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Article

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Chiral NHC Ligands Bearing a Pyridine Moiety in Copper-Catalyzed 1,2-Addition of Dialkylzinc Reagents to β-Aryl-α,β-unsaturated *N*-Tosylaldimines

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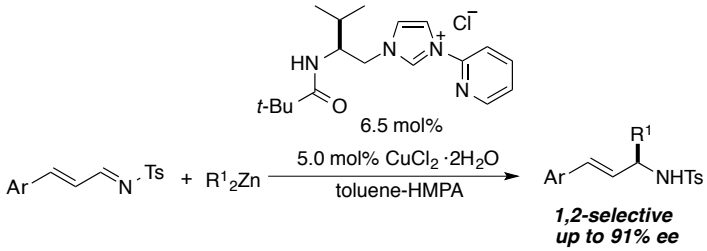
Abstract

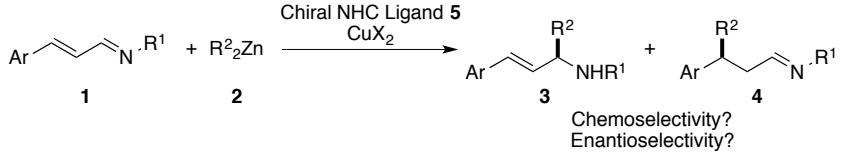


Asymmetric 1,2-addition of dialkylzinc reagents to α,β-unsaturated *N*-tosylaldimines was catalyzed by copper salt in the presence of chiral imidazolium salts having a pyridine ring, which were derived from amino acid, to afford the corresponding chiral allylic amines with up to 91% ee in reasonably high yields. The chiral *N*-heterocyclic carbene (NHC) ligand played an important role in controlling chemoselectivity.

Introduction

Allylic amines are common in biologically active compounds, such as the antifungal drug naftifine[1] and the calcium channel blocker flunarizine.[2] Chiral allylic amines, in particular, are synthetically and biologically relevant, not only for their therapeutic properties but also because they have been proven to be useful intermediates—for example, in the synthesis of conformationally restricted peptide isosteres.[3] Several methods of obtaining such compounds stereoselectively have recently been developed,

based either on control of asymmetric induction in the new C-C bond, or functional group transformation in a suitable precursor. In particular, catalytic asymmetric addition of organometallic reagents to the C=N double bond of imines constitutes an important method of obtaining optically active amines with a stereogenic center at the α-position.[4] Three types of enantioselective 1,2-addition to aldimines have been developed by various research groups: chiral-ether-mediated addition of organolithium reagents to 4-methoxyphenylimines, [5] copper(I)-chiral-amidophosphane-catalyzed addition of dialkylzinc reagents to *N*-sulfonylimines, [6] and rhodium-chiral-amidophosphane-catalyzed addition of arylboroxine reagents to *N*-sulfonylimines.[7] As part of our continuing effort to broaden the scope of copper-chiral-NHC-catalyzed addition of dialkylzinc reagents to imines,[8] we explored the possibility of controlling 1,4- and 1,2-addition to aldimines of α,β-unsaturated aldehydes to afford the corresponding chiral allylic amines (Scheme 1)[9]. We demonstrate herein that a combination of $CuCl_2 \cdot 2H_2O$ and amino acid-based chiral imidazolium salts bearing a pyridine ring catalyzes selective 1,2-addition of dialkylzinc reagents to aldimines of α,β-unsaturated aldehydes to give the corresponding allylic amines in reasonably high yields with up to 91% ee.



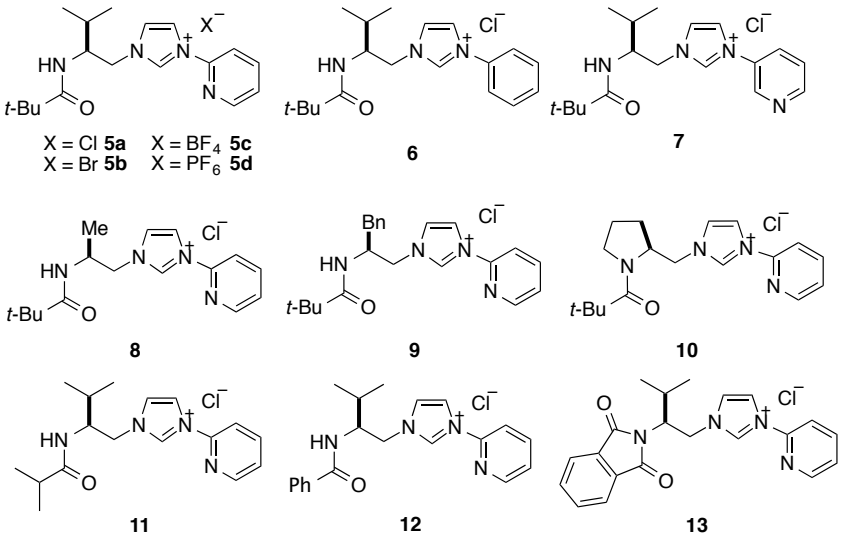
Scheme 1. Chemo- and enantioselective alkylation of α,β-unsaturated aldimines.

After the discovery of the first stable nucleophilic carbene around 1990[10c] by Bertrand, Arduengo and coworkers, the utilization of *N*-heterocyclic carbenes (NHCs) has been paid attention in organic synthesis.[10] NHCs have become popular ligands, along with phosphine, in organometallic chemistry.[11] Recently, chiral NHCs have been examined in the area of asymmetric synthesis. During the course of studies, chiral multidendate NHC has been developed.[12] In particular, Katsuki,[13] Sakaguchi,[14] Williams,[15] Hayashi,[16] and Tomioka[17] all independently developed chiral multidendate imidazolium salts as a NHC precursors, whicn were used for copper-catalyzed

asymmetric reactions.[18] We have also reported the synthesis of a series of chiral imidazolium salts, derived from commercially available L-amino acids and each bearing a pyridine moiety, and the corresponding NHC generated in situ from the salts act as a ligand for copper catalytic asymmetric reaction of *N*-sulfonylimines with dialkylzinc reagents (Figure 1)[8].

Results and Discussion

Figure 1. Chiral imidazolium salts derived from amino acid bearing a pyridine ring and phenyl ring.

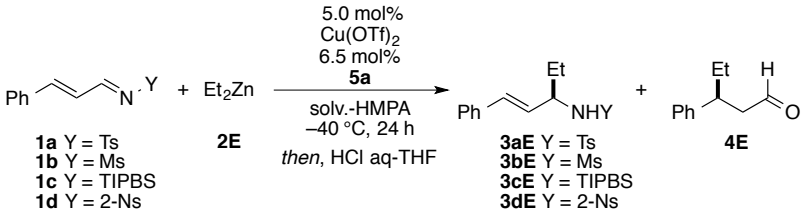


At first, we have examined the reaction of α,β-unsaturated *N*-sulfonylaldimine **1a** with diethylzinc (**2E**) in the presence of 5.0 mol% copper(II) triflate and the chiral imidazolium salt **5a** (6.5 mol%) in toluene at 0 °C. Surprisingly, the main product was the 1,2-adduct (*R*)-**3aE**,[19] with a yield of 64% and an ee of 85%, while the 1,4-adduct (*S*)-**4E**[20] was obtained in 25% yield (Table 1, entry 1). Generally, in the case of copper-catalyzed addition reactions of organometallic reagents to α,β-unsaturated carbonyl compounds in the absence of an NHC ligand, the predominant reaction is 1,4-addition, as shown in Table 1, entry 2. These results indicate that the NHC ligand generated from the chiral imidazolium salt **5a** controls the chemoselectivity of this

reaction system. In the absence of hexamethylphosphoric triamide (HMPA), although the desired ethylated products **3aE** and **4E** were obtained in 22% yield and 52% yield, respectively, there was no enantioselectivity (Table 1, entry 3). We have found that HMPA was efficient co-solvent for chemical yield and enantioselectivity (entry 3). The enantioselectivity increased to 89% ee when the reaction was carried out at –40 °C (entry 4). To confirm the influence of the substituent on the imine nitrogen group on the chemoselectivity of the reaction, we examined various substituents on the *N*-sulfonyl group (entries 5–7). For substrates bearing a methyl or 2,4,6-triisopropylphenyl group on the sulfonyl group (TIPBS), the same levels of chemoselectivity and enantioselectivity were observed as for the 4-tolyl group (entries 5 and 6). When there was a 2-nitrophenyl group on the sulfonyl group, the reaction did not proceed at all, and the starting **1d** was recovered (entry 7).

Since it was evident that the reaction was influenced by the solvent,, we examined different solvents in the ethylation of α,β-unsaturated *N*-tosylaldimine **1a** with diethylzinc (entries 8–11). When dichloromethane was used as a solvent, the reaction proceeded smoothly to give the ethylated product **3aE** in 55% yield with 69% ee (entry 8). In addition, diethylether and THF, which are coordinative solvents, were also effective to this reaction, affording **3aE** with good enantioselectivity (entries 9 and 10). When acetonitrile was used as a solvent, the reaction proceeded slowly, affording an almost 1:1 mixture of 1,2- and 1,4-adducts with lower enantioselectivity (entry 11).

