Palladium-Catalyzed Asymmetric Allylic Substitution Reactions Using New Chiral Phosphinooxathiane Ligands

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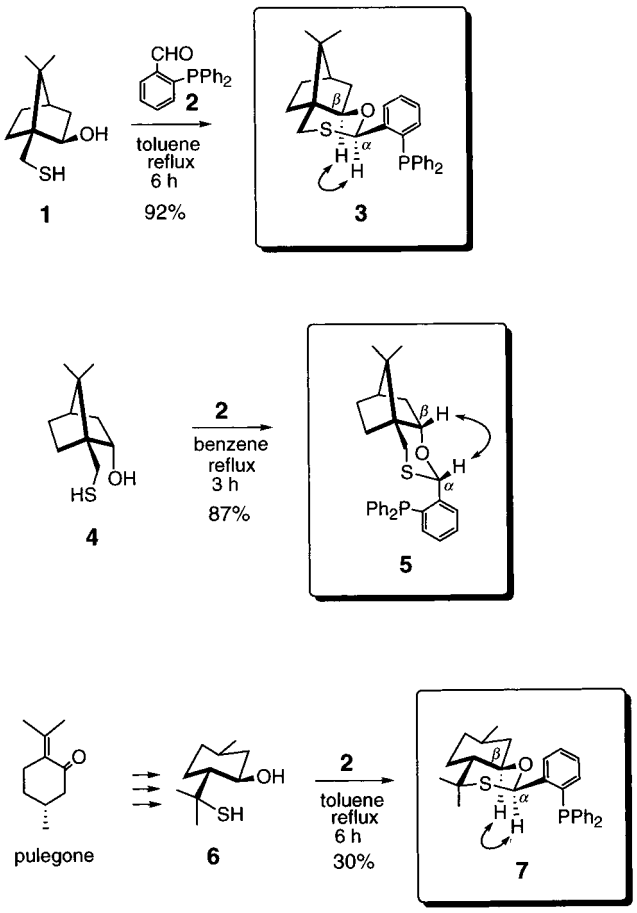
The development of the new chiral ligands for use in asymmetric catalytic reactions has drawn considerable interest in the last 10 years. In this area, palladium-catalyzed allylic substitution reactions have been shown to be effective tools for the construction of carbon−carbon and carbon−heteroatom bond[1] formation, and several efficient enantioselective catalysts such as C_2- and C_1-symmetric bidentate chiral ligands[1b] and non-C_2-symmetric[2] ligands such as phosphineoxazoline[3] have been explored for these reactions. Oxathianes,[4] however, have not been studied extensively as chiral ligands, and to the best of our knowledge, they have been used only in asymmetric carbonyl epoxidations.[5] In this paper, we report the synthesis of novel norbornane-based phosphinooxathianes **3**, **5** and pulegone-based phosphinooxathiane **7** and their application to asymmetric palladium-catalyzed allylic substitution reactions such as the alkylation and amination of allylic acetates **8** and **10**.[6]

Scheme 1. Synthesis of Chiral Oxathianes 3, 5, and 7



Results and Discussion

Synthesis of Phosphinooxathiane Ligands. The preparations of chiral ligands **3**, **5**, and **7** are described in Scheme 1. The chiral norbornane-based phosphinooxathiane **3** was readily synthesized as a single stereoisomer in 92% yield by the condensation of commercially available (1*S*)-(−)-10-mercaptoisoborneol **1** with 2-(diphenylphosphino)benzaldehyde **2** in refluxing toluene using a Dean−Stark apparatus. The chiral ligand **5** was also prepared stereoselectively from commercially available (*1S*)-(−)-10-mercaptoborneol **4** with **2** in refluxing benzene in 87% yield. (+)-Pulegone-based phosphinooxathiane **7**[4c] was obtained stereoselectively from the hydroxy thiol **6** (a diastereomeric mixture of which the major component **6** constitutes 82% as indicated by ^{13}C NMR)[4c] with **2** in refluxing toluene in 30% yield. In all three cases (**3**, **5**, and **7**), the assigned stereochemistry at the α-position of the 1,3-oxathiane ring was determined by the NOE difference spectrum (NOEDS). Thus,

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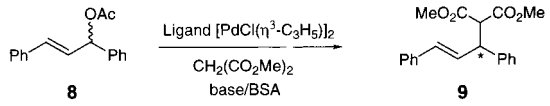
Table 1. Asymmetric Pd-Catalyzed Allylation of Acetate 8



