π-Allylic Sulfonylation in Water with Amphiphilic Resin-Supported Palladium–Phosphine Complexes

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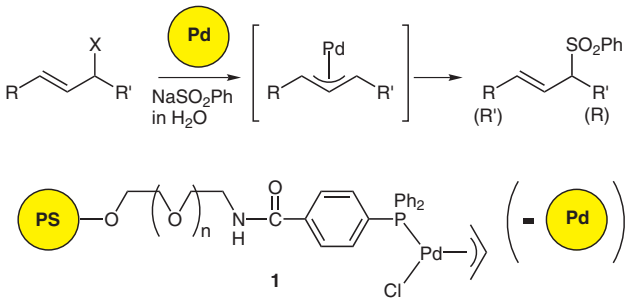
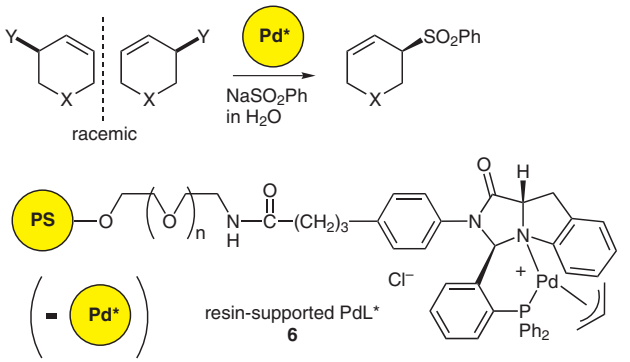
Abstract: π-Allylic substitution of allyl esters with sodium arylsulfinate was performed with an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phosphine-palladium complex in water as a single reaction medium under heterogeneous conditions to give allyl sulfones in good to high yields. Catalytic asymmetric allylic substitution of cycloalkenyl esters also took place in water using a PS-PEG resin-supported chiral imidazoindolephosphine-palladium complex to give cycloalkenyl sulfones with up to 81% ee.

Key words: π-allylpalladium, sulfone, aqueous media, polymer support, palladium catalyst



Scheme 1 π-Allylic sulfonylation



Scheme 2 Asymmetric π-allylic sulfonylation

The palladium-catalyzed allylic substitution reaction, the Tsuji–Trost reaction, has been recognized as one of the most powerful carbon–carbon and carbon–nitrogen bond-forming reactions in use today. However, in spite of the widespread synthetic utility of allyl sulfones,[1,2] the well-developed research on π-allylic sulfonylation has been limited to isolated reports.[3–5] One of the major problems associated with the π-allylic sulfonylation lies in the low solubility of the sulfone nucleophiles, for example, sodium sulfinates, in organic solvents. We have recently developed amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phosphine–palladium complexes which promote various catalytic transformations,[6] including allylic substitution,[7] smoothly in water[8] under heterogeneous conditions[9,10] to meet the requirements of safe, green, and high-throughput chemical processes. Our continuing interest in the aquacatalytic utility of PS-PEG resin-supported palladium complexes led us to examine the π-allylic sulfonylation in water with the PS-PEG-Pd complexes.[11] We report herein a heterogeneous aquacatalytic π-allylic substitution of various allyl esters with sodium arylsulfinate (Scheme 1), and also describe our preliminary studies on the asymmetric π-allylic sulfonylation of cycloalkenyl esters (up to 81% ee) (Scheme 2).[12]

The reaction of methyl cinnamyl carbonate (**2a**) with sodium benzenesulfinate was carried out in water at 25 °C for 12 hours in the presence of 5 mol% palladium of the PS-PEG (TentaGel)[13] resin-supported π-allylpalladium–triarylphosphine complex **1**.

