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Enantioselective Heck-Type Reaction Catalyzed by *tropos*-Pd(II) Complex with Chiraphos Ligand

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Abstract: The Pd(II)-catalyzed enantioselective organoboron-mediated Heck-type reaction is shown to proceed under molecular oxygen as an oxidant. The $Pd(OAc)_2$/(*S,S*)-chiraphos catalyst gives good yield and the best enantioselectivity. Among the two possible δ- and λ-conformations in equilibrium, this reaction proceeds *via* the λ-conformation of chiraphos with the two methyl groups in a diaxial orientation.

Keywords: aerobic oxidation; asymmetric catalysis; chiraphos; Heck-type reaction; palladium

Introduction

Palladium-catalyzed C–C bond formation is one of the most important and useful reactions in recent organic synthesis[1]. Palladium-catalyzed C–C bond forming reactions are classified into two types: Pd(0)- or Pd(II)-catalyzed reactions (Figure 1). The Pd(0) catalysis has been widely studied in synthetically useful reactions, for example, Suzuki–Miyaura and Mizoroki–Heck reactions. In contrast, the Pd(II)-catalyzed reaction has been limited so far,[2] particularly in an asymmetric version.

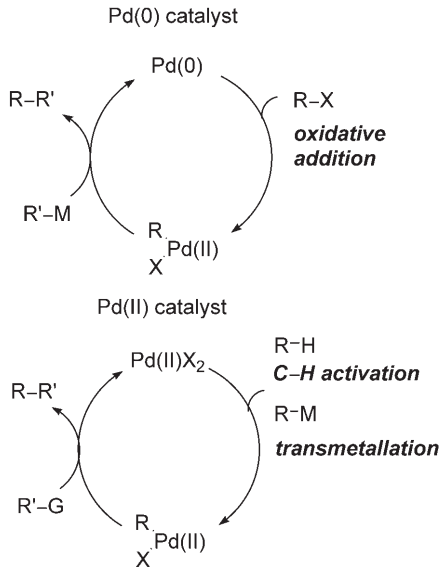


Figure 1. Pd(0) and Pd(II) catalytic cycles.

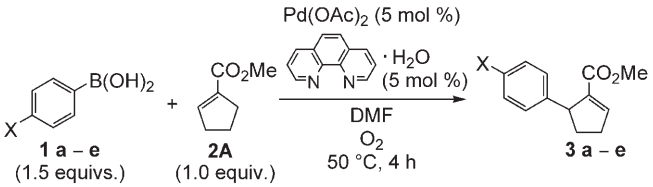
However, Pd(II) catalysis has a unique feature that the first catalytic step should involve C–H activation[3,4] or transmetallation[5] (Figure 1).

One of the most attractive Pd(II)-catalyzed reactions is the organoboron-mediated Heck-type reaction first reported by Heck with stoichiometric amounts of a Pd(II) complex.[6] The first catalytic system was reported by Uemura,[7] however, with a Pd(0) catalyst. The oxidative addition to the carbon-boron bond was proposed to be the initial catalytic step. Recently, Mori reported the Pd(II)-catalyzed organoboron-mediated Heck-type reaction using $Cu(OAc)_2$ as an oxidant.[8] Jung reported molecular oxygen as an oxidant.[9] Furthermore, Larhed reported the first ligand-modulated reaction using 2,9-dimethyl-1,10-phenanthroline.[10] To the best of our knowledge, however, there is no report on the asymmetric catalysis. Herein we report the first Pd(II)-catalyzed, enantioselective organoboron-mediated Heck-type reaction using a Pd/chiraphos complex. Among the two possible δ- and λ-conformations in equilibrium, this reaction is found to proceed *via* the λ-conformation of chiraphos with two methyl groups in an axial orientation.

Result and Discussion

We examined phenylboronic acid (**1c**) and methyl 1-cyclopentenecarboxylate (**2A**) as reaction substrates. The coupling reaction was carried out in the presence of $Pd(OAc)_2$ and an achiral ligand, 1,10-phenanthroline monohydrate under an oxygen atmosphere in DMF to give the product **3c** in 11% yield (Table 1, entry 3).