Table 1. Asymmetric ethylation of *N*-α,β-unsaturated *N*-sulfonylaldimines with diethylzinc in the presence of Copper salts.

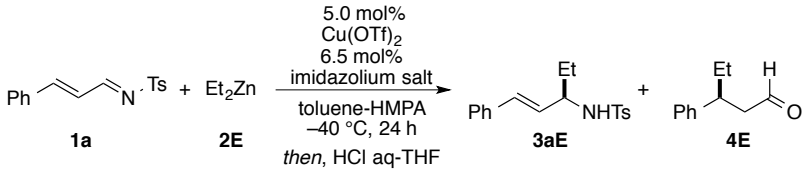


Entry[a]	**1**	Solvent	Yield of **3**/%	ee of **3**/%	Yield of **4**/%	ee of **4**/%[b]
1[c]	**1a**	toluene	64	85	25	30
2[c, d]	**1a**	toluene	21	-	60	-
3[e]	**1a**	toluene	22	0	52	2
4	**1a**	toluene	64	89	17	29
5	**1b**	toluene	63	87	21	22
6	**1c**	toluene	50	89	28	28
7	**1d**	toluene	nr	-	nr	-
8	**1a**	CH_2Cl_2	55	69	26	27
9	**1a**	Et_2O	52	82	24	29
10	**1a**	THF	62	83	27	26
11	**1a**	MeCN	47	47	38	21

[a] 2.0 equiv of **2E** and 10 equiv of HMPA were used unless otherwise noted. [b] The ee was determined by HPLC after conversion to the corresponding alcohol using $NaBH_4$. [c] The reaction was carried out at 0 °C. [d] In the absence of HMPA and **5a**. [e] In the absence of HMPA.

We examined the various kind of chiral imizolium salts **5**–**13**. We found that Cl^- (as in **5a**) was suitable counter anion of the imidazolium salt, however, the reactions using chiral imidazolium salts with Br^- (**5b**), BF_4^- (**5c**), and PF_6^- (**5d**) all resulted in slightly lower enantioselectivities, especially in the case of **5c**, in which the 1,2- and 1,4-adducts were obtained in a ratio of almost 1:1 (Table 2, entries 1–4). Next, we carried out present asymmetric ethylation of the α,β-unsaturated *N*-tosylaldimine **1a** with the imidazolium salt **6** bearing a phenyl ring. The reaction proceeded slower than that using **5a**, affording the product **3aE** in 39% yield with 70% ee (entry 5). This result indicated clealy that the pyridinyl group is critical in realizing the high chemical yield and stereoselectivity. Furthermore, introduction of a nitrogen atom onto the C3-position of the aromatic ring (**7**) lowered the enantioselectivity (entry 6). Chiral imidazolium salts prepared from L-alanine (**8**), L-phenylalanine (**9**), and L-proline (**10**) were examined in the present asymmetric reaction (entries 7-9). In all cases, reaction proceeded efficiently, however, the enantioselectivities of the product was lower. The amidocarbonyl group of the imidazolium salt played an important role for the enantioselectivity. Thus, the imidazolium salt **5a** bearing pivaloyl group was found to be the best ligand for the present catalytic asymmetric reaction, affording **3aE** with 89% ee, whereas, chiral imidazolium salts bearing isobutylamide or benzamide groups were not effective to this reaction (entries 10 and 11). Finally, the hydrogen atom of the amidocarbonyl group was found to be a critical factor in realizing high enantio- and chemoselectivity. Thus, when a imidazolium salt **13** bearing phthalimide group was used for asymmetric copper-catalyzed ethylation of **1a**, the significant decreace of enantioselectivity was observed, and the 1,4-adduct **4E** was obtained as the major product with a yield of 60% and 10% ee (entry 12).

Table 2. Copper-catalyzed asymmetric ethylation of α,β-unsaturated *N*-tosylaldimine using various chiral imidazolium salts.

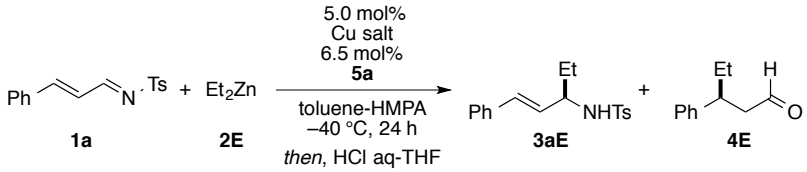


Entry[a]	Imidazolium salt	Yield of **3**/%	ee of **3**/%	Yield of **4**/%	ee of **4**/%
1	**5a**	64	89	17	29
2	**5b**	63	86	25	37
3	**5c**	48	88	35	16
4	**5d**	69	88	23	38
5	**6**	39	70	15	30
6	**7**	17	66	22	36
7	**8**	49	32	38	13
8	**9**	52	44	30	27
9	**10**	45	–29	26	23
10	**11**	72	75	19	24
11	**12**	49	63	37	24
12	**13**	26	45	60	–10

[a] 2.0 equiv of **2E** and 10 equiv of HMPA were used.

The use of other copper salts in the asymmetric alkylation of α,β-unsaturated *N*-tosylaldimine was also investigated (Table 3). In the case of $CuCl_2 \cdot 2H_2O$ in particular, higher chemoselectivity was observed, and the chiral allylic amine **3aE** was obtained in 75% yield with 91% ee (entry 2). Other copper(I) salts were also good candidates in this reaction, affording the product with excellent enantioselectivity and high yields, whereas only in the case of CuCN, the 1,4-adduct was obtained as the major product in 64% with 4% ee (entry 11).

Table 3. The effect of copper salts in the catalytic asymmetric ethylation of α,β-unsaturated *N*-tosylaldimine



1a **2E** **3aE** **4E**

Entry[a]	Cu salt	Yield of **3**/%	ee of **3**/%	Yield of **4**/%	ee of **4**/%
1	$Cu(OTf)_2$	64	89	17	29
2	$CuCl_2 \cdot 2H_2O$	75	91	11	54
3	$CuCl_2$	68	90	21	53
4	$Cu(acac)_2$	72	90	14	41
5	$(CuOTf)_2$-PhH	76	89	12	47
6	$Cu(MeCN)_4BF_4$	70	89	15	41
7	CuTC[b]	74	90	10	62
8	CuCl	72	90	9	44
9	CuBr	70	91	15	34
10	CuI	73	89	17	51
11	CuCN	17	88	64	4

[a] 2.0 equiv of **2E** and 10 equiv of HMPA were used.. [b] CuTC = copper(I) thiophene-2-carboxylate.

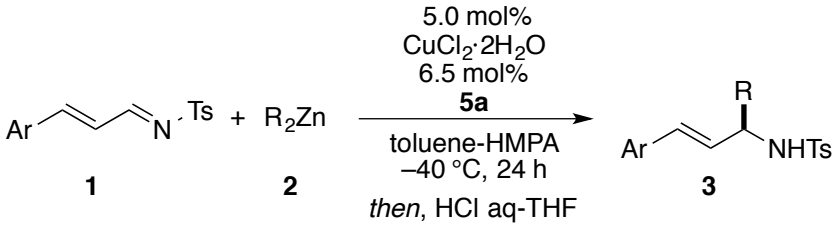
Under the optimized reaction conditions, the scope of the catalytic asymmetric alkylation was demonstrated with various kinds of β-aryl α,β-unsaturated *N*-tosylaldimines and dialkylzinc reagents (Table 4). It was gratifying to observe that

wide range of α,β-unsaturated *N*-tosylaldimines were applicable to the present catalytic system when the reactions were carried out using 5 mol% $CuCl_2 \cdot 2H_2O$ and 6.5 mol% of the imidazolium salt **5a**. The α,β-unsaturated *N*-tosylaldimines **1e** and **1f**, bearing a 1- or 2-naphthyl group at the β-position, were good substrates, giving the 1,2-adducts **3eE** and **3fE** as major products with 82% ee and 86% ee, respectively (entries 2 and 3). Even the relatively deactivated α,β-unsaturated *N*-tosylaldimine **1g**, derived from 4-methoxycinnamaldehyde, was successfully used in the reaction, affording the product **3gE** in 53% yield with 91% ee (entry 4). Other substituted α,β-unsaturated *N*-tosylaldimines bearing an electron-withdrawing group at the *para*-position of the phenyl group at the β-position were investigated: the reactions of diethylzinc (**2E**) with α,β-unsaturated *N*-tosylaldimines **1h** and **1i**, derived from 4-(trifluoromethyl)cinnamaldehyde and 4-bromocinnamaldehyde, gave the products **3hE** and **3iE** with 85% ee and 88% ee, respectively (entries 5 and 6). The reaction of **1j**, derived from 3-(furan-2-yl)acrylaldehyde, gave **3jE** in 62% yield with 91% ee (entry 7).

