Supplementary Material (ESI) for Organic and Biomolecular Chemistry


# Preparation of new axially chiral bridged 2,2'-bipyridines and Pyridyl monooxazoline (Pymox). Evaluation in copper (I)-catalyzed enantioselective cyclopropanation.

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## Supplementary information

**Methyl 2-(3-acetylpyridyl)benzoate (12).** To a solution of boronic ester **11** (2.46g, 8.66 mmol) and 2-chloro-3-acetylpyridine **10** (1.12 g, 7.2 mmol) in toluene (140 mL), ethanol (15 mL), water (778 µL), were added $K_2CO_3$ (2.99 g, 21.6 mmol) and $Pd[(PPh_3)]_4$ (455 mg, 0.34 mmol). The mixture was degassed by $N_2$ for 30 min and then stirred at 60°C for 4 hours. The reaction mixture was quenched with water (50 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2 x 40 mL) and the combined organic layers were evaporated under vacuum. Flash chromatography (eluent: EtOAc/cyclohexane: 1/1) of the residue provided **12** as a yellow oil (1.81 g, 98%). $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.63 (dd, *J* = 4.9 Hz and 1.7 Hz, 1H), 7.97 (dd, *J* = 7.8 Hz and 1.5 Hz, 2H), 7.48 (m, 2H), 7.30 (dd, *J* = 7.7 Hz and 4.7 Hz, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 3.61 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 201.3, 167.6, 158.7, 151.2, 142.3, 136.6, 135.0, 132.4, 130.9, 130.8, 130.1, 129.1, 122.5, 52.5, 29.8. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2952, 1724, 1694, 1561, 1269. Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.45; H, 5.04; N, 5. 63.

***Trans*-(3*R*,13b*S*,a*S*)-13b-methyl-3-phenyl-2,3-dihydro-13b*H*-benz[e]oxazolo[3,2-a]pyrido[2,3-c]azepin-5-one (13).** To a solution of methyl 2-(3-acetylpyridyl)benzoate **12** (1.80 g, 7.06 mmol) in toluene (50 mL) was added (*R*)-phenylglycinol (1.07 g, 7.80 mmol). The mixture was refluxed for 2 days and then cooled to room temperature. Solvent was removed under vacuum. Flash chromatography (eluent: $CH_2Cl_2$) provided **13** (1.55 g, 60%) as a yellow solid. Mp: 84°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.75 (dd, *J* = 4.8 and 1.5 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.96 (dd, *J* = 7.8 and 1.7 Hz, 1H), 7.90 (dd, *J* = 7.7 and 1.1 Hz, 1H), 7.10-7.70 (m, 8H), 5.48 (m, 1H), 4.33 (m, 2H), 1.58 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 164.8, 153.3, 150.0, 140.8, 137.7, 136.4, 133.5, 131.8, 131.1, 130.6, 129.9, 129.8, 129.0, 128.0, 127.2, 123.1, 93.0, 71.4, 62.3, 26.0. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2924,

1723, 1635, 1423, 1395. Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.94; H, 5.16; N, 8.39. $[\alpha]^{20}_D$ = - 16.0 (*c* = 1.0, $CH_2Cl_2$).

***Trans*-(3*R*,13b*S*,a*S*)-13b-methyl-3-phenyl-2,3-dihydro-13b*H*-benz[e]oxazolo[3,2-a]-*N*-oxide-pyrido[2,3-c]azepin-5-one (14).** To a solution of lactam **13** (1.55 g, 4.53 mmol) in $CH_2Cl_2$ (30 mL) was added *m*-chloroperbenzoic acid (70%, 3.35 g, 13.6 mmol). The mixture was stirred for 3 days and 2N aqueous potassium carbonate (50 mL) was added. After phase separation, the aqueous phase was extracted with dichloromethane (50 mL). Drying ($MgSO_4$) and evaporation of $CH_2Cl_2$ afforded 1.5 g of a pale brownish oil. Flash chromatography on silica gel (eluent: EtOAc then EtOH) of the crude product provided **14** (1.32 g, 81%) as a white solid. Mp: 104°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.27 (m, 2H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.19-7.46 (m, 10H), 5.37 (m, 1H), 4.18 (m, 2H), 1.34 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 164.0, 144.0, 143.2, 140.9, 140.4, 134.6, 130.9, 130.3, 130.1, 129.1, 128.2, 127.3, 127.2, 124.8, 120.7, 92.3, 71.6, 61.7, 25.0. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 3063, 2883, 1644, 1394. Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.64; H, 5.17; N, 7.79. $[\alpha]^{20}_D$ = - 218.2 (*c* = 0.55, $CH_2Cl_2$).

