Supporting Information

Hydroaminations of Unactivated Alkenes with Basic Alkylamines: Group 4 Metal Halide Catalysts and Brønsted-Acid Organocatalysts

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General Remarks:

Reactions were carried out on a 0.5-1.0 mmol scale under N₂ using pre-dried glassware. Chemicals were obtained from Aldrich, Fluka, Lancaster, Strem and Acros, and were used without further purification. Toluene and 1,4-dioxane were distilled from sodium under N₂. Starting materials **1a**, **1b**, **S1c-S1I** were prepared as described in the literature.^[1,2] Yields refer to isolated compounds, estimated to be > 95% pure as determined by ¹H-NMR and GC analysis. Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on Varian 300, 400 and 600 in CDCl₃; chemical shifts are given in ppm, coupling constants (*J*) in Hz. IR: wavenumber in cm⁻¹.



Representative procedure for MCl₄-catalyzed intramolecular hydroaminations of unactivated olefins

1-Trifluoroacetyl-2-methyl-4,4-diphenylpyrrolidine (2a, Table 1, entry 6):

An oven dried seal tube was charged under a positive pressure of nitrogen with ZrCl₄ (47 mg, 0.20 mmol, 20 mol %), toluene (2 mL) and LDA (2.0 M in THF/*n*-heptane/ethylbenzene, 0.40 mL, 0.80 mmol). The resulting solution was stirred for 30 min at ambient temperature, followed by addition of **1a** (237 mg, 1.00 mmol). The reaction mixture was stirred at 120 °C for 18 h. The cold solution was subsequently treated with trifluoroacetic anhydride (420 mg, 2.00 mmol). After stirring for 15 min at ambient temperature, Et₂O (50 mL) and saturated aqueous (NH₄)₂CO₃ (30 mL) were added. The separated aqueous phase was extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O = 60/1→30/1) to yield **2a** (290 mg, 0.87 mmol, 87 %) as a light yellow solid (mp: 78.8-79.6 °C).

¹H-NMR (300 MHz, CDCl₃): δ = 7.34-7.37 (m, 10H), 4.61 (dt, *J* = 11.5, 1.8 Hz, 1H), 4.12-4.02 (m, 1H), 3.98 (d, *J* = 11.5 Hz, 1H), 3.06-2.97 (m, 1H), 2.32-2.25 (m, 1H), 1.40 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 155.3 (q, *J* = 36.1 Hz, CO), 144.7 (C_q), 143.6 (C_q), 128.8 (CH), 128.7 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 116.1 (q, *J* = 288.0 Hz, CF₃), 56.2 (q, *J* = 2.6 Hz, CH₂), 54.6 (CH), 53.3 (C_q), 44.4 (CH₂), 18.9 (CH₃). ¹⁹F-NMR (275 MHz, CDCl₃): δ = -72.37 (s). IR (ATR): 3060, 2932, 1685, 1496, 1446, 1253, 1205, 1180, 1136, 1033, 753, 696 cm⁻¹. MS (EI), *m/z* (relative intensity) 334 (18) [M+H⁺], 333 (90) [M⁺], 220 (19), 207 (46), 193 (66), 179 (100), 115 (40), 91 (31), 69 (35). HR-MS (EI) *m/z* calcd for C₁₉H₁₈F₃NO 333.1340, found 333.1322.



Representative Procedure for NH₄O₂CCF₃-catalyzed hydroamination reactions (A): 1-Benzyl-2-methyl-4,4-diphenylpyrrolidine (2b, Table 2, entry 16):

A solution of **1b** (328 mg, 1.00 mmol) and NH₄O₂CCF₃ (26.2 mg, 0.20 mmol, 20 mol %) in dry 1,4-dioxane (2.0 mL) was stirred in a sealed tube under N₂ for 24 h at 130 °C. At ambient temperature, saturated aqueous NaHCO₃ (80 mL) and Et₂O (80 mL) were added. The separated aqueous phase was extracted with Et₂O (2 × 80 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O = 30/1) to yield **2b** (243 mg, 74 %) as a yellow solid (mp. 70.6-72.2 °C).

