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Expanding the scope of atropisomeric monodentate P-donor ligands in asymmetric catalysis. Asymmetric allylic alkylation of 1,3-diphenylpropenyl-1-esters by Pd/BINEPINE catalysts

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Dedicated to Professor Henri Kagan for his seminal contribution in establishing fundamental concepts of enantioselective catalysis

ABSTRACT

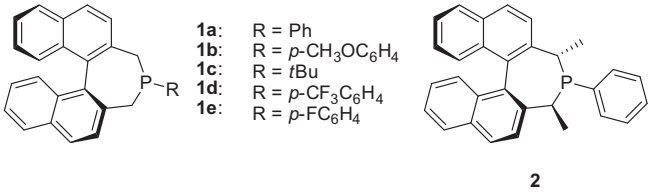
Monodentate binaphthophosphepines (BINEPINES) have been tested in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylallyl esters. Stereoselectivities of up to 92% ee have been achieved in the alkylation of the acetate ester with the *C*-nucleophile, generated in situ by the action of BSA (*N*,*O*-bis(trimethylsilyl)acetamide) on dimethylmalonate in the presence of a catalytic amount of sodium acetate.

1. Introduction

The last 10 years have witnessed the successful application of diverse monodentate phosphorus ligands to several catalytic- and organocatalytic reactions. This marked the renaissance of this class of chiral inducers against the established belief that only bidentate diphosphines could be properly suited for asymmetric catalysis. This event, anticipated by Kagan in a seminal paper,[1] was the result of the efforts of several groups which independently were pursuing this goal at the same time. Thus, in a short time, a range of monodentate phosphorus ligands capable of providing excellent enantioselectivities in a variety of metal-catalyzed reactions have appeared in the literature. Chronologically, the first entry in this family of highly efficient monodentate ligands was a phospholane derivative reported by Fiaud.[2] The real breakthrough in the field, however, was achieved in 2000 when almost simultaneously three independent groups pointed out the exceptional stereoselective ability displayed in the Rh-catalyzed asymmetric hydrogenation of α-acyldehydroaminoacid derivatives by the phosphites[3] phosphonites[4] and phosphoramidites of binaphthol.[5]

Following the early contributions of one of us (S.G.)[6] and parallel to the work of Zhang,[7] in recent years we have focussed our efforts in this field on a class of phosphines based on the 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphepine structure (nicknamed BINEPINES, Scheme 1).[8]

BINEPINES share some common features with the binaphthol derivatives mentioned above: they possess an endocyclic P-donor



Scheme 1. Structure of the phosphepine ligands tested in this study.

inserted in a seven-membered ring embedded in the C_2-symmetrical environment created by the naphthalene template and feature a stereogenic axis as the unique chiral element. Due to the absence of *P*-heteroatom bonds (heteroatom = *O*, *N*) BINEPINES are expected to have a comparably lower π-acidity and a higher σ-donating propensity than their binaphthol counterparts.

The ability of BINEPINES to enable high stereoselectivities in a variety of asymmetric reactions catalyzed by a range of different transition metals has been demonstrated in a set of recent papers and has been reviewed recently.[9] To the best of our knowledge, however, no application of these ligands to asymmetric allylic alkylation has been reported so far. This reaction constitutes a powerful synthetic tool for the formation of new bonds.[10] The reaction typically involves the metal-promoted ionization of a properly substituted unsaturated substrate followed by addition of a suitable nucleophile on the resulting π-allyl metal complex. The versatility of this catalytic process lies in the possibility of creating C–H, C–N, C–O and C–C bonds relying on different metals such as Pd, but also Rh, Ru, Ir, Mo and Cu as catalysts. This allows the reaction to be adjusted to a large variety of diverse synthetic targets. Informed by

