Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 1457–1464

TETRAHEDRON: *ASYMMETRY*

Remote electronic control of the ligand in the enantioselective palladium-catalyzed allylic alkylation with chiral oxazolinylpyridines

Giorgio Chelucci,* Sebastiano P. Deriu, Antonio Saba and Raffaela Valenti

Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

Received 22 February 1999; accepted 26 March 1999

Abstract

New chiral oxazolinylpyridines bearing electron-donating and withdrawing groups in the 4-position of the pyridine ring have been prepared and assessed in the enantioselective palladium catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate. The electronic properties of substituents strongly affect the catalytic activity and only slightly affect the enantioselectivity of the substitution reaction. Enantioselectivity up to 93% was obtained.

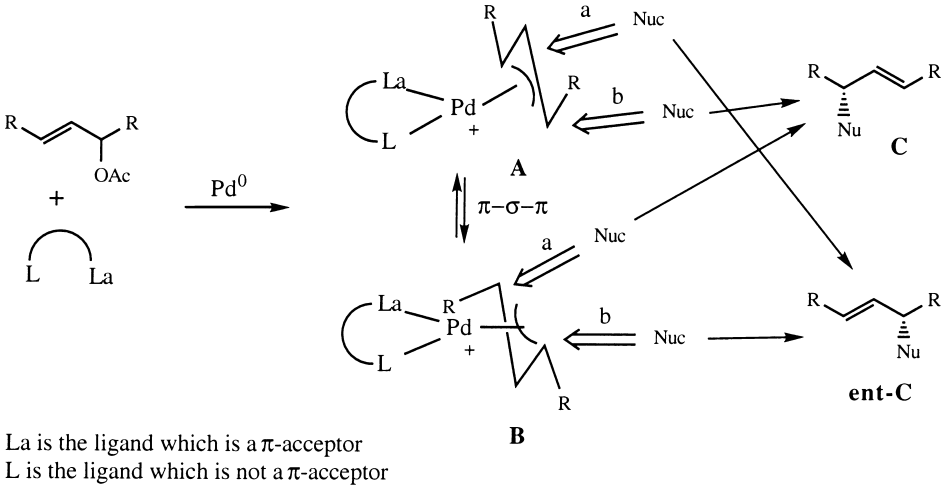
1. Introduction

Asymmetric induction with chiral metal-catalysts has been recognized as depending mainly on steric repulsion (i.e. non-bonding interactions) between an active metal-center decorated by chiral ligands and substrates. However, the chemo-, regio- and stereoselectivity in asymmetric catalytic reactions can be determined not only by steric (steric control) but also by electronic properties of the ligand (electronic control). Palladium-catalyzed asymmetric allylic substitution is a catalytic process in which these concepts have found useful applications.[1] The accepted mechanism for palladium-catalyzed allylic substitutions which proceed through a meso η^3-allyl intermediate, foresees that the nucleophile attacks the allylic termini of two alternative diastereomeric π-allyl palladium complexes (**C** and **D**, Scheme 1). As a consequence, there are, in principle, four main reaction pathways, of which two lead to product **E** and the remainder to the other enantiomer *ent*-**E**. With ligands containing two coordination sites such as phosphinooxazolines or thiophenooxazolines, while the steric properties of the ligand affect the ratio at equilibrium between the intermediates **C** and **D**, the electronically different properties of the two donor centers can control the approach of an incoming nucleophile on **C** or **D**. For instance, it has been

* Corresponding author. E-mail: chelucci@ssmain.uniss.it

0957-4166/99/$ - see front matter
PII: S0957-4166(99)00116-0

demonstrated that in the allylic palladium–phosphinooxazoline complexes the nucleophile attacks the carbon atom *trans* to the phosphane ligand (in Scheme 1: b in **C** and **D** if La=P and L=N) because this group is a better π-acceptor than the nitrogen ligand and so it withdraws electron density *trans* to itself making this carbon more susceptible to nucleophilic attack.[2] Moreover, this electronic effect has been increased in this class of ligands by making the Pd center more electrophilic, for instance by replacing the phosphane substituent with a phosphite group.[3]



Scheme 1.