***Trans*-(3*R*,13b*S*,a*S*)-13b-methyl-3-phenyl-2,3-dihydro-13bH-benz[e]oxazolo[3,2-a](6-cyano)pyrido[2,3-c]azepin-5-one (15).** Prepared as described for **9** according to procedure A from pyridine *N*-oxide **14** (750 mg, 2.09 mmol), trimethysilyl cyanide (229 mg, 2.31 mmol) and dimethylcarbamoyl chloride (199 µL, 2.36 mmol). Flash chromatography (eluent: cyclohexane/EtOAc: 1/1) provided **15** (443 mg, 58%) as a yellow solid. Mp: 94°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.78 (dd, *J* = 7.7 and 0.8 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.53 (dt, *J* = 7.5 Hz and 1.3 Hz, 1H), 7.41-7.49 (m, 3H), 7.20-7.30 (m, 3H), 5.37 (d, *J* = 4.9 Hz, 1H), 4.18 (m, 2H), 1.46 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 163.5, 154.7, 140.7, 139.9, 134.1, 133.5, 133.1, 132.2, 131.7, 130.4, 129.9, 128.6, 127.8, 127.4, 126.8, 116.9, 92.2, 71.1, 62.0, 25.1. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2924, 2850, 1636, 1394. Anal. Calcd. for $C_{23}H_{17}N_3O_2$: C, 75.19; H, 4.66; N, 11.44. Found: C, 75.27; H, 4.73; N, 11.33. $[\alpha]^{20}_D$ = - 36.8 (*c* = 1.1, $CH_2Cl_2$).

**Phenyl(3-carboxypyridin-2-yl)methanone (16).** To a solution of 2,3-pyridinedicarboxylic anhydride (7.46 g, 50 mmol) in dry THF (80 mL) at -78°C was added dropwise phenylmagnesium chloride in THF (2M, 26.2 mL, 52.5 mmol). The mixture was stirred for 2 hours, warmed to room temperature and quenched with 1M HCl

(55 mL). After phase separation, the aqueous phase was extracted with $CH_2Cl_2$ (2 x 30 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. Solvent was removed under vacuum and the residue was triturated in ether. Filtration provided **16** (4.20 g, 37%) as a pale powder. Mp: 134°C. $^1$H NMR 300 MHz, (DMSO) δ 8.84 (d, *J* = 3.8 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.75 (m, 1H), 7.66 (m, 3H), 7.53 (m, 2H). $^{13}$C NMR 75 MHz, (DMSO) δ 194.8, 166.5, 150.5, 147.4, 137.0, 136.8, 136.7, 133.9, 129.4, 129.2, 126.7. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2853, 1797, 1668, 1287. Anal. Calcd. for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.96; H, 4.14; N, 6.00.

***Trans*-(3*R*,13b*S*,a*S*)-13b-methyl-3-phenyl-2,3-dihydro-13b*H*-benz[e]oxazolo[3,2-a]-6-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-pyrido[2,3-c]azepin-5-one (2d).** Prepared as described for **2a** according to procedure B from dry $ZnCl_2$ (16.7 mg, 0.12 mmol), cyanopyridine **15** (450 mg, 1.22 mmol) and 2-amino-2-methylpropanol (120.3 mg, 1.35 mmol) in chlorobenzene (6 mL). Flash chromatography of the residue on neutral alumina (eluent: EtOAc/cyclohexane: 1/1) provided ligand **2d** (323 mg, 60%) as a white solid. Mp: 106°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.15 (m, 2H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.88 (dd, *J* = 7.7 and 1.1 Hz, 1H), 7.64 (dt, *J* = 7.5 and 1.1 Hz, 1H), 7.52 (m, 3H), 7.42-7.31 (m, 3H), 5.47 (dd, *J* = 4.1 and 2.8 Hz, 1H), 4.31 (m, 2H), 4.24 (s, 2H), 1.57 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 164.4, 161.4, 153.3, 147.6, 140.8, 139.6, 135.9, 133.5, 132.1, 131.9, 130.6, 130.5, 130.0, 129.1, 128.1, 127.3, 123.6, 93.1, 80.2, 77.0, 68.5, 62.3, 28.8, 25.9. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 3435, 2925, 2852, 1633. Anal. Calcd. for $C_{27}H_{25}N_3O_3$: C, 73.78; H, 5.73; N, 9.56. Found: C, 73.61, H, 5.99; N, 9.37. $[\alpha]^{20}_D$ = - 39.9 (*c* = 5.96, $CH_2Cl_2$).

**(3*S*,9b*R*)-2,3-Dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]pyrrolo[3,4-b]pyridin-5-(9b*H*)-one (17)**. To a solution of benzoylnicotinic acid **16** (4.00 g, 15.5 mmol) in toluene (200 mL) was added (*R*)-phenylglycinol (2.41 g, 17.6 mmol). The solution was refluxed overnight in a Dean-Stark apparatus and then cooled to room temperature. Toluene was evaporated under vacuum. Crystallisation of the residue by addition of cyclohexane afforded after filtration lactam **17** (2.89 g, 50%) as a beige solid. Mp: 176°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.60 (d, *J* = 4.1 Hz, 1H), 7.35 (m, 3H), 7.13 (m, 4H), 6.98 (m, 5H), 5.11 (t, *J* = 8.3 Hz, 1H), 4.69 (t, *J* = 8.5 Hz, 1H), 3.99 (*J* = 8.7 Hz, 1H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 173.0, 153.0, 149.1, 142.1, 138.3, 137.2, 132.0, 129.2, 129.1, 128.6, 127.7, 126.9, 126.7, 125.9, 99.7, 76.7, 60.1. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2853, 2448, 1667, 1287,

934. Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.71; H, 5.09; N, 8.46. $[\alpha]^{20}_D$ = - 247.0 (*c* = 2.13, $CH_2Cl_2$).

