Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ligand Accelerated Site-Selective C–H Alkynylation of Alcohols via Pd(II) Catalysis

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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:

1) General procedure for the synthesis of alcohol oximes 1, 4:

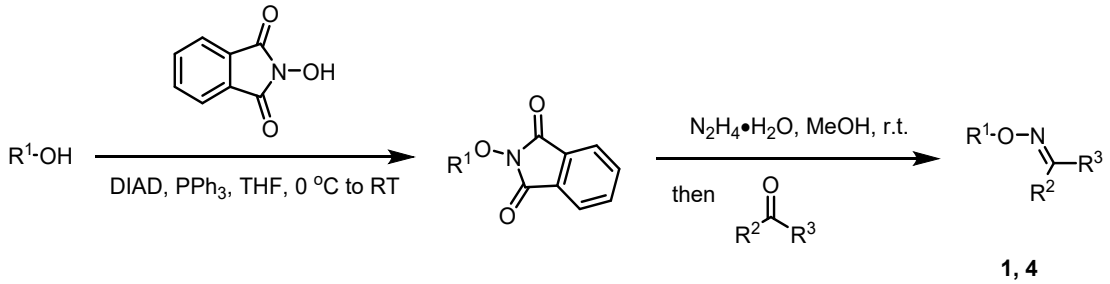


Figure SI-1. General procedure for the synthesis of alcohol oximes **1**, **4**

To a solution of alcohol (5 mmol, 1.0 equiv), N-hydroxyphthalimide (978 mg, 6 mmol, 1.2 equiv) and PPh_3 (1.572 g, 6 mmol, 1.2 equiv) in 20 mL THF was added diisopropyl azodicarboxylate (1.2 mL, 6 mmol, 1.2 equiv) dropwise at 0 °C. Then the reaction was allowed to warm to room temperature and stirred overnight. Upon done, the solvent was removed under reduced pressure. The residue was used for the second step without further purification.

To a solution of N-alkoxyphthalimide (1.1 equiv) in MeOH (5 mL/mmol) was added hydrazine monohydrate (1.15 equiv) at room temperature. The reaction was monitored by TLC and usually completed in 30 min. Then aldehyde or ketone (1.0 equiv) was added. The reaction was monitored by TLC. After 0.5 h the mixture was filtered to remove precipitate if formed and then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the title compounds **1**, **4**.

2) General procedure for the synthesis of alcohol oximes 9:

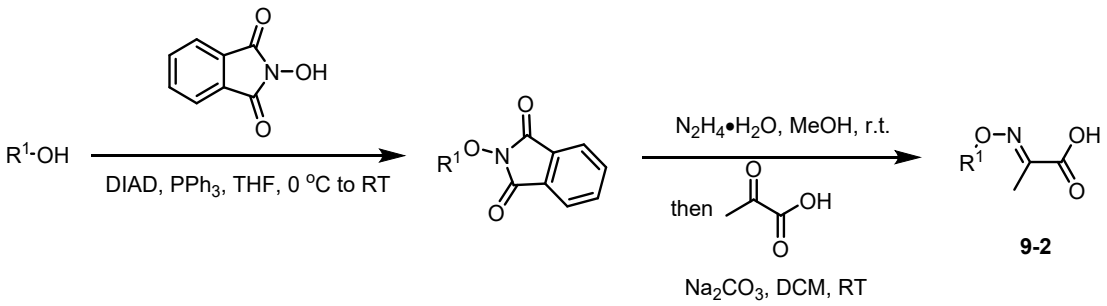


Figure SI-2. General procedure for the synthesis of alcohol oximes **9-2**

To a solution of alcohol (10 mmol, 1.0 equiv.), N-hydroxyphthalimide (1.96 g, 12 mmol, 1.2 equiv.), PPh_3 (3.14 g, 12 mmol, 1.2 equiv.) in THF (50 mL) was added Diisopropyl azodicarboxylate (DIAD, 2.4 mL, 12 mmol, 1.2 equiv.) dropwise at 0 °C. Then the solution was allowed to stir at room temperature overnight. Upon completion, the mixture was concentrated under reduced pressure, then purified by flash column chromatography on silica gel to give the title compounds.

To a solution of N-alkoxyphthalimide (5 mmol, 2.5 equiv.) in MeOH (20 mL) was added hydrazine monohydrate (0.32 g, 5.4 mmol, 2.7 equiv., 85% w/w in water) at room temperature. The reaction was monitored by TLC and usually completed in 30 min. Then Na_2CO_3 (0.64 g, 6 mmol, 3.0 equiv.), pyruvic acid (0.44 g, 5 mmol, 2.5 equiv.) was added to the mixture and stirred for 5 h at the same temperature. Upon completion, MeOH was removed by reduced pressure and CH_2Cl_2 (15 mL) was added, filtered to remove the precipitate, then the filtrate was washed with CH_2Cl_2 and water. The resulting mixture was treated with diluted HCl (1.0 mol/L), adjusted the pH to 4.0~5.0, and extracted with CH_2Cl_2 (6×10 mL). The combined organic layer was dried over $MgSO_4$ and concentrated to provide the crude pyruvic acid oxime ether.

3) General procedure for the synthesis of alcohol oximes 9:

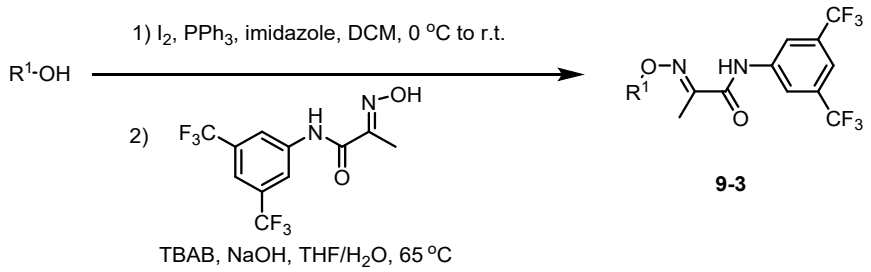


Figure SI-3. General procedure for the synthesis of alcohol oximes **9-3**

Iodinate: A 100 mL round bottom flask was charged with alcohol (10 mmol, 1.0 equiv.), PPh_3 (3.67 g, 14 mmol, 1.4 equiv.), imidazole (1.06 g, 15.5 mmol, 1.55 equiv.) and CH_2Cl_2 (50 mL). To this stirring solution was added I_2 (3.81 g, 15 mmol, 1.5 equiv.) in one portion at 0 ℃. The mixture was allowed to warm to room temperature and stirred for 3 h, then the solvent was evaporated to give a thick oil. This residue was triturated with n-hexane and the organic phase was washed with sat. $Na_2S_2O_3$, dried by $MgSO_4$, filtered and concentrated to afford the alkyl iodides as a colorless oil.

Etherification: A mixture of N-trifluoromethylphenyl pyruvamide oxime (0.54 g, 2.0 mmol, 1.0 equiv.), tetrabutylammonium bromide (77.3 mg, 0.24 mmol), NaOH (0.12 g, 3.0 mmol, 1.5 equiv.), THF (14 mL) and H_2O (7 mL) was heated to 65 ℃. Then a solution of alkyl iodide (3 mmol, 1.5 equiv.) in THF (4 mL) was added dropwise, and the mixture was stirred for 3.5 h. Upon completion, the mixture was evaporated to leave the aqueous layer, which was extracted by CH_2Cl_2 (3×15 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give a crude product, which was purified by flash column chromatography on silica gel using a mixture of petroleum ether (60~90 ℃) and EtOAc as the eluent to give the target compounds.

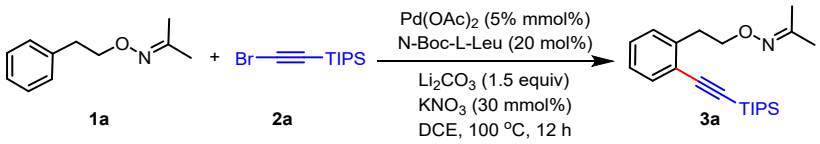
4) General procedure for the Pd(II)-Catalyzed C–H alkynylation of alcohols:

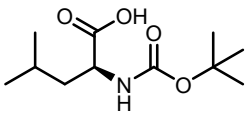
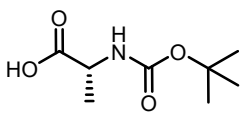
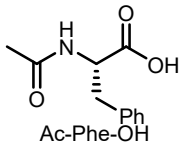
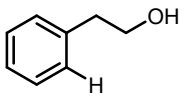
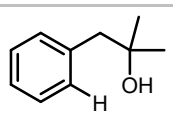
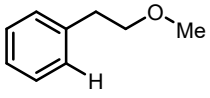
With C-H alkynylation of alcohols 1 to afford 3 as examples:

An oven-dried 10 mL Schlenk Tube was charged with **1** (0.2 mmol), $PdCl_2$ (0.01 mmol, 1.77 mg), N-Boc-L-Leu-OH (0.04 mmol, 9.2 mg), KNO_3 (0.06 mmol, 6.1 mg), Li_2CO_3 (0.3 mmol, 22.2 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**.

5) Investigation of reaction conditions:

1) Table S1. Conditions optimization for aryl C–H alkynylation.[a]



Entry	Variation of standard conditions	Yield[b] (%)
1	None	78
2	$NiCl_2$ instead of $PdCl_2$	15
3	$[Ru(p\text{-cymene})Cl_2]_2$ instead of $PdCl_2$	36
4	$[IrCp^*Cl_2]_2$ instead of $PdCl_2$	47
5	without $PdCl_2$	n. p.
6	without N-Boc-L-Leu-OH	39
7	without KNO_3	31
8	$AgNO_3$ instead of KNO_3	78
9	LiOAc, Cs_2CO_3 instead of Li_2CO_3	62, 25
10	PivOH instead of Li_2CO_3	< 10
11	N-Boc-L-Ala instead of N-Boc-L-Leu-OH	71
12	Ac-Phe-OH instead of N-Boc-L-Leu-OH	49
13	CH_3CN, HFIP, toluene instead of DCE	52, 53, 62
14	40 °C, 60 °C, 120 °C	37, 56, 75
	 N-Boc-L-Leu-OH	 N-Boc-L-Ala
	 Ac-Phe-OH	
	 **1a-1**, trace	 **1a-2**, trace
	 **1a-3**, trace	

[a] Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), N-Boc-L-Leu-OH (20 mol%), Li_2CO_3 (1.5 equiv.), KNO_3 (20 mol%), DCE (1 mL), 100 ℃, 12 h. [b] Isolated yield.

2) Investigation of Csp^3-H alkynylation of aliphatic alcohols

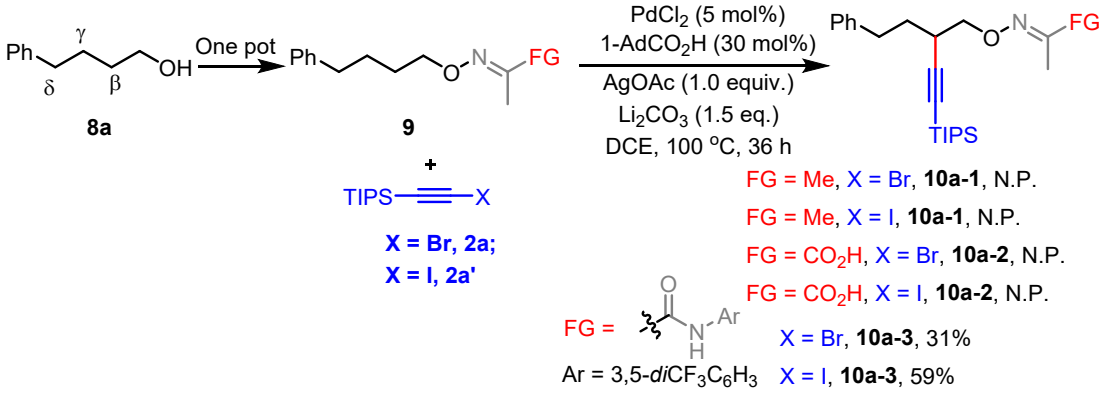
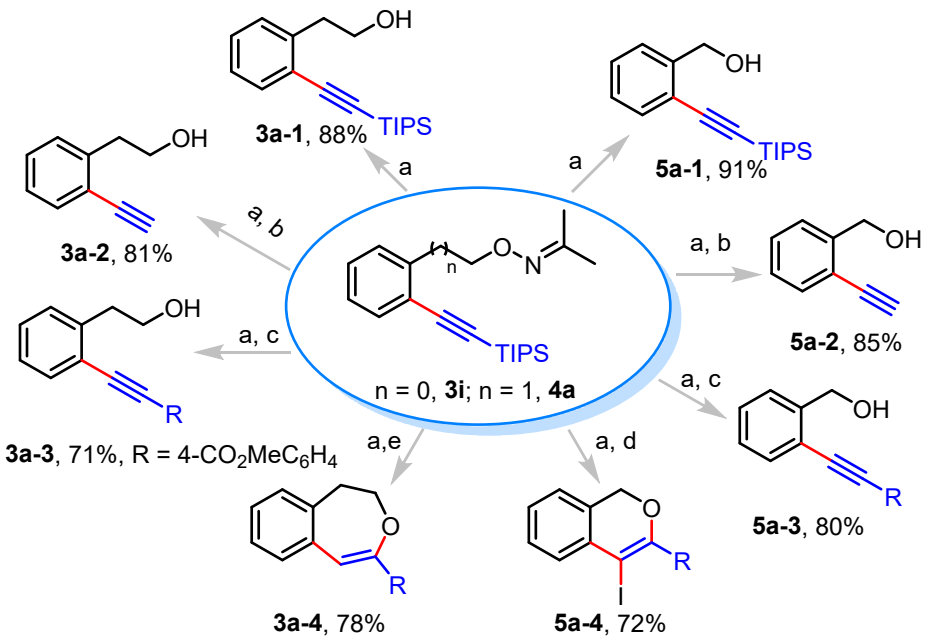


Figure SI-4. Amide-attached oximes enabled Csp^3–H alkynylation under Pd(II) catalysis

After extensive investigation of reaction conditions for Csp^3–H alkynylation of aliphatic alcohols under Pd(II) catalysis, we are grateful to find that with amide-attached oxime substrates, site-selective β Csp^3–H alkynylation of **8** was achieved. Further optimization revealed that the use of 1-$AdCO_2H$ enhanced the efficiency, it was speculated that 1-$AdCO_2H$ might enhance the formation of stronger electrophilic Pd(II) catalyst, and/or facilitate the product releasing step (*J. Am. Chem. Soc*. **2013**, *135*, 12135−12141. *Acc. Chem. Res*. **2013**, *47*, 281−295.).

C. Synthetic applications

To further demonstrate the synthetic potential of this transformation, selective N–O reduction of the obtained products could be readily transformed to the corresponding alcohols (**3a-1**, **4a-1**), and subsequent desilylation or desilylation/Sonogashira reaction afforded to the terminal alkynes (**3a-2**, **4a-2**) and internal alkynes (**4a-3**, **5a-3**), proving complementary approach for alkyne delivery. Notably, *ortho* alkyne substituted aryl alcohols serve as versatile synthons for concise delivery of 6 and 7-memebered oxygen heterocycles (**3a-4**, **5a-4**).



Conditions: a) Zn, HOAc/THF/H_2O = 3:1:1, RT; b) TBAF (2.0 equiv.), THF, RT; c) 4-$CO_2MeC_6H_4I$ (1.0 equiv.), TBAF (2.0 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mol%), Et_3N/THF, 50 °C; d) I_2, CH_3CN; e) $Pd(CH_3CN)_2Cl_2$ (10 mol%), THF, RT.

Figure SI-5. Synthetic transformations.

D. Mechanistic studies

According to the literature and experimental observations, it was proposed that ligand exchange of Pd(II) catalyst to the alcohol substrates initiated this transformation (**Figure SI-6**). Notably, with the assistance of MPAA, deprotonation took place with lower activation barrier, delivering to the corresponding 6, 7 or 8-membered palladacycle intermediate **B**. Further oxidation of the palladacycle intermediate with bromoalkyne **2** might procced to give Pd^{IV} species **C**, which underwent subsequent reductive elimination to afford the desired alkynes. Alternatively, alkyne migratory insertion into the palladacycle **B** led to the palladacycle species **C'**, which followed by *trans* β elimination to release the desired alkyne products.

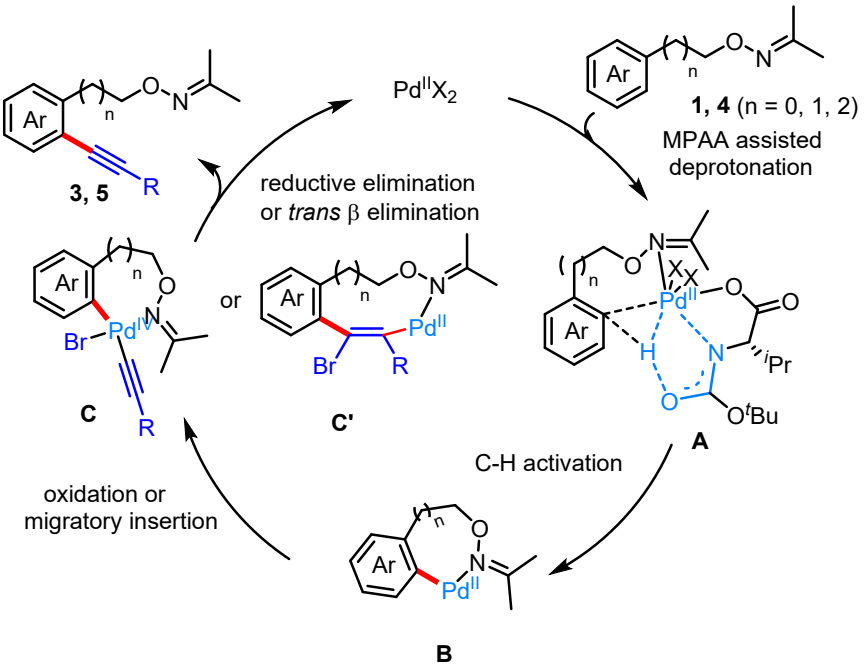


Figure SI-6. Proposed mechanism for remote C−H alkynylation under Pd(II)/MPAA catalysis.

For secondary and tertiary Csp^3–H alkynylation (**Figure SI-7**) enabled by amide attached oximes under Pd(II) catalysis, a bidentate [5. 5] palladacycle intermediates **9-A**, was the key intermediate, to achieve simultaneous site-selectivity and efficiency of this transformation. Subsequent haloalkyne migratory insertion or further oxidation, affording to seven-membered palladacycle or Pd(IV) intermediate **9B** or **9B'**. Finally, *trans* β-elimination or reductive elimination afforded to the alkyne products **10**. Notably, sequential secondary Csp^3–H alkynylation followed tertiary Csp^3–H alkynylation, might proceed to afford iterative Csp^3–H activation product **10b**. We speculated that the secondary Csp^3–H alkynylation product might enhance the acidity of the β Csp^3–H to alcohols, and thus, acerating the further tertiary Csp^3–H alkynylation.

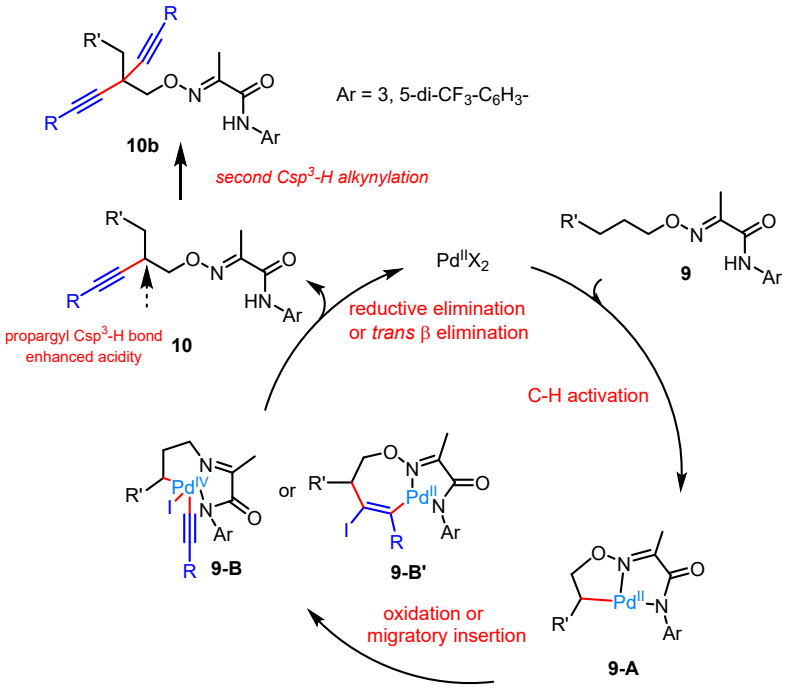
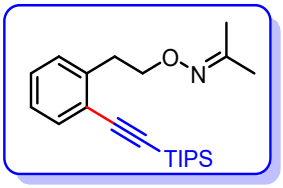
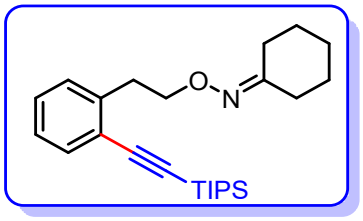


Figure SI-7. Proposed mechanism for secondary and tertiary Csp^3–H alkynylation enabled by amide attached oximes.

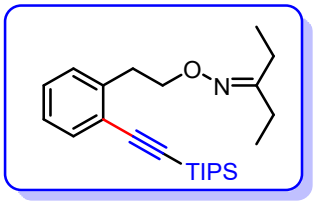
E. Analytical data for the alkyne products:



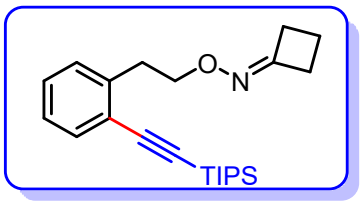
Propan-2-one *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3a), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.17-7.13 (m, 1H), 4.27 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 6.8 Hz, 2H), 1.87 (s, 3H), 1.81 (s, 3H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 154.8, 141.3, 132.9, 129.8, 128.4, 126.2, 123.5, 105.5, 94.5, 72.8, 34.9, 22.0, 18.8, 15.7, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{36}NOSi$: 358.2561, found: 358.2566.



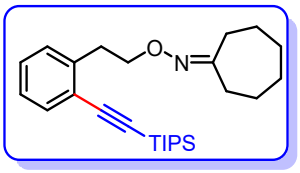
Cyclohexanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3b), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.23-7.22 (m, 2H), 7.17-7.14 (m, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.43-2.40 (m, 2H), 2.23-2.18 (m, 2H), 1.67 (s, 2H), 1.59-1.57 (m, 4H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 160.3, 141.4, 132.9, 129.8, 128.3, 126.1, 123.5, 105.5, 94.5, 72.7, 34.8, 32.3, 27.2, 25.9, 18.8, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{40}NOSi$: 398.2874, found: 398.28746.



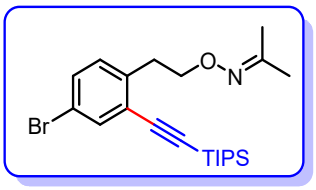
Pentan-3-one *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3c), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.23-7.22 (m, 2H), 7.18-7.13 (m, 1H), 4.27 (t, J = 7.2 Hz, 2H), 4.22 (t, J = 6.8 Hz, 2H), 3.17 (t, J = 6.8 Hz, 2H), 2.96 (t, J = 7.2 Hz, 2H), 2.29-2.25 (m, 3H), 2.19 (q, J = 4 Hz, 3H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 163.4, 141.4, 132.9, 129.8, 128.3, 126.1, 123.4, 105.5, 94.5, 72.7, 34.8, 27.2, 21.4, 18.8, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{40}NOSi$: 386.2874, found: 386.2871.



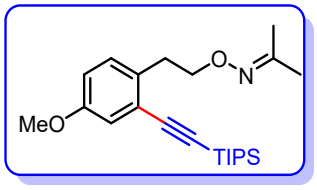
Cyclobutanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3d), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.18-7.13 (m, 1H), 4.25 (t, J = 7.2 Hz, 2H), 3.17 (t, J = 7.2 Hz, 2H), 2.93-2.84 (m, 4H), 1.99 (t, J = 4 Hz, 2H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.7, 141.1, 132.9, 128.4, 128.4, 126.2, 123.5, 105.4, 94.6, 73.1, 34.9, 31.8, 18.8, 14.7, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{36}NOSi$: 370.2561, found: 370.2563.



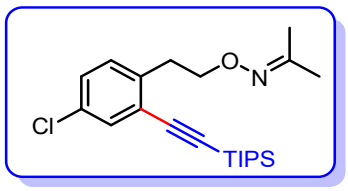
Cycloheptanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3e), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.23-7.22 (m, 2H), 7.17-7.13 (m, 1H), 4.28 (t, J = 6.8 Hz, 3H), 3.18 (t, J = 6.8 Hz, 3H), 2.48-2.45 (m, 2H), 2.38-2.35 (m, 2H), 1.64-1.54 (m, 8H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 153.7, 141.4, 132.9, 128.3, 126.1, 123.5, 110.3, 105.5, 91.3, 72.8, 33.8, 30.6, 29.3, 28.0, 24.8, 18.8, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{42}NOSi$: 412.3030, found: 412.3035.



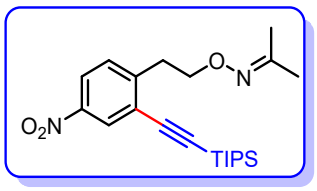
Propan-2-one *O*-(4-bromo-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3f), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.59 (d, J = 2 Hz, 1H), 7.34 (dd, J = 2.4 Hz, J = 8.4 Hz, 1H), 7.08 (d, J = 8 Hz, 1H), 4.23 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 6.8 Hz, 2H), 1.87 (s, 3H), 1.80 (s, 3H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 140.4, 135.2, 131.4, 131.3, 125.4, 119.5, 103.9, 96.3, 72.4, 34.3, 22.0, 18.8, 15.7, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{35}BrNOSi$: 436.1666, found: 436.1660.



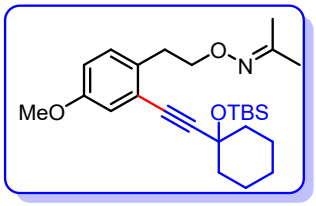
Propan-2-one *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3g), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 2.8 Hz, 1H), 6.80 (dd, J = 2.8 Hz, J = 8.4 Hz, 1H), 4.22 (t, J = 7.2 Hz, 2H), 3.80 (s, 3H), 3.10 (t, J = 6.8 Hz, 2H), 1.87 (s, 3H), 1.81 (s, 3H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.7, 154.7, 133.7, 130.8, 130.1, 124.2, 117.2, 115.1, 105.4, 94.3, 73.1, 55.5, 34.0, 22.0, 18.8, 15.7, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{38}NO_2Si$: 388.2666, found: 388.2662.



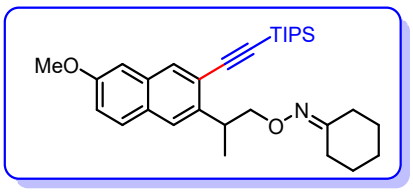
Propan-2-one *O*-(4-chloro-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3h), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.44 (d, J = 2.0 Hz, 1H), 7.19 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H), 7.15 (s, 1H), 4.23 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.6 Hz, 2H), 1.87 (s, 3H), 1.80 (s, 3H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 139.9, 132.4, 131.7, 131.0, 128.5, 125.0, 104.0, 96.2, 72.5, 34.3, 29.8, 22.0, 18.8, 15.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{35}ClNOSi$: 392.2171, found: 392.2175.



Propan-2-one *O*-(4-nitro-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3i), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.29 (d, J = 2.4 Hz, 1H), 8.06 (dd, J = 2.4 Hz, J = 8.4 Hz, 1H), 7.38 (d, J = 3.6 Hz, 1H), 4.29 (t, J = 6.8 Hz, 2H), 3.26 (t, J = 6.4 Hz, 2H), 1.87 (s, 3H), 1.79 (s, 3H), 1.14 (d, J = 3.8 Hz, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.3, 149.0, 146.4, 130.7, 127.6, 124.9, 122.9, 102.9, 98.2, 71.9, 58.6, 34.9, 22.0, 18.8, 15.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{35}N_2O_3Si$: 403.2411, found: 403.2414.

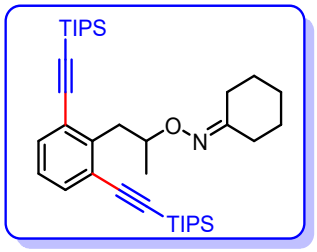


Propan-2-one *O*-(2-((1-((tert-butyldimethylsilyl) oxy) cyclohexyl) ethynyl) -4-methoxyphenethyl) oxime (3j), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.13 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 2.8 Hz, J = 8.4 Hz, 1H), 4.20 (t, J = 6.8 Hz, 2H), 3.80 (s, 3H), 3.07 (t, J = 7.2 Hz, 2H), 1.87 (s, 3H), 1.82 (s, 3H), 0.90 (s, 9H), 0.21 (s, 3H), 0.07 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.8, 154.7, 133.1, 130.8, 129.8, 124.0, 116.9, 114.5, 113.9, 97.6, 83.3, 73.2, 55.4, 41.4, 33.9, 29.8, 25.5, 23.1, 22.0, 18.3, 15.7, 1.17, -2.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{42}NO_3Si$: 444.2928, found: 444.2925.

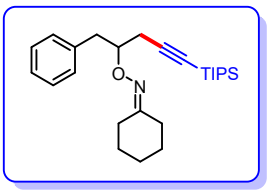


Cyclohexanone *O*-(2-(6-methoxy-3-((triisopropylsilyl)ethynyl) naphthalen-2-yl) propyl) oxime (3k), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.92 (s, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.58 (s, 1H), 7.11 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 4.40-4.36 (m, 1H), 4.19-4.15 (m, 1H), 3.90 (s, 3H), 3.86-3.81 (m, 1H), 2.39 (t, J = 6.4 Hz, 2H), 2.16 (t, J = 6.0 Hz, 2H), 1.65-1.60 (m, 2H), 1.56-1.51 (m, 4H), 1.39 (d, J = 6.8 Hz,

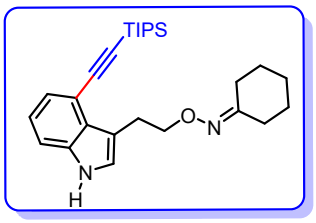
3H), 1.17 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.2, 157.7, 140.5, 132.7, 132.0, 131.2, 129.2, 128.9, 124.8, 122.3, 119.6, 106.0, 105.1, 94.7, 77.6, 55.4, 36.9, 32.3, 27.2, 26.0, 25.9, 18.9, 11.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{46}NO_2Si$: 492.3292, found: 492.3295.



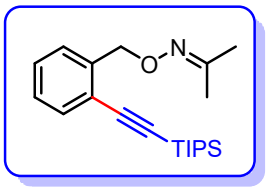
Cyclohexanone *O*-(1-(2,6-bis((triisopropylsilyl)ethynyl)phenyl)propan-2-yl) oxime (3m), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 4.69-4.61 (m, 1H), 3.47-3.42 (m, 1H), 3.27-3.22 (m, 1H), 2.50-2.34 (m, 2H), 2.09-2.04 (m, 4H), 1.93-1.91 (m, 2H), 1.75-1.73 (m, 2H), 1.13 (s, 42H), 1.08-1.05 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.7, 143.9, 133.0, 125.7, 124.5, 105.8, 94.5, 77.8, 55.9, 39.7, 35.1, 32.2, 27.2, 18.9, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{62}NOSi_2$: 592.4364, found: 592.4361.



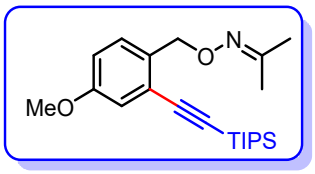
Cyclohexanone *O*-(1-phenyl-5-(triisopropylsilyl)pent-4-yn-2-yl) oxime (3m'), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.26 (m, 4H), 7.23-7.18 (m, 1H), 4.37-4.31 (m, 1H), 3.11 (dd, J = 5.6 Hz, 8.8 Hz, 1H), 3.02 (dd, J = 6.8 Hz, 14.0 Hz, 1H), 2.58-2.49 (m, 2H), 2.47-2.43 (m, 2H), 2.19-2.16 (m, 2H), 1.65-1.56 (m, 6H), 1.25 (s, 2H), 1.10-1.09 (m, 19H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 160.6, 138.4, 129.7, 128.1, 126.1, 105.3, 82.5, 80.8, 38.4, 32.2, 29.7, 27.1, 25.8, 24.2, 18.7, 18.6, 18.5, 18.4, 17.7, 12.3, 11.4, 11.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{41}NOSi$: 411.2957; Found: 411.2961.



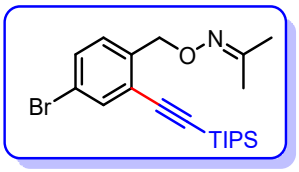
Cyclohexanone *O*-(2-(4-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)ethyl) oxime (3l), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.08 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.17-7.16 (m, 1H), 7.13-7.09 (m, H), 7.01-6.98 (m, 1H), 4.20 (t, J = 6.8 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 2.34-2.31 (m, 2H), 2.12 (t, J = 6.0 Hz, 2H), 1.58-1.57 (m, 2H), 1.48-1.47 (m, 4H), 1.07 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 160.2, 135.7, 127.7, 123.6, 120.4, 119.9, 119.8, 117.5, 110.8, 98.2, 97.7, 73.0, 32.3, 27.1, 26.0, 18.8, 17.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{41}N_2OSi$: 437.2983, found: 437.2989.



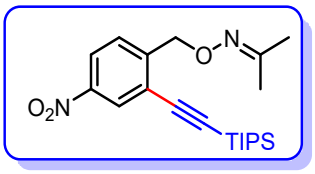
Propan-2-one *O*-(2-((triisopropylsilyl)ethynyl)benzyl) oxime (5a), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.23-7.22 (m, 2H), 7.17-7.14 (m, 1H), 4.29-4.25 (m, 2H), 1.88 (d, J = 2.0 Hz, 3H), 1.81 (d, J = 2 Hz, 3H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 160.9, 140.8, 132.8, 128.4, 127.6, 127.1, 122.2, 104.5, 95.6, 73.5, 32.3, 27.2, 18.9, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{34}NOSi$: 344.2404, found: 344.2401.



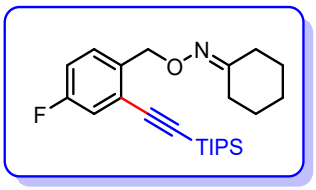
Propan-2-one *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5b), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.30 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 2.8 Hz, 1H), 6.86 (dd, J = 2.8 Hz, J = 8.8 Hz, 1H), 5.18 (s, 2H), 3.80 (s, 3H), 1.87 (d, J = 2.8 Hz, 6H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.8, 155.0, 132.8, 130.0, 123.9, 114.9, 104.6, 95.1, 73.4, 55.5, 22.0, 18.8, 15.9, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{36}NO_2Si$: 374.2510, found: 374.2513.



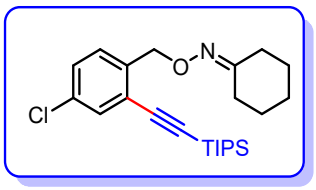
Propan-2-one *O*-(4-bromo-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5c), ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 4.8 Hz, 1H), 5.22 (s, 2H), 1.93 (s, 3H), 1.90 (s, 3H), 1.16 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 155.7, 139.8, 135.2, 131.5, 129.3, 124.2, 120.7, 102.9, 97.4, 73.0, 22.0, 18.8, 15.9, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{33}BrNOSi$: 422.1509, found: 422.1507.



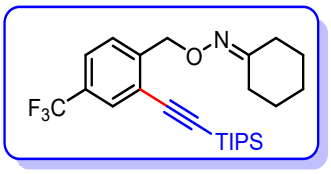
Propan-2-one-*O*-(4-nitro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5d), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* =1.6 Hz, 1H), 8.13 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 5.13 (s, 2H), 1.96 (s, 3H), 1.89 (s, 3H), 1.15 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 156.4, 148.4, 146.9, 127.8, 127.4, 123.1, 123.0, 101.7, 99.6, 72.8, 22.0, 18.8, 16.0, 11.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{33}N_2O_3Si$: 389.2255, found: 389.2258.



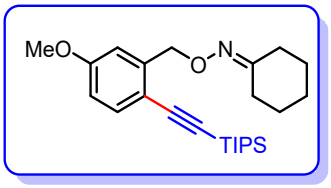
Cyclohexanone *O*-(4-fluoro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5e), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.33 (dd, *J* = 6.0 Hz, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 2.4 Hz, *J* = 9.2 Hz, 1H), 7.02-6.97 (m, 1H), 5.20 (s, 1H), 2.51 (t, *J* = 5.6 Hz, 2H), 2.20 (t, *J* = 6.0 Hz, 2H), 1.67-1.63 (m, 2H), 1.60 (brs, 4H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.6 (d, *J* = 250.0 Hz), 161.1, 136.7 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 8.0 Hz), 124.0, 119.2 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 21.0 Hz), 103.3, 96.8, 72.9, 32.3, 27.2, 25.6, 18.8, 11.4. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -115.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{37}FNOSi$: 402.2623, found: 402.2627.



Cyclohexanone *O*-(4-chloro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5f), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 2.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 5.20 (s, 2H), 2.53-2.50 (m, 2H), 2.21-2.18 (m, 2H), 1.69-1.65 (m,2H), 1.61-1.60 (m, 4H), 1.13 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.2, 139.4, 132.8, 132.3, 129.0, 128.6, 123.8, 103.0, 97.3, 72.8, 32.3, 27.2, 25.9, 18.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{37}ClNOSi$: 418.2327, found: 418.2322.

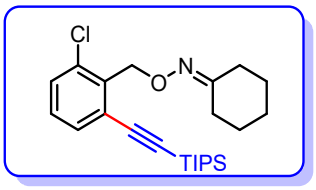


Cyclohexanone *O*-(4-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5g), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.69 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.28 (s, 2H), 2.54 (t, J = 5.6 Hz, 2H), 2.20 (t, J = 5.6 Hz, 2H), 1.67-1.65 (m, 2H), 1.59 (s, 4H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.5, 145.0, 130.2 (q, J = 32.0 Hz), 129.7, 129.4 (q, J = 3.0 Hz) 127.6, 124.9 (q, J = 4.0 Hz), 124.1 (q, J = 270.0 Hz) 122.5, 102.8, 98.0, 72.9, 32.3, 27.2, 25.9, 18.8, 11.4. **^{19}F NMR (300 MHz, $CDCl_3$)** δ -62.7 (3F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{37}F_3NOSi$: 452.2591, found: 452.2595.

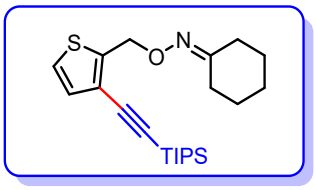


Cyclohexanone *O*-(5-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5h), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.74 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 5.24 (s, 1H), 3.81 (d, J = 0.8 Hz, 1H), 2.55 (t, J = 6.0 Hz, 2H), 2.23-2.20 (m, 2H), 1.70-1.65 (m, 2H), 1.61-1.59 (m, 4H), 1.12 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.1, 159.8, 142.8, 134.2, 124.5, 114.2, 113.1, 112.7, 104.5, 93.7, 73.4, 55.4, 32.3, 27.2, 25.7, 18.9, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd

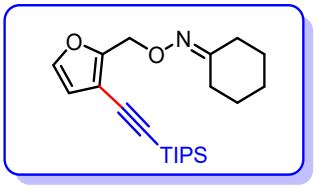
for $C_{25}H_{40}NO_2Si$: 414.2823, found: 414.2819.



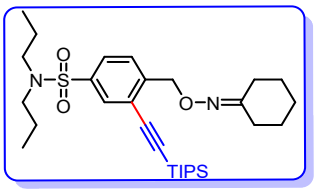
Cyclohexanone *O*-(2-chloro-6-((triisopropylsilyl)ethynyl)benzyl) oxime (5i), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 8 Hz, 1H), 7.13-7.09 (m, 1H), 5.28 (s, 1H), 2.35-2.33 (m, 2H), 2.12 (t, J = 6.4 Hz, 2H), 1.57 (d, J = 6.0 Hz, 2H), 1.47 (d, J = 2.8 Hz, 4H), 1.06 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.1, 136.2, 136.4, 131.6, 129.9, 129.1, 127.1, 104.3, 95.9, 70.9, 32.3, 27.1, 26.0, 18.8, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{37}ClNOSi$: 418.2327, found: 418.2322.



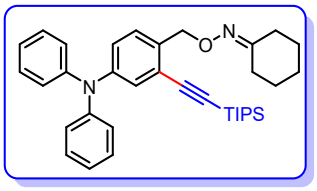
Cyclohexanone *O*-((3-((triisopropylsilyl)ethynyl)thiophen-2-yl)methyl) oxime (5j), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.08 (d, J = 3.6 Hz, 1H), 6.85 (d, J = 3.6 Hz, 1H), 5.11 (s, 2H), 2.46-2.44 (m, 2H), 2.21 (t, J = 6 Hz, 2H), 1.67 (brs, 2H), 1.57 (brs, 4H), 1.11 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.7, 142.9, 132.2, 126.0, 124.1, 99.8, 95.5, 69.8, 32.3, 27.1, 25.9, 18.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{36}NOSSi$: 390.2281, found: 390.2283.



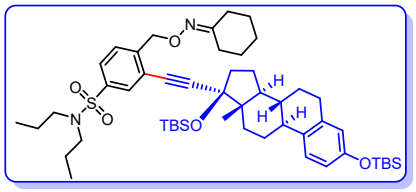
Cyclohexanone *O*-((3-((triisopropylsilyl)ethynyl)furan-2-yl)methyl) oxime (5k), ^{1}H NMR (400 MHz,$CDCl_3$) δ 6.55 (d, J = 3.2 Hz, 1H), 6.31 (d, J = 3.2 Hz, 1H), 4.93 (s, 2H), 2.46-2.44 (m, 2H), 2.21-2.17 (s, 2H), 1.67-1.66 (m, 2H), 1.58-1.57 (m, 4H), 1.12 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.6, 152.9, 142.8, 137.3, 116.7, 110.4, 96.7, 67.2, 32.3, 27.1, 25.9, 18.7, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{36}NO_2Si$: 374.2510, found: 374.2516.



4-(((Cyclohexylideneamino)oxy)methyl)-N,N-dipropyl-3-((triisopropylsilyl) ethynyl)benzenesulfonamide (5l), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.86 (d, J = 1.60 Hz, 1H), 7.70 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.28 (s, 2H), 3.07 (t, J = 7.6 Hz, 4H), 2.55 (t, J = 6.0 Hz, 2H), 2.20 (t, J = 6.0 Hz, 2H), 1.68-1.61 (m, 6H), 1.57-1.54 (m, 4H), 1.14 (s, 21H), 0.88 (t, J = 3.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.7, 145.7, 138.9, 131.0, 127.5, 126.6, 122.6, 102.5, 98.6, 72.8, 50.2, 32.2, 25.9, 25.7, 18.8, 11.4, 11.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{51}N_2O_3SSi$: 547.3384, found: 547.3387.

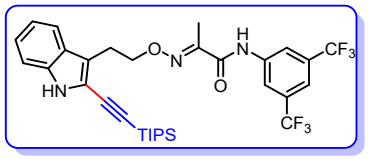


Cyclohexanone *O*-(4-(diphenylamino)-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5m), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.27-7.26 (m, 2H), 7.25-7.24 (m, 2H), 7.23-7.21 (m, 2H), 7.08-7.06 (m, 4H), 7.03-6.99 (m, 3H), 5.22 (s, 2H), 2.52 (t, J = 6.0 Hz, 2H), 2.22 (t, J = 6.8 Hz, 2H), 1.66-1.64 (m, 2H), 1.60-1.58 (m, 4H), 1.10 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.2, 147.7, 147.0, 135.0, 129.4, 129.3, 127.8, 124.7, 124.3, 123.4, 123.0, 104.2, 95.7, 73.4, 32.3, 27.2, 25.7, 18.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{47}N_2OSi$: 551.3452, found: 551.3457.

