Anti-Markovnikov Rearrangement in Sulfur Mediated Allylic C-H Amination of Olefins

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I. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. Dichloromethane was refluxed over CaH$_2$, and freshly distilled prior to use. Tetrahydrofuran (THF) was refluxed with sodium/benzophenone, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200-300 mesh) from Branch of Qingdao Haiyang Chemical. Petroleum ether used for column chromatography were 60-90 °C fraction, and the removal of residue solvent was accomplished under rotovap with repeated azeotrope with chloroform, and then evaporation under vacuum (< 1 mmHg pressure). Reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates from Yantai Chemical Industry Research Institute. The plates were visualized under UV light, as well as other TLC stains (phosphomolybdic acid: 10% in ethanol; potassium permanganate: 1% in water; iodine: 10 g iodine absorbed on 30g silica gel). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in CDCl$_3$ with TMS as an internal standard, and the chemical shifts ($\delta$) were reported in parts per million (ppm). The IR spectra (KBr pellets, $\nu$ [cm$^{-1}$]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. The thin layer chromatography silica gel preparative plates were brought from Anhui LiangChen Silicon Material Co. Ltd.
II. Compounds Chart

1a\textsuperscript{a}  
1b  
1c  
1d  
1e  
1f  
1g  
1h  
1i  
1j  
1k\textsuperscript{a}  
1l

\textsuperscript{a} commercially available, used as received
III. Experimental Procedures and Characterization Data

Preparation of alkene substrates

(1) General Procedure 1 for preparation of alkenes $1b - 1e, 1g - 1h$: [1]
Under a N$_2$ atmosphere, a dry 100 mL three-necked flask, fitted with a reflux condenser, and pressure-equalizing dropping funnel, was charged with a magnetic stirring bar and magnesium turnings (1.2 equiv.). Aryl bromide (1 equiv.) and an iodide grain were dissolved in Et$_2$O (1.6 M, for $1b, 1d$) or THF (1.6 M, for $1c, 1e, 1g-1h$) in the funnel. Part of the solution (~2 mL) was added to the flask and stirred. After the color of the mixture suddenly faded, the rest solution was added dropwise via the dropping funnel. Then the mixture was refluxed for 2h. The reaction solution was decanted into another dry flask and allyl bromide (1.5 equiv.) was added at ice bath temperature. When the mixture had reached room temperature, it was carefully hydrolyzed with aqueous saturated NH$_4$Cl solution. The aqueous phase was removed and extracted with Et$_2$O. The combined organic phases were dried with MgSO$_4$ and concentrated under reduced pressure. The crude product was applied to flash column chromatography afford pure allyl arene.


(2) General Procedure 2 for preparation of alkenes $1f$ and $1i$: [2]
The arylamine (3.0 mmol) was added during 20 min to a solution of tert-butyl nitrite (535 µL, 4.5 mmol) and allyl bromide (1.9 mL, 22.5 mmol) in dry and degassed CH$_3$CN (3 mL) under argon atmosphere while maintaining the specified temperature ($1f$ in 50 ºC and $1i$ in 30 ºC). At the end of the addition of arylamine, extra tert-butyl nitrite (180 µL, 1.5 mmol) was added. The reaction mixture was then stirred at a temperature specified in Table 1 for 1 h. The volatile material in the reaction mixture was then removed at reduced pressure. The crude product was applied to flash column chromatography afford pure allyl arene.


(3) General Procedure 3 for preparation of alkene $1j$: [3]
To a solution of tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol), sodium carbonate (252 mg, 3 mmol), and o-methylphenylboronic acid (136 mg, 1 mmol) in a mixed solvent (dimethoxyethane/H$_2$O = 1/1, 5 mL), allyl bromide (260 mL, 3 mmol) was added. The resultant mixture was heated under reflux for 6 hours. The mixture was dissolved into dichloromethane (30 mL), and washed with water (20 mL). Furthermore, the aqueous layer was extracted with dichloromethane (30 mL x 3). The combined organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel) using petroleum ether.

Sulfur mediated allylic amination reactions

General Procedure

To a flame-dried Schlenk tube, 1 eq alkene (1a) (47 mg, 0.4 mmol) and 1.2 eq diphenyl sulfoxide (97 mg, 0.48 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -78 °C (liquid nitrogen/ethyl acetate bath). 1.2 eq Tf$_2$O (81 μL, 0.48 mmol) were added dropwise, and then gradually warmed up to 0 °C. And a solution of 5 eq diisopropylamine (2a) (202 mg, 2.0 mmol) in 1 mL CH$_2$Cl$_2$ was added. After 12 hours of reaction at room temperature, the solution was quenched by 10 mL 0.1 M aqueous solution of sodium hydroxide. The aqueous phase extracted with CH$_2$Cl$_2$ (10 mL×3). The combined organic phases were dried with Na$_2$SO$_4$ and concentrated under reduced pressure to give the crude amine products. Crude $^1$H NMR was taken for determination of isomer ratio. The crude product was then purified by repeated flash column chromatography and preparative thin layer chromatography to give pure isolated products.
Characterization data of new compounds

**N,N-diisopropyl-2-phenylprop-2-en-1-amine (4aa) and (E)-N,N-diisopropyl-3-phenylprop-2-en-1-amine (3aa)** were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/5/1, to give 61 mg product 4aa as a yellow oil in 70% yield and 10 mg product 3aa as a yellow oil in 12% yield.

**3aa**: R\textsubscript{f} = 0.39 (CHCl\textsubscript{3}/MeOH = 10:1)

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.37 (d, \( J = 7.2 \) Hz, 1H), 7.29 (t, \( J = 7.6 \) Hz, 2H), 7.19 (t, \( J = 7.2 \) Hz, 2H), 6.50 (d, \( J = 15.6 \) Hz, 1H), 6.24 (dt, \( J = 15.6, 6.0 \) Hz, 1H), 3.29 (d, \( J = 6.0 \) Hz, 2H), 3.10 (hept, \( J = 6.8, 2H) \), 1.04 (d, \( J = 6.6 \) Hz, 12H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 137.6, 131.7, 130.0, 128.5, 127.0, 126.1, 48.4, 47.7, 20.7.

IR (KBr) \( \nu (\text{cm}^{-1}) \) 2962, 2924, 1495, 1382, 1362, 1178, 965, 748, 691.

