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Monophosphite ligands derived from carbohydrates and H_8-BINOL: highly enantioselective Rh-catalyzed asymmetric hydrogenations

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Abstract—A series of monophosphite ligands derived from carbohydrates and H_8-BINOL have been synthesized. Excellent enantioselectivities (over 99% ee) were obtained when these ligands were applied in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate and enamides.

1. Introduction

Catalytic asymmetric hydrogenation is one of the most useful processes to synthesis of enantiopure compounds, which has attracted a great deal of attention from both academia and industry.[1] As enantioselectivities and catalytic activities are highly affected by chiral ligands, one of the challenges in this area is to develop highly enantioselective and inexpensive chiral ligands. In recent years, some of the monodentate chiral phosphorus ligands, which are easily prepared and highly enantioselective, have attracted much attention. A large variety of chiral monophosphoramidites, monophosphites and monophosphinites have been prepared and their applicability in Rh-catalyzed asymmetric hydrogenation demonstrated.[2]

Recently, over the course of our studies in the field of asymmetric synthesis and reactions, we have designed and synthesized a new class of chiral monophosphite ligands **1**–**3** from inexpensive carbohydrates and commercially available BINOL, which have proven to be excellent ligands in the Rh-catalyzed asymmetric hydrogenation of functionalized olefins.[3] Our previous studies also demonstrated that the attached carbohydrate backbones in these ligands are important for achieving high enantioselectivity. We reasoned that this may attribute to the additional groups contained in the carbohydrate backbones to effectively restrain the rotation of M–P bond by hemilabile coordination[4] of the ligand to metal. In view of these benefits of carbohydrate backbones, as well as recent successes with H_8-BINOL based ligands,[5] we decided to design new monophosphites, which incorporated these advantageous features. Herein, we report a new class of monophosphites, based on carbohydrates with an appropriate configuration and H_8-BINOL, as ligands for the Rh-catalyzed enantioselective hydrogenation of functionalized olefins with excellent enantioselectivity (Fig. 1).

2. Results and discussion

2.1. Synthesis of chiral monophosphite ligands

The novel ligands **4**–**6** were easily prepared by literature procedures[3] with H_8-BINOL and the corresponding monosaccharides with an appropriate configuration. The RO–PCl_2 intermediates were prepared by the reaction of alcohols with PCl_3 in the absence of Et_3N. These were then directly reacted with H_8-BINOL in the presence of Et_3N to afford the desired product (Scheme 1). Ligands **4**–**6** were purified through a short silica gel plug and were stable in the solid state. Their structures were fully characterized by ^1H, ^{13}C, ^{31}P NMR and HRMS.

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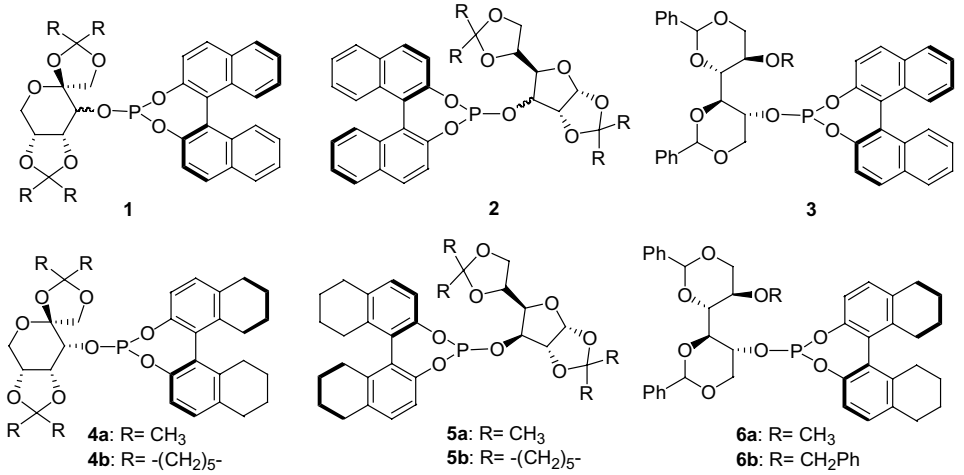
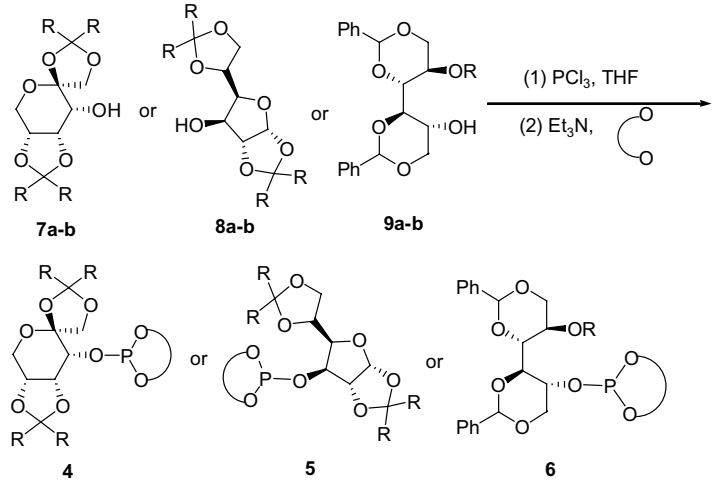


