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P-Chiral Monophosphorus Ligands for Asymmetric Copper-Catalyzed Allylic Alkylation

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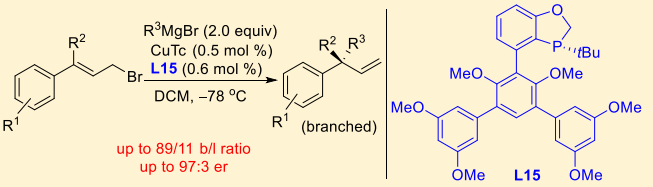
Supporting Information

ABSTRACT: Asymmetric copper-catalyzed allylic alkylation between allyl bromides and alkyl Grignard reagents using a P-chiral monophosphorus ligand is described. A range of terminal olefins bearing tertiary or quaternary carbon centers were formed in good branched/linear selectivities and excellent enantioselectivities at copper loadings as low as 0.5 mol %.



INTRODUCTION

Development of an efficient asymmetric catalytic carbon−carbon bond-forming reaction remains an important goal in the field of organic chemistry. Transition metal catalyzed allylic substitution with carbon nucleophiles is a powerful carbon−carbon bond-forming reaction.[1] A number of enantioselective transformations have been realized with various transition metal catalysts including Pd,[2] Mo,[3] W,[4] Ru,[5] Rh,[6] and Ir[7] by employing stabilized carbon nucleophiles such as malonates. For enantioselective allylic alkylation with nonstabilized carbon nucleophiles, Cu catalyst is most frequently employed, allowing the enantioselective installation of simple alkyl groups at the allylic position.[8]

In 1995, Bäckvall and co-workers reported the first Cu-catalyzed asymmetric allylic alkylation between allylic chlorides and alkyl Grignard reagents with moderate enantioselectivity-(up to 42% ee) by employing a chiral arenethiolatocopper(I) catalyst (Scheme 1, equation a).[9] The enantioselectivity was improved to 64% ee when a chiral ferrocenyl thiolate ligand was employed.[9c] Dübner and Knochel later developed an enantioselective reaction with dialkylzinc reagents employing a chiral ferrocenyl amine ligand.[10] Because of their relatively low activity, organozinc reagents were more frequently employed.[11] With a TADDOL-based phosphite ligand, Alexakis and co-workers achieved up to 73% ee in Cu-catalyzed allylic alkylation of cinnamyl chloride.[12] However, greater enantioselectivities and higher regioselectivities were not achieved. Until 2004, they employed a chiral phosphoramidite ligand in Cu-catalyzed allylic alkylation of cinnamyl chloride with Grignard reagents.[13b] Since then, increasing efforts have been focused on diversifying the toolbox of allylic electrophiles and organometallic nucleophiles by employing chiral phosphoramidite ligands.[14] The Cu-catalyzed asymmetric allylic alkylation with alkyl Grignard reagents has served as a model reaction to test the performance of new chiral ligands including a chiral diphosphine Taniaphos,[15] a phosphine−phosphite ligand,[16] and a chiral NHC ligand.[17] To the best of our knowledge, P-chiral monophosphorus ligand[18] has not been applied in asymmetric Cu-catalyzed allylic alkylation. Herein we described the structural properties of a Cu(I) complex of a P-chiral monophosphorus ligand and the application of a P-chiral monophosphorus ligand in asymmetric Cu-catalyzed allylic alkylation with alkyl Grignard reagents.

RESULTS AND DISCUSSION

Although many studies are reported on Pd or Rh catalysis with chiral monophosphorus ligand BI-DIME,[19] the preparation of its copper complex and applications in catalysis are rarely explored. We successfully prepared the [Cu((*S*)-BI-DIME)-$(MeCN)_2$]PF_6 complex by mixing (*S*)-BI-DIME and Cu-$(MeCN)_4PF_6$ in dichloromethane, and its X-ray crystal structure was shown in Figure 1 and was deposited with the Cambridge Crystallographic Data Centre as CCDC 1906544. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223−336−033; or deposit@ccdc.cam.ac.uk). Interestingly, the Cu(I) center coordinated with two nitrogen atoms from two acetonitrile molecules as well as the phosphorus atom of (*S*)-BI-DIME, forming an almost planar geometry with the dihedral angle of N1CuPN2 at 171.9°. A weak coordination perpendicular to the N1CuPN2 "plane" from one methoxy group to the Cu(I) center was also observed, with a bond length of 2.627 Å. The geometric

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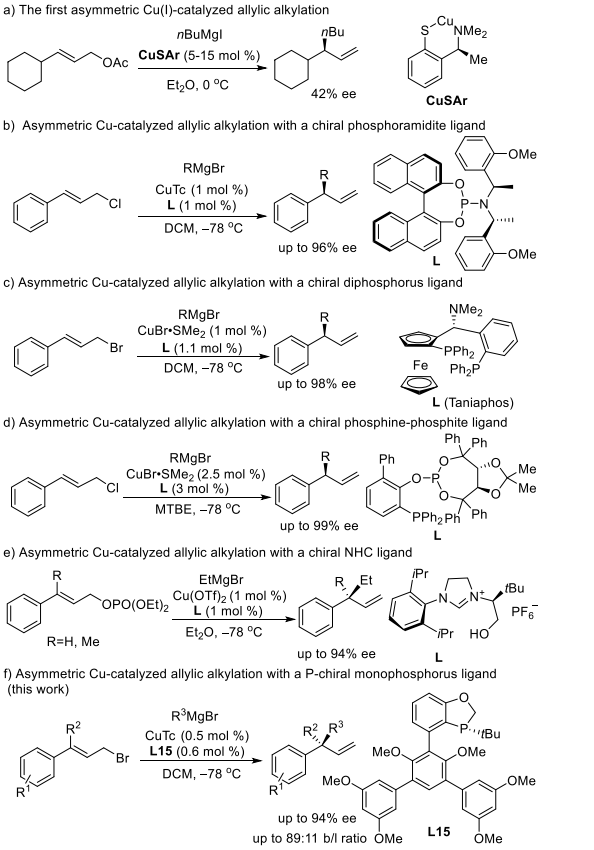
Scheme 1. Asymmetric Cu-Catalyzed Allylic Alkylation with Grignard Reagents



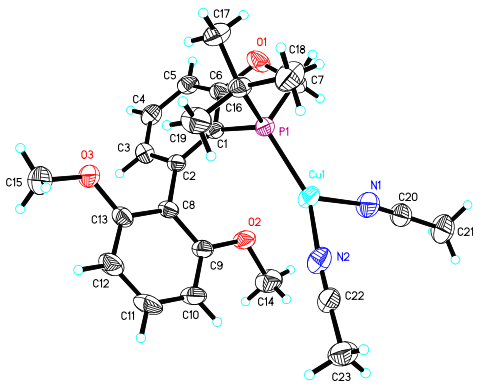


Figure 1. X-ray crystal structure of $[Cu((S)\text{-BI-DIME})(MeCN)_2]PF_6$. The PF_6^- anion was omitted; key bond lengths: 2.181 Å (Cu–P), 2.019 Å (Cu–N1), 1.197 Å (Cu–N2), 2.627 Å (Cu–O2); key bond angles: 117.8° (∠N1CuP), 141.6° (∠N2CuP), 99.8° (∠N1CuN2); dihedral angle: 171.9° (∠N1CuPN2).

information on $[Cu((S)\text{-BI-DIME})(MeCN)_2]PF_6$ provided guidance in understanding the coordination of chiral BI-DIME and related ligands in copper catalysis.

We then prepared a set of BI-DIME-related chiral monophosphorus ligands and applied them in Cu-catalyzed allylic alkylation of cinnamyl chloride or bromide with ethylmagnesium bromide. The reactions were performed in dichloromethane at −78 °C under nitrogen with slow addition of 2 equiv of EtMgBr over 0.5 h in the presence of Cu(I) salt (5 mol %) and chiral ligand (6 mol %). Initial investigation on cinnamyl chloride as the substrate showed good regioselectivity (branched/linear = 97:3) but low enantioselectivities with various chiral ligands (see the Supporting Information). Employment of cinnamyl bromide showed promising enantioselectivities, and copper(I) cyanide was chosen as the metal precursor for further study (Table 1). Although known P-chiral monophosphorus ligands **L1**–**L4** provided little or no enantioselectivity (entries 1–4), **L5** bearing two methyl substituents at 3,5-positions provided a much improved er (86:14, entry 5), albeit with a branched/linear ratio of 60:40. A similar er but with an improved branched/linear ratio of 72:28 was obtained with **L6** bearing two phenyl groups at 3,5-positions of the lower benzene ring (entry 6). We thus developed a series of P-chiral monophosphorus ligands with substituents at 3,5-positions of the lower benzene ring, **L7**–**L19**, for copper-catalyzed asymmetric allylic alkylation. The results showed that the substituents at 3,5-positions provided a profound influence on both enantioselectivity and branched/linear ratio (entries 7–18). Moreover, the weak coordination of a methoxy group at 2, 6 positions to the Cu(I) center was also substantiated to be indispensable by the reaction result of **L19** (entry 19). Among those chiral ligands, **L15** (entry 15) provided the best er (93:7) and the highest branched/linear ratio (76:24). This could be due to a combination effect of both electronic and steric properties. Work is ongoing to gain a better understanding of the effect of substituents on enantioselectivity as well as the branched/linear ratio. With **L15** as the ligand, various copper salts were further screened (entries 20–25). The enantioselectivity (97:3 er) and branched/linear ratio (80:20) was further improved with CuTC as the catalyst precursor. Further screening of reaction conditions including solvent, temperature, catalyst loading, and leaving group of the allylic substrate allowed us to identify the optimal reaction conditions as using CuTC (0.5 mol %) and **L15** (0.6 mol %) as the catalysts, dichloromethane as the solvent, allylic bromide as the substrate, and −78 °C as the reaction temperature (see the Supporting Information).

Under the optimized reaction conditions, the substrate scope of asymmetric allylic alkylation of disubstituted allyl bromides with ethylmagnesium bromide was studied with CuTC/**L15** catalyst system. A series of substituted cinnamyl bromides were successfully applied to the transformation to provide chiral products in excellent er values and good branched/linear ratios (Table 2). In particular, *p*- and *m*-substituted allyl bromides preferentially led to desired branched products **3ba**–**ha** (67:33–88:12 b/l) with excellent enantioselectivities (74:26–97:3 er). The relative low er obtained with **3ea** was probably due to the partial involvement of cationic pathway due its electron-rich character. *o*-Substituted allyl bromides were more sterically hindered substrates, leading to **3ja**–**la** with poor branched/linear selectivities (32:68–48:52 b/l) but good enantioselectivities (81:19–86:14 er). Interestingly, the cyclohexyl-substituted allyl bromide (**1i**) led to formation of **3ia** in excellent regioselectivity (89:11 b/l) and good enantioselectivity (92:8 er). 1-Naphthyl (**1m**) and 2-naphthyl allyl bromides (**1n**) were also applicable, leading to corresponding products **3ma** and **3na** in good enantioselectivities and moderate branched/linear selectivities.

