Supporting Information for:

Asymmetric Synthesis of Either Diastereomer of Trifluoromethylated Allylic Amines by the Selective Reduction of Trifluoromethyl α,β-Unsaturated *N-tert*-Butanesulfinyl Ketoimines

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1. Supplementary Data.

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. THF was freshly distilled over Na/benzophenone. Melting points were measured on a Melt-Temp apparatus and uncorrected. ¹H NMR spectra were recorded on Bruker AM-300 or Mercury 300 (300 MHz) spectrometers with TMS as internal standard. ¹⁹F NMR spectra were recorded on Bruker AM-300 or Mercury 300 (282 MHz) spectrometers with CFCl₃ as external standard. ¹³C NMR spectra were recorded on Bruker 300 (75.5 MHz) or DPX-400 (100.7 MHz) spectrometers. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra were taken on a HP5989A spectrometer. High-resolution mass data were obtained on a high-resolution mass spectrometer in the EI or MALDI mode. The trifluoromethyl unsaturated ketones were prepared according to literature.¹

2. General Procedure for the Preparation of Trifluoromethyl α , β -Unsaturated *N*-tert-Butanesulfinyl Ketoimines.

Into a 25-mL round-bottomed flame-dried flask fitted with a magnetic stirring bar were added 0.9 mmol of trifluoromethyl unsaturated ketones, 1.0 mmol (*R*)-*tert*-butanesulfinyl amide and 2.0-2.5 mmol Ti(OEt)₄ in 8 mL of THF under a N₂ atmosphere. The resulting mixture was stirred under reflux and monitored by TLC. After reaction the mixture was poured into an equal volume of brine with rapid stirring and filtered immediately through celite. The filter cake was washed with EtOAc. The combined filtrate was washed twice with EtOAc, dried over Na₂SO₄ and filtered. After the removal of solvents under vacuum, the residue was purified by chromatography on silica gel to give 1.

Table S1. Preparation of trifluoromethyl α , β -unsaturated *N*-tert-butanesulfinimines **1**

| F ₃ C R | + \times | Ti(OEt) ₄ | N ^{-S} O ⊢ F ₃ C R 1 |
|------------------------------|------------------------------------|----------------------|---|
| entry | R | 1 | yield ^a (%) |
| 1 | Ph | 1a | 91 |
| 2 | 4-MeOC ₆ H ₄ | 1b | 86 |
| 3 | $4-MeC_6H_4$ | 1c | 85 |
| 4 | $4-ClC_6H_4$ | 1d | 80 |
| 5 | $4-BrC_6H_4$ | 1e | 76 |
| 6 | $2-MeOC_6H_4$ | 1 f | 86 |
| 7 | $3-BrC_6H_4$ | 1g | 65 |
| 8 | 1-Naphthyl | 1h | 80 |
| 9 | 2-Furyl | 1i | 72 |
| 10 | PhC≡C | 1j | 56 |
| 11 | $n-C_8H_{17}$ | 1k | 51 |
| 12 | $C_{6}H_{5}(CH_{2})_{3}$ | 11 | 91 |
| ^a Isolated yield. | | | |

3. General Procedure for the Reduction of Trifluoromethyl α , β -Unsaturated *N*-tert-Butanesulfinyl Ketoimines in DIBAL-H System.



Into a dried 20-mL Schlenk flask containing trifluoromethyl α,β -unsaturated *N-tert*-butanesulfinyl ketoimines (**R**)-1 (0.25 mmol) in 3 mL THF was slowly added a solution of DIBAL-H (0.75 mL, 0.75 mmol, 1.0 M solution in toluene) at -78 °C under N₂ atmosphere. The reaction mixture was stirred at this temperature for half an hour, followed by adding a saturated aqueous NH₄Cl solution (5 mL) at the same temperature. The resulting mixture was extracted with CH₂Cl₂ (10 mL x 3). The combined organic solution was dried over Na₂SO₄. After the removal of volatile solvents under vacuum, the crude product was further purified by column chromatography on silica gel to give product **2**.

4. General Procedure for the Reduction of Trifluoromethyl α , β -Unsaturated *N*-tert-Butanesulfinyl Ketoimines in L-Selectride System.



Into a dried 20-mL Schlenk flask containing trifluoromethyl α , β -unsaturated *N-tert*-butanesulfinyl ketoimines (**R**)-1 (0.25 mmol) in 3 mL THF and 0.6 mL HMPA was slowly added a solution of L-Selectride (0.75 mL, 0.75 mmol, 1.0 M solution in THF) at -78 °C under N₂ atmosphere. The reaction mixture was then stirred at this temperature for 0.5-1 h, followed by adding a saturated aqueous NH₄Cl solution (5 mL) at the same temperature. The resulting mixture was extracted with CH₂Cl₂ (10 mL x 3). The combined organic solution was dried over Na₂SO₄. After the removal of volatile solvents under vacuum, the crude product was further purified by column chromatography on silica gel to give product **3**.

[Caution]: HMPA is a suspected human carcinogen.

5. Determination of the Diastereoselectivity.

The diastereoselectivity of trifluoromethylated allylic amines was determined according to 19 F NMR spectra of the crude reaction mixture. In the case of **1a**, the diastereomeric excess of the product was further measured by chiral HPLC to ensure the accuracy.



HPLC: Chiralpak AD-H column, 90:10 hexane/2-propanol; 0.8 mL/min; 254 nm; (*Rs*, *S*), $t_r = 6.23 \text{ min}$, (*Rs*, *R*), $t_r = 8.98 \text{ min}$.

6. The Configuration Assignment.

The configuration of the reduction product was assigned by comparison with literature data of trifluoromethylated allylic amine hydrochlorides.



7. Characterization Data of 1-6.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-ylidene)-*tert*-butanesulfinamide (1a)



Yellow solid, yield 91%; mp 55-56 °C; $[\alpha]_D^{20}$ -985.76 (c = 0.70, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2964, 2932, 1617, 1583, 1451, 1197, 1144, 1126, 1079, 977, 762, 698; ¹H NMR (CDCl₃): δ 8.00 (d, *J* = 16.8 Hz, 1H), 7.44-7.47 (m, 2H), 7.27-7.30 (m, 3H), 7.23 (d, *J* = 16.8 Hz, 1H), 1.25 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.26 (s, 3F); ¹³C NMR (CDCl₃): δ 158.66 (q, *J* = 32.9 Hz), 143.77 (q, *J* = 2.7 Hz), 134.65, 130.86, 128.89, 128.35, 118.88 (q, *J* = 282.4 Hz), 115.09, 60.58, 22.89; EIMS (*m/z*, %): 304 (M⁺+1, 0.54), 247 (M⁺-^tBu+1, 39.62), 198 (38.91), 57 (100.00); HRMS(EI) calcd. for C₁₀H₇F₃NOS [M⁺-^tBu]: 246.0200; Found: 246.0206.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-ylidene)-*tert*-butane-sulfinamide (1b)



