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Chiral N-Heterocyclic Carbene−Copper(I)-Catalyzed Asymmetric Allylic Arylation of Aliphatic Allylic Bromides: Steric and Electronic Effects on γ-Selectivity

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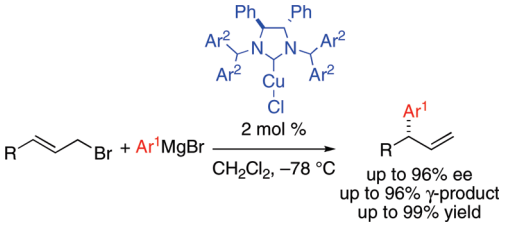

Chiral N-heterocyclic carbene ligands were electronically and sterically tuned to improve γ-selectivity in copper(I)-catalyzed asymmetric allylic arylation of aliphatic allylic bromides with several aryl Grignard reagents. High γ-selectivity was realized when either the aryl group of the Grignard reagent or the aryl group on the N-substituent of the carbene ligand was electron-deficient or when either the carbene ligand or allylic bromide was bulky. The results indicated that electron deficiency and steric hindrance of the initially formed σ-allyl copper intermediate enhance the rate of the reductive elimination to give γ-products as major isomers.

Introduction

Among transition metal-catalyzed allylic substitutions,[1] a method using a chiral copper catalyst with hard nucleophiles is a potentially useful asymmetric C−C bond-forming reaction.[2] Regioselectivity and enantioselectivity, however, are greatly affected by the structural and electronic features of the substrates and chiral catalyst, as well as the reagent reactivity. Many reports have documented powerful methods to control the regio- and enantioselectivities of the reaction products with alkyl coppers derived from alkyl Grignard or dialkylzinc reagents using different types of chiral ligands.[3,4] The power of these catalysts, however, remains insufficient for less reactive aryl, alkenyl, and alkynyl anions.[5,6] Hoveyda recently reported efficient chiral

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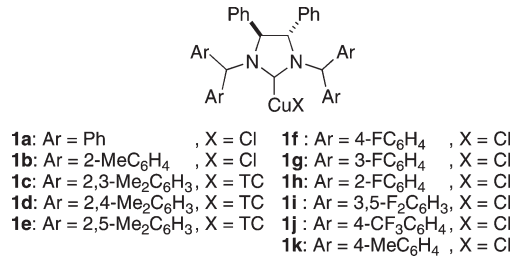
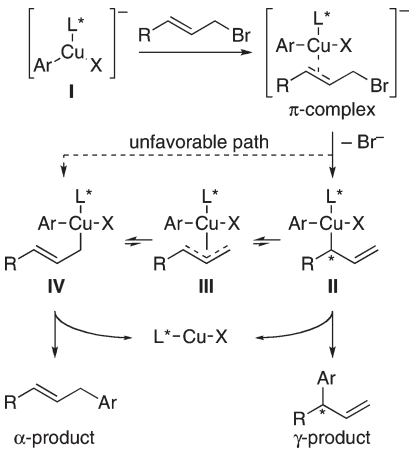


FIGURE 1. Chiral N-heterocyclic carbene−copper(I) complexes.

bidentate N-heterocyclic carbenes (NHCs) for allylic substitution with aryl copper reagents derived from diarylzincs[7] and aryldialkylaluminums,[8] as well as alkenyl copper reagents derived from vinylaluminums.[9] Nonetheless, significant approaches using aryl Grignard reagents under copper-catalyzed allylic substitution have yet to be developed.[10]

Recently, we introduced the first successful copper-catalyzed asymmetric allylic arylation (AAAr) of aliphatic allylic substrates with aryl Grignard reagents in the presence of a chiral amidophosphane ligand.[11] Further, highly enantioselective and γ-selective copper-catalyzed allylic arylation of cinnamyl bromides was achieved using an air-tolerant monodentate chiral NHC[12]−CuCl catalyst **1** with aryl Grignard reagents, in which the γ-selectivity was improved (up to 99% yield, 97% γ-selectivity, and 98% ee) by steric tuning of the catalyst, i.e., from **1a** to **1b** (Figure 1).[13] The primary merit of this method is its compatibility with several aryl Grignard reagents, which are generally less reactive and less regioselective toward allylic substrates, in addition to the easy preparation of the NHC−copper catalysts from imidazolinium salts and CuCl. In the reaction of an aliphatic substrate hex-2-enyl bromide with PhMgBr, however, the enantioselectivity of the γ-product was unsatisfactory (74% ee), despite its high yield (98%) and high γ-selectivity (91% γ-product). Having achieved this allylic arylation, we next directed our attention to enhance the selectivity of the reaction toward *aliphatic allylic substrates* using a sterically and/or electronically tuned monodentate chiral NHC−copper catalyst.

SCHEME 1. Possible Pathway to α- and γ-Products in AAAr with Chiral NHC−Cu Catalysts



Herein, we report a γ-selective AAAr of aliphatic allylic bromide using aryl Grignard reagents under the catalysis of NHC−copper(I) complexes, as well as steric and electronic effects on the γ-selectivity.[14] The reactions proceeded with exceptional regioselectivity (up to 96:4) and high enantioselectivity (up to 96% ee), and transformations were completed within 0.5 h with a variety of aryl Grignard reagents and 2.0 mol % of a chiral NHC−Cu complex **1a** or **1f**, derived from commercially available and air-stable CuCl.

Results and Discussion

Working Hypothesis. Scheme 1 shows a possible pathway of the formation of α- and γ-products based on previous reports.[15] First, the Grignard reagent undergoes transmetalation with a Cu(I) complex to give arylcuprate **I**, which then preferentially reacts with the allylic bromide in an S_N2' fashion through the π-complex to form σ-allyl copper(III) complex **II**.[15e,f,h] Reductive elimination of **II** produces the γ-product, while isomerization of **II** into π-allyl complex **III** leads to exclusive formation of the less sterically hindered terminal σ-allyl complex **IV**, whose reductive elimination gives the α-product. Therefore, the regioselectivity depends on the relative rates of the reductive elimination of **II** and the isomerization of **II** to **IV** and the following reductive elimination. We speculated that increased steric hindrance or electron deficiency in complex **II** promotes its reductive elimination step, which liberates the copper from the steric hindrance and electron deficiency, and improves γ-selectivity.[16,15d,15e,15h] We thus tested the regio- and stereocontrolling ability of chiral NHC−Cu(I) complexes **1b**−**j** bearing *N*-benzhydryl groups with bulky or electron-deficient

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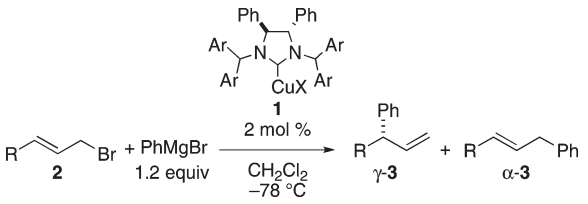
TABLE 1. Steric and Electronic Tuning of NHC−Cu 1 in AAAr with PhMgBr[a]



entry	2	R	1	Ar	time (h)	3	yield (%)[b,c]	γ/α[d]	ee (%)[c]
1	**2a**	C_5H_{11}	**1a**	Ph	0.5	**3aa**	98	67:33	89
2	**2a**	C_5H_{11}	**1b**	2-MeC_6H_4	0.5	**3aa**	100	92:8	76
3	**2a**	C_5H_{11}	**1c**	2,3-$Me_2C_6H_3$	0.5	**3aa**	(89)	90:10	72
4	**2a**	C_5H_{11}	**1d**	2,4-$Me_2C_6H_3$	0.5	**3aa**	97	76:24	63
5	**2a**	C_5H_{11}	**1e**	2,5-$Me_2C_6H_3$	0.5	**3aa**	(93)	74:26	4
6	**2a**	C_5H_{11}	**1f**	4-FC_6H_4	0.5	**3aa**	93	84:16	87
7	**2a**	C_5H_{11}	**1g**	3-FC_6H_4	0.5	**3aa**	99	77:23	76
8	**2a**	C_5H_{11}	**1h**	2-FC_6H_4	0.5	**3aa**	90	86:14	47
9	**2a**	C_5H_{11}	**1i**	3,5-$F_2C_6H_3$	0.5	**3aa**	(100)	74:26	25
10	**2a**	C_5H_{11}	**1j**	4-$CF_3C_6H_4$	0.5	**3aa**	(100)	79:21	31
11	**2a**	C_5H_{11}	**1k**	4-MeC_6H_4	0.5	**3aa**	95	53:47	68
12	**2b**	Pr	**1a**	Ph	0.5	**3ba**	100	68:32	86
13	**2b**	Pr	**1b**	2-MeC_6H_4	0.5	**3ba**	98	91:9	74
14	**2b**	Pr	**1f**	4-FC_6H_4	0.5	**3ba**	96	80:20	81
15	**2c**	*c*-Hex	**1a**	Ph	0.5	**3ca**	97	89:11	94
16	**2c**	*c*-Hex	**1b**	2-MeC_6H_4	0.5	**3ca**	(100)	94:6	83
17	**2c**	*c*-Hex	**1f**	4-FC_6H_4	0.5	**3ca**	97	89:11	93
18	**2d**	*t*-Bu	**1a**	Ph	6	**3da**	(97)[e]	47:53	86
19	**2d**	*t*-Bu	**1b**	2-MeC_6H_4	17	**3da**	(99)[e]	25:75	12
20	**2d**	*t*-Bu	**1f**	4-FC_6H_4	3.5	**3da**	61[e]	53:47	87

[a]The NHC−Cu complexes (X = Cl) were isolated and used in the reaction except for in entries 3−5, where the complexes (X = TC) were generated *in situ* from CuTC, BF_4 salts of the corresponding imidazolinium, and BuLi (see ref 13). Grignard reagents were added over 30 min in the reactions with 1.0 mmol of **2** (entries 1−14), and over 15 min in those with 0.5 mmol of **2** (entries 15−20). Conversion of **2** was 100%, unless otherwise mentioned. [b]The combined isolated yield of γ- and α-**3** is presented, unless otherwise mentioned. [c]The yields in parentheses and the enantioselectivity were determined by GC. [d]The γ/α ratios were determined by GC or ^{1}H NMR of the crude material. [e]Remaining **2d** was detected by GC in entries 18−20 (2%, 1%, and 22%, respectively).

aryl groups in the copper(I)-catalyzed AAAr with Grignard reagents (Figure 1). According to the previously described methods,[13] NHC−Cu complexes **1a**, **1b**, and **1f**−**k** were prepared and isolated, and complexes **1c**−**e** were generated *in situ* from the corresponding imidazolinium salt and copper(I) thiophene-2-carboxylate (CuTC).

Steric Tuning of the NHC−Cu Complex in AAAr of Linear Allylic Bromides. A 3 M diethyl ether solution of PhMgBr (0.4 mL, 1.2 mmol) diluted with CH_2Cl_2 (0.5 mL) was added over 30 min at −78 °C to a solution of NHC−CuCl catalyst **1a** (2 mol %), with prototype benzhydryl groups on the nitrogen atoms, and oct-2-enyl bromide (**2a**; 1.0 mmol) in CH_2Cl_2 (2 mL). Allylic bromide **2a** was completely consumed within 30 min after the addition of the Grignard reagent to give γ-**3aa** with 89% ee and moderate γ-selectivity (γ/α 67:33; Table 1, entry 1).

Sterically tuned NHC−Cu complexes **1b**−**e** were then evaluated in the reaction. In the allylic arylation with catalyst **1b**, having *ortho*-methyl substituents, γ-selectivity was dramatically improved (γ/α 92:8), but at the expense of enantioselectivity (76% ee; entry 2). The introduction of a second methyl group was then systematically examined at three positions, as shown in complexes **1c**−**e** (entries 3−5). The use of complexes **1c**−**e** was not beneficial, however, and resulted in the formation of γ-**3aa** with decreased enantioselectivity (72%, 63%, and 4% ee) and less improved γ-selectivity (γ/α 90:10, 76:24, and 74:26), respectively.[17]

AAAr of substrate **2b** in the presence of catalyst **1a** or **1b** gave similar results to those of **2a**; γ-selectivity was 68:32 with 86% ee and 91:9 with 74% ee for **1a** and **1b**, respectively (entries 12 and 13).[13]

Electronic Tuning of the NHC−Cu Complex in AAAr of Linear Allylic Bromides. Next, electronically tuned NHC−Cu complexes **1f**−**j** were investigated in the reaction. When complex **1f**, having *para*-fluorophenyl groups, was used as a catalyst, γ-**3aa** with 87% ee, comparable to entry 1, was obtained with improved γ-selectivity (γ/α 84:16; entry 6).