Excellent enantioselectivities and good regioselectivities were also obtained on chiral products **3oa**–**za** bearing a quaternary all-carbon center (Table 3) when a series of trisubstituted allyl bromides were employed with CuTC (5 mol %) and **L15** (6 mol %) as the catalysts. The alkyl

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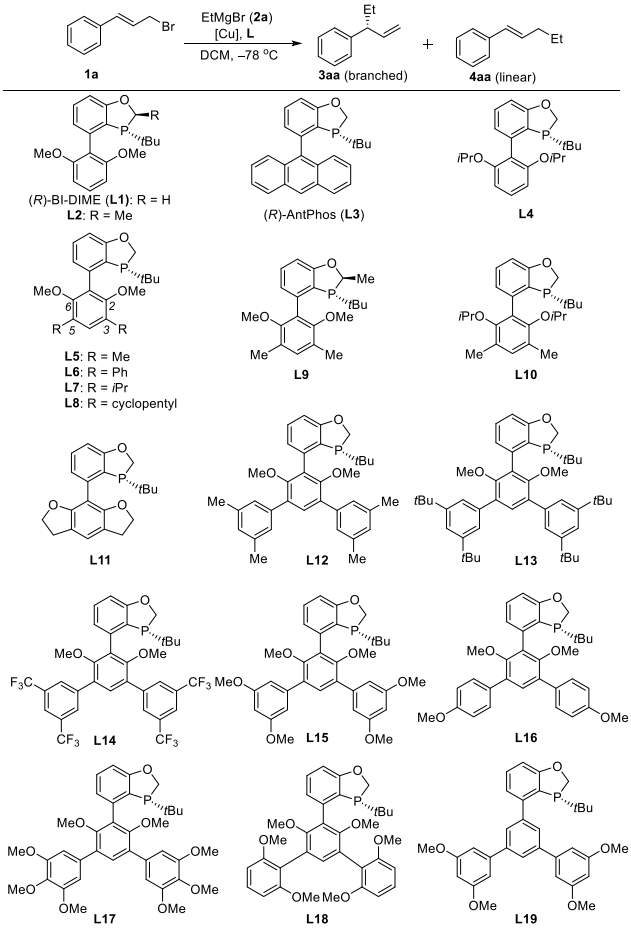
Table 1. Cu-Catalyzed Asymmetric Allylic Alkylation of Cinnamyl Bromide (1a) with EtMgBr (2a) by Employing a P-Chiral Monophosphorus Ligand[a]



entry	5 mol % [Cu]	6 mol % L	3aa/4aa[b]	er (3aa)[c]
1	CuCN	L1	62:38	56:44
2	CuCN	L2	60:40	53:47
3	CuCN	L3	53:47	54:46
4	CuCN	L4	28:72	53:47
5	CuCN	L5	60:40	86:14
6	CuCN	L6	72:28	85:15
7	CuCN	L7	43:57	79:21
8	CuCN	L8	30:70	81:19
9	CuCN	L9	46:54	54:46
10	CuCN	L10	41:59	70:30
11	CuCN	L11	75:25	72:28
12	CuCN	L12	67:33	86:14
13	CuCN	L13	55:45	71:29
14	CuCN	L14	58:42	69:31
15	CuCN	L15	76:24	93:7
16	CuCN	L16	66:34	84:16
17	CuCN	L17	49:51	63:37
18	CuCN	L18	50:50	52:48
19	CuCN	L19	45:55	55:45
20[d]	CuTc	L15	80:20	97:3
21	$[Cu(MeCN)_4]PF_6$	L15	70:30	94:6
22	CuCl	L15	76:24	93:7
23	CuBr	L15	71:29	93:7
24	$CuBr{\cdot}SMe_2$	L15	83:17	81:19
25	CuI	L15	80:20	94:6

[a]Unless otherwise specified, the reactions were performed under nitrogen in DCM at −78 °C in the presence of 5 mol % [Cu] and 6 mol % L with cinnamyl bromide (1a, 0.25 mmol) and EtMgBr (3 M solution in diethyl ether, 0.5 mmol, 2.0 equiv). Slow addition of EtMgBr over 0.5 h. The absolute configuration of 3aa was determined by comparing the sign of its optical rotation with reported data and based on the absolute configuration of 5a.[13c] [b]All reactions gave full conversion. The ratios of 3aa/4aa were determined by ^{1}H NMR spectroscopy. [c]The er values of 3aa were determined by chiral HPLC analysis. [d]The isolated yield of mixed 3aa and 4aa products was 73%.

substituent at γ-position of allyl bromides were not limited to methyl group (Table 3). Substituents such as *n*-Pr and *i*-Pr groups were also applicable to form **3x′a** and **3y′a**, albeit with diminished enantioselectivities and moderate regioselectivities.

Various alkyl Grignard reagents, even the challenging methyl Grignard reagent, were also applicable to allylic alkylation of **1a**, providing the corresponding products in excellent enantioselectivities and moderate to good branch/linear selectivities (Table 4). Both primary and secondary alkyl Grignard reagents can be employed successfully. Allylmagnesium bromide formed product **3ah** in moderate er and ∼1:1 branched/linear selectivity. *tert*-Butyl Grignard reagent did not form the desired chiral product, leading to linear product **4ai** exclusively. A poor branched/linear selectivity and enantioselectivity was also observed on **3cj** when a phenyl Grignard reagent was employed.

On the basis of the X-ray crystal structure of [Cu((*S*)-BI-DIME)$(MeCN)_2$]PF_6 and Hoveyda's work[20] on copper-catalyzed allylic alkylation, a stereochemical model for the reaction between cinnamyl bromide and EtMgBr with the Cu-**L15** catalyst at reductive elimination stage is proposed in Figure 2. Because of the unique P-chiral biaryl skeleton of **L15**, the coordination of the cinnamyl component as well as the ethyl group with the copper(III) center are almost parallel to the low aryl ring of the biaryl skeleton. The steric bulk of the aryl group at 3-position of the low aryl ring in combination with the *tert*-butyl group of **L15** would push the cinnamyl coordination to the relatively open side (left in Figure 2) with the phenyl group directing upward, leading to the alkylation product **3aa** with the observed *R* configuration after reductive elimination.

To demonstrate the practicality of the allylic substitution reaction, a gram-scale reaction between cinnamyl bromide **1a** and ethylmagnesium bromide (**2a**) was carried out to provide olefin product with a branch/linear ratio of 79:21 and 97:3 er in 75% yield (Scheme 2). The results were identical to the experiments at milligram scales, showing excellent repeatability. The chiral terminal olefin can be further transformed. Hydroboration−oxidation of olefin product led to the formation of alcohol **5a** in 92% ee and 70% yield.

CONCLUSION

In summary, we have successfully developed an effective P-chiral monophosphorus ligand for asymmetric Cu-catalyzed allylic alkylation with alkyl Grignard reagents, providing a range of olefin products containing tertiary or quaternary carbon centers in good branched/linear ratios and excellent enantioselectivities at copper loading as low as 0.5 mol %. The

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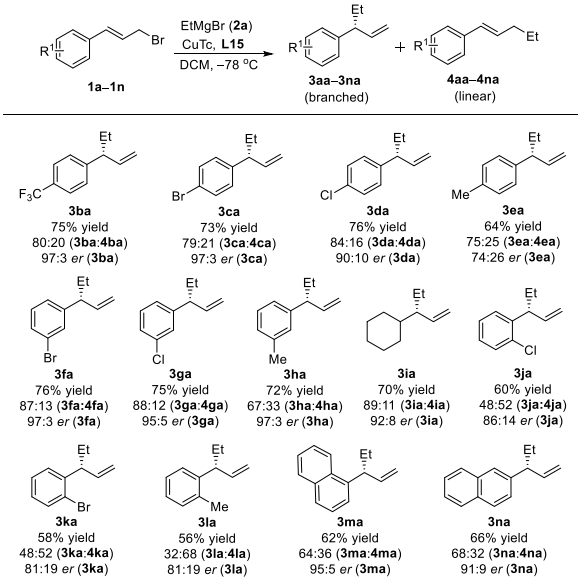
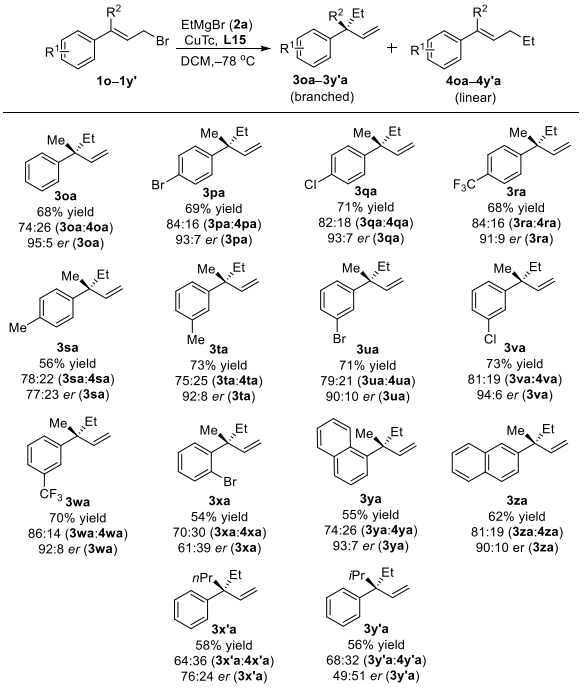
Table 2. Asymmetric Cu-Catalyzed Allylic Alkylation of Disubstituted Allyl Bromides[a]



[a]Unless otherwise specified, the reactions were performed under nitrogen in DCM at −78 °C in the presence of 0.5 mol % CuTC and 0.6 mol % **L15** with disubstituted allyl bromides (**1a−1n**, 0.5 mmol) and EtMgBr (3 M solution in diethyl ether, 1 mmol, 2.0 equiv). Slow addition of EtMgBr was carried out over 0.5 h. All reactions gave full conversion. The yields were isolated yields of mixed **3** and **4** products. The ratios of **3**/**4** were determined by ^{1}H NMR spectroscopy. The er values of **3** were determined by chiral HPLC or GC analysis.

Table 3. Asymmetric Cu-Catalyzed Allylic Alkylation of Trisubstituted Allyl Bromides[a]



[a]Unless otherwise specified, the reactions were performed under nitrogen in DCM at −78 °C in the presence of 5 mol % CuTC and 6 mol % **L15** with trisubstituted allyl bromides (**1o−1y′**, 0.25 mmol) and EtMgBr (3 M solution in diethyl ether, 0.5 mmol, 2 equiv). Slow addition of EtMgBr was carried out over 0.5 h. All reactions gave full conversion. The yields were isolated yields of mixed **3** and **4** products. The ratios of **3**/**4** were determined by ^{1}H NMR spectroscopy. The er values of **3** were determined by chiral HPLC or GC analysis.

structural information on Cu-BI-DIME complex as well as the substitution effect at the 3,5-positions of the lower benzene ring of the P-chiral monophosphorus ligand has provided guidance in understanding the copper catalysis and laid strong foundation for developing more efficient asymmetric alkylation. Further investigation in this field with P-chiral monophosphorus ligands is ongoing in our laboratory.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to the standard methods prior to use.