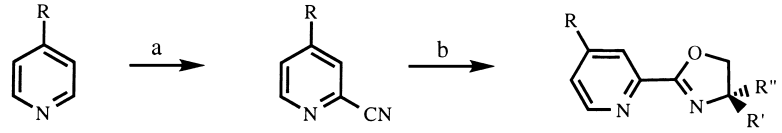
We have recently synthesized and assessed the palladium-catalyzed asymmetric allylic alkylations in a number of chiral oxazolinylpyridines having different substituents on the pyridine and oxazoline rings and we have disclosed their cross effects on the catalytic activity and stereoselectivity of the process (steric control).[4] Continuing our interest in this field,[5] we have evaluated the possibility of electronically controlling the catalytic process by differentiation of the electronic properties of the two very similar oxazolinylpyridine nitrogens (electronic control) in order to synthesize oxazolinylpyridines in which steric and electronic factors work together so as to optimize the asymmetric reaction. We thought that by modifying the electron-donating properties of the pyridine nitrogen by the introduction on the pyridine ring of electron-donating or withdrawing groups we could achieve this goal.[6] Moreover, we decided to synthesize oxazolinylpyridines where the electronic differentiating substituents are far from the catalytic center, in order to differentiate the electronic effects from the steric effects.

We report here on the synthesis of chiral oxazolinylpyridines bearing electron-donating and withdrawing groups in the 4-position of the pyridine ring and the results obtained with these ligands in the palladium-catalyzed alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate.

2. Results and discussion

We have synthesized oxazolinylpyridines with a methoxy- or a chloro-group in the 4-position of the pyridine ring and an *iso*-propyl- or phenyl-substituent on the oxazoline moiety (Scheme 2). Ligands **5c–f** were prepared by heating a chlorobenzene solution of the corresponding cyanoheterocycles **3** and **4** under reflux with the appropriate aminoalcohol in the presence of a catalytic amount of zinc chloride[7] (30–61% yields). Compounds **3** and **4** were obtained by oxidation of **1** and **2** with 3-chloroperbenzoic

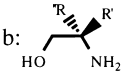
acid in CH_2Cl_2 at room temperature for 24 h and then treating the obtained oxide with dimethylcarbamoyl chloride and trimethylsilylcyanide in CH_2Cl_2 at room temperature for 6 days.[8]



1: R= Cl
2: R= OCH_3

3: R= Cl
4: R= OCH_3

	5a	5b	5c	5d	5e	5f
R	H	H	Cl	OCH_3	Cl	OCH_3
R'	H	Ph	H	H	Ph	Ph
R''	*i*-Pr	H	*i*-Pr	*i*-Pr	H	H

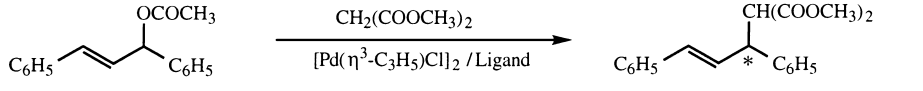
a: MCPA, CH_2Cl_2, rt, 24 h then Me_3SiCN, Me_2NCOCl, CH_2Cl_2, rt, 6 d; b:  , $ZnCl_2$, C_6H_5Cl, reflux.

Scheme 2.

With the ligands **5c–f** in hand, their ability to provide asymmetric induction in the palladium-catalyzed alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate was examined. Allylic substitutions were carried out at room temperature employing Trost's procedure which used $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as procatalyst and a mixture of dimethyl malonate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and potassium acetate in a methylene chloride solution.[9]

The results obtained under control of the new ligands are summarized in Table 1 from which the following conclusions can be made: (i) a dramatic effect on the catalytic activity is observed by the presence in the pyridine ring of the pyridyloxazolines of electron-donating (**5c**, **5e**) or withdrawing

Table 1
Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate[a]



