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Palladium-catalyzed asymmetric hydrovinylation under mild conditions using monodentate chiral spiro phosphoramidite and phosphite ligands

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Abstract—Palladium complexes of chiral spiro phosphoramidite and phosphite ligands are effective catalysts in the asymmetric hydrovinylation of vinylarenes with ethylene. The hydrovinylation products were obtained in modest selectivity with enantioselectivities up to 92% ee. The structures of the palladium catalysts have been analyzed by X-ray diffraction. The active catalyst contained one monodentate ligand. A kinetic resolution accompanied the isomerization of the hydrovinylation product in the reaction.

1. Introduction

The catalytic asymmetric hydrovinylation of olefins is an important stereoselective carbon–carbon bond forming reaction in organic synthesis.[1] In particular the asymmetric hydrovinylation of vinylarenes can afford chiral 3-aryl-1-butenes, which are starting materials for the synthesis of 2-arylpropionic acids, anti-inflammatory drugs, such as Ibuprofen and Naproxen. Recently, the nickel-catalyzed hydrovinylation of olefins has been intensively studied and high regioselectivity and excellent enantioselectivity (up to 95% ee) have been achieved.[2] However, much less attention has been paid to palladium-catalyzed asymmetric hydrovinylation, due to the concomitant isomerization of the hydrovinylation product 3-aryl-1-butene to achiral 2-aryl-2-butenes. Salzer reported a remarkable enantioselectivity (92% ee) in the palladium-catalyzed asymmetric hydrovinylation of styrene using a chiral phosphine ligand derived from tricarbonyl(η^6-ethylbenzene)chromium, but the yield of the desired product 3-phenyl-1-butene was not high.[3] Employing P-stereogenic ligands, such as benzylmesitylphenylphosphine, Granell et al. obtained the hydrovinylation product in excellent yield and good enantioselectivity (84% ee) in the reaction of 2-vinylnaphthalene.[4] These results indicated that palladium-catalyzed asymmetric hydrovinylation could surmount the concomitant isomerization of the products and provided 3-aryl-1-butene in high enantioselectivity by choosing a suitable chiral ligand. Recently, we have developed a new type of monodentate phosphoramidite and phosphite ligands containing a 1,1′-spirobiindane backbone and demonstrated they were highly efficient for the rhodium-catalyzed asymmetric hydrogenation of functionalized olefins,[5] copper-catalyzed 1,4-addition of dialkylzincs to enones,[6] and other reactions.[7] Herein, we describe the application of these highly rigid spiro phosphoramidite and phosphite ligands in the palladium-catalyzed asymmetric hydrovinylation of vinylarenes.

2. Results and discussion

Chiral ligands are crucial for the palladium-catalyzed asymmetric hydrovinylation of vinylarenes with ethylene. Besides the enantioselectivity of the primary products 3-aryl-1-butenes, the regioselectivity and the isomerization of the 3-aryl-1-butene to 2-aryl-2-butene also vary according to the ligand used. To search for efficient chiral ligands in Pd-catalyzed asymmetric hydrovinylation, we investigated various monodentate phosphorus ligands including those with a hemilabile coordinating group. Preliminary experiments showed that spiro phosphoramidite and phosphite ligands (Fig. 1) are effective.

The hydrovinylation reaction took place in dichloromethane at 25 °C under 10 bar of ethylene in the presence

