Synthesis of (+) or (−)-2-(8′-Diphenylphosphino-1′-naphthyl) oxazoline Ligands and Their Application in Pd-Catalyzed Allylic Alkylation Reaction†

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We synthesized optically active 2-(8′-diphenylphosphino-1′-naphthyl) oxazoline ligands by palladium-catalyzed coupling reactions of (trimethylsilyl) diphenylphosphine with 2-(8′-bromo-1′-naphthyl) oxazolines, which, in turn, were prepared from 8-bromo-1-naphthoyl chloride by the reaction with natural optical active amino alcohols. Pd-Catalyzed allylic alkylation reaction induced by these chiral ligands gave the allylic substituted products in high yields and moderate *ee* values.

Keywords 2-(8′-diphenylphosphino-1′-naphthyl) oxazoline, Pd catalysis, allylic alkylation

Introduction

With the famous DIOP ligand, Kagan introduced the important concept of C_2-symmetry in ligand design.[1] However, it is not always true that a C_2-symmetric ligand should necessarily be superior to a non-symmetric counterpart. Transition metal-catalyzed allylic alkylation via symmetric allyl complexes is a good example.[2] In such reactions, the ratio of the two enantiomeric products is determined with the regioselectivity of nucleophilic attack. Consequently, it can be argued that chiral ligands possessing two different coordinating atoms should allow more effective control of regioselectivity than C_2-symmetric ligands. Because of the high enantioselectivities induced by C_2-symmetric bisoxazolines in transition metal-reactions,[3] some research groups were intrigued by the idea that replacement of one of the oxazoline rings by a phosphino group might lead to even more efficient ligands. These typical ligands include (phosphinoaryl) oxazolines,[4] chiral phosphino-oxazoline ligands with the 1,1-binaphthyl skeleton,[5] phosphino-substituted ferrocenyl oxazolines,[6] and JM-PHOS ligands.[7]

To the nonsymmetric ligands, the rigidity of the backbone may play an important role in determining the enantioselectivity of the asymmetric allylic substitution reaction. With this assumption in mind, we synthesized 1, 8-phosphinooxazoline ligands with a naphthyl skeleton and applied them to the allylic substitution reaction.

Results and discussion

Syntheses of 2-(8′-*diphenylphosphino*-1′-*naphthyl*) *oxazolines*

In the phosphino-oxazoline ligands, obviously the oxazoline ring is quite stable, while the phosphino group is easily oxidized to the corresponding phosphine oxide. So we first constructed the oxazoline ring. At 0 ℃, a solution of 8-bromo-1-naphthoyl chloride (**1**)[8] in CH_2Cl_2 was added dropwise to the solution of 1.0 equiv. of amino

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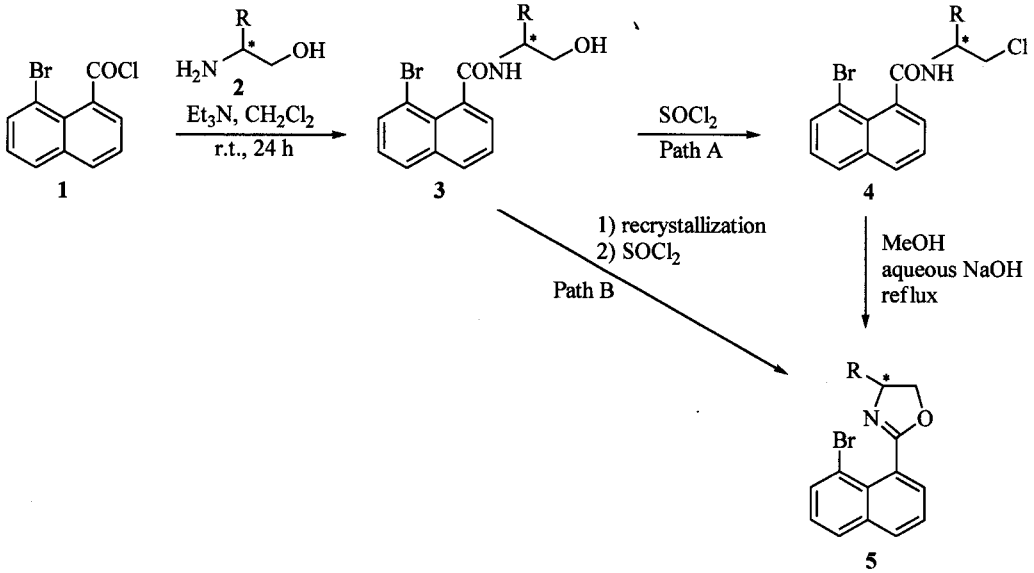
alcohol **2** in CH_2Cl_2 in the presence of triethyl amine. Then the mixture was stirred for 24 h at room temperature to give an amido alcohol **3**. The direct treatment of the amido alcohol **3** with thionyl chloride afforded predominantly the corresponding amido chloride **4**. 2-(8′-Bromo-1′-naphthyl) oxazoline (**5**) was obtained from the compound **4** by its reaction with MeOH/aqueous NaOH under reflux (Path A of Scheme 1). An alternative route is that the amido alcohol **3** was purified by recrystallization from H_2O/EtOH, then treated with freshly distilled thionyl chloride to directly afford the cyclization product **5** (Path B of Scheme 1).

