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Nickel(0)-catalysed asymmetric cross-coupling reactions of allylic compounds with Grignard reagents using optically active oxazolinylferrocenylphosphines as ligands

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Optically active oxazolinylferrocenylphosphines work effectively as chiral P–N ligands in nickel(0)-catalysed cross-coupling reactions of allylic compounds with Grignard reagents, which are known to behave as "hard" nucleophiles, to give the expected coupling products in high yields and high enantioselectivities (30–100% chemical yield and 14–95% ee). These ligands are revealed to be more effective than optically active oxazolinylphenylphosphines which have only a central chirality.

Introduction

Asymmetric synthesis catalysed by transition metals is now a field of great attention and various kinds of optically active ligands which coordinate to the metal have been devised in order to achieve high enantioselectivities. Optically active oxazolinylferrocenylphosphines (4,5-dihydrooxazolylferrocenylphosphines) (Chart 1, **I**–**V**)[1] having both planar and central

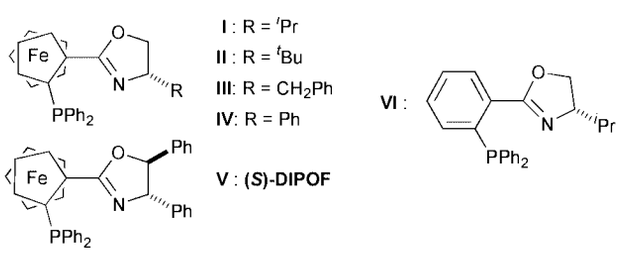
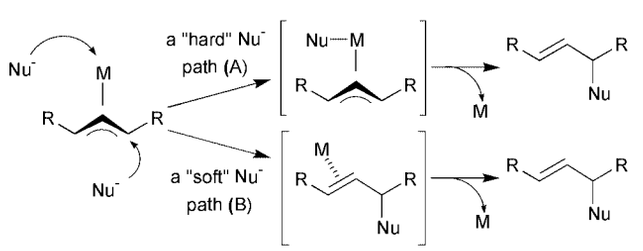


Chart 1

chiralities function as such ligands quite effectively in several reductive reactions such as rhodium(I)-, iridium(I)-, or ruthenium(II)-catalysed hydrosilylation of ketones or imines[2] and ruthenium(II)-catalysed transfer hydrogenation of ketones.[3] Furthermore, they are utilized in some carbon–carbon bond forming reactions[4] including palladium(0)[5]- or nickel(0)[6]-catalysed allylic substitution reaction using either "soft" or "hard" nucleophiles, respectively, to construct new carbon–carbon bonds.

Mechanistically, the allylic substitution reaction with a "hard" nucleophile is considered to proceed differently from that with a "soft" nucleophile; a "hard" nucleophile attacks a transition metal first [Scheme 1, path (A)], while a "soft" one attacks an allylic carbon directly [Scheme 1, path (B)].[7] Excellent selectivities have been attained using transition metal catalysts with various chiral ligands in the allylation with "soft" nucleophiles such as dimethyl malonate.[8] However, examples of the reaction with the corresponding "hard" nucleophiles are quite limited, most of which are nickel-catalysed allylic substitutions with Grignard reagents in the presence of chiral P–P ligands.[9,10] Very recently, we reported that arylboronic acids behave as "hard" nucleophiles in the cross-coupling reaction with allylic compounds catalysed by nickel(0) with optically active oxazolinylferrocenylphosphines as chiral P–N ligands to give the corresponding arylated products with moderate enantioselectivities (up to 53% ee).[6] This, to the best of our knowledge, was the first example of allylation using not only organoheteroatom reagents but also chiral P–N ligands. We have now disclosed that Grignard reagents can also be employed as "hard" nucleophiles in place of arylboronic acids in nickel(0)-catalysed asymmetric cross-coupling reaction of allylic compounds using optically active oxazolinylferrocenylphosphines (Chart 1, **I**–**V**) as chiral P–N ligands, the expected coupling products being obtained more stereoselectively. These phosphines have been revealed to be more effective than the corresponding phosphines only having central chirality such as **VI**.[2d,3c]



