Chiral Bis-π-allylpalladium Complex Catalyzed Asymmetric Allylation of Imines: Enhancement of Enantioselectivity and Chemical Yield in the Presence of Water

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Supporting Information
(32 pages)

General Information. Commercially available imines were procured from Aldrich Chemical Co.; while most were prepared by refluxing equimolar amount of corresponding aldehyde and amine in toluene or benzene with Dean-Stark removal of water. They were then purified by either high vacuum distillation or recrystallization. Most commercially supplied chemicals were freshly distilled or recrystallized before use. Solvents were dried by standard procedures. Dry THF refers to commercial dehydrated THF procured from Kanto Chem. Co., Inc, Japan. 1H and 13C NMR spectra were recorded on a Jeol JNM LA-300 spectrometer. The chemical shifts are reported in δ units relative to internal tetramethylsilane for 1H NMR and CDCl3 was used as internal standard (δ = 77.0) for 13C NMR. IR spectra were recorded on a Shimadzu FTIR-8200 A spectrometer. Mass spectra were recorded on Jeol JMS-HX 110 in EI mode. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter. HPLC was performed on Shimadzu LC9A using Daicel CHIRALCEL OD or CHIRALCEL OD-R columns (0.46 cm x 25 cm). The absolute configuration was determined by converting amine 13a into 1-phenylbutylamine which exhibited optical rotation with + value. The literature value of (S)-1-phenylbutylamine is [α]D = −21.3 (c 1.3, CHCl3). Hence the absolute configuration of 13a is confirmed to be (R). Thus, by analogy the homoallylamines obtained are assumed to have (R) configuration2 (unless otherwise indicated).

Preparation of the catalyst, 2a

(1R)-(+) nopinone is available in Aldrich Chemical Co. in 90% ee. But its precursor (1S)-(−)-β-pinene is available in 97% ee. So we preferred to prepare (1R)-(+) nopinone from (1S)-(−)-β-pinene. The ozonolysis of exocyclic double bond of (1S)-(−)-β-pinene afforded (1R)-(+) nopinone in 75% yield, [α]D = 39.4 (c =1, MeOH). Wittig reaction with ethyltriphenylphosphonium bromide and t-BuOK by known procedure4 gave the olefin 7 (E:Z = 1:1) in 83% yield.
From olefin 7 we followed the literature procedure\textsuperscript{5} to prepare the 2a:2b mixture. To a solution of Pd(OCOCF\textsubscript{3})\textsubscript{2} (5 g, 15.04 mmol) in dry acetone (125 mL) in a two necked round bottom flask under argon atmosphere was added olefin 7 (2.26 g, 15.04 mmol). The reaction mixture was stirred for 1 h at room temperature (TLC monitored). \textsuperscript{6}Bu\textsubscript{4}NCl (4.56 g, 16.55 mmol) in acetone (30 mL) was added and the reaction mixture was stirred for 1 h. The clear brown-orange solution was then filtered through a plug of celite to remove suspended Pd-black. The filtrate was concentrated to thick amber colored oil. This was purified by silica gel column chromatography using hexane/EtOAc = 5:1 as eluent to give 2a/2b mixture as semi solid (6.92 g). \textsuperscript{1}H NMR indicated 2a:2b = 1.3:1. This was dissolved in minimum CH\textsubscript{2}Cl\textsubscript{2} and hexane (30 mL) was added. The crystallized solid was filtered through sintered funnel, washed with hexane and dried with suction to afford 2a:2b = 4.8:1 (3.2 g) as yellow powder (I). Further upgradation is as shown in the flow chart below (II-V). During propionitrile recrystallization boiling of solvent to dissolve the solid should be avoided to prevent catalyst decomposition. To recover the catalyst the filtrates after each recrystallization F1-F3 as shown below were combined and concentrated to yellow colored solid foam. This was subjected to benzene column chromatography. Elution with benzene gave in first few fractions the catalyst 2b (0.45 g) having $[\alpha]_D^{22} + 47.5$ (c = 0.4, CHCl\textsubscript{3}). The later fractions were mixture of 2a and 2b. The filtrates F4 and F5 were combined and concentrated to yellow powder (1 g). This on successive three recrystallizations in propionitrile gave 2a:2b = 100:1 (0.452 g), $[\alpha]_D^{22} - 17.2$ (c = 0.4, CHCl\textsubscript{3}). Further three repeated recrystallizations in propionitrile afforded 2a:2b = >400:1 (0.215 g), $[\alpha]_D^{22} - 19.8$ (c = 0.4, CHCl\textsubscript{3}).
Mixture 2a:2b = 1.3:1 [semisolid 6.92 g], after column chromatography [5:1, Hexane:EtOAc]

I →
Yellow powder, 3.2 g [2a:2b = 4.8:1] Filtrate (foam, 3.6 g) F1
Filtrate concentrated

II →
Yellow powder, 2.32 g [2a:2b = 12.3:1] Filtrate (yellow powder, 0.832 g [2a:2b = 1.5:1]) F2

III →
Yellow powder, 1.56 g [2a:2b = 33:1] Filtrate (yellow powder, 0.701 g [2a:2b = 2.7:1]) F3

IV →
Yellow needles, 0.852 g [2a:2b = 100:1] Filtrate (yellow powder, 0.628 g [2a:2b = 8.8:1]) F4

[α]D22 = -19.4 (c = 0.4, CHCl3)

V →
Yellow needles, 0.443 g [2a:2b = >400:1] Filtrate (yellow powder, 0.381 g [2a:2b = 17:1]) F5

[α]D22 = -19.9 (c = 0.4, CHCl3)

Recovery of the catalyst

Filtrates F1 - F3 Combined and subjected to benzene column separation

2b ligand was separated (0.45 g), [α]D22 + 47.5 (c = 0.4, CHCl3)

Filtrates F4 and F5 [1.0 g]
Three repeated recrystallizations in EtCN

Yellow needles, 0.452 g [2a:2b = 100:1]
[α]D22 = -17.2 (c = 0.4, CHCl3)

Three repeated recrystallizations in EtCN

Yellow needles, 0.215 g [2a:2b = >400:1]
[α]D22 = -19.8 (c = 0.4, CHCl3)

1H NMR of 2a:2b = 1.3:1
$^1$H NMR of 2a:2b = 100:1
$^1$H NMR of 2a:2b = >400:1

2a: (CDCl$_3$) $\delta$ 3.84–3.80 (m, 1H), 3.78–3.68 (m, 1H), 2.7–2.64 (m, 1H), 2.55 (brt, $J = 5.5$ Hz, 1H), 2.44–2.33 (m, 1H), 2.08–2.03 (m, 1H), 1.77–1.74 (m, 2H), 1.34 (s, 3H), 1.13 (d, $J = 6.5$ Hz, 3H), 0.91 (s, 3H).
$^{13}$C NMR 2a: (CDCl$_3$) $\delta$ 136.0, 72.2, 71.0, 40.5, 39.9, 37.8, 33.8, 29.9, 26.1, 21.7, 13.9.
IR (KBr) 2982, 2951, 2912, 2870, 1499, 1466, 1448, 1429, 1367, 1265, 1219, 1101, 1051, 1032, 974, 860, 758 cm⁻¹.

\[ \text{Pd-Cl} \]

\[ \text{2b} \]

\[ \text{1H NMR of 2b: (CDCl}_3\text{)} \] \( \delta \) 4.47–4.41 (m, 1H), 4.33–4.22 (m, 1H), 2.67–2.52 (m, 1H), 2.36–2.3 (m, 1H), 2.2–2.13 (m, 1H), 2.08–2.02 (m, 1H), 1.87–1.74 (m, 2H), 1.29 (s, 3H), 1.03 (d, \( J = 6.8 \text{ Hz} \), 3H), 0.71 (s, 3H).
$^{13}$C NMR 2b: (CDCl$_3$) $\delta$ 132.5, 72.7, 70.8, 46.5, 39.9, 38.0, 34.4, 29.9, 26.0, 21.7, 16.2.