^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 MHz Agilent spectrometer with $CDCl_3$ as the solvent. ^{1}H chemical shifts were referenced to $CDCl_3$ at 7.26 ppm. ^{13}C chemical shifts were referenced to $CDCl_3$ at 77.16 ppm and obtained with ^{1}H decoupling. ^{31}P chemical shifts were referenced to 85% H_3PO_4 in D_2O at 0.0 ppm as external standard and obtained with ^{1}H decoupling. ^{19}F NMR chemical shifts were referenced relative to $CFCl_3$. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet−doublet (dd), triplet−doublet (td), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). Mass spectroscopy (MS) was carried out on Shimadzu LCMS-2010EV (EI) or Brukerdaltonics APEX III (HR-EI) mass spectrometers. Chiral HPLC analysis were performed on an Agilent 1200 system using chiral column described below in detail. Chiral GC analysis were performed on an Agilent 6890N GC using the chiral column described below in detail. The optical rotations were measured on a Jacsco P-1010 polarimeter.

General Procedure for Cu-L15-Catalyzed Asymmetric Allylic Alkylation with Grignard Reagents. A flame-dried Schlenk tube equipped with stirring bar at room temperature was charged copper salt and ligand. The tube was evacuated and backfilled with nitrogen. To the mixture was added freshly distilled solvent, and the resultant solution was stirred for 20 min at room temperature. Allyl bromide was then added. After stirring for another 20 min, the reaction mixture was cooled to −78 °C. Grignard reagent (2.0 equiv) diluted in dry solvent was added dropwise to the reaction mixture over 30 min via syringe pump. After the addition was complete, the mixture was stirred at −78 °C for additional 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution. The organic phase was separated, and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography with *n*-hexane to give a mixture of branched and linear products. The branched/linear ratios were determined by ^{1}H NMR, and the er values were determined by chiral HPLC or GC analysis.

*(R)-Pent-1-en-3-ylbenzene (**3aa**).* Colorless oil; 73% yield; **3aa**/**4aa** = 80/20; 94% ee. $[\alpha]_D^{25}$ − 11.7° (*c* = 0.25, $CHCl_3$); lit. $[\alpha]_D^{25}$ − 30° (*c* = 0.6, $CHCl_3$) (76/24 b/l, 85% ee).[23] NMR experiments were performed on the mixture of products, but only data of branched product **3aa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 3H), 6.04−5.95 (m, 1H), 5.08 (dd, *J* = 8.4, 7.9 Hz, 2H), 3.18 (q, *J* = 7.5 Hz, 1H), 1.79 (dt, *J* = 14.2, 7.0 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.3, 128.4, 127.7, 126.1, 114.1, 51.8, 28.3, 12.2. EI-MS: *m*/*z* 146.2 $[M]^+$. HRMS (EI) *m*/*z* calcd for $C_{11}H_{14}$ $[M]^+$: 146.1096. Found: 146.1100. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.66 (major) and 10.01 (minor).

*(R)-1′-(Pent-1-en-3-yl)-4′-(trifluoromethyl)benzene (**3ba**).* Colorless oil; 75% yield; **3ba**/**4ba** = 80/20; 94% ee. $[\alpha]_D^{25}$ − 20.7° (*c* = 1.0, $CHCl_3$); lit. $[\alpha]_D^{25}$ − 32° (*c* = 0.9, $CHCl_3$) (76/24 b/l, 90% ee).[23]

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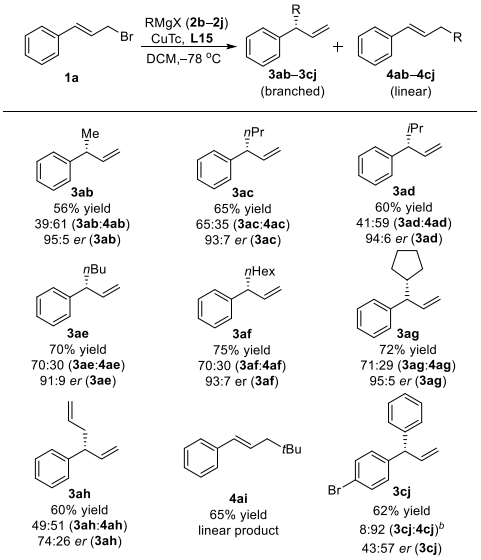
Table 4. Asymmetric Cu-Catalyzed Allylic Alkylation with Various Alkyl Grignard Reagents[a]



[a]Unless otherwise specified, the reactions were performed under nitrogen in DCM at −78 °C in the presence of 0.5 mol % CuTC and 0.6 mol % **L15** with cinnamyl bromide (**1a**, 0.5 mmol) and RMgX (different concentration solutions in diethyl ether, 1 mmol, 2 equiv). Slow addition of RMgX was carried out over 0.5 h. All reactions gave full conversion. The yields were isolated yields of mixed **3** and **4** products. The ratios of **3**/**4** were determined by ^{1}H NMR spectroscopy. Theer values of **3** were determined by chiral HPLC or GC analysis. [b]The reaction was conducted with **1c** as substrate.

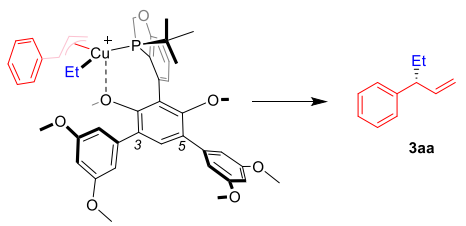
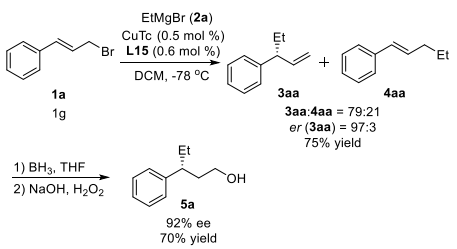


Figure 2. Proposed stereochemical model for the reaction between cinnamyl bromide and EtMgBr with the Cu-**L15** catalyst at reductive elimination stage.

Scheme 2. Gram-Scale Experiment



NMR experiments were performed on the mixture of products, but only data of branched product **3ba** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.99–5.89 (m, 1H), 5.07 (t, J = 13.0 Hz, 2H), 3.22 (q, J = 7.4 Hz, 1H), 1.85–1.66 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 141.6, 131.5, 131.4, 129.4, 127.5, 114.5, 51.1, 28.2, 12.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.7. EI-MS: m/z 214.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{13}F_3$ $[M]^+$: 214.0969. Found: 214.0973. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 5.88 (minor) and 6.42 (major).

*(R)-1′-Bromo-4′-(pent-1-en-3-yl)benzene (**3ca**).* Colorless oil; 73% yield; **3ca**/**4ca** = 79/21; 94% ee. $[\alpha]_D^{25}$ − 14.8° (c = 1.0, $CHCl_3$); lit. $[\alpha]_D^{25}$ + 46° (c = 0.228, $CHCl_3$) (97/3 b/l, 96% ee, *S*).[24] NMR experiments were performed on the mixture of products, but only data of branched product **3ca** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 5.92 (ddd, J = 17.6, 10.3, 7.5 Hz, 1H), 5.05 (dd, J = 13.2, 11.9 Hz, 2H), 3.13 (q, J = 7.4 Hz, 1H), 1.82–1.62 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 141.6, 131.4, 129.4, 127.5, 114.5, 51.1, 28.2, 12.1. EI-MS: m/z 224.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Br$ $[M]^+$: 224.0201. Found: 224.0204. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 230 nm, retention times (min): 9.91 (minor) and 10.27 (major).

*(R)-1′-Chloro-4′-(pent-1-en-3-yl)benzene (**3da**).* Colorless oil; 76% yield; **3da**/**4da** = 84/16; 80% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3da** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.92 (ddd, J = 17.6, 10.3, 7.5 Hz, 1H), 5.13–4.92 (m, 2H), 3.14 (q, J = 7.4 Hz, 1H), 1.85–1.62 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 141.7, 129.0, 128.5, 127.1, 114.4, 51.0, 28.2, 12.1. EI-MS: m/z 180.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Cl$ $[M]^+$: 180.0706. Found: 180.0710. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral GC: CP-Chiralsil-Dex-CB (25 m × 0.25 mm), initial temperature 50 °C, then 10 °C/min to 120 °C (hold for 30 min), then 10 °C/min to 160 °C (final temperature), retention times (min): 13.95 (major) and 14.44 (minor).

*(R)-1′-Methyl-4′-(pent-1-en-3-yl)benzene (**3ea**).* Colorless oil; 64% yield; **3ea**/**4ea** = 75/25; 48% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ea** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (q, J = 8.0 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 5.96 (ddd, J = 17.1, 10.4, 7.7 Hz, 1H), 5.07–5.02 (m, 2H), 3.13 (q, J = 7.5 Hz, 1H), 2.35 (s, 3H), 1.73 (dt, J = 7.2, 4.2 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 141.5, 135.6, 129.2, 127.5, 113.8, 51.4, 28.3, 21.1, 12.2. EI-MS: m/z 160.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ $[M]^+$: 160.1252. Found: 160.1257. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral GC: CP-Chiralsil-Dex-CB (25 m × 0.25 mm), initial temperature 70 °C, 1 °C/min to 115 °C, then 20 °C/min to 170 °C (final temperature), retention times (min): 28.70 (major) and 29.51 (minor).

*(R)-1′-Bromo-3′-(pent-1-en-3-yl)benzene (**3fa**).* Colorless oil; 76% yield; **3fa**/**4fa** = 87/13; 94% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3fa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, J = 9.7, 8.7 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.13 (dd, J = 7.6, 0.8 Hz, 1H), 5.96–5.86 (m, 1H), 5.06 (ddd, J = 13.8, 9.6, 3.1 Hz, 2H), 3.13 (q, J = 7.4 Hz, 1H), 1.81–1.66 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 141.4, 130.7, 129.9, 129.2, 126.3, 122.5, 114.7, 51.4, 28.2, 12.1. EI-MS: m/z 224.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Br$ $[M]^+$: 224.0201. Found: 224.0208. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 60/40, flow rate 0.7 mL/min, 214 nm, retention times (min): 14.18 (major) and 14.87 (minor).

*(R)-1′-Chloro-3′-(pent-1-en-3-yl)benzene (**3ga**).* Colorless oil; 75% yield; **3ga**/**4ga** = 88/12; 90% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ga** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.21 (m, 1H), 7.19 (d, J = 7.0 Hz, 2H), 7.08 (d, J = 7.5 Hz, 1H), 5.96–5.86 (m, 1H), 5.06 (dd, J = 13.5, 8.5 Hz, 2H), 3.14 (q, J = 7.4 Hz, 1H), 1.77–1.70 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 141.4, 129.6, 127.8, 126.3, 125.9, 114.7, 51.4, 28.2, 12.1. EI-MS: m/z 180.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Cl$

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[M]$^+$: 180.0706. Found: 180.0711. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 65/35, flow rate 0.7 mL/min, 214 nm, retention times (min): 10.30 (major) and 10.81 (minor).

*(R)-1′-Methyl-3′-(pent-1-en-3-yl)benzene (**3ha**).* Colorless oil; 72% yield; **3ha**/**4ha** = 67/33; 94% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ha** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24−7.21 (m, 1H), 7.05 (t, J = 8.6 Hz, 3H), 6.05−5.89 (m, 1H), 5.19−4.96 (m, 2H), 3.15 (q, J = 7.5 Hz, 1H), 2.38 (s, 3H), 1.83−1.72 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.4, 128.4, 128.3, 126.9, 124.6, 113.9, 51.8, 28.3, 21.5, 12.2. EI-MS: m/z 160.2 [M]$^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ [M]$^+$: 160.1252. Found: 160.1256. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.60 (major) and 9.54 (minor).

