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Imidazolium-tagged ferrocenyl diphosphanes in allylic substitution with heteroatom nucleophiles

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ABSTRACT

Imidazolium-tagged ferrocenyl diphosphanes are useful ligands in palladium-catalyzed allylic substitutions with heteroatom nucleophiles. Substitution with phthalimide proceeds with high enantioselectivity (up to 92% ee) in various ionic liquids. Reaction with *p*-cresol as nucleophile affords allylation product in up to 62% ee, while using tolylsulfinate as a nucleophile gives a product with very little or no enantioselectivity. Under these reaction conditions, catalyst recyclability is challenging, and decrease in activity as well as enantioselectivity was observed.

1. Introduction

Enantioselective catalytic carbon–carbon and carbon–heteroatom bond formations are important tools for the construction of complex molecules. From a large array of available methods, nucleophilic attack on a transition metal-stabilized allylic cation has been a greatly studied reaction, because it leads to many useful structural motifs.[1] From among many metals capable of catalyzing allylic substitution, palladium occupies a prominent position. Numerous asymmetric ligands have been successfully utilized in this reaction,[2] including a range of chiral ferrocene derivatives.[3]

One of the important issues in modern asymmetric catalysis is a question of catalyst recycling or practical product separation. Heterogeneous catalysis offers solutions to some of the issues.[4] On the other hand, heterogeneous systems often suffer from decreased activities compared to homogeneous catalysts. Therefore, a concept of homogeneous-supported catalysis was suggested as an interesting alternative to address this problem, and was aimed at combining positive features of both heterogeneous and homogeneous catalyses. These catalytic systems, usually in connection with an appropriate reaction medium such as fluorous solvents, soluble polymers or ionic liquids, offer interesting possibilities for the development of efficient recyclable catalysts.[5] In this context, diverse ionically tagged catalysts have been successfully used for a variety of asymmetric catalytic reactions in ionic liquids.[6] However, little attention has been devoted to asymmetric allylic substitution in this direction. Several polymer-supported palladium catalysts have been shown to be active in allylic substitution.[7] Polyethylene glycol (PEG)-supported catalysts again appear as interesting soluble alternatives to cross-linked polymer supports. Bandini and Ding prepared PEG-supported palladium catalysts for allylic substitution.[8] Gavrilov and Reetz described ionic phosphites which were used in asymmetric hydrogenation as well as allylic substitution.[9] Using an ionic-tag strategy, we prepared soluble imidazolium ferrocenyl phosphanes, which also proved to be useful ligands in Pd-catalyzed allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate.[10] At the same time, the imidazolium cation was also attached to *Josiphos* diphosphanes but the resulting ligands were used for Rh-catalyzed hydrogenation.[11] Our BPPFA **1**-derived imidazolium diphosphane **3** afforded an allylation product with high enantioselectivity (92% ee). However, we also noted problems with recyclability of these catalysts.[10] Encouraged by the initial results we decided to explore the allylic substitution reaction with heteroatom nucleophiles. Herein we report that imidazolium-tagged ferrocenyl diphosphanes are useful ligands in Pd-catalyzed allylic substitution with heteroatom nucleophiles. We also tried to address the issue of catalyst recycling by modification of its structure.

2. Results and discussion

Imidazolium-tagged ferrocenyl diphosphanes **3** and **4** (Scheme 1) were prepared from the BPPFA ligand[12] by a procedure developed in our laboratory.[10] Ligand **4** was suggested as a possible improvement of ligand **3**. The acidic proton at the 2-position was replaced by a methyl group to prevent carbene formation under basic conditions.[13]

As a prototype reaction, we chose allylic substitution with potassium phthalimide as a nucleophile (Scheme 2). A palladium

