**Supporting Information**

# A Facile Stereocontrolled Synthesis of *anti*-α-(Trifluoromethyl)-β-Amino Alcohols

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**6a**: $^1$H NMR (360 MHz, $CDCl_3$) δ 2.16 (s, 3H), 3.37 (d, 1H, $J$ = 13.4 Hz), 3.63 (d, 1H, $J$ = 13.4 Hz), 4.02 (d, 1H, $J$ = 6.9 Hz), 4.52 (m, 1H), 6.31 (m, 1H), 7.20–7.25 (d, 4H, $J$ = 3.4 Hz), 7.44 (m, 1H); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 38.6, 59.5, 60.5, 70.2, (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 110.2, 110.6, 124.4, (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.2, 128.3, 128.5, 138.5, 142.6, 149.2; $^{19}$F NMR (360 MHz, $CDCl_3$): δ= –76.52 (d, $J_{F\text{-}H}$ = 5.9 Hz); HRMS (DEI) *m/z* 299.1127 [$M^+$], calcd for $C_{15}H_{16}F_3NO_2$ 299.1133.

**6b** $^1$H NMR (360 MHz, $CDCl_3$) δ 3.27 (d, 2H, $J$ = 14.3 Hz), 3.90 (d, 1H, $J$ = 14.3 Hz), 4.83 (m, 1H),5.15 (d, 1H, $J$ = 6.9 Hz), 7.23–7.39 (m, 11H), 7.47–7.52 (m, 1H), 7.57–7.66 (m, 2H), 7.77–7.79 (m, 1H), 7.88–7.92 (m, 1H); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 29.6, 55.2, 71.0, (q, $^2J_{C\text{-}F}$ = 29.3 Hz), 123.8, 124.7, 124.9, (q, $^1J_{C\text{-}F}$ = 281 Hz), 125.8, 126.2, 126.7, 127.2, 128.3, 128.7, 128.8, 129.0, 130.0, 133.7, 134.0, 1.39.1; $^{19}$F NMR (360 MHz, $CDCl_3$) δ –75.16 (d, $J_{F\text{-}H}$ = 5.7 Hz); HRMS (CI, $NH_3$) *m/z* 392.1303 [$M^+$], calcd for $C_{21}H_{21}F_3NOS$ 392.1295.

**6c** $^1$H NMR (360 MHz, $CDCl_3$): δ 3.25 (d, 2H, $J$ = 13.7 Hz), 3.86 (d, 2H, $J$ = 13.6 Hz), 4.35 (d, 1H, $J$ = 5.9 Hz), 4.47 (m, 1H), 6.94 (d, 1H, $J$ = 3.3 Hz), 7.05 (m, 1H), 7.16–7.35 (m, 11H); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 54.9, 58.1, 71.7, (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 124.4, (q, $^1J_{C\text{-}F}$ = 283 Hz), 126.0, 126.8, 127.3, 128.4, 128.7, 128.8, 134.7, 138.5; $^{19}$F NMR (360 MHz, $CDCl_3$) δ –76.29 (d, $J_{F\text{-}H}$ = 6.3); HRMS (CI, $NH_3$) *m/z* 436.1869 [$M^+$], calcd for $C_{27}H_{25}F_3NO$ 436.1888.

**6d** $^1$H NMR (360 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.66 (d, 1H, $J$ = 12.9 Hz), 3.83 (d, 1H, $J$ = 12.9 Hz), 4.16 (dd, 1H, $J$ = 9.6, 4.4 Hz), 4.3 (m, 1H), 6.43 (d, 1H, $J$ = 9.7 Hz), 7.10–7.50 (m, 10H); $^{13}$C NMR (90 MHz, $CDCl_3$) δ 39.0, 59.5, 64.6, 70.7, (q, $^2J_{C\text{-}F}$ = 28.8 Hz), 123.9, 124.6, (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.3, 127.8, 128.3, 128.4, 129.2, 130.4, 138.4, 139.5;127.2, 128.3, 128.5, 138.5, 139.5 $^{19}$F NMR (360 MHz, $CDCl_3$) δ –75.50 (d, $J_{F\text{-}H}$ = 7.4 Hz); HRMS (CI, $NH_3$) *m/z* 414.0670 [$M^+$], calcd for $C_{19}H_{20}F_3BrNO$ 414.0680.

**6e** $^1$H NMR (360 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.40–3.50 (m, 2H), 3.77 (d, 1H, $J$ = 13.4 Hz), 4.26 (m, 1H), 6.31 (dd, 1H, $J$ = 15.7, 9.8 Hz), 6.61 (d, 1H, 15.7 Hz), 7.22–7.43 (m,

10H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 38.7, 59.2, 65.6, 70.8, (q, $^2J_{C\text{-}F}$ = 29.2 Hz), 121.7, 124.8, (q, $^1J_{C\text{-}F}$ = 283 Hz), 126.6, 127.3, 128.0, 128.4, 128.6, 136.2, 136.3, 136.5; $^{19}F$ NMR (360 MHz, $CDCl_3$) δ –75.48 (d, $J_{F\text{-}H}$ = 6.6); HRMS (CI, $NH_3$) *m/z* 336.1584 [$M^+$], calcd for $C_{19}H_{21}F_3NO$ 336.1575.