8 9

entry	ligand	ligand (mol %)	temp (°C)	solvent	base	time (h)	yield[d] (%)	ee[e] (%)	config[f]
1[a]	3	2	rt	CH_2Cl_2	CH_3CO_2K	3	96	89	*R*
2	3	2	0	CH_2Cl_2	CH_3CO_2K	7	75	91	*R*
3	3	2	−30	CH_2Cl_2	CH_3CO_2K	24	80	94	*R*
4	3	2	−50	CH_2Cl_2	CH_3CO_2K	24	62	94	*R*
5	3	2	−78	CH_2Cl_2	CH_3CO_2K	24	13	90	*R*
6	3	2	−30	toluene	CH_3CO_2K	24	44	93	*R*
7[b]	3	2	−30	CH_3CN	TBAF	24	39	88	*R*
8[c]	3	1	−30	CH_2Cl_2	CH_3CO_2K	24	41	92	*R*
9	5	2	rt	CH_2Cl_2	CH_3CO_2K	3	98	52	*S*
10	5	2	0	CH_2Cl_2	CH_3CO_2K	20	90	69	*S*
11	5	2	−30	CH_2Cl_2	CH_3CO_2K	24	82	78	*S*
12	5	2	−50	CH_2Cl_2	CH_3CO_2K	24	66	86	*S*
13	5	2	−78	CH_2Cl_2	CH_3CO_2K	24	16	85	*S*
14	7	2	−30	CH_2Cl_2	CH_3CO_2K	48	42	16	*R*

[a] Molar ratio for entries 1−6 and 9−14: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.01 equiv), dimethyl malonate (3 equiv), *N*,*O*-bis(trimethylsilyl)acetoamide (BSA) (3 equiv), potassium acetate (0.02 equiv), **8** (1 equiv), ligands **3**, **5**, **7** (0.02 equiv). [b] Molar ratio for entry 7: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.01 equiv), dimethyl malonate (3 equiv), BSA (3 equiv), TBAF (3 equiv), **8** (1 equiv), ligand **3** (0.02 equiv). [c] Molar ratio for entry 8: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.005 equiv), dimethyl malonate (3 equiv), BSA (3 equiv), potassium acetate (0.02 equiv), **8** (1 equiv), ligand **3** (0.01 equiv). [d] Isolated yields. [e] Determined by HPLC analysis using a DAICEL Chiralcel OD-H column (entries 1−14). [f] *R* or *S* configurations based on the specific rotation with literature data.[3a,b,m]

NOE enhancement was observed between the hydrogen at the α-position and the hydrogen at the *β*-position when the α- and *β*-positions were irradiated, respectively (Scheme 1).

Asymmetric Allylic Alkylation. We investigated the palladium-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate **8** with dimethyl malonate using the chiral ligands **3**, **5**, and **7**. The reaction was carried out in the presence of *π*-allylpalladium chloride dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[7] (entries 1−14) to give the allylation product **9**. The results are summarized in Table 1. When the reactions were carried out at room temperature and 0 °C in dichloromethane using 1 mol % $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 2 mol % ligand **3** (entries 1 and 2), diester **9** was obtained in high yields with good enantioselectivities (rt: 96%, 89% ee, 0 °C: 75%, 91% ee). The enantioselectivity of the reaction was improved by lowering the temperature to −30 °C (80%, 94% ee) (entry 3); however, dropping the temperature to −50 °C only resulted in a moderate chemical yield (62%), but no improved enantioselectivity (94% ee) (entry 4). The same reaction at −78 °C gave the product **9** in a quite low chemical yield (13%) (entry 5). When the solvent was changed to toluene, a high enantiomeric excess (93% ee) was observed, but the chemical yield was poor (44%) (entry 6). Using tetrabutylammonium fluoride (TBAF) as base, the reaction also gave a lower chemical yield (39%) as compared to potassium acetate (entry 7). The reaction was also tried using 0.5 mol % $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 1 mol % ligand **3** under the same reaction conditions as entry 3 (entry 8); however, these reaction conditions did not give any better results in comparison with entry 3. Next, we tested the effectiveness of the chiral ligand **5** which is the stereoisomer of **3**. The reaction was carried out under the same conditions as entries 1−5. At room temperature and 0 °C, the enantioselectivities were poor (rt: 52% ee, 0 °C: 69% ee) (entries 9 and 10); however, when the reactions were performed at −30 °C and −50 °C, diester **9** was prepared in moderate yields and respectable enantioselectivities (−30 °C: 82%, 78% ee, −50 °C: 66%, 86% ee) (entries 11 and 12). As with ligand **5** at −78 °C, the product was obtained in a high enantiomeric excess (85% ee), with a low yield (entry 13). Finally, we examined the effectiveness of the chiral ligand **7** in this allylation reaction (entry 14). However, the ligand **7** was also less effective than ligand 3. From the above results, it is seen that phosphinooxathiane **3** is an excellent ligand for the allylation reaction described above.