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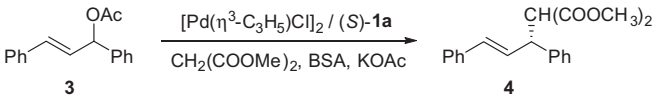
the principles of ligand rational design,[11] several classes of bidentate ligands have been synthesized and successfully applied to asymmetric allylic alkylation.[10e,12] The potential of monodentate phosphorus donor ligands, however, appears to be poorly explored, despite a few excellent results.[13] Of specific relevance to the present study is the case of binaphthalene-templated monodentate phosphorus ligands. Phosphoramidites and phosphites have been applied to asymmetric allylic alkylation promoted by diverse metals achieving, in some cases, very high selectivities.[14] For instance, allylic alkylation of 1,3-diphenylprop-2-enyl-1-acetate with dimethylmalonate in the presence of a cationic complex of palladium modified with an axially chiral phosphoramidite afforded the product in quantitative yield and 90% ee.[14c] Phosphoramidites of bulky secondary chiral amines induced enantioselectivities higher than 90% in the iridium-catalyzed allylic alkylations of unsymmetrically substituted allylic acetates[14i] and in the copper-catalyzed asymmetric allylic alkylation of cyclohex-1-enyl-3-bromide with primary alkyl Grignard reagents.[14h] Herein we report on the utility of BINEPINES in the Pd-catalyzed process.

2. Results and discussion

At the start of our work, Ph-BINEPINE, the parent compound of this class of ligands, was tested in the asymmetric palladium-catalyzed alkylation of 1,3-diphenylprop-2-enyl-1-acetate (*rac*-**3**) with the *C*-nucleophile, generated by action of an organic base BSA (*N*,*O*-bis(trimethylsilyl)acetamide) on dimethylmalonate in the presence of a catalytic amount of sodium acetate (Scheme 2). The active catalyst was generated in situ from $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and an appropriate amount of the chiral ligand.



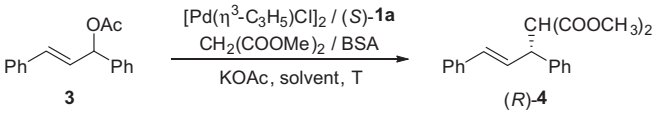
Scheme 2.

As the results reported in Table 1 show, the rate and selectivity of the reaction turned out to be strongly dependent on the solvent and for a complete conversion to be achieved quite different reaction times were required. Oxygenated solvents (Table 1, entries 4–12) performed far better than chlorinated ones (Table 1, entries 1 and 2) and simple hydrocarbons (Table 1, entry 3). Among them, THF and dioxane were the most effective, in terms of both activity and selectivity. These solvents were then chosen to explore the temperature influence on selectivity. As it frequently occurs, a decrease of the temperature was accompanied by an increase of enantioselectivity (Table 1, compare entries 6 and 8, entries 11 and 12). Unfortunately below 0 °C the reactions become sluggish, beyond any practical application (Table 1, entry 10). The best ee was achieved in dioxane at 0 °C (Table 1, entry 12). Under these conditions, the substrate was fully converted in 5 h to afford the product in 86% ee.

Decreasing the substrate concentration from 0.133 M to 0.0133 M had a slightly positive effect on the selectivity but at the expense of a decrease in the rate (Table 1, entries 6 and 7).

To gain insight into the coordination mode of Binepine during the catalytic reaction, the dependence of enantioselectivity on the ligand-to-palladium ratio was checked (Table 2). In the presence of an equimolar amount of chiral ligand, the enantioselectivity recorded in THF dropped dramatically compared to the one obtained when employing a L/Pd of 2 (Table 2, entries 1 and 2). A further increase of the relative amount of ligand to 4:1 brought about only a modest gain of selectivity regardless of the solvent used, either THF or dioxane (Table 2, entries 2 and 3, entries 5 and 6). Based on these results and although no investigation into non-linear effects was performed,[15] it can be confidently assumed that the active catalyst contains two molecules of BINEPINE coordinated to palladium. This assumption was confirmed by the results obtained when using a hetero-combinations of ligands (vide infra).