**(3*S*,9b*R*)-2,3-Dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]*N*-oxyde-pyrrolo[3,4-b]pyridin-5(9b*H*)-one (18)**. To a solution of lactam **17** (2.72 g, 8.3 mmol) in $CH_2Cl_2$ (50 mL) was added *m*-chloroperbenzoic acid (6.14 g, 35.6 mmol). The mixture was stirred for 3 days. The organic phase was washed with 15% aqueous potassium carbonate (50 mL). After drying ($MgSO_4$) and evaporation of $CH_2Cl_2$ under vacuum, the residue was dissolved in a minimal amount of $CH_2Cl_2$. Then a large excess of ether was added. The resulting oil was vigorously triturated and the solid formed was filtered off to afford **18** (2.17 g, 76%) as a beige powder. Mp: 208°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.24 (d, *J* = 6.4 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.05-7.36 (m, 10 H), 5.31 (t, *J* = 8.1 Hz, 1H), 4.90 (t, *J* = 8.6 H, 1H), 4.17 (t, *J* = 8.6 Hz, 1H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 167.3, 147.0, 142.6, 138.3 (x2), 136.6, 129.9, 129.7, 129.6, 128.9, 128.1, 127.0, 126.3, 120.5, 98.6, 76.7, 60.6. IR $\upsilon_{max}$ $cm^{-1}$ (KBr): 3069, 1736, 1438, 1325, 1242. Anal. Calcd. for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.10; H, 4.64; N, 8.26. $[\alpha]^{20}_D$ = - 341.7 (*c* = 2.71, $CH_2Cl_2$).

**(3*S*,9b*R*)-2,3-Dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]pyrrolo[3,4-b](6-chloro)pyridin-5(9b*H*)-one (19).** To a solution of pyridine *N*-oxide **18** (200 mg, 0.61 mmol) in dry $CH_2Cl_2$ (10 mL) were added phosphorus oxychloride (33 µL, 3.54 mmol) and triethylamine (611 µL, 4.38 mmol). The mixture was refluxed for 1 night and then cooled to 0°C. The solution was quenched with water (10 mL) and neutralized with 20% aqueous potassium carbonate. After phase separation, the aqueous phase was extracted with $CH_2Cl_2$ (2 x 10 mL). After drying ($MgSO_4$), the solvent was removed under vacuum and the resultant crude product was purified by flash chromatography (eluent: cyclohexane/EtOAc: 1/1) providing 2-chloropyridine **19** (90 mg, 41%) as a white product. Mp: 80°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 7.54 (m, 3H), 7.34 (m, 4H), 7.10-7.21 (m, 5H), 5.30 (t, *J* = 8.3 Hz, 1H), 4.89 (dd, *J* = 9.0 and 8.3 Hz, 1H), 4.19 (t, *J* = 9 Hz, 1H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 171.8, 155.6, 149.8, 141.4, 138.3, 137.1, 134.8, 129.7, 129.6, 129.0, 128.3, 128.2, 127.1, 126.2, 99.6, 77.2, 60.7. IR $\upsilon_{max}$ $cm^{-1}$ (KBr): 2926, 1736, 1588, 1434, 1320. Anal. Calcd. for $C_{21}H_{15}ClN_2O_2$: C, 69.52; H, 4.17; N, 7.72. Found: C, 69.41; H, 4.31; N, 7.77. $[\alpha]^{20}_D$ = - 365.1 (*c* = 1.06, $CH_2Cl_2$).

