Supporting Information

Weak Coordinated Nitrogen Functionality Enabled Regioselective C-H Alkynylation via Pd(II)/Mono-N-Protected Amino Acid Catalysis

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A. General procedure

^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts for 1 H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet). Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS–QP 5000 spectrometer. HRMS was carried out on a MAT 95XP (Thermo).

General reaction procedure for the synthesis of trifluoromethanesulfonamides:

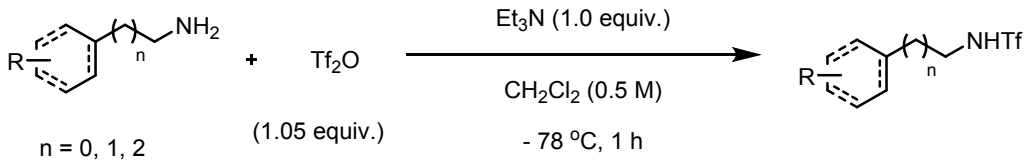


Figure S1. Synthesis of trifluoromethanesulfonamide substrates.

General Procedure: To a stirred solution of benzylamine (50 mmol, 1.0 equiv.) in dichloromethane (100 mL) was added triethylamine (7.0 mL, 50 mmol, 1.0 equiv.) at -78 °C under nitrogen. After stirring for 5 min at -78 °C, trifluoromethanesulfonic anhydride (8.8 mL, 52.5 mmol, 1.05 equiv.) was added dropwise and the mixture was stirred for 1 h at that temperature before being quenched by water (100 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (50 mL × 2). The combined organic phase was washed with brine (100 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (ethyl acetate/hexane = 1:100-1:5 as eluant) afforded corresponding trifluoromethanesulfonamides.

General reaction procedure for the synthesis of amides:

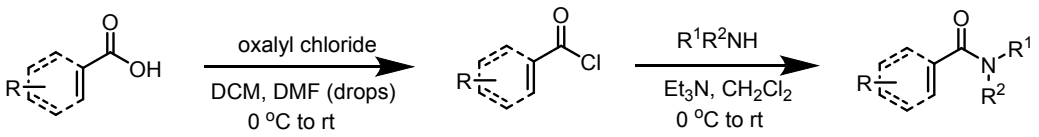


Figure S2. Synthesis of amide substrates.

1) The acid was dissolved in anhydrous CH_2Cl_2 (20 mL) and cooled with ice water. Oxalyl chloride (1.5 eq.) was added dropwise to the solution followed with the addition of catalytic amount of DMF (2 drops). The resulting mixture was allowed to stir at room temperature for additional two hours and the solvent was evaporated to afford crude acid chloride, which was used directly in the next step.

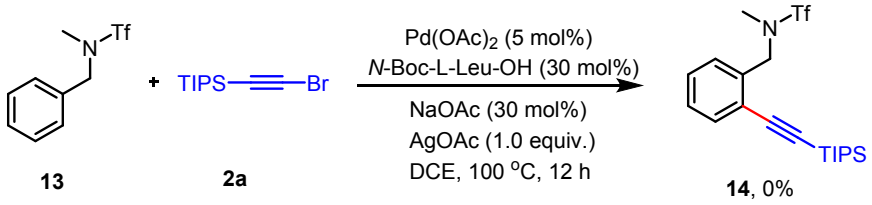
2) To a solution of amine R^1R^2NH (1 eq.) in a mixture of Et_3N (1 M), CH_2Cl_2 (1 M), the resulting solution was cooled to 0 ºC, followed by dropwise addition of the substituted benzoyl chloride (1.0 eq.). The reaction mixture was warmed to rt and stirred overnight. The organic phase was separated and the aqueous phase was extracted with EtOAc (20 mL×3). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The pure products were obtained by flash column chromatography.

General procedure for the Pd(II)-Catalyzed C-H alkynylation of amines:

An oven-dried 10 mL Schlenk Tube was charged with **1** (0.2 mmol), $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), NaOAc (0.06 mmol, 4.9 mg), N-Boc-L-Leu (0.06 mmol, 13.0 mg), AgOAc (0.2 mmol, 33.4 mg) in sequence, followed by adding alkyne **2** (0.3 mmol) in DCE (1.0 mL) through syringe. The resulting reaction mixture was stirred at 100 ºC for 12 h and then diluted with CH_2Cl_2 and filtered through diatomite. Removing the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired annulation product **3**.

B. Preliminary mechanistic studies:

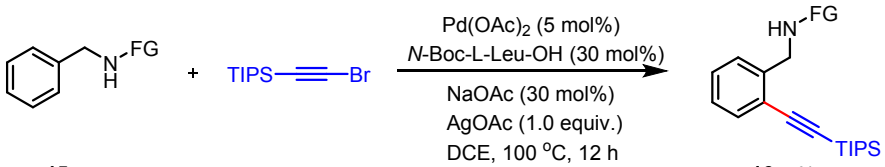
a) To further elucidate the role of the NHTf group in this regioselective C-H alkynylation, we used N-Me-N-Tf benzylamine **13** substrate under Pd(II)/MPAA catalysis, and the result revealed that no desired *ortho* C–H alkynylation product **14** was obtained (**Figure S3**). This observation indicated that ligand exchange between Pd(II) catalyst and NHTf group might take place to initiate this C–H alkynylation process.



13 **2a** **14**, 0%

Figure S3. Attempt for the C–H alkynylation of tertiary N–Tf benzylamine

b) We also conducted some control experiments using other NH-substituted benzylamines in this C–H alkynylation, as depicted in **Figure S4**, NHAc and NHTs benzylamines showed no reactivity for the *ortho* C–H alkynylation under Pd(II)/MPAA catalysis.



15, R = Ac
17, R = Ts

2a

16, 0%
18, 0%

Figure S4. Effect of N-substituted benzylamines in this *ortho* C–H alkynylation

c) The achievement of site-selective C–H functionalization of complex molecules, which contained multiple reactive C–H bonds, would provide valuable insight into the regiospecific modification of biologically active molecules. Along this line, we selected substrate **4m** that contained weak coordinated ester and NHTf group under this Pd(II)/MPAA catalyzed catalysis, and C–H alkynylation took place exclusively at C-H postition *ortho* to NHTf group (**Figure S5**).

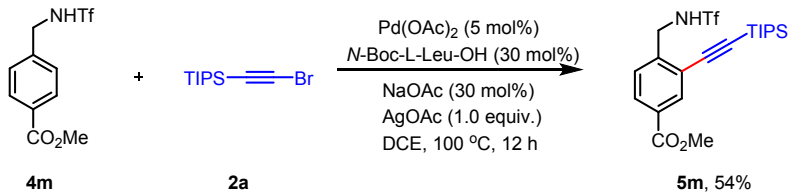
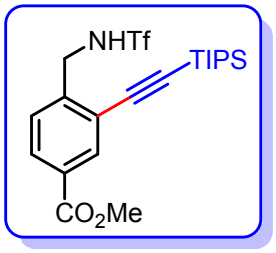
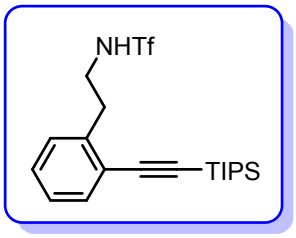


Figure S5. Regioselective C-H alkynylation of multiple functionalized arenes

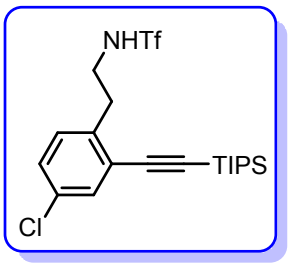


Methyl 4-(((trifluoromethyl)sulfonamido)methyl)-3-((triisopropylsilyl)ethynyl) benzoate (**5m**), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (dd, J = 1.6 Hz, 1H), 8.00 (dd, J = 1.6 Hz, 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 4.65 (s, 2H), 3.94 (s, 3H), 1.15-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.9, 142.1, 134.1, 130.5, 130.1, 129.2, 128.2, 122.8, 102.9, 100.0, 98.9, 52.5, 46.8, 29.7, 18.6, 11.2. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{31}F_3NO_4SSi$: 478.1690; Found: 478.1693.

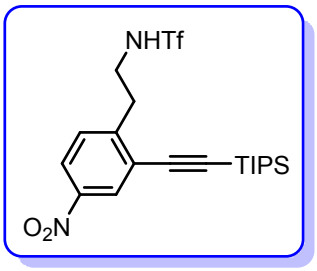
C. Analytical data for the alkynylated compounds:



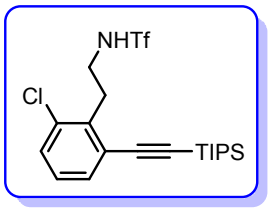
1,1,1-Trifluoro-*N*-(2-((triisopropylsilyl)ethynyl)phenethyl)methanesulfonamide (3a), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 1H), 7.30 (dt, J = 1.6 Hz, 7.6 Hz, 2H), 7.25 (dd, J = 0.8 Hz, 1H), 7.22-7.20 (m, 1H), 4.88 (brs, 1H), 3.65 (dd, J = 6.4 Hz, 12.4 Hz, 2H), 3.11 (t, J = 6.4 Hz, 2H), 1.15-1.05 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.75, 133.5, 129.5, 129.0, 127.2, 123.3, 104.9, 95.8, 44.6, 35.2, 18.6, 11.3. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.43. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_2SSi$: 434.1791, found: 434.1796.



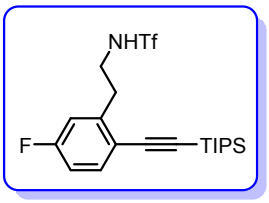
***N*-(4-Chloro-2-((triisopropylsilyl)ethynyl)phenethyl)-1,1,1-trifluoromethane sulfonamide (3b), ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, J = 2.0 Hz, 1H), 7.28 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 4.84 (brs, 1H), 3.62 (t, J = 6.4 Hz, 2H), 3.08 (t, J = 6.8 Hz, 2H), 1.135-1.127 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.2, 133.0, 130.8, 129.1, 124.9, 118.0, 103.4, 97.5, 44.4, 34.8, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.39. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{30}ClF_3NO_2SSi$: 468.1402, found: 468.1405.



1,1,1-Trifluoro-*N*-(4-nitro-2-((triisopropylsilyl)ethynyl)phenethyl)methane sulfonamide (3c), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 2.4 Hz, 1H), 8.13 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 3.68 (t, J = 2.0 Hz, 1H), 3.21 (t, J = 6.8 Hz, 1H), 1.17-1.12 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.0, 145.8, 130.6, 128.4, 125.0, 123.4, 102.3, 99.5, 43.9, 35.5, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.35. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{30}F_3N_2O_4SSi$: 479.1642, found: 479.1644.

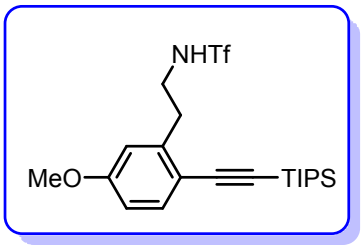


***N*-(2-Chloro-6-((triisopropylsilyl)ethynyl)phenethyl)-1,1,1-trifluoromethane sulfonamide (3d), ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 (dd, J = 1.2 Hz, 7.6 Hz, 1H), 7.37 (dd, J = 0.8 Hz, 8.0 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 5.02 (brs, 1H), 3.64 (dd, J = 9.6 Hz, 2H), 3.34 (t, J = 6.8 Hz, 1H), 1.16-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.5, 134.7, 131.9, 128.2, 125.6, 104.4, 97.0, 43.6, 32.0, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.43. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{30}ClF_3NO_2SSi$: 468.1402, found: 468.1405.

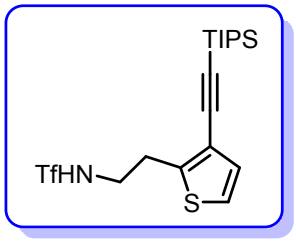


1,1,1-Trifluoro-*N*-(5-fluoro-2-((triisopropylsilyl)ethynyl)phenethyl)methane sulfonamide (3e), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 1H), 6.97-6.93 (m, 2H), 7.31 (s, 1H), 4.96 (brs, 1H), 3.64 (d, J = 4.0 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H),

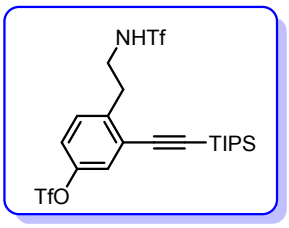
1.13-1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 161.2, 141.4, 135.3, 135.2, 119.4, 116.8, 116.5, 114.7, 103.8, 95.6, 44.4, 35.2, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** **-**77.45, -109.43. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{30}F_4NO_2SSi$: 452.1697, found: 452.1695.



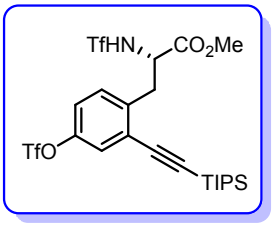
1,1,1-Trifluoro-*N*-(5-methoxyl-2-((triisopropylsilyl)ethynyl)phenethyl) methanesulfonamide (3f), ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.45 (d, *J* = 8.4 Hz, 1H), 6.82-6.77 (m, 1H), 6.76-6.73 (m, 1H), 4.96 (brs, 1H), 3.81 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H), 1.15-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 159.9, 140.6, 134.9, 115.4, 115.3, 112.8, 105.0, 93.9, 55.4, 44.5, 35.4, 18.7, 11.3. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** **-**77.44. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{33}F_3NO_3SSi$: 464.1897, found: 464.1903.



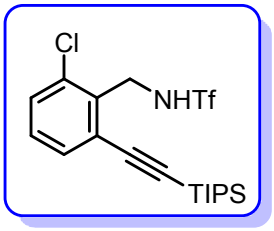
1,1,1-Trifluoro-*N*-(2-(3-((triisopropylsilyl)ethynyl)thiophen-2-yl)ethyl)methane sulfonamide (3g), ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.12 (d, *J* = 5.2 Hz, 1H), 7.05 (d, *J* = 5.2 Hz, 1H), 4.98 (brs, 1H), 3.64 (dd, *J* = 6.0 Hz, 12.0 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 1.125-1.120 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 142.2, 130.6, 123.5, 121.8, 100.4, 94.6, 44.8, 29.7, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** -77.40. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{29}F_3NO_2S_2Si$: 440.1356, found: 440.1358.



4-(2-((Trifluoromethyl)sulfonamido)ethyl)-3-((triisopropylsilyl)ethynyl)phenyl trifluoromethanesulfonate (3h), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.39 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H),7.22 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 4.89 (brs, 1H), 3.63 (dd, *J* = 6.8 Hz, 14.4 Hz, 2H), 3.13 (t, *J* = 6.4 Hz, 2H), 1.17-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 159.9, 140.6, 134.9, 115.4, 115.3, 112.8, 105.0, 93.9, 55.4, 44.5, 35.4, 18.7, 11.3. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** **-**72.8, -77.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{30}F_6NO_5S_2Si$: 582.1233, found: 582.1235.

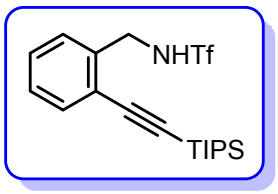


Methyl (*S*)-2-((trifluoromethyl)sulfonamido)-3-(4-(((trifluoromethyl)sulfonyl)oxy) -2-((triisopropylsilyl)ethynyl)phenyl)propanoate (3i), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.40 (d, *J* = 2.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 1.6 Hz, 2.4 Hz, 1H), 4.52 (dd, *J* = 0.8 Hz, 10.8 Hz, 1H), 3.80 (s, 3H), 3.48 (q, *J* = 0.8 Hz, 1H), 3.12 (dd, *J* = 10.8 Hz, 14.0 Hz, 1H), 1.18-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 170.6, 148.4, 137.4, 131.8, 125.7, 121.7, 102.7, 99.4, 57.6, 53.2, 37.1, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** -72.7, -77.9. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{23}H_{32}F_6NO_7S_2Si$: 640.1288, found: 640.1293.

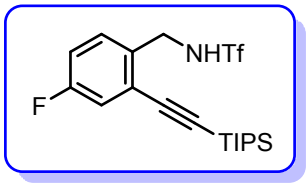


***N*-(2-Chloro-6-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethanesulfon-**

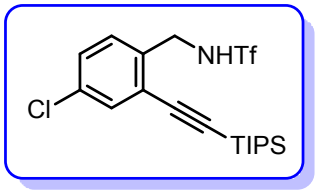
amide (5a), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 5.53 (brs, 1H), 4.78 (d, J = 5.6 Hz, 2H), 1.13-1.06 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 134.6 (d, J = 6.0 Hz), 132.0, 130.3, 129.7, 125.5, 121.2, 118.0, 103.1, 98.7, 44.1, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ 77.37. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{28}ClF_3NO_2SSi$: 454.1245, found: 454.1249.



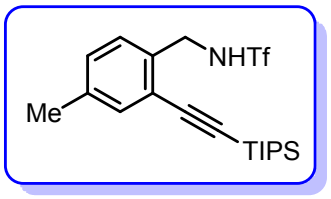
1,1,1-Trifluoro-*N*-(2-((triisopropylsilyl)ethynyl)benzyl)methanesulfonamide (5b), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.2 Hz, 1H), 7.36-7.34 (m, 2H), 7.33-7.30 (m, 1H), 5.57 (brs, 1H), 4.60 (s, 2H), 1.16-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.6, 133.2, 129.2, 128.5, 128.4, 122.5, 104.1, 97.5, 47.2, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.49. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{29}F_3NO_2SSi$: 420.1635, found: 420.1639.



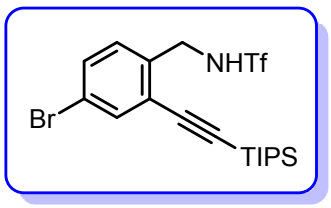
1,1,1-Trifluoro-*N*-(4-fluoro-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5c), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, J = 5.2 Hz, 8.8 Hz, 1H), 7.22 (dd, J = 2.8 Hz, 8.8 Hz, 1H), 7.07 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 5.60 (br, 1H), 4.57 (s, 2H), 1.16-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 133.7, 130.4, 130.3, 129.8, 124.4, 121.2, 119.9, 119.7, 118.0, 116.6, 116.4, 116.0, 102.8, 98.9, 46.4, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.18, -77.50, -112.75. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{28}F_4NO_2SSi$: 438.1541, found: 438.1545.



***N*-(4-Chloro-2-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5d), ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, J = 1.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 7.31 (s, 1H), 4.56 (s, 2H), 1.16-1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.1, 134.4, 132.8, 129.7, 129.4, 124.1, 102.6, 99.2, 46.5, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.46. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{28}ClF_3NO_2SSi$: 454.1245, found: 454.1242.

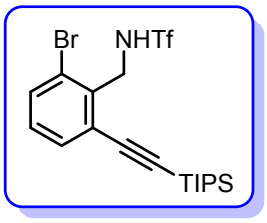


1,1,1-Trifluoro-*N*-(4-methyl-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5e), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.19-7.16 (m, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.52 (brs, 1H), 4.50 (s, 2H), 2.28 (s, 3H), 1.12-1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.5, 134.7, 133.6, 130.1, 128.4, 122.3, 104.4, 96.9, 46.9, 20.9, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.50, -77.51. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_2SSi$: 434.1791, found: 434.1796.

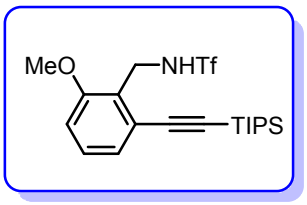


***N*-(4-Bromo-2-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5f), ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, J = 1.6 Hz, 1H), 7.32 (d, J = 1.6 Hz, 1H), 7.31 (s, 1H), 4.56 (s, 2H), 1.16-1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.6, 135.6, 132.3, 129.8, 122.2, 102.5, 46.5, 18.6, 11.2. **^{19}F NMR (100**

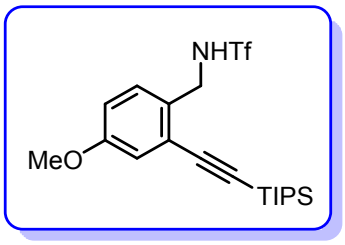
MHz, $CDCl_3$): ***δ*** -77.45. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{28}BrF_3NO_2SSi$: 498.0740, found: 498.0744.



N*-(2-Bromo-6-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5g), ^{1}H NMR (400 MHz, $CDCl_3$):** ***δ 7.45 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 5.70 (brs, 1H), 4.56 (s, 2H), 3.78 (s, 3H), 1.17-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 160.1, 139.4, 134.6, 114.5, 114.05, 114.0, 104.2, 95.5, 55.5, 47.2, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** -77.28. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{28}BrF_3NO_2SSi$: 498.0740, found: 498.0745.

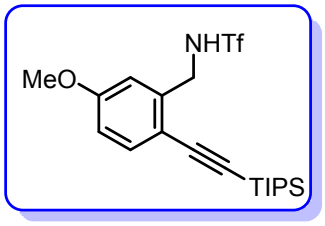


1,1,1-Trifluoro-*N*-(2-methoxy-6-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5h), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.30-7.24 (m, 1H), 7.16 (dd, *J* = 0.8 Hz, 3.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.70 (brs, 1H), 5.70 (brs, 1H), 4.76 (d, *J* = 5.6 Hz, 2H), 3.90 (s, 3H), 1.16-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 157.5, 130.2, 129.5, 125.5, 121.0, 11.1, 110.5, 103.5, 96.8, 55.8, 41.8, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** -77.51, -77.52. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_3SSi$: 450.1741, found: 450.1743.

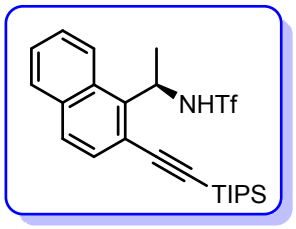


1,1,1-Trifluoro-*N*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl)methane

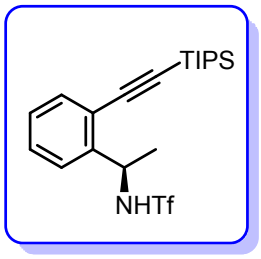
sulfonamide (5i), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, J = 4.4 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.84 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 4.50 (s, 2H), 3.78 (s, 2H), 1.11-1.10 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.4, 130.2, 129.9, 123.6, 118.0, 115.3, 104.1, 97.0, 55.5, 46.7, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.47, -77.49. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_3SSi$: 450.1741, found: 450.1743.



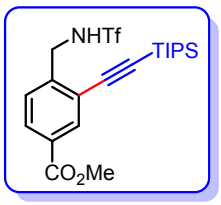
1,1,1-Trifluoro-*N*-(5-methoxy-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5j), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 5.60 (brs, 1H), 4.86 (d, J = 6.0 Hz, 2H), 1.15-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.2, 133.6, 132.7, 129.9, 125.6, 124.6, 103.2, 98.8, 65.9, 46.7, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -77.47. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_3SSi$: 450.1741, found: 450.1743.



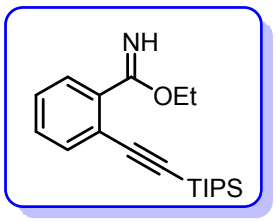
(*R*)-1,1,1-Trifluoro-*N*-(1-(2-((triisopropylsilyl)ethynyl)naphthalen-1-yl)ethyl) methanesulfonamide (5k), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.56-7.53 (m, 2H), 5.79 (brs, 1H), 1.86 (d, J = 7.2 Hz, 3H), 1.19 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.2, 130.5, 129.3, 129.0, 128.3, 127.7, 127.1, 121.9, 106.7, 101.3, 60.4, 18.7, 14.2, 11.3. **^{19}F NMR (100 MHz, $CDCl_3$)**: δ -78.17. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{24}H_{33}F_3NO_2SSi$: 484.1948, found: 484.1945.



(*R*)-1,1,1-Trifluoro-*N*-(1-(2-((triisopropylsilyl)ethynyl)phenyl)ethyl)methane sulfonamide (5l), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.53 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 5.2 Hz, 1H), 5.04-4.97 (m, 2H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.17-1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 143.2, 134.4, 129.2, 127.8, 126.4, 120.0, 104.8, 98.3, 55.6, 23.5, 18.6, 11.3. **^{19}F NMR (100 MHz, $CDCl_3$)**: ***δ*** -77.50. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}F_3NO_2SSi$: 434.1791, found: 434.1794.

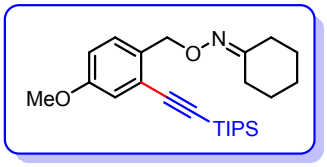


Methyl 4-(((trifluoromethyl)sulfonamido)methyl)-3-((triisopropylsilyl)ethynyl) benzoate (5m), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 8.16 (dd, *J* = 1.6 Hz, 1H), 8.00 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 4.65 (s, 2H), 3.94 (s, 3H), 1.15-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 165.9, 142.1, 134.1, 130.5, 130.1, 129.2, 128.2, 122.8, 102.9, 100.0, 98.9, 52.5, 46.8, 29.7, 18.6, 11.2. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{31}F_3NO_4SSi$: 478.1690; Found: 478.1693.

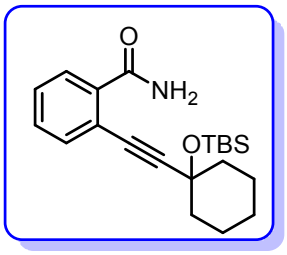


Ethyl 2-((triisopropylsilyl)ethynyl)benzimidate (7a), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 8.79 (brs, 1H), 7.75 (q, *J* = 3.6 Hz, 1H), 7.57 (q, *J* = 3.2 Hz, 1H), 7.35 (q, *J* = 3.6 Hz, 2H), 4.34 (q, *J* = 3.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.16-1.11 (m, 21H). **^{13}C NMR**

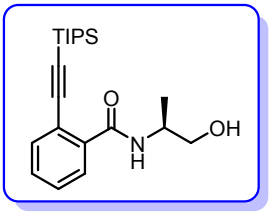
(100 MHz, $CDCl_3$): ***δ*** 165.8, 134.6, 134.5, 129.6, 128.4, 127.9, 121.2, 104.6, 98.3, 61.7, 18.7, 14.2, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{32}NOSi$: 330.2248, found: 330.2245.



Cyclohexanone *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (7b), ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.30 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.89-6.84 (m, 1H), 5.18 (s, 2H), 3.80 (s, 3H), 2.50-2.47 (m, 2H), 2.21-2.18 (m, 2H), 1.66-1.57 (m, 8H), 1.13 (s, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 158.5, 132.7, 129.7, 129.6, 123.6, 113.7, 104.4, 94.9, 73.1, 55.4, 55.2, 32.2, 32.1, 25.7, 18.7, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{25}H_{40}NO_2Si$: 414.2823; found: 414.2825.

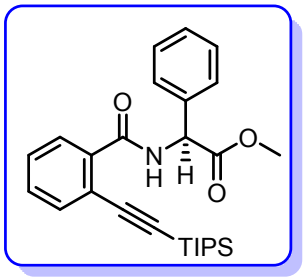


2-((1-((*tert*-Butyldimethylsilyl)oxy)cyclohexyl)ethynyl)benzamide (7c), ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 (d, *J* = 7.2 Hz, 1H), 7.31 (dd, *J* = 1.2 Hz, 6.4 Hz, 2H), 7.29-7.27 (m, 1H), 5.85 (brs, 1H), 5.52 (brs, 1H), 3.76 (s, 2H), 1.92-1.86 (m, 2H), 1.74-1.69 (m, 4H), 1.57-1.52 (m, 2H), 1.48-1.44 (m, 1H), 1.38-1.32 (m, 1H), 0.90 (s, 9H), 0.19 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 173.1, 136.6, 132.5, 130.0, 128.9, 127.6, 123.3, 99.2, 69.8, 42.1, 41.1, 27.1, 25.8, 25.3, 22.9, 2.7. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{34}NO_2Si$: 372.2353; found: 372.2356.

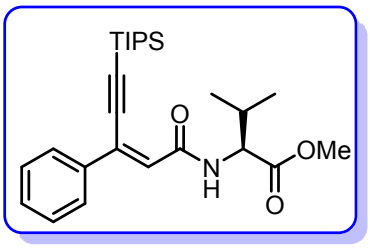


(*S*)-*N*-(1-Hydroxypropan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide (7d), ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.14 (brs, 1H), 8.11-8.08 (t, J = 4.4 Hz, 1H), 7.57-7.55

(m, 1H), 7.42 (t, J = 4.4 Hz, 2H), 4.05-4.01 (m, 1H), 3.59-3.53 (m, 1H), 3.43-3.36 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H), 1.14-1.13 (m, 21H) ; **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.6, 134.6, 134.5, 130.7, 130.2, 129.0, 119.8, 105.5, 99.1, 67.9, 48.2, 20.9, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{34}NO_2Si$: 360.2353; found: 360.2357.

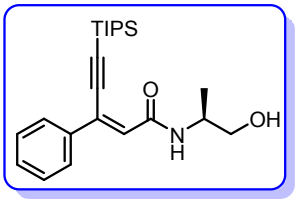


Methyl (*S*)-2-phenyl-2-(2-((triisopropylsilyl)ethynyl)benzamido)acetate (7e), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (m, 1H), 7.71-7.70 (d, *J* = 7.2 Hz, 1H), 7.58-7.55 (m, 1H), 7.40-7.38 (m, 2H), 7.25-7.21 (m, 2H), 7.19-7.17 (m, 1H), 5.01 (q, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 3.28 (q, *J* = 6.8 Hz, 1H), 3.19 (dd, *J* = 6.4 Hz, 13.6 Hz, 1H), 1.15-1.13 (m, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 171.7, 166.0, 136.3, 135.2, 134.8, 130.5, 129.4, 129.3, 128.7, 128.5, 127.0, 120.4, 105.1, 98.7, 54.5, 52.1, 38.1, 18.7, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{27}H_{36}NO_3Si$: 450.2459; found: 450.2456.

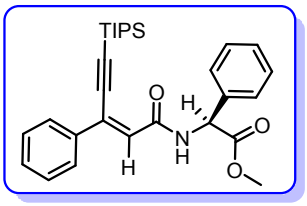


Methyl (*Z*)-(3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynoyl)-L-valinate (7f), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.67 (m, 2H), 7.66-7.63 (m, 2H), 7.38-7.36 (m, 3H), 6.56 (s, 1H), 4.68 (dd, *J* = 6.4 Hz, 8.4 Hz, 1H), 3.73 (s, 3H), 2.23-2.15 (m, 1H), 1.18-1.13 (m, 21H), 1.00 (q, *J* = 3.2 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 172.2, 164.7, 137.7, 129.8, 129.4, 128.53, 128.48, 127.1, 106.8, 103.0, 57.85,52.0, 31.4,

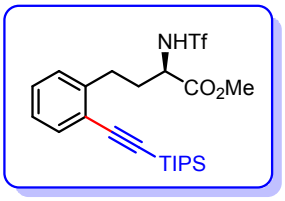
19.1, 18.9, 18.7, 11.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{26}H_{40}NO_3Si$: 442.2772; found: 442.2776.



(*S*,*Z*)-*N*-(1-Hydroxypropan-2-yl)-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7g), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (brs, 1H), 7.67-7.65 (m, 2H), 7.375-7.370 (m, 3H), 6.12 (s, 1H), 4.08-3.99 (m, 1H), 3.52-3.46 (m, 1H), 3.36-3.29 (m, 2H), 2.15 (s, 2H), 1.21 (d, J = 6.0 Hz, 3H), 1.15-1.13 (m, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 166.7, 136.9, 129.6, 129.4, 128.9, 128.7, 126.9, 106.5, 103.1, 67.9, 47.9, 20.9, 18.6, 11.2; **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{23}H_{36}NO_2Si$: 386.2510; found: 386.2512.

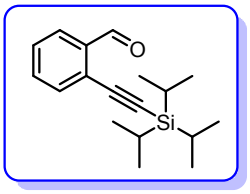


Methyl (*S*, *Z*)-2-phenyl-2-(3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamido) acetate (7h), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 6.0 Hz, 1H), 7.68-7.65 (m, 2H), 7.45-7.43 (m, 2H), 7.38-7.33 (m, 6H), 6.58 (s, 1H), 5.71 (d, J = 6.4 Hz, 1H), 3.75 (s, 3H), 1.05-1.02 (m, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 171.0, 164.7, 137.4, 136.0, 130.0, 129.5, 128.9, 128.6, 128.1, 127.7, 127.0, 107.1, 102.7, 57.2, 52.6, 18.6, 11.2; **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{29}H_{38}NO_3Si$: 476.2615; found: 476.2618.

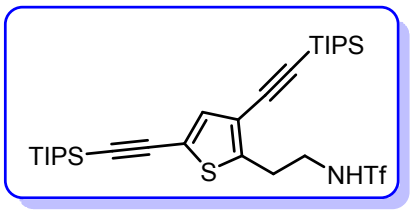


Methyl (*R*)-2-((trifluoromethyl)sulfonamido)-4-(2-((triisopropylsilyl)ethynyl)

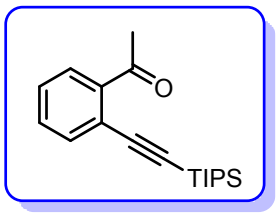
phenyl)butanoate (9), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 5.51 (brs, 1H), 4.23-4.19 (m, 2H), 4.17-4.12 (m, 1H), 3.00-2.93 (m, 2H), 2.35-2.26 (m, 1H), 2.11-2.02 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.14 (s, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 170.7, 141.8, 133.4, 128.9, 128.7, 126.5, 123.1, 100.0, 95.1, 62.4, 57.1, 33.9, 30.5, 18.7, 14.0, 11.3; **^{19}F NMR (100 MHz, $CDCl_3$): δ** -77.51, -77.52. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{23}H_{35}F_3NO_4SSi$: 506.2003; found: 506.2007.



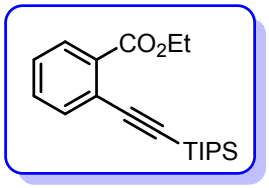
2-((Triisopropylsilyl)ethynyl)benzaldehyde (10), ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.62 (brs, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.59-7.54 (m, 2H), 7.45-7.43 (m, 1H), 1.15-1.09 (m, 21H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.8 (d, J = 9.0 Hz), 136.2, 135.3, 133.9, 133.7, 129.9, 128.7, 127.9, 127.2, 126.8, 102.0, 99.2, 18.7, 11.3; **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{27}OSi$: 287.1826; found: 287.1828.



***N*-(2-(3,5-Bis((triisopropylsilyl)ethynyl)thiophen-2-yl)ethyl)-1,1,1-tifluoro methanesulfonamide (3g-2), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.16 (s, 1H), 3.61 (t, J = 6.4 Hz, 2H), 3.17 (t, J = 6.4 Hz, 1H), 1.11 (s, 42H). **^{13}C NMR (100 MHz, $CDCl_3$)**: **δ** 143.1, 135.3, 126.9, 125.5, 124.0, 121.8, 121.6, 99.5, 97.9, 96.8, 94.9, 44.6, 29.7, 18.6, 11.2 (d, J = 6 Hz). **^{19}F NMR (100 MHz, $CDCl_3$): δ** -77.33. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{49}F_3NO_2S_2Si_2$: 620.2690; Found: 620.2693.



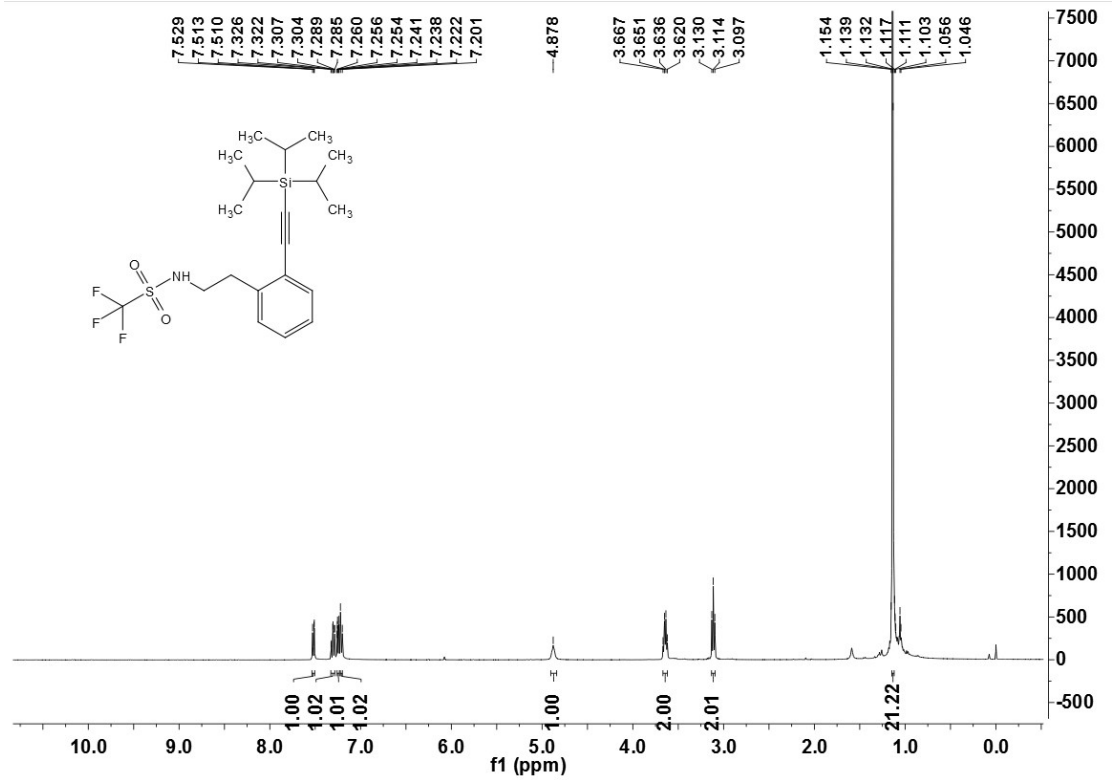
1-(2-((Triisopropylsilyl)ethynyl)phenyl)ethan-1-one (7a-1), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.75 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 199.8, 140.3, 133.8, 130.0, 127.4, 127.2, 120.7, 104.5, 97.2, 29.3, 28.7, 17.6, 10.3. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{28}OSiNa$ 323.1807; Found 323.1802.