Table 1. The effect of *para* substituent on phenylboronic acid.



Entry	X	Yield [%][a]
1	OMe (**1a**)	-
2	Me (**1b**)	trace
3	H (**1c**)	11%
4	Cl (**1d**)	15%
5	CF_3 (**1e**)	48%
6[b]	CF_3 (**1e**)	trace

[a] NMR yield (1,1,1,2-tetrachloroethane as internal standard).
[b] Reaction under argon.

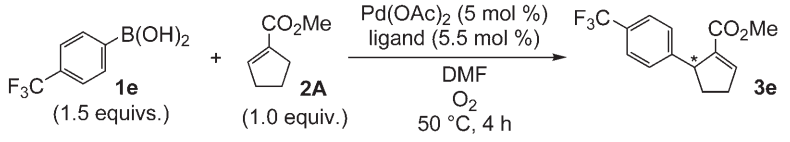
The low reactivity may be due to the difficulty in transmetallation. Therefore we examined several phenylboronic acids **1a**–**e** with a substituent at the *para* position to control the electronic environment on the boron atom. Upon introducing electron-donating groups as in **1a** and **1b** (X = OMe and Me), the product was not obtained (entries 1 and 2). In contrast, the electron-withdrawing groups in **1d** (X = Cl) and **1e** (X = CF_3) increase the reactivity (entries 4 and 5). Using the trifluoromethyl substituent in **1e** (X = CF_3), **3e** was obtained in the highest yield (49%) (entry 5). Under an argon atmosphere the same reaction of **1e** and **2A** did not proceed (entry 6). This result indicates that oxygen is essential to regenerate the Pd(II) catalyst.

We examined several chiral ligands; five- and six-membered chelating bis-oxazoline ligands **4**, **5a**, **5b**, five-membered chelating oxazoline-pyridine ligands **6a**, **6b**, and five-, six-, and seven-membered chelating bis-phosphine ligands, (*S,S*)-chiraphos, (*R,R*)-Me-BPE, (*S,S*)-skewphos, (*R,R*)-DIOP, and (*S*)-BINAP (Table 2). Five-membered chelating ligands **4**, **6a**, **6b** (entries 1, 4, and 5), (*S,S*)-chiraphos (entry 6), and (*R,R*)-Me-BPE (entry 7) provided higher yields than six- or seven-membered chelating ligands. Particularly, **6a**, **6b**, (*S,S*)-chiraphos, and (*R,R*)-Me-BPE gave good yields (69–77%). These results suggest that five-membered chelating ligands provide higher catalytic activity in the Pd complexes. Especially (*S,S*)-chiraphos gave a good yield and the highest enantioselectivity (73%, 46% ee).

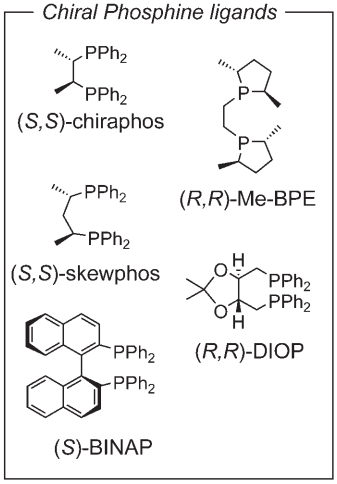
The solvent effect was examined using the $Pd(OAc)_2$/(*S,S*)-chiraphos complex **7** (Table 3). Methanol, toluene, 1,2-dichloroethane, THF, DMSO, DMF, and acetic acid were examined. The highest enantioselectivity was obtained using methanol (59% ee), although the yield was low (entry 1). In contrast, DMF gave the highest yield (68%, 46% ee) (entry 6).