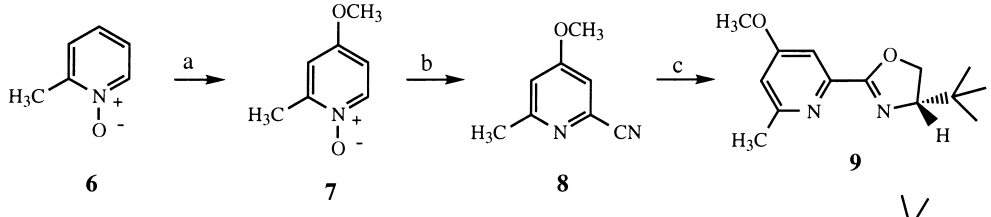
Entry	Ligand	React. time, h	Conv.[b]	Yield[c]	% Ee[d]	Conf.[e]
1	**5a**	1	100	84	24	S[f]
2	**5c**	168	40	n.d.	18	S
3	**5d**	0.45	100	97	16	S
4	**5b**	2.5	100	86	55	R[f]
5	**5e**	168	23	n.d.	54	R
6	**5f**	1.1	100	93	60	R
7	**9**	4.5	100	94	93	R
8	**10**	2.3	100	92	91	S[f]

[a]Reaction of the ligand (10 mol %) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol %) with 1,3-diphenylprop-2-enyl acetate (0.4 mmol), $CH_2(COOMe)_2$ (1.2 mmol), N,O-bis(trimethylsilyl)acetamide (BSA) (1.2 mmol) and KOAc (3.5 % mol) in CH_2Cl_2 (2 ml) at room temperature. [b]Determined by ^{1}H-NMR of the crude reaction mixture. [c]Isolated yields. [d]Determined by ^{1}H-NMR using Eu(hfc)$_3$ as chiral shift reagent. [e]The assignement is based on the sign of the optical rotation: Leutenegger, U.; Umbricht, G.; Fahrni, C.; Matt, P.V.; Pfaltz, A. *Tetrahedron*, **1992**, *48*, 2143. [f]Data taken from ref. 4

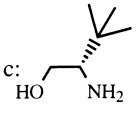
(**5d**, **5f**) groups. The electron-donating group (**5c**, **5e**) increases the reaction rate with respect to the 4-unsubstituted oxazolinylpyridine **5a** (entry 2 versus 1 and entry 5 versus 4) whereas the electron-withdrawing substituent decreases it drastically (entry 3 versus 1 and entry 6 versus 4); (ii) in contrast, the enantioselectivity of the substitution reaction appears to be scarcely affected by the electronic properties of the ligand. Thus, the ligands containing both electron-donating or withdrawing groups give a product possessing a similar enantiomeric excess and the same sense of chirality from that obtained from the related 4-unsubstituted ligands (entries 2, 3 versus 1 and entries 5, 6 versus 4).

These results indicate that the catalytic activity of the ligand is strongly dependent on its electronic properties, whereas its stereodifferentiating ability appears to be chiefly determined by its steric properties, although a favorable affect (albeit modest) on the enantioselectivity is observed with the ligand **5f** bearing an electron-donating substituent on the pyridine and a crowded group on the oxazoline ring (Table 1: entry 6 versus 4).

Starting from these observations, it appeared interesting to synthesize an oxazolinylpyridine in which steric and electronic factors work together so as to optimize the asymmetric reaction. To this end we decided to synthesize oxazolinylpyridine **9** (Scheme 3) using both a methoxy and a methyl group on the 4- and 6-positions of the pyridine ring and a *tert*-butyl substituent on the oxazoline, since good results have been obtained in the enantioselective palladium-catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate using as a ligand the related 2-[4,5-dihydro-4-(1,1-dimethylethyl)oxazol-2-yl]-6-methylpyridine **10** (91% ee, Table 1). In other words, we decided to prepare **9** with the aim of combining the favorable electronic effect of the methoxy group and the steric effect of the methyl and *tert*-butyl groups.



a: Literature; b: $(CH_3)_3SiCN$, $(CH_3)_2NCOCl$, CH_2Cl_2, r.t., 96h, 92 % yield; c: $ZnCl_2$, C_6H_5Cl, 24 h reflux, 72% yield.



