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Highly regioselective asymmetric copper-catalyzed allylic alkylation with dialkylzincs using monodentate chiral spiro phosphoramidite and phosphite ligands

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Abstract—The copper complexes of chiral spiro phosphoramidite and phosphite ligands were found to be effective catalysts in the asymmetric allylic alkylations of cinnamyl halides with dialkylzincs. The allylic alkylation products were obtained in high regioselectivities (S_N2'/S_N2 up to 98:2) and enantiomeric excesses of up to 74% for S_N2' products.
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1. Introduction

The alkylation of allylic substrates is an important reaction for carbon–carbon bond formation in organic synthesis. Highly enantioselective palladium-catalyzed allylic alkylations with stabilized carbon anions such as malonates or related species as carbon nucleophiles have been described.[1] However, enantioselective copper-catalyzed allylic alkylation with organometallic reagents is quite limited.[2] In 1995, Bäckvall and van Koten reported the first asymmetric copper-catalyzed allylic alkylation with Grignard reagent in moderate enantioselectivity.[3] Asymmetric copper-catalyzed allylic alkylation with dialkylzinc reagents was described by Knochel et al. Employing the copper complexes of chiral ferrocenylamine ligands Knochel achieved 87% e.e. in the reaction of cinnamyl chloride with sterically hindered zinc reagent dineopentylzinc.[4] The enantioselectivity of copper-catalyzed allylic alkylation with dialkylzinc was further improved by Hoveyda et al. Using peptidic Schiff base ligands they obtained up to 97% e.e. in the alkylation of α,β-unsaturated esters bearing a primary γ-phosphate with dialkylzincs.[5] Feringa et al. reported that monodentate phosphoramidites derived from BINOL could also be efficient ligands in the copper-catalyzed allylic alkylation of cinnamyl bromide with dialkylzincs, affording S_N2'/S_N2 ratio of 85:15 and enantiomeric excesses up to 77% for the S_N2' products.[6]

In the previous paper, we have demonstrated that the chiral spiro phosphoramidite ligands **1**–**3** were highly effective in the rhodium-catalyzed hydrogenations of functionalized olefins [7] and copper-catalyzed 1,4-addition of dialkylzincs to enones.[8] Here we describe an asymmetric copper-catalyzed allylic alkylations of cinnamyl halides with dialkylzincs using spiro phosphoramidite and phosphite ligands **1**–**9** (Fig. 1), resulting in S_N2'/S_N2 ratio up to 98:2 and enantiomeric excesses up to 74% for the S_N2' products.

2. Results and discussion

The chiral spiro phosphoramidites and phosphites **1**–**9** were readily prepared from enantiomerically pure 1,1′-spirobiindane-7,7′-diol.[9] Heating the mixture of 1,1′-spirobiindane-7,7′-diol and $P(NMe_2)_3$ in toluene afforded ligand **1** in 92% yield. Condensation of 1,1′-spirobiindane-7,7′-diol with PCl_3, followed by treatment with the corresponding lithium dialkylamides or alkoxides provided ligands **2**–**9** in 40–69% yield.

The allylic alkylation reaction was initially carried out with cinnamyl bromide and diethylzinc (1.2 eq. to cinnamyl bromide) in the presence of copper catalyst (1 mol%) prepared in situ from $(CuOTf)_2.C_6H_6$ and ligand (*R*,*S*,*S*)-**3** in ether (Scheme 1). After 3 days at −30°C, 50% of substrate was converted and the alkylation products were produced in 36% yield. The ratio of two regioisomers (S_N2'/S_N2) was 64:36, and the enan-