Table 1
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate in the presence of in situ-generated Pd/(*S*)-Ph-Binepine[a]: Effect of solvent, temperature and concentration



Entry	Solvent	Temp (°C)	Time	Conv. (%)	ee[b] (%)
1	$CHCl_3$	30	4 h	>99	27
2	CH_2Cl_2	30	12 min	>99	30
3	Toluene	15	18 h	>99	30
4	$(CH_3OCH_2)_2$	30	2 h	>99	48
5	Acetone	25	16 h	60	48
6	THF	30	10 min	>99	74
7	THF[c]	30	20 min	>99	81
8	THF	0	1 h	>99	80
9	THF	−10	10 h	77	80
10	THF	−30	16 h	nd	—
11	Dioxane	30	10 min	>99	75
12	Dioxane	0	5 h	>99	86

[a] General experimental conditions $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ 0.01 mmol, (*S*)-**1a** 0.04 mmol, substrate 0.4 mmol, dimethyl malonate 1.2 mmol, BSA 1.2 mmol, KOAc 0.012 mmol, [1,3-diphenylprop-2-enyl acetate] = 0.133 M.
[b] All experiments provided (*R*)-dimethyl[1,3-diphenylprop-2-enyl]malonate.
[c] [1,3-diphenylprop-2-enyl acetate] = 0.0133 M.

Table 2
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate in the presence of in situ-generated Pd/(*S*)-**1a**: Effect of L/Pd ratio[a]

Entry	Solvent	L/Pd	ee[b] (%)
1	THF	1	10
2	THF	2	74
3	THF	4	76
5	Dioxane	2	75
6	Dioxane	4	78

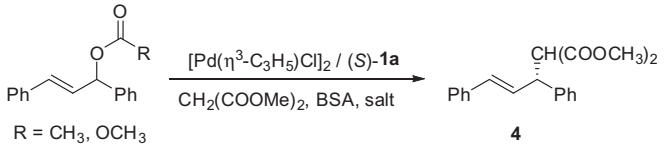
[a] General experimental conditions $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ 0.01 mmol, substrate 0.4 mmol, dimethyl malonate 1.2 mmol, BSA 1.2 mmol, KOAc 0.012 mmol, [1,3-diphenylprop-2-enyl acetate] = 0.133 M, room temperature.
[b] All experiments provided (*R*)-dimethyl[1,3-diphenylprop-2-enyl]malonate.

The stereoselectivity was not affected by the leaving ability of the ionizable group of the substrate as almost identical ees were obtained for the acetate (R = Me) and the carbonate (R = OMe) esters (Table 3, entries 1 and 2).

Since the nucleophile is directly involved in the enantiodiscriminating step of the process, its structure is expected to affect the ee.[16] As Table 3 shows, by changing the ion pair through the use of different acetate salts, a dramatic variation in the selectivity as well as in the activity was observed. The best result of this set (74% ee) was obtained with CH_3COOK (Table 3, entry 1). The selectivity was reduced to 68% ee (Table 3, entry 3) with CH_3COOCs and dropped dramatically with CH_3COOLi (Table 3, entry 4). In the latter case, the cation effect was so pronounced as to cause a switch of handedness from the (*R*)- to (*S*)-configured product. Surprisingly, no conversion was observed in the presence of CH_3COONa even after a prolonged reaction time (Table 3, entry 5).

A representative selection of the available members of the BINEPINE ligand library, featuring alkyl (Scheme 1, **1c**) and substituted aryl groups (Scheme 1, **1b**, **1d**, **1e**) onto the phosphorus

Table 3
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate in the presence of in situ-generated Pd/(*S*)-Ph-Binepine: Effect of leaving group and of the cation[a]



Entry	Leaving group RCOO⁻	Salt	Time	Conv. (%)	ee (%)	Configuration
1	AcO^-	KOAc	10 min	>99	74	(*R*)
2	$MeOCO_2^-$	KOAc	15 h	>99	73	(*R*)
3	AcO^-	CsOAc	10 min	>99	68	(*R*)
4	AcO^-	LiOAc	5 min	>99	8	(*S*)
5	AcO^-	NaOAc	48 h	nd	—	

[a] General experimental conditions $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ 0.01 mmol, **(*S*)-1a** 0.04 mmol, substrate 0.4 mmol, Dimethyl malonate 1.2 mmol, BSA 1.2 mmol, salt 0.012 mmol, [1,3-diphenylprop-2-enyl acetate] = 0.133 M, THF, room temperature.

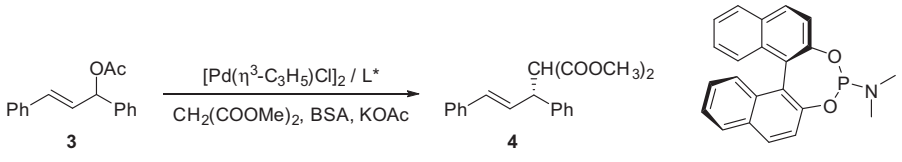
donor and including an α,α′-alkylated phosphepine (Scheme 1, **2**) were tested in the allylic alkylation of 1,3-diphenylprop-2-en-1-acetate.