On the basis of these results, several 1-cyclopentenecarboxylates **2A**–**E** were examined using the $Pd(OAc)_2$/(*S,S*)-chiraphos catalyst. The ethyl ester **2B**

Table 2. Chiral ligands for the enantioselective Heck-type reaction.

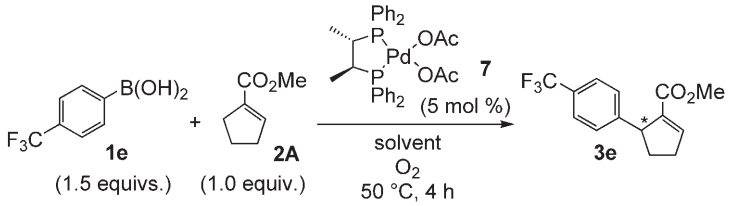


Entry	Chelate ring	Ligand	Yield [%][a]	ee [%]
1	5	**4** (*S,S*)	47	16
2	6	**5** (*R,R*) R = Ph (**5a**)	15	10
3		= *i*-Pr (**5b**)	21	13
4	5	**6** (*S*) R= *i*-Pr (**6a**)	77	23
5		= *t*-Bu (**6b**)	69	15
6	5	(*S,S*)-chiraphos	73	46
7		(*R,R*)-Me-BPE	73	1
8	6	(*S,S*)-skewphos	trace	20
9	7	(*R,R*)-DIOP	31	0
10		(*S*)-BINAP	-	-



[a] Yield of isolated product.

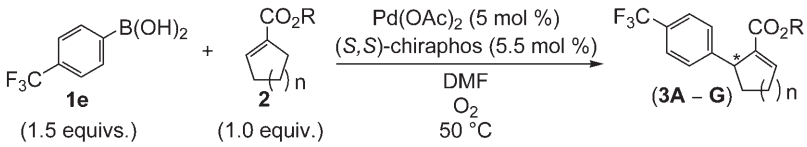
Table 3. The solvent effect on the Pd(II)$(OAc)_2$/(*S,S*)-chiraphos complex-catalyzed enantioselective Heck-type reaction.



Entry	Solvent	Yield [%][a]	ee [%]
1	MeOH	25	59
2	toluene	17[b]	58
3	CH_2ClCH_2Cl	trace	-
4	THF	25	54
5	DMSO	42	51
6	DMF	68	45
7	AcOH	5	-

[a] Yield of isolated products.
[b] NMR yield (1,1,1,2-tetrachloroethane as internal standard).

Table 4. Olefin substrates for enantioselective Heck-type reactions.



Entry	Substrate	Time [h]	Yield [%][a]	ee [%]
1	R= Me (**2A**)	4	73	46
2	Et (**2B**)		72	46
3	*i*-Pr (**2C**)		49	35
4	Ph (**2D**)		31	22
5	Bn (**2E**)		58	49
6	(**2F**)	24	trace	-
7	(**2G**)	24	trace	-

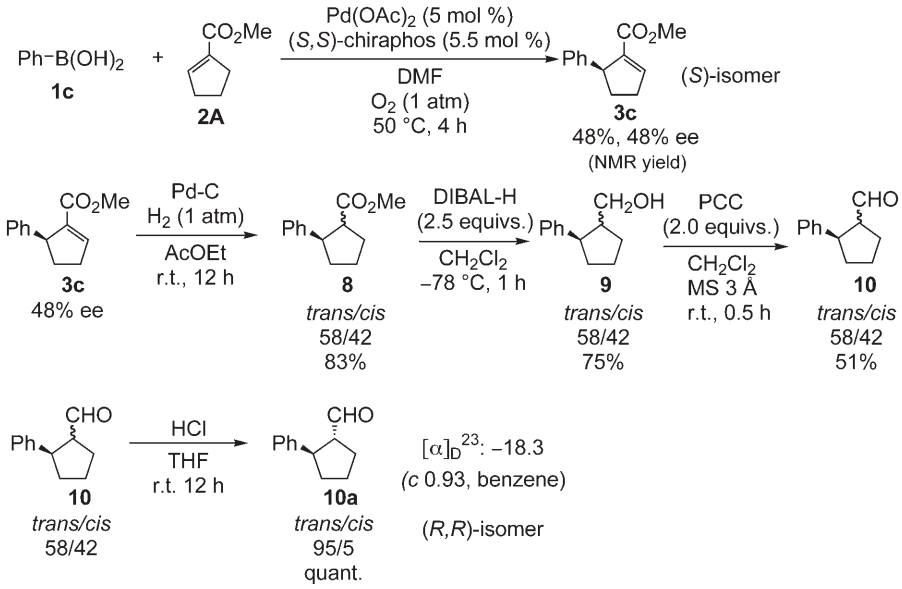
[a] Yield of isolated products.

