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Furanoside thioether–phosphinite ligands for Pd-catalyzed asymmetric allylic substitution reactions

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Abstract—A new series of thioether–phosphinite ligands, easily prepared in a few steps from inexpensive D-(+)-xylose, was tested in the Pd-catalyzed allylic substitution of substrates with different steric properties. The results show that the enantiomeric excesses are strongly dependent on the steric properties of the substituent in the thioether moiety. Enantiomeric excesses of up to 93% with high activities were obtained for the substrate *rac*-1,3-diphenyl-3-acetoxyprop-1-ene **7** with dimethyl malonate as the nucleophile.

1. Introduction

Palladium-catalyzed asymmetric allylic substitution is a versatile, widely used process in organic synthesis for the enantioselective formation of C–C and C–heteroatom bonds.[1] Many chiral ligands, bidentate nitrogen and phosphorus donors (both homo- and heterodonors), have been successfully applied.[1] Mixed phosphorus–nitrogen ligands have played a dominant role among the heterodonor ligands. To a lesser extent, phosphorus–thioether ligands have also demonstrated their potential utility in Pd-catalyzed asymmetric allylic substitution.[2] Evans et al. have developed a family of thioether–phosphinite ligands that proved to be effective[3] but, despite this success, the use of other thioether–phosphinite ligands has not been reported. As far as carbohydrate ligands are concerned, despite their advantages such as availability at low price and easy modular constructions, they have only very recently shown their huge potential as a source of highly effective chiral ligands in this process.[4] In this context, several combinations of S–P ligands such as thioether–phosphine,[5] thioether–phospholane,[6] thioether–phosphite[7] have been studied and have proven to be effective. However, to our knowledge, carbohydrate-based thioether–phosphinite ligands have not been tested in this process.

Following our interest in carbohydrates as an inexpensive and highly modular chiral source for preparing ligands, and encouraged by the success of Evans' thioether–phosphinite ligands, we have designed the furanoside thioether–phosphinites ligands **1**–**3** (Fig. 1).

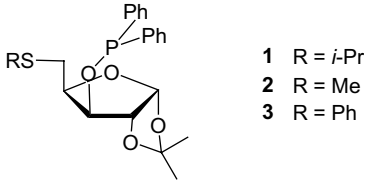

Figure 1. Thioether–phosphinite ligands **1**–**3**.

Herein we report the synthesis of the thioether–phosphinite ligands **1**–**3** and their use in Pd-catalyzed enantioselective asymmetric allylic substitution.

2. Results and discussion

2.1. Synthesis of the chiral thioether–phosphinite ligands

The new ligands **1**–**3** were synthesized very efficiently in one step from the corresponding thioether-alcohols **4**–**6**, which are easily prepared on a large scale from D-(+)-xylose using a standard procedure (Scheme 1).[8] Reaction of the corresponding thioethers **4**–**6** with one equivalent of chlorodiphenylphosphine in dry THF, under nitrogen and in the presence of pyridine and 4-(dimethylamino)-pyridine (DMAP), then provided the desired ligands **1**–**3** in 71%, 87% and 89% yields, respectively.

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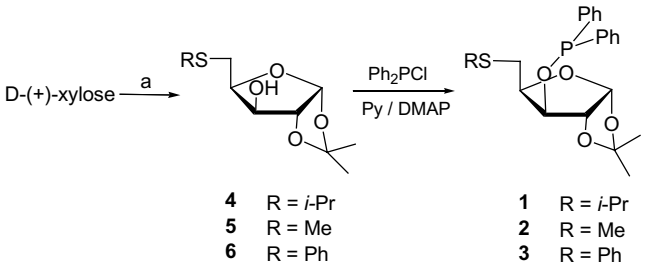
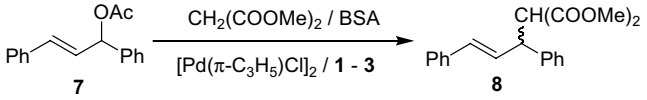


Scheme 1. Synthesis of ligands **1**–**3**. a—Ref. 8.