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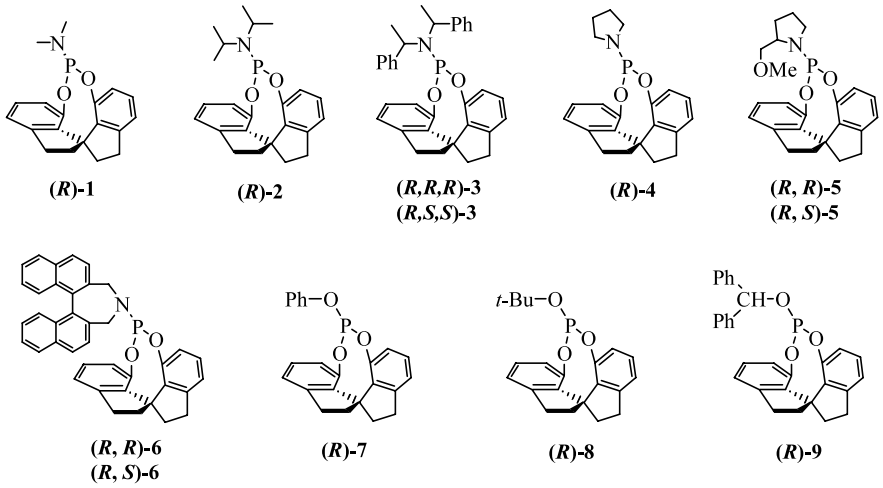
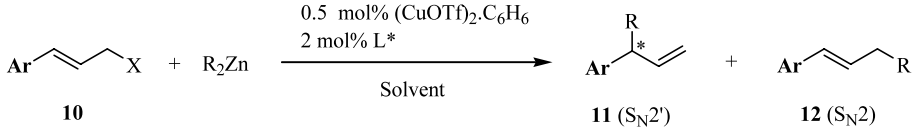


Figure 1. Spiro phosphoramidite and phosphite ligands.



Scheme 1.

tiomeric excess of S_N2' product was 56%. Screening of the solvents led to the finding that both regioselectivity and enantioselectivity are improved in chelating solvent, with dimethoxyethane (DME) and diglyme being the solvents of choice (Table 1). In diglyme, the alkylation products were obtained in 62% yield with 88:12 of S_N2'/S_N2 ratio and 71% e.e. for the S_N2' product (entry 4). Both regioselectivity and enantioselectivity decreased when the reaction was performed at 0°C or 15°C although the rates of reactions were faster and the yields of alkylation products were higher at these temperatures (entries 5 and 6).

The source of copper has been reported to have a strong influence on the activity and selectivity of catalyst in copper-catalyzed allylic alkylation with organometallic reagents.[2c,6] We examined different copper(I) and copper(II) salts with ligands (*R*,*S*,*S*)-**3** and (*R*)-**8** in the reaction of cinnamyl bromide and diethylzinc. As shown in Table 2, all the copper salts tested can be used as copper source of the catalyst. In the reactions using phosphoramidite ligand (*R*,*S*,*S*)-**3**, $(CuOTf)_2.C_6H_6$ gave highest enantioselectivity. But, in the reactions using phosphite ligand (*R*)-**8**, $Cu(OTf)_2$ was superior to other copper salts in both regioselectivity and enantioselectivity. The optimal copper/ligand ratio was found to be 1:2. Lowering or increasing the Cu/L ratio resulted in a decrease in either yield of reaction or enantiomeric excess of S_N2' product (entries 3 and 4 versus entry 2).

Table 1. Enantioselective copper-catalyzed allylic alkylation of cinnamyl bromide with diethylzinc using ligand (*R*,*S*,*S*)-**3**. Solvent effect[a]

Entry	Solvent	Temp. (°C)	Time (h)	Yield (%)[b] $S_N2'+S_N2$	S_N2'/S_N2 [c]	E.e. (%)[d] S_N2'
1	Et_2O	−30	72	36	64:36	56
2	THF	−30	72	81	89:11	58
3	DME	−30	72	50	86:14	71
4	Diglyme	−30	72	62	88:12	71
5	Diglyme	0	5	72	81:19	54
6	Diglyme	15	5	77	76:24	28
7	EA	−30	72	45	83:17	63
8	CH_2Cl_2	−30	72	53	73:27	9
9	toluene	−30	72	64	78:22	5

[a] 0.5 mol% $(CuOTf)_2{\cdot}C_6H_6$, Cu/L = 1:2.
[b] Determined by GC.
[c] Determined by GC.
[d] Determined by chiral GC using a Suplco β-DEX 120 column.

