Supporting Information

Asymmetric 1,3-Dipolar Cycloaddition Reactions of Nitrile Oxides Catalyzed by Chiral Binaphthyldiimine-Ni(II) Complexes

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Experimental Section

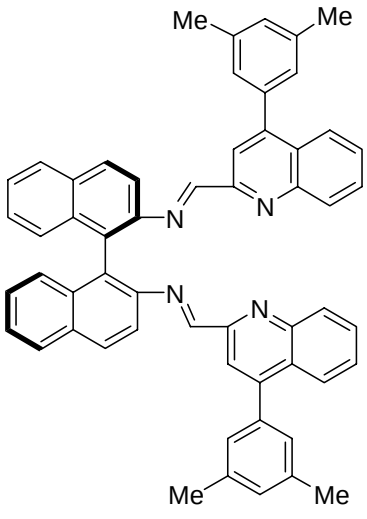
General. Melting points were determined on a melting point apparatus and are uncorrected. IR spectra were taken with a FT/IR spectrophotometer. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer using broadband proton decoupling. Chemical shifts are expressed in parts per million using the middle resonance of $CDCl_3$ (77.0 ppm) as an internal standard. For preparative column chromatography, Wakogel C-300HG was employed. All reactions were carried out under an argon atmosphere in dried glassware.

Materials. 2,4,6-Trimethylbenzonitrile oxide (**1a**) was prepared according to the procedure in the previous paper.[1] Hydroximoyl chlorides as the precursors for the corresponding nitrile oxides were prepared by the procedure in the literature.[1a] Chiral Binaphthyldiimine (BINIM) ligands were prepared by the procedure reported previously.[2] 3-Crotonoyl-2-oxazolidinone (**2**),[3] 3-crotonoyl-5,5-dimethyl-2-oxazozolidinone (**3**),[3] 5,5-dimethyl-3-(2-pentenoyl)-2-oxazolidinone (**11**),[3] 3-acryloyl-5,5-dimethyl-2-oxazolidinone (**12**),[3] and 5,5-dimethy-3-[3-(ethoxycarbonyl)propenoyl]-2-oxazolidinone (**13**)[4] were prepared according to the procedure reported by Evans. 1-Benzyl-2-crotonyl-5,5-dimethyl-3-pyrazolidinone (**4**),[5] 2-acryloyl-1-benzyl-5,5-dimethyl-3-pyrazolidinone (**14**),[6] and 1-benzyl-2-[3-(ethoxycarbonyl)propenoyl]-5,5-dimethy-3-pyrazolidinone (**15**)[5] were prepared according to the procedure reported in the literature. Powdered 4Å molecular sieves (MS 4Å) is commercially available (Aldrich) and dried *in vacuo* at 200 ^{o}C for 12 h before use. $Ni(ClO_4)_2 \cdot 6H_2O$ is commercially available, and used without further purification. CH_2Cl_2 was purified by distillation first from $CaCl_2$ and then CaH_2 under argon before used.

General Procedure for the Preparation of (*R*)-BINIM-4X-2QN was Exemplified by the Reaction of (*R*)-1,1'-Binaphthyl-2,2'-diamine with 4-(3,5-Xylyl)-2-quinolinecarbaldehyde. A suspension of (*R*)-1,1'-binaphthyl-2,2'-diamine (0.341 g, 1.2 mmol), 4-(3,5-xylyl)-2-quinolinecarbaldehyde (0.627 g, 2.4 mmol), and MS 4Å (10.0 g) in benzene (25 mL) was heated under reflux for 10 h. After removal of MS 4 Å by filtration, the solvent was evaporated *in vacuo*. The

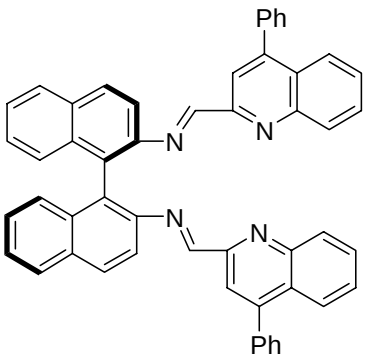
residual solid was recrystallized from diethyl ether-hexane to give the corresponding (*R*)-BINIM-4(3,5-xylyl)-2QN (0.488 g, 52%).

