Organic & Biomolecular Chemistry

Accepted Manuscript

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Metal and Base Free Synthesis of Primary Amines via *ipso* Amination of Organoboronic Acids Mediated by [bis(trifluoroacetoxy)iodo]benzene (PIFA)

Nachiketa Chatterjee and Avijit Goswami*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A metal and base free synthesis of primary amine has been developed at ambient temperature through *ipso* amination of diversely functionalized organoboronic acids, employing a combination of [bis(trifluoroacetoxy)iodo]benzene (PIFA) – N-Bromosuccinimide (NBS) and methoxyamine hydrochloride as the aminating reagent. The amines were primarily obtained as their trifluoroacetate salts which on subsequent aqueous alkaline work up provided the corresponding free amines. The combination of PIFA-NBS is found to be the mildest choice compared to the commonly used strong bases (e.g. n-BuLi, Cs_2CO_3) for activating the aminating agent. The reaction is expected to proceed via activation of the aminating reagent followed by B-N 1,2- aryl migration.

Amines, both aromatic and aliphatic, are ubiquitous in various natural products, pharmaceuticals, agrochemicals and dyes.[1] As a result, these compounds have significant applications in the pharmaceutical industry and medicinal chemistry (Figure 1).[2] Therefore, developing novel methodologies to access variedly functionalized aromatic and aliphatic amines always have a great research importance.

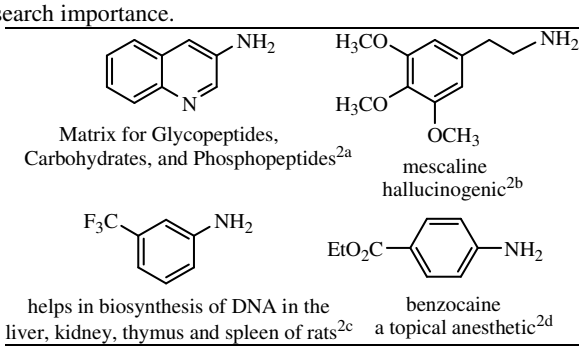

Figure 1 Selected bio-active primary amines

In this context, it is needless to say that over the recent decades, significant advancements have taken place in the field of syntheses of secondary and tertiary anilines starting from palladium catalyzed Buchwald-Hartwig coupling of aryl halides and cupper catalysed Chan-Lam coupling of arylboronic acids/esters.[3] In spite of such notable progress in the methodologies for syntheses of *N*-substituted arylamines, much less attention has been drawn towards the development of advanced protocols for facile syntheses of primary amines under mild reaction conditions. The traditional approach to prepare the primary aromatic amines are the metal mediated reductions of the nitro compounds and treatment of metal amide in liquid ammonia to the benzynes.[1c,1d,4] Later on, transition metal catalyzed amination of aryl halides with ammonia were achieved.[5] However, these transformations have several drawbacks of their own, such as, limited functional groups compatibility, use of metal and harsh reaction conditions, the concomitant formation of undesired diaryl amines and many often the requirement of costly ligands. From the pharmaceutical point of view, metal free processes are always preferred over metal promoted methods. In this perspective, transition metal free protocols towards syntheses of primary amines from organoboronic acids have been documented using $ArONH_2/Cs_2CO_3$,[6] $MeONH_2.HCl/n\text{-}BuLi$[7] and $HSO_3ONH_2/NaOH$[8] as the aminating agents (Scheme 1).

Previous work:

$$R\text{-}B(OH)_2 \xrightarrow{\text{reaction conditions}} R\text{-}NH_2$$

reaction conditions

1. $C_6H_3(NO_2)_2ONH_2/Cs_2CO_3$; ***50 ^{0}C, 24-48 h***; **ref.6**
2. $MeONH_2.HCl/n\text{-}BuLi$; ***-78 ^{0}C - 60 ^{0}C, 12 h***; **ref.7**
3. $HSO_3ONH_2/NaOH$; ***RT, 16 h***; **ref.8**