The reactions of **1k**, **1l**, and **1m**, which contain a 2-, 3-, or 4-methylphenyl group at the β-position, gave **3kE**, **3lE**, and **3mE** with 85% ee, 89% ee, and 88% ee, respectively, and a significant improvement in chemoselectivity was achieved by introducing a 2-substituted phenyl group at the β-position (entries 8–10). Since a trimethylsilyl (TMS) group on a phenyl ring is easily convertible to a proton or halogen, the ethylation reaction was examined using the 2-TMS-cinnamaldehyde imine **1n**. The ratio of the 1,2- to 1,4- product was dramatically improved to 11:1, giving **3nE** in 80% yield with 90% ee (entry 11). Furthermore, the α,β-unsaturated *N*-tosylaldimine **1o**, bearing a bulky 2,4,6-trimethylphenyl group at the β-position, was found to be 1,2-selectively converted to **3oE**, with 88% ee and a yield of 93% (entry 12). Diisopropylzinc (**2I**) was also employed in this reaction, and the reaction proceeded with high chemoselectivity to afford the 1,2-adduct (*R*)-**3nI** with 72% ee and 87% yield (entry 13). On the other hand, the methylation of **1n** with 5.0 equiv of dimethylzinc (**2M**) was sluggish at 0 °C, generating (*R*)-**3nM** with 88% ee and a yield of 59% after 120 h (entry 14). Alkylation of **1o** with diisopropylzinc (**2I**) and dimethylzinc (**2M**) selectively afforded the 1,2-adducts **3oI** and **3oM** with good enantioselectivities (entries 15 and 16). Furthermore, diphenylzinc (**2P**) and diallylzinc (**2A**) were employed in this reaction. The reactions of **1n** and **1o** with diphenylzinc (**2P**) proceeded smoothly to afford the

products **3nP** and **3oP** with good to high enantioselectivities but chemoselectivities were lower (entries 17 and 18). In the case of diallylzinc (**2A**), the 1,2-adducts were obtained predominantly in excellent yields, however, no enantioselectivities were observed (entries 19 and 20).

Table 4. Catalytic asymmetric 1,2-addition reactions of α,β-unsaturated *N*-tosylaldimines with various dialkylzinc reagents.

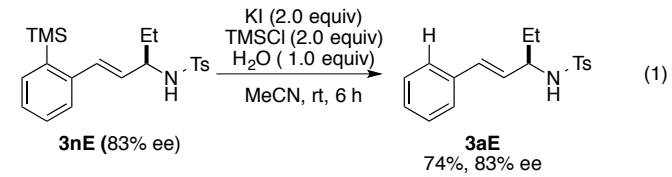


Entry [a]	Ar	R	Yield of	ee of	1,2-/1,4-
			3/%	**3**/%	
1	C_6H_5 (**1a**)	Et (**2E**)	75 (**3aE**)	91	7:1
2 [d]	1-naphthyl (**1e**)	Et (**2E**)	60 (**3eE**)	82	3:1
3 [d]	2-naphthyl (**1f**)	Et (**2E**)	63 (**3fE**)	86	3:1
4	4-$MeOC_6H_4$ (**1g**)	Et (**2E**)	53 (**3gE**)	91	3:1
5	4-$CF_3C_6H_4$ (**1h**)	Et (**2E**)	71 (**3hE**)	85	6:1
6	4-BrC_6H_4 (**1i**)	Et (**2E**)	67 (**3iE**)	88	5:1
7	2-furyl (**1j**)	Et (**2E**)	62 (**3jE**)	91	3:1
8	2-MeC_6H_4 (**1k**)	Et (**2E**)	60 (**3kE**)	85 [f]	15:1
9 [e]	3-MeC_6H_4 (**1l**)	Et (**2E**)	69 (**3lE**)	89	4:1
10 [e]	4-MeC_6H_4 (**1m**)	Et (**2E**)	56 (**3mE**)	88	2:1
11 [d]	2-$TMSC_6H_4$ (**1n**)	Et (**2E**)	80 (**3nE**)	90	11:1
12 [d,]	2,4,6-$Me_3C_6H_2$ (**1o**)	Et (**2E**)	93 (**3oE**)	88	>20:1
13 [d]	2-$TMSC_6H_4$ (**1n**)	*i*-Pr (**2I**)	87 (**3nI**)	72	15:1
14 [h]	2-$TMSC_6H_4$ (**1n**)	Me (**2M**)	59 (**3nM**)	88	3:1
15 [d,g]	2,4,6-$Me_3C_6H_2$ (**1o**)	*i*-Pr (**2I**)	93 (**3oI**)	73	>20:1
16 [h]	2,4,6-$Me_3C_6H_2$ (**1o**)	Me (**2M**)	55 (**3oM**)	79	nd[i]
17 [d i]	2-$TMSC_6H_4$ (**1n**)	Ph (**2P**)	60 (**3nP**)	86	3:1

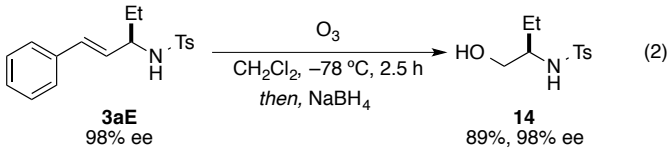
18 [d i]	2,4,6-$Me_3C_6H_2$ (**1o**)	Ph (**2P**)	37 (**3oP**)	70	1:1
19 [d j]	2-$TMSC_6H_4$ (**1n**)	CH_2=CH-CH_2 (**2A**)	99 (**3nA**)	0	>20:1
20 [d j]	2,4,6-$Me_3C_6H_2$ (**1o**)	CH_2=CH-CH_2 (**2A**)	99 (**3oA**)	0	>20:1

[a] 2.0 equiv of **2** and 10 equiv of HMPA were used unless otherwise noted. [b] The ratio was determined by ^{1}H-NMR. [c] The absolute configurations of **3**, except for **3aE**, were determined based on the analogous reactions in Table 1 (also see reference 18). [d] The reaction was carried out at 0 °C. [e] The reaction was carried out at –20 °C. [f] The ee was determined by HPLC using the corresponding amino alcohol, which was prepared from **3kE** by treatment of ozonolysis followed by reduction. [g] Using 3.0 equiv of **2E**. [h] Using 5.0 equiv of **2M** at 0 °C for 120 h. [i] The peaks of the 1,2- and 1,4-adducts overlapped in ^{1}H-NMR. [j] Diphenylzinc was prepared by following literature.[21] [j] Diallylzinc was prepared by following literature[22].

The 2-TMS group on the phenyl ring of **3nE** was easily converted to other functional groups. Thus, **3nE** was protodesilylated with potassium iodide and TMSCl in the presence of water to afford (*R*)-**3aE** in 74% yield without any racemization (eq. 1).[23] The chiral allylic amines obtained from these catalytic asymmetric reactions could be transformed to the corresponding 2-aminoalcohols. We demonstrated ozonolysis of **3aE** with 98% ee, which was obtained by recrystallization, followed by reduction to afford the 2-aminoalcohol **14** in 89% yield without any loss of enantioselectivity (eq. 2).[24]



3nE (83% ee) **3aE** 74%, 83% ee



3aE 98% ee **14** 89%, 98% ee

Conclusion

Asymmetric 1,2-addition of dialkylzinc reagents to α,β-unsaturated *N*-tosylaldimines was catalyzed by copper salt in the presence of chiral imidazolium salts having a pyridine ring, which were derived from amino acid, to afford the corresponding chiral allylic amines with up to 91% ee in reasonably high yields. We have found that the chiral NHC ligand played an important role in controlling chemo- and enantioselectivity. In addition, the obtained allylic amine was able to convert the corresponding chiral amino alcohol without any loss of enantioselectivities.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded using a 400 MHz NMR spectrometer. Chemical shifts were given in ppm downfield from TMS with chloroform as an internal standard. Infrared spectra (IR) were recorded as FT-IR spectra are reported in terms of frequency of absorption (cm^{-1}). HRMS (FAB and DART) were measured with a quadrupole and TOF mass spectrometers. Unless otherwise noted, all reagents were reagent grade and used without further purification.

The substrates **1** were prepared following the reported literatures.[8, 25]

4-Methyl-*N*-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (1a)

White solid of mp = 116–117 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.44 (s, 3H), 7.00 (dd, *J* = 9.6, 14.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.40–7.56 (m, 6H), 7.86 (d, *J* = 8.0 Hz, 2H), 8.79 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 124.6, 127.9, 128.6, 129.1, 129.7, 131.6, 134.0, 135.2, 144.4, 153.8, 170.8. IR (KBr): 2980, 1620, 1580, 1490, 1450, 1360, 1310, 1290, 1170, 1150, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{16}H_{16}NO_2S$ $[M+H]^+$: 286.0902. Found: 286.0892.

N-((1*E*,2*E*)-3-Phenylallylidene)methanesulfonamide (1b)

White solid of mp = 103–104 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 3.07 (s, 3H), 7.00 (dd, *J* = 9.6, 16.0 Hz, 1H), 7.34–7.59 (m, 6H), 8.75 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 40.2, 124.2, 128.4, 128.6, 129.1, 131.7, 133.9, 154.4. IR (KBr): 2970, 1620, 1580, 1460, 1360, 1310, 1260, 1160, 1040 1010, 970 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{10}H_{12}NO_2S$ $[M+H]^+$: 210.0589. Found: 210.0596.