HRMS (ESI) calcd for C\textsubscript{15}H\textsubscript{24}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \) : 218.1903, found: 218.1908.

**4aa**: R\textsubscript{f} = 0.38 (petroleum ether/ethyl acetate = 5:1).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.46 – 7.44 (m, 2H), 7.32 – 7.22 (m, 3H), 5.42 (d, \( J = 2.0 \) Hz, 1H), 5.36 (d, \( J = 1.2 \) Hz, 1H), 3.43 (s, 2H), 3.07 (hept, \( J = 6.4 \) Hz, 2H), 0.99 (d, \( J = 6.4 \) Hz, 12H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 148.2, 141.3, 127.9, 127.1, 126.4, 113.5, 49.3, 47.7, 20.6.

IR (KBr) \( \nu (\text{cm}^{-1}) \) 2963, 2927, 1629, 1600, 1464, 1179, 1026, 902, 778, 700.

HRMS (ESI) calcd for C\textsubscript{15}H\textsubscript{24}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \) : 218.1903, found: 218.1903.

**N,N-diethyl-2-phenylprop-2-en-1-amine (4ab) and (E/Z)-N,N-diethyl-3-phenylprop-2-en-1-amine (3ab)** were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/5/1, to give 36 mg product 4ab as a yellow oil in 47% yield and 12 mg product 3ab as a yellow oil in 16% yield (E/Z = 95:5 according to the NMR).

**3ab**: R\textsubscript{f} = 0.39 (CHCl\textsubscript{3}/MeOH = 10:1).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.38 (d, \( J = 7.6 \) Hz, 2H), 7.30 – 7.22 (m, 3H), 5.42 (d, \( J = 2.0 \) Hz, 1H), 5.36 (d, \( J = 1.2 \) Hz, 1H), 3.43 (s, 2H), 3.07 (hept, \( J = 6.4 \) Hz, 2H), 0.99 (d, \( J = 6.4 \) Hz, 12H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 137.2, 132.2, 128.5, 127.6, 127.3, 126.2, 113.5, 49.3, 46.7, 11.7.

IR (KBr) \( \nu (\text{cm}^{-1}) \) 2965, 2920, 1659, 1623, 1469, 1383, 965, 735, 691.

HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{20}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \) : 190.1590, found: 190.1591.

**4ab**: R\textsubscript{f} = 0.20 (petroleum ether/ethyl acetate = 5:1).
\[ \text{δ} \] 7.51 – 7.48 (m, 2H), 7.33 – 7.24 (m, 3H), 5.41 (d, \( J = 1.6 \text{ Hz}, 1\text{H} \)), 5.27 (d, \( J = 1.6 \text{ Hz}, 1\text{H} \)), 3.41 (s, 2H), 2.53 (q, \( J = 7.0 \text{ Hz}, 4\text{H} \)), 1.00 (t, \( J = 7.0 \text{ Hz}, 6\text{H} \)).

\[ \text{δ} \] 146.0, 140.8, 128.1, 127.3, 126.4, 114.7, 57.7, 46.8, 11.5.

\[ \text{δ} \] 146.3, 140.8, 128.0, 127.2, 126.5, 114.5, 59.2, 55.9, 20.0, 11.9.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

\[ \text{δ} \] 7.37 (d, \( J = 7.2 \text{ Hz}, 2\text{H} \)), 7.30 (t, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 7.24 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 5.40 (s, 1H), 5.27 (s, 1H), 3.39 (s, 2H), 2.38 (t, \( J = 7.2 \text{ Hz}, 4\text{H} \)), 1.44 (sext, \( J = 7.2 \text{ Hz}, 4\text{H} \)), 0.80 (t, \( J = 7.2 \text{ Hz}, 6\text{H} \)).

\[ \text{δ} \] 146.3, 140.8, 128.0, 127.2, 126.5, 114.5, 59.2, 55.9, 20.0, 11.9.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.

HRMS (ESI) calcd for \( \text{C}_{15}\text{H}_{24}\text{N}^+ (\text{M}+\text{H})^+ \) m/z: 218.1903, found: 218.1896.
minor), 3.55 (d, J = 6.4 Hz, 2H, minor), 3.43 (d, J = 6.4 Hz, 2H, major), 2.91 (hept, J = 6.2 Hz, 1H), 1.11 (d, J = 6.2 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.1, 131.4, 128.5, 128.3, 127.4, 126.3, 49.3, 48.2, 22.7.

IR (KBr) ν (cm$^{-1}$) 3360, 2956, 2921, 1660, 1632, 1470, 1383, 1138, 1074, 748.

HRMS (ESI) calcd for C$_{12}$H$_{18}$N$^+$ (M+H)$^+$ m/z: 176.1434, found: 176.1431.

4ad: R$_f$ = 0.27 (CHCl$_3$/MeOH = 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.29 (d, J = 6.8 Hz, 1H), 5.39 (s, 1H), 5.39 (s, 1H), 5.24 (d, J = 0.8 Hz, 1H), 3.66 (s, 2H), 2.85 (hept, J = 6.2 Hz, 1H), 1.60 (br, 1H), 1.06 (d, J = 6.2 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.7, 140.0, 128.5, 127.6, 126.2, 113.2, 51.0, 47.9, 22.8.

IR (KBr) ν (cm$^{-1}$) 3354, 2957, 2921, 1659, 1632, 1469, 1383, 1180, 1141, 1075, 901, 777, 703, 617.

HRMS (ESI) calcd for C$_{12}$H$_{18}$N$^+$ (M+H)$^+$ m/z: 176.1434, found: 176.1434.

5ad: R$_f$ = 0.27 (CHCl$_3$/MeOH = 10:1). (Mixed with 3ad)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.19 (m, 5H), 3.81 – 3.77 (m, 2H), 3.70 (quint, J = 15.6 Hz, 1H), 3.10 – 3.06(m, 2H), 2.36 (hept, J = 6.2 Hz, 1H), 0.97 (d, J = 6.2 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) mixture δ 137.1, 131.2, 128.7, 128.5, 128.3, 128.2, 127.3, 127.0, 126.3, 126.2, 60.1, 58.6, 49.4, 48.1, 34.4, 23.5, 22.8, 19.5.

HRMS (ESI) calcd for C$_{12}$H$_{18}$N$^+$ (M+H)$^+$ m/z: 176.1434, mixture found: 176.1432.