*(R)-Pent-1-en-3-ylcyclohexane (**3ia**).* Colorless oil; 70% yield; **3ia**/**4ia** = 89/11; 84% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ia** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58−5.49 (m, 1H), 4.99 (dd, J = 10.2, 2.3 Hz, 1H), 4.94−4.88 (m, 1H), 1.75−1.60 (m, 6H), 1.51−1.44 (m, 1H), 1.23 (tdd, J = 9.3, 7.7, 4.5 Hz, 4H), 1.15−1.08 (m, 1H), 1.04−0.97 (m, 1H), 0.93−0.86 (m, 1H), 0.88−0.80 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 114.9, 52.0, 41.5, 31.2, 29.7, 26.8, 26.7 (d, J = 3.5 Hz), 24.3, 12.0. EI-MS: m/z 152.0 [M]$^+$. HRMS (EI) m/z calcd for $C_{11}H_{20}$ [M]$^+$: 152.1565. Found: 152.1570. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral GC: Chirasil DEX-CB column (30 m × 0.25 mm), initial temperature70 °C for 50 min, then 20 °C/min to 170 °C (final temperature), retention times (min): 46.94 (major) and 48.39 (minor).

*(R)-1′-Chloro-2′-(pent-1-en-3-yl)benzene (**3ja**).* Colorless oil; 60% yield; **3ja**/**4ja** = 48/52; 72% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ja** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.8, 1.4 Hz, 1H), 7.25−7.23 (m, 2H), 7.22−7.18 (m, 1H), 6.00−5.86 (m, 1H), 5.12−5.03 (m, 2H), 3.79 (q, J = 7.3 Hz, 1H), 1.88−1.65 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 140.5, 134.0, 132.5, 128.2, 127.1, 126.8, 114.9, 46.7, 27.7, 11.9. EI-MS: m/z 180.1 [M]$^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Cl$ [M]$^+$: 180.0706. Found: 180.0705. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 214 nm, retention times (min): 6.98 (minor) and 7.40 (major).

*(R)-1′-Bromo-2′-(pent-1-en-3-yl)benzene (**3ka**).* Colorless oil; 58% yield; **3ka**/**4ka** = 48/52; 62% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ka** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.18 (m, 3H), 7.07 (t, J = 1.9 Hz, 1H), 5.98−5.84 (m, 1H), 5.09 (ddt, J = 9.7, 2.8, 1.5 Hz, 2H), 3.77 (q, J = 7.3 Hz, 1H), 1.84−1.65 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 140.5, 132.9, 128.4, 127.5, 125.0, 123.1, 115.0, 49.3, 27.9, 11.9. EI-MS: m/z 224.1 [M]$^+$. HRMS (EI) m/z calcd for $C_{11}H_{13}Br$ [M]$^+$: 224.0201. Found: 224.0202. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 214 nm, retention times (min): 7.75 (minor) and 8.55 (major).

*(R)-1′-Methyl-2′-(pent-1-en-3-yl)benzene (**3la**).* Colorless oil; 56% yield; **3la**/**4la** = 32/68; 62% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3la** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19−7.13 (m, 4H), 5.94 (ddd, J = 17.4, 10.2, 7.5 Hz, 1H), 5.05 (dd, J = 18.5, 13.7 Hz, 2H), 3.46 (q, J = 7.4 Hz, 1H), 2.38 (s, 3H), 1.87−1.74 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 141.8, 135.9, 130.3, 126.3, 126.1, 125.8, 114.0, 46.8, 27.9, 19.6, 12.2. EI-MS: m/z 160.2 [M]$^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ [M]$^+$: 160.1252. Found: 160.1251. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral GC: CP-Chiralsil-Dex-CB (25 m × 0.25 mm × 0.25 μm), initial temperature 40 °C, then 10 °C/min to 75 °C, then 0.5 °C/min to 120 °C (final temperature), retention times (min): 70.07 (minor) and 71.03 (major).

*(R)-1′-(Pent-1-en-3-yl)naphthalene (**3ma**).* Colorless oil; 62% yield; **3ma**/**4ma** = 64/36; 90% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ma** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24−8.22 (m, 1H), 7.95 (t, J = 9.0 Hz, 1H), 7.82 (t, J = 8.5 Hz, 1H), 7.58−7.56 (m, 1H), 7.56−7.52 (m, 2H), 7.48 (d, J = 7.1 Hz, 1H), 6.21−6.12 (m, 1H), 5.23−5.18 (m, 2H), 4.11 (q, J = 7.2 Hz, 1H), 2.05−1.98 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 140.5, 134.4, 129.0, 128.5, 126.8, 125.8, 125.6, 125.4, 124.0, 123.5, 114.7, 46.1, 28.2, 12.5. EI-MS: m/z 196.2 [M]$^+$. HRMS (EI) m/z calcd for $C_{15}H_{16}$ [M]$^+$: 196.1252. Found: 196.1255. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 98/2, flow rate 0.7 mL/min, 230 nm, retention times (min): 6.45 (minor) and 6.82 (major).

*(R)-2′-(Pent-1-en-3-yl)naphthalene (**3na**).* Colorless oil; 66% yield; **3na**/**4na** = 68/32; 82% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3na** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dt, J = 14.0, 8.8 Hz, 4H), 7.51−7.42 (m, 3H), 6.14−5.99 (m, 1H), 5.18−5.05 (m, 2H), 3.35 (q, J = 7.4 Hz, 1H), 1.93−1.79 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 141.9, 133.6, 132.3, 128.0, 127.6 (d, J = 2.1 Hz), 126.3, 126.0, 125.9, 125.3, 114.3, 51.8, 28.2, 12.3. EI-MS: m/z 196.1 [M]$^+$. HRMS (EI) m/z calcd for $C_{15}H_{16}$ [M]$^+$: 196.1252. Found: 196.1255. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 230 nm, retention times (min): 20.57 (major) and 21.52 (minor).

*(R)-(3-Methylpent-1-en-3-yl)benzene (**3oa**).* Colorless oil; 68% yield; **3oa**/**4oa** = 74/26; 90% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3oa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.28 (m, 4H), 7.21−7.16 (m, 1H), 6.03 (ddd, J = 17.5, 10.8, 1.6 Hz, 1H), 5.08 (dd, J = 31.8, 14.1 Hz, 2H), 1.89−1.71 (m, 2H), 1.36 (d, J = 1.7 Hz, 3H), 0.80−0.74 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 146.9, 128.0, 126.7, 125.6, 111.7, 44.5, 33.4, 24.3, 8.9. EI-MS: m/z 160.1 [M]$^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ [M]$^+$: 160.1252. Found: 160.1245. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.44 (minor) and 10.62 (major).

*(R)-1′-Bromo-4′-(3-methylpent-1-en-3-yl)benzene (**3pa**).* Colorless oil; 69% yield; **3pa**/**4pa** = 84/16; 86% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3pa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.4, 1.2 Hz, 2H), 7.18 (dd, J = 8.5, 1.3 Hz, 2H), 5.97 (ddd, J = 17.5, 10.8, 1.3 Hz, 1H), 5.07 (dd, J = 42.2, 14.1 Hz, 2H), 1.85−1.65 (m, 2H), 1.32 (d, J = 1.2 Hz, 3H), 0.76 (td, J = 7.4, 1.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 146.3, 131.0, 128.6, 127.2, 112.2, 44.3, 33.3, 24.3, 8.8. EI-MS: m/z 238.0 [M]$^+$. HRMS (EI) m/z calcd for $C_{12}H_{15}Br$ [M]$^+$: 238.0357. Found: 238.0366. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.15 (minor) and 8.61 (major).

*(R)-1′-Chloro-4′-(3-methylpent-1-en-3-yl)benzene (**3qa**).* Colorless oil; 71% yield; **3qa**/**4qa** = 82/18; 86% ee. NMR experiments

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were performed on the mixture of products, but only data of branched product **3qa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.28−7.26 (m, 1H), 7.25 (t, J = 1.9 Hz, 2H), 7.24 (d, J = 2.6 Hz, 1H), 5.98 (dd, J = 17.5, 10.8 Hz, 1H), 5.07 (ddd, J = 18.7, 14.1, 1.2 Hz, 2H), 1.86−1.68 (m, 2H), 1.33 (s, 3H), 0.76 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 145.9, 128.2, 128.0, 126.8, 112.2, 44.3, 33.4, 24.4, 8.8. EI-MS: m/z 194.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{15}Cl$ $[M]^+$: 194.0862. Found: 194.0858. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, 210 nm, retention times (min): 9.17 (minor) and 9.73 (major).

*(R)-1′-(3-Methylpent-1-en-3-yl)-4′-(trifluoromethyl) benzene (**3ra**).* Colorless oil; 68% yield; **3ra**/**4ra** = 84/16; 82% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ra** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 6.00 (dd, J = 17.5, 10.8 Hz, 1H), 5.26−4.93 (m, 2H), 1.94−1.67 (m, 2H), 1.37 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 145.9, 127.1, 125.8, 124.9 (q, J = 3.8 Hz), 112.6, 44.7, 33.4, 24.3, 8.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.7. EI-MS: m/z 228.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{13}H_{15}F_3$ $[M]^+$: 228.1126. Found: 228.1134. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 75/25, 0.7 mL/min, 214 nm, retention times (min): 6.24 (minor) and 6.49 (major).

*(R)-1′-Methyl-4′-(3-methylpent-1-en-3-yl)benzene (**3sa**).* Colorless oil; 56% yield; **3sa**/**4sa** = 78/22; 54% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3sa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.01 (dd, J = 17.5, 10.8 Hz, 1H), 5.06 (dd, J = 28.8, 14.1 Hz, 2H), 2.32 (s, 3H), 1.88−1.68 (m, 2H), 1.33 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 144.5, 128.8, 128.7, 126.6, 111.5, 44.2, 33.4, 24.4, 20.8, 8.9. EI-MS: m/z 174.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{13}H_{18}$ $[M]^+$: 174.1409. Found: 174.1416. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column: *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 10.12 (minor) and 13.16 (major).

*(R)-1′-Methyl-3′-(3-methylpent-1-en-3-yl)benzene (**3ta**).* Colorless oil; 73% yield; **3ta**/**4ta** = 75/25; 84% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ta** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dt, J = 7.9, 4.4 Hz, 2H), 7.13 (d, J = 5.8 Hz, 2H), 6.03 (dd, J = 17.5, 10.8 Hz, 1H), 5.13−5.02 (m, 2H), 2.19 (dd, J = 14.7, 7.3 Hz, 2H), 1.35 (s, 3H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 147.0, 127.9, 127.5, 126.4, 123.7, 111.6, 44.4, 33.4, 24.3, 21.7, 8.9. EI-MS: m/z 174.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{13}H_{18}$ $[M]^+$: 174.1409. Found: 174.1407. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 7.75 (minor) and 9.45 (major).

*(R)-1′-Bromo-3′-(3-methylpent-1-en-3-yl)benzene (**3ua**).* Colorless oil; 71% yield; **3ua**/**4ua** = 79/21; 80% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ua** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.34−7.30 (m, 1H), 7.26−7.22 (m, 1H), 7.17 (d, J = 7.8 Hz, 1H), 5.97 (dd, J = 17.5, 10.8 Hz, 1H), 5.09 (dd, J = 42.1, 14.1 Hz, 2H), 1.78 (dtd, J = 21.1, 13.9, 7.4 Hz, 2H), 1.33 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 146.0, 130.0, 129.5, 128.8, 125.4, 112.4, 44.6, 33.4, 24.3, 8.8. EI-MS: m/z 238.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{15}Br$ $[M]^+$: 238.0357. Found: 238.0355. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, 210 nm, retention times (min): 8.75 (minor) and 9.40 (major).

