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[3]Ferrocenophane Ligands with an Inserted Methylene Group

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New planar chiral [3]ferrocenophane aminosulfane and aminophosphane ligands displayed interesting results in model Pd-catalyzed allylic substitution reactions. The phosphane derivative having a methylene group between the cyclopentadienyl ring and the phosphane group showed enantioselectivities up to 86 % *ee*, whereas the ligand without the methylene group afforded almost racemic allylation products. Analogous sulfane ligands showed the opposite trend. Tentative catalytic complexes were studied by ^{31}P NMR spectroscopy and DFT computational methods.

Introduction

Asymmetric catalysis with the use of transition-metal complexes with chiral ligands is an important strategy for the preparation of enantiomerically pure or enriched compounds.[1] At present, a great variety of potent catalytic systems is already known and the number of catalytic enantioselective processes is growing rapidly. Nevertheless, syntheses of new and supposedly even more capable ligands continue to be an area of active research. Particularly, the rational design of efficient catalysts still remains one of the challenges in this field.[2]

Ferrocene derivatives represent a prominent ligand class due to their interesting stereochemical properties and the availability of reliable methods for their synthesis and functionalization. Notably, chiral ferrocenylphosphanes proved to be valuable ligands for various enantioselective transformations.[3] Sulfur-containing ferrocene derivatives also found use in asymmetric catalysis.[4] Heterobidentate ligands often positively influence catalyzed asymmetric reactions because of additional electronic stereodifferentiation in the coordination sphere of the transition metal.[5] Chiral ferrocene heterobidentate P,N ligands proved useful, especially for Pd-catalyzed allylic substitution reactions.[6] Among various structural scaffolds of ferrocene ligands, carbon-bridged ferrocenophanes appear to be interesting alternatives to unbridged compounds.[7] Weissensteiner showed the utility of [3]ferrocenophane derivatives in several asymmetric reactions. In the Pt-catalyzed carbonylation of styrene, only small enantioselectivities were obtained.[8] Several homo- and heteroannularly bridged ferrocenyldiphosphanes were used more successfully in Rh-catalyzed hydrogenations of olefins and ketones with medium-to-high enantioselectivities.[9] The rigidness of the ligand caused by the three-atom bridge was suggested as a possible reason for the lower enantioselectivities relative to those obtained with unbridged derivatives. These compounds were also tested in Pd-catalyzed allylic substitution reactions: enantioselectivities up to 71 % were obtained. Interestingly, P,N ligands of this type were unsuccessful in this allylation reaction.[10] We recently demonstrated that [5]ferrocenophane derivatives are also useful ligands in Pd-catalyzed allylic substitution, Rh-catalyzed hydrogenation, and Cu-catalyzed conjugate addition reactions.[11] Erker described [3]ferrocenophane diphosphanes with a slightly different framework. By using these diphosphanes, dimethyl itaconate was hydrogenated in up to 95 % *ee*.[12]

Inspired by the work of Weissensteiner,[10] we decided to prepare [3]ferrocenophane ligands with an additional methylene group between the Cp ring and the donor atoms. The idea was that it could lead to a more flexible ligand, with better catalytic performance, especially in terms of enantioselectivity. Here we present the synthesis of such derivatives along with their testing in model Pd-catalyzed allylic substitution reactions. For evaluation of the influence of the methylene group on the ligand performance, we also performed allylation reactions with the parent compounds without the methylene group.

Results and Discussion

Amine **1** was prepared from ferrocene according to described methods.[13] Directed *ortho*-lithiation of amine **1** with BuLi proceeded highly diastereoselectively.[14] We used $(CH_2O)_n$ as the electrophile to introduce a hydroxymethyl group on the cyclopentadienyl (Cp) ring. Column chromatography afforded pure alcohol **2** in 65 % yield with no minor diastereoisomer detectable by NMR spectroscopy.