Yellow solid, yield 86%; mp 47-48 °C; $[\alpha]_D^{20}$ -1095.62 (c = 0.89, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2964, 1618, 1599, 1579, 1512, 1263, 1174, 1129, 1070, 829, 689; ¹H NMR (CDCl₃): δ 7.92 (d, *J* = 17.0 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 17.0 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 9H); ¹⁹F NMR (CDCl₃): δ -65.76 (s, 3F); ¹³C NMR (CDCl₃): δ 161.94, 158.89 (q, *J* = 32.9 Hz), 143.63 (q, *J* = 2.7 Hz), 130.21, 127.41, 118.99 (q, *J* = 282.4 Hz), 114.35, 112.83, 60.26, 55.29, 22.83; EIMS (*m*/*z*, %): 334 (M⁺+1, 0.67), 277 (M⁺-^tBu+1, 61.34), 228 (89.80), 57 (100.00); HRMS(EI) calcd. for C₁₁H₁₀F₃NO₂S [M⁺-^tBu+1]: 277.0384; Found: 277.0390.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-*p*-tolylbut-3-en-2-ylidene)-*tert*-butanesulfinamide (1c)



Yellow solid, yield 85%; mp 85-87 °C; $[\alpha]_D^{20}$ -1072.16 (c = 0.74, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2988, 2974, 1615, 1578, 1341, 1275, 1183, 1142, 1085, 971, 816, 690; ¹H NMR (CDCl₃): δ 8.02 (d, *J* = 17.1 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 17.1 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H), 1.34 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.15 (s, 3F); ¹³C NMR (CDCl₃): δ 158.88 (q, *J* = 33.0 Hz), 143.95 (q, *J* = 2.8 Hz), 141.57, 131.99, 129.67, 128.43, 118.96 (q, *J* = 282.4 Hz), 114.14, 60.44, 22.90, 21.46; EIMS (*m*/*z*, %): 318 (M⁺+1, 0.17), 261 (M⁺-^tBu+1, 41.86), 212 (38.84), 57 (100.00); HRMS(EI) calcd. for C₁₁H₁₀F₃NOS [M⁺-^tBu+1]: 261.0435; Found: 261.0441.

(*R*,*E*)-*N*-((*E*)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-ylidene)-*tert*-butane-sulfinamide (1d)



Yellow solid, yield 80%; mp 68-69 °C; $[\alpha]_D^{20}$ -896.59 (c = 0.72, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2988, 2970, 1615, 1577, 1491, 1344, 1268, 1187, 1144, 1089, 973, 821, 690; ¹H NMR (CDCl₃): δ 7.99 (d, *J* = 16.8 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* =

8.7 Hz, 2H), 7.16 (d, J = 16.8 Hz, 1H), 1.26 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.32 (s, 3F); ¹³C NMR (CDCl₃): δ 158.33 (q, J = 32.9 Hz), 142.11 (q, J = 2.7 Hz), 136.81, 133.18, 129.46, 129.19, 118.80 (q, J = 282.4 Hz), 116.93, 60.78, 22.94; EIMS (*m*/*z*, %): 338 (M⁺+1, 0.83), 281 (M⁺-^tBu+1, 25.54), 232 (24.34), 57 (100.00); HRMS(EI) calcd. for C₁₀H₇ClF₃NOS [M⁺-^tBu+1]: 280.9889; Found: 280.9886.

(*R*,*E*)-*N*-((*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-ylidene)-*tert*-butanesulfinamide (1e)



Yellow solid, yield 76%; mp 72-73 °C; $[\alpha]_D^{20}$ -806.16 (c = 0.785, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2988, 2970, 1614, 1576, 1487, 1339, 1267, 1186, 1143, 1088, 973, 817, 689; ¹H NMR (CDCl₃): δ 8.09 (d, *J* = 17.1 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 17.1 Hz, 1H), 1.35 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.31 (s, 3F); ¹³C NMR (CDCl₃): δ 158.34 (q, *J* = 33.0 Hz), 142.24 (q, *J* = 2.8 Hz), 133.61, 132.18, 129.68, 125.30, 118.81 (q, *J* = 282.4 Hz), 115.59, 60.84, 22.99; EIMS (*m/z*, %): 325 (M⁺-^tBu+1, 9.53), 276 (6.45), 57 (100.00); HRMS(EI) calcd. for C₁₀H₇BrF₃NOS [M⁺-^tBu+1]: 324.9384; Found: 324.9391.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-(2-methoxyphenyl)but-3-en-2-ylidene)-*tert*-butane-sulfinamide (1f)



Viscous yellow oil, yield 86%; $[\alpha]_D^{20}$ -860.64 (c = 0.515, CHCl₃); FT-IR (film, cm⁻¹): v 2966, 1611, 1573, 1488, 1340, 1252, 1191, 1134, 1107, 752, 691; ¹H NMR (CDCl₃): δ 8.08 (d, *J* = 17.0 Hz, 1H), 7.76 (d, *J* = 17.0 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 3H), 1.34 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.27 (s, 3F); ¹³C NMR (CDCl₃): δ 159.32 (q, *J* = 32.5 Hz), 158.22, 138.98 (q, *J* = 3.3 Hz), 132.29, 128.02, 124.60, 120.77, 118.98 (q, *J* = 282.5 Hz), 115.13, 111.01, 60.29, 55.50, 22.83; EIMS (*m*/*z*, %): 334 (M⁺+1, 0.89), 277 (M⁺-^tBu+1, 38.28), 228 (11.15), 198 (100.00), 57 (76.19); HRMS(EI) calcd. for C₁₅H₁₈F₃NO₂S [M⁺]: 333.1010; Found: 333.1005.

(*R*,*E*)-*N*-((*E*)-4-(3-bromophenyl)-1,1,1-trifluorobut-3-en-2-ylidene)-*tert*-butane-sulfinamide (1g)



Yellow solid, yield 65%; mp 50-51 °C; $[\alpha]_D^{20}$ -757.04 (c = 0.605, CHCl₃); FT-IR (KBr, cm⁻¹): v 2923, 1619, 1583, 1478, 1344, 1272, 1193, 1127, 1087, 967, 782, 689; ¹H NMR (CDCl₃): δ 8.05 (d, *J* = 17.4 Hz, 1H), 7.65 (s, 1H), 7.45-7.50 (m, 2H), 7.17-7.26 (m, 2H), 1.33 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.76 (s, 3F); ¹³C NMR (CDCl₃): δ 158.18 (q, *J* = 33.0 Hz), 141.90 (q, *J* = 2.2 Hz), 136.73, 133.55, 131.08, 130.35, 126.69, 123.08, 118.77 (q, *J* = 282.4 Hz), 116.25, 60.90, 22.98; EIMS (*m/z*, %): 382 (M⁺, 0.21), 325 (M⁺-^tBu+1, 9.53), 276 (5.50), 57 (100.00); HRMS(EI) calcd. for C₁₀H₇BrF₃NOS [M⁺-^tBu+1]: 324.9384; Found: 324.9396.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-(naphthalen-1-yl)but-3-en-2-ylidene)-*tert*-butane-sulfinamide (1h)



Yellow solid, yield 80%; mp 62-63 °C; $[\alpha]_D^{20}$ -763.29 (c = 0.56, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2974, 2929, 1606, 1570, 1510, 1459, 1192, 1133, 1076, 975, 771, 686; ¹H NMR (CDCl₃): δ 8.23 (d, *J* = 17.1 Hz, 1H), 8.08-8.16 (m, 2H), 7.84-7.93 (m, 3H), 7.47-7.63 (m, 3H), 1.37 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.12 (s, 3F); ¹³C NMR (CDCl₃): δ 158.67 (q, *J* = 33.0 Hz), 140.52 (q, *J* = 2.8 Hz), 133.55, 131.76, 131.29, 131.23, 128.83, 127.08, 126.22, 125.51, 125.37, 122.66, 119.07 (q, *J* = 282.4 Hz), 117.29, 60.66, 22.94; EIMS (*m*/*z*, %): 297 (M⁺-^tBu+1, 29.09), 248 (62.54), 57 (100.00); HRMS(EI) calcd. for C₁₄H₁₀F₃NOS [M⁺-^tBu+1]: 297.0435; Found: 297.0445.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-4-(furan-2-yl)but-3-en-2-ylidene)-*tert*-butanesulfinamide (1i)