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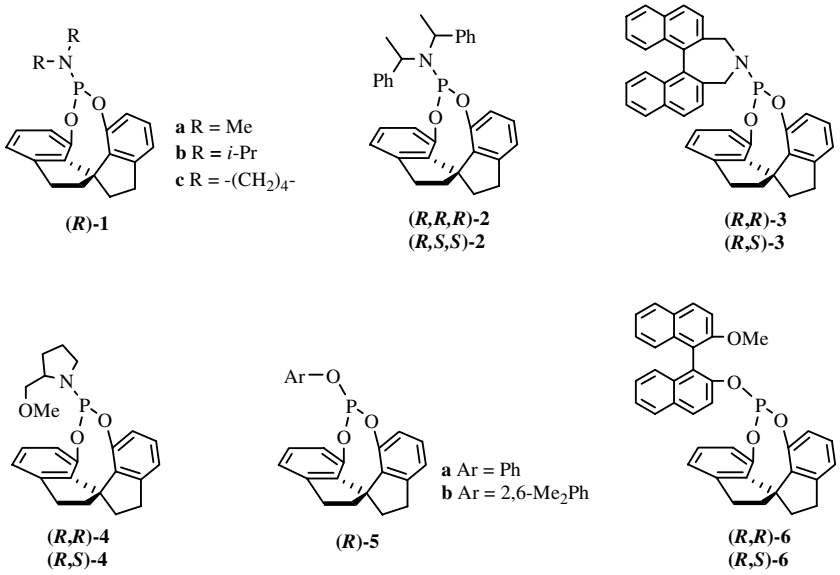


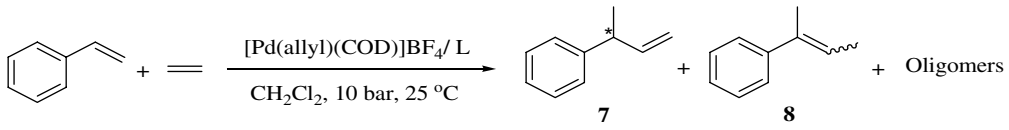
Figure 1. Spiro phosphoramidite and phosphite ligands.

of 0.5 mol% of palladium catalyst prepared in situ from $[Pd(\eta^3\text{-}C_3H_5)(COD)]BF_4$ and the ligand (0.5 mol%). After stirring for several hours, the reaction was quenched with aqueous ammonium chloride, and the products were purified by chromatography on a short silica gel column and analyzed by GC. It was found that the hydrovinylation reaction was accompanied by the isomerization of product **7**. Prolonging the reaction time increased the conversion of styrene, but the amount of isomerization product **8** increased simultaneously. Table 1 summarizes the best results obtained with spiro monodentate ligands **1**–**6**.

From the data in Table 1, some conclusions can be drawn: (1) The phosphoramidite ligands bearing larger alkyl groups on the nitrogen atom gave higher conversion of styrene and higher enantioselectivity of the hydrovinylation product **7**. (2) Introducing a chiral amino moiety into the phosphoramidite ligand did not give a positive influence on the selectivity of reaction. (3) Adding a hemilabile methoxy group to the ligands did not significantly improve the reaction.

Using (*R*)-**1b** as a standard ligand, we further studied the influence of counter anions, which play an important

Table 1. Pd-catalyzed asymmetric hydrovinylation, ligand comparison[a]



Entry	Ligand	Time (h)	Conv (%)[b]	Selectivity (%)[c]			Ee of **7** (%)[d]
				7	**8**	Oligomers	
1	(*R*)-**1a**	7	11	88	9	3	17 (*S*)
2	(*R*)-**1b**	7	86	51	48	1	38 (*S*)
3	(*R*)-**1c**	12	6	83	4	13	18 (*S*)
4	(*R*,*R*,*R*)-**2**	7	10	80	4	16	24 (*S*)
5	(*R*,*S*,*S*)-**2**	3	80	61	38	1	23 (*S*)
6	(*R*,*R*)-**3**	12	42	69	25	6	26 (*S*)
7	(*R*,*S*)-**3**	12	33	69	27	4	9 (*S*)
8	(*R*,*R*)-**4**	12	Trace	—	—	—	—
9	(*R*,*S*)-**4**	12	28	79	15	6	20 (*S*)
10	(*R*)-**5a**	13	47	64	30	6	34 (*S*)
11	(*R*)-**5b**	1	61	69	25	6	33 (*S*)
12	(*R*,*S*)-**6**	8	70	44	55	1	21 (*S*)
13	(*R*,*R*)-**6**	5	85	26	73	1	36 (*S*)

[a] Reaction conditions: Styrene/Pd/L = 200:1:1, 3 mL CH_2Cl_2, $[Pd(\eta^3\text{-}C_3H_5)(COD)]BF_4$ as catalyst precursor.
[b] Determined by GC using a HP-5 column.
[c] Based on the converted styrene.
[d] Determined by chiral GC using a Suplco β-DEX 120 column.