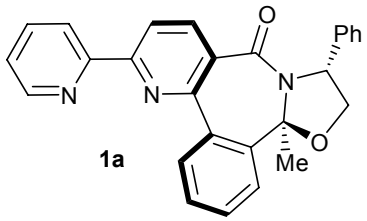
**6,6'Bis(3*S*,9b*R*)-2,3-dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]pyrrolo[3,4-b]pyridin-5(9b*H*)-one (1c)**. To a stirred solution of nickel(II) chloride hexahydrate (300 mg, 1.26 mmol) and triphenylphosphine (1.33 g, 5.07 mmol) in dry, degassed DMF (6 mL) was added zinc dust (<10 μm, 106.7 mg, 1.63 mmol) and the resultant suspension was heated at 60 °C for 1 hour. A solution of chloropyridine **19** (451 mg, 1.24 mmol) in dry, degassed DMF (6 mL) was then added. The resultant mixture was heated at 60°C for 4 hours. The reaction mixture was then allowed to cool to room temperature and was poured into an aqueous solution of ammonia (10% w/w, 50 mL). The resultant mixture was extracted with $CH_2Cl_2$ (3 x 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography of the residue on silica gel (eluent: EtOAc/cyclohexane 1:4) provided ligand **1c** (370 mg, 91%) as a white solid. Mp: 192 °C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.5 and 1.7 Hz, 4H), 7.26 (m, 6H), 7.12 (m, 10H), 5.28 (t, *J* = 8.5 Hz, 2H), 4.86 (t, *J* = 4.9 Hz, 2H), 4.15 (t, *J* = 8.7 Hz, 2H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 173.1, 158.4, 149.2, 143.0, 138.5, 137.4, 133.2, 129.5, 129.4, 128.9, 128.0, 127.0, 126.2, 125.7, 99.8, 77.0, 60.5. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 1736, 1318, 698. Anal. Calcd. for $C_{42}H_{30}N_4O_4$: C, 77.05; H, 4.62; N, 8.56. Found: C, 76.91, H, 4.51, N, 8.42. $[\alpha]^{20}_D$ = -321.4 (*c* = 0.28, $CH_2Cl_2$).

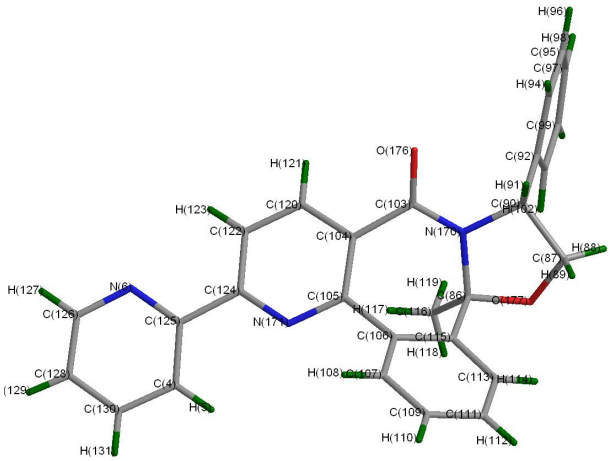
**(3*S*,9b*R*)-2,3-Dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]pyrrolo[3,4-b](6-cyano)pyridin-5(9b*H*)-one (20).** Prepared as described for **9** according to procedure A from pyridine *N*-oxide **18** (1.00 g, 2.90 mmol), trimethysilyl cyanide (294 mg, 2.96 mmol) and dimethylcarbamoyl chloride (305 μL, 3.32 mmol). Flash chromatography (eluent: cyclohexane/EtOAc: 1/1) provided **20** (571 mg, 56%) as a yellow solid. Mp: 86°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 7.72 (m, 2H), 7.50 (m, 2H), 7.30 (m, 3H), 7.02-7.13 (m, 5H), 5.25 (t, *J* = 8.3 Hz, 1H), 4.85 (t, *J* = 8.8 Hz, 1H), 4.14 (t, *J* = 8.6 Hz, 1H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 171.0, 150.9, 144.5, 137.9, 136.9, 136.4, 134.1, 131.9, 130.1, 129.8, 129.1, 128.3, 127.1, 126.2, 116.7, 99.6, 77.1, 60.8. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2926, 1736, 1323, 1211. Anal. Calcd. for $C_{22}H_{15}N_3O_2$: C, 74.78; H, 4.28; N, 11.89. Found: 74.70; H, 4.39; N, 11.81. $[\alpha]^{20}_D$ = - 331.8 (*c* = 1.07, $CH_2Cl_2$).

**(3*S*,9b*R*)-2,3-Dihydro-9b-phenyl-3-phenyl-oxazolo[3',2':1,2]pyrrolo[3,4-b][6-(4,5-dihydro-4,4-dimethyloxazol-2-yl)]-pyridin-5(9b*H*)-one (2e).** Prepared as described for **2a** according to procedure B from dry $ZnCl_2$ (14.0 mg, 0.10 mmol), cyanopyridine **20**

(353.4 mg, 1.00 mmol) and 2-amino-2-methylpropanol (151.0 mg, 1.10 mmol) in chlorobenzene (5 mL). Flash chromatography (eluent: $CH_2Cl_2$/EtOAc: 4/1) provided ligand **2e** (340 mg, 80%) as a white powder. Mp: 114°C. $^1$H NMR 300 MHz, ($CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.55 (m, 2H), 7.34 (m, 3H), 7.20 (m, 3H), 7.13 (m, 2H), 5.34 (t, *J* = 8.3 Hz, 1H), 4.91 (t, *J* = 7.1 Hz, 1H), 4.22 (s, 2H), 4.21 (t, *J* = 7.6 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H). $^{13}$C NMR 75 MHz, ($CDCl_3$) δ 172.0, 161.0, 150.9, 149.6, 143.8, 138.5, 137.4, 132.9, 129.6, 129.5, 128.9, 128.1, 127.6, 127.1, 126.3, 99.7, 77.2, 68.6, 60.7, 28.8, 28.7. IR $\upsilon_{max}$ cm$^{-1}$ (KBr): 2972, 1729, 1327, 1097. Anal. Calcd. for $C_{26}H_{23}N_3O_3$: C, 73.39; H, 5.45; N, 9.88. Found: C, 73.24; H, 5.37; N, 10.03. $[\alpha]^{20}_D$ = - 300.0 (*c* = 0.96, $CH_2Cl_2$).