The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ = 7.42-7.37 (m, 15H), 4.12 (d, *J* = 13.3 Hz, 1H), 3.70 (d, *J* = 10.0 Hz, 1H), 3.30 (d, *J* = 13.3 Hz, 1H), 2.99-2.83 (m, 3H), 2.25 (dd, *J* = 12.2, 7.2 Hz, 1H), 1.21 (d, *J* = 6.1 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 150.5 (C_q), 148.6 (C_q), 139.9 (C_q), 128.6 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.2 (CH), 126.8 (CH), 125.8 (CH), 125.4 (CH), 66.4 (CH₂), 59.7 (CH), 58.0 (CH₂), 52.5 (C_q), 47.9 (CH₂), 19.5 (CH₃). IR (ATR): 3061, 3029, 2960, 2924, 2788, 1491, 1445, 1373, 730, 695 cm⁻¹. MS (EI) *m/z* (relative intensity) 327 (18) [M⁺], 312 (75), 147 (100), 91 (64), 56 (98). HR-MS (EI) *m/z* calcd for C₂₄H₂₅N 327.1987, found 327.2002.



1-(4-Methoxybenzyl)-2-methyl-4,4-diphenylpyrrolidine (2c, Table 3, entry 1):

The representative procedure A was followed using **S1c** (358 mg, 1.00 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 15/1) yielded **2c** (224 mg, 63 %) as a white solid (mp. 84.5-85.7 °C).

¹H NMR (300 MHz, CDCl₃): δ = 7.32-7.18 (m, 11H), 7.15-7.12 (m, 1H), 6.91-6.88 (m, 2H), 4.05 (d, *J* = 13.2 Hz, 1H), 3.84 (s, 3H), 3.66 (d, *J* = 9.7 Hz, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 2.94 (dd, *J* = 12.8, 7.9 Hz, 1H), 2.85-2.79 (m, 2H), 2.23 (dd, *J* = 13.2, 7.9 Hz, 1H), 1.19 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 158.5 (C_q), 151.5 (C_q), 150.6 (C_q), 132.1 (C_q), 129.7 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.2 (CH), 125.8 (CH), 125.4 (CH), 113.6 (CH), 66.3 (CH₂), 59.5 (CH), 57.3 (CH₂), 55.2 (OCH₃), 52.5 (C_q), 48.0 (CH₂), 19.5 (CH₃). IR (ATR): 2922, 2852, 2782, 1448, 1374, 734, 696 cm⁻¹. MS (EI) *m/z* (relative intensity) 357 (17) [M⁺], 342 (35), 176 (59), 120 (100), 56 (52). HR-MS (EI) *m/z* calcd for C₂₅H₂₇NO 357.2093, found 357.2097.



1-(4-Chlorobenzyl)-2-methyl-4,4-diphenylpyrrolidine (2d, Table 3, entry 2):

The representative procedure A was followed using **S2d** (362 mg, 1.00 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 30/1) yielded **2d** (303 mg, 84 %) as a white solid (mp. 96.2-97.4 °C).

¹H NMR (300 MHz, CDCl₃): δ = 7.39-7.14 (m, 14H), 4.06 (d, *J* = 13.3 Hz, 1H), 3.65 (d, *J* = 9.7 Hz, 1H), 3.27 (d, *J* = 13.2 Hz, 1H), 2.99-2.86 (m, 2H), 2.81 (d, *J* = 9.7 Hz, 1H), 2.26 (dd, *J* = 12.2, 7.1 Hz, 1H), 1.19 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 150.3

(C_q), 148.5 (C_q), 138.6 (C_q), 132.4 (C_q), 129.8 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 125.8 (CH), 125.5 (CH), 66.3 (CH₂), 59.6 (CH), 57.2 (CH₂), 52.5 (C_q), 47.8 (CH₂), 19.5 (CH₃). IR (ATR): 3062, 2962, 2798, 1489, 1444, 1373, 1013, 802, 763, 700 cm⁻¹. MS (EI) m/z (relative intensity) 361 (12) [M⁺], 346 (53), 181 (84), 125 (43), 56 (100). HR-MS (EI) m/z calcd for C₂₄H₂₄CIN 361.1597, found 361.1581.