Table 2. The counter anion effect in Pd-catalyzed hydrovinylation of styrene[a]

Entry	Ligand	Anion	Time (h)	Conv (%)	Selectivity (%)			Ee of **7** (%)
					7	**8**	Oligomers	
1	(*R*)-**1b**	OTf^-	5.0	31	65	9	26	27 (*S*)
2	(*R*)-**1b**	BF_4^-	7.0	86	51	48	1	38 (*S*)
3	(*R*)-**1b**	PF_6^-	5.0	56	77	17	6	40 (*S*)
4[b]	(*R*)-**1b**	SbF_6^-	7.0	63	66	19	15	47 (*S*)
5	(*R*)-**1b**	$BARF^-$	1.5	48	76	14	10	58 (*S*)

[a] Reaction conditions: Styrene/Pd/**1b** = 200:1:1, 10 bar (initial pressure) ethylene, 25 °C, 3 mL CH_2Cl_2, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as catalyst precursor; AgX or NaBARF ($[3,5\text{-}(CF_3)_2C_6H_3]_4\ B^-\ [Na]^+$) as coactivator.
[b] At 0 °C.

role in various olefin dimerization and related reactions.[8] The results are summarized in Table 2. Consistent with the Ni-catalyzed asymmetric hydrovinylation reported by RajanBabu[2b] and Leinter and co-workers,[2c] a counter anion effect was observed in palladium-catalyzed hydrovinylation. The catalyst with the weakly coordinating anion TfO^- gave a poorer result in terms of both reactivity and enantioselectivity (Table 2, entry 1). Using a bulkier and more dissociating anions, such as BF_4^-, PF_6^-, and SbF_6^- significantly improved the reactivity and the enantioselectivity of the reaction (entries 2–4). The highest enantioselectivity (58% ee) was achieved by using the catalyst with $BARF^-$ anion.

Further optimization of the reaction conditions for asymmetric hydrovinylation of styrene was performed employing ligand **1b** and coactivitor NaBARF. Solvent screening showed that the reaction was very sensitive to the solvent used. In coordinating solvents, such as THF, no reaction occurred (Table 3, entry 6). However, higher reactivity and enantioselectivity were obtained in weakly coordinating nonpolar solvents, such as toluene and chlorobenzene (entries 2 and 3). As for protic solvents, for example, methanol, even a small amount completely quenched the reaction. The hydrovinylation under 1 bar of ethylene gave almost the same results as the reaction under 10 bar of ethylene, implying that the pressure of ethylene is not a controlling factor to the reaction (entry 7). When the reaction was carried out at 0 °C, the enantioselectivity increased to 68% ee, but the reaction became very slow (entry 8). The hydrovinylation reaction can also be performed with a lower catalyst loading ($S/C = 600$), providing a similar result (entry 9).

Under the optimized conditions, various vinylarenes were investigated in the hydrovinylation reaction. As shown in Table 4, the reactions for all vinylarene substrates were fast, finishing in 2 h. An electronic effect of substituents on the phenyl ring of styrene was observed. The styrenes substituted with electron-withdrawing groups, such as Cl or Br, gave poor enantioselectivities (entries 2 and 3), whereas those with electron-donating groups, such as methyl and *iso*-butyl, provided higher enantioselectivities (entries 4–6). The highest enantioselectivity was achieved in the hydrovinylation of 4-methylstyrene.