X-ray data of 2,2'-bipyridine **1a**:



# Bond lengths [Å] and angles [°] for compound **1a**.

| | |
|---|---|
| C(4)-C(125) | 1.410 |
| C(4)-C(130) | 1.373 |
| C(4)-H(5) | 0.948 |
| N(6)-C(125) | 1.328 |
| N(6)-C(126) | 1.328 |
| C(86)-C(115) | 1.529 |
| C(86)-C(116) | 1.513 |
| C(86)-N(170) | 1.489 |
| C(86)-O(177) | 1.419 |
| C(87)-C(90) | 1.534 |
| C(87)-O(177) | 1.441 |
| C(87)-H(88) | 0.991 |
| C(87)-H(89) | 0.989 |
| C(90)-C(92) | 1.514 |
| C(90)-N(170) | 1.467 |
| C(90)-H(91) | 1.002 |
| C(92)-C(93) | 1.415 |
| C(92)-C(101) | 1.374 |
| C(93)-C(95) | 1.382 |
| C(93)-H(94) | 0.951 |
| C(95)-C(97) | 1.348 |
| C(95)-H(96) | 0.950 |
| C(97)-C(99) | 1.343 |
| C(97)-H(98) | 0.949 |
| C(99)-C(101) | 1.365 |
| C(99)-H(100) | 0.950 |
| C(101)-H(102) | 0.951 |
| C(103)-C(104) | 1.498 |
| C(103)-N(170) | 1.342 |
| C(103)-O(176) | 1.240 |
| C(104)-C(105) | 1.416 |
| C(104)-C(120) | 1.381 |
| C(105)-C(106) | 1.481 |
| C(105)-N(171) | 1.352 |
| C(106)-C(107) | 1.406 |
| C(106)-C(115) | 1.409 |
| C(107)-C(109) | 1.379 |
| C(107)-H(108) | 0.950 |
| C(109)-C(111) | 1.377 |
| C(109)-H(110) | 0.949 |
| C(111)-C(113) | 1.377 |
| C(111)-H(112) | 0.950 |
| C(113)-C(115) | 1.392 |
| C(113)-H(114) | 0.950 |
| C(116)-H(117) | 0.980 |
| C(116)-H(118) | 0.980 |
| C(116)-H(119) | 0.981 |
| C(120)-C(122) | 1.377 |
| C(120)-H(121) | 0.950 |
| C(122)-C(124) | 1.394 |
| C(122)-H(123) | 0.951 |
| C(124)-C(125) | 1.492 |
| C(124)-N(171) | 1.340 |
| C(126)-C(128) | 1.355 |
| C(126)-H(127) | 0.950 |
| C(128)-C(130) | 1.361 |

| | |
|---|---|
| C(128)-H(129) | 0.951 |
| C(130)-H(131) | 0.950 |
| C(125)-C(4)-C(130) | 118.713 |
| H(5)-C(4)-C(125) | 120.685 |
| H(5)-C(4)-C(130) | 120.602 |
| C(125)-N(6)-C(126) | 116.994 |
| C(115)-C(86)-C(116) | 113.479 |
| C(115)-C(86)-N(170) | 109.753 |
| C(115)-C(86)-O(177) | 110.513 |
| C(116)-C(86)-N(170) | 114.338 |
| C(116)-C(86)-O(177) | 105.811 |
| N(170)-C(86)-O(177) | 102.255 |
| C(90)-C(87)-O(177) | 103.837 |
| H(88)-C(87)-C(90) | 111.033 |
| H(88)-C(87)-O(177) | 110.925 |
| H(88)-C(87)-H(89) | 108.947 |
| H(89)-C(87)-C(90) | 111.032 |
| H(89)-C(87)-O(177) | 111.017 |
| C(87)-C(90)-C(92) | 113.428 |
| C(87)-C(90)-N(170) | 100.801 |
| C(87)-C(90)-H(91) | 109.165 |
| C(92)-C(90)-N(170) | 115.049 |
| H(91)-C(90)-C(92) | 109.034 |
| H(91)-C(90)-N(170) | 109.013 |
| C(90)-C(92)-C(93) | 121.102 |
| C(90)-C(92)-C(101) | 123.808 |
| C(93)-C(92)-C(101) | 114.831 |
| C(92)-C(93)-C(95) | 121.461 |
| C(92)-C(93)-H(94) | 119.247 |
| H(94)-C(93)-C(95) | 119.292 |
| C(93)-C(95)-C(97) | 119.213 |
| C(93)-C(95)-H(96) | 120.255 |
| H(96)-C(95)-C(97) | 120.532 |
| C(95)-C(97)-C(99) | 121.551 |
| C(95)-C(97)-H(98) | 119.196 |
| H(98)-C(97)-C(99) | 119.252 |
| C(97)-C(99)-C(101) | 119.252 |
| C(97)-C(99)-H(100) | 120.402 |
| H(100)-C(99)-C(101) | 120.346 |
| C(92)-C(101)-C(99) | 123.433 |
| C(92)-C(101)-H(102) | 118.287 |
| C(99)-C(101)-H(102) | 118.280 |
| C(104)-C(103)-N(170) | 119.012 |
| C(104)-C(103)-O(176) | 119.493 |
| N(170)-C(103)-O(176) | 121.436 |
| C(103)-C(104)-C(105) | 124.666 |
| C(103)-C(104)-C(120) | 117.577 |
| C(105)-C(104)-C(120) | 117.447 |
| C(104)-C(105)-C(106) | 123.634 |
| C(104)-C(105)-N(171) | 122.005 |
| C(106)-C(105)-N(171) | 114.353 |
| C(105)-C(106)-C(107) | 118.231 |
| C(105)-C(106)-C(115) | 123.365 |
| C(107)-C(106)-C(115) | 118.404 |
| C(106)-C(107)-C(109) | 121.738 |
| C(106)-C(107)-H(108) | 119.209 |
| H(108)-C(107)-C(109) | 119.053 |
| C(107)-C(109)-C(111) | 118.968 |
| C(107)-C(109)-H(110) | 120.478 |
| H(110)-C(109)-C(111) | 120.553 |

