C–H Functionalization of Cyclic Amines: Redox-Annulations with α,β-Unsaturated Carbonyl Compounds

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Supporting Information

General Information: (E)-α-Methylcinnamaldehyde was purchased from Alfa Aesar and distilled under vacuum prior to use. Other α,β-unsaturated aldehydes were prepared according to previously reported methods.1 (E)-Chalcone was purchased from Acros and was recrystallized prior to use. Other chalcones were prepared according to previously reported procedures.2 Secondary amines were purchased from commercial sources and were distilled prior to use. Benzoic acid was purchased from Sigma-Aldrich and was recrystallized prior to use. 3Å powdered molecular sieves were purchased from Alfa Aesar and were activated before use by heating in a furnace to 300 °C for 2 h and were stored in a desiccator. Reagent grade toluene was purchased from Sigma-Aldrich and distilled over sodium. Purification of reaction products was carried out by flash column chromatography using Sorbent Technologies Standard Grade silica gel (60 Å, 230–400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60 F254 plates. Visualization was accomplished with UV light, potassium permanganate and Dragendorff-Munier stains followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (1H-NMR) were recorded on a Varian VNMRS-500 MHz and are reported in ppm using chloroform as the internal standard (7.26 ppm). Data are reported as app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, comp = complex, br = broad; and coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (13C-NMR) were recorded on a Varian VNMRS-500 MHz, Varian VNMRS-300 MHz and are reported in ppm using chloroform as the internal standard (77.0 ppm). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer.
**General Procedure:** α,β–Unsaturated aldehyde or ketone (1 mmol) was added to a 25 mL round bottom flask containing a stir bar. The flask was charged with toluene (10 mL), 3 Å molecular sieves (200 mg), benzoic acid (1 mmol) and secondary amine (5 mmol). A reflux condenser with a nitrogen inlet was placed on top of the flask which was then heated in an oil bath at reflux until the aldehyde or ketone was consumed. Once cooled to room temperature, the mixture was filtered through a pad of celite and rinsed with EtOAc (50 mL). The filtrate was concentrated under reduced pressure and the resulting residue purified via silica gel chromatography.

(±) 1a: Following the general procedure, (E)-chalcone and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et3N, resulting in the isolation of 201 mg of (±) 1a as a yellow oil (77% yield). Rf = 0.14 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3058, 3024, 2962, 2870, 1594, 1671, 1601, 1508, 1358, 1223, 1155, 1028, 838, 697; 1H NMR (500 MHz, CDCl3) δ 7.69–7.62 (comp, 2H), 7.43–7.26 (comp, 8H), 5.18 (d, J = 2.5 Hz, 1H), 4.44 (dd, J = 11.0, 2.5 Hz, 1H), 4.37 (app dt, J = 11.0, 7.6 Hz, 1H), 3.25 (ddd, J = 10.4, 7.0, 4.9 Hz, 1H), 2.92 (app dt, J = 10.5, 7.5 Hz, 1H), 1.70–1.59 (comp, 2H), 1.34–1.25 (comp, 2H); 13C NMR (125 MHz, CDCl3) δ 154.47, 141.60, 134.08, 128.65, 128.22, 128.04, 127.85, 126.97, 126.21, 104.15, 69.03, 51.96, 49.49, 27.53, 25.83; m/z (ESI–MS) 262.3 [M+H]+.

(±) 1b: Following the general procedure, 4-fluorochalcone and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et3N, resulting in the isolation of 185 mg of (±) 1b as a yellow oil (66% yield). Rf = 0.14 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3058, 2961, 2870, 2870, 1594, 1891, 1671, 1601, 1508, 1358, 1223, 1155, 1028, 838, 697; 1H NMR (500 MHz, CDCl3) δ 7.69–7.62 (comp, 2H), 7.43–7.26 (comp, 2H), 7.35–7.30 (m, 1H), 7.29–7.23 (comp, 2H), 7.07–7.01 (comp, 2H), 5.10 (d, J = 2.4 Hz, 1H), 4.41–4.27 (comp, 2H), 3.26–3.18 (m, 1H), 2.89 (app dt, J = Hz, 1H), 1.67–1.57 (comp, 2H), 1.30–1.19 (comp, 2H); 13C NMR (75 MHz, CDCl3) δ 161.57 (d, J = 244.2 Hz), 159.95, 154.73, 137.35, 134.03, 130.08, 129.98, 128.32, 128.04, 127.06, 115.08, 114.75, 103.88, 77.49, 76.64, 69.04, 51.99, 48.81, 27.59, 25.90; m/z (ESI–MS) 280.6 [M + H]+.