Scheme 1

Results and discussion

First, similar reaction conditions to those employed in the case of arylboronic acids[6] were applied to the cross-coupling reactions between Grignard reagents and allylic compounds; namely, in tetrahydrofuran (THF) at reflux with 3-acetoxycyclohexene (**1a**, 1 equiv.) and phenylmagnesium bromide (3 equiv. to **1a**, 1.0 M THF solution) in the presence of nickel(II) acetylacetonate [$Ni(acac)_2$] (5 mol%), diisobutylaluminium hydride (DIBAL-H) (16 mol%), and an optically active oxazolinylferrocenylphosphine (**I**, 10 mol%) as a chiral ligand. However, the reaction did not proceed well and the amount of desired coupling product, 3-phenylcyclohexene (**3w**), was low and not enough to measure its optical yield on a polarimeter. Next, the reaction was conducted at room temperature with the other conditions kept constant (Scheme 2); **3w** was then obtained in 33% chemical yield with 84% ee after 17 h together with a by-product, biphenyl (Table 1, Entry 1). The result is better than the case using phenylboronic acid from the standpoint that

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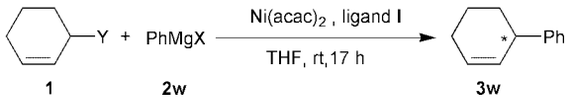


Scheme 2

Table 1 Nickel-catalysed cross-coupling reactions between 3-substituted cyclohexenes and phenylmagnesium halides[a]

Entry	1X	2w	Yield (%)[b]	Ee (%)[c]	Ph–Ph (%)[d]
1[e]	**1a**	Br	33	84	15
2	**1a**	Br	97	84	64
3	**1a**	Cl	53	87	13
4[f]	**1a**	I	63	74	45
5	**1b**	Br	79	69	47
6	**1c**	Br	93	88	60
7	**1c**	Cl	83	84	23
8	**1d**	Br	98	87	57
9	**1e**	Br	36	82	45
10	**1f**	Br	95	15	68

[a] Reaction conditions: **1** (0.50 mmol), **2w** (1.5 mmol, THF solution), $Ni(acac)_2$ (0.025 mmol), ligand **I** (0.050 mmol), THF (total 3 mL), at rt for 17 h. [b] Determined by GLC based on **1**. [c] Determined by optical rotation; (*S*)-configuration predominated in all cases. [d] Determined by GLC; 0.75 mmol of biphenyl corresponds to 100%. [e] In the presence of DIBAL-H (0.080 mmol). [f] THF (total 5 mL).

the reaction proceeded even at room temperature with higher enantioselectivity, whereas the compound **3w** was not detected by GLC analysis in the reaction using phenylboronic acid which proceeded only under reflux in THF and in the presence of potassium hydroxide.[6] Furthermore, a drastic improvement in chemical yield was observed when the reaction was carried out in the absence of DIBAL-H which was employed as a reductant of Ni(II) to Ni(0) (Entry 2). In this case, apparently the reactant PhMgBr itself acted as a reducing agent. Hoping to achieve higher selectivities, the experiments at temperatures below room temperature were also attempted. In the reaction at 0 °C or −20 °C, a slight decrease in enantioselectivity (69% ee and 72% ee, respectively) as well as yield (81% and 79%, respectively) of **3w** was observed, while **3w** was obtained at −78 °C in trace quantities. When phenylmagnesium chloride was used in place of the bromide, the yield of **3w** as well as the by-product, biphenyl, was reduced without loss of any enantioselectivity of **3w** (Entry 3), while the reaction using the iodide resulted in a lower optical yield (Entry 4). As to the effect of the nature of the leaving group (Chart 2), cyclohex-2-enyl carbonate (**1b**),