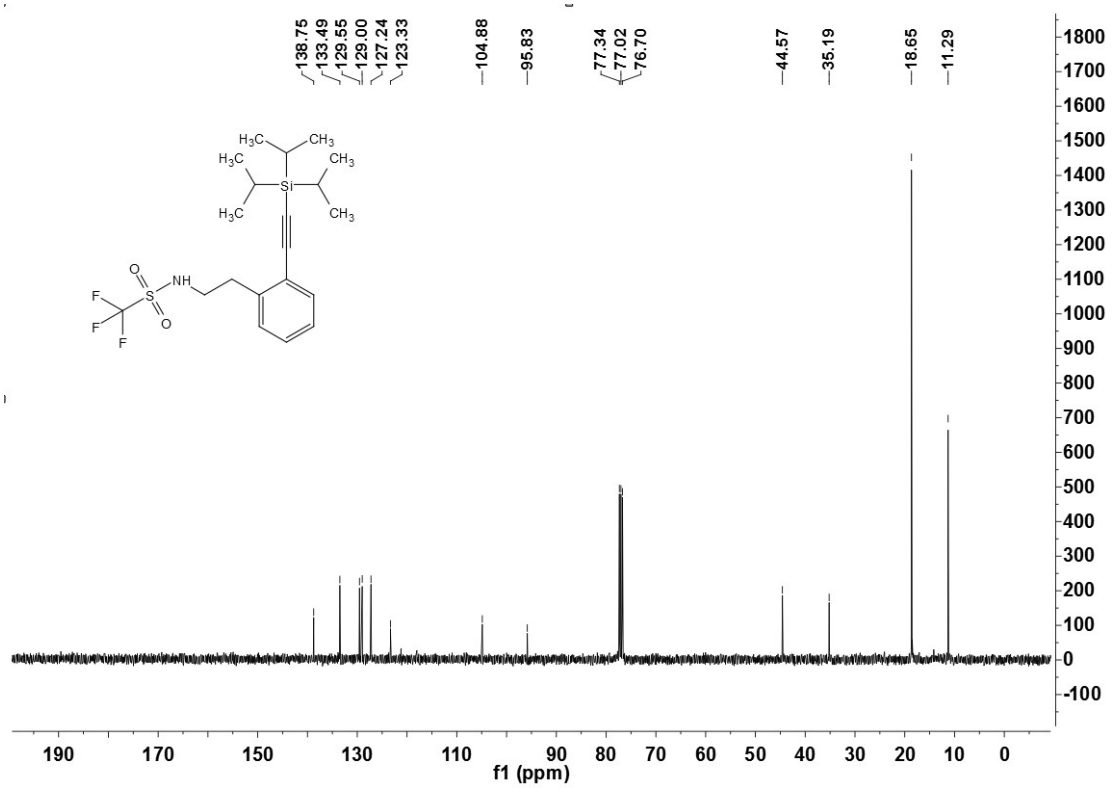


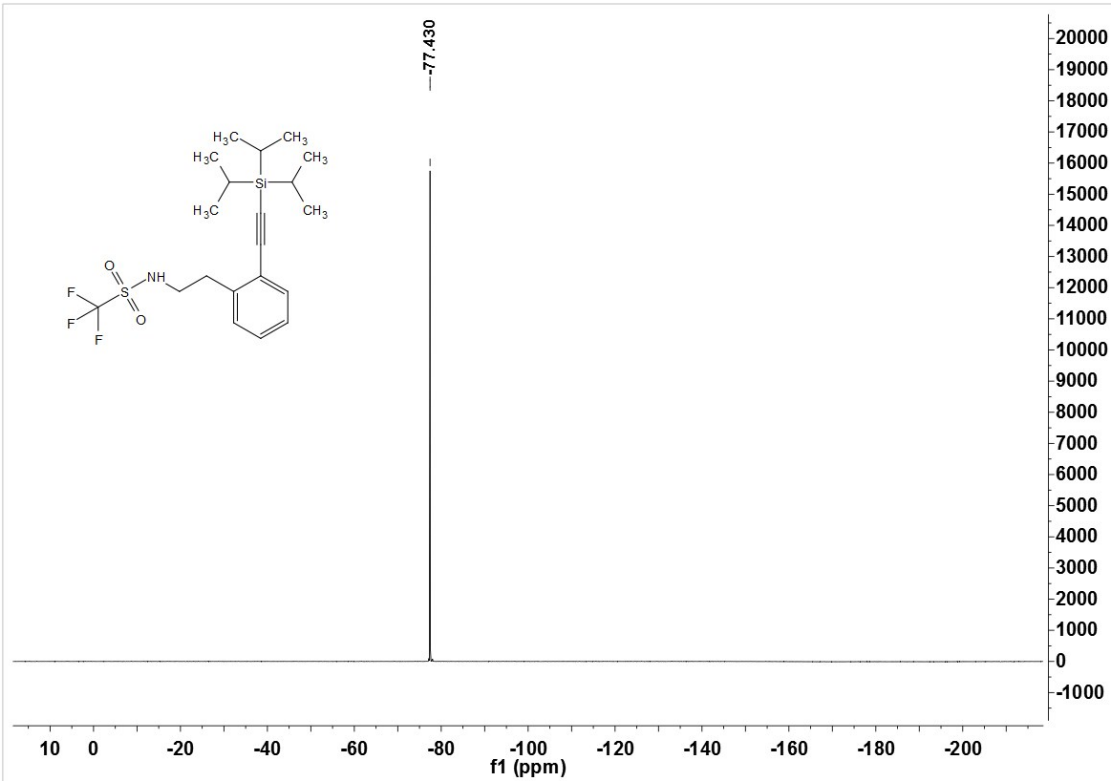
Ethyl 2-((triisopropylsilyl)ethynyl)benzoate (7a-2), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.85 (dd, *J* = 0.8 Hz, 7.6 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.42 (dt, *J* = 1.2 Hz, 7.6 Hz, 1H), 7.34 (dt, *J* = 1.2 Hz, 8.0 Hz, 1H), 4.39 (dd, *J* = 7.2 Hz, 14.0 Hz, 2H), 1.38 (t, *J* =7.2 Hz, 3H), 1.15 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)**: ***δ*** 166.6, 135.0, 133.1, 131.1, 129.9, 127.9, 123.4, 105.2, 96.3, 61.2, 18.7, 18.6, 14.3, 11.4. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{30}NaO_2Si$: 353.1913; Found: 353.1907.

D. NMR spectra

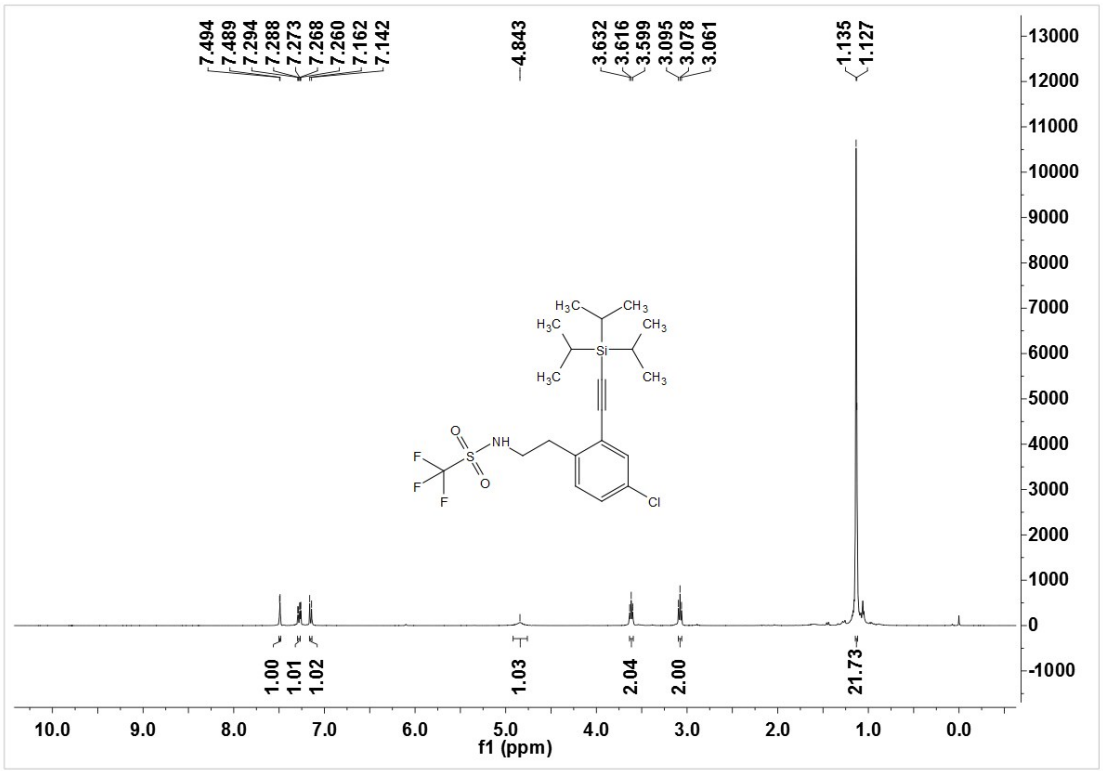
1,1,1-Trifluoro-*N*-(2-((triisopropylsilyl)ethynyl)phenethyl)methanesulfonamide (3a)

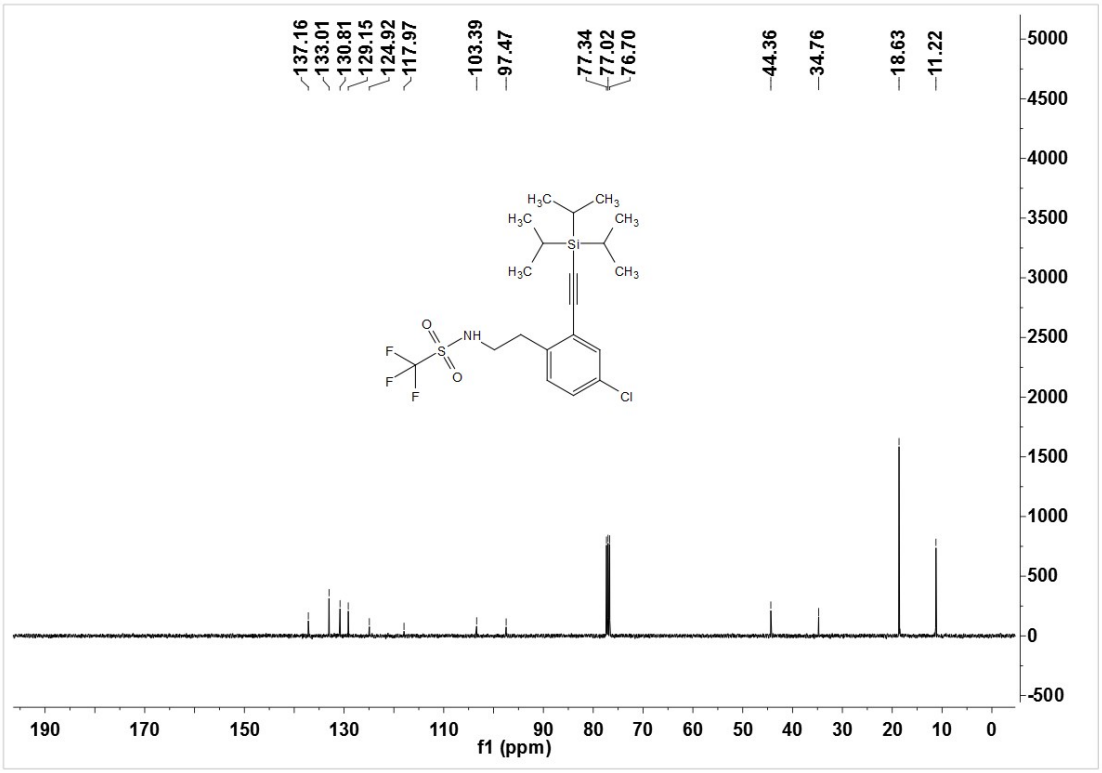


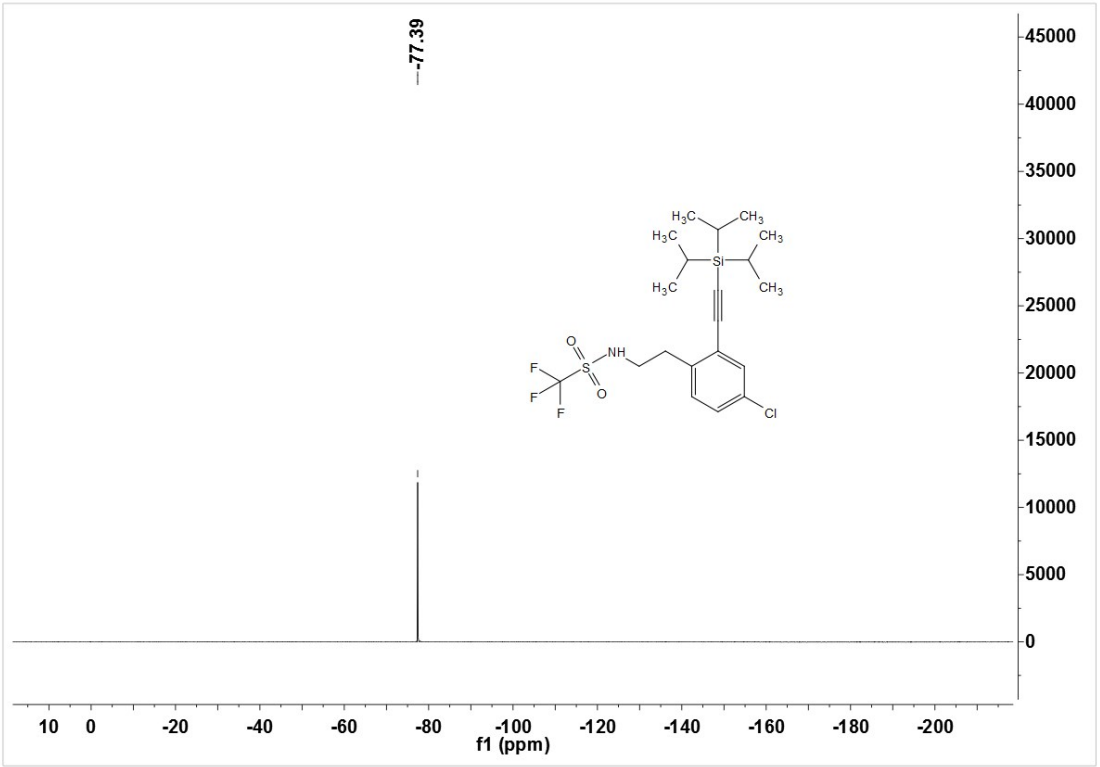




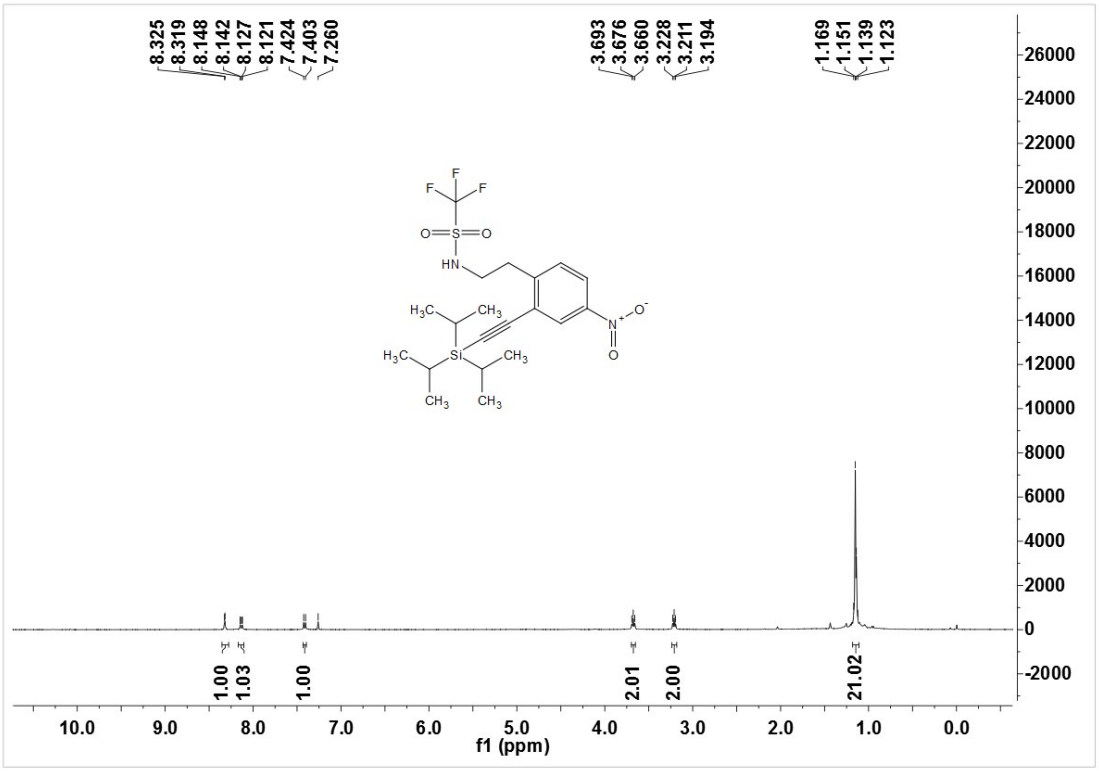
_N_-(4-Chloro-2-((triisopropylsilyl)ethynyl)phenethyl)-1,1,1-trifluoromethane sulfonamide (3b)

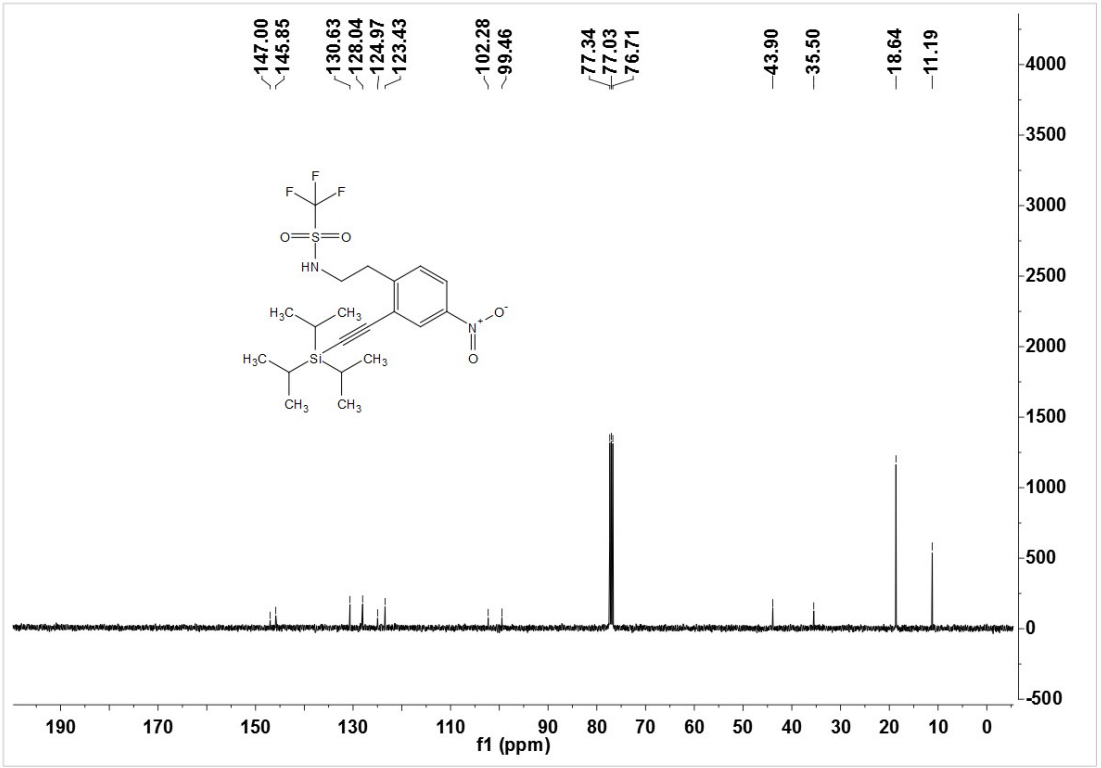


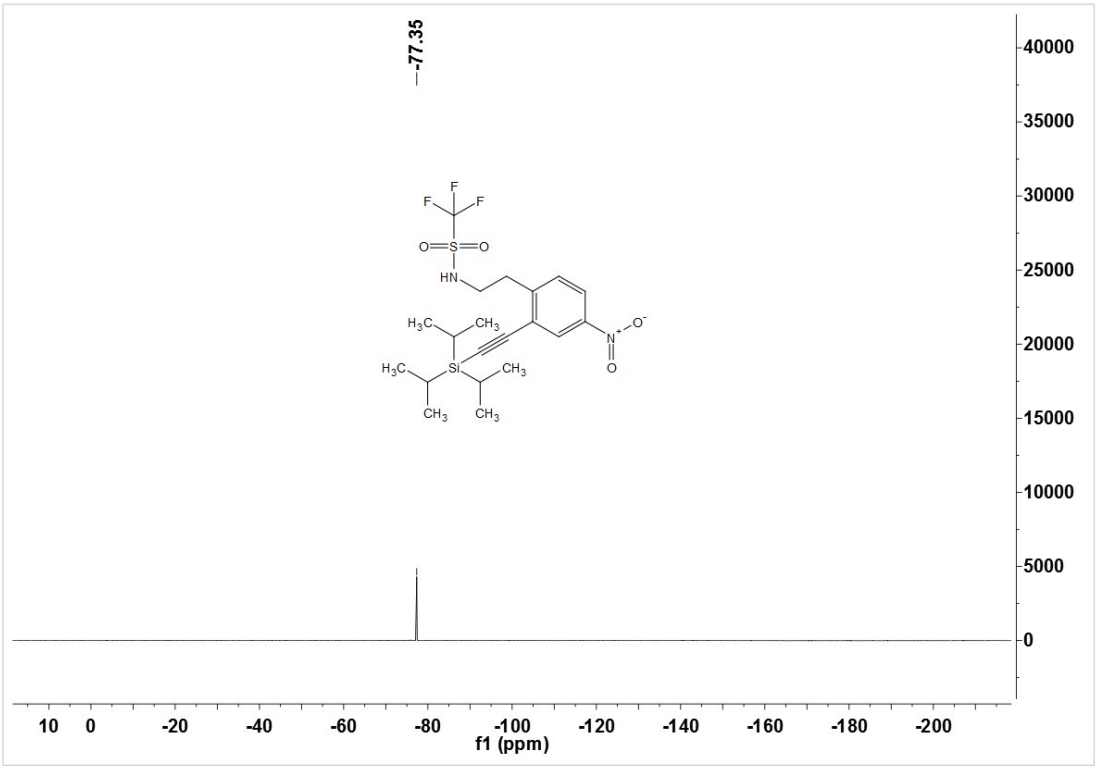

137.16
133.01
130.81
129.15
124.92
117.97
103.39
97.47
77.34
77.02
76.70
44.36
34.76
18.63
11.22
f1 (ppm)


-77.39
f1 (ppm)

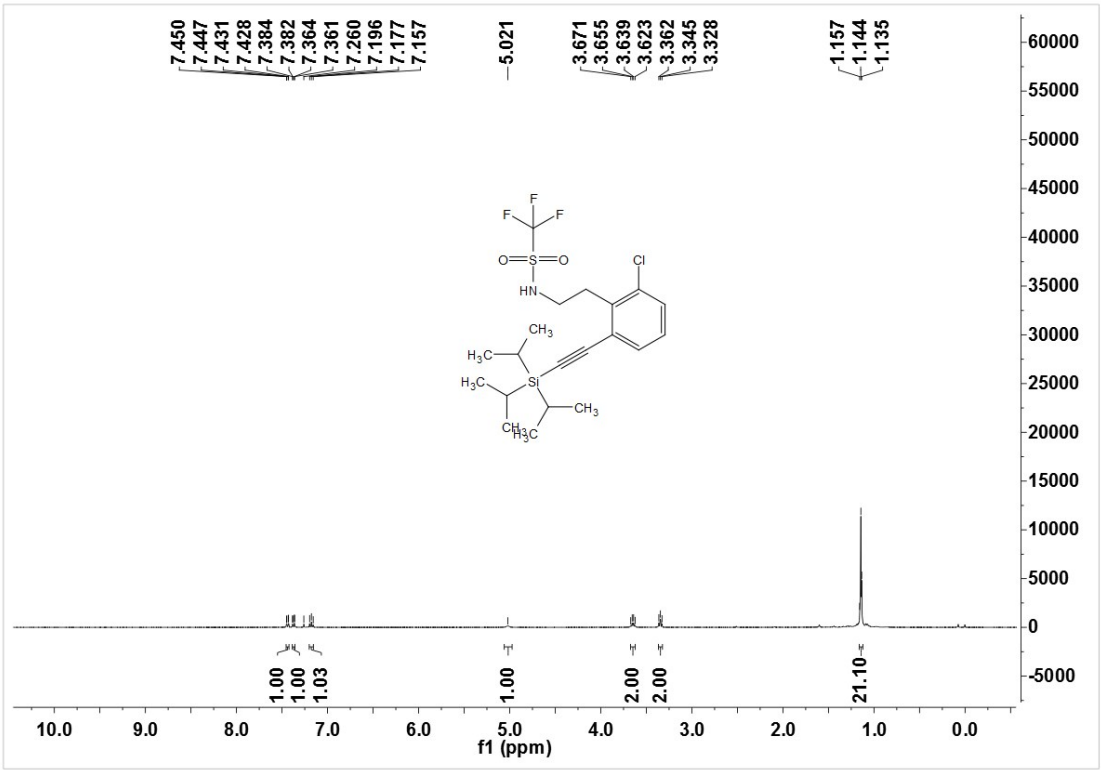
1,1,1-Trifluoro-*N*-(4-nitro-2-((triisopropylsilyl)ethynyl)phenethyl)methane sulfonamide (3c)

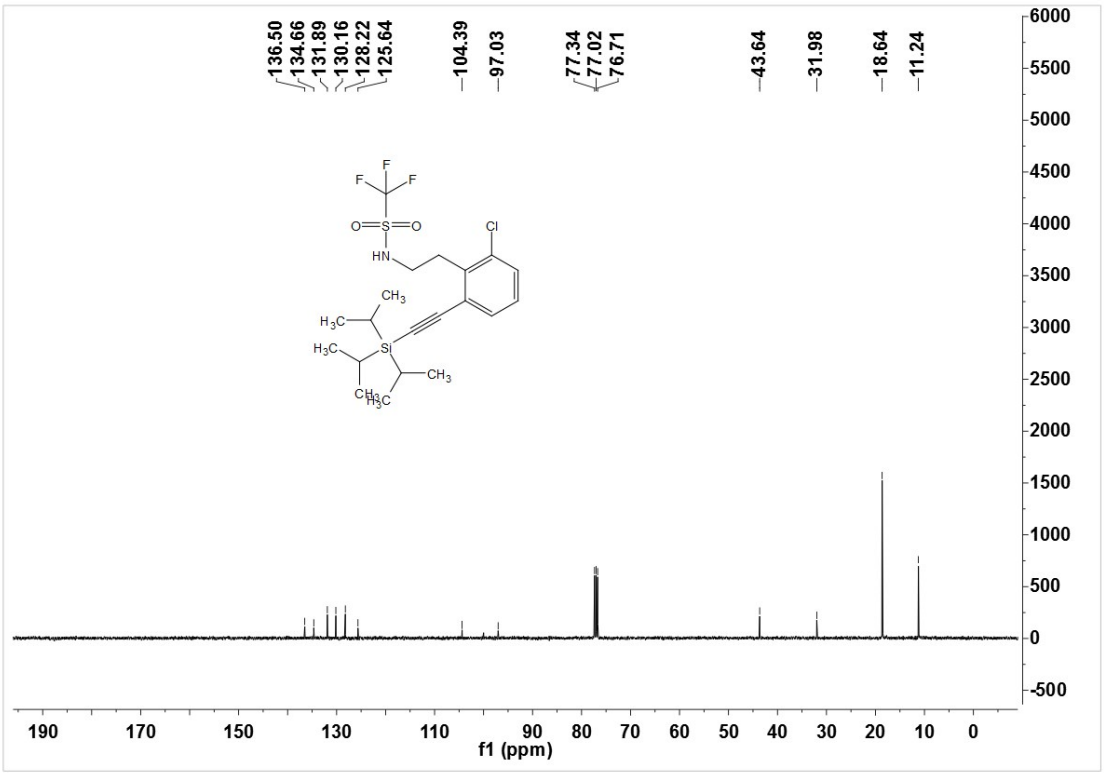


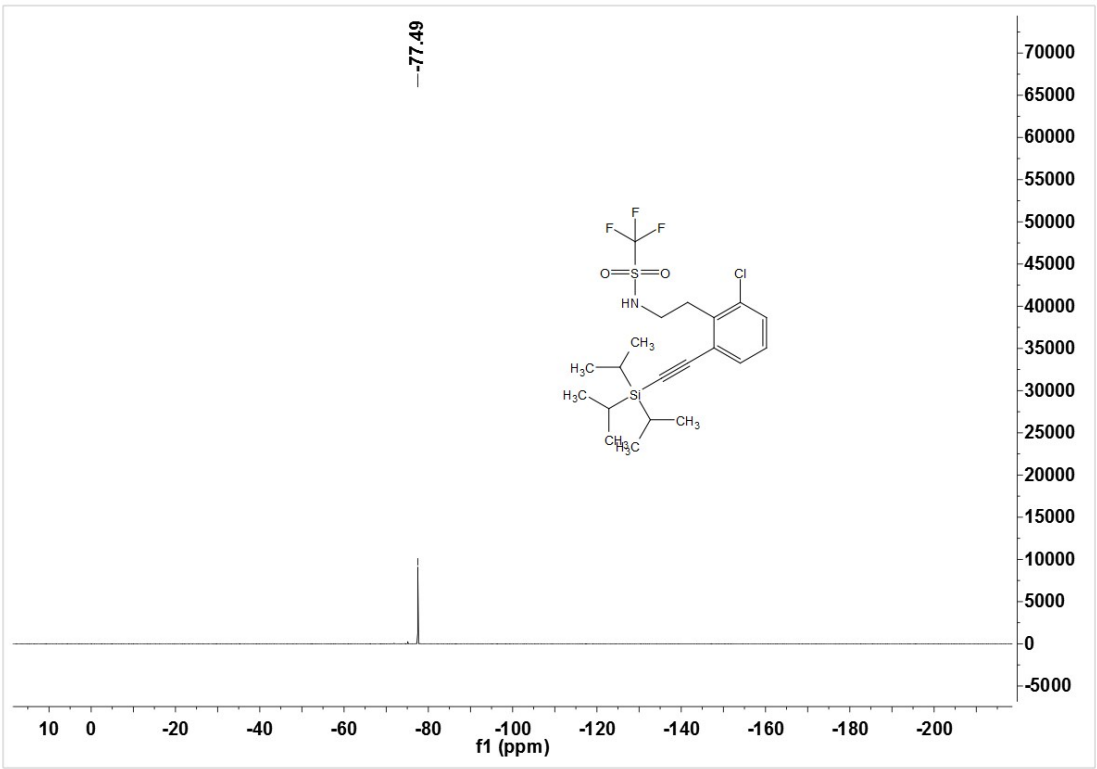




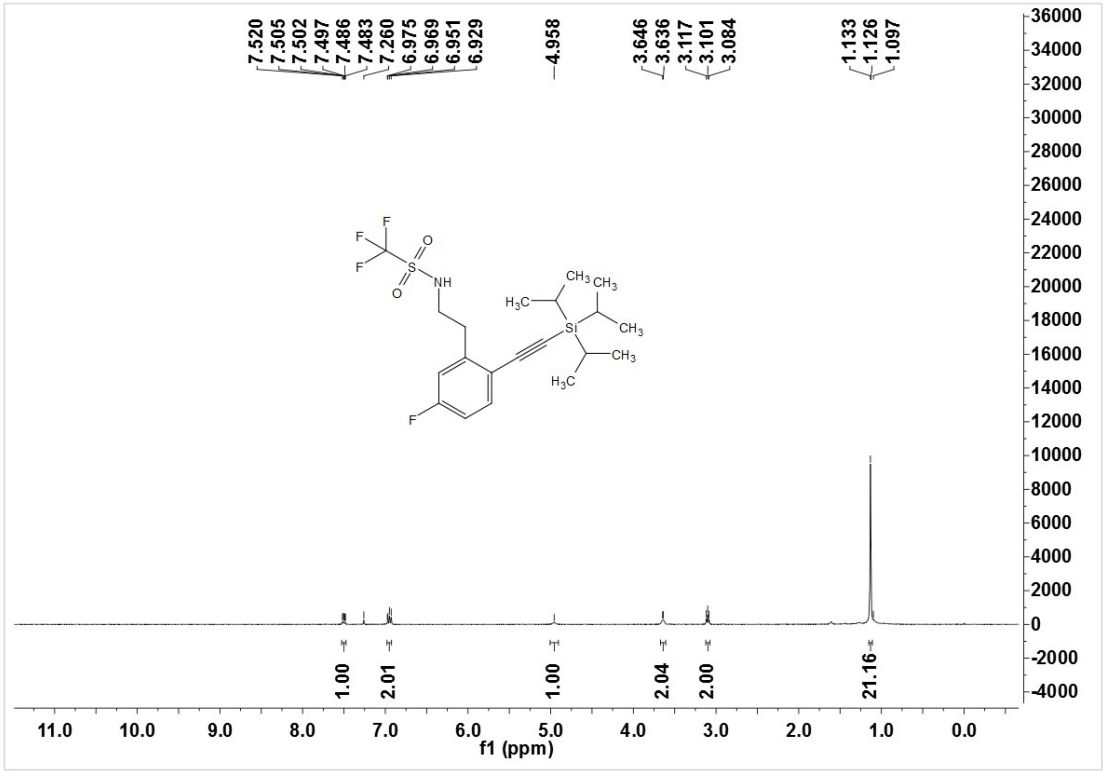
N-(2-Chloro-6-((triisopropylsilyl)ethynyl)phenethyl)-1,1,1-trifluoromethane sulfonamide (3d)

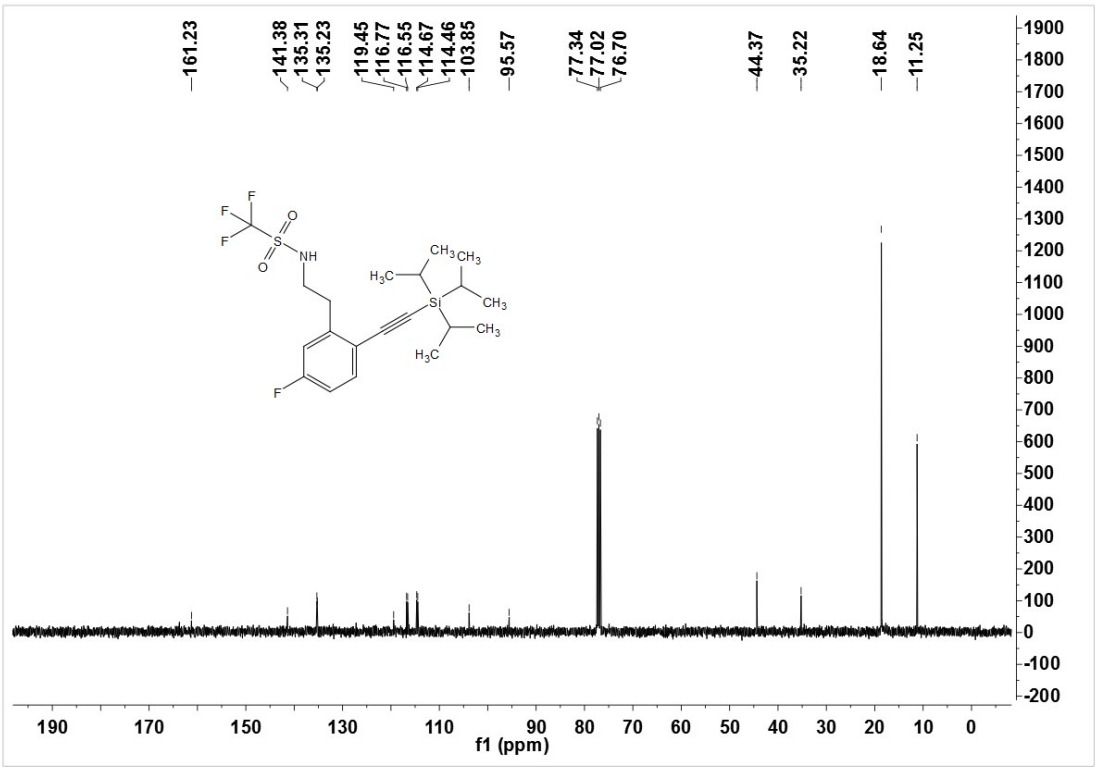


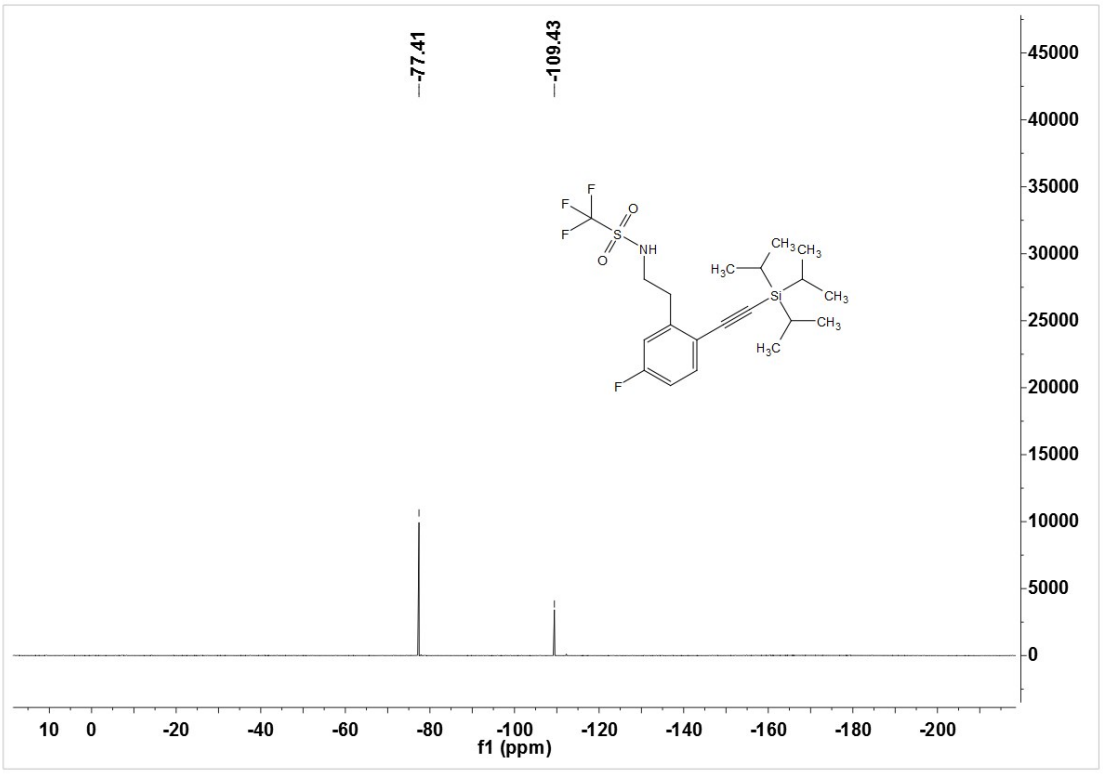

136.50
134.66
131.89
130.16
128.22
125.64
104.39
97.03
77.34
77.02
76.71
43.64
31.98
18.64
11.24
f1 (ppm)


-77.49
f1 (ppm)