Viscous yellow oil, yield 72%; $[\alpha]_D^{20}$ -1148.04 (c = 1.04, CHCl₃); FT-IR (film, cm⁻¹): v 2966, 2929, 1617, 1588, 1469, 1343, 1187, 1128, 1084, 969, 689; ¹H NMR (CDCl₃): δ 7.88 (d, *J* = 16.8 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.08 (d, *J* = 16.8 Hz, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 6.50 (dd, *J_I* = 3.6 Hz, *J₂* = 1.8 Hz, 1H), 1.34 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.59 (s, 3F); ¹³C NMR (CDCl₃): δ 158.34 (q, *J* = 33.0 Hz), 150.97, 145.87, 129.60 (q, *J* = 2.8 Hz), 118.92 (q, *J* = 281.9 Hz), 116.56, 112.81, 112.57, 60.43, 22.82; EIMS (m/z, %): 293 (M⁺, 0.10), 294 (M⁺+1, 0.11), 237 (M⁺-^tBu+1, 25.60), 189 (27.98), 57 (100.00); HRMS(EI) calcd. for C₈H₆F₃NO₂S [M⁺-^tBu+1]: 237.0071; Found: 237.0064.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-6-phenylhex-3-en-5-yn-2-ylidene)-*tert*-butanesulfinamide (1j)



Yellow solid, yield 56%; mp 58-60 °C; $[\alpha]_D^{20}$ -1021.22 (c = 0.54, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2964, 2932, 2191, 1600, 1583, 1489, 1336, 1191, 1144, 1129, 1083, 954, 757, 690; ¹H NMR (CDCl₃): δ 7.86 (d, *J* = 16.8 Hz, 1H), 7.46-7.49 (m, 2H), 7.31-7.39 (m, 3H), 6.63 (d, *J* = 16.8 Hz, 1H), 1.33 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.74 (s, 3F); ¹³C NMR (CDCl₃): δ 157.38 (q, *J* = 33.5 Hz), 132.03, 129.59, 128.45, 126.27, 124.61 (q, *J* = 3.3 Hz), 121.91, 118.63 (q, *J* = 282.4 Hz), 102.23, 87.75, 61.16, 23.01; EIMS (*m/z*, %): 271 (M⁺-^tBu+1, 15.32), 223 (9.64), 57 (100.00); HRMS(EI) calcd. for C₁₂H₈F₃NOS [M⁺-^tBu+1]: 271.0279; Found: 271.0273.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluorododec-3-en-2-ylidene)-*tert*-butanesulfinamide (1k)



Viscous yellow oil, yield 51%; $[\alpha]_D^{20}$ -331.54 (c = 1.115, CHCl₃); FT-IR (film, cm⁻¹): v 2959, 2930, 2858, 1631, 1593, 1459, 1340, 1195, 1143, 1113; ¹H NMR (CDCl₃): δ 7.18 (d, *J* = 15.6 Hz, 1H), 6.54-6.65 (m, 1H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.35-1.44 (m, 2H), 1.23 (s, 9H), 1.15-1.22 (m, 10H), 0.81 (t, *J* = 7.2 Hz, 3H); ¹⁹F NMR (CDCl₃): δ -66.69 (s, 3F); ¹³C NMR (CDCl₃): δ 159.02 (q, *J* = 32.5 Hz), 150.30 (q, *J* = 2.3 Hz), 118.83 (q, *J* = 282.4 Hz), 118.39, 60.01, 34.20, 31.75, 29.25, 29.15, 29.12, 28.00, 22.78, 22.60, 14.03; EIMS (*m*/*z*, %): 340 (M⁺+1, 0.62), 283 (M⁺-^tBu+1, 3.90), 235 (4.92), 57 (100.00); HRMS(EI) calcd. for C₁₆H₂₈F₃NOS [M⁺]: 339.1844; Found: 339.1856.

(*R*,*E*)-*N*-((*E*)-1,1,1-trifluoro-7-phenylhept-3-en-2-ylidene)-*tert*-butanesulfinamide (1)



Yellow oil, yield 91%; $[\alpha]_D^{20}$ -388.26 (c = 1.21, CHCl₃); FT-IR (film, cm⁻¹): *v* 3029, 2932, 2863, 1631, 1593, 1455, 1340, 1195, 1141, 1123, 700; ¹H NMR (CDCl₃): δ 7.15-7.23 (m, 3H), 7.06-7.12 (m, 3H), 6.51-6.63 (m, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.17-2.25 (m, 2H), 1.67-1.77 (m, 2H), 1.22 (s, 9H); ¹⁹F NMR (CDCl₃): δ -66.61 (s, 3F); ¹³C NMR (CDCl₃): δ 158.78 (q, *J* = 32.7 Hz), 149.40 (q, *J* = 2.3 Hz), 141.40, 128.36, 128.33, 125.90, 118.78 (q, *J* = 282.4 Hz), 118.65, 60.07, 35.25, 33.52, 29.63, 22.77; ESI MS (*m*/*z*): 346.2 (M⁺+1), 368.1 (M⁺+Na); HRMS(MALDI) calcd. for C₁₇H₂₂F₃NOSNa⁺¹ [M⁺+Na]: 368.1266; Found: 368.1280.

(Rs,R)-N-((E)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)-tert-butanesulfinamide (2a)



White solid, yield 99%; mp 50-52 °C; $[\alpha]_D^{20}$ -204.43 (c = 0.67, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3168, 2968, 2868, 1450, 1364, 1267, 1165, 1123, 1053, 970, 751, 693; ¹H NMR (CDCl₃): δ 7.31-7.46 (m, 5H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J*₁ = 15.9 Hz, *J*₂ = 8.4 Hz, 1H), 4.43-4.54 (m, 1H), 3.71 (d, *J* = 4.5 Hz, 1H), 1.26 (s, 9H); ¹⁹F NMR (CDCl₃): δ -76.17 (d, *J* = 5.4 Hz, 3F); ¹³C NMR (CDCl₃): δ 138.58, 135.06, 128.74, 128.57, 126.85, 124.35 (q, *J* = 281.4 Hz), 118.48, 59.22 (q, *J* = 30.8 Hz), 56.23, 22.26; EIMS (*m*/*z*, %): 306 (M⁺+1, 0.19), 249 (M⁺-^tBu+1, 3.15), 185 (20.92), 57 (100.00); HRMS(EI) calcd. for C₁₄H₁₈F₃NOS [M⁺]: 305.1061; Found: 305.1055.

