Supporting Information for

Copper-Catalyzed Direct Propargylation of Polyfluoroarenes with Secondary Propargyl Phosphates

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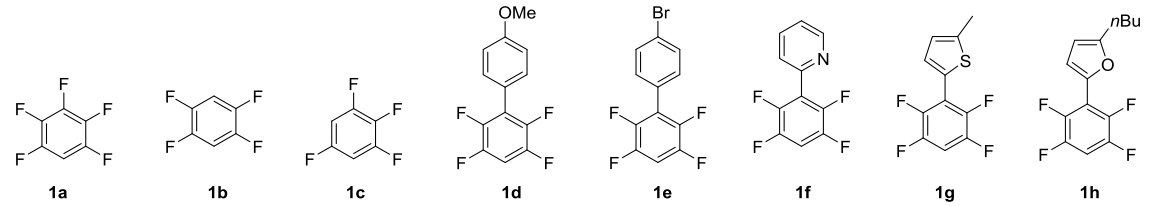
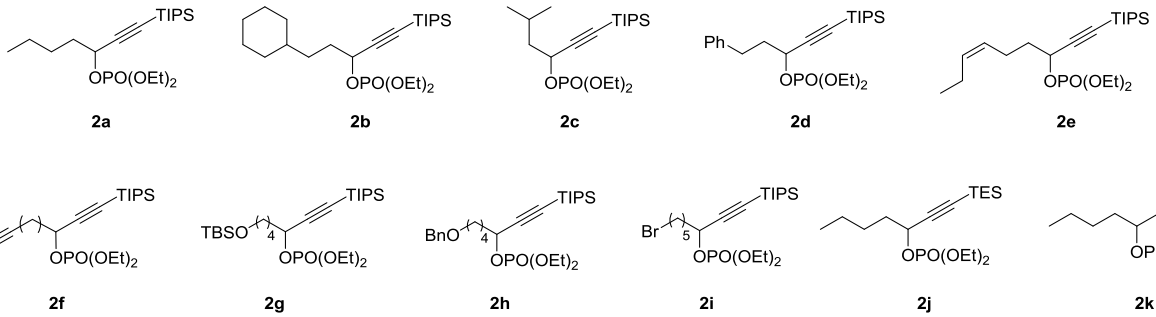
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 and AM500 spectrometer. ^{19}F NMR was recorded on a Bruker AM400 spectrometer ($CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature. THF was distilled from sodium and benzophenone before use. Propargyl phosphates were prepared from corresponding propargyl alcohol and diethyl chlorophosphate according to the literature.[1] Dans-$(CH_2)_3$-N_3 was prepared according to the literature.[2]



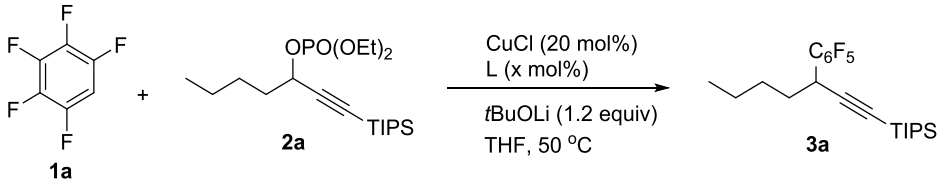


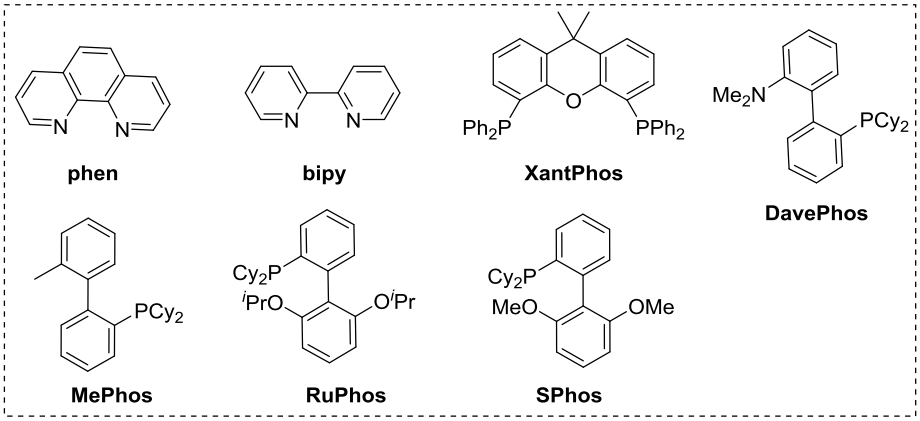
[1] Uehling, M. R.; Marionni, S. T.; Lalic, G. *Org. Lett*. **2012**, *14*, 362.

[2] Frei, R.; Waser, J. *J. Am. Chem. Soc*. **2013**, *135*, 9620.

Screening for Copper-Catalyzed Cross-Coupling of Pentafluorobenzene 1a with Secondary Propargyl Phosphate 2a (Table S1-S3). To a septum capped 25 mL of Schlenck tube were added [Cu] (10 - 20 mol%), ligand (20 mol%), base (1.2 - 2.4 equiv) under N_2, followed by solvent (1 mL). Propargyl phosphate **2a** (0.3 mmol, 1.0 equiv) and pentafluorobenzene **1a** (2.0 - 3.0 equiv) were then added. The tube was screw capped and put into an oil bath (preheated to 50 or 80 ^oC). After stirring for 8 h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

Table S1. Ligand Effect on Cu-Catalyzed Cross-Coupling of 1a with 2a.[a]

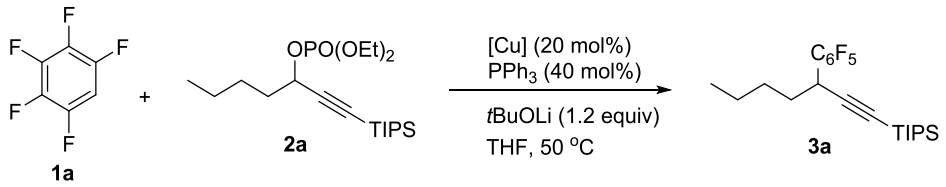




Entry	Ligand, x	Yield (%)[b]	Entry	Ligand, x	Yield (%)[b]
1	phen, 20	ND	5	PPh_3, 40	20
2	bipy, 20	ND	6	MePhos, 40	10
3	XantPhos, 20	10	7	RuPhos, 40	11
4	DavePhos, 20	13	8	SPhos, 40	9

[a]Reaction conditions (unless otherwise specified): **1a** (0.6 mmol, 2.0 equiv), **2a** (0.3 mmol, 1.0 equiv),THF (1 mL), 50 ^oC, 8 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. ND = Not detected.

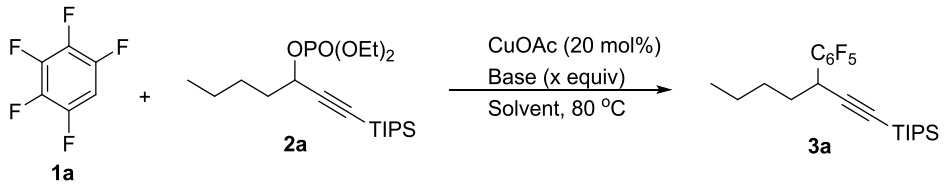
Table S2. Screening of Copper Catalysts for Cross-Coupling of 1a with 2a.[a]



Entry	[Cu]	Ligand, x	Yield (%)[b]	Entry	[Cu]	Ligand, x	Yield (%)[b]
1	CuI	PPh_3, 40	21	5	$Cu(OAc)_2$	PPh_3, 40	15
2	CuBr	PPh_3, 40	18	6	CuOAc	PPh_3, 40	30
3	$CuCl_2$	PPh_3, 40	ND	7	CuOAc	/	45
4	CuSCN	PPh_3, 40	23	8[c]	CuOAc	/	68

[a]Reaction conditions (unless otherwise specified): **1a** (0.6 mmol, 2.0 equiv), **2a** (0.3 mmol, 1.0 equiv),THF (1 mL), 50 °C, 8 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. [c]Reaction run at 80 °C.

Table S3. Screening of Solvents and Bases for Cu-Catalyzed Cross-Coupling of 1a with 2a.[a]



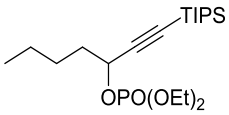
Entry	Base, x	Solvent	Yield (%)[b]	Entry	Base, x	Solvent	Yield (%)[b]
1	*t*BuOLi, 1.2	Toluene	20	5	*t*BuOK, 1.2	THF	40
2	*t*BuOLi, 1.2	Dioxane	ND	6	K_2CO_3, 1.2	THF	ND
3	*t*BuOLi, 1.2	DMF	ND	7	*t*BuOLi, 2.4	THF	75
4	*t*BuONa, 1.2	THF	55	8[c]	*t*BuOLi, 2.4	THF	90 (85)

[a]Reaction conditions (unless otherwise specified): **1a** (0.6 mmol, 2.0 equiv), **2a** (0.3 mmol, 1.0 equiv),THF (1 mL), 80 °C, 8 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. [c]**1a** (1.8 mmol, 3.0 equiv), **2a** (0.6 mmol, 1.0 equiv), CuOAc (10 mol%), THF (2 mL), 80 °C, 12 h. Number in parenthesis is isolated yield.

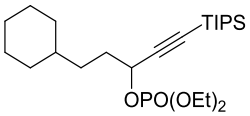
General Procedure for the Preparation of Secondary Propargyl Phosphates 2

To a solution of (triisopropylsilyl)acetylene (1.0 equiv) in THF was added dropwise *n*BuLi (1.6 M hexane solution, 1.0 equiv) at 0 ℃ under N_2. After the resulting mixture was stirred for 30 min at same temperature, the corresponding aldehyde (1.0 equiv) was added via a syringe. The resulting mixture was allowed to warm to room temperature and stirred for additional 2 h. The resulting suspension was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate three times. The combined organic layers were dried over sodium sulfate and concentrated. The residue was used directly in the next step without further purification.

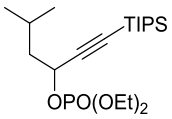
To a flask were added propargylic alcohol (1.0 equiv), 4-dimethylaminopyridine (0.1 equiv), dry CH_2Cl_2, and diethylchlorophosphate (1.3 equiv) under N_2. The resulting mixture was then cooled to 0 ℃ and triethylamine (1.2 equiv) was added. The reaction mixture was allowed to warm to room temperature with stirring. After consumption of the alcohol (monitored by TLC), the mixture was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate three times. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography to give desired propargyl phosphates.



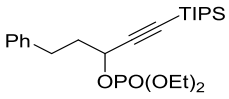
Diethyl (1-(triisopropylsilyl)hept-1-yn-3-yl) phosphate (2a). The product (73% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (dd, *J* = 14.2, 6.7 Hz, 1H), 4.17-4.07 (m, 4H), 1.85-1.78 (m, 2H), 1.50-1.43 (m, 2H), 1.38-1.30 (m, 8H), 1.05-0.94 (m, 21H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.6 (d, *J* = 4.3 Hz), 87.6, 68.5 (d, *J* = 5.7 Hz), 63.7 (dd, *J* = 5.7 Hz, *J* = 4.2 Hz), 36.4 (d, *J* = 5.7 Hz), 26.8, 22.0, 18.4, 16.0 (dd, *J* = 7.0, 3.3 Hz), 13.8, 11.0. IR (thin film) ν_{max} 2944, 2867, 2176, 1724, 1034 cm^{-1}. MS (EI): *m/z* (%) 405 $[M+H]^+$. HRMS: Calculated for $C_{20}H_{42}O_4PSi$: 405.2584; Found: 405.2582.



5-Cyclohexyl-1-(triisopropylsilyl)pent-1-yn-3-yl diethyl phosphate (2b). The product (65% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (dd, *J* = 14.0, 6.7 Hz, 1H), 3.97-3.89 (m, 4H), 1.66-1.63 (m, 2H), 1.51-1.44 (m, 6H), 1.23-1.19 (m, 2H), 1.16-1.13 (m, 5H), 1.17-0.93 (m, 4H), 0.95-0.79 (m, 21H), 0.74-0.67 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.6 (d, *J* = 4.4 Hz), 87.3, 77.4, 68.5 (d, *J* = 5.6 Hz), 63.4 (dd, *J* = 5.7, 3.7 Hz), 36.9, 34.1 (d, *J* = 5.6 Hz), 33.1, 33.0, 32.1, 26.4, 26.0, 18.3, 15.8 (dd, *J* = 6.9, 4.8 Hz), 10.9. IR (thin film) ν_{max} 2925, 2865, 2176, 1035, 679 cm^{-1}. MS (DART): *m/z* (%) 459 $[M+H]^+$. HRMS: Calculated for $C_{24}H_{48}O_4PSi$: 459.3054; Found: 459.3052.

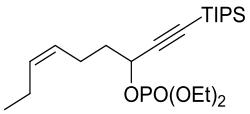


Diethyl (5-methyl-1-(triisopropylsilyl)hex-1-yn-3-yl) phosphate (2c). The product (70% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (q, *J* = 7.4 Hz, 1H), 4.03-3.94 (m, 4H), 1.79-1.71 (m, 1H), 1.66-1.60 (m, 1H), 1.55-1.49 (m, 1H), 1.18 (dd, *J* = 7.1, 0.7 Hz, 6H), 0.98-0.86 (m, 21H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.7 (d, *J* = 3.7 Hz), 87.5, 67.1 (d, *J* = 5.8 Hz), 63.5 (dd, *J* = 5.9, 2.9 Hz), 45.6 (d, *J* = 6.0 Hz), 24.5, 22.2, 22.1, 18.3, 15.9 (dd, *J* = 7.0, 4.5 Hz), 10.9. IR (thin film) ν_{max} 2958, 2867, 2176, 1279, 679 cm^{-1}. MS (EI): *m/z* (%) 361 $(M-C_3H_7)^+$, 267, 211 (100). HRMS: Calculated for $C_{17}H_{34}O_4PSi$: 361.1964; Found: 361.1956.

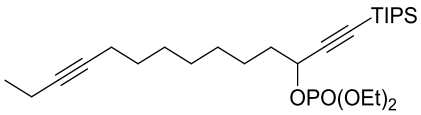


Diethyl (5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl) phosphate (2d). The product (79% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.21 - 7.20 (m, 3H), 5.06 (dd, *J* = 13.8, 6.5 Hz, 1H), 4.17-4.11 (m, 4H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.18-2.11 (m, 2H), 1.34 (td, *J* = 7.0, 2.1 Hz, 6H), 1.08-1.07

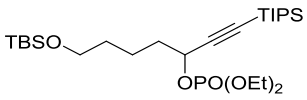
(m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 128.5, 128.4, 126.1, 104.2 (d, *J* = 4.3 Hz), 88.3, 68,0 (d, *J* = 5.7 Hz), 63.8 (dd, *J* = 5.9, 2.7 Hz), 38.7 (d, *J* = 5.8 Hz), 31.1, 18.5, 16.1 (dd, *J* = 6.8, 5.6 Hz), 11.1. IR (thin film) ν_{max} 2944, 2866, 2175, 1009 cm^{-1}. MS (EI): *m/z* (%) 409 $(M\text{-}C_3H_7)^+$, 267, 211 (100). HRMS: Calculated for $C_{21}H_{34}O_4PSi$: 409.1964; Found: 409.1972.



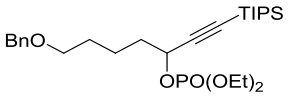
(*Z*)-Diethyl (1-(triisopropylsilyl)non-6-en-1-yn-3-yl) phosphate (2e). The product (63% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dt, *J* = 10.5, 7.1 Hz, 1H), 5.30 (dt, *J* = 8.6, 7.2 Hz, 1H), 5.00 (dd, *J* = 14.2, 6.6 Hz, 1H), 4.16-4.07 (m, 4H), 2.23-2.19 (m, 2H), 2.06-1.99 (m, 2H), 1.87-1.81 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 6H), 1.08-1.05 (m, 21H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.9, 126.9, 104.3 (d, *J* = 4.4 Hz), 87.9, 68.1 (d, *J* = 5.7 Hz), 67.0, 63.7 (d, *J* = 5.9 Hz, 5.7 Hz), 36.9 (d, *J* = 5.6 Hz), 22.5, 20.4, 18.4, 16.0 (d, *J* = 6.9 Hz, 7.0 Hz), 14.2, 11.0. IR (thin film) ν_{max} 2944, 2867, 1724, 1265, 680 cm^{-1}. MS (EI): *m/z* (%) 387 $(M\text{-}C_3H_7)^+$, 267, 211 (100). HRMS: Calculated for $C_{19}H_{36}O_4SiP$: 387.2121; Found: 387.2126.



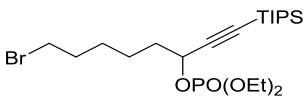
Diethyl (1-(triisopropylsilyl)tetradeca-1,11-diyn-3-yl) phosphate (2f). The product (68% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (dd, *J* = 13.9, 6.8 Hz, 1H), 4.14-4.07 (m, 4H), 2.14-2.08 (m, 4H), 1.85-1.73 (m, 2H), 1.47-1.41 (m, 4H), 1.33-1.29 (m, 12H), 1.11-1.04 (m, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.6 (d, *J* = 4.4 Hz), 87.6, 81.4, 79.3, 68.4 (d, *J* = 5.7 Hz), 63.6 (dd, *J* = 5.8, 3.9 Hz), 36.7 (d, *J* = 5.6 Hz), 29.0, 28.9, 28.8, 28.6, 24.6, 18.6, 18.4, 16.0 (dd, *J* = 7.0, 4.0 Hz), 14.3, 12.3, 11.0. IR (thin film) ν_{max} 3397, 2938, 2865, 2175, 1265, 1035 cm^{-1}. MS (DART): *m/z* (%) 499 $[M+H]^+$. HRMS: Calculated for $C_{27}H_{52}O_4PSi$: 499.3367; Found: 499.3367.



