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Development of the First Menthane-Based Chiral Bis(π-allylpalladium) Catalysis: Asymmetric Allylation of Imines

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Dedicated to Professor Yoshinori Yamamoto on the occasion of his 70th birthday

Keywords: Asymmetric catalysis / Homogeneous catalysis / C-C coupling / Allylation / Palladium / Enantioselectivity

A new ethylidene menthane-based chiral π-allylpalladium complex catalyzes the asymmetric allylation of various imines with allyltributylstannane and 1 equiv. of water to give chiral homoallylamines in good yields and enantioselectivities. The reaction was carried out essentially under neutral conditions and displayed a good transfer of chiral information from the menthane skeleton through the formation of a bis(π-allylpalladium) species. This is the first example of menthane-based chiral bis(π-allylpalladium) catalysis.

Introduction

A π-allylpalladium complex was first prepared by the addition of palladium chloride to butadiene, although the structure was not originally known as a π-allyl complex.[1] Various π-allylpalladium complexes have been reported from a wide range of olefins with different substitution patterns.[2] These complexes are electrophilic and widely used in reactions with a variety of nucleophiles. Although this chemistry is well explored (e.g., allylic alkylation and the oxidation of alkenes and conjugated dienes),[3–8] the umpolung of the π-allyl palladium complex is a new arena in organometallic chemistry with new applications in the area of catalysis. The key intermediate in such reactions is the bis(π-allylpalladium) species which has nucleophilic character. It has been demonstrated that under catalytic conditions, the bis(π-allylpalladium) complex can undergo an initial electrophilic attack on one of the allyl moieties followed by a nucleophilic attack on the other, thereby, displaying amphiphilic character.[9] The evidence for the in situ formation of the bis(π-allylpalladium) species is well documented,[10] and the mechanism and regioselectivity of the electrophilic attack of the bis(π-allylpalladium) complex has also been studied.[11] Various synthetic applications of the bis(π-allylpalladium) species including the first catalytic asymmetric allyation of imines were explored by Yamamoto's group.[12–14] The *exo*-ethylidene (–)-β-pinene-based π-allylpalladium-catalyzed asymmetric allylation of imines occurred with an enantioselectivity of up to 82%.[12] The reaction was further improved by meticulously preparing the *exo*-ethylidene-based π–allylpalladium chloride in high regioisomeric purity (*Z*/*E*, 400:1) and by using water (1 equiv.) to affect the asymmetric allylation which occurred in good reproducible yields and enantioselectivity (28 examples, up to 94% yield and up to 91%*ee*).[14a] The use of allylsilanes, instead of stannanes, was also explored in the presence of TBAF (tetra-*n*-butylammonium fluoride) and MeOH. The former helped to activate the C–Si bond cleavage, and the latter promoted the facile protonation of the intermediate palladium amide.[13,14b]

The asymmetric allylation of imines or hydrazones represents an important C–C bond forming reaction in organic synthesis.[15–18] Although several catalytic asymmetric methods have been developed, work in this area goes unabated. Yamamoto's catalyst based on the *exo*-ethylidene (–)-β-pinene required extensive purification using column chromatography followed by repeated recrystallizations to achieve a regiosiomeric purity of 400:1 and resulted in a low overall yield for the preparation of the catalyst.[14a] Noting this difficulty and that a limited number of chiral skeletons were examined, we embarked on investigating the framework of menthane-based chiral π-allylpalladium chloride. The menthane framework has been extensively used as a chiral auxiliary.[19] However, until now, a chiral π-allyl palladium chloride complex based on the menthane structure has not been studied as a catalyst. We believe that the stereochemical information from the menthane framework, previously used as a chiral auxiliary in synthetic transformations, could be translated through the formation of chiral bis(π-allylpalladium) species. In addition, the men-

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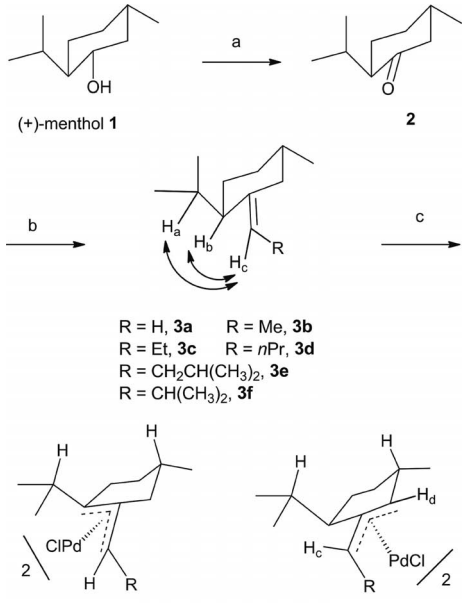
thane skeleton (as menthol) is available in both enantiomeric forms to enable synthesis of either enantiomeric catalyst.

Results and Discussion

We prepared several olefins from (+)-menthone **2** [prepared from (+)-menthol **1**] as shown in Scheme 1.[20] Olefins **3a**–**f** were prepared in yields of 51–72% by a conventional Wittig olefination using alkyltriphenylphosphonium halide and either *n*BuLi or *t*BuOK as the base. Gratifyingly, the olefins were isolated as single diastereomers (*E* isomers), indicated by the presence of a single peak in the olefin region of the ^{1}H NMR spectra. The *E* geometry was assigned using the ^{1}H-^{1}H COSY correlations between H_b and H_c and also the ^{1}H-^{1}H NOESY correlations between H_a and H_c in **3b** (Scheme 1). The reaction of these olefins with $Pd(OCOCF_3)_2$ and nBu_4NCl in acetone furnished in each case the π-allylpalladium chloride complexes **4a**–**f** along with the minor regioisomeric complexes **5a**–**f** (^{1}H NMR shows **4b**–**f**/**5b**–**f**, 3.5–4.5:1 and **4a**/**5a**, 3:2). ^{1}H NMR spectroscopy was used to characterize the mixture of regioisomeric π-allylpalladium chloride complexes. For example, a clear distinction of peaks was observed in the ^{1}H NMR spectrum of **4b** containing **5b**. Only one allyl proton for **4b** was observed as a quartet, and as expected for **5b**, minor peaks were observed as a singlet for H_d and a quartet for H_c (Scheme 1). Similarly, this was the case for other complexes (R ≠ H, **4c**–**e**) with the only allyl proton assigned as a triplet. The major complexes **4b**–**f** were purified by flash column chromatography, however, pure forms of complexes **5b**–**f** were not obtained by column chromatography, and always contained **4b**–**f** as well. The mixture of complexes **4a**/**5a** obtained in 3:2 ratio were not separated by flash column chromatography or by recrystallization. Hence, complexes **4a**/**5a** were used as a mixture. Complexes **4**/**5** were observed to be stereochemically stable unlike earlier reports of *E* to *Z* conversion.[14d]