gave **3B** in almost the same yield and enantioselectivity as those obtained with methyl ester **2A** (72%, 46% ee) (entry 2). The sterically demanding groups such as isopropyl **2C** and phenyl **2D** led to lower yield and enantioselectivity (entries 3 and 4). The highest enantioselectivity was obtained with benzyl ester **2E**, although the yield of **3E** was lower than that of the methyl ester **3A** (58%, 49% ee) (entry 5). Unfortunately, the six-membered olefin **2F** and cyano-substituted **2G** did not give the desired products (entries 6 and 7).

The absolute configuration was determined in the following way (Scheme1). The reaction of phenylboronic acid (**1c**) and methyl 1-cyclopentenecarboxylate (**2A**) gave methyl 5-phenylcyclopent-1-enecarboxylate (**3c**; 48%, 48% ee) using the Pd$(OAc)_2$/(*S,S*)-chiraphos catalyst. The double bond of **3c** was reduced with H_2/Pd-C to give the saturated methyl ester **8** (*trans/cis* = 58/42), and **8** was transformed to the alcohol **9** (*trans/cis* = 58/42) by DIBAL reduction. The alcohol **9** was oxidized with PCC to the aldehyde **10** (*trans/cis* = 58/42). The *trans/cis* mixture of the aldehyde **10** was isomerized using concentrated HCl in THF to give the *trans* isomer **10a** (*trans/cis* = 95/5). Comparing to the literature data of $[\alpha]_D$ value, **10a** was confirmed to be the (*R,R*)-isomer.[11] Therefore, the Pd$(OAc)_2$/(*S,S*)-chiraphos catalyst gave the (*S*)-product **3**.

Therefore, we suggest a plausible catalytic cycle as shown in Figure 2. The Pd(II) species **A** reacts with arylboronic acid *via* transmetallation to form Pd–Ar species **B**. The olefin substrate coordinates to the Pd catalyst and migratory insertion takes place to provide the intermediate **D**, followed by β-elimination to give the product with a regioisomeric double bond and the Pd–H species **E**. The Pd–H species **E** is oxidized with molecular oxygen to reproduce the Pd(II) peroxohydride species **A**.[12]

The enantiodetermining step can be assumed to be the olefin coordination and migratory insertion step. There are two conformations of the Pd-(*S,S*)-chiraphos complex: δ- and λ-conformations in equilibrium (Figure 3). The δ-conformation with two methyl groups in an equatorial orientation has been recognized to be more stable than the methyl-axial λ-conformation.[13] The sense of enantioselectivity should be determined in terms of the steric repulsion between the equatorial phenyl group of chiraphos and the cyclopentene ring of the substrate. Accordingly, the (*R*)-**3** product should be obtained *via* the δ-conformation, because the quadrants I and III were occupied with equatorial phenyl groups. In contrast, (*S*)-**3** should be obtained *via* the λ-conformation, because the quadrants II and IV were occupied with equatorial phenyl groups. In our experi-



Scheme 1. The determination of absolute configuration of the product.

