RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advance

RSCPublishing

ARTICLE

An Efficient and Metal Free Synthesis of Benzylpyridines Using HI through Deoxygenation Reaction

Selvaraj Chandrasekar,[a] Iyyanar Karthikeyan[a] and Govidasamy Sekar*[a]

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

An efficient and practical method for the synthesis of benzylpyridine derivatives has been developed using *aqueous* hydroiodic acid in acetic acid. This method is also successfully applied for the synthesis of 2,6-disubstituted pyridine derivatives under the same reaction conditions. Using readily available *aqueous* hydroiodic acid as reducing agent made this process economical. When the aryl group of secondary alcohol is replaced by alkyl group, the reaction gives exclusively acetoxylation instead of deoxygenation reaction.

Introduction

Functionalization of pyridine and related heterocycles are very important process in organic chemistry due to their biological properties and applications in material science.[1] 2-Substituted pyridine derivatives are frequently found in several natural products and play an important role in the field of medicinal chemistry.[2] For example, 2-benzylpyridine and their derivatives act as dopamine receptor antagonists.[3] 4-Benzylpyridine derivatives are widely used as selective *N*-methyl-D-aspartate (NMDA) antagonists,[4] and they have shown tendency to act as central nervous system receptors such as $5HT_{1A}$ or $5HT_2$.[5] Particularly, methylene linked biaryls and aryl(di)azinyl methanes are medicinally important compounds and methylene linkage present in these compounds can lead to the unique binding properties (Figure 1).[6]

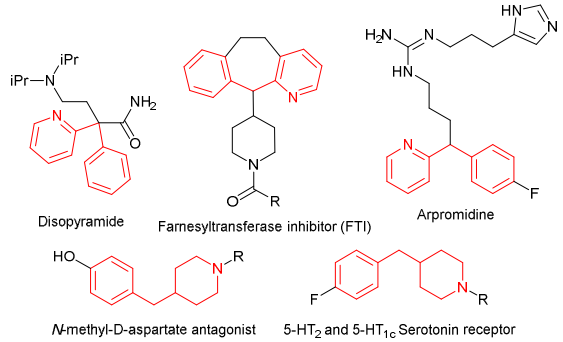
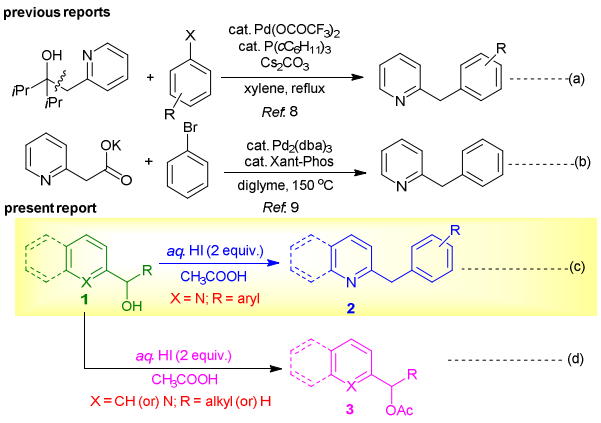


Figure 1. Some of the representative example for benzylpyridine containing biologically important compounds.

By owing the important of benzylpyridine derivatives, various methods are available[7] for the synthesis of these molecules using transition metal coupling reactions. In 2007, Oshima *et al.* reported palladium catalyzed 2-pyridylmethyl transfer to aryl halides for the synthesis of benzylpyridine derivatives (Scheme 1a).[8] Later, Liu *et al*. demonstrated decarboxylative coupling reactions of 2-(2-azaaryl)acetate with aryl halide using palladium catalyst to synthesize benzylpyridine derivatives (Scheme 1b).[9] In addition, benzylpyridine derivatives have been synthesized through Friedel-Crafts acylation,[10] catalytic carbonylation[11] followed by reduction of 2-pyridylaryl carbonyl compound with hydrazine.[4,10]



Scheme 1. Synthesis of 2-benzylpyridines.

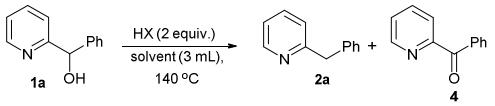
As part of our ongoing research towards developing metal free organic transformations,[12] herein we report metal free synthesis of

benzylpyridine derivatives **2** from readily available secondary alcohols **1** through HI mediated deoxygenation reaction[13] (Scheme 1c). The same reaction yields corresponding acetate **3** as product through acetoxylation when the secondary alcohol **1** is aryl(alkyl)methanol (Scheme 1d).

Results and discussion

Initially, we have chosen 2-pyridyl(phenyl)methanol **1a** as model substrate for this deoxygenation reaction and **1a** was reacted with 2 equivalents of HI in acetic acid at 140 ^{o}C (Table 1, entry 1). This reaction took place smoothly and gave 92% isolated yield of 2-benzylpyridine **2a** in 10 hours. To increase the efficiency of this deoxygenation reaction, other acids such as formic acid and pivalic acid were screened as solvent. In pivalic acid the reaction gave only oxidized product **4** (entry 2). In formic acid, the reaction took place but yield of **2a** got reduced to 72% after 14 hours (entry 3).