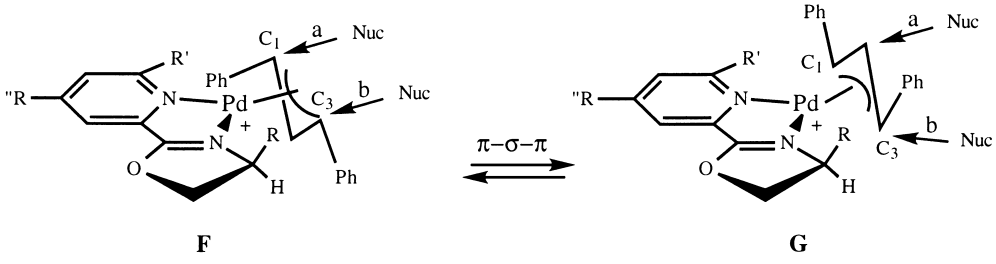
Scheme 3.

The oxazolinylpyridine **9** was prepared from the pyridine *N*-oxide **7** which was accessible following the literature procedure[10] (Scheme 3). Treatment of **7** with dimethylcarbamoyl chloride and trimethylsilylcyanide in CH_2Cl_2 at room temperature for 6 days afforded cyanoheterocycle **8** in very good yield (92%).[8] Finally, oxazolinylpyridine **9** was obtained by heating a chlorobenzene solution of **8** under reflux with *tert*-leucinol in the presence of a catalytic amount of zinc chloride[7] (72% yield).

Having prepared ligand **9**, we studied its properties as a catalyst under the usual conditions. The data, reported in Table 1, show that this ligand gives, with respect to the unsubstituted ligand **10**, a slightly better enantioselectivity but at a slightly worse reaction rate.

The results obtained can be tentatively explained as follows. With oxazolinylpyridines the two main reactive diastereomeric π-allyl palladium complexes **F** and **G** [depicted in Scheme 4 for ligands with (*S*)-configuration] interconvert through a π–σ–π mechanism and they are present at the equilibrium in a different ratio. This ratio is determined by both the substituents on the 6-position of the pyridine and on the 4-position of the oxazoline. In the absence of a substituent on the 6-position of the pyridine (i.e., with ligand **5**) diastereomer **F** should be slightly more stable than **G** because of the steric repulsion in

this diastereomer between the phenyl group of the π-allyl moiety and the substituent on the oxazoline ring, while the percentage of **F** would increase with the ligand **9** which has a bulkier substituent than hydrogen on the 6-position of the pyridine ring. The stereochemical outcome suggests that the nucleophile predominantly attacks the allylic terminus *trans* to the oxazoline nitrogen in the diastereomer **F** (a in **F**) or *cis* in **G** (b in **G**). An electron-donating group makes the pyridine nitrogen a better σ-donor than that of the oxazoline, whereas a withdrawing substituent makes it a worse σ-donor and, therefore, it should increase or decrease the electronic density on the metal. In both cases, the two termini of the allylic unit would respond in different ways to the electronic effect created on the metal by such a ligand since the electronic properties of the ligand are predominantly relayed in a *trans* manner across the complex. This electronic distortion upon the allylic moiety created by ligands with an electron-donating group (**5d**, **5f**) increases the reaction rate by making one of the two allylic termini of both diastereomers **F** and **G** more susceptible to nucleophilic attack, but the absence of a preferred reactive complex, because none of these diastereomers is particularly favored at the equilibrium, causes only a little change in the enantioselection.[11] On these grounds, a reduction of the catalytic activity should be expected with ligands bearing a withdrawing group but not as dramatic as that observed in this case. The electronic control of the reaction by the substituent could be otherwise rationalized considering the catalytic cycle of the reaction caused by the oxidative addition of the allylic substrate to the palladium(0) catalyst (Scheme 1). The rate of this step is dependent on the nature of the ligand and, in general, increases with increasing basicity (ability to donate electrons to the metal) of the ligand which increases the electronic density on the palladium and so its nucleophilic ability. These considerations are consistent with the observation that electron donating groups increase the reaction rate, whereas electron withdrawing groups decrease it drastically.