2,4,6-Triisopropyl-*N*-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (1c)

White solid of mp = 163–165 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 1.19–1.26 (m, 18H), 2.89 (septet, *J* = 6.8 Hz, 1H), 4.21 (septet, *J* = 6.8 Hz, 2H), 6.98 (dd, *J* = 9.6, 15.6 Hz, 1H), 7.16 (s, 2H), 7.40–7.55 (m, 6H), 8.72 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 23.5, 24.7, 29.7, 34.2, 123.8, 125.0, 128.5, 129.1, 131.0, 131.4, 134.2, 151.0, 152.8, 153.5, 169.3. IR (KBr): 2950, 1620, 1580, 1460, 1360, 1300, 1260, 1150, 1040 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{24}H_{32}NO_2S$ $[M+H]^+$: 398.2154. Found: 398.2150.

2-Nitro-*N*-((1*E*,2*E*)-3-phenylallylidene)benzenesulfonamide (1d)

White solid of mp = 150–152 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 7.04 (dd, *J* = 9.6, 16.0 Hz, 1H), 7.43–7.46 (m, 3H), 7.58–7.60 (m, 2H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.77–7.89 (m, 3H), 8.34–8.36 (m, 1H), 8.81 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 124.2, 124.7, 129.0, 129.2, 131.9, 132.0, 132.1, 132.6, 134.0, 134.5, 143.8, 156.0, 174.5. IR (KBr): 2960, 1610, 1580, 1540, 1460, 1360, 1320, 1260, 1160, 1120, 1050 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{15}H_{13}N_2O_4S$ $[M+H]^+$: 317.0596. Found: 317.0587.

4-Methyl-*N*-((1*E*,2*E*)-3-(naphthalen-1-yl)allylidene)benzenesulfonamide (1e)

White solid of mp = 152–153 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.45 (s, 3H), 7.12 (dd, *J* = 8.4, 15.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.51–7.65 (m, 3H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.89–7.92 (m, 3H), 7.96 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 15.6 Hz, 1H), 8.93 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 122.6, 125.4, 125.8, 126.4, 126.6, 127.4, 127.9, 128.9, 129.8, 130.9, 131.1, 132.0, 133.6, 135.3, 144.5, 150.2, 170.8. IR (KBr): 2960, 1620, 1590, 1370, 1320, 1180, 1150, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{20}H_{18}NO_2S$ $[M+H]^+$: 336.1058. Found: 336.1054.

4-Methyl-*N*-((1*E*,2*E*)-3-(naphthalen-2-yl)allylidene)benzenesulfonamide (1f)

White solid of mp = 166–167 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.44 (s, 3H), 7.10 (dd, J = 9.6, 15.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.56 (m, 2H), 7.65 (d, J = 15.6 Hz, 1H), 7.67–7.68 (m, 1H), 7.83–7.89 (m, 5H), 7.98 (s, 1H), 8.83 (d, J = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 123.2, 124.8, 127.0, 127.8, 127.9, 128.0, 128.8, 129.1, 129.8, 131.3, 131.7, 133.1, 134.7, 135.4, 144.4, 153.8, 170.8. IR (KBr): 2950, 1610, 1560, 1340, 1310, 1290, 1240, 1160, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{20}H_{18}NO_2S$ $[M+H]^+$: 336.1058. Found: 336.1057.

***N*-((1*E*,2*E*)-3-(4-Methoxyphenyl)allylidene)-4-methylbenzenesulfonamide (1g)**

White solid of mp = 101–103 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.43 (s, 3H), 3.86 (s, 3H), 6.88 (dd, J = 9.6, 15.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 15.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 8.74 (d, J = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 55.5, 114.6, 122.3, 127.0, 127.8, 129.2, 130.6, 135.6, 144.2, 153.9, 162.6, 171.1. IR (KBr): 2950, 1630, 1600, 1570, 1360, 1300, 1260, 1150, 1080, 1010 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{17}H_{18}NO_3S$ $[M+H]^+$: 316.1007. Found: 316.0998.

4-Methyl-*N*-((1*E*,2*E*)-3-(4-(trifluoromethyl)phenyl)allylidene)benzenesulfonamide (1h)

White solid of mp = 153–155 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.45 (s, 3H), 7.04 (d, J = 9.2, 15.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 15.6 Hz, 1H), 7.63–7.68 (m, 4H), 7.86 (d, J = 8.0 Hz, 2H), 8.79 (d, J = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 123.6 ($^1J_{C\text{-}F}$ = 271.8 Hz), 126.1 ($^3J_{C\text{-}F}$ = 2.9 Hz), 128.0, 128.6, 129.9, 132.7 ($^2J_{C\text{-}F}$ = 32.4 Hz), 134.9, 137.3, 144.8, 151.1, 170.1. IR (KBr): 2960, 1630, 1590, 1460, 1320, 1160, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{17}H_{15}NO_2SF_3$ $[M+H]^+$: 354.0776. Found: 354.0772.

***N*-((1*E*,2*E*)-3-(4-Bromophenyl)allylidene)-4-methylbenzenesulfonamide (1i)**

White solid of mp = 193–194 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.44 (s, 3H), 6.96 (dd, J = 9.2, 16.0 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7..39–7.44 (m, 3H), 7.57 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.8 Hz, 2H), 8.77 (d, J = 9.2

Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.6, 125.2, 126.1, 127.9, 129.6, 129.8, 132.4, 133.0, 135.1, 144.6, 152.0, 170.5. IR (KBr): 2960, 1620, 1570, 1480, 1320, 1160, 1090, 1070, 1000 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{16}H_{15}NO_2SBr$ $[M+H]^+$: 364.0007. Found: 364.0000.

_N_-((1_E_,2_E_)-3-(Furan-2-yl)allylidene)-4-methylbenzenesulfonamide (1j)

White solid of mp = 110–111 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.43 (s, 3H), 6.54 (dd, *J* = 1.6, 3.2 Hz, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.84 (dd, *J* = 9.6, 15.2 Hz, 1H), 7.22 (d, *J* = 15.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.68 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.5, 113.1, 117.6, 122.1, 127.8, 129.7, 135.4, 138.5, 144.3, 146.5, 150.8, 170.2. IR (KBr): 2960, 1630, 1590, 1460, 1390, 1350, 1310, 1290, 1170, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{14}H_{14}NO_3S$ $[M+H]^+$: 276.0694. Found: 276.0703.

4-Methyl-_N_-((1_E_,2_E_)-3-(_o_-tolyl)allylidene)benzenesulfonamide (1k)

White solid of mp = 122–124 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.44 (s, 3H), 2.46 (s, 3H), 6.94 (dd, *J* = 9.6. 15.6 Hz, 1H), 7.25–7.26 (m, 2H), 7.31–7.35 (m, 3H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 8.81 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 19.7, 21.6, 125.5, 126.7, 126.8, 127.9, 129.8, 131.1, 131.4, 132.9, 135.4, 138.3, 144.5, 151.4, 171.1. IR (KBr): 2980, 1620, 1580, 1350, 1310, 1290, 1170, 1150, 1080 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1058. Found: 300.1064.

4-Methyl-_N_-((1_E_,2_E_)-3-(_m_-tolyl)allylidene)benzenesulfonamide (1l)

White solid of mp = 90–91 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.38 (s, 3H), 2.44 (s, 3H), 6.97 (dd, *J* = 9.6, 15.6 Hz, 1H), 7.24–7.37 (m, 6H), 7.46 (d, *J* = 15.6 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.77 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.2, 21.5, 124.4, 125.7, 127.8, 129.0, 129.2, 129.7, 132.4, 134.0, 135.4, 138.8, 144.4, 154.1, 170.9. IR (KBr): 2970, 1620, 1570, 1320, 1290, 1160, 1150, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1058. Found: 300.1063.

4-Methyl-_N_-((1_E_,2_E_)-3-(_p_-tolyl)allylidene)benzenesulfonamide (1m)

White solid of mp = 150–151 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR

($CDCl_3$): 2.40 (s, 3H), 2.44 (s, 3H), 6.94 (dd, *J* = 9.6, 15.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 15.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 8.75 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.5, 123.5, 127.8, 128.6, 129.7, 129.8, 131.4, 135.3, 142.4, 144.3, 154.0, 171.0. IR (KBr): 2960, 1610, 1580, 1460, 1370, 1320, 1300, 1180, 1160, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1058. Found: 300.1056.

4-Methyl-*N*-((1*E*,2*E*)-3-(2-(trimethylsilyl)phenyl)allylidene)benzenesulfonamide (1n)

White solid of mp = 124–125 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 0.39 (s, 9H), 2.45 (s, 3H), 6.93 (dd, *J* = 9.2, 15.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.39–7.43 (m, 2H), 7.58–7.60 (m, 1H), 7.67–7.69 (m, 1H), 7.85–7.86 (m, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 8.81 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): 0.0, 21.2, 125.0, 126.3, 127.5, 129.3, 129.4, 129.9, 134.7, 135.0, 139.1, 142.0, 144.1, 154.3, 170.3. IR (KBr): 2960, 1620, 1580, 1320, 1260, 1160, 1120, 1090, 970 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{19}H_{24}NO_2SSi$ $[M+H]^+$: 358.1297. Found: 358.1298.