Fluoro substitution at different positions was then examined. Catalysts **1g** and **1h**, having 3- and 2-fluorophenyl groups, gave γ-**3aa** with decreased regio- and enantioselectivity (γ/α 77:23, 76% ee; entry 7) and with lower enantioselectivity and comparable regioselectivity (47% ee, γ/α 86:14; entry 8), respectively. 3,5-Difluoro-substituted NHC−Cu **1i** was also tested in the reaction of **2a**, but poor enantioselectivity (25% ee) was observed with less effective improvement in γ-selectivity (γ/α 74:26; entry 9).

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(17) Evaluation of the NHCs using the *in situ*-generated NHC−CuTC can be justified because the reaction with the *in situ*-generated CuTC analogues of **1a** and **1b** gave almost the same results (97% yield, 88% ee, γ/α 67:33 and 82% yield, 77% ee, γ/α 90:10, respectively) as those of **1a** and **1b** shown in Table 1, entries 1 and 2.

On the basis of these results, the best position of the electron-withdrawing substituent should be the *para*-position; therefore a more powerful electron-withdrawing group, trifluoromethyl, was introduced on the phenyl groups. The reaction using catalyst **1j**, however, provided γ-**3aa** with significantly lower enantioselectivity (31% ee), though the γ/α ratio was improved to 79:21 (entry 10). The reaction using catalyst **1k**, having methyl groups at the *para*-position, resulted in decreased regio- and enantioselectivity (γ/α 53:47, 68% ee; entry 11). Obviously, the electron-withdrawing *para*-substituents increased the γ-selectivity, but the bulkiness of the *para*-substituents seems to have decreased enantioselectivity in this reaction.

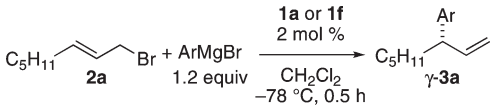
The best catalyst, **1f**, was applied to the reaction of **2b**, and γ-**3ba** was obtained with better γ-selectivity (γ/α 80:20) and similar enantioselectivity (81% ee; entry 14).

AAAr of Branched Allylic Bromides. As a branched allylic substrate, 3-cyclohexylprop-2-enyl bromide (**2c**) was examined. There was a dramatic increase in both the γ-selectivity (γ/α 89:11) and enantioselectivity (94% ee), compared to those in the reactions of **2a** and **2b**, when the reaction of **2c** was conducted in the presence of catalyst **1a** (entry 15). This result indicates that the increased steric repulsion between the allylic substrate and the copper complex accelerated the rate of reductive elimination of the initially formed γ-σ-allyl complex **II** (Scheme 1). The reaction with sterically tuned **1b** gave γ-**3ca** with decreased enantioselectivity (83% ee) and improved γ/α ratio (94:6; entry 16). Introduction of a fluorine atom, an electron-withdrawing substituent, did not affect the selectivity; the reaction with **1f** afforded γ-**3ca** with comparable regio- and enantioselectivity (γ/α 89:11, 93% ee; entry 17). These results suggested that steric hindrance of γ-σ-allyl complex **II** derived from **1a** and **2c** was sufficient to promote reductive elimination, and further electronic tuning would be unnecessary.

The reactions of more sterically hindered allylic substrate **2d**, having a *tert*-butyl group at the γ-position, were also examined. In the presence of catalyst **1a**, the reaction rate was significantly slower, giving γ-**3da** with 86% ee without regioselectivity (γ/α 47:53) along with a trace amount (2%) of recovered **2d** after 6 h (entry 18). The use of bulky catalyst **1b** further increased the reaction time to 17 h, and γ-**3da** with 12% ee was obtained along with α-**3da** as a major isomer (γ/α 25:75; entry 19). Electronic tuning of the catalyst slightly improved the γ-preference (γ/α 53:47), and γ-**3da** with 87% ee was obtained in 61% yield with 22% recovery of **2d** (entry 20). Although the yield and regioselectivity were unsatisfactory, good enantioselectivity was realized in the reaction of the bulky allylic substrate. A possible explanation for the observed low regioselectivity is as follows: (1) accumulation of the aryl Grignard reagent, due to the slow reaction, led to the formation of diarylcuprate species (X = Ar, Scheme 1), which might facilitate isomerization to the terminal σ-allyl complex **IV** through π-allyl complex **III**;[5,15h] (2) an S_N2 pathway leading directly to the terminal σ-allyl complex **IV** was concomitant in the presence of severe steric repulsion during the nucleophilic attack of complex **I** to the γ-position of allylic substrate **2** (Scheme 1).

Electronic Effects of Aryl Grignard Reagents on AAAr of Linear Allylic Bromide. The reaction of allylic bromide **2a** with various aryl Grignard reagents was examined (Table 2). In the presence of **1f**, Grignard reagents with an aryl group having an electron-donating methyl or methoxy group at the *para*-positions improved the γ-selectivity with a similar level of enantioselectivity (entries 4 and 6). Thus, using catalysts **1a** and **1f**, the reactions with 4-tolylmagnesium bromide produced γ-**3ab** with 88% and 84% ee in a γ/α ratio of 64:36 and 82:18, respectively (entries 3 and 4), and those with 4-methoxyphenylmagnesium bromide produced γ-**3ac** with 85% and 79% ee in a γ/α ratio of 67:33 and 79:21, respectively (entries 5 and 6).

TABLE 2. NHC−Cu-Catalyzed AAAr of 2a with Aryl Grignard Reagents[a]



entry	1	Ar	3	yield (%)[b]	γ/α[c]	ee (%)[d]
1[e]	**1a**	Ph	**3aa**	98	67:33	89
2[e]	**1f**	Ph	**3aa**	93	84:16	87
3	**1a**	4-MeC_6H_4	**3ab**	98	64:36	88
4	**1f**	4-MeC_6H_4	**3ab**	92	82:18	84
5	**1a**	4-MeOC_6H_4	**3ac**	99	67:33	85
6	**1f**	4-MeOC_6H_4	**3ac**	99	79:21	79
7	**1a**	4-ClC_6H_4	**3ad**	98	87:13	80
8	**1f**	4-ClC_6H_4	**3ad**	99	83:17	56
9	**1a**	4-FC_6H_4	**3ae**	96	82:18	86
10	**1f**	4-FC_6H_4	**3ae**	96	88:12	66
11	**1a**	3-FC_6H_4	**3af**	96	84:16	82
12	**1f**	3-FC_6H_4	**3af**	96	79:21	52

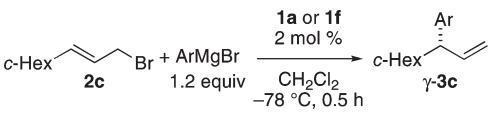
[a]The reactions were conducted with 0.5 mmol of **2a**, and Grignard reagents were added over 1 h except for entries 1 and 2, where 1.0 mmol of **2a** was used, and the addition time was 30 min. Conversion of **2a** was 100%. [b]The combined isolated yield of γ- and α-**3a** is presented. [c]The γ/α ratio was determined by ^{1}H NMR of the crude material. [d]The enantioselectivity was determined by GC. [e]The results in Table 1, entries 1 and 6, are shown again for comparison.

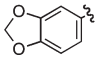
In reactions using Grignard reagents with an electron-deficient aryl group, good regio- and enantioselectivity were realized by catalyst **1a**, whereas electronically tuned catalyst **1f** did not improve γ-selectivity, but decreased enantioselectivity (entries 7−12). Thus, the reactions with a 4-chlorophenyl Grignard reagent using **1a** and **1f** provided γ-**3ad** in 80% and 56% ee with a γ/α ratio of 87:13 and 83:17, respectively (entries 7 and 8). When a 4-florophenyl Grignard reagent was utilized, γ-**3ae** with 86% and 66% ee were produced by complexes **1a** and **1f** with a γ/α ratio of 82:18 and 88:12, respectively (entries 9 and 10). A 3-fluorophenyl Grignard reagent also showed the same tendency; the reactions with **1a** and **1f** afforded γ-**3af** with 82% and 52% ee in a γ/α ratio of 84:16 and 79:21, respectively (entries 11 and 12). As illustrated in Scheme 1, these electron-deficient aryl species of the Grignard reagents were incorporated into γ-σ-allyl intermediate **II**; thus, these results also indicate that electron deficiency of the γ-σ-allyl intermediate increased the formation of γ-products by promoting reductive elimination.

In short, the best catalyst for the reaction of **2a** depended on the Grignard reagents; **1a** was the appropriate catalyst for Grignard reagents with an electron-deficient aryl group, and **1f** was more appropriate for the others.

Electronic Effects of Aryl Grignard Reagents on AAAr of Branched Allylic Bromide. The reaction of allylic bromide **2c** with various aryl Grignard reagents was examined (Table 3). Similar to the reactions in entries 1 and 2, comparable results were obtained in the reaction of a 4-tolyl Grignard reagent,

TABLE 3. NHC−Cu-Catalyzed AAAr of 2c with Aryl Grignard Reagents[a]



entry	1	Ar	3	yield (%)[b]	γ/α[c]	ee (%)[d]
1[e]	**1a**	Ph	**3ca**	97	89:11	94
2[e]	**1f**	Ph	**3ca**	97	89:11	93
3	**1a**	4-MeC_6H_4	**3cb**	99	87:13	96
4	**1f**	4-MeC_6H_4	**3cb**	99	84:16	94
5	**1a**	4-ClC_6H_4	**3cd**	97	96:4	93
6	**1a**	4-FC_6H_4	**3ce**	98	95:5	92
7[f]	**1a**	3,4-$Cl_2C_6H_3$	**3cg**	84[g]	96:4	86
8[f]	**1a**		**3ch**	41[g]	91:9	93[h]

[a]The reactions were conducted with 0.5 mmol of **2c**, and Grignard reagents were added over 15 min, except for entries 7 and 8, where Grignard reagents were added over 1 h. Conversion of **2a** was 100%, unless otherwise mentioned. [b]The combined isolated yield of γ- and α-**3a** is presented. [c]The γ/α ratio was determined by GC or ^{1}H NMR of the crude material. [d]The enantioselectivity was determined by GC, unless otherwise mentioned. [e]The results in Table 1, entries 15 and 17, are shown again for comparison. [f]The Grignard reagent was added over 1 h. [g]Remaining **2c** was detected by GC in entries 7 and 8 (16% and 40%, respectively). [h]The enantioselectivity was determined by HPLC after conversion to alcohol.

and regardless of whether **1a** or **1f** was used as a catalyst, **3cb** with high enantiopurity (96% and 94% ee) was obtained in good γ-selectivity (γ/α 87:13 and 84:16), respectively (entries 3 and 4). Therefore, the following reactions were conducted using catalyst **1a**.

As expected, Grignard reagents bearing electron-withdrawing 4-chloro and 4-fluoro substituents underwent AAAr in a highly γ-selective manner, and **3cd** and **3ce** were obtained in 93% and 92% ee with a γ/α ratio of 96:4 and 95:5, respectively (entries 5 and 6). When a 3,4-dichlorophenyl Grignard reagent was used, **3cg** with 86% ee was obtained also with high γ-selectivity (96:4) along with 16% of recovered **2c** (entry 7). With a benzodioxolanyl Grignard reagent, the reaction was also slow without complete conversion of **2c**, but **3ch** was obtained with high enantioselectivity (93% ee) and a high γ/α ratio (91:9) in moderate yield (41%; entry 8).

These results clearly indicate that the electron deficiency of the γ-σ-allyl intermediate also promotes the formation of γ-products in the reaction of **2c**.