This work:

$$R\text{-}B(OH)_2 \xrightarrow{\text{reaction conditions}} R\text{-}NH_2$$

reaction conditions

PIFA/NBS/$MeONH_2.HCl$; ***RT, 2-3 h***

Scheme 1 Transition metal free syntheses of primary amines from organoboronic acids

In spite of the novelties associated with these protocols, these methods suffer from certain drawbacks. In the presence of aminating reagent HSO_3ONH_2 or excess amount of very strong base like n-BuLi, the functional groups like carbonyls, nitriles and esters could not be expected to tolerate the reaction conditions[9] and this phenomenon imposes a limitation to the functional group compatibility of these protocols. Furthermore, no documentation has been made in the above mentioned literature for amination of the *N*-heteroarylboronic acids.

In the present work, attention has been devoted to overcome these problems by using easily available aminating reagent $MeONH_2.HCl$ without using a base so that a wide range of functional groups could tolerate the reaction conditions. In this connection, it is mention worthy that our group has reported a

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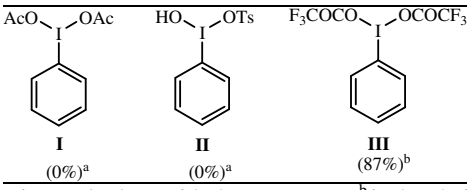
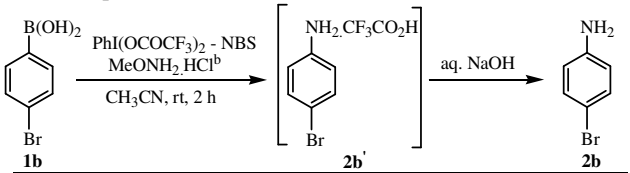
novel methodology for *ipso* nitration[10] of organoboronic acids where the combination of PIFA[11] and NBS is anticipated to produce a succinimidyl radical which could be used as an effective as well as milder proton scavenger compared to a base, required to activate the aminating reagent for the amination reaction to take place. With this idea from our earlier work, we herein report a facile PIFA-NBS mediated regioselective amination of aryl-, *N*-heteroaryl- and alkylboronic acids by using easily available methoxyamine hydrochloride ($MeONH_2.HCl$) as the aminating reagent. To the best of our knowledge, it is the first example of using a novel combination of PIFA-NBS-$MeONH_2.HCl$ to generate primary amines under base and metal free conditions.



[a]no amination took place with these reagents; [b]isolated yield

Figure 2 Different organohypervalent iodine reagents employed for the amination reaction

Table 1 Optimization of reaction conditions[a]



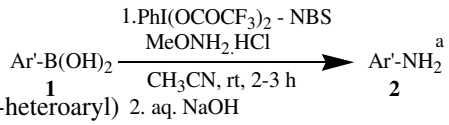
entry	eq. of PIFA	eq. of NBS as an additive	solvent	yield (%)[c]
1	3.0	-	CH_3CN	n.r[d]
2	-	3.0	CH_3CN	n.r[e]
3	1.0	1.0	CH_3CN	49
4	2.0	1.0	CH_3CN	66
5	2.0	2.0	CH_3CN	87[f]
6	2.0	2.0	CH_2Cl_2	69
7	2.0	2.0	THF	64
8	2.0	2.0	$CHCl_3$	67
7	2.0	2.0	EtOH	n.r[d]
8	2.0	2.0	CH_3CN	85[g]

