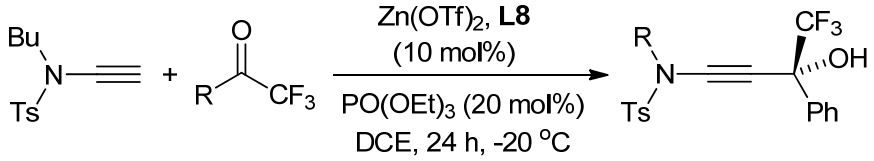
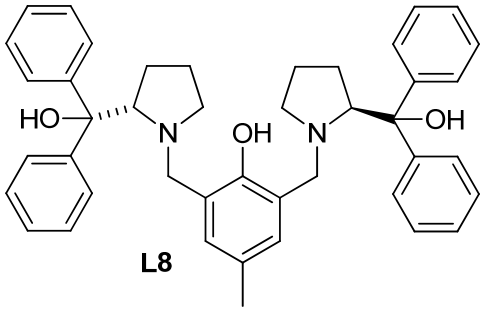
Contents:

1. Synthetic Procedures

Commercially available trifluoromethyl ketones, reagents and solvents were used as purchased without further purification. NMR spectra were obtained at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) in deuterated chloroform. Chemical shifts are reported in ppm relative to TMS. Reaction products were purified by column chromatography on silica gel (particle size 40-63 μm) as described below.

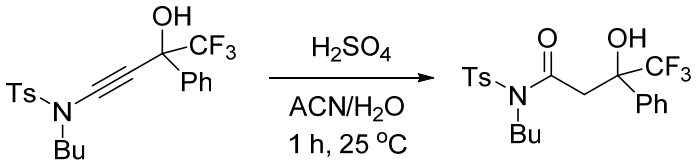
General Zinc Catalyzed Ynamide Addition Procedure





Zinc triflate (7.4 mg, 0.02 mmol), (*R*,*R*)-(-)-2,6-bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol (14.8 mg, 0.022 mmol), *N*-butyl-*N*-ethynyl-4-tolylsulfonamide (75.3 mg, 0.30 mmol), ketone (0.20 mmol) and triethyl phosphate (7.3 mg, 0.04 mmol) were dissolved in 1,2-dichloroethane (0.2 mL) under nitrogen atmosphere. The mixture was stirred at -20 to -17 ^{o}C for 22-24 h. The crude mixture was purified by flash chromatography with 1% NEt_3 in CH_2Cl_2 as mobile phase on silica gel.

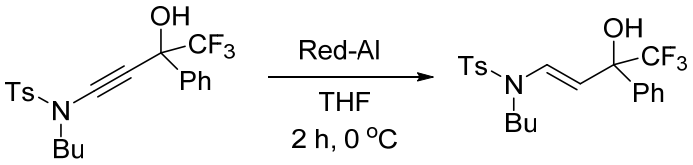
Acid Mediated Hydration of N-(3-Phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-N-butyl-4-toluenesulfonamide



To a solution of *N*-(3-phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide (90 mg, 0.21 mmol) in CH_3CN (2 mL) was added 1M H_2SO_4 (1 mL). The resulting mixture was stirred vigorously for 1 hour and then extracted with Et_2O (3 x 15 mL). The combined organics were washed with brine (1 x 5 mL), and dried over $MgSO_4$ followed by removal of solvents under reduced pressure. The resulting colorless oil was purified by flash chromatography on silica gel (2:1 hexanes:CH_2Cl_2) to give 86 mg (0.19 mmol, 91%) of a cloudy white oil.

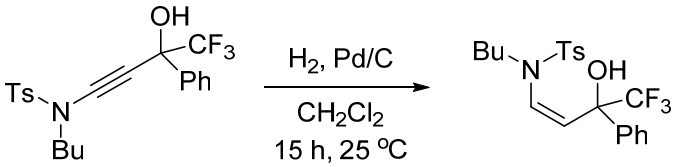
Stereoselective Partial Reduction of N-(3-Phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-N-butyl-4-toluenesulfonamide

a) Formation of the (E)-Enamide



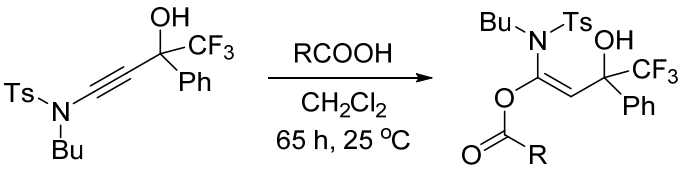
Adopting a procedure from Meyer,[1] a solution of *N*-(3-phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide (120 mg, 0.28 mmol) in THF (2 mL) was added to a solution of Red-Al (0.12 mL, 3.4 M in toluene) in THF (2 mL) at 0 °C under nitrogen atmosphere. After stirring for 1 hour an additional portion of Red-Al (0.12 mL, 3.4 M in toluene) was added and the solution was stirred for another hour. A saturated solution of Rochelle's salt (10 mL) was added and the resulting mixture was stirred for 2 hours and then extracted with EtOAc (3 x 15 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel with hexanes and CH_2Cl_2 (6:4) as the mobile phase to give 99 mg (0.23 mmol, 82%) of a colorless oil.

b) Formation of the (Z)-Enamide



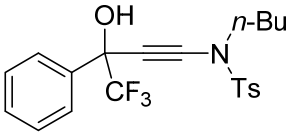
N-(3-Phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide (80 mg, 0.19 mmol) and 10 wt.% Pd on carbon (4 mg, 5 wt.%) were added to CH_2Cl_2 (15 mL) and stirred under H_2 atmosphere (10 bar) for 15 hours. The mixture was filtered through celite and concentrated under reduced pressure. The resulting white solid was purified by flash chromatography on silica gel with hexanes and CH_2Cl_2 (4:3) as the mobile phase to give 69 mg (0.16 mmol, 84%, 89:11 *Z:E*) of a white solid.

Stereoselective Hydroacyloxylation of N-(3-Phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-N-butyl-4-toluenesulfonamide

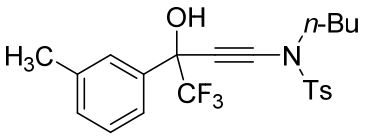


To a solution of *N*-(3-phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide (87 mg, 0.20 mmol) in CH_2Cl_2 were added 8-10 equivalents of a carboxylic acid. The resulting mixture was stirred for 3 days and then purified directly by flash chromatography on silica gel with CH_2Cl_2: hexanes (1:1) as the mobile phase.

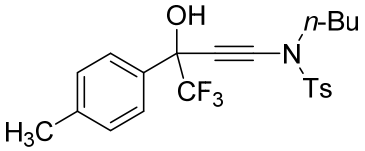
2. Product Characterization



***N*-(3-Phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 2,2,2-trifluoroacetophenone (35 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 ^{o}C to give 82 mg (0.19 mmol, 96%, 96% ee) of a colorless oil after 24 hours.^{1}H NMR (400 MHz) δ = 7.76 (d, *J* = 8.1 Hz, 2H), 7.69 (m, 2H), 7.43 – 7.36 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.44 – 3.32 (m, 2H), 3.05 (s, 1H), 3.05 (s, 3H), 1.67 – 1.58 (m, 2H), 1.40 – 1.29 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.0, 135.4, 134.3, 129.9, 129.4, 128.2, 127.7, 127.2, 123.4 (q, *J* = 285.6 Hz), 81.7, 73.4 (q, *J* = 32.5 Hz), 67.4, 50.9, 29.8, 21.7, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 6.4 min (minor), t_2 = 9.9 min (major). α = 2.18. Anal. Calcd. for $C_{21}H_{22}F_3NO_3S$: C, 59.28; H, 5.21; N, 3.29. Found: C, 59.02; H, 5.12; N, 3.29.

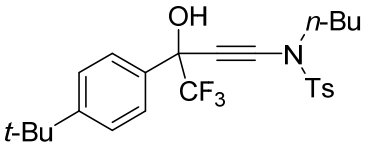


***N*-(3-(3'-Tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 3'-methyl-2,2,2-trifluoroacetophenone (38 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 ^{o}C to give 85 mg (0.19 mmol, 97%, 95% ee) of a colorless oil after 24 hours.^{1}H NMR (400 MHz) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.53 (m, 1H), 7.48 (m, 1H), 7.35 – 7.26 (m, 3H), 7.22 (m, 1H), 3.44 – 3.32 (m, 2H), 3.16 (s, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 1.67 – 1.58 (m, 2H), 1.40 – 1.29 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.0, 137.9, 135.3, 134.3, 130.2, 129.9, 128.0, 127.7, 127.6, 124.3, 123.4 (q, *J* = 284.5 Hz), 81.6, 73.4 (q, *J* = 32.0 Hz), 67.5, 50.9, 29.8, 21.7, 21.5, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 6.3 min (minor), t_2 = 7.4 min (major). α = 1.34. Anal. Calcd. for $C_{22}H_{24}F_3NO_3S$: C, 60.12; H, 5.50; N, 3.19. Found: C, 60.06; H, 5.88; N, 3.25.



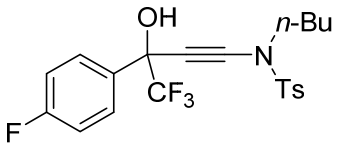
***N*-(3-(4'-Tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-methyl-2,2,2-trifluoroacetophenone (38 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 ^{o}C to give 86 mg (0.19 mmol, 97%, 94% ee) of a colorless oil after 24 hours.^{1}H NMR (400 MHz) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.44 – 3.31 (m, 2H), 3.00 (s, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 1.68 – 1.57 (m, 2H), 1.40 – 1.27 (m, 2H),

0.90 (t, *J* = 7.3 Hz, 3H).[13]C NMR (100 MHz) δ = 145.0, 139.4, 134.3, 132.5, 129.9, 128.9, 127.7, 127.0, 123.4 (q, *J* = 285.0 Hz), 81.5, 73.3 (q, *J* = 32.1 Hz), 67.5, 50.9, 29.8, 21.7, 21.2, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 6.3 min (minor), t_2 = 9.8 min (major). α = 2.22. Anal. Calcd. for $C_{22}H_{24}F_3NO_3S$: C, 60.12; H, 5.50; N, 3.19. Found: C, 59.76; H, 5.84; N, 3.28.



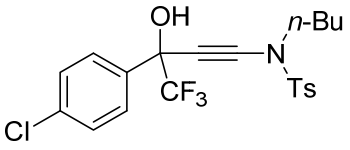
***N*-(3-(4'-*Tert*-butylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**

The reaction with 4'-*tert*-butyl-2,2,2-trifluoroacetophenone (46 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -18 °C to give 92 mg (0.19 mmol, 95%, 96% ee) of a colorless oil after 24 hours.[1]H NMR (400 MHz) δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 3.44 – 3.32 (m, 2H), 3.02 (s, 1H), 2.45 (s, 3H), 1.68 – 1.58 (m, 2H), 1.40 – 1.30 (m, 2H), 1.33 (s, 9H), 0.90 (t, *J* = 7.4 Hz, 3H).[13]C NMR (100 MHz) δ = 152.53, 145.0, 134.3, 132.4, 129.9, 127.7, 126.9, 125.1, 123.5 (q, *J* = 284.6 Hz), 81.5, 73.3 (q, *J* = 32.1 Hz), 67.5, 50.9, 34.6, 31.3, 29.8, 21.7, 19.4, 13.5. The ee was determined by HPLC on Chiralcel OD using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 6.9 min (minor), t_2 = 9.3 min (major). α = 1.66. Anal. Calcd. for $C_{25}H_{30}F_3NO_3S$: C, 62.35; H, 6.28; N, 2.91. Found: C, 62.32; H, 6.58; N, 3.01.

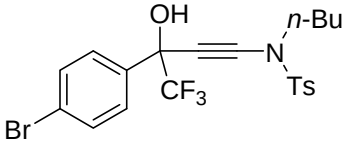


***N*-(3-(4'-Fluorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**

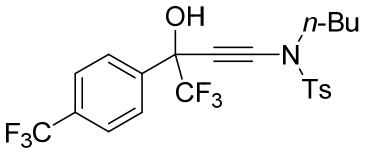
The reaction with 4'-fluoro-2,2,2-trifluoroacetophenone (39 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 °C to give 86 mg (0.19 mmol, 97%, 94% ee) of a colorless oil after 24 hours.[1]H NMR (400 MHz) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.67 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.08 (m, *J* = 8.6 Hz, 2H), 3.45 – 3.30 (m, 2H), 3.03 (s, 1H), 2.46 (s, 3H), 1.67 – 1.58 (m, 2H), 1.40 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).[13]C NMR (100 MHz) δ = 164.64, 162.16, 145.2, 134.3, 131.3, 129.9, 129.3 (d, *J* = 85.4 Hz), 127.6, 123.5 (q, *J* = 284.0 Hz), 115.1 (d, *J* = 21.7 Hz), 81.9, 73.0 (q, *J* = 32.6 Hz), 67.2, 50.9, 29.8, 21.7, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min t_1 = 6.2 min (minor), t_2 = 7.1 min (major). α = 1.32. Anal. Calcd. for $C_{21}H_{21}F_4NO_3S$: C, 56.88; H, 4.77; N, 3.16. Found: C, 56.78; H, 5.13; N, 3.25.



***N*-(3-(4'-Chlorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-chloro-2,2,2-trifluoroacetophenone (44 mg, 0.21 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 ^{o}C to give 86 mg (0.20 mmol, 95%, 93% ee) of a colorless oil after 24 hours.^{1}H NMR (400 MHz) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.44 – 3.30 (m, 2H), 3.40 (s, 1H), 2.45 (s, 3H), 1.67 – 1.57 (m, 2H), 1.40 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.1, 135.6, 134.2, 134.0, 129.9, 128.6, 128.3, 127.6, 123.2 (q, *J* = 284.7 Hz), 81.9, 72.9 (q, *J* = 32.6 Hz), 67.0, 50.8, 29.8, 21.6, 19.3, 13.4. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (95:5) as the mobile phase at 1.0 mL/min. t_1 = 8.2 min (minor), t_2 = 9.6 min (major). α = 1.29. Anal. Calcd. for $C_{21}H_{21}ClF_3NO_3S$: C, 54.84; H, 4.60; N, 3.05. Found: C, 54.71; H, 4.77; N, 3.09.

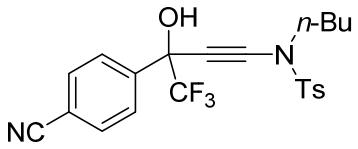


***N*-(3-(4'-Bromophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-bromo-2,2,2-trifluoroacetophenone (50 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -17 ^{o}C to give 98 mg (0.19 mmol, 97%, 90% ee) of a colorless oil after 24 hours.^{1}H NMR (400 MHz) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.33 (d, *J* = 8.3 Hz, 2H), 3.44 – 3.31 (m, 2H), 3.32 (s, 1H), 2.46 (s, 3H), 1.67 – 1.57 (m, 2H), 1.40 – 1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.2, 134.6, 134.2, 131.3, 129.9, 129.0, 127.6, 123.9, 123.1 (q, *J* = 284.7 Hz), 82.0, 73.0 (q, *J* = 32.6 Hz), 67.0, 50.9, 29.8, 21.7, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 17.1 min (minor), t_2 = 18.8 min (major). α = 1.12. Anal. Calcd. for $C_{21}H_{21}BrF_3NO_3S$: C, 50.01; H, 4.20; N, 2.78. Found: C, 50.08; H, 4.54; N, 2.73.

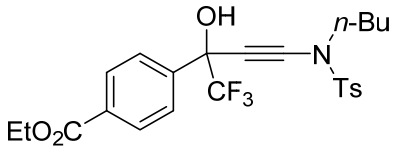


***N*-(3-(4'-Trifluoromethylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-trifluoromethyl-2,2,2-trifluoroacetophenone (50 mg, 0.21 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (77 mg, 0.31 mmol) at -18 ^{o}C to give 98 mg (0.20 mmol, 99%, 92% ee) of a colorless oil after 22 hours.^{1}H NMR (400 MHz) δ = 7.82 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.49 (s, 1H), 3.45 – 3.31 (m, 2H), 2.45 (s, 3H), 1.66 – 1.58 (m, 2H), 1.39 – 1.29 (m, 2H), 0.90 (t,

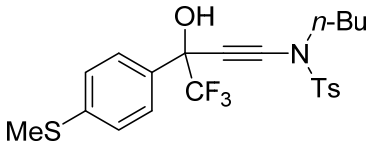
J = 7.4 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.2, 139.3, 134.1, 131.6 (q, J = 32.6 Hz), 129.9, 127.7, 127.6, 125.1 (q, J = 3.8 Hz), 123.8 (q, J = 270.9 Hz), 123.1 (q, J = 284.5 Hz), 82.2, 73.0 (q, J = 32.5 Hz), 66.8, 50.8, 29.8, 21.6, 19.3, 13.4. The ee was determined by HPLC on Phenomenex® Cellulose-4 using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 13.7 min (minor), t_2 = 14.6 min (major). α = 1.09. Anal. Calcd. for $C_{22}H_{21}F_6NO_3S$: C, 53.55; H, 4.29; N, 2.84. Found: C, 53.54; H, 4.42; N, 2.87.



***N*-(3-(4'-Cyanophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-cyano-2,2,2-trifluoroacetophenone (42 mg, 0.21 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (77 mg, 0.31 mmol) at -17 ^{o}C to give 86 mg (0.19 mmol, 91%, 90% ee) of a colorless oil after 22 hours.^{1}H NMR (400 MHz) δ = 7.83 (d, J = 8.2 Hz, 2H), 7.77 – 7.67 (m, 4H), 7.34 (d, J = 8.1 Hz, 2H), 3.60 (s, 1H), 3.46 – 3.30 (m, 2H), 2.46 (s, 3H), 1.66 – 1.57 (m, 2H), 1.38 – 1.27 (m, 2H), 0.90 (t, J = 7.4, 3H).^{13}C NMR (100 MHz) δ = 145.3, 140.4, 134.1, 131.9, 129.9, 128.1, 127.5, 123.0 (q, J = 285.6 Hz), 118.2, 113.4, 82.5, 72.9 (q, J = 32.5 Hz), 50.8, 61.2, 50.8, 29.8, 21.6, 19.3, 13.4. The ee was determined by HPLC on Phenomenex® Cellulose-4 using hexanes: EtOH (97:3) as the mobile phase at 1.0 mL/min. t_1 = 23.4 min (minor), t_2 = 26.3 min (major). α = 1.14. Anal. Calcd. for $C_{22}H_{24}F_3N_2O_3S$: C, 58.66; H, 4.70; N, 6.22. Found: C, 58.77; H, 5.10; N, 6.14.

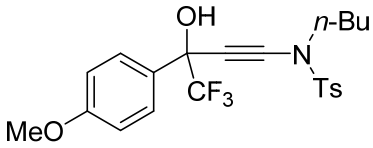


***N*-(3-(4'-Ethoxycarbonylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**
The reaction with 4'-ethoxycarbonyl-2,2,2-trifluoroacetophenone (50 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -17 ^{o}C to give 99 mg (0.20 mmol, 99%, 89% ee) of a colorless oil after 22 hours.^{1}H NMR (400 MHz) δ = 8.06 (d, J = 8.5 Hz, 2H), 7.79 – 7.71 (m, 4H), 7.33 (d, J = 8.1 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.73 (s, 1H), 3.46 – 3.31 (m, 2H), 2.46 (s, 3H), 1.68 – 1.56 (m, 2H), 1.41 (t, J = 7.1 Hz, 3H), 1.38 – 1.29 (m, 2H), 0.90 (t, J = 7.4, 3H).^{13}C NMR (100 MHz) δ = 166.1, 145.1, 140.0, 134.1, 131.4, 129.9, 129.3, 127.6, 127.2, 123.2 (q, J = 284.6 Hz), 82.0, 73.1 (q, J = 32.6 Hz), 67.0, 61.2, 50.8, 29.8, 21.6, 19.3, 14.3, 13.4. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 7.5 min (minor), t_2 = 8.9 min (major). α = 1.34. Anal. Calcd. for $C_{24}H_{26}F_3NO_5S$: C, 57.94; H, 5.27; N, 2.82. Found: C, 57.92; H, 5.53; N, 2.88.