The catalyst resin beads were filtered off and extracted with a small portion of ethyl acetate to give 86% yield of cinnamyl phenyl sulfone (**3a**) (Table 1, entry 1). A range of acyclic and cyclic carbonates of the corresponding primary, secondary, and tertiary allylic alcohols were readily sulfonylated under similar conditions. Representative results are summarized in Table 1. The carbonate ester **2b**, the allylic isomer of cinnamyl carbonate **2a**, gave exclusively cinnamyl phenyl sulfone **3a** (entry 2), when the same procedure for entry 1 was employed, in which the isomeric sulfone **3b** (Figure 1) was not detected on GC. The sulfonylation of the aryl vinyl carbinol esters **2c** and **2d** bearing electron-donating and -withdrawing substituents at their para positions gave the cinnamyl sulfones **3c** and **3d** in 84 and 83% yield, respectively (entries 3 and 4).

The diphenylpropenyl ester **2e** also underwent sulfonylation to give **3e** in 90% yield (entry 5). Geranyl, neryl, and linalyl carbonates **2f**, **2g**, and **2h** reacted with sodium sulfinate under similar conditions to give 62, 78, and 89% yield, respectively, of a mixture of regioisomeric sulfonylation products **3f** and **3h** (entries 6, 7, and 8). The ratios of the geranyl sulfone **3f** and the linalyl sulfone **3h** obtained from the reactions of **2f**, **2g**, and **2h** were almost the

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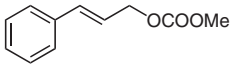
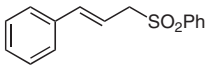
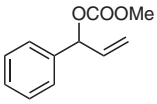
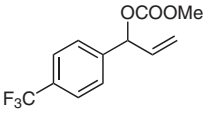
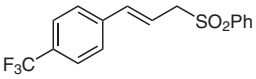
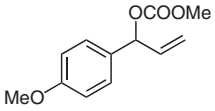
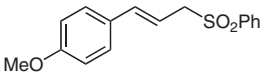
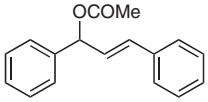
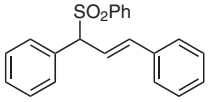
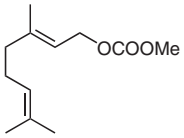
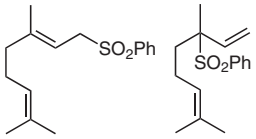
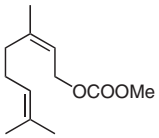
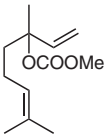
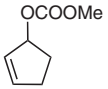
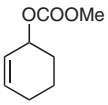
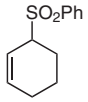
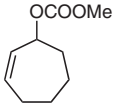
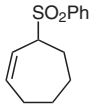
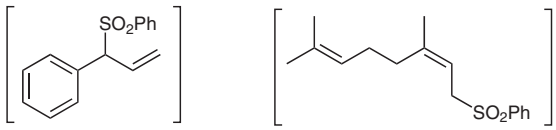
Table 1 π-Allylic Sulfonylation of Allyl Carbonates **2** in H_2O[a]

Entry	Allyl ester **2**	Product **3**	Yield (%)
1	 **2a**	 **3a**	86
2	 **2b**	**3a**	84
3	 **2c**	 **3c**	84
4	 **2d**	 **3d**	83
5	 **2e**	 **3e**	90
6	 **2f**	 **3f** (11:89) **3h**	62
7	 **2g**	**3f/3h** (11:89)	78
8	 **2h**	**3f/3h** (11:89)	89
9	 **2i**	 **3i**	80
10	 **2j**	 **3j**	84
11	 **2k**	 **3k**	86

