Supporting Information

Photo-induced Reduction of Nitrobenzenes to Primary Aromatic Amines

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Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise specified. Purified compounds were further dried under high vacuum (0.01-0.05 Torr). All the photoreactions were carried out in quartz tube under UV irradiation (306 nm) by using Photochemical Reactor PR-2000 from PANCHUM. Yields refer to purified and spectroscopically pure compounds. Thin layer chromatography (TLC) was performed using Merck TLC Aluminum sheets silica gel 60 F254 plates and visualized by fluorescence quenching under UV light and KMnO4 stain. Flash chromatography was performed using silica gel (230-400 mesh) purchased by Merck. NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 300 MHz for 1H and 75 MHz for 13C, Bruker AVANCE II operating at 400 MHz for 1H and 100 MHz for 13C acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. The following solvent chemical shifts were used as reference values (ppm): CDCl3 = 7.26 (1H), 77.0 (13C); (CD3)2SO 2.50 (1H), 39.52 (13C). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained on JMS-700 at the National Central University or Bruker Daltonics Esquire 2000 spectrometers at the Chung Yuan Christian University Mass Spectrometry Facilities.

All of the nitroarene are commercial available purchased from Alfa, Aldrich, Acros and TCI.

**General procedure I for the photo-induced reduction in isopropanol**: Nitroarene (20 mg) was added into 20 mL isopropanol. The quartz tube containing the solution was degassed by ultrasonic cleaner for 1 h prior to use. The reaction was stirred at room temperature under UV irradiation (306 nm). Consumption of starting material was monitored by TLC. Solvent was removed under reduced pressure and the crude mixture was transferred to a separatory funnel containing 1 M HCl. The aqueous layer was extracted two times with dichloromethane. The aqueous layer was then basified using 1 N NaOH and extracted two times with ethyl acetate. The combined organic layers were washed with brine, dried (MgSO4) and concentrated to provide the desired primary aromatic amines.

**General procedure II for the photo-induced reduction in THF**: Nitroarene (50 mg) was added into 25 mL THF. The quartz tube containing the solution was degassed by ultrasonic cleaner for 1 h prior to use. The reaction was stirred at room temperature under UV irradiation (306 nm). Consumption of starting material was monitored by TLC. The reaction mixture was transferred to a flask which was contained Al2O3 (5 g) and then reflux until the intermediate was consumed. Solvent was removed under reduced pressure and the crude mixture was transferred to a separatory funnel containing 1 M HCl. The aqueous layer was extracted two times with dichloromethane. The aqueous layer was then basified using 1 N NaOH and extracted two times with ethyl acetate. The combined organic layers were washed with brine, dried (MgSO4) and concentrated to provide the desired primary aromatic amines.
Experimental Data

Compound Characterization

4-aminobenzonitrile (2a)

Following the general procedure I, using 4-nitrobenzonitrile (20.0 mg, 0.135 mmol), provided the title compound 12 mg (75% yield) as a yellowish powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.41 (d, $J = 8.6$ Hz, 2H), 6.64 (d, $J = 8.7$ Hz, 2H), 4.11 (s, 2H).

3-aminobenzonitrile (2b)

Following the general procedure I, using 3-nitrobenzonitrile (20.0 mg, 0.135 mmol), provided the title compound 5 mg (63% yield) as a yellowish powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.22 (t, 1H, $J = 7.9$ Hz), 7.02 (d, 1H, $J = 7.6$ Hz), 6.90-6.85 (m, 2H), 3.85 (s, 2H).

2-aminobenzonitrile (2c)

Following the general procedure I, using 2-nitrobenzonitrile (20.0 mg, 0.135 mmol), provided the title compound 4 mg (50% yield) as a yellowish powder.
Following the **general procedure II**, using 2-nitrobenzonitrile (50.0 mg, 0.338 mmol), provided the title compound 30 mg (75% yield) as a yellowish powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 $^\circ$C, $\delta$): 7.42-7.30 (m, 2H), 6.77-6.72 (m, 2H), 6.64 (d, $J = 8.7$ Hz, 2H), 4.38 (s, 2H).

1-(4-aminophenyl)ethanone (2d)$^1$

Following the **general procedure I**, using 1-(4-nitrophenyl)ethanone (20.0 mg, 0.121 mmol), provided the title compound 10 mg (57% yield) as a yellowish powder.

Following the **general procedure II**, using 1-(4-nitrophenyl)ethanone (50.0 mg, 0.303 mmol), provided the title compound 43 mg (70% yield) as a yellowish powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 $^\circ$C, $\delta$): 7.80 (d, $J = 8.6$ Hz, 2H), 6.65 (d, $J = 8.3$ Hz, 2H), 4.10 (s, 2H), 2.51 (s, 3H).

1-(3-aminophenyl)ethanone (2e)$^3$

Following the **general procedure I**, using 1-(3-nitrophenyl)ethanone (20.0 mg, 0.121 mmol), provided the title compound 9 mg (52% yield) as a yellowish powder.