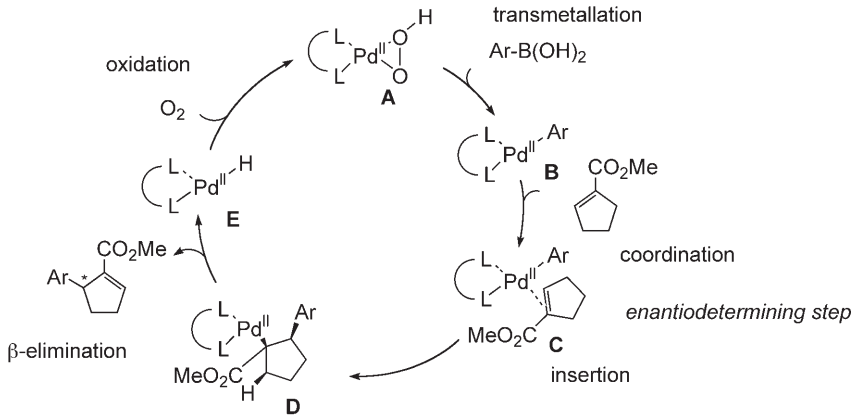


Figure 2. Plausible mechanism for the Pd(II)-catalyzed enantioselective Heck-type reaction.

ment, the (*S*)-product **3** was obtained using the Pd/(*S,S*)-chiraphos complex. Therefore, this Pd(II)-catalyzed Heck-type reaction should proceed *via* the λ-conformation. When the substrate approaches to the catalyst, a steric repulsion can be maximized between equatorial methyl groups and equatorial phenyl groups in the δ-conformation of the chiraphos ligand. Therefore, the δ-conformation changes over to the λ-conformation because of the dynamic (*tropos*) nature[14] of the Pd complex with the chiraphos ligand to give the (*S*)-product.

Conclusion

We have reported the first example of a Pd(II)-catalyzed, organoboron-mediated enantioselective Heck-type reaction. In the examination of chiral ligand, (*S,S*)-chiraphos gave good yields and highest enantioselectivity up to 59% ee. Among the δ- and λ-conformations of the *tropos* Pd(II)/(*S,S*)-chirapos complex, the reaction could proceed *via* the λ-conformation of chiraphos with the two methyl groups in a diaxial orientation to give the (*S*)- product.

Experimental Section

General

^{1}H NMR and ^{13}C NMR were measured on a Varian Gemini 300 (300 MHz) spectrometer and ^{31}P NMR and ^{19}F NMR were measured on an INOVA 400 (400 MHz) spectrometer. Chemical shifts of ^{1}H NMR are expressed in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in $CDCl_3$. Chemical shifts of ^{13}C NMR are expressed in parts per million downfield from $CDCl_3$ as an internal standard

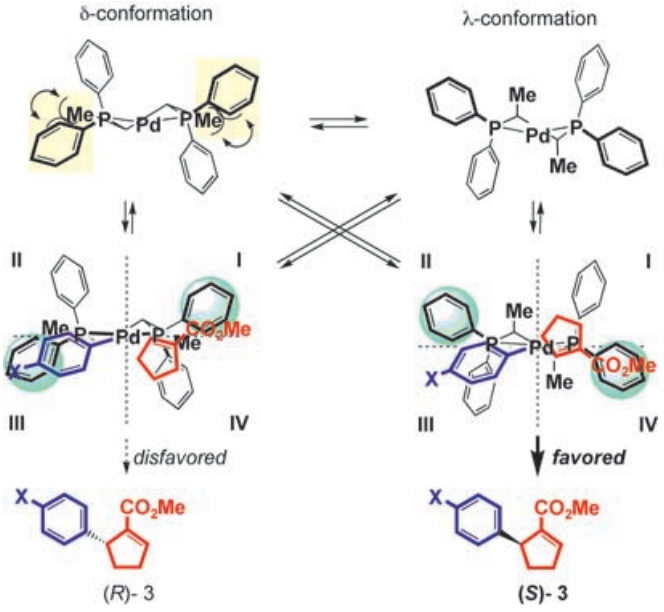


Figure 3. Plausible enantiodetermining step of Pd/(*S,S*)-chiraphos-catalyzed Heck-type reaction.