Table 1. Optimization of HI mediated deoxygenation reaction



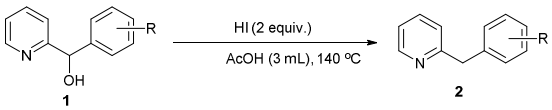
entry	HX	solvent	time (h)	yield (%)[a]	
				2a	**4**
1	**HI**	**CH_3COOH**	**10**	**92**	-
2	HI	pivalic acid	16	trace	63[b]
3	HI	HCOOH	14	72	-
4	HI	toluene	32	trace	-
5	HI	xylene	24	28	-
6	HI	H_2O	28	trace	-
7	HI	CH_3CN	20	62	-
8	HI	DMF	20	68	-
9	HI	1,4-dioxane	18	72	-
10	HI	DMSO	16	68	-
11	HI	CH_3COOH	18	38	-[c]
12	HI	CH_3COOH	18	61	-[d]
13	HBr	CH_3COOH	10	27	-
14	HCl	CH_3COOH	25	-	-
15	HI	CH_3COOH	10	70	-[e]

[a] Isolated yield. [b] Reference No.:14. [c] 1 Equiv. of HI was used. [d] 3 Equiv. of HI was used. [e] 120 ^{o}C.

To improve the efficiency of this deoxygenation reaction, the reaction was carried out in various solvents like toluene, xylene, water, acetonitrile, dimethylformamide, 1,4-dioxane and dimethyl sulfoxide. Unfortunately, all the solvents gave less yield than acetic acid. Decreasing the amount of hydroiodic acid from 2 equivalents to 1 equivalent, the yield of the reaction also decreased from 92% to 38% (entry 11). At the same time, when the reaction was carried out with 3 equivalents of HI, the reaction gave only 61% yield after 18 hours (entry 12). Instead of hydroiodic acid, when the reaction was carried out with HBr, yield of **2a** got reduced to 27% (entry 13). Then the same reaction with hydrochloric acid gave inseparable complex reaction mixture (entry 14). Reducing the reaction temperature to 120 ^{o}C, reduced the yield of **2a** to 70% (entry 15).

With this optimized conditions in our hand, the substrate scope was explored for this HI mediated deoxygenated reaction and the results are summarized in Table 2. All the substrates containing substitution at the pyridine ring as well as aryl ring were well tolerated under the optimized reaction conditions and gave good to excellent yields. *Para*-vinyl, *para*-thiomethyl and *para*-chloro substituted secondary alcohols undergone smoothly for the deoxygenation reaction and gave excellent yields (entries 2-4).

Table 2. Substrate scope for HI mediated deoxygenation reaction

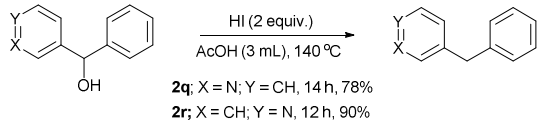


entry	substrate	product	time (h)	yield (%)[a]
1	**1a**	**2a**	8	92
2	**1b**	**2b**	8	85
3	**1c**	**2c**	10	80
4	**1d**	**2d**	14	72
5	**1e**	**2e**	6	86
6	**1f**	**2f**	4	95
7	**1g**	**2g**	6	95
8	**1h**	**2h**	8	72
9	**1i**	**2i**	6	88
10	**1j**	**2j**	7	86
11	**1k**	**2k**	7	83
12	**1l**	**2l**	25	75
13	**1m**	**2m**	18	66
14	**1n**	**2n**	6	92
15	**1o**	**2o**	22	43
16	**1p**	**2p**	20	53

[a] Isolated yield.

Also, substitution at the 6th position of heteroaryl ring such as methyl and bromo groups were well tolerated and gave excellent yield (entries 6 and 7). Sterically hindered substrates such as **1h** and **1i** also gave the expected products in good yields (entries 8 and 9). Interestingly, other heterocycles such as pyrimidine and quinoline containing substrates were successfully converted to corresponding deoxygenated product under the optimized reaction conditions (entries 15 and 16).

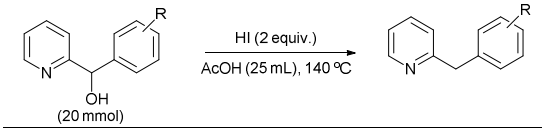
In the same optimized reaction conditions, the analogue alcohol of **1a** such as 3-phenylpyridylmethanol **1q** and 4-phenylpyridylmethanol **1r** were subjected to deoxygenation reactions. Both of these reactions underwent smoothly for deoxygenation reaction and gave corresponding benzylpyridines **2q** and **2r** with excellent yield (Scheme 2). This result clearly shows that changing the nitrogen position in the pyridine ring does not change the course of the deoxygenation reaction.



Scheme 2. HI mediated deoxygenation reaction of 3 and 4-phenylpyridylmethanols.

To find out the large scale synthetic utility of this deoxygenation reaction, we have chosen the substrates **1i**, **1j** and **1n** for this deoxygenation reaction and the results are summarized in Table 3. All the substrates were subjected for this deoxygenation reaction under optimized reaction condition in 20 mmol scale (~5 grams). It is important to mention that all these large scale reactions gave corresponding 2-benzylpyridine derivatives in good to excellent yield (Table 3).

Table 3. Large scale synthesis of 2-benzylpyridines



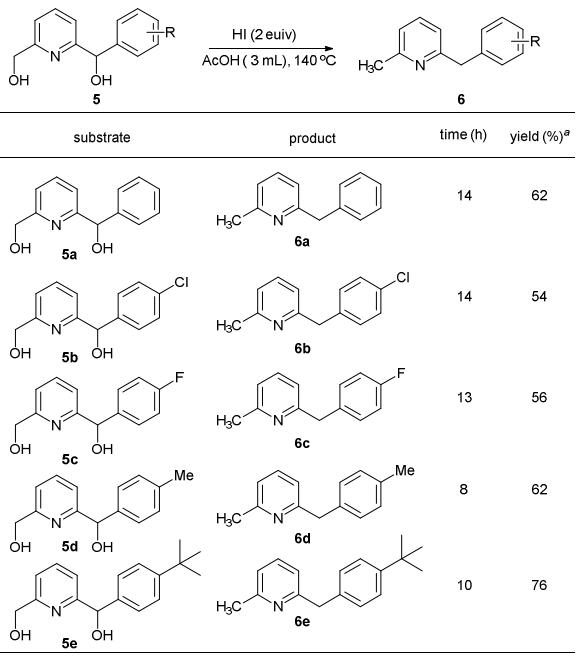
entry	substrate	product	time (h)	yield (%)[a]
1	**1i**	**2i**	12	82
2	**1j**	**2j**	10	85
3	**1n**	**2n**	10	94

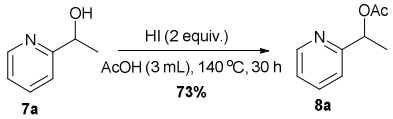
[a] Isolated yield.