$N$-benzyl-2-phenylprop-2-en-1-amine (4ae), (E)-$N$-benzyl-3-phenylprop-2-en-1-amine (3ae) and 1-benzyl-3-phenylazetidine (5ae) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give product 4ae/5ae mixture and 8 mg product 3ae as a yellow oil in 9% yield. The mixture of 4ae/5ae was purified by preparative TLC to give 23 mg 4ae as a yellow oil in 26% yield and 29 mg 5ae as a yellow oil in 32% yield (E/Z = 92:8 according to the NMR).

3ae: R$_f$ = 0.34 (CHCl$_3$/MeOH = 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.19 (m, 10H), 6.55 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 6.0 Hz, 1H, major), 5.81 (dt, J = 12.4, 6.6 Hz, 1H, minor), 3.85 (s, 2H, major), 3.79 (s, 1H, minor), 3.57 (dd, J = 6.6, 1.4 Hz, 1H, minor), 3.45 (d, J = 6.0 Hz, 2H, major), 2.19 (br, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.9, 137.1, 131.7, 128.53, 128.46, 128.3, 128.1, 127.4, 127.1, 126.3, 126.2, 53.2, 51.1.

IR (KBr) ν (cm$^{-1}$) 3356, 2921, 2850, 1659, 1494, 1452, 1383, 1141, 966, 736, 696.

HRMS (ESI) calcd for C$_{16}$H$_{18}$N$^+$ (M+H)$^+$ m/z: 224.1434, found: 224.1438.

4ae: R$_f$ = 0.34 (CHCl$_3$/MeOH = 10:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.22 (m, 8H), 5.42 (s, 1H), 5.26 (d, J = 1.2 Hz, 1H), 3.80 (s, 2H), 3.67 (s, 2H), 1.55 (br, 1H).
13C NMR (100 MHz, CDCl3) δ 146.3, 140.2, 139.9, 128.4, 128.3, 128.2, 127.6, 126.9, 126.2, 113.5, 53.0, 52.7.

IR (KBr) ν (cm⁻¹) 3359, 2953, 2920, 1632, 1494, 1453, 1180, 1027, 903, 778, 698.

HRMS (ESI) calcd for C₁₆H₁₈N⁺ (M+H)⁺ m/z: 224.1434, found: 224.1433.

5ae: Rᶠ = 0.34 (CHCl₃/MeOH = 10:1).

1H NMR (400 MHz, CDCl₃) δ 7.32 – 7.19 (m, 10H), 3.78 – 3.72 (m, 3H), 3.67 (s, 2H), 3.23 – 3.16 (m, 2H).

13C NMR (100 MHz, CDCl₃) δ 142.6, 138.2, 128.5, 128.4, 128.3, 126.98, 126.93, 126.3, 63.8, 61.5, 35.8.

IR (KBr) ν (cm⁻¹) 2957, 2920, 1725, 1462, 1408, 1383, 1259, 1180, 1074, 806.

HRMS (ESI) calcd for C₁₂H₁₈N⁺ (M+H)⁺ m/z: 176.1434, found: 176.1437.

2-phenyl-N-propylprop-2-en-1-amine (4af), (E/Z)-3-phenyl-N-propylprop-2-en-1-amine (3af) and 3-phenyl-1-propylazetidine (5af) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give 35 mg product 4af as a yellow oil in 50% yield and mixture 3af/5af. The mixture of 3af/5af was purified by preparative TLC to give 6 mg 3af as a yellow oil in 9% yield (E/Z = 93:7 according to the NMR) and 25 mg 5af as a yellow oil in 35% yield.

3af: Rᶠ = 0.29 (CHCl₃/MeOH = 10:1).

1H NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 6.53 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 15.9, 6.4 Hz, 1H, major), 5.78 (dt, J = 12.0, 6.4 Hz, 1H, minor), 3.55 (d, J = 6.4 Hz, 2H, minor), 3.43 (d, J = 6.4 Hz, 2H, major), 2.64 (t, J = 7.2 Hz, 2H, major), 2.59 (t, J = 7.2 Hz, 2H, minor), 1.55 (sext, J = 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ 137.1, 131.6, 128.5, 128.0, 127.4, 126.3, 126.2, 113.3, 53.3, 51.0, 23.0, 11.8.

IR (KBr) ν (cm⁻¹) 3345, 2956, 2853, 1460, 1029, 801, 693.

HRMS (ESI) calcd for C₁₂H₁₈N⁺ (M+H)⁺ m/z: 176.1434, found: 176.1429.

4af: Rᶠ = 0.29 (CHCl₃/MeOH = 10:1).

1H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.5 Hz, 2H), 7.37 – 7.27 (m, 3H), 5.40 (s, 1H), 5.25 (s, 1H), 3.68 (s, 2H), 2.60 (t, J = 7.4 Hz, 2H), 1.50 (sext, J = 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ 146.3, 139.9, 128.4, 127.6, 126.2, 113.3, 53.3, 51.0, 23.0, 11.7.

IR (KBr) ν (cm⁻¹) 3357, 2957, 2928, 1723, 1632, 1460, 1295, 1075, 1046.

HRMS (ESI) calcd for C₁₂H₁₈N⁺ (M+H)⁺ m/z: 176.1434, found: 176.1435.

5af: Rᶠ = 0.29 (CHCl₃/MeOH = 10:1).

1H NMR (400 MHz, CDCl₃) δ 7.34 – 7.19 (m, 5H), 3.85 – 3.73 (m, 3H), 3.18 – 3.09 (m, 2H), 2.48 (t, J = 7.4 Hz, 2H), 1.42 (sext, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ 142.3, 128.4, 127.0, 126.4, 61.7, 61.6, 35.8, 20.8, 11.8.

IR (KBr) ν (cm⁻¹) 2955, 2923, 1631, 1462, 1383, 1141, 1075, 699.
HRMS (ESI) calcd for C\textsubscript{12}H\textsubscript{18}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \): 176.1434, found: 176.1435.