1-(4-Methoxycarbonylbenzyl)-2-methyl-4,4-diphenylpyrrolidine (2e, Table 3, entry 3):

The representative procedure A was followed using **S1e** (386 mg, 1.00 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 8/1) yielded **2e** (361 mg, 93 %) as an orange solid (mp. 67.1-69.0 °C).

The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.25-7.08 (m, 10H), 4.08 (d, *J* = 13.7 Hz, 1H), 3.89 (s, 3H), 3.59 (d, *J* = 9.7 Hz, 1H), 3.31 (d, *J* = 13.7 Hz, 1H), 2.90 (dd, J = 12.8, 7.5 Hz, 1H), 2.86-2.81 (m, 1H), 2.77 (d, *J* = 9.7 Hz, 1H), 2.22 (dd, *J* = 12.8, 7.5 Hz, 1H), 1.15 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 166.9 (CO), 150.1 (C_q), 148.3 (Cq), 145.5 (C_q), 129.4 (CH), 128.5 (C_q), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.1 (CH), 126.9 (CH), 125.6 (CH), 125.3 (CH), 66.2 (CH₂), 59.5 (CH), 57.5 (CH₂), 52.4 (C_q), 51.8 (OCH₃), 47.6 (CH₂), 19.3 (CH₃). IR (ATR): 2932, 2895, 1719, 1435, 1275, 1108, 757, 699 cm⁻¹. MS (EI) *m/z* (relative intensity) 385 (15) [M⁺], 350 (67), 205 (100), 149 (18), 121 (6), 91 (5), 56 (80). HR-MS (EI) *m/z* calcd for C₂₆H₂₇NO₂ 385.2042, found 385.2057.



2-Methyl-1-(4-nitrobenzyl)- 4,4-diphenylpyrrolidine (2f, Table 3, entry 4):

The representative procedure A was followed using **S1f** (373 mg, 1.00 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 10/1) yielded **2f** (300 mg, 80 %) as an orange solid (mp. 127.3-128.5 °C).

The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ = 8.18-8.17 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.29-7.14 (m, 10H), 4.12 (d, *J* = 14.1 Hz, 1H), 3.61 (d, *J* = 9.7 Hz, 1H), 3.43 (d, *J* = 14.1 Hz, 1H), 2.95-2.90 (m, 2H), 2.86 (d, *J* = 9.7 Hz, 1H) , 2.31-2.27 (m, 1H), 1.19 (d, *J* = 5.7 Hz, 3H).¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 150.0 (C_q), 148.3 (C_q), 148.2 (C_q), 147.0 (C_q), 129.0 (CH), 128.2 (CH), 127.9 (CH), 127.3 (CH), 127.0 (CH), 126.0 (CH), 125.6 (CH), 123.5 (CH), 66.4 (CH₂), 59.7 (CH), 57.3 (CH₂), 52.7 (C_q), 47.6 (CH₂), 19.5 (CH₃). IR (ATR): 2964, 2793, 1598, 1514, 1490, 1342, 844, 763, 737, 702 cm⁻¹. MS (EI) *m/z* (relative intensity) 372 (16) [M⁺], 357 (70), 192 (100), 177 (7), 115 (7), 91 (5), 56 (84). HR-MS (EI) *m/z* calcd for C₂₄H₂₄N₂O₂ 372.1838, found 372.1818.



1-(4-Cyanobenzyl)-2-methyl-4,4-diphenylpyrrolidine (2g, Table 3, entry 5):

The representative procedure A was followed using **S1g** (353 mg, 1.00 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 10/1) yielded **2g** (289 mg, 82 %) as a white solid (mp. 113.2-115.0 °C).