***N*-((1*E*,2*E*)-3-Mesitylallylidene)-4-methylbenzenesulfonamide (1o)**

White solid of mp = 157–158 °C (recrystallized from hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$): 2.30 (s, 3H), 2.36 (s, 6H), 2.44 (s, 3H), 6.68 (dd, *J* = 9.2, 15.6 Hz, 1H), 6.92 (s, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J*= 15.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 8.78 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): 21.3, 21.5, 21.6, 127.9, 129.2, 129.8, 129.9, 130.2, 135.4, 137.8, 140.3, 144.5, 152.9, 171.7. IR (KBr): 2920, 1620, 1580, 1380, 1320, 1290, 1180, 1150, 1090 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{19}H_{22}NO_2S$ $[M+H]^+$: 328.1371. Found: 328.1359.

General procedure for the alkylation of β-Aryl-α,β-unsaturated *N*-Toluenesulfonylaldimines with dialkylzinc reagentes catalyzed by NHC-copper(I) complex

Under Ar atmosphere, the solution of imidazolium salt **4** (11.4 mg, 0.033 mmol) in 0.9 mL of HMPA and 2 mL of toluene was added to $CuCl_2{\cdot}2H_2O$ (4.2 mg, 0.025 mmol). The mixture was diluted with toluene (10.1 mL) and the whole was cooled to –40 °C. After 15 min, a hexane solution of dialkyllzinc (1.0 mL, 1.0 mmol) was added dropwise

over 3 min at –40 °C and stirred for 30 min. A solution of imine **1** (0.5 mmol) in 3.0 mL of toluene was added dropwise over 4 min at –40 °C. After 24 h, the reaction was quenched with satd. NH_4Cl aq and stirred at room temperature for another 0.5 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with satd. $NaHCO_3$ and brine, and then dried over Na_2SO_4. Concentration gave a pale yellow oil, which was treated with 6 M HCl aq (1 mL) in THF (5 mL) for 0.5 h at room temperature. The reaction mixture was neutralized by satd. $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, and then dried over Na_2SO_4. Concentration and purification by silica gel column chromatography.

In the case of the asymmetric methylation, dimethylzinc (1.0 M in toluene) was used.

Absolute configuration of (*R*)-**3aE** was determined by comparison of the specific rotation with the reported value[18]. Those of other **3** were assigned by the reaction analogy.

(*R*,*E*)-4-Methyl-*N*-(1-phenylpent-1-en-3-yl)benzenesulfonamide (3aE)

Silica gel column chromatography (hexane/ ethyl acetate = 20/1~3/1) gave **3aE** (119 mg, 75% yield, 0.5 mmol scale) as a white solid of mp = 98–99 °C and $[\alpha]^{25}_{D}$ +97.5 (*c* 0.53, $CHCl_3$). The ee was determined to be 91% by HPLC (Daicel Chiralcel IA, hexane/*i*-PrOH = 20/1, 0.7 mL/min, 254 nm, major 37.9 min and minor 33.9 min). ^{1}H NMR ($CDCl_3$): 0.89 (t, *J* = 7.2 Hz, 3H), 1.57–1.64 (m, 2H), 2.31 (s, 3H), 3.84–3.88 (m, 1H), 4.46 (d, *J* = 8.0 Hz, 1H), 5.71 (dd, *J* = 7.6, 15.6 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.18–7.27 (m, 5H), 7.72 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.3, 38.8, 57.8, 126.2, 127.2, 127.5, 128.3, 128.6, 129.4, 131.4, 136.2, 138.0, 143.1. IR (KBr): 3260, 2960, 1600, 1500, 1460, 1440, 1320, 1160, 1030, 970 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{18}H_{22}NO_2S$ $[M+H]^+$: 316.1371. Found: 316.1368.

(*R*,*E*)-*N*-(1-Phenylpent-1-en-3-yl)methanesulfonamide (3bE)

Silica gel column chromatography (hexane/ ethyl acetate = 20/1~3/1) gave **3bE** (75 mg, 63% yield, 0.5 mmol scale) as a colorless oil and $[\alpha]^{25}_{D}$ +47.8 (*c* 0.21, $CHCl_3$). The ee was determined to be 87% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.5

mL/min, 254 nm, major 22.5 min and minor 17.1 min). ^{1}H NMR ($CDCl_3$): 1.00 (t, J = 7.2 Hz, 3H), 1.66–1.71 (m, 2H), 2.95 (s, 3H), 3.97–4.04 (m, 1H), 4.59 (d, J = 6.4 Hz, 1H), 6.05 (dd, J = 8.4, 15.6 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 7.25–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$): 10.2, 29.1, 42.2, 58.0, 126.4, 128.0, 128.6, 129.2, 132.0, 136.0. IR (KBr): 3280, 2970, 1600, 1490, 1450, 1440, 1320, 1150, 1040, 970 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{12}H_{18}NO_2S$ $[M+H]^+$: 240.1058. Found: 240.1041.

(*R*,*E*)-2,4,6-Triisopropyl-*N*-(1-phenylpent-1-en-3-yl)benzenesulfonamide (3cE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3cE** (107 mg, 50% yield, 0.5 mmol scale) as a colorless oil and $[\alpha]^{25}_D$ +63.7 (*c* 0.27, $CHCl_3$). The ee was determined to be 89% by HPLC (Daicel Chiralcel IB x2, hexane/*i*-PrOH = 20/1, 0.7 mL/min, 254 nm, major 11.9 min and minor 8.8 min). ^{1}H NMR ($CDCl_3$): 0.92 (t, J = 7.2 Hz, 3H), 1.18 (d, J = 7.6 Hz, 3H), 1.19 (d, J = 7.6 Hz, 3H), 1.22 (d, J = 7.2 Hz, 6H), 1.26 (d, J = 6.8 Hz, 6H), 1.59–1.67 (m, 2H), 2.82 (septet, J = 7.2 Hz, 1H), 3.94–3.97 (m, 1H), 4.13 (septet, J = 6.8 Hz, 2H), 4.45 (d, J = 6.0 Hz, 1H), 5.71 (dd, J = 7.6, 15.6 Hz, 1H), 6.22 (d, J = 15.6 Hz, 1H), 7.02–7.03 (m, 2H), 7.08 (s, 2H), 7.15–7.25 (m, 3H). ^{13}C NMR ($CDCl_3$): 10.0, 23.5, 24.6, 24.6, 24.9, 29.0, 29.7, 34.0, 57.5, 123.6, 126.2, 127.6, 128.3, 128.8, 131.6, 134.2, 136.2, 149.6, 152.4. IR (KBr): 3290, 2960, 1600, 1560, 1490, 1460, 1390, 1320, 1150, 1060, 960 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{26}H_{38}NO_2S$ $[M+H]^+$: 428.2623. Found: 428.2606.

(*R*,*E*)-4-Methyl-*N*-(1-(naphthalen-1-yl)pent-1-en-3-yl)benzenesulfonamide (3eE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3eE** (110 mg, 60% yield, 0.5 mmol scale) as a yellow solid of mp = 144–146 °C and $[\alpha]^{25}_D$ +63.1 (*c* 0.36, $CHCl_3$). The ee was determined to be 82% by HPLC (Daicel Chiralcel IB x2, hexane/*i*-PrOH = 20/1, 0.8 mL/min, 240 nm, major 88.2 min and minor 82.5 min). ^{1}H NMR ($CDCl_3$): 0.97 (t, J = 7.2 Hz, 3H), 1.63–1.73 (m, 2H), 2.27 (s, 3H), 3.96–4.04 (m, 1H), 4.70 (brs, 1H), 5.79 (dd, J = 7.6, 15.6 Hz, 1H), 7.01 (d, J = 15.6 Hz, 1H), 7.17–7.21 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.45–7.49 (m, 2H), 7.72–7.82 (m, 5H). ^{13}C NMR ($CDCl_3$): 10.0, 21.4, 29.2, 57.9, 123.6, 123.8, 125.4, 125.8, 126.0, 127.2, 128.0, 128.4, 128.9, 129.6, 130.9, 132.0, 133.4, 134.0, 138.2, 143.2. IR (KBr): 3290, 2960, 1590, 1490, 1430, 1400, 1330, 1160, 1080, 970 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{22}H_{24}NO_2S$ $[M+H]^+$: 366.1528. Found: 366.1517.

(*R*,*E*)-4-Methyl-*N*-(1-(naphthalen-2-yl)pent-1-en-3-yl)benzenesulfonamide (3fE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3fE** (115 mg, 63% yield, 0.5 mmol scale) as a white solid of mp = 144–146 °C and $[\alpha]^{25}_{D}$ +86.2 (*c* 0.36, $CHCl_3$). The ee was determined to be 86% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 25.0 min and minor 22.4 min). ^{1}H NMR ($CDCl_3$): 0.92 (t, *J* = 7.6 Hz, 3H), 1.57–1.71 (m, 2H), 2.25 (s, 3H), 3.88–3.95 (m, 1H), 4.63 (d, *J* = 7.6 Hz, 1H), 5.53 (dd, *J* = 7.6, 15.6 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 4.6, 8.8 Hz, 1H), 7.41–7.48 (m, 3H), 7.70–7.78 (m, 5H). ^{13}C NMR ($CDCl_3$): 10.0, 21.3, 28.9, 57.9, 123.4, 125.9, 126.3, 126.4, 127.2, 127.3, 127.6, 127.9, 129.1, 129.5, 131.7, 132.9, 133.4, 133.7, 138.2, 143.2. IR (KBr): 3250, 2930, 1600, 1500, 1420, 1330, 1160, 1080, 1040, 980 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{22}H_{24}NO_2S$ $[M+H]^+$: 366.1528. Found: 366.1529.

