## Supporting Information

# Asymmetric Synthesis of Trifluoromethylated Allylic Amines Using α,β-Unsaturated *N-tert*-Butanesulfinimines

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**3a: (*R*)-(–)-*N*-(3-phenyl-allylidene)-2-methylpropanesulfinamide:** Yield 90%. $[\alpha]^{20}_{D}$ – 289 (*c* 3.7, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.23 (9H, s), 7.08 (1H, dd, *J* = 15.7 Hz, *J* = 9.04 Hz), 7.22 (1H, d, *J* = 15.7 Hz), 7.38 (3H, m), 7.53 (2H, m), 8.37 (1H, d, *J* = 9.07 Hz): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.3, 55.4, 125.5, 127.8, 128.8, 130, 134.9, 146.2, 163.6.

**3b: (*R*)-(–)-*N*-(2-methyl-3-phenyl-allylidene)-2-methylpropanesulfinamide:** Yield 87%. $[\alpha]^{20}_{D}$ – 406 (*c* 0.99, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.24 (9H, s), 2.20 (3H, s), 7.11 (1H, s), 7.32 – 7.47 (5H, m), 8.30 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 13.0, 22.5, 57.4, 128.5, 127.6, 129.7, 135,2, 135.9, 144.0, 167.

**3c: (*R*)-(–)-*N*-(3-furyl-allylidene)-2-methylpropanesulfinamide:** Yield 85%. $[\alpha]^{20}_{D}$ – 265 (*c* 1.2, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.22 (9H, s), 6.49 (1H, m), 6.63 (1H, d, *J* = 3.23 Hz), 6.97 (2H, m), 7.51 (1H, s), 8.30 (1H, d, *J* = 7.9 Hz): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.4, 57.5, 112.4, 114.3, 123.5, 131.9, 144.7, 151.3, 162.9.

**3d: (*R*)-(–)-*N*-(3-furyl-2-methyl-allylidene)-2-methylpropanesulfinamide:** Yield 83%. $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.22 (9H, s), 2.26 (3H, s), 6.52 (1H, m), 6.65 (1H, d, *J* = 3.46 Hz), 6.84 (1H, s), 7.56 (1H, m), 8.22 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 12.8, 22.4, 57.4, 112.2, 114.8, 130.0, 132.3, 144.2, 152.1, 165.9.

**3e: (*R*)-(–)-*N*-(3,3-diphenyl-allylidene)-2-methylpropanesulfinamide:** Yield 80%. $[\alpha]^{20}_{D}$ – 488 (*c* 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.22 (9H, s), 7.01 (1H, d, $J$ = 9.75 Hz), 7.21 – 7.41 (5H, m), 8.30 (1H, d, $J$ = 9.8 Hz): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.5, 57.5, 124.4, 128.4, 128.5, 128.9, 129.5, 130.4, 137.4, 140.6, 156.3, 162.3

**3f: (*R*)-(–)-*N*-(2-pentyl-3-phenyl-allylidene)-2-methylpropanesulfinamide:** Yield 75%. $[\alpha]^{20}_{D}$ – 231 (*c* 4.5, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, $J$ = 6.97 Hz), 1.24 (9H, s), 1.36 (4H, m), 1.59 (2H, m), 2.64 (2H, m), 7.06 (1H, s), 7.32 – 7.43 (5H, m), 8.30 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 13.9, 22.3, 26.6, 28.1, 32.0, 57.4, 128.5, 128.6, 129.3, 135.8, 140.1, 143.9, 166.8.

**3g: (*R*)-(–)-*N*-(2-hexyl-3-phenyl-allylidene)-2-methylpropanesulfinamide:** Yield 70%. $[\alpha]^{20}_{D}$ – 233 (*c* 4.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, $J$ = 6.97 Hz), 1.24 (9H, s), 1.30 (4H, m), 1.39 (2H, m), 1.58 (2H, m), 2.64 (2H, m), 7.05 (1H, s), 7.32 – 7.43 (5H, m), 8.23 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 13.9, 22.4, 26.6, 28.4, 29.5, 31.4, 57.3, 128.5, 128.6, 129.3, 135.7, 140.1, 143.9, 166.8.