*(R)-1′-Chloro-3′-(3-methylpent-1-en-3-yl)benzene (**3va**).* Colorless oil; 73% yield; **3va**/**4va** = 81/19; 88% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3va** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 1.7 Hz, 1H), 7.24−7.21 (m, 1H), 7.21−7.18 (m, 1H), 7.18−7.15 (m, 1H), 5.98 (dd, J = 17.5, 10.8 Hz, 1H), 5.16−5.02 (m, 2H), 1.86−1.69 (m, 2H), 1.34 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H,). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 146.1, 129.2, 127.1, 125.9, 124.9, 112.4, 44.6, 33.3, 24.3, 8.8. EI-MS: m/z 194.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{15}Cl$ $[M]^+$: 194.0862. Found: 194.0867. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column: *n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, 210 nm, retention times (min): 7.53 (minor) and 8.19 (major).

*(R)-1′-(3-Methylpent-1-en-3-yl)-3′-(trifluoromethyl)benzene (**3wa**).* Colorless oil; 70% yield; **3wa**/**4wa** = 86/14; 84% ee. $[\alpha]_D^{25}$ − 10.9° (c = 0.5, $CHCl_3$); lit. $[\alpha]_D^{20}$ − 14.2° (c = 1.07, $CHCl_3$) (30/1 b/l, 88% ee, *R*).[25] NMR experiments were performed on the mixture of products, but only data of branched product **3wa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.48−7.43 (m, 1H), 7.42 (d, J = 7.7 Hz, 1H), 6.00 (dd, J = 17.5, 10.8 Hz, 1H), 5.12 (ddd, J = 18.4, 14.1, 1.0 Hz, 2H), 1.90−1.73 (m, 2H), 1.37 (s, 3H), 0.77 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 145.9, 130.2, 128.4, 123.4 (q, J = 3.9 Hz), 122.6 (q, J = 3.8 Hz), 112.7, 44.7, 33.4, 24.3, 8.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.8. EI-MS: m/z 228.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{13}H_{15}F_3$ $[M]^+$: 228.1126. Found: 228.1129. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 60/40, flow rate 0.7 mL/min, 214 nm, retention times (min): 9.63 (minor) and 9.96 (major).

*(R)-1′-Bromo-2′-(3-methylpent-1-en-3-yl)benzene (**3xa**).* Colorless oil; 54% yield; **3xa**/**4xa** = 70/30; 22% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3xa** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.26 (d, J = 7.3 Hz, 1H), 7.07 (dt, J = 15.0, 7.6 Hz, 1H), 6.20 (ddd, J = 17.6, 10.7, 1.9 Hz, 1H), 5.10 (dd, J = 10.7, 0.9 Hz, 1H), 4.93 (dd, J = 17.6, 0.8 Hz, 1H), 2.15 (dd, J = 14.5, 7.2 Hz, 2H), 1.49 (s, 3H), 0.71 (ddd, J = 7.4, 4.6, 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 144.9, 132.6, 131.0, 130.2, 127.9, 127.1, 112.4, 46.2, 31.1, 25.6, 9.0. EI-MS: m/z 238.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{15}Br$ $[M]^+$: 238.0357. Found: 238.0360. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 70/30, flow rate 0.7 mL/min, 214 nm, retention times (min): 9.51 (minor) and 10.39 (major).

*(R)-1′-(3-Methylpent-1-en-3-yl)naphthalene (**3ya**).* Colorless oil; 55% yield; **3ya**/**4ya** = 74/26; 86% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ya** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 1H), 7.89−7.85 (m, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 7.3 Hz, 1H), 7.48 (dd, J = 3.6, 2.4 Hz, 1H), 7.45 (dd, J = 10.0, 4.9 Hz, 2H), 6.34 (dd, J = 17.6, 10.7 Hz, 1H), 5.10 (dd, J = 50.8, 14.2 Hz, 2H), 2.01 (dq, J = 14.4, 7.4 Hz, 2H), 1.59 (s, 3H), 0.69 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 144.3, 142.3, 129.1, 127.7, 127.6, 125.1, 125.0, 124.8, 124.3, 112.0, 45.5, 32.8, 27.4, 9.0. EI-MS: m/z 210.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{16}H_{18}$ $[M]^+$: 210.1409. Found: 210.1415. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 16.47 (major) and 17.03 (minor).

*(R)-2′-(3-Methylpent-1-en-3-yl)naphthalene (**3za**).* Colorless oil; 62% yield; **3za**/**4za** = 81/19; 80% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3za** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.79 (m, 3H), 7.74 (d, J = 1.6 Hz, 1H), 7.50−7.44 (m, 3H), 6.12 (dd, J = 17.5,

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10.8 Hz, 1H), 5.14 (dd, J = 10.8, 1.3 Hz, 1H), 5.10 (dd, J = 17.5, 1.3 Hz, 1H), 1.97 (dd, J = 13.7, 7.4 Hz, 1H), 1.87 (dd, J = 13.7, 7.4 Hz, 1H), 1.47 (s, 3H), 0.81 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 144.8, 127.9, 127.5, 127.4, 125.8, 125.7, 125.4, 124.8, 112.1, 44.7, 33.2, 24.3, 9.0. EI-MS: m/z 210.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{16}H_{18}$ $[M]^+$: 210.1409. Found: 210.1413. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 230 nm, retention times (min): 16.54 (minor) and 19.26 (major).

*(S)-(3-Ethylhex-1-en-3-yl)benzene (**3x′a**).* Colorless oil; 58% yield; **3x′a**/**4x′a** = 64/36; 52% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3x′a** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 4.8 Hz, 4H), 7.18 (dt, J = 5.2, 4.1 Hz, 1H), 5.92 (dd, J = 17.7, 10.9 Hz, 1H), 5.19 (dd, J = 10.9, 1.2 Hz, 1H), 5.09 (dd, J = 17.7, 1.2 Hz, 1H), 1.87−1.69 (m, 4H), 1.16−1.06 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 145.7, 127.8, 127.8, 125.6, 112.6, 55.5, 39.1, 29.6, 17.2, 14.8, 8.5. EI-MS: m/z 188.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{14}H_{20}$ $[M]^+$: 188.1565. Found: 188.1560. The absolute configuration was assigned by analogy based on **3wa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 75/25, flow rate 0.7 mL/min, 214 nm, retention times (min): 15.14 (major) and 16.69 (minor).

*(3-Ethyl-4-methylpent-1-en-3-yl)benzene (**3y′a**).* Colorless oil; 56% yield; **3y′a**/**4y′a** = 68/32; 2% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3y′a** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.29 (m, 3H),7.28−7.26 (m, 1H), 7.18−7.16 (m, 1H), 6.01 (dd, J = 17.9, 11.2 Hz, 1H), 5.37 (dd, J = 11.2, 1.3 Hz, 1H), 5.13 (dd, J = 17.9, 1.3 Hz, 1H), 2.29 (dt, J = 13.5, 6.8 Hz, 1H), 1.78 (dd, J = 14.8, 7.3 Hz, 2H), 0.85 (d, J = 6.7 Hz, 3H), 0.75 (d, J = 6.9 Hz, 3H), 0.59 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 140.8, 128.2, 127.6, 125.5, 115.1, 51.6, 33.1, 29.2, 21.8, 17.5, 8.7. EI-MS: m/z 188.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{14}H_{20}$ $[M]^+$: 188.1565. Found: 188.1560. Enantiomeric excess was determined by chiral GC: CP-Chiralsil-Dex-CB (25 m × 0.25 mm), initial temperature 80 °C for 140 min, then 0.5 °C/min to 140 °C (hold for 5 min), then 10 °C/min to 180 °C (final temperature), retention times (min): 44.79 (major) and 46.37 (minor).

*(R)-But-3-en-2-ylbenzene (**3ab**).* Colorless oil; 56% yield; **3ab**/**4ab** = 39/61; 90% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ab** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 6.0 Hz, 2H), 7.19 (d, J = 7.0 Hz, 1H), 6.07−5.99 (m, 1H), 5.09−5.03 (m, 2H), 3.58−3.37 (m, 1H), 1.39 (dd, J = 7.0, 0.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 143.2, 137.9, 128.4, 127.2, 126.1, 113.1, 43.2, 20.7. EI-MS: m/z 132.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{10}H_{12}$ $[M]^+$: 132.0939. Found: 132.0944. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.88 (major) and 9.75 (minor).

*(R)-Hex-1-en-3-ylbenzene (**3ac**).* Colorless oil; 65% yield; **3ac**/**4ac** = 65/35; 86% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ac** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.37 (m, 1H), 7.33 (dt, J = 7.9, 4.9 Hz, 4H), 6.05−5.94 (m, 1H), 5.07 (ddd, J = 10.1, 2.4, 1.1 Hz, 2H), 3.30 (q, J = 7.5 Hz, 1H), 1.80−1.66 (m, 2H), 1.39−1.23 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 142.5, 128.4, 127.6, 126.1, 113.8, 49.7, 37.7, 20.7, 14.1, 14.0. EI-MS: m/z 160.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ $[M]^+$: 160.1252. Found: 160.1254. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 9.83 (major) and 11.60 (minor).

*(R)-(4-Methylpent-1-en-3-yl)benzene (**3ad**).* Colorless oil; 60% yield; **3ad**/**4ad** = 41/59; 88% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ad** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 1.9 Hz, 1H), 7.33 (d, J = 1.4 Hz, 2H), 7.26−7.22 (m, 2H), 6.08−5.99 (m, 1H), 5.09−5.05 (m, 2H), 2.91 (t, J = 9.0 Hz, 1H), 2.02−1.95 (m, 1H), 1.00 (d, J = 6.9 Hz, 3H), 0.80 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 141.2, 128.4, 127.9, 126.0, 115.0, 58.6, 32.6, 28.6, 21.1. EI-MS: m/z 160.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{16}$ $[M]^+$: 160.1252. Found: 160.1256. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 65/35, flow rate 0.7 mL/min, 214 nm, retention times (min): 26.35 (major) and 28.01 (minor).

*(R)-Hept-1-en-3-ylbenzene (**3ae**).* Colorless oil; 70% yield; **3ae**/**4ae** = 70/30; 82% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ae** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.9 Hz, 1H), 7.38−7.32 (m, 2H), 7.27−7.22 (m, 2H), 6.08−5.96 (m, 1H), 5.13−5.03 (m, 2H), 3.29 (q, J = 7.5 Hz, 1H), 1.83−1.70 (m, 2H), 1.45−1.30 (m, 4H), 0.93 (td, J = 7.1, 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 142.6, 128.4, 127.6, 126.1, 113.8, 50.0, 35.2, 29.8, 22.7, 14.1. EI-MS: m/z 174.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{13}H_{18}$ $[M]^+$: 174.1409. Found: 174.1408. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Phenomenex Lux 5u Cellulose-3 (0.46 × 25 cm), CH_3CN/H_2O = 60/40, flow rate 0.7 mL/min, 214 nm, retention times (min): 23.29 (major) and 24.42 (minor).