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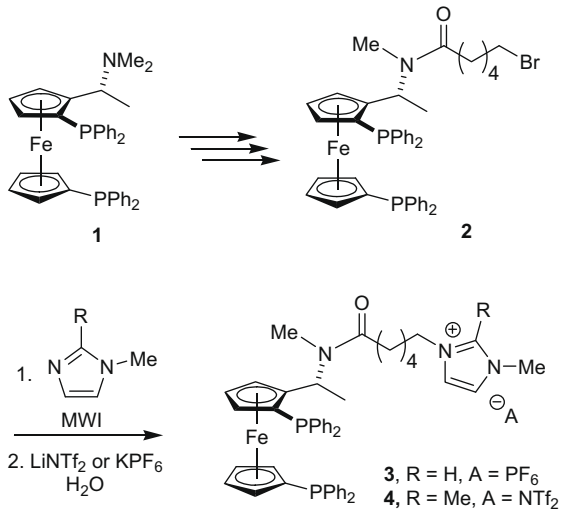
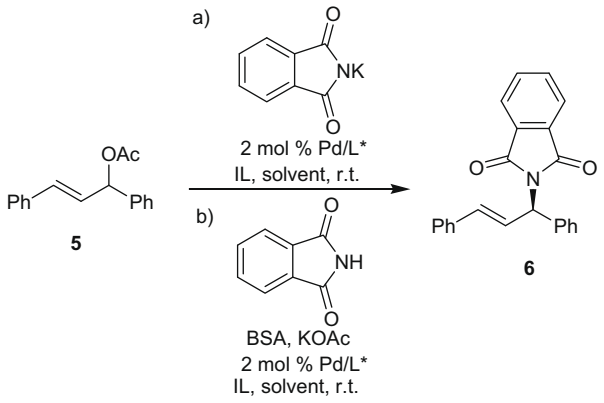


Scheme 1.



Scheme 2.

complex of BPPFA afforded compound **6** in small to medium yields and with enantioselectivities from 37 to 90% ee (Table 1, entry 3). The strong influence of the reaction medium on the reactivity and enantioselectivity should be noted (Table 1).

Table 1
Allylic substitution with potassium phthalimide using BPPFA ligand

Entry	Solvent	Time (h)	Yield[a] (%)	ee[b] (%)
1	CH_2Cl_2	24	19	70
2	THF	160	5	37
3	EtOAc	120	50	90
4	Toluene	120	5	68
5	$ClCH_2CH_2Cl$	120	22	80
6	[emim]$EtOSO_3$/H_2O	168	34	60
7	[emim]$EtOSO_3$/EtOH	168	10	70
8	[bdmim]PF_6/CH_2Cl_2	48	55	70

[a] Isolated yield of pure compound **6**.
[b] Determined by HPLC on Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min.

When ionic liquids and ionic ligand **3** were used in this reaction, product **6** was isolated in up to 84% yield with high enantioselectivities (up to 92% ee). The small solubility of potassium phthalimide in ionic liquid led to the formation of very viscous reaction mixtures, resulting in inadequate stirring. In order to avoid this problem we added a polar organic solvent, miscible with the ionic liquid, into the reaction mixture (Table 2). The best results were obtained with ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([emim]$EtOSO_3$, other imidazolium ionic liquids are abbreviated similarly; [bdmim] stands for 1-butyl-2,3-dimethylimidazolium) and CH_2Cl_2 or CH_3CN (Table 2, entries 1–5). It is also noteworthy that ligand **3** in ionic liquids performs better than the parent BPPFA ligand **1** in terms of both chemical yield and enantioselectivity (Table 1, entry 8 cf. Table 2 entry 6). After consumption of all the starting material, followed by TLC, the reaction mixture was extracted with toluene to obtain crude product **6**. In ionic liquids immiscible with water, the unreacted potassium phthalimide together with potassium acetate was removed by extraction with water. The catalytic system, comprised the palladium complex of ligand **3** dissolved in ionic liquid and was, before reuse, dried in vacuum and degassed. Unfortunately, the recycled catalytic system with ligand **3** was considerably less active (Table 2, entries 8 and 11). The situation did not improve in other ionic liquids, at lower temperatures or excesses of organic solvent. We hypothesized that the presence of a large amount of basic potassium phthalimide can be a problem, leading to ligand or ionic liquid degradation. For this reason we prepared ligand **4** with a 1,2-dimethyl imidazolium moiety, which should be more resistant to basic conditions. In our reaction, ligand **4** behaves similarly to ligand **3**, but there was no improvement in the recycled experiments (Table 2, entry 13). Even a combination of 2-methyl-substituted imidazolium ionic liquids, such as [bdmim]PF_6 and [bdmim]NTf_2, and ligand **4** did not improve the situation (Table 2, entries 12–14).

