Supporting Information

Efficient ipso-nitration of arylboronic acids with iron nitrate as the nitro source

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General experimental procedures

All reagents and solvents were obtained from commercial suppliers and used without further purification. Fe(NO₃)₃·9H₂O was purchased from Sigma-Aldrich, and other reagents were purchased from Beijing Ouhe Technology Ltd. Co.. All reagents were weighed and handled in air at room temperature. Flash chromatography was performed on silica gel (200 ~ 300 mesh). Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded using tetramethylsilane (TMS) in solvent of CDCl₃ as the internal standard (¹H NMR: TMS at 0.00 ppm, CHCl₃ at 7.24 ppm, ¹³C NMR: CDCl₃ at 77.1 ppm) or using tetramethylsilane (TMS) in the solvent of DMSO-d₆ as the internal standard (¹H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm, ¹³C NMR: DMSO at 40.0 ppm).

General procedure for synthesis of nitroarenes (2a-v)

A 10 mL schlenk tube equipped with a magnetic stirrer, Fe(NO₃)₃·9H₂O (0.5 mmol, 202 mg), aromatic boronic acid (1 mmol), toluene (1.5 mL) were added to the tube, and the tube with an N₂ ballon (1 atm) was sealed and put into a pre-heated oil bath at 80 °C for 18 h. After the resulting solution was cooled to room temperature, toluene was removed by a vacuum, and the residue was purified by a column chromatography on silica gel to provide the desire product.

The characterization data of compounds 2a-v

Nitrobenzene (2a).¹ Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield 92% (113 mg). ¹H NMR (CDCl₃, 600 MHz) δ 8.16 (d, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.52 (t, 2H, J = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) 147.7, 134.3, 128.9, 122.9. GC-MS 123.1.

4-Nitrotoluene (2b).¹ Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 92% (126.1 mg), mp 51 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.08 (d, 2H, J = 8.7 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.52 (t, 2H, J = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) 147.7, 134.3, 128.9, 122.9.
GC-MS m/z 137.1.

2, 6-Dimethyl-1-Nitrobenzene (2c).\(^2\) Eluent: Ethyl acetate/petroleum ether (1:100). Colorless oil. Yield 60% (90.6 mg). 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.23 (t, 1H, \(J = 7.33\) Hz), 7.09 (d, 2H, \(J = 7.33\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 152.03, 130.04, 129.52, 128.9, 17.46. GC-MS m/z 151.2.

1-Isopropyl-4-Nitrobenzene (2d).\(^3\) Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield 88% (145.4 mg). 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.06 (d, 2H, \(J = 8.7\) Hz), 7.29 (d, 2H, \(J = 8.7\) Hz), 2.94 (m, 1H), 1.2 (d, 2H, \(J = 6.87\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 155.7, 145.4, 126.4, 122.8, 33.4, 22.7. GC-MS m/z 165.2.

3-Nitroanisole (2e).\(^1\) Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 87% (133.2 mg), mp 34°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.83 (dd, 1H, \(J = 2.1, 8.3\) Hz), 7.74 (dd, 2H, \(J = 2.8, 8.3\) Hz), 7.43 (t, 1H, \(J = 8.3\) Hz), 7.23 (dd, 1H, \(J = 2.8, 8.3\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 160.2, 149.3, 130.0, 121.3, 115.8, 108.2, 55.9. GC-MS m/z 153.1.

4-Nitrobenzylalcohol (2f).\(^1\) Eluent: Ethyl acetate/petroleum ether (1:10). Yellow solid. Yield 78% (119.3 mg), mp 90°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.16 (d, 2H, \(J = 8.7\) Hz), 7.5 (d, 2H, \(J = 8.7\) Hz), 4.81 (s, 2H), 2.09 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 148.3, 147.3, 127.1, 123.8, 64.0. GC-MS m/z 153.1.

4-Fluoronitrobenzene (2g).\(^1\) Eluent: Ethyl acetate/petroleum ether (1:100). Yellow oil. Yield
85% (119.1 mg). 1H NMR (CDCl$_3$, 600MHz) $\delta$ 8.28 (m, 2H), 7.22 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) 167.6, 165.0, 144.3, 126.4, 126.3, 116.6, 116.3. 19F NMR (CDCl$_3$, 400MHz) 101.87. GC-MS m/z 141.1.

2-Nitrochlorobenzene (2h).\textsuperscript{4} Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 68% (106.8mg), mp 30 °C. 1H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.85 (d, 1H, $J = 8.24$ Hz), 7.52 (m, 2H), 7.40 (t, 1H, $J = 8.24$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz) 148.0, 133.3, 131.9, 127.7, 127.1, 125.7. GC-MS m/z 157.5.