Scheme 4.

Neither of these mechanistic interpretations rationalize the unexpected decrease of the reaction rate obtained with ligand **9**. Clearly, in this case the catalytic activity is strongly dependent on the steric properties of the ligand. In fact, the rate of the oxidative addition step can be decreased not only by reducing the electronic density on the palladium but also by improving the steric requirement of the ligand. Thus, the electronic effect of the methoxy group appears relevant for the slightly crowed ligands **5d**, **5f** but it becomes unimportant in the case of the more sterically demanding ligand **9**. However, the observed improved enantioselectivity obtained with the ligand **9** confirms the favorable electronic effect on the stereoselectivity of the methoxy group which favors the nucleophilic attack on the C_1 carbon of the preferred diastereomer **F**, as previously observed with ligand **5f**.

3. Conclusions

The catalytic activity in the palladium-catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate, with dimethyl malonate using chiral oxazolinylpyridines bearing electron-donating and withdrawing

groups in the pyridine ring, was found to be highly dependent upon the electronic properties of the ligands. As previously mentioned, the electron-donating group increases the reaction rate, whereas the electron-withdrawing group decreases it drastically. In contrast, the enantioselectivity of the substitution reaction was scarcely affected by the electronic properties of the ligand. With the aim of obtaining a ligand in which steric and electronic factors work together so as to optimize the asymmetric reaction, we prepared oxazolinylpyridine **9** which gave a slightly better enantioselectivity (93% ee) with respect to the unsubstituted ligand **10**. The catalytic activity and stereochemical results has been tentatively rationalized on the basis of considerations on the transition states and related rates.

4. Experimental

4.1. General methods

Boiling points are uncorrected. Melting points were determined on a Buchi 510 capillary apparatus and are uncorrected. The ^{1}H NMR (300 MHz) spectra were obtained with a Varian VXR-300 spectrometer. Optical rotations were measured with a Perkin–Elmer 241 polarimeter in a 1 dm tube. Elemental analyses were performed on a Perkin–Elmer 240 B analyzer. 4-Chloro-2-cyanoypyridine **3**,[12] 2-cyano-4-methoxypyridine[13] **4**, 4-methoxy-2-methylpyridine-*N*-oxide **7**[10] were prepared following a literature procedure.

*4.2. 2-Cyano-3-methoxy-6-methylpyridine **8***

Dimethylcarbamoyl chloride (1.44 g, 13.5 mmol) was added dropwise to a solution of *N*-oxide of **7** (1.87 g, 13.5 mmol) and trimethylsilylcyanide (1.59 g, 14.8 mmol) in CH_2Cl_2 (100 ml). The solution was stirred at room temperature for 5 days, then 10% K_2CO_3 was added and stirring continued for 15 min. The organic phase was separated and dried (Na_2SO_4), and the solvent was evaporated. The residue was taken up with ethyl ether and the solid formed was filtered to give **8**: 1.84 g (92% yield); mp 105–107°C; ^{1}H NMR ($CDCl_3$) δ: 7.09 (d, 1H, J=2.4 Hz), 6.87 (d, 1H, J=2.4 Hz), 3.90 (s, 3H), 2.55 (s, 3H). Anal. calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.66; H, 5.41; N, 18.76.

4.3. General procedure for the preparation of oxazolinylpyridines

In a 25 ml two-necked flask zinc chloride (14 mg, 0.10 mmol) was melted under high vacuum and cooled under argon. After cooling to room temperature, chlorobenzene (12 ml) was added followed by the nitrile (2 mmol) and the amino alcohol (3.0 mmol). The resulting mixture was heated under reflux for the proper time (vide infra) and then the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (6 ml) and the resulting solution was washed with water (3×4 ml). The aqueous solution was extracted with CH_2Cl_2 (6 ml), the combined organic phases were dried over anhydrous Na_2SO_4, and the solvent evaporated. The residue was purified by chromatography on a silica gel column with the indicated eluent.