(±) 1c: Following the general procedure, 4-chlorochalcone and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et3N, resulting in the isolation of 223 mg of (±) 1c as a colorless oil (75% yield). Rf = 0.10 in hexanes/EtOAc 70:30 v/v; IR (KBr) 2962, 2870, 1640, 1489, 1445, 1406, 1358, 1245, 1176, 1088, 1014, 751, 695 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.65–7.52 (comp, 2H), 7.41–7.34 (comp, 2H), 7.34–7.28 (comp, 3H), 7.25–7.16 (comp, 2H), 5.07 (d, J = 2.0 Hz, 1H), 4.45–4.24 (comp, 2H), 3.28–3.14 (m, 1H), 2.86 (app dt, J = 10.5, 7.5 Hz, 1H), 1.66–1.53 (comp, 2H), 1.32–1.12 (comp, 2H); 13C NMR (125 MHz, CDCl3) δ 140.21, 133.93, 132.01, 130.00, 128.31, 128.23, 128.06, 127.05, 104.76, 103.46, 68.93, 51.95, 48.91, 27.58, 25.88; m/z (ESI–MS) 296.2 [M+H]+.
Following the general procedure, 4-bromo(chalcone and pyrrolidine were heated at reflux for 5 h. The residue was purified via silica gel chromatography in 80:19:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 221 mg of (±) 1d as a colorless oil (65% yield). R$_f$ = 0.33 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3058, 2961, 2870, 1954, 1891, 1813, 1758, 1671, 1508, 1446, 1358, 1223, 1155, 1094, 980, 919, 838, 761, 697; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.60–7.58 (comp, 2H), 7.49–7.42 (comp, 2H), 7.40–7.35 (comp, 2H), 7.34–7.29 (m, 1H), 7.18–7.16 (comp, 2H), 5.06 (d, $J$ = 2.2 Hz, 1H), 4.37–4.27 (comp, 2H), 3.21 (ddd, $J$ = 11.5, 7.2, 4.8 Hz, 1H), 2.86 (app dt, $J$ = 10.4, 7.5 Hz, 1H), 1.67–1.55 (comp, 2H), 1.33–1.13 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 154.93, 140.66, 133.85, 131.10, 130.35, 128.24, 128.00, 126.98, 120.04, 103.23, 68.78, 51.87, 48.91, 27.53, 25.84; m/z (ESI–MS) [(79Br) 340.3 [M+H]$^+$, (81Br) 342.2 [M+H]$^+$].

Following the general procedure, 4-methoxychalcone and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 199 mg of (±) 1e as a colorless oil (68% yield). R$_f$ = 0.08 in hexanes/EtOAc 70:30 v/v; IR (KBr) 2968, 2833, 1609, 1509, 1445, 1357, 1245, 1173, 1066, 1035, 833, 761 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.66–7.55 (comp, 2H), 7.41–7.34 (comp, 2H), 7.34–7.28 (m, 1H), 7.23–7.15 (comp, 2H), 6.93–6.84 (comp, 2H), 5.11 (d, $J$ = 2.4 Hz, 1H), 4.29 (dd, $J$ = 2.4 Hz, 1H), 4.29 (ddd, $J$ = 10.9, 7.8, 6.9 Hz, 1H), 3.82 (s, 3H), 3.20 (ddd, $J$ = 10.4, 7.1, 4.9 Hz, 1H), 2.87 (app dt, $J$ = 10.4, 7.4 Hz, 1H), 1.67–1.54 (comp, 2H), 1.33–1.20 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.12, 154.20, 134.17, 133.81, 129.61, 128.26, 127.87, 127.01, 113.49, 104.71, 69.18, 55.26, 52.06, 48.83, 27.58, 25.90; m/z (ESI–MS) (79Br) 304.3 [M+H]$^+$, (81Br) 342.2 [M+H]$^+$.

Following the general procedure, (E)-3-mesityl-1-phenylprop-2-en-1-one and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 279 mg of (±) 1f as a colorless oil (92% yield). R$_f$ = 0.15 in hexanes/EtOAc 70:30 v/v; IR (KBr) 2959, 2916, 1633, 1492, 1478, 1445, 1357, 1258, 1026, 851, 749, 695 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.60–7.59 (comp, 2H), 7.41–7.40 (comp, 2H), 7.32–7.31 (m, 1H), 6.86 (s, 2H), 5.39 (d, $J$ = 2.7 Hz, 1H), 4.71 (dd, $J$ = 11.3, 2.7 Hz, 1H), 4.45 (ddd, $J$ = 11.4, 8.6, 7.5 Hz, 1H), 3.20 (ddd, $J$ = 10.8, 6.9, 5.1 Hz, 1H), 3.03 (app dt, $J$ = 10.7, 7.3 Hz, 1H), 2.50 (br s, 6H), 2.30 (s, 3H), 1.79–1.63 (comp, 2H), 1.50–1.32 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 149.37, 137.31, 135.45, 134.42, 133.87, 129.73, 128.26, 127.50, 126.70, 108.90, 67.81, 52.16, 46.67, 28.17, 25.81, 21.63, 20.64.; m/z (ESI–MS) 304.4 [M+H]$^+$. 

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(±) Ig: Following the general procedure, (E)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 268 mg of (±) Ig as a yellow oil (86% yield). R$_f$ = 0.13 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3058, 2962, 2869, 1635, 1596, 1492, 1445, 1359, 1263, 1251, 1090, 1072, 1023, 779, 739, 695 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.11–8.09 (m, 1H), 7.89–7.88 (m, 1H), 7.77–7.76 (m, 1H), 7.68–7.67 (comp, 2H), 7.60–7.46 (comp, 4H), 7.41–7.39 (comp, 2H), 7.37–7.30 (m, 1H), 5.26 (d, $J = 2.5$ Hz, 1H), 5.04 (dd, $J = 11.1$, 2.5 Hz, 1H), 4.65 (ddd, $J = 11.1$, 8.3, 7.0 Hz, 1H), 3.24 (ddd, $J = 10.6$, 7.4, 4.4 Hz, 1H), 2.88 (ddd, $J = 10.5$, 8.1, 6.9 Hz, 1H), 1.67–1.47 (comp, 2H), 1.17–1.03 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 154.20, 138.31, 134.22, 133.70, 132.15, 128.68, 128.32, 127.96, 127.08, 126.15, 125.87, 125.51, 125.30, 123.74, 104.04, 68.71, 52.07, 45.59, 27.42, 25.77; m/z (ESI–MS) 312.2 [M$^+$]+.