Table 2
Allylic substitution with potassium phthalimide

Entry	Ligand	Solvent	Time (h)	Yield[c] (%)	ee[d] (%)
1	3	[emim]$EtOSO_3$/CH_2Cl_2	4.5	67	92
2	3	[emim]$EtOSO_3$/CH_2Cl_2[a]	48	47	91
3	4	[emim]$EtOSO_3$/CH_2Cl_2[b]	18	84	89
4	3	[emim]$EtOSO_3$/THF	24	39	88
5	3	[emim]$EtOSO_3$/CH_3CN	20	70	92
6	3	[bmim]PF_6/CH_2Cl_2	72	49	90
7	3	[bdmim]PF_6/CH_2Cl_2	21	70	92
8	3	rec. [bdmim]PF_6/CH_2Cl_2	168	<5	n.d.
9	3	[bdmim]PF_6/THF	120	24	90
10	3	[bdmim]NTf_2/CH_2Cl_2	72	15	92
11	3	rec. [bdmim]NTf_2/CH_2Cl_2	72	15	92
12	4	[bdmim]NTf_2/CH_2Cl_2	168	47	91
13	4	rec. [bdmim]NTf_2/CH_2Cl_2	168	9	90
14	4	[bdmim]NTf_2/CH_2Cl_2 (1:4)	72	50	91
15	3	[Bu_3EtP]$(EtO)_2PO_2$/CH_2Cl_2	20	67	78
16	4	[emim]$EtOSO_3$/EtOAc	168	<5	88
17	3	[1-Bu-3-Me-pyr]PF_6	48	20	91

[a] Reaction was performed at 0 °C.
[b] 5 mol % of catalyst was used.
[c] Isolated yield of pure compound **6**.
[d] Determined by HPLC on Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min.

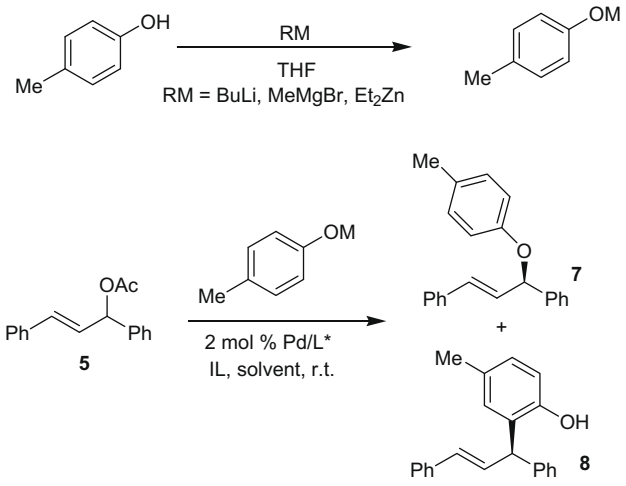
In order to minimize the amount of the base present in the reaction mixture, we tried to use phthalimide with bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc, a well known strategy for the generation of stabilized anions from active methylene compounds (Scheme 2, procedure b). Interestingly, the reaction proceeded well in some ionic liquids, such as [emim]$EtOSO_3$. Product **6** was isolated in up to 68% yield and 92% ee (Table 3, entries 1 and 5). However recycling was again difficult because this ionic liquid is miscible with water (Table 3, entry 3).

As a representative oxygen nucleophile, we chose 4-methylphenolate. Lithium alkoxide was generated from the corresponding alcohol and BuLi in THF. The resulting THF solution was added into the ionic liquid containing the Pd-complex of ligand **3** (Scheme 3). In [emim]$EtOSO_3$, compound **7** was formed in medium yields but with only 62% ee (Table 4, entry 2). Using [bdmim]NTf_2 as the reaction medium, the enantioselectivity decreased to 54% ee but partial recycling of catalytic system was possible (Table 4, entries 5 and 6). However catalytic activity as well as enantioselectivity decreased. We attempted to use BSA and KOAc for the generation of a better

Table 3
Ligand 3 in Pd-catalyzed allylic substitution with phthalimide, BSA, and KOAc

Entry	Solvent	Time (h)	Yield[a] (%)	ee[b] (%)
1	[emim]$EtOSO_3$/CH_2Cl_2	32	64	90
2	[bmim]PF_6/CH_2Cl_2	72	6	92
3	rec. [bmim]PF_6/CH_2Cl_2	168	5	92
4	[bmim]PF_6/CH_2Cl_2 (1:4)	120	7	92
5	[emim]$EtOSO_3$/CH_2Cl_2 (1:4)	48	68	91

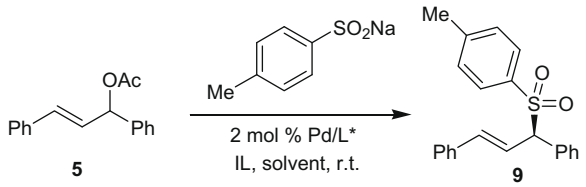
[a] Isolated yield of pure compound **6**.
[b] Determined by HPLC on Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min.