The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ = 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.26-7.13 (m, 10H), 4.08 (d, *J* = 14.1 Hz, 1H), 3.62 (s, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.95-2.85 (m, 3H), 2.31-2.27 (m, 1H), 1.18 (d, *J* = 5.3 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 151.1 (C_q), 148.4 (C_q), 146.2 (C_q), 132.1 (CH), 129.1 (CH), 128.2 (CH), 127.9 (CH), 127.2 (CH), 127.0 (CH), 126.0 (CH), 125.6 (CH), 119.0 (CN), 110.9 (C_q), 66.3 (CH₂), 59.7 (CH), 57.6 (CH₂), 52.7 (C_q), 47.5 (CH₂), 19.4 (CH₃). IR (ATR): 3062, 2964, 2787, 2226, 1608, 1492, 1444, 1375, 852, 822, 762, 702 cm⁻¹. MS (EI) *m/z* (relative intensity) 352 (18) [M⁺], 337 (71), 193 (7), 172 (100), 116 (22), 56 (78). HR-MS (EI) *m/z* calcd for C₂₅H₂₄N₂ 352.1939, found 352.1924.



Representative procedure for PhMe₂NHB(C₆F₅)₄-catalyzed hydroamination reactions (B):

1-(4-Hydroxybenzyl)-2-methyl-4,4-diphenylpyrrolidine (2h, Table 3, entry 6):

A solution of **S1h** (172 mg, 0.50 mmol) and PhMe₂NHB(C₆F₅)₄ (40 mg, 0.05 mmol, 10 mol %) in dry 1,4-dioxane (1.0 mL) was stirred in a sealed tube under N₂ for 24 h at 120 °C. At ambient temperature, saturated aqueous NaHCO₃ (80 mL) and Et₂O (80 mL) were added. The separated aqueous phase was extracted with Et₂O (2 × 80 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O = 2/1) to yield **2h** (145 mg, 84%) as a white solid (mp. 63.6-65.2 °C).

¹H NMR (300 MHz, CDCl₃): δ = 7.33-7.14 (m, 12H), 6.80 (d, *J* = 7.9 Hz, 2H), 4.25 (s, br, 1H), 4.04 (d, *J* = 13.2 Hz, 1H), 3.80 (d, *J* = 10.6 Hz, 1H), 3.24 (d, *J* = 12.4 Hz, 1H), 2.99-2.83 (m, 3H), 2.25 (dd, *J* = 12.4, 7.1 Hz, 1H), 1.21 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT,

CDCl₃): $\delta = 154.2$ (C_q), 150.5 (C_q), 148.7 (C_q), 131.9 (C_q), 129.9 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.2 (CH), 125.8 (CH), 125.4 (CH), 115.1 (CH), 66.2 (CH₂), 59.5 (CH), 57.3 (CH₂), 52.5 (C_q), 48.0 (CH₂), 19.4 (CH₃). IR (ATR): 3298, 2963, 2792, 1612, 1596, 1513, 1493, 1445, 1232, 757, 697 cm⁻¹. MS (EI) *m/z* (relative intensity) 343 (63) [M⁺], 328 (17), 220 (14), 178 (25), 163 (80), 115 (21), 107 (100), 91 (19), 77 (20), 56 (100). HR-MS (EI) *m/z* calcd for C₂₄H₂₅NO 343.1936, found 343.1924.



1-Benzyl-2,4,4-trimethylpyrrolidine (2i, Table 3, entry 7):

The representative procedure B was followed using **S1i** (102 mg, 0.50 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 10/1) yielded **2i** (79.0 mg, 75 %) as a yellow oil. The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ 7.36-7.23 (m, 5H), 4.04 (d, *J* = 13.2 Hz, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 2.69 (d, *J* = 9.3 Hz, 1H), 2.62-2.61 (m, 1H), 1.99 (d, *J* = 9.3 Hz, 1H), 1.74 (dd, *J* = 12.4, 7.1 Hz, 1H), 1.39-1.35 (m, 1H), 1.18 (d, *J* = 5.7 Hz, 3H), 1.09 (s, 3H), 0.99 (s, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 139.9 (C_q), 128.8 (CH), 128.1 (CH), 126.7 (CH), 68.1 (CH₂), 59.9 (CH), 57.9 (CH₂), 49.0 (CH₂), 35.4 (C_q), 30.5 (CH₃), 29.2 (CH₃), 19.2 (CH₃). IR (ATR): 2953, 2866, 2784, 1453, 1373, 1219, 735, 696 cm⁻¹. MS (EI) *m*/*z* (relative intensity) 203 (11) [M⁺], 188 (100), 91 (97), 56 (27). HR-MS (EI) *m*/*z* calcd for C₁₄H₂₁N 203.1674, found 203.1685.