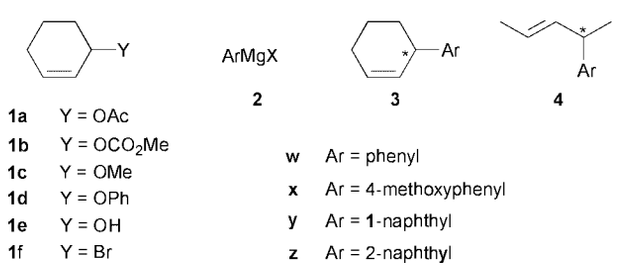


Chart 2

3-methoxycyclohexene (**1c**) and 3-phenoxycyclohexene (**1d**) could be employed in place of **1a** (Entries 5–8), although a slight decrease in both chemical and optical yields was observed in the case of **1b**. The utilization of cyclohex-2-enol (**1e**) resulted in lower chemical yield (Entry 9) and a great decrease in enantioselectivity was observed in the reaction with 3-bromocyclohexene (**1f**, Entry 10). In contrast to the reactions using phenylboronic acid where biphenyl was scarcely produced, the formation of variable amounts of biphenyl was observed in the reaction using phenylmagnesium bromide. Additionally, the enhancement of selectivity for the formation of **3w** over

Table 2 Effect of chiral ligands on nickel-catalysed asymmetric substitution[a]

Entry	Ligand	Yield (%)[b]	Ee (%)[c]	Ph–Ph (%)[d]
1	**I**	83	86	23
2	**II**	74	32	29
3	**III**	100	76	44
4	**IV**	94	84	26
5	**V**	80	71	33
6	**VI**	91	52	36

[a] Reaction conditions: **1c** (0.50 mmol), PhMgCl (1.5 mmol, 2.0 M THF solution), $Ni(acac)_2$ (0.025 mmol), ligand (0.050 mmol), THF (total 3 mL), at rt for 17 h. [b] Determined by GLC based on **1c**. [c] Determined by optical rotation; (*S*)-configuration predominated in all cases. [d] Determined by GLC; 0.75 mmol of biphenyl corresponds to 100%.

biphenyl was not observed either by carrying out the reactions for shorter periods (0.5–8 h) than 17 h, by using a smaller amount of PhMgBr (1.2 equiv. to **1a**), or by a quite slow addition of PhMgBr (2 h *vs.* 5 min).

Next, oxazolinylferrocenylphosphines other than **I** (Chart 1) were examined under the conditions of Entry 7 in Table 1 and typical results are shown in Table 2. The same trend was seen as observed in the reactions using phenylboronic acid; each ligand including **V** ((*S*,*S*,*S*)-[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine, abbreviated as **(*S*)-DIPOF**) was found to be efficient except **II** and, especially, the ligand **IV** showed similar effectiveness to **I** (84% ee, Entry 4). It is noteworthy that in the reaction using the ligand **VI**,[11] which has no planar chirality, the product showed only moderate enantioselectivity (52% ee, Entry 6). This result clearly shows the importance of the presence of planar chirality in **I**.

Using the conditions described above, the reactions of other Grignard reagents (Chart 2) with 5- or 6-membered cyclic compounds were carried out (Table 3). In each reaction using cyclohexenyl compounds, the expected coupling products were obtained with high enantioselectivities; especially **1d** and 2-naphthylmagnesium bromide (**2z**, X = Br) underwent coupling to give 3-(2-naphthyl)cyclohexene (**3z**) of 95% ee (Entry 8). In the cases using sterically hindered 1-naphthyl or 2-naphthylmagnesium bromide, an improvement in chemical yields was achieved by adding a catalytic amount of DIBAL-H as a reductant (Entries 7 and 9). 3-(4-Methoxyphenyl)cyclohexene (**3x**) was also prepared from 4-methoxyphenylmagnesium chloride (**2x**, X = Cl), but the chemical yield was much lower (Entry 5). From a five-membered cyclic compound, 3-phenoxycyclopentene, the expected product was obtained quantitatively, but with a moderate enantioselectivity (47% ee, Entry 10).