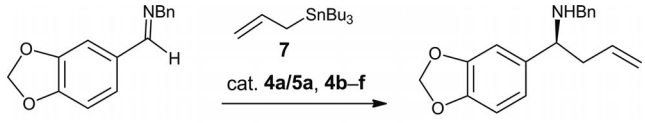


R	**4**/**5** (yield)	pure π-allyl complex
H	3:2 (55%)	**4a**/**5a** (mixture)
Me	3.5:1 (78%)	**4b** (45%)
Et	4:1 (68%)	**4c** (41%)
*n*Pr	3.5:1 (62%)	**4d** (38%)
$CH_2CH(CH_3)_2$	3.5:1 (65%)	**4e** (40%)
*i*Pr	3.8:1 (55%)	**4f** (31%)

Scheme 1. Synthesis of menthane-based chiral π-allylpalladium complexes. Reagents and conditions: (a) PCC (pyridinium chlorochromate), MS (molecular sieves, 4 Å), CH_2Cl_2, 0 °C to room temp., 4 h, 94%; (b) $Ph_3P^+CH_2RX^-$ (X = Br, I), THF (tetrahydrofuran), *n*BuLi, 0 °C, 30 min, 80 °C, 48 h or *t*BuOK, room temp., 30 min, 80 °C, 48 h, 51–72%; (c) $Pd(OCOCF_3)_2$, acetone, room temp., 1 h then nBu_4NCl, room temp., 1 h, 55–78%.

Our initial investigation commenced with screening the mixture of complexes **4a**/**5a** and **4b**–**f** in the asymmetric allylation of model imine **6a**. The results are shown in Table 1. We employed similar conditions as in the literature[14a] using water (1 equiv.) and allyltributylstannane (1.25 equiv.) in the THF solvent. The mixture of inseparable complexes **4a**/**5a** catalyzed the reaction giving homoallylamine **8a** in good yields and enantioselectivity (Table 1, Entry 1, 68% *ee*). A better yield and enantioselectivity was obtained by changing to the *exo*-ethylidene group in **4b** providing **8a** in 68% yield and 78% *ee* (Table 1, Entry 2). Increasing the alkyl chain length further from the ethylidene to the butylidene group (Table 1, Entries 2–4, complexes **4b**–**4d**,) resulted in lower enantioselectivities. Branching on the alkyl chain (Table 1, Entries 5 and 6, complexes **4e** and **f**) did not have any positive influence on the enantioselectivity. Thus, the optimum chain length was with the ethylidene group in **4b** as shown in Entry 2. In addition, we investigated the catalyst loading with 1 and 2 mol-% of **4b**, which resulted in a decrease in both the yields and enantio-

Table 1. Asymmetric allylation of imine **6a** with **7** and **4a**/**5a** mixture or **4b**–**f**.[a]

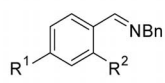
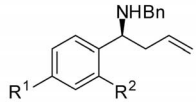
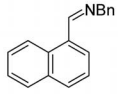
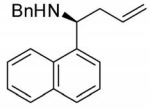
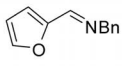
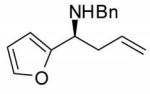
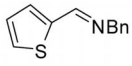
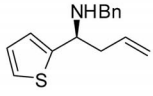
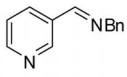
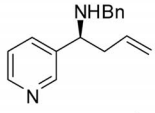
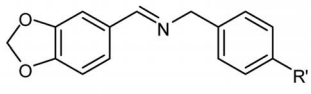
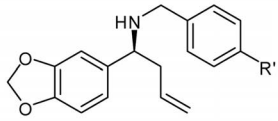
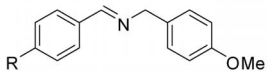
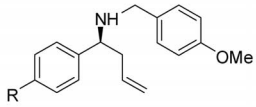
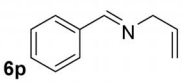
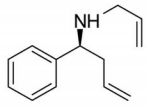
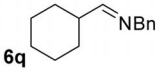
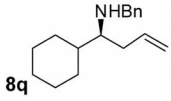
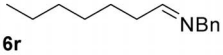
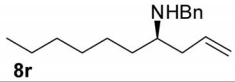


Entry	π-Allylpalladium chloride complex [mol-%]	% Yield **8a**	% *ee*[b] **8a**
1	**4a**/**5a** (5)	62	68
2	**4b** (5)	68	78
3	**4c** (5)	66	52
4	**4d** (5)	45	48
5	**4e** (5)	60	46
6	**4f** (5)	38	48
7	**4b** (1)	52	68
8	**4b** (2)	56	68
9	**4b** (10)	65	72
10	**4b** (20)	71	74

[a] Allyltributylstannane (1.25 equiv.). [b] *ee* determined by HPLC.

selectivities (Table 1, Entries 7 and 8). An increase in the catalyst loading to 10 or 20 mol-% gave comparable results (Table 1, Entries 9 and 10). The latter case resulted in better yields (71%), but a lower *ee* of 74% (Table 1, Entry 10). Thus, 5 mol-% of catalyst was the optimum requirement for the reaction.

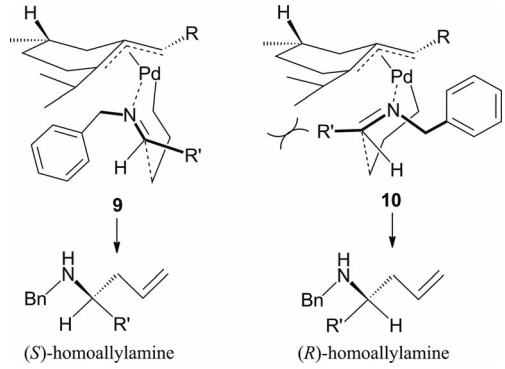
Table 2. Catalytic asymmetric allylation of imines with allyltributylstannane using catalyst **4b**.[a]

Entry	Imine	Product	Time (h)	% Yield	% *ee*[b]
					
1	**6b** $R^1 = R^2 = H$	**8b**	48	70	70
2	**6c** $R^1 = CH_3$, $R^2 = H$	**8c**	70	79	76
3	**6d** $R^1 = OCH_3$, $R^2 = H$	**8d**	98	74	72
4	**6e** $R^1 = H$, $R^2 = OCH_3$	**8e**	74	64	42
5	**6f** $R^1 = NO_2$, $R^2 = H$	**8f**	72	62	22
6	**6g** $R^1 = Cl$, $R^2 = H$	**8g**	75	68	56
7	**6h** 	**8h** 	96	72	62
8	**6i** 	**8i** 	74	67	36
9	**6j** 	**8j** 	90	61	48
10	**6k** 	**8k** 	140	41	52
					
11	**6a** R′ = H	**8a**	84	79	78
12	**6l** R′ = OMe	**8l**	84	77	64
					
13	**6m** R = H	**8m**	73	80	68
14	**6n** R = Me	**8n**	74	79	60
15	**6o** R = OMe	**8o**	88	78	56
16	**6p** 	**8p** 	78	72	64
17	**6q** 	**8q** 	68	60	36
18	**6r** 	**8r** 	96	55	30

[a] Allyltributylstannane (1.25 equiv.), H_2O (1 equiv.), catalyst **4b** (5 mol-%), 0 °C. [b] *ee* determined by HPLC.