Figure 1. Monophosphite ligands derived from carbohydrates.



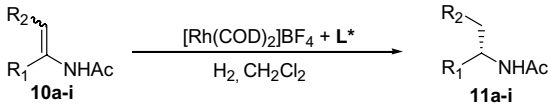
Scheme 1. The synthesis of the monophosphite ligands.

2.2. Asymmetric hydrogenation of enamides

The performance of ligands **4–6** was thoroughly explored in the Rh-catalyzed enantioselective hydrogenation of enamides. In the first set of experiments, we chose *N*-(1-phenylethenyl)acetamide **10a** as a model substrate for testing the catalytic performance of the catalyst precursors containing with ligands **4–6**. The catalyst was prepared in situ by mixing $[Rh(COD)_2]BF_4$ and the monophosphite ligand under an inert atmosphere. All the hydrogenation reactions were typically carried out at room temperature under 10 atm pressure of H_2 and with a substrate, Rh and ligand ratio of 1.0/0.01/0.022. Although a standard reaction time of 12 h was chosen, most of the reactions were complete within 3 h. Entries 1–6 in Table 1 summarize the results of the asymmetric hydrogenation when employing our new ligands. The reaction was carried out in CH_2Cl_2 with full conversion and excellent enantioselectivities (96.4–99.0% ee) when monophosphites **4–6** were used as ligands. The results also demonstrated that the capability of asymmetric induction of these ligands was again sensitive to the carbohydrate moiety and that the D-fructose derived monophosphite **4a** has the highest capability of asymmetric induction among **4–6** (Table 1, entry 1).

With the best ligand **4a**, we examined the Rh-catalyzed enantioselective hydrogenation of a variety of enamides under the optimal condition. In all cases, ligands **4a** exhibited excellent enantioselectivities (97.3–99.6% ee). The electronic nature of the *para*-substituents in α-arylenamides appeared to affect the enantioselectivity observed. Hydrogenation of α-arylenamides with electron-withdrawing substituents (Table 1, entries 7–9) on the phenyl ring gave higher enantioselectivities than those with electron-donating substituents (entry 10). Hydrogenation of 2-naphthyl derivative also gave an excellent ee value (Table 1, entry 12). β-Substituted isomeric mixtures of (*E*/*Z*) arylenamides were also reduced with excellent enantioselectivities (entries 13 and 14), regardless of the various β-substituents. It is notable that the ee values obtained by the H_8-BINOL derived ligands **4a** are higher than those obtained with the BINOL derived parent ligands.[3] This might be attributed to the larger torsion dihedral angle in H_8-BINOL derived ligands.[5a]

Table 1. Rh-catalyzed asymmetric hydrogenation of enamides **10**[a]