*(R)-Non-1-en-3-ylbenzene (**3af**).* Colorless oil; 75% yield; **3af** /**4af** = 70/30; 86% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3af** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.30 (m, 2H), 7.23 (dd, J = 7.4, 4.1 Hz, 3H), 6.06−5.93 (m, 1H), 5.06 (dd, J = 9.4, 8.8 Hz, 2H), 3.27 (q, J = 7.5 Hz, 1H), 1.79−1.67 (m, 2H), 1.40−1.18 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 142.6, 128.4, 127.6, 126.1, 113.8, 50.0, 35.5, 31.8, 29.3, 27.5, 22.7, 14.1. EI-MS: m/z 202.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{15}H_{22}$ $[M]^+$: 202.1722. Found: 202.1727. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.92 (major) and 11.86 (minor).

*(S)-(1-Cyclopentylallyl)benzene (**3ag**).* Colorless oil; 72% yield; **3ag**/**4ag** = 71/29; 90% ee. $[\alpha]_D^{25}$ − 41.9° (c = 1.0, $CHCl_3$); lit. [α] + 67.2° (c = 1.0, $CHCl_3$) (98/2 b/l, 85% ee, *R*).[26] NMR experiments were performed on the mixture of products, but only data of branched product **3ag** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, J = 7.6 Hz, 2H), 7.27−7.21 (m, 3H), 6.11−6.02 (m, 1H), 5.09−5.00 (m, 2H), 3.04 (t, J = 9.2 Hz, 1H), 1.88 (dddd, J = 18.8, 17.0, 11.8, 7.3 Hz, 2H), 1.77−1.67 (m, 2H), 1.66−1.57 (m, 3H), 1.57−1.46 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7, 142.1, 128.4, 127.9, 126.0, 114.1, 56.8, 44.8, 31.4, 25.3. EI-MS: m/z 186.2 $[M]^+$. HRMS (EI) m/z calcd for $C_{14}H_{18}$ $[M]^+$: 186.1409. Found: 184.1412. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 8.44 (major) and 9.38 (minor).

*(R)-Hexa-1,5-dien-3-ylbenzene (**3ah**).* Colorless oil; 60% yield; **3ah**/**4ah** = 49/51; 48% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3ah** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.1 Hz, 2H), 7.33 (q, J = 6.6 Hz, 3H), 6.06−5.97 (m, 1H), 5.81−5.69 (m, 1H), 5.09 (d, J = 8.8 Hz, 2H), 5.04 (d, J = 13.4 Hz, 2H), 3.39 (q, J = 7.1 Hz, 1H), 2.57−2.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 141.6, 136.6, 128.4, 127.7, 126.3, 116.1, 114.4, 49.6, 39.8. EI-MS: m/z 158.1 $[M]^+$. HRMS (EI) m/z calcd for $C_{12}H_{14}$ $[M]^+$: 158.1096. Found: 158.1098. The absolute configuration was assigned by analogy based on **3aa** through a similar stereochemical model. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-

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PrOH = 100/0, flow rate 0.7 mL/min, 210 nm, retention times (min): 16.68 (major) and 22.3 (minor).

*1-Bromo-4-(1-phenylallyl)benzene (**3cj**).* Colorless oil; 62% yield; **3cj**/**4cj** = 8/92; 14% ee. NMR experiments were performed on the mixture of products, but only data of branched product **3cj** are given. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.3, 1.2 Hz, 3H), 7.52−7.49 (m, 2H), 7.49−7.48 (m, 1H), 7.43−7.40 (m, 1H), 7.23−7.20 (m, 1H), 7.11 (dd, J = 6.1, 4.5 Hz, 1H), 6.31 (ddd, J = 17.2, 10.2, 7.1 Hz, 1H), 5.30 (dt, J = 10.2, 1.3 Hz, 1H), 5.05 (dt, J = 17.1, 1.4 Hz, 1H), 4.74 (d, J = 7.1 Hz, 1H). EI-MS: m/z 272.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{15}H_{13}Br$ $[M]^+$: 272.0201. Found: 272.0205. Enantiomeric excess was determined by chiral HPLC: Chiralcel OJ-H column, *n*-hexane/*i*-PrOH = 100/0, flow rate 0.7 mL/min, 230 nm, retention times (min): 7.29 (minor) and 7.62 (major).

Procedure for Hydroboration−Oxidation of Alkene Product 3aa.[21] To a solution of alkene product mixture **3aa**/**4aa** (0.2 mmol, 1.0 equiv) in dry THF (2.0 mL) at 0 °C was added BH_3·THF (1.0 M solution in THF, 0.4 mmol, 2.0 equiv) over 5 min. The mixture was stirred at 0 °C for 10 min and then warmed to room temperature and stirred for additional 1 h. To the reaction mixture at 0 °C was added 15% aqueous NaOH (2.0 mL) followed by 30% aqueous H_2O_2 (2.0 mL). The resulting mixture was stirred at room temperature for 1 h and then diluted with brine (2.0 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography with *n*-hexane/EA to afford corresponding alcohol **5a** with 92% ee as colorless liquid in 70% yield. **5a**: $[\alpha]_D^{25}$ − 1.6° (c = 0.5, $CHCl_3$); lit. $[\alpha]_D^{20}$ − 2.4° (c = 0.8, $CDCl_3$) (*R*).[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.5 Hz, 2H), 7.20 (dd, J = 7.6, 1.4 Hz, 1H), 7.19−7.14 (m, 2H), 3.58−3.43 (m, 2H), 2.59 (ddd, J = 14.8, 9.9, 5.2 Hz, 1H), 1.96 (dtd, J = 12.2, 7.2, 5.0 Hz, 1H), 1.85−1.77 (m, 1H), 1.75−1.54 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 128.4, 127.7, 126.1, 61.2, 44.3, 39.2, 29.8, 12.1. EI-MS: m/z 164.0 $[M]^+$. HRMS (EI) m/z calcd for $C_{11}H_{16}O$ $[M]^+$: 164.1201. Found: 164.1198. Enantiomeric excess was determined by chiral HPLC: Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95/5, flow rate 0.7 mL/min, 214 nm, retention times (min): 13.30 (major) and 15.78 (minor).

Procedure for the Preparation of Copper Complex.[22] A mixture of complex $[Cu(CH_3CN)_4][PF_6]$ (111.8 mg, 0.3 mmol) and (*S*)-BIDIME (99.1 mg, 0.3 mmol) was dissolved in dichloromethane (2 mL). The solution was stirred at 45 °C under nitrogen atmosphere. The stirring was maintained for 15 h. Then, the resulting mixture was diluted with additional CH_2Cl_2(2 mL), filtered, and the supernatant evaporated to dryness at 45 °C under vacuum to yield the corresponding copper complex 158.8 mg as an off-white solid in 85% yield. $[Cu(I)((S)\text{-BIDIME})(MeCN)_2]PF_6$: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, J = 7.9 Hz, 1H), 7.37 (t, J = 8.4 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.87 (dd, J = 7.3, 4.2 Hz, 2H), 6.66 (d, J = 8.1 Hz, 1H), 4.90 (dd, J = 12.9, 3.8 Hz, 1H), 4.63−4.57 (m, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 2.24 (s, 6H), 0.83 (d, J = 15.8 Hz, 9H). Elem. Anal. Calcd for $C_{23}H_{29}CuF_6N_2O_3P_2$: C, 44.49; H, 4.71; N, 4.51. Found: C, 42.50; H, 5.09; N, 4.03. Crystals of the complex suitable for X-ray crystallography were obtained by recrystallization from dichloromethane/*n*-hexane (1/5) by standing at room temperature for 48 h.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00194.

Experimental details, characterization data, crystallographic data, NMR spectra, and HPLC data (PDF)

Accession Codes

CCDC 1906544 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Lu, Z.; Ma, S. Metal-Catalyzed Enantioselective Allylation in Asymmetric Synthesis. *Angew. Chem., Int. Ed.* **2008**, *47*, 258−297. (b) Negishi, E. Magical Power of Transition Metals: Past, Present, and Future (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6738−6764.

(2) (a) Trost, B. M.; Van Vranken, D. L. Asymmetric Transition Metal-Catalyzed Allylic Alkylations. *Chem. Rev.* **1996**, *96*, 395−422. (b) Williams, J. M. J. The Ups and Downs of Allylpalladium Complexes in Catalysis. *Synlett* **1996**, 705−710. (c) Garrido, J. L.; Alonso, I.; Carretero, J. C. One-Step Palladium-Catalyzed Synthesis of Substituted Dihydrofurans from the Carbonate Derivatives of γ-Hydroxy-α,β-unsaturated Sulfones. *J. Org. Chem.* **1998**, *63*, 9406−9413. (d) Trost, B. M.; Crawley, M. L. Asymmetric Transition-Metal-Catalyzed Allylic Alkylations: Applications in Total Synthesis. *Chem. Rev.* **2003**, *103*, 2921−2944.

(3) (a) Belda, O.; Lundgren, S.; Moberg, C. Recoverable Resin-Supported Pyridylamide Ligand for Microwave-Accelerated Molybdenum-Catalyzed Asymmetric Allylic Alkylations: Enantioselective Synthesis of Baclofen. *Org. Lett.* **2003**, *5*, 2275−2278. (b) Belda, O.; Moberg, C. Molybdenum-Catalyzed Asymmetric Allylic Alkylations. *Acc. Chem. Res.* **2004**, *37*, 159−167. (c) Zhang, Y.; Trost, B. M. Mo-Catalyzed Regio-, Diastereo-, and Enantioselective Allylic Alkylation of 3-Aryloxindoles. *J. Am. Chem. Soc.* **2007**, *129*, 14548−14549. (d) Bandini, M.; Eichholzer, A.; Kotrusz, P.; Umani-Ronchi, A. Highly Efficient Molybdenum(II)-Catalyzed Intramolecular Allylic Alkylation of Arenes. *Adv. Synth. Catal.* **2008**, *350*, 531−536. (e) Zhang, Y.; Trost, B. M. Catalytic Double Stereoinduction in Asymmetric Allylic Alkylation of Oxindoles. *Chem. - Eur. J.* **2010**, *16*, 296−303. (f) Zhang, Y.; Trost, B. M. Molybdenum-Catalyzed Asymmetric Allylic Alkylation of 3-Alkyloxindoles: Reaction Development and Applications. *Chem. - Eur. J.* **2011**, *17*, 2916−2922. (g) Trost, B. M.; Miller, J. R.; Hoffman, C. M. A Highly Enantio- and Diastereoselective Molybdenum-Catalyzed Asymmetric Allylic Alkylation of Cyanoesters. *J. Am. Chem. Soc.* **2011**, *133*, 8165−8167. (h) Ozkal, E.; Pericàs, M. A. A Bis(Triazolecarboxamido) Ligand for Enantio- and Regioselective Molybdenum-Catalyzed Asymmetric Allylic Alkylation Reactions. *Adv. Synth. Catal.* **2014**, *356*, 711−717. (i) Trost, B. M.; Osipov, M.; Kruger, S.; Zhang, Y. A Catalytic Asymmetric Total Synthesis of (−)-Perophoramidine. *Chem. Sci.* **2015**, *6*, 349−353.

