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Asymmetric aza-Claisen rearrangement of allyl imidates catalyzed by homochiral cationic palladium(II) complexes

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Abstract

The asymmetric aza-Claisen rearrangement of (*E*)-3-alkyl-2-propenyl *N*-[4-trifluoromethyl)phenyl]benzimidates was catalyzed by a homochiral cationic palladium(II) complex generated from $PdCl_2$\{(*S*)-2-(2-diphenylphosphino)phenyl-4-benzyloxazoline\} and silver tetrafluoroborate (Pd:silver=1:1) to give (*S*)-*N*-(1-alkyl-2-propenyl)-*N*-[4-(trifluoromethyl)phenyl]benzamide of up to 81% ee.

1. Introduction

Transition metal catalyzed [3,3]-sigmatropic rearrangements are among the important transformations in modern synthetic organic chemistry.[1,2] However, only scattered attention has been paid to catalytic asymmetric [3,3]-sigmatropic rearrangements which would constitute a powerful strategy for the synthesis of a variety of optically active compounds. The aza-Claisen rearrangement of allyl imidates catalyzed by divalent palladium species is a typical case.[3] Recently, Overman reported the first example of a catalytic asymmetric rearrangement of allyl imidate **1a**, where a cationic palladium(II) complex bearing an optically active tertiary diamine as a ligand catalyzed the rearrangement to give *N*-allyl amide **2a** in up to 60% ee.[4]

On the other hand, we have reported the palladium-catalyzed asymmetric Heck reaction[5] and the Wacker-type reaction[6] where a cationic palladium(II) species plays a key role in the activation of the carbon–carbon double bond as well as in the enantioface selection.[7,8] As a part of our efforts to develop a wide utility of the cationic chiral palladium(II) catalysts, the asymmetric aza-Claisen rearrangement of allyl imidates was examined. We describe herein that higher enantioselectivity (up to 81% ee) was obtained by use of a cationic palladium(II) catalyst of 2-(2-diphenylphosphino)phenyl-4-alkyloxazoline

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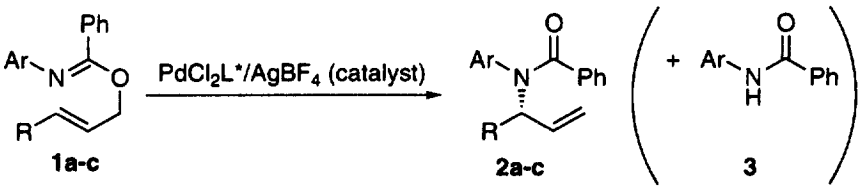
(phox, **4**) in the asymmetric aza-Claisen rearrangement of 3-alkyl-2-propenyl *N*-arylbenzimidates **1** to *N*-(1-alkyl-2-propenyl)-*N*-arylbenzamide **2** of up to 81% ee (Scheme 1).



1a-c **2a-c** **3**

1a: Ar = 4-$CF_3C_6H_4$, R = $CH_2CH_2CH_3$
1b: Ar = C_6H_5, R = $CH_2CH_2CH_3$
1c: Ar = 4-$CF_3C_6H_4$, R = $CH(CH_3)_2$

Scheme 1.