Scheme 3.

nucleophile from *p*-cresol but no product **7** was isolated (Table 4, entry 7). When phenolate was generated with MeMgBr instead of BuLi, a typical product of allylic substitution with phenolate, ether **7**, was only isolated as a minor component. The major product, compound **8**, resulted from Friedel–Craft alkylation of phenolate in position 2 by allyl cation (Table 4, entries 8 and 9). Compound **8**, however, was usually obtained with low enantioselectivity or as a racemate. Using Et_2Zn as a base product **7** was isolated in 35% yield but with no enantioselectivity. The results with *p*-cresol are summarized in Table 4.

With sodium *p*-tolylsulfinate as a nucleophile, product **9** can be obtained in good yield but with little (up to 29% ee) to no enantioselectivity (Scheme 4) (Table 5). Competitive complexation of the nucleophile to palladium could be a possible explanation for the small enantioselectivity. In an attempt to minimize this effect,



Scheme 4.

Table 5
Allylic substitution with sodium *p*-tolylsulfinate.

Entry	Solvent	Mol % of **3**	Time (h)	Yield[a] (%)	ee[b] (%)
1	[bmim]PF_6/CH_2Cl_2	2	24	53	15
2	[bmim]PF_6/CH_2Cl_2	3	20	81	10
3	rec. [bmim]PF_6/CH_2Cl_2	3	168	15	26
4	[emim]$EtOSO_3$/CH_2Cl_2	3	16	86	0
5	[bdmim]NTf_2/THF	2	24	33	29
6	[bmim]PF_6/CH_2Cl_2[c]	3	96	75	7

[a] Isolated yield of pure compound **9**.
[b] Determined by HPLC on Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min.
[c] $Pd_2dba_3.CHCl_3$ was used as palladium source.

we increased the ligand to palladium ratio from 1:1 to 1.5:1, however, the enantioselectivity of the reaction did not improve.

The NMR experiments confirmed that imidazolium diphosphane ligands form palladium complexes in ionic liquid. Figure 1 shows ^{31}P NMR of the free ligand **4** (a) and its Pd-complex in [bdmim]NTf_2 (b). The spectrum displays a typical shift from negative to positive chemical shift values, thus confirming complexation of both phosphorus atoms to palladium. NMR spectrum (c) of ionic liquid phase after reaction and extraction of product shows significant ligand decomposition.

Recycling experiments as well as NMR studies suggest that imidazolium-tagged ferrocenyl diphosphanes are sensitive under the reaction conditions of allylic substitution. Substitution of the hydrogen at the 2-position with a methyl group did not lead to significant improvement. This could be explained by the possible formation of C4-carbene under basic conditions.[14]

3. Conclusions

We have demonstrated that allylic substitution with heteroatom nucleophiles in ionic liquids can be conveniently performed. Allylation products with nitrogen and oxygen nucleophiles were formed with high enantioselectivities (up to 92% ee and 62% ee,

Table 4
Allylic substitution with 4-methylphenolate using ligand 3.

Entry	Base	Solvent	Time (h)	7[b,c] (yield/ee)	8[d,e] (yield/ee)
1[a]	BuLi	[emim]$EtOSO_3$/THF	24	79/50	-
2	BuLi	[emim]$EtOSO_3$/THF	43	41/62	-
3	BuLi	[bmim]PF_6/THF	18	46/46	37/34
4	BuLi	rec. [bmim]PF_6/THF	42	16/14	22/3
5	BuLi	[bmim]NTf_2/THF	43	43/54	-
6	BuLi	rec. [bmim]NTf_2/THF	72	25/24	-
7	BSA/KOAc	[emim]$EtOSO_3$/THF	168	0	0
8	MeMgBr	[bmim]PF_6/THF	18	12/0	74/2
9	MeMgBr	rec. [bmim]PF_6/THF	18	0	65/0
10	Et_2Zn	[bmim]NTf_2/THF	18	35/0	39/0

[a] BPPFA was used as a ligand.
[b] Isolated yield of pure compounds **7**.
[c] Enantiomeric excess determined by HPLC on Chiralcel OD-H column, hexane/*i*-PrOH, 98:2; 0.5 mL/min).
[d] Isolated yield of pure compounds **8**.
[e] Enantiomeric excess determined by HPLC on Chiralcel OD-H column, hexane/*i*-PrOH, 80:20; 0.75 mL/min)