(±) Ih: Following the general procedure, 4'-chlorochalcone and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 242 mg of (±) Ih as a colorless oil (82% yield). R$_f$ = 0.11 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3060, 3025, 2962, 2870, 1621, 1593, 1488, 1451, 1401, 1357, 1246, 1176, 1091, 1012, 835, 762, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53–7.52 (comp, 2H), 7.37–7.31 (comp, 4H), 7.28–7.22 (comp, 3H), 5.13 (d, $J = 2.4$ Hz, 1H), 4.38 (dd, $J = 11.2$, 2.5 Hz, 1H), 4.32 (app dt, $J = 11.0$, 7.5 Hz, 1H), 3.18 (ddd, $J = 11.2$, 6.9, 4.9 Hz, 1H), 2.81 (app dt, $J = 10.4$, 7.5 Hz, 1H), 1.69–1.54 (comp, 2H), 1.32–1.16 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 153.48, 141.41, 133.53, 132.63, 128.68, 128.48, 128.23, 128.13, 126.35, 104.80, 69.10, 51.99, 49.57, 27.60, 25.91; m/z (ESI–MS) 296.2 [M$^+$]+.

(±) II: Following the general procedure, 3',4'-dimethoxychalcone and pyrrolidine were heated at reflux for 4 h. The residue was purified via silica gel chromatography in 94:5:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 182 mg of (±) II as a colorless oil (57% yield). R$_f$ = 0.09 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3058, 2959, 2834, 1601, 1581, 1514, 1463, 1451, 1417, 1360, 1267, 1136, 1027, 862, 810, 764, 703 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34–7.30 (m, 1H), 5.26 (d, $J = 2.0$ Hz, 1H), 5.04 (d, $J = 2.0$ Hz, 1H), 4.39 (dd, $J = 11.1$, 2.4 Hz, 1H), 4.32 (app dt, $J = 10.8$, 7.6 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.24–3.16 (m, 1H), 2.88 (app dt, $J = 10.2$, 7.5 Hz, 1H), 1.67–1.57 (comp, 2H), 1.29–1.20 (comp, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.88, 141.78, 128.73, 128.08, 127.14, 126.27, 119.61, 110.92, 110.13, 102.99, 69.10, 55.95, 55.94, 52.17, 49.57, 27.61, 25.93; m/z (ESI–MS) 322.2 [M$^+$]+.
(±) 1j: Following the general procedure, (E)-3-(4-bromophenyl)-1-(3-chlorophenyl)prop-2-en-1-one and pyrrolidine were heated at reflux for 3 h. The residue was purified via silica gel chromatography in 60:40 hexanes/EtOAc resulting in the isolation of 191 mg of (±) 1j as a colorless oil (51% yield). Rf = 0.33 in hexanes/EtOAc 60:40 v/v; IR (KBr) 3069, 2971, 2921, 2876, 2829, 2366, 2318, 1901, 1737, 1683, 1620, 1588, 1480, 1421, 1355, 1240, 1067, 1005, 765; 1H NMR (500 MHz, CDCl3) δ 7.59 (s, 1H), 7.49–7.44 (comp, 3H), 7.31–7.28 (comp, 2H), 7.15–7.13 (comp, 2H), 5.09 (d, J = 1.7 Hz, 1H), 4.41–4.36 (comp, 2H), 3.20 (ddd, J = 11.7, 7.2, 4.7 Hz, 1H), 2.81 (app dt, J = 10.3, 7.5 Hz, 1H), 1.64–1.58 (comp, 2H), 1.34–1.23 (m, 1H), 1.23–1.12 (m, 1H); 13C NMR (125 MHz, CDCl3) δ 153.73, 140.29, 135.76, 134.19, 131.15, 130.30, 129.51, 127.96, 127.00, 125.03, 120.16, 104.49, 68.76, 51.87, 48.91, 27.54, 25.83; m/z (ESI–MS) (79Br, 35Cl) 374.3 [M+H]+, (81Br, 35Cl) 376.1 [M+H]+, (81Br, 37Cl) 378.1 [M+H]+.

(±) 2a: Following the general procedure, (E)-chalcone and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 24 h. The residue was purified via silica gel chromatography in 90:10 hexanes/EtOAc, resulting in the isolation of 257 mg of (±) 2a as a yellow oil (79% yield). Rf = 0.18 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3025, 2932, 2828, 1951, 1595, 1493, 1455, 1390, 1319, 1262, 1234, 1152, 1129, 1042, 1028, 912, 755, 735, 699 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.55–7.53 (comp, 3H), 7.47–7.34 (comp, 4H), 7.36–7.27 (comp, 3H), 7.22–7.21 (m, 1H), 7.18–7.08 (comp, 2H), 6.92 (dd, J = 8.4, 5.9, 2.7 Hz, 1H), 4.28 (dd, J = 13.3, 9.7 Hz, 1H), 3.23–3.01 (comp, 3H), 2.93 (dd, J = 15.4, 13.2 Hz, 1H), 2.83 (app dt, J = 15.6, 3.5 Hz, 1H), 2.74 (app td, J = 10.9, 3.7 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 142.67, 139.58, 139.11, 135.32, 128.97, 128.73, 128.50, 128.48, 128.46, 127.59, 127.43, 127.32, 126.52, 126.06, 125.47, 111.85, 69.76, 46.19, 46.08, 30.63; m/z (ESI–MS) 324.3 [M+H]+.