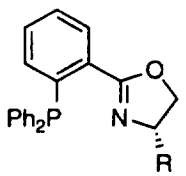
2. Results and discussion

Rearrangement of (*E*)-2-hexenyl *N*-[4-(trifluoromethyl)phenyl]benzimidate **1a** to *N*-(1-hexen-3-yl)-*N*-[4-(trifluoromethyl)phenyl]benzamide **2a** was examined in the presence of palladium(II) catalysts coordinated with chiral bis(oxazoline), phosphino-oxazoline, and bis(phosphine) ligands under several reaction conditions (Scheme 1). The *N*-allyl amide **2a** was isolated by chromatography on silica gel and the enantiomeric excess was determined by HPLC analysis using a chiral stationary column (Chiralpack AD; eluent: hexane:isopropanol=9:1). The absolute configuration was determined by comparison of the specific rotation with that reported for optically active **2a**.[4] The results summarized in Table 1 reveal that the most stereoselective ligand is (*S*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazoline ((*S*)-bn-phox **4a**)[9] (entry 1). According to the procedures reported by Overman,[4] a cationic palladium catalyst was generated from dichloro[(*S*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazolyl]palladium(II) [$PdCl_2$\{(*S*)-bn-phox\}] by treatment with 1 equiv. (to Pd) of silver tetrafluoroborate.[10] The rearrangement of **1a** proceeded in refluxing 1,2-dichloroethane to give 81% yield of *N*-allyl amide (*S*)-**2a** of 70% ee ($[\alpha]_D^{25}$ +50.5 (*c* 0.23, dichloromethane), lit.[4] for (*R*)-**2a** of 55% ee: $[\alpha]_D^{25}$ −37.2 (*c* 0.5, dichloromethane)). The reaction carried out at 40°C raised the enantiomeric excess to 76% ee, though the reaction is slower (entry 2). Dicationic palladium(II) catalyst generated by addition of 2 equiv. (to Pd) of silver tetrafluoroborate is not effective for the rearrangement to **2a**, resulting in carbon–oxygen bond cleavage to give *N*-[4-(trifluoromethyl)phenyl]benzamide (**3**) (entry 3). The effects of the added silver salts on the reaction pathway are consistent with those reported by Overman.[4] Without silver salt, $PdCl_2$\{(*S*)-bn-phox)\} did not catalyse the rearrangement at all. The reaction with other phosphino-oxazoline ligands, which have isopropyl **4b**[9] and *t*-butyl **4c**[9] substituents at the C4-position, proceeded with 36% and 50% enantioselectivity, respectively (entries 5 and 6). Ferrocene analog **5**[11] exhibited moderate catalytic activity and stereoselectivity (entry 7). Chiral bis(oxazoline) ligands,[12] 2,2-bis(oxazolyl)propane **6**,[13] 2,2′-bioxazolyl **7**[14] and 2,2′-bis[4-(benzyl)oxazolyl]-1,1′-binaphthyl ((*S,S*)-bn-boxax) **8**[15] gave **2a** with much lower enantioselectivity (entries 8, 9 and 10). The palladium complex of (*S*)-BINAP **9**[16] was found to be stereoselective, but less catalytically active (entry 11).

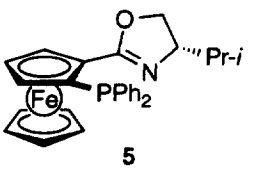
Table 1
Asymmetric rearrangement of **1** catalyzed by cationic palladium(II) complexes[a]

entry	substrate	catalyst	time (h)	yield of products[b] 2 (%)	3 (%)	% ee of 2[c] (abs. config.)[d]
1	**1a**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/$AgBF_4$	15	81	0	70 (*S*)
2[e]	**1a**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/$AgBF_4$	24	41	3	76 (*S*)
3[f]	**1a**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/2$AgBF_4$	24	2	71	52 (*S*)
4[g]	**1a**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/none	24	0	0	-
5	**1a**	$PdCl_2$\{(*S*)-ip-phox **4b**\}/$AgBF_4$	24	34	4	36 (*S*)
6	**1a**	$PdCl_2$\{(*S*)-tb-phox **4c**\}/$AgBF_4$	24	12	44	50 (*S*)
7	**1a**	$PdCl_2$(**5**)/$AgBF_4$	24	54	30	50 (*S*)
8[h]	**1a**	$PdCl_2(CH_3CN)_2$/**6**/$AgBF_4$	24	69	10	2 (*S*)
9[h]	**1a**	$PdCl_2(CH_3CN)_2$/**7**/$AgBF_4$	24	52	24	5 (*S*)
10	**1a**	$PdCl_2$\{(*S,S*)-bn-boxax **8**\}/$AgBF_4$	24	44	33	17 (*S*)
11	**1a**	$PdCl_2$\{(*S*)-BINAP **9**\}/$AgBF_4$	72	24	36	67 (*R*)
12	**1a'**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/$AgBF_4$	15	56	27	28 (*R*)
13	**1b**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/$AgBF_4$	24	88	6	47 (*S*)
14	**1c**	$PdCl_2$\{(*S*)-bn-phox **4a**\}/$AgBF_4$	24	30	37	81 (*S*)