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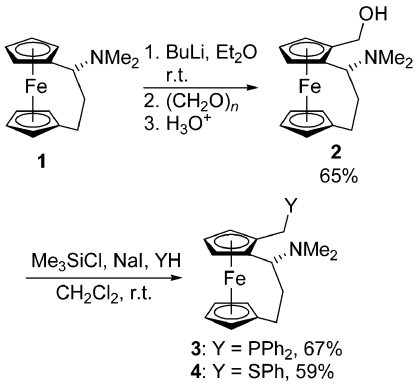
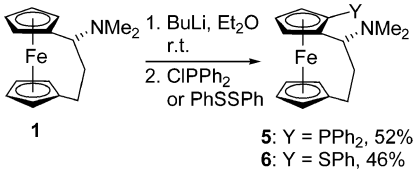
To transform the hydroxy group into a phosphanyl or sulfanyl group, we modified a method for the preparation of iodo derivatives.[15] We found that it is possible to perform the desired nucleophilic substitution reaction in one pot by adding the appropriate phosphane or sulfane directly into the reaction mixture together with NaI and Me_3SiCl. This leads, presumably, to the formation of an intermediate iodo derivative, which then undergoes nucleophilic substitution. Under these conditions, desired phosphane **3** and sulfane **4** were obtained only in rather moderate yields of 67 and 59%, respectively (Scheme 1). In contrast, this simple one-pot procedure is very convenient from a practical point of view.



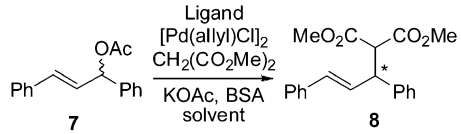
Scheme 1.

For the sake of comparison, we also prepared ligands with PPh_2 and SPh groups attached directly to the Cp ring. Lithiated amine **1** was quenched with Ph_2PCl and PhSSPh as electrophiles to produce ligands **5**[14] and **6**, respectively (Scheme 2).



Scheme 2.

With the ligands in hand, we performed the catalysis experiments. Asymmetric Pd-catalyzed reactions involving an allylic moiety are important tools for creating new carbon–carbon bonds, as well as carbon–heteroatom bonds.[16] Therefore, we chose Pd-catalyzed allylic alkylation as a benchmark reaction. As the allylic substrate we used 1,3-diphenyl-1-acetoxypropene (**7**) and generated the nucleophile in situ from dimethyl malonate with the use of KOAc/BSA. The catalyst (2 mol-%) was formed by mixing the appropriate free ligand with $[Pd(allyl)Cl]_2$ before the reaction (Scheme 3).



Scheme 3.

With the use of ligand **5**, allylic substitution afforded product **8** only with 7%*ee*, which is in agreement with the literature.[10] By using aminophosphane **3**, which contains an additional methylene group between the Cp and PPh_2 groups, we obtained diester **8** under various conditions, generally in good yields and enantioselectivities (up to 86%*ee*). Surprisingly, in the sulfur pair, allylation with the use of ligand **6** proceeded with 68%*ee* but ligand **4** (with an inserted methylene group) afforded racemic compound **8**. An interesting detail is that with a Pd/ligand **3** ratio of 1:2, we isolated diester **8** with 65%*ee* (*R* enantiomer), but with a Pd/**3** ratio of 1:1, we obtained (*S*)-**8**. No such effect was observed with sulfane **6**. Results of the catalysis experiments are summarized in Table 1.

Table 1. Pd-catalyzed allylic substitution.

L	Pd/L	Solvent	*T*	Time [h]	Yield[a] [%]	*ee*[b] [%]
3	1:1	CH_2Cl_2	r.t.	3	92	82 (*S*)
3	1:1	CH_2Cl_2	0	5	94	84 (*S*)
3	1:1	toluene	r.t.	22	85	86 (*S*)
3	1:1	$CHCl_3$	r.t.	18	82	85 (*S*)
3	1:1	THF	r.t.	20	87	71 (*S*)
3	1:2	CH_2Cl_2	r.t.	18	84	43 (*R*)
3	1:2	CH_2Cl_2	0	21	88	65 (*R*)
4	1:1	CH_2Cl_2	r.t.	48	–	–
4	1:2	CH_2Cl_2	r.t.	48	6	0
5	1:1	CH_2Cl_2	r.t.	18	15	7 (*S*)
6	1:1	CH_2Cl_2	r.t.	48	41	68 (*R*)
6	1:2	CH_2Cl_2	r.t.	48	48	67 (*R*)

[a] Isolated yield of purified diester **8**. [b] Determined by HPLC on a Chiralcel AD-H column (hexane/*i*PrOH, 9:1; 0.75 mL min^{-1}).