Table 2. Asymmetric allylic alkylation of cinnamyl bromide with diethylzinc. Copper salt effect[a]

Entry	Ligand	Cu salt	Yield (%) $S_N2'+S_N2$	S_N2'/S_N2	E.e. (%) S_N2'
1	(*R*,*S*,*S*)-**3**	$CuBr{\cdot}Me_2S$	77	83:17	46
2	(*R*,*S*,*S*)-**3**	$(CuOTf)_2{\cdot}C_6H_6$	62	88:12	71
3[b]	(*R*,*S*,*S*)-**3**	$(CuOTf)_2{\cdot}C_6H_6$	78	82:18	41
4[c]	(*R*,*S*,*S*)-**3**	$(CuOTf)_2{\cdot}C_6H_6$	35	89:11	74
5	(*R*,*S*,*S*)-**3**	$(CuOTf)_2{\cdot}Tol$	70	85:15	60
6	(*R*,*S*,*S*)-**3**	$Cu(MeCN)_4PF_6$	77	86:14	55
7	(*R*,*S*,*S*)-**3**	$CuBr_2$	84	79:21	46
8	(*R*,*S*,*S*)-**3**	$Cu(OTf)_2$	77	91:9	62
9	(*R*,*S*,*S*)-**3**	$Cu(OAc)_2{\cdot}H_2O$	74	88:12	56
10	(*R*,*S*,*S*)-**3**	$CuSO_4{\cdot}5H_2O$	45	85:15	64
11	(*R*)-**8**	$CuBr.Me_2S$	72	88:12	21
12	(*R*)-**8**	$(CuOTf)_2{\cdot}C_6H_6$	86	93:7	42
13	(*R*)-**8**	$(CuOTf)_2{\cdot}Tol$	83	94:6	46
14	(*R*)-**8**	$Cu(MeCN)_4PF_6$	83	91:9	27
15	(*R*)-**8**	$CuBr_2$	97	94:6	53
16	(*R*)-**8**	$Cu(OTf)_2$	90	98:2	59

[a] 1 mol% Cu, Cu/L = 1:2 unless stated otherwise, diglyme as solvent, −30°C.
[b] Cu/L = 1:1.
[c] Cu/L = 1:3.

Ligands **1**–**9** were compared in the copper-catalyzed allylic alkylation of cinnamyl bromide with diethylzinc, and the results are summarized in Table 3. Among the phosphoramidite ligands tested, ligands **1** and **4**, having smallest alkyl groups at nitrogen atom afforded highest regioselectivity (entries 1 and 4). However, ligand (*R*,*S*,*S*)-**3**, bearing a (*S*,*S*)-di(1-phenylethyl)amine moiety, gave best enantioselectivity (entry 3). In contrast with phosphoramidite ligands, phosphite ligands **7**–**9** are more active. The reactions with these ligands completed within one day and the yields of allylic alkylation products were higher. It was more exciting to see that the reactions using phosphite ligands have excellent regioselectivities (S_N2'/S_N2 up to 98:2).

The allylic alkylations of different cinnamyl halides were performed with diethylzinc using ligand (*R*,*S*,*S*)-**3** and $(CuOTf)_2{\cdot}C_6H_6$ (Table 4). Comparing to cinnamyl

Table 3. Enantioselective copper-catalyzed allylic alkylation of cinnamyl bromide using spiro phosphoramidite and phosphite ligands[a]

Entry	Ligand	Cu salt	Time (h)	Yield (%) $S_N2'+S_N2$	S_N2'/S_N2	E.e. (%) S_N2'
1	**1**	$(CuOTf)_2{\cdot}C_6H_6$	72	86	93:7	17
2	**2**	$(CuOTf)_2{\cdot}C_6H_6$	72	80	87:13	47
3	(*R*,*S*,*S*)-**3**	$(CuOTf)_2{\cdot}C_6H_6$	72	62	88:12	71
4	(*R*,*R*,*R*)-**3**	$(CuOTf)_2{\cdot}C_6H_6$	72	39	80:20	61
5	**4**	$(CuOTf)_2{\cdot}C_6H_6$	72	80	93:7	16
6	(*R*,*R*)-**5**	$(CuOTf)_2{\cdot}C_6H_6$	72	70	90:10	27
7	(*R*,*S*)-**5**	$(CuOTf)_2{\cdot}C_6H_6$	72	58	82:18	−11
8	(*R*,*R*)-**6**	$(CuOTf)_2{\cdot}C_6H_6$	72	82	88:12	8
9	(*R*,*S*)-**6**	$(CuOTf)_2{\cdot}C_6H_6$	72	81	87:13	28
10	**7**	$Cu(OTf)_2$	24	82	96:4	34
11	**8**	$Cu(OTf)_2$	24	90	98:2	59
12	**9**	$Cu(OTf)_2$	24	95	98:2	56

[a] 1 mol% of Cu, Cu/L = 1:2, diglyme as solvent, −30°C.