(*R*,*E*)-*N*-(1-(4-Methoxyphenyl)pent-1-en-3-yl)-4-methylbenzenesulfonamide (3gE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3gE** (92 mg, 53% yield, 0.5 mmol scale) as a white solid of mp = 95–97 °C and $[\alpha]^{25}_{D}$ +94.3 (*c* 0.45, $CHCl_3$). The ee was determined to be 91% by HPLC (Daicel Chiralcel IB x 2, hexane/*i*-PrOH = 20/1, 0.5 mL/min, 254 nm, major 103.6 min and minor 100.4 min). ^{1}H NMR ($CDCl_3$): 0.80 (t, *J* = 7.6 Hz, 3H), 1.43–1.59 (m, 2H), 2.26 (s, 3H), 3.74 (s, 3H), 3.72–3.79 (m, 1H), 4.40 (brs, 1H), 5.50 (dd, *J* = 8.0, 15.6 Hz, 1H), 6.08 (d, *J* = 15.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 10.0, 21.4, 29.0, 55.3, 57.8, 113.4, 126.4, 127.3, 127.5, 129.0, 129.5, 131.1, 138.2, 143.1, 159.2. IR (KBr): 3300, 2960, 1610, 1510, 1460, 1420, 1330, 1160, 1030, 970 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1477. Found: 346.1452.

(*R*,*E*)-4-Methyl-*N*-(1-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl)benzenesulfonamide (3hE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3hE** (137 mg, 71% yield, 0.5 mmol scale) as a white solid of mp = 67–68 °C and $[\alpha]^{25}_{D}$ +85.4 (*c* 0.85, $CHCl_3$). The ee was determined to be 85% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 17.3 min and minor 16.2 min). ^{1}H

NMR ($CDCl_3$): 0.85 (t, J = 7.2 Hz, 3H), 1.56–1.65 (m, 2H), 2.31 (s, 3H), 3.81–3.92 (m, 1H), 4.66 (d, J = 6.4 Hz, 1H), 5.83 (dd, J = 7.2, 15.6 Hz, 1H), 6.28 (d, J = 15.6 Hz, 1H), 7.18–7.27 (m, 4H), 7.50 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.3, 28.7, 57.5, 123.5 ($^1J_{C\text{-}F}$ = 271.8 Hz), 125.3 ($^3J_{C\text{-}F}$ = 2.9 Hz), 126.5, 127.2, 129.3 ($^2J_{C\text{-}F}$ = 26.7 Hz), 129.5, 130.1, 131.5, 138.1, 139.8, 143.3. IR (KBr): 3270, 2960, 1610, 1420, 1320, 1160, 1100, 1080, 970 cm^{-1}. HRMS–FAB (*m/z*): Calcd for $C_{19}H_{21}F_3NO_2S$ $[M+H]^+$: 384.1245. Found: 384.1263.

(*R*,*E*)-*N*-(1-(4-Bromophenyl)pent-1-en-3-yl)-4-methylbenzenesulfonamide (3iE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3iE** (132 mg, 67% yield, 0.5 mmol scale) as a white solid of mp = 83–84 °C and $[\alpha]^{25}_D$ +78.1 (*c* 1.23, $CHCl_3$). The ee was determined to be 88% by HPLC (Daicel Chiralcel IB x 2, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 17.3 min and minor 16.2 min). ^{1}H NMR ($CDCl_3$): 0.87 (t, J = 7.2 Hz, 3H), 1.54–1.63 (m, 2H), 2.30 (s, 3H), 3.81–3.88 (m, 1H), 4.45 (d, J = 7.6 Hz, 1H), 5.72 (dd, J = 7.2, 15.6 Hz, 1H), 6.17 (d, J = 15.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.3, 28.7, 57.6, 121.2, 127.2, 127.8, 129.4, 129.6, 130.2, 131.3, 135.2, 138.0, 143.1. IR (KBr): 3230, 2960, 1600, 1490, 1460, 1330, 1150, 1080, 980 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{18}H_{21}BrNO_2S$ $[M+H]^+$: 394.0476. Found: 394.0457.

(*R*,*E*)-*N*-(1-(Furan-2-yl)pent-1-en-3-yl)-4-methylbenzenesulfonamide (3jE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3jE** (94 mg, 62% yield, 0.5 mmol scale) as a white solid of mp = 64–66 °C and $[\alpha]^{25}_D$ +124.6 (*c* 0.63, $CHCl_3$). The ee was determined to be 91% by HPLC (Daicel Chiralcel IA, hexane/*i*-PrOH = 20/1, 1.5 mL/min, 254 nm, major 19.5 min and minor 15.2 min). ^{1}H NMR ($CDCl_3$): 0.86 (t, J = 7.2 Hz, 3H), 1.48–1.59 (m, 2H), 2.35 (s, 3H), 3.77–3.86 (m, 1H), 4.60 (brs, 1H), 5.72 (dd, J = 8.8, 15.6 Hz, 1H), 6.07 (d, J = 15.6 Hz, 1H), 6.09 (s, 1H), 6.31 (dd, J = 2.0, 3.6 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.26 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.4, 28.5, 57.3, 108.2, 111.2, 119.9, 127.2, 127.3, 129.5, 138.0, 141.9, 143.2, 151.8. IR (KBr): 3240, 2970, 1640, 1490, 1440, 1320, 1160, 1090, 1070, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{16}H_{20}NO_3S$ $[M+H]^+$: 306.1164 Found: 306.1157.

(*R*,*E*)-4-Methyl-*N*-(1-(*o*-tolyl)pent-1-en-3-yl)benzenesulfonamide (3kE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3kE** (123 mg, 60% yield, 0.5 mmol scale) as a white solid of mp = 53–54 °C and $[\alpha]^{25}_{D}$ +83.8 (*c* 1.22, $CHCl_3$). The ee was determined to be 85% by HPLC (Daicel Chiralcel IA, hexane/*i*-PrOH = 10/1, 1.0 mL/min, 254 nm, major 48.4 min and minor 23.5 min) after conversion to the corresponding amino alcohol **13**. ^{1}H NMR ($CDCl_3$): 0.89 (t, *J* = 7.2 Hz, 3H), 1.51–1.67 (m, 2H), 2.19 (s, 3H), 2.31 (s, 3H), 3.79–3.90 (m, 1H), 5.07 (brs, 1H), 5.62 (dd, *J* = 7.2, 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 7.02–7.13 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 19.5, 21.3, 29.0, 57.9, 125.5, 125.7, 127.1, 127.4, 129.2, 129.4, 130.0, 130.1, 135.2, 135.4, 138.1, 143.0. IR (KBr): 3280, 2970, 1600, 1490, 1460, 1320, 1160, 1100, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{19}H_{24}NO_2S$ $[M+H]^+$: 330.1528. Found: 330.1524.

(*R*,*E*)-4-Methyl-*N*-(1-(*m*-tolyl)pent-1-en-3-yl)benzenesulfonamide (3lE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3lE** (113 mg, 69% yield, 0.5 mmol scale) as a white solid of mp = 84–85 °C and $[\alpha]^{25}_{D}$ +92.8 (*c* 0.68, $CHCl_3$). The ee was determined to be 89% by HPLC (Daicel Chiralcel IA x 2, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 38.3 min and minor 35.1 min). ^{1}H NMR ($CDCl_3$): 0.81 (t, *J* = 7.2 Hz, 3H), 1.43–1.56 (m, 2H), 2.22 (s, 3H), 2.25 (s, 3H), 3.73–3.80 (m, 1H), 4.63 (brs, 1H), 5.62 (dd, *J* = 7.2, 15.6 Hz, 1H), 6.11(d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.2, 21.3, 28.8, 57.8, 123.5, 126.9, 127.2, 128.2, 128.3, 128.4, 129.4, 131.5, 136.2, 137.8, 138.2, 143.0. IR (KBr): 3270, 2930, 1600, 1490, 1430, 1330, 1160, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{19}H_{24}NO_2S$ $[M+H]^+$: 330.1528. Found: 330.1507.