7-((*tert*-Butyldimethylsilyl)oxy)-1-(triisopropylsilyl)hept-1-yn-3-yl diethyl phosphate (2g). The product (61% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.96 (dd, *J* = 14.3, 6.5 Hz, 1H), 4.12 - 4.02 (m, 4H), 3.56 - 3.54 (m, 2H), 1.83-1.78 (m, 2H), 1.54-1.49 (m, 4H), 1.29 – 1.26 (m, 6H), 1.02 - 0.95 (m, 21H), 0.83 (s, 9H), -0.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.5 (d, *J* = 4.3 Hz), 87.7, 68.4 (d, *J* = 5.7 Hz), 63.7 (dd, *J* = 5.6, 4.9 Hz), 62.9, 36.7 (d, *J* = 5.7 Hz), 32.2, 25.9, 21.3, 18.4, 18.2, 16.0 (dd, *J* = 7.0, 4.0 Hz), 11.0, -5.4. IR (thin film) ν_{max} 3435, 2944, 2866, 2176, 1036 cm^{-1}. MS (DART): *m/z* (%) 535 $[M+H]^+$. HRMS: Calculated for $C_{26}H_{56}O_5PSi_2$: 535.3398; Found: 535.3398.

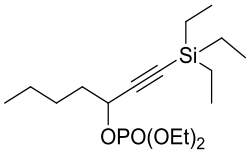


7-(Benzyloxy)-1-(triisopropylsilyl)hept-1-yn-3-yl diethyl phosphate (2h). The product (57% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 5.03 (dd, *J* = 14.2, 6.5 Hz, 1H), 4.49 (d, *J* = 3.2 Hz, 2H), 4.17 - 4.08 (m, 4H), 3.47 (t, *J* = 6.0 Hz, 2H), 1.89-1.83 (m, 2H), 1.69-1.60 (m, 4H), 1.34-1.30 (m, 6H), 1.06-1.03 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 128.3, 127.5, 127.4, 104.5 (d, *J* = 4.2 Hz), 87.8, 72.8, 70.0, 68.3 (d, *J* = 5.7 Hz), 63.7 (dd, *J* = 5.6, 3.0 Hz), 36.6 (d, *J* = 5.7 Hz), 29.1, 21.6, 18.5, 16.0 (dd, *J* = 7.0, 2.2 Hz), 11.0. IR (thin film) ν_{max} 3327, 2943, 2866, 2176, 1719, 1034 cm^{-1}. MS (DART): *m/z* (%) 511 $[M+H]^+$, 490. HRMS: Calculated for $C_{27}H_{48}O_5PSi$: 511.3003; Found: 511.3003.

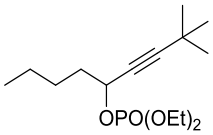


8-Bromo-1-(triisopropylsilyl)oct-1-yn-3-yl diethyl phosphate (2i). The product (59% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.00 (dd, *J* = 13.7, 6.8 Hz, 1H), 4.15-4.09 (m, 4H), 3.38 (t, *J* = 6.7 Hz, 2H), 1.87-

1.79 (m, 4H), 1.55-1.46 (m, 4H), 1.32 (t, *J* = 7.0 Hz, 6H), 1.05-1.03 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 104.3, 87.9, 68.2 (d, *J* = 5.5 Hz), 63.7 (dd, *J* = 4.7, 3.5 Hz), 36.5 (d, *J* = 5.5 Hz), 33.3, 32.5, 27.5, 23.8, 18.4, 16.0 (dd, *J* = 6.5, 4.8 Hz), 11.0. IR (thin film) ν_{max} 2943, 2866, 2176, 1724, 1006 cm^{-1}. MS (DART): *m/z* (%) 497 $[M+H]^+$. HRMS: Calculated for $C_{21}H_{42}BrO_4PSi$: 497.1846; Found: 497.1846.



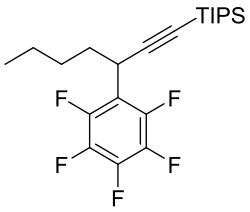
Diethyl (1-(triethylsilyl)hept-1-yn-3-yl) phosphate (2j). The product (70% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 4:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.97 (dd, *J* = 13.7, 6.8 Hz, 1H), 4.14-4.09 (m, 4H), 1.83-1.76 (m, 2H), 1.48-1.36 (m, 2H), 1.34-1.30 (m, 8H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.57 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 103.7, 88.5, 68.3, 63.6, 36.1, 26.7, 21.9, 15.8, 13.6, 7.0, 4.0. IR (thin film) ν_{max} 2957, 2876, 2177, 1725, 1264 cm^{-1}. MS (EI): *m/z* (%) 347 $(M-CH_3)^+$, 239, 183 (100). HRMS: Calculated for $C_{15}H_{30}O_4SiP$: 333.1651; Found: 333.1649.



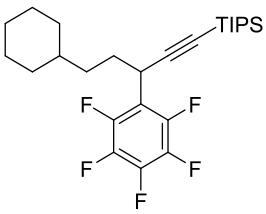
2,2-Dimethylnon-3-yn-5-yl diethyl phosphate (2k). The product (62% overall yield, 2 steps) as a colorless oil was purified with silica gel chromatography (Pentane / EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 (q, *J* = 6.8 Hz, 1H), 4.10-4.00 (m, 4H), 1.75-1.64 (m, 2H), 1.38-1.24 (m, 10H), 1.13 (s, 9H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 95.2, 76.2 (d, *J* = 4.1 Hz), 68.5 (d, *J* = 5.8 Hz), 67.0, 63.5 (t, *J* = 6.4 Hz), 36.5 (d, *J* = 6.2 Hz), 30.6, 27.2, 26.9, 22.0, 16.0 (d, *J* = 7.1 Hz), 13.8. IR (thin film) ν_{max} 3472, 2869, 2242, 1265 cm^{-1}. MS (EI): *m/z* (%) 304 (M^+), 275, 155 (100). HRMS: Calculated for $C_{15}H_{29}O_4P$: 304.1803; Found: 304.1800.

General Procedure for Cu-Catalyzed Cross-Coupling of Propargyl Phosphates 2 with Polyfluoroarenes 1

To a septum capped 25 mL of Schlenck tube were added CuOAc (10 mol%), *t*BuOLi (2.4 equiv) under N_2, followed by THF (2.0 mL), propargyl phosphate **2** (0.6 mmol, 1.0 equiv), and polyfluoroarene **1** (3.0 or 4.0 equiv). The tube was screw capped and put into an oil bath (preheated to 80 ^oC). After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product **3** or **4**.

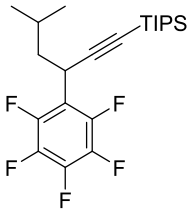


Triisopropyl (3-(perfluorophenyl)hept-1-yn-1-yl)silane (3a). The product (213 mg, 85% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (400 MHz, $CDCl_3$) δ 4.02 (t, *J* = 7.6 Hz, 1H), 2.06-1.96 (m, 1H), 1.81-1.73 (m, 1H), 1.49-1.34 (m, 4H), 1.12-0.94 (m, 21H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.4 (dd, *J* = 21.4, 6.8 Hz, 2F), -157.1 (t, *J* = 21.0 Hz, 1F), -162.8 (td, *J* = 21.3, 7.1 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1 (dm, *J* = 252.1 Hz), 140.32 (dm, *J* = 252.7 Hz), 137.79 (dm, *J* = 252.0 Hz), 115.86 (td, *J* = 15.9, 3.9 Hz), 106.0, 82.9, 35.1, 29.9, 28.1, 22.3, 18.7, 14.0, 11.4. IR (thin film) ν_{max} 3853, 2943, 2866, 2174, 1522 cm^{-1}. MS (EI): *m/z* (%) 418 (M^+), 419 $[M+H]^+$, 375 (100). HRMS: Calculated for $C_{22}H_{31}F_5Si$: 418.2115; Found: 418.2120.

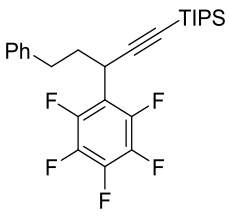


(5-Cyclohexyl-3-(perfluorophenyl)pent-1-yn-1-yl)triisopropylsilane (3b). The product (235 mg, 83% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H

NMR (400 MHz, $CDCl_3$) δ 3.97 (t, *J* = 7.7 Hz, 1H), 1.98-1.93 (m, 1H), 1.79-1.63 (m, 5H), 1.46-1.40 (m, 1H), 1.26-1.14 (m, 5H), 1.11-0.96 (m, 21H), 0.91-0.80 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.0 (dd, *J* = 21.7, 7.5 Hz, 2F), -156.8 (t, *J* = 21.0 Hz, 1F), -162.5 (td, *J* = 21.7, 7.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 248.3 Hz), 140.1 (dm, *J* = 253.1 Hz), 137.5 (dm, *J* = 255.5 Hz), 115.7 (tm, *J* = 15.6 Hz), 105.8, 82.7, 37.2, 35.2, 33.4, 33.1, 32.7, 26.6, 26.3, 18.4, 11.2. IR (thin film) ν_{max} 2926, 2866, 2175, 1653 cm^{-1}. MS (EI): *m/z* (%) 472 (M^+), 473 $[M+H]^+$, 429 (100). HRMS: Calculated for $C_{26}H_{37}F_5Si$: 472.2585; Found: 472.2580.

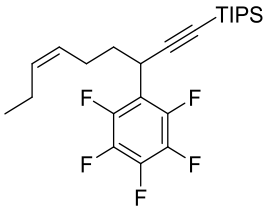


Triisopropyl(5-methyl-3-(perfluorophenyl)hex-1-yn-1-yl)silane (3c). CuOAc (20 mol%) was used. The product (221 mg, 88% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (t, *J* = 7.8 Hz, 1H), 1.98-1.91 (m, 1H), 1.83-1.73 (m, 1H), 1.63-1.56 (m, 1H), 1.10-1.06 (m, 21H), 0.99-0.97 (m, 6H) . ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.4 (dd, *J* = 21.2, 7.0 Hz, 2F), -157.1 (t, *J* = 20.8 Hz, 1F), -162.7 (td, *J* = 21.5, 7.7 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 252.4 Hz), 140.08 (dm, *J* = 252.6 Hz), 137.56 (dm, *J* = 252.6 Hz), 115.77 (td, *J* = 16.2, 4.4 Hz), 105.7, 82.6, 44.0, 26.2, 26.0, 22.3, 21.6, 18.4, 11.2. IR (thin film) ν_{max} 2959, 2867, 2174, 1521 cm^{-1}. MS (EI): *m/z* (%) 418 (M^+), 419 $[M+H]^+$, 375 (100). HRMS: Calculated for $C_{22}H_{31}F_5Si$: 418.2115; Found: 418.2120.

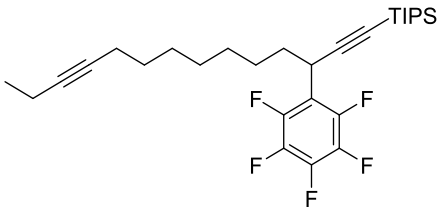


Triisopropyl(3-(perfluorophenyl)-5-phenylpent-1-yn-1-yl)silane (3d). The product (240 mg, 86% yield) as a white solid (m.p. 36 °C) was purified with silica gel chromatography (Petroleum ether/ EtOAc = 50:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 -7.25 (m, 2H), 7.18-7.16 (m, 3H), 4.03 (t, *J* = 7.6 Hz, 1H), 3.00-2.87 (m, 1H), 2.75-2.69 (m, 1H), 2.34-2.27 (m, 1H), 2.08-2.00 (m, 1H), 1.25-0.93 (m,

21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.9 (dd, *J* = 20.7, 6.9 Hz, 2F), -158.2 (t, *J* = 20.4 Hz, 1F), -163.9 (dt, *J* = 21.3, 7.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 245.4 Hz), 140.5, 140.3 (dm, *J* = 253.2 Hz), 137.6 (dm, *J* = 252.3 Hz), 128.5, 128.4, 126.2, 115.3 (tm, *J* = 15.5 Hz), 105.3, 83.6, 36.8, 33.8, 27.5, 18.6, 11.3. IR (KBr disk) ν_{max} 3028, 2943, 2890, 2865, 2175, 2723, 1506 cm^{-1}. MS (EI): *m/z* (%) 423 [$(M-C_3H_7)^+$, 100], 395, 381. HRMS: Calculated for $C_{23}H_{24}F_5Si$: 423.1567; Found: 423.1563. Anal. Calcd. For $C_{23}H_{24}F_5Si$: C, 66.93; H, 6.70; Found: C, 66.89; H, 6.61.

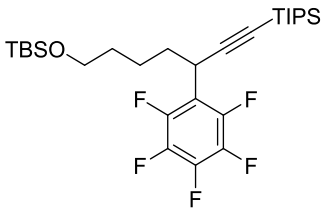


(*Z*)-Triisopropyl(3-(perfluorophenyl)non-6-en-1-yn-1-yl)silane (3e). The product (186 mg, 70% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/ EtOAc = 100:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (ddd, *J* = 12.8, 9.7, 7.3 Hz, 1H), 5.29 (ddd, *J* = 10.7, 9.7, 7.3 Hz, 1H), 4.05 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.28-2.19 (m, 2H), 2.10-2.02 (m, 3H), 1.78-1.71 (m, 1H), 1.12-1.00 (m, 21H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.0 (dd, *J* = 21.5, 7.0 Hz, 2F), -156.7 (t, *J* = 21.0 Hz, 1F), -162.4 (td, *J* = 21.6, 7.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 248.9 Hz), 140.1 (dm, *J* = 258.0 Hz), 137.5 (dm, *J* = 245.3 Hz), 133.5, 126.8, 115.5 (td, *J* = 16.3, 3.5 Hz), 105.5, 83.0, 35.1, 27.3, 25.1, 20.6, 18.5, 14.2, 11.2. IR (thin film) ν_{max} 3008, 2944, 2867, 2175, 1521, 1504 cm^{-1}. MS (EI): *m/z* (%) 401 [$(M-C_3H_7)^+$, 100], 395, 381. HRMS: Calculated for $C_{21}H_{26}F_5Si$: 401.1724; Found: 401.1717.

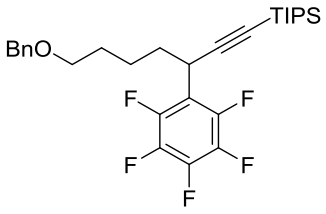


Triisopropyl(3-(perfluorophenyl)tetradeca-1,11-diyn-1-yl)silane (3f). The product (280 mg, 91% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (t, *J* = 7.6 Hz, 1H), 2.18-2.11 (m, 4H), 1.96-1.91 (m, 2H), 1.74-1.70 (m, 2H), 1.48-1.45 (m, 4H), 1.33-1.26 (m, 4H), 1.13-0.92 (m, 24H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

142.0 (dd, *J* = 21.5, 7.0 Hz, 2F), -156.7 (t, *J* = 21.0 Hz, 1F), -162.4 (td, *J* = 21.6, 7.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (d, *J* = 248.4 Hz), 140.0 (d, *J* = 253.2 Hz), 137.5 (d, *J* = 252.3 Hz), 115.6 (tm, *J* = 16.1 Hz), 105.7, 82.7, 81.6, 79.4, 35.1, 29.7, 29.1, 28.9, 28.8, 28.7, 27.8, 27.5, 18.5, 14.4, 12.4, 11.2. IR (thin film) ν_{max} 2939, 2865, 2175, 1504 cm^{-1}. MS (EI): *m/z* (%) 512 (M^+), 469, 427, 73 (100). HRMS: Calculated for $C_{29}H_{41}F_5Si$: 512.2898; Found: 512.2892.

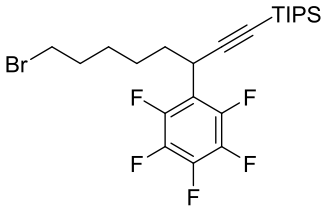


***tert*-Butyldimethyl((5-(perfluorophenyl)-7-(triisopropylsilyl)hept-6-yn-yl)oxy)silane (3g).** The product (256 mg, 78% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/ EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (t, *J* = 7.6 Hz, 1H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.04-1.95 (m, 1H), 1.80- 1.76 (m, 1H), 1.59-1.54 (m, 3H), 1.47-1.40 (m, 1H), 1.08-1.01 (m, 21H), 0.87 (s, 9H), 0.03 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) -141.9 (dd, *J* = 21.5, 7.3 Hz, 2F), -156.7 (t, *J* = 20.9 Hz, 2F), -162.5 (td, *J* = 21.7, 7.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) 144.8 (dm, *J* = 250.5 Hz), 140.1 (dm, *J* = 253.2 Hz), 137.5 (dm, *J* = 251.6 Hz), 115.4 (tm, *J* = 14.4 Hz), 105.6, 82.7, 62.8, 35.0, 32.1, 27.9, 25.9, 24.0, 18.5, 18.3, 11.2, -5.4. IR (thin film) ν_{max} 2944, 2865, 2175, 1653, 1504 cm^{-1}. MS (MALDI): *m/z* (%) 549 $[M+H]^+$, 532, 520. HRMS: Calculated for $C_{28}H_{46}F_5OSi_2$: 549.3002; Found: 549.2990.