(Rs,S)-N-((E)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)-tert-butanesulfinamide (3a)



White solid, yield 99%; mp 109-111 °C; $[\alpha]_D^{20}$ -13.88 (c = 0.66, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3206, 2968, 1656, 1497, 1368, 1262, 1173, 1128, 1068, 969, 748, 692; ¹H NMR (CDCl₃): δ 7.40-7.43 (m, 2H), 7.29-7.37 (m, 3H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.22 (dd, *J*₁ = 16.1 Hz, *J*₂ = 6.0 Hz, 1H), 4.42-4.54 (m, 1H), 3.47 (d, *J* = 7.5 Hz, 1H), 1.27 (s, 9H); ¹⁹F NMR (CDCl₃): δ -76.53 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CD₃OD): δ 137.76, 137.22, 129.78, 129.62, 127.92, 126.36 (q, *J* = 281.1 Hz), 121.72, 62.73 (q, *J* = 31.0 Hz), 58.20, 23.06; EIMS (*m*/*z*, %): 306 (M⁺+1, 0.21), 249 (M⁺-^tBu+1, 3.93), 185 (21.10), 57 (100.00); HRMS(EI) calcd. for C₁₀H₁₀F₃NOS [M⁺-^tBu+1]: 249.0435; Found: 249.0443.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)-*tert*-butanesulfin -amide (2b)



White solid, yield 95%; mp 71-72 °C; $[\alpha]_D^{20}$ -235.76 (c = 0.61, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3154, 2961, 2872, 1656, 1611, 1515, 1467, 1365, 1259, 1164, 1122, 1066, 973, 834; ¹H NMR (CDCl₃): δ 7.37 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 15.9 Hz, 1H), 5.89 (dd, *J*₁ = 15.9 Hz, *J*₂ = 8.4 Hz, 1H), 4.39-4.50 (m, 1H), 3.82 (s, 3H), 3.72 (d, *J* = 4.2 Hz, 1H), 1.25 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.50 (d, *J* = 7.1 Hz, 3F); ¹³C NMR (CDCl₃): δ 160.11, 138.32, 128.29, 127.90, 124.47 (q, *J* = 281.4 Hz), 115.97, 114.02, 59.40 (q, *J* = 30.8 Hz), 56.23, 55.24, 22.37; EIMS (*m*/*z*, %): 279 (M⁺-^tBu+1, 14.66), 215 (68.01), 57 (100.00); HRMS(EI) calcd. for C₁₁H₁₂F₃NO₂S [M⁺-^tBu+1]: 279.0541; Found: 279.0541.

(*Rs*,*S*)-*N*-((*E*)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)-*tert*-butanesulfin -amide (3b)



White solid, yield 92%; mp 113-114 °C; $[\alpha]_D^{20}$ -8.09 (c = 0.675, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3211, 2963, 2870, 1658, 1608, 1514, 1464, 1363, 1257, 1175, 1125, 1033, 970, 804; ¹H NMR (CDCl₃): δ 7.35 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J*₁ = 15.9 Hz, *J*₂ = 6.6 Hz, 1H), 4.39-4.51 (m, 1H), 3.81 (s, 3H), 3.46 (d, *J* = 7.5 Hz, 1H), 1.27 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.81 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CD₃OD): δ 160.12, 135.93, 128.48, 127.81, 124.99 (q, *J* = 280.7 Hz), 117.84, 113.72, 61.36 (q, *J* = 30.8 Hz), 56.76, 54.35, 21.63; EIMS (*m*/*z*, %): 279 (M⁺-^tBu+1, 13.07), 215 (56.12), 57 (100.00); HRMS(EI) calcd. for C₁₁H₁₂F₃NO₂S [M⁺-^tBu+1]: 279.0541; Found: 279.0531.

(Rs,R)-N-((E)-1,1,1-trifluoro-4-p-tolylbut-3-en-2-yl)-tert-butanesulfinamide (2c)



White solid, yield 97%; mp 97-98 °C; $[\alpha]_D^{20}$ -228.64 (c = 0.79, CHCl₃); FT-IR (KBr, cm⁻¹): v 3199, 2950, 2925, 1656, 1611, 1516, 1474, 1365, 1261, 1171, 1129, 1075, 972, 797; ¹H NMR (CDCl₃): δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.83

(d, J = 15.9 Hz, 1H), 5.98 (dd, $J_1 = 15.9$ Hz, $J_2 = 8.4$ Hz, 1H), 4.41-4.51 (m, 1H), 3.72 (d, J = 3.6 Hz, 1H), 2.36 (s, 3H), 1.25 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.45 (d, J = 7.3 Hz, 3F); ¹³C NMR (CDCl₃): δ 138.98, 138.79, 132.49, 129.42, 126.42, 124.52 (q, J = 281.3 Hz), 117.49, 59.43 (q, J = 30.7 Hz), 56.33, 22.45, 21.28; EIMS (*m/z*, %): 263 (M⁺-^tBu+1, 7.09), 199 (42.44), 57 (100.00); HRMS(EI) calcd. for C₁₅H₂₀F₃NOS [M⁺]: 319.1218; Found: 319.1211.

(Rs,S)-N-((E)-1,1,1-trifluoro-4-p-tolylbut-3-en-2-yl)-tert-butanesulfinamide (3c)



White solid, yield 95%; mp 147-148 °C; $[\alpha]_D^{20}$ -13.03 (c = 0.72, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3135, 2964, 2866, 1659, 1515, 1363, 1268, 1160, 1124, 1054, 971, 797; ¹H NMR (CD₃OD): δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J*₁ = 15.9 Hz, *J*₂ = 7.5 Hz, 1H), 4.53-4.63 (m, 1H), 2.33 (s, 3H), 1.27 (s, 9H); ¹⁹F NMR (CD₃OD): δ -78.20 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CD₃OD): δ 138.29, 136.28, 133.06, 128.96, 126.44, 124.97 (q, *J* = 280.7 Hz), 119.21, 61.32 (q, *J* = 31.0 Hz), 56.77, 21.62, 19.88; EIMS (*m*/*z*, %): 263 (M⁺-^tBu+1]: 263.0592; Found: 263.0595.

(*Rs*,*R*)-*N*-((*E*)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (2d)



White solid, yield 95%; mp 86-87 °C; $[\alpha]_D^{20}$ -226.13 (c = 0.71, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3151, 2958, 2932, 1656, 1596, 1493, 1364, 1257, 1166, 1121, 1065, 967, 736; ¹H NMR (CDCl₃): δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J*₁ = 15.9 Hz, *J*₂ = 8.1 Hz, 1H), 4.41-4.52 (m, 1H), 3.76 (d, *J* = 3.9 Hz, 1H), 1.26 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.50 (d, *J* = 6.8 Hz, 3F); ¹³C NMR (CDCl₃): δ 137.52, 134.68, 133.72, 128.91, 128.21, 124.40 (q, *J* = 281.5 Hz), 119.34, 59.21 (q, *J* = 30.9 Hz), 56.47, 22.42; EIMS (*m*/*z*, %): 283 (M⁺-^tBu+1, 0.68), 219 (7.04), 57 (100.00); HRMS(MALDI) calcd. for C₁₄H₁₇ClF₃NOSNa⁺¹ [M⁺+Na]: 362.0564; Found: 362.0573.

(*Rs*,*S*)-*N*-((*E*)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (3d)



White solid, yield 88%; mp 143-145 °C; $[\alpha]_D^{20}$ -14.22 (c = 0.58, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3138, 2983, 2966, 2916, 1659, 1595, 1491, 1363, 1270, 1161, 1127, 1054, 970, 798; ¹H NMR (CDCl₃): δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.20 (dd, *J*₁ = 16.2 Hz, *J*₂ = 6.2 Hz, 1H), 4.41-4.53 (m, 1H), 3.48 (d, *J* = 8.1 Hz, 1H), 1.27 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.91 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CD₃OD): δ 135.00, 134.58, 133.84, 128.48, 127.96, 124.86 (q, *J* = 280.9 Hz), 121.30, 61.20 (q, *J* = 31.0 Hz), 56.83, 21.63; EIMS (*m*/*z*, %): 283 (M⁺-^tBu+1, 0.89), 219 (7.26), 57 (100.00); HRMS(MALDI) calcd. for C₁₄H₁₇ClF₃NOSNa⁺¹ [M⁺+Na]: 362.0564; Found: 362.0559.