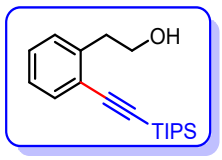


3-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Bis((tert-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11, 12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)ethynyl)-4-(((cyclohexylideneamino)oxy)methyl)-N,N-dipropylbenzenesulfonamide (5n), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.82 (d, J = 1.6 Hz, 1H), 7.71 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.61 (dd, J = 2.4 Hz, J = 8.4 Hz, 1H), 6.55 (s, 1H), 5.25

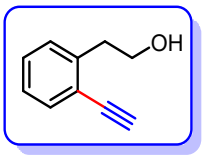
(s, 2H), 3.07 (t, J = 7.6 Hz, 4H), 2.83-2.79 (m, 2H), 2.52 (t, J = 2.8 Hz, 2H), 2.38-2.33 (m, 2H), 2.14 (t, J = 6.0 Hz, 2H), 2.08-2.04 (m, 1H), 1.93-1.75 (m, 7H), 1.61-1.54 (m, 8H), 1.46-1.40 (m, 3H), 0.90 (s, 18H), 0.88 (d, J = 0.8 Hz, 6H), 0.86 (s, 3H), 0.19 (t, J = 3.2 Hz, 12H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.7, 153.4, 144.9, 139.1, 137.9, 133.2, 130.3, 126.3, 122.7, 120.0, 117.3, 100.9, 82.8, 81.5, 72.9, 50.3, 48.9, 43.9, 40.5, 39.6, 33.4, 32.2, 29.8, 27.5, 27.1, 25.9, 25.8, 25.6, 23.3, 22.2, 18.3, 13.4, 11.3, -2.7, -4.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{51}H_{81}N_2O_5SSi_2$: 889.5399, found: 889.5403.



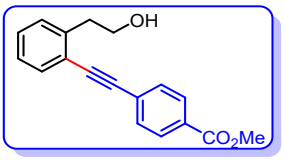
(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-((2-(2-((triisopropylsilyl)ethynyl)-1*H*-indol-3-yl)ethoxy)imino)propanamide (3l'), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.24 (s, 1H), 8.11 (s, 1H), 7.88 (s, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.21 (d, J = 5.6 Hz, 2H), 4.63 (t, J = 6.4 Hz, 2H), 3.29 (t, J = 6.4 Hz, 2H), 2.03 (s, 3H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.4, 149.7, 138.9, 135.7, 132.5, 132.2 (q, J = 33.5 Hz), 127.2, 124.6, 124.1 (q, J = 3.0 Hz), 121.9 (q, J = 272.8 Hz), 120.9, 120.4, 119.3 (q, J = 4.0 Hz), 117.9, 117.4 (q, J = 3.0 Hz), 111.2 (d, J = 2.0 Hz), 98.2, 97.9, 75.3, 36.6, 18.8, 11.4, 9.54. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -62.9 (6F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{38}F_6N_3O_2Si$: 638.2632, found: 638.2635.



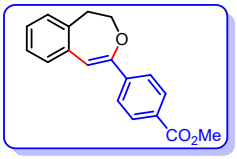
2-(2-((Triisopropylsilyl)ethynyl)phenyl)ethan-1-ol (3a-1), ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 1H), 7.27-7.25 (m, 2H), 7.21-7.17 (m, 1H), 3.92-3.91 (m, 2H), 3.09 (t, J = 6.4 Hz, 2H), 1.14 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 140.8, 133.2, 129.9, 128.6, 126.5, 123.5, 105.5, 94.8, 63.0, 38.3, 18.8, 11.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{31}OSi$: 303.2139, found: 303.2135.



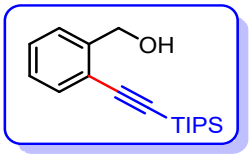
2-(2-Ethynylphenyl)ethan-1-ol (3a-2),[1] **^{1}H NMR (400 MHz,$CDCl_3$)** ***δ*** 7.50 (d, *J* = 3.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.20 (td, *J* = 1.6 Hz, *J* = 7.6 Hz, 1H), 3.91 (td, *J* = 2.0 Hz, *J* = 6.8 Hz, 1H), 3.26 (s, 1H), 3.08 (t, *J* = 6.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 141.1, 133.2, 129.1, 126.6, 122.1, 82.3, 81.1, 63.0, 37.9.



Methyl 4-((2-(2-hydroxyethyl)phenyl)ethynyl)benzoate (3a-3), ^{1}H NMR (400 MHz,$CDCl_3$) ***δ*** 7.98 (d, *J* = 8.4 Hz, 2H), 7.56-7.51 (m, 3H), 7.28-7.26 (m, 2H), 7.23-7.20 (m, 1H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.89 (s, 3H), 3.12 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 166.6, 140.7, 132.6, 131.4, 129.8, 128.0, 126.5, 122.5, 92.4, 90.9, 62.7, 52.3, 38.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}O_3$: 281.1172, found: 281.1177.

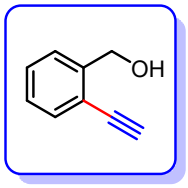


Methyl 4-(4,5-dihydrobenzo[d]oxepin-2-yl)benzoate (3a-4), ^{1}H NMR (400 MHz,$CDCl_3$) ***δ*** 7.90 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.63-7.60 (m, 1H), 7.20-7.16 (m, 2H), 7.08-7.06 (m, 1H), 4.22 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 2.87 (t, *J* = 5.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 167.3, 152.4, 141.5, 134.4, 130.4, 129.6, 128.6, 128.3, 128.2, 127.2, 126.6, 124.6, 102.5, 65.1, 52.0, 29.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}O_3$: 281.1172, found: 281.1177.

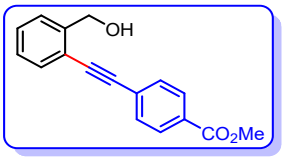


(2-((Triisopropylsilyl)ethynyl)phenyl)methanol (5a-1), ^{1}H NMR (400 MHz,$CDCl_3$) ***δ*** 7.49 (dd, *J* = 0.8 Hz, *J* = 6.8 Hz, 1H), 7.42 (dd, *J* = 0.4 Hz, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 7.24 (td, *J* = 1.2 Hz, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 6.8 Hz,

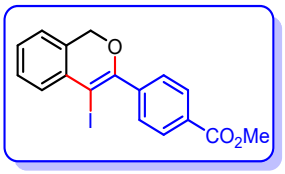
2H), 1.14 (d, J = 2.0 Hz, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 143.2, 132.9, 127.2, 121.6, 104.5, 96.2, 64.3, 18.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{29}OSi$: 289.1982, found: 289.1985.



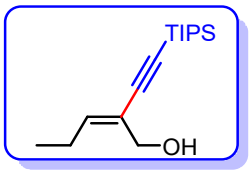
(2-Ethynylphenyl)methanol (5a-2),[2] **^{1}H NMR (400 MHz,$CDCl_3$) δ** 7.49 (dd, J = 0.8 Hz, J = 7.6 Hz, 1H), 7.45 (dd, J = 0.8 Hz, J = 8.0 Hz, 1H), 7.35 (td, J = 1.2 Hz, J = 7.2 Hz, 1H), 7.24 (td, J = 1.2 Hz, J = 8.0 Hz, 1H), 4.82 (s, 2H), 3.33 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 143.4, 132.9, 129.3, 127.4, 127.3, 120.2, 82.1, 81.3, 63.7, 29.8.



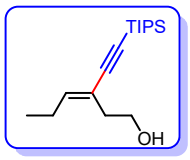
Methyl 4-((2-(hydroxymethyl)phenyl)ethynyl)benzoate (5a-3), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.59-7.50 (m, 4H), 7.39 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 4.93 (s, 2H), 3.93 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 166.6, 142.9, 132.5, 132.0, 131.6, 130.7, 129.7, 129.4, 127.7, 127.4, 120.9, 93.4, 89.8, 64.0, 52.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}O_3$: 267.1016, found: 267.1019.



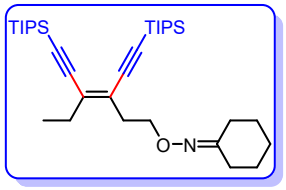
Methyl 4-(4-iodo-1H-isochromen-3-yl)benzoate (5a-4), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.24 (s, 2H), 7.00-6.96 (m, 1H), 6.48 (d, J = 8.0 Hz, 2H), 5.44 (s, 2H), 3.93 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 166.8, 157.7,145.7,142.6, 131.0, 130.5, 130.3, 129.9, 129.4, 128.0, 123.2, 121.6, 73.6, 61.6, 52.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}IO_3$: 392.9982, found: 392.9985.



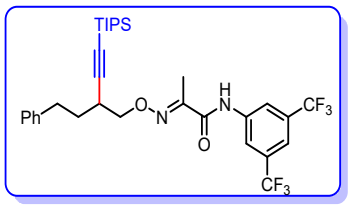
(*Z*)-2-((Triisopropylsilyl)ethynyl)pent-2-en-1-ol (7a), ^{1}H NMR (400 MHz,$CDCl_3$) *δ* 5.97 (t, *J* = 7.2 Hz, 1H), 4.10 (s, 2H), 2.37-2.30 (m, 1H), 1.09 (s, 21H), 1.02 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 141.0, 123.0, 103.3, 96.6, 66.1, 23.9, 18.8, 13.5, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{31}OSi$: 267.2139, found: 267.2137.



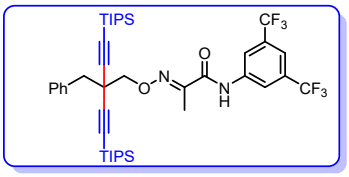
(*E*)-3-((Triisopropylsilyl)ethynyl)hex-3-en-1-ol (7b), ^{1}H NMR (400 MHz,$CDCl_3$) *δ* 6.06 (t, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 6.0 Hz, 2H), 2.42 (t, *J* = 6.4 Hz, 2H), 2.18-2.11 (m, 2H), 1.09-1.08 (m, 21H), 1.00 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 143.3, 119.1, 108.8, 88.2, 61.4, 33.9, 21.9, 18.8, 13.8, 11.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{33}OSi$: 281.2295, found: 281.2291.



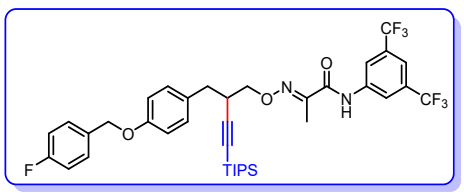
(*Z*)-Cyclohexanone *O*-(4-ethyl-6-(triisopropylsilyl)-3-((triisopropylsilyl) ethynyl) hex-3-en-5-yn-1-yl) oxime (7c), ^{1}H NMR (400 MHz,$CDCl_3$) *δ* 4.19 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.44-2.42 (m, 2H), 2.17 (t, *J* = 6.0 Hz, 2H), 1.65-1.63 (m, 2H), 1.58-1.55 (m, 4H), 1.12-1.11 (m, 3H), 1.09-1.08 (m, 42H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 160.0, 133.7, 126.0, 105.6, 105.5, 101.3, 101.0, 71.2, 35.0, 32.2, 28.6, 27.1, 25.9, 25.8, 25.3, 18.5, 12.8, 11.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{62}NOSi_2$: 556.4364, found: 556.4367.



(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-phenethyl-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10a-3), ^{1}H NMR (400 MHz,$CDCl_3$) *δ* 8.72 (s, 1H), 8.10 (s, 2H), 7.62 (s, 1H), 7.30-7.27 (m, 2H), 7.21-7.15 (m, 3H), 4.39-4.34 (m, 1H), 4.31-4.23 (m, 1H), 3.01-2.94 (m, 1H), 2.92-2.85 (m, 1H), 2.83-2.77 (m, 1H), 2.11 (s, 3H), 1.84-1.78 (m, 2H), 1.11-1.09 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 161.2 (d, *J* = 25.0 Hz), 150.4 (d, *J* = 69.0 Hz), 141.7 (d, *J* = 46.0 Hz), 138.8 (d, *J* = 10.0 Hz), 132.4 (q, *J* = 33.0 Hz), 128.4 (q, *J* = 5.0 Hz), 126.5 (q, *J* = 125.0 Hz), 126.1, 124.5 (q, *J* = 272.8 Hz), 121.7, 119.3 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 3.0 Hz), 119.0, 117.4 (q, *J* = 4.0 Hz), 107.6, 83.8, 77.8, 33.2, 33.1, 32.5, 18.6, 11.2, 9.6. **^{19}F NMR (300 MHz, $CDCl_3$) *δ*** -63.0 (6F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{41}F_6N_2O_2Si$: 627.2836, found: 627.2839. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{41}F_6N_2O_2Si$: 627.2836, found: 627.2839.

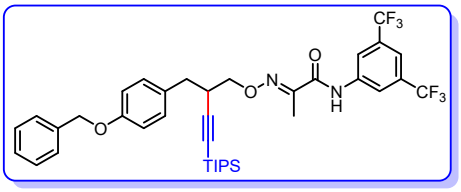


(*E*)-2-(((2-Benzyl-4-(triisopropylsilyl)-2-((triisopropylsilyl)ethynyl)but-3-yn-1-yl) oxy)imino)-N-(3,5-bis(trifluoromethyl)phenyl)propanamide (10b), ^{1}H NMR (400 MHz,$CDCl_3$) *δ* 8.87 (s, 1H), 8.06 (s, 1H), 7.98-7.96 (m, 2H), 7.60 (s, 1H), 7.36-7.32 (m, 3H), 5.31 (s, 2H), 2.15 (s, 3H), 1.57 (s, 2H), 1.12-1.09 (m, 21H), 1.02-1.00 (m, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) *δ*** 161.3, 150.6, 139.0, 136.7, 132.7, 132.4(q, *J* = 33.0 Hz), 129.0 (q, *J* = 3.0 Hz), 128.0, 125.2 (q, *J* = 4.0 Hz), 124.6 (q, *J* = 272.2 Hz), 121.9, 119.4 (q, *J* = 4.0 Hz), 117.5 (q, *J* = 4.0 Hz), 105.0, 104.8, 104.7, 104.4, 77.6, 29.8, 18.8, 18.7, 11.5, 11.4, 9.7. **^{19}F NMR (300 MHz, $CDCl_3$) *δ*** -63.0 (6F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{59}F_6N_2O_2Si_2$: 793.4014, found: 793.4017.

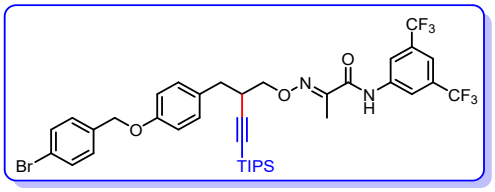


(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-((4-fluorobenzyl)oxy)benzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10c), ^{1}H NMR (400

MHz,$CDCl_3$) ***δ*** 8.82 (s, 1H), 8.13 (s, 2H), 7.62 (s, 1H), 7.42-7.38 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.00 (s, 2H), 4.37-4.33 (m, 1H), 4.29-4.25 (m, 1H), 3.17-3.11 (m, 1H), 2.93-2.88 (m, 1H), 2.82-2.77 (m, 1H), 2.15 (s, 3H), 1.03 (d, *J* = 3.6 Hz, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 161.0, 157.5, 150.8, 138.8, 132.8(d, *J* = 3.0 Hz), 132.5 (q, *J* = 32.0 Hz), 130.7, 130.5 (d, *J* = 4.0 Hz), 129.2 (d, *J* = 8.0 Hz), 128.5, 123.1 (q, *J* = 271.0 Hz), 119.3 (d, *J* = 2.0 Hz), 117.5 (q, *J* = 4.0 Hz), 115.6, 115.4, 114.7, 107.3, 84.2, 69.4, 60.4, 36.7, 35.0, 18.6, 11.2, 9.6. **^{19}F NMR (300 MHz, $CDCl_3$)** ***δ*** -63.0, -114.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{44}F_7N_2O_3Si$: 737.3004, found: 737.3008.

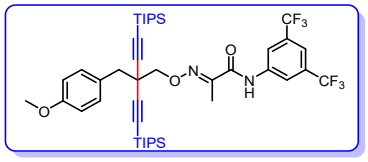


(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-phenoxybenzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10d), ^{1}H NMR (400 MHz,$CDCl_3$) ***δ*** 8.81 (s, 1H), 8.13 (s, 2H), 7.63 (s, 1H), 7.45-7.37 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 2H), 4.37-4.33 (m, 1H), 4.29-4.25 (m, 1H), 3.17-3.10 (m, 1H), 2.92-2.87 (m, 1H), 2.83-2.77 (m, 1H), 2.15 (s, 3H), 1.03 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$)** ***δ*** 161.2, 157.8, 150.9, 138.9, 137.2, 132.5 (q, *J* = 33.0 Hz), 130.7, 130.5, 128.7, 128.1, 127.6, 126.2 (q, *J* = 271.0 Hz), 124.6 (q, *J* = 3.7 Hz), 124.1, 121.9, 119.5 (q, *J* = 4.5 Hz), 117.6 (q, *J* = 4.0 Hz), 114.8, 107.5, 100.1, 84.3, 70.2, 36.8, 35.1, 18.7, 11.3, 9.7. **^{19}F NMR (300 MHz, $CDCl_3$)** ***δ*** -63.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{45}F_6N_2O_3Si$: 719.3098, found: 719.3002.

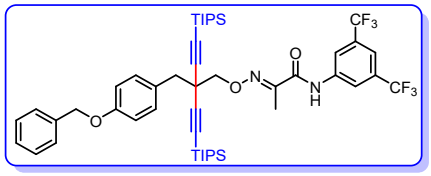


(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-((4-bromobenzyl)oxy)benzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10e), ^{1}H NMR (400 MHz,$CDCl_3$) ***δ*** 8.72 (s, 1H), 8.04 (s, 2H), 7.54 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32-7.22 (m, 3H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.83-6.73 (m, 2H), 4.93 (d, *J* = 21.2 Hz, 2H),

4.28 (m, 1H), 4.20-4.16 (m, 1H), 3.08-3.01 (m, 1H), 2.83-2.78 (m, 1H), 2.73-2.67 (m, 1H), 2.05 (s, 3H), 0.94 (s, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.2, 157.5, 150.9, 138.9, 137.2, 136.3, 132.6 (d, J = 34.0 Hz), 131.8, 130.9, 130.6 (d, J = 5.6 Hz), 126.0 (d, J = 270Hz), 129.1, 128.7, 128.1, 127.6, 124.6 (d, J = 4.0 Hz), 122.02, 121.9, 119.5 (d, J = 4.0 Hz), 117.6 (q, J = 3.0 Hz), 114.8 (d, J = 2.0 Hz), 107.4, 84.3, 70.2, 69.4, 36.8, 35.1, 18.7, 11.3, 9.7. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -63.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{44}BrF_6N_2O_3Si$: 797.2203, found: 797.2207.



(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-methoxybenzyl)-4-(triisopropylsi lyl)-2-((triisopropylsilyl)ethynyl)but-3-yn-1-yl)oxy)imino)propanamide (10f), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.90 (s, 1H), 8.06 (s, 2H), 8.03 (dd, J = 2.0 Hz, J = 6.8 Hz, 2H), 7.60 (s, 1H), 6.86 (dd, J = 2.0 Hz, J = 7.2 Hz, 2H), 5.31 (s, 2H), 3.83 (s, 3H), 2.15 (s, 3H), 1.41 (s, 2H), 1.10 (d, J = 3.6 Hz, 21H), 1.03 (d, J = 2.4 Hz, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.3, 160.2, 150.4, 139.0, 132.5 (q, J = 33.0 Hz), 131.9, 130.5, 129.1, 123.3 (q, J = 271.0 Hz), 123.2, 119.4 (d, J = 3.0 Hz), 117.5 (q, J = 4.0 Hz), 113.3, 105.6, 104.9, 104.4, 104.1, 77.9, 55.4, 25.5, 18.7, 17.8, 11.4, 9.6. **^{19}F NMR (300 MHz, $CDCl_3$) δ** -63.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{43}H_{61}F_6N_2O_3Si_2$: 823.4119, found: 823.4116.



(*E*)-2-(((2-(4-(Benzyloxy)benzyl)-4-(triisopropylsilyl)-2-((triisopropylsilyl)ethynyl) but-3-yn-1-yl)oxy)imino)-N-(3,5-bis(trifluoromethyl)phenyl)propanamide (10g), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.87 (s, 1H), 8.05 (s, 2), 8.01 (d, J = 8.8 Hz, 2H), 7.60 (s, 1H), 7.44-7.37 (m, 5H), 6.94 (d, J = 9.2 Hz, 2H), 5.30 (s, 2H), 5.09 (s, 2H), ,2.14 (s, 3H), 2.09 (s, 2H), 1.10 (d, J = 8.0 Hz, 21H), 1.01 (d, J = 2.0 Hz, 21H). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 161.3, 159.4, 150.5, 139.0, 136.9, 132.5 (q, J = 33.0Hz), 130.5, 125.9

(q, J = 271.0 Hz), 129.6, 129.4, 128.7 (d, J = 5.0 Hz), 128.2, 128.1, 127.6, 123.2, 119.4 (q, J = 4.0 Hz), 115.0, 114.2, 105.5, 104.9, 104.4, 104.2, 77.9, 70.2, 32.0, 29.8, 18.7, 17.8, 11.5, 11.4, 9.7, **^{19}F NMR (300 MHz, $CDCl_3$)** δ -63.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{49}H_{65}F_6N_2O_3Si_2$: 899.4432, found: 899.4435.

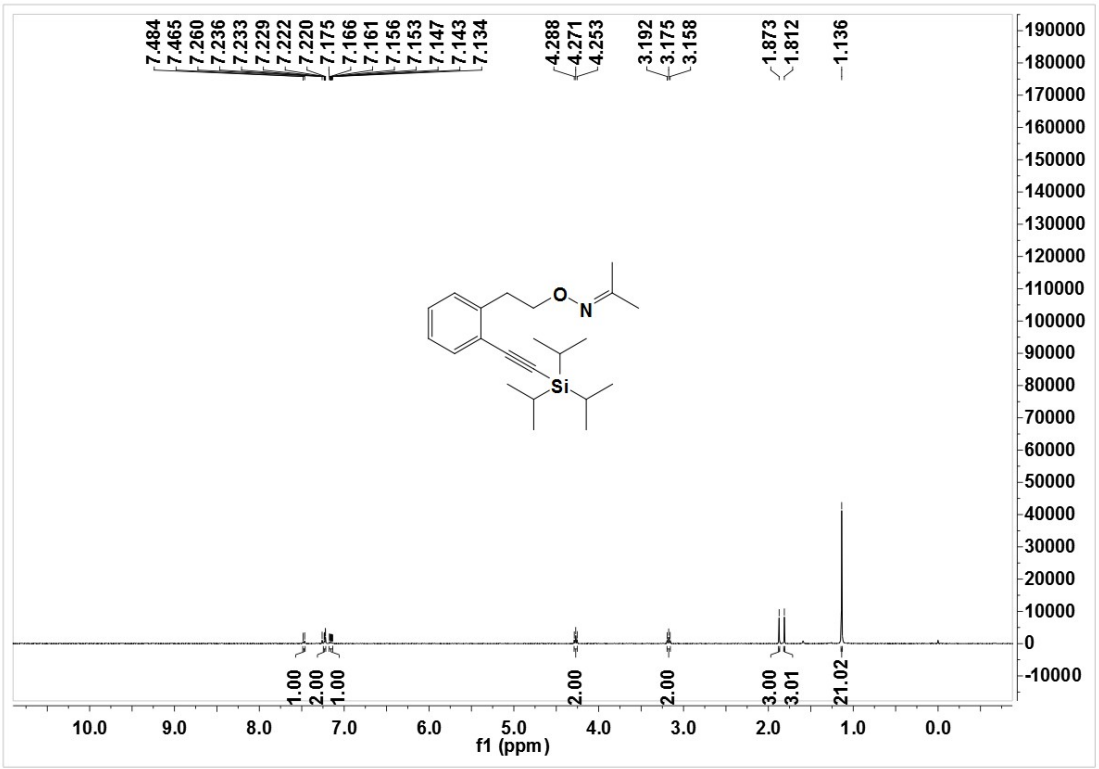
E. References

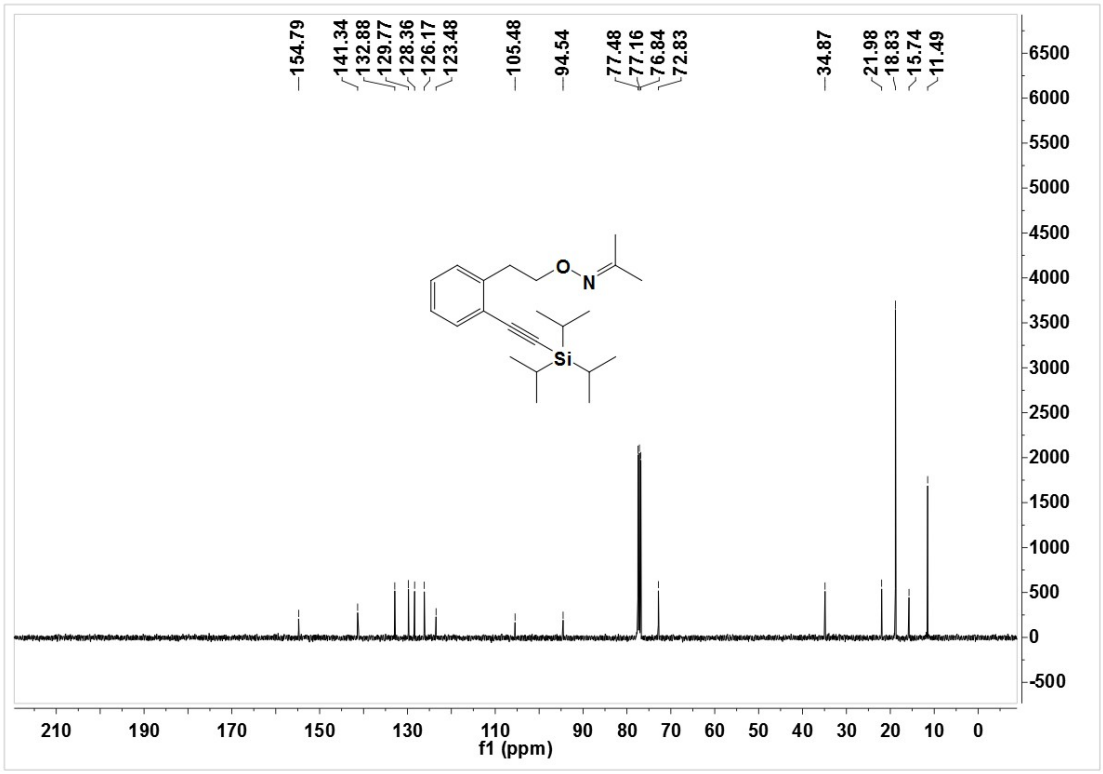
1) K. Hiroya, R. Jouka, M. Kameda, A. Yasuhara, T. Sakamoto, *Tetrahedron*, **2001**, *57*, 9697.

2) L. A. Aronica, L. Giannotti, S. Giuntini, A. M. Caporusso, *Eur. J. Org. Chem*., **2014**, 6858.

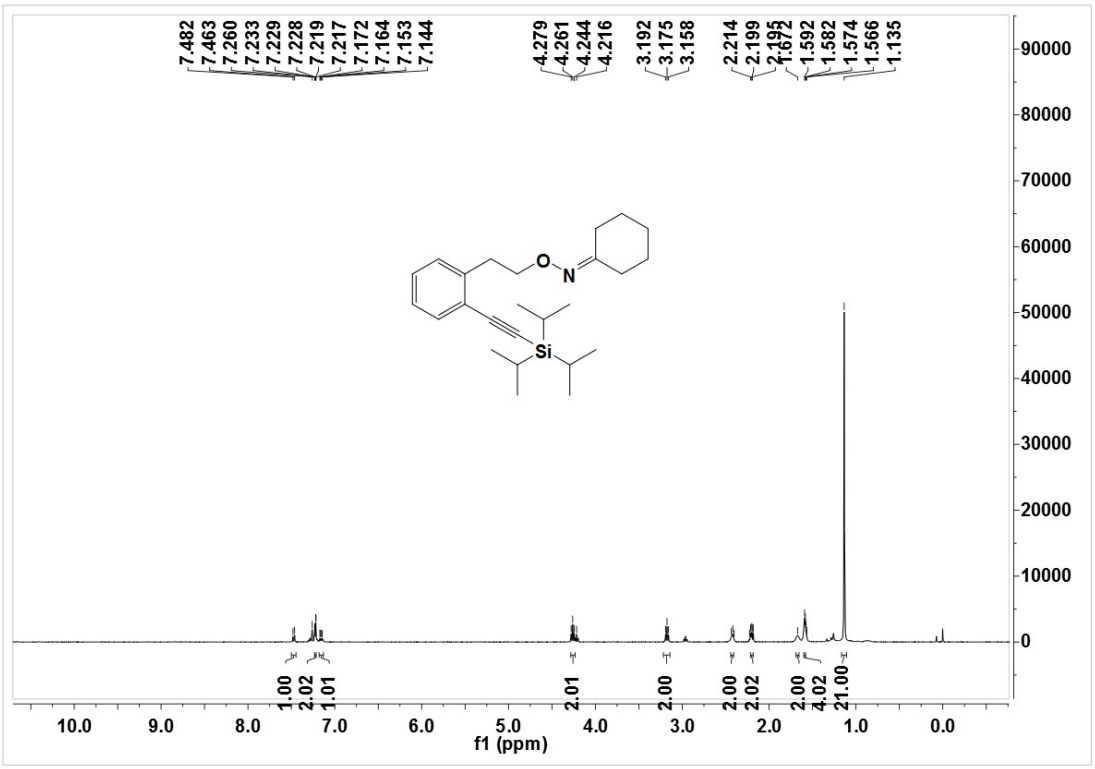
F. NMR spectra

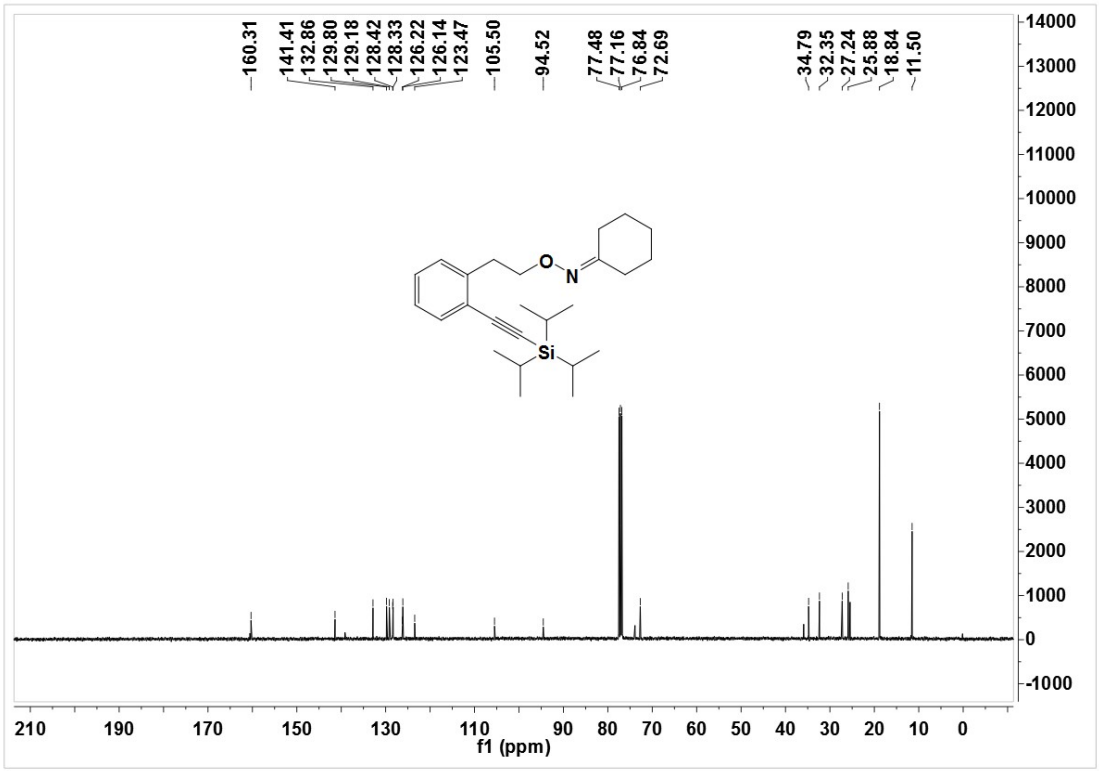
Propan-2-one *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3a)



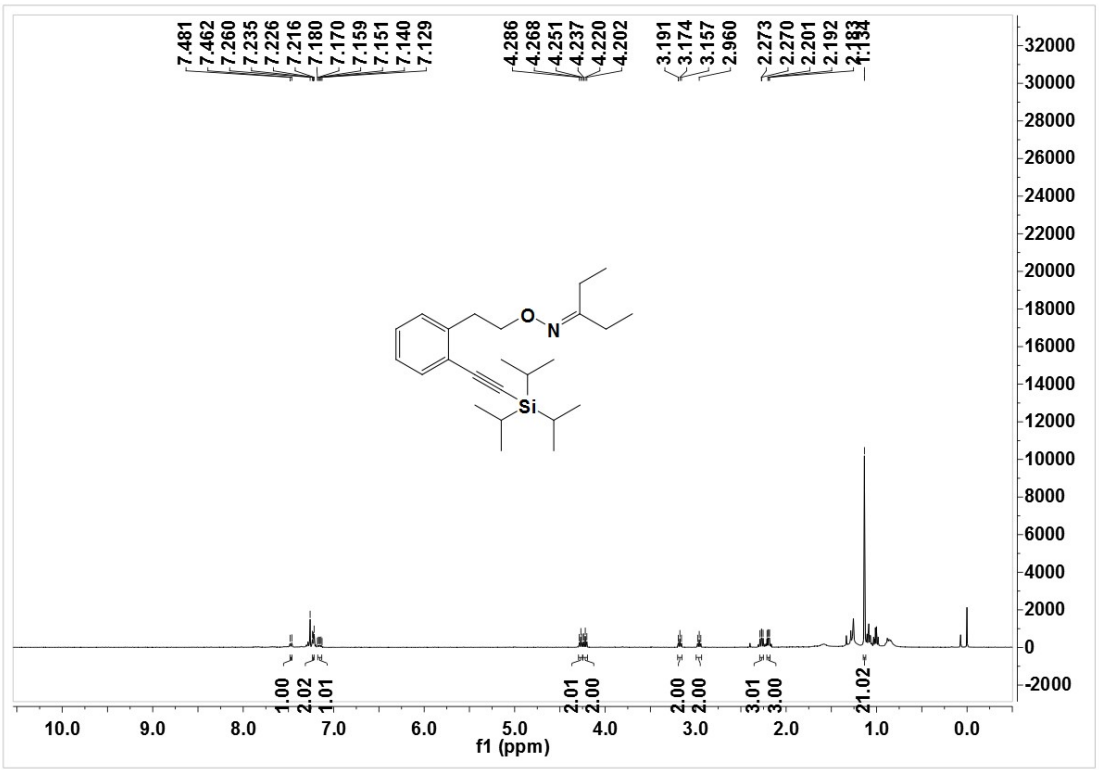


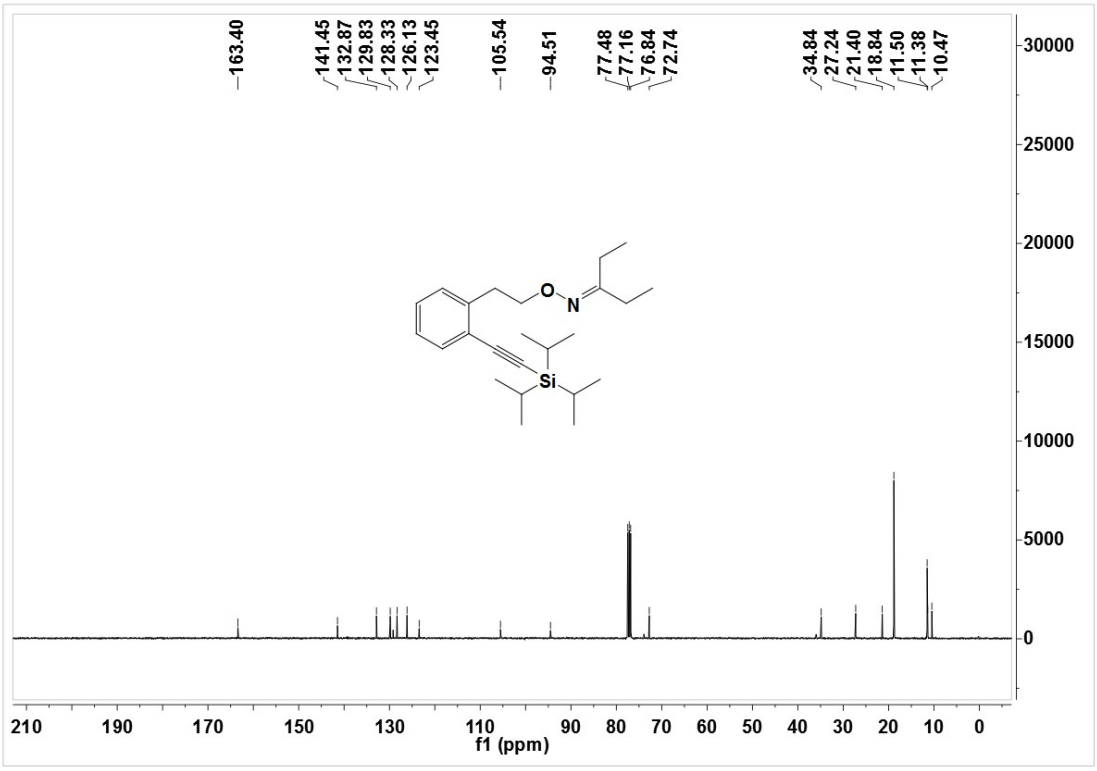
Cyclohexanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3b)



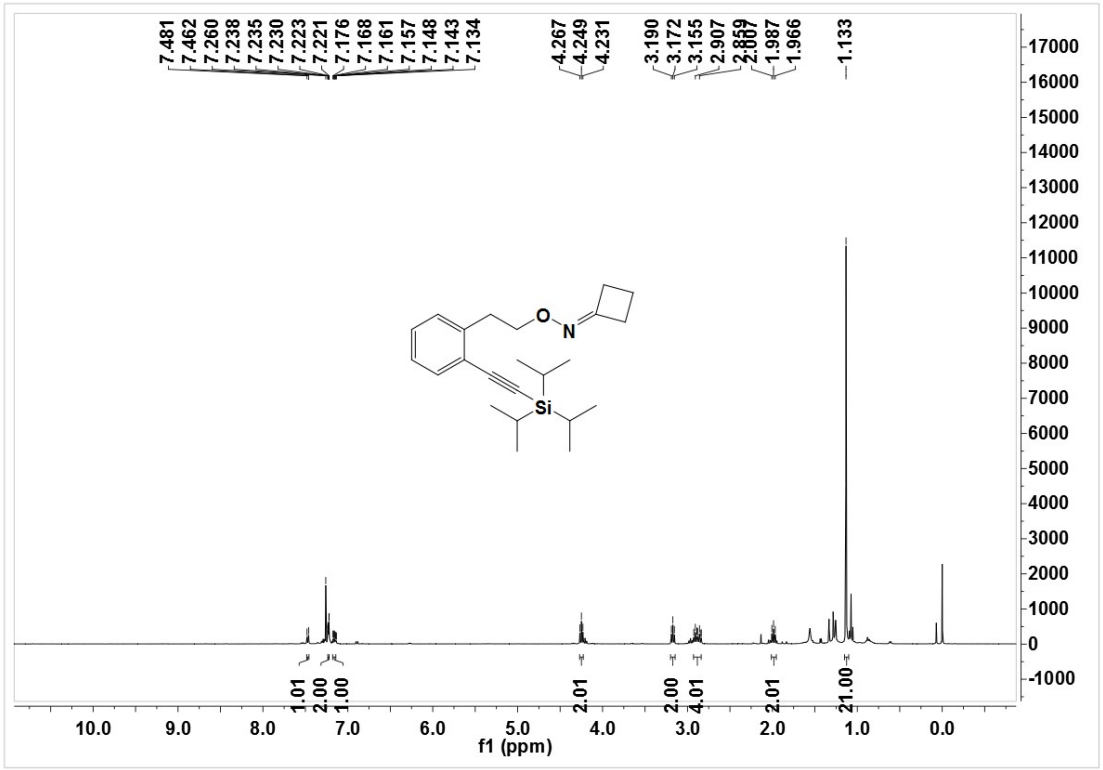


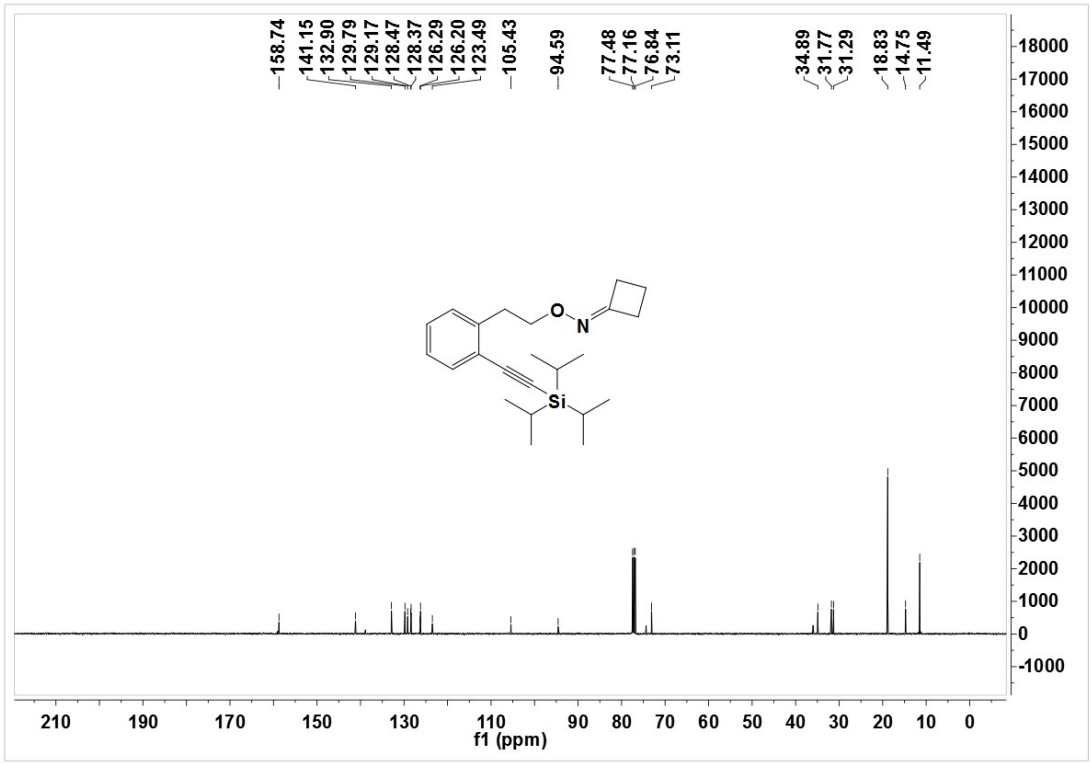
Pentan-3-one *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3c)