IR (KBr) 2980, 2918, 2872, 2833, 1468, 1454, 1429, 1369, 1265, 1221, 1099, 1042, 968, 920, 762 cm$^{-1}$.

General equation for allylation of imines with allyltributylstannane and catalyst 2a

\[
\begin{align*}
\text{5} & \overset{\text{cat} \ 2a}{\underset{1 \text{ eq } H_2O, \text{ THF, } 0^\circ C}{\longrightarrow}} \text{6}
\end{align*}
\]
Table. Catalytic asymmetric allylation of imines with allyltribuylstannane in the presence of the catalyst 2a

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
<th>time (h)</th>
<th>% yield</th>
<th>%ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12a (R_1 = R_2 = R_3 = H)</td>
<td>13a</td>
<td>48</td>
<td>86</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>12b (R_1 = R_3 = H, R_2 = \text{OMe})</td>
<td>13b</td>
<td>98</td>
<td>82</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>12c (R_1 = R_3 = H, R_2 = \text{Me})</td>
<td>13c</td>
<td>67</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>12d (R_1 = R_2 = H, R_3 = \text{OMe})</td>
<td>13d</td>
<td>73</td>
<td>78</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>12e (R_1 = R_2 = \text{OMe}, R_3 = H)</td>
<td>13e</td>
<td>116</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>14</td>
<td>15</td>
<td>74</td>
<td>84</td>
<td>50</td>
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<tr>
<td>7</td>
<td>16</td>
<td>17</td>
<td>72</td>
<td>84</td>
<td>69</td>
</tr>
<tr>
<td>8</td>
<td>18a (X = \text{O})</td>
<td>19a</td>
<td>73</td>
<td>90</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>18b (X = \text{S})</td>
<td>19b</td>
<td>90</td>
<td>90</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>10a (R_1 = R_2 = H, R_3 = \text{OMe})</td>
<td>11a</td>
<td>73</td>
<td>89</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td>10b (R_1 = R_3 = \text{OMe}, R_2 = H)</td>
<td>11b</td>
<td>88</td>
<td>78</td>
<td>85</td>
</tr>
<tr>
<td>12</td>
<td>10c (R_1 = \text{Me}, R_2 = H, R_3 = \text{OMe})</td>
<td>11c</td>
<td>72</td>
<td>81</td>
<td>86</td>
</tr>
<tr>
<td>13</td>
<td>10d (R_1 = \text{NO}_2, R_2 = H, R_3 = \text{OMe})</td>
<td>11d</td>
<td>70</td>
<td>94</td>
<td>42</td>
</tr>
<tr>
<td>14</td>
<td>10e (R_1 = R_3 = H, R_2 = \text{OMe})</td>
<td>11e</td>
<td>78</td>
<td>82</td>
<td>89</td>
</tr>
</tbody>
</table>
All reactions were carried out with 1.25 equivalent of allyltributylstannane and one equivalent of water in the presence of 5 mol% of 2a and at 0°C for the specified time. In some cases additional 0.5 equivalent of allyltributylstannane was added if it was completely consumed and the reaction was not complete (checked by GC-MS); determined by 1H NMR of the crude reaction mixture with CH₃NO₂ as internal standard. ee based on known [α]₀ values (see reference 6)
N−Benzyl−1−phenyl−3−butenylamine, 13a

![Structure of 13a](image)

Colorless oil; [α]D23 = + 51.2 (c 1.45, CHCl₃); IR, ¹H NMR, ¹³C NMR, HRMS and analysis data (see ref. 2). The enantiomeric excess was determined by using CHIRALCEL OD-R column, CH₃CN/1M NaClO₄ aq = 40/60, flow rate = 0.8 mL/min, UV detection at 254 nm, t'R = 16.38 min (major enantiomer), t'R = 18.48 min (minor enantiomer); 85% ee.

N−Benzyl−1−(4−methoxyphenyl)−3−butenylamine, 13b

![Structure of 13b](image)

Colorless oil; [α]D22 = + 56.1 (c 0.745, CHCl₃); IR, ¹H NMR, ¹³C NMR, HRMS and analysis data (see ref. 2). The enantiomeric excess was determined by using CHIRALCEL OD-R column, CH₃CN/1M NaClO₄ aq = 40/60, flow rate = 0.8 mL/min, UV detection at 254 nm, t'R = 18.02 min (major enantiomer), t'R = 21.5 min (minor enantiomer); 85% ee.

N−Benzyl−1−(4−methylphenyl)−3−butenylamine, 13c

![Structure of 13c](image)

Colorless oil; [α]D22 = + 50.4 (c 1.0, CHCl₃); IR (neat) 3325, 3061, 3025, 2977, 2921, 1638, 1603, 1513, 1495, 1454, 1350, 1304, 1176, 1029, 995, 916, 816, 735 cm⁻¹; ¹H NMR (CDCl₃) δ 7.28−7.13 (m, 7H), 7.09 (d, J = 8 Hz, 2H), 5.6 (ddt, J = 17.1 Hz, 10.3 Hz, 7.1 Hz, 1H), 5.02 (ddt, J = 17.1 Hz, 2 Hz, 2 Hz, 1H), 4.97 (ddt, J = 10.3 Hz, 2 Hz, 2 Hz, 1H), 3.61−3.59 (m, 1H), 3.6 (d, J = 13.4 Hz, 1H), 3.45 (d, J = 13.4 Hz, 1H), 2.34−2.32 (m, 2H), 2.3 (s, 3H), 1.66 (brs, 1H);
\(^{13}\text{C NMR (CDCl}_3\text{)} \) \(\delta\) 140.7, 136.5, 135.5, 129.0, 128.2, 128.0, 127.2, 126.7, 117.4, 61.2, 51.3, 43.1, 21.0; MS (EI) \(m/z\) (relative intensity) 210 [M+−allyl] (5.7), 132 (0.7), 118 (1.2), 105 (2.9), 91 (100); Anal. Calcd for C\(_{18}\)H\(_{21}\)N (251.37): C, 86.00; H, 8.42; N, 5.57. Found: C, 85.82; H, 8.66; N, 5.52. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH\(_3\text{CN/1M NaClO}_4\) aq = 40/60, flow rate = 0.8 mL/min, UV detection at 254 nm, \(t_R\) = 22.82 min (major enantiomer), \(t_R\) = 27.20 min (minor enantiomer); 90% ee.