(*Rs*,*R*)-*N*-((*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (2e)



White solid, yield 96%; mp 90-92 °C; $[\alpha]_D^{20}$ -205.09 (c = 0.71, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3155, 2960, 2910, 1656, 1590, 1489, 1364, 1256, 1166, 1121, 1069, 968, 735; ¹H NMR (CDCl₃): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J*₁ = 15.9 Hz, *J*₂ = 8.4 Hz, 1H), 4.41-4.52 (m, 1H), 3.76 (d, *J* = 4.5 Hz, 1H), 1.26 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.29 (d, *J* = 7.1 Hz, 3F); ¹³C NMR (CDCl₃): δ 137.66, 134.13, 131.89, 128.50, 124.36 (q, *J* = 281.4 Hz), 122.93, 119.45, 59.21 (q, *J* = 30.8 Hz), 56.45, 22.44; EIMS (*m*/*z*, %): 327 (M⁺-^tBu+1, 0.50), 263 (3.36), 57 (100.00); HRMS(EI) calcd. for C₁₀H₉BrF₃NOS [M⁺-^tBu+1]: 326.9540; Found: 326.9545.

(*Rs*,*S*)-*N*-((*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (3e)



White solid, yield 93%; mp 141-143 °C; $[\alpha]_D^{20}$ -9.59 (c = 0.58, CH₃OH); FT-IR (KBr, cm⁻¹): v 3209, 2958, 1488, 1364, 1259, 1186, 1131, 1037, 972, 798; ¹H NMR

(CD₃OD): δ 7.52 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 16.2 Hz, 1H), 6.37 (dd, $J_I = 16.2$ Hz, $J_2 = 7.4$ Hz, 1H), 4.59-4.70 (m, 1H), 1.29 (s, 9H); ¹⁹F NMR (CD₃OD): δ -76.86 (d, J = 7.9 Hz, 3F); ¹³C NMR (CD₃OD): δ 135.06, 134.99, 131.50, 128.22, 124.83 (q, J = 280.9 Hz), 121.91, 121.42, 61.20 (q, J = 31.0 Hz), 56.82, 21.62; EIMS (m/z, %): 327 (M⁺-^tBu+1, 0.67), 263 (3.47), 57 (100.00); HRMS(EI) calcd. for C₁₀H₉BrF₃NOS [M⁺-^tBu+1]: 326.9540; Found: 326.9538.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluoro-4-(2-methoxyphenyl)but-3-en-2-yl)-*tert*-butanesulfin -amide (2f)



Viscous oil, yield 97%; $[\alpha]_D^{20}$ -151.94 (c = 0.55, CHCl₃); FT-IR (film, cm⁻¹): v 3193, 2962, 2872, 1650, 1600, 1581, 1491, 1466, 1366, 1249, 1175, 1125, 1068, 977, 753; ¹H NMR (CDCl₃): δ 7.37 (dd, J_I = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.19 (td, J_I = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.10 (d, J = 16.5 Hz, 1H), 6.85 (t, J = 7.8 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.01 (dd, J_I = 16.5 Hz, J_2 = 8.3 Hz, 1H), 4.34-4.45 (m, 1H), 3.75 (s, 3H), 3.73 (d, J = 5.1 Hz, 1H), 1.17 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.39 (d, J = 7.3 Hz, 3F); ¹³C NMR (CDCl₃): δ 157.17, 133.55, 129.98, 127.38, 124.59 (q, J = 281.6 Hz), 124.25, 120.63, 119.01, 111.06, 59.88 (q, J = 30.7 Hz), 56.40, 55.45, 22.42; EIMS (*m*/*z*, %): 336 (M⁺+1, 0.85), 279 (M⁺-^tBu+1, 10.00), 215 (91.22), 57 (100.00); HRMS(MALDI) calcd. for C₁₅H₂₀F₃NO₂SNa⁺¹ [M⁺+Na]: 358.1059; Found: 358.1072.

(*Rs*,*S*)-*N*-((*E*)-1,1,1-trifluoro-4-(2-methoxyphenyl)but-3-en-2-yl)-*tert*-butanesulfin -amide (3f)



White solid, yield 96%; mp 84-86 °C; $[\alpha]_D^{20}$ -50.39 (c = 0.63, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3144, 2958, 1600, 1492, 1365, 1251, 1163, 1120, 1057, 975, 754; ¹H NMR (CD₃OD): δ 7.46 (dd, J_I = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.27 (td, J_I = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.16 (d, J = 15.9 Hz, 1H), 6.95 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.35 (dd, J_I = 15.9 Hz, J_2 = 7.7 Hz, 1H), 4.49-4.59 (m, 1H), 3.85 (s, 3H), 1.26 (s, 9H); ¹⁹F NMR (CD₃OD): δ -78.01 (d, J = 6.8 Hz, 3F); ¹³C NMR (CD₃OD): δ 157.28, 131.65, 129.45, 127.13, 125.00 (q, J = 280.6 Hz), 124.44, 120.81, 120.30, 110.83, 61.65 (q, J = 30.9 Hz), 56.76, 54.58, 21.63; EIMS (m/z, %): 279 (M⁺-^tBu+1, 9.16), 215 (57.31), 57 (100.00); HRMS(EI) calcd. for C₁₁H₁₂F₃NO₂S [M⁺-^tBu+1]: 279.0541; Found: 279.0538.

(*Rs*,*R*)-*N*-((*E*)-4-(3-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (2g)



Viscous oil, yield 93%; $[\alpha]_D^{20}$ -176.58 (c = 0.50, CHCl₃); FT-IR (film, cm⁻¹): *v* 3192, 2963, 2871, 1654, 1593, 1564, 1474, 1427, 1366, 1264, 1177, 1127, 1072, 968, 757; ¹H NMR (CDCl₃): δ 7.51 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.12-7.20 (m, 1H), 6.72 (d, *J* = 15.9 Hz, 1H), 5.99 (dd, *J*₁ = 15.9 Hz, *J*₂ = 8.0 Hz, 1H), 4.34-4.45 (m, 1H), 3.75 (d, *J* = 4.5 Hz, 1H), 1.19 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.23 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CDCl₃): δ 137.30, 131.77, 130.25, 129.69, 125.81, 124.37 (q, *J* = 281.4 Hz), 122.89, 120.31, 59.15 (q, *J* = 31.0 Hz), 56.50, 22.44; EIMS (*m/z*, %): 384 (M⁺+1, 0.77), 327 (M⁺-^tBu+1, 0.40), 263 (2.81), 57 (100.00); HRMS(MALDI) calcd. for C₁₄H₁₇BrF₃NOSNa⁺¹ [M⁺+Na]: 406.0059; Found: 406.0072.