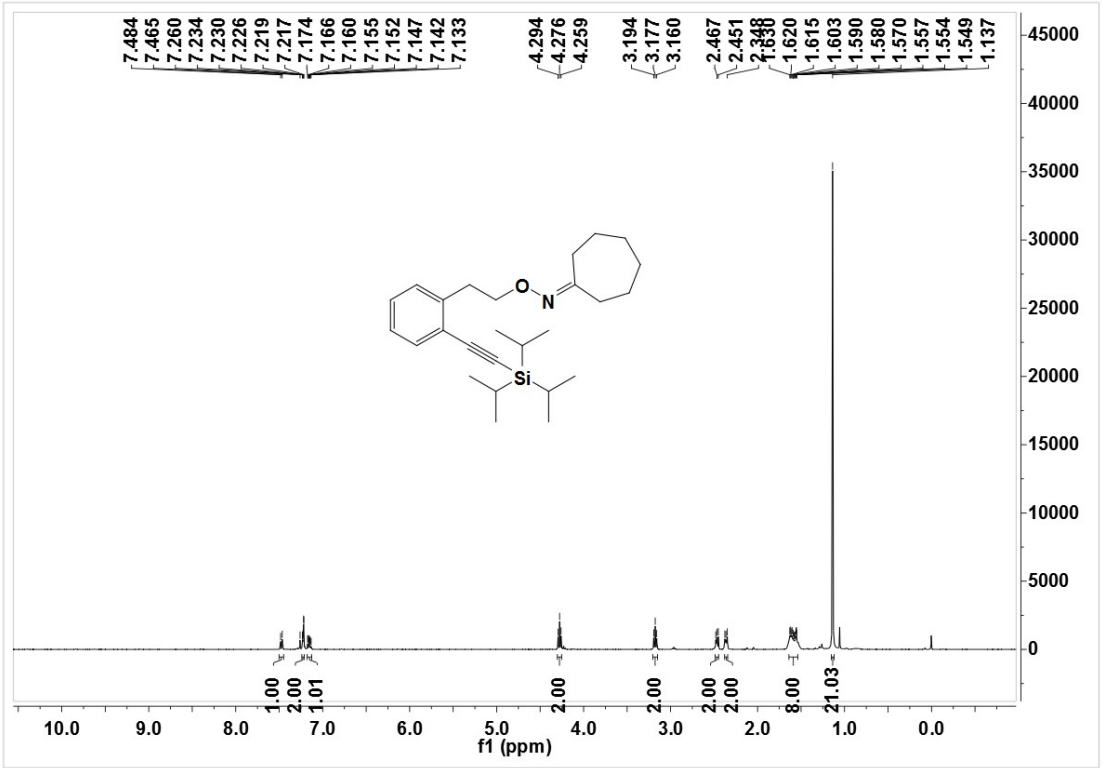


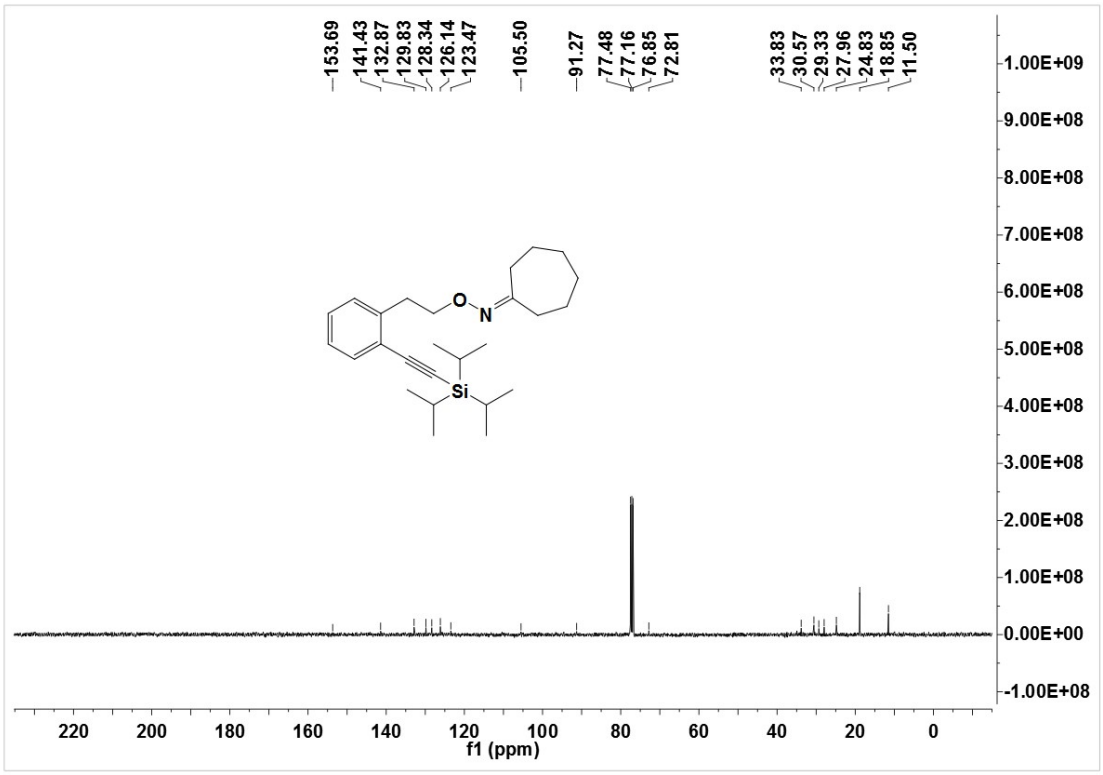
Cyclobutanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3d)



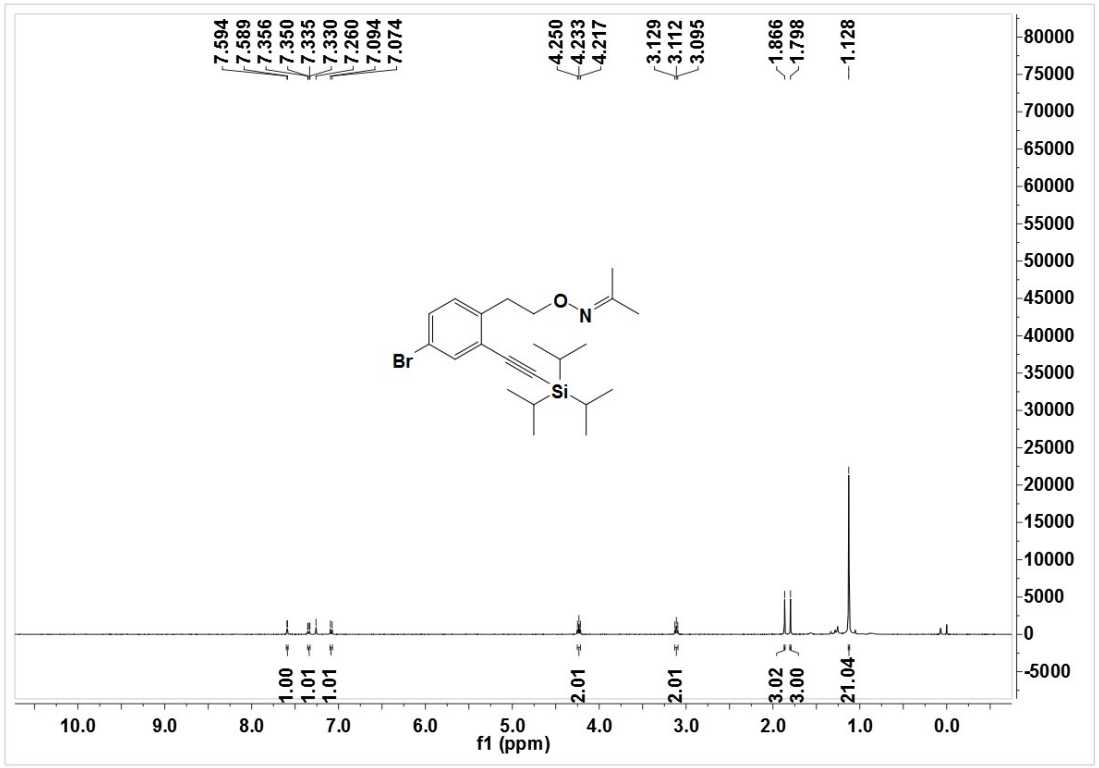


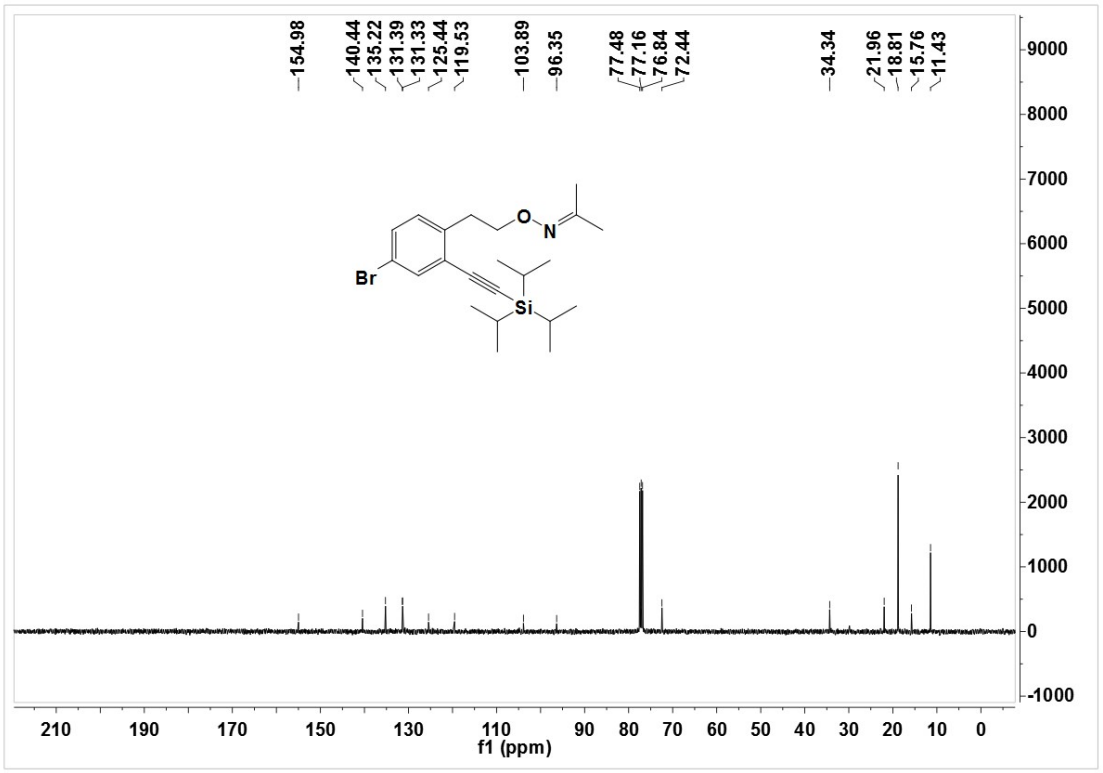
Cycloheptanone *O*-(2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3e)



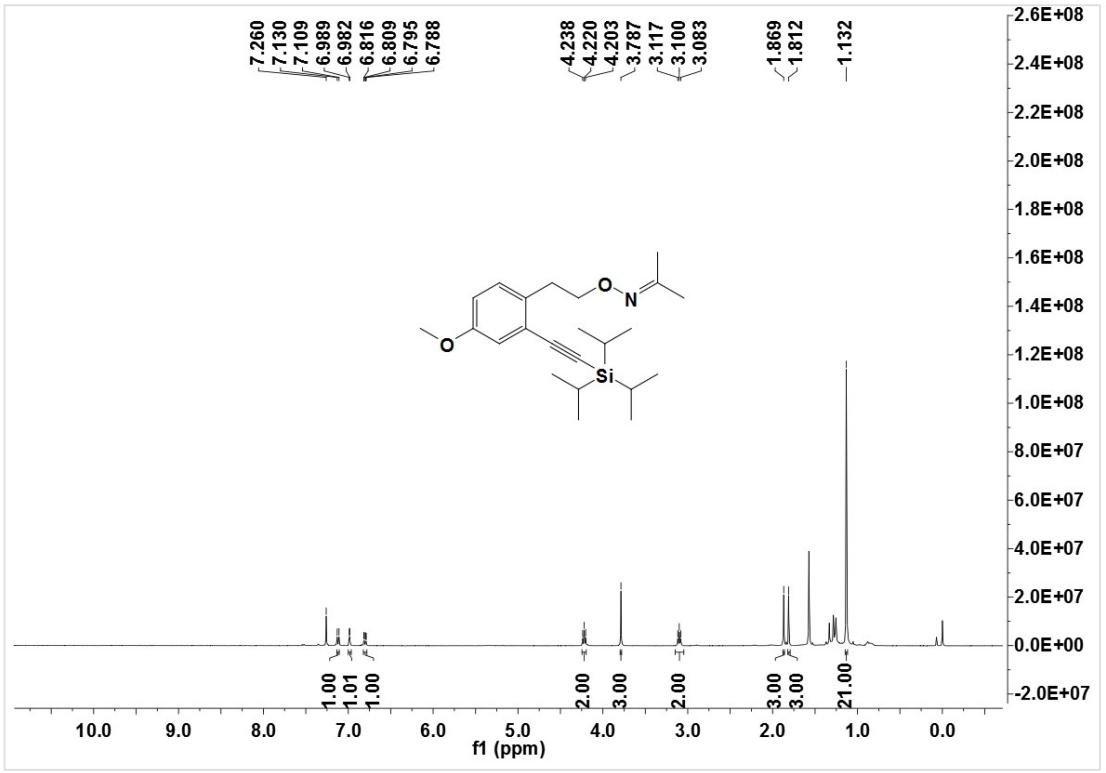


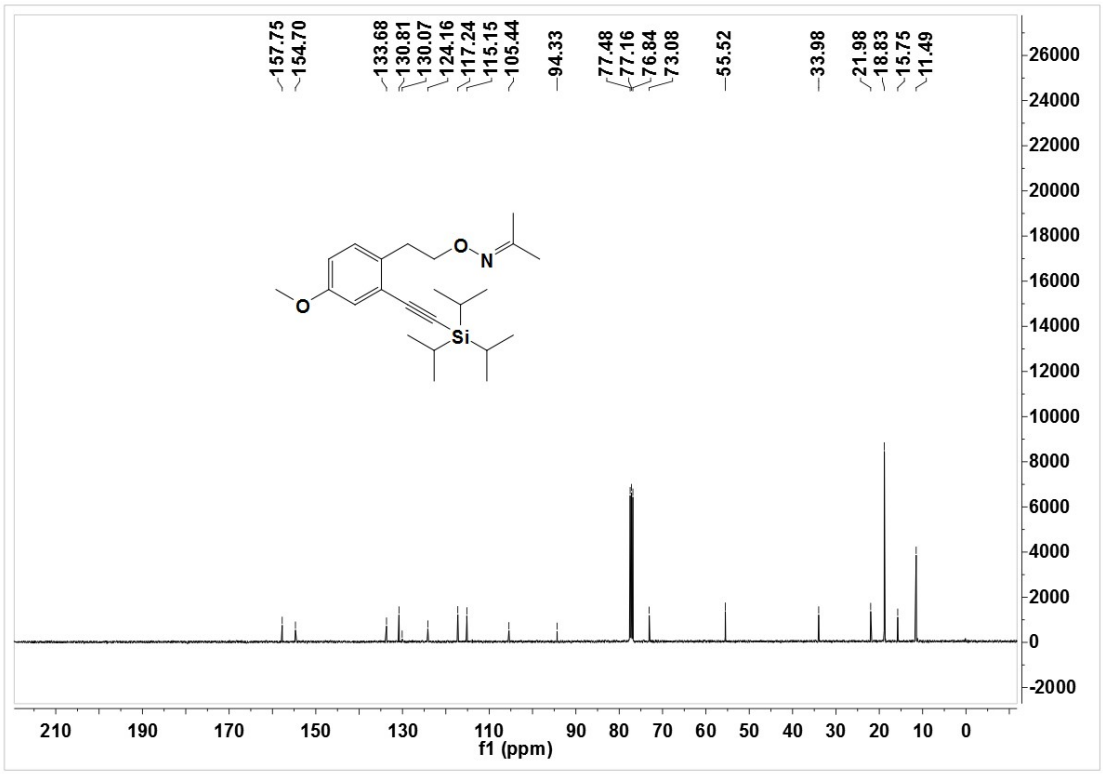
Propan-2-one *O*-(4-bromo-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3f)



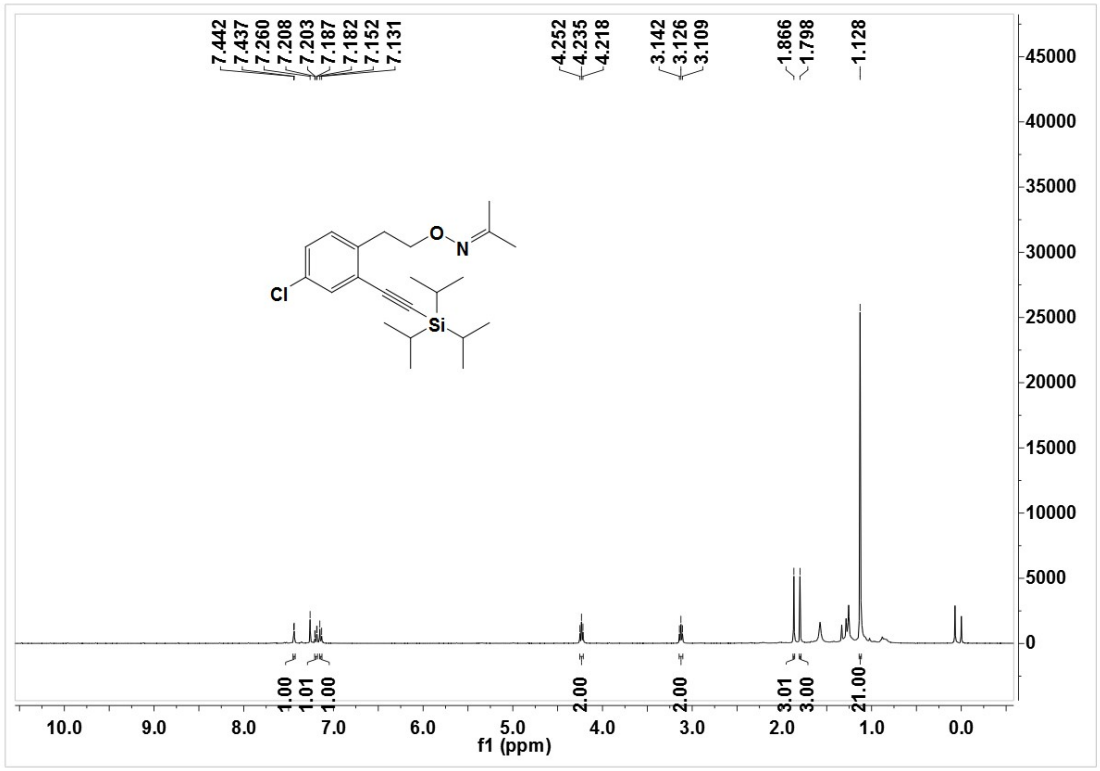


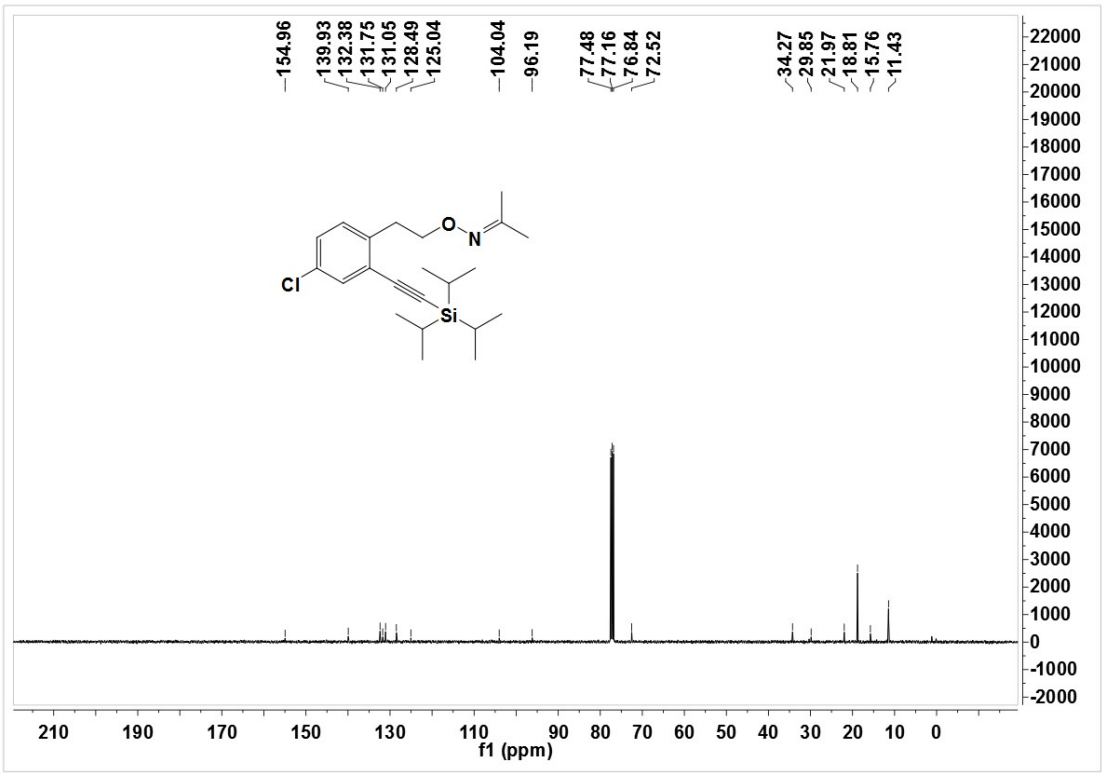
Propan-2-one *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3g)



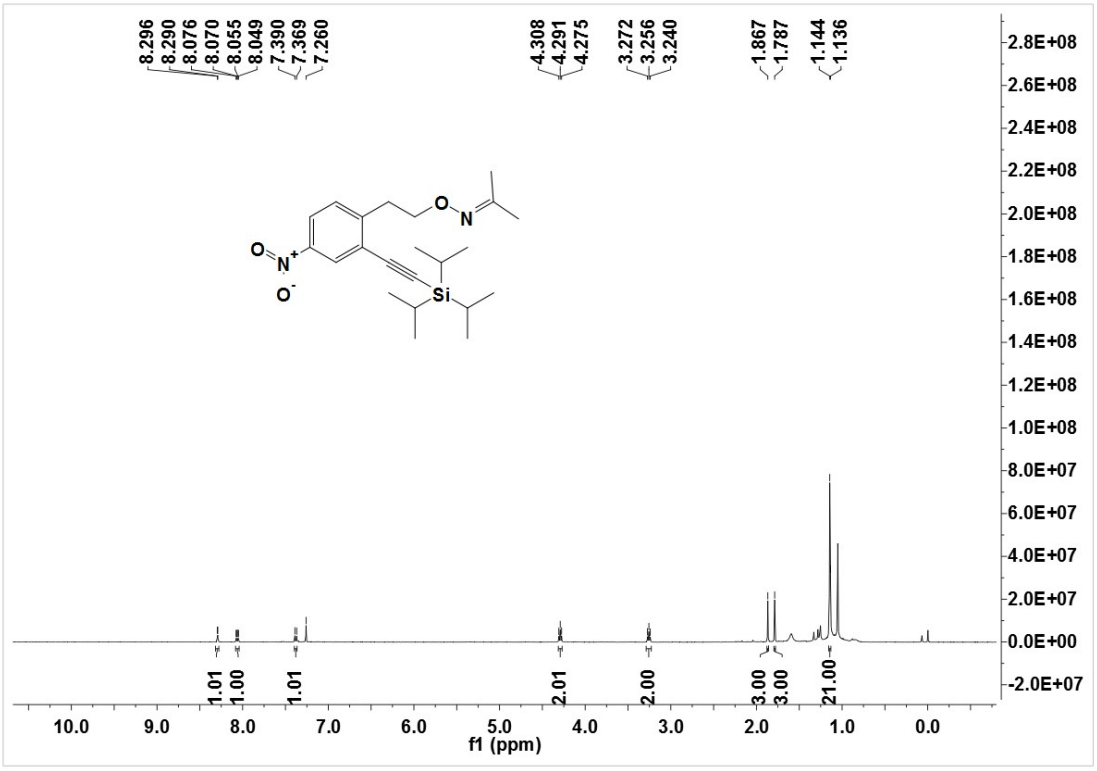


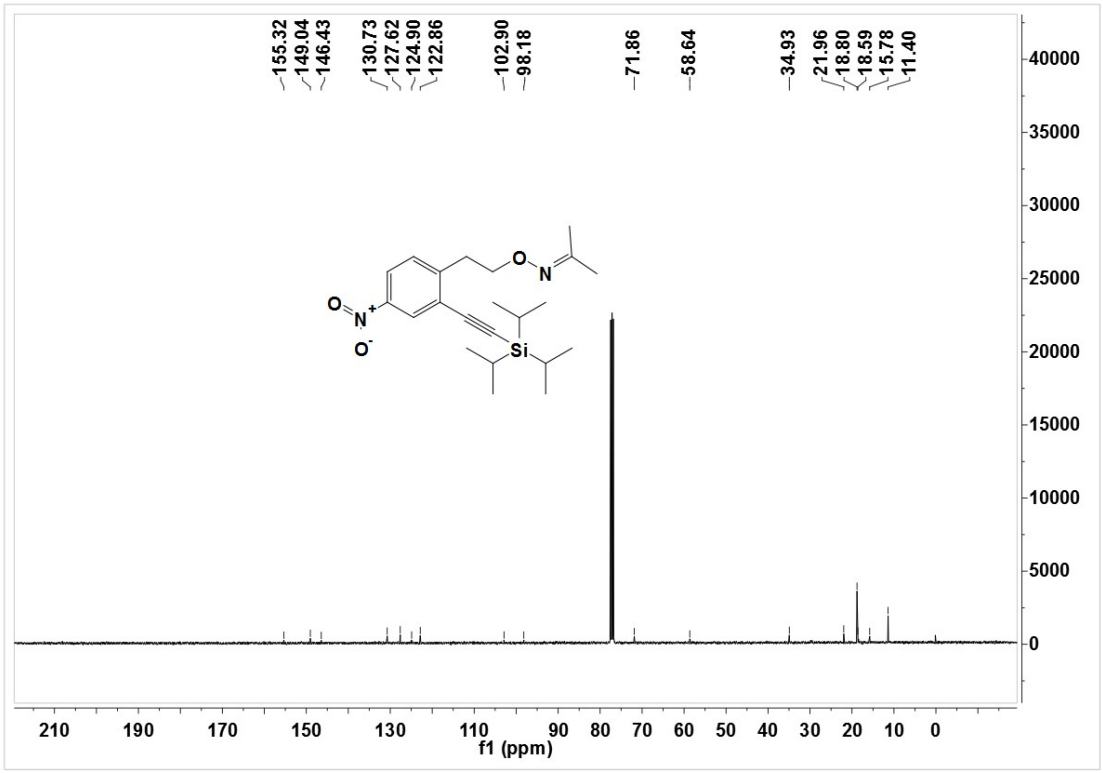
Propan-2-one *O*-(4-chloro-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3h)



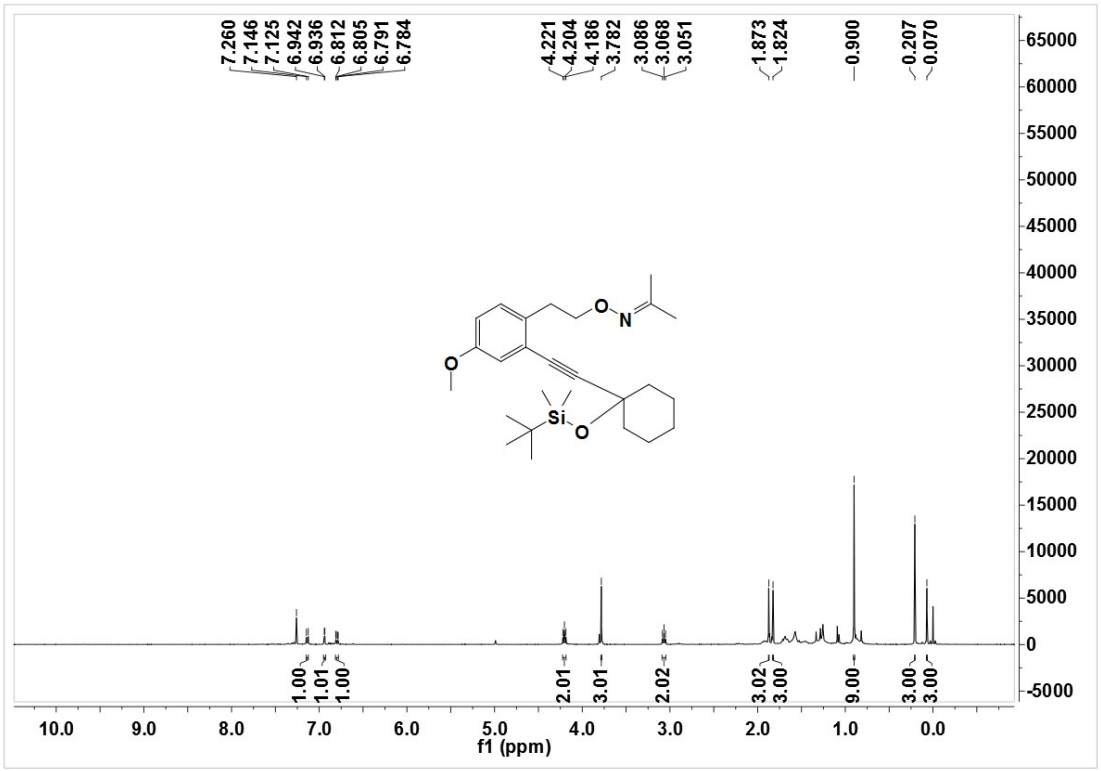


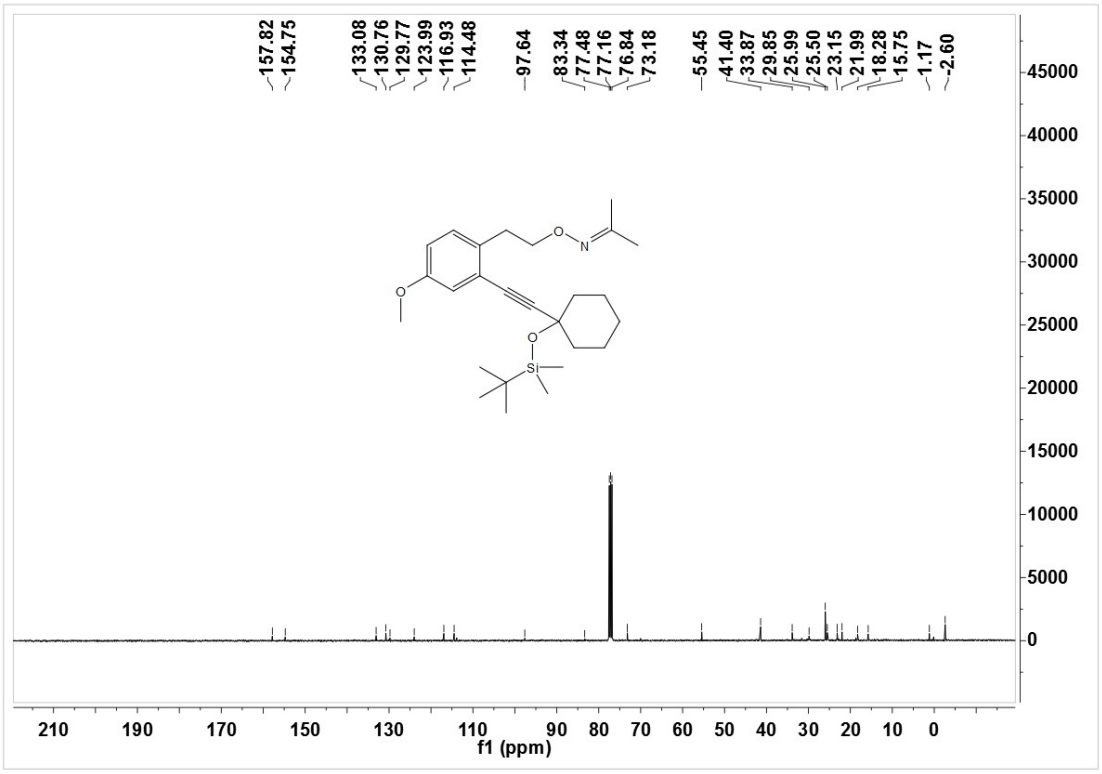
Propan-2-one *O*-(4-nitro-2-((triisopropylsilyl)ethynyl)phenethyl) oxime (3i)



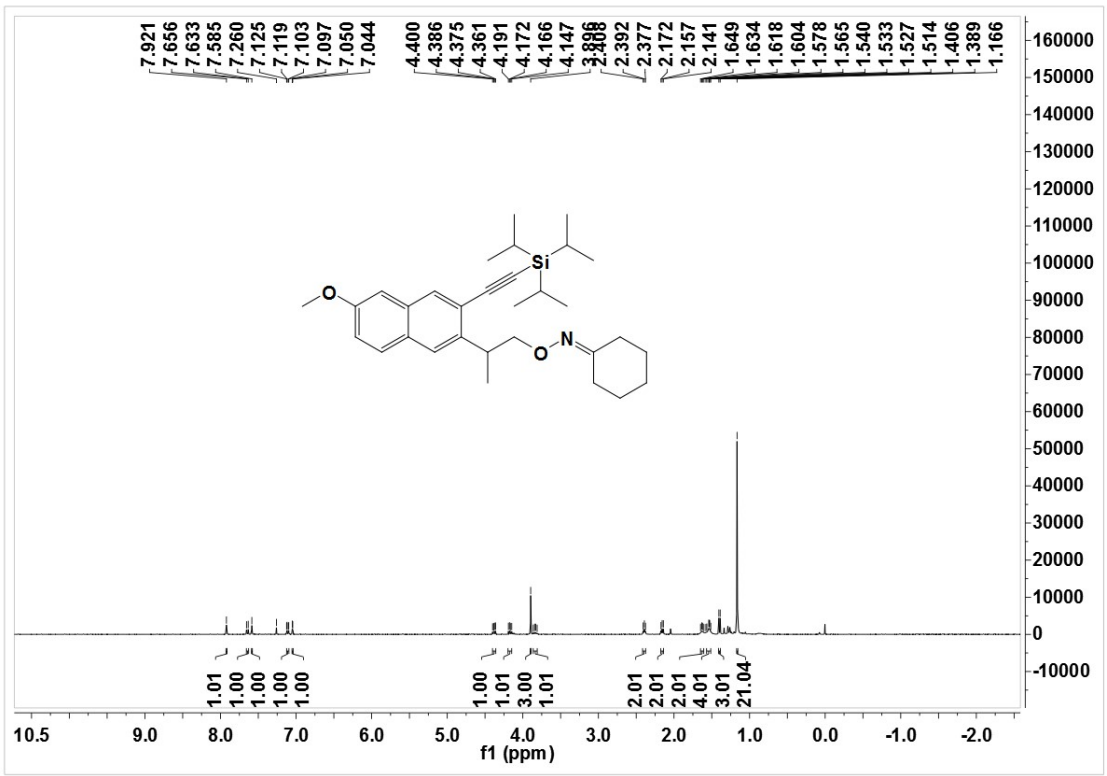


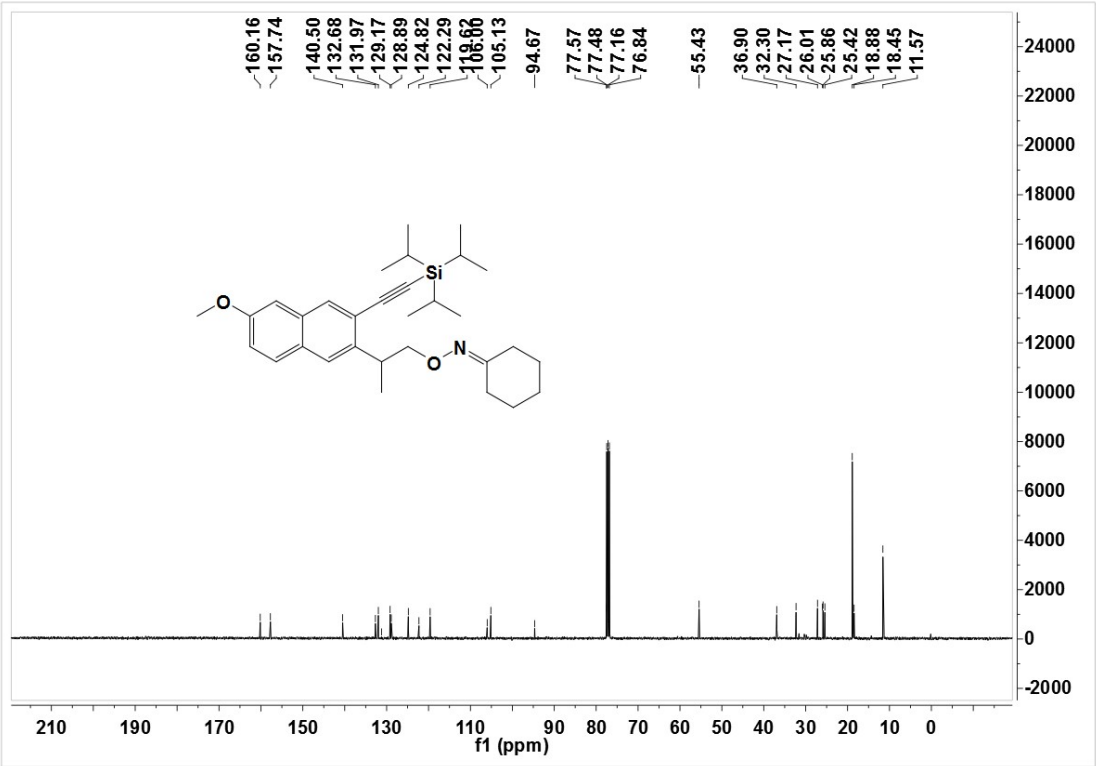
Propan-2-one *O*-(2-((1-((tert-butyldimethylsilyl) oxy) cyclohexyl) ethynyl) -4-methoxyphenethyl) oxime (3j)



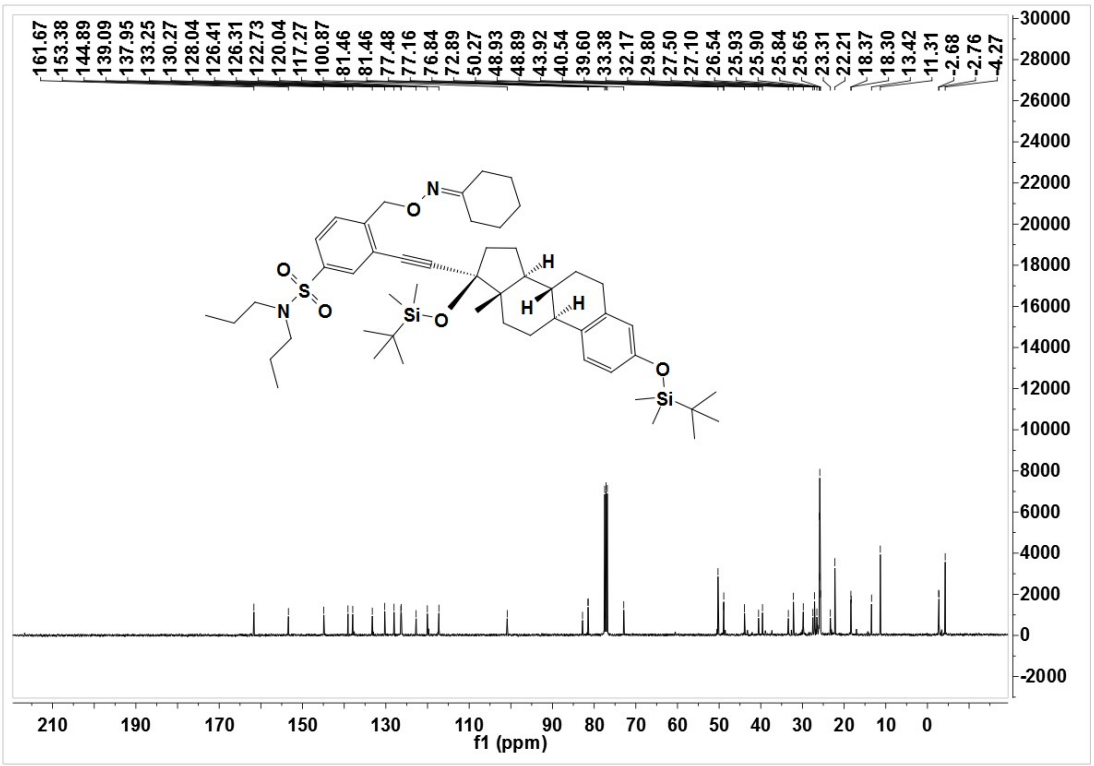


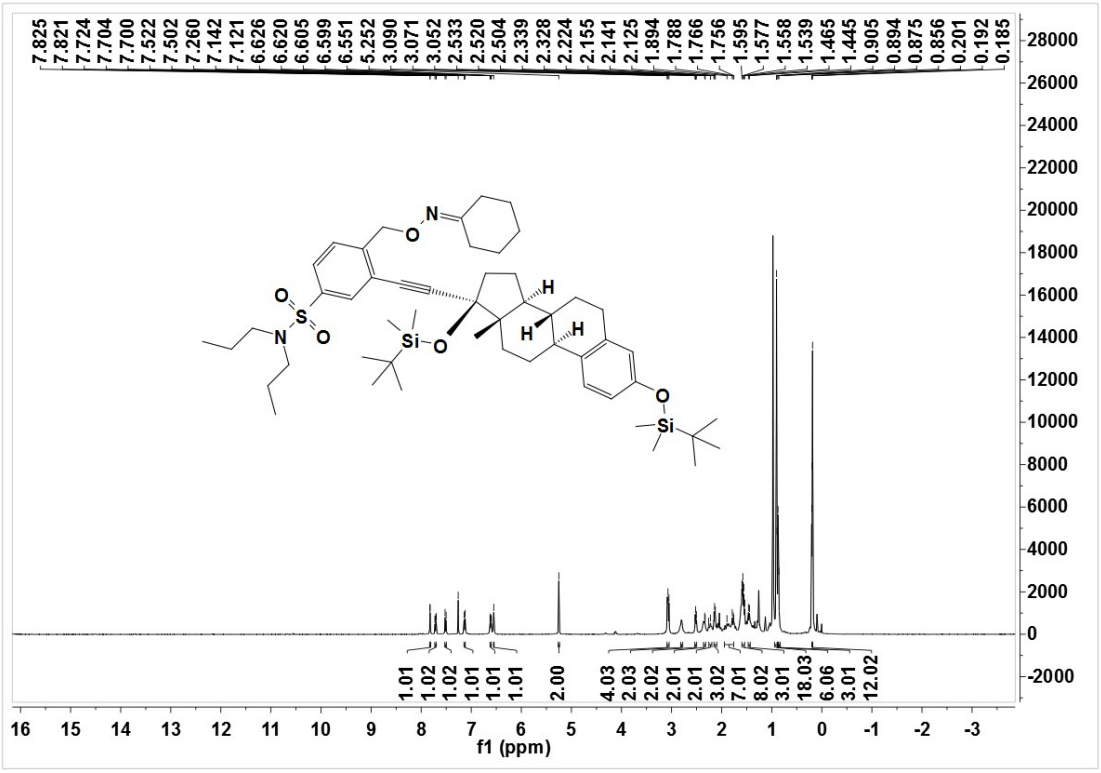
Cyclohexanone *O*-(2-(6-methoxy-3-((triisopropylsilyl)ethynyl) naphthalen-2-yl) propyl) oxime (3k)



