Supporting Information

for

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

Nachiketa Chatterjee and Avijit Goswami*

Department of Chemistry, Indian Institute of Technology, Ropar, (IIT Ropar), Nangal Road Punjab 140001, India

* E-mail: agoswami@iitrpr.ac.in

CONTENTS:

1. General Information................................................................................................02

2. Syntheses and Characterizations of Aliphatic and Aromatic Amino Compounds.....03-08

3. Copies of the $^1$H NMR, $^{13}$C NMR spectra of all compounds and selected GC-MS Spectra.........09-34
1. General information

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvent (CH$_2$CN) 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 ($^1$H) 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 $^1$H 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.
2. Syntheses and Characterizations of the Aromatic and Aliphatic Nitro Compounds

General procedure for syntheses of the amino compounds:

To a stirred solution of appropriate organoboronic acids (2.0 mmol, 1.0 eq.), PIFA (4.0 mmol, 2.0 eq.) and NBS (4.0 mmol, 2.0 eq.) in CH$_3$CN (6 mL), MeONH$_2$.HCl (2.0 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 obtained, 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$_2$SO$_4$. After evaporating the solvent, the residue was purified by column chromatography over silica gel using pentane/ether as eluent to provide the pure target product.

Characterization of compounds:

2a

Aniline (2a): 2a was obtained as a pale yellow liquid (78%, 145.1 mg) following the general procedure. $^1$H 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.

2b

4-Bromoaniline (2b): 2b was obtained as a off-white solid (87%, 299.2 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.23 (dd, $J = 6.8$ Hz, 1.8 Hz, 2H), 6.55 (dd, $J = 6.4$Hz, 2.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 145.3, 132.1, 116.8, 110.1.

2c

4-Fluoroaniline (2c): 2c was obtained as a light brown liquid (71%, 157.6 mg) following the general procedure. $^1$H 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$_3$): $\delta$ 157.6, 155.3, 142.4, 116.2, 116.1, 115.8, 115.6.

\[ \text{Cl} \quad \text{NH}_2 \quad \text{Cl} \]

**3,4-Dichloroaniline (2d):** 2d was obtained as a grey solid (84%, 272.2 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 146.1, 132.7, 130.6, 121.2, 116.9, 114.9.

\[ \text{NH}_2 \quad \text{I} \quad \text{2e} \]

**2-iodoaniline (2e):** 2e was obtained as a brownish solid (80%, 350.4 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (dd, $J = 8.2$ Hz, 1.4 Hz, 1H), 7.13 (dt, $J = 7.3$ Hz, 1.8 Hz, 1H), 6.75 (dd, $J = 8.2$ Hz, 1.8 Hz, 1H), 4.08 (s, br, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.8, 139.2, 129.4, 119.6, 114.5, 84.2.

\[ \text{CH}_3 \quad \text{NH}_2 \]

**2-Methylaniline (2f):** 2f was obtained as a pale yellow liquid (78%, 166.9 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.07-7.10 (m, 2H), 6.76 (t, $J = 7.4$ Hz, 1H), 6.52-6.54 (m, 2H), 3.54 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.9, 131.2, 127.0, 121.8, 118.6, 114.6, 17.4.

\[ \text{H}_3\text{C} \quad \text{NH}_2 \]

**3-Methylaniline (2g):** 2g was obtained as a light yellow liquid (74%, 158.4 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 146.2, 139.1, 129.0, 119.5, 116.0, 112.3, 21.8.
4-Methylaniline (2h): 2h was obtained as off-white semi-solid (82%, 175.5 mg) following the general procedure. $^1$H 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): 2i was obtained as a light yellow liquid (79%, 194.3 mg) following the general procedure. $^1$H 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): 2j was obtained as a pale off-white solid (86%, 211.6 mg) following the general procedure. $^1$H 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): 2k was obtained as a pale yellowish solid (75%, 177.0 mg) following the general procedure. $^1$H 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):** 2l was obtained as an off-white solid (77%, 232.6 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 166.6, 150.7, 131.6, 120.1, 113.9, 60.1, 14.8.

