**Supporting Information**

for

**Evaluation of the enantioselectivity of new chiral ligands based on imidazolidine-4-one derivatives**

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**General information and experimental data of prepared compounds, copies of 1H and 13C NMR spectra and DFT calculations**

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6. **Experimental procedures**

**1.1. General procedures**

The starting chemicals and solvents were obtained from TCI Chemicals or Fluorochem and used without further purification. (*S*)-2-amino-2,3-dimethylbutanamide was prepared according to the method described previously [1]. Column chromatography was performed using 60 Å (60–200 μm) silica gel. TLC was performed on aluminium-backed silica gel plates (Merck DC, Alufolien Kieselgel 60 F254) with spots visualised by UV light. The melting point temperatures are uncorrected. The IR spectra were measured at room temperature using Thermo Scientific Nicolet iS50 FT-IR Spectrometer with ATR technique, the resolution was 4 cm–1, FT-IR data are presented in cm–1. 1H NMR spectra were recorded on a Bruker Avance 400 instrument (400.13 MHz for 1H) or Bruker Ascend 500 instrument (500.13 MHz for 1H). Chemical shifts *δ* were referenced to the residual peak of CDCl3 at 7.26 ppm or MeOD-*d*4 at 3.31 ppm. The 13C NMR spectra were calibrated with respect to the middle signal in the triplet of CDCl3 (*δ* = 77.23 ppm). High-resolution mass spectra were measured on the Thermo Fisher Scientific MALDI LTQ Orbitrap instrument. The used matrix was a 0.2M solution of 2,5-dihydroxybenzoic acid (DHB) in MeCN/H2O (95/5). Spectra were calibrated with respect to the used matrix. The optical rotation was measured on a Perkin–Elmer 341 instrument; the concentration *c* was given in g/100 mL. HPLC analyses were performed on the Watrex HPLC instrument with UV-Vis DAD (200–800 nm) SYKAM 3240 and with chiral Daicel columns Chilacel OD-H, Chiralpak AD-H, Chiralpak IA and Chiralpak AS-H (250 mm × 4.6 mm). Hydrogenations were performed in pressure vessel Berghof BR-100. To evaluate the effectiveness of the catalysts, the values of Turnover Number (TON) and Turnover Frequency (TOF) related to the production of the major stereoisomer were calculated using the following equations:

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**1.2. Synthesis**

**2,6-Bis(5-isopropyl-5-methylimidazolidine-4-on-2-yl)pyridines Ia-c**



A solution of pyridine-2,6-dicarbaldehyde (271.2 mg, 2 mmol), (*S*)-2-amino-2,3-dimethylbutanamide (780 mg, 6 mmol) and TsOH (30 mg) in *n*BuOH (6 mL) was heated at 80 °C under argon for 5 d. TEA (50 µl) was added to the cooled reaction mixture, and the solvent was evaporated under reduced pressure. The residue was at least twice chromatographed (SiO2; acetone/AcOEt /MeOH (13/7/1; v/v/v)) to afford individual diastereomers of ligand **I**.

(2*R*,2´*R*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-5-methylimidazolidine-4-on-2-yl)pyridine (Ia)

Yield: 150 mg (20%), white crystalline solid; *R*f 0.51; mp 235–⁠⁠⁠237 °C; +32.6 (*c* 0.212; DCM/MeOH (9/1; v/v); 1H NMR (500 MHz, CD3OD): *δ* 7.91 (t, 1H, *J* = 7.8 Hz), 7.52 (d, 2H, *J* = 7.8 Hz), 5.54 (s, 2H), 1.93 (sp, 2H, *J* = 6.5 Hz), 1.33 (s, 6H), 1.03 (m, 12H); 13C NMR (125 MHz, CD3OD): *δ* 182.3, 160.6, 139.8, 123.1, 72.6, 66.4, 36.2, 24.1, 18.1, 16.7; FT-IR (ATR, cm–1): 3171, 2962, 2922, 2871, 1709, 1681, 1453, 1333, 1080, 1058, 804, 627; HR-MALDI-MS (DHB): Calcd for C19H29N5O2 m*/z* 360.23940 [M+H]+; found 360.23984.

