Substrate Structural Effects in Yttrium(III) catalyzed Hydroamination/Cyclizations of Aminoalkenes Terminated by 2-(Phenyl)ethenyl and 2-(2-Heteroarenyl)ethenyl Groups.

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Experimental Supporting Information

1. Materials and methods
Reactions employed oven- or flame-dried glassware under nitrogen unless otherwise noted. THF and diethyl ether were distilled from sodium/benzophenone under nitrogen. CH$_2$Cl$_2$ was distilled from CaH$_2$ under nitrogen. All other materials were used as received from commercial sources. Thin-layer chromatography (TLC) employed 0.25 mm glass silica gel plates with UV indicator. Flash chromatographic columns were packed with Silicycle SiliaFlash F60 silica gel as a slurry in the initial elution solvent. Nuclear magnetic resonance (NMR) data were obtained from Bruker DPX-300 (300 MHz) and Bruker DPX-500 (500 MHz). Infrared spectra (IR) were obtained from JASCO FTIR-4100. High-resolution mass spectra (HRMS) were obtained from Bruker MicroTOF with an Agilent 1100 HPLC.
2. Procedures and characterization data for new compounds.

2.1 Amino alkene syntheses and characterization data.
General nitrile preparation procedure: \((E)\)-2,2-Dimethyl-5-phenylpent-4-enenitrile

A 200-mL, round-bottomed flask equipped with a magnetic stirring bar and a N\(_2\) inlet was charged with anhydrous diisopropylamine (5.6 mL, 39.6 mmol) and anhydrous THF (100 mL) was subsequently added. The resulting solution was cooled to 0 °C with an ice-water bath and \(n\)-BuLi (10 M, 4.0 mL, 40.0 mmol) was slowly added dropwise. The reactant mixture was stirred for 30 min at 0 °C, then cooled to −78 °C with a Dry Ice-acetone bath. Isobutyronitrile (3.6 mL, 39.6 mmol) was added and the reactant mixture
was stirred for 2 h at -78 °C. Cinnamyl chloride (2.73 mL, 19.8 mmol) in anhydrous THF (5 mL) was then slowly added. The reactant mixture was warmed to room temperature and stirred for 2 h when judged complete by TLC. The reactant mixture was diluted with diethyl ether (100 mL), washed with saturated NaHCO₃ (30 mL), brine (30 mL). The organic phase was dried with Na₂SO₄. Concentration in vacuo followed by flash chromatography on silica gel (20:1 hexane/EtOAc for elution) afforded (E)-2,2-dimethyl-5-phenylpent-4-enenitrile (2.5 g, 13.5 mmol, 68%) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.37 (d, J=7.5 Hz, 2H, 2Ar-H), 7.31 (t, J=7.0 Hz, 2H, 2Ar-H), 7.23 (t, J=8.0 Hz, 1H, Ar-H), 6.50 (d, J=15.5 Hz, 1H, Ar-C=CH=C), 6.25 (ddd, apparent dt, J=15.0, 7.5 Hz, 1H, Ar-C=CH), 2.43 (d, J=7.0 Hz, 2H, CH₂), 1.37 (s, 6H, 2CH₃); ¹³C NMR (500 MHz, CDCl₃): δ 136.7, 134.8, 128.6, 127.7, 126.4, 124.8, 123.6, 44.3, 32.6, 26.3; IR (film) 2979, 2233, 1450, 969, 744, 696 cm⁻¹.

**General LiAlH₄ reduction procedure:** (E)-2,2-Dimethyl-5-phenylpent-4-enylamine (3aₑ)

A 50-mL, round-bottomed flask equipped with a magnetic stirring bar and a N₂ inlet was charged with LiAlH₄ (81 mg, 2.12 mmol) and anhydrous diethyl ether (8 mL) was subsequently added. The resulting mixture was cooled to 0 °C with an ice-water bath. (E)-2,2-Dimethyl-5-phenylpent-4-enenitrile (0.26 g, 1.42 mmol) in anhydrous diethyl ether (2 mL) was then added at 0 °C. The reactant mixture was stirred for 10 h when judged complete by TLC. Water was slowly added dropwise until no hydrogen was evolved. The reactant mixture was diluted with diethyl ether (10 mL) and subsequently
was dried with Na₂SO₄. The white solid was removed by vacuum filtration. Concentration in vacuo followed by bulb to bulb distillation from CaH₂ afforded (E)-2,2-dimethyl-5-phenylpent-4-enylamine (3αₑ) (0.22 g, 1.18 mmol, 83%) as a colorless oil. ¹H NMR (500 MHz, toluene-D₈): δ 7.22 (d, J=7.0 Hz, 2H, 2Ar-H), 7.12 (t, J=7.5 Hz, 2H, 2Ar-H), 7.03 (t, J=7.5 Hz, 1H, Ar-H), 6.29 (d, J=16.0 Hz, 1H, Ar-CH2=C), 6.15 (ddd, apparent dt, J=15.5, 7.5 Hz, 1H, Ar-C=CH), 2.27 (s, 2H, CH₂NH₂), 1.98 (d, J=7.0 Hz, 2H, C=C-CH₂), 0.78 (s, 6H, 2CH₃), 0.63 (s, 2H, NH₂); ¹³C NMR (500 MHz, toluene-D₈): δ 132.2, 128.3, 127.3, 126.7, 126.0, 52.4, 42.9, 35.4, 24.5; IR (film) 2957, 1576, 1472, 1364, 1309, 969, 751, 692 cm⁻¹.

**General H/D exchange procedure**: (E)-2,2-dimethyl-5-phenylpent-4-enylamine-Ν,N-D₂ [3αₑ (D₂)]

A 15-mL, round-bottomed flask equipped with a magnetic stirring bar and a N₂ inlet was charged with (E)-2,2-dimethyl-5-phenylpent-4-enylamine (3αₑ) (0.88 g, 4.67 mmol) and anhydrous benzene (2.5 mL) was subsequently added. D₂O (1.88 g, 93.0 mmol) was subsequently added. The reactant mixture was stirred for 12 h. The lower D₂O layer was removed by syringe and the H/D exchange was repeated three times. Concentration in vacuo followed by bulb to bulb distillation afforded (E)-2,2-dimethyl-5-phenylpent-4-enylamine-Ν,N-D₂ [3αₑ (D₂)] (0.69 g, 3.61 mmol, 78%) as a colorless oil. ¹H NMR (500 MHz, toluene-D₈): δ 7.22 (d, J=7.5 Hz, 2H, 2Ar-H), 7.12 (t, J=7.5 Hz, 2H, 2Ar-H), 7.03 (t, J=7.5 Hz, 1H, Ar-H), 6.29 (d, J=16.0 Hz, 1H, Ar-CH2=C), 6.15 (ddd, apparent dt,
$J=15.5, 7.5 \text{ Hz, } 1 \text{H, Ar-C=CH}, 2.26 \text{ (s, } 2 \text{H, CH}_2\text{ND}_2), 1.99 \text{ (d, } J=7.0 \text{ Hz, } 2 \text{H, C=C-CH}_2), 0.78 \text{ (s, } 6 \text{H, } 2 \text{CH}_3); ^{13}\text{C NMR (500 MHz, toluene-D}_8\text{): } \delta 137.9, 132.2, 128.3, 127.3, 126.7, 126.0, 52.2, 42.9, 35.4, 24.5; \text{ IR (film) 2954, 1598, 1469, 1364, 1309, 966, 751, 692 cm}^{-1}; \text{ HRMS (ESI): Calcd for } C_{13}H_{17}D_2ND [M+D]^+ 193.1779, \text{ found 193.1779.}

3-Phenyl-prop-2-yn-1-ol

\[
\text{Ph} \rightleftharpoons \text{Ph} \quad \underset{1) \text{n-BuLi}}{\overset{2) (\text{CH}_2\text{O})_x}{\longrightarrow}} \quad 86\%
\]

A 500-mL, round-bottomed flask equipped with a magnetic stirring bar and a N$_2$ inlet was charged with phenylethyne (20 mL, 179 mmol) and anhydrous THF (180 mL) was subsequently added. The resulting solution was cooled to $-78 ^\circ\text{C}$ with a Dry Ice-acetone bath, n-BuLi (2.6M, 82.4 mL, 214 mmol) was slowly added dropwise, and the reactant mixture was stirred at $-78 ^\circ\text{C}$ for 40 min. Paraformaldehyde (6.43 g, 217 mmol) was added and the reactant mixture was warmed to room temperature and stirred for 10 h. The reactant mixture was diluted with diethyl ether (200 mL), washed with saturated NH$_4$Cl (50 mL), brine (50 mL), and the organic phase was subsequently dried with Na$_2$SO$_4$. Concentration in vacuo followed by flash chromatography on silica gel (3:1 hexane/EtOAc for elution) afforded 3-phenyl-prop-2-yn-1-ol (20.2 g, 153 mmol, 86%) as a light yellow oil. $^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.43$-$7.24$ (m, 5H, 5Ar-H), 4.49 (d, $J=6.0$ Hz, 2H, CH$_2$), 1.69 (dd, apparent triplet, $J=5.5$ Hz, 1H, OH); $^{13}\text{C NMR (500 MHz, CDCl}_3\text{): } \delta 131.7, 128.5, 128.3, 85.7, 51.7; \text{ IR (film) 3324, 1491, 1033, 755, 692 cm}^{-1}.$
(Z)-3-Phenyl-prop-2-en-1-ol

A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and a N₂ inlet was charged with anhydrous ethanol (30 mL), Ni(OAc)₂•4H₂O (0.83 g, 3.32 mmol) and NaBH₄ (0.13 g, 3.32 mmol) were added in succession. The reactant mixture was purged by hydrogen gas three times. Ethylenediamine (0.45 mL, 6.63 mmol) and 3-phenyl-prop-2-yn-1-ol (2.19 g, 16.6 mmol) in absolute ethanol (5 mL) were added in succession. The reactant mixture was stirred under hydrogen at room temp for 10 h. Filtration of the reactant mixture through silica gel followed by concentration in vacuo afforded (Z)-3-phenyl-prop-2-en-1-ol (2.16 g, 16.1 mmol, 98%) as a colorless oil, which is used without further purification. ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.18 (m, 5H, 5Ar-H), 6.56 (d, J=12.0 Hz, 1H, Ar-CH=C), 5.86 (ddd, apparent dt, J=13.0, 6.5 Hz, 1H, Ar-C=C=H), 4.43 (d, J=6.0 Hz, 2H, CH₂), 1.56 (s, 1H, OH); ¹³C NMR (500 MHz, CDCl₃): δ 131.1, 131.0, 128.8, 128.3, 127.3, 59.7; IR (film) 3328, 1498, 1013, 769, 700 cm⁻¹.

