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Bridged Dimers

# Menthane-Based Chloride-Bridged $\eta^3$-Bis-$\pi$-Allylpalladium Chloride Dimers: Catalytic Asymmetric Allylation of Imines

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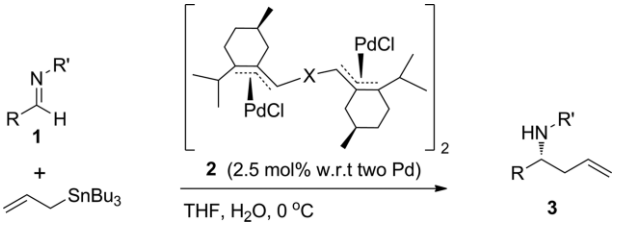
**Abstract:** Menthane-based $\eta^3$-bis-$\pi$-allylpalladium chloride dimer complexes have been prepared for the first time. They exist as dimeric $\eta^3$-bis-$\pi$-allylpalladium with four chloride bridges. The complexes catalyze the asymmetric allylation of various imines with allyltributylstannane and one equivalent of water to give chiral homoallylamines in yields of 60–77 % and enantioselectivity up to *er* = 93:7. The stereochemical information from the menthane framework was translated successfully through the $\eta^3$-bis-$\pi$-allylpalladium catalysts in asymmetric allylation of imines.

## Introduction

$\eta^3$-Allylpalladium chloride dimers were first prepared by Hüttel[1] and Hafner[2] independently in 1959. These were later employed as allylating agents by Tsuji and co-workers.[3] Trost et al.[4] combined both Hüttel's method of preparation and Tsuji's allylation and disclosed the synthetic potential of these species. This chemistry today is widely referred to as "Tsuji-Trost" reaction and the species involved as "$\pi$-allylpalladium". Various $\pi$-allylpalladium complexes have been prepared by Trost and co-workers[5] involving both aliphatic and cyclic olefins. Moving away from stoichiometry to catalytic version of their use was a remarkable achievement.[6] Today most reactions involving $\pi$-allylpalladium are catalytic in nature with respect to palladium.

Yamamoto and co-workers[7] reported the first catalytic enantioselective synthesis of homoallylamines by the use of various chiral $\pi$-allylpalladium catalysts prepared from different chiral moieties. Although the simple $\pi$-allylpalladium complexes derived from allyl acetate or halide act as electrophiles,[8] the bis-$\pi$-allylpalladium formed in situ exhibit nucleophilic character in delivering the allyl unit to the prochiral imine.[9] It has been demonstrated that the bis-$\pi$-allylpalladium complex under catalytic conditions, can undergo an initial electrophilic attack on one of the allyl moieties followed by a nucleophilic attack on the other, thereby, displaying amphiphilic character.[9,10] Considering the limited chiral frameworks examined by Yamamoto and co-workers and low overall yield in catalyst preparation,[7,9,11] in 2012 we reported the improved synthesis of $\pi$-allylpalladium chloride complexes based on pinene skeleton and also achieved higher enantioselectivity up to 99:1 er.[12a] In the same year, we also developed the first menthane-based chiral $\pi$-allylpalladium catalysts;[12b] since before the menthane moiety had been used extensively as a chiral auxiliary.[13] The menthane-based chiral catalyst effected asymmetric allylation of imines up to 89:11 er.[12b] Various monomeric $\pi$-allylpalladium complexes have been reported till date,[5,7,8] but there is no report on $\eta^3$-bis-$\pi$-allylpalladium chloride complexes to the best of our knowledge. Knowing that monomer complexes exist as dimers through chloride bridges, the proposed synthesis of bis complexes intrigued us to study their formation and dimerization similar to the monomeric complexes. The intriguing question at this juncture was whether the complexes would dimerize intramolecular or intermolecular. Therefore, in continuation to our ongoing research,[12] we have synthesized various menthane-based $\eta^3$-bis-$\pi$-allylpalladium chloride complexes **2** and noted that dimerization of these complexes occurs intermolecular through four chloride bridges as can be seen in the X-ray structure. The complexes were then employed in the asymmetric allylation of imines **1** (Scheme 1).




Scheme 1. Menthane-based dimeric $\eta^3$-bis-$\pi$-allylpalladium chloride complexes and asymmetric allylation of imines.

## Results and Discussion

Our initial efforts focused on the preparation of several dimeric olefins **6a-f** starting from (–)-menthone **5** [prepared by PCC oxidation of (–)-menthol **4**][14] with various dimeric phosphonium salts[15] (Scheme 2). Treatment of these Wittig salts with *t*-BuOK generated the ylides and further reaction with (–)-menthone **5** provided the olefins **6a-f** in 30–50 % yields (Scheme 2) as single diastereomers (*E*-olefins). The single peak in the olefinic region in the $^1$H NMR spectrum clearly indicated