To test the effect of this deoxygenation reaction on the substrate having both primary and secondary alcohol group, diol **5a** was prepared[14] and subjected for this deoxygenated reaction (Table 4, entry 1). It is our delight to observe that both the alcohol groups of **5a** got deoxygenated and gave the product **6a** in 62% isolated yield after 14 hours. Similar kind of substrates containing electron withdrawing and electron donating groups were prepared and subjected under optimized reaction conditions and all the substrates gave the di-deoxygenated products as shown in (Table 4).

When the 2-pyridylethanol **7a** was subjected under this deoxygenative reaction conditions, instead of expected deoxygenated product, acetylated product **8a** was observed in 73% isolated yield after 30 hours (Scheme 3). This result clearly shows that second aryl group is necessary for deoxygenation reaction. To find out the synthetic utility of this acetoxylation reaction, various alkyl substituted substrates were subjected for this transformation and the results are summarized in Table 5. Both aryl and heteroaryl secondary alcohols underwent for this acetoxylation reaction in the presence of hydroiodic acid and gave excellent yield. Substrates containing electron withdrawing groups as well as electron donating groups were successfully converted to corresponding acetylated product in good to excellent yield (Table 5).

Table 4. HI mediated deoxygenative reaction of dihydroxy molecules

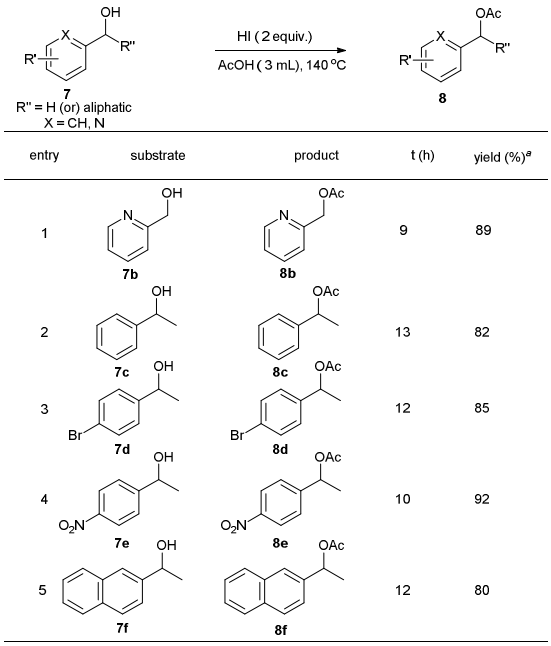


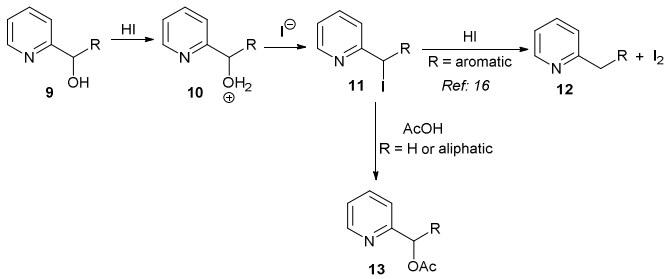


Scheme 3. Acetoxylation reaction of (heteroaryl)alkylmethanol **7a**.

The plausible mechanism for these deoxygenation and acetoxylation reaction can be explained as shown in Scheme 4. Initially, the secondary alcohol group of **9** may be protonated to give the intermediate **10** where the nucleophilic attack can take place by iodide anion to form secondary iodo compound **11**. This iodo compound in the presence of HI at high temperature may form the deoxygenated product **12** exclusively.[15] If the R group is hydrogen or aliphatic group, exclusively it gives acetylated product **13** where as if the R group is aromatic, then the reaction gives exclusively deoxygenated product **12**. In case of deoxygenation, when the starting material is having two aryl groups, the iodo compound **11** may be giving highly stable dibenzylic radical which may be quenched by hydrogen radical generated by HI at higher temperature in the reaction medium.[15,16] On the other hand, when the starting material is arylmethanol or arylalkymethanol, it may give acetylated product **13** via simple S_N^2 displacement by acetic acid due to mono benzylic nature of substrate may not generate the stable radical for deoxygenation. Alternatively, acetoxylation may happen in the compound **10** by S_N^2 displacement by acetic acid due to its monobenzylic nature of the alcohol starting material.

Table 5. Substrate scope for HI mediated acetoxylation





Scheme 4. Plausible reaction mechanism for HI mediated deoxygenation and acetoxylation reaction

Conclusions

In conclusion, an efficient and practical method for the synthesis of 2, 3 and 4-benzylpyridine derivatives have been developed using *aqueous* hydroiodic acid in acetic acid. This method also successfully applied for the synthesis of 2,6-disubstituted pyridine derivatives under the same reaction conditions. Using readily available *aqueous* hydroiodic acid as reducing agent made this process atom and cost economical. When the aryl group of secondary alcohol is replaced by alkyl group, the reaction gives exclusively acetoxylation instead of deoxygenation.