General allylic chloride preparation procedure¹: [(Z)-3-Chloro-propenyl]-benzene

A 50-mL, round-bottomed flask equipped with a magnetic stirring bar and a N₂ inlet was charged with LiCl (780 mg, 18.4 mmol) and anhydrous DMF (30 mL) was subsequently added. The resulting mixture was stirred at 0 °C for 10 min until the LiCl had dissolved. (Z)-3-Phenyl-prop-2-en-1-ol (2.1 g, 15.3 mmol) and anhydrous 2,6-lutidine (2.1 mL, 18.4 mmol) were added in succession. MsCl (1.42 mL, 18.4 mmol) was then slowly added.
The reactant mixture was stirred for 3 h when judged complete by TLC. The reactant mixture was diluted with diethyl ether (20 mL), washed with water (5 mL), and the ether layer was subsequently dried with Na$_2$SO$_4$. Concentration in vacuo followed by flash chromatography on silica gel (10:1 hexane/EtOAc for elution) afforded [(Z)-3-chloro-propenyl]-benzene (1.82 g, 11.9 mmol, 73%) as a light yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.38-7.18 (m, 5H, 5Ar-H), 6.65 (d, $J$=11.5 Hz, 1H, Ar-CH=C), 5.89 (m, 1H, Ar-C=CH), 5.89 (d, $J$=8.0 Hz, 2H, CH$_2$); $^{13}$C NMR (500 MHz, CDCl$_3$): δ 135.6, 133.4, 128.7, 128.5, 127.7, 126.9, 40.8; IR (film) 3028, 1495, 1446, 1257, 811, 773, 700 cm$^{-1}$.

(Z)-2,2-Dimethyl-5-phenylpent-4-enenitrile

The title compound (Z)-2,2-dimethyl-5-phenylpent-4-enenitrile (0.85 g, 4.62 mmol, 52%) was obtained as a light yellow oil from [(Z)-3-chloro-propenyl]-benzene (1.35 g, 8.85 mmol) by the general nitrile preparation procedure. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.35-7.21 (m, 5H, 5Ar-H), 6.68 (d, $J$=11.5 Hz, 1H, Ar-CH=C), 5.78 (ddd, apparent dt, $J$=12.0, 7.0 Hz, 1H, Ar-C=CH), 2.54 (d, $J$=7.0 Hz, 2H, CH$_2$), 1.32 (s, 6H, 2CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): δ 136.8, 132.8, 128.7, 128.3, 127.0, 125.9, 124.8, 39.1, 32.5, 26.4; IR (film) 2979, 2233, 1495, 1446, 1368, 807, 773, 703 cm$^{-1}$; HRMS (ESI): Calcd for C$_{13}$H$_{16}$N [M+H]$^+$: 186.12773, found: 186.12706; Calcd for C$_{13}$H$_{16}$NO [M+OH]$^+$: 202.12264, found: 202.12331; C$_{13}$H$_{15}$NONa [M+Na]$^+$: 208.10967, found: 208.10906.
\((Z)-2,2\text{-dimethyl-5-phenylpent-4-enylamine (3a)}\)

\[
\begin{array}{c}
\text{Ph} \\
\text{H}_2\text{N} \\
\end{array}
\]

The title compound \((Z)-2,2\text{-dimethyl-5-phenylpent-4-enylamine (3a)}\) (0.53 g, 2.78 mmol, 79\%) was obtained as a colorless oil from \((Z)-2,2\text{-dimethyl-5-phenylpent-4-enenitrile (0.65 g, 3.51 mmol)}\) by the general LiAlH\(_4\) reduction procedure. \(^1\)H NMR (500 MHz, toluene-D\(_8\)): \(\delta\) 7.24 (d, \(J=7.5\) Hz, 2H, 2Ar-H), 7.14 (t, \(J=7.5\) Hz, 2H, 2Ar-H), 7.02 (t, \(J=7.5\) Hz, 1H, Ar-H), 6.46 (d, \(J=12.0\) Hz, 1H, Ar-CH=C), 5.63 (ddd, apparent dt, \(J=11.5, 7.5\) Hz, 1H, Ar-C=CH), 2.23 (s, 2H, CH\(_2\)NH\(_2\)), 2.20 (dd, \(J=7.5, 1.5\) Hz, 2H, C=C-CH\(_2\)), 0.74 (s, 6H, 2CH\(_3\)), 0.40 (s, 2H, NH\(_2\)); \(^1\)C NMR (500 MHz, toluene-D\(_8\)): \(\delta\) 137.1, 130.3, 129.1, 128.8, 128.0, 126.4, 52.2, 37.2, 35.1, 24.4; IR (film) 2954, 1602, 1469, 1364, 807, 773, 696 cm\(^{-1}\).

\((Z)-2,2\text{-Dimethyl-5-phenylpent-4-enylamine-}N,N\text{-D}_2 [3a(D)]\)

\[
\begin{array}{c}
\text{Ph} \\
\text{D}_2\text{N} \\
\end{array}
\]

The title compound \((Z)-2,2\text{-dimethyl-5-phenylpent-4-enylamine-}N,N\text{-D}_2 [3a(D)]\) (0.65 g, 3.4 mmol, 67\%) was obtained as a colorless oil from \((Z)-2,2\text{-dimethyl-5-phenylpent-4-enylamine (3a)}\) (0.96 g, 5.1 mmol) by the general H/D exchange procedure. \(^1\)H NMR (500 MHz, benzene-D\(_6\)): \(\delta\) 7.37 (d, \(J=7.5\) Hz, 2H, 2Ar-H), 7.25 (t, \(J=7.5\) Hz, 2H, 2Ar-H), 7.12 (t, \(J=7.0\) Hz, 1H, Ar-H), 6.58 (d, \(J=12.0\) Hz, 1H, Ar-CH=C), 5.73 (ddd, apparent dt, \(J=12.0, 7.5\) Hz, 1H, Ar-C=CH), 2.31 (dd, \(J=7.5, 1.5\) Hz, 2H, C=C-CH\(_2\)), 2.30 (s, 2H, CH\(_2\)ND\(_2\)), 0.82 (s, 6H, 2CH\(_3\)); \(^1\)C NMR (500 MHz, benzene-D\(_6\)): \(\delta\) 138.0, 130.5, 129.4,
129.0, 128.2, 126.6, 52.1, 37.4, 35.2, 24.5; IR (film) 2954, 1364, 1450, 1495, 1469, 803, 769, 700 cm\(^{-1}\); HRMS (ESI): Calcd for C\(_{13}\)H\(_{17}\)D\(_2\)ND \([\text{M+D}]^+\) 193.1779, found 193.1767.

**General Hornor-Wadsworth-Emmons procedure:** \((E)\)-2-Methyl-oct-2-enoic acid ethyl ester

A 250-mL, round-bottomed flask equipped with a magnetic stirring bar and a \(\text{N}_2\) inlet was charged with NaH (60% in oil, 1.96 g, 49.1 mmol) and anhydrous THF (100 mL) was added. After cooling to 0 °C, triethyl 2-phosphonopropionate (10.7 mL, 49.1 mmol) was slowly added. The reactant mixture was stirred at 0 °C for 30 min. Hexanal (5 mL, 40.9 mmol) was then slowly added and the reactant mixture was stirred for 30 min. The reactant mixture was diluted with diethyl ether (200 mL), washed with saturated NaHCO\(_3\) (50 mL), brine (50 mL), and the ether layer was subsequently dried with Na\(_2\)SO\(_4\). Concentration in vacuo followed distillation afforded \((E)\)-2-methyl-oct-2-enoic acid ethyl ester (4.79 g, 26.0 mmol, \(E/Z\): 5.4/1, 64%) as a colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \((E)\) isomer \(\delta\) 6.72 (t, \(J=7.5\) Hz, 1H, \(\text{CH}=\text{C}\)), 4.15 (ddd, apparent quartet, \(J=7.0\) Hz, 2H, OCH\(_2\)), 2.12 (ddd, apparent quartet, \(J=7.5\) Hz, 2H, C=\(\text{C-CH}_2\)), 1.79 (s, 3H, C=\(\text{C-CH}_3\)), 1.32-1.21 (m, 9H, 3\(\text{CH}_2\) and \(\text{CH}_3\)), 0.85 (dd, apparent triplet, \(J=6.5\) Hz, 3H, OCH\(_2\)\(\text{CH}_3\)); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)): \((E)\) and \((Z)\) mixture \(\delta\) 168.3, 143.1, 142.4, 127.6, 60.3, 60.0, 31.5, 29.5, 29.1, 28.6, 28.2, 22.5, 20.6, 14.3, 14.0, 12.3; IR (film): \((E)\) and \((Z)\)
mixture 2957, 2932, 2862, 1712, 1650, 1461, 1368, 1254, 1195, 1143, 1098, 1029, 741 cm$^{-1}$.