All ligands were stable during purification on neutral alumina under an atmosphere of argon and were isolated as colourless oils. The ^{1}H, ^{31}P and ^{13}C NMR spectra were as expected for these C_1 ligands (see Experimental section).

2.2. Asymmetric allylic substitution reactions

We first investigated the Pd-catalyzed allylic substitution of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene **7**, which is widely used as a model substrate, with dimethyl malonate using the chiral thioether–phosphinite ligands **1**–**3** (Scheme 2). The catalysts were generated in situ from 0.5 mol % of π-allyl-palladium chloride dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$, the corresponding ligand and a catalytic amount of the corresponding base.



Scheme 2.

The effect of the solvent, base and the ligand-to-palladium ratio were investigated using the catalyst precursor containing ligand **1** (Table 1). Our results indicate that both solvent and base affected catalytic performance. Dichloromethane as solvent and potassium acetate as base provided the best combination of activity and enantioselectivity (entries 1–4 and 5–7). Good activity [TOF > 200 mol × (mol × h)$^{-1}$] and good enantioselectivity [(*S*) 86% ee] were obtained. Varying the ligand-to-palladium ratio showed that excess ligand was not needed to obtain good enantioselectivities and activities (entries 1 and 8). At higher ligand-to-palladium ratios, activities and enantioselectivities were lower. This was probably due to the fact that the thioether–phosphinite ligand acts as a monodentate ligand.

Under the optimized conditions, we studied how the thioether substituents affect the catalytic performance with ligands **2** and **3** (Table 1). The use of ligand **2** with methyl substituents in the thioether moieties showed higher activities but lower asymmetric induction than those obtained with the catalytic system Pd/**1** (entry 9). The use of ligand **3** with phenyl substituents in the thioether moieties showed the lowest activity and asymmetric induction (entry 10).

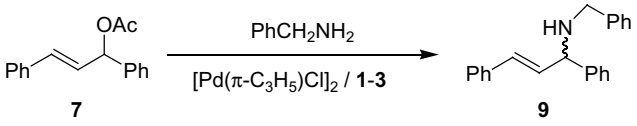
Table 1. Pd-catalyzed allylic alkylation of 1,3-diphenyl-3-acetoxyprop-1-ene **7** using ligands **1**–**3**[a]

Entry	Ligand	Solvent	Base	% Conv (min)[b]	% Ee[c]
1	**1**	CH_2Cl_2	KOAc	100 (30)	86 (*S*)
2	**1**	DMF	KOAc	100 (5)	67 (*S*)
3	**1**	THF	KOAc	77 (30)	84 (*S*)
4	**1**	Toluene	KOAc	60 (30)	86 (*S*)
5	**1**	CH_2Cl_2	K_2CO_3	72 (30)	83 (*S*)
6	**1**	CH_2Cl_2	NaOAc	95 (30)	83 (S)
7	**1**	CH_2Cl_2	Li_2CO_3	95 (30)	82 (*S*)
8[d]	**1**	CH_2Cl_2	KOAc	70 (30)	72 (*S*)
9	**2**	CH_2Cl_2	KOAc	91 (5)	61 (*S*)
10	**3**	CH_2Cl_2	KOAc	90 (30)	47 (*S*)
11[e]	**1**	CH_2Cl_2	KOAc	100 (90)	93 (*S*)
12[f]	**1**	CH_2Cl_2	KOAc	100 (60)	88 (*S*)

[a] 0.5 mol % $[Pd(\pi\text{-}C_3H_5)Cl]_2$, 1.1 mol % ligand, room temperature, 30 min; 3 equiv of $CH_2(COOMe)_2$ and *N*,*O*-bis(trimethylsilyl)acetamide (BSA), a pinch of the corresponding base.
[b] Measured by ^{1}H NMR. Reaction time in minutes shown in parentheses.
[c] Determined by HPLC (Chiralcel OD). Absolute configuration drawn in parentheses.
[d] L/Pd = 2.
[e] Reaction carried out at 0 °C.
[f] Substrate/Pd ratio of 1000.