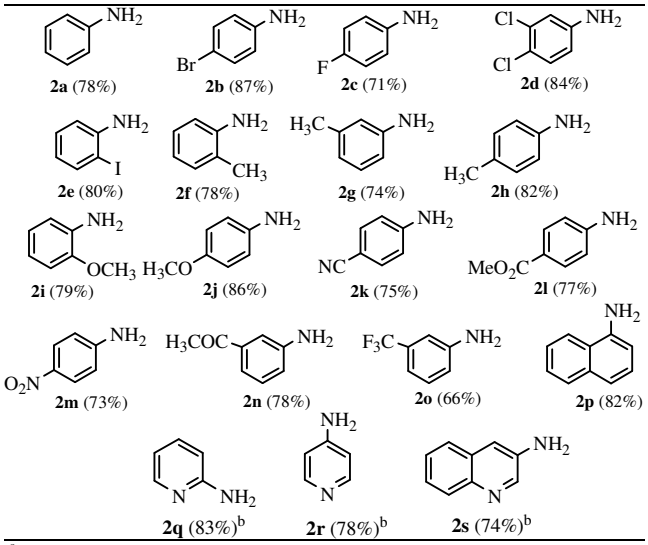
[a]optimized reaction conditions: **1b** (2.0 mmol, 1.0 eq.), $PhI(OCOCF_3)_2$ (4.0 mmol, 2.0 eq.), $MeONH_2HCl$ (2.0 mmol, 1.0 eq.), NBS (4.0 mmol, 2.0 eq.), CH_3CN (6 mL), rt, 2 h, open air; [b]all optimization reactions were carried out with 2.0 mmol of $MeONH_2.HCl$; [c]isolated yield of **2b**; [d]no amination took place by stirring the reaction mixture for 24 h at room temperature; [e]no amination was observed; however, bromination took place on heating the mixture at 60 ^{0}C for 4 h; [f]these reaction conditions were taken as optimized reaction conditions; [g]the reaction was carried out under argon atmosphere

The primary investigations were carried out with 4-Bromophenylboronic acid (**1b**), taken as the model substrate for obtaining 4-bromoaniline (**2b**). An initial screening of the organo-hypervalent iodine species disclosed that the reagents **I** and **II** were unable to provide the desired arylamines regardless of the presence or absence of NBS as additive, whereas, the hypervalent iodine (**III**) was successful to promote the reaction and the arylamines were obtained in high yield in the presence of NBS as an additive (Figure 2).

Table 1 represents the optimization results of PIFA-NBS mediated *ipso* amination of organoboronic acids in open air under ambient temperature. Early experiments confirmed that for the reaction to be successful, the presence of both PIFA and NBS are essential (entries 1 and 2). The optimization process revealed that complete conversion of **1b** to its corresponding trifluoroacetate salt took place when 2.0 eq. of PIFA and NBS were employed using acetonitrile as solvent (entries 3-5). Dichloromethane and ethanol were examined as solvent for the said reaction. In dichloromethane amination was found to occur in a comparatively lower yield (entry 6) whereas, in ethanol no amination was found to take place (entry 7). No significant change in the reaction outcome was noticed while performing the reaction under inert environment (entry 8).

Keeping the optimized reaction conditions in mind, the investigations were further explored to other substrates in order to figure out the substrate scope of this methodology and the results are documented in Scheme 2.





[a]reaction conditions: **1** (2.0 mmol), $PhI(OCOCF_3)_2$ (4.0 mmol), $MeONH_2.HCl$ (2.0 mmol), NBS (4.0 mmol), CH_3CN (6 mL), rt, 2-3 h, open air; [b]the reactions with **1q**, **1r** and **1s** were carried out in 3.0 mmol scale

Scheme 2 PIFA Mediated *ipso*-Amination of Arylboronic Acids

Employing this methodology, variedly functionalized arylboronic acids were efficiently transformed to their corresponding amines which demonstrated the excellent functional group (*e.g.* halide, nitro, ester, keto and nitrile) compatibility of the protocol. The

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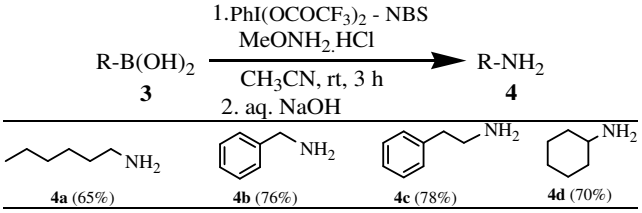
arylboronicacids with a wide range of substitution in the *ortho-*, *meta-* and *para* position were successfully converted to the corresponding arylamines indicating the negligible steric (**2e, 2f** and **2i)** and electronic effect (**2j-2n**) on the reaction outcome. However, with fluorinated arylboronic acids, the amination was found to undergo in lower yield (**2c** and **2o**). It was delightful to find that using the optimized reaction conditions, *N*-hetero-arylboronic acids are also conveniently transformed to their corresponding amines (**2q**, **2r** and **2s**) in excellent yields which were not possible to synthesize through the previously mentioned reported protocols for synthesizing primary amines from organoboronic acids. On the other hand, aryl- and heteroboronates were not found to undergo amination under this reaction conditions.