Furthermore, Monophos® (Table 4, **5**), a phosphoramidite ligand based on the binaphthol scaffold, was as well included in the screening because it was interesting to compare the influence of a ligand of higher π-acidity than BINEPINE on the efficiency of the reaction.

The results are reported in Table 4. The catalytic performances (activity and selectivity) of the reaction were highly affected by the substituent on phosphorus and on the benzylic carbons adjacent to phosphorus. In comparison with Ph-BINEPINE (*S*)-**1a**, ligand (*S*)-**1b**, featuring a more electron-donating *p*-anisyl substituent on phosphorus, gave higher stereoselectivities (Table 4, compare entries 2–4 and 3–5). The highest ee among the ligands screened in this investigation was achieved by (*S*)-**1b** at 0 °C (92% ee; Table 4, entry 2). For the other derivatives, different reaction conditions were to be assessed for the best result to be obtained with each ligand. The introduction of electron-withdrawing groups on the P-phenyl substituent, as in the case of the fluoroaryl derivatives (*S*)-**1d** and (*S*)-**1e**, led to a decrease in stereoselectivity (Table 4, entries 9 and 10). Interestingly, in the case of the *tert*-butyl-substituted ligand (*S*)-**1c** a stereoreversion of the reaction was noticed and the handedness of the prevailing enantiomer was opposite as compared to the general trend (Table 4, entry 7). Such a behaviour is not a novelty for this ligand as it was previously noticed also in the Rh-catalyzed asymmetric hydrogenations.[8c,e,17] Ligand (*S,S,S*)-**2** is prepared via a deprotonation–alkylation protocol of the oxygen-[8e] or sulfur-protected Ph-BINEPINE.[18] The reaction is completely stereoselective and only the (*S,S,S*)-dialkylated diastereomer is obtained from the (*S*)-configured starting product. Much at our surprise, when this ligand was applied to the Pd-promoted allylic alkylation, the resulting product was racemic (Table 4, entry 11) thus suggesting that the stereogenic elements of the ligand operate in an antagonist mode in this reaction. A modest selectivity was achieved with the phosphoramidite Monophos (*R*)-**5** (Table 4, entry 12). In this case the absolute configuration of the prevailing enantiomer is the same as that of the one obtained with the phosphepine ligands (with the exception of ligand (*S*)-**1c**) of like configuration.[19]

One advantage inherent with monodentate ligands resides in the possibility of preparing mixed-ligand complexes. Recently, it has been shown that the combination of two different monodentate P-donor ligands, either both chiral or one chiral and the other achiral, may in some cases afford a more stereoselective and/or more active catalyst.[20] This strategy has been exploited with success in the Rh-catalyzed asymmetric hydrogenation using various combinations of phosphines, phosphites, phosphinites and phosphoramidites. This 'mixed-ligand approach' may change the outcome of a reaction when at least two monodentate ligands are bound to the metal of the active catalyst in the transition state. We have exploited this strategy by screening four binary combinations, three made up each by Ph-BINEPINE **1a** and one different chiral ligand, the fourth one by Ph-BINEPINE and PPh_3. If the catalyst resulting from a heterocombination of ligands is more active than the one containing two identical monophosphines, the electronic disparity of the two ligands might positively impact on the stereoselectivity of the reaction. Actually the nucleophilic attack

Table 4
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate in the presence of in situ-generated Pd/(S)-chiral ligand: Screening of different ligands[a]