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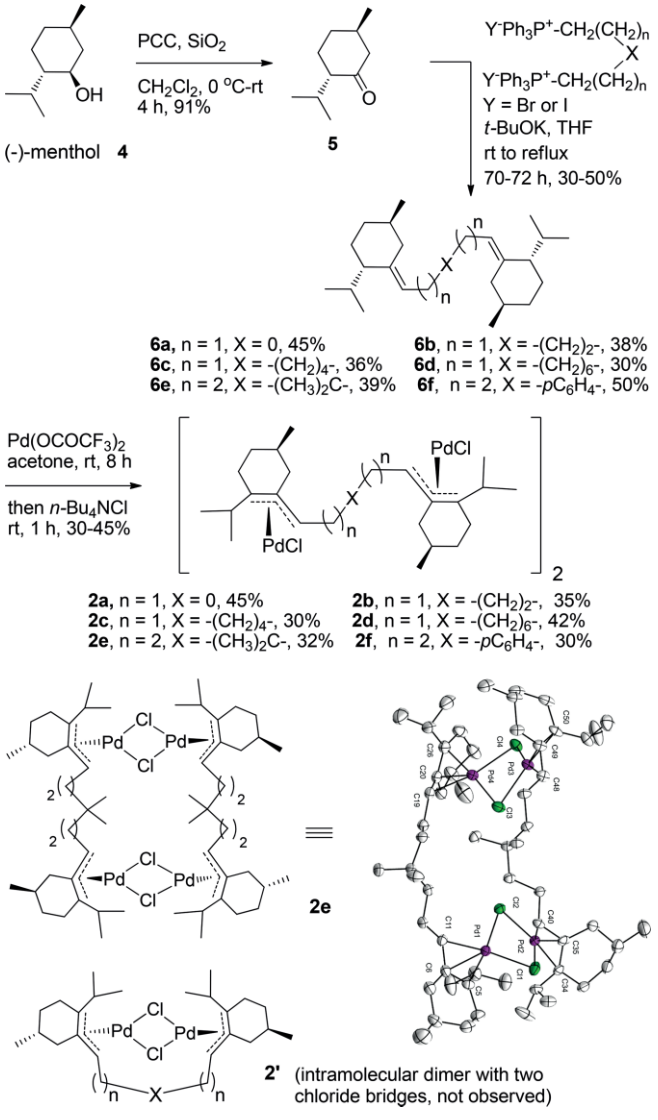
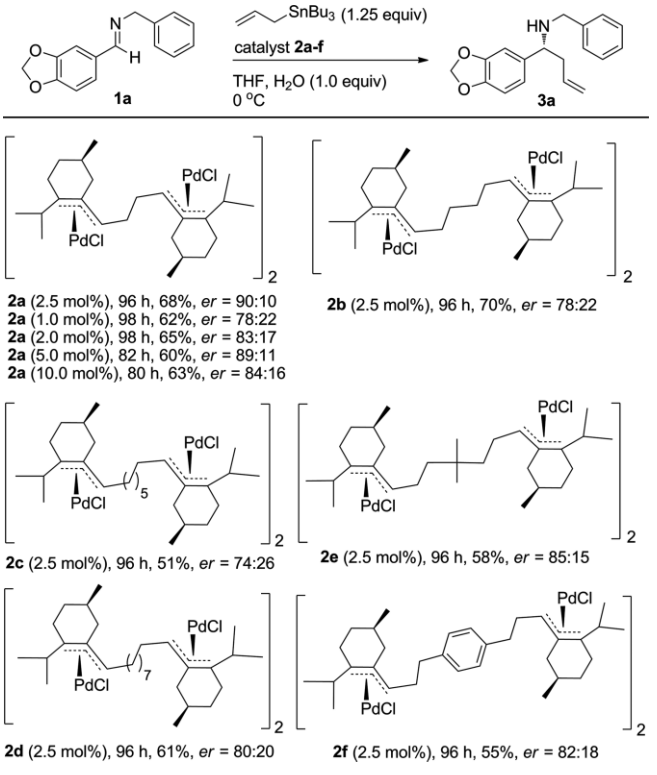
the formation of single diastereomer (see Supporting Information). The *E*-geometry of olefins was confirmed by $^1$H-$^1$H COSY, $^1$H-$^1$H NOESY correlations and also with the help of NOE similar to our earlier report for monomeric olefins.[12b] We could not prepare the dimeric olefin with a three carbon spacer between the menthyl moieties. The Wittig reaction failed in this case. The reaction of these dimeric olefins with $Pd(OCOCF_3)_2$ and $nBu_4NCl$ in acetone furnished the desired $\eta^3$-bis-$\pi$-allylpalladium chloride complexes **2a-f** as single regioisomers. The complexes **2a-d** have long un-substituted carbon chains separating the two menthyl moieties. The complex **2e** has a quaternary carbon mid-way with gem-dimethyl group. An aryl spacer is present in complex **2f**. The structure of these complexes was determined by $^1$H-$^1$H COSY, NOE, HSQC, and with the help of HRMS (see Supporting Information). The complex **2e** gave crystals for X-ray analysis indicating the dimeric nature with four chloride bridges[16] (Scheme 2). From the HRMS data of all complexes **2a-e** and crystal structure of **2e**, it was remarkable to note that these complexes get associated intermolecular as dimers with four chloride bridges involving two molecules of the $\eta^3$-bis-$\pi$-allylpalladium chloride. We did not observe the formation of an intramolecular dimer with two chloride bridges, such as **2′** (Scheme 2).

The allylation of aldimines and derivatives has been established as one of the important C–C bond forming reactions. Due to the strong coordinating ability of nitrogen in comparison to oxygen, the enantioselective allylation of aldimines shows incredible selectivity toward the synthesis of chiral homoallylamines.[7,11,12,17–19] The latter are found to be consequential intermediates for a wide range of pharmaceuticals, agrochemicals, and *N*-heterocyclic compounds.[20] Thus, the development of a general and efficient method for the synthesis of this type of chiral amines has been of great interest. We screened the prepared complexes **2a-f** for the asymmetric allylation of model imine **1a** (Scheme 3). We employed similar reaction conditions as reported by us earlier using water (1.0 equiv.) and allyltributylstannane (1.25 equiv.) in THF solvent at 0 °C.[12] Among the catalysts **2a-d** with un-substituted long chain separating the two menthyl moieties, **2a** delivered the homoallylamine **3a** in 68 % yield and 90:10 *er,* indicating that the longer chains were not as effective. We could not prepare the dimer catalyst with a three-carbon spacer as the corresponding olefin was not accessible. However, we believe an optimum chain length would be required for the Pd complexes to be formed considering over-crowding between the menthyl moieties. A gem-dimethyl group containing catalyst **2e** offered **3a** in 58 % yield and 85:15 *er*. We also attempted the preparation of the