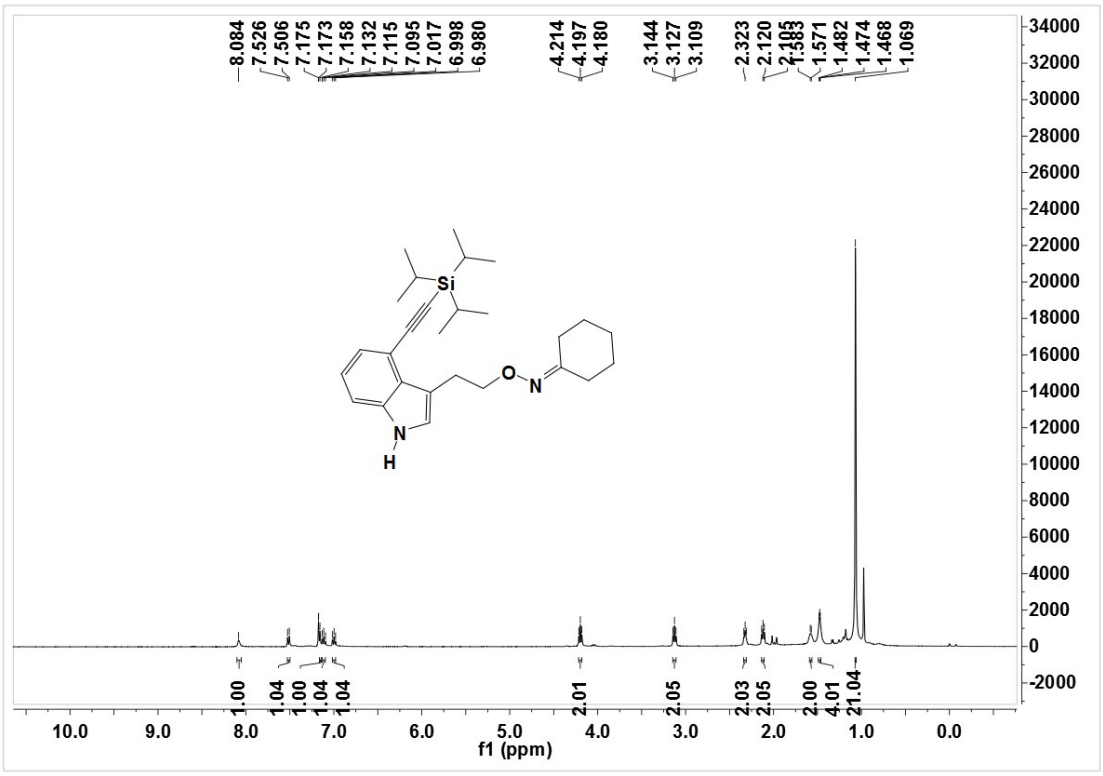


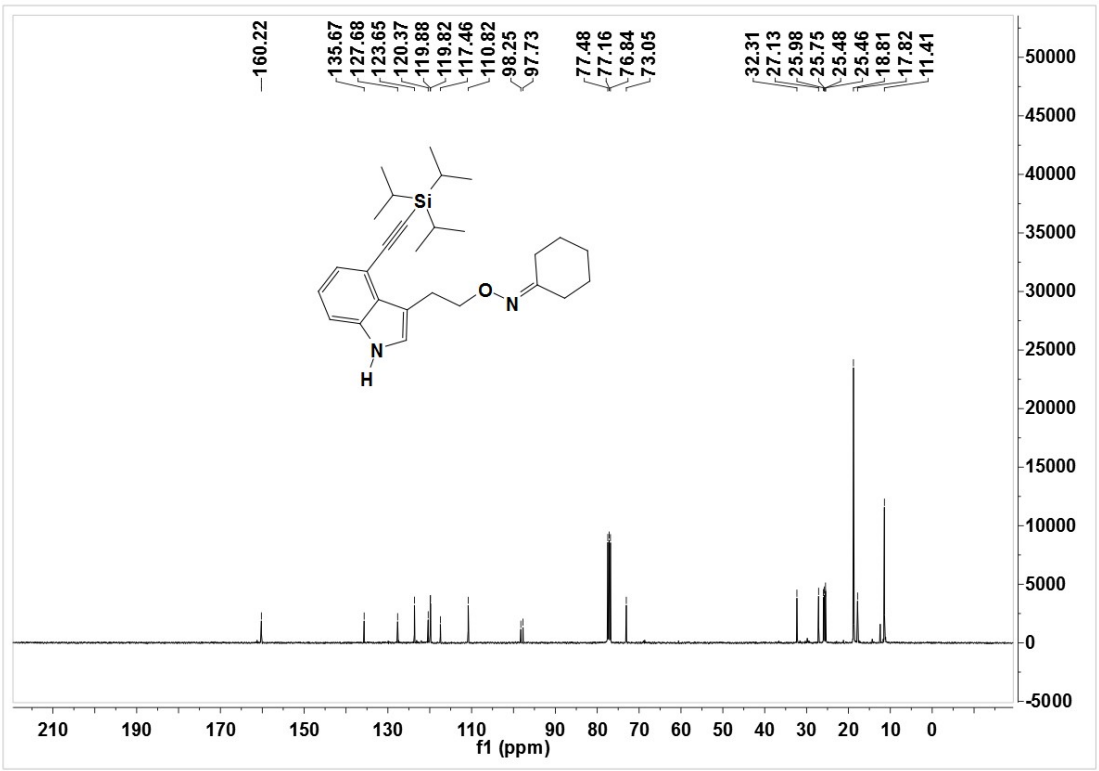
3-(((8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-Bis((tert-butyldimethylsilyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-yl)ethynyl)-4-(((cyclohexylideneamino)oxy)methyl)-N,N-dipropylbenzenesulfonamide (5n)



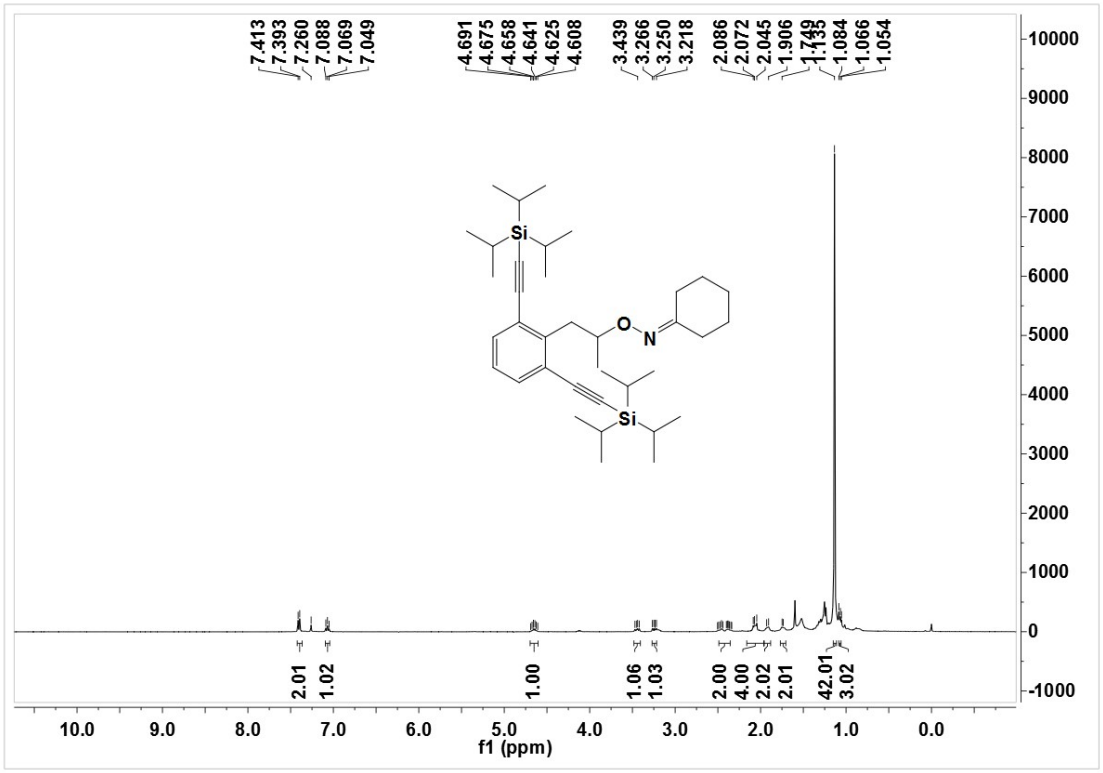


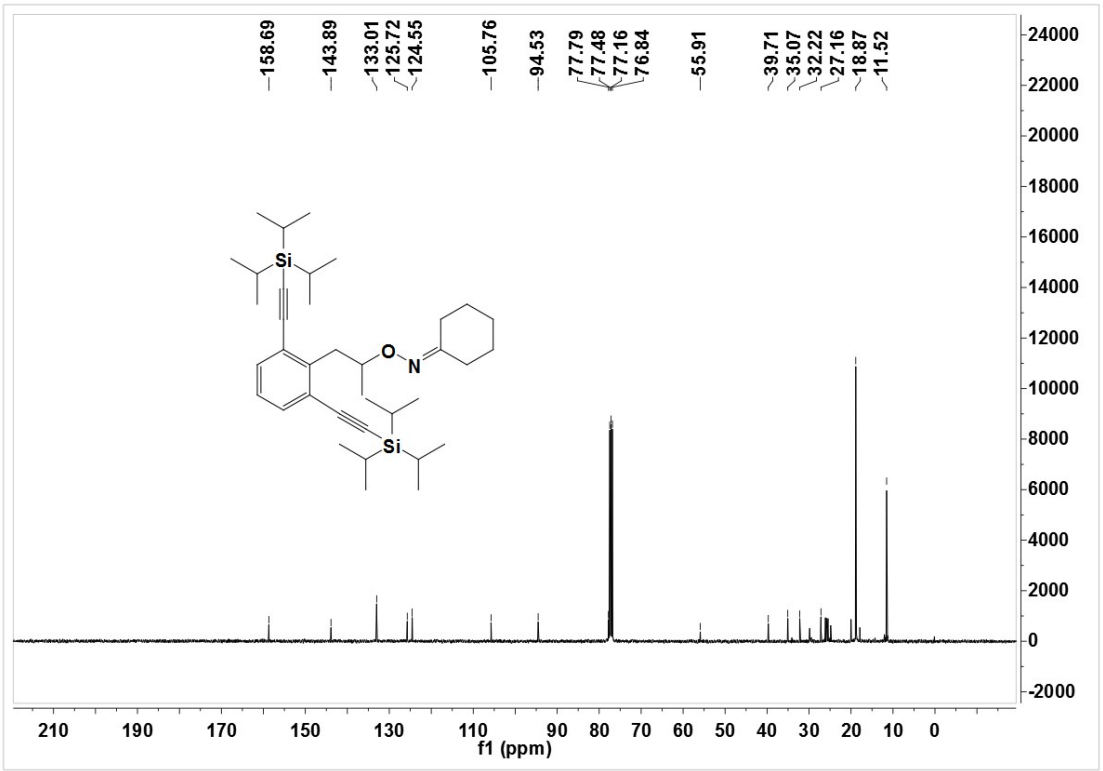
Cyclohexanone *O*-(1-(2,6-bis((triisopropylsilyl)ethynyl)phenyl)propan-2-yl) oxime (3l)



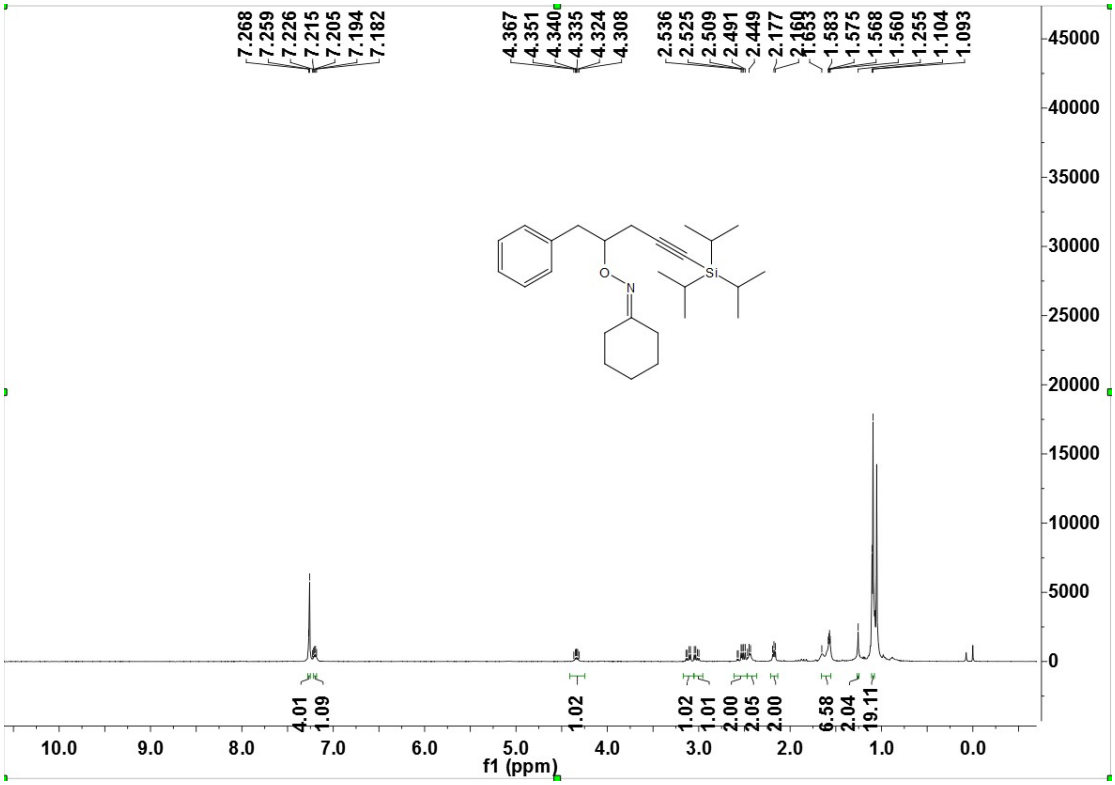


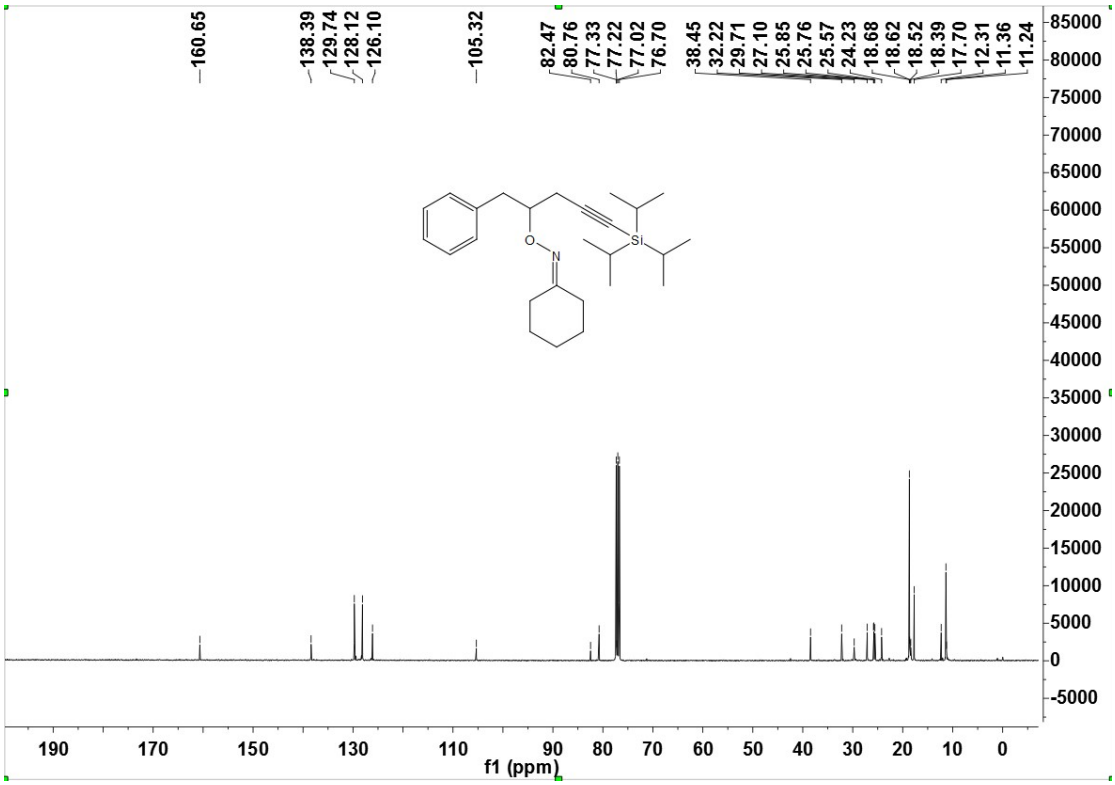
Cyclohexanone *O*-(2-(4-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)ethyl) oxime (3m)



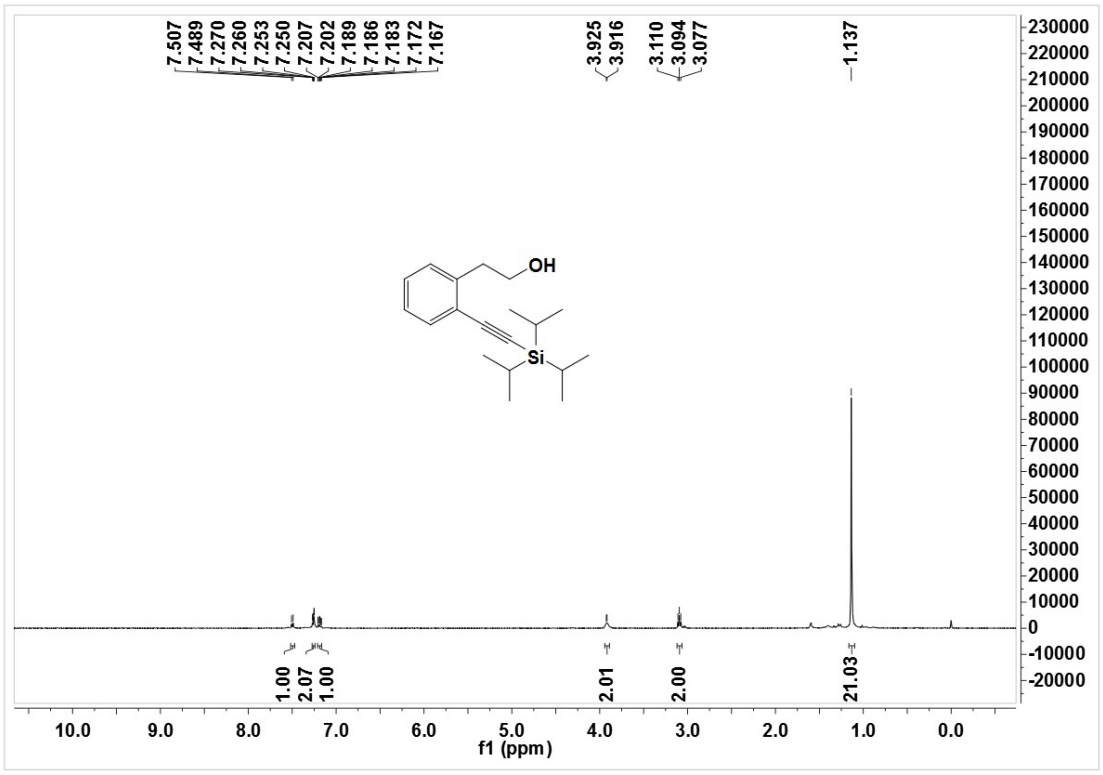


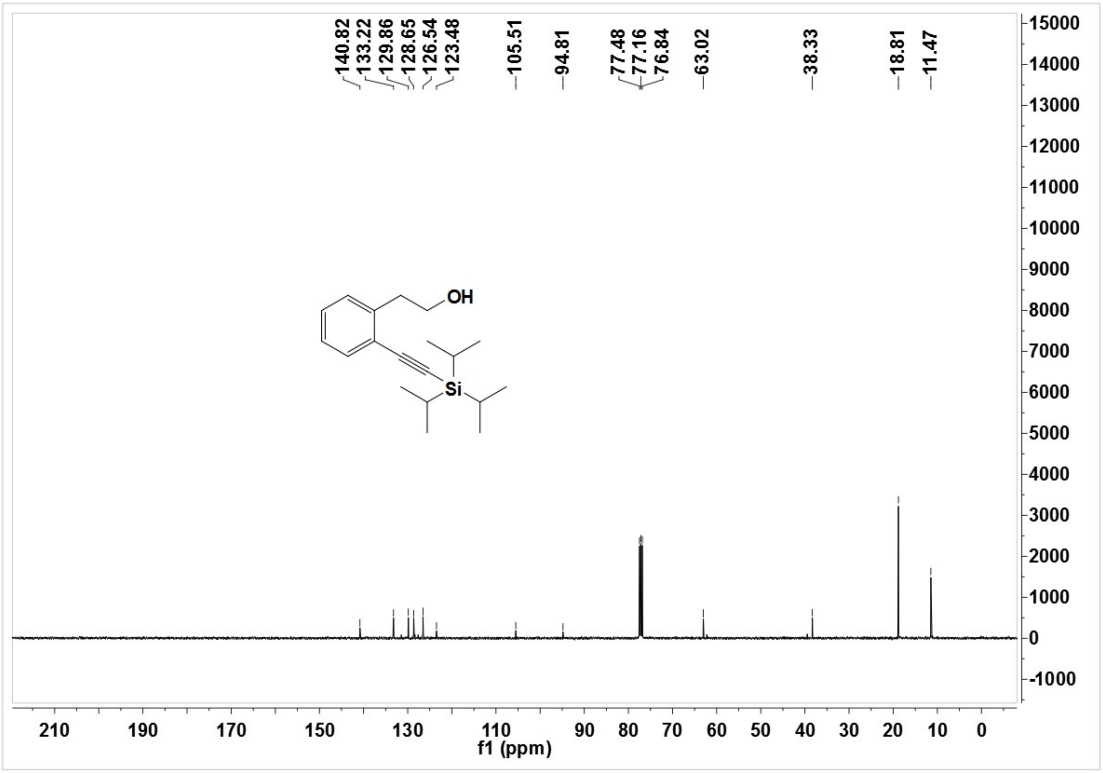
Cyclohexanone *O*-(1-phenyl-5-(triisopropylsilyl)pent-4-yn-2-yl) oxime (3m')



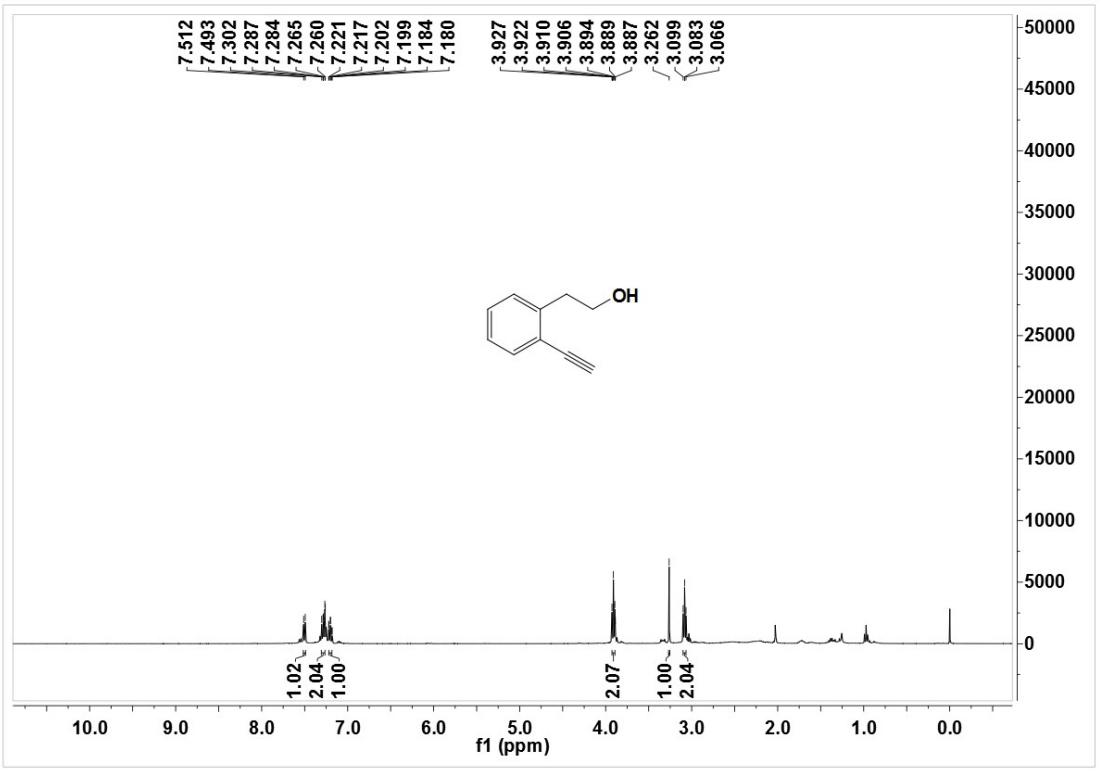


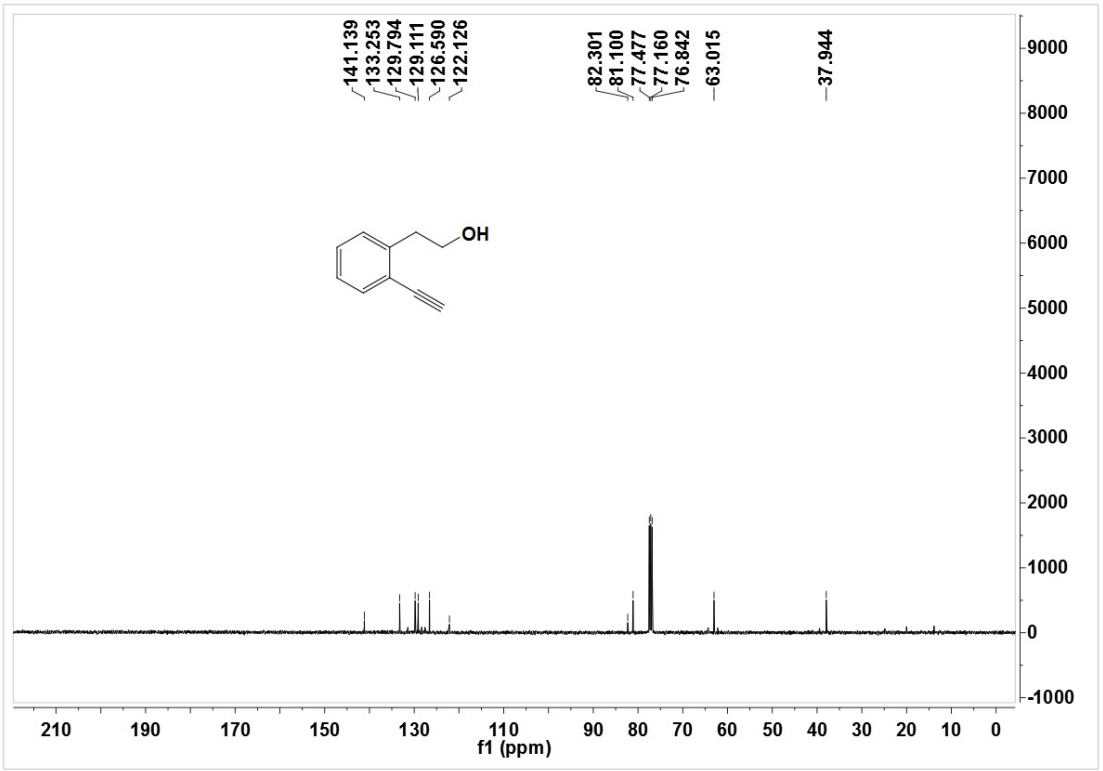
2-(2-((Triisopropylsilyl)ethynyl)phenyl)ethan-1-ol (3a-1)



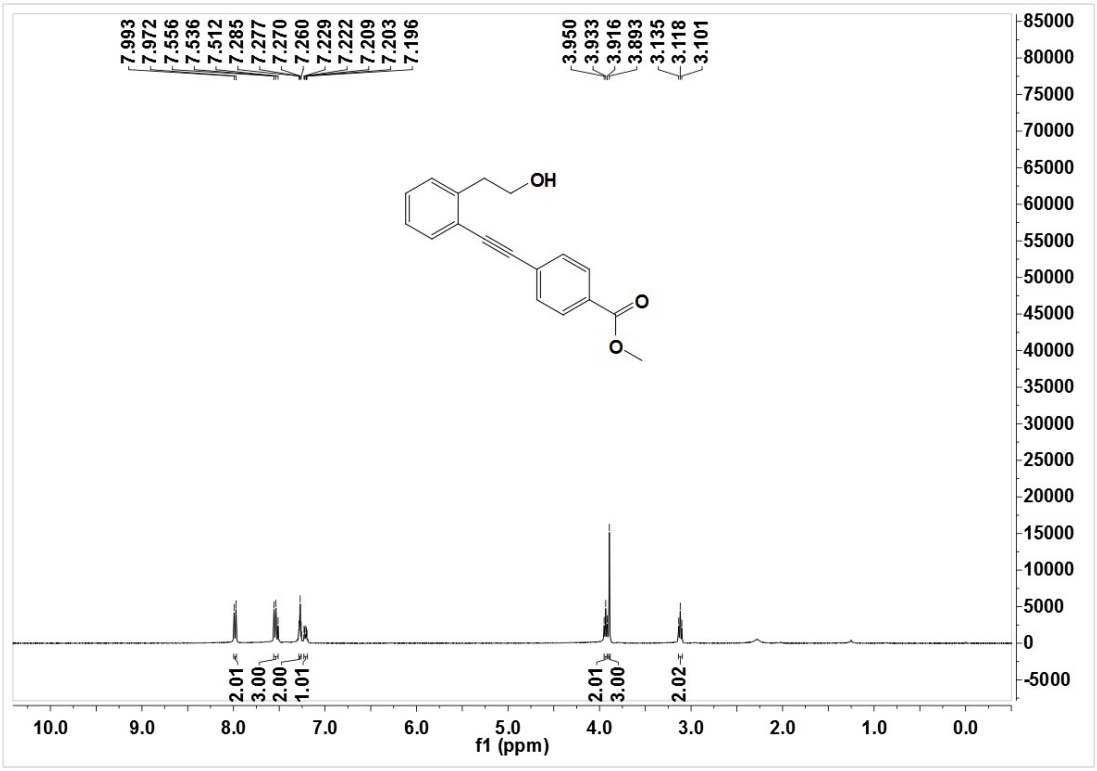


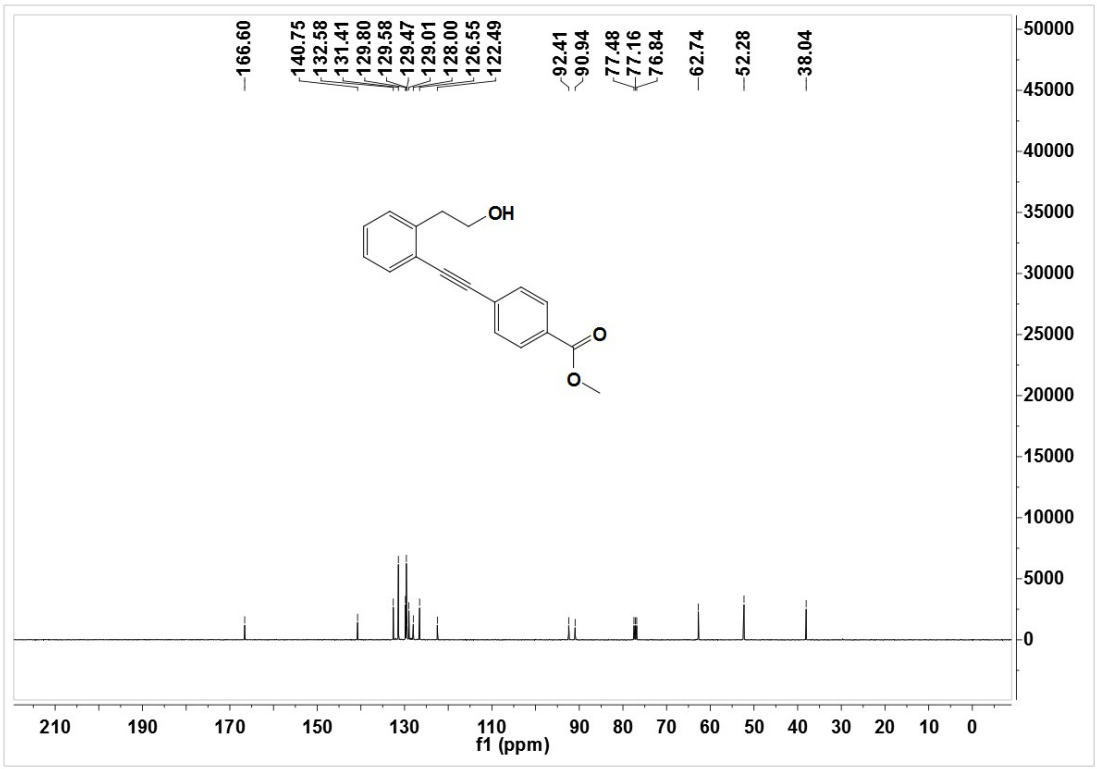
2-(2-Ethynylphenyl)ethan-1-ol (3a-2)



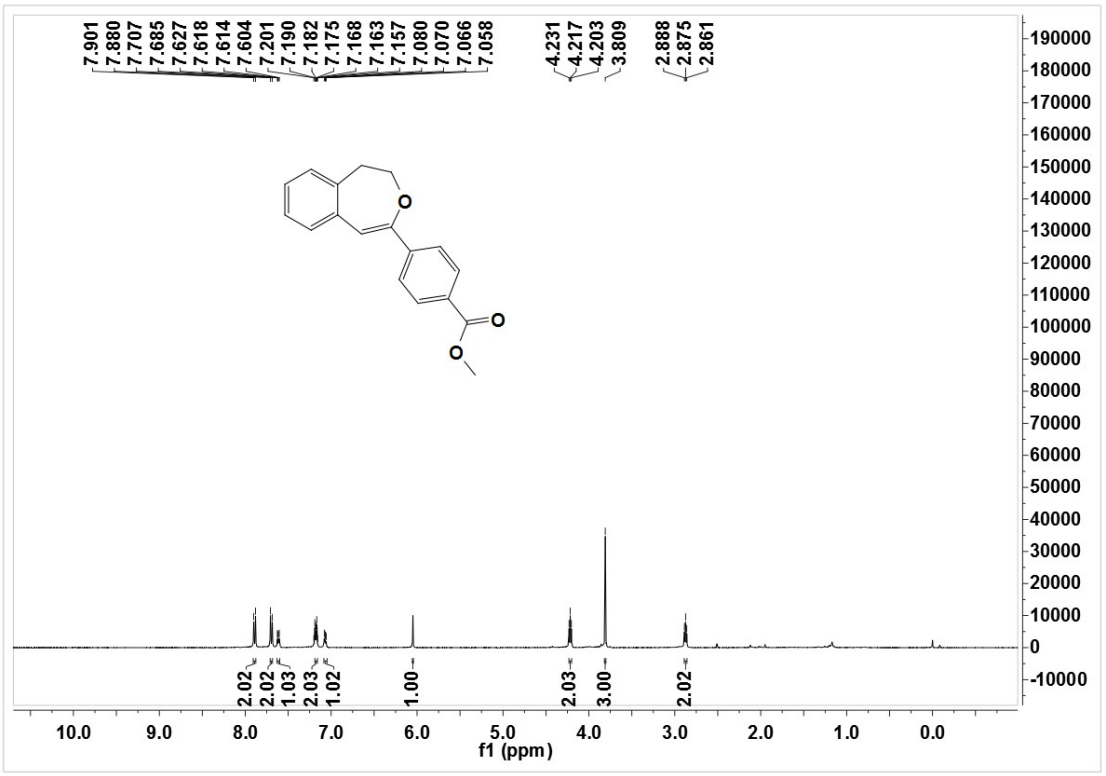


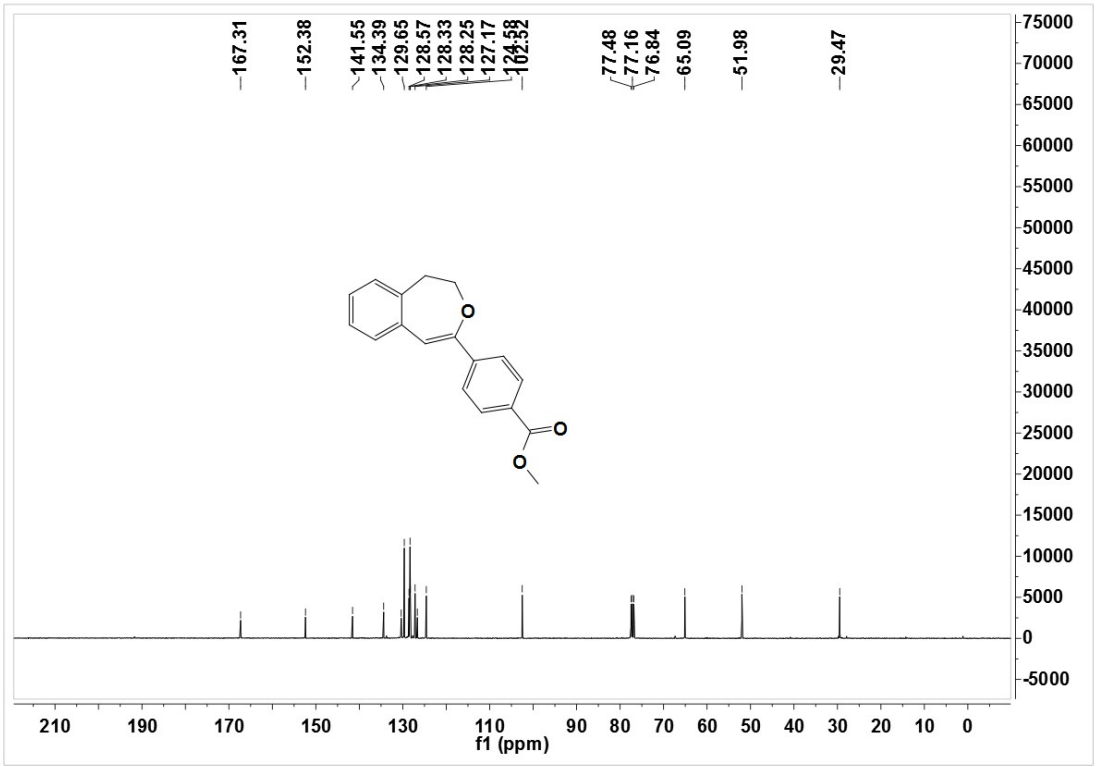
Methyl 4-((2-(2-hydroxyethyl)phenyl)ethynyl)benzoate (3a-3)



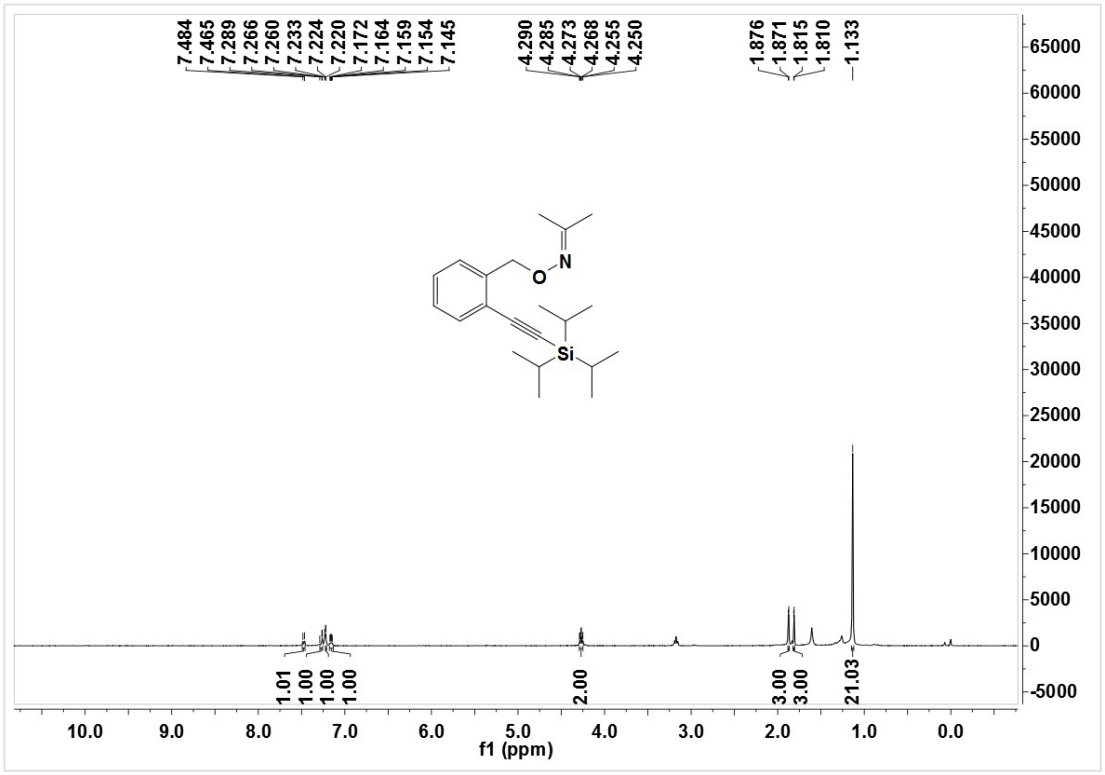


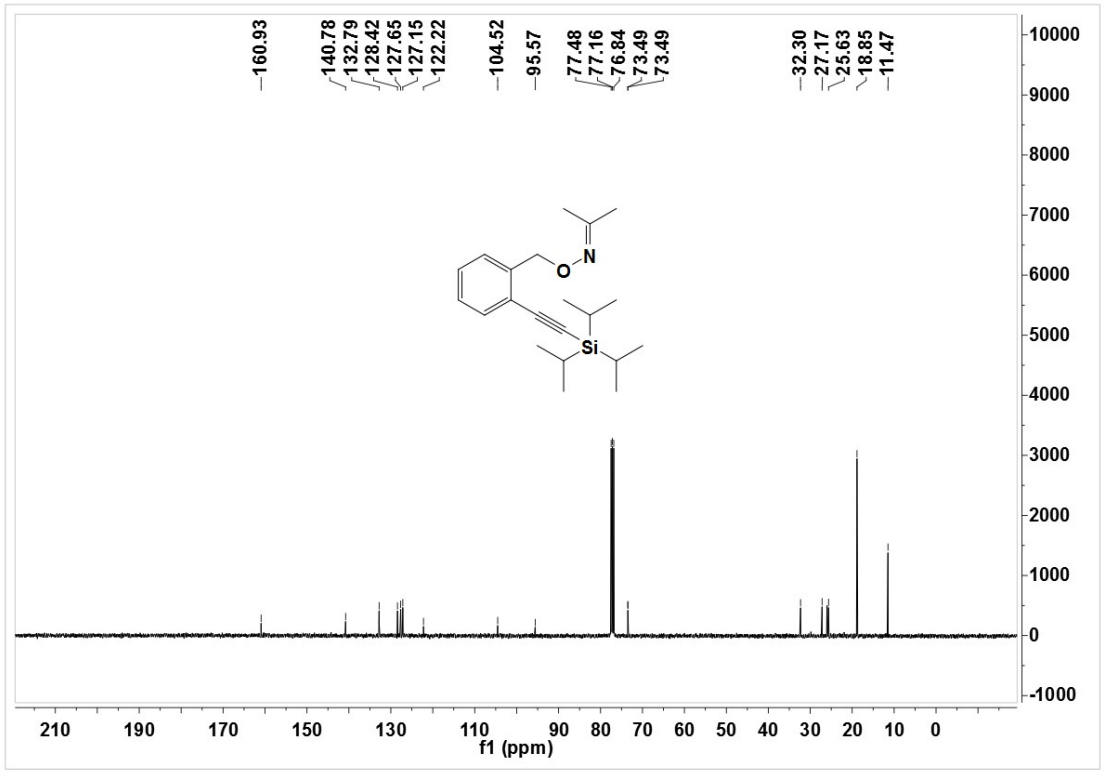
Methyl 4-(4,5-dihydrobenzo[d]oxepin-2-yl)benzoate (3a-4)