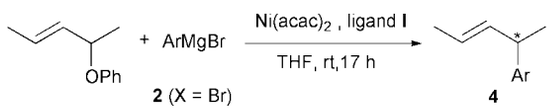
When the reaction was applied to an acyclic compound, 4-phenoxypent-2-ene, the coupling products showed only moderate enantioselectivities (Scheme 3, Table 4); in each case, the formation of a small amount of its *cis* isomer (*trans*/*cis* = 92–95/5–8) was observed by ^{1}H-NMR analysis. Unsymmetrical acyclic substrates, 1-phenoxyhex-2-ene and 1-phenoxybut-2-ene, were also applied to this reaction system (Schemes 4 and 5). In each case, the regioselectivity for the phenylated product with a chiral center as well as the enantioselectivity of the product was low.[12,13]

We believe that the catalytic cycle of this reaction is as follows (*cf.* Scheme 1, path (a) and ref. 8): (1) reduction of Ni(II) to Ni(0) by ArMgX producing biaryl where a chiral P–N ligand coordinates to Ni(0), (2) oxidative addition of Ni(0) to an allylic compound to give an allylic nickel(II) species, (3) nucleophilic attack of a Grignard reagent to the nickel(II) species (transmetallation) to give an allylic arylnickel(II) species and (4) reductive elimination to produce a cross-coupling product and to regenerate Ni(0). However, details of the structure of the

Table 3 Effect of 3-substituted cyclohexenes and Grignard reagents on nickel-catalysed asymmetric allylic substitution[a]

Entry	1	2 (X = Br)	Yield of 3 (%)[b]	Ee (%)	$[\alpha]_D^{25}$
1	**1c**	**2w**	93	88[c]	−140 (*c* 0.53, benzene)[d]
2	**1d**	**2w**	98	87[c]	−139 (*c* 0.53, benzene)[d]
3	**1c**	**2x**	73	91[e]	−135 (*c* 0.30, EtOH)
4	**1d**	**2x**	69	91[e]	
5	**1d**	**2x**[f]	28	85[e]	
6	**1d**	**2y**	7	64[e]	
7[g]	**1d**	**2y**	39	80[e]	+22 (*c* 0.50, EtOH)
8	**1d**	**2z**	50	95[e]	
9[g]	**1d**	**2z**	72	88[e]	−169 (*c* 0.50, EtOH)
10	—[h]	**2w**	100[i]	47[c]	−99 (*c* 0.60, $CHCl_3$)[j]

[a] Reaction conditions; the allylic compound (0.50 mmol), ArMgX (1.5 mmol, 1.0 M THF solution), $Ni(acac)_2$ (0.025 mmol), ligand **I** (0.050 mmol), THF (total 3 mL), at rt for 17 h. [b] Determined by GLC based on the allylic compound. [c] Determined by optical rotation; (*S*)-configuration predominated in all cases. [d] See ref. 16. [e] Determined by HPLC analysis using suitable chiral columns. [f] X = Cl. [g] In the presence of DIBAL-H (0.080 mmol). [h] 3-Phenoxycyclopentene was used. [i] The yield of 3-phenylcyclopentene. [j] See ref. 17.

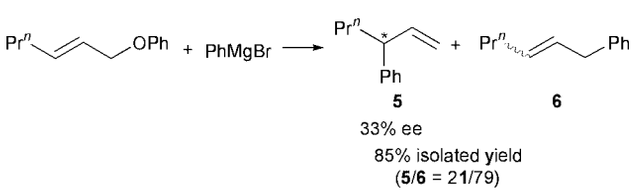


Scheme 3

Table 4 Nickel-catalysed cross-coupling reactions between 4-phenoxypent-2-ene and Grignard reagents[a]