*4.3.1. (S)-4-Chloro-2-[4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]pyridine **5c***

Reaction time: 48 h; chromatographic eluent: benzene:acetone, 8:2; 0.217 g (48%); oil; $[\alpha]_D^{25}$ −61.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 8.60 (d, 1H, J=5.2 Hz), 8.08 (d, 1H, J=2.0 Hz), 7.41 (dd, 1H, J=5.2, 2.0 Hz), 4.51 (t, 1H, J=8.5 Hz), 4.26–4.12 (m, 2H), 1.91 (m, 1H), 1.07 (d, 3H, J=6.9 Hz), 0.95 (d, 3H,

J=6.9 Hz). Anal. calcd for $C_{11}H_{13}ClN_2O$: C, 58.80; H, 5.83; N, 12.47; Cl, 15.78. Found: C, 58.65; H, 5.84; N, 12.43; Cl, 15.60.

*4.3.2. (S)-2-[4,5-Dihydro-4-(1-methylethyl)oxazol-2-yl]-4-methoxypyridine **5d***

Reaction time: 48 h; chromatographic eluent (Al_2O_3): benzene:acetone, 1:1; 0.130 g (30%); oil; $[\alpha]_D^{25}$ −64.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 8.49 (d, 1H, J=5.7 Hz), 7.60 (d, 1H, J=2.5 Hz), 6.89 (dd, 1H, J=5.7, 2.5 Hz), 4.50 (t, 1H, J=8.5 Hz), 4.25–4.11 (m, 2H), 3.89 (s, 3H, CH_3O), 1.91 (m, 1H), 1.07 (d, 3H, J=6.9 Hz), 0.95 (d, 3H, J=6.9 Hz). Anal. calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.35; H, 7.18; N, 12.58.

*4.3.3. (S)-4-Chloro-2-(4,5-dihydro-4-phenyloxazol-2-yl)pyridine **5e***

Reaction time: 48 h; chromatographic eluent: benzene:acetone, 8:2; 0.29 g (57%); oil; $[\alpha]_D^{25}$ +4.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 8.61 (d, 1H, J=5.1 Hz), 8.20 (d, 1H, J=1.8 Hz), 7.42–7.23 (m, 6H), 5.47 (dd, 1H, J=9.6, 9.0 Hz), 4.90 (dd, 1H, J=9.6, 9.0 Hz), 4.42 (t, 1H, J=8.7 Hz). Anal. calcd for $C_{14}H_{11}ClN_2O$: C, 65.00; H, 4.29; N, 10.83; Cl, 13.70. Found: C, 64.88; H, 4.53; N, 10.70; Cl, 13.54.

*4.3.4. (R)-2-(4,5-Dihydro-4-phenyloxazol-2-yl)-4-methoxypyridine **5f***

Reaction time: 48 h; chromatographic eluent: benzene:acetone, 8:2; 0.30 g (61%); oil; $[\alpha]_D^{25}$ +83.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 8.51 (d, 1H, J=5.7 Hz), 7.68 (d, 1H, J=2.4 Hz), 7.39–7.24 (m, 5H), 6.91 (dd, 1H, J=5.7, 2.4 Hz), 5.48 (dd, 1H, J=9.6, 9.0 Hz), 4.91 (dd, 1H, J=9.6, 9.0 Hz), 4.43 (t, 1H, J=8.7 Hz), 3.85 (s, 3H, CH_3O). Anal. calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.93; H, 5.68; N, 10.77.