Conclusions

We performed steric and electronic tuning of chiral NHC and developed chiral NHC−Cu(I)-catalyzed γ-selective AAAr of aliphatic allylic bromides with aryl Grignard reagents. The suitable catalyst depended on the allylic substrates as well as the Grignard reagents; catalyst **1a**, bearing *N*-benzhydryl groups, afforded good results for linear allylic substrates with Grignard reagents having an electron-deficient aryl group (up to 86% ee, 88% γ-product) and for branched allylic substrates with any Grignard reagents (up to 96% ee, 96% γ-product), and catalyst **1f**, bearing *N*-(4,4′-difluorobenzhydryl) groups, for linear allylic substrates with Grignard reagents having no electron-withdrawing group (up to 87% ee, 84% γ-product). The results showed that electron deficiency and moderate steric hindrance of the complex derived from the catalysts, Grignard reagents, and allylic substrates are important factors for achieving high γ-selectivity and support the hypothesis that γ-selectivity is governed by the relative rates of reductive elimination of the γ-σ-allyl intermediate and isomerization to the α-σ-allyl intermediate and the subsequent reductive elimination.

Experimental Section

General Procedures. All reactions were carried out under argon atmosphere in flame-dried glassware. Complexes **1a** and **1b** were prepared according to the reported procedure.[13] CuCl was purchased and used as received. CuTC was prepared according to the reported procedure.[18] Grignard reagents were purchased from Aldrich. A 3 M solution of PhMgBr in Et_2O was used as received. Solutions of 4-FC_6H_4MgBr (2 M), 4-ClC_6H_4MgBr (1 M), and 4-$CH_3C_6H_4MgBr$ (0.5 M) in Et_2O were concentrated to ca. 3 M *in vacuo* prior to use. Solutions of 3-FC_6H_4MgBr (1 M), 4-$MeOC_6H_4MgBr$ (0.5 M), and 3,4-$Cl_2C_6H_3MgBr$ (0.5 M) in THF, and 3,4-(methylenedioxy)-phenylMgBr (1 M) in toluene/THF (1:1), were used after replacing most of the solvents with toluene by two consecutive additions of toluene followed by vacuum removal of the solvent to give a final concentration of approximately 3 M. CH_2Cl_2 was distilled from CaH_2 and stored with MS 4A under argon. Substrates **2a**,[19] **2b**,[19] **2c**[20] and **2d**[20] were prepared according to the literature procedures. Column chromatography was performed using silica gel. TLC was performed using precoated silica gel plates (0.25 mm thick, 60 F_{254}), and the products were observed under UV light and with either phosphomolybdic acid or $KMnO_4$ reagents.

The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 and 125 MHz, respectively, unless otherwise mentioned. Chemical shifts and coupling constants are presented in ppm δ relative to tetramethylsilane and Hz, respectively. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), coupling constants, assignment. ^{13}C peak multiplicity assignments were made on the basis of DEPT data. The ^{1}H and ^{13}C NMR data are reported for γ-products. Specific rotation was measured in a 10 cm cell. For the AAAr products, the specific rotation and *c* of the α,γ-mixture were reported. The enantioselectivity of chiral products was determined by comparison of the chiral stationary phase GC or HPLC traces with those of the corresponding racemic products. The absolute configurations of the products other than γ-**3aa** and γ-**3ca** were tentatively assigned by analogy.

Preparation of Chiral NHC−Cu Complexes. Synthesis of Chiral Imidazolinium Salts. Typical Procedure for the Synthesis of *N,N′*-Dibenzohydryldiamines. (1*S*,2*S*)-*N,N′*-Bis(bis(2,3-dimethylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (C). A mixture of (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (1.14 g, 5.4 mmol), bis(2,3-dimethylphenyl)methyl bromide (3.60 g, 11.9 mmol), and Na_2CO_3 (2.29 g, 21.6 mmol) in DMPU (16 mL) was stirred at 120 °C. After 2 h, water (60 mL) was added, and the

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(19) Tallman, K. A.; Roschek, B., Jr.; Porter, N. A. *J. Am. Chem. Soc.* **2004**, *126*, 9240–9247.
(20) Tallman, K. A.; Rector, C. L.; Porter, N. A. *J. Am. Chem. Soc.* **2009**, *131*, 5635–5641.

whole was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over Na_2SO_4, and then concentrated *in vacuo*. The resulting crude mixture was purified by column chromatography (hexane/EtOAc = 15:1) to afford the title compound (68%) as a colorless, amorphous solid of mp 83−86 °C: $[\alpha]^{25}_D$ −73.7 (*c* 1.00, $CHCl_3$). IR (KBr): 3336, 2918, 1585, 1458, 1094, 725, 700. ^{1}H NMR: 1.71 (6H, s), 1.87 (6H, s), 2.20 (6H, s), 2.23 (6H, s), 2.51 (2H, s), 3.78 (2H, s), 4.96 (2H, s), 6.91−7.00 (10H, m), 7.02−7.09 (10H, m), 7.56−7.59 (2H, m). ^{13}C NMR: 14.4 (CH_3), 14.5 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 56.2 (CH), 65.9 (CH), 125.2 (CH), 125.3 (CH), 125.8 (CH), 126.4 (CH), 126.9 (CH), 127.7 (CH), 128.1 (CH), 128.3 (CH), 128.7 (CH), 134.7 (C), 134.9 (C), 136.56 (C), 136.58 (C), 140.5 (C), 141.6 (C), 141.7 (C). EIMS: *m*/*z* 328 (M/2). Anal. Calcd for $C_{48}H_{52}N_2 \cdot 0.5H_2O$: C, 86.57; H, 8.02; N, 4.21. Found: C, 86.51; H, 8.02; N, 4.09.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(2,4-dimethylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (D). Column chromatography (hexane/EtOAc = 15:1) gave the title compound (54%) as a colorless, amorphous solid of mp 87−90 °C: $[\alpha]^{25}_D$ −45.0 (*c* 0.97, $CHCl_3$). IR (KBr): 3328, 2918, 1612, 1499, 1454, 804, 700. ^{1}H NMR: 1.78 (6H, s), 1.96 (6H, s), 2.26 (6H, s), 2.31 (6H, s), 2.48 (2H, s), 3.75 (2H, s), 4.76 (2H, s), 6.84 (2H, s), 6.86−6.90 (4H, m), 6.91−6.94 (4H, m), 6.96−7.02 (4H, m), 7.06−7.08 (6H, m), 7.56 (1H, s), 7.58 (1H, s). ^{13}C NMR: 18.9 (CH_3), 19.0 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.3 (CH), 65.8 (CH), 126.5 (CH), 126.7 (CH), 126.8 (CH), 127.6 (CH), 127.7 (CH), 128.3 (CH), 128.6 (CH), 131.1 (CH), 131.3 (CH), 135.6 (C), 136.01 (C), 136.03 (C), 136.2 (C), 137.3 (C), 138.8 (C), 141.6 (C). EIMS *m*/*z*: 328 (M/2). Anal. Calcd for $C_{48}H_{52}N_2$: C, 87.76; H, 7.98; N, 4.26. Found: C, 87.70; H, 8.05; N, 4.13.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(2,5-dimethylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (E). Column chromatography (hexane/EtOAc = 15:1) gave the title compound (57%) as a colorless, amorphous solid of mp 80−82 °C: $[\alpha]^{25}_D$ −96.6 (*c* 1.00, $CHCl_3$). IR (KBr): 3326, 2920, 1498, 1454, 808, 700. ^{1}H NMR: 1.82 (6H, s), 1.88 (6H, s), 2.21 (6H, s), 2.22 (6H, s), 2.49 (2H, s), 3.72 (2H, s), 4.81 (2H, s), 6.87−6.97 (14H, m), 7.06−7.11 (6H, m), 7.59 (2H, s). ^{13}C NMR: 18.4 (CH_3), 18.8 (CH_3), 21.2 (CH_3), 55.7 (CH), 65.9 (CH), 126.9 (CH), 127.0 (CH), 127.4 (CH), 127.8 (CH), 128.4 (CH), 128.6 (CH), 129.0 (CH), 130.2 (CH), 130.3 (CH), 133.0 (C), 133.3 (C), 135.07 (C), 135.09 (C), 140.2 (C), 141.3 (C), 141.9 (C). CIMS *m*/*z*: 657 ($M + H^+$). HRMS-CI *m*/*z*: $[M + H]^+$ calcd for $C_{48}H_{53}N_2$ 657.4209, found 657.4203.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(4-fluorophenyl)methyl)-1,2-diphenylethane-1,2-diamine (F). Column chromatography (hexane/EtOAc = 10:1) gave the title compound (75%) as a white, amorphous solid of mp 162−164 °C: $[\alpha]^{21}_D$ +35.8 (*c* 0.65, $CHCl_3$). IR (KBr): 3317, 3032, 2839, 1605, 1504, 1450, 1227, 1157, 1095, 833, 702. ^{1}H NMR: 2.49 (2H, s), 3.59 (2H, s), 4.49 (2H, s), 6.90−6.95 (8H, m), 6.99−7.02 (8H, m), 7.17−7.20 (10H, m). ^{13}C NMR: 62.1 (CH), 65.7 (CH), 115.2 (d, *J* = 22, CH), 115.4 (d, *J* = 22, CH), 127.2 (CH), 127.9 (CH), 128.2 (CH), 128.7 (d, *J* = 8.3, CH), 129.1 (d, *J* = 8.3, CH), 137.6 (d, *J* = 4.1, C), 140.3 (d, *J* = 3.1, C), 140.7 (C), 161.8 (d, *J* = 246, C), 161.9 (d, *J* = 245, C). EIMS *m*/*z*: 308 (M/2). Anal. Calcd for $C_{40}H_{32}F_4N_2$: C, 77.90; H, 5.23; N, 4.54. Found: C, 78.17; H, 5.36; N, 4.60.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(3-fluorophenyl)methyl)-1,2-diphenylethane-1,2-diamine (G). Column chromatography (hexane/EtOAc = 1:0−40:1−10:1) gave the title compound (81%) as an off-white, amorphous solid of mp 52−54 °C: $[\alpha]^{21}_D$ +36.7 (*c* 1.54, $CHCl_3$). IR (KBr): 3310, 3032, 2847, 1589, 1481, 1450, 1242, 1134, 1072, 880, 772, 694. ^{1}H NMR: 2.60 (2H, s), 3.62 (2H, s), 4.51 (2H, s), 6.83−7.01 (16H, m), 7.17−7.27 (10H, m). ^{13}C NMR: 62.6 (CH), 65.8 (CH), 114.0 (d, *J* = 21, CH), 114.1 (d, *J* = 23, CH), 114.3 (d, *J* = 22, CH), 114.5 (d, *J* = 22, CH), 122.7 (d, *J* = 3, CH), 123.3 (d, *J* = 2, CH), 127.4 (CH), 127.9 (CH), 128.2 (CH), 129.9 (d, *J* = 8, CH), 130.2 (d, *J* = 8, CH), 140.3 (C), 145.5 (d, *J* = 6, C), 146.6 (d, *J* = 6, C), 162.9 (d, *J* = 246, C), 163.2 (d, *J* = 246, C). EIMS *m*/*z*: 308 (M/2). Anal. Calcd for $C_{40}H_{32}F_4N_2$: C, 77.90; H, 5.23; N, 4.54. Found: C, 77.84; H, 5.27; N, 4.54.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(2-fluorophenyl)methyl)-1,2-diphenylethane-1,2-diamine (H). Column chromatography (hexane/EtOAc = 14:1) gave the title compound (74%) as a pale yellow, amorphous solid of mp 131−132 °C: $[\alpha]^{25}_D$ +52.3 (*c* 1.01, $CHCl_3$). IR (KBr): 3433, 3071, 3040, 1583, 1489, 1458, 1227, 756. ^{1}H NMR: 2.86 (2H, br s), 3.67 (2H, s), 5.13 (2H, s), 6.89−6.95 (4H, m), 7.00−7.05 (6H, m), 7.08−7.10 (2H, m), 7.14−7.21 (12H, m), 7.44−7.47 (2H, m). ^{13}C NMR: 51.5 (CH), 66.2 (CH), 115.4 (d, *J* = 22, CH), 115.5 (d, *J* = 22, CH), 124.03 (d, *J* = 9, CH), 124.05 (d, *J* = 9, CH), 127.1 (CH), 128.01 (CH), 128.04 (CH), 128.49 (d, *J* = 9, CH), 128.54 (d, *J* = 3, CH), 128.57 (d, *J* = 9, CH), 129.07 (d, *J* = 3, CH), 129.12 (d, *J* = 13, C), 130.4 (d, *J* = 13, C), 140.5 (C), 160.2 (d, *J* = 247, C), 161.0 (d, *J* = 247, C). FABMS *m*/*z*: 617 ($M + H^+$), 308 (M/2). Anal. Calcd for $C_{40}H_{32}F_4N_2$: C, 77.90; H, 5.23; N, 4.54. Found: C, 77.64; H, 5.10; N, 4.62.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(3,5-difluorophenyl)methyl)-1,2-diphenylethane-1,2-diamine (I). Column chromatography (hexane/EtOAc = 20:1) gave the title compound (71%) as an off-white, amorphous solid of mp 64−66 °C: $[\alpha]^{21}_D$ +33.9 (*c* 1.24, $CHCl_3$). IR (KBr): 3317, 3094, 2855, 1605, 1458, 1319, 1119, 988, 856, 764, 702. ^{1}H NMR: 2.47 (2H, s), 3.63 (2H, s), 4.45 (2H, s), 6.53−6.57 (4H, m), 6.64−6.77 (8H, m), 7.02−7.04 (4H, m), 7.24−7.26 (6H, m). ^{13}C NMR: 62.4 (CH), 65.7 (CH), 102.9 (t, *J* = 25, CH), 103.2 (t, *J* = 25, CH), 110.0 (dd, *J* = 6.2, 20, CH), 110.3 (dd, *J* = 6.2, 20, CH), 127.6 (CH), 127.9 (CH), 128.6 (CH), 139.5 (C), 146.2 (t, *J* = 8.3, C), 147.0 (t, *J* = 8.3, C), 163.1 (dd, *J* = 12.4, 249, C), 163.3 (dd, *J* = 12.4, 250, C). EIMS *m*/*z*: 344 (M/2). Anal. Calcd for $C_{40}H_{28}F_8N_2$: C, 69.76; H, 4.10; N, 4.07. Found: C, 69.82; H, 4.16; N, 3.98.