($\delta = 77.0$) in $CDCl_3$. Chemical shifts of ^{19}F NMR are expressed in parts per million downfield from BTF as an external standard ($\delta = -63.24$) in $CDCl_3$. Chemical shifts of ^{31}P NMR are expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$) in $CDCl_3$. IR spectra were measured on a JASCO FT/IR-5000 spectrometer. Optical rotations were measured on a JASCO DIP-370. High performance liquid chromatographic analyses (HPLC) were conducted on Shimadzu PU-980, LG-980-02, DG-980-50, AS-950 and CO-966 instruments equipped with model UV-975 spectrometers as ultraviolet detectors. Peak area was calculated by JASCOBORWIN (Windows NT) as an automatic integrator. Capillary gas chromatographic analyses (GC) were conducted on a Shimadzu GC-14B instrument equipped with an FID detector and a capillary column coated with CP-Chirasil-Dex CB (GL Science Inc.) by using He as a carrier gas. Peak area was calculated by the Shimadzu C-R6A as an automatic integrator. Analytical thin layer chromatography (TLC) were performed on a glass plates and/or aluminum sheets pre-coated with silica gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 and 0.2 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid. Column chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral), employing hexane-ethyl acetate mixtures as eluent unless otherwise noted. All experiments were carried out under an argon atmosphere otherwise noted.

Diethyl ether (dehydrate), benzene (dehydrate), toluene (dehydrate), dichloromethane (dehydrate), hexane (dehydrate), *N,N*-dimethylformamide (dehydrate), and acetonitrile (dehydrate) were purchased from Kanto chemical Co., Inc. Dimethyl sulfoxide was freshly distilled over CaH_2. Palladium acetate, (2*S*,3*S*)-(−)-bis(diphenylphosphino)butane [(*S,S*)-chiraphos], 4-chlorophenylboronic acid, 4-methylphenylboronic acid, and 4-methoxyphenylboronic acid were purchased from Aldrich Chemical Co. and used without further purification. Methyl 1-cyclopentenecarboxylate, and methyl 1-cyclohexenecarboxylate were purchased from Aldrich Chemical Co. and purified by distillation before use. Phenylboronic acid, 4-trifluoromethylphenylboronic acid, and 1,10-phenanthroline monohydrate were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd. and used without further purification. Ethyl 1-cyclopentene-1-carboxylate, isopropyl 1-cyclopentene-1-carboxylate, benzyl 1-cyclopentene-1-carboxylate, and phenyl 1-cyclopentene-1-carboxylate were prepared by typical DCC condensation from 1-cyclopentenecarboxylic acid and the corresponding alcohol.

Typical Procedure for the Enantioselective, Organoboron-Mediated Heck-Type Reaction

To a solution of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and (*S,S*)-chiraphos (9.4 mg, 0.022 mmol) in DMF (0.8 mL) was added methyl 1-cyclopentene-1-carboxylate (**2A**; 50.5 mg, 0.40 mmol) and 4-trifluoromethylphenylboronic acid (**1e**; 114.0 mg, 0.6 mmol) under air. The reaction vessel was equipped with an oxygen balloon and the reaction mixture was stirred at 50 °C for 4 h. After stirring, the mixture was diluted with Et_2O, filtered through a pad of celite, washed with water and brine, and dried over with $MgSO_4$. After evaporation under reduced pressure, the residue was analyzed by NMR [NMR yield was determined using 1,1,1,2-tetrachloroethane (10 μL 0.0929 mmol) as internal standard]. The residue was purified by column chromatography to give the product **3e**. The enantiomeric excess was determined by capillary gas chromatographic (GC) analyses. Capillary gas chromatographic analyses (GC) were conducted on Shimadzu GC-14B instrument equipped with an FID detector and a capillary column coated with CP-Chirasil-Dex CB (GL Science Inc.) by using He as a carrier gas. Peak area was calculated by the Shimadzu C-R6A as an automatic integrator.