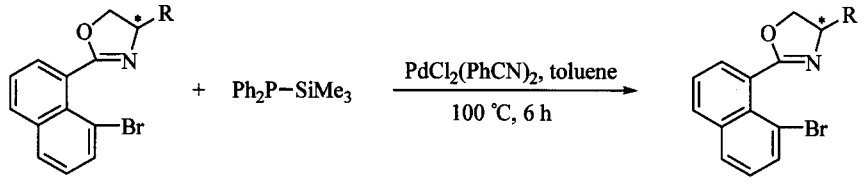
Unlike PHOX ligands,[4] the treatment of compound **5** with *n*-BuLi led to the lithiation not only at 8-position, but also at 2-position.[9] The strategy by Grignard reaction required highly active magnesium and risked the racemization of the chiral oxazoline ring.[10] After screening over some methods for the preparation of aryldiphenylphosphine, we selected the Pd-catalyzed cross-coupling reaction of α-naphthyl bromide **5** with (trimethylsilyl)-diphenylphosphine (**6**) for the synthesis of 2-(8′-diphenylphosphino-1′-naphthyl) oxazoline ligands (**7**). The mixture of the naphthyl bromides **5**, Ph_2PSiMe_3 (**6**) and 2.5 mol% of $PdCl_2(PhCN)_2$ in toluene was heated to 100 ℃ for 6 h to afford the corresponding phosphinonaphthyloxazolines **7** in moderate yields (Scheme 2).[11]

Scheme 1



Amino alcohol **2**	Path	Overall yield from **2**
R = $PhCH_2$, (*S*)-**2a**	B	(*S*)-**5a**, 59%
R = Ph, (*S*)-**2b**	B	(*S*)-**5b**, 42%
Rac-**2b**	A	*Rac*-**5b**, 19%
(*R*)-**2b**	B	(*R*)-**5b**, 34%
R = *i*-Pr, (*S*)-**2c**	B	(*S*)-**5c**, 62%

Scheme 2



5 **6** **7**

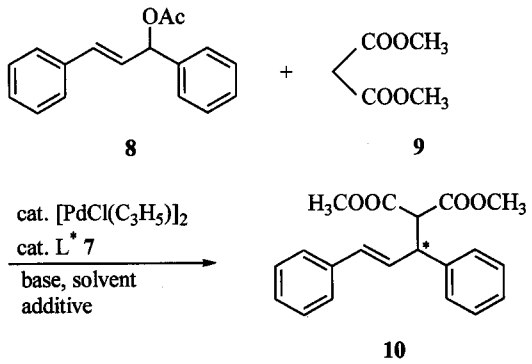
R = $PhCH_2$, (*S*)-**5a** — (*S*)-**7a**, 51%
R = Ph, (*S*)-**5b** — (*S*)-**7b**, 57%
R = Ph, (*R*)-**5b** — (*R*)-**7b**, 70%
R = *i*-Pr, (*S*)-**5c** — (*S*)-**7c**, 30%

To exclude the possibility of racemization of the chiral oxazoline ring, we synthesized *rac*-**7b** from *rac*-2-(8′-bromo-1′-naphthyl)-4-phenyloxazoline (**5b**), which, in turn, was obtained from acyl chloride **4** by the reaction with *rac*-phenylglycinol via path A. With the racemic ligand **7b** in hand, we determined the enantiomeric excess values of (*S*)-**7b** (99.3% *ee*) and (*R*)-**7b** (98.5% *ee*) by HPLC with a chiral AD column (eluent: *n*-hexane/2-propanol, 80 : 20), which means that no racemization took place in the whole process from amino alcohols **2** to ligands **7**.