Entry	Ligand	Substrate (R_1, R_2)	Ee% (config)[b]
1	**4a**	**10a** (Ph, H)	99.0 (*S*)
2	**4b**	**10a** (Ph, H)	98.6 (*S*)
3	**5a**	**10a** (Ph, H)	97.3 (*S*)
4	**5b**	**10a** (Ph, H)	96.4 (*S*)
5	**6a**	**10a** (Ph, H)	97.1 (*S*)
6	**6b**	**10a** (Ph, H)	98.5 (*S*)
7	**4a**	**10b** (*p*-FC_6H_4, H)	99.3 (*S*)
8	**4a**	**10c** (*p*-BrC_6H_4, H)	99.6 (*S*)
9	**4a**	**10d** (*p*-ClC_6H_4, H)	99.5 (*S*)
10	**4a**	**10e** (*p*-$CH_3OC_6H_4$, H)	98.9 (*S*)
11	**4a**	**10f** (*p*-$CF_3C_6H_4$, H)	99.3 (*S*)
12	**4a**	**10g** (2-Naphthyl, H)	99.5 (*S*)
13[c]	**4a**	**10h** (Ph, Me)	97.3 (*S*)
14[d]	**4a**	**10i** (Ph, Et)	99.0 (*S*)

[a] Solvent: CH_2Cl_2; $p(H_2) = 10$ atm; $T = 20$ °C; reaction time: 12 h; substrate:$[Rh(COD)_2]BF_4$:**L** = 1:0.01:0.022; 100% conversion was obtained in all cases.

[b] Determined by chiral capillary GC on a Varian Chirasil-L-Val column and a Supelco Chiral select 1000 column. The absolute configuration was assigned by comparison of the specific rotation with reported data.

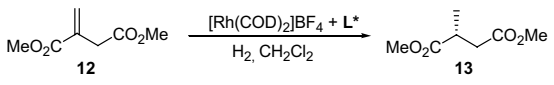
[c] *E*/*Z* = 67/33.

[d] *E*/*Z* = 40/60.

2.3. Asymmetric hydrogenation of dimethyl itaconate

Dimethyl itaconate was also hydrogenated with these catalysts. As shown in Table 2, these monophosphites, which we prepared, are efficient ligands for the asymmetric hydrogenation reaction, with good to excellent ee values (up to 99.5% ee) and full conversions being observed in the hydrogenation of this substrate. However, the enantioselectivities also proved to be influenced by the structure of the carbohydrate backbones contained in these ligands. The results in Table 2 show that the D-fructose derived monophosphite **4a** is the most effective ligand, which gave the best ee value 99.5% (Table 2, entry 1). These observations further demonstrate that carbohydrate backbones are important to these catalysts.

Table 2. Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate **12**[a]



Entry	Ligand	Ee% (Config)[b]
1	**4a**	99.5 (*R*)
2	**4b**	96.3 (*R*)
3	**5a**	95.6 (*R*)
4	**5b**	95.0 (*R*)
5	**6a**	97.0 (*R*)
6	**6b**	96.1 (*R*)

[a] Solvent: CH_2Cl_2; $p(H_2) = 10$ atm; $T = 20$ °C; reaction time: 12 h; substrate:$[Rh(COD)_2]BF_4$:**L** = 1:0.01:0.022; 100% conversion was obtained in all cases.

[b] Determined by chiral capillary GC on a γ-DEX 225 column. The absolute configuration was assigned by comparison of the optical rotation with reported data.

3. Conclusions

In summary, a new class of monophosphite ligands **4–6** derived from carbohydrates and H_8-BINOL has been designed and synthesized. Excellent ee values were obtained in the Rh-catalyzed asymmetric hydrogenation of enamides and dimethyl itaconate. In contrast to the other H_8-BINOL derived monodentate ligands,[2f,l,m] the ligands reported here are more efficient in the Rh-catalyzed asymmetric hydrogenations. This may be attributed to the function of the carbohydrate backbones attached in these ligands. The design and synthesis of more effective chiral monophosphorus ligands from carbohydrates and their applications in asymmetric catalytic hydrogenation are currently in progress.