(1*S*,2*S*)-*N*,*N*′-Bis(bis(4-trifluoromethylphenyl)methyl)-1,2-diphenylethane-1,2-diamine (J). Column chromatography (hexane/EtOAc = 1:0−20:1) gave the title compound (80%) as a white, amorphous solid of mp 95−97 °C: $[\alpha]^{25}_D$ +34.5 (*c* 0.54, $CHCl_3$). IR (KBr): 3317, 3062, 1620, 1458, 1327, 1172, 1126, 1065, 826, 702. ^{1}H NMR: 2.55 (2H, s), 3.64 (2H, s), 4.64 (2H, s), 7.04−7.06 (4H, m), 7.12 (4H, d, *J* = 8.3), 7.24−7.26 (6H, m), 7.33 (4H, d, *J* = 8.3), 7.48 (4H, d, *J* = 8.3), 7.53 (4H, d, *J* = 8.3). ^{13}C NMR: 62.9 (CH), 65.8 (CH), 124.06 (q, *J* = 272, CF_3), 124.11 (q, *J* = 272, CF_3), 125.6 (q, *J* = 4, CH), 125.7 (q, *J* = 4, CH), 127.5 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 129.7 (q, *J* = 32, C), 129.8 (q, *J* = 33, C), 140.0 (C), 146.3 (C), 147.4 (C). EIMS *m*/*z*: 408 (M/2). HRMS-FAB *m*/*z*: $[M + H]^+$ calcd for $C_{44}H_{33}F_{12}N_2$ 817.2452, found 817.2432.

(1*S*,2*S*)-*N*,*N*′-Bis(di-*p*-tolylmethyl)-1,2-diphenylethane-1,2-diamine (K). Column chromatography (hexane/$CHCl_3$ = 1:0−1:2) gave the title compound (56%) as a white, amorphous solid of mp 65−67 °C: $[\alpha]^{25}_D$ +39.6 (*c* 1.08, $CHCl_3$). IR (KBr): 3310, 3024, 2924, 2862, 1512, 1450. ^{1}H NMR: 2.29 (6H, s), 2.32 (6H, s), 2.68 (2H, s), 3.63 (2H, s), 4.46 (2H, s), 6.95−6.96 (4H, m), 7.06 (8H, m), 7.07 (4H, m), 7.11−7.12 (6H, m), 7.18 (4H, d, *J* = 8.0). ^{13}C NMR: 21.0 (CH_3), 21.1 (CH_3), 62.6 (CH), 65.8 (CH), 126.7 (CH), 127.0 (CH), 127.5 (CH), 127.8 (CH), 128.1 (CH), 128.9 (CH), 129.1 (CH), 136.18 (C), 136.21 (C), 140.5 (C), 141.2 (C), 142.3 (C). EIMS *m*/*z*: 300 (M/2), 195. Anal. Calcd for $C_{44}H_{44}N_2$: C, 87.96; H, 7.38; N, 4.66. Found: C, 87.77; H, 7.31; N, 4.56.

Typical Procedure for the Synthesis of Imidazolinium Salts. (4*S*,5*S*)-1,3-Bis(bis(2,3-dimethylphenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (C1). A suspension of **C** (2.17 g, 3.31 mmol) and NH_4BF_4 (0.38 g, 3.65 mmol) in $CH(OEt)_3$ (20 mL) was stirred at 120 °C for 2 h. The mixture was cooled to rt, filtrated, and concentrated *in vacuo*. After azeotropic evaporation with toluene (3 × 10 mL), the resulting residue was purified by column chromatography (hexane/EtOAc = 1:1) to afford the title compound (76%) as a colorless, amorphous solid of mp

134−136 °C: $[\alpha]^{25}_D$ −383 (*c* 1.01, $CHCl_3$). IR (KBr): 2918, 1630, 1458, 1035, 729. ^{1}H NMR: 1.71 (6H, s), 2.08 (6H, s), 2.20 (6H, s), 2.24 (6H, s), 5.34 (2H, s), 5.92 (2H, s), 6.70−6.72 (2H, m), 6.76 (1H, s), 6.91−6.94 (2H, m), 7.03−7.05 (2H, m), 7.16−7.21 (8H, m), 7.40−7.44 (8H, m). ^{13}C NMR: 14.2 (CH_3), 14.5 (CH_3), 20.56 (CH_3), 20.63 (CH_3), 58.9 (CH), 73.2 (CH), 124.6 (CH), 126.2 (CH), 126.4 (CH), 126.5 (CH), 128.5 (CH), 129.9 (CH), 130.9 (CH), 131.3 (CH), 131.8 (C), 132.2 (C), 132.5 (C), 135.0 (C), 135.1 (C), 138.6 (C), 138.7 (C), 154.6 (CH). FABMS *m*/*z*: 668 (M + H − BF_4). Anal. Calcd for $C_{49}H_{51}BF_4N_2\cdot 0.3H_2O$: C, 77.42; H, 6.84; N, 3.69. Found: C, 77.25; H, 6.89; N, 3.69.

(4*S*,5*S*)-1,3-Bis(bis(2,4-dimethylphenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (D1). Column chromatography ($CHCl_3$/EtOH = 1:0−9:1) gave the title compound (68%) as a pale yellow, amorphous solid of mp 132−135 °C: $[\alpha]^{25}_D$ −382 (*c* 1.08, $CHCl_3$). IR (KBr): 2922, 1631, 1499, 1055, 758. ^{1}H NMR: 1.69 (6H, s), 2.21 (6H, s), 2.23 (6H, s), 2.36 (6H, s), 5.29 (2H, s), 5.63 (2H, s), 6.62 (1H, s), 6.71−6.73 (2H, m), 6.79−6.81 (2H, m), 6.94 (2H, s), 7.01 (2H, s), 7.19−7.21 (4H, m), 7.23−7.25 (2H, m), 7.40−7.41 (2H, m), 7.46−7.48 (6H, m). ^{13}C NMR: 18.4 (CH_3), 18.6 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 57.6 (CH), 72.9 (CH), 126.2 (CH), 127.6 (CH), 127.8 (CH), 128.3 (C), 128.4 (CH), 128.6 (C), 128.8 (CH), 130.0 (CH), 131.0 (CH), 132.37 (C), 132.44 (CH), 132.8 (CH), 136.0 (C), 136.5 (C), 139.2 (C). 139.9 (C), 153.7 (CH). FABMS *m*/*z*: 668 (M + H − BF_4). Anal. Calcd for $C_{49}H_{51}BF_4N_2\cdot 0.5H_2O$: C, 77.06; H, 6.86; N, 3.67. Found: C, 76.98; H, 6.69; N, 3.93.

(4*S*,5*S*)-1,3-Bis(bis(2,5-dimethylphenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (E1). Recrystallization from EtOH gave the title compound (60%) as colorless needles of mp 255−257 °C: $[\alpha]^{25}_D$ −442 (*c* 1.04, $CHCl_3$). IR (KBr): 2922, 1627, 1504, 1055, 758. ^{1}H NMR: 1.78 (6H, s), 2.14−2.15 (12H, m), 2.54 (6H, s), 5.22 (2H, s), 5.76 (2H, s), 6.71 (2H, s), 6.89 (1H, s), 6.97−7.01 (4H, m), 7.08−7.12 (4H, m), 7.20−7.24 (6H, m), 7.45−7.49 (6H, m). ^{13}C NMR: 18.1 (CH_3), 18.2 (CH_3), 20.8 (CH_3), 21.3 (CH_3), 58.1 (CH), 73.0 (CH), 127.0 (CH), 128.2 (CH), 129.1 (CH), 129.9 (CH), 130.0 (CH), 130.4 (CH), 131.0 (CH), 131.5 (C), 131.6 (C), 131.7 (CH), 132.0 (CH), 133.4 (C), 136.6 (C), 136.9 (C), 154.8 (CH). FABMS *m*/*z*: 668 (M + H − BF_4). Anal. Calcd for $C_{49}H_{51}BF_4N_2$: C, 77.98; H, 6.81; N, 3.71. Found: C, 78.01; H, 6.78; N, 3.51.

(4*S*,5*S*)-1,3-Bis(bis(4-fluorophenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (F1). Column chromatography ($CHCl_3$/EtOH = 10:1) gave a white, amorphous solid, which was recrystallized from $CHCl_3/Et_2O$ to give the title compound (77%) as colorless needles of mp 115−117 °C: $[\alpha]^{21}_D$ −290.3 (*c* 0.71, $CHCl_3$). IR (KBr): 3078, 1628, 1512, 1234, 1165, 1057, 833. ^{1}H NMR: 4.97 (2H, s), 5.73 (2H, s), 7.02 (4H, dd, *J* = 8.6, 8.6), 7.07 (4H, dd, *J* = 8.6, 8.6), 7.12−7.14 (4H, m), 7.23−7.29 (8H, m), 7.43−7.45 (6H, m), 7.54 (1H, s). ^{13}C NMR: 64.5 (CH), 74.4 (CH), 116.6 (d, *J* = 22, CH), 116.7 (d, *J* = 22, CH), 127.7 (CH), 129.9 (d, *J* = 3, C), 130.06 (d, *J* = 8, CH), 130.11 (CH), 130.4 (CH), 130.5 (d, *J* = 3, C), 131.1 (d, *J* = 8, CH), 134.0 (C), 156.4 (CH), 163.0 (d, *J* = 249, C), 163.1 (d, *J* = 250, C). FABMS *m*/*z*: 627 (M − BF_4). Anal. Calcd for $C_{41}H_{31}BF_8N_2$: C, 68.92; H, 4.37; N, 3.92. Found: C, 68.63; H, 4.34; N, 3.96.