Methyl 5-Phenylcyclopent-1-enecarboxylate (3c): ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.93$ (m, 1H), 2.48–2.70 (m, 3H), 3.60 (s, 3H), 4.14 (br d, $J = 8.7$ Hz, 1H), 6.99 (q, $J = 2.1$ Hz, 1H), 7.16–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.2$, 34.1, 50.1, 51.2, 126.2, 126.9, 128.4, 139.3, 144.7, 145.1, 165.1. IR (neat): $\nu = 2950$, 1717, 1630, 1493, 1437, 1338, 1272, 1193, 1094, 1019, 758, 700 cm^{-1}; GC (column, Cp-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 135 °C; injection and detection temperatures, 160 °C; split ratio, 100:1): $t_R = 17.8$ min, (*R*)-isomer; 18.9 min, (*S*)-isomer.

Methyl 5-(4-Chlorophenyl)cyclopent-1-enecarboxylate (3d): ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.87$ (m, 1H), 2.47–2.73 (m, 3H), 3.61 (s, 3H), 4.11 (br d, $J = 10.5$ Hz, 1H), 6.99 (q. $J = 2.1$ Hz, 1H), 7.09 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.2$, 33.9, 49.5, 51.3, 128.3, 128.5, 131.8, 138.9, 143.6, 145.1, 164.9. IR (neat): $\nu = 2952$, 2848, 1721, 1630, 1491, 1437, 1410, 1348, 1270, 1199, 1093, 1015, 826, 775 cm^{-1}.

Methyl 5-(4-Trifluoromethylphenyl)cyclopent-1-enecarboxylate (3e, 3A): ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.90$ (m, 1H), 2.48–2.75 (m, 3H), 3.61 (s, 3H), 4.19 (br d, $J = 10.5$ Hz, 1H), 7.03 (m, 1H), 7.27 (d, $J = 7.5$ Hz, 2H), 7.53 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 32.2$, 33.8, 50.0, 51.4, 124.3 (q, $J = 270.2$ Hz), 125.4 (q, $J = 3.7$ Hz), 127.3, 128.6 (q, $J = 32.0$ Hz), 138.6, 145.5, 149.2, 164.9; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -62.8$; IR (neat): $\nu = 2956$, 1721, 1620, 1439, 1423, 1328, 1276, 1164, 1114, 1069, 1019, 839, 766 cm^{-1}; GC

(CP-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, N_2; 75 kPa; column, 125 °C; injection and detection temperatures, 155 °C; split ratio, 100:1): t_R = 31.2 min, 40.0 min.

Ethyl 5-(4-Trifluoromethylphenyl)cyclopent-1-enecarboxylate (3B): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.2 Hz, 3H), 1.90 (m, 1H), 2.48–2.75 (m, 3H), 4.05 (m, *J* = 7.2 Hz, 2H), 4.19 (br d, *J* = 7.2 Hz, 1H), 7.03 (q, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 32.2, 33.9, 50.1, 60.1, 124.3 (q, *J* = 270.2 Hz), 125.3 (q, *J* = 3.6 Hz), 127.4, 128.5 (q, *J* = 32.1 Hz), 139.0, 145.2, 149.4, 164.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8; IR (neat): ν = 2944, 1717, 1620, 1421, 1373, 1328, 1274, 1166, 1112, 1069, 1019, 953, 839, 768 cm^{-1}; GC (column, Cp-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 135 °C; injection and detection temperatures: 155 °C; split ratio, 100:1): t_R = 26.6 min, 31.2 min.