4. Experimental

4.1. General methods

All reactions were carried out under a N_2 atmosphere. Melting points were measured on a Metter FP5 melting apparatus and are uncorrected. NMR spectra were measured on a Bruker DRX-400 NMR spectrometer. Optical rotations were measured with a JASCO P-1020 automatic polarimeter. High resolution mass spectra were recorded on Applied Biosystems Mariner System 5303. Enantiomeric excess (ee) determination was carried out using GC with a Supelco Chiral Select 1000, a CP-chiralsil-L-Val capillary column and a γ-DEX 225 chiral capillary column on an Agilent HP-4890 GC instrument with FID as detector. All solvents were dried and degassed by standard methods. 1,2:4,5-Di-*O*-isopropylidene-β-D-fructopyranose **7a**, 1,2:4,5-di-*O*-cyclohexylidene-β-D-fructopyranose **7b**, 1,2:5,6-di-*O*-isopropylidene-D-glucose **8a**, 1,2:4,5-di-*O*-cyclohexylidene-D-glucose **8b**, 1,3:4,6-di-*O*-benzyllidene–2–*O*-methyl-D-mannitol **9a**, 1,3:4,6-di-*O*-benzyllidene–2–*O*-benzyl-D-mannitol **9b** and (*R*)-2,2′–dihydroxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl were prepared according to the literature procedures.[3,6] Enamides were synthesized by using procedures describe elsewhere.[7] All other chemicals were obtained commercially.

4.2. General procedures for the synthesis of monophosphite ligands 4–6

To a stirred solution of **7**, **8** or **9** (2.5 mmol) in THF (5 mL) was slowly added PCl_3 (218 μL, 2.5 mmol) as a solution in THF (4 mL) at 0 °C and the resulting mixture stirred for 1 h at room temperature. The reaction mixture was then cooled to −10 °C and Et_3N (1.07 mL, 7.6 mmol) slowly added. The reaction mixture was allowed to warm to room temperature, maintained under these conditions for 0.25 h and then cooled to 0 °C, solid H_8-BINOL was added and the resulting mixture allowed to warm to room temperature and stirred

overnight prior to dilution with diethyl ether. The solids were removed by filtration through a pad of Celite, the solvent removed in vacuo and the residue purified by flash chromatography (EtOAc–hexane, 1:20 ~ 1:10), furnished the title ligands as a white foam in 75–85% yield.

4.2.1. 1,2:4,5-Di-*O*-isopropylidene-3-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)dioxophosphite)-D-fructose, 4a. The above procedure was followed using **7a** and (*R*)-H_8-BINOL. After work-up, it gave **4a**. Mp 113–114 °C; $[\alpha]_D^{10} = -184.5$ (*c* 0.93, THF); ^{1}H NMR (DMSO-d_6): δ 1.29–1.40 (m, 14H), 1.73 (d, J = 3.6 Hz, 6H), 2.12–2.16 (m, 2H), 2.62 (d, J = 6.8 Hz, 2H), 2.79 (d, J = 2.0 Hz, 4H), 3.53 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 9.2 Hz, 1H), 3.80 (d, J = 12.4 Hz, 1H), 4.05 (d, J = 9.2 Hz, 1H), 4.36 (d, J = 8.0 Hz, 1H), 4.59 (dd, J = 7.8, 1.8 Hz, 1H), 4.75 (dd, J = 10.6, 1.8 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 7.01 (dd, J = 15.6, 8.0 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 21.96, 24.59, 25.88, 26.10, 26.18, 27.22, 27.30, 28.44, 62.55, 70.54, 70.68, 73.41, 73.80, 104.74, 108.62, 108.94, 118.69, 118.95, 129.11, 129.60, 133.69, 133.99; ^{31}P NMR (DMSO-d_6): δ 145.60; HRMS (APCI) calcd for $C_{32}H_{40}O_8P$ (M+1): 583.2455, found: 583.2505.