Following the **general procedure II**, using 1-(3-nitrophenyl)ethanone (50.0 mg, 0.303 mmol), provided the title compound 23 mg (52% yield) as a yellowish powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 $^\circ$C, $\delta$): 7.34-7.20 (m, 3H), 6.87 (d, $J = 7.8$ Hz, 1H), 3.28 (s, 2H).

methyl 4-aminobenzoate (2g)$^2$

Following the **general procedure I**, using methyl 4-nitrobenzoate (20.0 mg, 0.110 mmol), provided the title compound 9 mg (54% yield) as a white powder.
Following the general procedure II, using methyl 4-nitrobenzoate (50.0 mg, 0.276 mmol), provided the title compound 30 mg (72% yield) as a white powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.85 (d, $J = 8.5$ Hz, 2H), 6.64 (d, $J = 8.5$ Hz, 2H), 4.11 (s, 2H).

methyl 3-aminobenzoate (2h)$^4$

Following the general procedure I, using methyl 3-nitrobenzoate (20.0 mg, 0.110 mmol), provided the title compound 8 mg (48% yield) as a white powder.

Following the general procedure II, using methyl 3-nitrobenzoate (50.0 mg, 0.276 mmol), provided the title compound 24 mg (58% yield) as a white powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.42 (d, $J = 7.5$ Hz, 1H), 7.35 (s, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 6.86 (dd, $J = 8.1$, 7.8 Hz, 1H), 3.89 (s, 3H), 3.80 (s, 2H).

4-nitroaniline (2j)$^4$

Following the general procedure I, using 1,4-dinitrobenzene (20.0 mg, 0.119 mmol), provided the title compound 12 mg (73% yield) as a pale yellow powder.

Following the general procedure II, using 1,4-dinitrobenzene (50.0 mg, 0.297 mmol), provided the title compound 32 mg (78% yield) as a pale yellow powder.

NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.85 (d, $J = 8.5$ Hz, 2H), 6.64 (d, $J = 8.5$ Hz, 2H), 4.11 (s, 2H).

4-aminobenzoic acid (2k)$^1$

Following the general procedure I, using 4-nitrobenzoic acid (20.0 mg, 0.120 mmol), provided the title compound 27 mg (65% yield) as a pale yellow powder.

Following the general procedure II, using 4-nitrobenzoic acid (50.0 mg, 0.299 mmol), could not
provide the title compound.
NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 7.23 (d, $J = 8.5$ Hz, 2H), 6.62 (d, $J = 8.5$ Hz, 2H).

4-methoxyaniline (2l)$^2$

Following the general procedure I, using 1-methoxy-4-nitrobenzene (20.0 mg, 0.131 mmol), provided the title compound 13 mg (81% yield) as a pale yellow powder.
Following the general procedure II, using 1-methoxy-4-nitrobenzene (50.0 mg, 0.327 mmol), could not provide the title compound.
NMR Spectroscopy: $^1$H NMR (300 MHz, CDCl$_3$, 24 °C, δ): 6.79 (d, $J = 8.6$ Hz, 2H), 6.61 (d, $J = 8.6$ Hz, 2H), 3.72 (s, 3H), 3.59 (s, 2H).

4-aminobenzenesulfonamide (2p)$^4$

Following the general procedure I, using 4-nitrobenzenesulfonamide (20.0 mg, 0.131 mmol), provided the title compound trace as a pale yellow powder.
Following the general procedure II, using 4-nitrobenzenesulfonamide (50.0 mg, 0.327 mmol), provide the title compound in 58% NMR yield (using the nitromethane as the internal standard).
NMR Spectroscopy: $^1$H NMR (300 MHz, CD$_3$OD, 24 °C, δ): 7.57 (d, $J = 8.9$ Hz, 2H), 6.68 (d, $J = 8.9$ Hz, 2H).
References

Spectroscopic Data

$^1$H NMR of 2a, CDCl$_3$, 300 MHz, 24 °C

$^1$H NMR of 2b, CDCl$_3$, 300 MHz, 24 °C
1H NMR of 2c, CDCl₃, 300 MHz, 24 °C

1H NMR of 2d, CDCl₃, 300 MHz, 24 °C
$^1$H NMR of 2e, CDCl$_3$, 300 MHz, 24 °C

$^1$H NMR of 2g, CDCl$_3$, 300 MHz, 24 °C
$^1$H NMR of 2h, CDCl$_3$, 300 MHz, 24 °C

$^1$H NMR of 2j, CDCl$_3$, 300 MHz, 24 °C
$^1$H NMR of 2k, CDCl$_3$, 300 MHz, 24 °C

$^1$H NMR of 2l, CDCl$_3$, 300 MHz, 24 °C
$^1$H NMR of 2p, CDCl$_3$, 300 MHz, 24 °C