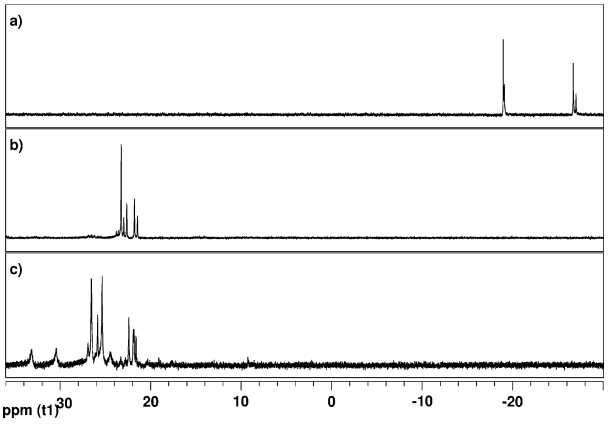


Figure 1. NMR spectra of free ligand **4** (a), its Pd-complex (b), and ionic liquid after reaction and work-up (c).

respectively). Magnesium alcoholate undergoes interesting Friedel–Crafts alkylation with allyl cation. The efficient recycling of the catalytic system is a challenging task, presumably due to the decomposition of the catalyst in the inherently basic conditions present. However further work in this area is currently underway in our laboratory.

4. Experimental

4.1. General

All reactions were carried out under an inert atmosphere of N_2. The solvents were purified by standard methods. Ionic liquids were purchased from Merck. NMR spectra were recorded on Varian Mercury plus instrument (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.5 MHz for ^{31}P). Chemical shifts (δ) are given in ppm relative to tetramethylsilane for ^{1}H NMR; to residual solvent peak for ^{13}C NMR and to H_3PO_4 as external standard for ^{31}P NMR. Specific rotations were measured on Perkin–Elmer instrument and are given in deg cm^{-3} g^{-1} dm^{-1}. Flash chromatography was performed on Merck Silica Gel 60. Thin-layer chromatography was performed on Merck TLC-plates Silica Gel 60, F-254. Enantiomeric excesses were determined by HPLC on Chiralpak AD-H (Daicel Chemical Industries) column using hexane/*i*PrOH = 9:1 as a mobile phase and detection with UV-detector at 254 nm. Mass spectrum was recorded on Waters Premium QTOF instrument. Compound **2** was prepared according to the literature procedure.[10] The absolute configuration of compound **6** was assigned by comparison of the sign of the specific rotation with the literature values. Configurations of compound **7**, **8,** and **9** were assigned in analogy to compound **6**.

4.2. Preparation of ligand 4

Compound **2** (355 mg, 0.450 mmol) and 1,2-dimethylimidazole (1.08 g, 11.2 mmol) were dissolved in CH_2Cl_2 and the solution was concentrated. The residue was subjected to microwave irradiation (6 × 10 s, 300 W) and (2 × 10 s, 500 W). After cooling, the resulting mixture was washed with *t*-BuOMe (5 × 5 mL). The oily residue was dissolved in MeOH (10 mL), the solution was filtered through Celite, and the filtrate was concentrated. The crude product was dissolved in degassed deionized H_2O (30 mL) and MeOH (0.5 mL). Into this solution, $LiNTf_2$ (194 mg, 0.675 mmol) in H_2O (5 mL) was added and the resulting mixture was stirred for 5 h at rt. The pale yellow precipitate was filtered off and washed with H_2O (100 mL). Purification of the crude product by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) afforded pure ligand **4** (387 mg, 79%) as a yellow solid. Mp 71–74 °C. ^{1}H NMR (300 MHz, $CDCl_3$): (peaks of minor amide rotamer shown in italics) δ 1.04–1.20 (m, 2H, CH_2), 1.31 (d, J = 6.9 Hz, 3H CH_3), 1.32–1.47 (m, 2H, CH_2), 1.48–1.64 (m, 2H, CH_2), 1.65–1.84 (m, 2H, CH_2), 2.14, *2.19* (s, 3H, N–CH_3), 2.58, *2.63* (s, 3H, Im–CH_3), 3.59 (m, 1H), 3.62 (m, 1H), 3.79, *3.82* (s, 3H, Im–CH_3), 4.03 (m, 2H, CH_2); 4.14 (m, 3H, Fc), 4.45 (m, 1H, Fc), 4.50 (m, 1H, Fc), 5.23, *6.01* (dd, J = 13.4, 7.0 Hz, 1H, FcCH), 7.00–7.12 (m, 2H, Ph), 7.13–7.35 (m, 18H, Ph + Im), 7.36–7.48 (m, 2H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): (peaks of minor amide rotamer shown in italics) δ 170.7, *170.6* (CO), *143.8*, 143.7 (qC), 139.0 (d, J = 8.4 Hz), 138.3 (d, J = 9.0 Hz), 136.6 (d, J = 8.1 Hz), 135.0, 134.9 (d, J = 21.4 Hz), 133.63, *133.61* (d, J = 20.0 Hz), *133.1*, 133.0 (d, J = 19.1 Hz), 132.4 (d, J = 19.6 Hz), *131.9*, 128.9 (d, J = 32.0 Hz), 128.2 (d, J = 42.2 Hz), *128,16*, 128.15 (d, J = 15.8 Hz), 128.09 (d, J = 15.8 Hz), 122,4, 122.0, 121.0, *120.9* (Ph, Im), 94.1, *93.7* (d, J = 25.5 Hz, C_{Fc}), 77.2 (CH_{Fc}), 76.8 (d, J = 9.2 Hz), 75.5, *75.4* (d, J = 19.7 Hz), 74.5 (dd, J = 4.5, 1.8 Hz, CH_{Fc}); 73.4, 73.2 (d, J = 4.8 Hz, C_{Fc}), 73.1, 72.4 (d, J = 4.6 Hz, CH_{Fc}), 71.2 (d, J = 2.4 Hz, CH_{Fc}), 48.5, *48.4* (CH_2), 35.4, *35.37* (CH_3), 32.1 (CH_2), *29.7*, 29.3 (CH_2), 28.6 (CH_3), *25.8*, 25.7 (CH_2), *23.5*, 23.3 (CH_2), 15.9, *15.6* (CH_3), 9.7, *9.66* (CH_3). ^{31}P NMR (121 MHz, $CDCl_3$): δ −17.9, −18.2; −26.9, −27.0. $[\alpha]_D$ = −212 (*c* 0.51, $CHCl_3$). HRMS calcd for $C_{48}H_{52}FeN_3OP_2$: 804.2930; found: 804.2842.