Table 4. Enantioselective copper-catalyzed allylic alkylation of cinnamyl halides[a]

Entry	Subs.	R_2Zn	Yield (%) $S_N2'+S_N2$	S_N2'/S_N2	E.e. (%) S_N2'
1	Ar = Ph, X = Cl	R = Et	11	86:14	47
2	Ar = Ph, X = Br	R = Et	62	88:12	71
3	Ar = Ph, X = Br	R = *i*-Pr	82	91:9	67
4	Ar = Ph, X = I	R = Et	53	42:58	71
5	Ar = 4-MePh, X = Br	R = Et	80	88:12	74
6	Ar = 2-ClPh, X = Br	R = Et	42	80:20	60
7	Ar = 4-ClPh, X = Br	R = Et	57	82:18	59

[a] 0.5 mol% $(CuOTf)_2{\cdot}C_6H_6$, 2 mol% (*R*,*S*,*S*)-**3**, diglyme as solvent, −30°C.

bromide, cinnamyl chloride was less reactive (entry 1) and cinnamyl iodide provided the allylic alkylation products in low regioselectivity (entry 4). 4-Methylcinnamyl bromide showed the activity (80% yield) and enantioselectivity (74% e.e.) which are slightly better than those with cinnamyl bromide (entry 5). The reactions of 2-chloro- and 4-chlorocinnamyl bromides produced allylic alkylation products in lower yields and lower enantioselectivities (entries 6 and 7). The cinnamyl acetate and carbonate were not active under the same reaction conditions. In addition to diethylzinc, diisopropylzinc, a bulkier zinc reagent, was also tested in the allylic alkylation of cinnamyl bromide using ligand (*R*,*S*,*S*)-**3** and $(CuOTf)_2 \cdot C_6H_6$ with 91:9 of regioselectivity and 67% of e.e. (entry 3), which are close to those obtained from diethylzinc.

To investigate the structure of catalyst, we grew a single crystal of copper complex from $CuBr \cdot Me_2S$ and phosphoramidite ligand **1** suitable for X-ray crystallography. The structure of $[CuBr((R)\text{-}\mathbf{1})_2]_2$ is shown in Figure 2.[10] Selected bond lengths and bond angles are listed in Table 5. The complex in the crystal is C_2-symmetric dimer with two bromine atoms as bridges. Each copper atom was coordinated with two phosphoramidite ligands. This structure is different from the copper complex of Feringa's MonoPhos ligand, which is a monomer with three ligands coordinated to copper.[11]

3. Conclusion

We have found that the spiro phosphoramidites and phosphites are effective ligands in the copper-catalyzed allylic alkylation of cinnamyl halides with dialkylzinc reagents. The alkylation products were obtained in good yields with high regioselectivities up to 98:2 of S_N2'/S_N2 ratio and enantiomeric excesses up to 74% for S_N2' products. Phosphoramidite ligands possessed higher enantioselectivity, while phosphite ligands provided higher regioselectivity and faster rate of reaction. Studies of other transition metal-catalyzed reactions using novel spiro phosphoramidite and phosphite ligands are in progress in our laboratory.

