General Methods.

All reactions, unless otherwise specified, were performed under an inert atmosphere of nitrogen. All chemicals were purchased commercially, were purified prior to use, and were stored in an MBraun glove box. Distilled solvents were transferred under vacuum into vacuum-tight glass vessels and were stored in the glove box. Lithium aluminum hydride and lithium aluminum deuteride was purified before use.\textsuperscript{1} Ti(NMe\textsubscript{2})\textsubscript{4} was synthesized using the literature procedure.\textsuperscript{2} Allyl-1-\textit{d}\textsubscript{2}-alcohol\textsuperscript{3} and 3-buten-1-ol-1,1-\textit{d}\textsubscript{2}\textsuperscript{4} were prepared using the literature procedures. All the allyl alcohols were bought commercially, purified before use by distilling from magnesium, and stored in the glove box. 2-phenyl-3-buten-2-ol\textsuperscript{5} and 2-phenyl-2-propen-1-ol\textsuperscript{6} were synthesized according to the literature procedures. Thin layer chromatography was performed on 0.20 mm thick aluminum-backed silica gel plates. Components were visualized with ultraviolet light (\(\lambda = 254\) nm). \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{2}H NMR spectra were recorded in CDCl\textsubscript{3} and CHCl\textsubscript{3} respectively, at 25 ºC in 5 mm NMR tubes on a 500 MHz Varian Inova spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the trimethylsilane (TMS) internal standard at 0 ppm for deuterated chloroform. The experiments were heated in a constant oil bath maintained at 160 ºC, using Barnstead Electrothermal Set-Temp apparatus. The deuteration for allyl-1-\textit{d}\textsubscript{2}-alcohol and 3-buten-1-ol-1,1-\textit{d}\textsubscript{2} were more than 99.5% for the indicated positions.

Preparation of N-phenyl allylamine (Table 1 Entry 1)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe$_2$)$_4$ (0.50 g, 2.23 mmol), and allyl alcohol (152.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 24 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO$_3$ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na$_2$SO$_4$. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 51% isolated yield (1.14 mmol). $^1$H NMR ($500$ MHz, CDCl$_3$): $\delta = 7.30$ (app t, 2 H, i), 6.84 (tt, 1 H, j, $J = 7.4$, 1.04 Hz), 6.72 (dd, 2 H, h), 6.06 (m, 1 H, d), 5.40 (dq, 1 H, b, $J = 17.3$, 1.7 Hz), 5.28 (dq, 1 H, c, $J = 10.2$, 1.5 Hz), 3.85 (dt, 2 H, a, $J = 5.3$, 1.7 Hz). $^{13}$C($^1$H) NMR ($500$ MHz, CDCl$_3$): 148.2 (g), 135.6 (d), 129.3 (i), 117.6 (j), 116.3 (f), 113.1 (h), 46.6 (a). MS(EI) m/z = 133 (M$^+$).

Preparation of N-benzhydryl allylamine (Table 1 Entry 2)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and allyl alcohol (152.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and benzhydrylamine (1155 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 16 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:9 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 42% yield (0.90 mmol). The product is inseparable from small amount of benzhydrylamine, [MS(EI) m/z = 183 (M⁺)] and an unidentified compound [MS(EI) m/z = 347 (M⁺)] that is formed as the minor product. ¹H NMR⁸ (500 MHz, CDCl₃): δ = 7.0-7.7 (m, 10 H, h, i, and j), 5.95 (m, 1 H, d), 5.19 (dq, 1 H, b, J = 17.2 Hz), 5.11 (dq, 1 H, c, J = 10.47 Hz), 4.78 (s, 1 H, k), 3.22 (dt, 2 H, a, J = 5.90, 1.4 Hz), 1.65 (s, 1 H e). ¹³C{¹H} NMR⁸ (500 MHz, CDCl₃): 148.0-126 (g, h, i, and j), 124.2 (d), 114.7 (f), 67.8 (k), 47.1 (a). MS(EI) m/z = 233 (M⁺).