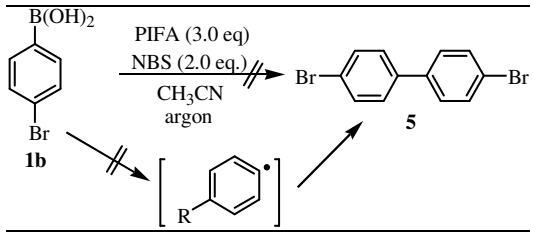


reaction conditions: **3** (3.0 mmol), $PhI(OCOCF_3)_2$ (6.0 mmol), $MeONH_2.HCl$ (3.0 mmol), NBS (6.0 mmol), CH_3CN (6 mL), rt, 3 h, open air

Scheme 3 PIFA Mediated *ipso*-Amination of Alkylboronic Acids

To further explore the spectrum of this protocol, the alkylboronic acids were also employed for amination reactions (Scheme 3). Greatly, through this newly developed protocol, primary aliphatic amines (4**a-d**) were successfully synthesized in high yields.

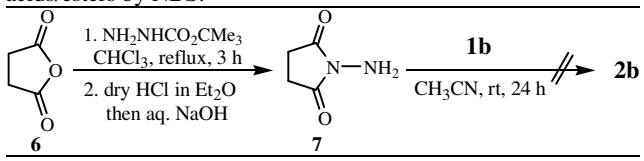
There might be three probable mechanistic rationales for this *ipso* amination reaction of the organoboronic acid to happen. It was hypothesised that if in the presence of the combination of PIFA-NBS, methoxyamine hydrochloride and arylboronic acid could produce the MeONH and an aryl radical respectively, then these two radicals (aryl and MeONH) might combine to provide arylamines in a single pot. Therefore, in order to be confirmed for the radial mechanistic pathway, radical scavenging experiment with TEMPO was performed.[12] It was observed in the presence of TEMPO, no amination took place at ambient temperature after 3 h which clearly confirms the radical pathway for this amination reaction of the organoboronic acids.



Scheme 4 Reactions of 1b with PIFA-NBS in attempted syntheses of biaryls

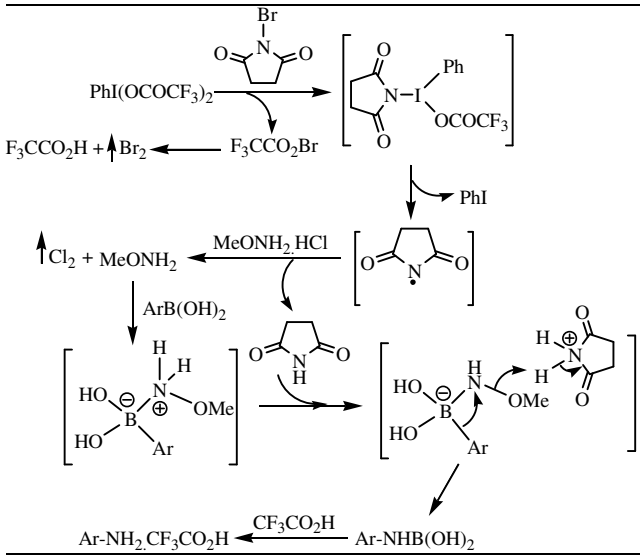
On the other hand, in a separate reaction, the arylboronic acid **1b** when applied to react with PIFA and NBS (Scheme 4) did not afford any biaryl compound (**5)** which suggests that aryl radical is not getting formed in the course of the reaction. Hence the combination of aryl radical and metoxyamine radical for the generation of the arylamines might be ruled out, although a radical nature of the reaction pathway is being indicated.