Application of ligands **7** *in asymmetric allylic alkylation reaction*

The asymmetric allylic alkylation of racemic diphenylallyl acetate **8** with dimethyl malonate **9**, as a model reaction, is often used to measure the asymmetric inducing abilities of some new ligands (Scheme 3).[12]

Scheme 3



When the allylpalladium(II) complexes, generated *in situ* from $\{PdCl(\eta\text{-}C_3H_5)\}_2$ and the ligand (*S*)-**7b**, were used as the catalyst, the reaction with BSA/KOAc as the base gave higher yields and *ee* values than that with NaH (compare Entries 1 and 2, Table 1). The solvents and the additives also affected the enantioselectivity. When anhydrous MeCN was used as the solvent, the best asymmetric inducing result (44.6% *ee*) was obtained with the catalyst (compare Entry 5 with Entries 1, 3 and 4, Table 1). KOAc and CsOAc were better additives than LiOAc, NaOAc and Bu_4NF (compare Entries 5 and 10 with Entries 6—8, Table 1). The best ligand is 2-(8′-diphenylphosphino-1′-naphthyl)-4-isopropyloxazoline (**7c**). Under the optimized conditions, the reaction induced by ligand **7c** gave the highest enantiomeric excess (48.6%). The amounts of $\{PdCl(\eta\text{-}C_3H_5)\}_2$ and chiral ligand only changed the reaction rate, but did not affect the enantioselectivity (compare Entry 11 with Entry 13, Entry 16 and Entry 17, Table 1). Unexpectedly the reaction temperature has no effect on the enantiomeric excess. The reaction at − 20 ℃ became quite slow and gave almost the same *ee* value as that at room temperature (compare Entry 17 and Entry 18, Table 1). Noteworthily the reaction induced by (*R*)-**7b** gave (*S*)-configuration product **10** (Entries 10—13, Table 1), while the same reaction induced by (*S*)-**7b** gave *R*-product **10** (Entries 1—9, Table 1).

Conclusion

A class of new ligands, *i.e.*, 2-(8′-diphenylphosphino-1′-naphthyl)oxazolines (**7**) was prepared and applied to the enantioselective allylic alkylation of malonate in high yields and moderate *ee* values. Although excellent enantioselective results have not been observed in the reaction, this type of ligands may show their potentials in catalytic enantioselective reactions.

Experimental

Starting materials

8-Bromo-1-naphthoyl chloride[8] (**1**) and trimethylsilyl-diphenylphosphine (**6**)[11] were prepared according to the reported methods. All amino alcohols were obtained by the reduction of the corresponding amino acids with $NaBH_4/I_2$.[13] 1,3-Diphenylallyl acetate (**8**) was prepared from 1,3-diphenylprop-2-enol,[14] which was obtained from the reduction of 1,3-diphenylprop-2-en-1-one with $NaBH_4$.[15] 1,3-Diphenylallylic acetate (**8**), a colorless oil, 145—147 ℃/40 Pa [Lit.[14] 136—140 ℃/0.2 mmHg (26.6 Pa)]; ^1H NMR ($CDCl_3$) δ: 7.08—7.62 (m, 10H), 6.66 (d, J = 15.7 Hz, 1H), 6.33—6.48 (m, 2H), 2.17 (s, 3H).