**3h: (*R*)-(–)-*N*-(2,3-diphenyl-allylidene)-2-methylpropanesulfinamide:** Yield 86%. $[\alpha]^{20}_{D}$ – 473 (*c* 0.96, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.21 (9H, s), 7.35 – 7.48 (11H, m), 8.88 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.6, 57.7, 127.9, 128.6, 129.0, 129.1, 129.9, 134.9, 138.0, 143.2, 161.6.

**4a: ($R_S$, *S*)-(–)-*N*-(3-phenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_{D}$ – 27.3 (*c* 0.66, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.27 (9H, s), 3.47 (1H, d, $J$ = 8.2 Hz), 4.47 (1H. m), 6.21 (1H, dd, $J$ = 15.8 Hz, $J$ = 6.0 Hz), 6.91 (1H, d, $J$ = 15.8 Hz), 7.29-7.43 (5H, m): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.3, 57.0, 60.4 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 120.1, 124.6 (q, $^1J_{C\text{-}F}$ = 281 Hz), 127.0, 128.6, 128.7, 135.2, 137.2: $^{19}F$ NMR (500 MHz, $CDCl_3$): δ= – 76.3 (d, $J_{F\text{-}H}$ = 9.6 Hz).

**4b: ($R_S$, $S$)-(–)-*N*-(2-methyl-3-phenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 66.1 (*c* 1.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.26 (9H, s), 1.96 (3H, s), 3.67 (1H, d, $J$ = 8.3 Hz), 4.32 (1H, m), 6.70 (1H, s), 7.24-7.36 (5H, m): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 14.6, 22.0, 56.9, 65.1 (q, $^2J_{C\text{-}F}$ = 27.6 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.3, 128.2, 129.0, 130.4, 132.8, 136.0: $^{19}F$ NMR (500 MHz, $CDCl_3$): δ= – 73.4(d, $J_{F\text{-}H}$ = 7.5 Hz).

**4c: ($R_S$, $S$)-(–)-*N*-(3-furyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 19.6 (*c* 3.0, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.24 (9H. s), 3.54 (1H, d, $J$ = 8.1 Hz), 4.43 (1H, m), 6.17 (1H, dd, $J$ = 15.8 Hz, $J$ = 6.6 Hz), 6.37 (2H. m), 6.72 (1H, d, $J$ = 15.8 Hz), 7.37 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.4, 57.0, 60.2 ((q, $^2J_{C\text{-}F}$ = 28.7 Hz), 110.6, 111.5, 118.4, 124.5 (q, $^1J_{C\text{-}F}$ = 280 Hz), 124.8, 142.9, 151.0: $^{19}F$ NMR (500 MHz, $CDCl_3$): δ= – 76.4 (d, $J_{F\text{-}H}$ = 7.6 Hz).

**4d: ($R_S$, $S$)-(–)-*N*-(3-furyl-2-methyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 61.6 (*c* 1.5, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 9H), 2.12 (s, 3H), 3.61 (d, 1H, $J$ = 8.3 Hz), 4.26 (1H, m), 6.36-6.44 (3H, m), 7.42 (1H, s): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 15.5, 22.3, 57.0, 65.0 (q, $^2J_{C\text{-}F}$ = 31.0 Hz), 111.3, 111.4, 121.8, 124.6 (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.4, 142.3, 151.5. $^{19}F$ NMR (500 MHz, $CDCl_3$): δ= – 73.5 (d, $J_{F\text{-}H}$ = 6.8 Hz).

**4e: ($R_S$, $S$)-(–)-*N*-(3,3-diphenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 88.7 (*c* 0.98, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 1.19 (9H, s), 3.44 (1H, d, $J$ = 7.4 Hz), 4.39 (1H, m), 6.01 (1H, d, $J$ = 9.8 Hz), 7.25-7.47 (10H, m): $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 22.3, 57.0, 58.0 (q, $^2J_{C\text{-}F}$ = 29.6 Hz), 118.6, 124.7 (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.7, 128.1, 128.3, 128.5, 128.7, 129.5, 138.0, 140.6, 149.6: $^{19}F$ NMR (500 MHz, $CDCl_3$): δ= – 75.8 (d, $J_{F\text{-}H}$ = 6.7 Hz).

