Supporting Information

Cross-Dehydrogenative Alkynylation of Sulfonamides and Amides with Terminal Alkynes via Ir(III) Catalysis

Xianwei Li,[a*] Guocai Wu,[a] Wensen Ouyang,[a] Qian Chen,[a] Yanping Huo,[a]

[a] School of Chemical Engineering and Light Industry, Guangdong University of Technology, No. 100 Waihuan Xi Road Guangzhou, Higher Education Mega Center, Guangzhou, 510006, China.

E-mail: **xwli@gdut.edu.cn**

List of Contents

A. General information

^{1}H 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); dq (doublets of quartet). 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).

B. General procedure

General reaction procedure for the synthesis of amides:

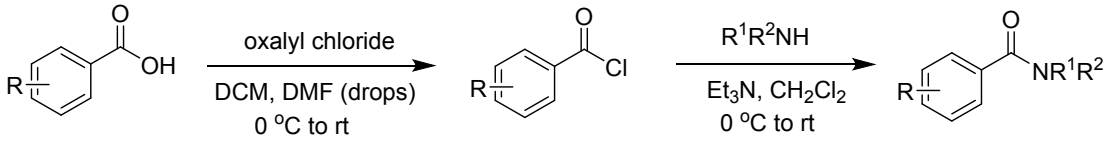


Fig SI-1. Synthesis of amides.

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.

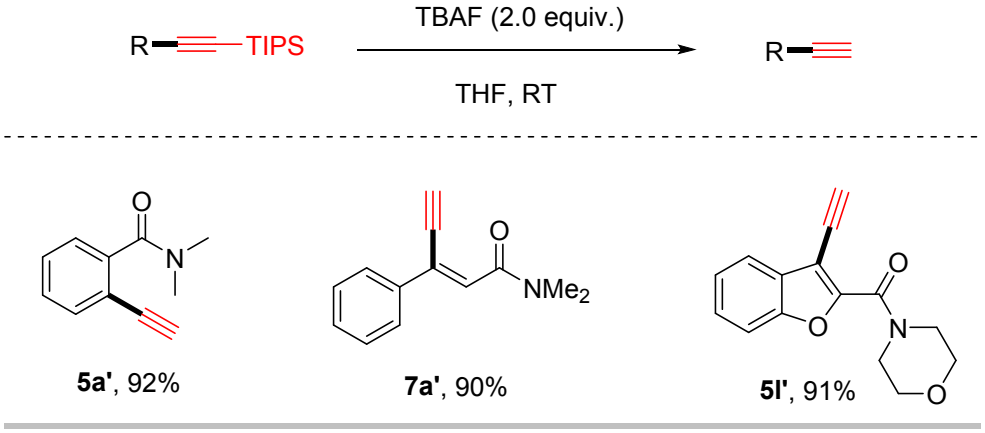
2) To a solution of amine R^1R^2NH (1 eq.) in a mixture of Et_3N (1 M), CH_2Cl_2 (1 M), the resulting solution was cooled to 0 ºC, followed by dropwise addition of the substituted benzoyl chloride (1.0 eq.). The reaction mixture was warmed to rt and stirred overnight. The organic phase was separated 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 Ir(III)-Catalyzed C-H alkynylation of sulfonamides:

An oven-dried 10 mL Schlenk Tube was charged with **1** (0.1 mmol), $[IrCp^*Cl_2]_2$ (0.004 mmol), $AgNTf_2$ (0.016 mmol), NaOAc (0.03 mmol), Cs_2CO_3 (0.05 mmol) and AgOAc (0.20 mmol) in sequence, followed by adding alkyne **2** (0.2 mmol) in DCE/HFIP (0.8/0.2 mL) through syringe. The resulting reaction mixture was stirred at 90 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**.

C. Desilylations of the obtained alkynes:

Terminal alkynes could be easily obtained from TIPS-substituted alkynes generated in this transformation, by treatment of TBAF in THF, terminal alkynes such as **5a'**, **5d'** and **7a'** were obtained in quantitive yield. The compounds (0.2 mmol) dissolved in freshly distilled THF (2 mL) was added TBAF (1M in THF, 2.0 equiv) under N_2. The reaction mixture was stirred at rt for 40 min until starting material disappeared on TLC. The mixture was filtered through Celite using CH_2Cl_2 (15 mL) and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate to give the desired product.



5a', 92% **7a'**, 90% **5l'**, 91%

Fig SI-2. Desilylations of the obtained alkynes

D. Mechanism studies

Preliminary KIE studies:

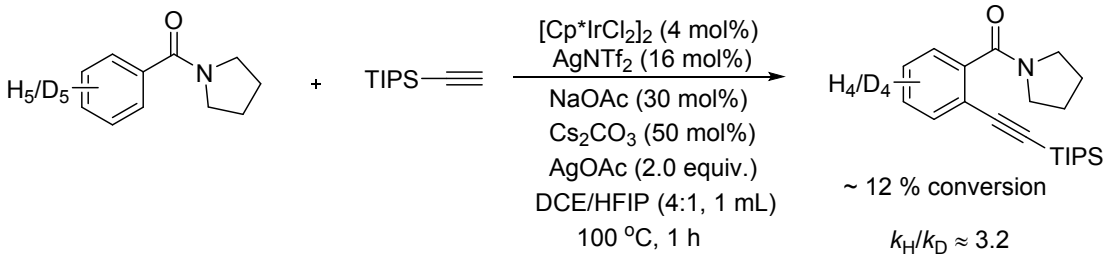


Fig SI-3. Preliminary KIE studies

$[Cp^*IrCl_2]_2$ (1.6 mg, 4.0 mol%), $AgNTf_2$ (6.2 mg, 16 mol%), NaOAc (4.9 mg, 0.03 mmol), Cs_2CO_3 (16.3 mg, 0.05 mmol) and AgOAc (33.4 mg, 0.2 mmol) in sequence, amide (**4d**) (17.5 mg, 0.10 mmol) or D5-**4d** (18.0 mg, 0.10 mmol), alkyne (**2**) (38.4 mg, 0.20 mmol) and DCE/HFIP (1.0 mL) were added in two separated Schlenk tubes. They were stirred at 100 ºC under Ar for 60 minutes, then immediately quenched with EtOAc at the same time. Then two reaction mixture were combined and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: Petroleum ether/ethyl acetate = 5: 1), a kinetic isotope effect (KIE) of $k_H/k_D \approx 3.2$ was observed.

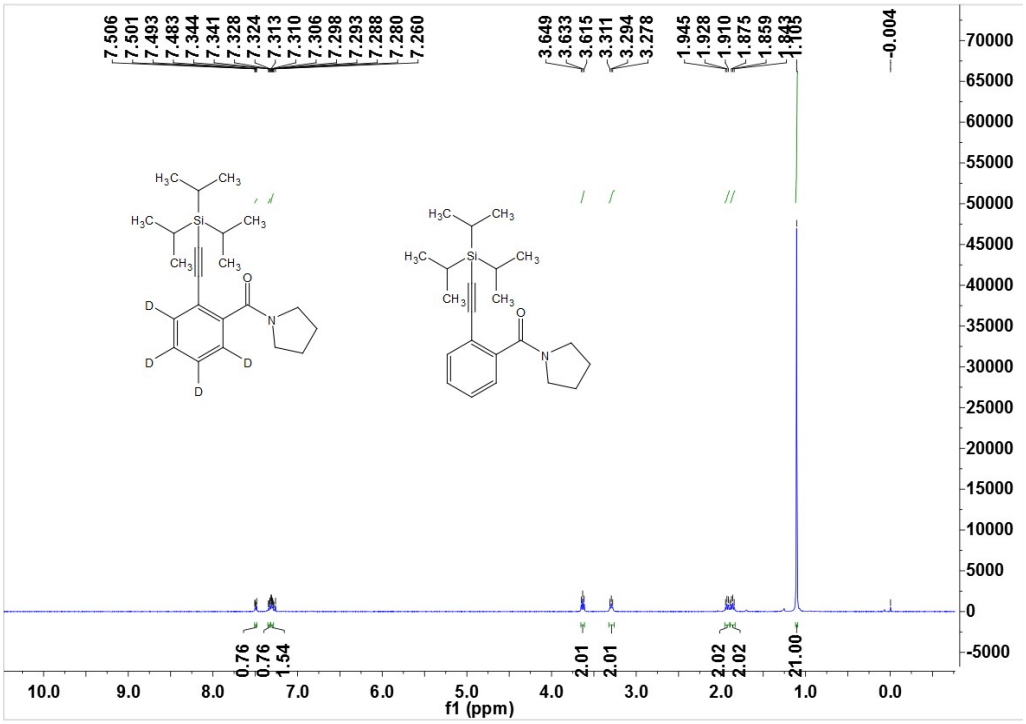


Fig SI-4. ^{1}H NMR of preliminary KIE studies

Silver acetylide in this transformation:

We also performed experiment with stoichoimetric silver acetylide in this catalytic C-H alkynylation with amide **4d**, as depict below, we found that the desired product **5d** was observed in 58% yield.

Silver acetylide in this transformation:

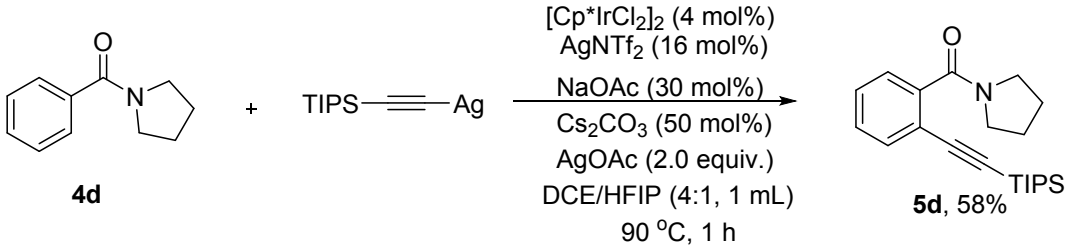


Fig SI-5. Silver acetylide in this transformation

Although further investigation is needed to elucidate the mechanism, a process that involved the C-H activation facilated by Ir^{III} catalyst, which was assisted by $AgNTf_2$ and ^{-}OAc ; On the other side, silver acetylide was generated in situ, which underwent transmetalation to afford alkynyl-Ir^{III} complex, subsequent reductive elimination to give the desired product.

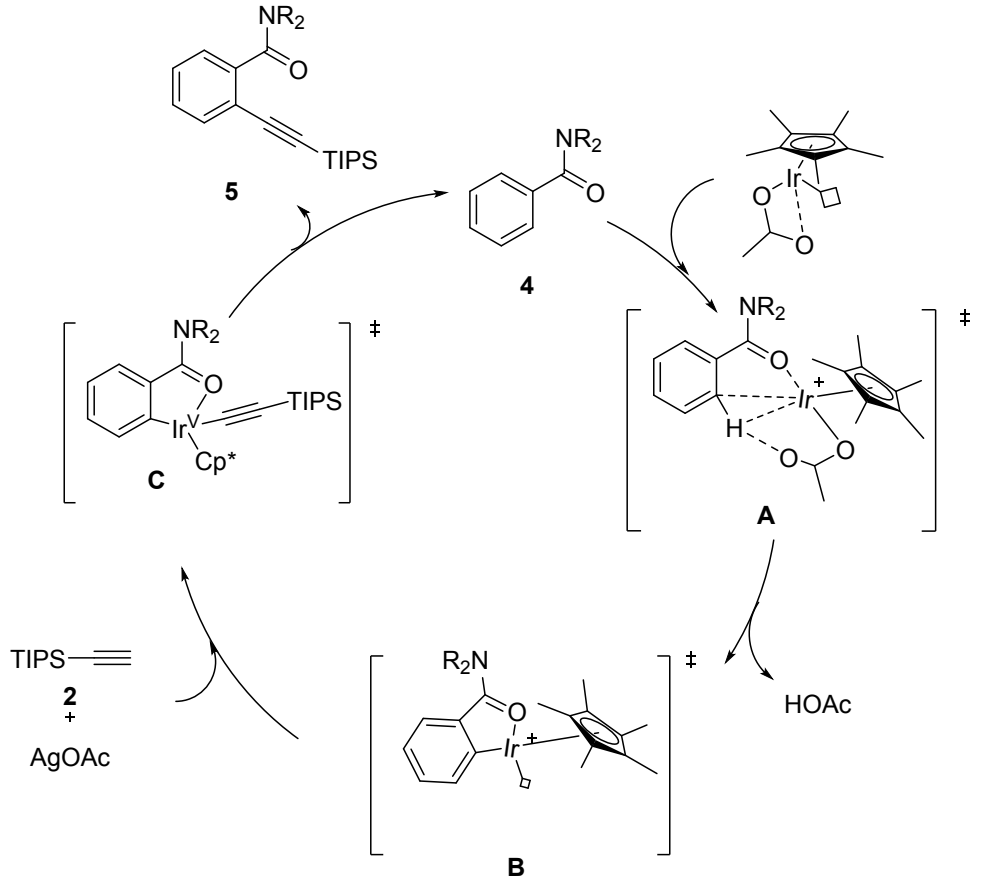
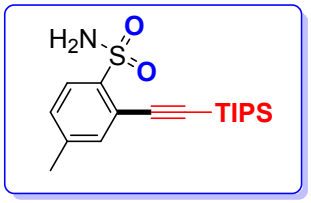
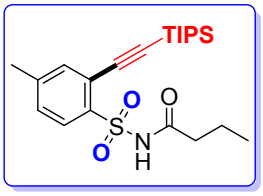


Fig SI-6. A tentive mechanism for this C-H alkynylation of sulfonamides and amides

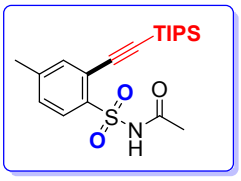
E. Analytical data for the alkynylated compounds



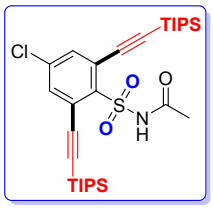
4-Methyl-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3a), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.90 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.24 (d, J = 8.0Hz, 1H), 5.25 (brs, 2H), 2.40 (s, 3H), 1.18-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 141.8, 139.9, 134.4, 128.3, 126.2, 119.3, 102.3, 100.0, 20.1, 17.6, 10.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{30}NO_2SSi$: 352.1761; Found: 352.1769.



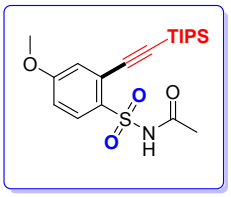
***N*-((4-Methyl-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)butyramide (3b), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.04 (d, J = 8.0 Hz, 1H), 7.44 (s, 1H), 7.28-7.26 (m, 1H), 2.40 (s, 3H), 2.23 (t, J = 7.6 Hz, 2H), 1.62-1.53 (m, 2H), 1.18-1.15 (m, 21H), 0.86 (t, J = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 171.0, 144.2, 137.0, 136.1, 130.4, 129.3, 121.3, 102.8, 100.7, 38.2, 21.2, 18.7, 17.8, 13.4, 11.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{36}NO_3SSi$: 422.2180, Found: 422.2184.



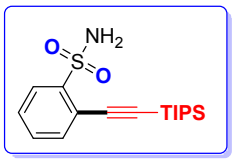
***N*-((4-Methyl-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3c), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.04 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.28 (d, J = 7.2 Hz, 1H), 2.41 (s, 3H), 2.07 (s, 3H), 1.19-1.15(m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.8, 144.4, 136.9, 136.1, 130.1, 129.3, 121.4, 102.6, 101.1, 23.3, 21.3, 18.7, 11.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{32}NO_3SSi$: 394.1867, Found: 394.1864.



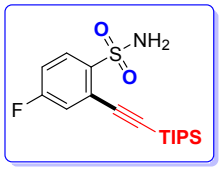
N*-((4-Chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3f), ^{1}H NMR (400 MHz, $CDCl_3$): *δ 7.55 (s, 2H), 2.18 (s, 3H), 1.17-1.13 (m, 42H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 168.5, 139.1, 138.2, 104.4, 135.4, 125.3, 101.5, 23.0, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{30}H_{49}ClNO_3SSi_2$: 594.2655, Found: 594.2653.



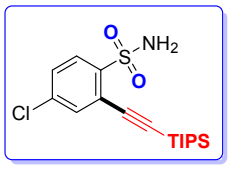
N*-((4-Methoxy-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3g), ^{1}H NMR (400 MHz, $CDCl_3$): *δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 6.95 (dd, *J* = 8.8Hz, 2.8 Hz, 1H), 3.87 (s, 3H), 2.07 (s, 3H), 1.19-1.16 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 167.7, 163.1, 132.5, 131.4, 123.4, 121.2, 113.5, 102.2, 101.3, 55.8, 23.3, 18.7, 11.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{32}NO_4SSi$: 410.1816, Found: 410.1818.



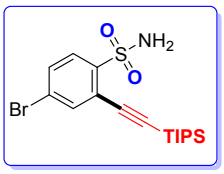
((Triisopropylsilyl)ethynyl)benzenesulfonamide (3h), **^{1}H NMR (400 MHz, $CDCl_3$): *δ*** 8.02 (dd, *J* = 7.8 Hz, 1.0 Hz 1H), 7.67-7.65 (m, 1H), 7.52 (td, *J* = 7.6 Hz, 1.2 Hz 1H), 7.46 (td, *J* = 7.6 Hz, 1.2 Hz 1H), 5.32 (brs, 2H), 1.18-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 142.5, 134.0, 131.0, 127.7, 126.1, 119.4, 102.2, 100.7, 17.6, 10.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{17}H_{28}NO_2SSi$: 338.1605; found: 338.1608.



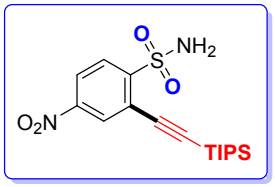
4-Fluoro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3i), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 8.8 Hz, 5.6 Hz, 1H), 7.33 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 7.15-7.10 (m, 1H), 5.26 (s, 2H), 1.18-1.13 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 164.3, 163.2, 138.8, 128.9, 128.8, 122.1, 122.0, 121.0, 120.8, 115.0, 114.8, 102.3, 100.8, 17.6, 10.3. **^{19}F NMR (376 MHz, $CDCl_3$): δ** -106.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{17}H_{27}FNO_2SSi$:356.1510, Found: 356.1515.



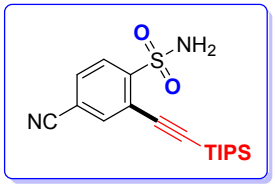
4-Chloro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3j), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.41 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 5.27 (s, 2H), 1.18-1.15 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 142.0, 138.4, 134.6, 128.8, 128.6, 122.2, 103.4, 101.8, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{17}H_{27}ClNO_2SSi$: 372.1215, Found: 372.1217.



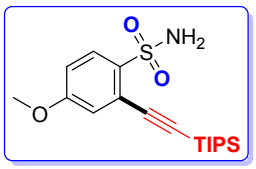
4-Bromo-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3k), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.58 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 5.26 (s, 2H), 1.18-1.13 (m, 21H).**^{13}C NMR (100 MHz, $CDCl_3$): δ** 142.5, 137.4, 131.8, 128.6, 126.5, 122.2, 103.5, 101.7, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{17}H_{27}BrNO_2SSi$: 416.0710, Found: 416.0713.



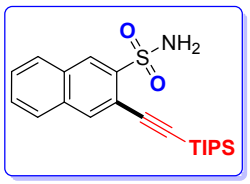
4-Nitro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3l), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 2.0 Hz, 1H), 8.26 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 5.37 (s, 2H), 1.18-1.15 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 149.5, 148.5, 129.6, 128.7, 123.2, 122.5, 105.7, 101.0, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{17}H_{27}N_2O_4SSi$: 383.1455, Found: 383.1458.



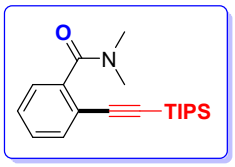
4-Cyano-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3m), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.72 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 5.37 (s, 2H), 1.18-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 147.1, 138.1, 131.7, 128.0, 122.0, 116.5, 116.3, 105.4, 100.9, 18.6, 18.3, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2O_2SSi$: 363.1557, Found: 363.1560.



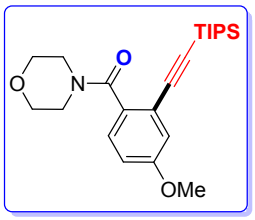
4-Methoxy-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3n), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.91 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 5.21 (s, 2H), 3.87 (s, 3H), 1.18-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 162.0, 135.8, 129.3, 122.1, 120.4, 113.6, 103.0, 101.3, 55.8, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{30}NO_3SSi$: 368.1710, Found: 368.1713.



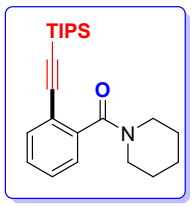
3-((Triisopropylsilyl)ethynyl)naphthalene-2-sulfonamide (3o), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.14 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.67-7.59 (m, 2H), 5.36 (s, 2H), 1.12 -1.18 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 139.4, 135.8, 134.0, 131.3, 129.4, 129.3, 128.5, 128.3, 127.5, 115.9, 103.8, 99.5, 18.7, 11.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{30}NO_2SSi$: 388.1761, Found: 388.1764.



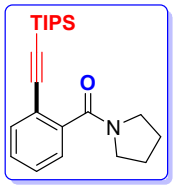
***N*, *N*-Dimethyl-2-((triisopropylsilyl)ethynyl)benzamide (5a), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.50-7.48 (m, 1H), 7.35-7.27 (m, 3H), 3.09 (s, 3H), 2.89 (s, 3H), 1.11 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 170.0, 139.9, 132.8, 128.8, 128.5, 126.4, 120.2, 104.0, 94.2, 38.3, 34.8, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M+ H]^+$ Calcd for $C_{20}H_{32}NOSi$: 330.2248, Found: 330.2249.



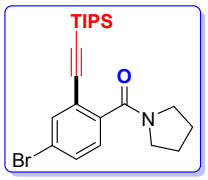
(4-Methoxy-2-((triisopropylsilyl)ethynyl)phenyl)(morpholino)methanone (5b), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.8 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 8.8, 2.8 Hz, 1H), 4.03 (brs, 1H), 3.80 (s, 3H), 3.67-3.27 (m, 7H), 1.11-1.09 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 168.9, 159.9, 131.6, 128.4, 122.0, 118.0, 115.5, 104.1, 95.1, 67.3, 67.1, 55.8, 47.7, 42.4, 19.0, 11.6. **HRMS (ESI-TOF) m/z**: $[M + Na]^+$ Calcd for $C_{23}H_{35}NNaO_3Si$: 424.2278; found: 424.2280.



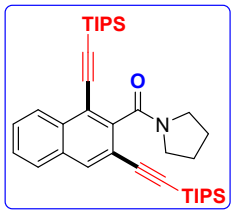
Piperidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone (5c), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.50-7.47 (m, 1H), 7.35-7.28 (m, 2H), 7.25-7.24(m, 1H), 4.09 (d, *J* = 12.8 Hz, 1H), 3.34–3.29 (m,1H), 3.23–3.14 (m,2H), 1.68(s, 3H), 1.57 (d, *J* = 7.2 Hz,3H), 1.11 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 168.3, 139.9, 133.0, 128.6, 128.3, 126.1, 120.3, 104.1, 94.4, 47.9, 42.5, 26.5, 25.5, 24.6, 18.7, 11.3. **HRMS (ESI-TOF) m/z**: $[M+ H]^+$ Calcd for $C_{23}H_{36}NOSi$: 370.2561, Found: 370.2565.



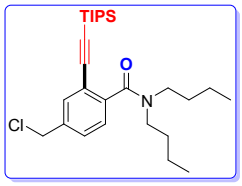
Pyrrolidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone (5d), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.50-7.48 (m, 1H), 7.36-7.32 (m, 1H), 7.31-7.27 (m, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 1.96-1.89 (m, 2H), 1.87-1.82 (m, 2H), 1.10 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 168.3, 141.0, 133.0, 128.7, 128.5, 126.1, 120.0, 104.2, 94.0, 47.8, 45.6, 25.9, 24.5, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M +Na]^+$ Calcd for $C_{22}H_{33}NNaOSi$: 378.2224, found: 378.2229.



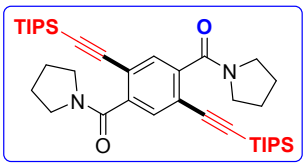
(4-Bromo-2-((triisopropylsilyl)ethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.62 (d, *J* = 2.0 Hz, 1H), 7.47 (dd, *J* = 2.0 Hz, 8.0 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 3.60 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.4 Hz, 2H), 1.94-1.85 (m, 4H), 1.09 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 167.4, 139.8, 135.5, 131.9, 127.8, 122.3, 122.0, 102.6, 96.0, 47.8, 45.7, 25.9, 24.5, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{33}BrNOSi$: 434.1509, found: 434.1513.



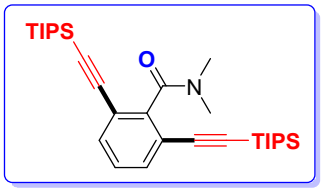
(1,3-Bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)(pyrrolidin-1-yl)methanone (5f), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.35 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.60-7.50 (m, 2H), 3.69 (t, *J* = 6.8 Hz, 2H), 3.28-3.22 (m, 2H), 1.95-1.85 (m, 4H), 1.17-1.13 (m, 42H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.0, 141.8, 133.9, 133.2, 132.6, 128.4, 128.3, 127.7, 126.8, 118.3, 118.0, 104.1, 101.7, 100.6, 94.3, 47.8, 45.8, 26.3, 24.9, 19.1, 19.0, 11.69, 11.65. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{37}H_{56}NOSi_2$: 586.3895, Found: 586.3902.



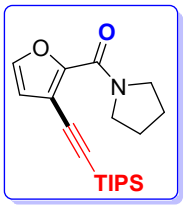
***N,N*-Dibutyl-4-(chloromethyl)-2-((triisopropylsilyl)ethynyl)benzamide (5g)**, **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.49 (d, *J* = 1.2 Hz, 1H), 7.35 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.54 (s, 2H), 3.44 (brs, 2H), 3.09 (brs, 2H), 1.78 (s, 1H), 1.69-1.61 (m, 2H), 1.42-1.35 (m, 3H), 1.25 (s, 1H), 1.10 (s, 21H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 169.4, 140.4, 137.9, 133.5, 128.9, 127.2, 121.1, 103.9, 95.5, 49.0, 45.5, 45.3, 31.2, 30.2, 20.8, 20.1, 19.0, 14.2, 13.9, 11.6. **HRMS (ESI-TOF) m/z**: $[M + Na]^+$ Calcd for $C_{27}H_{45}ClNOSi$: 462.2953; found: 462.2957.



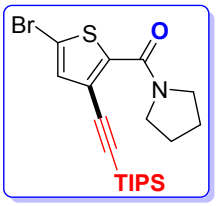
(2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(pyrrolidin-1-ylmethanone) (5h), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.45 (s, 2H), 3.61 (t, *J* = 6.8 Hz, 4H), 3.30 (s, 4H), 1.95-1.91 (m, 4H), 1.90-1.86 (m, 4H), 1.09 (s, 42H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.0, 141.0 , 130.9, 120.4, 103.2, 97.2, 47.9, 45.8, 25.9, 24.5, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{38}H_{61}N_2O_2Si_2$: 633.4266, Found: 633.4268.



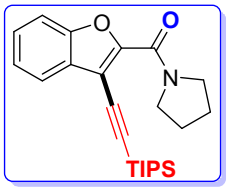
***N*,*N*-Dimethyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5i)**, **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.44 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 3.07 (s, 3H), 2.86 (s, 3H), 1.10 (s, 42H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 168.1, 142.9, 132.5, 127.9, 120.7, 103.3, 94.7, 37.6, 34.6, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{31}H_{52}NOSi_2$: 510.3582, Found: 510.3580.



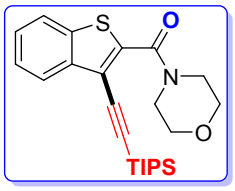
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)furan-2-yl)methanone (5j), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.37 (d, J = 1.6 Hz, 1H), 6.47 (d, J = 2.0 Hz, 1H), 3.78 (t, J = 6.0 Hz, 2H), 3.62 (t, J = 6.4 Hz, 2H), 1.90-1.89 (m, 4H), 1.10 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 158.6, 150.0, 142.8, 114.8, 110.3, 97.9, 97.6, 47.8, 46.5, 26.2, 24.1, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{32}NO_2Si$:346.2197 Found: 346.2203.



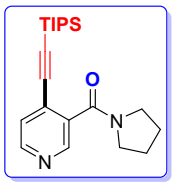
(5-Bromo-3-((triisopropylsilyl)ethynyl)thiophen-2-yl)(pyrrolidin-1-yl)methanone (5k), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 6.98 (s, 1H), 3.61 (d, J = 20.4 Hz, 4H), 1.91 (d, J = 2.4 Hz, 4H), 1.08 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 161.6, 143.1, 133.0, 122.0, 113.9, 99.6, 96.4, 48.6, 46.8, 26.3, 24.8, 18.9, 11.5. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{31}BrNOSSi$: 440.1074, Found: 440.1069.



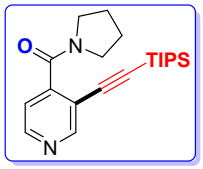
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)benzofuran-2-yl)methanone (5l), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.68 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.87 (brs, 2H), 3.68 (brs, 2H), 1.95-1.91 (m, 4H), 1.15 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 159.3, 153.9, 151.2, 128.6, 127.1, 124.1, 121.4, 112.2, 106.4, 101.3, 96.2, 48.2, 46.9, 26.5, 24.4, 18.9, 11.5. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{24}H_{34}NO_2Si$: 396.2353, Found: 396.2355.



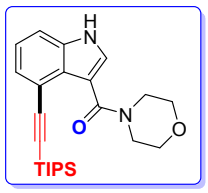
Morpholino(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)methanone (5m), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.92 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.49-7.41 (m, 2H), 3.73 (brs, 8H), 3.68 (s, 2H), 1.19-1.16 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 163.3, 139.4, 139.2, 138.6, 126.5, 125.7, 124.0, 122.7, 117.7, 98.9, 98.7, 67.2, 48.4, 43.2, 19.0, 11.6. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{24}H_{34}NO_2SSi$: 428.2074, Found: 428.2076.



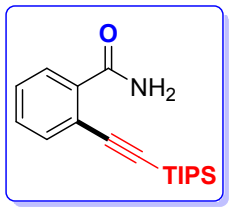
Pyrrolidin-1-yl(4-((triisopropylsilyl)ethynyl)pyridin-3-yl)methanone (5n), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.61 (d, *J* = 3.6 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.30-7.27(m, 1H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.31 (brs, 2H), 1.96-1.89 (m, 4H), 1.12 (s, 21H). **^{13}C NMR (101 MHz, $CDCl_3$): δ** 166.4, 150.1, 139.0, 134.3, 127.8, 123.0, 103.3, 95.3, 47.9, 45.9, 26.0, 24.5, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{33}N_2OSi$: 357.2357, Found: 357.2361.



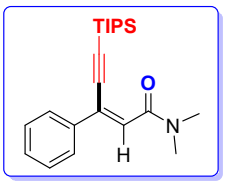
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)pyridin-4-yl)methanone (5o), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.73 (s, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.28 (t, *J* = 6.4 Hz, 2H), 1.96–1.93 (m, 2H), 1.91–1.88 (m, 2H), 1.11 (s, 20H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 165.9, 153.6 149.1, 147.5, 120.1, 116.6, 100.8, 98.4, 47.7, 45.7, 25.9, 24.4, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{21}H_{33}N_2OSi$:357.2357, Found: 357.2361.



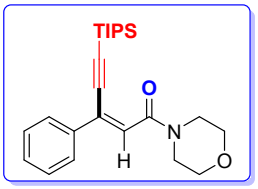
Morpholino(2-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)methanone (5p), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.75-8.69 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.24–7.22 (m, 1H), 7.18–7.15 (m, 1H), 3.71 (brs, 8H), 1.17–1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 165.5, 135.6, 126.5, 124.8, 121.9, 120.8, 118.0, 116.2, 111.2, 100.0, 97.2, 67.6, 30.0, 19.0, 11.6. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{24}H_{35}N_2O_2Si$: 411.2462, Found: 411.2466.



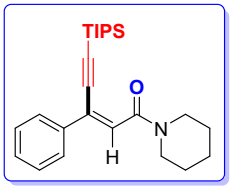
2-((Triisopropylsilyl)ethynyl)benzamide (5q), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 8.18-8.16 (m, 1H), 7.87 (brs, 1H), 7.59-7.56 (m, 1H), 7.46-7.43 (m, 2H), 5.84 (brs, 1H), 1.16-1.14 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.9, 134.7, 134.5, 131.4, 130.9, 129.4, 120.6, 106.1, 99.6, 19.0, 11.6. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{18}H_{28}NOSi$: 302.1935, found: 302.1939.



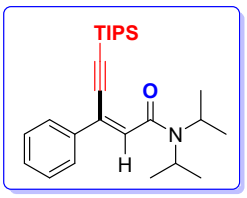
***(Z)*-*N*,*N*-Dimethyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7a)**, **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.69-7.67 (m, 2H), 7.39-7.33 (m, 3H), 6.68 (s, 1H), 3.13 (s, 3H), 3.03 (s, 3H), 1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 167.8, 136.3, 128.9, 128.5, 128.0, 127.4, 126.3, 102.4, 99.7, 37.9, 34.7, 18.6, 11.3. **HRMS (ESI-TOF) m/z**:[M +Na]$^+$ Calcd for $C_{22}H_{33}NNaOSi$: 378.2224, found: 378.2229.



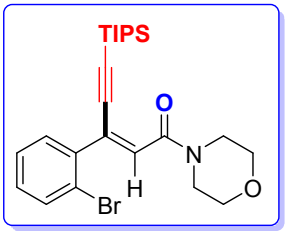
(*Z*)-1-Morpholino-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7b), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.68 (dd, *J* = 8.0Hz, 2.0 Hz, 2H), 7.39-7.34 (m, 3H), 6.67 (s, 1H), 3.72 (brs, 4H), 3.67 (d, *J* = 4.4 Hz, 2H), 3.63 (d, *J* = 4.8 Hz, 2H), 1.13-1.12 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 166.3, 136.1, 129.1, 128.6, 128.2, 126.9, 126.3, 102.2, 100.6, 67.1, 66.7, 47.0, 41.8, 18.7, 11.3. **HRMS (ESI-TOF) m/z**:[M +H]$^+$ Calcd for $C_{24}H_{36}NO_2Si$: 398.2510, found: 398.2514.



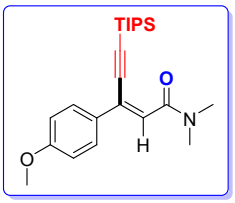
***(Z)*-3-Phenyl-1-(piperidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7c)**, **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.68 (d, *J* = 6.4 Hz, 2H), 7.38-7.32 (m, 3H), 6.70 (s, 1H), 3.65-3.63 (m, 2H), 3.54 (t, *J* = 5.6 Hz 2H), 1.65-1.57 (m, 6H), 1.53-1.12 (m, 21H).**^{13}C NMR (100 MHz, $CDCl_3$): δ** 166.1, 136.4, 128.8, 128.5, 128.3, 127.1, 126.3, 102.5, 99.6, 47.7, 42.4, 26.8, 25.4, 24.6, 18.7, 11.3. **HRMS (ESI-TOF) m/z**: [M + H]$^+$ Calcd for $C_{25}H_{38}NOSi$: 418.2537, Found: 418.2531.



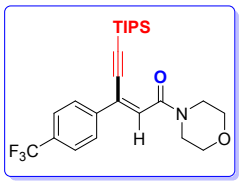
***(Z)*-*N*,*N*-Diisopropyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7d)**, **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.70-7.68 (m, 2H), 7.38-7.32 (m, 3H), 6.71 (s, 1H), 4.13-4.07 (m, 1H), 3.59-3.53 (m, 1H), 1.47 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.4 Hz, 3H), 1.12 (s, 21H).**^{13}C NMR (100 MHz, $CDCl_3$): δ** 166.5, 137.1, 130.3, 128.5, 128.4, 126.3, 126.1, 102.7, 99.0, 50.2, 45.6, 21.2, 20.6, 18.7, 11.4. **HRMS (ESI-TOF) m/z**:$[M+H]^+$ Calcd for $C_{26}H_{42}NOSi$: 412.3030, found: 412.3036.



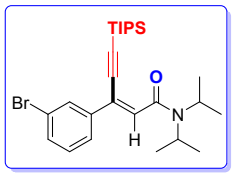
(*E*)-3-(2-Bromophenyl)-1-morpholino-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7e), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.85 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.66 (s, 1H), 3.72 (brs, 4H), 3.68-3.67 (m, 2H), 3.60 (brs, 2H), 1.13-1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 165.8, 138.2, 131.9, 130.0, 129.7, 127.7, 126.9, 124.7, 122.7, 101.6, 101.4, 67.0, 66.7, 47.0, 41.8, 18.7, 11.3. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{24}H_{35}BrNO_2Si$: 476.1615, Found: 476.1624.



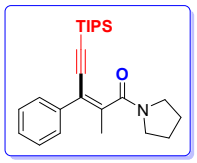
(*Z*)-3-(4-Methoxyphenyl)-*N*, *N*-dimethyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7f), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.61 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.57 (s, 1H), 3.81 (s, 3H), 3.12 (s, 3H), 3.01 (s, 3H), 1.11 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 168.0, 160.3, 128.8, 127.6, 126.9, 126.1, 113.9, 102.7, 99.4, 55.3, 38.0, 34.7, 18.6, 11.3. **HRMS (ESI-TOF) m/z**:$[M+H]^+$ Calcd for $C_{23}H_{36}NO_2Si$: 386.2510, found: 386.2513.



(*Z*)-1-Morpholino-3-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7g), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 6.74 (s, 1H), 3.73 (brs, 4H), 3.69 (t, J = 4.0 Hz, 2H), 3.61 (d, J = 4.4 Hz, 2H), 1.14-1.11 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 165.7, 139.6, 131.1, 130.8, 128.7, 127.0, 126.7, 125.6 (q, $J_{C\text{-}F}$ = 3Hz), 101.6, 101.5, 67.0, 66.7, 46.9, 41.8, 18.7, 11.3. **^{19}F NMR (300 MHz, $CDCl_3$)** δ -63.5. **HRMS (ESI-TOF) m/z**:[M +H]$^+$ Calcd for $C_{25}H_{35}F_3NO_2Si$: 466.2384, found: 466.2387.

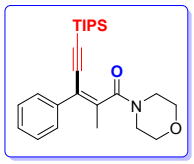


(*Z*)-3-(3-Bromophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7h), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.86 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 6.70 (s, 1H), 4.09-4.04 (m, 1H), 3.59-3.54 (m, 1H), 1.47 (d, J = 6.8 Hz, 6H), 1.22 (d, J = 6.4 Hz, 6H), 1.07-1.12 (m, 21H). **^{13}C NMR (100MHz, $CDCl_3$):** δ 166.0, 139.2, 131.4, 131.0, 129.9, 129.7, 124.72, 124.68, 122.6, 102.1, 99.9, 50.3, 45.7, 29.7, 21.2, 20.5, 18.7, 11.4. **HRMS (ESI-TOF) m/z**:[M +H]$^+$ Calcd for $C_{26}H_{41}BrNOSi$: 490.2135, found: 490.2132.

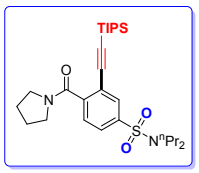


(*Z*)-2-Methyl-3-phenyl-1-(pyrrolidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7i), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 6.77 (s, 1H), 3.62–3.55 (m, 4H), 1.95-1.90 (m, 4H), 1.25 (s, 3H), 1.14–1.08 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.0, 141.6, 137.2, 128.9, 128.1, 127.7, 121.4, 105.6, 94.1, 46.7, 45.4,

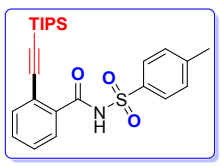
26.0, 24.4, 18.6, 17.3, 11.30. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{25}H_{37}NOSi$: 418.2537, Found: 418.2531.



(*Z*)-2-Methyl-1-morpholino-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7j), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40-7.36 (m, 4H), 7.34-7.30 (m, 1H), 3.79- 3.59(m, 8H), 2.01 (s, 3H), 1.02-1.12(m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 170.3, 139.1, 136.8, 128.9, 128.2, 127.9, 122.1, 105.1, 95.5, 67.1, 66.7, 46.5, 41.6, 18.7, 17.9, 11.4. **HRMS (ESI-TOF) m/z**:$[M+H]^+$ Calcd for $C_{25}H_{38}NO_2Si$: 412.2666, found: 412.2669.

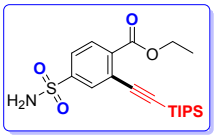


***N,N*-dipropyl-4-(pyrrolidine-1-carbonyl)-3-((triisopropylsilyl)ethynyl)benzene sulfonamide (9a)**, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (d, J = 1.2 Hz, 1H), 7.72 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 3.60 (t, J = 6.8 Hz, 2H), 3.22 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 7.2 Hz, 4H), 1.95-1.83 (m, 4H), 1.59-1.50 (m, 4H), 1.08 (s, 21H), 0.86 (t, J = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.2, 144.5, 140.9, 131.7, 127.3, 127.2, 121.5, 102.7, 97.2, 50.3, 48.1, 46.0, 26.2, 24.7, 22.3, 18.9, 11.5, 11.4. **HRMS (ESI-TOF) m/z**: $[M+H]^+$ Calcd for $C_{28}H_{47}N_2O_3SSi$: 519.3071, Found: 519.3081.

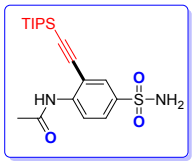


***N*-Tosyl-2-((triisopropylsilyl)ethynyl)benzamide (9b)**, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.82 (brs, 1H), 8.14 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 1.21-1.20 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.9, 145.2, 136.2, 135.4, 132.8, 131.33,

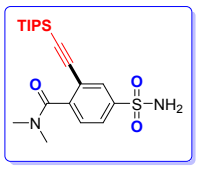
131.26, 129.7, 129.6, 129.1, 120.8, 105.1, 103.5, 22.0, 19.0, 11.5. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{25}H_{34}NO_3SSi$: 456.2023, Found: 456.2027.



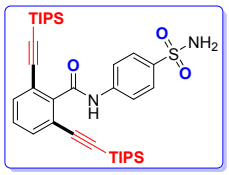
Ethyl 4-sulfamoyl-2-((triisopropylsilyl)ethynyl)benzoate (9c), ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.26 (d, *J* = 1.2 Hz, 1H), 8.11-8.08 (m, 2H), 5.33 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.17-1.15 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 164.6, 146.9, 135.9, 133.9, 129.4, 127.3, 120.8, 103.0, 102.4, 62.0, 18.6, 14.2, 11.3.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{32}NO_4SSi$: 410.1816, Found: 410.1815.



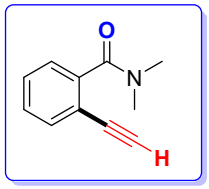
N*-(4-sulfamoyl-2-((triisopropylsilyl)ethynyl)phenyl)acetamide (9d), ^{1}H NMR (400 MHz, $CDCl_3$): *δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.65 (s, 1H), 7.49 (d, *J* = 8.8Hz, 1H), 5.31 (s, 2H), 2.20 (s, 3H), 1.17-1.12 (m, 21H). **^{13}C NMR (100 MHz, MeOD): *δ*** 170.8, 142.0, 138.6, 127.8, 124.7, 121.0, 118.6, 103.2, 99.6, 22.6, 17.7, 11.1. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{19}H_{31}N_2O_3SSi$: 395.1819, Found: 395.1816.