(±) 2b: Following the general procedure, (E)-chalcone and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline were heated at reflux for 5 h. The residue was purified via silica gel chromatography in 60:39:1 hexanes/EtOAc/Et3N, resulting in the isolation of 195 mg of (±) 2b as a colorless oil (51% yield). Rf = 0.43 in EtOAc; IR (KBr) 3054, 3004, 2949, 2925, 2830, 1660, 1605, 1513, 1409, 1351, 1228, 1148, 1096, 1015, 873, 760, 700; 1H NMR (500 MHz, CDCl3) δ 7.57–7.56 (comp, 2H), 7.45–7.44 (comp, 2H), 7.41–7.30 (comp, 5H), 7.22–7.19 (m, 1H), 7.06 (s, 1H, 6.61 (s, 1H), 4.25 (dd, J = 13.1, 9.7 Hz, 1H), 3.85 (s, 3H), 3.36 (s, 3H), 3.25–3.03 (comp, 3H), 3.02–2.88 (m, 1H), 2.76–2.69 (comp, 2H); 13C NMR (125 MHz, CDCl3) δ 148.52, 146.52, 142.58, 139.57, 139.28, 129.19, 128.38, 128.05, 127.36, 127.22, 126.06, 121.14, 110.54, 110.19, 109.17, 69.90, 55.65, 55.03, 46.53, 45.99, 30.05; m/z (ESI–MS) 384.3 [M+H]+.
4a: Following the general procedure, trans-cinnamaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 15 min. The residue was purified via silica gel chromatography in 79:20:1 hexanes/EtOAc/Et₃N, resulting in the isolation of 4a as a yellow oil (3–6% yield). R₇ = 0.06 in hexanes/EtOAc v/v/v; IR (KBr) 3054, 2935, 2827, 1606, 1493, 1475, 1456, 1333, 1291, 1258, 1155, 1043, 757, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.45–7.44 (m, 1H), 7.40–7.36 (comp, 2H), 7.36–7.31 (comp, 2H), 7.25–7.20 (m, 1H), 7.15–7.07 (comp, 2H), 6.91–6.85 (m, 1H), 3.25 (2H), 6.90 (±) 7.34–7.33 (comp, 2H). Following the general procedure, (±) 4b as a yellow oil (68% yield). R₇ = 0.12 in hexanes/EtOAc 70:30 v/v; IR (KBr) 3075, 2954, 2925, 2808, 1626, 1493, 1472, 1456, 1393, 1330, 1289, 1260, 1156, 756, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.4–7.34 (comp, 2H); 7.31–7.25 (comp, 3H), 7.18 (app d, J = 8.1 Hz, 1H), 7.11 (app d, J = 7.6 Hz, 1H), 7.09–7.04 (m, 1H), 6.82 (app t, J = 7.6 Hz, 1H), 3.48 (app t, J = 8.7 Hz, 1H), 3.21–2.89 (comp, 5H), 2.78 (app t, J = 8.7 Hz, 1H), 1.04 (d, J = 6.7 Hz, 3H); ¹⁳C NMR (125 MHz, CDCl₃) δ 139.58, 138.60, 135.03, 129.77, 128.65, 128.52, 127.20, 126.38, 126.29, 125.44, 120.00, 104.75, 61.52, 48.41, 41.60, 30.43, 17.85; m/z (ESI–MS) 262.3 [M+H]+.

(±) 4c: Following the general procedure, (E)-3-(4-fluorophenyl)-2-methylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et₃N, resulting in the isolation of 163 mg of (±) 4c as a yellow oil (51% yield). R₇ = 0.24 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3059, 2959, 2901, 2886, 2849, 2814, 1891, 1618, 1593, 1495, 1487, 1445, 1390, 1330, 1285, 1153, 932, 825, 770; ¹H NMR (500 MHz, CDCl₃) δ 7.31–7.24 (comp, 2H); 7.20–7.18 (m, 1H), 7.17–7.08 (comp, 4H), 6.90–6.87 (m, 1H), 3.50 (app t, J = 8.7 Hz, 1H), 3.24–3.00 (comp, 4H), 2.99–2.93 (m, 1H), 2.81 (app t, J = 8.6 Hz, 1H), 1.07 (d, J = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.60 (d, J = 245.1 Hz) 139.91, 135.08, 134.41 (d, J = 3.4 Hz), 131.30 (d, J = 7.7 Hz), 128.58, 128.55, 127.30, 126.08, 125.45, 118.49, 115.61 (d, J = 21.1 Hz), 61.35, 48.22, 41.54, 30.36, 17.75; m/z (ESI–MS) 280.2 [M+H]+.

(±) 4d: Following the general procedure, (E)-3-(4-chlorophenyl)-2-methylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et₃N, resulting in the isolation of 194 mg of (±) 4d as a colorless oil (66% yield). R₇ = 0.28 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3020, 2961, 2905, 2825, 1610, 1488, 1475, 1456, 1298, 1259, 1159, 1087, 820 737; ¹H NMR (500 MHz, CDCl₃) δ 7.34–7.33 (comp, 2H), 7.23–7.21 (comp, 3H), 7.15–7.07 (comp, 2H), 6.90–6.84 (m, 1H),
3.47 (app t, J = 8.8 Hz, 1H), 3.11–3.11 (m, 1H), 3.10–2.99 (comp, 3H), 2.99–2.90 (m, 1H), 2.80 (app t, J = 8.5 Hz, 1H), 1.04 (d, J = 6.8 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 140.10, 137.05, 135.14, 131.90, 131.05, 128.80, 128.54, 128.40, 127.42, 126.12, 125.46, 117.86, 61.22, 48.01, 41.26, 30.31, 17.75; m/z (ESI–MS) (35Cl) 296.3 [M+H]⁺, (37Cl) 298.3 [M+H]⁺.