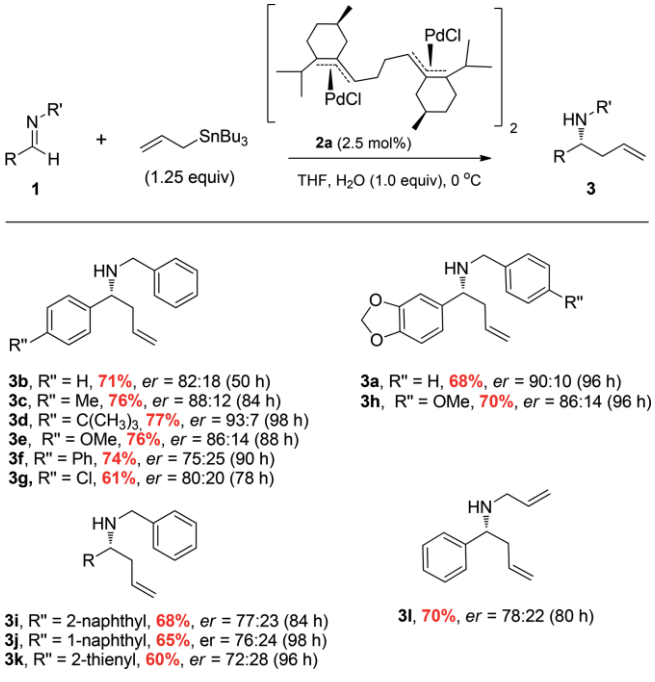

Scheme 2. Synthesis of menthane-based dimeric $\eta^3$-bis-$\pi$-allylpalladium chloride complexes **2a-f** and crystal structure of **2e**.




Scheme 3. Asymmetric allylation of model imine **1a** with allyltributylstannane using catalysts **2a-f**. Note: mol-% of **2** is with respect to two Pd.

olefin with two methylene groups less as in **2e** and having the gem-dimethyl group, but this was not successful. The catalyst with an aryl spacer **2f** provided **3a** in 55 % yield and 82:18 *er*. Considering **2a** to be better, we further reduced the catalyst loading to observe that 1–2 mol-% was not as effective and gave lower *er* for **3a**. An increase in catalyst loading to 5–10 mol-% of **2a** gave no beneficial results. Thus, we chose **2a** under 2.5 mol-% as optimum requirement for asymmetric allylation of imines.

We next investigated the scope of complex **2a** for asymmetric allylation of various imines using allyltributylstannane (1.25 equiv.) and water (1.0 equiv.) at 0 °C (Scheme 4). The imine **1b** delivered the homoallylamine **3b** in good yield of 71 % and *er* = 82:18. Imines with electron donating groups like **1c**, **1d** and **1e** worked well with increased *er* of **3c** (88:12), **3d** (93:7) and **3e** (86:14), respectively. The imine **1f** with *p*-Ph group provided the corresponding amine **3f** in 74 % yield and *er* = 75:25. The *p*-Cl-aryl imine **1g** worked well giving **3g** in 61 % yield and *er* = 80:20. The piperonyl imine **1a** gave **3a** in good yield (68 %) and *er* = 90:10. The similar imine with PMB group on *N* for **1h** lowered the *er* of **3h** to 86:14. The naphthyl based imines **1i** and **1j** provided the corresponding homoallylamines **3i** (*er* = 77:23) and **3j** (*er* = 76:24). The 2-thienyl imine **1k** reacted well to furnish the homoallylamine **3k** with *er* = 72:28. Change of Bn to allyl group on *N*, i.e. imine **1l** also worked well providing the homoallylamine **3l** in 70 % yield and *er* = 78:22.




Scheme 4. Catalytic asymmetric allylation of imines **1** with allyltributylstannane using catalyst **2a**. Allyltributylstannane (1.25 equiv.), $H_2O$ (1.0 equiv.), catalyst **2a** (2.5 mol-%), THF, 0 °C. *er* determined by HPLC. Note: 2.5 mol-% of **2a** is with respect to two Pd.

The reaction would follow similar mechanistic path (Figure 1) as described by us earlier using the monomeric catalyst.[12b] The sign of optical rotation of the homoallylamines matched well with those prepared by us using the pinene-based catalyst[12a] indicating them to have the (*R*) configuration. This is also opposite to our work reported earlier[12b] [using (+)-menthol] as here, we used (–)-menthol **4**. The addition of the allyl group to the *Si* face of the imine is disfavored in having the R group of the imine in a sterically hindered position with respect to the isopropyl group (Figure 1, model **A**). However, attack on the *Re* face of the imine is favored as the R group of the imine is placed away from the menthyl moiety resulting in the formation of (*R*)-homoallylamines (model **B**). It is remarkable to note that the dimeric complexes also catalyzed the asymmetric allylation of imines similar to monomeric complexes and transferred the chiral information from the menthane skeleton to the product.

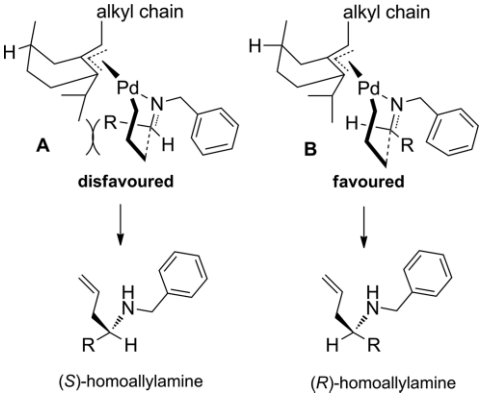



Figure 1. Probable transition state models.

## Conclusions

We have synthesized various menthane-based dimeric chiral $\eta^3$-bis-π-allylpalladium chloride complexes for the first time. It was remarkable to note that the complexes exist as intermolecular dimers with four chloride bridges. They catalyze the asymmetric allylation of various imines to afford chiral homoallylamines in good yields and enantioselectivities. The homoallylamines have the same configuration as those obtained by us previously using a pinene-based catalyst.[12a] Currently, we are investigating the nature of the dimerization to find out whether it can occur within the bis complex (intramolecular) while having an optimum chain and substituents to fold as **2′** with two chloride bridges (Scheme 2).