Experimental Section

General consideration:

Hydroiodic acid (~57% *aqueous* solution) was purchased from Spectrochem and acetic acid (AR grade) is from RANKEM chemical company. Solvents used for extraction and purification were technical grade and distilled before use. Reactions were monitored by thin layer chromatography on pre-coated aluminium-packed plates (0.25 mm, Merck Kieselgel 60 with fluorescent indicator UV254) and visualized by fluorescence quenching. Column chromatography was performed with silica gel (particle size 100-120 mesh, RANKEM). Infrared spectra were recorded on a FTIR 4000 Series Spectrometer using dry KBr pellet. The wave numbers of recorded IR signals are quoted in cm^{-1}. Silica gel for column chromatography (particle size 100-200 mesh) was purchased from SRL India. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. ^1H NMR spectra were reported relative to Me_4Si (δ 0.0 ppm) or residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16 ppm). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. ^1H and ^{13}C NMR and HRMS Spectral data have been included for all compounds.

General experimental procedure for HI mediated deoxygenation reaction:

In a pressure tube hydroiodic acid (~57% *aqueous* solution) (155 µl, 2 mmol) and phenyl-2-pyridylmethanol **1a** (185 mg, 1mmol) in 3 mL of acetic acid was stirred at 140 °C. The reaction was monitored by TLC. After 10 hours, the reaction mixture was diluted with water and neutralized by *aqueous* $NaHCO_3$ solution. The resulting aqueous layer was extracted with ethyl acetate (3x5 mL) and the combined organic layer was washed with saturated *aqueous* sodium thiosulfate solution to remove the iodine generated during the reaction. Then the organic layer was dried over anhydrous Na_2SO_4 and evaporated in vaccuo and the resulting residue was purified by silica gel column chromatography (eluents: hexanes-ethylacetate) to give the pure 2-benzylpyridine **2a** (170 mg, yield 92%).

2-Benzylpyridine (2a): Pale yellow colour oil; R_f 0.35; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, J = 5.2 Hz, 1H), 7.59 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.28-7.35 (m, 4H), 7.22-7.26 (m, 1H), 7.12-7.15 (m, 2H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 149.4, 139.6, 136.7, 129.2, 128.7, 126.5, 123.3, 123.3, 121.4, 44.8; IR (neat) 3060, 3026, 2920, 1661, 1589, 1472, 1433 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{12}N$: 170.0970; found: 170.0963.

2-(4-Vinylbenzyl)pyridine (2b): Colourless oil; R_f 0.42; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.8 Hz, 1H), 7.58 (td, J = 1.6 Hz, J = 7.8 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 8 Hz, 2H), 7.12 (t, J = 4.8 Hz, 2H), 6.69 (q, J = 6.4 Hz, 1H), 5.7 (dd, J = 0.8 Hz, J = 17.6 Hz, 1H), 5.20 (dd, J = 0.4 Hz J = 11Hz, 1H), 4.16(s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 149.2, 139.1, 136.9, 136.7, 136.0, 129.4, 126.6, 123.3, 121.4, 113.5, 44.4; IR (neat) 3055, 1916, 1701, 1591, 900, 622 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{14}N$: 196.1126; found: 196.1117.

2-(4-Methylthio)benzyl)pyridine (2c): Green colour oil; R_f 0.29; (hexanes : ethyl acetate, 80:20 v/v): ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.58 (td, J = 1.6 Hz, J = 7.6Hz, 1H), 7.17-7.22 (m, 4H), 7.10 (t, J = 5.5 Hz, 2H), 4.12 (s, 2H), 2.44 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 149.2, 136.9, 136.5, 136.4, 129.7, 127.3, 123.3, 121.5, 44.0, 16.2; IR (neat) 3051, 1904, 1590, 1266, 737 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{14}NS$, 216.0847: found: 216.0855.

2- (4-Chlorobenzyl)pyridine (2d): Pale yellow oil; R_f 0.54; (hexanes : ethyl acetate, 70:30 v/v): ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.4 Hz, 1H), 7.58 (td, J =1.6 Hz, J =7.6 Hz, 1H), 7.24-7.27 (m, 2H), 7.19 (d, J =7.6 Hz, 2H), 7.08-7.13 (m, 2H), 4.11(s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 149.6, 138.1, 136.8, 132.4, 130.5, 128.8, 123.2, 121.6, 44.0; IR (neat) 3055, 3011, 1901, 1663, 1588, 848, 799 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{11}NCl$: 204.0580; found: 204.0589.

2-(4-Methylbenzyl)pyridine (2e): Pale yellow oil; R_f 0.45; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.4 Hz, 1H) 7.57 (td, J = 1.6 Hz, J = 7.6Hz, 1H), 7.09-7.17 (m, 6H), 4.13 (s, 2H), 2.32 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 149.1, 136.9, 136.4, 136.0, 129.4, 129.1, 123.3, 121.4, 44.1, 21.1; IR (neat) 3010, 2923, 1905, 1587, 789, 752 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}N$: 184.1126; found: 184.1127.

2-Benzyl-6-methylpyridine (2f): Pale yellow oil; R_f 0.48; (hexanes : ethyl acetate, 80:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 7.6 Hz, 1H), 7.22-7.24 (m, 1H), 7.18-7.21 (m, 3H), 7.13 (m, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 4.07 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 157.9, 139.6, 137.0, 129.3, 128.7, 126.5, 121.0, 120.3, 44.5, 24.4; IR (neat) 3027, 2923, 1962, 1714, 1585, 773, 704 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}N$: 184.1126; found: 184.1117.

