Supporting Information

Palladium-Catalyzed Highly Selective *gem*-Difluoroallylation of Propargyl Sulfonates with *gem*-Difluoroallylboron

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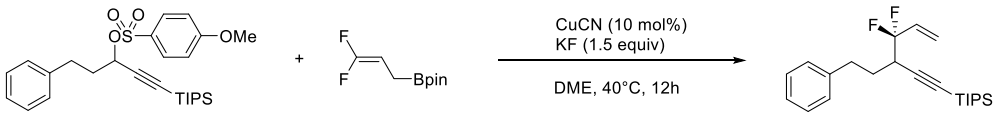
1. General Information and Materials

General Information: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent MR 400 and Agilent MR 500 spectrometer. ^{19}F NMR was recorded on an Agilent MR 400 spectrometer ($CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction. High-performance liquid chromatography was performed on Waters 2487-600E, Waters ACQUITY UPC2, and Agilent Series HPLC.

Materials: All reagents were used as received from commercial sources unless otherwise stated, or prepared as described in the literature. All solvents used in the reaction were anhydrous and purchased from J&K. KOH was purchased from Adamas and its purity is 99.999% metals basis.

2. Optimization of the Reaction Conditions

Cu-catalyzed *gem*-difluoroallylation of propargyl sulfonate 1a.[a]



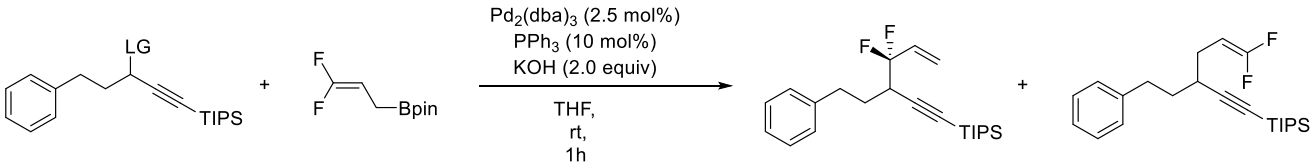
1a **2** **3a**, nd

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), DME (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

Optimizations for the Pd-catalyzed *gem*-difluoroallylation of propargyl sulfonate (Tables S1-S6):

To a 25 mL of Schlenk tube were added Pd_2dba_3 (2.5 mol %), base (2.0 equiv), and ligand (10 mol %). The mixture was evacuated and backfilled with argon three times. The solvent (2.0 mL) was added, and the solution was stirred for 5 minutes. Then, *gem*-difluoroallylboron **2** (1.5 equiv) was added, and the reaction mixture was stirred for 5 minutes. Secondary propargyl sulfonate **1a** (0.2 mmol, 1.0 equiv) was added slowly. The Schlenk tube was screw-capped. After stirring for 1 h at room temperature, the resulting mixture was filtered with a pad of celite. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard.

Table S1. Effect of the leaving groups on the reaction.[a]

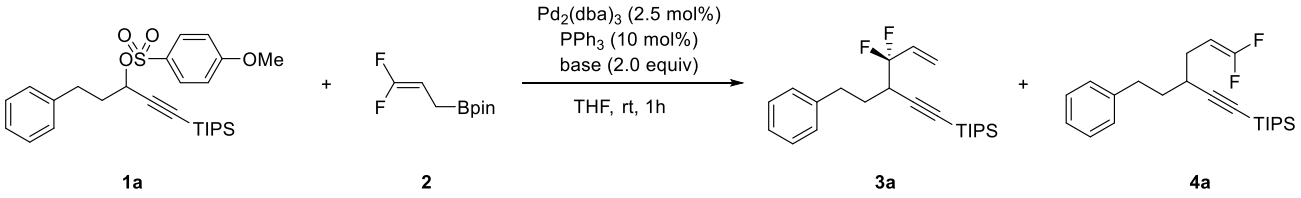


1a **2** **3a** **4a**

Entry	**1**, LG	**3a/4a**, yield (%)[b]	γ/α
1	**1ab**, OAc	nd	-
2	**1ac**, $^tBuCO_2$	nd	-
3	**1ad**, $PhCO_2$	nd	-
4	**1ae**, *p*-MeO-$PhCO_2$	nd	-
5	**1af**, *p*-MeO-$PhSO_2O$	66/6	11:1

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), THF (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

Table S2. Effect of the bases on the reaction.[a]

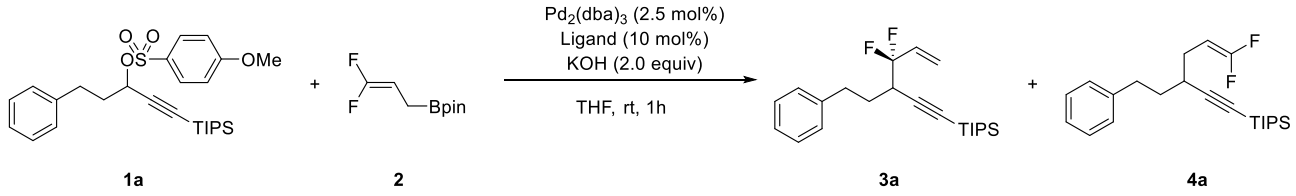


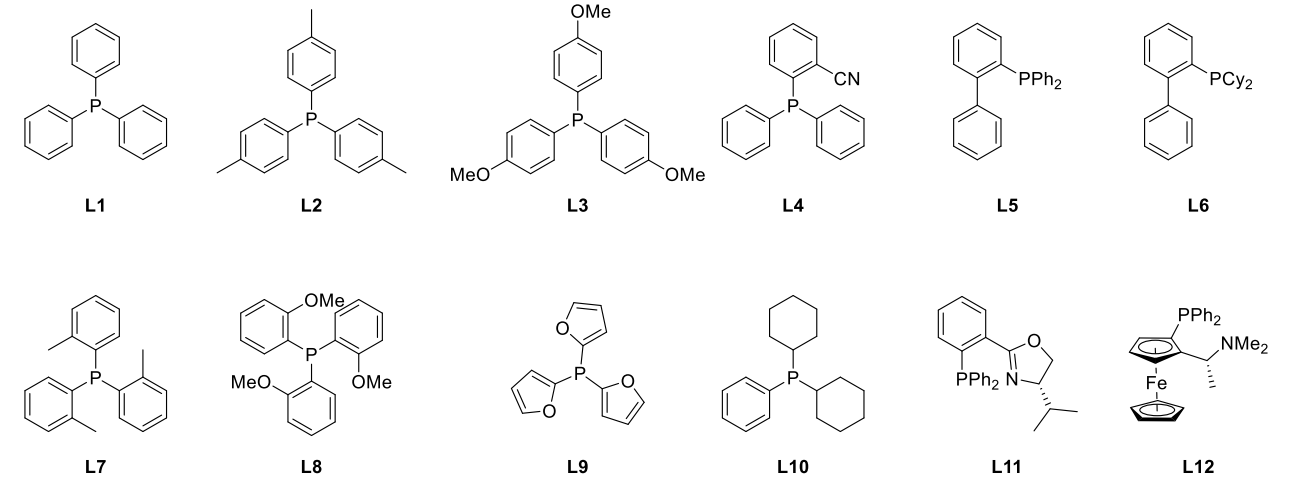
1a **2** **3a** **4a**

Entry	Base	**3a/4a**, yield (%)[b]	γ/α
1	KOH	66/6	11:1
2	NaOH	48/2	24:1
3	K_2CO_3	nd	-
4	Cs_2CO_3	nd	-
5	K_3PO_4	nd	-
6	KF	nd	-
7	LiF	nd	-
8	LiOMe	nd	-
9	LiO^{t}Bu	18/2	9:1

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), THF (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

Table S3. Effect of the ligands on the reaction.[a]

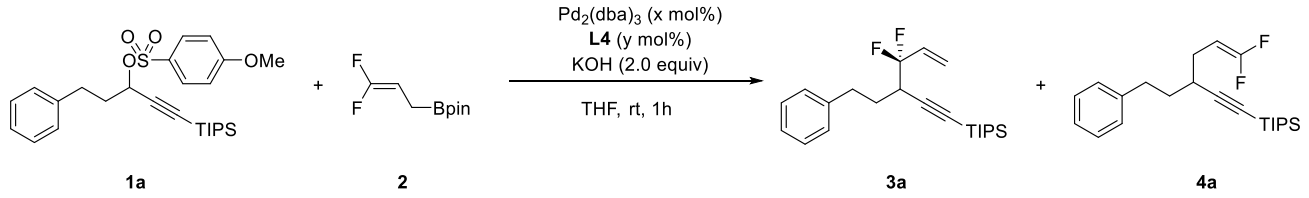




Entry	**Ligand**	**3a/4a**, yield (%)[b]	γ/α
1	**L1**	66/6	11:1
2	**L2**	62/8	7.7:1
3	**L3**	62/16	3.8:1
4	**L4**	80/4	20:1
5	**L5**	9/2	4.5:1
6	**L6**	nd	-
7	**L7**	nd	-
8	**L8**	10/8	1.2:1
9	**L9**	56/8	7:1
10	**L10**	2/0	-
11	**L11**	nd	-
12	**L12**	nd	-

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), THF (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

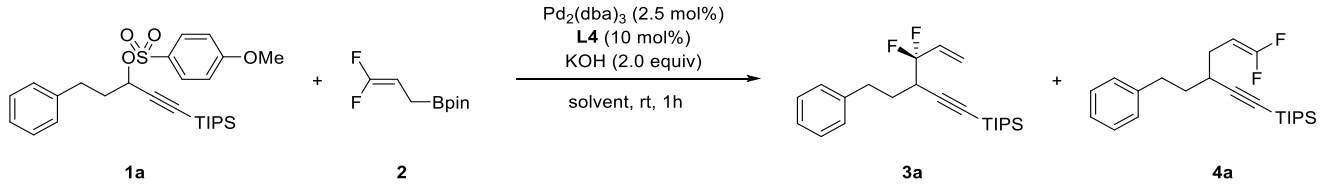
Table S4. Effect of the loading amount of the Pd-catalyst on the reaction.[a]



Entry	$Pd_2(dba)_3$ (x mol%)	**L4** (y mol%)	**3a/4a**, yield (%)[b]	γ/α
1	0.5	2	nd	-
2	0.75	3	42/6	7:1
3	1	4	48/6	8:1
4	1.25	5	58/4	14.5:1
5	2.5	10	80/4	20:1
6	5	20	80/4	20:1

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), THF (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

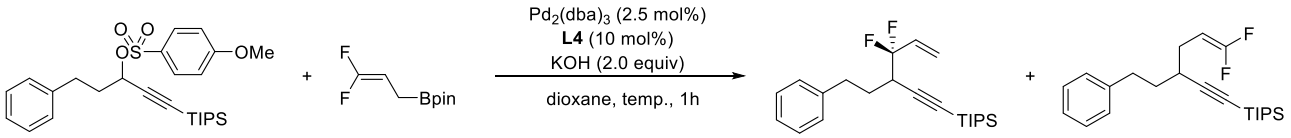
Table S5. Effect of the solvents on the reaction.[a]



Entry	Solvent	**3a/4a**, yield (%)[b]	γ/α
1	THF	80/4	20:1
2	Dioxane	92/4	23:1
3	DME	92/12	7.7:1
4	MeOH	nd	-
5	MeCN	22/6	3.7:1
6	DMF	4/0	-
7	DMSO	6/2	3:1
8	DCM	20/6	3.3:1
9	2-MeTHF	66/6	11:1
10	CPME	66/14	4.7:1

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), solvent (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

Table S6. Effect of the reaction temperature on the reaction.[a]

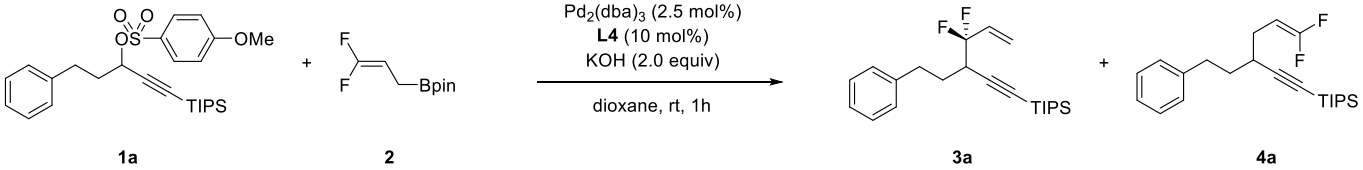


1a 2 3a 4a

Entry	Temp (°C)	**3a/4a**, yield (%)[b]	γ/α
1	rt	92/4	23:1
2	0	20/2	10:1
3	40	48/4	12:1

[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), dioxane (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nd = not detected.

Table S7. Control experiments.[a]

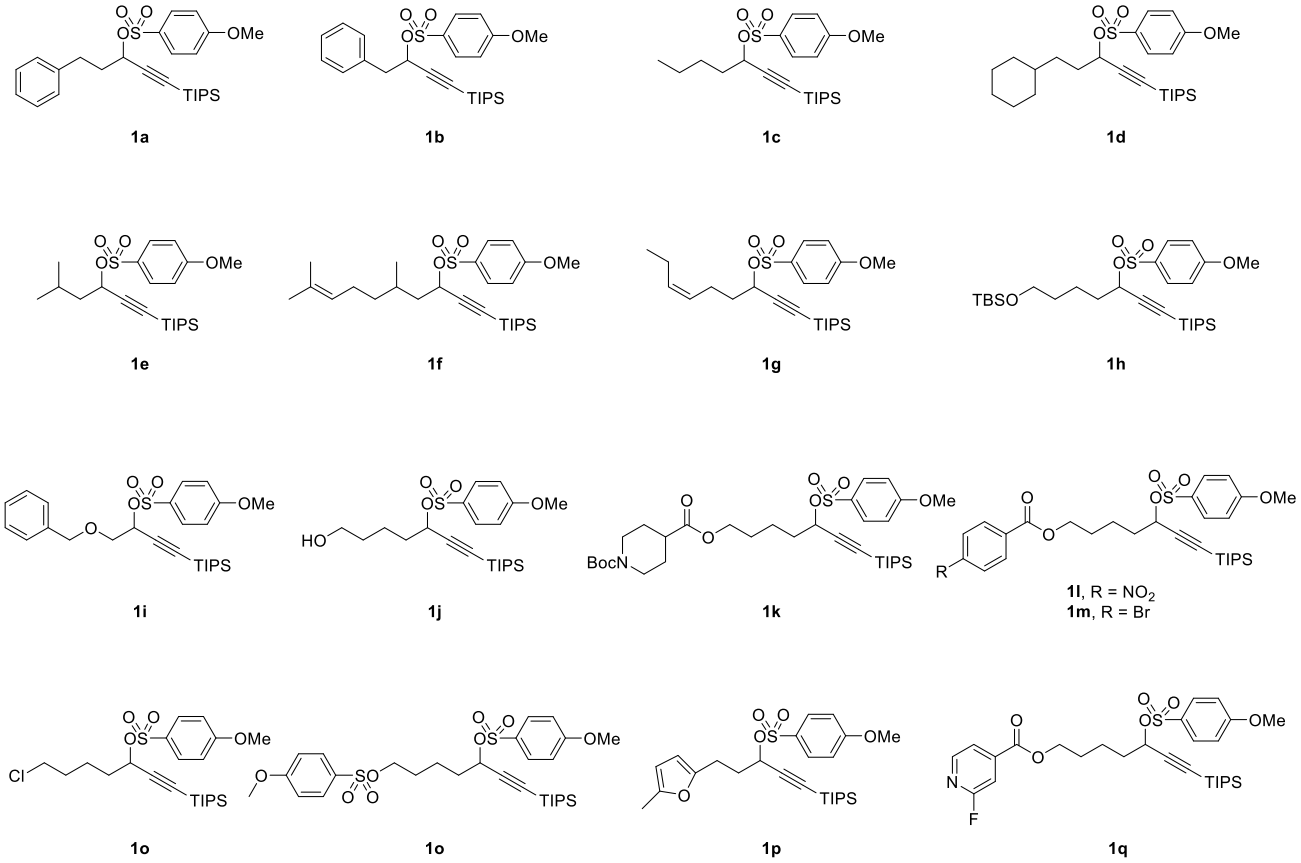


1a 2 3a 4a

Entry	Conditions	**3a/4a**, yield (%)[b]	γ/α
1	---	92(90)/4	23:1
2	No Pd catalyst	nd	-
3	No ligand	nd	-
4	No KOH	nd	-
5	aerobic condition	18/4	4.5:1
6	H_2O (0.56 equiv) was added	72/6	12:1
7	H_2O (0.83 equiv) was added	72/6	12:1
8	H_2O (1.11 equiv) was added	72/6	12:1
9	H_2O (1.39 equiv) was added	74/6	12.3:1

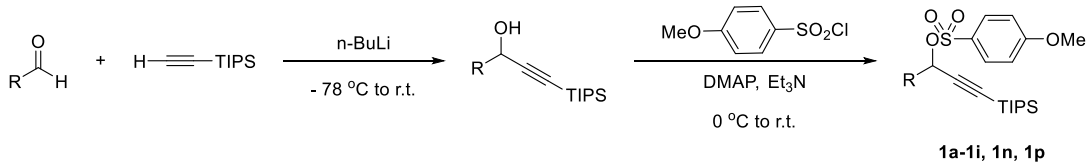
[a]Reaction conditions (unless otherwise specified): **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), dioxane (2 mL). [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard, and the number in parenthesis is the isolated yield. nd = not detected.

3. Procedure for the Preparation of Propargyl Sulfonates 1

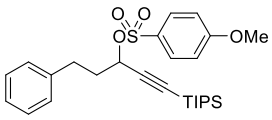


Structure of Propargyl Sulfonates 1

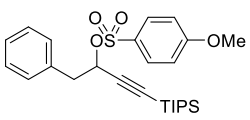
3.1 Synthesis of compounds 1a-1i, 1n, and 1p



General procedure for the preparation of secondary propargyl sulfonates 1. To a solution of triisopropyl acetylene (1.4 mL, 6.25 mmol, 1.25 equiv) in THF (20 mL) was added dropwise *n*-butyllithium (2.6 mL, 2.5 M in hexane, 6.5 mmol, 1.3 equiv) at -78 °C under Ar. The reaction was stirred at -78 °C for 0.5 h and room temperature for another 1 h. Then the mixture was cooled to -78 °C, and aldehyde (0.66 mL, 5 mmol, 1.0 equiv, in 20 mL THF) was added slowly. After stirring at room temperature for 1 h, the reaction was quenched by saturated NH_4Cl solution, extracted with ethyl acetate (30 mL× 2), and concentrated to afford the secondary propargyl alcohol. To a solution of the alcohol in dry DCM (5 mL) were added DMAP (30.5 mg, 0.25 mmol, 0.05 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv). Then, 4-methoxybenzenesulfonyl chloride (1.10 g, 5.5 mmol, 1.1 equiv) was slowly added at 0 °C. After stirring at room temperature overnight, the reaction was quenched by saturated NH_4Cl solution, extracted with DCM (30 mL× 2), and concentrated to afford the crude product. The residue was purified by flash column chromatography to give product **1a**.

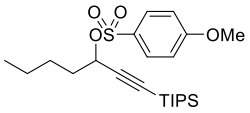


5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1a). The compound **1a** was obtained in 88% yield (2.14 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.24 - 7.17 (m, 3H), 6.97 (d, *J* = 9.0 Hz, 2H), 5.11 (t, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 2.88 - 2.77 (m, 2H), 2.23 - 2.11 (m, 2H), 1.05 - 0.96 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 140.3, 130.1, 128.5, 128.4, 128.3, 126.2, 114.2, 101.8, 90.2, 71.3, 55.5, 38.0, 30.9, 18.4, 10.9. MS (DART): m/z (%) 504 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{27}H_{42}O_4NSSi$: 504.2598; Found: 504.2597.

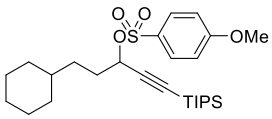


1-Phenyl-4-(triisopropylsilyl)but-3-yn-2-yl 4-methoxybenzenesulfonate (1b). The product was obtained in 81% yield (1.92 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.31 - 7.26 (m, 1H), 7.25 - 7.21 (m, 4H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.22 (dd,

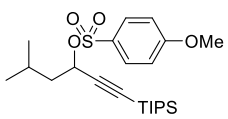
J = 7.4, 6.3 Hz, 1H), 3.85 (s, 3H), 3.22 - 3.07 (m, 2H), 0.96 - 0.91 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 134.7, 130.0, 129.8, 128.4, 128.3, 127.1, 114.2, 101.6, 90.8, 72.2, 55.5, 42.6, 18.4, 10.9. MS (DART): m/z (%) 490 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{26}H_{40}O_4NSSi$: 490.2442; Found: 490.2441.



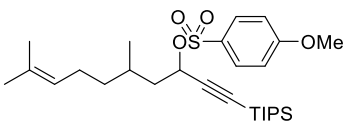
1-(Triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1c). The product was obtained in 87% yield (1.91 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.07 (t, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 1.89 - 1.79 (m, 2H), 1.48 - 1.42 (m, 2H), 1.37 - 1.31 (m, 2H), 0.99 - 0.92 (m, 21H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 130.1, 128.7, 114.2, 102.3, 89.7, 72.1, 55.5, 36.0, 26.8, 22.0, 18.4, 13.8, 11.0. MS (DART): m/z (%) 456 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{42}O_4NSSi$: 456.2598; Found: 456.2599.



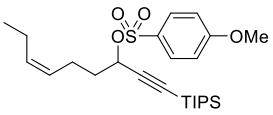
5-Cyclohexyl-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1d). The product was obtained in 34% yield (0.82 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.05 (t, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 1.89 - 1.81 (m, 2H), 1.70 - 1.61 (m, 5H), 1.37 - 1.31 (m, 2H), 1.26 - 1.14 (m, 4H), 0.99 - 0.91 (m, 21H), 0.89 - 0.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 130.1, 128.7, 114.2, 102.3, 89.7, 72.1, 55.5, 37.0, 33.8, 33.2, 33.1, 32.2, 26.5, 26.2, 18.4, 10.9. MS (DART): m/z (%) 510 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{27}H_{48}O_4NSSi$: 510.3068; Found: 510.3065.



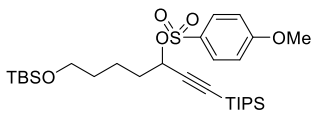
5-Methyl-1-(triisopropylsilyl)hex-1-yn-3-yl 4-methoxybenzenesulfonate (1e). The product was obtained in 99% yield (2.52 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.12 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 1.92 - 1.78 (m, 2H), 1.70 - 1.63 (m, 1H), 0.97 - 0.91 (m, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 130.1, 128.7, 114.2, 102.5, 89.7, 70.9, 55.5, 45.1, 24.5, 22.3, 22.1, 18.4, 10.9. MS (DART): m/z (%) 456 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{42}O_4NSSi$: 456.2598; Found: 456.2598.



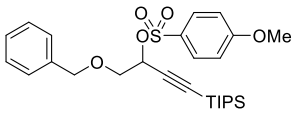
5,9-Dimethyl-1-(triisopropylsilyl)dec-8-en-1-yn-3-yl 4-methoxybenzenesulfonate (1f). The product was obtained in 60% yield (1.52 g, dr = 63:37) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.83 (m, 2H), 7.00 - 6.92 (m, 2H), 5.18 - 5.10 (m, 1H), 5.10 - 5.04 (m, 1H), 3.86 (s, 3H), 2.00 - 1.90 (m, 2H), 1.75 - 1.65 (m, 5H), 1.62 - 1.56 (m, 4H), 1.40 - 1.30 (m, 1H), 1.23 - 1.11 (m, 1H), 0.98 - 0.90 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ Major: 163.6, 131.4, 130.1, 128.8, 124.3, 114.3, 102.3, 89.9, 71.1, 55.5, 43.3, 36.8, 29.2, 25.7, 25.2, 19.1, 18.4, 17.6, 10.9. Minor: 163.6, 131.4, 130.1, 128.8, 124.3, 114.3, 102.7, 89.9, 70.7, 55.5, 43.7, 36.7, 28.9, 25.7, 25.3, 19.1, 18.4, 17.6, 10.9. MS (DART): m/z (%) 524 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{28}H_{50}O_4NSSi$: 524.3224; Found: 524.3224.



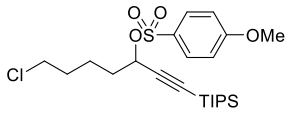
(*Z*)-1-(Triisopropylsilyl)non-6-en-1-yn-3-yl 4-methoxybenzenesulfonate (1g). The product was obtained in 99% yield (2.38 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.46 - 5.38 (m, 1H), 5.32 - 5.24 (m, 1H), 5.09 (t, *J* = 6.5 Hz, 1H), 3.86 (s, 3H), 2.26 - 2.18 (m, 2H), 2.07 - 1.99 (m, 2H), 1.93 - 1.86 (m, 2H), 0.99 - 0.92 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 133.4, 130.1, 128.6, 126.6, 114.3, 102.1, 89.9, 71.6, 55.5, 36.4, 22.5, 20.5, 18.4, 14.2, 10.9. MS (DART): m/z (%) 482 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{25}H_{44}O_4NSSi$: 482.2755; Found: 482.2751.



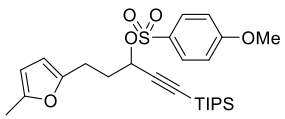
7-((Tert-butyldimethylsilyl)oxy)-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1h). The reaction was carried out on an 18.6 mmol scale. Compound **1h** was obtained in 52.4% yield (5.54 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.08 (t, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.61 - 3.57 (m, 2H), 1.93 - 1.83 (m, 2H), 1.55 - 1.48 (m, 4H), 0.99 - 0.93 (m, 21H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 130.1, 128.7, 114.3, 102.2, 89.7, 72.0, 62.9, 55.5, 36.2, 32.1, 26.0, 21.3, 18.4, 18.3, 10.9, -5.3.



1-(Benzyloxy)-4-(triisopropylsilyl)but-3-yn-2-yl 4-methoxybenzenesulfonate (1i). Compound **1i** was obtained in 99% yield (2.52 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.37 - 7.26 (m, 5H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.28 (dd, *J* = 7.2Hz, 4.4 Hz, 1H), 4.62 - 4.53 (m, 2H), 3.84 (s, 3H), 3.79 - 3.69 (m, 2H), 0.97 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 137.5, 130.1, 128.3, 128.3, 127.6, 127.5, 114.2, 99.6, 91.0, 73.2, 72.8, 70.5, 55.5, 18.3, 10.8.

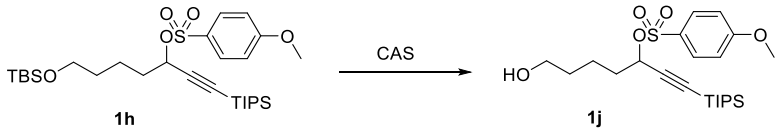


7-Chloro-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1n). Compound **1n** was obtained in 99% yield (2.48 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.10 (t, *J* = 6.2 Hz, 1H), 3.86 (s, 3H), 3.51 (t, *J* = 6.2 Hz, 2H), 1.93 - 1.85 (m, 2H), 1.84 - 1.74 (m, 2H), 1.70 - 1.60 (m, 2H), 1.00 - 0.92 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 130.1, 128.5, 114.3, 101.8, 90.2, 71.6, 55.6, 44.5, 35.6, 31.8, 22.2, 18.6, 10.9. MS (DART): m/z (%) 490 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{41}O_4NClSSi$: 490.2209; Found: 490.2210.



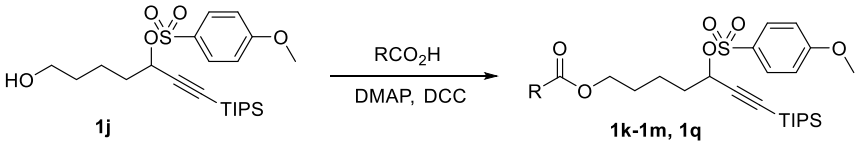
5-(5-Methylfuran-2-yl)-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1p). Compound **1p** was obtained in 99% yield (2.50 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.88 (d, *J* = 3.0 Hz, 1H), 5.84 (d, *J* = 3.0 Hz, 1H), 5.12 (t, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 2.80 - 2.73 (m, 2H), 2.24 (s, 3H), 2.22 - 2.11 (m, 2H), 1.00 - 0.39 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 151.9, 150.7, 130.1, 128.5, 114.3, 106.2, 105.9, 101.8, 90.2, 71.1, 55.5, 34.9, 23.5, 18.4, 13.5, 10.9. MS (DART): m/z (%) 508 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{26}H_{42}O_5NSSi$: 508.2547; Found: 508.2548.

3.2 Synthesis of compound 1j

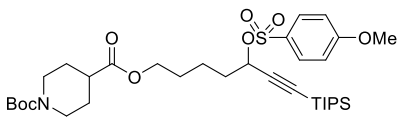


7-Hydroxy-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1j). To a solution of compound **1h** (11.4 g, 20 mmol, 1.0 equiv) in CH_3OH/DCM (50 mL, v:v = 5:1) was added slowly *D*-camphor sulfonic acid (CAS) (2.3 g, 10 mmol, 0.5 equiv) at 0 °C. After stirring for 1.5 h at 0 °C, the reaction was quenched with triethylamine (2.8 mL, 20 mmol, 1.0 equiv). The resulting mixture was concentrated and purified by flash column chromatography on silica gel (hexane/EtOAc = 3:1) to give compound **1j** (3.10 g, 34% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.09 (t, *J* = 6.4 Hz, 1H), 3.86 (s, 3H), 3.65 - 3.60 (m, 2H), 1.95 - 1.84 (m, 2H), 1.62 (br s, 1H), 1.61 - 1.52 (m, 4H), 0.98 - 0.92 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 130.1, 128.5, 114.3, 102.1, 89.9, 71.8, 62.6, 55.6, 36.1, 31.9, 21.1, 18.4, 10.9. MS (DART): m/z (%) 472 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{42}O_5NSSi$: 472.2547; Found: 472.2552.

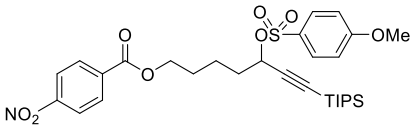
3.3 Synthesis of esters 1k-1m and 1q



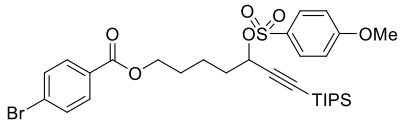
Typical procedure for the synthesis of esters 1k.[1] To a solution of compound **1j** (0.91 g, 2 mmol, 1.0 equiv) in dry DCM (5 mL) was added N-Boc-piperidine-4-carboxylic acid (0.92 g, 4 mmol, 2.0 equiv) and DMAP (24.4 mg, 0.2 mmol, 0.1 equiv). To the resulting mixture was added a solution of DCC (0.83 g, 4 mmol, 2 equiv) in DCM (5 mL). After stirring overnight at room temperature, the reaction mixture was filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give compound **1k**.



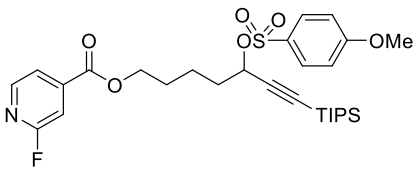
1-(*tert*-Butyl) 4-(5-(((4-methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl) piperidine-1,4-dicarboxylate (1k). Compound **1k** was obtained in 85% yield (1.13 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.09 (t, *J* = 6.5 Hz, 1H), 4.12 – 3.94 (m, 4H), 3.86 (s, 3H), 2.88 - 2.75 (m, 2H), 2.49 - 2.39 (m, 1H), 1.93 - 1.82 (m, 4H), 1.66 - 1.55 (m, 6H), 1.45 (s, 9H), 1.01 - 0.91 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 163.6, 154.7, 130.1, 128.4, 114.3, 101.8, 89.9, 79.5, 71.5, 64.2, 55.6, 43.4, 41.1, 35.9, 28.4, 27.9, 27.9, 21.3, 18.4, 10.9. MS (DART): m/z (%) 666 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{34}H_{56}O_8NSSi$: 666.3490; Found: 666.3492.



5-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 4-nitrobenzoate (1l). The reaction was conducted on a 1.2 mmol scale. Compound **1l** was obtained in 57% yield (0.41 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.13 (t, *J* = 6.4 Hz, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 2.00 - 1.91 (m, 2H), 1.88 - 1.81 (m, 2H), 1.73 - 1.65 (m, 2H), 0.96 - 0.91 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 163.7, 150.5, 135.6, 130.7, 130.1, 128.4, 123.5, 114.3, 101.8, 90.0, 71.4, 65.6, 55.6, 35.9, 27.9, 21.3, 18.4, 10.9. MS (DART): m/z (%) 621 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{30}H_{45}O_8N_2SSi$: 621.2660; Found: 621.2665.

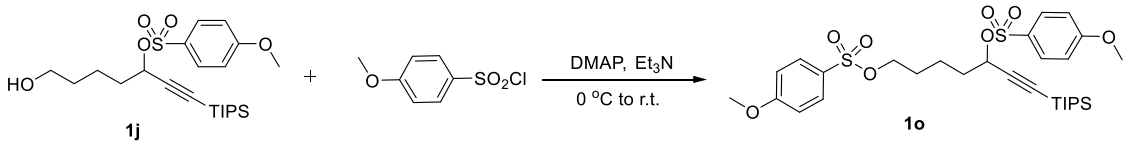


6-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 4-cyanobenzoate (1m). The reaction was conducted on a 2.0 mmol scale. Compound **1m** was obtained in 58% yield (0.74 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.83 (m, 4H), 7.57 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.12 (t, *J* = 6.4 Hz, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.02 - 1.89 (m, 2H), 1.87 - 1.75 (m, 2H), 1.70 - 1.63 (m, 2H), 0.97 - 0.89 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 163.6, 131.7, 131.1, 130.1, 129.2, 128.4, 128.0, 114.3, 101.8, 90.0, 71.5, 64.9, 55.6, 35.9, 28.0, 21.4, 18.4, 10.9. MS (DART): m/z (%) 654 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{30}H_{45}O_6NBrSSi$: 654.1915; Found: 654.1916.



5-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 2-fluoroisonicotinate (1q). The reaction was conducted on a 1.0 mmol scale.Compound **1q** was obtained in 87% yield (0.50 g) as a colorless oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.2 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 5.2 Hz, 1H), 7.48 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.13 (t, *J* = 6.3 Hz, 1H), 4.36 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 1.99 - 1.90 (m, 2H), 1.88 - 1.79 (m, 2H), 1.71 - 1.63 (m, 2H), 0.96 - 0.91 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1 (d, *J* = 240.6 Hz), 163.7 (d, *J* = 4.0 Hz), 163.6, 148.5 (d, *J* = 15.1 Hz), 142.8, 130.0, 128.3, 120.7, 114.3, 109.8, 109.3, 101.7, 90.0, 71.4, 65.8, 55.5, 35.8, 27.8, 21.3, 18.3, 10.8. MS (DART): m/z (%) 578 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{29}H_{41}O_6NFSSi$: 578.2402; Found: 578.2393.

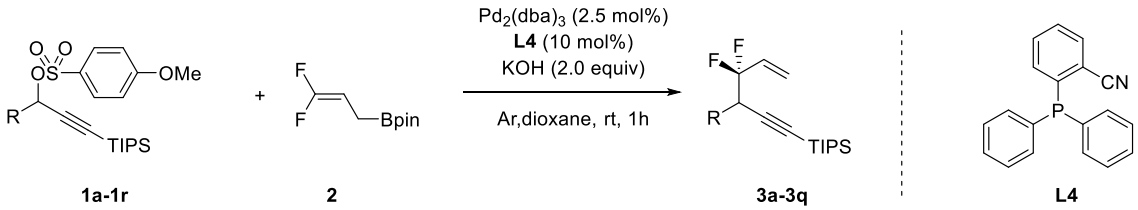
3.4 Synthesis of compound 1o



7-(Triisopropylsilyl)hept-6-yne-1,5-diyl bis(4-methoxybenzenesulfonate) (1o). To a solution of **1j** (3.0 g, 6 mmol, 1.0 equiv) in DCM (20 mL) were added DMAP (80.6 mg, 0.66 mmol, 0.1 equiv) and triethylamine (1 mL, 7.26 mmol, 1.1 equiv) at 0 °C. 4-Methoxybenzenesulfonyl chloride (1.50 g, 7.26 mmol, 1.1 equiv) was then added. After stirring for 1 h at 0 °C, the reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 40:1) to give compound **1o** (2.58 g, 69% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 4H), 7.04 - 6.99 (m, 2H), 6.98 - 6.94 (m, 2H), 5.03 (t, *J* = 6.1 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 1.86 - 1.75 (m, 2H), 1.72 - 1.63 (m, 2H), 1.55 - 1.45 (m, 2H), 0.98 - 0.91 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 163.7, 130.1, 130.1, 128.4, 127.4, 114.5, 114.3, 101.7, 90.2, 71.4, 69.7, 55.7, 55.6, 35.6, 28.2, 20.9,

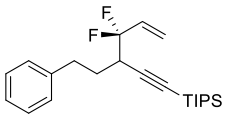
18.4, 10.9. MS (DART): m/z (%) 642 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{30}H_{48}O_8NS_2Si$: 642.2585; Found: 642.2588.

4. General Procedure for the Pd-Catalyzed *gem*-Difluoroallylation of Propargyl Sulfonates 1 and Characterization Data for Compounds 3.

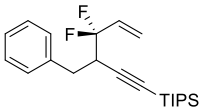


To a 25 mL of Schlenk tube were added Pd_2dba_3 (9.2 mg, 0.01 mmol, 2.5 mol %), KOH (44.8 mg, 0.8 mmol, 2.0 equiv), and **L4** (11.4 mg, 0.04 mmol, 10 mol %). The mixture was evacuated and backfilled with argon three times. Dioxane (4.0 mL) was added, and the solution was stirred for 5 minutes. Then, *gem*-difluoroallylboron **2** (122 mg, 0.6 mmol, 1.5 equiv) was added, and the resulting mixture was stirred for 5 minutes. Secondary propargyl sulfonate **1** (0.4 mmol, 1.0 equiv) was added slowly. The Schlenk tube was screw-capped. After stirring for 1 h at room temperature, the resulting mixture was filtered with a pad of celite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (pure petroleum) to give product **3.**

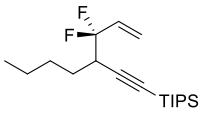
Note: The γ- and α-regioisomers can be separated by column chromatography, and the yields given were the isolated yields of pure **3**.



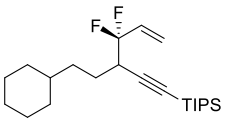
(4,4-Difluoro-3-phenethylhex-5-en-1-yn-1-yl)triisopropylsilane (3a). Compound **3a** was obtained in 90% yield (135 mg, γ/α = 21:1 determined by ^{19}F NMR before purification) as a yellow oil after flash column chromatography (100% hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 2H), 7.25 - 7.18 (m, 3H), 6.13 - 5.97 (m, 1H), 5.69 (dt, *J* = 17.2 Hz, 2.8 Hz, 1H), 5.49 (d, *J* = 11.2, 1H), 3.05 - 2.85 (m, 2H), 2.80 - 2.89 (m, 1H), 2.07 - 1.97 (m, 1H), 1.90 - 1.78 (m, 1H), 1.13 - 1.09 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.9 (dt, *J* = 239.3 Hz, 8.3 Hz, 1F), -106.2 (dt, *J* = 239.3 Hz, 13.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 131.0 (t, *J* = 26.3 Hz), 128.5, 128.5, 126.1, 120.4 (t, *J* = 9.1 Hz), 119.8 (dd, *J* = 245.4 Hz, 244.4 Hz), 103.7, 85.9, 40.8 (t, *J* = 29.3Hz), 33.1, 30.4, 18.6, 11.2. MS (DART): m/z (%) 394 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{38}NF_2Si$: 394.2736; Found: 394.2738.



(3-Difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3b). Compound **3b** (106 mg, 73% yield, γ/α = 8.5:1 determined by ^{19}F NMR before purification) was purified with FP ECOFLEX C18 (20 g) (100% MeCN) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.26 (m, 4H), 7.24 - 7.18 (m, 1H), 6.19 - 6.05 (m, 1H), 5.76 (dt, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.54 (d, *J* = 11.2, 1H), 3.21 - 3.09 (m, 2H), 2.77 - 2.70 (m, 1H), 1.01 - 0.98 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.1 (dt, *J* = 238.8 Hz, 10.2 Hz, 1F), -106.9 (dt, *J* = 238.8 Hz, 14.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 130.9 (t, *J* = 26.5 Hz), 129.3, 128.2, 126.5, 120.7 (t, *J* = 10.1 Hz), 119.6 (dd, *J* = 246.9Hz, 244.4 Hz), 103.2 (t, *J* = 6.3 Hz), 86.4, 43.7 (t, *J* = 29.0 Hz), 34.8 (t, *J* = 3.8 Hz), 18.5, 11.1. MS (DART): m/z (%) 380 $(M+NH_4)^+$. HRMS (DART): $(M+NH_4)^+$ Calculated for $C_{22}H_{36}NF_2Si$: 380.2580; Found: 380.2581.

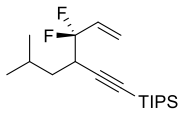


(3-(1,1-Difluoroallyl)hept-1-yn-1-yl)triisopropylsilane (3c). Compound **3c** (85 mg, 65% yield, γ/α = 14.5:1 determined by ^{19}F NMR before purification) was purified with FP ECOFLEX C18 (20 g) (100% MeCN) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 - 5.98 (m, 1H), 5.69 (dt, *J* = 17.6, 2.0 Hz, 1H), 5.48 (d, *J* = 10.4 Hz, 1H), 2.97 - 2.85 (m, 1H), 1.74 - 1.59 (m, 2H), 1.53 - 1.41 (m, 2H), 1.40 - 1.31 (m, 2H), 1.08 - 1.05 (m, 21H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.7 (dt, *J* = 239.0 Hz, 10.7 Hz, 1F), -106.3 (dt, *J* = 239.0 Hz, 13.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1 (t, *J* = 26.3 Hz), 120.2 (t, *J* = 9.1 Hz), 120.1 (t, *J* = 243.4 Hz, 237.4 Hz), 104.3 (t, *J* = 6.1 Hz), 85.1, 41.4 (t, *J* = 29.3 Hz), 29.2, 28.1 (dd, *J* = 3.0 Hz, 2.0 Hz), 22.2, 18.5, 13.9, 11.2. MS (DART): m/z (%) 346 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{19}H_{38}NF_2Si$: 346.2736; Found: 346.2737.

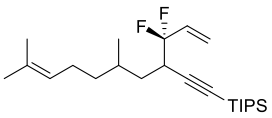


(3-(2-Cyclohexylethyl)-4,4-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3d). Compound **3d** was obtained in 75% yield (114 mg, γ/α = 14.3:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 - 5.97 (m, 1H), 5.69 (d, *J* = 17.2 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H), 2.92 - 2.81 (m, 1H), 1.76 - 1.64 (m, 6H), 1.54 - 1.41 (m, 2H), 1.35 - 1.18 (m, 5H), 1.08 - 1.04 (m, 21H), 0.94 - 0.86 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.6 (dt, *J* = 238.8 Hz, 10.2 Hz, 1F), -106.3 (dt, *J* = 238.8 Hz, 13.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.1 (t, *J* = 26.6 Hz), 120.2 (t, *J* = 9.6 Hz), 119.9 (dd, *J* = 245.4 Hz, 244.4 Hz), 104.3 (t, *J* = 6.1 Hz), 85.1, 41.7 (t, *J* = 29.3

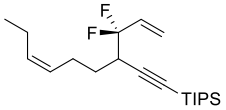
Hz), 37.3, 34.7, 33.6, 32.9, 26.6, 26.3, 26.3, 25.9 (t, *J* = 2.0 Hz), 18.6, 11.2. MS (DART): m/z (%) 400 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{44}NF_2Si$: 400.3206; Found: 400.3207.



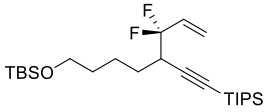
(4,4-Difluoro-3-isobutylhex-5-en-1-yn-1-yl)triisopropylsilane (3e). Compound **3e** was obtained in 61% yield (80 mg, γ/α = 11.7 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 6.13 - 5.97 (m, 1H), 5.68 (dt, *J* = 17.2 Hz, 3.2 Hz, 1H), 5.49 (d, *J* = 11.2 Hz, 1H), 3.02 - 2.92 (m, 1H), 1.98 - 1.86 (m, 1H), 1.58 - 1.47 (m, 1H), 1.44 - 1.34 (m, 1H), 1.07 - 1.04 (m, 21H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.7 (dt, *J* = 238.2 Hz, 10.4 Hz, 1F), -106.5 (dt, *J* = 238.2 Hz, 13.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.0 (t, *J* = 26.4 Hz), 120.3 (t, *J* = 9.4 Hz), 120.0 (dd, *J* = 245.4 Hz, 244.4 Hz), 104.1 (t, *J* = 6.1 Hz), 85.0, 39.7 (t, *J* = 28.7 Hz), 37.2, 25.7, 23.6, 20.9, 18.5, 11.2. MS (DART): m/z (%) 346 $(M+NH_4)^+$. HRMS (DART): $(M+NH_4)^+$ Calculated for $C_{19}H_{38}NF_2Si$: 346.2736; Found: 346.2738.



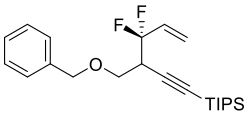
(3-(1,1-Difluoroallyl)-5,9-dimethyldec-8-en-1-yn-1-yl)triisopropylsilane (3f). Compound **3f** was obtained in 60% yield (95 mg, dr = 56:44, γ/α = 8.3:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 6.13 - 5.95 (m, 1H), 5.68 (dd, *J* = 17.6 Hz, 2.4 Hz, 1H), 5.49 (d, *J* = 11.2 Hz, 1H), 5.09 (t, *J* = 8.0 Hz, 1H), 3.06 - 2.94 (m, 1H), 2.10 - 1.86 (m, 2H), 1.84 - 1.74 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.55 - 1.39 (m, 2H), 1.37 - 1.19 (m, 2H), 1.07 - 1.03 (m, 21H), 0.97 (d, *J* = 6.8 Hz, 1.31H, minor), 0.89 (d, *J* = 6.8 Hz, 1.69H, major). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.8 (dt, *J* = 238.4 Hz, 8.6 Hz, 1F), -106.1 – -107.0 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ Major: 131.3, 131.0 (t, *J* = 26.3 Hz), 124.5, 120.3 (t, *J* = 9.2 Hz), 120.0 (t, *J* = 245.3 Hz), 103.9 (t, *J* = 6.3 Hz), 85.0, 39.5 (t, *J* = 29.2 Hz), 37.9, 35.2, 29.9, 25.7, 25.5, 18.5, 18.4, 17.6, 11.2. Minor: 131.3, 131.0 (t, *J* = 26.3 Hz), 124.5, 120.3 (t, *J* = 9.2 Hz), 120.0 (t, *J* = 246.3 Hz), 104.3 (t, *J* = 6.0 Hz), 84.9, 39.4 (t, *J* = 29.2 Hz), 35.9, 35.2, 30.2, 25.7, 25.2, 20.3, 18.5, 17.6, 11.2. MS (DART): m/z (%) 397 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{24}H_{43}F_2Si$: 397.3097; Found: 397.3098.



(Z)-(3-(1,1-Difluoroallyl)non-6-en-1-yn-1-yl)triisopropylsilane (3g). Compound **3g** was obtained in 70% yield (99 mg, γ/α = 15.4:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 - 5.97 (m, 1H), 5.68 (dt, *J* = 17.2 Hz, 2.4 Hz, 1H), 5.48 (d, *J* = 11.2 Hz, 1H), 5.47 - 5.39 (m, 1H), 5.34 - 5.25 (m, 1H), 2.98 - 2.86 (m, 1H), 2.37 - 2.27 (m, 1H), 2.27 - 2.16 (m, 1H), 2.11 - 2.02 (m, 2H), 1.72 (m, 1H), 1.62 - 1.56 (m, 1H), 1.08 - 1.05 (m, 21H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.9 (dt, *J* = 239.0 Hz, 10.2 Hz, 1F), -106.2 (dt, *J* = 239.0 Hz, 12.8 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 130.9 (t, *J* = 26.5 Hz), 127.4, 120.3 (t, *J* = 8.8 Hz), 119.9 (dd, *J* = 245.7 Hz, 243.2 Hz), 103.9 (t, *J* = 6.3 Hz), 85.2, 40.8 (t, *J* = 29.0 Hz), 28.7, 24.5, 20.6, 18.5, 14.4, 11.2. MS (DART): m/z (%) 372 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{21}H_{40}NF_2Si$: 372.2893; Found: 372.2894.