**Preparation of N-cyclohexyl allylamine** (Table 1 Entry 3)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe$_2$)$_4$ (0.50 g, 2.23 mmol), and allyl alcohol (152.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (766 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 24 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO$_3$ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na$_2$SO$_4$. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 0.5:9.5 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 30% isolated yield (0.67 mmol). $^1$H NMR$^9$ (500 MHz, CDCl$_3$): δ = 5.84 (m, 1 H, d), 5.10 (dq, 1 H, b, $J$ = 17.3, 1.5 Hz), 5.00 (dq, 1 H, c, $J$ = 10.2, 1.30 Hz), 3.21 (dt, 2 H, a, $J$ = 6.0, 1.3 Hz), 2.39 (m, 1 H, g), 1.0-1.9 (m, 11 H, h, i, and e). $^{13}$C{$^1$H}$^9$ NMR$^9$ (500 MHz, CDCl$_3$): 137.3 (d), 115.5 (f), 56.2 (a), 49.5 (g), 33.6 (h), 26.2 (j), 25.1 (i). MS(EI) $m/z$ = 139 (M$^+$).

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Preparation of N-(3-methylbut-2-enyl)aniline (Table 1 Entry 4)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-methyl-3-buten-2-ol (233.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 10 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 7:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 74% isolated yield (1.56 mmol).

1H NMR (500 MHz, CDCl₃): δ = 7.20 (m, 2 H, i), 6.72 (tt, 1 H, j, J = 7.2, 1.2 Hz), 6.62 (m, 2 H, h), 5.36 (tt, 1 H, d, J = 6.9, 1.4 Hz), 3.70 (d, 2 H, a, J = 6.9 Hz), 3.60 (br s, 1 H, e), 1.76 (s, 3 H, b), 1.72 (s, 3 H, e).

13C{1H} NMR (500 MHz, CDCl₃): 148.7 (g), 135.8 (f), 129.5 (i), 122.0 (d), 117.6 (j), 113.2 (h), 42.3 (d), 26.0 (b), 18.3 (e). MS(EI) m/z = 161 (M⁺).

Preparation of N-benzhydryl-3-methylbut-2-en-1-amine (Table 1 Entry 5)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-methyl-3-buten-2-ol (233.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and benzhydrylamine (1155 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 10 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 7:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 72% isolated yield (1.59 mmol). The product is inseparable from diphenylmethane [MS(EI) m/z =168 (M⁺)], benzhydrylamine, [MS(EI) m/z = 183 (M⁺)] and an unidentified compound [MS(EI) m/z = 347 (M⁺)]. ¹H NMR (500 MHz, CDCl₃): δ = 7.0-7.7 (m, 10 H, h, i, and j), 5.18 (t, 1 H, d), 4.68 (s, 1 H, k) 3.20 (d, 2 H, a, J= 7.2 Hz), 1.56 (s, 1 H, b or c), 1.36 (s, 1 H, b or c). ¹³C{¹H} NMR (500 MHz, CDCl₃): 144.0-126 (g, h, i, j, and f), 123.6 (d), 67.4 (k), 46.1 (a), 26.3 (b or c), 18.4 (b or c). MS(EI) m/z = 251 (M⁺).
Preparation of \(N\)-(3-methylbut-2-enyl)cyclohexanamine (Table 1 Entry 6)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe\(_2\))\(_4\) (0.50 g, 2.23 mmol), and 2-methyl-3-buten-2-ol (233.0 \(\mu\)L, 2.23 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (765 \(\mu\)L, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 24 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO\(_3\) was added to the reaction mixture. The solution was extracted with ether (4 \(\times\) 20 mL) and was dried over Na\(_2\)SO\(_4\). The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 100 g of Florisil\textsuperscript{®} and 9.5:0.5 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 69% isolated yield (1.15 mmol). \(^1\)H NMR\(^{11}\) (500 MHz, CDCl\(_3\)): \(\delta = 5.16\) (tt, 1 H, d, \(J = 6.9, 1.5\) Hz), 3.12 (d, 2 H, a, \(J = 6.8\) Hz), 2.34 (m, 1 H, g), 1.58 (s, 3 H, b), 1.52 (s, 3 H, c), 0.9-1.8 (m, 10 H, h, i and j), 0.8 (br s, 1 H, e). \(^{13}\)C\{\(^1\)H\} NMR\(^{11}\) (500 MHz, CDCl\(_3\)): 133.8 (f), 123.7 (d), 56.2 (a), 44.3 (g), 33.8 (h), 26.3 (j), 25.6 (i), 25.0 (b), 17.8 (c). MS(EI) \(m/z = 167\) (M\(^+\)).