It is considered that the enantiodifferentiation step in Pd-catalyzed allylation is the substitution of *π*-allyl complexes with nucleophiles, and nucleophilic attack occurs predominantly at the allyl terminus from trans to the better *π*-acceptor (P ≫ S).[8] Since the (*R*) product is obtained as the major enantiomer, the reaction probably proceeds through an M-type **A** rather than a W-type **B** intermediate.[8] In addition, the differentiation of chemical yields and enantiomeric excesses for the ligands **3** and **7** may be explained by steric difference. Thus, the ligand **7** has a bulky *gem*-dimethyl group in the oxathiane ring that obstructs the construction of the *π*-allyl palladium complex **C** (Figure 1).

Next, we investigated the regio- and stereoselective allylic alkylation[2e,3g,h,p] of cinnamyl acetate **10** with dimethyl malonate in the presence of the palladium catalyst and the chiral ligands **3** and **5**, the products

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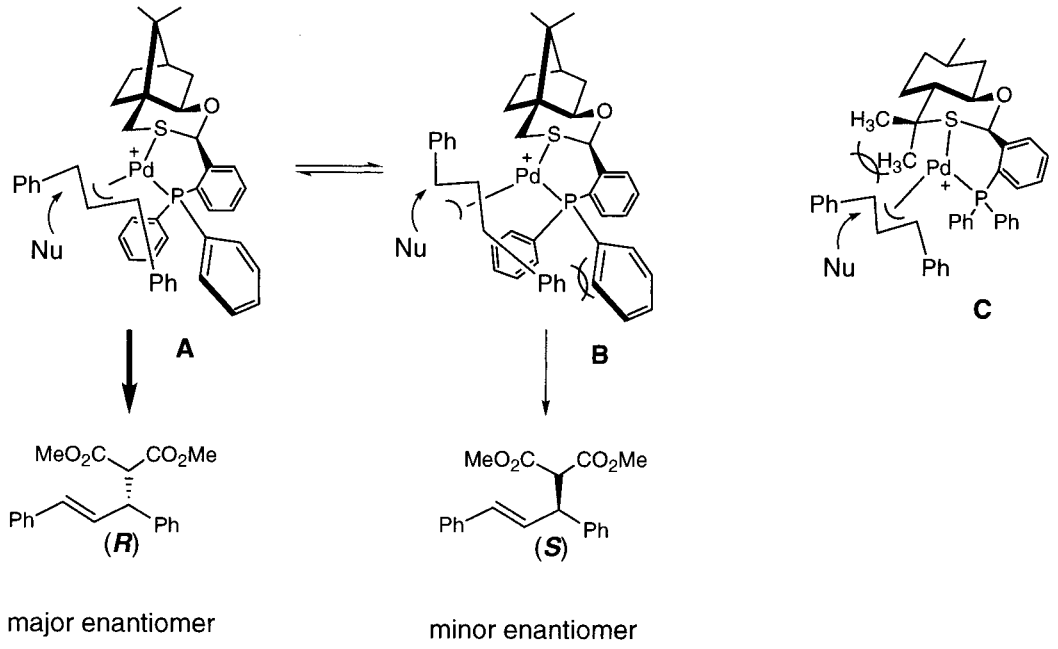
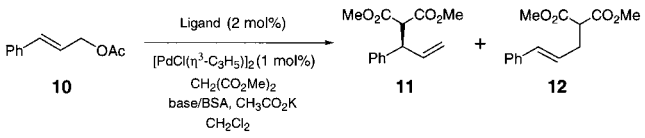


Figure 1. A plausible reaction course in the reaction of **8**.