2-Benzyl-3-methyl-2-aza-spiro[4.5]decane (2j, Table 3, entry 8):

The representative procedure B was followed using **S1j** (122 mg, 0.50 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 3/1) yielded **2j** (102 mg, 84 %) as a yellow oil. The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃): δ 7.37-7.23 (m, 5H), 4.05 (d, *J* = 13.2 Hz, 1H), 3.14 (d, *J* = 13.2 Hz, 1H), 2.82 (d, *J* = 9.7 Hz, 1H), 2.60-2.48 (m, 1H), 1.92 (d, *J* = 8.8 Hz, 1H), 1.77 (dd, *J* = 12.4, 7.1 Hz, 1H), 1.50-1.29 (m, 11H), 1.18 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 139.8 (C_q), 128.7 (CH), 128.1 (CH), 126.6 (CH), 68.5 (CH₂), 59.0 (CH), 57.9 (CH₂), 46.9 (CH₂), 39.3 (C_q), 39.2 (CH₂), 38.5 (CH₂), 26.0 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 19.2 (CH₃). IR (ATR): 3027, 2922, 2852, 2782, 1697, 1492, 1448, 1374, 734, 696 cm⁻¹. MS (EI) *m/z* (relative intensity) 243 (9) [M⁺], 228 (100), 91 (84), 56 (28). HR-MS (EI) *m/z* calcd for C₁₇H₂₅N 243.1987, found 243.1989.



1-Benzyl-4-(4-methoxyphenyl)-2-methylpyrrolidine (2k, Table 3, entry 9):

The representative procedure B was followed using **S1k** (141 mg, 0.50 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 1/1) yielded **2k** (116 mg, 82 %, diastereomeric ratio: 2.6:1) as a yellow oil.

The spectral data were in accordance with those reported in the literature.^[1]

¹H NMR (300 MHz, CDCl₃, major diastereomer): δ 7.38-7.21 (m, 7H), 6.81-6.79 (m, 2H), 4.11 (d, J = 13.2 Hz, 1H), 3.77 (s, 3H), 3.26 (d, J = 7.5 Hz, 1H), 3.15 (ddd, J = 12.8, 8.8, 4.4 Hz, 1H), 2.94-2.93 (m, 1H), 2.63-2.60 (m, 2H), 2.41 (ddd, J = 12.8, 8.8, 6.2 Hz, 1H), 1.58-1.53 (m, 1H), 1.24 (d, J = 6.2 Hz, 3H). ¹H NMR (300 MHz, CDCl₃, minor diastereomer): δ 7.38-7.21 (m, 5H), 7.13-7.11 (m, 2H), 6.81-6.79 (m, 2H), 4.06 (d, J = 12.8 Hz, 1H), 3.78 (s, 3H), 3.31-3.29 (m, 1H), 3.28-3.22 (m, 2H), 2.77-2.74 (m, 1H), 2.19 (t, J = 9.5 Hz, 1H), 2.01-2.05 (m, 1H), 2.00-1.95 (m, 1H), 1.24 (d, J = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃, major diastereomer): $\delta = 157.7$ (C_q), 140.0 (C_q), 128.6 (CH), 128.1 (CH), 128.0 (CH), 127.0 (C_q), 126.6 (CH), 113.6 (CH), 61.7 (CH₂), 60.5 (CH), 58.0 (CH₂), 55.2 (CH), 44.0 (CH₂), 40.4 (OCH₃), 19.0 (CH₃). ¹³C-NMR (75 MHz, DEPT, CDCl₃, minor diastereomer): $\delta = 157.9$ (C_q), 139.6 (C_q), 129.1 (CH), 128.2 (CH), 128.2 (CH), 127.6 (C_q), 126.9 (CH), 113.7 (CH), 63.0 (CH₂), 60.0 (CH), 58.5 (CH₂), 55.3 (CH), 41.3 (CH₂), 40.6 (OCH₃), 20.0 (CH₃). IR (ATR): 3028, 2958, 2929, 2785, 1611, 1511, 1453, 1243, 1176, 1035, 828, 734, 697 cm⁻¹. MS (EI) *m*/*z* (relative intensity) 281 (27) [M⁺], 266 (95), 147 (23), 121 (7), 91 (100), 56 (54). HR-MS (EI) *m*/*z* calcd for C₁₉H₂₃NO 281.1780, found 281.1771.