(4) (a) Trost, B. M.; Hung, M. H. Tungsten-Catalyzed Allylic Alkylations. New Avenues for Selectivity. *J. Am. Chem. Soc.* **1983**, *105*, 7757−7759. (b) Lloyd-Jones, G. C.; Pfaltz, A. Chiral Phosphanodihydrooxazoles in Asymmetric Catalysis: Tungsten-Catalyzed Allylic

DOI: 10.1021/acs.organomet.9b00194
Organometallics XXXX, XXX, XXX−XXX

Substitution. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 462−464. (c) Lehmann, J.; Lloyd-Jones, G. C. Regiocontrol and Stereoselectivity in Tungsten-Bipyridine Catalysed Allylic Alkylation. *Tetrahedron* **1995**, *51*, 8863−8874. (d) Faller, J. W.; Fontaine, P. P. Stereodynamics and Conformational Equilibria in Some Chiral Pseudo-Octahedral Tungsten Crotyl Complexes. *J. Organomet. Chem.* **2006**, *691*, 4667−4675.

(5) (a) Matsushima, Y.; Onitsuka, K.; Kondo, T.; Mitsudo, T.; Takahashi, S. Asymmetric Catalysis of Planar-Chiral Cyclopentadienylruthenium Complexes in Allylic Amination and Alkylation. *J. Am. Chem. Soc.* **2001**, *123*, 10405−10406. (b) Kanbayashi, N.; Hosoda, K.; Kato, M.; Takii, K.; Okamura, T.; Onitsuka, K. Enantio- and Diastereoselective Asymmetric Allylic Alkylation Catalyzed by a Planar-Chiral Cyclopentadienyl Ruthenium Complex. *Chem. Commun.* **2015**, *51*, 10895−10898. (c) Kanbayashi, N.; Hosoda, K.; Okamura, T.; Aoshima, S.; Onitsuka, K. Enantio- and Diastereoselective Polymerization: Asymmetric Allylic Alkylation Catalyzed by a Planar-Chiral Cp'Ru complex. *Polym. Chem.* **2016**, *7*, 3691−3699.

(6) (a) Evans, P. A.; Kennedy, L. J. Regioselective Rhodium-Catalyzed Allylic Alkylation/Ring-Closing Metathesis Approach to Carbocycles. *Tetrahedron Lett.* **2001**, *42*, 7015−7018. (b) Hayashi, T.; Okada, A.; Suzuka, T.; Kawatsura, M. High Enantioselectivity in Rhodium-Catalyzed Allylic Alkylation of 1-Substituted 2-Propenyl Acetates. *Org. Lett.* **2003**, *5*, 1713−1715. (c) Sieber, J. D.; Angeles-Dunham, V. V.; Chennamadhavuni, D.; Fandrick, D. R.; Haddad, N.; Grinberg, N.; Kurouski, D.; Lee, H.; Song, J. J.; Yee, N. K.; Mattson, A. E.; Senanayake, C. H. Rhodium-Catalyzed Asymmetric Allenylation of Sulfonylimines and Application to the Stereospecific Allylic Allenylation. *Adv. Synth. Catal.* **2016**, *358*, 3062−3068.

(7) (a) Lipowsky, G.; Miller, N.; Helmchen, G. Regio- and Enantioselective Iridium-Catalyzed Allylic Alkylation with In Situ Activated P,C-Chelate Complexes. *Angew. Chem., Int. Ed.* **2004**, *43*, 4595−4597. (b) Tosatti, P.; Nelson, A.; Marsden, S. P. Recent Advances and Applications of Iridium-Catalysed Asymmetric Allylic Substitution. *Org. Biomol. Chem.* **2012**, *10*, 3147−3163. (c) Shockley, S. E.; Hethcox, J. C.; Stoltz, B. M. Intermolecular Stereoselective Iridium-Catalyzed Allylic Alkylation: An Evolutionary Account. *Synlett* **2018**, *29*, 2481−2492. (d) Hethcox, J. C.; Shockley, S. E.; Stoltz, B. M. Enantioselective Synthesis of Vicinal All-Carbon Quaternary Centers via Iridium-Catalyzed Allylic Alkylation. *Angew. Chem., Int. Ed.* **2018**, *57*, 8664−8667. (e) Butcher, T. W.; Hartwig, J. F. Enantioselective Synthesis of Tertiary Allylic Fluorides by Iridium-Catalyzed Allylic Fluoroalkylation. *Angew. Chem., Int. Ed.* **2018**, *57*, 13125−13129.

(8) For a recent review on Cu-catalyzed allylic substitution, see (a) Yorimitsu, H.; Oshima, K. Recent Progress in Asymmetric Allylic Substitutions Catalyzed by Chiral Copper Complexes. *Angew. Chem., Int. Ed.* **2005**, *44*, 4435−4439. (b) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. Catalytic Asymmetric Conjugate Addition and Allylic Alkylation with Grignard Reagents. *Chem. Rev.* **2008**, *108*, 2824−2852. (c) Falciola, C. A.; Alexakis, A. Copper-Catalyzed Asymmetric Allylic Alkylation. *Eur. J. Org. Chem.* **2008**, 3765−3780. (d) Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pàmies, O.; Diéguez, M. Enantioselective Copper-Catalyzed Conjugate Addition and Allylic Substitution Reactions. *Chem. Rev.* **2008**, *108*, 2796−2823.

(9) (a) van Klaveren, M.; Persson, E. S. M.; del Villar, A.; Grove, D. M.; Bäckvall, J. E.; van Koten, G. Chiral arenethiolatocopper(I) Catalyzed Substitution Reactions of Acyclic Allylic Substrates with Grignard Reagents. *Tetrahedron Lett.* **1995**, *36*, 3059−3062. (b) Meuzelaar, G. J.; Karlström, A. S. E.; Klaveren, M. V.; Persson, E. S. M.; Villar, A. D.; Koten, G. V.; Bäckvall, J. E. Asymmetric Induction in the Arenethiolatocopper(I)-Catalyzed Substitution Reaction of Grignard Reagents with Allylic Substrates. *Tetrahedron* **2000**, *56*, 2895−2903. (c) Karlström, A. S. E.; Huerta, F. F.; Meuzelaar, G. J.; Bäckvall, J. E. Ferrocenyl Thiolates as Ligands in the Enantioselective Copper-Catalyzed Substitution of Allylic Acetates with Grignard Reagents. *Synlett* **2001**, *2001*, 923−926. (d) Cotton, H. K.; Norinder, J.; Bäckvall, J. E. Screening of Ligands in the Asymmetric Metallocenethiolatocopper(I)-Catalyzed Allylic Substitution with Grignard Reagents. *Tetrahedron* **2006**, *62*, 5632−5640.

(10) (a) Dübner, F.; Knochel, P. Copper(I)-Catalyzed Enantioselective Substitution of Allyl Chlorides with Diorganozinc Compounds. *Angew. Chem., Int. Ed.* **1999**, *38*, 379−381. (b) Dübner, F.; Knochel, P. Highly Enantioselective Copper-Catalyzed Substitution of Allylic Chlorides with Diorganozincs. *Tetrahedron Lett.* **2000**, *41*, 9233−9237.

(11) (a) Malda, H.; Van Zijl, A. W.; Arnold, L. A.; Feringa, B. L. Enantioselective Copper-Catalyzed Allylic Alkylation with Dialkylzincs Using Phosphoramidite Ligands. *Org. Lett.* **2001**, *3*, 1169−1171. (b) Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. Modular Pyridinyl Peptide Ligands in Asymmetric Catalysis: Enantioselective Synthesis of Quaternary Carbon Atoms Through Copper-Catalyzed Allylic Substitutions. *Angew. Chem., Int. Ed.* **2001**, *40*, 1456−1460. (c) Piarulli, U.; Daubos, P.; Claverie, C.; Roux, M.; Gennari, C. A Catalytic and Enantioselective Desymmetrization of *meso* Cyclic Allylic Bisdiethylphosphates with Organozinc Reagents. *Angew. Chem., Int. Ed.* **2003**, *42*, 234−236. (d) Goldsmith, P. J.; Teat, S. J.; Woodward, S. Enantioselective Preparation of β,β-Disubstituted α-Methylenepropionates by MAO Promotion of the Zinc Schlenk Equilibrium. *Angew. Chem., Int. Ed.* **2005**, *44*, 2235−2237. (e) Yoshikai, N.; Miura, K.; Nakamura, E. Enantioselective Copper-Catalyzed Allylic Substitution Reaction with Aminohydroxyphosphine Ligand. *Adv. Synth. Catal.* **2009**, *351*, 1014−1018. (f) Jennequin, T.; Wencel-Delord, J.; Rix, D.; Daubignard, J.; Crévisy, C.; Mauduit, M. Chelating Hydroxyalkyl NHC as Efficient Chiral Ligands for Room-Temperature Copper-Catalyzed Asymmetric Allylic Alkylation. *Synlett* **2010**, *2010*, 1661−1665.

(12) Alexakis, A.; Malan, C.; Lea, L.; Benhaim, C.; Fournioux, X. Enantioselective Copper-Catalyzed S_N2' Substitution with Grignard Reagents. *Synlett* **2001**, *2001*, 927−930.

(13) (a) Alexakis, A.; Croset, K. Tandem Copper-Catalyzed Enantioselective Allylation-Metathesis. *Org. Lett.* **2002**, *4*, 4147−4149. (b) Tissot-Croset, K.; Polet, D.; Alexakis, A. A Highly Effective Phosphoramidite Ligand for Asymmetric Allylic Substitution. *Angew. Chem., Int. Ed.* **2004**, *43*, 2426−2428. (c) van Zijl, A. W.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L. Highly Enantioselective Copper-Catalyzed Allylic Alkylation with Phosphoramidite Ligands. *Adv. Synth. Catal.* **2004**, *346*, 413−420.

(14) (a) Tissot-Croset, K.; Alexakis, A. Copper Catalyzed Enantioselective Allylic Substitution by MeMgX. *Tetrahedron Lett.* **2004**, *45*, 7375−7378. (b) Falciola, C. A.; Tissot-Croset, K.; Alexakis, A. β-Disubstituted Allylic Chlorides: Substrates for the Cu-Catalyzed Asymmetric S_N2' Reaction. *Angew. Chem., Int. Ed.* **2006**, *45*, 5995−5998. (c) Falciola, C. A.; Alexakis, A. 1, 4-Dichloro- and 1, 4-Dibromo-2-butenes as Substrates for Cu-Catalyzed Asymmetric Allylic Substitution. *Angew. Chem., Int. Ed.* **2007**, *46*, 2619−2622. (d) Fañanás-Mastral, M.; Feringa, B. L. Copper-Catalyzed Regio- and Enantioselective Synthesis of Chiral Enol Acetates and β-Substituted Aldehydes. *J. Am. Chem. Soc.* **2010**, *132*, 13152−13153. (e) Fang, F.; Zhang, H.; Xie, F.; Yang, G.; Zhang, W. Highly Enantioselective Copper-Catalyzed Allylic Alkylation with Atropos Phosphoramidites Bearing a D_2-Symmetric Biphenyl Backbone. *Tetrahedron* **2010**, *66*, 3593−3598. (f) Langlois, J. B.; Alexakis, A. Identification of a Valuable Kinetic Process in Copper-Catalyzed Asymmetric Allylic Alkylation. *Angew. Chem., Int. Ed.* **2011**, *50*, 1877−1881. (g) Giannerini, M.; Fañanás-Mastral, M.; Feringa, B. L. Z-Selective Copper-Catalyzed Asymmetric Allylic Alkylation with Grignard Reagents. *J. Am. Chem. Soc.* **2012**, *134*, 4108−4111. (h) Hornillos, V.; Pérez, M.; Fañanás-Mastral, M.; Feringa, B. L. Copper-Catalyzed Enantioselective Allyl-Allyl Cross-Coupling. *J. Am. Chem. Soc.* **2013**, *135*, 2140−2143.