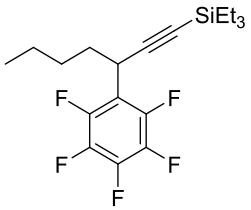


(7-(Benzyloxy)-3-(perfluorophenyl)hept-1-yn-1-yl)triisopropylsilane (3h). The product (255 mg, 81% yield) as a light yellow oil was purified with silica gel chromatography (Petroleum ether/ EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 4.48 (s, 2H), 4.03 (t, *J* = 7.6 Hz, 1H), 3.46 (t, *J* = 6.2 Hz, 2H), 2.02-1.95 (m, 1H), 1.81-1.72 (m, 1H), 1.69-1.57 (m, 3H), 1.48-1.40 (m, 1H), 1.08-1.00 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.0 (dd, *J* = 21.5, 7.4 Hz, 2F), -156.6 (t, *J* = 21.0 Hz,

1F), -162.4 (td, *J* = 21.7, 7.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 244.9 Hz), 140.1 (dm, *J* = 253.0 Hz), 138.5, 137.6 (dm, *J* = 252.7 Hz), 128.3, 127.6, 127.5, 115.4 (dd, *J* = 16.3, 3.6 Hz), 105.6, 82.9, 72.9, 69.9, 35.0, 29.1, 27.8, 24.3, 18.5, 11.2. IR (thin film) ν_{max} 2943, 2866, 2174, 1504 cm^{-1}. MS (MALDI): *m/z* (%) 525 $[M+H]^+$, 481, 451. HRMS: Calculated for $C_{29}H_{38}F_5OSi$: 525.2607; Found: 525.2595.

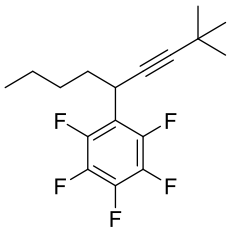


(8-Bromo-3-(perfluorophenyl)oct-1-yn-1-yl)triisopropylsilane (3i). The product (190 mg, 62% yield) as a light yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (t, *J* = 7.6 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.04-1.95 (m, 1H), 1.90-1.83 (m, 1H), 1.81-1.72 (m, 1H), 1.58-1.41 (m, 4H), 1.05-0.90 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.0 (dd, *J* = 21.0, 6.5 Hz, 2F), -156.6 (t, *J* = 20.9 Hz, 1F), -162.3 (td, *J* = 21.2, 6.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 248.3 Hz), 140.1 (dm, *J* = 253.0 Hz), 137.6 (dm, *J* = 251.0 Hz), 115.4 (td, *J* = 16.9, 3.5 Hz), 105.4, 83.0, 34.9, 33.4, 32.5, 27.8, 27.5, 26.7, 18.5, 11.2. IR (thin film) ν_{max} 2943, 2866, 2176, 1503 cm^{-1}. MS (EI): *m/z* (%) 469 $(M-C_3H_7)^+$, 427, 167 (100). HRMS: Calculated for $C_{20}H_{25}BrF_5Si$: 467.0829; Found: 467.0827.

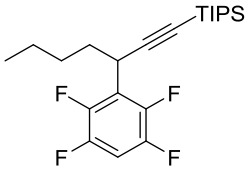


Triethyl(3-(perfluorophenyl)hept-1-yn-1-yl)silane (3j). The product (165 mg, 73% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, *J* = 7.7 Hz, 1H), 1.98-1.93 (m, 1H), 1.79-1.74 (m, 1H), 1.48-1.41 (m, 1H), 1.39-1.26 (m, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.58 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.0 (dd, *J* = 21.6, 7.5 Hz, 2F), -156.8 (t, *J* = 20.9 Hz, 1F), -162.5 (td, *J* = 21.7, 7.7 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 251.4 Hz), 140.08 (dm, *J* = 252.2 Hz),

137.56 (dm, *J* = 246.4 Hz), 115.45 (tm, *J* = 16.8 Hz), 105.3, 83.8, 34.8, 29.6, 27.8, 22.0, 13.8, 7.3, 4.4. IR (thin film) ν_{max} 2958, 2877, 2175, 1506 cm^{-1}. MS (EI): *m/z* (%) 376 (M^+), 347 (100), 319. HRMS: Calculated for $C_{19}H_{25}F_5Si$: 376.1646; Found: 376.1646.

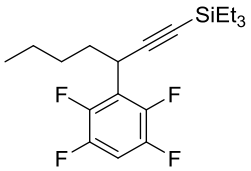


1-(2,2-Dimethylnon-3-yn-5-yl)-2,3,4,5,6-pentafluorobenzene (3k). The product (168 mg, 88% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (400 MHz, $CDCl_3$) δ 3.93 (t, *J* = 7.7 Hz, 1H), 1.94-1.87 (m, 1H), 1.79-1.68 (m, 1H), 1.46-1.38 (m, 1H), 1.37-1.23 (m, 3H), 1.20 (s, 9H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.5 (dd, *J* = 20.9, 7.1 Hz, 2F), -158.8 (t, *J* = 20.3 Hz, 1F), -164.1 (td, *J* = 20.8, 6.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 248.7 Hz), 139.9 (dm, *J* = 252.3 Hz), 137.5 (dm, *J* = 251.9 Hz), 116.4 (td, *J* = 16.0, 4.4 Hz), 90.4, 76.6, 35.0, 30.8, 29.6, 27.3, 26.9, 22.0, 13.7. IR (thin film) ν_{max} 2968, 2933, 2867, 1504 cm^{-1}. MS (EI): *m/z* (%) 318 (M^+), 261, 181(100). HRMS: Calculated for $C_{17}H_{19}F_5$: 318.1407; Found: 318.1408.

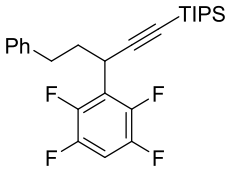


Triisopropyl(3-(2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4a). 4.0 equiv of fluoroarene was used. The product (192 mg, 80% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (500 MHz, $CDCl_3$) δ 6.95 (tt, *J* = 9.6, 7.3 Hz, 1H), 4.07 (t, *J* = 7.7 Hz, 1H), 2.00-1.97 (m, 1H), 1.78-1.76 (m, 1H), 1.50-1.48 (m, 1H), 1.38-1.33 (m, 3H), 1.09-1.01 (m, 21H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.5 (m, 2F), -142.6 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2 (d, *J* = 181.4 Hz), 144.2 (d, *J* = 181.7 Hz), 121.4 (t, *J* = 15.4 Hz), 106.1, 104.3 (t, *J* = 22.6 Hz), 82.4, 34.8, 29.7, 28.2, 22.0, 18.5, 13.8, 11.2. IR (thin film) ν_{max} 2944, 2866, 2172, 1502 cm^{-1}. MS (EI): *m/z* (%) 400 (M^+), 401 $[M+H]^+$, 357 (100). HRMS: Calculated for $C_{22}H_{32}F_4Si$: 400.2209; Found: 400.2214.

Gram-Scale Synthesis of 4a. To a septum capped 100 mL of Schlenck tube were added CuOAc (10 mol%), *t*BuOLi (2.4 equiv) under N_2, followed by THF (15 mL). Propargyl phosphate **2a** (4 mmol, 1.0 equiv), pentafluorobenzene (16 mmol, 4.0 equiv) were then added. The tube was screw capped and then conducted on oil bath (preheated to 80 ^oC). After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%) to provide pure **4a** (1.2 g, 75% yield).

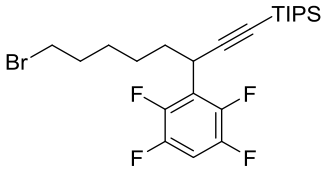


Triethyl(3-(2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4b). 4.0 equiv of fluoroarene was used. The product (193 mg, 90% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (tt, *J* = 9.6, 7.3 Hz, 1H), 4.05 (t, *J* = 7.7 Hz, 1H), 1.99-1.96 (m, 1H), 1.80-1.76 (m, 1H), 1.47-1.43 (m, 1H), 1.39-1.27 (m, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.91-0.85 (m, 4H), 0.58 (q, *J* = 7.9 Hz, 5H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.5 (m, 2F), -142.6 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9 (dm, *J* = 247.6 Hz), 144.5 (dm, *J* = 252.2 Hz), 121.3 (t, *J* = 15.5 Hz), 105.6, 104.3 (t, *J* = 22.6 Hz), 83.5, 34.7, 29.6, 28.2, 22.1, 13.8, 7.3, 4.4. IR (thin film) ν_{max} 2958, 2930, 2173, 1509 cm^{-1}. MS (EI): *m/z* (%) 358 (M^+), 359 $[M+H]^+$, 329 (100). HRMS: Calculated for $C_{19}H_{26}F_4Si$: 358.1740; Found: 358.1740.

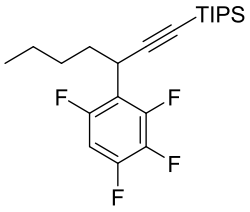


Triisopropyl(5-phenyl-3-(2,3,5,6-tetrafluorophenyl)pent-1-yn-1-yl)silane (4c). 4.0 equiv of fluoroarene was used. The product (223 mg, 83% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21-7.17 (m, 3H), 6.95 (tt, *J* = 9.5 Hz, 7.5 Hz, 1H), 4.10-4.06 (m, 1H), 2.93-2.86 (m, 1H), 2.76-2.69 (m, 1H), 2.35-2.26 (m, 1H), 2.20-2.01 (m, 1H), 1.09-1.06 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

139.3 (m, 2F), -142.4 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.9 (dm, *J* = 247.9 Hz), 144.5 (dm, *J* = 248.0 Hz), 140.7, 128.5, 128.4, 126.2, 121.0 (t, *J* = 15.3 Hz), 105.5, 104.5 (t, *J* = 22.6 Hz), 83.3, 36.6, 33.8, 27.9, 18.6, 11.2. IR (thin film) ν_{max} 3066, 2943, 2177, 1502 cm^{-1}. MS (EI): *m/z* (%) 448 (M^+), 405 (100), 363. HRMS: Calculated for $C_{26}H_{32}F_4Si$: 448.2209; Found: 448.2202.

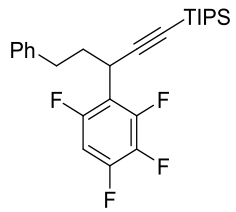


(8-Bromo-3-(2,3,5,6-tetrafluorophenyl)oct-1-yn-1-yl)triisopropylsilane (4d). 20 mol% of CuOAc and 4.0 equiv of fluoroarene were used. The product (215 mg, 73% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (tt, *J* = 9.6, 7.3 Hz, 1H), 4.08 (t, *J* = 7.7 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.05-1.96 (m, 1H), 1.90-1.83 (m, 2H), 1.81-1.74 (m, 1H), 1.61-1.36 (m, 4H), 1.08-1.05(m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.3 (m, 2F), -142.5 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2 (dm, *J* = 183.7 Hz), 144.2 (dm, *J* = 178.9 Hz), 121.1 (t, *J* = 15.4 Hz), 105.7, 104.4 (t, *J* = 22.6 Hz), 82.8, 34.8, 33.5, 32.5, 28.2, 27.5, 26.7, 18.5, 11.2. IR (thin film) ν_{max} 3080, 2943, 2866, 2175, 1503 cm^{-1}. MS (EI): *m/z* (%) 449 $(M\text{-}C_3H_7)^+$, 451, 370. HRMS: Calculated for $C_{20}H_{26}F_4SiBr$: 449.0923; Found: 449.0933.

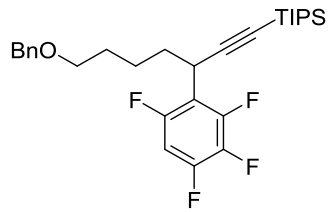


Triisopropyl(3-(2,3,4,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4e). 20 mol% of CuOAc and 4.0 equiv of fluoroarene were used. The product (194 mg, 81% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78-6.72 (m, 1H), 4.01 (t, *J* = 7.7 Hz, 1H), 2.01-1.95 (m, 1H), 1.80-1.73 (m, 1H), 1.54-1.48 (m, 1H), 1.41-1.33 (m, 3H), 1.12-1.00 (m, 21H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9 (t, *J* = 9.9 Hz, 1F), -134.4 (d, *J* = 20.0 Hz, 1F), -134.8 (ddd, *J* = 20.8, 9.3, 5.2 Hz, 1F), -165.2 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9 (dm, *J* = 247.1 Hz), 149.7 (dm, *J* = 246.6 Hz), 149.4 (dm, *J* = 250.0 Hz), 137.3

(dm, *J* = 253.7 Hz), 115.54 (tm, *J* = 17.2 Hz), 106.6, 100.6 (m), 81.9, 34.8, 29.7, 27.7, 22.0, 18.5, 13.8, 11.2. IR (thin film) ν_{max} 2943, 2866, 2173, 1640 cm^{-1}. MS (EI): *m/z* (%) 400 (M^+), 401 $[M+H]^+$, 357 (100). HRMS: Calculated for $C_{22}H_{32}F_4Si$: 400.2209; Found: 400.2212.

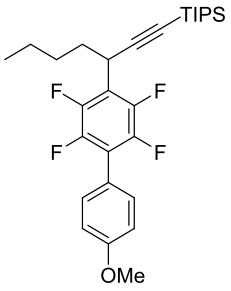


Triisopropyl(5-phenyl-3-(2,3,4,6-tetrafluorophenyl)pent-1-yn-1-yl)silane (4f). 4.0 equiv of fluoroarene was used. The product (188 mg, 70% yield) as a light yellow oil was purified with silica gel chromatography (Petroleum ether/ EtOAc 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.22-7.18 (m, 3H), 6.77-6.70 (m, 1H), 4.03-3.99 (m, 1H), 2.93-2.85 (m, 1H), 2.76-2.68 (m, 1H), 2.33-2.24 (m, 1H), 2.08-1.99 (m, 1H), 1.20 – 0.94 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.6 (t, *J* = 10.3 Hz, 1F), -134.2 (d, *J* = 20.5 Hz, 1F), -134.3 (m, 1F), -165.0 (tdd, *J* = 20.9, 10.9, 6.0 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9 (dm, *J* = 251.9 Hz), 149.6 (dm, *J* = 251.8 Hz), 149.5 (dm, *J* = 249.1 Hz), 140.8, 137.3 (dm, *J* = 243.2 Hz), 128.5, 128.4, 126.1, 115.2 (tm, *J* = 17.2 Hz), 106.1, 100.8 (ddd, *J* = 28.6, 21.1, 3.6 Hz), 82.8, 36.8, 33.8, 27.4, 18.6, 11.3. IR (thin film) ν_{max} 3028, 2943, 2174, 1518 cm^{-1}. MS (EI): *m/z* (%) 448 (M^+), 405 (100), 363. HRMS: Calculated for $C_{26}H_{32}F_4Si$: 448.2209; Found: 448.2206.

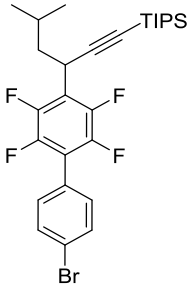


(7-(Benzyloxy)-3-(2,3,4,6-tetrafluorophenyl)hept-1-yn-1-yl)triisopropylsilane (4g). 4.0 equiv of fluoroarene was used. The product (216 mg, 71% yield) as a light yellow oil was purified with silica gel chromatography (Petroleum ether/ EtOAc = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) 7.36-7.31 (m, 4H), 7.30-7.24 (m, 1H), 6.78-6.71 (m, 1H), 4.52-4.40 (m, 2H), 4.02 (t, *J* = 7.6 Hz, 1H), 3.53-3.46 (m,2H), 2.05-1.97 (m, 1H), 1.82 -1.74 (m, 1H), 1.71-1.62 (m, 3H), 1.50-1.43 (m, 1H), 1.10-0.90 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8 (t, *J* = 10.3 Hz), -134.3 (dd, *J* = 20.6, 3.9 Hz), -134.6 (m), -165.1

(tdd, *J* = 21.0, 10.9, 6.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9 (dm, *J* = 247.6 Hz), 149.7 (dm, *J* = 246.1 Hz), 149.4 (dm, *J* = 235.1 Hz), 138.6, 137.3 (dm, *J* = 248.9 Hz), 128.3, 127.6, 127.5, 115.4 (tm, *J* = 19.3 Hz), 106.4, 100.8 (ddd, *J* = 28.8, 21.2, 3.6 Hz), 82.2, 72.9, 70.0, 35.0, 29.1, 27.7, 24.3, 18.5, 11.2. IR (thin film) ν_{max} 2985, 1742, 1654, 1374 cm^{-1}. MS (EI): *m/z* (%) 463 $[M-C_3H_7]^+$, 464, 421. HRMS: Calculated for $C_{26}H_{31}OF_4Si$: 463.2080; Found: 463.2075.

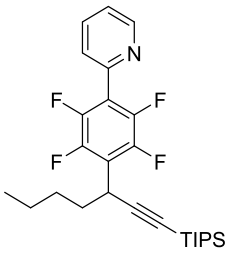


Triisopropyl(3-(2,3,5,6-tetrafluoro-4'-methoxy-[1,1'-biphenyl]-4-yl)hept-1-yn-1-yl)silane (4h). 20 mol% of CuOAc and 3.0 equiv of fluoroarene were used, the reaction was conducted at 100 ºC. The product (246 mg, 81% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / EtOAc = 100:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.03-7.01 (m, 2H), 4.10 (t, *J* = 7.7 Hz, 1H), 3.87 (s, 3H), 2.05-1.98 (m, 1H), 1.85-1.78 (m, 1H), 1.57-1.50 (m, 1H), 1.41-1.36 (m, 3H), 1.10 – 1.04 (m, 21H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -143.2 (dd, *J* = 22.2, 12.2 Hz, 2F), -145.1 (dd, *J* = 22.3, 12.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 145.2 (dm, *J* = 130.1 Hz), 143.3 (dm, *J* = 126.0 Hz), 131.4, 119.6, 118.9, 114.1, 110.0, 106.3, 82.3, 55.3, 34.97, 29.7, 28.2, 22.1, 18.6, 13.9, 11.3. IR (thin film) ν_{max} 3358, 2942, 2865, 2172, 1480 cm^{-1}. MS (DART): *m/z* (%) 507 $[M+H]^+$. HRMS: Calculated for $C_{29}H_{39}F_4OSi$: 507.2701; Found: 507.2702.