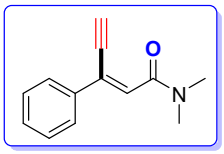
N*,*N*-Dimethyl-4-sulfamoyl-2-((triisopropylsilyl)ethynyl)benzamide (9e), ^{1}H NMR (400 MHz, $CDCl_3$): *δ 8.01 (d, *J* = 1.6 Hz, 1H), 7.84 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 3.03 (s, 3H), 2.88 (s, 3H), 1.11 (brs, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 168.8, 143.0, 142.8, 130.8, 126.9, 126.7, 121.1, 102.4, 96.7, 41.6, 38.2, 18.6, 11.2. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{20}H_{33}N_2O_3SSi$: 409.1976, Found: 409.1979.



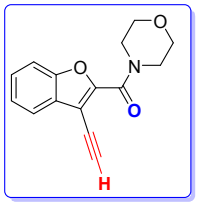
***N*-(4-Sulfamoylphenyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (9f), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.88 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 4.82 (s, 2H), 0.98 (brs, 42H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 142.3, 142.0, 136.8, 132.6, 129.3, 127.6, 121.3, 119.2, 102.6, 96.8, 18.5, 11.1. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{35}H_{53}N_2O_3SSi_2$: 637.3310, Found: 637.3313.



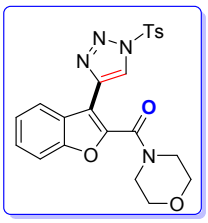
Ethynyl-*N*,*N*-dimethylbenzamide (5a'), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 3.16 (s, 1H), 3.12 (s, 3H), 2.88 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 169.9, 140.3, 132.8, 129.8, 129.2, 128.6, 126.4, 119.0, 80.8, 80.4, 38.3, 34.8.



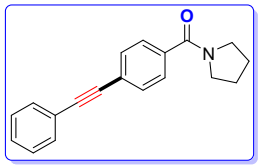
***N, N*-Dimethyl-3-phenylpent-2-en-4-ynamide (7a'), ^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.66 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.39-7.36 (m, 3H),6.80 (s, 1H), 3.47 (s, 1H), 3.11 (s, 3H), 3.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$): δ** 166.8, 136.3, 129.2, 128.6, 128.2, 126.5, 85.9, 79.9, 37.7, 34.9.



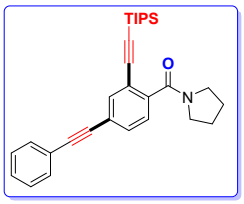
(3-Ethynylbenzofuran-2-yl)(morpholino)methanone (5l'), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.73 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46-7.42 (m, 1H), 7.38-7.34 (m, 1H), 3.79 (brs, 8H), 3.57 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 159.3, 153.7, 150.2, 127.7, 127.3, 124.2, 121.2, 112.0, 105.8, 86.3, 73.1, 66.9, 47.7, 43.1. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{15}H_{14}NO_3$: 256.0968, Found: 256.0964.



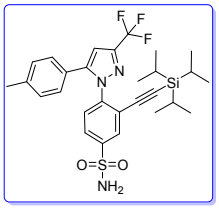
Morpholino(3-(1-tosyl-1H-1,2,3-triazol-4-yl)benzofuran-2-yl)methanone (5l''), **^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.91 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 6.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.24-7.21(m, 2H), 6.55 (s, 1H), 4.05 (s, 4H), 3.87 (s, 4H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 160.6, 159.0, 148.6, 145.1, 141.9, 140.8, 132.9, 129.1, 126.5, 124.2, 123.7, 121.4, 112.3, 85.5, 66.4, 46.3, 21.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{21}N_4O_5S$: 453.1227, Found: 453.1232.



(4-(Phenylethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e'), ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.56-7.49 (m, 6H), 7.35-7.33 (m, 3H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 1.95 (t, *J* = 6.8 Hz, 2H), 1.87 (t, *J* = 6.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** ***δ*** 169.0, 136.7, 131.6, 131.4, 128.5, 128.4, 127.2, 124.9, 122.9, 90.8, 88.7, 49.6, 46.3, 26.4, 24.4. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{22}H_{21}N_4O_5S$: 276.1383, Found: 276.1386.



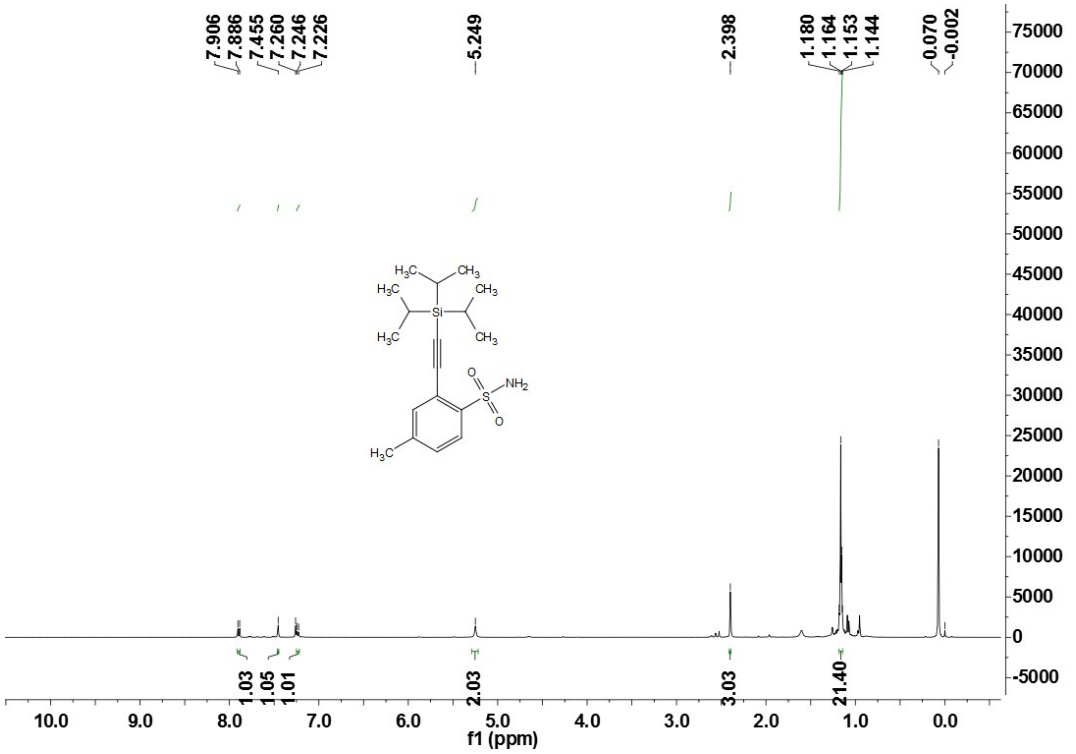
(4-**(Phenylethynyl)-2-((triisopropylsilyl)ethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e''), ^{1}H NMR (400 MHz, $CDCl_3$):** ***δ*** 7.67 (d, *J* = 1.2 Hz, 1H), 7.54-7.52 (m, 2H), 7.50 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.37-7.35 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.31 (t, *J* = 6.8 Hz, 2H), 1.96-1.86 (m, 4H), 1.11 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$): *δ*** 167.8, 140.3, 135.9, 131.7, 128.6, 128.4, 126.4, 124.0, 122.8, 120.4, 103.4, 94.9, 90.8, 87.9, 47.8, 45.7, 25.9, 24.5, 18.6, 11.3. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{30}H_{38}NOSi$: 456.2717, Found: 456.2719.

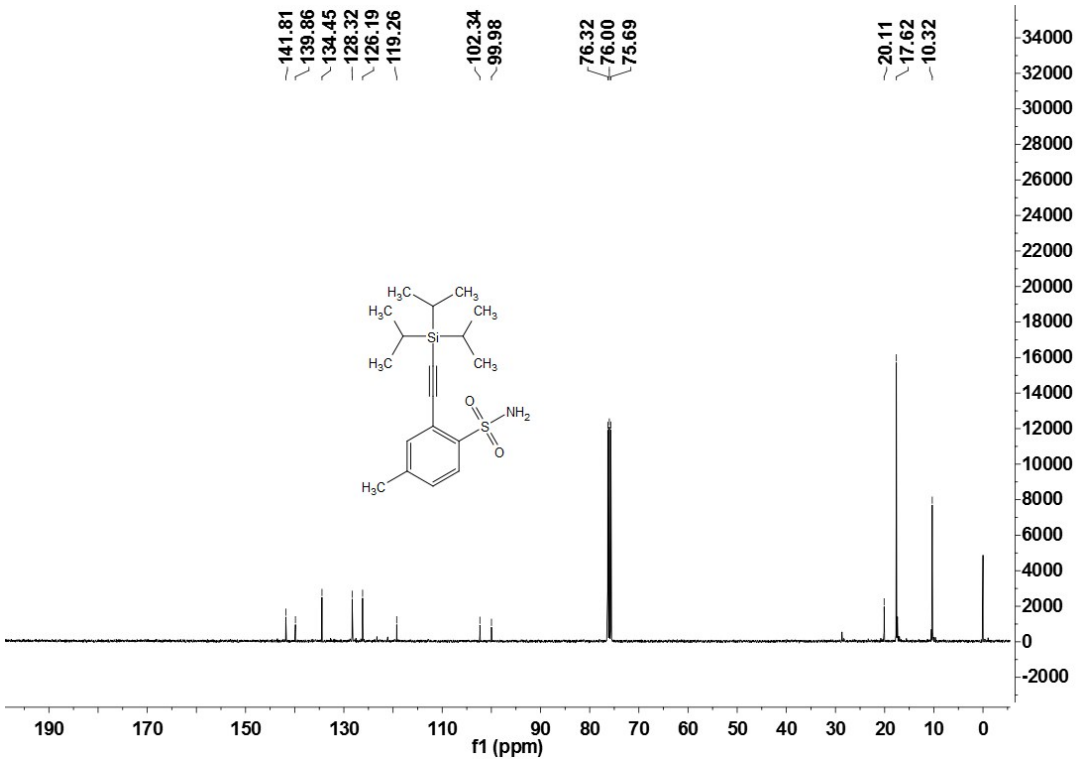


4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl) benzenesulfonamide (), ^{1}H NMR (400 MHz, $CDCl_3$) ***δ*** 7.94 (d, *J* = 8.8Hz, 1H), 7.71 (s, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.26 (brs, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 5.29 (s, 1H), 2.38 (s, 3H), 1.13-1.10 (m, 21H). **^{13}C NMR (150 MHz, $CDCl_3$)** *δ* 145.4, 144.3 (q, $J_{C\text{-}F}$ = 39.0 Hz), 142.5, 141.9, 140.0, 130.7, 129.8, 128.8, 128.1, 125.6, 124.5, 121.7, 121.0 (q, $J_{C\text{-}F}$ = 267.0 Hz), 106.5, 103.6, 101.9, 21.3, 18.6, 11.2. **^{19}F NMR (100 MHz, $CDCl_3$) *δ*** -62.5. **HRMS (ESI-TOF) m/z**: $[M + H]^+$ Calcd for $C_{28}H_{35}F_3N_3O_2SSi$: 562.21659, found: 562.21600.

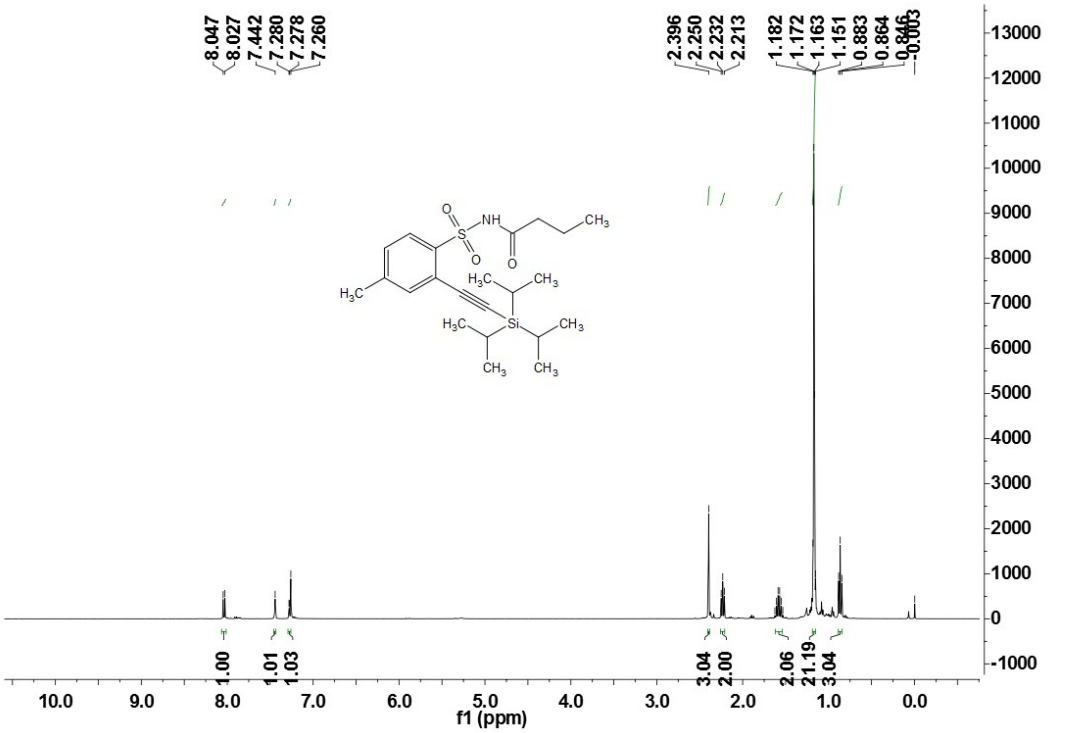
F. NMR spectra

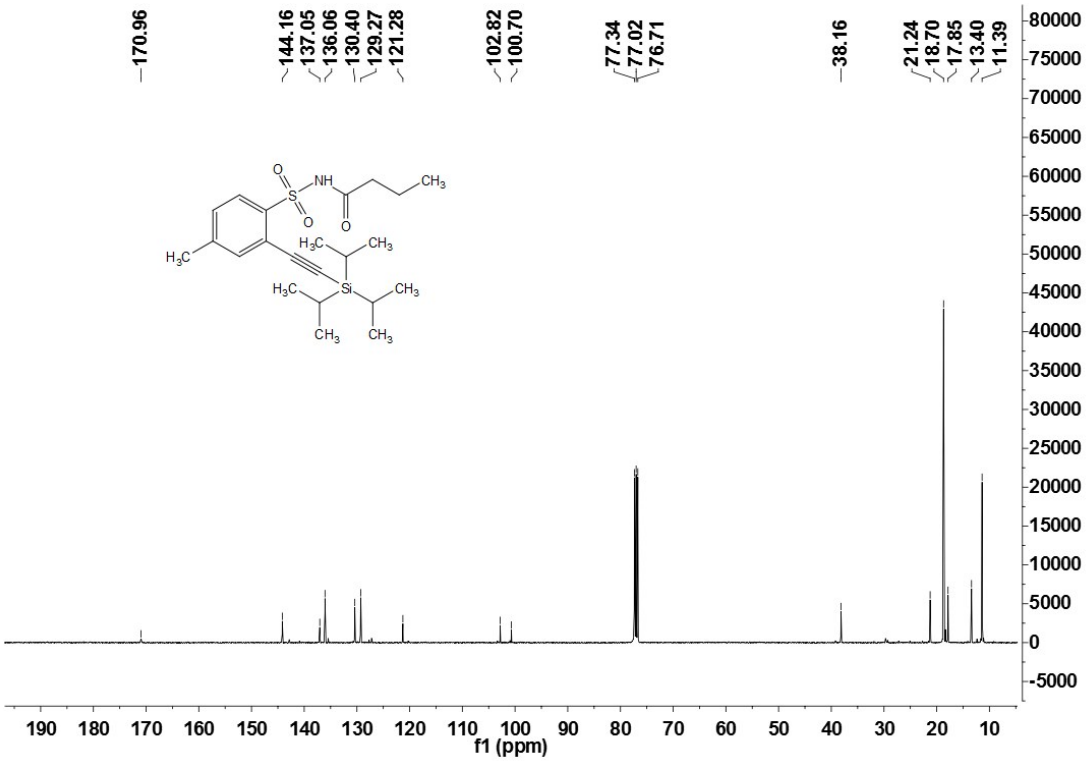
4-Methyl-2-((triisopropylsilyl)ethynyl)benzenesulfonamide(3a)



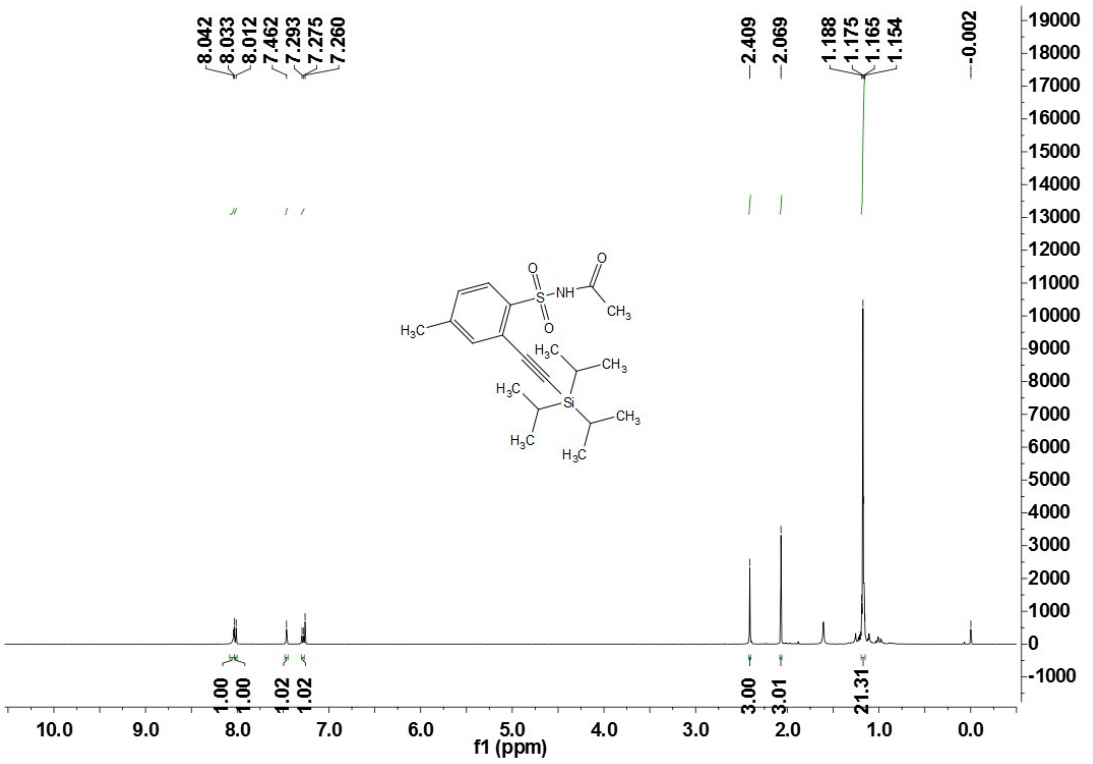


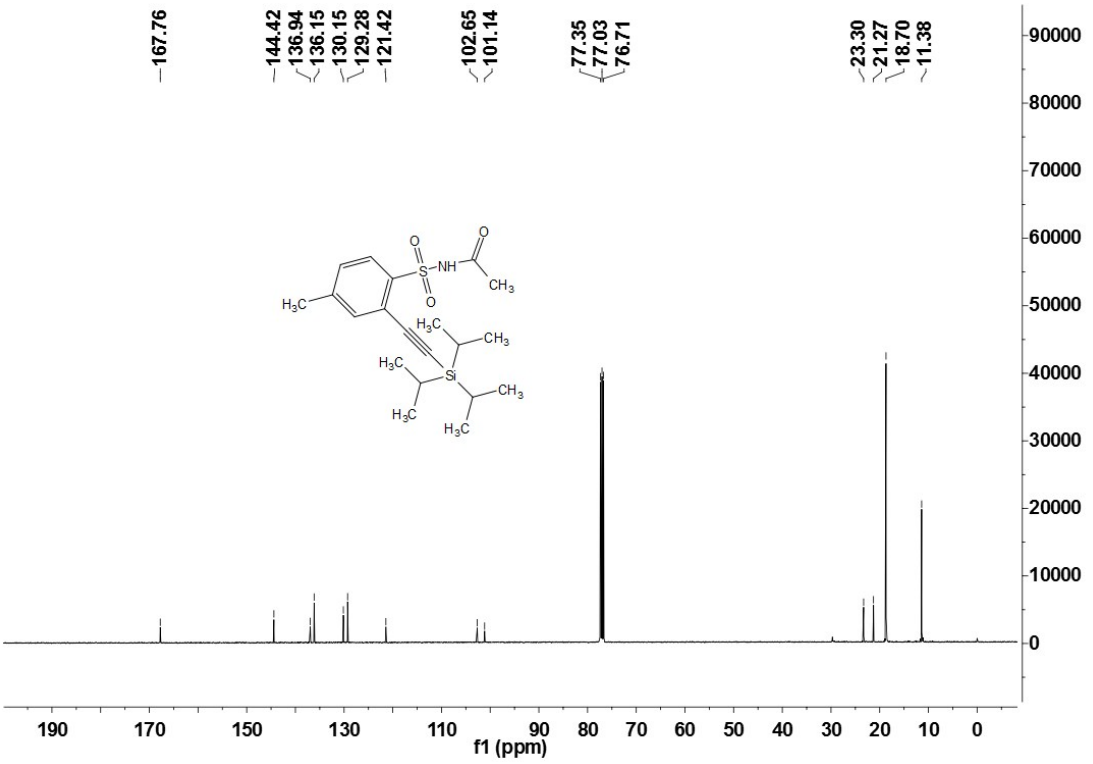
_N_-((4-Methyl-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)butyramide (3b)



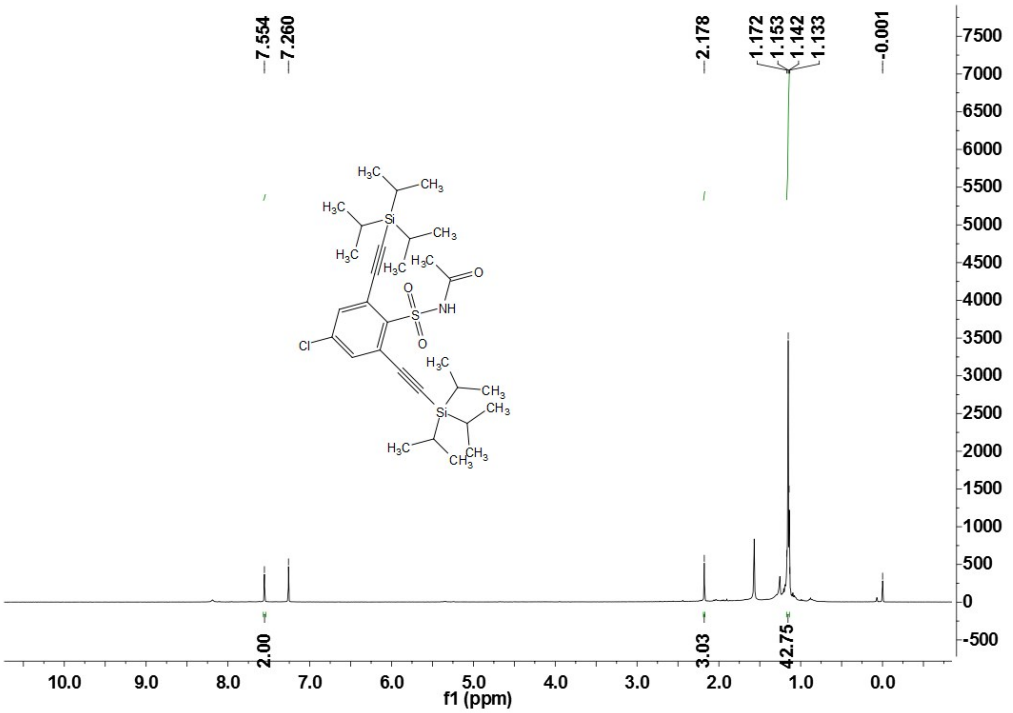


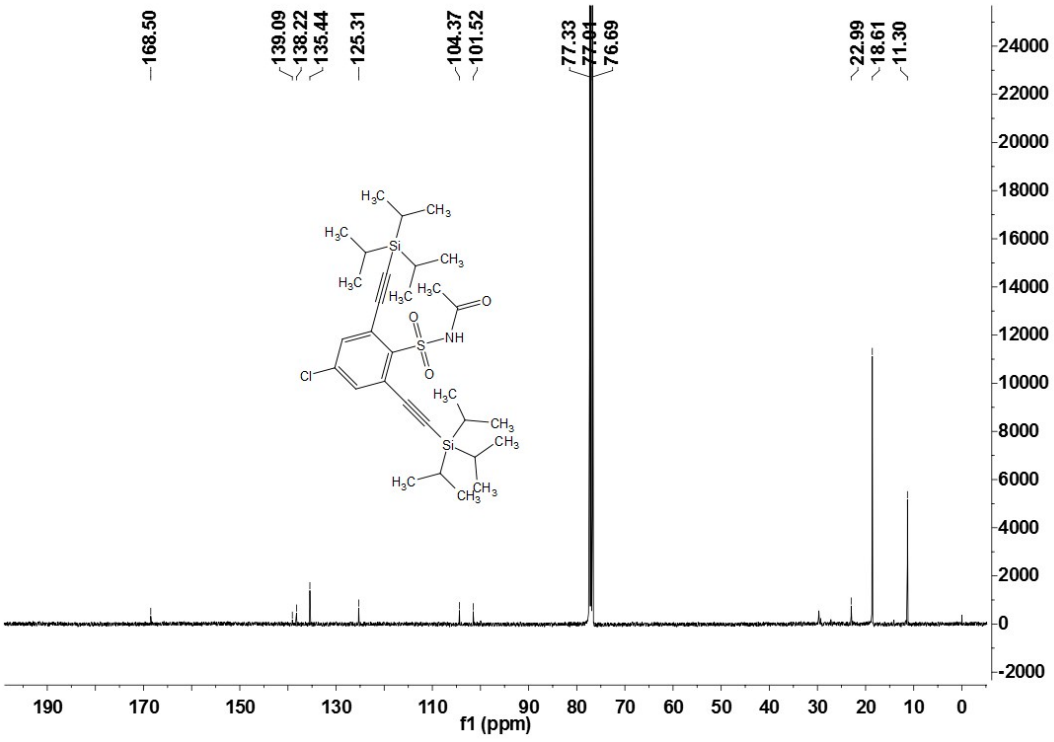
***N*-((4-Methyl-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3c)**



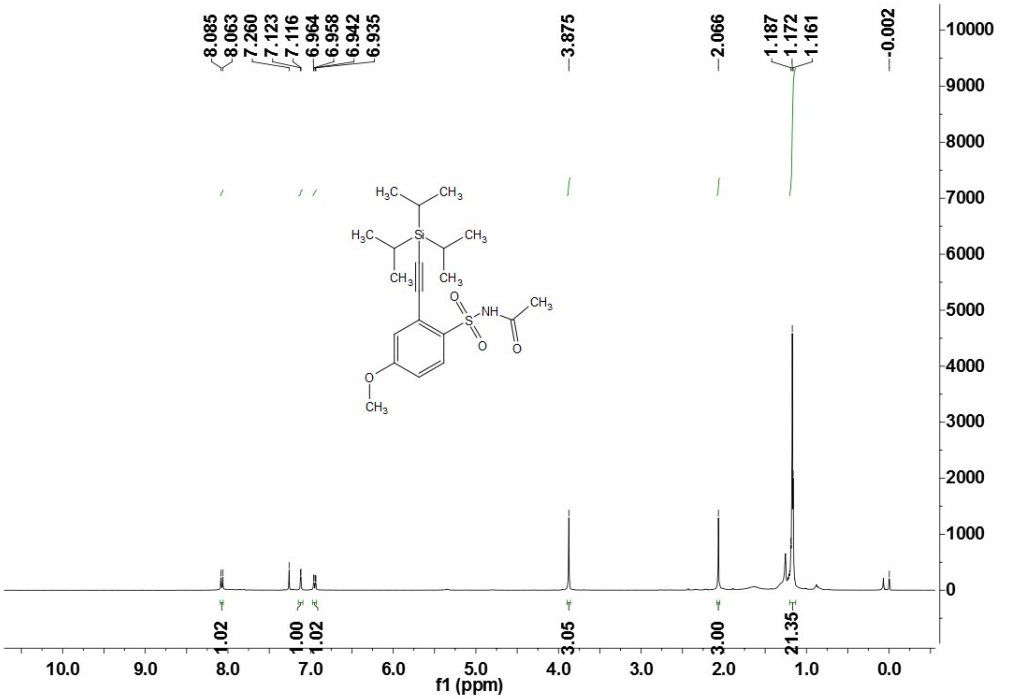


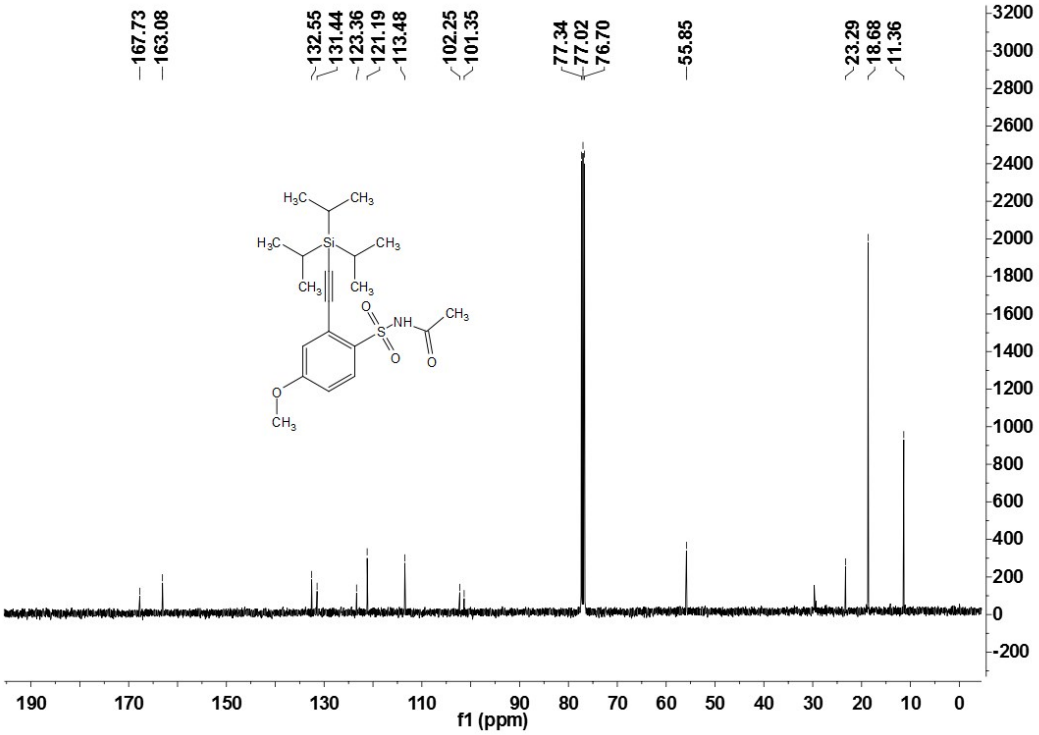
***N*-((4-Chloro-2,6-bis((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3f)**



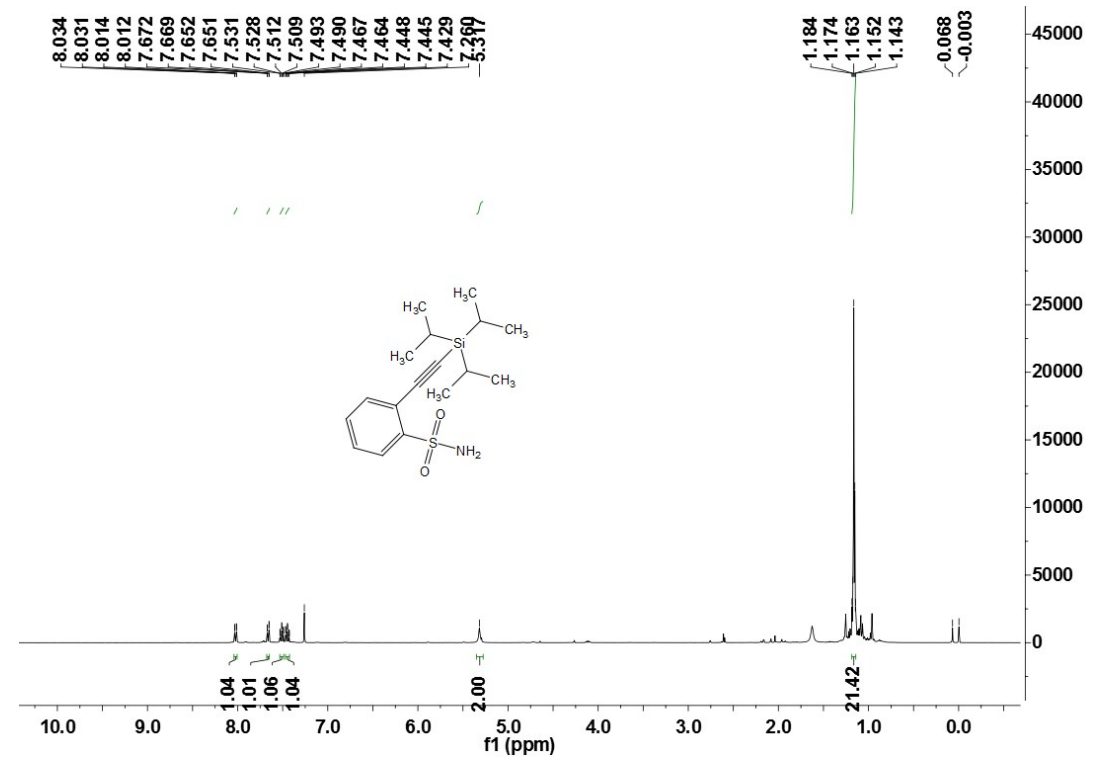


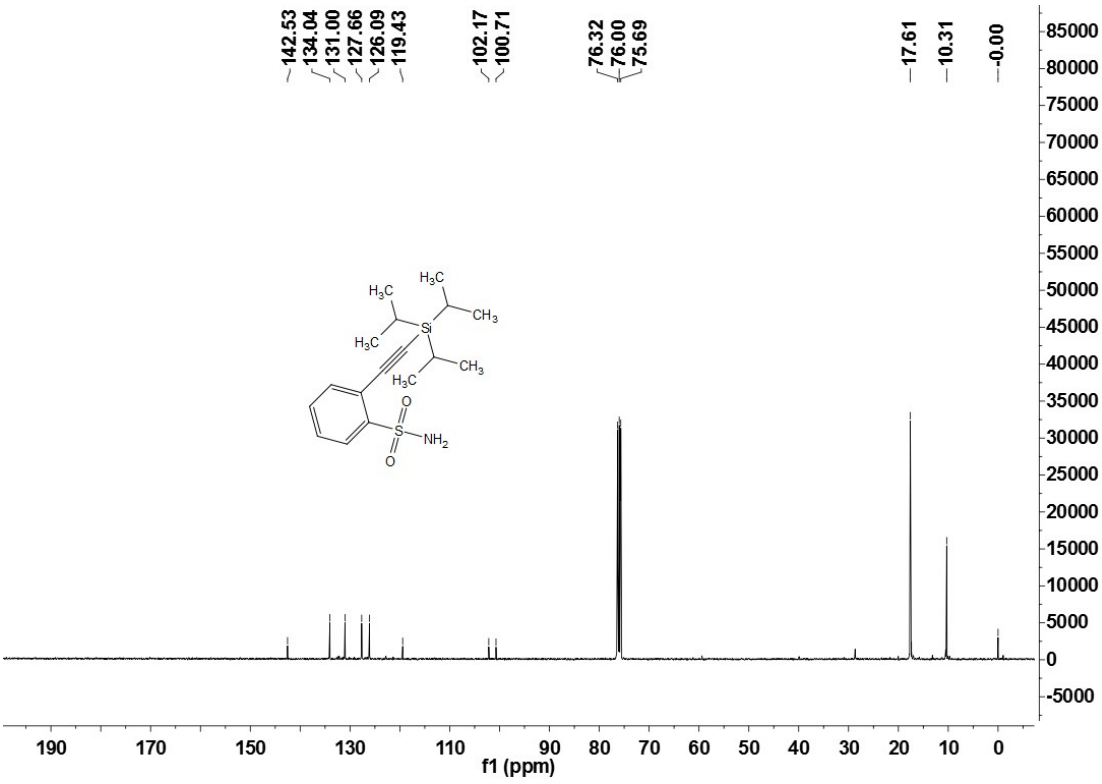
N-((4-Methoxy-2-((triisopropylsilyl)ethynyl)phenyl)sulfonyl)acetamide (3g)



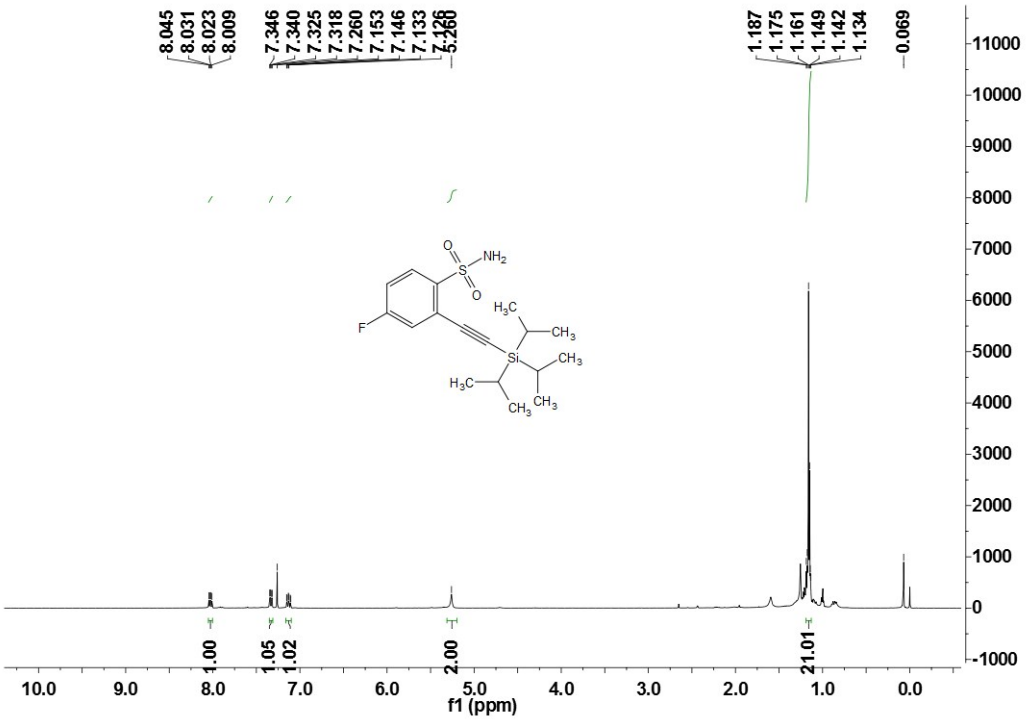


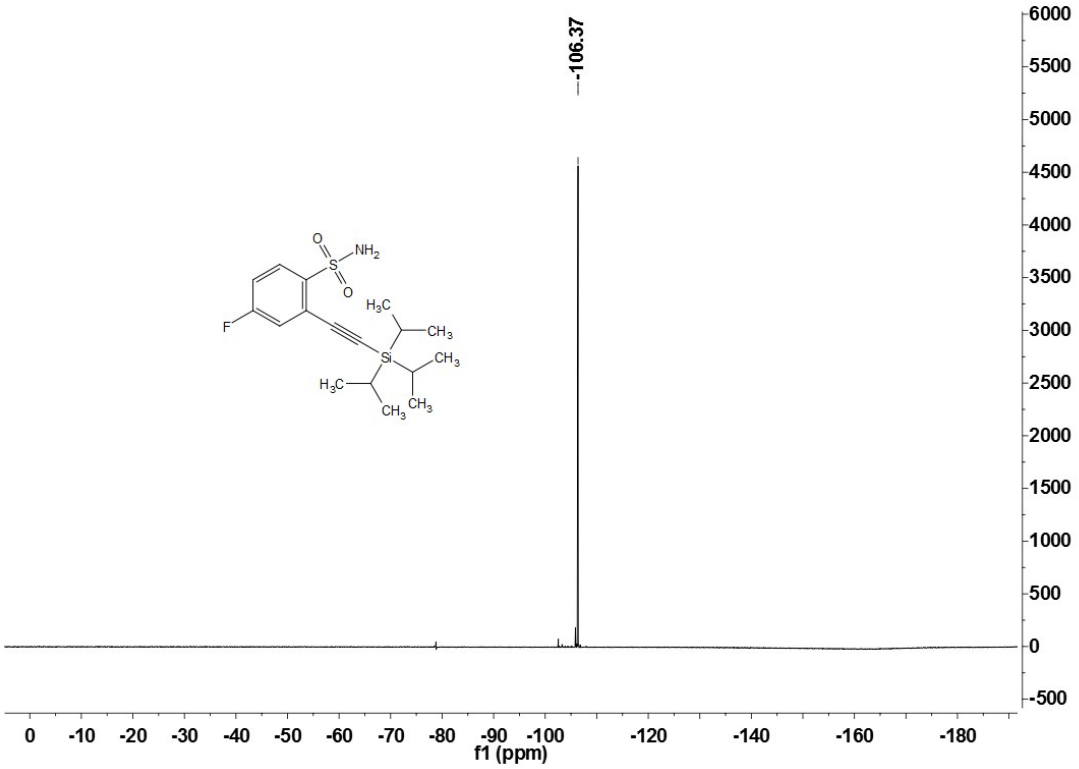
((Triisopropylsilyl)ethynyl)benzenesulfonamide (3h)