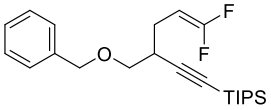


tert-Butyl((6,6-difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl)oxy)dimethylsilane (3h). Compound **3h** was obtained in 68% yield (124 mg, γ/α = 15.2:1 determined by ^{19}F NMR before purification) as a yellow oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 - 5.98 (m, 1H), 5.68 (d, *J* = 16.8 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H), 3.61 (t, *J* = 6.0 Hz, 2H), 2.97 - 2.85 (m, 1H), 1.75 - 1.65 (m, 2H), 1.55 - 1.39 (m, 4H), 1.07 - 1.04 (m, 21H), 0.89 (s, 9H), 0.04 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 98.7 (dt, *J* = 238.8 Hz, 8.7 Hz, 1F), - 106.3 (dt, *J* = 238.8 Hz, 13.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.0 (t, *J* = 26.5 Hz), 120.3 (t, *J* = 8.8 Hz), 119.9 (t, *J* = 244.4 Hz, 243.2 Hz), 104.0 (t, *J* = 6.3 Hz), 85.1, 63.1, 41.4 (t, *J* = 29.0 Hz), 32.4, 28.4, 26.0, 23.6, 18.6, 18.4, 11.1, -5.3. MS (DART): m/z (%) 476 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{25}H_{52}NF_2Si_2$: 476.3550; Found: 476.3550.

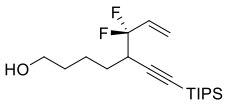


(3-((Benzyloxy)methyl)-4,4-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3i). Compound **3i** was obtained in 70% yield (109 mg) as a colorless oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.27 (m, 5H), 6.15 - 5.98 (m, 1H), 5.70 (d, *J* = 17.2 Hz, 1H), 5.48 (d, *J* = 11.2 Hz, 1H), 4.59 (s, 2H), 3.81 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.67 (dd, *J* = 9.6 Hz, 7.2 Hz, 1H), 3.36 - 3.25 (m, 1H), 1.08 - 1.05 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.4 (dt, *J* = 242.5 Hz, 10.8 Hz, 1F), -103.4 (dt, *J* = 242.5

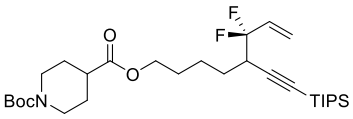
Hz, 12.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 130.9 (t, *J* = 26.5 Hz), 128.3, 127.6, 127.5, 120.4 (t, *J* = 10.1 Hz), 119.2 (t, *J* = 243.2 Hz), 102.1 (t, *J* = 6.3 Hz), 85.8, 73.3, 68.6, 42.2 (t, *J* = 29.0 Hz), 18.5, 11.1. MS (DART): m/z (%) 410 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{23}H_{38}ONF_2Si$: 410.2685; Found: 410.2684.



(3-((Benzyloxy)methyl)-6,6-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (4i). Compound **4i** was obtained in 22% yield (35 mg) as a yellow oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.28 (m, 5H), 4.58 - 4.55 (m, 2H), 4.30 (dtd, *J* = 25.2 Hz, 8.0 Hz, 2.4 Hz, 1H), 3.60 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 3.44 (t, *J* = 9.2 Hz, 1H), 2.84 - 2.77 (m, 1H), 2.40 - 2.33 (m, 1H), 2.26 - 2.18 (m, 1H), 1.08 - 1.00 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.7 (d, *J* = 44.7 Hz, 1F), -90.1 (dd, *J* = 44.7 Hz, 25.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 288.4 Hz, 285.6 Hz), 138.1, 128.4, 127.6, 127.5, 107.5, 83.0, 75.2 (dd, *J* = 24.1 Hz, 20.2 Hz), 73.1, 71.9, 33.4, 24.7, 18.5, 11.1. MS (DART): m/z (%) 410 $[M+NH_4]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{23}H_{35}ONF_2Si$: 393.2420; Found: 393.2416.

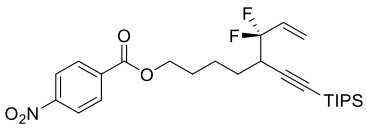


5,5-Difluoro-4-((triisopropylsilyl)ethynyl)hept-6-en-1-ol (3j). Compound **3j** was obtained in 54% yield (74 mg, γ/α = 4.2:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 - 5.97 (m, 1H), 5.69 (d, *J* = 17.3 Hz, 1H), 5.49 (d, *J* = 10.8 Hz, 1H), 2.98 - 2.86 (m, 1H), 2.81 (t, *J* = 12.4 Hz, 2H), 2.42 (tt, *J* = 11.1 Hz, 3.9 Hz, 1H), 1.77 - 1.69 (m, 2H), 1.63 - 1.55 (m, 4H), 1.07 - 1.03 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.8 (dt, *J* = 238.8 Hz, 8.6 Hz, 1F), -106.5 (dt, *J* = 239.1 Hz, 12.8 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.9 (t, *J* = 26.5 Hz), 120.4 (t, *J* = 8.8 Hz), 119.2 (dd, *J* = 254.7 Hz, 244.4 Hz), 103.8 (t, *J* = 6.3 Hz), 85.3, 62.7, 41.3 (t, *J* = 29.0 Hz), 32.2, 28.2, 23.3, 18.5, 11.1. MS (DART): m/z (%) 344 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{19}H_{38}ONF_2Si$: 344.2685; Found: 344.2686.

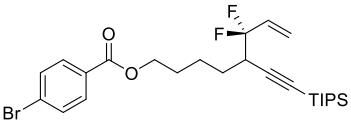


1-(Tert-butyl) 4-(6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl) piperidine-1,4-dicarboxylate (3k). Compound **3k** was obtained in 74% yield (164 mg, γ/α = 12.6:1 determined by ^{19}F NMR before

purification) as a colorless oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 - 5.97 (m, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.49 (d, *J* = 11.6 Hz, 1H), 4.10 - 3.99 (m, 4H), 2.96 - 2.88 (m, 1H), 2.81 (t, *J* = 12.0 Hz, 2H), 2.46 - 2.37 (m, 1H), 1.89 - 1.84 (m, 2H), 1.78 - 1.66 (m, 4H), 1.66 - 1.58 (m, 4H), 1.45 (s, 9H), 1.06 - 1.03 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.8 (dt, *J* = 238.8 Hz, 8.8 Hz, 1F), -106.5 (dt, *J* = 238.8 Hz, 13.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 154.7, 130.8 (t, *J* = 26.3 Hz), 120.5 (t, *J* = 9.1Hz), 119.8 (dd, *J* = 245.7 Hz, 244.4 Hz), 103.6 (t, *J* = 6.3 Hz), 84.5, 79.6, 64.4, 43.4, 41.3 (t, *J* = 29.5 Hz), 41.1, 28.4, 28.2, 28.1, 28.0, 23.7, 18.5, 11.1. MS (DART): m/z (%) 556 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{30}H_{52}O_4NF_2Si$: 556.3628; Found: 556.3628.

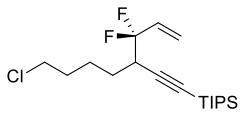


6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-nitrobenzoate (3l). Compound **3l** was obtained in 79% yield (156 mg, γ/α = 11.5:1 determined by ^{19}F NMR before purification) as a yellow oil after flash column chromatography (hexane/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 - 8.25 (m, 2H), 8.23 - 8.17 (m, 2H), 6.12 - 5.97 (m, 1H), 5.70 (d, *J* = 17.2 Hz, 1H), 5.50 (d, *J* = 11.6 Hz, 1H), 4.38 (t, *J* = 6.1 Hz, 2H), 3.00 - 2.88 (m, 1H), 1.89 - 1.76 (m, 4H), 1.69 - 1.57 (m, 2H), 1.05 - 1.01 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.8 (dt, *J* = 239.1 Hz, 8.1 Hz, 1F), -106.5 (dt, *J* = 239.1 Hz, 12.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 131.7, 131.1, 130.9 (t, *J* = 26.3 Hz), 129.3, 128.0, 120.4 (t, *J* = 9.7 Hz), 119.8 (dd, *J* = 246.4 Hz, 244.4 Hz), 103.7 (t, *J* = 5.8 Hz), 85.6, 65.1, 41.4 (t, *J* = 29.3 Hz), 28.3, 28.2 (dd, *J* = 3.0 Hz, 1.0 Hz), 23.8, 18.5, 11.1. MS (DART): m/z (%) 511 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{26}H_{41}O_4N_2F_2Si$: 511.2798; Found: 511.2797.

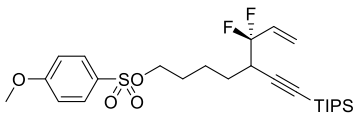


6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-bromobenzoate (3m). Compound **3m** was obtained in 88% yield (185 mg, γ/α = 21:1 determined by ^{19}F NMR before purification) as a yellow oil after flash column chromatography (hexane/ EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.12 - 5.96 (m, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.49 (d, *J* = 11.2 Hz, 1H), 4.32 (t, *J* = 5.6 Hz, 2H), 2.98 - 2.88 (m, 1H), 1.86 - 1.74 (m, 4H), 1.61 - 1.52 (m, 2H), 1.05 - 1.01 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.8 (dt, *J* = 239.1 Hz, 8.0 Hz, 1F), -106.5 (dt, *J* = 239.1 Hz, 13.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 131.6, 131.1, 130.9 (t, *J* = 26.3 Hz),

129.3, 127.9, 120.4 (t, *J* = 9.1 Hz), 119.7 (dd, *J* = 245.3 Hz, 243.4 Hz), 103.6 (t, *J* = 13.1 Hz), 85.6, 65.1, 43.3 (t, *J* = 29.3 Hz), 28.3, 28.2, 23.8, 18.5, 11.1. MS (DART): m/z (%) 544 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{26}H_{41}O_2NBrF_2Si$: 544.2053; Found: 544.2048.



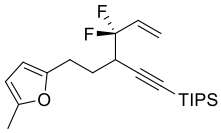
(7-Chloro-3-(1,1-difluoroallyl)hept-1-yn-1-yl)triisopropylsilane (3n). Compound **3n** (89 mg, 62% yield, γ/α = 12.4:1 determined by ^{19}F NMR before purification) was purified with FP ECOFLEX C18 (20 g) (100% MeCN) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.13 - 5.97 (m, 1H), 5.70 (dt, *J* = 17.2 Hz, 2.4 Hz, 1H), 5.50 (d, *J* = 11.2 Hz, 1H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.98 - 2.86 (m, 1H), 1.87 - 1.76 (m, 3H), 1.76 - 1.68 (m, 1H), 1.59 - 1.54 (m, 2H), 1.08 - 1.05 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.9 (dt, *J* = 239.1 Hz, 10.3 Hz, 1F), -106.6 (dt, *J* = 239.1 Hz, 14.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.9 (t, *J* = 26.3 Hz), 120.4 (t, *J* = 10.1 Hz), 119.8 (dd, *J* = 246.4 Hz, 244.4Hz), 103.6 (t, *J* = 7.1 Hz), 85.7, 44.6, 41.3 (t, *J* = 29.3Hz), 32.1, 27.8, 24.5, 18.5, 11.2. MS (DART): m/z (%) 380 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{19}H_{37}NClF_2Si$: 380.2346; Found: 380.2348.



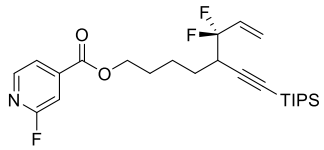
6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-methoxybenzenesulfonate (3o). Compound **3o** was obtained in 70% yield (144 mg, γ/α = 17.8:1 determined by ^{19}F NMR before purification) as a yellow oil after flash column chromatography (hexane/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.09 - 5.94 (m, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.48 (d, *J* = 11.2 Hz, 1H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.89 (s, 3H), 2.89 - 2.78(m, 1H), 1.78 - 1.58 (m, 4H), 1.55 - 1.38 (m, 2H), 1.07 - 1.02 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 98.9 (dt, *J* = 239.1 Hz, 8.0 Hz, 1F), - 106.5 (dt, *J* = 239.1 Hz, 12.6 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 130.8 (t, *J* = 26.5 Hz), 130.0, 127.5, 120.5 (t, *J* = 10.1 Hz), 119.7 (dd, *J* = 245.7 Hz, 244.4Hz), 114.4, 103.4 (t, *J* = 6.3 Hz), 85.7, 69.9, 55.7, 41.3 (t, *J* = 29.0 Hz), 28.4, 27.7, 23.0, 18.5, 11.1. MS (DART): m/z (%) 532 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{26}H_{44}O_4NF_2SSi$: 532.2723; Found: 532.2726.

Procedure of Gram-Scale Synthesis 3o: To a 100 mL of Schlenk tube were added Pd_2dba_3 (114.5 mg, 0.125 mmol, 2.5 mol %), KOH (0.56 g, 10 mmol, 2.0 equiv), and **L4** (143.6 mg, 0.5 mmol, 10

mol %). The mixture was evacuated and backfilled with argon three times. Dioxane (40.0 mL) was added, and the solution was stirred for 5 minutes. Then, *gem*-difluoroallylboron **2** (1.52 g, 7.5 mmol, 1.5 equiv) was added, and the resulting mixture stirred for 10 minutes. **1o** (3.12 g, 5 mmol, 1.0 equiv) was added slowly. The Schlenk tube was screw-capped. After stirring overnight at room temperature, the mixture was filtered with a pad of celite. The filtrate was concentrated, and compound **3o** was obtained in 72% yield (1.85 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 20:1).



(4,4-Difluoro-3-(2-(5-methylfuran-2-yl)ethyl)hex-5-en-1-yn-1-yl)triisopropylsilane (3p). Compound **3p** was obtained in 64% yield (97 mg, γ/α = 10.1:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 - 5.95 (m, 1H), 5.87 (d, *J* = 3.2 Hz, 1H), 5.82 (d, *J* = 3.2 Hz, 1H), 5.68 (dt, *J* = 17.2 Hz, 2.0 Hz, 1H), 5.48 (d, *J* = 11.1 Hz, 3H), 2.99 - 2.83 (m, 2H), 2.77 - 2.65 (m, 1H), 2.23 (s, 3H), 2.09 - 1.99 (m, 1H), 1.81 - 1.72 (m, 1H), 1.07 - 1.04 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.0 (dt, *J* = 239.5 Hz, 9.9 Hz, 1F), -106.2 (dt, *J* = 239.5 Hz, 13.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 150.7, 130.9 (t, *J* = 26.3 Hz), 120.5 (t, *J* = 9.1 Hz), 119.8 (dd, *J* = 246.4, 244.4 Hz), 106.1, 105.8, 103.4 (t, *J* = 6.1 Hz), 85.9, 40.7 (t, *J* = 29.3 Hz), 27.3, 25.5, 18.6, 13.5, 11.2. MS (FI): m/z (%) 380 $[M]^+$. HRMS (FI): $[M]^+$ Calculated for $C_{22}H_{34}OF_2Si$: 380.2342 Found: 380.2326.

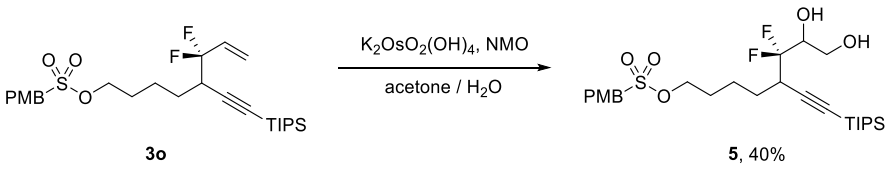


6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 2-fluoroisonicotinate (3q). Compound **3q** was obtained in 68% yield (127 mg, γ/α = 13.1:1 determined by ^{19}F NMR before purification) as a colorless oil after flash column chromatography (100% hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.1 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.48 (s, 1H), 6.12 – 5.92 (m, 1H), 5.69 (dt, *J* = 17.4, 2.6 Hz, 1H), 5.50 (d, *J* = 11.0 Hz, 1H), 4.41 – 4.35 (m, 2H), 2.99 – 2.87 (m, 1H), 1.98 – 1.78 (m, 4H), 1.62 – 1.52 (m, 2H), 1.04 – 1.00 (m, 21H).. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.29 (s, 1F), -98.38 – -99.30 (m, 1F), -106.63 (dt, *J* = 239.1, 13.6 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (d, *J* = 240.2 Hz), 163.8 (d, *J* = 8.4 Hz), 163.8, 148.6 (d, *J* = 14.4 Hz), 143.24, 130.82 (t, *J* = 26.3 Hz), 120.54 (t, *J* = 9.3 Hz), 119.73 (t, *J* = 224.4 Hz), 109.75 (d, *J* = 37.6 Hz), 103.49 (t, *J* = 6.2 Hz), 85.66, 66.05, 41.29 (t, *J* =

29.5 Hz), 29.43, 28.10, 23.72, 18.60, 11.09. MS (DART): m/z (%) 468 $[M+NH_4]^+$. HRMS (DART): $[M+NH_4]^+$ Calculated for $C_{25}H_{37}O_2NF_3Si$: 468.2540; Found: 468.2538.

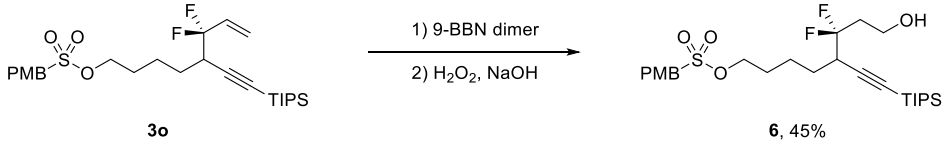
5. Transformations of Compound 3o.

Synthesis of compound 5[2]



3,3-Difluoro-8-((((4-methoxyphenyl)peroxy)thio)oxy)-4-((triisopropylsilyl)ethynyl)octane-1,2-diol (5). To a 25 mL of Schlenk tube was added compound **3o** (103 mg, 0.2 mmol, 1.0 equiv), $K_2OsO_4{\cdot}2H_2O$ (3.7 mg, 0.01 mmol, 0.05 equiv), *N*-methylmorpholine oxide (NMO) (117 mg, 0.4 mmol, 2.0 equiv), and acetone/H_2O (2 ml, v:v = 5:1). After stirring for 24 h, the reaction was quenched with saturated aqueous Na_2SO_3 and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Compound **5** was obtained in 40% yield (44 mg) as a colorless oil after flash column chromatography (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* =8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.25 – 4.12 (m, 1 H), 4.02 (t, *J* = 6.2 Hz, 2H), 3.96 - 3.89 (m, 2H), 3.89 (s, 3H), 3.21 – 3.08 (m, 1H), 2.85 - 2.71 (m, 1H), 1.81 - 1.64 (m, 5H), 1.60 - 1.57 (m, 2H), 1.50 - 1.40 (m, 1H), 1.06 - 1.02 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.9 (dd, *J* = 246.5 Hz, 24.1 Hz, 1F), -119.9 (ddd, *J* = 246.5 Hz, 21.8 Hz, 3.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 130.0, 127.5, 122.3 (t, *J* = 253.3 Hz), 114.4, 103.4 (d, *J* = 12.6 Hz), 86.2, 71.1 (dd, *J* = 32.8 Hz, 23.9 Hz), 69.9, 60.6, 55.7, 37.1 (dd, *J* = 32.8 Hz, 23.9 Hz), 28.4, 25.9, 23.1, 18.5, 11.1. MS (DART): m/z (%) 549 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{26}H_{43}O_6F_2SSi$: 549.2512; Found: 549.2511.

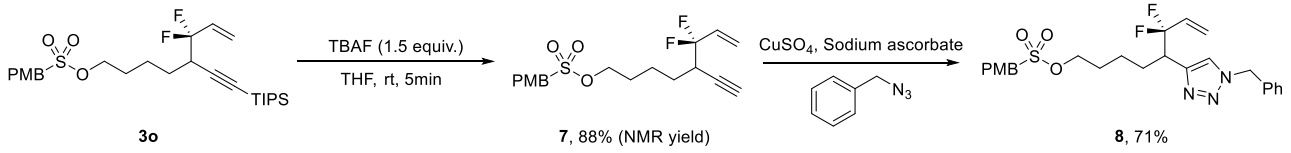
Synthesis of compound 6



3,3-Difluoro-8-((((4-methoxyphenyl)peroxy)thio)oxy)-4-((triisopropylsilyl)ethynyl)octan-1-ol (6). To a 25 mL of Schlenk tube was added 9-BBN dimer (146 mg, 0.6 mmol, 3.0 equiv) in the glove

box. The tube was removed from the glovebox, evacuated, and backfilled with argon three times. Compound **3o** (103 mg, 0.2 mmol, 1.0 equiv) and THF (2 mL) were then added. The Schlenk tube was sealed with a screwed cap and put into a 60 °C oil bath. After stirring for 12 h, the reaction mixture was cooled to room temperature, aqueous H_2O_2 (1 mL, 30 wt%) and aqueous NaOH (1 mL, 3.0 M) were added. The resulting mixture was heated to reflux for 3h. Upon cooling to room temperature, the mixture was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. Compound **6** was obtained in 45% yield (48 mg) as a colorless oil after flash column chromatography (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 3.92 - 3.91 (m, 2H), 3.88 (s, 3H), 2.94 - 2.78 (m, 1H), 2.42 - 2.20 (m, 2H), 1.73 - 1.63 (m, 5H), 1.55 - 1.41 (m, 2H), 1.09 - 1.02 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.5 - -101.4 (m, 1F), -103.5 - -104.3 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 130.1, 127.5, 123.7 (dd, *J* = 248.2 Hz, 245.7 Hz), 114.4, 103.7 (dd, *J* = 8.8 Hz, 5.0 Hz), 86.0, 69.9, 56.8 (dd, *J* = 6.3 Hz, 5.0 Hz), 55.7, 40.8 (t, *J* = 27.7 Hz), 37.4 (t, *J* = 23 Hz), 28.4, 27.3, 23.2, 18.5, 11.1. MS (DART): m/z (%) 533 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{26}H_{43}O_5F_2SSi$: 533.2563; Found: 533.2560.

Synthesis of compound 8[3]



1-Benzyl-4-(3,3-difluoro-8-((((4-methoxyphenyl)peroxy)thio)oxy)oct-1-en-4-yl)-1*H*-1,2,3-triazole (8). To a solution of **3o** (90 mg, 0.42 mmol, 1.0 equiv) in THF (2 mL) was added TBAF (0.5 mL, 0.5 mmol, 1.2 equiv, 1 M in THF) at 0 °C. The mixture was stirred for 5 minutes before being quenched with H_2O (2 mL). Then, (azidomethyl)benzene (58.6 mg, 0.44 mmol, 1.2 equiv), $CuSO_4$ (11.8 mg, 0.074 mmol, 0.2 equiv) and sodium ascorbate (44 mg, 0.22 mmol, 0.6 equiv) were added at room temperature. The resulting mixture was stirred for 12 hours at room temperature and concentrated. The residue was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated. Compound **8** (129 mg, 63% yield, 2

steps) was purified with silica gel chromatography (Petroleum ether/EtOAc = 6:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz , 2H), 7.42 - 7.33 (m, 4H), 7.25 - 7.21 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.87 - 5.72 (m, 1H), 5.56 - 5.47 (m, 3H), 5.35 (d, *J* = 10.8 Hz, 1H), 3.97 - 3.91 (m, 2H), 3.89 (s, 3H), 3.37 - 3.25 (m, 1H), 1.86 - 1.76 (m, 1H), 1.68 - 1.58 (m, 3H), 1.27 - 1.20 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 100.4 (dt, *J* = 242.5 Hz, 12.1 Hz, 1F), - 104.1 (dt, *J* = 242.5 Hz, 14.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 134.6, 131.2 (t, *J* = 26.5 Hz), 130.0, 129.1, 128.7, 127.9, 127.3, 122.6, 122.6, 120.6 (t, *J* = 243.2 Hz), 120.4 (t, *J* = 8.8 Hz), 114.4, 69.9, 55.7, 54.2, 44.7 (t, *J* = 26.5 Hz), 28.5, 27.6, 23.0. MS (DART): m/z (%) 492 $[M+H]^+$. HRMS (DART): $[M+H]^+$ Calculated for $C_{24}H_{28}O_4N_3F_2S$: 492.1762; Found: 492.1764.

6. References

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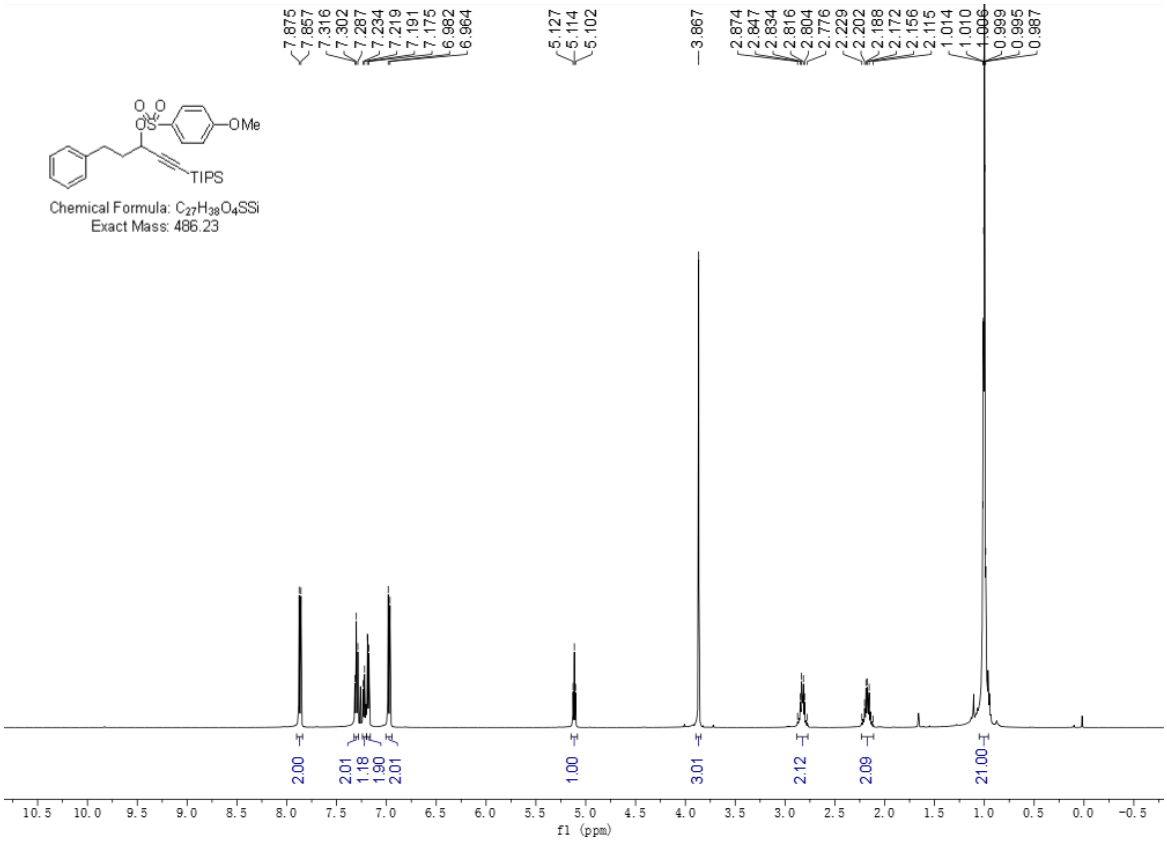
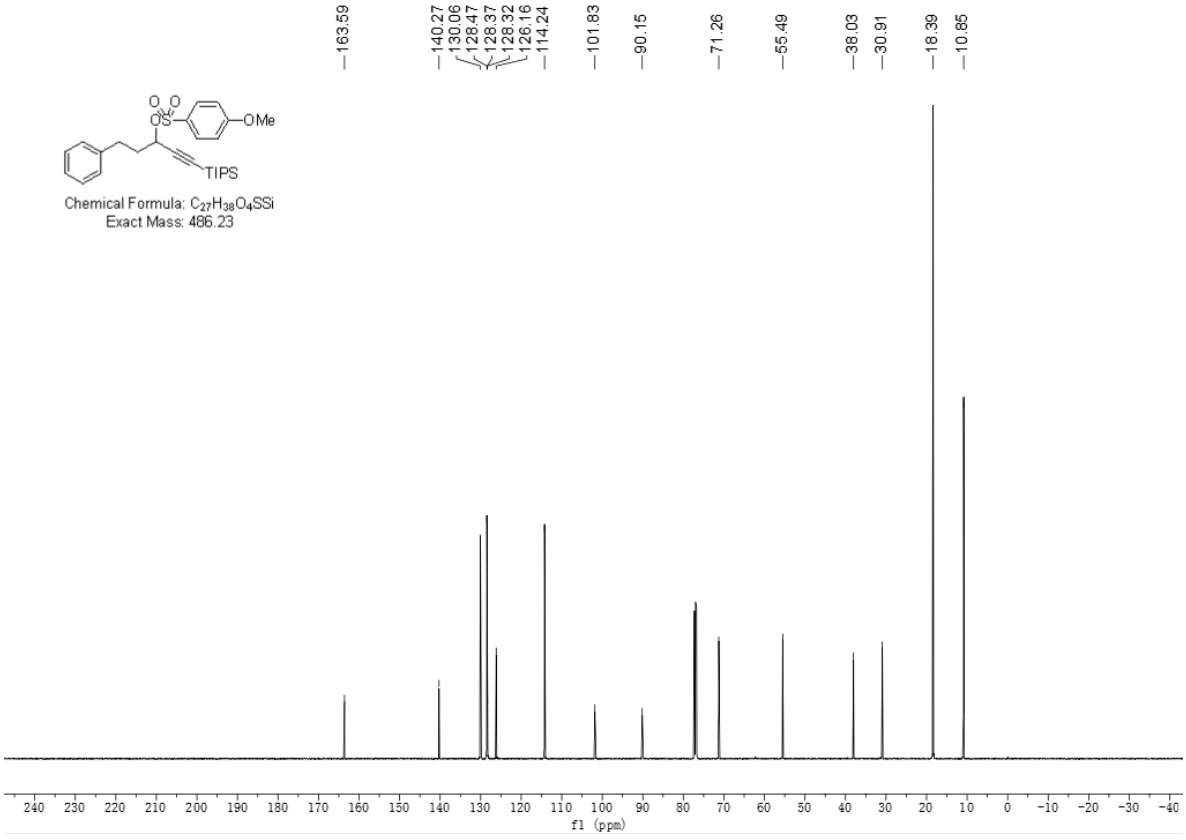
2 J. C. Hethcox, S. E. Shockley, B. M. Stoltz, *Angew. Chem., Int. Ed.* **2016**, *55*, 16092; *Angew. Chem.* **2016**, *128*, 16326.

3 a) F. E. Michael, A. P. Duncan, Z. K. Sweeney, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 1752; b) C. Deraedt, N. Pinaud, D. Astruc, *J. Am. Chem. Soc.* **2014**, *136*, 12092.

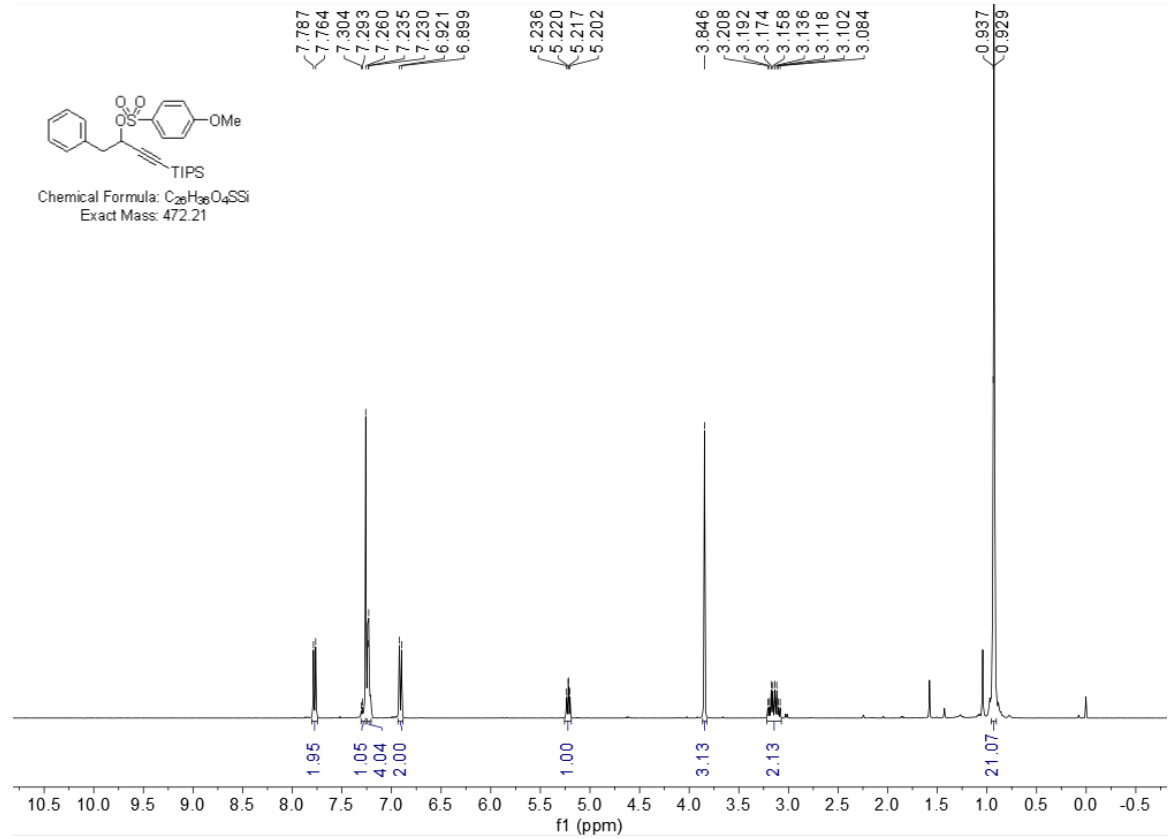
7. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra

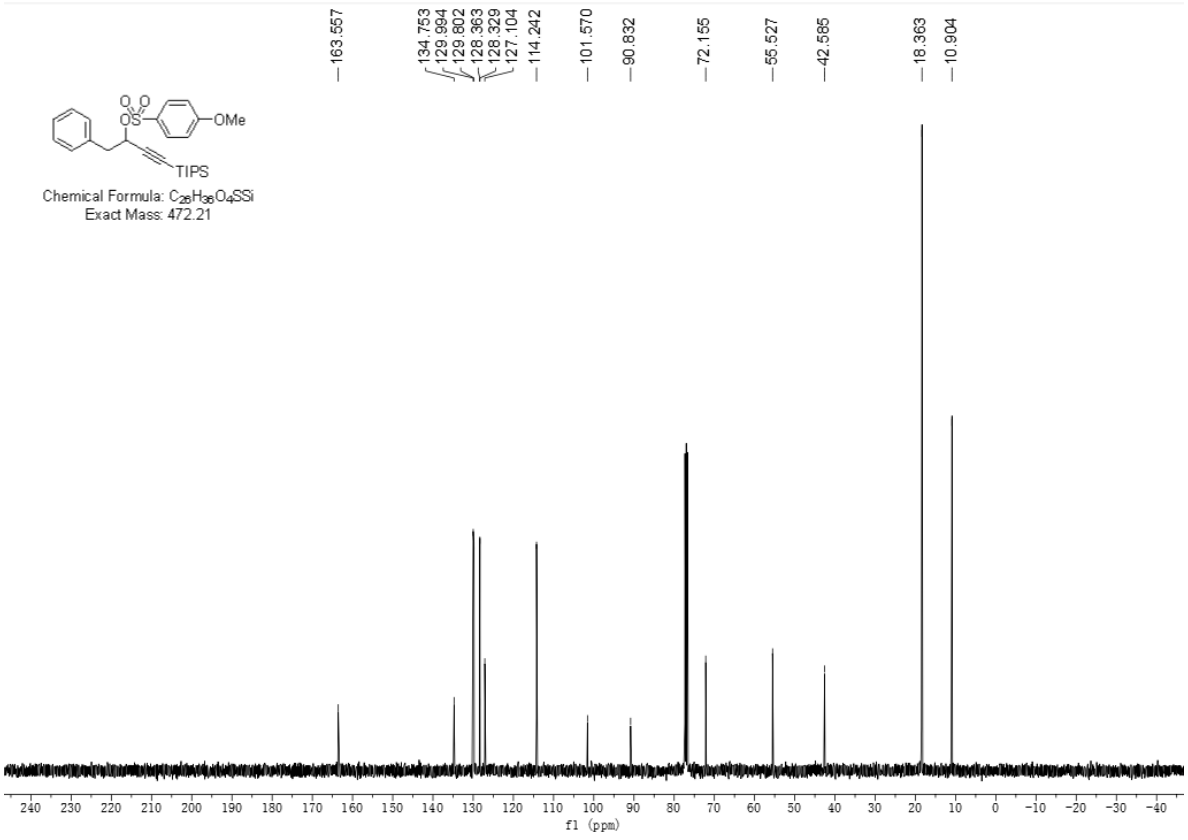
5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1a)



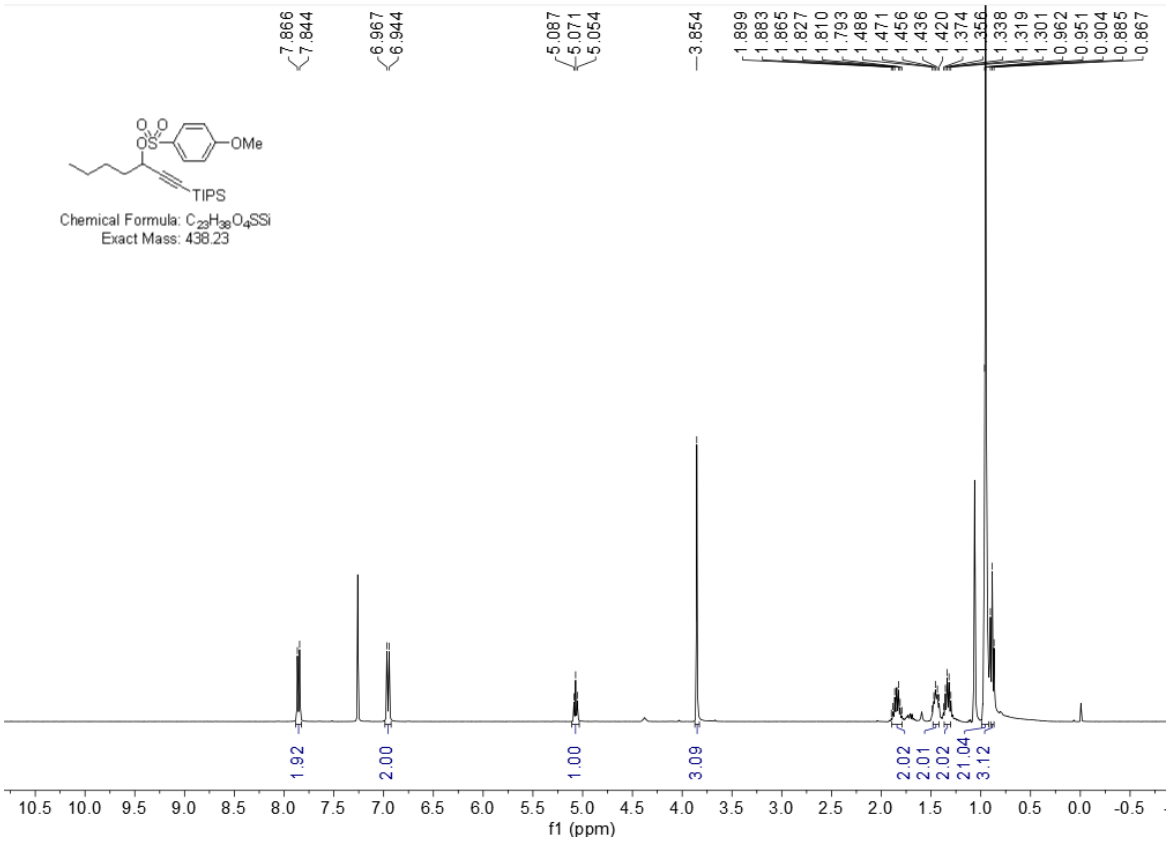


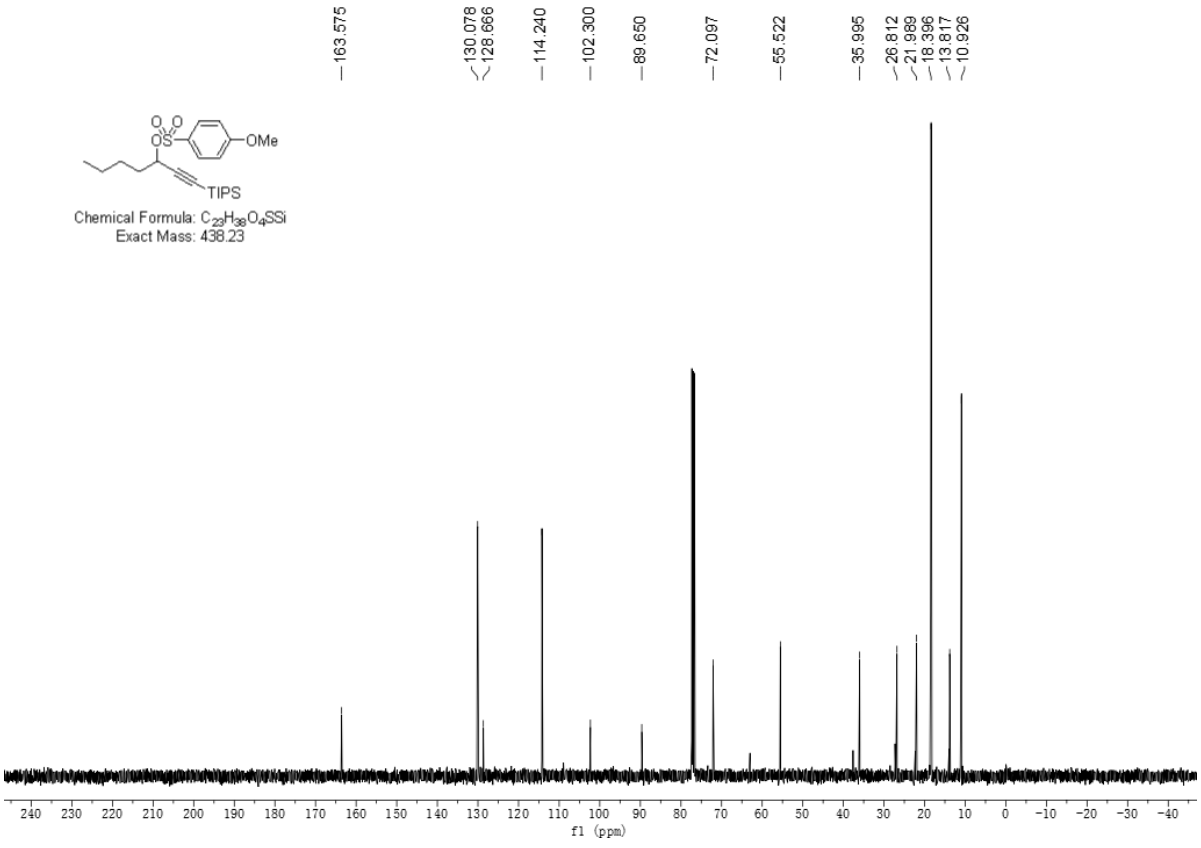
1-Phenyl-4-(triisopropylsilyl)but-3-yn-2-yl 4-methoxybenzenesulfonate (1b)



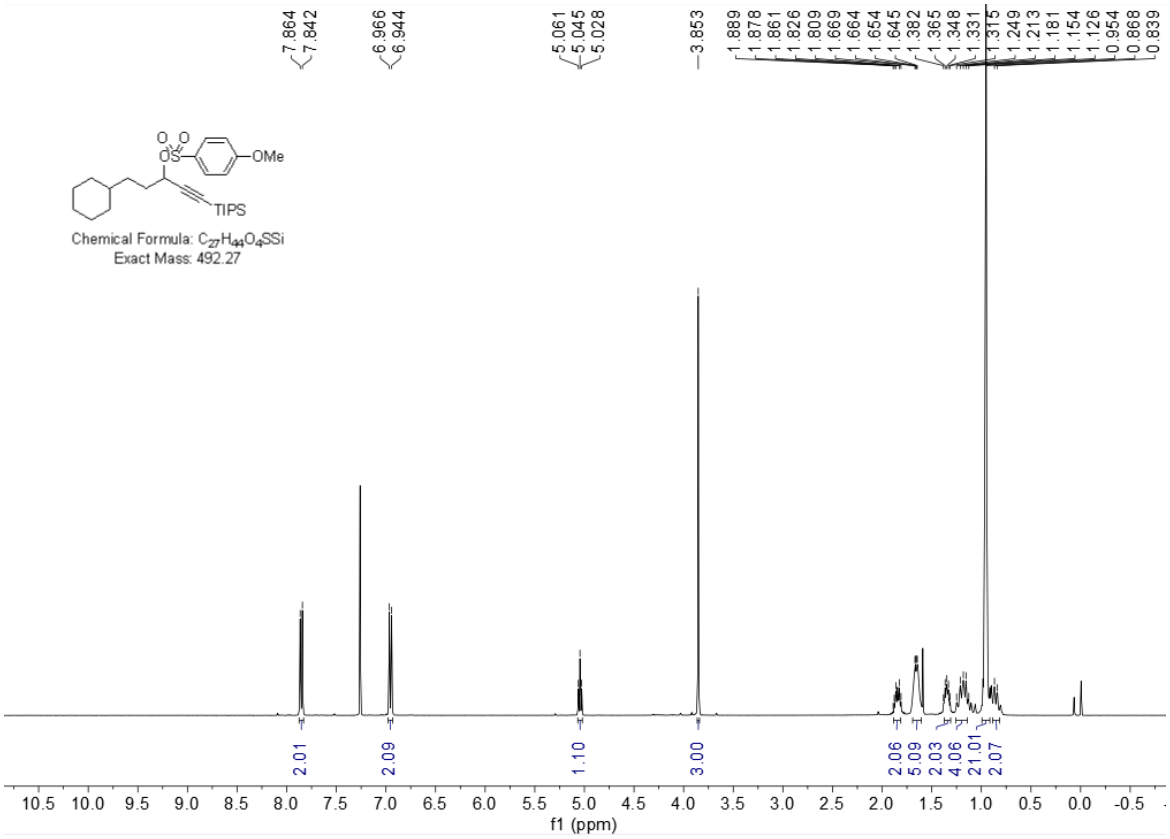


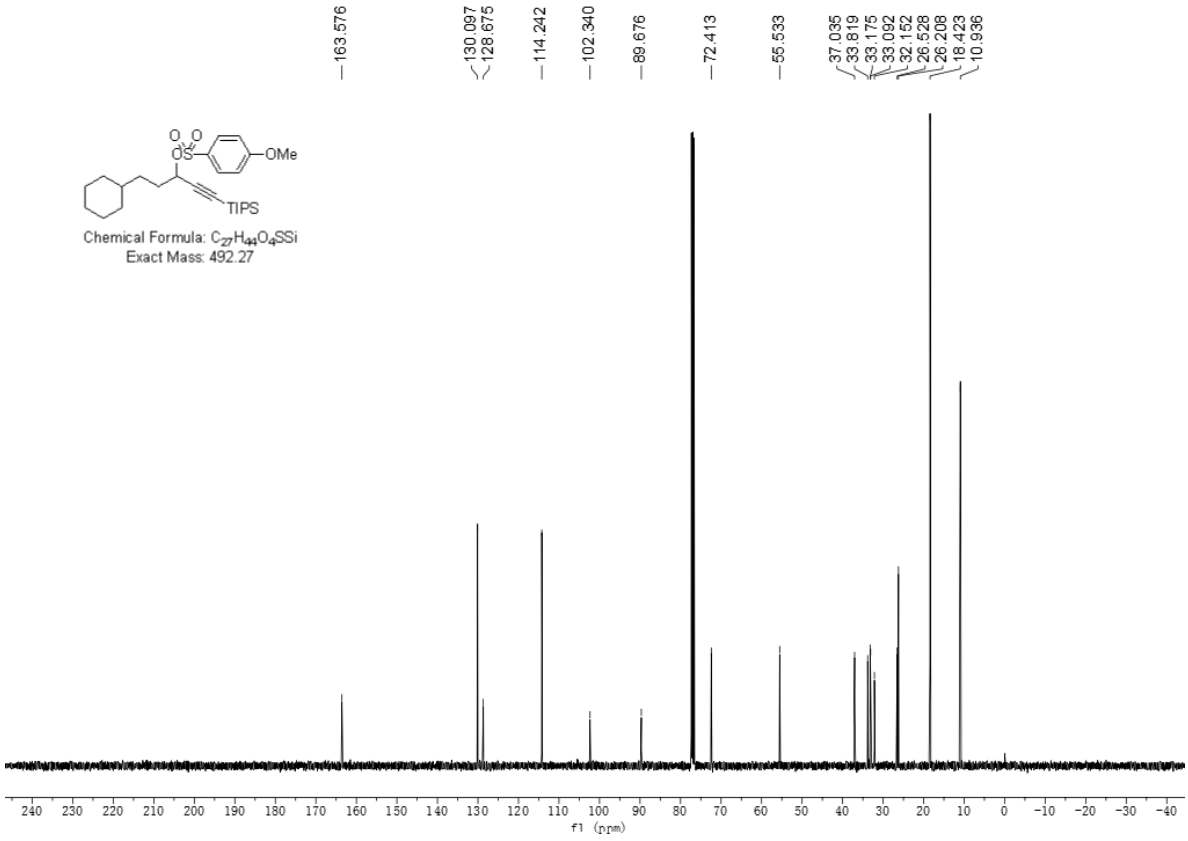
1-(Triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1c)