We then focused on investigating the scope of complex **4b** in the asymmetric allylation of various imines using allyltributylstannane and 1 equiv. of water at 0 °C. The results are presented in Table 2. Benzaldehyde imine **6b** delivered homoallylamine **8b** in good yield (70%) and an enantioselectivity of 70%*ee* (Table 2, Entry 1). Imines with electron-donating groups in the *para* position resulted in a slight increase in enantioselectivity, for example, **6c** and **d** gave homoallylamines **8c** and **d** in 76 and 72%*ee*, respectively (Table 2, Entries 2 and 3). However, the *ortho*-methoxy group in **6e** yielded **8e** with a remarkably lower enantioselectivity (42%*ee*, Table 2, Entry 4). Similarly, having the electron-withdrawing NO_2 group in the *para* position of the imine also resulted in a lower enantioselectivity (**6f** gave **8f**, 22%*ee*, Table 2, Entry 5). 4-Chlorobenzaldehyde imine **6g** reacted well giving homoallylamine **8g** in good yield (68%, Table 2, Entry 6) and a moderate enantioselectivity of 56%*ee*. α-Naphthaldehyde imine **6h** gave homoallylamine **8h** in 72% yield and a moderate 62%*ee* (Table 2, Entry 7). Heterocyclic imines **6i**–**k** reacted well to produce the corresponding homoallylamines **8i**–**k** in good yields of 67, 61, and 41% and enantioselectivities of 36, 48, and 52%*ee*, respectively (Table 2, Entries 8–10). The pyridine-based imine **6k** was sluggish in the reaction and required a longer reaction time (Table 2, Entry 10). Piperonyl imine **6a** with the benzyl group furnished **8a** in good yields and the best *ee* of 78% (Table 2, Entry 11). However, substituting a *p*-methoxybenzyl group for the benzyl group as in **6l** resulted in **8l** with a slight decrease in enantioselectivity, 64%*ee* (Table 2, Entry 12). Homoallylamine **8a** is a precursor for α-propylpiperonylamine which is an important building block of the human leukocyte elastase inhibitor L-694,458.[21] The *p*-methoxybenzyl group containing imines **6m**–**o** reacted well with good yields of 80, 79, and 78% and moderate enantioselectivities of 68, 60, and 56%*ee*, respectively (Table 2, Entries 13–15). Benzaldehyde imine **6p** with the *N*-allyl group furnished homoallylamine **8p** in 72% yield and a moderate 64%*ee* (Table 2, Entry 16). Nonaryl imines like cyclohexylimine **6q** and *n*-heptylimine **6r** produced homoallylamines **8q** and **8r** in moderate yields and enantioselectivities of 36 and 30%*ee*, respectively (Table 2, Entries 17 and 18).

The reaction is expected to follow a similar mechanistic pathway as reported in the literature.[14a] The bis(π-allylpalladium) complex is initially formed. It is this key intermediate that is nucleophilic and transfers the allyl group to the imine, directed by the chiral menthane skeleton and resulting in the observed chiral induction. The transfer of the bulky menthane allyl moiety was not observed, which is a remarkable feature. The opposite sign of optical rotation for the homoallylamines were obtained using Yamamoto's (–)-ethylidene pinene π-allylpalladium complex, whereas, the homoallylamines in our work have the (*S*) configuration. The probable transition state models are shown in Scheme 2. The backside of palladium complex **9** is occupied by an alkyl group, and thus, the imine is forced to approach from front α side. In η^3,η^1-π-allylpalladium complex **9**, the smaller allyl group is transferred to the coordinated imine through a six-membered chair-like transition state to the *si* face of the imine. This explains the formation of the (*S*)-homoallylamines. In transition-state model **10** which gives the (*R*)-homoallylamines, the imine R′ group encounters steric repulsion from bulky isopropyl group of the complex, and therefore the structure is less favored. A smaller sized R group, such as R = Me (as in **4b**), is required for complexation to occur from front α side and not from the rear side. A further increase in the chain length or branching in the alkyl R group has no influence. For Yamamoto's catalyst,[12,14] the complexation of imine occurs from backside of the ethylidene pinene catalyst, and in our case, it occurs from front α side which explains the formation of the opposite enantiomer of homoallylamines.



Scheme 2. Transition-state models.

Conclusions

In summary, we have developed for the first time a menthane-based chiral π-allylpalladium catalyst which catalyzed the asymmetric allylation of various imines to give chiral homoallylamines in good yields and enantioselectivities. The homoallylamines have the opposite configuration to that obtained in previous reports.[14a] The reaction was carried out essentially under neutral conditions and displayed a good transfer of chiral information from the menthane skeleton through formation of a bis(π-allylpalladium) complex.

Experimental Section

General Remarks: The solvents were dried by standard procedures. Thin layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. ^1H and ^{13}C NMR spectroscopic data were recorded with a Bruker Avance^{III} 400 spectrometer, and the chemical shifts are based on the TMS peak at δ = 0.00 pm for the ^1H NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) for the ^{13}C NMR spectra. IR spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer. Optical rotations were measured with a Jasco P-2000 polarimeter. The HRMS data were recorded with a Micromass: Q-Tof micro (YA-105) spectrometer. HPLC was performed with a JASCO-(PU-2089PLUS) quaternary gradient pump equipped with a MD-2010PLUS mutiwavelength detector. Imines were prepared as previously reported.[22] Though

solids, we did not determine melting points of the π-allylpalladium chloride complexes, as they decomposed upon slight heating.