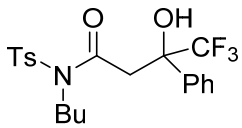
***N*-(3-((4'-Methylthio)phenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**

The reaction with 4'-methylthio-2,2,2-trifluoroacetophenone (44 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (75 mg, 0.30 mmol) at -20 ^{o}C to give 94 mg (0.20 mmol, 99%, 90% ee) of a colorless oil after 22 hours.^{1}H NMR (400 MHz) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.44 – 3.30 (m, 2H), 3.39 (s, 1H), 2.50 (s, 3H), 2.45 (s, 3H), 1.66 – 1.58 (m, 2H), 1.39 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 145.9, 141.2, 134.9, 132.7, 130.6, 128.3, 128.2, 126.3, 124.0 (q, *J* = 285.8 Hz), 82.0, 73.5 (q, *J* = 32.5 Hz), 67.7, 51.1, 29.9, 21.8, 19.4, 15.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 10.9 min (minor), t_2 = 18.8 min (major). α = 2.06. Anal. Calcd. for $C_{22}H_{24}F_3NO_3S_2$: C, 57.94; H, 5.27; N, 2.82. Found: C, 57.92; H, 5.53; N, 2.88.



***N*-(3-(4'-Methoxyphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**

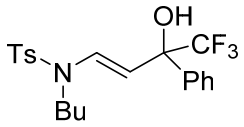
The reaction with 4'-methoxy-2,2,2-trifluoroacetophenone (41 mg, 0.20 mmol) was performed using *N*-butyl-*N*-ethynyl-4-toluenesulfonamide (74 mg, 0.29 mmol) at 0 ^{o}C to give 85 mg (0.19 mmol, 91%, 85% ee) of a colorless oil after 52 hours.^{1}H NMR (400 MHz) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.44 – 3.30 (m, 2H), 3.26 (s, 1H), 2.44 (s, 3H), 1.67 – 1.57 (m, 2H), 1.39 – 1.28 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 161.0, 145.6, 134.7, 130.4, 129.0, 128.1, 128.0, 123.9 (q, *J* = 285.6 Hz), 113.9, 81.8, 73.4 (q, *J* = 32.4 Hz), 67.7, 55.5, 51.1, 29.8, 21.7, 19.4, 13.5. The ee was determined by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (95:5) as the mobile phase at 1.0 mL/min. t_1 = 13.8 min (minor), t_2 = 26.2 min (major). α = 2.20. Anal. Calcd. for $C_{22}H_{24}F_3NO_4S$: C, 58.01; H, 5.31; N, 3.08. Found: C, 57.70; H, 5.54; N, 3.13.



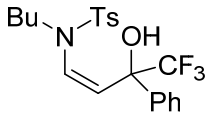
***N*-Butyl-4,4,4-trifluoro-3-hydroxy-3-phenyl-*N*-tosylbutanamide**

^{1}H NMR (400 MHz) δ = 7.76 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.21 (m, 5H), 5.45 (s, 1H), 3.86 (d, *J* = 17.1 Hz, 1H), 3.79 – 3.63 (m, 2H), 3.23 (d, *J* = 17.0 Hz, 1H), 2.48 (s, 3H), 1.56 – 1.36 (m, 2H), 1.28 – 1.14 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 171.5, 145.7, 137.1, 136.2, 130.2, 128.6, 128.3, 127.4, 126.2, 124.2 (q, *J* = 283.5 Hz), 76.2 (q, *J*

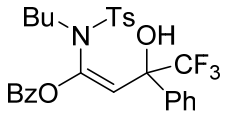
= 28.7 Hz), 46.8, 39.4, 31.3, 29.7, 21.6, 19.8, 13.5. The ee was determined as 94% ee (starting material: 94% ee) by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (95:5) as the mobile phase at 1.0 mL/min. t_1 = 8.2 min (minor), t_2 = 10.0 min (major). α = 1.38. Anal. Calcd. for $C_{21}H_{24}F_3NO_4S$: C, 56.88; H, 5.46; N, 3.16. Found: C, 57.17; H, 5.78; N, 3.18.



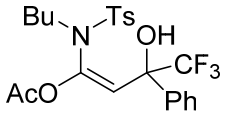
(*E*)-*N*-(4,4,4-Trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide
^{1}H NMR (400 MHz) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.43 – 7.36 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 14.4 Hz, 1H), 5.24 (d, *J* = 14.4 Hz, 1H), 3.40 – 3.26 (m, 2H), 2.60 (s, 1H), 2.42 (s, 3H), 1.60 – 1.51 (m, 2H), 1.39 – 1.28 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz) δ = 140.1, 133.7, 131.9, 128.1, 125.9, 124.9, 124.3, 122.9, 122.8 (q, *J* = 1.5 Hz), 121.0 (q, *J* = 284.6 Hz), 103.0, 72.9 (q, *J* = 29.0 Hz), 41.6, 24.9, 17.6 (q, *J* = 1.3 Hz), 9.6. The ee was determined as 93% ee (starting material: 94% ee) by HPLC on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 10.0 min (minor), t_2 = 14.9 min (major). α = 1.75. Anal. Calcd. for $C_{21}H_{24}F_3NO_3S$: C, 59.00; H, 5.66; N, 3.28. Found: C, 59.17; H, 6.01; N, 3.30.



(*Z*)-*N*-(4,4,4-Trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide
^{1}H NMR (400 MHz) δ = 7.64 – 7.58 (m, 4H), 7.40 – 7.29 (m, 5H), 6.30 (d, *J* = 8.9 Hz, 1H), 5.46 (d, *J* = 8.9 Hz, 1H), 5.41 (s, 1H), 3.00 (m, 1H), 2.75 (m, 1H), 2.44 (s, 3H), 1.10 – 1.01 (m, 4H), 0.69 – 0.63 (m, 3H).^{13}C NMR (100 MHz) δ = 144.5, 137.7, 133.0, 131.3, 129.8, 129.6, 128.5, 128.0, 127.8, 126.7, 124.7 (q, *J* = 285.3 Hz), 76.5 (q, *J* = 28.4 Hz), 51.0, 29.7, 21.5, 19.6, 13.4. The ee was determined by HPLC as 93% ee (starting material: 94% ee) on Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 6.5 min (minor), t_2 = 7.5 min (major). α = 1.33. Mp. 117-120 ^{o}C. Anal. Calcd. for $C_{21}H_{24}F_3NO_3S$: C, 59.00; H, 5.66; N, 3.28. Found: C, 59.23%; H, 5,81%; N, 3.23%.



(*E*)-*N*-(2-Benzoyloxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide
Employing benzoic acid (244 mg, 2.0 mmol) in the procedure described above gave 105 mg (0.19 mmol, 93%) of a white solid.^{1}H NMR (400 MHz) δ = 7.82 – 7.71 (m, 4H), 7.56 (m, 1H) 7.46 – 7.27 (m, 9H), 6.58 (s, 1H), 5.40 (s, 1H), 3.23 (m, 1H), 2.86 (m, 1H), 2.42 (s, 3H), 1.15 – 0.85 (m, 4H), 0.65 – 0.45 (m, 3H).^{13}C NMR (100 MHz) δ = 164.1, 145.2, 140.5, 138.6, 135.8, 134.6, 130.4, 129.1, 128.9, 128.7, 128.5, 127.9, 125.2 (q, *J* = 287.0 Hz), 123.1, 76.5 (q, *J* = 28.7 Hz), 48.6, 29.8, 21.6, 19.8, 13.3. The ee was determined by HPLC as 89% ee (starting material: 87% ee) on Phenomenex® Cellulose-4 using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 12.4 min (minor), t_2 = 13.4 min (major). α = 1.11. Mp. 120-123 ^{o}C. Anal. Calcd. for $C_{28}H_{28}F_3NO_5S$: C, 61.42; H, 5.15; N, 2.56. Found: C, 61.33; H, 5.36; N, 2.56.

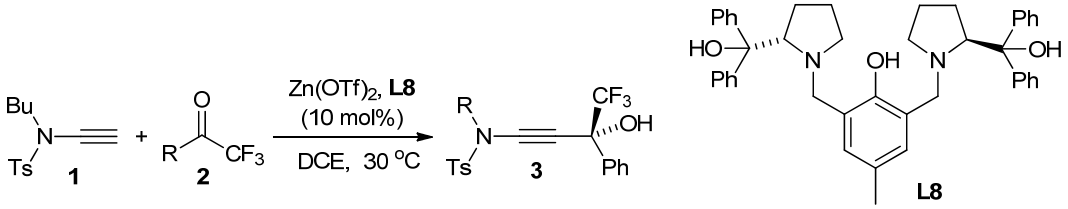


(*E*)-*N*-(2-Acetoxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide

Employing acetic acid (103 mg, 1.72 mmol) in the procedure described above gave 88 mg (0.18 mmol, 89%) of a colorless oil. ^{1}H NMR (400 MHz) δ = 7.75 – 7.63 (m, 4H), 7.41 – 7.27 (m, 5H), 6.39 (s, 1H), 5.16 (s, 1H), 3.03 (m, 1H), 2.79 (m, 1H), 2.43 (s, 3H), 1.81 (s, 3H), 1.05 – 0.75 (m, 4H), 0.64 – 0.47 (m, 3H). ^{13}C NMR (100 MHz) δ = 168.2, 145.2, 140.6, 138.4, 135.3, 130.0, 129.1, 128.7, 128.4, 127.8, 125.1 (q, *J* = 286.8 Hz), 122.3, 75.5 (q, *J* = 29.0 Hz), 48.7, 29.6, 21.6, 20.4, 19.7, 13.3. The ee was determined as 88% ee (starting material: 87% ee) by HPLC on Chiralcell OJ using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 11.3 min (minor), t_2 = 14.2 min (major). α = 1.36. Anal. Calcd. for $C_{23}H_{26}F_3NO_5S$: C56.90; H, 5.40; N, 2.88. Found: C, 57.00; H, 5.57; N, 2.91.

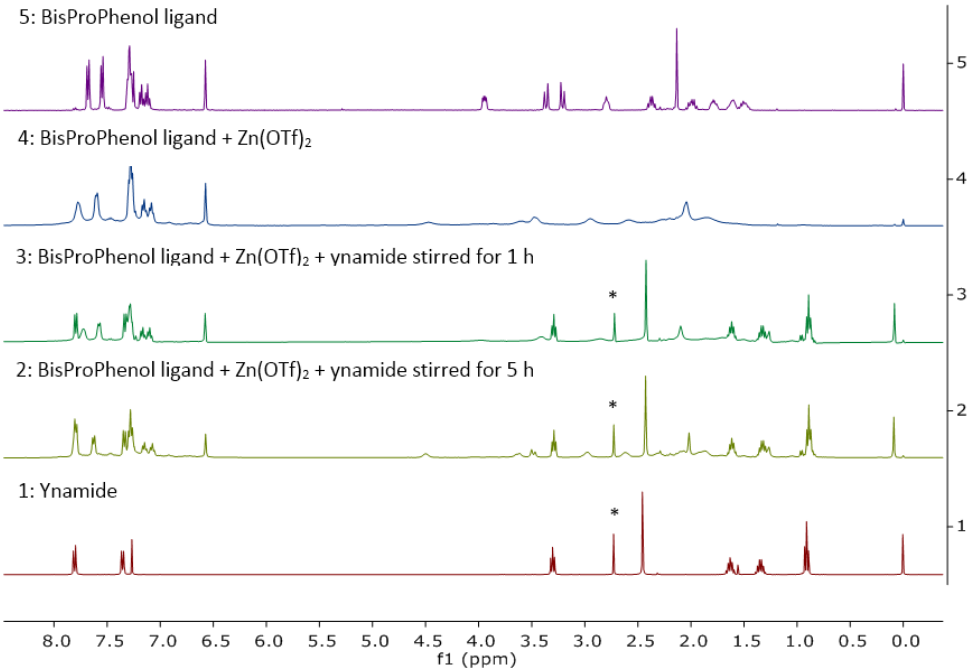
3. Investigation of the Effect of the Ligand and the Ynamide/Ketone Ratio

Reaction analysis at 30 °C showed that the same results can be obtained using either 1.5 equivalents of the ynamide **1** or 1.5 equivalents of the trifluoromethyl ketone **2** (compare entries 1 and 5). Monitoring the reaction by ^{1}H and ^{19}F NMR showed that the catalysis is ligand-accelerated. In the presence of 10 mol% of **L8** the reaction is almost complete after 8 hours while in the absence of the ligand the conversion to **3** is only 47% after 26 hours (entries 4 and 6).



Entry	1	2	L8	time	conversion	ee
1	1.5 equiv.	1.0 equiv.	10 mol%	16 h	100%	-87%
2	1.0 equiv.	1.5 equiv.	10 mol%	2 h	41%	n.d.
3				4 h	82%	n.d.
4				8 h	97%	-87%
5				16 h	100%	-87%
6	1.0 equiv.	1.5 equiv.	none	26 h	47%	0%

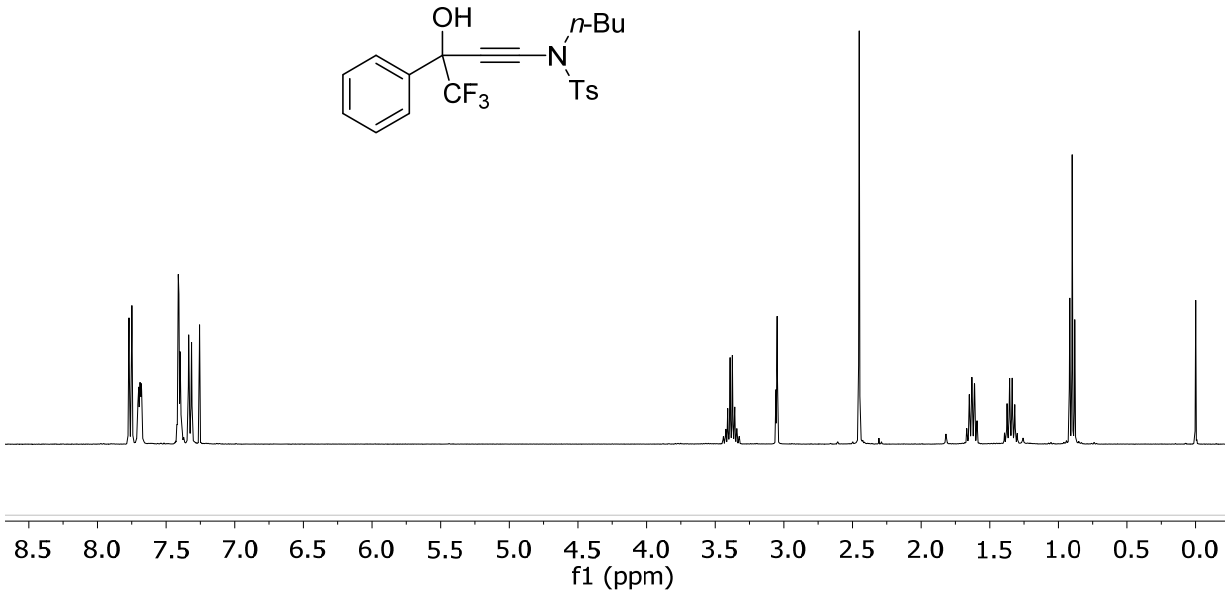
^{1}H NMR analysis of stoichiometric mixtures of zinc triflate, the Bis-ProPhenol ligand and **1** showed formation of a Zn-**L8** complex in deuterated chloroform which is evident from line broadening and shifts of some ligand NMR signals. We observed no sign of coordination and activation of the ynamide. The signal of the terminal alkyne proton remained unchanged even after 5 hours.



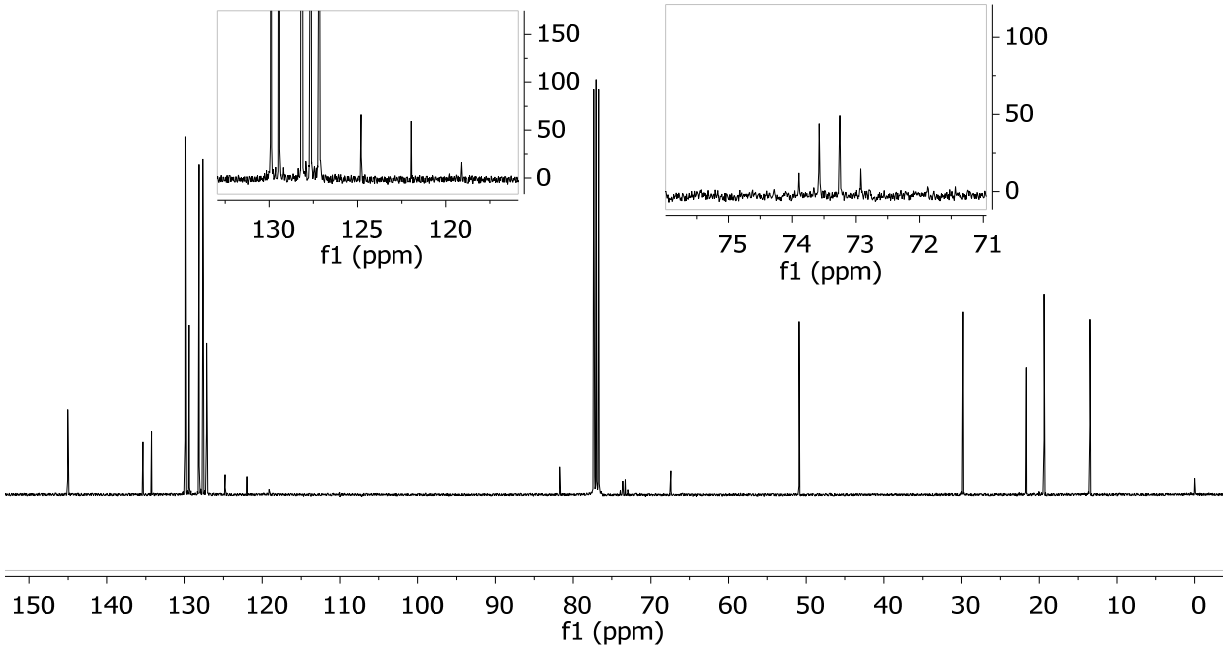
*R-C≡CH.

