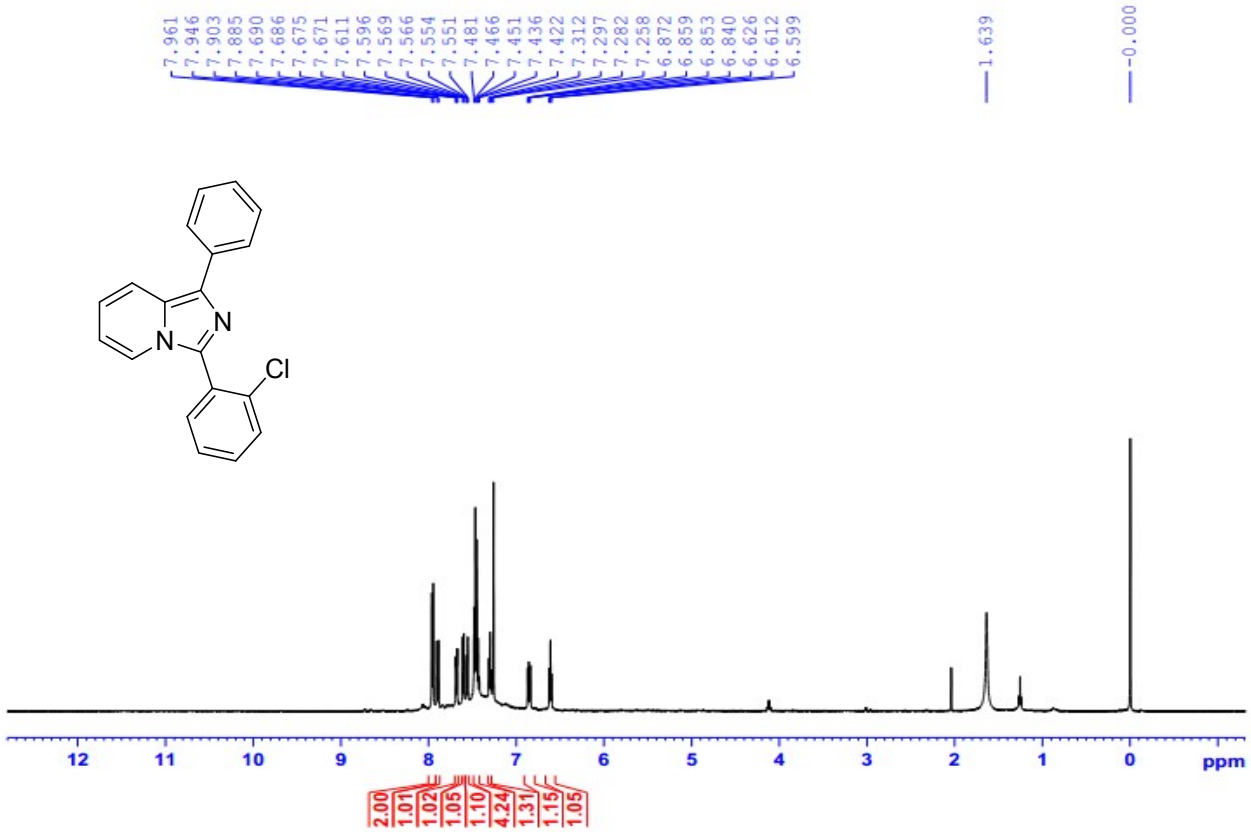

Fig. S11. ^{1}H-NMR spectra of 3-(2-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

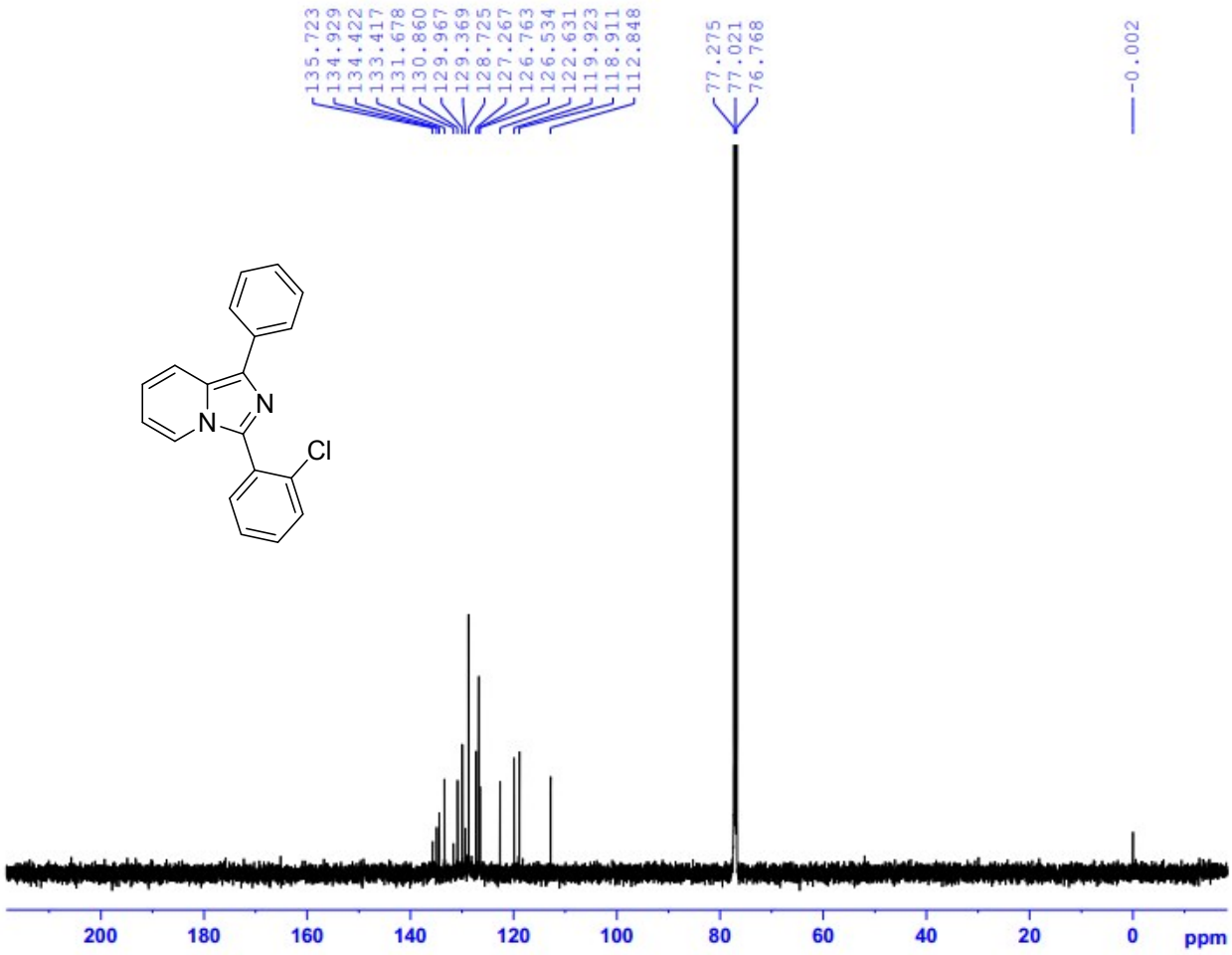

Fig. S12. ^{13}C-NMR spectra of 3-(2-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(2-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:4): yellow oil, 53% yield. 1H-NMR (500 MHz, CDCl3) δ 7.95 (d, J= 7.5 Hz, 2H), 7.89 (d, J= 9 Hz, 1H), 7.68 (m, 1H), 7.6 (d, J= 7.5, 1H), 7.56 (m, 1H), 7.48 - 7.42 (m, 4H), 7.31 - 7.26 (m, 1H), 6.87 - 6.84 (m, 1H), 6.61 (t, J= 6.8Hz, 1H); 13C-NMR (125 MHz, CDCl3) δ 135.72, 134.93, 134.42, 133.42, 131.8, 130.86, 129.97, 129.37, 128.72, 127.27, 126.76, 126.53, 122.63, 119.92, 118.91, 112.85.