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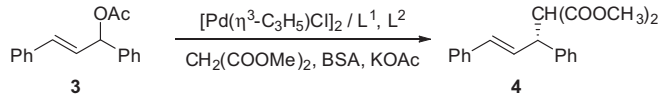
Entry	Ligand (L*)	Solvent	L/Pd	Temp (°C)	Time	Conv. (%)	ee (%)	Configuration
1	**(*S*)-1a**	Dioxane	2	0	5 h	>99	86	(*R*)
2	**(*S*)-1a**	Dioxane	2	25	10 min	>99	75	(*R*)
3	**(*S*)-1a**	Dioxane	4	25	10 min	>99	78	(*R*)
4	**(*S*)-1b**	Dioxane	2	25	40 min	>99	90	(*R*)
5	**(*S*)-1b**	Dioxane	4	25	15 min	>99	90	(*R*)
6	**(*S*)-1b**	Dioxane	4	0	3.2 h	>99	92	(*R*)
7	**(*S*)-1c**	Dioxane	2	25	20 h	0	—	—
8	**(*S*)-1c**	DCM	4	25	24 h	60	18	(*S*)
9	**(*S*)-1d**	DCM	2	25	20 h	70	12	(*R*)
10	**(*S*)-1e**[b]	DCM	2	25	15 min	>99	54	(*R*)
11	**(*S,S,S*)-2**	THF	2	25	1 h	>99	*rac*	
12	**(*R*)-5**	DCM	2	25	15 min	>99	25	(*S*)

[a] General experimental conditions $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ 0.01 mmol, substrate 0.4 mmol, Dimethyl malonate 1.2 mmol, BSA 1.2 mmol, KOAc 0.012 mmol, [1,3-diphenylprop-2-enyl acetate] = 0.133 M.

[b] Ligand (*S*)-**1e** is about 75% pure, the rest being unknown P-containing impurities.

Table 5
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate in the presence of in situ generated: mixed-ligand Pd catalysts[a] (see text)



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Entry	L^1	L^2	L^1/L^2/Pd ratio	Time	ee (%)	Configuration
1[b]	(*S*)-**1a**	—	2/—/1	12 min	30	(*R*)
2[b]	—	(*S*)-**1c**	—/2/1	24 h[c]	18	(*S*)
3[b]	(*S*)-**1a**	(*S*)-**1c**	2/2/1	15 min	18	(*R*)
4	(*S*)-**1a**	—	2/—/1	10 min	74	(*R*)
5	—	(*S*)-**1c**	—/2/1	36 h[d]	—	—
6	(*S*)-**1a**	(*S*)-**1c**	2/2/1	10 min	74	(*R*)
7	(*S*)-**1a**	(*S*)-**1c**	1/1/1	15 min	78	(*R*)
8	—	(*S*)-**1b**	—/2/1	2 h	82	(*R*)
9	(*S*)-**1a**	(*S*)-**1b**	1/1/1	5 min	81	(*R*)
10	(*R*)-**1a**	(*S*)-**1b**	1/1/1	45 min	56	(*R*)
11	—	(*R*)-**5**	—/2/1	1 h 10 min	23	(*S*)
12	(*S*)-**1a**	(*R*)-**5**	1/1/1	30 min	26	(*S*)
13	(*R*)-**1a**	(*R*)-**5**	1/1/1	1 h 30 min	81	(*S*)
14	(*R*)-**1a**	PPh_3	1/1/1	55 min	29	(*S*)

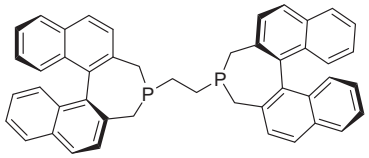
[a] General experimental conditions $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ 0.01 mmol, substrate 0.4 mmol, dimethyl malonate 1.2 mmol, BSA 1.2 mmol, KOAc 0.012 mmol, [1,3-diphenylprop-2-enyl acetate] = 0.133 M, THF, room temperature.
[b] Reactions performed in CH_2Cl_2.
[c] 60% conversion.
[d] No conversion.

is expected to proceed preferentially *trans* to the ligand with the higher *trans* influence, because of the higher electrophilicity of the corresponding π-allyl *terminus*.

The results of the catalytic reactions performed with these hetero-combinations of ligands are presented in Table 5. For ease of comparison, the results obtained with the homocombinations under otherwise identical experimental conditions are reported as well. No clear evidence of the involvement of a hetero-complex was noticed in the case of the combination **1a/1c**, even if a modest improvement of the selectivity (78% vs 74%) was recorded at 1/1/1 ratio (Table 5, entry 7). The decrease in rate and selectivity observed with the combination (*R*)-**1a**/(*S*)-**1b** (Table 5, entry 10) indicates that the relevant hetero-complex can have a significant albeit detrimental role in the catalytic process. This seems to occur only when the two ligands have opposite configuration. The results observed when Ph-BINEPINE **1a** is used in combination with Monophos **5** or with PPh_3 provide strong evidence that in both cases the hetero-complex is the main player in the catalytic reaction.