4.2.2. 1,2:4,5-Di-*O*-cyclohexylidene-3-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)dioxophosphite)-D-fructose, 4b. The above procedure was followed using **7b** and (*R*)-H_8-BINOL. After work-up, it gave **4b**. Mp 62–63 °C; $[\alpha]_D^{10} = -162.4$ (*c* 0.91, THF); ^{1}H NMR (DMSO-d_6): δ 1.34-1.82 (m, 28H), 2.22 (d, J = 16.0 Hz, 2H), 2.71 (d, J = 11.6 Hz, 2H), 2.86–2.92 (m, 4H), 3.63 (d, J = 13.2 Hz, 1H), 3.77 (d, J = 8.8 Hz, 1H), 3.91 (d, J = 12.8 Hz, 1H), 4.17 (d, J = 8.8 Hz, 1H), 4.46 (d, J = 7.6 Hz, 1H), 4.69 (d, J = 7.6 Hz, 1H), 4.88 (d, J = 10.4 Hz, 1H), 6.99 (dd, J = 16.6, 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 21.93, 22.06, 23.19, 23.34, 23.52, 24.58, 27.24, 28.49, 33.75, 35.15, 35.34, 35.53, 62.64, 70.09, 70.68, 70.88, 73.12, 73.56, 104.20, 109.18, 109.55, 118.62, 118.98, 118.98, 127.33, 128.74, 128.95, 129.56, 133.69, 134.80, 136.93, 137.99, 145.16, 145.42; ^{31}P NMR (DMSO-d_6): δ 146.01; HRMS (APCI) calcd for $C_{38}H_{48}O_8P$ (M+1): 663.3081, found: 663.3033.

4.2.3. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)dioxophosphite)-D-glucose, 5a. The above procedure was followed using **8a** and (*R*)-H_8-BINOL. After work-up, it gave **5a**. Mp 108–109 °C; $[\alpha]_D^{10} = -168.6$ (*c* 0.90, THF); ^{1}H NMR (DMSO-d_6): δ 1.30–1.72 (m, 20H), 2.12 (d, J = 16.0 Hz, 2H), 2.60 (s, 2H), 2.78 (s, 4H), 3.71–3.75 (m, 1H), 3.93–3.97 (m, 1H), 4.01–4.03 (m, 1H), 4.08–4.12 (m, 1H), 4.63–4.71 (m, 2H), 5.86–5.87 (d, J = 3.2 Hz, 1H), 6.98–7.05 (m, 2H), 7.11–7.15 (m, 2H); ^{13}C NMR (DMSO-d_6): δ 21.88, 21.98, 25.29, 26.12, 26.57, 27.23, 28.43, 66.35, 71.72, 77.18, 77.36, 80.19, 83.70, 104.57, 108.46, 111.51, 118.77, 118.83, 126.97, 128.66, 129.26, 129.57, 133.70, 134.78, 136.97, 137.97, 145.45; ^{31}P NMR (DMSO-d_6): δ 142.17; HRMS (APCI) calcd for $C_{32}H_{40}O_8P$ (M+1): 583.2455, found: 583.2475.

4.2.4. 1,2:5,6-Di-*O*-cyclohexylidene-3-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)dioxophosphite)-D-glucose, 5b. The above procedure was followed using **8b** and (*R*)-H_8-BINOL. After work-up, it gave **5b**. Mp 106–107 °C; $[\alpha]_D^{10} = -139.4$ (*c* 0.90, THF); ^{1}H NMR (DMSO-d_6): δ 1.33–1.70 (m, 28H), 2.21–2.25 (m, 2H), 2.67–2.73 (m, 2H), 2.87 (d, J = 5.2 Hz, 4H), 3.80 (dd, J = 8.4, 5.6 Hz, 1H), 4.04–4.17 (m, 3H), 4.77–4.79 (m, 2H), 5.95 (d, J = 3.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 13.8, 8.2 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 21.98, 23.24, 23.59, 24.33, 24.65, 27.23, 28.43, 34.45, 35.17, 36.00, 66.29, 71.43, 77.31,77.52, 80.40, 83.29, 104.33, 108.94, 112.01, 118.61, 118.85, 127.06, 128.70, 129.26, 129.57, 133.70, 134.77, 137.00, 137.99, 145.47; ^{31}P NMR (DMSO-d^6): δ 144.10; HRMS (APCI) calcd for $C_{38}H_{48}O_8P$ (M+1): 663.3081, found: 663.3074.