Typical procedure for the preparation of rac-2-(8′-Bromo-1′-naphthyl) oxazoline [*rac*-**5**] (*path A*)

To a 100 mL round bottom flask charged with (*D*)-(−)-phenylglycinol (0.323 g, 2.5 mmol), (*L*)-(+)-phenylglycinol (0.323 g, 2.5 mmol), triethyl amine (2.0 mL) and CH_2Cl_2 (20 mL) was added dropwise a solution of 8-bromo-1-naphthoyl chloride (**1**) (1.348 g,

Table 1 Enantioselective allylic alkylation of *rac*-**8** with dimethyl malonate under the catalysis of $\{Pd(\eta\text{-}C_3H_5)Cl\}_2$ and (phosphinonaphthyl)-oxazoline **7**[a]

Entry	Ligand (mol%)	Additative (mol%)	Solvent	Temp. (℃)	Time (h)	Yield[b] (%)	ee[c] (%)	*R*/*S*[d]
1	(*S*)-**7b** (2.5)	KOAc (2)	CH_2Cl_2	13	14	90	41.4	*R*
2[e]	(*S*)-**7b** (2.5)	—	THF	12	4	77	34.0	R
3	(*S*)-**7b** (2.5)	KOAc (2)	Toluene	13	14	99	38.3	*R*
4	(*S*)-**7b** (2.5)	KOAc (2)	THF	8	15	76	35.9	*R*
5	(*S*)-**7b** (2.5)	KOAc (2)	MeCN	8	2	89	44.6	*R*
6	(*S*)-**7b** (2.5)	Bu_4NF (300)	MeCN	12	3.5	73	40.9	*R*
7	(*S*)-**7b** (2.5)	NaOAc (2)	MeCN	25	16	75	39.5	*R*
8	(*S*)-**7b** (2.5)	LiOAc (2)	MeCN	25	16	81	27.8	*R*
9	(*S*)-**7b** (2.5)	KOAc (2)	MeCN	-10	24	91	44.8	*R*
10	(*S*)-**7b** (2.5)	CsOAc (2)	MeCN	28	0.5	99	41.8	*S*
11	(*S*)-**7b** (2.5)	KOAc (2)	MeCN	-20	24	38	46.2	*S*
12[f]	(*S*)-**7b** (8.0)	KOAc (2)	MeCN	26	0.5	88	42.8	*S*
13[f]	(*S*)-**7b** (8.0)	KOAc (2)	MeCN	-20	21	38	47.1	*S*
14	(*S*)-**7b** (2.5)	KOAc (2)	MeCN	8	2	99	30.1	*R*
15	(*S*)-**7b** (2.5)	KOAc (2)	MeCN	19	12	86	48.6	*R*
16	(*S*)-**7b** (5.0)	KOAc (2)	MeCN	19	1	88	46.7	*R*
17[f]	(*S*)-**7b** (8.0)	KOAc (2)	MeCN	26	0.5	93	48.3	*R*
18[f]	(*S*)-**7b** (8.0)	KOAc (2)	MeCN	-20	21	68	47.3	*R*

[a] 0.5 mmol of 1,3-diphenylallyl acetate, dimethyl malonate (3 equiv.), ligand, BSA (3.0 equiv.) and 1 mol% $\{Pd(\eta\text{-}C_3H_5)Cl\}_2$ were used unless otherwise stated. [b] Purified products after column chromatography. [c] Determined by chiral HPLC. [d] (*R*) or (*S*)-Configuration according to the $[\alpha]_D$ value given in Ref. 12. [e] Dimethyl malonate (1.20 equiv.) and NaH (1.20 equiv.) as the base. [f] 2.0 mol% $\{Pd(C_3H_5)Cl\}_2$ was used.

5.0 mmol) in CH_2Cl_2(20 mL) at 0 ℃. After the mixture was stirred at room temperature for 24 h, thionyl chloride (6.0 mL) was cautiously added dropwise and continued to stir for 4 h at room temperature. The mixture was concentrated and neutralized with saturated aqueous $NaHCO_3$ until pH value was 7—8. The mixture was extracted with CH_2Cl_2, dried with Na_2SO_4, and chromatographed on silica gel to afford 0.499 g (26%) of the racemic amido chloride. The amido chloride was treated subsequently with MeOH (11 mL) and 2.5 mol/L aqueous NaOH (13 mL). The mixture was heated to 80 ℃ for 4 h. After it was concentrated to 1/2 volume, extracted with CH_2Cl_2 and evaporated, the residue was purified by chromatography on silica gel to afford *rac*-2-(8′-bromo-1′-naphthyl)-5-phenyloxazoline (**5b**) as a colorless oil (0.334 g, 73%). ^1H NMR ($CDCl_3$) δ: 7.70—8.00 (m, 4H), 7.10—7.59 (m, 7H), 5.43 (t, J = 8.9 Hz, 1H), 4.88 (t, J = 8.9 Hz, 1H), 4.33 (t, J = 8.9 Hz, 1H). For other data see (*S*)-**5b**.