(±) 4e: Following the general procedure, (E)-3-(4-bromophenyl)-2-methylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et3N, resulting in the isolation of 217 mg of (±) 4e as a yellow oil (64% yield). Rf = 0.28 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3059, 3037, 3018, 2955, 2928, 2901, 2813, 1902, 1679, 1648, 1606, 1487, 1389, 1262, 1157, 1070, 1010, 815, 730; 1H NMR (500 MHz, CDCl3) δ 7.55–7.46 (comp, 2H), 7.27–7.25 (m, 1H), 7.20–7.18 (comp, 2H), 7.15–7.08 (comp, 2H), 6.91–6.88 (m, 1H), 3.49 (app t, J = 8.8 Hz, 1H), 3.19–3.13 (m, 1H), 3.10–3.01 (comp, 3H), 3.01–2.94 (m, 1H), 2.83 (app t, J = 8.5 Hz, 1H), 1.06 (d, J = 6.8 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 140.48, 137.91, 135.52, 132.09, 131.78, 128.91, 128.75, 127.82, 126.50, 125.84, 120.37, 118.11, 61.56, 48.33, 41.55, 30.68, 18.14; m/z (ESI–MS) (79Br) 340.3 [M+H]⁺, (81Br) 342.2 [M+H]⁺.

(±) 4f: Following the general procedure, (E)-3-(3-chlorophenyl)-2-methylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et3N, resulting in the isolation of 168 mg of (±) 4f as a colorless oil (57% yield). Rf = 0.32 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3059, 3019, 2954, 2924, 2901, 2809, 2774, 1678, 1583, 1455, 1325, 1260, 1158, 735, 1H NMR (500 MHz, CDCl3) δ 7.30–7.23 (comp, 3H), 7.22–7.15 (comp, 2H), 7.14–7.07 (comp, 2H), 6.92–6.84 (m, 1H), 3.47 (app t, J = 8.8 Hz, 1H), 3.17–3.11 (m, 1H), 3.09–3.00 (comp, 3H), 2.99–2.92 (m, 1H), 2.80 (app t, J = 8.5 Hz, 1H), 1.04 (d, J = 6.7 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 140.62, 140.39, 135.25, 134.33, 129.85, 129.63, 128.59, 128.35, 128.04, 127.55, 126.40, 126.28, 125.56, 117.77, 61.29, 48.03, 41.31, 30.34, 17.83; m/z (ESI–MS) (35Cl) 296.3 [M+H]⁺, (37Cl) 298.2 [M+H]⁺.

(±) 4g: Following the general procedure, (E)-2-(4-chlorobenzylidene)butanal and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 80:19:1 hexanes/EtOAc/Et3N, resulting in the isolation of 135 mg of (±) 4g as a colorless oil (44% yield). Rf = 0.31 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3057, 3046, 3019, 2958, 2931, 2898, 2813, 1611, 1490, 1475, 1457, 1265, 1157, 1089, 834, 730; 1H NMR (500 MHz, CDCl3) δ 7.34–7.33 (comp, 2H), 7.26–7.16 (comp, 3H), 7.16–7.07 (comp, 2H), 6.89–6.86 (m, 1H), 3.44 (app t, J = 8.8 Hz, 1H), 3.07–2.94 (comp, 5H), 2.90 (app t, J = 8.5 Hz, 1H), 1.50–1.44 (m, 1H), 1.35–1.24 (m, 1H), 0.86 (t, J = 7.4 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ 140.38, 137.31, 135.21, 131.93, 131.17, 128.86, 128.60, 128.49, 127.45, 126.25, 125.51, 116.82, 58.55, 48.42, 48.07, 30.44, 25.12, 11.67; m/z (ESI–MS) (35Cl) 310.5 [M+H]⁺, (37Cl) 312.4 [M+H]⁺.
(±) 4h: Following the general procedure, (E)-3-(4-bromophenyl)-2-ethylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 80:19:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 245 mg of (±) 4h as a yellow oil (69% yield). R$_f$ = 0.31 in hexanes/EtOAc 50:50 v/v; IR (KBr) 2956, 2929, 2871, 2809, 1645, 1485, 1388, 1330, 1260, 1153, 1070, 1008, 737; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53–7.43 (comp, 2H), 7.22–7.21 (m, 1H), 7.19–7.15 (m, 2H), 7.14–7.08 (comp, 2H), 6.90–6.85 (m, 1H), 3.44 (app t, $J$ = 8.8 Hz, 1H), 3.11–2.94 (comp, 5H), 2.90 (app t, $J$ = 8.4 Hz, 1H), 1.51–1.44 (m, 1H), 1.34–1.25 (m, 1H), 0.86 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.39, 137.80, 135.22, 131.78, 131.53, 128.60, 128.46, 127.48, 126.57, 125.52, 120.02, 116.72, 58.51, 48.33, 48.02, 30.43, 25.11, 11.66; m/z (ESI–MS) $^{79}$Br 354.3 [M+H]$^+$, $^{81}$Br 356.2 [M+H]$^+$.