(2*R*,2´*S*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-5-methylimidazolidine-4-on-2-yl)pyridine (Ib)

Yield: 311 mg (41%), white crystalline solid; *R*f 0.43; mp 208–210 °C; –13.0 (*c* 0.432; DCM/MeOH (9/1; v/v); 1H NMR (500 MHz, CD3OD): *δ* 7.92 (t, 1H, *J* = 7.8 Hz), 7.61 (d, 1H, *J* = 7.8 Hz), 7.53 (d, 1H, *J* = 7.8 Hz), 5.64 (s, 1H), 5.55 (s, 1H), 1.94 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 1.03 (m, 6H); 1.00 (d, 3H, *J* = 6.8 Hz), 0.96 (d, 3H, *J* = 6.8 Hz);  13C NMR (125 MHz, CD3OD): *δ* 182.2, 182.0, 160.1, 160.0, 139.7, 123.2, 123.1, 72.6, 70.8, 66.5, 66.4, 36.2, 34.7, 24.0, 21.9, 18.5, 18.1, 16.7; FT-IR (ATR, cm–1): 3220, 2965, 2873, 1690, 1447, 1320, 1108, 758, 666. HR-MALDI-MS (DHB): Calcd for C19H29N5O2 m*/z* 360.23940 [M+H]+; found 360.23992.

(2*S*,2´*S*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-5-methylimidazolidine-4-on-2-yl)pyridine (1c)

Yield: 115 mg (15%), white crystalline solid; *R*f 0.36; mp 172–174 °C; –70.0 (*c* 0.216; DCM/MeOH (9/1; v/v); 1H NMR (500 MHz, CD3OD): *δ* 7.95 (t, 1H, *J* = 7.8 Hz), 7.62 (d, 2H, *J* = 7.8 Hz), 5.68 (s, 2H), 1.96 (sp, 2H, *J* = 6.8 Hz), 1.38 (s, 6H), 1.01 (d, 6H, *J* = 6.8 Hz), 0.95 (d, 6H, *J* = 6.8 Hz); 13C NMR (125 MHz, CD3OD): *δ* 181.5, 159.6, 139.7, 123.2, 70.7, 66.7, 34.6, 21.5, 18.4, 16.7; FT-IR (ATR, cm–1): 3209, 2962, 2872, 2854, 1688, 1446, 1320, 1077, 756; HR-MALDI-MS (DHB): Calcd for C19H29N5O2 m*/z* 360.23940 [M+H]+; found 360.23976.

**2,6-Bis(5-isopropyl-2,5-dimethylimidazolidine-4-on-2-yl)pyridines IIa-c**



A solution of 2,6-diacetyl pyridine (332.8 mg, 2 mmol), (*S*)-2-amino-2,3-dimethylbutanamide (780 mg, 6 mmol) and TsOH (30 mg) in *ortho-*dichlorobenzene (6 mL) was heated at 140 °C under argon for 4 d. TEA (50 µl) was added to the cooled reaction mixture, and the solvent was evaporated under reduced pressure. The residue was at least twice chromatographed (SiO2; AcOEt/MeOH (20/1; v/v)) to afford individual diastereomers of ligand **II**.

(2*R*,2´*R*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-2,5-dimethylimidazolidine-4-on-2-yl)pyridine (IIa)

Yield: 186 mg (23%), white crystalline solid; *R*f 0.39; mp 188–190 °C; +80.5 (*c* 0.41; DCM); 1H NMR (500 MHz, CDCl3): *δ* 8.73 (bs, 2H), 7.63 (t, 1H, *J* = 8.0 Hz), 7.54 (d, 2H, *J* = 8.0 Hz), 2.30 (bs, 2H), 2.05 (sp, 2H, *J* = 6.8 Hz), 1.53 (s, 6H), 1.00 (d, 12H, *J* = 6.8 Hz), 0.97 (s, 6H); 13C NMR (125 MHz, CDCl3): *δ* 180.3, 164.2, 137.5, 117.7, 75.1, 66.2, 33.7, 31.4, 23.7, 18.2, 16.6; FT-IR (ATR, cm–1): 3199, 2964, 2874, 1693, 1574, 1343, 1236, 1101, 949, 820, 680; HR-MALDI-MS (DHB): Calcd for C21H33N5O2 m*/z* 388.27070 [M+H]+; found 388.27151.