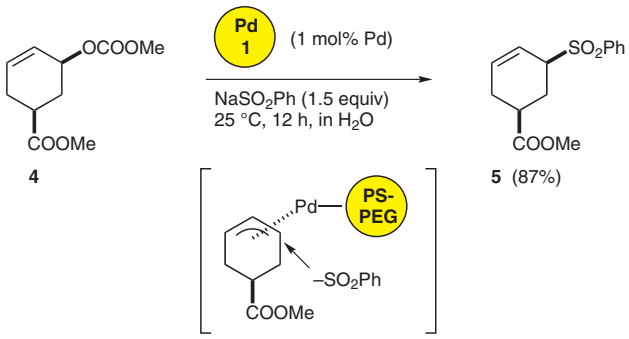
[a] All reactions were carried out in H_2O at 25 °C for 12 h. The ratio of **2** (mol)/$NaSO_2Ph$ (mol)/Pd (mol)/H_2O (L) = 1:1.5:0.05:2.

same (**3f/3h** = 1:9); the neryl sulfone **3g** (Figure 1) was not observed at all. These results demonstrate that the reactions of **2f–h** proceeded by way of the same π-allylpalladium intermediate. The cyclic substrates **2i**, **2j**, and **2k** also underwent π-allylic sulfonylation to afford the corresponding sulfones **3i**, **3j**, and **3k** in 80, 84, and 86% isolated yield, respectively. The sulfonylation of *cis*-5-methoxycarbonylcyclohex-2-enyl methyl carbonate (**4**) was also catalyzed by the PS-PEG palladium **1** in water at 25 °C to afford the *cis*-5-methoxycarbonylcyclohex-2-enyl phenyl sulfone (**5**) in 87% yield (Scheme 3). The exclusive formation of the cycloalkenyl sulfone **5** having the *cis*-configuration from the *cis*-allylic ester **4** revealed that this π-allylic sulfonylation proceeds via a double-inversion pathway (π-allylpalladium formation and nucleophilic attack with a sulfinate anion) in water under these conditions.



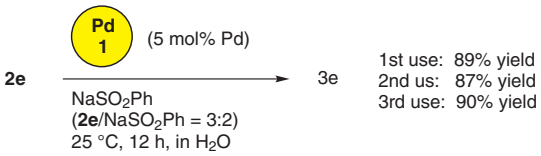
3b **3g**

Figure 1



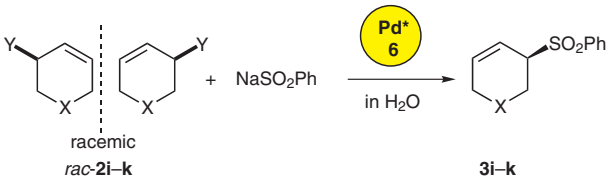
Scheme 3

Recycling experiments were examined for sulfonylation of the diphenylpropenyl ester **2e**. After the first use of the polymeric palladium catalyst **1** (Table 1, entry 5) to give 87% yield of the adduct **3e**, the recovered catalyst beads were taken on to two reuses and exhibited stable catalytic activity (Scheme 4).



Scheme 4 Recycling experiments

Using this π-allylic sulfonylation protocol, we examined next the catalytic asymmetric sulfonylation in water with an amphiphilic PS-PEG resin-supported chiral palladium complex.[14,15] We previously reported the heterogeneous



(*S*)-**3i**: X = none; 25 °C, 1 h; 80% yield, 45% ee
(*S*)-**3j**: X = CH_2; 25 °C, 1 h; 78% yield, 33% ee
(*S*)-**3k**: X = CH_2CH_2; 25 °C, 1 h; 84% yield, 71% ee
25 °C, 12 h; 83% yield, 10% ee
0 °C, 0.5 h; 52% yield, 81% ee