(*R*)-*N,N'*-Bis[4-(3,5-xylyl)-2-quinolylmethylene]-1,1'-binaphthyl-2,2'-diamine: Yellow prisms;



mp 136.0-138.0 ^{o}C; (diethyl ether-hexane), $[\alpha]_D^{25}$ = -120.4 ^{o} (*c* = 0.50, CH_2Cl_2); IR (KBr) 3449, 3055, 2918, 1587, 1552, 1504, 1425, 1377, 1224, 1026, 956, 854, 823, 767, 746 cm^{-1}; ^{1}H NMR (C_6D_6) δ2.14 (12H, s), 6.76 (4H, s), 6.83 (2H, s), 6.93-7.30 (10H, m), 7.53-7.65 (6H, m), 7.84 (2H, d, *J* = 8.1 Hz), 7.95 (2H, s), 8.16 (2H, d, *J* = 8.1 Hz), 9.01 (2H, s); ^{13}C NMR (C_6D_6) δ 21.6 (CH_3), 118.86 (CH), 118.92 (CH), 125.3 (CH), 126.2 (CH), 126.9 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 127.9 (CH), 128.5 (CH), 129.2 (CH), 129.6 (CH), 130.0 (CH), 130.8 (CH), 131.3 (CH), 132.6 (C), 134.2 (C), 137.8 (C), 138.3 (C), 148.0 (C), 149.0 (C), 149.1 (C), 155.1 (C), 161.9 (CH); MS (EI) m/z 544, 295, 274, 144, 44. Satisfactory elemental analysis was not obtained because of instability of the compound under the analytical conditions.

(*R*)-*N,N'*-Bis(4-phenyl-2-quinolylmethylene)-1,1'-binaphthyl-2,2'-diamine: Yellow prisms; mp



126.0-128.0 ^{o}C (Et_2O); $[\alpha]_D^{23}$ = -111.9 ^{o} (*c* = 0.50, CH_2Cl_2); IR (KBr) 3055, 2953, 2926, 1633, 1614, 1589, 1552, 1504, 1408, 1221, 1026, 968, 920, 821, 798, 769, 747, 700 cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.94-7.05 (4H, m), 7.07-7.19 (12H, m), 7.24-7.29 (4H, m), 7.54-7.64 (6H, m), 7.72 (2H, d, *J* = 8.3 Hz), 7.90 (2H, s), 8.15 (2H, d, *J* = 8.3 Hz), 8.96 (2H, s); ^{13}C NMR (C_6D_6) δ 119.1 (CH), 119.3 (CH), 125.7 (CH), 126.1 (CH), 127.1 (CH), 127.6 (CH), 127.76 (CH), 727.78 (CH), 128.1 (CH), 128.8 (CH), 129.5 (CH), 129.9 (CH), 130.1 (CH), 131.1 (CH), 132.8 (C), 134.5 (C), 138.5 (C), 148.1 (C), 148.7 (C), 149.3 (C), 155.3 (C), 161.9 (CH); MS (EI) m/z 510 (M^+ - 4-phenylquinoline), 499, 482, 357, 295, 278, 267, 219, 204, 176, 40, 29, 12. Anal. Calcd for $C_{52}H_{34}N_4$: C, 87.37; H, 4.79; N, 7.84 %. Found: C, 87.28; H, 5.01; N, 7.71 %.