Enantioselectivity can be further improved (ee's up to 93% (*S*)) using ligand **1** by lowering the reaction temperature to 0 °C (entry 11). We also performed the reaction at a low catalyst concentration (**7**/Pd = 1000) using ligand **1**. Good enantioselectivity [(*S*) 88% ee] and excellent activity (100% conversion after 1 h at room temperature, TOF > 1000 mol × (mol × h)$^{-1}$) were achieved.

To investigate further the catalytic efficiency of these Pd/**1**–**3** systems, we then tested these ligands in the Pd-catalyzed allylic amination of **7** with benzylamine (Scheme 3). The results, which are summarized in Table 2, indicate that the catalytic performance (activities and enantioselectivities) followed the same trend as for the allylic alkylation of **7**, however, the activities were lower.



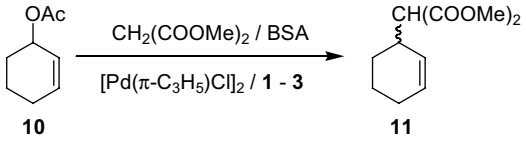
Scheme 3.

Table 2. Pd-catalyzed allylic amination of 1,3-diphenyl-3-acetoxyprop-1-ene **7** using ligands **1**–**3**[a]

Entry	Ligand	% Conv (h)[b]	% Ee[c]
1	**1**	100 (4)	88 (*R*)
2	**2**	100 (4)	63 (*R*)
3	**3**	100 (10)	40 (*R*)

[a] 0.5 mol % $[Pd(\pi\text{-}C_3H_5)Cl]_2$, 1.1 mol % ligand, room temperature, 30 min; 3 equiv of benzylamine. Dichloromethane as solvent.
[b] Measured by ^{1}H NMR. Reaction time in hours shown in parentheses.
[c] Determined by HPLC (Chiralcel OJ).

Encouraged by the good results obtained so far we also tested ligands **1**–**3** in the Pd-catalyzed allylic alkylation of *rac*-3-acetoxycyclohexene **10** (Scheme 4), which is usually used as a model cyclic substrate. It is usually more difficult to control enantioselectivity in cyclic substrates, mainly because of the presence of less sterically *syn* substituents, which are thought to play a crucial role in the enantioselection observed with acyclic substrates in the corresponding Pd-allyl intermediate.[1]



Scheme 4.

Our preliminary investigations into the solvent effect, the ligand-to-palladium ratio and base using ligand **1** provided the same trends as those observed in the previously tested linear substrate **7** (Table 3). The optimum compromise between enantioselectivities and reaction rates was therefore obtained when dichloromethane was used as solvent, the ligand-to-palladium ratio was 1.1 and potassium acetate was used as base (entry 1). Under optimized conditions, the results obtained with ligands **1**–**3** indicate that the catalytic performance (activities and enantioselectivities) followed the same trend as for the allylic alkylation of 1,3-diphenyl-3-acetoxyprop-1-ene **7**. However, the activities and enantiomeric excesses were lower. Lowering the temperature to a 0 °C increased enantioselectivity up to 51% (entry 11 vs 1).

Table 3. Pd-catalyzed allylic alkylation of 3-acetoxycyclohexene **10** with ligands **1**–**3**[a]

Entry	Ligand	Solvent	Base	% Conv (min)[b]	% Ee[c]
1	**1**	CH_2Cl_2	KOAc	100 (30)	41 (*R*)
2	**1**	DMF	KOAc	51 (30)	30 (*R*)
3	**1**	THF	KOAc	53 (30)	30 (*R*)
4	**1**	Toluene	KOAc	53 (30)	31 (*R*)
5	**1**	CH_2Cl_2	K_2CO_3	162 (30)	29 (*R*)
6	**1**	CH_2Cl_2	NaOAc	88 (30)	33 (*R*)
7	**1**	CH_2Cl_2	Li_2CO_3	81 (30)	32 (*R*)
8[d]	**1**	CH_2Cl_2	KOAc	24 (30)	20 (*R*)
9	**2**	CH_2Cl_2	KOAc	100 (30)	21 (*R*)
10	**3**	CH_2Cl_2	KOAc	98 (30)	4 (*R*)
11[e]	**1**	CH_2Cl_2	KOAc	98 (90)	51 (*R*)

[a] 0.5 mol % $[Pd(\pi\text{-}C_3H_5)Cl]_2$, 1.1 mol % ligand, room temperature, 30 min; 3 equiv of $CH_2(COOMe)_2$ and *N*,*O*-bis(trimethylsilyl)acetamide (BSA), a pinch of the corresponding base.