1-Benzyl-2-methylpyrrolidine (2l, Table 3, entry 10):

The representative procedure B was followed at 130 °C using **S11** (87.7 mg, 0.50 mmol). Purification by column chromatography (*n*-pentane/Et₂O = 1/1) yielded **21** (64.8 mg, 74 %) as a yellow oil.

The spectral data were in accordance with those reported in the literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.34-7.26 (m, H), 4.05 (d, *J* = 12.4 Hz, 1H), 3.17 (d, *J* = 12.4 Hz, 1H), 2.96-2.90 (m, 1H), 2.45-2.39 (m, 1H), 2.18-2.02 (m, 1H), 1.97-1.91 (m, 1H), 1.78-1.69 (m, 2H), 1.55-1.43 (m, 1H), 1.20 (d, *J* = 6.2 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 139.6 (C_q), 129.1 (CH), 128.1 (CH), 126.7 (CH), 59.6 (CH), 58.3 (CH₂), 54.0 (CH₂), 32.7 (CH₂), 21.5 (CH₂), 19.2 (CH₃). IR (ATR): 3028, 2962, 2784, 1495, 1453, 1374,

1260, 1100, 1028, 802, 734, 696 cm⁻¹. MS (EI) *m/z* (relative intensity) 175 (11) [M⁺], 160 (85), 91 (100), 65 (12), 56 (11), 41 (9). HR-MS (EI) *m/z* calcd for C₁₂H₁₇N 175.1361, found 175.1352.



1-Trifluoroacetyl-2-methyl-4,4-diphenylpyrrolidine (2a, Table 3, entry 11):

The representative procedure was followed using **1a** (119 mg, 0.50 mmol), dry 1,4-dioxane (1 mL) and PhMe₂NHB(C₆F₅)₄ (80 mg, 0.10 mmol, 20 mol %). The reaction mixture was stirred at 120 °C for 18 h. The cold reaction mixture was subsequently treated with trifluoroacetic anhydride (210 mg, 1.00 mmol). After stirring for 15 min, Et₂O (50 mL) and saturated aqueous (NH₄)₂CO₃ (30 mL) were added. The separated aqueous phase was extracted with Et₂O (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O = $60/1 \rightarrow 30/1$) to yield **2a** (138 mg, 0.41 mmol, 83 %) as a light yellow solid.



Representative procedure for the reductive amination of benzaldehyde derivatives:

(4-Methoxybenzyl)-(2,2-diphenylpent-4-enyl)amine (S1c):

A solution of 2,2-diphenylpent-4-enylamine (2.37g, 10.0 mmol) and 4-anisaldehyde (1.57 g, 10.5 mmol) in MeOH (40 mL) was stirred at room temperature for 3 h, subsequently treated with NaBH₄ (0.57 mg, 15.0 mmol), and stirred overnight. The resulting mixture was quenched with water (100 mL) and aqueous NaOH (30 mL, 1 M), and then extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography on silica gel (*n*-pentane/Et₂O = 8/1) yielded **S1c** (3.21 g, 90 %) as a colorless viscous oil.