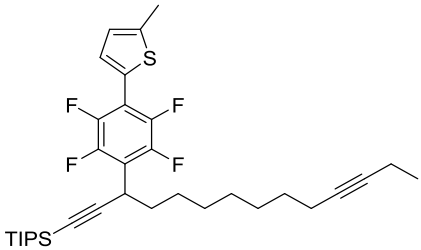


(3-(4'-Bromo-2,3,5,6-tetrafluoro-[1,1'-biphenyl]-4-yl)-5-methylhex-1-yn-1-yl)triisopropylsilane

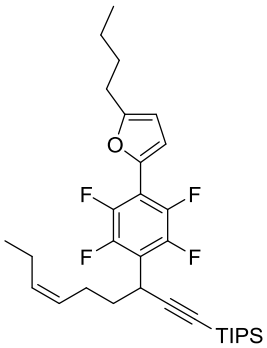
(4i). 3.0 equiv of fluoroarene was used. The product (283 mg, 85% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.20 (t, *J* = 7.9 Hz, 1H), 1.99-1.93 (m, 1H), 1.84-1.76 (m, 1H), 1.67-1.61 (m, 1H), 1.09-1.06 (m, 21H), 0.99 (d, *J* = 6.6, 3H), 0.98 (d, *J* = 6.6, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -142.6 (dd, *J* = 21.9, 12.3 Hz, 2F), -144.5 (dd, *J* = 22.1, 12.3 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3 (dm, *J* = 150.9 Hz), 143.3 (dm, *J* = 148.9 Hz), 131.8, 131.7, 126.4, 123.5, 120.2 (t, *J* = 15.8 Hz), 117.9 (t, *J* = 17.2 Hz), 106.0, 82.5, 44.0, 26.4, 26.2, 22.5, 21.8, 18.5, 11.2. IR (thin film) ν_{max} 2959, 2867, 2173, 1742, 1478 cm^{-1}. MS (DART): *m/z* (%) 554 (M^+), 556. HRMS: Calculated for $C_{28}H_{36}BrF_4Si$: 555.1700; Found: 555.1702.



2-(2,3,5,6-Tetrafluoro-4-(1-(triisopropylsilyl)hept-1-yn-3-yl)phenyl)pyridine (4j). 3.0 equiv of fluoroarene was used. The product (215 mg, 75% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / EtOAc = 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81-8.76 (m, 1H), 7.85-7.80 (m, 1H), 7.55-7.47 (m, 1H), 7.37-7.34 (m, 1H), 4.13 (t, *J* = 7.8 Hz, 1H), 2.05-2.01 (m, 1H), 1.84-1.82 (m, 1H), 1.55-1.51 (m, 1H), 1.42-1.37 (m, 3H), 1.11-1.08 (m, 21H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -142.51 (dd, *J* = 21.8, 12.5 Hz, 2F), -144.67 (dd, *J* = 21.9, 12.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 147.8, 145.4 (dm, *J* = 65.5 Hz), 143.5 (dm, *J* = 67.3 Hz), 136.5, 125.9, 123.5, 120.8 (t, *J* = 15.7 Hz), 118.4 (t, *J* = 16.2 Hz), 106.0, 82.5, 34.9, 29.6, 28.2, 22.1, 18.5, 13.8, 11.2. IR (thin film) ν_{max} 2943, 2865, 2172, 1485, 675 cm^{-1}. MS (DART): *m/z* (%) 478 $[M+H]^+$. HRMS: Calculated for $C_{27}H_{36}F_4NSi$: 478.2548; Found: 478.2546.



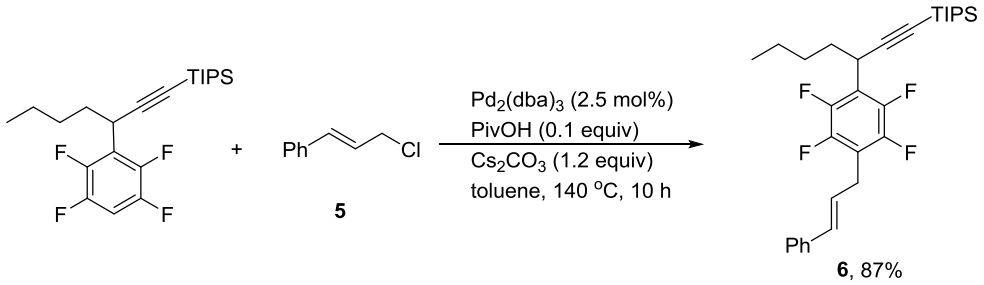
Triisopropyl(3-(2,3,5,6-tetrafluoro-4-(5-methylthiophen-2-yl)phenyl)tetradeca-1,11-diyn-1-yl)silane (4k). 3.0 equiv of fluoroarene was used. The product (283 mg, 80% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / EtOAc = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 4.07 (t, *J* = 7.6 Hz, 1H), 2.55 (s, 3H), 2.19-2.12 (m, 4H), 2.05-1.95 (m, 1H), 1.81-1.75 (m, 1H), 1.56-1.25 (m, 10H), 1.13-0.93 (m, 24H). ^{19}F NMR (376 MHz, $CDCl_3$) -141.4 (dd, *J* = 21.1, 11.2 Hz, 2F), -143.3 (dd, *J* = 21.1, 11.3 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 240.7 Hz), 143.3 (dm, *J* = 248.5 Hz), 142.9 (t, *J* = 4.2 Hz), 130.2 (t, *J* = 6.0 Hz), 125.6, 125.4 (t, *J* = 2.7 Hz), 118.1 (t, *J* = 16.1 Hz), 113.2 (t, *J* = 15.2 Hz), 106.1, 82.4, 81.6, 79.4, 35.2, 29.1, 29.0, 28.9, 28.7, 28.1, 27.5, 18.7, 18.5, 15.1, 14.4, 12.4, 11.2. IR (thin film) ν_{max} 2938, 2864, 2175, 1479 cm^{-1}. MS (DART): *m/z* (%) 591 $[M+H]^+$. HRMS: Calculated for $C_{34}H_{47}F_4SSi$: 591.3098; Found: 591.3099.



(Z)-(3-(4-(5-butylfuran-2-yl)-2,3,5,6-tetrafluorophenyl)non-6-en-1-yn-1-yl)triisopropylsilane (4l). The product (227 mg, 69% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83-6.72 (m, 1H), 6.17 (d, *J* = 3.3 Hz, 1H), 5.46 (dt, *J* = 10.7, 7.2 Hz, 1H), 5.32 (dt, *J* = 10.7, 7.2 Hz, 1H), 4.10 (t, *J* = 7.4 Hz, 1H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.32-2.20 (m, 2H), 2.08-2.05 (m, 3H), 1.83-1.75 (m, 1H), 1.73-1.66 (m, 2H), 1.47-1.37 (m, 2H), 1.08-1.06 (m, 21H), 0.99-0.94 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) -142.7 (dd, *J* = 20.8, 11.5 Hz, 2F), -143.5 (dd, *J* = 20.7, 11.4 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 145.0

(dm, *J* = 247.7 Hz), 142.7 (dm, *J* = 249.5 Hz), 140.4, 133.4, 127.0, 117.8 (t, *J* = 16.0 Hz), 114.6 (t, *J* = 6.3 Hz), 110.0, 107.0, 106.0, 82.6, 35.2, 30.0, 27.8, 27.6, 25.2, 22.2, 20.6, 18.5, 14.3, 13.8, 11.2. IR (thin film) ν_{max} 2960, 2866, 2175, 1486, 787, 678 cm^{-1}. MS (DART): *m/z* (%) 549 $[M+H]^+$. HRMS: Calculated for $C_{32}H_{45}F_4OSi$: 549.3170; Found: 549.3169.

Unsymmetrical Synthesis of Dialkylated Fluoroarenes by Iterative C-H Functionalization of 1,2,4,5-Tetrafluorobenzene

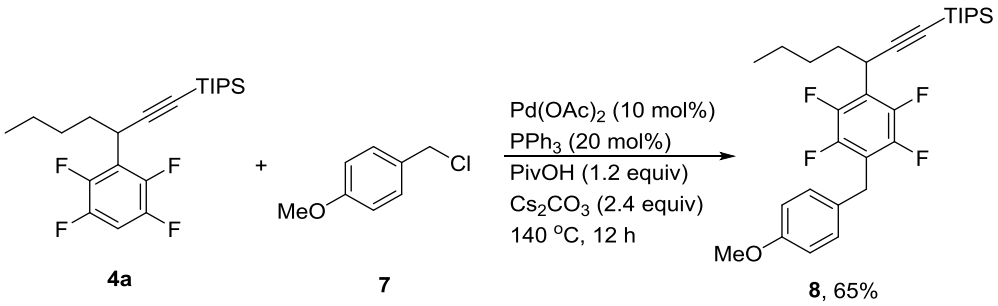


The reaction was conducted according to the literature.[3] To a septum capped 25 mL of Schlenck tube were added $Pd_2(dba)_3$ (2.5 mol%), Cs_2CO_3 (1.2 equiv) under N_2, followed by toluene 2.0 mL, PivOH (0.1 equiv), **4a** (0.43 mmol, 1.5 equiv), **5** (0.23 mmol, 1.0 equiv), the tube was screw capped and heated to 140 °C with an oil bath. After stirring for 10 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to give compound **6** (103 mg, 87% yield) as a yellow oil.

(3-(4-Cinnamyl-2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)triisopropylsilane (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.21 (m, 1H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.27 (dt, *J* = 15.7 Hz, 7.6 Hz, 1H), 4.08 (t, *J* = 7.6 Hz, 1H), 3.62 (d, *J* = 6.4 Hz, 2H), 2.06-1.96 (m, 1H), 1.84-1.75 (m, 1H), 1.55-1.51 (m, 1H), 1.37 (d, *J* = 6.5 Hz, 3H), 1.12-1.02 (m, 21H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.3 (dd, *J* = 21.6, 12.5 Hz, 2F), -145.1 (dd, *J* = 21.7, 12.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8 (dm, *J* = 248.8 Hz), 144.5 (dm, *J* = 243.4 Hz), 136.8, 132.3, 128.5, 127.5, 126.2, 124.7, 118.6 (t, *J* = 15.7 Hz), 116.7 (t, *J* = 18.5 Hz), 106.4, 82.3,

[3] Yu, Y.-B, S Fan, X Zhang. *Chem. Eur. J*., **2012**, *18*, 14643.

35.0, 29.7, 28.1, 26.2, 22.1, 18.6, 13.9, 11.3. IR (thin film) ν_{max} 2998, 2869, 2186, 1513 cm^{-1}. MS (EI): *m/z* (%) 516 (M^+), 517 $[M+H]^+$, 473 (100). HRMS: Calculated for $C_{31}H_{40}F_4Si$: 516.2835; Found: 516.2831.



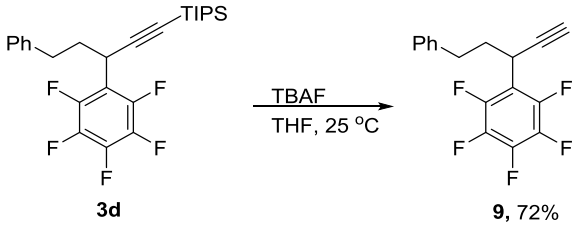
The reaction was conducted according to the literature.[4] To a septum capped 25 mL of Schlenck tube were added $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), Cs_2CO_3 (2.4 equiv) under N_2, followed by toluene 2.0 mL, PivOH (0.1 equiv), **4a** (0.2 mmol, 2.0 equiv), and **7** (0.1 mmol, 1.0 equiv), the tube was screw capped and heated to 140 °C with an oil bath. After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to give compound **8** (34 mg, 65% yield) as a colorless oil.

Triisopropyl(3-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)hept-1-yn-1-yl)silane (8). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.02 (t, *J* = 7.7 Hz, 1H), 3.97 (s, 2H), 3.78 (s, 3H), 1.97-1.91 (m, 1H), 1.77-1.69 (m, 1H), 1.49-1.47 (m, 1H), 1.35-1.33 (m, 3H), 1.09-1.02 (m, 21H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.2 (dd, *J* = 21.7, 12.4 Hz, 2F), -144.8 (dd, *J* = 21.8, 12.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) 158.4, 144.5 (dm, *J* = 244.3 Hz), 129.9, 129.6, 118.5 (t, *J* = 15.4 Hz), 118.2 (t, *J* = 18.7 Hz), 114.1, 106.4, 82.2, 55.2, 34.9, 29.6, 28.0, 27.7, 22.1, 18.5, 13.9, 11.2. IR (thin film) ν_{max} 2984, 2963, 1743, 1242, 1048 cm^{-1}. MS (DART): *m/z* (%) 521 $[M+H]^+$. HRMS: Calculated for $C_{30}H_{41}F_4OSi$: 521.2857; Found: 521.2857.

[4] S Fan, C He, X Zhang. *Chem. Commun*., **2010**, *46*, 4926.

Transformations of Compound 9

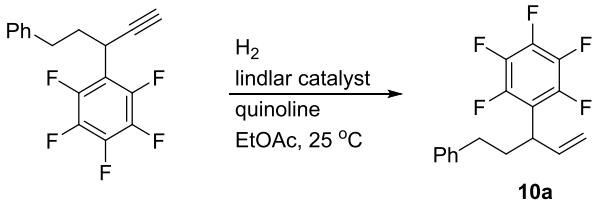
Synthesis of 9



3d **9**, 72%

1,2,3,4,5-Pentafluoro-6-(5-phenylpent-1-yn-3-yl)benzene (9). To a solution of HOAc (17.4 mmol, 2.9 equiv) and TBAF (1.0 M in THF, 13.2 mL 13.2 mmol, 2.2 equiv) in THF (80 mL) was added TIPS protected alkyne **3d** (2.8g, 6 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred for 3h and then quenched with sat.NH_4Cl. The reaction mixture was then diluted with water and extracted with EtOAc. The organic layers were dried over $NaSO_4$, filtered and concentrated. The resulting crude product was purified by flash chromatography (Pentane / EtOAc = 100:1) to afford terminal alkyne **9** (1.34 g, 72% yield) as a white solid (m.p. 31°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.25 (m, 2H), 7.22 - 7.16 (m, 3H), 3.99 (t, *J* = 7.3 Hz, 1H), 2.88-2.81 (m, 1H), 2.73-2.65 (m, 1H), 2.12-2.03 (m, 1H), 2.24 (d, *J* = 2.5 Hz, 1H), 2.07 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.8 (dd, *J* = 21.2, 7.1 Hz, 2F), -155.8 (t, *J* = 21.0 Hz, 1F), -161.9 (td, *J* = 21.6, 7.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 248.9 Hz), 140.4 (dm, *J* = 253.3 Hz), 140.2, 137.6 (d, *J* = 253.1 Hz), 128.5, 128.3, 126.3, 114.6 (td, *J* = 15.9, 4.2 Hz), 81.7, 70.6, 35.9, 33.6, 26.2. IR (KBr disk) ν_{max} 3311, 2962, 1948, 1503 cm^{-1}. MS (EI): *m/z* (%) 310 (M^+), 311 $[M+H]^+$, 105 (100). HRMS: Calculated for $C_{17}H_{11}F_5$: 310.0781; Found: 310.0769.

Synthesis of Compound 10a

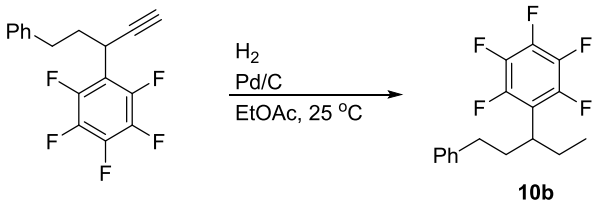


10a

1,2,3,4,5-Pentafluoro-6-(5-phenylpent-1-en-3-yl)benzene (10a). To a solution of **9** (62 mg, 0.2 mmol) in 10 mL of anhydrous EtOAc was added Lindlar catalyst (10 mg), followed by quinoline (10 mg). The reaction mixture was stirred for 0.5 h at room temperature under hydrogen atmosphere. The

reaction mixture was filtrated through a pad of Celite® and concentrated. The resulting crude product was purified by flash chromatography (Pentane) to afford alkene **10a** (53 mg , 85% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 2H), 6.09-6.00 (m, 1H), 5.14-5.10 (m, 2H), 3.76 (q, *J* = 7.8 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.55 – 2.48 (m, 1H), 2.17-2.10 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) -143.0 (dd, *J* = 21.3, 6.7 Hz, 2F), -159.2 (t, *J* = 20.3 Hz, 1F), -164.1 (dt, *J* = 20.9, 7.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (dm, *J* = 246.2 Hz), 141.0, 139.7 (dm, *J* = 257.9 Hz), 137.6 (dm, *J* = 257.7 Hz), 137.5, 128.4, 128.3, 126.1, 116.9, 110.0 (m), 39.7, 34.7, 33.9. IR (thin film) ν_{max} 3086, 2932, 1499, 975 cm^{-1}. MS (EI): *m/z* (%) 312 (M^+), 313 $[M+H]^+$, 105 (100). HRMS: Calculated for $C_{17}H_{13}F_5$: 312.0937; Found: 312.0942.