[a] All reactions were carried out in the presence of palladium catalysts (10 mol %) prepared from palladium dichloride complexes and silver tetrafluoroborate (Pd/silver = 1/1) in refluxing dichloroethane unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis with chiral stationary phase column, Chiralpack AD. [d] The absolute configuration was determined by comparison of the optical rotation with that reported for optically active **2a** (ref. 4). [e] The reaction was carried out at 40 °C. [f] The reaction with 20 mol % of silver tetrafluoroborate (Pd/silver = 1/2). [g] Without silver salt. [h] Palladium(II)-bis(oxazoline) complexes were prepared from $PdCl_2(CH_3CN)_2$ and optically active bis(oxazoline) ligands **6** and **7**, and then used without purification.



(*S*)-bn-phox (**4a**): R = CH_2Ph
(*S*)-ip-phox (**4b**) : R = $CH(CH_3)_2$
(*S*)-tb-phox (**4c**) : R = $C(CH_3)_3$



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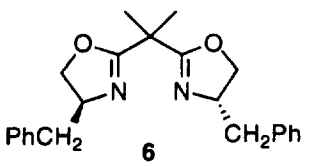

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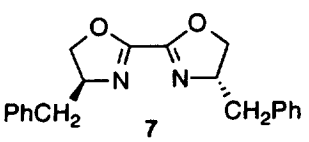

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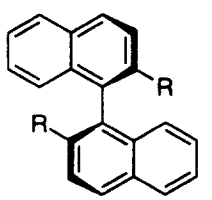
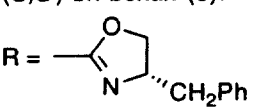


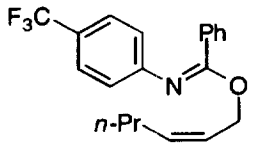
(*S,S*)-bn-boxax (**8**):



(*S*)-BINAP (**9**): R = PPh_2

The rearrangement of (*Z*) isomer **1a'** gave an enantiomeric product (*R*)-**2a** though the selectivity was lower than that observed for (*E*) isomer **1a** (entry 12). Allyl imidate **1b** which has a phenyl substituent

at the imidate nitrogen instead of 4-trifluoromethylphenyl gave *N*-allyl benzamide **2b** in high yield with moderate enantiomeric purity (entry 13). The highest stereoselectivity was observed in the reaction of **1c**, which gave **2c** in 81% ee under the same reaction conditions (entry 14).



1a'

In conclusion, it was found that a cationic palladium(II) complex generated from $PdCl_2$\{(*S*)-bn-phox\} and silver tetrafluoroborate was an efficient catalyst for asymmetric aza-Claisen rearrangement of allyl imidates giving *N*-allyl amide derivatives of high % ee.

3. Experimental

3.1. General

Optical rotations were measured with a JASCO DIP-370 polarimeter. ^{1}H NMR spectra were measured with a JEOL JNM-LA500 (500 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Chemical shifts are reported in δ ppm. HPLC analyses were performed on a Shimadzu LC-9A liquid chromatograph system with chiral stationary phase column, Daicel Chemical Co. Ltd, Chiralpack AD.

3.2. Materials

Optically active ligands, (*S*)-bn-phox **4a**,[9] (*S*)-ip-phox **4b**,[9] (*S*)-tb-phox **4c**,[9] (*S*)-(−)-2-[(*S*)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline **5**,[11] 2,2-bis(oxazolyl)propane **6**,[13] 2,2′-bioxazolyl **7**,[14] and 2,2′-bis[4-(benzyl)oxazolyl]-1,1′-binaphthyl ((*S,S*)-bn-boxax) **8**[15] were prepared according to the reported procedures. Optically active palladium(II) complex $PdCl_2$\{(*S*)–BINAP\} was prepared according to the reported procedure.[5e,17] THF, benzene and hexane were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane and dichloroethane were distilled from calcium hydride under nitrogen.