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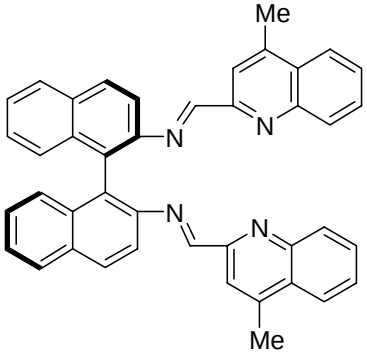
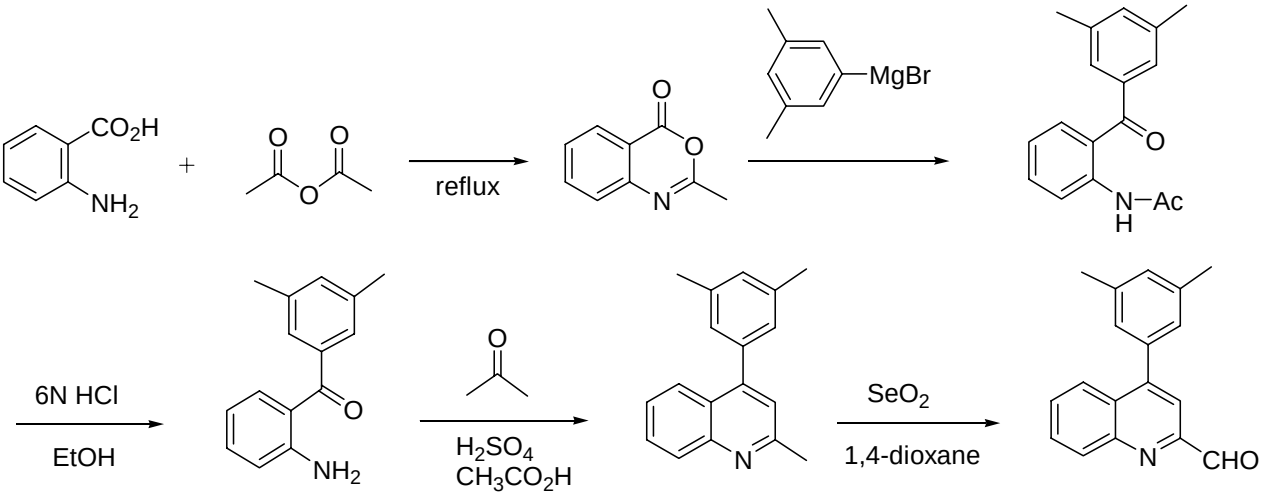
(*R*)-*N*,*N*'-Bis(4-methyl-2-quinolylmethylene)-1,1'-binaphthyl-2,2'-diamine: Yellow prisms; mp 192.0-193.0 °C (Et_2O); $[\alpha]_D^{25}$ = -4.00 ° (*c* = 0.50, CH_2Cl_2); IR (KBr) 3056, 2953, 2922, 2868, 1595, 1557, 1505, 1447, 1427, 1412, 1379, 1346, 1281, 1217, 1157, 1128, 1026, 961, 866, 823, 799, 758 cm^{-1}; ^1H NMR (C_6D_6) δ 1.91 (6H, s), 7.00-7.18 (6H, m), 7.25-7.42 (6H, m), 7.57-7.77 (8H, m), 8.12 (2H, d, *J* = 8.3 Hz), 8.94 (2H, s); ^{13}C NMR (C_6D_6) δ 18.4 (CH_3), 119.3 (CH), 123.9 (CH), 125.4 (CH), 127.0 (CH), 127.4 (CH), 127.9 (C), 128.3 (CH), 128.5 (CH), 129.0 (CH), 129.1 (CH), 129.8 (CH), 131.0 (CH), 132.6 (C), 134.2 (C), 144.3 (C), 148.3 (C), 148.7 (C), 154.9 (C), 126.6 (CH); MS (EI) m/z 590 (M^+), 176, 138, 86, 69, 57, 43, 27, 17. Anal. Calcd for $C_{42}H_{30}N_4$: C, 85.40; H, 5.12; N, 9.48 %. Found: C, 85.63; H, 5.29; N, 9.33 %.



Preparation of 4-(3,5-xylyl)-2-quinolinecarbaldehyde. 4-(3,5-Xylyl)-2-quinolinecarbaldehyde was prepared from anthranilic acid by 5 step shown in Scheme S1.



Scheme S1. Preparation of of 4-(3,5-xylyl)-2-quinolinecarbaldehyde

2-Methyl-4H-3,1-benzoxazoline-4-one was prepared according to the procedure reported in the literature.[7] 2-Amino-3',5'-dimethylbenzophenone was synthesized according to the procedure reported for the synthesis of 2-amino-3'-chlorobenzophenone in the literature.[7] To a solution of 2-methyl-4H-