*(E)-2-Methyl-oct-2-en-1-ol*

\[
\text{C}_8\text{H}_{11} = \text{C} = \text{C} - \text{OH}
\]

The title compound *(E)-2-methyl-oct-2-en-1-ol* (3.85 g, 25.0 mmol, *E/Z*: 4/1, 98%) was obtained as a colorless oil from *(E)-2-methyl-oct-2-enoic acid ethyl ester* (4.70 g, 25.5 mmol) by the general LiAlH$_4$ reduction procedure. $^1$H NMR (500 MHz, CDCl$_3$): *(E)* isomer $\delta$ 5.38 (t, $J$=7.0 Hz, 1H, CH=C), 3.97 (s, 2H, OC$_2$H$_2$), 1.99 (ddd, apparent quartet, $J$=6.5 Hz, 2H, C=C-CH$_2$), 1.63 (s, 3H, C=C-CH$_3$), 1.40-1.21 (m, 6H, 3C$_2$H$_2$), 0.86 (dd, apparent triplet, $J$=7.0 Hz, 3H, CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): *(E)* and *(Z)* mixture $\delta$ 134.5, 128.9, 126.7, 69.0, 61.6, 31.5, 31.4, 30.3, 29.7, 29.2, 27.5, 22.6, 21.2, 14.1, 13.6; IR (film): *(E)* and *(Z)* mixture 3309, 2925, 2858, 1460, 1380, 1013 cm$^{-1}$.

*(E)-1-Chloro-2-methyl-oct-2-ene*

\[
\text{C}_8\text{H}_{11} = \text{C} = \text{C} - \text{Cl}
\]

The title compound *(E)-1-chloro-2-methyl-oct-2-ene* (2.49 g, 15.5 mmol, *E/Z*: 3.5/1, 63%) was obtained as a colorless oil from *(E)-2-methyl-oct-2-en-1-ol* (3.50 g, 24.7 mmol) by the general allylic chloride preparation procedure. $^1$H NMR (500 MHz, CDCl$_3$): *(E)* isomer $\delta$ 5.51 (t, $J$=7.0 Hz, 1H, CH=C), 4.00 (s, 2H, Cl-CH$_2$), 2.00 (ddd, apparent quartet, $J$=5.5 Hz, 2H, C=C-CH$_2$), 1.71 (s, 3H, C=C-CH$_3$), 1.40-1.21 (m, 6H, 3CH$_2$), 0.86 (dd, apparent triplet, $J$=6.5 Hz, 3H, CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): *(E)* and *(Z)* mixture $\delta$
The title compound (E)-2,2,4-trimethyl-dec-4-enenitrile (1.12 g, 5.79 mmol, E/Z: 3.5/1, 93%) was obtained as a colorless oil from (E)-1-chloro-2-methyl-oct-2-ene (1.0 g, 6.23 mmol) by the general nitrile preparation procedure. $^1$H NMR (500 MHz, CDCl$_3$): (E) isomer $\delta$ 5.24 (t, $J$=7.0 Hz, 1H, CH=C), 2.18 (s, 2H, C=C-CH$_2$), 1.99 (ddd, apparent quartet, $J$=7.0 Hz, 2H, C=C-CH$_2$), 1.74 (s, 3H, C=C-CH$_3$), 1.36-1.22 (m, 6H, 3CH$_2$), 1.29 (s, 6H, 2 CH$_3$), 0.86 (dd, apparent triplet, $J$=6.5 Hz, 3H, CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): (E) and (Z) mixture $\delta$ 131.4, 131.1, 129.9, 125.7, 50.5, 42.3, 31.7, 31.5, 29.5, 29.2, 28.5, 28.1, 27.3, 27.0, 24.9, 22.5, 17.5, 14.1; IR (film): (E) and (Z) mixture 2957, 2932, 2858, 2233, 1469, 1390, 1368, 1280, 1195, 1140, 914, 877, 729, 692 cm$^{-1}$.

(E)-2,2,4-Trimethyl-dec-4-enylamine (3b)

The title compound (E)-2,2,4-trimethyl-dec-4-enylamine (3b) (1.04 g, 5.27 mmol, E/Z: 3.7/1, 92%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-dec-4-enenitrile (1.10 , 5.70 mmol) by the general LiAlH$_4$ reduction procedure. $^1$H NMR (500 MHz, CDCl$_3$): (E) isomer $\delta$ 5.08 (t, $J$=7.0 Hz, 1H, CH=C), 2.41 (s, 2H, C=C-CH$_2$), 1.95 (ddd, apparent quartet, $J$=7.0 Hz, 2H, C=C-CH$_2$), 1.87 (s, 2H, N-CH$_2$), 1.62 (s, 3H, C=C-CH$_3$),
1.34-1.22 (m, 6H, 3CH$_3$), 1.05 (s, 2H, NH$_2$), 0.86 (dd, apparent triplet, $J$=6.5 Hz, 3H, CH$_3$), 0.81 (s, 6H, 2CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): (E) and (Z) mixture $\delta$ 132.2, 129.2, 129.1, 54.1, 53.3, 49.2, 41.3, 35.9, 31.7, 31.6, 30.3, 29.6, 29.4, 28.8, 28.2, 26.8, 25.5, 25.3, 22.6, 18.9, 14.1; IR (film): (E) and (Z) mixture 2961, 2925, 2858, 1579, 1465, 1380, 1062, 807, 725 cm$^{-1}$; HRMS (ESI): Calcd for C$_{13}$H$_{27}$N [M+H]$^+$: 198.2216, found: 198.2250.

Ethyl (E)-2-methyl-3-phenyl-2-propenoate

Ph\[\begin{array}{c} \bigarrow{\text{CO}_2}\text{Et} \end{array}\]

The title compound ethyl (E)-2-methyl-3-phenyl-2-propenoate (3.78 g, 19.9 mmol, 97%) was obtained as colorless oil from benzaldehyde (2.1 mL, 20.6 mmol) by the general Hornor-Wadsworth-Emmons procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.68 (s, 1H, Ar-CH=C), 7.39-7.23 (m, 5H, 5Ar-H), 4.26 (ddd, apparent quartet, $J$=7.0 Hz, 2H, CH$_2$), 2.10 (s, 3H, CH$_3$), 1.33 (dd, apparent triplet, $J$=7.0 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 138.6, 135.9, 129.6, 128.3, 128.2, 60.9, 14.3, 14.1; IR (film) 2983, 1705, 1634, 1446, 1364, 1254, 1202, 1110, 1033, 763, 700 cm$^{-1}$.

(E)-2-Methyl-3-phenylprop-2-en-1-ol

Ph\[\begin{array}{c} \bigarrow{\text{CH}_2}\text{OH} \end{array}\]

The title compound (E)-2-methyl-3-phenylprop-2-en-1-ol (2.8 g, 18.9 mmol, 96%) was obtained as a colorless oil from ethyl (E)-2-methyl-3-phenyl-2-propenoate (3.78 g, 19.9 mmol) by the general LiAlH$_4$ reduction procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.35-
7.21 (m, 5H, 5Ar-H), 6.52 (s, 1H, Ar-CH=CH), 4.18 (s, 2H, CH₂), 1.89 (s, 3H, CH₃), 1.71 (s, 1H, OH); ¹³C NMR (500 MHz, CDCl₃): δ 137.7, 137.5, 128.9, 128.2, 126.4, 125.0, 69.0, 15.3; IR (film) 3324, 2913, 2858, 1602, 1491, 1439, 1372, 1069, 1007, 918, 844, 741, 696 cm⁻¹.