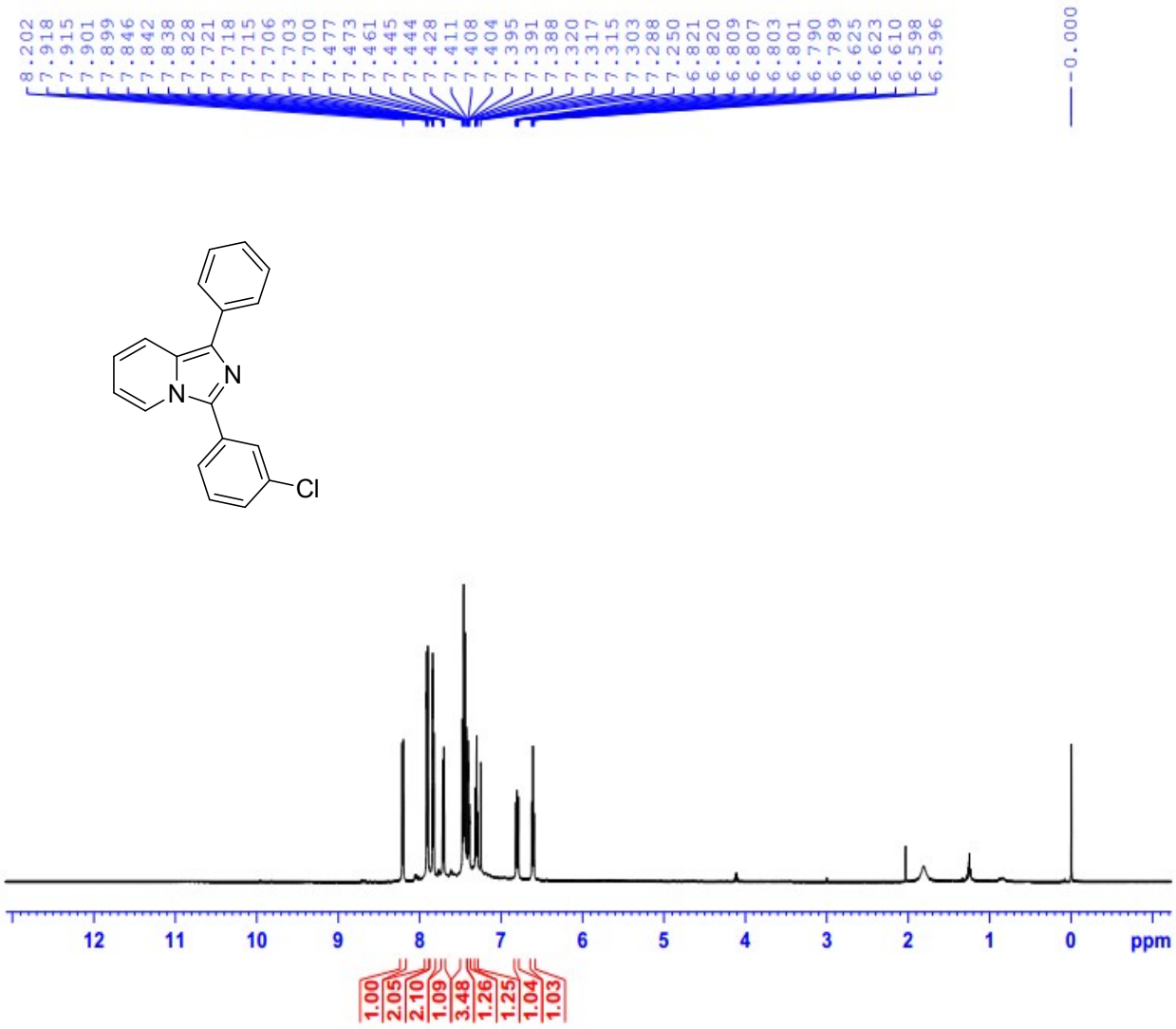

Fig. S13. ^{1}H-NMR spectra of 3-(3-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

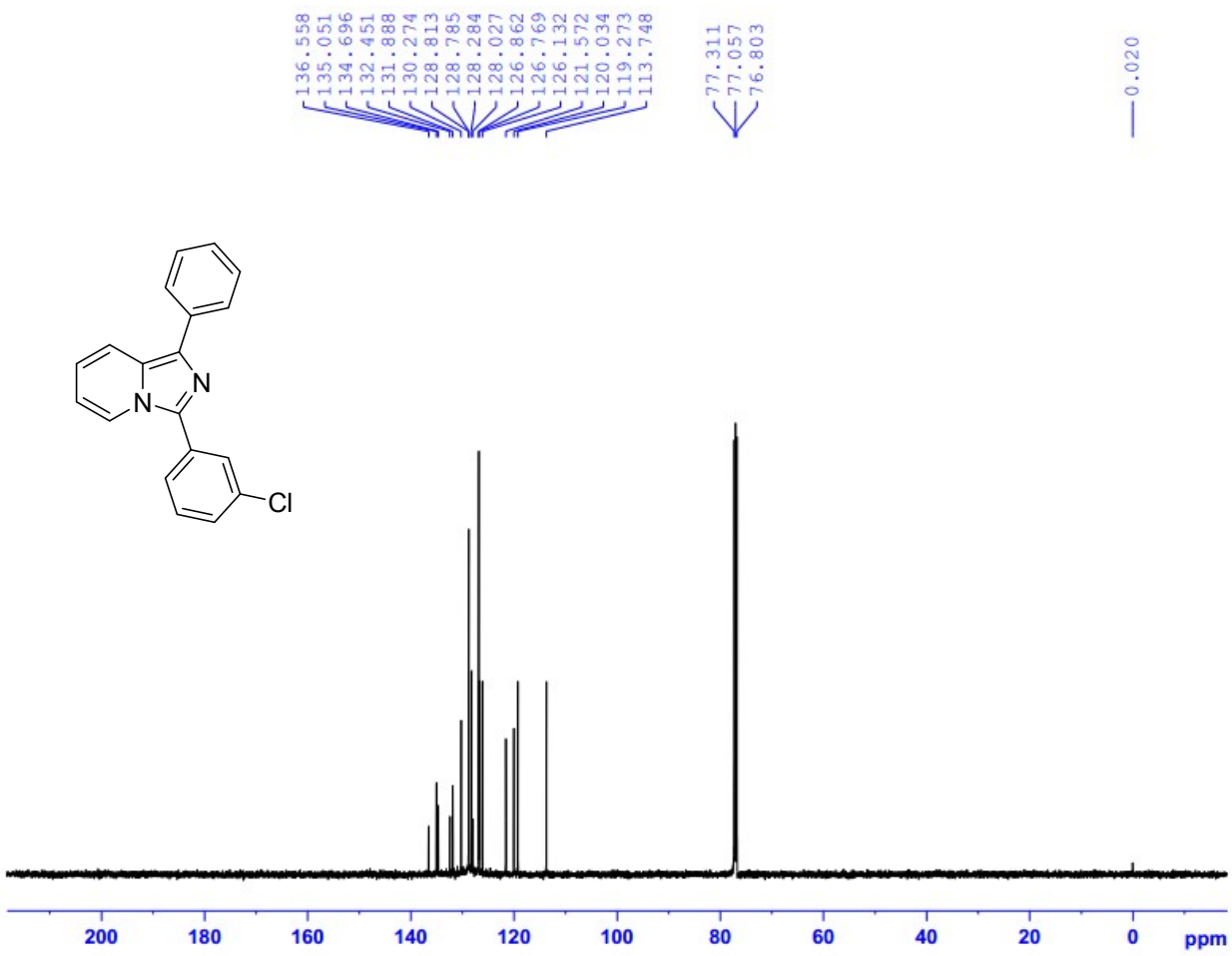

Fig. S14. ^{13}C-NMR spectra of 3-(3-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(3-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:2): yellow oil, 54% yield. This compound is known [1]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J*= 7.5 Hz, 1H), 7.92 (s, 1H), 7.9 (s, 1H), 7.85 - 7.82 (m, 2H), 7.72 - 7.7 (m, 1H), 7.48 - 7.39 (m, 4H), 7.32 - 7.25 (m, 1H), 6.81- 6.78 (m, 1H), 6.61 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.6, 135.05, 134.70, 132.45, 131.89, 130.27, 128.81, 128.79, 128.28, 128.03, 126.86, 126.77, 126.13, 121.57, 120.03, 119.27, 113.75.