Scheme 5 Asymmetric substitution in H_2O

aquacatalytic chiral process by catalytic asymmetric π-allylic alkylation and amination of cycloalkenyl esters using a palladium catalyst coordinated with a novel optically active ligand, (3*R*,9a*S*)-[2-aryl-3-(2-diphenylphosphino)phenyl]tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one, anchored onto PS-PEG resin (Scheme 2, polymeric ligand **6**). Preliminary studies on the aquacatalytic asymmetric allylic sulfonylation of cycloalkenyl esters was examined with cycloheptenyl methyl carbonate **2k** (Scheme 5). When a mixture of the cycloheptenyl carbonate **2k** and 1.5 equivalents of sodium sulfinate in water was shaken at 25 °C for 1 hour in the presence of the PS-PEG resin-supported chiral palladium–imidazoindole phosphine **6** (5 mol% palladium), the 3-(phenylsulfonyl)cyclohept-1-ene (**3k**) was obtained in 84% yield. The enantiomeric purity of **3k** was determined by HPLC analysis [Chiralcel OD-H (500 mm), *n*-hexane–*i*-PrOH, 9:1] to be 71% ee, and the absolute configuration was determined to be *S* by measurement of the specific rotation ($[\alpha]_D^{25}$ –145 (*c* 1.0, CH_2Cl_2)). The cyclohexenyl and cyclopentenyl carbonates **2j** and **2i** gave the corresponding cycloalkenyl sulfones **3j** and **3i** in 33 and 45% ee, respectively. The enantiomeric purity of the sulfonylated product **3k** decreased as the reaction time was prolonged. Thus, the sulfonylation of **2k** for 12 hours gave only 10% ee of the product **3k** under otherwise similar reaction conditions, whereas 71% ee of **3k** was obtained in one hour. It has been reported that allyl sulfones can react with dialkyl malonate derivatives under basic conditions in the presence of a palladium(0) catalyst via π-allylpalladium intermediates.[16] During the asymmetric sulfonylation of **2k**, the enantiomerically enriched **3k** generated in situ should undergo the π-allylpalladium formation and subsequent (nonproductive) sulfonylation to result in the racemization of **3k**. The highly enantiomerically enriched **3k** of 81% ee was obtained when the asymmetric sulfonylation of the cycloheptenyl carbonate **2k** was carried out at 0 °C for 30 minutes.

In summary, the palladium-catalyzed π-allylic sulfonylation was achieved with sodium benzenesulfinate in water with polymeric palladium complexes to meet safe and green chemical requirements. Asymmetric π-allylic sulfonylation of cycloalkenyl carbonates was also carried out in water without any organic solvent to give up to 81% ee.

All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Water was deionized with a Millipore system as Milli-Q grade. NMR spectra were recorded on a JEOL JNM-AL400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a JEOL JNM-LA500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C. Chemical shifts were reported in ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR were given relative to $CDCl_3$ as an internal standard (δ = 77.0 ppm). The mass spectral data were measured on an Agilent 6890 GC/5973N MS detector (GC-MS) and JEOL JMS-700 (EI-MS); the abbreviation 'bp' is used to denote the base peak. IR analysis was performed on a JASCO FTIR-460. Optical rotations were measured on a JASCO P-1020 polarimeter. HPLC analysis was performed on a JASCO PU-1580 liquid chromatograph system. PS-PEG-supported catalysts were prepared from PS-PEG amino-resin (TentaGelS NH_2, average diameter 0.90 μm, 1% divinylbenzene cross-linked, loading value of amino residue 0.31 mmol/g; purchased from RAPP POLYMERETM) according to the reported procedure.[7b,12c]

CAS Registry No.: **3a**, 16212-07-0; **3d**, 863310-91-2; **3e**, 191542-63-9; **3f**, 56691-80-6; **3h**, 91940-11-3; **3i**, 140396-96-9; **3j**, 87413-32-9; **3k**, 131179-47-0; **5**, 74866-39-0.

Palladium-Catalyzed Allylic Substitution of Allyl Esters with Sodium Benzenesulfinate; 3-(Phenylsulfonyl)-1-phenylpropene (3a); Typical Procedure

To a mixture of the catalyst **1** (92 mg, 0.025 mmol) and cinnamyl carbonate (**2a**; 96.0 mg, 0.5 mmol) in H_2O (2.0 mL) was added sodium benzenesulfinate (150 mg, 0.75 mmol) and the mixture was stirred at 25 °C for 12 h. The mixture was filtered and the recovered resin beads were rinsed with EtOAc (3 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (5 mL). The combined EtOAc extracts were washed with brine (2 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (hexane–EtOAc, 1:1) to give 110.8 mg (86%) of **3a** (Table 1).