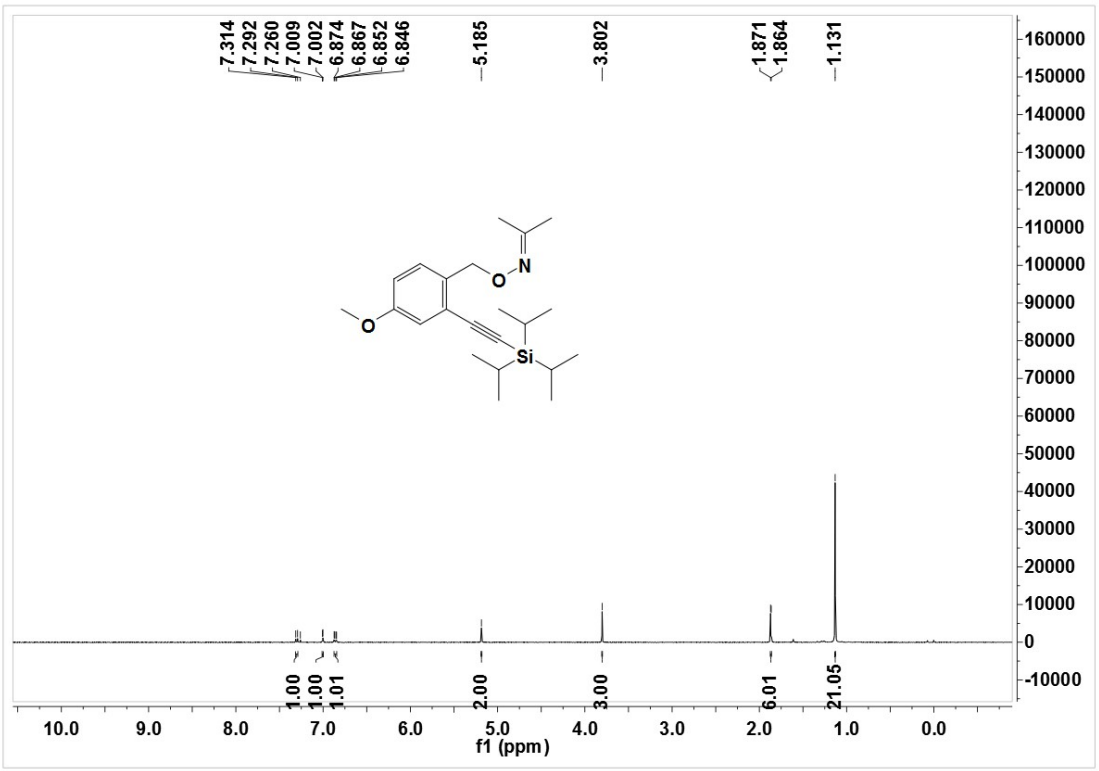


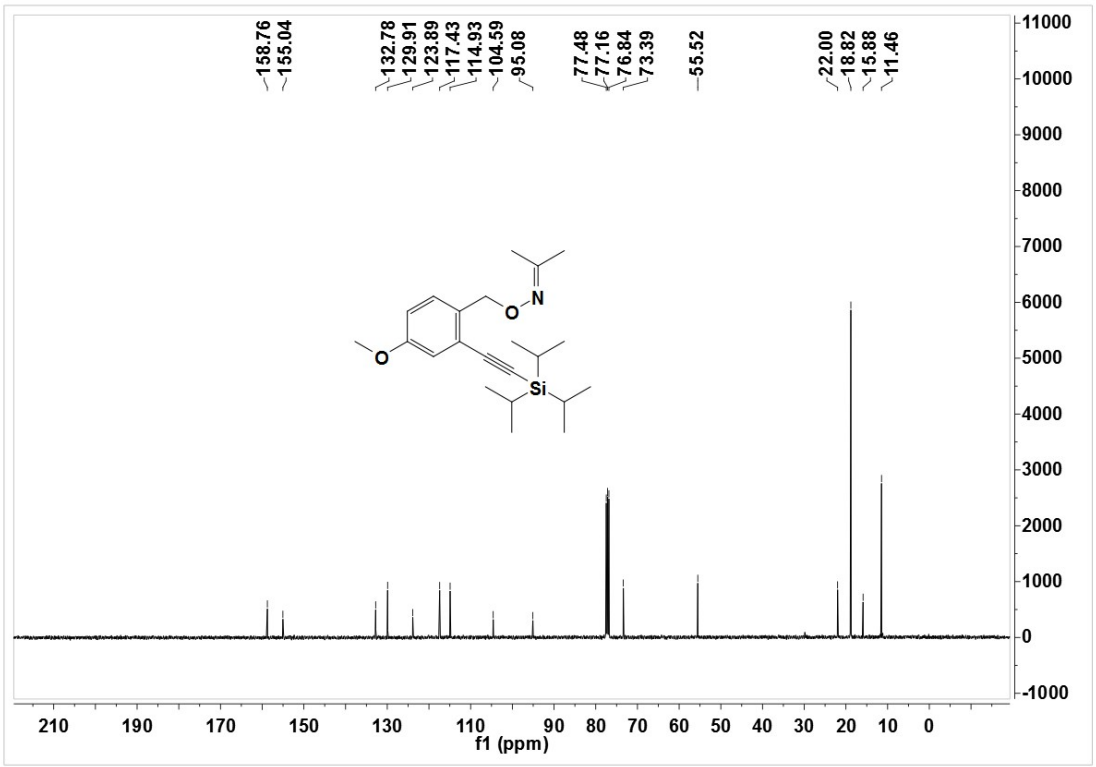
Propan-2-one *O*-(2-((triisopropylsilyl)ethynyl)benzyl) oxime (5a)



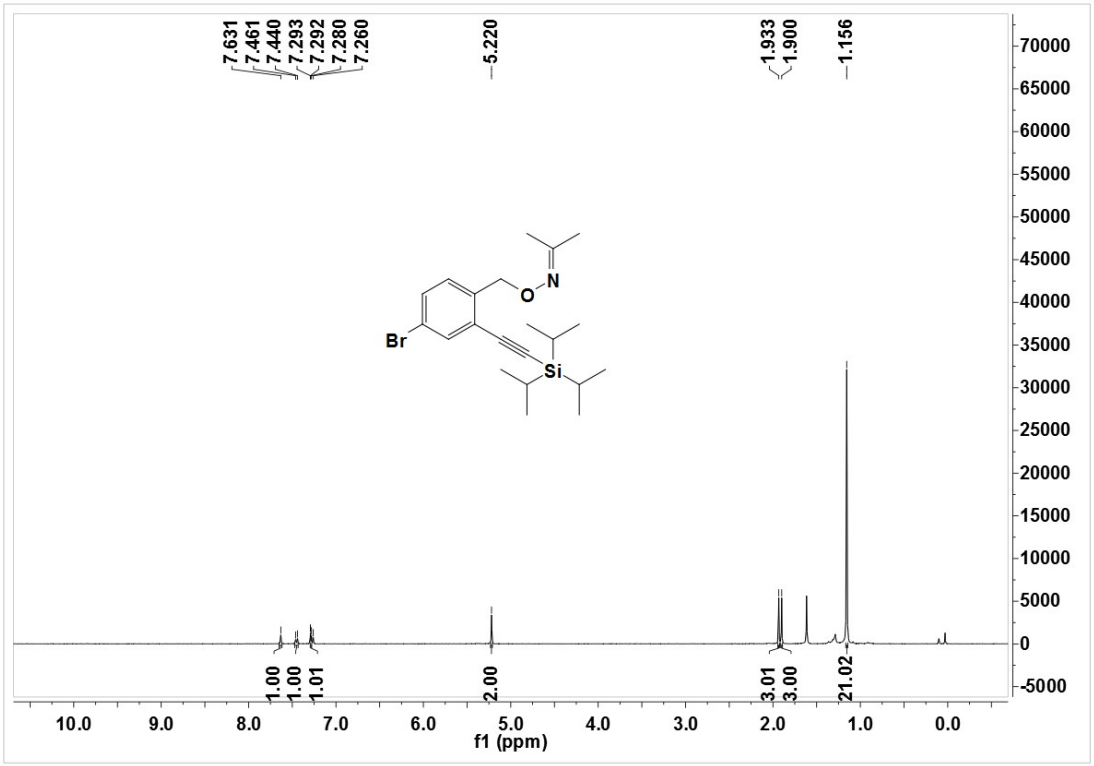


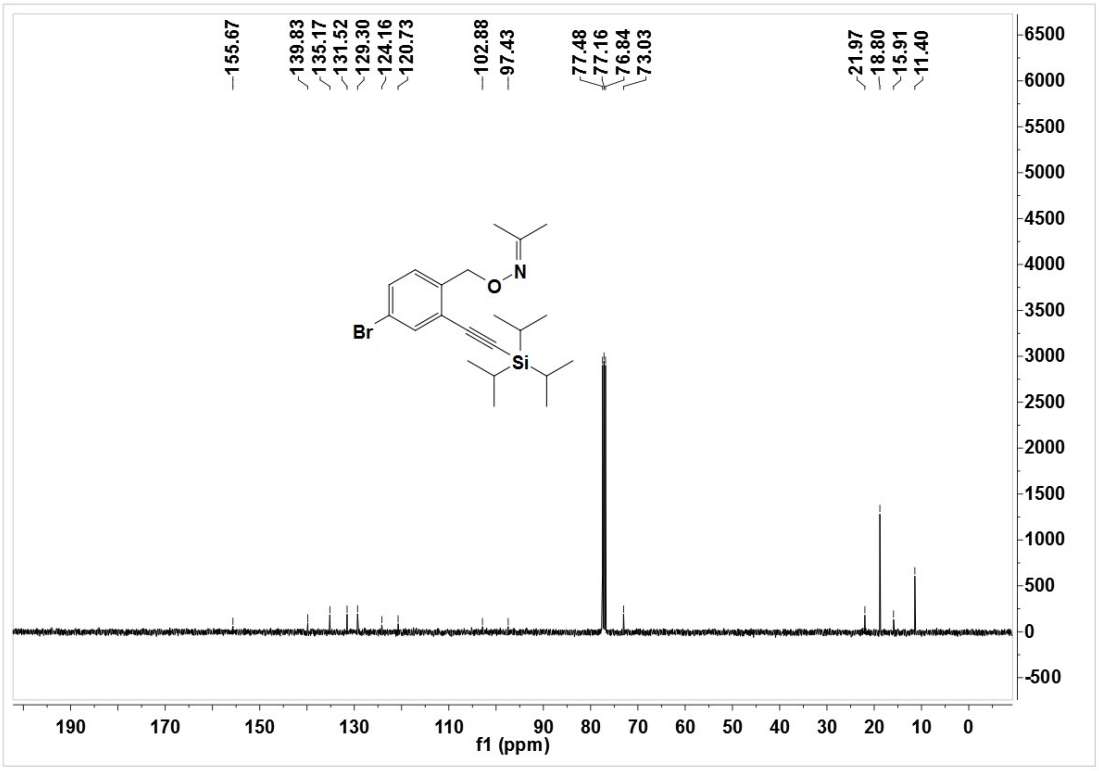
Propan-2-one *O*-(4-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5b)



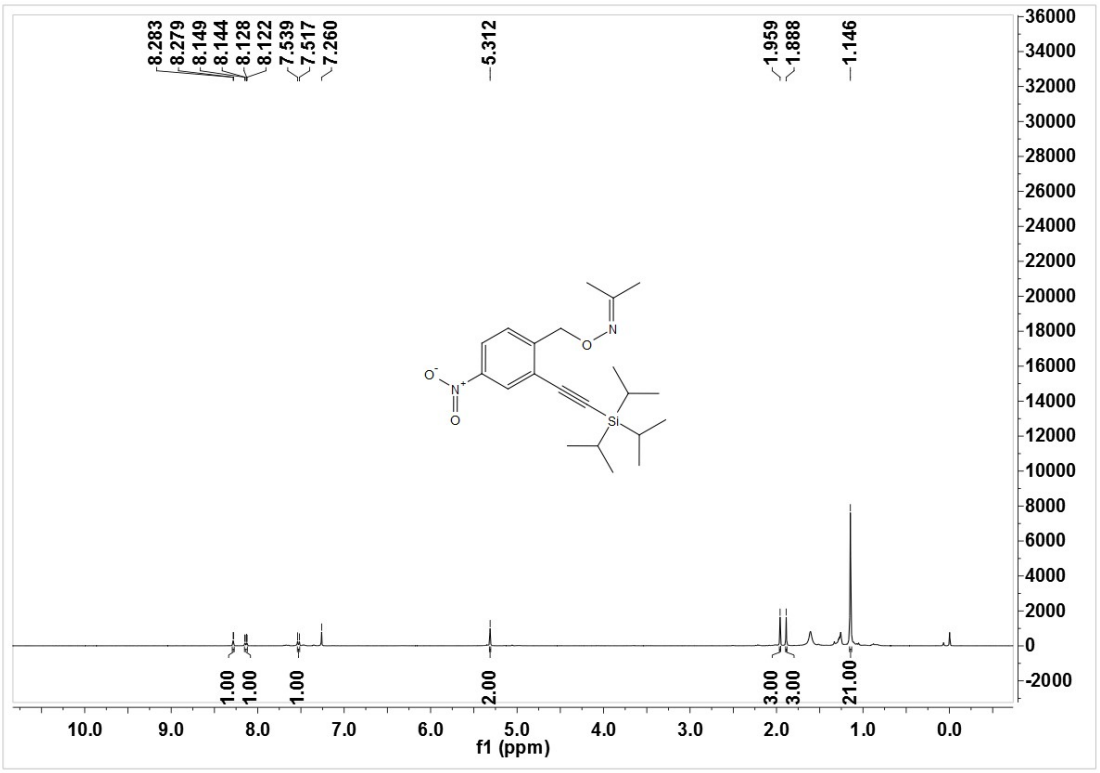


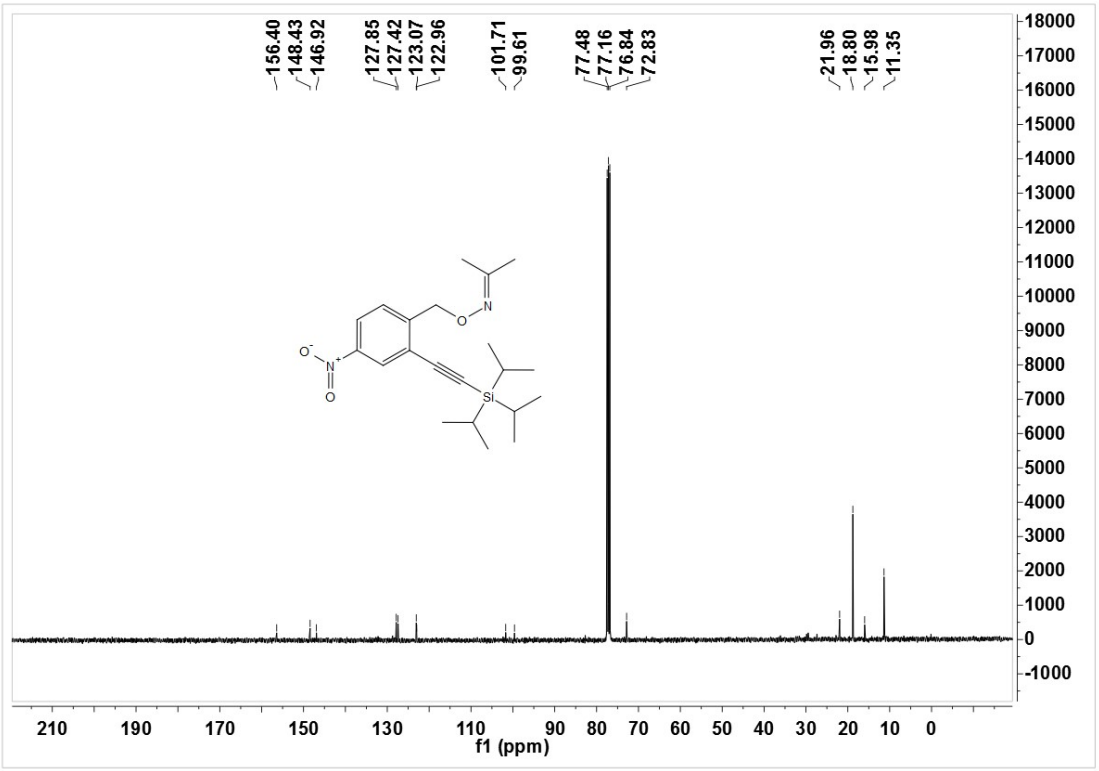
Propan-2-one *O*-(4-bromo-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5c)



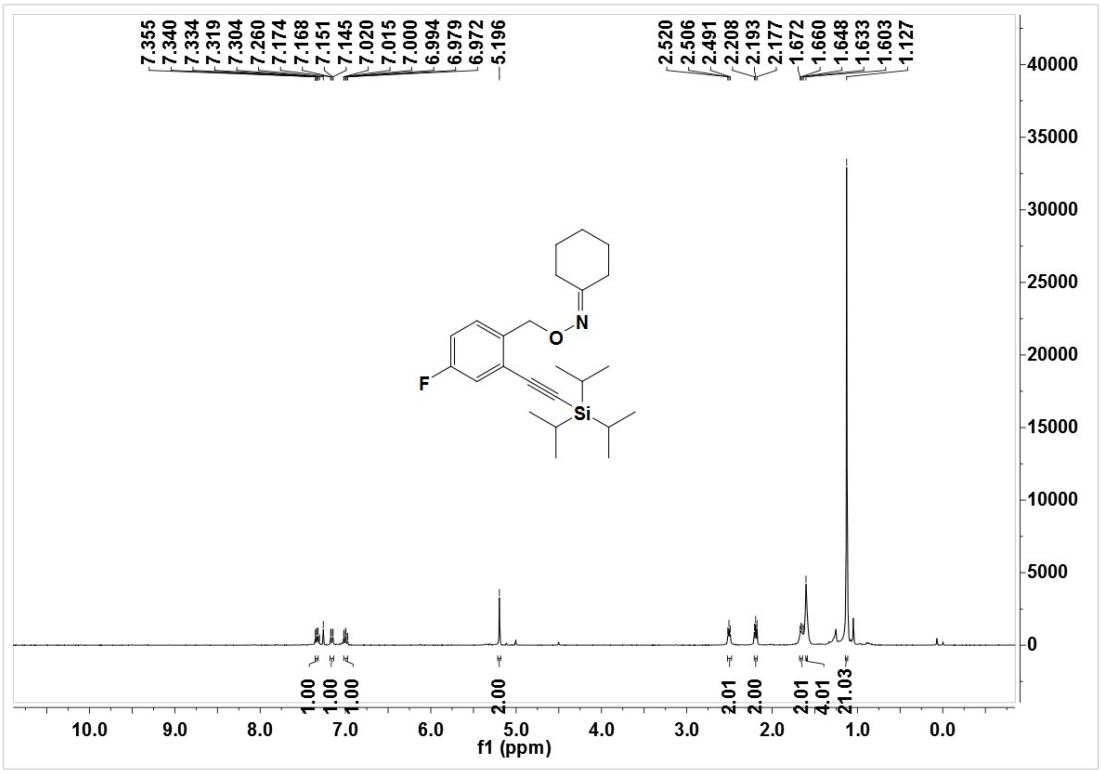


Propan-2-one-*O*-(4-nitro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5d)





Cyclohexanone *O*-(4-fluoro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5e)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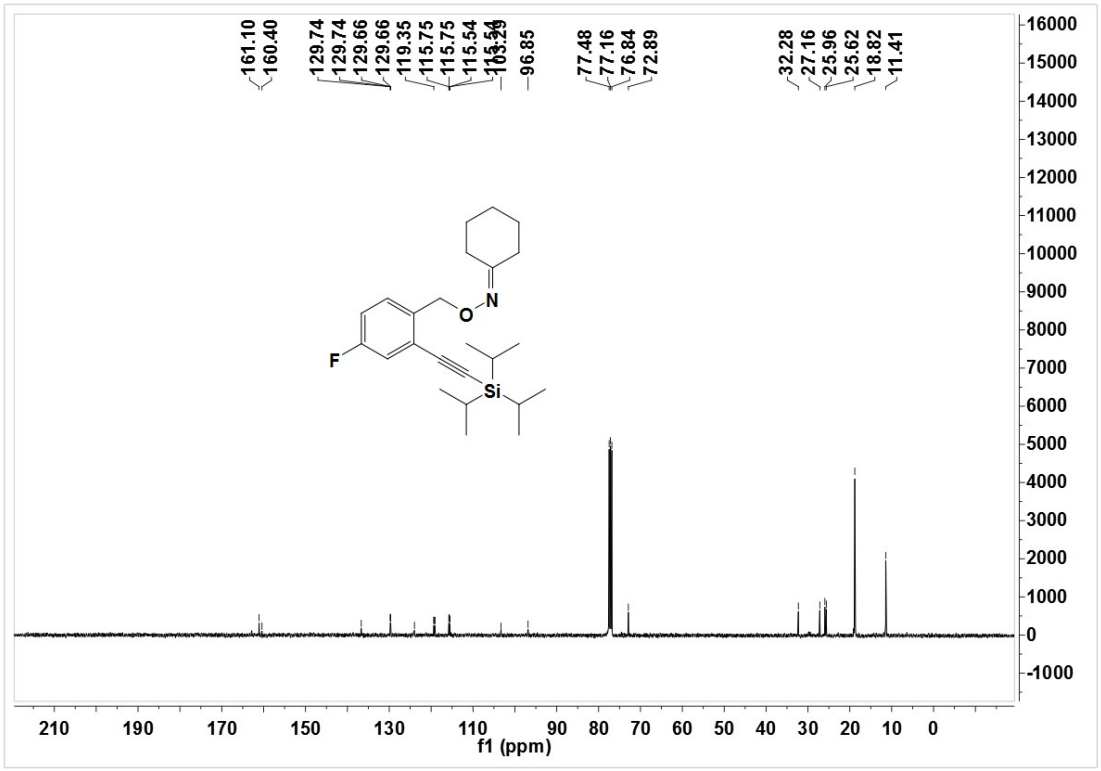
7.340
7.334
7.319
7.304
7.260
7.174
7.168
7.151
7.145
7.020
7.015
7.000
6.994
6.979
6.972
5.196
2.520
2.506
2.491
2.208
2.193
2.177
1.672
1.660
1.648
1.633
1.603
1.127
N
O
F
Si
1.00
1.00
1.00
2.00
2.01
2.00
2.01
4.01
21.03
f1 (ppm)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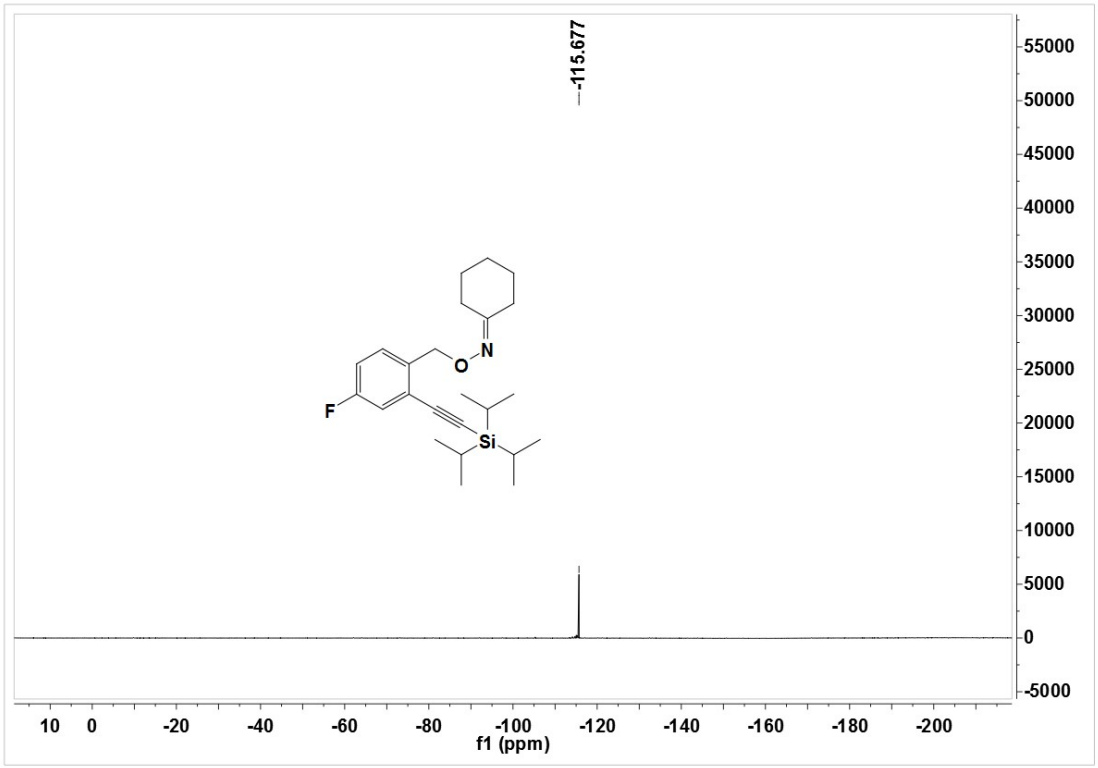
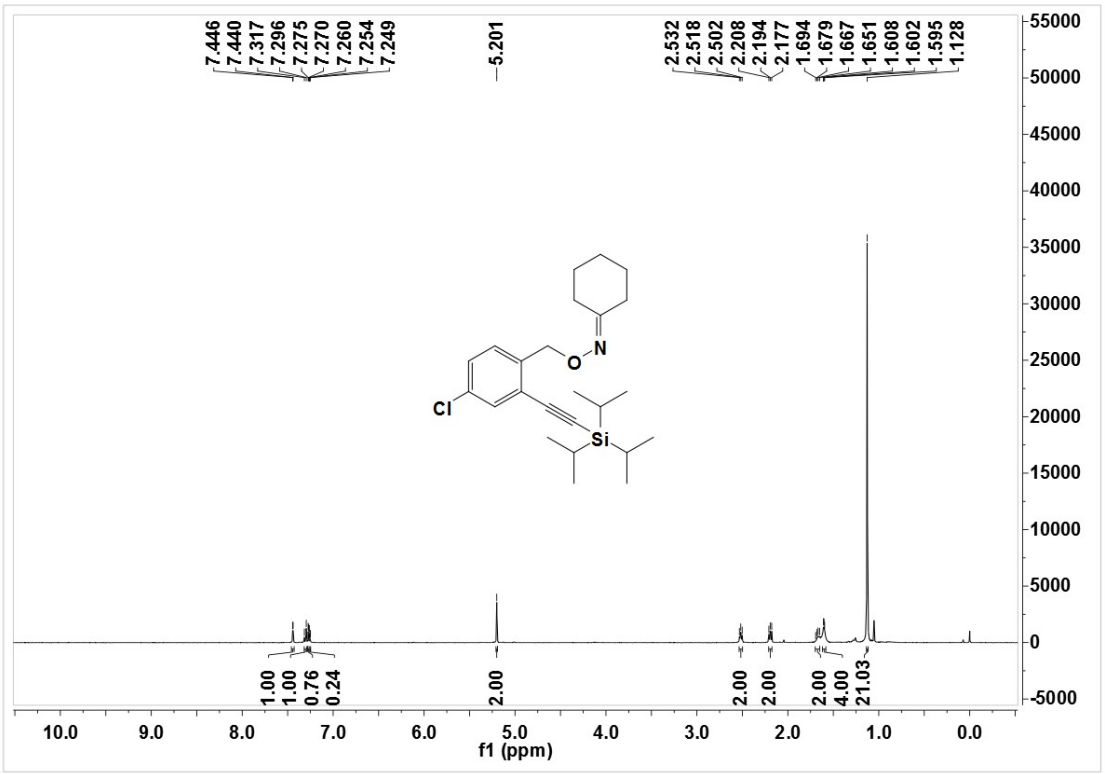
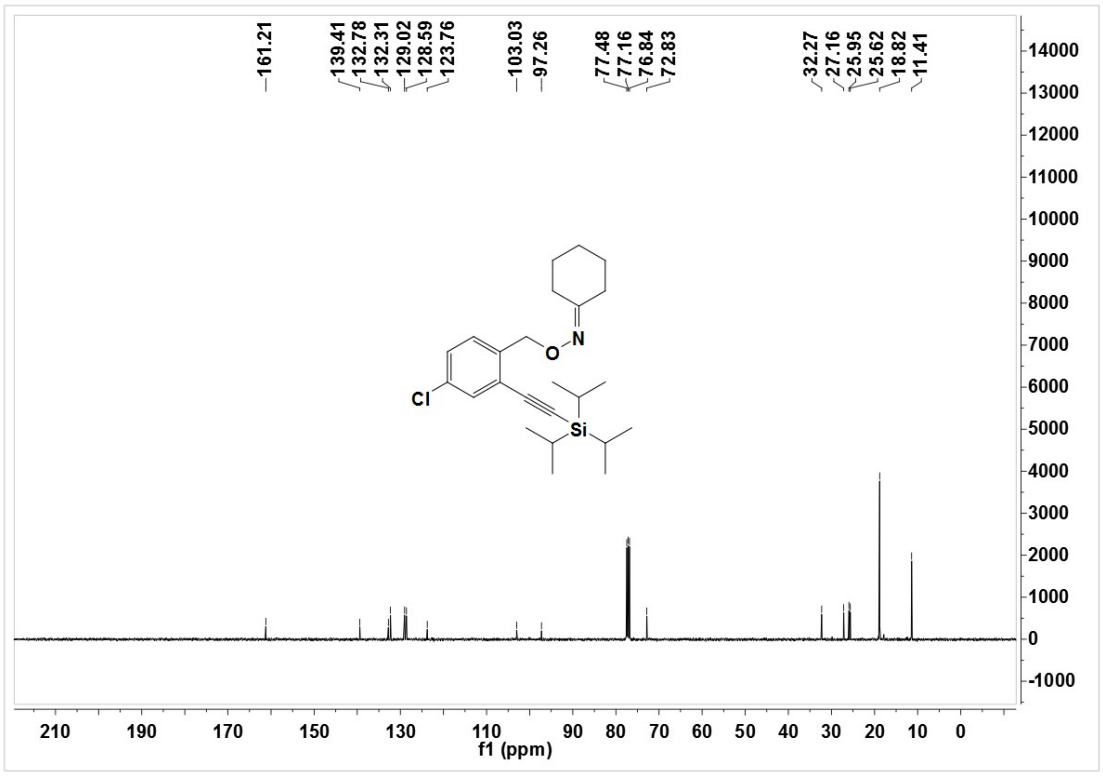
160.40
129.74
129.74
129.66
129.66
119.35
115.75
115.75
115.54
96.85
77.48
77.16
76.84
72.89
32.28
27.16
25.96
25.62
18.82
11.41
N
O
F
Si
f1 (ppm)

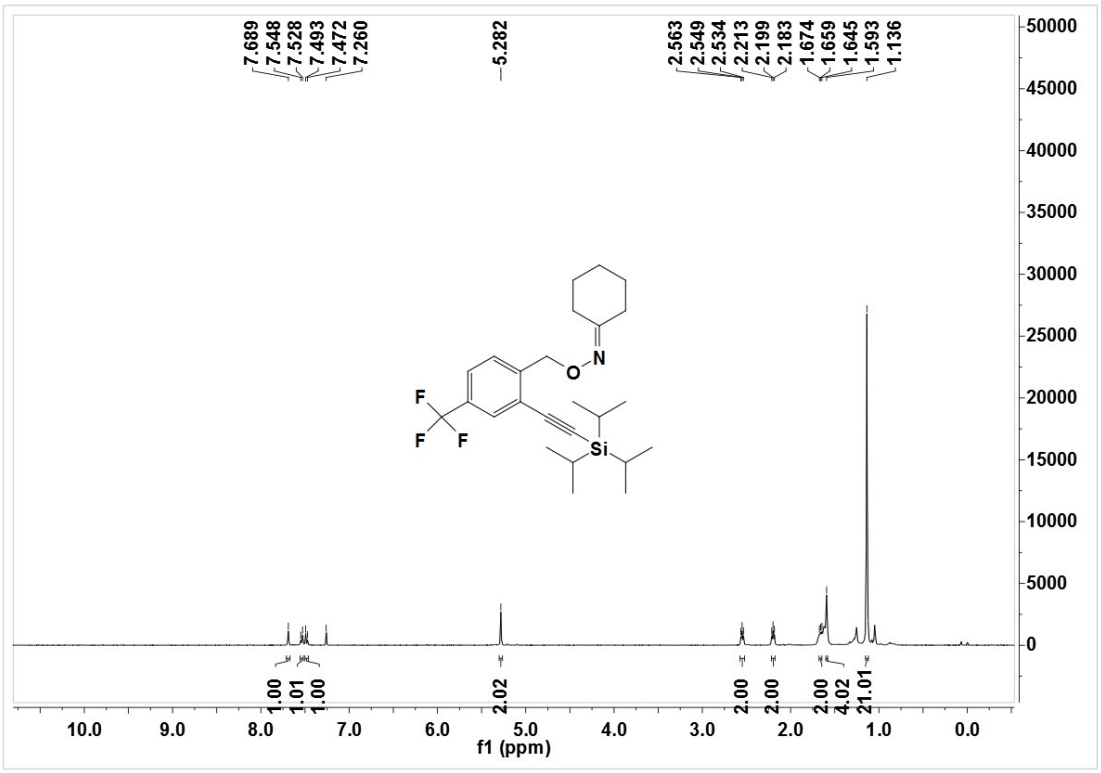


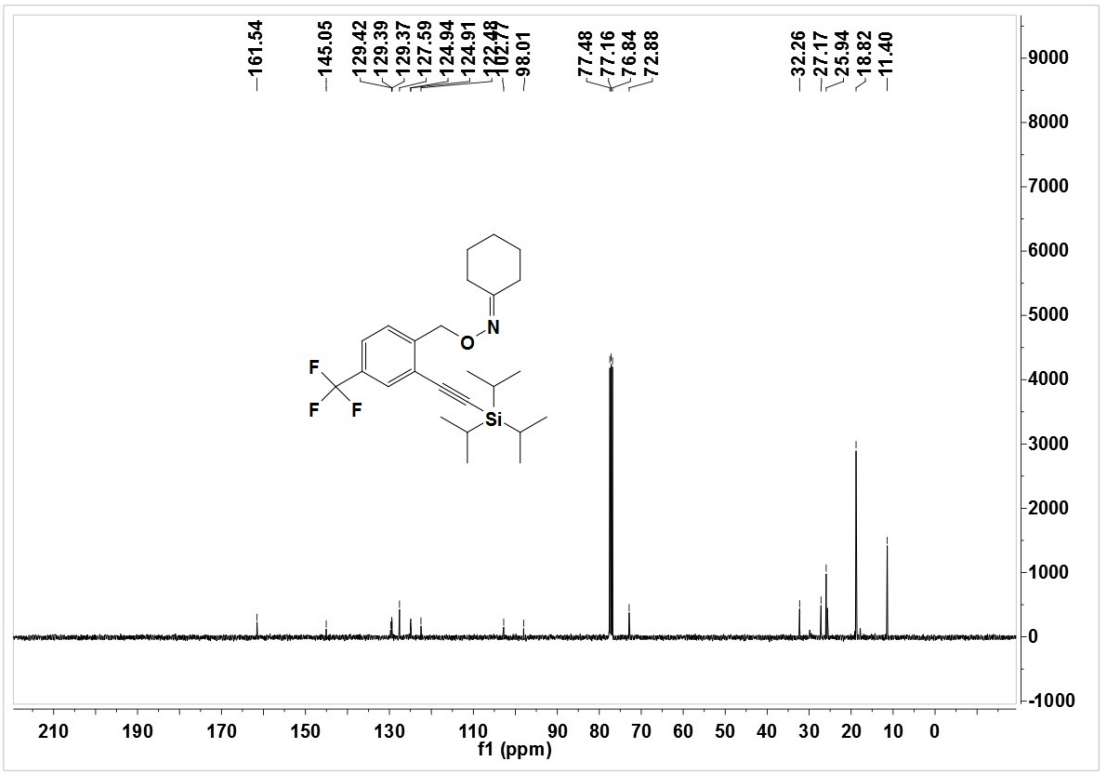
Cyclohexanone *O*-(4-chloro-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5f)





Cyclohexanone *O*-(4-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5g)

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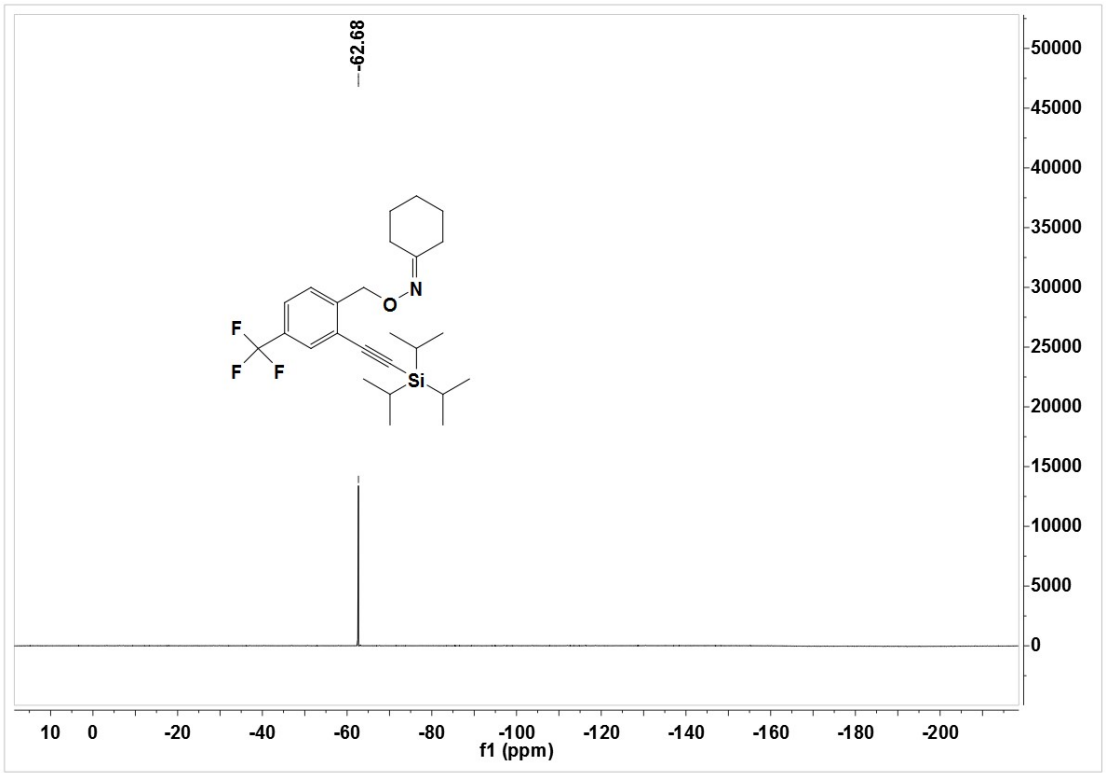
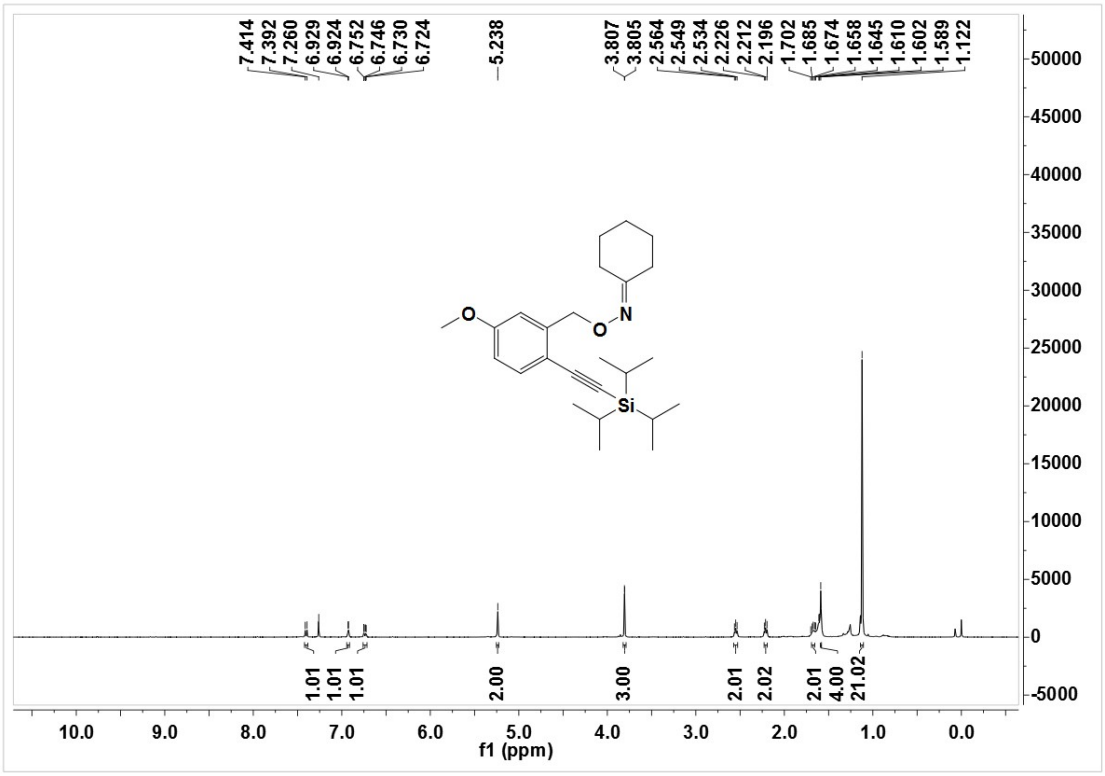
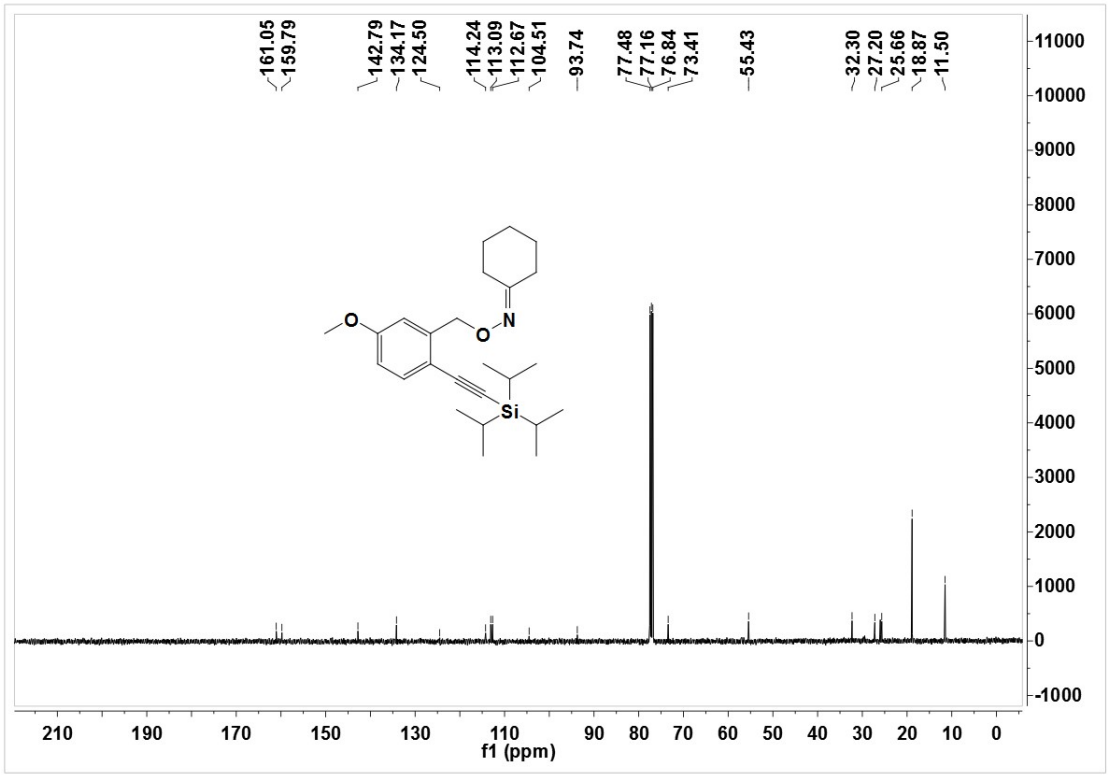
129.42
129.39
129.37
127.59
124.94
124.91
102.77
98.01
77.48
77.16
76.84
72.88
32.26
27.17
25.94
18.82
11.40
O
N
F
F
F
Si
f1 (ppm)