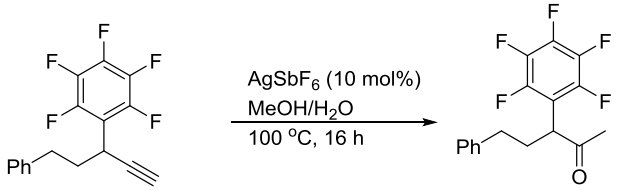
Synthesis of Compound 10b



10b

1,2,3,4,5-Pentafluoro-6-(1-phenylpentan-3-yl)benzene (10b). To a solution of **9** (62 mg, 0.2 mmol) in 10 mL of anhydrous EtOAc was added Pd/C (10 mg). The reaction mixture was stirred for 4 h at room temperature under hydrogen atmosphere. The reaction mixture was filtrated through a pad of Celite® and concentrated. The resulting crude product was purified by flash chromatography (Pentane) to afford alkane **10b** (59 mg , 95% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 7.6, 7.1 Hz, 2H), 7.15 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.08 (d, *J* = 6.9 Hz, 2H), 3.01 (tt, *J* = 9.4, 5.9 Hz, 1H), 2.56-2.42 (m, 2H), 2.11-1.99 (m, 2H), 1.79-1.70 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -142.1 (dd, *J* = 22.5, 7.9 Hz, 2F), -157.6 (t, *J* = 21.0 Hz, 1F), -162.8 (td, *J* = 22.7, 8.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4 (dm, *J* = 245.7 Hz), 141.4, 139.4 (dm, *J* = 238.3 Hz), 137.4 (dm, *J* = 237.9 Hz), 128.3, 128.2, 125.9, 117.6 (tm, *J* = 16.8 Hz), 38.0, 35.1, 34.3, 27.0, 12.3. IR (thin film) ν_{max} 3087, 2933, 1499, 973 cm^{-1}. MS (EI): *m/z* (%) 314 (M^+), 181, 91 (100). HRMS: Calculated for $C_{17}H_{15}F_5$: 314.1094; Found: 314.1091.

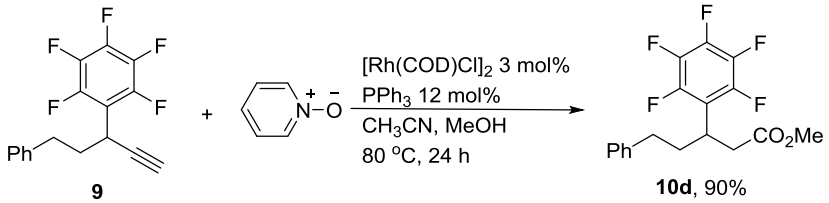
Synthesis of Compound 10c[5]



9 **10c**, 84%

3-(Perfluorophenyl)-5-phenylpentan-2-one (10c). To a septum capped 25 mL of Schlenck tube were added $AgSbF_6$ (0.02 mmol, 10 mol%), **9** (62 mg, 0.2 mmol), MeOH (0.3 mL) and H_2O (30 μL), the tube was screw capped and then heated to 100 °C with an oil bath. After stirring for 16 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 10:1) to product **10c** (55 mg, 84% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.20-7.16 (m, 1H), 7.12-7.10 (m, 2H), 3.90 (dd, *J* = 9.5, 4.4 Hz, 1H), 2.58-2.53 (m, 3H), 2.18-2.10 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) -141.0 (dd, *J* = 21.2, 6.8 Hz, 2F), -154.7 (t, *J* = 20.9 Hz, 1F), -161.4 (qd, *J* = 9.2, 2.4 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 145.2 (dm, *J* = 250.4 Hz), 140.5 (dm, *J* = 254.5 Hz), 140.3, 137.7 (dm, *J* = 253.4 Hz), 128.5, 128.3, 126.3, 112.7 (td, *J* = 16.6 Hz, 4.0 Hz), 48.3, 33.7, 30.3, 28.1. IR (thin film) ν_{max} 3029, 2929, 1727, 1501, 968 cm^{-1}. MS (EI): *m/z* (%) 328 (M^+), 329 $[M+H]^+$, 43 (100). HRMS: Calculated for $C_{17}H_{13}F_5O$: 328.0887; Found: 328.0881.

Synthesis of Compound 10d[6]



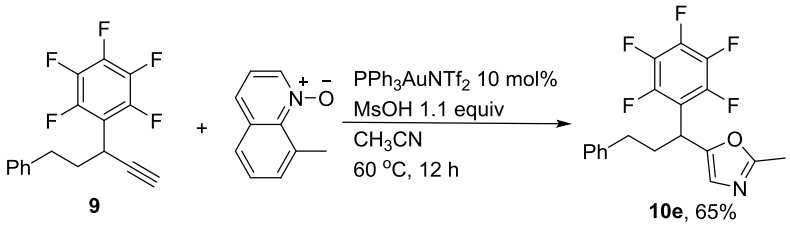
9 **10d**, 90%

Methyl 3-(perfluorophenyl)-5-phenylpentanoate (10d). To a septum capped 25 mL of Schlenck tube were added $[Rh(COD)Cl]_2$ (3mg, 0.006 mmol, 3 mol%), PPh_3 (0.024 mmol, 12 mol%), Pyridine *N*-oxide (0.24 mmol, 1.2 mol equiv), **9** (0.2 mmol, 1.0 equiv), MeOH (1.0 mmol, 5.0 equiv), and CH_3CN

[5] Thuong, M. B. T.; Mann, A.; Wagner, A. *Chem. Commun.* **2012**, *48*, 434–436.
[6] Kim, I.; Lee, C. *Angew. Chem., Int. Ed*. **2013**, *52*, 10023.

(1.5 mL). The tube was screw capped and then heated to 80 °C with an oil bath and. After stirring for 24 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 10:1) to give product **10d** (65 mg, 90% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 3.68-3.60 (m, 4H), 2.79 (d, *J* = 8.1 Hz, 2H), 2.62-2.54 (m, 1H), 2.50-2.43 (m, 1H), 2.16-1.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) -141.8 (dd, *J* = 22.0, 7.1 Hz, 2F), -156.4 (t, *J* = 21.0 Hz, 1F), -162.2 (dt, *J* = 21.9, 7.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 145.3 (dm, *J* = 246.8 Hz), 140.6, 139.9 (dm, *J* = 238.7 Hz), 137.5 (dm, *J* = 250.9 Hz), 128.4, 128.1, 126.1, 116.3 (tm, *J* = 16.2 Hz), 51.8, 38.2, 35.0, 33.9, 32.1. IR (thin film) ν_{max} 3064, 2954, 1742, 1298, 1199 cm^{-1}. MS (EI): *m/z* (%) 358 (M^+), 359 $[M+H]^+$, 91 (100). HRMS: Calculated for $C_{18}H_{15}F_5O_2$: 358.0992; Found: 358.0994.

Synthesis of Compound 10e[7]

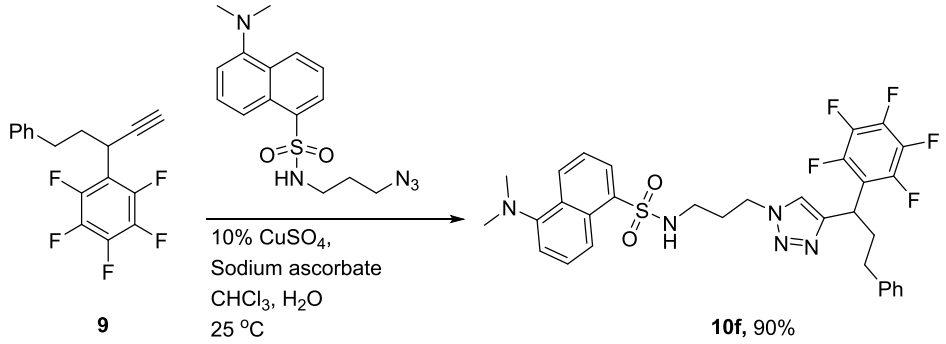


2-Methyl-5-(1-(perfluorophenyl)-3-phenylpropyl)oxazole (10e). To a septum capped 25 mL of Schlenck tube were added PPh_3AuNTf_2 (0.02 mmol, 10 mol%), **9** (0.2 mmol, 1.0 equiv), 8-methylquinoline 1-oxide (0.26 mmol, 1.3 equiv) under N_2, followed by CH_3CN (1.5 mL) and MsOH (0.22 mmol, 1.1 equiv), the tube was screw capped and then heated to 60 °C with an oil bath. After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 5:1) to give product **10e** (48 mg, 65% yield) as a white solid (m.p. 68 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.74 (s, 1H), 4.39 (t, *J* = 7.8 Hz, 1H), 2.67-2.56 (m, 2H), 2.54-2.43 (m, 1H), 2.41-2.37 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.8 (dd, *J* = 21.8, 7.4 Hz, 2F), -155.4 (t, *J* = 21.0

[7] He, W.; Li, C.; Zhang, L. *J. Am. Chem. Soc*. **2011**, *133*, 8482.

Hz, 1F), -161.7 (td, *J* = 21.8, 7.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 150.5, 145.2 (dm, *J* = 248.9 Hz), 140.3 (dm, *J* = 253.9 Hz), 140.2, 137.6 (dm, *J* = 244.1 Hz), 128.5, 128.2, 126.3, 123.1, 114.2 (tm, *J* = 16.8 Hz), 33.7, 32.5, 32.2, 13.93. IR (KBr disk) ν_{max} 3028, 2933, 1739, 1502, 701 cm^{-1}. MS (EI): m/z (%) 367 (M^+), 368 $[M+H]^+$, 105 (100). HRMS: Calculated for $C_{19}H_{14}NOF_5$: 367.0996; Found: 367.0992.

Synthesis of Compound 10f[8]



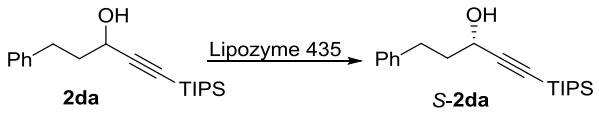
5-(Dimethylamino)-N-(3-(4-(1-(perfluorophenyl)-3-phenylpropyl)-1H-1,2,3-triazol-1-yl)propyl)naphthalene-1-sulfonamide (10f). To a solution of **9** (0.43 mmol, 1.0 equiv) in 3.0 mL of $CHCl_3$ and H_2O (0.2 mL) were added Dans-$(CH_2)_3$-N_3 (0.43 mmol, 1.0 equiv), $CuSO_4$ (0.043 mmol, 0.1 equiv), and sodium ascorbate (0.086 mmol, 0.2 equiv). After stirring for 24 h at room temperature, the mixture was quenched by NH_4Cl (sat.), and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 2:1 to 1:2) to give product **10f** (249 mg, 90% yield) as a yellow solid (m.p. 59 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.24 – 7.20 (m, 2H), 7.16-7.09 (m, 4H), 6.05 (t, *J* = 6.2 Hz, 1H), 4.56 (dd, *J* = 9.1, 6.3 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 2H), 2.83 (s, 8H), 2.69 – 2.31 (m, 4H), 1.99-1.96 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.5 (dd, *J* = 22.3, 7.0 Hz, 2F), -156.3 (t, *J* = 21.1 Hz, 1F), -162.0 (td, *J* = 22.1, 7.4 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 147.8, 145.2 (dm, *J* = 249.8 Hz), 140.6, 140.1 (dm, *J* = 245.7 Hz), 137.6 (dm, *J* = 250.1 Hz) , 134.3, 130.7, 129.9, 129.6, 129.5, 128.6, 128.5, 128.3, 126.2, 123.2, 121.8, 118.4, 115.9 (tm, *J* = 16.3 Hz), 115.3, 47.0, 45.3, 39.8, 34.1, 34.0, 32.6, 30.2. IR (KBr disk) ν_{max} 3289, 3140, 2929, 1654, 1575, 1522, 1500 cm^{-1}. MS (MALDI):

[8] Lewis, W. G.; Magallon, F. G.; Fokin, V. V.; Finn, M. G. *J. Am. Chem. Soc*. **2004**, *126*, 9152.

m/z (%) 643 (M^+), 644 [$(M+H)^+$, 100)]. HRMS: Calculated for $C_{32}H_{30}F_5N_5O_2S$: 644.2113; Found: 644.2103. Anal. Calcd. For $C_{32}H_{30}F_5N_5O_2S$: C, 59.71; H, 4.70; Found: C, 59.47; H, 4.72.

Mechanistic studies

Synthesis of Optically Pure Propargyl Alcohol[9]



(*S*)-5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-ol (*S*-2da). To a solution of 5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-ol (**2da**) 1.93 g (6.1 mmol, 1.0 equiv) in vinyl acetate (12 mL) was added Lipozyme 435 (250 mg). The reaction mixture was heated to 80 ^oC and stirred for 24 h. The reaction was then cooled to room temperature and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 30:1) to give product *S*-**2da** (0.81 g, 42% yield) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.26-7.16 (m, 3H), 5.42 (t, *J* = 6.5 Hz, 1H), 4.41 (t, *J* = 6.5 Hz, 1H), 2.86-2.80 (m, 2H), 2.16-1.95 (m, 2H), 1.24-0.88 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 128.5, 128.5, 126.0, 108.6, 85.9, 62.3, 39.7, 31.6, 18.7, 11.2. IR (thin film) ν_{max} 3355, 2943, 2865, 2169, 1463 cm^{-1}. MS (EI): *m/z* (%) 314 $[M-2H]^+$, 273, 255, 91(100). HRMS: Calculated for $C_{20}H_{30}OSi$: 314.2069; Found: 314.2074. $[\alpha]^{26}_D$ = +26.8 (*c* = 0.95, $CHCl_3$) for a 99% ee sample. Enantiomeric purity was determined by chiral HPLC analysis (Cellulose-1, flow 0.7 mL/min, MeOH/H_2O = 90:10, 214 nm, t_R = 11.406 min (major) and t_R = 13.022 (minor).

Characterization of Absolute Configuration of Propargyl Alcohol *S*-2da by Mosher's Method[10]

To a stirred solution of ***S*-2da** (42 mg, 0.13 mmol) in CH_2Cl_2 (3.0 mL) was added (*S*)-(+)-MTPA-Cl (0.2 mmol, 1.5 equiv), DMAP (0.01 mmol, 0.05 equiv) and NEt_3(0.4 mmol, 2.0 equiv) at room temperature. After the reaction mixture was stirred for 16 h, the solvent was removed. The residue was purified by flash chromatography (EtOAc/pentane = 10:100) to afford the (*R*)-MTPA ester.

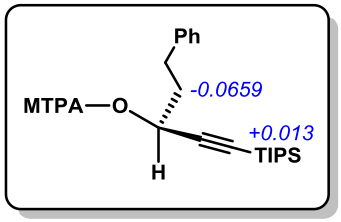
Data for the (*R*)-MTPA ester of *S*-2da: ^1H NMR (400 MHz, CDCl3) δ 7.59-7.51 (m, 2H), 7.44-7.35 (m, 3H), 7.31-7.29 (m, 2H), 7.22 (dd, *J* = 7.7, 6.5 Hz, 1H), 7.18 (dd, *J* = 8.9, 4.3 Hz, 2H), 5.55

[9] X. Zhang; Z. Lu; C. Fu; S. Ma. *Org. Biomol. Chem*. **2009**, *7*, 3258.
[10] Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc*. **1973**, *95*, 512.

(t, *J* = 6.6 Hz, 1H), 3.55 (s, 3H), 2.83-2.78 (m, 2H), 2.27-2.07 (m, 2H), 1.07-1.05 (m, 21H).

Similarly, the (*S*)-MTPA ester was prepared with (*R*)-(-)-MTPA-Cl.

Data for the (*S*)-MTPA ester of *S*-2da: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 2H), 7.45-7.35 (m, 3H), 7.29-7.25 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 2H), 5.57 (t, *J* = 6.5 Hz, 1H), 3.60 (s, 3H), 2.82-2.59 (m, 2H), 2.21-2.01 (m, 2H), 1.09-1.07 (m, 21H).

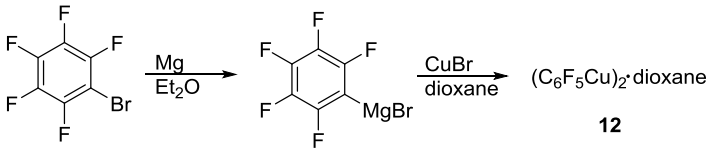


A Δδ ppm ($\Delta\delta_S$-$\Delta\delta_R$) was observed by comparison of ^{1}H -NMR resonances of *S*- and *R*- Mosher ester derivatives. On the basis of the Mosher's conformational model, the configuration of **2da** should be *S*.