Table 2. Asymmetric Pd-Catalyzed Allylation of Acetate 10



entry	ligand	temp (°C)	time (h)	yield[b]	11:12	ee[c] (%)	config[d]
1[a]	**3**	rt	1	100	25:75	13	*R*
2	**3**	0	3	97	22:78	57	*R*
3	**3**	−30	3	92	42:58	85	*R*
4	**5**	−30	3	94	23:77	79	*R*

[a] Molar ratio for entries 1−4: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.01 equiv), dimethyl malonate (3 equiv), *N*,*O*-bis(trimethylsilyl)acetoamide (BSA) (3 equiv), potassium acetate (0.02 equiv), **10** (1 equiv), ligands **3,5** (0.02 equiv). [b] Isolated yields. [c] Determined by HPLC analysis using a DAICEL Chiralcel OJ column. [d] *R*-Configuration based on the specific rotation with literature data.[3g,m]

being a mixture of regioisomers **11** and **12** (Table 2). We examined the reaction in CH_2Cl_2 in the range of room temperature to −30 °C using 1 mol % $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 2 mol % chiral ligands. The results are listed in Table 2. The reaction when performed at room temperature using the chiral ligand **3** proceeded in a quantitative yield (entry 1). The regioselectivity and enantiomeric excess for **11**, however, were not high. Next, this reaction was tested at 0 °C using the chiral ligand **3** (entry 2). Unfortunately, this case also provided poor enantioselectivity. A good result was obtained at −30 °C (entry 3). Thus, the reaction gave the products **11** (85% ee) and **12** in a ratio of 42:58. In addition, the reaction was also tried using the chiral ligand **5** under the same reaction conditions as entry 3 (entry 4); however, any better results was not obtained in comparison with entry 3.

The plausible intermediates in the alkylation of **10** are illustrated in Figure 2. The predominant formation of the linear product **12** may suggest that intermediate **A** is most favored. Considering the previous report[8] and that the absolute configuration of the branched product **11** is (*R*), the next plausible reaction course is suggested. Thus, the reaction probably proceeds through the intermediate **B** rather than the intermediate **C** because of the steric interaction between the phenyl group of the alkene of the alkene−Pd complex and the methylene moiety of the oxathiane ring of the ligand. For this reason, the *R* product may be given preferentially, as is observed experimentally.

Asymmetric Allylic Amination. We examined the palladium-catalyzed allylic amination[9] of **8** with benzylamine **13** using the chiral ligands **3** and **5**. The reaction was carried out in CH_2Cl_2 using a catalyst generated by mixing 1 mol % $[PdCl(\eta^3\text{-}C_3H_5)]_2$ with 2 mol % chiral ligands **3** (entries 1−6) and **5** (entries 7−9), respectively, to give the aminated product **14a**. The results are listed in Table 3. When the reaction was carried out at room temperature using 1 equiv of benzylamine to a substrate, the product **14a** was obtained in a low chemical yield (30%) and a good enantiomeric excess (77% ee) (entry 1). Interestingly, the product **14a** was obtained in almost quantitative yield without the decrease of the enantioselectivity (76% ee), when 10 equiv of benzylamine to the substrate was used (entry 2). Next, the reactions were tried at 0 °C for 3 h (entries 3 and 4) by using both 1 and 10 equiv of benzylamine, respectively, and satisfactory results (67% yield, 82% ee) were obtained with 10 equiv of benzylamine (entry 4). The same reactions at −30 °C provided the high enantiomeric excesses (85% ee and 86% ee), although the chemical yields were quite low (12 and 15%) in both cases (entries 5 and 6). We also tested the effectiveness of the chiral ligand **5** for this asymmetric amination. Unfortunately, **5** did not work as an effective ligand at −30 and 0 °C (entries 7−9). Furthermore, the same reaction was tried using potassium phthalimide **15** (3 equiv to the substrate **8**) as a nitrogen nucleophile. The reaction was carried out in CH_2Cl_2 using 2.5 mol %