(1*R*,4*S*)-1-Isopropyl-4-methyl-2-methylenecyclohexane (3a):[23] To a stirred solution of $Ph_3P^+CH_3I^-$ (2.37 g, 5.83 mmol) in THF (15 mL) at 0 °C under an argon atmosphere was added *n*BuLi (1.6 M in hexane, 5.5 mL, 8.75 mmol, 1.5 equiv.), and the mixture was stirred for 30 min. A solution of (+)-**2**[20] (0.6 g, 3.89 mmol) in THF (5 mL) was added, and the mixture was stirred for 48 h at 80 °C. It was then cooled to room temp. and quenched with a saturated aqueous solution of NH_4Cl (1 mL), and the resulting mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated. Silica gel column chromatography of the crude product using petroleum ether as the eluent gave **3a** (0.37 g, 62%) as a colorless oil. $[\alpha]_D^{25}$ = +40.5 (*c* = 0.12, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3084, 2954, 2928, 1645, 1457, 1385, 1163, 891, 861 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.7 Hz, 3 H), 0.90 (d, *J* = 6.5 Hz, 3 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 1.04–1.25 (m, 3 H), 1.55–1.81 (m, 4 H), 1.92–1.98 (m, 1 H), 2.27 (dd, *J* = 12.6, 4.0 Hz, 1 H), 4.58 (s, 1 H), 4.69 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 21.4, 22.1, 27.1, 27.4, 33.4, 34.0, 44.4, 49.4, 106.1, 151.2 ppm. LRMS (ESI): calcd. for $C_{11}H_{21}$ $[M + H]^+$ 153.1; found 153.1.

(1*R*,4*S*,*E*)-2-Ethylidene-1-isopropyl-4-methylcyclohexane (3b): To a stirred solution of $Ph_3P^+CH_2CH_3\,Br^-$ (2.41 g, 6.48 mmol, 2.0 equiv.) in THF (20 mL) at room temp. under an argon atmosphere was added *t*BuOK (0.547 g, 4.86 mmol, 1.5 equiv.), and the mixture was stirred for 30 min. A solution of (+)-**2** (0.5 g, 3.24 mmol) in THF (5 mL) was added, and the mixture was stirred for 48 h at 80 °C. It was then quenched with a saturated aqueous solution of NH_4Cl (1 mL), and the resulting mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated. Silica gel column chromatography of the crude product using petroleum ether as the eluent gave **3b** (0.355 g, 66%) as a colorless oil. $[\alpha]_D^{25}$ = +55.9 (*c* = 0.32, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3033, 2954, 2927, 1666, 1455, 1382, 1367, 1093, 1062, 862, 829, 805 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.5 Hz, 3 H), 0.91 (d, *J* = 6.4 Hz, 3 H), 1.07–1.17 (m, 1 H), 1.24–1.32 (m, 1 H), 1.58 (d, *J* = 6.7 Hz, 3 H), 1.54–1.61 (m, 1 H), 1.62–1.82 (m, 4 H), 1.86–1.96 (m, 1 H), 2.29–2.35 (m, 1 H), 5.17 (q, *J* = 6.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 19.7, 20.5, 22.1, 26.4, 26.8, 32.0, 32.2, 34.6, 51.2, 115.1, 140.6 ppm. LRMS (ESI): calcd. for $C_{12}H_{23}$ $[M + H]^+$ 167.1; found 167.09.

(1*R*,4*S*,*E*)-1-Isopropyl-4-methyl-2-propylidenecyclohexane (3c): The title compound was prepared from (+)-**2** (0.6 g, 3.89 mmol) and $Ph_3P^+CH_2CH_2CH_3\,Br^-$ (3.0 g, 7.78 mmol, 2.0 equiv.) by a similar procedure to that described for **3b** to give **3c** (0.505 g, 72%) as a colorless oil. $[\alpha]_D^{25}$ = +33.7 (*c* = 1.14, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2955, 2929, 2870, 1661, 1455, 1378, 1265, 1164, 1063, 895, 877, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.7 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.90 (d, *J* = 6.6 Hz, 3 H), 0.94 (t, *J* = 7.5 Hz, 3 H), 1.08–1.16 (m, 1 H), 1.24–1.33 (m, 1 H), 1.54–1.60 (m, 1 H), 1.63–1.83 (m, 4 H), 1.87–1.96 (m, 1 H), 1.97–2.08 (m, 2 H), 2.28–2.35 (m, 1 H), 5.07 (t, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 19.8, 20.5 (2 C), 22.1, 26.4, 26.7, 31.8, 32.3, 34.8, 51.2, 123.6, 139.0 ppm. LRMS (ESI): calcd. for $C_{13}H_{25}$ $[M + H]^+$ 181.2; found 181.2.

(1*R*,4*S*,*E*)-2-Butylidene-1-isopropyl-4-methylcyclohexane (3d): The title compound was prepared from (+)-**2** (0.6 g, 3.89 mmol) and $Ph_3P^+CH_2CH_2CH_2CH_3\,Br^-$ (3.11 g, 7.78 mmol, 2.0 equiv.) by a similar procedure to that described for **3b** to give **3d** (0.491 g, 65%) as a colorless oil. $[\alpha]_D^{25}$ = +42.7 (*c* = 0.86, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2957, 2930, 2871, 1662, 1456, 1382, 1366, 1065, 923, 885, 867, 818, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.91 (t, *J* = 7.4 Hz, 3 H), 1.09–1.15 (m, 1 H), 1.23–1.40 (m, 3 H), 1.53–1.61 (m, 1 H), 1.62–1.81 (m, 4 H), 1.88–2.03 (m, 3 H), 2.29–2.34 (m, 1 H), 5.09 (t, *J* = 7.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.8, 20.6, 22.1, 23.4, 26.4, 26.8, 29.3, 31.9, 32.3, 35.0, 51.2, 121.7, 139.8 ppm. LRMS (ESI): calcd. for $C_{14}H_{27}$ $[M + H]^+$ 195.2; found 195.1.

(1*R*,4*S*,*E*)-1-Isopropyl-4-methyl-2-(3-methylbutylidene)cyclohexane (3e): The title compound was prepared from (+)-**2** (0.6 g, 3.89 mmol) and $Ph_3P^+CH_2CH_2CH(CH_3)_2\,Br^-$ (3.21 g, 7.78 mmol, 2.0 equiv.) by a similar procedure to that described for **3b** to give **3e** (0.526 g, 65%) as a colorless oil. $[\alpha]_D^{25}$ = +42.2 (*c* = 0.34, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2955, 2928, 2870, 1661, 1464, 1382, 1366, 1258, 1166, 1086, 1063, 867, 774 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.95 (m, 15 H), 1.0–1.18 (m, 1 H), 1.23–1.32 (m, 1 H), 1.51–1.84 (m, 6 H), 1.85–1.98 (m, 3 H), 2.27–2.35 (m, 1 H), 5.10 (t, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 20.8, 22.3, 22.6, 22.8, 26.7, 27.1, 29.4, 32.2, 32.6, 35.4, 36.6, 51.5, 120.9, 140.4 ppm. LRMS (ESI): calcd. for $C_{15}H_{29}$ $[M + H]^+$ 209.2; found 209.2.