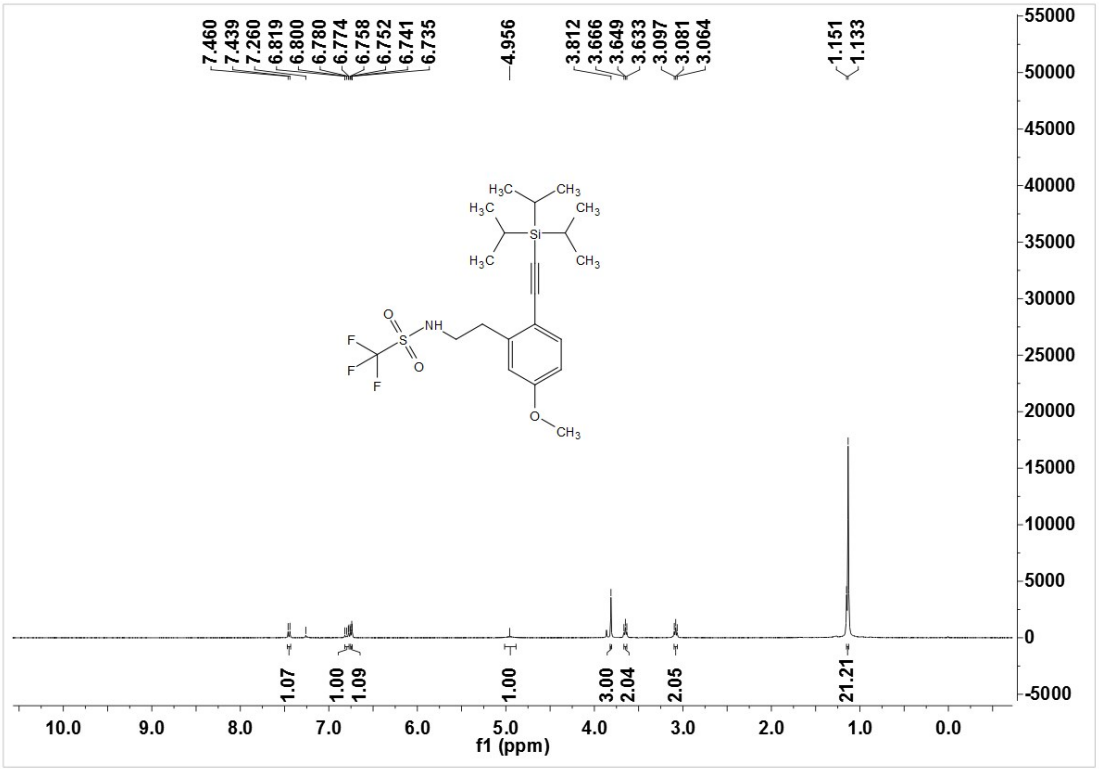
1,1,1-Trifluoro-*N*-(5-fluoro-2-((triisopropylsilyl)ethynyl)phenethyl)methane sulfonamide (3e)

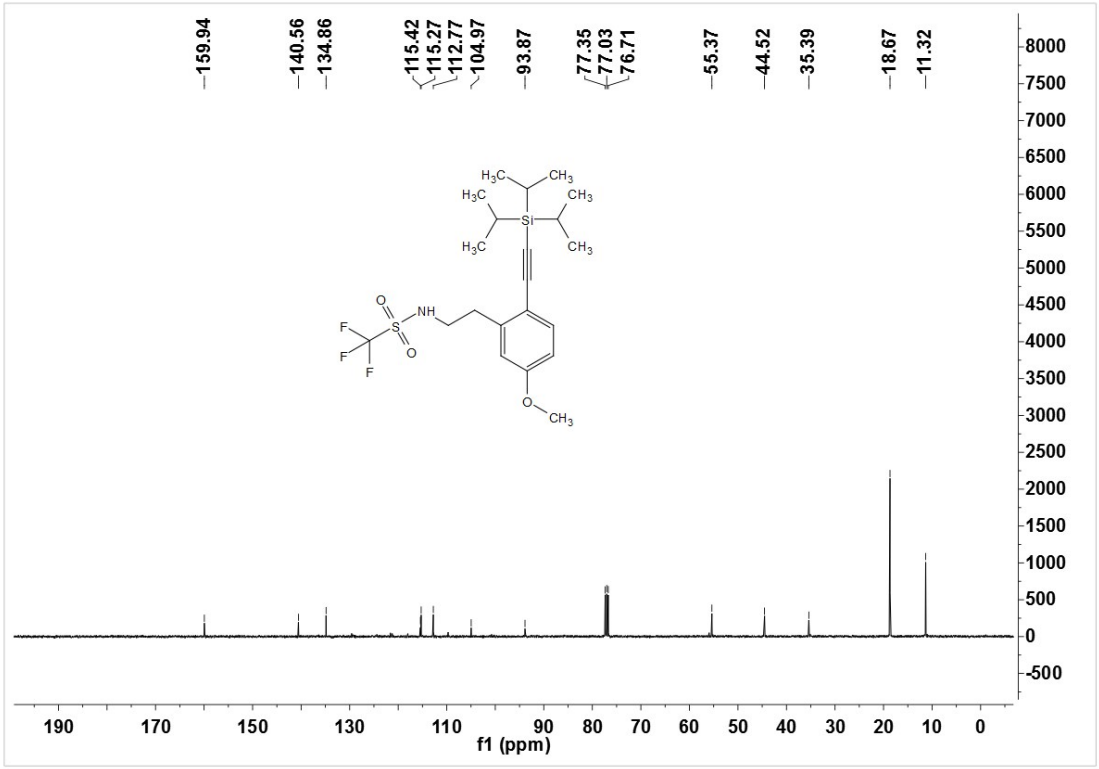


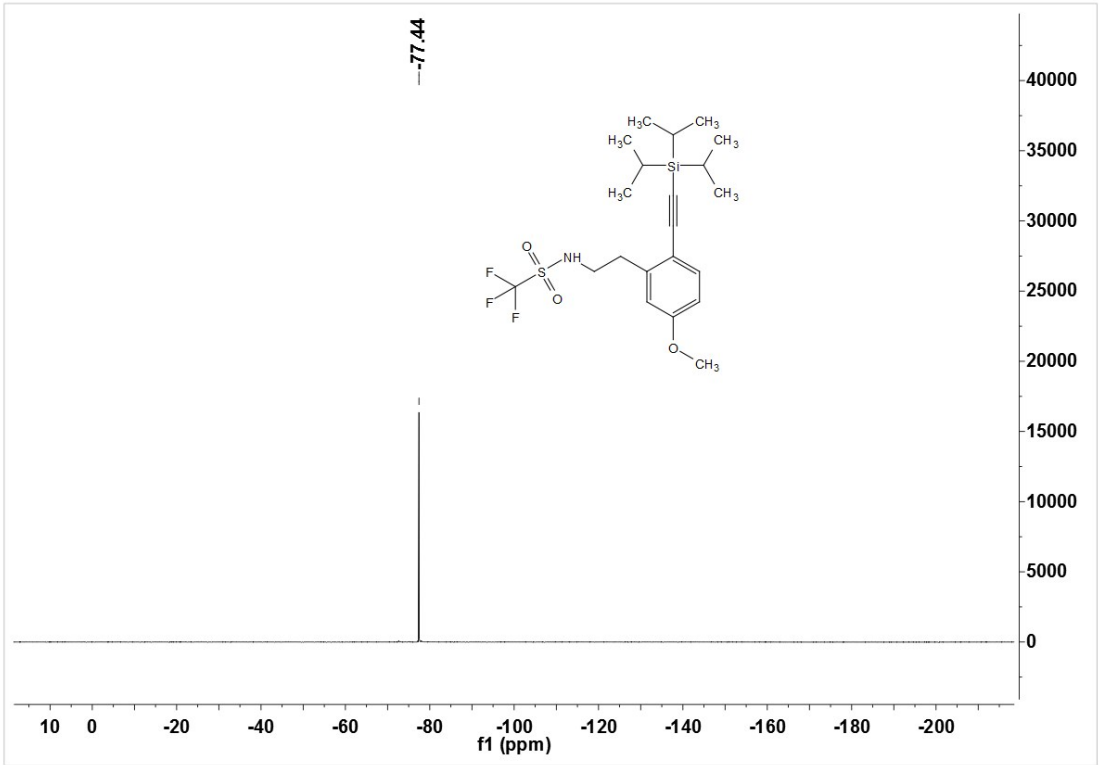




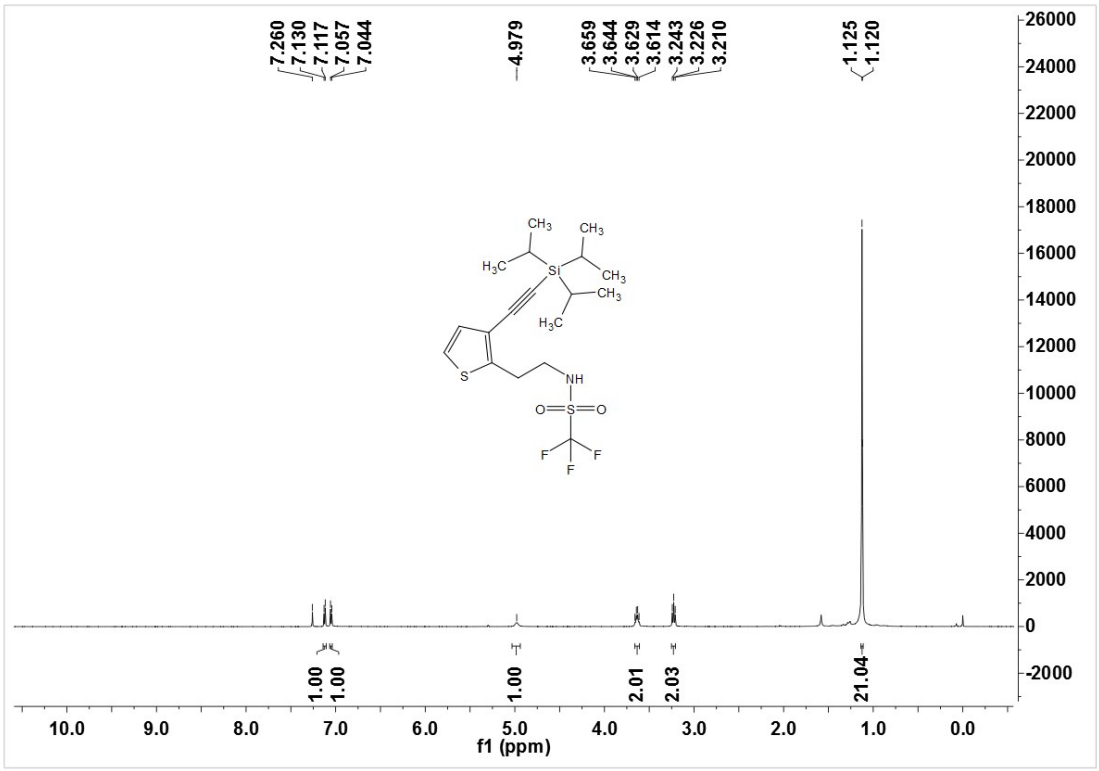
1,1,1-Trifluoro-*N*-(5-methoxyl-2-((triisopropylsilyl)ethynyl)phenethyl) methanesulfonamide (3f)

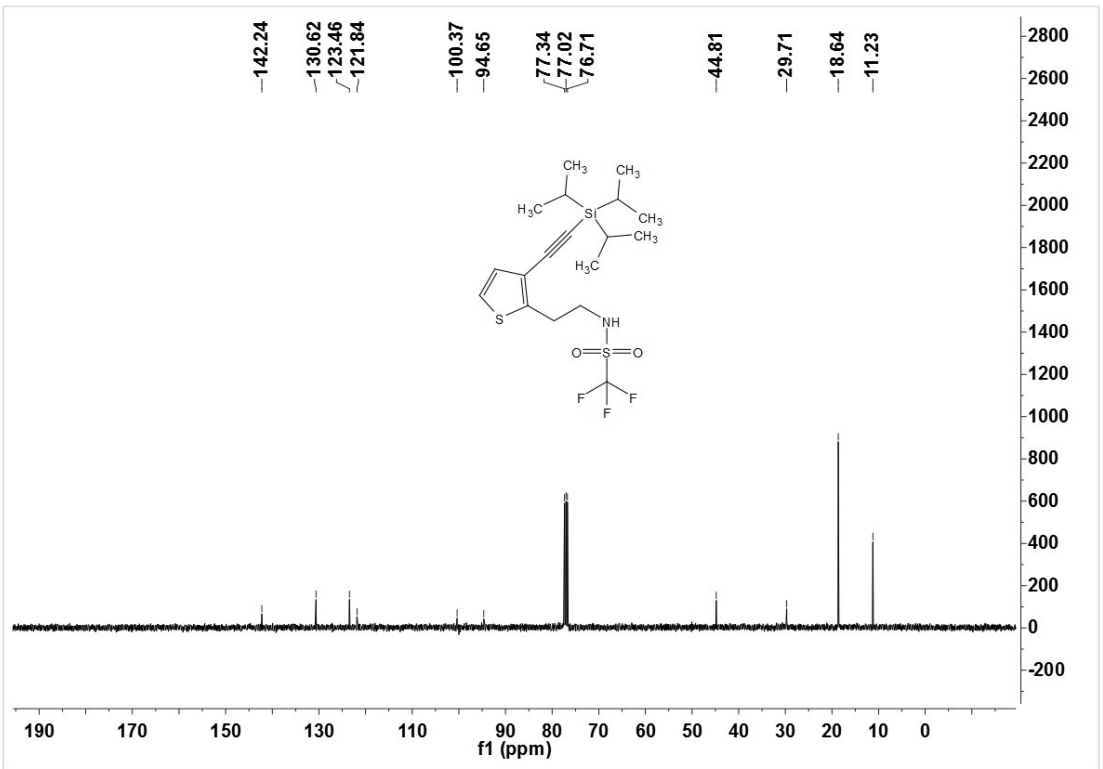


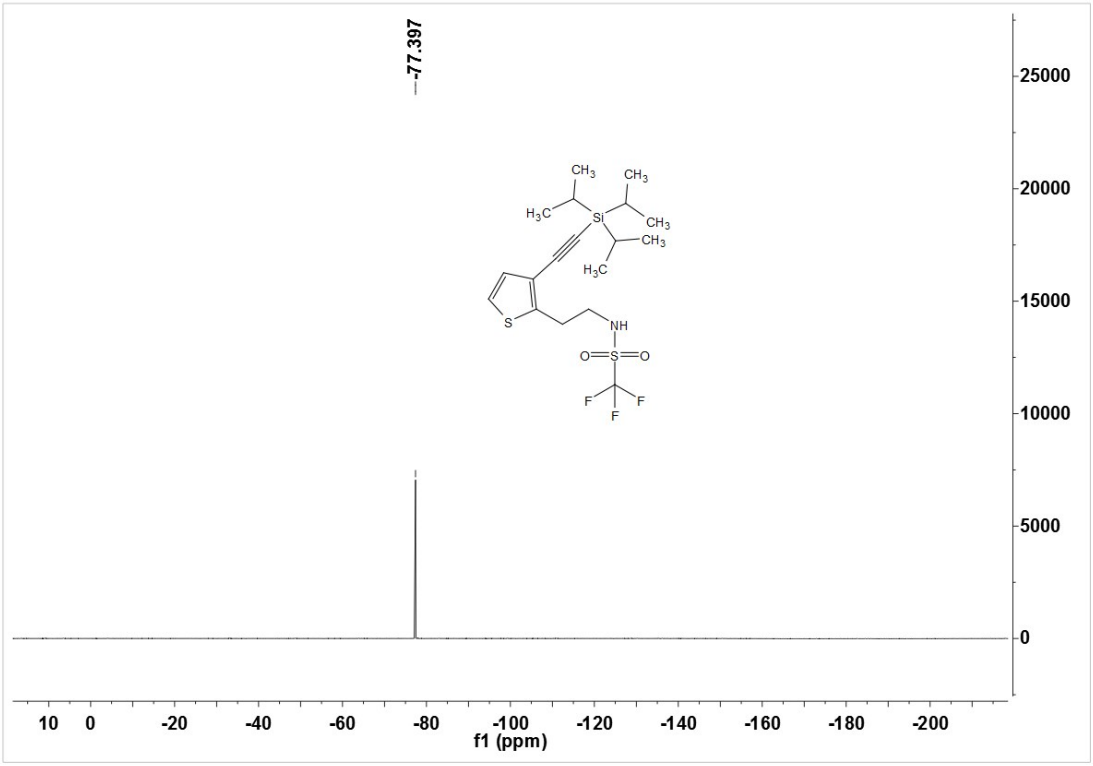

159.94
140.56
134.86
115.42
115.27
112.77
104.97
93.87
77.35
77.03
76.71
55.37
44.52
35.39
18.67
11.32
f1 (ppm)


-77.44
f1 (ppm)

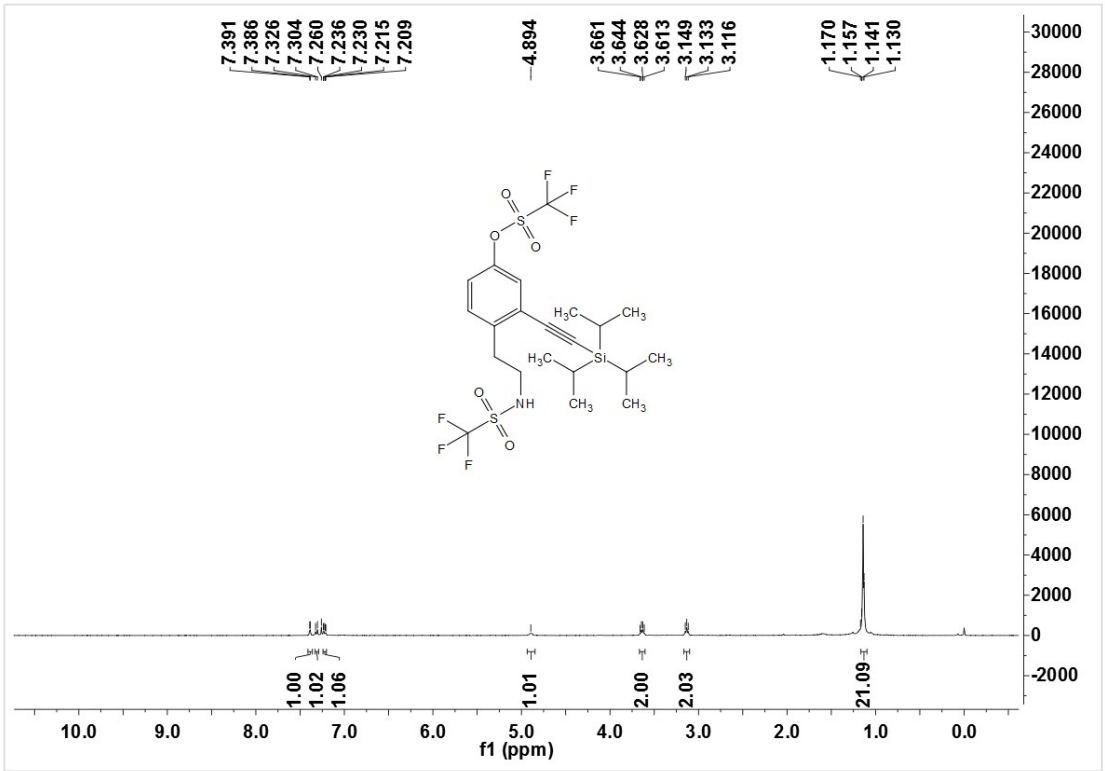
1,1,1-Trifluoro-*N*-(2-(3-((triisopropylsilyl)ethynyl)thiophen-2-yl)ethyl)methane sulfonamide (3g)

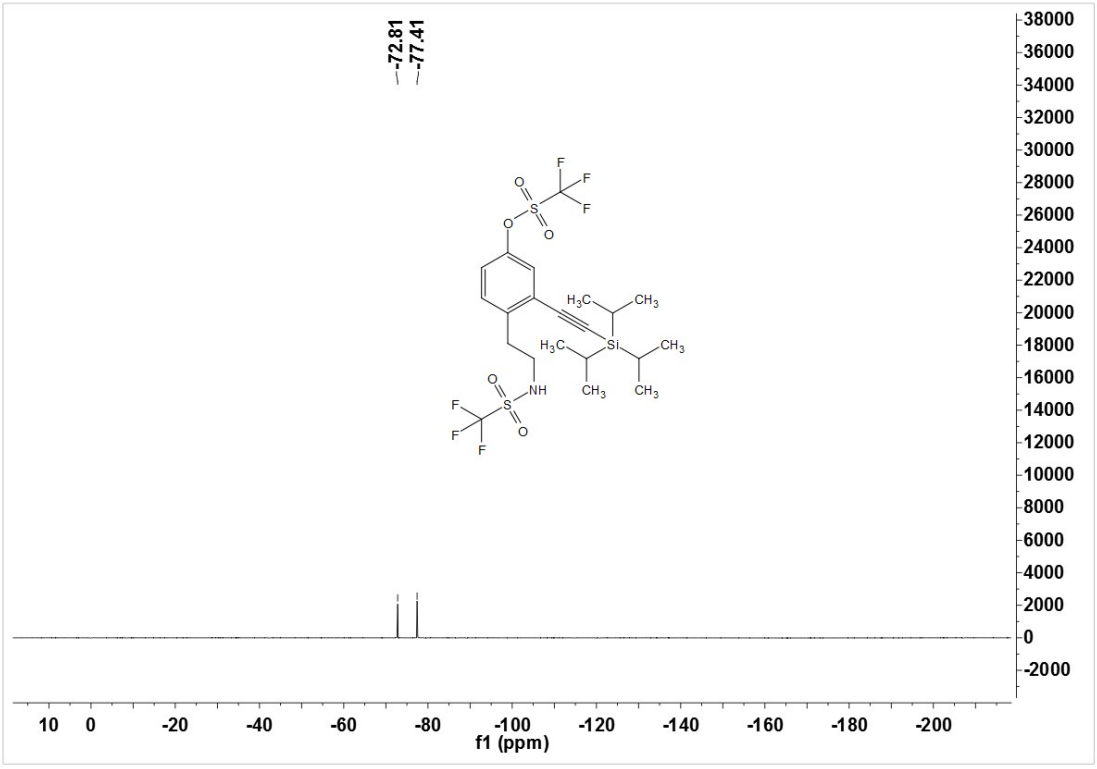




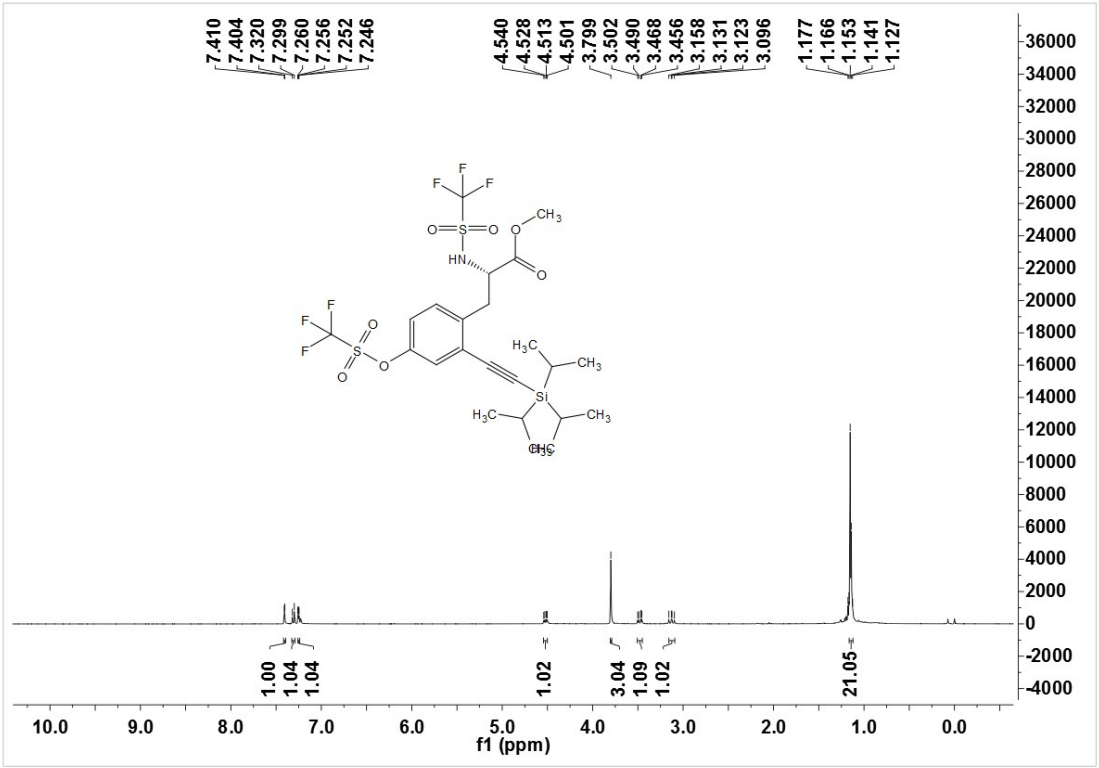


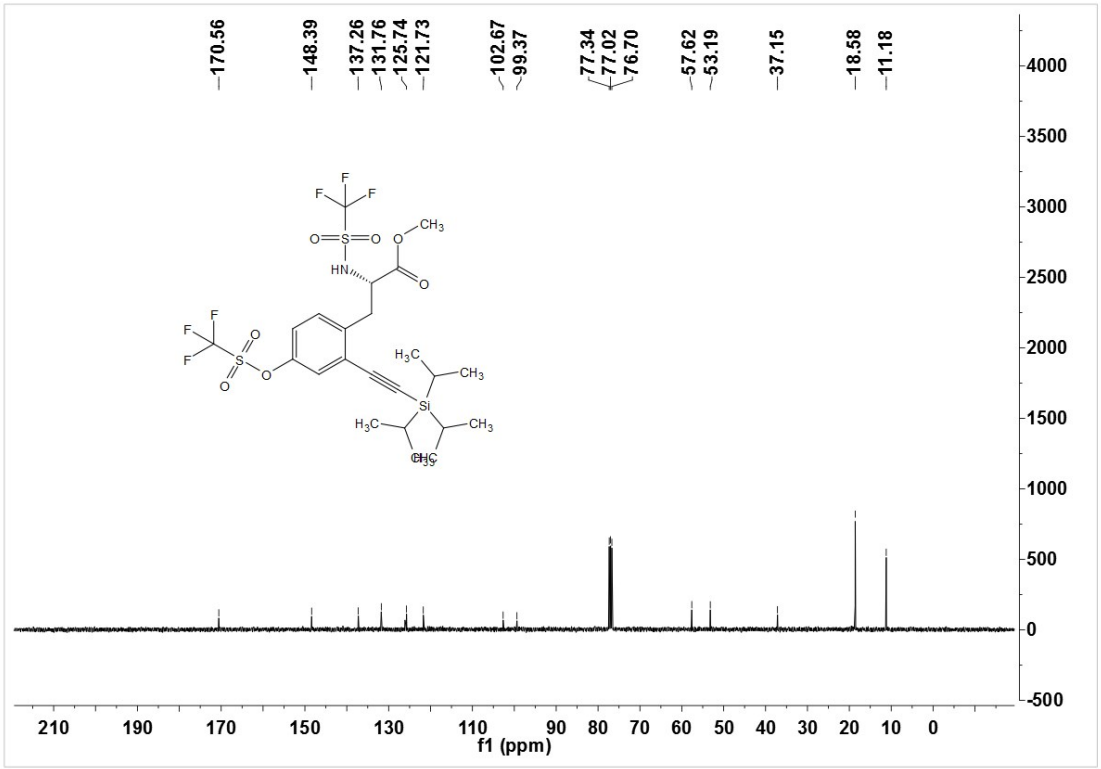
4-(2-((Trifluoromethyl)sulfonamido)ethyl)-3-((triisopropylsilyl)ethynyl)phenyl trifluoromethanesulfonate (3h)

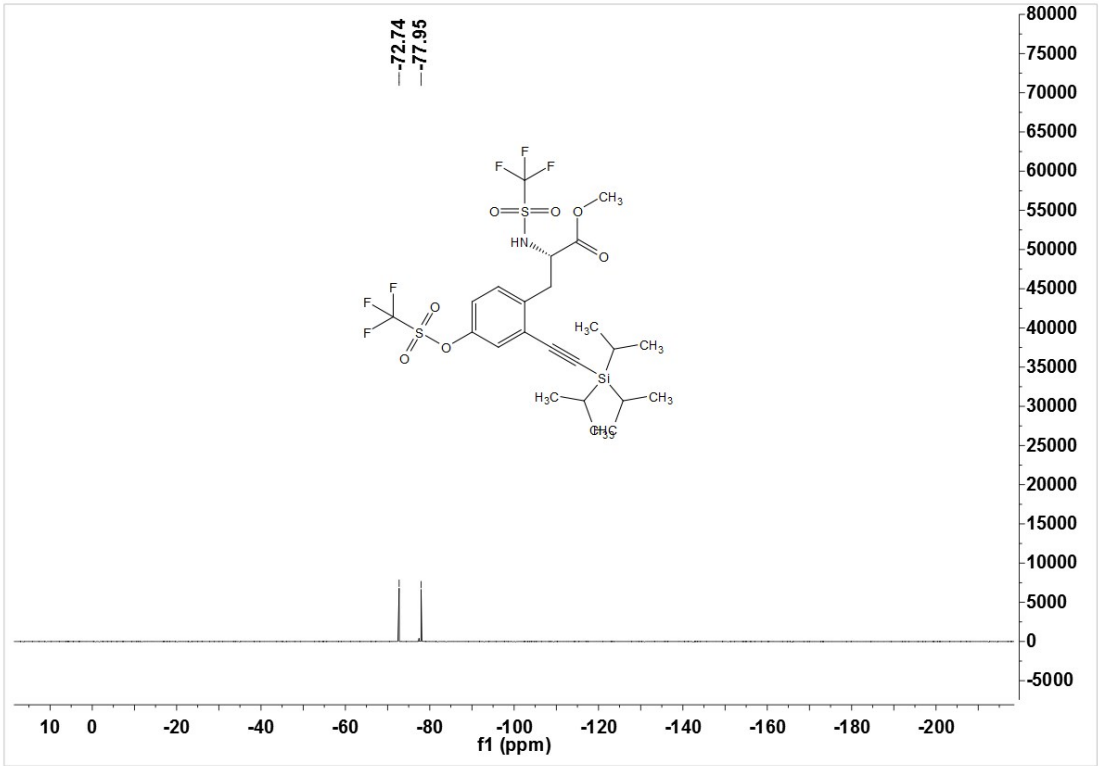




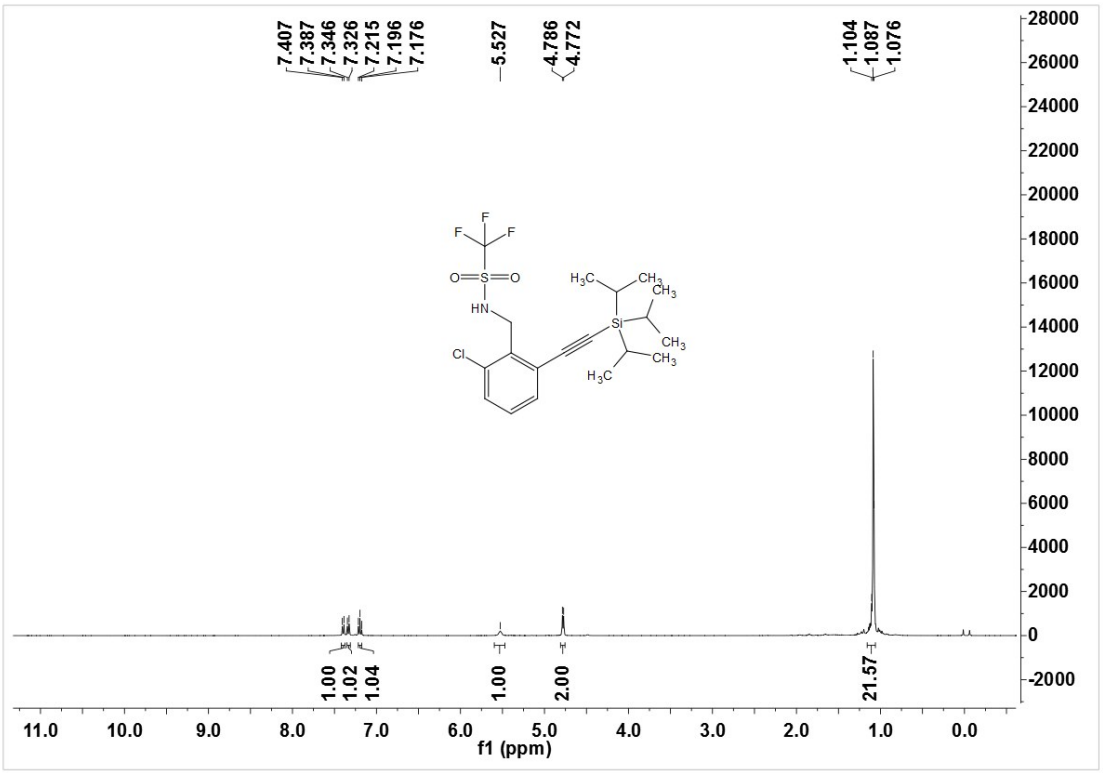
Methyl (*S*)-2-((trifluoromethyl)sulfonamido)-3-(4-(((trifluoromethyl)sulfonyl)oxy)-2-((triisopropylsilyl)ethynyl)phenyl)propanoate (3i)

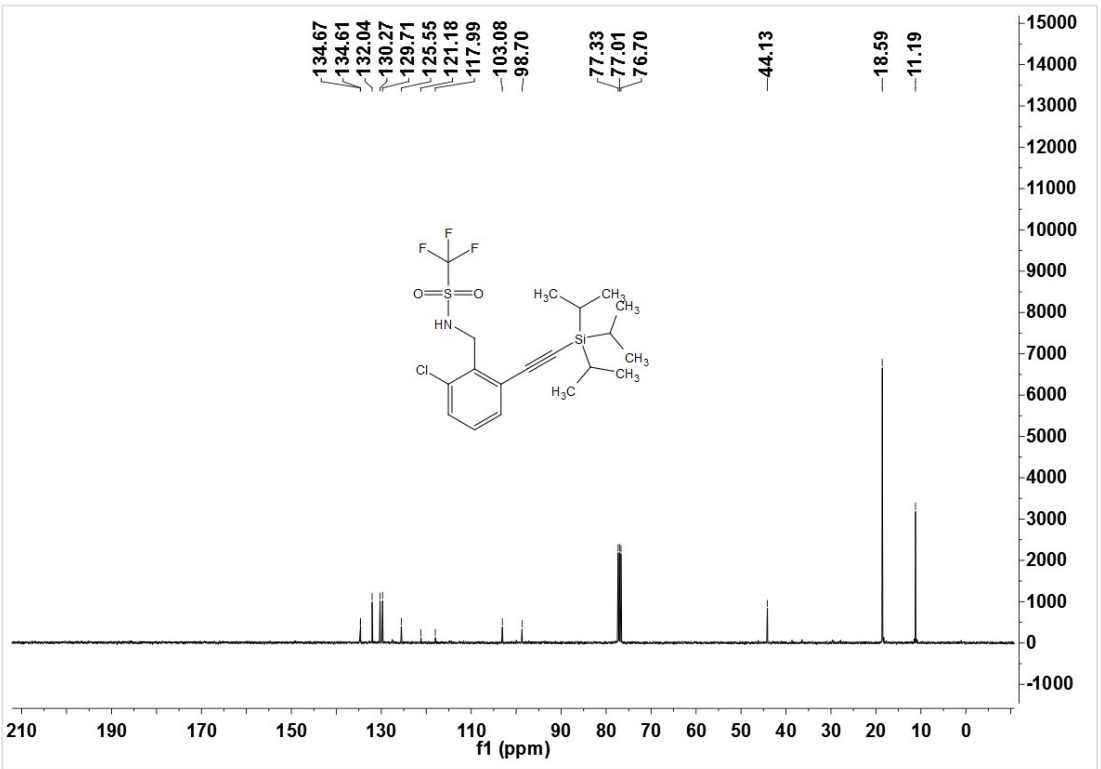


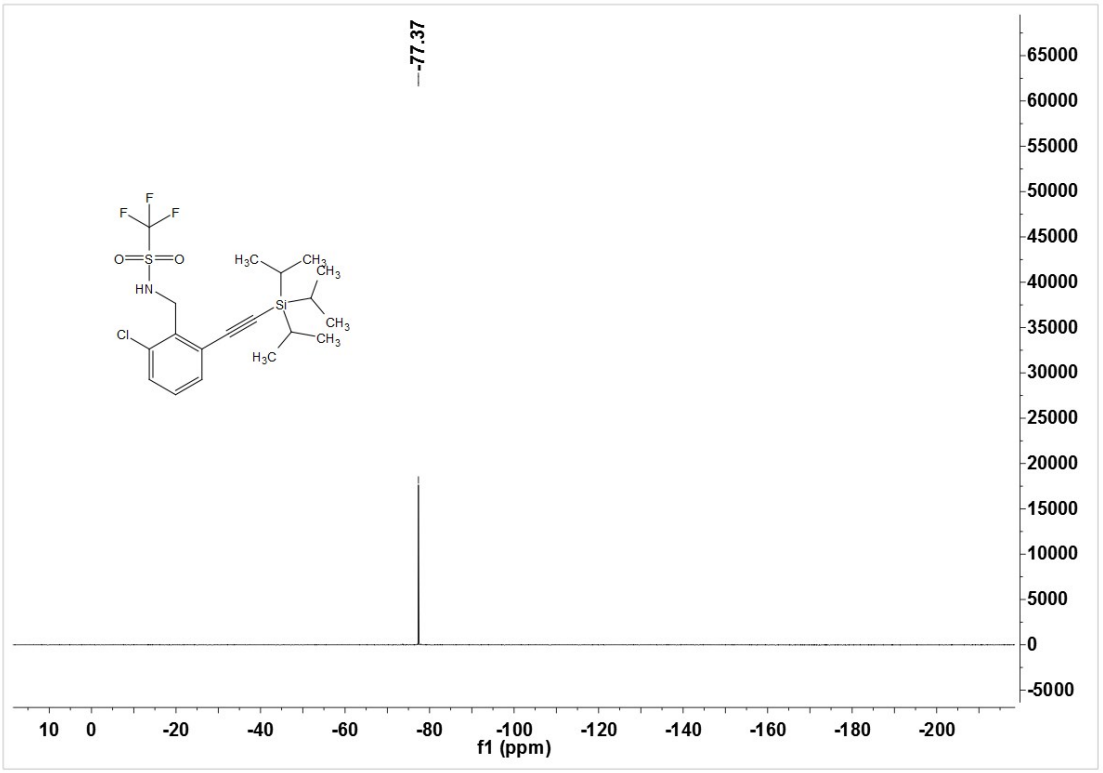

170.56
148.39
137.26
131.76
125.74
121.73
102.67
99.37
77.34
77.02
76.70
57.62
53.19
37.15
18.58
11.18
f1 (ppm)


72.74
77.95
f1 (ppm)