## 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. (–)-Menthol, palladium(II) trifluoroacetate, allyltributylstannane and $nBu_4NCl$ were purchased from Sigma Aldrich Chemical Co. $^1H$ and $^{13}C$ NMR were recorded at 400 or 500 MHz and 100 or 125 MHz respectively as $CDCl_3$ solutions and the chemical shifts are based on the TMS peak at $\delta$ = 0.00 pm for the $^1H$ NMR and the $CDCl_3$ peak at $\delta$ = 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 multi-wavelength detector. Imines were prepared as previously reported under microwave conditions.[21] For the π-allylpalladium chloride complexes although are solids, we did not determine melting points as they decomposed upon slight heating.

**General procedure for synthesis of olefins (6a-f): The following preparation of 6a is representative.**

**(1*E*,4*E*)-1,4-bis[(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-butane (6a):** To a stirred slurry of $Br^-Ph_3P^+CH_2(CH_2)_2CH_2Ph_3P^+Br^-$ (3.0 g, 4.05 mmol) in dry THF (30 mL) was added *t*-BuOK (1.363 g, 12.15 mmol, 3.0 equiv.) in portions at room temperature under an argon atmosphere. After stirring for 30 min, a solution of (–)-**5** (1.313 g, 8.51 mmol) in dry THF (5 mL) was added dropwise to the orange colored ylide solution and the mixture was stirred from room temperature to reflux for 72 h. It was then cooled to room temperature and quenched with a saturated aqueous solution of $NH_4Cl$ (5 mL), and the resulting mixture was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine, dried ($Na_2SO_4$) and concentrated. The crude residue was purified by silica gel column chromatography using petroleum ether as the eluent to afford **6a** (602.5 mg, 45 %) as a colorless oil. $[\alpha]_D^{25}$ –48.8 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2954, 2869, 1661, 1457, 1380, 1267, 1163, 1062, 865, 739, 613, 545 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.7 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.91 (d, *J* = 6.4 Hz, 6H), 1.07–1.15 (m, 2H), 1.23–1.31 (m, 2H), 1.53–1.60 (m, 2H), 1.62–1.70 (m, 4H), 1.70–1.81 (m, 4H), 1.87–1.97 (m, 2H), 2.03–2.08 (m, 4H), 2.30–2.37 (m, 2H), 5.12 (t, *J* = 6.3 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 19.7, 20.6, 22.1, 26.5, 26.8, 28.0, 32.1, 32.4, 35.2, 51.2, 121.5, 139.8 ppm; HRMS (ESI-TOF): *m/z* $[M + K]^+$ calcd. for $C_{24}H_{42}K$ 369.2918, found 369.2917.

**(1*E*,6*E*)-1,6-bis[(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-hexane (6b):** The title compound was prepared from (–)-**5** (1.313 g, 8.51 mmol) and $Br^-Ph_3P^+CH_2(CH_2)_4CH_2Ph_3P^+Br^-$ (3.113 g, 4.05 mmol) by a similar procedure to that described for **6a** to deliver **6b** (552 mg, 38 %, reaction time = 70 h) as a colorless oil; $[\alpha]_D^{25}$ –31.0 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2955, 2926, 2854, 1658, 1463, 1115, 1021, 858 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.7 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.91 (d, *J* = 6.3 Hz, 6H), 1.06–1.16 (m, 2H), 1.23–1.30 (m, 2H), 1.30–1.39 (m, 4H), 1.53–1.61 (m, 2H), 1.62–1.81 (m, 8H), 1.86–2.06 (m, 6H), 2.27–2.38 (m, 2H), 5.09 (t, *J* = 7.1 Hz, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 19.8, 20.6, 22.1, 26.4, 26.8, 27.1, 29.9, 32.0, 32.3, 35.1, 51.2, 121.8, 139.6 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{47}$ 359.3672, found 359.3669.

**(1*E*,8*E*)-1,8-bis[(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-octane (6c):** The title compound was prepared from (–)-**5** (1.313 g, 8.51 mmol) and $Br^-Ph_3P^+CH_2(CH_2)_6CH_2Ph_3P^+Br^-$ (3.226 g, 4.05 mmol) by a similar procedure to that described for **6a** to give **6c** (563.8 mg, 36 %, reaction time = 72 h) as a colorless oil; $[\alpha]_D^{25}$ –34.2 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2927, 2854, 1662, 1455, 1381, 1168, 1095, 1022, 868 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.7 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.92 (d, *J* = 6.4 Hz, 6H), 1.09–1.17 (m, 2H), 1.25–1.34 (m, 12H), 1.55–1.61 (m, 2H), 1.64–1.73 (m, 4H), 1.75–1.82 (m, 2H), 1.90–1.98 (m, 2H), 1.98–2.08 (m, 4H), 2.30–2.35 (m, 2H), 5.10 (t, *J* = 7.2 Hz, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 19.7, 20.6, 22.1, 26.4, 26.8, 27.2, 29.2, 30.3, 31.9, 32.3, 35.0, 51.2, 121.9, 139.5 ppm; HRMS (ESI-TOF): *m/z* $[M + K]^+$ calcd. for $C_{28}H_{50}K$ 425.3544, found 425.3540.

**(1*E*,10*E*)-1,10-bis[(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene] decane (6d):** The title compound was prepared from (–)-**5** (1.313 g, 8.51 mmol) and $Br^-Ph_3P^+CH_2(CH_2)_8CH_2Ph_3P^+Br^-$ (3.34 g, 4.05 mmol) by a similar procedure to that described for **6a** to produce **6d** (504 mg, 30 %, reaction time = 72 h) as a colorless oil; $[\alpha]_D^{25}$ –25.3 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2953, 2923, 2861, 1457, 1376, 907, 734, 678 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.7 Hz, 6H), 0.89 (d, *J* = 6.5 Hz, 6H), 0.92 (d, *J* = 6.1 Hz, 6H), 1.09–1.18 (m, 2H), 1.22–1.38 (m, 16H), 1.55–1.63 (m, 2H), 1.63–1.75 (m, 4H), 1.75–1.83 (m, 2H), 1.86–2.08 (m, 6H), 2.27–2.39 (m, 2H), 5.10 (t, *J* = 7.3 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 19.8, 20.6, 22.1, 26.4, 26.8, 27.2, 29.3, 29.6, 30.3, 31.9, 32.3, 35.0, 51.2, 121.9, 139.5 ppm; HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{55}$ 415.4298, found 415.4296.