Second probable reaction pathway might be such that in the presence of PIFA, methoxyamine hydrochloride could combine with NBS, in a radical pathway, to form *N*-aminosuccinimide (**7**) which then reacted with arylboronic acid in the same fashion as proposed by Petasis *et al.* for bromination of organoboronic acids/esters by NBS.[13]



Scheme 5 Preparation of *N*-aminoosuccinimide (7) and its reaction with 1b

However, in a separate reaction performed at ambient temperature with NBS and $MeONH_2.HCl$ in the presence of PIFA, formation of **7** was not observed in GC-MS analysis of the crude reaction mixture. Furthermore, 4-bromoaniline (**2b**) was not obtained when 4-bromophenylboronic acid (**1b)** was allowed to react with **7**, synthesized separately following the reported literature procedure (Scheme 5).[14] Thus, this pathway could also be eliminated.



Scheme 6 Tentative reaction pathway

As the reaction is occurring in the absence of a base and having a radical nature, the third possibility of PIFA-NBS mediated activation of the aminatig reagent via a radical pathway followed by B-N 1,2- aryl migration sounds logical for the reaction to proceed. Based on the above mentioned experimental facts, it could be speculated that PIFA readily reacts with NBS to generate a succinimidyl radical[10] along with generation of trifluoroacetic acid and evolution of bromine gas. The succinimdyl radical is expected to activate the aminating reagent by abstracting the proton[10] of the associated HCl molecule, leaving behind the chlorine radical to go out as chlorine gas. Then, nucleophilic attack of the activated methoxyamine takes place to the boron centre of organoboronic acid to provide the tetracoordinated boronate species. Finally, amine salts are produced via intermolecular B-N 1,2-aryl migration from the tetracordinated boronate species (Scheme 6).

Afterwards, the amination reaction was performed on a gram scale to understand its practicality (Scheme 7). When **1b** and **1k** were subjected for primary amination on a 10.0 mmol scale, the corresponding primary amines were obtained in comparable

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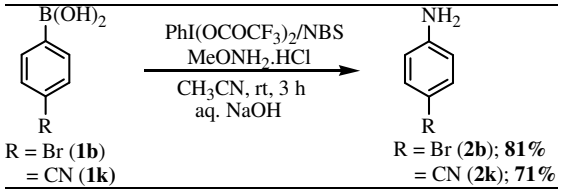
yields as obtained on the low scale experiments demonstrating the practical applicability of the protocol.



reaction conditions: **1b** (2.0 g, 10.0 mmol)/**1k** (1.47 g, 10 mmol) $PhI(OCOCF_3)_2$ (20.0 mmol), $MeONH_2.HCl$ (10.0 mmol), NBS (20.0 mmol), CH_3CN (20 mL), rt, 3 h, open air

Scheme 7 PIFA Mediated *ipso*-amination of arylboronic acids on gram-scale

In conclusion, we have developed a novel metal and base free methodology for synthesising primary amines via *ipso* amination of organoboronic acids using a combination of PIFA-NBS and $MeONH_2.HCl$ as the aminating agent. The method is applicable for aryl-, heteroaryl-, and alkylboronic acids and produces amino compounds at ambient temperature in significantly less reaction time. The reaction conditions employed in the protocol show a wide range of functional groups tolerance especially to the carbonyl, nitrile ester and halogen which are hard to synthesise through some of the previously reported methods. The simplicity, use of easily available inexpensive reagents and the utilization of PIFA-NBS combination, as a milder alternative to a base as proton scavenger, are the remarkable features of this method**.**

Experimental

General experimental section

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvent (CH_3CN) used in the reactions was dried and freshly distilled before use. Thin layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). GC-MS analyses were carried out on SHIMADZU GCMS-QP Ultra 2010 instrument. NMR spectra were recorded in $CDCl_3$, on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz (^1H) or 100 MHz (^{13}C) as indicated in the individual spectrum. Chemical shifts (δ) are given in ppm relative to residual solvent (chloroform, δ= 7.26 for ^1H and 77.16 for proton decoupled ^{13}C NMR) and coupling constants (*J*) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quartet, dd for doublet of doublet, dt for doublet of triplet and m for multiplet.