4.3. (*R*)-(*E*)-2-(1,3-Diphenylprop-1-enyl)isoindolin-1,3-dione 6

4.3.1. Procedure a

Ligand (0.02 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.01 mmol) were dissolved in degassed ionic liquid (2 mL), and the resulting solution was stirred for 30 min at rt. Then acetate **5** (252 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) was added to this solution and the mixture was stirred for additional 15 min at rt. Solid potassium phthalimide (371 mg, 2 mmol) was added and the reaction mixture was stirred. The reaction was monitored by TLC and stopped when no starting material was detected or after the selected time. The mixture was then washed with water (3 × 10 mL). The reaction product was extracted with small portions of toluene and the combined organic extracts were concentrated. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc, 8:1).

4.3.2. Procedure b

The ligand (0.02 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.01 mmol) were dissolved in an ionic liquid (2 mL), and the resulting solution was stirred for 30 min at room temperature. Acetate **5** (252 mg, 1.0 mmol) in an appropriate solvent (2 mL) was added to this solution and the resulting solution was stirred for additional 15 min at room temperature. Then phthalimide (294 mg, 2 mmol), BSA (0.49 mL, 407 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 the selected time. The mixture was then washed with water (3 × 10 mL) and the product was extracted with toluene. The combined organic extracts were concentrated and the crude product was purified by column chromatography (SiO_2; hexane/EtOAc 8:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.13 (d, J = 8.6 Hz, 1H, CH), 6.72 (d, J = 15.9 Hz, 1H, CH), 7.07 (dd, J = 15.9, 8.6 Hz, CH), 7.20–7.39 (m, 6H, Ph), 7.40–7.53 (m, 4H, Ph), 7.67–7.75 (m, 2H, Ph-Phtal), 7.80–7.89 (m, 2H, Ph-Phtal). NMR data are in agreement with the literature.[15] $[\alpha]_D$ = −20 (*c* 1.7, $CHCl_3$); Lit.[16] $[\alpha]_D$ = −17 (*c* 1.7, $CHCl_3$). HPLC (Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min): t_R(minor) 11.8 min, t_R(major) 14.5 min.