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|---|---|
| C(109)-C(111)-C(113) | 120.783 |
| C(109)-C(111)-H(112) | 119.513 |
| H(112)-C(111)-C(113) | 119.703 |
| C(111)-C(113)-C(115) | 121.199 |
| C(111)-C(113)-H(114) | 119.414 |
| H(114)-C(113)-C(115) | 119.387 |
| C(86)-C(115)-C(106) | 120.860 |
| C(86)-C(115)-C(113) | 120.270 |
| C(106)-C(115)-C(113) | 118.857 |
| C(86)-C(116)-H(117) | 109.505 |
| C(86)-C(116)-H(118) | 109.519 |
| C(86)-C(116)-H(119) | 109.443 |
| H(117)-C(116)-H(118) | 109.506 |
| H(117)-C(116)-H(119) | 109.397 |
| H(118)-C(116)-H(119) | 109.457 |
| C(104)-C(120)-C(122) | 120.554 |
| C(104)-C(120)-H(121) | 119.823 |
| H(121)-C(120)-C(122) | 119.623 |
| C(120)-C(122)-C(124) | 118.860 |
| C(120)-C(122)-H(123) | 120.510 |
| H(123)-C(122)-C(124) | 120.630 |
| C(122)-C(124)-C(125) | 121.843 |
| C(122)-C(124)-N(171) | 122.049 |
| C(125)-C(124)-N(171) | 116.107 |
| C(4)-C(125)-N(6) | 121.766 |
| C(4)-C(125)-C(124) | 121.570 |
| N(6)-C(125)-C(124) | 116.658 |
| N(6)-C(126)-C(128) | 124.966 |
| N(6)-C(126)-H(127) | 117.541 |
| H(127)-C(126)-C(128) | 117.493 |
| C(126)-C(128)-C(130) | 118.652 |
| C(126)-C(128)-H(129) | 120.691 |
| H(129)-C(128)-C(130) | 120.657 |
| C(4)-C(130)-C(128) | 118.852 |
| C(4)-C(130)-H(131) | 120.602 |
| C(128)-C(130)-H(131) | 120.546 |
| C(86)-N(170)-C(90) | 111.586 |
| C(86)-N(170)-C(103) | 126.883 |
| C(90)-N(170)-C(103) | 120.402 |
| C(105)-N(171)-C(124) | 119.016 |
| C(86)-O(177)-C(87) | 108.696 |

## Torsion angles [°] for compound **1a**

| | |
|---|---|
| C(130)-C(4)-C(125)-N(6) | -2.416 |
| C(130)-C(4)-C(125)-C(124) | 178.467 |
| H(5)-C(4)-C(125)-N(6) | 177.777 |
| H(5)-C(4)-C(125)-C(124) | -1.341 |
| C(125)-C(4)-C(130)-C(128) | 2.873 |
| C(125)-C(4)-C(130)-H(131) | -177.220 |
| H(5)-C(4)-C(130)-C(128) | -177.319 |
| H(5)-C(4)-C(130)-H(131) | 2.588 |
| C(126)-N(6)-C(125)-C(4) | 0.852 |
| C(126)-N(6)-C(125)-C(124) | -179.989 |
| C(125)-N(6)-C(126)-C(128) | 0.210 |
| C(125)-N(6)-C(126)-H(127) | -179.842 |
| C(116)-C(86)-C(115)-C(106) | -67.180 |