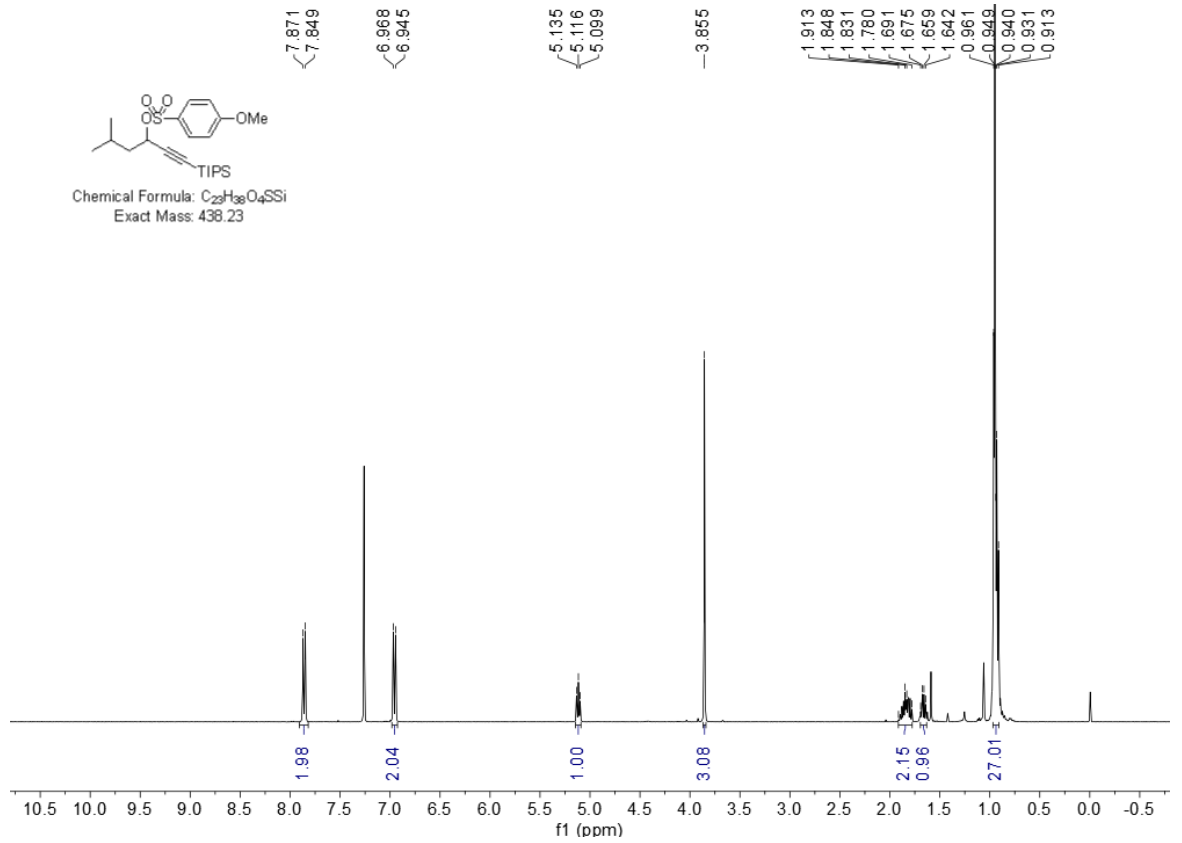


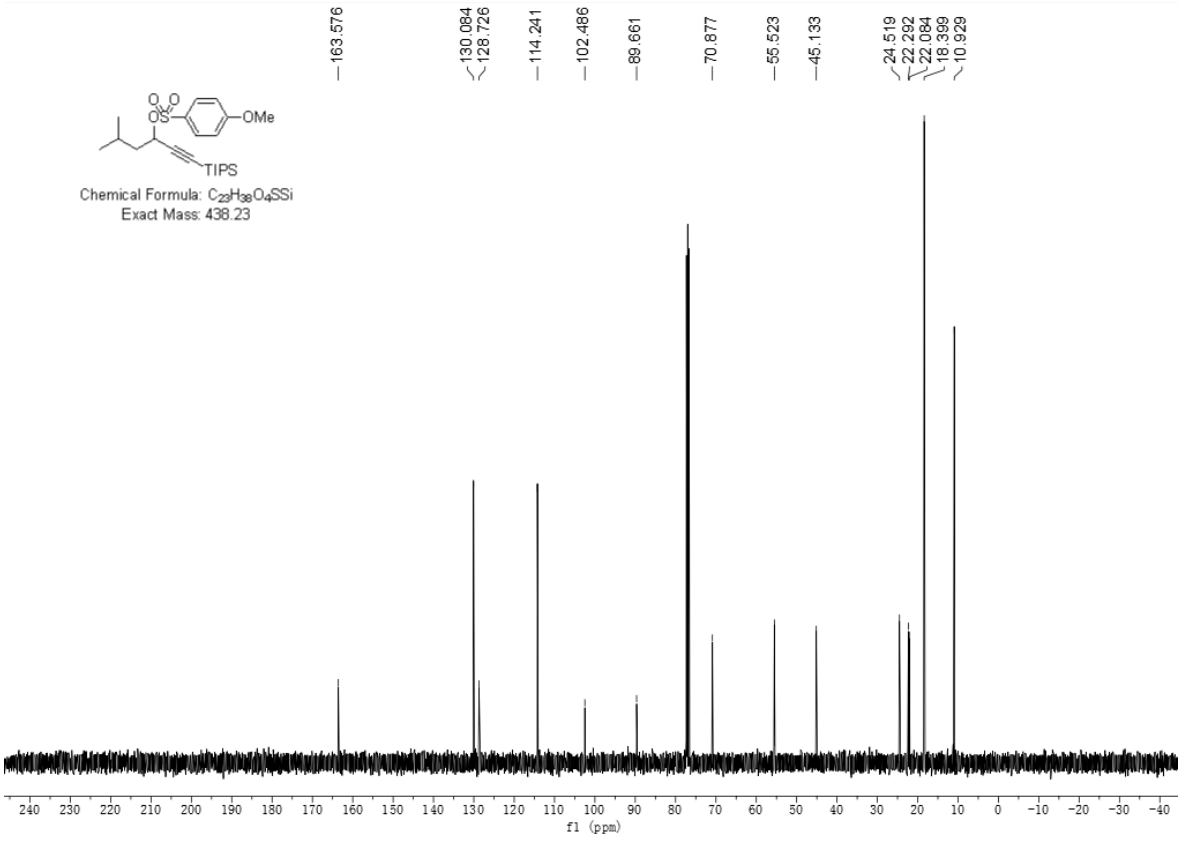
5-Cyclohexyl-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1d)



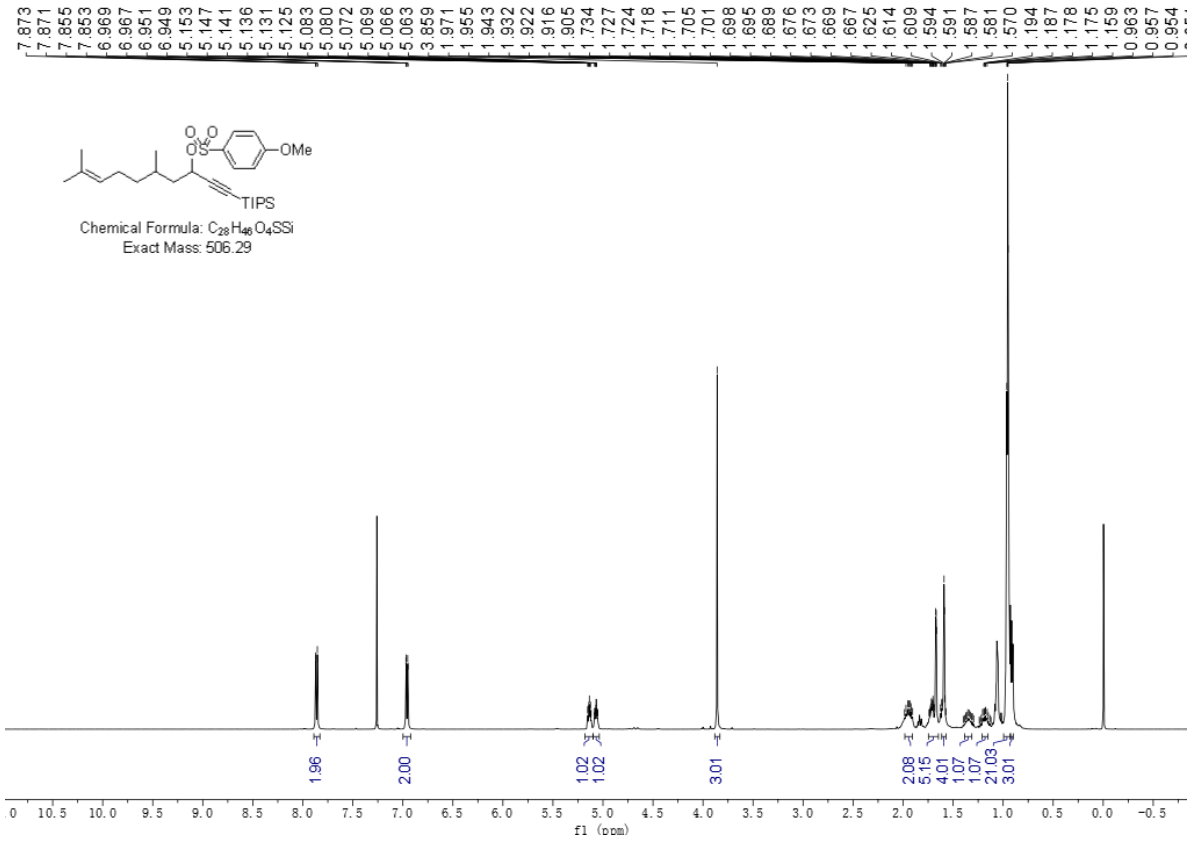


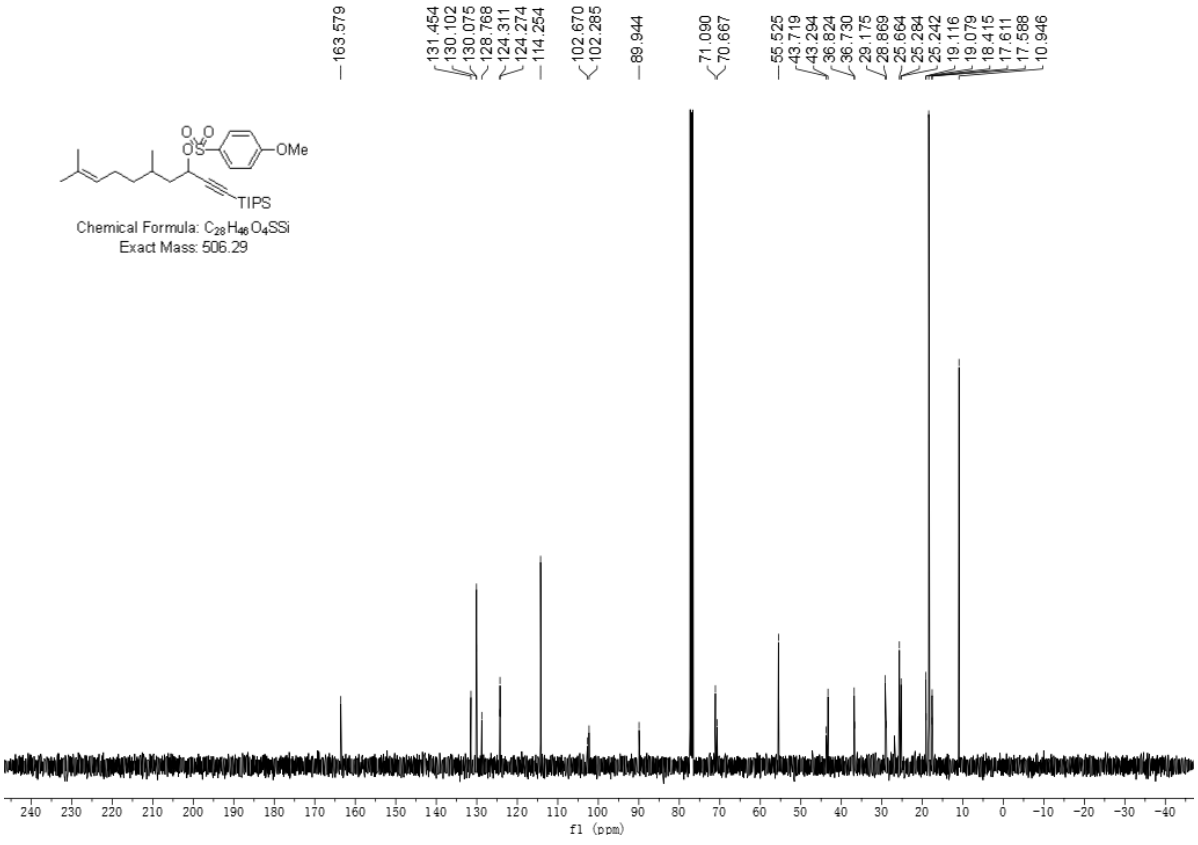
5-Methyl-1-(triisopropylsilyl)hex-1-yn-3-yl 4-methoxybenzenesulfonate (1e)



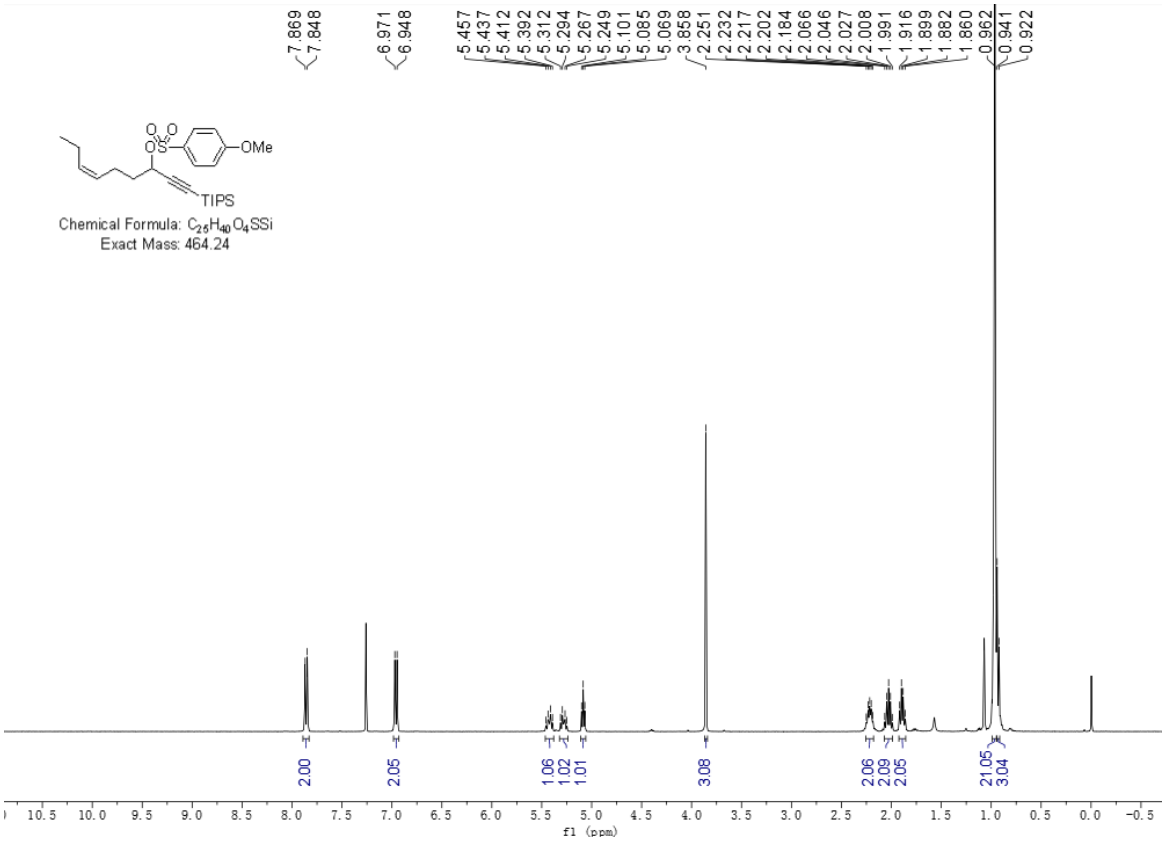


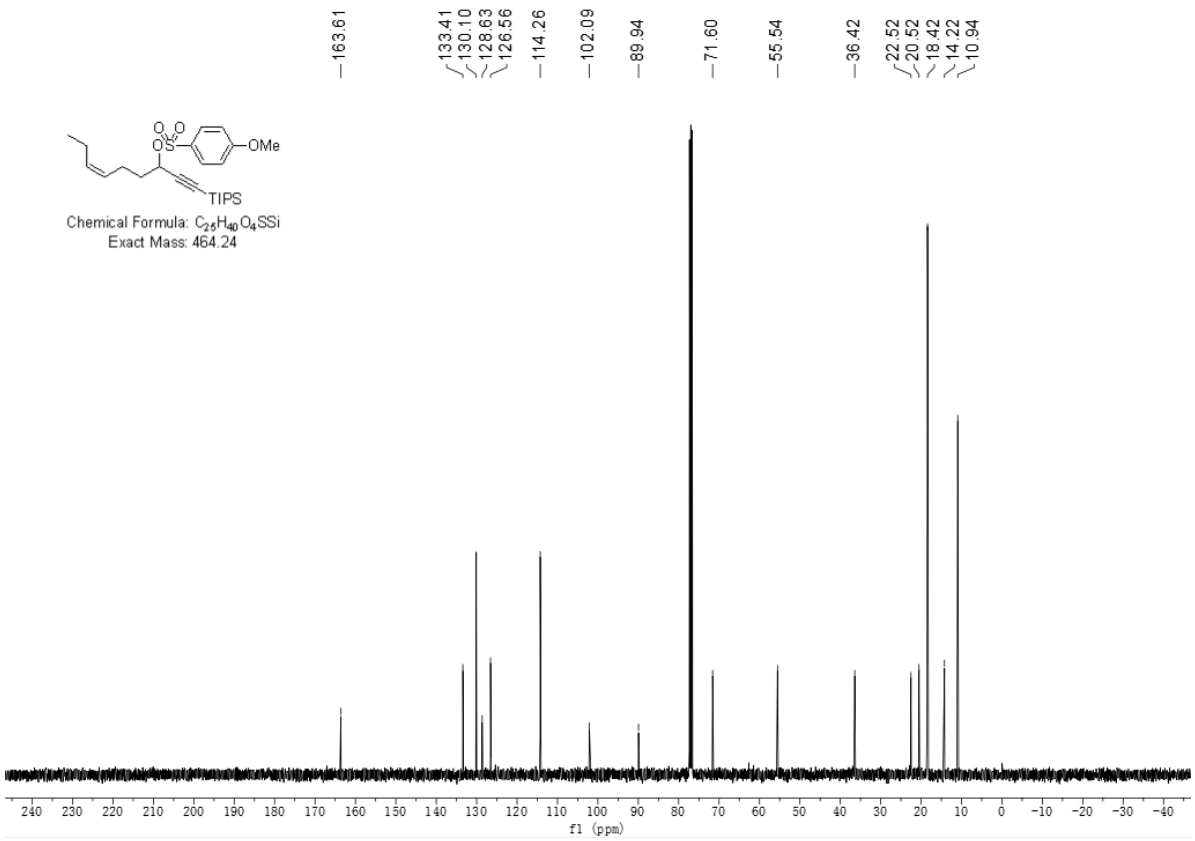
5,9-Dimethyl-1-(triisopropylsilyl)dec-8-en-1-yn-3-yl 4-methoxybenzenesulfonate (1f)



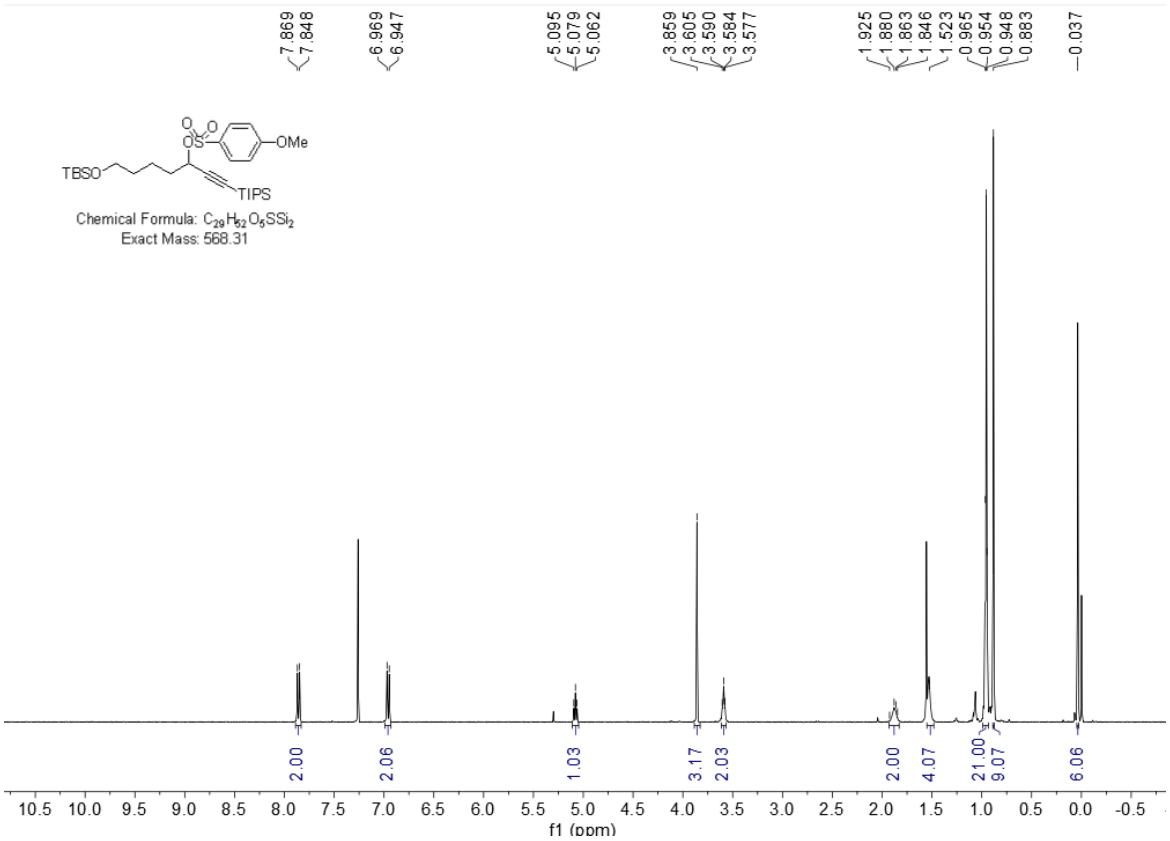


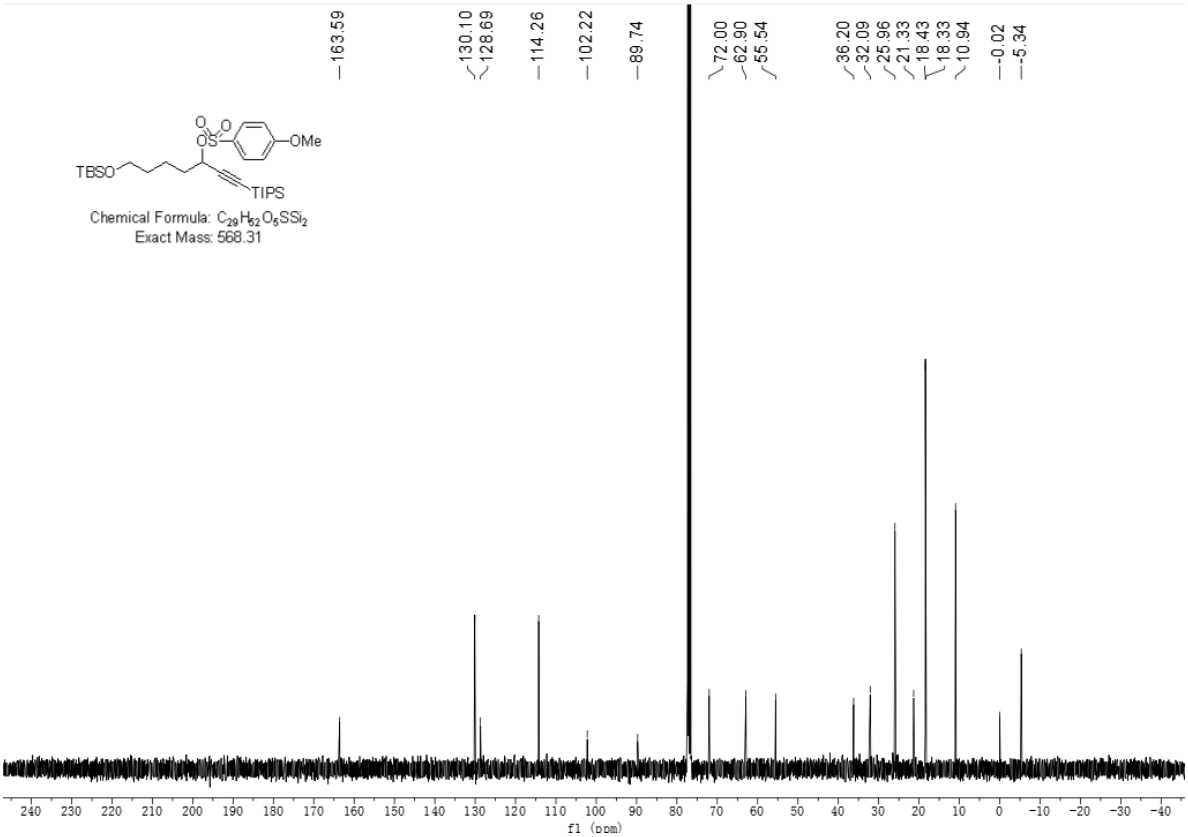
(*Z*)-1-(Triisopropylsilyl)non-6-en-1-yn-3-yl 4-methoxybenzenesulfonate (1g)



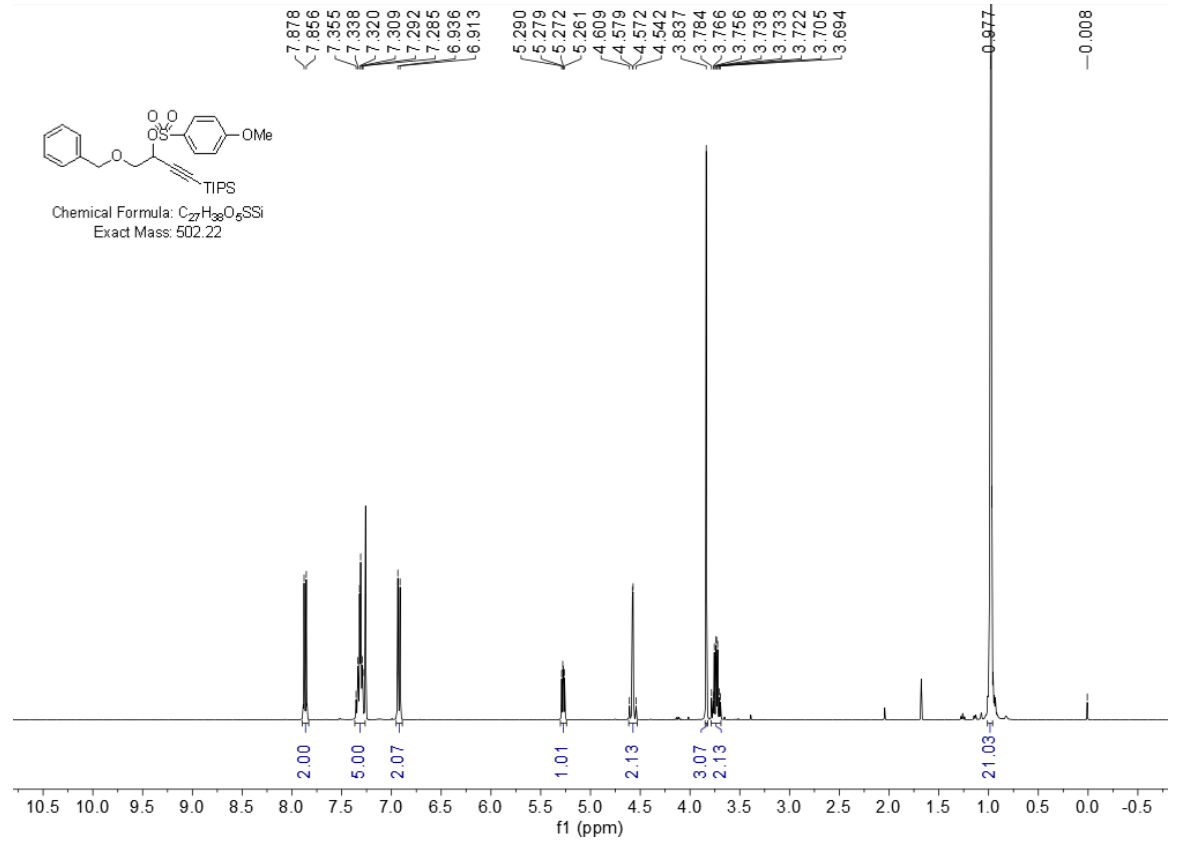


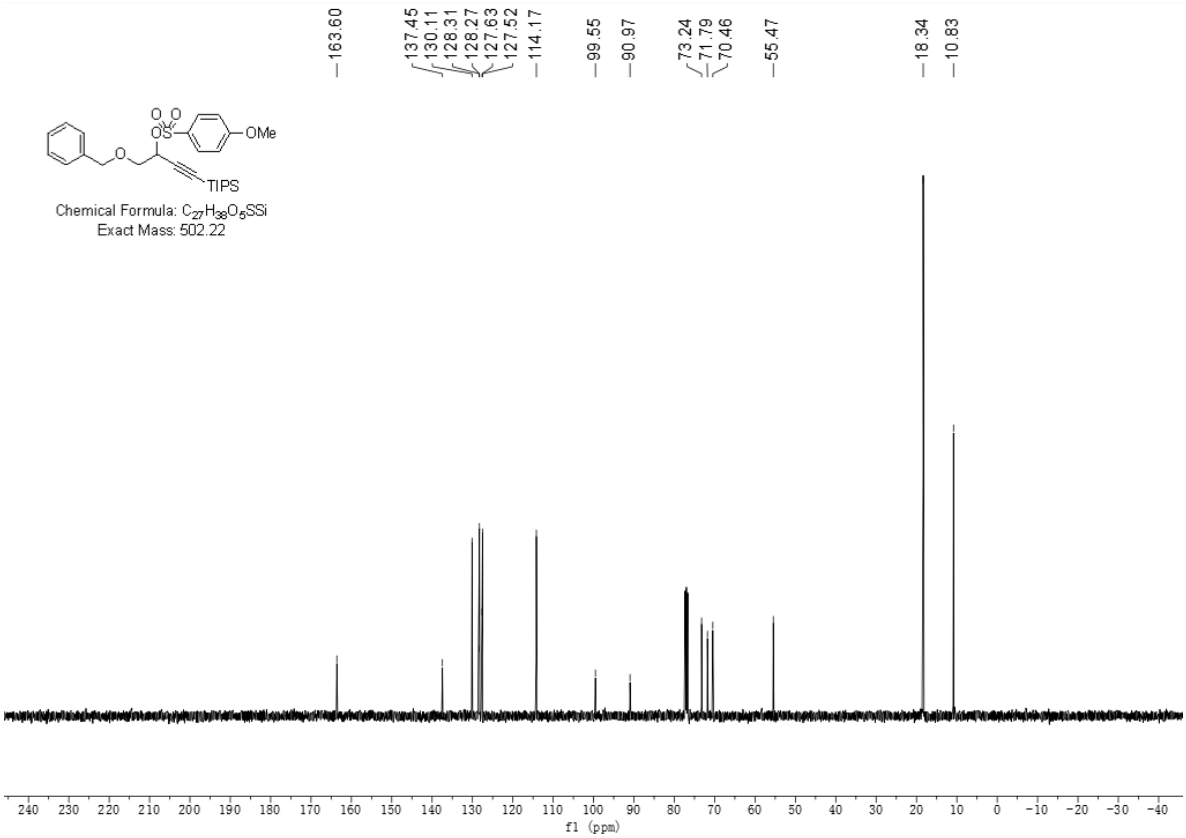
7-((*tert*-Butyldimethylsilyl)oxy)-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1h)



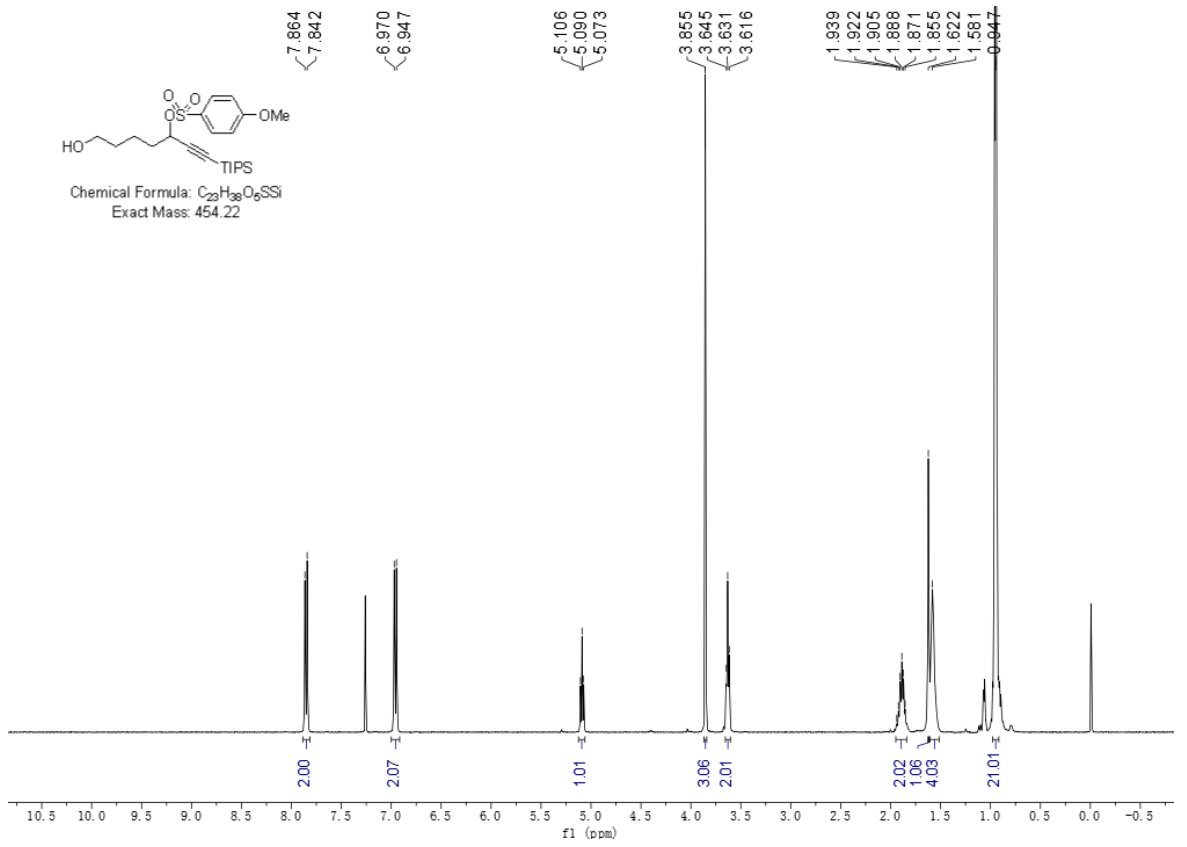


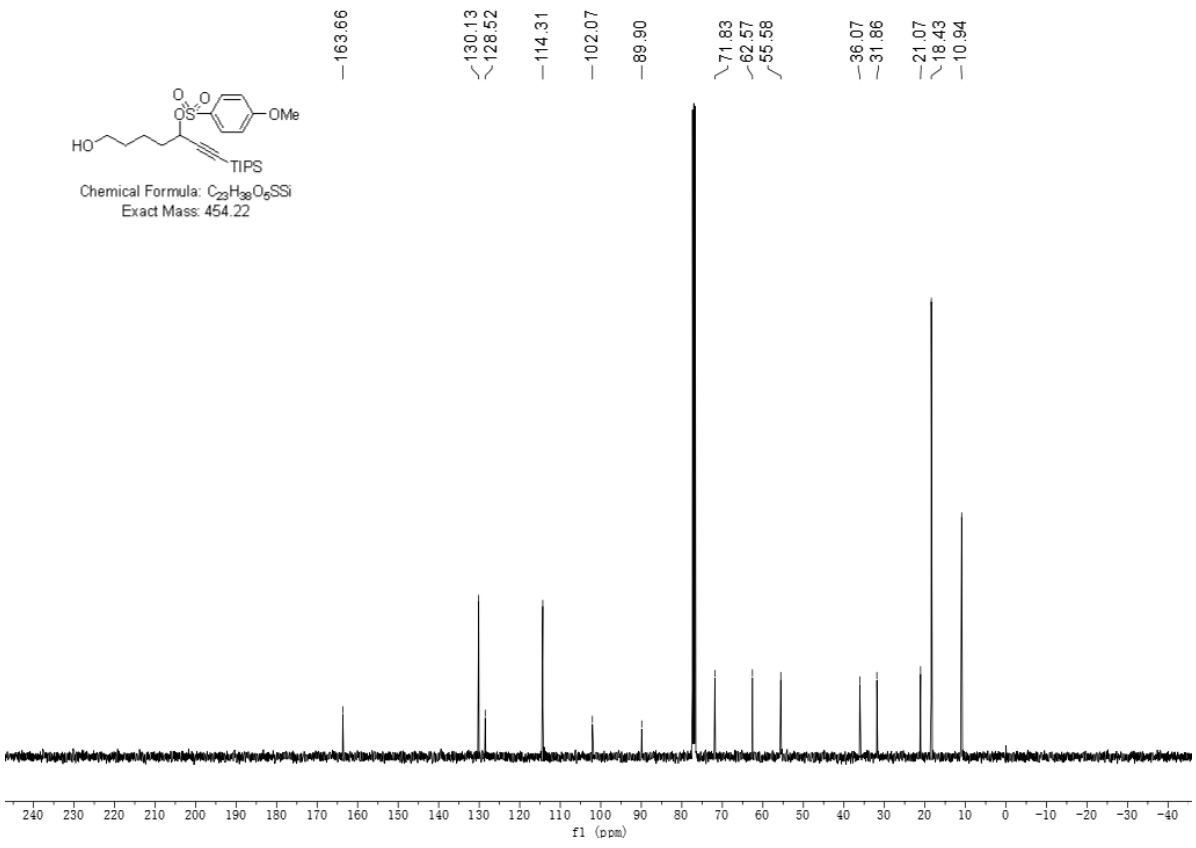
1-(Benzyloxy)-4-(triisopropylsilyl)but-3-yn-2-yl 4-methoxybenzenesulfonate (1i)



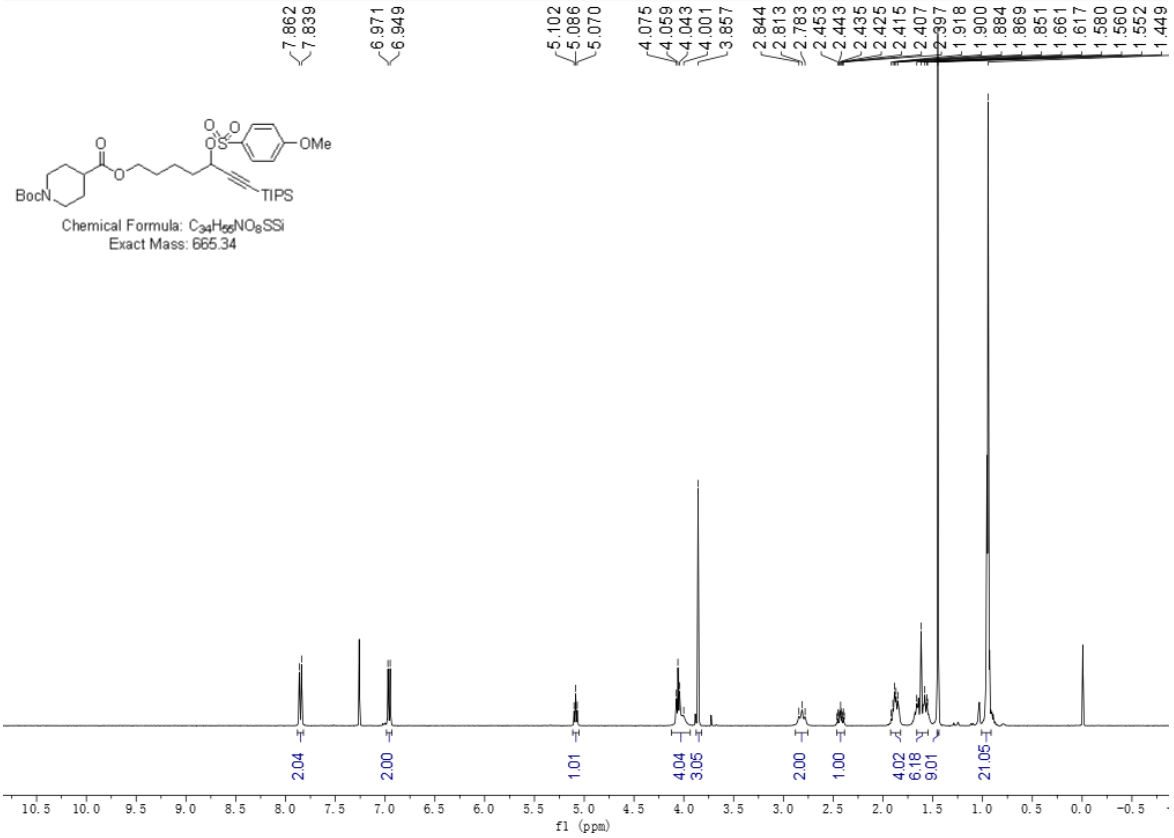


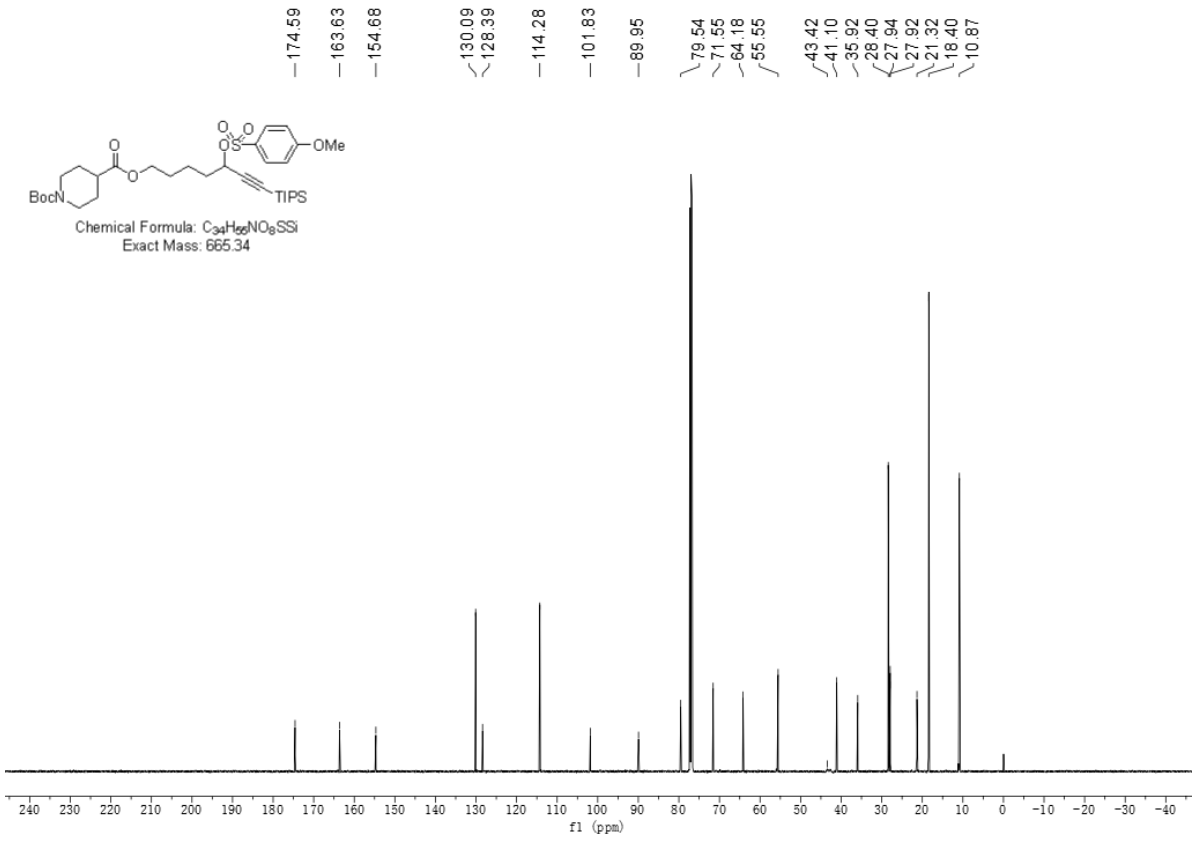
7-Hydroxy-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1j)