N–Benzyl–1–(2–methoxyphenyl)–3–butenylamine, 13d

\[
\begin{array}{c}
\text{NHBn} \\
\text{OMe}
\end{array}
\]

Colorless oil; [\(\alpha\)]\(_D\)\(^{22}\) = +37.2 (c 1.0, CHCl\(_3\)); IR (neat) 3330, 3063, 3027, 3001, 2935, 2835, 1638, 1600, 1586, 1489, 1437, 1363, 1281, 1239, 1173, 1095, 1050, 1029, 996, 914, 754 cm\(^{-1}\); \(^1\text{H NMR (CDCl}_3\text{)} \) \(\delta\) 7.38–7.35 (m, 1H), 7.26–7.16 (m, 6H), 6.95–6.83 (m, 2H), 5.72 (ddt, \(J = 16.1\) Hz, 10.2 Hz, 6.7 Hz, 1H), 5.03–4.93 (m, 2H), 4.07–4.03 (m, 1H), 3.77 (s, 3H), 3.65 (d, \(J = 13\) Hz, 1H), 3.51 (d, \(J = 13\) Hz, 1H), 2.5–2.34 (m, 2H), 1.8 (brs, 1H);
$^{13}$C NMR (CDCl₃) δ 157.2, 140.7, 136.0, 131.2, 128.0, 127.9, 127.7, 127.4, 127.1, 126.5, 120.4, 116.6, 110.3, 55.8, 55.0, 51.4, 40.7; MS (EI) m/z (relative intensity) 226 [M$^+$–allyl] (15.8), 209 (6.7), 197 (3.1), 194 (4.9), 134 (3.8), 121 (17.6), 91 (100); Anal. Caled for C₁₈H₂₁NO (267.37): C, 80.86; H, 7.91; N, 5.23. Found: C, 80.81; H, 8.11; N, 5.28. The enantiomeric excess was determined by converting to trifluoroacetylamide form, $[\alpha]_D^{22} = +31.0$ (c 2.8, CHCl₃) and using CHIRALCEL OD column, hexane/i-PrOH = 100/1, flow rate = 0.7 mL/min, UV detection at 254 nm, $t_R = 9.04$ min (major enantiomer), $t_R = 10.43$ min (minor enantiomer); 88% ee.

N–Benzyl–1–(3,4–dimethoxyphenyl)–3–butenylamine, 13e

Colorless oil; $[\alpha]_D^{23} = +38.6$ (c 1.75, CHCl₃); IR (neat) 3325, 3062, 2998, 2932, 2833, 1638, 1593, 1463, 1417, 1358, 1262, 1233, 1139, 1029, 916, 856, 808, 747 cm$^{-1}$; $^1$H NMR (CDCl₃) δ 7.32–7.19 (m, 5H), 6.95–6.81 (m, 3H), 5.72 (ddt, $J = 16.2$ Hz, 10.2 Hz, 7.2 Hz, 1H), 5.06 (ddt, $J = 16.2$ Hz, 2 Hz, 2 Hz, 1H), 5.03 (ddt, $J = 10.2$ Hz, 2 Hz, 2 Hz, 1H), 3.9 (s, 3H), 3.88 (s, 3H), 3.69 (d, $J = 13.2$ Hz, 1 H), 3.63–3.59 (m, 1H), 3.54 (d, $J = 13.2$ Hz, 1H), 2.41–2.34 (m, 2H), 1.81 (brs, 1H);
$^{13}$C NMR (CDCl$_3$) δ 149.0, 147.9, 140.6, 136.3, 128.3, 128.1, 126.8, 119.5, 117.5, 110.8, 109.9, 61.2, 55.8, 51.3, 43.2; MS (EI) $m/z$ (relative intensity) 256 [M$^+$–allyl] (14.8), 239 (5), 214 (9.4), 151 (20.8), 91 (100); Anal.

Calcd for C$_{19}$H$_{23}$NO$_2$ (297.39): C, 76.73; H, 7.79; N, 4.71. Found: C, 76.68; H, 8.06; N, 4.72. The enantiomeric excess was determined by using CHIRALCEL OD-R column, CH$_3$CN/1M NaClO$_4$ aq = 30/70, flow rate = 0.8 mL/min, UV detection at 254 nm, $t_R$ = 28.57 min (major enantiomer), $t_R$ = 32.58 min (minor enantiomer); 70% ee.

N–Benzyl–1–cyclohexyl–3–butenylamine, 15

![Chemical Structure](image)

Colorless oil; $[\alpha]_D^{21} = -5.4$ (c 0.5, CHCl$_3$); IR, $^1$H NMR, $^{13}$C NMR, HRMS and analysis data (see ref. 2). The enantiomeric excess was determined by converting to trifluoroacetylamide form, $[\alpha]_D^{22} = -7.8$ (c 0.6, CHCl$_3$) and using CHIRALCEL OD column, hexane/i-PrOH = 800/1, flow rate = 0.6 mL/min, UV detection at 254 nm, $t_R$ = 26.04 min (minor enantiomer), $t_R$ = 30.41 min (major enantiomer); 50% ee.

N–Benzyl–1–phenyl–1,5–hexadien–3–ylamine, 17

![Chemical Structure](image)

Colorless oil; $[\alpha]_D^{23} = +77.2$ (c 1.0, CHCl$_3$); IR, $^1$H NMR, $^{13}$C NMR, HRMS and analysis data (see ref. 2). The
enantiomeric excess was determined using CHIRALCEL OD-R column, CH$_3$CN/1M NaClO$_4$ aq = 60/40, flow rate = 0.6 mL/min, UV detection at 254 nm, $t_R$ = 10.03 min (major enantiomer), $t_R$ = 12.17 min (minor enantiomer); 69% ee.

**N-Benzyl-1-([2-furfuryl]-3-butenyl)amine, 19a**

Colorless oil; $[\alpha]_D^{22}$ = +55.9 (c 1.0, CHCl$_3$); IR (neat) 3330, 3063, 3028, 2978, 2914, 2837, 1640, 1604, 1512, 1495, 1455, 1346, 1248, 1176, 1148, 1108, 1073, 1028, 918, 884, 807, 734 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.31–7.13 (m, 6H), 6.25 (dd, $J$ = 3.2 Hz, 2 Hz, 1H), 6.11 (d, $J$ = 3.2 Hz, 1H), 5.68 (ddt, $J$ = 17.1 Hz, 10.2 Hz, 6.6 Hz, 1H), 5.05 (ddt, $J$ = 17.1 Hz, 2.2 Hz, 2 Hz, 1H), 5.03 (ddt, $J$ = 10.2 Hz, 2.2 Hz, 2 Hz, 1H), 3.72–3.70 (m, 1H), 3.69 (d, $J$ = 13.2 Hz, 1H), 3.54 (d, $J$ = 13.2 Hz, 1H), 2.46 (dd, $J$ = 6.6 Hz, 1.3 Hz, 2H), 1.65 (brs, 1H);