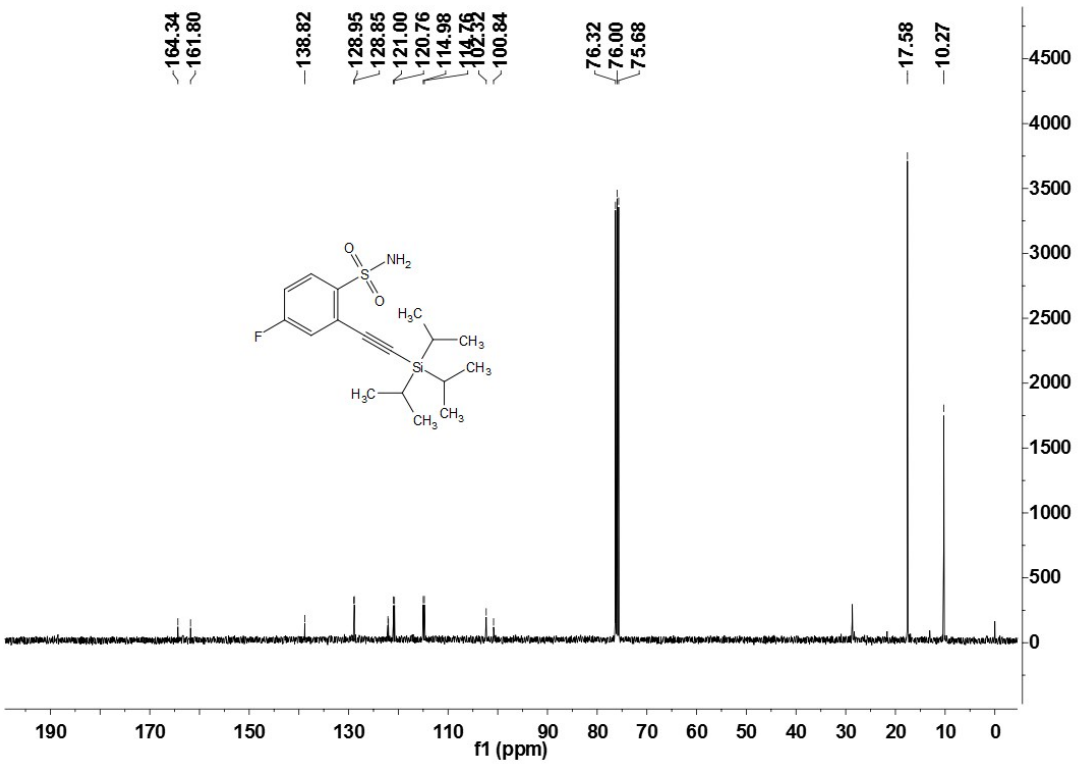




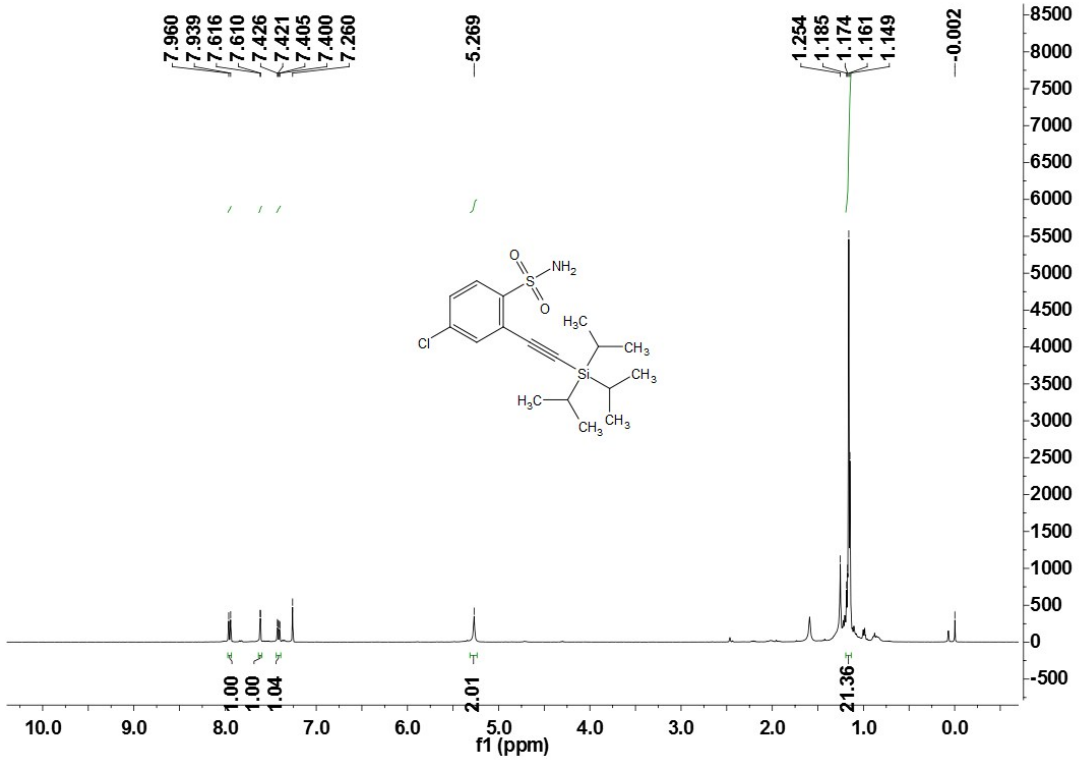
4-Fluoro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3i)

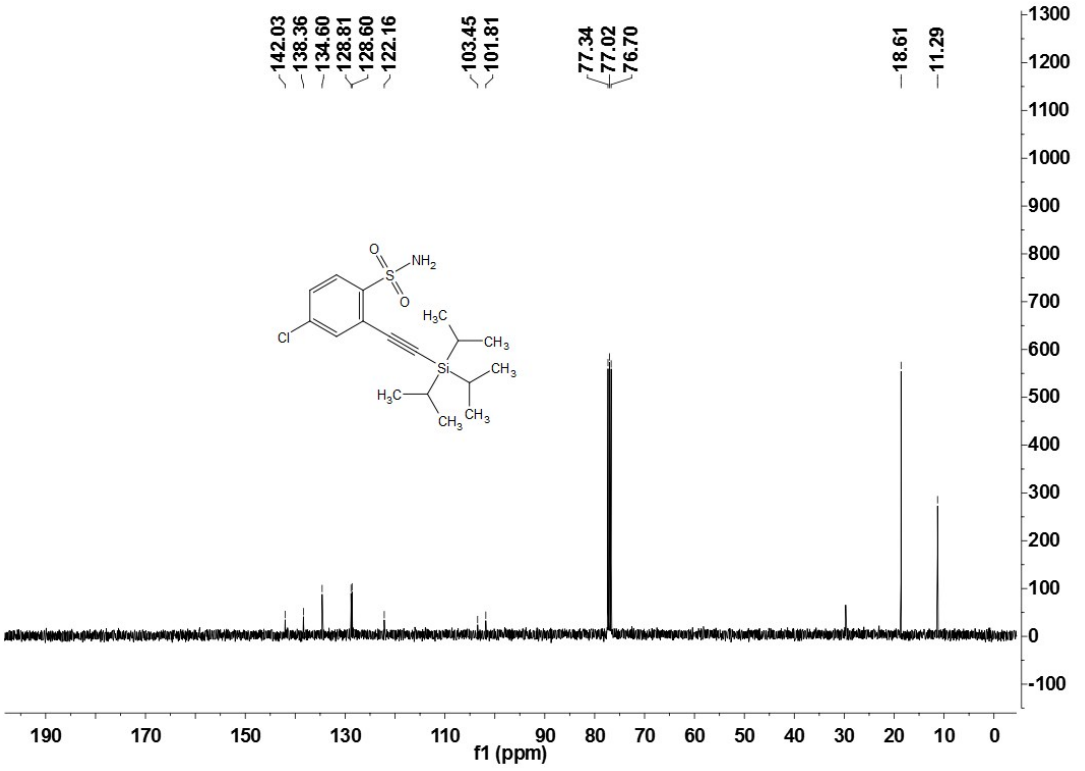




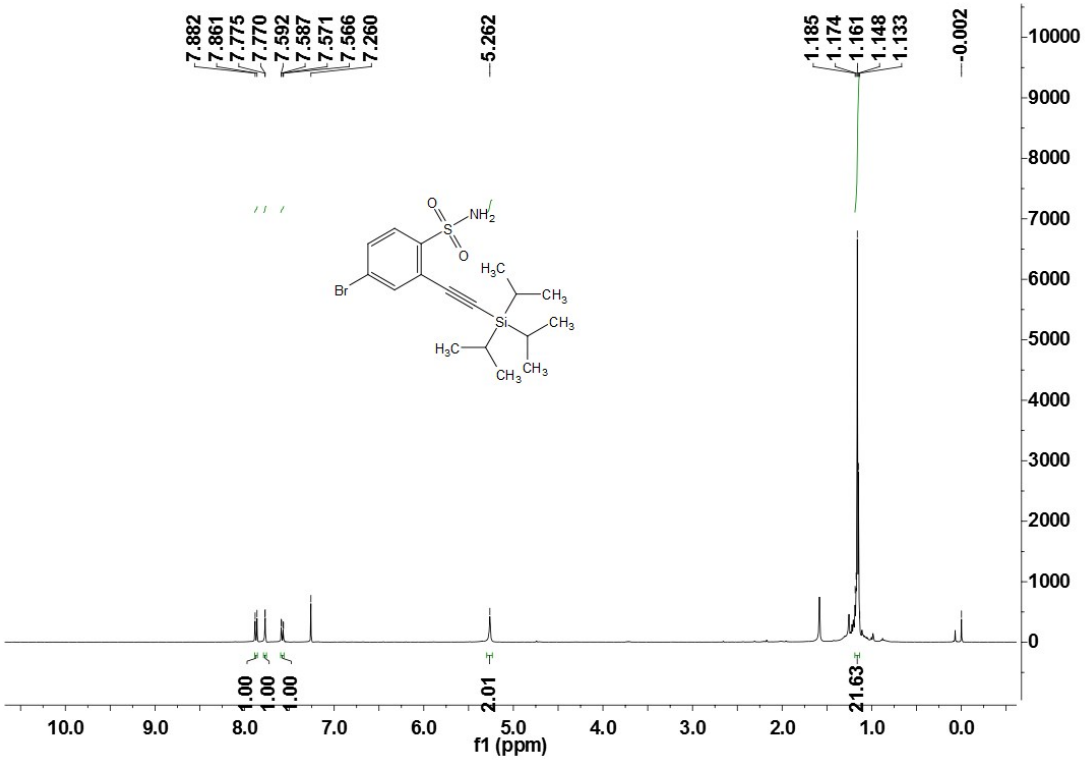


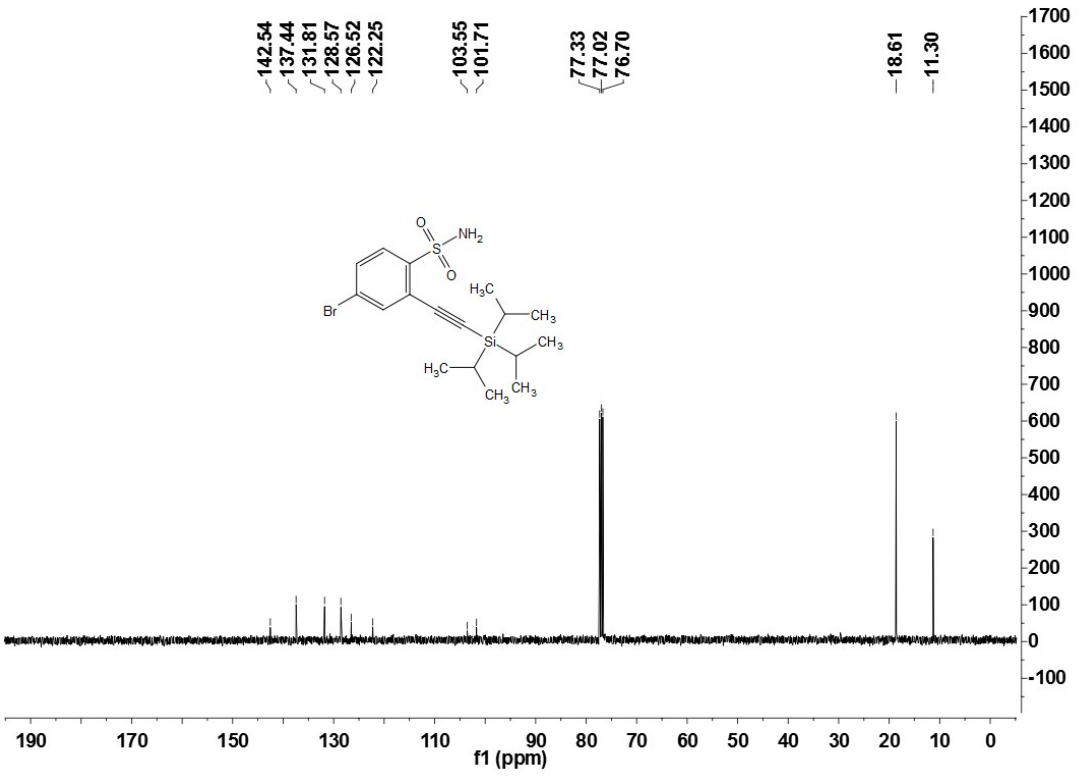
4-Chloro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3j)



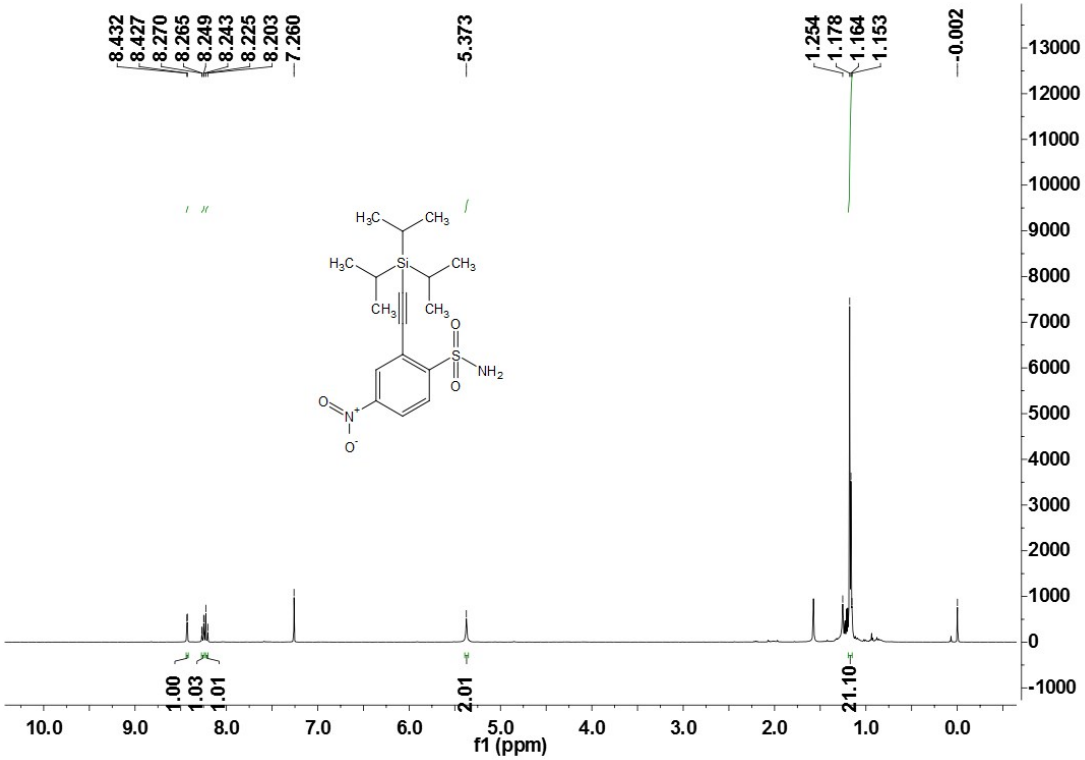


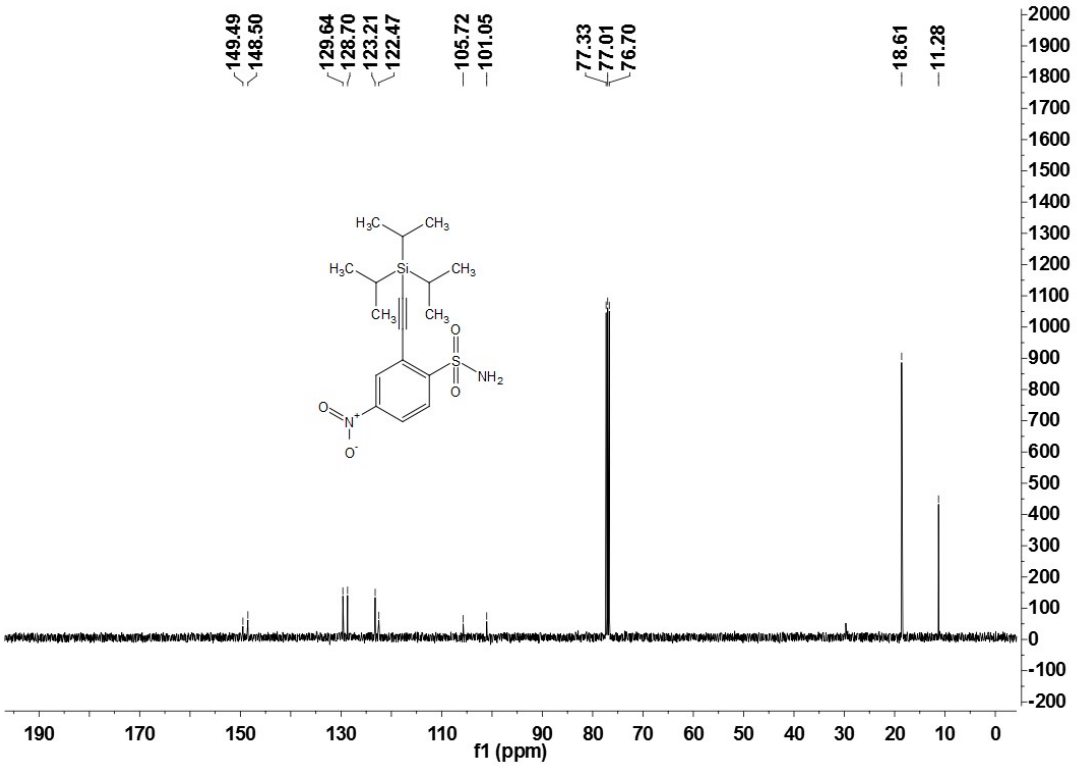
4-Bromo-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3k)



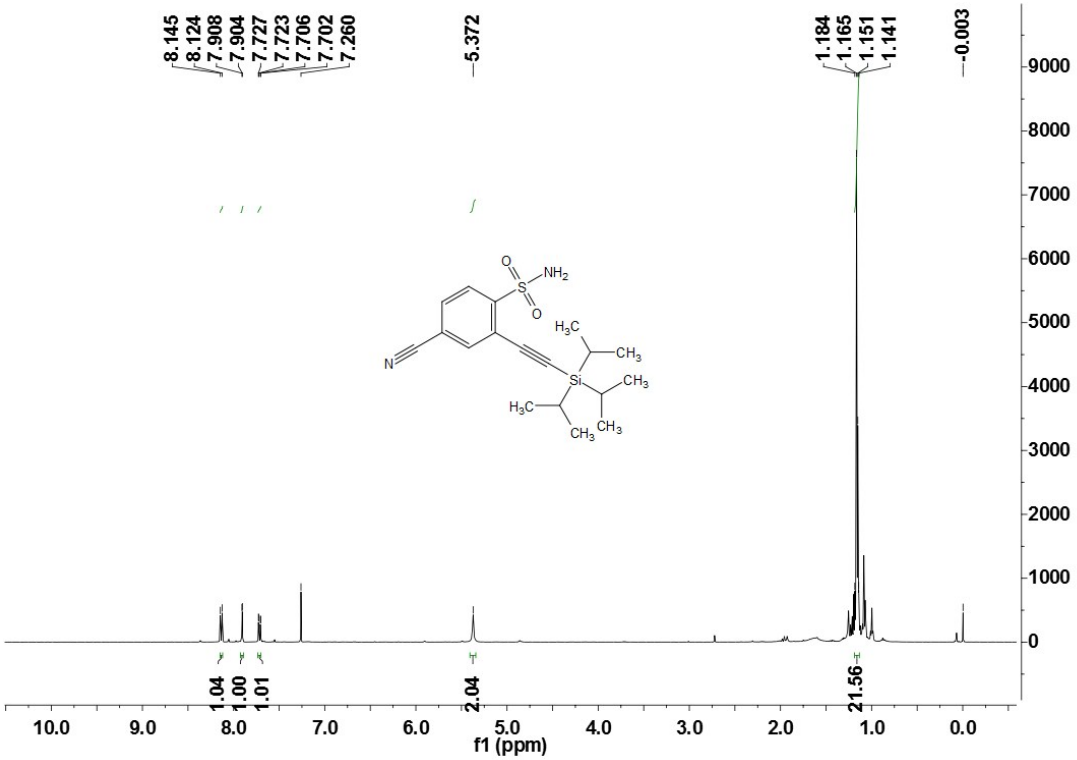


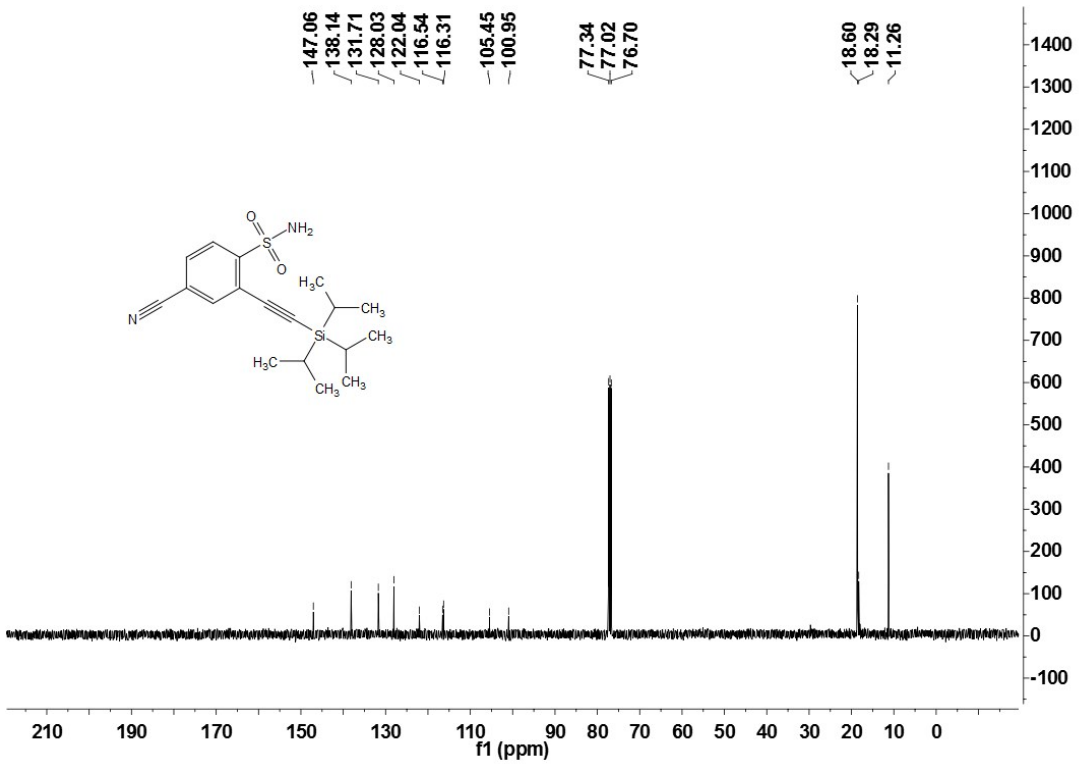
4-Nitro-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3l)



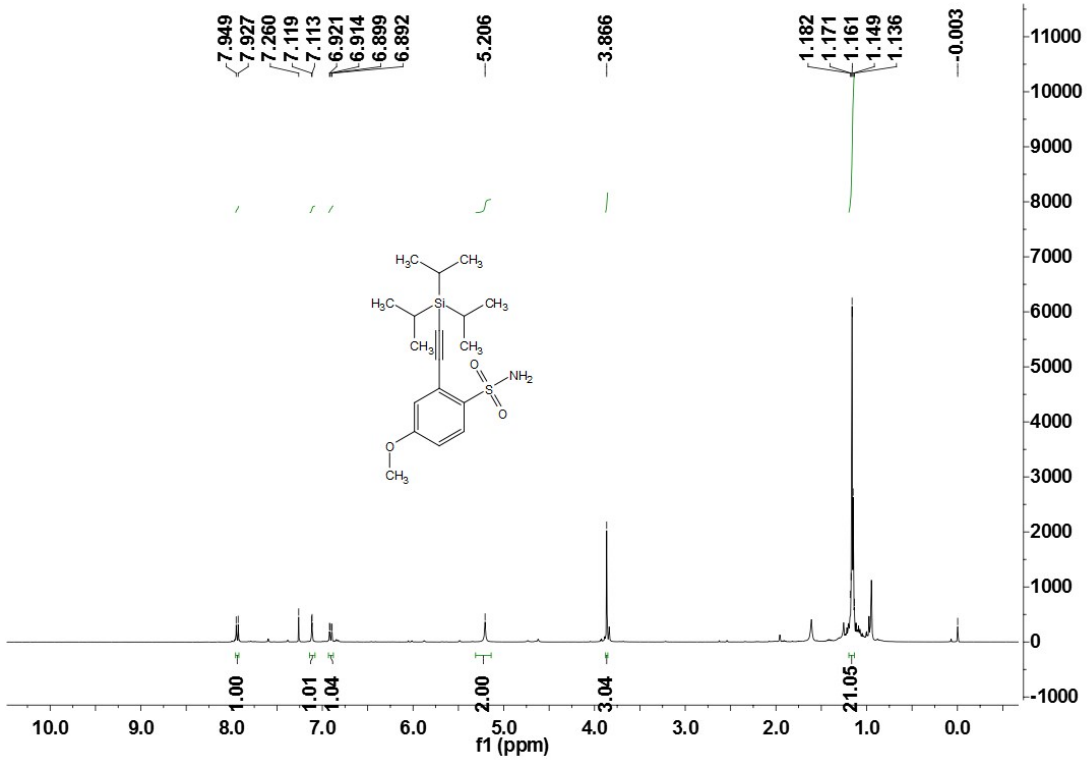


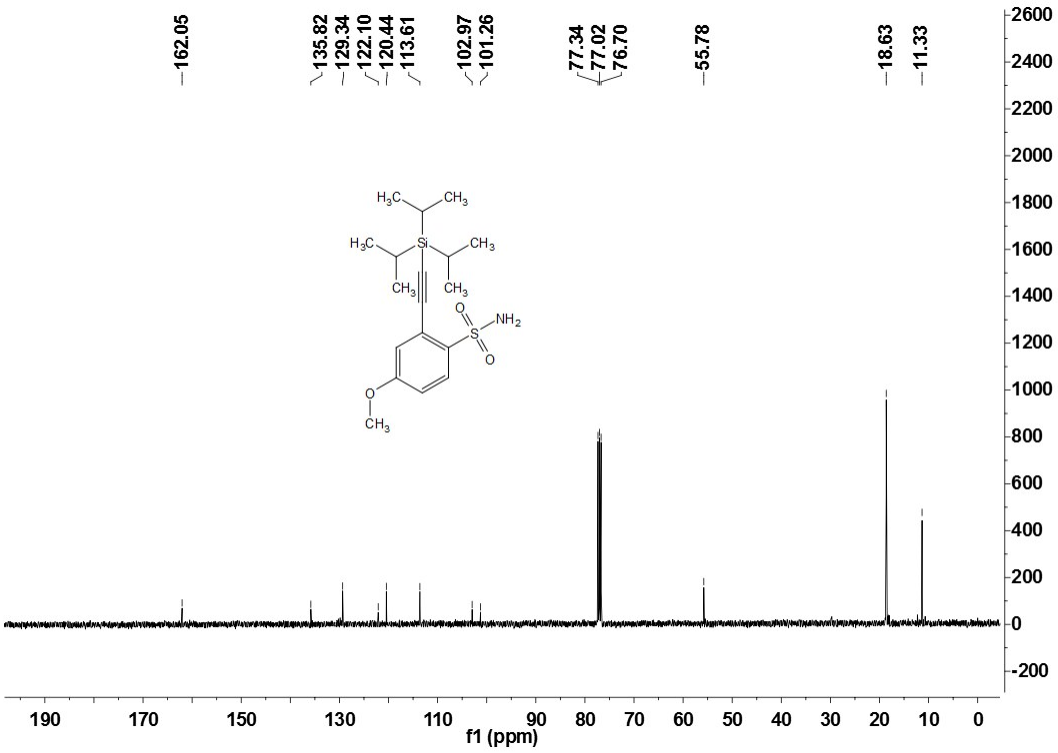
4-Cyano-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3m)



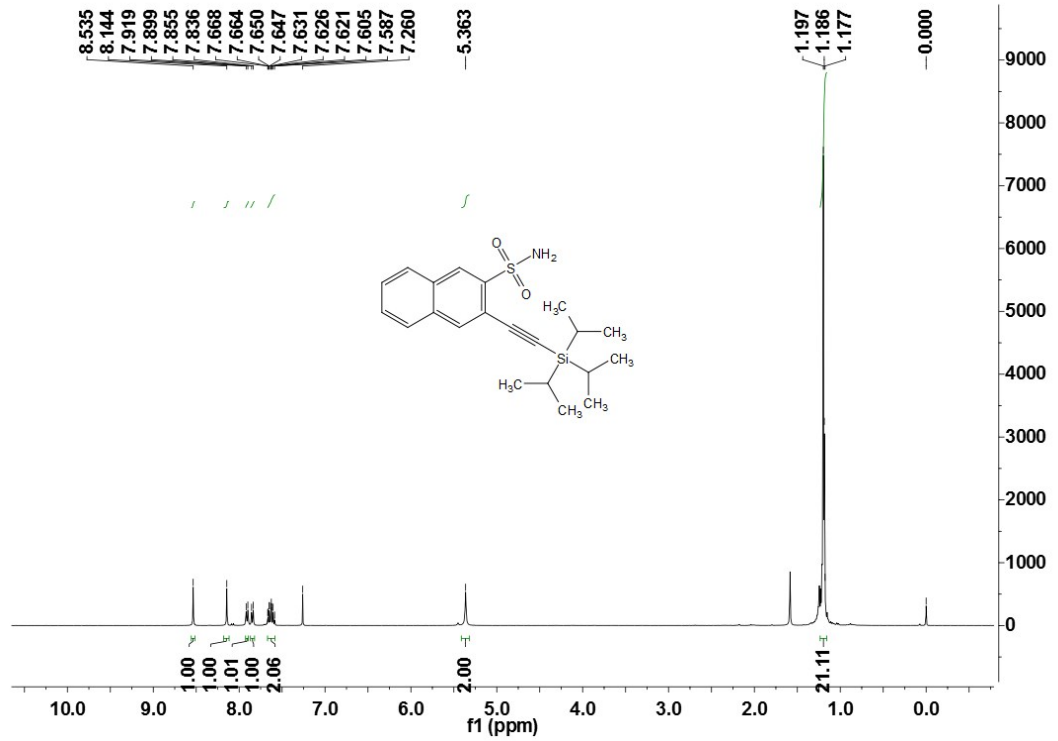


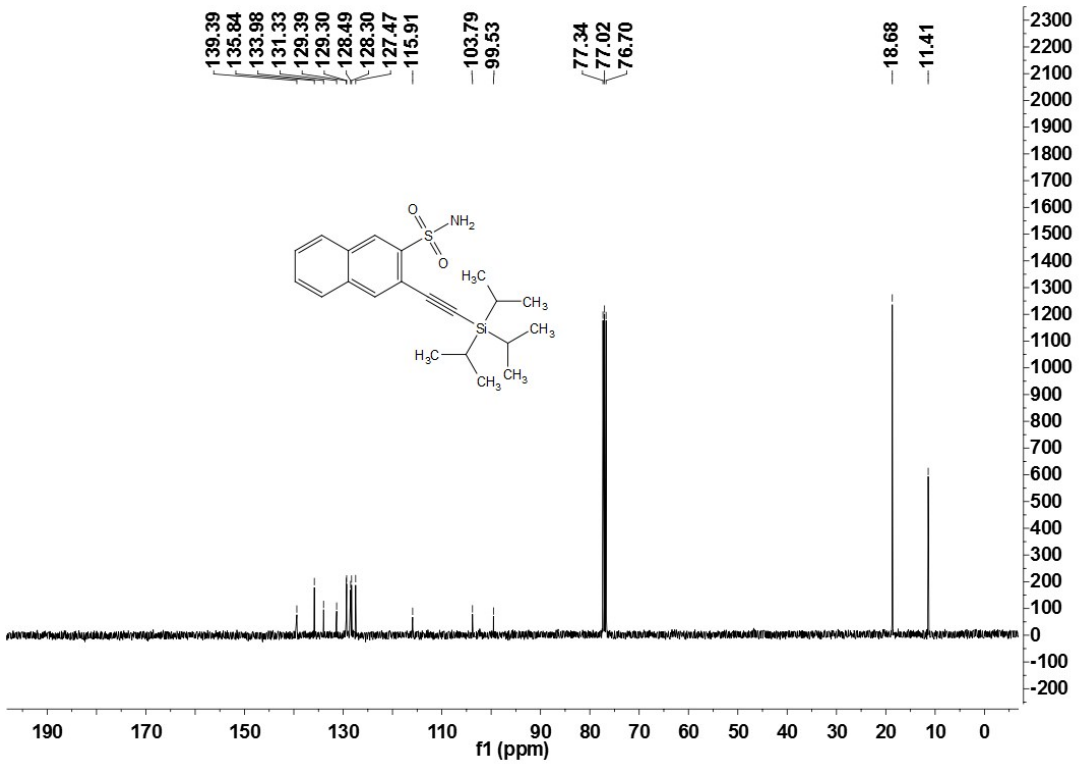
4-Methoxy-2-((triisopropylsilyl)ethynyl)benzenesulfonamide (3n)



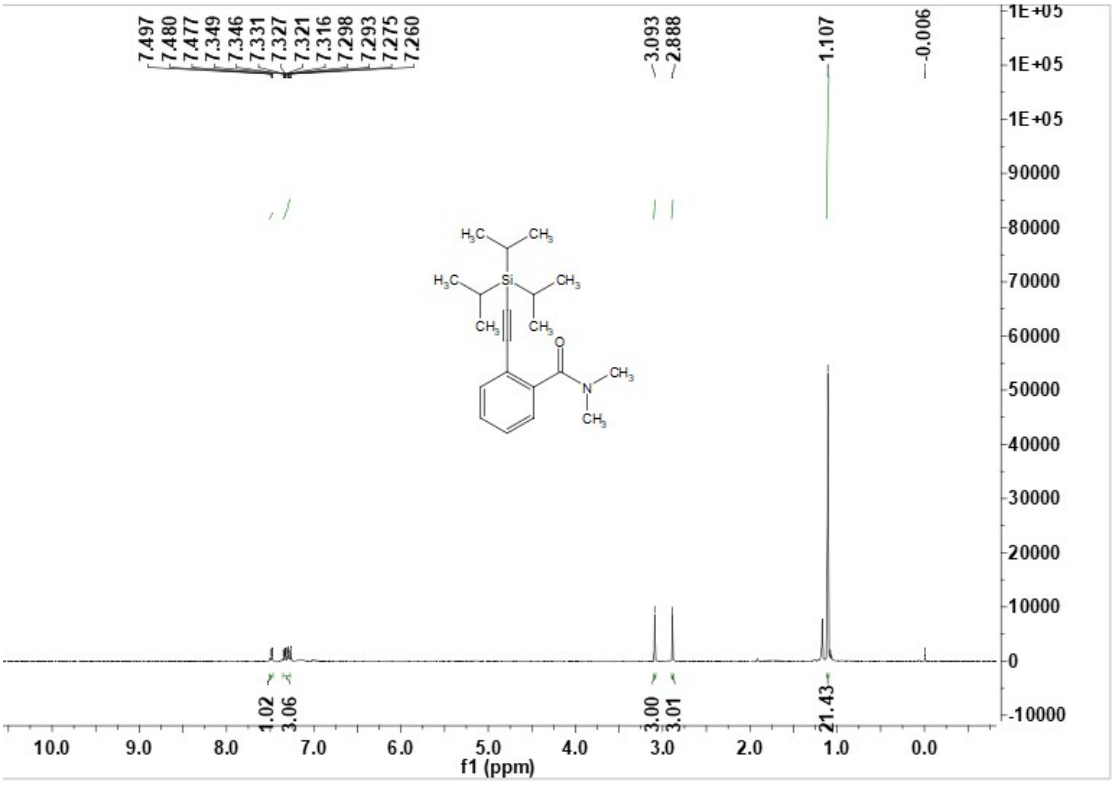


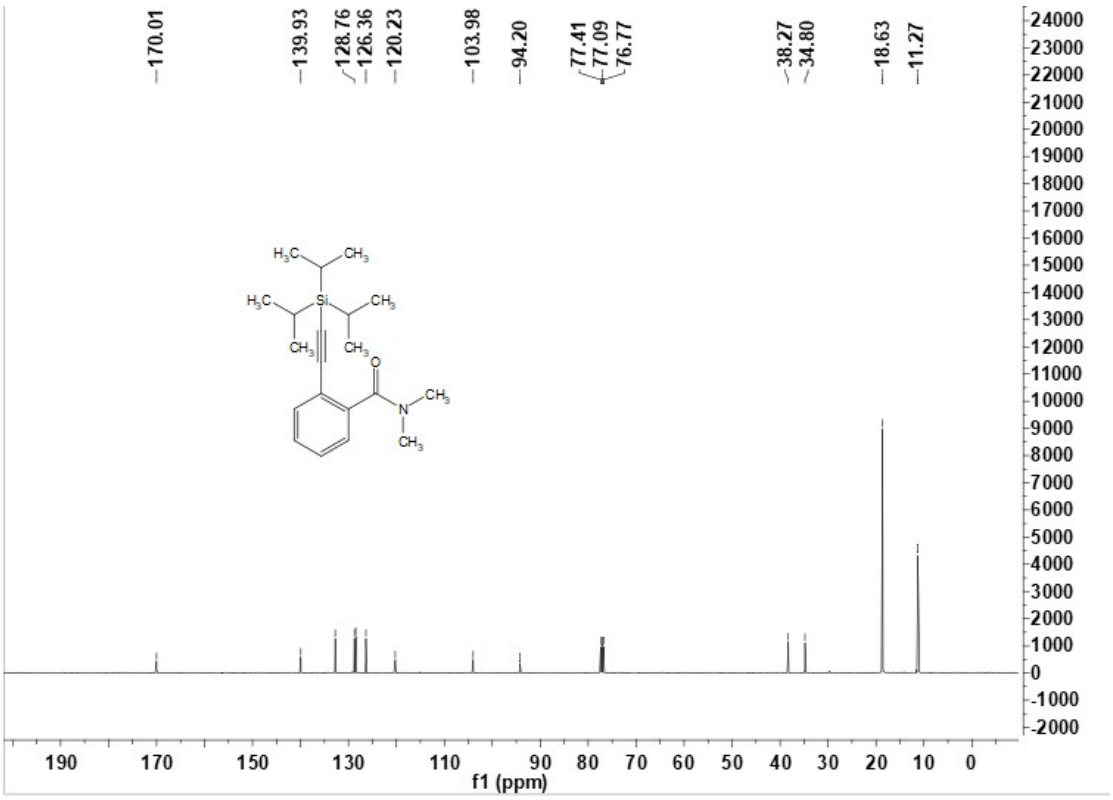
3-((Triisopropylsilyl)ethynyl)naphthalene-2-sulfonamide (3o)



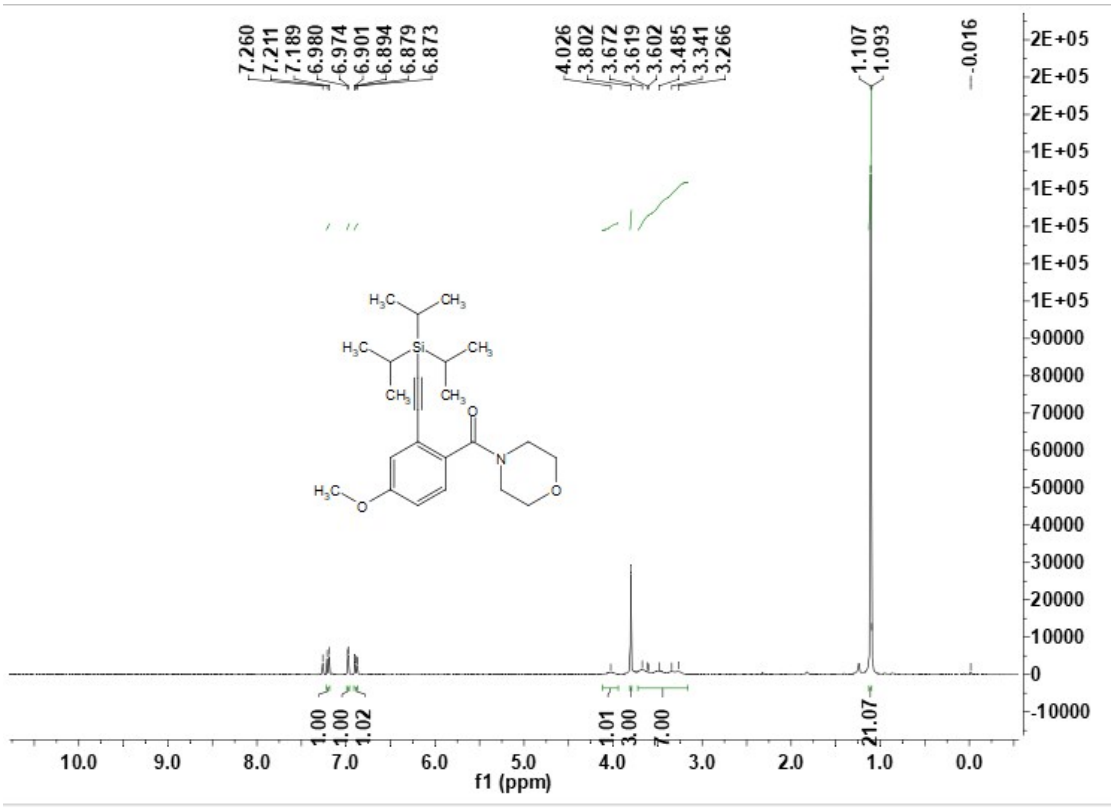


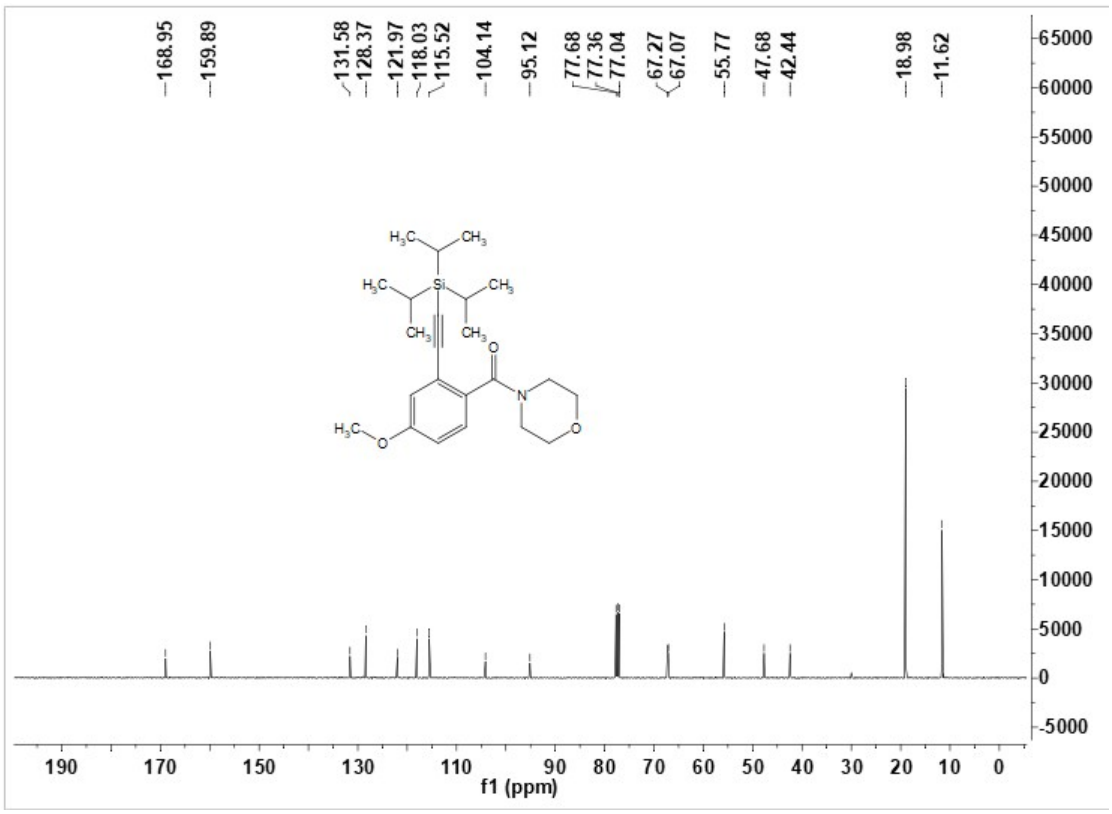
***N*, *N*-Dimethyl-2-((triisopropylsilyl)ethynyl)benzamide (5a)**