(4*S*,5*S*)-1,3-Bis(bis(3-fluorophenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (G1). Column chromatography ($CHCl_3$/EtOH = 30:1) gave a white solid, which was recrystallized from CH_2Cl_2/Et_2O to give the title compound (83%) as colorless needles of mp 184−185 °C: $[\alpha]^{21}_D$ −247.0 (*c* 0.6, $CHCl_3$). IR (KBr): 3071, 1620, 1489, 1450, 1250, 1211, 1065, 756. ^{1}H NMR: 5.06 (2H, s), 5.86 (2H, s), 6.79−6.84 (4H, m), 6.97−7.05 (4H, m), 7.15−7.22 (8H, m), 7.36−7.44 (10H, m), 7.72 (1H, s). ^{13}C NMR: 64.8 (CH), 74.5 (CH), 115.3 (d, *J* = 22, CH), 115.7 (d, *J* = 23, CH), 116.5 (d, *J* = 21, CH), 116.7 (d, *J* = 21, CH), 124.0 (d, *J* = 3, CH), 125.1 (d, *J* = 3, CH), 127.7 (CH), 130.1 (CH), 130.4 (CH), 131.6 (d, *J* = 7, CH), 134.0 (C), 136.4 (d, *J* = 7, C), 136.8 (d, *J* = 6, C), 157.4 (CH), 162.9 (d, *J* = 249, C), 163.1 (d, *J* = 249, C). FABMS *m*/*z*: 627 (M − BF_4). Anal. Calcd for $C_{41}H_{31}BF_8N_2$: C, 68.92; H, 4.37; N, 3.92. Found: C, 69.06; H, 4.36; N, 3.96.

(4*S*,5*S*)-1,3-Bis(bis(2-fluorophenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (H1). Column chromatography ($CHCl_3$/EtOH = 1:0−9:1) gave the title compound (86%) as a yellow, amorphous solid of mp 85−88 °C: $[\alpha]^{25}_D$ −199.2 (*c* 1.02, $CHCl_3$). IR (KBr): 1636, 1489, 1219, 1057. ^{1}H NMR: 5.11 (2H, s), 6.08 (2H, s), 6.96−7.00 (2H, m), 7.07−7.11 (2H, m), 7.13−7.16 (2H, m), 7.20−7.21 (4H, m), 7.28−7.32 (6H, m), 7.37−7.42 (8H, m), 7.47−7.51 (3H, m). ^{13}C NMR: 55.1 (CH), 74.9 (CH), 115.7 (d, *J* = 21, CH), 116.3 (d, *J* = 21, CH), 120.3 (d, *J* = 11, C), 120.5 (d, *J* = 12, C), 125.6 (d, *J* = 3, CH), 125.8 (d, *J* = 3, CH), 127.9 (CH), 129.8 (CH), 130.6 (CH), 130.6 (CH), 131.1 (CH), 132.0 (d, *J* = 7, CH), 133.1 (C), 155.8 (CH), 159.9 (d, *J* = 249, C), 160.3 (d, *J* = 249, C). FABMS *m*/*z*: 627 (M − BF_4). Anal. Calcd for $C_{41}H_{31}BF_8N_2$: C, 68.92; H, 4.37; N, 3.92. Found: C, 68.62; H, 4.46; N, 3.99.

(4*S*,5*S*)-1,3-Bis(bis(3,5-difluorophenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (I1). Recrystallization from CH_2Cl_2/Et_2O gave the title compound (77%) as a white powder of mp 258−260 °C: $[\alpha]^{21}_D$ −175.9 (*c* 0.51, $CHCl_3$). IR (KBr): 3094, 1620, 1458, 1327, 1211, 1126, 1065, 856, 718. ^{1}H NMR: 5.04 (2H, s), 6.04 (2H, s), 6.74−6.83 (12H, m), 7.14−7.16 (4H, m), 7.44−7.45 (6H, m), 8.19 (1H, s). ^{13}C NMR (CD_2Cl_2): 64.7 (CH), 75.0 (CH), 105.7 (t, *J* = 25, CH), 105.8 (t, *J* = 25, CH), 112.2. (dd, *J* = 7.2, 21, CH), 112.6 (dd, *J* = 7.2, 21, CH), 128.0 (CH), 130.5 (CH), 131.1 (CH), 134.1 (C), 137.7 (t, *J* = 9.3, C), 138.2 (t, *J* = 9.3, C), 158.7 (CH), 163.8 (dd, *J* = 12.4, 252, C), 164.0 (dd, *J* = 12.4, 252, C). FABMS *m*/*z*: 699 (M − BF_4). Anal. Calcd for $C_{41}H_{27}BF_{12}N_2\cdot 0.5H_2O$: C, 61.90; H, 3.55; N, 3.52. Found: C, 61.77; H, 3.39; N, 3.90.

(4*S*,5*S*)-1,3-Bis(bis(4-trifluoromethylphenyl)methyl)-4,5-diphenylimidazolinium Tetrafluoroborate (J1). Column chromatography ($CHCl_3$/EtOH = 15:1) gave the title compound (83%) as a white solid of mp 238−240 °C: $[\alpha]^{21}_D$ −238.6 (*c* 0.56, benzene). IR (KBr): 3071, 2368, 1628, 1420, 1327, 1173, 1126, 1072, 826, 702. ^{1}H NMR (CD_2Cl_2): 5.14 (2H, s), 5.96 (2H, s), 7.19 (4H, m), 7.44−7.47 (14H, m), 7.59−7.67 (9H, m). ^{13}C NMR (CD_2Cl_2): 65.3 (CH), 75.0 (CH), 124.0 (q, *J* = 273, CF_3), 124.1 (q, *J* = 272, CF_3), 127.05 (q, *J* = 3, CH), 127.13 (q, *J* = 3, CH), 128.1 (CH), 129.3 (CH), 130.0 (CH), 130.6 (CH), 131.1 (CH), 132.0 (q, *J* = 32, C), 132.2 (q, *J* = 34, C), 134.0 (C), 137.9 (C), 138.6 (C), 157.6 (CH). FABMS *m*/*z*: 827 (M − BF_4). Anal. Calcd for $C_{45}H_{31}BF_{16}N_2$: C, 59.10; H, 3.42; N, 3.06. Found: C, 59.08; H, 3.52; N, 3.17.

(4*S*,5*S*)-1,3-Bis(di-*p*-tolylmethyl)-4,5-diphenylimidazolinium Tetrafluoroborate (K1). Column chromatography ($CHCl_3$/EtOH = 1:0−9:1) gave the title compound (99%) as a pale yellow, amorphous solid of mp 101−103 °C: $[\alpha]^{25}_D$ −279.0 (*c* 1.03, $CHCl_3$). IR (KBr): 3032, 2924, 1628, 1211, 1057. ^{1}H NMR: 2.27 (6H, s), 2.33 (6H, s), 4.99 (2H, s), 5.53 (2H, s), 7.08 (3H, m), 7.10 (8H, m), 7.15−7.17 (4H, m), 7.21−7.23 (4H, m), 7.25−7.27 (2H, m), 7.42−7.47 (6H, m). ^{13}C NMR: 21.0 (CH_3), 21.1 (CH_3), 65.0 (CH), 73.9 (CH), 127.6 (CH), 127.7 (CH), 128.7 (CH), 130.0 (CH), 130.1 (CH), 130.2 (CH), 130.9 (C), 131.9 (C), 134.2 (C), 139.1 (C), 139.4 (C), 155.5 (CH). FABMS *m*/*z*: 611 (M − BF_4). HRMS-FAB *m*/*z*: $[M - BF_4]^+$ calcd for $C_{45}H_{43}N_2$, 611.3421; found, 611.3417. Anal. Calcd for $C_{45}H_{43}BF_4N_2\cdot 0.05CHCl_3$: C, 76.79; H, 6.16; N, 3.98. Found: C, 76.54; H, 6.34; N, 4.08.

Preparation of NHC−Cu Complexes 1f−k. Typical Procedure. [(4*S*,5*S*)-1,3-Bis(bis(4-fluorophenyl)methyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1f). A mixture of **F1** (140 mg, 0.20 mmol), NaO*t*Bu (21 mg, 0.22 mmol), and CuCl (20 mg, 0.20 mmol) in THF (3 mL) was stirred at rt for 3 h. The mixture was filtrated through Celite and concentrated *in vacuo* to give a crude mixture, which was purified by column

chromatography (benzene to $CHCl_3$/EtOH = 20:1) to afford the title compound as an off-white, amorphous solid (117 mg, 81%) of mp 205−207 °C (dec): $[\alpha]^{25}_D$ −246.5 (*c* 0.5, $CHCl_3$). IR (KBr): 3060, 1605, 1504, 1458, 1227, 1157, 833. ^{1}H NMR: 4.52 (2H, s), 5.39 (2H, s), 6.97−7.05 (12H, m), 7.14−7.17 (4H, m), 7.29−7.32 (4H, m), 7.40−7.41 (6H, m). ^{13}C NMR: 63.8 (CH), 74.6 (CH), 116.3 (d, *J* = 22, CH), 116.5 (d, *J* = 22, CH), 127.4 (CH), 129.6 (CH), 129.7 (CH), 130.1 (d, *J* = 8, CH), 130.4 (d, *J* = 8, CH), 132.4 (d, *J* = 3, C), 133.7 (d, *J* = 3, C), 137.5 (C), 162.8 (d, *J* = 248, C), 163.0 (d, *J* = 248, C), 198.6 (C). FABMS *m*/*z*: 689 (M − Cl). Anal. Calcd for $C_{41}H_{30}ClCuF_4N_2 \cdot H_2O$: C, 66.21; H, 4.34; N, 3.77. Found: C, 66.08; H, 4.29; N, 3.79.

[(4*S*,5*S*)-1,3-Bis(bis(3-fluorophenyl)methyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1g). Column chromatography (benzene to $CHCl_3$/EtOH = 50:1) gave the title compound as an off-white, amorphous solid (209 mg, 96%) of mp 219−221 °C (dec): $[\alpha]^{25}_D$ −226.7 (*c* 0.47, $CHCl_3$). IR (KBr): 3063, 1589, 1489, 1443, 1265, 1142, 764. ^{1}H NMR: 4.57 (2H, s), 5.40 (2H, s), 6.69 (2H, d, *J* = 9.8), 6.86 (2H, d, *J* = 7.7), 6.99−7.05 (4H, m), 7.09−7.11 (4H, m), 7.12−7.16 (2H, m), 7.19 (2H, d, *J* = 7.7), 7.30−7.34 (2H, m), 7.41−7.42 (6H, m), 7.46−7.51 (2H, m). ^{13}C NMR: 64.1 (CH), 74.7 (CH), 115.5 (d, *J* = 23, CH), 115.99 (d, *J* = 21, CH), 116.01 (d, *J* = 24, CH), 116.1 (d, *J* = 22, CH), 123.9 (d, *J* = 2, CH), 124.3 (d, *J* = 3, CH), 127.5 (CH), 129.7 (CH), 129.8 (CH), 131.1 (d, *J* = 8, CH), 137.2 (C), 138.8 (d, *J* = 6, C), 139.9 (d, *J* = 7, C), 163.2 (d, *J* = 249, C), 163.3 (d, *J* = 248, C), 199.3 (C). Anal. Calcd for $C_{41}H_{30}ClCuF_4N_2$: C, 67.86; H, 4.17; N, 3.86. Found: C, 67.65; H, 4.31; N, 3.99.

[(4*S*,5*S*)-1,3-Bis(bis(2-fluorophenyl)methyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1h). Column chromatography (benzene to $CHCl_3$/EtOH = 19:1) gave the title compound as a pale yellow, amorphous solid (206 mg, 94%) of mp 87−89 °C: $[\alpha]^{25}_D$ −160.0 (*c* 1.00, $CHCl_3$). IR (KBr): 3040, 2908, 1589, 1489, 1450, 1273, 1219, 756. ^{1}H NMR: 4.73 (2H, s), 5.92 (2H, s), 6.94−6.98 (2H, m), 7.02−7.15 (10H, m), 7.28−7.36 (10H, m), 7.40−7.48 (4H, m). ^{13}C NMR: 53.0 (CH), 75.7 (CH), 115.7 (d, *J* = 22, CH), 115.9 (d, *J* = 22, CH), 123.9 (d, *J* = 13, C), 124.3 (d, *J* = 13, C), 125.1 (d, *J* = 3, CH), 125.3 (d, *J* = 3, CH), 128.3 (CH), 129.0 (CH), 129.3 (CH), 129.5 (d, *J* = 3, CH), 130.5 (d, *J* = 3, CH), 130.6 (d, *J* = 8, CH), 130.9 (d, *J* = 8, CH), 136.3 (C), 160.3 (d, *J* = 249, C), 160.7 (d, *J* = 249, C), 197.5 (C). FABMS *m*/*z*: 689 (M − Cl). HRMS-FAB *m*/*z*: $[M - Cl]^+$ calcd for $C_{41}H_{30}CuF_4N_2$, 689.1641; found, 689.1639. Anal. Calcd for $C_{41}H_{30}ClCuF_4N_2 \cdot 0.5CHCl_3$: C, 63.47; H, 3.91; N, 3.57. Found: C, 63.35; H, 3.97; N, 3.65.