$^{13}$C NMR (CDCl$_3$) $\delta$ 156.0, 141.4, 140.1, 134.8, 128.2, 128.0, 126.7, 117.5, 109.7, 106.5, 54.7, 50.93, 39.2; MS (EI) $m/z$ (relative intensity) 186 [M$^-$-allyl] (33.9), 131 (1.5), 95 (1.8), 91 (100); Anal. Calcd for C$_{15}$H$_{17}$NO (227.3): C, 79.26; H, 7.53; N, 6.16. Found: C, 79.11; H, 7.84; N, 6.15. The enantiomeric excess was determined by converting to trifluoroacetylamide form, $[\alpha]_D^{22}$ = +54.7 (c 1.0, CHCl$_3$) and using CHIRALCEL OD column, hexane/i-PrOH = 500/1, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 22.18 min (major enantiomer), $t_R$ = 25.2 min (minor enantiomer); 67% ee.
N–Benzyl–1–(2–thiophenyl)–3–butenylamine, 19b

Colorless oil; \([\alpha]_D^{22} = + 24.5\) (c 1.0, CHCl₃); IR (neat) 3325, 3064, 3027, 2977, 2910, 2835, 1639, 1603, 1495, 1454, 1434, 1368, 1225, 1168, 1029, 995, 917, 850, 735 cm⁻¹; \(^1\)H NMR (CDCl₃) \(\delta\) 7.27–7.14 (m, 6H), 6.9–6.84 (m, 2H), 5.69 (ddt, \(J = 16.1\) Hz, 10.0 Hz, 6.9 Hz, 1H), 5.05 (ddt, \(J = 16.1\) Hz, 2.1 Hz, 2 Hz, 1H), 5.0 (ddt, \(J = 10.0\) Hz, 2.1 Hz, 2 Hz, 1H), 3.92 (t, \(J = 6.7\) Hz, 1H), 3.74 (d, \(J = 13.2\) Hz, 1H), 3.55 (d, \(J = 13.2\) Hz, 1H), 2.44–2.34 (m, 2H), 1.73 (brs, 1H);

\(^{13}\)C NMR (CDCl₃) \(\delta\) 149.2, 140.2, 134.8, 128.3, 128.2, 126.9, 126.3, 124.2, 123.9, 117.9, 57.0; MS (EI) \(m/z\) (relative intensity) 202 [M⁺–allyl] (18.9), 111 (2), 106 (1.3), 97 (7.9), 91 (100); Anal. Calcd for C₁₅H₁₇NS (243.37): C, 74.03; H, 7.04; N, 5.75; S, 13.17. Found: C, 73.96; H, 7.32; N, 5.66; S, 13.18. The enantiomeric excess was determined by converting to trifluoroacetylamide form, \([\alpha]_D^{22} = + 43.4\) (c 1.0, CHCl₃) and using CHIRALCEL OD column, hexane/i-PrOH = 500/1, flow rate = 0.5 mL/min, UV detection at 254 nm, \(t_R = 27.55\) min (major enantiomer), \(t_R = 30.59\) min (minor enantiomer); 53% ee.

N–(4–Methoxybenzyl)–1–phenyl–3–butenylamine, 11a
Colorless oil; $[\alpha]_D^{23} = +49.1$ (c 1.0, CHCl$_3$); IR, $^1$H NMR, $^{13}$C NMR, HRMS and analysis data (see ref. 2). The enantiomeric excess was determined by converting to trifluoroacetylamide form, $[\alpha]_D^{22} = +75.0$ (c 1.75, CHCl$_3$) and using CHIRALCEL OD column, hexane/i-PrOH = 100/1, flow rate = 0.6 mL/min, UV detection at 254 nm, $t_R = 17.02$ min (major enantiomer), $t_R = 20.19$ min (minor enantiomer); 90% ee.

N–(4–Methoxybenzyl)–1–(4-methoxyphenyl)–3–butenylamine, 11b

Colorless oil; $[\alpha]_D^{22} = +48.3$ (c 1.0, CHCl$_3$); IR (neat) 3325, 3072, 2998, 2932, 2907, 2834, 2059, 1638, 1611, 1585, 1512, 1463, 1351, 1301, 1245, 1174, 1106, 1036, 997, 917, 831, 781, 756 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.26 (d, $J$ = 8.6 Hz, 2H), 7.15 (d, $J$ = 8.6 Hz, 2H), 6.89 (d, $J$ = 8.6 Hz, 2H), 6.84 (d, $J$ = 8.6 Hz, 2H), 5.7 (ddt, $J$ = 16.2 Hz, 10.1 Hz, 6.5 Hz, 1H), 5.07−4.9 (m, 2H), 3.8 (s, 3H), 3.78 (s, 3H), 3.63−3.61 (m, 1H), 3.58 (d, $J$ = 13 Hz, 1H), 3.44 (d, $J$ = 13 Hz, 1H), 2.38−2.33 (m, 2H), 1.69 (brs, 1H);

$^{13}$C NMR (CDCl$_3$) $\delta$ 158.5, 135.7, 135.6, 132.7, 129.2, 128.2, 117.3, 113.6, 60.7, 55.2, 55.1, 50.6, 43.1; MS (EI) $m/z$ (relative intensity) 256 [M$^+$–allyl] (9.4), 160 (6), 122 (8.8), 121 (100), 91 (6.7), 77 (2.9); Anal. Caled for C$_{19}$H$_{23}$NO$_2$ (297.39): C, 76.73; H, 7.79; N, 4.71. Found: C, 76.6; H, 7.98; N, 4.68. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH$_3$CN/1M NaClO$_4$ aq = 35/65, flow rate = 0.8 mL/min, UV detection at 254 nm, $t_R = 31.9$ min (major enantiomer), $t_R = 36.22$ min (minor enantiomer); 85% ee.
N-(4-Methoxybenzyl)-1-(4-methylphenyl)-3-butenylamine, 11c

Colorless oil; [α]D22 = +48.5 (c 1.0, CHCl3); IR (neat) 3325, 3002, 2910, 2833, 1638, 1612, 1512, 1512, 1463, 1349, 1301, 1247, 1173, 1105, 1037, 996, 917, 817, 781, 757 cm⁻¹; ¹H NMR (CDCl3) δ 7.32 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8 Hz, 4H), 6.92 (d, J = 8.5 Hz, 2H), 5.78 (ddt, J = 16 Hz, 10.2 Hz, 6.8 Hz, 1H), 5.07–5.15 (m, 2H), 3.85 (s, 3H), 3.72–3.7 (m, 1H), 3.69 (d, J = 13 Hz, 1H), 3.53 (d, J = 13 Hz, 1H), 2.47–2.45 (m, 2H), 2.42 (s, 3H), 1.73 (bss, 1H);