An explanation for the reversal in the enantioselectivity upon changing the ratio of Pd/**3** could be that different catalytically active complexes are formed. It is generally accepted that nitrogen is a weaker donor than phosphorus. Therefore, we supposed that by increasing the amount of ligand to two equivalents relative to the amount of palladium, the corresponding 2:1 complex will be formed. However, ^{31}P NMR spectroscopic experiments suggest that the situation is more complicated. In the ^{31}P NMR spectrum of the 1:1 Pd complex of ligand **3** (prepared from $[Pd(allyl)Cl]_2$ and free ligand **3** in $CDCl_3$) one major signal at δ = 18.2 ppm was observed, probably corresponding to 1:1 Pd/**3** complex having phosphorus and nitrogen as donor atoms. If more ligand **3** was added, up to a Pd/**3** ratio of 1:2, the 1:1 complex seemed to be still predominant, but it was in equilibrium with other species. The dynamic nature of the solution was also noticeable from peak broadening, which was even more evident upon heating to 40 °C. Certainly,

different species were present when the Pd/**3** ratio was 1:1 and 1:2, and a signal for the uncomplexed ligand (–15.1 ppm) was absent in both cases (Figure 1).

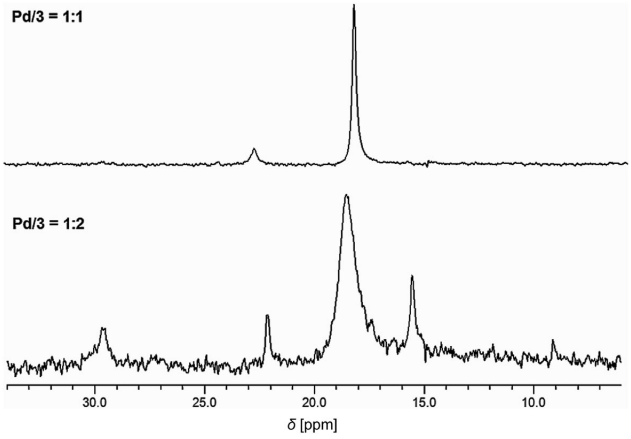
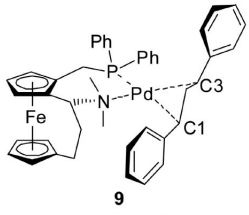


Figure 1. ^{31}P NMR spectra of Pd/**3** complexes.

The structure of the likely intermediate in the reaction, the Pd complex of ligand **3** and the diphenylpropenylium cation, was optimized in DGauss engine in the CaChe package[17] with the DFT method by using the B88-LYP functional and the DZVP basis set. Attack of the nucleophile at the carbon atom *trans* to the phosphorus atom[18] would lead to the observed (*S*) enantiomer of diester **8**. Figure 2 depicts the DFT-optimized structure of this intermediate. In an attempt to understand the influence of the ligand structure on the catalyzed reaction, we examined also similar intermediates with ligands **5** and **6**. We were not able to produce any optimized structure with ligand **4**, which suggests, as also supported by catalytic experiments, that no productive, catalytically active complex is formed in this case.



9

Figure 2. DFT optimized structure of **9**.

One of the most important parameters for ligands in transition-metal catalysts is the ligand bite angle.[19] The additional methylene group in ligand **3** increased the bite angle (N–Pd–P) from 89.0° in ligand **5** (without the methylene group) to 94.4°. This modification resulted in a considerably more-active and enantioselective catalyst, probably because of the increased steric influence of the ligand on the allylic cation. Calculations also predict a *trans* effect of phosphorus leading to elongation of the Pd–C1 bond. Table 2 shows selected geometrical parameters of DFT-optimized Pd complexes with ligands **3**, **5**, and **6**. Orientation of the 1,3-diphenylallyl cation was W-type for ligands **3** and **5**, which would lead to the observed (*S*) enantiomer of compound **8**; for ligand **6**, the cation was M-type.