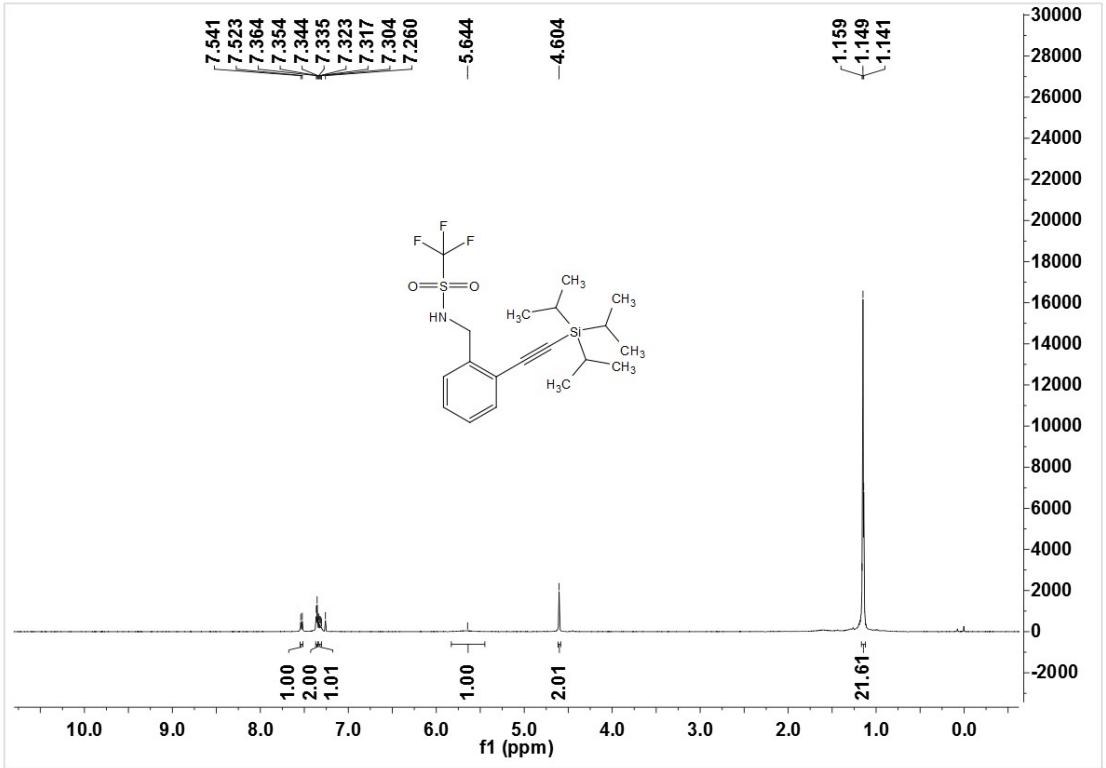
_N_-(2-Chloro-6-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethanesulfonamide (5a)

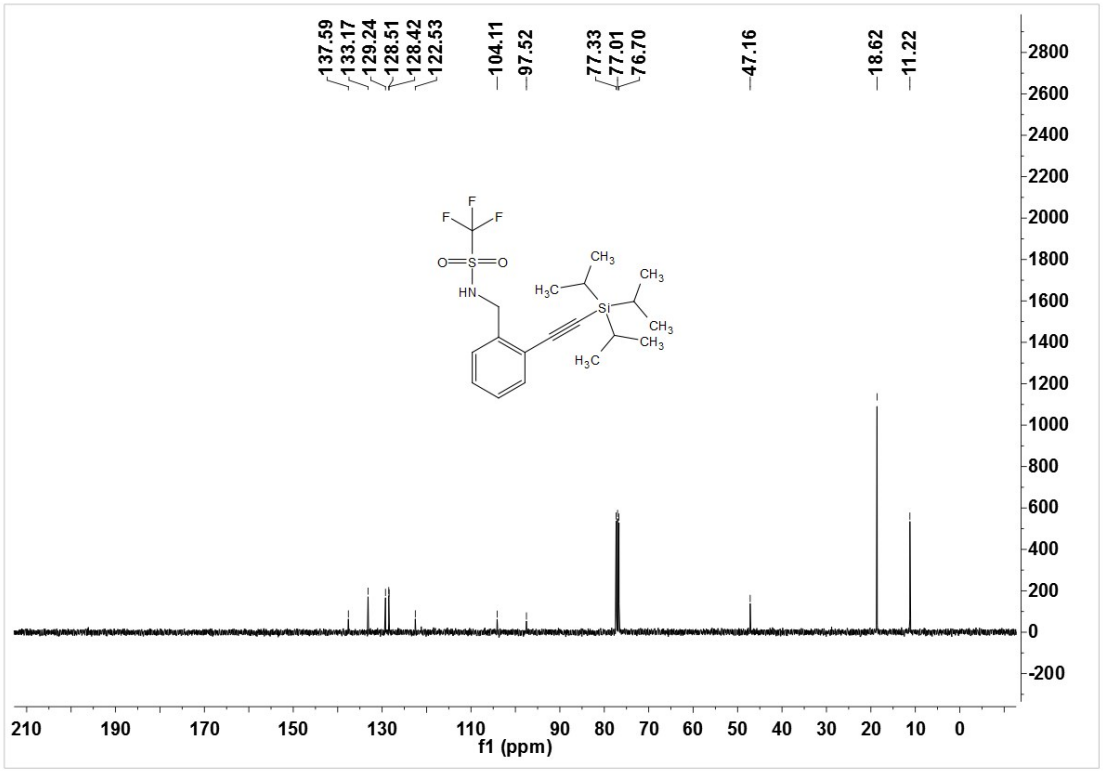


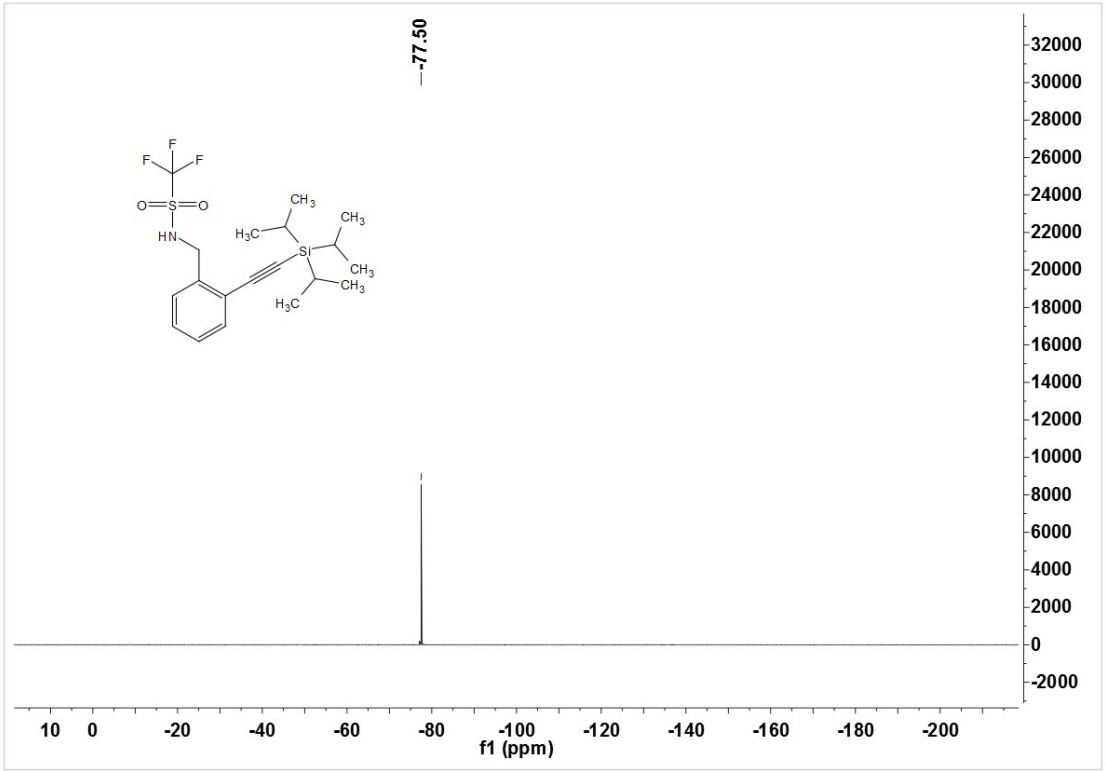




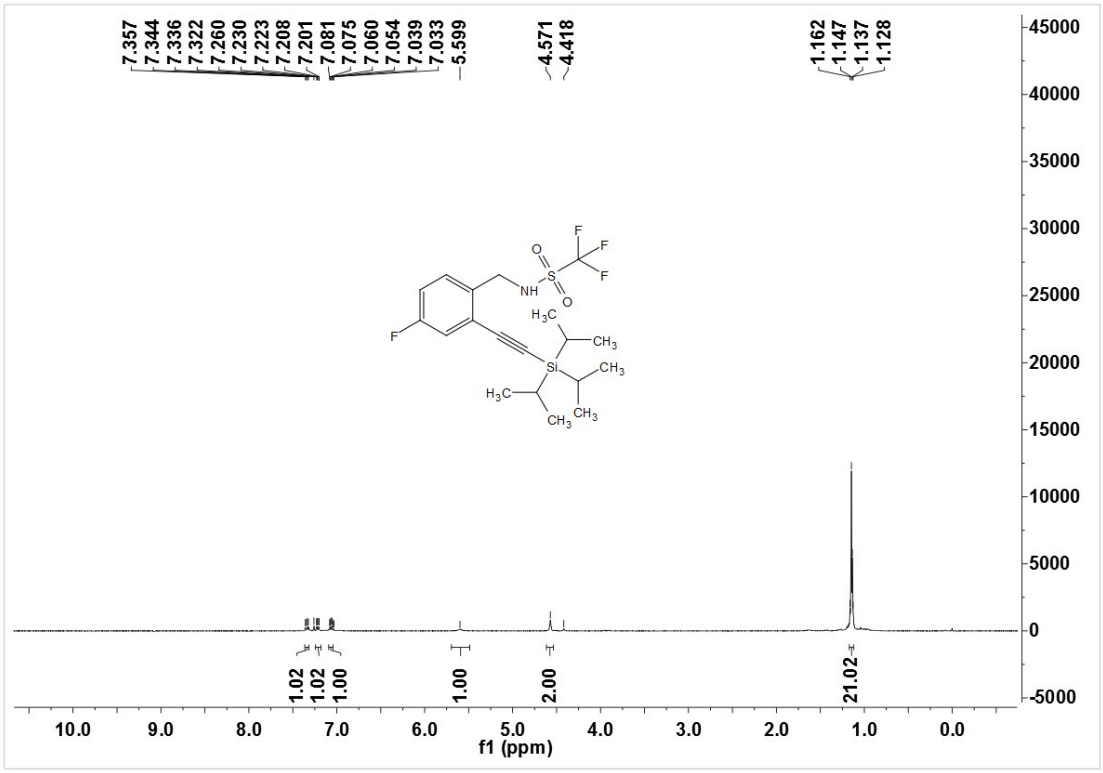
1,1,1-Trifluoro-*N*-(2-((triisopropylsilyl)ethynyl)benzyl)methanesulfonamide (5b)

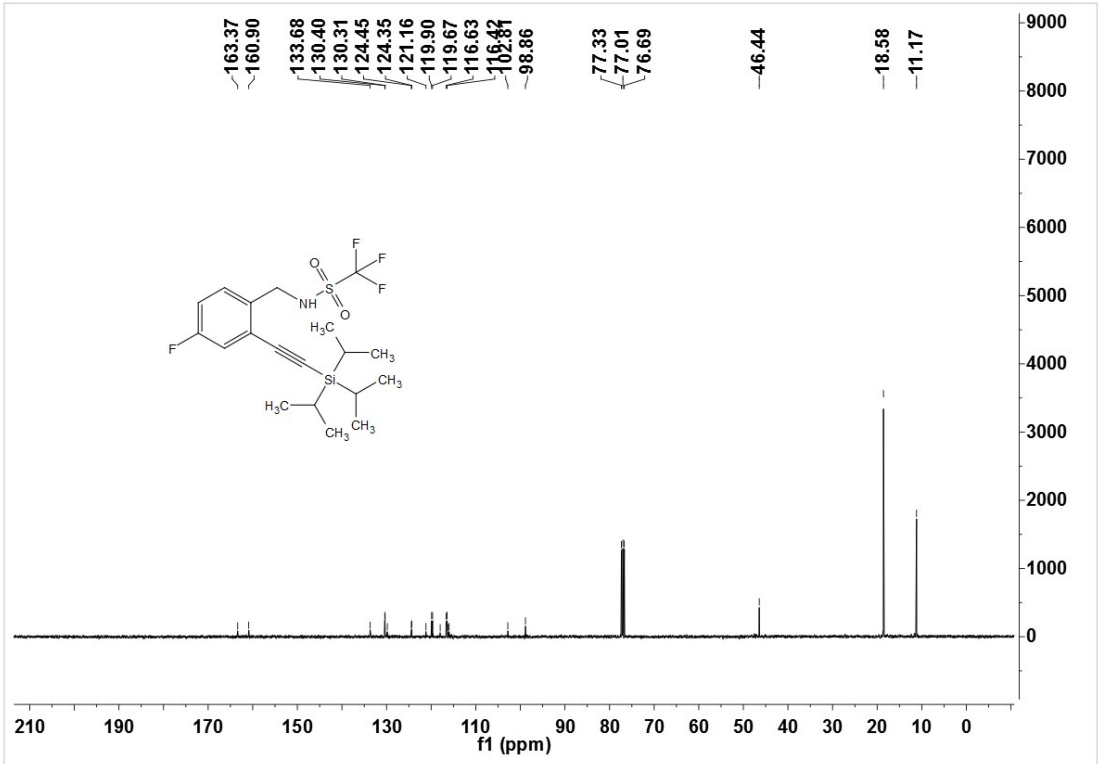


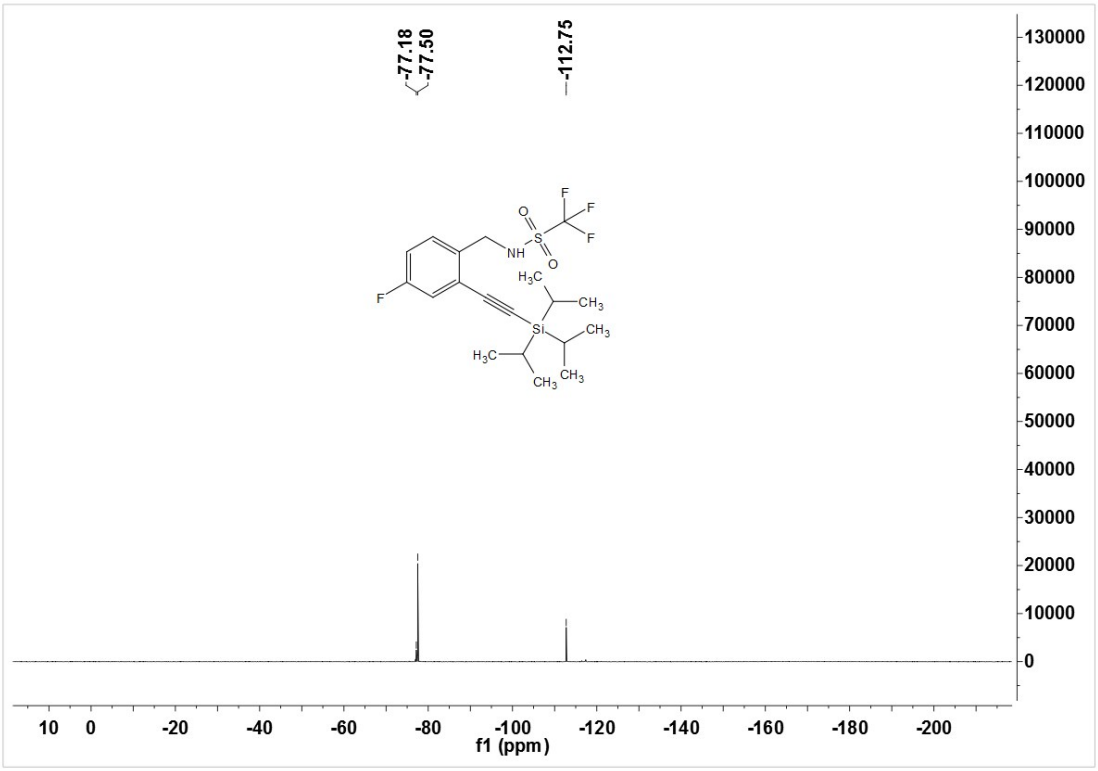

137.59
133.17
129.24
128.51
128.42
122.53
104.11
97.52
77.33
77.01
76.70
47.16
18.62
11.22
f1 (ppm)


-77.50
f1 (ppm)

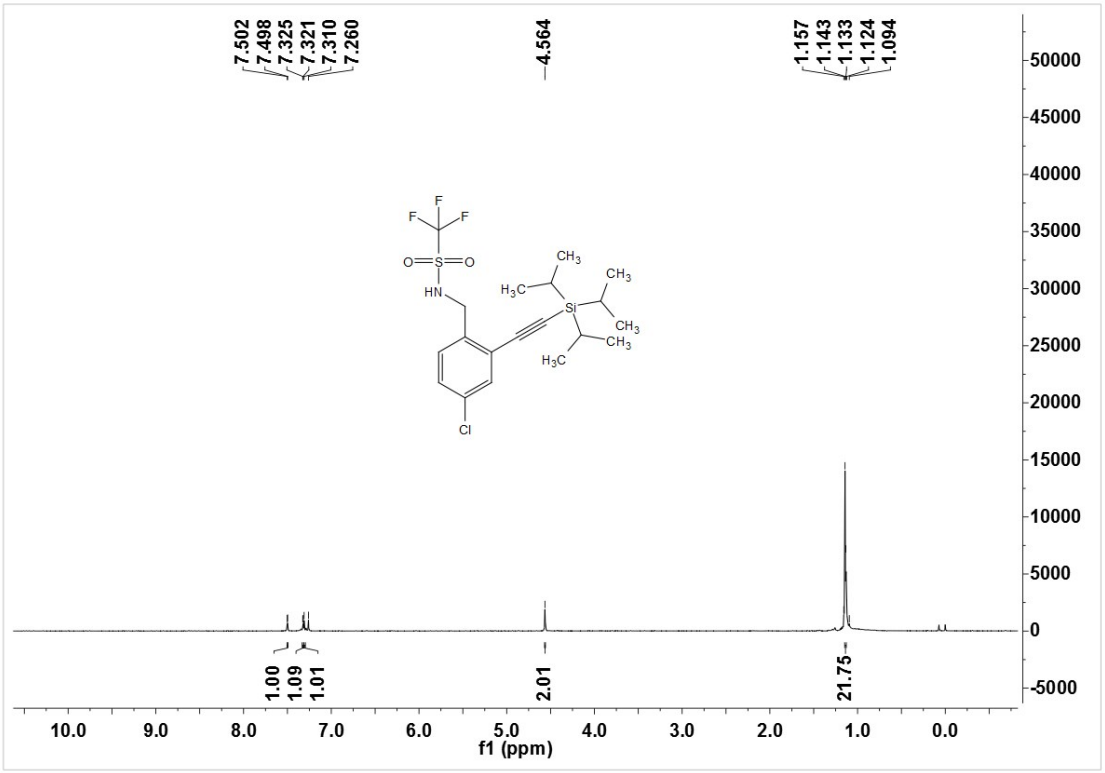
1,1,1-Trifluoro-*N*-(4-fluoro-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5c)

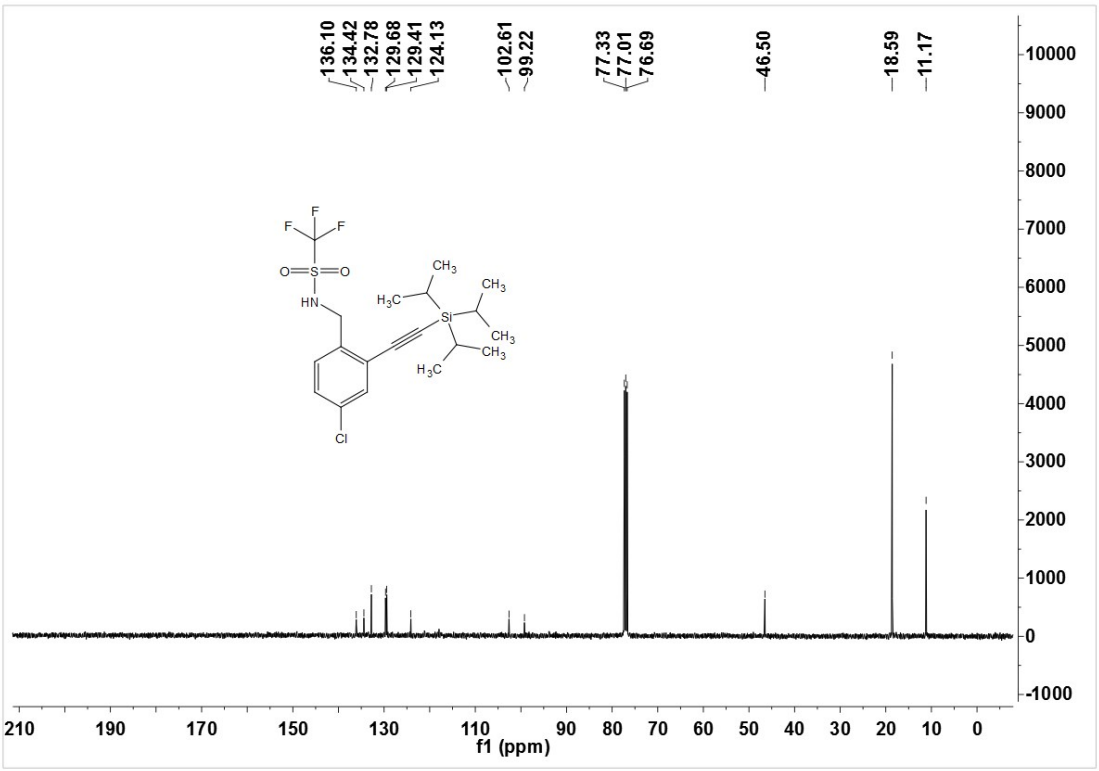


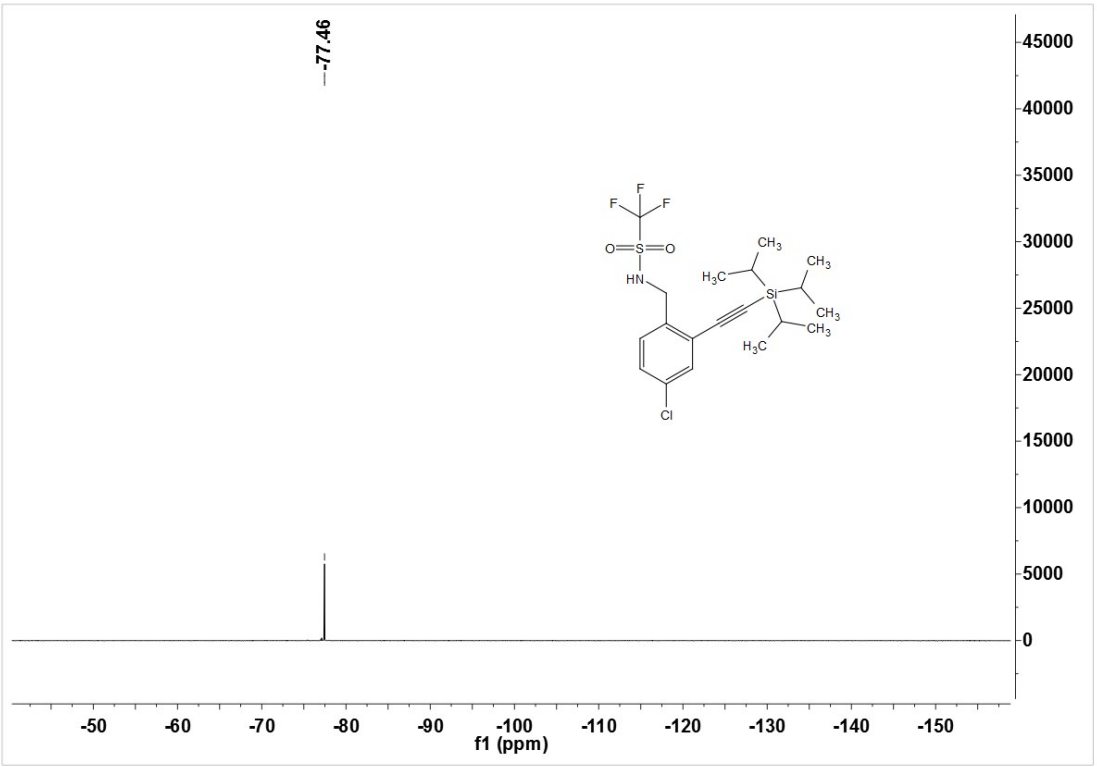




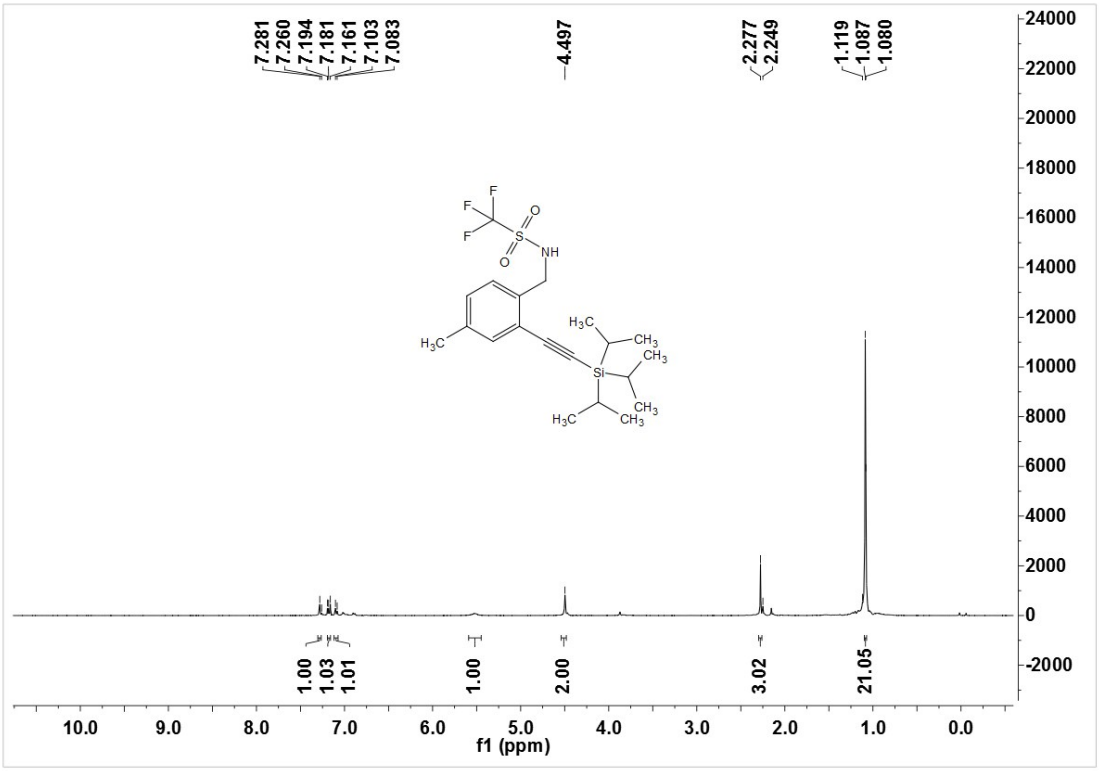
***N*-(4-Chloro-2-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5d)**

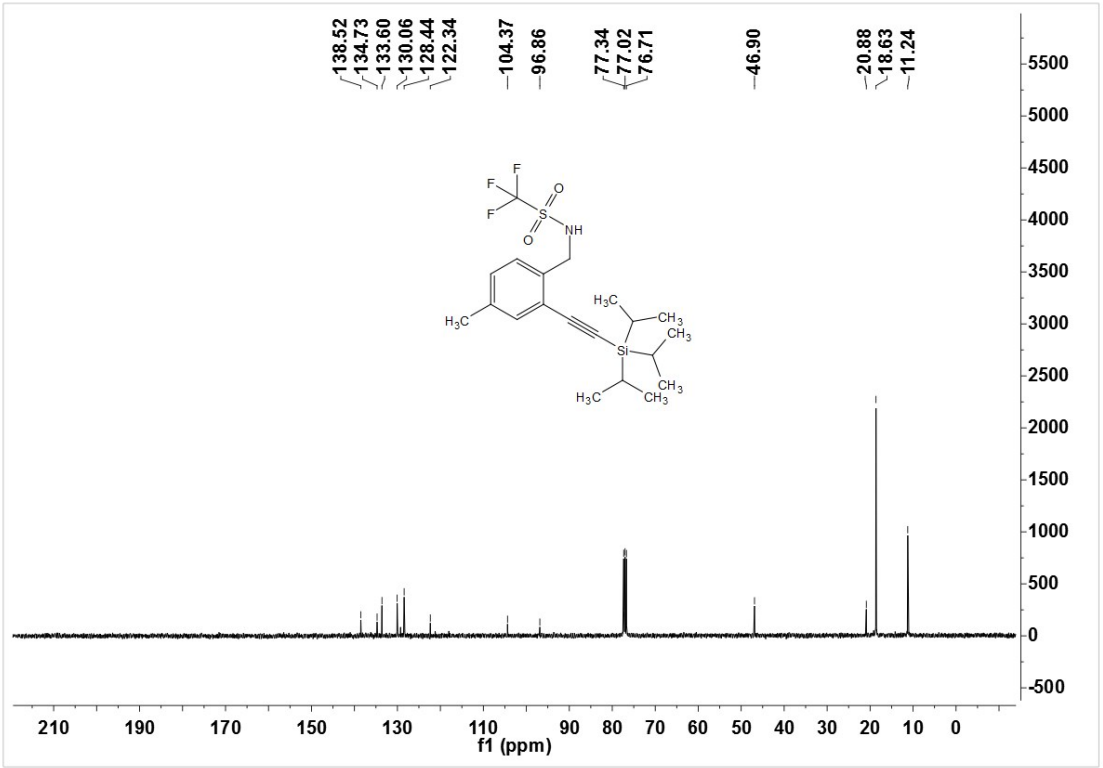


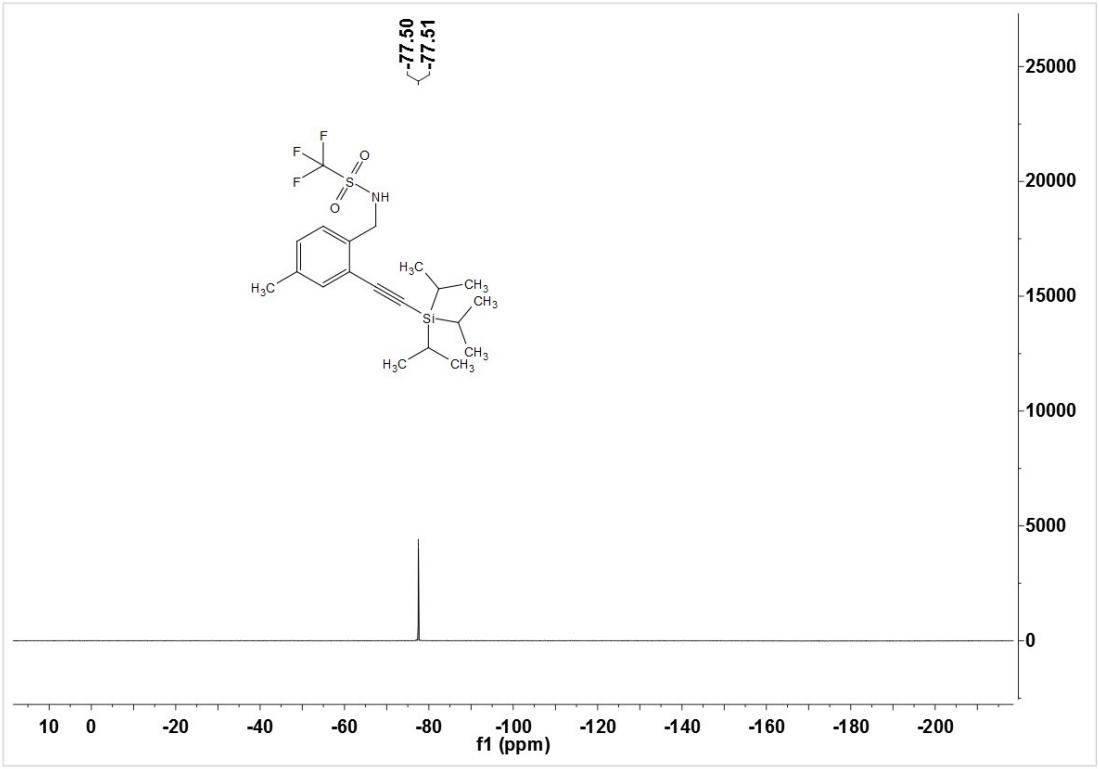

136.10
134.42
132.78
129.68
129.41
124.13
102.61
99.22
77.33
77.01
76.69
46.50
18.59
11.17
f1 (ppm)


-77.46
f1 (ppm)

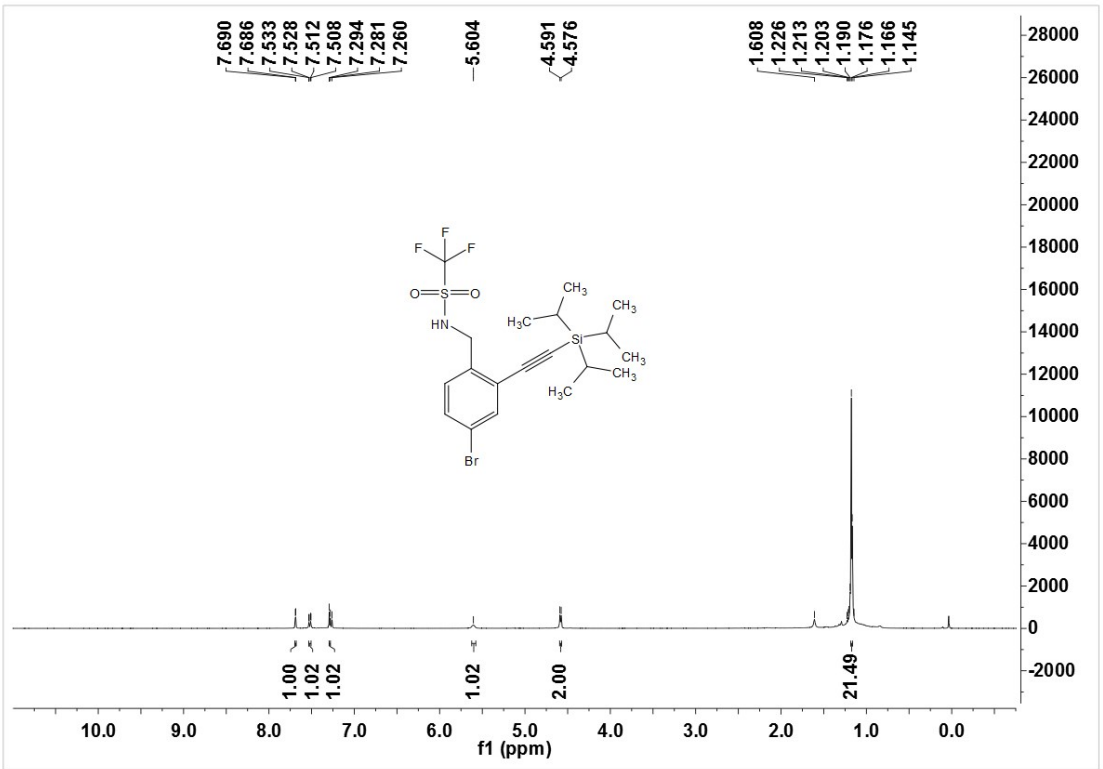
1,1,1-Trifluoro-*N*-(4-methyl-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5e)

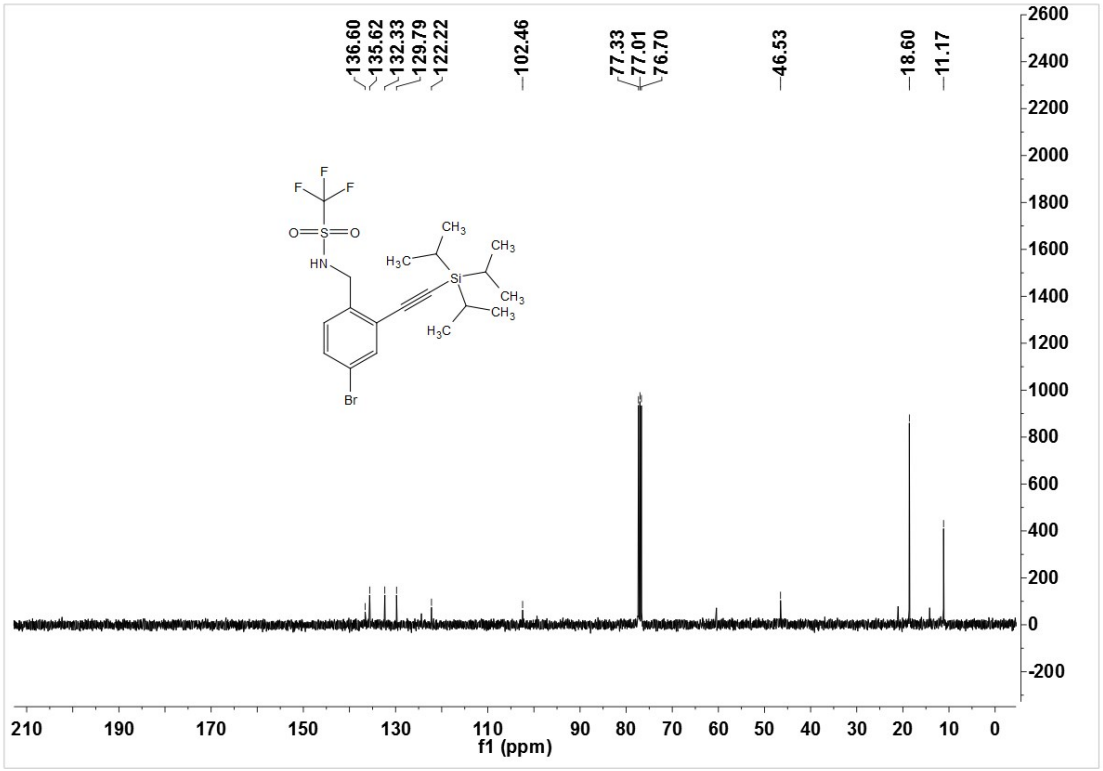


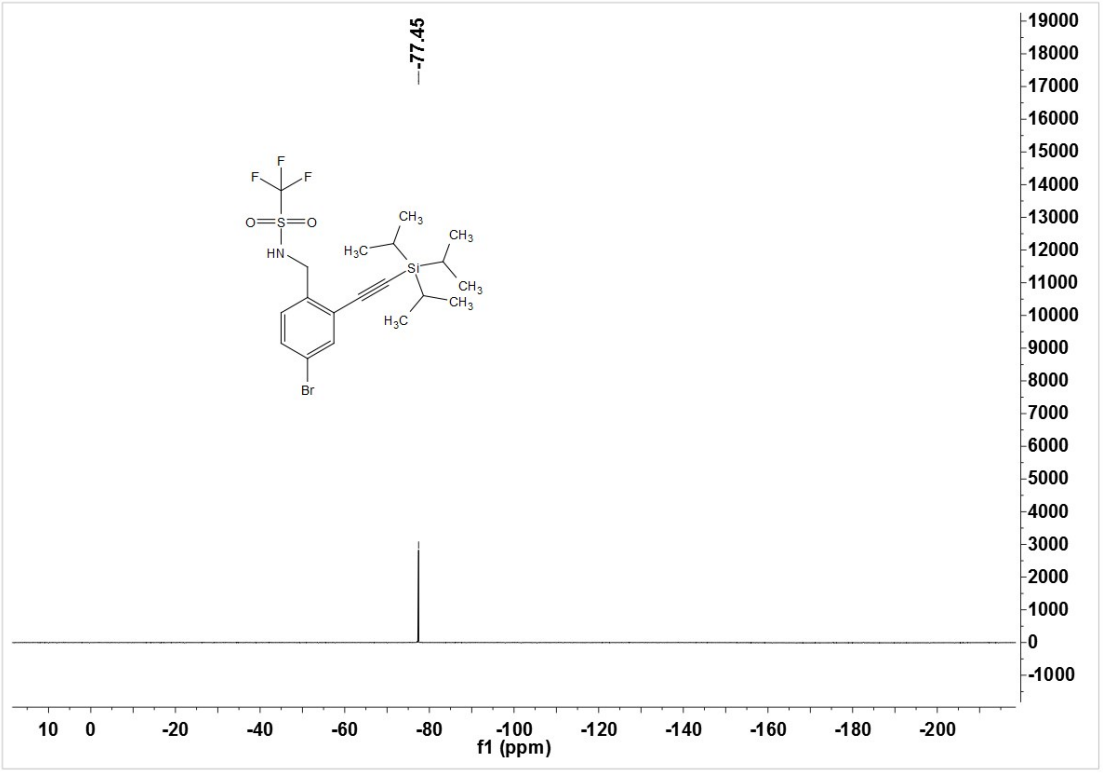




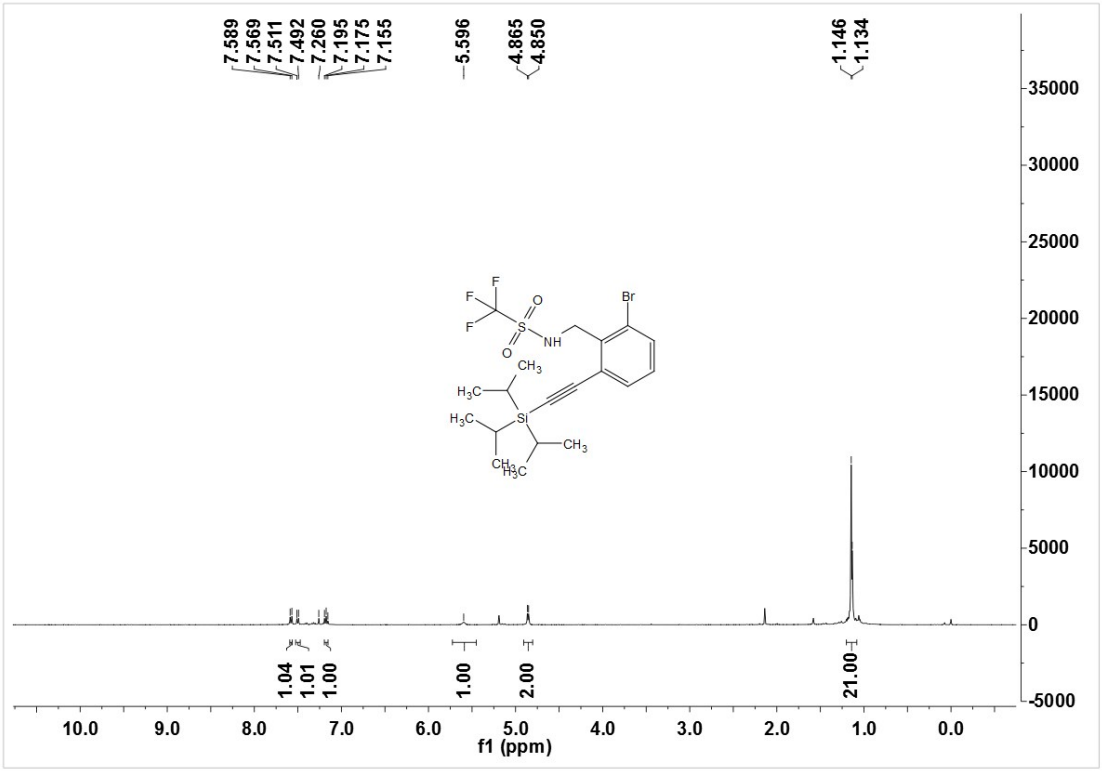
_N_-(4-Bromo-2-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5f)

