Supporting Information

for

A Novel Transition Metal Free, [bis-(trifluorocetoxy)iodo]benzene (PIFA) Mediated Oxidative ipso Nitration of Organoboronic Acids

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1. General information

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvent (CH$_3$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, dd for doublet of doublet, t for triplet, and m for multiplet.
2. Syntheses and Characterizations of the Aromatic and Aliphatic Nitro Compounds

General procedure for syntheses of aromatic, heteroaromatic and aliphatic nitro compounds:

To a stirred solution of appropriate organoboronic acids (0.5 mmol, 1.0 eq.) in CH$_3$CN, PIFA (1.5 mmol, 3 eq.), NBS (1 mmol, 2 eq.) and NaNO$_2$ (1.5 mmol, 3 eq.) were added and the mixture was stirred for 3 h. After completion of the reaction (checked by TLC), the mixture was concentrated under vacuum. It was then washed with distilled water (3×4 mL) and extracted with CH$_2$Cl$_2$ (3×7 mL). The combined organic phase was dried over Na$_2$SO$_4$ and 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:

Nitrobenzene (2a)$^1$: 2a was obtained as a pale yellow liquid (82%, 50.4 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.20 (dd, $J$ = 8.7 Hz, 0.9 Hz, 2H), 7.69 (tt, $J$ = 7.3 Hz, 1.4 Hz, 1H), 7.55-7.50 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.1, 134.7, 129.4, 123.5; GC-MS (m/z): 123 [M$^+$]

3-Nitrotoluene (2b)$^1$: 2b was obtained as a yellowish liquid (93%, 63.7 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.99 (d, $J$ = 8.2, 2H), 7.48 (d, $J$ = 7.3 Hz, 1H), 7.39(t, $J$ = 7.8 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.2, 139.8,135.4, 129.11, 123.9, 120.4, 21.3; GC-MS (m/z): 137 [M$^+$].

2-Nitrotoluene (2c)$^1$: 2c was obtained as a pale yellow liquid (90%, 61.6 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.90 (d, $J$ = 8.7, 1H), 7.45 (t, $J$ = 7.6, 1H),
7.27-7.30 (m, 2H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.1, 133.5, 133.0, 132.7, 126.9, 124.5, 20.1; GC-MS (m/z): 137 [M$^+$]

![2d](image)

1, 3 Dimethyl-2-Nitrobenzene (2d)$^1$: 2d was obtained as a yellow liquid (89%, 67.2 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.14 (t, $J$ = 7.8 Hz, 1H), 7.00 (d, $J$ = 7.8 Hz, 2H), 2.19 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.7, 130.0, 129.4, 128.9, 17.4; GC-MS (m/z): 151 [M$^+$]

![2e](image)

4-Nitrotoluene (2e)$^1$: 2e was obtained as a pale yellow crystalline solid (92%, 63.0 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.10 (d, $J$ = 8.7 Hz, 2H), 7.31 (d, $J$ = 8.2, 2H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.1, 129.9, 123.6, 21.7; (one peak wasn’t observed); GC-MS (m/z): 137 [M$^+$]

![2f](image)

3,4-Dimethoxy nitrobenzene (2f)$^1$: 2f was obtained as a yellow crystalline powder (92%, 84.2 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (dd, $J$ = 9.2 Hz, 0.7 Hz, 1H), 7.74 (d, $J$ = 2.3 Hz, 1H), 6.91 (d, $J$ = 9.2 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.6, 148.9, 141.5, 117.9, 109.9, 106.4, 56.6, 56.4; GC-MS (m/z): 183 [M$^+$]

![2g](image)

1-Nitronaphthalene (2g)$^1$: 2g was obtained as a yellow crystalline powder (88%, 76.1 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.55 (d, $J$ = 8.7 Hz, 1H), 8.22 (d, $J$ = 7.4 Hz, 1H), 8.11 (d, $J$ = 8.2 Hz, 1H), 7.94 (d, $J$ = 8.2 Hz, 1H), 7.71 (t, $J$ = 8.2 Hz, 1H), 7.61 (t, $J$ = 6.9 Hz, 1H), 7.53 (t, $J$ = 8.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.5, 134.8, 134.4, 129.6, 128.7, 127.4, 125.2, 124.2, 124.1, 123.2; GC-MS (m/z): 173 [M$^+$]
3-Nitrobenzenetrifluoride (2h): 2h was obtained as a clear yellow liquid (80%, 76.4 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.40 (d, $J = 9.2$ Hz, 2H), 7.96 (d, $J = 7.8$ Hz, 1H), 7.75 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.8, 132.2 (q, $J_{C-F} = 34.3$ Hz), 131.2 (d, $J_{C-F} = 1.91$ Hz), 130.5, 124.3, 121.6, 120.7 (d, $J_{C-F} = 3.82$ Hz), 118.9; GC-MS (m/z): 191 [M$^+$]

1, 3-Dinitrobenzene (2i): 2i was obtained as a yellow crystalline powder (87%, 73.1 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 9.07 (s, 1H), 8.58 (dd, $J = 8.2$ Hz, 0.5 Hz, 2H), 7.82 (t, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.6, 130.8, 129.0, 119.2; GC-MS (m/z): 168 [M$^+$]