IR (ATR): 2982, 1237, 1086 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 7.3 Hz, 2 H), 7.63 (t, *J* = 7.3 Hz, 1 H), 7.54 (t, *J* = 7.3 Hz, 2 H), 7.32–7.25 (m, 5 H), 6.36 (d, *J* = 15.8 Hz 1 H), 6.09 (td, *J* = 7.9, 15.8 Hz, 1 H), 3.95 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 139.1 (2 C), 138.3, 135.6, 133.7, 129.0, 128.6 (4 C), 126.5, 115.0, 60.4.

MS (EI): *m*/*z* (%) = 258 (2, M^+), 198 (7), 117 (bp), 77 (75).

3-(Phenylsulfonyl)-1-(4-trifluoromethylphenyl)propene (3c)

IR (ATR): 2925, 1302, 1084, 892 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 7.3 Hz, 2 H), 7.66 (t, *J* = 7.3 Hz, 1 H), 7.55 (t, *J* = 7.3 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 6.42 (d, *J* = 16.1 Hz, 1 H), 6.21 (td, *J* = 7.3, 16.1 Hz 1 H), 3.97 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 139.0, 138.3, 137.7, 133.9, 130.3 (q, *J* = 36.4 Hz), 129.1, 128.4, 126.7, 125.6 (q, *J* = 4.1 Hz), 123.9 (q, *J* = 267.8 Hz), 117.9, 60.2.

MS (EI): *m*/*z* (%) = 307 (1, M^+ – F), 165 (51), 115 (67), 77 (bp), 51 (58).

Anal. Calcd for $C_{16}H_{13}F_3O_2S$: C, 58.89; H, 4.02. Found: C, 58.44; H, 4.11.

3-(Phenylsulfonyl)-1-(4-methoxyphenyl)propene (3d)

IR (ATR): 2983, 1606, 1509, 1249, 1135 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 7.9 Hz, 2 H), 7.63 (t, *J* = 7.9 Hz, 1 H), 7.53 (t, *J* = 7.9 Hz, 1 H), 7.21 (d, *J* = 9.1 Hz, 2 H), 6.84 (d, *J* = 9.1 Hz, 2 H), 6.30 (d, *J* = 15.8 Hz, 1 H), 5.95 (td, *J* = 7.3, 15.8 Hz 1 H), 3.56 (d, *J* = 7.3 Hz, 2 H), 3.80 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 159.8, 138.6, 133.6, 130.9, 129.0, 128.5, 127.8, 127.6, 114.0, 112.5, 60.5, 55.2.

MS (EI): *m*/*z* (%) = 288 (10, M^+), 197 (9), 115 (bp), 51 (67).

3-(Phenylsulfonyl)-1,3-diphenylprop-2-ene (3e)
IR (ATR): 3060, 1142, 1082 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.65 (d, *J* = 7.3 Hz, 2 H), 7.54 (t, *J* = 7.3 Hz, 1 H), 7.39 (t, *J* = 7.3 Hz, 2 H), 7.35–7.25 (m, 10 H), 6.56 (dd, *J* = 15.6, 8.7 Hz, 1 H), 6.49 (d, *J* = 15.6 Hz, 1 H), 4.81 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 156.4, 155.6, 154.1, 150.5, 148.0, 147.6, 147.2, 147.0, 146.9, 146.9, 146.8, 145.0, 138.2, 93.7.

MS (EI): *m*/*z* (%) = 334 (0.5, M^+), 191 (42), 115 (bp), 91 (41).