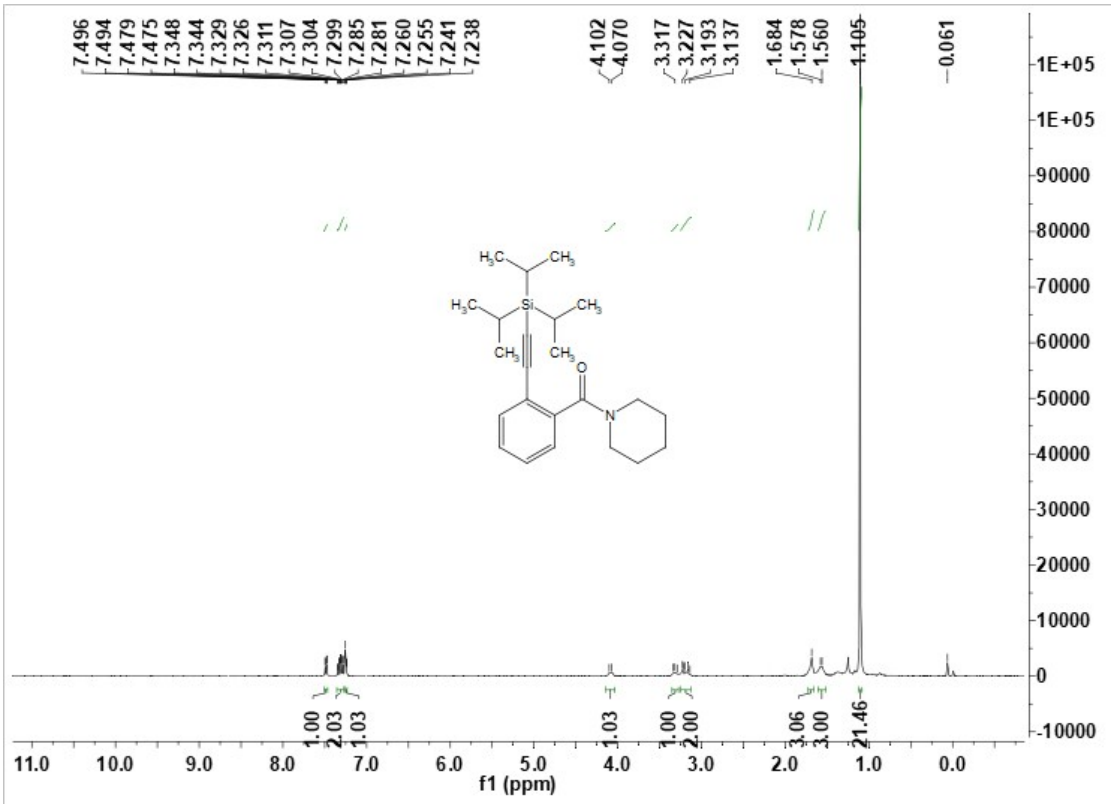


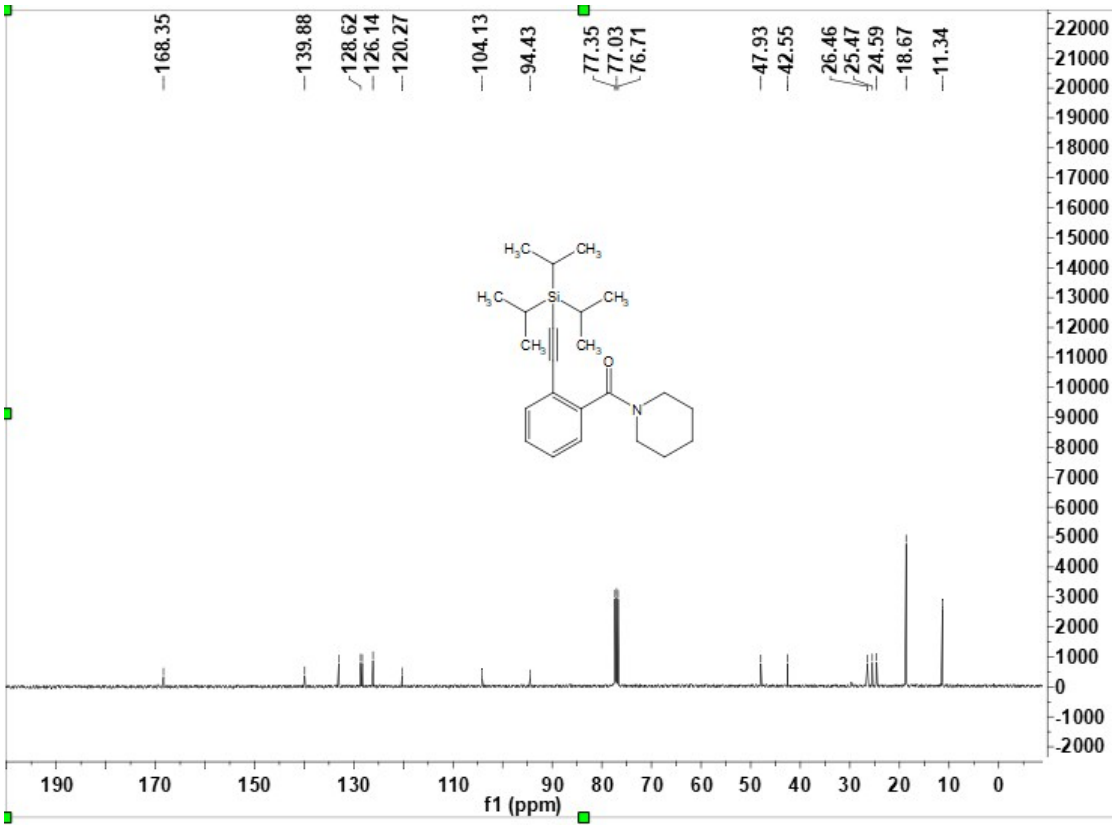
(4-Methoxy-2-((triisopropylsilyl)ethynyl)phenyl)(morpholino)methanone (5b)



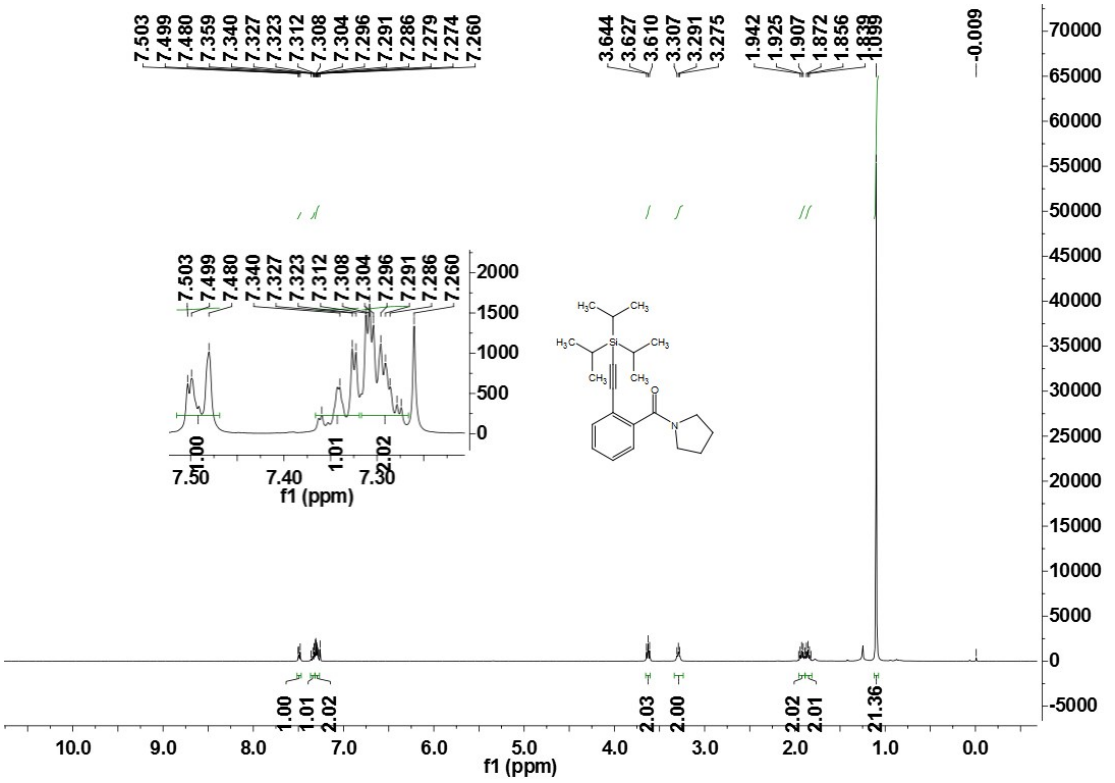


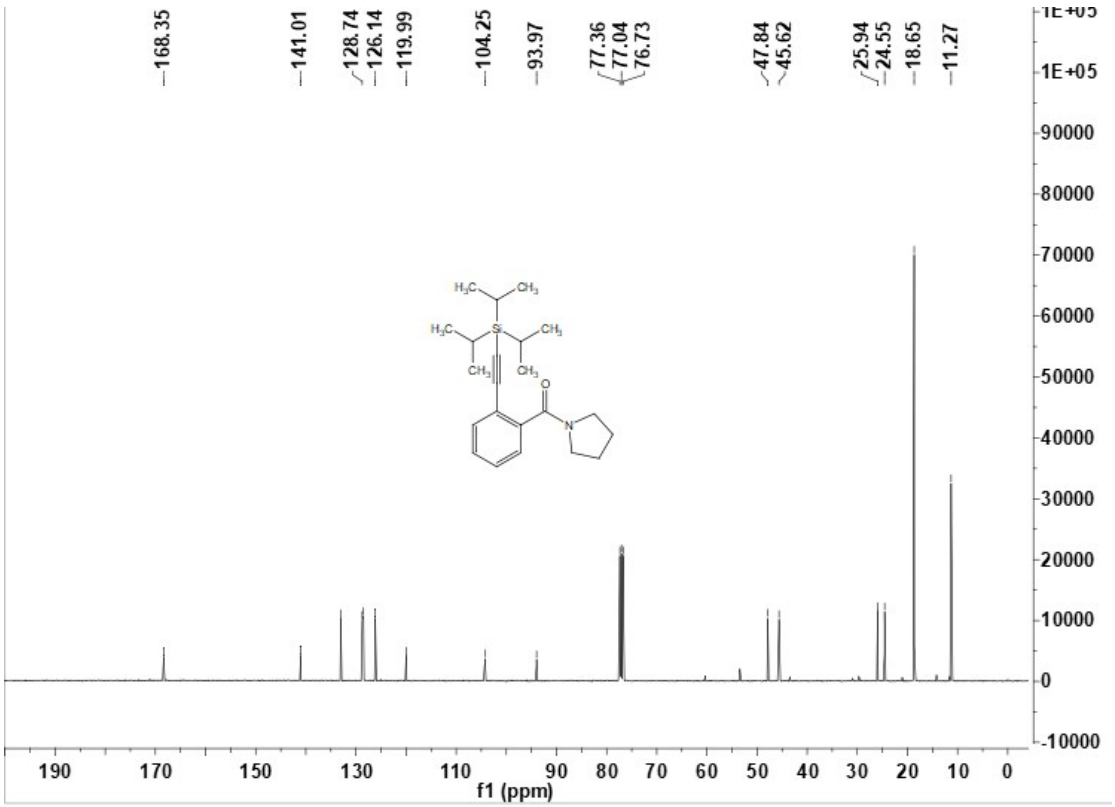
Piperidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone (5c)



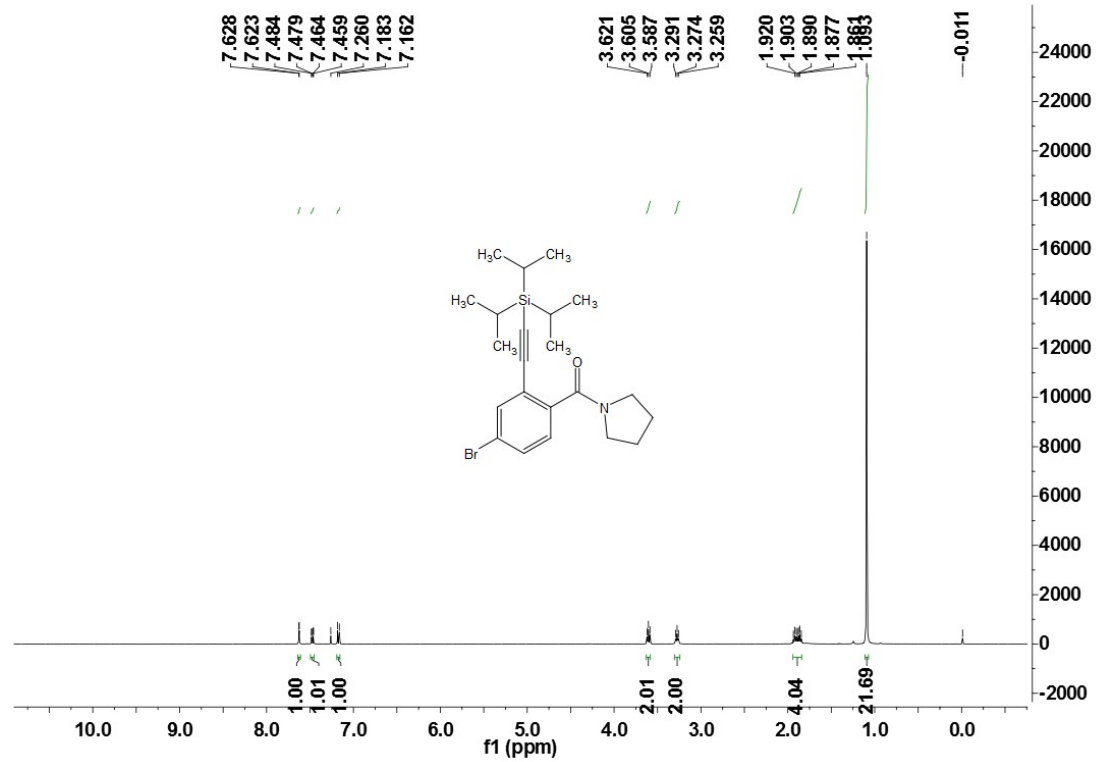


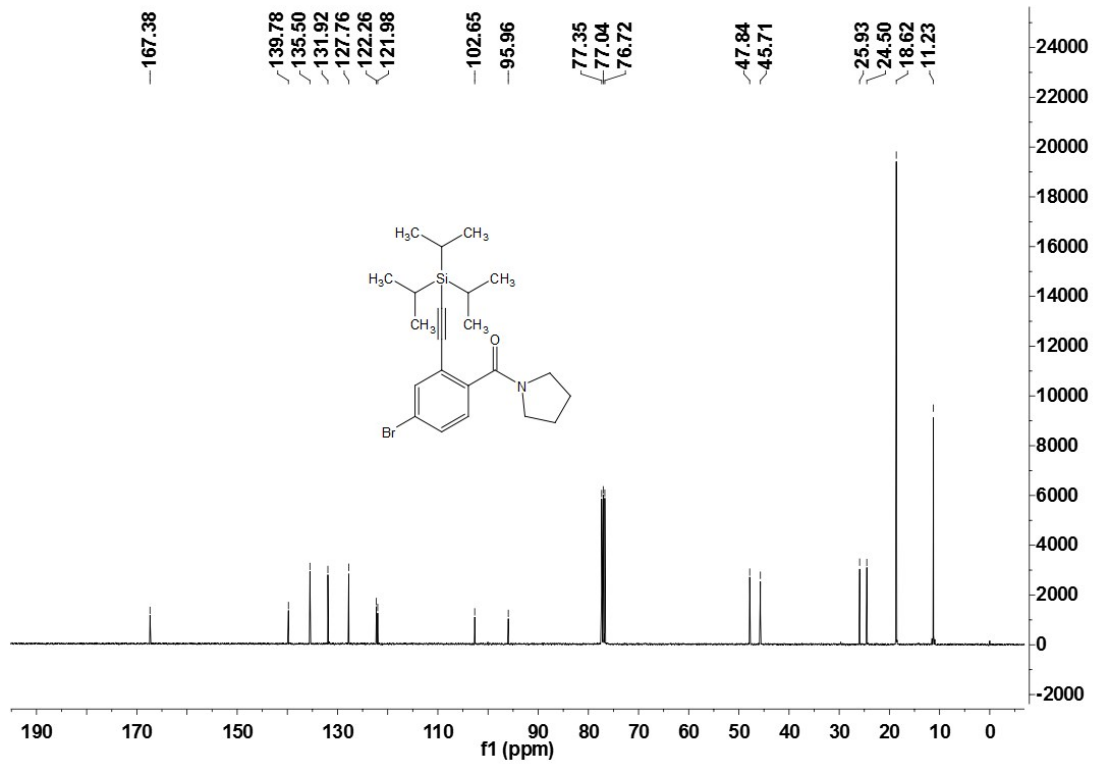
Pyrrolidin-1-yl(2-((triisopropylsilyl)ethynyl)phenyl)methanone (5d)



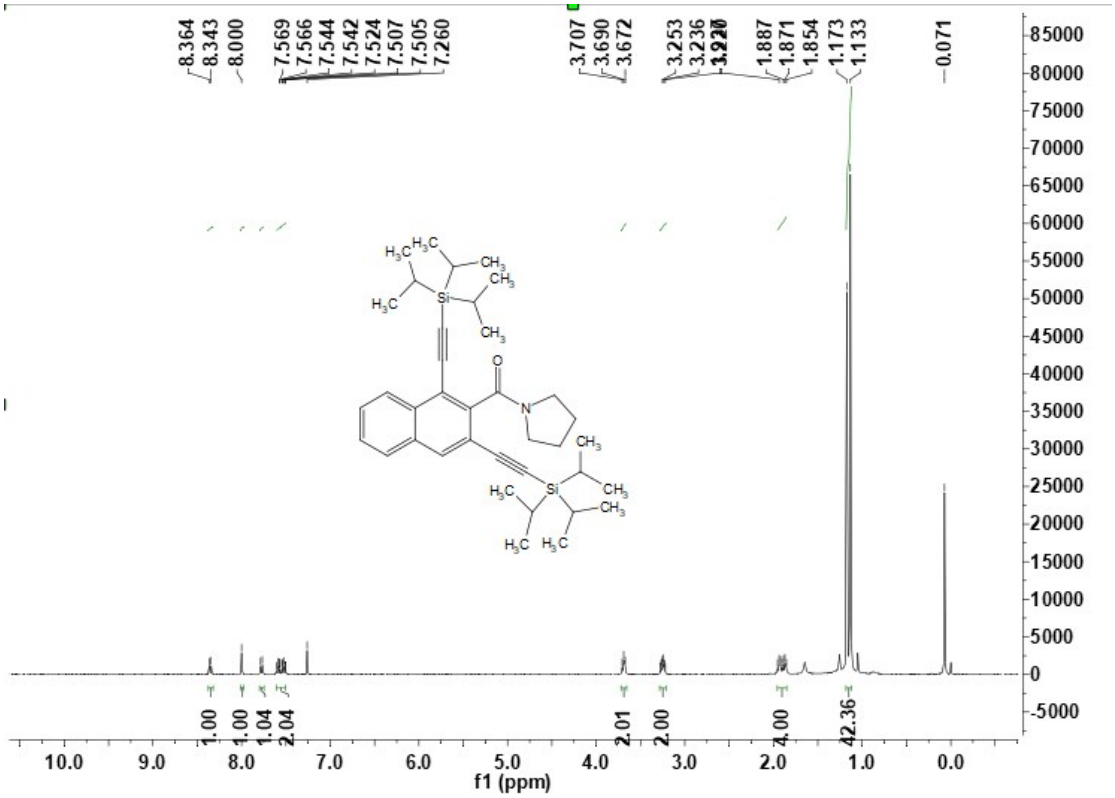


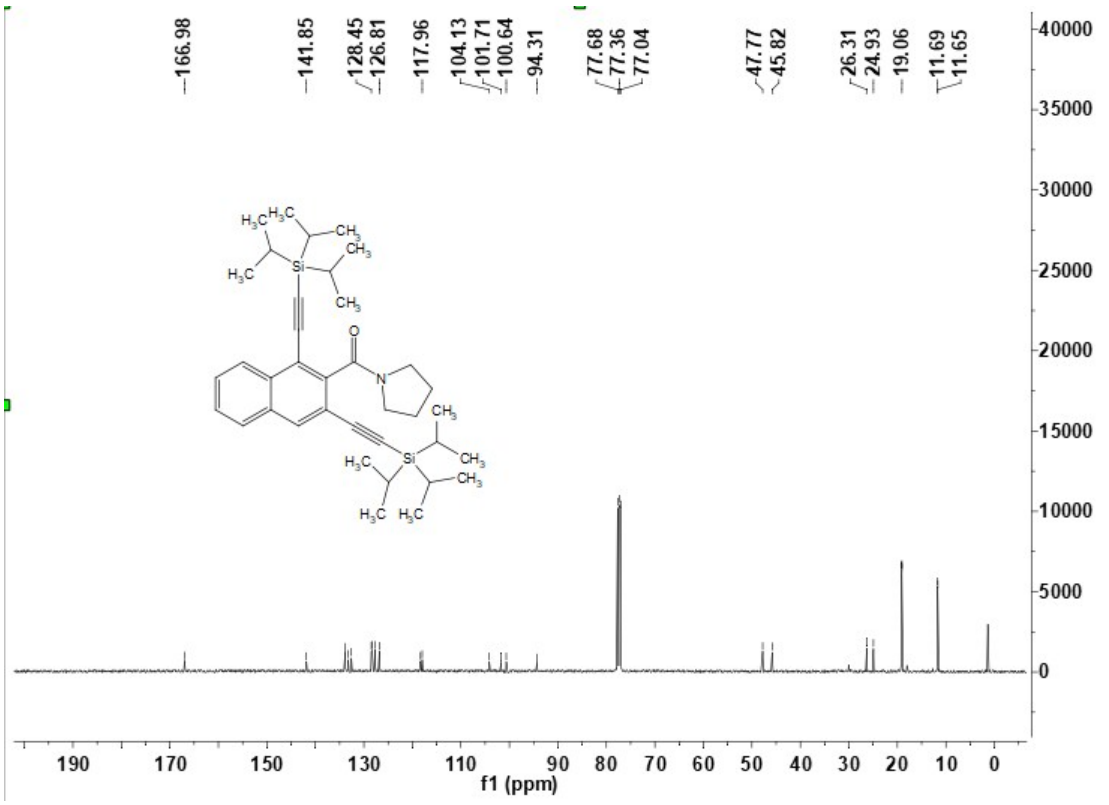
(4-Bromo-2-((triisopropylsilyl)ethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e)



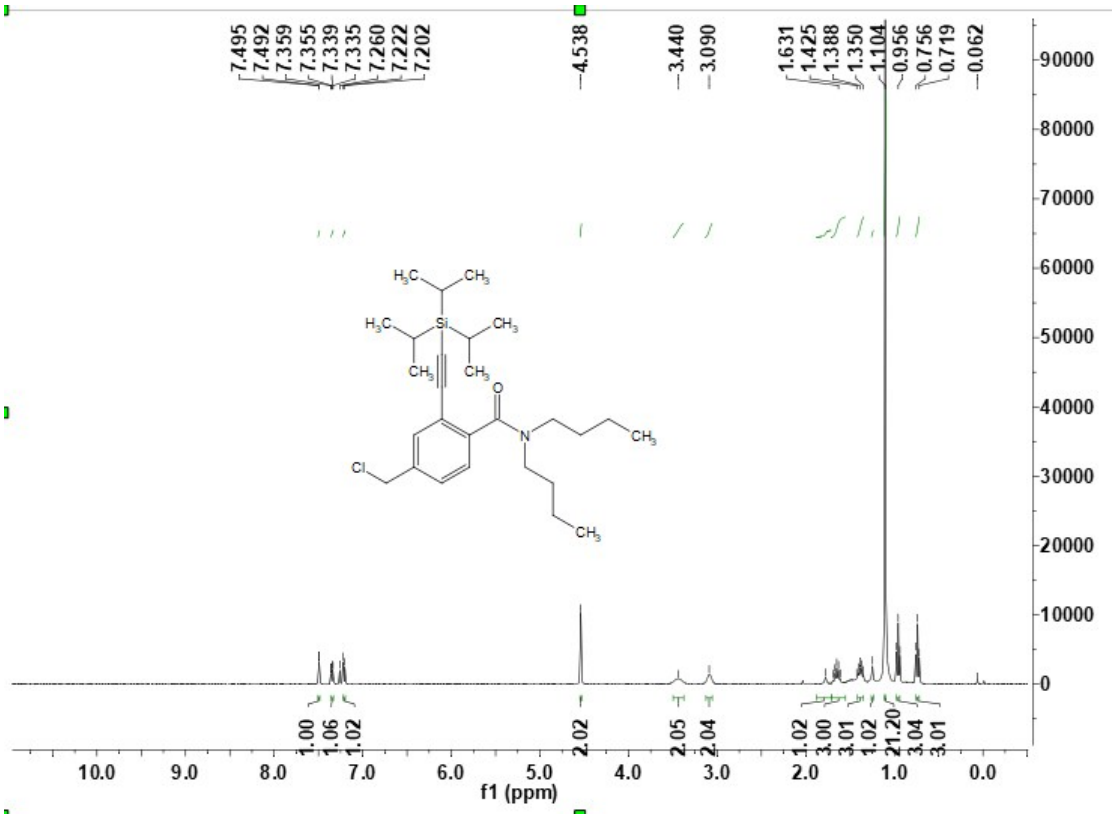


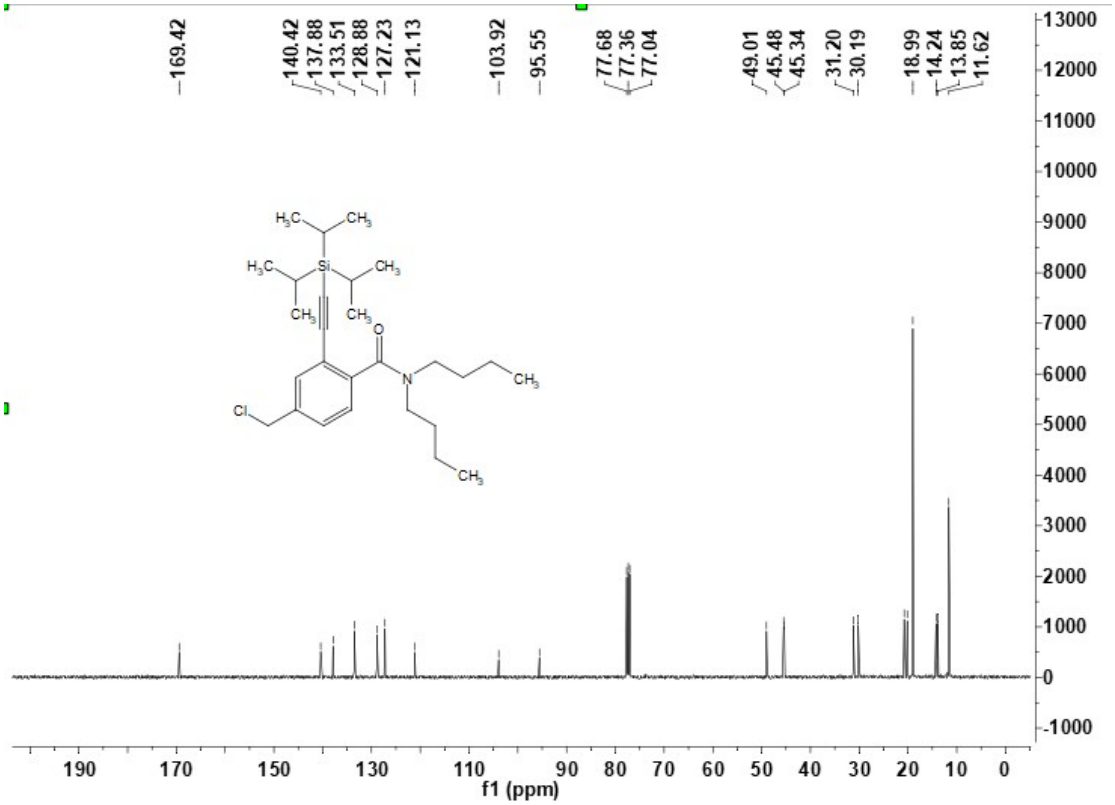
(1,3-Bis((triisopropylsilyl)ethynyl)naphthalen-2-yl)(pyrrolidin-1-yl)methanone (5f)



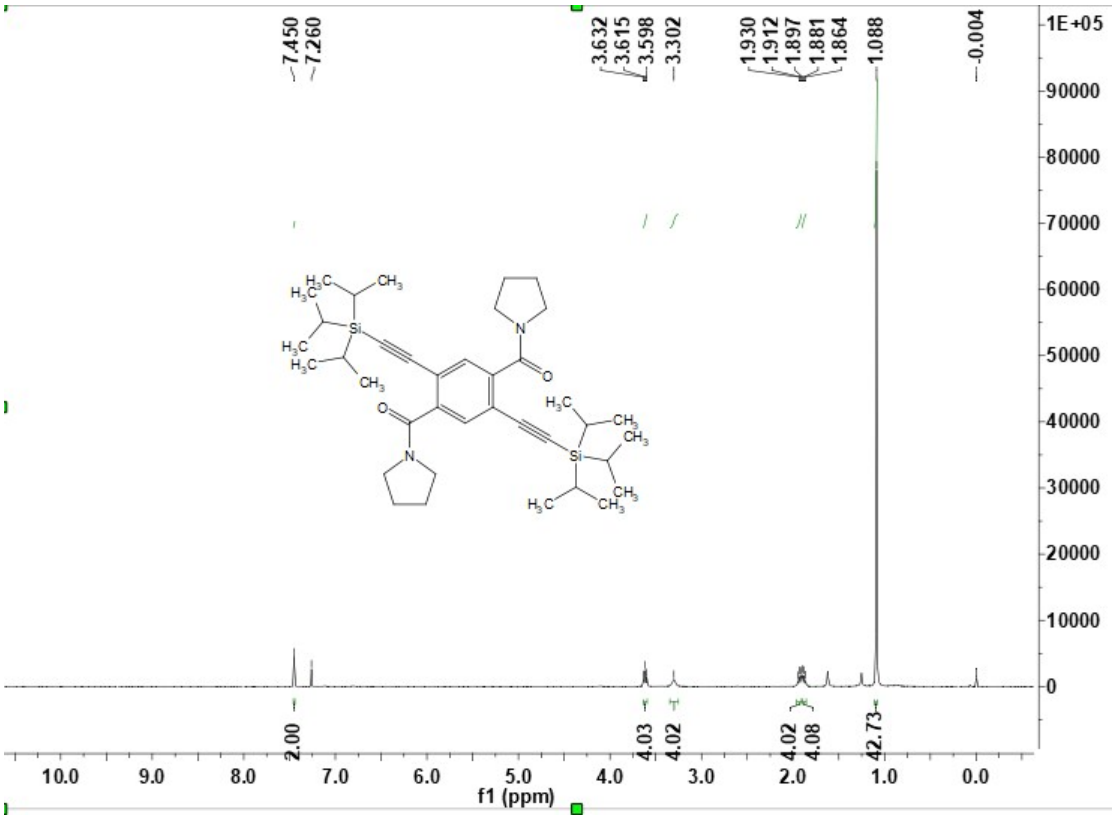


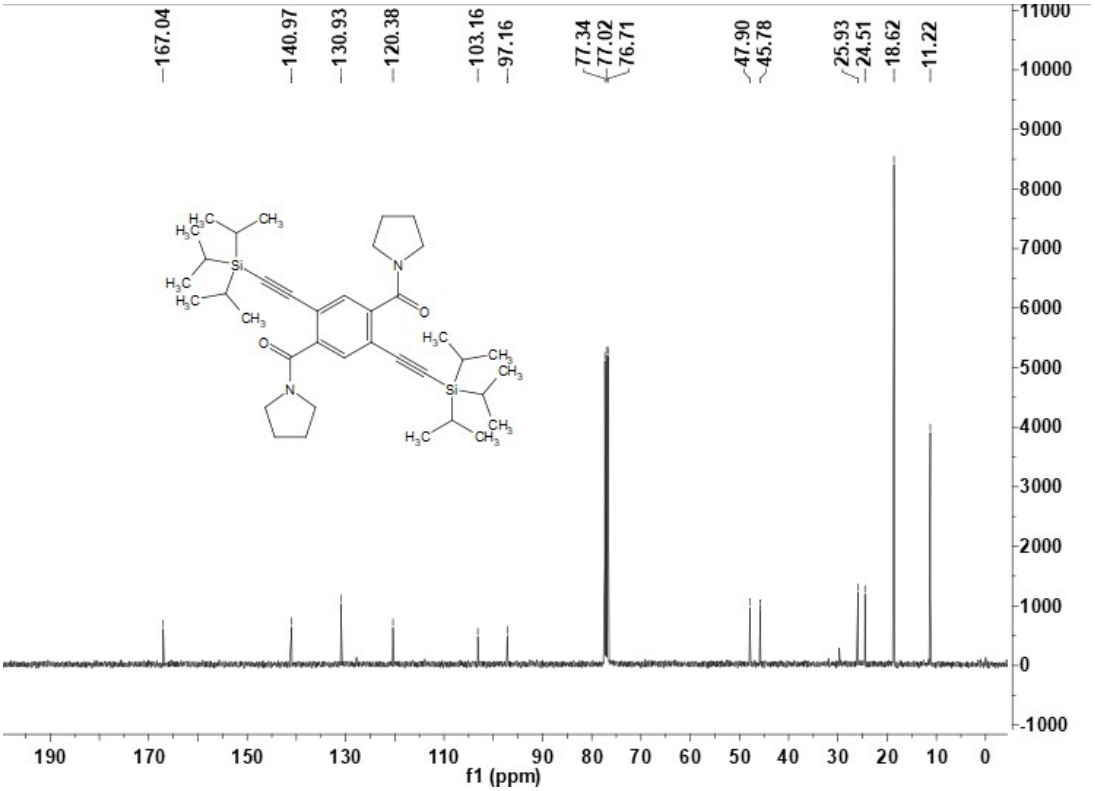
***N,N*-Dibutyl-4-(chloromethyl)-2-((triisopropylsilyl)ethynyl)benzamide (5g)**



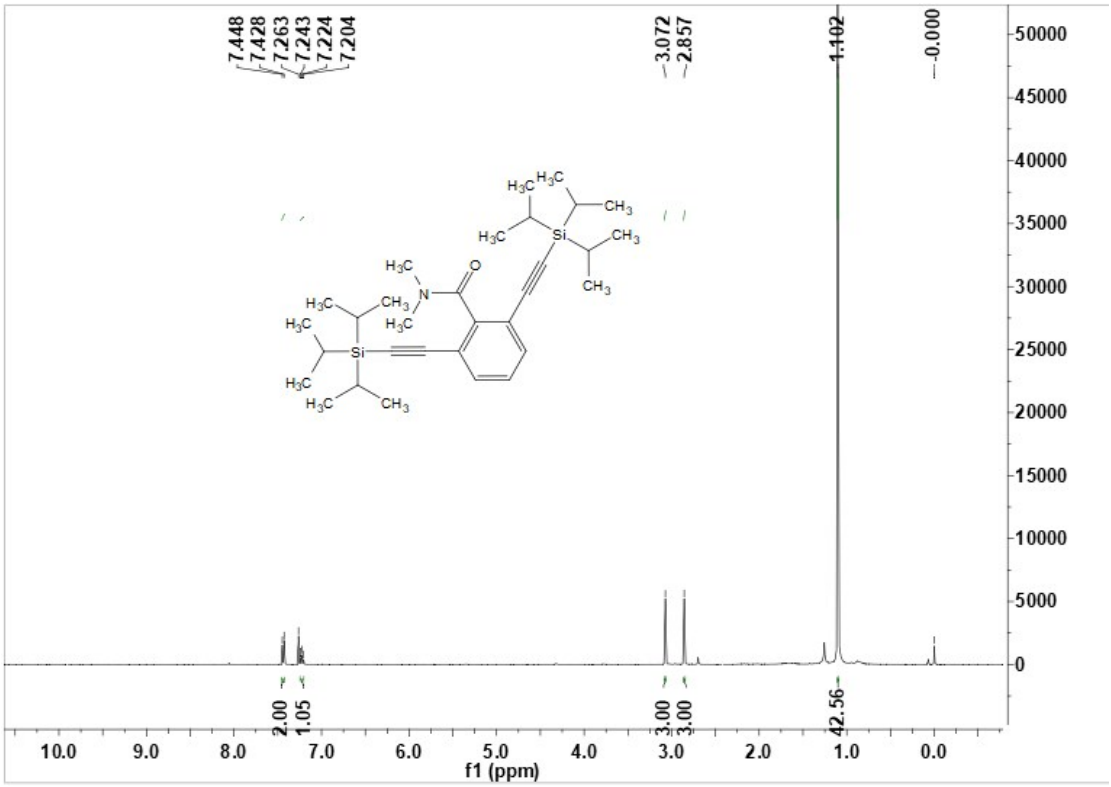


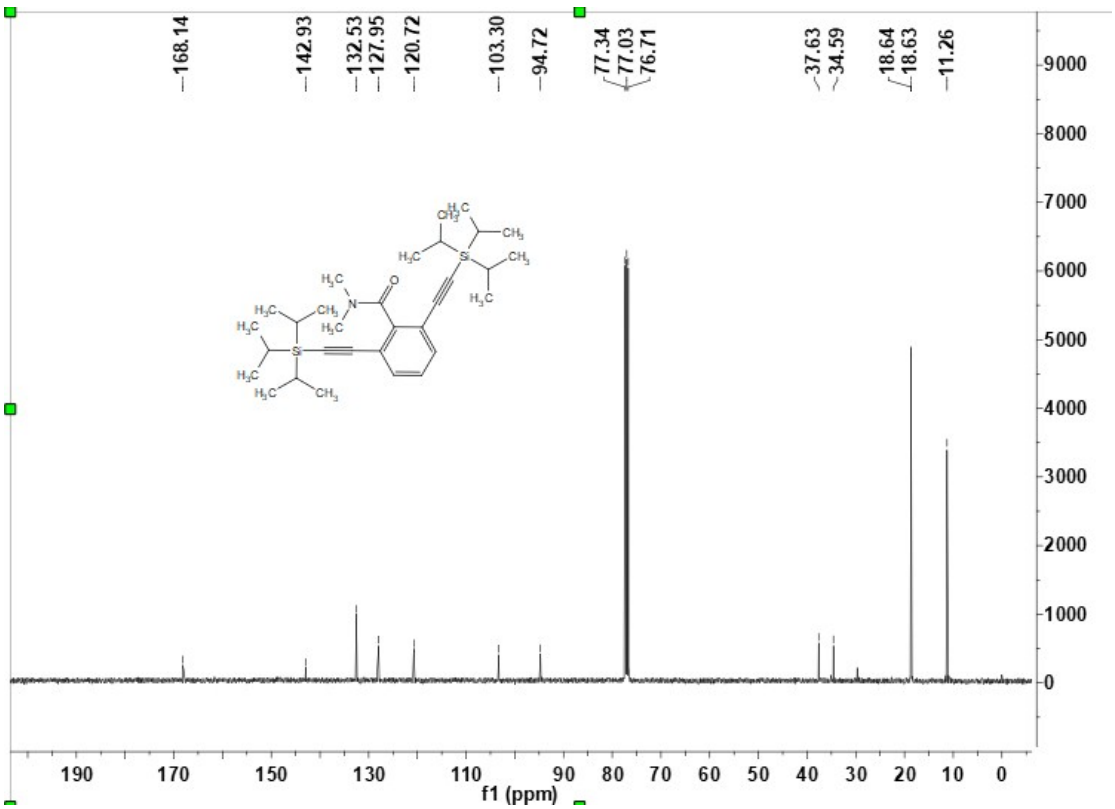
(2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bis(pyrrolidin-1-ylmethanone) (5h)



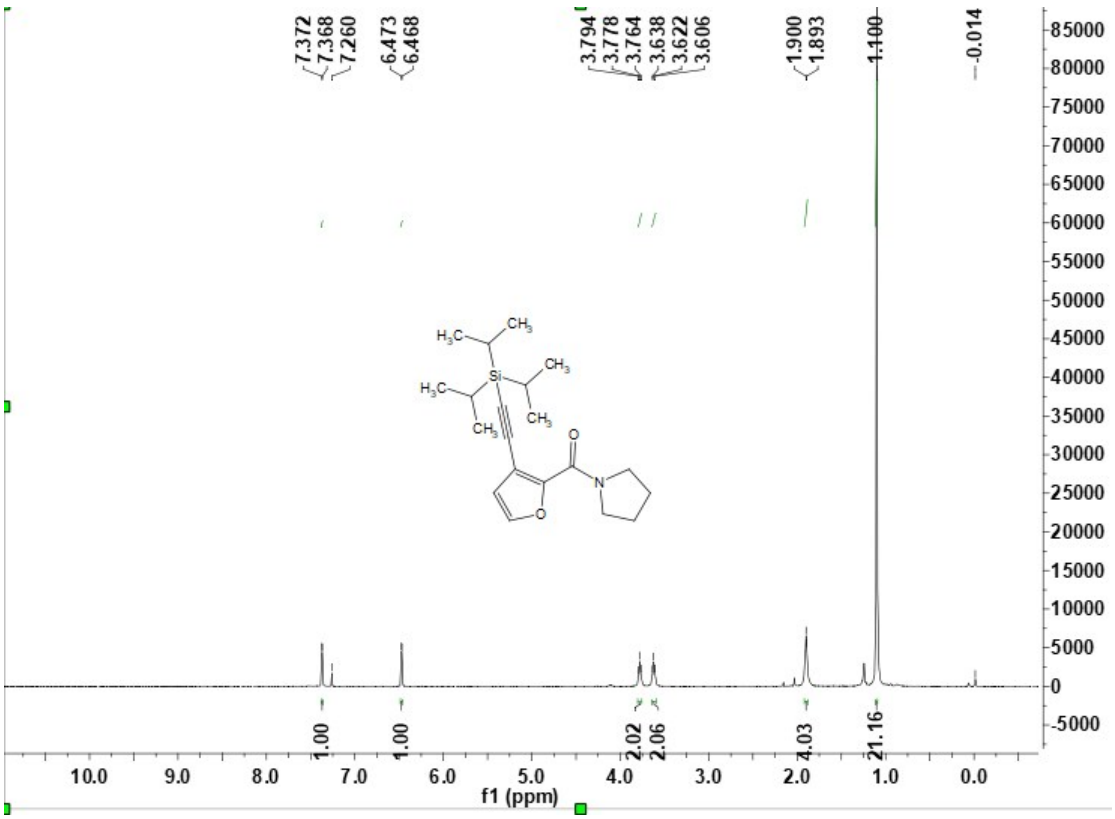


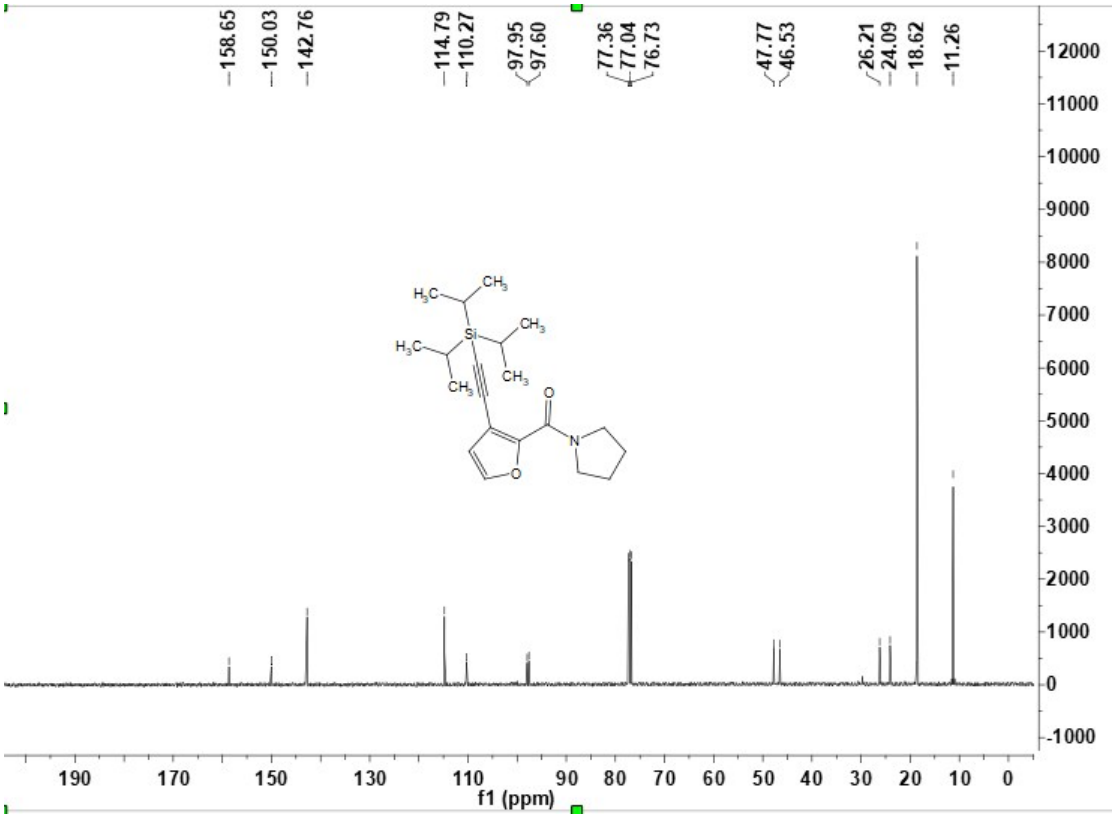
***N*,*N*-Dimethyl-2,6-bis((triisopropylsilyl)ethynyl)benzamide (5i)**