3,1-benzoxazoline-4-one (2.42 g, 15 mmol) in benzene (30 mL) and diethyl ether (10 mL) was added a solution of 3,5-dimethylphenylmagnesium bromide, which was prepared from magnesium (0.301 g, 12.4 mmol) and 1-bromo-3,5-dimethylbenzene (1.5 mL, 11.3 mmol), in diethyl ether (50 mL) over a period of 2 h at 0 ^{o}C. After stirring the mixture at room temperature for 2 h, the mixture was quenched with 2N hydrochloric acid (16.8 mL) at -15 ^{o}C. A stirring was continued for 10 min at -10 ^{o}C, and then the organic layer was separated. The organic layer was washed with water (50 mL), 5% NaOH solution (30 mL x 2), and then water (50 mL). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was reflux with 6N hydrochloric acid (7.5 mL) in ethanol (15 mL) for 10 h. After cooling the mixture to room temperature, 5N ammonium hydroxide solution (12.1 mL) was added. The mixture was extracted with benzene (12 mL), and then the organic layer was dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel with hexane-ethyl acetate (9 : 1 v/v) to give 2-amino-3',5'-dimethylbenzophenone (0.575 g, 37% (2 steps)).

2-Amino-3',5'-dimethylbenzophenone: Yellow needles; mp 66.0-67.0 ^{o}C (diethyl ether-hexane); IR (KBr) 3450, 3333, 2920, 2860, 1622, 1545, 1477, 1446, 1334, 1309, 1221, 1161, 1032, 966, 852, 785 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 2.37, (6H, s), 6.06 (2H, brs), 6.58-6.62 (1H, m), 6.72-6.74 (1H, m), 7.14-7.17 (1H, m), 7.22-7.24 (2H, m), 7.27-7.31 (1H, m), 7.45-7.47 (1H, m); ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3), 115.4 (CH), 116.8 (CH), 118.3 (C), 126.7 (CH), 132.6 (CH), 134.0 (CH), 134.5 (CH), 137.6 (C), 140.0 (C), 150.7 (C), 199.4 (C); MS (EI) m/z 225 (M^+), 210, 120, 105, 92, 65; HRMS (EI) Calcd for $C_{15}H_{15}NO$ (M^+): 225.1154. Found: 225.1173.

4-(3,5-Xylyl)-2-methylquinoline was synthesized by the procedure reported for the synthesis of 2-methyl-4-phenylqunoline.[8] A solution of 2-amino-3',5'-dimethylbenzophenone (1.14 g, 5.1 mmol), acetone (0.74 mL, 10.3 mmol), and concentrated sulfuric acid (0.1 mL) was heated under reflux in acetic acid (10 mL) for 7 h. After cooling the mixture to 0 ^{o}C, the solution was neutralized with concentrated ammonium hydroxide solution and the mixture was extracted with dichloromethane (30 mL x 3). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was chromatographed on silica gel with hexane-ethyl acetate (9 : 1 v/v) to give 4-(3,5-xylyl)-2-methylquinoline (1.07 g, 85%).

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4-(3,5-Xylyl)-2-methylquinoline: Colorless needles; mp 89.5-90.0 ^{o}C (CH_2Cl_2-hexane); IR (KBr) 3003, 2916, 2860, 2361, 1701, 1589, 1556, 1508, 1448, 1406, 1373, 1319, 1292, 1259, 1222, 956, 879, 852, 773, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (6H, s), 2.77(3H, s), 7.10 (2H, s), 7.11 (1H, s), 7.21 (1H, s), 7.40-7.45 (1H, m), 7.65-7.69 (1H, m), 7.86-7.89 (1H, m), 8.07-8.09 (1H, m); ^{13}C NMR ($CDCl_3$) δ 21.3 (CH_3), 25.3 (CH_3), 121.8 (CH), 124.9 (C), 125.3 (CH), 125.5 (CH), 127.0 (CH), 128.7 (CH), 128.9 (CH), 129.6 (CH), 137.7 (C), 137.8 (C), 148.1 (C), 148.6 (C), 158.0 (C); MS (EI) m/z 247 (M^+), 230, 217, 202, 189, 165, 115, 101, 77, 49, 35, 24; HRMS (EI) Calcd for $C_{18}H_{17}N$ (M^+): 247.1361. Found: 247.1380. Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66 %. Found: C, 87.20; H, 7.24; N, 5.56 %.

4-(3,5-Xylyl)-2-quinolinecarbaldehyde was synthesized by the procedure reported for the synthesis of 4-methyl-2-quinolinecarbaldehyde.[9] A solution of 4-(3,5-Xylyl)-2-methylquinoline (1.04 g, 4.20 mmol) and SeO_2 (0.515 g, 4.60 mmol) in 1,4-dioxane (25 mL) was heated under reflux for 6 h. After filtration of insoluble materials, the filtrate was evaporated *in vacuo*. The residue was chromatographed over silica gel with hexane-ethyl acetate (99 : 1 v/v) to give 4-(3,5-xylyl)-2-quinolinecarbaldehyde (0.966 g, 88%).