[(E)-3-Chloro-2-methylpropenyl]-benzene

\[
\begin{align*}
\text{Ph} & \quad \text{CH₂OH} & \quad \text{SOCl₂} & \quad \text{Ph} & \quad \text{CH₂Cl} \\
\text{58\%}
\end{align*}
\]

A 250-mL, round-bottomed flask equipped with a magnetic stirring bar and a N₂ inlet was charged with (E)-2-methyl-3-phenylprop-2-en-1-ol (2.8 g, 18.9 mmol) and anhydrous diethyl ether (100 mL) was subsequently added. After cooling to 0 °C, freshly distilled SOCl₂ (1.33 mL, 18.9 mmol) was slowly added. The reactant mixture was stirred for 30 min when judged complete by TLC. The reactant mixture was diluted with diethyl ether (100 mL), washed with saturated NaHCO₃ (50 mL), brine (50 mL), and the organic layer was subsequently dried with Na₂SO₄. Concentration in vacuo followed by flash chromatography on silica gel (hexane for elution) afforded [(E)-3-chloro-2-methylpropenyl]-benzene (1.83 g, 11.0 mmol, 58%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.23 (m, 5H, 5Ar-H), 6.58 (s, 1H, Ar-CH=CH), 4.18 (s, 2H, CH₂), 1.98 (s, 3H, CH₃); ¹³C NMR (500 MHz, CDCl₃): δ 136.8, 134.1, 129.7, 129.0, 128.5, 128.2, 127.1, 52.9, 15.9; IR (film) 3024, 2951, 1491, 1439, 1261, 1013, 922, 855, 747, 696, 515 cm⁻¹.
(E)-2,2,4-Trimethyl-5-phenylpent-4-enenitrile

\[
\text{Ph} \equiv \text{C} = \text{N}
\]

The title compound (E)-2,2,4-trimethyl-5-phenylpent-4-enenitrile (0.5 g, 2.56 mmol, 85%) was obtained as a light yellow oil from [(E)-3-chloro-2-methylpropenyl]-benzene (0.5 g, 3.0 mmol) by the general nitrile preparation procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.35-7.19 (m, 5H, 5Ar-H), 6.36 (s, 1H, Ar-CH=H=C), 2.40 (s, 2H, CH\(_2\)), 2.03 (s, 3H, CH\(_3\)), 1.40 (s, 6H, 2CH\(_3\)); \(^1\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 130.6, 128.9, 128.1, 126.5, 51.5, 27.1, 19.5; IR (film) 2979, 2935, 2233, 1598, 1491, 1469, 1446, 1390, 1368, 1364, 1273, 1187, 1021, 918, 744, 696, 515 cm\(^{-1}\).

(E)-2,2,4-Trimethyl-5-phenylpent-4-enylamine (3c)

\[
\text{Ph} \equiv \text{C} = \text{N} \equiv \text{H}_{2}\text{N}
\]

The title compound (E)-2,2,4-trimethyl-5-phenylpent-4-enylamine (3c) (0.38 g, 1.87 mmol, 93%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5-phenylpent-4-enenitrile (0.4 g, 2.0 mmol) by the general LiAlH\(_4\) reduction procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.32-7.15 (m, 5H, 5Ar-H), 6.23 (s, 1H, Ar-CH=C), 2.51 (s, 2H, N-CH\(_2\)), 2.10 (s, 2H, C=CH=CH\(_2\)), 1.92 (s, 3H, CH\(_3\)), 1.29 (s, 2H, NH\(_2\)), 0.92 (s, 6H, 2CH\(_3\)); \(^1\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 138.4, 136.6, 128.9, 128.8, 128.0, 125.9, 53.4, 50.4, 36.4, 25.3, 21.1; IR (film) 2957, 1572, 1469, 1372, 1309, 751, 700 cm\(^{-1}\); HRMS (ESI): Calcd for C\(_{14}\)H\(_{21}\)N [M+H]\(^+\): 204.175, found: 2104.170.
General silylation procedure: \((E)-3-[5-(\text{Trimethylsilyl})\text{thiophen-2-yl}]\)-prop-2-en-1-ol

\[
\text{Thiophen-2-yl-prop-2-en-1-ol} \rightarrow \text{TMSCl} \rightarrow (E)-3-[5-(\text{Trimethylsilyl})\text{thiophen-2-yl}]\)-prop-2-en-1-ol \quad 74\%
\]

A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and a \(\text{N}_2\) inlet was charged with \((E)-3\)-thiophen-2-y1-prop-2-en-1-ol (1.0 g, 7.14 mmol) and anhydrous THF (40 mL) was subsequently added. The resulting solution was cooled to \(-78\ ^\circ\text{C}\) with a dry ice-acetone bath and \(n\)-BuLi (2.5 M, 7.15 mL, 17.9 mmol) was slowly added dropwise. The reactant mixture was warmed up to \(-15\ ^\circ\text{C}\) and stirred for 20 min, and then re-cooled back to \(-78\ ^\circ\text{C}\). The freshly distilled TMSCl (2.3 mL, 17.9 mmol) was slowly added and the reactant mixture was stirred for another 30 min at \(-78\ ^\circ\text{C}\). The reactant mixture was diluted with diethyl ether (100 mL), washed with aqueous 10\% HCl (10 mL), brine (30 mL), and the ether layer was subsequently dried with Na\(_2\)SO\(_4\). Concentration in vacuo followed by flash chromatography on silica gel (4:1 hexane/EtOAc for elution) afforded \((E)-3-[5-(\text{trimethylsilyl})\text{thiophen-2-yl}]\)-prop-2-en-1-ol (1.12 g, 5.28 mmol, 74\%) as a colorless oil. \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\ 7.07\ (d, J=3.0\ Hz, 1\ H, \text{Ar-H}), 6.99\ (d, J=3.0\ Hz, 1\ H, \text{Ar-H}), 6.74\ (d, J=16.0\ Hz, 1\ H, \text{Ar-CH=C}), 6.20\ (ddd,\ apparent\ dt, J=16.0, 6.0\ Hz, 1\ H, \text{Ar-C=CH}), 4.27\ (dd,\ apparent\ triplet, J=6.0\ Hz, 2\ H, \text{C=C-CH}_2), 1.38\ (dd,\ apparent\ triplet, J=5.5\ Hz, 1\ H, \text{OH}), 0.28\ (s, 9\ H, 3\text{SiCH}_3); \(^{13}\text{C}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\ 134.3, 128.5, 127.1, 124.2, 63.5, -0.16;\) IR (film) 3305, 2954, 1254, 1251, 984, 840 cm\(^{-1}\).
The title compound \((E)-2,2\text{-dimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enenitrile}\) (0.31 g, 1.18 mmol, 37 %) was obtained as a colorless oil from \((E)-3\text{-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-ol}\) (0.68 g, 3.20 mmol) by the general nitrile preparation procedure in which the highly unstable intermediate \((E)-3\text{-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-chloride}\) was prepared by treating \((E)-3\text{-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-ol}\) with 1 eq SOCl\(_2\) in THF at 0 ºC and the crude product was used directly without work up. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.08 (d, \(J=3.5\) Hz, 1H, Ar-H), 6.98 (d, \(J=3.5\) Hz, 1H, Ar-H), 6.64 (d, \(J=15.5\) Hz, 1H, Ar-CH=C), 6.09 (ddd, apparent dt, \(J=15.5, 8.0\) Hz, 1H, Ar-C=CH), 2.39 (d, \(J=7.5\) Hz, 2H, C=C-C\(_2\)H), 1.36 (s, 6H, 2CH\(_3\)), 0.30 (s, 9H, 3SiCH\(_3\)); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 146.8, 140.0, 134.3, 127.7, 126.9, 124.7, 123.5, 44.2, 32.6, 26.3, -0.14; IR (film) 2957, 2233, 1469, 1435, 1251, 1202, 1065, 988, 958, 848, 755, 700, 626, 523 cm\(^{-1}\).

The title compound \((E)-2,2\text{-dimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enylamine}\) (3d) (0.22 g, 0.80 mmol, 87 %) was obtained as a light yellow oil from \((E)-2,2\text{-dimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enenitrile}\) (0.24 g, 0.93 mmol) by the general LiAlH\(_4\) reduction procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.05 (d, \(J=3.0\) Hz, 1H, Ar-H), 6.90 (d, \(J=3.0\) Hz, 1H, Ar-H), 6.51 (d, \(J=15.5\) Hz, 1H, Ar-CH=C), 6.07
(ddd, apparent dt, \(J=15.5, 7.5\) Hz, 1H, Ar-\(\text{C}=\text{CH}\)), 2.47 (s, 2H, N-\(\text{CH}_2\)), 2.07 (d, \(J=7.5\) Hz, 2H, C=\(\text{C}-\text{CH}_2\)), 1.21 (s, 2H, NH\(_2\)), 0.88 (s, 6H, 2CH\(_3\)), 0.28 (3, 9H, 3SiCH\(_3\)); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 134.3, 127.8, 125.8, 125.2, 52.7, 43.0, 35.7, 24.7, -0.13; IR (film) 2954, 1472, 1435, 1247, 1199, 1065, 984, 955, 840, 795, 755 cm\(^{-1}\); HRMS (ESI): Calcd for C\(_{14}\)H\(_{25}\)NSSi [M+H]\(^+\): 268.155, found: 268.161.

\((E)-3-[5-(\text{trimethylsilyl})\text{furan-2-yl}]-\text{prop-2-en-1-ol}\)

The title compound \((E)-3-[5-(\text{trimethylsilyl})\text{furan-2-yl}]-\text{prop-2-en-1-ol}\) (2.70 g, 13.8 mmol, 74%) was obtained as a colorless oil from \((E)-3\text{-furan-2-yl-prop-2-en-1-ol}\) (2.32 g, 18.7 mmol) by the general silylation procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.56 (d, \(J=3.0\) Hz, 1H, Ar-\(\text{H}\)), 6.46 (d, \(J=16.0\) Hz, 1H, Ar-\(\text{CH}=\text{C}\)), 6.33 (ddd, apparent dt, \(J=15.5, 5.5\) Hz, 1H, Ar-\(\text{C}=\text{CH}\)), 6.21 (d, \(J=3.0\) Hz, 1H, Ar-\(\text{H}\)), 4.29 (m, 1H, CH\(_2\)), 1.60 (s, 1H, OH), 0.25 (s, 9H, 3SiCH\(_3\)); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 156.1, 127.4, 121.1, 119.5, 108.2, 63.4, -1.57; IR (film) 3324, 2957, 1251, 1092, 1013, 962, 929, 844, 759, 630 cm\(^{-1}\).