\( \text{N-tert-butyl-2-phenylprop-2-en-1-amine (4ag), (E)-N-tert-butyl-3-phenylprop-2-en-1-amine (3ag) and 1-tert-butyl-3-phenylazetidine (5ag) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 10/1 to petroleum ether/ethyl acetate/triethylamine = 100/30/1, to give 36 mg product 4ag as a yellow oil in 48\% yield and 26 mg product 3ag/5ag as a yellow oil in 34\% mixture yield (NMR yield for 3ag is 14\%, NMR yield for 5ag is 20\%).}

\text{Mixture of 3ag and 5ag:} \( R_f = 0.32 \) (CHCl\textsubscript{3}/MeOH = 10:1).

\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta \text{ 3ag: 7.37 (d, } J = 7.6 \text{ Hz, 2H), 7.29 (t, } J = 7.6 \text{ Hz, 2H), 7.21 (t, } J = 7.2 \text{ Hz, 1H), 6.53 (d, } J = 15.8 \text{ Hz, 1H), 6.34 (dt, } J = 15.8, 6.4 \text{ Hz, 1H), 3.38 (d, } J = 6.4 \text{ Hz, 2H), 1.17 (s, 9H).}

\(^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta \text{ 142.8, 137.2, 130.7, 129.4, 128.5, 128.3, 127.2, 127.0, 126.3, 126.2, 53.6, 52.0, 50.4, 45.2, 33.7, 29.1, 24.2.}

\text{HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{20}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \): 190.1590, mixture found: 190.1590.}

\text{4ag:} \( R_f = 0.32 \) (CHCl\textsubscript{3}/MeOH = 10:1).

\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta \text{ 7.48 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 5.38 (s, 1H), 5.28 (d, } J = 1.2 \text{ Hz, 1H), 3.62 (s, 2H), 3.09 (hept, } J = 6.6 \text{ Hz, 2H), 1.04 (d, } J = 6.6 \text{ Hz, 12H).}

\(^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta \text{ 147.2, 140.2, 128.4, 127.6, 126.2, 113.0, 50.5, 46.6, 29.0.}

\text{IR (KBr) } \nu \text{ (cm\textsuperscript{−1}) 3353, 2959, 2921, 1631, 1469, 1361, 1229, 901, 778, 704.}

\text{HRMS (ESI) calcd for C\textsubscript{13}H\textsubscript{20}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \): 190.1590, found: 190.1590.}

\( N,N\text{-diisopropyl-2-p-tolylprop-2-en-1-amine (4ba) and (E)-N-N\text{-diisopropyl-3-p-tolylprop-2-en-1-amine (3ba) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 54 mg product 4ba as a yellow oil in 58\% yield and 8mg product 3ba as a yellow oil in 9\% yield.}

\text{3ba:} \( R_f = 0.39 \) (CHCl\textsubscript{3}/MeOH = 10:1).

\(^1\text{H NMR (400 MHz, CDCl}_3\text{)} \delta \text{ 7.26 (d, } J = 8.0 \text{ Hz, 2H), 7.10 (d, } J = 8.0 \text{ Hz, 2H), 6.46 (d, } J = 16.0 \text{ Hz, 1H), 6.18 (dt, } J = 16.0, 6.6 \text{ Hz, 1H), 3.27 (d, } J = 6.6 \text{ Hz, 2H), 3.09 (hept, } J = 6.6 \text{ Hz, 2H), 2.32 (s, 3H), 1.04 (d, } J = 6.6 \text{ Hz, 12H).}

\(^13\text{C NMR (100 MHz, CDCl}_3\text{)} \delta \text{ 136.7, 134.8, 130.8, 129.9, 129.2, 126.0, 48.3, 47.7, 21.1, 20.7.}

\text{IR (KBr) } \nu \text{ (cm\textsuperscript{−1}) 2960, 2919, 1658, 1632, 1470, 1380, 1174, 967, 793.}

\text{HRMS (ESI) calcd for C\textsubscript{16}H\textsubscript{26}N\textsuperscript{+} (M+H\textsuperscript{+}) \( m/z \): 232.2060, found: 232.2063.}
4ba: Rf = 0.30 (petroleum ether/ethyl acetate = 5:1).

1H NMR (400 MHz, CDCl3) δ 7.35 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.38 (d, J = 2.0 Hz, 1H), 5.33 (d, J = 2.0 Hz, 1H), 3.41 (s, 2H), 3.07 (hept, J = 6.6 Hz, 2H), 2.34 (s, 3H), 0.99 (d, J = 6.6 Hz, 12H).

13C NMR (100 MHz, CDCl3) δ 147.8, 138.4, 136.8, 128.6, 126.2, 112.8, 49.3, 47.8, 21.1, 20.6.

IR (KBr) ν (cm⁻¹) 2963, 2925, 1630, 1513, 1463, 1362, 1179, 1118, 900, 823, 740.

HRMS (ESI) calcd for C16H26N+ (M+H)+ m/z: 232.2060, found: 232.2063.

2-(4-fluorophenyl)-N,N-diisopropylprop-2-en-1-amine (4ca) and (E)-3-(4-fluorophenyl)-N,N-diisopropylprop-2-en-1-amine (3ca) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 35 mg product 4ca as a yellow oil in 38% yield and 16 mg product 3ca as a yellow oil in 17% yield.

3ca: Rf = 0.39 (CHCl3/MeOH = 10:1)

1H NMR (400 MHz, CDCl3) δ 7.36 – 7.28 (m, 2H), 6.98 (t, J = 8.8 Hz, 2H), 6.46 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 5.8 Hz, 1H), 3.27 (d, J = 5.8 Hz, 2H), 3.09 (hept, J = 6.6 Hz, 2H), 1.04 (d, J = 6.6 Hz, 12H).

13C NMR (100 MHz, CDCl3) δ 162.0 (d, J = 243 Hz, 1C), 133.8 (d, J = 3 Hz, 1C), 131.6, 128.8, 127.5 (d, J = 2 Hz, 1C), 115.3 (d, J = 22 Hz, 1C), 48.3, 47.5, 20.7.

19F NMR (376 MHz, CDCl3) δ -115.65.

IR (KBr) ν (cm⁻¹) 2962, 2925, 1601, 1508, 1461, 1380, 1231, 1156, 966, 845, 774.

HRMS (ESI) calcd for C15H23FN+ (M+H)+ m/z: 236.1809, found: 236.1811.