(±) 4i: Following the general procedure, (E)-3-(furan-2-yl)-2-methylacrylaldehyde and 1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 181 mg of (±) 4i as a yellow oil (72% yield). R$_f$ = 0.25 in hexanes/EtOAc 50:50 v/v; IR (KBr) 2956, 2907, 2820, 2782, 1612, 1495, 1457, 1400, 1371, 1290, 1158, 1013, 799, 768, 732 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.66–7.64 (m, 1H), 7.46–7.40 (m, 1H), 7.24–7.14 (comp, 2H), 7.12–7.06 (m, 1H), 6.48 (ddd, $J$ = 2.9, 1.9, 0.9 Hz, 1H), 6.31–6.30 (m, 1H), 3.45–3.38 (m, 1H), 3.23–3.14 (m, 1H), 3.09–3.00 (comp, 4H), 2.98–2.94 (m, 1H), 1.19 (dd, $J$ = 6.7, 0.6 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.01, 143.05, 140.72, 135.81, 128.56, 128.53, 128.26, 127.04, 126.07, 111.30, 107.60, 107.24, 61.03, 47.51, 39.75, 30.60, 18.76; m/z (ESI–MS) $^{79}$Br 252.3 [M+H]$^+$.

(±) 4j: Following the general procedure, (E)-α-methylcinnamaldehyde and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 163 mg of (±) 4j as a yellow oil (51% yield). R$_f$ = 0.14 in hexanes/EtOAc 50:50 v/v; IR (KBr) 3059, 3001, 2954, 2926, 2901, 2829, 2053, 1951, 1881, 1810, 1628, 1603, 1468, 1275, 1220, 1148, 1095, 1020, 867, 760, 700; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39–7.36 (comp, 2H), 7.33–7.29 (comp, 2H), 7.25–7.22 (m, 1H), 6.70 (s, 1H), 6.56 (s, 1H), 3.81 (s, 3H), 3.47 (app t, $J$ = 8.6 Hz, 1H), 3.23 (s, 3H), 3.20–3.10 (m, 1H), 3.11–2.96 (comp, 2H), 2.96–2.83 comp, 2H), 2.74 (app t, $J$ = 8.7 Hz, 1H), 1.06 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.16, 146.43, 139.64, 138.77, 130.19, 128.52, 127.71, 126.29, 121.00, 118.06, 110.52, 108.89, 61.60, 55.57, 54.70, 48.75, 41.34, 29.78, 17.85; m/z (ESI–MS) 322.2 [M+H]$^+$.
Following the general procedure, (E)-α-methylcinnamaldehyde and 2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole were heated at reflux for 1 h. The residue was purified via silica gel chromatography in 70:29:1 hexanes/EtOAc/Et$_3$N, resulting in the isolation of 92 mg of (±) 4k as a colorless oil (31% yield). $R_f = 0.23$ in hexanes/EtOAc 50:50 v/v; IR (KBr) 3453, 3053, 2895, 2815, 1952, 1915, 1881, 1813, 1763, 1632, 1537, 1494, 1265, 1189, 1154, 780; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (br s, 1H), 7.54–7.52 (m, 1H), 7.50–7.47 (comp, 4H), 7.38–7.35 (m, 1H), 7.21–7.13 (comp, 2H), 7.12–7.06 (m, 1H), 3.56 (app t, $J = 8.5$ Hz, 1H), 3.45–3.37 (m, 1H), 3.23–3.15 (m, 1H), 3.14–3.01 (comp, 3H), 2.86 (app t, $J = 8.6$ Hz, 1H), 1.16 (d, $J = 6.7$ Hz, 3H); $m/z$ (ESI–MS) 301.3 [M+H]$^+$. Reduction of (±) 1d

To a stirred solution of (±) 1d (0.441 mmol, 0.15 g) in MeOH (4.4 mL) at 0 °C was added NaBH$_4$ (3.97 mmol, 0.15 g). The reaction mixture was stirred at room temperature for 15 h. The reaction was then quenched by addition of saturated NaHCO$_3$ (aq) (10 mL). The resulting mixture was stirred vigorously for 1 h, diluted with EtOAc (50 mL) and the organic layer was washed with NaHCO$_3$ (3 x 30 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$. Solvent was removed under reduced pressure and the residue was purified by silica gel chromatography in 70:30 hexanes/EtOAc. Products (±) 5 and (±) 5'$^*$ were obtained in a 1.1:1 ratio, 78% combined yield.

(±) 5: Colorless oil. $R_f = 0.11$ in hexanes/EtOAc 50:50 v/v; IR (KBr) 3081, 3056, 3025, 2954, 2926, 2869, 1676, 1600, 1478, 1449, 1403, 1365, 1288, 1071, 823, 700; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48–7.47 (comp, 2H), 7.45–7.42 (comp, 2H), 7.39–7.35 (comp, 2H), 7.32–7.27 (m, 1H), 7.21–7.19 (comp, 2H), 4.18 (dd, $J = 11.0, 5.0$ Hz, 1H), 3.73–3.63 (m, 1H), 3.57–3.48 (m, 1H), 2.41–2.31 (comp, 3H), 2.30–2.17 (m, 1H), 1.79–1.59 (comp, 2H), 1.49–1.37 (m, 1H), 1.00–0.91 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.89, 139.96, 131.08, 129.81, 128.20, 128.07, 127.09, 119.73, 69.16, 65.02, 49.36, 45.22, 34.80, 27.72, 26.28; $m/z$ (ESI–MS) (81)Br 342.2 [M+H]$^+$, (81)Br 344.2 [M+H]$^+$.
(±) 5°: Colorless oil. \( R_f = 0.33 \) in hexanes/EtOAc 60:40 v/v; IR (KBr) 3057, 3026, 2958, 2869, 2788, 2371, 2319, 2270, 1949, 1896, 1736, 1601, 1489, 1450, 1264, 1170, 1072, 1009, 737; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.47–7.40 \) (comp, 3H), 7.36–7.33 (comp, 2H), 7.28–7.26 (comp, 2H), 7.11–7.09 (comp, 2H), 4.03 (dd, \( J = 8.0, 4.1 \) Hz, 1H), 4.00–3.92 (m, 1H), 3.68 (app q, \( J = 7.7 \) Hz, 1H), 3.21 (ddd, \( J = 11.2, 7.5, 4.2 \) Hz, 1H), 2.75 (app dt, \( J = 10.3, 7.5 \) Hz, 1H), 2.53 (ddd, \( J = 12.3, 10.0, 8.3 \) Hz, 1H), 2.13 (ddd, \( J = 12.2, 7.3, 4.2 \) Hz, 1H), 1.86 1.83 (m, 1H), 1.79–1.66 (m, 1H), 1.37–1.34 (m, 1H), 1.20–1.09 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta 140.59, 131.20, 129.49, 128.26, 126.64, 126.53, 119.76, 69.40, 69.07, 55.37, 44.16, 36.78, 27.97, 25.90; \( m/z \) (ESI–MS) (\(^{79}\)Br) 342.2 [M+H]+, (\(^{81}\)Br) 344.2 [M+H]+.