4. NMR Spectroscopy

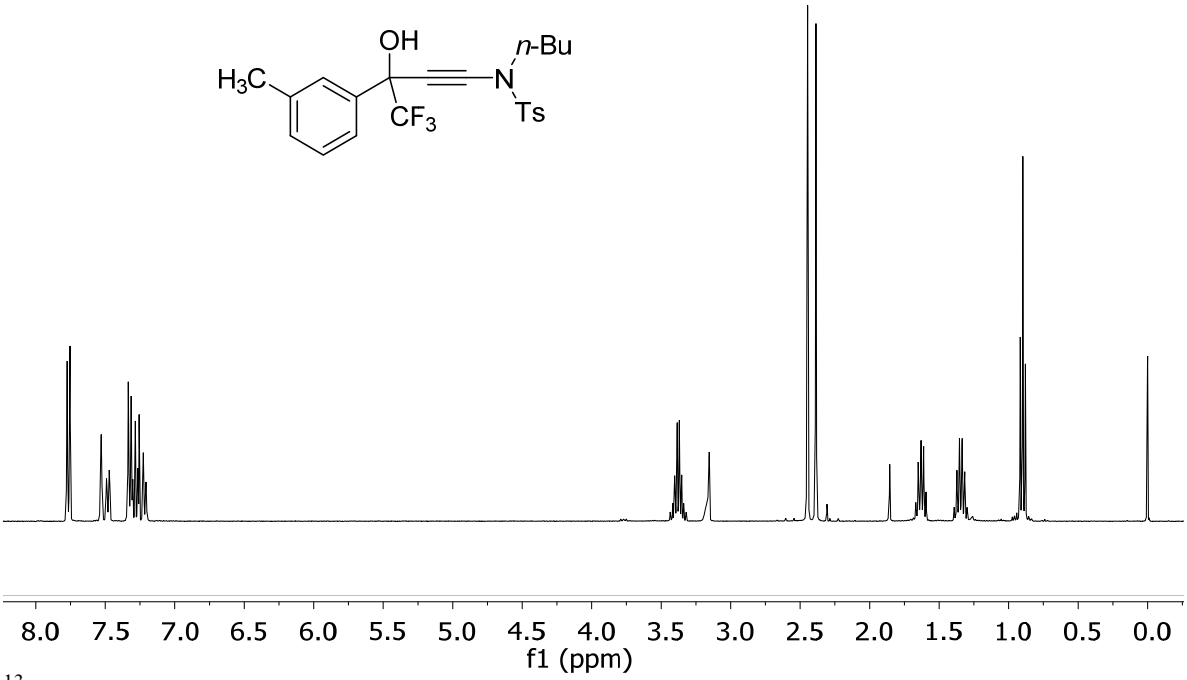
^{1}H NMR Spectrum of *N*-(3-phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



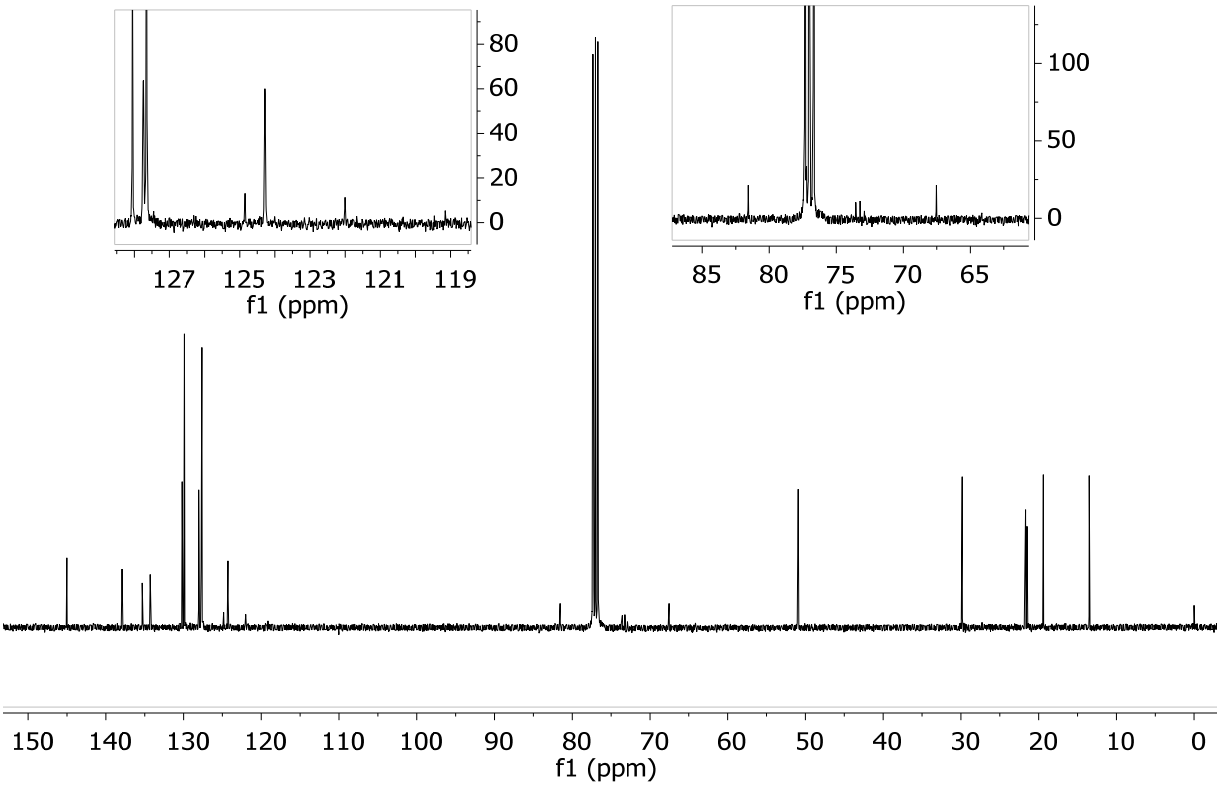
^{13}C NMR Spectrum of *N*-(3-phenyl-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



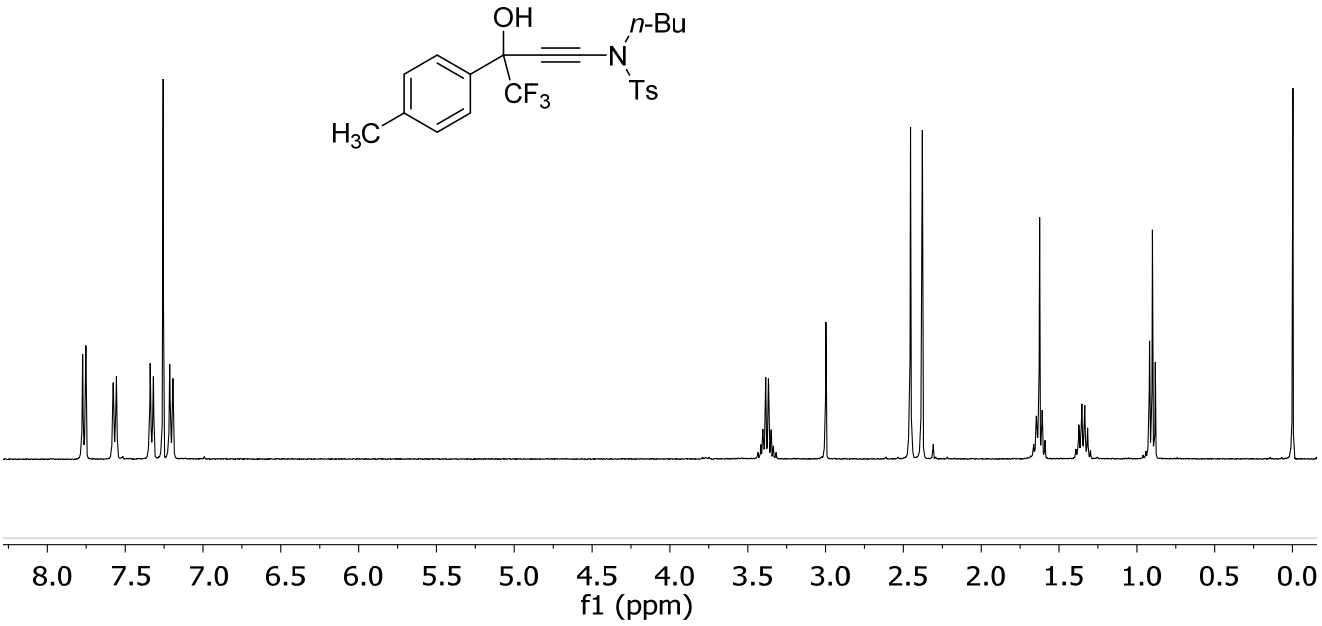
[1]H NMR Spectrum of *N*-(3-(3'-tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



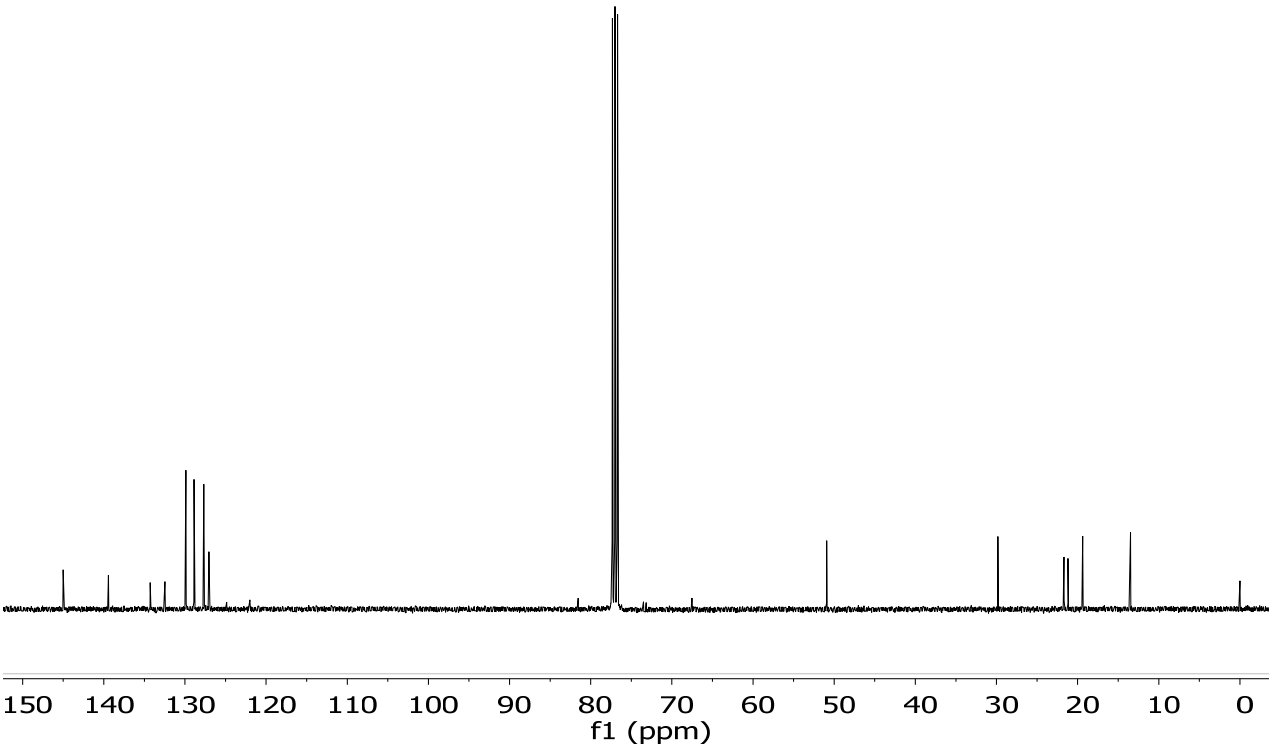
[13]C NMR Spectrum of *N*-(3-(3'-tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



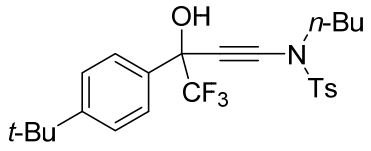
^{1}H NMR Spectrum of *N*-(3-(4'-tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



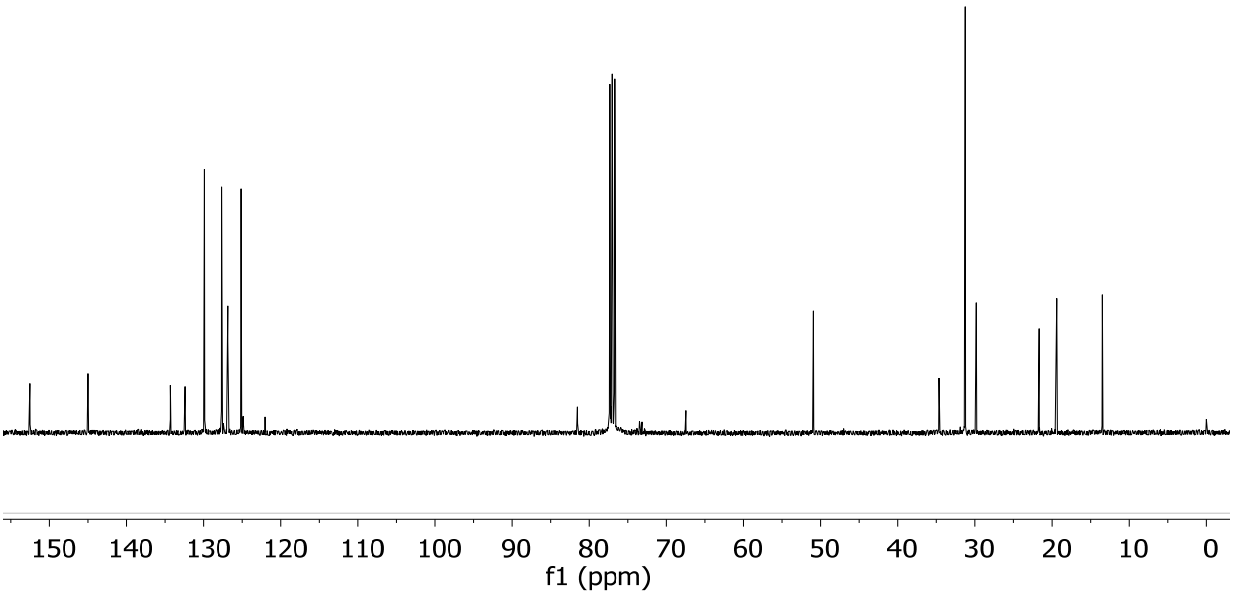
^{13}C NMR Spectrum of *N*-(3-(4'-tolyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



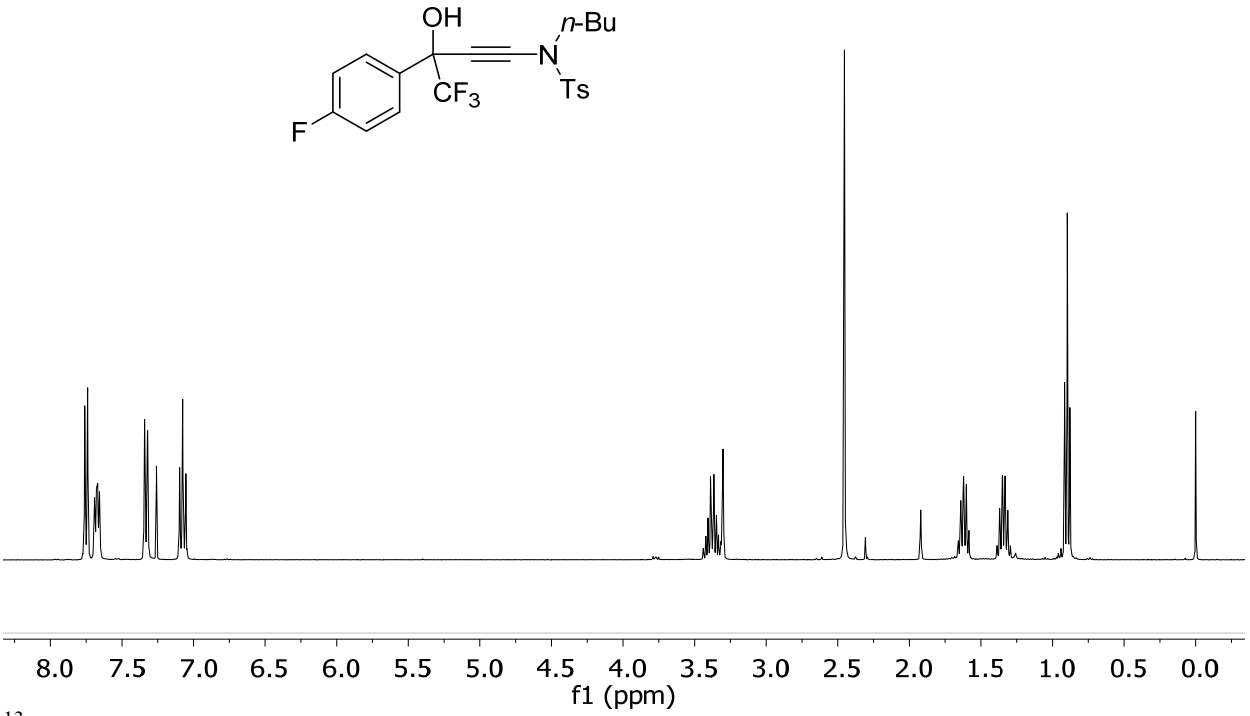
^{1}H NMR Spectrum of *N*-(3-(4'-*tert*-butylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



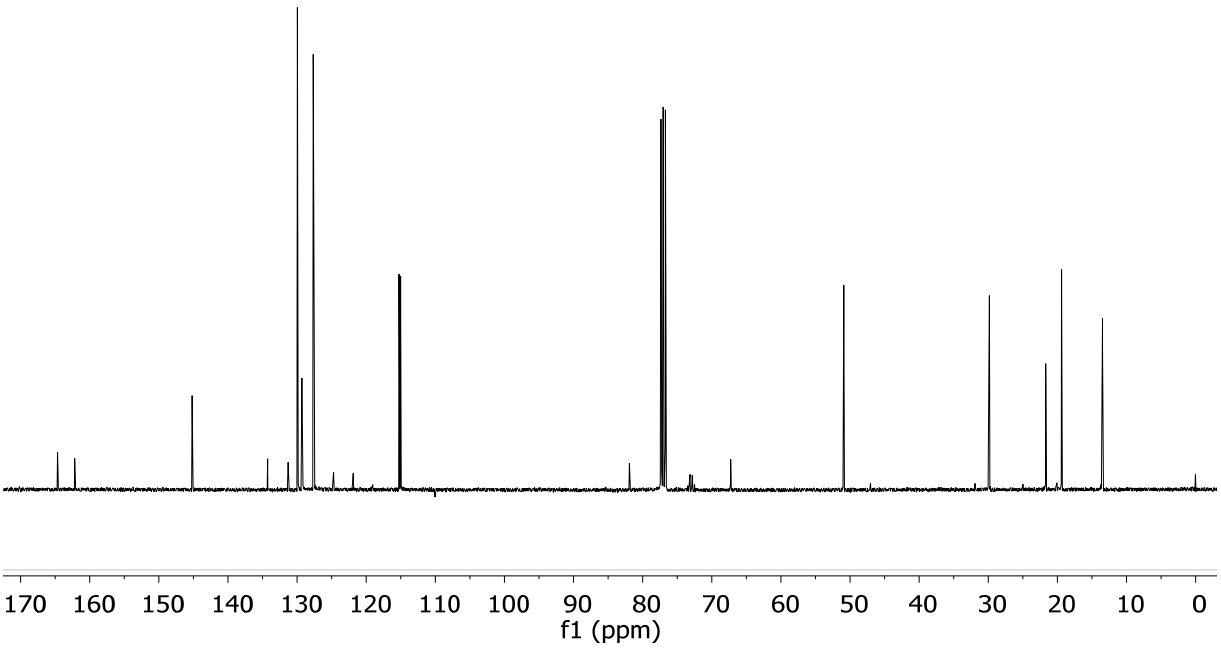
^{13}C NMR Spectrum of *N*-(3-(4'-*tert*-butylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



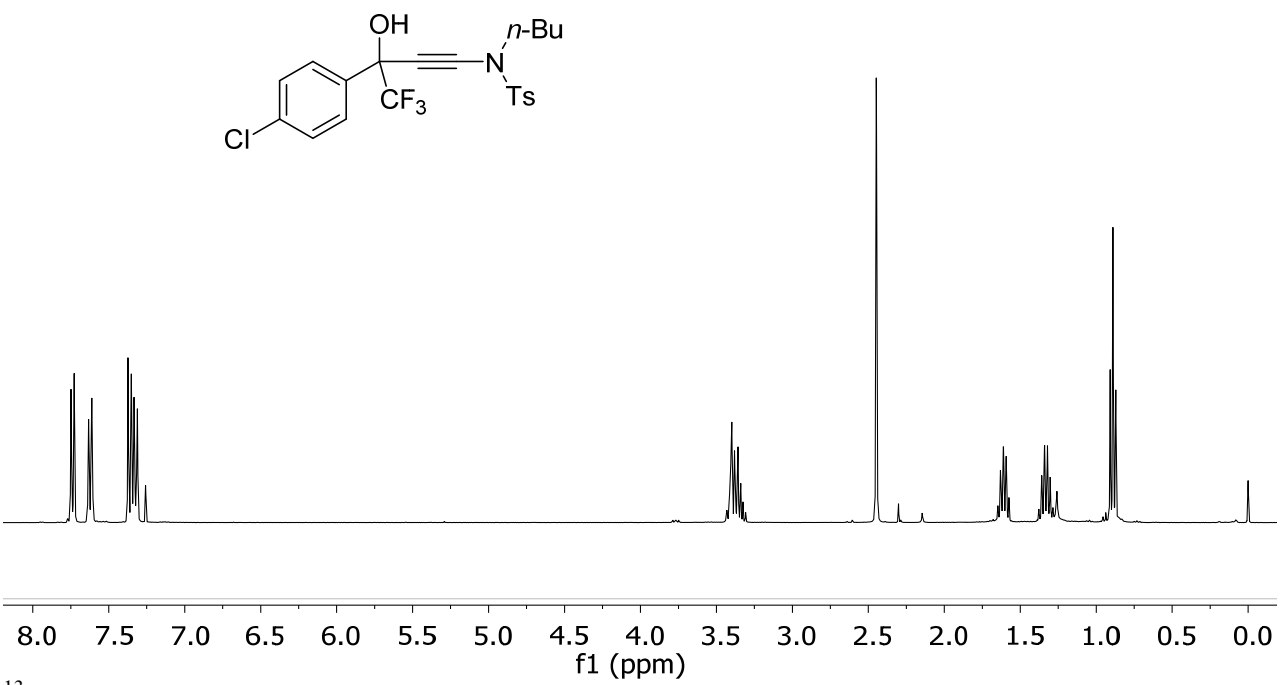
^{1}H NMR Spectrum of *N*-(3-(4'-fluorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