Synthesis of *S*-2d[1]

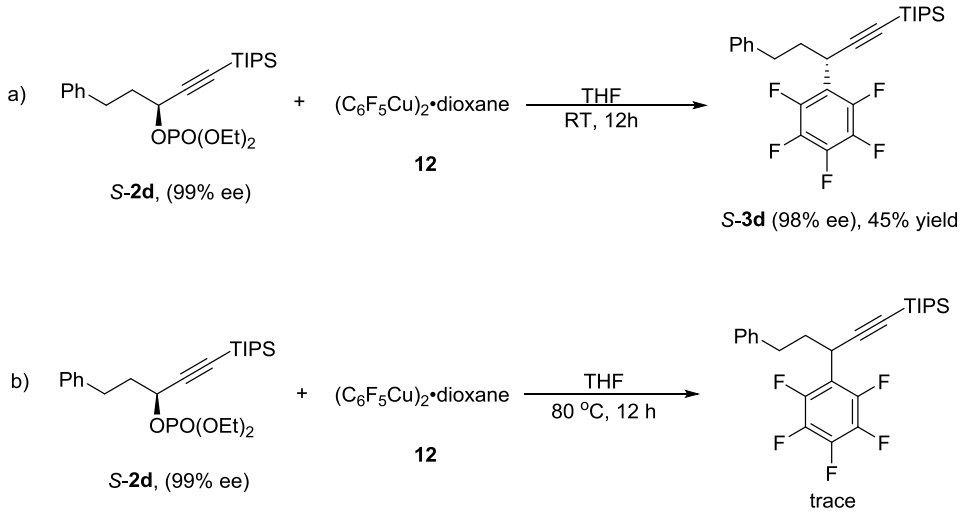
(*S*)-Diethyl (5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl) phosphate (*S*-2d). To a flask were added ***S*-2da** (0.81 g, 4.0 mmol, 1.0 equiv), 4-dimethylaminopyridine (0.4 mmol, 0.1 equiv), anhydrous CH_2Cl_2, and diethylchlorophosphate (5.2 mmol, 1.3 equiv). The resulting mixture was then cooled to 0 ℃ and triethylamine (4.8 mmol, 1.2 equiv) was added. The reaction mixture was allowed to warm to room temperature with stirring. After consumption of the alcohol (TLC monitoring), the mixture was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography (Petroleum ether / EtOAc 3:1) to give product *S*-**2d** (1.35 g, 75% yield) as a colorless oil. *S*-**2d**: $[\alpha]^{26}_D$ = -8.9 (*c* = 1.2, $CHCl_3$) for a 99% ee sample. Enantiomeric purity was determined by chiral HPLC analysis (ID3, flow 0.7 mL/min, Hexane:*i*-PrOH = 98:2, 214 nm, t_R = 11.48 min (major) and t_R = 13.35 (minor).

Synthesis of Complex C_6F_5H·dioxane[11]



To a three-necked, round-bottomed flask fitted with a condenser bearing a nitrogen inlet were charged with magnesium turnings (1.1 g, 46 mmol, 1.0 equiv), Et_2O 37 mL, and a few iodine seed. Then 1-bromo-2,3,4,5,6-pentafluorobenzene (46 mmol, 1.0 equiv) was added dropwise at a rate that maintains a gentle reflux. The reflux is maintained for another 1 h by heating at 35 °. The resulting black solution is cooled to room temperature, and 92 mmol (2.0 equiv) of powdered and anhydrous copper(I) bromide (92 mmol, 2.0 equiv) was added in three intervals. The brown mixture is stirred for 30 minutes, 20 mL of Et_2O is added, and the mixture heated at reflux for another 30 minutes. After the mixture was cooled to room temperature, Et_2O (80 mL) and dioxane (20 mL) was added carefully and stirred for another 0.5 h at room temperature. The supernatant was transferred to a Schlenck flask by double-point needles with an attached nitrogen atmosphere. The solution was evaporated to dryness under reduced pressure with an oil bath at 40 °, and the pale-yellow solid **12** (2.74 g, 22% yield) was obtained. Compound **12** is known.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 8H), ^{19}F NMR (376 MHz, $CDCl_3$) -102.9 (m, 2F), -140.4 (t, *J* = 20 Hz, 1F), -156.8 (m, 2F).

Scheme S1. Scheme Reaction of Complex $(C_6F_5Cu)_2$·dioxane 12 with *S*-2d



11 Cairncross, A.; Sheppard, W. A.; Wonchoba, E.; Guildford, W. J.; House, C. B.; Coates, R. M. *Org. Synth.* **1980**, *59*, 122.

To a septum capped 25 mL of Schlenck tube were added $(C_6F_5Cu)_2$·dioxane (164 mg, 0.3 mmol, 0.5 equiv), under N_2, followed by THF (2.0 mL) and *S*-**2d** (0.6 mmol, 2.0 equiv), the tube was screw capped and the reaction was stirred at room temperature or at 80 °C. After stirring for 12 h, the reaction mixture was cooled to room temperature and the yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. If necessary, the mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, concentrated and purified with silica gel chromatography.

When the reaction was conducted at 80 °C, only trace amount of **3d** was obtained due to the decomposition of copper complex **12**.

However, when the reaction was conducted at room temperature, *S*-**3d** was obtained. The product **(**125.8 mg, 45% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / EtOAc 50:1). *S*-**3d**: $[\alpha]^{26}_D$ = +0.15 (*c* = 1.0, $CHCl_3$) for a 98% ee sample. Enantiomeric purity was determined by chiral HPLC analysis (Cellulose-1, flow 0.7 mL/min, CH_3CN:H_2O = 80:20, 214 nm, t_R = 11.406 min (major) and t_R = 13.022 (minor).

The absolute configuration of *S*-**3d** was characterized by X-ray crystallographic analysis (Figure S1). The crystal of *S*-**3d** was obtained by recrystallization from *n*-pentane and methanol at room temperature.

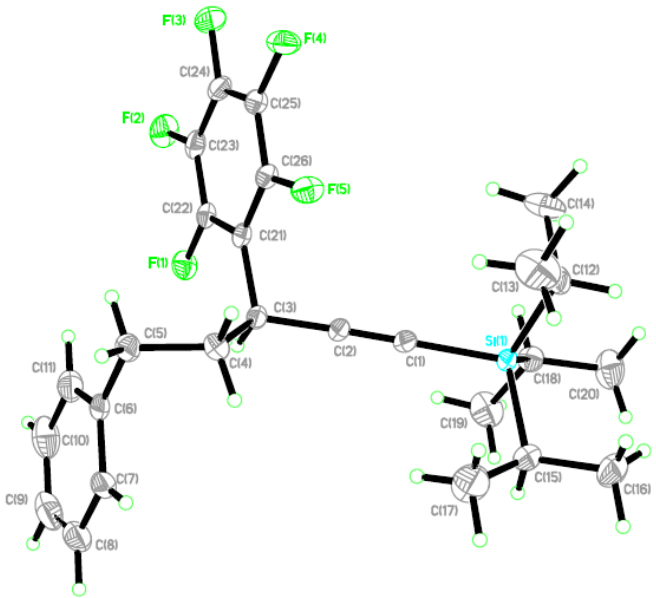
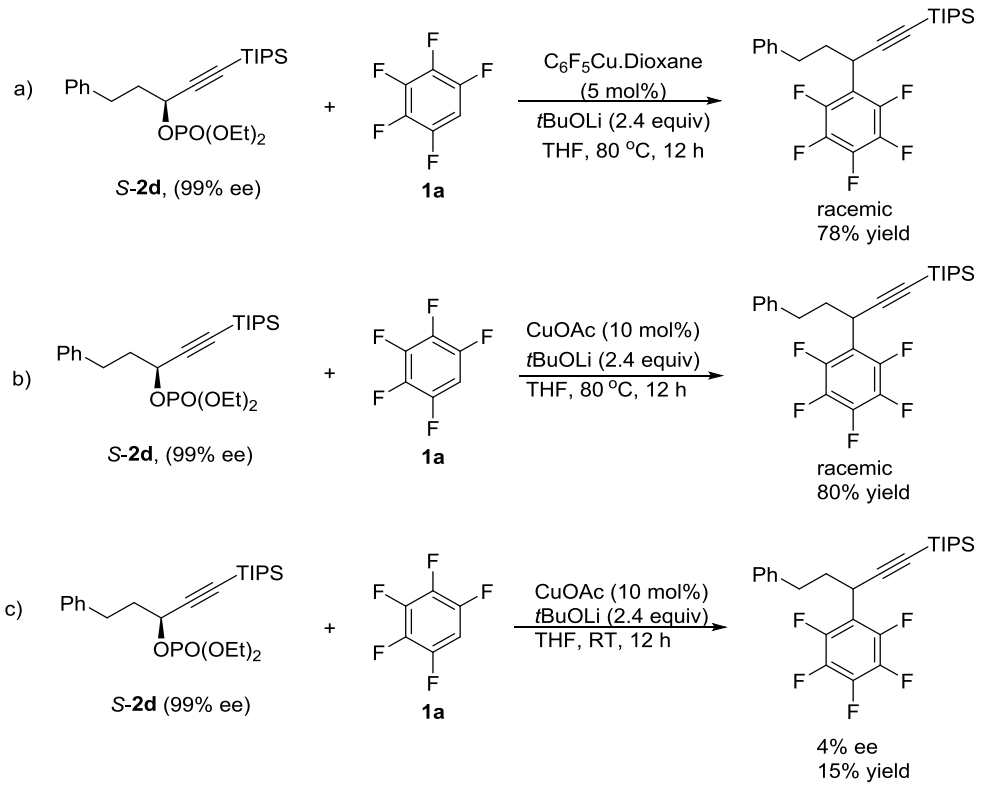


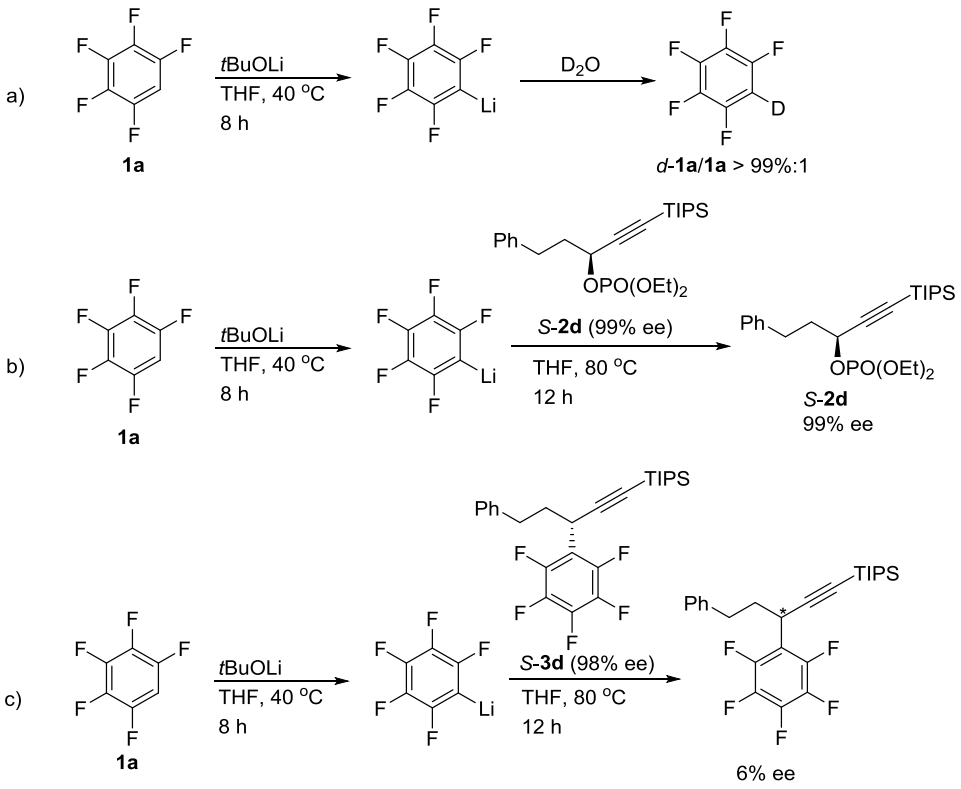
Figure S1. X-Ray Crystal Structure of Compound *S*-**3d**

Scheme S2. Reaction of *S*-2d with 1a catalyzed by [Cu]



To a septum capped 25 mL of Schlenck tube were added CuOAc (0.06 mmol, 10 mol%) or $(C_6F_5Cu)_2$·dioxane (0.03 mmol, 5 mol%), and *t*BuOLi (1.44 mmol 2.4 equiv) under N_2, followed by THF (2.0 mL), ***S*-2d** (0.6 mmol, 1.0 equiv), and C_6F_5H (1.8 mmol 3.0 equiv). The tube was screw capped and the reaction was performed at 80 °C or room temperature. After stirring for 12 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered, concentrated and purified with silica gel chromatography.

Scheme S3. Reaction of C_6F_5Li with *S*-2d or *S*-3d



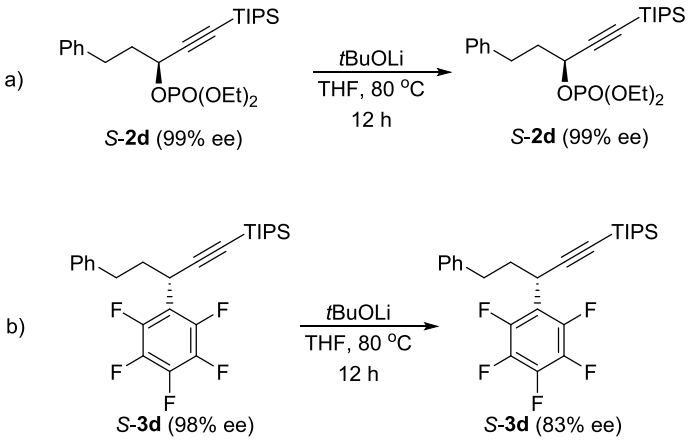
Preparation of C_6F_5Li (Scheme S3a)

To a septum capped 25 mL of Schlenck tube were added *t*BuOLi (1.44 mmol 2.4 equiv), C_6F_5H (1.8 mmol 3.0 equiv), and THF (2.0 mL) under N_2, the tube was screw capped and the reaction was heated to 40 °C with stirring for 8 h. The formation of C_6F_5Li was confirmed by deuteration of C_6F_5Li with D_2O (2.0 equiv), in which 99% yield of C_6F_5D was provided, suggesting that C_6F_5Li was formed.

Reaction of C_6F_5Li with *S*-2d or *S*-3d (Scheme S3b-c)

To a septum capped 25 mL of Schlenck tube were added *t*BuOLi (1.44 mmol 2.4 equiv), C_6F_5H (1.8 mmol 3.0 equiv), and THF (2.0 mL) under N_2, the tube was screw capped and the reaction was stirred at 40 °C for 2 h. The resulting solution was then cooled to room temperature, *S*-**2d** (0.6 mmol, 1.0 equiv) or *S*-**3d** (0.6 mmol, 1.0 equiv) was added. After the reaction mixture was stirred at 80 °C for 12 h, the reaction was cooled to room temperature and the resulting sample was used for the ee determination.

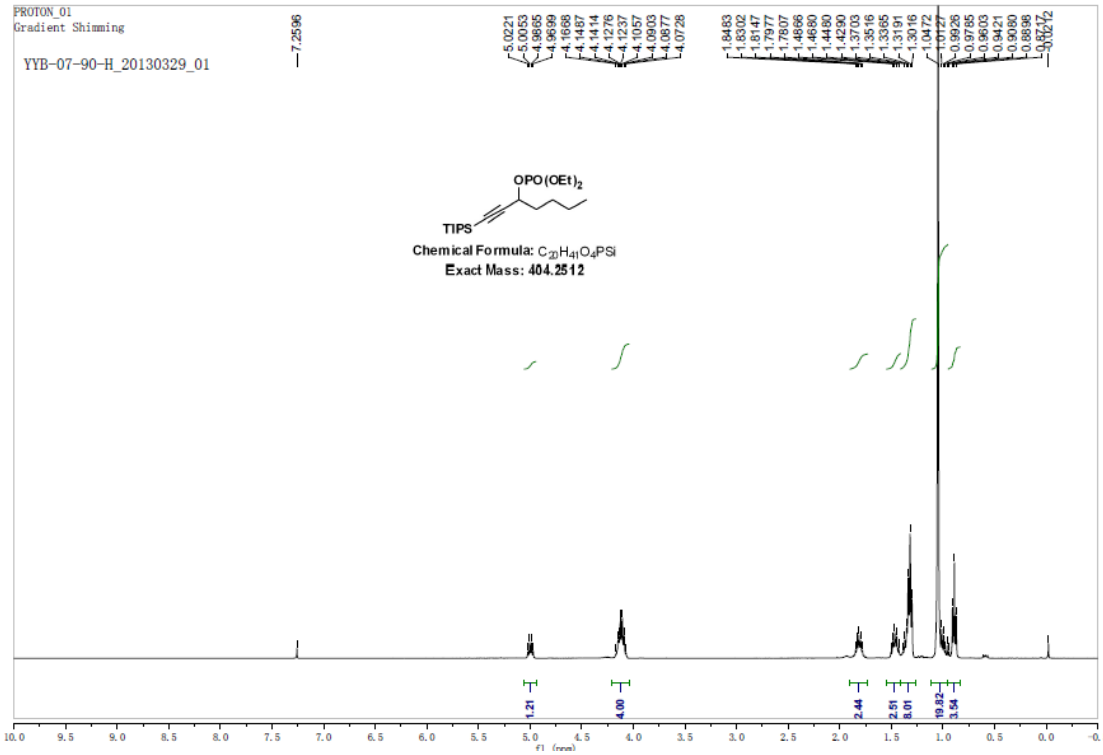
Scheme S4. Reaction of *t*BuOLi with *S*-2d or *S*-3d