2-(4-bromophenyl)-N,N-diisopropylprop-2-en-1-amine (4da) and (E/Z)-3-(4-bromophenyl)-N,N-diisopropylprop-2-en-1-amine (3da) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 79 mg product 4da as a yellow oil in 67% yield and 24 mg product 3da as a yellow oil in 20% yield (E/Z = 89:11 according to the NMR).
3da: \( R_f = 0.39 \) (CHCl\textsubscript{3}/MeOH = 10:1)

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.66 – 7.62 (m, 2H, minor), 7.46 – 7.44 (m, 2H, minor), 7.41 – 7.36 (m, 2H, major) 7.24 – 7.20 (m, 2H, major), 6.81 (d, \( J = 15.8 \) Hz, 1H, minor), 6.44 (d, \( J = 15.8 \) Hz, 1H, major), 6.23 (dt, \( J = 15.8, 6.4 \) Hz, 1H), 3.30 (dd, \( J = 6.4, 1.6 \) Hz, 2H, minor), 3.26 (dd, \( J = 6.4, 1.6 \) Hz, 2H, major), 3.08 (hept, \( J = 6.6, 1H \)), 1.04 (d, \( J = 6.6, 12H \)).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 136.5, 134.0, 132.8, 131.5, 131.0, 130.9, 129.8, 129.3, 128.8, 127.7, 124.8, 120.6, 48.6, 48.4, 47.5, 47.3, 20.8, 20.7.

IR (KBr) \( \nu (\text{cm}^{-1}) \) 2963, 2923, 1632, 1487, 1463, 1382, 1175, 1072, 1008, 967.

HRMS (ESI) calcd for C\textsubscript{15}H\textsubscript{23}BrN\textsuperscript{+} (M+H)
\( m/z \): 296.1008, found: 296.1014.

4da: \( R_f = 0.36 \) (petroleum ether/ethyl acetate = 5:1).

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.30 – 7.22 (m, 4H), 6.46 (d, \( J = 15.8 \) Hz, 1H), 6.21 (d, \( J = 15.8 \) Hz, 2H), 3.27 (d, \( J = 5.8 \) Hz, 2H), 3.14 – 3.02 (hept, \( J = 6.4 \) Hz, 2H), 3.05 (hept, \( J = 6.6 \) Hz, 2H), 0.98 (d, \( J = 6.6 \) Hz, 12H).
N,N-diisopropyl-2-(4-nitrophenyl)prop-2-en-1-amine (4fa) and (E)-N,N-diisopropyl-3-(4-nitrophenyl)prop-2-en-1-amine (3fa) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 25 mg product 4fa as a bright yellow oil in 24% yield and 21 mg product 3fa as a bright yellow oil in 20% yield.

3fa: \( R_f = 0.38 \) (CHCl3/MeOH = 10:1)

\(^1\)H NMR (400 MHz, CDCl3) \( \delta \) 8.16 (d, \( J = 8.8 \) Hz, 2H), 7.48 (d, \( J = 8.8 \) Hz, 2H), 6.61 (d, \( J = 15.6 \) Hz, 1H), 6.46 (dt, \( J = 15.6, 5.4 \) Hz, 1H), 3.32 (d, \( J = 5.4 \) Hz, 2H), 3.08 (hept, \( J = 12.9, 6.4 \) Hz, 2H), 1.05 (d, \( J = 6.4 \) Hz, 12H).

\(^13\)C NMR (100 MHz, CDCl3) \( \delta \) 146.5, 144.2, 137.9, 127.8, 126.5, 123.9, 48.6, 47.5, 20.8.

IR (KBr) \( \nu \) (cm\(^{-1}\)) 2964, 2927, 1596, 1517, 1383, 1342, 1180, 1109, 859.

HRMS (ESI) calcd for C15H23N2O2+ (M+H)+ \( m/z \): 263.1754, found: 263.1754.

4fa: \( R_f = 0.42 \) (petroleum ether/ethyl acetate = 5:1).

\(^1\)H NMR (400 MHz, CDCl3) \( \delta \) 8.16 (d, \( J = 8.8 \) Hz, 2H), 7.61 (d, \( J = 8.8 \) Hz, 2H), 5.54 (d, \( J = 1.2 \) Hz, 1H), 5.49 (s, 2H), 3.48 (s, 2H), 3.04 (hept, \( J = 6.6 \) Hz, 2H), 0.98 (d, \( J = 6.6 \) Hz, 12H).

\(^13\)C NMR (100 MHz, CDCl3) \( \delta \) 147.2, 144.8, 129.1 (q, \( J = 32 \) Hz, 1C), 126.3, 124.4 (q, \( J = 4 \) Hz, 1C), 124.3 (q, \( J = 270 \) Hz, 1C), 48.4, 47.49, 47.49, 20.71.

\(^19\)F NMR (376 MHz, CDCl3) \( \delta \) -62.42.

IR (KBr) \( \nu \) (cm\(^{-1}\)) 2962, 2923, 1616, 1467, 1382, 1326, 1165, 1126, 1068, 1017, 969, 856.

HRMS (ESI) calcd for C15H23F3N+ (M+H)+ \( m/z \): 286.1777, found: 236.1784.

N,N-diisopropyl-2-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (4ga) and (E)-N,N-diisopropyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (3ga) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 25 mg product 4ga as a yellow oil in 22% yield and 46 mg product 3ga as a yellow oil in 40% yield.

3ga: \( R_f = 0.39 \) (CHCl3/MeOH = 10:1)

\(^1\)H NMR (400 MHz, CDCl3) \( \delta \) 7.53 (d, \( J = 8.2 \) Hz, 2H), 7.44 (d, \( J = 8.2 \) Hz, 2H), 6.55 (d, \( J = 15.8 \) Hz, 1H), 6.34 (dt, \( J = 15.8, 5.6 \) Hz, 1H), 3.29 (dd, \( J = 5.6, 0.8 \) Hz, 2H), 3.08 (hept, \( J = 6.6 \) Hz, 2H), 1.04 (d, \( J = 6.6 \) Hz, 12H).

\(^13\)C NMR (100 MHz, CDCl3) \( \delta \) 141.1, 135.1, 128.7 (q, \( J = 32 \) Hz, 1C), 128.5, 126.2, 125.4 (q, \( J = 4 \) Hz, 1C), 124.3 (q, \( J = 270 \) Hz, 1C), 48.49, 47.49, 20.71.

\(^19\)F NMR (376 MHz, CDCl3) \( \delta \) -62.42.