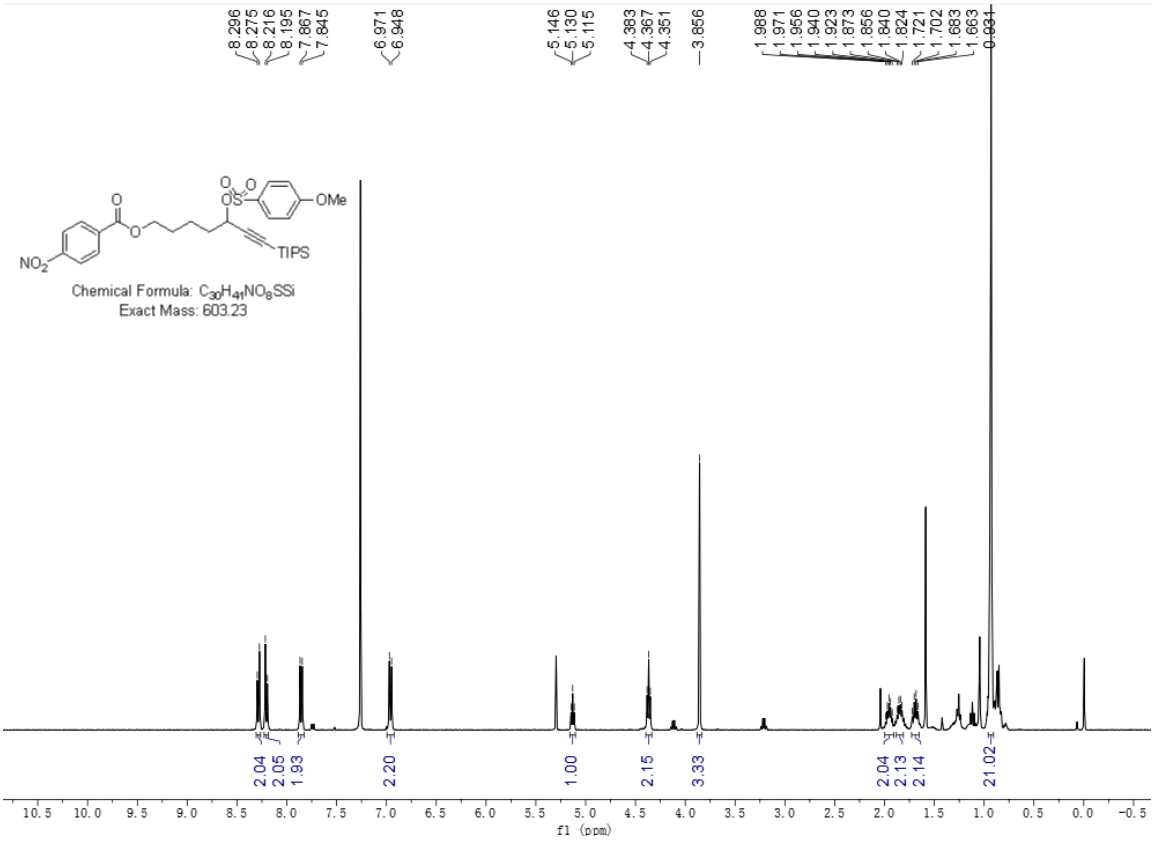


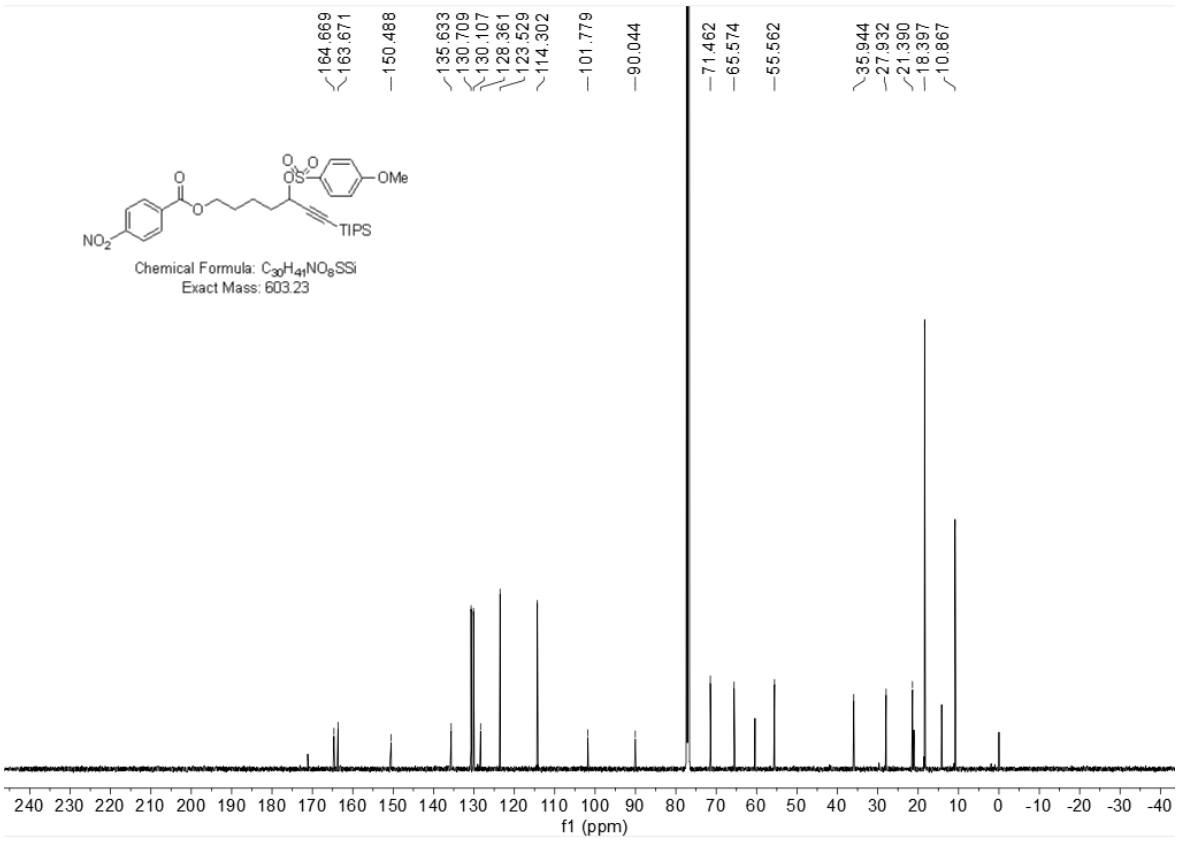
1-(*tert*-Butyl) 4-(5-(((4-methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl) piperidine-1,4-dicarboxylate (1k)



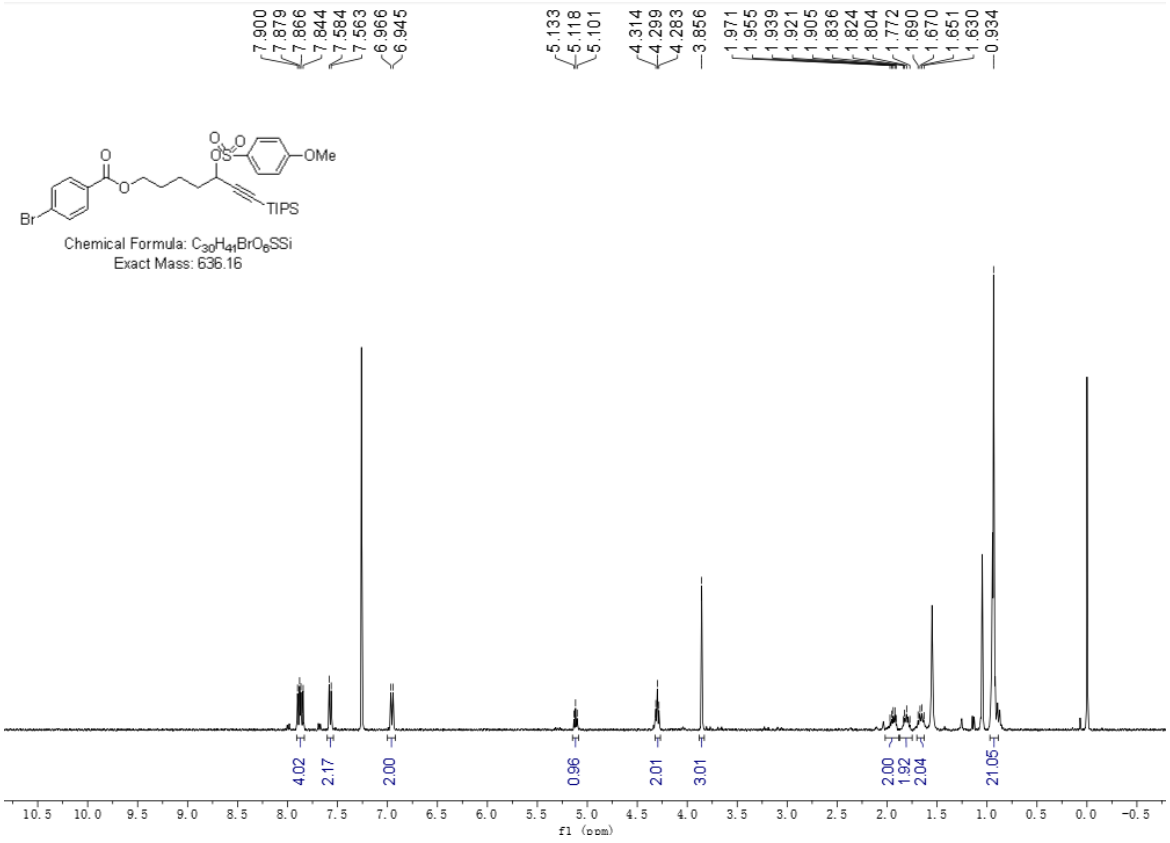


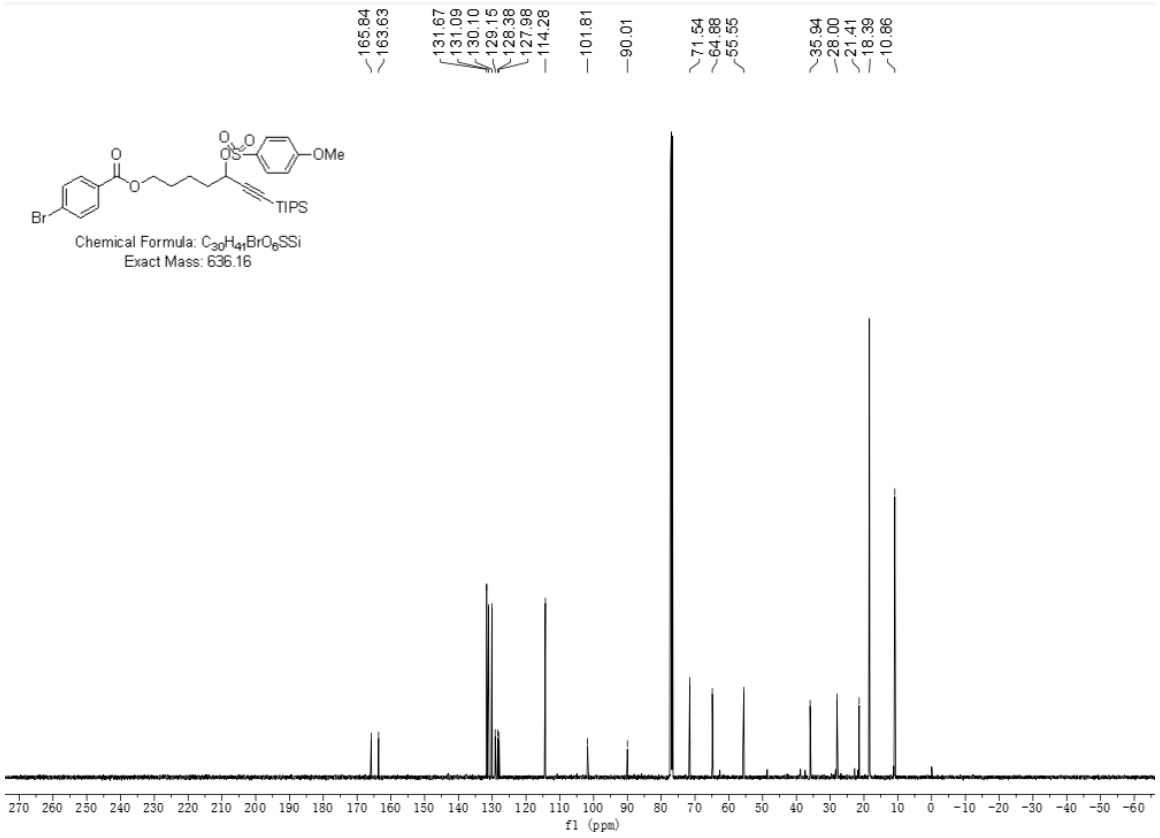
1-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 4-nitrobenzoate (1l)



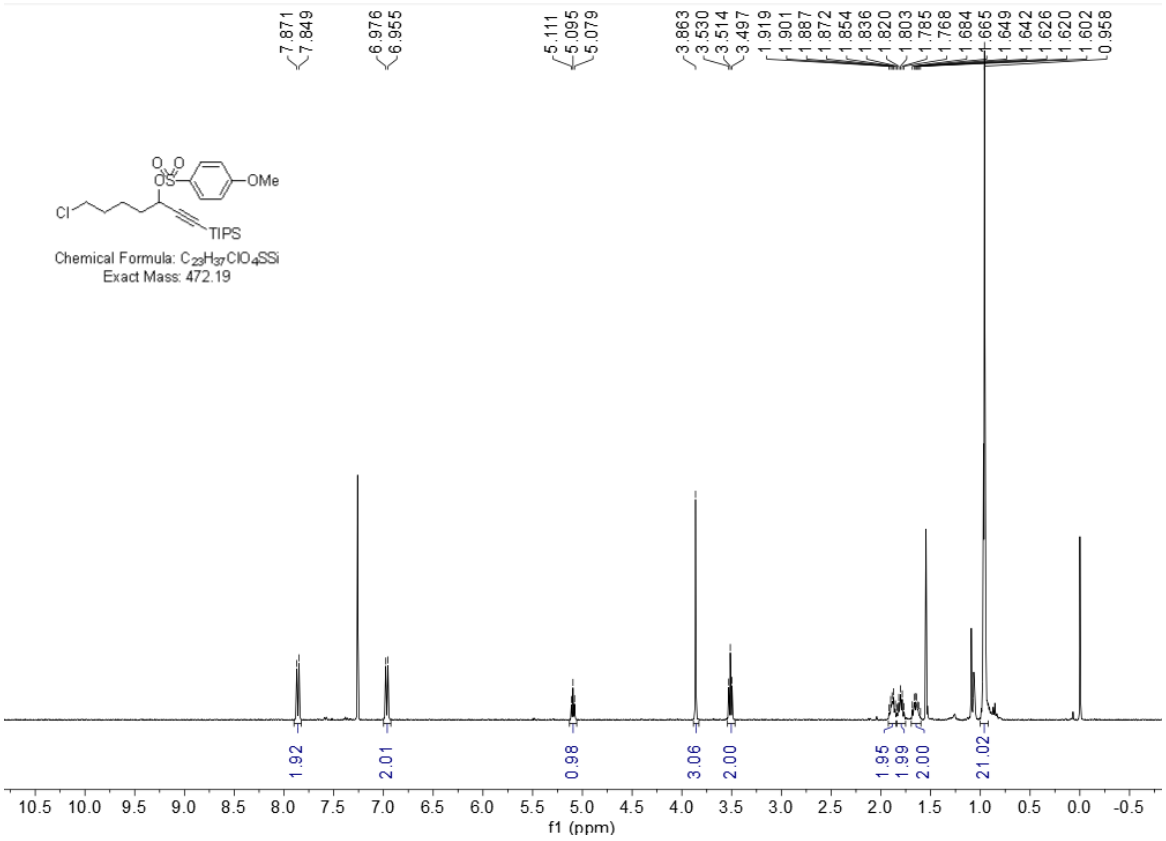


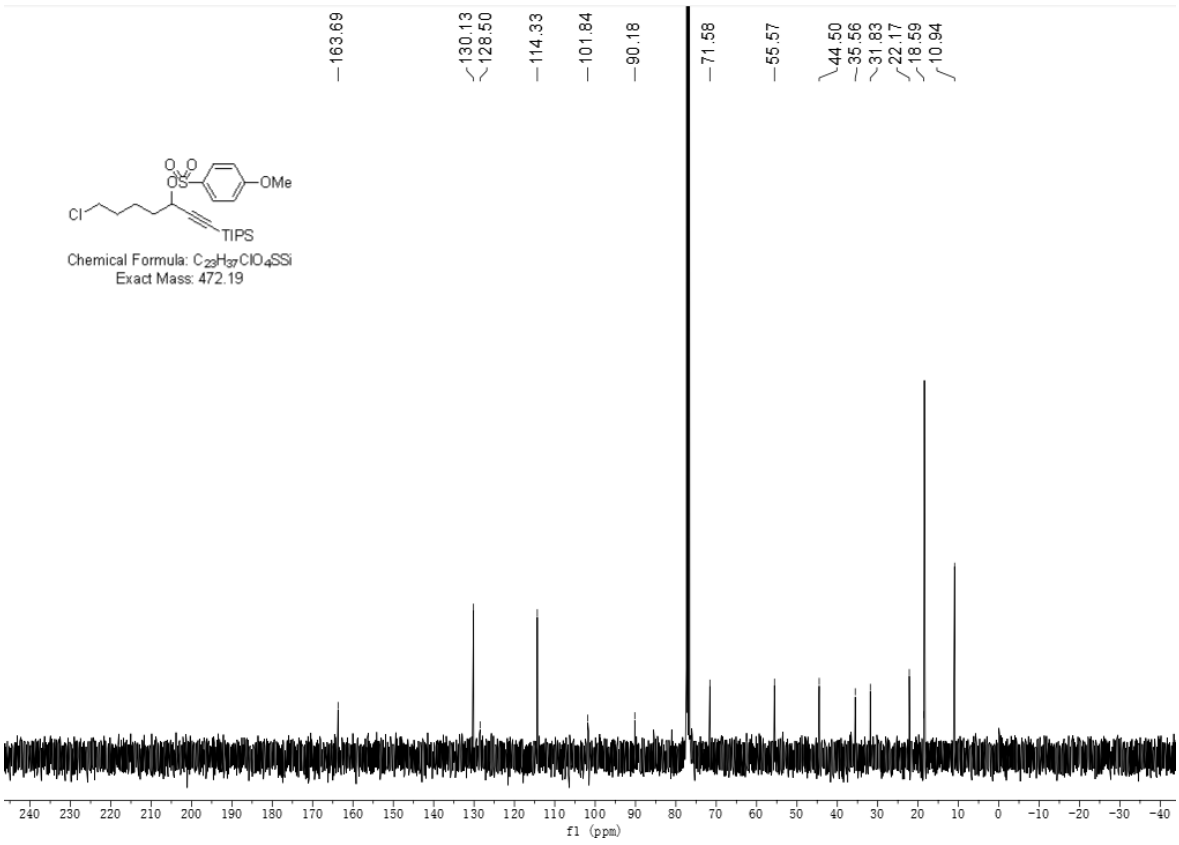
5-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 4-cyanobenzoate (1m)



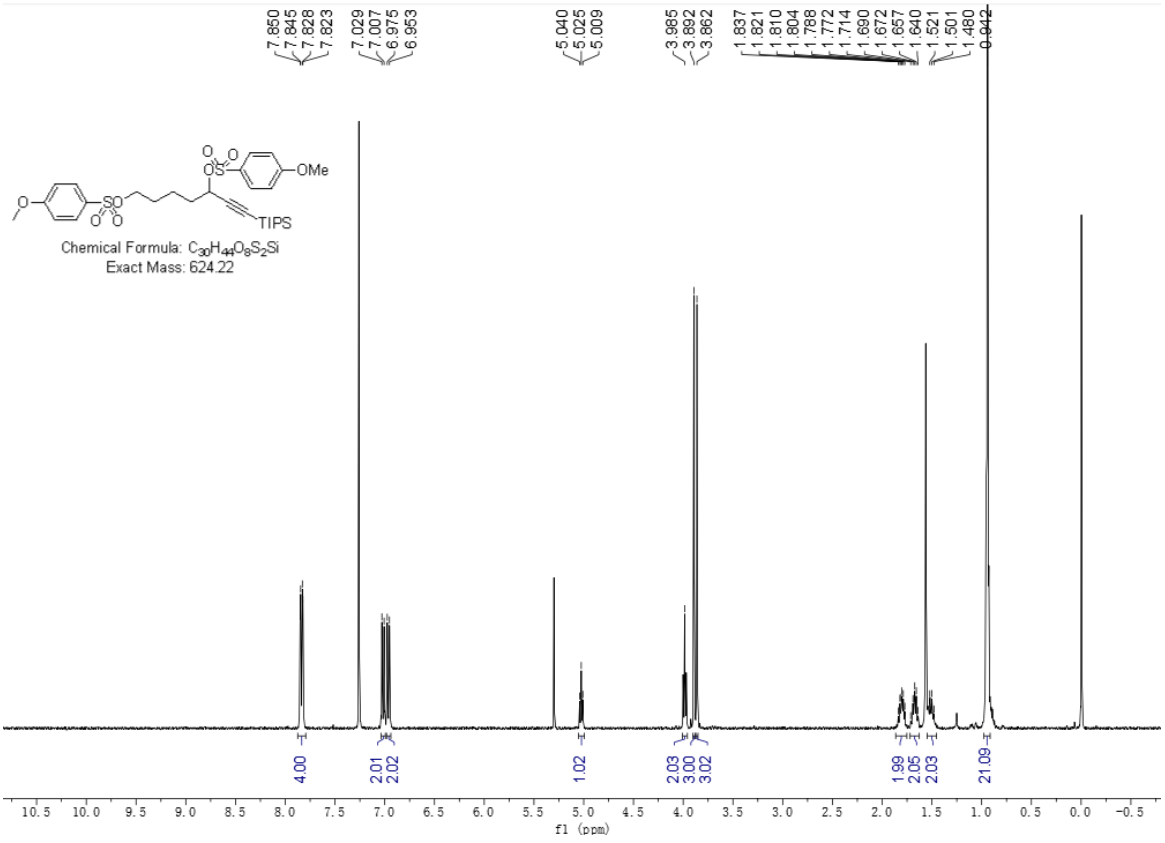


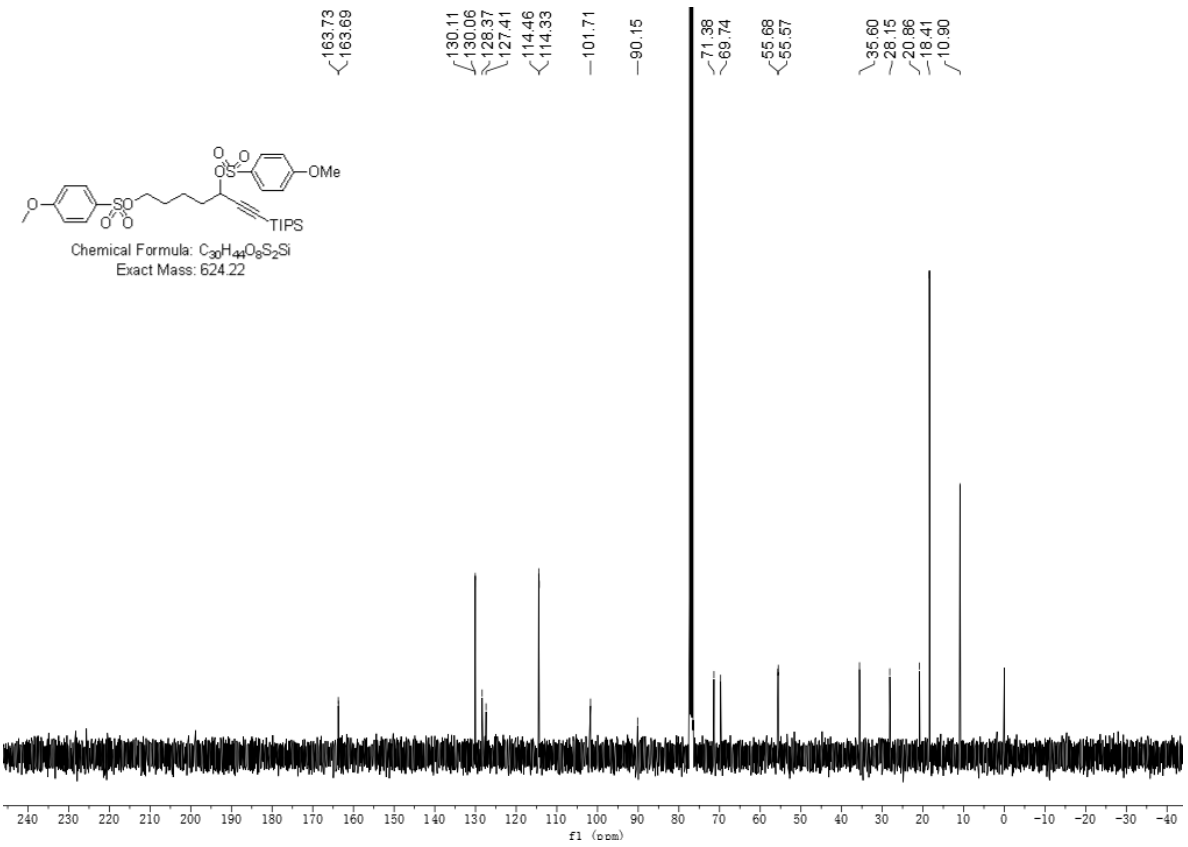
7-Chloro-1-(triisopropylsilyl)hept-1-yn-3-yl 4-methoxybenzenesulfonate (1n)



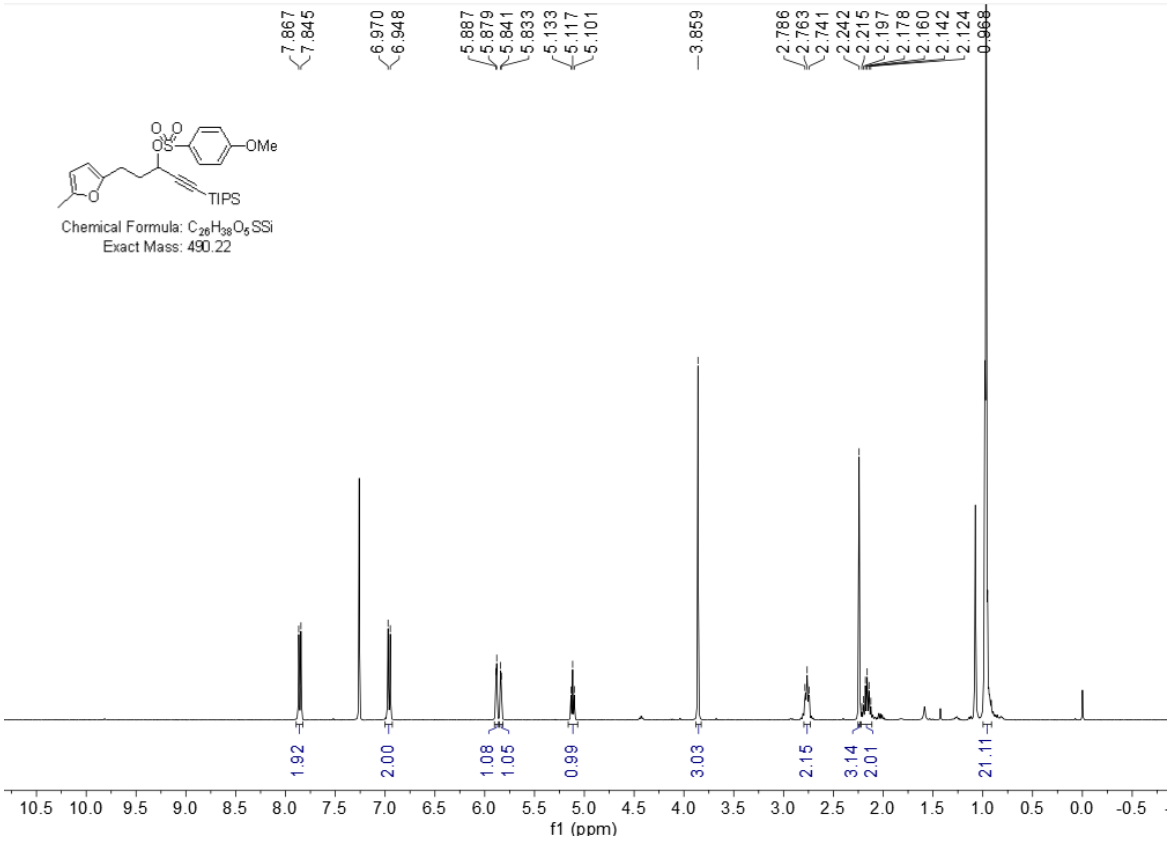


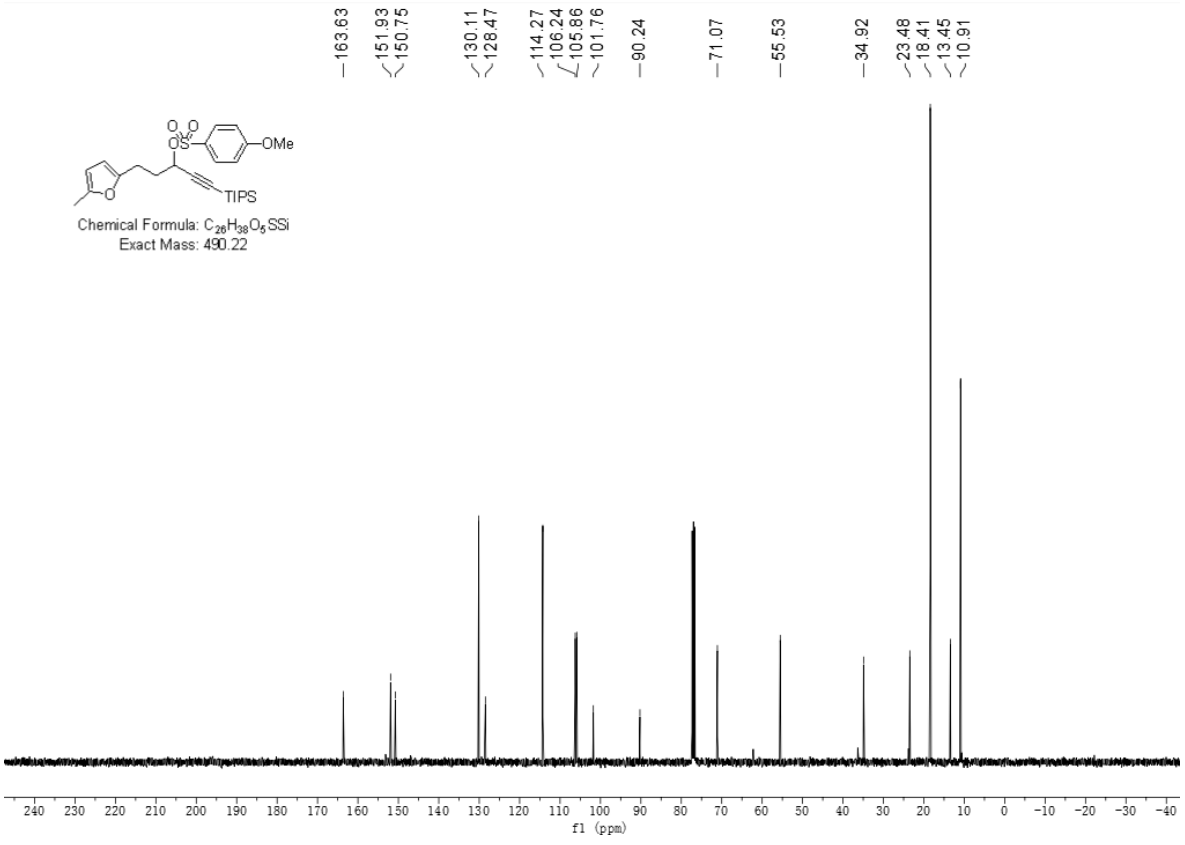
7-(Triisopropylsilyl)hept-6-yne-1,5-diyl bis(4-methoxybenzenesulfonate) (1o)



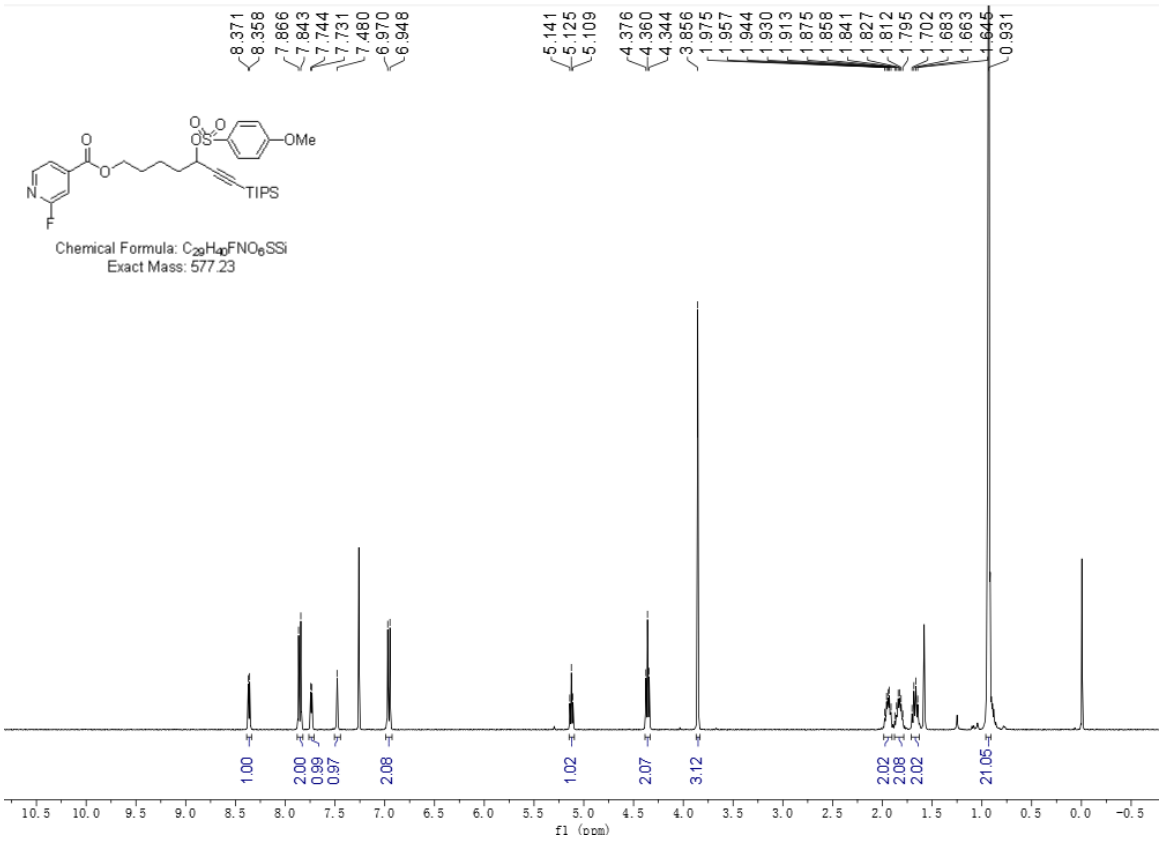


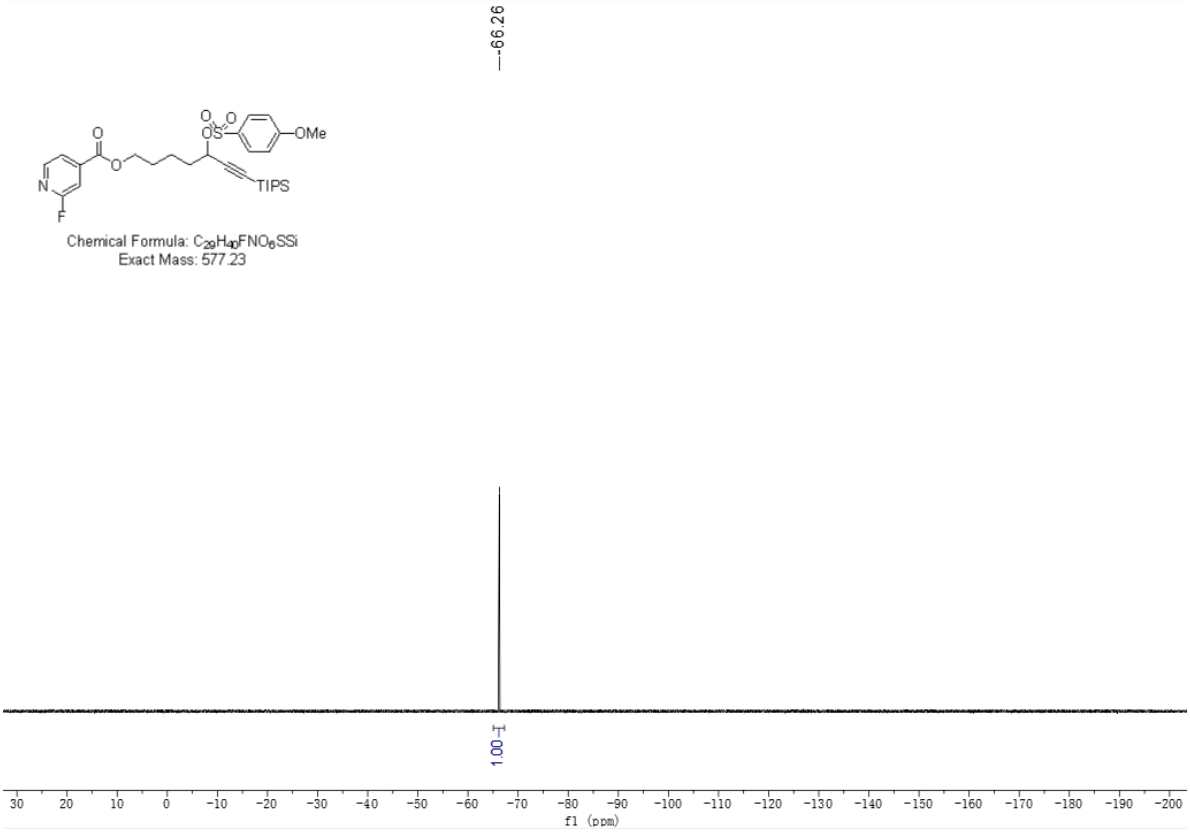
5-(5-Methylfuran-2-yl)-1-(triisopropylsilyl)pent-1-yn-3-yl 4-methoxybenzenesulfonate (1p)

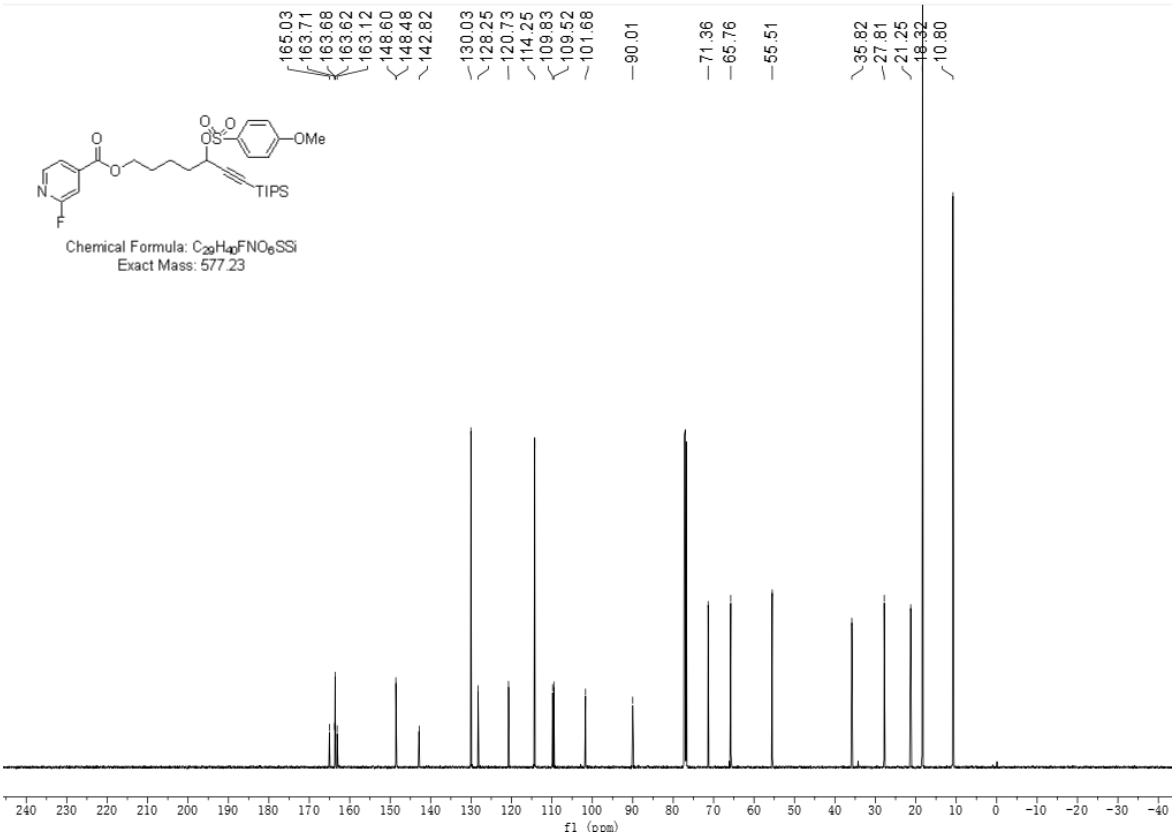




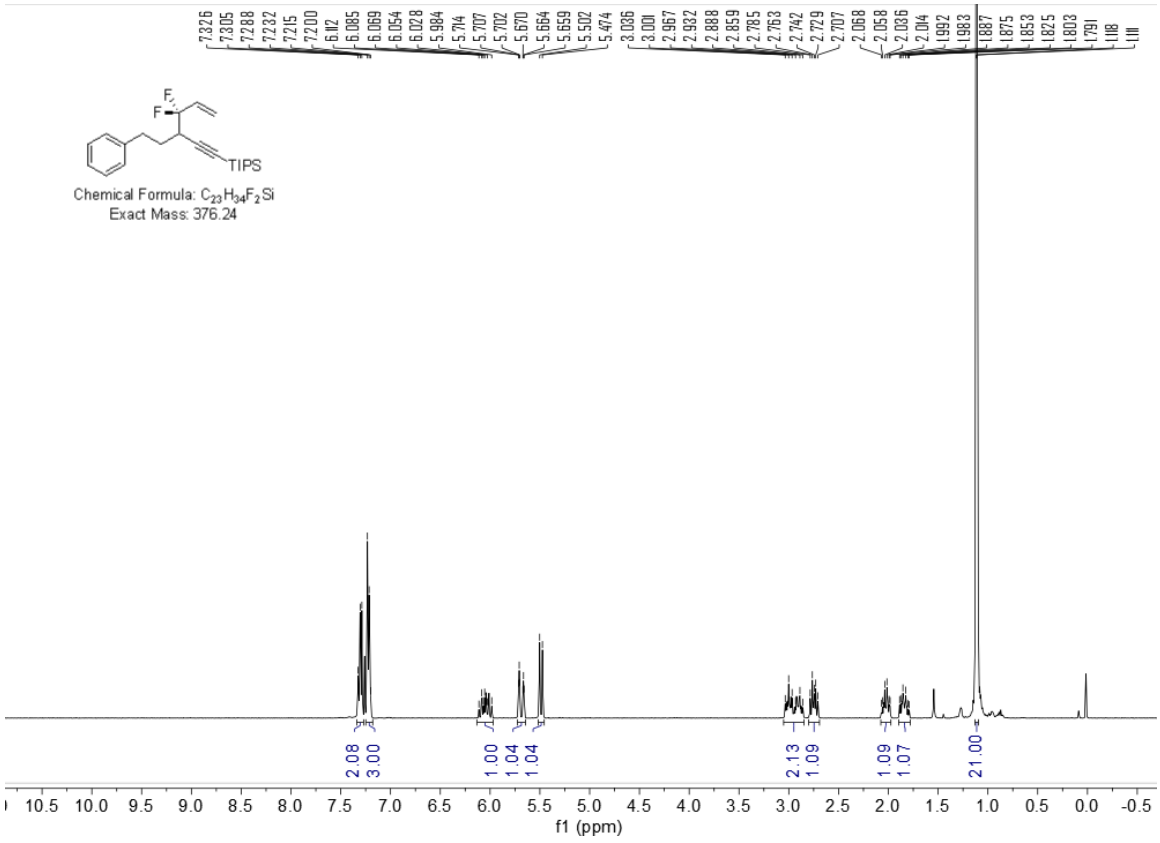
5-(((4-Methoxyphenyl)sulfonyl)oxy)-7-(triisopropylsilyl)hept-6-yn-1-yl 2-fluoroisonicotinate (1q)

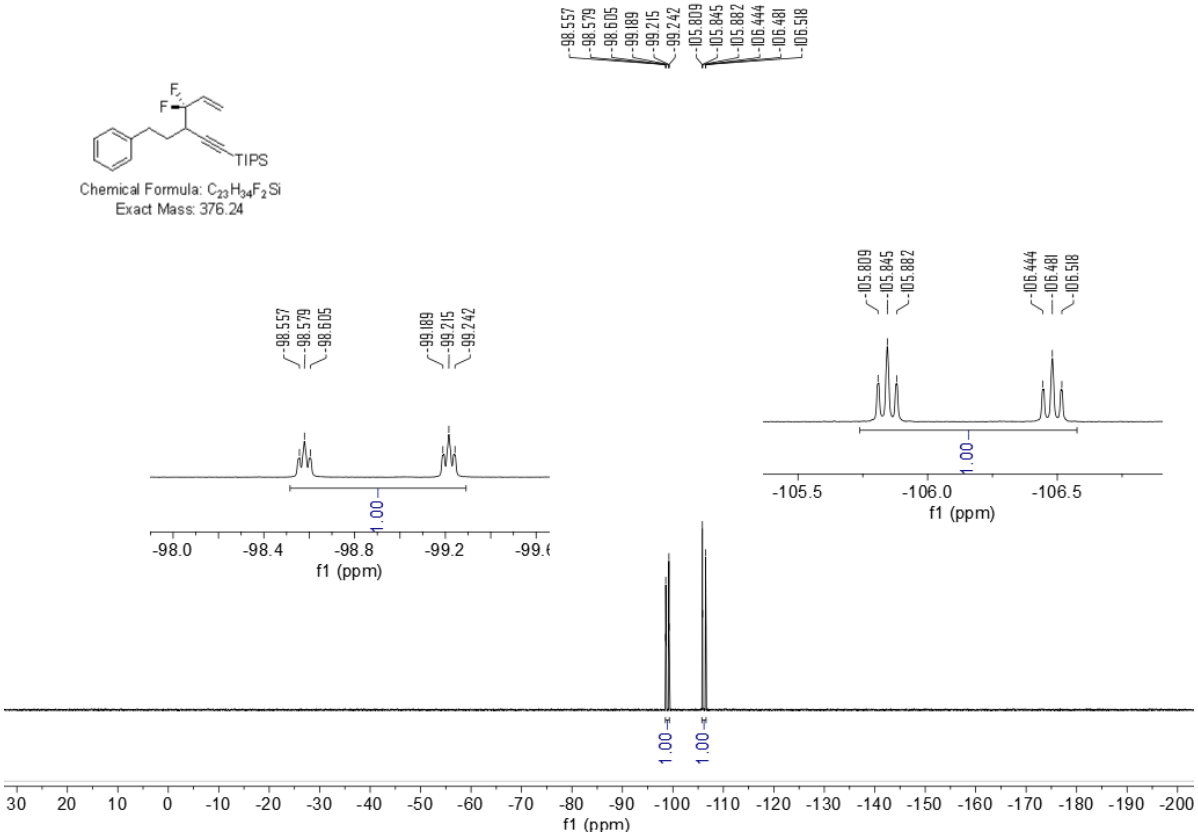


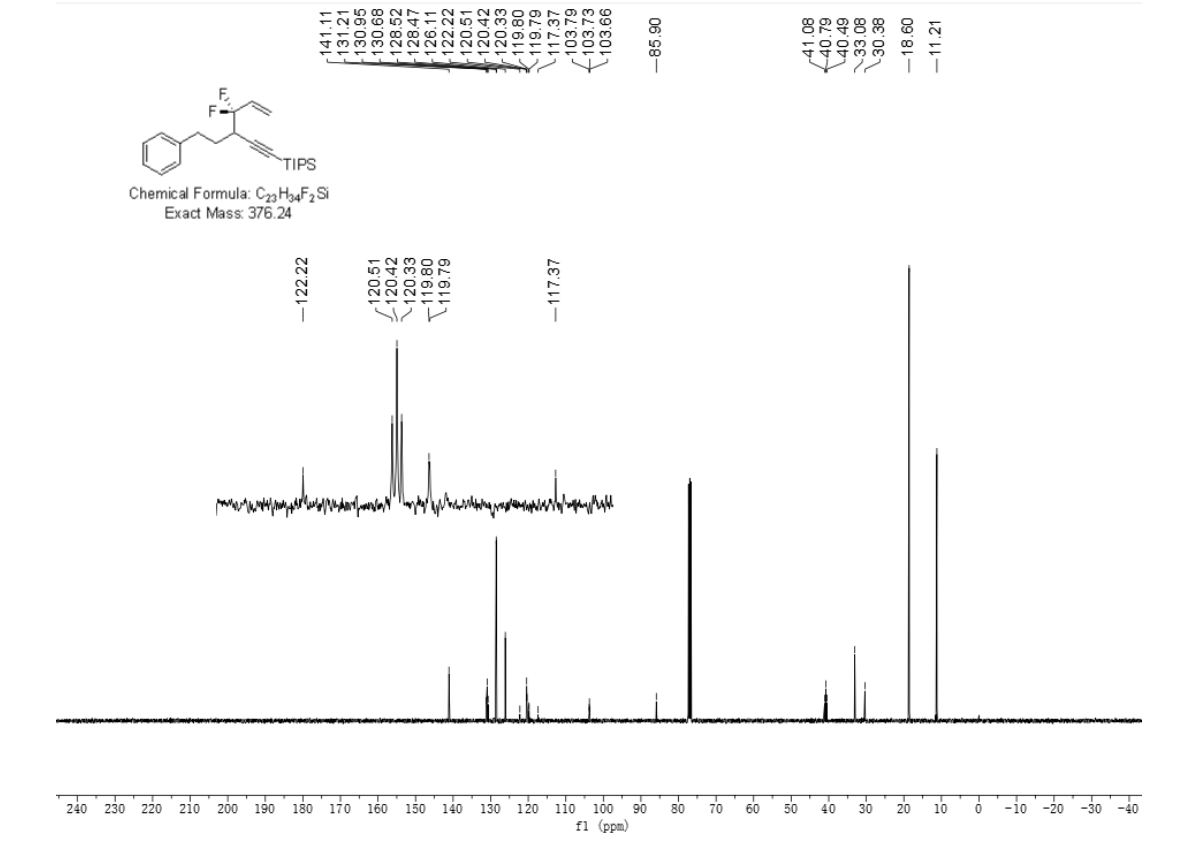




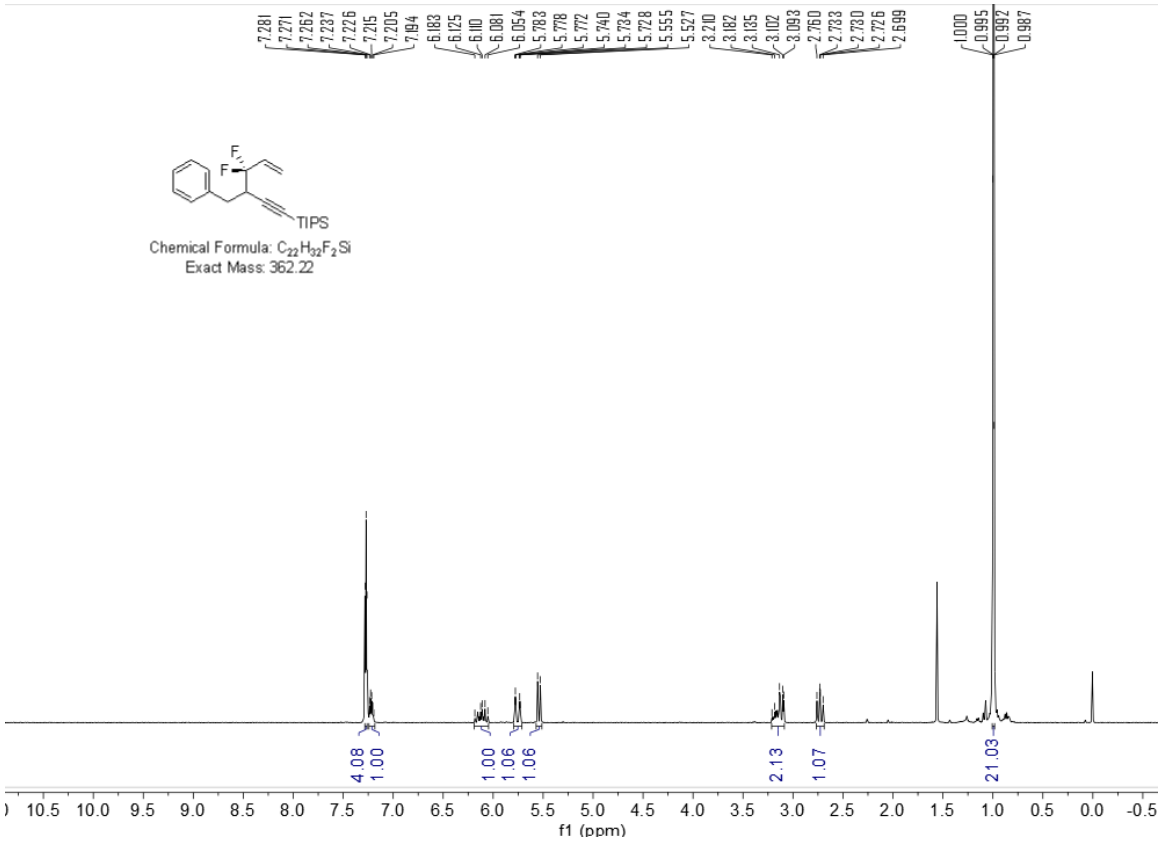
(4,4-Difluoro-3-phenethylhex-5-en-1-yn-1-yl)triisopropylsilane (3a)