2-Benzyl-6-bromopyridine (2g): Green oil; R_f 0.48; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8 Hz, 1H), 7.20-7.26 (m, 2H), 7.16 (t, J = 8.4 Hz, 3H), 7.09 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H) 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 138.7, 138.0, 132.5, 129.3, 128.8, 126.8, 122.3, 117.7, 44.4; IR (neat) 2918, 1666, 1553, 1424, 767, 737 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}$ BrN: 248.0069; found: 248.0073.

2-(Naphthalen-1-ylmethyl)pyridinine (2h): Pale green oil; R_f 0.43; (hexanes : ethyl acetate, 75:25 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dq, J = 0.8, Hz J = 5.2 Hz, 1H), 7.90-8.8 (m, 1H), 7.83-7.88 (m, 1H), 7.79 (d, J = 8 Hz, 1H), 7.39–7.50 (m, 5H), 7.06-7.12 (m ,1H), 6.96 (d, J = 8 Hz, 1H), 4.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 149.2, 136.7, 135.4, 134.1, 132.3, 128.8, 127.8, 127.6, 126.2, 125.8, 125.7, 124.7 123.0, 121.3, 42.3; IR (neat) 3053, 1941, 1587, 1432, 781 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{12}N$: 220.1121; found: 220.1122.

2-(2-Methylbenzyl)pyridine (2i): Pale yellow oil; R_f 0.45; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dq, J = 0.8Hz, J = 5 Hz, 1H), 7.53 (td, J = 2 Hz, J = 7.6 Hz, 1H), 7.18 (s, 4H), 7.08-7.11 (m, 1H), 6.96 (d, J= *7.6* Hz 1H), 4.19 (s, 2H) 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.3, 137.6, 136.9, 136.5, 130.5, 130.3, 126.8, 126.2, 122.8, 121.2, 42.5, 19.8 ; IR (neat) 3017, 2960, 1586, 1435, 743 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}N$: 184.1126; found: 184.1132.

2-**(4-Tert-butyl)benzyl)pridine (2j):** Green oil; R_f 0.54; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dq, J = 0.8 Hz, J = 4.8 Hz, 1H), 7.46 (td, J = 2 Hz, J = 7.6 Hz, 1H), 7.23 (td, J = 2 Hz, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 4.03 (s, 2H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 149.3, 149.2, 136.7, 136.5, 128.8, 125.6, 123.3, 121.3, 44.2, 34.5, 31.5; IR (neat) 2958, 1590, 1432, 755, 605, 545 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{20}N$: 226.1590; found: 226.1586.

2-(3-Methylbenzyl)pyridine (2k): Pale yellow oil; R_f 0.45; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dq, J = 0.8 Hz, J = 5 Hz, 1H), 7.53 (td, J = 2 Hz, J = 7.6Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.03-7.12 (m, 5H), 4.13 (s, 2H) , 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 149.3, 139.4, 138.3, 136.7, 130.0, 128.6, 127.2, 126.2, 123.2, 121.3, 44.6, 21.5 ; IR (neat) 3018, 2920, 1711, 1664, 1590, 756, 701 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}N$: 184.1126; found: 184.1131.

2-(3-(Trifloromethyl)benzyl)pyridine (2l): Pale yellow oil; R_f 0.31; (hexanes : ethyl acetate, 70:30 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J = 0.8 Hz, J = 4.8 Hz 1H), 7.62 (td, J = 1.6 Hz , J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.38-7.48 (m, 3H), 7.11-7.17 (m, 2H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 149.4, 140.3, 137.3, 132.7, 131.2, 130.9, 129.1, 125.9 (q, J = 4 Hz), 123.5, 123.4, 121.9, 44.2; IR (neat) 2932, 1714, 1591, 1164, 734 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{11}NF_3$: 238.0844; found: 238.0855.

2-**(4-Fluorobenzyl)pyridine (2m):** Pale yellow oil. R_f 0.51; (hexanes : ethyl acetate, 70:30 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (t, J = 4.4 Hz, 1H), 7.58 (td, J = 1.6, Hz J = 7.6 Hz, 1H), 7.19-7.22 (m, 2H), 7.08-7.13 (m, 2H), 6.95-6.99 (m, 2H), 4.12(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J = 243 Hz), 160.8, 160.5, 149.5, 136.8, 135.3 (d, J = 3.4Hz), 130.6 (d, J = 7.7 Hz), 123.2, 121.5, 115.5 (d, J = 21.1 Hz), 43.8; IR (neat) 3029, 2921, 1659, 1550, 1426, 1104, 773, 737 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{11}NF$: 188.0876; found: 188.0871.

2-(3,5-Dimethylbenzyl)pyridine (2n): Pale yellow oil; R_f 0.38; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dt, J = 1.2, Hz J = 4.4 Hz, 1H), 7.59 (td, J = 2 Hz, J = 7.6Hz, 1H), 7.12-7.15 (m, 2H), 6.88 (d, J = 8Hz, 3H), 4.10 (s, 2H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.03, 148.8, 139.1, 138.2, 137.1, 128.2, 127.0, 123.5, 121.5, 44.1, 21.3; IR (neat) 2953, 2120, 1654, 1454, 1244, 1034, 762 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{16}N$: 198.1277; found: 198.1275.

2-Benzylpyrimidine (2o): Pale green oil ; R_f 0.26; (hexanes : ethyl acetate, 75:25 v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 4.8 Hz, 2H) , 7.26 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 2H) , 7.11 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 2.8 Hz, 1H), 4.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.11, 157.4, 138.3, 132.2, 129.3, 128.6, 126.7, 118.8, 46.1; IR (neat) 3033, 1637, 1565, 739, 700 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{11}N2$: 171.0922; found: 171.0922.