3-Nitrochlorobenzen (2i).\textsuperscript{1} Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 88% (138.7mg), mp 42 °C. 1H NMR (CDCl$_3$, 600MHz) $\delta$ 8.24 (s, 1H), 8.14 (d, 1H, $J = 8.3$ Hz), 7.69 (d, 1H, $J = 8.3$ Hz), 8.14 (t, 1H, $J = 8.3$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz) 148.7, 135.5, 134.8, 130.5, 123.9, 121.8. GC-MS m/z 157.5.

1-Bromo-2-nitrobenzene (2j).\textsuperscript{1} Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 72% (145.5 mg), mp 38 °C. 1H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.84 (d, 1H, $J = 7.6$ Hz), 7.75 (d, 1H, $J = 8.3$ Hz), 7.46 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz) 149.8, 135.1, 133.3, 128.3, 125.7, 114.5. GC-MS m/z 202.0.

1-Bromo-4-nitrobenzene (2k).\textsuperscript{5} Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 89% (179.2mg), mp 120 °C. 1H NMR (CDCl$_3$, 600MHz) $\delta$ 8.09 (d, 2H, $J = 8.25$ Hz), 7.68 (d, 2H, $J = 8.25$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz) GC-MS m/z=202.0.
2-Nitroaniline (2l).\(^1\) Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 60% (82.8 mg), mp 110°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.57 (d, 1H, \(J = 8.2\) Hz), 7.49 (s, 1H), 7.27 (t, 1H, \(J = 8.2\) Hz), 6.95 (d, 2H, \(J = 8.2\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 149.3, 147.5, 130.0, 120.7, 113.2, 109.1. GC-MS m/z 138.1.

4-Nitroaniline (2m).\(^6\) Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 60% (82.8 mg), mp 145°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.06 (d, 2H, \(J = 8.94\) Hz), 6.61 (d, 2H, \(J = 8.94\) Hz), 4.28 (s, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 152.6, 152.5, 126.4, 113.4. GC-MS m/z 138.1.

3-Nitrophenol (2n).\(^7\) Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 70% (97.4 mg), mp 40°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 10.57 (s, 1H), 8.09 (d, 1H, \(J = 8.24\) Hz), 7.57 (t, 1H, \(J = 7.79\) Hz), 7.14 (t, 1H, \(J = 8.7\) Hz), 6.98 (t, 1H, \(J = 7.79\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 155.2, 137.6, 133.7, 125.2, 120.3, 120.0. GC-MS m/z 139.1.

4-Nitrophenol (2o).\(^8\) Eluent: Ethyl acetate/petroleum ether (1:15). Yellow solid. Yield 90% (125.2 mg), mp 111°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.16 (d, 2H, \(J = 9.16\) Hz), 6.92 (d, 2H, \(J = 9.16\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 161.6, 141.6, 126.4, 115.8. GC-MS m/z 139.1.

4-Nitrobenzaldelyde (2p).\(^1\) Eluent: Ethyl acetate/petroleum ether (1:80). Yellow solid. Yield 74% (111.7 mg), mp 101°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 10.17 (s, 1H), 8.40 (d, 2H, \(J = 8.3\) Hz), 8.08 (d, 2H, \(J = 8.3\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 190.4, 151.1, 140.1, 130.5, 124.4.
4-Nitrobenzonic acid (2q).\textsuperscript{1} Eluent: Ethyl acetate/petroleum ether (1:2.5). Yellow solid. Yield 82\% (137.0 mg), mp 236°C. \( ^1 \text{H} \) NMR (CDCl\textsubscript{3}, 600 MHz) \( \delta \) 13.72 (s, 1H), 8.33 (d, 2H, \( J = 8.7 \) Hz), 8.18 (d, 2H, \( J = 8.7 \) Hz). \( ^{13} \text{C} \) NMR (CDCl\textsubscript{3}, 100 MHz) 166.3, 150.5, 136.9, 131.2, 124.2. GC-MS m/z 167.1.

3-Nitrobenzonic acid (2r).\textsuperscript{1} Eluent: Ethyl acetate/petroleum ether (1:2.5). Yellow solid. Yield 75\% (125.30 mg), mp 138°C. \( ^1 \text{H} \) NMR (CDCl\textsubscript{3}, 600 MHz) \( \delta \) 13.76 (s, 1H), 8.62 (d, 2H, \( J = 1.4 \) Hz), 8.47 (dd, 1H, \( J = 1.4, 8.3 \) Hz), 8.35 (d, 1H, \( J = 7.6Hz \)), 7.82 (dd, 1H, \( J = 8.3, 7.6 \) Hz) \( ^{13} \text{C} \) NMR (CDCl\textsubscript{3}, 100 MHz) 166.0, 148.4, 135.8, 132.9, 131.0, 127.8, 124.2. GC-MS m/z 167.1.