**4f: ($R_S$, $S$)-(–)-*N*-(2-pentyl-3-phenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 55.8 (*c* 0.98, $CHCl_3$). $^1H$ NMR (500 MHz, $CDCl_3$): δ 0.86 (3H. m), 1.27

(13H, m), 1.54 (2H, m), 2.28-2.42 (2H. m), 3.52 (1H, d, $J$ = 6.6 Hz), 4.29 (1H, m), 6.72 (1H), s), 7.23-7.36 (5H. m): $^{13}$C NMR (125 MHz, $CDCl_3$): δ 13.9, 22.2, 23.0, 27.8, 30.7, 31.8, 56.9, 61.7 (q, $^2J_{C\text{-}F}$ = 30.9 Hz), 124.8 (q, $^1J_{C\text{-}F}$ = 280 Hz), 127.4, 128.3, 128.6, 131.2, 136.2, 136.9: $^{19}$F NMR (500 MHz, $CDCl_3$): δ= – 73.5 (d, $J_{F\text{-}H}$ = 9.3 Hz).

**4g: ($R_S$, $S$)-(–)-*N*-(2-hexyl-3-phenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 59.1 (*c* 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 0.85 (3H, t, $J$ = 7.0 Hz), 1.27 (15H, m), 1.53 (2H, m), 2.28-2.42 (2H. m), 3.52 (1H, d, $J$ = 6.5 Hz), 4.28 (1H, m), 6.71 (1H, s), 7.23-7.36 (5H. m): $^{13}$C NMR (125 MHz, $CDCl_3$): δ 13.9, 22.4, 22.5, 28.0, 29.2, 30.4, 31.4, 56.8, 61 (q, $^2J_{C\text{-}F}$ = 29.7 Hz), 124.8 (q, $^1J_{C\text{-}F}$ = 281 Hz), 127.4, 128.3, 128.6, 131.2, 136.2, 136.8. $^{19}$F NMR (500 MHz, $CDCl_3$): δ= – 73.6 (d, $J_{F\text{-}H}$ = 7.4 Hz).

**4h: ($R_S$, $S$)-(–)-*N*-(2,3-diphenyl-1-trifluoromethyl-allyl)-2-methylpropanesulfinamide:** $[\alpha]^{20}_D$ – 152 (*c* 1.0, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): δ 1.14 (9H, s), 3.77 (1H, d, $J$ = 10.3 Hz), 5.01 (1H, m), 6.85 (1H, s), 7.35 – 7.46 (10H, m): $^{13}$C NMR (125 MHz, $CDCl_3$): δ 22.3, 56.9, 58.7 (q, $^2J_{C\text{-}F}$ = 30.7 Hz), 124.6 (q, $^1J_{C\text{-}F}$ = 282 Hz), 127.8, 128.0, 128.3, 128.6, 128.8, 130.3, 135.7, 135.8, 136.9, 137.7: $^{19}$F NMR (500 MHz, $CDCl_3$): δ= – 71.6 (d, $J_{F\text{-}H}$ = 7.83 Hz).

**6: (*S*)-(+)-3-phenyl-1-trifluoromethyl allylamine hydrochloride:** $[\alpha]^{20}_D$ + 51.4 (*c* 1.0, $CH_3OH$). $^1$H NMR (360 MHz, $CD_3OD$): δ 6.20 (1H, dd, $J$ = 15.9 Hz, $J$ = 8.7 Hz), 7.10 (1H, d, $J$ = 15.7 Hz), 7.38 (3H, m), 7.52 (2H, m): $^{13}$C NMR (90 MHz, $CD_3OD$): δ 55.7 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 115.0, 124.7 (q, $^1J_{C\text{-}F}$ = 279 Hz), 128.3, 129.9, 130.7, 135.8, 142.9: $^{19}$F NMR (360 MHz, $CD_3OD$): δ= – 73.8 (d, $J_{F\text{-}H}$ = 5.03 Hz).