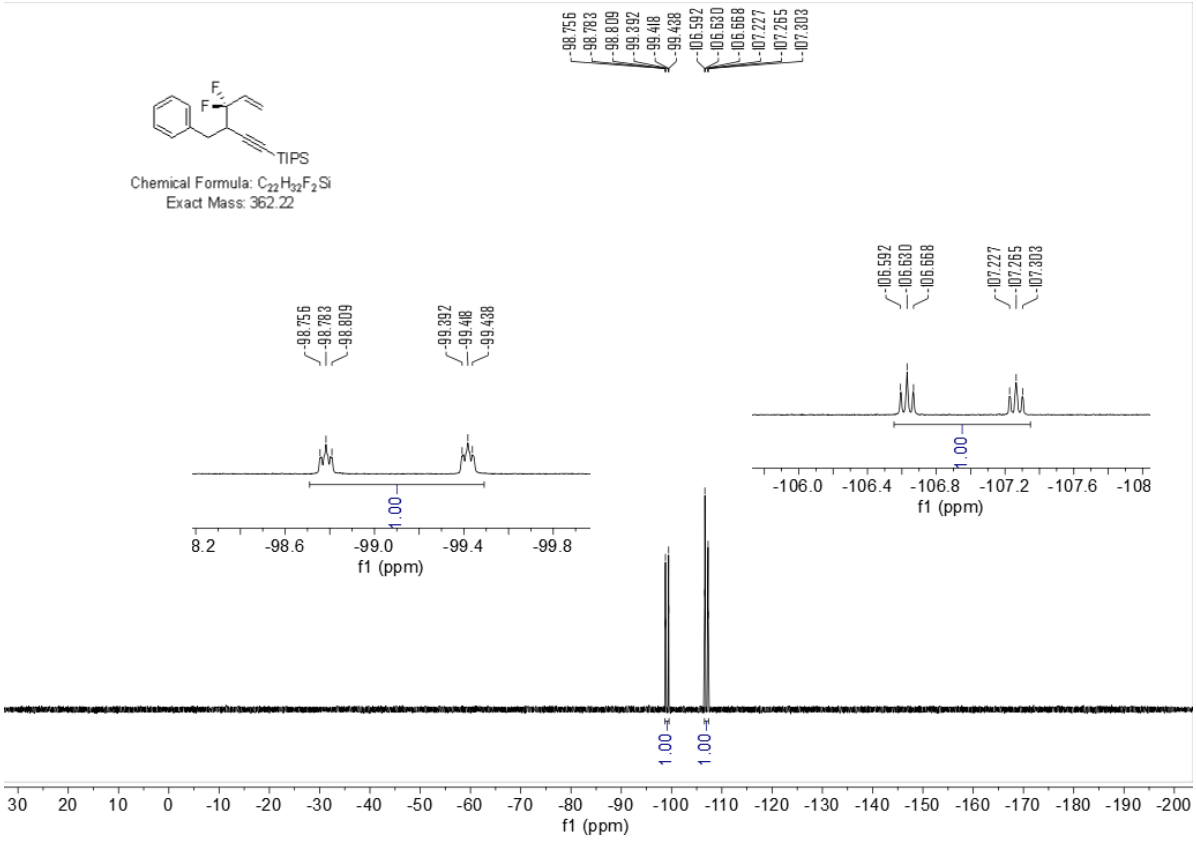


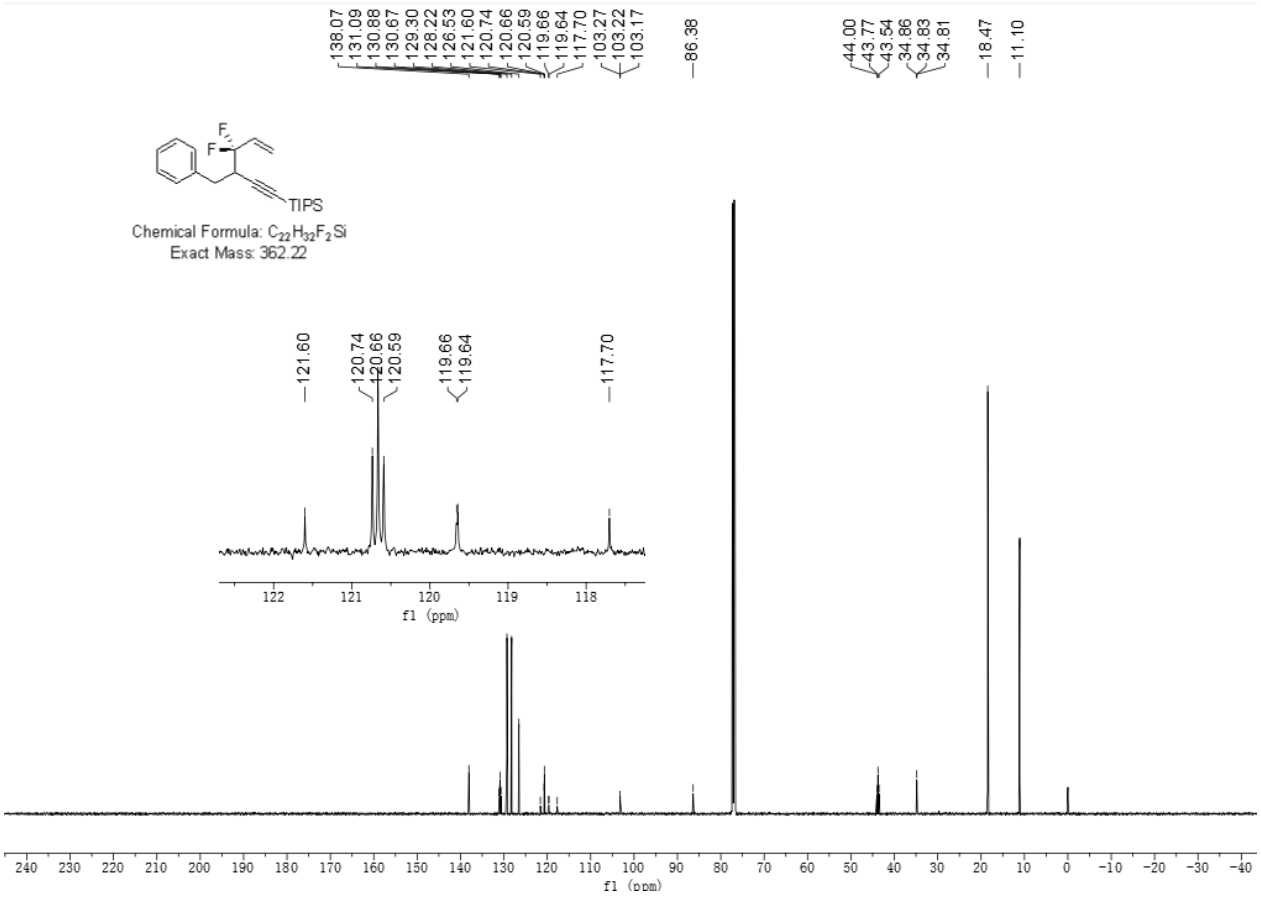

-98.557
-98.579
-98.605
-99.189
-99.215
-99.242
-105.809
-105.845
-105.882
-106.444
-106.481
-106.518
F
F
TIPS
Chemical Formula: C23H34F2Si
Exact Mass: 376.24
1.00
1.00
1.00
f1 (ppm)


141.11
131.21
130.95
130.68
128.52
128.47
126.11
122.22
120.51
120.42
120.33
119.80
119.79
117.37
103.79
103.73
103.66
85.90
41.08
40.79
40.49
33.08
30.38
18.60
11.21
F
F
TIPS
Chemical Formula: C23H34F2Si
Exact Mass: 376.24
f1 (ppm)

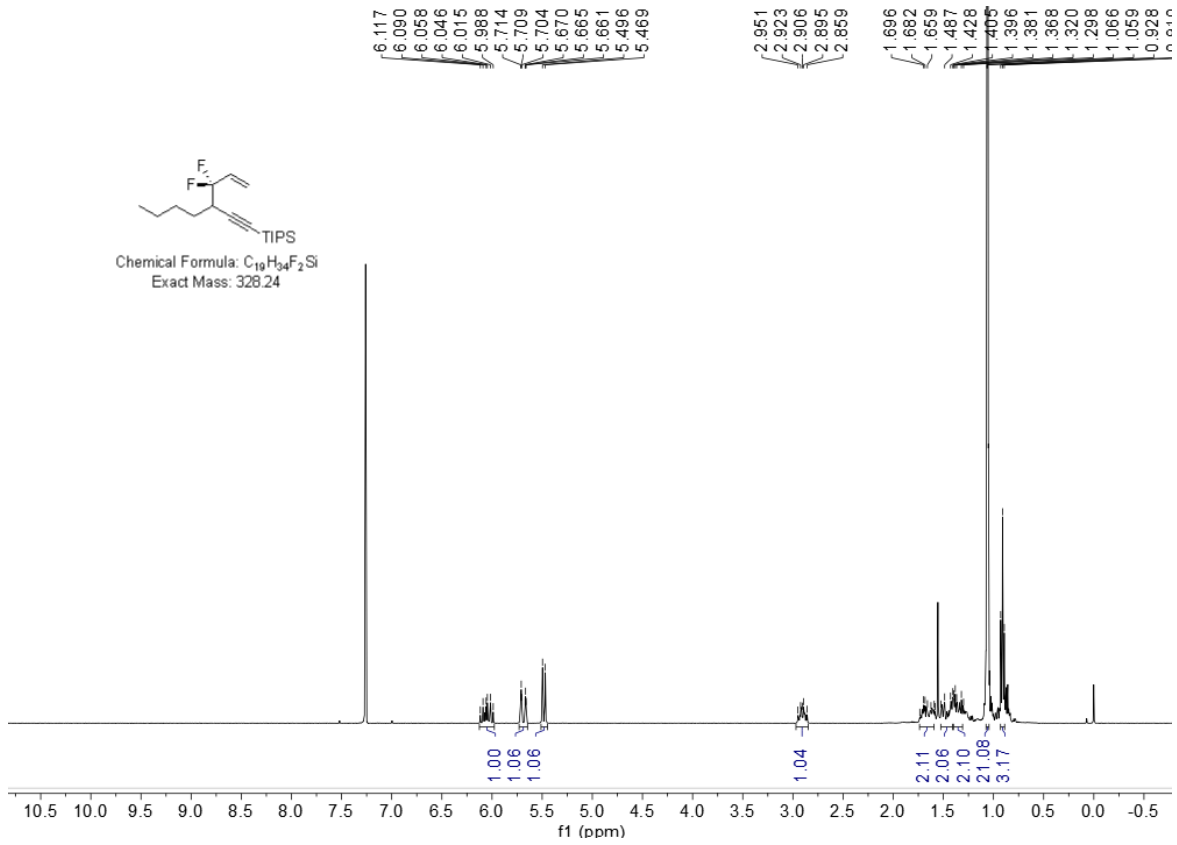
Difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3b)

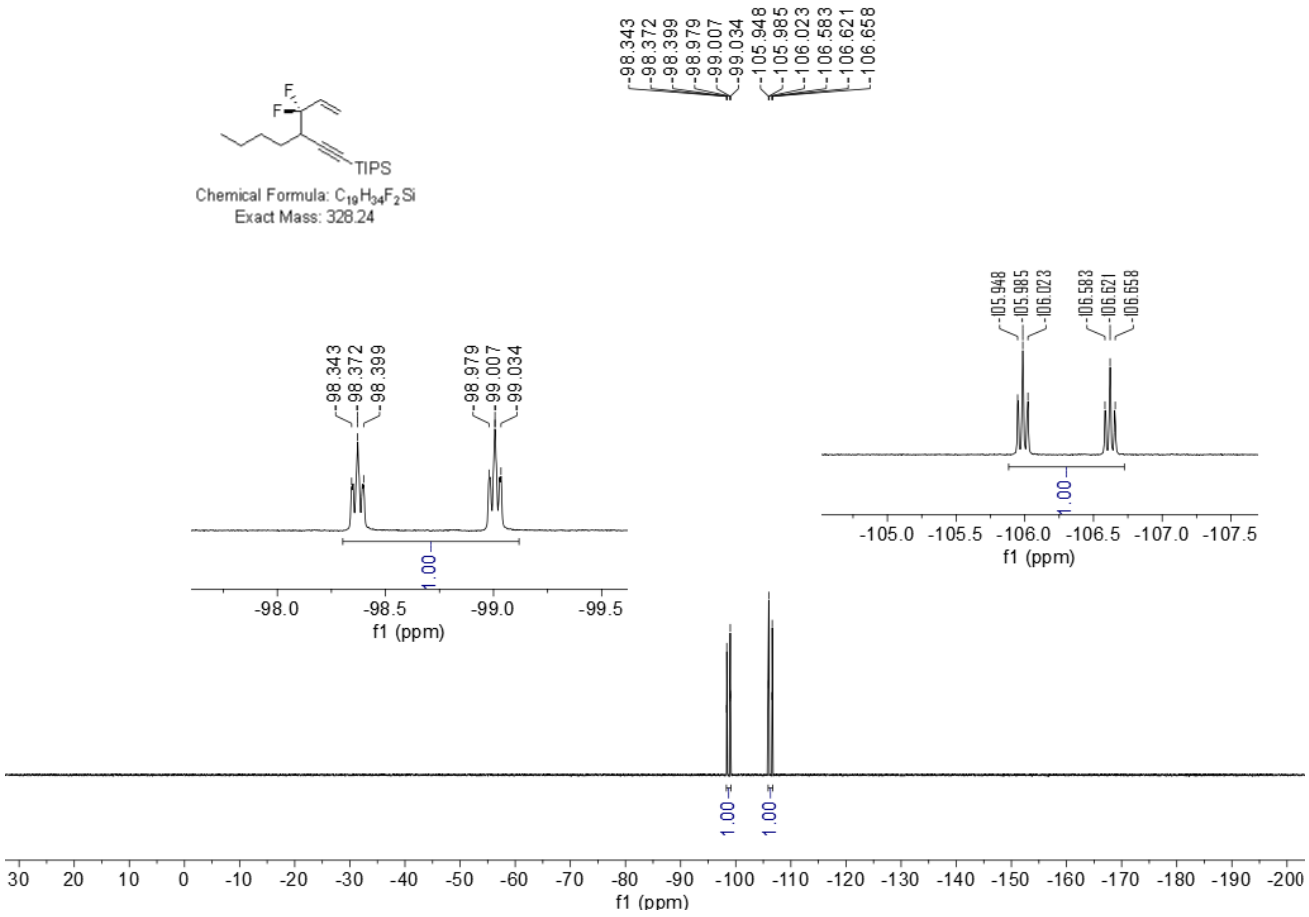


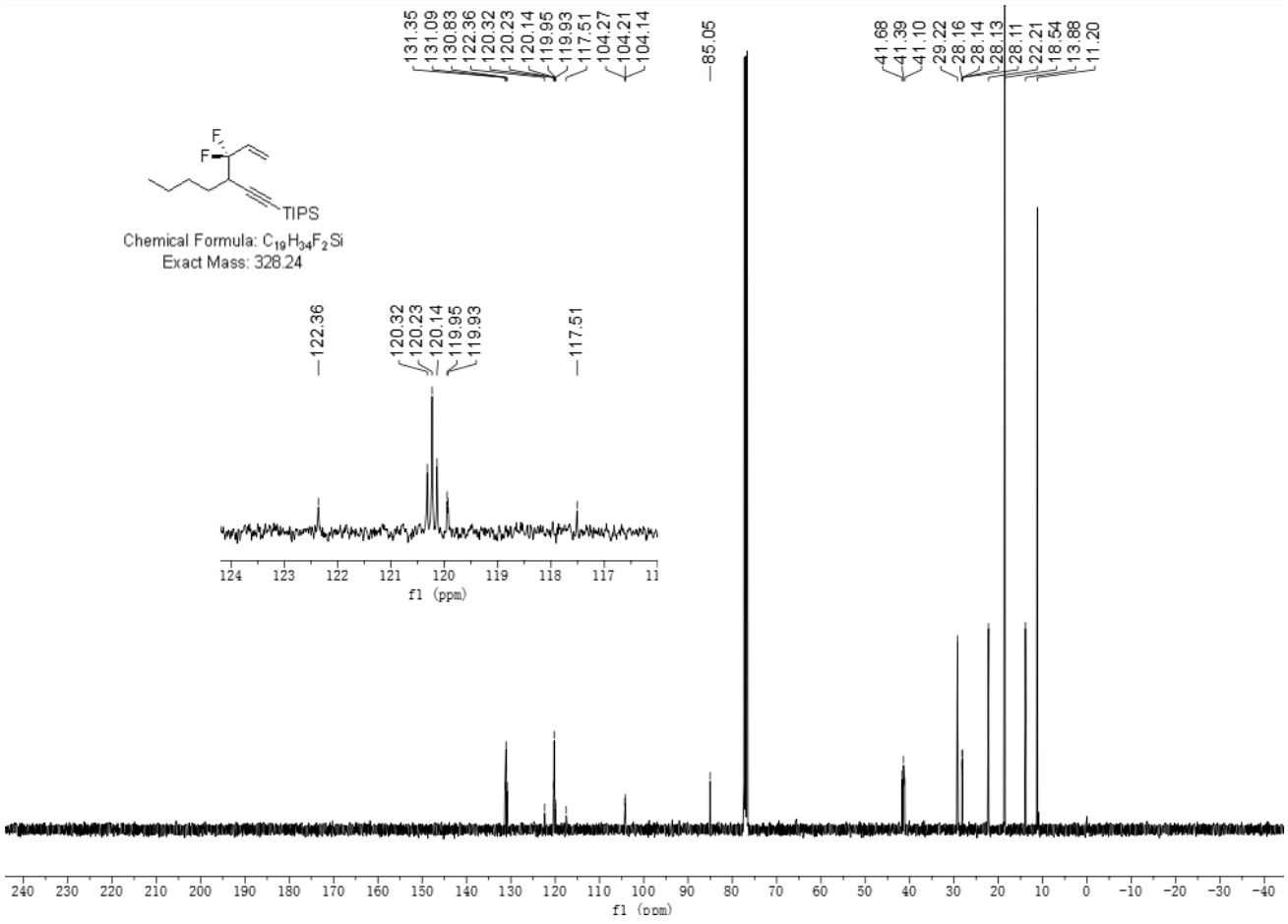




(1,1-Difluoroallyl)hept-1-yn-1-yl)triisopropylsilane (3c)




-98.343
-98.372
-98.399
-98.979
-99.007
-99.034
-105.948
-105.985
-106.023
-106.583
-106.621
-106.658
F
F
TIPS
Chemical Formula: C19H34F2Si
Exact Mass: 328.24
1.00
1.00
1.00
f1 (ppm)


131.35
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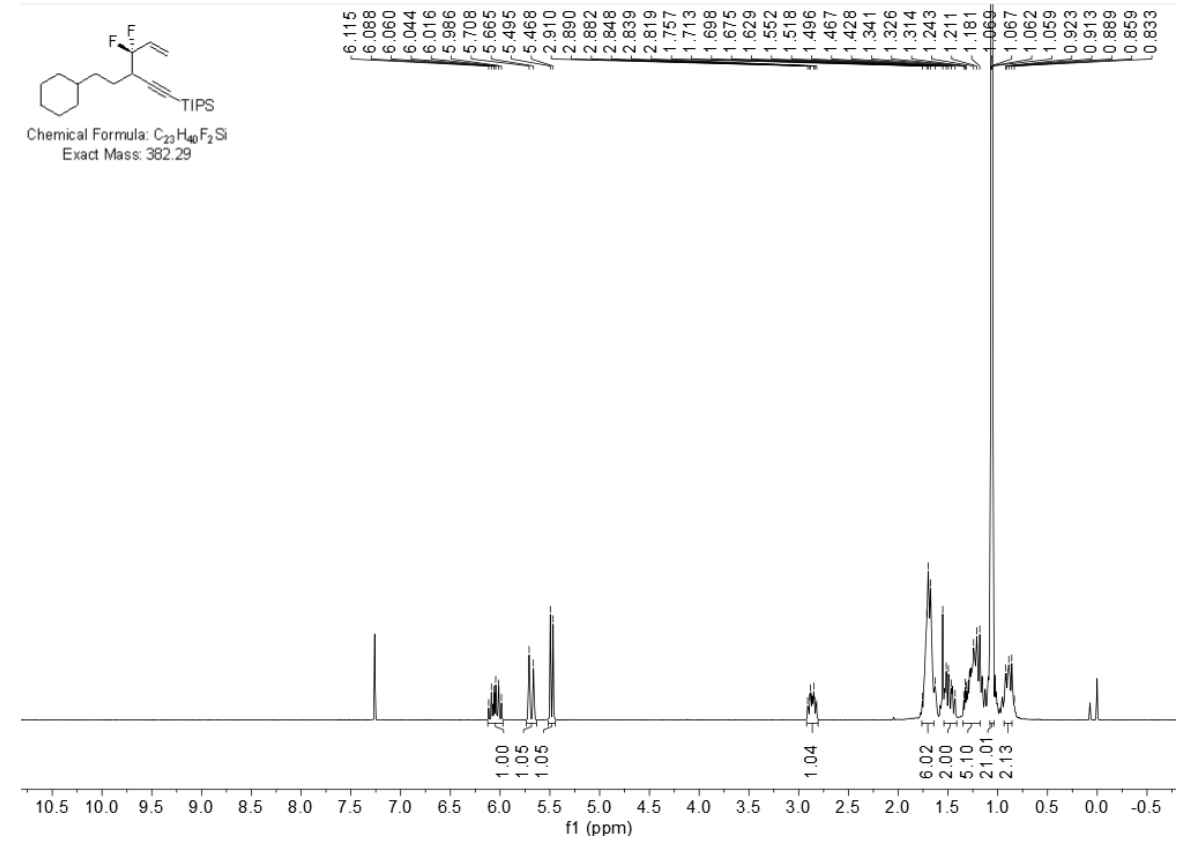
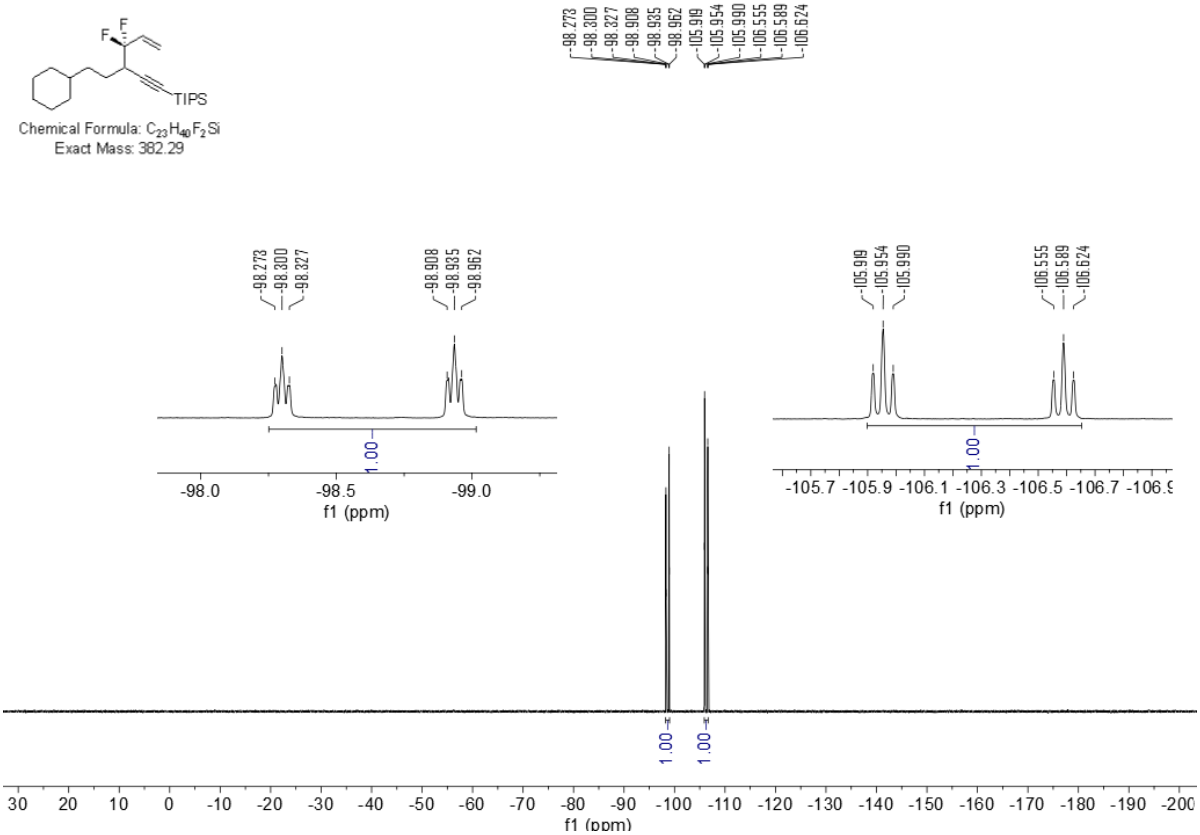
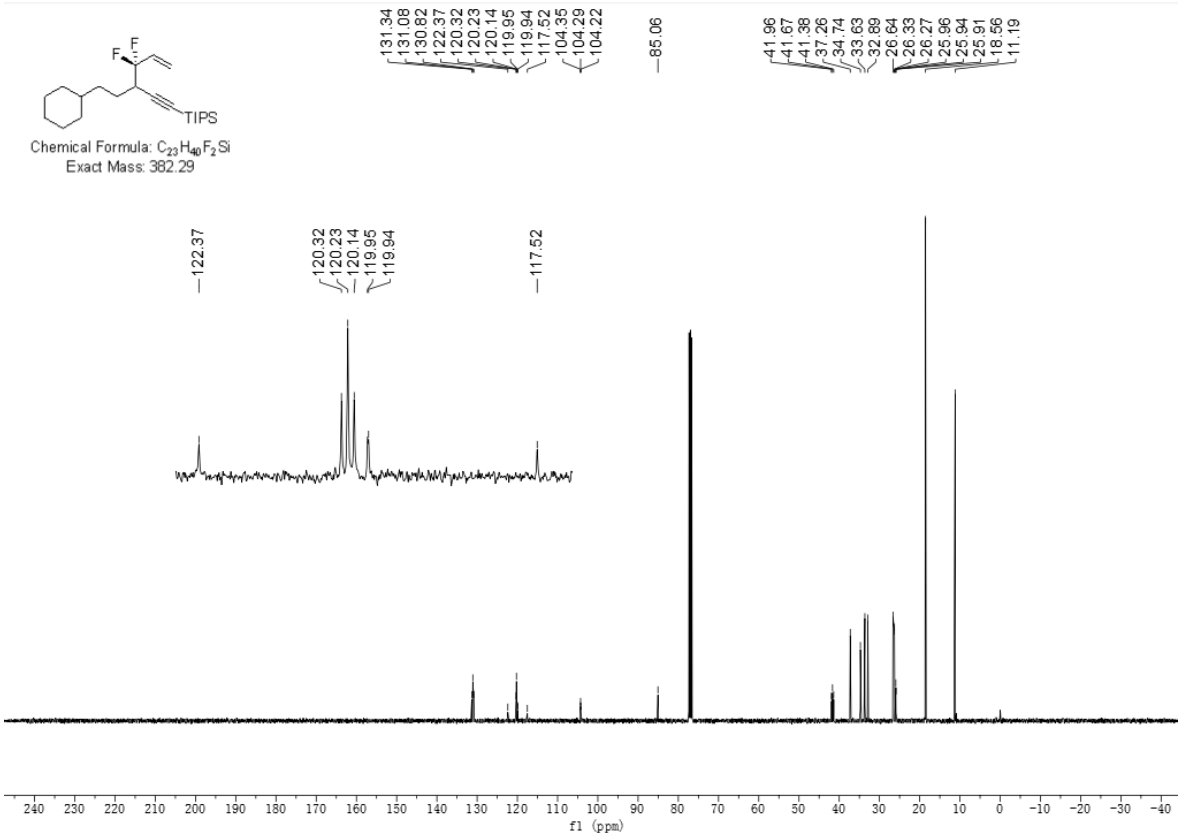
130.83
122.36
120.32
120.23
120.14
119.95
119.93
117.51
104.27
104.21
104.14
85.05
41.68
41.39
41.10
29.22
28.16
28.14
28.13
28.11
22.21
18.54
13.88
11.20
F
F
TIPS
Chemical Formula: C19H34F2Si
Exact Mass: 328.24
f1 (ppm)

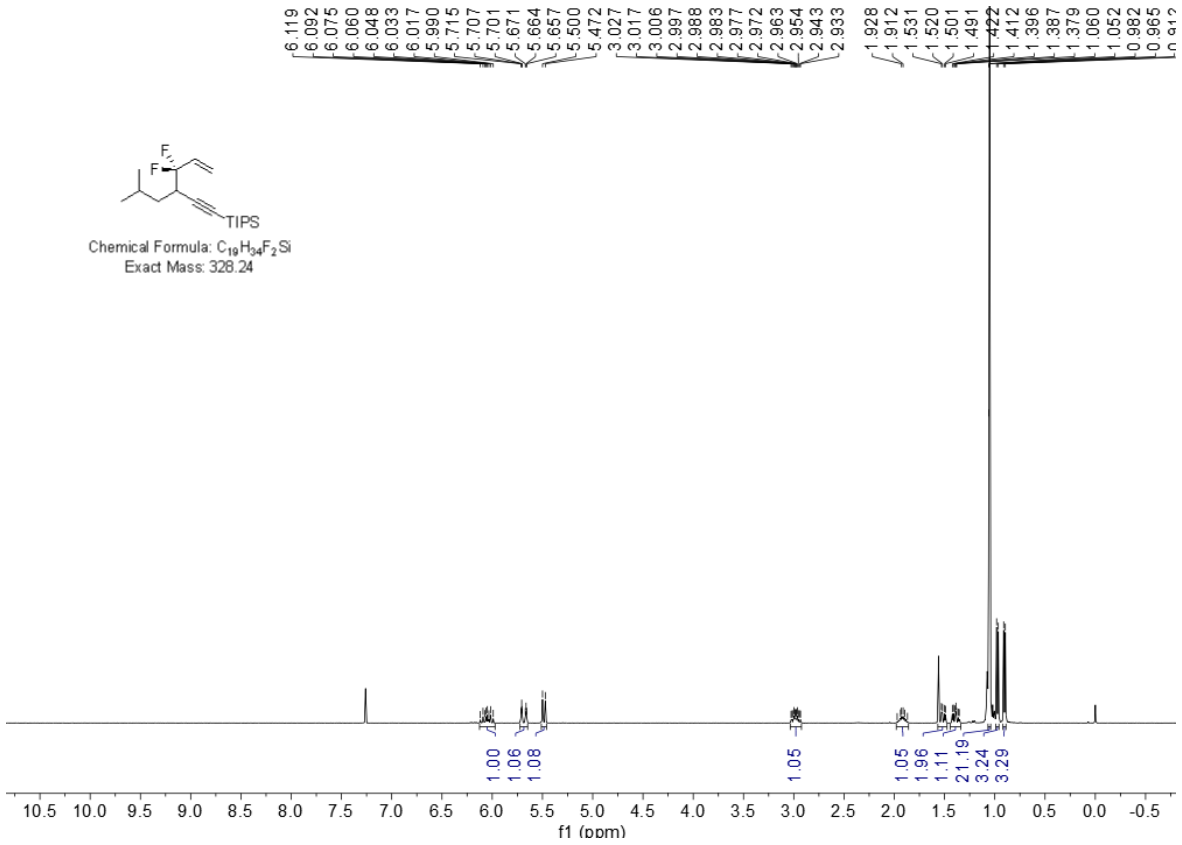
(3-(2-Cyclohexylethyl)-4,4-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3d)

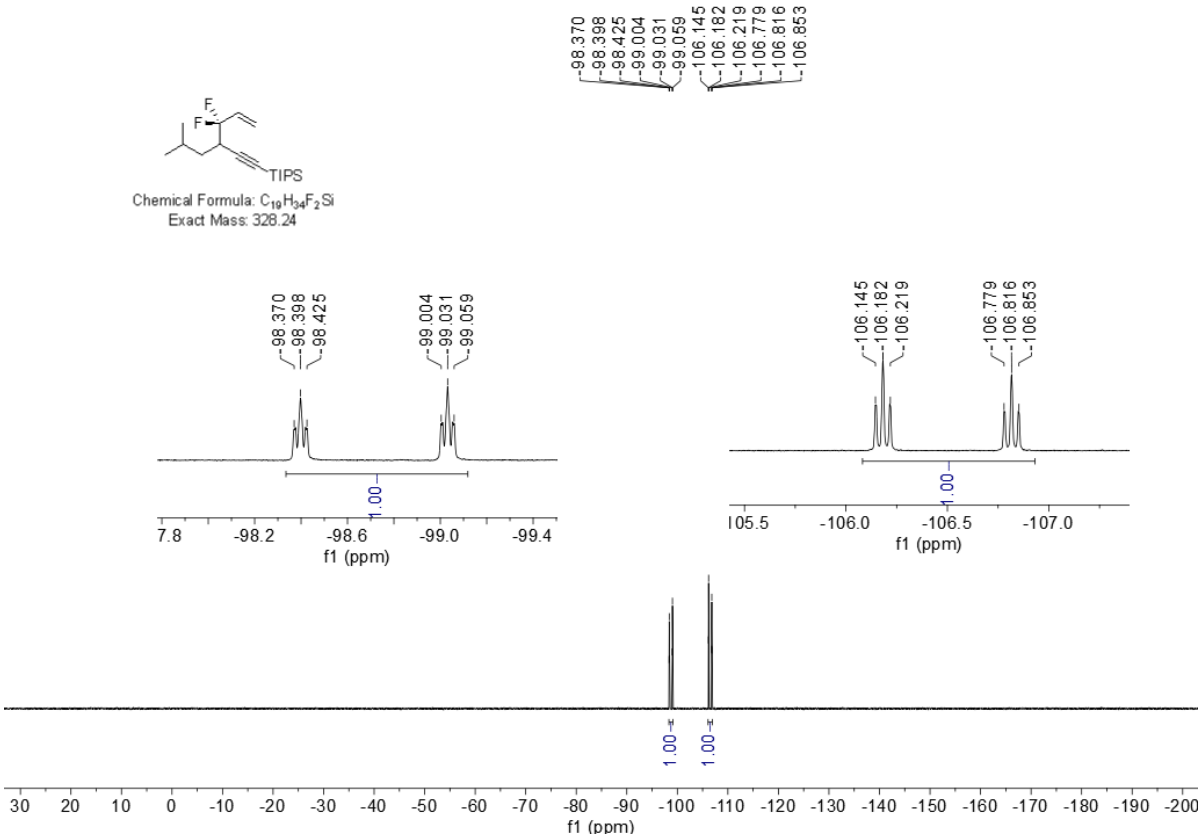


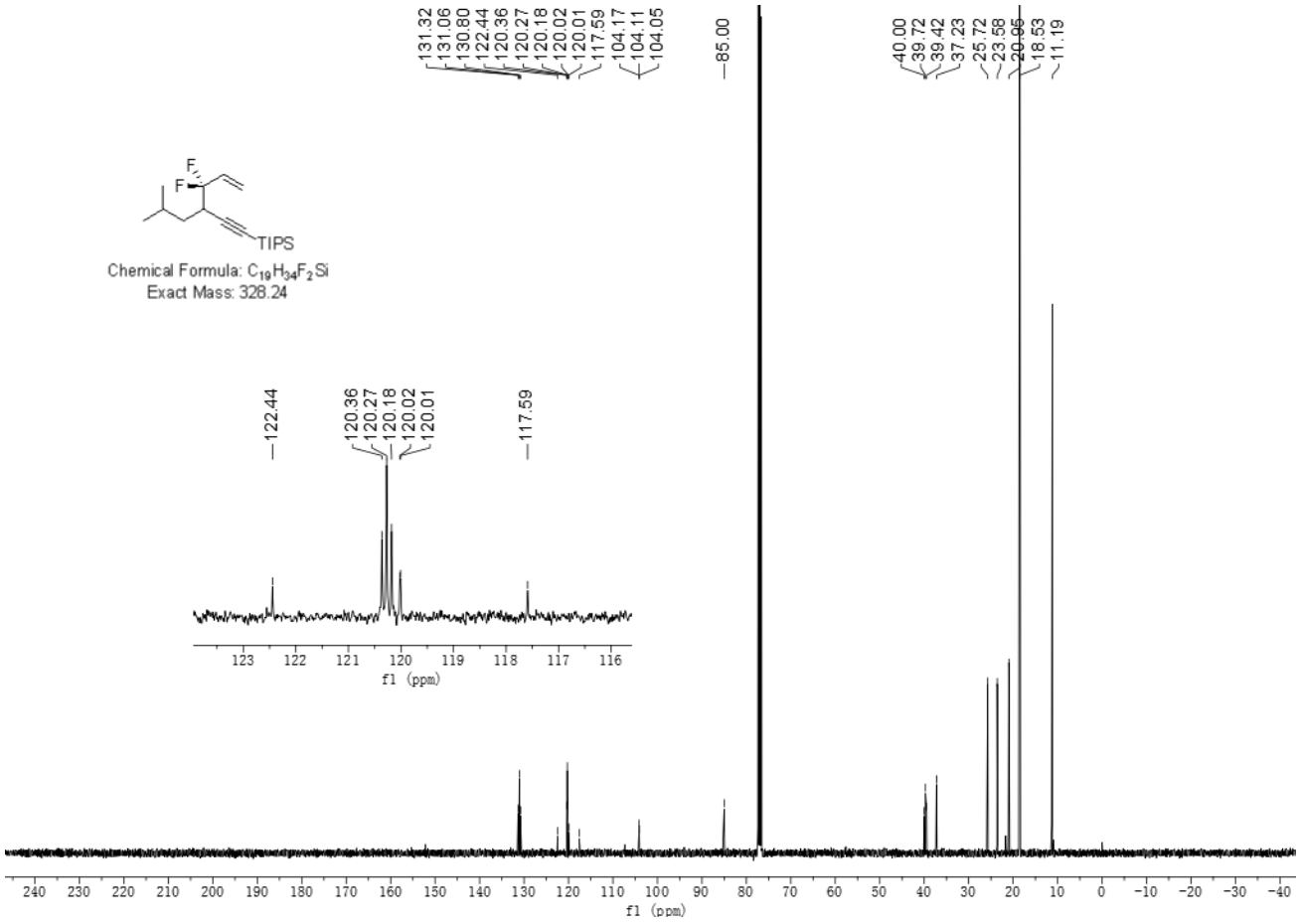




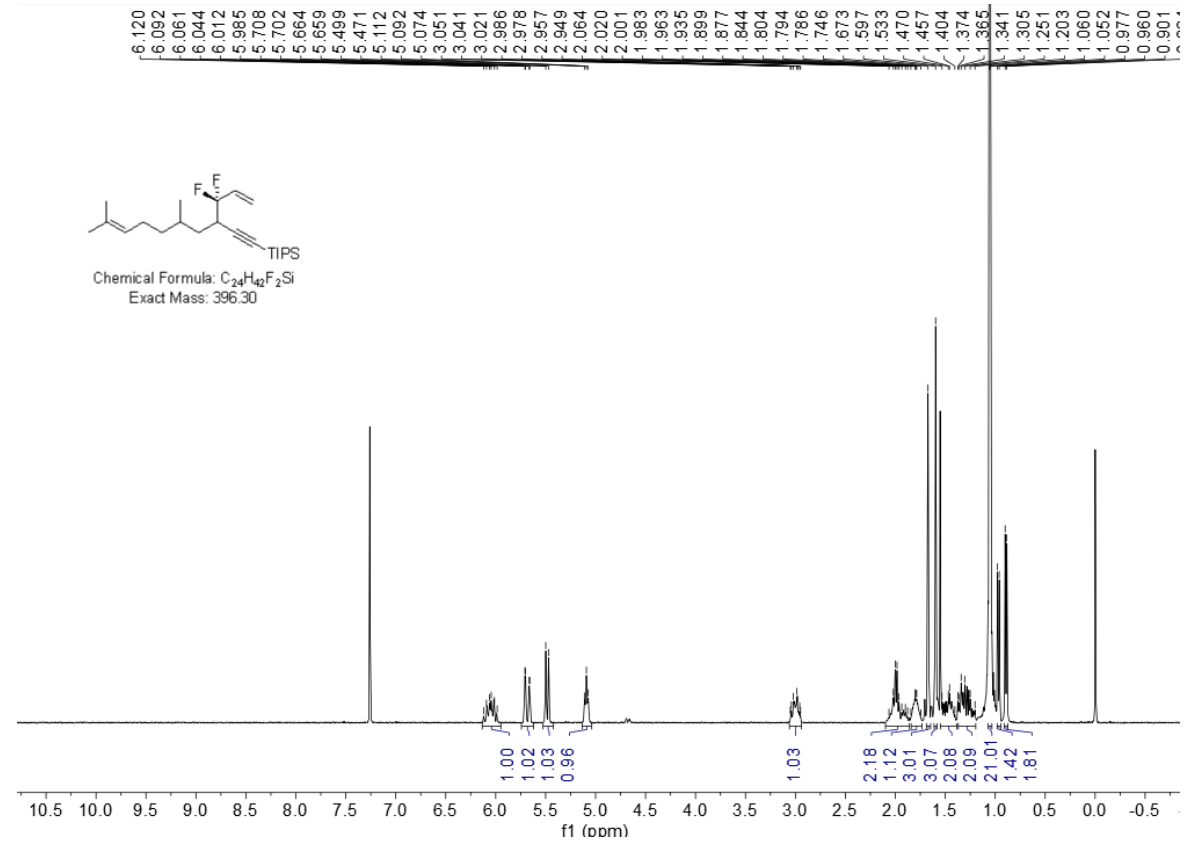
(4,4-Difluoro-3-isobutylhex-5-en-1-yn-1-yl)triisopropylsilane (3e)

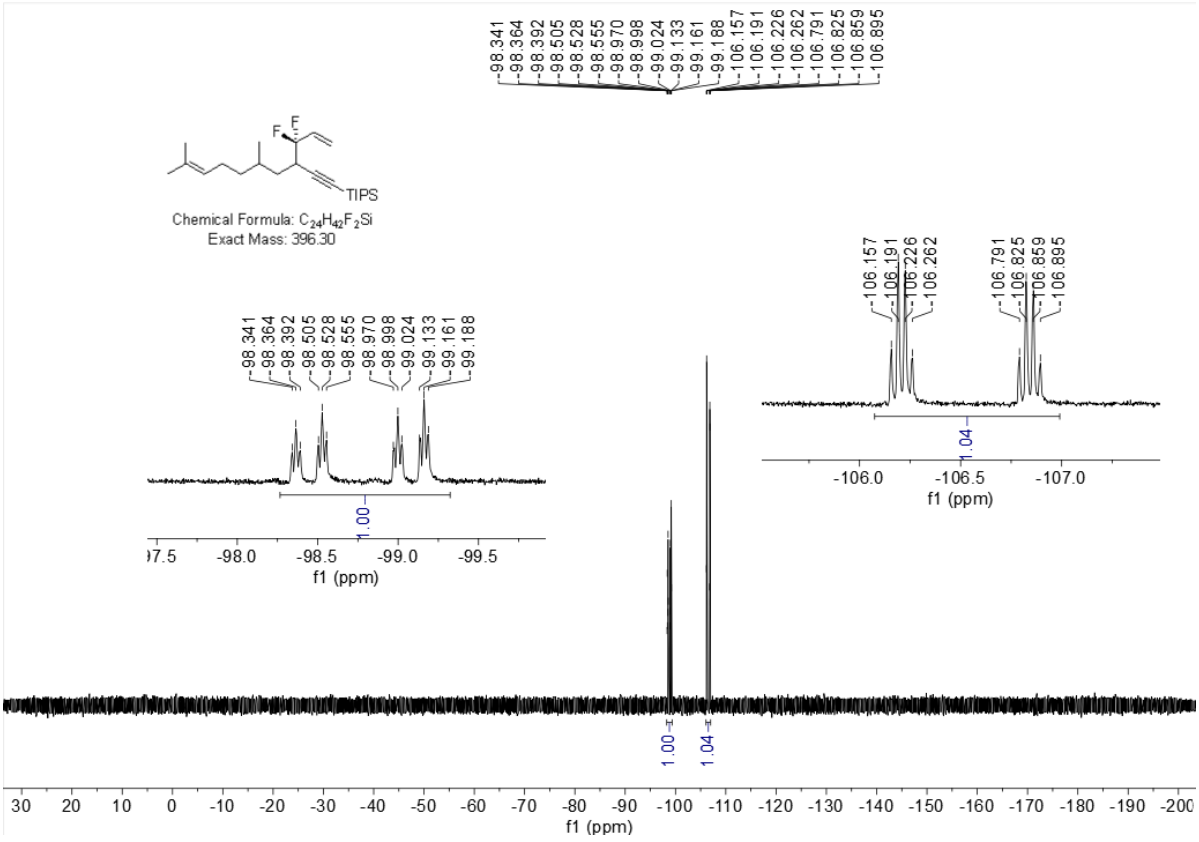


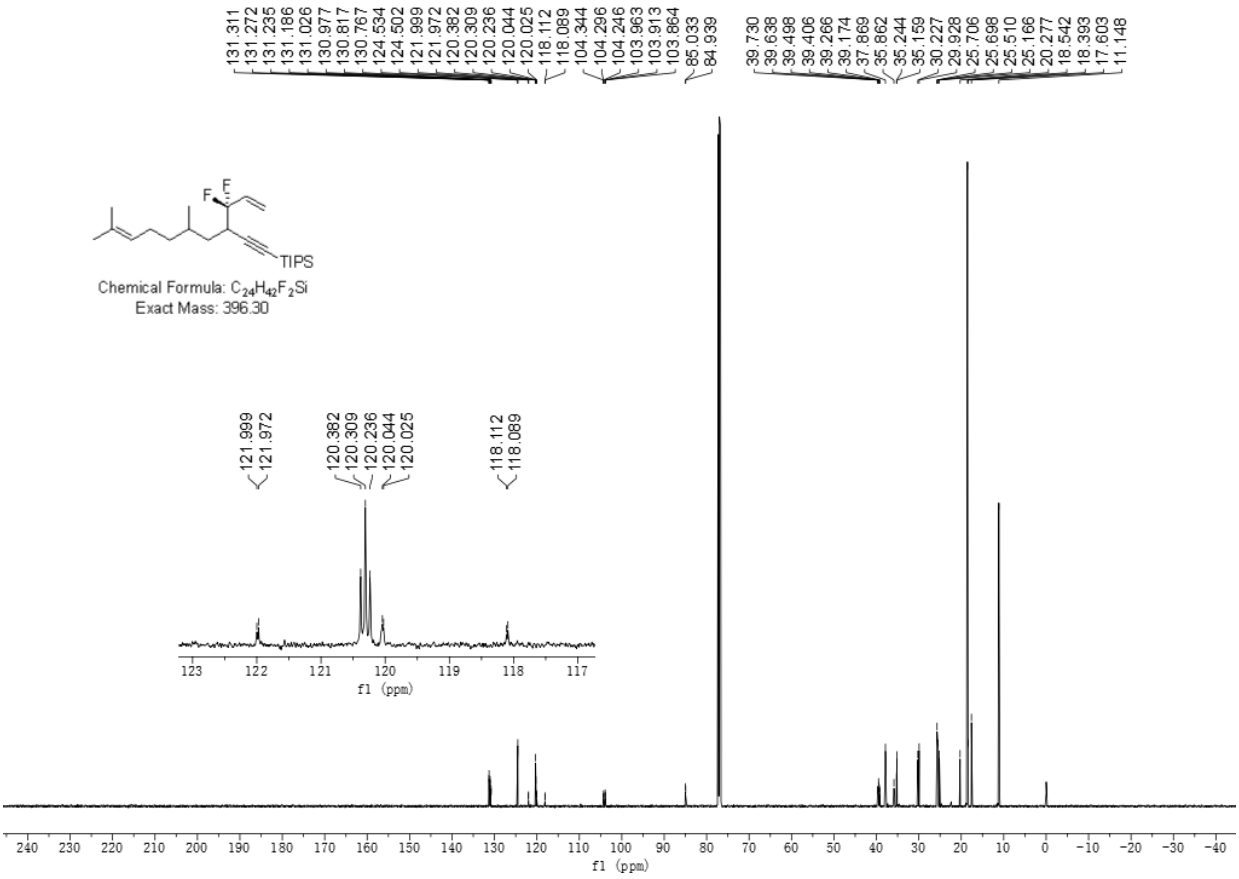

98.370
98.398
98.425
99.004
99.031
99.059
106.145
106.182
106.219
106.779
106.816
106.853
F
F
TIPS
Chemical Formula: C19H34F2Si
Exact Mass: 328.24
1.00
1.00
1.00
f1 (ppm)
f1 (ppm)
f1 (ppm)