2-Benzyl quinoline (2p): Green oil; R_f 0.33; (hexanes : ethyl acetate, 70:30 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.62 (t, J = 8 Hz, 1H), 7.41(t, J = 7.6Hz, 1H), 7.12-7.22 (m, 6H), 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 147.9, 139.3, 136.7, 129.6, 129.4, 129.0, 128.8, 127.8, 126.9, 126.6, 126.1, 121.7, 45.6 ; IR (neat) 3055, 1660, 1601, 754, 710 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{14}N$: 220.1126; found: 220.1128.

3-Benzylpyridine (2q): Pale yellow oil; R_f 0.29; (hexanes: ethyl acetate, 80:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 2 Hz, 1H), 8.46 (dd, J = 1.6 Hz, J = 4.8 Hz, 1H), 7.46 (dq, J = 0.8 Hz, J = 7.8 Hz, 1H), 7.28-7.32 (m, 2H), 7.16-7.24 (m, 4H), 3.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.7, 139.9, 136.6, 136.5, 129.0, 128.8, 126.6, 123.6, 39.1; IR (neat) 3028, 2919, 1581, 1427, 780, 708 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{12}N$: 170.0970; found: 170.0963.

4-Benylpyridine (2r): Green oil; R_f 0.32; (hexanes: ethyl acetate, 75:25 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.31 (td, J = 1.2 Hz, J = 6 Hz, 2H), 7.21-7.26 (m, 1H), 7.16 (dd, J = 1.2 Hz, J = 8 Hz, 2H), 7.09 (d, J = 5.2 Hz, 2H), 3.95 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.8, 138.9, 129.1, 128.8, 126.7, 124.3, 41.3; IR (neat) 3026, 1667, 1596, 786, 700 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{12}H_{12}N$: 170.0970; found: 170.0963.

2-Benzyl-3-methylpyridine (6a): yellow colour oil; R_f 0.48; (hexanes : ethyl acetate, 80:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.6 Hz, 1H), 7.22-7.24 (m, 1H), 7.18-7.21 (m, 3H), 7.13 (tt, 1H), 6.90 (d, J = 7.6 Hz, 1H) 6.78 (d, J = 7.6 Hz, 1H), 4.07 (s,

2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 157.9, 139.6, 137.0, 129.3, 128.7, 126.5, 121.0, 120.3, 44.5, 24.4; IR (neat) 3027, 2923, 1962, 1714, 1585, 773, 704 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{14}N$: 184.1126; found: 184.1117.

2-(4-Chlorobenzyl)-6-methylpyridine (6b): Pale yellow oil; R_f 0.32; (hexanes : ethyl acetate, 70:30 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.18 (dt, *J* = 1.6 Hz, *J* = 8.6 Hz, 2H), 7.12 (dt, *J* = 2 Hz, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.02 (s, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz,) δ 159.8, 158.1, 138.2, 137.1, 132.3, 130.6, 128.8, 121.1, 120.1, 44.1, 24.6; IR (neat) 3058, 2922, 2842, 1652, 1589, 794, 758 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{13}NCl$: 218.0731; found: 218.0730.

(4-Fluorobenzyl)6-methylpyridine (6c): Pale green oil R_f 0.3; (hexanes : ethyl acetate, 75:25 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.6 Hz, 1H), 7.19-7.24 (m, 2H), 6.94-7.0 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.10 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 242.7 Hz), 160.2, 158.0, 137.0, 135.4 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 7.7 Hz), 121.0, 120, 24.6, 115.5 (d, *J* = 21.1 Hz), 43.8; IR (neat): 3062, 2932, 1588, 1509, 1455, 1222, 1103, 763 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{13}FN$: 202.1027; found: 202.1025.

2-Methyl-6-(4-methylbenzyl)pyridine (6d): Yellow oil; R_f 0.42; (hexanes : ethyl acetate, 80:20 v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 6.3 Hz, 1H), 7.17 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 4.12 (s, 2H), 2.57 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 157.8, 137.0, 136.6, 135.9, 129.3, 129.2, 120.9, 120.9, 44.2, 24.4, 21.1; IR (neat): 2953, 1650, 1512, 1244, 822, 762, 620 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{16}N$: 198.1277; found: 198.1275.

2-**(4-Tert-butyl)benzyl)-6-pyridine (6e):** Pale yellow oil; R_f 0.54; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 11.2 Hz, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.22 (d, *J* =8.4 Hz, 2H), 6.93 (dd, *J* = 8 Hz, *J* =31.6 Hz, 2H), 4.14 (s, 2H), 2.57 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 157.7, 149.2, 137.0, 136.5, 128.9, 125.5, 120.9, 120.2, 44.0, 34.4, 31.5, 24.4; IR (neat): 3073, 2960, 1586, 910, 734, cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{22}N$: 240.1747; found: 240.1748.

1-(Pyridin-2-yl)ethyl acetate (8a): Pale yellow oil; R_f 0.43; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dt, *J* = 0.8 Hz, *J* = 4.8 Hz, 1H), 7.67 (td, *J* = 1.6 Hz, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.17–7.21 (m, 1H), 5.90 (q, *J* = 6.4 Hz, 1H), 2.10 (d, *J* = 1.2 Hz, 3H), 1.58 (dd, *J* = 0.8 Hz, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.3, 149.2, 137.0, 122.8, 120.6, 73.0, 36.8, 21.3, 20.8; IR (neat) 2929, 2860, 1739, 1373, 1240 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_9H_{12}NO_2$: 166.0868; found: 166.0861.

Pyridin-2-ylmethyl acetate (8b): Pale yellow oil; R_f 0.32; (hexanes : ethyl acetate, 80:20 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.4 Hz, 1H), 7.70 (td, *J* = 1.6 Hz, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.21-7.25 (m, 1H), 5.21 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 155.8, 149.5, 137.0, 123.1, 122.0, 66.8, 53.5, 21.0 ; IR (neat): 2924, 1724, 1596, 1436, 1232, 1047, 766 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_8H_{10}NO_2$: 152.0712; found: 152.0716.