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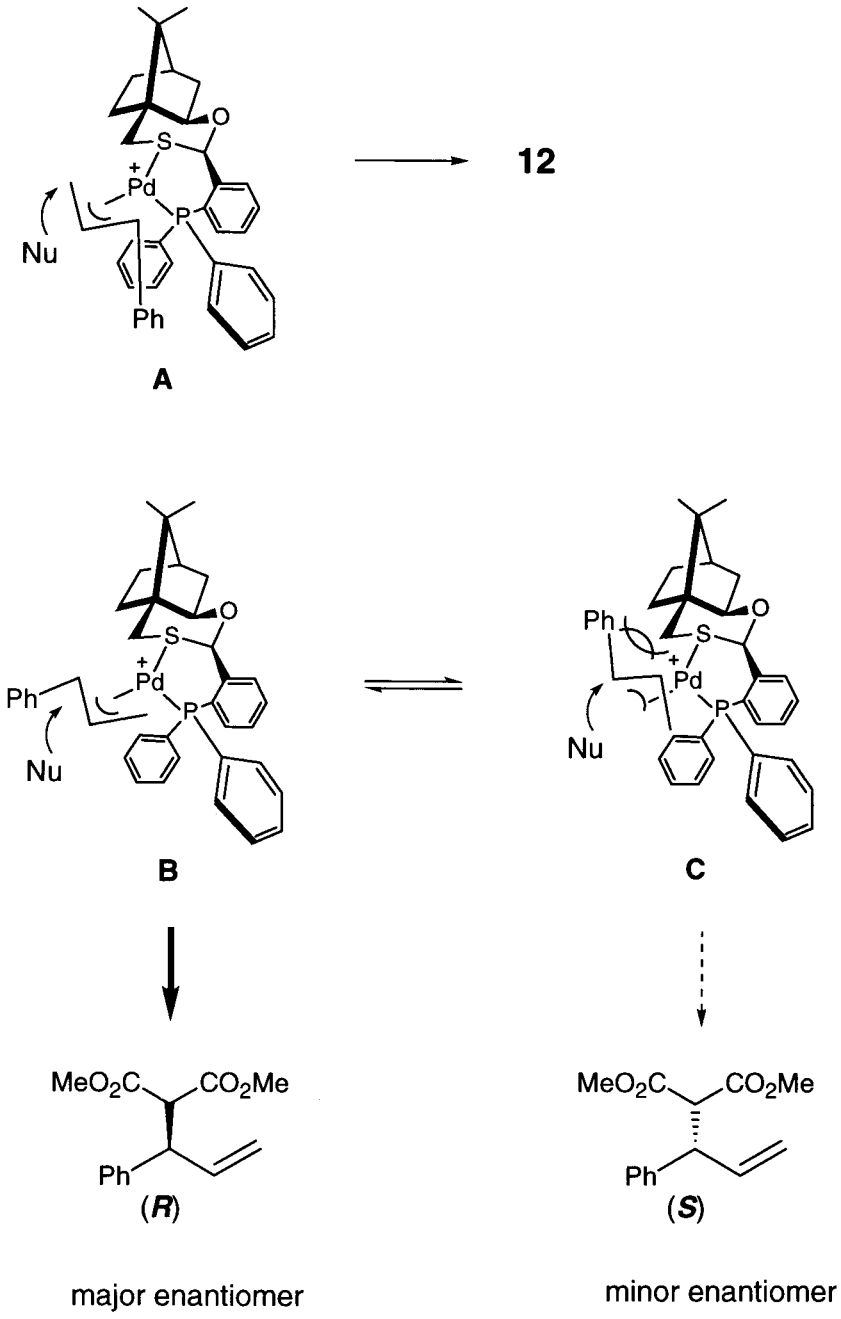


Figure 2. A plausible reaction course in the reaction of **10**.

$[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 5 mol % chiral ligands **3** (entries 10−13) and **5** (entries 14 and 15), respectively, to give the aminated product **14b**. The results are listed in Table 3. When the reaction was carried out at 50 °C, the product **14b** was obtained in a quantitative yield and good enantiomeric excess (73% ee) (entry 10). The same reactions at room temperature and 0 °C also provided satisfactory results for the chemical yield (rt: 86%, 0 °C: 74%) and enantiomeric excesses (rt: 88% ee, 0 °C: 90% ee) (entries 11 and 12). At −30 °C, a high enantiomeric excess (89% ee) was achieved, although the chemical yield was low (31%) (entry 13). Unfortunately, the chiral ligand **5** was not an effective ligand for this asymmetric reaction at both room temperature and 0 °C (entries 14 and 15).