General procedure for syntheses of the amino compounds:

To a stirred solution of appropriate boronic acids (**1/ 3**, 2.0 mmol/3.0 mmol, 1.0 eq.), PIFA (4.0 mmol/6.0 mmol, 2.0 eq.) and NBS (4.0 mmol/6.0 mmol, 2.0 eq.) in CH_3CN (6 mL), $MeONH_2.HCl$ (2.0 mmol/3.0 mmol, 1.0 eq.) were added and the mixture was stirred for 2-3 h. After completion of the reaction (checked by TLC), the mixture was concentrated under vacuum. The solid mass was washed with dry hexane to remove the iodobenzene and other less polar impurities. The solid was then dissolved to its optimum extent in minimum volume of water. The solution was made completely alkaline with saturated aq. NaOH solution under cold condition and the aq. solution was extracted with ethyl acetate (5×20 mL). The combined organic phase was washed with distilled water (3×7 mL) and was dried over Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography over silica gel using pentane/ether as eluent to provide the pure target products (**2/4**).

Aniline (2a): pale yellow liquid (78%, 145.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.19-7.23 (m, 2H), 6.80-6.84 (m, 1H), 6.71-6.73 (m, 2H), 3.58 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 129.3, 118.3, 115.2.

4-Bromoaniline (2b): off-white solid (87%, 299.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 6.8 Hz, 1.8 Hz, 2H), 6.55 (dd, *J* = 6.4Hz, 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 132.1, 116.8, 110.1.

4-Fluoroaniline (2c): light brown liquid (71%, 157.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 6.83-6.87 (m, 2H), 6.59-6.63 (m, 2H), 3.45 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 155.3, 142.4, 116.2, 116.1, 115.8, 115.6.

3,4-Dichloroaniline (2d)*:* grey solid (84%, 272.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.7 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.48-6.51 (m, 1H), 3.71 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 132.7, 130.6, 121.2, 116.9, 114.9.

2-Iodoaniline (2e): brownish solid (80%, 350.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.2 Hz, 1.4Hz, 1H), 7.13 (dt, *J* = 7.3 Hz, 1.8 Hz, 1H), 6.75 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 6.47 (dt, *J* = 8.2 Hz, 1.8 Hz, 1H) 4.08 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 139.2, 129.4, 119.6, 114.5, 84.2.

2-Methylaniline (2f): pale yellow liquid (78%, 166.9 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.07-7.10 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.61 (s, 3H), 3.96 (s, br, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 131.2, 127.0, 121.8, 118.6, 114.6, 17.4.

3-Methylaniline (2g)*:* light yellow liquid (74%, 158.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.52-6.54 (m, 2H), 3.54 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 139.1, 129.0, 119.5, 116.0, 112.3, 21.8.

4-Methylaniline (2h)*:* off-white semi-solid (82%, 175.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 6.97-6.99 (m, 2H), 6.61-6.64 (m, 2H), 3.39 (s, br, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 129.8, 127.9, 115.3, 20.5.

2-Methoxyaniline (2i): light yellow liquid (79%, 194.3 mg);. ^1H NMR (400 MHz, $CDCl_3$): δ 6.73-6.83 (m, 4H), 3.86 (s, 3H), 3.69 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 136.1, 121.2, 118.2, 115.3, 110.4, 55.4.

4-Methoxyaniline (2j)*:* off-white solid (86%, 211.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 6.75 (dd, *J* = 8.6 Hz, 2.3 Hz, 2H), 6.65 (dd, *J* = 8.7 Hz, 2.3 Hz, 2H), 3.74 (s, 3H), 3.19 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 139.8, 116.5, 114.7, 55.7.