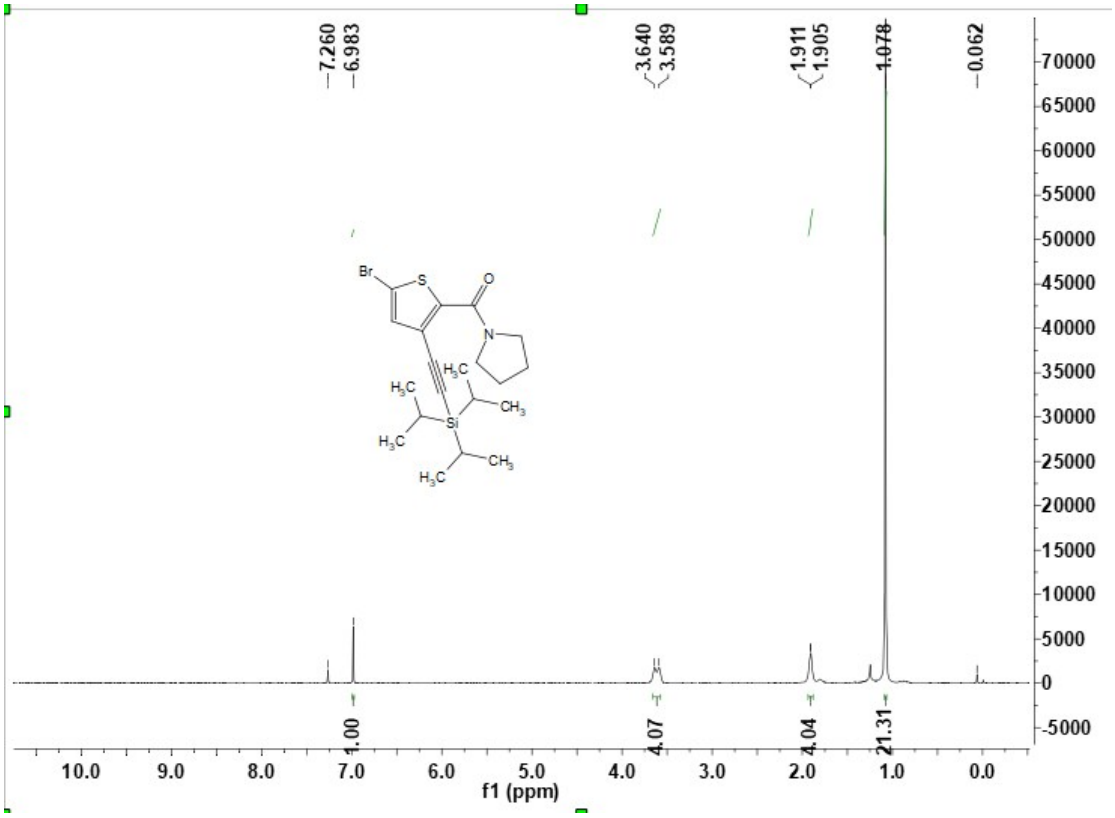


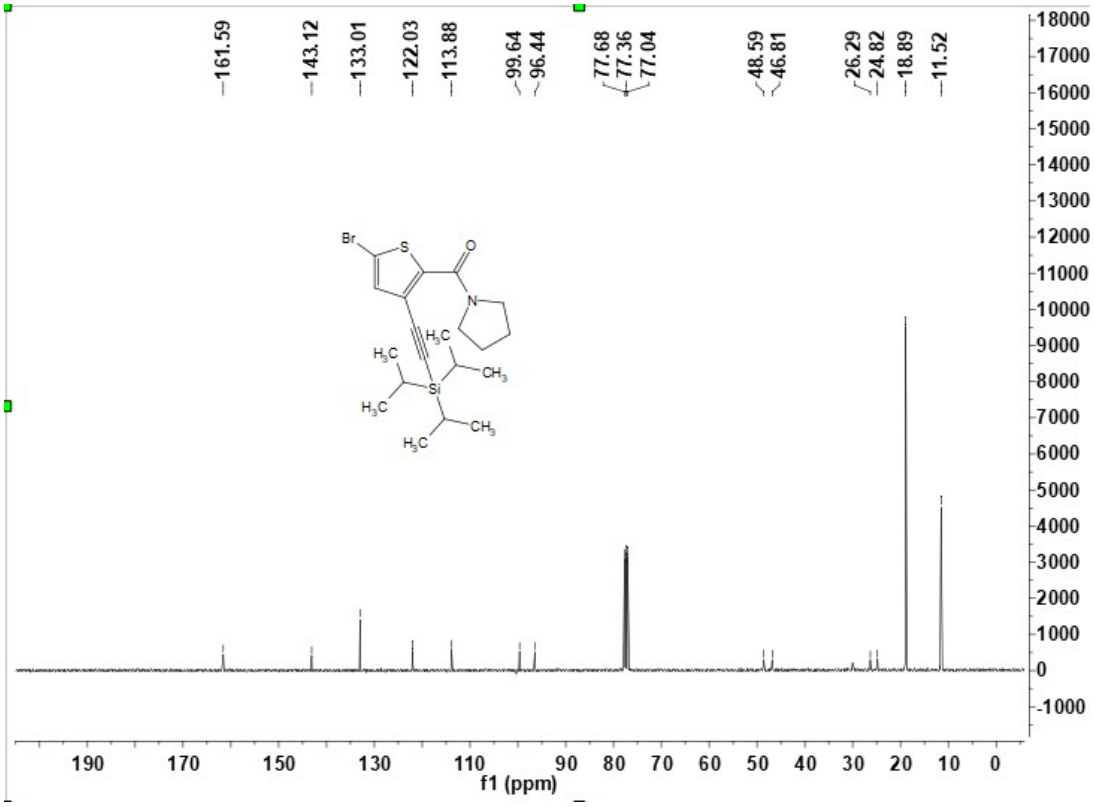
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)furan-2-yl)methanone (5j)



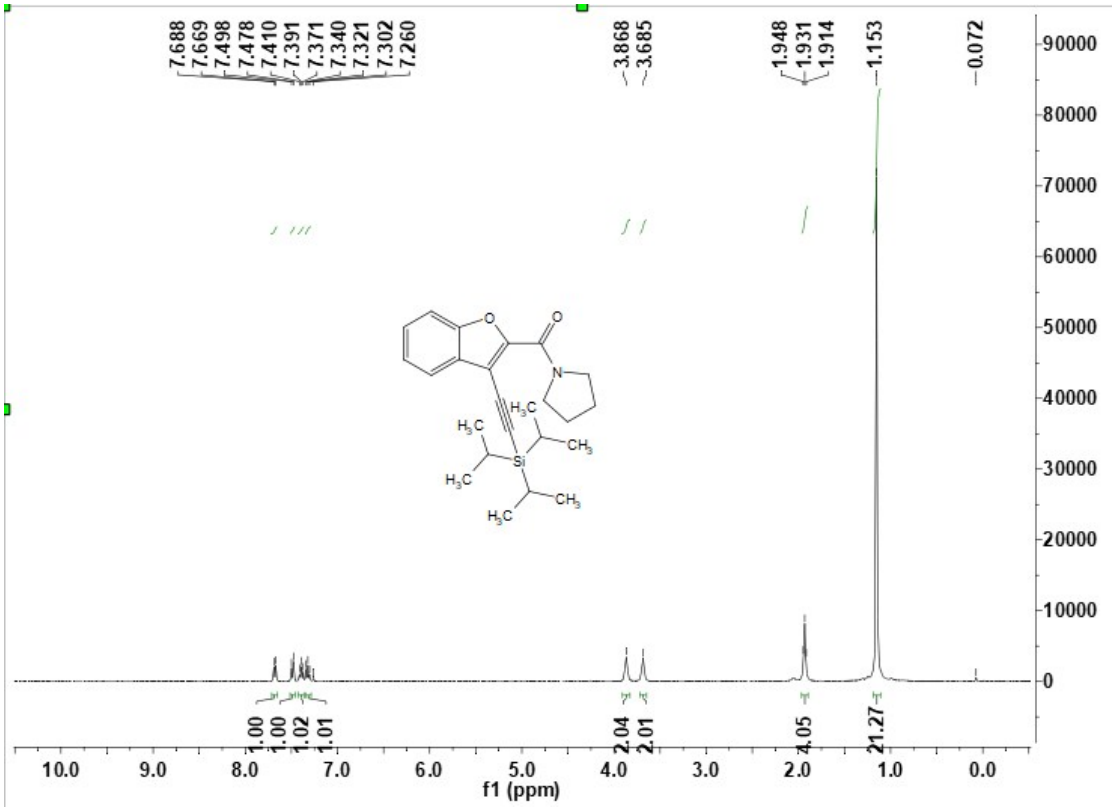


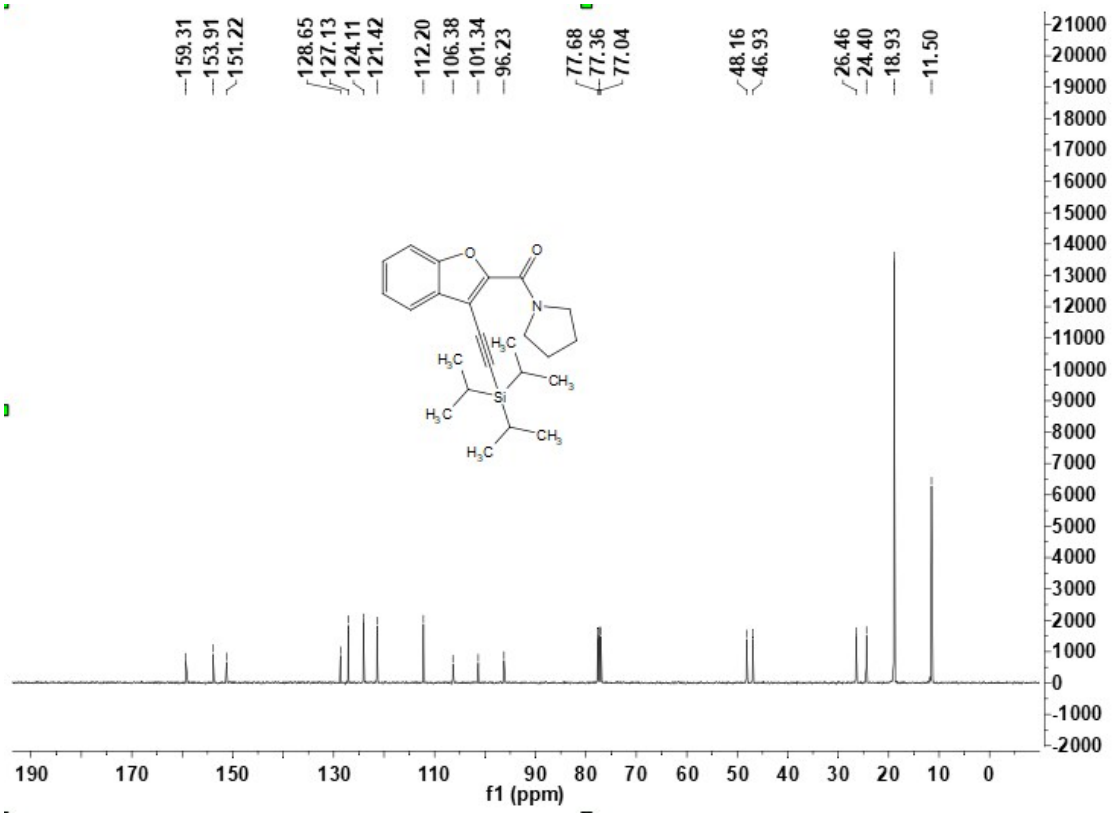
(5-Bromo-3-((triisopropylsilyl)ethynyl)thiophen-2-yl)(pyrrolidin-1-yl)methanone (5k)



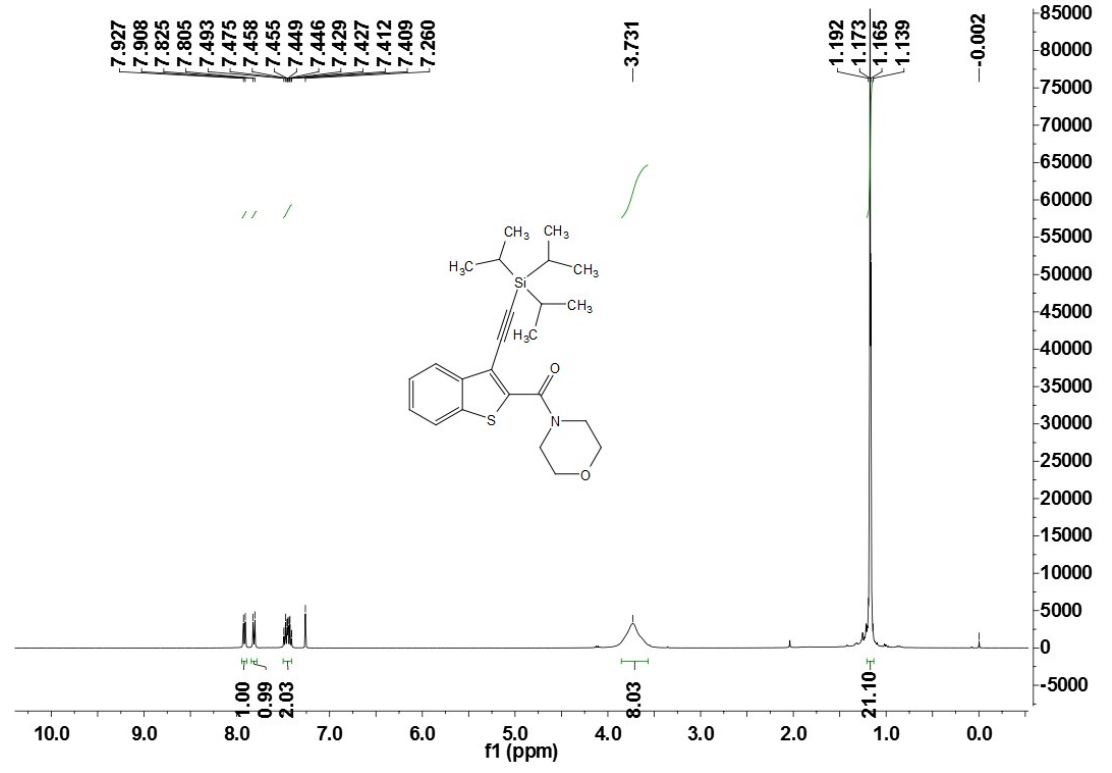


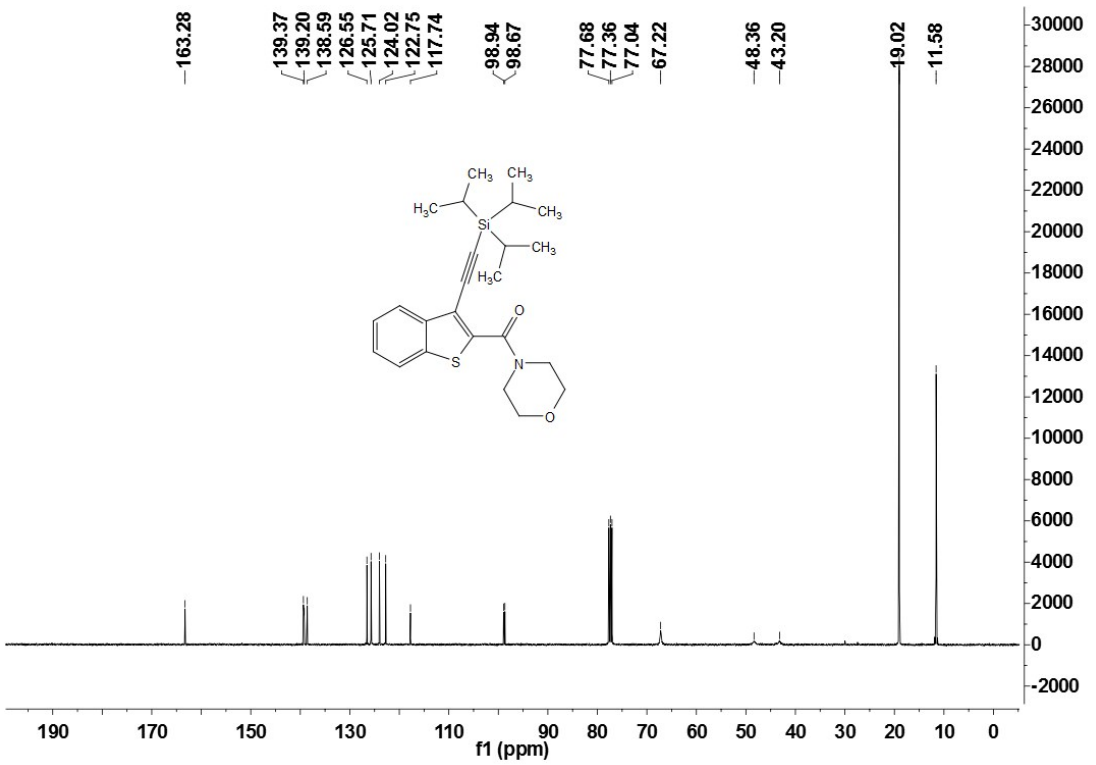
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)benzofuran-2-yl)methanone (5l)



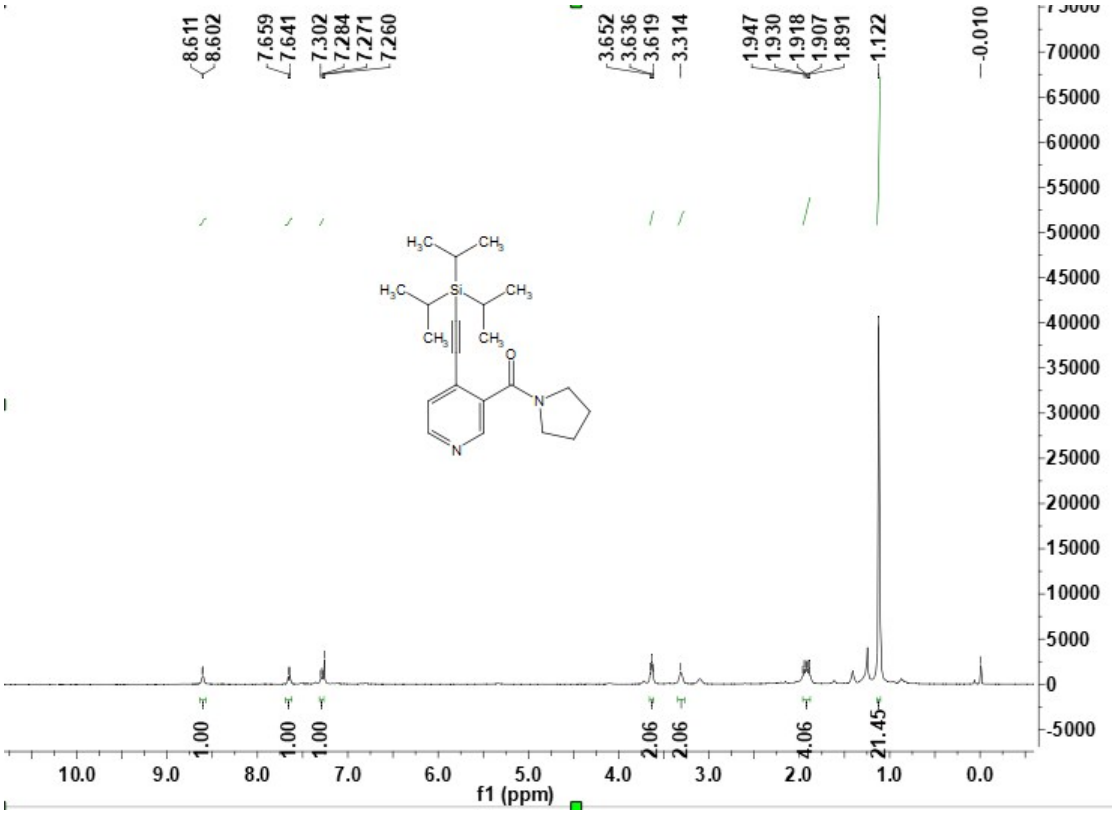


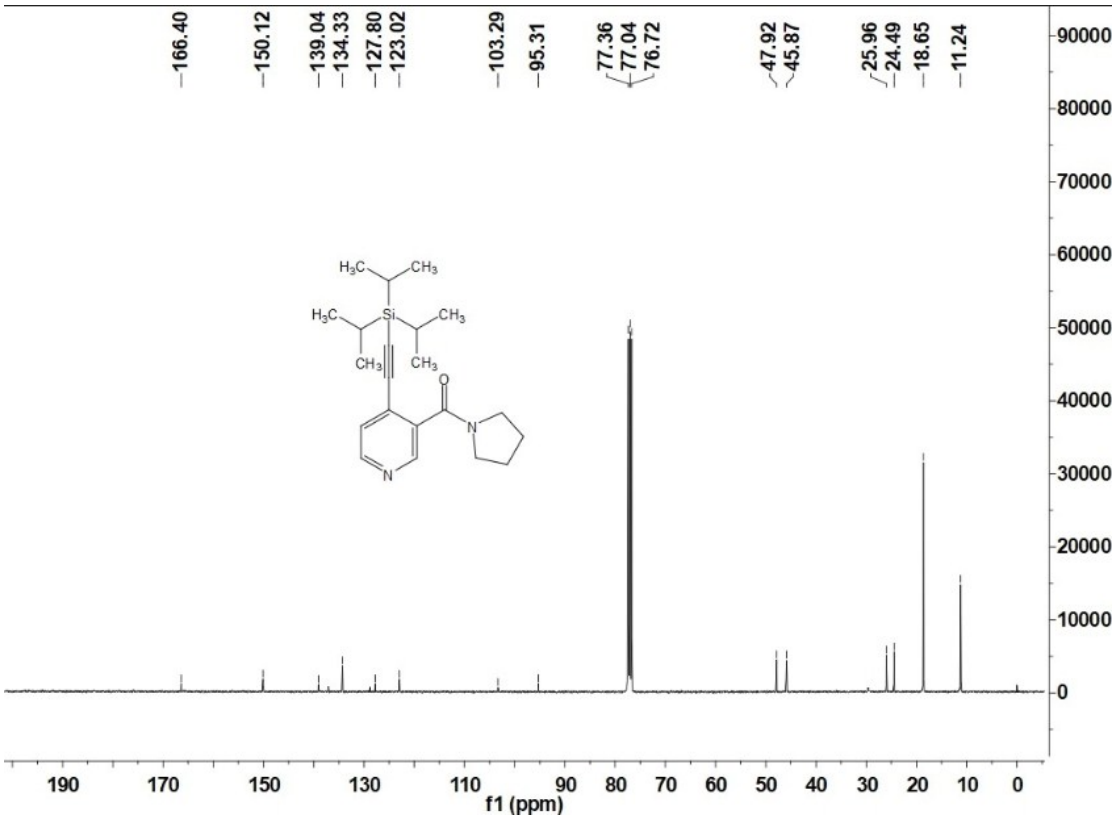
Morpholino(3-((triisopropylsilyl)ethynyl)benzo[b]thiophen-2-yl)methanone (5m)



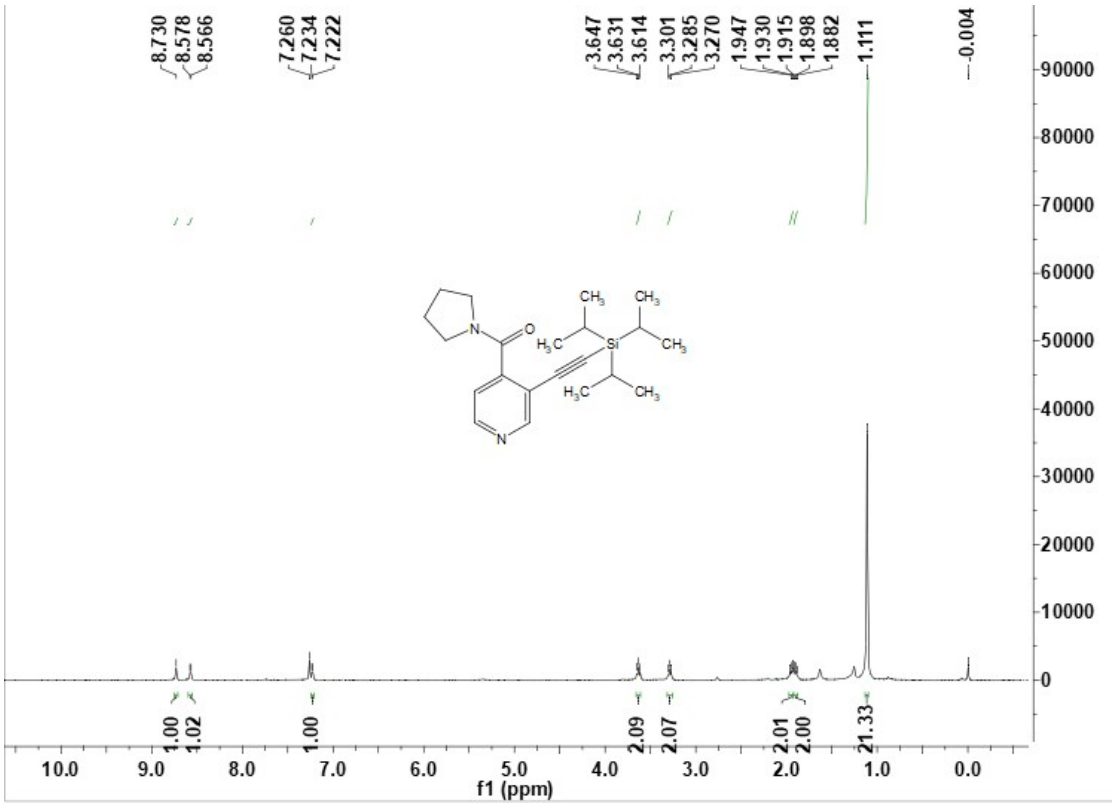


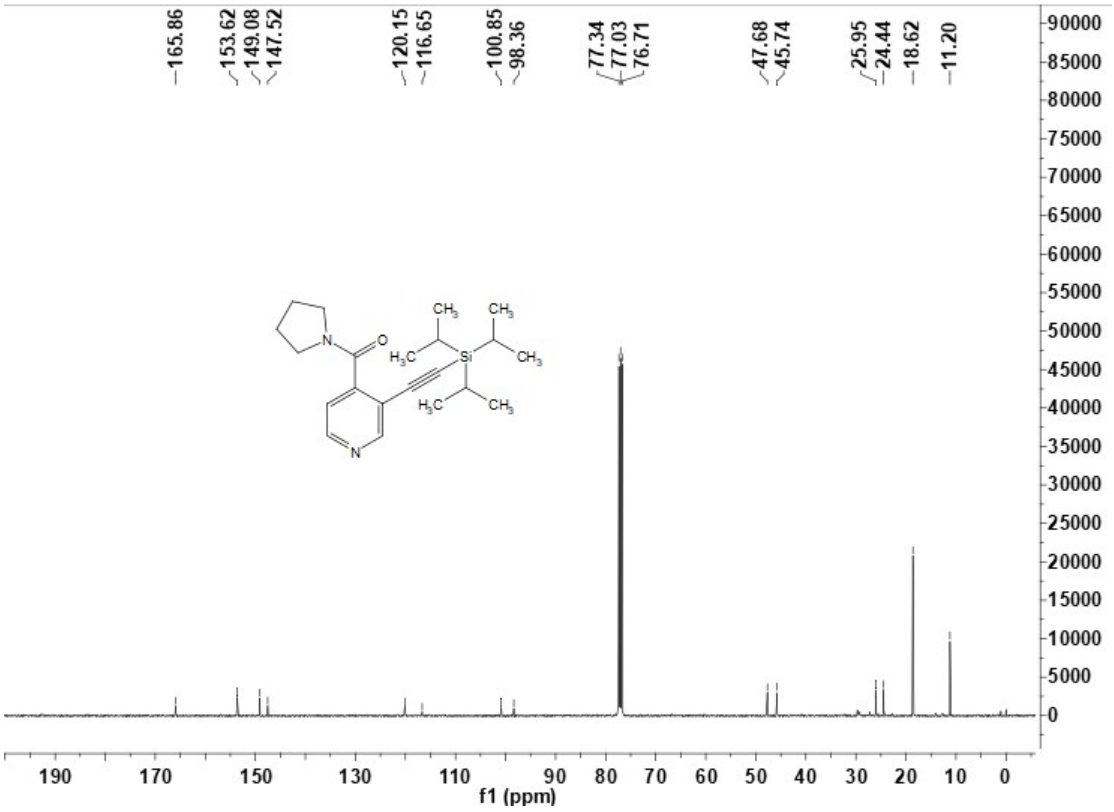
Pyrrolidin-1-yl(4-((triisopropylsilyl)ethynyl)pyridin-3-yl)methanone (5n)



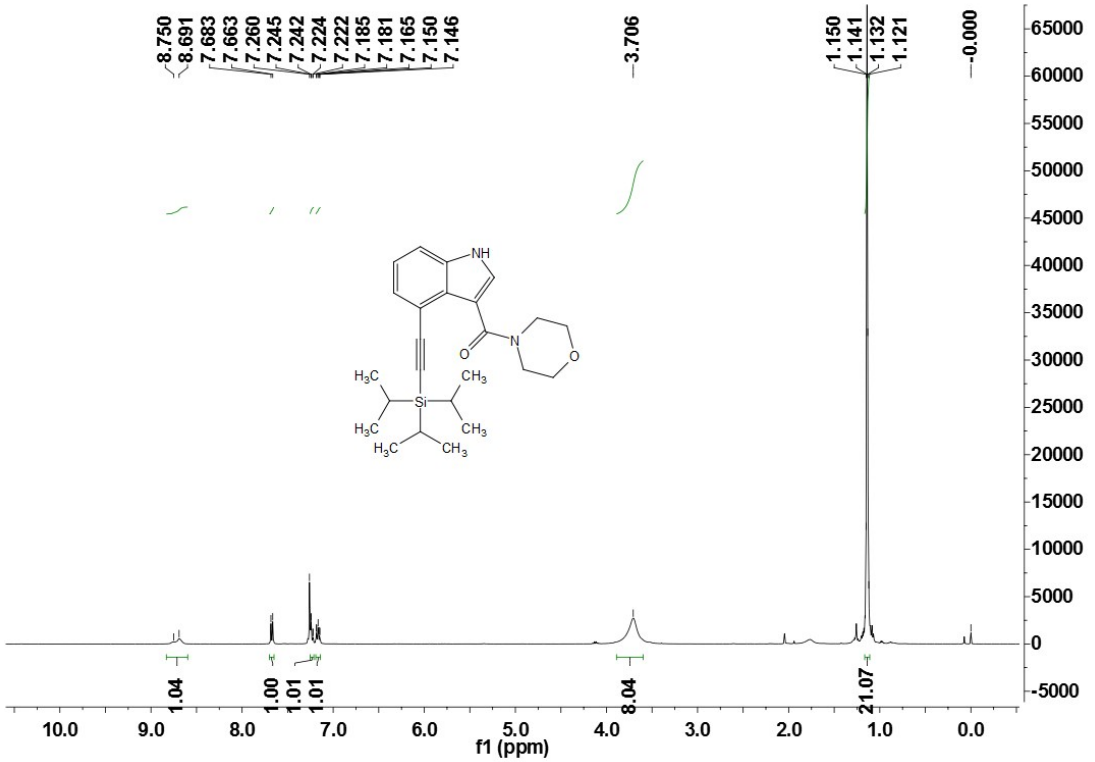


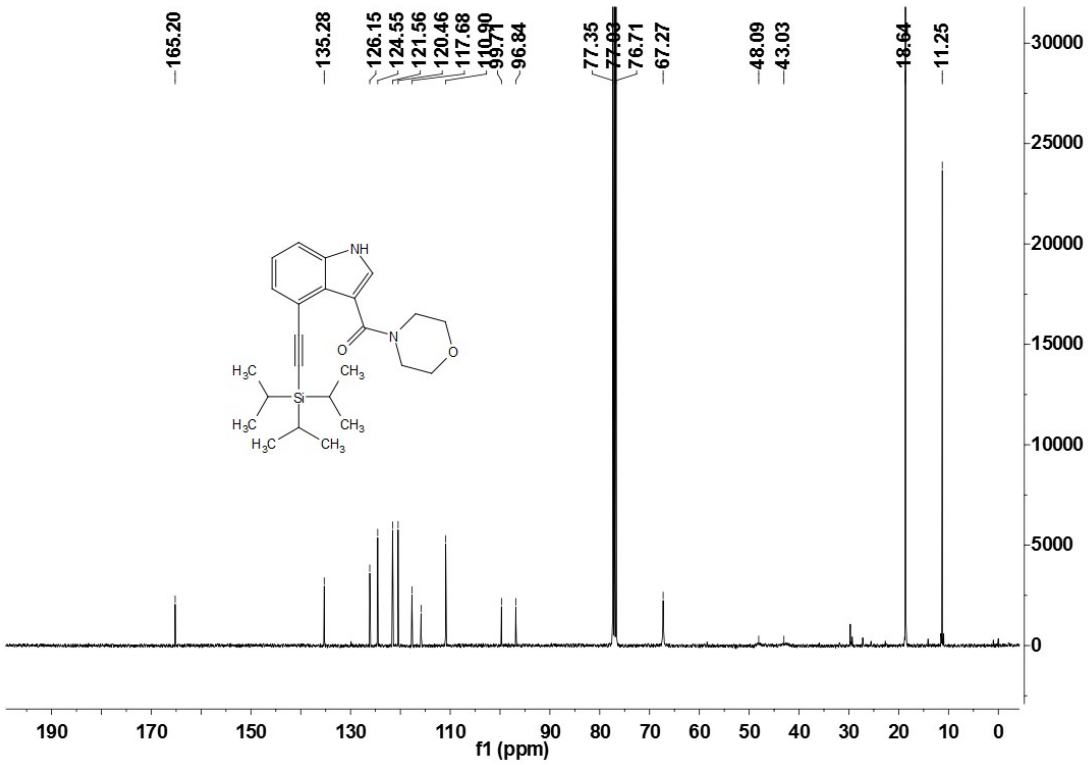
Pyrrolidin-1-yl(3-((triisopropylsilyl)ethynyl)pyridin-4-yl)methanone (5o)



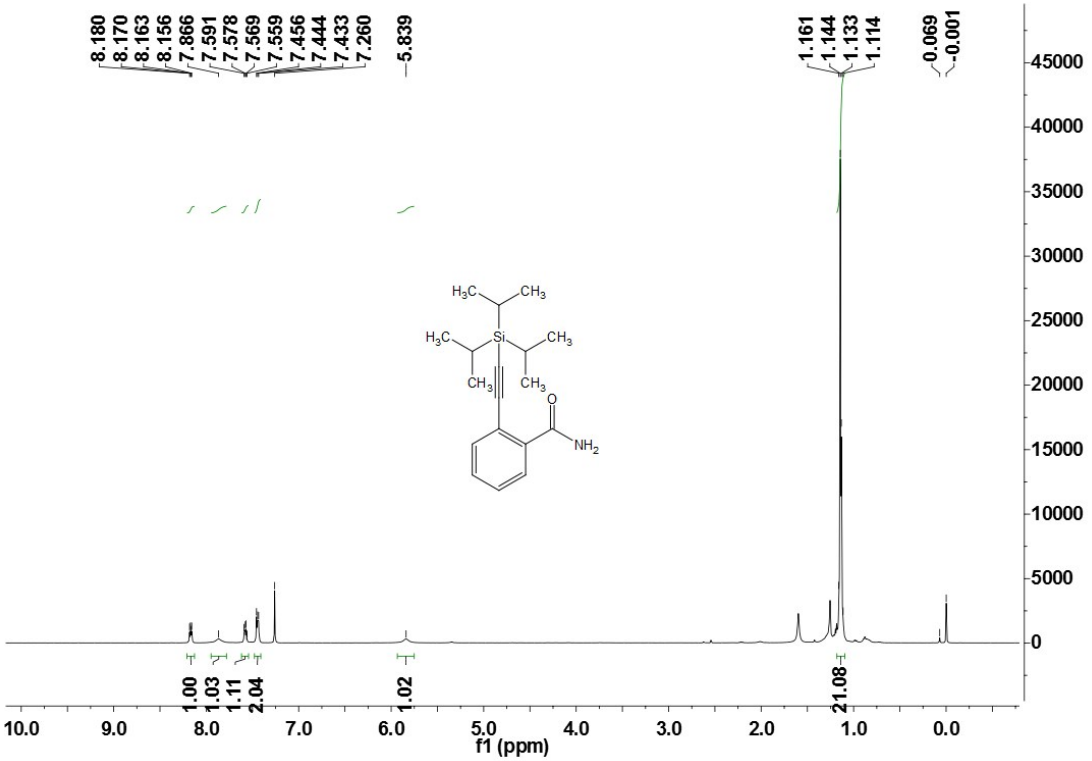


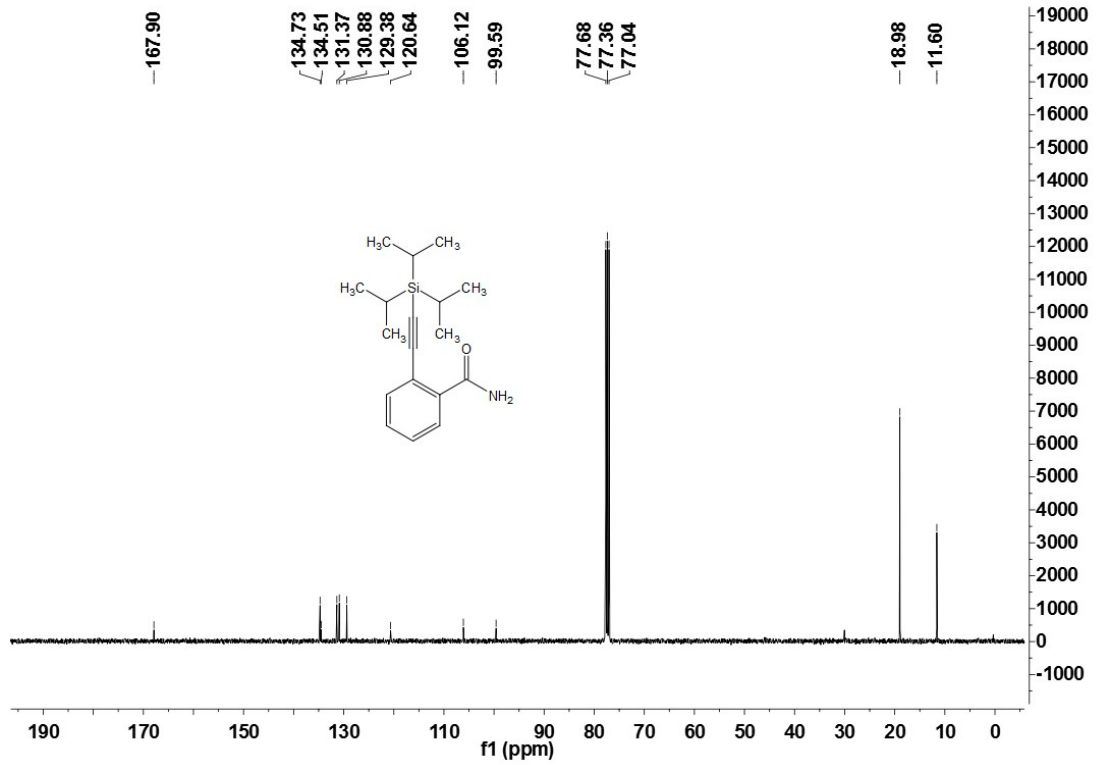
Morpholino(2-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)methanone (5p)



