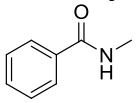
Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

General comments: All reactions were carried out under air. $ZnBr_2$, pyridine, *tert*-butyl hydroperoxide (70% in water) and all the substrates were purchased from Aldrich and used as received. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 μm film thickness) using helium carrier gas.

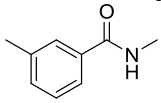
General procedure for the oxidation of *N*-methyl benzylamine *N*-methyl benzamide: In a 50 mL reaction tube, $ZnBr_2$ (10 mol%) and a stirring bar was added. And followed by the addition of *N*-methylbenzyl amine (1 mmol) and pyridine (0.1 mL) by syringe, at the end *tert*-butyl hydroperoxide (3 mmol; 70% aqueous) was added in one pot to the solution and keep the final solution at 80°C for 16 hours. Then cool it down to room temperature, the reaction tube was washed three times with ethyl acetate (3 ml). The combined organic solutions were evapotated with adsorption on silica gel and the crude product was purified by column chromatography using n-heptane/AcOEt (4:1-1:1) as the eluent.

***N*-Methylbenzamide**



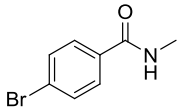
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65-7.72 (m, 2H), 7.30-7.44 (m, 3H), 6.27 (br s, 1H), 2.93 (d, 3H, *J* = 4.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 134.6, 131.4, 128.6, 126.9, 26.9.

***N*,3-dimethylbenzamide**



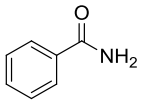
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.52 (m, 2H), 7.18-7.22 (m, 2H), 6.44 (bs, 1H), 2.90 (d, 3H, *J* = 4.9 Hz), 2.29 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 138.4, 134.6, 132.1, 128.4, 127.7, 123.9, 26.8, 21.4.

4-Bromo-*N*-methylbenzamide



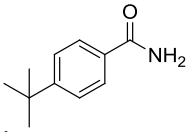
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.64 (m, 4H), 6.24 (bs, 1H), 2.92 (d, 3H, *J* = 4.8 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 133.4, 131.8, 128.5, 126.1, 26.9.

Benzamide



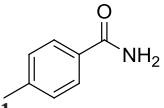
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73-7.80 (m, 2H), 7.34-7.51 (m, 3H), 6.04 (bs, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.9, 133.3, 132.1, 128.7, 127.4.

4-*tert*-Butylbenzamide



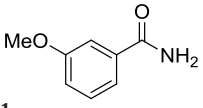
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 2H, *J* = 8.6 Hz), 7.37 (d, 2H, *J* = 8.8 Hz), 6.21 (bs, 2H), 1.26 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 155.6, 130.5, 127.3, 125.6, 35.0, 31.2.

4-Methylbenzamide



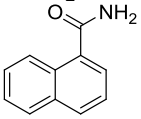
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 2H, *J* = 8.3 Hz), 7.17 (d, 2H, *J* = 7.9 Hz), 6.09 (bs, 2H), 2.33 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 142.6, 130.5, 129.3, 127.4, 21.5.

3-Methoxybenzamide



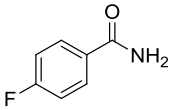
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23-7.36 (m, 3H), 6.93-7.05 (m, 1H), 6.05 (bs, 2H), 3.78 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 159.9, 134.8, 129.7, 119.2, 118.3, 112.6, 55.5.

1-Naphthamide



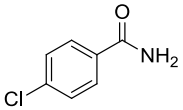
^{1}H NMR (300 MHz, $DMSO^{d6}$): δ 8.31-8.41 (m, 1H), 7.97-8.11 (m, 3H), 7.55-7.72 (m, 5H).
^{13}C NMR (75 MHz, $DMSO^{d6}$): δ 170.5, 134.6, 133.1, 129.72, 129.66, 128.1, 126.6, 126.1, 125.5, 125.1, 124.9.

4-Fluorobenzamide



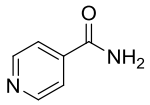
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (dd, 2H, J^1 = 8.9 Hz, J^2 = 5.3 Hz), 7.06 (t, 2H, *J* = 7.1 Hz), 5.99 (bs, 2H).

4-Chlorobenzamide



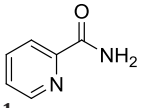
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 2H, *J* = 8.7 Hz), 7.36 (d, 2H, *J* = 8.5 Hz), 6.04 (bs, 2H).

Isonicotinamide



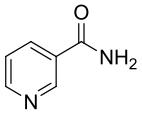
^{1}H NMR (400 MHz, DMSO^{d6}): δ 8.72 (d, 2H, *J* = 5.9 Hz), 8.26 (s, 1H), 7.78 (d, 2H, *J* = 6.1 Hz), 7.73 (s, 1H).
^{13}C NMR (100 MHz, DMSO^{d6}): δ 166.2, 150.1, 141.3, 121.4.

Picolinamide



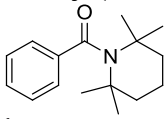
^{1}H NMR (400 MHz, DMSO^{d6}): δ 8.63 (d, 1H, *J* = 4.8 Hz), 8.12 (s, 1H), 8.05 (d, 1H, *J* = 7.9 Hz), 7.98 (dt, 1H, J^1 = 15.4 Hz, J^2 = 7.6 Hz, J^3 = 1.7 Hz), 7.65 (s, 1H), 7.55-7.61 (m, 1H).
^{13}C NMR (100 MHz, DMSO^{d6}): δ 166.0, 150.3, 148.4, 137.6, 126.4, 121.9.

Nicotinamide



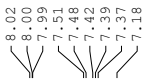
^{1}H NMR (400 MHz, DMSO^{d6}): δ 9.04 (d, 1H, *J* = 2.5 Hz), 8.70 (dd, 1H, J^1 = 4.9 Hz, J^2 = 1.7 Hz), 8.21 (td, 1H, J^1 = 7.9 Hz, J^2 = 1.9 Hz), 8.17 (s, 1H), 7.61 (s, 1H), 7.47-7.52 (m, 1H).
^{13}C NMR (100 MHz, DMSO^{d6}): δ 166.4, 151.9, 148.6, 135.1, 129.6, 123.4.

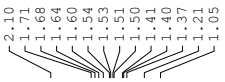
Phenyl(2,2,6,6-tetramethylpiperidin-1-yl)methanone

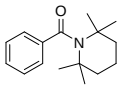


^{1}H NMR (400 MHz, DMSO^{d6}): δ 8.01 (d, 2H, J = 8.0 Hz), 7.45-7.55 (m, 1H), 7.32-7.43 (m, 2H), 1.35-1.75 (m, 6H), 1.21 (s, 6H), 1.05 (s, 6H).
^{13}C NMR (100 MHz, DMSO^{d6}): δ 166.4, 132.9, 129.8, 129.6, 128.5, 60.5, 39.1, 32.0, 20.9, 17.1.
GC-MS: 246 (50), 105 (100), 77 (10).

Xiao-Feng/ XWCB-76
Au1H CDCl3 /opt/topspin 1208 31







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PROCNO 1

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