\((E)-2,2\text{-Dimethyl-5-[5-(\text{trimethylsilyl})\text{furan-2-yl}]-pent-4-enenitrile}\)

The title compound \((E)-2,2\text{-dimethyl-5-[5-(\text{trimethylsilyl})\text{furan-2-yl}]-pent-4-enenitrile}\) was obtained (0.15 g, 0.61 mmol, 33%) as a colorless oil from \((E)-3-[5-(\text{trimethylsilyl})\text{furan-2-yl}]-\text{prop-2-en-1-ol}\) (0.36 g, 1.84 mmol) by the general nitrile preparation procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.56 (d, \(J=3.5\) Hz, 1H, Ar-\(\text{H}\)), ...
6.35 (d, J=16.0 Hz, 1H, Ar-CH=C), 6.21 (d, J=3.5 Hz, 1H, Ar-H), 6.19 (ddd, apparent dt, J=15.5, 7.5 Hz, 1H, Ar-CH=C), 2.39 (d, J=7.5 Hz, 2H, CH=CH₂), 1.36 (s, 6H, 2CH₃), 0.26 (s, 9H, 3SiCH₃); ¹³C NMR (500 MHz, CDCl₃): δ 160.2, 156.0, 124.8, 123.4, 122.3, 121.2, 108.0, 44.3, 32.6, 26.3, −1.50; IR (film) 2957, 2233, 1469, 1254, 1180, 1114, 1013, 962, 929, 844, 785, 759, 700, 634 cm⁻¹.

(E)-2,2-Dimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3e)

The title compound (E)-2,2-dimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3e) (0.16 g, 95%) was obtained as colorless oil from (E)-2,2-dimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enenitrile (0.17 g, 0.68 mmol) by the general LiAlH₄ reduction procedure. ¹H NMR (500 MHz, CDCl₃): δ 6.54 (d, J=2.5 Hz, 1H, Ar-H), 6.19 (d, J=15.0 Hz, 1H, Ar-CH=C), 6.17 (m, 2H, Ar-C=CH and Ar-H), 2.47 (s, 2H, CH₂-NH₂), 2.07 (d, J=7.0 Hz, 1H, C=CH₂), 1.05 (s, 2H, NH₂), 0.88 (s, 6H, 2CH₃), 0.24 (s, 9H, 3SiCH₃); ¹³C NMR (500 MHz, CDCl₃): δ 159.3, 157.0, 126.6, 121.1, 106.4, 52.7, 43.1, 35.7, 29.7, 24.7, −1.50; IR (film) 2961, 1475, 1251, 910, 840, 737 cm⁻¹; HRMS (ESI): Calcd for C₁₄H₂₆NOSi [M+H]⁺: 252.17782, found: 252.17721.

(E)-2-Methyl-3-thiophen-2-yl-acrylic acid ethyl ester

The title compound (E)-2-methyl-3-thiophen-2-yl-acrylic acid ethyl ester (4.1 g, 20.0 mmol, 98%) was obtained as a colorless oil from 2-thiophencarboxaldehyde (1.96 mL,
20.6 mmol) by the general Hornor-Wadsworth-Emmons procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.83 (s, 1H, Ar-CH=CH)=C), 7.46 (d, $J$=5.0 Hz, 1H, Ar-H), 7.25 (d, $J$=3.5 Hz, 1H, Ar-H), 7.09 (t, $J$=3.5 Hz, 1H, Ar-H), 4.24 (ddd, apparent quartet, $J$=7.0 Hz, 2H, OCH$_2$), 2.19 (s, 3H, C=C-CH$_3$), 1.32 (dd, apparent triplet, $J$=7.5 Hz, 3H, CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 168.5, 139.3, 131.6, 131.4, 129.1, 127.3, 124.9, 60.9, 14.4, 14.3; IR (film) 2979, 1701, 1624, 1364, 1269, 1106, 700 cm$^{-1}$.

$(E)$-2-Methyl-3-thiophen-2-yl-prop-2-en-1-ol

![Chemical structure](image)

The title compound $(E)$-2-methyl-3-thiophen-2-yl-prop-2-en-1-ol (3.0 g, 19.7 mmol, 94%) was obtained as a colorless oil from $(E)$-2-methyl-3-thiophen-2-yl-acrylic acid ethyl ester (4.1 g, 20.0 mmol) by the general LiAlH$_4$ reduction procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.24 (s, 1H, Ar-CH=CH)=C), 7.01 (t, $J$=3.5 Hz, 1H, Ar-H), 7.00 (d, $J$=4.5 Hz, 1H, Ar-H), 6.66 (m, 1H, Ar-H), 4.18 (d, 2H, $J$=5.5 Hz, C=C-CH$_2$), 1.99 (s, 3H, C=C-CH$_3$), 1.48 (dd, apparent triplet, $J$=6.0 Hz, 3H, OH); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 127.0, 126.8, 124.9, 118.4, 68.9, 16.0; IR (film) 3213, 2913, 1439, 1243, 1033, 874, 855, 703 cm$^{-1}$. 
(\(E\))-2-Methyl-3-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-ol

\[
\begin{align*}
\text{S} & \quad \text{CH}_3 \quad \text{S} \quad \text{C} \quad \text{H}_2 \quad \text{C} \\
\text{TMS} & \quad \text{OH} 
\end{align*}
\]

The title compound \((E\))-2-methyl-3-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-ol (3.62 g, 16.0 mmol, 54%) was obtained as a colorless oil from \((E\))-2-methyl-3-thiophen-2-yl-prop-2-en-1-ol (4.57 g, 30.0 mmol) by the general silylation procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.13 (d, \(J=3.0\) Hz, 1H, Ar-\(H\)), 7.03 (d, \(J=3.0\) Hz, 1H, Ar-\(H\)), 6.68 (s, 1H, Ar-C\(\text{H} \equiv \text{C}\)), 4.11 (s, 2H, C\(\text{H}_2\)), 2.02 (s, 3H, C=\(\text{C}-\text{CH}_3\)), 1.70 (s, 1H, \(\text{O}H\)), 0.30 (s, 9H, 3Si\(\text{C}_3\)H\(_3\)); \(^13\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 145.9, 140.0, 136.2, 133.8, 128.4, 118.3, 68.9, 16.1, -0.07; IR (film) 3294, 2957, 1431, 1247, 988, 840, 747, 626 cm\(^{-1}\).

\((E\))-2,2,4-Trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enenitrile

\[
\begin{align*}
\text{S} & \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{C} \quad \text{CN} \\
\text{TMS} & 
\end{align*}
\]

The title compound \((E\))-2,2,4-trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enenitrile (1.0 g, 3.61 mmol, 37%) was obtained as a light yellow solid from \((E\))-2-methyl-3-[5-(trimethylsilyl)thiophen-2-yl]-prop-2-en-1-ol (2.2 g, 9.73 mmol) by the general nitrile preparation procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.13 (d, \(J=3.0\) Hz, 1H, Ar-\(H\)), 7.03 (d, \(J=3.0\) Hz, 1H, Ar-\(H\)), 6.52 (s, 1H, Ar-\(\text{CH} \equiv \text{C}\)), 2.41 (s, 2H, C=\(\text{C}-\text{CH}_2\)), 2.16 (s, 3H, C=\(\text{C}-\text{CH}_3\)), 1.36 (s, 6H, 2CH\(_3\)), 0.30 (s, 9H, 3SiCH\(_3\)); \(^13\)C NMR (500 MHz, CDCl\(_3\)): \(\delta\) 133.8, 132.1, 128.5, 125.3, 123.7, 51.8, 32.1, 27.0, 20.4, -0.10; IR (film) 2957, 1446, 1251, 1209, 1073, 1069, 988, 840, 755, 696, 630, 533 cm\(^{-1}\).
(E)-2,2,4-Trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enylamine (3f)

The title compound (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enylamine (3f) (0.37 g, 1.32 mmol, 91%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enenitrile (0.4 g, 1.44 mmol) by the general LiAlH₄ reduction procedure. \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 7.13 (d, \(J=3.0\) Hz, 1H, Ar-H), 6.98 (d, \(J=3.0\) Hz, 1H, Ar-H), 6.41 (s, 1H, Ar-CH=CH), 2.48 (s, 2H, NCH₂), 2.11 (s, 2H, C=CH₂), 2.04 (s, 3H, C=CH₃), 1.08 (s, 2H, NH₂), 0.88 (s, 6H, 2CH₃), 0.29 (s, 9H, 3SiCH₃); \(^1\)C NMR (500 MHz, CDCl₃): \(\delta\) 146.9, 139.0, 135.8, 133.8, 127.5, 121.9, 53.3, 50.7, 36.6, 25.1, 21.9, -0.06; IR (film) 2954, 1431, 1251, 1073, 988, 836, 795, 751 cm\(^{-1}\); HRMS (ESI): Calcd for C₁₅H₂₇NSSi [M+H]\(^+\): 282.171, found: 282.164.