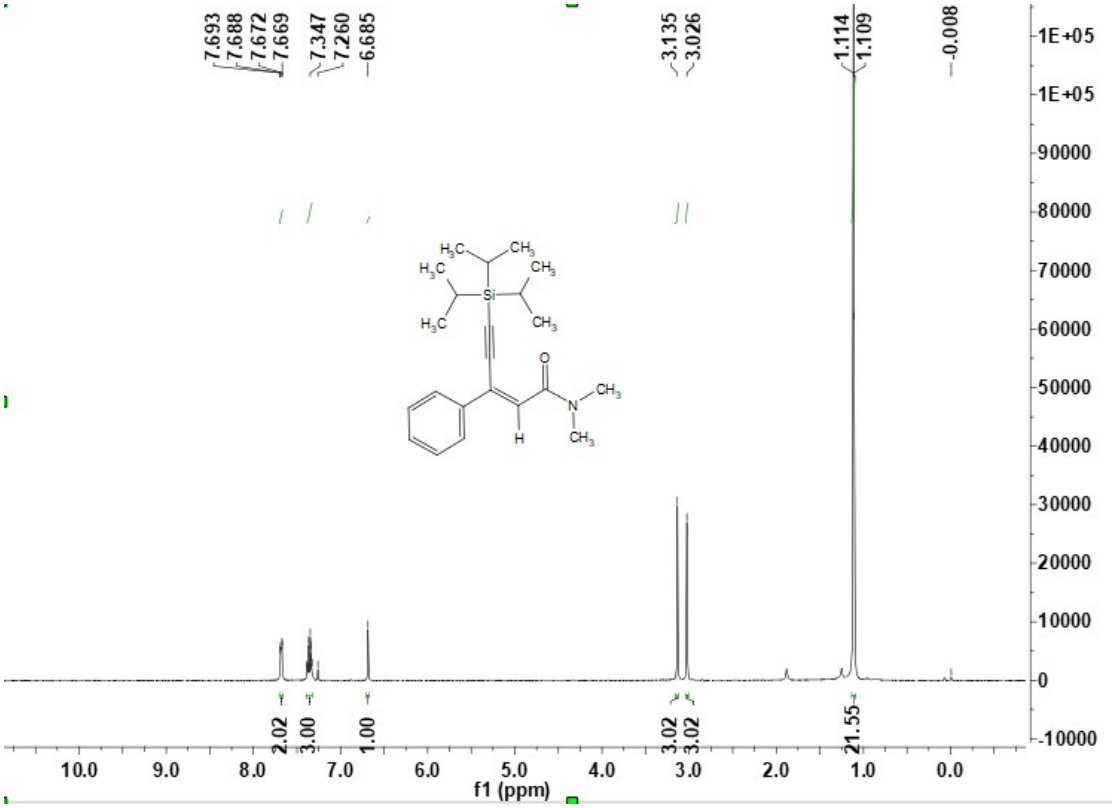


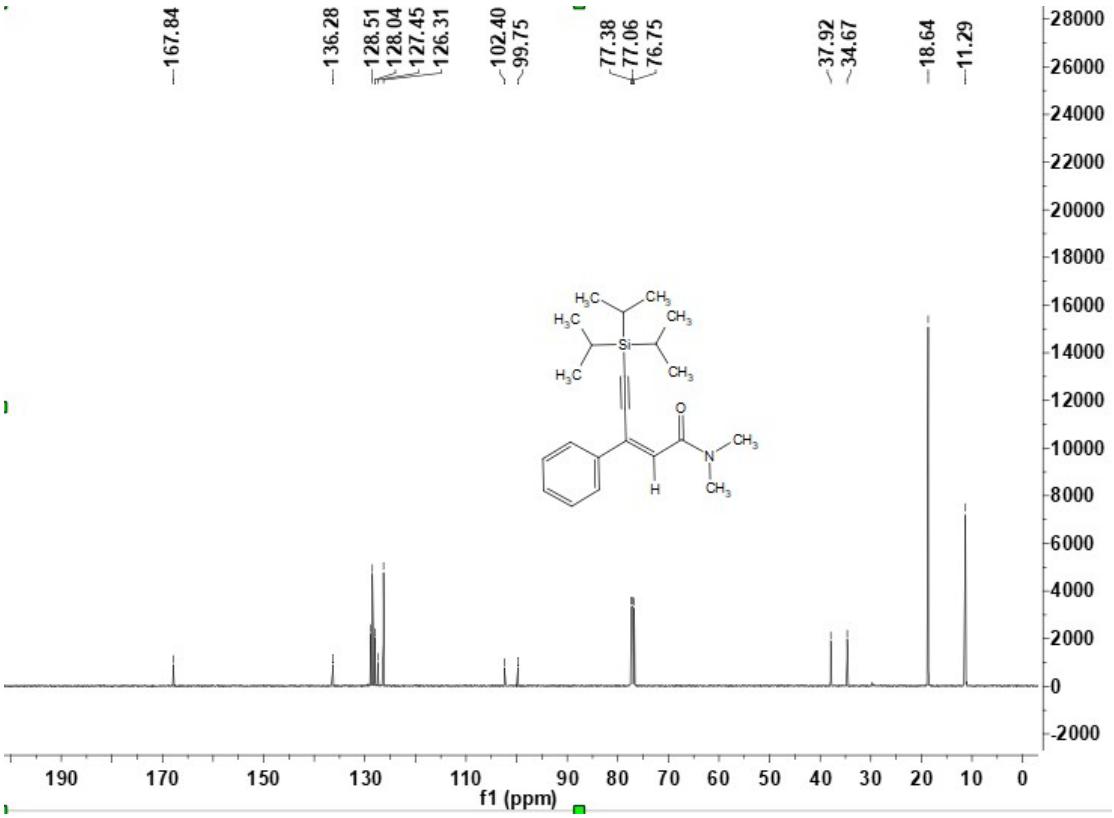
2-((Triisopropylsilyl)ethynyl)benzamide (5q)



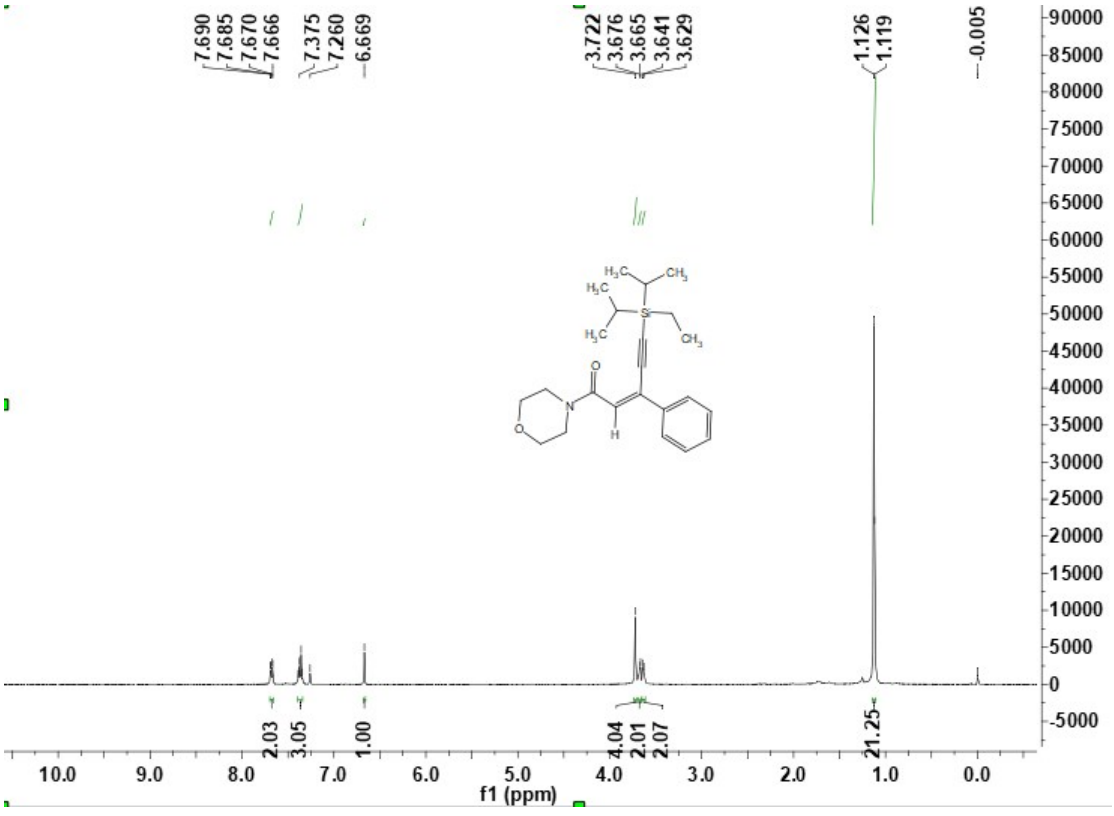


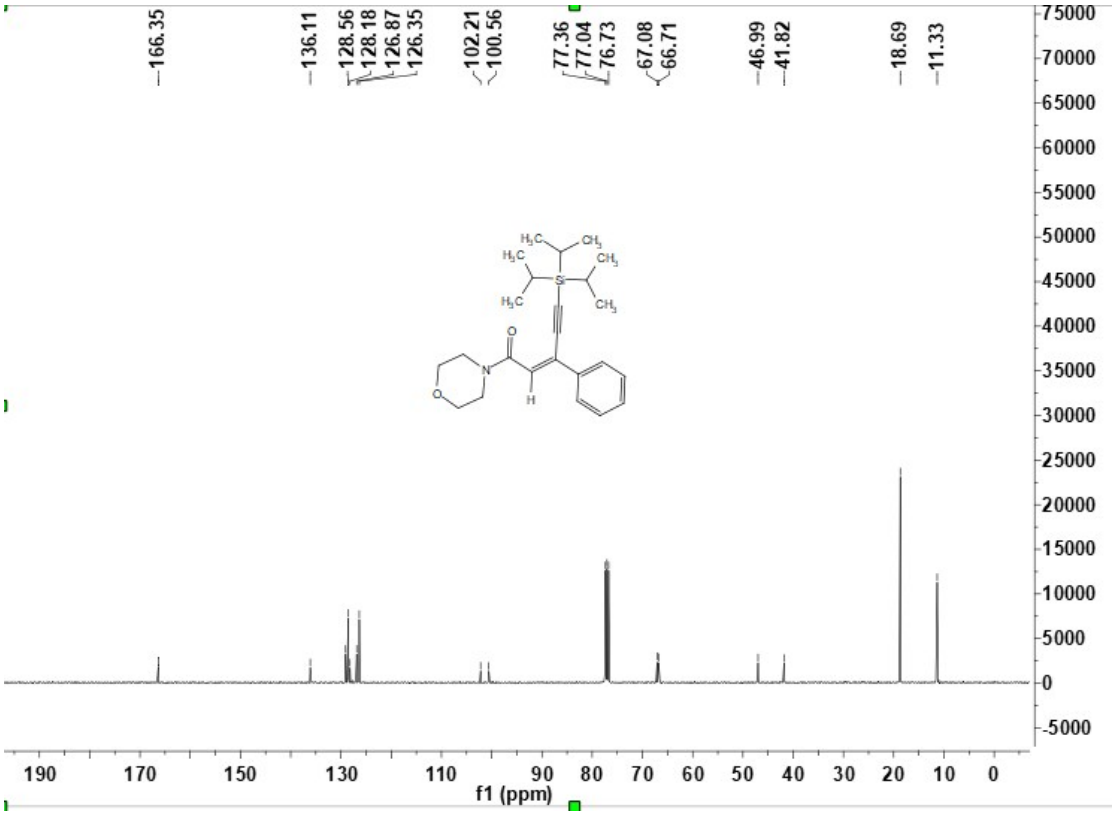
***(Z)*-*N*,*N*-Dimethyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7a)**



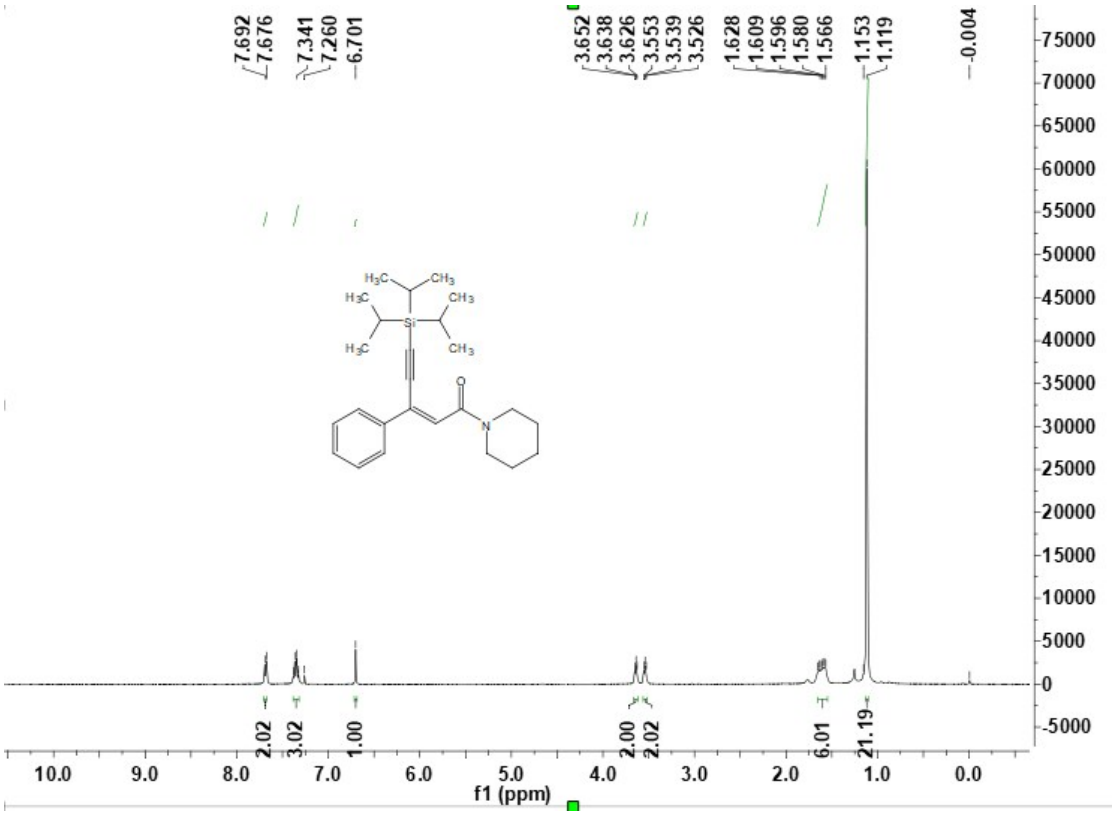


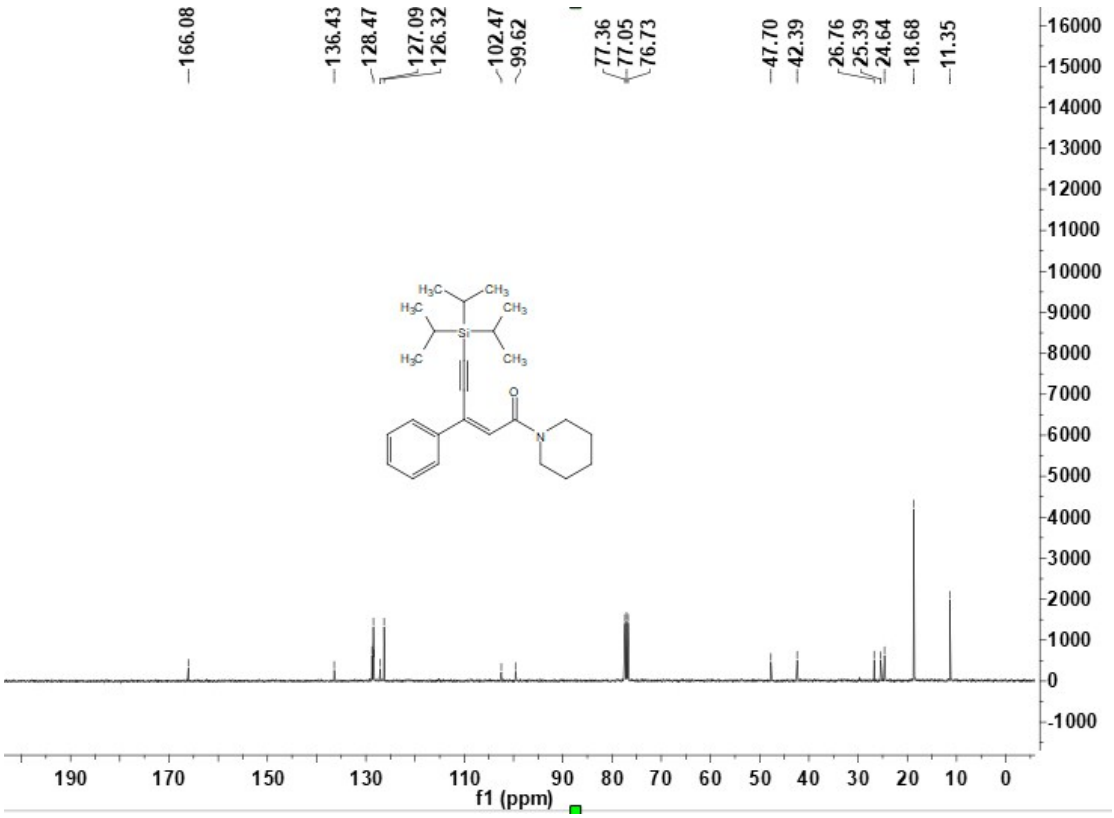
(*Z*)-1-Morpholino-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7b)



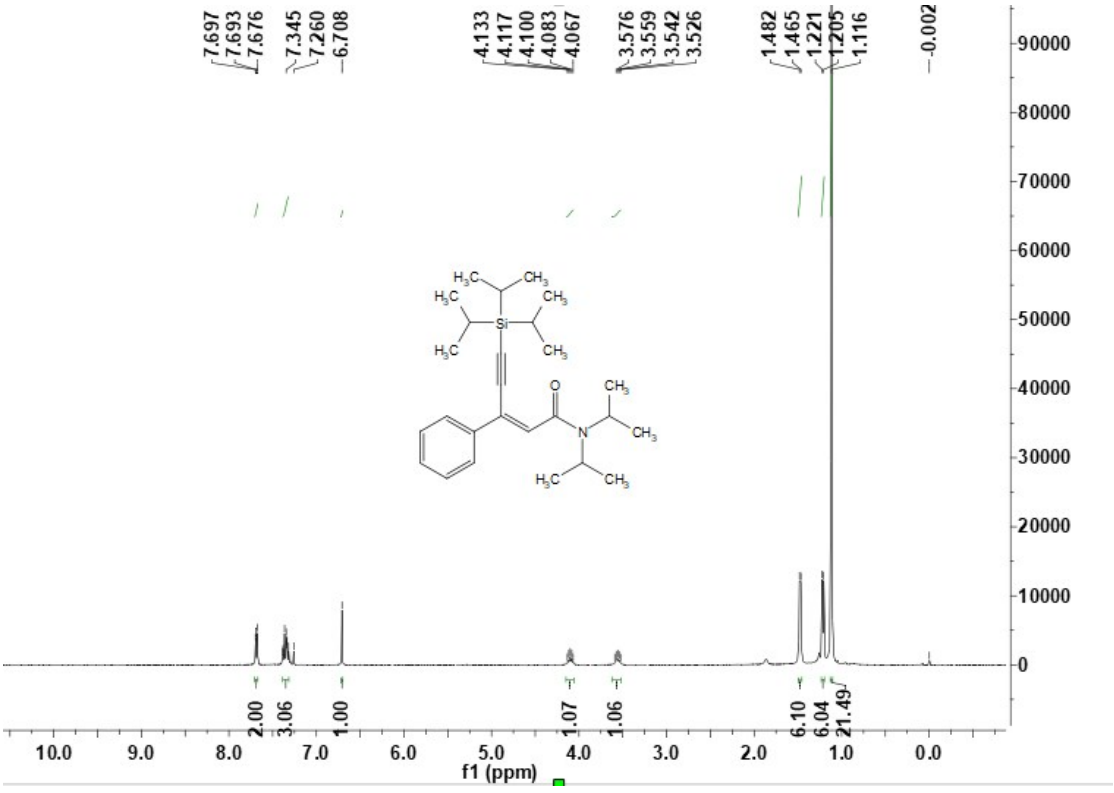


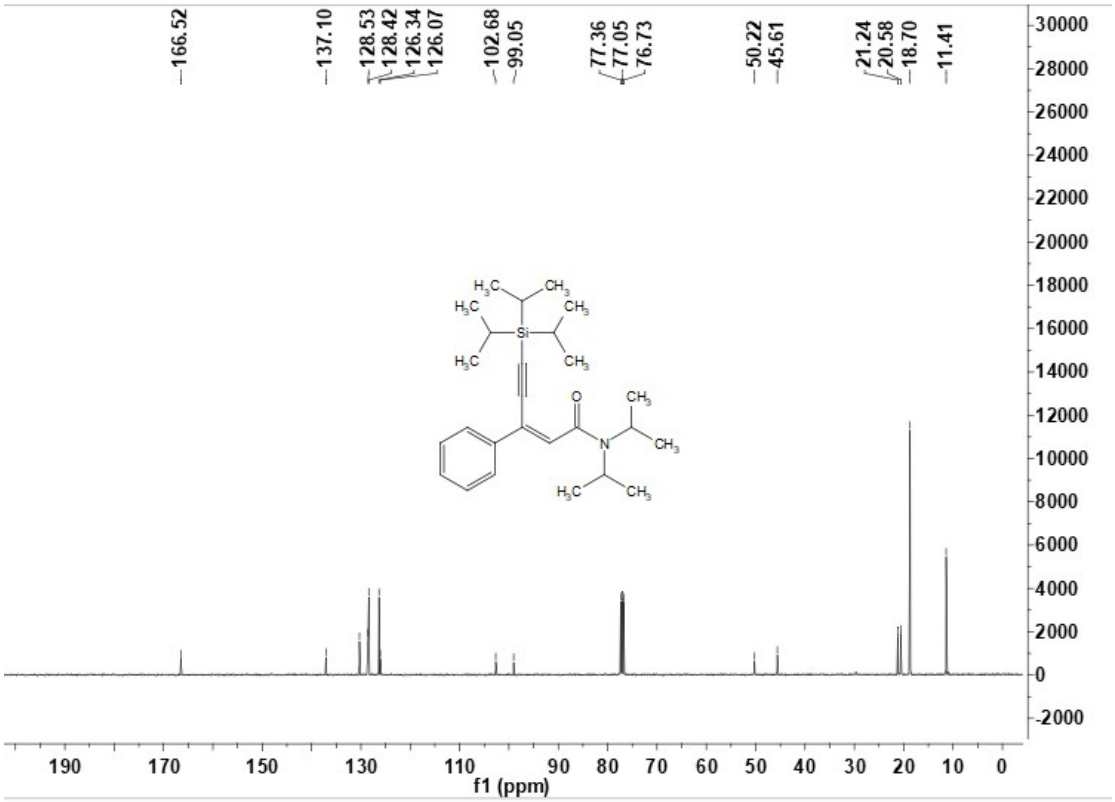
***(Z)*-3-Phenyl-1-(piperidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7c)**



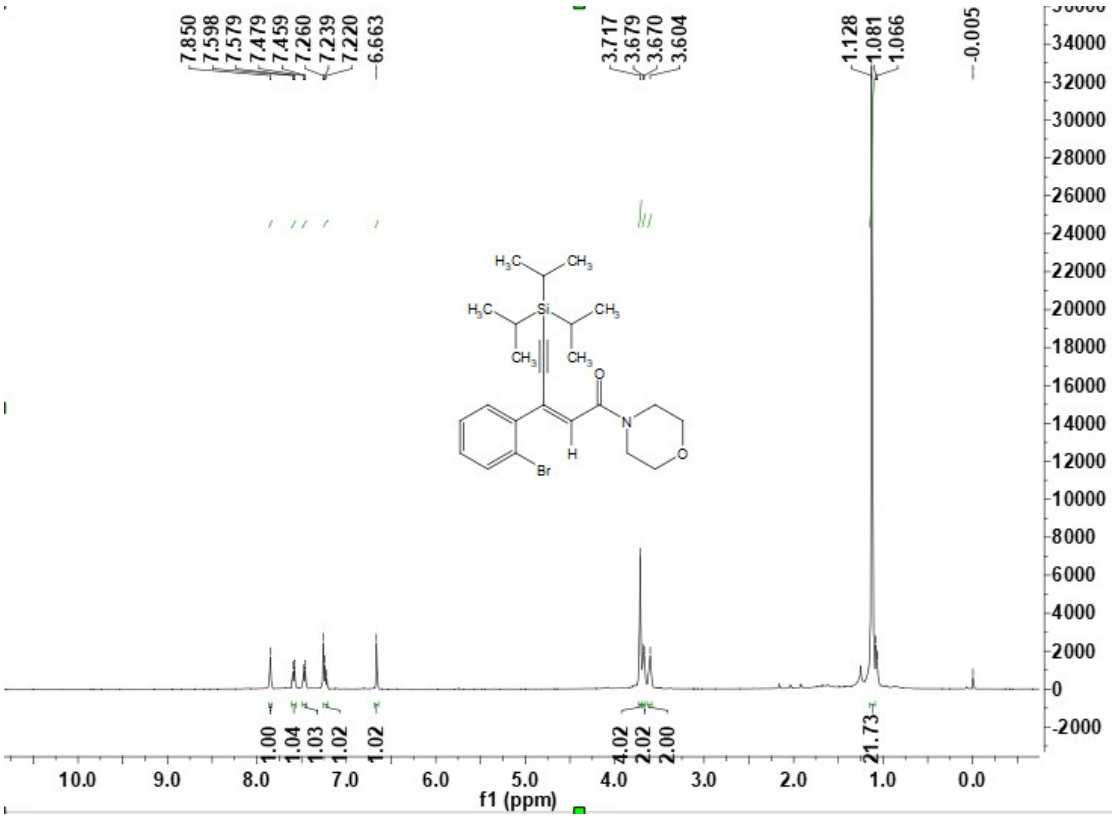


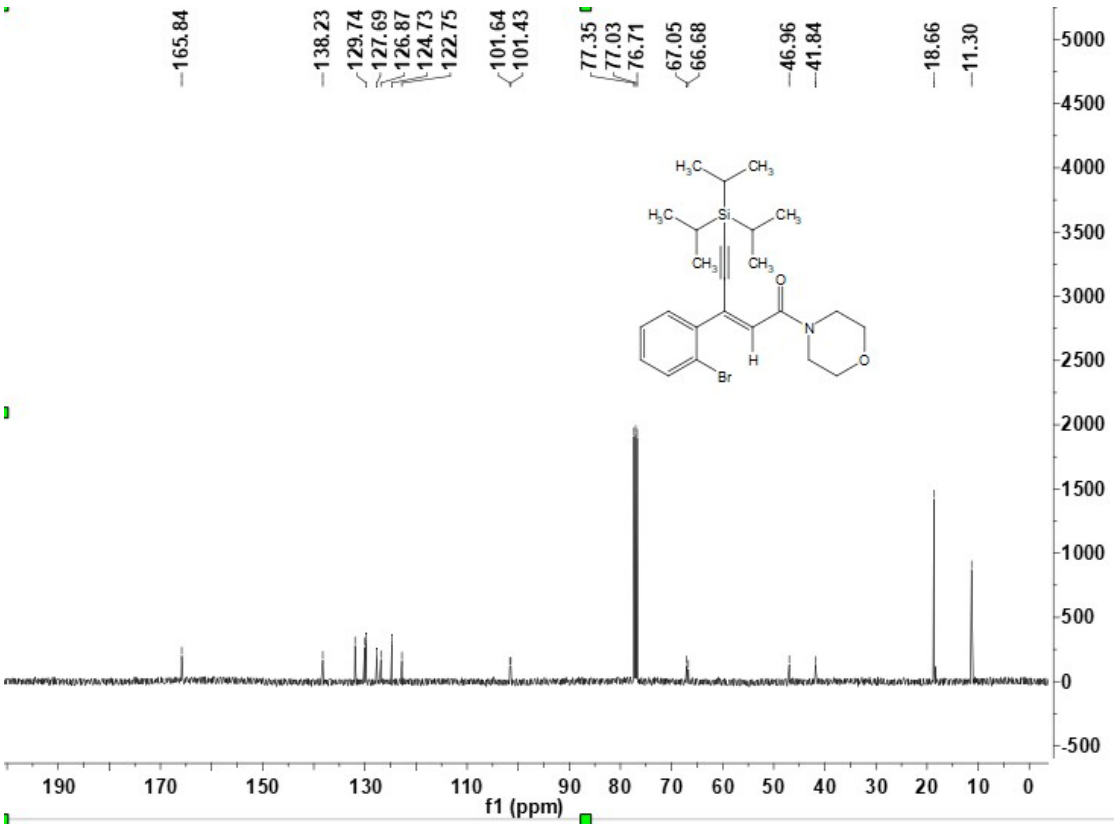
***(Z)*-*N*,*N*-Diisopropyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7d)**



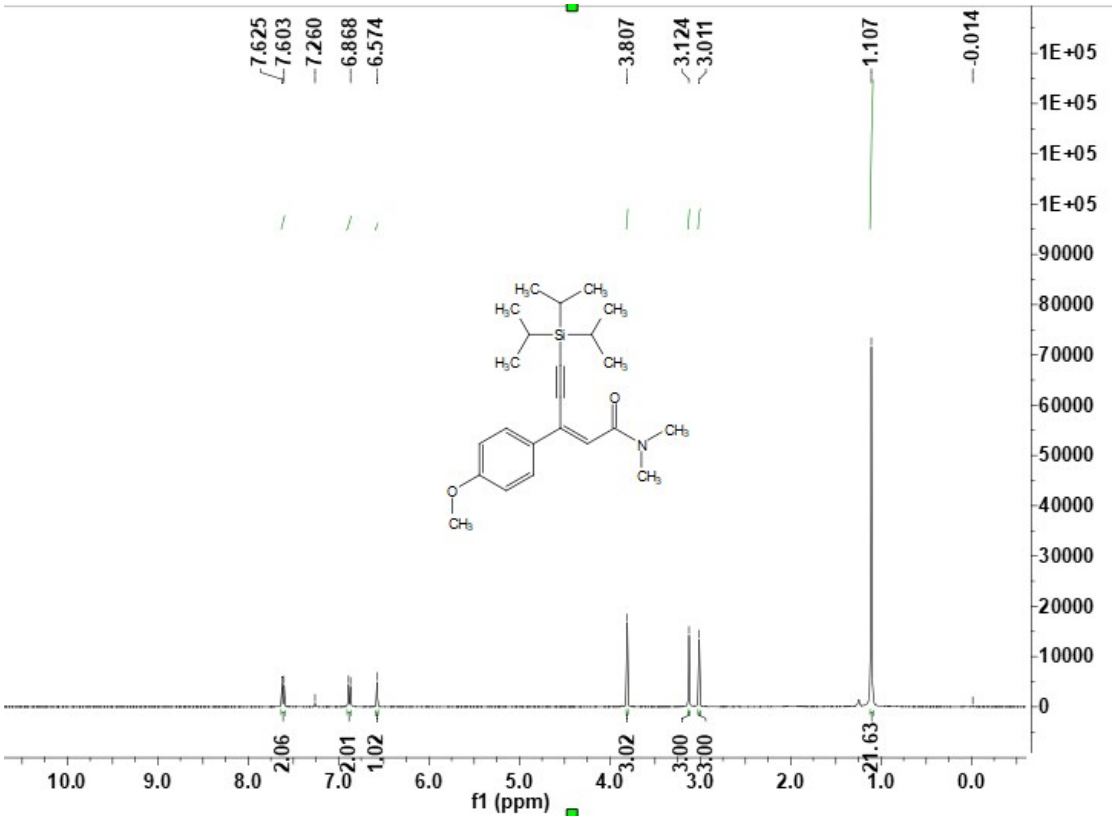


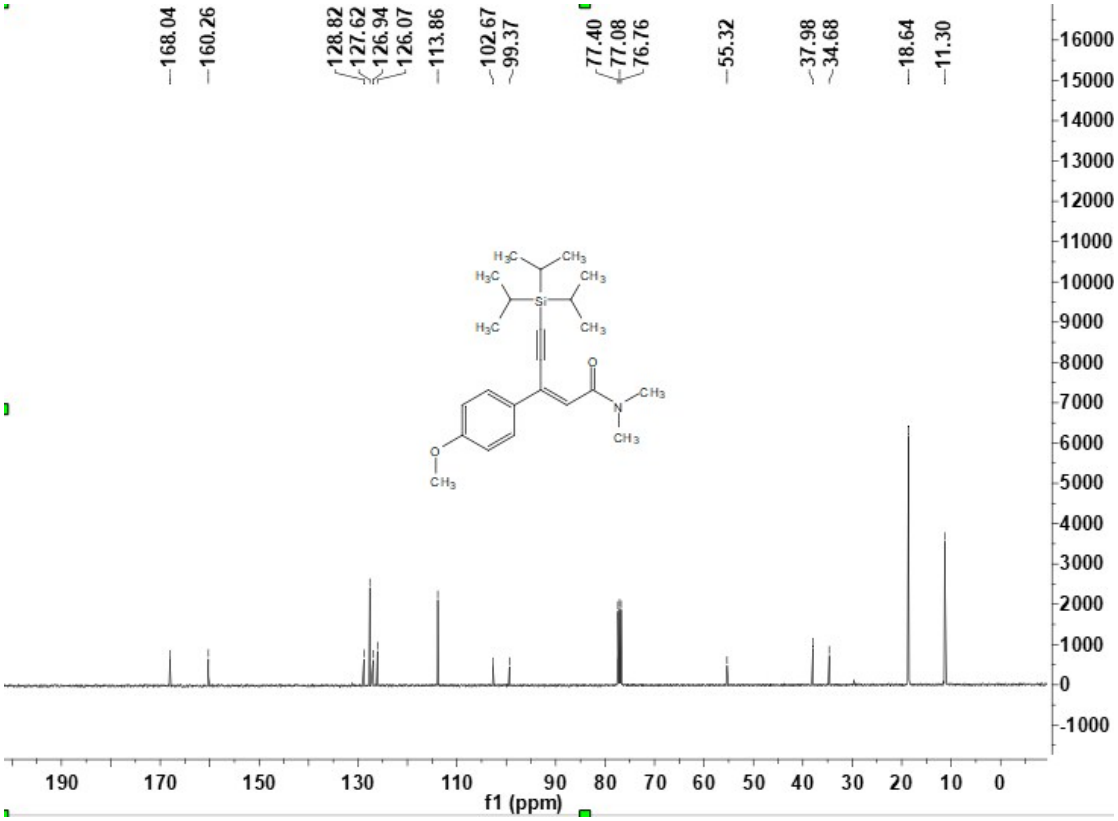
(*E*)-3-(2-Bromophenyl)-1-morpholino-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7e)



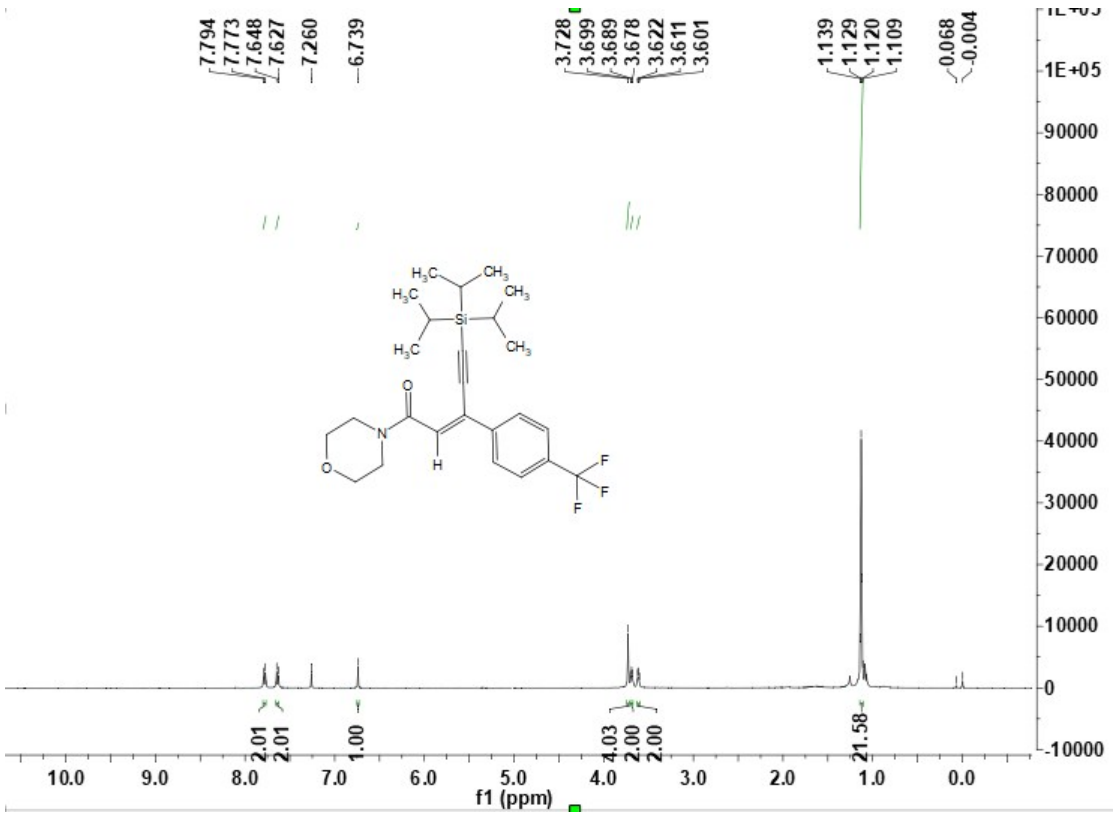


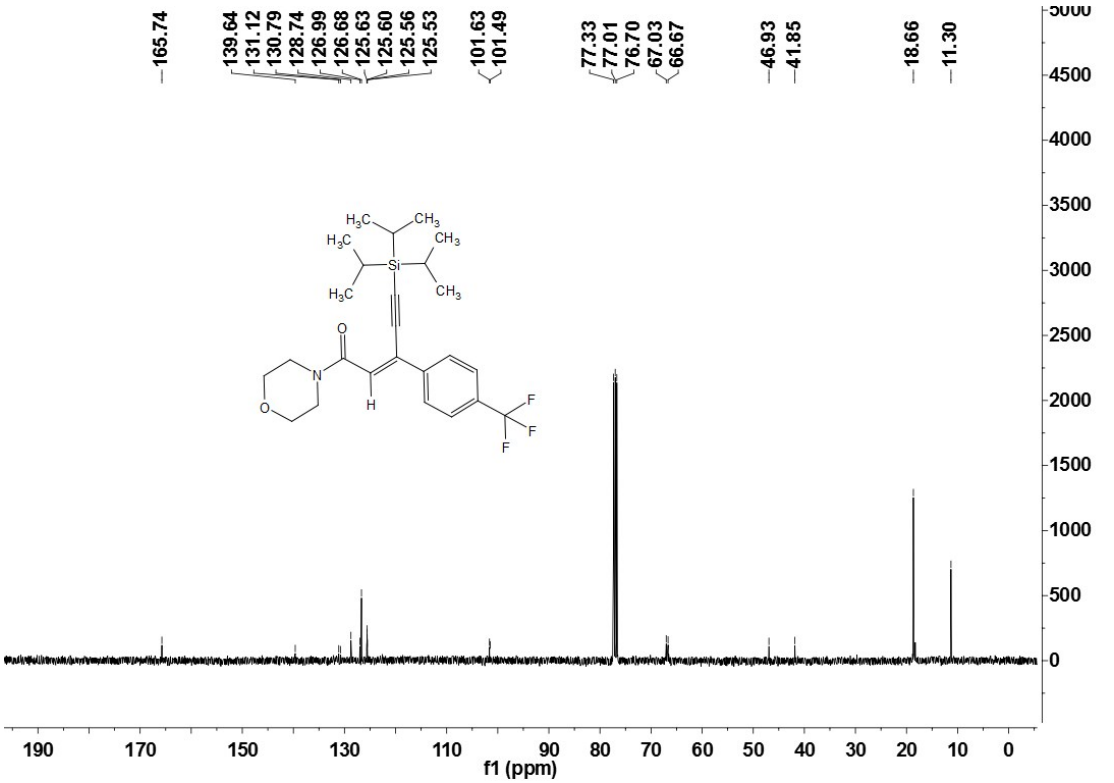
(*Z*)-3-(4-Methoxyphenyl)-*N*,*N*-dimethyl-5-(triisopropylsilyl)pent-2-en-4-ynamide (7f)

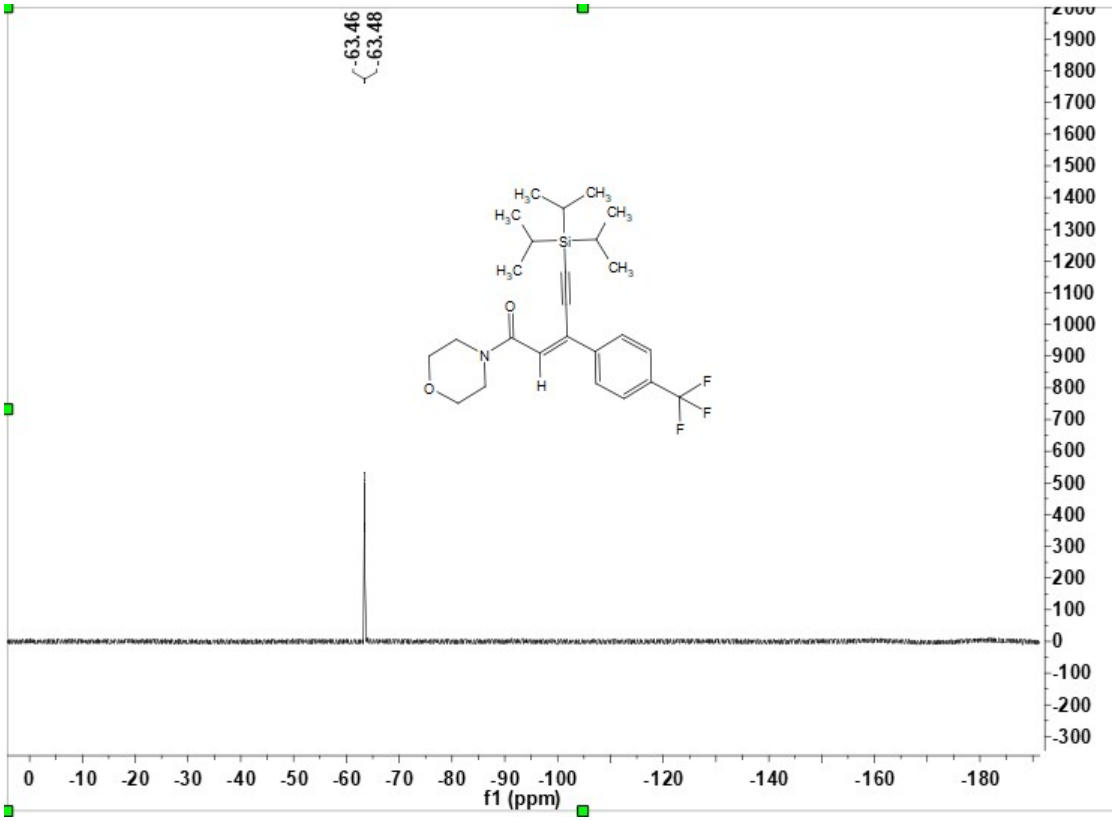




(*Z*)-1-Morpholino-3-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7g)

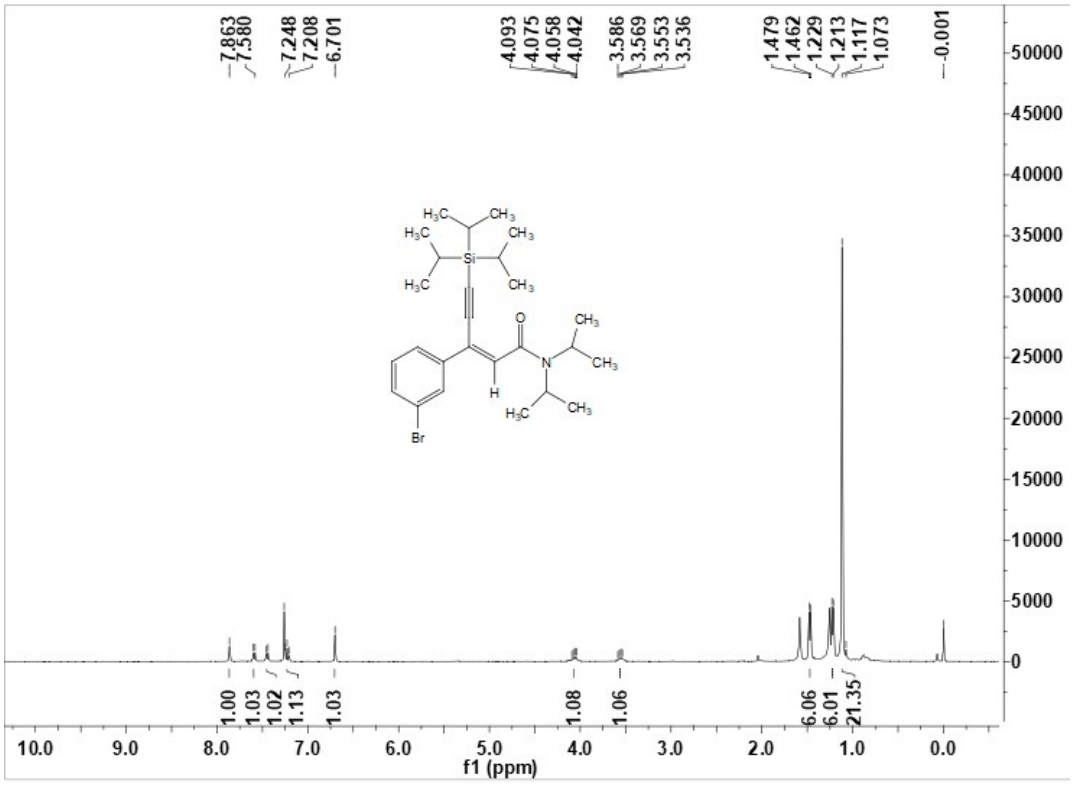


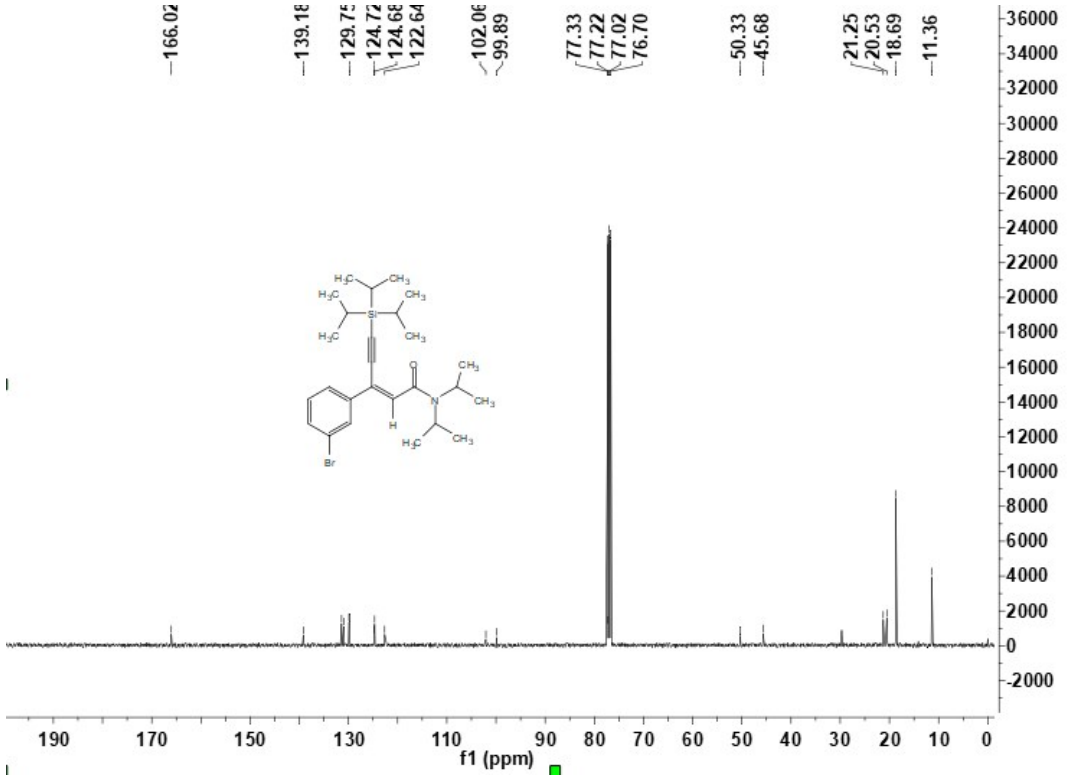

165.74
139.64
131.12
130.79
128.74
126.99
126.68
125.63
125.60
125.56
125.53
101.63
101.49
77.33
77.01
76.70
67.03
66.67
46.93
41.85
18.66
11.30
f1 (ppm)