IR (KBr) \( \nu \) (cm\(^{-1}\)) 2962, 2923, 1616, 1467, 1382, 1326, 1165, 1126, 1068, 1017, 969, 856.

HRMS (ESI) calcd for C16H23F3N+ (M+H)+ \( m/z \): 286.1777, found: 236.1784.

4ga: \( R_f = 0.42 \) (petroleum ether/ethyl acetate = 5:1).

\(^1\)H NMR (400 MHz, CDCl3) \( \delta \) 7.60 – 7.49 (m, 4H), 5.48 (d, \( J = 1.3 \) Hz, 1H), 5.41 (s, 1H), 3.45 (s, 2H), 3.05 (hept, \( J = 6.6 \) Hz, 2H), 0.98 (d, \( J = 6.6 \) Hz, 12H).

\(^13\)C NMR (100 MHz, CDCl3) \( \delta \) 147.2, 144.8, 129.1 (q, \( J = 32 \) Hz, 1C), 124.4 (q, \( J = 270 \) Hz, 1C), 126.8, 124.8 (q, \( J = 4 \) Hz, 1C), 115.7, 49.3, 47.5, 20.5.
$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.42.

IR (KBr) $\nu$ (cm$^{-1}$) 2965, 2927, 1617, 1383, 1364, 1165, 1126, 1067, 1016, 847, 617.

HRMS (ESI) calcd for C$_{16}$H$_{23}$F$_3$N$^+$ (M+H)$^+$ $m/z$: 286.1777, found: 236.1781.

2-(3-chlorophenyl)-N,N-diisopropylprop-2-en-1-amine (4ha) and (E)-3-(3-chlorophenyl)-N,N-diisopropylprop-2-en-1-amine (3ha) were synthesized according to General Procedure, eluted by petroleum ether/ethyle acetate = 50/1 to petroleum ether/ethyle acetate/triethylamine = 100/10/1, to give 43 mg product 4ha as a yellow oil in 43% yield and 26 mg product 3ha as a yellow oil in 26% yield.

3ha: $R_f = 0.44$ (CHCl$_3$/MeOH = 10:1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (s, 1H), 7.22 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 6.25 (dt, $J = 16.0$, 6.0 Hz, 1H), 3.27 (dd, $J = 6.0$, 0.4 Hz, 2H), 3.08 (hept, $J = 6.6$ Hz, 2H), 1.04 (d, $J = 6.6$ Hz, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.5, 134.4, 133.7, 129.6, 128.6, 126.8, 126.1, 124.3, 48.4, 47.4, 20.7.

IR (KBr) $\nu$ (cm$^{-1}$) 2963, 2920, 1658, 1632, 1470, 1384, 1180, 1141, 1076, 1049.

HRMS (ESI) calcd for C$_{15}$H$_{23}$ClN$^+$ (M+H)$^+$ $m/z$: 252.1514, found: 252.1514.

4ha: $R_f = 0.48$ (petroleum ether/ethyle acetate = 5:1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (s, 1H), 7.33 (t, $J = 4.2$ Hz, 1H), 7.23 (d, $J = 4.2$ Hz, 2H), 5.44 (s, 1H), 5.38 (s, 1H), 3.41 (s, 2H), 3.06 (hept, $J = 6.6$ Hz, 2H), 0.99 (d, $J = 6.6$ Hz, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.0, 133.8, 129.10, 127.1, 126.7, 124.6, 114.9, 49.3, 47.6, 20.5.

IR (KBr) $\nu$ (cm$^{-1}$) 2963, 2926, 1593, 1562, 1465, 1383, 1207, 1180, 1141, 787.

HRMS (ESI) calcd for C$_{15}$H$_{23}$ClN$^+$ (M+H)$^+$ $m/z$: 252.1514, found: 252.1514.

2-(3,5-dichlorophenyl)-N,N-diisopropylprop-2-en-1-amine (4ia) and (E)-3-(3,5-dichlorophenyl)-N,N-diisopropylprop-2-en-1-amine (3ia) were synthesized according to General Procedure, eluted by petroleum ether/ethyle acetate = 50/1 to petroleum ether/ethyle acetate/triethylamine = 100/10/1, to give 27 mg product 4ia as a yellow oil in 24% yield and 53 mg product 3ia as a yellow oil in 46% yield.

3ia: $R_f = 0.27$ (CHCl$_3$/MeOH = 10:1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (s, 1H), 7.21 (s, 1H), 7.17 (m, 1H), 6.41 (d, $J = 15.8$ Hz, 1H), 6.27 (dt, $J = 15.8$, 5.7 Hz, 1H), 3.26 (d, $J = 5.7$ Hz, 2H), 3.06 (hept, $J = 6.6$ Hz, 2H), 1.03 (d, $J = 6.6$ Hz, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.7, 135.5, 135.0, 127.3, 126.6, 124.5, 48.5, 47.3, 20.7.

IR (KBr) $\nu$ (cm$^{-1}$) 2960, 2922, 1585, 1560, 1416, 1205, 1141, 1179, 1116, 1075, 799.

HRMS (ESI) calcd for C$_{15}$H$_{22}$Cl$_2$N$^+$ (M+H)$^+$ $m/z$: 286.1124, found: 286.1118.
4ia: R_f = 0.55 (petroleum ether/ethyl acetate = 5:1).

^1^H NMR (400 MHz, CDCl_3) δ 7.37 (s, 2H), 7.24 (s, 1H), 5.44 (s, 1H), 5.39 (s, 1H), 3.38 (s, 2H), 3.05 (hept, J = 6.4 Hz, 2H), 0.99 (d, J = 6.4 Hz, 12H).

^1^C NMR (100 MHz, CDCl_3) δ 145.8, 144.0, 134.4, 126.9, 125.1, 116.0, 77.3, 47.5, 20.4.

IR (KBr) ν (cm⁻¹) 2963, 2925, 1583, 1558, 1383, 1363, 1207, 1180, 1141, 1095, 801.

HRMS (ESI) calcd for C_{15}H_{22}Cl_2N^+ (M+H)^+ m/z: 286.1124, found: 286.1118.

2-(2-chlorophenyl)-N,N-diisopropylprop-2-en-1-amine (4ja) and (E)-3-(2-chlorophenyl)-N,N-diisopropylprop-2-en-1-amine (3ja) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 4 mg product 4ja as a yellow oil in 4% yield and 44 mg product 3ja as a yellow oil in 44% yield.