¹H NMR (300 MHz, CDCl₃): $\delta = 7.27$ (t, J = 7.5 Hz, 4H), 7.19-7.16 (m, 6H), 7.12 (d, J = 8.8 Hz, 2H), 6.83-6.81 (m, 2H), 5.35 (tdd, J = 16.8, 10.1, 7.1 Hz, 1H), 4.99 (md, J = 16.8 Hz, 1H), 4.90 (md, J = 10.1 Hz, 1H), 3.79 (s, 3H), 3.65 (s, 2H), 3.19 (s, 2H), 3.03 (d, J = 7.1 Hz, 2H), 0.79 (s, br, 1H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): $\delta = 158.4$ (C_q), 146.8 (C_q), 134.9 (CH), 132.9 (C_q), 129.0 (CH), 128.1 (CH), 127.9 (CH), 125.9 (CH), 117.5 (CH₂), 113.7 (CH), 55.3 (CH₃), 55.2 (CH₂), 53.6 (CH₂), 50.2 (C_q), 41.6 (CH₂). IR (ATR): 3058, 2907, 1610, 1510, 1495, 1443, 1244, 1172, 1033, 914, 755, 697 cm⁻¹. MS (EI) *m/z* (relative intensity) 357 (1) [M⁺], 150 (60), 121 (100), 91 (8). HR-MS (EI) *m/z* calcd for C₂₅H₂₇NO 357.2093, found 357.2111.



(4-Chlorobenzyl)-(2,2-diphenylpent-4-enyl)amine (S1d):

The representative procedure was followed using 2,2-diphenylpent-4-enylamine (2.37 g, 10.0 mmol) and *p*-chlorobenzaldehyde (1.48 g, 10.5 mmol). Purification by column chromatography on silica gel (*n*-pentane/Et₂O = 8/1) yielded **S1d** (3.48 g, 96%) as a viscous yellow oil.

¹H NMR (300 MHz, CDCl₃): $\delta = 7.32-7.15$ (m, 14H), 5.37 (tdd, J = 16.8, 9.7, 7.1 Hz, 1H), 5.04-4.99 (m, 1H), 4.94 (dd, J = 9.7, 2.7 Hz, 1H), 3.70 (s, 2H), 3.20 (s, 2H), 3.06 (d, J = 7.1 Hz, 2H), 1.00 (s, br, 1H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): $\delta = 146.7$ (C_q), 139.2 (C_q), 134.8 (CH), 132.3 (C_q), 129.2 (CH), 128.3 (CH), 128.0 (CH), 128.0 (CH), 126.0 (CH), 117.6 (CH₂), 55.2 (CH₂), 53.4 (CH₂), 50.1 (C_q), 41.6 (CH₂). IR (ATR): 3027, 2955, 2870, 2811, 1605, 1495, 1453, 1102, 1028, 911, 820, 732, 696 cm⁻¹. MS (EI) *m/z* (relative intensity) 361 (8) [M⁺], 345 (9), 181 (18), 154 (100), 125 (90), 91 (16), 56 (39). HR-MS (EI) *m/z* calcd for C₂₄H₂₄CIN 361.1597, found 361.1593.



4-[(2,2-Diphenylpent-4-enylamino)-methyl]phenole (S1h):

The representative procedure was followed using 2,2-diphenylpent-4-enylamine (2.37g, 10.0 mmol) and 4-hydroxybenzaldehyde (1.28 g, 10.5 mmol). Purification by column chromatography on silica gel (*n*-pentane/Et₂O = 2/1) yielded **S1h** (2.70 g, 79%) as a white solid (m.p. 126.7-127.9 °C).

¹H NMR (300 MHz, CDCl₃): δ = 7.31-7.16 (m, 10H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.68 (md, *J* = 7.9 Hz, 2H), 7.22-7.15 (m, 6H), 5.37 (tdd, *J* =16.7, 9.7, 7.1 Hz, 1H), 5.04-4.91 (m, 2H), 3.64 (s, 2H), 3.23 (s, 2H), 3.15 (s, br, 2H), 3.04 (d, *J* = 7.1 Hz, 2H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 154.7 (C_q), 146.6 (C_q), 134.7 (CH), 132.1 (C_q), 129.3 (CH), 128.0 (CH), 128.0 (CH), 125.8 (CH), 117.7 (CH₂), 115.2 (CH), 55.1 (CH₂), 53.6 (CH₂), 50.1 (C_q), 41.6 (CH₂). IR (ATR): 3290, 3053, 2826, 1615, 1594, 1519, 1494, 1443, 1274, 1257, 1092, 818, 756, 699 cm⁻¹. MS (LC/ESI) *m*/*z* (relative intensity) 344 (100) [M⁺+H]. HR-MS (EI) *m*/*z* calcd for C₂₄H₂₆NO 344.2014, found 344.1997.

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S15









































