(2*R*,2´*S*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-2,5-dimethylimidazolidine-4-on-2-yl)pyridine (IIb)

Yield: 288 mg (35%), white crystalline solid; *R*f 0.34; mp 172–174 °C; –30.6 (*c* 0.252; DCM); 1H NMR (500 MHz, CDCl3): *δ* 8.41 (bs, 1H), 8.22 (bs, 1H), 7.68 (t, 1H, *J* = 7.8 Hz), 7.59 (m, 2H), 2.32 (bs, 2H), 2.03 (sp, 1H, *J* = 6.8 Hz), 1.77 (sp, 1H, *J* = 6.8 Hz), 1.69 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H), 1.06 (s, 3H), 1.01 (m, 6H), 0.92 (d, 3H, *J* = 6.8 Hz), 0.64 (d, 3H, *J* = 6.8 Hz); 13C NMR (125 MHz, CDCl3): *δ* 180.0, 178.8, 164.1, 163.8, 137.7, 117.6, 117.5, 75.0, 74.8, 66.0, 65.7, 34.5, 34.0, 33.5, 31.5, 24.7, 24.0, 18.3, 18.2, 16.6; FT-IR (ATR, cm–1): 3196, 2965, 2873, 1697, 1574, 1445, 1364, 1237, 1111, 758, 674; HR-MALDI-MS (DHB): Calcd for C21H33N5O2 m*/z* 388.27070 [M+H]+; found 388.27113.

(2*S*,2´*S*,5*S*,5´*S*)-2,6-Bis(5-isopropyl-2,5-dimethylimidazolidine-4-on-2-yl)pyridine (IIc)

Yield: 96 mg (12%), white crystalline solid; *R*f 0.30; mp 141–143 °C; –133.5 (*c* 0.212; DCM); 1H NMR (500 MHz, CDCl3): *δ* 9.45 (bs, 2H), 7.65 (t, 1H, *J* = 7.8 Hz), 7.45 (d, 2H, *J* = 7.8 Hz), 2.14 (bs, 2H), 1.75 (sp, 2H, *J* = 6.8 Hz), 1.54 (s, 6H), 1.44 (s, 6H), 0.84 (d, 6H, *J* = 6.8 Hz), 0.44 (d, 6H, *J* = 6.8 Hz); 13C NMR (125 MHz, CDCl3): *δ* 179.3, 163.8, 137.3, 117.2, 75.5, 66.2, 34.1, 33.9, 24.5, 18.2, 16.5; FT-IR (ATR, cm–1): 3214, 2964, 2872, 1673, 1575, 1370, 1260, 1097, 793; HR-MALDI-MS (DHB): Calcd for C21H33N5O2 m*/z* 388.27070 [M+H]+; found 388.27104.

**5-Isopropyl-5-methyl-2-(1*H*-imidazole-2-yl)imidazolidine-4-one III**



A solution of 1*H*-imidazole-2-carbaldehyde (380 mg, 4 mmol), (*S*)-2-amino-2,3-dimethylbutanamide (390 mg, 3 mmol) and AcOH (3 drops) in *n*BuOH (4 mL) was heated to reflux under argon for 17h. The reaction mixture was diluted with DCM (10 mL) and washed with a saturated solution of Na2CO3 (10 mL). The organic layer was dried over Na2SO4 and evaporated under reduced pressure. The residue was chromatographed (SiO2; acetone) to afford individual diastereomers of ligand **III**.

**(2*R*,5*S*)-5-Isopropyl-5-methyl-2-(1*H*-imidazole-2-yl)imidazolidine-4-one IIIa**

Yield: 175 mg (28%), yellow crystalline solid; *R*f 0.25; mp 82–84 °C; –8.5 (*c* 0.52; DCM); 1H NMR (500 MHz, CDCl3): *δ* 8.53 (bs, 1H), 6.98 (s 2H), 5.60 (s, 1H), 1.89 (sp, 1H, *J* = 6.8 Hz), 1.20 (s, 3H), 0.95 (d, 6H, *J* = 6.8 Hz); 13C NMR (125 MHz, CDCl3): *δ* 180.6, 148.0, 122.7, 65.3, 64.8, 34.9, 23.7, 17.9, 16.5; HR-MALDI-MS (DHB): Calcd for C10H16N4O m*/z* 209.13969 [M+H]+; found 209.13972.