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|---|---|
| C(116)-C(86)-C(115)-C(113) | 111.464 |
| N(170)-C(86)-C(115)-C(106) | 62.121 |
| N(170)-C(86)-C(115)-C(113) | -119.235 |
| O(177)-C(86)-C(115)-C(106) | 174.155 |
| O(177)-C(86)-C(115)-C(113) | -7.201 |
| C(115)-C(86)-C(116)-H(117) | 58.133 |
| C(115)-C(86)-C(116)-H(118) | -61.960 |
| C(115)-C(86)-C(116)-H(119) | 178.046 |
| N(170)-C(86)-C(116)-H(117) | -68.801 |
| N(170)-C(86)-C(116)-H(118) | 171.107 |
| N(170)-C(86)-C(116)-H(119) | 51.112 |
| O(177)-C(86)-C(116)-H(117) | 179.470 |
| O(177)-C(86)-C(116)-H(118) | 59.378 |
| O(177)-C(86)-C(116)-H(119) | -60.617 |
| C(115)-C(86)-N(170)-C(90) | 107.488 |
| C(115)-C(86)-N(170)-C(103) | -60.275 |
| C(116)-C(86)-N(170)-C(90) | -123.680 |
| C(116)-C(86)-N(170)-C(103) | 68.556 |
| O(177)-C(86)-N(170)-C(90) | -9.835 |
| O(177)-C(86)-N(170)-C(103) | -177.599 |
| C(115)-C(86)-O(177)-C(87) | -87.356 |
| C(116)-C(86)-O(177)-C(87) | 149.410 |
| N(170)-C(86)-O(177)-C(87) | 29.422 |
| O(177)-C(87)-C(90)-C(92) | -94.979 |
| O(177)-C(87)-C(90)-N(170) | 28.554 |
| O(177)-C(87)-C(90)-H(91) | 143.226 |
| H(88)-C(87)-C(90)-C(92) | 24.282 |
| H(88)-C(87)-C(90)-N(170) | 147.815 |
| H(88)-C(87)-C(90)-H(91) | -97.513 |
| H(89)-C(87)-C(90)-C(92) | 145.652 |
| H(89)-C(87)-C(90)-N(170) | -90.815 |
| H(89)-C(87)-C(90)-H(91) | 23.857 |
| C(90)-C(87)-O(177)-C(86) | -37.723 |
| H(88)-C(87)-O(177)-C(86) | -157.058 |
| H(89)-C(87)-O(177)-C(86) | 81.656 |
| C(87)-C(90)-C(92)-C(93) | -125.284 |
| C(87)-C(90)-C(92)-C(101) | 48.555 |
| N(170)-C(90)-C(92)-C(93) | 119.379 |
| N(170)-C(90)-C(92)-C(101) | -66.782 |
| H(91)-C(90)-C(92)-C(93) | -3.415 |
| H(91)-C(90)-C(92)-C(101) | 170.423 |
| C(87)-C(90)-N(170)-C(86) | -11.625 |
| C(87)-C(90)-N(170)-C(103) | 157.039 |
| C(92)-C(90)-N(170)-C(86) | 110.783 |
| C(92)-C(90)-N(170)-C(103) | -80.552 |
| H(91)-C(90)-N(170)-C(86) | -126.412 |
| H(91)-C(90)-N(170)-C(103) | 42.253 |
| C(90)-C(92)-C(93)-C(95) | 179.232 |
| C(90)-C(92)-C(93)-H(94) | -0.922 |
| C(101)-C(92)-C(93)-C(95) | 4.871 |
| C(101)-C(92)-C(93)-H(94) | -175.283 |
| C(90)-C(92)-C(101)-C(99) | -179.320 |
| C(90)-C(92)-C(101)-H(102) | 0.787 |
| C(93)-C(92)-C(101)-C(99) | -5.132 |
| C(93)-C(92)-C(101)-H(102) | 174.976 |
| C(92)-C(93)-C(95)-C(97) | -1.089 |
| C(92)-C(93)-C(95)-H(96) | 179.064 |
| H(94)-C(93)-C(95)-C(97) | 179.065 |
| H(94)-C(93)-C(95)-H(96) | -0.782 |
| C(93)-C(95)-C(97)-C(99) | -2.914 |