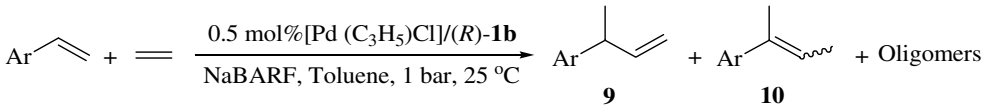
The catalytic hydrovinylation of vinylarenes is concomitant with the isomerization of the product 3-aryl-1-butene to the achiral 2-aryl-2-butene, which increased with prolonging reaction time. In the hydrovinylation of 4-methylstyrene, we found that when the reaction was quenched in 60 min, the conversion was 65%, and the selectivity of 3-(4-methylphenyl)-1-butene was 71% in 68% ee (entry 4). When the reaction time was prolonged to 120 min, the substrate 4-methylstyrene was completely converted, and the selectivity of 3-(4-methylphenyl)-1-butene dramatically dropped to 10%, while the enantioselectivity increased to 92% ee (entry 6). These

Table 3. Solvent, pressure, and temperature effect in the hydrovinylation of styrene[a]

Entry	Solvent	Time (h)	Conv (%)	Selectivity (%)			Ee of **7** (%)
				7	**8**	Oligomers	
1	CH_2Cl_2	1.5	48	76	14	10	58 (*S*)
2	Toluene	0.5	85	58	30	12	63 (*S*)
3	PhCl	0.5	62	76	16	8	62 (*S*)
4	CH_3NO_2	15.0	38	78	13	10	26 (*S*)
5	Et_2O	15.0	20	86	4	10	60 (*S*)
6	THF	15.0	N.R.[b]	—	—	—	—
7[c]	Toluene	1.0	88	57	32	11	64 (*S*)
8[c,d]	Toluene	12.0	83	63	24	13	68 (*S*)
9[e]	Toluene	1.5	86	49	23	28	63 (*S*)

[a] Reaction conditions: Styrene/[Pd]/**1b** = 200:1:1, 10 bar ethylene, 25 °C, 3 mL solvent, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as catalyst precursor, NaBARF as coactivator unless otherwise stated.
[b] No reaction.
[c] Under 1 bar ethylene.
[d] At 0 °C.
[e] $S/C = 600$.

Table 4. Palladium-catalyzed asymmetric hydrovinylation of vinylarenes and ethylene[a]



Entry	Substrate	Time (min)	Conv (%)	Selectivity (%)[b]			Ee of **9** (%)[c]
				9	**10**	Oligomers	
1	Styrene	60	88	57	32	11	64 (*S*)
2	4-Bromostyrene	15	56	78	18	4	20
3	3-Chlorostyrene	45	72	62	32	6	36
4	4-Methylstyrene	60	65	71	11	18	68
5	4-Methylstyrene	100	98	41	45	14	77
6	4-Methylstyrene	120	100	10	75	15	92
7	3-Methystyene	30	75	72	15	13	72
8	4-*i*-Bu-styrene	45	79	72	25	3	76
9	2-Vinylnaphthanlene	120	73	85	15	0	55 (*S*)[d]

[a] Reaction conditions: vinylarene/Pd/**1b** = 200:1:1, 1 bar ethylene, 25 °C, 3 mL toluene, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as catalyst precursor, NaBARF as coactivator.
[b] Determined by GC using a HP-5 column.
[c] Determined by chiral GC using a Suplco β-DEX 120 column.
[d] Determined by chiral HPLC using a Chiralcel OJ column.

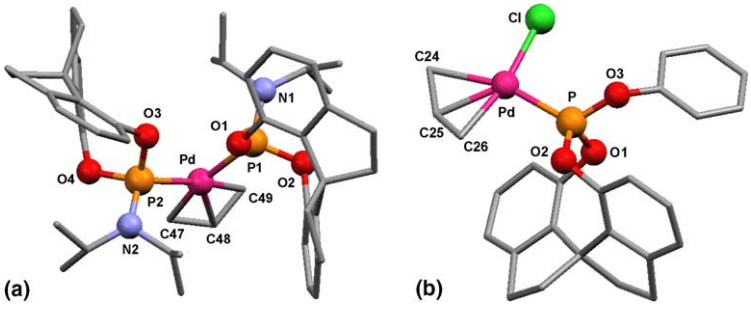


Figure 2. Crystal structures of $[Pd(\eta^3\text{-}C_3H_5)((R)\text{-}1\mathbf{b})2]BF_4$ (a) and $[Pd(\eta^3\text{-}C_3H_5)Cl((R)\text{-}5\mathbf{a})]$ (b), anions are omitted for clarity.