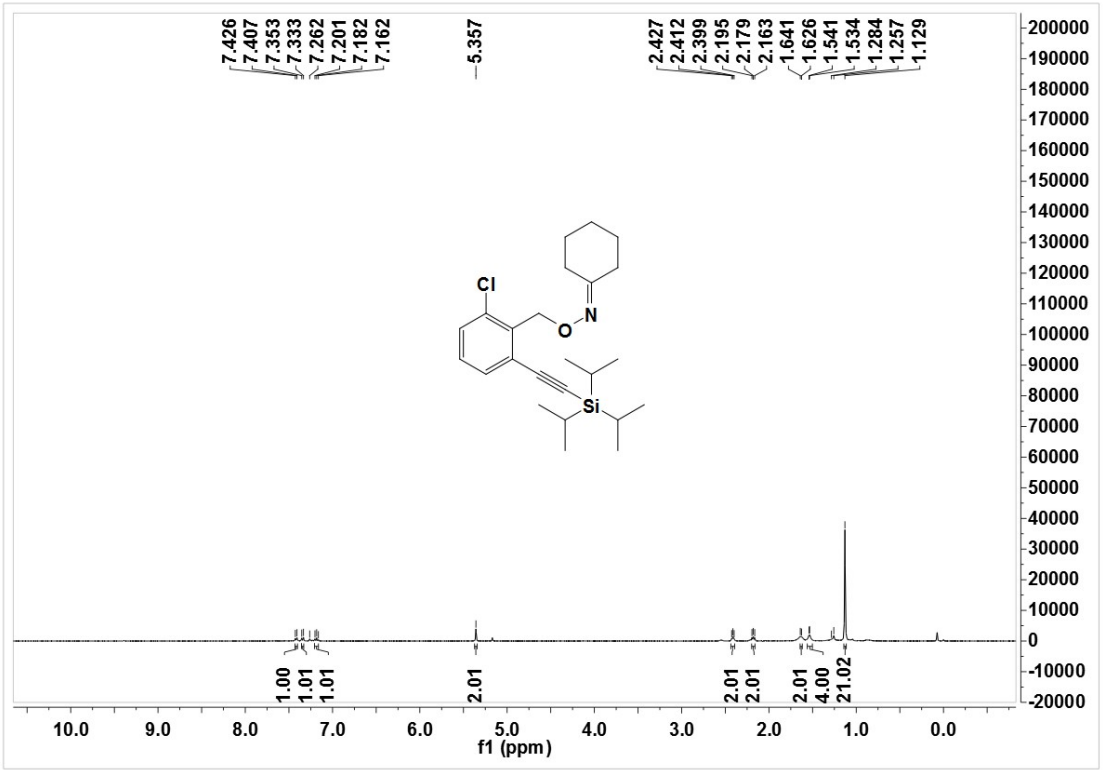

-62.68
O
N
F
F
F
Si
f1 (ppm)

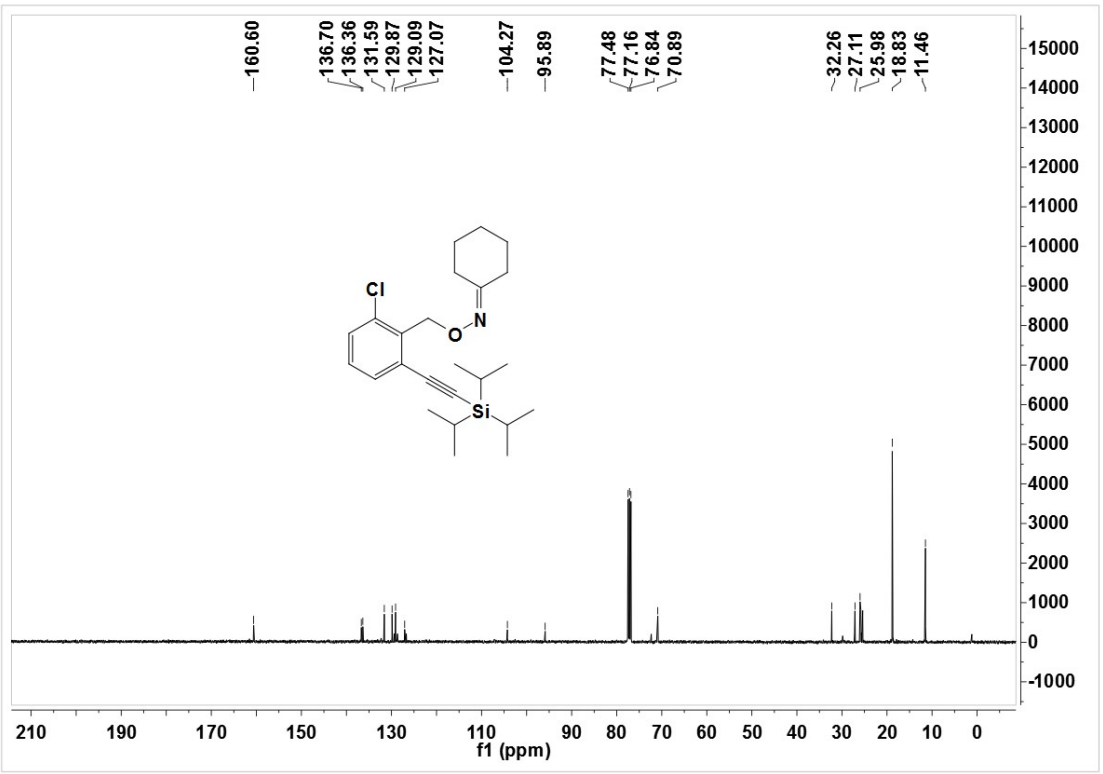
Cyclohexanone *O*-(5-methoxy-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5h)



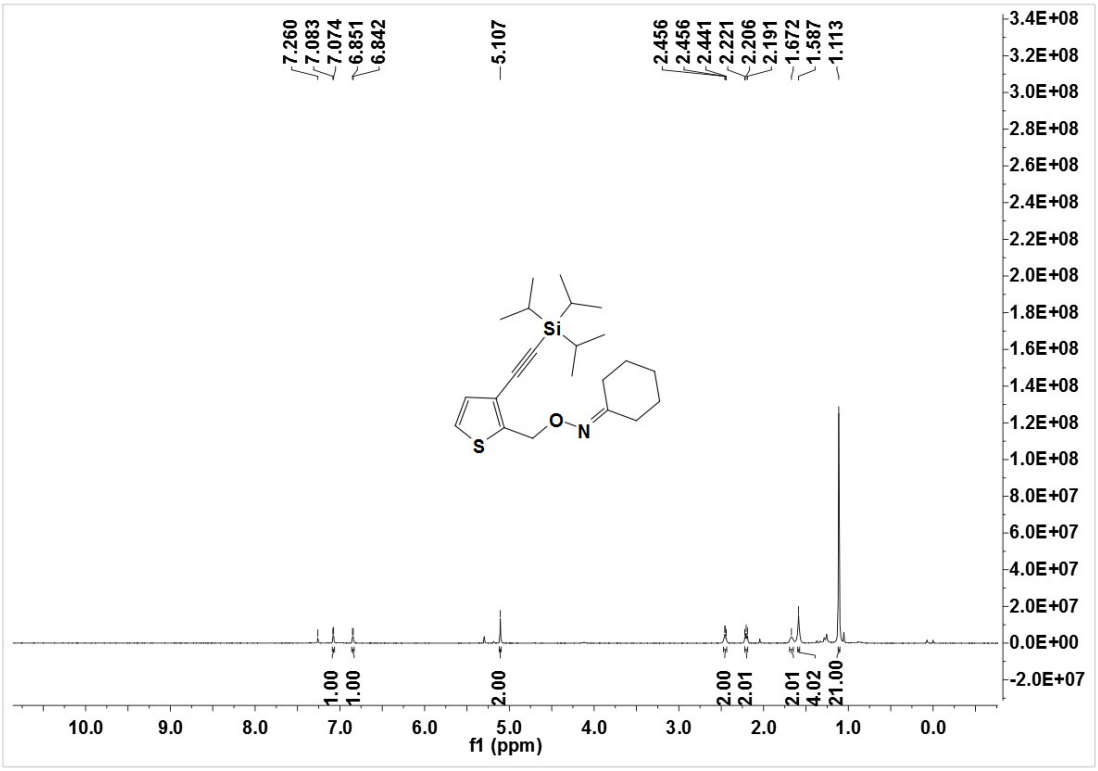


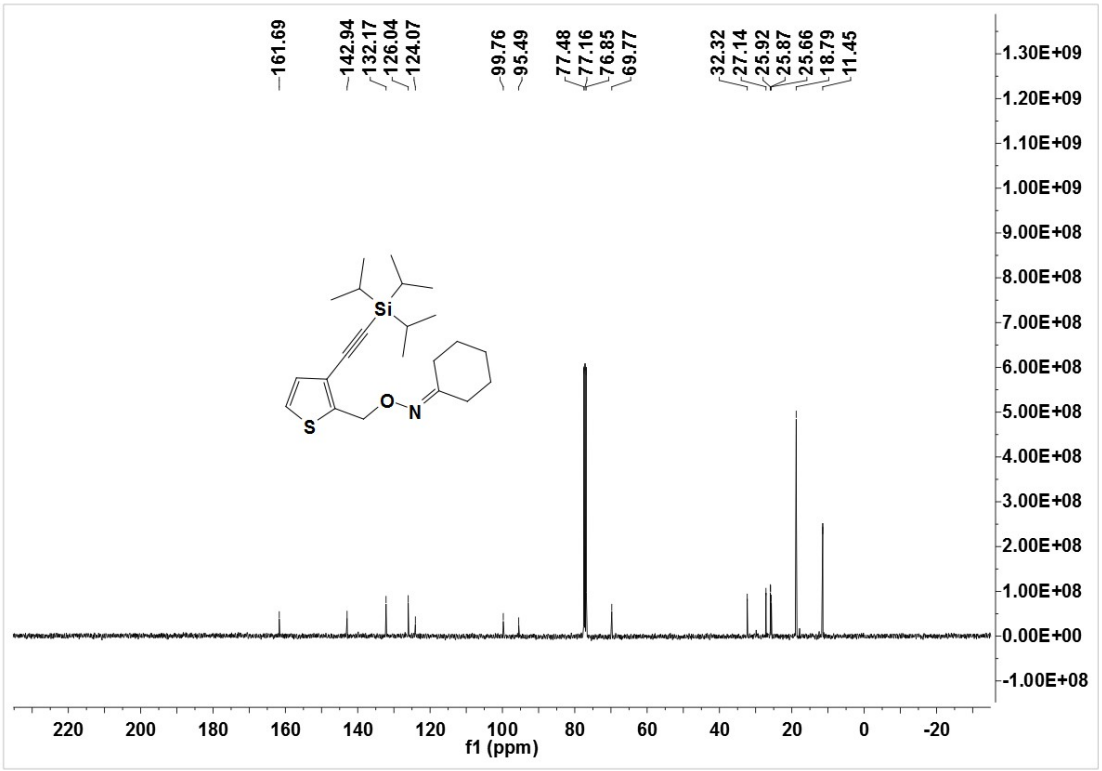
Cyclohexanone *O*-(2-chloro-6-((triisopropylsilyl)ethynyl)benzyl) oxime (5i)



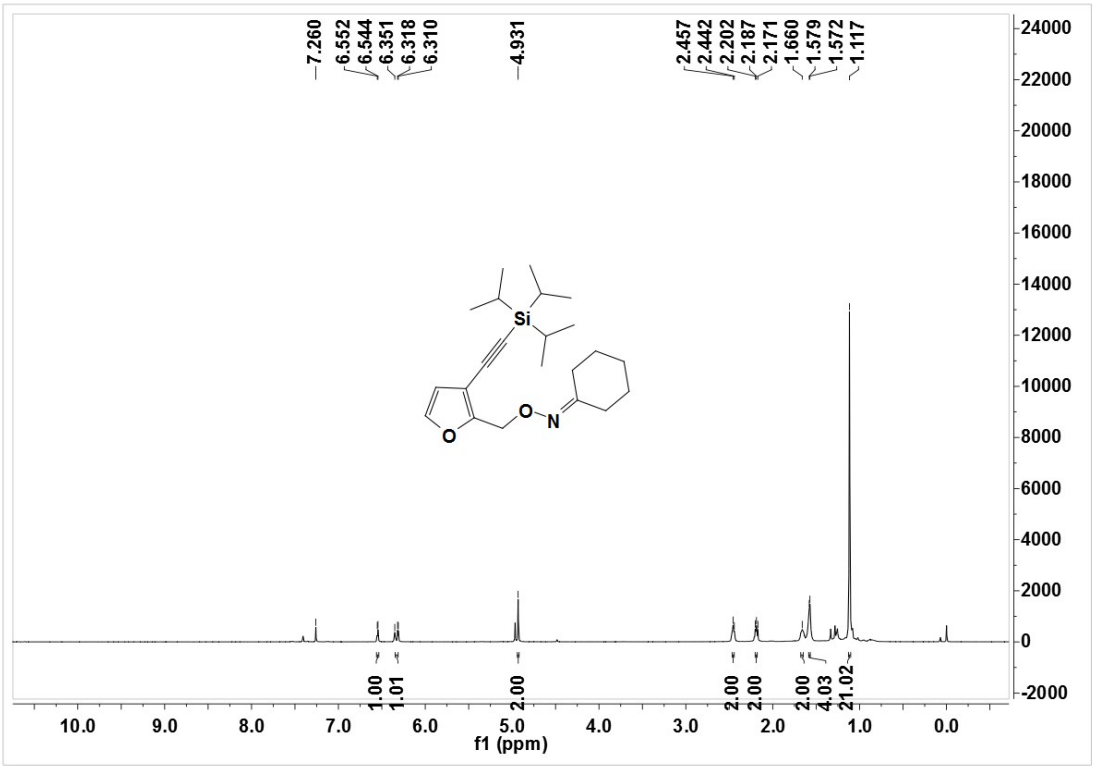


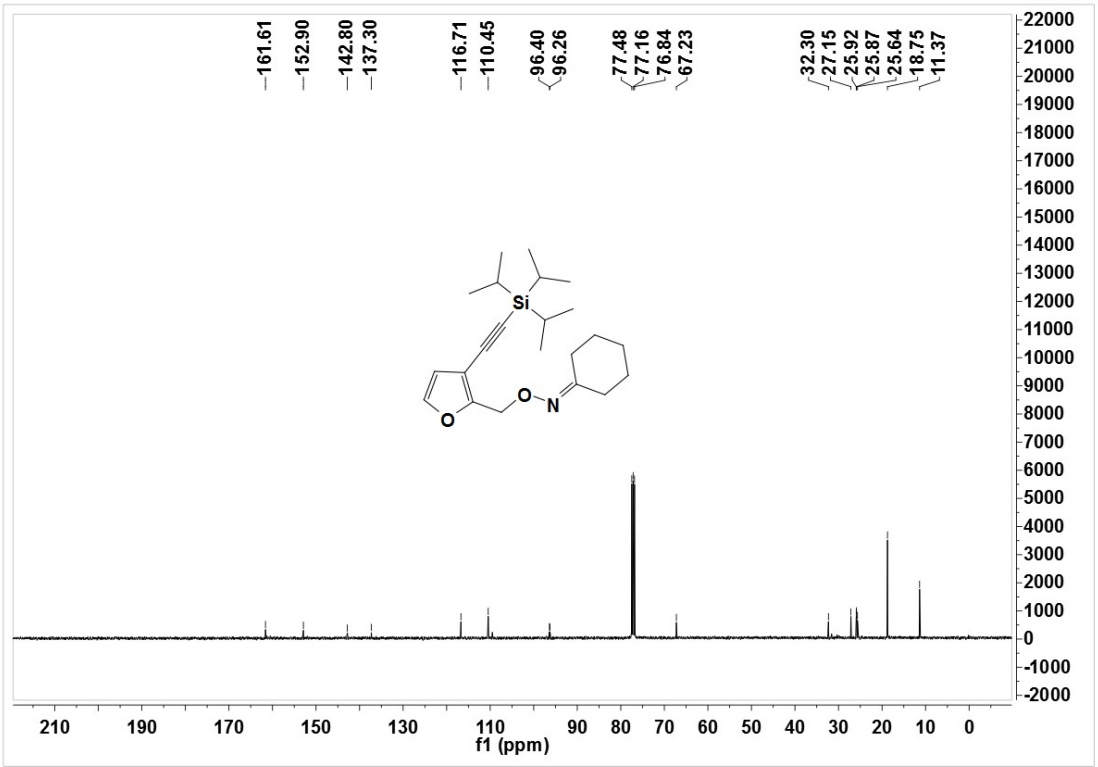
Cyclohexanone *O*-((3-((triisopropylsilyl)ethynyl)thiophen-2-yl)methyl) oxime (5j)





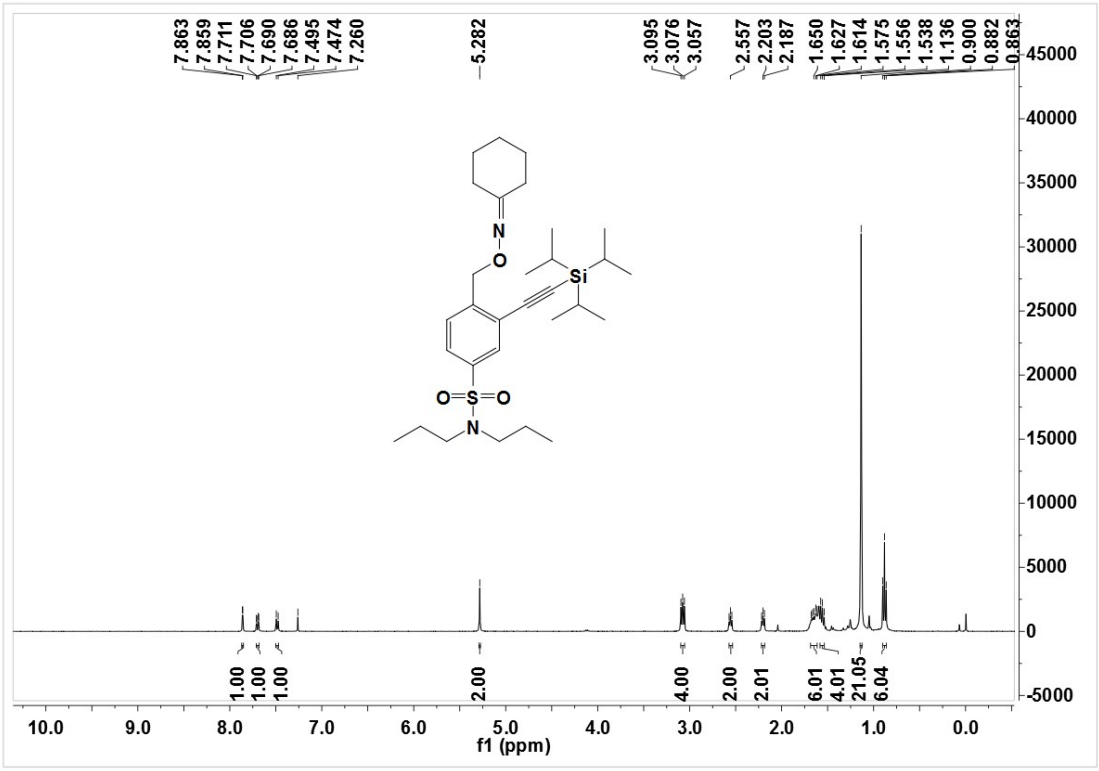
Cyclohexanone *O*-((3-((triisopropylsilyl)ethynyl)furan-2-yl)methyl) oxime (5k)

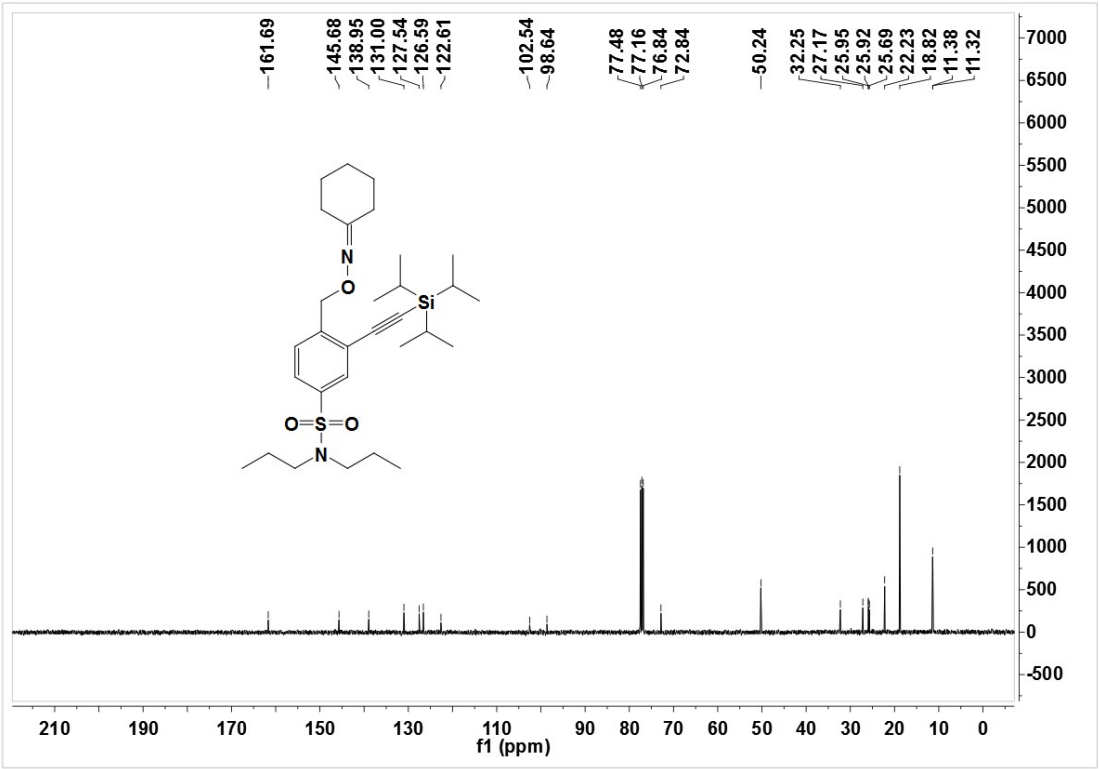




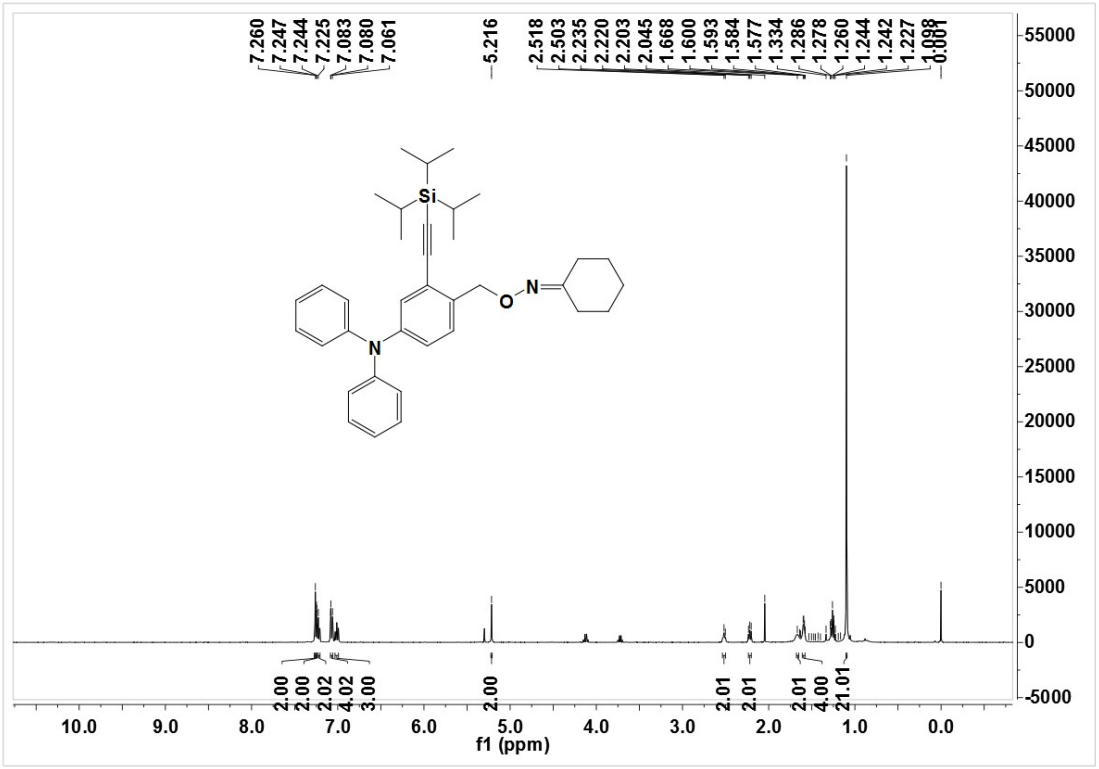
4-(((Cyclohexylideneamino)oxy)methyl)-N,N-dipropyl-3-((triisopropylsilyl)

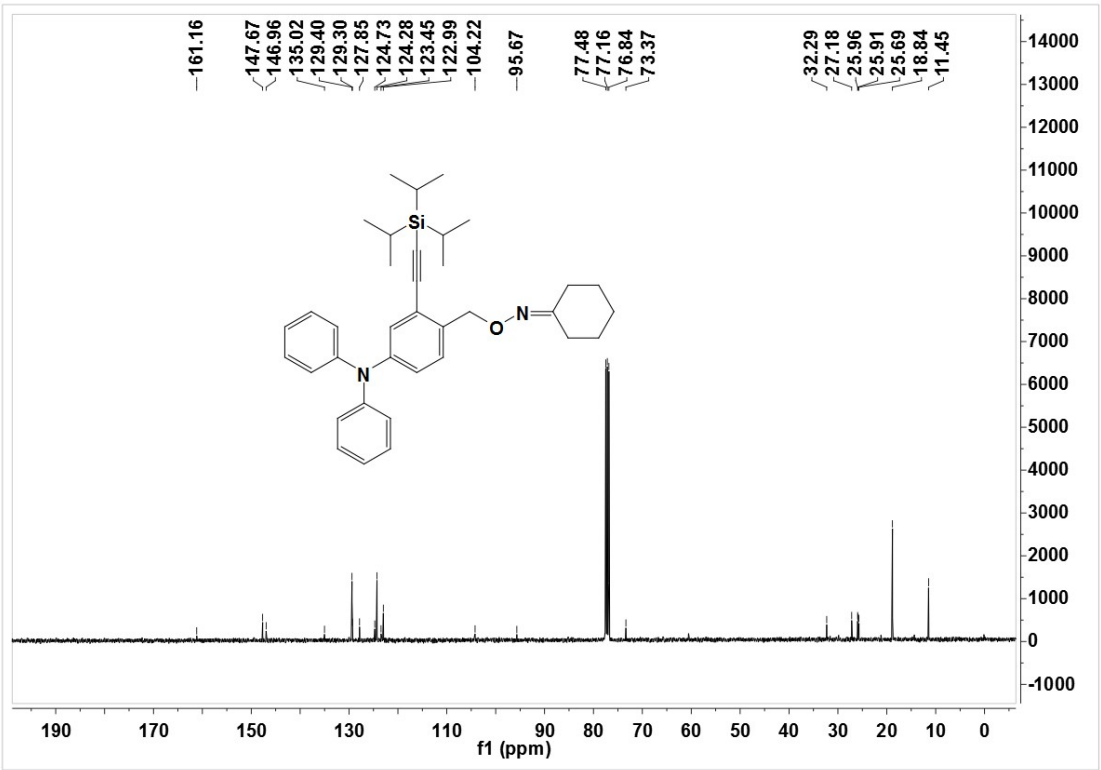
ethynyl)benzenesulfonamide (5l)





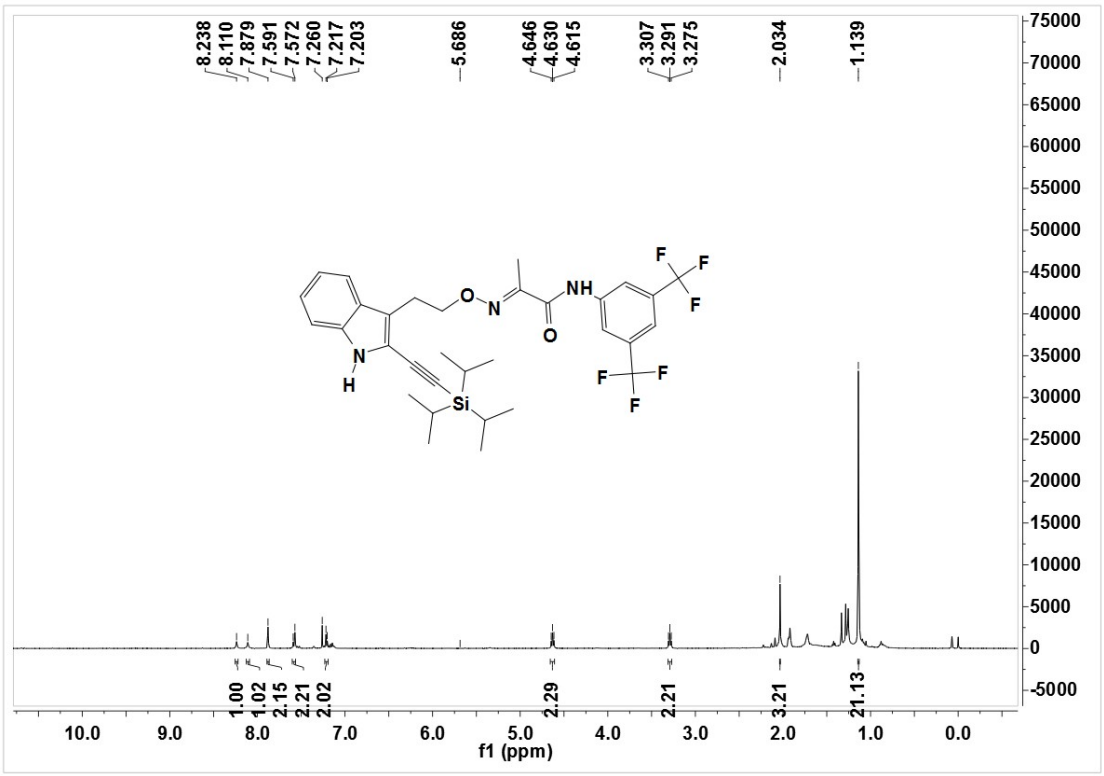
Cyclohexanone *O*-(4-(diphenylamino)-2-((triisopropylsilyl)ethynyl)benzyl) oxime (5m)

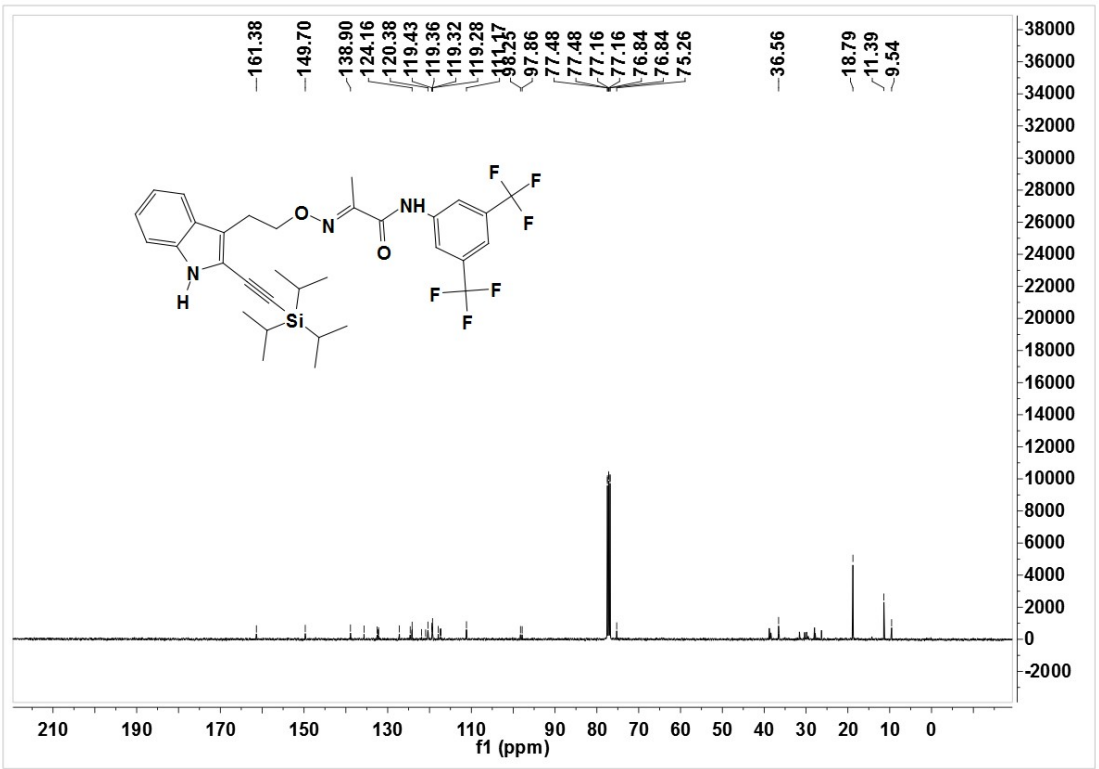


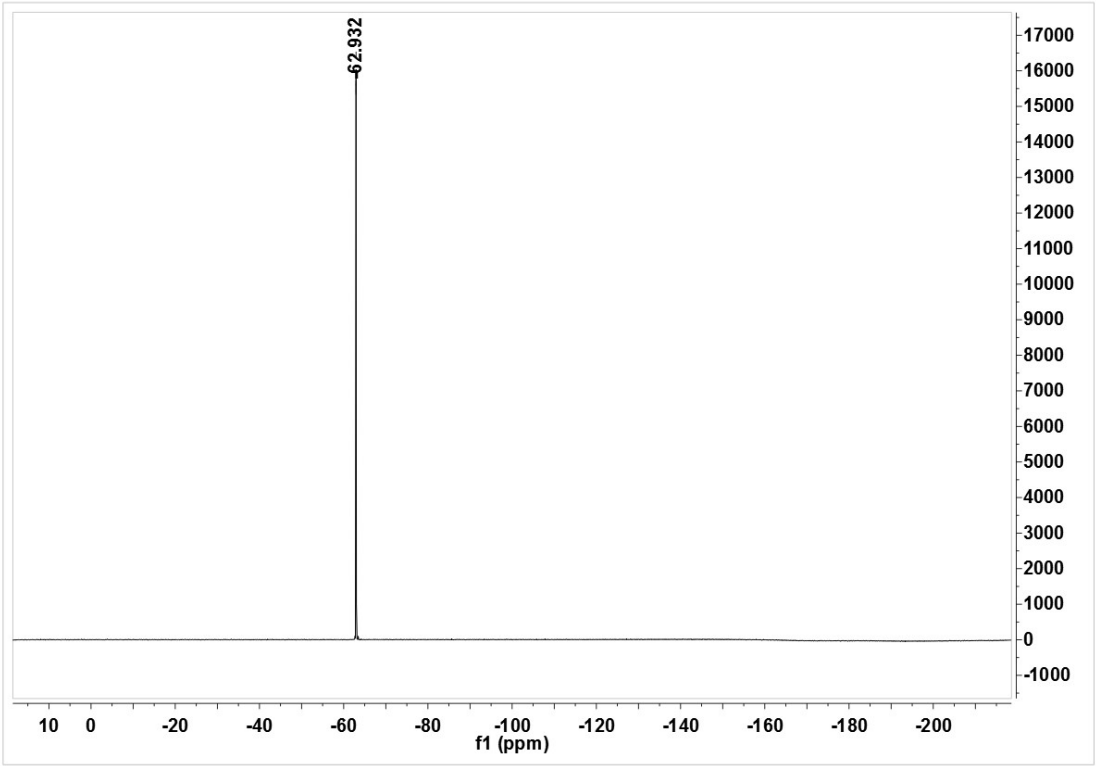


(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-((2-(2-((triisopropylsilyl)ethynyl)-1*H*-

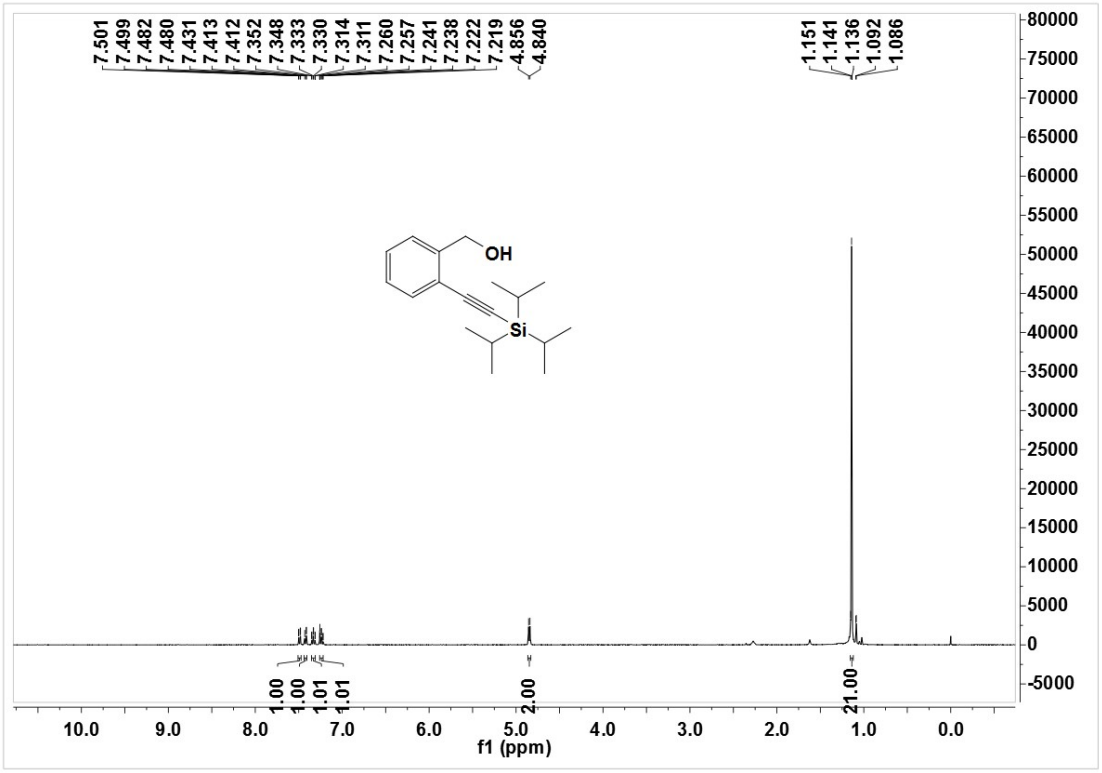
indol-3-yl)ethoxy)imino)propanamide (3l')

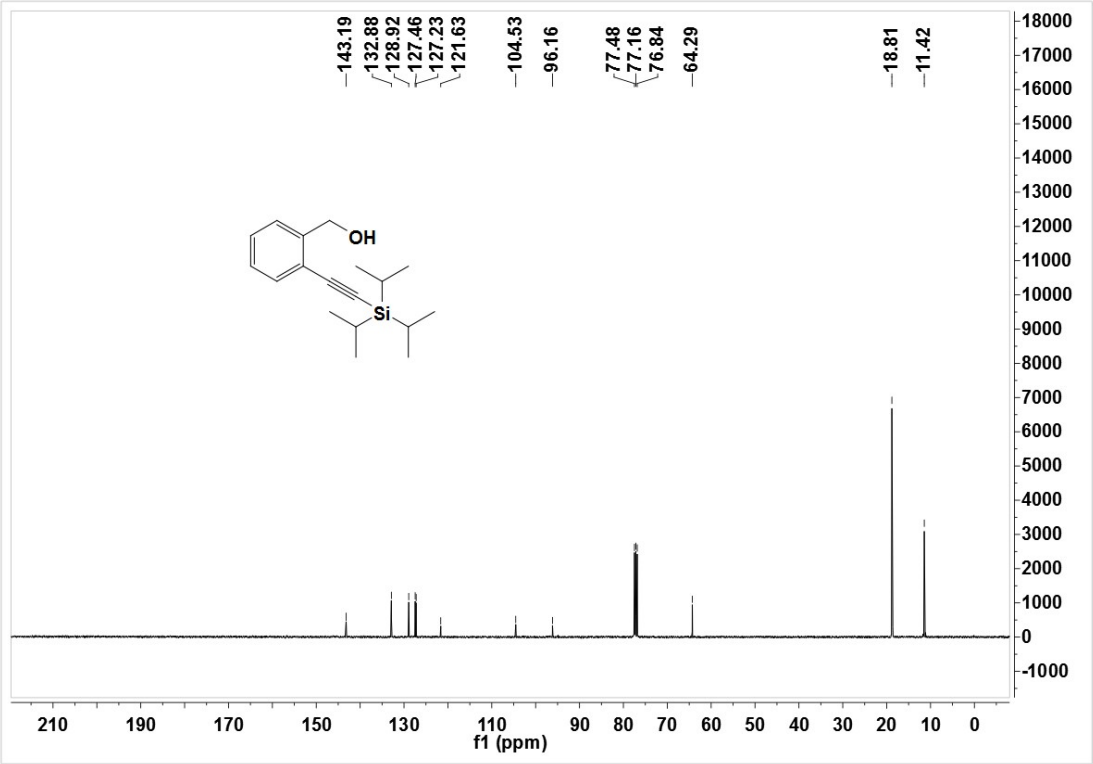




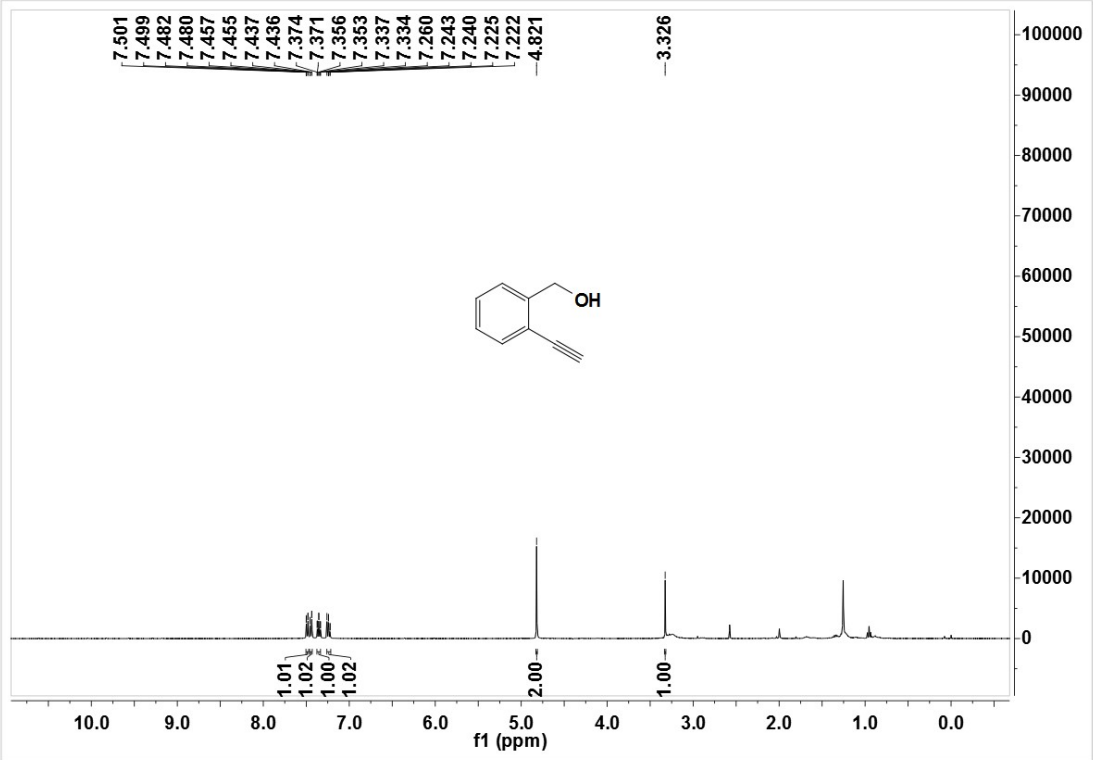


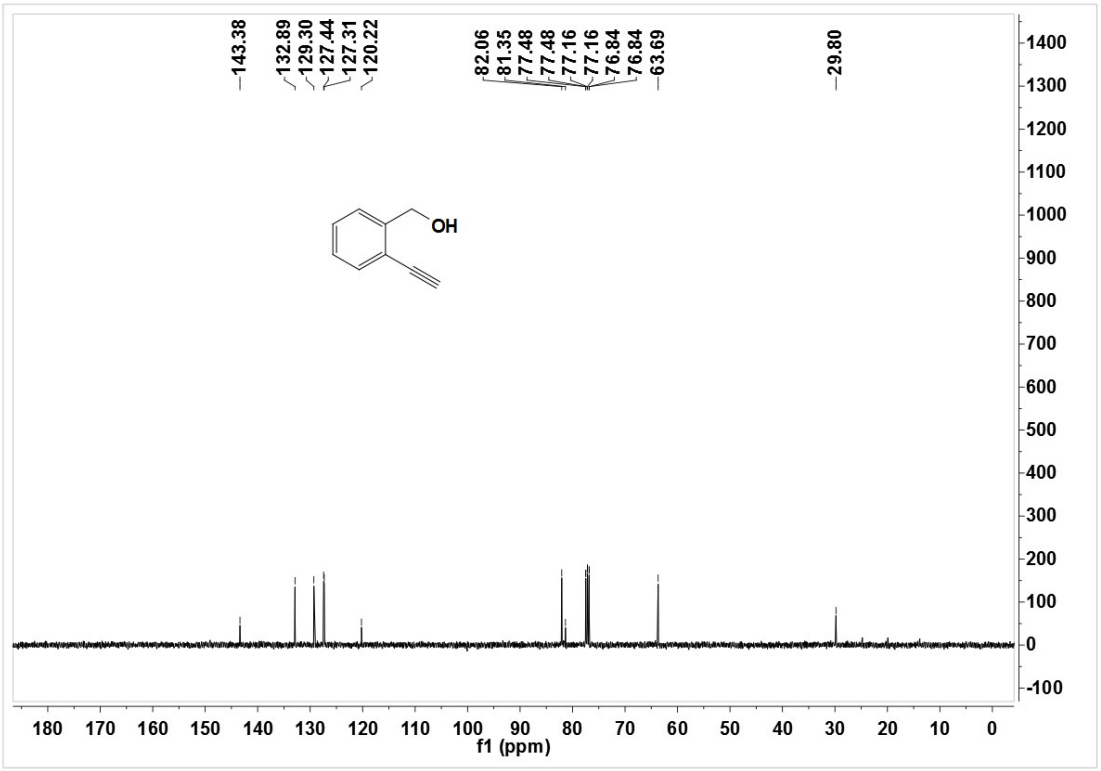
(2-((Triisopropylsilyl)ethynyl)phenyl)methanol (5a-1)