3.3. Preparation of $PdCl_2$(phosphine-oxazoline) complexes

A typical procedure is given for the preparation of dichloro[(*S*)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazoline]palladium(II) ($PdCl_2$\{(*S*)-bn-phox\}):

3.3.1. Dichloro[(S)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazoline]palladium(II) ($PdCl_2$\{(S)-bn-phox\})

A solution of 250 mg (0.59 mmol) of (*S*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazoline ((*S*)-bn-phox **4a**) in 5 mL of benzene was added to a mixture of 154 mg (0.59 mmol) of $PdCl_2(CH_3CN)_2$ and 5 mL of benzene. The reaction mixture was stirred for 20 min. A yellow precipitate was collected by filtration and washed with benzene to give 352 mg (98% yield) of dichloro[(*S*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazoline]palladium(II): mp 247°C (dec); $[\alpha]_D^{20}$ +497 (*c* 0.27,

chloroform); ^{1}H NMR δ 1.68 (br t, *J*=12.7 Hz, 1H), 3.87 (dd, *J*=13.3, 3.5 Hz, 1H), 4.30 (dd, *J*=8.8, 4.9 Hz, 1H), 4.39 (br t, *J*=9.3 Hz, 1H), 5.80 (m, 1H), 6.99 (m, 1H), 7.21 (m, 5H), 7.45 (m, 4H), 7.58 (m, 5H), 7.74 (m, 3H), 8.10 (m, 1H); ^{13}C NMR δ 40.64, 67.98, 72.39, 162.09; ^{31}P NMR δ 26.70. Anal. calcd for $C_{28}H_{24}NOPCl_2Pd$: C, 56.16; H, 4.01; N, 2.34. Found: C, 56.39; H, 3.89; N, 2.15.

3.3.2. Dichloro[(S)-2-(2-(diphenylphosphino)phenyl)-4-(isopropyl)oxazoline]palladium(II) ($PdCl_2$[(S)-ip-phox])

89% Yield: mp 239°C (dec); $[\alpha]_D^{20}$ +704 (*c* 0.08, chloroform); ^{1}H NMR δ 0.02 (d, *J*=6.9 Hz, 3H), 0.82 (d, *J*=7.4 Hz, 3H), 2.68 (m, 1H), 4.38 (dd, *J*=9.3, 5.4 Hz, 1H), 4.50 (br t, *J*=9.3 Hz, 1H), 5.61 (m, 1H), 6.82 (m, 1H), 7.36–7.60 (m, 9H), 7.71 (m, 3H), 8.14 (m, 1H); ^{13}C NMR δ 12.80, 18.57, 30.47, 68.99, 71.30, 161.40; ^{31}P NMR δ 21.01. Anal. calcd for $C_{24}H_{24}NOPCl_2Pd$: C, 52.34; H, 4.39; N, 2.54. Found: C, 52.05; H, 4.33; N, 2.53.

3.3.3. Dichloro[(S)-2-(2-(diphenylphosphino)phenyl)-4-(t-butyl)oxazoline]palladium(II) ($PdCl_2$[(S)-tb-phox])

78% Yield: mp 263°C (dec); $[\alpha]_D^{20}$ +464 (*c* 0.18, chloroform); ^{1}H NMR δ 1.56 (s, 9H), 4.54 (m, 2H), 5.53 (dd, *J*=7.9, 5.6 Hz, 1H), 6.93 (m, 1H), 7.40 (m, 4H), 7.49–7.64 (m, 7H), 7.72 (br t, 1H), 8.19 (m, 1H); ^{13}C NMR δ 25.86, 29.71, 34.39, 70.72, 74.58, 162.49; ^{31}P NMR δ 25.42. Anal. calcd for $C_{25}H_{26}NOPCl_2Pd$: C, 46.90; H, 4.09; N, 2.19. Found: C, 46.71; H, 4.01; N, 2.25.