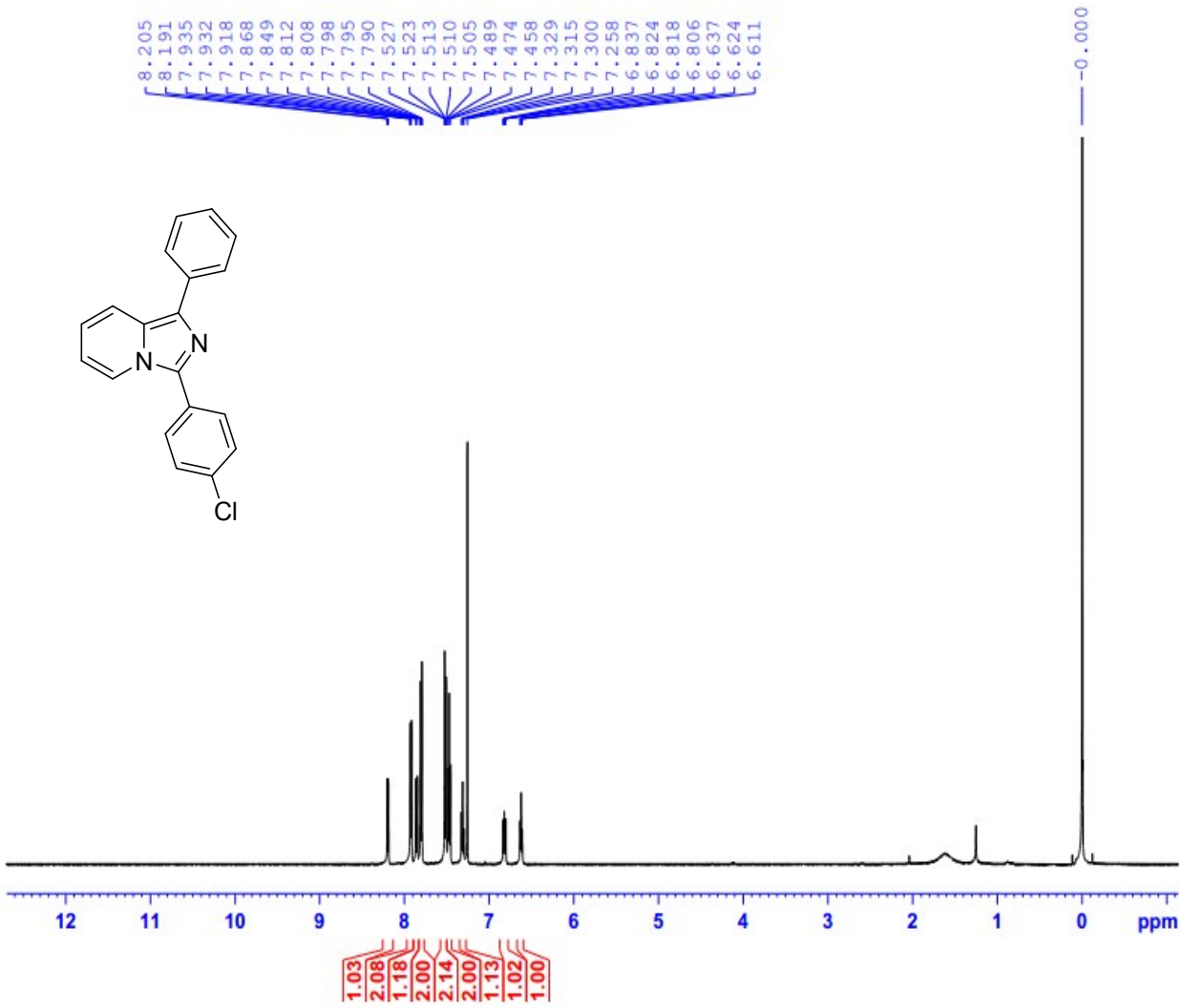

Fig. S15. ^{1}H-NMR spectra of 3-(4-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

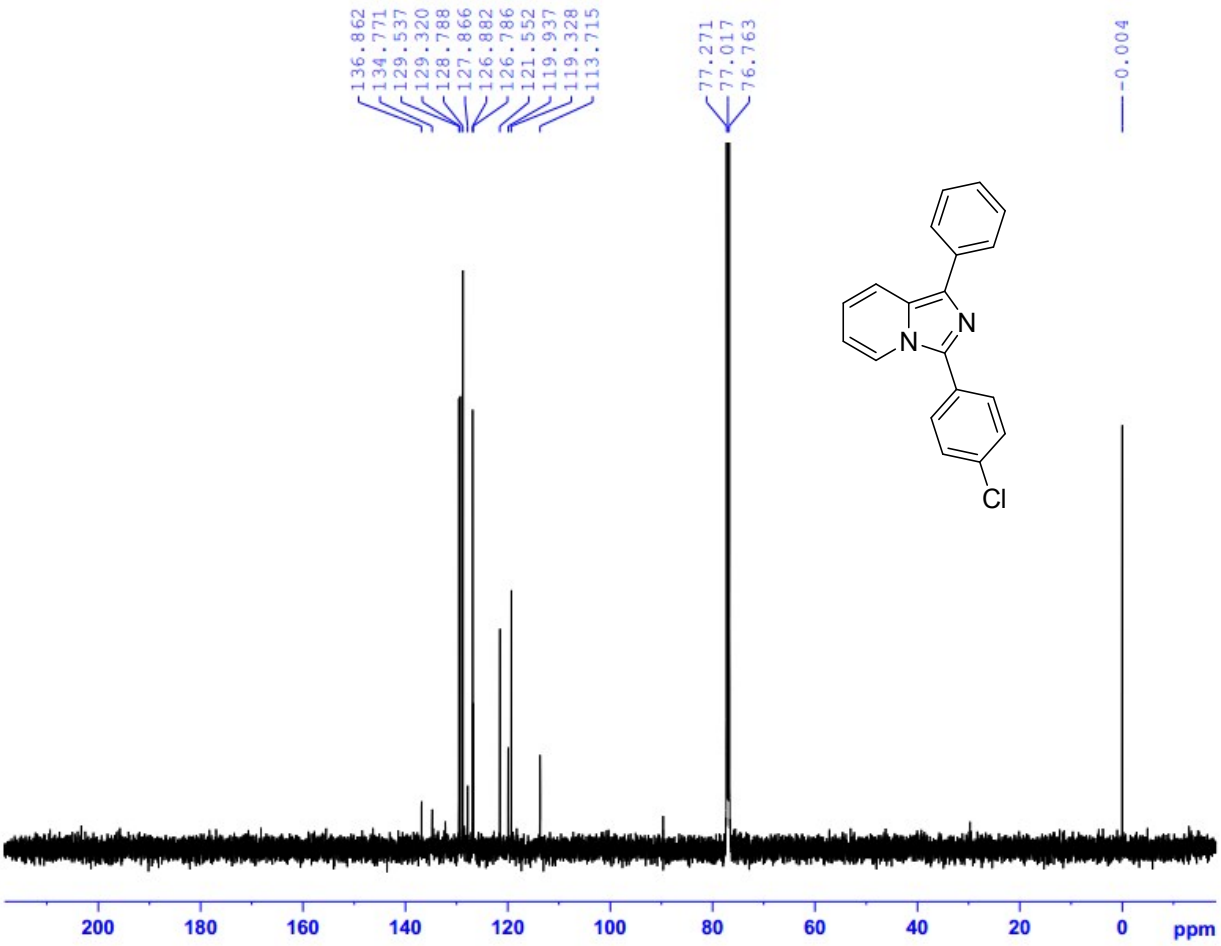

Fig. S16. ^{13}C-NMR spectra of 3-(4-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(4-chlorophenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:8): yellow solid, 53% yield. This compound is known [2] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J*= 7 Hz, 1H), 7.93 (s, 1H), 7.92 (s, 1H), 7.86 (d, *J*= 9.5 Hz, 1H), 7.81 – 7.79 (m, 2H), 7.53 - 7.45 (m, 4H), 7.33 - 7.26 (m, 1H), 6.84 - 6.81 (m, 1H), 6.62 (t, *J*= 6.5 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 136.86, 134.77, 129.54, 129.32, 128.79, 127.87, 126.88, 126.79, 121.55, 119.94, 119.33, 113.72.