3ja: R_f = 0.33 (CHCl_3/MeOH = 10:1)

^1^H NMR (400 MHz, CDCl_3) δ 7.53 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 15.6 Hz, 1H), 6.22 (dt, J = 15.6, 6.0 Hz, 1H), 3.32 (d, J = 6.0 Hz, 2H), 3.16 – 3.04 (hept, J = 6.4 Hz, 2H), 1.05 (d, J = 6.4 Hz, 12H).

^1^C NMR (100 MHz, CDCl_3) δ 135.7, 135.0, 132.7, 129.5, 127.9, 126.8, 126.7, 126.1, 48.5, 47.7, 20.8.

IR (KBr) ν (cm⁻¹) 2962, 2923, 1469, 1440, 1382, 1204, 1180, 1075, 1033, 749.

HRMS (ESI) calcd for C_{15}H_{23}ClN^+ (M+H)^+ m/z: 252.1514, found: 252.1519.

4ja: R_f = 0.50 (petroleum ether/ethyl acetate = 5:1).

^1^H NMR (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 1H), 7.21 – 7.13 (m, 3H), 5.55 (s, 1H), 5.05 (s, 1H), 3.31 (s, 2H), 3.07 (hept, J = 6.6 Hz, 2H), 0.95 (d, J = 6.6 Hz, 12H).

^1^C NMR (100 MHz, CDCl_3) δ 148.8, 141.6, 132.1, 130.9, 129.2, 128.0, 126.2, 115.3, 50.1, 47.6, 20.7.

IR (KBr) ν (cm⁻¹) 2962, 2924, 1456, 1363, 1331, 1207, 1179, 1147, 1046, 160.

HRMS (ESI) calcd for C_{15}H_{23}ClN^+ (M+H)^+ m/z: 252.1514, found: 252.1514.

(E/Z)-N-tert-butyl-2-methyl-3-phenylprop-2-en-1-amine (3kg) and 2-benzyl-N-tert-butylprop-2-en-1-amine (3kg') were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to give 30 mg mixture product 3kg and 3kg' as a yellow oil in 37 % yield (3kg: 3kg' = 1:0.3 according to the NMR, for 3kg, the E/Z ratio is 89:11).

Mixture of 3kg and 3kg': R_f = 0.29 (CHCl_3/MeOH = 10:1)

^1^H NMR (400 MHz, CDCl_3) δ (3kg) 7.34 – 7.16 (m, 5H), 6.45 (s, 1H, major), 6.38 (s, 1H, minor), 3.28 (s, 2H, major), 3.26 (s, 2H, minor), 1.96 (d, J = 1.6 Hz, 3H, minor), 1.91 (s, 3H, major), 1.16 (s, 9H, major), 1.08 (s, 9H, major); (3kg') 7.34 – 7.16 (m, 5H), 5.02 (s, 1H), 4.82 (s, 1H), 3.42 (s, 2H), 3.08 (s, 2H), 1.06 (s, 9H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.4, 139.7, 138.3, 138.0, 131.0, 129.0, 128.9, 128.5, 128.2, 128.02, 127.97, 127.4, 126.2, 126.03, 126.00, 125.1, 124.8, 111.5, 51.3, 50.5, 50.4, 46.8, 44.0, 41.6, 29.7, 29.3, 29.1, 29.0, 23.4, 17.1.

HRMS (ESI) calcd for C\(_{14}\)H\(_{22}\)N\(^+\) (M+H\(^+\)) \(m/z\): 204.1747, mixture found: 204.1747.

\((E/Z)-N,N\)-diisopropyl-2-phenylbut-2-en-1-amine (4la) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate = 50/1 to petroleum ether/ethyl acetate/triethylamine = 100/10/1, to give 49 mg product 4la as a yellow oil in 53% yield (\(E/Z = 3:1\) according to the NMR).

4la: \(R_f\) = 0.27 (CHCl\(_3\)/MeOH = 10:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.20 (m, 5H), 5.87 (q, \(J = 7.0\) Hz, 1H, major), 5.82 (q, \(J = 6.8\) Hz, 1H, minor), 3.55 (s, 2H, major), 3.29 (s, 2H, minor), 3.20 – 2.96 (m, 2H), 1.91 (d, \(J = 7.0\) Hz, 3H, major, \(E\) product), 1.64 (dd, \(J = 6.8, 1.2\) Hz, 3H, minor, \(Z\) product), 1.02 – 0.97 (m, \(J = 7.2\) Hz, 12H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.9, 141.0, 140.0, 128.8, 127.6, 127.4, 127.1, 126.2, 126.1, 126.0, 122.1, 52.2, 47.1, 46.1, 42.7, 20.5, 14.5, 14.0.

IR (KBr) \(\nu\) (cm\(^{-1}\)) 2962, 2925, 1463, 1380, 1361, 1179, 1116, 1029, 698.

HRMS (ESI) calcd for C\(_{16}\)H\(_{26}\)N\(^+\) (M+H\(^+\)) \(m/z\): 232.2060, found: 232.2060.

\((E/Z)-N\)-isopropyl-2-phenyl-N-((E/Z)-2-phenylbut-2-enyl)but-2-en-1-amine (4ld') and \((E/Z)-N\)-isopropyl-2-phenylbut-2-en-1-amine (\(E/Z\)-4ld) were synthesized according to General Procedure, eluted by petroleum ether/ethyl acetate =50/1 to petroleum ether/ethylacetate/triethylamine = 100/10/1, to give 18 mg product 4ld' as a yellow oil in 28% yield and 54 mg product \(E/Z\)-4ld as a yellow oil in 71% yield (\(E/Z = 3:1\) according to the NMR). The mixture \(E/Z\)-4ld was purified by preparative TLC.

\(E\)-4ld: \(R_f\) = 0.29 (CHCl\(_3\)/MeOH = 10:1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (m, 2H), 7.31 (m, 2H), 7.23 (m, 1H), 5.87 (q, \(J = 7.0\) Hz, 1H, major), 3.67 (s, 2H, major), 2.79 (hept, \(J = 6.2\) Hz, 1H), 1.86 (d, \(J = 7.0\) Hz, 3H), 1.03 (d, \(J = 6.2\) Hz, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.0, 139.1, 128.4, 126.7, 126.2, 125.2, 48.1, 45.0, 22.9, 14.1.