-63.46
-63.48
f1 (ppm)

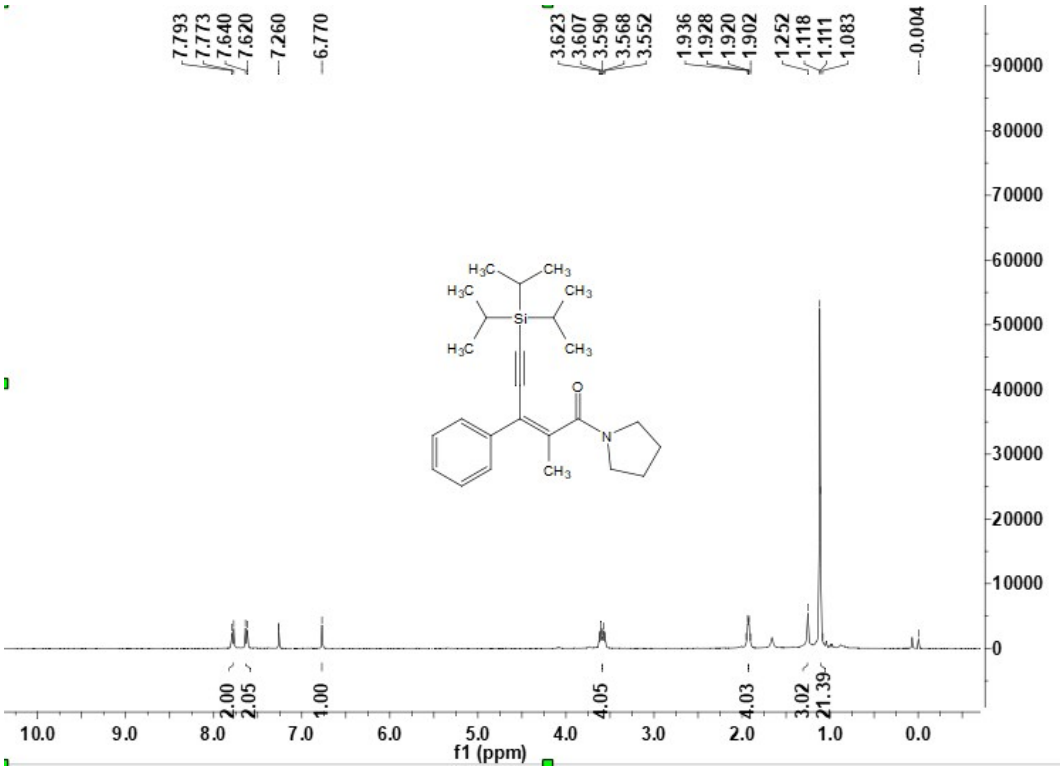
(*Z*)-3-(3-Bromophenyl)-*N*,*N*-diisopropyl-5-(triisopropylsilyl)pent-2-en-4-ynamide

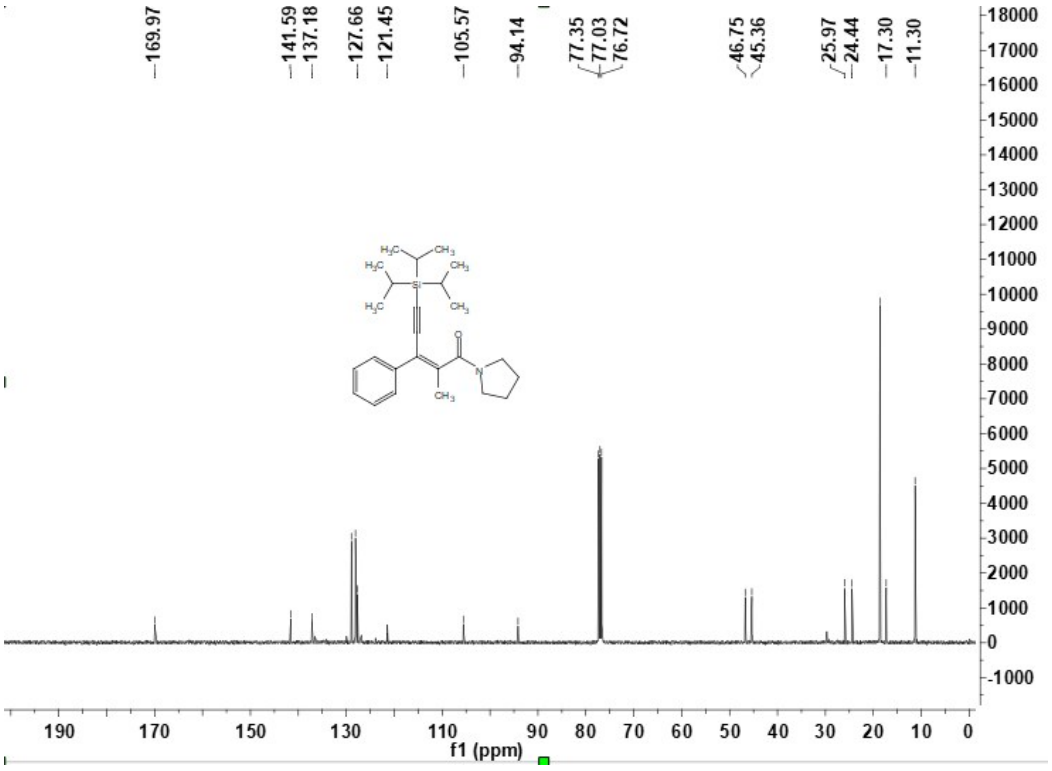
(7h)





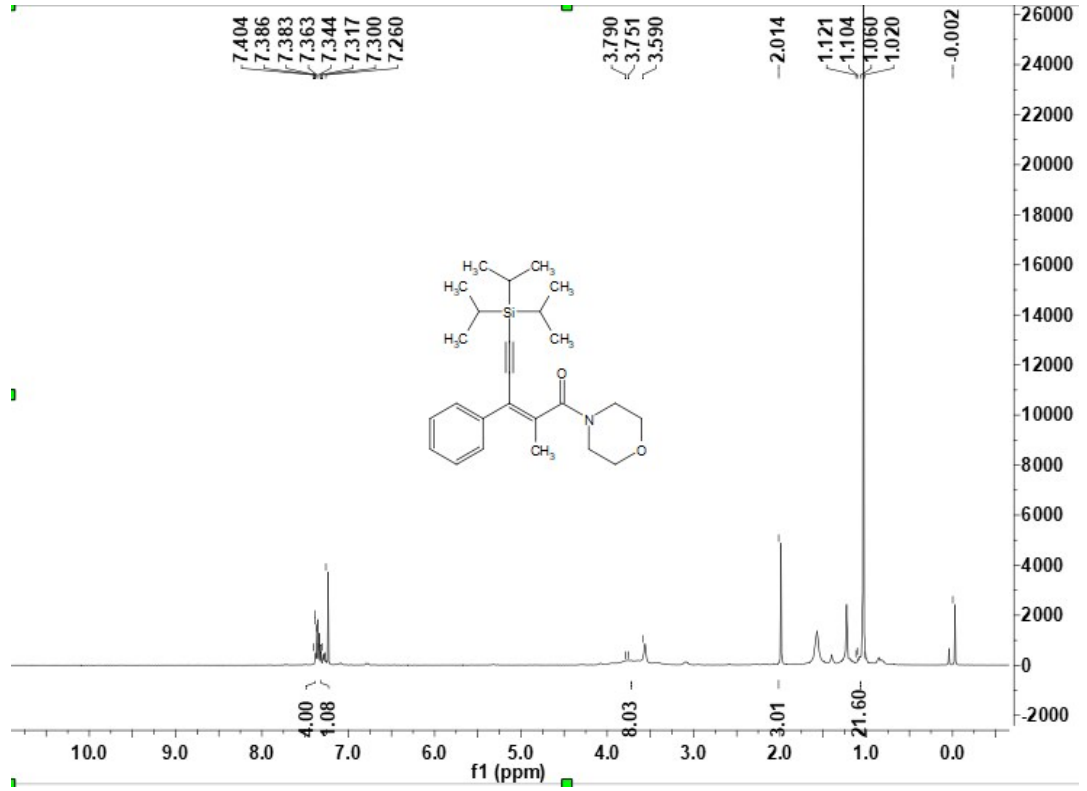
(*Z*)-2-Methyl-3-phenyl-1-(pyrrolidin-1-yl)-5-(triisopropylsilyl)pent-2-en-4-yn-1-one (7i)

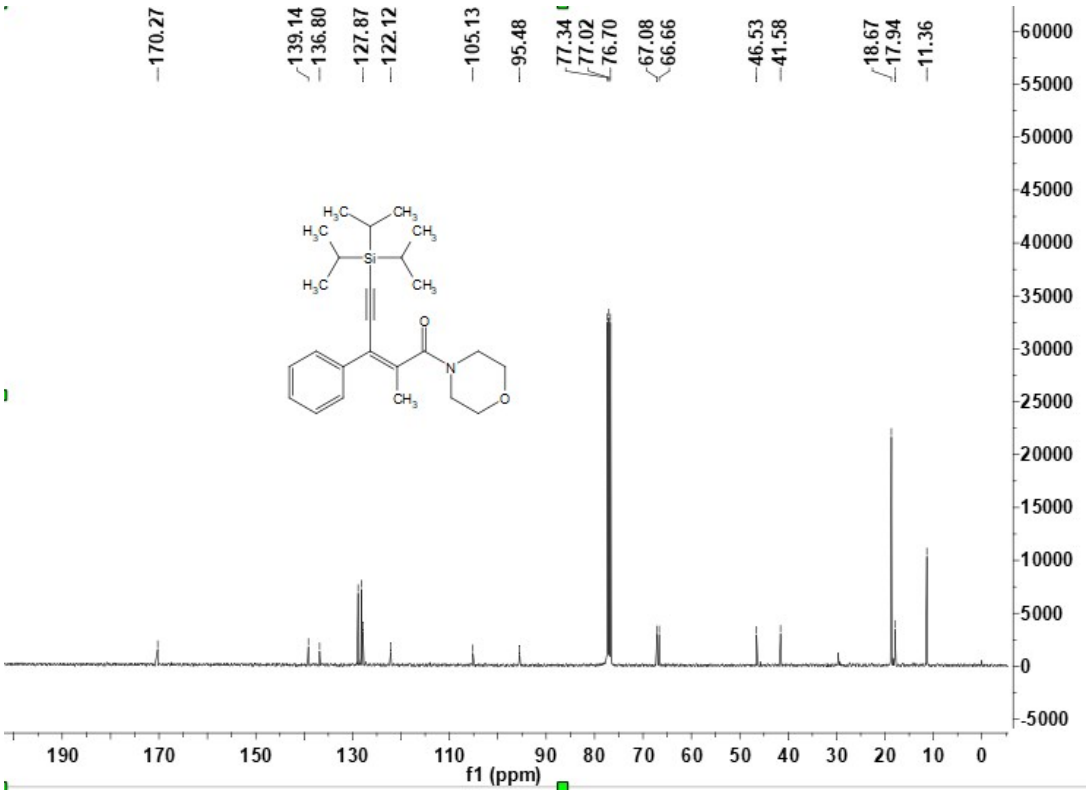




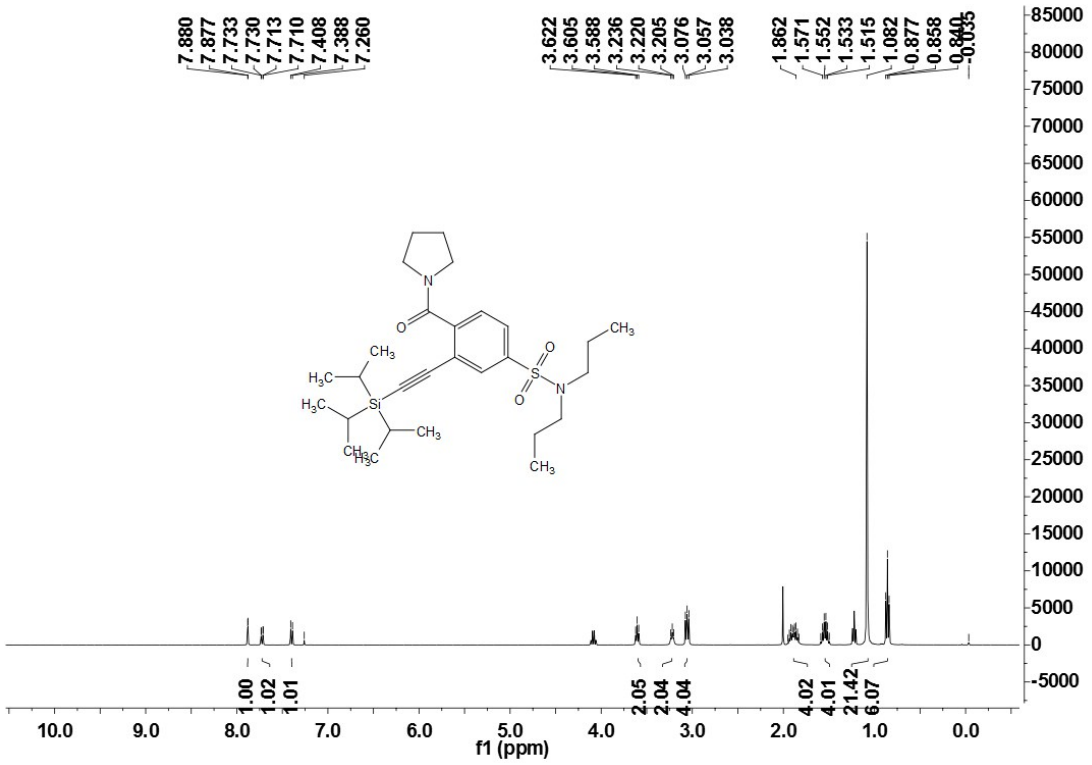
(*Z*)-2-Methyl-1-morpholino-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-yn-1-one

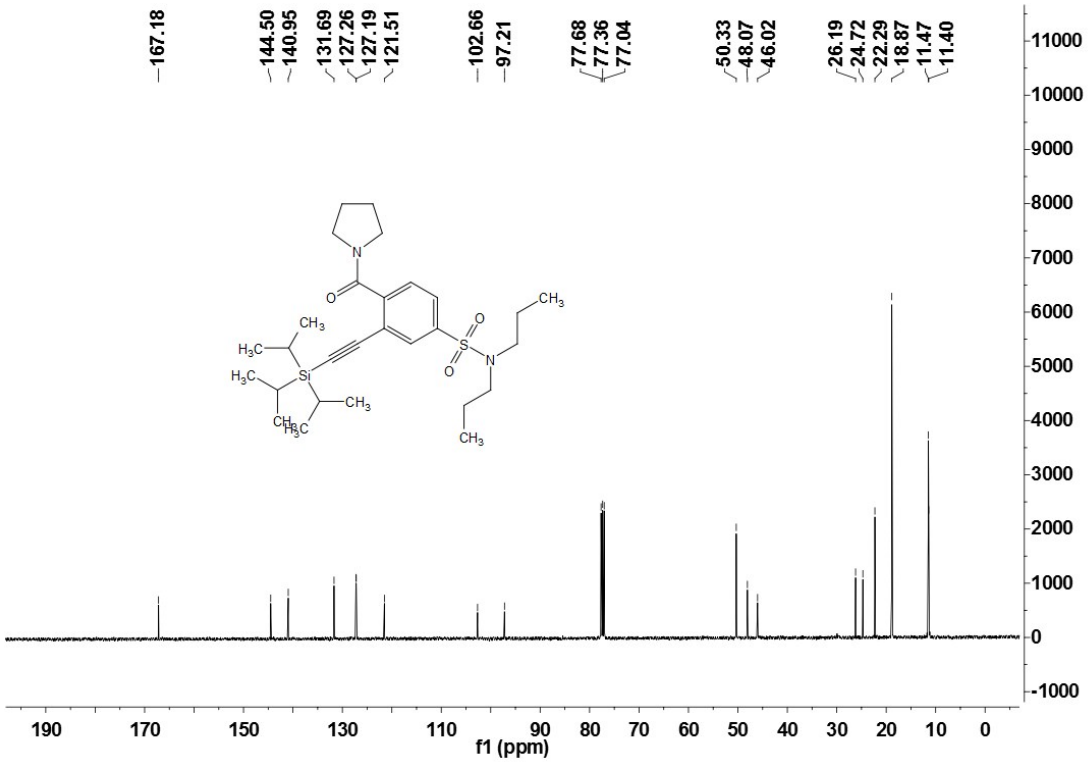
(7j)



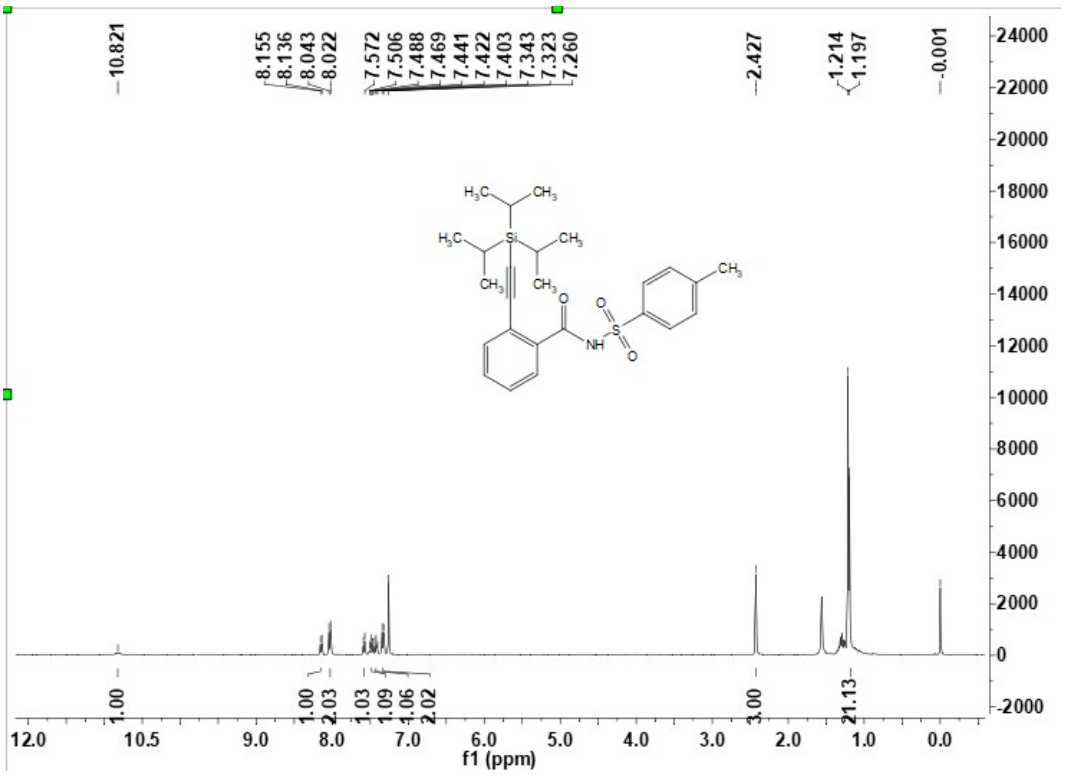


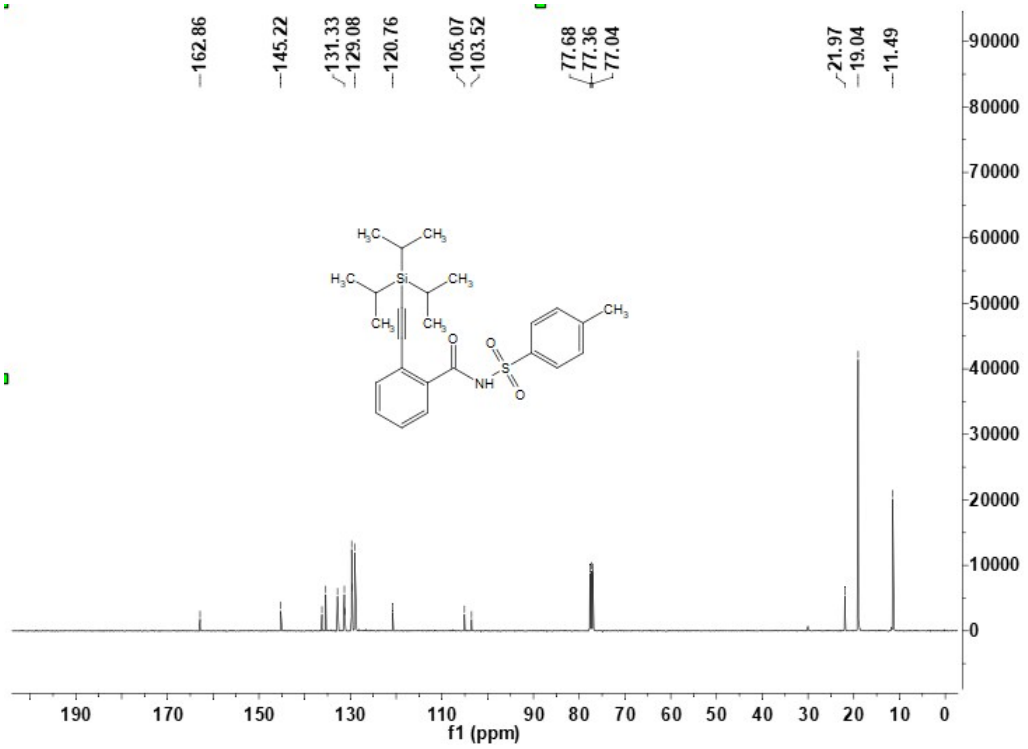
***N,N*-dipropyl-4-(pyrrolidine-1-carbonyl)-3-((triisopropylsilyl)ethynyl)benzene sulfonamide (9a)**



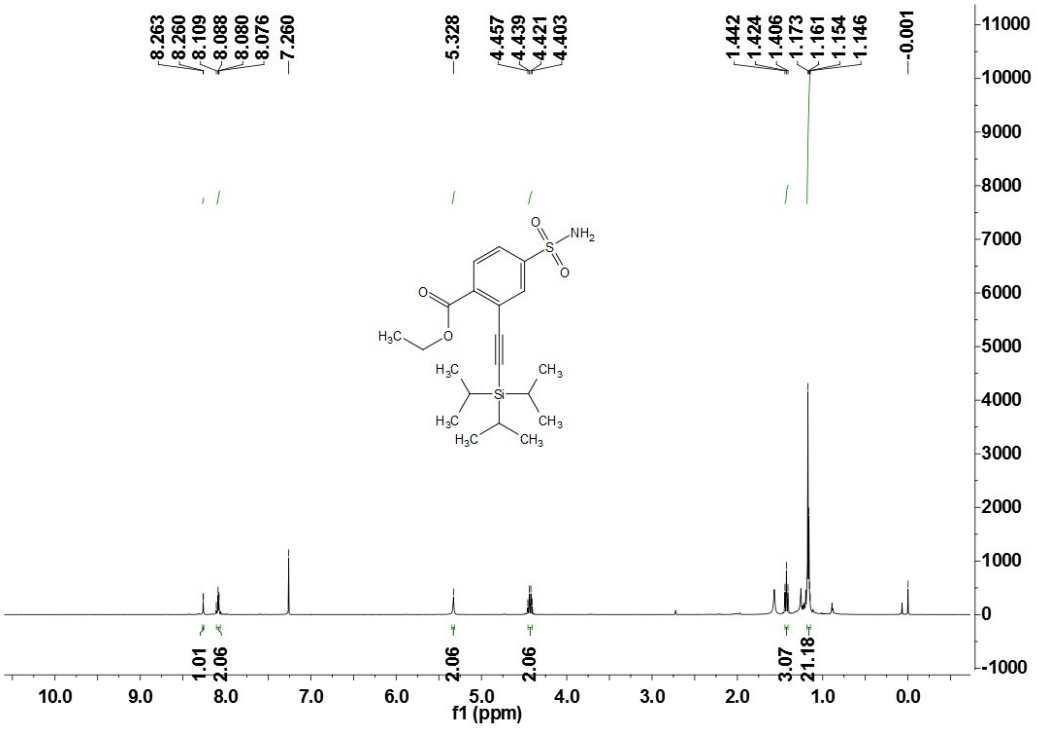


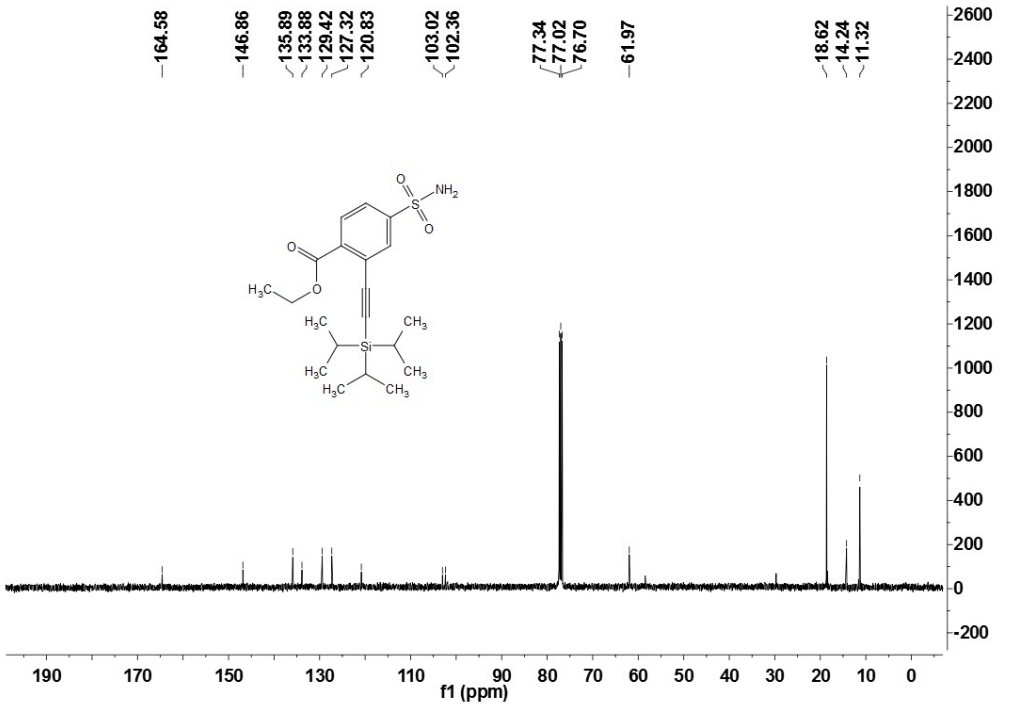
N-Tosyl-2-((triisopropylsilyl)ethynyl)benzamide (9b)



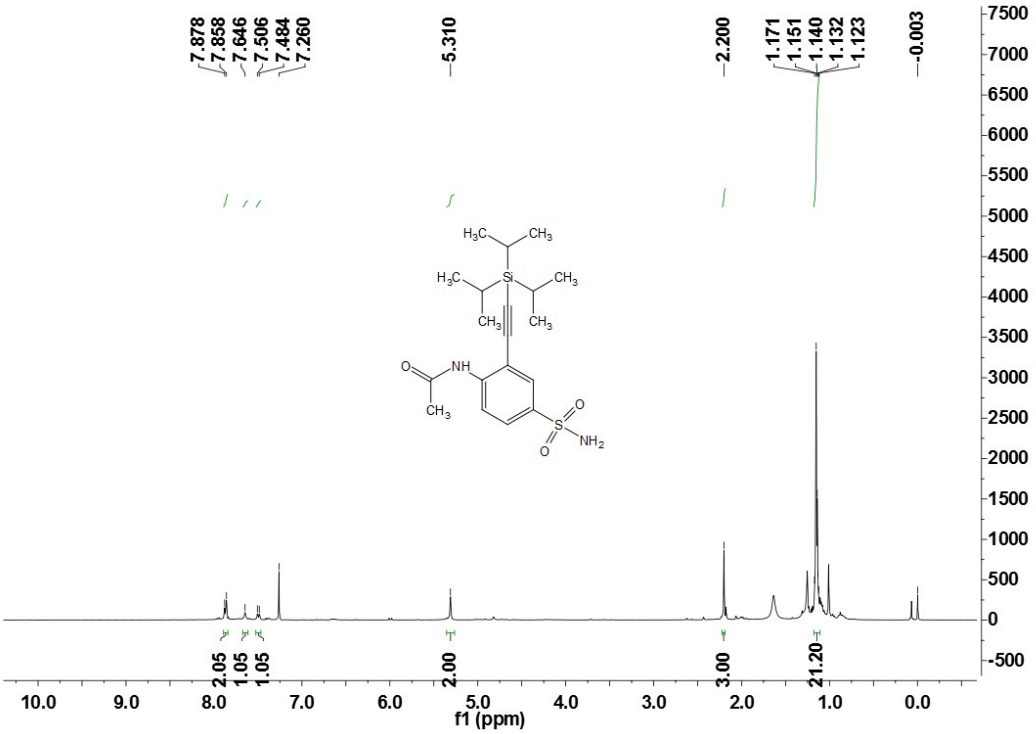


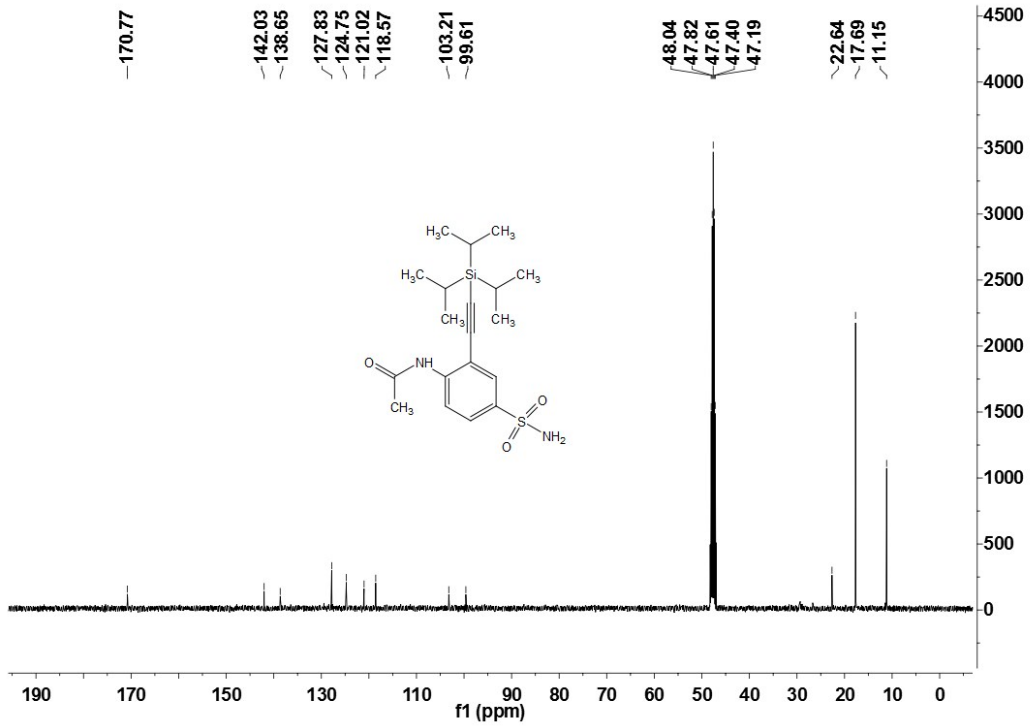
Ethyl 4-sulfamoyl-2-((triisopropylsilyl)ethynyl)benzoate (9c)



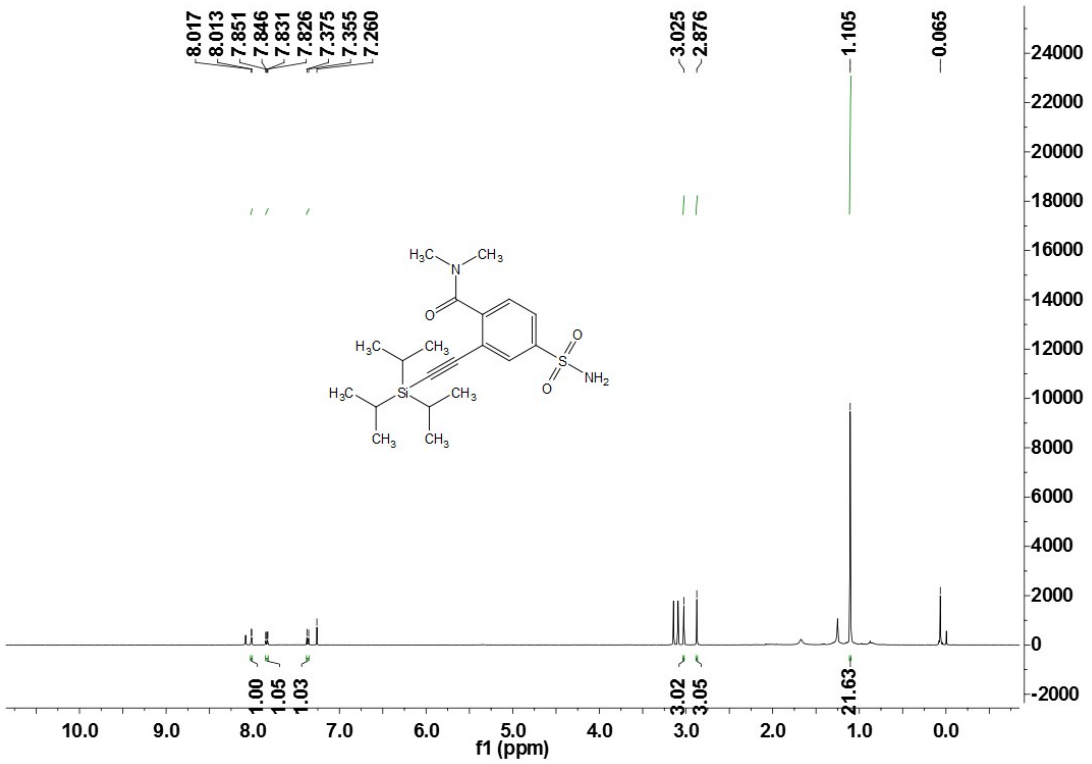


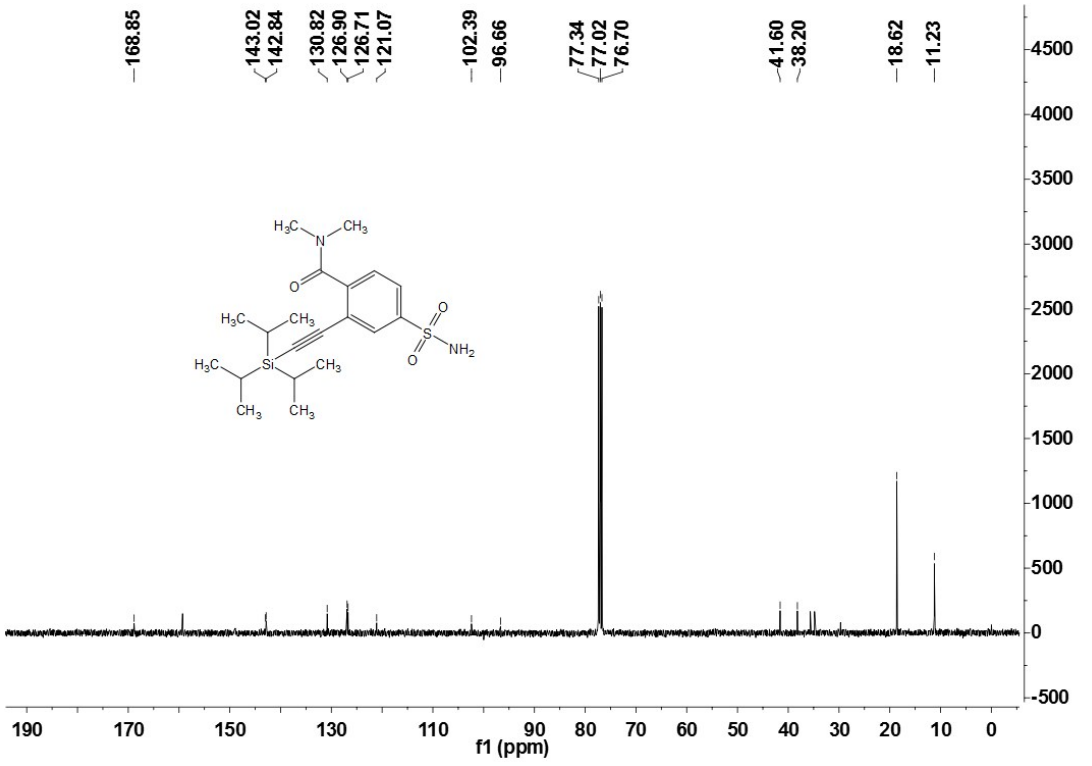
_N_-(4-Sulfamoyl-2-((triisopropylsilyl)ethynyl)phenyl)acetamide (9d)



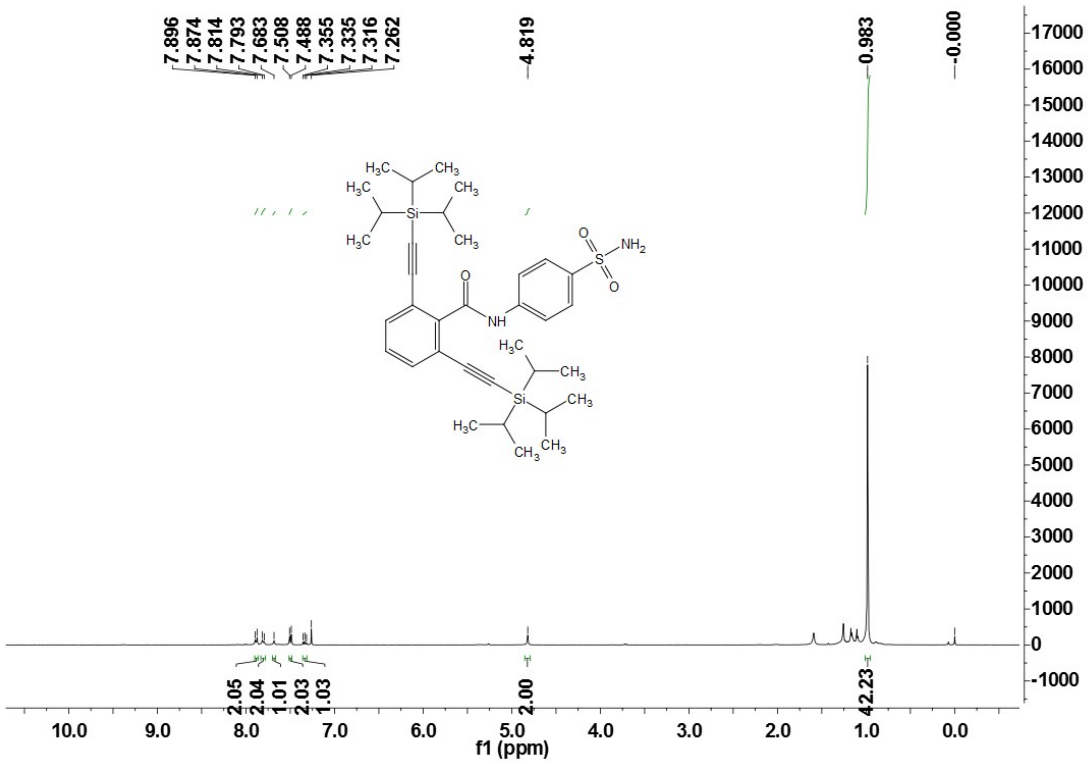


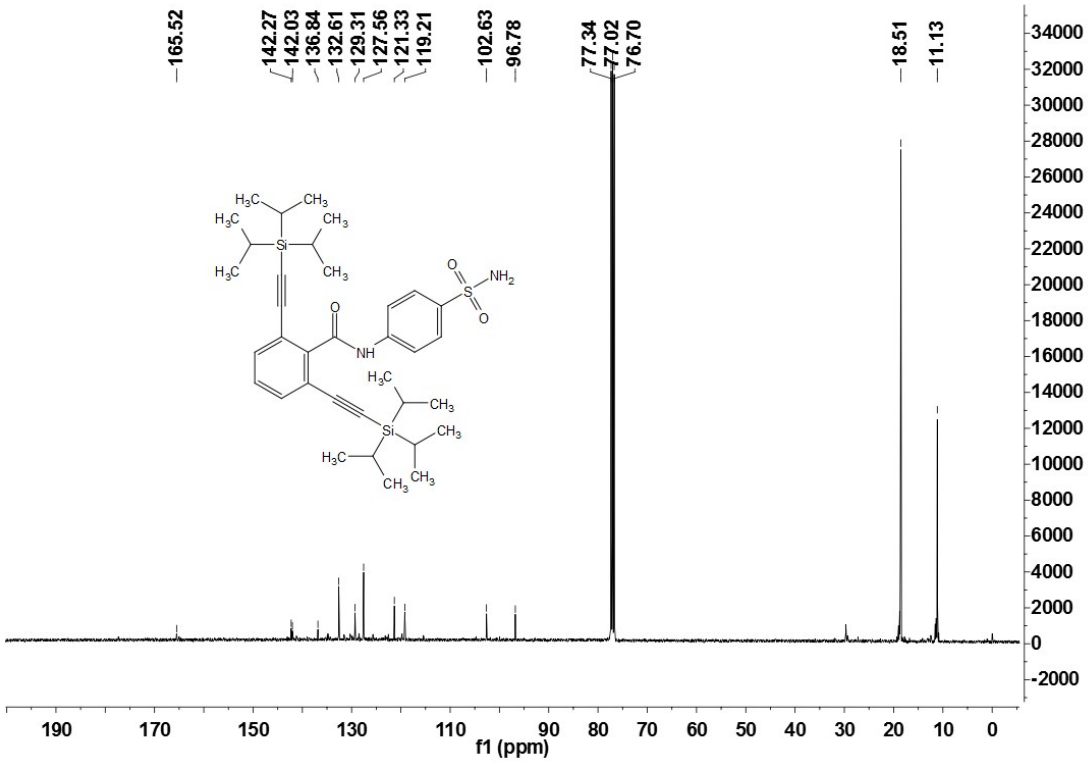
***N*, *N*-Dimethyl-4-sulfamoyl-2-((triisopropylsilyl)ethynyl)benzamide (9e)**