131.32
131.06
130.80
122.44
120.36
120.27
120.18
120.02
120.01
117.59
104.17
104.11
104.05
85.00
40.00
39.72
39.42
37.23
25.72
23.58
20.96
18.53
11.19
F
F
TIPS
Chemical Formula: C19H34F2Si
Exact Mass: 328.24
f1 (ppm)
f1 (ppm)

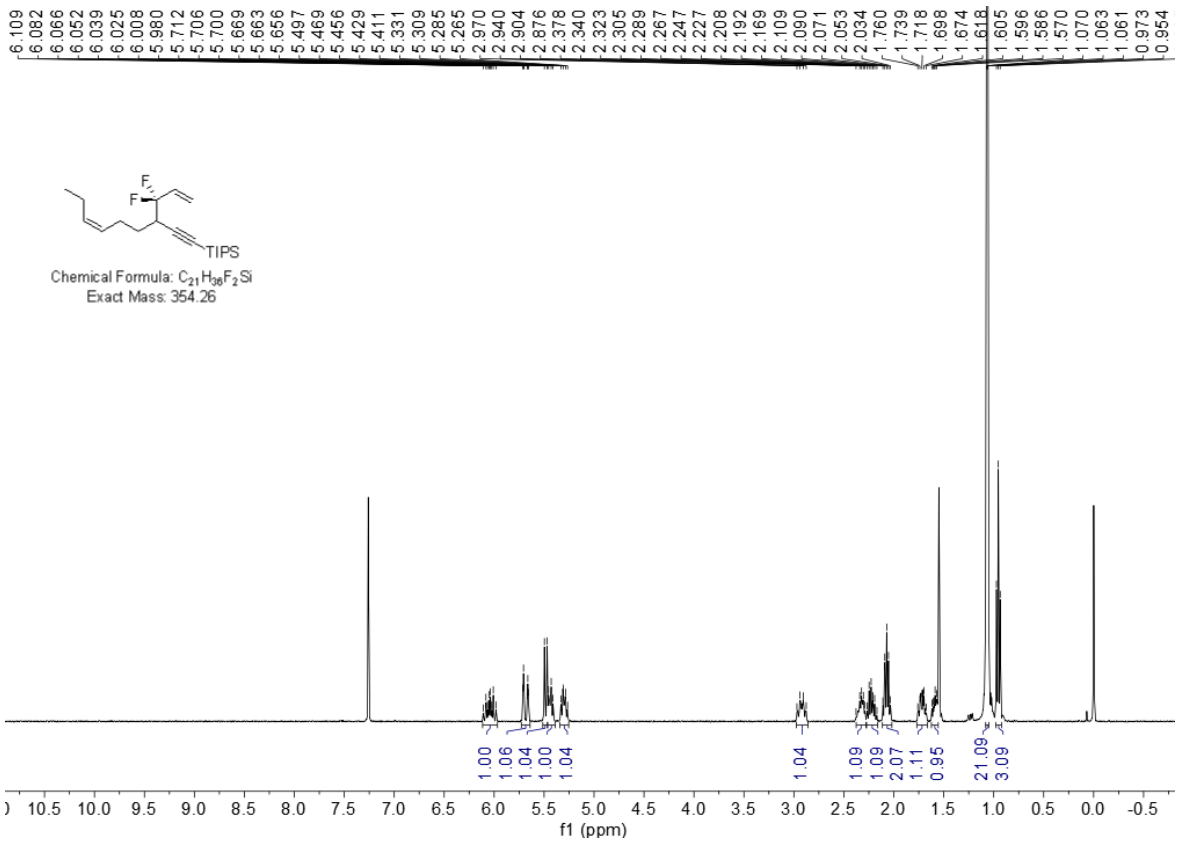
(1,1-Difluoroallyl)-5,9-dimethyldec-8-en-1-yn-1-yl)triisopropylsilane (3f)

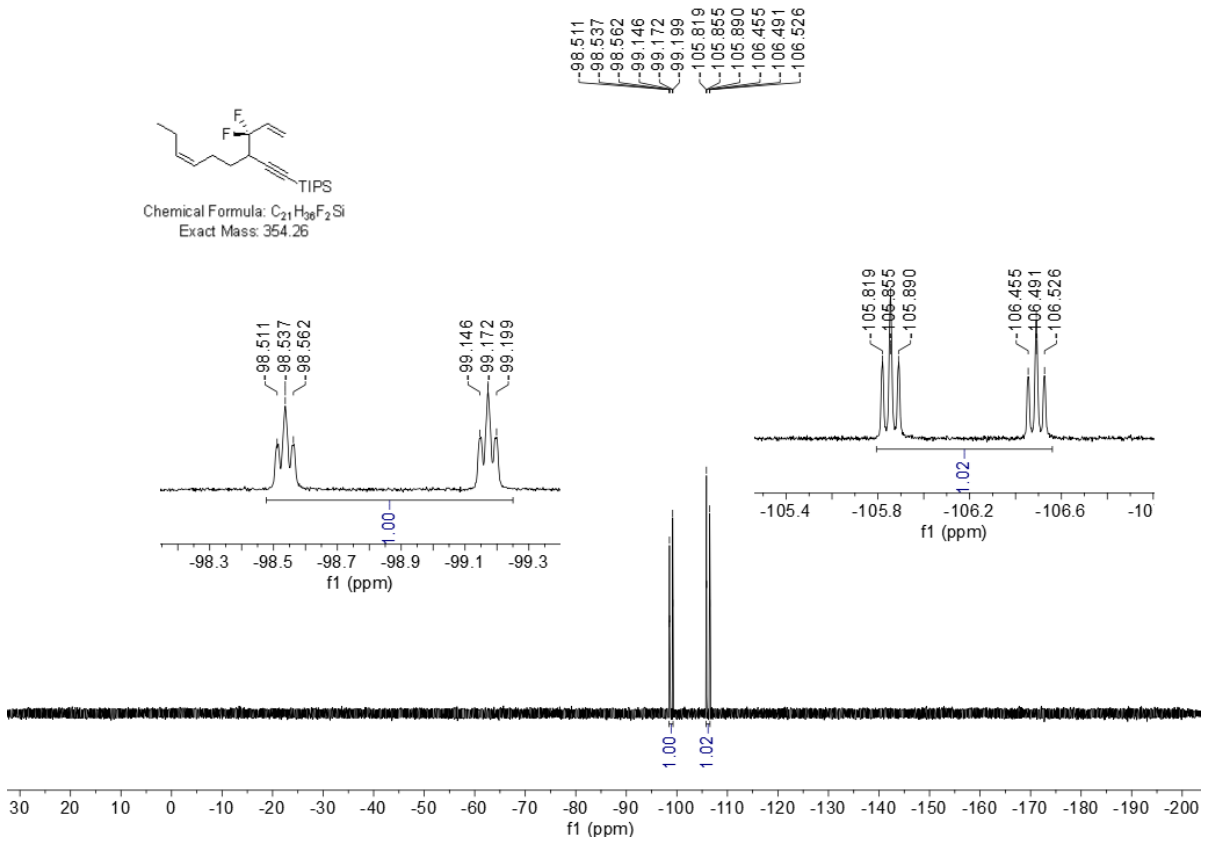


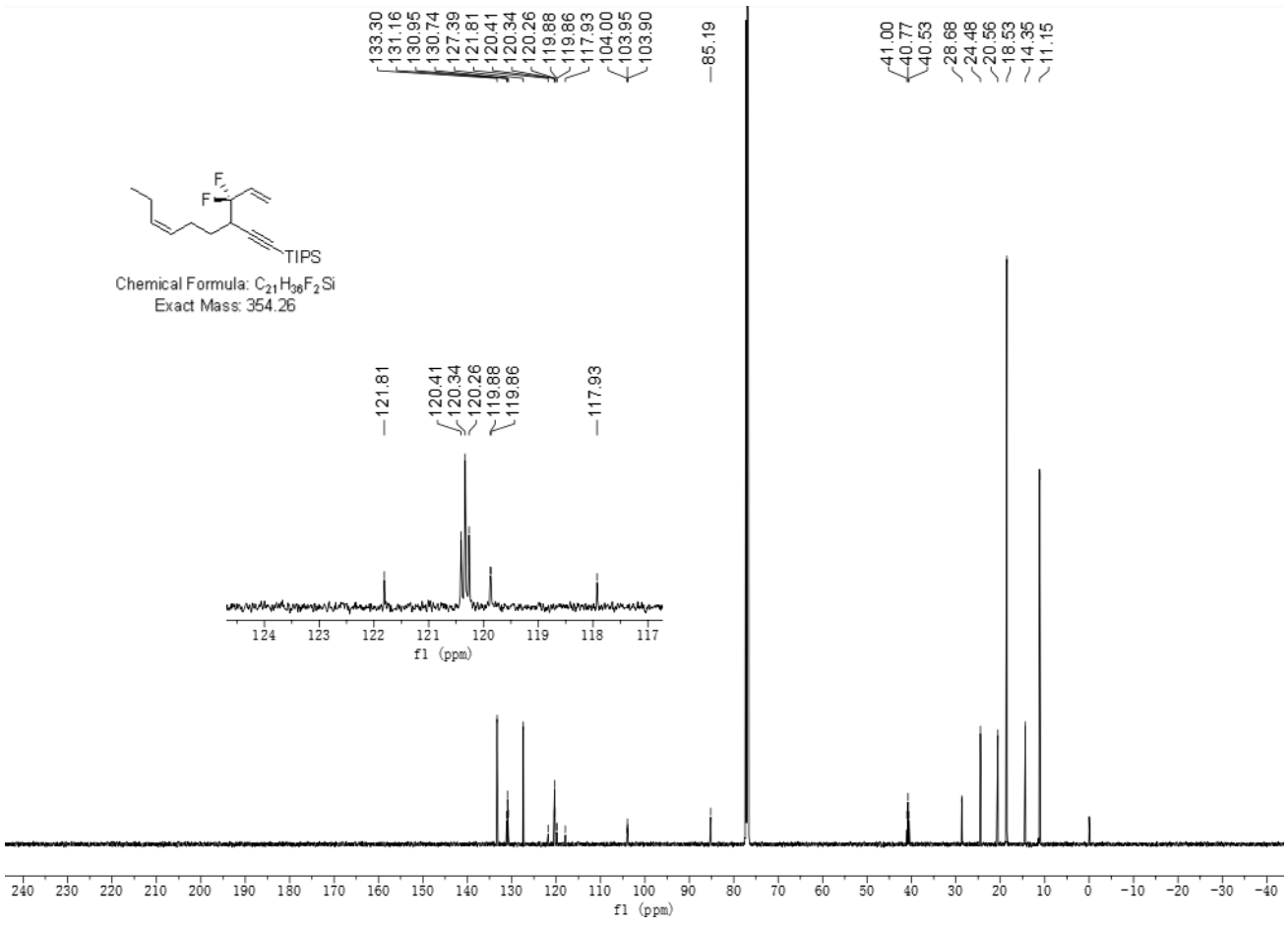




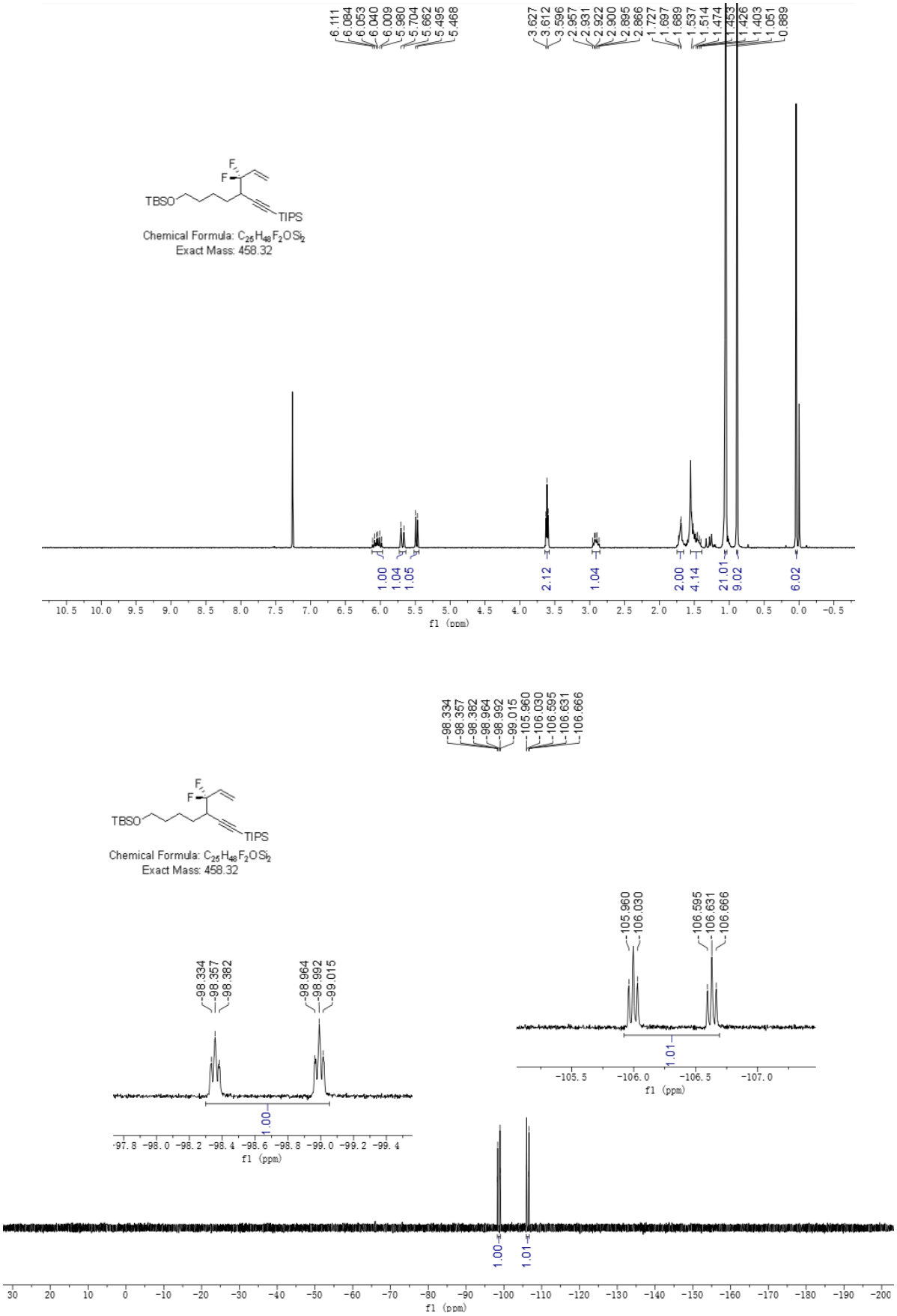
(*Z*)-(3-(1,1-Difluoroallyl)non-6-en-1-yn-1-yl)triisopropylsilane (3g)

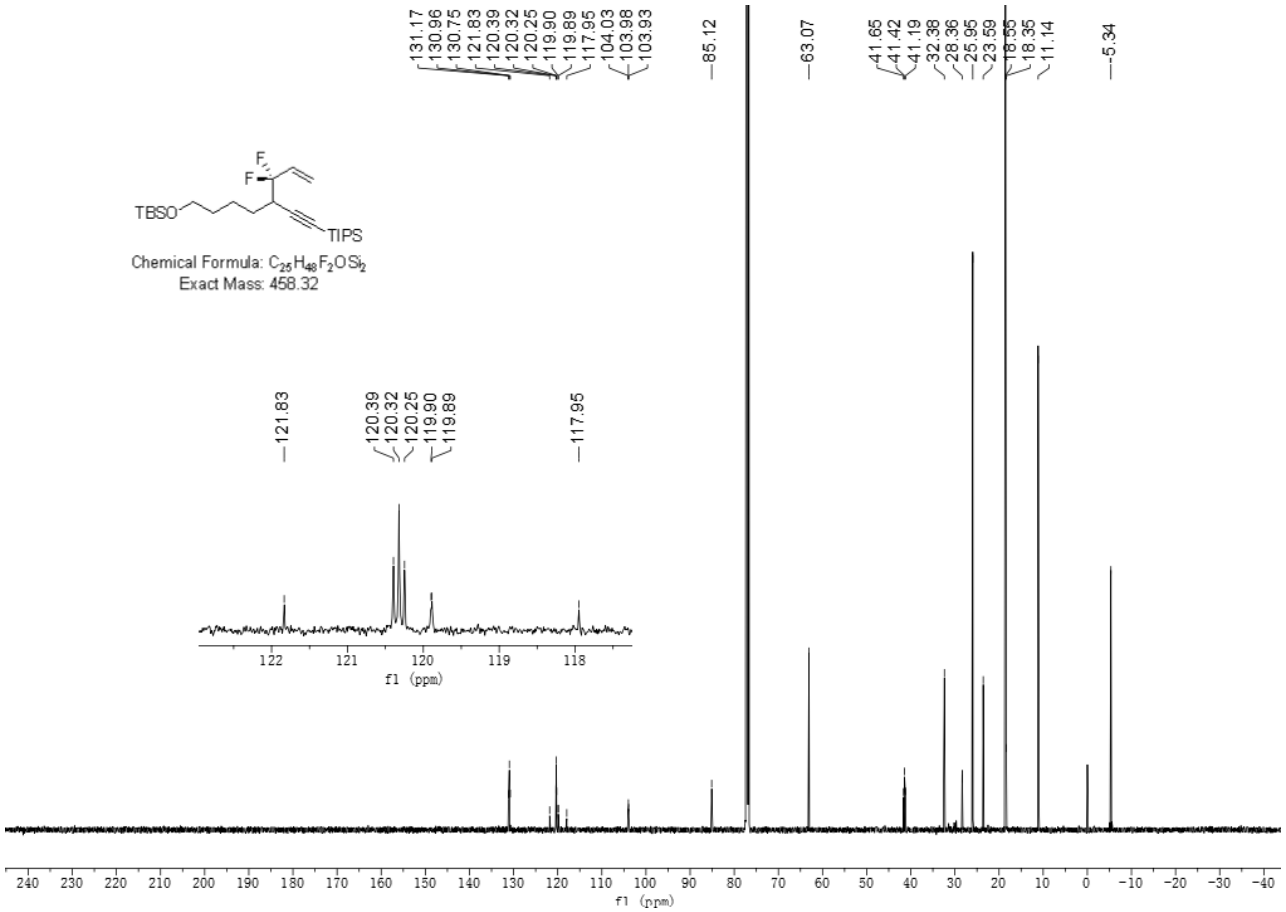



98.511
98.537
98.562
99.146
99.172
99.199
105.819
105.855
105.890
106.455
106.491
106.526
F
F
TIPS
Chemical Formula: C21H36F2Si
Exact Mass: 354.26
1.00
1.02
f1 (ppm)

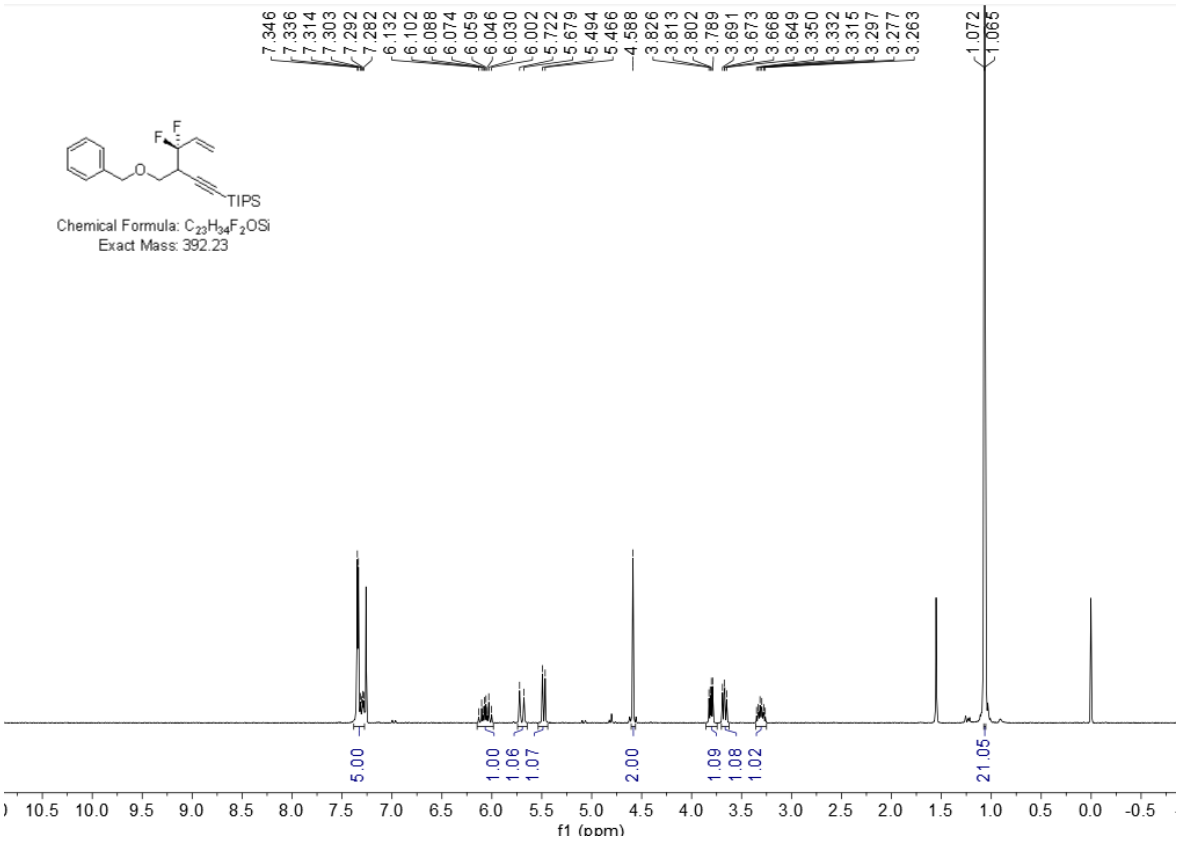

133.30
131.16
130.95
130.74
127.39
121.81
120.41
120.34
120.26
119.88
119.86
117.93
104.00
103.95
103.90
85.19
41.00
40.77
40.53
28.68
24.48
20.56
18.53
14.35
11.15
F
F
TIPS
Chemical Formula: C21H36F2Si
Exact Mass: 354.26
f1 (ppm)

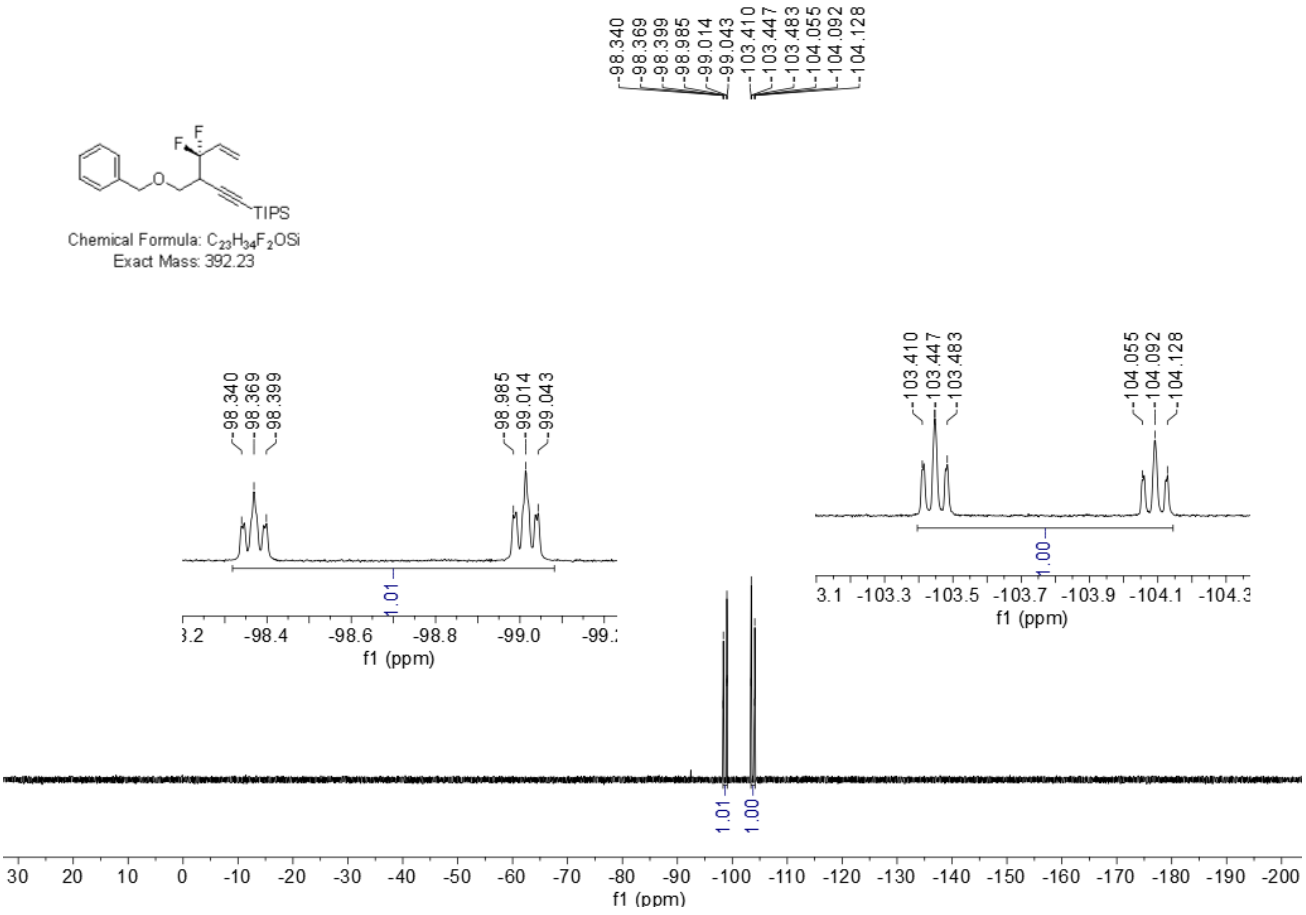
tert-Butyl((6,6-difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl)oxy)dimethylsilane (3h)

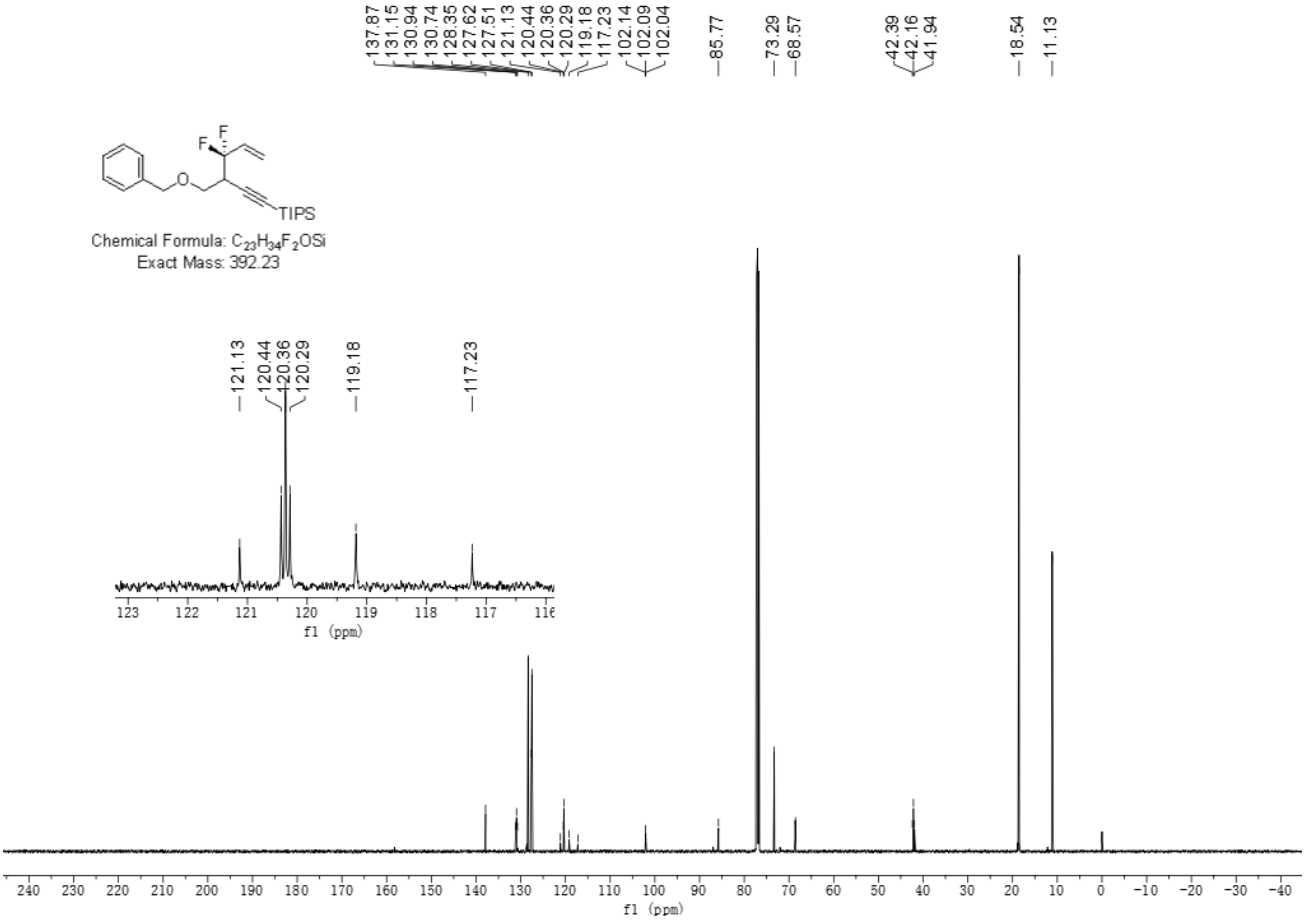




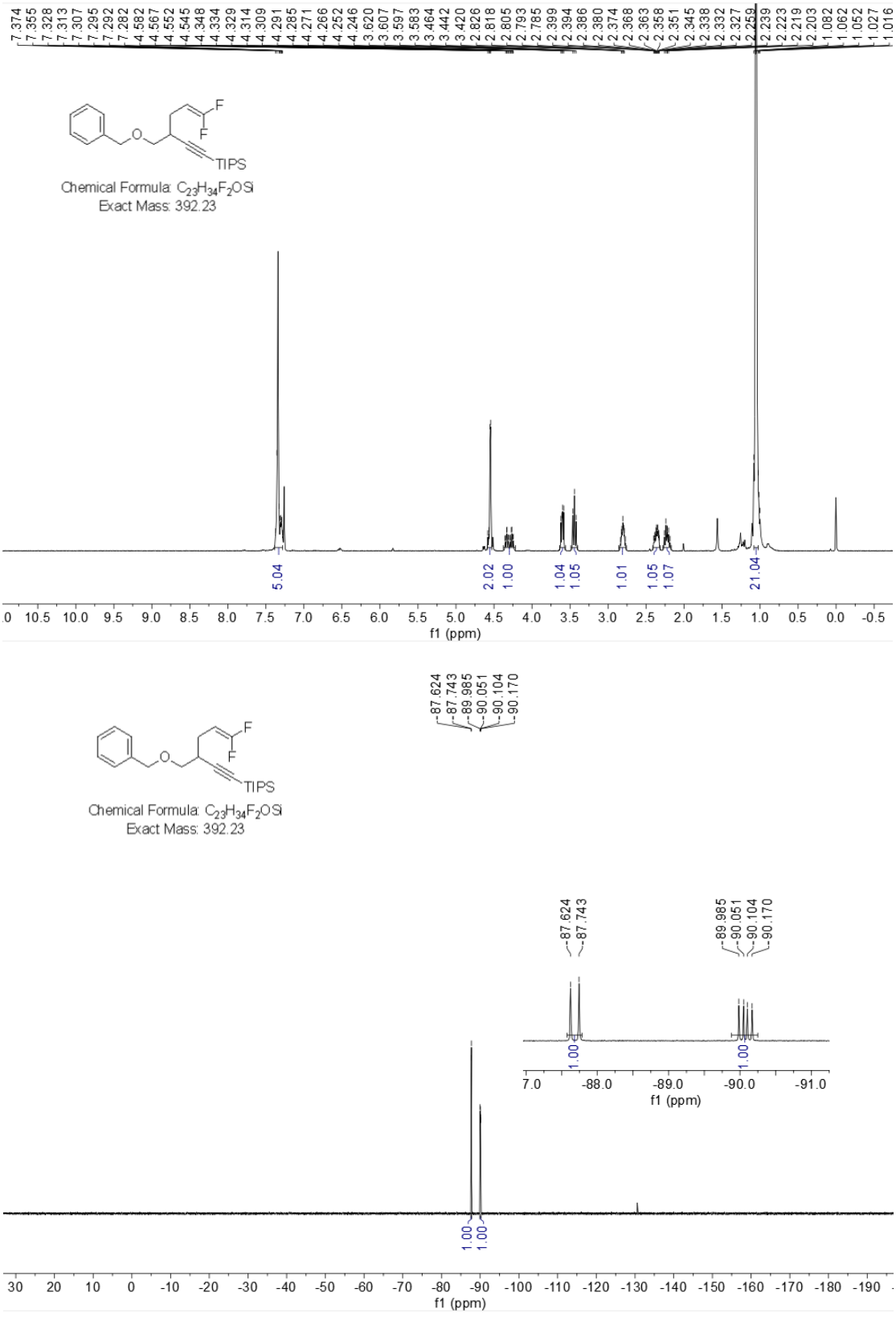
(3-((Benzyloxy)methyl)-4,4-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (3i)

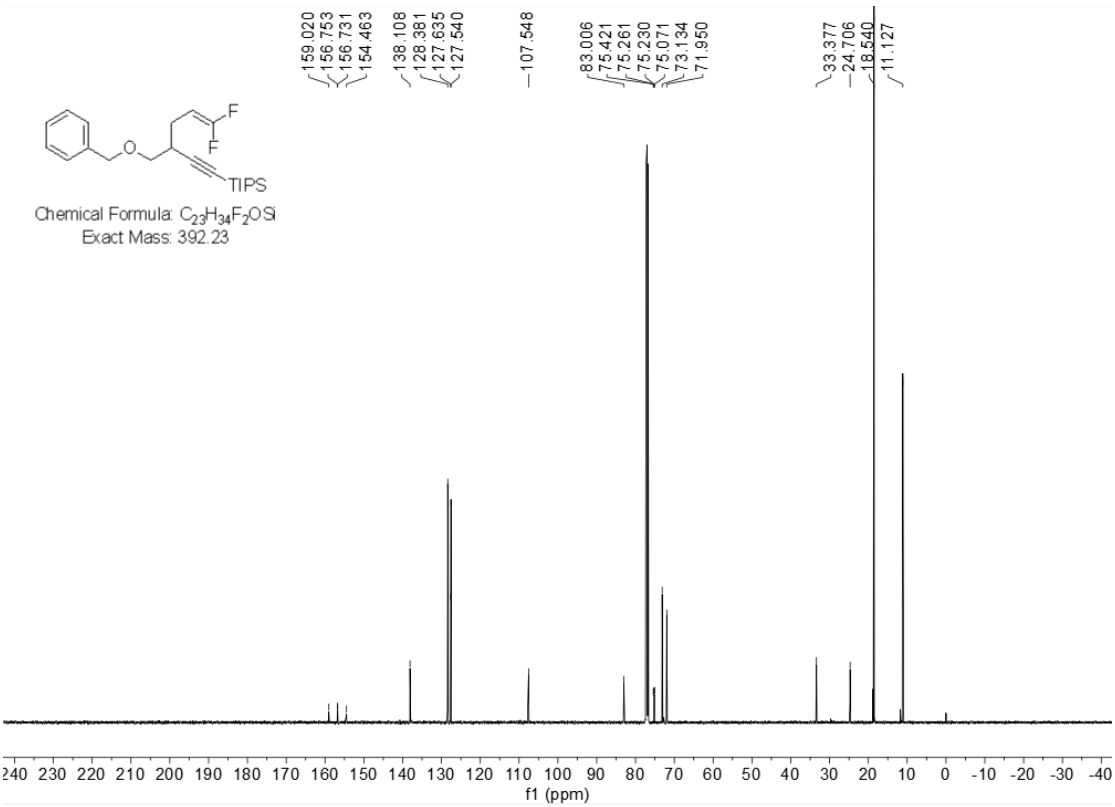



-98.340
-98.369
-98.399
-98.985
-99.014
-99.043
-103.410
-103.447
-103.483
-104.055
-104.092
-104.128
F
F
O
TIPS
Chemical Formula: C23H34F2OSi
Exact Mass: 392.23
1.01
1.00
f1 (ppm)

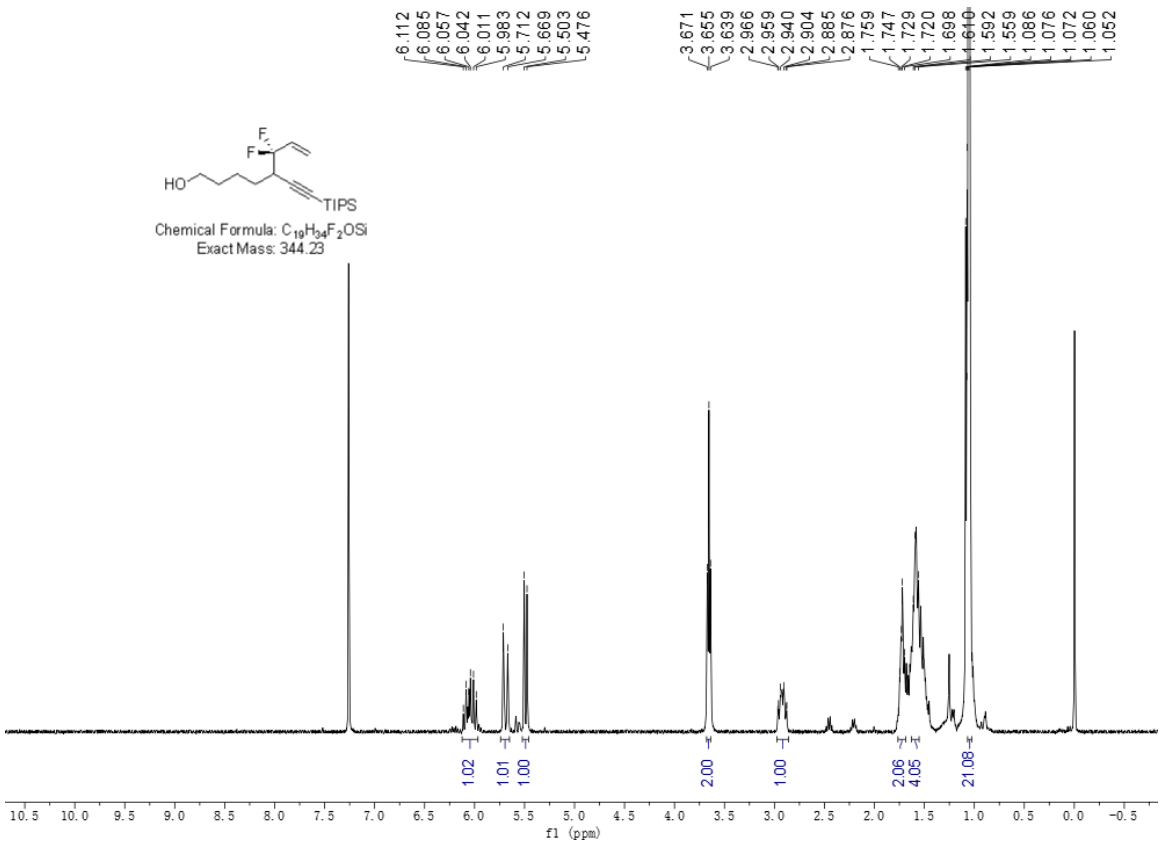

137.87
131.15
130.94
130.74
128.35
127.62
127.51
121.13
120.44
120.36
120.29
119.18
117.23
102.14
102.09
102.04
85.77
73.29
68.57
42.39
42.16
41.94
18.54
11.13
F
F
O
TIPS
Chemical Formula: C23H34F2OSi
Exact Mass: 392.23
f1 (ppm)

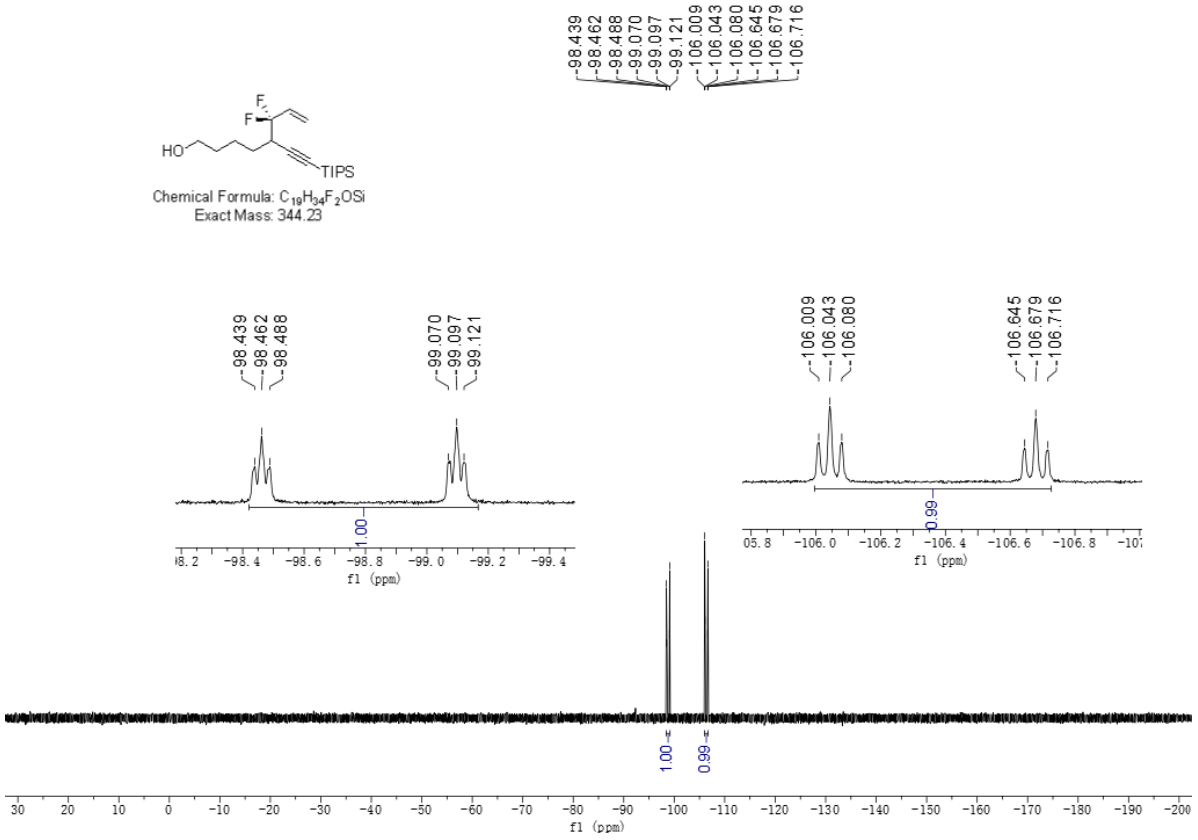
(3-((Benzyloxy)methyl)-6,6-difluorohex-5-en-1-yn-1-yl)triisopropylsilane (4i)

