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SUPPLEMENTARY MATERIAL TO

RuO_4-mediated oxidation of secondary amines. 2. Imines as main reaction intermediates

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*2,2'-[Methylenebis(benzylimino)]bisacetonitrile (**14d**)*

To a solution of **16a** (390 mg, 2.67 mmol) in ethanol (2 mL), aqueous formaldehyde (37 %, 0.1 mL, 1.33 mmol) was added and the reaction mixture stirred at room temperature for 7 h. The solvent was evaporated and the residue was purified by column chromatography on silica gel 60 (Merck, 70–230 mesh) eluted with EtOAc:hexane (15:85 volume ratio). The desired compound **14d** was obtained as a colourless solid (380 mg).

Yield: 94 %; m.p.: 63–65 °C. Anal. Calcd. for $C_{19}H_{20}N_4$: C, 74.97; H, 6.62; N, 18.41 %. Found: C, 74.69; H, 6.80; N, 18.19 %; FT-IR (solid, cm^{-1}): 3033 (C–H stretching of aromatic ring), 2842 (C–H stretching of CH_2 group), 2236 (C–N stretching of C≡N group), 1497 and 1456 (C–C stretching of aromatic ring), 1369, 1161, 1126 and 1029 (C–N stretching of tertiary amine), 738 and 698 (C–H bending of monosubstituted aromatic ring); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 3.58 (4H, *s*, CH_2CN), 3.79 (4H, *s*, C**H**$_2$Ph), 7.25–7.40 (10H, *m*, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 39.0 (**C**H_2CN), 56.0 (**C**H_2Ph), 72.8 (NCH_2N), 114.7 (CN), 128.2 (*p*), 128.97 (*m*), 129.02 (*o*), 136.4 (*i*).

SPECTRAL DATA OF SELECTED COMPOUNDS

The ^{1}H- and ^{13}C-NMR chemical shifts of the following compounds are referenced to internal $(CH_3)_4Si$ (δ_H = 0) and $CDCl_3$ (δ_C = 77.16 ppm, as suggested in H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **62** (1997) 7512). Aromatic *ortho*, *meta*, *para*, and *ipso* carbons are labelled as *o*, *m*, *p* and *i*, respectively.

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The MS data of the new compounds are also presented, except for compounds **14d**, **26** and **27**, which were too unstable under the used analytical conditions and their mass spectra could not be recorded.

N-*Benzylethanimine (**3b**, moderately stable compound)*. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.95 (3H, *dt*, ^{3}J = 4.9 Hz & ^{5}J = 1.1 Hz, CH_3), 4.49 (2H, *m*, C**H**$_2$Ph), 7.11–7.31 (5H, *m*, Ar-H), 7.77 (1H, *qt*, ^{3}J = 4.9 Hz & ^{4}J = 1.4 Hz, CH=N); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 22.5 (CH_3), 65.3 (C**H**$_2$Ph), 127.1 (*p*), 128.1 (*o*), 128.6 (*m*), 139.4 (*i*), 162.0 (CH=N); EI-MS [70 eV; *m*/*z*, (relative abundance, %)]: 133 (5, M^+), 92 (35), 91 (100, BP), 89 (5), 65 (10), 63 (4), 51 (4), 39 (4).

N-*Benzyl*-N-*(cyanomethyl)formamide (**8f**, mixture of E/Z isomers; the underlined values belong to the main isomer)*. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 4.01+<u>4.13</u> (2H, *s*+*s*, CH_2CN), <u>4.55</u>+4.67 (2H, *s*+*s*, C**H**$_2$Ph), 7.14–7.47 (5H, *m*, Ar-H), 8.22+<u>8.32</u> (1H, *s*+*s*, CHO); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): <u>29.4</u>+34.9 (**C**H_2CN), 45.8+<u>51.1</u> (**C**H_2Ph), <u>114.40</u> (CN), <u>128.0</u>+128.8 (*o*), 128.7+<u>129.1</u> (*p*), 129.3+<u>129.5</u> (*m*), <u>133.5</u>+134.1 (*i*), 161.8+<u>162.1</u> (CHO); EI-MS [70 eV; *m*/*z*, (relative abundance, %)]: 174 (35, M^+), 134 (100, BP), 107 (14), 106 (81), 91 (54), 89 (10), 79 (49), 77 (17), 65 (21), 51 (11).

*1,3,5-Tribenzylhexahydro-1,3,5-triazine (**26**)*. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 3.41 (6H, *brs*, NCH_2N), 3.66 (6H, *s*, C**H**$_2$Ph), 7.15–7.40 (15H, *m*, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 57.2 (**C**H_2Ph), 73.9 (NCH_2N), 127.1 (*p*), 128.3 (*m*), 129.0 (*o*), 138.5 (*i*).

N-*Benzyl*-N-*[(benzylamino)methyl]formamide* (***27**, mixture of* E/Z *isomers; the underlined values belong to the main isomer. Sign prime (′) refers to the **Ph**–C**H**$_2$–NH atoms)*. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): <u>3.62</u>+3.68 (2H, *s*+*s*, C**H**$_2$′Ph), <u>4.08</u>+4.23 (2H, *s*+*s*, NCH_2N), 4.38+<u>4.57</u> (2H, *s*+*s*, C**H**$_2$Ph), 7.27–7.40 (10H, *m*, Ar-H), <u>8.11</u>+8.33 (1H, *s*+*s*, CHO); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): <u>44.2</u>+50.6 (**C**H_2Ph), <u>49.2</u>+50.9 (**C**′H_2Ph), 56.7+<u>61.2</u> (NCH_2N), 126.96+127.04+127.94+128.36+128.18+128.51+128.72+128.89 (*m*+*m*′+*p*+*p*′), 127.54+<u>128.28</u> (*o*), 128.00+<u>128.07</u> (*o*′), 136.3+<u>136.7</u> (*i*), <u>138.9</u>+139.7 (*i*′), <u>162.7</u>+163.6 (CHO).

N-*Ethylacetamide (**28**)*. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.09 (3H, *t*, *J* = 7.3 Hz, C**H**$_3$–CH_2), 1.91 (3H, *s*, CH_3CO), 3.23 (2H, *m*, CH_2), 8.58–8.62 (1H, *brs*, NH, D_2O exchangeable); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 14.8 (CH_3), 23.3 (**C**H_3CO), 34.4 (CH_2), 170.0 (CO); EI-MS [70 eV; *m*/*z*, (relative abundance, %)]: 87 (100, M^+, BP), 72 (21), 44 (55), 43 (72), 42 (17), 30 (83), 29 (13), 28 (11).