![2m](image)

**4-nitroaniline (2m):** 2m was obtained as a brown solid (73%, 201.5 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.06 (d, \(J = 8.7\) Hz, 2H), 6.62 (d, \(J = 9.2\) Hz, 2H), 4.39 (s, br, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 152.4, 126.3, 122.0, 113.4.

![2n](image)

**3-Aminoacetophenone (2n):** 2n was obtained as a brownish solid (78%, 210.6 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 198.9, 146.8, 138.1, 129.5, 119.9, 119.0, 113.8, 26.8.

![2o](image)

**3-Trifluoromethylaniline (2o):** 2o was obtained as a light yellow liquid (66%, 212.5 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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\(_3\)): \(\delta\) 146.7, 131.7, 131.5, 131.1, 129.8, 128.3, 125.6, 122.9, 118.0, 115.1, 115.0, 114.1, 111.3.

![2p](image)

**1-Aminonapthaline (2p):** 2p was obtained as a grey solid (82%, 234.5 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.81-7.84 (m, 2H), 7.46-7.48 (m, 2H), 7.29-7.35 (m, 2H), 6.90 (d, \(J = 6.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.1, 134.4, 128.6, 126.4, 125.9, 124.9, 123.7, 120.8, 119.0, 109.7.
2-Aminopyridine (4a): 4a was obtained as a light yellow solid (83%, 234.1 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 158.2, 148.1, 137.8, 114.0, 108.2.

4-Aminopyridine (4b): 4b was obtained as a white solid (78%, 219.9 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 152.7, 150.4, 109.7.

3-Aminoquinoline (4c): 4c was obtained as a brownish solid (74%, 319.7mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 143.1, 142.6, 139.9, 129.2, 128.9, 127.0, 125.9, 125.7, 115.1.

Hexylamine (6a): 6a was obtained as a light yellow liquid (65%, 196.9 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 42.3, 39.9, 31.6, 26.4, 22.7, 14.0.
Benzylamine (6b): 6b was obtained as a light yellow liquid (76%, 244.0 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.14-7.27 (m, 5H), 3.77 (s, 2H), 1.43 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.2, 128.5, 127.1, 126.8, 46.5.

\[ \text{C} \text{H} \text{N}_2 \]

2-Phenylethylamine (6c): 6c was obtained as a light brown liquid (78%, 283.1 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 139.8, 128.9, 128.4, 126.0, 43.8, 40.0.

\[ \text{C} \text{H} \text{N}_2 \]

Cyclohexylamine (6d): 6d was obtained as a colourless liquid (70%, 207.9 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 50.5, 36.9, 25.7, 25.2.

References:


(3) Voth, S.; Hollet, J. W.; McCubbin, J. A. J. Org. Chem. 2015, 80, 2545


GC-MS of crude $p$-bromoanilinetrifluoroacetate salt ($2b'$)

![Chemical reaction diagram]

the solid $2b'$ obtained was washed with hexane to make it free from PhI as much as possible

(GC-MS of crude solid $2b'$ after washing it with hexane)
Radical scavenging experiment with TEMPO

Two different reactions were performed at the same time under similar standard reaction conditions except that one of the reactions were carried out in presence of TEMPO as a radical scavenger. No aminated product was observed in the presence of TEMPO after 3 h, whereas in the other reaction, amination was found to take place as usual within 3 h.
GC-MS of crude $m$-aminoacetophenonetrifluoroacetate salt (2n')

The solid product obtained was as usual washed with hexane to make it free from PhI as much as possible.

(GC-MS of crude solid 2n' after washing it with hexane)
$\text{I}$

$\text{NH}_2$

$2e$
H$_3$C=CH$_2$
\[
\text{NH}_2
\]
$\text{NH}_2$

6b