Methyl-4-Nitrobenzoate (2s).\textsuperscript{2} Eluent: Ethyl acetate/petroleum ether (1:5). Yellow solid. Yield 86\% (155.7 mg), mp 95°C. \( ^1 \text{H} \) NMR (CDCl\textsubscript{3}, 600 MHz) \( \delta \) 8.30 (d, 2H, \( J = 8.7 \) Hz), 8.22 (d, 2H, \( J = 8.7 \) Hz), 3.99 (s, 3H). \( ^{13} \text{C} \) NMR (CDCl\textsubscript{3}, 100 MHz) 165.2, 150.5, 135.5, 130.8, 123.6, 52.9. GC-MS m/z 181.2.

Methyl-3-Nitrobenzoate (2t).\textsuperscript{9} Eluent: Ethyl acetate/petroleum ether (1:5). Yellow solid. Yield 78\% (141.2 mg), mp 79°C. \( ^1 \text{H} \) NMR (CDCl\textsubscript{3}, 600 MHz) \( \delta \) 8.87 (s, 1H), 8.40 (m, 2H), 7.66 (t, 1H, \( J = 7.79 \) Hz), 3.99 (s, 3H). \( ^{13} \text{C} \) NMR (CDCl\textsubscript{3}, 100 MHz) 165.0, 148.3, 135.4, 131.9, 129.7, 127.4, 124.7, 52.9. GC-MS m/z 181.2.
1-Nitronophthalene (2u).\(^5\) Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 82% (141.9 mg), mp 55°C. 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.55 (d, 1H, \(J = 8.24\) Hz), 8.21 (d, 1H, \(J = 7.79\) Hz), 7.10 (d, 1H, \(J = 8.24\) Hz), 7.94 (d, 1H, \(J = 8.24\) Hz), 7.70 (m, 1H), 7.71 (m, 1H), 7.52 (d, 1H, \(J = 7.79\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 146.6, 134.8, 134.4, 129.5, 128.7, 127.4, 125.2, 124.2, 124.1, 123.2. GC-MS m/z 173.2.

Dibenzo[\(b,d\)]furan (2v).\(^7\) Eluent: Ethyl acetate/petroleum ether (1:100). Yellow solid. Yield 78% (166.1 mg), mp 96°C 1H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 8.27 (d, 1H, \(J = 8.25\) Hz), 8.23 (d, 1H, \(J = 7.56\) Hz), 7.98 (d, 1H, \(J = 7.56\) Hz), 7.94 (d, 1H, \(J = 8.24\) Hz), 7.73 (m, 1H, \(J = 8.25\) Hz), 7.56 (t, 1H, \(J = 7.22\) Hz), 7.45 (m, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 156.8, 148.5, 133.9, 128.8, 128.3, 126.9, 124.0, 122.9, 122.6, 122.2, 120.8, 112.4. GC-MS m/z 213.0.

EPR measurement

The EPR measurement was performed on a X-band EPR (10.0 GHz) instrument JES FA200 (JEOL). The mixture of 4-methylphenyl boronic acid (0.1 mmol) and Fe(NO\(_3\))\(_3\) (0.05 mmol) in 0.5 mL of toluene was added into an EPR tube. Conditions of EPR measurements were as follows: microwave power (1 mW), central field (250 mT), magnetic width (150 mT), modulation width (0.2 mT), time constant (0.3 s), measure time (4 min) in Figure 1 in text. Conditions of EPR measurements were as follows: microwave power (10 mW), central field (323 mT), magnetic width (4 mT), modulation (0.03 mT), time constant (0.3 s), measurement time (8 min) in Figure 2 in text. The simulation of the hyperfine structure on the free radical was taken by the ISO-SIMU software from JEOL company. Based on the measurement spectrum and references\(^{[10]}\), the simulation parameters are as follows: \(A_N = 1.001\) mT, \(A_{11}^{11B} = 0.190\) mT, \(A_{10}^{10B} = 0.064\) mT, \(A_{ortho}^H = 0.185\) mT, \(A_{meta}^H = 0.81\) mT, \(A_{methyl}^H = 0.205\) mT.
References

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