4.4. (*E*)-3-(4-Methylphenyloxy)-1,3-diphenylprop-1-ene 7

Ligand **2** (0.02 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.01 mmol) were dissolved in an ionic liquid (2 mL), and the resulting solution

was stirred for 30 min at rt. Acetate **5** (252 mg, 1.0 mmol) was added to this solution and the resulting mixture was stirred for additional 15 min at rt. Into a THF (2 mL) solution of 4-methylphenol (324 mg, 3 mmol), cooled to 0 °C in an ice-bath, BuLi was added dropwise (1.6 M in hexane, 0.75 mL, 1.2 mmol); alternatively MeMgBr (3 M in Et_2O) or Et_2Zn (1 M in toluene) was used). This solution was stirred for 15 min and then added via syringe pump to the reaction mixture over 3 h. The reaction was monitored by TLC and stopped when no starting material was detected or after the selected time. The product was extracted with toluene and the combined extracts were concentrated. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 8:1) to give ether **7** and alcohol **8**.

Compound **7**: mp 66–67.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 5.75 (d, J = 6.4 Hz, 1H, CH), 6.43 (dd, J_1 = 15.9 Hz, J_2 = 6.4 Hz, 1H, CH), 6.66 (d, J = 15.9 Hz, 1H, CH), 6.83–6.91 (m, 2H, Ph-cresol), 6.99–7.07 (m, 2H, Ph-cresol), 7.18–7.50 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (CH_3), 80.9 (CH-O), 116.1 (CH), 126.6 (CH), 127.79 (CH), 127.82 (CH), 129.4 (CH), 129.8 (CH), 130.3(qC), 131.4 (CH), 136.4 (qC), 140.5 (qC), 155.7 (qC). $[\alpha]_D = -24.6$ (c 1.0, $CHCl_3$, 48% ee). Anal. Calcd for $C_{22}H_{20}0$: C 87.97, H 6.71. Found: C 88.14, H 6.70. HPLC (Chiralcel OD-H column, hexane/*i*-PrOH, 98:2; 0.5 mL/min): t_R = 7.6, t_R = 8.0 min.

Compound **8**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 4.75 (s, 1H, OH), 5.09 (d, J = 7.1 Hz, 1H, CH), 6.35 (dd, J = 15.9, 1.0 Hz, 1H), 6.69 (dd, J = 14.3, 7.1 Hz, 1H), 6.72 (d, J = 7.2 Hz, 1H, Ph), 6.95 (m, 2H, Ph), 7.45–7.17 (m, 10H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7 (CH_3), 48.6 (CH), 116.3 (CH), 126.4 (CH), 126.8 (CH), 127.4 (CH), 128.5 (CH), 128.52 (CH), 128.6 (CH), 128.7 (CH), 129.1 (qC), 130.20 (CH), 130.22 (qC), 131.3 (CH), 131.8 (CH), 137.1 (qC), 142.1 (qC), 151.2 (qC). $[\alpha]_D$ = +1.4 (*c* 1.1, $CHCl_3$, 34% ee). HPLC (Chiralcel OD-H column, hexane/*i*-PrOH, 80:20; 0.75 mL/min): t_R = 8.1 min, t_R = 10.7 min.

4.5. (*E*)-3-(4-Methylphenyl)sulfonyl-1,3-diphenylprop-1-ene 9

Ligand **2** (0.01 mmol) and $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol) were dissolved in ionic liquid (2 mL), and the resulting solution was stirred for 30 min at rt. Acetate **5** (126 mg, 0.5 mmol) in organic solvent (2 mL) was added to this solution and the resulting mixture was stirred for additional 15 min at rt. Then sodium tolylsulphinate (178 mg, 1 mmol) was added, and the resulting mixture was stirred at rt. in nitrogen atmosphere. The reaction was monitored by TLC and stopped when no starting material was detected or after the selected time. The mixture was then washed with water (3 × 3 mL), the product was extracted with toluene, and the combined organic extracts were concentrated. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc, 8:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 1H, CH_3), 4.81 (dd, J = 7.3, 0.8 Hz, 1H, CH), 6.66–6.45 (m, 2H, CH), 7.16–7.23 (m, 2H, Ph), 7.27–7.39 (m, 10H, Ph), 7.60–7.42 (m, 2H, Ph). NMR data are in agreement with the literature.[17] $[\alpha]_D$ = +2.6 (*c* 1.0, $CHCl_3$, 29% ee). HPLC (Chiralcel OD-H, hexane/*i*-PrOH, 90:10; 0.75 mL/min): t_R = 24.5, t_R = 29.9 min.