(*R*,*E*)-4-Methyl-*N*-(1-(*p*-tolyl)pent-1-en-3-yl)benzenesulfonamide (3mE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3mE** (92 mg, 56% yield, 0.5 mmol scale) as a white solid of mp = 98–99 °C and $[\alpha]^{25}_{D}$ +98.8 (*c* 0.16, $CHCl_3$). The ee was determined to be 88% by HPLC (Daicel Chiralcel IB x2, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 32.8 min and minor 39.2 min). ^{1}H NMR ($CDCl_3$): 0.88 (t, *J* = 7.2 Hz, 3H), 1.54–1.65 (m, 2H), 2.31 (s, 3H), 2.32 (s, 3H),

3.80–3.88 (m, 1H), 4.41 (d, J = 7.6 Hz, 1H), 5.66 (dd, J = 7.6, 16.0 Hz, 1H), 6.18 (d, J = 16.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 21.3, 21.4, 28.9, 57.8, 126.2, 127.3, 127.6, 129.0, 129.5, 131.5, 133.5, 137.5, 138.1, 143.1. IR (KBr): 3290, 2960, 1600, 1510, 1420, 1310, 1160, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{19}H_{24}NO_2S$ $[M+H]^+$: 330.1528. Found: 330.1515.

(*R*,*E*)-4-Methyl-*N*-(1-(2-(trimethylsilyl)phenyl)pent-1-en-3-yl)benzenesulfonamide (3nE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3nE** (155 mg, 80% yield, 0.5 mmol scale) as a white solid of mp = 82–83 °C and $[\alpha]^{25}_D$ +99.8 (*c* 0.39, $CHCl_3$). The ee was determined to be 90% by HPLC (Daicel Chiralcel IB x 2, hexane/*i*-PrOH = 20/1, 0.5 mL/min, 254 nm, major 38.7 min and minor 41.7min). ^{1}H NMR ($CDCl_3$): 0.21 (s, 9H), 0.80 (t, J = 7.2 Hz, 3H), 1.45–1.63 (m, 2H), 2.23 (s, 3H), 3.77 (m, 1H), 4.85 (d, J = 7.6 Hz, 1H), 5.57 (dd, J = 7.2, 15.2 Hz, 1H), 6.57 (d, J = 15.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 7.09–7.13 (m, 3H), 7.16 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 0.1, 10.0, 21.3, 28.9, 57.9, 125.4, 126.7, 127.2, 129.0, 129.5, 129.9, 132.8, 134.2, 138.1, 138.3, 142.2, 143.2. IR (KBr): 3250, 2960, 1600, 1490, 1430, 1310, 1250, 1170, 1120, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{21}H_{30}NO_2SSi$ $[M+H]^+$: 388.1767. Found: 388.1785.

(*R*,*E*)-*N*-(1-Mesitylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3oE)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3oE** (166 mg, 93% yield, 0.5 mmol scale) as a white solid of mp = 111–113 °C and $[\alpha]^{25}_D$ +82.8 (*c* 0.93, $CHCl_3$). The ee was determined to be 88% by HPLC (Daicel Chiralcel IB x 2, hexane/*i*-PrOH = 20/1, 0.5 mL/min, 254 nm, major 42.7 min and minor 49.2 min). ^{1}H NMR ($CDCl_3$): 0.92 (t, J = 7.2 Hz, 3H), 1.58–1.64 (m, 2H), 2.08 (s, 6H), 2.24 (s, 3H), 2.41 (s, 3H), 3.84–3.91 (m, 1H), 4.49 (d, J = 7.2 Hz, 1H), 5.39 (dd, J = 7.2, 16.0 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 6.81 (s, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 9.9, 20.6, 20.9, 21.4, 29.3, 57.8, 127.0, 128.4, 129.0, 129.6, 133.0, 133.8, 135.7, 136.2, 138.1, 143.2. IR (KBr): 3290, 2920, 1610, 1510, 1430, 1320, 1160, 1090, 990 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{21}H_{28}NO_2S$ $[M+H]^+$: 358.1841.

Found: 358.1836.

(*R*,*E*)-4-Methyl-*N*-(4-methyl-1-(2-(trimethylsilyl)phenyl)pent-1-en-3-yl)benzenesulfonamide (3nI)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3nI** (175 mg, 87% yield, 0.5 mmol scale) as a white solid of mp = 94–96 °C and $[\alpha]^{25}_{D}$ +83.3 (*c* 0.51, $CHCl_3$). The ee was determined to be 72% by HPLC (Daicel Chiralcel IA x 2, hexane/*i*-PrOH = 20/1, 0.8 mL/min, 254 nm, major 21.1 min and minor 22.5 min). ^{1}H NMR ($CDCl_3$): 0.28 (s, 9H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.85 (septet, *J* = 6.8 Hz, 1H), 2.27 (s, 3H), 3.72–3.78 (m, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 5.65 (dd, *J* = 8.0, 15.6 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.16–7.24 (m, 4H), 7.43–7.46 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 0.1, 18.3, 18.7, 21.3, 33.4, 62.1, 125.4, 126.7, 127.2, 128.0, 129.0, 129.5, 133.5, 134.2, 138.1, 138.3, 142.1, 143.1. IR (KBr): 3250, 2960, 1600, 1440, 1320, 1160, 1100, 1040, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{22}H_{32}NO_2SSi$ $[M+H]^+$: 402.1923. Found: 402.1901.

(*R*,*E*)-4-Methyl-*N*-(4-(2-(trimethylsilyl)phenyl)but-3-en-2-yl)benzenesulfonamide (3nM)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3nM** (111 mg, 59% yield, 0.5 mmol scale) as a white solid of mp = 94–96 °C and $[\alpha]^{25}_{D}$ +83.9 (*c* 0.51, $CHCl_3$). The ee was determined to be 88% by HPLC (Daicel Chiralcel IA x 2, hexane/*i*-PrOH = 20/1, 0.8 mL/min, 254 nm, major 42.9 min and minor 46.1 min). ^{1}H NMR ($CDCl_3$): 0.28 (s, 9H), 1.30 (d, *J* = 6.8 Hz, 3H), 2.38 (s, 3H), 4.06–4.14 (m, 1H), 4.40 (d, *J* = 7.2 Hz, 1H), 5.75 (dd, *J* = 6.4, 15.6 Hz, 1H), 6.73 (d, *J* = 15.6 Hz, 1H), 7.16–7.28 (m, 5H), 7.44–7.47 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 0.3, 21.3, 21.6, 51.5, 125.3, 126.6, 127.1, 129.0, 129.5, 131.2, 131.6, 134.1, 137.8, 138.2, 142.1, 143.2. IR (KBr): 3280, 2960, 1590, 1420, 1320, 1150, 1120, 1090, 960 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{20}H_{28}NO_2SSi$ $[M+H]^+$: 374.1610. Found: 374.1619.

(*R*,*E*)-*N*-(1-Mesityl-4-methylpent-1-en-3-yl)-4-methylbenzenesulfonamide (3oI)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3oI** (173 mg, 93% yield, 0.5 mmol scale) as a white solid of mp = 97–99 °C and $[\alpha]^{25}_{D}$ +60.7 (*c* 1.06,

$CHCl_3$). The ee was determined to be 73% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 0.7 mL/min, 254 nm, major 13.1 min and minor 15.1 min). ^1H NMR ($CDCl_3$): 0.93 (d, *J* = 6.8 Hz, 6H), 1.86 (septet, *J* = 6.8 Hz, 1H), 2.05 (s, 6H), 2.24 (s, 3H), 2.37 (s, 3H), 3.77–3.82 (m, 1H), 4.80 (brs, 1H), 5.40 (dd, *J* = 7.6, 16.8 Hz, 1H), 6.25 (d, *J* = 16.8 Hz, 1H), 6.80 (s, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): 18.1, 18.4, 20.7, 20.8, 21.4, 33.4, 61.7, 126.9, 128.4, 129.5, 129.6, 131.9, 133.2, 135.7, 136.1, 138.3, 143.0. IR (KBr): 3280, 2960, 1600, 1440, 1320, 1160, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{22}H_{30}NO_2S$ $[M+H]^+$: 372.1997. Found: 372.1974.

(*R*,*E*)-*N*-(4-Mesitylbut-3-en-2-yl)-4-methylbenzenesulfonamide (3oM)

Silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **3oM** (94 mg, 55% yield, 0.5 mmol scale) as a white solid of mp = 95–97 °C and $[\alpha]^{25}_D$ +65.2 (*c* 0.48, $CHCl_3$). The ee was determined to be 79% by HPLC (Daicel Chiralcel IB x 2, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 24.7 min and minor 27.8 min). ^1H NMR ($CDCl_3$): 1.31 (d, *J* = 6.8 Hz, 3H), 2.10 (s, 6H), 2.26 (s, 3H), 2.40 (s, 3H), 4.05–4.13 (m, 1H), 4.51 (brs, 1H), 5.40 (dd, *J* = 6.4, 16.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.81 (s, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 20.6, 20.9, 21.5, 22.4, 51.8, 127.0, 128.0, 128.5, 129.6, 132.9, 135.2, 135.7, 136.3, 138.0, 143.3. IR (KBr): 3270, 2920, 1610, 1460, 1430, 1320, 1160, 1100, 1090, 970 cm^{-1}. HRMS–FAB(*m/z*): Calcd for $C_{20}H_{26}NO_2S$ $[M+H]^+$: 344.1684. Found: 344.1671.