(1*R*,4*S*,*E*)-1-Isopropyl-4-methyl-2-(2-methylpropylidene)cyclohexane (3f): The title compound was prepared from (+)-**2** (0.6 g, 3.89 mmol) and $Ph_3P^+CH_2CH(CH_3)_2\,Br^-$ (3.21 g, 7.78 mmol, 2.0 equiv.) by a similar procedure to that described for **3a** to give **3f** (0.385 g, 51%) as a colorless oil. $[\alpha]_D^{25}$ = +8.6 (*c* = 0.36, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3021, 2957, 2929, 2871, 1639, 1456, 1378, 1019, 901, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.94 (m, 15 H), 1.05–1.18 (m, 1 H), 1.22–1.41 (m, 3 H), 1.60–1.81 (m, 3 H), 1.89–2.08 (m, 2 H), 2.28–2.36 (m, 1 H), 5.10 (t, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 20.6, 22.1, 23.4, 26.4, 26.8, 29.3, 29.7, 31.9, 32.3, 35.0, 51.2, 121.7, 139.8 ppm. LRMS (ESI): calcd. for $C_{14}H_{27}$ $[M + H]^+$ 195.2; found 195.1.

General Procedure for the Preparation of π-Allylpalladium Chloride Complexes 4a–f: To a solution of $Pd(OCOCF_3)_2$ (0.2 g, 0.6 mmol, 1.0 equiv.) in dry acetone (10 mL) at room temp. and under an argon atmosphere was added olefin **3** (0.722 mmol, 1.2 equiv.). The mixture was stirred for 1 h (TLC monitored). nBu_4NCl (0.183 g, 0.66 mmol, 1.1 equiv.) in acetone (2 mL) was added, and the reaction mixture was stirred for 1 h. The clear brown solution was then filtered through a plug of Celite to remove the suspended Pd-black. The filtrate was concentrated, and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (5:1) as the eluent to give a mixture of complexes **4** and **5** (analyzed by ^1H NMR) as a yellow semisolid. Complex **4** was separated from **5** by flash column chromatography using petroleum ether as the eluent to give pure complex **4** as a yellow solid. [Yields are based on $Pd(OCOCF_3)_2$ and are given below for the **4**/**5** mixture and isolated major complex **4**]. In the case of **4a**/**5a**, the mixture could not be separated.

π-Allylpalladium Chloride Complexes 4a/5a: Obtained as a 3:2 inseparable mixture of **4a**/**5a** (97.0 mg, 55%). R_f = 0.29 (petroleum ether). IR ($CHCl_3$): $\tilde{\nu}$ = 2958, 2928, 2871, 1652, 1455, 1363, 1261, 1040, 930, 805, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75–1.05 (m, 12 H), 1.2 (d, *J* = 6.8 Hz, 3 H), 1.2–1.41 (m, 7 H), 1.42–1.55 (m, 2 H), 1.56–1.65 (m, 2 H), 1.7–1.85 (m, 2 H), 1.86–2.05 (m, 2 H), 2.25–2.51 (m, 1 H), 2.52–2.65 (m, 1 H), 2.72–2.82 (m, 1 H), 3.0 (s, 1 H), 3.14 (s, 1 H), 3.52 (s, 1 H), 3.66 (s, 1 H), 4.12 (s, 1 H) ppm. HRMS (ESI-TOF) calcd. for $C_{22}H_{38}Pd_2Cl$ $[M - Cl]^+$ 549.0728; found 549.0733.

π-Allylpalladium Chloride Complex 4b: Obtained as a 3.5:1 mixture of **4b/5b** (143.9 mg, 78%). Pure complex **4b** (83.3 mg, 45%) was isolated as a yellow powder. R_f = 0.28 (petroleum ether). $[\alpha]_D^{25}$ = +15.7 (c = 0.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2959, 2927, 2871, 1660, 1456, 1424, 1375, 1318, 1257, 1230, 1085, 1032, 986, 666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.8 Hz, 3 H), 1.02 (d, J = 6.0 Hz, 3 H), 1.22 (d, J = 6.4 Hz, 3 H), 1.25 (d, J = 7.0 Hz, 3 H), 1.26–1.35 (m, 2 H), 1.45–1.53 (m, 1 H), 1.61–1.70 (m, 1 H), 1.77–1.88 (m, 1 H), 1.89–1.96 (m, 1 H), 2.34–2.45 (m, 2 H), 3.99 (q, J = 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 20.1, 21.9, 24.0, 27.4, 29.1, 30.0, 32.3, 36.2, 69.2, 100.4, 118.1 ppm. HRMS (ESI-TOF) calcd. for $C_{24}H_{42}Pd_2Cl$ [M – Cl]$^+$ 577.1041; found 577.1026.

π-Allylpalladium Chloride Complex 4c: Obtained as a 4:1 mixture of **4c/5c** (131 mg, 68%). Pure complex **4c** (79 mg, 41%) was isolated as a yellow powder. R_f = 0.27 (petroleum ether). $[\alpha]_D^{25}$ = +12.5 (c = 0.42, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3033, 2954, 2929, 2870, 1638, 1455, 1382, 1262, 1120, 1093, 1045, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.9 Hz, 3 H), 1.00 (d, J = 6.0 Hz, 3 H), 1.16 (t, J = 7.4 Hz, 3 H), 1.26 (d, J = 6.8 Hz, 3 H), 1.28–1.32 (m, 1 H), 1.45–1.56 (m, 3 H), 1.62–1.72 (m, 2 H), 1.78–1.88 (m, 1 H), 1.89–1.97 (m, 1 H), 2.38–2.45 (m, 2 H), 3.78 (t, J = 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0, 20.0, 21.9, 22.6, 24.1, 27.4, 29.0, 29.9, 32.3, 35.9, 76.4, 100.5, 116.9 ppm. HRMS (ESI-TOF) calcd. for $C_{26}H_{46}Pd_2Cl$ [M – Cl]$^+$ 605.1358; found 605.1365.

π-Allylpalladium Chloride Complex 4d: Obtained as a 3.5:1 mixture of **4d/5d** (125 mg, 62%). Pure complex **4d** (76.7 mg, 38%) was isolated as a yellow powder. R_f = 0.28 (petroleum ether). $[\alpha]_D^{25}$ = +15.1 (c = 0.34, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2961, 2927, 2870, 1686, 1460, 1384, 1261, 1117, 1088, 1036, 899 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.8 Hz, 3 H), 0.96 (t, J = 7.1 Hz, 3 H), 1.0 (d, J = 5.9 Hz, 3 H), 1.26 (d, J = 5.4 Hz, 3 H), 1.21–1.31 (m, 3 H), 1.44–1.59 (m, 3 H), 1.61–1.72 (m, 2 H), 1.75–1.88 (m, 1 H), 1.89–1.98 (m, 1 H), 2.41–2.50 (m, 2 H), 3.85 (t, J = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 20.0, 21.8, 21.9, 24.1, 27.4, 29.1, 29.9, 31.2, 32.4, 36.0, 74.6, 100.5, 117.0 ppm. HRMS (ESI-TOF) calcd. for $C_{28}H_{50}Pd_2Cl$ [M – Cl]$^+$ 633.1671; found 633.1684.