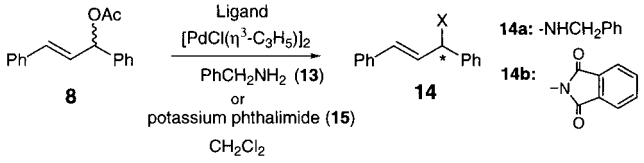
In conclusion, we have prepared three new chiral ligands **3**, **5**, and **7**. Particularly, phosphinooxathiane **3** proved to be the most effective ligand for asymmetric allylic substitution reactions, providing the products in high chemical yields and high enantiomeric excesses. Further applications and modifications of the ligand **3** are in progress.

Experimental Section

IR spectra were measured with a Perkin Elmer 1725X spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX 270 and a JEOL JNM-LA 600 spectrometers with TMS as an internal standard. MS were taken on a JEOL-JNM-DX 303 spectrometer. Elemental analyses were performed by a Perkin Elmer 2400 Elemental Analyzer. Optical rotations were measured with a JASCO-DIP-370 digital polarimeter.

(1*R*,3*R*,5*R*,8*S*)-11,11-Dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0^{3,8}]undecane (3). (1*S*)-(−)-10-Mercaptoisoborneol **1** (100 mg, 0.54 mmol), 2-(diphenylphosphino)benzaldehyde **2** (157 mg, 0.54 mmol), *p*-toluenesulfonic acid monohydrate (10 mg, 0.054 mmol), and toluene (10 mL) were placed in a flask equipped with a Dean−Stark trap. The mixture was refluxed for 6 h. The solvent was evaporated under

Table 3. Asymmetric Pd-Catalyzed Amination of Acetate 8 Using Benzylamine or Potassium Phthalimide



entry	ligand	nucleophile	nucleophile (equiv to **8**)	temp (°C)	time (h)	yield[c] (%)	ee[d] (%)	config[e]
1[a]	**3**	**13**	1	rt	3	30	77	*S*
2	**3**	**13**	10	rt	1	98	76	*S*
3	**3**	**13**	1	0	3	16	81	*S*
4	**3**	**13**	10	0	3	67	82	*S*
5	**3**	**13**	1	−30	24	12	85	*S*
6	**3**	**13**	10	−30	24	15	86	*S*
7	**5**	**13**	1	0	3	8	46	*R*
8	**5**	**13**	10	0	3	30	52	*R*
9	**5**	**13**	10	−30	24	27	60	*R*
10[b]	**3**	**15**	3	50	18	100	73	*S*
11	**3**	**15**	3	rt	24	86	88	*S*
12	**3**	**15**	3	0	48	74	90	*S*
13	**3**	**15**	3	−30	48	31	89	*S*
14	**5**	**15**	3	rt	24	100	50	*R*
15	**5**	**15**	3	0	48	98	51	*R*

[a] Molar ratio for entries 1−9: $[PdCl(\eta^3\text{-}C^3H_5)]_2$ (0.01 equiv), benzylamine [entries 1, 3, 5, 7: (1 equiv), entries 2, 4, 6, 8, 9: (10 equiv), **8** (1 equiv), ligands 3, 5 (0.02 equiv). [b] Molar ratio for entries 10−15: $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.025 equiv), potassium phthalimide (3 equiv), **8** (1 equiv), ligands **3**, **5** (0.05 equiv). [c] Isolated yields. [d] Determined by HPLC analysis using a DAICEL Chiralcel OD-H column. [e] *R* or *S* configurations based on the specific rotation with literature data.[3m,9a,d]

a reduced pressure, and the residue was purified by preparative TLC (hexane:ether = 6:1) to give a pure **3** (230 mg) in 92% yield. mp 52−54 °C, $[\alpha]^{23}_D = -96.1$ (*c* 1.51, $CHCl_3$). IR (film) cm^{-1}: 746, 719, 702. ^1H NMR ($CDCl_3$) δ: 7.71 (m, 1H), 7.35−7.46 (m, 12H), 6.92 (m, 1H), 6.39 (d, J = 7.6 Hz, 1H), 3.59 (dd, J = 7.0, 3.0 Hz, 1H), 3.19 (d, J = 14.2 Hz, 1H), 2.70 (d, J = 14.2 Hz, 1H), 1.88 (m, 1H), 1.59−1.72 (m, 3H) 1.47 (m, 1H), 1.46 (s, 3H), 0.88−1.10 (m, 2H), 0.92 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 137.2, 137.1, 136.7, 134.0, 133.9, 133.8, 133.8, 133.7, 133.5, 129.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 127.3, 85.6, 81.3, 81.0, 46.8, 45.6, 37.9, 34.3, 30.0, 27.3, 23.4, 20.5. Anal. Calcd for $C_{29}H_{31}OPS$: C, 75.97; H, 6.80. Found: C, 75.68; H, 6.53. MS *m*/*z*: 458 (M^+).