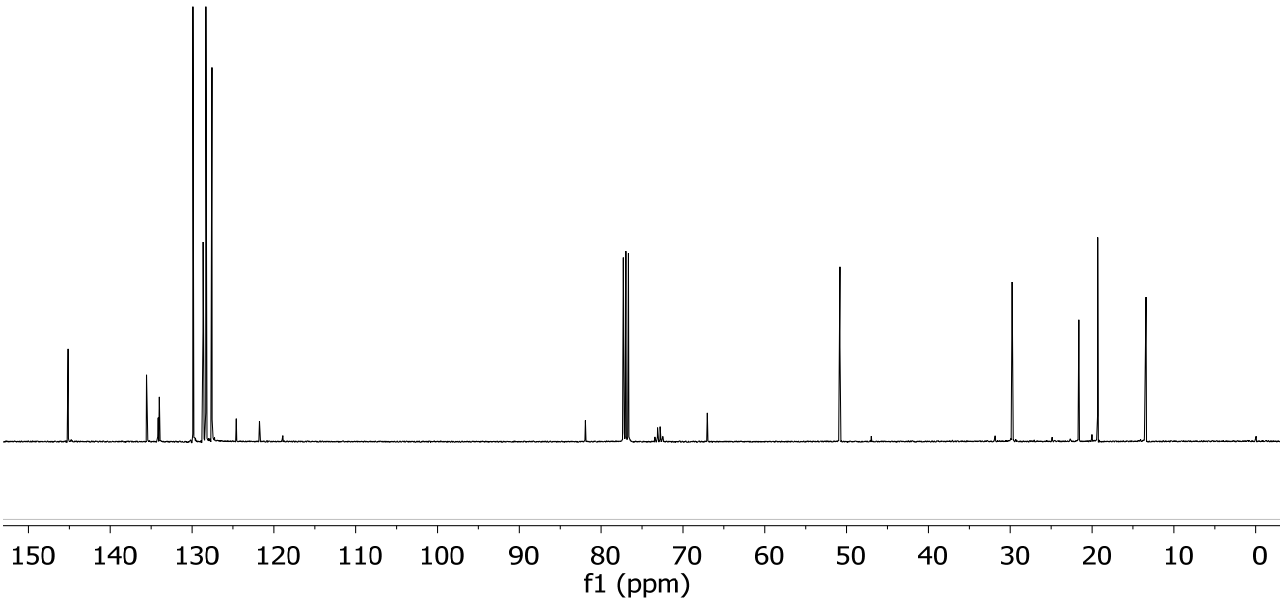
^{13}C NMR Spectrum of *N*-(3-(4'-fluorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



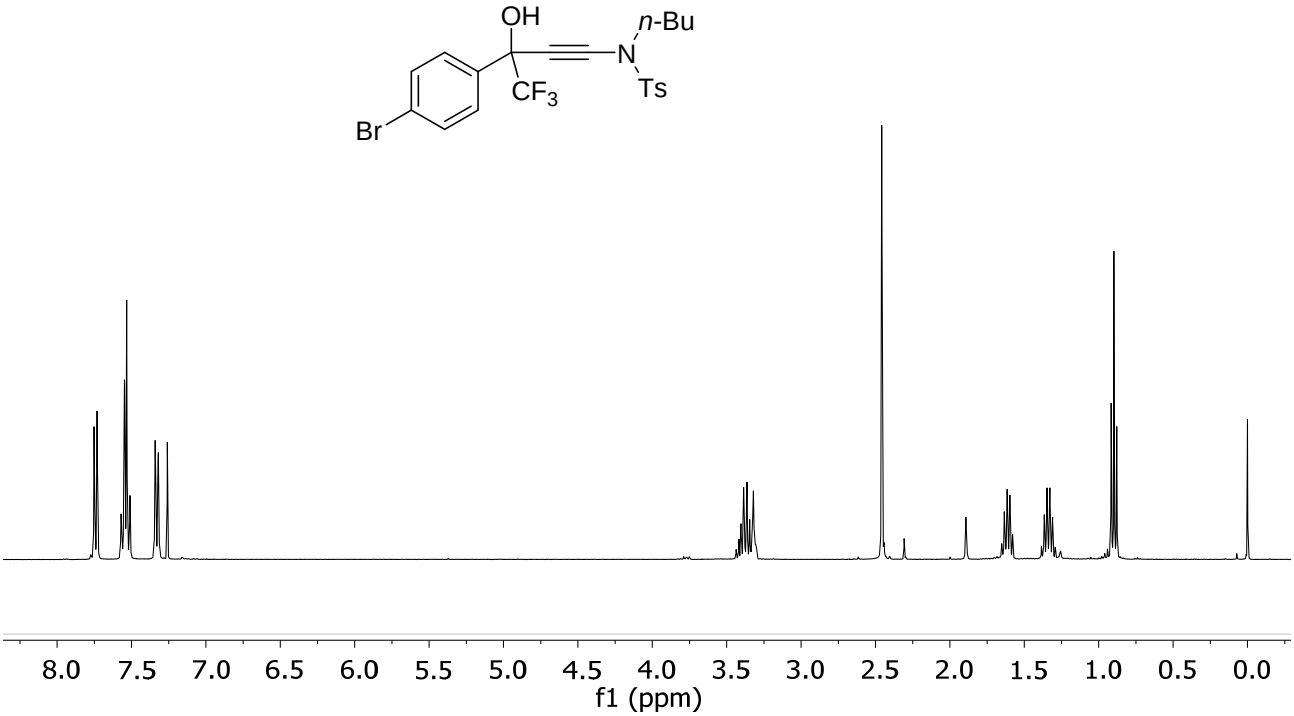
^{1}H NMR Spectrum of *N*-(3-(4'-chlorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



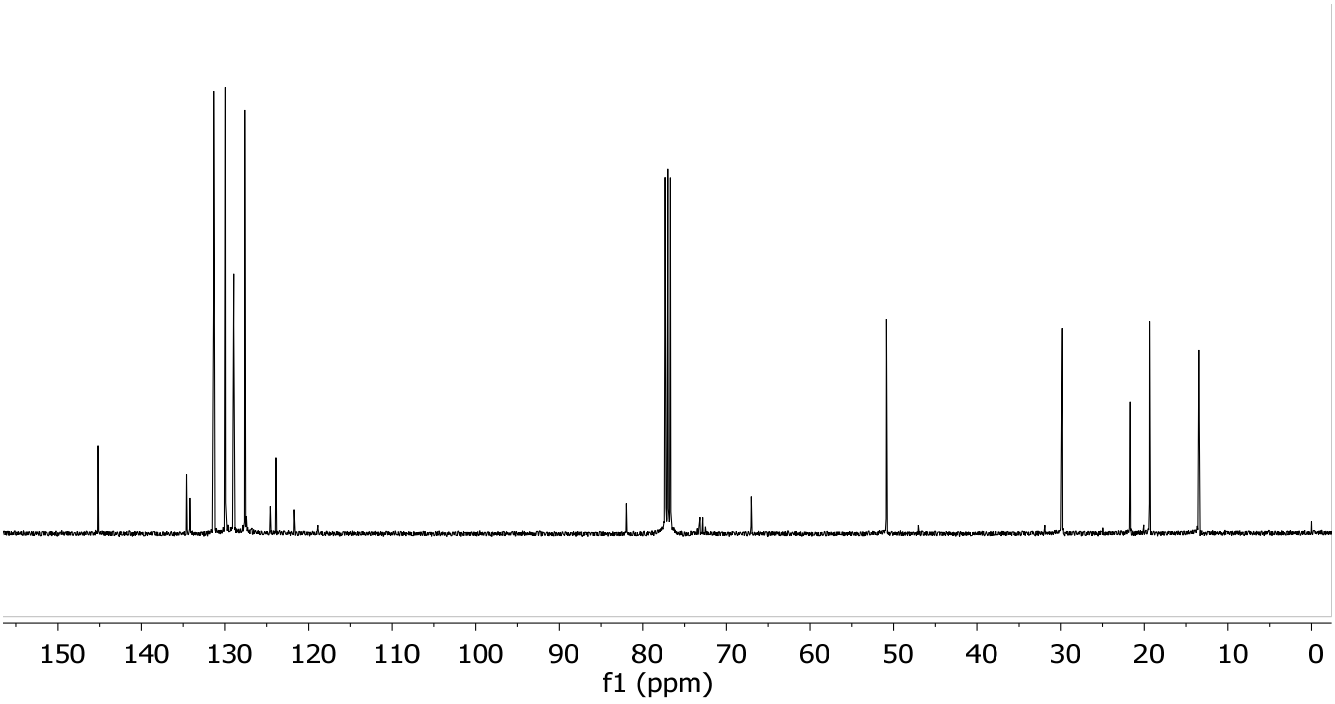
^{13}C NMR Spectrum of *N*-(3-(4'-chlorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-
toluenesulfonamide



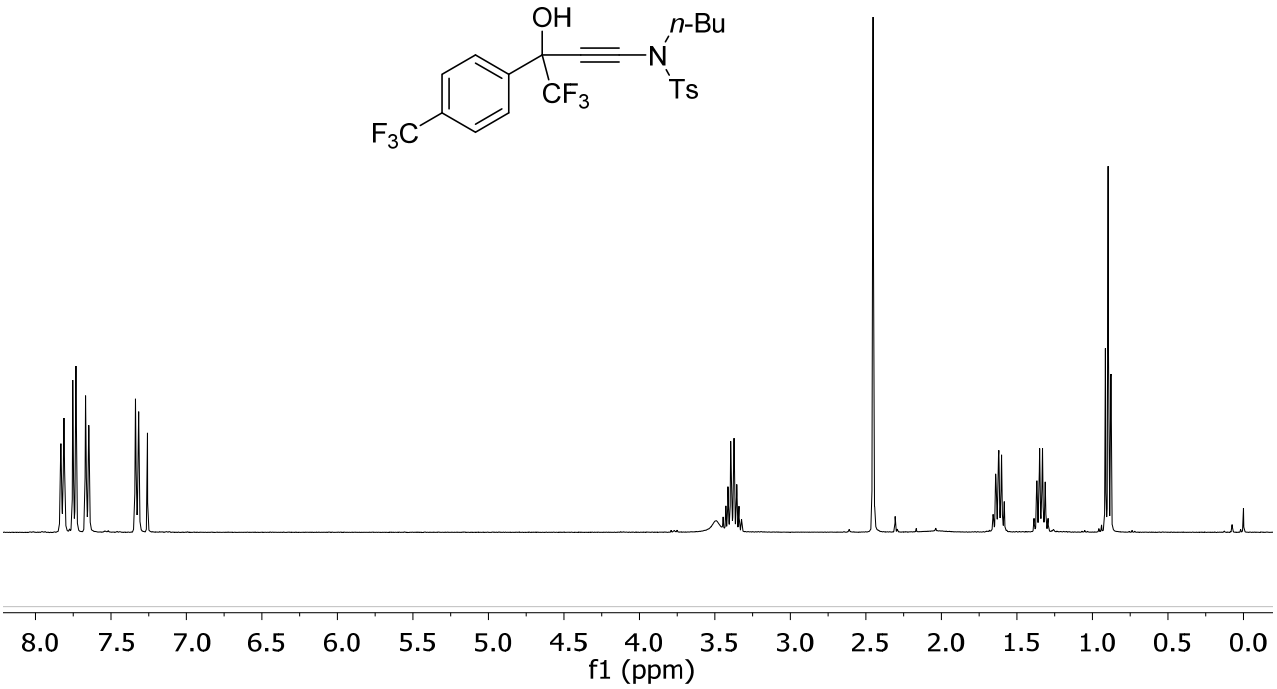
^{1}H NMR Spectrum of *N*-(3-(4'-bromophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-
toluenesulfonamide



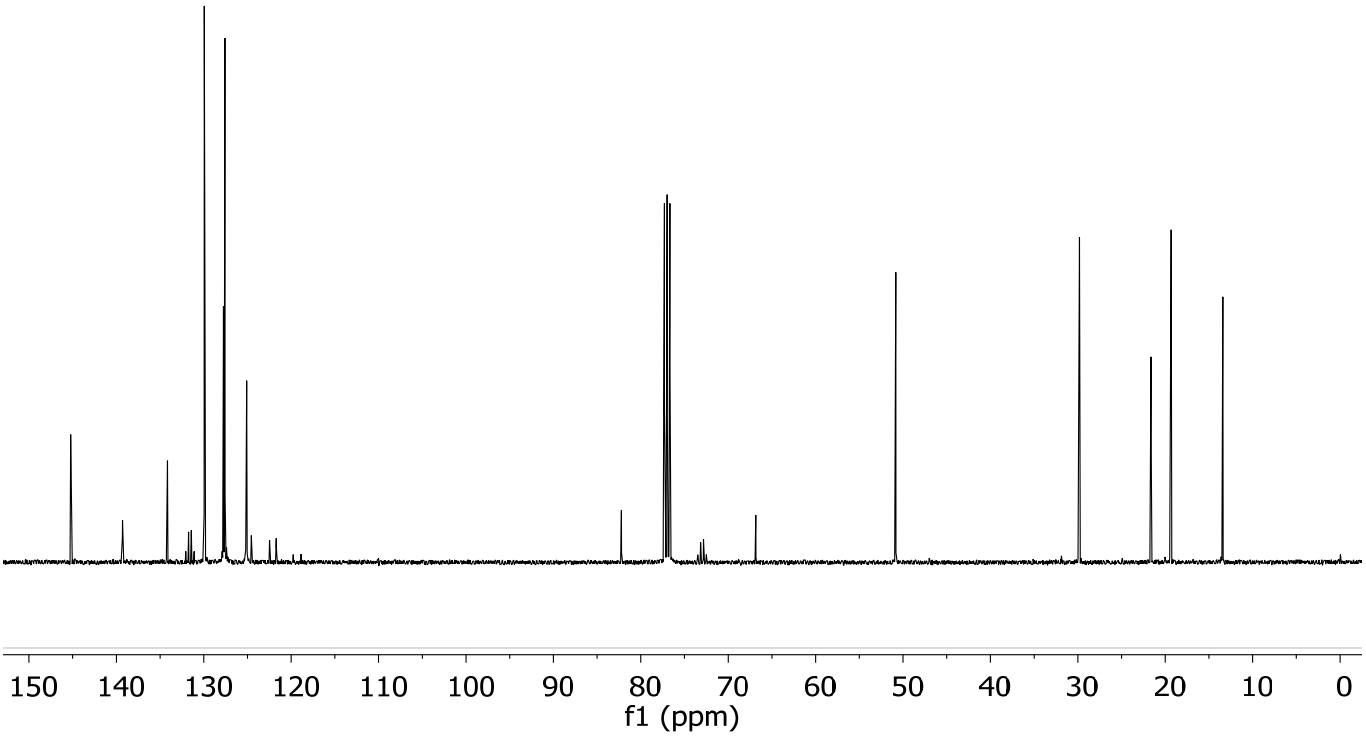
^{13}C NMR Spectrum of *N*-(3-(4'-bromophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-
toluenesulfonamide



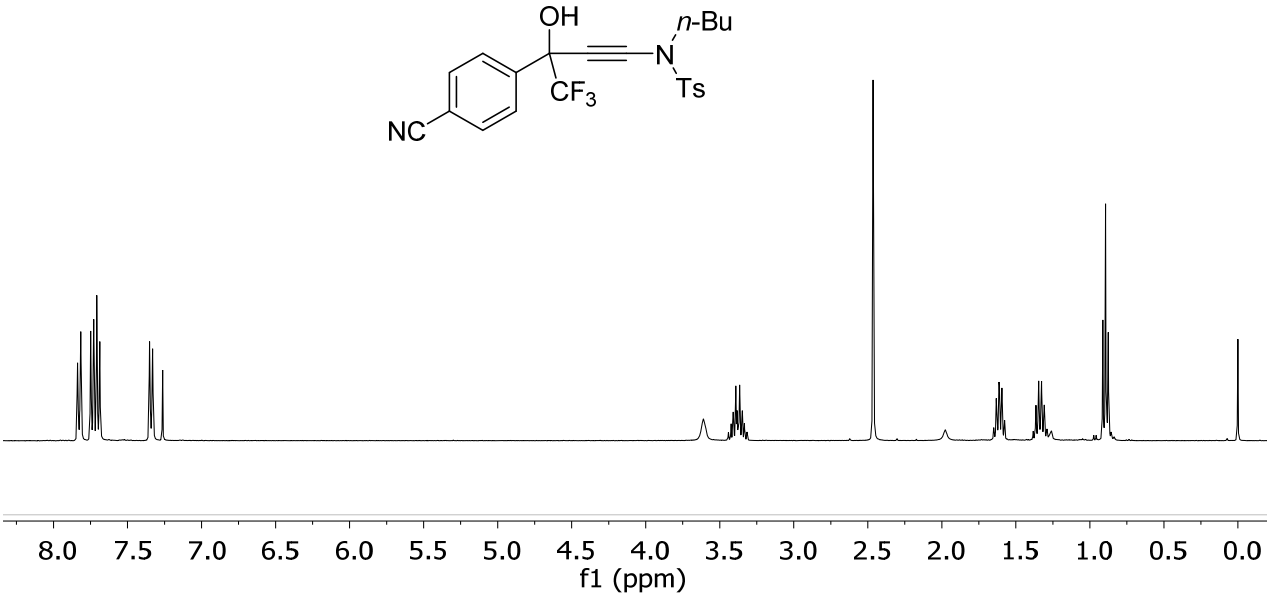
^{1}H NMR Spectrum of *N*-(3-(4'-trifluoromethylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



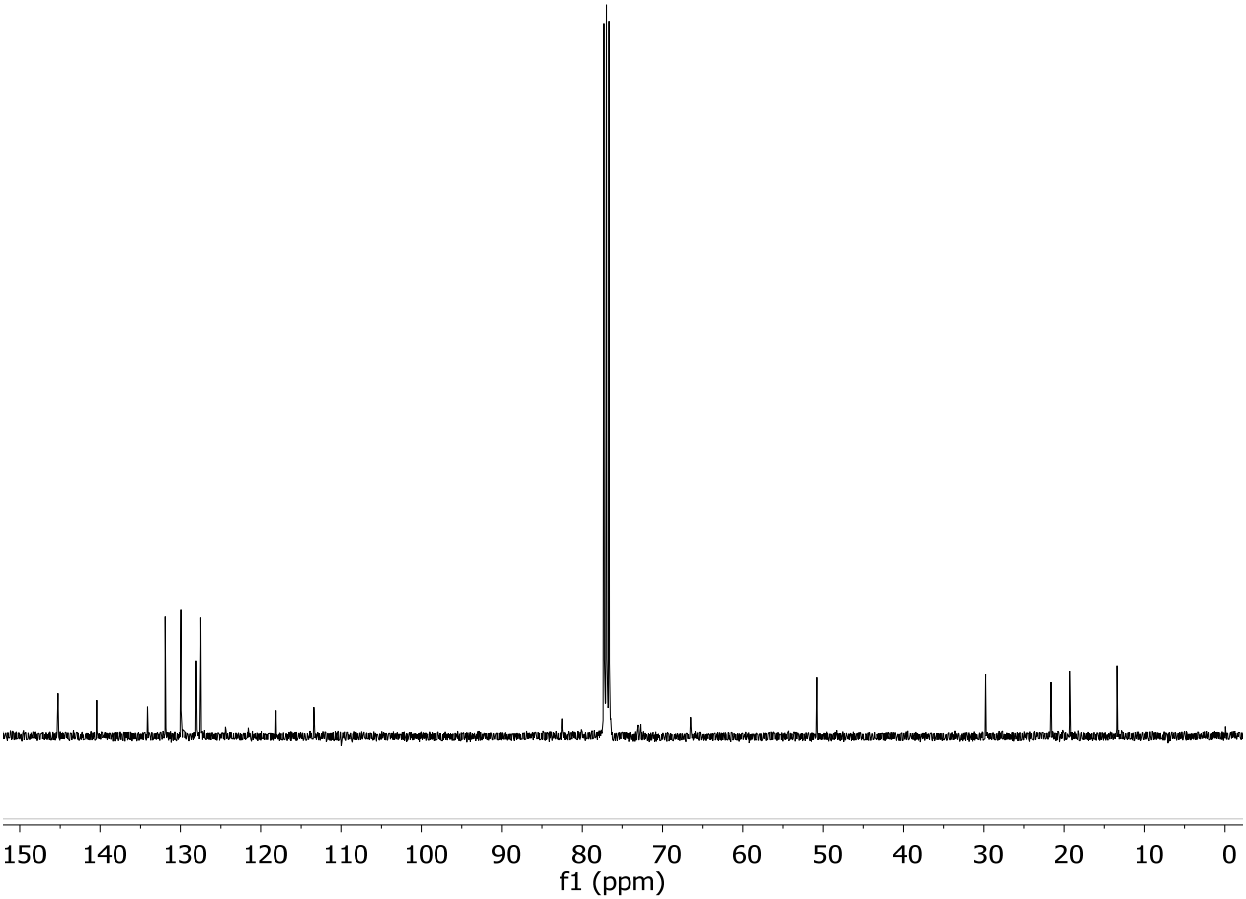
^{13}C NMR Spectrum of *N*-(3-(4'-trifluoromethylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



