

## Electronic Supplementary Information

### The Selective Reduction of Nitroarenes to N-arylhydroxylamines using Zn in CO<sub>2</sub>/H<sub>2</sub>O System

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#### Characterisation data for the products

##### HPLC data for the mixture after the reaction of nitrobenzene

Eluent: water (solvent A) + methanol (solvent B), a linear gradient of 50% of B to 100% over 30 min, UV detector: 254 nm, flow rate: 1.0 mL min<sup>-1</sup>, retention time: N-phenylhydroxylamine, 4.9 min; aniline, 5.7 min; nitrobenzene, 11.1 min; azoxybenzene, 24.7 min.

##### Characteristic data of N-arylhydroxylamines

**N-phenylhydroxylamine** mp 80 - 81 °C. (lit.,<sup>s1</sup> 81 °C).  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)<sup>s2</sup> 6.32 (2 H, br s, NH and OH), 6.97 - 7.00 (3 H, m, 2-H, 4-H and 6-H), 7.23- 7.29 (2 H, m, 3-H and 5-H).

**N-(4-chlorophenyl) hydroxylamine** mp 83 - 84 °C. (lit.,<sup>s1</sup> 86 °C).  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)<sup>s3</sup> 6.01 (2 H, br s, NH and OH), 6.92 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.8, A-H and A'-H), 7.23 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.8, X-H and X'-H).

**N-(4-acetophenyl) hydroxylamine** mp 116 - 117 °C. (lit.,<sup>s4</sup> 110 - 116 °C).  $\delta_{\text{H}}$  (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si)<sup>s5</sup> 2.50 (3 H, s, COMe), 6.93 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.4, A-H and A'-H), 7.82 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.4, X-H and X'-H), 8.16 (1 H, s, OH), 8.49 (1 H, s, NH).

**N-(4-cyanophenyl) hydroxylamine** mp 85 - 86 °C. (lit.,<sup>s6</sup> 86 °C).  $\delta_{\text{H}}$  (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si)<sup>s5</sup> 6.85 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.8, A-H and A'-H), 7.55 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.8, X-H and X'-H), 8.76 (1 H, s, OH), 9.11 (1 H, s, NH).

**N-(3-nitrophenyl) hydroxylamine** mp 118 - 119 °C. (lit.,<sup>S7</sup> 120 - 121 °C).  $\delta_{\text{H}}$  (400 MHz; DMSO- $d_6$ ; Me<sub>4</sub>Si)<sup>S3</sup> 7.21 (1 H, br d,  $J$  8.0, 6-H), 7.44 (1 H, t,  $J$  8.0, 5-H), 7.59 (1 H, br d,  $J$  8.0, 4-H), 7.63 (1 H, br s, 2-H), 8.76 (1 H, s, NH), 8.88 (1 H, s, OH).

**N-(*p*-tolyl) hydroxylamine** mp 82 - 84 °C. (lit.,<sup>S7</sup> 81 - 85 °C).  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si)<sup>S8</sup> 2.29 (3 H, s, Me), 6.70 (2 H, br s, NH and OH), 6.89 (2 H, pseudo-q,  $J_{\text{AX}}+J_{\text{AX}'}$  8.0, A-H and A'-H), 7.07 (2 H, pseudo-quarted,  $J_{\text{AX}}+J_{\text{AX}'}$  8.0, X-H and X'-H).

## References

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