¹³C NMR (CDCl₃) δ 158.4, 140.7, 136.4, 135.6, 132.7, 129.2, 129.0, 127.1, 117.4, 113.6, 61.0, 55.1, 50.6, 43.1, 21.0; MS (EI) m/z (relative intensity) 240 [M⁺-allyl] (13.3), 160 (4.9), 121 (100), 119 (4.9), 91 (12.4), 77 (5.3); Anal. Calcd for C₁₉H₂₃NO (281.39): C, 81.10; H, 8.24; N, 4.97. Found: C, 81.02; H, 8.47; N, 4.97. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH₃CN/1M NaClO₄ aq = 35/65, flow rate = 0.8 mL/min, UV detection at 254 nm, tᵣ = 41.41 min (major enantiomer), tᵣ = 46.64 min (minor enantiomer); 86% ee.
N-(4-Methoxybenzyl)-1-(4-nitrophenyl)-3-butenylamine, 11d

Pale yellow oil; [α]_D^22 = +26.9 (c 1.0, CHCl_3); IR (neat) 3331, 3075, 3001, 2935, 2835, 1639, 1609, 1515, 1463, 1346, 1301, 1247, 1176, 1108, 1035, 1013, 996, 920, 856, 825, 753 cm^-1; ^1H NMR (CDCl_3) δ 8.14 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 5.62 (ddt, J = 16.4 Hz, 10.1 Hz, 6.4 Hz, 1H), 5.52–4.96 (m, 2H), 3.74–3.73 (m, 1H), 3.72 (s, 3H), 3.52 (d, J = 13 Hz, 1H), 3.38 (d, J = 13 Hz, 1H), 2.37–2.21 (m, 2H), 1.7 (brs, 1H);

^13C NMR (CDCl_3) δ 158.6, 151.8, 147.0, 134.2, 131.9, 129.1, 128.0, 123.6, 118.5, 113.7, 60.9, 55.2, 50.9, 42.8; MS (EI) m/z (relative intensity) 271 [M^+–allyl] (2), 186 (14.6), 150 (4.3), 121 (44.6), 91 (100), 81 (10.2), 77 (11.8); Anal. Calcd for C_{18}H_{20}N_2O_3 (312.37): C, 69.21; H, 6.45; N, 8.96. Found: C, 68.98; H, 6.73; N, 8.8. The enantiomeric excess was determined by converting to trifluoroacetylamide form, [α]_D^22 = +30.6 (c 1.5, CHCl_3) and using CHIRALCEL OD column, hexane/i-PrOH = 50:1, flow rate = 0.8 mL/min, UV detection at 254 nm, t_R = 27.43 min (minor enantiomer), t_R = 29.75 min (major enantiomer); 42% ee.

S-19
N-(2–Methoxybenzyl)–1–phenyl–3–butenylamine, 11e

![Chemical structure](image)

Colorless oil; \([\alpha]_D^{22} = + 51.6 \text{ (c 1.0, CHCl}_3\); IR (neat) 3343, 3062, 3026, 3001, 2934, 2835, 1638, 1601, 1588, 1492, 1463, 1358, 1288, 1241, 1175, 1117, 1048, 1029, 955, 916, 836, 754, 702 \text{ cm}^{-1}; ^1\text{H NMR (CDCl}_3\) \(\delta\) 7.34–7.18 (m, 6H), 7.1–7.05 (m, 1H), 6.89–6.82 (m, 2H), 5.66 (ddt, \(J = 16.8 \text{ Hz}, 10.1 \text{ Hz}, 6.8 \text{ Hz}, 1\text{H})\), 5.07 (ddt, \(J = 16.8 \text{ Hz}, 2.2 \text{ Hz}, 2 \text{ Hz}, 1\text{H})\), 5.02 (ddt, \(J = 10.1 \text{ Hz}, 2.2 \text{ Hz}, 2 \text{ Hz}, 1\text{H})\), 3.8 (s, 3H), 3.72 (d, \(J = 13.4 \text{ Hz}, 1\text{H})\), 3.63–3.6 (m, 1H), 3.58 (d, \(J = 13.4 \text{ Hz}, 1\text{H})\), 2.39–2.35 (m, 2H), 2.12–1.91 (brs, 1H);

\[^{13}\text{C NMR (CDCl}_3\) \(\delta\) 157.6, 143.8, 135.5, 129.8, 128.2, 128.1, 128.0, 127.3, 126.8, 120.1, 117.3, 110.0, 60.9, 54.9, 47.1, 43.1; MS (El) \(m/z\) (relative intensity) 226 [M–allyl] (11.9), 160 (3.9), 122 (9.2), 121 (100), 105 (2.3), 94 (3.1), 93 (37.6), 91 (7.2), 79 (1.3), 77 (1); Anal. Calcd for C\(_{18}\)H\(_{21}\)NO (267.37): C, 80.86; H, 7.91; N, 5.23. Found: C, 80.83; H, 8.18; N, 5.2. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH\(_3\)CN/1M NaClO\(_4\) aq = 50/50, flow rate = 0.8 mL/min, UV detection at 254 nm, \(t_R = 10.03 \text{ min (minor enantiomer)}\), \(t_R = 12.66 \text{ min (major enantiomer)}\); 89% ee.
N−Benzyl−1−(2−naphthyl)−3−butenylamine, 21a

Colorless oil; [\(\alpha\)\(D\)]\(21\) = + 64.0 (c 1.5, CHCl\(_3\)); IR, \(^1\)H NMR, \(^{13}\)C NMR, HRMS and analysis data (see ref. 2). The enantiomeric excess was determined by using CHIRALCEL OD-R column, CH\(_3\)CN/1M NaClO\(_4\) aq = 40/60, flow rate = 0.8 mL/min, UV detection at 254 nm, \(t_R = 58.3\) min (major enantiomer), \(t_R = 67.45\) min (minor enantiomer); 91% ee.

N−(4−Methoxybenzyl)−1−(2−naphthyl)−3−butenylamine, 21b

Colorless oil; [\(\alpha\)\(D\)]\(22\) = + 54.3 (c 1.0, CHCl\(_3\)); IR (neat) 3330, 3076, 3026, 2978, 2911, 2833, 1640, 1602, 1492, 1454, 1415, 1357, 1115, 1070, 1027, 994, 759 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.95−7.86 (m, 4H), 7.63−7.51 (m, 3H), 7.26 (d, \(J = 8.6\) Hz, 2H), 6.94 (d, \(J = 8.6\) Hz, 2H), 5.85 (ddt, \(J = 16.4\) Hz, 10.2 Hz, 6.9 Hz, 1H), 5.2−5.1 (m, 2H), 3.95−3.91 (m, 1H), 3.87 (s, 3H), 3.74 (d, \(J = 13\) Hz, 1H), 3.5 (d, \(J = 13\) Hz, 1H), 2.62−2.52 (m, 2H), 1.87 (brs, 1H);
$^{13}$C NMR (CDCl$_3$) $\delta$ 158.4, 141.1, 135.3, 133.3, 132.7, 129.1, 128.0, 127.6, 126.1, 125.8, 125.3, 125.2, 117.5, 113.6, 61.4, 55.0, 50.6, 42.8; MS (EI) $m/z$ (relative intensity) 276 [M$^+$–allyl] (7.7), 160 (6.6), 122 (8.7), 121 (100), 91 (4.8), 77 (2.4); Anal. Calcd for C$_{22}$H$_{23}$NO (317.43): C, 83.24; H, 7.3; N, 4.41. Found: C, 83.19; H, 7.49; N, 4.58. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH$_3$CN/1M NaClO$_3$ aq = 50/50, flow rate = 0.7 mL/min, UV detection at 254 nm, $t_R$ = 38.16 min (major enantiomer), $t_R$ = 42.87 min (minor enantiomer); 82% ee.