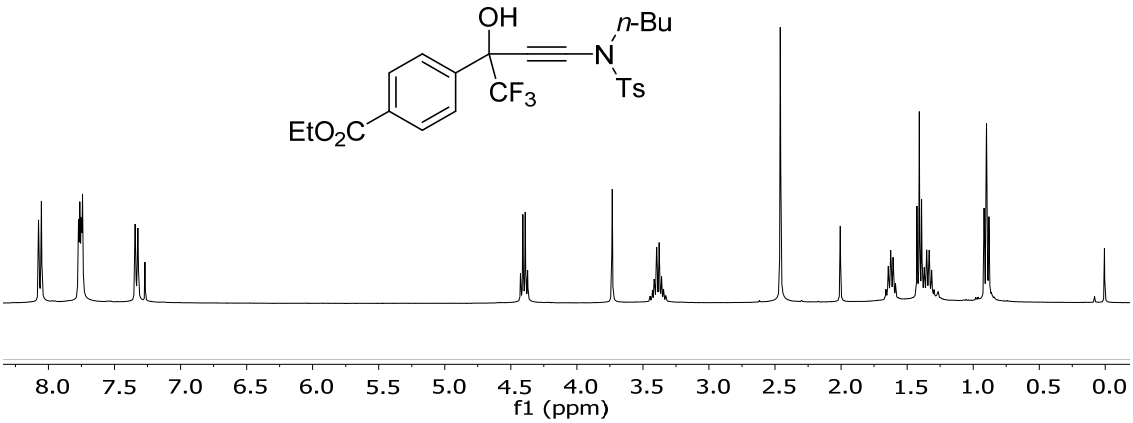
^{1}H NMR Spectrum of *N*-(3-(4'-cyanophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



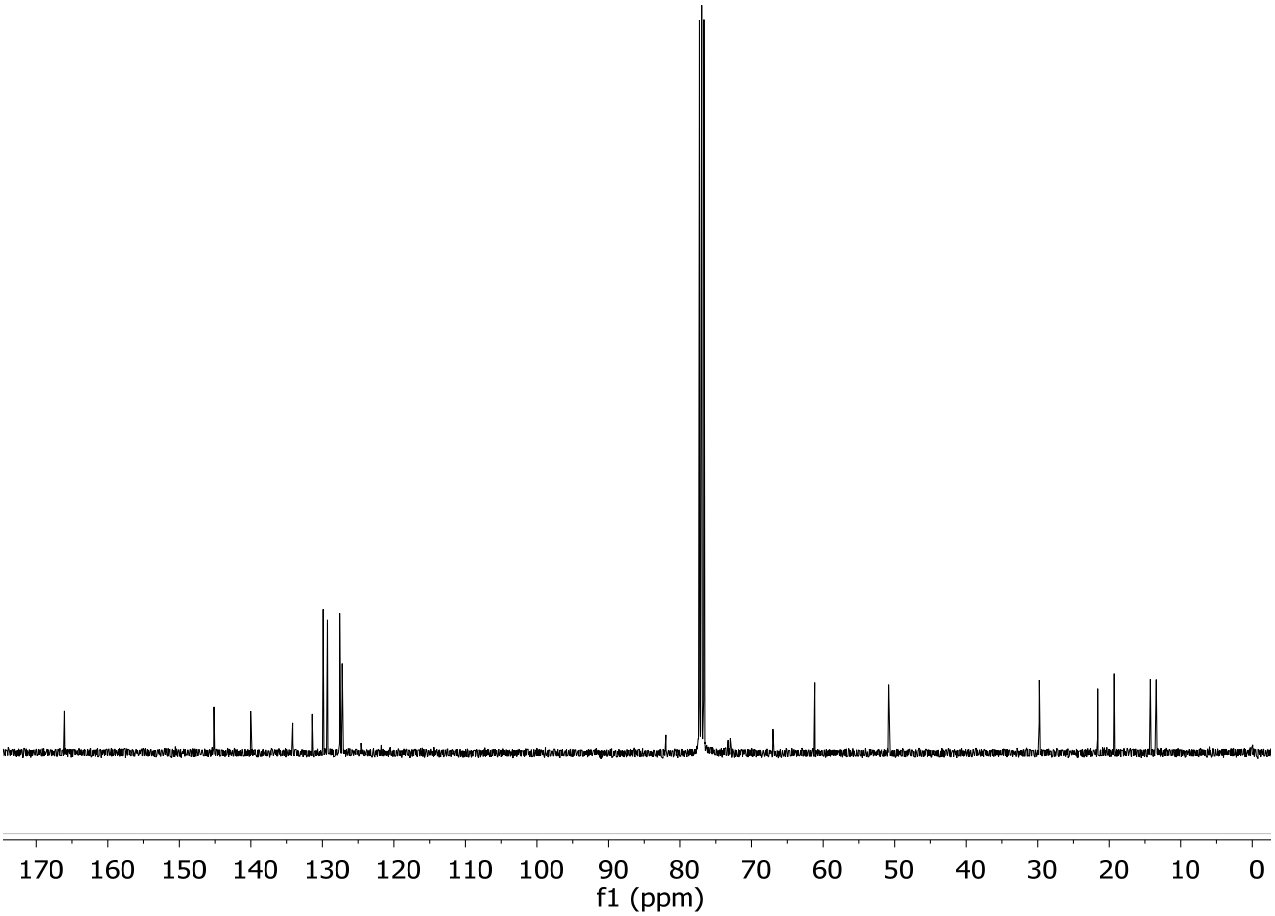
^{13}C NMR Spectrum of *N*-(3-(4'-cyanophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



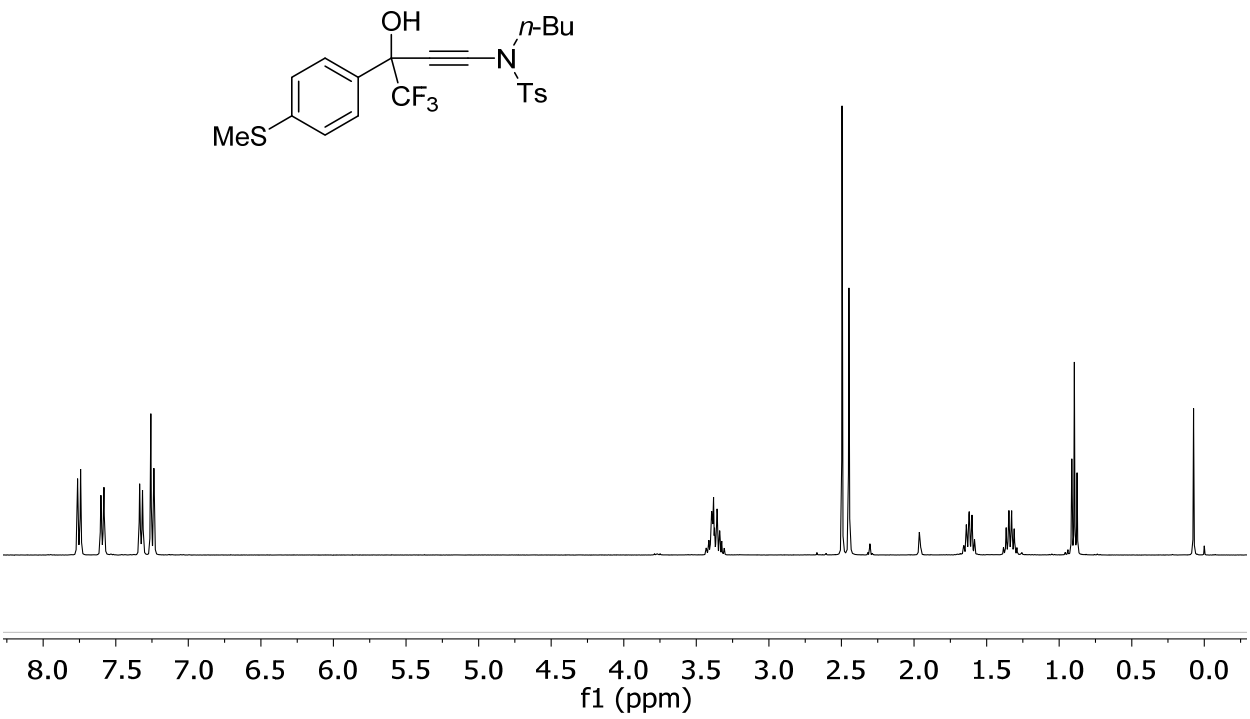
^{1}H NMR Spectrum of *N*-(3-(4-ethoxycarbonylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



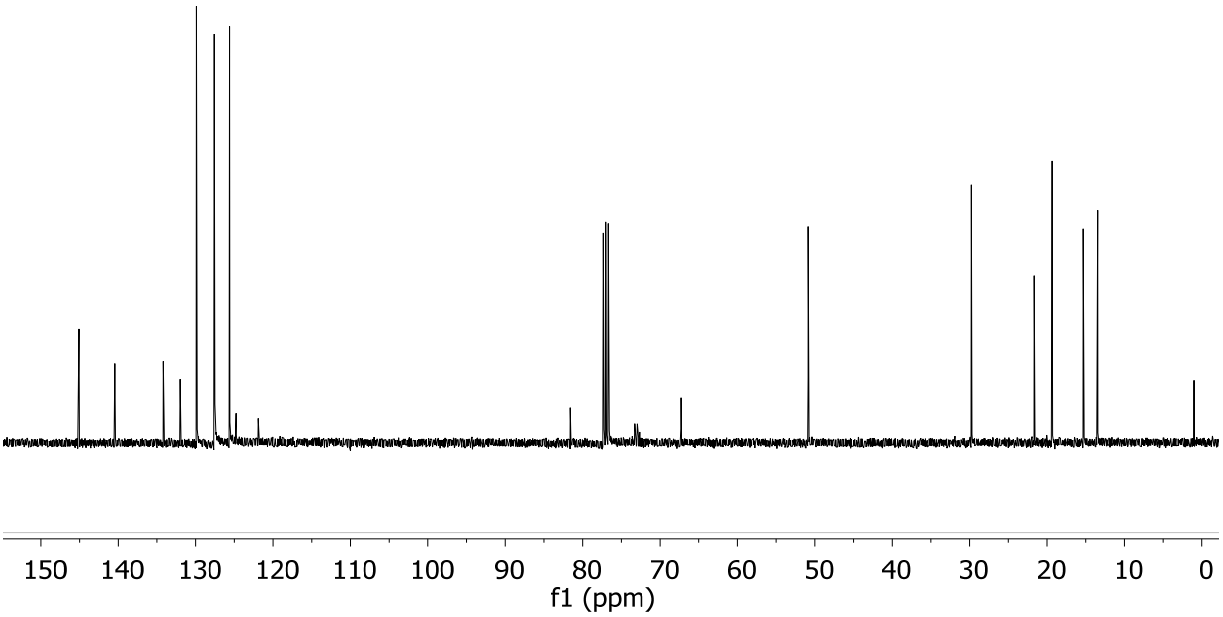
^{13}C NMR Spectrum of *N*-(3-(4-ethoxycarbonylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



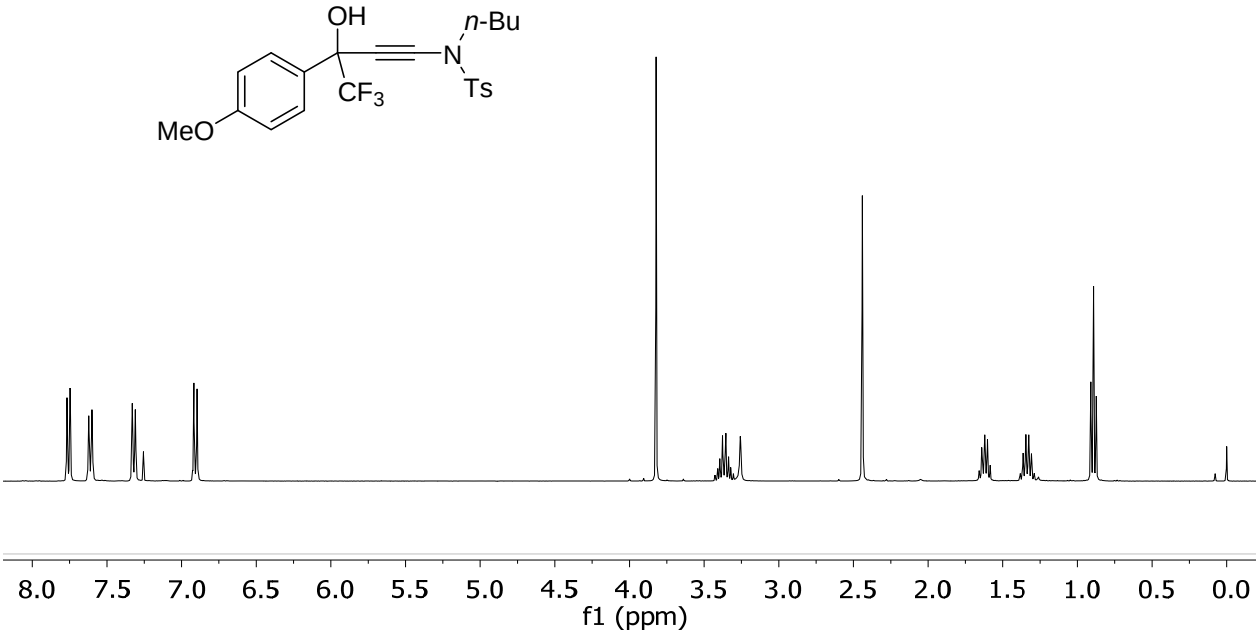
^{1}H NMR Spectrum of *N*-(3-((4'-methylthio)phenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



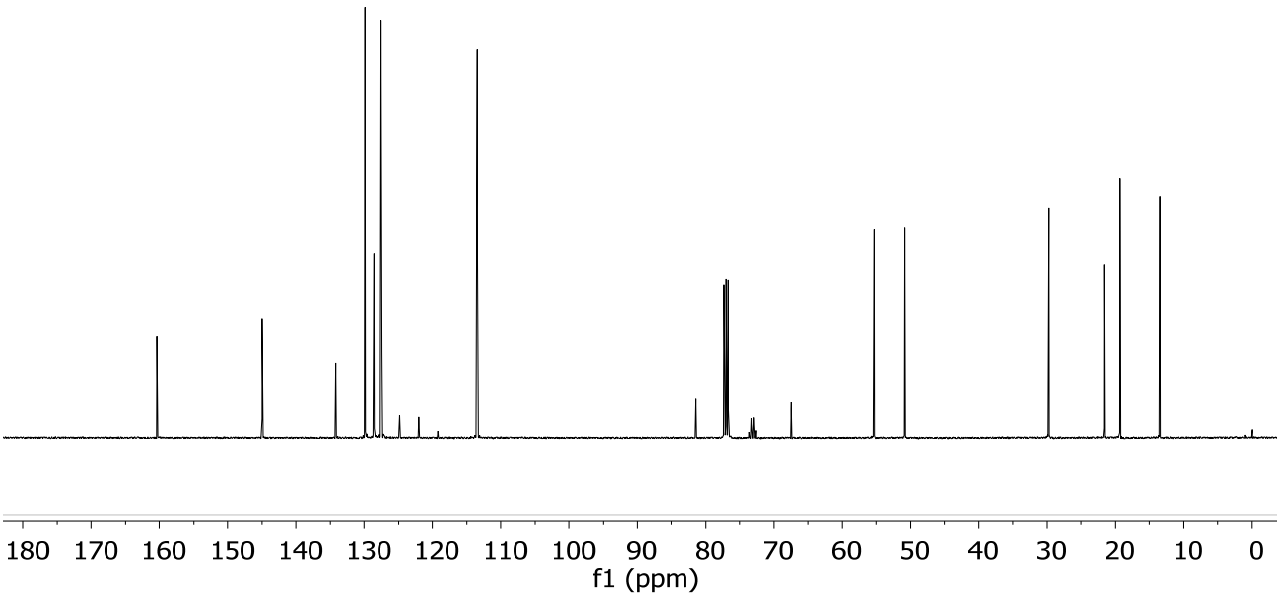
^{13}C NMR Spectrum of *N*-(3-((4'-methylthio)phenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide



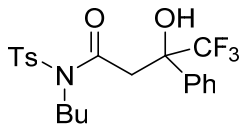
^{1}H NMR Spectrum of *N*-(3-(4'-methoxyphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide

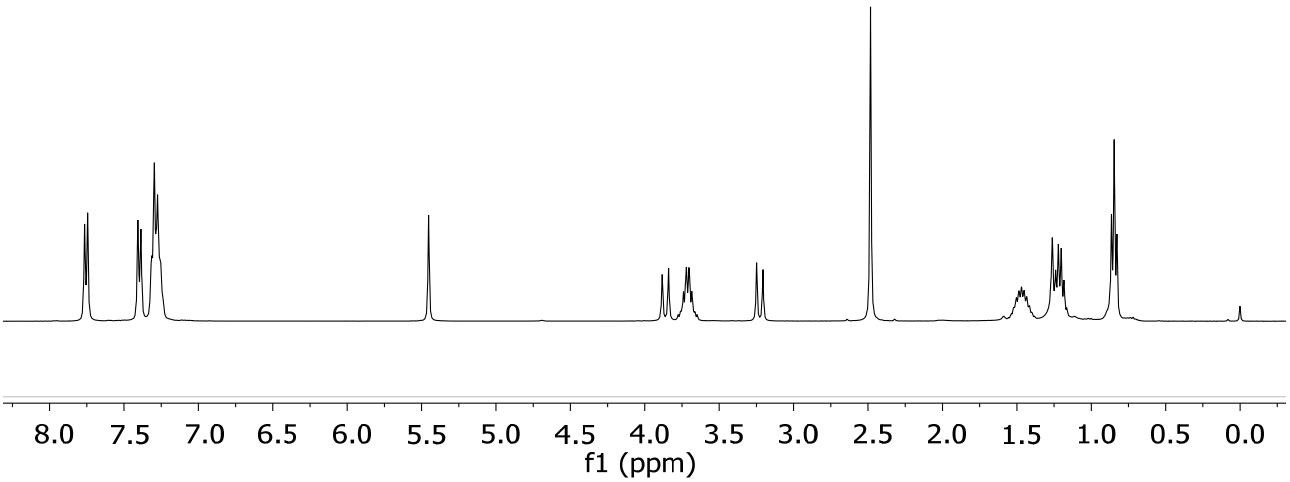


^{13}C NMR Spectrum of *N*-(3-(4'-methoxyphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide