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Preparation of (±)-N-(but-3-en-2-yl)aniline (Table 1 Entry 7)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)_4 (0.50 g, 2.23 mmol), and (±)-2-buten-1-ol (191.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 8 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:9 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 31% isolated yield (0.75 mmol). The product contains a small amount of trans-N-(but-2-enyl)aniline, which was confirmed by NMR spectroscopy and MS(EI). The trans-N-(but-2-enyl)aniline was inseparable from the product. This could be due to the competition that exists between the proposed [2+2]/retro-[2+2] mechanism and the pathway for the homoallylic alcohol case. Alternatively, a second transfer to imido from the amine may be occurring, which would also lead to this product. Further mechanistic investigations are underway to understand this result. ¹H NMR¹² (500 MHz, CDCl₃): δ = 7.18 (m, 2 H, i), 6.50 (m, 1 H, j), 6.42 (m, 2 H, h), 5.66 (m, 1 H, d), 5.04 (dt, 1 H, b, J = 17.3, 1.5 Hz), 4.90 (dt, 1 H, c, J = 10.3, 1.3 Hz), 3.80 (m, 1 H, a), 3.42 (br s, 1 H, e), 1.56 (d, 3 H, k, J = 6.1 Hz). ¹³C{¹H} NMR¹² (500 MHz, CDCl₃): 147.5 (g), 141.3 (d), 129.2 (i), 117.3 (f), 114.2.8 (j), 113.5 (h), 51.1 (a), 21.7 (k). MS(EI) m/z = 147 (M⁺).

Preparation of (E,Z)-N-(but-2-enyl)aniline (Table 1 Entry 8)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 3-buten-2-ol (193.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 10 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 2:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 80% isolated yield (1.78 mmol). The cis:trans ratio is 1:2 respectively. The product contains a small amount of (±)-N-(but-3-en-2-yl)aniline, which was confirmed by NMR spectroscopy and MS(EI). The N-(but-3-en-2-yl)aniline was inseparable from the product. This could be due to the competition that exists between the proposed [2+2]/retro-[2+2] mechanism and the pathway for the homoallylic alcohol case. Alternatively, a second transfer to imido from the amine may be occurring, which would also lead to this product. Further mechanistic investigations are underway to understand this result. ¹H NMR¹³ (500 MHz, CDCl₃): δ = 7.26 (m, 2 H, i), 6.82 (m, 1 H, j), 6.72 (m, 2 H, h), 5.2-5.8 (m, 1 H, d, b and l), 3.80 (br s, 1 H, e), 3.7-3.9 (d, 2 H, a and m, J = 5.8 Hz) 1.80 (d, 3 H, c, J = 6.1 Hz), 1.40 (d, 3 H, k, J = 6.7 Hz). ¹³C{¹H} NMR¹³ (500 MHz, CDCl₃): 148.2 (g), 129.3 (i), 128.3 (d), 127.7 (f), 127.3 (f₁), 117.6 (j), 113.2 (h), 46.2 (a), 41.1 (m), 17.9 (c), 13.5 (k). MS(EI) m/z = 147 (M⁺).

Preparation of (E,Z)-N-(but-2-enyl)cyclohexanamine (Table 1 Entry 10)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 3-buten-2-ol (193.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (766 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 10 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 9.5:0.5 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 30% isolated yield (0.65 mmol). The cis–trans ratio is 2:1 respectively. 

\(^{1}\)H NMR\(^{14}\) (500 MHz, CDCl₃): δ = 5.4-5.6 (m, 2 H, n, b, and l), 3.26 (d, 2 H, m, J = 5.8 Hz), 3.14 (d, 2 H, a, J = 4.9 Hz), 2.40 (m, 1 H, g), 1.0-1.8 (m, 13 H, h, i, j, k and c).