**(1*E*,7*E*)-1,7-bis[(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene]-4,4-dimethylheptane (6e):** The title compound was prepared from (–)-**5** (1.313 g, 8.51 mmol) and $I^-Ph_3P^+CH_2(CH_2)_2C(CH_3)_2(CH_2)_2-CH_2Ph_3P^+I^-$ (3.664 g, 4.05 mmol) by a similar procedure to that described for **6a** to afford **6e** (633 mg, 39 %, reaction time = 70 h) as a colorless oil; $[\alpha]_D^{25}$ –34.6 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2952, 2868, 1660, 1455, 1383, 1364, 1326, 1163, 1089, 1063, 1017, 866, 810, 610, 545 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.6 Hz, 6H), 0.87–0.90 (m, 12H), 0.92 (d, *J* = 6.4 Hz, 6H), 1.07–1.17 (m, 2H), 1.18–1.24 (m, 4H), 1.25–1.33 (m, 4H), 1.53–1.62 (m, 2H), 1.64–1.74 (m, 4H), 1.74–1.81 (m, 2H), 1.85–2.0 (m, 6H), 2.27–2.37 (m, 2H), 5.10 (t, *J* = 7.1 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 19.8, 20.6, 22.0, 22.1, 26.5, 26.7, 27.3, 31.9, 32.3, 32.9, 34.9, 42.4, 51.2, 122.4, 139.1 ppm; HRMS (ESI-TOF): *m/z* $[M + K]^+$ calcd. for $C_{29}H_{52}K$ 439.3701, found 437.3704.

**1,4-Bis[(*E*)-3-((2*S*,5*R*)-2-Isopropyl-5-methylcyclohexylidene)-propyl] benzene (6f):** The title compound was prepared from (–)-**5** (1.313 g, 8.51 mmol) and $I^-Ph_3P^+CH_2(CH_2)_2$-$pC_6H_4$-$(CH_2)_2CH_2Ph_3P^+I^-$ (3.801 g, 4.05 mmol) by a similar procedure to that described for **6a** to give **6f** (880 mg, 50 %, reaction time = 72 h) as a colorless oil; $[\alpha]_D^{25}$ –36.0 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 3013, 2952, 2927, 2867, 1661, 1513, 1454, 1381, 1365, 1163, 1021, 862, 805, 670 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.85–0.94 (m, 18H), 1.09–1.18 (m, 2H), 1.24–1.36 (m, 2H), 1.53–1.83 (m, 10H), 1.86–2.0 (m, 2H), 2.26–2.43 (m, 6H), 2.54–2.71 (m, 4H), 5.19 (t, *J* = 6.8 Hz, 2H), 7.13 (d, *J* = 1.8 Hz, 4H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 19.7, 20.6, 22.1, 26.5, 26.8, 29.5, 31.9, 32.3, 35.1, 36.3, 51.2, 120.8, 128.25, 128.3, 139.7, 140.4 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. for $C_{32}H_{50}Na$ 457.3805, found 457.3803.

**General procedure for the synthesis of π-allylpalladium chloride complexes (2a–f):** To a solution of $Pd(OCOCF_3)_2$ (0.2 g, 0.6 mmol, 3.0 equiv.) in dry acetone (10 mL) at room temperature and under an argon atmosphere was added olefin **6** (0.2 mmol, 1.0 equiv.). The mixture was stirred for 8 h (monitored by TLC). $nBu_4NCl$ (0.23 g, 0.8 mmol, 4.0 equiv.) in dry acetone (2 mL) was added and the reaction mixture stirred for additional 1 h. The clear brown colored solution was then filtered through a plug of celite to remove suspended Pd-black and washed with acetone (2 × 10 mL). 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 complex **2a-f**.

**π-Allylpalladium chloride complex (2a):** Isolated yield (55.1 mg, 45 %); yellow powder; $[\alpha]_D^{25}$ +24.0 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2956, 2921, 2868, 1742, 1644, 1463, 1363, 1378, 1260, 1183, 1081, 806, 722, 604 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 6H), 1.0 (d, *J* = 6.2 Hz, 6H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.29–1.39 (m, 2H), 1.41–1.69 (m, 8H) 1.81–1.95 (m, 4H), 2.11–2.27 (m, 2H), 2.34–2.52 (m, 4H), 3.84 (t, *J* = 5.4 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 20.1, 21.8, 24.1, 27.6, 29.1, 29.2, 30.0, 32.2, 36.3, 75.5, 99.4,

117.0 ppm; HRMS (ESI-TOF): *m/z* [M – Cl]$^+$ calcd. for $C_{48}H_{80}Pd_4Cl_3$ 1189.1482, found 1189.1480.

**π -Allylpalladium chloride complex (2b):** Isolated yield (44.8 mg, 35 %); yellow powder; $[\alpha]_D^{25}$ +34.2 (*c* 2.2, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2955, 2925, 2868, 1734, 1661, 1456, 1382, 1361, 1322, 1261, 1034, 666 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 6H), 1.01 (d, *J* = 6.1 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.44–1.69 (m, 12H), 1.73–1.83 (m, 4H), 1.83–1.96 (m, 4H), 2.33–2.54 (m, 4H), 3.80 (t, *J* = 5.6 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 20.1, 21.9, 24.0, 27.3, 28.9, 29.1, 29.2, 29.9, 32.3, 36.1, 74.9, 99.9, 117.1 ppm; HRMS (ESI-TOF): *m/z* [M – Cl]$^+$ calcd. for $C_{52}H_{88}Pd_4Cl_3$ 1245.2110, found 1245.2125.