(*Rs*,*S*)-*N*-((*E*)-4-(3-bromophenyl)-1,1,1-trifluorobut-3-en-2-yl)-*tert*-butanesulfinamide (3g)



White solid, yield 90%; mp 89-92 °C; $[\alpha]_D^{20}$ -14.38 (c = 0.62, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3211, 2958, 2866, 1593, 1565, 1480, 1353, 1272, 1170, 1124, 1048, 964, 777; ¹H NMR (CD₃OD): δ 7.64 (d, *J* = 1.5 Hz, 1H), 7.44 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.5 Hz, 2H), 7.27 (t, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.37 (dd, *J*₁ = 15.6 Hz, *J*₂ = 7.2 Hz, 1H), 4.59-4.69 (m, 1H), 1.27 (s, 9H); ¹⁹F NMR (CD₃OD): δ -77.99 (d, *J* = 8.5 Hz, 3F); ¹³C NMR (CD₃OD): δ 138.20, 134.77, 130.99, 130.11, 129.33, 125.24, 124.82 (q, *J* = 280.9 Hz), 122.36, 122.24, 61.11 (q, *J* = 30.1 Hz), 56.84, 21.61; EIMS (*m*/*z*, %): 327 (M⁺-^tBu+1, 0.42), 263 (2.05), 57 (100.00); HRMS(MALDI) calcd. for C₁₄H₁₇BrF₃NOSNa⁺¹ [M⁺+Na]: 406.0059; Found: 406.0056.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluoro-4-(naphthalen-1-yl)but-3-en-2-yl)-*tert*-butanesulfinamide (2h)



White solid, yield 96%; mp 81-83 °C; $[\alpha]_D^{20}$ -110.35 (c = 0.62, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3198, 2950, 2866, 1656, 1590, 1508, 1473, 1366, 1266, 1168, 1118, 1077, 963, 780; ¹H NMR (CDCl₃): δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.43-7.62 (m, 4H), 6.10 (dd, *J_I* = 15.5 Hz, *J₂* = 8.0 Hz, 1H), 4.57-4.68 (m, 1H), 3.87 (d, *J* = 4.2 Hz, 1H), 1.27 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.40 (d, *J* = 6.8 Hz, 3F); ¹³C NMR (CDCl₃): δ 136.51, 133.57, 133.22, 131.06, 129.16, 128.60, 126.60, 126.09, 125.49, 124.62, 124.55 (q, *J* = 281.5 Hz), 123.62, 122.10, 59.42 (q, *J* = 30.7 Hz), 56.47, 22.48; EIMS (*m*/*z*, %): 355 (M⁺, 0.24), 299 (M⁺-^tBu+1); 14.23), 235 (36.06), 57 (100.00); HRMS(EI) calcd. for C₁₄H₁₂F₃NOS [M⁺-^tBu+1]: 299.0592; Found: 299.0588.

(*Rs*,*S*)-*N*-((*E*)-1,1,1-trifluoro-4-(naphthalen-1-yl)but-3-en-2-yl)-*tert*-butanesulfinamide (3h)



White solid, yield 94%; mp 94-96 °C; $[\alpha]_D^{20}$ -76.34 (c = 0.625, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3173, 2981, 2870, 1593, 1511, 1478, 1394, 1366, 1268, 1171, 1123, 1052, 966, 789; ¹H NMR (CD₃OD): δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.74-7.87 (m, 3H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.42-7.56 (m, 3H), 6.36 (dd, *J*₁ = 15.9 Hz, *J*₂ = 6.6 Hz, 1H), 4.72-4.82 (m, 1H), 1.29 (s, 9H); ¹⁹F NMR (CD₃OD): δ -77.91 (d, *J* = 7.3 Hz, 3F); ¹³C NMR (CD₃OD): δ 133.75, 133.46, 131.17, 128.43, 128.13, 126.02, 125.63, 125.19, 124.99 (q, *J* = 280.9 Hz), 123.67, 123.47, 61.41 (q, *J* = 30.7 Hz), 56.85, 21.66; EIMS (*m*/*z*, %): 355 (M⁺, 0.46), 299 (M⁺-^tBu+1, 14.35), 235 (35.00), 57 (100.00); HRMS(EI) calcd. for C₁₄H₁₂F₃NOS [M⁺-^tBu+1]: 299.0592; Found: 299.0595.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluoro-4-(furan-2-yl)but-3-en-2-yl)-*tert*-butanesulfinamide (2i)



White solid, yield 94%; mp 60-63 °C; $[\alpha]_D^{20}$ -268.38 (c = 2.7, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3185, 2983, 2870, 1660, 1565, 1492, 1365, 1267, 1176, 1125, 1068, 967, 744; ¹H NMR (CDCl₃): δ 7.40 (d, *J* = 1.5 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.41 (dd, *J_I* = 3.3 Hz, *J₂* = 1.5 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 5.98 (dd, *J_I* = 15.9 Hz, *J₂* = 8.1 Hz, 1H), 4.37-4.48 (m, 1H), 3.71 (d, *J* = 4.2 Hz, 1H), 1.26 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.44 (d, *J* = 8.2 Hz, 3F); ¹³C NMR (CDCl₃): δ 150.82, 143.08, 126.24, 124.32 (q, *J* = 281.4 Hz), 116.58, 111.56, 110.76, 59.12 (q, *J* = 30.7 Hz), 56.43, 22.37; EIMS (*m/z*,

%): 295 (M⁺, 0.37), 239 (M⁺-^tBu+1, 6.49), 175 (29.76), 57 (100.00); HRMS(EI) calcd. for $C_8H_8F_3NO_2S$ [M⁺-^tBu+1]: 239.0228; Found: 239.0230.

(*Rs*,*S*)-*N*-((*E*)-1,1,1-trifluoro-4-(furan-2-yl)but-3-en-2-yl)-*tert*-butanesulfinamide (3i)



White solid, yield 98%; mp 124-126 °C; $[\alpha]_D^{20}$ -11.59 (c = 0.87, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3221, 2985, 2871, 1593, 1365, 1268, 1170, 1122, 1055, 963, 748; ¹H NMR (CD₃OD): δ 7.48 (s, 1H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.42-6.45 (m, 2H), 6.20 (dd, *J_I* = 15.9 Hz, *J₂* = 7.2 Hz, 1H), 4.54-4.64 (m, 1H), 1.26 (s, 9H); ¹⁹F NMR (CD₃OD): δ -78.20 (d, *J* = 8.5 Hz, 3F); ¹³C NMR (CD₃OD): δ 151.47, 142.84, 124.85 (q, *J* = 280.9 Hz), 124.17, 118.47, 111.15, 109.77, 60.96 (q, *J* = 31.1 Hz), 56.80, 21.62; EIMS (*m/z*, %): 295 (M⁺, 0.47), 239 (M^{+-t}Bu+1, 6.23), 175 (28.86), 57 (100.00); HRMS(EI) calcd. for C₈H₈F₃NO₂S [M^{+-t}Bu+1]: 239.0228; Found: 239.0221.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluoro-6-phenylhex-3-en-5-yn-2-yl)-*tert*-butanesulfinamide (2j)



White solid, yield 93%; mp 56-58 °C; $[\alpha]_D^{20}$ -211.39 (c = 0.65, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3185, 2982, 2864, 1639, 1596, 1491, 1366, 1270, 1174, 1124, 1047, 951, 757; ¹H NMR (CDCl₃): δ 7.44-7.47 (m, 2H), 7.31-7.34 (m, 3H), 6.21 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J*₁ = 15.9 Hz, *J*₂ = 7.5 Hz, 1H), 4.36-4.47 (m, 1H), 3.76 (d, *J* = 4.8 Hz, 1H), 1.27 (s, 9H); ¹⁹F NMR (CDCl₃): δ -75.05 (d, *J* = 7.1 Hz, 3F); ¹³C NMR (CDCl₃): δ 131.69, 131.44, 128.83, 128.40, 124.10 (q, *J* = 281.3 Hz), 122.46, 118.71, 92.98, 85.87, 59.05 (q, *J* = 31.2 Hz), 56.72, 22.42; EIMS (*m*/*z*, %): 272 (M⁺-^tBu, 0.18), 273 (M⁺-^tBu+1, 0.55), 209 (12.68), 57 (100.00); HRMS(EI) calcd. for C₁₂H₁₀F₃NOS [M⁺-^tBu+1]: 273.0435; Found: 273.0440.