[(4*S*,5*S*)-1,3-Bis(bis(3,5-difluorophenyl)methyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1i). Column chromatography (benzene to $CHCl_3$/EtOH = 30:1) gave the title compound as a white, amorphous solid (219 mg, 92%) of mp 229−231 °C (dec): $[\alpha]^{25}_D$ −205.9 (*c* 0.84, $CHCl_3$). IR (KBr): 3062, 1620, 1597, 1443, 1327, 1203, 1119, 995, 856, 702. ^{1}H NMR: 4.57 (2H, s), 5.38 (2H, s), 6.55 (4H, d, *J* = 5.5), 6.80−6.86 (6H, m), 6.90−6.94 (2H, m), 7.10−7.12 (4H, m), 7.47−7.49 (6H, m). ^{13}C NMR: 63.6 (CH), 74.8 (CH), 105.1 (t, *J* = 25, CH), 105.2 (t, *J* = 25, CH), 111.3 (dd, *J* = 7.2, 21, CH), 112.0 (dd, *J* = 7.2, 21, CH), 127.3 (CH), 130.1 (CH), 130.2 (CH), 136.4 (C), 139.5 (t, *J* = 8.3, C), 140.3 (t, *J* = 8.3, C), 163.6 (dd, *J* = 12.4, 252, C), 163.8 (dd, *J* = 13.5, 251, C), 199.6 (C). FABMS *m*/*z*: 761 (M−Cl). HRMS-FAB *m*/*z*: $[M - Cl]^+$ calcd for $C_{41}H_{26}CuF_8N_2$, 761.1264; found, 761.1273. Anal. Calcd for $C_{41}H_{26}ClCuF_8N_2 \cdot 0.5CHCl_3$: C, 58.14; H, 3.12; N, 3.27. Found: C, 58.09; H, 3.29; N, 3.27.

[(4*S*,5*S*)-1,3-Bis(bis(4-trifluoromethylphenyl)methyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1j). Column chromatography (benzene to $CHCl_3$/EtOH = 20:1) gave the title compound as a beige solid (231 mg, 83%) of mp 227−229 °C (dec): $[\alpha]^{25}_D$ −214.2 (*c* 0.29, $CHCl_3$). IR (KBr): 3070, 1620, 1420, 1327, 1165, 1126, 1065, 818. ^{1}H NMR: 4.57 (2H, s), 5.59 (2H, s), 7.05−7.07 (4H, m), 7.14 (4H, d, *J* = 8.2), 7.40−7.43 (6H, m), 7.45 (4H, d, *J* = 8.2), 7.59 (4H, d, *J* = 8.2), 7.75 (4H, d, *J* = 8.2). ^{13}C NMR: 64.5 (CH), 74.8 (CH), 123.74 (q, *J* = 271, CF_3), 123.75 (q, *J* = 273, CF_3), 126.5 (q, *J* = 4, CH), 126.7 (q, *J* = 3, CH), 127.3 (CH), 128.9 (CH), 129.1 (CH), 129.9 (CH), 130.0 (CH), 131.4 (q, *J* = 32, C), 131.5 (q, *J* = 33, C), 136.8 (C), 140.0 (C), 141.0 (C), 199.5 (C). Anal. Calcd for $C_{45}H_{30}ClCuF_{12}N_2$: C, 58.39; H, 3.27; N, 3.03. Found: C, 58.16; H, 3.25; N, 3.09.

[(4*S*,5*S*)-1,3-Bis(di-*p*-tolylmethyl)-4,5-diphenylimidazolidin-2-ylidene]copper(I) Chloride (1k). Column chromatography (benzene to $CHCl_3$/EtOH = 19:1) gave the title compound as a colorless, amorphous solid (199 mg, 93%) of mp 102−106 °C: $[\alpha]^{25}_D$ −251 (*c* 1.01, $CHCl_3$). IR (KBr): 3024, 2924, 1612, 1512, 1450. ^{1}H NMR: 2.31 (6H, s), 2.41 (6H, s), 4.51 (2H, s), 5.33 (2H, s), 6.90−6.91 (4H, m), 7.08−7.11 (8H, m), 7.20−7.24 (8H, m), 7.35−7.36 (6H, m). ^{13}C NMR: 21.10 (CH_3), 21.11 (CH_3), 64.5 (CH), 74.3 (CH), 127.5 (CH), 128.3 (CH), 128.6 (CH), 129.0 (CH), 129.3 (CH), 129.6 (CH), 129.9 (CH), 133.8 (C), 135.3 (C), 138.0 (C), 138.2 (C), 138.4 (C), 198.2 (C). FABMS *m*/*z*: 673 (M − Cl). HRMS-FAB *m*/*z*: $[M - Cl]^+$ calcd for $C_{45}H_{42}CuN_2$, 673.2644; found, 673.2664. Anal. Calcd for $C_{45}H_{43}BF_4N_2 \cdot 0.55CHCl_3$: C, 70.55; H, 5.53; N, 3.61. Found: C, 70.40; H, 5.60; N, 3.57.

Typical Procedure for the AAAr of Aliphatic Allylic Bromides. (+)-(*S*)-3-Phenyloct-1-ene (γ-3aa)[11,21] (Table 1, entry 6). In a 10 mL tube capped with a rubber septum, **1f** (14.5 mg, 0.02 mmol) and **2a** (190 mg, 1.0 mmol) were dissolved in CH_2Cl_2 (2 mL) and stirred for 10 min at −78 °C. A 3.0 M solution of PhMgBr (0.40 mL, 1.2 mmol) in Et_2O was diluted with CH_2Cl_2 (0.5 mL) and added over 30 min to the above mixture using a syringe pump. After the addition of PhMgBr, the mixture was stirred for 30 min and diluted with Et_2O (6 mL). The reaction was quenched with 10% HCl (1 mL), and the aqueous phase was separated and extracted with Et_2O (3 × 3 mL). The combined organic layers were dried over Na_2SO_4 and filtered. A small part of the filtrate was passed through a short plug of silica gel to remove residual metal and subjected to a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 160 °C at 5 °C/min) to determine conversion and regioselectivity. The remainder of the filtrate was concentrated *in vacuo* and purified by column chromatography (pentane/Et_2O = 1:0−50:1) to give an 84:16 mixture of γ-**3aa** with 87% ee and α-**3aa** (176 mg, 93%) as a colorless oil: $[\alpha]^{20}_D$ +19.8 (*c* 1.65, $CHCl_3$); lit.[11] $[\alpha]^{20}_D$ −20.8 (*c* 1.52, $CHCl_3$) for the *R*-enantiomer. ^{1}H and ^{13}C NMR, IR, and MS were identical to those reported.[11] Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 40 °C for 20 min and then to 70 °C at 2 °C/min; major 116.2 min, minor 117.8 min).

(+)-(*S*)-3-Phenylhex-1-ene (γ-3ba)[22] (Table 1, entry 13). The typical procedure with column chromatography (pentane/Et_2O = 1:0−50:1) gave a 91:9 mixture of γ-**3ba** with 74% ee and α-**3ba** (98%) as a colorless oil: $[\alpha]^{20}_D$ +34.8 (*c* 1.19, $CHCl_3$). IR (neat): 3071, 3024, 2955, 2924, 1636, 1597, 1489, 1458, 1373, 995, 910, 764. ^{1}H NMR: 0.89 (3H, t, *J* = 7.3), 1.19−1.34 (2H, m), 1.63−1.74 (2H, m), 3.25 (1H, dt, *J* = 7.6, 7.6), 5.00 (1H, m), 5.02 (1H, m), 5.95 (1H, ddd, *J* = 7.6, 10.4, 18.0), 7.17−7.20 (3H, m), 7.28−7.31 (2H, m). ^{13}C NMR: 13.9 (CH_3), 20.6 (CH_2), 37.6 (CH_2), 49.6 (CH), 113.8 (CH_2), 126.1 (CH), 127.6 (CH), 128.4 (CH), 142.6 (CH), 144.7 (C). EIMS *m*/*z*: 161 (M + 1, 2%), 160 (M^+, 7%), 159 (M − 1, 9%), 131 (24), 117 (97), 105 (32), 84 (100). Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 70 °C for 25 min and then to 120 °C at 10 °C/min; major 22.8 min, minor 23.3 min).

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(+)-(***R***)**-2-Cyclohexyl-2-phenylprop-1-ene (*γ*-3ca) (Table 1, entry 17).** The typical procedure was performed in half-scale (0.5 mmol of **2c**). The Grignard reagent was diluted with CH_2Cl_2 (0.25 mL) and added over 15 min. Column chromatography (pentane) gave an 89:11 mixture of *γ*-**3ca** with 93% ee and α-**3ca** (97%) as a colorless oil: $[\alpha]^{21}_D$ +63.9 (*c* 1.33, $CHCl_3$). IR (neat): 3024, 2924, 2855, 1636, 1597, 1490, 1450, 1381, 910, 702. ^{1}H NMR: 0.76−1.91 (11H, m), 2.92 (1H, dd, *J* = 9.2, 9.2), 4.98−5.02 (2H, m), 5.97 (1H, dt, *J* = 9.2, 17.4), 7.14−7.19 (3H, m), 7.25−7.29 (2H, m). ^{13}C NMR: 26.3 (CH_2), 26.5 (CH_2), 31.26 (CH_2), 31.30 (CH_2), 42.1(CH), 57.6 (CH), 114.9 (CH_2), 126.0 (CH), 128.0 (CH), 128.4 (CH), 141.3 (CH), 144.2 (C). EIMS *m*/*z*: 201 (M + 1), 200 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{20}$, 200.1565; found, 200.1570. Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 40 °C for 10 min, to 100 °C at 1 °C/min, 100 °C for 30 min, and to 170 °C at 5 °C/min; minor 94.4 min, major 95.3 min).

(+)-(***R***)**-4,4-Dimethyl-3-phenylpent-1-en (*γ*-3da)**[23] **(Table 1, entry 20).** Modification of the typical procedure, as in Table 1, entry 17, and column chromatography (pentane) gave a 53:47 mixture of *γ*-**3da** with 87% ee and α-**3da** (61%) as a volatile pale yellow oil: $[\alpha]^{25}_D$ +45.3 (*c* 0.67, $CDCl_3$); lit.[23] $[\alpha]^{25}_D$ +101 (neat) for optically pure (*R*)-*γ*-**3da**. IR (neat): 3063, 3024, 2955, 1636, 1605, 1458, 1366, 972, 910, 741. ^{1}H NMR: 0.89 (9H, s), 3.02 (1H, dd, *J* = 0.7, 9.8), 5.03 (1H, ddd, *J* = 0.7, 2.1, 16.8), 5.08 (1H, dd, *J* = 2.1, 10.1), 6.26 (1H, ddd, *J* = 9.8, 10.1, 16.8), 7.16−7.20 (5H, m). ^{13}C NMR: 28.0 (CH_3), 33.8 (C), 61.5 (CH), 116.2 (CH_2), 126.0 (CH), 127.9 (CH), 129.2 (CH), 138.9 (CH), 142.9 (C). EIMS *m*/*z*: 175 (M + 1, 1%), 174 (M^+, 4%), 131 (7), 117 (30), 91 (15), 84 (100). Enantioselectivity was determined by chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 90 °C for 30 min and then to 160 °C at 5 °C/min; minor 9.8 min, major 10.5 min).