**Synthesis of (±) 5-BH\(_3\)**

\[
\begin{align*}
\text{(±) 1d} & \quad \xrightarrow{\text{NaBH}_4, \text{MeOH}} \quad \text{(±) 5-BH}_3 \\
& \quad + \quad \text{(±) 5} \\
& \quad + \quad \text{(±) 5°}
\end{align*}
\]

Ratio of 5-BH\(_3\), 5, and 5° = 1:1:2

To a stirred solution of (±) 1d (0.441 mmol, 0.15 g) in MeOH (4.4 mL) at 0 °C was added NaBH\(_4\) (3.97 mmol, 0.15 g). The reaction mixture was stirred at room temperature for 15 h. The reaction was then quenched by addition of water (10 mL) and diluted with EtOAc (50 mL) and the organic layer was washed with water (3 x 30 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\). Solvent was removed under reduced pressure and the residue purified by silica gel chromatography in 90:10 hexanes/EtOAc to give (±) 5-BH\(_3\) as an off-white solid in 19% yield.

(±) 5-BH\(_3\): Off-white solid. mp: 144–145 °C; \( R_f = 0.33 \) in hexanes/EtOAc 90:10 v/v; IR (KBr) 3064, 3039, 2949, 2924, 2851, 2406, 2361, 2316, 2263, 1943, 1891, 1743, 1488, 1453, 1378, 1165, 1070, 815, 760, 692; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.79–7.63 \) (comp, 2H), 7.49–7.48 (comp, 2H), 7.44–7.35 (comp, 3H), 7.16–7.14 (comp, 2H), 4.76 (dd, \( J = 13.2, 4.4 \) Hz, 1H), 4.35–4.15 (m, 1H), 3.90 (ddd, \( J = 13.1, 8.3, 5.1 \) Hz, 1H), 2.73–2.53 (comp, 3H), 2.34–2.23 (m, 1H), 1.99–1.94 (m, 1H), 1.67–1.64 (comp, 2H), 1.31–1.15 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta 137.25, 133.57, 131.61, 130.43, 129.27, 129.07, 128.21, 120.80, 78.74, 73.70, 58.46, 42.25, 30.88, 29.72, 24.72; \( m/z \) (ESI–MS) (\(^{79}\)Br) 342.3 [M–BH\(_3\)]+, (\(^{81}\)Br) 344.3 [M–BH\(_3\)]+. 

S 10
(±) 5-BH$_3$ was further characterized by X-ray crystallography: The compound was crystallized from hexanes/ethyl acetate through slow diffusion at room temperature. The relative configuration was assigned by X-ray crystallography.

The requisite CIF has been deposited with the CCDC (deposition # 1061075).

**Reduction of (±) 4b**

![Reduction of (±) 4b](image)

To a stirred solution of (±) 4b (0.131 g, 0.5 mmol) and AcOH (0.057 mL, 1.0 mmol) in MeOH (5 mL) at 0 °C was added NaBH$_4$ (1.5 mmol, 0.057 g). Three equivalents of NaBH$_4$ were added every half hour until a total of 9 equivalents was added. The reaction mixture was stirred at room temperature for 15 h, quenched with K$_2$CO$_3$ (aq) (10 mL) and extracted with EtOAc (3 x 20 mL). The organic layers were dried over anhydrous Na$_2$SO$_4$. Solvent was removed under reduced pressure and the residue purified by silica gel chromatography in 60:40 hexanes/EtOAc to give product (±) 6 as a colorless oil in 4:1 ratio, 85% combined yield.

(±) 6: Colorless oil. R$_f$ = 0.33 in hexanes/EtOAc 60:40 v/v; IR (KBr) 3060, 3023, 2952, 2925, 2782 1679, 1651, 1602, 1492, 1453, 1373, 1161, 735, 701; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.23–7.24 (comp, 2H), 7.13–7.08 (comp, 2H), 7.05–7.00 (comp, 2H), 6.97–6.92 (m, 1H), 6.81–6.78 (m, 1H), 6.58–6.67 (m, 1H), 3.69 (d, $J$ = 7.4 Hz, 1H), 3.44 (app t, $J$ = 8.0 Hz, 1H), 3.34 (dd, $J$ = 10.9, 6.4 Hz, 1H), 3.26–3.15 (comp, 2H), 2.77 (dd, $J$ = 16.2, 3.6 Hz, 1H), 2.47 (app td, $J$ = 11.1, 3.6 Hz, 1H), 2.40–2.25 (m, 1H), 2.11 (app t, $J$ = 8.6 Hz, 1H), 1.22 (dd, $J$ = 6.9, 0.8 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.53, 136.34, 135.30, 129.07, 128.26, 127.72, 126.94, 125.46, 125.18, 124.89, 68.18, 62.44, 55.31, 49.74, 42.91, 29.79, 19.46; m/z (ESI–MS) 264.6 [M+H]$^+$. 