Typical procedure for the preparation of 2-(8′-*bromo*-1′-*naphthyl*) *oxazoline* (**5**) (*path B*)

To a 250 mL round bottom flask charged with (*L*)-2-amino-3-methylbutan-1-ol (1.545 g, 15.0 mmol), triethyl amine (6.0 mL) and CH_2Cl_2(60 mL) was added dropwise a solution of 8-bromo-1-naphthoyl chloride (**1**) (4.043 g, 15.0 mmol) in CH_2Cl_2(60 mL) at 0 ℃. After the mixture was stirred at room temperature for 24 h, water (20 mL) was added. After evaporation, ethanol (30 mL) was added to recrystallize the amido alcohol. Although only a single recrystallization could not afford the completely pure amido alcohol, the purity is enough for the further transformation. To the partially purified amido alcohol (4.150 g) in CH_2Cl_2(100 mL) was added dropwise freshly distilled $SOCl_2$(15 mL). After the mixture was stirred for 5 h at room temperature, most of $SOCl_2$ was removed *in vacuo*. The residue was neutralized with 2.5 mol/L aqueous NaOH, extracted, dried and flash chromatographed on silica gel to afford (*S*)-(−)-2-(8′-bromo-1′-naphthyl)-5′-isopropyloxazoline (**5c**) (2.978 g, 62% overall yield from amino alcohol) as a colorless oil. $[\alpha]_D^{20}$ −73.0 (*c* 1.1, $CHCl_3$); FT-IR (KBr) ν: 2958, 1665, 761 cm^{-1}; ^1H NMR δ: 7.70—8.10 (m, 4H), 7.45—7.55 (m, 1H), 7.26—7.33 (m, 1H), 4.55 (dd, J = 8.3, 9.6 Hz, 1H), 4.25 (t, J = 8.3 Hz, 1H), 4.05—4.30 (m, 1H), 1.90—2.10 (m, 1H), 1.12 (d, J = 6.7 Hz, 3H), 1.01 (d,

J = 6.7 Hz, 3H); MS m/z (%): 320 [M^+ (^{81}Br) + 1, 24], 318 [M^+ (^{79}Br) + 1, 24], 238 (100); HRMS calcd for $C_{16}H_{16}{}^{79}BrNO$ (M^+) 317.0615, found 317.0438.

(*S*)-**5a** (*S*)-(−)-2-(8′-Bromo-1′-naphthyl)-5-benzyloxazoline [(*S*)-**5a**] was obtained via path B. A colorless oil, 59% overall yield; $[\alpha]_D^{20}$ − 12.6 (*c* 1.2, $CHCl_3$); FT-IR (KBr) ν: 3060, 1660, 821, 763, 701 cm^{-1}; ^{1}H NMR δ: 7.80—8.02 (m, 3H), 7.71 (d, J = 6.9 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.23—7.36 (m, 6H), 4.63—4.74 (m, 1H), 4.52 (t, J = 8.5 Hz, 1H), 4.25 (t, J = 8.5 Hz, 1H), 3.31 (dd, J = 14.0, 5.6 Hz, 1H), 2.94 (dd, J = 14.0, 8.2 Hz, 1H); MS m/z (%): 368 [M^+ (^{81}Br) + 1, 14], 366 [M^+ (^{79}Br) + 1, 14], 286 (100); HRMS calcd for $C_{20}H_{16}{}^{79}BrNO$ (M^+) 365.0615, found 365.0445.

(*S*)-**5b** (*S*)-(−)-2-(8′-Bromo-1′-naphthyl)-5-phenyloxazoline [(*S*)-**5b**] was obtained via path B. Colorless oil (solidified in a refrigerator), 42% overall yield; $[\alpha]_D^{20}$ − 79.6 (*c* 1.375, $CHCl_3$); FT-IR (KBr) ν: 2925, 1656, 825, 757, 702 cm^{-1}; ^{1}H NMR δ: 7.80—8.13 (m, 4H), 7.15—7.71 (m, 7H), 5.52 (t, J = 8.5 Hz, 1H), 4.96 (t, J = 8.5 Hz, 1H), 4.41 (t, J = 8.5 Hz, 1H); MS m/z (%): 354 [M^+ (^{81}Br) + 1, 13], 352 [M^+ (^{79}Br) + 1, 14], 293 (100); HRMS calcd for $C_{19}H_{14}{}^{79}BrNO$ (M^+) 351.0459, found 351.0229.