In the case of Monophos this is true whatever the relative configuration of the two ligands. The unlike pair (*S*)-**1a**/(*R*)-**5** is the more active of the two but is poorly selective (Table 5, entry 12). The like pair (*R*)-**1a**/(*R*)-**5** is more stereoselective providing a quantitative conversion in 1,5 h with 81% ee (Table 5, entry 13). Notably, this value is definitely higher than the one obtained with (*R*)-**1a** alone (74% ee). On the contrary, the catalyst arising from the hetero-combination (*R*)-**1a**/PPh_3 is by far less active and stereoselective than the one with (*R*)-**1a** alone.

Several attempts aimed at intercepting the BINEPINE containing Pd/1,3-diphenylallyl complex, the putative intermediate of the reaction, have been performed but all were inconclusive. This failure does not allow to draw any sound conclusion on the origin of the stereoselectivity in the alkylation step. Anyway, it is worth of note that when two binepine fragments are linked together to build up a C_2-symmetric bidentate ligand such as (*S*,*S*)-**7** (Fig. 1) the alkylated product which is obtained in even higher ee shows the opposite configuration.[21] This indicates that the substituent



(*S*,*S*)-7

Figure 1.

at the P-atom plays a fundamental role in addressing the stereochemistry of this reaction. A confirmation of this fact comes from the inversion of handedness observed with the *t*-butyl-substituted BINEPINE **3a** as compared to the aryl-substituted counterparts.

3. Conclusions

By proper choice of reaction conditions and substituent onto the phosphorus, stereoselectivities up to 92% have been achieved in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl-1-acetate with palladium complexes modified by monodentate BINEPINES. Only a small number of the derivatives pertaining to this library of ligands have been screened and the potential of BINEPINES as chiral modifiers for this reaction is far from being completely assessed. The conditions have been highlighted for a combinatorial approach to be performed. This could be advantageously exploited for improving the efficiency of this catalytic system.

4. Experimental

4.1. General

All reactions were carried out under a dry nitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried by means of standard procedures and stored under nitrogen. *N*,*O*-bis(trimethylsilyl)acetamide (BSA), dimethyl malonate and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ were used as received. The BINEPINE derivatives were prepared as described.[6a,8a,c] ^1H and ^{13}C spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts were reported in ppm relative to TMS and were referenced by means of the residual solvent signal. Optical rotations were measured with a Perkin-Elmer 241 polarimeter, using a cell of 1 dm path length.

4.2. General procedure for the palladium-catalyzed allylic alkylation

A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2 mg, 0.01 mmol) and the free ligand (0.04 mmol) in the desired solvent (1 ml) was stirred at room temperature under nitrogen. After 30 min, a solution of 1,3-diphenylprop-2-enyl acetate (101 mg, 0.4 mmol) in the same solvent (0.5 ml) was added. Dimethyl malonate (159 mg, 1.2 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (244 mg, 1.2 mmol) dissolved in the same solvent (1.5 ml) and potassium acetate (1.2 mg, 0.012 mmol) were added to the reaction mixture which was then stirred at the required temperature until a quantitative conversion was observed by tlc monitoring. The reaction mixture was diluted with diethyl ether (25 mL) and washed with saturated NH_4Cl. The organic phase was dried over Na_2SO_4, concentrated under reduced pressure and the residue was purified by flash chromatography (petroleum ether–diethylether, 3:1) to give dimethyl[1,3-diphenylprop-2-enyl]malonate. Conversions were determined by means of NMR. *ee*s were determined from the integrals of the methoxy groups of (1,3-diphenylprop-2-enyl) malonate, as split by the chiral shift reagent Europium(III) tris

[3-(heptafluoropropylhydroxymethylene)-*d*camphorate]. The absolute configuration of the product (1,3-diphenylprop-2-enyl)malonate was assigned by comparison of the sign of the measured value of the specific rotation with published data.

Acknowledgements

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