[b] Conversion percentage determined by GC. Reaction time in minutes shown in parentheses.

[c] Enantiomeric excesses determined by GC (FS-β-Cyclodex). Absolute configuration drawn in parentheses.

[d] L/Pd = 2.

[e] Reaction carried out at 0 °C.

3. Conclusions

We have designed and synthesized a new family of readily available thioether–phosphinite ligands for Pd-catalyzed allylic substitution reactions of several substrates with different steric properties. Our results show that the enantiomeric excesses are strongly dependent on the steric proprieties of substituent in the thioether moiety of the carbohydrate backbone. Enantiomeric excesses of up to 93% with high activities were obtained using KOAc as base and CH_2Cl_2 as solvent.

Interestingly, these thioether–phosphinite ligands showed a much higher degree of enantioselectivity and higher reaction rates than their thioether–phosphite analogues under similar reaction conditions.[7]

We are confident that further development of new ligands, taking advantage of the high modularity of this family of ligands, will improve enantioselectivities so far obtained in cyclic substrates. Such studies and mechanistic are currently under way.

4. Experimental section

4.1. General comments

All syntheses were performed using standard Schlenk techniques under argon atmosphere. Solvents were purified by standard procedures. Compounds **4**–**6** were prepared by previously described methods.[8] All other reagents were used as commercially available. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by ^1H–^1H and ^{13}C–^1H spectra. Racemics 1,3-diphenyl-3-acetoxyprop-1-ene **7**[9] and 3-acetoxycyclohexene **10**[10] were prepared as previously reported.

4.2. Synthesis of the chiral thioether–phosphinite ligands

4.2.1. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-isopropylsulfanyl-D-xylofuranose 1. A solution of 0.6 mL (3.3 mmol) of chlorodiphenylphosphine in 12 mL of THF was slowly added at 0 °C to a solution of 744 mg (3 mmol) of **4** and 18.3 mg (0.15 mmol) of DMAP in 3 mL of pyridine. The reaction mixture was stirred overnight at room temperature. Ether ethylic was then added and the pyridine salts were removed by filtration. The residue was purified by flash chromatography (eluent: toluene/NEt_3 100:1, R_f 0.9) to produce 0.92 g (71%) of a colourless oil. ^{31}P NMR, δ: 116.1 (s). ^1H NMR ($CDCl_3$), δ: 1.16 (d, 3H, CH_3, *i*-Pr, $^3J_{Me-CH}$ = 1.2 Hz), 1.18 (d, 3H, CH_3, *i*-Pr, $^3J_{Me-CH}$ = 1.2 Hz), 1.26 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.72 (m, 1H, H-5′), 2.78 (m, 1H, CH–S), 2.82 (m, 1H, H-5), 4.33 (m, 1H, H-4), 4.48 (dd, 1H, H-3, $^3J_{3-P}$ = 9.2 Hz, $^3J_{3-4}$ = 2.4 Hz), 4.56 (d, 1H, H-2, $^3J_{2-1}$ = 3.2 Hz), 5.91 (d, 1H, H-1, $^3J_{1-2}$ = 3.2 Hz), 7.3–7.6 (m, 10H, CH=). ^{13}C NMR ($CDCl_3$), δ: 23.5 (CH_3, *i*-Pr), 23.6 (CH_3, *i*-Pr), 26.5 (CH_3), 27.0 (CH_3), 28.5 (C-5), 35.8 (CH–S), 80.8 (d, C-4, $^3J_{4-P}$ = 6.9 Hz), 82.7 (d, C-3, $^2J_{3-P}$ = 19.8 Hz), 84.0 (d, C-2, $^3J_{2-P}$ = 6.1 Hz), 105.1 (C-1), 112.1 (CMe_2), 128.5 (CH=), 128.6 (CH=), 128.8 (CH=), 129.8 (CH=),