N–allyl–1–phenyl–3–butenylamine, 23a

Colorless oil; [$\alpha$]$_D^{23}$ = + 24.8 (c 1.0, CHCl$_3$); IR (neat) 3329, 3077, 3026, 3003, 2977, 2910, 2833, 1640, 1602, 1542, 1492, 1454, 1357, 1307, 1235, 1199, 1069, 1027, 994, 917, 758 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.35–7.23 (m, 5H), 5.86–5.73 (m, 1H), 5.73–5.7 (m, 1H), 5.14–5.03 (m, 4H), 3.72 (dd, $J = 6.2$ Hz, 1.2 Hz, 1H), 3.11–3.02 (m, 2H), 2.44–2.39 (m, 2H), 1.71 (brs, 1H);

$^{13}$C NMR (CDCl$_3$) $\delta$ 143.4, 136.4, 135.2, 128.5, 126.9, 126.7, 117.3, 115.4, 61.4, 49.7, 42.8; MS (EI) $m/z$ (relative intensity) 188 [M$^+$+1] (0.9), 146 [M$^+$–allyl] (16.1), 129 (14.9), 119 (2.6), 104 (4.8), 91 (100), 77 (2.1); Anal. Calcd for C$_{13}$H$_{17}$N (187.28): C, 83.37; H, 9.14; N, 7.47. Found: C, 83.07; H, 9.35; N, 7.4. The enantiomeric excess was determined by converting to trifluoroacetylamide form, [$\alpha$]$_D^{22}$ = + 93.2 (c 1.0, CHCl$_3$)
and using CHIRALCEL OD column, hexane/i-PrOH = 300/1, flow rate = 0.6 mL/min, UV detection at 254 nm, $t_R = 16.17$ min (major enantiomer), $t_R = 17.85$ min (minor enantiomer); 78% ee.

N–Methyl–1–(3–pyridyl)–3–butenylamine, 25

![Image of N–Methyl–1–(3–pyridyl)–3–butenylamine](image)

Yellow liquid; $[\alpha]_D^{22} = +43.1$ (c 1.66, CHCl$_3$); IR (neat) 3324, 3082, 2979, 2936, 1666, 1640, 1578, 1476, 1428, 1098, 1027, 996, 734 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 8.45–8.41 (m, 2H), 7.62–7.58 (m, 1H), 7.23–7.2 (m, 1H), 5.69–5.59 (m, 1H), 5.08–5.01 (m, 2H), 3.64–3.60 (m, 1H), 3.51 (t, $J = 6.8$ Hz, 1H), 2.47–2.4 (m, 2H), 2.2 (s, 3H); $^1$C NMR (CDCl$_3$) $\delta$ 149.2, 148.5, 138.6, 134.7, 134.3, 123.5, 118.3, 62.1, 42.4, 34.7; MS (EI) $m/z$ (relative intensity) 163 [M$^+$+ H] (3.5), 161 [M$^+$–H] (6.3), 121 [M$^+$–allyl] (100), 119 (9.6), 94 (92), 80 (18.7), 78 (9.4); Anal. Calcd for C$_{10}$H$_{14}$N$_2$ (162.23): C, 74.04; H, 8.69; N, 17.27. Found: C, 74.24; H, 8.85; N, 16.94. The enantiomeric excess was determined by converting to trifluoroacetylamide form, $[\alpha]_D^{22} = +90.5$ (c 0.5, CHCl$_3$) and using CHIRALCEL OD column, hexane/i-PrOH = 10/1, flow rate = 0.7 mL/min, UV detection at 254 nm, $t_R = 24.13$ min (minor enantiomer), $t_R = 32.58$ min (major enantiomer); 55% ee.
N−Benzyl−1−(3,4,5−trimethoxyphenyl)−3−butenylamine, 27

Colorless syrupy liquid; \([\alpha]_D^{22} = +15.3\) (c 1.0, CHCl₃); IR (neat) 3325, 3062, 2997, 2936, 2835, 1638, 1590, 1505, 1462, 1419, 1325, 1233, 1183, 1128, 1009, 917, 831, 739 cm⁻¹; ¹H NMR (CDCl₃) \(\delta\) 7.34−7.21 (m, 5H), 6.6 (s, 2H), 5.73 (ddt, \(J = 16.6\) Hz, 10.0 Hz, 6.9 Hz, 1H), 5.13−5.05 (m, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 3.71 (d, \(J = 13.2\) Hz, 1H), 3.63−3.59 (m, 1H), 3.56 (d, \(J = 13.2\) Hz, 1H), 2.45−2.31 (m, 2H), 1.81 (brs, 1H);

¹³C NMR (CDCl₃) \(\delta\) 153.2, 140.5, 139.6, 136.6, 135.4, 128.3, 128.1, 126.8, 117.7, 103.8, 61.8, 60.8, 56.0, 51.4, 43.3; MS (EI) \(m/z\) (relative intensity) 286 [M⁺−allyl] (14.9), 254 (8.4), 238 (23.2), 209 (6.1), 195 (6.9), 181 (13.8), 169 (4), 125 (1.2), 91 (100); Anal. Calcd for C₂₀H₂₅NO₃ (327.42): C, 73.36; H, 7.69; N, 4.27. Found: C, 73.12; H, 7.89; N, 4.57. The enantiomeric excess was determined using CHIRALCEL OD−R column, CH₃CN/1M NaClO₄aq = 30/70, flow rate = 0.8 mL/min, UV detection at 254 nm, \(t_R = 31.15\) min (major enantiomer), \(t_R = 34.64\) min (minor enantiomer); 34% ee.
N-Benzyl-1-piperonyl-3-butenylamine, 9a

\[
\begin{array}{c}
\text{NH}_{\text{Bn}} \\
\text{C}_6\text{H}_5
\end{array}
\]

Colorless oil; \(\alpha_D^{22} = +59.1\) (c 1.0, CHCl\(_3\)); IR (neat) 3327, 3063, 3026, 2976, 2894, 1638, 1607, 1468, 1439, 1376, 1243, 1183, 1100, 1040, 996, 865, 736 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.32–7.21 (m, 5H), 6.91 (s, 1H), 6.77 (s, 2H), 5.95 (s, 2H), 5.69 (ddt, \(J = 17.0\) Hz, 10.2 Hz, 7.2 Hz, 1H), 5.09 (ddt, \(J = 17.0\) Hz, 2.2 Hz, 2 Hz, 1H), 5.03 (ddt, \(J = 10.2\) Hz, 2.2 Hz, 2 Hz, 1H), 3.66 (d, \(J = 13.2\) Hz, 1H), 3.6 (t, \(J = 6.8\) Hz, 1H), 3.51 (d, \(J = 13.2\) Hz, 1H), 2.38–2.28 (m, 2H), 1.7 (brs, 1H);

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 147.8, 146.4, 140.5, 137.8, 135.3, 128.3, 128.0, 126.8, 120.5, 117.5, 107.9, 107.2, 100.8, 61.3, 51.3, 43.2; MS (EI) \(m/z\) (relative intensity) 240 [M–allyl] (100), 148 (3.9), 117 (2.5), 91 (81), 65 (5.7); Anal. Calcd for C\(_{18}\)H\(_{19}\)NO\(_2\) (281.35): C, 76.84; H, 6.8; N, 4.97. Found: C, 76.52; H, 6.68; N, 5.21. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH\(_3\)CN/1M NaClO\(_4\) aq = 40/60, flow rate = 0.8 mL/min, UV detection at 254 nm, \(t_R = 18.4\) min (major enantiomer), \(t_R = 22.2\) min (minor enantiomer); 90% ee.