(E)-3-Furan-2-yl-2-methyl-acrylic acid ethyl ester

The title compound (E)-3-furan-2-yl-2-methyl-acrylic acid ethyl ester (3.66 g, 20.3 mmol, 98%) was obtained as a colorless oil from 2-furaldehyde (1.8 mL, 20.6 mmol) by the general Hornor-Wadsworth-Emmons procedure. \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 7.50 (m, 1H, Ar-H), 7.42 (s, 1H, Ar-CH=CH), 6.58 (d, \(J=3.0\) Hz, 1H, Ar-H), 6.46 (m, 1H, Ar-H), 4.22 (ddd, apparent quartet, \(J=7.0\) Hz, 2H, CH₂), 2.19 (s, 3H, C=CH₃), 1.31 (dd, apparent triplet, \(J=7.0\) Hz, 3H, CH₂CH₃); \(^1\)C NMR (500 MHz, CDCl₃): \(\delta\) 168.5, 152.0, 143.9, 125.6, 125.1, 114.6, 112.0, 60.8, 14.3, 14.1; IR (film) 2979, 1705, 1634, 1475, 1372, 1269, 1209, 1176, 1114, 1021, 740 cm\(^{-1}\).
(E)-3-Furan-2-yl-2-methyl-prop-2-en-1-ol

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{F} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

The title compound (E)-3-furan-2-yl-2-methyl-prop-2-en-1-ol (2.70 g, 19.6 mmol, 98\%) was obtained as a colorless oil from (E)-3-furan-2-yl-2-methyl-acrylic acid ethyl ester (3.60 g, 20.0 mmol) by the general LiAlH\textsubscript{4} reduction procedure. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \delta 7.36 (s, 1H, Ar-CH=), 6.38 (m, 1H, Ar-H), 6.31 (m, 1H, Ar-H), 6.24 (d, \textit{J}=3.0 Hz, 1H, Ar-H), 4.15 (s, 2H, CH\textsubscript{2}), 2.04 (s, 1H, OH), 1.97 (s, 3H, C=C-CH\textsubscript{3}); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \delta 153.1, 141.2, 136.3, 113.6, 111.1, 108.7, 68.5, 15.8; IR (film) 3324, 2917, 2858, 1495, 1446, 1380, 1069, 1021, 737, 592 cm\textsuperscript{-1}.

(E)-2-Methyl-3-[5-(trimethylsilyl)furan-2-yl]-prop-2-en-1-ol

\[
\begin{align*}
\text{TMS} & \quad \text{O} \\
\text{F} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

The title compound (E)-2-methyl-3-[5-(trimethylsilyl)furan-2-yl]-prop-2-en-1-ol (2.52 g, 12.0 mmol, 61\%) was obtained as a colorless oil from (E)-3-furan-2-yl-2-methyl-prop-2-en-1-ol (2.70 g, 19.6 mmol) by the general silylation procedure. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \delta 6.60 (d, \textit{J}=3.0 Hz, 1H, Ar-H), 6.37 (s, 1H, Ar-CH=), 6.24 (d, \textit{J}=3.0 Hz, 1H, Ar-H), 4.15 (d, \textit{J}=3.0 Hz, 2H, CH\textsubscript{2}), 2.02 (s, 3H, C=C-CH\textsubscript{3}), 1.47 (t, \textit{J}=6.0 Hz, 1H, OH), 0.29 (s, 9H, 3CH\textsubscript{3}); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \delta 120.9, 114.0, 108.9, 68.7, 15.9, -1.66; IR (film) 3320, 2957, 1254, 1013, 932, 840, 781, 751, 630 cm\textsuperscript{-1}. 
(E)-2,2,4-Trimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enenitrile

The title compound (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enenitrile (0.99 g, 3.81 mmol, 32%) was obtained as a colorless oil from (E)-2-methyl-3-[5-(trimethylsilyl)furan-2-yl]-prop-2-en-1-ol (2.5 g, 11.9 mmol) by the general nitrile preparation procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.60 (d, $J$=2.5 Hz, 1H, Ar-H), 6.24 (d, $J$=3.0 Hz, 1H, Ar-H), 6.20 (s, 1H, Ar-CH=C), 2.38 (s, 2H, CH$_2$), 2.16 (s, 3H, C=C-CH$_3$), 1.37 (s, 6H, 2CH$_3$), 0.25 (s, 9H, 3CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 125.3, 121.0, 119.6, 109.2, 51.7, 32.0, 27.0, 20.3, -1.65; IR (film) 2961, 1469, 1251, 1199, 1128, 1021, 983, 840, 789, 755, 634 cm$^{-1}$.

(E)-2,2,4-Trimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3g)

The title compound (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3g) (0.39 g, 1.45 mmol, 95%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5,[5-(trimethylsilyl)furan-2-yl]-pent-4-enenitrile (0.4 g, 1.53 mmol) by the general LiAlH$_4$ reduction procedure. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.60 (d, $J$=3.0 Hz, 1H, Ar-H), 6.17 (d, $J$=3.0 Hz, 1H, Ar-H), 6.10 (s, 1H, Ar-CH=C), 2.47 (s, 2H, N-CH$_2$), 2.08 (s, 2H, C=C-CH$_2$), 2.01 (s, 3H, C=C-CH$_3$), 1.08 (s, 2H, NH$_2$), 0.88 (s, 6H, 2CH$_3$), 0.23 (s, 9H, 3SiCH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 158.2, 157.5, 136.1, 121.0, 117.9, 107.9, 53.3, 50.5, 36.6, 25.1, 21.9, -1.62; IR (film) 2954, 1475, 1247, 1021, 936, 840, 781, 755, 630 cm$^{-1}$; HRMS (ESI): Calcd for C$_{15}$H$_{27}$NOSi [M+H]$^+$: 266.193, found: 266.200.
(E)-6-Phenyl-hex-5-en-2-one

\[
\begin{array}{c}
\text{NNMe}_2 \\
1) n-\text{BuLi} \\
2) \text{cinnamyl chloride} \\
3) \text{aq HCl/CH}_2\text{Cl}_2 \\
\text{67%}
\end{array}
\]

A 100-mL, round-bottomed flask equipped with a magnetic stirring bar and a N\textsubscript{2} inlet was charged with acetone dimethylhydrazone (3.0 g, 30.0 mmol) and anhydrous THF (50 mL) was subsequently added. The resulting solution was cooled to −78 °C with a Dry Ice-acetone bath and n-BuLi (5.2 M, 5.77 mL, 30 mmol) was slowly added dropwise. The reactant mixture was warmed to 0 °C and stirred for 2 h, and then cooled back to −78 °C. Cinnamyl chloride (2.76 mL, 20.0 mmol) in THF (6 mL) was slowly added and the reactant mixture was warmed to 0 °C and stirred for 6 h. The reactant mixture was diluted with diethyl ether (60 mL), washed with saturated NaHCO\textsubscript{3} (10 mL), brine (10 mL) and concentrated in vacuo. CH\textsubscript{2}Cl\textsubscript{2} (30 mL) and diluted aqueous HCl (6.0 M, 30 mL, 180 mmol) were added in succession and the reactant mixture was stirred for 10 h at room temperature. The organic phase was separated, washed with saturated NaHCO\textsubscript{3} (10 mL), brine (10 mL) and subsequently dried with Na\textsubscript{2}SO\textsubscript{4}. Concentration in vacuo followed by flash chromatography on silica gel (15:1 hexane/EtOAc for elution) afforded (E)-6-phenyl-hex-5-en-2-one (2.36 g, 13.6 mmol, 68%) as a colorless oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.33-7.17 (m, 5H, 5Ar-H), 6.39 (d, J=15.5 Hz, 1H, Ph-CH=C), 6.19 (ddd, apparent dt, J=15.5, 6.5 Hz, 1H, Ph-C=CH), 2.60 (m, 2H, CH\textsubscript{2}), 2.47 (m, 2H, CH\textsubscript{2}), 2.15 (s, 3H, CH\textsubscript{3}); \textsuperscript{13}C NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 208.1, 137.4, 130.7, 128.8, 128.5, 127.1, 126.0, 43.2, 30.1, 27.1; IR (film): 3028, 2917, 1712, 1362, 1158, 966, 744, 692 cm\textsuperscript{−1}. 
(E)-1-Methyl-5-phenylpent-4-enylamine (3h)

\[
\text{Ph} \equiv \text{C(\equiv \text{C})(\text{CH}_2)} \quad \text{NH}_2
\]

75%

NH$_4$OAc

NaBH$_3$CN

A 15-mL, round-bottomed flask equipped with a magnetic stirring bar and a N$_2$ inlet was charged with (E)-6-phenyl-hex-5-en-2-one (0.2 g, 1.15 mmol) and anhydrous methanol (5 mL) was subsequently added. NH$_4$OAc (1.33 g, 17.2 mmol) and NaBH$_3$CN (0.11 g, 1.72 mmol) were added in succession. The reactant mixture was stirred at room temperature for 24 h until judged complete by TLC. Aqueous 10% NaOH was slowly added until pH was raised to 10. The reactant mixture was extracted with diethyl ether (10 mL), and the organic phase was dried with Na$_2$SO$_4$. Concentration in vacuo followed by bulb-to-bulb distillation from CaH$_2$ afforded (E)-1-methyl-5-phenylpent-4-enylamine (3h) (0.15 g, 0.86 mmol, 75%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.33-7.16 (m, 5H, 5Ar-H), 6.39 (d, J=16.0 Hz, 1H, Ph-CH=C), 6.21 (ddd, apparent dt, J=15.5, 7.0 Hz, 1H, Ph-C=CH), 2.93 (m, 1H, CH-NH$_2$), 2.24 (m, 2H, CH$_2$), 1.47 (m, 2H, CH$_2$), 1.26 (s, 2H, NH$_2$), 1.08 (d, J=6.5 Hz, 3H, CH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): δ 130.5, 129.9, 128.5, 126.9, 125.9, 46.5, 39.6, 30.0, 24.0; IR (film): 2932, 2356, 1576, 1446, 1372, 966, 741, 692 cm$^{-1}$; HRMS (ESI): Calcd for C$_{12}$H$_{17}$N [M+H]$^+$: 176.1434, found: 176.1476.
2.2 Hydroamination results:

**General hydroamination procedure:** in an argon-filled glove box, Y[N(TMS)2]3 (5.70 mg, 0.01 mmol) and benzene-D6 (0.5 mL) were added into a J. Young NMR tube equipped with teflon screw cap. Then (E)-2,2-dimethyl-5-phenylpent-4-enylamine (3aE) (19 mg, 0.1 mmol) and p-xylene (10 µL) were added and the reactant mixture was subsequently held at 60 ºC in an oil bath for 2 h until ring closure was judged complete (≥90% by 1H NMR integration).