Entry	2 (X = Br)	Yield (%) of 4[b]	Ee (%)[c]
1	**2w**	90[d]	40[e]
2	**2x**	40	37
3[f]	**2y**	30	14[g]
4	**2z**	49	38

[a] Reaction conditions; the allylic compound (0.50 mmol), ArMgBr (1.5 mmol, 1.0 M THF solution), $Ni(acac)_2$ (0.025 mmol), ligand **I** (0.050 mmol), THF (total 3 mL), at rt for 17 h. [b] Determined by GLC based on the allylic compound; *trans*/*cis* = 92–95/5–8. [c] Determined by HPLC analysis. [d] Isolated yield. [e] (*S*)-configuration predominated. [f] In the presence of DIBAL-H. [g] Determined by ^{1}H-NMR analysis of methyl ester derived from 4-(1-naphthyl)pent-2-ene in the presence of $Eu(hfc)_3$ (see Experimental).



Scheme 4

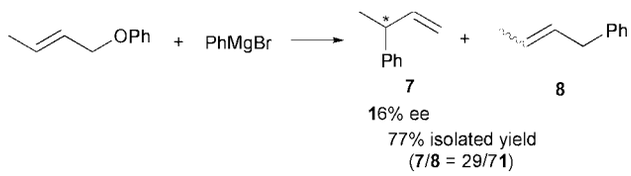
intermediate species as well as the origin of the high enantioselectivity are not yet clear at present.

In summary, we have found that optically active oxazolinylferrocenylphosphines function as chiral P–N ligands in nickel(0)-catalysed cross-coupling reactions of allylic compounds with Grignard reagents. The reaction proceeded at much lower temperature than the case of similar coupling reactions using arylboronic acids, and the desired coupling product was obtained in higher yield with much higher enantioselectivities (up to 100% chemical yield and 95% ee).

Experimental

General

^{1}H- and ^{13}C-NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300, and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a CPB 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 mm film thickness)



Scheme 5

column using helium as carrier gas. GLC yields were determined using bibenzyl or pentamethylbenzene as an internal standard. Optical rotations were measured on JASCO DIP-1000 instrument. HPLC analyses were carried out on an L-7300 instrument with an L-7400 detector (HITACHI) using a Daicel Chiralcel OB, OD or OJ column. Column chromatographies were performed with Merck silica gel 60.

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Other commercially available compounds including $Ni(acac)_2$ (not dried) and diisobutylaluminium hydride (DIBAL-H) were used without further purification. Chiral oxazolinylferrocenylphosphines (**I**–**V**)[1a,1b] as well as the compound **VI**[11] were prepared by the reported methods. Cyclohex-2-enol (**1e**) was prepared by reduction of cyclohex-2-en-1-one with $NaBH_4$ and $CeCl_3 \cdot 7H_2O$ in methanol.[14] 3-Acetoxycyclohexene (**1a**) and 1-acetoxyhex-2-ene were prepared by acetylation of the corresponding alcohol with acetic anhydride. Cyclohex-2-enyl carbonate (**1b**) was prepared from **1e** and methyl chlorocarbonate. 3-Methoxycyclohexene was prepared by methylation of **1e** with iodomethane. 3-Bromocyclohexene (**1f**) was prepared by treatment of cyclohexene with NBS (*N*-bromosuccinimide). All phenyl ethers were prepared according to the literature procedure.[15]

General procedure for Ni(0)-catalysed cross-coupling reaction of 3-acetoxycyclohexene (1a) with phenylmagnesium bromide (Table 1, Entry 1)

