ELECTRONIC SUPPLEMENTARY INFORMATION

Iridium catalysed synthesis of piperazines from diols

Lars Ulrik Nordstrøm and Robert Madsen*
Center for Sustainable and Green Chemistry, Department of Chemistry, Building 201
Technical University of Denmark, DK-2800 Lyngby, Denmark

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General methods:
[Cp*IrCl$_2$]$_2$ was purchased from Strem while all other chemicals were obtained from Aldrich and used as received. Toluene was distilled from sodium. NMR spectra were recorded on a Varian Mercury 300 spectrometer with residual solvent signals$^1$ or TMS as reference. Assignments were made based on one dimensional spectra as well as COSY and HSQC spectra. HRMS were obtained at the Department of Chemistry, University of Copenhagen (ionisation method: ESP+).
General procedure for N-heterocyclisation:
To 5 mL screw-top vial were added \([\text{Cp}^*\text{IrCl}_2]_2\), (8 mg, 10 \(\mu\)mol), diamine (2 mmol), diol (2 mmol), NaHCO₃ (10 mg, 0.12 mmol), and solvent (1 mL). The vial was flushed with argon, sealed, and heated to the indicated temperature overnight. After cooling to room temperature aqueous K₂CO₃ and CH₂Cl₂ were added. The phases were separated and the aqueous phase was extracted twice with CH₂Cl₂. The combined organic phases were dried (K₂CO₃) and concentrated. The residue was further purified by column chromatography (heptane/EtOAc or MeOH/CH₂Cl₂ mixtures).

\((\pm)\)-\(\text{trans}\)-Decahydroquinoxaline
\(\delta_H\) (300 MHz, CDCl₃): 2.98-2.78 (m, 4H), 2.25-2.10 (m, 2H), 1.80-1.10 (m, 10H, H₁, H₄, H₆, H₇, H₈, H₉); \(\delta_C\) (75 MHz, CDCl₃): 61.4 (C₅, C₁₀), 47.1 (C₂, C₃), 32.1 (C₆, C₉), 25.0 (C₇, C₈); MS: \(m/z\) 140 \([M^+\]).

\((\pm)-(\text{2S,4aR,8aR})\)-Decahydro-2-methylquinoxaline
\(\delta_H\) (300 MHz, CDCl₃): 2.88 (dd, 1H, \(J_{3\text{eq}-2} = 2.9\) Hz, \(J_{3\text{gem}} = 11.6\) Hz, H₂), 2.38 (dd, 1H, \(J_{3\text{ax}-2} = 10.2\) Hz, \(J_{3\text{gem}} = 11.6\) Hz, H₃ax), 2.26-2.05 (m, 2H, H₅, H₁₀), 1.75-1.55 (6H, H₁, H₄, 2 × H₆, 2 × H₉, H₁₁); \(\delta_C\) (75 MHz, CDCl₃): 61.7, 60.7, 54.2, 52.2, 32.2, 32.0, 25.2, 25.0 (C₆, C₉); HRMS calcd. for C₉H₁₉N₂ \([M+H]^+\) \(m/z\) 155.1548, found \(m/z\) 155.1556.

Minor isomer
\(\delta_H\) (300 MHz, CDCl₃): 3.41 (tq, 1H, \(J_{2-3} = 1.8\) Hz, \(J_{2-11} = 7.0\) Hz, H₂), 2.16-2.07 (m, 2H, H₅, H₁₀), 1.85-1.05 (m, 8H, H₆, H₇, H₈, H₉), 0.96 (d, 3H, \(J_{2-11} = 6.6\) Hz, H₁₁); \(\delta_C\) (75 MHz, CDCl₃): 62.9, 60.8, 56.5, 50.0, 32.3, 32.0, 25.1, 19.2 (C₁₁, C₁₂); MS: \(m/z\) 154 \([M^+\]).

\((\pm)-(\text{2R,3S,4aR,8aR})\)-Decahydro-2,3-dimethylquinoxaline (major isomer)
\(\delta_H\) (300 MHz, CDCl₃): 3.05, 2.88 (2×dq, 1H each, \(J = 3.6\) Hz, \(J = 6.7\) Hz, H₂, H₃), 2.44-2.15 (m, 2H, H₅, H₁₀), 1.67-1.50 (m, 6H, H₁, H₄, 2 × H₆, 2 × H₉), 1.30-1.15 (m, 4H, 2 × H₇, 2 × H₈), 1.08, 0.91 (2×d, 3H each, \(J = 6.7\) Hz, H₁₁, H₁₂); \(\delta_C\) (75 MHz, CDCl₃): 62.6, 54.4, 53.4, 52.1 (C₂, C₃, C₅, C₁₀), 31.2, 31.9 (C₆, C₉), 25.0, 24.9 (C₇, C₈), 19.2 (C₁₁), 12.8 (C₁₂); HRMS calcd. for C₁₀H₂₁N₂ \([M+H]^+\) \(m/z\) 169.1705, found \(m/z\) 169.1705.

Minor isomer
\(\delta_C\) (75 MHz, CDCl₃): 61.3 (C₅, C₁₀), 57.9 (C₂, C₃), 31.7 (C₆, C₉), 19.0 (C₁₁, C₁₂).

1,4-Dibenzylpiperazine
\(\delta_H\) (300 MHz, CDCl₃): 7.35-7.21 (m, 10H, Ar), 3.52 (s, 4H, Ph-CH₂-N), 2.49 (bs, 8H, N-CH₂-CH₂-N); \(\delta_C\) (75 MHz, CDCl₃): 138.2 (C₁₃), 129.4, 128.3 (C₂, C₃, C₅, C₆, C₉), 25.0, 24.9 (C₇, C₈), 19.2 (C₁₁), 12.8 (C₁₂); MS: \(m/z\) 266 \([M^+\]).