results indicated that a kinetic resolution accompanied isomerization of the hydrovinylation product.[3]

To understand the structure of catalyst and the features of the reaction, we grew two single crystals of palladium complex of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands **1b** and **5a**, which are suitable for X-ray diffraction analysis (Fig. 2). The complex $[Pd(\eta^3\text{-}C_3H_5)((R)\text{-}\mathbf{1b})_2]BF_4$[9] (Fig. 2, **a**) has a C_2-symmetric structure with two phosphoramidite ligands coordinated to palladium in a square planar geometry. The complex $[Pd(\eta^3\text{-}C_3H_5)Cl((R)\text{-}\mathbf{5a})]$[10] (Fig. 2, **b**) has a tetrahedron geometry with one ligand coordinated to palladium. When the crystal of $[Pd(\eta^3\text{-}C_3H_5)Cl((R)\text{-}\mathbf{5a})]$ was used as catalyst, the hydrovinylation of styrene proceeded smoothly, and the results are the same as those with the in situ prepared catalyst. But using the crystal of $[Pd(\eta^3\text{-}C_3H_5)((R)\text{-}\mathbf{1b})_2]BF_4$, which has two ligands coordinated, as a catalyst gave no reaction. These experimental results demonstrated that more than one monodentate ligands coordinated to palladium strongly inhibit the hydrovinylation reaction. This might be due to the lack of coordinating site on palladium for a second olefin coming into the putative benzylic metal intermediate.[11]

3. Conclusion

In summary, we have established a new efficient catalytic system for palladium-catalyzed asymmetric hydrovinylation of vinylarenes using monodentate chiral spiro phosphoramidite and phosphite ligands. Moderate to good chemoselectivity and enantioselectivity have been achieved in the reaction. The isomerization of hydrovinylation products 3-aryl-1-butene to the achiral 2-aryl-2-butene was accompanied by a kinetic resolution, which is beneficial to the increase of enantiomerical purity of hydrovinylation product. X-ray analysis of crystal structures revealed that the active catalyst contained one monodentate ligand.

4. Experimental

4.1. General

All reactions and manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Brucker-300 spectrometers. Chemical shifts were

reported in ppm downfield from internal $Si(CH_3)_4$ and external 85% H_3PO_4, respectively. Optical rotations were determined using a Perkin Elmer 341 polarimeter. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were measured on a RY-I apparatus and uncorrected. GC analyses were performed using Hewlett Packard Model HP 6890 Series. Toluene and THF were distilled from sodium-benzophenone ketyl under nitrogen. Methylene chloride, chlorobenzene, and nitromethane were distilled from CaH_2 under nitrogen atmosphere. Styrene was distilled from CaH_2 and stored at low temperature. All vinylarenes were purchased from Aldrich except 4-*iso*-butylstyrene that was prepared from 4-bromostyrene according to the reported literature.[12] The ethylene used had a purity of >99.99%. $[Pd(\eta^3\text{-}C_3H_5)(COD)]BF_4$[13] and NaBARF[14] were prepared according to the literature methods. Ligands **1**, **2**, **3**, **4** and **5a** were prepared by the previously reported methods.[7a]