4-(3,5-Xylyl)-2-quinolinecarbaldehyde: Colorless needles; mp 112.5-114.0 ^{o}C (CH_2Cl_2-hexane); IR(KBr) 3391, 3001, 2916, 2816, 2361, 1979, 1705, 1604, 1583, 1462, 1437, 1413, 1379, 1359, 1305, 1267, 1178, 1128, 1030, 993, 949, 912, 900, 873, 846, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (6H, s), 7.12-7.15 (2H, m), 7.15-7.17 (1H, m), 7.63-7.67 (1H, m), 7.81-7.86 (1H, m), 7.97 (1H, s), 8.03-8.06 (1H, m), 8.30-8.32 (1H, m), 10.3 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.4 (CH_3), 117.4 (CH), 126.2 (CH), 127.2 (CH), 128.6 (C), 129.0 (CH), 130.1 (CH), 130.3 (CH), 130.6 (CH), 137.2 (C), 138.2 (C), 148.3 (C), 150.3 (C), 151.9 (C), 193.8 (CH); MS (EI) m/z 261 (M^+), 233, 218; HRMS (EI) Calcd for $C_{18}H_{15}NO$ (M^+): 261.1154. Found: 261.1138. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36 %. Found: C, 82.68; H, 5.78; N, 5.42 %.

Preparation of 4-phenyl-2-quinolinecarbaldehyde. 2-Methyl-4-phenylqunoline was prepared by the procedure reported in the literature.[8] 4-Penyl-2-quinolinecarbaldehyde was synthesized by the procedure reported for the synthesis of 4-methyl-2-quinolinecarbaldehyde.[9] A solution of 4-Pheny-2-methylquinoline (0.934 g, 4.30 mmol) and SeO_2 (0.520 g, 4.70 mmol) in 1,4-dioxane (20 mL) was

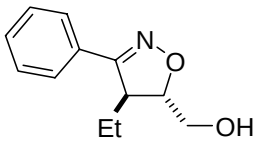
heated under reflux for 15 h. After filtration of insoluble materials, the filtrate was evaporated *in vacuo*. The residue was chromatographed over silica gel with hexane-ethyl acetate (99 : 1 v/v) to give 4-phenyl-2-quinolinecarbaldehyde (0.751 g, 76%).

4-Phenyl-2-quinolinecarbaldehyde: Colorless prisms; mp 92.0-94.0 ^{o}C (Et_2O-hexane); IR (KBr) 3057, 2824, 1711, 1585, 1512, 1489, 1446, 1415, 1358, 1194, 1124, 1078, 1030, 908, 896, 783, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.50-7.59 (5H, m), 7.63-7.67 (1H, m), 7.82-7.86 (1H, m), 7.99 (1H, s), 8.01-8.03 (1H, m), 8.31-8.34 (1H, m), 10.3 (1H, s); ^{13}C NMR ($CDCl_3$) δ 117.3, 125.9, 128.3, 128.5, 128.6, 129.0, 129.3, 130.0, 130.6, 137.1, 148.2, 149.7, 151.8, 193.5; MS (EI) m/z 233 (M^+), 219, 204, 190, 178, 165, 151, 138, 77, 61, 57, 43, 32, 27, 17. Anal. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00%. Found: C, 82.42; H, 4.68; N, 6.03%.

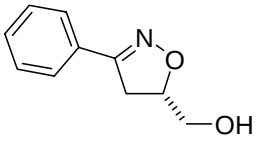
4-Methyl-2-quinolinecarbaldehyde was prepared from commercially available 2,4-dimethylquinoline by the procedure reported in the literature.[9]

Spectroscopic Data of 5-Hydroxymethyl-4,5-dihydroisoxazoles derived from isoxazolines 4-Me-**16b**, 4-Me-**17b**, 4-Me-**18b**, 4-Me-**19c**, and 4-Me-**19e** were shown below.