**π-Allylpalladium chloride complex (2c):** Isolated yield (40.1 mg, 30 %); yellow powder; $[\alpha]_D^{25}$ +23.9 (*c* 0.70, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2945, 2925, 2867, 1742, 1666, 1456, 1044, 909, 765, 699, 616 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.6 Hz, 6H), 1.01 (d, *J* = 5.8 Hz, 6H), 1.23 (d, *J* = 6.6 Hz, 6H), 1.33–1.53 (m, 12H), 1.59–1.73 (m, 8H), 1.77–1.85 (m, 2H), 1.86–1.95 (m, 2H), 2.35–2.50 (m, 4H), 3.8 (t, *J* = 5.6 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 20.0, 21.8, 24.1, 27.3, 29.08, 29.1, 29.4, 29.9, 30.1, 32.2, 36.1, 75.3, 99.7, 117.1 ppm; HRMS (ESI-TOF): *m/z* [M + H – Cl]$^+$ calcd. for $C_{56}H_{97}Pd_4Cl_3$ 1301.2814, found 1301.2819.

**π-Allylpalladium chloride complex (2d):** Isolated yield (58.5 mg, 42 %); yellow powder; $[\alpha]_D^{25}$ +44.6 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2955, 2924, 2852, 1645, 1463, 1044, 909 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 6H), 1.0 (d, *J* = 6.1 Hz, 6H), 1.23 (d, *J* = 6.6 Hz, 6H), 1.30–1.37 (m, 8H), 1.41–1.55 (m, 8H), 1.56–1.73 (m, 8H), 1.76–1.86 (m, 2H), 1.86–1.98 (m, 2H), 2.37–2.53 (m, 4H), 3.82 (t, *J* = 6.15 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 20.0, 21.9, 24.1, 27.3, 28.7, 29.1, 29.4, 29.8, 29.9, 32.3, 36.1, 75.2, 99.9, 117.1 ppm; HRMS (ESI-TOF): *m/z* [M – Cl]$^+$ calcd. for $C_{60}H_{104}Pd_4Cl_3$ 1357.3365, found 1357.3365.

**π-Allylpalladium chloride complex (2e):** Isolated yield (43.7 mg, 32 %); yellow powder; $[\alpha]_D^{25}$ +38.20 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2955, 2927, 2868, 1643, 1459, 1378, 1363, 1272, 912, 806, 734 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 0.85–0.91 (m, 12H), 1.03 (d, *J* = 6.6 Hz, 6H), 1.24 (m, 8H), 1.46–1.53 (m, 4H), 1.55–1.68 (m, 8H), 1.79–1.88 (m, 4H), 1.88–1.95 (m, 2H), 2.36–2.51 (m, 4H), 3.71 (t, *J* = 5.4 Hz, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 20.1, 21.9, 24.05, 24.1, 26.7, 27.2, 29.2, 29.7, 29.9, 31.9, 32.2, 33.0, 36.1, 41.4, 75.2, 99.9, 116.7 ppm; HRMS (ESI-TOF): *m/z* [M – Cl]$^+$ calcd. for $C_{58}H_{100}Pd_4Cl_3$ 1329.3051, found 1329.3051.

**π-Allylpalladium chloride complex (2f):** Isolated yield (43 mg, 30 %); yellow powder; $[\alpha]_D^{25}$ –9.0 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 2956, 2921, 2851, 1742, 1642, 1463, 1378, 1260, 1022, 804, 722, 612 cm$^1$; $^1$H NMR (400 MHz, $CDCl_3$) δ 0.90 (d, *J* = 6.7 Hz, 6H), 1.0 (d, *J* = 5.9 Hz, 6H) 1.20–1.28 (m, 8H), 1.46–1.75 (m, 10H), 1.80–1.95 (m, 6H), 2.42–2.49 (m, 2H), 2.75–2.90 (m, 2H), 3.09–3.23 (m, 2H), 3.82–3.91 (m, 2H), 7.21 (s, 4H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.8, 24.1, 27.4, 29.1, 29.9, 31.9, 32.3, 34.7, 36.3, 74.6, 99.9, 117.3, 128.4, 139.7 ppm; HRMS (ESI-TOF): *m/z* [M – Cl]$^+$ calcd. for $C_{64}H_{96}Pd_4Cl_3$ 1397.2740, found 1397.2740.

**General procedure for asymmetric allylation of imines 1 using catalyst 2a:** The imine **1** (0.334 mmol) was placed in a Wheaton micro reactor (5 mL capacity), and under an argon atmosphere, dry THF (1.0 mL), degassed water (6 μL, 0.334 mmol, 1.0 equiv.), and allyltributylstannane (130 μL, 0.420 mmol, 1.25 equiv.) were added sequentially. The mixture was cooled to 0 °C, and the chiral palladium chloride complex **2a** (5.2 mg, 0.0042 mmol, 2.5 mol-% with respect to two Pd) 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, 2.0 mL). $CH_3CN$ (1.0 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, 1.0 mL), and the resulting solution was stirred for 5 min. The solution was extracted with EtOAc (2 × 5 mL), and the combined organic layers were dried ($Na_2SO_4$) and concentrated. Purification of the residue by silica gel column chromatography using petroleum ether/EtOAc (5:1) offered the corresponding homoallylamines **3** as colorless oils. The characterization data for most of the homoallylamines is same as reported by us earlier.[12] The enantiomeric excess was determined by HPLC of the trifluoroacetylamide forms of all of the homoallylamines with UV detection at 254 nm.

**(*R*)-*N*-Benzyl-1-phenyl-3-butenylamine (3b):**[12a] Isolated yield (56.3 mg, 71 %), colorless oil; $[\alpha]_D^{25}$ +39.1 (*c* 0.60, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.01 (br s, 1H), 2.43–2.52 (m, 2H), 3.55–3.61 (m, 1H), 3.69–3.79 (m, 2H), 5.05–5.16 (m, 2H), 5.69–5.81 (m, 1H), 7.25–7.45 (m, 10H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 43.0, 51.3, 61.5, 117.5, 126.8, 127.0, 127.3, 128.1, 128.3, 128.4, 135.4, 140.4, 143.6 ppm; HPLC analysis: *er* = 82:18, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99.8:0.2, flow rate 0.5 mL/min, ($t_{major}$ = 12.64 min, $t_{minor}$ = 15.63 min).