IR (KBr) \(\nu\) (cm\(^{-1}\)) 3361, 2960, 2926, 2854, 1725, 1599, 1462, 1378, 1179, 1074, 760, 698.

HRMS (ESI) calcd for C\(_{13}\)H\(_{20}\)N\(^+\) (M+H\(^+\)) \(m/z\): 190.1590, found: 190.1590.

\(Z\)-4ld: \(R_f\) = 0.29 (CHCl\(_3\)/MeOH = 10:1)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 (m, 2H), 7.26 (m, 1H), 7.20 (m, 2H), 5.72 (q, \(J = 6.8\) Hz, 1H), 3.48 (s, 2H, major), 2.80 (hept, \(J = 6.2\) Hz, 1H), 1.59 (d, \(J = 6.8\) Hz, 3H), 1.00 (d, \(J = 6.2\) Hz, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.7, 139.4, 128.6, 128.2, 126.8, 123.0, 54.2, 47.3, 22.7, 14.5.

IR (KBr) \(\nu\) (cm\(^{-1}\)) 2956, 2925, 1494, 1463, 1378, 1179, 1074, 768, 701.
HRMS (ESI) calcd for C_{13}H_{20}N^+ (M+H)^+ m/z: 190.1590, found: 190.1594.

4ld': R_f = 0.43 (petroleum ether/ethyl acetate = 5:1)

^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.00 (m, 10H), 5.94 (q, J = 7.0 Hz, 0.8H), 5.85 (q, J = 7.0 Hz, 0.5H), 5.60 (q, J = 7.0 Hz, 0.5H), 5.54 (q, J = 7.0 Hz, 0.2H), 3.43 (s, 1H), 3.41 (s, 1H), 3.21 (s, 1H), 3.18 (s, 0.4H), 3.13 – 2.89 (m, 1H), 1.83 (d, J = 7.0 Hz, 2.4H), 1.79 (d, J = 7.0 Hz, 1.5H), 1.59 (d, J = 7.0 Hz, 1.5H), 1.53 (d, J = 7.0 Hz, 0.6H), 0.93 (d, J = 6.7 Hz, 2.4H), 0.87 (d, J = 6.7 Hz, 3.0H), 0.83 (d, J = 6.7 Hz, 0.6H).

^13C NMR (100 MHz, CDCl_3) δ 143.4, 142.9, 140.1, 139.4, 138.8, 138.4, 128.83, 128.81, 127.6, 127.50, 127.48, 126.9, 126.8, 126.6, 126.5, 126.1, 126.04, 126.00, 123.8, 123.3, 56.4, 47.5, 47.4, 47.0, 46.5, 17.2, 17.1, 14.65, 14.23, 14.15.

IR (KBr) ν (cm\(^{-1}\)) 2959, 2924, 1494, 1462, 1383, 1260, 1166, 1098, 1021, 750, 698.

HRMS (ESI) calcd for C_{23}H_{30}N^+ (M+H)^+ m/z: 320.2373, found: 320.2375.
IV. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra

the $^1$H and $^{13}$C NMR spectra of 3aa
the $^1$H and $^{13}$C NMR spectra of 4aa
the $^1$H and $^{13}$C NMR spectra of 3ab
the $^1$H and $^{13}$C NMR spectra of 4ab
the $^1$H and $^{13}$C NMR spectra of 3ac
the $^1$H and $^{13}$C NMR spectra of 4ac
the $^1$H and $^{13}$C NMR spectra of 3ad
the $^1$H and $^{13}$C NMR spectra of $4\text{ad}$
the $^1$H and $^{13}$C NMR spectra of mixture 5ad and 3ad
the $^1$H and $^{13}$C NMR spectra of 3ae
the $^1$H and $^{13}$C NMR spectra of 4ae
the $^1$H and $^{13}$C NMR spectra of 5ae
the $^1$H and $^{13}$C NMR spectra of 3af
the $^1$H and $^{13}$C NMR spectra of 4af
the $^1$H and $^{13}$C NMR spectra of 5af
the $^1$H and $^{13}$C NMR spectra of mixture 5ag and 3ag

mixture 5ag and 3ag

mixture 5ag and 3ag
the $^1$H and $^{13}$C NMR spectra of 4ag
the $^1$H and $^{13}$C NMR spectra of 3ba
the $^1$H and $^{13}$C NMR spectra of 4ba
the $^1$H, $^{13}$C and $^{19}$F NMR spectra of 3ca
the $^1$H, $^{13}$C and $^{19}$F NMR spectra of 4ca
the $^1$H and $^{13}$C NMR spectra of 3da
the $^1$H and $^{13}$C NMR spectra of 4da

![NMR Spectra of 4da](image-url)
the $^1$H and $^{13}$C NMR spectra of 3ea
the $^1$H and $^{13}$C NMR spectra of 4ea
the $^1$H and $^{13}$C NMR spectra of 3fa
the $^1$H and $^{13}$C NMR spectra of 4fa

4fa

4fa
the $^1$H, $^{13}$C and $^{19}$F NMR spectra of 3ga
the $^1$H, $^{13}$C and $^{19}$F NMR spectra of 4ga
the $^1$H and $^{13}$C NMR spectra of 3ha
the $^1$H and $^{13}$C NMR spectra of $4\text{ha}$
the $^1$H and $^{13}$C NMR spectra of 3ia
the $^1$H and $^{13}$C NMR spectra of 4ia
the $^1$H and $^{13}$C NMR spectra of 3ja

3ja

3ja
the $^1$H and $^{13}$C NMR spectra of 4ja
the $^1$H NMR spectra of crude mixture to determine the ratio of \textbf{3kg} and \textbf{3kg'}

Mixture product $\textbf{3kg}: \textbf{3kg'} = 3: 1$
the $^1$H and $^{13}$C NMR spectra of mixture 3kg and 3kg'
the $^1$H and $^{13}$C NMR spectra of 4la
the $^1$H and $^{13}$C NMR spectra of $E$-4ld
the $^1$H and $^{13}$C NMR spectra of Z-4ld
the $^1$H and $^{13}$C NMR spectra of 4ld$'$.
V. Copies of crude $^1$H NMR spectra for determination of the product ratio (3:4) in Table 2

4aa: 3aa

4ba: 3ba
4ga: 3ga

4ha: 3ha