4.2.5. 1,3:4,6-Di-*O*-benzyllidene-2-*O*-methyl-5-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)-dioxophosphite)-D-mannitol, 6a. The above procedure was followed using **9a** and (*R*)-H_8-BINOL. After work-up, it gave **6a**. Mp 133–134 °C; $[\alpha]_D^{10} = -156.5$ (*c* 0.87, THF); ^{1}H NMR (DMSO-d_6): δ 1.50–1.75 (m, 8H), 2.11–2.81 (m, 4H), 3.42 (s, 3H), 3.61–3.92 (m, 4H), 4.12–4.59 (m, 4H), 5.51 (s, 1H), 5.77 (s, 1H), 6.96–7.48 (m, 14H); ^{13}C NMR (DMSO-d_6): δ 21.98, 22.08, 27.25, 28.43, 28.51, 58.18, 62.52, 62.72, 68.23, 68.37, 68.81, 76.26, 76.55, 99.96, 118.84, 119.03, 125.90, 127.32, 128.08, 128.19, 128.71, 128.82, 129.27, 129.56, 133. 79, 134.83, 137.00, 137.47, 137.65, 138.01, 144.97, 145.39; ^{31}P NMR (DMSO-d_6): δ 145.42; HRMS (APCI) calcd for $C_{41}H_{44}O_8P$ (M+1): 695.2768, found: 695.2740.

4.2.6. 1,3:4,6-Di-*O*-benzyllidene-2-*O*-benzyl-5-*O*-((*R*)-2,2′-*O*,*O*-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl)dioxophosphite)-D-mannitol, 6b. The above procedure was followed using **9b** and (*R*)-H_8-BINOL. After work-up, it gave **6b**. Mp 125–126 °C; $[\alpha]_D^{10} = -148.9$ (*c* 0.76, THF); ^{1}H NMR (DMSO-d_6): δ 1.55–2.24 (m, 11H), 2.68–2.88 (m, 6H), 3.74–3.77 (m, 1H), 3.86–3.87 (m, 1H), 3.96–3.98 (m, 2H), 4.21–4.24 (m, 1H), 4.52–4.57 (m, 2H), 4.64–4.73 (m, 3H), 5.60 (s, 1H), 5.74 (s, 1H), 7.02–7.53 (m, 20H); ^{13}C NMR (DMSO-d_6): δ 21.95, 27.22, 28.48, 62.50, 62.69, 65.73, 68.60, 68.73, 71.25, 76.15, 76.42, 99.95, 118.84, 119.00, 125.86, 125.96, 127.28, 127.73, 127.83, 128.06, 128.28, 128.70, 129.26, 129.54, 133.76, 134.81, 136.98, 137.35, 137.59, 138.00, 144.92, 145.37; ^{31}P NMR (DMSO-d_6): δ 145.46; HRMS (APCI) calcd for $C_{47}H_{48}O_8P$ (M+1): 771.3081, found: 771.3132.

4.3. General procedures for asymmetric hydrogenation

In a nitrogen-filled glove box, to a solution of $[Rh(COD)_2]BF_4$ (2.0 mg, 0.005 mmol) in anhydrous and degassed CH_2Cl_2 (1 mL) was added the ligand (0.011 mmol). After stirring the mixture for 30 min, a substrate (0.5 mmol) dissolved in CH_2Cl_2 (1 mL) was added. The reaction mixture was then transferred to an autoclave. The autoclave was purged three times with hydrogen and the pressure set to the desired pressure;

hydrogenation was performed at room temperature for 12 h. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica gel plug to remove the catalyst. The resulting solution was directly used for chiral GC to determine enantiomeric excesses.

Acknowledgements

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