Isopropyl 5-(4-Trifluoromethylphenyl)cyclopent-1-enecarboxylate (3C): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.3 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.90 (m, 1H), 2.48–2.73 (m, 3H), 4.17 (br d, *J* = 9.3 Hz, 1H), 4.90 (sep, *J* = 6.2 Hz, 1H), 7.01 (q, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 21.7, 32.2, 33.9, 50.1, 67.5, 124.3 (q, *J* = 270.2 Hz), 125.3 (q, *J* = 3.6 Hz), 127.4, 128.5 (q, *J* = 32.1 Hz), 139.4, 144.9, 149.6, 164.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8; IR (neat): ν = 2984, 1715, 1620, 1458, 1421, 1375, 1328, 1274, 1166, 1112, 1069, 1017, 953, 839, 766 cm^{-1}; GC (column, Cp-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 150 °C; injection and detection temperatures, 180 °C; split ratio, 100:1): t_R = 23.0 min, 25.6 min.

Phenyl 5-(4-Trifluoromethylphenyl)cyclopent-1-enecarboxylate (3D): ^{1}H NMR (300 MHz, $CDCl_3$): d = 2.02 (m, 1H), 2.57–2.85 (m, 3H), 4.31 (br, 1H), 7.17 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (m, 4H), 6.91 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.5, 33.9, 50.1, 121.4, 124.3 (q, *J* = 270.2 Hz), 125.5 (q, *J* = 3.7 Hz), 125.6, 127.4, 128.7 (q, *J* = 32.1 Hz), 129.2, 138.3, 147.5, 149.1, 150.5, 162.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.7; IR (KBr): ν = 2930, 1725, 1620, 1595, 1491, 1458, 1423, 1328, 1292, 1241, 1199, 1164, 1135, 1112, 1067, 1017, 961, 919, 893, 843, 764, 737, 690, 611 cm^{-1}; GC (column, Cp-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 185 °C; injection and detection temperatures, 220 °C; split ratio, 100:1): t_R = 33.0 min, 35.1 min.

Benzyl 5-(4-Trifluoromethylphenyl)cyclopent-1-enecarboxylate (3E): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.91 (m, 1H), 2.49–2.76 (m, 3H), 4.21 (br d, *J* = 9.3 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 5.15 (d, *J* = 12.6 Hz, 1H), 7.08 (m, *J* = 2.1 Hz, 3H), 7.28 (m, 4H), 7.51 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.3, 34.0, 50.1, 66.0, 124.3 (q, *J* = 274.2 Hz), 125.4 (q, *J* = 3.7 Hz), 127.4, 127.8, 128.0, 128.4, 128.5 (q, *J* = 35.8 Hz) 135.9, 138.6, 146.2, 149.3, 164.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.7; IR (neat): ν = 2952, 2366, 1717, 1620, 1499, 1458, 1421, 1379, 1328, 1272, 1166, 1114, 1069, 1017, 839, 739, 696 cm^{-1}; GC (column, Cp-Chirasil-Dex CD, i.d. 0.32 mm × 25 m, CHROMPACK; carrier gas, nitrogen 75 kPa; column, 185 °C; injection and detection temperatures, 220 °C; split ratio, 100:1): t_R = 40.2 min, 42.3 min.

Palladium-(*S,S*)-Chiraphos Acetate Complex 7[15]

A mixture of (*S,S*)-chiraphos (103.8 mg, 0.42 mmol) and $PdCl_2(CH_3CN)_2$ (179.1 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature under an argon atmosphere. After 11 h, the pinkish precipitate was filtered and washed with CH_2Cl_2 and dried under reduced pressure. The resultant precipitate was suspended in CH_2Cl_2 (10 mL) and silver acetate (133.5 mg, 0.8 mmol) added under an argon atmosphere. After stirring for 24 hours, the mixture was filtered through a pad of celite and recrystallized with hexane and CH_2Cl_2 to give the title product (palladium/(*S,S*)-chiraphos 1:1/1:2 complex = 97/3); yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (m, 6H), 1.61 (s, 6H), 2.34 (br s, 2H), 7.45–7.62 (m, 16H), 8.27 (t, *J* = 8.7 Hz, 4H); ^{31}P NMR (400 MHz, $CDCl_3$): δ = 59.9.

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