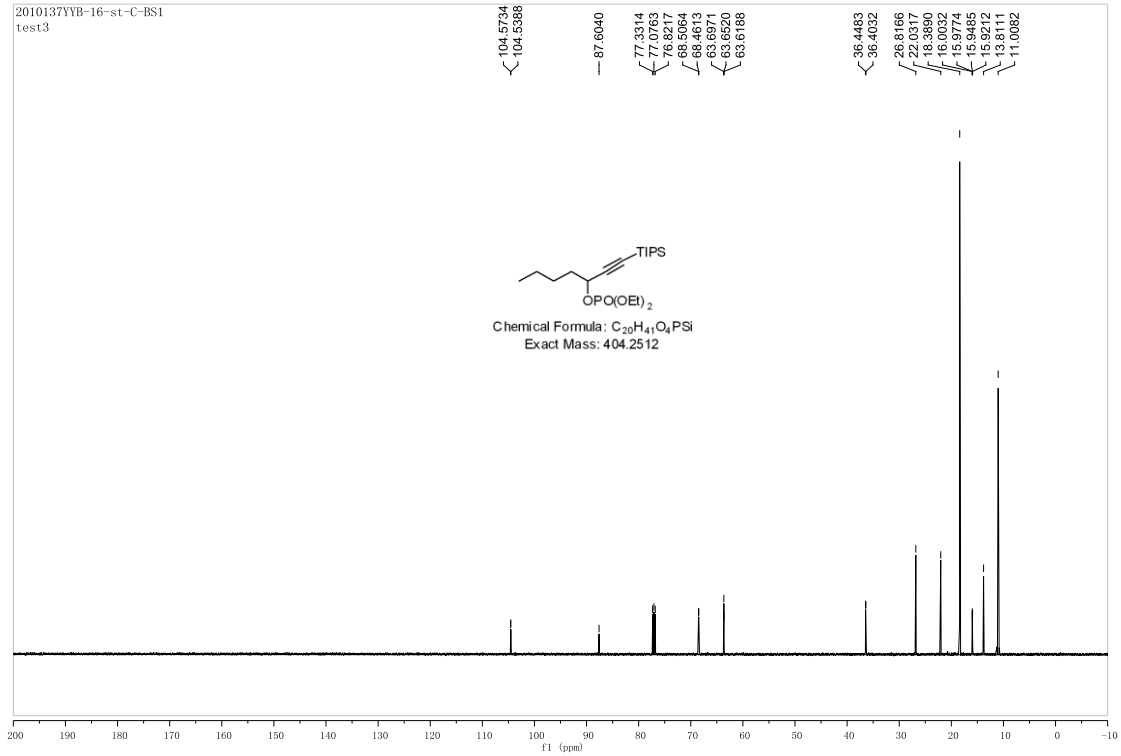


Procedure：

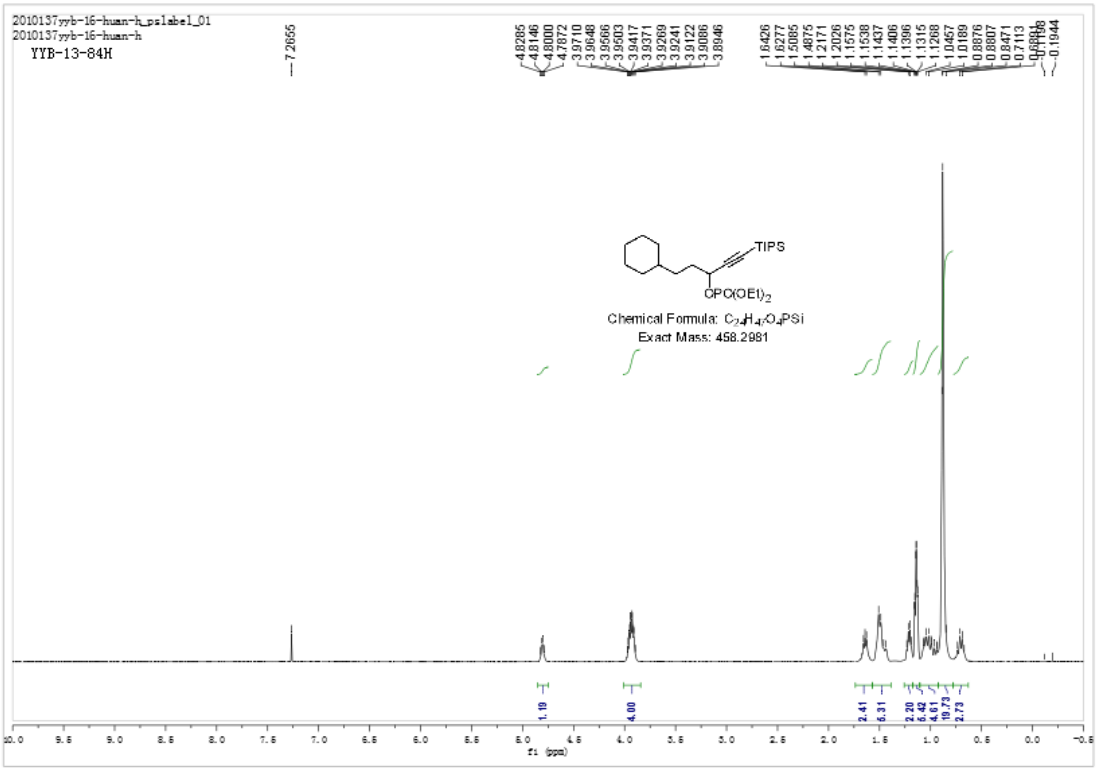
To a septum capped 25 mL of Schlenck tube were added *t*BuOLi (0.1 mmol, 1.0 equiv), *S*-**2d** or *S*-**3d** (0.1 mmol, 1.0 equiv) and THF (2.0 mL) under N_2. The tube was screw capped and the reaction was heated to 80 ^oC with stirring for 12 h. The reaction was then cooled to room temperature and the resulting sample was used for the ee determination.

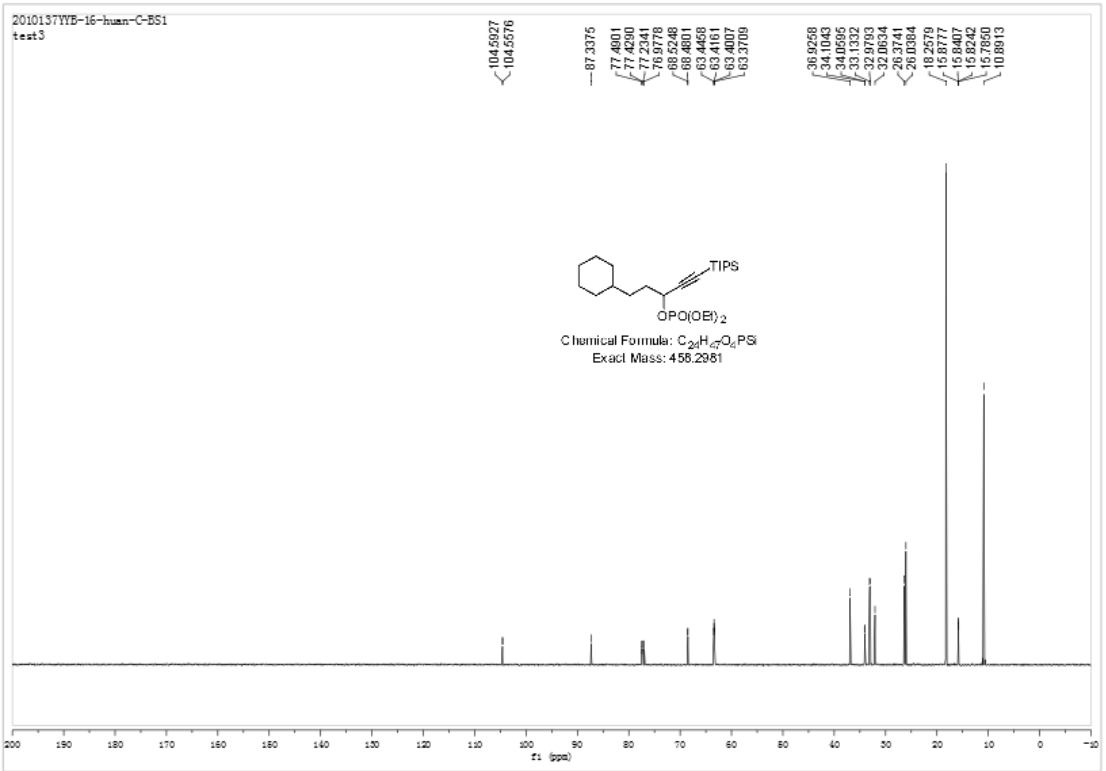
Diethyl (1-(triisopropylsilyl)hept-1-yn-3-yl) phosphate (2a)



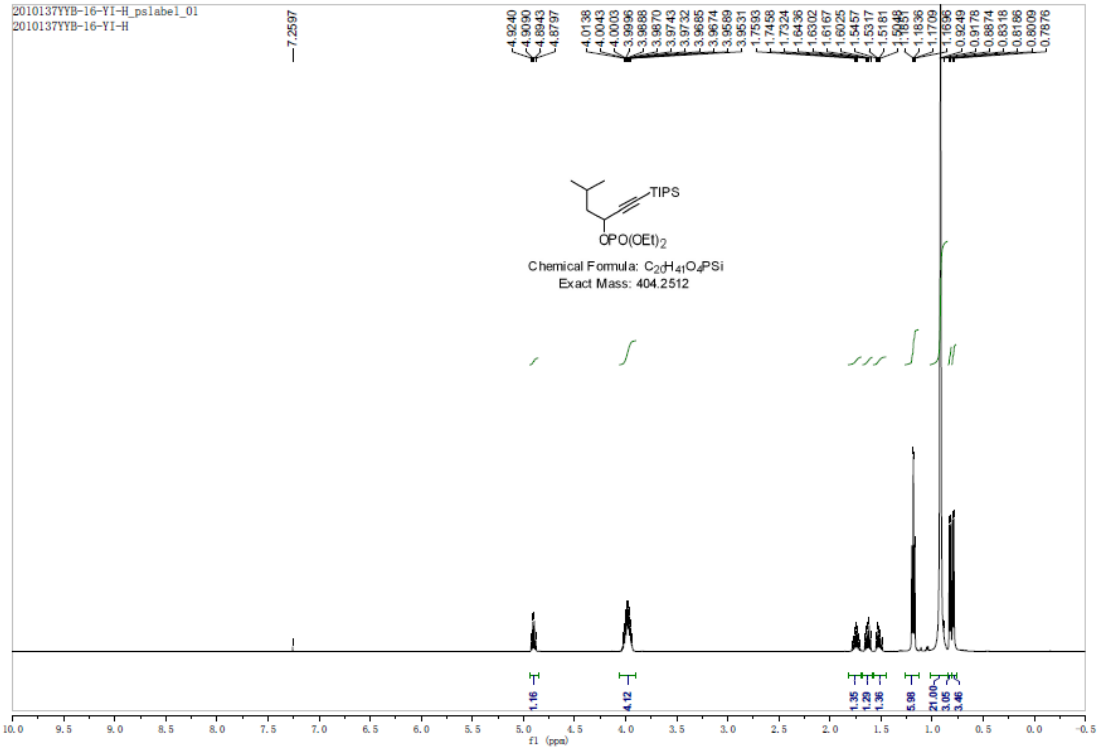


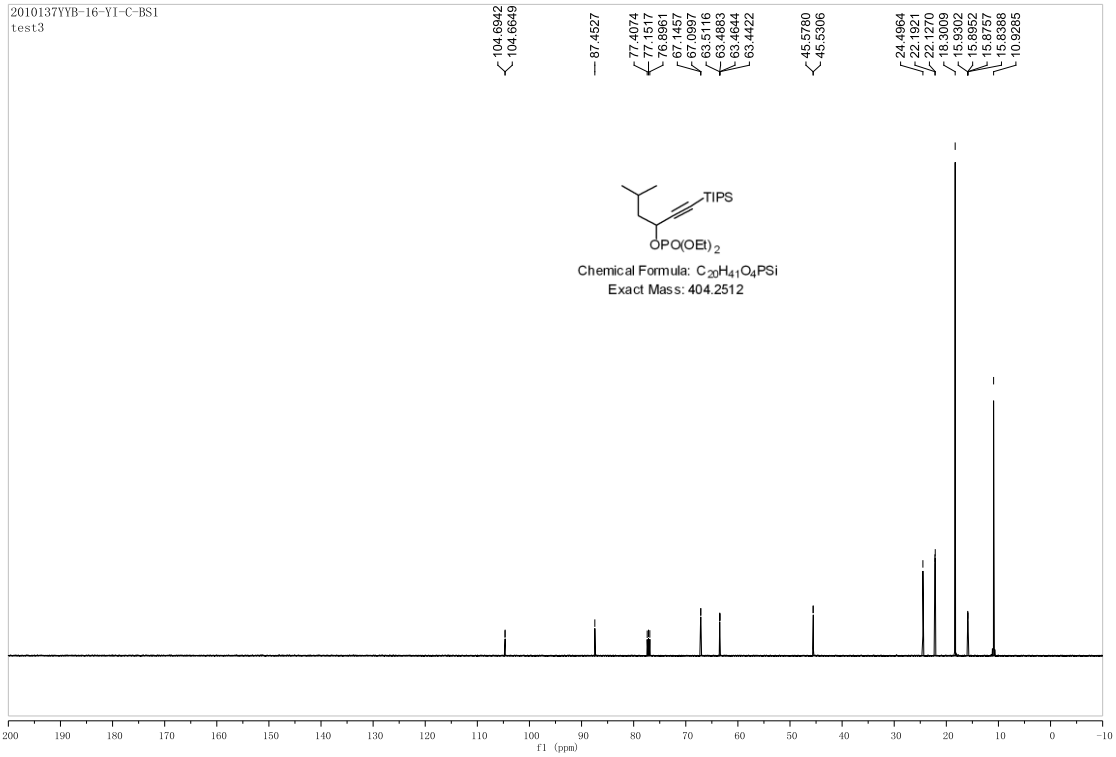
5-Cyclohexyl-1-(triisopropylsilyl)pent-1-yn-3-yl diethyl phosphate (2b)



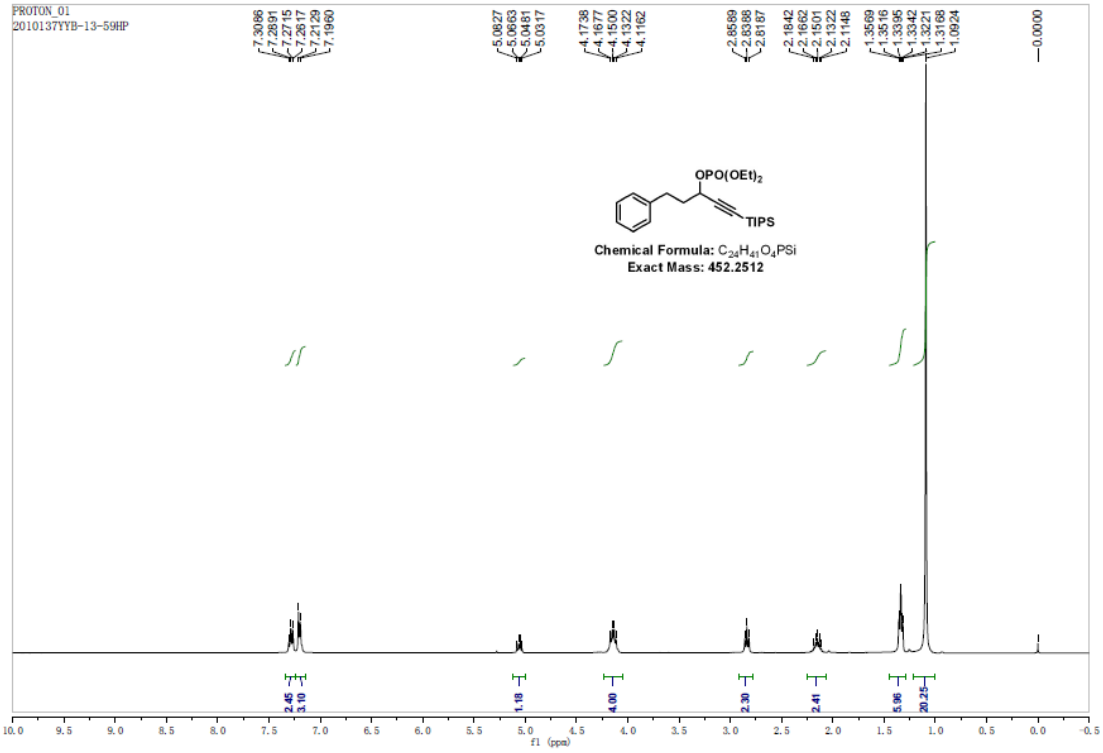


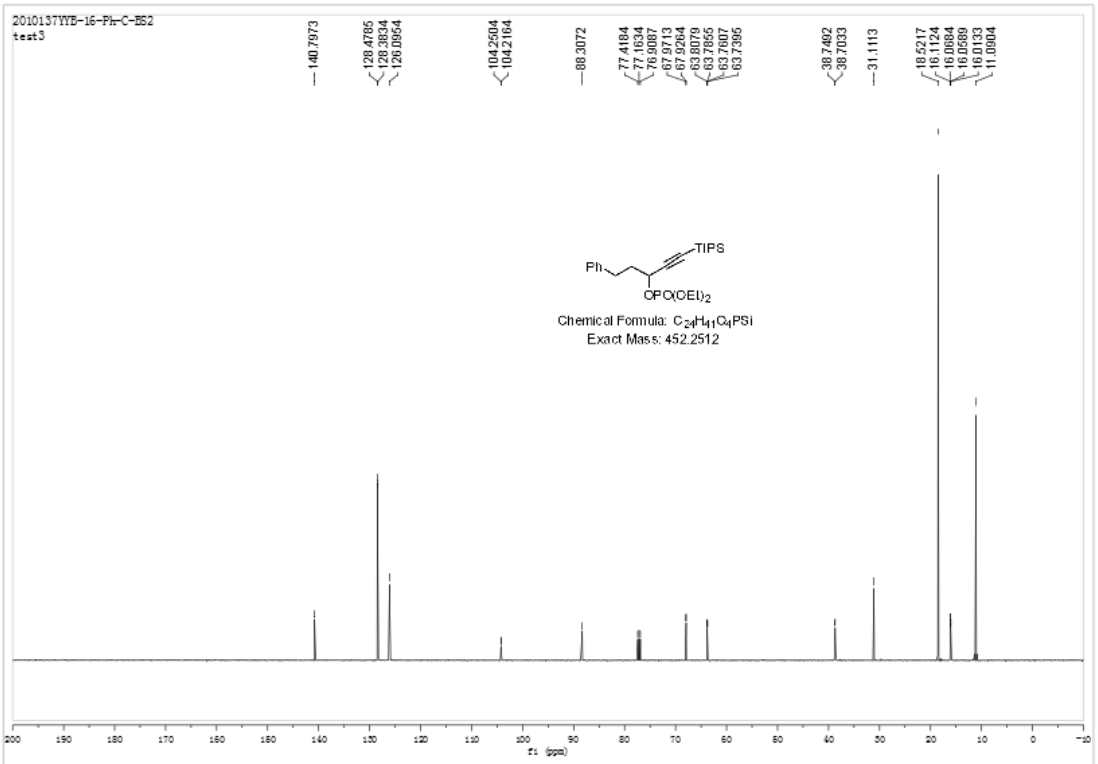
Diethyl (5-methyl-1-(triisopropylsilyl)hex-1-yn-3-yl) phosphate (2c)