(*Rs*,*S*)-*N*-((*E*)-1,1,1-trifluoro-6-phenylhex-3-en-5-yn-2-yl)-*tert*-butanesulfinamide (3j)



White solid, yield 81%; mp 139-140 °C; $[\alpha]_D^{20}$ -4.74 (c = 0.59, CH₃OH); FT-IR (KBr, cm⁻¹): *v* 3147, 2985, 2868, 1634, 1490, 1364, 1261, 1168, 1125, 1056, 956, 756; ¹H NMR (CD₃OD): δ 7.41-7.45 (m, 2H), 7.32-7.37 (m, 3H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J*₁ = 15.9 Hz, *J*₂ = 5.7 Hz, 1H), 4.58-4.68 (m, 1H), 1.26 (s, 9H); ¹⁹F NMR (CD₃OD): δ -77.90 (d, *J* = 6.2 Hz, 3F); ¹³C NMR (CD₃OD): δ 133.42, 131.18, 128.40, 128.30 (q, *J* = 280.7 Hz), 128.16, 122.68, 116.43, 91.53, 85.73, 60.80 (q, *J* = 31.2 Hz), 56.86, 21.59; EIMS (*m*/*z*, %): 272 (M⁺-^tBu, 0.19), 273 (M⁺-^tBu+1, 0.45), 209 (11.00), 57 (100.00); HRMS(EI) calcd. for C₁₂H₈F₃N [M⁺-^tBu-SO-1]: 223.0609; Found: 223.0610.

(*Rs*,*R*)-*N*-((*E*)-1,1,1-trifluorododec-3-en-2-yl)-*tert*-butanesulfinamide (2k)



Viscous oil, yield 87%; $[\alpha]_D^{20}$ -95.09 (c = 0.47, CHCl₃); FT-IR (film, cm⁻¹): *v* 3196, 2926, 2856, 1671, 1465, 1366, 1267, 1175, 1120, 1073, 972, 722; ¹H NMR (CDCl₃): δ 5.93 (dt, J_I = 15.9 Hz, J_2 = 7.4 Hz, 1H), 5.28 (dd, J_I = 15.9 Hz, J_2 = 8.4 Hz, 1H), 4.13-4.24 (m, 1H), 3.55 (d, J = 3.9 Hz, 1H), 2.06 (q, J = 6.8 Hz, 2H), 1.33-1.37 (m, 2H), 1.20-1.24 (m, 10H), 1.17 (s, 9H), 0.81 (t, J = 6.8 Hz, 3H); ¹⁹F NMR (CDCl₃): δ -76.45 (d, J = 5.1 Hz, 3F); ¹³C NMR (CDCl₃): δ 141.69, 124.53 (q, J = 281.1 Hz), 119.60, 59.18 (q, J = 30.6 Hz), 56.12, 32.35, 31.83, 29.31, 29.24, 28.98, 28.45, 22.64, 22.42, 14.06; EIMS (*m*/*z*, %): 342 (M⁺+1, 5.17), 285 (M⁺-^tBu+1, 1.92), 236 (6.60), 57 (100.00); HRMS(MALDI) calcd. for C₁₆H₃₀F₃NOSNa⁺¹ [M⁺+Na]: 364.1892; Found: 364.1899.

(Rs,S)-N-((E)-1,1,1-trifluorododec-3-en-2-yl)-tert-butanesulfinamide (3k)



Viscous oil, yield 60%; $[\alpha]_D^{20}$ -53.43 (c = 0.88, CHCl₃); FT-IR (film, cm⁻¹): v 3197, 2929, 2858, 1673, 1467, 1365, 1265, 1174, 1120, 1071, 971; ¹H NMR (CDCl₃): δ 6.02 (dt, J_1 = 15.3 Hz, J_2 = 7.3 Hz, 1H), 5.50 (dd, J_1 = 15.3 Hz, J_2 = 6.3 Hz, 1H), 4.18-4.30 (m, 1H), 3.29 (d, J = 7.5 Hz, 1H), 2.08 (q, J = 6.9 Hz, 2H), 1.34-1.44 (m, 2H), 1.25-1.29 (m, 10H), 1.23 (s, 9H), 0.87 (t, J = 6.9 Hz, 3H); ¹⁹F NMR (CDCl₃): δ

-76.59 (d, J = 5.9 Hz, 3F); ¹³C NMR (CDCl₃): δ 139.60, 124.60 (q, J = 281.1 Hz), 121.17, 60.22 (q, J = 30.5 Hz), 56.90, 32.40, 31.85, 29.34, 29.21, 29.10, 28.49, 22.66, 22.35, 14.10; ESI MS (*m/z*): 342.3 (M⁺+1), 364.3 (M⁺+Na), 396.3 (M⁺+Na+MeOH); HRMS(MALDI) calcd. for C₁₆H₃₀F₃NOSNa⁺¹ [M⁺+Na]: 364.1892; Found: 364.1878.

(Rs,R)-N-((E)-1,1,1-trifluoro-7-phenylhept-3-en-2-yl)-tert-butanesulfinamide (21)



Viscous oil, yield 81%; $[\alpha]_D^{20}$ -100.55 (c = 1.015, CHCl₃); FT-IR (film, cm⁻¹): *v* 3196, 2931, 2862, 1671, 1456, 1366, 1266, 1175, 1125, 1070, 971, 747; ¹H NMR (CDCl₃): δ 7.18-7.23 (m, 2H), 7.08-7.13 (m, 3H), 5.94 (dt, $J_I = 15.3$ Hz, $J_2 = 6.8$ Hz, 1H), 5.31 (dd, $J_I = 15.3$ Hz, $J_2 = 8.4$ Hz, 1H), 4.13-4.24 (m, 1H), 3.61 (s, 1H), 2.55 (t, J = 7.4 Hz, 2H), 2.05-2.13 (m, 2H), 1.63-1.73 (m, 2H), 1.15 (s, 9H); ¹⁹F NMR (CDCl₃): δ -76.87 (d, J = 7.6 Hz, 3F); ¹³C NMR (CDCl₃): δ 141.95, 141.10, 128.46, 128.35, 125.84, 124.54 (q, J = 281.2 Hz), 120.19, 59.17 (q, J = 30.5 Hz), 56.20, 35.11, 31.78, 30.15, 22.44; ESI MS (m/z): 348.1 (M⁺+1), 370.1 (M⁺+Na), 402.2 (M⁺+Na+MeOH); HRMS(MALDI) calcd. for C₁₇H₂₄F₃NOSNa⁺¹ [M⁺+Na]: 370.1423; Found: 370.1439.