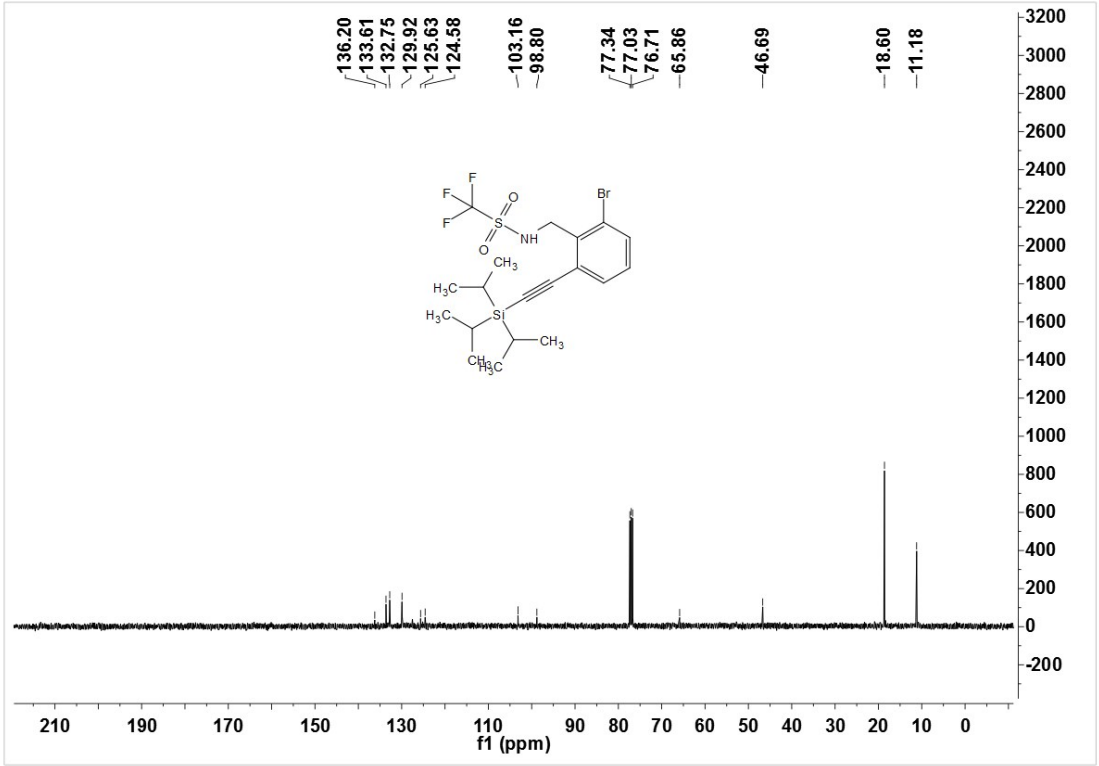


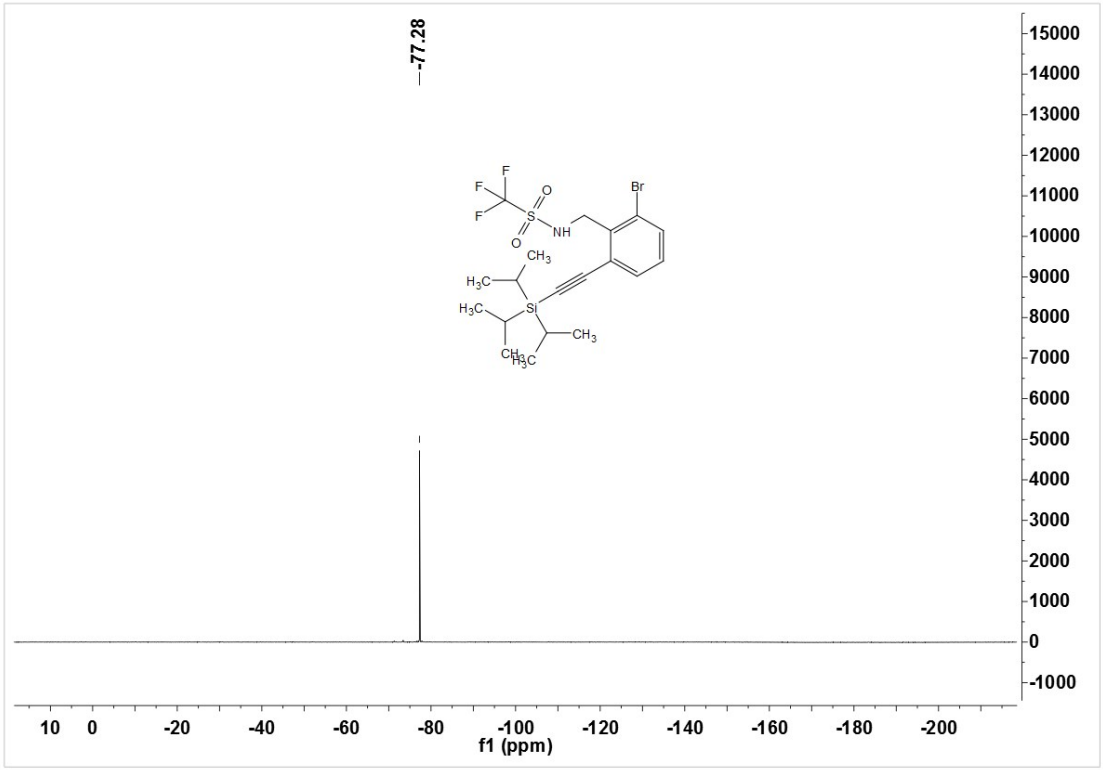

136.60
135.62
132.33
129.79
122.22
102.46
77.33
77.01
76.70
46.53
18.60
11.17
f1 (ppm)


-77.45
f1 (ppm)

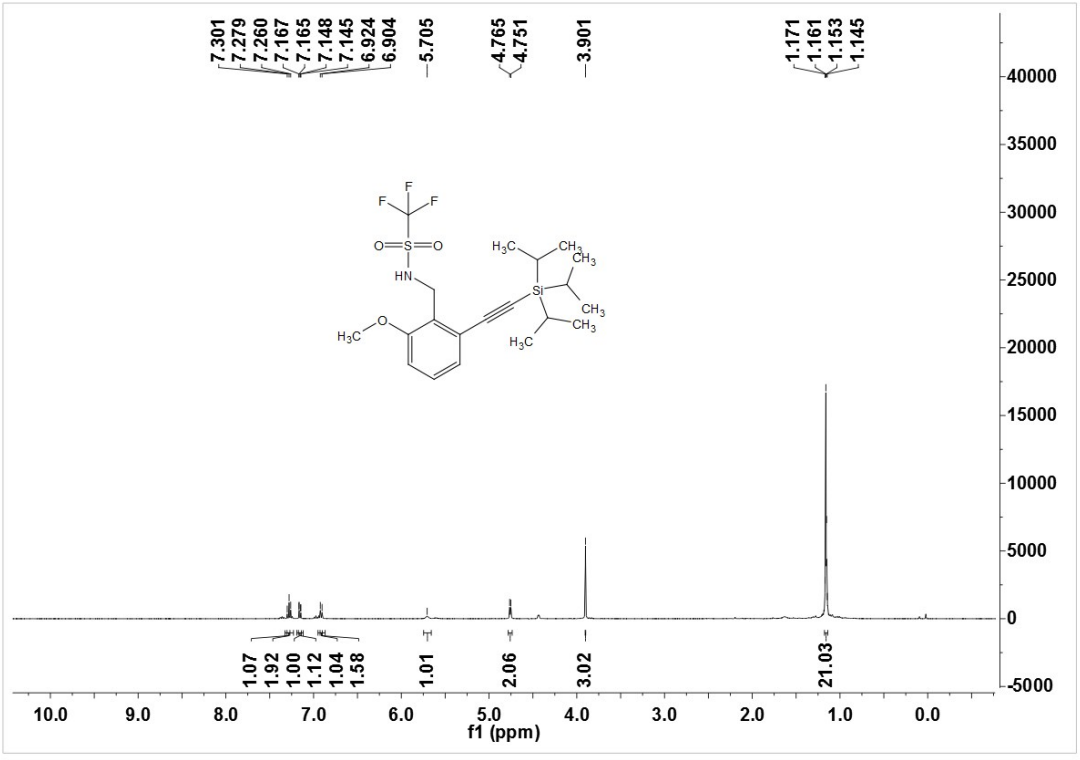
_N_-(2-Bromo-6-((triisopropylsilyl)ethynyl)benzyl)-1,1,1-trifluoromethane sulfonamide (5g)

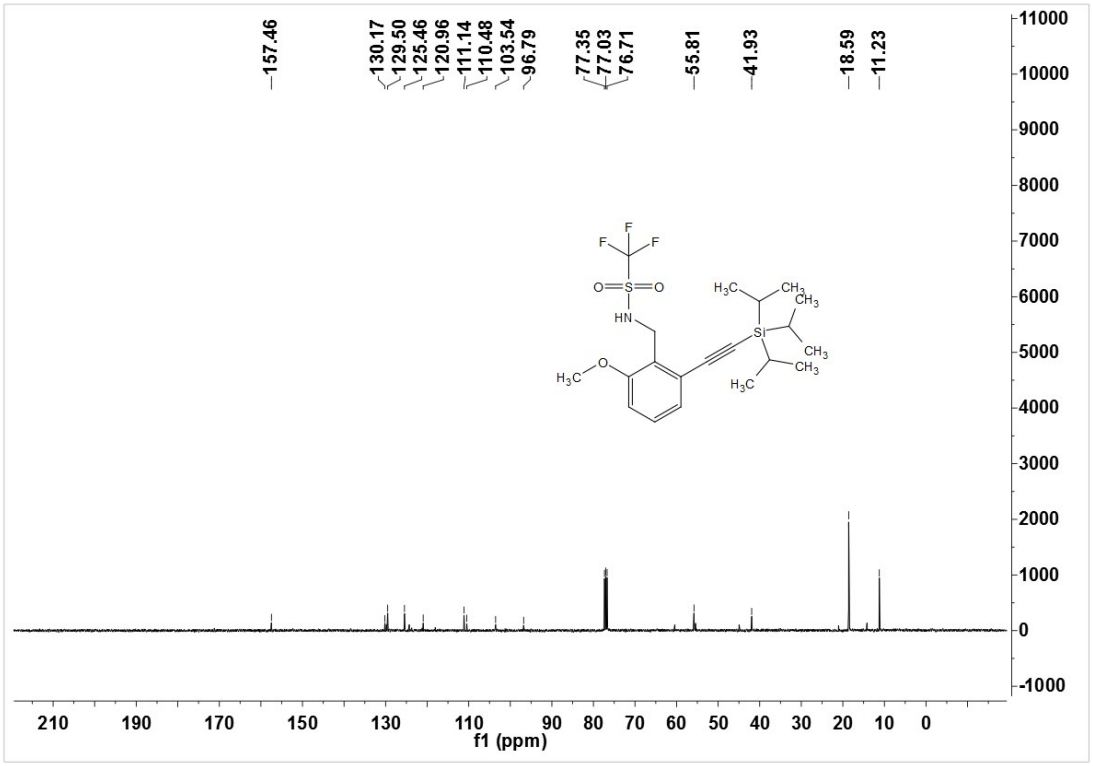


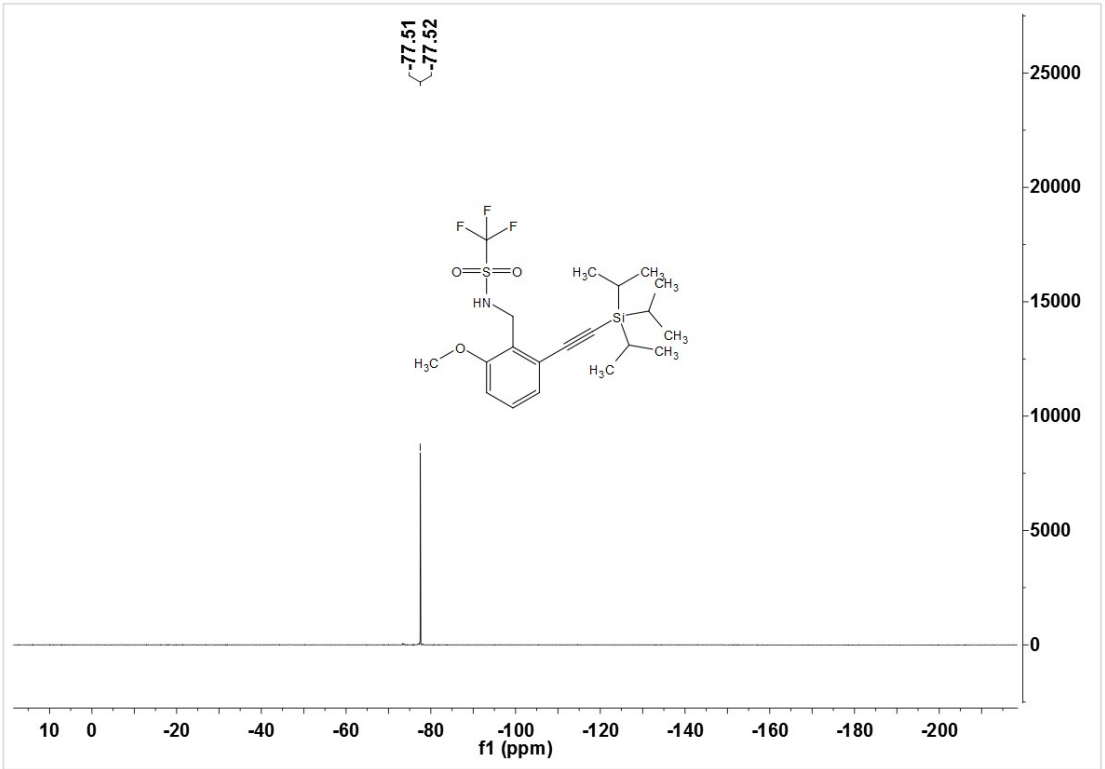




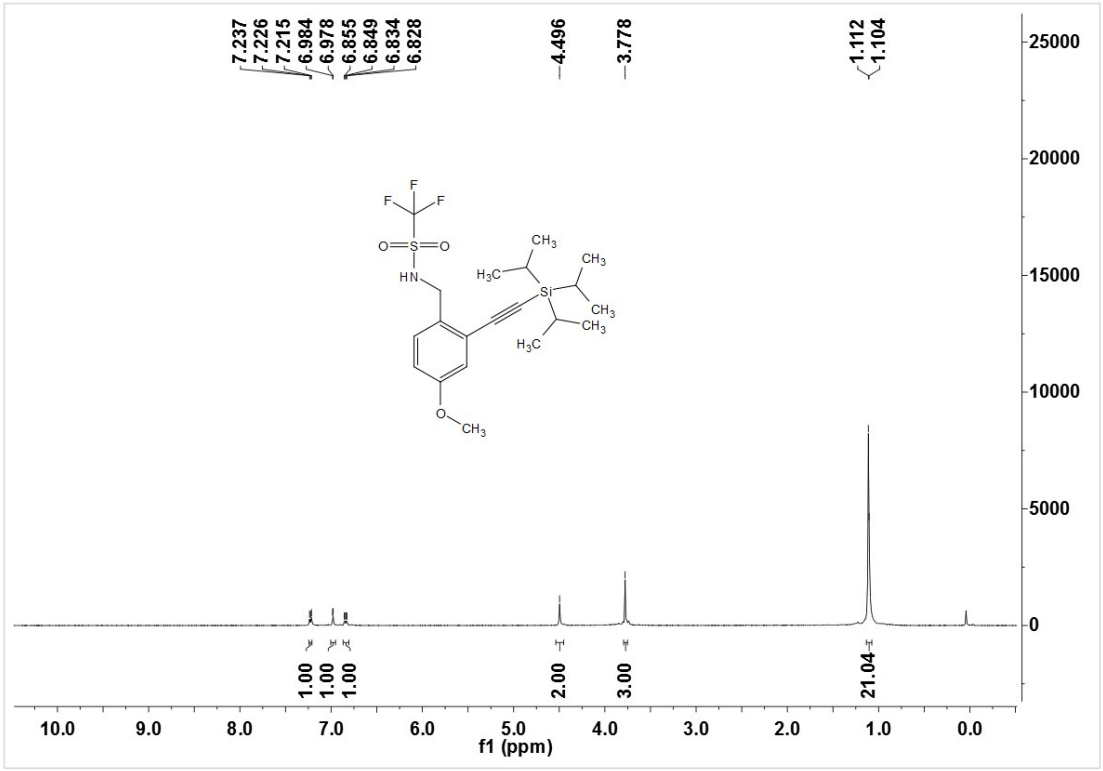
1,1,1-Trifluoro-*N*-(2-methoxy-6-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5h)

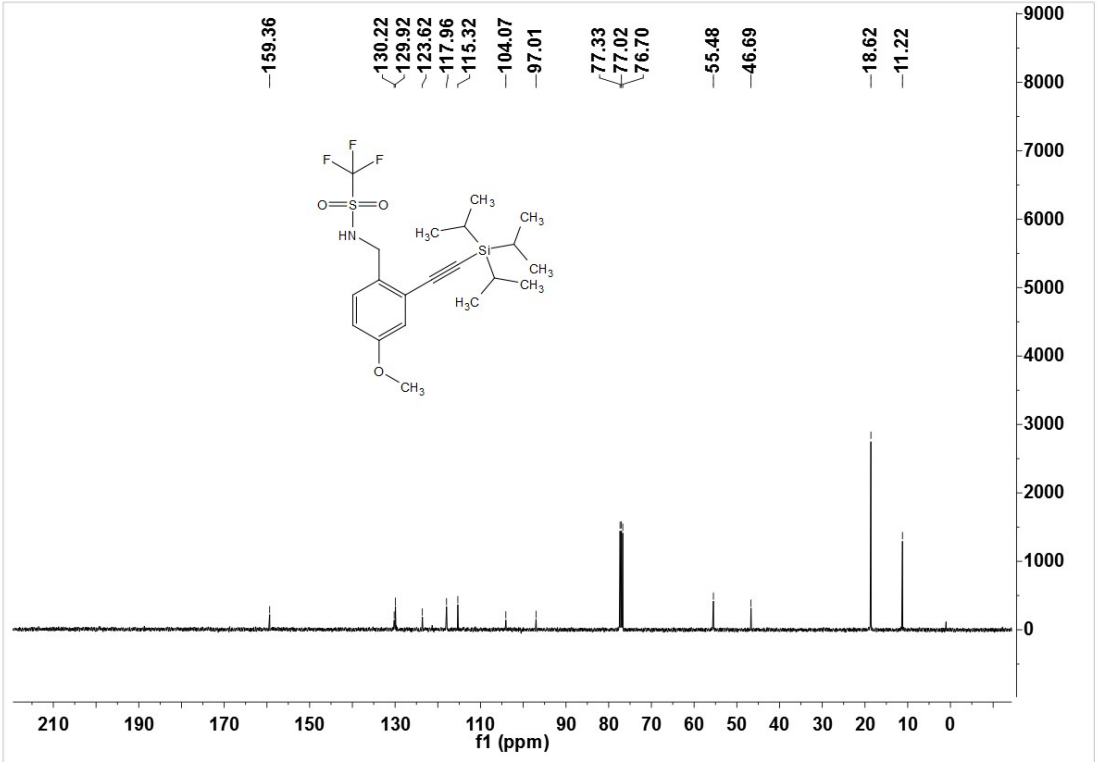


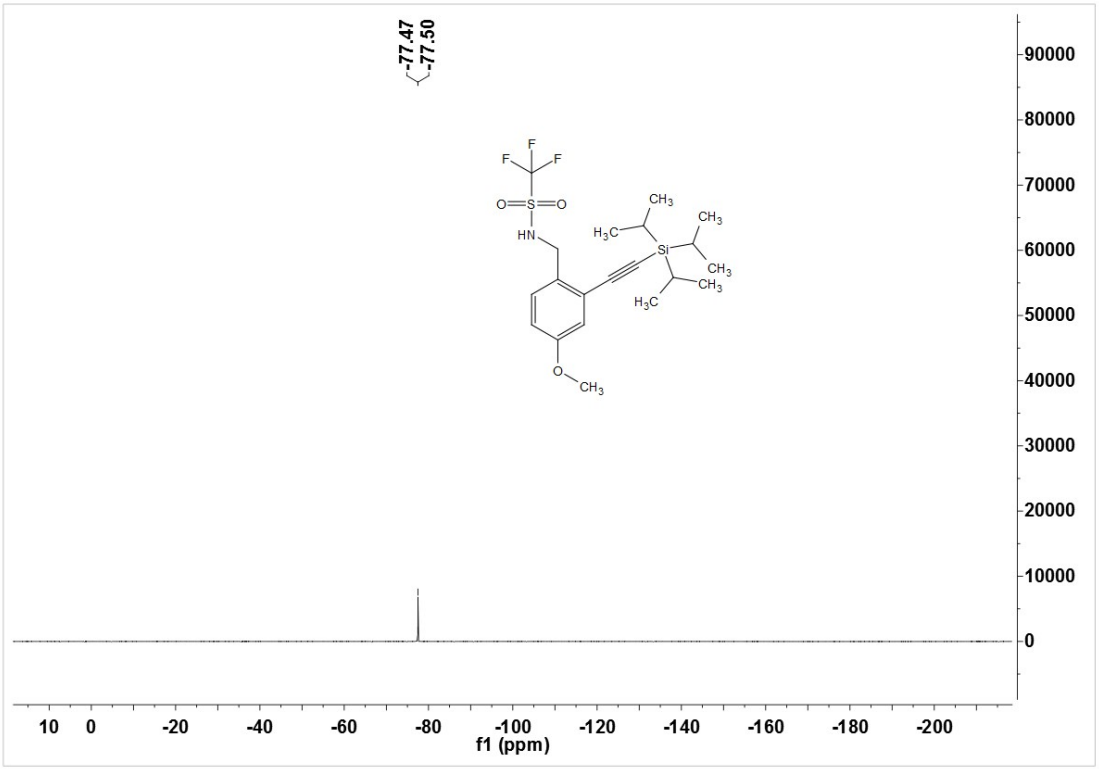

157.46
130.17
129.50
125.46
120.96
111.14
110.48
103.54
96.79
77.35
77.03
76.71
55.81
41.93
18.59
11.23
f1 (ppm)


77.51
77.52
f1 (ppm)

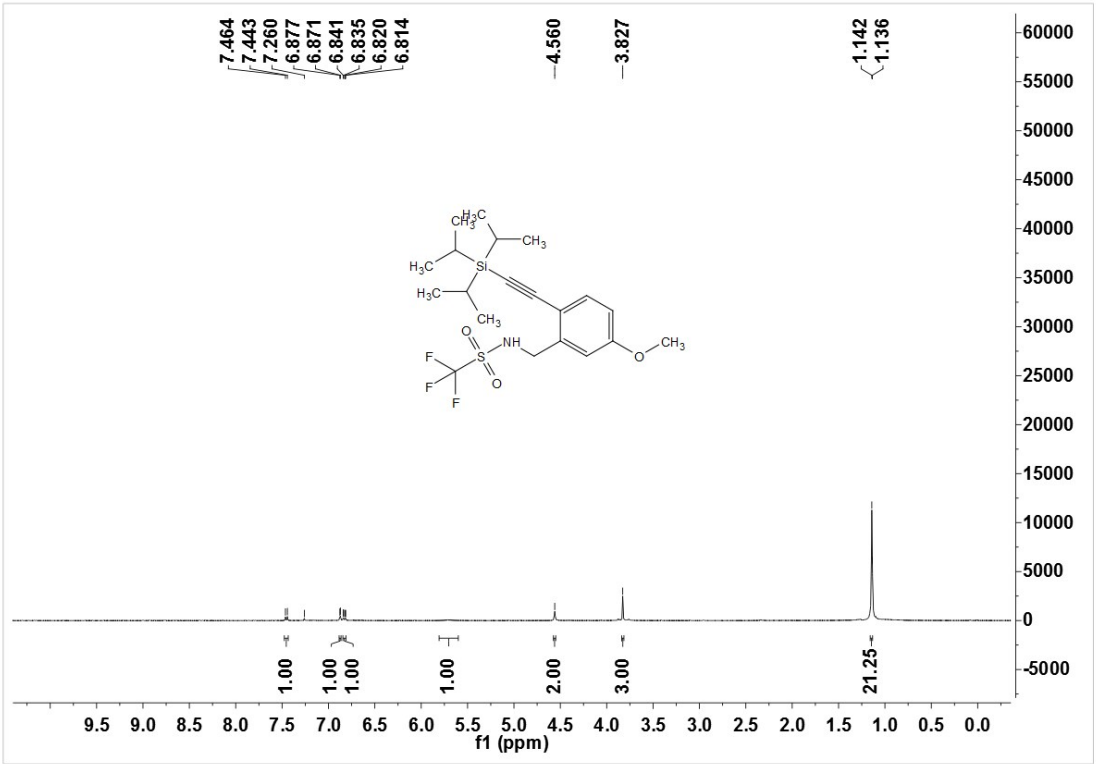
1,1,1-Trifluoro-*N*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5i)

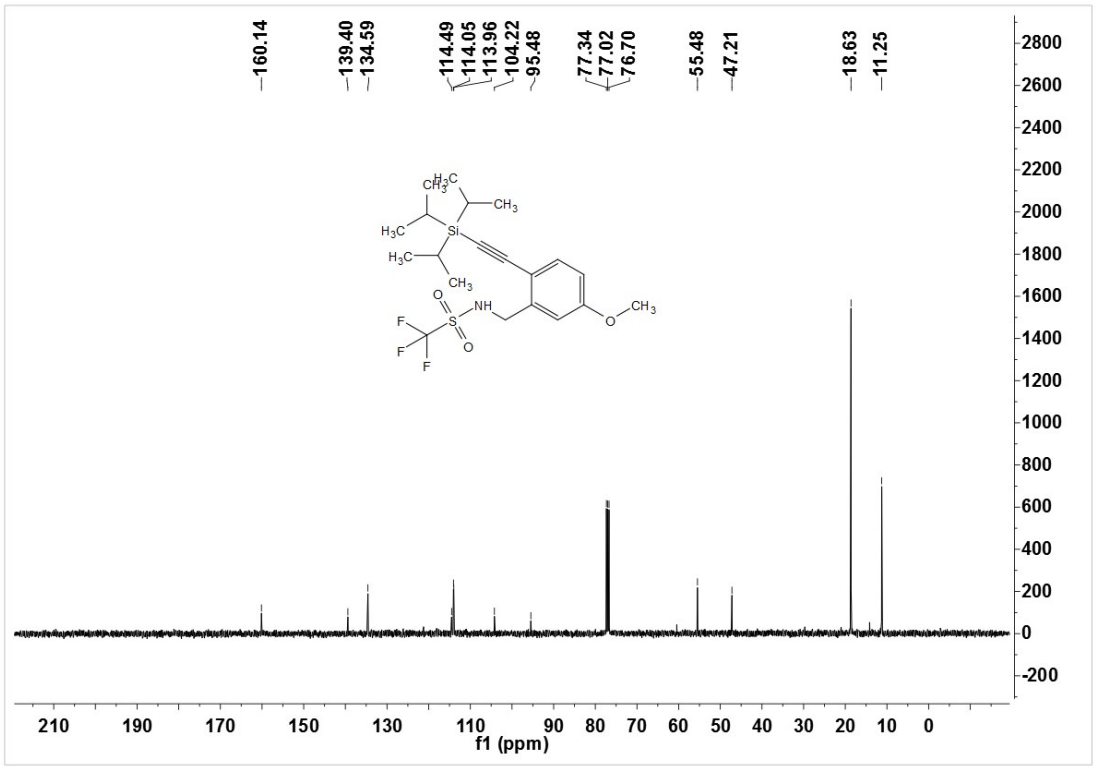


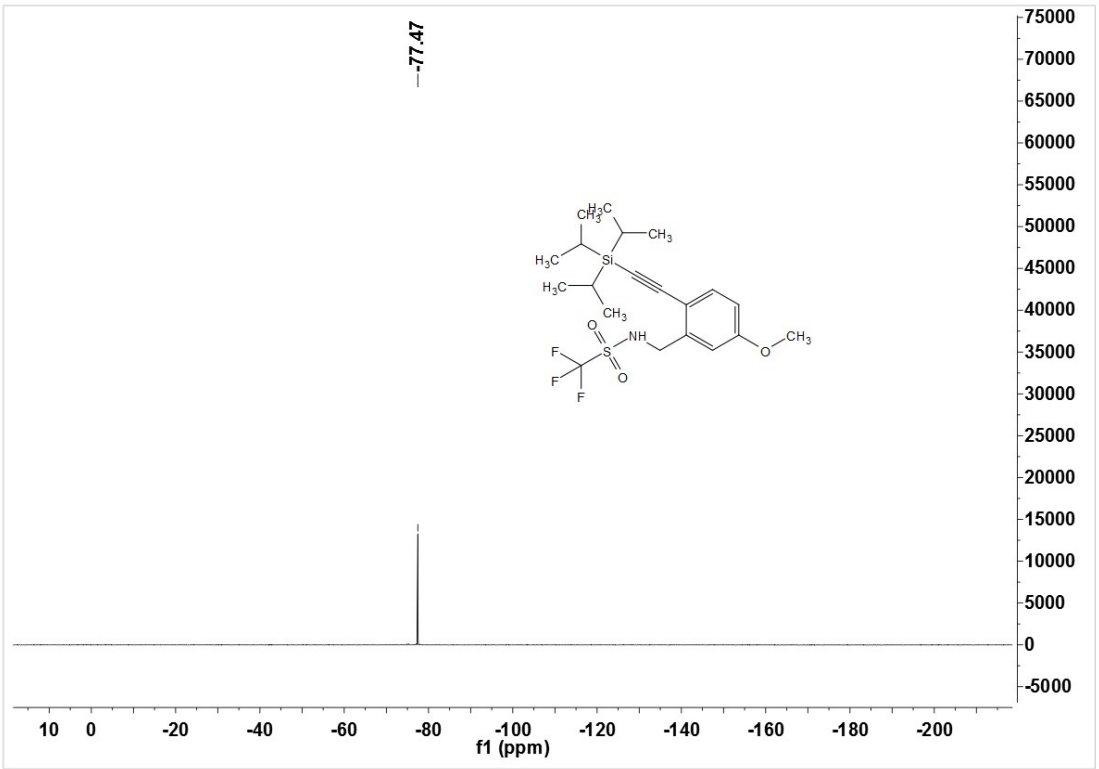




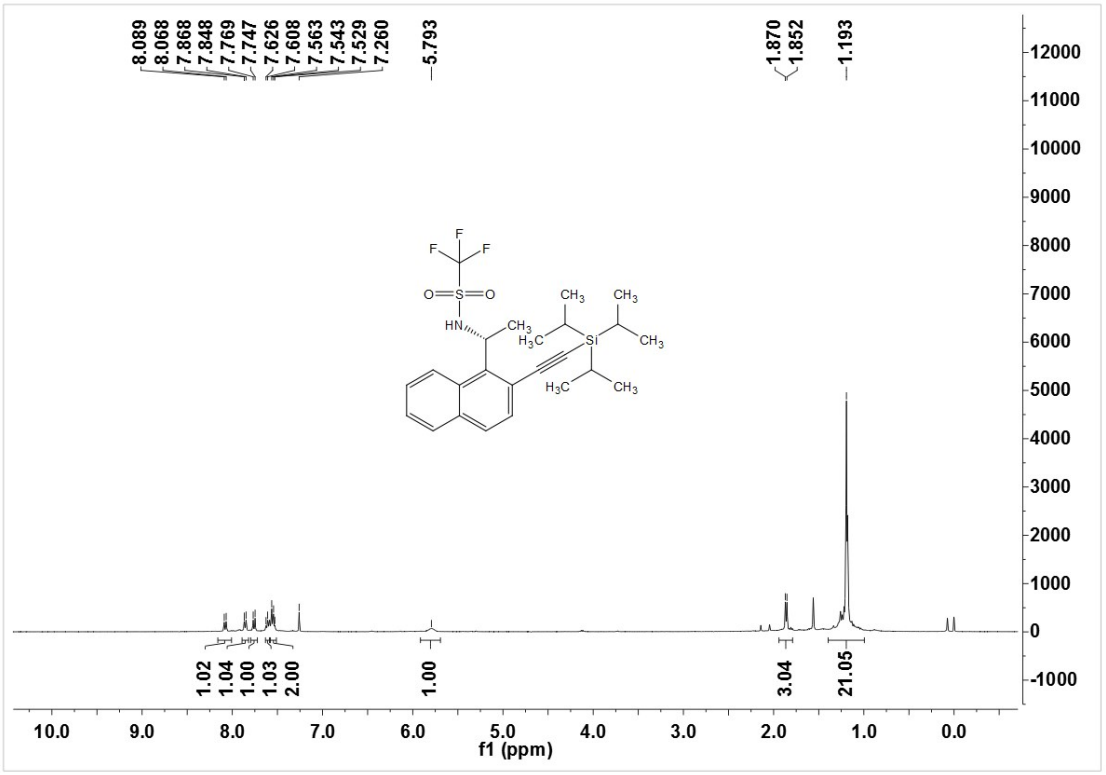
1,1,1-Trifluoro-*N*-(5-methoxy-2-((triisopropylsilyl)ethynyl)benzyl)methane sulfonamide (5j)