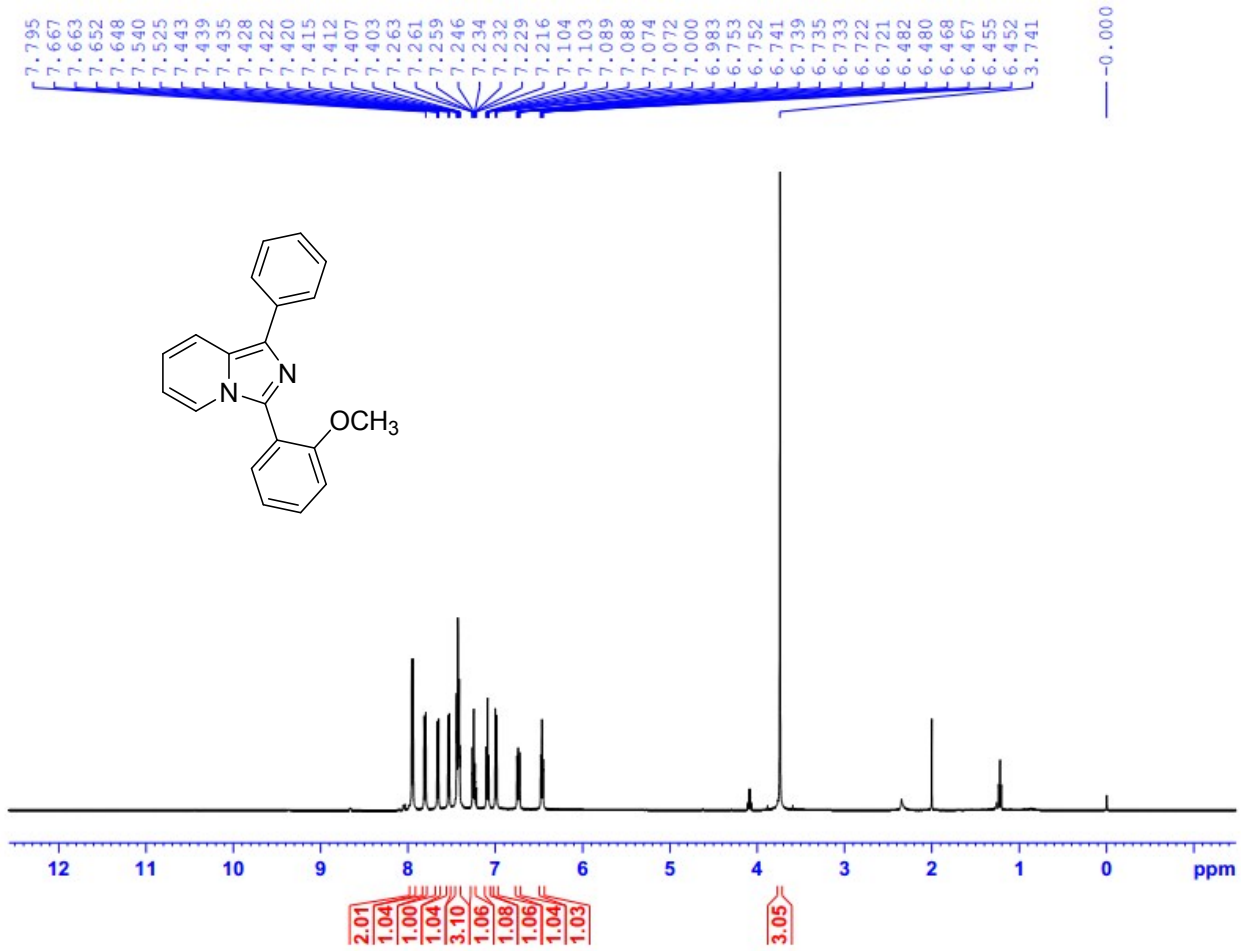

Fig. S17. [1]H-NMR spectra of 3-(2-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

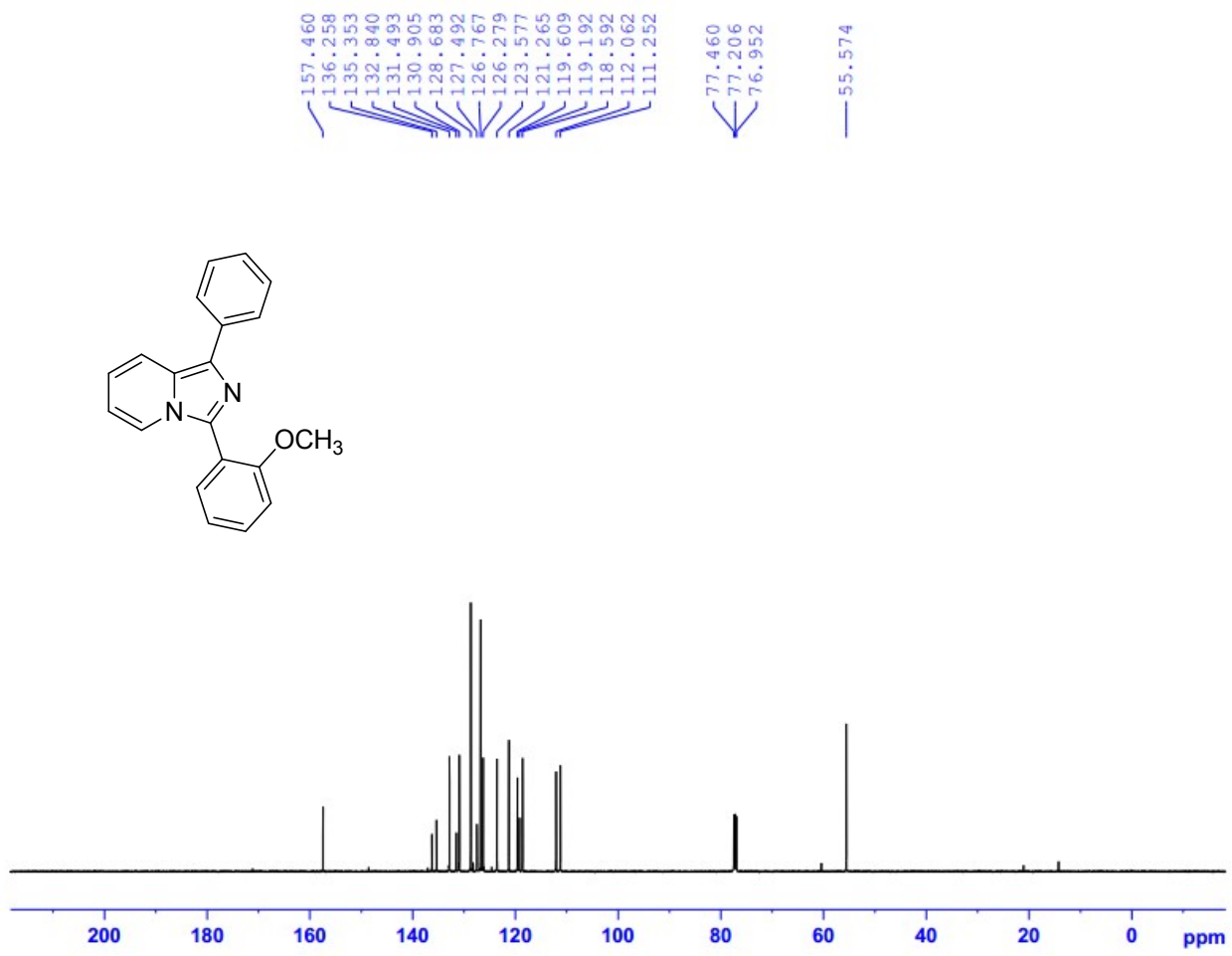

Fig. S18. ^{13}C-NMR spectra of 3-(2-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(2-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:14): yellow oil, 61% yield. This compound is known [3]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.94 (s, 1H), 7.80 (d, *J*= 9.5 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.53 (d, *J*= 8 Hz, 1H), 7.44 - 7.40 (m, 3H), 7.26 – 7.22 (m, 1H), 7.10 - 7.07 (m, 1H), 6.99 (d, *J*= 8.5 Hz, 1H), 6.75 – 6.72 (m, 1H), 6.48 – 6.45 (m, *J*= 7 Hz, 1H), 3.74 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 157.46, 136.26, 135.35, 132.84, 131.49, 130.91, 128.68, 127.49, 126.77, 126.28, 123.58, 121.27, 119.61, 119.19, 118.59, 112.06, 111.25, 55.57.