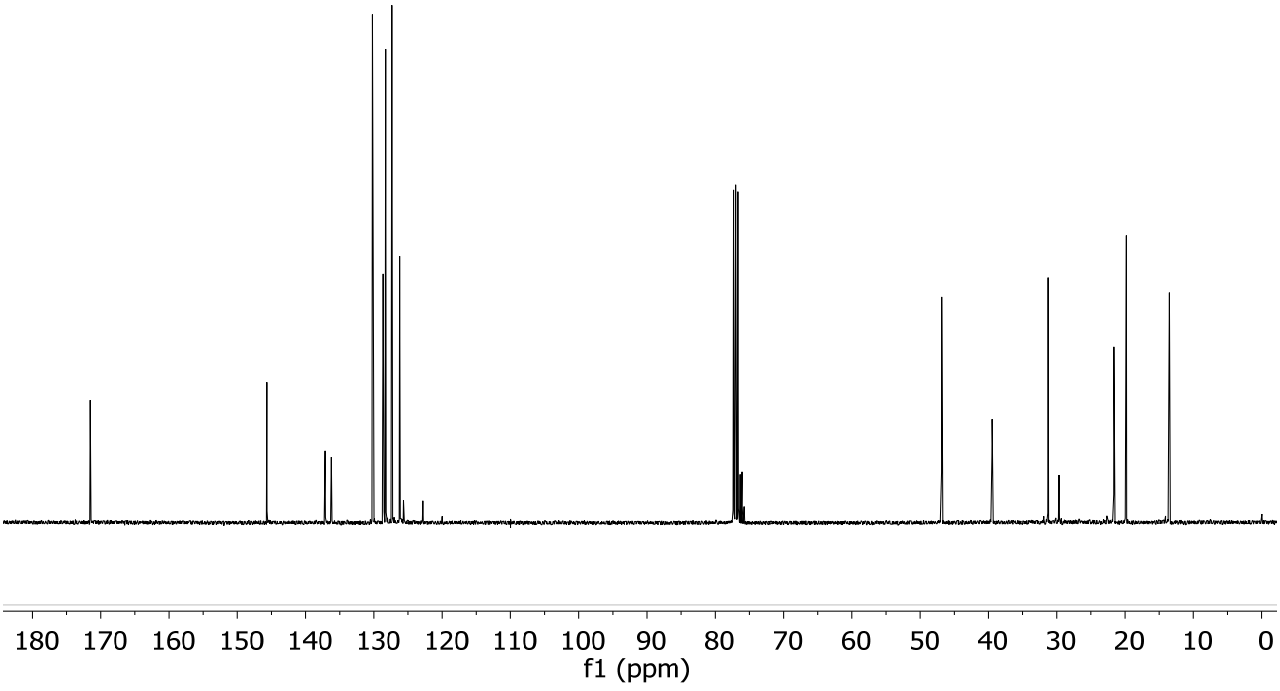


^{1}H NMR Spectrum of *N*-butyl-4,4,4-trifluoro-3-hydroxy-3-phenyl-*N*-tosylbutanamide

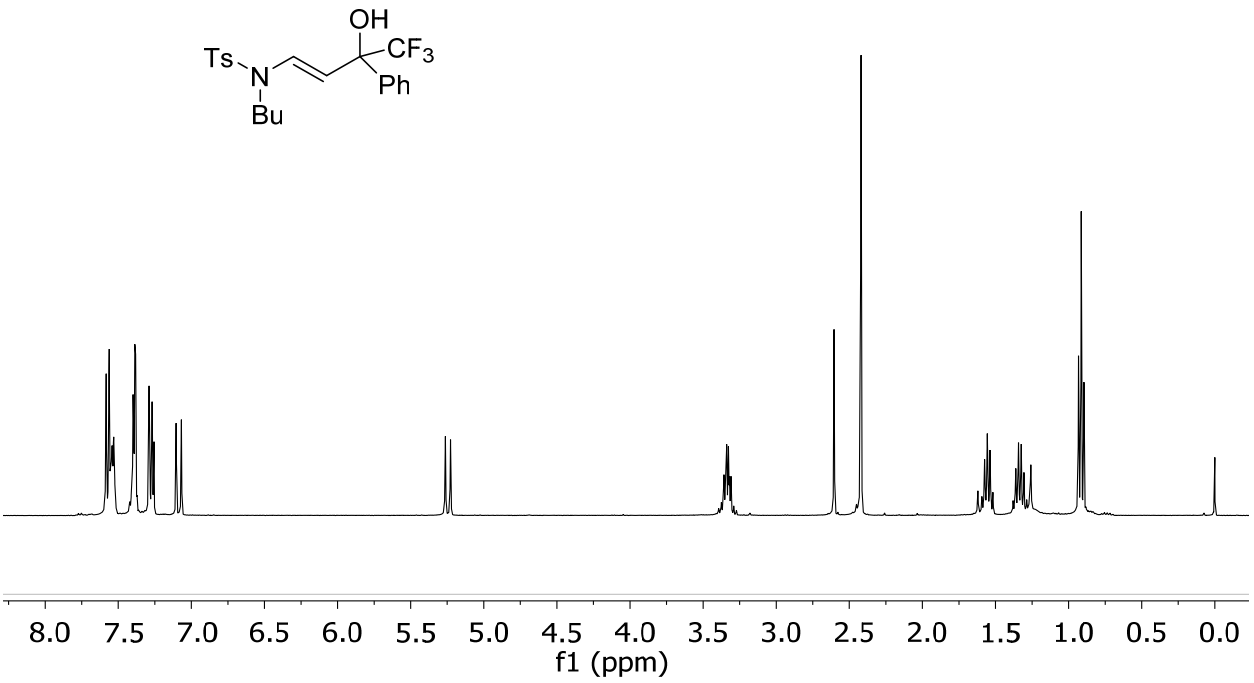




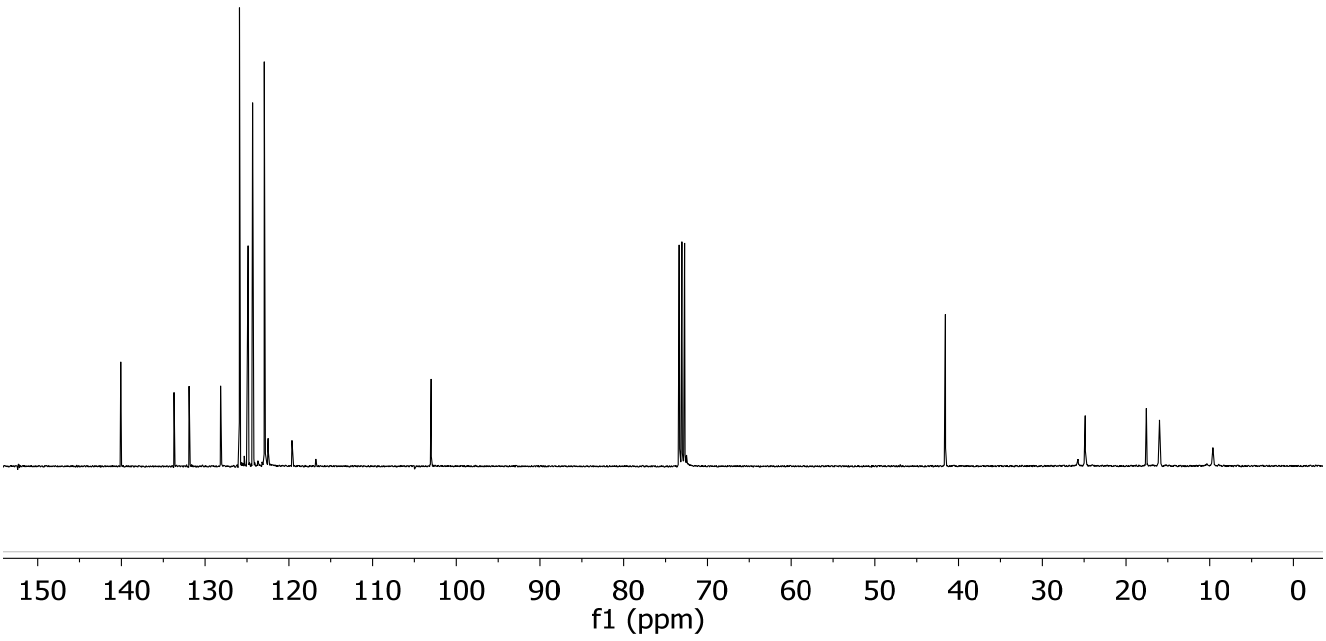
^{13}C NMR Spectrum of *N*-butyl-4,4,4-trifluoro-3-hydroxy-3-phenyl-*N*-tosylbutanamide



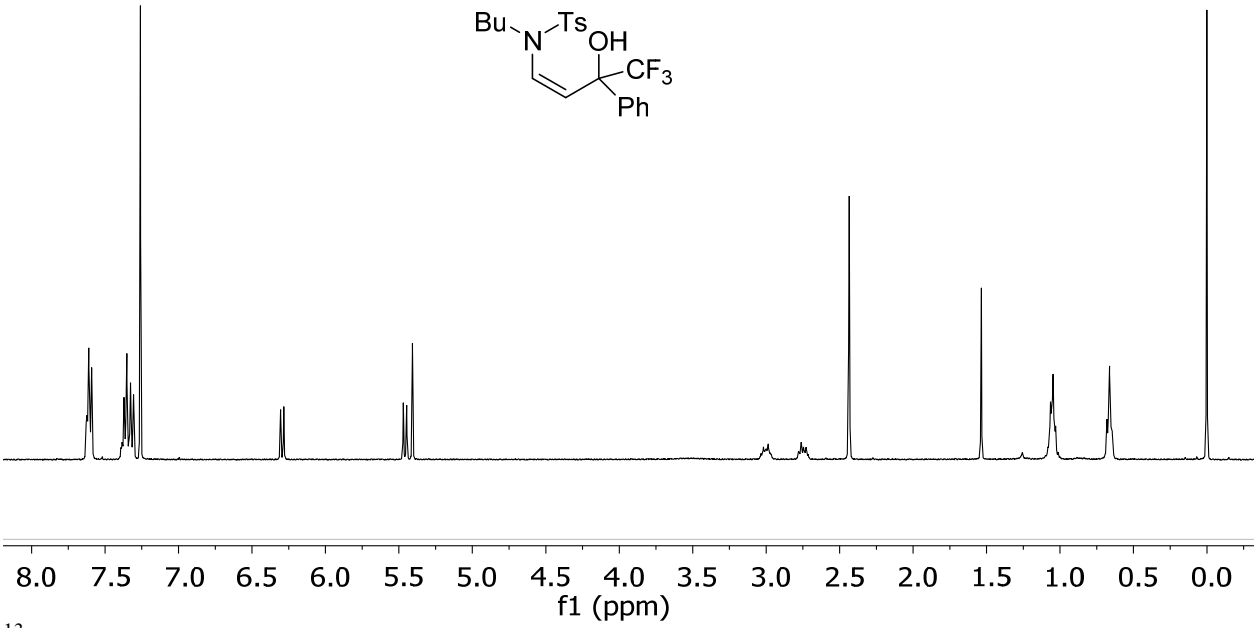
^{1}H NMR Spectrum of (*E*)-*N*-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



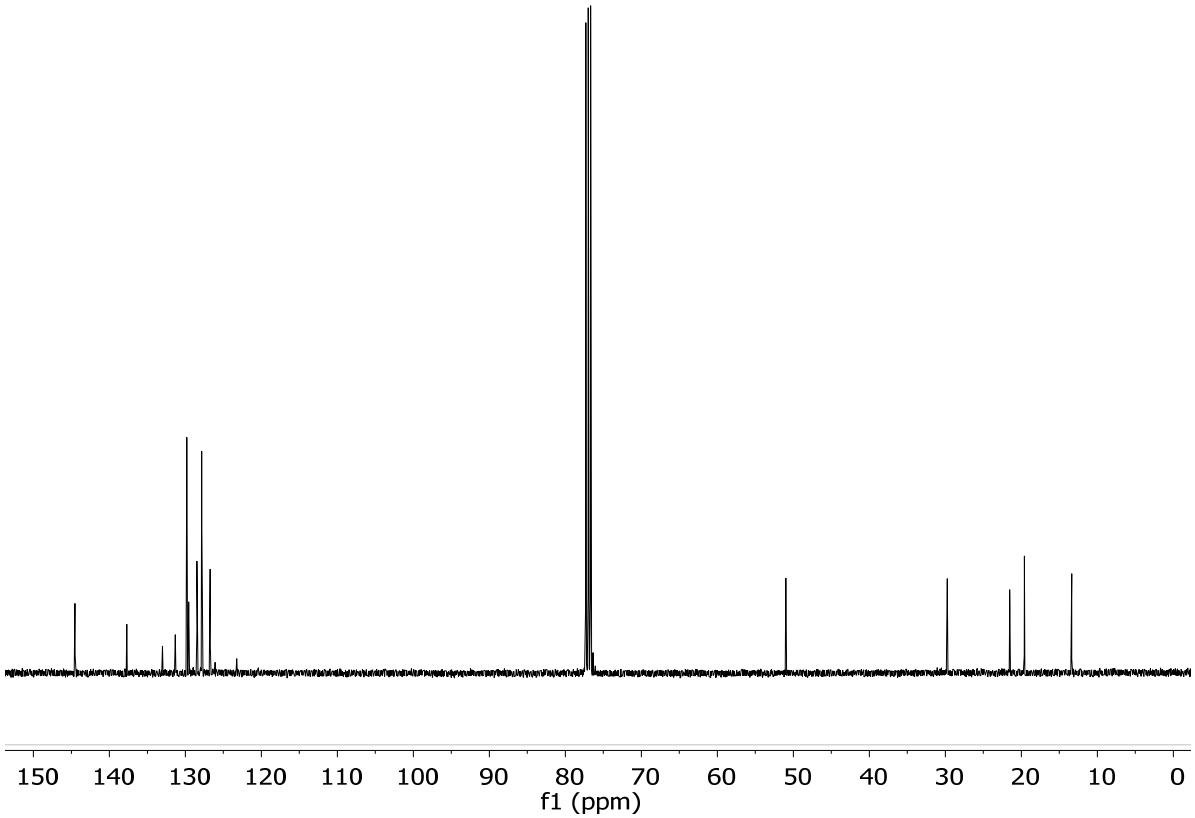
^{13}C NMR Spectrum of (*E*)-*N*-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



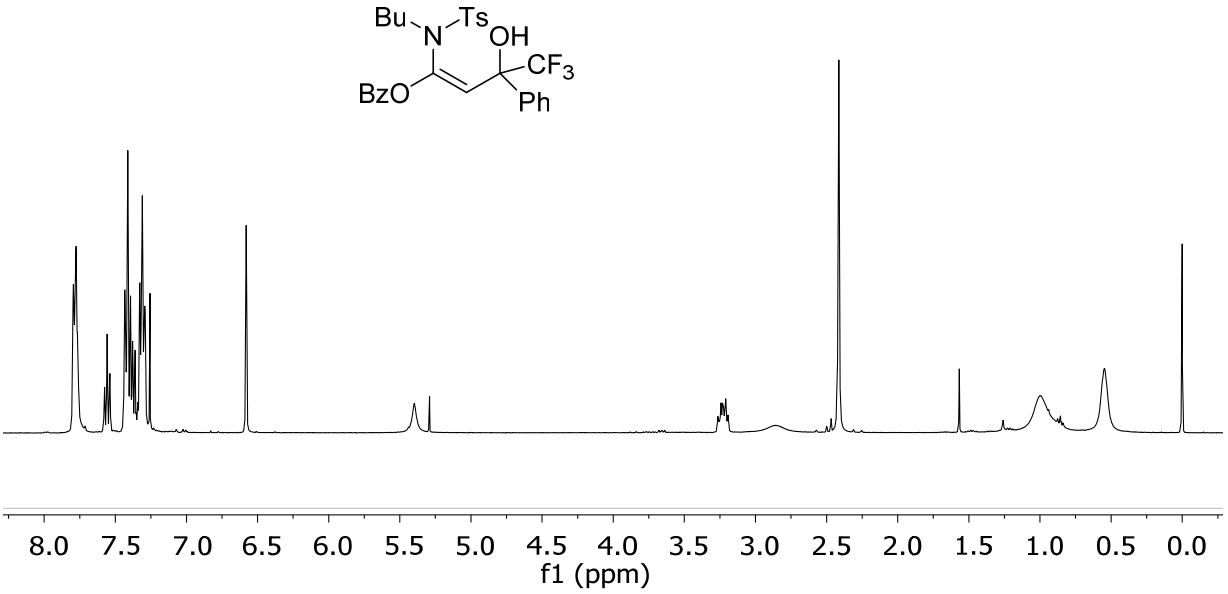
^{1}H NMR Spectrum of (*Z*)-*N*-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



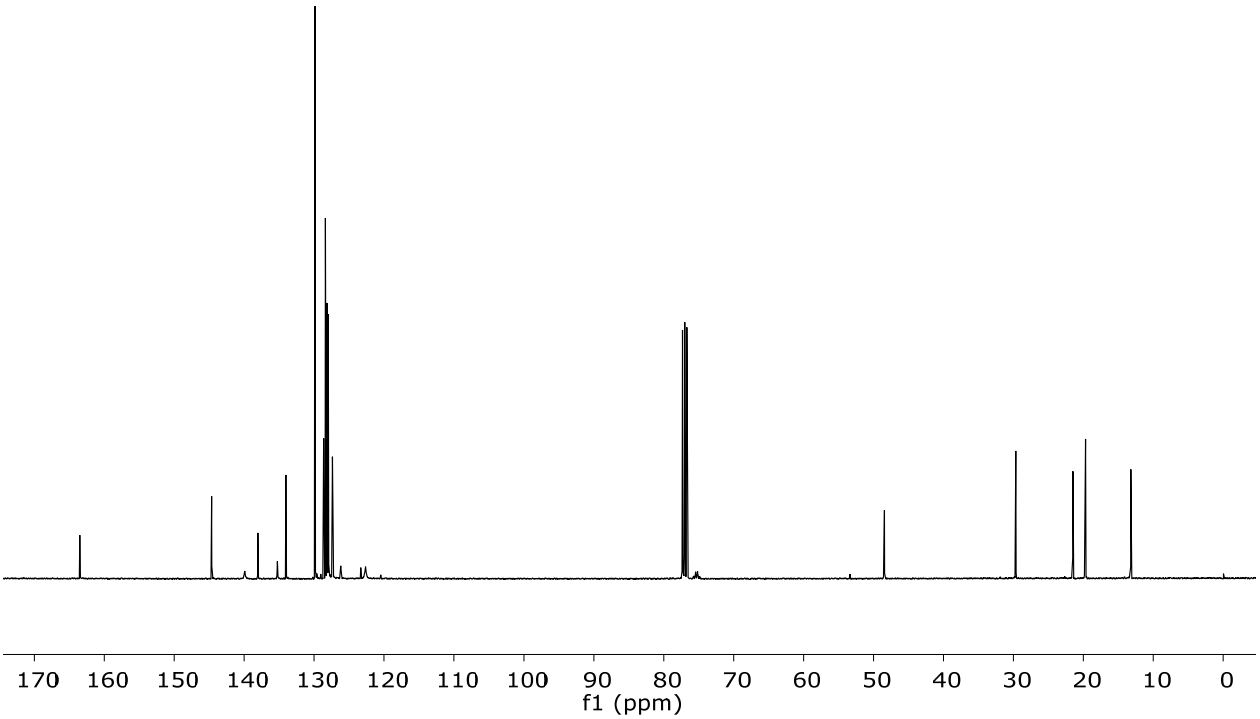
^{13}C NMR Spectrum of (*Z*)-*N*-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



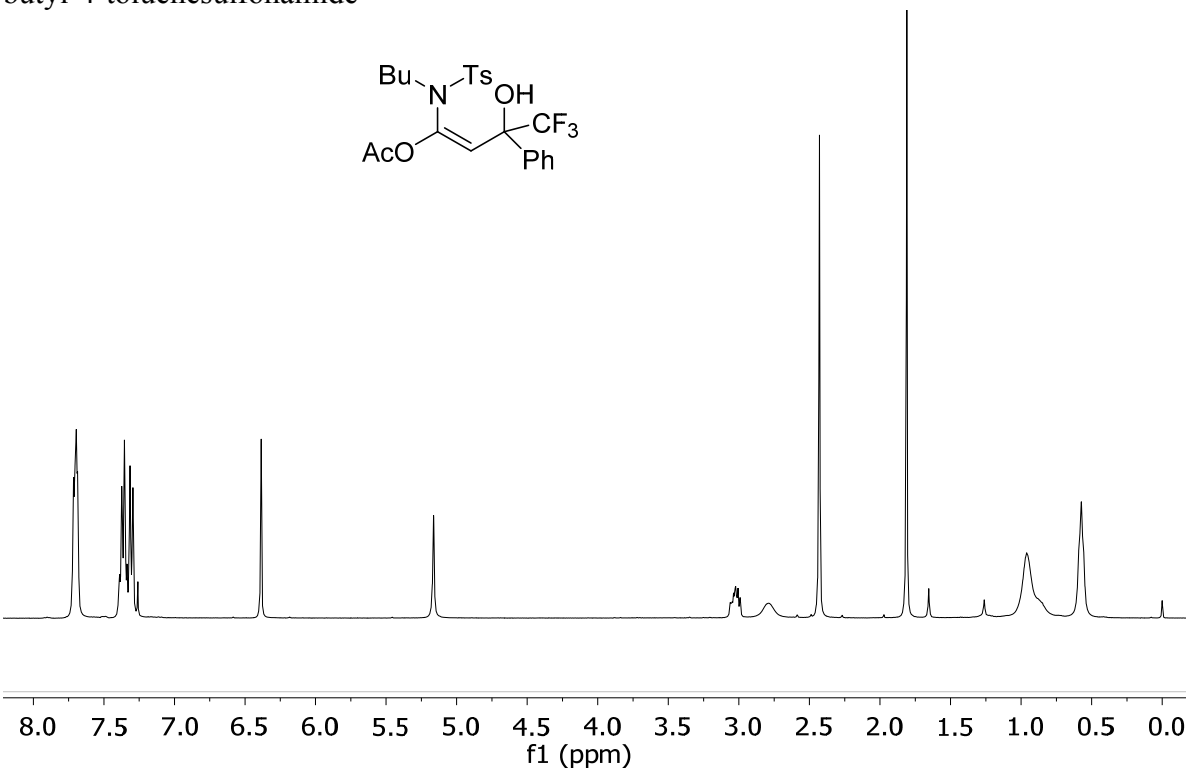
^{1}H NMR Spectrum of (*E*)-*N*-(2-benzoyloxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