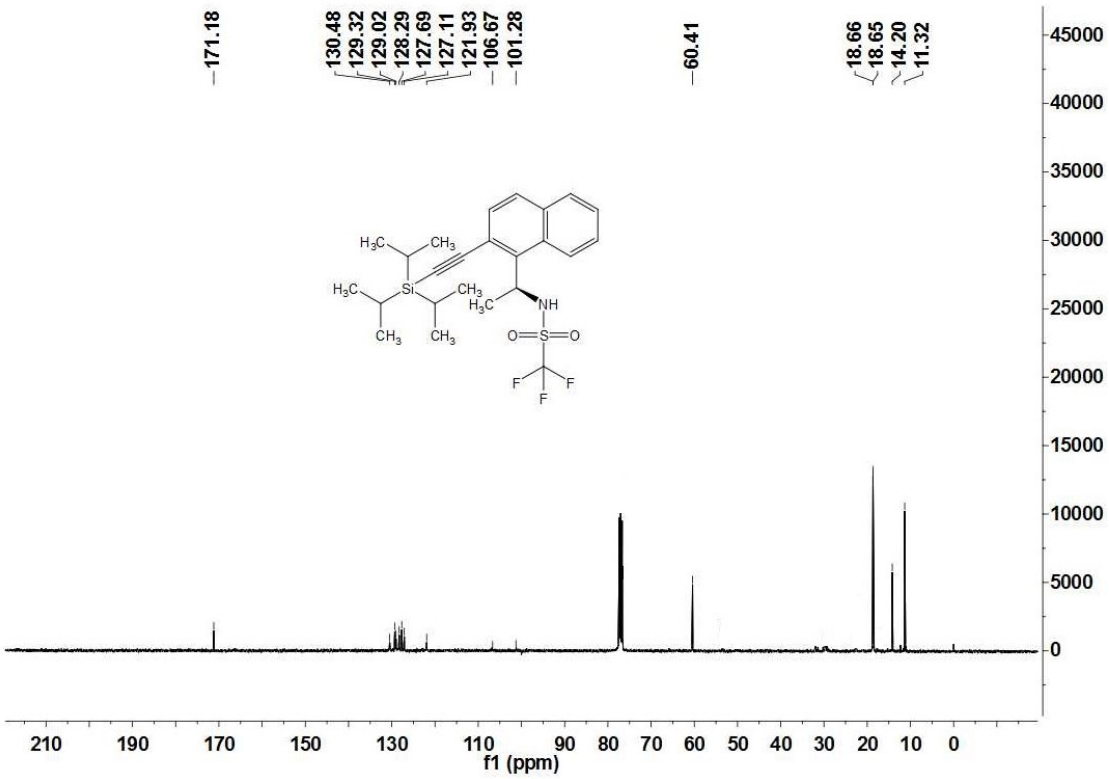


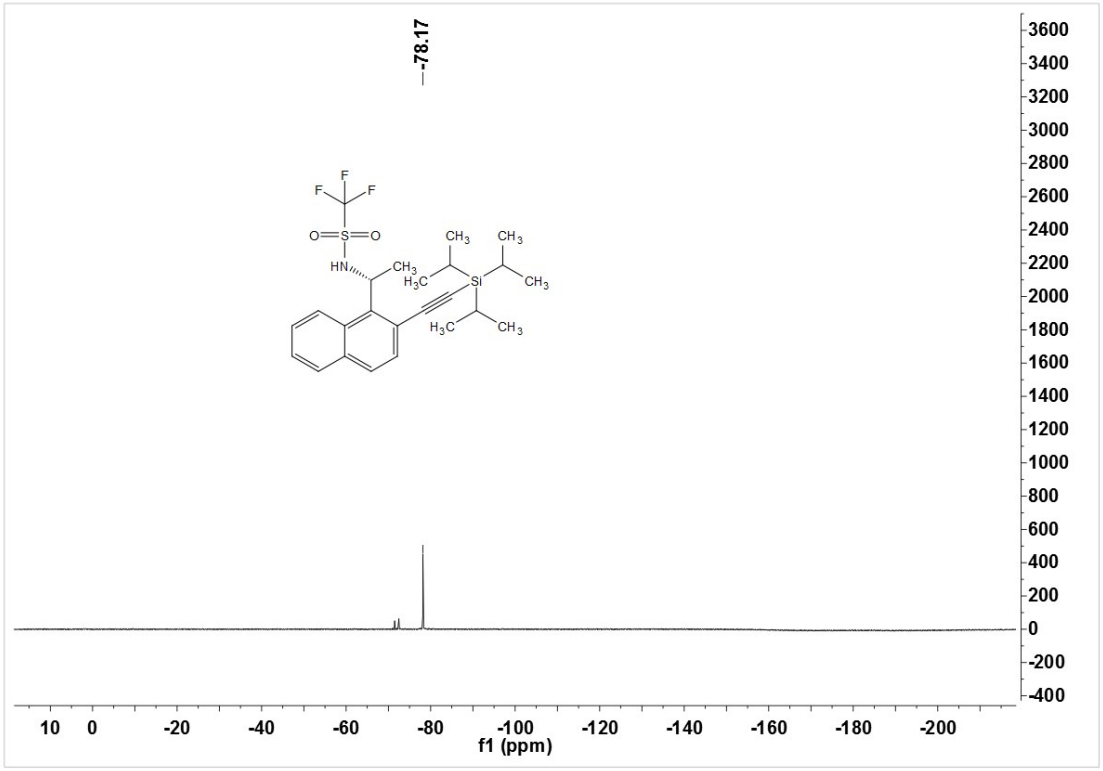

160.14
139.40
134.59
114.49
114.05
113.96
104.22
95.48
77.34
77.02
76.70
55.48
47.21
18.63
11.25
f1 (ppm)


-77.47
f1 (ppm)

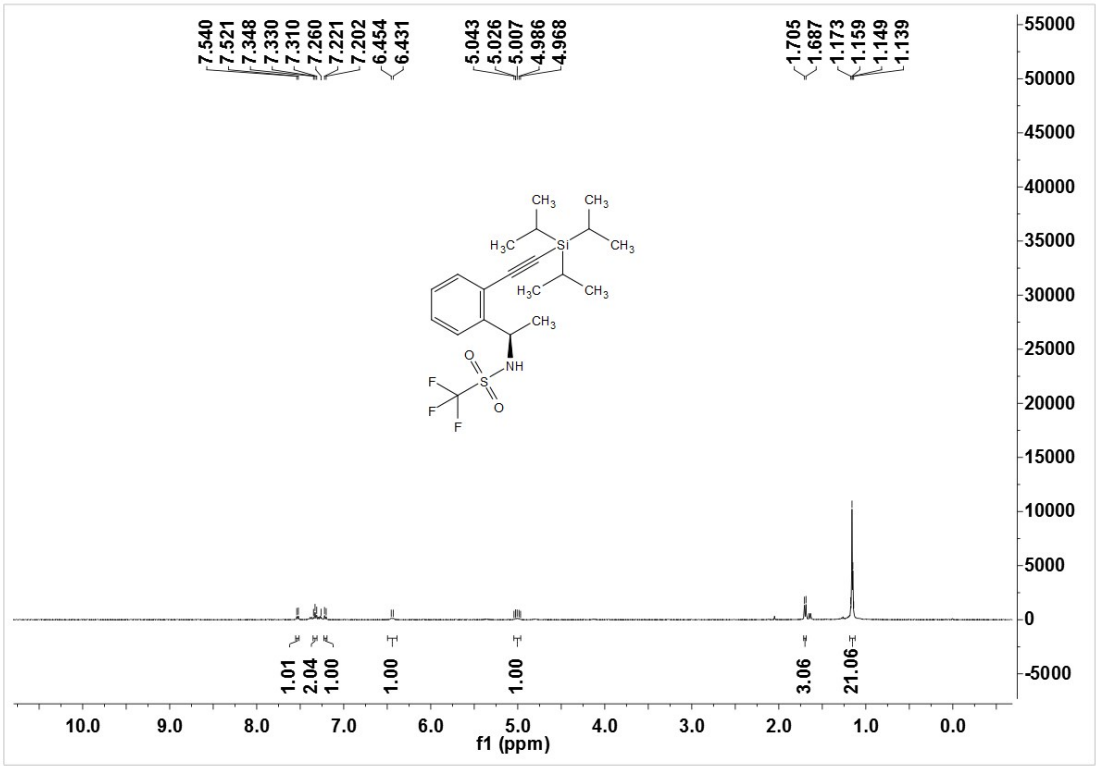
(*R*)-1,1,1-Trifluoro-*N*-(1-(2-((triisopropylsilyl)ethynyl)naphthalen-1-yl)ethyl) methanesulfonamide (5k)

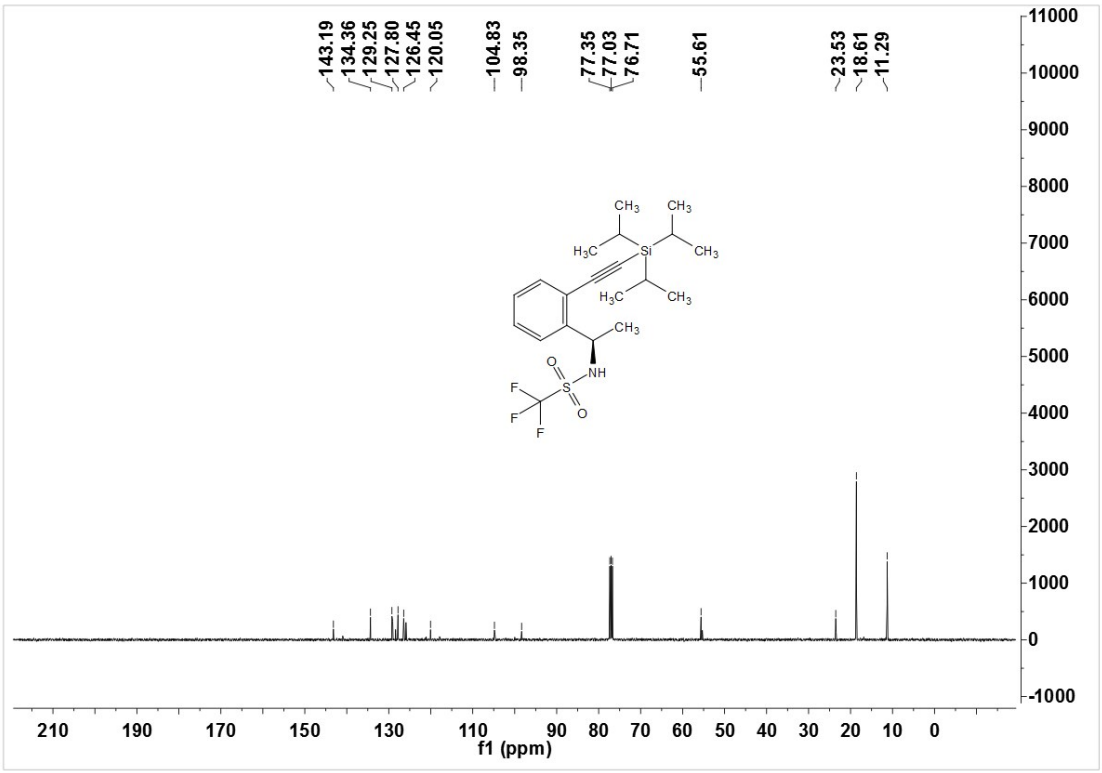


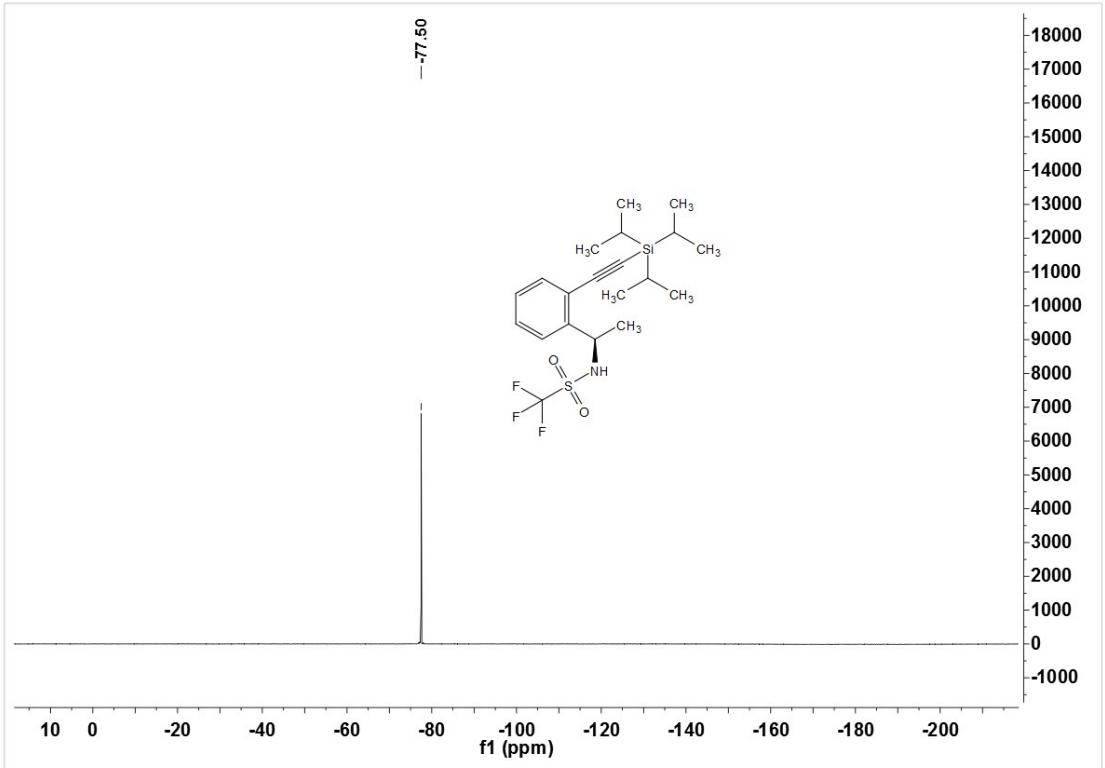




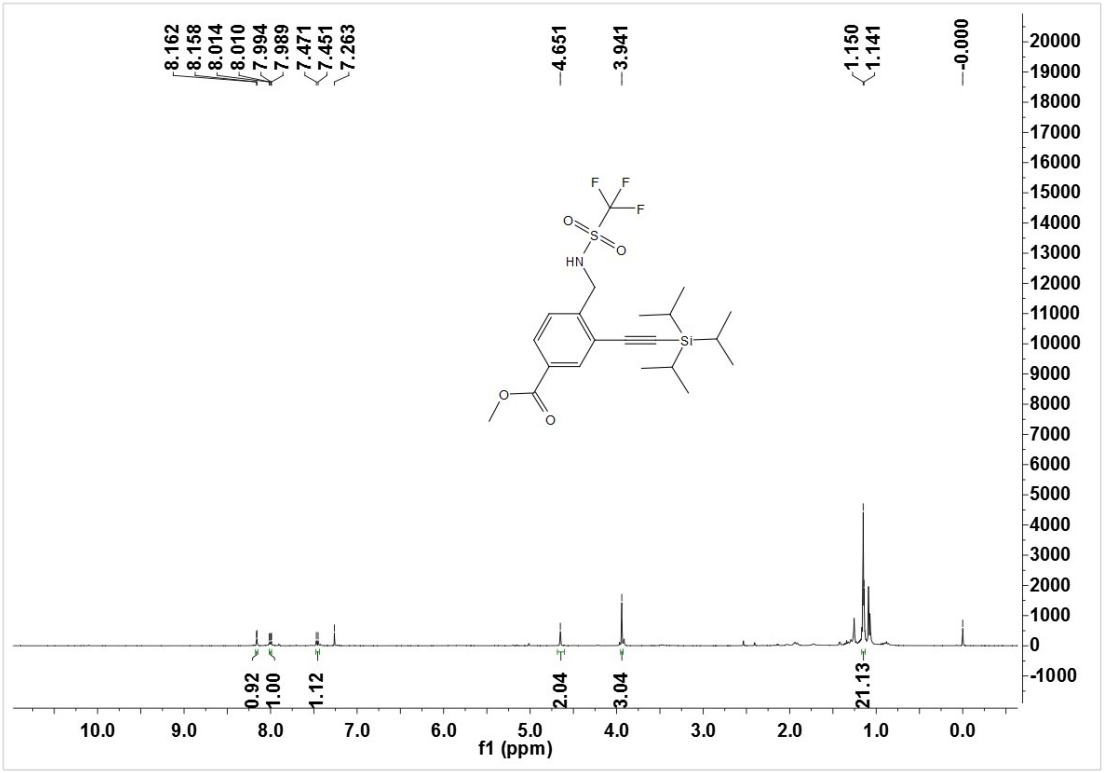
(*R*)-1,1,1-Trifluoro-*N*-(1-(2-((triisopropylsilyl)ethynyl)phenyl)ethyl)methane sulfonamide (5l)

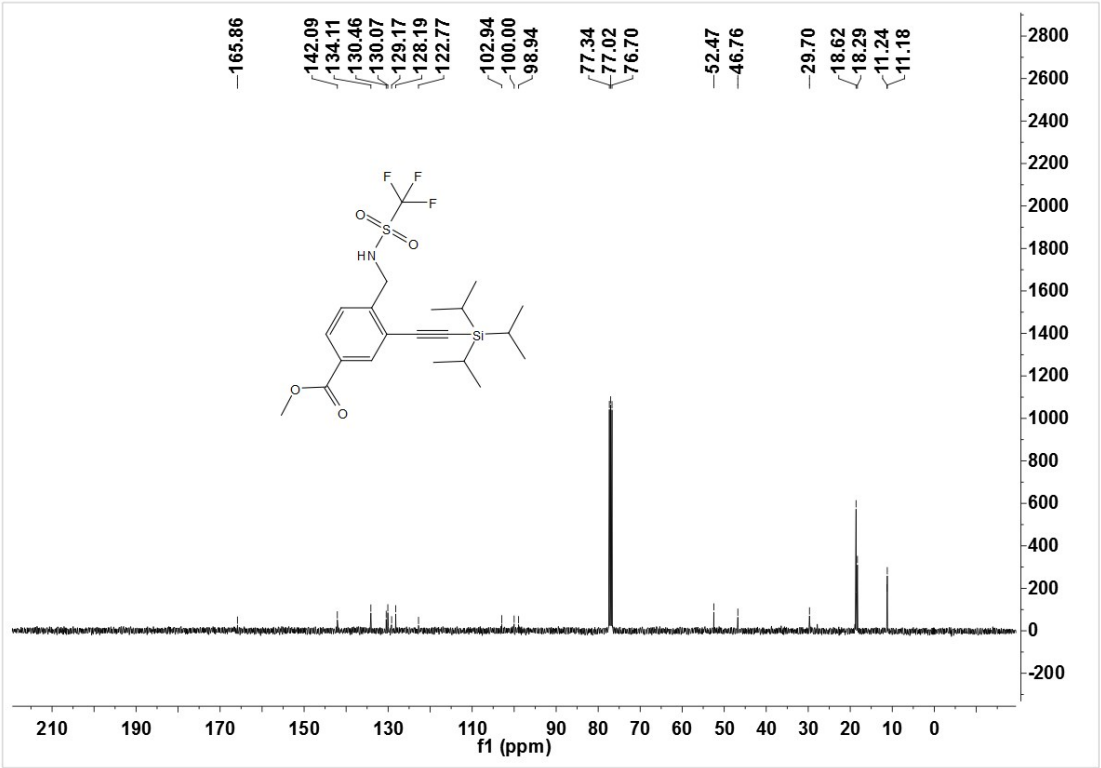



143.19
134.36
129.25
127.80
126.45
120.05
104.83
98.35
77.35
77.03
76.71
55.61
23.53
18.61
11.29
f1 (ppm)

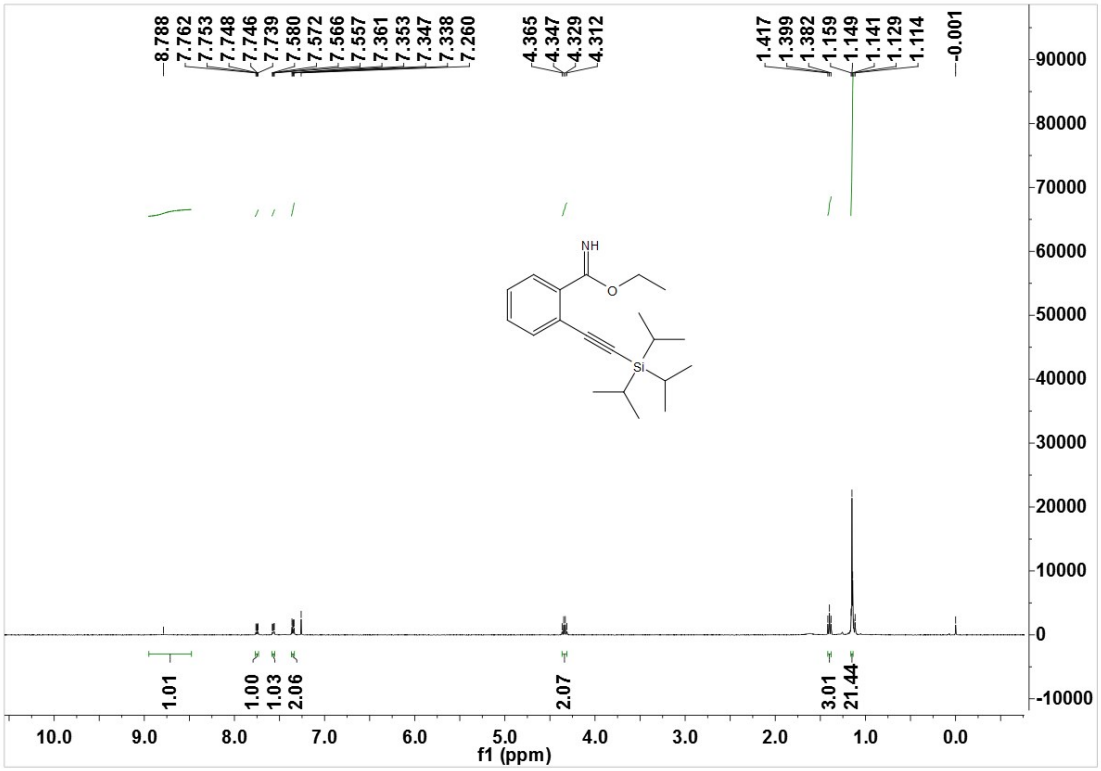

-77.50
f1 (ppm)

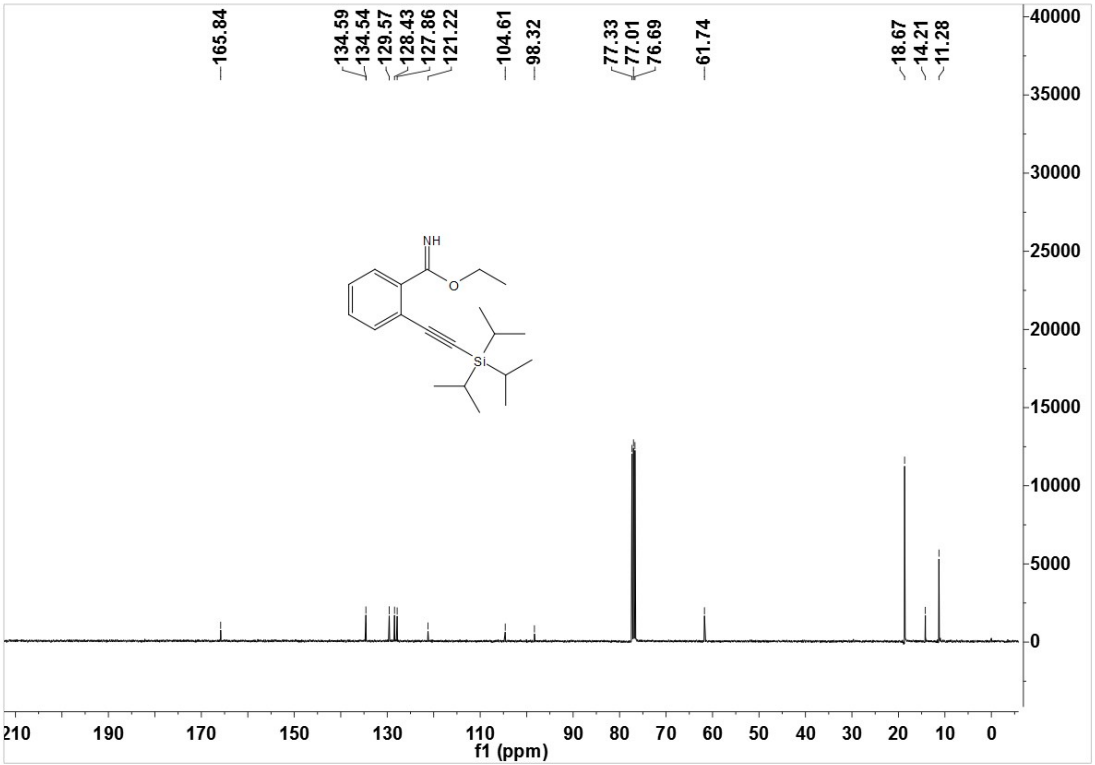
Methyl 4-(((trifluoromethyl)sulfonamido)methyl)-3-((triisopropylsilyl)ethynyl) benzoate (5m)



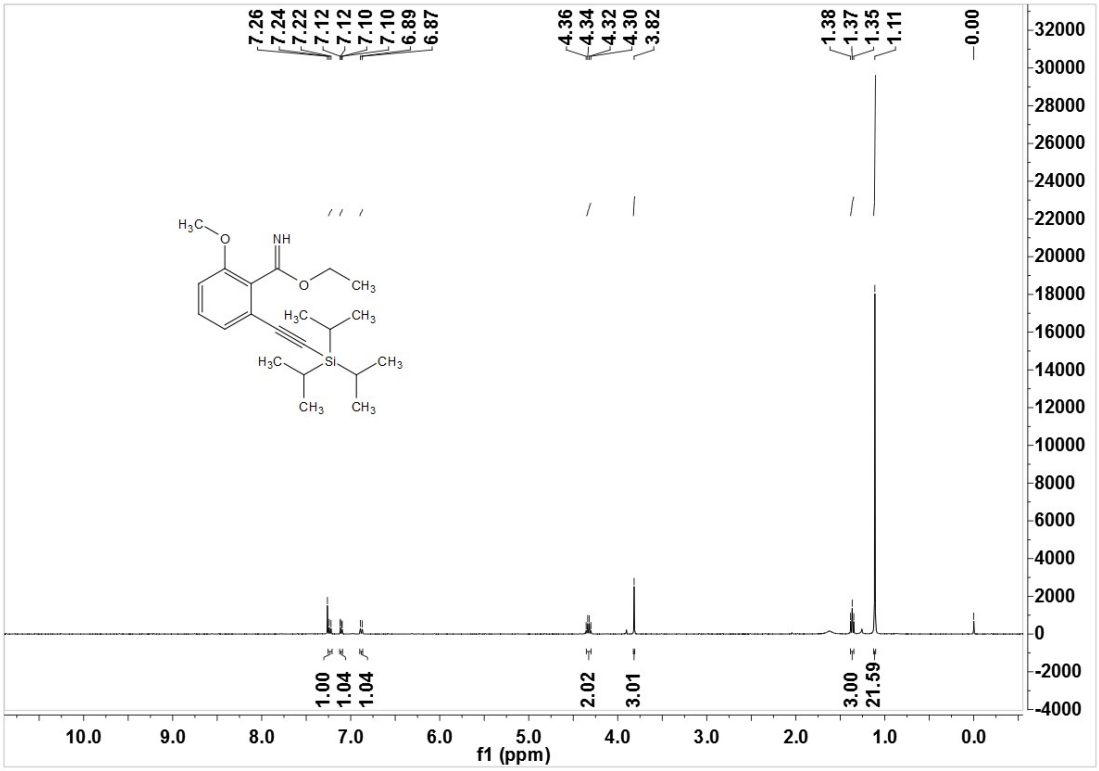


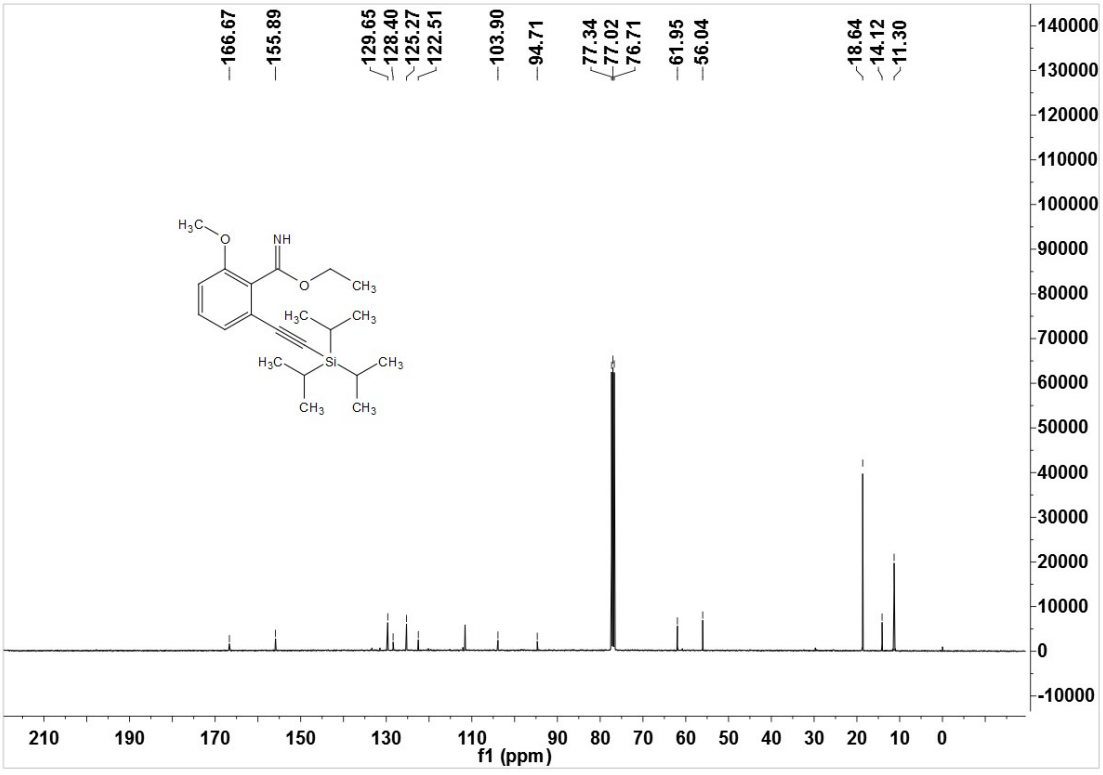
Ethyl 2-((triisopropylsilyl)ethynyl)benzimidate (7a)



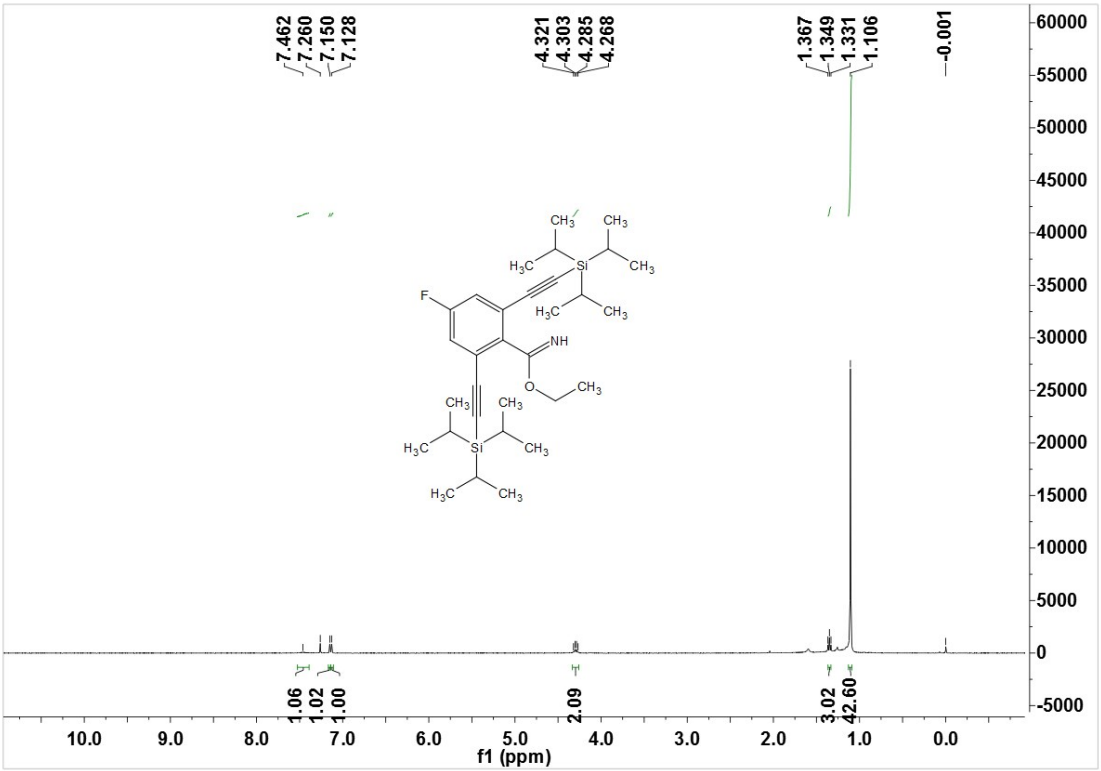


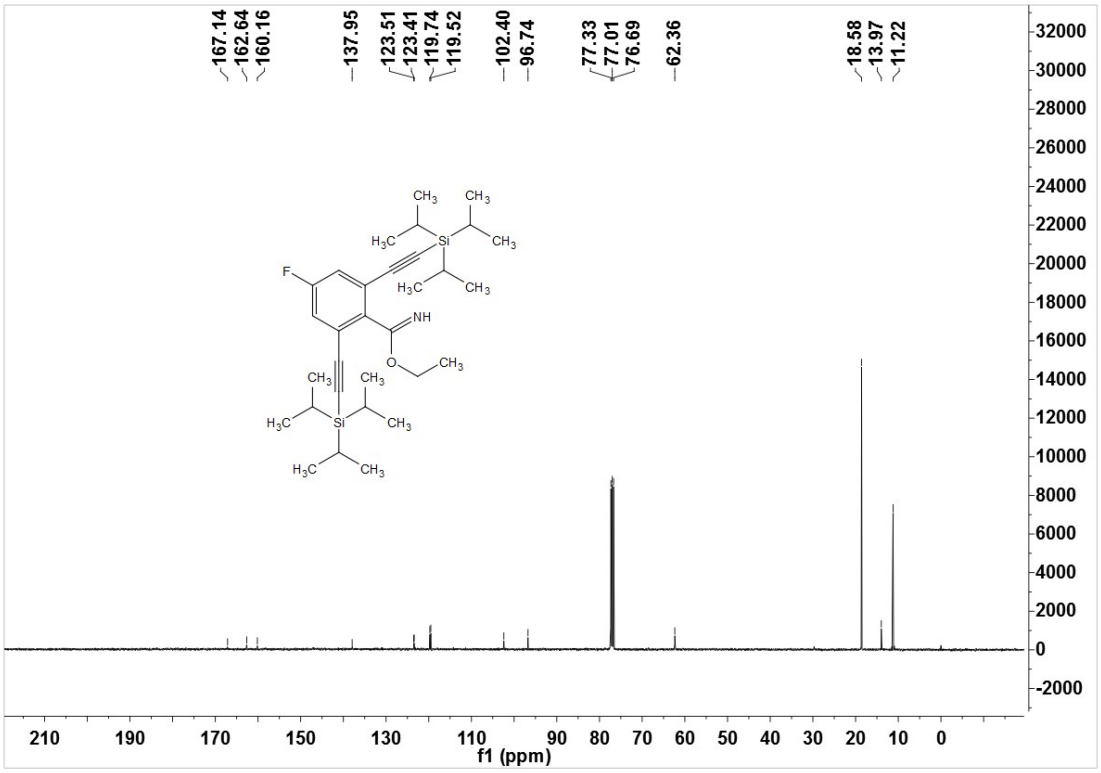
Ethyl 2-methoxy-6-((triisopropylsilyl)ethynyl)benzimidate (7b)



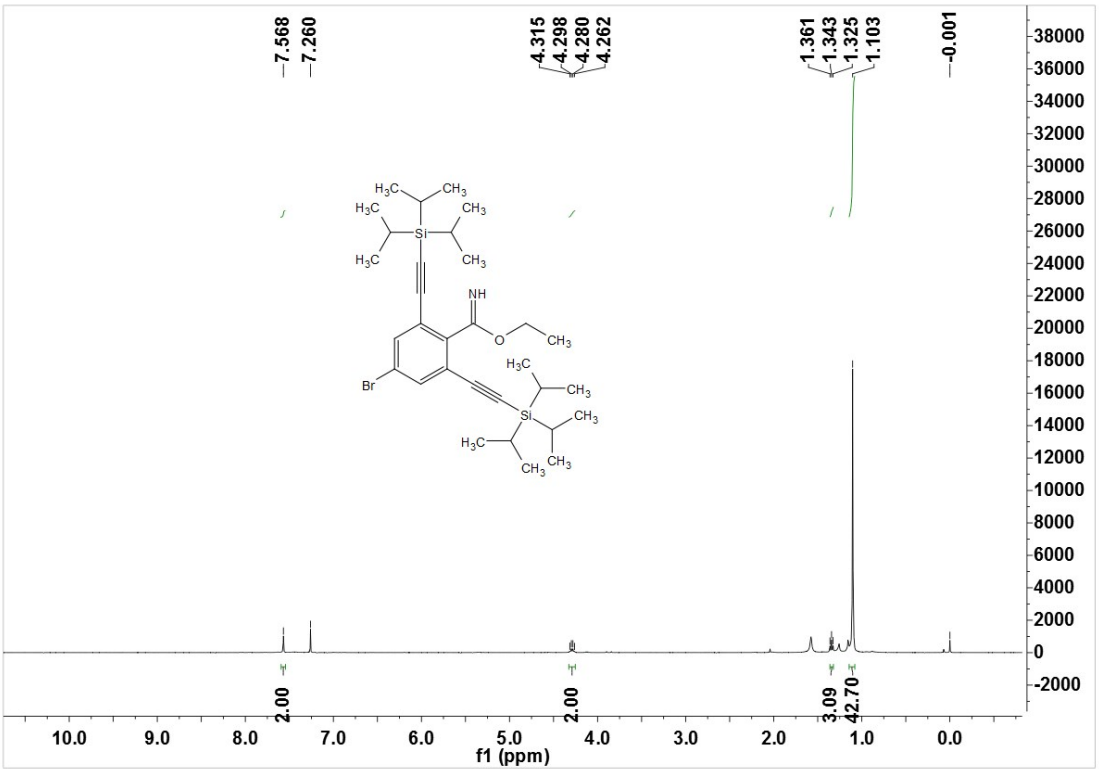


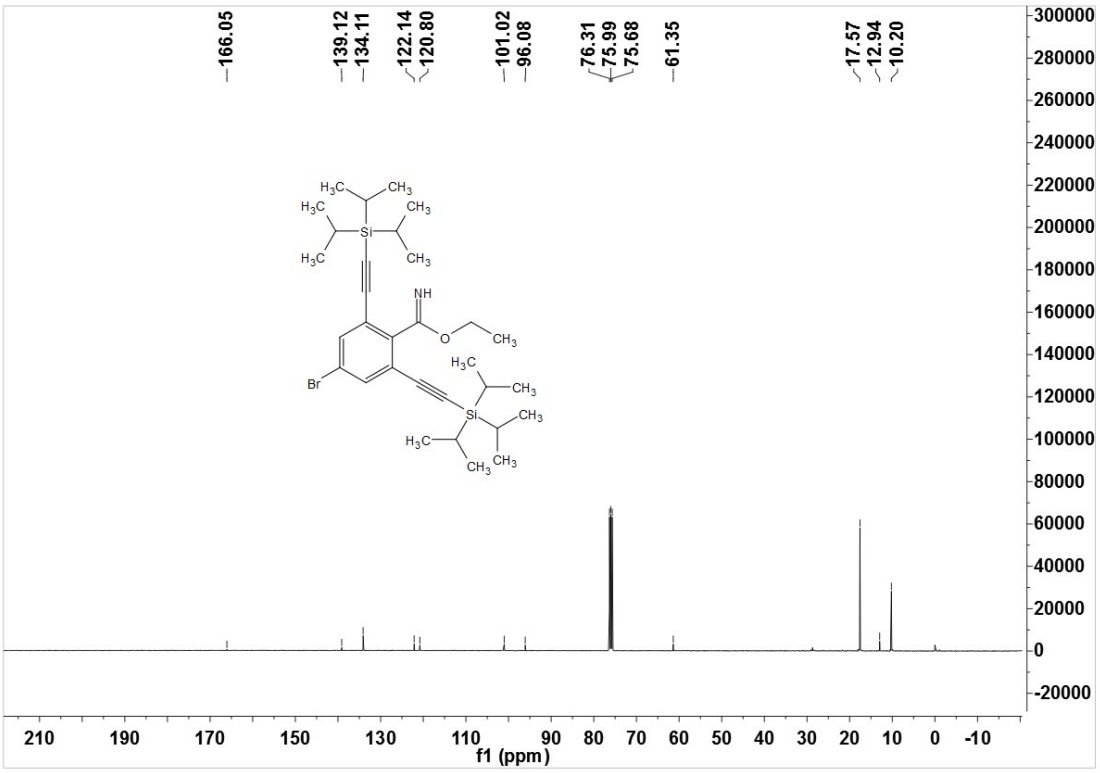
Ethyl 4-fluoro-2,6-bis((triisopropylsilyl)ethynyl)benzimidate (7c)