4-cyanoaniline (2k): pale yellowish solid (75%, 177.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 8.7 Hz, 1.8 Hz, 2H), 6.64 (dd, *J* = 8.6 Hz, 2.3 Hz, 2H), 4.17 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 133.9, 120.1, 114.5, 100.1.

Ethyl 4-aminobenzoate (2l): off-white solid (77%, 232.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.7 Hz, 2.3 Hz, 2H), 6.63 (dd, *J* = 8.7 Hz, 2.3 Hz, 2H), 4.31 (q, 2H), 4.05 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 150.7, 131.6, 120.1, 113.9, 60.1, 14.8.

4-nitroaniline (2m): brown solid (73%, 201.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 9.2

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Hz, 2H), 4.39 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 126.3, 122.0, 113.4.

3-Aminoacetophenone (2n): brownish solid (78%, 210.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.26 (m, 1H), 7.14-7.19 (m, 2H), 6.78-6.81 (m, 1H), 3.66 (s, br, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 146.8, 138.1, 129.5, 119.9, 119.0, 113.8, 26.8.

3-Trifluoromethylaniline (2o): light yellow liquid (66%, 212.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 7.15 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.79 (m, 1H), 6.70-6.73 (m, 1H), 3.66 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 131.7, 131.5, 131.1, 129,8, 128.3, 125.6, 122.9, 118.0, 115.1, 115.0, 111.4, 111.3.

1-Aminonapthaline (2p): grey solid (82%, 234.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 7.81-7.84 (m, 2H), 7.46-7.48 (m, 2H), 7.29-7.35 (m, 2H), 6.80 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.4, 128.6, 126.4, 125.9, 124.9, 123.7, 120.8, 119.0, 109.7.

2-Aminopyridine (2q): light yellow solid (83%, 234.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): 8.03-8.05 (m, 1H), 7.37-7.46 (m, 1H), 6.59-6.62 (m, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 4.52 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 148.1, 137.8, 114.0, 108.2.

4-Aminopyridine (2r): white solid (78%, 219.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, *J* = 6.4 Hz, 1.4 Hz, 2H), 6.51 (dd, *J* = 6.4 Hz, 1.4 Hz, 2H), 4.14 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 150.4, 109.7.

3-Aminoquinoline (2s): brownish solid (74%, 319.7mg);. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.94-7.96 (m, 1H), 7.55-7.58 (m, 1H), 7.39-7.44 (m, 2H), 7.21 (m, 1H), 3.65 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 142.6, 139.9, 129.2, 128.9, 127.0, 125.9, 125.7, 115.1.

Hexylamine (4a): light yellow liquid (65%, 196.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (t, *J* = 7.3 Hz, 2H), 1.36-1.41 (m, 2H), 1.21-1.31 (m, 6H), 1.16 (s, br, 2H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.3, 39.9, 31.6, 26.4, 22.7, 14.0.

Benzylamine (4b): light yellow liquid (76%, 244.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.27 (m, 5H), 3.77 (s, 2H), 1.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 128.5, 127.1, 126.8, 46.5.

2-Phenylethylamine (4c): light brown liquid (78%, 283.1 mg);. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.32 (m, 2H), 7.19-7.23 (m, 3H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 1.24 (s, br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 128.9, 128.4, 126.0, 43.8, 40.0.

Cyclohexylamine (4d): colourless liquid (70%, 207.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53-2.60 (m, 1H), 1.74-1.78 (m, 2H), 1.63-1.68 (m, 2H), 1.52-1.57 (m, 1H), 1.34 (s, br, 2H), 0.94-1.26 (m,6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.5, 36.9, 25.7, 25.2.

Acknowledgements

We are grateful to DST, New Delhi, India for their generous financial support and IIT Ropar for infrastructural facilities. NC would like to thank IIT Ropar for his fellowship.

Notes and references

Department of Chemistry, Indian Institute of Technology, Ropar (IIT Ropar), Nangal Road, Rupnagar, Punjab 140001, India
Tel: +91-1881-242121; E-mail: agoswami@iitrpr.ac.in

†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x

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