π-Allylpalladium Chloride Complex 4e: Obtained as a 3.5:1 mixture of **4e/5e** (136.5 mg, 65%). Pure complex **4e** (84 mg, 40%) was isolated as a yellow powder. R_f = 0.28 (petroleum ether). $[\alpha]_D^{25}$ = +17.2 (c = 0.3, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2928, 2957, 2870, 1653, 1463, 1383, 1367, 1166, 1086, 988, 936 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, J = 7.4 Hz, 3 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.96 (d, J = 6.6 Hz, 3 H), 1.00 (d, J = 5.9 Hz, 3 H), 1.20–1.35 (m, 6 H), 1.42–1.55 (m, 2 H), 1.58–1.68 (m, 2 H), 1.77–1.88 (m, 1 H), 1.90–2.01 (m, 1 H), 2.38–2.47 (m, 2 H), 3.95 (t, J = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 21.9, 22.4, 22.9, 24.1, 27.8, 29.1, 29.9, 32.5, 34.6, 36.3, 37.4, 73.8, 100.3, 117.2 ppm. HRMS (ESI-TOF) calcd. for $C_{30}H_{54}Pd_2Cl$ [M – Cl]$^+$ 661.1984; found 661.1974.

π-Allylpalladium Chloride Complex 4f: Obtained as a 3.8:1 mixture of **4f/5f** (111 mg, 55%). Pure complex **4f** (62.5 mg, 31%) was isolated as a yellow powder. R_f = 0.28 (petroleum ether). $[\alpha]_D^{25}$ = +15.2 (c = 0.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3033, 2960, 2929, 1654, 1456, 1427, 1383, 1262, 1089, 1054, 944 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, J = 6.7 Hz, 6 H), 0.96 (d, J = 6.9 Hz, 3 H), 1.01 (d, J = 5.5 Hz, 3 H), 1.24 (d, J = 6.7 Hz, 3 H), 1.21–1.31 (m, 1 H), 1.41–1.55 (m, 2 H), 1.56–1.75 (m, 2 H), 1.78–1.86 (m, 1 H), 1.87–1.98 (m, 1 H), 2.35–2.50 (m, 2 H), 3.85 (t, J = 6.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 20.0, 21.8, 21.9, 24.1, 27.4, 29.1, 29.9, 31.2, 32.4, 36.0, 74.6, 100.5, 117.0 ppm. HRMS (ESI-TOF) calcd. for $C_{28}H_{50}Pd_2Cl$ [M – Cl]$^+$ 633.1671; found 633.1681.

General Procedure for Asymmetric Allylation of Imines Using Catalyst 4b: The imine (0.5 mmol) was placed in a Wheaton microreactor (5 mL capacity), and under an argon atmosphere, dry THF (1.25 mL), degassed water (9 μL, 0.5 mmol, 1 equiv.), and allyltributylstannane (194 μL, 0.625 mmol, 1.25 equiv.) were added sequentially. The mixture was cooled to 0 °C, and the chiral palladium chloride complex **4b** (14.56 mg, 0.025 mmol, 5 mol-%) was added under argon. The reaction mixture was flushed with argon and stirred at 0 °C for the specified time. The reaction progress was monitored by TLC. After completion, the turbid reaction mixture was quenched with HCl (1 N solution, 2.5 mL). CH_3CN (1 mL) was added, and the reaction mixture was stirred at room temperature for 10 min. The two-layered solution was extracted with hexane (2 × 3 mL), and the hexane layer was discarded. The aqueous layer was basified with NaOH (10% aqueous solution, 1.25 mL), and the resulting solution was stirred for 5 min. The solution was extracted with EtOAc (2 × 5 mL), dried with Na_2SO_4, and concentrated. Purification by silica gel column chromatography (hexane/EtOAc, 5:1) gave the corresponding homoallylamine **8** as a colorless oil. Characterization data (^1H NMR is only included) for the known homoallylamines were identical to literature data.[14a] The enantiomeric excesses were determined by HPLC of the trifluoroacetylamide forms of all of the homoallylamines with UV detection at 254 nm.

***N*-Benzyl-1-phenyl-3-butenylamine (8b):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –44.8 (c = 0.14, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (br. s, 1 H), 2.38–2.45 (m, 2 H), 3.51 (d, J = 13.3 Hz, 1 H), 3.67 (dd, J = 7.6, 6.8 Hz, 2 H), 5.02–5.10 (m, 2 H), 5.65–5.75 (m, 1 H), 7.21–7.36 (m, 10 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99.8:0.2; flow rate: 0.5 mL/min): t_R (retention time) = 16.85 min (minor enantiomer) and 19.5 min (major enantiomer); 70% *ee*.

***N*-Benzyl-1-(4-methylphenyl)-3-butenylamine (8c):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –41.5 (c = 0.84, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (br. s, 1 H), 2.34 (s, 3 H), 2.32–2.40 (m, 2 H), 3.48 (d, J = 13.2 Hz, 1 H), 3.62–3.65 (m, 2 H), 5.03–5.09 (m, 2 H), 5.64–5.75 (m, 1 H), 7.15 (d, J = 7.4 Hz, 2 H), 7.21–7.31 (m, 7 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 0.7 mL/min): t_R = 8.40 min (minor enantiomer) and 10.06 min (major enantiomer); 76% *ee*.

***N*-Benzyl-1-(4-methoxyphenyl)-3-butenylamine (8d):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –32.1 (c = 0.56, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (ddt, J = 7.5, 6.4, 2.1 Hz, 2 H), 3.51 (d, J = 13.1 Hz, 1 H), 3.67 (t, J = 6.5 Hz, 1 H), 3.67 (d, J = 13.1 Hz, 1 H), 3.82 (s, 3 H), 5.03–5.09 (m, 2 H), 5.64–5.75 (m, 1 H), 6.9 (d, J = 8.7, Hz, 2 H), 7.22–7.33 (m, 7 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 0.7 mL/min): t_R = 10.42 min (minor enantiomer) and 11.20 min (major enantiomer); 72% *ee*.

***N*-Benzyl-1-(2-methoxyphenyl)-3-butenylamine (8e):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –19.2 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (br. s, 1 H), 2.43–2.60 (m, 2 H), 3.56 (d, J = 13.1 Hz, 1 H), 3.69 (d, J = 13 Hz, 1 H), 3.81 (s, 3 H), 4.09–4.13 (m, 1 H), 4.97–5.05 (m, 2 H), 5.71 (ddt, J = 15.6, 9.5, 7.1 Hz, 1 H), 6.90 (d, J = 7.9 Hz, 1 H), 6.97 (t, J = 7.7 Hz, 1 H), 7.23–7.51 (m, 7 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99:1; flow rate: 0.8 mL/min): t_R = 8.50 min (minor enantiomer) and 10.00 min (major enantiomer); 42% *ee*.