To a mixture of $Ni(acac)_2$ (6.5 mg, 0.025 mmol), (*S*,*S*)-[2-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine (**I**, 24.0 mg, 0.050 mmol), and bibenzyl (as an internal standard; 19.9 mg) in THF (0.5 mL) was added DIBAL-H (1.0 M solution in hexane; 0.080 mL, 0.080 mmol) at 0 °C under nitrogen. After stirring for 30 min, a solution of 3-acetoxycyclohexene (**1a**, 70.1 mg, 0.50 mmol) in THF (1.0 mL) was added. Fifteen minutes later, the 1.0 M THF solution of phenylmagnesium bromide (1.5 mL, 1.5 mmol) was added dropwise (for about 5 min) at 0 °C to the mixture which was stirred at rt for 17 h. The resulting mixture was quenched with a saturated aqueous solution of ammonium chloride, extracted three times with diethyl ether and the organic layer was dried over $MgSO_4$. The amount of the product **3w** was determined by

GLC analysis. For isolation of **3w** the solvent was evaporated and the residue was purified by column chromatography using hexane as an eluent. Typical spectroscopic data of the obtained coupling products are as follows.

3-Phenylcyclohexene (3w). Colorless liquid; ^{1}H-NMR δ = 1.49–2.11 (6H, m), 3.42 (1H, m), 5.71 (1H, m), 5.89 (1H, m), 7.16–7.33 (5H, m); ^{13}C-NMR δ = 21.19, 25.01, 32.60, 41.85, 125.94, 127.71, 128.24, 128.33, 130.18, 146.64. The ee value and the configuration of the product were determined using a polarimeter based on the reported rotation of an optically pure (*R*)-**3w**, $[\alpha]_D^{29}$ = +159.6 (*c* 0.53, benzene).[16]

3-(4-Methoxyphenyl)cyclohexene (3x). Colorless liquid; ^{1}H-NMR δ = 1.48–1.67 (3H, m), 1.69–1.77 (1H, m), 1.95–2.01 (1H, m), 2.06–2.10 (2H, m), 3.32–3.38 (1H, m), 3.79 (3H, s), 5.69 (1H, dd, *J* = 10.0, 2.2 Hz), 5.83–5.89 (1H, m), 6.84 (2H, d, *J* = 8.5 Hz), 7.13 (2H, d, *J* = 8.5 Hz); ^{13}C-NMR δ = 21.13, 25.03, 32.73, 40.97, 55.27, 113.69, 128.13, 128.61, 130.53, 138.81, 157.89. The ee value was determined by HPLC analysis with a Daicel Chiralcel OB column (eluent: hexane).

3-(1-Naphthyl)cyclohexene (3y). Colorless liquid; ^{1}H-NMR δ = 1.64–1.78 (3H, m), 2.15–2.21 (3H, m), 4.19–4.26 (1H, m), 5.83 (1H, dd, *J* = 10.0, 2.6 Hz), 5.98–6.05 (1H, m), 7.37–7.54 (4H, m), 7.72 (1H, dd, *J* = 7.4, 2.1 Hz), 7.87 (1H, dd, *J* = 7.4, 2.2 Hz), 8.13 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR δ = 20.86, 25.25, 30.91, 37.00, 123.41, 125.06, 125.27, 125.42, 125.71, 126.60, 126.77, 128.92, 130.22, 131.40, 134.10, 141.92; IR (neat) 724, 761, 778, 796, 2834, 2858, 2930, 3018, 3045, 3059 cm^{-1} (Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.50; H, 7.83%). The ee value was determined by HPLC analysis with a Daicel Chiralcel OB column (eluent: hexane).

3-(2-Naphthyl)cyclohexene (3z). Colorless liquid; ^{1}H-NMR δ = 1.62–2.23 (6H, m), 3.56–3.60 (1H, m), 5.81 (1H, dd, *J* = 10.0, 2.1 Hz), 5.92–6.00 (1H, m), 7.35–7.61 (3H, m), 7.64 (1H, s), 7.76–7.88 (3H, m); ^{13}C-NMR δ = 21.12, 25.09, 32.41, 41.91, 125.14, 125.79, 125.81, 126.71, 127.55, 127.58, 127.84, 128.64, 130.06, 132.16, 133.55, 144.06; IR (neat) 723, 744, 757, 815, 853, 2835, 2856, 2927, 3018, 3052 cm^{-1} (Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.45; H, 7.70%). The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ (eluent: hexane).