**General p-toluenesulfonamide preparation procedure:** 2-Benzyl-4,4-dimethyl-1-(4-methylbenzenesulfonyl)pyrrolidine (4aTs)

The tetrahydropyrrole was prepared from (E)-2,2-dimethyl-5-phenylpent-4-enylamine (3aE) (19 mg, 0.10 mmol) by the general hydroamination procedure. The teflon screw cap was then removed and crude product was diluted with anhydrous CH2Cl2 (3 mL). TsCl (22 mg, 0.12 mmol) and pyridine (9.70 µL, 0.12 mmol) were added in succession. The reactant mixture was stirred at room temperature for 12 h. The reactant mixture was diluted with diethyl ether (10 mL), washed with saturated NaHCO3 (3 mL) and brine (3 mL). The organic phase was subsequently dried with Na2SO4. Concentration in vacuo followed by flash chromatography on silica gel (15:1 hexane/EtOAc for elution) afforded 2-benzyl-4,4-dimethyl-1-(4-methylbenzenesulfonyl)pyrrolidine (4aTs) (32 mg, 0.09 mmol, 83%) as a colorless oil. 1H NMR (300 MHz, CDCl3): δ 7.77 (d, J=8.1 Hz, 2H, 2Ar-H), 7.25 (m, 7H, 7Ar-H), 3.77 (m, 1H, CH-N), 3.56 (dd, J=13.2, 3.3 Hz, 1H, Ph-CH), 3.10 (s, 2H, CH2NTs), 2.75 (dd, J=13.2, 9.9 Hz, 1H, Ph-CH), 2.41 (s, 3H, ArCH3), 1.45 (m, 2H, CH2-CH), 0.96 (s, 3H, CH3), 0.43 (s, 3H, CH3); 13C NMR (300 MHz,
The title compound 2-[2'-(2H)(phenyl)methyl]-4,4-dimethyl-1-(4-methylbenzenesulfonyl)-2\(\alpha\)H,2'\(\alpha\)H-pyrrolidine \([(R,R)-4a(D)_{Ts}]\)

\[
\begin{array}{c}
\text{\(\text{N}^\text{Ts}\)} \\
\text{Ph}
\end{array}
\]

was obtained as a white solid from \((E)-2,2\text{-dimethyl-5-phenylpent-4-enylamine-\(N,N\)-D}2\ (3a_e)\) \((41.0\ \text{mg}, 0.22\ \text{mmol})\) by the general hydroamination and \(p\)-toluenesulfonamide procedures. \(\text{\(^1\)H NMR (300 MHz, CDCl}_3): \delta 7.77 (d, J=8.0\ \text{Hz}, 2\text{H}, 2\text{Ar-H}), 7.26 (m, 7\text{H}, 7\text{Ar-H}), 3.75 (\text{ddd}, \text{apparent quartet}, J=8.0\ \text{Hz}, 1\text{H}, \text{CH-NTs}), 3.11 (s, 2\text{H}, \text{NCH}_2), 2.73 (d, J=9.5\ \text{Hz}, 1\text{H}, \text{Ph-CH}), 2.41 (s, 3\text{H}, \text{ArCH}_3), 1.45 (m, 2\text{H}, \text{CH-CH}_2), 0.97 (s, 3\text{H}, \text{CH}_3), 0.42 (s, 3\text{H}, \text{CH}_3); \text{\(^{13}\)C NMR (300 MHz, CDCl}_3): \delta 143.3, 138.5, 135.1, 129.6, 129.5, 128.4, 127.5, 126.3, 61.6, 61.5, 45.7, 42.9, 42.6 (triplet, \Delta J= 0.16), 37.2, 26.5, 25.8, 21.6; \text{\(^{2}\)D NMR (300 MHz, CDCl}_3\): \delta 3.47; IR (film) 2961, 1342, 1158, 1095, 700, 658, 589, 545 cm\(^{-1}\); HRMS (ESI): Calcd for C\(_{20}\)H\(_{24}\)NDO\(_2\)S [M+H]\(^+\): 345.1742, found: 345.1757.

2-[2'-(2H)(phenyl)methyl]-4,4-dimethyl-1-(4-methylbenzenesulfonyl)-2\(\alpha\)H,2'\(\beta\)H-pyrrolidine \([(R,S)-4a(D)_{Ts}]\)

\[
\begin{array}{c}
\text{\(\text{N}^\text{Ts}\)} \\
\text{Ph}
\end{array}
\]
The title compound 2-[2′-(2H)(phenyl)methyl]-4,4-dimethyl-1-(4-methylbenzenesulfonfonyl)-2αH,2′βH-pyrrolidine [(R,S)-4a(D)Ts] (70 mg, 0.20 mmol, 85%) was obtained as a white solid from (Z)-2,2-dimethyl-5-phenylpent-4-enylamine-N,N-D2 (3a2) (45 mg, 0.24 mmol) by the general hydroamination and p-toluenesulfonamide procedures. 1H NMR (500 MHz, CDCl3): δ 7.78 (d, J=8.0 Hz, 2H, 2Ar-H), 7.26 (m, 7H, 7Ar-H), 3.75 (m, 1H, N-CH), 3.55 (d, J=2.5 Hz, 1H, Ph-CH), 3.11 (s, 2H, NCH2), 2.41 (s, 3H, ArCH3), 1.45 (m, 2H, CH-C₂H₆), 0.96 (s, 3H, CH₃), 0.42 (s, 3H, CH₃); 13C NMR (500 MHz, CDCl3): δ 143.4, 138.4, 135.1, 129.6, 129.5, 128.4, 127.5, 126.3, 61.6, 61.5, 45.7, 45.6, 42.8, 42.5 (triplet, ΔJ= 0.16), 37.2, 26.4, 25.8, 21.6; 2D NMR (300 MHz, CDCl3) δ 2.65; IR (film) 2961, 1346, 1158, 1092, 1039, 814, 737, 703, 589, 548 cm⁻¹; HRMS (ESI): Calcd for C₂₀H₂₄NDO₂S [M+H]+: 345.1742, found: 345.1745.

2-Hexyl-2,4,4-trimethyl-1-(toluene-4-sulfonyl)-pyrrolidine (4bTs)

The title compound 2-hexyl-2,4,4-trimethyl-1-(toluene-4-sulfonyl)-pyrrolidine (4bTs) (47 mg, 1.26 mmol, 67%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-dec-4-enylamine (4b) (40 mg, 0.2 mmol) by the general hydroamination and p-toluenesulfonamide preparation procedures. 1H NMR (500 MHz, CDCl3): δ 7.71 (d, J=6.5 Hz, 2H, 2Ar-H), 7.24 (d, J=6.5 Hz, 2H, 2Ar-H), 3.05 (m, 1H, N-CH), 3.01 (m, 1H, N-CH), 2.39 (s, 3H, ArCH₃), 1.92 (m, 1H, CH), 1.83 (m, 1H, CH), 1.69 (m, 1H, CH), 1.45 (s, 3H, CH₃), 1.23 (m, 9H, CH and 4CH₂), 0.99 (s, 3H, CH₃), 0.95 (s, 3H, CH₃), 0.86 (m, 3H, CH₃); 13C NMR (500 MHz, CDCl3): δ 142.5, 129.2, 127.2, 69.2, 61.5, 53.1,

2-Benzyl-2,4,4-trimethyl-1-(4-methylbenzenesulfonyl)pyrrolidine (4cTs)

The title compound 2-benzyl-2,4,4-trimethyl-1-(4-methylbenzenesulfonyl)pyrrolidine (4cTs) (30.0 mg, 0.08 mmol, 76%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5-phenylpent-4-enylamine (4c) (23 mg, 0.11 mmol) by the general hydroamination and p-toluenesulfonamide procedures in which 1.2 eq 1-methylimidazole was used instead of pyridine because of the hindered substrate. ¹H NMR (500 MHz, CDCl₃): δ 7.76 (d, J=8.5 Hz, 2H, 2Ar-H), 7.32-7.18 (m, 7H, 7Ar-H), 3.27 (d, J=13.0 Hz, 1H, CH), 3.11 (d, J=13.0 Hz, 1H, CH), 3.03 (d, J=9.5 Hz, 1H, CH), 2.88 (d, J=9.5 Hz, 1H, CH), 2.40 (s, 3H, ArCH₃), 2.06 (d, J=13.5 Hz, 1H, CH), 1.49 (s, 3H, CH₃), 1.27 (d, J=13.0 Hz, 1H, CH), 0.90 (s, 3H, CH₃), 0.85 (s, 3H, CH₃); ¹³C NMR (500 MHz, CDCl₃): δ 142.7, 138.0, 131.1, 129.3, 128.0, 127.3, 126.4, 69.1, 61.7, 51.6, 47.8, 36.1, 27.6, 27.5, 27.2, 21.5; IR (film) 2957, 2869, 1602, 1495, 1450, 1339, 1154, 1058, 966, 814, 755, 711, 656, 592, 548 cm⁻¹; HRMS (ESI): Calcd for C₂₁H₂₇NO₂S [M+H]⁺: 358.1835, found: 358.1840.