(*R*)-**5b** (*R*)-(+)-2-(8′-Bromo-1′-naphthyl)-5-phenyloxazoline [(*R*)-**5b**] was obtained via path B. Colorless solid, m.p. 114—115 ℃ (from hexane/ethyl acetate), 34% overall yield. $[\alpha]_D^{20}$ + 64.0 (*c* 1.45, $CHCl_3$); FT-IR (KBr) ν: 1656, 825, 757, 702 cm^{-1}; ^{1}H NMR δ: 7.80—8.02 (m, 4H), 7.25—7.63 (m, 7H), 5.53 (t, J = 8.5 Hz, 1H), 4.98 (t, J = 8.5 Hz, 1H), 4.43 (t, J = 8.5 Hz, 1H); MS m/z (%): 354 [M^+ (^{81}Br) + 1, 11], 352 [M^+ (^{79}Br) + 1, 12], 273 (100). Anal. calcd for $C_{19}H_{14}BrNO$: C 64.79, H 4.01, N 3.98; found C 64.90, H 3.96, N 3.86.

Typical procedure for the preparation of 2-(8′-*diphenylphosphino*-1′-*naphthyl*) *oxazoline ligands* (**7**)

To 0.445 g (1.26 mmol) of (*S*)-(−)-2-(8′-bromo-1′-naphthyl)-5-phenyloxazoline (**5b**) was added 12 mg (0.32 mmol) of bis(benzonitrile) palladium dichloride, 3.2 mL of toluene and 0.56 mL (2.15 mmol) of trimethylsilyldiphenylphosphine. The reaction mixture was heated to 100 ℃ for 5 h, then cooled to room temperature. After most of toluene was evaporated, 5 mL of CH_2Cl_2 and 0.5 g of silica gel was added directly to the residue. After concentration, the dry silica gel was directly added to the top of silica gel column. Purification by flash chromatography on silica gel (hexane/CH_2Cl_2/ethyl acetate, 4 : 1 : 1) afforded (*S*)-(−)-2-(8′-diphenylphosphino-1′-naphthyl)-5-phenyloxazoline [(*S*)-**7b**] (0.326 g, 57%) as a colorless solid, m.p. 145—146 ℃ (hexane/ethyl acetate). $[\alpha]_D^{20}$ − 53.0 (*c* 1.0, $CHCl_3$); FT-IR (KBr) ν: 1651, 1432, 696 cm^{-1}; ^{1}H NMR δ: 7.81—7.93 (m, 3H), 7.18—7.48 (m, 18H), 5.24 (t, J = 9.2 Hz, 1H), 4.57 (t, J = 9.2 Hz, 1H), 4.07 (t, J = 9.2 Hz, 1H); ^{31}P NMR (121 MHz, H_3PO_4 as the external standard) δ: − 10.29; MS m/z (%): 457 [M^+, 17], 353 (100). Anal. calcd for $C_{31}H_{24}NOP$: C 81.38, H 5.29, N 3.06; found C 81.03, H 5.15, N 2.67.

(*S*)-(−)-2-(8′-*Diphenylphosphino*-1′-*naphthyl*)-5-*benzyloxazoline* [(*S*)-**7a**] 51% yield, 99.3% *ee*; colorless crystal, m.p. 138—140 ℃ (from hexane/ethyl acetate); $[\alpha]_D^{20}$ − 5.7 (*c* 1.4, $CHCl_3$); FT-IR (KBr) ν: 1662, 1432, 747, 696 cm^{-1}; ^{1}H NMR δ: 7.88 (d, J = 8.2 Hz, 1H), 7.77 (dd, J = 7.9, 7.0 Hz, 2H), 7.10—7.46 (m, 18H), 4.43—4.47 (m, 1H), 4.15 (t, J = 8.2 Hz, 1H), 3.87 (t, J = 8.2 Hz, 1H), 3.14 (dd, J = 14.0, 8.5 Hz, 1H), 2.81 (dd, J = 14.0, 5.5 Hz, 1H); ^{31}P NMR (121 MHz, H_3PO_4 as the external standard) δ: − 10.01; MS m/z (%): 471 (M^+, 2), 352 (100). Anal. calcd for $C_{32}H_{26}NOP$: C 81.51, H 5.56, N 2.97; found C 81.65, H 5.60, N 2.98.