**(2*S*,5*S*)-5-Isopropyl-5-methyl-2-(1*H*-imidazole-2-yl)imidazolidine-4-one IIIb**

Yield: 237 mg (38%), yellow oil; *R*f 0.17; –34.1 (*c* 0.50; DCM); 1H NMR (500 MHz, CDCl3): *δ* 7.47 (bs, 1H), 7.03 (s 2H), 5.72 (s, 1H), 1.93 (sp, 1H, *J* = 6.8 Hz), 1.33 (s, 3H), 0.95 (d, 3H, *J* = 6.8 Hz), 0.90 (d, 3H, *J* = 6.8 Hz); 13C NMR (125 MHz, CDCl3): *δ* 178.9, 147.5, 122.9, 64.6, 63.4, 33.7, 22.3, 18.3, 16.5; HR-MALDI-MS (DHB): Calcd for C10H16N4O m*/z* 209.13969 [M+H]+; found 209.13968.

**(*S*)-1-Cbz-Pyrrolidine-2-carbaldehyde**



(*S*)-1-Cbz-Pyrrolidine-2-carbaldehyde was prepared according to the method described in Ref. [2].To a solution of DMSO (3.32 mL, 50 mmol, 3 equiv.) in dry DCM (35 mL) was added dropwise a solution of oxalyl chloride (3.3 mL, 37.5 mmol, 2.25 equiv.) in dry DCM (15 mL) at –78 °C. The reaction mixture was stirred for 45 min and then, a solution of (*S*)-(1-Cbz-pyrrolidine-2-yl) methanol (3.05 mL, 16.7 mmol) in dry DCM (20 mL) was over 20 min. After being stirred for an additional 20 min, TEA (9.4 mL; 67 mmol, 4 equiv.) was added, the reaction mixture was gradually heated at 0 °C and stirred for 2 h. After the addition of DCM (75 mL), the mixture was washed with a saturated solution of NaHCO3 (75 mL) and brine (75 mL). The organic layer was dried over Na2SO4 and evaporated under reduced pressure to give 2.92 g (75 %) of aldehyde as a yellow oil, which was introduced into the next step without further purification. 1H NMR (500 MHz, CDCl3): *δ* 9.54 (d, 1H, *J* = 8.0 Hz), 7.38–7.31 (m, 5H), 5.29–5.13 (m, 2H), 4.30–4.19 (m, 1H), 3.60–3.51 (m, 2H), 2.17–2.00 (m, 2H), 1.94–1.85 (m, 2H).

**(*S*)-2-(1-CBz-pyrrolidine-2-yl)-1*H*-imidazole**



(*S*)-2-(1-CBz-pyrrolidine-2-yl)-1*H*-imidazole was prepared according to the method described in Ref. [3].To a solution of (*S*)-1-Cbz-pyrrolidine-2-carbaldehyde (2.62 g, 12.2 mmol) in MeOH (20 mL) was added 40% aqueous solution of glyoxal (4.8 mL, 42 mmol, 3.5 equiv.) and 26% aqueous solution of ammonia (5.6 mL, 70 mmol, 5.75 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 24 hours. The solvents were evaporated under reduced pressure, and the residue was mixed with AcOEt (50 mL). The precipitate was removed by filtration, and the organic phase was washed with a saturated solution of NaHCO3 (2× 25 mL). The organic layer was dried over Na2SO4 and evaporated under reduced pressure. The crude product was purified by column chromatography (*R*f 0.41; SiO2; acetone) to give the imidazole derivative as a white crystalline solid (1.36 g; 48%); mp 118–119 °C; = –58.7 (*c* 1.006; MeOH); 1H NMR (500 MHz, CDCl3): *δ* 10.37 (bs, 1H), 7.38–7.31 (m, 5H), 6.96 (s, 2H), 5.18 (d, 1H, *J* = 10.0 Hz), 5.13 (d, 1H, *J* = 10.0 Hz), 4.99 (m, 1H), 3.48 (m, 2H), 2.94 (m, 1H), 2.19–2.13 (m, 2H), 1.98 (m, 1H); 13C NMR (125 MHz, CDCl3): *δ* 156.9, 148.4, 148.1, 136.6, 128.8, 128.4, 128.0, 67.5, 54.7, 47.3, 28.3, 25.1; FT-IR (ATR, cm–1): 1697, 1456, 1408, 1348, 1099, 955, 773, 741, 731, 696;HR-MALDI-MS (DHB): Calcd for C15H17N3O2 m*/z* 272.13936 [M+H]+; found 272.13971.