(1*R*,3*S*,5*S*,8*S*)-11,11-Dimethyl-4-oxa-5-(2-diphenylphosphino)phenyl-6-thiatricyclo[6.2.1.0^{3,8}]undecane (5). (1*S*)-(−)-10-Mercaptoborneol **4** (100 mg, 0.54 mmol), 2-(diphenylphosphino)benzaldehyde **2** (157 mg, 0.54 mmol), *p*-toluenesulfonic acid monohydrate (10 mg, 0.054 mmol), and benzene (10 mL) were placed in a flask equipped with a Dean−Stark trap. The mixture was refluxed for 3 h. The solvent was evaporated under a reduced pressure, and the residue was purified by preparative TLC (hexane:ether = 6:1) to give a pure **5** (213 mg) in 87% yield. mp 56−58 °C, $[\alpha]^{23}_D = 40.9$ (*c* 1.10, $CHCl_3$). IR (film) cm^{-1}: 748, 721, 694. ^1H NMR ($CDCl_3$) δ: 7.90 (m, 1H), 7.41 (m, 1H), 7.27−7.33 (m, 10H), 7.21 (m, 1H), 6.95 (m, 1H), 6.56 (d, J = 8.4 Hz, 1H), 3.79 (m, 1H), 3.17 (d, J = 12.1 Hz, 1H), 2.75 (m, 1H), 2.43 (d, J = 12,1, 1H), 2.10 (m, 1H), 1.68−1.75 (m, 2H), 1.40 (m, 1H), 1.30 (m, 1H), 1.02 (dd, J = 13.6, 4.8 Hz, 1H), 0.90−0.97 (m, 6H). ^{13}C NMR($CDCl_3$) δ: 143.6, 143.2, 136.8, 136.5, 136.4, 133.7, 133.5, 133.4, 133.2, 129.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.5, 84.2, 83.1, 82.6, 44.7, 44.1, 34.3, 33.2, 27.9, 25.9, 19.6, 18.7. Anal. Calcd for $C_{29}H_{31}OPS$: C, 75.97; H, 6.80. Found: C, 75.72; H, 6.86. MS *m*/*z*: 458 (M^+).

(1*R*,3*R*,6*R*)-5,5,9-Trimethyl-2-oxa-3-(2-diphenylphosphino)phenyl-4-thiabicyclo[4.4.0]decane (7). 3,7,7-Trimethyl-7-mercaptomenthol **6** (100 mg, 0.54 mmol), 2-(diphenylphosphino)-benzaldehyde **2** (157 mg, 0.54 mmol), *p*-toluenesulfonic acid monohydrate (10 mg, 0.054 mmol), and toluene (10 mL) were placed in a flask equipped with a Dean−Stark trap. The mixture was refluxed for 6 h. The solvent was evaporated under a reduced pressure, and the residue was purified by preparative TLC (hexane: ether = 40:1) to give a pure **7** (75 mg) in 30% yield. mp 55−57 °C, $[\alpha]^{23}_D = -33.3$ (*c* 2.10, $CHCl_3$). IR (film) cm^{-1}: 745, 717, 706. ^1H NMR ($CDCl_3$): δ ($CDCl_3$): 7.76 (m, 1H), 7.25−7.39 (m, 11H), 7.17 (t, J = 7.4 Hz, 1H), 6.89 (m, 1H), 6.61 (d, J = 8.2 Hz, 1H), 3.39 (ddd, J = 10.2, 10.1, 4.0 Hz, 1H), 1.82 (m, 1H), 1.66−1.79 (m, 2H), 1.50 (m, 1H), 1.40 (m, 1H), 1.36 (s, 3H), 1.19 (s, 3H), 1.05 (br q, 1H), 0.87 (d, J = 6.6 Hz, 3H), 0.86 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 143.44, 143.10, 137.08, 136.28, 136.14, 134.23, 133.94, 133.73, 133.44, 133.39, 129.39, 128.59, 128.37, 128.35, 128.32, 128.25, 128.23, 127.56, 78.68, 78.21, 77.83, 50.59, 44.34, 41.72, 34.82, 31.51, 24.48, 22.48, 22.17. Anal. Calcd for $C_{29}H_{33}OPS$: C, 75.62; H, 7.22. Found: C, 75.45; H, 6.97. MS *m*/*z*: 460 (M^+).