(*S*)-(−)-2-(8′-*Diphenylphosphino*-1′-*naphthyl*)-5-*isopropyloxazoline* [(*S*)-**7c**] 30% yield, colorless crystal, m.p. 101—102 ℃ (from hexane/ethyl acetate); $[\alpha]_D^{20}$ − 37.5 (*c* 1.15, $CHCl_3$); FT-IR (KBr) ν: 3051, 2956, 1655, 1433 cm^{-1}; ^{1}H NMR δ: 7.72—7.86 (m, 3H), 7.16—7.42 (m, 13H), 4.17—4.28 (m, 1H), 3.81—3.95 (m, 2H), 1.66—1.87 (m, 1H), 0.88 (d, J = 6.7 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H); ^{31}P NMR (121 MHz, H_3PO_4 as the external standard) δ: − 10.05; MS m/z (%): 423 (M^+, 14), 352 (100). Anal. calcd for $C_{28}H_{26}NOP$: C 79.41, H 6.19, N 3.31; found C 79.54, H 6.42, N 3.12.

(R)-(+)-2-(8′-Diphenylphosphino-1′-naphthyl)-5-phenyloxazoline [(*R*)-**7b**] 70% yield, 98.5% *ee*; colorless solid, m.p. 66—68 ℃ (sample directly from chromatography on silica gel); $[\alpha]_D^{20}$ + 48.0 (*c* 1.1, $CHCl_3$). FT-IR (KBr) ν: 3052, 1650, 1433, 697 cm^{-1}; ^1H NMR δ: 7.90—8.02 (m, 3H), 7.27—7.58 (m, 18H), 5.34 (t, J = 8.5 Hz, 1H), 4.66 (t, J = 8.5 Hz, 1H), 4.16 (t, J = 8.5 Hz, 1H); ^{31}P NMR (121 MHz, H_3PO_4 as the external standard) δ: −10.25.

Typical procedure for palladium-catalyzed allylic alkylation

To 1.8 mg (5 μmol, 1 mol%) of $[(\eta\text{-}C_3H_5)PdCl]_2$ in a 10 mL Schlenck tube equipped with a magnetic stirring bar was added a solution of 5.3 mg (12.5 μmol, 2.5 mol%) of ligand (*S*)-**7c** in 0.5 mL of MeCN. The suspension was degassed by three freeze-thaw cycles. The evacuated tube was sealed and the solution was stirred at 40 ℃ for 1 h. After the resulting clear and colorless solution was treated with a solution of 127 mg (0.5 mmol) of *rac*-**8** in 1.5 mL of MeCN, the mixture was immediately degassed by three freeze-thaw cycles, then stirred for 30 min at room temperature. To this mixture was added successively 0.17 mL (1.5 mmol) of dimethyl malonate, 0.37 mL (1.5 mmol) of *N*, *O*-bis (trimethylsilyl) acetamide (BSA), and 2 mg (15 μmol) of anhydrous potassium acetate. The reaction mixture was stirred at room temperature and monitored by TLC. After 12 h, the pale yellow, turbid reaction mixture was diluted with 60 mL of diethyl ether, transferred to a separatory funnel, and washed twice with an ice-cold saturated aqueous NH_4Cl solution. The organic phase was dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed (hexane/ethyl acetate, 6∶1) to afford 139 mg (86%, 48.6% *ee*) of analytically pure (+)-dimethyl 2-(1′, 3′-diphenyl-2′-propenyl) malonate (**10**) as a colorless oil[16] (overnight, the product was solidified). ^1H NMR δ: 7.04—7.65 (m, 10H), 6.49 (d, J = 15.7 Hz, 1H), 6.33 (dd, J = 15.7, 9.4 Hz, 1H), 4.24 (t, J = 9.4 Hz, 1H), 3.99 (d, J = 9.4 Hz, 1H), 3.75 (s, 3H), 3.52 (s, 3H).

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