Table 5. Selected bond lengths [Å] and bond angles [°] in the complex $[CuBr((R)\text{-}\mathbf{1})_2]_2$

Bond lengths [Å]		Bond angles [°]	
Cu(1)-P(1)	2.260(2)	P(1)-Cu-P(2)	113.57(6)
Cu(1)-P(2)	2.254(2)	P(1)-Cu-Br(1)	115.56(5)
Cu(1)-Br(1)	2.542(1)	P(1)-Cu-Br(2)	111.98(5)
Cu(1)-Br(2)	2.523(1)	P(2)-Cu-Br(1)	106.72(5)
P(1)-N(1)	1.629(5)	P(2)-Cu-Br(2)	111.73(5)
P(1)-O(1)	1.649(4)	Br(1)-Cu-Br(2)	95.94(3)
P(1)-O(2)	1.635(4)	Cu(1)-Br(1)-Cu(2)	83.39(3)

4. Experimental

4.1. General

All reactions and manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. Toluene, ether, diglyme and THF were distilled from sodium-benzophenone ketyl under nitrogen. Methylene chloride and ethyl acetate were distilled from CaH_2. Starting (*R*)-1,1′-spirobiindane-7,7′-diol and the ligands **1**, **2** and **3** were prepared by the previously reported methods.[8,9]

4.2. Syntheses of spiro phosphoramidite ligands 4–6

4.2.1. *O*,*O*′-[(*R*)-1,1′-Spirobiindane-7,7′-diyl]-P-(1-pyrrolidinyl)phosphonite (*R*)-4. General procedure. A solution of (*R*)-1,1′-spirobiindane-7,7′-diol (505 mg, 2.0 mmol) in 8 mL THF was added over a period of 5 min to a cooled solution of PCl_3 (175 μL, 2.0 mmol), Et_3N (556

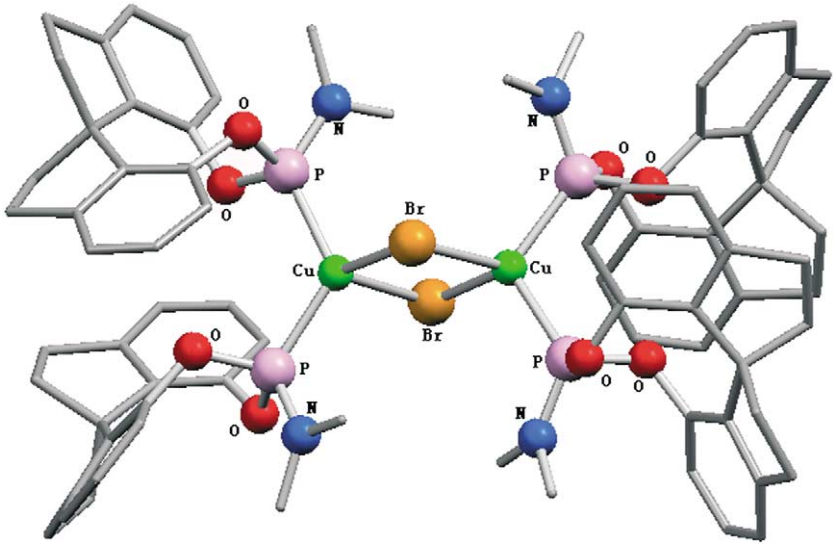


Figure 2. Crystal structure of complex $[CuBr((R)\text{-}\mathbf{1})_2]_2$.

μL, 4.0 mmol), and THF (50 mL) at −78°C. The reaction mixture was stirred for another 0.5 h, warmed to room temperature over a period of 2 h, and filtered. In a Schlenk tube, to the solution of pyrrolidine (167 μL, 2.0 mmol) and 5.0 mL THF, butyllithium (1.5 M solution in hexane, 1.4 mL, 2.1 mmol) was added at −30°C, then stirred for another 10 min. After warmed to room temperature, the solution was transferred to the above filtrate by syringe, the resulted mixture was stirred at −78°C for another 1 h, and warmed to room temperature. Concentration and chromatography purification using petroleum ether/EtOAc (10:1) on a silica gel column afforded (*R*)-**4** as a white powder (460 mg, 65% yield). Mp 140–142°C, $[\alpha]_D^{25}$ +366 (*c* 1.0, CH_2Cl_2). ^1H NMR: 7.20–6.65 (m, 6H), 3.00 (s, 4H), 2.85–2.77 (m, 2H), 2.51 (s, 2H), 2.17–2.18 (m, 2H), 2.04–1.91 (m, 2H), 1.67–1.56 (m, 4H). ^{13}C NMR: 149.0, 146.6, 146.0, 145.7, 142.6, 141.3, 128.7, 128.0, 122.2, 121.3, 120.6, 59.0, 45.6, 45.4, 44.8, 38.5, 38.3, 31.4, 31.2, 30.8, 26.1. ^{31}P NMR: 128.0. MS (*m*/*z*, %): 351 (M^+, 100). Anal. calcd for $C_{21}H_{22}NO_2P$: C, 71.76; H, 6.32; N, 3.99. Found: C, 71.90; H, 6.39; N, 3.73.