Geranyl Phenyl Sulfone (3f)
IR (ATR): 2918, 1446, 1294, 1144, 1085 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.88–7.85 (m, 2 H), 7.65–7.61 (m, 1 H), 7.55–7.51 (m, 2 H), 5.18 (t, *J* = 8.0 Hz, 1 H), 5.02 (m, 1 H), 3.80 (d, *J* = 8.0 Hz, 2 H), 2.18–1.94 (m, 4 H), 1.68 (s, 3 H), 1.58 (s, 3 H), 1.31 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 146.3, 138.6, 133.4, 132.0, 128.9, 128.5, 123.4, 110.2, 56.0, 39.6, 26.1, 25.6, 17.6, 16.1.

MS (EI): *m*/*z* (%) = 169 (1, $M^+ - O_2Ph$), 141 (10), 77 (91), 41 (bp).

Linalyl Phenyl Sulfone (3h)
IR (ATR): 2918, 1446, 1294, 1144, 1085 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 8.3 Hz, 1 H), 7.48 (t, *J* = 8.3 Hz, 2 H), 5.89 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.33 (d, *J* = 10.7 Hz, 1 H), 5.03 (d, *J* = 17.5 Hz, 1 H), 5.01 (m, 1 H), 1.96–1.83 (m, 4 H), 1.63 (s, 3 H), 1.52 (s, 3 H), 1.34 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 135.1, 133.4, 130.7, 128.8, 128.2, 123.0, 120.4, 110.2, 68.2, 32.7, 25.5, 22.4, 17.6, 16.1.

MS (EI): *m*/*z* (%) = 169 (1, $M^+ - O_2Ph$), 141 (10), 77 (91), 41 (bp).

3-(Phenylsulfonyl)cyclopent-1-ene (3i)
IR (ATR): 2936, 1302, 1138, 1084 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 7.3 Hz, 2 H), 7.65 (t, *J* = 7.3 Hz, 1 H), 7.54 (t, *J* = 7.3 Hz, 2 H), 6.12–6.10 (m, 1 H), 5.68–5.66 (m, 1 H), 4.29–4.27 (m, 1 H), 2.39–2.13 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 140.2, 137.5, 133.5, 129.0, 128.8, 123.7, 72.3, 31.8, 24.4.

MS (EI): *m*/*z* (%) = 209 (0.1, M^+ + H), 143 (6), 67 (bp).

3-(Phenylsulfonyl)cyclohex-1-ene (3j)
IR (ATR): 2938, 1302, 1084 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 7.8 Hz, 2 H), 7.65 (t, *J* = 7.8 Hz, 1 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 6.10–6.07 (m, 1 H), 5.79–5.77 (m, 1 H), 3.77–3.75 (m, 1 H), 2.01–1.73 (m, 5 H), 1.53–1.46 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 137.3, 135.2, 133.5, 129.1, 128.9, 118.4, 61.7, 24.3, 22.6, 19.4.

MS (EI): *m*/*z* (%) = 223 (33, M^+ + H), 143 (99), 77 (bp).

3-(Phenylsulfonyl)cyclohept-1-ene (3k)
IR (ATR): 2926, 1303, 1084 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.91 (d, *J* = 8.2 Hz, 2 H), 7.65 (t, *J* = 8.2 Hz, 1 H), 7.56 (t, *J* = 8.2 Hz, 2 H), 6.04–5.99 (m, 1 H), 5.82–5.79 (m, 1 H), 3.86–3.83 (m, 1 H), 2.23–2.19 (m, 2 H), 2.08–2.20 (m, 2 H), 1.72–1.58 (m, 3 H), 1.46–1.44 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 137.8, 136.8, 133.5, 129.0, 128.9, 123.7, 66.2, 27.9, 27.8, 26.8, 25.9.

MS (EI): *m*/*z* (%) = 237 (3, M^+ + H), 143 (99), 95 (bp).