\(^{13}\)C\(^{1}\)H NMR\(^{14}\) (500 MHz, CDCl₃): 130.0 (p), 129.4 (d), 126.9 (f), 125.7 (f₁), 56.4 (a), 48.8 (m), 43.1 (g), 33.6 (h), 26.2 (j), 25.1 (i), 17.8 (e), 13.5 (k). MS(EI) m/z = 153 (M⁺).

Preparation of (E,Z)-N-(3-phenyl-2-butenyl)aniline (Table 1 Entry 11)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-phenyl-3-buten-2-ol (331.0 mg, 2.23 mmol). The reaction mixture was stirred for twenty minutes and then aniline (609 µL, 6.69 mmol) was added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 36 h. The solution was acidified with 5% HCl and then saturated solution of NaHCO₃ was added to the reaction mixture. The solution was then extracted with ether (4 × 20 mL) and was then dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 7:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 57% isolated yield (1.26 mmol). The cis–trans ratio is 2:1. ¹H NMR (500 MHz, CDCl₃): δ = 7.20-7.50 (m, 16 H, g, h, i, l, and e), 6.50-6.80 (m, 6 H, k and m), 5.96 (dt, 1 H, p, J = 6.7, 1.4 Hz), 5.68 (dt, 1 H, d, J = 6.9, 1.6 Hz), 3.96 (d, 2 H, o, J = 6.8, 0.9, Hz), 3.72 (d, 2 H, a, J = 6.8, 1.2, Hz), 2.18 (s, 1 H, r), 2.15 (s, 1 H, b). ¹³C{¹H} NMR (500 MHz, CDCl₃): 148.0 (j or n), 147.9 (j or n), 137.2-142.8 (c, f, q and s), 124.2-129.2 (g, h, i, l and m), 117.4 (p), 117.2 (d), 112.8 (k), 42.6 (o), 42.5 (a), 25.3 (r), 16.0 (b). MS(EI) m/z = 223 (M⁺).
Preparation of (E,Z)-N-benzhydryl-3-phenylbut-2-en-1-amine (Table 1 Entry 12)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-methyl-3-buten-2-ol (233.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and benzhydrylamine (1155 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 36 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 9:1 hexanes–ethyl acetate as the eluent, followed by 8:2 pentane–ether. The product eluted in the first fractions in 54% isolated yield (1.20 mmol). The cis–trans ratio is 1:5 respectively. ¹H NMR (500 MHz, CDCl₃): δ = 7.10-7.50 (m, 20 H, h, i, and j), 5.95 (t, 1 H, p), 5.70 (t, 1 H, d), 4.94 (s, 1 H, u) 4.78 (s, 1 H, t) 3.42 (d, 2 H, o, J = 7.0 Hz), 3.16 (d, 2 H, a, J = 7.0 Hz), 2.08 (s, 1 H, b) 1.92 (s, 1 H, r), 1.72 (br s, 1 H, e). ¹³C{¹H} NMR (500 MHz, CDCl₃): 144.0-126 (f, g, h, i, j, k, l, m, c, q, d, p and n), 123.6 (d), 67.2 (u and t), 47.0 (a), 46.4 (o), 25.8 (b), 16.3 (r). MS(EI) m/z = 313 (M⁺).
Preparation of N-(2-methylallyl)aniline (Table 1 Entry 13)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-phenyl-2-propen-1-ol (299.0 mg, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 15 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 31% isolated yield (0.68 mmol). ¹H NMR¹⁵ (500 MHz, CDCl₃): δ = 7.36 (m, 2 H, l), 7.22 (m, 3 H, m and n), 7.04 (t, 2 H, h), 6.60 (t, 1 H, i J = 7.5 Hz), 6.52 (d, 2 H, g, J = 8.5 Hz), 5.36 (s, 1 H, b), 5.22 (s, 1 H, e), 4.04 (s, 2 H, a), 3.88 (br s, 1 H, e).

¹³C{¹H} NMR¹⁵ (500 MHz, CDCl₃): 147.9 (j), 144.6 (k), 139.2 (d), 127.5-129.5 (h, m and n), 126.0 (l), 117.4 (i), 113.5 (g), 112.8 (f), 47.9 (a). MS(EI) m/z = 209 (M⁺).