**(*S*)-2-(Pyrrolidine-2-yl)-1*H*-imidazole (IV)**



To a solution of (*S*)-2-(1-CBz-pyrrolidine-2-yl)-1*H*-imidazole (813 mg, 3.21 mmol) in EtOH (20 mL) was carefully added 10% Pd/C (318 mg, 0.3 mmol). The mixture was stirred under an atmosphere of hydrogen (40 bar) at room temperature for 5 d. After this period, the stream of argon was introduced to the mixture (ca. 5 min), the catalyst was removed by filtration and washed with MeOH (50 mL). The solvents were evaporated under reduced pressure to give compound **4** (0.42 g; 97%) as a yellow oil; = –41.2 (*c* 1.00; MeOH); 1H NMR (500 MHz, CDCl3): *δ* 7.15 (bs, 2H), 6.94 (s, 2H), 4.30 (d, 1H, *J* = 7.0 Hz), 3.03–2.96 (m, 1H), 2.94–2.91 (m, 1H), 2.21–2.14 (m, 1H), 2.11–2.04 (m, 1H), 1.88–1.83 (m, 2H); 13C NMR (125 MHz, CDCl3): *δ* 149.8, 122.1, 56.2, 46.5, 31.9, 25.6;FT-IR (ATR, cm–1): 2972, 1697, 1406, 1254, 1099, 741, 696; HR-MALDI-MS (DHB): Calcd for C7H117N3 m*/z* 138.10257 [M+H]+; found 138.10253.

**General procedure for asymmetric Henry reaction**

A mixture of ligand **I–IV** (27.5 μmol), Cu(OAc)2 (4.5 mg, 25 μmol) and nitromethane (0.5 mL, 9 mmol) in absolute ethanol (1 mL) was stirred for 1 h at room temperature. Then the mixture was cooled at 10 °C, aldehyde (0.5 mmol) was added, and a formed solution was stirred for the 2 d. The solvents were removed under reduced pressure, and the crude product was analysed by 1H NMR for determination of conversion. The nitroalcohol was purified by column or flash chromatography (AcOEt/hexane; 1/3 (v/v)**.** The enantiomeric excess was determined by HPLC. The characterisation data for corresponding nitroalcohols were in accordance with data published previously [4,5].

**General procedure for asymmetric aldol reaction**

To a solution of catalyst **IV** (13.6, 0.1 mmol) and TFA (0.1 mmol or 0.2 mmol) in an appropriate solvent (2 mL) was added cyclohexanone or acetone (5 mmol). The reaction mixture was cooled to the corresponding temperature, and the aldehyde (0.5 mmol) was added. The mixture was kept at the used temperature for the chosen reaction time. The catalyst was removed by flash chromatography (SiO2; PE/AcOEt 1/1 (v/v)) and the solvent and excess ketone were evaporated under reduced pressure. The crude product was analysed by 1H NMR for determination of diastereomeric ratio. The aldol was purified by column or flash chromatography (AcOEt/hexane; 1/1 (v/v)**.** The enantiomeric excess in the major diastereomer was determined by HPLC. The characterisation data for corresponding aldols were in accordance with data published previously [6,7].

1. **NMR spectra**

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1. **DFT calculations**

Detailed DFT calculations were employed to analyse the structural and electronic characteristics of three nitrogen-rich molecules. The calculation was performed using Orca 5.0.2 [8,9]. The geometry of individual structures was optimised at the B3LYP/def2-TZVP level of theory with Grimme’s dispersion correction D3. The optimised geometries, which do not contain imaginary frequencies, are listed below. We modelled the following compounds: Substance A (5,5-dimethyl-2-(pyridine-2-yl)imidazolidine-4-one), Substance B (2-(1*H*-imidazole-2-yl)-5,5-dimethylimidazolidine-4-one), and Substance C (2-(pyrrolidine-2-yl)-1*H*-imidazole). The primary objective of this modelling was to investigate the impact of substituting the pyridine unit with an imidazole group on the coordination potential of these molecules. A critical aspect of our study focused on comparing the Mulliken atomic charges of the coordinating nitrogen atoms.