1-Phenylethyl acetate (8c):[17] Pale green oil; R_f 0.43; (hexanes : ethyl acetate, 90:10 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.38 (m, 5H), 5.90 (q, *J* = 6.8Hz, 1H), 2.08 (s, 3H), 1.55 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4 141.8, 128.6, 128.0, 126.2, 72.3, 22.3, 21.4; IR (neat) cm^{-1}; 3065, 2984, 1733, 1372, 1244, 911.

1-(4-Bromophenyl) ethyl acetate (8d):[17] Pale green oil ; R_f 0.38; (hexanes : ethyl acetate, 90:10 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dt, *J* = 2 Hz, *J* = 8.8 Hz, 2H), 7.22 (dt, *J* = 1.6 Hz, *J* = 8.4 Hz, 2H), 5.82 (q, *J* = 6.4 Hz, 1H), 2.06 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.0, 131.8, 128.0, 121.9, 71.8, 22.3, 21.4; IR (neat) cm^{-1}; 2925, 2354, 1730, 1597, 818.

1-(4-Nitrolphenyl) ethyl acetate (8e): White semisolid; R_f 0.32; (hexanes : ethyl acetate, 70:30 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.50 (dd, *J* = 2 Hz, *J* = 7 Hz 2H), 5.92 (q, *J* = 13.2 Hz, 1H), 2.10 (s, 3H), 1.55 (d, *J* = 6.4 Hz, 3H), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 149.1, 147.6, 126.9, 124.0, 71.4, 22.4, 21.3; IR (neat) 2983, 1740, 1599, 1523, 1240, 1052, 853 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{11}O_4NNa$: 232.0580; found: 232.0578.

1-(Naphthalen-2-yl)ethyl acetate (8f):[18] Green colour oil; R_f 0.52; (hexanes : ethyl acetate, 90:10 v/v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.86 (m, 4H), 7.45-7.51(m, 3H), 6.07 (q, *J* = 6.8 Hz, 1H), 2.11 (s, 3H), 1.63 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 139.2, 133.3, 133.2, 128.5, 128.2, 127.8, 126.4, 126.2, 125.2, 124.2, 76.6, 22.3, 21.5; IR (neat) cm^{-1}; 3055, 2933, 1737, 1370, 1061, 818, 749.

Acknowledgements

We thank DST (project No.: SB/S1/OC-72/2013) and DST Nano mission (SR/NM/NS-1034/2012(G)) New Delhi for financial support. I. K thank CSIR, India for senior research fellowship and S. C thank UGC for junior research fellowship.

Notes and references

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India, Phone: (+91) 44-2257 4229, Fax: (+91) 44-2257-4202, E-mail: gsekar@iitm.ac.in.

† Electronic Supplementary Information (ESI) available: Experimental procedures, spectral data and copy of ^{1}H NMR and ^{13}C NMR spectra were given in SI. See DOI: 10.1039/c000000x/

1 (a) Kotschy, G. Timari and Editors, *Heterocycles from Transition Metal Catalysis: Formation and Functionalization*, Springer, 2005; (b) J. A. Bull, J. J. Mousseau, G. Pelletier and A. B. Charette, *Chem. Rev.* 2012, **112**, 2642-2713; (c) Y. Nakao, *Synthesis*, 2011, 3209-3219. (d) P. L. Diaconescu, *Curr. Org. Chem.*, 2008, **12**, 1388-1405; (e) K. C. Nicolaou, R. Scarpelli, B. Bollbuck, B. Werschkun, M. M. A. Pereira, M. Wartmann, K. H. Altmann, D. Zaharevitz, R. Gussio and P. Giannakakou, *Chem. Biol.*, 2000, **7**, 593-599; (f) J.-M. Lehn, *Science* 2002, **295**, 2400-2403

2 (a) G. D. Henry, *Tetrahedron*, 2004, **60**, 6043-6061. (b) J. P. Michael, *Nat. Prod. Rep.*, 2005, **22**, 627-646; (c) M. Schlosser and F. Mongin, *Chem. Soc. Rev.*, 2007, **36**, 1161-1172.

3 M. Cardellini, F. Claudi, V. Perlini, W. Balduini, F. Cattabeni and M. Cimino, *Farmaco, Ed. Sci.*, 1987, **42**, 307-317; *Chem. Abstr*, 1987, **107**, 32610.

4 (a) A. P. Guzikowski, A. P. Tamiz, M. Acosta-Burruel, S. Hong-Bae, S. X. Cai, J. E. Hawkinson, J. F. W. Keana, S. R. Kesten, C. T. Shipp, M. Tran, E. R. Whittemore, R. M. Woodward, J. L. Wright and Z.-L. Zhou,

J. Med. Chem., 2000, **43**, 984-994; (b) G. V. De Lucca, U. T. Kim, C. Johnson, B. J. Vargo, P. K. Welch, M. Covington, P. Davies, K. A. Solomon, R. C. Newton, G. L. Trainor, C. P. Decicco and S. S. Ko, *J. Med. Chem.*, 2002, **45**, 3794-3804.