S-25
N-(4-Methoxybenzyl)-1-piperonyl-3-butenylamine, 9b

Colorless oil; [α]D$^2_22$ = +54.9 (c 1.0, CHCl₃); IR (neat) 3327, 3072, 2934, 1638, 1611, 1584, 1512, 1376, 1300, 1244, 1177, 1101, 1038, 997, 814, 759 cm$^{-1}$; $^1$H NMR (CDCl₃) δ 7.26 (d, J = 8.4 Hz, 2H), 7.0 (s, 1H), 6.95 (d, J = 8.4 Hz, 2H), 6.85 (s, 2H), 6.04 (s, 2H), 5.78 (ddt, J = 16.1 Hz, 10.1 Hz, 6.6 Hz, 1H), 5.18 (ddt, J = 16.1 Hz, 2.1 Hz, 1H), 5.12 (ddt, J = 10.1 Hz, 2.1 Hz, 2 Hz, 1H), 3.87 (s, 3H), 3.71–3.7 (m, 1H), 3.67 (d, J = 13 Hz, 1H), 3.55 (d, J = 13 Hz, 1H), 2.46–2.42 (m, 2H), 1.77 (brs, 1H);

$^{13}$C NMR (CDCl₃) δ 158.4, 147.7, 146.4, 137.8, 135.4, 132.6, 129.2, 120.5, 117.4, 113.6, 107.8, 107.2, 100.8, 61.1, 55.2, 50.6, 43.1; MS (EI) m/z (relative intensity) 270 [M⁺-allyl] (8.4), 160 (5.4), 122 (9.8), 121 (100), 91 (7.4), 77 (2.8); Anal. Calcld for C₁₉H₂₁NO₃ (311.38): C, 73.28; H, 6.79; N, 4.49. Found: C, 73.07; H, 6.9; N, 4.78.

The enantiomeric excess was determined using CHIRALCEL OD-R column, CH₃CN/1M NaClO₄ aq = 35/65, flow rate = 0.8 mL/min, UV detection at 254 nm, tR = 34.37 min (major enantiomer), tR = 38.25 min (minor enantiomer); 89% ee.
N-(2-Methoxybenzyl)-1-piperonyl-3-butenylamine, 9c

Colorless oil; $[\alpha]_D^{22} = +57.8$ (c 1.0, CHCl$_3$); IR (neat) 3341, 3073, 3001, 2834, 1638, 1601, 1588, 1490, 1376, 1326, 1289, 1180, 1098, 996, 868, 755 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.18–7.12 (m, 1H), 7.03–7.0 (m, 1H), 6.85–6.76 (m, 3H), 6.69 (s, 2H), 5.87 (s, 2H), 5.6 (ddt, $J = 16.4$ Hz, 10.2 Hz, 6.6 Hz, 1H), 5.0 (ddt, $J = 16.4$ Hz, 2.1 Hz, 2 Hz, 1H), 4.96 (ddt, $J = 10.2$ Hz, 2.1 Hz, 2 Hz, 1H), 3.75 (s, 3H), 3.65 (d, $J = 13.4$ Hz, 1H), 3.48–3.46 (m, 1H), 3.42 (d, $J = 13.4$ Hz, 1H), 2.3–2.17 (m, 2H), 1.95 (brs, 1H);

$^{13}$C NMR (CDCl$_3$) $\delta$ 157.5, 147.0, 146.2, 137.9, 135.5, 129.8, 128.2, 128.0, 120.5, 120.1, 117.2, 110.0, 107.7, 107.3, 100.6, 60.7, 54.9, 46.9, 43.2; MS (EI) m/z (relative intensity) 270 [M$^+$-allyl] (10.5), 160 (5.9), 148 (1.4), 122 (8.9), 121 (100), 93 (23), 91 (3.5); Anal. Calcd for C$_{19}$H$_{21}$NO$_3$ (311.38): C, 73.28; H, 6.79; N, 4.49. Found: C, 73.1; H, 7.01; N, 4.4. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH$_3$CN/1M NaClO$_4$ aq = 50/50, flow rate = 0.7 mL/min, UV detection at 254 nm, $t_R = 13.3$ min (minor enantiomer), $t_R = 17.11$ min (major enantiomer); 89% ee.
N-Benzyl-1-(2-chloropiperonyl-3-butenylamine, 9d

Colorless oil; [α]D

22 = + 48.0 (c 1.0, CHCl3); IR (neat) 3330, 3075, 3027, 2977, 2896, 1639, 1603, 1502, 1475, 1408, 1391, 1375, 1269, 1237, 1159, 1110, 1038, 996, 935, 841, 796, 734 cm⁻¹; ³H NMR (CDCl₃) δ 7.92–7.21 (m, 5H), 7.2 (s, 1H), 6.77 (s, 1H), 5.94–5.92 (m, 2H), 5.74 (ddt, J = 16.8 Hz, 10.2 Hz, 6.8 Hz, 1H), 5.07–5.0 (m, 2H), 4.15 (dd, J = 4.8 Hz, 3.8 Hz, 1H), 3.62 (dd, J = 13.2 Hz, 1H), 3.5 (d, J = 13.2 Hz, 1H), 2.43–2.35 (m, 1H), 2.23–2.13 (m, 1H), 1.66 (brs, 1H);

¹³C NMR (CDCl₃) δ 147.1, 146.7, 140.3, 134.9, 134.2, 128.2, 128.0, 126.8, 124.9, 117.8, 109.5, 107.4, 101.5, 57.1, 51.4, 41.4; MS (EI) m/z (relative intensity) 274 [M⁺–allyl] (7.5), 169 (2), 115 (2.2), 91 (100); Anal. Calcd for C₁₈H₁₉ClNO₂ (315.8): C, 68.46; H, 5.75; N, 4.43; Cl, 11.23. Found: C, 68.4; H, 5.85; N, 4.46; Cl, 11.11. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH₃CN/1M NaClO₄ aq = 60/40, flow rate = 0.6 mL/min, UV detection at 254 nm, t₀ = 17.13 min (major enantiomer), tᵣ = 19.3 min (minor enantiomer); 87% ee.
N-Benzyl-1-(2-bromopiperonyl)-3-butynylamine, 9e