129.9 (CH=), 130.1 (CH=), 130.3 (CH=), 130.9 (CH=), 131.1 (CH=), 141.2 (d, C, J_{C-P} = 16.0 Hz), 142.2 (d, C, J_{C-P} = 17.6 Hz). Anal. Calcd (%) for $C_{23}H_{29}O_4PS$: C, 63.87; H, 6.76; S, 7.41. Found: C, 63.78, H, 6.84, S 7.34.

4.2.2. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-methylsulfanyl-D-xylofuranose 2. Treatment of **5** (3 mmol) with chlorodiphenylphosphine (0.6 mL, 3.3 mmol) as described for compound **4** afforded thioether–phosphinite **2**, which was purified by flash chromatography (eluent: toluene/NEt_3 100:1, R_f 0.9) to produce 1.05 g (87%) of a colourless oil. ^{31}P NMR, δ: 115.9 (s). ^1H NMR, δ: 1.27 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.04 (s, 3H, CH_3–S), 2.70 (dd, 1H, H-5′, $^3J_{H-H}$ = 8.0 Hz, $^2J_{H-H}$ = 13.2 Hz), 2.75 (dd, 1H, H-5, $^3J_{H-H}$ = 6.0 Hz, $^2J_{H-H}$ = 13.2 Hz), 4.37 (m, 1H, H-4), 4.48 (dd, 1H, H-3, $^3J_{H-H}$ = 2.8 Hz, J_{H-P} = 9.6 Hz), 4.58 (d, 1H, H-2, $^3J_{H-H}$ = 3.2 Hz), 5.92 (d, 1H, H-1, $^3J_{H-H}$ = 3.2 Hz), 7.3–7.6 (m, 10H, CH=). ^{13}C NMR, δ: 16.4 (CH_3–S), 26.5 (CH_3), 27.0 (CH_3), 31.9 (C-5), 80.3 (d, C-4, J_{C-P} = 6.8 Hz), 82.7 (d, C-3, J_{C-P} = 19.9 Hz), 84.0 (d, C-2, J_{C-P} = 5.3 Hz), 105.1 (C-1), 112.1 (CMe_2), 128.6 (CH=), 128.7 (CH=), 128.8 (CH=), 129.7 (CH=), 130.1 (CH=), 130.3 (CH=), 131.0 (CH=), 131.2 (CH=), 141.2 (d, C, J_{C-P} = 16.8 Hz), 142.1 (d, C, J_{C-P} = 16.0 Hz). Anal. Calcd (%) for $C_{21}H_{25}O_4PS$: C, 62.36; H, 6.23; S, 7.93. Found: C, 62.43, H, 6.34, S, 7.82.