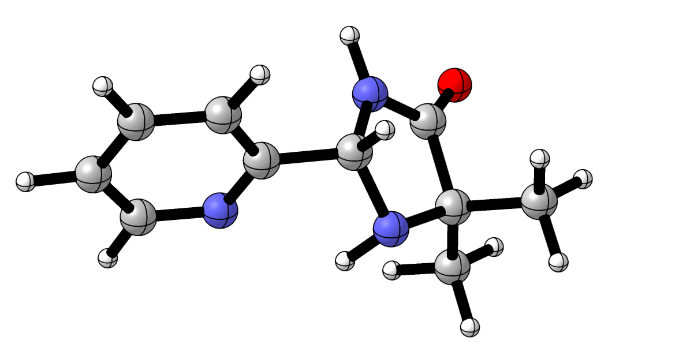
Obsah obrázku mapa

Popis byl vytvořen automaticky

In Substance A, the pyridine nitrogen exhibited a Mulliken charge of –0.282. Intriguingly, in Substance B, where the pyridine is replaced by an imidazole ring, the corresponding nitrogen showed a higher charge of –0.297. This trend was further accentuated in Substance C, with the imidazole nitrogen displaying a charge of –0.321. These findings compellingly suggest that the replacement of pyridine with imidazole leads to an increased negative charge on the coordinating nitrogen, likely due to electron donation from the adjacent imidazole nitrogen. Consequently, our DFT analysis strongly supports the hypothesis that such a substitution would result in compounds exhibiting coordination properties closely analogous to their pyridine-based counterparts.

**Optimised geometries of model compounds (in cartesian coordinates)**

**A – 5,5-dimethyl-2-(pyridine-2-yl)imidazolidine-4-one**



C 2.20699 –1.71209 –0.32207

C 2.58477 –2.90607 –0.92625

C 3.09198 –1.11438 0.56393

C 4.31421 –1.72839 0.80201

C 4.61087 –2.91357 0.13716

N 3.75823 –3.49387 –0.70701

H 1.91622 –3.41173 –1.61469

H 1.24235 –1.27260 –0.53721

H 2.83391 –0.19004 1.06475

H 5.02793 –1.30113 1.49494

C 5.95772 –3.58394 0.31828

N 5.86761 –5.03606 0.26144

N 6.87857 –3.24292 –0.76819

H 6.38098 –3.26083 1.27726

C 7.58688 –4.31255 –1.22177

C 7.08035 –5.52937 –0.42529

O 8.46081 –4.29954 –2.06318

H 5.05420 –5.24951 –0.30858

C 6.75795 –6.69263 –1.35030

H 5.99193 –6.41223 –2.07611

H 6.39866 –7.54593 –0.77221

H 7.65182 –6.98806 –1.89864

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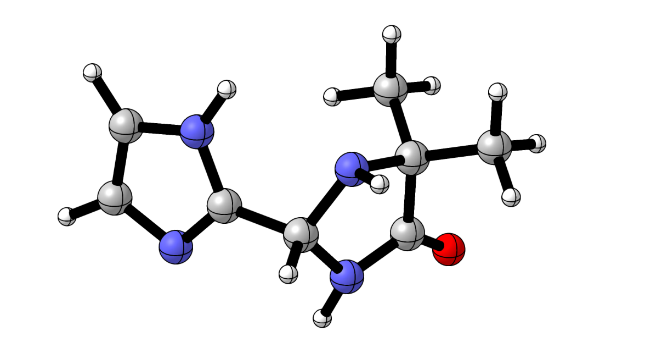
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H 9.08560 –6.17514 0.09223