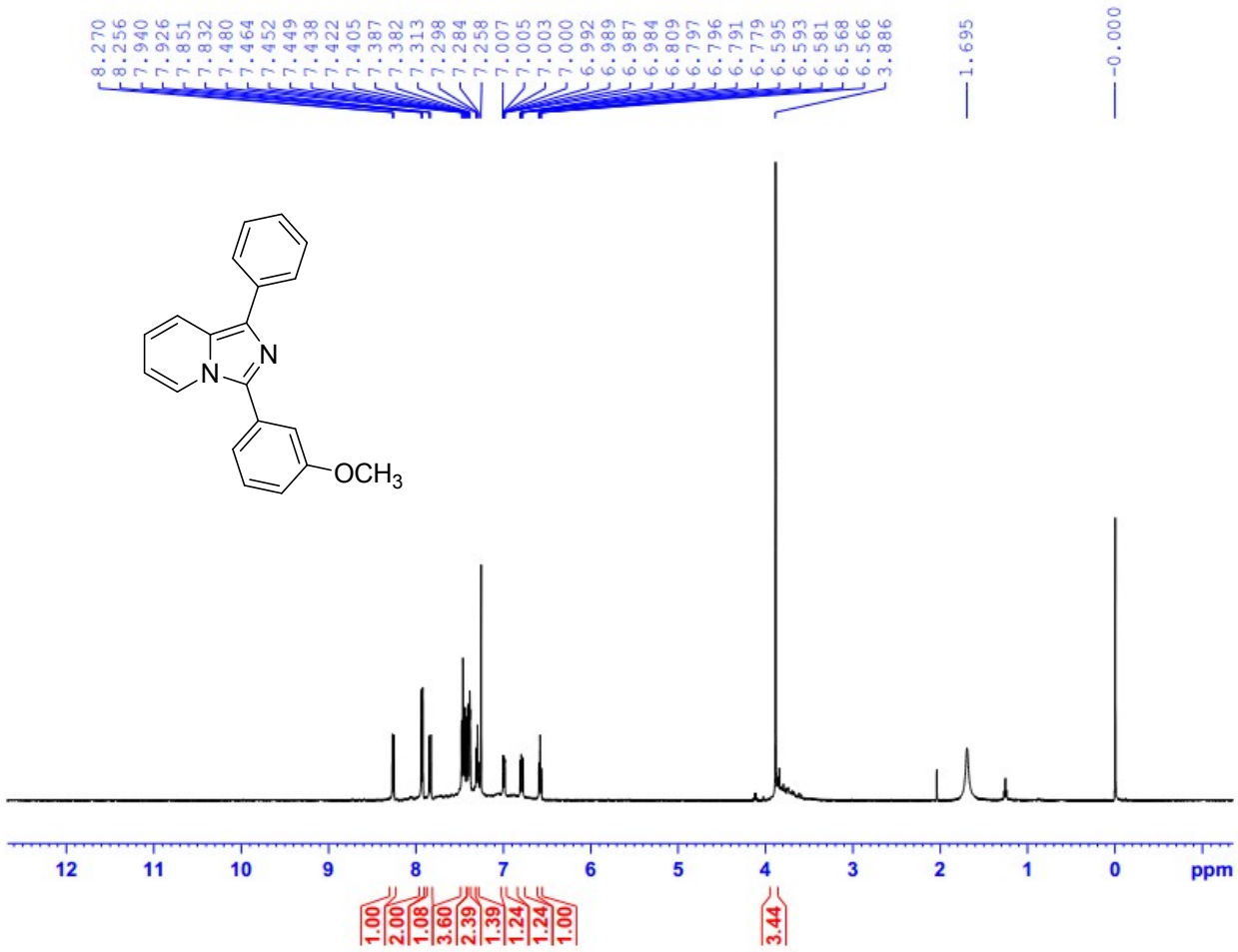

Fig. S19. [1]H-NMR spectra of 3-(3-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