4.2. Synthesis of spiro phosphite ligands 5b and 6

4.2.1. 2,6-Dimethylphenyl-[(*R*)-1,1′-spirobiindane-7,7′-diyl]-phosphite (*R*)-5b. *General procedure:* To a stirred solution of PCl_3 (110 μL, 1.3 mmol), Et_3N (380 μL, 2.7 mmol), and THF (25 mL) was added (*R*)-1,1′-spirobiindane-7,7′-diol (308 mg, 1.2 mmol) in 5 mL THF at −78 °C and the mixture was stirred for 2 h. After warming to room temperature, the reaction mixture was filtered, and the filtrate was cooled to −78 °C again. A solution of lithium phenolate prepared from 2,6-dimethylphenol (166 mg, 1.36 mmol) and *n*-butyllithium (1.6 M solution in hexane, 0.85 mL, 1.36 mmol) was added to the above filtrate. After the addition, the resulting solution was warmed to room temperature, and was stirred overnight. Then, the reaction mixture was concentrated in vacuo and the obtained residue was purified by a flash chromatography on silica gel using petroleum ether/EtOAc (30:1) as an eluent to give (*R*)-**5b** as a white solid (367 mg, 76% yield). Mp: 143–145 °C. $[\alpha]_D^{25} = +324$ (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 7.25–6.81 (m, 9H), 3.16–3.04 (m, 2H), 2.90–2.81 (m, 2H), 2.31–2.26 (m, 2H), 2.24 (s, 6H), 2.09–2.0 (m, 2H). ^{31}P NMR (300 MHz, $CDCl_3$): δ 122.7. ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.2, 146.2, 145.8, 145.1, 144.1, 144.0, 143.2, 140.2, 130.8, 129.1, 128.6, 127.8, 124.5, 123.0, 122.1, 121.9, 121.8, 121.6, 59.5, 38.9, 38.1, 31.2, 30.7, 18.0. HR-MS (FAB) calcd for $C_{25}H_{23}O_3P + H$: 403.1447. Found: 403.1457.

4.2.2. (*S*)-[2-(2′-Methoxy-1,1′-binaphthyl)]-[(*R*)-1,1′-spirobiindane-7,7′-diyl]-phosphite (*R*,*S*)-6. Ligand (*R*,*S*)-6 was synthesized in 70% yield with (*S*)-2′-methoxyl-1,1′-binaphthyl-2-ol using the same procedure as that for (*R*)-**5b**. Mp: 124–125 °C. $[\alpha]_D^{25} = +62$ (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 8.12–6.67 (m, 18H), 3.70 (s, 3H), 3.07–2.96 (m, 2H), 2.77–2.70 (m, 2H), 2.20–2.03 (m, 2H), 1.93–1.81 (m, 2H). ^{31}P NMR (300 MHz, $CDCl_3$): δ 118.9. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.6, 148.0, 145.9, 145.1, 143.4, 142.8, 139.5, 134.1, 133.9, 130.8, 130.0, 129.3, 129.2, 128.3, 128.0, 127.3, 126.8, 126.6, 125.9, 125.1, 124.8, 123.8, 122.2, 121.7, 121.2, 120.8, 120.6, 118.6, 113.9, 38.4, 37.8, 30.8, 30.4. HR-MS (FAB) calcd for $C_{38}H_{29}O_4$ P + H: 581.1876. Found: 581.1866.

4.2.3. (*R*)-[2-(2′-Methoxy-1,1′-binaphthyl)]-[(*R*)-1,1′-spirobiindane-7,7′-diyl]phosphite (*R*,*R*)-6. Ligand (*R*,*R*)-**6** was synthesized in 70% yield with (*R*)-2′-methoxyl-1,1′-binaphthyl-2-ol using the same procedure as that for (*R*)-**5b**. Mp: 210–212 °C. $[\alpha]_D^{25} = +68$ (*c* 0.5, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 8.10–6.17 (m, 18H), 3.79 (s, 3H), 3.07–2.87 (m, 2H), 2.80–2.64 (m, 2H), 2.18–2.07 (m, 2H), 1.94–1.78 (m, 2H). ^{31}P NMR (300 MHz, $CDCl_3$): δ 119.8. ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.1, 148.1, 145.9, 144.9, 143.1, 143.0, 139.3, 134.0, 131.0, 130.0, 129.4, 128.3, 128.1, 127.8, 127.1, 126.7, 126.0, 125.7, 124.9, 123.7, 122.3, 121.9, 121.8, 121.3, 121.2, 121.1, 118.5, 113.5, 59.0, 56.4, 38.5, 37.7, 30.9, 30.4. HR-MS (FAB) calcd for $C_{38}H_{29}O_4P + H$: 581.1876. Found: 581.1875.