(Rs,S)-N-((E)-1,1,1-trifluoro-7-phenylhept-3-en-2-yl)-tert-butanesulfinamide (31)



White solid, yield 62%; mp 45-50 °C; $[\alpha]_D^{20}$ -58.72 (c = 0.775, CHCl₃); FT-IR (film, cm⁻¹): *v* 3123, 2922, 2855, 1675, 1456, 1366, 1267, 1177, 1121, 1052, 969, 737; ¹H NMR (CDCl₃): δ 7.25-7.30 (m, 2H), 7.15-7.20 (m, 3H), 6.04 (dt, J_I = 15.9 Hz, J_2 = 6.3 Hz, 1H), 5.52 (dd, J_I = 15.9 Hz, J_2 = 6.5 Hz, 1H), 4.19-4.31 (m, 1H), 3.32 (d, J = 7.5 Hz, 1H), 2.62 (t, J = 7.4 Hz, 2H), 2.10-2.17 (m, 2H), 1.70-1.80 (m, 2H), 1.24 (s, 9H); ¹⁹F NMR (CDCl₃): δ -76.10 (d, J = 7.6 Hz, 3F); ¹³C NMR (CDCl₃): δ 141.95, 138.93, 128.47, 128.35, 125.83, 124.60 (q, J = 280.9 Hz), 121.79, 60.30 (q, J = 30.9 Hz), 56.93, 35.22, 31.81, 30.14, 22.37; ESI MS (*m*/*z*): 348.1 (M⁺+1), 370.1 (M⁺+Na), 402.1 (M⁺+Na+MeOH); HRMS(MALDI) calcd. for C₁₇H₂₄F₃NOSNa⁺¹ [M⁺+Na]: 370.1423; Found: 370.1438.

(*R*,*E*)-*N*-((*E*)-4,4-dimethyl-1-phenylpent-1-en-3-ylidene)-*tert*-butanesulfinamide (4b)



Yellow solid, yield 82%; mp 88-91 °C; $[\alpha]_D^{20}$ -288.15 (c = 1.025, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 2964, 2926, 1634, 1573, 1474, 1449, 1361, 1105, 1072, 977, 725; ¹H NMR (CDCl₃): δ 7.48-7.51 (m, 2H), 7.28-7.38 (m, 3H), 7.09 (d, *J* = 16.5 Hz, 1H), 6.96 (d, *J* = 16.5 Hz, 1H), 1.26 (s, 9H), 1.25 (s, 9H); ¹³C NMR (CDCl₃): δ 189.45, 139.10, 135.44, 129.26, 128.79, 127.38, 121.94, 56.46, 42.68, 28.51, 22.26; EIMS (*m/z*, %): 292 (M⁺+1, 0.76), 235 (M⁺-^tBu+1, 90.22), 57 (100.00); HRMS(EI) calcd. for C₁₃H₁₇NOS [M⁺-^tBu+1]: 235.1031; Found: 235.1027.

(Rs,R)-N-((E)-1,3-diphenylallyl)-tert-butanesulfinamide (5a)



White solid, yield 82%; mp 105-111 °C; $[\alpha]_D^{20}$ -95.03 (c = 1.09, CHCl₃); FT-IR (KBr, cm⁻¹): *v* 3028, 2957, 2871, 1598, 1495, 1454, 1362, 1184, 1103, 1060, 969, 753, 697; ¹H NMR (CDCl₃): δ 7.23-7.44 (m, 10H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J_I* = 15.9 Hz, *J₂* = 8.1 Hz, 1H), 5.15 (dd, *J_I* = 8.1 Hz, *J₂* = 2.1 Hz, 1H), 3.59 (d, *J* = 2.1 Hz, 1H), 1.27 (s, 9H); ¹³C NMR (CDCl₃): δ 141.60, 136.36, 132.45, 129.52, 128.88, 128.46, 128.01, 127.78, 127.09, 126.58, 60.99, 55.59, 22.65; EIMS (*m/z*, %): 314 (M⁺+1, 0.37), 208 (2.68), 194 (16.89), 193 (100.00); HRMS(MALDI) calcd. for C₁₉H₂₃NOSNa⁺¹ [M⁺+Na]: 336.1393; Found: 336.1404; HPLC (Chiralpak AD column, 90:10 hexane/2-propanol; 0.8 mL/min; 230 nm; (*Rs*, *S*), t_r = 8.78 min, (*Rs*, *R*), t_r = 10.48 min).

(Rs,S)-N-((E)-1,3-diphenylallyl)-tert-butanesulfinamide (6a)



White solid, yield 17%; mp 82-85 °C; $[\alpha]_D^{20}$ -46.52 (c = 0.51, CHCl₃); FT-IR (KBr, cm⁻¹): v 3192, 2924, 2856, 1600, 1494, 1455, 1365, 1267, 1060, 963, 750, 697; ¹H NMR (CDCl₃): δ 7.23-7.43 (m, 10H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J*₁ = 15.9 Hz, *J*₂ = 7.5 Hz, 1H), 5.15 (dd, *J*₁ = 7.5 Hz, *J*₂ = 3.0 Hz, 1H), 3.56 (d, *J* = 3.0 Hz, 1H), 1.23 (s, 9H); ¹³C NMR (CDCl₃): δ 140.61, 136.22, 132.03, 130.59, 128.71, 128.57, 128.00, 127.89, 127.82, 126.67, 61.33, 55.82, 22.62; ESI MS (*m*/*z*): 336.1 (M⁺+Na), 368.1 (M⁺+Na+MeOH); HRMS(MALDI) calcd. for C₁₉H₂₃NOSNa⁺¹ [M⁺+Na]:

336.1393; Found: 336.1400; HPLC (Chiralpak AD column, 90:10 hexane/2-propanol; 0.8 mL/min; 230 nm; (*Rs*, *S*), $t_r = 8.78 \text{ min}$, (*Rs*, *R*), $t_r = 10.48 \text{ min}$).

Mixture of (*Rs*,*R*)-*N*-((*E*)-4,4-dimethyl-1-phenylpent-1-en-3-yl)-*tert*-butanesulfinamide (5b) and (*Rs*,*S*)-*N*-((*E*)-4,4-dimethyl-1-phenylpent-1-en-3-yl)-*tert*-butanesulfinamide (6b)



White solid, total yield 96%; FT-IR (KBr, cm⁻¹): *v* 3326, 2953, 2865, 1598, 1498, 1468, 1365, 1233, 1186, 1116, 1068, 984, 744, 696; ¹H NMR (CDCl₃): δ 7.22-7.41 (m, 5H), 6.59 (d, *J* = 15.9 Hz, 0.85H), 6.56 (d, *J* = 15.6 Hz, 0.15H), 6.00 (dd, *J_I* = 15.9 Hz, *J*₂ = 9.0 Hz, 0.85H), 5.60 (dd, *J_I* = 15.6 Hz, *J*₂ = 9.3 Hz, 0.15H), 3.67 (dd, *J_I* = 9.0 Hz, *J*₂ = 2.4 Hz, 0.85H), 3.59 (dd, *J_I* = 9.3 Hz, *J*₂ = 2.4 Hz, 0.15H), 3.41 (s, 0.85H), 3.39 (s, 0.15H), 1.22 (s, 9H), 0.99 (s, 9H); ¹³C NMR (CDCl₃): δ 136.79, 134.38, 128.58, 127.69, 127.23, 126.56, 65.95, 55.46, 35.03, 26.51, 22.71; EIMS (*m*/*z*, %): 294 (M⁺+1, 1.35), 236 (M⁺-^tBu, 4.62), 237 (M⁺-^tBu+1, 2.14), 173 (76.34), 131 (61.85), 57 (100.00); HRMS(EI) calcd. for C₁₁H₂₇NOS [M⁺]: 293.1813; Found: 293.1809.

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8. Copies of NMR Spectra.






















































































































































































































9. ORTEP View of 1c.



10. ORTEP View of 3d.