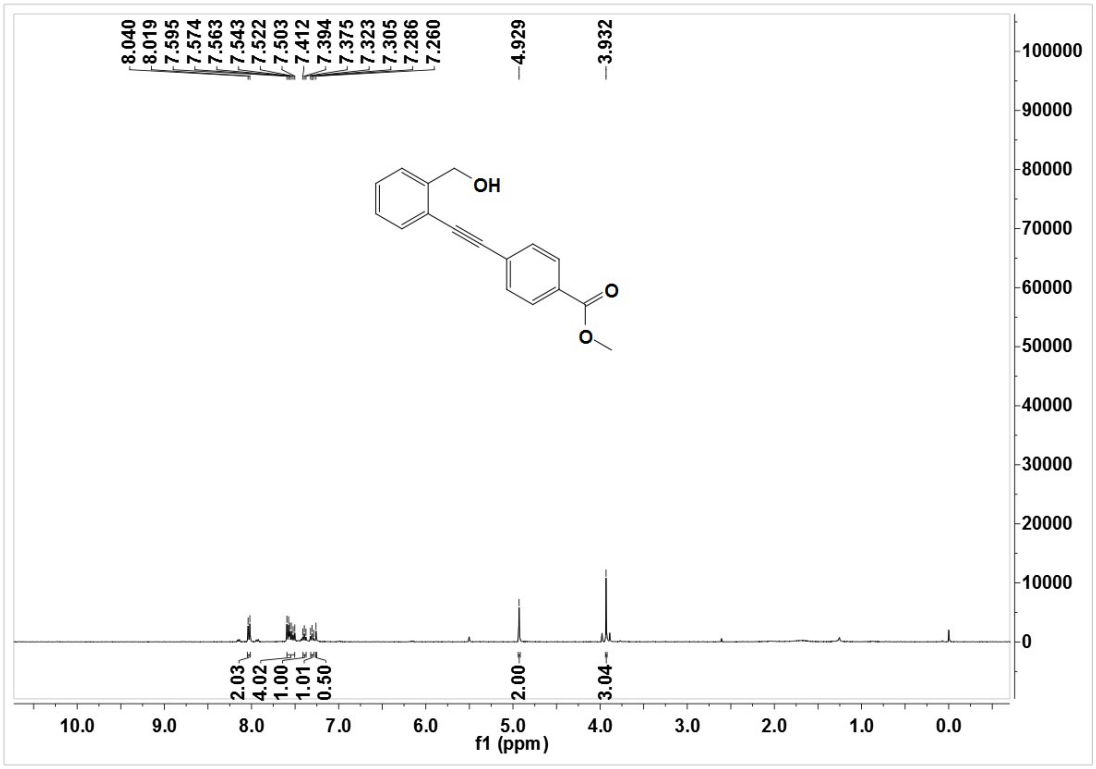


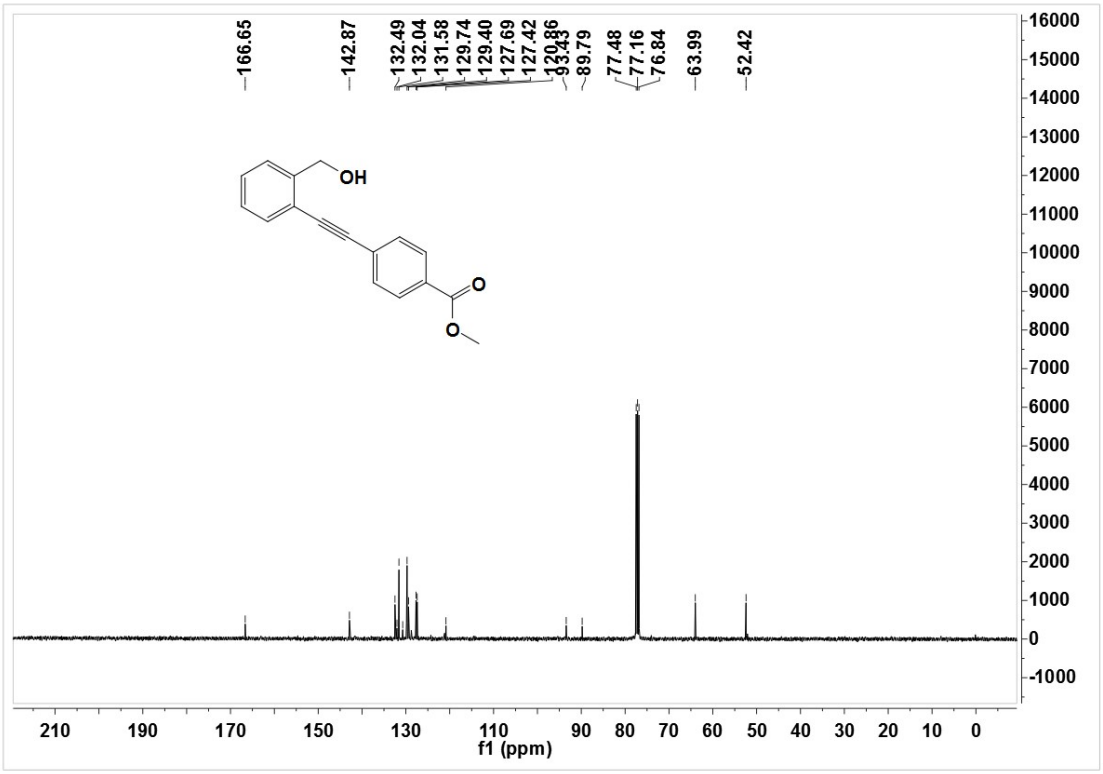
(2-Ethynylphenyl)methanol (5a-2)



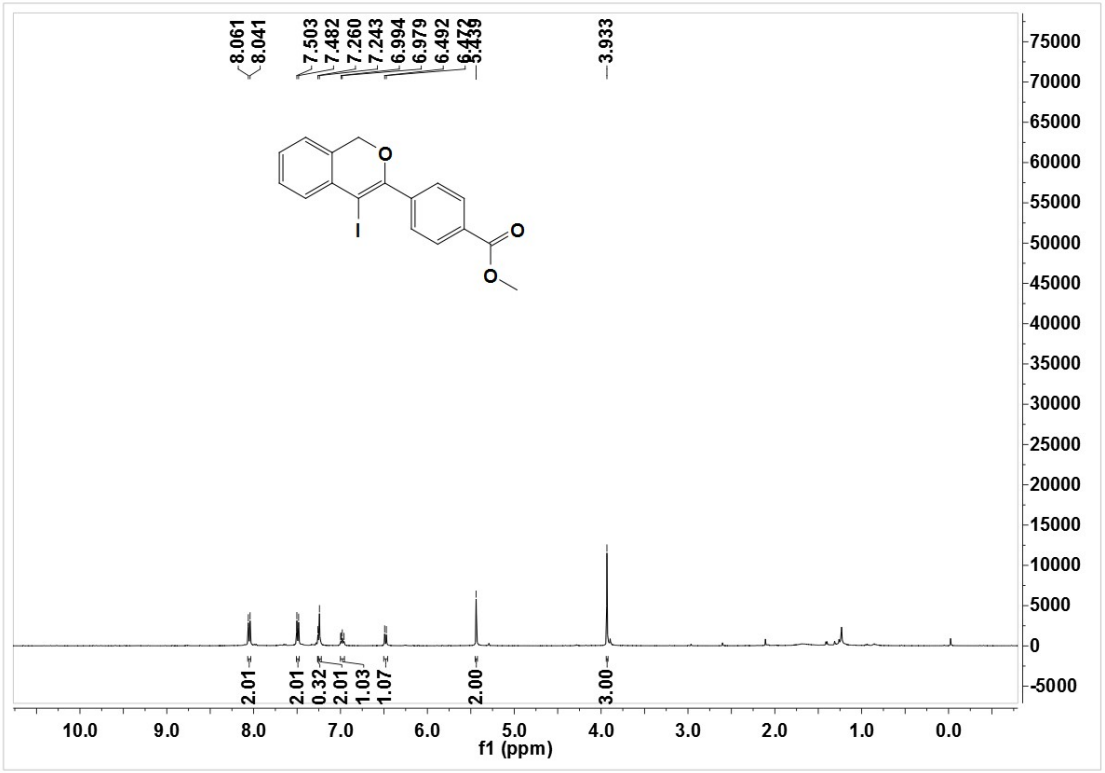


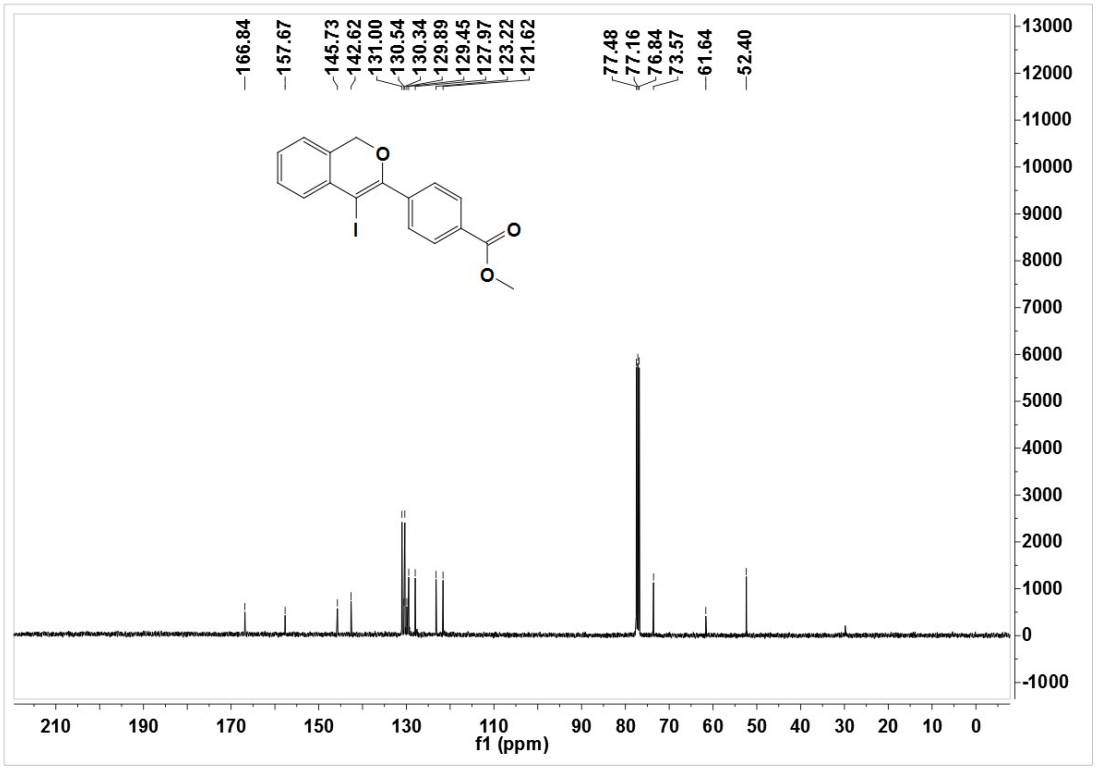
Methyl 4-((2-(hydroxymethyl)phenyl)ethynyl)benzoate (5a-3)



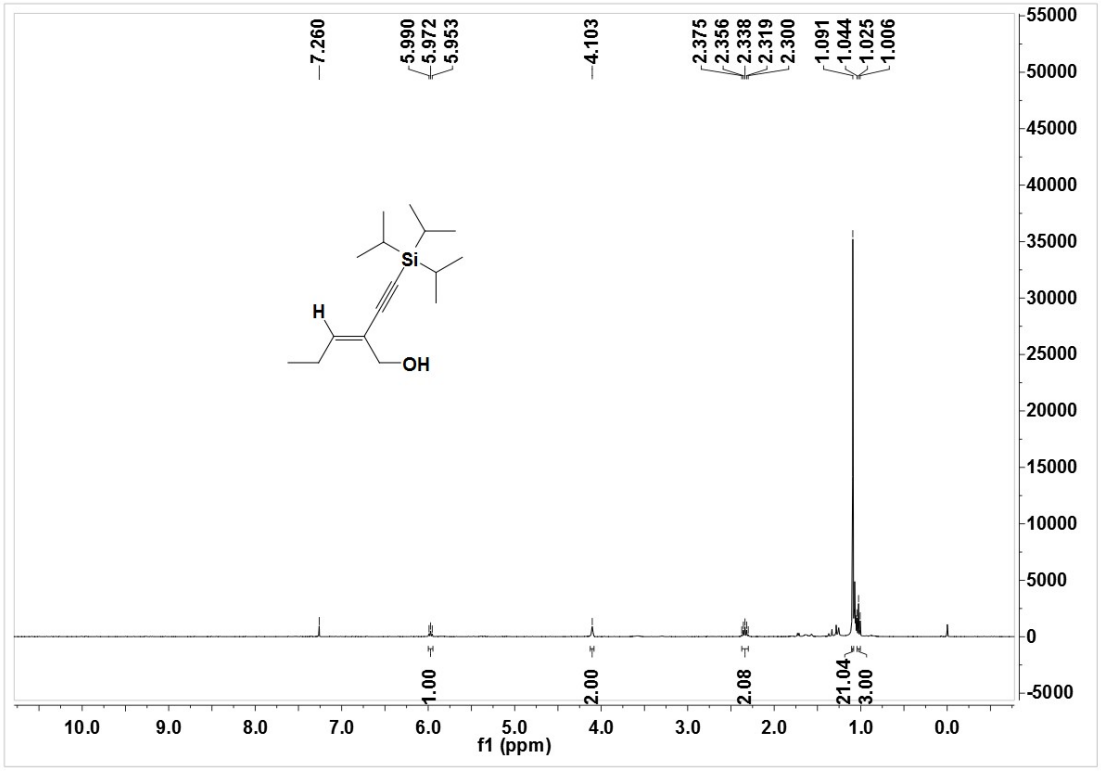


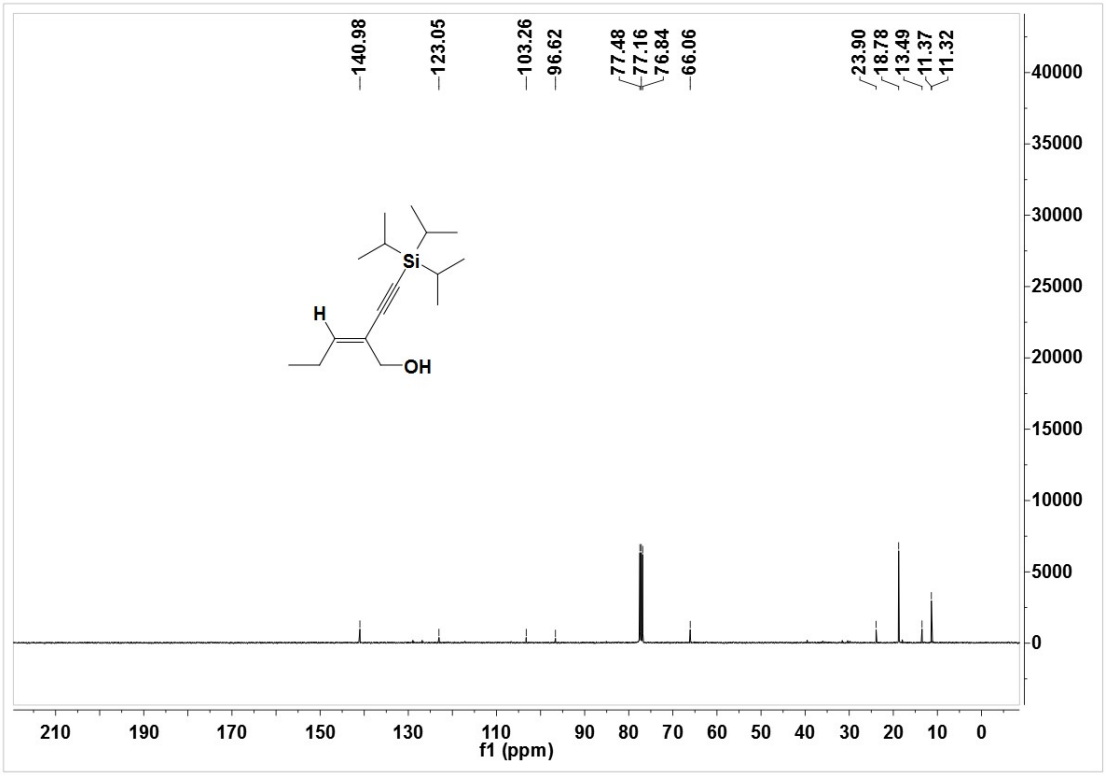
Methyl 4-(4-iodo-1*H*-isochromen-3-yl)benzoate (5a-4)



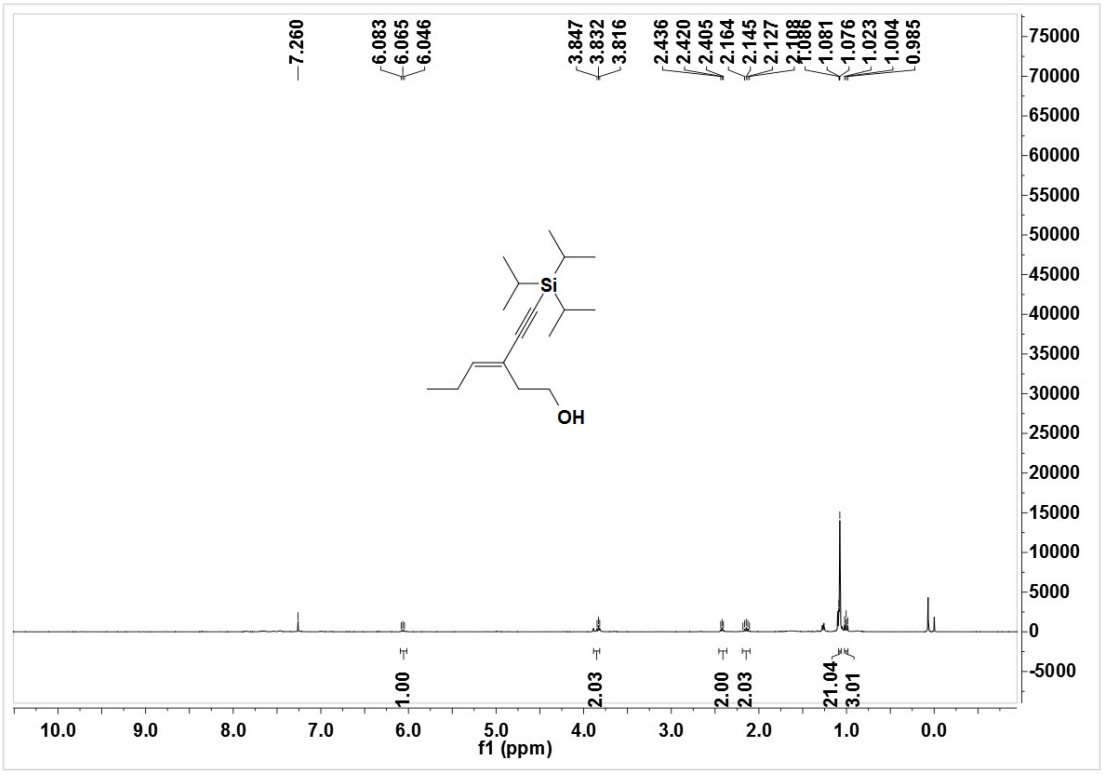


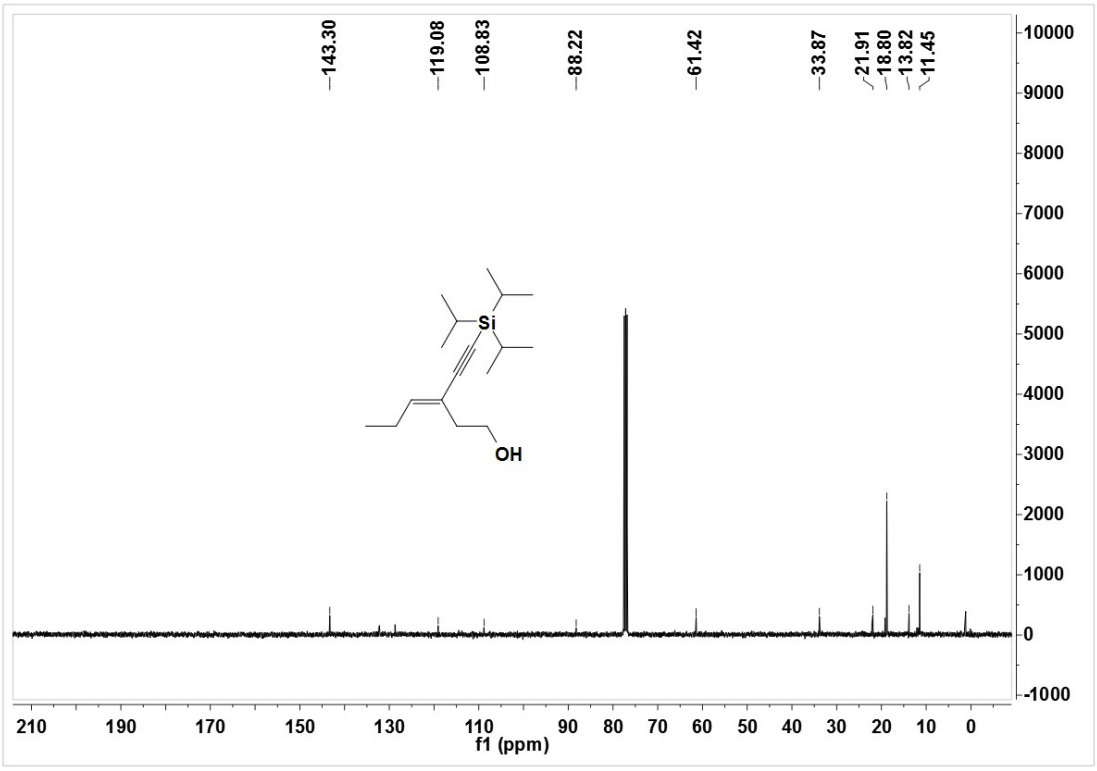
(*Z*)-2-((Triisopropylsilyl)ethynyl)pent-2-en-1-ol (7a)



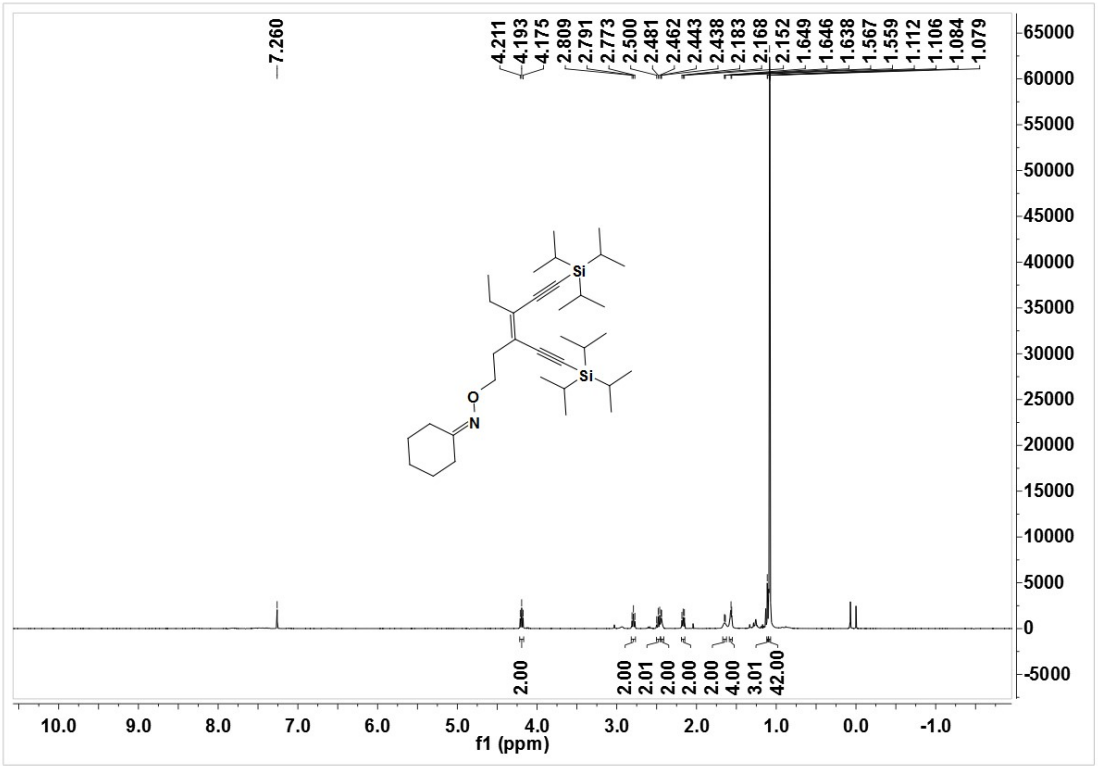


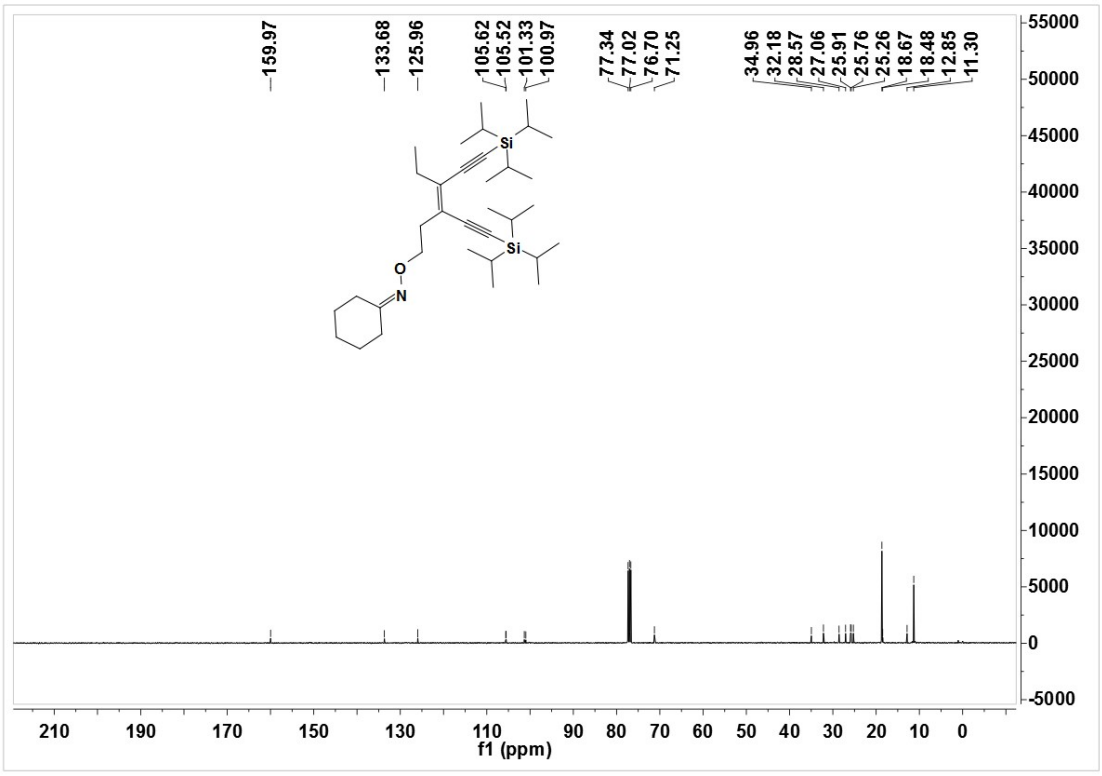
(*E*)-3-((Triisopropylsilyl)ethynyl)hex-3-en-1-ol (7b)



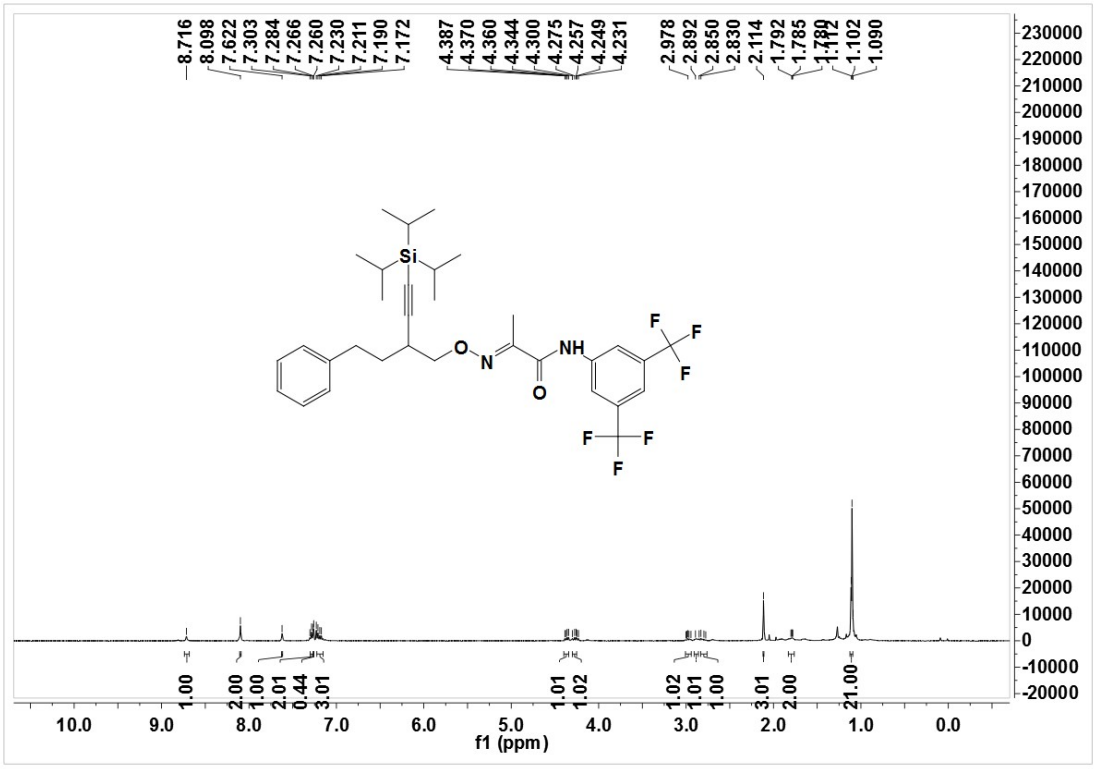


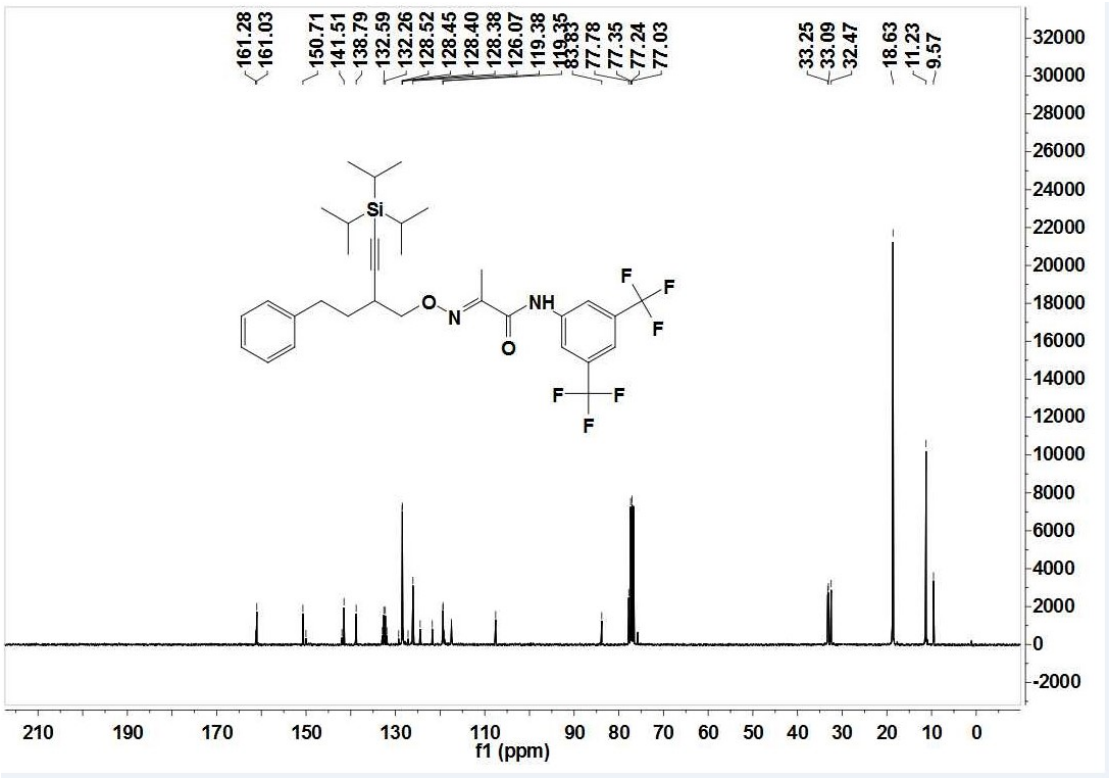
(*Z*)-Cyclohexanone *O*-(4-ethyl-6-(triisopropylsilyl)-3-((triisopropylsilyl) ethynyl) hex-3-en-5-yn-1-yl) oxime (7c)





(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-phenethyl-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10a-3)

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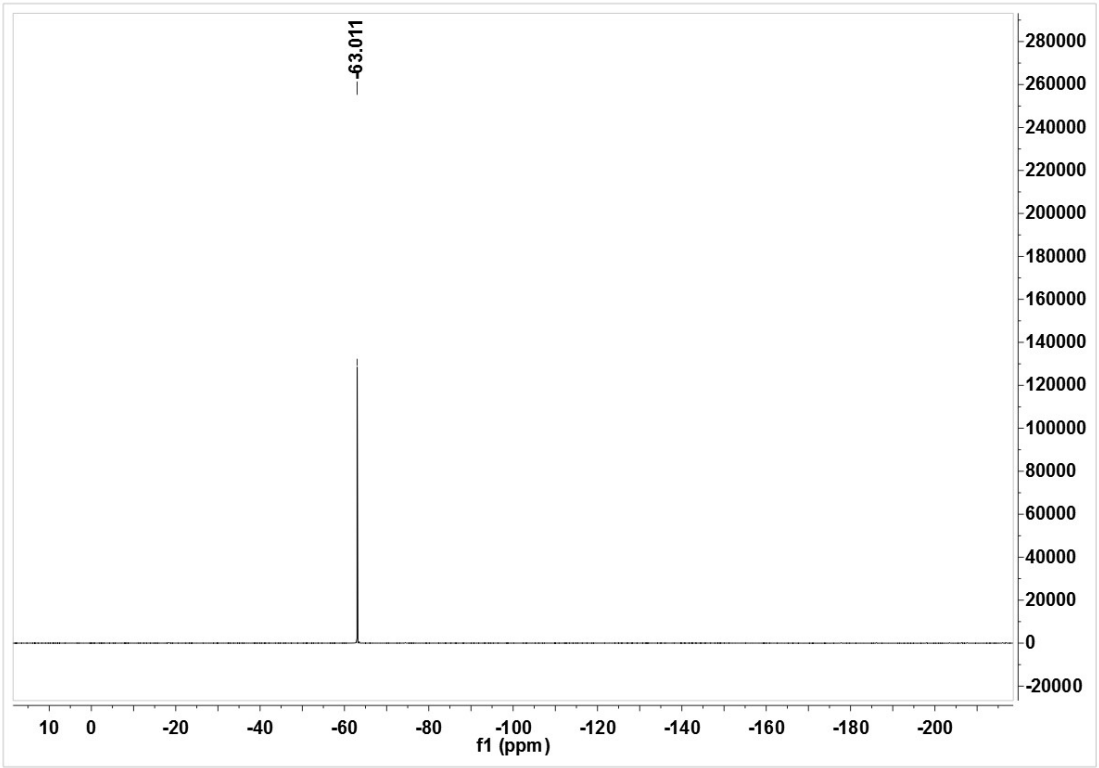
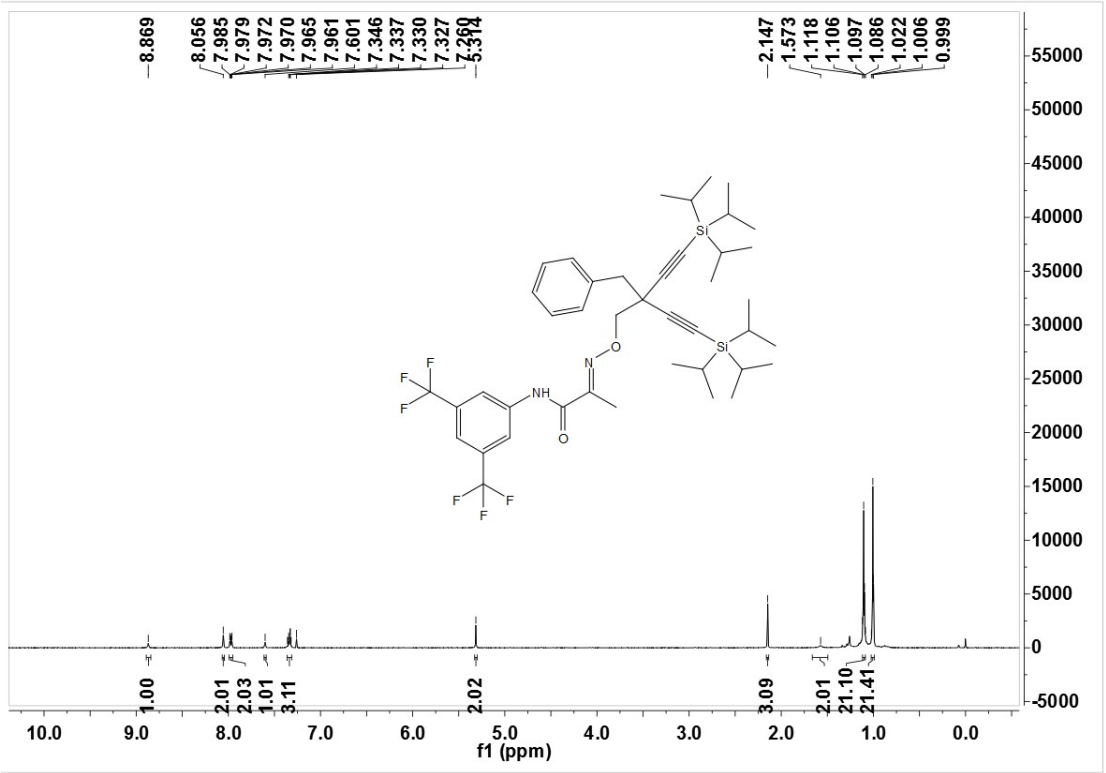
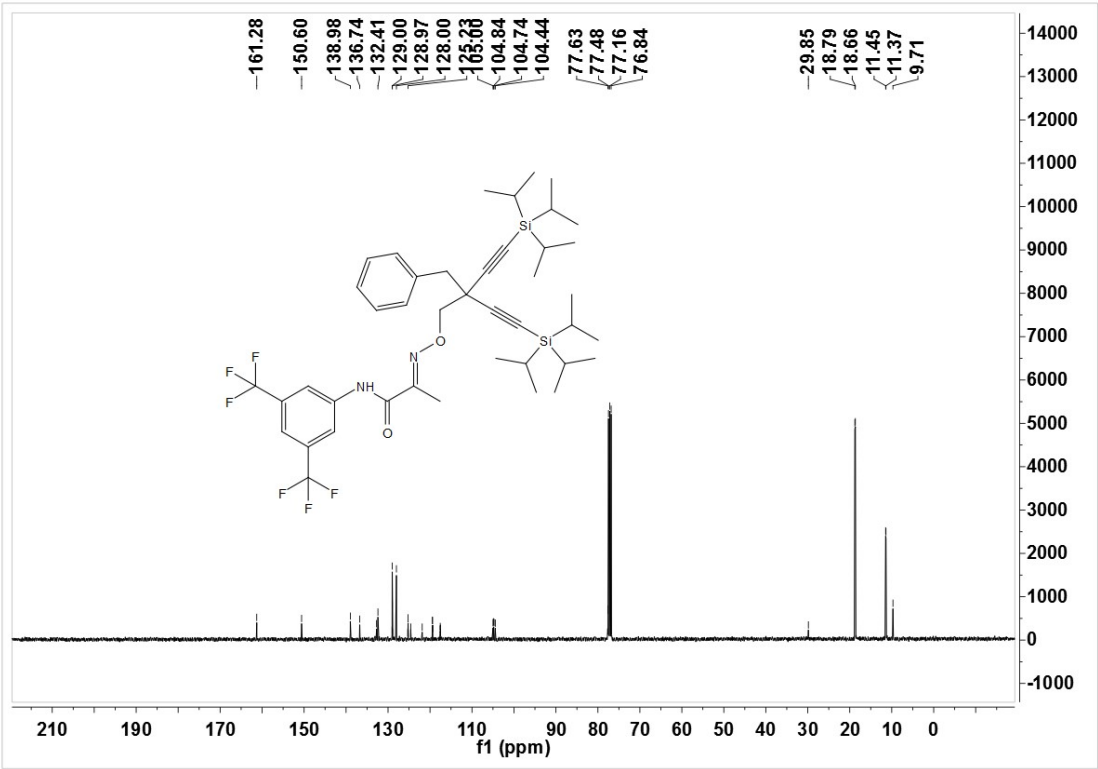
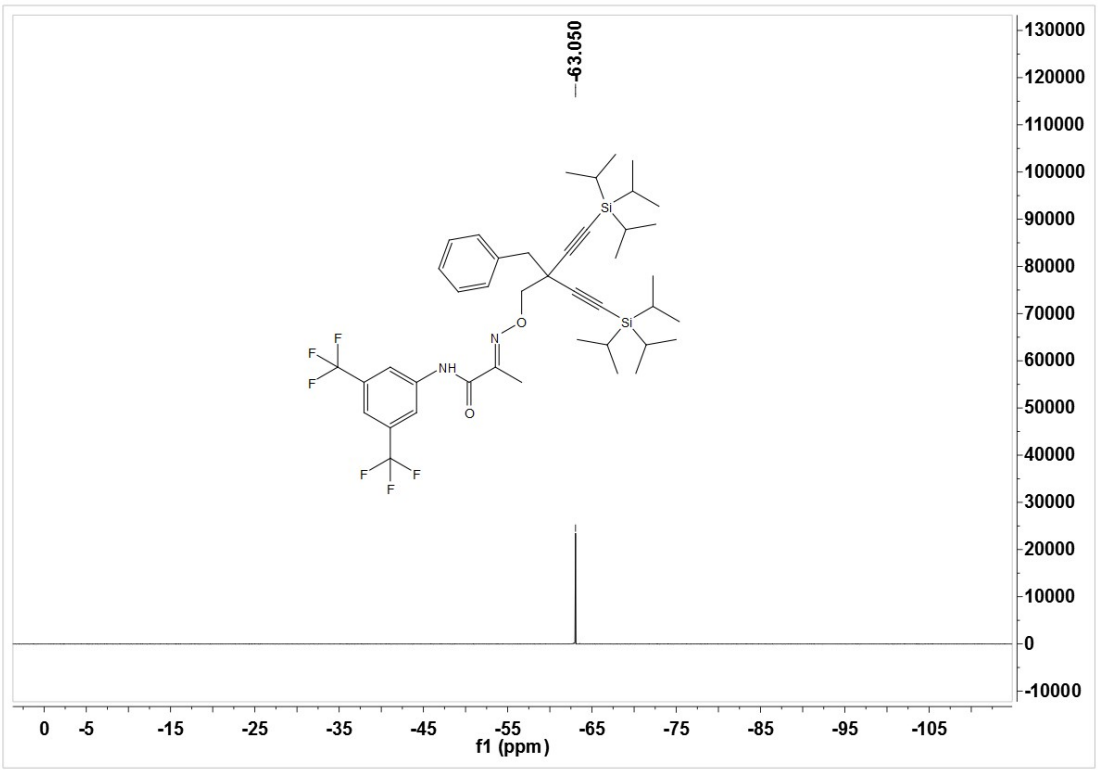
161.03
150.71
141.51
138.79
132.59
132.26
128.52
128.45
128.40
128.38
126.07
119.38
119.35
83.83
77.78
77.35
77.24
77.03
33.25
33.09
32.47
18.63
11.23
9.57
Si
O
N
NH
O
F
F
F
F
F
F
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.011
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