(4*S*,5*S*)-4-Ethyl-5-hydroxymethyl-3-phenyl-4,5-dihydroisoxazole: Colorless oil; $[\alpha]_D^{25}$ = +133.2 ^{o} (*c* = 0.08, $CHCl_3$, 88% ee); IR (neat) 2965, 2935, 2360, 1457, 1360, 1074, 1025, 914, 888, 768, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, t, *J* = 7.8 Hz), 1.58-1.69 (1H, m), 1.73-1.83 (1H, m), 2.08 (1H, brs), 3.50 (1H, ddd, *J* = 3.4, 4.3, 8.0 Hz), 3.64 (1H, dd, *J* = 5.8, 12.2 Hz), 3.74 (1H, dd, *J* = 3.6, 12.2 Hz), 4.56 (1H, ddd, *J* = 3.6, 4.3, 5.8), 7.37-7.44 (3H, m), 7.63-7.63 (2H, m); ^{13}C NMR ($CDCl_3$) δ 10.8 (CH_3), 24.1 (CH_2), 50.4 (CH), 64.3 (CH_2), 86.0 (CH), 126.9 (CH), 128.5 (C), 128.6 (CH), 129.9 (CH), 159.6 (C); MS (EI) m/z 205 (M^+) 175, 158, 145, 128, 102, 89, 75, 38; HRMS (EI) Calcd for $C_{12}H_{15}NO_2$ (M^+): 205.1102. Found: 205.1130. The enantiomeric excess was determined by HPLC analysis (Daicel Chiralpak AD-H, *i*-PrOH-hexane (3 : 97 vol/vol), detector: UV 254 nm, Flow rate = 0.5 ml/min, 35 ^{o}C). t_{minor} = 78.7 min, t_{major} = 90.3 min.

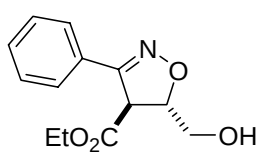


(5*S*)-5-Hydroxymethyl-3-phenyl-4,5-dihydroisoxazole: Colorless prisms; mp 76.0-77.0 ^{o}C (Et_2O); $[\alpha]_D^{25}$ = +159.5 ^{o} (*c* = 0.14, $CHCl_3$, 92% ee); IR (KBr) 5348, 2942, 1448, 1362, 1103, 1054, 901, 766,



694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (1H, brs), 3.29 (1H, dd, *J* = 8.0, 16.8 Hz), 3.39 (1H, dd, *J* = 10.8, 16.8 Hz), 3.69 (1H, dd, *J* = 4.6, 12.0 Hz), 3.88 (1H, dd, *J* = 2.9, 12.0 Hz), 4.84-4.91 (1H, m), 7.38-7.42 (3H, m), 7.66-7.68 (2H, m); ^{13}C NMR ($CDCl_3$) δ 36.4 (CH_2), 63.7 (CH_2), 81.2 (CH), 126.6 (CH), 128.6 (CH), 129.1 (C), 130.0 (CH), 156.9 (C); MS (EI) m/z 177(M^+), 146, 118, 104, 91, 78, 63. Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90 %. Found: C, 67.66; H, 6.22; N, 7.75 %. The enantiomeric excess was determined by HPLC analysis (Daicel Chiralpak AD-H, *i*-PrOH-hexane (3 : 97 vol/vol), detector: UV 254 nm, Flow rate = 0.5 ml/min, 35 ^oC). t_{minor} = 132.5 min, t_{major} = 149.3 min.