Preparation of N-(2-methylallyl)cyclohexanamine (Table 1 Entry 14)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 2-phenyl-2-propen-1-ol (299.0 mg, 2.23 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (765 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 16 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:2 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 45% isolated yield (1.0 mmol). ¹H NMR (500 MHz, CDCl₃): δ = 7.1–7.4 (m, 5 H, l, m and n), 5.30 (s, 1 H, b), 5.12 (s, 1 H, c), 3.58 (s, 2 H, a), 2.36 (m, 1 H, j), 1.8–0.9 (m, 11 H, g, h, i, and e). ¹³C{¹H} NMR (500 MHz, CDCl₃): 146.7 (k), 139.9 (d), 128.2 (m), 127.4 (l), 126.0 (n), 112.7 (f), 55.9 (a), 50.4 (j), 33.5 (g), 26.0 (i), 24.8 (h). MS(EI) m/z = 215 (M⁺).
Preparation of (±)-N-(1-phenylallyl)aniline (Table 1 Entry 15)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and (±)-3-phenyl-2-propen-1-ol (300 mg, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 40 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO₃ was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 10:1 hexanes–ethyl acetate as the eluent. The product eluted in the first fractions in 20% isolated yield (0.45 mmol). The product contains a small amount of unidentified impurity [MS(EI) m/z = 208 (M⁺)] which, was inseparable even after column chromatography. 

$^1$H NMR$^{16}$ (500 MHz, CDCl₃): δ = 7.2-7.4 (m, 7 H, h, l, m and n), 6.78 (tt, 1 H, i, J = 7.4, 1.2 Hz), 6.68 (m, 2 H, g), 6.1 (m, 1 H, d), 5.2-5.4 (m, 2 H, b and c), 5.04 (d, 1 H, a, J = 6.5 Hz), 4.01 (br s, 1 H, e). $^{13}$C{$^1$H} NMR$^{16}$ (500 MHz, CDCl₃): 147.5 (j), 139.4 (k), 126-130 (l, m, n, h and d), 118.0 (i), 116.4 (f), 113.9 (g), 61.2 (a). MS(EI) m/z = 209 (M⁺).

Preparation of 1-azaspiro-[5.5]-undecane (Scheme 6)

Under an atmosphere of dry nitrogen, a Schlenk tube was loaded with chlorobenzene (7.0 mL), Ti(NMe₂)₄ (0.50 g, 2.23 mmol), and 3-buten-1-ol (192 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (765 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 180 °C for 60 h. The solution was acidified with 15% HCl, and a 6 N solution of NaOH was added to the reaction mixture. The solution was extracted with ether (6 × 20 mL) and was dried over Na₂SO₄. The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 100 g of Florisil® and ethyl acetate as the eluent. The isolated yield obtained was 35% (0.72 mmol). ¹H NMR¹⁷ (500 MHz, CDCl₃): δ = 2.71 (t, 2 H, a, J = 5.8 Hz), 1.0-1.6 (m, 16 H, b, c, d, f, g and h). ¹³C{¹H} NMR (500 MHz, CDCl₃): 50.6 (e), 40.8 (a), 36.7 (f), 36.3 (d), 27.3 (b), 26.6 (h), 21.9 (e), 20.4(g). MS(EI) m/z = 153 (M⁺). The GC yield is 63% with toluene as the solvent for the reaction. The low isolated yield of the 1-azaspiro-[5.5]-undecane is due to the thick viscous emulsion that results after the addition of 6 N NaOH solution which, makes the extraction with ether harder than usual. We are currently pursuing better methods to quench the reaction.