3-Phenylcyclopentene. Colorless liquid; ^{1}H-NMR δ = 1.69–1.76 (1H, m), 2.35–2.54 (3H, m), 3.89 (1H, m), 5.78 (1H, m), 5.93 (1H, m), 7.18–7.20 (3H, m), 7.25–7.31 (2H, m); ^{13}C-NMR δ = 32.50, 33.78, 51.32, 125.96, 127.20, 128.36, 131.91, 134.28, 146.52. The ee value and the configuration of the product were determined by a polarimeter based on the reported rotation of an optically pure product of (*S*)-configuration, $[\alpha]_D^{30}$ = −212 (*c* 0.596, chloroform).[17]

4-Phenylpent-2-ene (4w). Colorless liquid; ^{1}H-NMR δ = 1.33 (3H, d, *J* = 7.3 Hz), 1.67 (3H, d, *J* = 7.3 Hz), 3.41 (1H, m, *trans* isomer), 3.79 (1H, m, *cis* isomer), 5.42–5.65 (2H, m), 7.16–7.31 (5H, m); ^{13}C-NMR δ = 17.88, 21.46, 42.33, 123.63, 125.90, 127.13, 128.32, 136.24, 146.48. The diastereoisomeric ratio of **4w** (*trans*/*cis* = 95/5) was determined by ^{1}H-NMR analysis and the ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column (eluent: hexane). The configuration of the product was determined by a polarimeter after conversion of **4w** into 2-phenylpropionic acid by an oxidative cleavage using $KMnO_4$ and $NaIO_4$, based on the reported rotation of an optically pure product of (*S*)-configuration of 2-phenylpropionic acid, $[\alpha]_D$ = +76.2 (*c* 3, chloroform).[18]

4-(4-Methoxyphenyl)pent-2-ene (4x). Colorless liquid; ^{1}H-NMR δ = 1.30 (3H, d, *J* = 7.0 Hz), 1.66 (3H, d, *J* = 6.1 Hz), 3.36 (1H, m, *trans* isomer), 3.76 (1H, m, *cis* isomer), 3.78 (3H, s), 5.39–5.49 (1H, m), 5.55–5.62 (1H, m), 6.84 (2H, d, *J* = 8.7 Hz), 7.12 (2H, d, *J* = 8.7 Hz); ^{13}C-NMR δ = 17.88, 21.57, 41.45, 55.25, 113.73, 123.33, 128.00, 136.58, 138.62, 157.79. The diastereoisomeric ratio could not be determined because the peak of the allylic proton of the *cis* isomer overlaps with that of the methyl protons of the methoxy group in the ^{1}H-NMR spectrum. The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column (eluent: hexane).

4-(1-Naphthyl)pent-2-ene (4y). Colorless liquid; ^{1}H-NMR δ = 1.47 (3H, d, *J* = 6.8 Hz, *trans* isomer), 1.48 (3H, d, *J* = 7.0 Hz, *cis* isomer), 1.69 (3H, dt, *J* = 6.4, 1.4 Hz, *trans* isomer), 1.74 (3H, dd, *J* = 6.6 Hz, *cis* isomer), 4.24 (1H, m, *trans* isomer), 4.53 (1H, m, *cis* isomer), 5.46–5.80 (2H, m), 7.36–7.53 (4H, m), 7.70 (1H, d, *J* = 7.7 Hz), 7.84 (1H, m), 8.13 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR δ = 17.98, 21.06, 37.02, 123.43, 123.61, 124.13, 125.25, 125.58, 125.63, 126.56, 128.84, 131.44, 133.96, 135.82, 142.34. The diastereoisomeric ratio of **4y** (*trans*/*cis* = 92/8) was determined by ^{1}H-NMR analysis and the ee value was determined by ^{1}H-NMR analysis in the presence of Eu(hfc)$_3$ (europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]) after conversion of **4y** to 2-(1-naphthyl)propionic acid by a similar method for **4w** and then into its methyl ester, methyl 2-(1-naphthyl)propionate.