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|---|---|
| C(93)-C(95)-C(97)-H(98) | 177.046 |
| H(96)-C(95)-C(97)-C(99) | 176.932 |
| H(96)-C(95)-C(97)-H(98) | -3.107 |
| C(95)-C(97)-C(99)-C(101) | 2.770 |
| C(95)-C(97)-C(99)-H(100) | -177.200 |
| H(98)-C(97)-C(99)-C(101) | -177.191 |
| H(98)-C(97)-C(99)-H(100) | 2.839 |
| C(97)-C(99)-C(101)-C(92) | 1.522 |
| C(97)-C(99)-C(101)-H(102) | -178.586 |
| H(100)-C(99)-C(101)-C(92) | -178.508 |
| H(100)-C(99)-C(101)-H(102) | 1.384 |
| N(170)-C(103)-C(104)-C(105) | 47.138 |
| N(170)-C(103)-C(104)-C(120) | -139.436 |
| O(176)-C(103)-C(104)-C(105) | -135.614 |
| O(176)-C(103)-C(104)-C(120) | 37.812 |
| C(104)-C(103)-N(170)-C(86) | -7.385 |
| C(104)-C(103)-N(170)-C(90) | -174.176 |
| O(176)-C(103)-N(170)-C(86) | 175.423 |
| O(176)-C(103)-N(170)-C(90) | 8.632 |
| C(103)-C(104)-C(105)-C(106) | -4.151 |
| C(103)-C(104)-C(105)-N(171) | 174.757 |
| C(120)-C(104)-C(105)-C(106) | -177.585 |
| C(120)-C(104)-C(105)-N(171) | 1.323 |
| C(103)-C(104)-C(120)-C(122) | -176.740 |
| C(103)-C(104)-C(120)-H(121) | 3.213 |
| C(105)-C(104)-C(120)-C(122) | -2.831 |
| C(105)-C(104)-C(120)-H(121) | 177.122 |
| C(104)-C(105)-C(106)-C(107) | 141.138 |
| C(104)-C(105)-C(106)-C(115) | -38.624 |
| N(171)-C(105)-C(106)-C(107) | -37.846 |
| N(171)-C(105)-C(106)-C(115) | 142.392 |
| C(104)-C(105)-N(171)-C(124) | -0.118 |
| C(106)-C(105)-N(171)-C(124) | 178.884 |
| C(105)-C(106)-C(107)-C(109) | 179.103 |
| C(105)-C(106)-C(107)-H(108) | -0.822 |
| C(115)-C(106)-C(107)-C(109) | -1.123 |
| C(115)-C(106)-C(107)-H(108) | 178.952 |
| C(105)-C(106)-C(115)-C(86) | 0.935 |
| C(105)-C(106)-C(115)-C(113) | -177.727 |
| C(107)-C(106)-C(115)-C(86) | -178.826 |
| C(107)-C(106)-C(115)-C(113) | 2.511 |
| C(106)-C(107)-C(109)-C(111) | -0.285 |
| C(106)-C(107)-C(109)-H(110) | 179.862 |
| H(108)-C(107)-C(109)-C(111) | 179.640 |
| H(108)-C(107)-C(109)-H(110) | -0.213 |
| C(107)-C(109)-C(111)-C(113) | 0.278 |
| C(107)-C(109)-C(111)-H(112) | -179.831 |
| H(110)-C(109)-C(111)-C(113) | -179.869 |
| H(110)-C(109)-C(111)-H(112) | 0.022 |
| C(109)-C(111)-C(113)-C(115) | 1.185 |
| C(109)-C(111)-C(113)-H(114) | -178.705 |
| H(112)-C(111)-C(113)-C(115) | -178.706 |
| H(112)-C(111)-C(113)-H(114) | 1.404 |
| C(111)-C(113)-C(115)-C(86) | 178.741 |
| C(111)-C(113)-C(115)-C(106) | -2.588 |
| H(114)-C(113)-C(115)-C(86) | -1.369 |
| H(114)-C(113)-C(115)-C(106) | 177.301 |
| C(104)-C(120)-C(122)-C(124) | 3.133 |
| C(104)-C(120)-C(122)-H(123) | -177.016 |
| H(121)-C(120)-C(122)-C(124) | -176.820 |

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| H(121)-C(120)-C(122)-H(123) | 3.031 |
| C(120)-C(122)-C(124)-C(125) | 177.638 |
| C(120)-C(122)-C(124)-N(171) | -1.899 |
| H(123)-C(122)-C(124)-C(125) | -2.213 |
| H(123)-C(122)-C(124)-N(171) | 178.251 |
| C(122)-C(124)-C(125)-C(4) | 169.123 |
| C(122)-C(124)-C(125)-N(6) | -10.037 |
| N(171)-C(124)-C(125)-C(4) | -11.314 |
| N(171)-C(124)-C(125)-N(6) | 169.526 |
| C(122)-C(124)-N(171)-C(105) | 0.398 |
| C(125)-C(124)-N(171)-C(105) | -179.164 |
| N(6)-C(126)-C(128)-C(130) | 0.318 |
| N(6)-C(126)-C(128)-H(129) | -179.728 |
| H(127)-C(126)-C(128)-C(130) | -179.631 |
| H(127)-C(126)-C(128)-H(129) | 0.324 |
| C(126)-C(128)-C(130)-C(4) | -1.888 |
| C(126)-C(128)-C(130)-H(131) | 178.205 |
| H(129)-C(128)-C(130)-C(4) | 178.157 |
| H(129)-C(128)-C(130)-H(131) | -1.750 |