\((\text{2S,3S})\)-2,3-Diphenylpiperazine

Supplementary Material (ESI) for Chemical Communications
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$[\alpha]_{D}^{25} = -102$ (c 1.0, CHCl$_3$) (lit.$^2$ $[\alpha]_{D}^{25} = -104.6$ (c 1.0, CHCl$_3$)); mp 93-95 ºC (lit.$^2$ mp 94-96 ºC); $\delta_{H}$(300 MHz, CDCl$_3$): 7.20-7.05 (m, 10H, Ar), 3.71 (s, 2H, H$_2$, H$_3$), 3.14 (s, 4H, H$_5$, H$_6$), 2.01 (bs, 2H, H$_1$, H$_4$); $\delta_{C}$(75 MHz, CDCl$_3$): 141.5 (C$_{ipso}$), 128.1, 127.9, 127.3 (Ar), 68.3 (C$_2$, C$_3$), 47.2 (C$_5$, C$_6$); MS: m/z 238 [M$^+$]. The starting material, (1$S$,2$S$)-1,2-diamino-1,2-diphenylethane, was prepared by resolution$^3$ and showed an optical rotation of $[\alpha]_{D}^{25} = -104$ (c 1.5, MeOH) (lit.$^3$ $[\alpha]_{D}^{23} = -106$ (c 1.1, MeOH)).

(±)-2-Phenylpiperazine
$\delta_{H}$(300 MHz, CDCl$_3$): 7.40-7.20 (m, 5H, Ar), 3.73 (dd, 1H, $J_{2-3eq} = 2.8$ Hz, $J_{2-3ax} = 10.2$ Hz, H$_2$), 3.11-2.80 (m, 5H, H$_3eq$, H$_5ax$, H$_5eq$, H$_6ax$, H$_6eq$), 2.69 (dd, 1H, $J_{gem} = 11.9$ Hz, H$_3ax$), 1.80 (bs, 2H, N-H); $\delta_{C}$(75 MHz, CDCl$_3$): 142.8 (C$_{ipso}$), 128.5, 127.5, 126.9 (Ar), 62.1 (C$_2$), 54.4, 47.9, 46.1 (C$_3$, C$_4$, C$_5$); HRMS calcd. for C$_{10}H_{15}N_2$ [M+H$^+$] m/z 163.1235, found m/z 163.0981.

(±)-1,4-Dibenzyl-2-phenylpiperazine
$\delta_{H}$(300 MHz, CDCl$_3$): 7.45-7.10 (m, 15H, Ar), 3.71 (d, 1H, $J_{gem} = 13.4$ Hz, Ph-CH$_2$H'-N), 3.43 (s, 2H, Ph-CH$_2$-N), 3.36 (dd, 1H, $J_{2-3eq} = 3.0$ Hz, $J_{2-3ax} = 10.3$ Hz, H$_2$), 2.85-2.67 (m, 4H, Ph-CH$_2$$^{'-}$-N, H$_{3eq}$, H$_5$, H$_6$), 2.25-2.05 (m, 3H, H$_{3ax}$, H$_5$', H$_6'$); $\delta_{C}$(75 MHz, CDCl$_3$): 142.3, 139.2, 138.0 (3 × C$_{ipso}$), 129.3, 128.9, 128.6, 128.3, 128.2, 127.5, 127.1, 126.8 (Ar), 67.4 (C$_2$), 63.1 (N-CH$_2$-Ph), 62.1 (C$^4$ or C$^5$), 59.1 (N-CH$_2$-Ph), 53.3 (C$^4$ or C$^5$), 51.9 (C$^3$); HRMS calcd. for C$_{24}H_{27}N_2$ [M+H$^+$] m/z 343.2174, found m/z 343.2153.

(±)-1,4-Dibenzyl-2-methylpiperazine (contains a small impurity of (±)-1,4-dibenzyl-dimethylpiperazine according to mass spectrometry)
$\delta_{H}$(300 MHz, CDCl$_3$): 7.35-7.20 (m, 10H, Ar), 4.05 (d, 1H, $J_{gem} = 13.3$ Hz, Ph-CH$_2$H'-N), 3.48 (s, 2H, Ph-CH$_2$-N), 3.19 (d, 1H, $J_{gem} = 13.2$ Hz, Ph-CH$_2$$^{'-}$-N), 2.75-2.60 (m, 3H, H$_{3eq}$, H$_5$, H$_6$), 2.50 (ddq, 1H, $J_{2-3eq} = 3.0$ Hz, $J_{2-Me} = 6.2$ Hz, J$_{2-3ax} = 9.1$ Hz, H$_2$), 2.26-2.12 (m, 2H, H$_5'$, H$_6'$), 2.02 (dd, 1H, $J = 9.7$ Hz, J = 10.5 Hz, H$_{3ax}$), 1.14 (d, 3H, $J_{2-Me} = 6.2$ Hz, -CH$_3$); $\delta_{C}$(75 MHz, C$_6$D$_6$): 140.1, 139.3 (2 × C$_{ipso}$), 129.2, 129.1, 128.5, 128.4 (2 × C$_{ortho}$, 2 × C$_{meta}$), 127.2, 127.0 (2 × C$_{para}$), 63.3, 61.1, 58.5, 55.7, 53.9, 51.5 (2 × Ph-CH$_2$-N, C$_2$, C$_3$, C$_5$, C$_6$), 16.7 (bs, -CH$_3$); HRMS calcd. for C$_{19}H_{25}N_2$ [M+H$^+$] m/z 281.2018, found m/z 281.2026.

References
Minor isomer can be seen in spectra.
Artifact at 51 ppm
Artifact at 51 ppm