***N*-Benzyl-1-(4-nitrophenyl)-3-butenylamine (8f):** Colorless oil. $[\alpha]_D^{25}$ = –6.8 (c = 1.2, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3335, 3078, 3029, 2924,

2849, 1640, 1599, 1520, 1455, 1347, 1109, 996, 920, 856, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (br. s, 1 H), 2.32–2.43 (m, 2 H), 3.49 (d, J = 13.1 Hz, 1 H), 3.63 (d, J = 13.2 Hz, 1 H), 3.66–3.84 (m, 1 H), 5.05–5.10 (m, 2 H), 5.62–5.72 (m, 1 H), 7.22–7.33 (m, 5 H), 7.54 (d, J = 8.4 Hz, 2 H), 8.19 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.8, 51.5, 61.1, 118.5, 123.6 (2 C), 127.0, 127.9 (2 C), 128.1 (2 C), 128.4 (2 C), 134.2, 139.9, 147.1, 151.8 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{19}N_2O_2$ $[M + H]^+$ 283.1447; found 283.1443. HPLC (CHIRALPAK AD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 0.5 mL/min): t_R = 50.32 min (minor enantiomer) and 54.87 min (major enantiomer); 22%*ee*.

***N*-Benzyl-1-(4-chlorophenyl)-3-butenylamine (8g):** Colorless oil. $[\alpha]_D^{25}$ = –39.1 (c = 0.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3396, 3077, 2931, 2844, 1646, 1460, 1046, 917, 765 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (br. s, 1 H), 2.35–2.37 (m, 2 H), 3.49 (d, J = 13.3 Hz, 1 H), 3.62 (d, J = 13.2 Hz, 1 H), 3.62–3.68 (m, 1 H), 5.03–5.08 (m, 2 H), 5.61–5.72 (m, 1 H), 7.2–7.4 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.0, 51.3, 60.9, 117.9, 126.9, 128.0 (2 C), 128.4 (2 C), 128.5 (2 C), 128.7 (2 C), 132.5, 134.9, 140.3, 142.3 ppm. LRMS (ESI): calcd. for $C_{17}H_{19}NCl$ $[M + H]^+$ 272.1; found 272.1. HPLC (CHIRALPAK IA column; hexane/*i*PrOH, 99:1; flow rate: 0.5 mL/min): t_R = 12.59 min (minor enantiomer) and 14.25 min (major enantiomer); 56%*ee*.

***N*-Benzyl-1-(1-naphthyl)-3-butenylamine (8h):** Colorless oil. $[\alpha]_D^{25}$ = –21.8 (c = 0.86, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3437, 3062, 2928, 2856, 1638, 1597, 1456, 1394, 1167, 1106, 1028, 997, 917, 800, 778 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (br. s, 1 H), 2.43–2.51 (m, 1 H), 2.64–2.68 (m, 1 H), 3.58 (d, J = 13.2 Hz, 1 H), 3.75 (d, J = 13.5 Hz, 1 H), 4.59 (dd, J = 7.7, 4.4 Hz, 1 H), 5.05–5.14 (m, 2 H), 5.75–5.85 (m, 1 H), 7.20–7.36 (m, 5 H), 7.47–7.52 (m, 3 H), 7.76–7.89 (m, 3 H), 8.18 (d, J = 6.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.1, 51.6, 57.1, 117.7, 123.0, 123.9, 125.3, 125.6, 125.7, 126.9, 127.4, 128.2 (2 C), 128.3 (2 C), 129.0, 131.6, 134.0, 135.5, 139.0, 140.6 ppm. HRMS (ESI-TOF): calcd. for $C_{21}H_{22}N$ $[M + H]^+$ 288.1752; found 288.1744. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 97:3; flow rate: 0.8 mL/min): t_R = 9.06 min (minor enantiomer) and 10.80 min (major enantiomer); 62%*ee*.

***N*-Benzyl-1-(2-furfuryl)-3-butenylamine (8i):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –25.8 (c = 0.56, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89 (br. s, 1 H), 2.51–2.55 (m, 2 H), 3.59 (d, J = 13.1 Hz, 1 H), 3.71 (d, J = 13.2 Hz, 1 H), 3.71–3.77 (m, 1 H), 5.03–5.11 (m, 2 H), 5.65–5.75 (m, 1 H), 6.18 (d, J = 2.8 Hz, 1 H), 6.33 (d, J = 2.8 Hz, 1 H), 7.23–7.31 (m, 6 H) ppm. HPLC (CHIRALCEL AD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 0.7 mL/min): t_R = 10.29 min (minor enantiomer) and 13.10 min (major enantiomer); 36%*ee*.

***N*-Benzyl-1-(2-thiophenyl)-3-butenylamine (8j):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –15.5 (c = 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (br. s, 1 H), 2.47–2.50 (m, 2 H), 3.60 (d, J = 13.5 Hz, 1 H), 3.79 (d, J = 13.5 Hz, 1 H), 3.97 (t, J = 6.6 Hz, 1 H), 5.05–5.11 (m, 2 H), 5.69 (ddt, J = 15.8, 9.6, 6.5 Hz, 1 H), 6.91–6.95 (m, 2 H), 7.21–7.32 (m, 6 H) ppm. HPLC (CHIRALCEL AD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 0.5 mL/min): t_R = 14.15 min (minor enantiomer) and 17.55 min (major enantiomer); 48%*ee*.

***N*-Benzyl-1-(3-pyridyl)-3-butenylamine (8k):** Colorless oil. $[\alpha]_D^{25}$ = –18.8 (c = 0.12, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3412, 3030, 2925, 2852, 1645, 1455, 1428, 1262, 1106, 1028, 995, 920, 808 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38–2.53 (m, 3 H), 3.51 (d, J = 13.3 Hz, 1 H), 3.65 (d, J = 13.3 Hz, 1 H), 3.73 (t, J = 7.1 Hz, 1 H), 5.01–5.08 (m, 2 H), 5.62–5.72 (m, 1 H), 7.22–7.34 (m, 6 H), 7.73 (d, J = 7.8 Hz, 1 H), 8.5 (d, J = 4.8 Hz, 1 H), 8.55 (d, J = 2 Hz 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.6, 51.3, 59.2, 118.5, 123.6, 127.1, 128.2 (3 C), 128.5 (3 C), 134.3, 135.0, 148.7, 149.4 ppm. HRMS (ESI-TOF): calcd. for $C_{16}H_{19}N_2$ $[M + H]^+$ 239.1548; found 239.1551. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 97:3; flow rate: 1 mL/min): t_R = 9.06 min (minor enantiomer) and 10.80 min (major enantiomer); 52%*ee*.