4.2.2. *O*,*O*′-[(*R*)-1,1′-Spirobiindane-7,7′-diyl]-P-[1-((*R*)-2-methoxymethylpyrro-lidinyl)]phosphonite (*R*,*R*)-5. Ligand (*R*,*R*)-**5** was synthesized in 40% yield from (*R*)-1,1′-spirobiindane-7,7′-diol and (*R*)-2-methoxymethylpyrrolidine by using the same procedure as that for (*R*)-**4**. White solid, mp 46–47°C. $[\alpha]_D^{25}$ +216 (*c* 0.5, $CHCl_3$). ^1H NMR: 7.27–6.75 (m, 6H), 3.73 (m, 1H), 3.42 (s, 3H), 3.38–1.82 (m, 16H). ^{13}C NMR: 149.1, 146.7, 146.6, 145.4, 142.5, 141.5, 128.7, 128.0, 122.1, 121.3, 120.6, 114.5, 59.0, 58.3, 58.0, 44.5, 38.5, 31.2, 30.8, 28.6, 28.6, 25.1. ^{31}P NMR: 120.7. HR-MS (FAB) calcd for $C_{23}H_{26}NO_3P$+H: 396.1723. Found 396.1723.

4.2.3. *O*,*O*′-[(*R*)-1,1′-Spirobiindane-7,7′-diyl]-P-[1-((*S*)-2-methoxymethylpyrro-lidinyl)]phosphonite (*R*,*S*)-5. Ligand (*R*,*S*)-**5** was synthesized in 50% yield from (*R*)-1,1′-spirobiindane-7,7′-diol and (*S*)-2-methoxymethylpyrrolidine by using the same procedure as that for (*R*)-**4**. White solid, mp 37–39°C. $[\alpha]_D^{25}$ +188 (*c* 0.5, $CHCl_3$). ^1H NMR: 7.26–6.67 (m, 6H), 3.80 (m, 1H), 3.42–1.50 (m, 19H). ^{13}C NMR: 148.7, 146.3, 145.7, 145.5, 142.1, 140.8, 128.5, 127.8, 122.0, 121.0, 120.4, 59.0, 58.8, 56.7, 56.4, 45.0, 38.2, 38.1, 30.9, 30.5, 29.4, 24.0. ^{31}P NMR: 128.7. HR-MS (FAB) calcd for $C_{23}H_{26}NO_3P$+H: 396.1723. Found 396.1723.

4.2.4. *O*,*O*′-[(*R*)-1,1′-Spirobiindane-7,7′-diyl]-P-[1-((*R*)-3,5 - dihydro - 4*H* - binaphth - [2,1 - c:1′,2′ - e] - azepinyl)]-phosphonite (*R*,*R*)-6. Ligand (*R*,*R*)-**6** was synthesized in 43% yield from (*R*)-1,1′-spirobiindane-7,7′-diol and (*R*)-3,5-dihydro-4*H*-binaphth-[2,1-c:1′,2′-e]-azepine by using the same procedure as that for (*R*)-**4**. White solid, mp 249–250°C. $[\alpha]_D^{25}$ −405 (*c* 0.1, $CHCl_3$). ^1H NMR: 8.00–7.95 (t, 4H), 7.60–6.14 (m, 14H), 4.15–4.09 (m, 2H), 3.20–2.71 (m, 6H), 2.35–1.84 (m, 4H). ^{13}C NMR: 148.8, 146.2, 145.0, 142.3, 141.0, 135.6, 133.8, 133.2, 131.6, 129.1, 128.7, 128.5, 127.5, 126.0, 120.0, 121.5, 120.6, 66.0, 58.9, 46.6, 38.5, 31.1, 30.7, 15.4. ^{31}P NMR: 122.1. HR-MS (FAB) calcd for $C_{39}H_{30}NO_2P$+H: 576.2087. Found 576.2080.