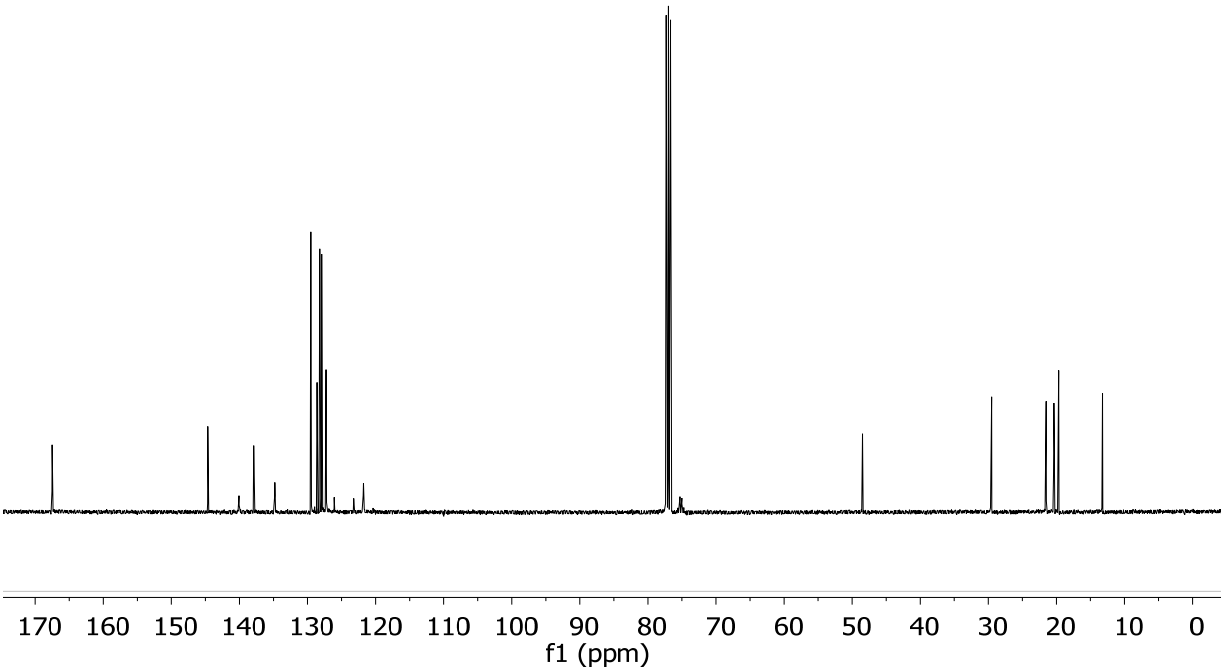
^{13}C NMR Spectrum of (*E*)-*N*-(2-benzoyloxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



^{1}H NMR Spectrum of (*E*)-*N*-(2-acetoxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide

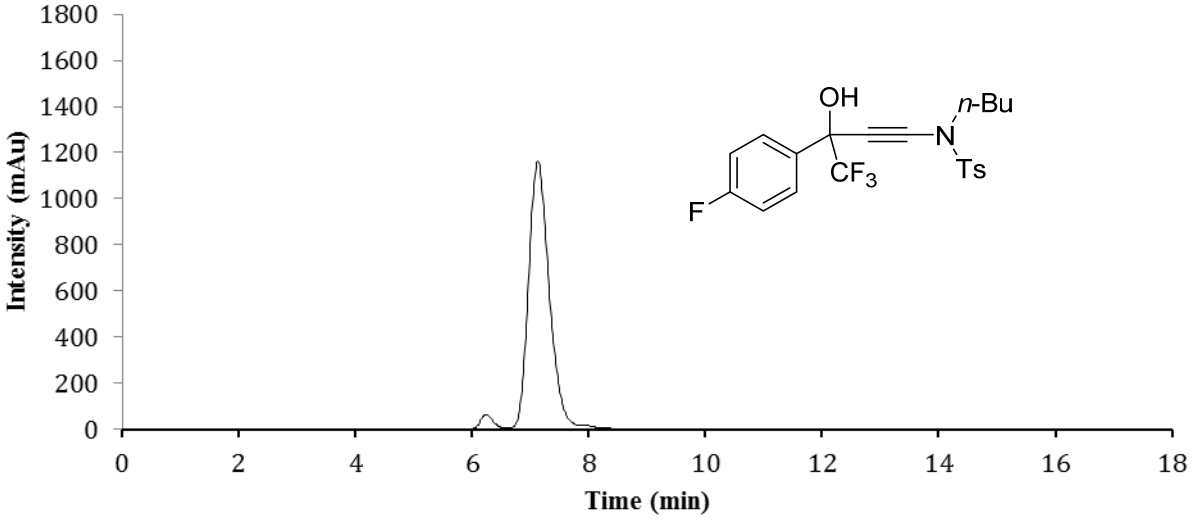


^{13}C NMR Spectrum of (*E*)-*N*-(2-acetoxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



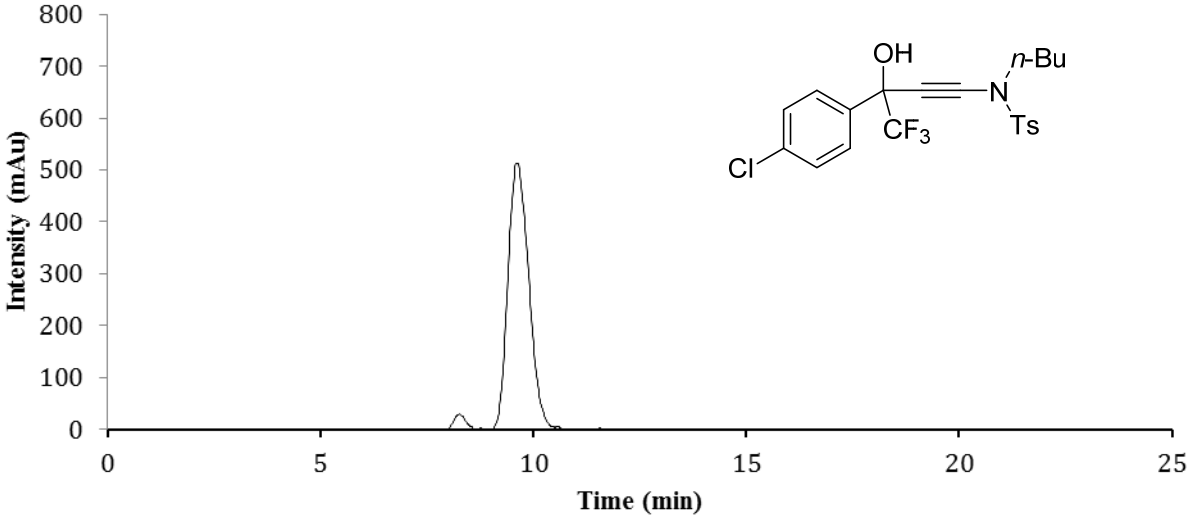
5. Chiral HPLC Chromatograms

***N*-(3-(4-Fluorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**



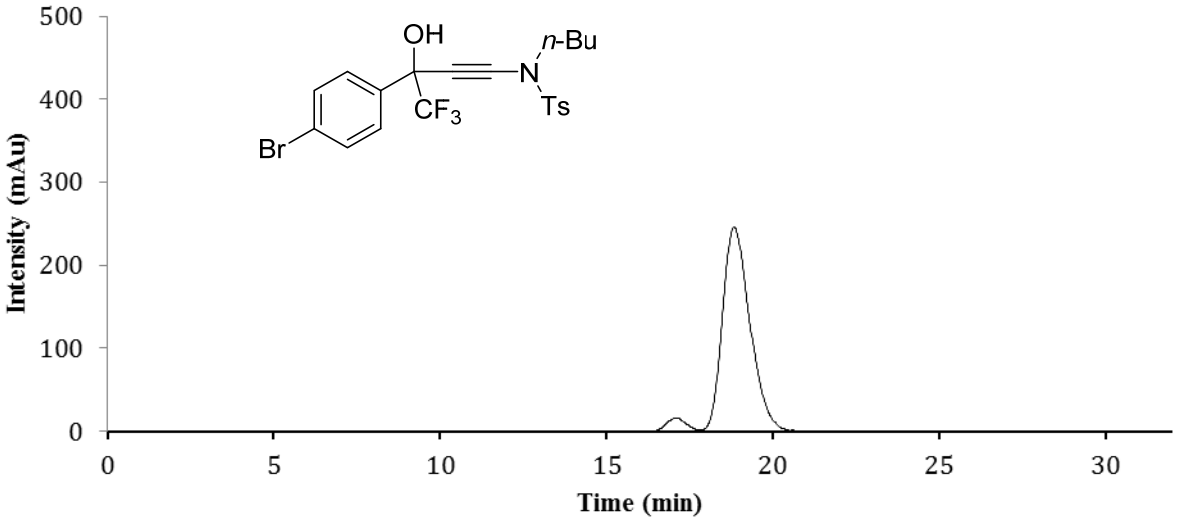
Phenomenex® Cellulose-3 using hexanes:EtOH (90:10) as the mobile phase at 1.0 mL/min, t_1 (minor) = 6.2 min, t_2 (major) = 7.1 min, α = 1.32

***N*-(3-(4-Chlorophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**



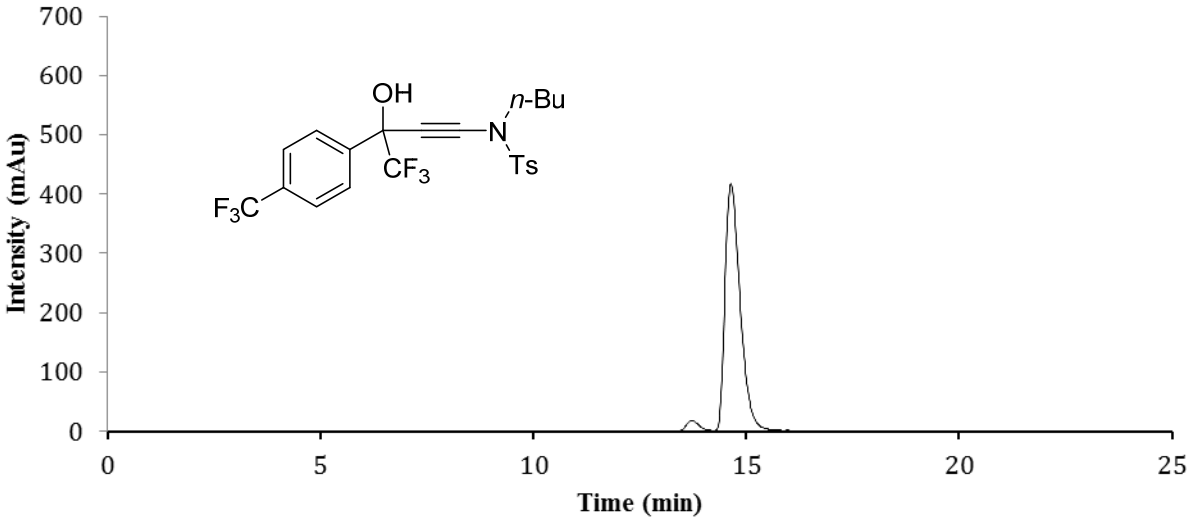
Phenomenex® Cellulose-3 using hexanes:EtOH (95:5) as the mobile phase at 1.0 mL/min, t_1 (minor) = 8.2 min, t_2 (major) = 9.6 min, α = 1.29

_N_-(3-(4-Bromophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-_N_-butyl-4-toluenesulfonamide



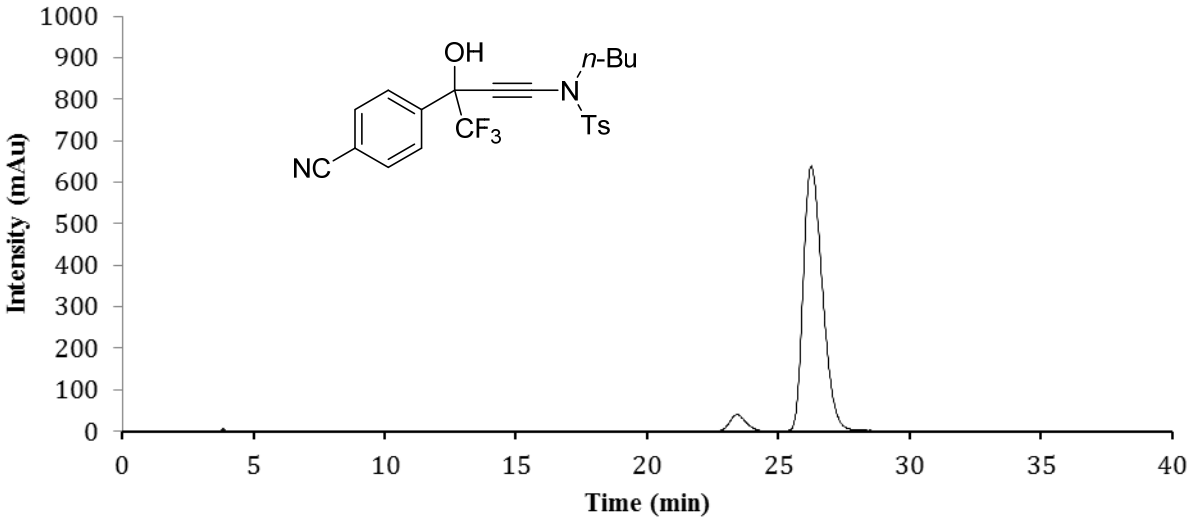
Phenomenex® Cellulose-3 using hexanes:EtOH (98:2) as the mobile phase at 1.0 mL/min, t_1 (minor) = 17.1 min, t_2 (major) = 18.8 min, α = 1.12

_N_-(3-(4-Trifluoromethylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-_N_-butyl-4-toluenesulfonamide



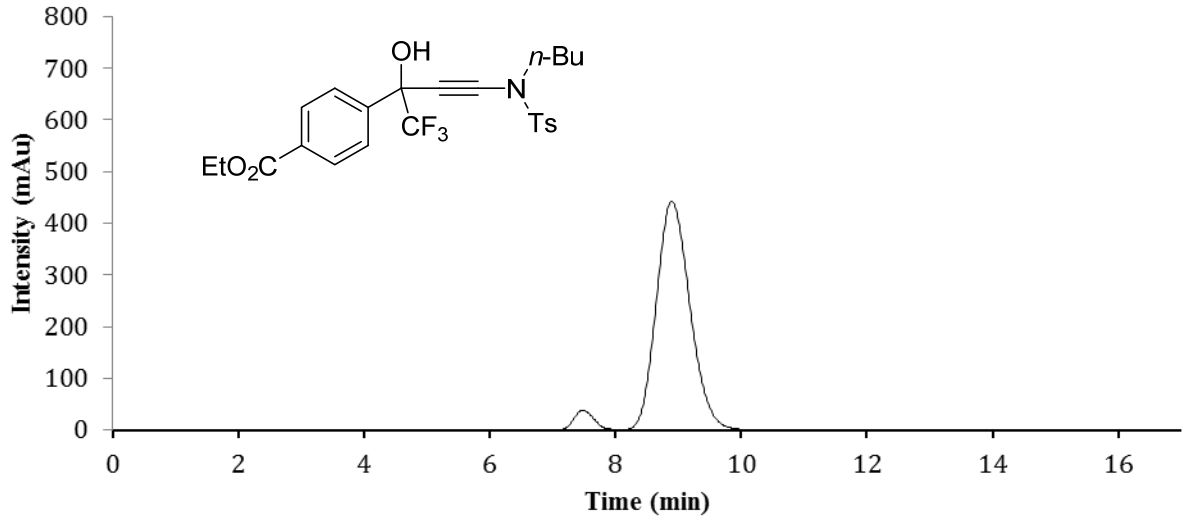
Phenomenex® Cellulose-4 using hexanes:EtOH (98:2) as the mobile phase at 1.0 mL/min, t_1 (minor) = 13.7 min, t_2 (major) = 14.6 min, α = 1.09

***N*-(3-(4-Cyanophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**



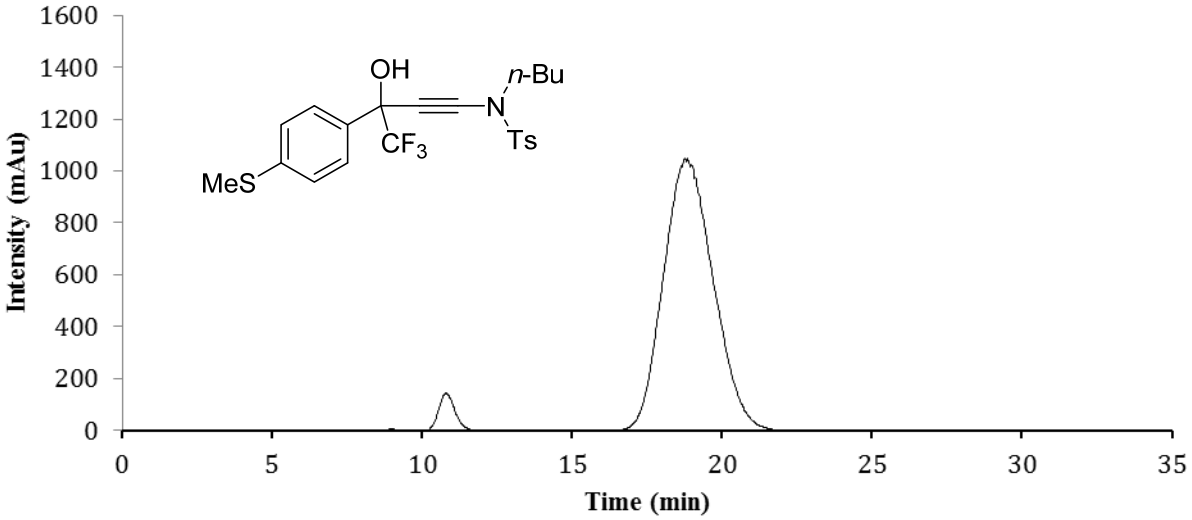
Phenomenex® Cellulose-4 using hexanes:EtOH (97:3) as the mobile phase at 1.0 mL/min, t_1 (minor) = 23.4 min, t_2 (major) = 26.3 min, α = 1.14