S 11
Preparation of (±) 6·HCl

To a stirred solution of 6 (0.536 mmol, 141.1 mg) in dioxane (1.0 mL) was added 4N HCl in dioxane (1.07 mmol, 0.268 mL). The resulting mixture was stirred for 1 h at rt. The solvent was then removed to yield the salt (±) 6·HCl.

(±) 6·HCl: Green solid. mp: 193–195 °C; R_f = 0.13 in EtOAc/MeOH 80:20 v/v; IR (KBr) 3059, 3031, 2961, 2929, 2906, 2875, 2578, 1709, 1453, 1376, 1218, 1111, 701; ¹H NMR (500 MHz, CDCl₃) δ 13.38 (br s, 1H), 7.25–7.14 (comp, 3H), 7.14–7.05 (m, 1H), 6.82–6.68 (comp, 3H), 5.88 (app d, J = 7.9 Hz, 1H), 5.31–5.20 (m, 1H), 3.71–3.61 (comp, 2H), 3.59–3.52 (m, 1H), 3.49–3.43 (m, 1H), 3.34 (app t, J = 12.2 Hz, 1H), 3.25–3.15 (m, 1H), 2.94 (app d, J = 16.9 Hz, 1H), 2.44–2.37, (m, 1H), 0.99 (d, J = 6.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 134.21, 132.33, 129.53, 129.04, 128.36, 128.20, 128.01, 127.83, 127.49, 126.06, 65.03, 58.19, 57.11, 47.72, 36.22, 23.29, 14.51; m/z (ESI–MS) 264.2 [M+H–Cl]⁺.

(±) 6·HCl was further characterized by X-ray crystallography: The compound was crystallized from hexanes/dichloromethane through slow diffusion at room temperature. The relative configuration was assigned by X-ray crystallography.

The requisite CIF has been deposited with the CCDC (deposition # 1061074).
Oxidation of (±) 1a

To a stirred solution of 1a (50 mg, 0.19 mmol) in toluene (2 mL) was added TEMPO (5.9 mg, 20 mol%). The reaction mixture was heated at reflux for 8 h under air, concentrated and the residue purified by silica gel chromatography in 95:5 hexanes/EtOAc to give 7 as a brown solid in 94% yield.

7: Brown solid. mp: 149–150 °C; Rf = 0.35 in hexanes/EtOAc 90:10 v/v; IR (KBr) 3096, 3051, 3024, 2986, 2954, 2899, 2874, 1948, 1871, 1813, 1745, 1600, 1518, 1485, 1383, 1295, 1278, 1183, 1143, 1070, 792, 695; 1H NMR (500 MHz, CDCl3) δ 7.59–7.56 (comp, 4H), 7.45–7.40 (comp, 4H), 7.30–7.27 (m, 1H), 7.23–7.21 (m, 1H), 6.79 (s, 1H), 4.18 (t, J = 7.1 Hz, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.70–2.51 (comp, 2H); 13C NMR (125 MHz, CDCl3) δ 136.64, 136.23, 133.64, 129.56, 128.95, 128.87, 126.20, 126.02, 125.43, 124.95, 116.40, 108.91, 46.92, 28.18, 25.61; m/z (ESI–MS) 260.4 [M+H]+.
References:


$^1\text{H NMR of (±) 1a}$
$^{13}$C NMR of (±) 1a
$^1$H NMR of (R) 1b
$^1$H NMR of (b) 1d
$^{13}$C NMR of (±) 1d
$^1$H NMR of (±) 1e

![NMR spectrum diagram]
$^{13}$C NMR of (t) 1e
$^1$H NMR of (±) 1f
$^{13}$C NMR of (d) 1g
$^{13}$C NMR of (±) 1h
$^{13}$C NMR of (±) 1i
$^1$H NMR of (±) 1
$^{13}$C NMR of (±) 1j
$^1$H NMR of 4a
$^1$H NMR of (2) 4b
$^{13}$C NMR of (±) 4b
$^1$H NMR of (±) 4c
$\text{H NMR of (t) 4d}$
$^1$H NMR of (±) 4e
$^{13}$C NMR of (±) 4e
$^1$H NMR of (4f)
$^{13}$C NMR of (2) 4f
$^1$H NMR of (±) 4g
$^1$H NMR of (3) 4h
$^{13}$C NMR of (4) 4h
$^1$H NMR of (±) 4i
$^{13}$C NMR of (t) 4l
$^1\text{H NMR of (4) 4j}$
$^1$H NMR of (±) 4k
$^{13}$C NMR of (±) 4k
$^{13}$C NMR of (±) 5
$^1$H NMR of (±) 5'
$^1$H NMR of (±) 5-BH$_3$
$^{13}$C NMR of (t) 5·$BH_3$
$^1$H NMR of (±) 6
$^{13}$C NMR of (3) 6
$^1$H NMR of (2) 6·HCl
$^{13}$C NMR of (8) 6-HCl
$^1$H NMR of 7