Table 2. Geometrical parameters of the calculated Pd–allyl complexes of type **9**.

Ligand	N–Pd–P [°]	Pd–C1 [Å]	Pd–C3 [Å]
3	94.4	2.605	2.287
5	89.0	2.524	2.267
6	90.8	2.424	2.288

Conclusions

We prepared new [3]ferrocenophane aminophosphane and aminosulfane derivatives, which showed promising results in Pd-catalyzed allylic substitution reactions. Our work shows that subtle changes in the structure of the ligand can have a dramatic influence on its catalytic performance. In the case of aminophosphane **3**, which has a methylene group inserted between the phosphorus atom and the Cp ring, a highly positive effect was observed; however, insertion of a methylene group into the corresponding aminosulfane derivative led to an inactive catalyst. Further work in this area is in progress in our laboratory.

Experimental Section

General: Homochiral amine (*R*)-**1** and ligand (R,S_P)-**5** were prepared by following literature procedures.[12,13] All reactions were carried out under an N_2 atmosphere and in the case of work with organometallic reagents by using standard Schlenk techniques. Column chromatography was performed on 40/100 mesh silica gel columns. NMR spectra were recorded with a Varian Gemini 2000 spectrometer at 300 MHz for ^{1}H, 75 MHz for ^{13}C and 121 MHz for ^{31}P nuclei. Tetramethylsilane was used as an internal standard. Elemental analyses were performed with a Carlo Erba Instrumentazione analyzer. Melting points were measured with a Kofler hotplate and are uncorrected. Mass spectra were recorded with a Waters Premium QTOF instrument.

(R,S_P)-2-Hydroxymethyl-[1,1′-(1-dimethylamino)propanediyl]-ferrocene (2): To a solution of amine **1** (413 mg, 1.60 mmol) in anhydrous Et_2O (5 mL) was dropwise added *n*BuLi (1.6 M in hexane, 2.0 mL, 2.40 mmol) at 0 °C. The reaction mixture was stirred for 4 h at room temperature, and an orange precipitate was formed. Then, solid $(CH_2O)_n$ (144 mg, 4.80 mmol) was added. The precipitate dissolved, and the reaction mixture was stirred for an additional 18 h at room temperature. The reaction was quenched with saturated $NaHCO_3$ (3 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic extract was washed with H_2O (2 × 15 mL) and dried (Na_2SO_4). The solvent was evaporated, and the residue was puri-

fied by column chromatography (SiO_2; hexane/EtOAc/Et_3N, 1:1:0.1) and crystallized from hexane to give pure alcohol **2** (300 mg, 65%) as orange crystals. M.p. 78–80 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.87–2.00 (m, 1 H), 2.16–2.30 (m, 1 H), 2.30–2.35 (s, 6 H, NMe_2), 2.42–2.57 (m, 2 H), 2.57–2.66 (ddd, J = 2.3, 4.3, 14.5 Hz, 1 H), 3.69–3.73 (m, 1 H, Cp), 3.92–3.97 (m, 2 H, Cp), 3.97–4.00 (m, 1 H, Cp), 4.03–4.07 (m, 2 H, Cp), 4.11 (d, J = 12.7 Hz, 1 H, CH_2OH), 4.12–4.16 (m, 1 H, Cp), 4.83 (d, J = 12.7 Hz, 1 H, CH_2OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2 (CH_2), 37.5 (CH_2), 44.9 (CH_3), 61.1 (CH_2OH), 66.1 (CH), 66.2 (CH), 67.1 (CH), 69.7 (CH), 71.19 (CH), 71.2 (CH), 71.4 (CH), 71.5 (CH), 85.5 (qC), 86.4 (qC), 87.33 (qC) ppm. $[\alpha]_D$ = –125 (c = 0.2, MeOH). $C_{16}H_{21}FeNO$ (299.19): calcd. C 64.23, H 7.07, N 4.68; found C 64.20, H 6.50, N 4.79.