H 7.81070 –6.76569 1.18475

H 7.11623 –2.30082 –1.03321

**B – 2-(1*H*-imidazole-2-yl)-5,5-dimethylimidazolidine-4-one**



C –0.48440 –1.37693 –0.15184

C –1.38549 –2.55964 –0.37351

N –1.99093 –3.02477 0.87892

C –1.24581 –4.23081 1.32062

C –0.45005 –4.66375 0.07507

N –0.65282 –3.71135 –0.87942

O 0.23952 –5.65511 –0.02061

C –0.24630 –3.88263 2.42811

N –0.53560 –0.61742 0.97143

C 0.39586 0.38707 0.83449

C 0.96908 0.17947 –0.39172

N 0.41008 –0.92230 –0.99897

H –2.17146 –2.27401 –1.07813

C –2.19483 –5.33261 1.77005

H –2.95340 –3.27773 0.70005

H –0.01510 –3.61834 –1.65586

H 0.43161 –3.08874 2.11253

H 0.35132 –4.75812 2.68128

H –0.78497 –3.54622 3.31568

H –1.13523 –0.81904 1.75474

H 0.56159 1.12711 1.59702

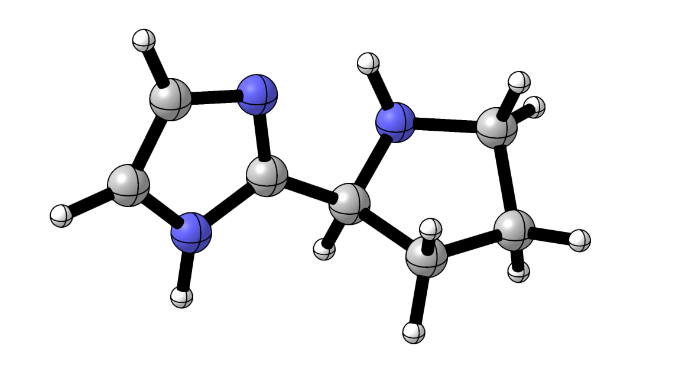
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H –2.90295 –5.58863 0.97862

H –2.75293 –5.01839 2.65450

H –1.62651 –6.22903 2.01487

**C – 2-(pyrrolidine-2-yl)-1*H*-imidazole**



C 2.074538 –2.370055 0.844080

C 2.269428 –3.787409 1.276012

N 0.984226 –4.486498 1.414732

C 1.043107 –5.772298 0.698673

C 2.537602 –6.038418 0.502699

C 3.095959 –4.633234 0.280229

N 2.960013 –1.370482 1.119865

C 2.486871 –0.213283 0.535040

C 1.317893 –0.574643 –0.071843

N 1.072350 –1.915148 0.126633

H 2.790871 –3.778196 2.244020

H 0.244571 –3.896392 1.057367

H 3.797163 –1.458166 1.669910

H 3.007378 0.724793 0.612477

H 0.639351 0.047015 –0.631797

H 0.558097 –6.561799 1.277297

H 0.542146 –5.716853 –0.275669

H 2.965018 –6.477765 1.407848

H 2.737387 –6.717314 –0.326580

H 4.170453 –4.552477 0.450765

H 2.884199 –4.298710 –0.737956

1. **Summarisation of the results of catalytic experiments**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | |
| **Ligand\*** | | **Time**  **(h)** | **Conversion (%)a** | **ee**  **(%)b** | **TON**  **(–)** | **TOF**  **(h–1)** |
| ref. [4] | (2*R*,5*S*) | 36 | 97 | 92 (*R*) | 18.62 | 0.52 |
| (2*S*,5*S*) | 48 | 85 | 25 (*S*) | 10.63 | 0.22 |
| ref. [4] | (2*R*, 5*S*) | 36 | 97 | 89 (*R*) | 18.33 | 0.51 |
| (2*S*,5*S*) | 48 | 80 | 23 (*S*) | 9.84 | 0.21 |
|  | **Ia**  (2*R*,2'*R*,5*S*,5'*S*) | 48 | 99 | 60 (*R*) | 15.84 | 0.33 |
| **Ib**  (2*S*,2'*R*,5*S*,5'*S*) | 48 | 99 | 38 (*R*) | 13.66 | 0.28 |
| **Ic**  (2*S*,2'*S*,5*S*,5'*S*) | 48 | 99 | 94 (*S*) | 19.21 | 0.40 |
|  | **IIa**  (2*R*,2'*R*,5*S*,5'*S*) | 48 | 99 | 80 (*R*) | 17.82 | 0.37 |
| **IIb**  (2*S*,2'*R*,5*S*,5'*S*) | 48 | 99 | 70 (*R*) | 16.83 | 0.35 |
| **IIc**  (2*S*,2'*S*,5*S*,5'*S*) | 48 | 99 | 90 (*S*) | 18.81 | 0.39 |
|  | **IIIa**  (2*R*,5*S*) | 48 | 63 | 89 (*R*) | 11.91 | 0.25 |
| **IIIb** (2*S*,5*S*) | 48 | 57 | 86 (*S*) | 10.60 | 0.22 |
|  | **IV**  (2*S*) | 48 | 97 | 50 (*S*) | 14.55 | 0.30 |
| a The conversion was determined by 1H NMR analysis of the crude product.  b The enantiomeric excess was determined by chiral HPLC. | | | | | | |

1. **References**

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