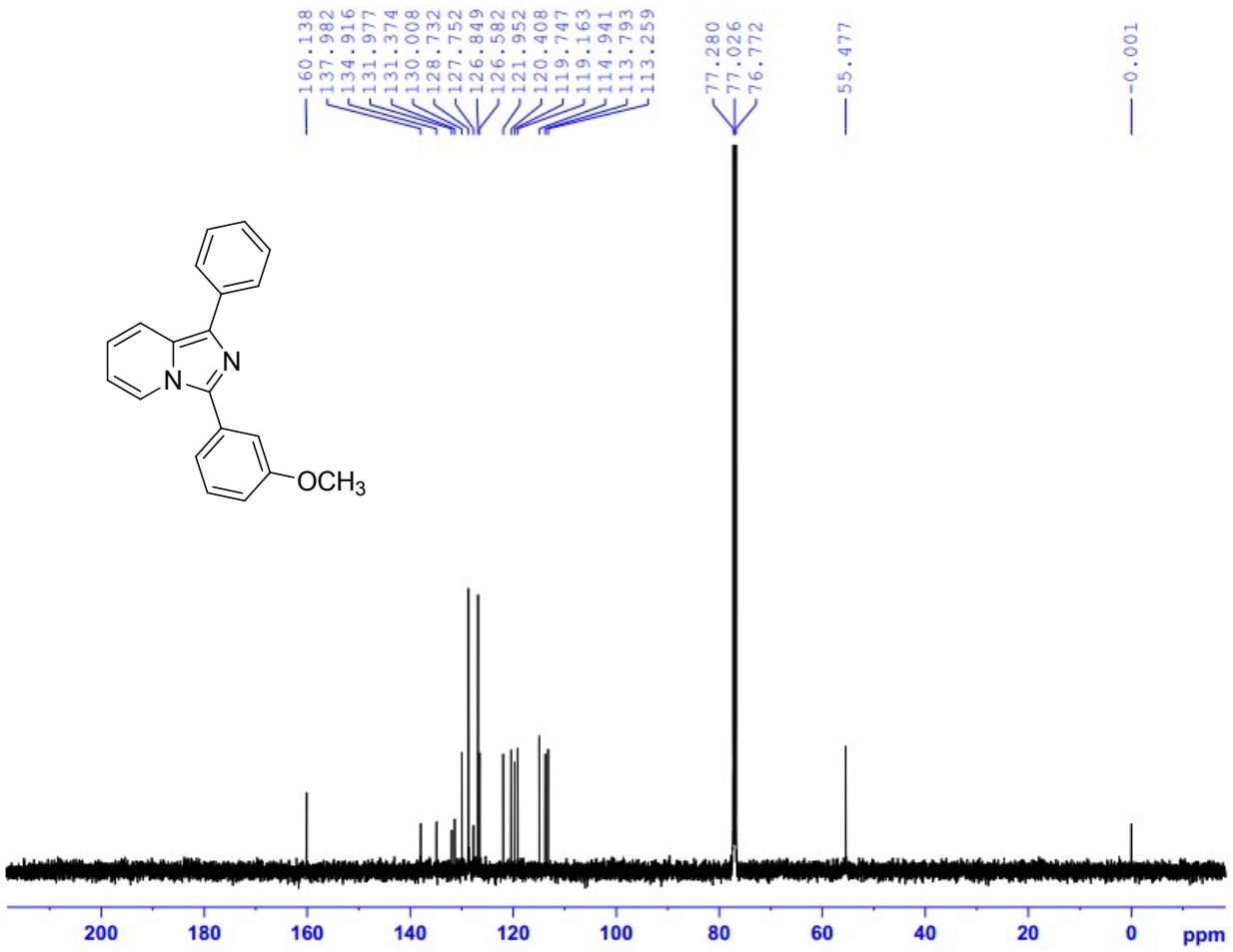

Fig. S20. ^{13}C-NMR spectra of 3-(3-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(3-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:2): yellow oil, 70% yield. This compound is known [3]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J*= 7 Hz, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 7.84 (d, *J*= 9.5 Hz, 1H), 7.48 - 7.38 (m, 5H), 7.31 - 7.26 (m, 1H), 7.01 - 6.98 (m, 1H), 6.81 - 6.78 (m, 1H), 6.60 - 6.57 (m, *J*= 7.3 Hz, 1H), 3.89 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 160.14, 137.98, 134.92, 131.98, 131.37, 130.01, 128.73, 127.75, 126.85, 126.58, 121.95, 120.41, 119.75, 119.16, 114.94, 113.79, 113.26, 55.48.

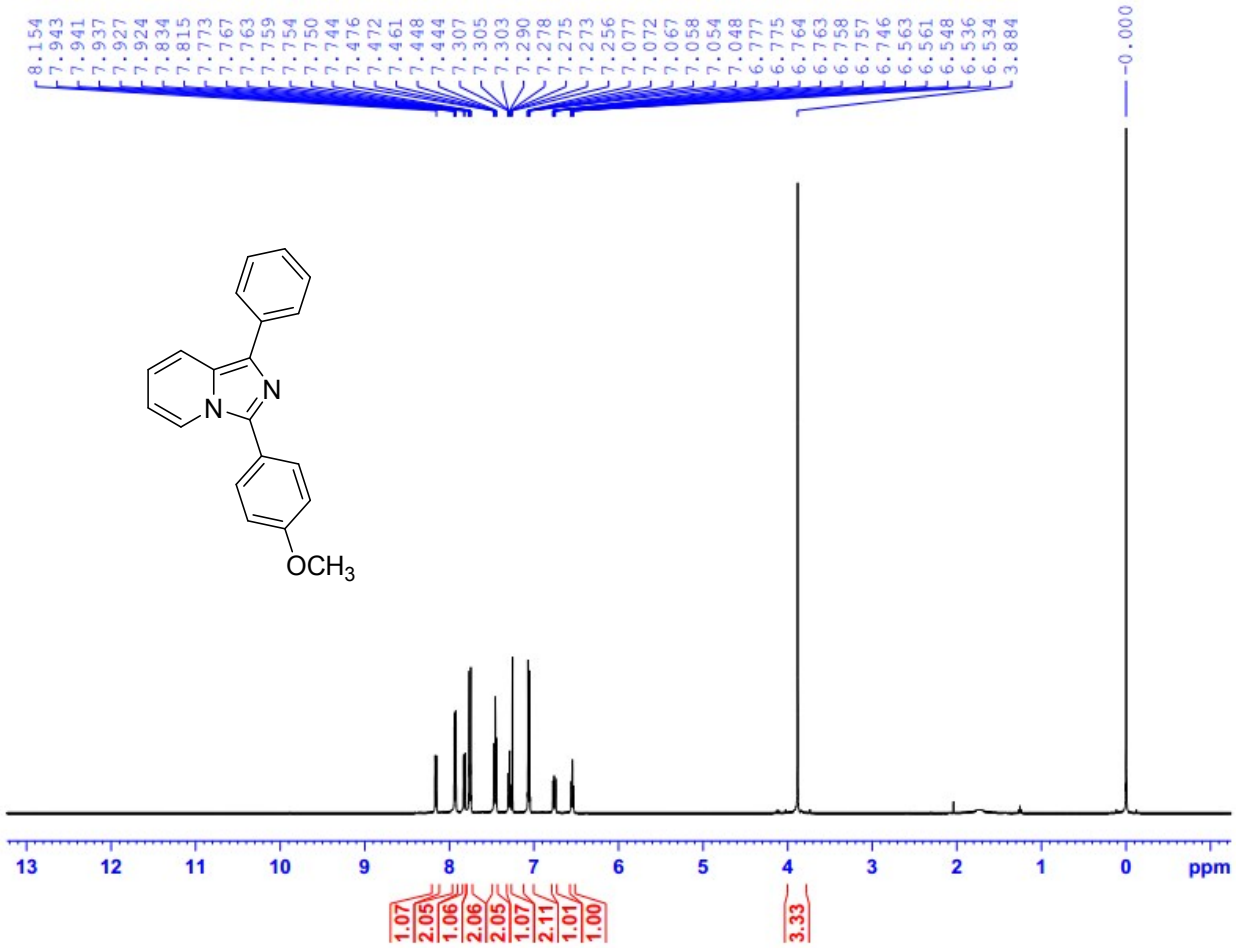

Fig. S21. ^{1}H-NMR spectra of 3-(4-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