(R,S_P)-2-Diphenylphosphanomethyl-[1,1′-(1-dimethylamino)propanediyl]ferrocene (3): To a solution of hydroxymethyl derivative **2** (272 mg, 0.94 mmol) and NaI (282 mg, 1.88 mmol) in anhydrous CH_3CN (5 mL) was dropwise added Me_3SiCl (324 μL, 2.55 mmol). A yellow precipitate was formed, the mixture was stirred for 5 min at room temperature, and then $HPPh_2$ (166 μL, 1.04 mmol) was added. The precipitate dissolved and the solution became orange. The reaction mixture was stirred for an additional 2 h at room temperature. The resulting solution was diluted with CH_2Cl_2 (10 mL) and extracted with H_2O (3 × 8 mL) and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography under a N_2 atmosphere (SiO_2; hexane/EtOAc/Et_3N, 1:1:0.1) to give pure phosphane **3** (293 mg, 67%) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.84–1.98 (m, 1 H), 2.18–2.34 (m, 1 H), 2.23–2.27 (s, 6 H, NMe_2), 2.38–2.52 (m, 2 H), 2.52–2.62 (m, 1 H), 3.26 (dd, J = 2.0, 14.7 Hz, 1 H), 3.48 (dd, J = 1.7, 14.7 Hz, 1 H), 3.68–3.74 (m, 2 H, Cp), 3.80–3.88 (m, 3 H, Cp), 3.98–4.02 (m, 1 H, Cp), 4.08–4.13 (m, 1 H, Cp) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7 (CH_2), 29.05 (d, J = 15.1 Hz, CH_2P), 38.8 (CH_2), 46.0 (CH_3), 66.6 (CH), 66.8 (CH), 68.2 (CH), 69.9 (CH), 70.9 (CH), 71.2 (d, J = 10.0 Hz, CH), 71.3 (CH), 73.4 (d, J = 3.2 Hz, CH), 83.6 (qC), 84.4 (d, J = 17.3 Hz, qC), 88.7 (qC), 128.3 (CH-Ph), 128.5 (d, J = 6.0 Hz, CH-Ph), 128.6 (d, J = 6.9 Hz, CH-Ph), 128.9 (CH-Ph), 132.6 (d, J = 18.0 Hz, CH-Ph), 133.8 (d, J = 20.0 Hz, CH-Ph), 139.6 (d, J = 15.8 Hz, qC-Ph), 140.1 (d, J = 16.3 Hz, qC-Ph) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –15.1 ppm. $[\alpha]_D$ = +77 (c = 0.5, MeOH). HRMS (ESI): calcd. for $C_{28}H_{30}NNaPFe$ $[M + Na]^+$ 490.1331; found 490.1061.

(R,S_P)-2-(Phenylsulfanyl)methyl-[1,1′-(1-dimethylamino)propanediyl]ferrocene (4): To a solution of hydroxymethyl derivative **2** (150 mg, 0.52 mmol) and NaI (156 mg, 1.04 mmol) in anhydrous CH_3CN (7 mL) was dropwise added Me_3SiCl (179 μL, 1.40 mmol). After the addition, a yellow precipitate was formed. The mixture was stirred for 5 min at room temperature and then HSPh (166 μL, 1.04 mmol) was added. The precipitate dissolved, and solution became darker. The reaction mixture was stirred for 4 h at room temperature. The solution was diluted with CH_2Cl_2 (10 mL) and extracted with H_2O (3 × 8 mL) and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by column chromatography under a N_2 atmosphere (SiO_2; hexane/EtOAc/Et_3N, 1:1:0.1) to give sulfane **4** (120 mg, 59%) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.84–1.96 (m, 1 H), 2.08–2.24 (m, 1 H), 2.24–2.29 (s, 6 H, NMe_2), 2.40–2.51 (m, 2 H), 2.51–2.61 (m, 1 H), 3.88–3.94 (m, 3 H, Cp), 3.98 (t, J = 2.5 Hz, 1 H, Cp), 4.03–4.07 (m, 1 H, Cp), 4.11 (d, J = 1.3 Hz, 2 H), 4.14–4.19 (m, 2 H, Cp), 7.13–7.21 (m, 1 H, Ph), 7.23–7.32 (m, 2 H, Ph), 7.37–7.43 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3 (CH_2), 34.0 (CH_2), 38.9 (CH_2), 45.6 (CH_3), 67.08 (CH), 67.15 (CH), 67.47 (CH), 70.0 (CH), 70.7 (CH), 71.1 (CH), 71.51 (CH), 71.52 (CH), 83.3 (qC), 83.6 (qC), 88.4 (qC), 125.8 (CH-Ph), 128.8 (CH-Ph), 129.4 (CH-Ph), 138.0 (qC-Ph) ppm. $[\alpha]_D$ = +158 (c = 0.5, EtOH). HRMS (ESI): calcd. for $C_{21}H_{23}FeNNaS$ $[M + Na]^+$ 400.0767; found 400.0625.