4.3. General procedure for the palladium-catalyzed asymmetric hydrovinylation of vinylarenes

The mixture of phosphoramidite (*R*)-**1b** (3.9 mg, 0.01 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol) in toluene (2 mL) in a Schlenk tube was stirred at room temperature for 1 h, and then transferred to another Schlenk tube which contained a suspension of NaBARF in toluene (1 mL). The resulted mixture was stirred at room temperature for 20 min and the color of the solution turned to yellow. After added styrenes (2.0 mmol), the oxygen-free ethene (1 atm) was introduced into the tube. The reaction mixture was vigorously stirred at 25 °C for several hours under the ethene atmosphere (1 atm). The reaction solution was then diluted with ether, quenched with a saturated aqueous NH_4Cl, and washed with brine. The organic layers were separated and dried over anhydrous Na_2SO_4, purified by a short silica gel column. The conversion, selectivity, and ee values of products were analyzed by GC or HPLC.

The GC and HPLC conditions for the determinations of ee values of hydrovinylation products are as follows:

3-Phenyl-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 1.2 mL/min; 65 °C (constant), t_R = 37.73 min (*R*), t_R = 38.55 min (*S*).

3-(4-Methylphenyl)-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 1.2 mL/min; 75 °C (constant), t_R = 59.18 (minor), t_R = 60.63 min (major).

3-(4-Bromophenyl)-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 1.2 mL/min; 100 °C for 50 min and then programmed at 1 °C/min to 120 °C, t_R = 62.70 (minor), t_R = 63.58 min (major).

3-(3-Methylphenyl)-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 1.1 mL/min; 80 °C (constant), t_R = 36.50 (minor), t_R = 37.32 min (major).

3-(3-Chlorophenyl)-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 1.1 mL/min; 75 °C for 60 min and then programmed at 1 °C/min to 100 °C, t_R = 72.75 (minor), t_R = 73.57 min (major).

3-(4-Isobutylphenyl)-1-butene: Supelco β-DEX™ 120 column, 25 m × 0.25 mm × 0.25 μm; N_2, 0.3 mL/min; 115 °C for 10 min, programmed at 0.5 °C/min to 130 °C, t_R = 53.74 (minor), t_R = 54.25 min (major).

3-(2-Naphthalenyl)-1-butene: Chiral Daciel OJ column, *n*-hexane as eluent, 0.3 mL/min; t_R = 56.76 min (*R*), t_R = 61.03 min (*S*).

Acknowledgements

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9. *Crystal data*: Orthorhombic, space group *P*2(1)2(1)2; *a* = 20.508(6), *b* = 24.183(7), *c* = 10.964(3) [Å]; *V* = 5437(3) [Å]^3, *Z* = 4, crystal dimensions = 0.2 × 0.20 × 0.12 mm, *T* = 293(2) K, radiation = MoKa, λ = 0.71073 [Å], unique data = 9503, *R* = 0.0424. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 259832. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ: [fax: +44(0) 1223-336033 or deposit@ccdc.cam.ac.uk].
10. *Crystal data*: Orthorhombic, space group *P*2(1)2(1)2; *a* = 7.306(8), *b* = 14.912(17), *c* = 21.25(3) [Å]; *V* = 2315(5) [Å]^3, *Z* = 4, crystal dimensions = 0.25 × 0.20 × 0.20 mm, *T* = 298(2) K, radiation = MoKa, λ = 0.71073 [Å], unique data = 4220, *R* = 0.0234. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 259831. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ: [fax: +44(0) 1223-336033 or deposit@ccdc.cam.ac.uk].
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