3.3.4. Dichloro[(S)-2-[(S)-2-(diphenylphosphino)ferrocenyl]-4-(isopropyl)oxazoline]palladium(II)

84% Yield: mp 265°C (dec); $[\alpha]_D^{20}$ −958 (*c* 0.04, chloroform); ^{1}H NMR δ 1.01 (d, *J*=6.9 Hz, 3H), 1.07 (d, *J*=6.9 Hz, 3H), 3.10 (m, 1H), 3.81 (s, 5H), 4.38 (br t, *J*=9.3 Hz, 1H), 4.49 (dd, *J*=8.8, 4.4 Hz, 1H), 4.53 (m, 1H), 4.77 (br s, 1H), 5.10 (br s, 1H), 5.33 (m, 1H), 7.26–7.41 (m, 5H), 7.64 (m, 3H), 8.33 (m, 2H); ^{13}C NMR δ 14.91, 18.77, 29.98, 73.14, 167.55; ^{31}P NMR δ 15.73. Anal. calcd for $C_{28}H_{28}NOPCl_2PdFe$: C, 51.06; H, 4.29; N, 2.13. Found: C, 51.17; H, 4.37; N, 1.99.

3.4. Preparation of imidates 1

A typical procedure is given for the preparation of (*E*)-2-hexenyl *N*-[4-(trifluoromethyl)phenyl]benzimidate **1a**.[8]

3.4.1. (E)-2-Hexenyl N-[4-(trifluoromethyl)phenyl]benzimidate 1a

To a mixture of 649 mg (4.03 mmol) of 4-trifluoromethylaniline and 608 mg (6.02 mmol) of triethylamine in 20 mL of dichloromethane was added 620 mg (4.41 mmol) of benzoyl chloride at 0°C and the reaction mixture was stirred for 30 min. The reaction mixture was washed with 10% hydrochloric acid. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give crude *N*-[4-(trifluoromethyl)phenyl]benzamide (1.04 g, 97% yield): ^{1}H NMR δ 7.52 (br t, *J*=7.9 Hz, 2H), 7.59 (br t, *J*=7.4 Hz, 1H), 7.64 (d, *J*=8.4 Hz, 2H), 7.79 (d, *J*=8.4 Hz, 2H), 7.88 (br d, *J*=8.3 Hz, 2H), 7.93 (br s, 1H).

A mixture of 596 mg (2.25 mmol) of *N*-[4-(trifluoromethyl)phenyl]benzamide and 469 mg (2.25 mmol) of phosphorus pentachloride was heated at 85°C for 1 h. After being cooled to room temperature, volatile materials were removed under reduced pressure to give crude *N*-[4-(trifluoromethyl)phenyl]benzimidoyl chloride (630 mg, 99% yield): ^{1}H NMR δ 7.07 (br d, *J*=8.35 Hz, 2H), 7.50 (br t, *J*=7.9 Hz, 2H), 7.58 (br t, *J*=7.4 Hz, 1H), 7.67 (d, *J*=8.4 Hz, 2H), 8.17 (br d, *J*=7.8 Hz, 2H).

To a suspension of 121 mg (2.20 mmol) of sodium hydride in 35 mL of THF was added a solution of 220 mg (2.20 mmol) of (*E*)-2-hexen-1-ol in THF (5 mL) at 0°C and the mixture was stirred for 10 min. To the mixture was added 610 mg (2.15 mmol) of *N*-[4-(trifluoromethyl)phenyl]benzimidoyl chloride at 0°C. The reaction mixture was stirred at room temperature for 4 h and a small amount of water was added. The entire solution was extracted with chloroform. The organic layer was dried over sodium sulfate, concentrated, and chromatographed on silica gel (eluent: EtOAc:hexane=1:19) to give 634 mg (83% yield) of (*E*)-2-hexenyl *N*-[4-(trifluoromethyl)phenyl]benzimidate (**1a**): ^{1}H NMR δ 0.92 (t, *J*=7.4 Hz, 3H), 1.45 (br sextet, *J*=7.4 Hz, 2H), 2.09 (br q, *J*=6.9 Hz, 2H), 4.81 (d, *J*=6.9 Hz, 2H), 5.75–5.91 (m, 2H), 6.78 (d, *J*=8.3 Hz, 2H), 7.22–7.34 (m, 5H), 7.42 (d, *J*=8.3 Hz, 2H).