(+)-(***S***)**-3-*p*-Tolyloct-1-ene (*γ*-3ab) (Table 2, entry 4).** The typical procedure was performed in half-scale (0.5 mmol of **2a**). The Grignard reagent was diluted with CH_2Cl_2 (0.4 mL) and added over 1 h. Column chromatography (pentane) gave an 82:18 mixture of *γ*-**3ab** with 84% ee and α-**3ab** (92%) as a pale yellow oil. Regioselectivity was determined by the integration area of ^{1}H NMR signals at 5.46−5.57 ppm for α-**3ab** and 5.92 ppm for *γ*-**3ab**: $[\alpha]^{25}_D$ +27.0 (*c* 1.03, $CHCl_3$). IR (neat): 2924, 2862, 1512, 1458. ^{1}H NMR: 0.84−0.90 (3H, m), 1.21−1.32 (6H, m), 1.63−1.70 (2H, m), 2.32 (3H, s), 3.19 (1H, dt, *J* = 7.5, 7.5), 4.98 (1H, m), 5.00 (1H, m), 5.92 (1H, ddd, *J* = 7.5, 10.3, 17.5), 7.06−7.11 (4H, m). ^{13}C NMR: 14.1 (CH_3), 21.0 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 31.8 (CH_2), 35.4 (CH_2), 49.5 (CH), 113.6 (CH_2), 127.4 (CH), 129.1 (CH), 135.5 (C), 141.7 (C), 142.8 (CH). EIMS *m*/*z*: 202 (M^+), 131. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{22}$, 202.1722; found, 202.1730. Enantioselectivity was determined after conversion to the corresponding terminal alcohol by hydroboration−oxidation (*vide infra*).

(+)-(***S***)**-3-(4-Methoxyphenyl)-1-octene (*γ*-3ac) (Table 2, entry 6).** Modification of the typical procedure, as in Table 2, entry 4, and column chromatography (pentane) gave a 79:21 mixture of *γ*-**3ac** with 79% ee and α-**3ac** (99%) as a pale yellow oil. Regioselectivity was determined by the integration area of ^{1}H NMR signals at 6.82−6.86 ppm for α-**3ac** and 5.92 ppm for *γ*-**3ac**: $[\alpha]^{25}_D$ +22.0 (*c* 1.27, $CHCl_3$). IR (neat): 2924, 2855, 1512, 1250. ^{1}H NMR: 0.85 (3H, t, *J* = 6.9), 1.18−1.31 (6H, m), 1.64−1.69 (2H, m), 3.18 (1H, dt, *J* = 7.5, 7.5), 3.79 (3H, s), 4.97 (1H, m), 5.00 (1H, m), 5.92 (1H, m), 6.82−6.86 (2H, m), 7.09−7.11 (2H, m). ^{13}C NMR: 14.0 (CH_3), 22.5 (CH_2), 27.2 (CH_2), 31.8 (CH_2), 35.4 (CH_2), 49.0 (CH), 55.0 (CH_3), 113.4 (CH_2), 113.7 (CH), 128.4 (CH), 136.6 (C), 142.8 (CH), 157.9 (C). EIMS *m*/*z*: 218 (M^+), 147. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{22}O$, 218.1671; found, 218.1674. Enantioselectivity was determined after conversion to the corresponding terminal alcohol by hydroboration−oxidation (*vide infra*).

(+)-(***S***)**-3-(4-Chlorophenyl)oct-1-ene (*γ*-3ad) (Table 2, entry 7).** Modification of the typical procedure, as in Table 2, entry 4, and column chromatography (pentane) gave an 87:13 mixture of *γ*-**3ad** with 80% ee and α-**3ad** (98%) as a pale yellow oil. Regioselectivity was determined by the integration area of ^{1}H NMR signals at 5.46−5.55 ppm for α-**3ad** and 5.90 ppm for *γ*-**3ad**: $[\alpha]^{25}_D$ +29.1 (*c* 1.14, $CHCl_3$). IR (neat): 2924, 2855, 1489. ^{1}H NMR: 0.85 (3H, t, *J* = 6.6), 1.15−1.31 (6H, m), 1.60−1.72 (2H, m), 3.21 (1H, dt, *J* = 7.6, 7.6), 5.00 (1H, d, *J* = 17.5), 5.02 (1H, d, *J* = 10.4), 5.90 (1H, ddd, *J* = 7.6, 10.4, 17.5), 7.10−7.12 (2H, m), 7.25−7.27 (2H, m). ^{13}C NMR: 14.0 (CH_3), 22.5 (CH_2), 27.1 (CH_2), 31.7 (CH_2), 35.3 (CH_2), 49.2 (CH), 114.2 (CH_2), 128.5 (CH), 128.9 (CH), 131.7 (C), 142.0 (CH), 143.1 (C). EIMS *m*/*z*: 224 (M + 2), 222 (M^+), 187 (M − Cl), 151. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{14}H_{19}Cl$, 222.1175; found, 222.1166. Enantioselectivity was determined by chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 100 °C; minor 57.7 min, major 59.2 min).

(+)-(***S***)**-3-(4-Fluorophenyl)oct-1-ene (*γ*-3ae) (Table 2, entry 10).** Modification of the typical procedure, as in Table 2, entry 4, and column chromatography (pentane) gave an 88:12 mixture of *γ*-**3ae** with 66% ee and α-**3ae** (96%) as a pale yellow oil. Regioselectivity was determined by the integration area of ^{1}H NMR signals at 5.46−5.55 ppm for α-**3ae** and 5.91 ppm for *γ*-**3ae**: $[\alpha]^{25}_D$ +18.1 (*c* 1.34, $CHCl_3$). IR (neat): 2924, 2862, 1512, 1227. ^{1}H NMR: 0.85 (3H, t, *J* = 6.3), 1.16−1.31 (6H, m), 1.65−1.70 (2H, m), 3.21 (1H, dt, *J* = 7.5, 7.5), 4.99 (1H, m), 5.01 (1H, m), 5.91 (1H, ddd, *J* = 7.5, 10.4, 17.2), 6.94−7.00 (2H, m), 7.11−7.15 (2H, m). ^{13}C NMR: 14.0 (CH_3), 22.6 (CH_2), 27.1 (CH_2), 31.8 (CH_2), 35.5 (CH_2), 49.1 (CH), 113.9 (CH_2), 115.1 (d, *J* = 20, CH), 128.9 (d, *J* = 7, CH), 140.2 (d, *J* = 2, C), 142.4 (CH), 161.3 (d, *J* = 244, C). EIMS *m*/*z*: 207 (M + 1), 206 (M^+), 135. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{14}H_{19}F$, 206.1471; found, 206.1476. Enantioselectivity was determined by chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 100 °C; minor 17.6 min, major 18.2 min).

(+)-(***S***)**-3-(3-Fluorophenyl)oct-1-ene (*γ*-3af) (Table 2, entry 12).** Modification of the typical procedure, as in Table 2, entry 4, and column chromatography (pentane) gave a 79:21 mixture of *γ*-**3af** with 52% ee and α-**3af** (96%) as a pale yellow oil. Regioselectivity was determined by the integration area of ^{1}H NMR signals at 5.49−5.58 ppm for α-**3af** and 5.90 ppm for *γ*-**3af**: $[\alpha]^{25}_D$ +13.0 (*c* 1.29, $CHCl_3$). IR (neat): 2932, 2862, 1589. ^{1}H NMR: 0.86 (3H, t, *J* = 6.9), 1.16−1.31 (6H, m), 1.62−1.72 (2H, m), 3.23 (1H, dt, *J* = 7.5, 7.5), 5.01 (1H, m), 5.04 (1H, m), 5.90 (1H, ddd, *J* = 7.5, 10.7, 18.3), 6.88−6.90 (2H, m), 6.95−6.97 (2H, m). ^{13}C NMR: 14.0 (CH_3), 22.5 (CH_2), 27.1 (CH_2), 31.7 (CH_2), 35.3 (CH_2), 49.7 (d, *J* = 2, CH), 112.9 (d, *J* = 22, CH), 114.3 (d, *J* = 20, CH), 114.4 (CH_2), 123.3 (d, *J* = 2, CH), 129.7 (d, *J* = 8, CH), 141.8 (CH), 147.3 (d, *J* = 7, C), 163.0 (d, *J* = 245, C). EIMS *m*/*z*: 207 (M + 1), 206 (M^+), 135. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{14}H_{19}F$, 206.1471; found, 206.1473. Enantioselectivity was determined by chiral GC analysis (Chiraldex B-DM, 25 m × 0.25 mm × 0.25 μm: 40 °C for 20 min and then to 70 °C at 1 °C/min; major 146.1 min, minor 148.9 min).

(+)-(***R***)**-3-Cyclohexyl-3-(4-tolyl)prop-1-ene (*γ*-3cb) (Table 3, entry 3).** The typical procedure was performed in half-scale (0.5 mmol of **2c**). The Grignard reagent was diluted with CH_2Cl_2 (0.4 mL) and added over 15 min. Column chromatography (pentane) gave an 87:13 mixture of *γ*-**3cb** with 96% ee and α-**3cb** (99%) as a colorless oil. Regioselectivity was determined by a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 160 °C at 5 °C/min; *γ* 25.7 min, α 28.3 min). $[\alpha]^{25}_D$ +68.8 (*c* 1.41, $CHCl_3$). IR (neat): 2924, 2855, 1636, 1512, 1381, 910, 818, 725. ^{1}H NMR: 0.75−1.89 (11H, m), 2.31 (3H, s), 2.89 (1H, dd, *J* = 9.2, 9.2), 4.97−5.01 (2H,

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m), 5.95 (1H, m), 7.03−7.10 (4H, m). ^{13}C NMR: 20.9 (CH_3), 26.3 (CH_2), 26.5 (CH_2), 31.3 (CH_2), 42.0 (CH), 57.1 (CH), 114.6 (CH_2), 127.8 (CH), 129.1 (CH), 135.4 (C), 141.2 (C), 141.5 (CH). EIMS *m*/*z*: 215 (M + 1), 214 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{16}H_{22}$, 214.1722; found, 214.1716. Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm; 40 °C for 30 min, to 100 °C at 1 °C/min, 100 °C for 70 min, and then to 170 °C at 5 °C/min; minor 149.4 min, major 151.0 min).

(+)-(*R*)-3-(4-Chlorophenyl)-3-cyclohexylprop-1-ene (*γ*-3cd) (Table 3, entry 5). Modification of the typical procedure, as in Table 3, entry 3, and column chromatography (pentane) gave a 96:4 mixture of *γ*-**2cd** with 93% ee and α-**2cd** (97%) as colorless oil. Regioselectivity was determined by a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 160 °C at 5 °C/min; *γ* 28.4 min, α 32.0 min). $[\alpha]^{25}_D$ +77.1 (*c* 1.72, $CHCl_3$). IR (neat): 2924, 2855, 1636, 1489, 1450, 1096, 910, 826. ^{1}H NMR: 0.74−1.88 (11H, m), 2.91 (1H, dd, *J* = 9.2, 9.2), 4.97−5.03 (2H, m), 5.92 (1H, ddd, *J* = 9.2, 10.1, 16.8), 7.07−7.26 (4H, m). ^{13}C NMR: 26.3 (CH_2), 26.4 (CH_2), 31.16 (CH_2), 31.19 (CH_2), 42.1 (CH), 56.8 (CH), 115.3 (CH_2), 128.5 (CH), 129.3 (CH), 131.6 (C), 140.7 (CH), 142.6 (C). EIMS *m*/*z*: 235 (M + 1), 234 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{19}Cl$, 234.1175; found, 234.1184. Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 40 °C for 30 min, to 100 °C at 1 °C/min, 100 °C for 70 min, and then to 170 °C at 5 °C/min; minor 171.2 min, major 171.4).

(+)-(*R*)-3-Cyclohexyl-3-(4-fluorophenyl)prop-1-ene (*γ*-3ce) (Table 3, entry 6). Modification of the typical procedure, as in Table 3, entry 3, and column chromatography (pentane) gave a 95:5 mixture of *γ*-**3ce** with 92% ee and α-**3ce** (98%) as a colorless oil. Regioselectivity was determined by a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 160 °C at 5 °C/min; *γ* 23.5 min, α 25.7 min). $[\alpha]^{25}_D$ +58.1 (*c* 1.84, $CHCl_3$). IR (neat): 2924, 2855, 1636, 1512, 1381, 1227, 1157, 910, 833. ^{1}H NMR: 0.74−1.89 (11H, m), 2.92 (1H, dd, *J* = 9.2, 9.2), 4.97−5.02 (2H, m), 5.92 (1H, ddd, *J* = 9.2, 10.1, 16.8), 6.94−7.13 (4H, m). ^{13}C NMR: 26.3 (CH_2), 26.4 (CH_2), 31.2 (CH_2), 42.2 (CH), 56.6 (CH), 115.0 (CH_2), 115.1 (CH, d, *J* = 21), 129.2 (CH, d, *J* = 7.3), 139.8 (C, d, *J* = 3.1), 141.0 (CH), 161.3 (C, d, *J* = 244). EIMS *m*/*z*: 219 (M + 1), 218 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{19}F$, 218.1471; found, 218.1467. Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 40 °C for 30 min, to 100 °C at 1 °C/min, 100 °C for 55 min, and then to 170 °C at 5 °C/min; minor 125.5 min, major 127.5 min).