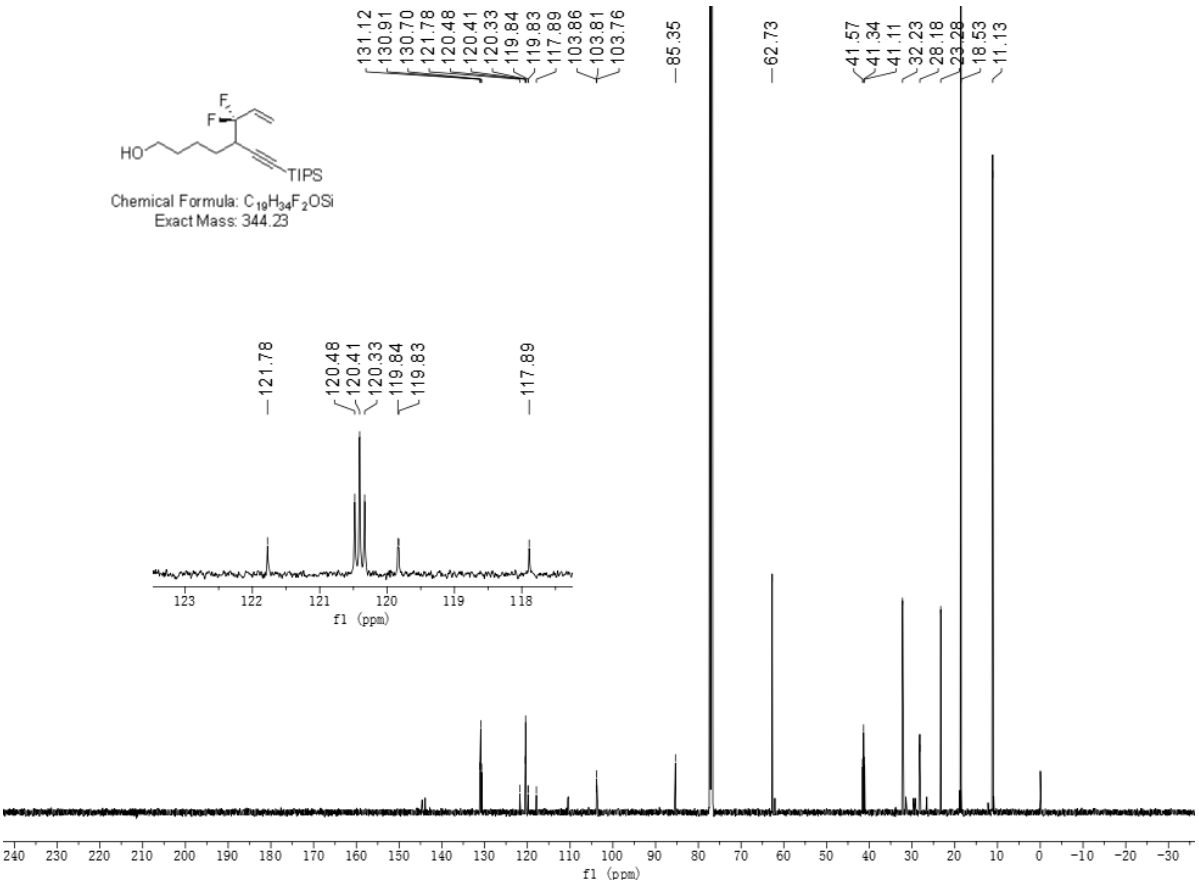




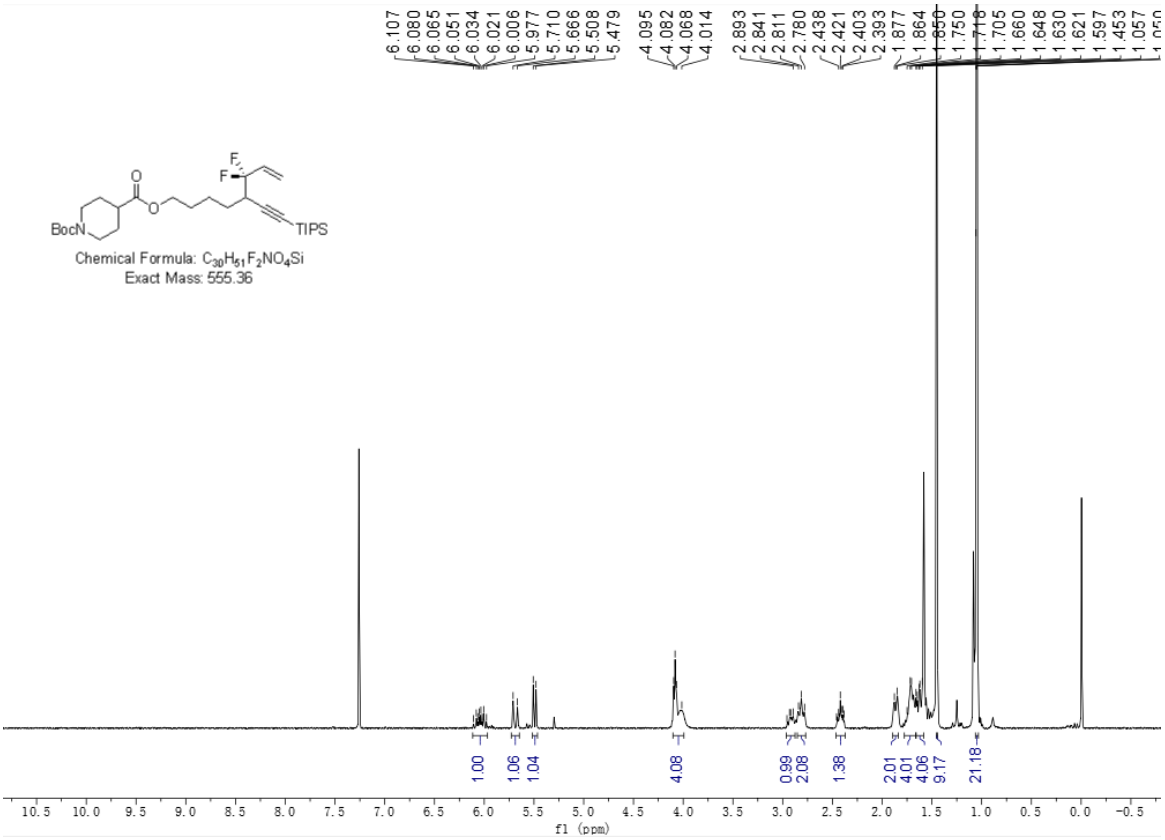
5,5-Difluoro-4-((triisopropylsilyl)ethynyl)hept-6-en-1-ol (3j)

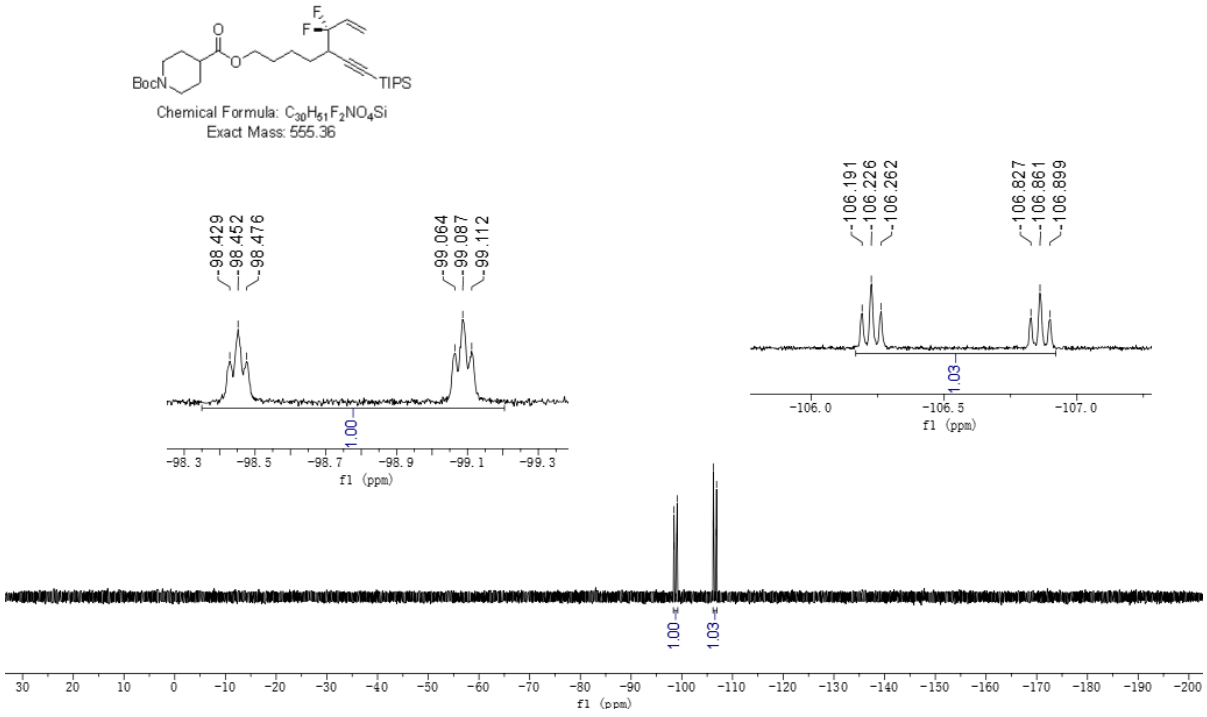


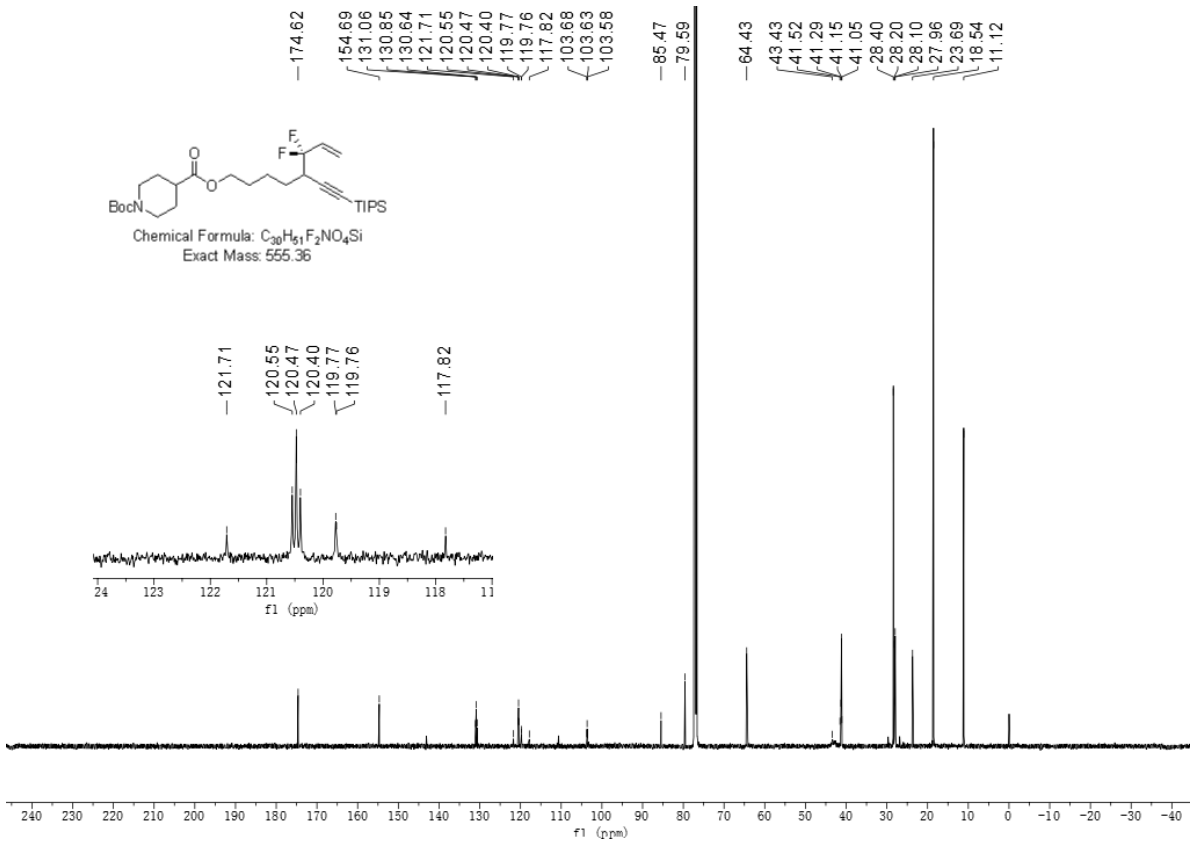

-98.439
-98.462
-98.488
-99.070
-99.097
-99.121
-106.009
-106.043
-106.080
-106.645
-106.679
-106.716
F
F
HO
TIPS
Chemical Formula: C19H34F2OSi
Exact Mass: 344.23
1.00
0.99
f1 (ppm)


131.12
130.91
130.70
121.78
120.48
120.41
120.33
119.84
119.83
117.89
103.86
103.81
103.76
85.35
62.73
41.57
41.34
41.11
32.23
28.18
23.28
18.53
11.13
F
F
HO
TIPS
Chemical Formula: C19H34F2OSi
Exact Mass: 344.23
f1 (ppm)

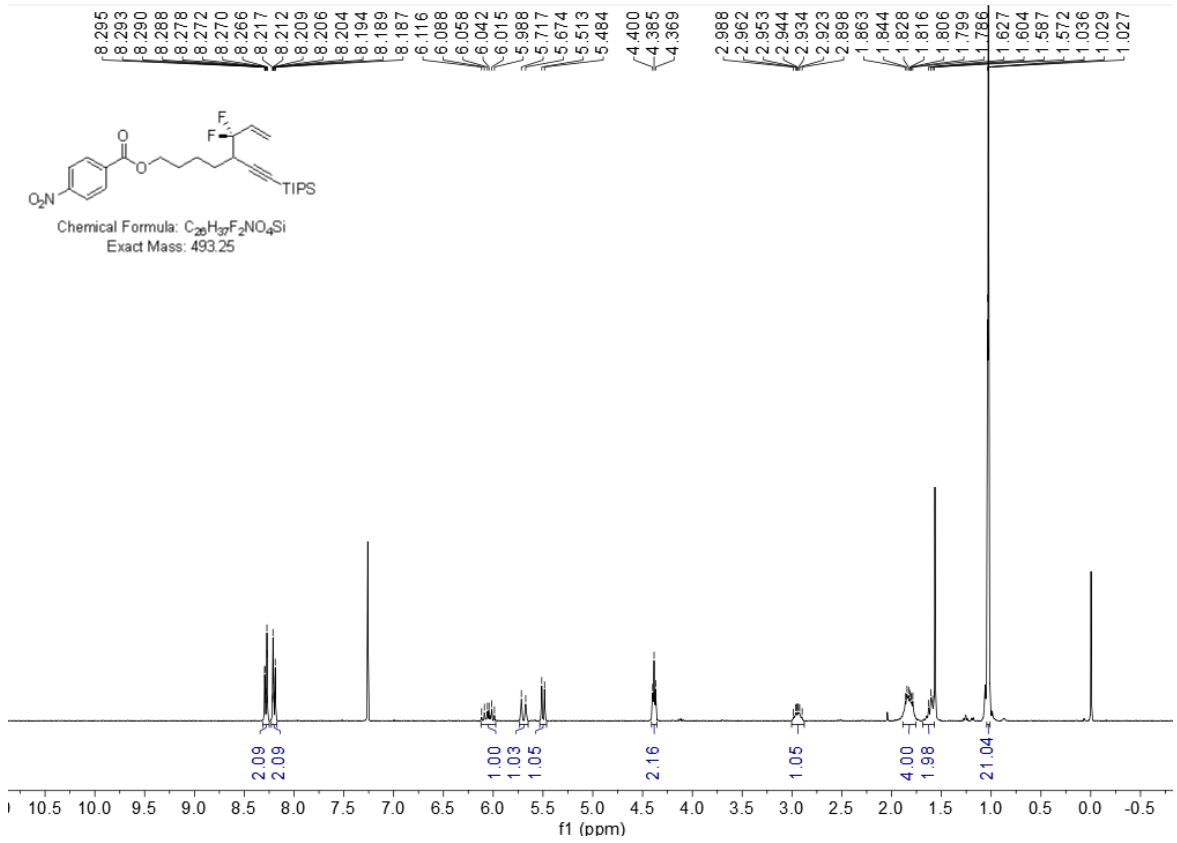
1-(*tert*-Butyl) 4-(6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl) piperidine-1,4-dicarboxylate (3k)

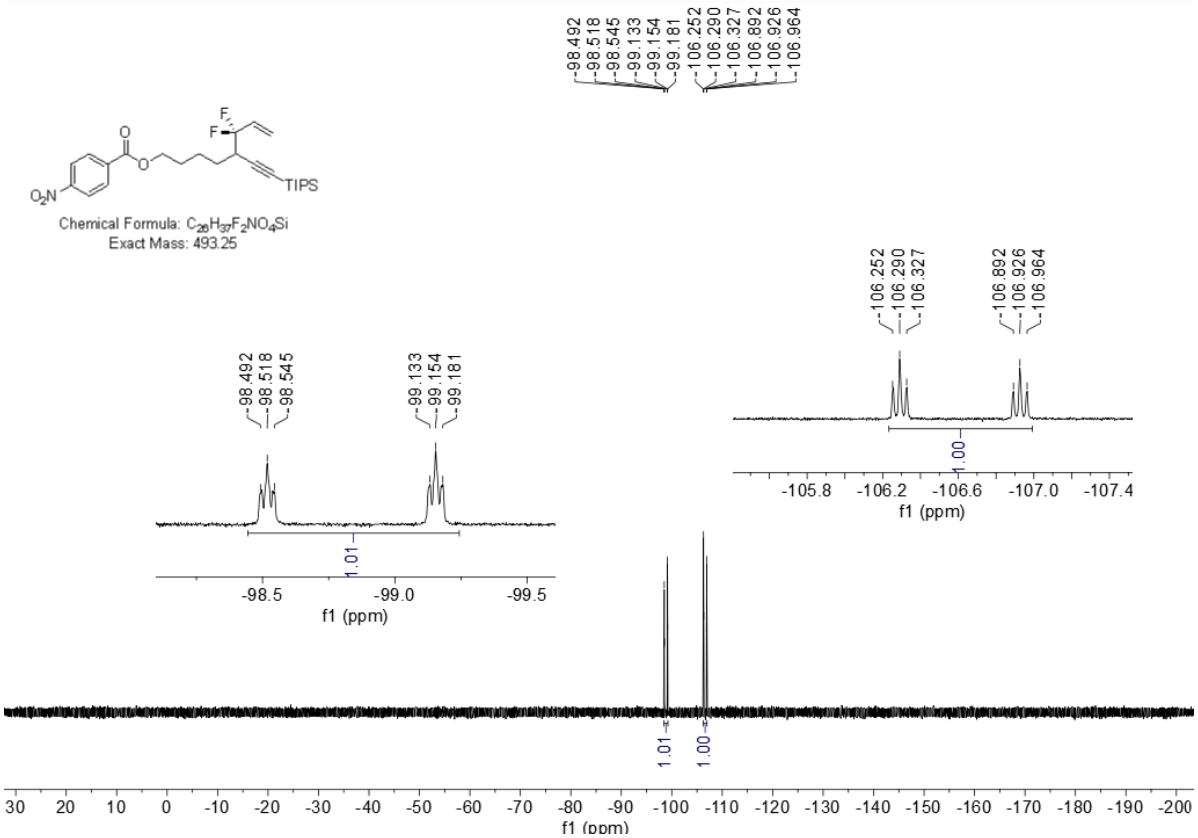


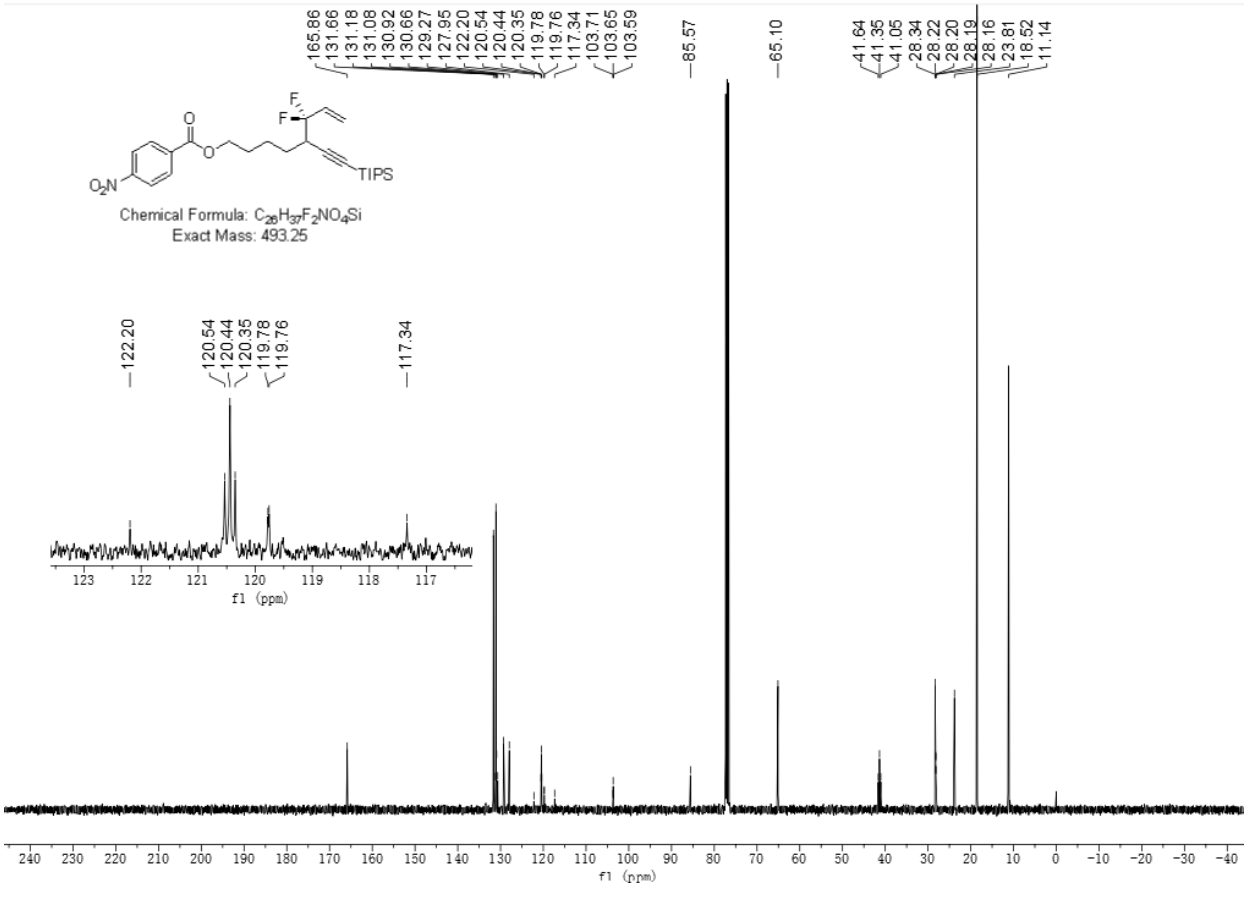




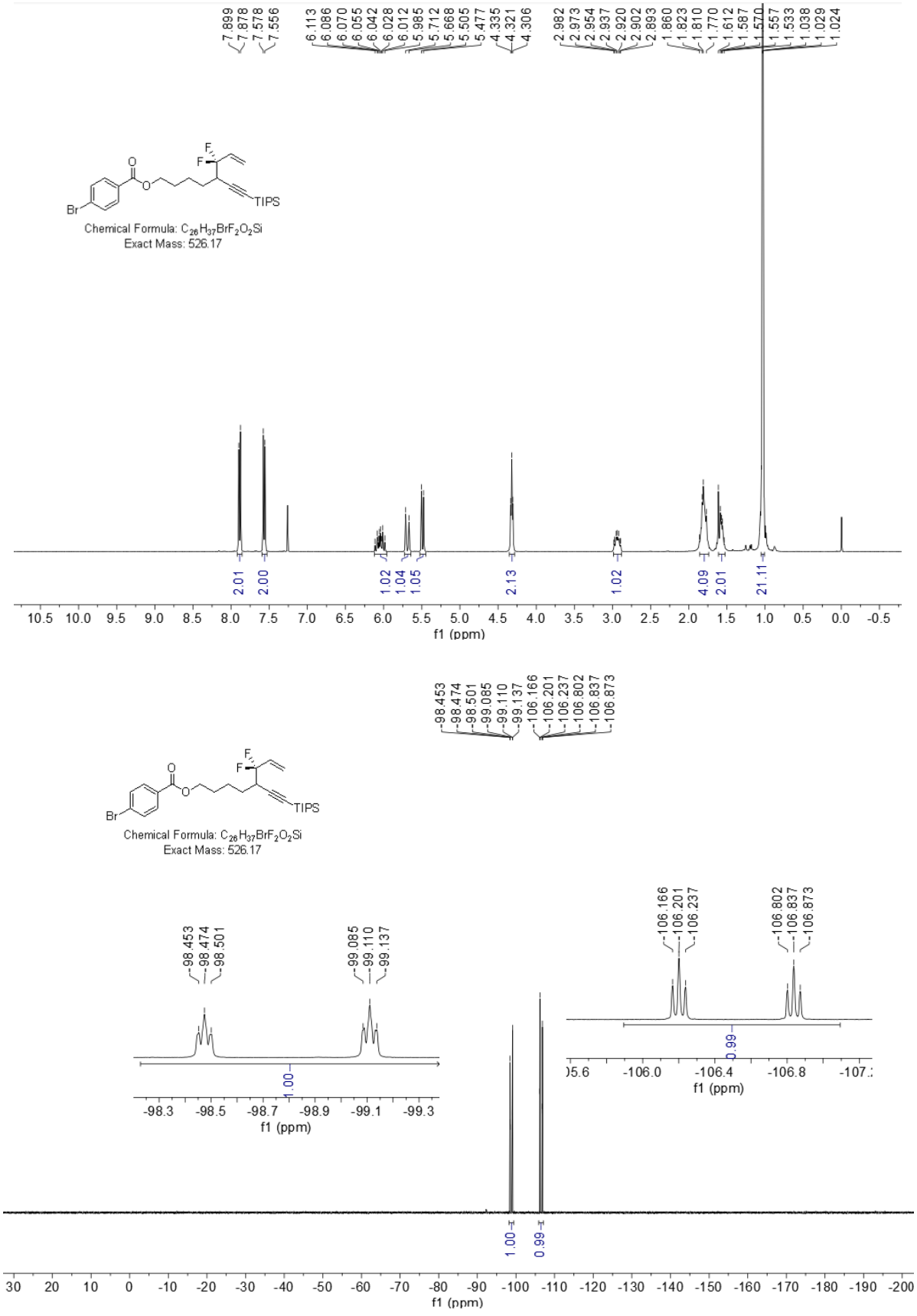
6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-nitrobenzoate (3l)

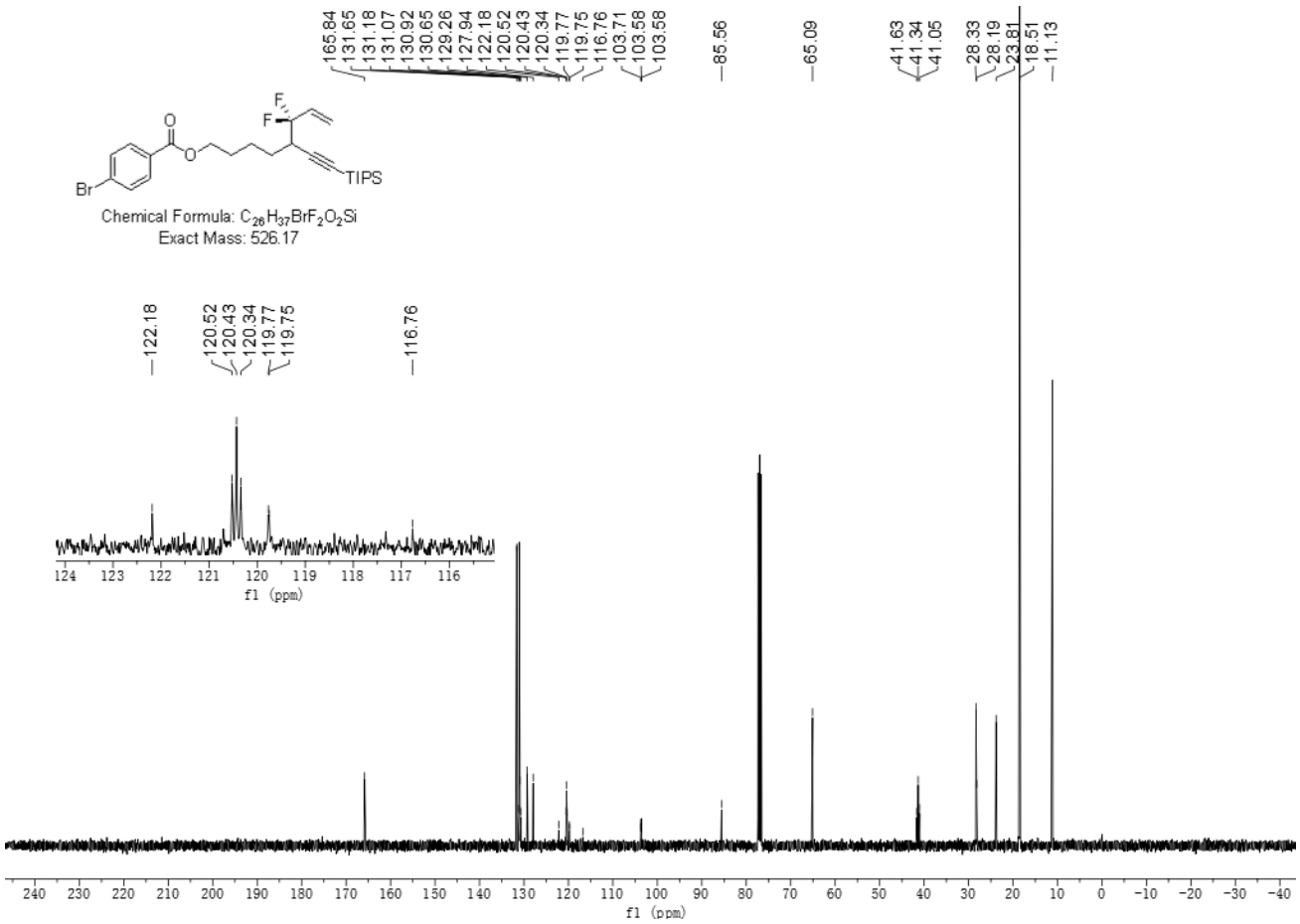



-98.492
-98.518
-98.545
-99.133
-99.154
-99.181
-106.252
-106.290
-106.327
-106.892
-106.926
-106.964
F
F
O
O
O2N
TIPS
Chemical Formula: C26H37F2NO4Si
Exact Mass: 493.25
1.01
1.00
f1 (ppm)

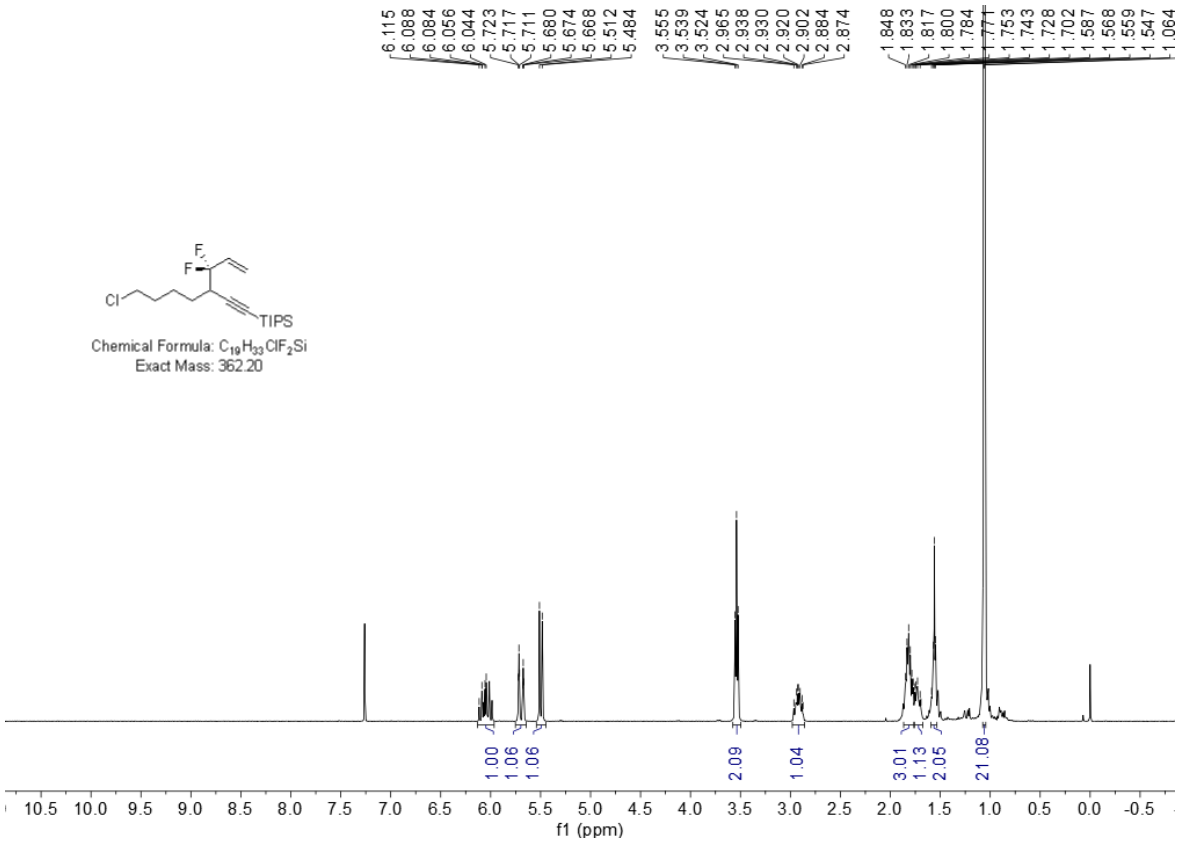

165.86
131.66
131.18
131.08
130.92
130.66
129.27
127.95
122.20
120.54
120.44
120.35
119.78
119.76
117.34
103.71
103.65
103.59
85.57
65.10
41.64
41.35
41.05
28.34
28.22
28.20
28.19
28.16
23.81
18.52
11.14
F
F
O
O
O2N
TIPS
Chemical Formula: C26H37F2NO4Si
Exact Mass: 493.25
f1 (ppm)

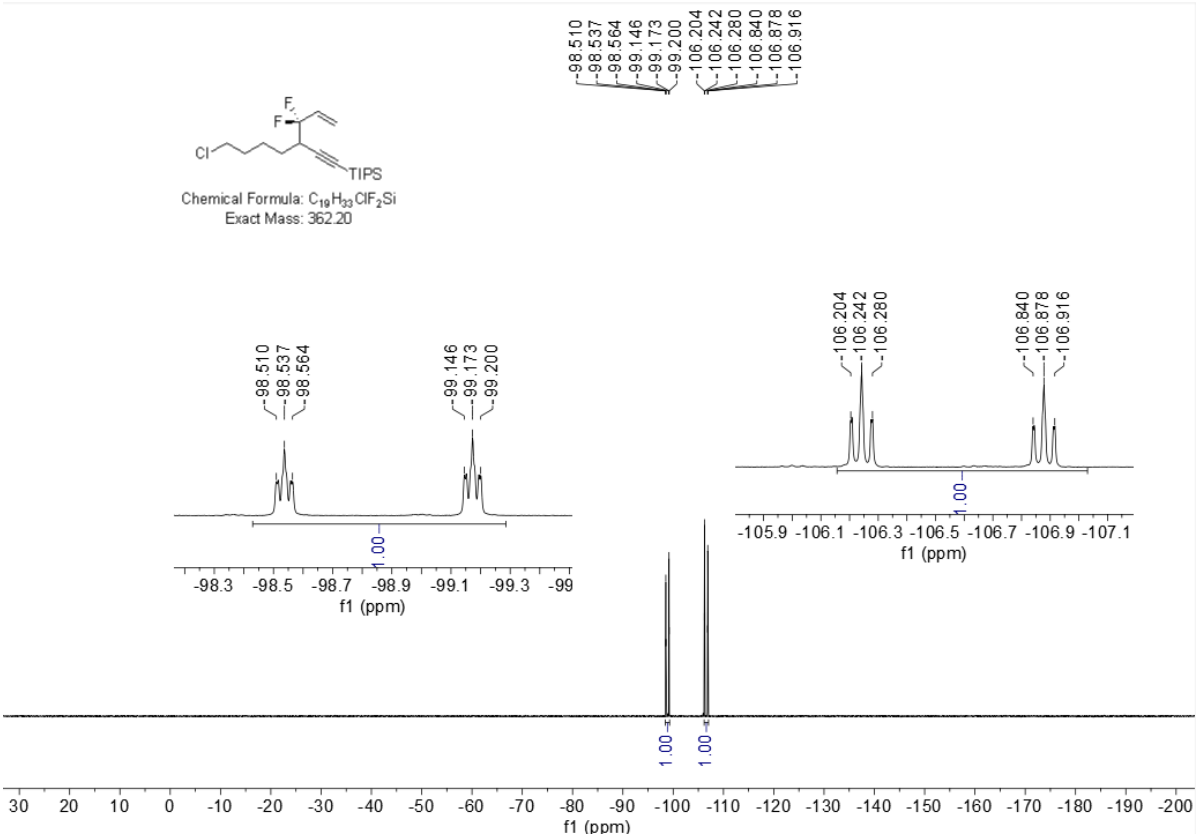
6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-bromobenzoate (3m)

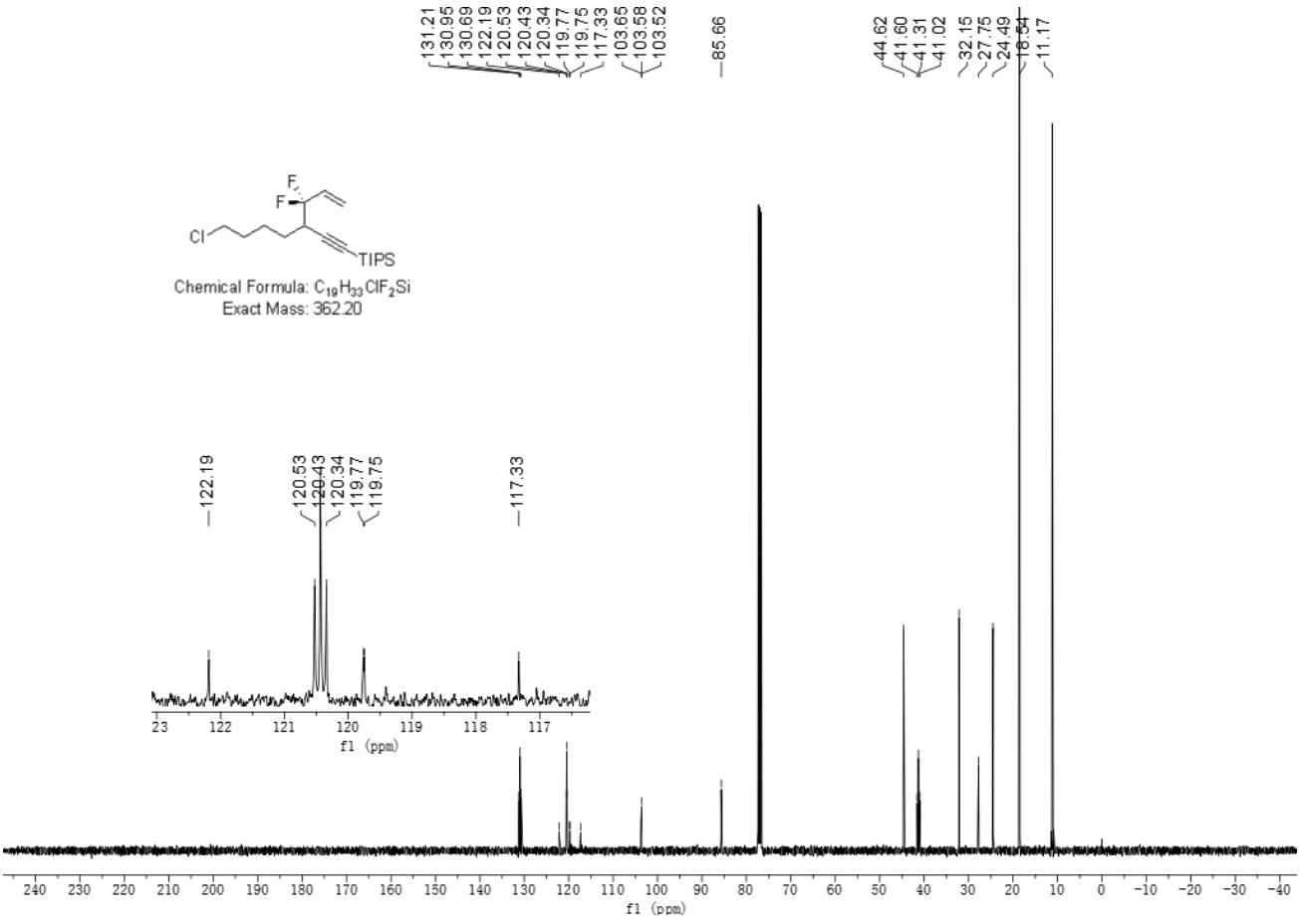




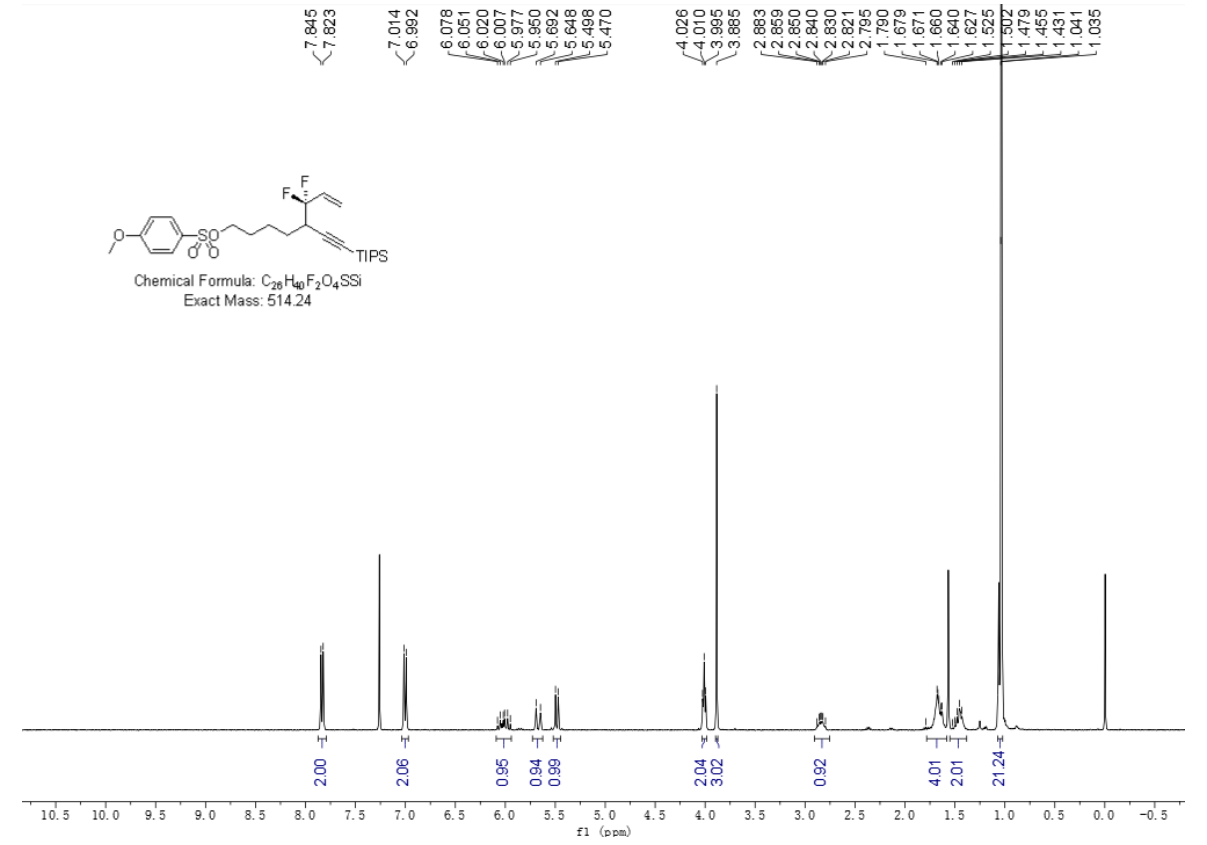
Chloro-3-(1,1-difluoroallyl)hept-1-yn-1-yl)triisopropylsilane (3n)

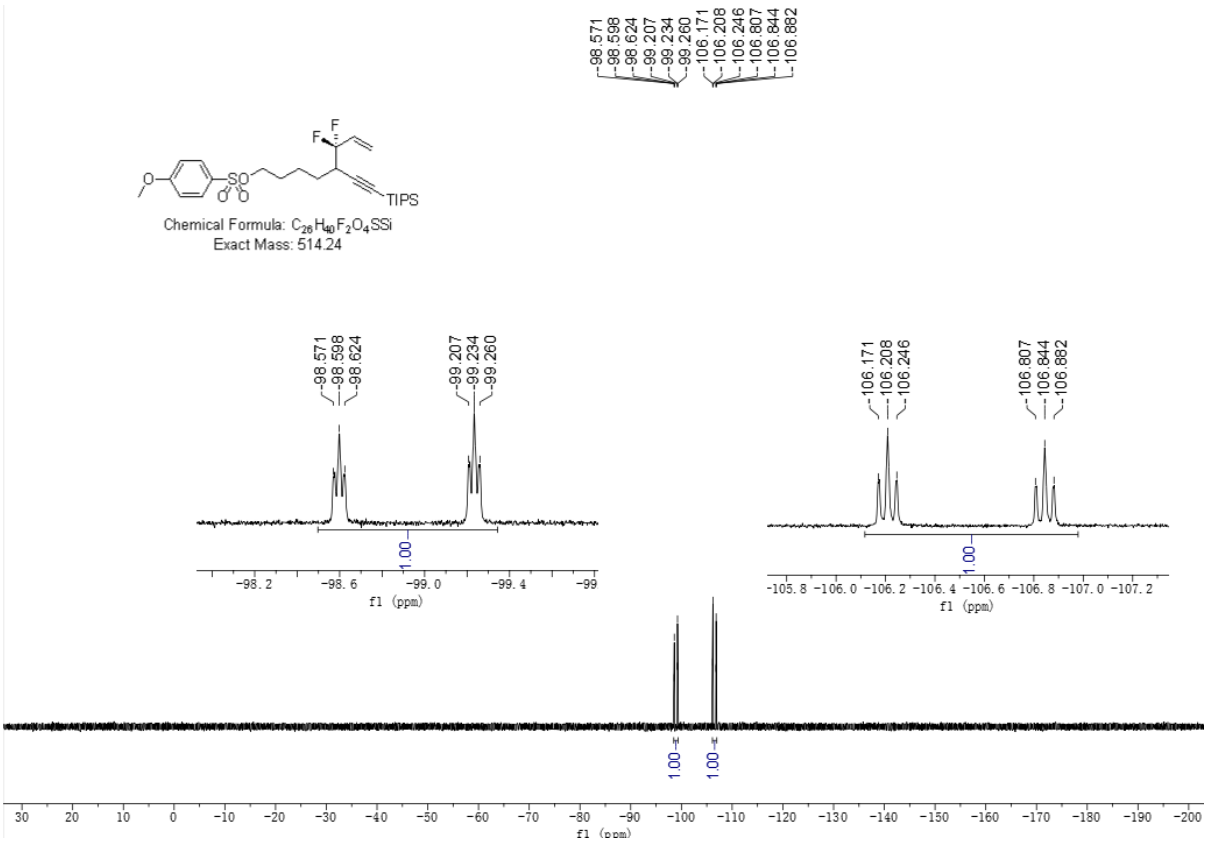


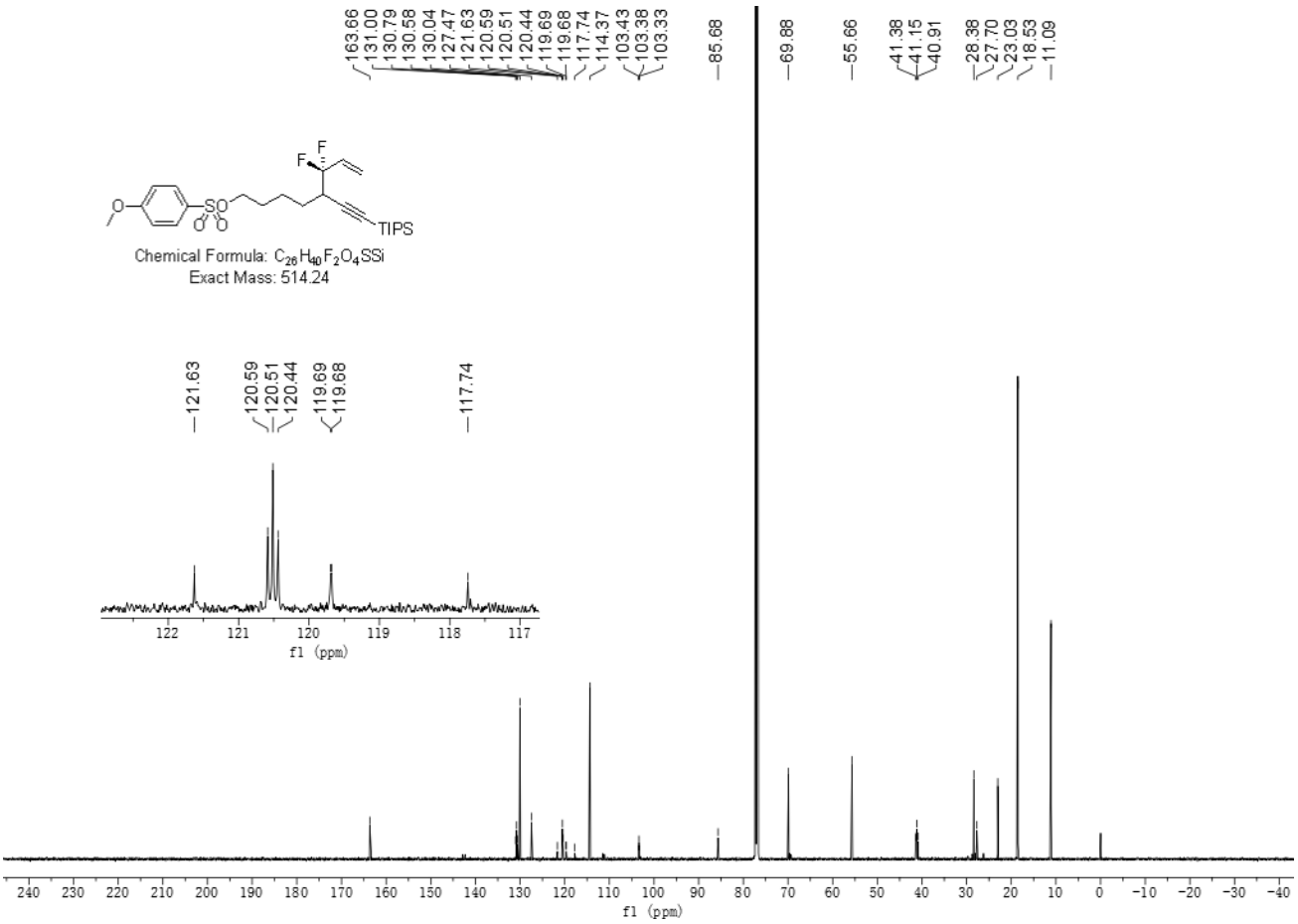

-98.510
-98.537
-98.564
-99.146
-99.173
-99.200
-106.204
-106.242
-106.280
-106.840
-106.878
-106.916
F
F
Cl
TIPS
Chemical Formula: C19H33ClF2Si
Exact Mass: 362.20
1.00
-98.3 -98.5 -98.7 -98.9 -99.1 -99.3 -99
f1 (ppm)
1.00
-105.9 -106.1 -106.3 -106.5 -106.7 -106.9 -107.1
f1 (ppm)
1.00
1.00
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