5 J. L. Herndon, A. Ismaiel, S. P. Ingher, M. Teitler and R. A. Glennon, *J. Med. Chem.*, 1992, **35**, 4903-4910

6 (a) B. Pieber and C. O. Kappe, *Green Chem*., 2013, **15**, 320-324; (b) Y. Wang, X. Li, F. Leng, H. Zhu, J. Li, D. Zou, Y. Wu and Y. Wu, *Adv. Synth. Catal*., 2014, **356**, 3307-3313; (c) Y.-Q. Long, X.-H. Jiang, R. Dayam, T. Sanchez, R. Shoemaker, S. Sei and N. Neamati, *J. Med. Chem.*, 2004, **47**, 2561-2573; (d) J. S. Wai, M. S. Egbertson, L. S. Payne, T. E. Fisher, M. W. Embrey, L. O. Tran, J. Y. Melamed, H. M. Langford, J. P. Guare, Jr., L. Zhuang, V. E. Grey, J. P. Vacca, M. K. Holloway, A. M. Naylor-Olsen, D. J. Hazuda, P. J. Felock, A. L. Wolfe, K. A. Stillmock, W. A. Schleif, L. J. Gabryelski and S. D. Young, *J. Med. Chem.*, 2000, **43**, 4923-4926.

7 (a) A. Flaherty, A. Trunkfield and W. Barton, *Org. Lett.*, 2005, **7**, 4975-4978; (b) J. D. St. Denis, C. C. G. Scully, C. F. Lee and A. K. Yudin, *Org. Lett.*, 2014, **16**, 1338-1341; (b) S. Duez, A. K. Steib, S. M. Manolikakes and P. Knochel, *Angew. Chem., Int. Ed.*, 2011, **50**, 7686-7690. (c) M. Haberberger, C. I. Someya, A. Company, E. Irran and S. Enthaler, *Catal. Lett.*, 2012, **142**, 557-565S. (d) Yamashita, N. Kurono, H. Senboku, M. Tokuda and K. Orito, *Eur. J. Org. Chem.*, 2009, 1173-1180. (e) B. Qian, S. Guo, J. Shao, Q. Zhu, L. Yang, C. Xia and H. Huang, *J. Am. Chem. Soc.*, 2010, **132**, 3650-3651; (f) X. Chen, L. Zhou, Y. Li, T. Xie and S. Zhou, *J. Org. Chem.*, 2014, **79**, 230-239; (g) P. M. Burton and J. A. Morris, *Org. Lett.*, 2010, **12**, 5359-5361.

8 T. Niwa, H. Yorimitsu and K. Oshima, *Angew. Chem., Int. Ed.*, 2007, **46**, 2643-2645.

9 R. Shang, Z.-W. Yang, Y. Wang, S.-L. Zhang and L. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 14391-14393.

10 A. Wick, J. Frost, B. Gaudilliere, J. Bertin, R. Dupant, J. Rouseau, FR 2534580, 1984 (*Chem. Abstr*. 1984, *101*, 210992e).

11 S. Couve-Bonnaire, J. F. Carpentier, A. Mortreux and Y. Castanet, *Tetrahedron Lett.*, 2001, **42**, 3689-3691.

12 (a) V. Rajeshkumar, S. Chandrasekar and G. Sekar, *Org. Biomol. Chem.*, 2014, **12**, 8512-8518; (b) I. Karthikeyan, D. Arunprasath and G. Sekar, *Chem. Commun.* 2015, **51**, 1701-1704; (c) N. C. Mamillapalli and G. Sekar, *RSC Adv.*, 2014, **4**, 61077-61085.

13 For metal mediated deoxygenation, see (a) B. R. Brown, *J. Chem. Soc.*, 1949, 2577-2579; (b) Y. Kato and T. Mase, *Tetrahedron Lett.*, 1999, **40**, 8823-8826; (c) G. A. Cain and E. R. Holler, *Chem. Commun.* 2001, 1168-1169; (d) T. D. Penning, N. S. Chandrakumar, B. B. Chen, H. Y. Chen, B. N. Desai, S. W. Djuric, S. H. Docter, A. F. Gasiecki, R. A. Haack, J. M. Miyashiro, M. A. Russell, S. S. Yu, D. G. Corley, R. C. Durley, B. F. Kilpatrick, B. L. Parnas, L. J. Askonas, J. K. Gierse, E. I. Harding, M. K. Highkin, J. F. Kachur, S. H. Kim, G. G. Krivi, D. Villani-Price, E. Y. Pyla, W. G. Smith and N. S. Ghoreishi-Haack, *J. Med. Chem.*, 2000, **43**, 721-735.

14 In this reaction, the oxidized product ketone **4** is the major product. The analyisis of crude reaction mixture by ^{1}H and ^{13}C NMR shows that the presence of pivalaldehyde. So, it is expected that initially the reaction may give pivalic ester of **1a** which may yielded oxidized product ketone **4** and reduced product pivalaldehyde.

15 .M. Dobmeier, J. M. Herrmann, D. Lenoir and B. Koenig, *Beilstein J. Org. Chem.*, 2012, **8**, 330-336; (b) D. Nguyen, B. Reiss, C. Dai and C. R. J. Stephenson, *Chem. Commun*. 2013, **49**, 4352-4354.

16 Acetate of **1a (13)** under the optimized reaction condition (HI (2 equiv.), CH_3COOH, 140 ^{o}C,8h) gave the deoxygenated **2a.** The result also confirms the proposed mechanistic pathway.

17 H. Baba, K. Moriyama and H. Togo, *Tetrahedron Lett.*, 2011, **52**, 4303-4307.

18 T. Mino, T. Hasegawa, Y. Shirae, M. Sakamoto and T. Fujita, *J. Organomet. Chem.*, 2007, **692**, 4389-4396.

An Efficient and Metal Free Synthesis of Benzylpyridines Using HI Through Deoxygenation Reaction

S. Chandrasekar, I. Karthikeyan and G. Sekar*

An efficient and practical method for the synthesis of benzylpyridines has been developed using *aqueous* hydroiodic acid in acetic acid.