3.4.2. (Z)-2-Hexenyl N-[4-(trifluoromethyl)phenyl]benzimidate ***1a'***

61% Yield; ^{1}H NMR δ 0.93 (t, *J*=7.3 Hz, 3H), 1.44 (br sextet, *J*=7.3 Hz, 2H), 2.17 (br q, *J*=7.3 Hz, 2H), 4.92 (d, *J*=6.4 Hz, 2H), 5.71 (m, 1H), 5.76 (m, 1H), 6.79 (d, *J*=8.3 Hz, 2H), 7.28 (m, 5H), 7.42 (d, *J*=8.3 Hz, 2H); ^{13}C NMR δ 13.69, 22.64, 29.73, 62.91, 121.70, 124.11, 124.49 (q, *J*=30 Hz), 124.52 (q, *J*=272 Hz), 126.10 (br t, *J*=5 Hz), 128.09, 129.26, 130.22, 130.78, 134.82, 151.78, 159.13. Anal. calcd for $C_{20}H_{20}NOF_3$: C, 69.15; H, 5.80; N, 4.03. Found: C, 69.22; H, 6.07; N, 4.05.

3.4.3. (E)-2-Hexenyl N-(phenyl)benzimidate ***1b***

77% Yield; ^{1}H NMR δ 0.94 (t, *J*=7.4 Hz, 3H), 1.45 (br sextet, *J*=7.4, 2H), 2.08 (br q, *J*=6.9 Hz, 2H), 4.81 (d, *J*=5.9 Hz, 2H), 5.77 (m, 1H), 5.88 (m, 1H), 6.71 (br d, *J*=7.4 Hz, 2H), 6.94 (br t, *J*=7.3 Hz, 1H), 7.15–7.32 (m, 7H).

3.4.4. (E)-4-Methyl-2-pentenyl N-[4-(trifluoromethyl)phenyl]benzimidate ***1c***

86% Yield; ^{1}H NMR δ 0.95 (d, *J*=6.9 Hz, 6H), 2.27 (br octet, 1H), 4.72 (d, *J*=5.9 Hz, 2H), 5.63 (dt, *J*=15.2, 5.9 Hz, 1H), 5.76 (dd, *J*=15.2, 6.4 Hz, 1H), 6.69 (d, *J*=8.3 Hz, 2H), 7.13 (m, 2H), 7.22 (m, 3H), 7.32 (d, *J*=8.3 Hz, 2H); ^{13}C NMR δ 22.12, 30.90, 67.80, 121.39, 121.68, 124.48 (q, *J*=32 Hz), 124.83 (q, *J*=270 Hz), 126.08 (q, *J*=4 Hz), 128.09, 129.26, 130.20, 130.88, 142.86, 151.81, 159.05. Anal. calcd for $C_{20}H_{20}NOF_3$: C, 69.15; H, 5.80; N, 4.03. Found: C, 69.05; H, 6.07; N, 3.76.