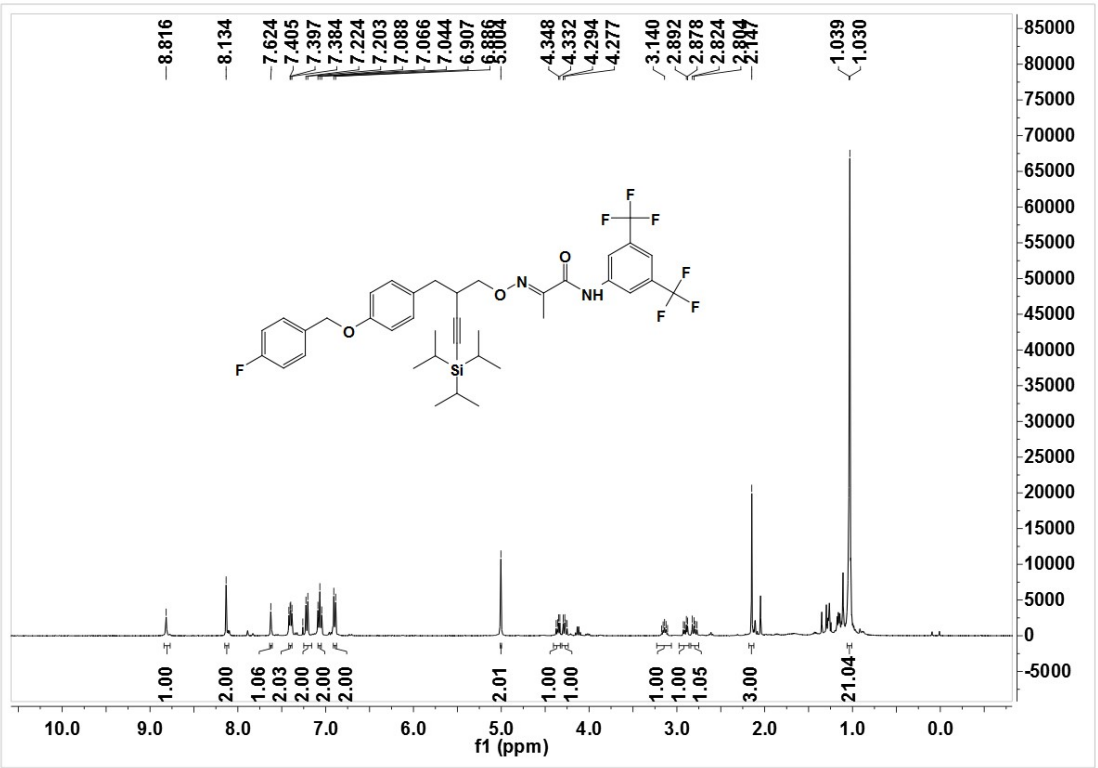
(*E*)-2-(((2-Benzyl-4-(triisopropylsilyl)-2-((triisopropylsilyl)ethynyl)but-3-yn-1-yl) oxy)imino)-N-(3,5-bis(trifluoromethyl)phenyl)propanamide (10b)

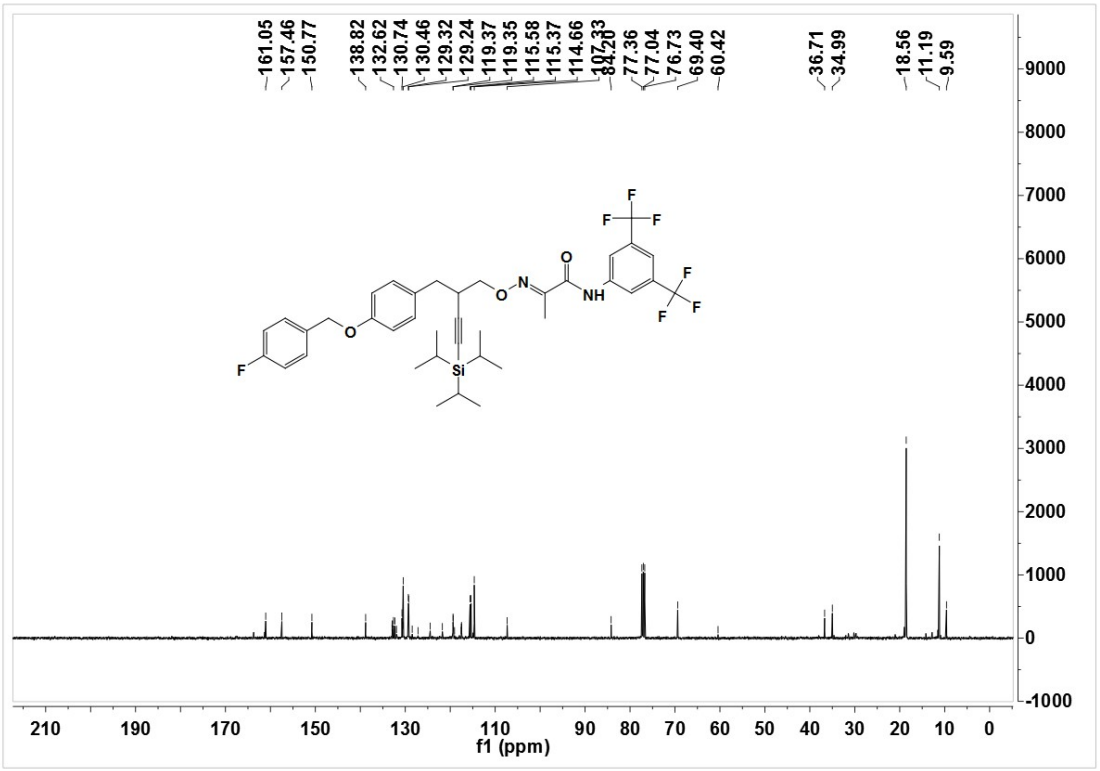






(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-((4-fluorobenzyl)oxy)benzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10c)

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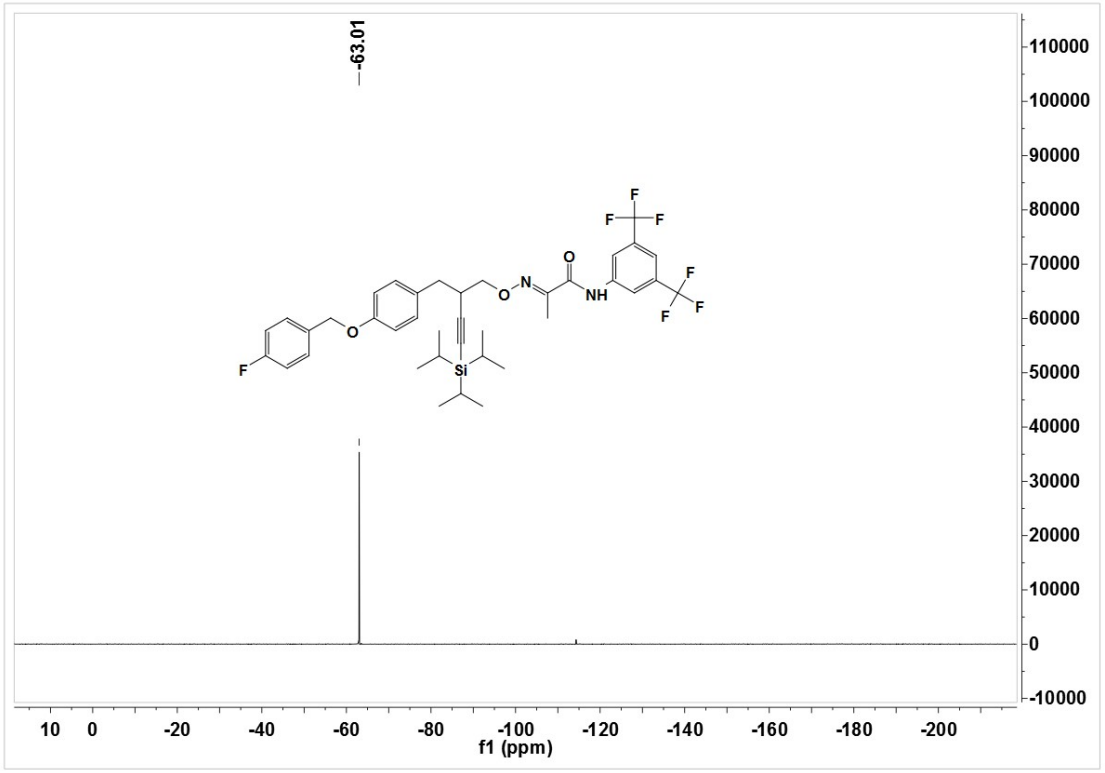
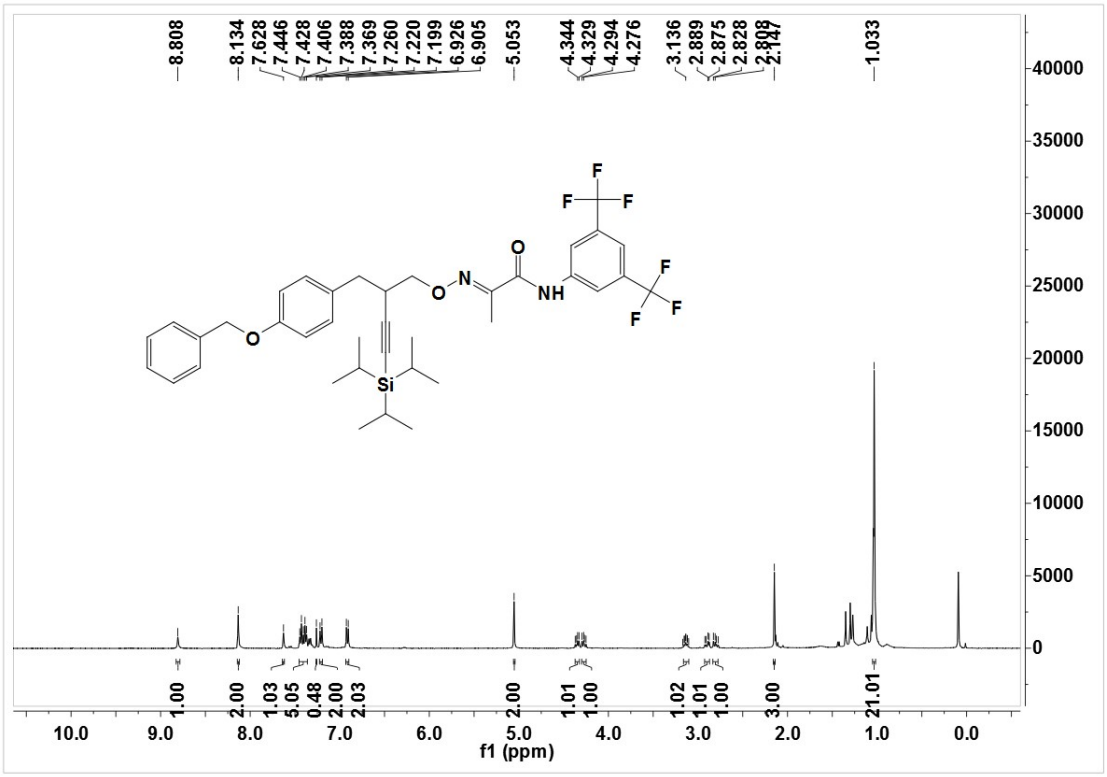
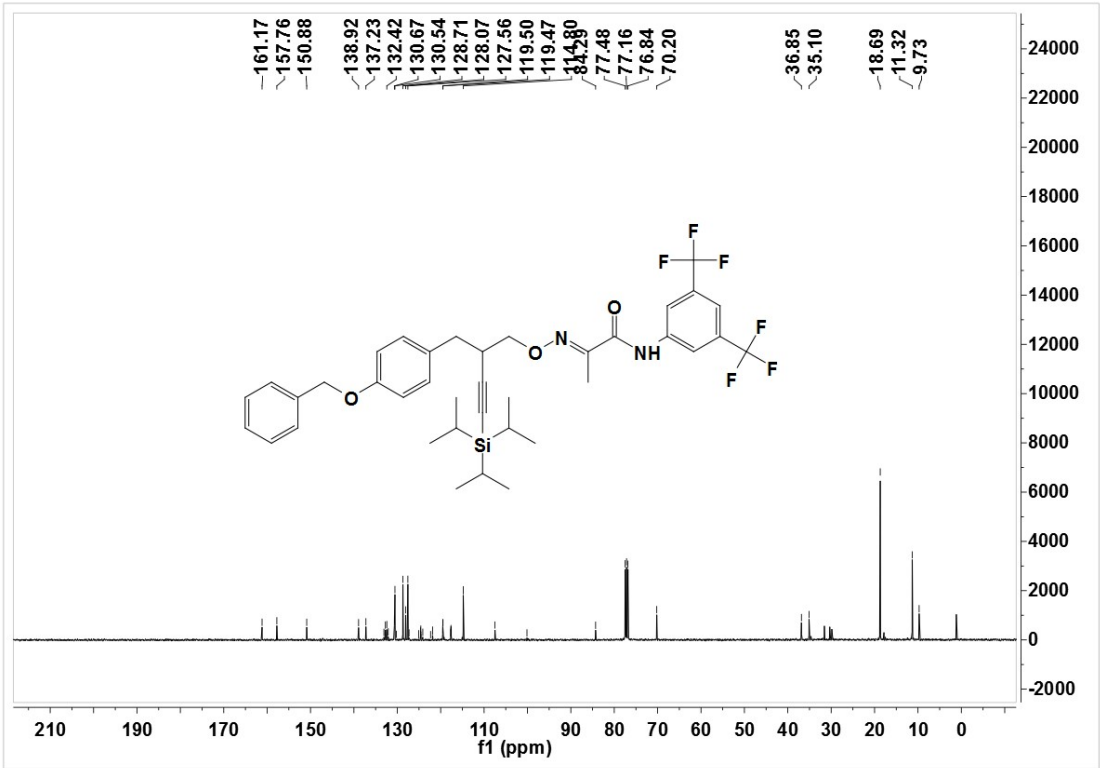
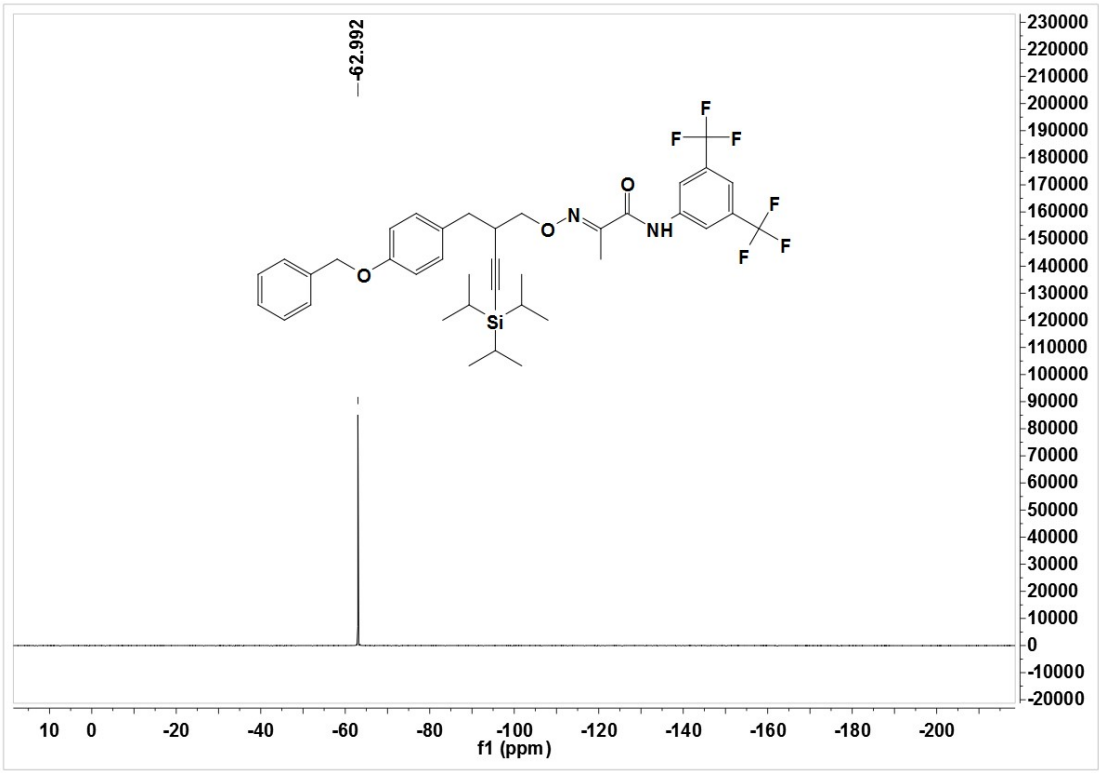
138.82
132.62
130.74
130.46
129.32
129.24
119.37
119.35
115.58
115.37
114.66
84.20
77.36
77.04
76.73
69.40
60.42
36.71
34.99
18.56
11.19
9.59
f1 (ppm)


-63.01
f1 (ppm)

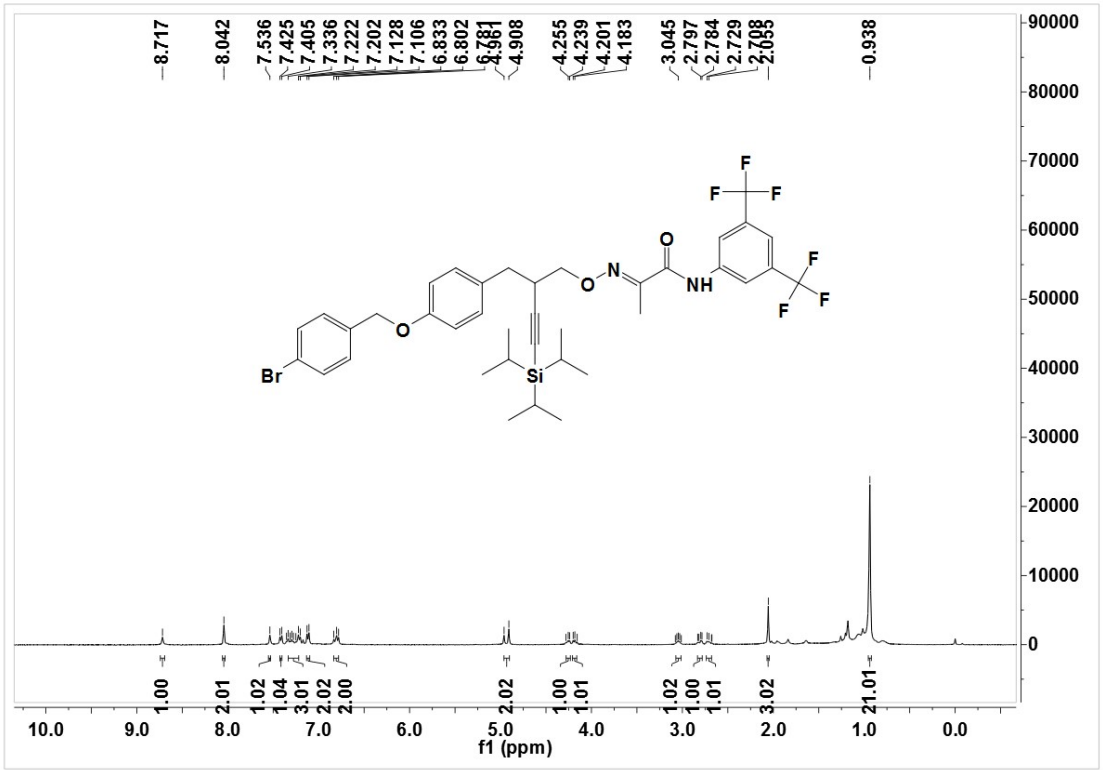
(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-phenoxybenzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10d)

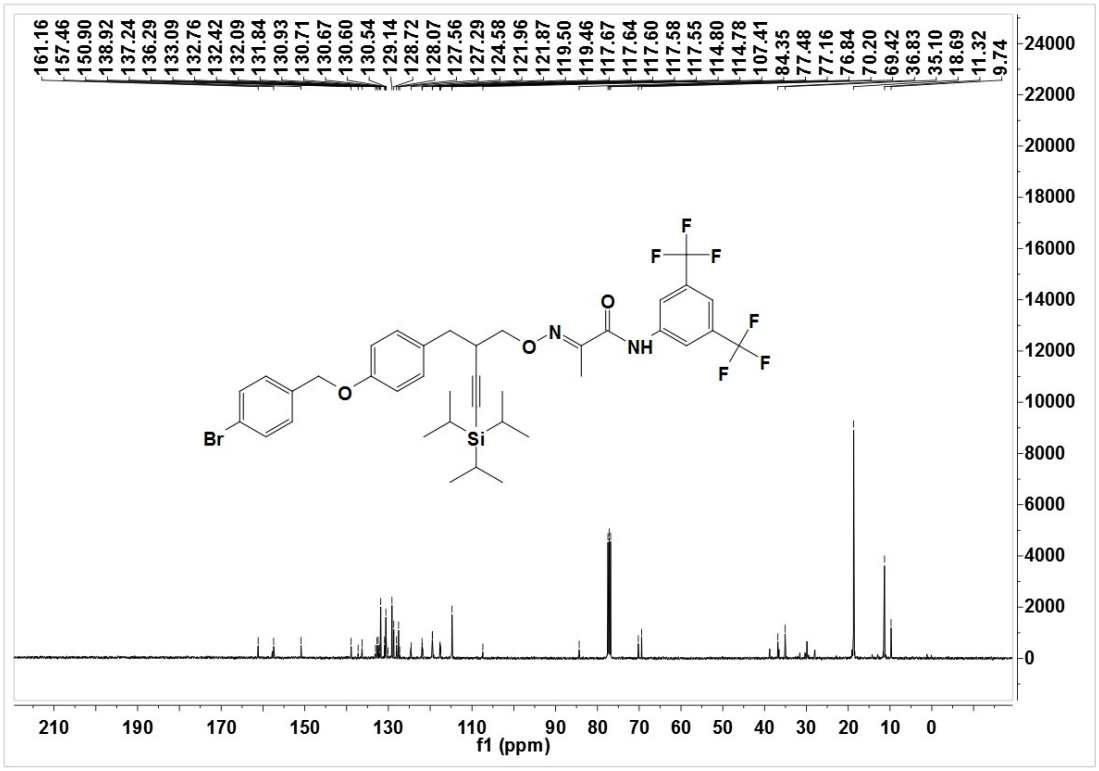






(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-((4-bromobenzyl)oxy)benzyl)-4-(triisopropylsilyl)but-3-yn-1-yl)oxy)imino)propanamide (10e)

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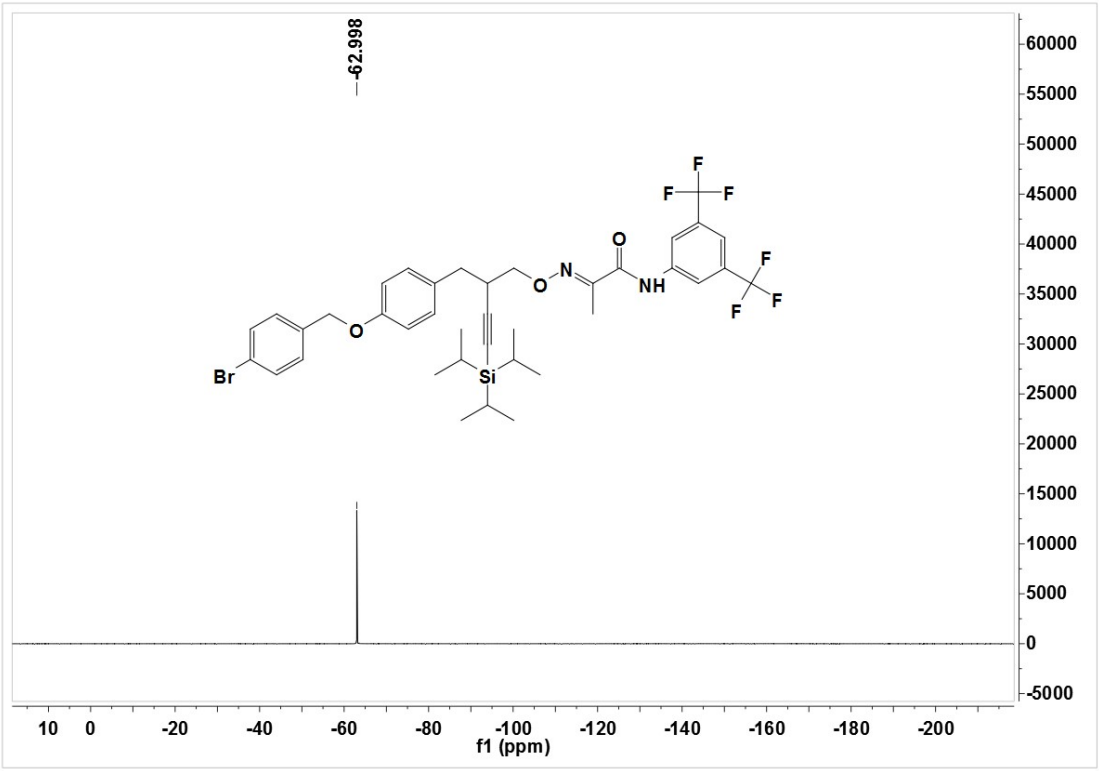
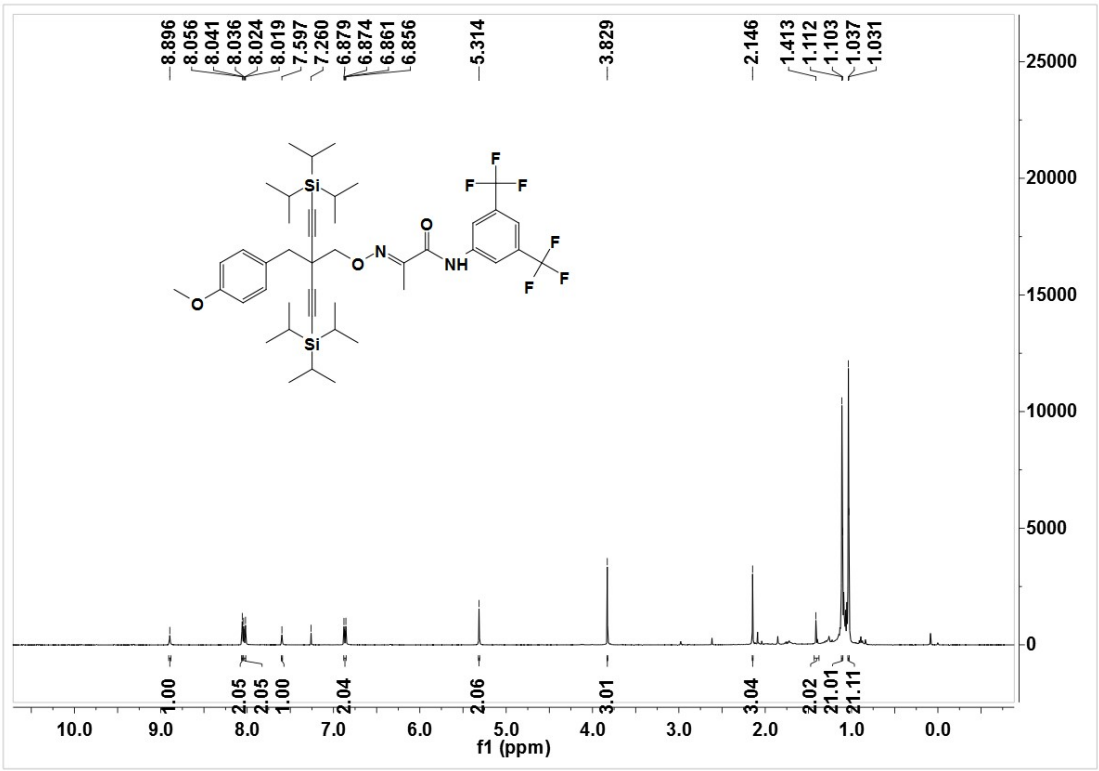
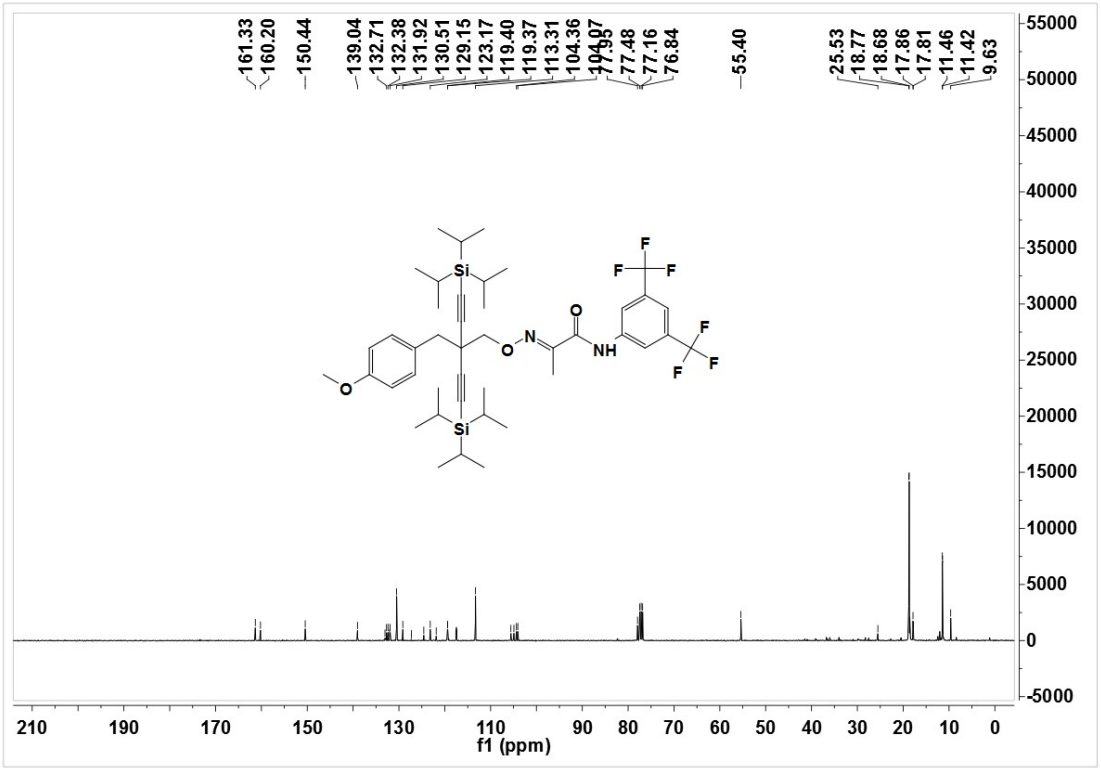
130.67
130.60
130.54
129.14
128.72
128.07
127.56
127.29
124.58
121.96
121.87
119.50
119.46
117.67
117.64
117.60
117.58
117.55
114.80
114.78
107.41
84.35
77.48
77.16
76.84
70.20
69.42
36.83
35.10
18.69
11.32
9.74
F
F
F
O
N
O
NH
F
F
F
O
Br
Si
f1 (ppm)

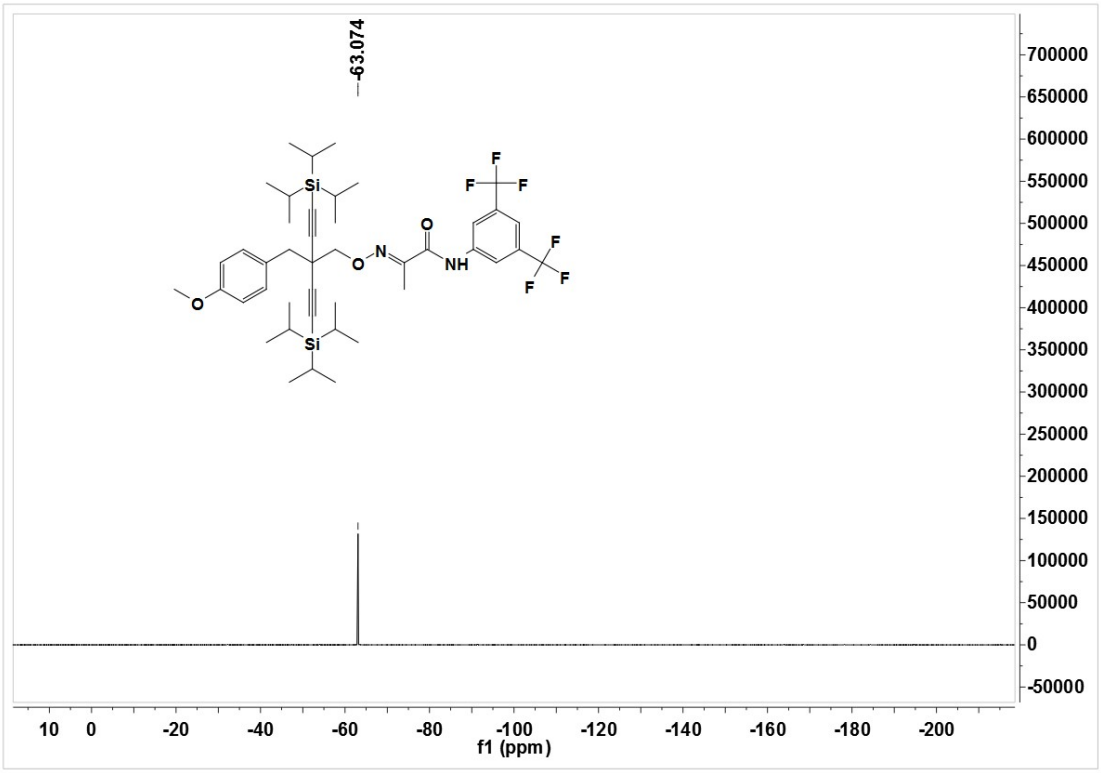

-62.998
F
F
F
O
N
O
NH
F
F
F
O
Br
Si
f1 (ppm)

(*E*)-N-(3,5-Bis(trifluoromethyl)phenyl)-2-(((2-(4-methoxybenzyl)-4-(triisopropylsi

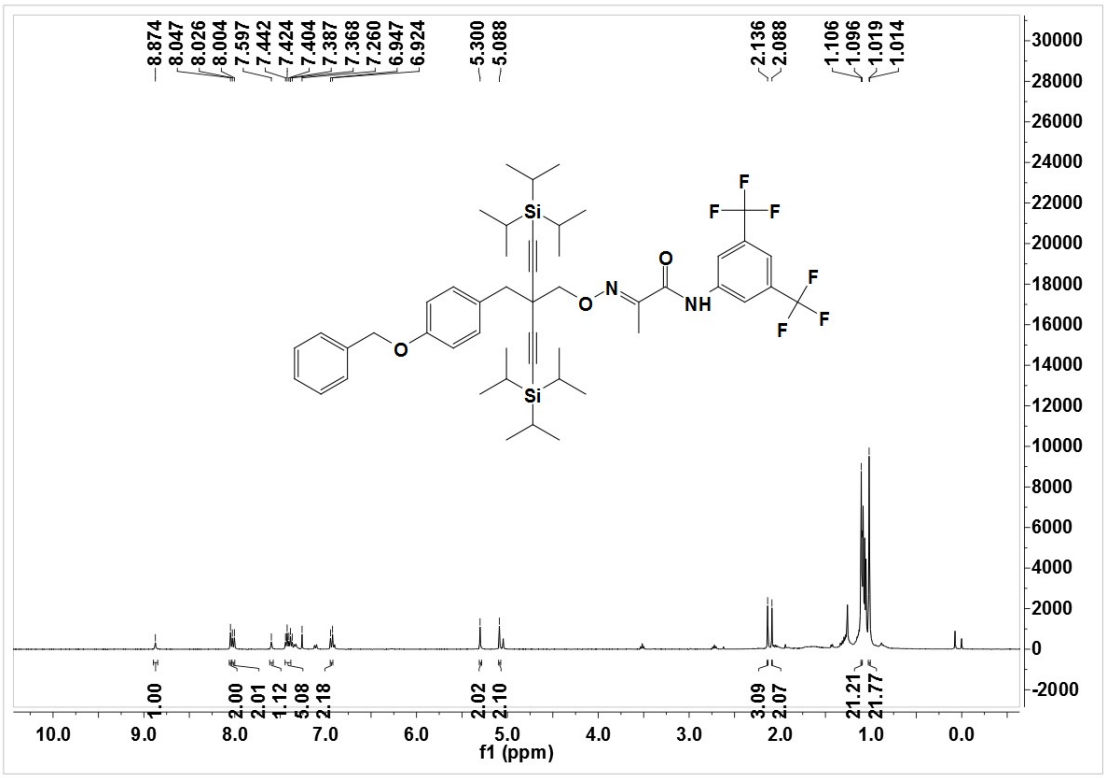
lyl)-2-((triisopropylsilyl)ethynyl)but-3-yn-1-yl)oxy)imino)propanamide (10f)







(*E*)-2-(((2-(4-(Benzyloxy)benzyl)-4-(triisopropylsilyl)-2-((triisopropylsilyl)ethynyl) but-3-yn-1-yl)oxy)imino)-N-(3,5-bis(trifluoromethyl)phenyl)propanamide (10g)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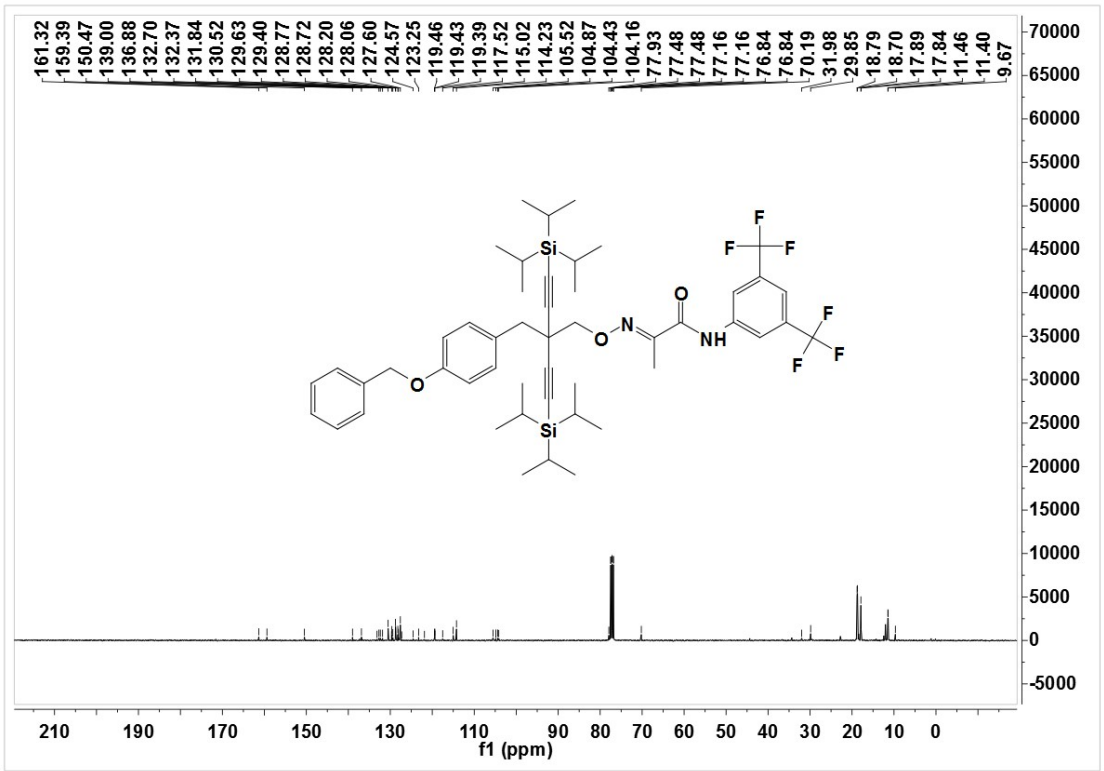
7.424
7.404
7.387
7.368
7.260
6.947
6.924
5.300
5.088
2.136
2.088
1.106
1.096
1.019
1.014
1.00
2.00
2.01
1.12
5.08
2.18
2.02
2.10
3.09
2.07
21.21
21.77
f1 (ppm)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128.06
127.60
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123.25
119.46
119.43
119.39
117.52
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105.52
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104.16
77.93
77.48
77.48
77.16
77.16
76.84
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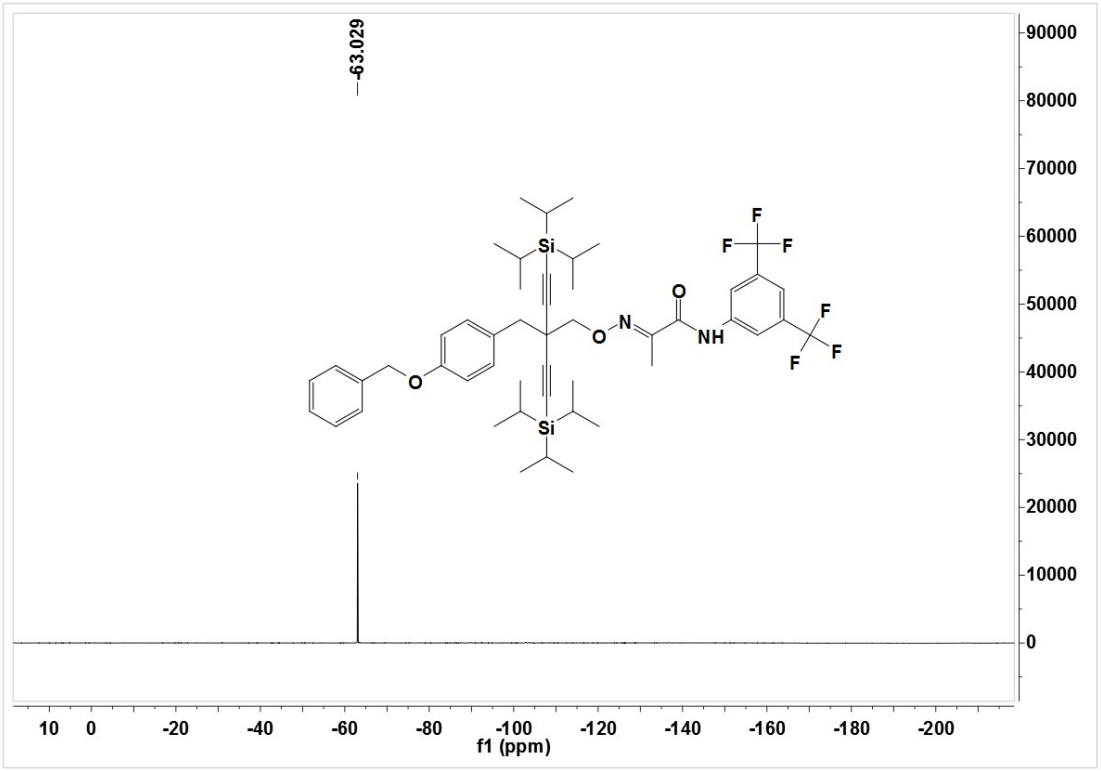
9.67
f1 (ppm)


-63.029
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60000
50000
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20000
10000
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10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)
Si
Si
O
O
N
NH
F
F
F
F
F
F