(+)-(*R*)-3-Cyclohexyl-3-(3,4-dichlorophenyl)prop-1-ene (*γ*-3cg) (Table 3, entry 7). The typical procedure was performed in half-scale (0.5 mmol of **2c**). The Grignard reagent was diluted with CH_2Cl_2 (0.4 mL) and added over 1 h. Column chromatography (pentane) gave a 96:4:19 mixture of *γ*-**3cg** with 86% ee (81%), α-**3cg** (3%), and **2c** (16%) as a pale yellow oil. Regioselectivity was determined by a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 160 °C at 5 °C/min; *γ* 36.2 min, α 41.7 min). A mixture of *γ*- and α-**3cg** (99 mg, 74%) was separated from **2c** by column chromatography (pentane/Et_2O = 1:0−10:1) after treatment with $CaCO_3$ in refluxing water/dioxane to convert **2c** into the corresponding alcohol: $[\alpha]^{25}_D$ +65.1 (*c* 1.20, $CHCl_3$). IR (neat): 2924, 2855, 1636, 1466, 1389, 1134, 918, 818. ^{1}H NMR: 0.76−1.87 (11H, m), 2.90 (1H, dd, *J* = 9.2, 9.2), 5.01 (1H, dd, *J* = 1.5, 16.8), 5.04 (1H, dd, *J* = 1.5, 10.1), 5.89 (1H, ddd, *J* = 9.2, 10.1, 16.8), 6.98 (1H, dd, *J* = 2.2, 8.3), 7.23 (1H, d, *J* = 2.2), 7.34 (1H, d, *J* = 8.3). ^{13}C NMR: 26.2 (CH_2), 26.3 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 42.0 (CH), 56.6 (CH), 115.9 (CH_2), 127.4 (CH), 129.8 (C), 129.9 (CH), 130.3 (CH), 132.3 (C), 140.0 (CH), 144.5 (C). EIMS *m*/*z*: 272 (M + 4), 270 (M + 2), 268 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{18}Cl_2$, 268.0786; found, 268.0783. Enantioselectivity was determined by a chiral GC analysis (CP-Chiralsil-Dex-CB, 25 m × 0.25 mm: 40 °C for 30 min, to 100 °C at 0.5 °C/min, 100 °C for 70 min, and then to 150 °C at 1 °C/min; minor 270.0 min, major 270.4 min).

(+)-(*R*)-3-Cyclohexyl-3-(3,4-methylenedioxyphenyl)prop-1-ene (*γ*-3ch) (Table 3, entry 8). Modification of the typical procedure, as in Table 3, entry 7, and column chromatography (pentane/Et_2O = 1:0−50:1) gave a 91:9 mixture of *γ*-**3ch** with 93% ee and α-**3ch** (41%) as a colorless oil. Regioselectivity was determined by a GC analysis (DB-1, 30 m × 0.25 mm: 35 to 200 °C at 5 °C/min; *γ* 31.2 min, α 33.3 min). $[\alpha]^{25}_D$ +64.9 (*c* 0.89, $CHCl_3$). IR (neat): 2924, 2855, 1636, 1489, 1443, 1242, 1042, 936, 810. ^{1}H NMR: 0.74−1.88 (11H, m), 2.84 (1H, dd, *J* = 9.2, 9.2), 4.98 (1H, d, *J* = 17), 4.99 (1H, d, *J* = 11), 5.87−5.95 (1H, m), 5.91 (2H, s), 6.58 (1H, dd, *J* = 1.5, 7.9), 6.65 (1H, d, *J* = 1.5), 6.72 (1H, d, *J* = 7.9). ^{13}C NMR: 26.3 (CH_2), 26.5 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 42.1 (CH), 57.2 (CH), 100.8 (CH_2), 108.09 (CH), 108.13 (CH), 114.7 (CH_2), 120.9 (CH), 138.1 (C), 141.3 (CH), 145.7 (C), 147.6 (C). EIMS *m*/*z*: 244 (M^+). HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{16}H_{20}O_2$, 244.1463; found, 244.1462. Enantioselectivity was determined after conversion to the corresponding terminal alcohol by hydroboration−oxidation (*vide infra*).

Determination of Enantioselectivity and Absolute Configuration. Absolute Configuration of *γ*-3ca. (+)-(*R*)-3-Cyclohexyl-3-phenylpropan-1-ol (4) (ref 24). To a solution of a mixture of α- and *γ*-**3ca** (60 mg, 0.3 mmol) in THF (2 mL) cooled in an ice/water bath was added a 0.5 M solution of 9-BBN (0.9 mL, 0.45 mmol) in THF. The mixture was stirred for 6 h and then allowed to reach rt. To the mixture were added sequentially EtOH (1.5 mL), 1 M NaOH (1.5 mL), and 30% H_2O_2 (1.2 mL). The mixture was stirred vigorously for 5 h, and then the reaction was quenched with 10% $Na_2S_2O_3$ (4 mL). The mixture was diluted with CH_2Cl_2 (20 mL), and the aqueous phase was separated and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Column chromatography (pentane/Et_2O = 3:1) gave **4** (58 mg, 89%) as a pale yellow oil: $[\alpha]^{22}_D$ +12.7 (*c* 0.95, pentane); lit.[24] $[\alpha]^{22}_D$ +12.4 (*c* 1.17, pentane). IR (neat): 3341(br), 2924, 2855, 1450, 1049, 702. ^{1}H NMR: 0.77−1.84 (12H, m), 1.92 (1H, m), 2.09 (1H, m), 2.45 (1H, m), 3.38 (1H, m), 3.47 (1H, m), 7.12−7.13 (2H, m), 7.19 (1H, m), 7.28−7.29 (2H, m). ^{13}C NMR: 26.4 (CH_2), 26.5 (CH_2), 31.0 (CH_2), 31.2 (CH_2), 35.5 (CH_2), 43.2 (CH), 48.6 (CH), 61.7 (CH_2), 126.1 (CH), 128.2 (CH), 128.5 (CH), 143.9 (C). EIMS *m*/*z*: 219 (M + 1, 2%), 218 (M^+, 14%), 136 (21), 118 (100), 105 (73), 91 (87).

Enantioselectivity of *γ*-3ab. (−)-(*S*)-3-*p*-Tolyloctan-1-ol (5). The above procedure and column chromatography (hexane/EtOAc = 14:1) gave **5** (89% from *γ*-**3ab** with 88% ee) as a colorless oil: $[\alpha]^{22}_D$ −4.14 (*c* 0.70, $CHCl_3$). IR (neat): 3333, 2924, 2862, 1512, 1458, 1049, 818. ^{1}H NMR: 0.83 (3H, t, *J* = 6.9), 1.07−1.25 (7H, m), 1.52−1.64 (2H, m), 1.77 (1H, m), 1.92 (1H, m), 2.32 (3H, s), 2.63 (1H, tt, *J* = 5.4, 9.2), 3.44−3.55 (2H, m), 7.04−7.06 (2H, m), 7.09−7.11 (2H, m). ^{13}C NMR: 14.1 (CH_3), 21.0 (CH_3), 22.5 (CH_2), 27.2 (CH_2), 31.9 (CH_2), 37.0 (CH_2), 39.7 (CH_2), 42.1 (CH), 61.3 (CH_2), 127.4 (CH), 129.1 (CH), 135.5 (C), 142.1 (C). EIMS *m*/*z*: 221 (M + 1), 220 (M^+), 175, 149. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{24}O$, 220.1827; found, 220.1823. Enantioselectivity was determined by a chiral GC analysis (Betadex 120, 25 m × 0.25 mm: 130 °C; minor 98.8 min, major 101.4 min).

Enantioselectivity of *γ*-3ac. (−)-(*S*)-3-(4-Methoxyphenyl)-octan-1-ol (6). The above procedure and column chromatography (hexane/EtOAc = 9:1) gave **6** (98% from *γ*-**3ac** with 85% ee) as a colorless oil: $[\alpha]^{25}_D$ −5.78 (*c* 0.65, $CHCl_3$). IR (neat): 3348, 2923, 2855, 1512, 1232, 1034, 826. ^{1}H NMR: 0.83 (3H, t, *J* = 6.8), 1.12−1.30 (7H, m), 1.50−1.63 (2H, m), 1.75 (1H, m), 1.92 (1H, m), 2.62 (1H, tt, *J* = 5.2, 9.5), 3.43−3.55 (2H, m), 3.79 (3H, s), 6.83−6.85 (2H, m), 7.06−7.09 (2H, m). ^{13}C NMR: 14.1

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(CH_3), 22.5 (CH_2), 27.1 (CH_2), 31.9 (CH_2), 37.1 (CH_2), 39.8 (CH_2), 41.6 (CH), 55.2 (CH_3), 61.3 (CH_2), 113.8 (CH), 128.4 (CH), 137.2 (C), 157.8 (C). EIMS *m*/*z*: 237 (M + 1), 236 (M^+), 191, 165. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{15}H_{24}O_2$, 236.1776; found, 236.1778. Enantioselectivity was determined by a chiral GC analysis (Betadex 120, 25 m × 0.25 mm: 130 °C for 200 min and then to 150 °C at 1 °C/min; minor 232.9 min, major 235.6 min).

Enantioselectivity of γ-3ch. (*R*)-3-Cyclohexyl-3-(3,4-methylenedioxyphenyl)propan-1-ol (7). To a solution of the 91:9 mixture of γ- and α-**3ch** (24 mg, 0.10 mmol) in THF (0.8 mL) cooled in an ice/water bath was added a 0.5 M solution of 9-BBN in THF (0.3 mL, 0.15 mmol). After the cooling bath was removed, the mixture was stirred for 10 h at rt, and then EtOH (0.6 mL), aqueous 1 M NaOH (0.6 mL), and aqueous 30% H_2O_2 (0.5 mL) were sequentially added. The mixture was stirred vigorously for 5 h, and then the reaction was quenched with 10% $Na_2S_2O_3$ (4 mL). The mixture was diluted with Et_2O (5 mL), and the aqueous phase was separated and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Column chromatography (hexane/EtOAc = 3:1) gave **7** (5 mg, 19%) with 93% ee as a colorless oil: $[\alpha]^{25}_D$ −3.74 (*c* 0.12, $CHCl_3$). IR (neat): 3356, 2924, 2855, 1489, 1242, 1042. ^{1}H NMR: 0.77−2.07 (14H, m), 2.37 (1H, m), 3.39 (1H, m), 3.48 (1H, m), 5.93 (2H, s), 6.56 (1H, dd, *J* = 7.9, 1.8), 6.63 (1H, d, *J* = 1.8), 6.72 (1H, d, *J* = 7.9). ^{13}C NMR: 26.46 (CH_2), 26.50 (CH_2), 26.52 (CH_2), 31.0 (CH_2), 31.3 (CH_2), 35.7 (CH_2), 43.3 (CH), 48.4 (CH), 61.6 (CH_2), 100.8 (CH_2), 107.9 (CH), 108.2 (CH), 121.5 (CH), 137.8 (C), 145.7 (C), 147.6 (C). EIMS *m*/*z*: 263 (M + 1), 262 (M^+), 179. HRMS-EI *m*/*z*: $[M]^+$ calcd for $C_{16}H_{22}O_3$, 262.1569; found, 262.1569. Enantioselectivity was determined by a chiral HPLC analysis (Chiralpak AD-H: hexane/*i*-PrOH = 98:2; 1 mL/min; 254 nm; major 35.2 min, minor 43.4 min).

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