**6f** $^1H$ NMR (360 MHz, $CDCl_3$) δ 3.10 (d, 2H, *J* = 13.6 Hz), 3.93 (d, 2H, *J* = 13.7 Hz), 4.02 (d, 1H, *J* = 7.7 Hz), 4.60 (m, 1H), 6.97 (d, 2H, *J* = 8.6 Hz), 7.20–7.35 (m, 12H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 54.8, 55.3, 62.3, 70.3, (q, $^2J_{C\text{-}F}$ = 28.5 Hz), 113.8, 124.4, 124.8, (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.2, 128.4, 128.8, 131.3, 138.8, 159.5; $^{19}F$ NMR (360 MHz, $CDCl_3$) δ –75.42 (d, $J_{F\text{-}H}$ = 6.5); HRMS (CI, $NH_3$) *m/z* 416.1841 [$M^+$], calcd for $C_{24}H_{25}F_3NO_2$ 416.1837.

**6g** $^1H$ NMR (360 MHz, $CDCl_3$) δ 2.20, (b, 1H), 2.80 (s, 3H), 3.43 (d, 1H, *J* = 13.4 Hz), 3.60 (d, 1H, *J* = 12.9 Hz), 4.60 (d, 1H, *J* = 7.8 Hz), 6.60 (m, 1H), 7.20–7.30 (m, 7H), 7.40 (m, 1H), 7.52 (m, 1H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 36.6, 59.6, 61.0, 69.9, (q, $^2J_{C\text{-}F}$ = 29.4 Hz), 107.5, 111.3, 121.1, 123.0, 124.4, 124.5, (q, $^1J_{C\text{-}F}$ = 283 Hz), 127.3, 127.7, 128.3, 128.8, 138.3, 151.7, 154.8; $^{19}F$ NMR (90 MHz, $CDCl_3$) δ –76.28 (d, $J_{F\text{-}H}$ = 6.1 Hz); HRMS (CI, $NH_3$) *m/z* 350.1368 [$M^+$], calcd for $C_{19}H_{19}F_3NO_2$ 350.1367.

**6h** $[\alpha]_D$ = + 33.0 (c = 1.0 g / 1.0 ml $CHCl_3$); $^1H$ NMR (360 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.66 (d, 1H, *J* = 12.9 Hz), 3.83 (d, 1H, *J* = 12.9 Hz), 4.16 (dd, 1H, *J* = 9.6, 4.4 Hz), 4.3 (m, 1H), 6.43 (d, 1H, *J* = 9.7 Hz), 7.10–7.50 (m, 10H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 39.0, 59.5, 64.6, 70.7, (q, $^2J_{C\text{-}F}$ = 28.8 Hz), 123.9, 124.6, (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.3, 127.8, 128.3, 128.4, 129.2, 130.4, 138.4, 139.5;127.2, 128.3, 128.5, 138.5, 139.5 $^{19}F$ NMR (360 MHz, $CDCl_3$) δ –75.50 (d, $J_{F\text{-}H}$ = 7.4 Hz); HRMS (CI, $NH_3$) *m/z* 280.09824 [$M^+$], calcd for $C_{12}H_{17}F_3NOS$ 280.0982. HPLC analysis (CHIRALCEL OD, 2-propanol/hexane/diethylamine 10/90/0.1, 1 mL $min^{-1}$, λ = 254 nm) showed the product to be of 92% ee; $t_R$: 5.60 min., minor; 10.06 min. major isomer.

Enantioselective reduction of *1,1,1-trifluoro-4-phenyl-3-buten-2-one* with BINAL-H:
The (*S*)-BINAL-H reagent was prepared by the dropwise addition of dry ethanol (0.61 ml, 0.61 mmol in 1 ml THF) and after 30 min. (*S*)-binaphthol (176 mg, 0.61 mmol in 1 ml THF) to $LiAlH_4$ (0.82 M THF solution, 0.75 ml, 0.61 mmol) at RT. After 30 min. the reducing agent was cooled to –100 °C and 1,1,1-trifluoromethyl-4-phenyl-3-buten-2-one (50 mg, 0.25 mmol in 0.25 ml THF) added over a period of 10 min. The solution was stirred at this temperature for 1 h and at –78 °C for 2 h, after which the reaction was quenched with 0.2 ml methanol and warmed up to room temperature. Water (1 ml) was added, and the mixture stirred for 1 h. Magnesiumsulfate was added, and the mixture filtered through celite. Concentration under vacuum, followed by flash chromatography (hexane/ether = 10/1) afforded 45 mg (90%) 1,1,1-trifluoro-4-phenyl-3-buten-2-ol in 71% ee.

Enantioselective reduction of *1,1,1-trifluoro-4-phenyl-3-buten-2-one* with *(S)-B-nBu-CBS*:

1,1,1-trifluoro-4-phenyl-3-buten-2-one (60 mg, 0.30 mmol) was treated with (*S*)-B-*n*Bu-CBS (0.5 M in toluene, 0.03 mmol) in 2 ml toluene. The solution was cooled down to −78 °C and catecholborane (72 mg, 0.60 mmol in 1 ml toluene) added dropwise over 1 h down the side of the flask. After the mixture had been stirred for 15 h the reaction was quenched with 0.1 ml methanol and warmed up to 0 °C. The solution was diluted with ether (20 ml), and washed with buffer (pH = 13. 1 N NaOH/sat. $NaHCO_3$ 2/1) until the aqueous washings were colorless. The dark aq. washings were extracted with ether (2 x 10 ml). The combined organic layers were washed with HCl solution (0.5 M), and the aq. layer extracted with ether (2 x 10 ml). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography (hexane/ether = 10 : 1) provided 55 mg (92%) 1,1,1-trifluoro-4-phenyl-3-buten-2-ol in 85% ee.