*4.3.5. (S)-2-[4,5-Dihydro-4-(1,1-dimethylethyl)oxazol-2-yl]-4-methoxy-6-methylpyridine **9***

Reaction time: 24 h; chromatographic eluent: benzene:acetone, 8:2; 0.57 g (72%); mp 97–98°C; $[\alpha]_D^{25}$ −77.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 7.50 (d, 1H, J=2.4 Hz), 6.76 (d, 1H, J=2.4 Hz), 4.44 (dd, 1H, J=10.2, 8.7 Hz), 4.31 (t, 1H, J=8.1 Hz), 4.09 (dd, 1H, J=10.2, 8.1 Hz), 3.88 (s, 3H, CH_3O), 2.58 (s, 3H, CH_3), 0.97 (s, 9H, *t*-bu). Anal. calcd for $C_{14}H_{20}N_2O_2$: C, 67.72; H, 8.12; N, 11.28. Found: C, 67.55; H, 8.35; N, 11.31.

4.4. Allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate: general procedure

A solution of ligand (0.04 mmol, 10 mol%) and $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ (4 mg, 2.5 mol%) in dry CH_2Cl_2 (2 ml) was stirred at room temperature for 15 min. This solution was treated successively with a solution of *rac*-(*E*)-1,3-diphenyl-2-propenyl acetate (0.4 mmol) in CH_2Cl_2 (1 ml), dimethyl malonate (1.2 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (1.2 mmol) and anhydrous potassium acetate (3.5 mol%). The reaction mixture was stirred for the appropriate time (see Table 1) until conversion was complete as shown by TLC analysis (light petroleum:ether, 3:1). The reaction mixture was diluted with ether (25 ml) and washed with ice-cold saturated aqueous ammonium chloride. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography (light petroleum:ether, 3:1) to afford dimethyl 1,3-diphenylprop-2-enylmalonate. The enantiomeric excess was determined from the ^{1}H NMR spectrum in the presence of enantiomerically pure shift reagent Eu(hfc)$_3$; splitting of the signals for one of the two methoxy groups was observed.

Acknowledgements

Financial support by M.U.R.S.T. and by Regione Autonoma Sardegna is gratefully acknowledged.

References

1. For reviews: Trost, M. B.; Van Vranken, D. L. *Chem. Rev*. **1996**, *96*, 395. Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: Weinheim, 1993. Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. For more recent references on palladium-catalyzed allylic alkylation reactions, see: Koning, B.; Meetsma, A.; Kellogg, R. M. *J. Org. Chem*. **1998**, *63*, 1604.
2. Ward, T. R. *Organometallics* **1996**, *15*, 2836. Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem., Int. Ed. Engl*. **1997**, 2108.
3. Prétôt, R.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl*. **1998**, 323.
4. Chelucci, G.; Medici, S.; Saba, A. *Tetrahedron: Asymmetry* **1999**, *10*, 543. Chelucci, G.; Medici, S.; Saba, A. *Tetrahedron: Asymmetry* **1997**, *8*, 3183. For a related study see: Nordström, K.; Macedo, E.; Moberg, C. *Tetrahedron: Asymmetry* **1998**, *9*, 3437.
5. Chelucci, G. *Tetrahedron: Asymmetry* **1997**, *8*, 2667. For other applications of oxazolinylpyridines for palladium-catalyzed allylic substitutions see: Nordström, K.; Macedo, E.; Moberg, C. *J. Org. Chem*. **1997**, *62*, 1604.
6. For analogue strategies see: Park, S.-B.; Murata, K.; Matsumoto, H.; Nishiyama, H. *Tetrahedron: Asymmetry* **1995**, *6*, 2487 and references therein.
7. Bolm, C.; Veickhardt, K.; Zehnder, M.; Ranff, T. *Chem. Ber*. **1991**, *124*, 1173.
8. Fife, W. K. *J. Org. Chem*. **1983**, *48*, 1375
9. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.
10. Deady, L. W.; Shanks, R. A.; Campbell, A. D.; Chooi, S. Y. *Aust. J. Chem*. **1971**, *24*, 385
11. Blöchl, P. E.; Togni, A. *Organometallics*, **1996**, *15*, 4125.
12. Tani, H. *Yakugaku Zasshi* **1960**, *80*, 1418. C.A. *55*, 9477
13. Shuman, R. T.; Ornstein, P. L.; Paschal, J. W.; Gesellchen, P. D. *J. Org. Chem.* **1990**, *55*, 738