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References

1. (a) Helmchen, G.; Ernst, M.; Paradies, G. *Pure Appl. Chem.* **2004**, *76*, 495–506; (b) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2943; (c) Pfaltz, A.; Lautens, M.. In *Comprehensive Asymmetric Catalysis I–III*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 2, pp 833–884.
2. Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258–297.
3. (a) Blaser, H.-U.; Chen, W.; Camponovo, F.; Togni, A.. In Štepnička, P., Ed.; Ferrocenes: Ligands, Materials and Biomolecules; Wiley: Chichester, 2008; pp 205–235; (b) Arrayas, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674–7715; (c) Hou, X. L.; You, S. L.; Tu, T.; Deng, W. P.; Wu, X. W.; Li, M.; Yuan, K.; Zhang, T. Z.; Dai, L. X. *Top. Catal.* **2005**, *35*, 87; (d) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131–2150; (e) Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.* **2004**, *33*, 313–328; (f) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101–3118; (g) Dai, L. X.; Tu, T.; You, S. L.; Deng, W. P.; Hou, X. L. *Acc. Chem. Res.* **2003**, *36*, 659–667; (h) Sutcliffe, O. B.; Bryce, M. R. *Tetrahedron: Asymmetry* **2003**, *14*, 2297–2325.
4. (a) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732–4762; (b) Corma, A.; Garcia, H. *Adv. Synth. Catal.* **2006**, *348*, 1391–1412; (c) Lemaire, M. *Pure Appl. Chem.* **2004**, *76*, 679–688; (d) Blaser, H.-U.; Studer, M.. In *Comprehensive Asymmetric Catalysis I–III*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 3, pp 1353–1363.
5. (a) Fache, F. *New J. Chem.* **2004**, *28*, 1277–1283; (b) Nakamura, Y.; Takeuchi, S.; Ohgo, Y. *J. Fluor. Chem.* **2003**, *120*, 121–129; (c) Bergbreiter, D. E.; Sung, S. D. *Adv. Synth. Catal.* **2006**, *348*, 1352–1366.
6. (a) Šebesta, R.; Kmentová, I.; Toma, Š. *Green Chem.* **2008**, *10*, 484–496; (b) Miao, W.; Chan, T. H. *Acc. Chem. Res.* **2006**, *39*, 897–908; (c) Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50–56.
7. (a) Uozumi, Y. *Pure Appl. Chem.* **2007**, *79*, 1481–1489; (b) Martín-Matute, B.; Pereira, S. I.; Peña-Cabrera, E.; Adrio, J.; Silva, A. M. S.; Carretero, J. C. *Adv. Synth. Catal.* **2007**, *349*, 1714–1724; (c) Uozumi, Y.; Suzuka, T. *J. Org. Chem.* **2006**, *71*, 8644–8646; (d) Trost, B. M.; Pan, Z.; Zambrano, J.; Kujat, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4691–4693; (e) Hallman, K.; Macedo, E.; Nordström, K.; Moberg, C. *Tetrahedron: Asymmetry* **1999**, *10*, 4037–4046.
8. (a) Bandini, M.; Benaglia, M.; Quinto, T.; Tommasi, S.; Umani-Ronchi, A. *Adv. Synth. Catal.* **2006**, *348*, 1521–1527; (b) Zhao, D.; Sun, J.; Ding, K. *Chem. Eur. J.* **2004**, *10*, 5952–5963.
9. Gavrilov, K. N.; Lyubimov, S. E.; Bondarev, O. G.; Maksimova, M. G.; Zheglov, S. V.; Petrovskii, P. V.; Davankov, V. A.; Reetz, M. T. *Adv. Synth. Catal.* **2007**, *349*, 609–616.
10. Šebesta, R.; Mečiarová, M.; Poláčková, V.; Veverková, E.; Kmentová, I.; Gajdošiková, E.; Cvengroš, J.; Buffa, R.; Gajda, V. *Collect. Czech. Chem. Commun.* **2007**, *72*, 1057–1068.
11. Feng, X.; Pugin, B.; Küsters, E.; Sedelmeier, G.; Blaser, H.-U. *Adv. Synth. Catal.* **2007**, *349*, 1803–1807.
12. Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138–1151.
13. Sato, Y.; Yoshino, T.; Mori, M. *Org. Lett.* **2003**, *5*, 31–33.
14. Albrecht, M. *Chem. Commun.* **2008**, 3601–3610.
15. Mancheno, O. G.; Priego, J.; Cabrera, S.; Arrayas, R. G.; Llamas, T.; Carretero, J. C. *J. Org. Chem.* **2003**, *68*, 3679–3686.
16. Sudo, A.; Saigo, K. *J. Org. Chem.* **1997**, *62*, 5508–5513.
17. Felpin, F.-X.; Landais, Y. *J. Org. Chem.* **2005**, *70*, 6441–6446.