Preparation of 1-azaspiro-2,2-\(2^H\{5.5\}\)-undecane (Scheme 7)

Under an atmosphere of dry nitrogen, a Schlenk tube was loaded with chlorobenzene (9.0 mL), Ti(\(\text{NMe}_2\))\(_4\) (1.00 g, 4.46 mmol), and 3-buten-1-ol-\(1,1\)-\(d_2\) (331 mg, 4.46 mmol). The reaction mixture was stirred for 20 min, and cyclohexylamine (1530 \(\mu\)L, 13.4 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 180 °C for 60 h. The solution was acidified with 15% HCl, and a 6 N solution of NaOH was added to the reaction mixture. The solution was extracted with ether (6 \(\times\) 20 mL) and was dried over Na\(_2\)SO\(_4\). The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 100 g of Florisil\textsuperscript{\textregistered} and ethyl acetate as the eluent. The isolated yield obtained was 32% (1.39 mmol). \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta = 1.0\text{--}1.6\) (m, 16 H, b, c, d, f, g and h). \(^{13}\text{C}\{^1\text{H}\}\) NMR (500 MHz, CDCl\(_3\)): 50.6 (e), 36.7 (f), 36.3 (d), 27.3 (b), 26.6 (h), 21.9 (c), 20.4 (g). MS(EI) \(m/z = 155\) (M\(^+\)).
Preparation of N-phenyl 3, 3-\(H^2\)-allylamine (Scheme 3)

Under an atmosphere of dry nitrogen, a threaded-top pressure tube was loaded with toluene (2.0 mL), Ti(NMe\(_2\))\(_4\) (0.50 g, 2.23 mmol), and allyl-\(l\)-\(d_2\)-alcohol (154.0 µL, 2.23 mmol). The reaction mixture was stirred for 20 min, and aniline (609 µL, 6.69 mmol) was then added. The tube was sealed with a Teflon cap, and the reaction mixture was heated at 160 °C for 24 h. The solution was acidified with 5% HCl, and a saturated solution of NaHCO\(_3\) was added to the reaction mixture. The solution was extracted with ether (4 × 20 mL) and was dried over Na\(_2\)SO\(_4\). The volatiles were removed from the reaction mixture in vacuo, and the residue was subjected to column chromatography using 300 g of silica gel and 1:1 hexanes–ethyl acetate as the eluent. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.30\) (app t, 2 H, i), 6.84 (tt, 1 H, j, \(J = 7.4, 1.04\) Hz), 6.72 (dd, 2 H, h), 5.88 (s, 1 H, d), 3.85 (d, 2 H, a, \(J = 5.3\) Hz). \(^{13}\)C\{\(^1\)H\} NMR (500 MHz, CDCl\(_3\)): 148.2 (g), 135.6 (d), 129.3 (i), 117.6 (j), 116.3 (f), 115.1 (h), 46.6 (a). MS(EI) \(m/z = 135\) (M\(^+\)).
S-phenyl-allyl-mesa-pure-021905

Archive directory: /home/lell/mersyn/data
Sample directory:

File logname: r1p1
metamethlamine trihydrochloride

NMR Spectrum: 390 MHz
Compound: 3-B-ethylamino-allylamine

Data Collected on:

Sample Directory:

File: MOTH

Pulse Sequence: alpd
2-methyl-1-butoxycarbonylalanine-Cl

Pulse Sequence: alpsl
benzyldimethylamine-2-ethyl-1-butene-2-ol-comp-4

Proton Sequence: s2pd1
2-butoxy-3-methyl-N-cyclohexanamine-complex-1H-NMR-Cl3

Archive directory:/home/bally/nnapsy/data
Sample directory:

File name: olpui
acilines-3-butene-2-ol-MeOH

NMR spectrum: signal

1H NMR (400 MHz, CDCl3): δ 1.64, 1.84, 2.18, 4.31, 2.53, 4.21
cycloexiphtane-3-oxime-1-ol-BM5-comp-11

Data collected on:
ra-1000N
Archive Directory:
/home/fall/macrop/data
Sample Directory:

File: FEGD3S

File Sequence: elk1
comp1-7,10a-20l-cyclosporin-C13-M5045

Data Collected on:

Archive directory:

Sample Directory:

File: CHRNW

Note: Acronyms: cyol
CH₃
N
H
H
O

C₈H₈N₄
O
H
H
N
O

CH₃
H
N
O
H
H
N
O

1H NMR spectrum: alpyl
A syn-epi-[2-]:-amino-2,2'-di-Cl-P
Pulse Sequence: tipol