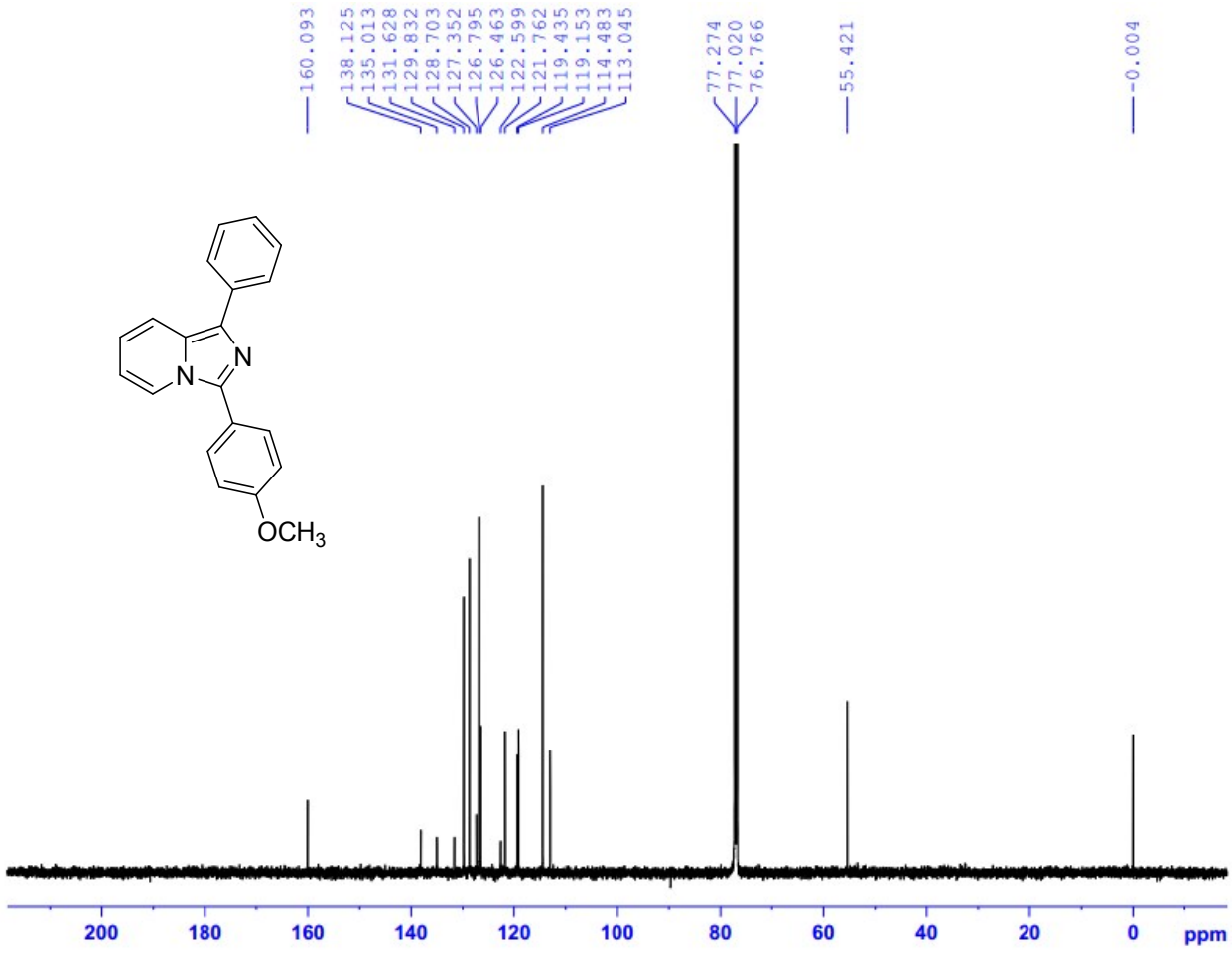

Fig. S22. ^{13}C-NMR spectra of 3-(4-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(4-methoxyphenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:1): yellow solid, 73% yield. This compound is known [4]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J*= 7.5 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.82 (d, *J*= 9.5 Hz, 1H), 7.77 - 7.74 (m, 2H), 7.48 - 7.44 (m, 2H), 7.31 - 7.26 (m, 1H), 7.07 – 7.05 (m, 2H), 6.78 - 6.75 (m, 1H), 6.56 - 6.53 (m, 1H), 3.88 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 160.09, 138.13, 135.01, 131.63, 129.83, 128.70, 127.35, 126.80, 126.46, 122.60, 121.76, 119.44, 119.15, 114.48, 113.05, 55.42.

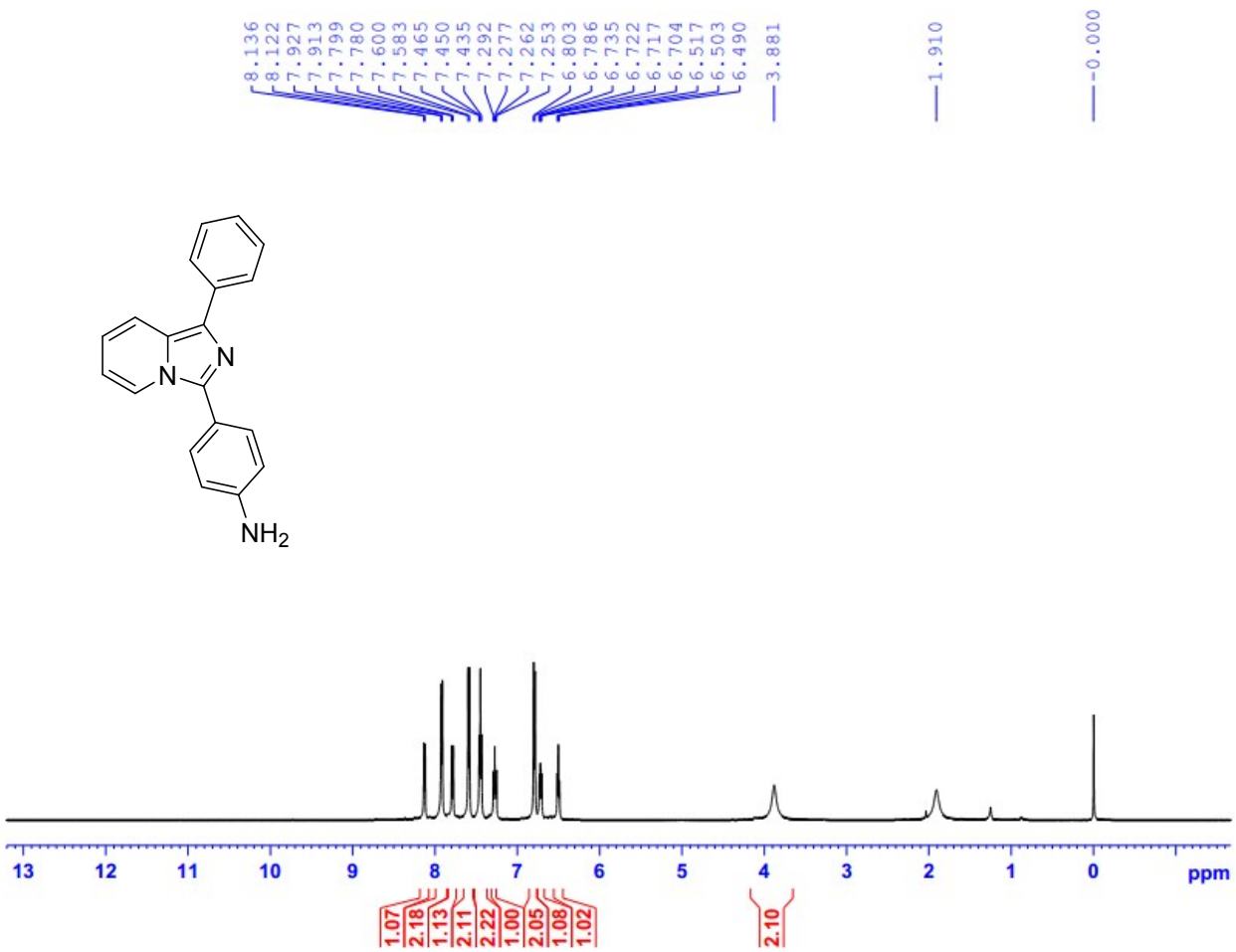

Fig. S23. ^{1}H-NMR spectra of 3-(4-aminophenyl)-1-phenylimidazo[1,5-a]pyridine.