(*S*,*E*)-4-methyl-*N*-(1-phenyl-3-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (3nP)

Silica gel column chromatography (hexane/ ethyl acetate = 20/1~3/1) gave **3nP** (130 mg, 60% yield, 0.5 mmol scale) as a colorless oil of $[\alpha]^{25}_D$ +37.5 (*c* 0.40, $CHCl_3$). The ee was determined to be 86% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 14.2 min and minor 11.7 min). ^1H NMR ($CDCl_3$): 0.15 (s, 9H), 2.34 (s, 3H), 5.00 (d, *J* = 6.2 Hz, 1H), 5.14 (t, *J* = 6.2 Hz, 1H), 6.07 (dd, *J* = 6.2, 15.6 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 7.14–7.30 (m, 10H), 7.41–7.44 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): –0.13, 21.3, 125.2, 126.8, 127.1, 127.1, 127.6, 128.5, 129.1, 129.4, 129.6, 133.8, 134.2, 137.6, 138.6, 139.3, 141.8, 143.1. IR (KBr): 3280, 2960, 1720, 1600, 1490, 1460, 1330, 1160, 840 cm^{-1}. HRMS–DART (*m/z*): Calcd for

$C_{25}H_{30}NO_2SSi$ $[M+H]^+$: 436.1767. Found: 436.1775.

(*S*,*E*)-*N*-(3-mesityl-1-phenylallyl)-4-methylbenzenesulfonamide (3oP)

Silica gel column chromatography (hexane/ ethyl acetate = 20/1~3/1) gave **3oP** (75 mg, 37% yield, 0.5 mmol scale) as a white solid of mp = 139–140 °C and $[\alpha]^{25}_D$ +10.0 (*c* 0.33, $CHCl_3$). The ee was determined to be 70% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, major 14.3 min and minor 18.8 min). ^{1}H NMR ($CDCl_3$): 2.11 (s, 6H), 2.24 (s, 3H), 2.38 (s, 3H), 4.80 (d, *J* = 6.2 Hz, 1H), 5.12 (t, *J* = 6.2 Hz, 1H), 5.71 (dd, *J* = 6.2, 16.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.81 (s, 2H), 7.20–7.29 (m, 7H), 7.69 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 20.7, 20.9, 21.4, 59.9, 127.0, 127.1, 127.7, 128.5, 128.7, 129.5, 129.9, 132.7, 133.3, 135.8, 136.4, 137.7, 140.0, 143.3. IR (KBr): 3280, 1450, 1320, 1150, 1090, 1060 cm^{-1}. HRMS–DART(*m/z*): Calcd for $C_{25}H_{28}NO_2S$ $[M+H]^+$: 406.1841. Found: 406.1868.

(*E*)-4-methyl-*N*-(1-(2-(trimethylsilyl)phenyl)hexa-1,5-dien-3-yl)benzenesulfonamide (3nA)

Silica gel column chromatography (hexane/ ethyl acetate = 5/1) gave **3nA** (198 mg, 99% yield, 0.5 mmol scale) as a white solid of mp = 58–59 °C. The ee was determined to be 0% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 1.0 mL/min, 254 nm, 13.1 min and 14.5 min). ^{1}H NMR ($CDCl_3$): 0.29 (s, 9H), 2.27–2.40 (m, 2H), 2.36 (s, 3H), 4.01–4.08 (m, 1H), 4.50 (d, *J* = 6.8 Hz, 1H), 5.08–5.14 (m, 2H), 5.59–5.69 (m, 1H), 5.74 (dd, *J* = 6.8, 15.6 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 7.14–7.28 (m, 5H), 7.45–7.47 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 0.05, 21.3, 40.1, 55.5, 119.1, 125.4, 126.6, 127.1, 129.0, 129.5, 129.5, 132.6, 132.8, 134.1, 137.9, 138.2, 142.0, 143.1. IR (KBr): 3310, 2960, 1440, 1320, 1250, 1160, 1100, 970, 910, 840 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{22}H_{30}NO_2SSi$ $[M+H]^+$: 400.1767. Found: 400.1760.

(*E*)-*N*-(1-mesitylhexa-1,5-dien-3-yl)-4-methylbenzenesulfonamide (3oA)

Silica gel column chromatography (hexane/ ethyl acetate = 5/1) gave **3oA** (183 mg, 99% yield, 0.5 mmol scale) as a white solid of mp = 84–86 °C. The ee was determined to be 0% by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 0.7 mL/min, 254 nm, 15.9 min and 17.6 min). ^{1}H NMR ($CDCl_3$): 2.10 (s, 6H), 2.24 (s, 3H), 2.31–2.44 (m, 2H), 2.40 (s, 3H), 4.01–4.07 (m, 1H), 4.53–4.57 (m, 1H), 5.07–5.15 (m, 2H), 5.46 (dd, *J*

= 6.4, 16.0 Hz, 1H), 5.62–5.72 (m, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.82 (s, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 20.6, 20.8, 21.3, 40.6, 55.4, 119.0, 127.0, 128.3, 128.9, 129.5, 132.9, 133.0, 133.3, 135.6, 136.1, 137.9, 143.1. IR (KBr): 3290, 2920, 1640, 1610, 1430, 1320, 1160, 1090, 1060 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{22}H_{28}NO_2S$ $[M+H]^+$: 370.1841. Found: 370.1864.

(*S*)-3-Phenylpentan-1-ol (4E')

The obtained aldehydes **4E** was treated with $NaBH_4$ (0.5 mmol) in methanol (4 mL) for 0.5 h at room temperature. After addition of water and ethyl acetate, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with satd $NaHCO_3$ and brine, and then dried over Na_2SO_4. Concentration and purification by silica gel column chromatography (hexane/ethyl acetate = 20/1~3/1) gave **4E'** as a colorless oil. The ee was determined by HPLC (Daicel Chiralcel IB, hexane/*i*-PrOH = 20/1, 0.3 mL/min, 220 nm, major 26.4 min and minor 23.9 min). ^{1}H NMR ($CDCl_3$): 0.78 (t, *J* = 7.6 Hz, 3H), 1.43 (brs, 1H), 1.59–1.98 (m, 4H), 2.57 (tt, *J* = 5.2, 5.2 Hz, 1H), 3.43–3.57 (m, 2H), 7.15–7.31 (m, 5H). ^{13}C NMR ($CDCl_3$): 12.1, 29.8, 39.2, 44.2, 61.2, 126.1, 127.7, 128.4, 144.9. IR (KBr): 3860, 2930, 1600, 1490, 1450, 1020 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{11}H_{17}O$ $[M+H]^+$: 165.1279. Found: 165.1281.

Protodesilation to (*R*,*E*)-4-Methyl-*N*-(1-phenylpent-1-en-3-yl)benzenesulfonamide (3aE)

To a solution of **3nE** (116 mg, 83% ee, 0.3 mmol scale), KI (100 mg, 0.6 mmol), and H_2O (5.4 μL, 0.3 mmol) in MeCN (4.5 mL), TMSCl (65 mg, 0.6 mmol) was added at room temperature. After 6 h, water was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate (5 mL x3). The combined organic layers were washed with brine and dried over Na_2SO_4. Silica gel column chromatography (hexane/ ethyl acetate = 5/1~3/1) gave **3aE** (116 mg, 74% yield). The ee was determined to be 83% by HPLC (Daicel Chiralcel IA, hexane/*i*-PrOH = 20/1, 0.7 mL/min, 254 nm, major 37.9 min and minor 33.9 min.

(*R*)-*N*-(1-Hydroxybutan-2-yl)-4-methylbenzenesulfonamide (14)

To a solution of **3aE** (158 mg, 98% ee, 0.5 mmol scale) in CH_2Cl_2 (4.0 mL), gentle

stream of ozone was passed through the solution at –78 °C. After 2.5 hours, $NaBH_4$ (95 mg, 2.5 mmol) in MeOH (2.0 mL) was added dropwise at –78 °C and the whole was steered for 15 min, then warmed to room temperature. Water was added and the aqueous layer was extracted with $CHCl_3$ (5 mL x3). The combined organic layers were washed with brine and dried over Na_2SO_4. Silica gel column chromatography (hexane/acetone/$CHCl_3$ = 1/1/1) gave **14** (108 mg, 89% yield, 2 steps) as an colorless oil of $[\alpha]^{25}_D$ +83.3 (*c* 0.51, $CHCl_3$). The ee was determined to be 98% by HPLC (Daicel Chiralcel IA, hexane/*i*-PrOH = 10/1, 1.0 mL/min, 254 nm, major 48.3 min and minor 23.5 min). ^{1}H NMR ($CDCl_3$): 0.75 (t, *J* = 7.2 Hz, 3H), 1.33 –1.44 (m, 1H), 1.45–1.52 (m, 1H), 1.98 (brs, 1H), 2.42 (s, 3H), 3.13–3.20 (m, 1H), 3.47–3.58 (m, 2H), 4.72 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): 10.0, 21.4, 24.5, 57.1, 64.2, 126.9, 129.6, 137.6, 143.3. IR (KBr): 3220, 2970, 1600, 1460, 1320, 1160, 1040 cm^{-1}. HRMS–DART (*m/z*): Calcd for $C_{11}H_{18}NO_3S$ $[M+H]^+$: 244.1007. Found: 244.1006.

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Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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