4,4-Dimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)thiophen-2-ylmethyl]-pyrrolidine (4dTs)
The title compound 4,4-dimethyl-1-(toluene-4-sulfonyl)-2-[5-trimethylsilyl-thiophen-2-ylmethyl]-pyrrolidine (4dTs) (36 mg, 0.1 mmol, 87%) was obtained as a colorless oil from (E)-2,2-dimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enylamine (3d) (27 mg, 0.1 mmol) by the general hydroamination and p-toluenesulfonamide preparation procedures. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J=8.0$ Hz, 2H, 2Ar-H), 7.31 (d, $J=7.5$ Hz, 2H, 2Ar-H), 7.05 (d, $J=3.0$ Hz, 1H, Ar-H), 6.88 (d, $J=3.0$ Hz, 1H, Ar-H), 3.80-3.66 (m, 2H, CH$_2$), 3.09 (m, 3H, CH$_2$-CH), 2.41 (s, 3H, ArCH$_3$), 1.65-1.50 (m, 2H, CH$_2$), 0.98 (s, 3H, CH$_3$), 0.45 (s, 3H, CH$_3$), 0.27 (s, 9H, 3SiCH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 145.8, 143.4, 139.1, 135.0, 133.9, 129.6, 127.6, 127.5, 61.7, 61.1, 45.9, 37.3, 36.9, 26.4, 25.8, 21.6, −0.01; IR (film) 2957, 1346, 1247, 1158, 1092, 1047, 981, 840, 814, 759, 662, 592, 548 cm$^{-1}$; HRMS (ESI): Calcd for C$_{21}$H$_{31}$NO$_2$S$_2$Si [M+H]$^+$: 422.164, found: 422.165.

4,4-Dimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)furan-2-ylmethyl]pyrrolidine (4eTs)

The title compound 4,4-dimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)furan-2-ylmethyl]pyrrolidine (4eTs) (37 mg, 0.09 mmol, 92 %) was obtained as a colorless oil from (E)-2,2-dimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3e) (25 mg, 0.1 mmol) by the general hydroamination and p-toluenesulfonamide procedures. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J=8.0$ Hz, 2H, 2Ar-H), 7.29 (d, $J=8.0$ Hz, 2H, 2Ar-H), 6.49 (d, $J=3.0$ Hz, 1H, Ar-H), 6.04 (d, $J=3.0$ Hz, 1H, Ar-H), 3.78 (m, 1H, N-CH), 3.50 (dd, $J=14.5$, 3.0 Hz, 1H, Ar-CH), 3.07 (AB, $J=14.5$ Hz, 2H, N-CH$_2$), 2.92 (dd, $J=14.5$, 

![Diagram](image-url)
9.5 Hz, 1H, Ar-CH), 2.41 (s, 3H, ArCH3), 1.60 (d, J=8.0 Hz, 2H, CH2-CH-N), 0.98 (s, 3H, CH3), 0.47 (s, 3H, CH3), 0.22 (s, 9H, 3SiCH3); 13C NMR (500 MHz, CDCl3): δ 156.9, 143.3, 129.6, 127.5, 120.4, 107.1, 61.5, 59.3, 46.0, 37.3, 35.2, 26.4, 25.8, 21.6, -1.58; IR (film) 2961, 1350, 1247, 1158, 1095, 844, 662, 589, 548 cm⁻¹; HRMS (ESI): Calcd for C21H32NO3SSi [M+H]⁺: 406.18667, found: 405.18537; Calcd for C21H31NNaO3SSi [M+Na]⁺: 428.16817, found: 428.16861.

2,4,4-Trimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)thiophen-2-ylmethyl]-pyrrolidine (4fTs)

The title compound 2,4,4-trimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)thiophen-2-ylmethyl]-pyrrolidine (4fTs) (36.2 mg, 0.08 mmol, 76%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)thiophen-2-yl]-pent-4-enylamine (3f) (31 mg, 0.11 mmol) by the general hydroamination and p-toluenesulfonylamide preparation procedures. 1H NMR (500 MHz, CDCl3): δ 7.75 (d, J=8.0 Hz, 2H, 2Ar-H), 7.26 (d, J=8.0 Hz, 2H, 2Ar-H), 7.07 (d, J=3.0 Hz, 1H, Ar-H), 6.98 (d, J=3.0 Hz, 1H, Ar-H), 3.57 (d, J=14.0 Hz, 1H, CH), 3.29 (d, J=14.0 Hz, 1H, CH), 3.06 (d, J=9.5 Hz, 1H, CH), 2.98 (d, J=10.0 Hz, 1H, CH), 2.40 (s, 3H, ArCH3), 2.15 (d, J=13.0 Hz, 1H, CH), 1.51 (s, 3H, CH3), 1.42 (d, J=13.5 Hz, 1H, CH), 0.97 (s, 3H, CH3), 0.90 (s, 3H, CH3), 0.27 (s, 9H, 3SiCH3); 13C NMR (500 MHz, CDCl3): δ 145.2, 142.8, 138.4, 133.9, 129.4, 129.3, 127.3, 68.7, 61.8, 52.6, 42.3, 36.2, 27.6, 27.2, 27.1, 21.5, −0.02; IR (film) 2957, 1439, 1342, 1251, 1209, 1154, 1092, 1055, 984, 840, 814, 759, 714, 659, 592, 548 cm⁻¹; HRMS (ESI): Calcd for C22H33NO2S2Si [M+H]⁺: 436.1816, found: 436.1897.
2,4,4-Trimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)furan-2-ylmethyl]-pyrrolidine (4gTs)

The title compound 2,4,4-trimethyl-1-(toluene-4-sulfonyl)-2-[5-(trimethylsilyl)furan-2-ylmethyl]-pyrrolidine (4gTs) (38 mg, 0.09 mmol, 83%) was obtained as a colorless oil from (E)-2,2,4-trimethyl-5-[5-(trimethylsilyl)furan-2-yl]-pent-4-enylamine (3g) (29 mg, 0.11 mmol) by the general hydroamination and p-toluenesulfonamide preparation procedures. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$=8.5 Hz, 2H, 2Ar-$H$), 7.25 (d, $J$=8.5 Hz, 2H, 2Ar-$H$), 6.52 (d, $J$=3.0 Hz, 1H, Ar-$H$), 6.15 (d, $J$=3.0 Hz, 1H, Ar-$H$), 3.33 (d, $J$=14.0 Hz, 1H, CH), 3.16 (d, $J$=14.0 Hz, 1H, CH), 3.01 (d, $J$=9.0 Hz, 1H, CH), 2.93 (d, $J$=9.5 Hz, 1H, CH), 2.40 (s, 3H, ArCH$_3$), 2.16 (d, $J$=13.0 Hz, 1H, CH), 1.47 (s, 3H, CH$_3$), 1.40 (d, $J$=13.0 Hz, 1H, CH), 0.93 (s, 3H, CH$_3$), 0.89 (s, 3H, CH$_3$), 0.20 (s, 9H, 3SiCH$_3$); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 156.9, 142.7, 129.3, 127.3, 120.5, 108.7, 68.4, 61.5, 52.8, 40.7, 36.0, 27.6, 27.4, 27.1, 21.5, −1.58; IR (film) 2957, 1339, 1251, 1154, 1095, 1011, 840, 755, 711, 662, 585, 545 cm$^{-1}$; HRMS (ESI): Calcd for C$_{22}$H$_{33}$NO$_3$Si [M+H]$^+$: 420.202, found: 420.205.
2-Benzyl-5-methyl-2αH,5βH-pyrrolidine (4h)

In an argon-filled glove box, Y[N(TMS)₂]₃ (6.5 mg, 0.01 mmol) and benzene-D₆ (0.5 mL) were introduced into a J. Young NMR tube equipped with teflon screw cap. p-xylene (10 μL) and (E)-1-methyl-5-phenylpent-4-enylamine (3h) (20 mg, 0.11 mmol) were subsequently added. The reactant mixture was maintained at 60 ºC in an oil bath for 9 days until ring closure was complete (90%, dr 6:1) as indicated by ¹H NMR spectrum. Removal of the solvent followed by bulb to bulb distillation from CaH₂ afforded 2-benzyl-5-methyl-2αH,5βH-pyrrolidine (4h) (16.5 mg, 0.09 mmol, 83%) as a colorless oil.

¹H NMR (500 MHz, C₆D₆): δ 7.26-7.10 (m, 5H, 5Ar-H), 3.38 (m, 1H, CH), 3.23 (m, 1H, CH), 2.68 (m, 1H, CH), 2.57 (m, 1H, CH), 1.80 (m, 2H, CH₂), 1.67 (m, 1H, CH), 1.32 (m, 1H, CH), 1.05 (s, 1H, NH), 1.00 (d, J=6.0 Hz, 3H, CH₃); ¹³C NMR (500 MHz, CDCl₃): δ 129.3, 128.0, 127.8, 127.6, 125.9, 59.3, 52.9, 43.6, 34.3, 32.4, 22.2; IR (film) 2957, 1495, 1453, 1402, 744, 700 cm⁻¹; HRMS (ESI): Calcd for C₁₂H₁₇N [M+H]⁺: 176.1434, found: 176.1473.

Reference