***N*-(3-(4-Ethoxycarbonylphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-*N*-butyl-4-toluenesulfonamide**



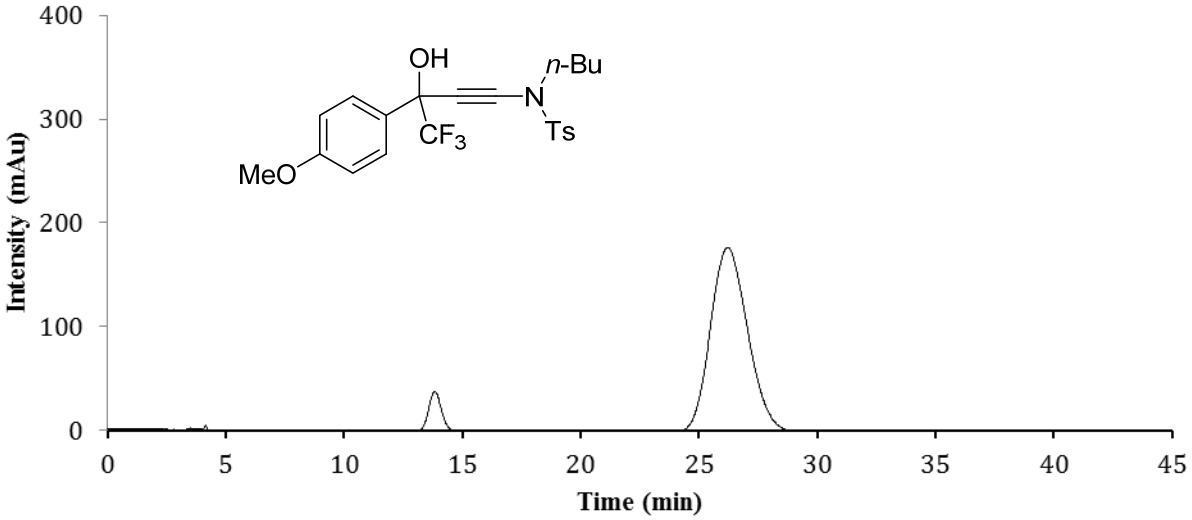
Phenomenex® Cellulose-3 using hexanes:EtOH (90:10) as the mobile phase at 1.0 mL/min, t_1 (minor) = 7.5 min, t_2 (major) = 8.9 min, α = 1.34

_N_-(3-(4-Methylthiophenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-_N_-butyl-4-toluenesulfonamide

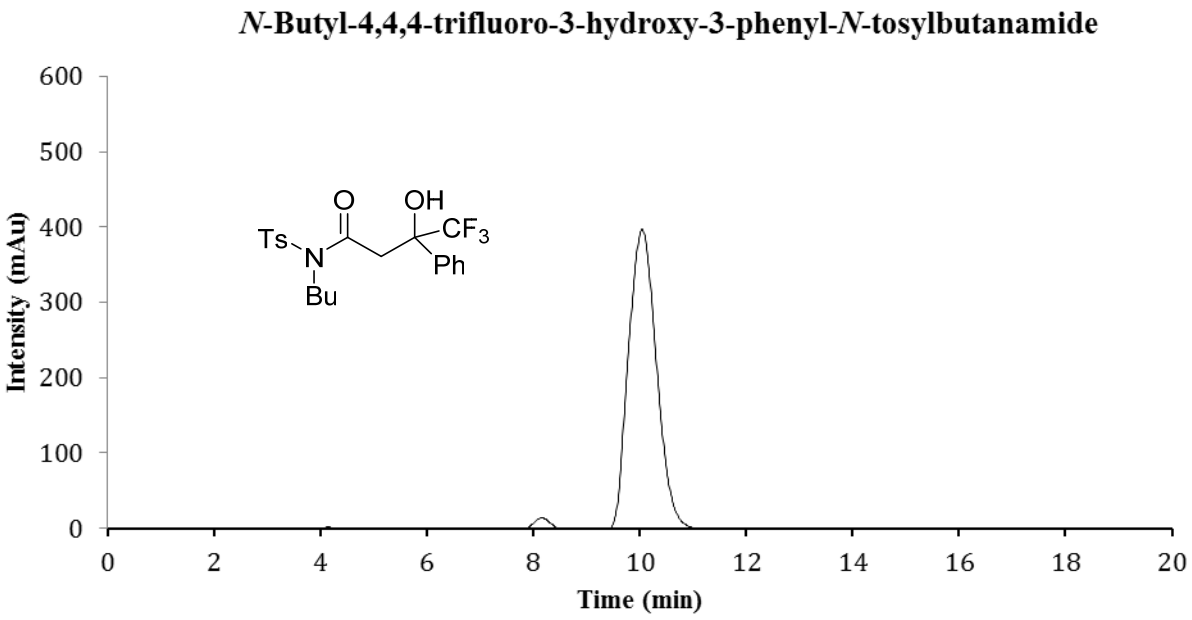


Phenomenex® Cellulose-3 using hexanes:EtOH (90:10) as the mobile phase at 1.0 mL/min, t_1 (minor) = 10.9 min, t_2 (major) = 18.8 min, α = 2.06

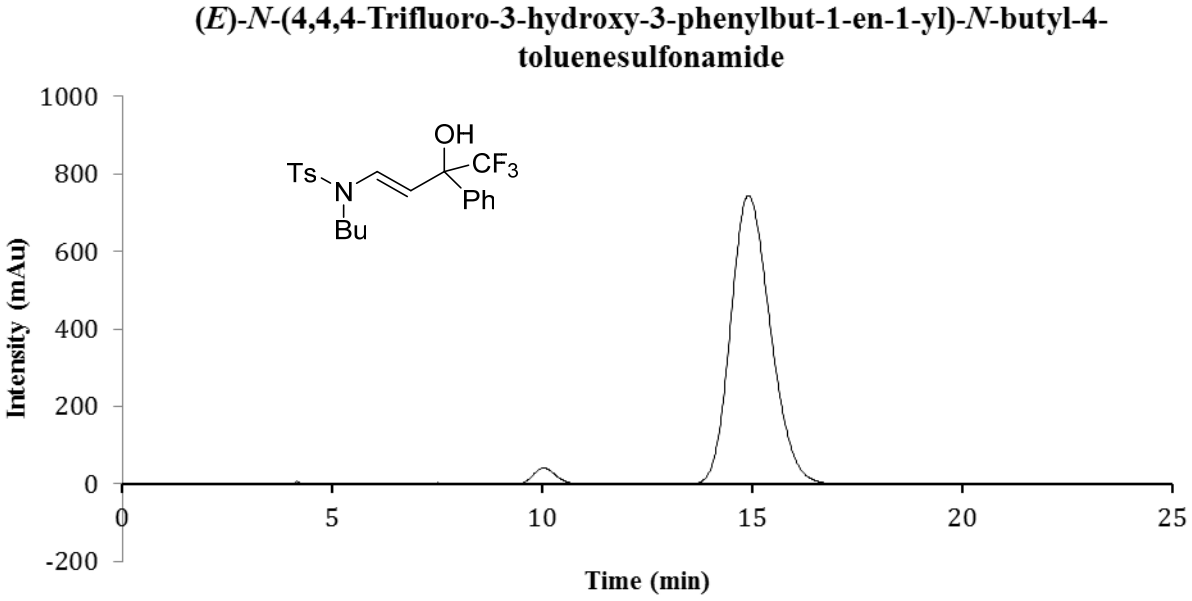
_N_-(3-(4-Methoxyphenyl)-4,4,4-trifluoro-3-hydroxy-but-1-yn-1-yl)-_N_-butyl-4-toluenesulfonamide



Phenomenex® Cellulose-3 using hexanes:EtOH (95:5) as the mobile phase at 1.0 mL/min, t_1 (minor) = 13.8 min, t_2 (major) = 26.2 min, α = 2.20

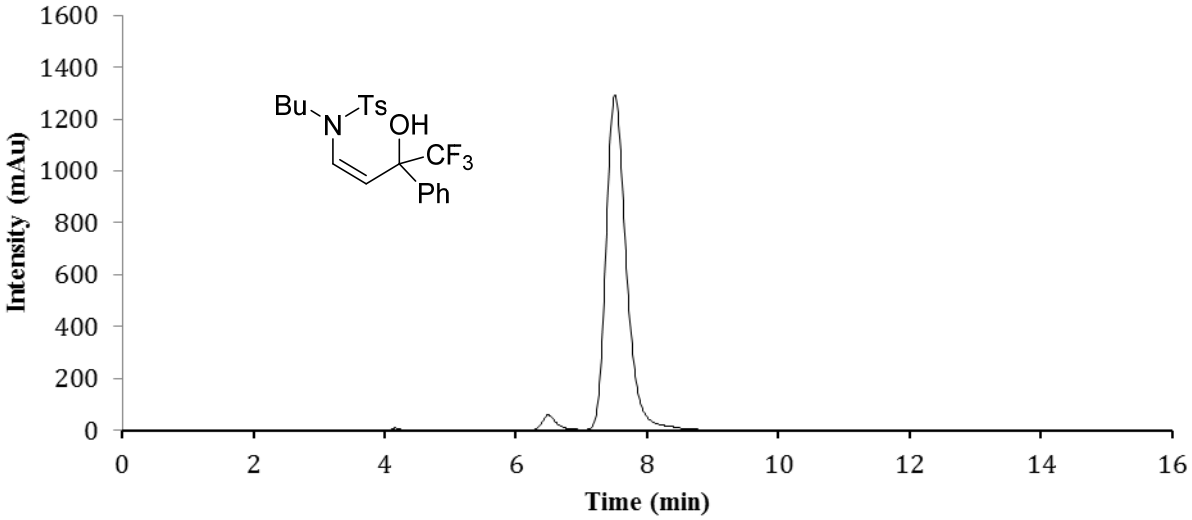


Phenomenex® Cellulose-3 using hexanes: EtOH (95:5) as the mobile phase at 1.0 mL/min. t_1 = 8.2 min (minor), t_2 = 10.0 min (major). α = 1.38



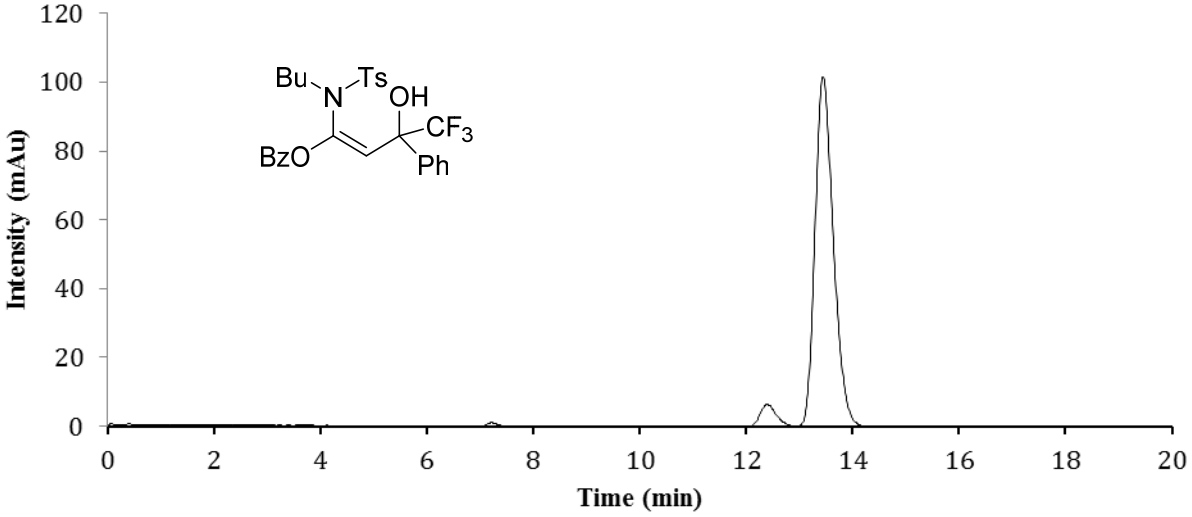
Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 10.0 min (minor), t_2 = 14.9 min (major). α = 1.75.

(*Z*)-*N*-(4,4,4-Trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



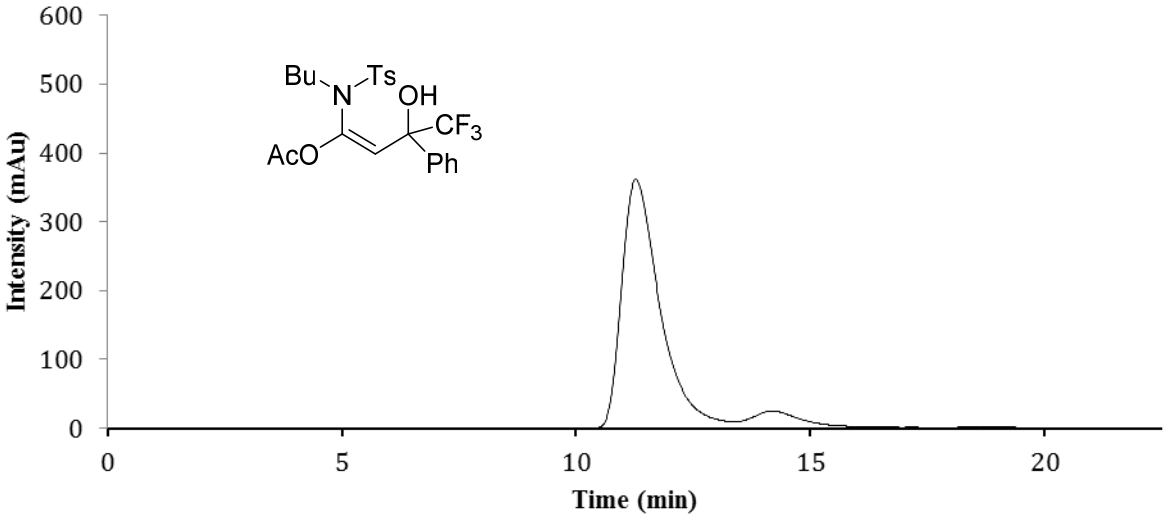
Phenomenex® Cellulose-3 using hexanes: EtOH (90:10) as the mobile phase at 1.0 mL/min. t_1 = 6.5 min (minor), t_2 = 7.5 min (major). α = 1.33.

(*E*)-*N*-(2-Benzoyloxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide



Phenomenex® Cellulose-4 using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 12.4 min (minor), t_2 = 13.4 min (major). α = 1.11.

(*E*)-*N*-(2-Acetoxy-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)-*N*-butyl-4-toluenesulfonamide

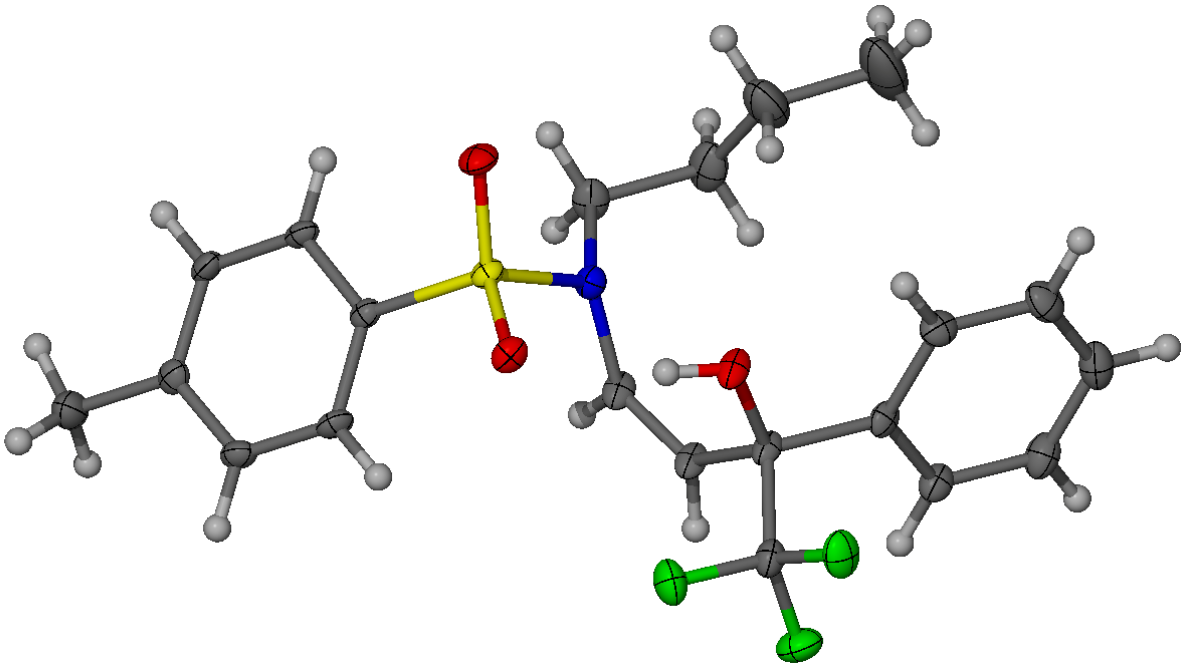


Chiralcell OJ using hexanes: EtOH (98:2) as the mobile phase at 1.0 mL/min. t_1 = 11.3 min (minor), t_2 = 14.2 min (major). α = 1.36.

6. Crystallographic Analysis

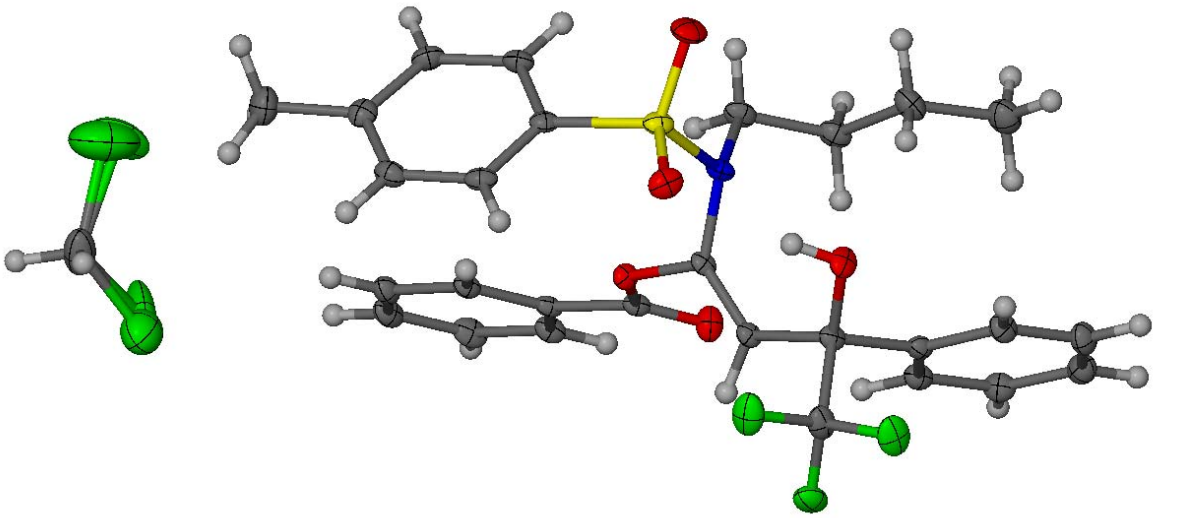
(*S*,*Z*)-*N*-butyl-4-methyl-*N*-(4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl)benzenesulfonamide

A single crystal was obtained by slow evaporation of a solution of the chiral alcohol in $CHCl_3$. Single crystal X-ray analysis was performed at 100 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated and corrected using the APEX 2 program. The structures were solved by intrinsic phasing and refined with full-matrix least-square analysis using SHELX-97-2 software. Non-hydrogen atoms were refined with anisotropic displacement parameter. Crystal data: $C_{21}H_{24}F_3NO_3S$, M = 427.42, colorless needle, 0.04 x 0.06 x 0.18 mm^3, orthorhombic, space group $P2_12_12_1$, a = 5.6103(5), b = 10.5760(9), c = 36.083(3) Å, V = 2141.0(3) $Å^3$, Z = 4. Absolute structure parameter = 0.01(3).[2]



(*S*,*E*)-2-((*N*-butyl-4-methylphenyl)sulfonamido)-4,4,4-trifluoro-3-hydroxy-3-phenylbut-1-en-1-yl benzoate

A single crystal was obtained by slow evaporation of a solution of the chiral alcohol in CH_2Cl_2. Single crystal X-ray analysis was performed at 173 K using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were integrated and corrected using the APEX 2 program. The structures were solved by direct methods and refined with full-matrix least-square analysis using SHELX-97-2 software. Non-hydrogen atoms were refined with anisotropic displacement parameter. Crystal data: $C_{28}H_{30}F_3NO_5S$, CH_2Cl_2, M = 632.50, colorless needle, 0.04 x 0.05 x 0.18 mm^3, orthorhombic, space group $P2_12_12_1$, a = 7.6073(6), b = 17.9032(13), c = 21.8189(16) Å, V = 2971.6(4) $Å^3$, Z = 4. Absolute structure parameter = 0.015(10).[2]



7. References

1. Barbazanges, M.; Meyer, C.; Cossy, J. *Org. Lett.* **2007**, *9*, 3245-3248.
2. Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881.