4.2.5. *O*,*O*′-[(*R*)-1,1′-Spirobiindane-7,7′-diyl]-P-[1-((*S*)-3,5 - dihydro - 4*H* - binaphth - [2,1 - c:1′,2′ - e] - azepinyl)]-phosphonite (*R*,*S*)-6. Ligand (*R*,*S*)-**6** was synthesized in 47% yield from (*R*)-1,1′-spirobiindane-7,7′-diol and (*S*)-3,5-dihydro-4*H*-binaphth-[2,1-c:1′,2′-e]-azepine by using the same procedure as that for (*R*)-**4**. White solid, mp 257–258°C. $[\alpha]_D^{25}$ −263 (*c* 0.1, $CHCl_3$). ^1H NMR: 7.95–7.93 (d, 3H, $J=8.4$ Hz), 7.48–6.68 (m, 15H), 3.87 (s, 2H), 3.57 (m, 2H), 3.20–2.80 (m, 4H), 2.30–1.90 (m, 4H). ^{13}C NMR: 146.1, 145.9, 135.1, 133.8, 133.3, 131.6, 128.9, 128.4, 128.0, 127.6, 126.0, 125.7, 122.4, 121.4, 120.7, 61.1, 59.7, 59.1, 50.5, 48.5, 44.1, 38.5, 38.4, 31.5, 31.1, 30.8, 29.9, 24.1, 18.4. ^{31}P NMR: 127.8. HR-MS (FAB) calcd for $C_{39}H_{30}NO_2P$+H: 576.2087. Found 576.2089.

4.3. Syntheses of spiro phosphite ligands 7-9

4.3.1. Phenyl-[(*R*)-1,1′-spirobiindane-7,7′-diyl]-phosphite (*R*)-7. General procedure. To the chilled solution of PCl_3 (110 μL, 1.3 mmol), Et_3N (380 μL, 2.7 mmol), and THF (25 mL), a solution of (*R*)-1,1′-spirobiindane-7,7′-diol (308 mg, 1.2 mmol) in 5 mL THF was added at −78°C. The reaction mixture was stirred for 2 h, then warmed to room temperature and filtered. The filtrate was cooled to −78°C and treated with lithium phenolate prepared from phenol (128 mg, 1.36 mmol) and butyllithium (1.6 M solution in hexane, 0.85 mL, 1.36 mmol) in 5 mL THF at −30°C. The resulted solution was warmed to room temperature, and stirred overnight. Concentration and flash chromatography purification on a silica gel column using petroleum ether/EtOAc (30:1) afforded (*R*)-**7** as a white solid (310 mg, 69% yield). Mp 104–105°C. $[\alpha]_D^{25}$ +72 (*c* 0.5, $CHCl_3$). ^1H NMR: 7.35–6.77 (m, 11H), 3.12–3.03 (m, 2H), 2.87–2.80 (m, 2H), 2.28–2.22 (m, 2H), 2.07–2.00 (m, 2H). ^{13}C NMR: 151.2, 145.1, 144.7, 143.8, 142.3, 141.9, 138.7, 128.7, 127.6, 126.9, 123.2, 122.8, 121.1, 120.9, 120.6, 119.7, 118.5, 58.2, 37.5, 36.9, 29.9, 29.4, 28.6. ^{31}P NMR: 120.5. HR-MS (FAB) calcd for $C_{23}H_{19}O_3P$+H: 375.1140. Found 375.1144.

4.3.2. *tert*-Butyl-[(*R*)-1,1′-spirobiindane-7,7′-diyl]-phosphite (*R*)-8. Ligand (*R*)-**8** was synthesized in 65% yield with sodium *tert*-butoxide by using the same procedure as that for (*R*)-**7**. White solid, mp 57–58°C. $[\alpha]_D^{25}$ +80 (*c* 0.5, $CHCl_3$). ^1H NMR: 7.20–6.76 (m, 6H), 3.08–3.02 (m, 2H), 2.85–2.81 (m, 2H), 2.24–2.18 (m, 2H), 2.04–2.00 (m, 2H), 1.48 (s, 9H). ^{13}C NMR: 145.1, 144.8, 144.4, 142.9, 142.0, 139.1, 127.3, 126.2, 121.8, 120.8, 120.5, 119.9, 58.0, 37.4, 36.9, 29.9, 29.5. ^{31}P NMR: 128.1. HR–MS (FAB) calcd for $C_{21}H_{23}O_3P$+H: 355.1457. Found 355.1463