**(*R*)-*N*-Benzyl-1-(4-methylphenyl)-3-butenylamine (3c):**[12a] Isolated yield (63.8 mg, 76 %), colorless oil; $[\alpha]_D^{25}$ +33.1 (*c* 0.25, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 1.86 (br s, 1H), 2.40 (s, 3H), 2.42–2.48 (m, 2H), 3.56 (d, *J* = 13.3 Hz, 1H), 3.66–3.75 (m, 2H), 5.04–5.16 (m, 2H), 5.70–5.81 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.26–7.32 (m, 5H), 7.32–7.37 (m, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 21.1, 43.1, 51.3, 61.2, 117.4, 126.7, 127.2, 128.1, 128.3, 129.1, 135.5, 136.5, 140.6, 140.7 ppm; HPLC analysis: *er* = 88:12, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99.5:0.5, flow rate 0.7 mL/min, ($t_{major}$ = 8.25 min, $t_{minor}$ = 9.38 min).

**(*R*)-*N*-Benzyl-1-(4-*tert*-butylphenyl)-3-butenylamine (3d):** Isolated yield (75.5 mg, 77 %), colorless oil; $[\alpha]_D^{25}$ +34.2 (*c* 0.75, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 3369, 2959, 2927, 2855, 1682, 1510, 1463, 1364, 1265, 1203, 1110, 1028, 919, 835, 745, 703 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 1.79 (br s, 1H), 2.37–2.50 (m, 2H), 3.54 (d, *J* = 13.3 Hz, 1H), 3.65–3.73 (m, 2H), 5.02–5.15 (m, 2H), 5.67–5.78 (m, 1H), 7.21–7.34 (m, 7H), 7.35–7.39 (m, 2H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 31.4, 34.4, 43.0, 51.4, 61.2, 117.4, 125.2, 126.8, 126.9, 128.1, 128.3, 135.7, 140.6, 149.8 ppm; HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd. for $C_{21}H_{28}N$ 294.2216, found 294.2211; HPLC analysis: *er* = 93:7, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99.5:0.5, flow rate 0.7 mL/min, ($t_{major}$ = 7.69 min, $t_{minor}$ = 8.28 min).

**(*R*)-*N*-Benzyl-1-(4-methoxyphenyl)-3-butenylamine (3e):**[12a] Isolated yield (67.9 mg, 76 %), colorless oil; $[\alpha]_D^{25}$ +31.8 (*c* 0.30, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 1.74 (br s, 1H), 2.38–2.43 (m, 2H), 3.53 (d, *J* = 13.3 Hz, 1H), 3.62–3.72 (m, 2H), 3.83 (s, 3H), 5.01–5.12 (m, 2 H), 5.65–5.78 (m, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.22–7.36 (m, 7H) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) δ 43.1, 51.3, 55.2, 60.9, 113.7, 117.4, 126.8, 128.1, 128.3, 128.3, 135.6, 135.7, 140.6, 158.6 ppm; HPLC analysis: *er* = 86:14 Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99.5:0.5, flow rate 1.0 mL/min, ($t_{major}$ = 16.47 min, $t_{minor}$ = 18.10 min).

**(*R*)-*N*-Benzyl-1-(biphenyl-4-yl)-3-butenylamine (3f):** Isolated yield (77.5 mg, 74 %), colorless oil; $[\alpha]_D^{25}$ +8.5 (*c* 0.24, $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}_{max}$ 3420, 3061, 3027, 2837, 1640, 1605, 1579, 1566, 1485, 1452, 1374, 1305, 1169, 112, 1080, 912, 836, 734, 695 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 1.78 (br s, 1H), 2.41–2.53 (m, 2H), 3.58 (d, *J* = 13.3 Hz, 1H), 3.70–3.79 (m, 2H), 5.06–5.16 (m, 2H), 5.70–5.81 (m, 1H), 7.25–7.38 (m, 6H), 7.43–7.48 (m, 4H), 7.58–7.67 (m, 4H) ppm; $^{13}$C

NMR (125 MHz, $CDCl_3$) δ 43.0, 51.4, 61.3, 117.7, 126.8, 127.0, 127.1, 127.7, 128.1, 128.3, 128.7, 135.4, 139.9, 140.5, 141.0 142.9 ppm; HRMS (ESI-TOF): *m/z* $[M + Na]^+$ calcd. for $C_{23}H_{23}NNa$ 336.1723, found 336.1725; HPLC analysis: *er* = 75:25, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99:1, flow rate 0.7 mL/min, ($t_{minor}$ = 13.63 min, $t_{major}$ = 17.43 min).

**(*R*)-*N*-Benzyl-1-(4-chlorophenyl)-3-butenylamine (3g):**[12b] Isolated yield (55.4 mg, 61 %), colorless oil; $[\alpha]_D^{25}$ +28.1 (*c* 0.5, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.79 (br s, 1H), 2.35–2.37 (m, 2H), 3.49 (d, *J* = 13.3 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.62–3.68 (m, 1H), 5.03–5.08 (m, 2H), 5.61–5.72 (m, 1H), 7.2–7.4 (m, 9H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 43.0, 51.4, 60.9, 117.9, 126.9, 128.1, 128.4, 128.5, 128.7, 132.6, 134.9, 140.3, 142.3 ppm; HPLC analysis: *er* = 80:20, Chiralpak IA column, *n*-hexane/*i*PrOH = 99:1, flow rate 0.5 mL/min, ($t_{major}$ = 10.45 min, $t_{minor}$ = 11.68 min).

**(*R*)-*N*-Benzyl-1-piperonyl-3-butenylamine (3a):**[12a] Isolated yield (63.9 mg, 68 %), Colorless oil; $[\alpha]_D^{25}$ +31.7 (*c* 0.4, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.91 (br s, 1H), 2.35–2.42 (m, 2H), 3.53 (d, *J* = 13.3 Hz, 1H), 3.62 (t, *J* = 7.1 Hz, 1H), 3.69 (d, *J* = 13.3 Hz, 1H), 5.01–5.11 (m, 2H), 5.64–5.75 (m, 1H), 5.96 (s, 2H), 6.79 (s, 2H), 6.93 (s, 1H), 7.21–7.35 (m, 5H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 43.1, 51.2, 61.3, 100.8, 107.3, 107.9, 117.5, 120.6, 126.8, 128.1, 128.3, 135.3, 137.7, 140.4, 146.5, 147.8 ppm; HPLC analysis: *er* = 90:10, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 98:2, flow rate 0.5 mL/min, ($t_{major}$ = 14.45 min, $t_{minor}$ = 15.69 min).