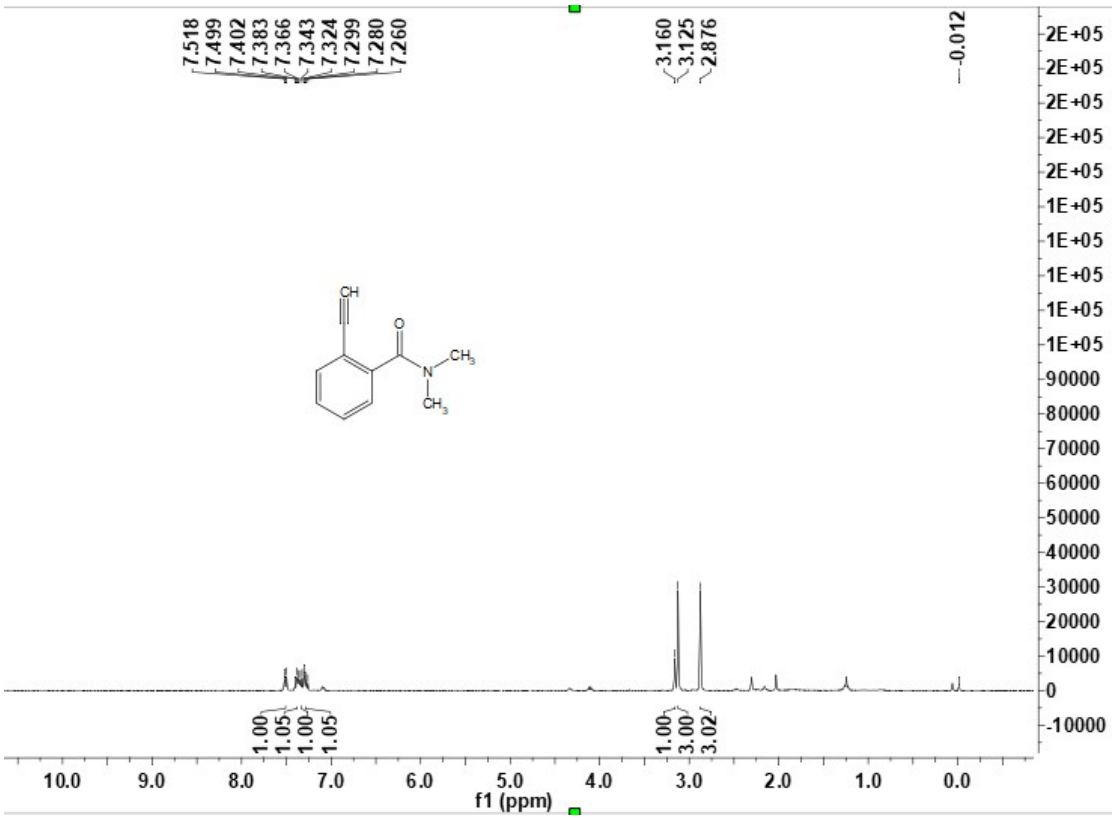


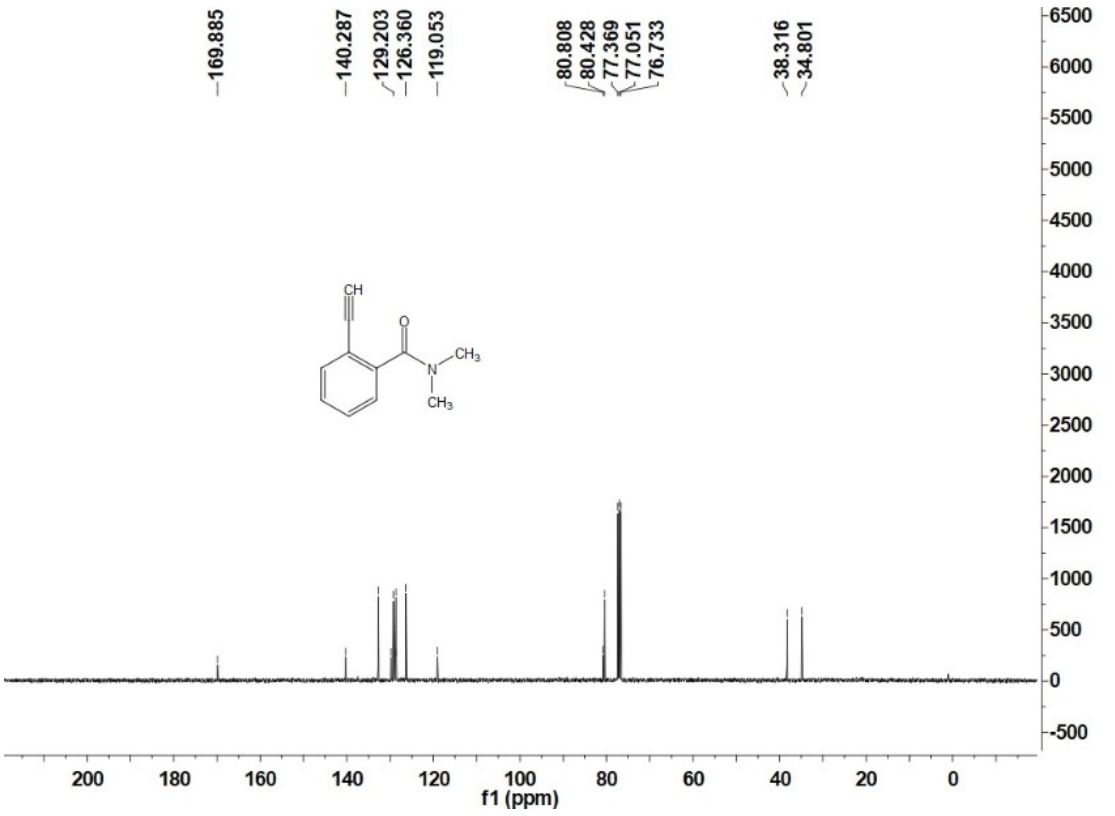
***N*-(4-Sulfamoylphenyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (9f)**



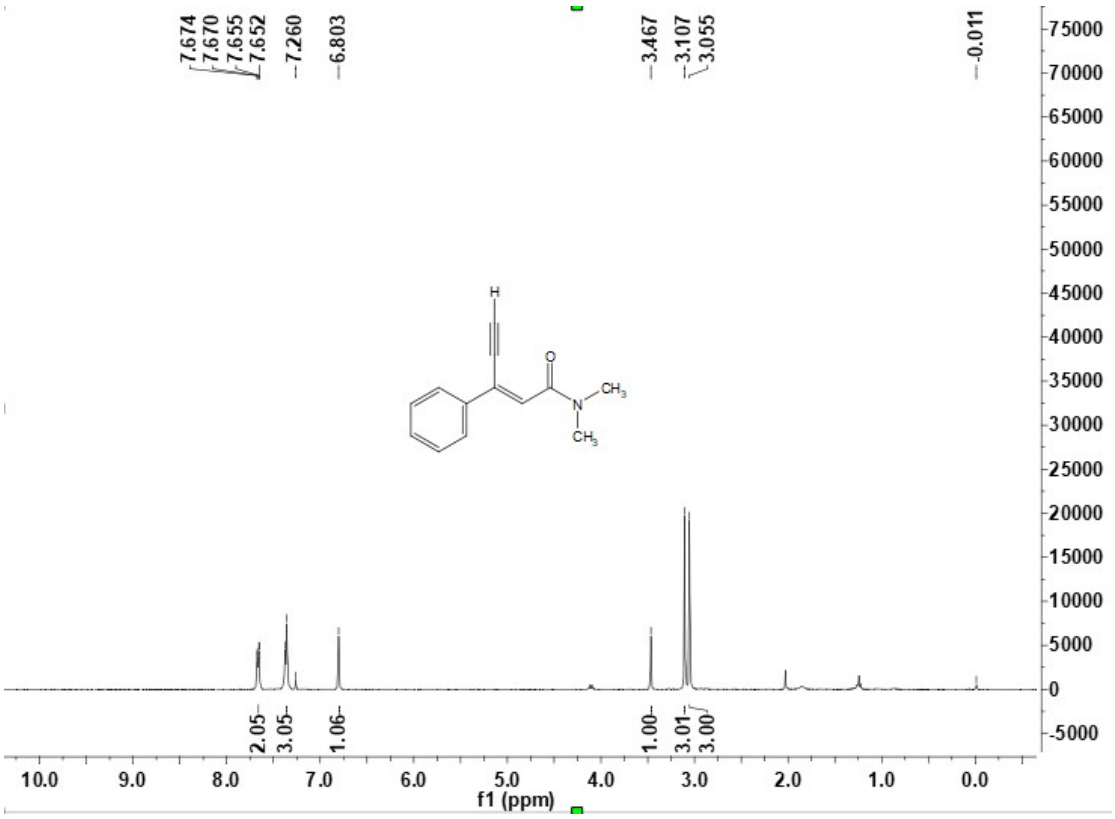


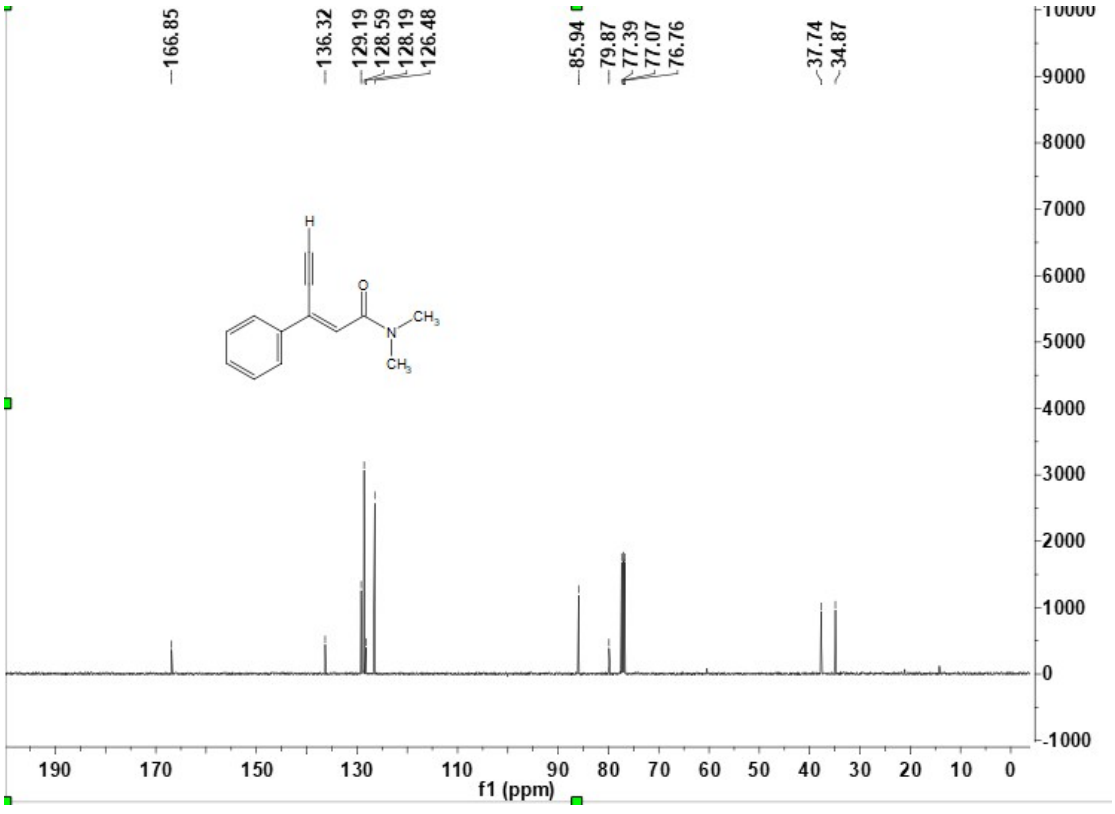
Ethynyl-*N*,*N*-dimethylbenzamide (5a')



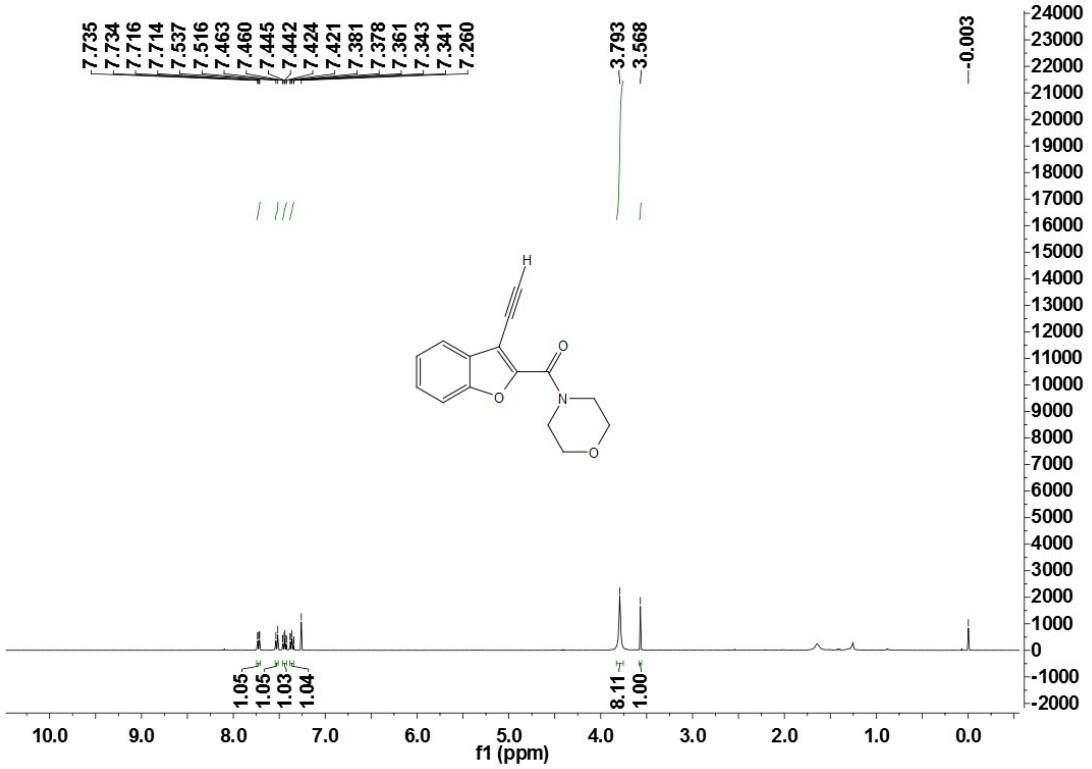


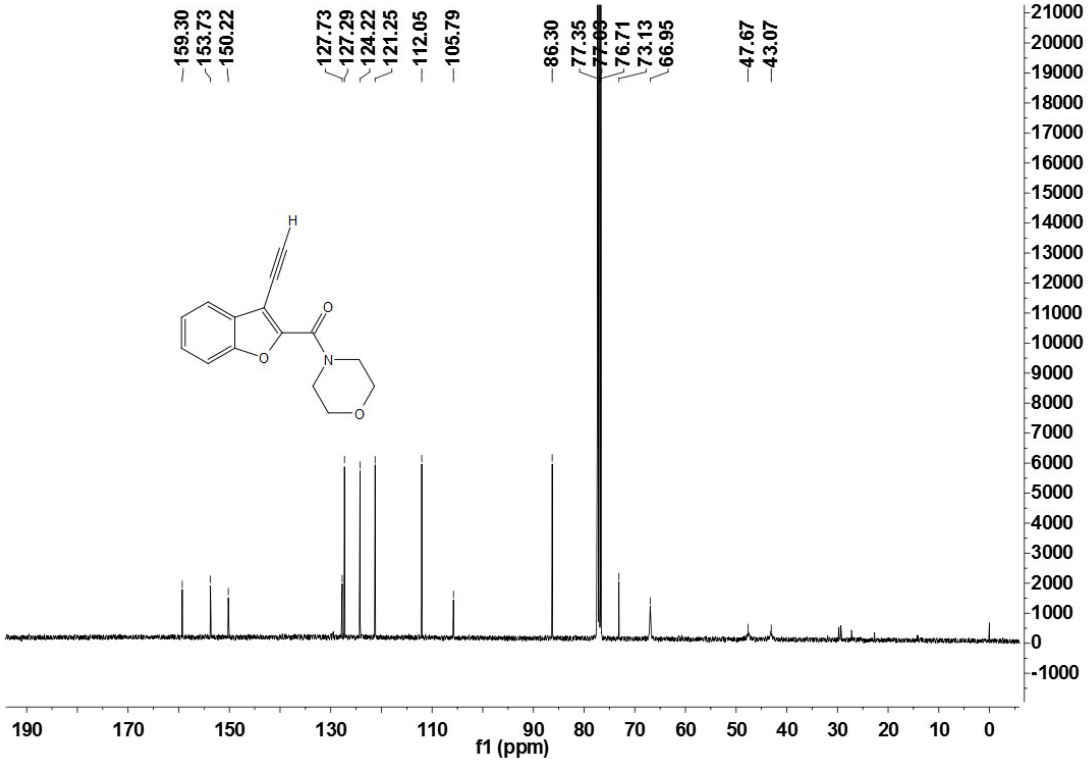
_N, N_-Dimethyl-3-phenylpent-2-en-4-ynamide (7a')



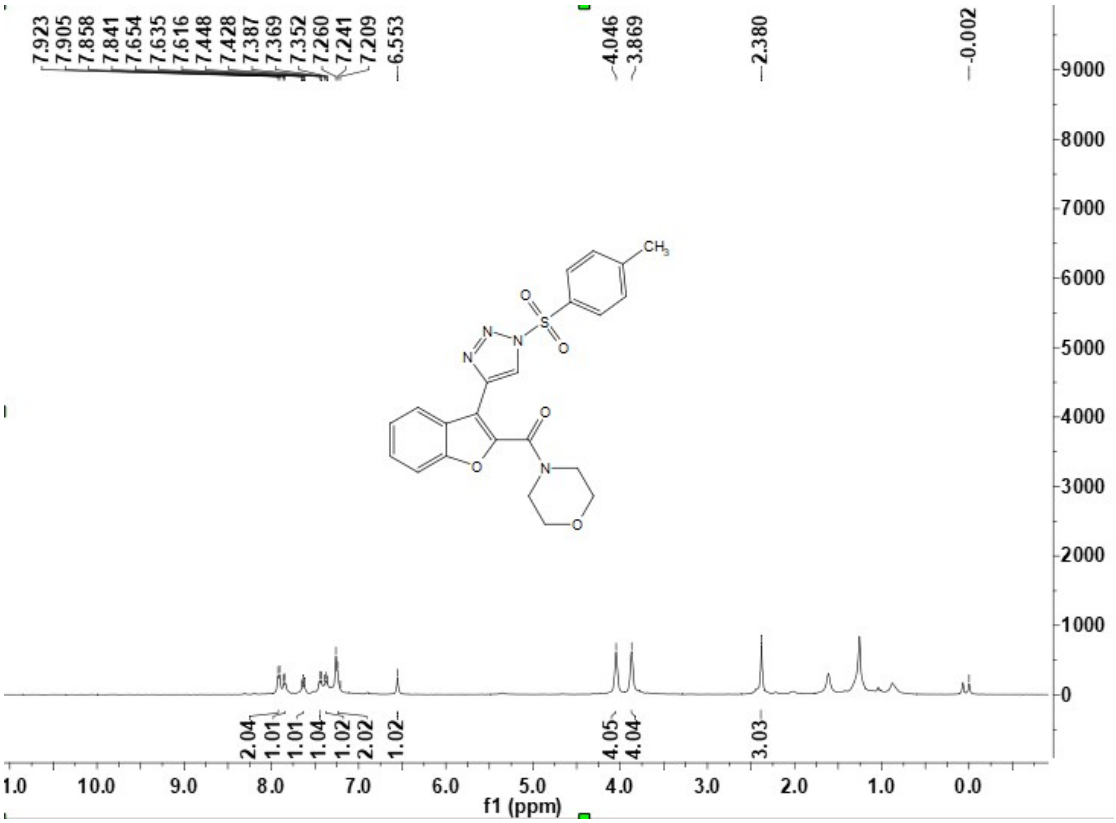


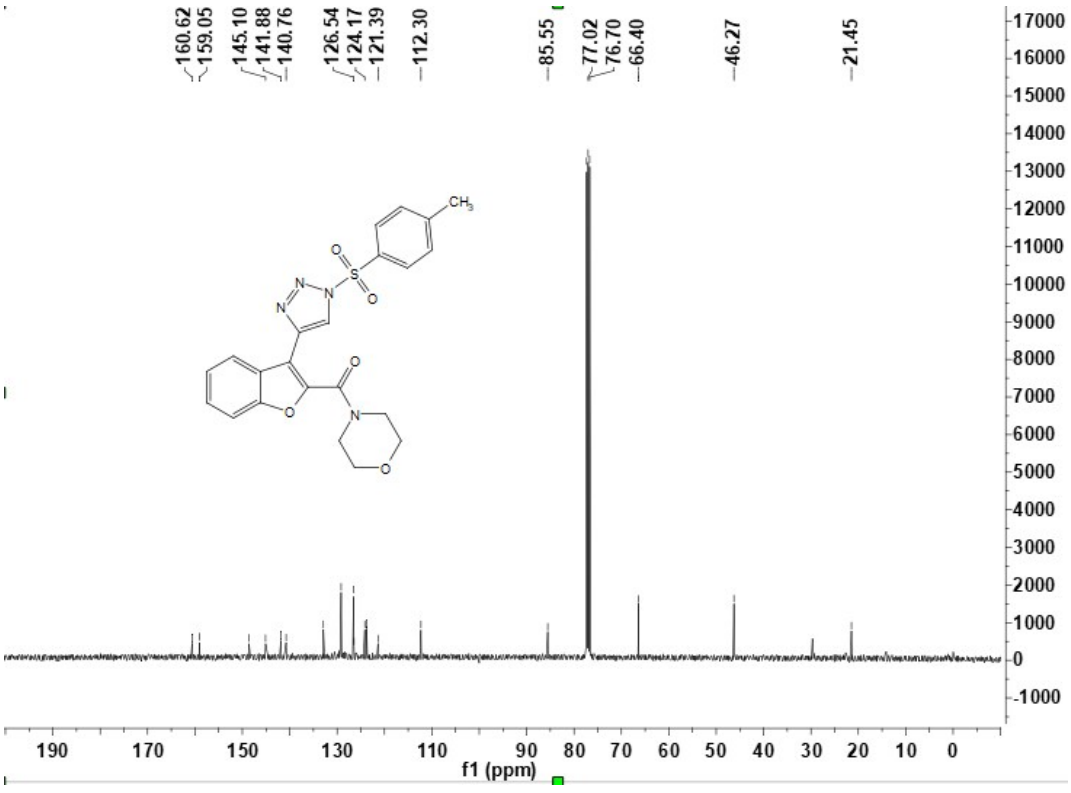
(3-Ethynylbenzofuran-2-yl)(morpholino)methanone (5l')



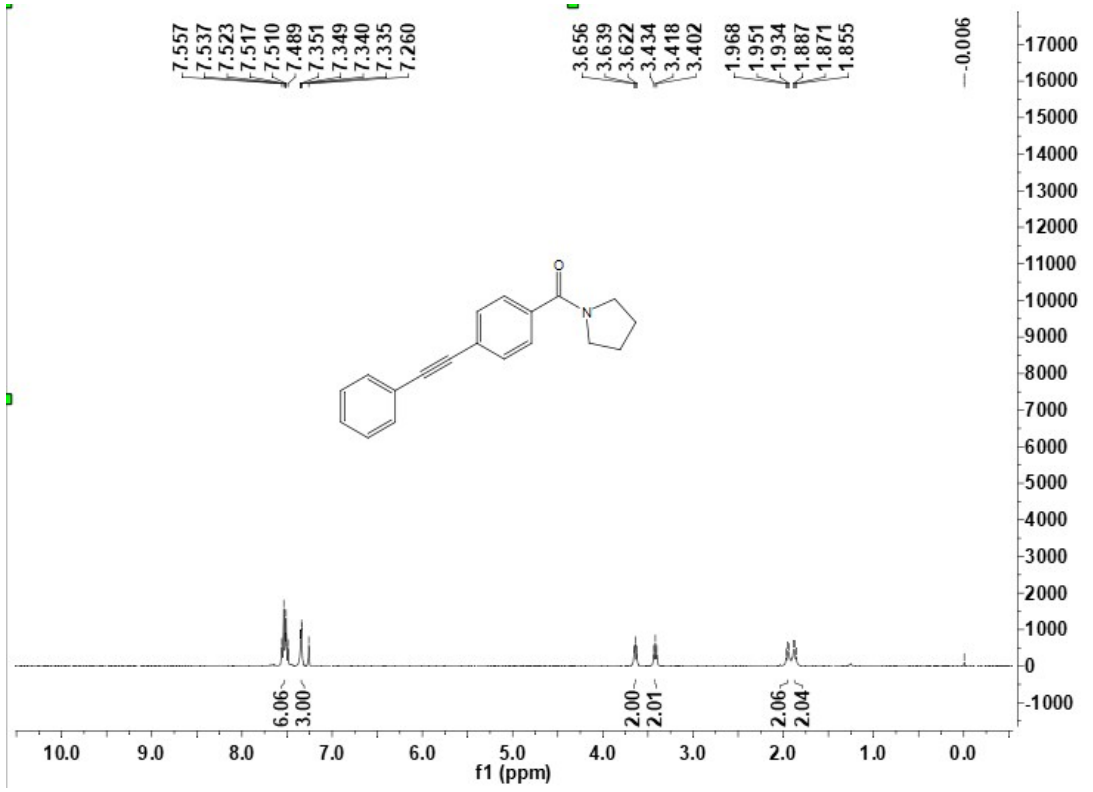


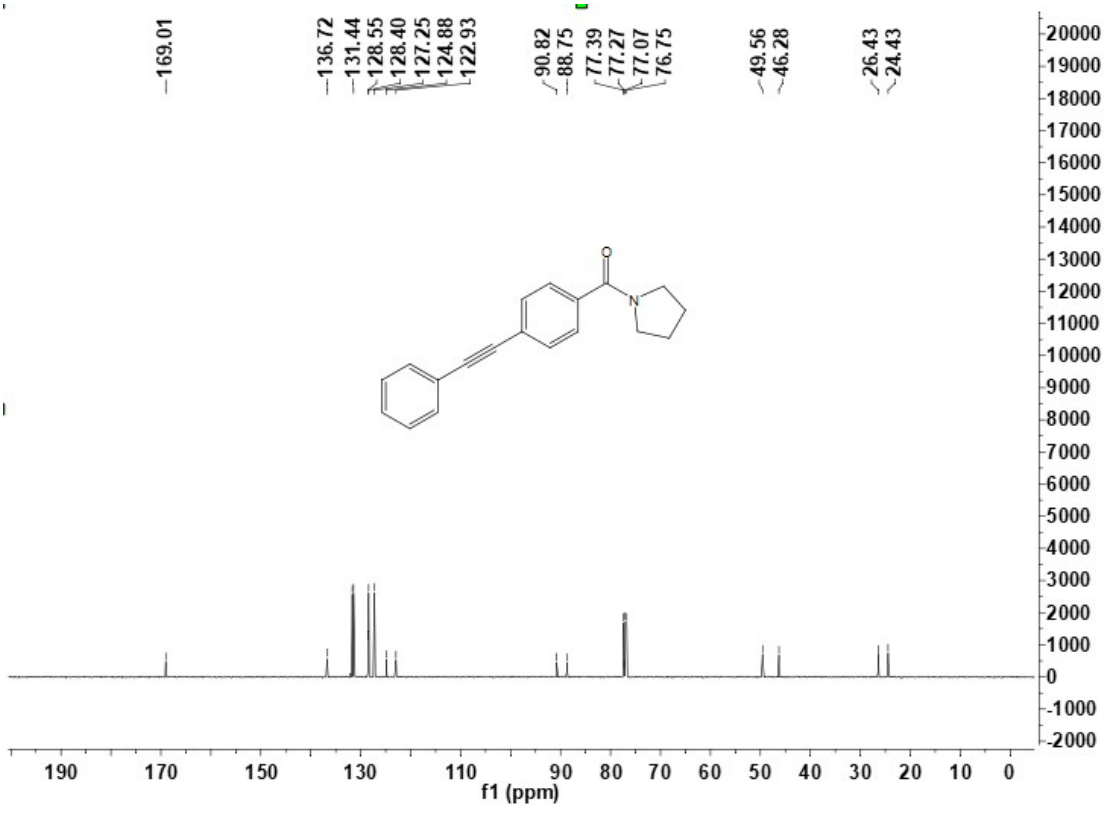
Morpholino(3-(1-tosyl-1*H*-1,2,3-triazol-4-yl)benzofuran-2-yl)methanone (5l'')



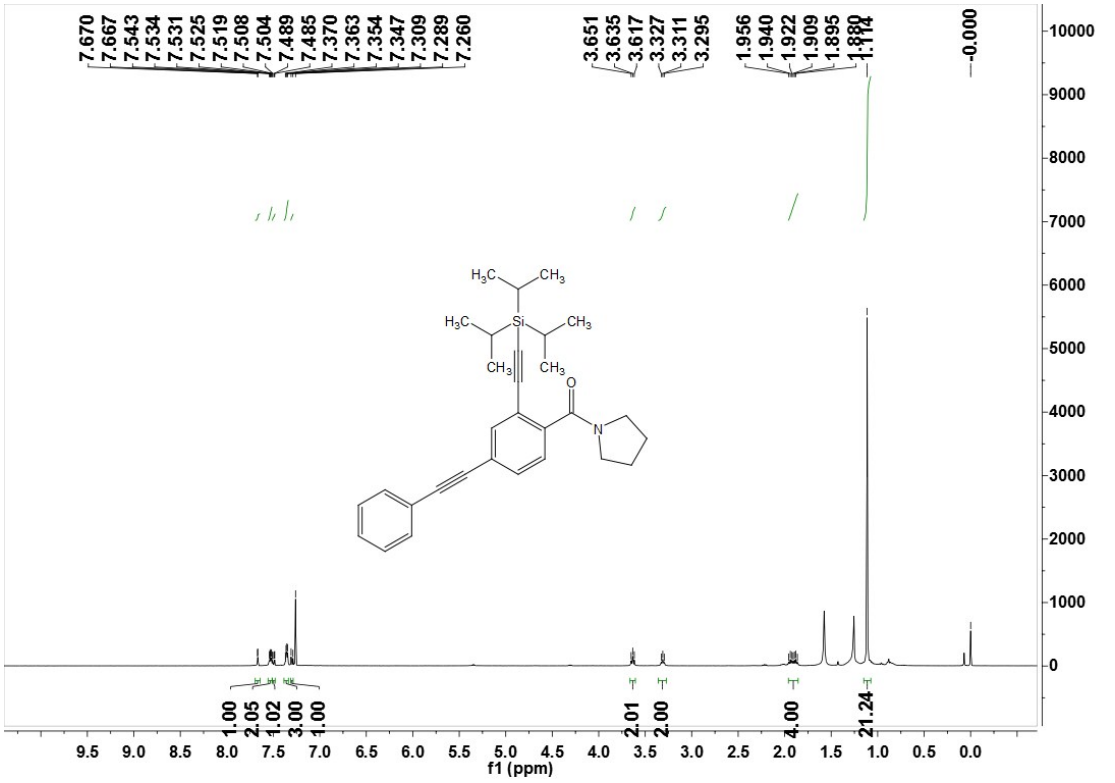


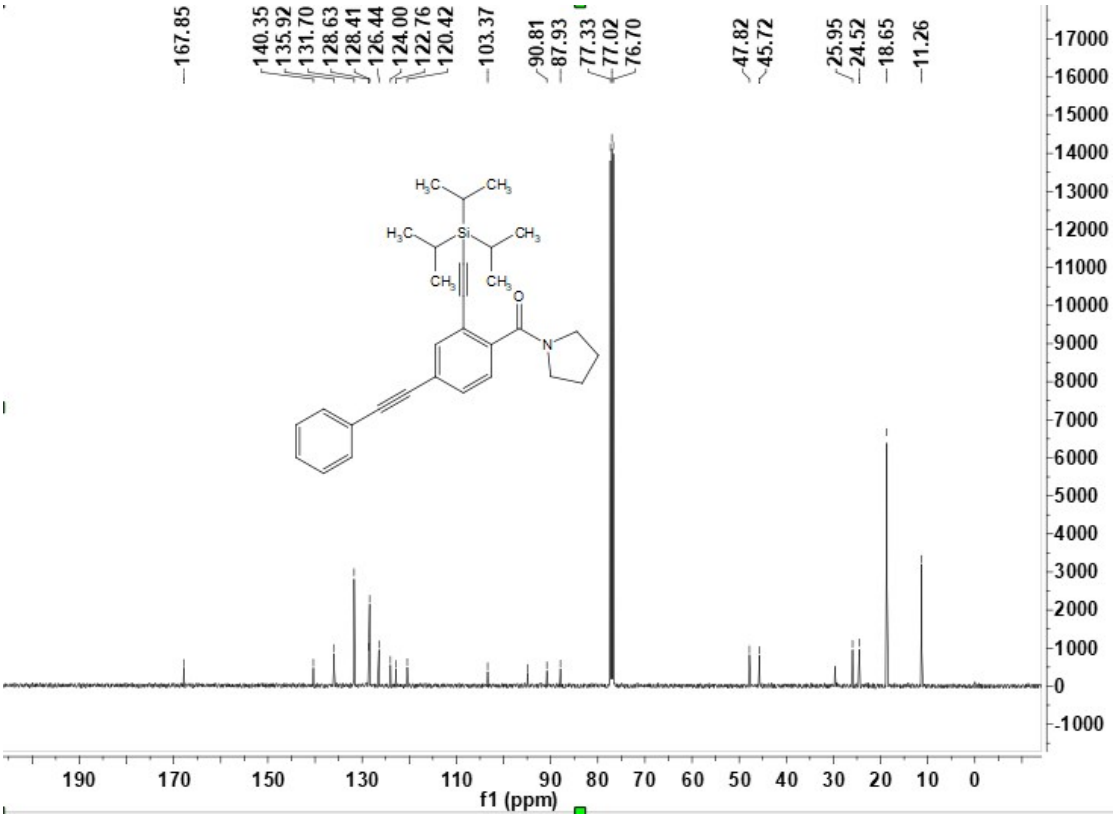
(4-(Phenylethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e')



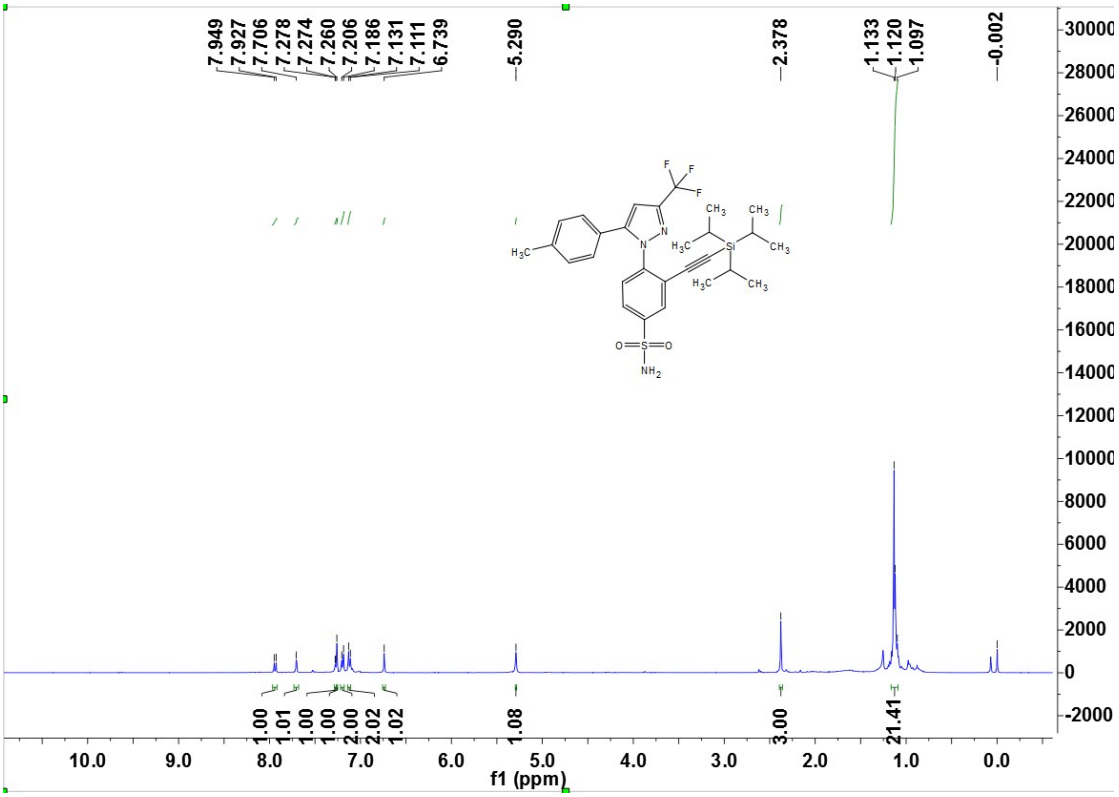


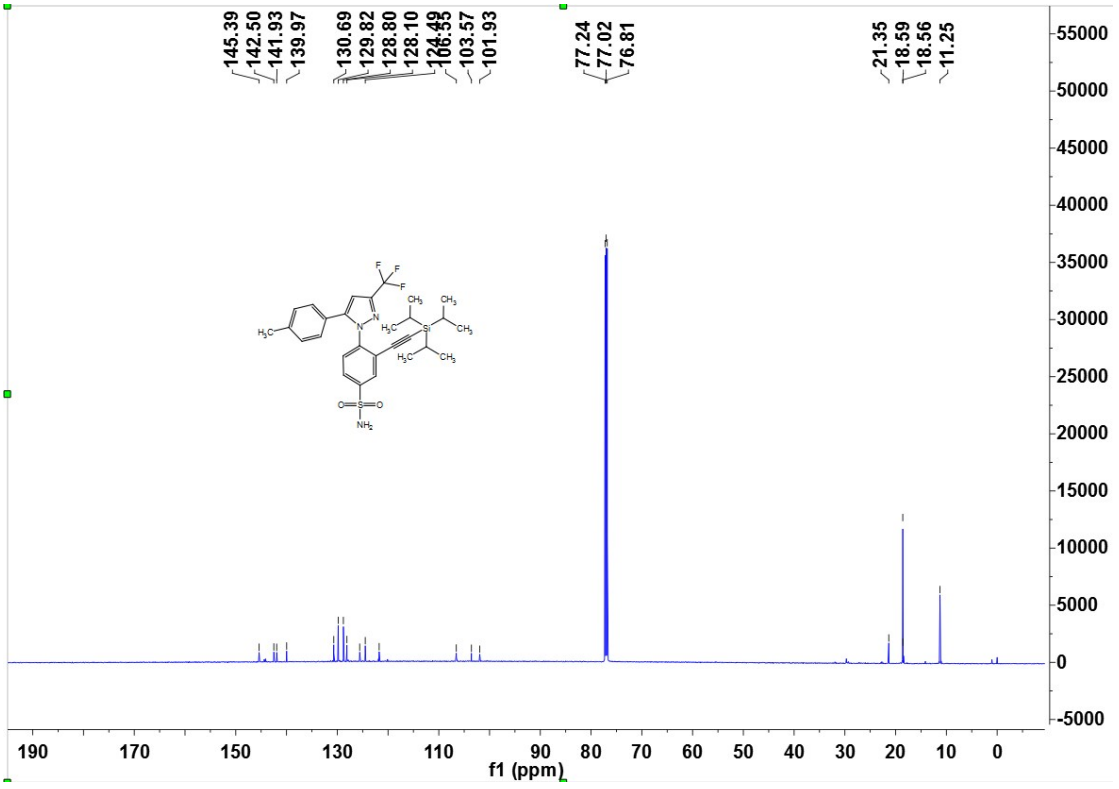
(4-(Phenylethynyl)-2-((triisopropylsilyl)ethynyl)phenyl)(pyrrolidin-1-yl)methanone (5e'')

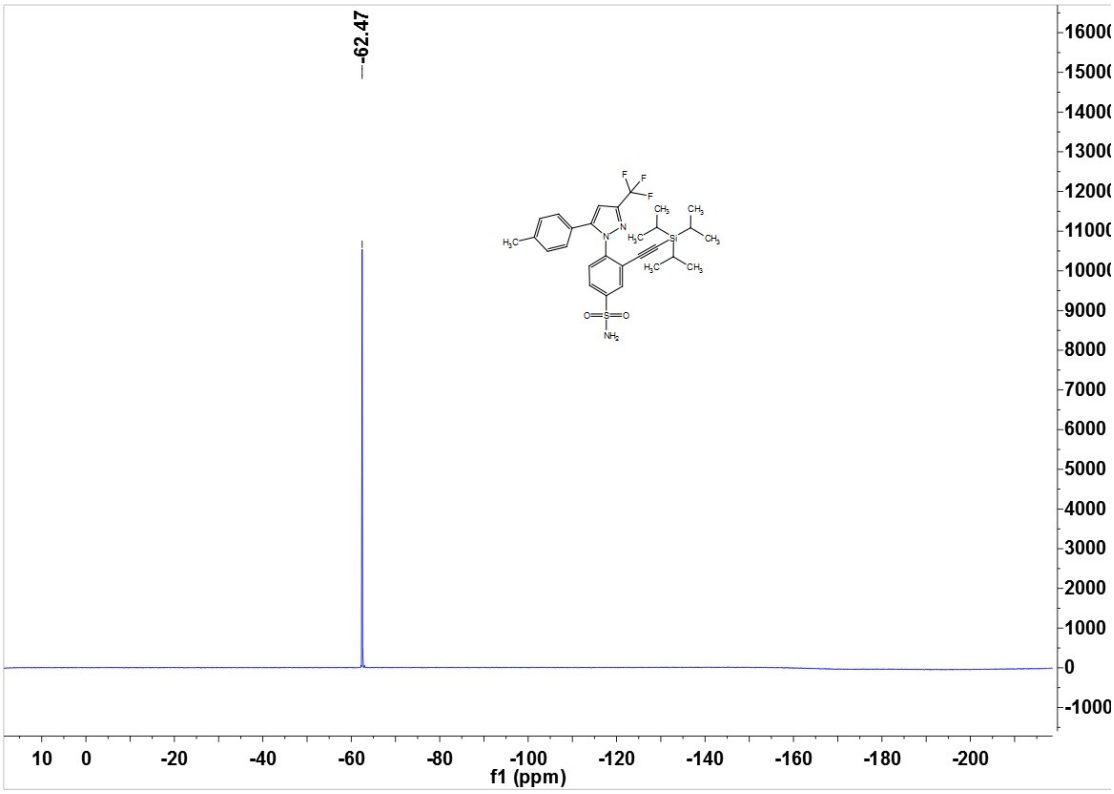




4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-3-((triisopropylsilyl)ethynyl) Benzenesulfonamide (9g)






-62.47
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)