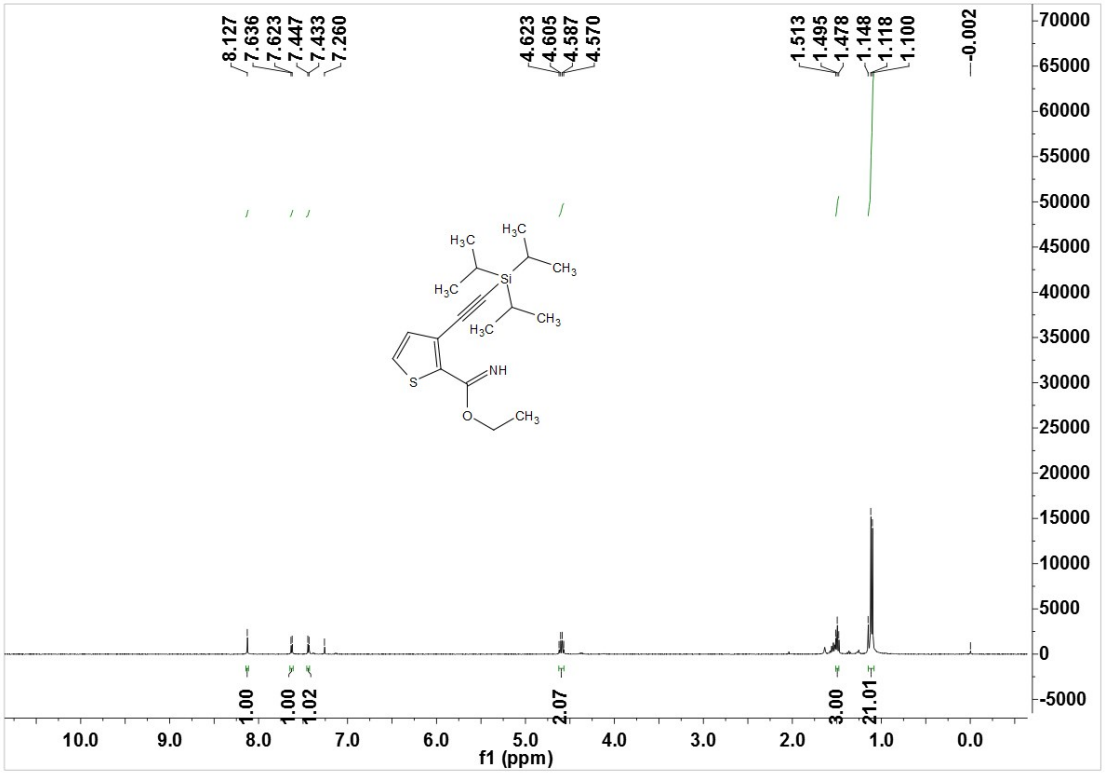


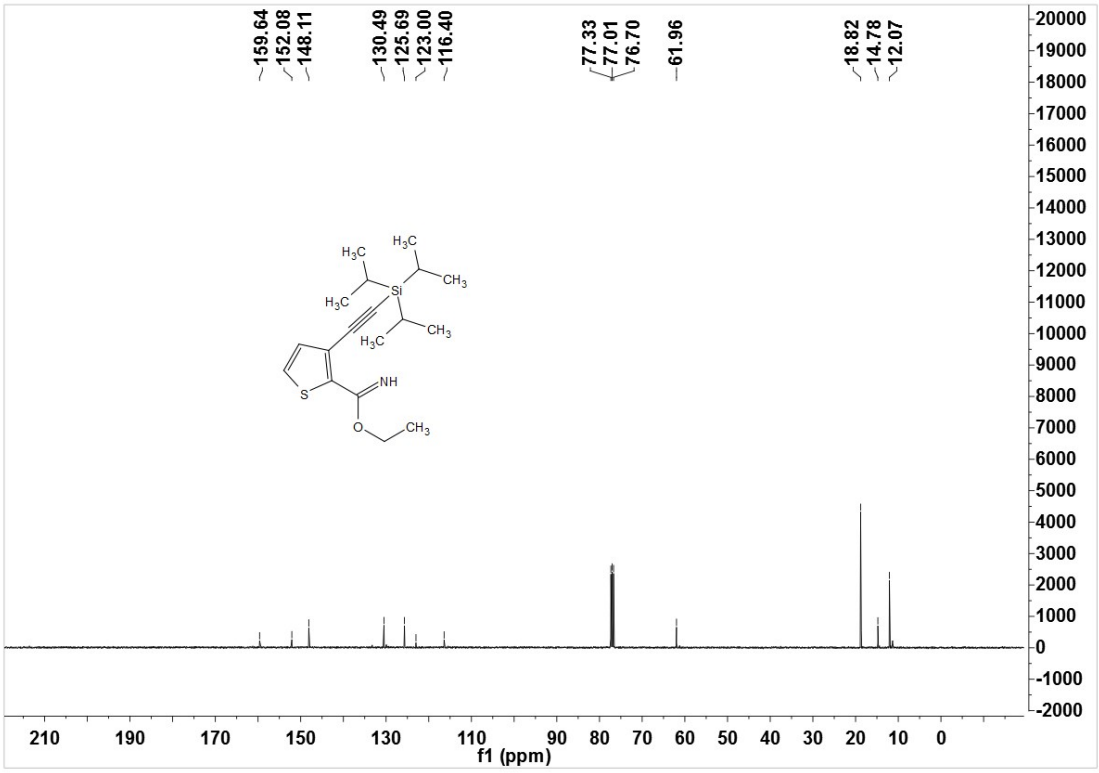
Ethyl 4-bromo-2,6-bis((triisopropylsilyl)ethynyl)benzimidate



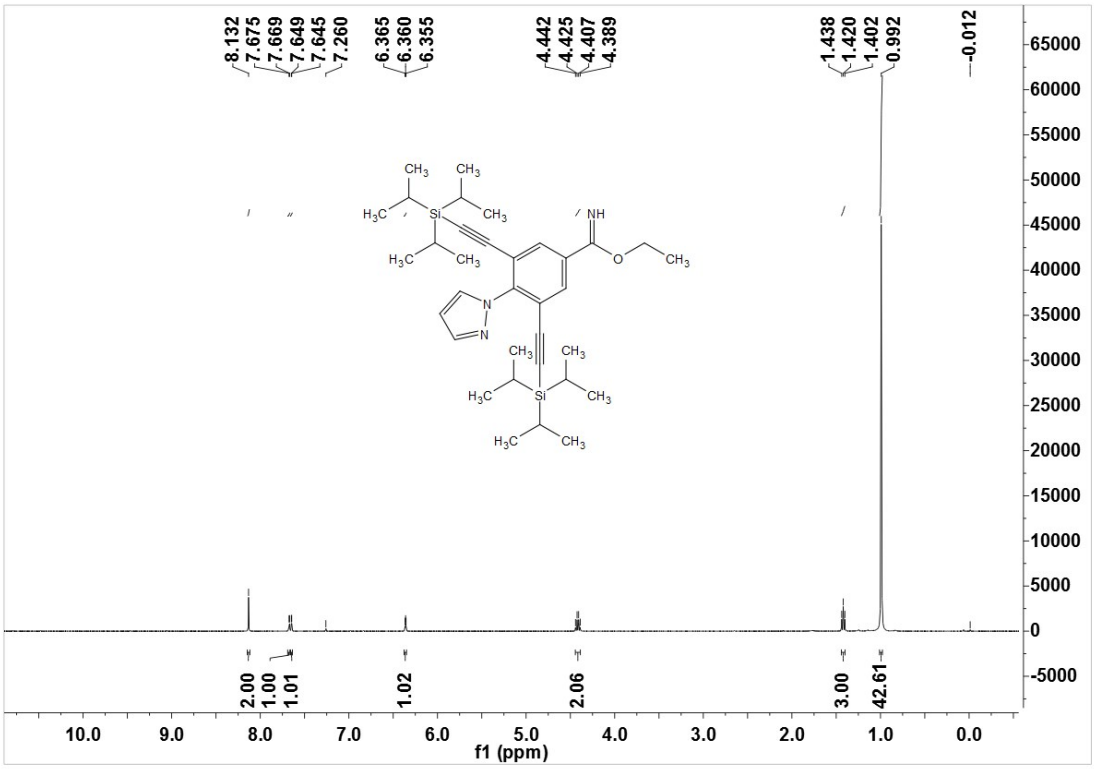


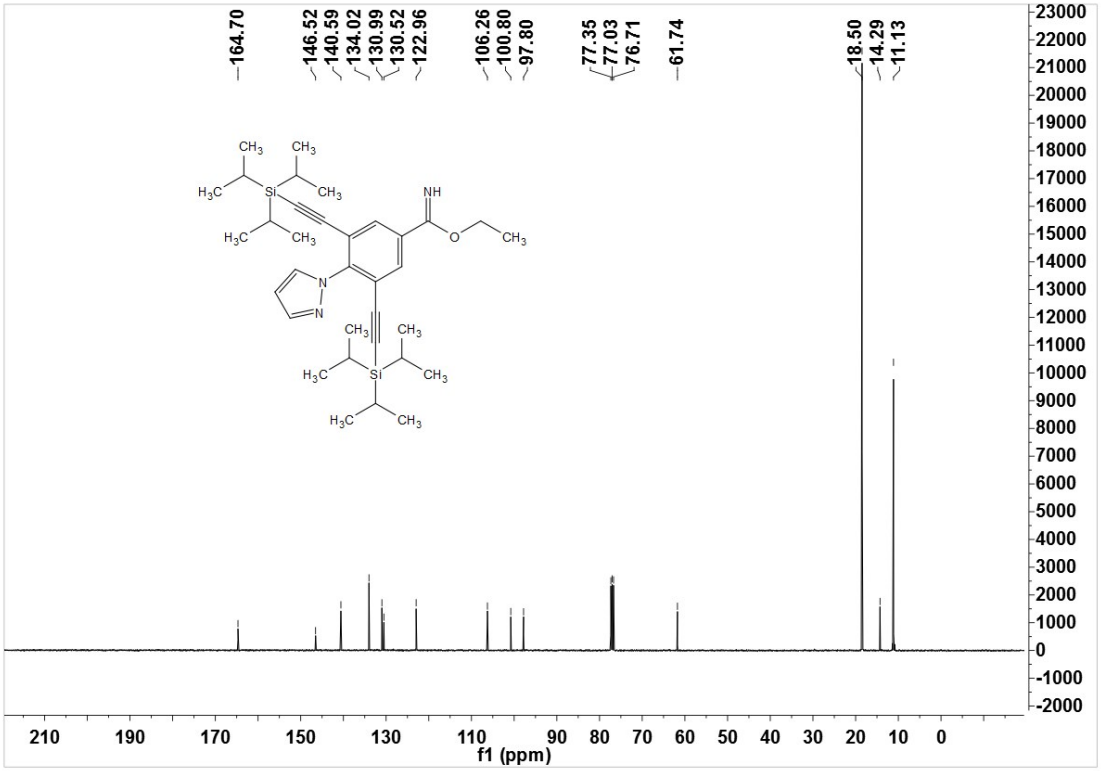
Ethyl 3-((triisopropylsilyl)ethynyl)thiophene-2-carbimidate (7d)



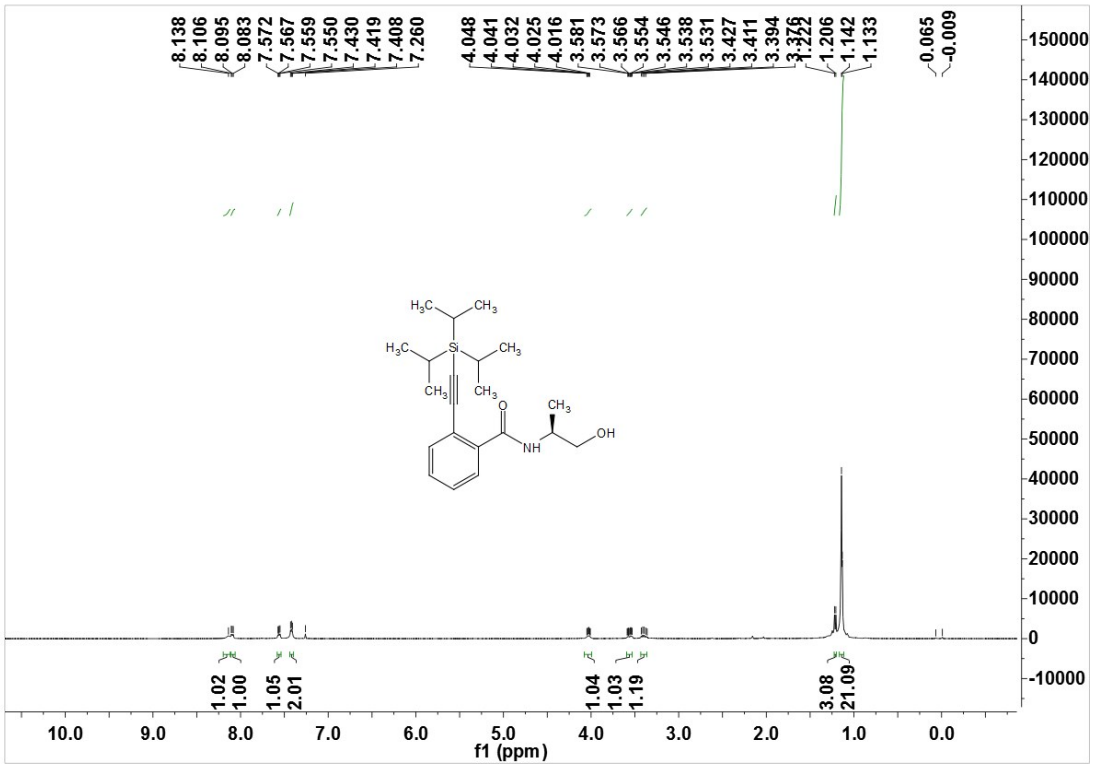


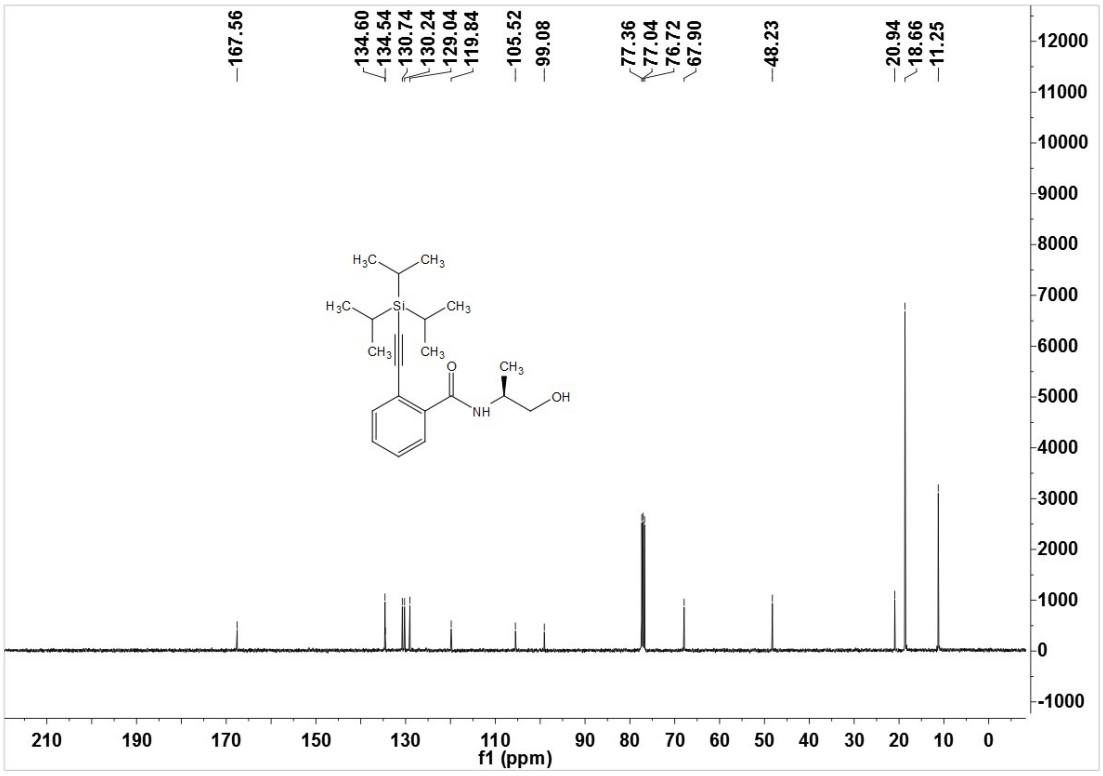
Ethyl 4-(1*H*-pyrazol-1-yl)-3,5-bis((triisopropylsilyl)ethynyl)benzimidate (7e)



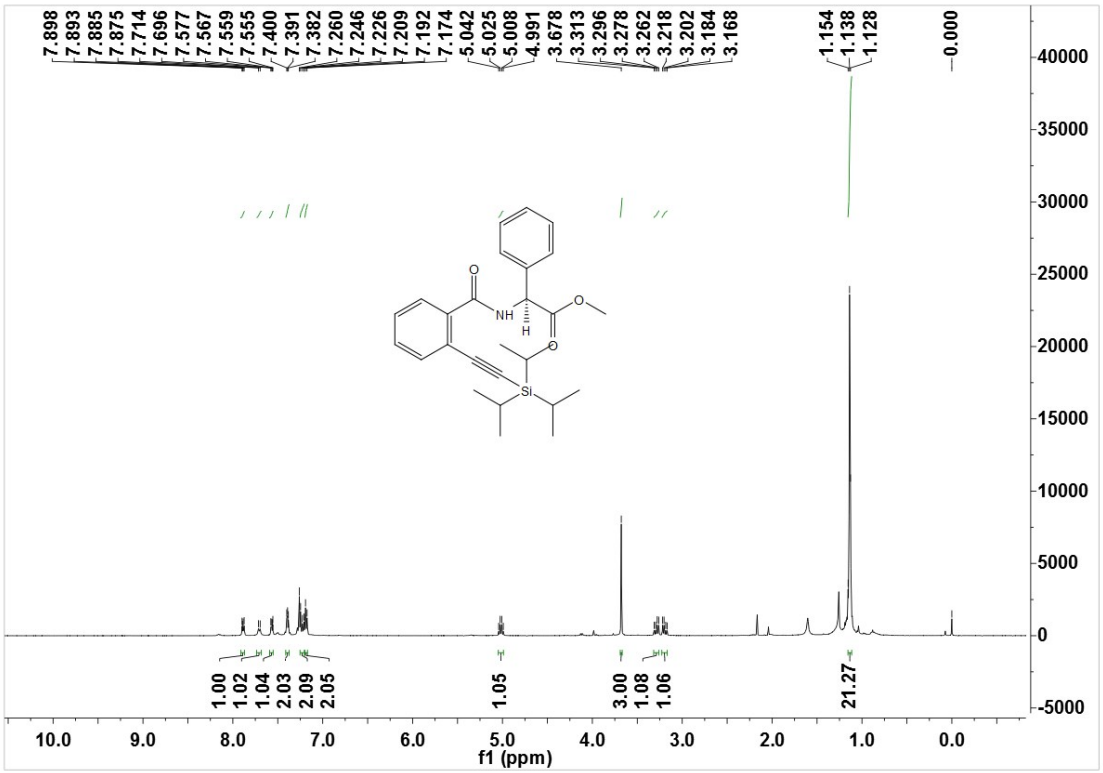


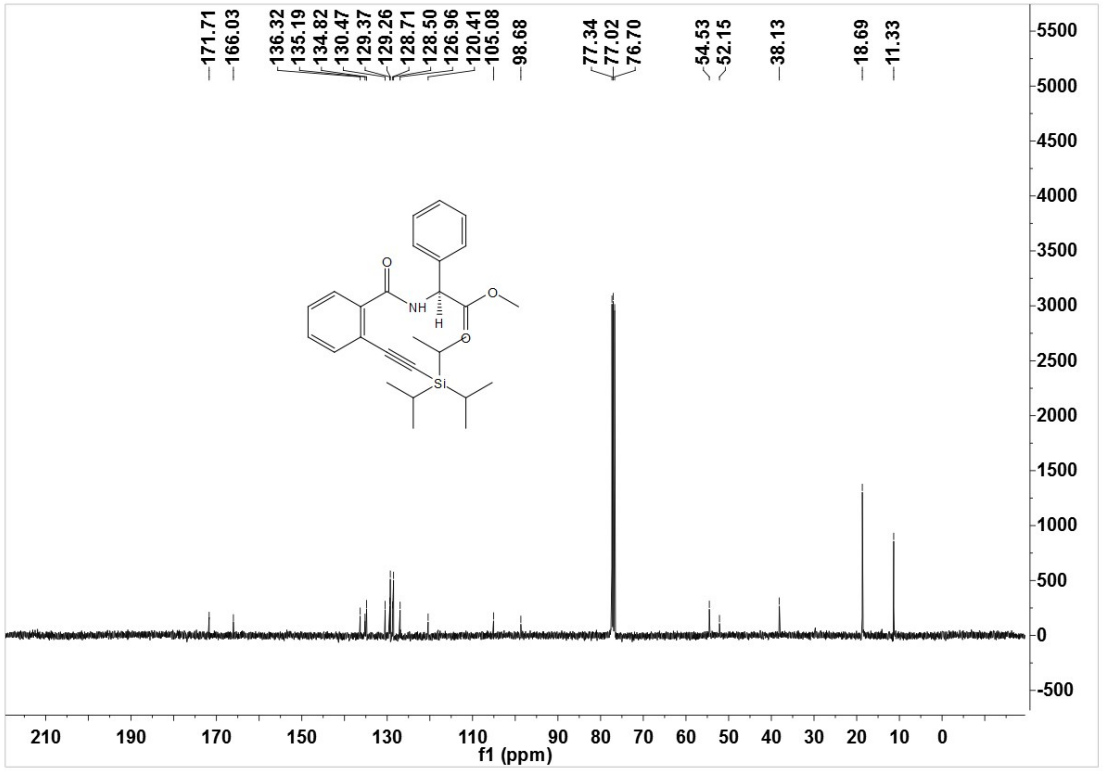
(*S*)-*N*-(1-Hydroxypropan-2-yl)-2-((triisopropylsilyl)ethynyl)benzamide (7f)



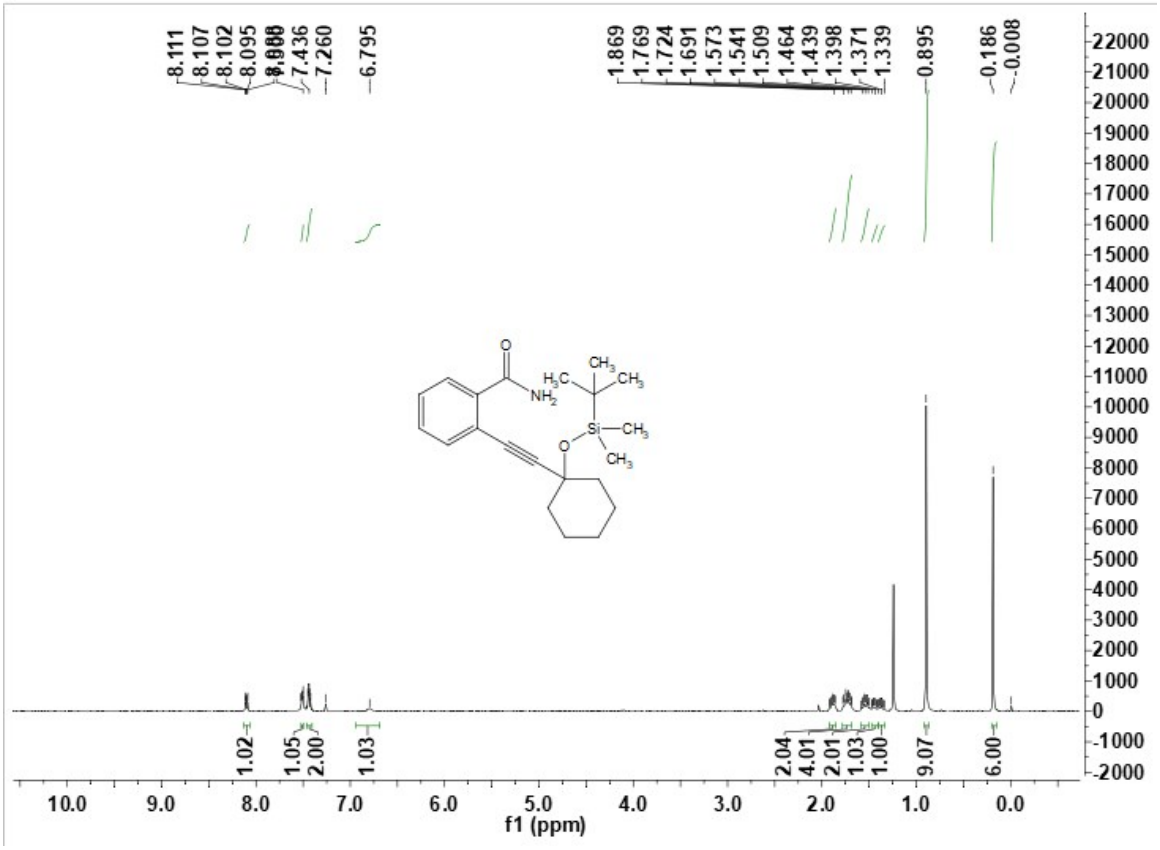


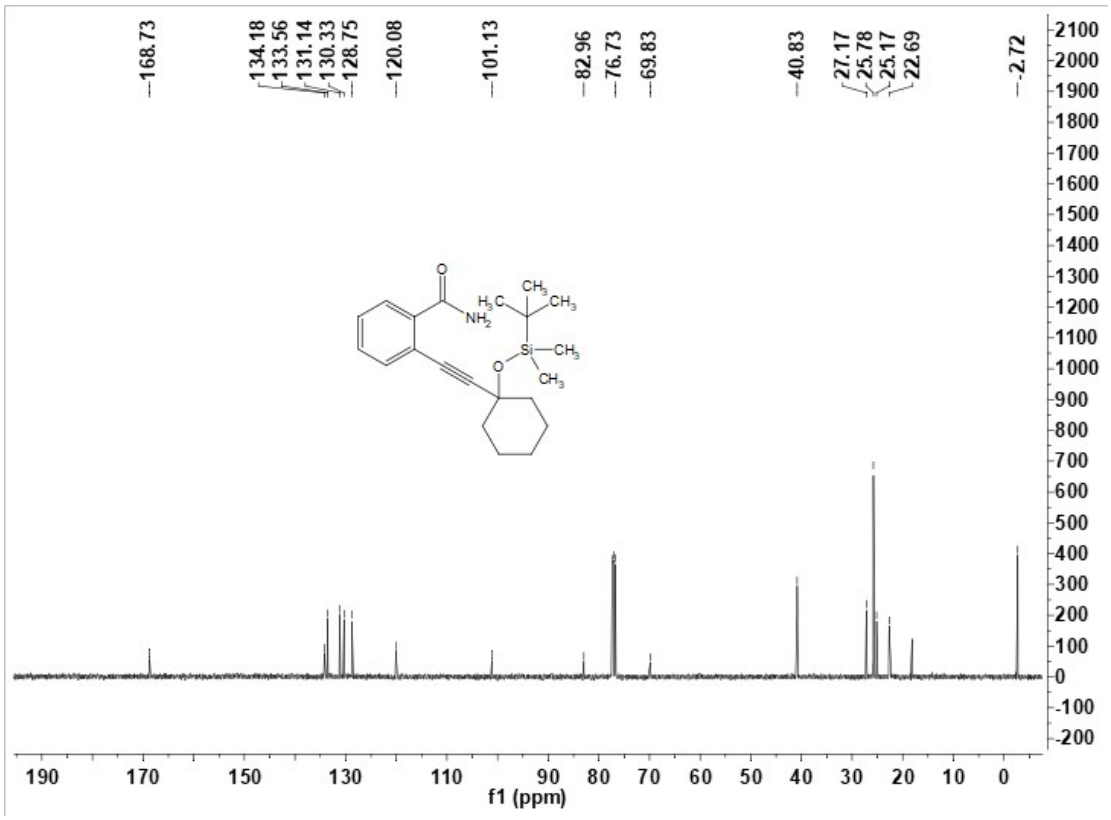
Methyl (*S*)-2-phenyl-2-(2-((triisopropylsilyl)ethynyl)benzamido)acetate (7g)



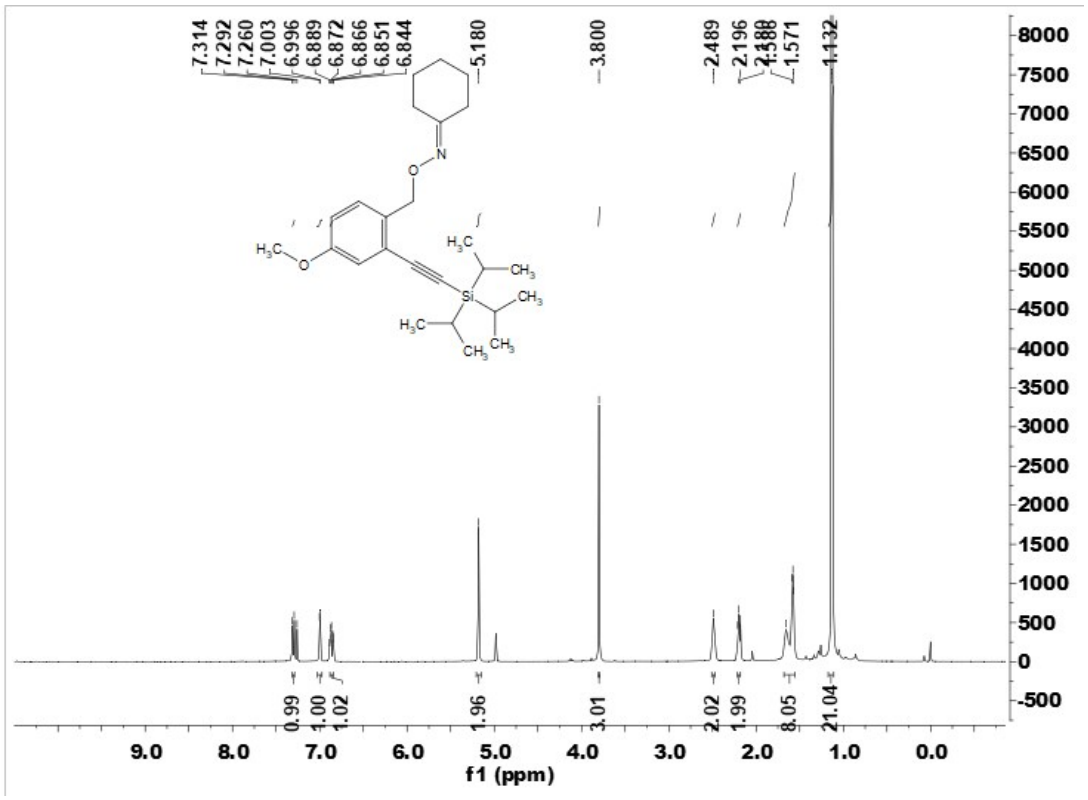


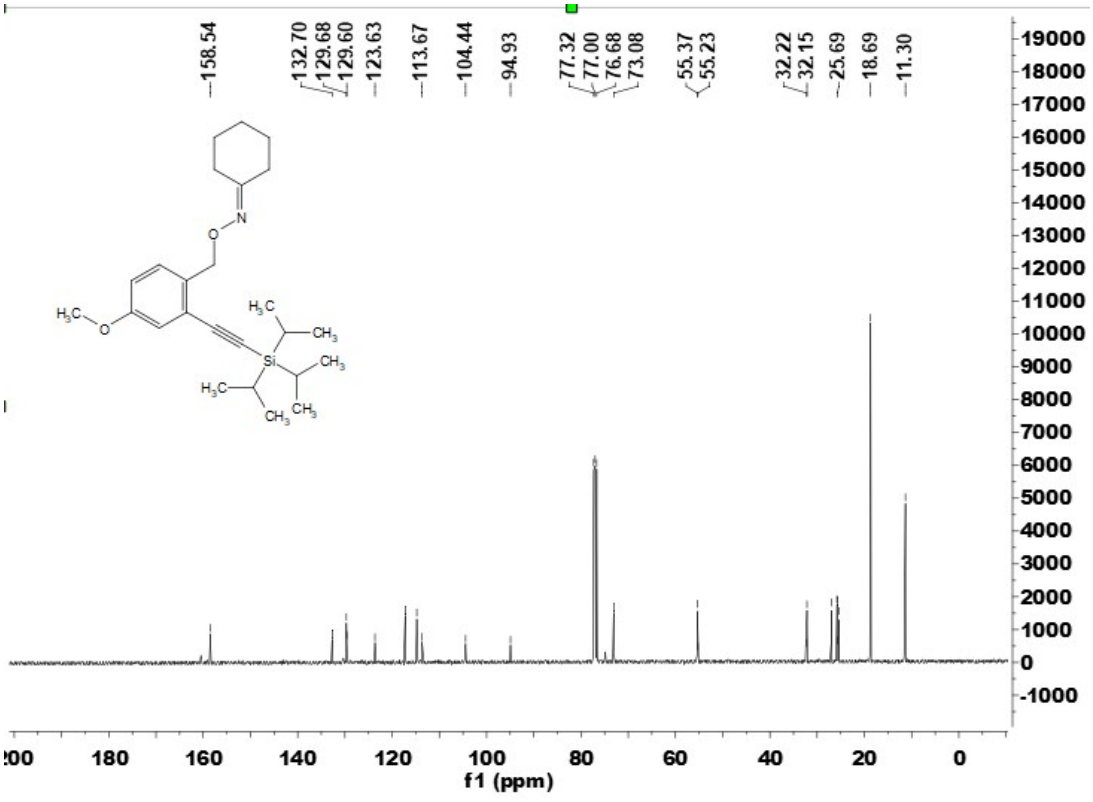
2-((1-((*tert*-Butyldimethylsilyl)oxy)cyclohexyl)ethynyl)benzamide (7h)



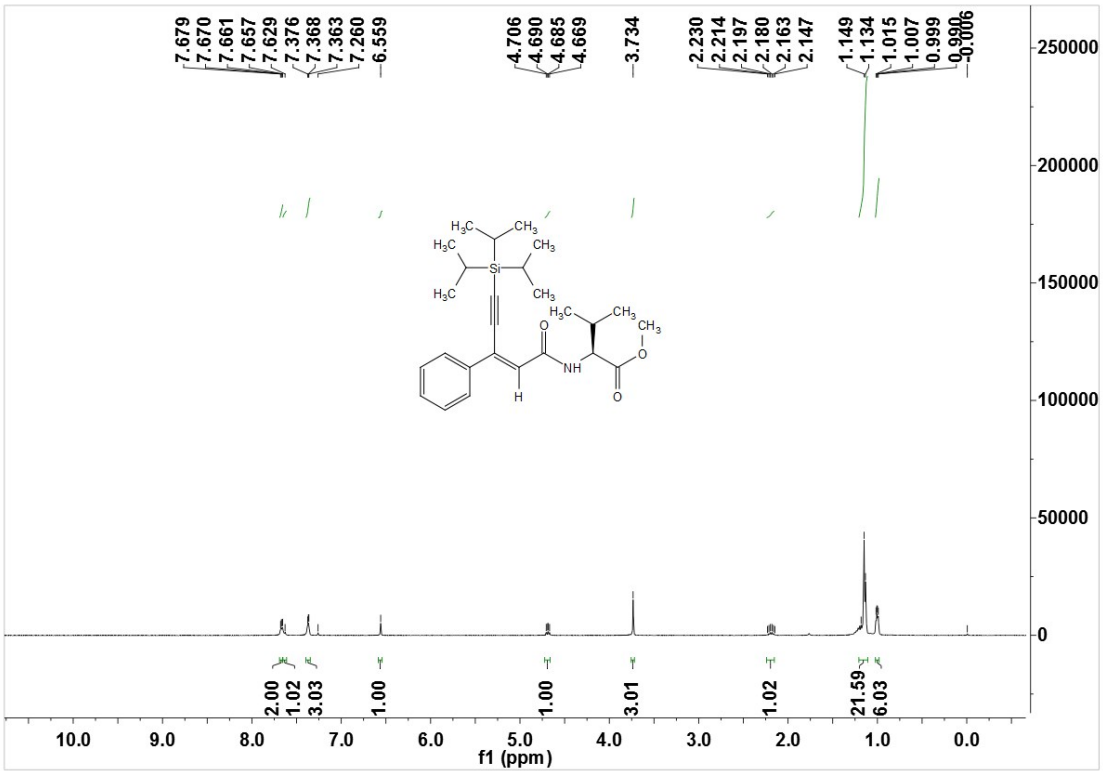


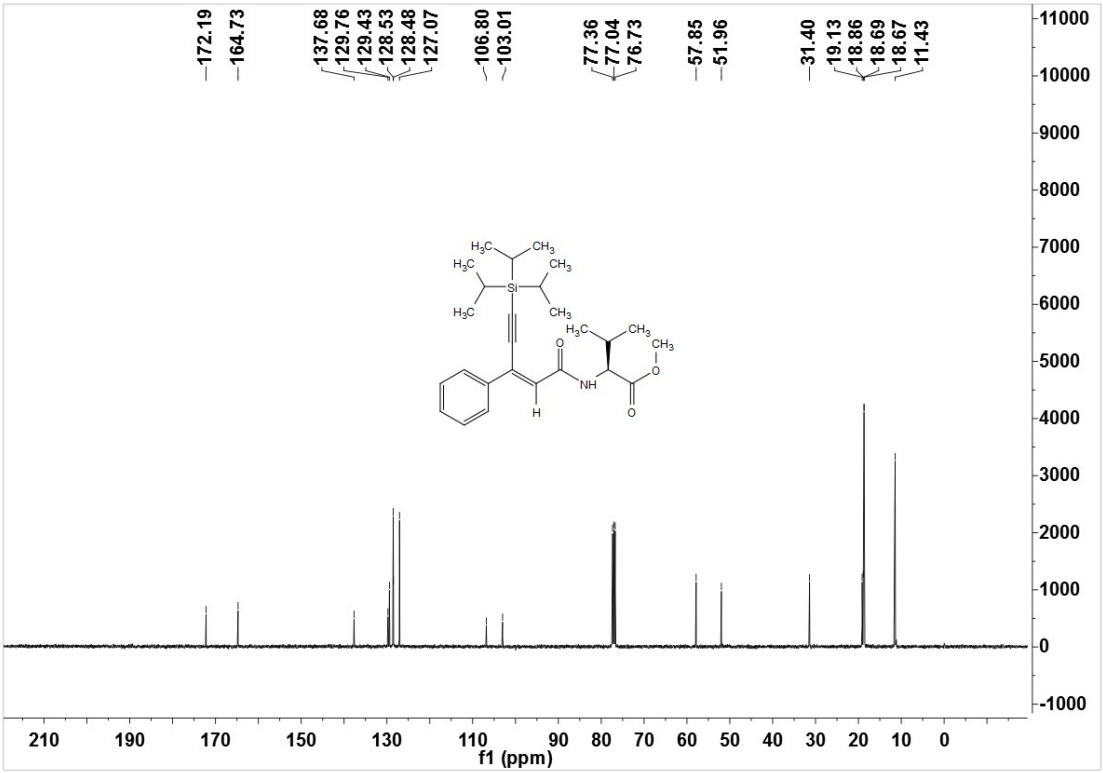
Cyclohexanone *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (7i)


7.314
7.292
7.260
7.003
6.996
6.889
6.872
6.866
6.851
6.844
5.180
3.800
2.489
2.196
1.571
1.132
0.99
1.00
1.02
1.96
3.01
2.02
1.99
8.05
21.04
f1 (ppm)