2-Nitrobenzaldehyde (2j): 2j was obtained as a pale yellow crystalline powder (91%, 68.7 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 10.4 (s, 1H), 8.12 (dd, $J = 7.8$ Hz, 1.4 Hz, 1H), 7.95 (dd, $J = 7.4$ Hz, 1.8 Hz, 1H), 7.74-7.82 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 188.8, 134.2, 133.8, 131.5, 129.8, 124.6, 29.8; GC-MS (m/z): 151 [M$^+$]

4-Nitroacetophenone (2k): 2k was obtained as a pale yellow semisolid (94%, 77.5 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.31 (d, $J = 8.7$ Hz, 2H), 8.11 (d, $J = 8.3$ Hz, 2H); GC-MS (m/z): 165 [M$^+$]
4-Nitrobenzonitrile (2l): 2l was obtained as a pale yellow crystalline powder (90%, 66.6 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.36 (d, J = 8.9 \text{ Hz}, 2\text{H}), 7.89 (d, J = 8.9 \text{ Hz}, 2\text{H})\); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 150.1, 133.6, 124.5, 118.4, 116.9\); GC-MS (m/z): 148 [M\(^+\)]

4-Bromo-1-nitrobenzene (2m): 2m was obtained as a pale yellow semisolid (92%, 92.4 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.10 (d, J = 8.5 \text{ Hz}, 2\text{H}), 7.69 (d, J = 8.7 \text{ Hz}, 2\text{H})\); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 134.4, 132.8, 130.1, 125.2\); GC-MS (m/z): 201 [M\(^+\)]

2-Flouro-1-nitrobenzene (2n): 2n was obtained as a yellowish brown liquid (80%, 56.4 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.01-8.05 (m, 1\text{H}), 7.62-7.68 (m, 1\text{H}), 7.28-7.32 (m, 2\text{H})\); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 155.4 (d, J_{C-F} = 263.2 \text{ Hz}), 135.8 (d, J_{C-F} = 8.6 \text{ Hz}), 126.1 (d, J_{C-F} = 2.86 \text{ Hz}), 124.7 (d, J_{C-F} = 3.82 \text{ Hz}), 118.4 (d, J_{C-F} = 20.02 \text{ Hz})\); GC-MS (m/z): 141 [M\(^+\)]

(2-Nitroethyl) benzene (2o): 2o was obtained as a colourless liquid (90%, 68.0 mg) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(7.31-7.35 (m, 2\text{H}), 7.27-7.28 (m, 1\text{H}), 7.22-7.23 (m, 2\text{H}), 4.64 (t, J = 6.9 \text{ Hz}, 2\text{H}), 3.02 (t, J = 7.3 \text{ Hz}, 2\text{H})\); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 136.3, 128.7, 127.1, 73.4, 33.4, 29.7\); GC-MS (m/z): 151 [M\(^+\)]
2-Nitropropane (2p): 2p was obtained as a colourless liquid (74%, 131.7 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): 4.56-4.63 (m, 1H), 1.49 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 78.6, 20.7; GC-MS (m/z): 89 [M$^+$]

2-Chloro-5-nitropyridine (4a): 4a was obtained as a light yellow solid (83%, 65.6 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): 9.24 (d, $J = 2.3$ Hz, 1H), 8.45 (dd, $J = 8.7$ Hz, 2.8 Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.1, 145.3, 143.7, 133.7, 125.0; GC-MS (m/z): 158 [M$^+$]

8-Nitroquinoline (4b): 4b was obtained as a light yellow crystalline powder (84%, 73.1 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.06 (dd, $J = 4.1$ Hz, 1.4 Hz, 1H), 8.26 (dd, $J = 8.7$ Hz, 1.8 Hz, 1H), 8.04 (d, $J = 7.8$ Hz, 2H), 7.54-7.63 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.6, 139.6, 136.3, 132.2, 129.3, 125.4, 123.9, 122.9; GC-MS (m/z): 174 [M$^+$]

1-Nitro-4,10-dihydro-thianthrene (4c): 4c was obtained as a dark yellow powder (83%, 108.3 mg) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.28 (dd, $J = 7.8$ Hz, 1.4 Hz, 1H), 7.99 (dt, 8.2 Hz, 1.4 Hz, 2H), 7.78 (t, $J = 7.8$ Hz, 1H), 7.62-7.67 (m, 2H), 7.46-7.50 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$131.0, 130.6, 130.4, 129.6, 129.3, 128.8, 128.2, 126.8, 126.2, 125.1, 124.4, 124.3; GC-MS (m/z): 261 [M$^+$]. This compound could not be obtained in perfectly pure condition; an inseparable impurity always remains there. The reported yield is along with the impurity associated with it.
2,3-Dihydro-6-nitro-1,4-benzdioxin (4d): 4d was obtained as a light yellow solid (85%, 76.9 mg) following the general procedure. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.77 (dd, \( J = 7.3 \) Hz, 2.3 Hz, 2H), 6.93 (dd, \( J = 7.3 \) Hz, 2.8 Hz, 1H), 4.36-4.30 (m, 4H); \( ^13C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 149.8, 143.3, 141.9, 117.8, 117.4, 113.7, 64.8, 64.2; GC-MS (m/z): 181 [M\(^+\)]

References:


Radical Scavenging Experiment: Successful nitrination with PIFA-NBS-NaNO$_2$ in the absence of TEMPO whereas no nitrination took place in the presence of TEMPO with the other reaction conditions remaining unaltered.

![Chemical reaction diagram]

No peak at m/z = 137, was observed.
NO₂
F
2n
(Mass fragmentation of 4c obtained from GCMS instrument)