(15) (a) López, F.; van Zijl, A. W.; Minnaard, A. J.; Feringa, B. L. Highly Enantioselective Cu-Catalysed Allylic Substitutions with Grignard Reagents. *Chem. Commun.* **2006**, *4*, 409−411. (b) Geurts, K.; Fletcher, S. P.; Feringa, B. L. Copper Catalyzed Asymmetric Synthesis of Chiral Allylic Esters. *J. Am. Chem. Soc.* **2006**, *128*, 15572−15573. (c) Teichert, J. F.; Zhang, S.-Y.; van Zijl, A. W.; Slaa, J.

DOI: 10.1021/acs.organomet.9b00194
Organometallics XXXX, XXX, XXX−XXX

W.; Minnaard, A. J.; Feringa, B. L. Asymmetric Allylic Alkylation in Combination with Ring-Closing Metathesis for the Preparation of Chiral N-Heterocycles. *Org. Lett.* **2010**, *12*, 4658−4660. (d) den Hartog, T. D.; Maciá, B.; Minnaard, A. J.; Feringa, B. L. Copper-Catalyzed Asymmetric Allylic Alkylation of Halocrotonates: Efficient Synthesis of Versatile Chiral Multifunctional Building Blocks. *Adv. Synth. Catal.* **2010**, *352*, 999−1013. (e) Fañanás-Mastral, M.; ter Horst, B.; Minnaard, A. J.; Feringa, B. L. Stereoselective Synthesis of syn and anti 1, 2-Hydroxyalkyl Moieties by Cu-Catalyzed Asymmetric Allylic Alkylation. *Chem. Commun.* **2011**, *47*, 5843−5845. (f) Huang, Y.; Fañanás-Mastral, M.; Minnaard, A. J.; Feringa, B. L. A Novel Catalytic Asymmetric Route towards Skipped Dienes with a Methyl-Substituted Central Stereogenic Carbon. *Chem. Commun.* **2013**, *49*, 3309−3311. (g) Mao, B.; Fañanás-Mastral, M.; Lutz, M.; Feringa, B. L. Diversity-Oriented Enantioselective Synthesis of Highly Functionalized Cyclic and Bicyclic Alcohols. *Chem. - Eur. J.* **2013**, *19*, 761−770. (h) Hornillos, V.; Pérez, M.; Fañanás-Mastral, M.; Feringa, B. L. Cu-Catalyzed Asymmetric Allylic Alkylation of Phosphonates and Phosphine Oxides with Grignard Reagents. *Chem. - Eur. J.* **2013**, *19*, 5432−5441.

(16) (a) Lölsberg, W.; Ye, S. T.; Schmalz, H. G. Enantioselective Copper-Catalysed Allylic Alkylation of Cinnamyl Chlorides by Grignard Reagents using Chiral Phosphine-Phosphite Ligands. *Adv. Synth. Catal.* **2010**, *352*, 2023−2031. (b) Lölsberg, W.; Werle, S.; Neudörfl, J. M.; Schmalz, H. G. An Enantioselective Total Synthesis of Helioporins C and E. *Org. Lett.* **2012**, *14*, 5996−5999.

(17) (a) Tominaga, S.; Oi, Y.; Kato, T.; An, D. K.; Okamoto, S. γ-Selective Allylic Substitution Reaction with Grignard Reagents Catalyzed by Copper N-Heterocyclic Carbene Complexes and Its Application to Enantioselective Synthesis. *Tetrahedron Lett.* **2004**, *45*, 5585−5588. (b) Seo, H.; Hirsch-Weil, D.; Abboud, K. A.; Hong, S. Development of Biisoquinoline-Based Chiral Diaminocarbene Ligands: Enantioselective S_N2'Allylic Alkylation Catalyzed by Copper-Carbene Complexes. *J. Org. Chem.* **2008**, *73*, 1983−1986. (c) Selim, K. B.; Matsumoto, Y.; Yamada, K. I.; Tomioka, K. Efficient Chiral N-Heterocyclic Carbene/Copper(I)-Catalyzed Asymmetric Allylic Arylation with Aryl Grignard Reagents. *Angew. Chem., Int. Ed.* **2009**, *48*, 8733−8735. (d) Magrez, M.; Le Guen, Y. L.; Baslé, O.; Crévisy, C.; Mauduit, M. Bidentate Hydroxyalkyl NHC Ligands for the Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Grignard Reagents. *Chem. - Eur. J.* **2013**, *19*, 1199−1203.

(18) (a) Xu, G.; Senanayake, C. H.; Tang, W. P-Chiral Phosphorus Ligands Based on a 2,3-Dihydrobenzo[*d*][1,3]oxaphosphole Motif forAsymmetric Catalysis. *Acc. Chem. Res.* **2019**, *52*, 1101−1112. (b) Fu, W.; Tang, W. Chiral Monophosphorus Ligands for Asymmetric Catalytic Reactions. *ACS Catal.* **2016**, *6*, 4814−4858.

(19) (a) Tang, W.; Capacci, A. G.; Wei, X.; Li, W.; White, A.; Patel, N. D.; Savoie, J.; Gao, J. J.; Rodriguez, S.; Qu, B.; Haddad, N.; Lu, B. Z.; Krishnamurthy, D.; Yee, N. K.; Senanayake, C. H. A General and Special Catalyst for Suzuki-Miyaura Coupling Processes. *Angew. Chem., Int. Ed.* **2010**, *49*, 5879−5883. (b) Zhao, Q.; Li, C.; Senanayake, C. H.; Tang, W. An Efficient Method for Sterically Demanding Suzuki-Miyaura Coupling Reactions. *Chem. - Eur. J.* **2013**, *19*, 2261−2265. (c) Tang, W.; Patel, N. D.; Xu, G.; Xu, X.; Savoie, J.; Ma, S.; Hao, M.-H.; Keshipeddy, S.; Capacci, A. G.; Wei, X.; Zhang, Y.; Gao, J. J.; Li, W.; Rodriguez, S.; Lu, B. Z.; Yee, N. K.; Senanayake, C. H. Efficient Chiral Monophosphorus Ligands forAsymmetric Suzuki-Miyaura Coupling Reactions. *Org. Lett.* **2012**, *14*, 2258−2261. (d) Xu, G.; Fu, W.; Liu, G.; Senanayake, C. H.; Tang, W. Efficient Syntheses of Korupensamines A, B and Michellamine B by Asymmetric Suzuki-Miyaura Coupling Reactions. *J. Am. Chem. Soc.* **2014**, *136*, 570−573. (e) Fu, W.; Nie, M.; Wang, A.; Cao, Z.; Tang, W. Highly Enantioselective Nickel-Catalyzed Intramolecular Reductive Cyclization of Alkynones. *Angew. Chem., Int. Ed.* **2015**, *54*, 2520−2524. (f) Hu, N.; Zhao, G.; Zhang, Y.; Liu, X.; Li, G.; Tang, W. Synthesis of Chiral α-Amino Tertiary Boronic Estersby Enantioselective Hydroboration of α-Arylenamides. *J. Am. Chem. Soc.* **2015**, *137*, 6746−6749. (g) Liu, J.; Nie, M.; Zhou, Q.; Gao, S.; Jiang, W.; Chung, L. W.; Tang, W.; Ding, K. Enantioselective Palladium-Catalyzed Diboration of 1,1-Disubstituted Allenes. *Chem. Sci.* **2017**, *8*, 5161−5165. (h) Rao, X.; Li, N.; Bai, H.; Dai, C.; Wang, Z.; Tang, W. Efficient Synthesis of (−)-Corynoline by Enantioselective Palladium-Catalyzed α-Arylation with Sterically Hindered Substrates. *Angew. Chem., Int. Ed.* **2018**, *57*, 12328−12332. (i) Liu, G.; Fu, W.; Mu, X.; Wu, T.; Nie, M.; Li, K.; Xu, X.; Tang, W. Pyrrolidines and piperidines bearing chiral tertiary alcohols by nickel-catalyzed enantioselective reductive cyclization of *N*-alkynones. *Commun. Chem.* **2018**, *1*, 90.

(20) (a) Gao, F.; Carr, J. L.; Hoveyda, A. H. A Broadly Applicable NHC-Cu-Catalyzed Approach for Efficient, Site-, and Enantioselective Coupling of Readily Accessible (Pinacolato)alkenylboron Compounds to Allylic Phosphates and Applications to Natural Product Synthesis. *J. Am. Chem. Soc.* **2014**, *136*, 2149−2161. (b) Lee, J.; Torker, S.; Hoveyda, A. H. Versatile Homoallylic Boronates by Chemo-, S_N2'-, Diastereo- and Enantioselective Catalytic Sequence of Cu−H Addition to Vinyl-B(Pin)/Allylic Substitution. *Angew. Chem., Int. Ed.* **2017**, *56*, 821−826.

(21) (a) Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Aryl- and Alkenylboronates. *Angew. Chem., Int. Ed.* **2011**, *50*, 8656−8659. (b) Takeda, M.; Takatsu, K.; Shintani, R.; Hayashi, T. Synthesis of Quaternary Carbon Stereocenters by Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Arylboronates. *J. Org. Chem.* **2014**, *79*, 2354−2367.

(22) Grirrane, A.; Álvarez, E.; García, H.; Corma, A. Deactivation of Cationic Cu^I and Au^I Catalysts for A^3 Coupling by CH_2Cl_2: Mechanistic Implications of the Formation of Neutral Cu^I and Au^I Chlorides. *Angew. Chem., Int. Ed.* **2014**, *53*, 7253−7258.

(23) Jackowski, O.; Alexakis, A. Copper-Free Asymmetric Allylic Alkylation with Grignard Reagents. *Angew. Chem., Int. Ed.* **2010**, *49*, 3346−3350.

(24) Yoshikai, N.; Miura, K.; Nakamura, E. Enantioselective Copper-Catalyzed Allylic Substitution Reaction with Aminohydroxyphosphine Ligand. *Adv. Synth. Catal.* **2009**, *351*, 1014−1018.

(25) Kacprzynski, M. A.; Hoveyda, A. H. Cu-Catalyzed Asymmetric Allylic Alkylations of Aromatic and Aliphatic Phosphates with Alkylzinc Reagents. An Effective Method for Enantioselective Synthesis of Tertiary and Quaternary Carbons. *J. Am. Chem. Soc.* **2004**, *126*, 10676−10681.

(26) Nguyen, T. N. T.; Thiel, N. O.; Teichert, J. F. Copper(I)-Catalyzed Asymmetric Allylic Reduction with Hydrosilanes. *Chem. Commun.* **2017**, *53*, 11686−11689.

(27) Sabbani, S.; Hedenström, E.; Andersson, J. Lipase Catalyzed Acylation of Primary Alcohols with Remotely Located Stereogenic Centres: the Resoution of (±)-4,4-Dimethyl-3-phenyl-1-pentanol. *Tetrahedron: Asymmetry* **2007**, *18*, 1712−1720.

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