Colorless oil; [α]_D^22 = +40.2 (c 1.0, CHCl₃); IR (neat) 3330, 3074, 3027, 2976, 2896, 1638, 1604, 1500, 1473, 1406, 1388, 1373, 1234, 1158, 1038, 996, 837, 735 cm⁻¹; ¹H NMR (CDCl₃) δ 7.38–7.31 (m, 5H), 7.3 (s, 1H), 7.03 (s, 1H), 6.02–6.01 (m, 2H), 5.81 (ddt, J = 16.8 Hz, 10.2 Hz, 6.7 Hz, 1H), 5.16–5.09 (m, 2H), 4.19 (dd, J = 4.6 Hz, 3.9 Hz, 1H), 3.70 (d, J = 13.2 Hz, 1H), 3.58 (d, J = 13.2 Hz, 1H), 2.52–2.43 (m, 1H), 2.29–2.18 (m, 1H), 1.76 (brs, 1H);

¹³C NMR (CDCl₃) δ 147.7, 147.0, 140.3, 135.7, 134.9, 128.2, 128.0, 126.8, 117.8, 113.9, 112.4, 107.8, 101.5, 59.6, 51.4, 41.5; MS (EI) m/z (relative intensity) 318 [M⁺–allyl] (1.8), 238 (2.9), 214 (2.1), 148 (2), 107 (2.2), 91 (100); Anal. Calcd for C₁₈H₁₈BrNO₂ (360.25): C, 60.01; H, 5.04; N, 3.89; Br, 22.18. Found: C, 59.71; H, 5.17; N, 3.98; Br, 22.48. The enantiomeric excess was determined using CHIRALCEL OD-R column, CH₃CN/1M NaClO₃ aq = 60/40, flow rate = 0.6 mL/min, UV detection at 254 nm, t_R = 21.97 min (major enantiomer), t_R = 24.92 min (minor enantiomer); 88% ee.
N-Diphenylmethylene-1-piperonyl-3-butenylamine, 9f

Colorless oil; [α]$_D^{22}$ = + 53.5 (c 1.58, CHCl$_3$); IR (neat) 3325, 3063, 3027, 2978, 2887, 2775, 1639, 1600, 1547, 1504, 1487, 1445, 1377, 1324, 1246, 1184, 1098, 1075, 1042, 941, 912, 864, 762 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.32–7.13 (m, 10H), 6.81 (d, $J$ = 2Hz, 1H), 6.74 (d, $J$ = 8Hz, 1H), 6.64 (dd, $J$ = 8 Hz, 2Hz, 1H), 5.92 (s, 2H), 5.65 (ddt, $J$ = 16.8 Hz, 10.1 Hz, 6.8 Hz, 1H), 5.05 (ddt, $J$ = 16.8 Hz, 2 Hz, 2 Hz, 1H), 4.97 (ddt, $J$ = 10.1 Hz, 2 Hz, 2 Hz, 1H), 4.59 (s, 1H), 3.46 (t, 6.5 Hz, 1H), 2.38–2.34 (m, 2H), 2.0–1.94 (brs, 1H); $^{13}$C NMR (CDCl$_3$) δ 147.7, 146.4, 144.5, 143.3, 137.8, 135.4, 128.4, 128.2, 127.7, 127.3, 126.9, 126.6, 120.5, 117.3, 107.9, 107.2, 100.8, 63.0, 58.9, 43.0; MS (EI) m/z (relative intensity) 316 [M$^+$–allyl] (8.6), 167 (100), 165 (17.3), 148 (1.8), 122 (3), 115 (4.2), 76 (5.7); Anal. Calcd for C$_{24}$H$_{23}$NO$_2$ (357.45): C, 80.64; H, 6.48; N, 3.92. Found: C, 80.52; H, 6.51; N, 3.8. The enantiomeric excess was determined by converting to trifluoroacetylamide form, [α]$_D^{22}$ = + 78.2 (c 1.0, CHCl$_3$) and using CHIRALCEL OD column, hexane/i-PrOH = 50/1, flow rate = 0.8 mL/min, UV detection at 254 nm, $t_R$ = 14.44 min (major enantiomer), $t_R$ = 18.95 min (minor enantiomer); 83% ee.
(S)-2-Allylpiperidine

$^1$H NMR of the hydrochloride (D$_2$O + CH$_3$NO$_2$ internal standard) $\delta$ 5.877–5.73 (m, 1H), 5.26–5.2 (m, 2H), 3.39–3.35 (m, 1H), 3.17–3.13 (m, 1H), 3.06–2.87 (m, 1H), 2.52–2.29 (m, 2H), 2.00–1.43 (m, 6H);

$^{13}$C NMR (CDCl$_3$) $\delta$ 135.5, 117.2, 56.0, 47.0, 41.9, 32.6, 26.2, 24.8. The enantiomeric excess was determined by converting into N-tosylamide, pale yellow oil; $[\alpha]_D^{21} = -0.43$ (c, 0.9, CH$_2$Cl$_2$); and using CHIRALCEL OD column, hexane/i-PrOH = 50/1, flow rate = 1.0 mL/min, UV detection at 254 nm, $t_R = 9.91$ min (minor enantiomer), $t_R = 11.12$ min (major enantiomer); 2% ee. Configurational assignment was made by comparison with the reported optical rotation.$^6$,$^7$

(R)-2-Allylpiperidine

$^1$H NMR and $^{13}$C NMR same as above. The enantiomeric excess was determined by converting into N-tosylamide, pale yellow oil; $[\alpha]_D^{23} = +4.1$ (c, 0.995, CH$_2$Cl$_2$); and using CHIRALCEL OD column, hexane/i-PrOH = 50/1, flow rate = 1.0 mL/min, UV detection at 254 nm, $t_R = 9.92$ min (major enantiomer), $t_R = 11.42$ min (minor enantiomer); 18% ee.
(R)-1-Allyl-1,2,3,4-tetrahydroisoquinoline

Yellow oil; [α]D<sub>22</sub> = + 6.2 (c 0.61, THF); 7% ee based on [α]D reported in literature. Configurational assignment was made by comparison with the reported optical rotation. IR (neat) 3072, 3018, 2920, 2833, 2803, 2728, 1638, 1492, 1454, 1430, 1315, 1132, 997, 914, 741 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.17−7.07 (m, 4H), 5.85−5.79 (m, 1H), 5.2−5.12 (m, 2H), 4.05 (dd, J = 9.0 Hz, 3.5 Hz, 1H), 3.26−3.2 (m, 1H), 3.01−2.93 (m, 1H), 2.83−2.63 (m, 3H), 2.55−2.48 (m, 1H), 1.81 (brs, 1H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 138.7, 135.8, 129.1, 126.4, 125.5, 117.8, 55.3, 41.2, 29.8; MS (EI) m/z (relative intensity) 173 [M<sup>+</sup>] (0.3), 172 [M<sup>+</sup>−H] (1.9), 132 [M<sup>+</sup>−allyl] (100), 117 (6.9), 105 (5.1), 91 (1.2), 77 (3.5).

(S)-1-Allyl-1,2,3,4-tetrahydroisoquinoline

Yellow oil; [α]D<sub>22</sub> = − 16.1 (c 0.61, THF); 19% ee based on [α]D reported in literature. IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS data same as above.
References and Notes