***cis*-5-Methoxycarbonylcyclohex-2-enyl Phenyl Sulfone (5)**
IR (ATR): 2979, 1731, 1085 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 7.8 Hz, 2 H), 7.67 (t, *J* = 7.8 Hz, 1 H), 7.57 (t, *J* = 7.8 Hz, 2 H), 6.05–6.02 (m, 1 H), 5.90 (d, *J* = 10.2 Hz, 1 H), 3.92–3.89 (m, 1 H), 3.69 (s, 3 H), 2.57–2.53 (m, 1 H), 2.40–2.38 (m, 1 H), 2.33–2.25 (m, 1 H), 2.10–2.02 (m, 1 H), 5.67 (d, *J* = 10.3 Hz, 1 H), 3.99 (br s, 1 H), 3.72 (s, 3 H), 2.67 (dddd, *J* = 12.2, 9.7, 6.4, 2.4 Hz, 1 H), 2.42–2.24 (m, 3 H), 1.72 (ddd, *J* = 12.3, 12.3, 12.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 174.1, 136.3, 133.8, 132.5, 129.1, 129.0, 118.9, 62.7, 52.1, 38.1, 27.2, 25.5.

MS (EI): *m*/*z* (%) = 280 (0.3, M^+), 139 (16), 79 (bp), 51 (30).

Palladium-Catalyzed Asymmetric Allylic Substitution of Cyclic Allyl Esters with Sodium Benzenesulfinate; (*S*)-3-(Phenylsulfonyl)cyclohept-1-ene [(*S*)-3k]; Typical Procedure
To a mixture of the catalyst **6** (89 mg, 0.025 mmol) and methyl cycloheptenyl carbonate (**2k**; 85.0 mg, 0.5 mmol) in H_2O (2.0 mL) was added sodium benzenesulfinate (150 mg, 0.75 mmol) and the mixture was stirred at 25 °C for 1 h. The mixture was filtered and the recovered resin beads were rinsed with EtOAc (3 mL). The EtOAc layer was separated and the aqueous layer was extracted with EtOAc (5 mL). The combined EtOAc extracts were washed with brine (2 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (hexane–EtOAc, 2:1) to give 65 mg (84%) of (*S*)-**3k**; $[\alpha]_D^{19}$ –145 (*c* 1.0, CH_2Cl_2); ee 71% {Lit.[15] $[\alpha]_D^{25}$ –89.6 (*c* 3.84, CH_2Cl_2) for (*S*)-**3k** of 94% ee}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Chiralcel OD-H (500 mm); eluent: *n*-hexane–*i*-PrOH, 9:1; flow rate: 0.5 mL/min; t_R: major isomer 59 min and minor isomer 62 min].

Spectral data of (*S*)-**3k** were identical with that of **3k** given above.

(*S*)-3i
$[\alpha]_D^{20}$ –179.9 (*c* 0.45, CH_2Cl_2); ee 45% {Lit.[15] $[\alpha]_D^{20}$ –216.6 (*c* 1.56, CH_2Cl_2) for (*S*)-**3i** of 98% ee}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Chiralcel OD-H (500 mm); eluent: *n*-hexane–*i*-PrOH, 9:1; flow rate: 0.5 mL/min; t_R: major isomer 77 min and minor isomer 82 min].

Spectral data of (*S*)-**3i** were identical with that of **3i** given above.

(*S*)-3j
$[\alpha]_D^{20}$ –60.0 (*c* 0.4, CH_2Cl_2); ee 33% {Lit.[15] $[\alpha]_D^{20}$ –136.8 (*c* 3.84, CH_2Cl_2) for (*S*)-**3j** of 98% ee}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [Chiralcel AD-H (500 mm); eluent: *n*-hexane–*i*-PrOH, 9:1; flow rate: 0.5 mL/min; t_R: major isomer 68 min and minor isomer 71 min].

Spectral data of (*S*)-**3j** were identical with that of **3j** given above.

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