4.2.3. 1,2-*O*-Isopropylidene-3-diphenylphosphinite-5-phenylsulfanyl-D-xylofuranose 3. Treatment of **6** (3.5 mmol) with chlorodiphenylphosphine (0.7 mL, 3.9 mmol) as described for compound **4** afforded thioether–phosphinite **3**, which was purified by flash chromatography (eluent: toluene/NEt_3 100:1, R_f 0.9) to produce 1.47 g (89%) of a colourless oil. ^{31}P NMR, δ: 116.8 (s). ^1H NMR, δ: 1.25 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.06 (dd, 1H, H-5′, $^3J_{H-H}$ = 8.4 Hz, $^2J_{H-H}$ = 12.8 Hz), 3.19 (dd, 1H, H-5, $^3J_{H-H}$ = 6.0 Hz, $^2J_{H-H}$ = 12.8 Hz), 4.32 (m, 1H, H-4), 4.51 (dd, 1H, H-3, $^3J_{H-H}$ = 2.1 Hz, J_{H-P} = 9.6 Hz), 4.59 (d, 1H, H-2, $^3J_{H-H}$ = 3.6 Hz), 5.93 (d, 1H, H-1, $^3J_{H-H}$ = 3.6 Hz), 7.1–7.6 (m, 15H, CH=). ^{13}C NMR, δ: 26.6 (CH_3), 26.9 (CH_3), 31.7 (C-5), 79.3 (d, C-4, J_{C-P} = 6.9 Hz), 82.5 (d, C-3, J_{C-P} = 20.0 Hz), 84.0 (d, C-2, J_{C-P} = 5.6 Hz), 105.1 (C-1), 112.1 (CMe_2), 126.5 (CH=), 128.7 (CH=), 128.8 (CH=), 129.1 (CH=), 129.8 (CH=), 129.9 (CH=), 130.1 (CH=), 130.4 (CH=), 131.0 (CH=), 131.3 (CH=), 135.6 (C), 141.0 (d, C, J_{C-P} = 16.8 Hz), 142.0 (d, C, J_{C-P} = 16.8 Hz) Anal. Calcd (%) for $C_{26}H_{27}O_4PS$: C, 66.94; H, 5.83; S 6.87. Found: C, 70.01, H, 5.79, S, 6.85.

4.3. Typical procedure of allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene 7

A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and the thioether–phosphinite ligand (0.011 mmol) in dichloromethane (0.5 mL) was stirred for 30 min. Subsequently, a solution of *rac*-**7** (126 mg, 0.5 mmol) in dichloromethane (1.5 mL), dimethyl malonate (171 μL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)-acetamide (370 μL, 1.5 mmol) and a pinch of KOAc were added. The reaction mixture was stirred at room temperature. After 5 min the reaction mixture was diluted with Et_2O (5 mL) and a saturated NH_4Cl (aq) (25 mL) was added. The mixture was extracted with Et_2O (3 × 10 mL) and the extract dried over $MgSO_4$. Solvent was removed and conversion was measured by ^1H NMR. To determine the ee by HPLC (Chiralcel OD, 0.5% 2-propanol/hexane, flow 0.5 mL/min), a sample was filtered over basic alumina using dichloromethane as the eluent.

4.4. Typical procedure of allylic alkylation of *rac*-3-acetoxycyclohexene 10

A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and the thioether–phosphinite ligand (0.011 mmol) in dichloromethane (0.5 mL) was stirred for 30 min. Subsequently, a solution of *rac*-**10** (70 mg, 0.5 mmol) in dichloromethane (1.5 mL), dimethyl malonate (171 μL, 1.5 mmol), *N*,*O*-bis(trimethylsilyl)-acetamide (370 μL, 1.5 mmol) and a pinch of KOAc were added. The reaction mixture was stirred at room temperature. After 30 min the reaction mixture was diluted with Et_2O (5 mL) and a saturated NH_4Cl (aq) (25 mL) was added. The mixture was extracted with Et_2O (3 × 10 mL) and the extract dried over $MgSO_4$. Conversion and enantiomeric excess were determined by GC using a FS-β-Cyclodex 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 100 kPa He, FID detector).

4.5. Typical procedure of allylic amination of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene 7

A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and the thioether–phosphinite ligand (0.011 mmol) in dichloromethane (0.5 mL) was stirred for 30 min. Subsequently, a solution of *rac*-**7** (126 mg, 0.5 mmol) in dichloromethane (1.5 mL) and benzylamine (131 μL, 1.5 mmol) was added. The reaction mixture was stirred at room temperature. After 1 h the reaction mixture was diluted with Et_2O (5 mL) and a saturated NH_4Cl (aq) (25 mL) was added. The mixture was extracted with Et_2O (3 × 10 mL) and the extract dried over $MgSO_4$. Solvent was removed and conversion was measured by ^1H NMR. To determine the ee by HPLC (Chiralcel OJ, 13% 2-propanol/hexane, flow 0.5 mL/min), a sample was filtered over silica using 10% Et_2O/hexane mixture as the eluent.

Acknowledgements

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