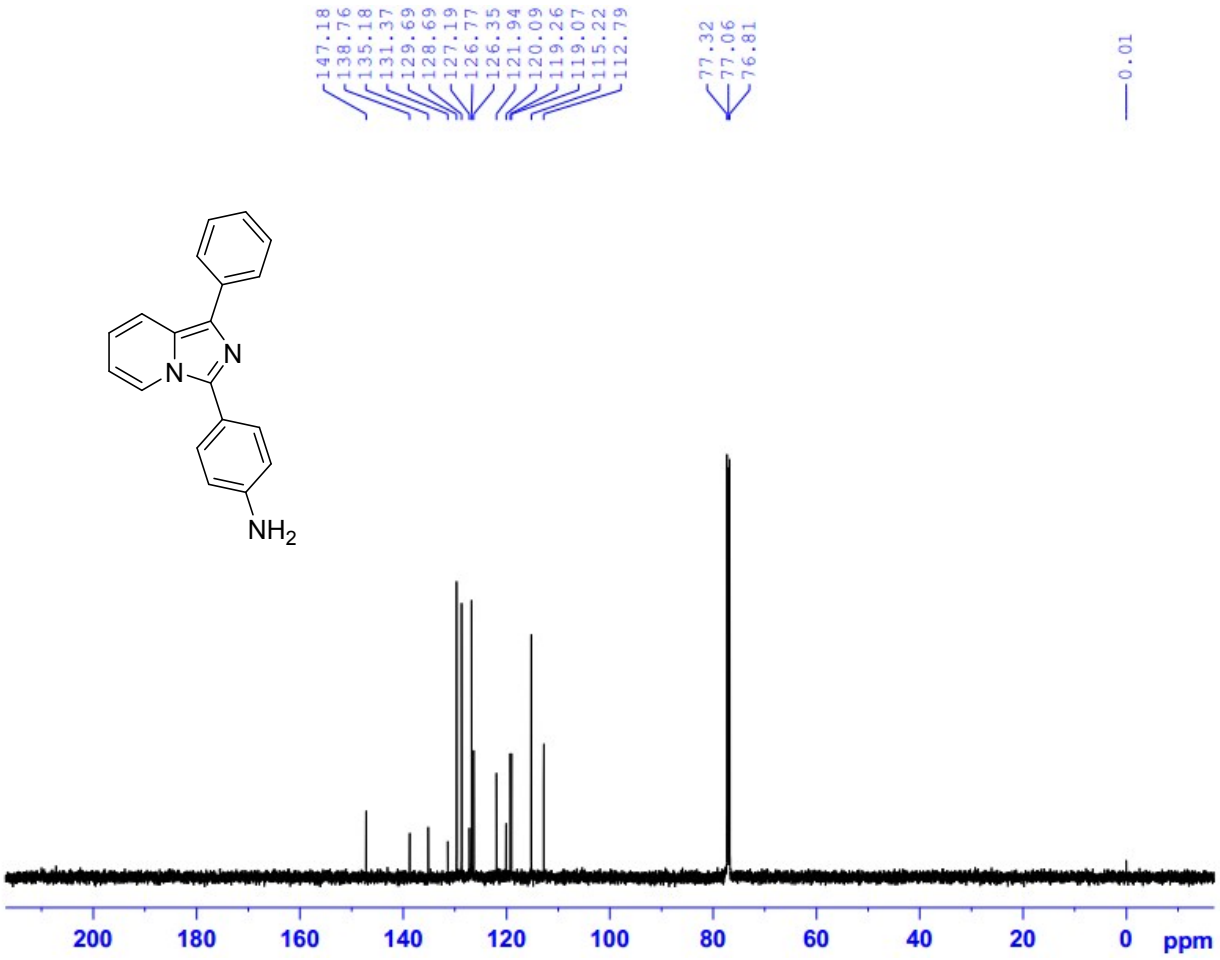

Fig. S24. ^{13}C-NMR spectra of 3-(4-aminophenyl)-1-phenylimidazo[1,5-a]pyridine.

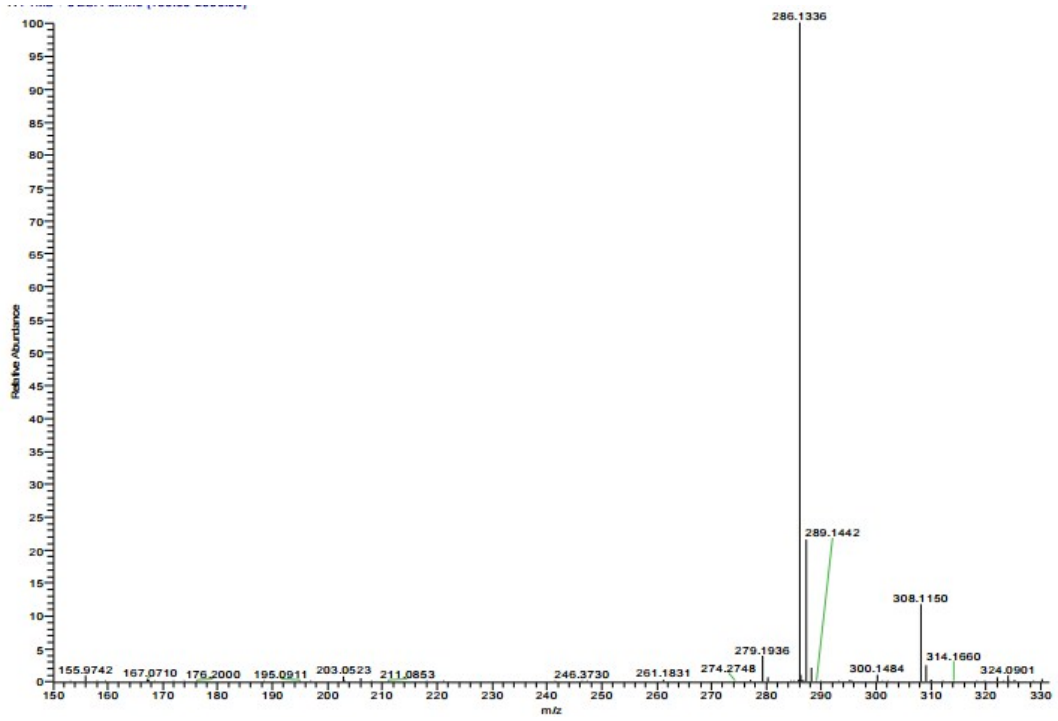

Fig. S25. HRMS (EIS+) of 3-(4-aminophenyl)-1-phenylimidazo[1,5-a]pyridine.

Characterization Data for 3-(4-aminophenyl)-1-phenylimidazo[1,5-a]pyridine

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:1): light orange solid, 67% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7 Hz, 1H), 7.92 (d, *J* = 7 Hz, 2H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.72 (dd, *J* = 9, 6.5 Hz, 1H), 6.50 (t, *J* = 6.8 Hz, 1H), 3.88 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 147.18, 138.76, 135.18, 131.37, 129.69, 128.69, 127.19, 126.77, 126.35, 121.94, 120.09, 119.26, 119.07, 115.22, 112.79. HRMS (EIS+): Calculated for $C_{19}H_{15}N_3$ $[M+H]^+$ 286.1344, Found 286.1336.

Table S1. Optimization of reaction conditions.

Entry	Temperature (°C)	Catalyst concentration (mol%)	Reactant molar ratio	Solvent	Yield (%)
1	RT	10	1:3	DMF	0
2	100	10	1:3	DMF	24
3	110	10	1:3	DMF	49
4	120	10	1:3	DMF	71
5	130	10	1:3	DMF	63
6	120	0	1:3	DMF	14
7	120	2.5	1:3	DMF	39
8	120	5	1:3	DMF	40
9	120	7.5	1:3	DMF	56
10	120	10	1:3	DMF	71
11	120	12.5	1:3	DMF	72
12	120	15	1:3	DMF	71
13	120	10	1:1	DMF	21
14	120	10	1:2	DMF	51
15	120	10	1:3	DMF	71
16	120	10	1:4	DMF	50
17	120	10	1:3	NMA	68
18	120	10	1:3	NMP	63
19	120	10	1:3	toluene	58

20	120	10	1:3	chlorobenzene	45
21	120	10	1:3	DMF	71
22	120	10	1:3	DMSO	60
23	120	10	1:3	*n*-butanol	61
24	120	10	1:3	*p*-xylene	37
25	120	10	1:3	benzonitrile	69
26	120	10	1:3	*tert*-butanol	44

Table S2. Different catalysts for the condensation-cyclization reaction [a].

Entry	Homogeneous catalyst	Heterogeneous catalyst	Yield (%)
1	$Cu(NO_3)_2$		40
2	$CuCl_2$		27
3	$CuSO_4$		16
4	$Cu(OAc)_2$		78
5	$Cu(acac)_2$		48
6	$CuBr_2$		30
7	CuBr		29
8	CuI		28
9	CuCl		36
10	$Co(OAc)_2$		22
11	$Zn(OAc)_2$		15
12	$Mn(OAc)_2$		13

13	$Ni(OAc)_2$		19
14	AgOAc		9
15	2,5-dihydroxyterephthalic acid		17
16		Cu(BDC)	37
17		$Cu_2(BDC)_2(DABCO)$	33
18		$Cu_3(BTC)_2$	22
19		$Cu_2(BPDC)_2(BPY)$	33
20		Cu(OBA)	48
21		$Cu_2(OBA)_2(BPY)$	46
22		$Cu(INA)_2$	56
23		Cu-MOF-74	71

[a]: The reaction was then carried out in DMF under air at 120 ^oC for 8 h, using 3 equivalents of benzylamine, in the presence of 10 mol% catalyst, at 2-benzoyl pyridine concentration of 0.2 M.

References

1. M. Li, Y. Xie, Y. Ye, Y. Zou, H. Jiang, W. Zeng, Org. Lett. 16 (2014) 6232-6235.
2. H. Wang, W. Xu, Z. Wang, L. Yu, K. Xu, J. Org. Chem. 80 (2015) 2431-2435
3. A. Joshi, D. C. Mohan, S. Adimurthy, Org. Lett., 18 (2016), 464–467.
4. J.M. Crawforth, M. Paoletti, Tetrahedron Lett. 50 (2009) 4916-4918.