***N*-Benzyl-1-piperonyl-3-butenylamine (8a):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –49.1 (c = 0.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84 (br. s, 1 H), 2.31–2.39 (m, 2 H), 3.51 (d, J = 13.3 Hz, 1 H), 3.6 (t, J = 6.5 Hz, 1 H), 3.68 (d, J = 13.3 Hz, 1 H) 5.03–5.10 (m, 2 H), 5.7 (ddt, J = 15.6, 9.7, 6.9 Hz, 1 H), 5.96 (s, 2 H), 6.78 (s, 2 H), 6.92 (s, 1 H), 7.23–7.35 (m, 5 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 98:2; flow rate: 0.8 mL/min): t_R = 9.61 min (minor enantiomer) and 10.40 min (major enantiomer); 78%*ee*.

***N*-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine (8l):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –38.6 (c = 0.28, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (br. s, 1 H), 2.34–2.40 (m, 2 H), 3.46 (d, J = 13.0 Hz, 1 H), 3.62 (d, J = 13.0 Hz, 1 H), 3.61–3.65 (m, 1 H), 3.79 (s, 3 H), 5.01–5.07 (m, 2 H), 5.62–5.72 (m, 1 H), 5.95 (s, 2 H), 6.77 (s, 2 H), 6.84 (d, J = 8.7 Hz, 2 H), 6.9 (s, 1 H), 7.17 (d, J = 8.6 Hz, 2 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99:1; flow rate: 1 mL/min): t_R = 15.87 min (minor enantiomer) and = 20.61 min (major enantiomer); 64%*ee*.

***N*-(4-Methoxybenzyl)-1-phenyl-3-butenylamine (8m):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –32.6 (c = 0.31, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (br. s, 1 H), 2.35–2.42 (m, 2 H), 3.45 (d, J = 13 Hz, 1 H), 3.6 (d, J = 13 Hz, 1 H), 3.67 (dd, J = 7.5, 6.2 Hz 1 H), 3.78 (s, 3 H), 5.01–5.08 (m, 2 H), 5.63–5.74 (m, 1 H), 6.84 (ddd, J = 8.7, 2.9, 2.4 Hz, 2 H), 7.15 (dd, J = 8.6, 2.3 Hz, 2 H), 7.23–7.28 (m, 1 H), 7.32–7.35 (m, 4 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99.8:0.2; flow rate: 1 mL/min): t_R = 6.29 min (minor enantiomer) and 7.64 min (major enantiomer); 68%*ee*.

***N*-(4-Methoxybenzyl)-1-(4-methylphenyl)-3-butenylamine (8n):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –31.5 (c = 0.19, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (br. s, 1 H), 2.35 (s, 3 H), 2.38–2.41 (m, 2 H), 3.46 (d, J = 13.0 Hz, 1 H), 3.62 (d, J = 13.0 Hz, 1 H), 3.58–3.66 (m, 1 H), 3.79 (s, 3 H), 5.01–5.08 (m, 2 H), 5.68 (ddt, J = 16.0, 9.9, 6.9 Hz, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 7.15 (d, J = 8.1 Hz, 4 H), 7.25 (d, J = 8.0 Hz, 2 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 99.3:0.7; flow rate: 1 mL/min): t_R = 7.23 min (minor enantiomer) and 9.70 min (major enantiomer); 60%*ee*.

***N*-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-3-butenylamine (8o):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –35.2 (c = 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (br. s, 1 H), 2.35–2.39 (m, 2 H), 3.44 (d, J = 13.1 Hz, 1 H), 3.61 (d, J = 13.0 Hz, 1 H), 3.58–3.64 (m, 1 H), 3.79 (s, 3 H), 3.81 (s, 3 H), 5.0–5.08 (m, 2 H), 5.68 (ddt, J = 16.0, 9.5, 6.4 Hz, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 7.15 (d, J = 8.6 Hz, 2 H), 7.26 (d, J = 7.8 Hz, 2 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 98:2; flow rate: 1 mL/min): t_R = 8.45 min (minor enantiomer) and 9.73 min (major enantiomer); 56%*ee*.

***N*-Allyl-1-phenyl-3-butenylamine (8p):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –21.3 (c = 0.15, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (br. s, 1 H), 2.40–2.44 (m, 2 H), 2.98–3.04 (m, 1 H), 3.09–3.14 (m, 1 H), 3.70 (dd, J = 6.2, 1.2 Hz, 1 H), 5.03–5.13 (m, 4 H), 5.68–5.76 (m, 1 H), 5.8–5.90 (m, 1 H), 7.22–7.34 (m, 5 H) ppm. HPLC (CHIRALCEL OD-H column; hexane/*i*PrOH, 98.2:1.8; flow rate: 0.6 mL/min): t_R = 8.48 min (minor enantiomer) and, = 9.0 min (major enantiomer); 64%*ee*.

***N*-Benzyl-1-cyclohexyl-3-butenylamine (8q):**[14a] Colorless oil. $[\alpha]_D^{25}$ = –1.7 (c = 0.14, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.1–1.76 (m, 11 H), 2.09–2.15 (m, 1 H), 2.24–2.31 (m, 1 H), 2.38–2.42

(m, 1 H), 3.75 (br. s, 2 H), 5.03–5.1 (m, 2 H), 5.74–5.83 (m, 1 H), 7.2–7.34 (m, 5 H) ppm. HPLC (CHIRALCEL OD column; hexane/*i*PrOH, 99:1; flow rate: 0.4 mL/min): t_R = 20.2 min (minor enantiomer) and 22.8 min (major enantiomer); 36%*ee*.

***N*-Benzyl-1-heptyl-3-butenylamine (8r):** Colorless oil. $[\alpha]_D^{25}$ = –0.72 (*c* = 0.44, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3411, 2928, 2856, 1653, 1455, 1074, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.22–1.40 (m, 11 H), 2.13–2.20 (m, 1 H), 2.23–2.30 (m, 1 H), 2.57–2.63 (m, 1 H), 3.77 (s, 2 H), 5.06–5.11 (m, 2 H), 5.73–5.83 (m, 1 H), 7.21–7.41 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.7, 29.5, 31.8, 33.8, 38.2, 51.0, 56.1, 117.2, 126.9, 128.2 (2 C), 128.4 (2 C), 135.7, 141.1 ppm. HRMS (ESI-TOF): calcd. for $C_{17}H_{28}N$ $[M + H]^+$ 246.2221; found 246.2222. HPLC (CHIRALCEL AD-H column; hexane/*i*PrOH, 99.5:0.5; flow rate: 1 mL/min): t_R = 4.8 min (minor enantiomer) and 7.7 min (major enantiomer); 30%*ee*.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra for compounds **3a**–**f**, **4a**/**5a** mixture, **4b**–**f**, **8f**, **8g**, **8h**, **8k**, and **8r**.

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