**(*R*)-*N*-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine (3h):**[12a] Isolated yield (72.8 mg, 70 %), Colorless oil; $[\alpha]_D^{25}$ +33.4 (*c* 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.81 (br s, 1H), 2.37–2.45 (m, 2H), 3.45 (d, *J* = 13.3 Hz, 1 H), 3.57–3.64 (m, 2H), 3.79 (s, 3H), 5.00–5.09 (m, 2H), 5.62–5.73 (m, 1H), 5.95 (s, 2H), 6.77 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 1H), 7.17 (d, *J* = 8.6 Hz, 2H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 43.1, 50.6, 55.2, 61.2, 100.8, 107.3, 107.9, 113.7, 117.5, 120.6, 129.3, 132.5, 135.4, 137.8, 146.5, 147.8, 158.5 ppm; HPLC analysis: *er* = 86:14, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99:1, flow rate 1 mL/min, ($t_{major}$ = 15.01 min, $t_{minor}$ = 22.55 min).

**(*R*)-*N*-Benzyl-1-(2-naphthyl)-3-butenylamine (3i):**[12a] Isolated yield (65.3 mg, 68 %), colorless oil; $[\alpha]_D^{25}$ +46.5 (*c* 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.87 (br s, 1H), 2.48–2.57 (m, 2H), 3.58 (d, *J* = 13.3 Hz, 1H), 3.72 (d, *J* = 13.4 Hz, 1H), 3.89 (t, *J* = 6.8 Hz, 1H), 5.03–5.15 (m, 2H), 5.69–5.80 (m, 1H), 7.23–7.36 (m, 5H), 7.45–7.52 (m, 2H), 7.54–7.58 (m, 1H), 7.80 (s, 1H), 7.83–7.90 (m, 3H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 42.9, 51.4, 61.7, 117.7, 125.3, 125.5, 125.9, 126.2, 126.9, 127.7, 127.8, 128.1, 128.2, 128.4, 133.0, 133.4, 135.3, 140.4, 141.1 ppm; HPLC analysis: *er* = 77:23, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 98:2, flow rate 0.5 mL/min, ($t_{major}$ = 15.34 min, $t_{minor}$ = 19.38 min).

**(*R*)-*N*-Benzyl-1-(1-naphthyl)-3-butenylamine (3j):**[12a] Isolated yield (62.4 mg, 65 %), Colorless oil; $[\alpha]_D^{25}$ +26.5 (*c* 0.55, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.90 (br s, 1H), 2.47–2.55 (m, 1H), 2.65–2.73 (m, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 3.78 (d, *J* = 13.2 Hz, 1H), 4.62 (dd, *J* = 8.2, 4.7 Hz, 1H), 5.07–5.18 (m, 2H), 5.78–5.88 (m, 1H), 7.24–7.36 (m, 5H), 7.48–7.57 (m, 3H), 7.78–7.85 (m, 2H), 7.89–7.93 (m, 1H), 8.20 (d, *J* = 7.1 Hz, 1H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 42.1, 51.6, 57.0, 117.7, 123.0, 123.9, 125.3, 125.6, 125.7, 126.8, 127.4, 128.2, 128.3, 129.0, 131.6, 134.0, 135.5, 139.0, 140.6 ppm; HPLC analysis: *er* = 76:24, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99:1, flow rate 0.8 mL/min, ($t_{major}$ = 9.13 min, $t_{minor}$ = 10.79 min).

**(*R*)-*N*-Benzyl-1-(2-thiophenyl)-3-butenylamine (3k):**[12a] Isolated yield (48.8 mg, 60 %), Colorless oil; $[\alpha]_D^{25}$ 12.7 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.0 (br s, 1H), 2.48–2.57 (m, 2H), 3.64 (d, *J* = 13.3 Hz, 1H), 3.82 (d, *J* = 13.3 Hz, 1H), 4.03 (t, *J* = 6.8 Hz, 1H), 5.04–5.17 (m, 2H), 5.69–5.81 (m, 1H), 6.91–6.95 (m, 1H), 6.96–6.99 (m, 1H), 7.23–7.28 (m, 2H), 7.28–7.37 (m, 4H) ppm; $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 43.5, 51.2, 57.0, 118.0, 124.0, 124.2, 126.3, 126.9, 128.2, 128.4, 134.8, 140.2, 148.9 ppm; HPLC analysis: *er* = 72:28, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 99.5:0.5, flow rate 0.7 mL/min, ($t_{major}$ = 9.83 min, $t_{minor}$ = 11.99 min).

**(*R*)-*N*-Allyl-1-phenyl-3-butenylamine (3l):**[12b] Isolated yield (43.8 mg, 70 %), Colorless oil; $[\alpha]_D^{25}$ 18.8 (*c* 1.250, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.05 (br s, 1H), 2.41–2.48 (m, 2H), 2.99–3.06 (m, 1H), 3.10–3.17 (m, 1H), 3.70 (dd, *J* = 6.3, 1.2 Hz, 1H), 5.04–5.16 (m, 4H), 5.64– 5.78 (m, 1H), 5.81–5.93 (m, 1H), 7.22–7.34 (m, 5H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 42.7, 49.9, 61.7, 116.0, 117.6, 127.1, 127.4, 128.3, 135.2, 136.5, 143.3 ppm; HPLC analysis: *er* = 78:22, Chiralpak OD-H column, *n*-hexane/*i*PrOH = 98:2, flow rate 0.6 mL/min, ($t_{major}$ = 8.13 min $t_{minor}$ = 8.98 min).

### Conflict of interest

The authors declare no conflict of interest

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