3.5. Asymmetric aza-Claisen rearrangement of imidates ***1*** *with catalysts prepared from $PdCl_2${(S)-bn-phox}*

A typical procedure is given for the asymmetric rearrangement of **1a** (Table 1, entry 1). To a suspension of 2.0 mg (10 μmol) of $AgBF_4$ in 0.1 mL of dichloromethane was added a solution of 6.6 mg (11 μmol) of dichloro[(*S*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-(benzyl)oxazolyl]palladium(II) [$PdCl_2${(*S*)-bn-phox}] in 0.1 mL of dichloromethane at room temperature. After 5 min, precipitated silver chloride was removed by filtration. The filtrate was concentrated in vacuo to give an orange solid. The orange solid was dissolved in 0.2 mL of 1,2-dichloroethane and 34.7 mg (0.10 mmol) of (*E*)-2-hexenyl-*N*-[4-(trifluoromethyl)phenyl]benzimidate **1a** in 0.1 mL of 1,2-dichloroethane was added. The reaction mixture was stirred at 40°C for 24 h. After being cooled to room temperature, removal of solvent followed by preparative TLC on silica gel (hexane:EtOAc=19:1) gave 14.2 mg (41%) of *N*-(1-hexen-3-yl)-*N*-[4-(trifluoromethyl)phenyl]benzamide **2a**, (41% yield, 76% ee): $[\alpha]_D^{20}$ +51.3 (*c* 0.18, chloroform). ^{1}H NMR δ 0.94 (t, *J*=7.4 Hz, 3H), 1.43 (br sextet, *J*=7.4 Hz, 2H), 1.57–1.65 (m, 1H), 1.68–1.76 (m, 1H), 5.22 (d, *J*=10.3 Hz, 1H), 5.23 (m, 1H), 5.29 (d, *J*=17.6 Hz, 1H), 5.89 (ddd, *J*=17.6, 10.3, 7.4 Hz, 1H), 7.14 (br d, *J*=8.8 Hz, 2H), 7.17 (br d, *J*=7.8 Hz, 2H), 7.24 (m, 3H), 7.14 (br d, *J*=8.4 Hz, 2H). The enantiomeric purity of **2a** was determined by HPLC analysis with a chiral stationary phase column.

Conditions: column, Daicel Chemical Industries Ltd, Chiralpack AD; eluent: hexane:isopropanol=9:1; detection 254 nm light. The absolute configuration was determined to be (*S*) by measurement of the specific rotation: $[\alpha]_D^{25}$ +50.5 (*c* 0.23, dichloromethane), lit.[8] for (*R*)-**2a** of 55% ee: $[\alpha]_D^{25}$ −37.2 (*c* 0.5, dichloromethane).

3.5.1. (S)-(+)-N-(1-Hexen-3-yl)-N-phenylbenzamide ***2b***

88% Yield, 47% ee: $[\alpha]_D^{20}$ +28.4 (*c* 0.15, chloroform); ^{1}H NMR δ 0.94 (t, *J*=7.4 Hz, 3H), 1.45 (sextet, *J*=7.4 Hz, 2H), 2.08 (q, *J*=6.9 Hz, 2H), 4.81 (d, *J*=5.9 Hz, 2H), 5.77 (m, 1H), 5.85 (m, 1H), 6.71 (br d, *J*=7.4 Hz, 2H), 6.94 (br t, *J*=7.3 Hz, 1H), 7.15–7.32 (m, 7H).

3.5.2. (S)-(+)-N-(4-Methyl-1-penten-3-yl)-N-(4-trifluoromethyl)phenyl]benzamide ***2c***

30% Yield, 81% ee: $[\alpha]_D^{20}$ +71.9 (*c* 0.10, chloroform); ^{1}H NMR δ 0.94 (d, *J*=6.9 Hz, 3H), 1.19 (d, *J*=6.9 Hz, 3H), 2.30 (m, 1H), 4.48 (br t, *J*=9.8 Hz, 1H), 5.21 (d, *J*=9.8 Hz, 1H), 5.22 (d, *J*=17.2 Hz, 1H), 5.91 (br t, *J*=9.8 Hz, 1H), 7.14 (d, *J*=8.3, 2H), 7.15–7.26 (m, 5H), 7.45 (d, *J*=8.3 Hz, 2H); ^{13}C NMR δ 20.24, 20.37, 29.81, 70.36, 119.09, 123.71 (q, *J*=274 Hz), 125.91 (br s), 127.90, 128.39 (q, *J* =34 Hz), 128.71, 129.43, 129.66, 135.96, 136.48, 146.11, 170.55. Anal. calcd for $C_{20}H_{20}NOF_3$: C, 69.15; H, 5.80; N, 4.03. Found: C, 69.08; H, 5.84; N, 3.97.

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