(R,S_P)-2-Phenylsulfanyl-[1,1′-(1-dimethylamino)propanediyl]ferrocene (6): To a solution of amine **1** (470 mg, 1.82 mmol) in anhydrous Et_2O (10 mL) was dropwise added nBuLi (1.6 M in hexane, 1.70 mL, 2.73 mmol) at 0 °C. The reaction mixture was stirred for 4 h at room temperature and an orange precipitate was formed. Then, PhSSPh (720 mg, 3.28 mmol) was added. The precipitate dissolved, and the reaction mixture was stirred for an additional 18 h at room temperature. The reaction was quenched with saturated $NaHCO_3$ (7 mL). The layers were separated, and aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried with Na_2SO_4. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2; hexane/EtOAc/Et_3N, 1:1:0.1) and crystallized from EtOH to give compound **6** (320 mg, 46%) as orange crystals. M.p. 140–142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.90–2.05 (m, 1 H), 2.15–2.20 (s, 6 H, NMe_2), 2.20–2.30 (m, 1 H), 2.55–2.65 (ddd, J = 2.7, 3.8, 14.4 Hz, 1 H), 2.80–3.00 (m, 2 H), 3.94–3.98 (m, 1 H, Cp), 4.00–4.05 (m, 1 H, Cp), 4.10–4.14 (m, 1 H, Cp), 4.17–4.21 (m, 1 H, Cp), 4.21–4.25 (dd, J = 2.5 Hz, 1 H, Cp), 4.28–4.34 (m, 2 H, Cp), 7.03–7.12 (m, 1 H, Ph), 7.15–7.23 (m, 4 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1 (CH_2), 38.4 (CH_2), 43.9 (CH_3), 67.5 (CH), 67.7 (CH), 69.7 (CH), 70.6 (CH), 71.6 (CH), 73.5 (CH), 74.6 (CH), 77.3 (qC), 78.1 (CH), 82.6 (qC), 89.7 (qC), 125.0 (CH-Ph), 127.0 (CH-Ph), 128.4 (CH-Ph), 140.1 (qC-Ph) ppm. $[\alpha]_D$ = +219 (c = 0.5, MeOH). HRMS (ESI): calcd. for $C_{20}H_{19}FeS$ (molecular ion was not observed because of rapid elimination of the NMe_2 group leading to a stable α-carbocation) 347.0526; found 347.0341.

General Procedure for Allylic Substitution: Ligand (0.02 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.01 mmol) were dissolved in CH_2Cl_2 (3 mL), and the resulting solution was stirred for 10 min at room temperature. This solution was added to acetate **7** (252 mg, 1.0 mmol) in CH_2Cl_2 (2 mL). Then, bis(trimethylsilyl)acetamide (0.49 mL, 407 mg, 2.0 mmol), dimethyl malonate (230 μL, 264 mg, 2.0 mmol) and KOAc (5 mg, 0.05 mmol) were added, and the resulting mixture was stirred. The reaction was monitored by TLC and stopped when no starting material was detected or after 48 h. The mixture was then diluted with CH_2Cl_2 (10 mL) and extracted with saturated aqueous NH_4Cl (3 × 10 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc, 9:1). Enantiomeric excesses were determined by HPLC on a Chiralcel AD-H column. HPLC (hexane/iPrOH, 9:1; 0.75 mL min^{-1}): t_R = 16.6 [(*R*)-**8**], 23.7 [(*S*)-**8**] min.

Acknowledgments

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