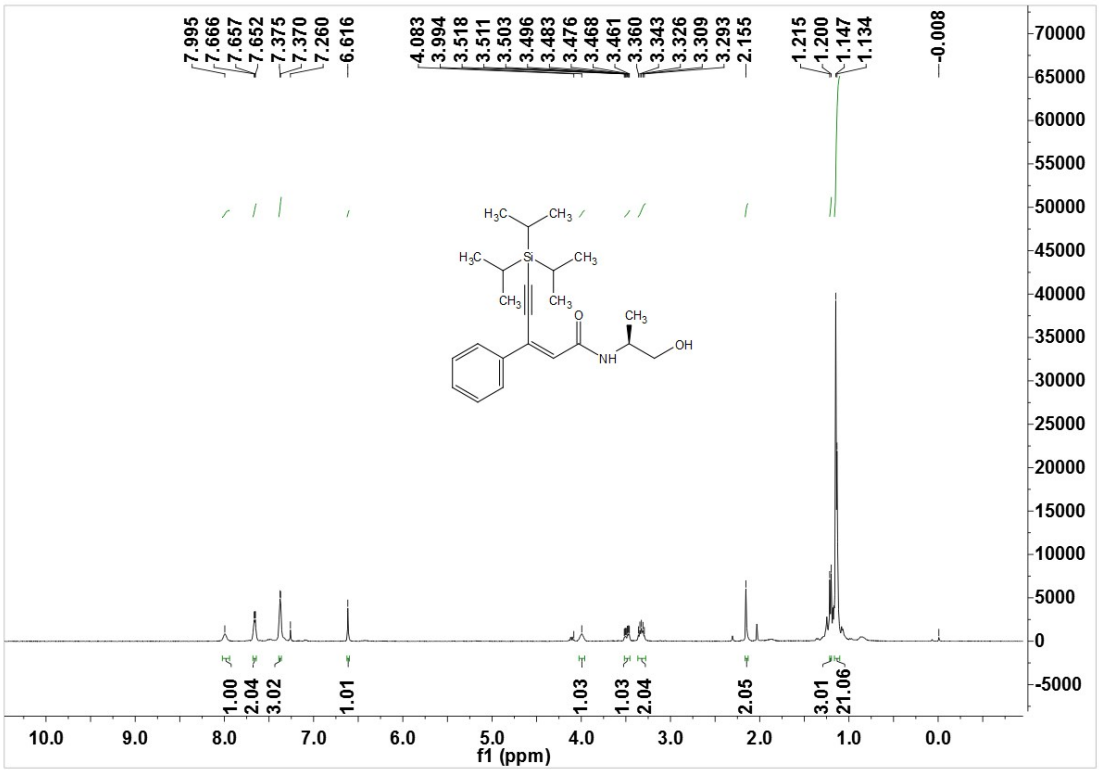

158.54
132.70
129.68
129.60
123.63
113.67
104.44
94.93
77.32
77.00
76.68
73.08
55.37
55.23
32.22
32.15
25.69
18.69
11.30
f1 (ppm)

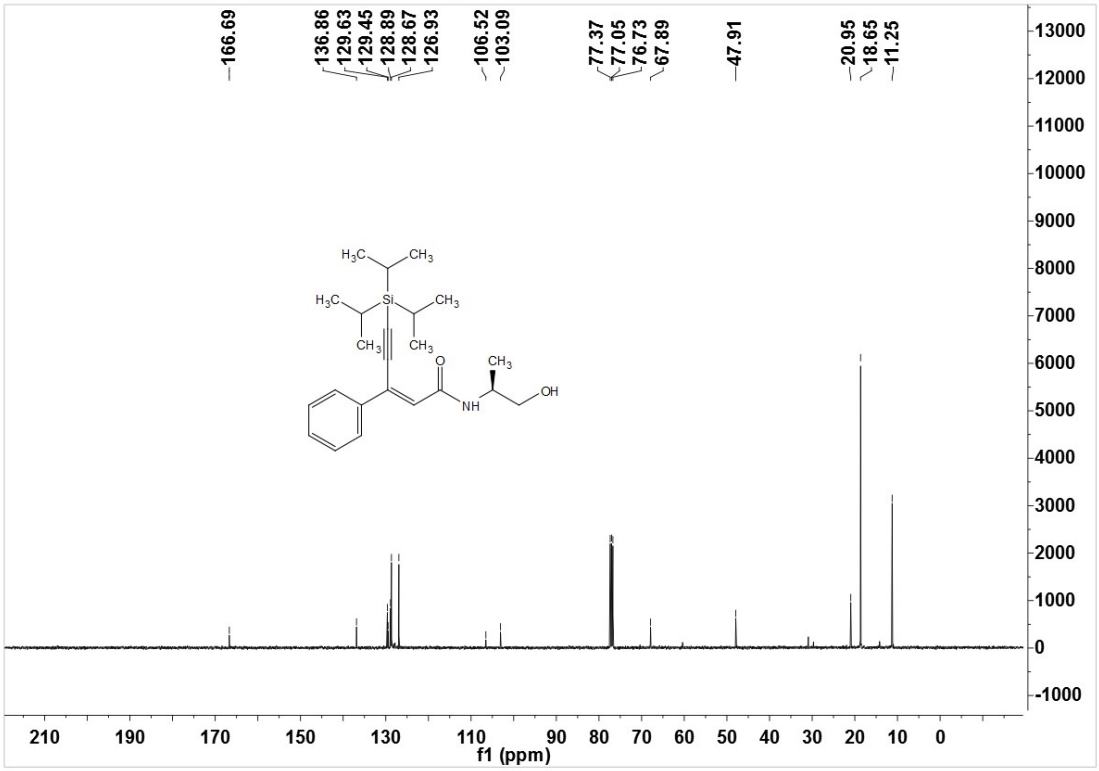
Methyl (*Z*)-(3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynoyl)-L-valinate (7j)



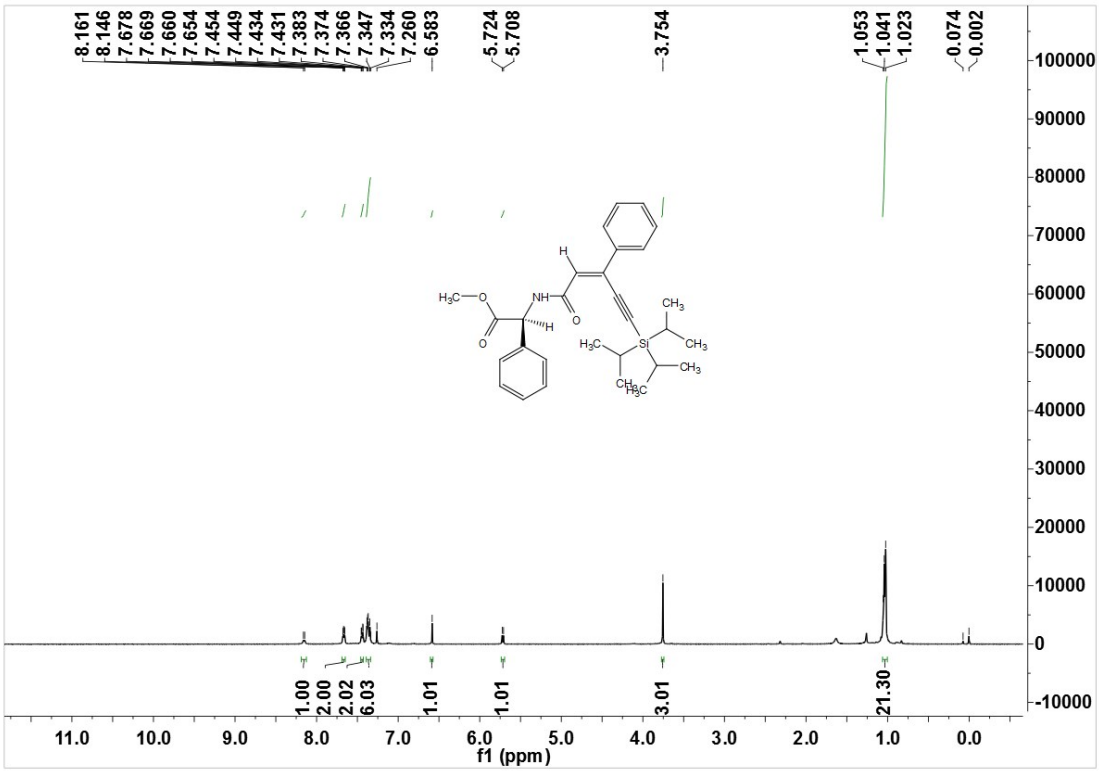


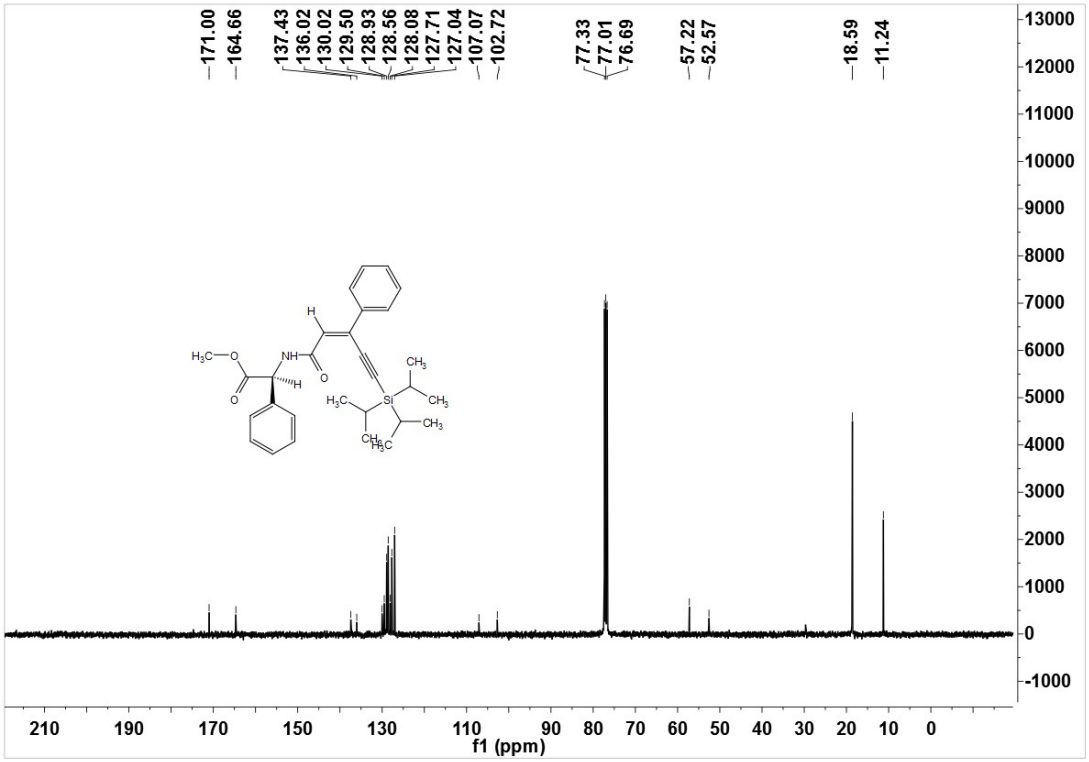
(*S*,*Z*)-*N*-(1-Hydroxypropan-2-yl)-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7k)



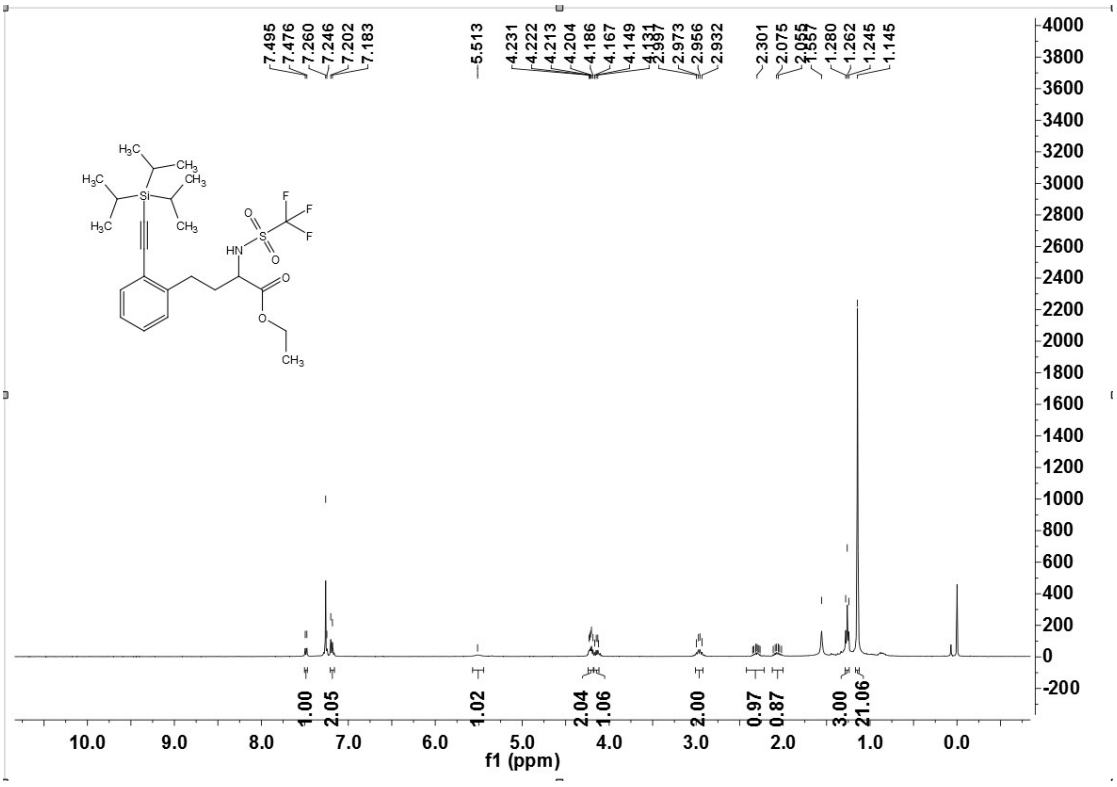


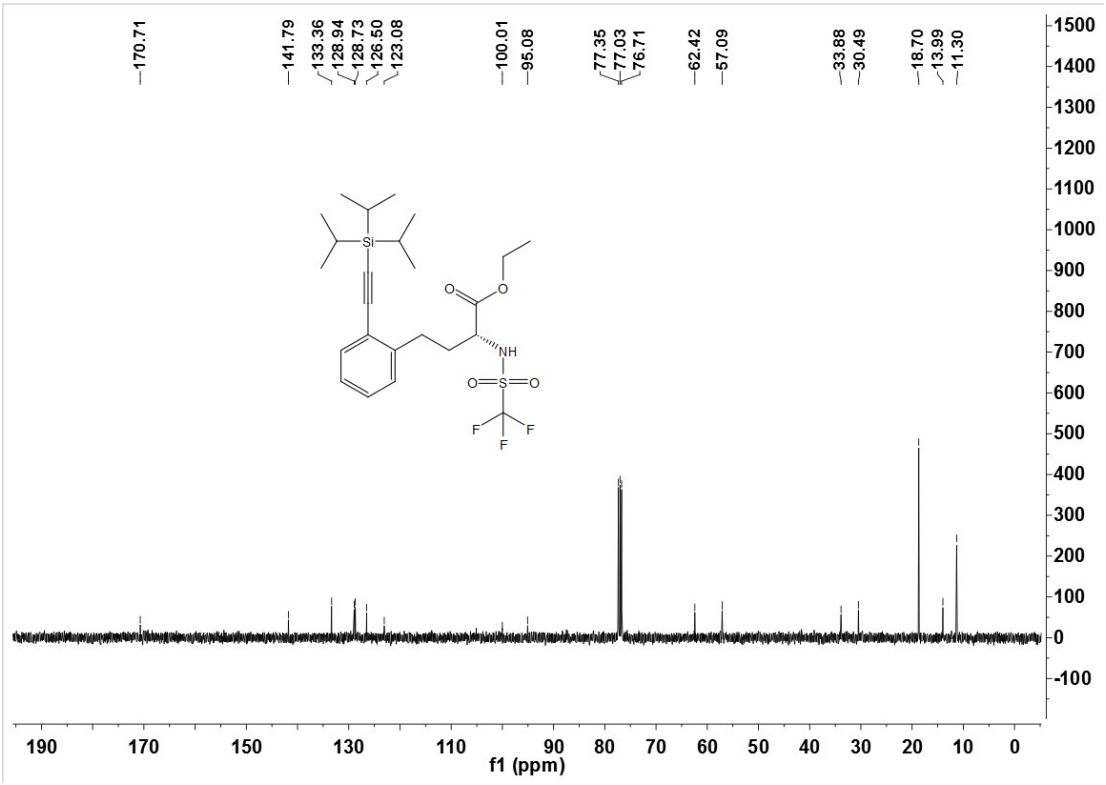
Methyl (*S*, *Z*)-2-phenyl-2-(3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamido) acetate (7l)

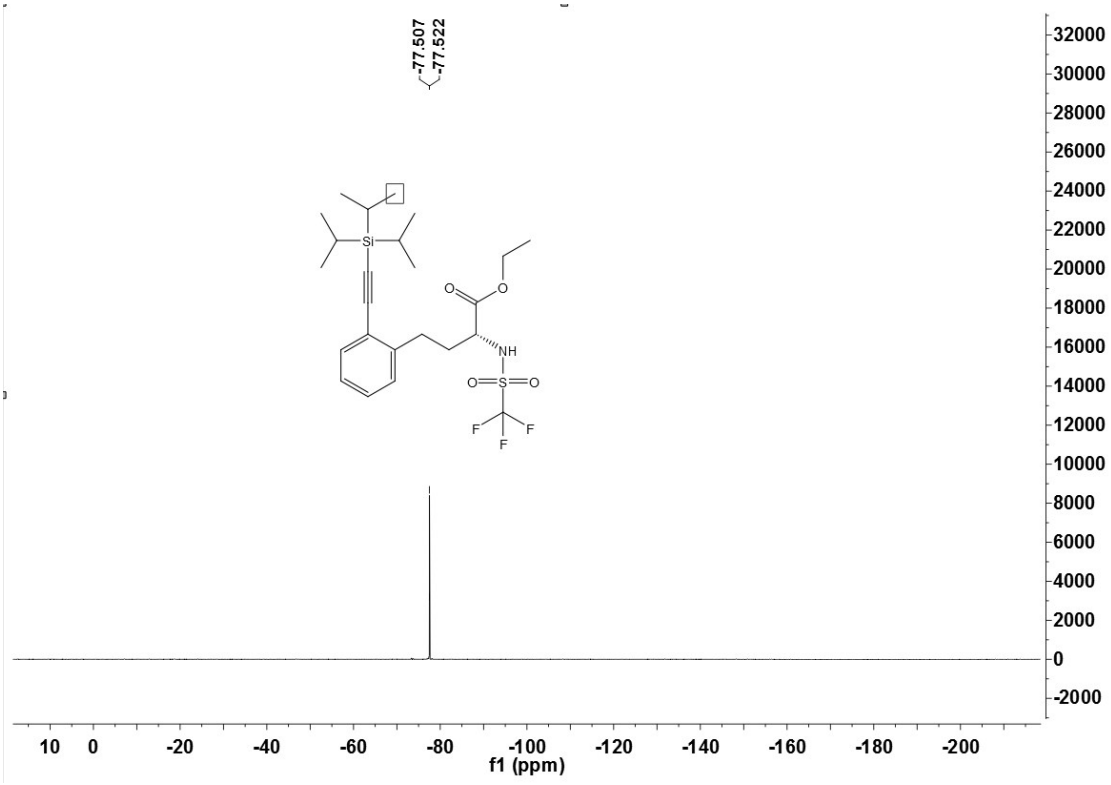




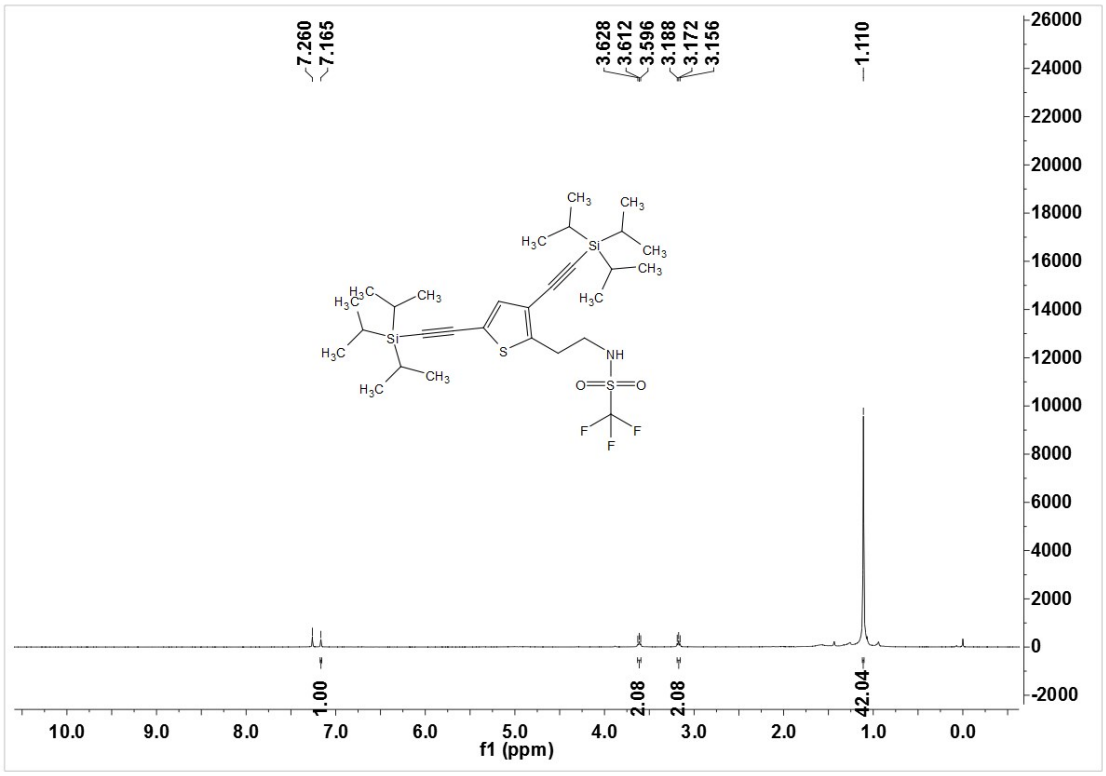
Methyl (*R*)-2-((trifluoromethyl)sulfonamido)-4-(2-((triisopropylsilyl)ethynyl) phenyl)butanoate (9)

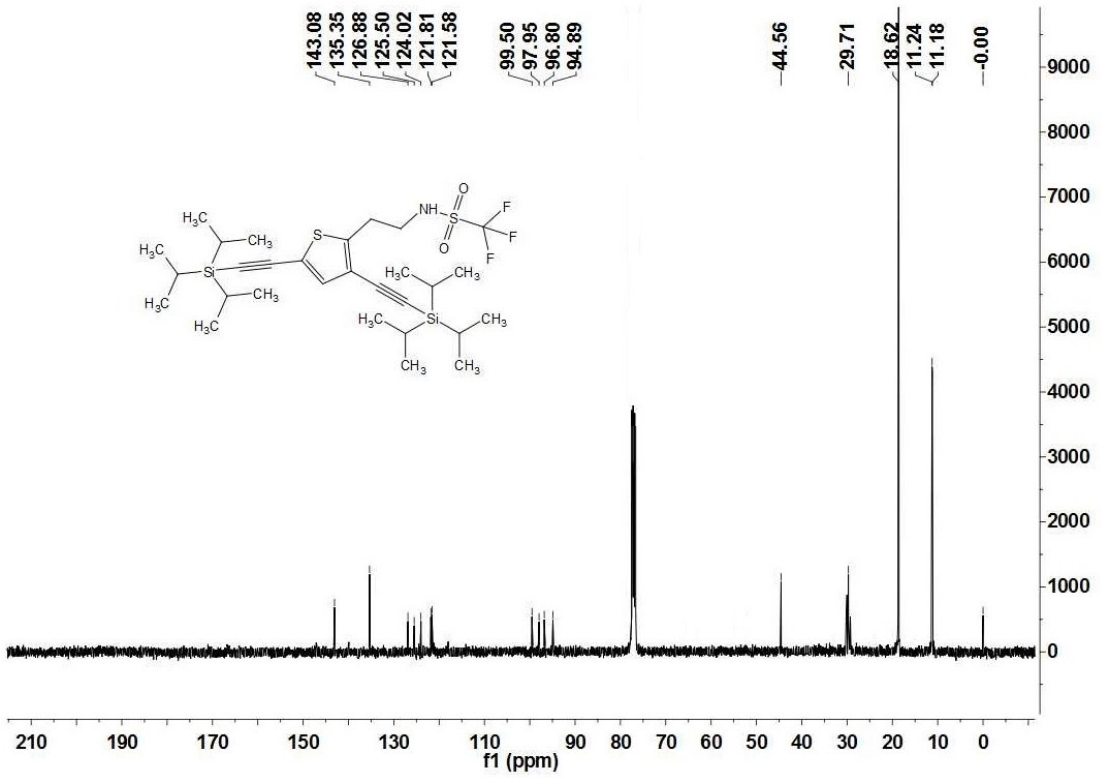


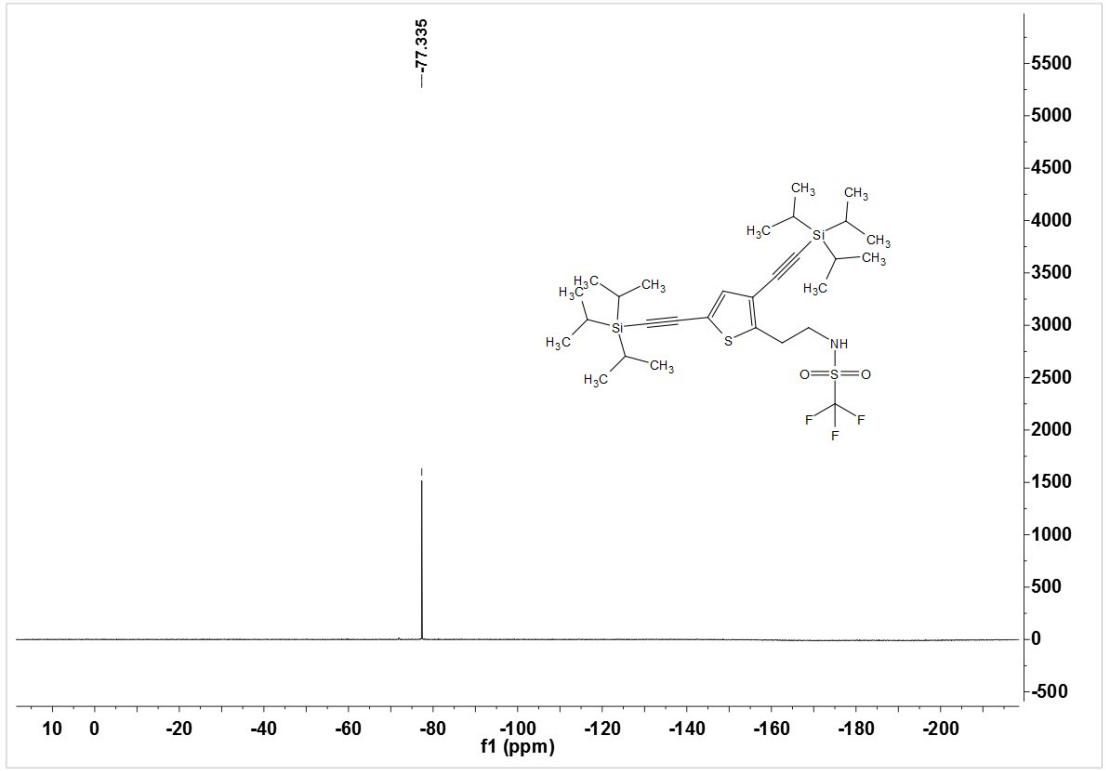




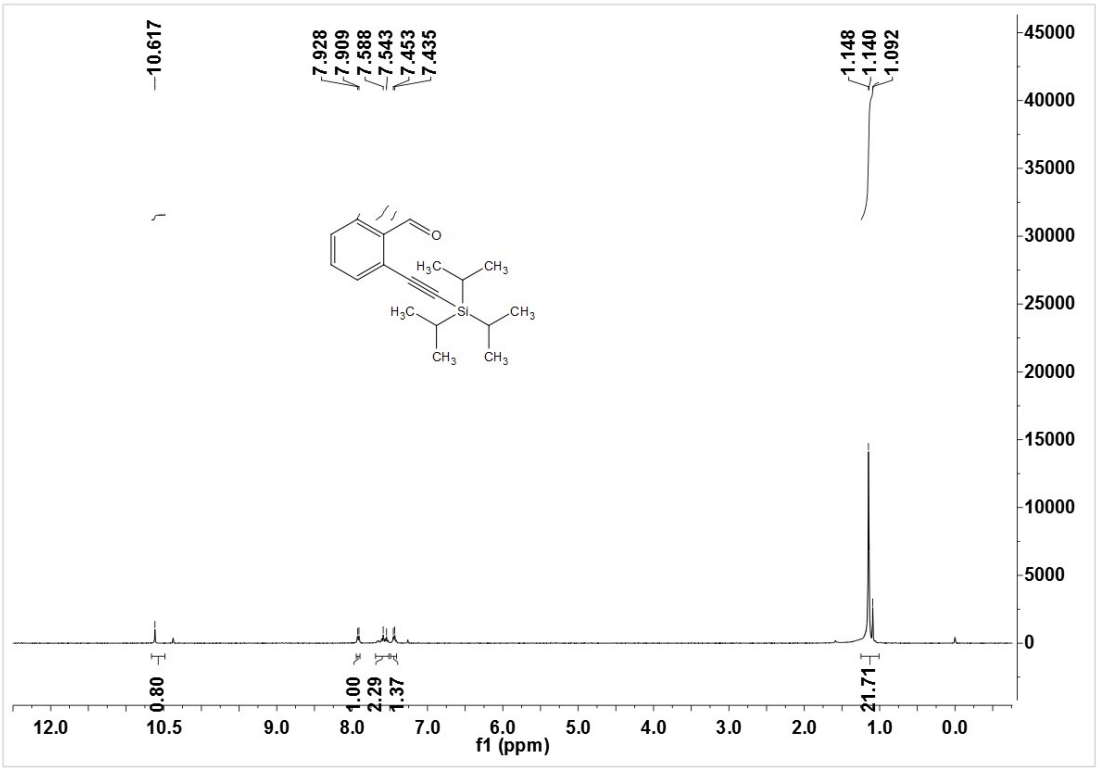
_N_-(2-(3,5-Bis((triisopropylsilyl)ethynyl)thiophen-2-yl)ethyl)-1,1,1-tifluoromethanesulfonamide (3g-2)

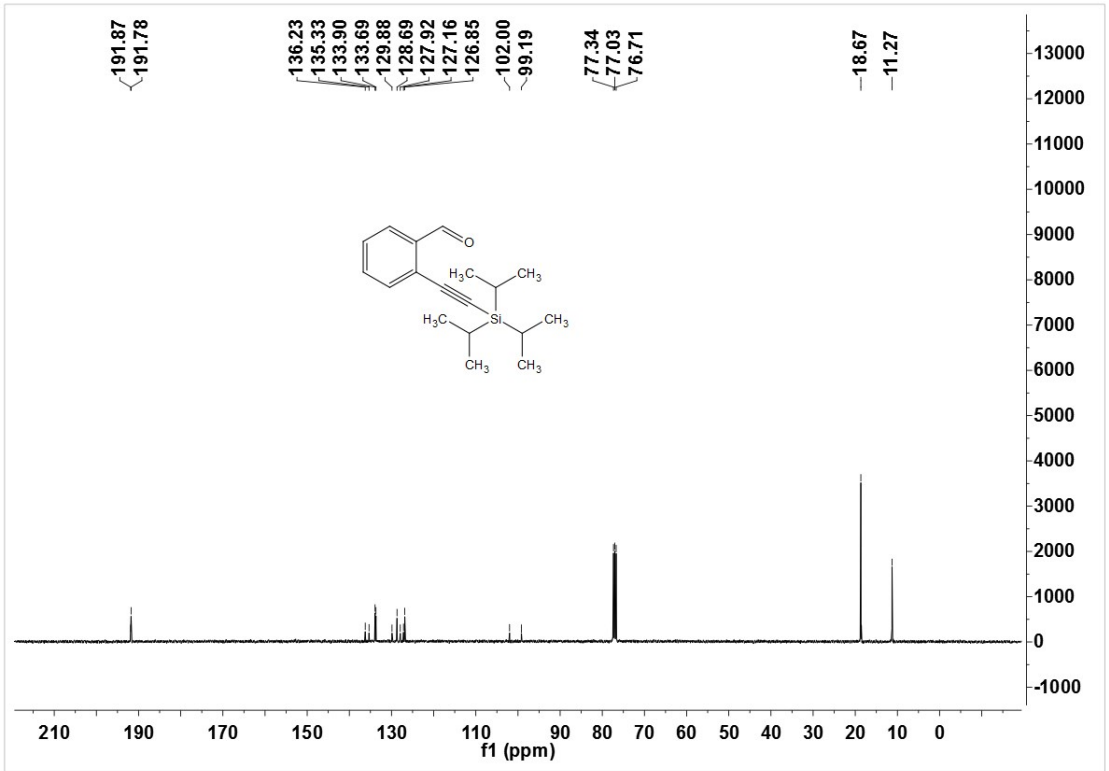



143.08
135.35
126.88
125.50
124.02
121.81
121.58
99.50
97.95
96.80
94.89
44.56
29.71
18.62
11.24
11.18
0.00
f1 (ppm)

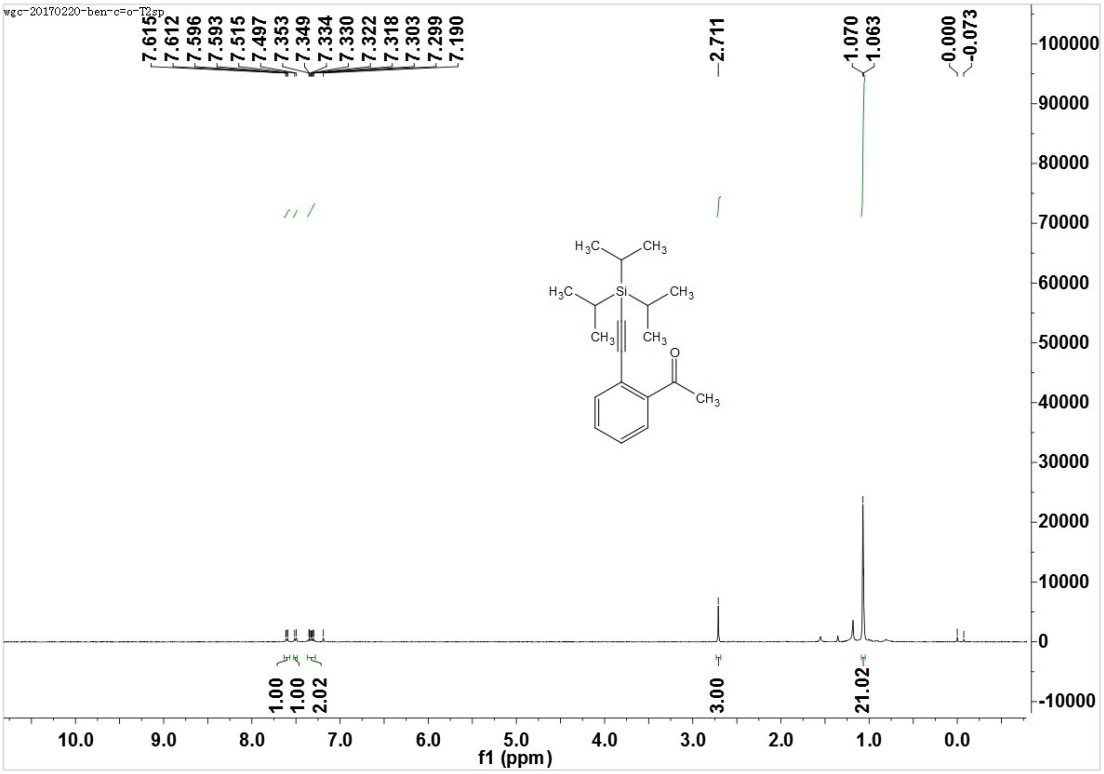

77.335
f1 (ppm)

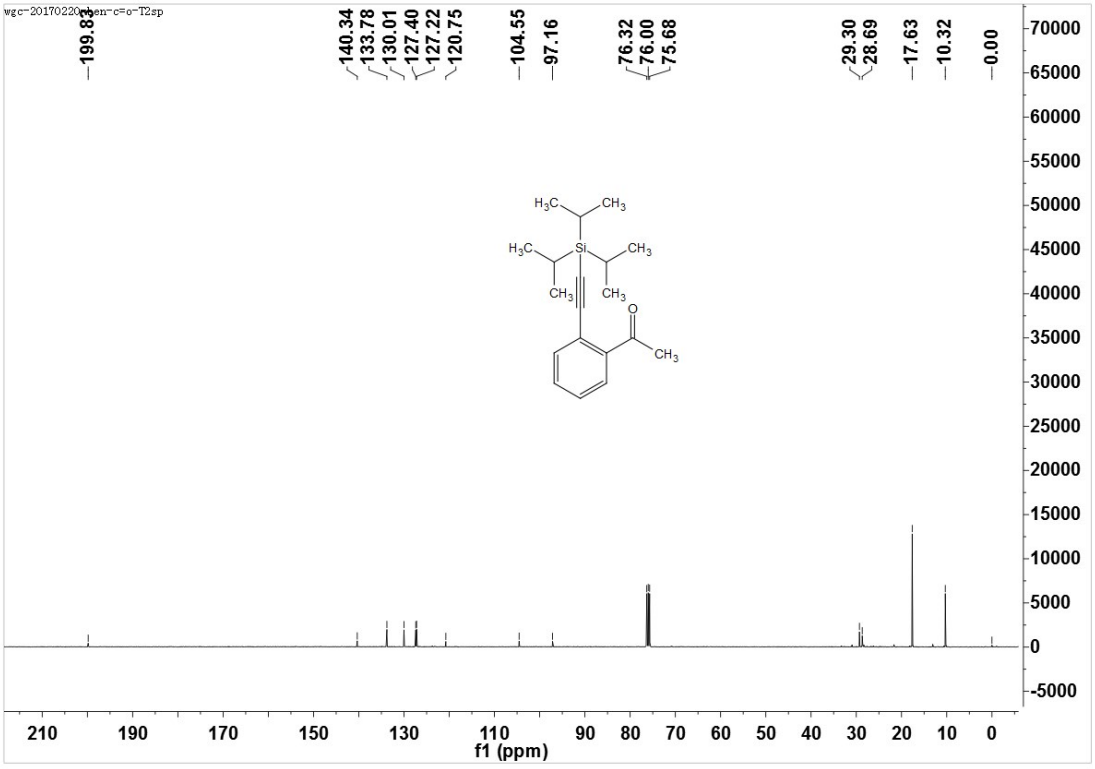
2-((Triisopropylsilyl)ethynyl)benzaldehyde (10)





1-(2-((Triisopropylsilyl)ethynyl)phenyl)ethan-1-one (7a-1)





Ethyl 2-((triisopropylsilyl)ethynyl)benzoate (7a-2)