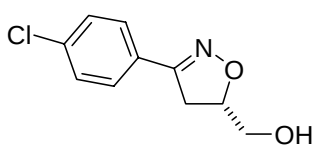
(4*S*,5*S*)-4-Ethoxycarbony-5-hydroxymethyl-3-phenyl-4,5-dihydroisoxazole: Colorless oil; $[\alpha]_D^{25}$ = +75.3^o (*c* = 0.09, $CHCl_3$, 75% ee); IR (neat) 3439, 3020, 1736, 1261, 1217, 925, 771, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (3H, t, *J* = 7.1 Hz), 1.95 (1H, brs, OH), 3.74 (1H, dd, *J* = 3.9, 12.4 Hz), 3.94 (1H, dd, *J* = 3.4, 12.4 Hz), 4.18 (2H, dq, *J* = 3.9, 7.1 Hz), 4.49 (1H, d, *J* = 6.6 Hz), 5.06 (1H, ddd, *J* = 3.4, 3.9, 6.6 Hz), 7.35-7.46 (3H, m), 7.69-7.73 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 29.8 (CH_2), 55.2 (CH), 62.1 (C), 63.3 (CH_2), 85.8 (CH), 126.9 (CH), 128.5 (CH), 130.2 (CH), 154.6 (C), 159.0 (C); MS (EI) m/z 249 (M^+), 218, 190, 146, 77, 37. HRMS (EI) Calcd for $C_{13}H_{15}NO_4$ (M^+): 249.1001. Found: 249.1024. The enantiomeric excess was determined by HPLC analysis (Daicel Chiralpak AD-H, *i*-PrOH-hexane (1 : 19 vol/vol), detector: UV 254 nm, Flow rate = 0.5 ml/min, 35 ^oC). t_{minor} = 54.9 min, t_{major} = 68.5 min.



(5*S*)-5-Hydroxymethyl-3-(*p*-methoxyphenyl)-4,5-dihydroisoxazole: Colorless prisms; mp 143.0-144.0 ^oC (Et_2O-hexane); $[\alpha]_D^{25}$ = +125.7 ^{o} (*c* = 0.20, $CHCl_3$, 90% ee); IR (KBr) 3357, 2940, 1701, 1612, 1519, 1366, 1265, 901, 833, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (1H, brs), 3.24 (1H, dd, *J* = 7.8, 16.6 Hz), 3.35(1H, dd, *J* = 10.2, 16.6 Hz), 3.65 (1H, dd, *J* = 4.6, 12.2 Hz), 3.82 (1H, dd, *J* = 3.4, 12.2 Hz), 3.83 (3H, s), 4.81 (1H, dddd, *J* = 3.4, 4.6, 7.8, 10.2 Hz), 6.90-6.93 (2H, m), 7.58-7.62 (2H, m); ^{13}C NMR ($CDCl_3$) δ 36.7 (CH_2), 55.4 (CH_3), 63.8 (CH_2), 80.9 (CH), 114.0 (CH), 121.7 (C), 128.1 (CH), 156.4 (C), 160.9 (C); MS (EI) m/z 207(M^+), 176, 121, 91, 77, 56. Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76 %. Found: C, 63.47; H, 6.03; N, 6.60 %. The enantiomeric excess was determined by HPLC

analysis (Daicel Chiralpak AD-H, *i*-PrOH-hexane (1 : 19 vol/vol), detector: UV 254 nm, Flow rate = 0.5 ml/min, 35 ^{o}C). t_{minor} = 111.4 min, t_{major} = 124.2 min.

(5*S*)-3-(*p*-Chlorophenyl)-5-hydroxymethyl-4,5-dihydroisoxazole: Colorless prisms; mp 87.0-88.0 ^{o}C (Et_2O-hexane); $[\alpha]_D^{25}$ = +127.8 ^{o} (*c* = 0.20, $CHCl_3$, 79% ee); IR (KBr) 3389, 2942, 1597, 1496, 1405, 1352, 1093, 1045, 905, 834, 809 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.27 (1H, dd, *J* = 7.6, 16.6 Hz), 3.37 (1H, dd, *J* = 10.7, 16.6 Hz), 3.68 (1H, dd, *J* = 4.4, 12.4 Hz), 3.90 (1H, dd, *J* = 3.2, 12.4 Hz), 4.88 (1H, dddd, *J* = 3.2, 4.4, 7.6, 10.7 Hz), 7.35-7.39 (2H, m), 7.56-7.60 (2H, m); ^{13}C NMR ($CDCl_3$) δ 36.3 (CH_2), 63.6 (CH_2), 81.5 (CH), 81.5 (C), 127.8 (CH), 128.9 (CH), 136.0 (C), 156.0 (C); MS (EI) m/z 211(M^+), 180, 111, 75, 61, 41. Anal. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62 %. Found: C, 56.87; H, 4.63; N, 6.46 %. The enantiomeric excess was determined by HPLC analysis (Daicel Chiralpak AD-H, *i*-PrOH-hexane (1 : 19 vol/vol), detector: UV 254 nm, Flow rate = 0.5 ml/min, 35 ^{o}C). t_{minor} = 68.5 min, t_{major} = 78.8 min.



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