131.21
130.95
130.69
122.19
120.53
120.43
120.34
119.77
119.75
117.33
103.65
103.58
103.52
85.66
44.62
41.60
41.31
41.02
32.15
27.75
24.49
18.84
11.17
F
F
Cl
TIPS
Chemical Formula: C19H33ClF2Si
Exact Mass: 362.20
122.19
120.53
120.43
120.34
119.77
119.75
117.33
23 122 121 120 119 118 117
f1 (ppm)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

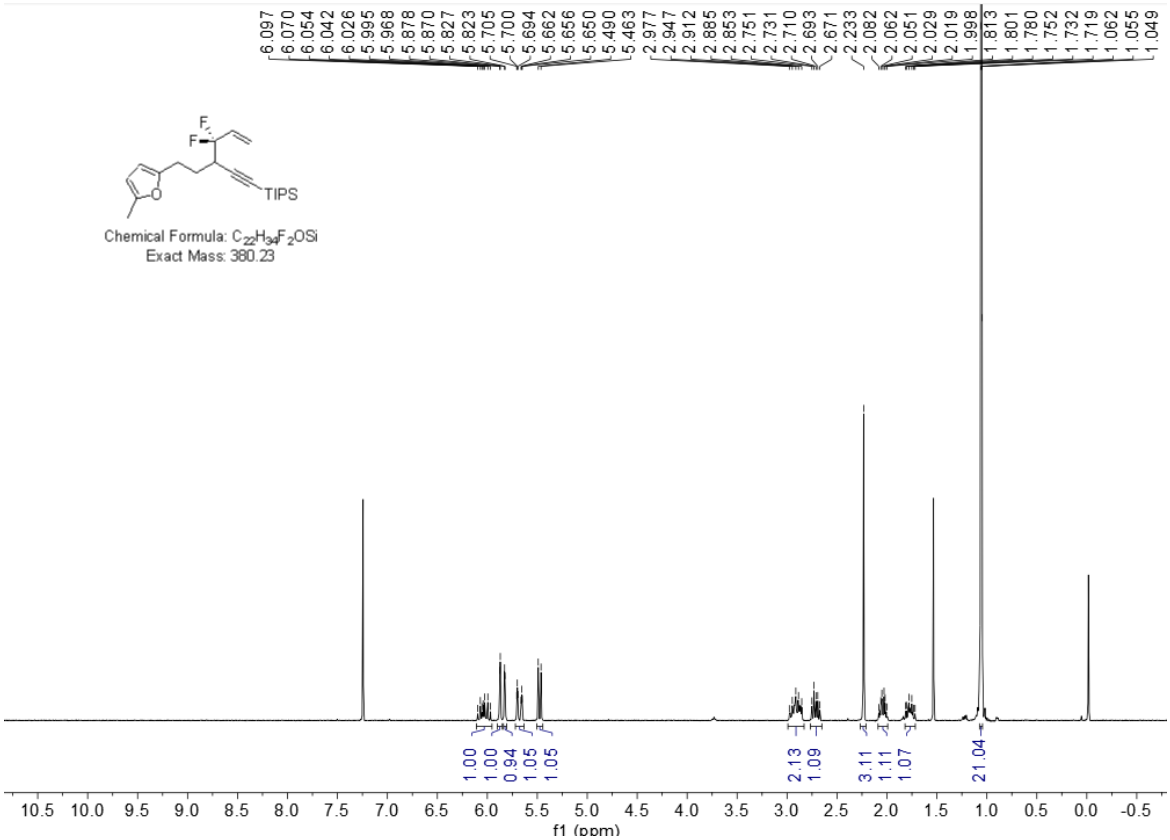
6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 4-methoxybenzenesulfonate (3o)

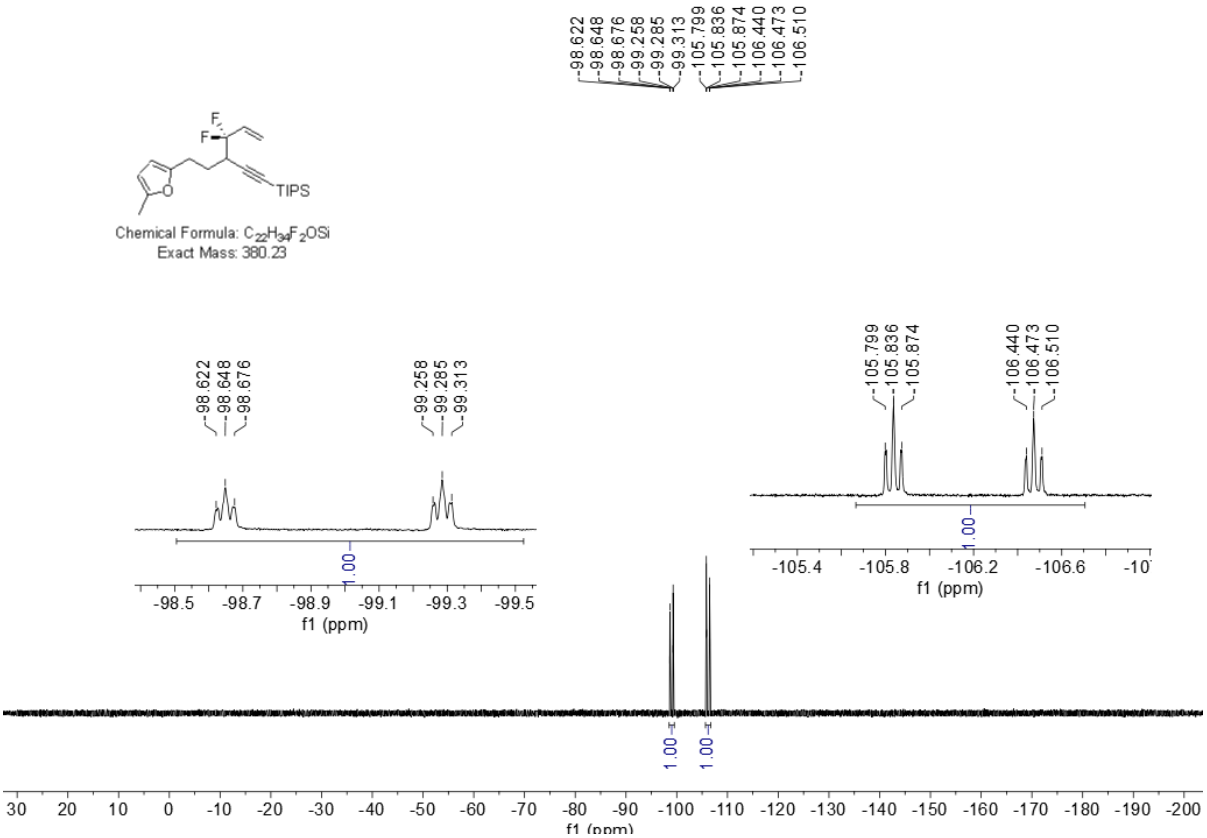


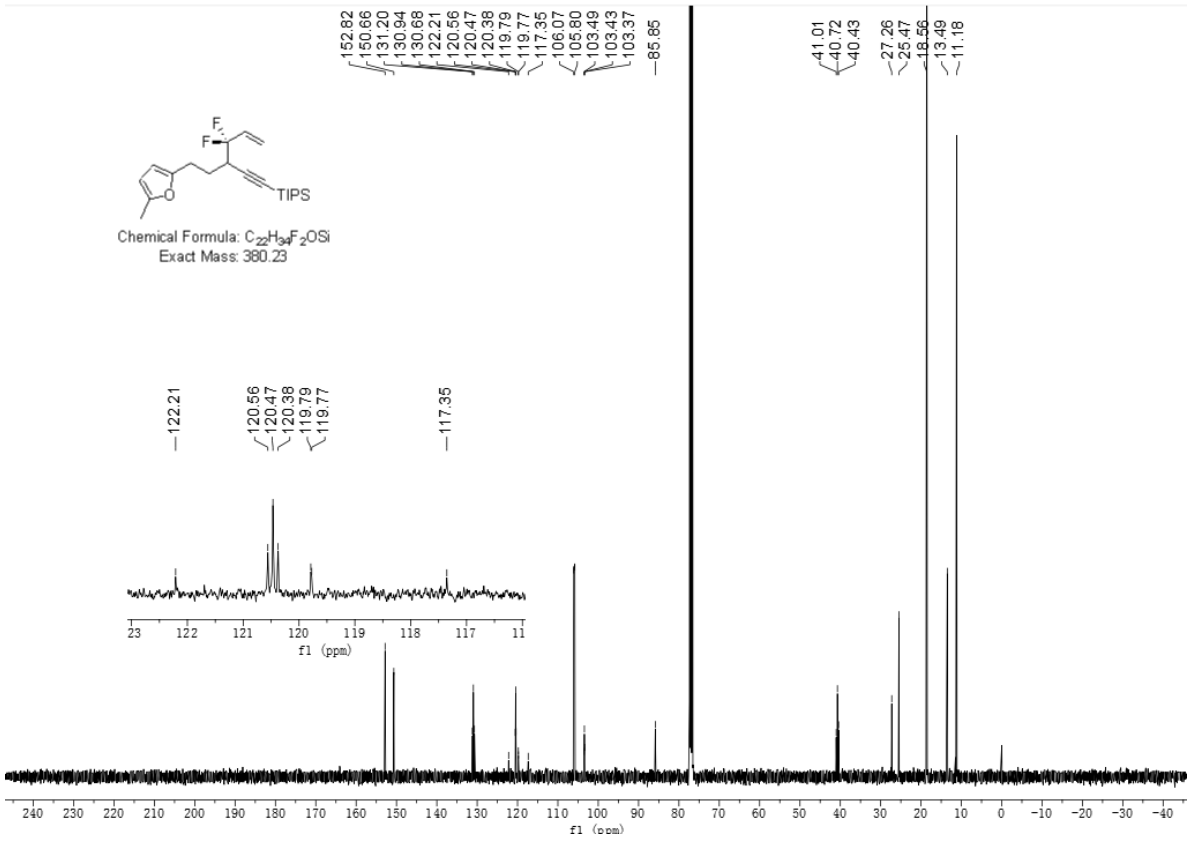




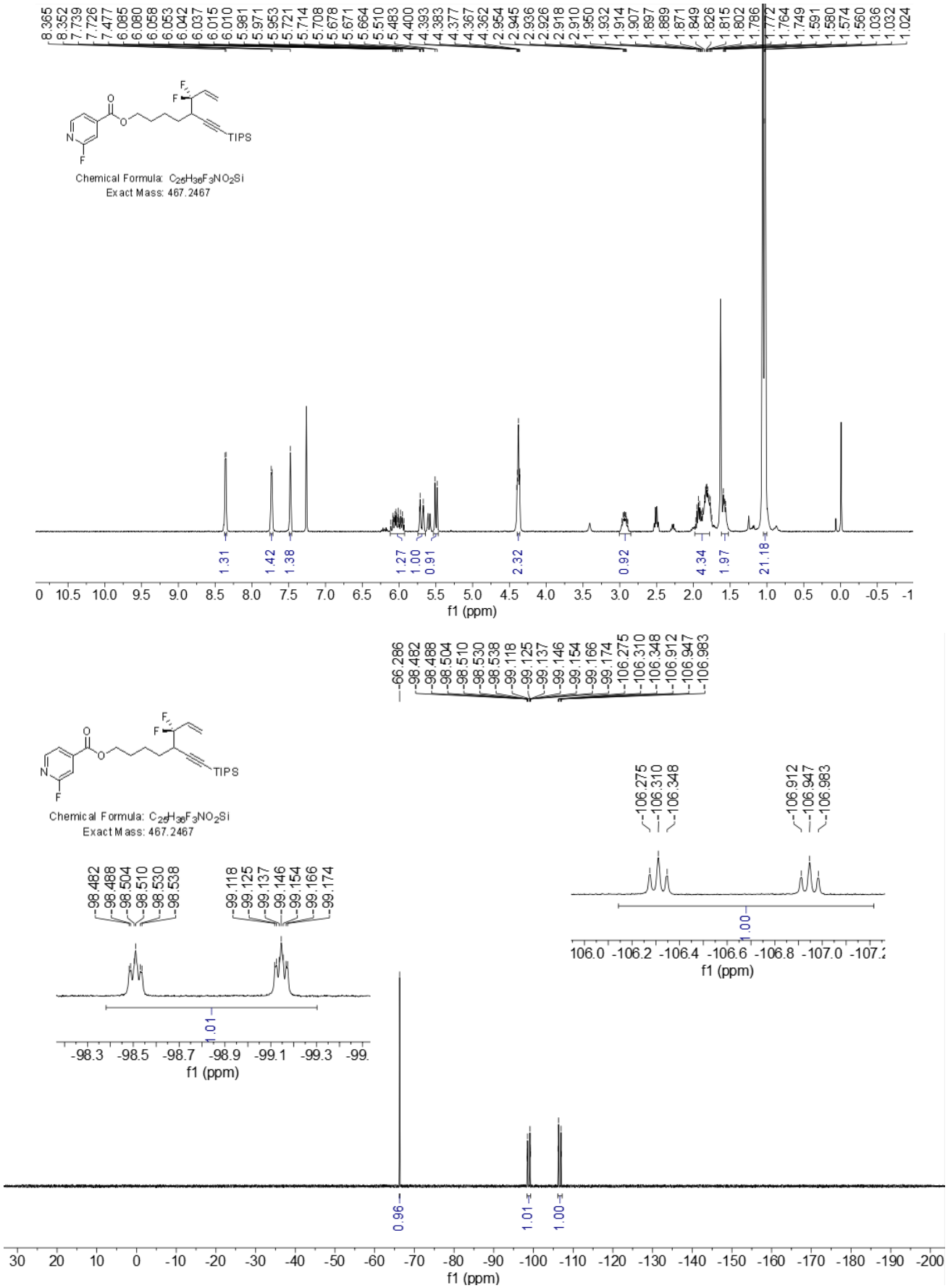
(4,4-Difluoro-3-(2-(5-methylfuran-2-yl)ethyl)hex-5-en-1-yn-1-yl)triisopropylsilane (3p)

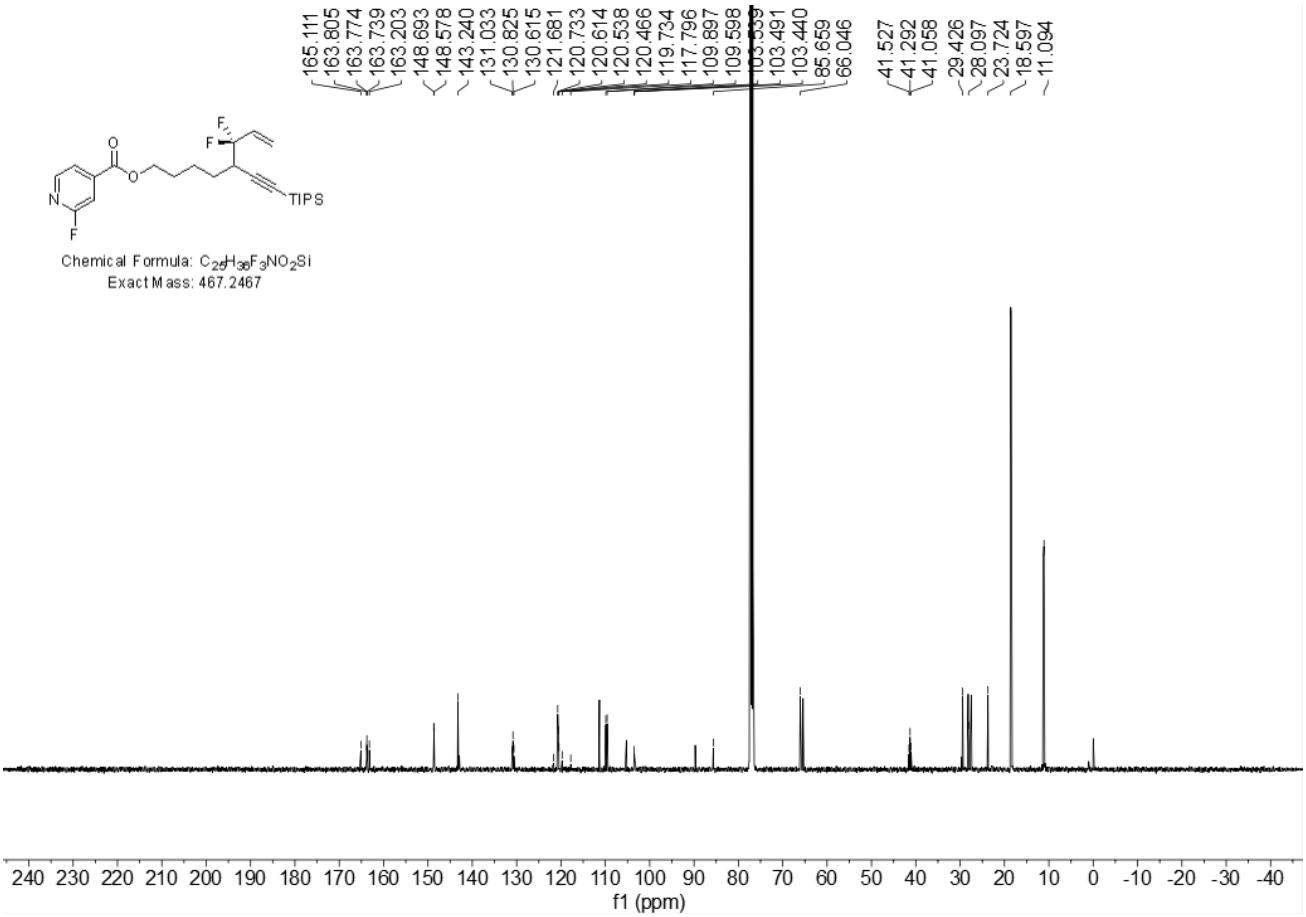



98.622
98.648
98.676
99.258
99.285
99.313
105.799
105.836
105.874
106.440
106.473
106.510
F
F
TIPS
Chemical Formula: C22H34F2OSi
Exact Mass: 380.23
1.00
f1 (ppm)
1.00
1.00
f1 (ppm)

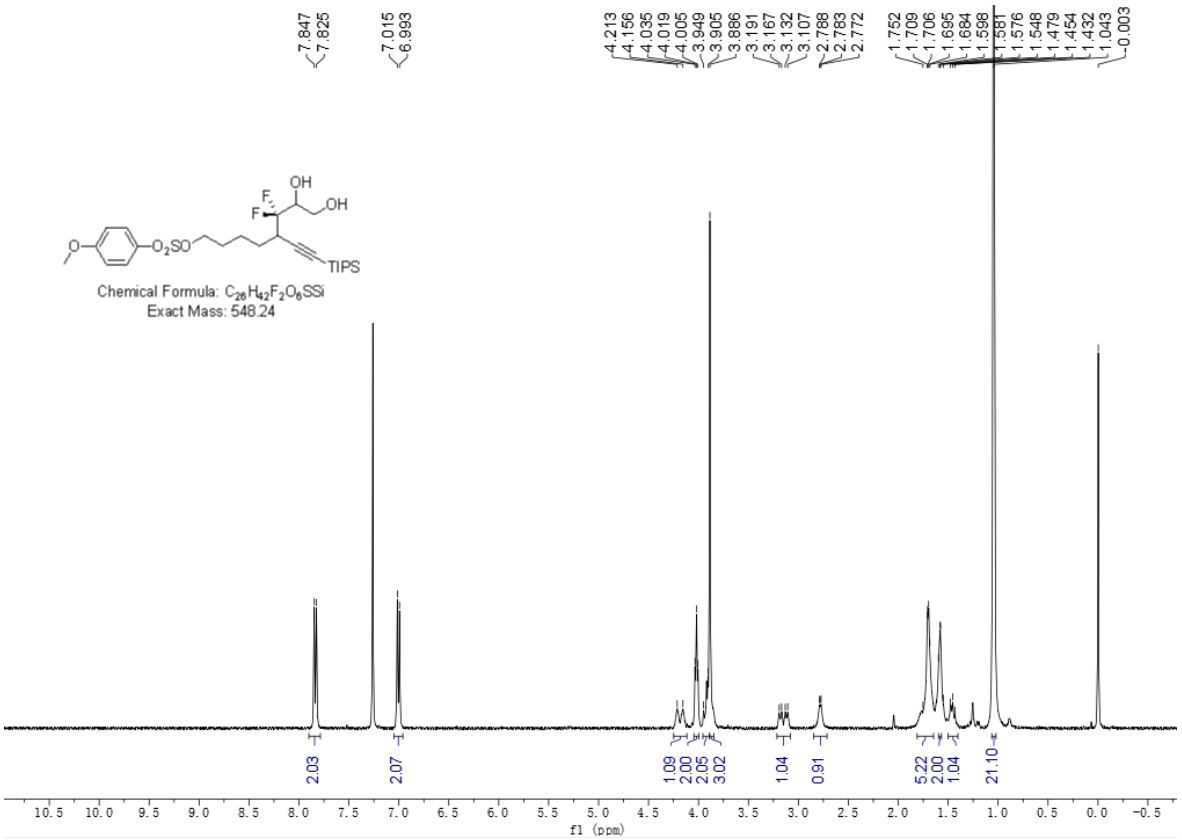

152.82
150.66
131.20
130.94
130.68
122.21
120.56
120.47
120.38
119.79
119.77
117.35
106.07
105.80
103.49
103.43
103.37
85.85
41.01
40.72
40.43
27.26
25.47
18.56
13.49
11.18
F
F
TIPS
Chemical Formula: C22H34F2OSi
Exact Mass: 380.23
122.21
120.56
120.47
120.38
119.79
119.77
117.35
f1 (ppm)
f1 (ppm)

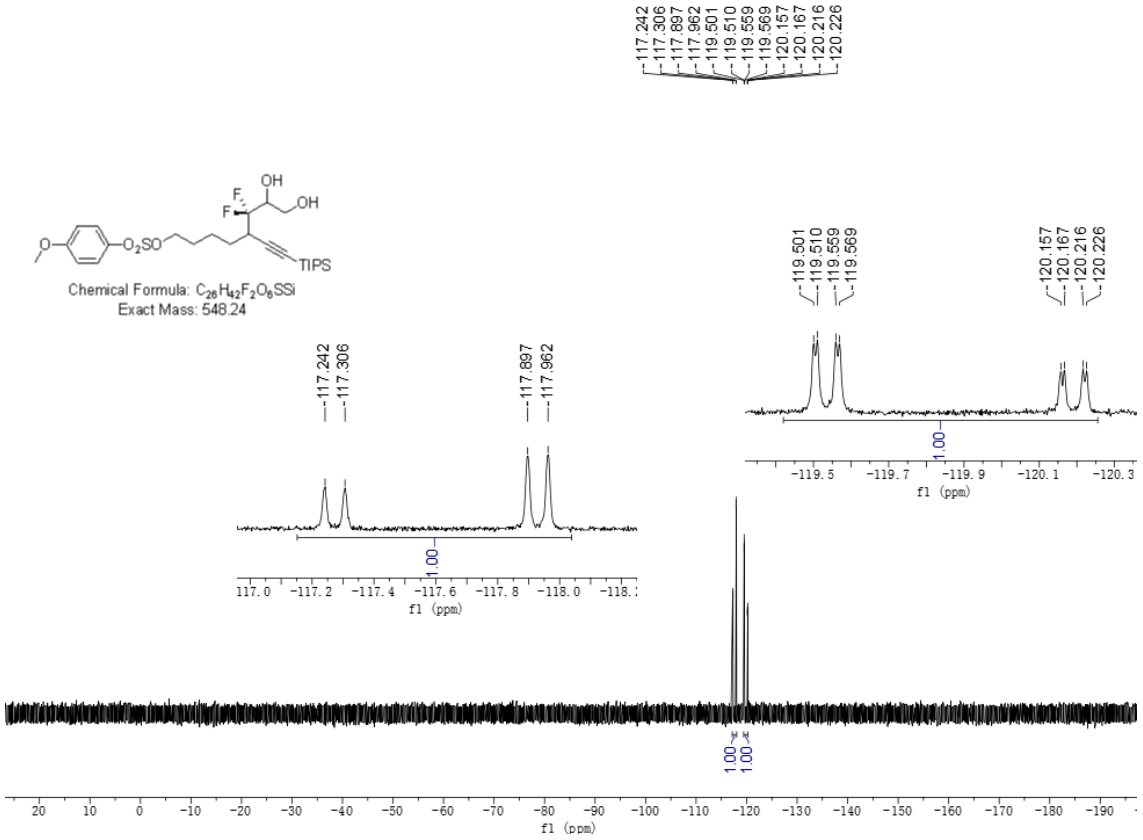
6,6-Difluoro-5-((triisopropylsilyl)ethynyl)oct-7-en-1-yl 2-fluoroisonicotinate (3q)

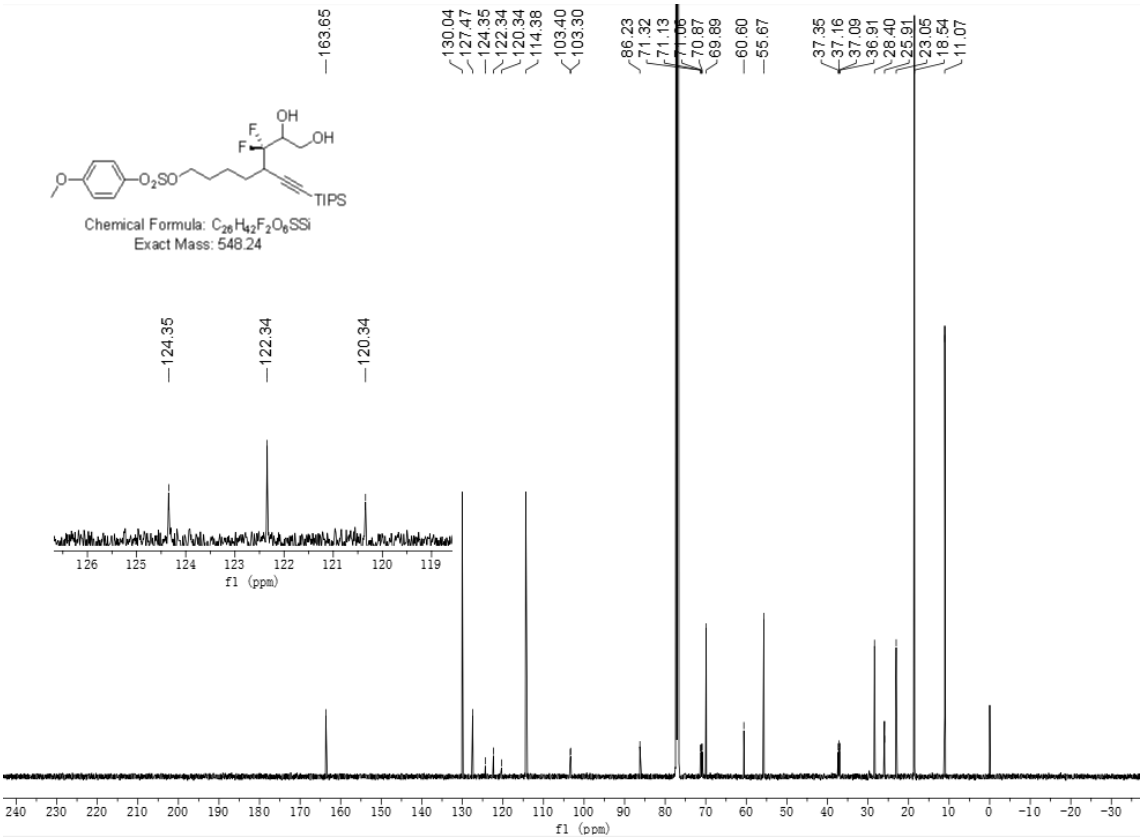




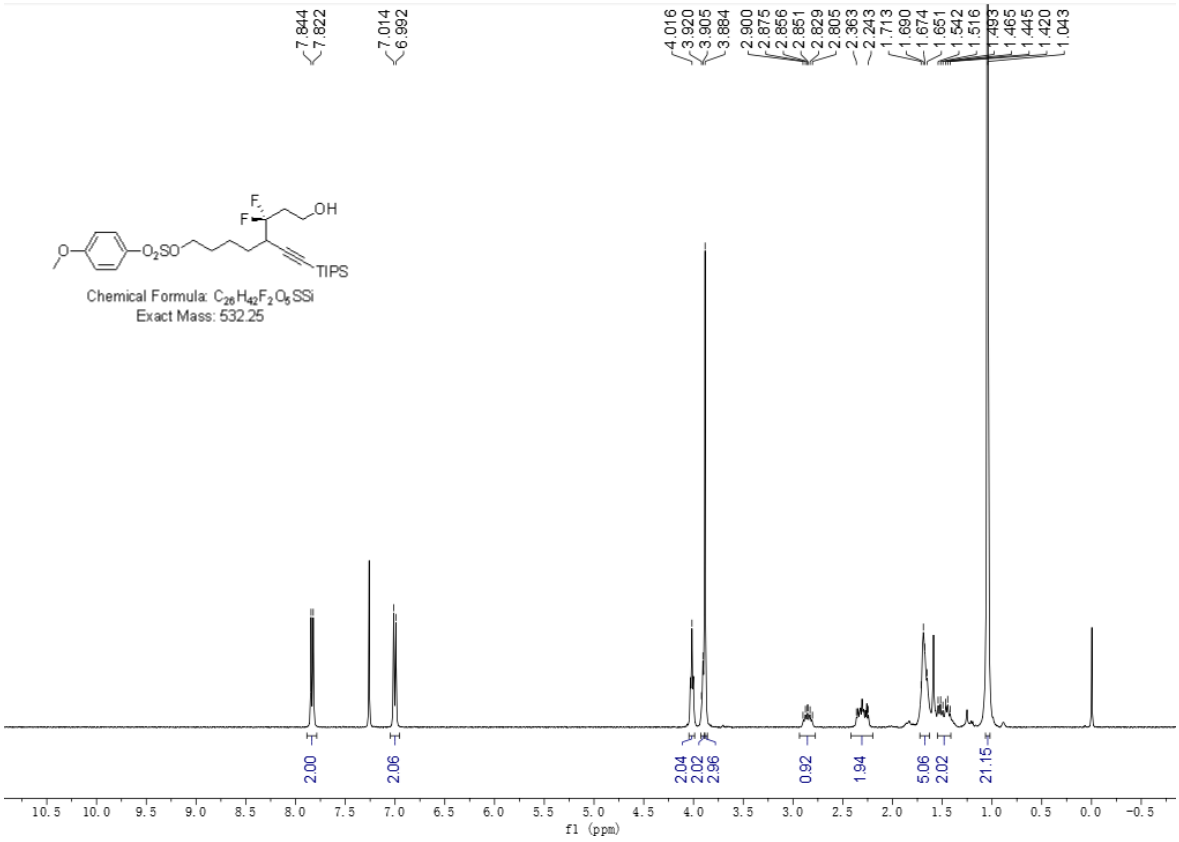
3,3-Difluoro-8-((((4-methoxyphenyl)peroxy)thio)oxy)-4-((triisopropylsilyl)ethynyl)octane-1,2-diol (5)

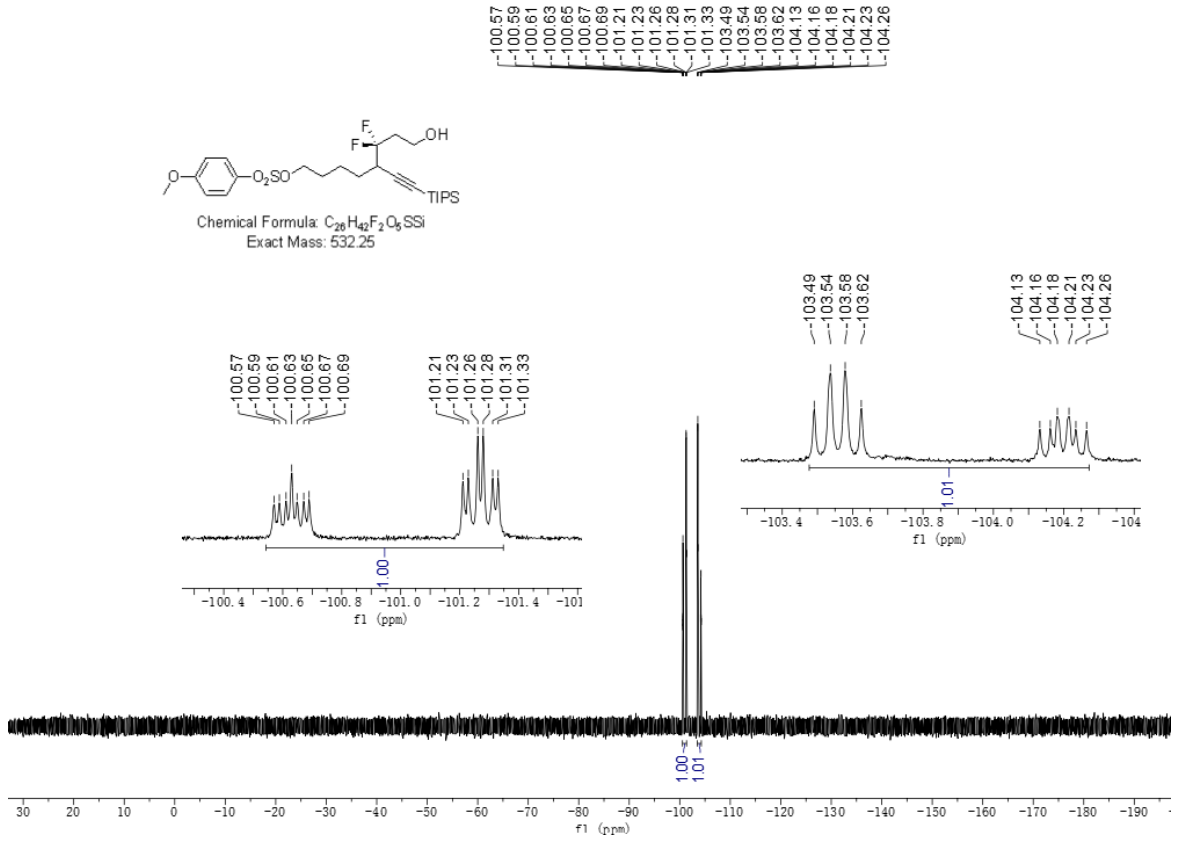


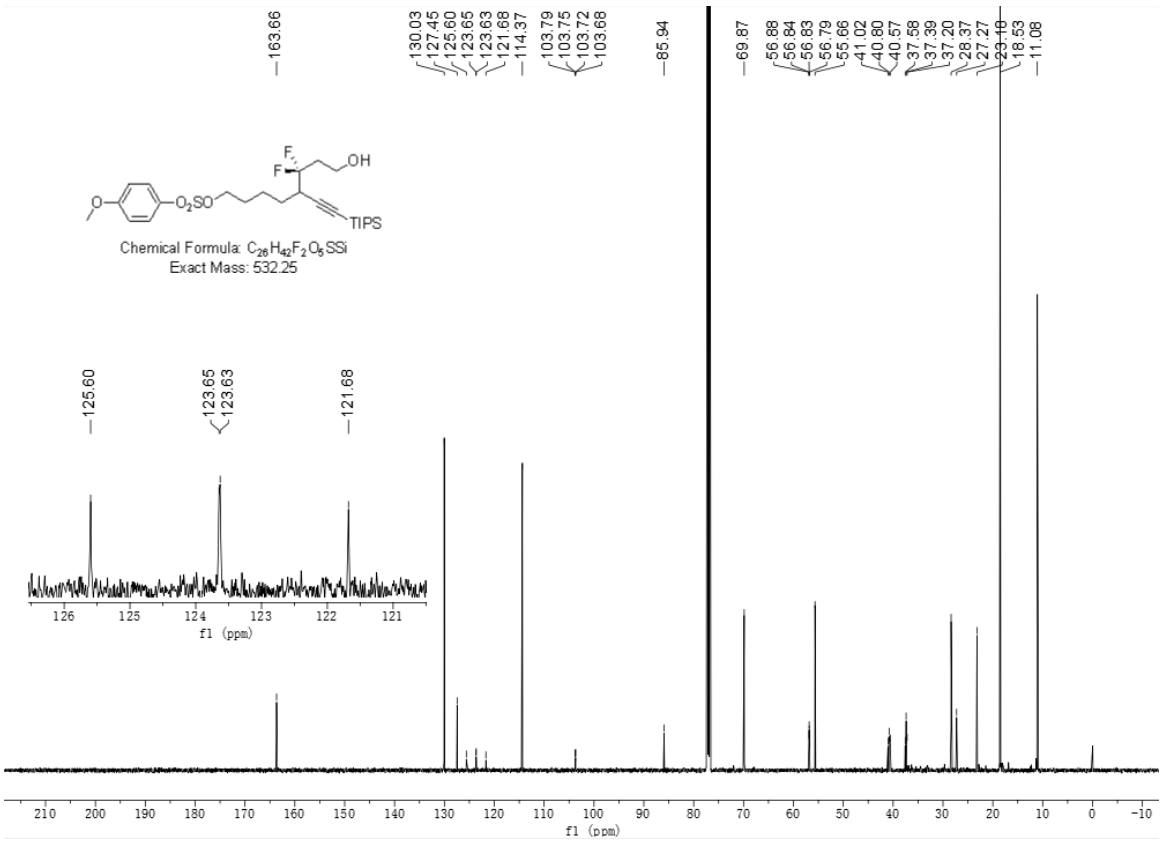

117.242
117.306
117.897
117.962
119.501
119.510
119.559
119.569
120.157
120.167
120.216
120.226
OH
F
F
OH
O
O2SO
TIPS
Chemical Formula: C26H42F2O6SSi
Exact Mass: 548.24
1.00
1.00
1.00
f1 (ppm)


163.65
130.04
127.47
124.35
122.34
120.34
114.38
103.40
103.30
86.23
71.32
71.13
71.06
70.87
69.89
60.60
55.67
37.35
37.16
37.09
36.91
28.40
25.91
23.05
18.54
11.07
124.35
122.34
120.34
OH
F
F
OH
O
O2SO
TIPS
Chemical Formula: C26H42F2O6SSi
Exact Mass: 548.24
f1 (ppm)

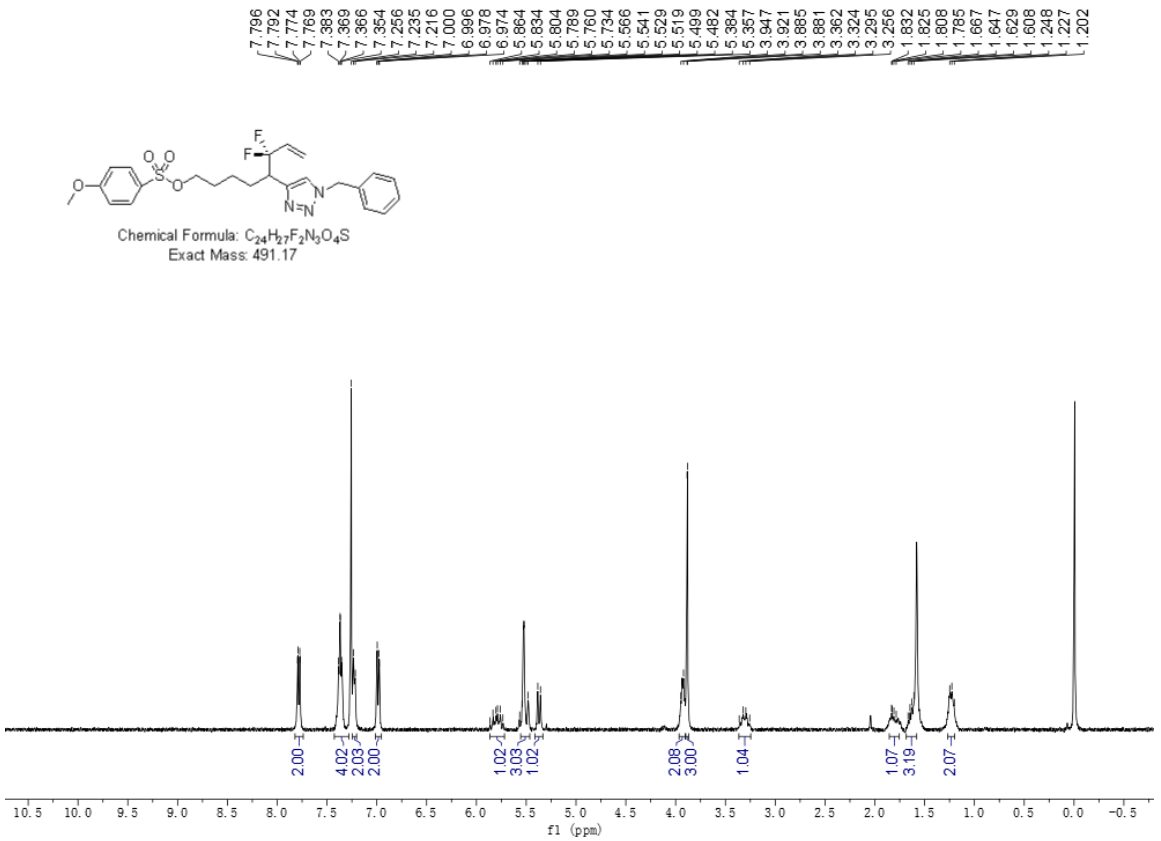
3,3-Difluoro-8-((((4-methoxyphenyl)peroxy)thio)oxy)-4-((triisopropylsilyl)ethynyl)octan-1-ol (6)

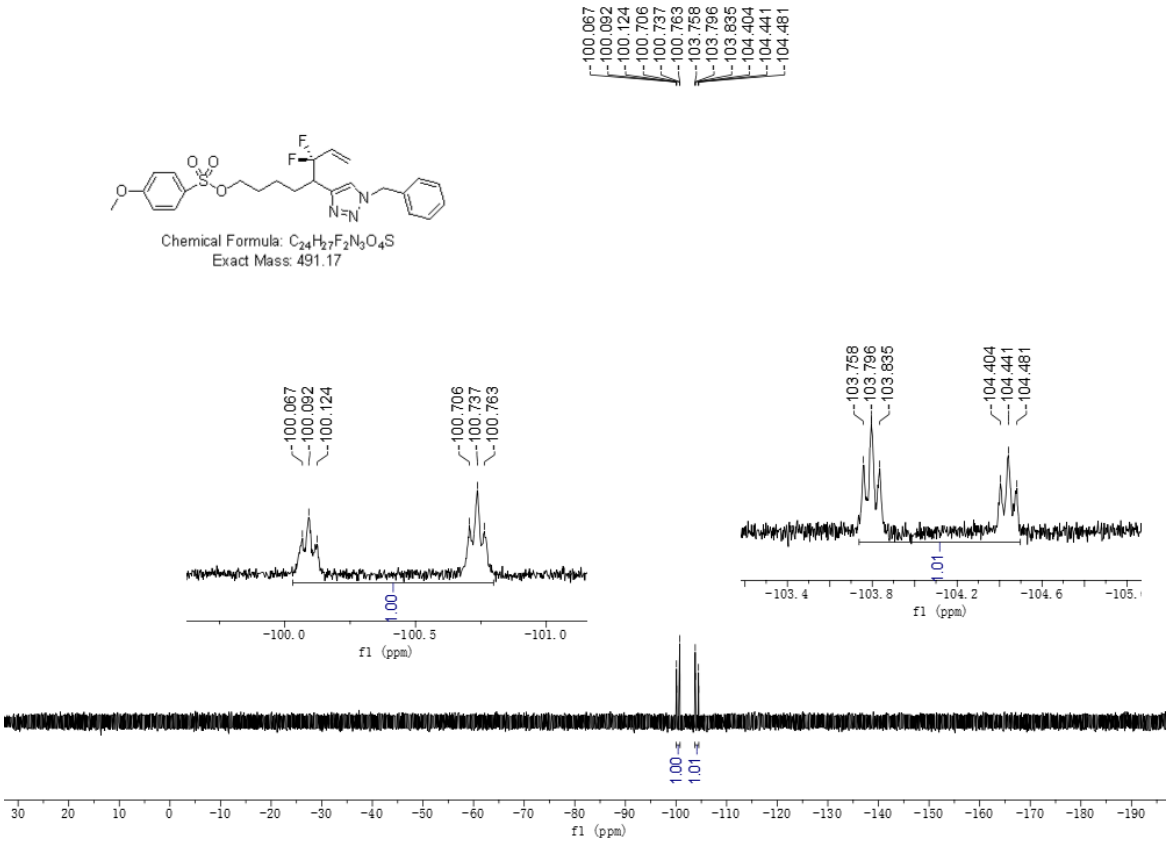


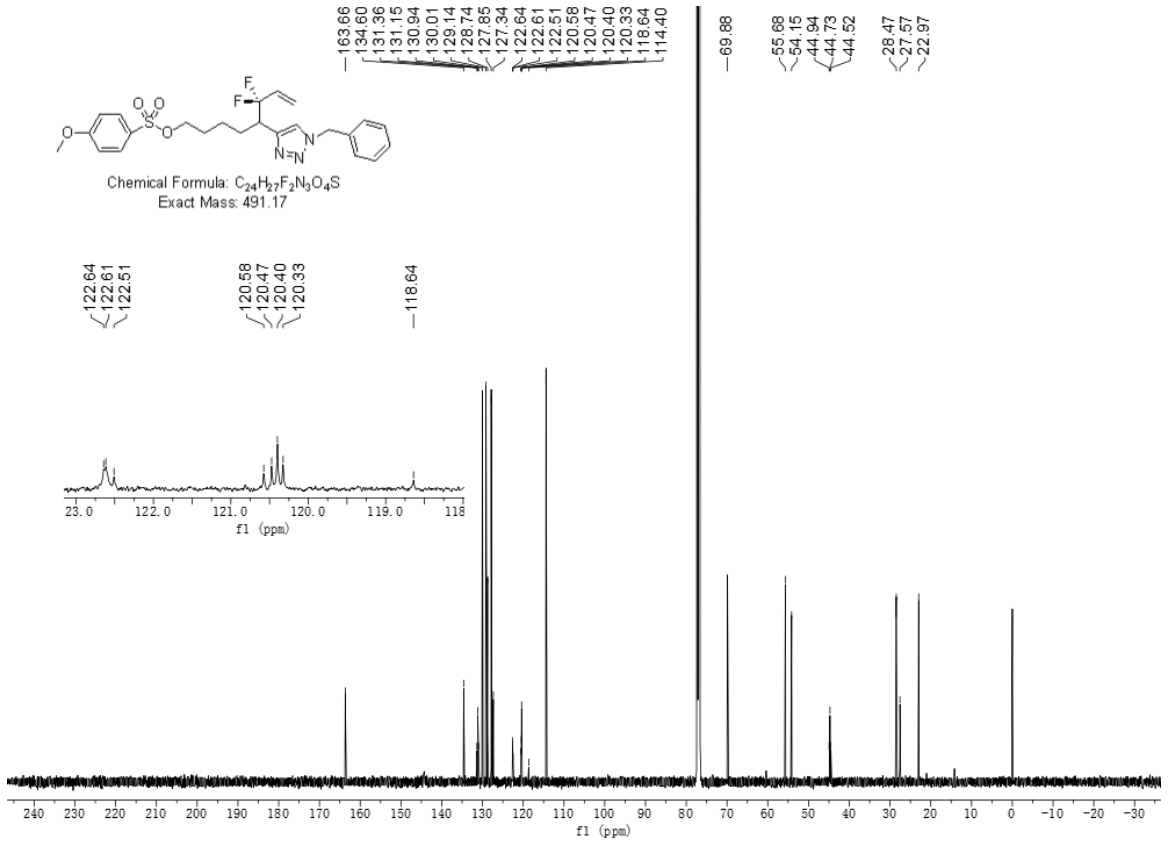




5-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-6,6-difluorooct-7-en-1-yl 4-methoxybenzenesulfonate (8)




Chemical Formula: C24H27F2N3O4S
Exact Mass: 491.17
f1 (ppm)


Chemical Formula: C24H27F2N3O4S
Exact Mass: 491.17
f1 (ppm)