Typical Procedure of Pd-Catalyzed Asymmetric Allylation of *rac*-1,3-Diphenyl-2-propenyl Acetate (8) with Dimethyl Malonate. A mixture of the ligand **3** (3.67 mg, 0.008 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.46 mg, 0.004 mmol) in dry dichloromethane (1 mL) was stirred at room temperature for 1 h, and the resulting yellow solution was added to a mixture of acetate **8** (100 mg, 0.40 mmol) and potassium acetate (0.8 mg, 0.008 mmol) in dry dichloromethane (1 mL) followed by the addition of dimethyl malonate (160 mg, 1.20 mmol) and BSA (240 mg, 1.20 mmol). The reaction was carried out an ambient temperature. The reaction mixture was diluted with ether and quenched with sat. NH_4Cl. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated under a reduced pressure, and the residue was purified by preparative TLC (hexane:ether = 5:1) to give a pure product **9**. The enantiomeric excess was determined by HPLC (Chiralcel OD-H, 0.5 mL/min, hexane:2-propanol = 98:2). The absolute configuration was determined by the specific rotation.[3a,b,m]

Typical Procedure of Pd-Catalyzed Asymmetric Allylation of Cinnamyl Acetate (10) with Dimethyl Malonate. A mixture of ligands **3** or **5** (5.23 mg, 0.0114 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.09 mg, 0.0057 mmol) in dry dichloromethane (1 mL) was stirred at room temperature for 1 h, and the resulting yellow solution was added to a mixture of acetate **10** (100 mg, 0.57 mmol) and potassium acetate (1.1 mg, 0.011 mmol) in dry dichloromethane (1 mL), followed by the addition of dimethyl malonate (226 mg, 1.71 mmol) and BSA (348 mg, 1.71 mmol). The mixture was stirred at the temperature as shown in Table 2, diluted with ether, and quenched with sat. NH_4Cl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under a reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/AcOEt (5:1) as an eluent to afford a mixture of **11** and **12**. The enantiomeric excess of **11** was determined by HPLC (Chiralcel OJ, 0.5 mL/min, hexane:2-propanol = 93:7). The absolute configuration was determined by the specific rotation.[3g,m]

Typical Procedure of Pd-Catalyzed Asymmetric Allylic Amination of *rac*-1,3-Diphenyl-2-propenyl Acetate (8) with Benzylamine. The chiral ligands **3** or **5** (3.67 mg, 0.008 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.46 mg, 0.004 mmol) were dissolved in dry dichloromethane (1 mL) under Ar, and the solution was stirred at room temperature. After 1 h, the solution of the acetate **8** (100 mg, 0.40 mmol) in dry dichloromethane (1 mL) and benzylamine (1.1 mg, 10 mmol) was added to the above solution, and the mixture was stirred at the temperature as shown in Table 3. The mixture was subjected to column chromatography on silica gel with hexane/AcOEt (5:1) as an eluent to give compound **14a**. The enantiomeric excess was determined by HPLC (Chiralcel OD-H, 0.5 mL/min, hexane:2-propanol = 199:1). The absolute configuration was determined by the specific rotation.[9a]

Typical Procedure of Pd-Catalyzed Asymmetric Allylic Amination of *rac*-1,3-Diphenyl-2-propenyl Acetate (8) with Potassium Phthalimide. The chiral ligands **3** or **5** (9.16 mg, 0.02 mmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.66 mg, 0.01 mmol) were dissolved in dry dichloromethane (1 mL) under Ar, and the solution was stirred at room temperature. After 1 h, the above solution and the solution of acetate **8** (100 mg, 0.40 mmol) in dry dichloromethane (1 mL) were added to the suspension of potassium phthalimide (222 mg, 1.2 mmol) in dry dichloromethane (1 mL). The reaction mixture was stirred at the temperature as shown in Table 3, quenched by the addition of water, and diluted with ether. The combined organics were dried and concentrated under a reduced pressure. Purification of the residue by column chromatography on silica gel with hexane/AcOEt (5:1) afforded the compound **14b**. The enantiomeric excess was determined by HPLC (Chiralcel OD-H, 0.5 mL/min, hexane:2-propanol = 98:2). The absolute configulation was determined by the specific rotation.[9d]

Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **3**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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