4-(2-Naphthyl)pent-2-ene (4z). Colorless liquid; ^{1}H-NMR δ = 1.42 (3H, d, *J* = 6.9 Hz), 1.69 (3H, dt, *J* = 6.0, 1.2 Hz, *trans* isomer), 1.73 (3H, d, *J* = 1.4 Hz, *cis* isomer), 3.53–3.63 (1H, m, *trans* isomer), 3.89–4.01 (1H, m, *cis* isomer), 5.44–5.57 (1H, m), 5.65–5.74 (1H, ddq, *J* = 15.3, 6.6, 1.4 Hz), 7.36 (1H, dd, *J* = 8.5, 1.9 Hz), 7.40–7.47 (2H, m), 7.62 (1H, s), 7.75–7.81 (3H, m); ^{13}C-NMR δ = 17.94, 21.37, 42.41, 124.01, 124.93, 125.15, 125.81, 126.31, 127.55, 127.60, 127.84, 132.14, 133.64, 136.10, 143.91. The diastereoisomeric ratio of **4z** (*trans*/*cis* = 95/5) was determined by ^{1}H-NMR analysis and the ee value was determined by HPLC analysis with a Daicel Chiralcel OD column (eluent: hexane).

3-Phenylhex-1-ene (5). Colorless liquid; ^{1}H-NMR δ = 0.89 (3H, t, *J* = 7.8 Hz), 1.16–1.42 (2H, m), 1.65–1.71 (2H, m), 3.25 (1H, dt, *J* = 7.6, 7.6 Hz), 5.01 (1H, d, *J* = 13.9 Hz), 5.03 (1H, d, *J* = 8.9 Hz), 5.95 (1H, ddd, *J* = 13.9, 8.9, 7.6 Hz), 7.17–7.19 (3H, m), 7.26–7.31 (2H, m); ^{13}C-NMR δ = 13.98, 20.62, 37.63, 49.62, 113.80, 126.05, 127.60, 128.39, 142.53, 144.67. The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column (eluent: hexane).

1-Phenylhex-2-ene (6). Colorless liquid; ^{1}H-NMR δ = 0.90 (3H, t, *J* = 7.3 Hz), 1.35–1.44 (2H, m), 2.00 (2H, dt, *J* = 6.8, 7.3 Hz, *trans* isomer), 2.14 (2H, dt, *J* = 7.1, 7.3 Hz, *cis* isomer), 3.33 (2H, d, *J* = 6.3 Hz, *trans* isomer), 3.40 (2H, d, *J* = 6.4 Hz, *cis* isomer), 5.47–5.61 (2H, m), 7.17–7.19 (3H, m), 7.25–7.30 (2H, m); ^{13}C-NMR δ = 13.67, 22.59, 34.59, 39.05, 125.83, 128.30, 128.46, 128.88, 131.88, 141.14.

3-Phenylbut-1-ene (7). Colorless liquid; ^{1}H-NMR δ = 1.37 (3H, d, *J* = 7.1 Hz), 3.40–3.52 (1H, m), 5.01 (1H, m), 5.07 (1H, m), 6.01 (1H, ddd, *J* = 17.0, 10.4, 6.5 Hz), 7.16–7.23 (3H, m), 7.28–7.33 (2H, m); ^{13}C-NMR δ = 20.72, 43.17, 113.08, 126.09, 127.23, 128.39, 143.25, 145.56. The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column (eluent: hexane–^{i}PrOH = 99 : 1) after conversion of **7** to 2-phenylpropionic acid and then into its methyl ester, methyl 2-phenylpropionate.

1-Phenylbut-2-ene (8). Colorless liquid; ^{1}H-NMR δ = 1.68–1.74 (3H, m), 3.32 (2H, m), 5.49–5.59 (2H, m), 7.20–7.34 (5H, m).

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