4.3.3. Diphenylmethyl-[(*R*)-1,1′-spirobiindane-7,7′-diyl]-phosphite (*R*)-9. Ligand (*R*)-**9** was synthesized in 43% yield with diphenylmethanol by using the same procedure as that for (*R*)-**7**. White solid, mp 77–79°C. $[\alpha]_D^{25}$ +218 (*c* 0.53, $CHCl_3$). ^1H NMR: 7.31–6.30 (m, 16H), 6.153 (d, 1H), 3.13–1.91 (m, 8H). ^{13}C NMR: 146.4, 145.9, 145.5, 144.0, 143.8, 142.8, 141.8, 141.7, 139.9, 128.3, 128.2, 127.9, 127.6, 127.5, 127.4, 126.6, 123.3,

122.6, 121.7, 121.1, 79.2, 19.0, 59.1, 38.5, 37.9, 31.0, 30.5. ^{31}P NMR: 126.4. HR-MS (EI) calcd for $C_{30}H_{25}O_3P$: 464.1541. Found 464.1546.

4.4. General procedure for enantioselective copper-catalyzed allylic alkylation

Under a nitrogen atmosphere the phosphite ligand (*R*)-**9** (9.3 mg, 0.02 mmol) and $Cu(OTf)_2$ (3.5 mg, 0.01 mmol) were dissolved in diglyme (10 mL) and stirred at room temperature for 30 min. After cooling to −30°C, the solution was added Et_2Zn (1 M in hexane, 1.2 mL, 1.2 mmol) and stirred for 5 min. Then cinnamyl bromide (198 mg, 1.0 mmol) was added and the resulting mixture was stirred at −30°C for 24 h. The reaction was quenched with 10% aqueous H_2SO_4, and 68.0 mg *n*-tridecane was added as a standard. The aqueous layer was extracted 2 times with diethyl ether. The combined organic layers were treated with brine, dried over anhydrous Na_2SO_4. After purification on a short silica gel pad, the yield and S_N2'/S_N2 ratio of allylic alkylation products were determined to be 95% and 98:2 respectively by GC [HP-5 column, started at 35°C, programmed at 5°C/min to 160°C, t_R (S_N2') = 10.50 min, t_R (S_N2) = 14.06 min, and t_R(*n*-$C_{13}H_{28}$) = 16.15 min]. The enantiomeric excess of S_N2' product was determined to be 56% by chiral GC (Supelco β-DEX-120 column, 30 m, 0.25 mm, 65°C constant, t_R = 65.15 and 66.62 min). The GC conditions for the determinations of e.e. values of other allylic alkylation products are as follows.

3-(4-Methylphenyl)-1-pentene: Supelco β-DEX-120 column (30 m, 0.25 mm ID) at 75°C constant, t_R = 74.61 and 76.37 min.

3-(2-Chlorophenyl)-1-pentene: Chiraldex G-TA column (50 m, 0.25 mm ID) at 100°C constant, t_R = 28.48 and 31.68 min.

3-(4-Chlorophenyl)-1-pentene: Supelco β-DEX-120 column (30 m, 0.25 mm ID) at 100°C constant, t_R = 45.24 and 46.47 min.

4-Methyl-3-phenyl-1-pentene: Supelco β-DEX-120 column (30 m, 0.25 mm ID) at 75°C constant, t_R = 51.27 and 53.78 min.

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10. *Crystal data*: Monoclinic, space group *P*2(1); *a* = 11.2872(2), *b* = 27.1587(16), *c* = 12.0384(7) [Å]; *V* = 3642.5(4) [Å^3], *Z* = 4, Crystal dimensions = 0.22 x 0.20 x 0.12 mm, *T* = 293(2) K, radiation = *MoKa*, λ = 0.71073 [Å], unique data = 13500, *R* = 0.0343. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 210546. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ: [fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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