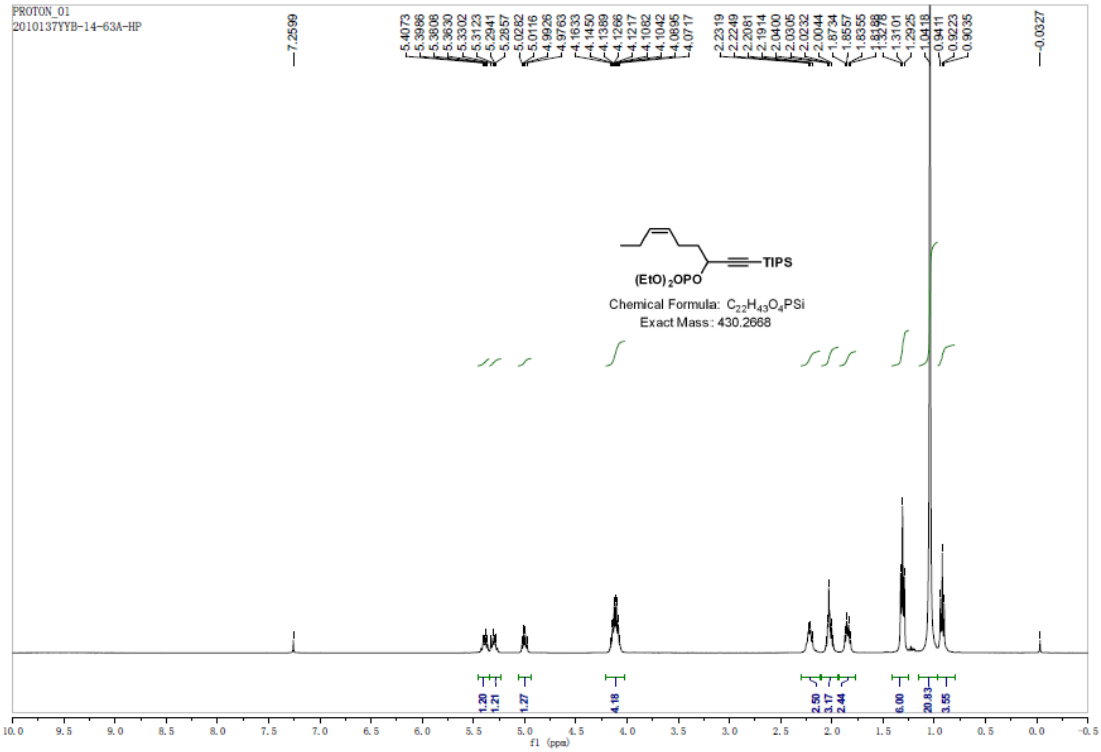


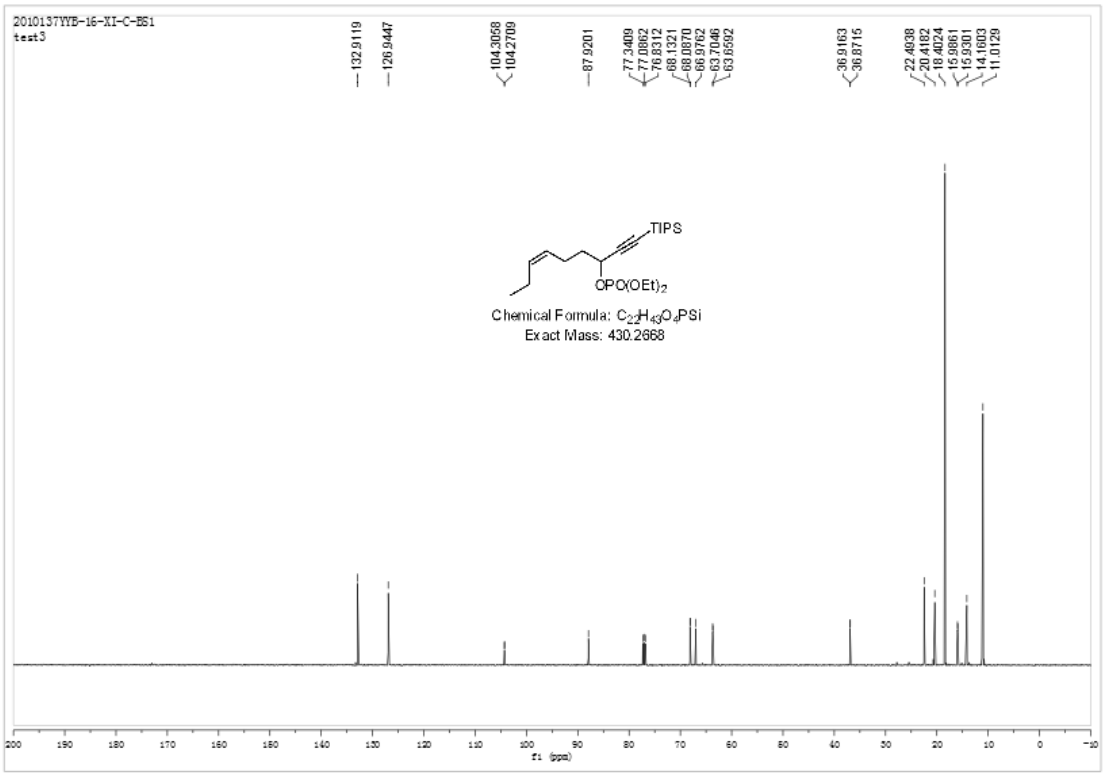
Diethyl (5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-yl) phosphate (2d)



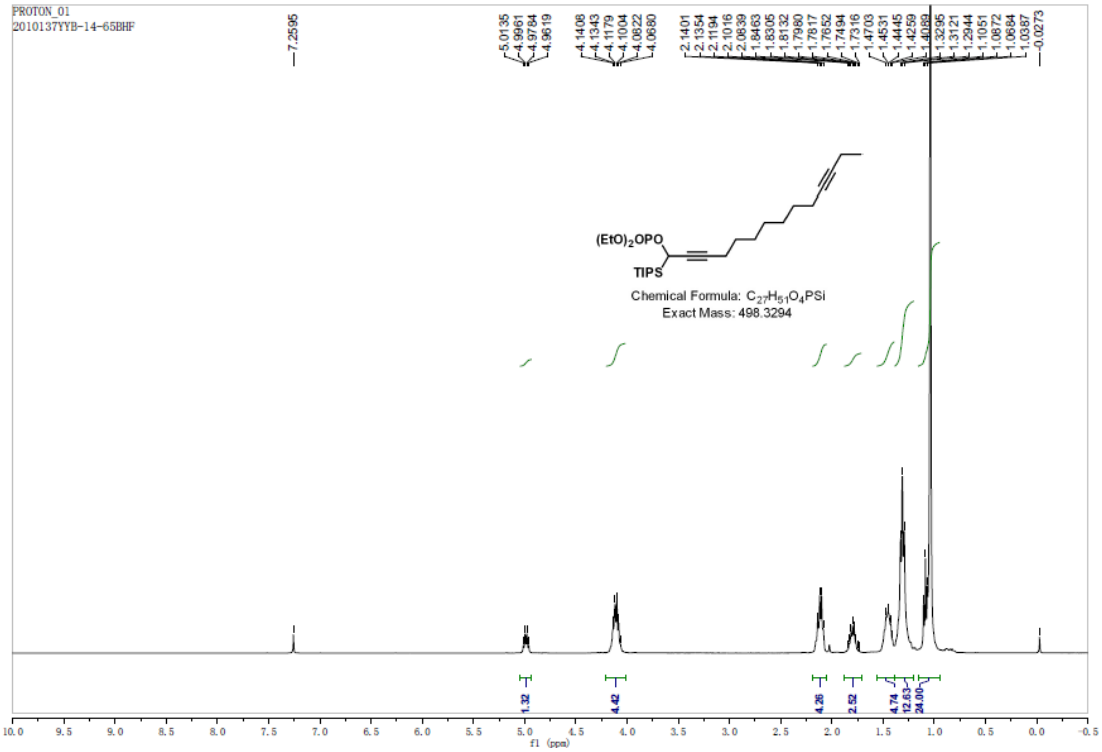


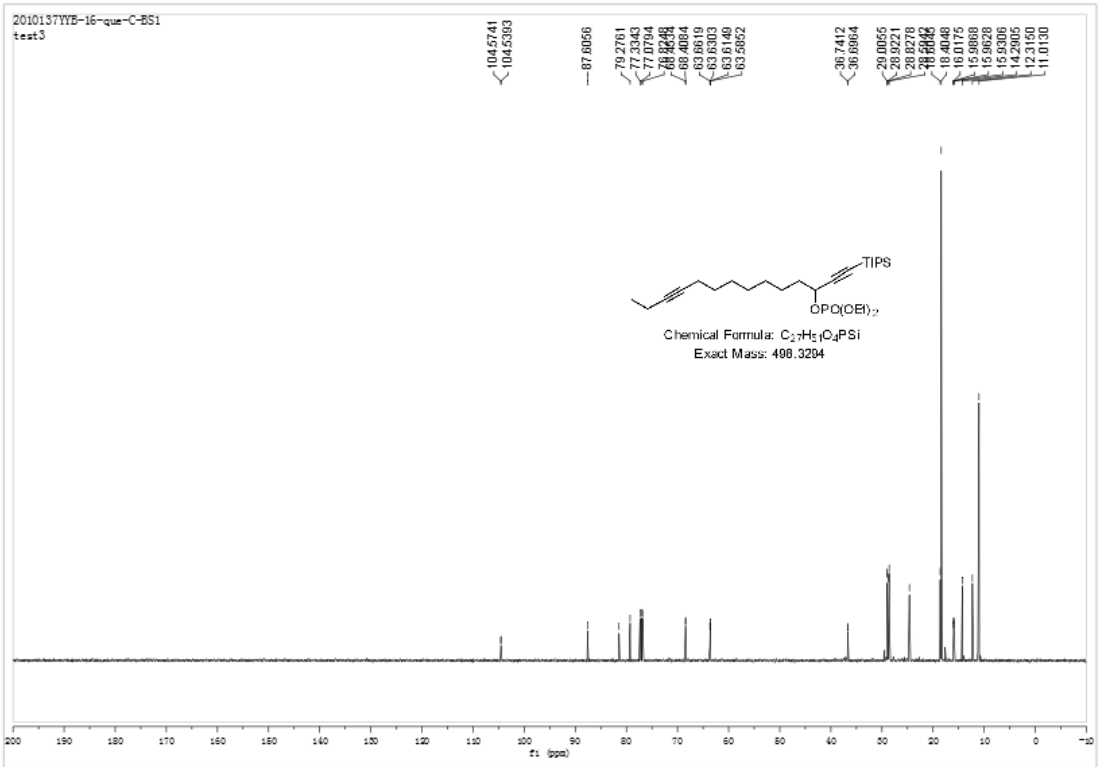
(*Z*)-Diethyl (1-(triisopropylsilyl)non-6-en-1-yn-3-yl) phosphate (2e)



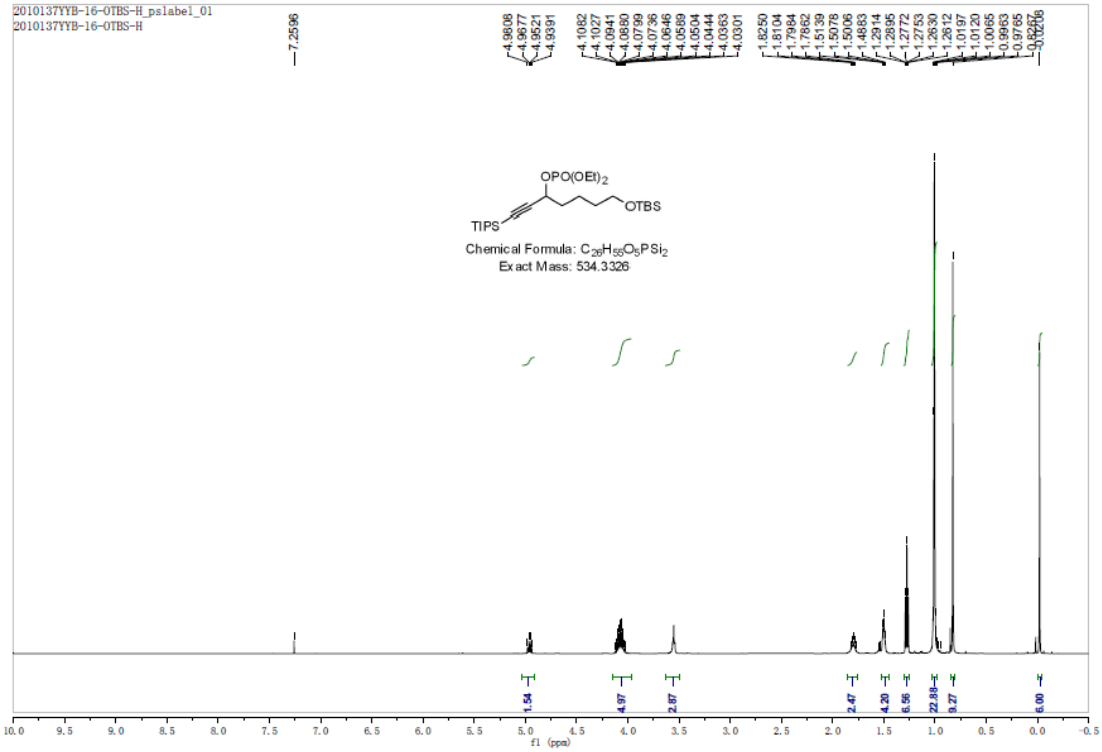


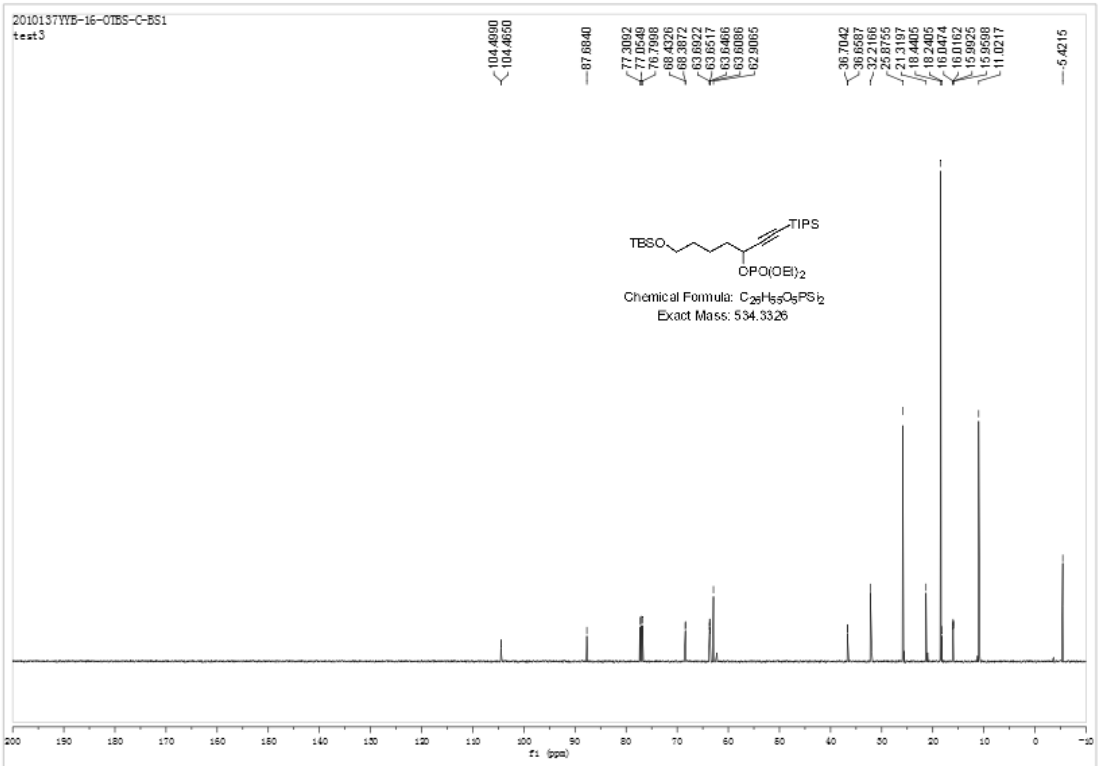
Diethyl (1-(triisopropylsilyl)tetradeca-1,11-diyn-3-yl) phosphate (2f)



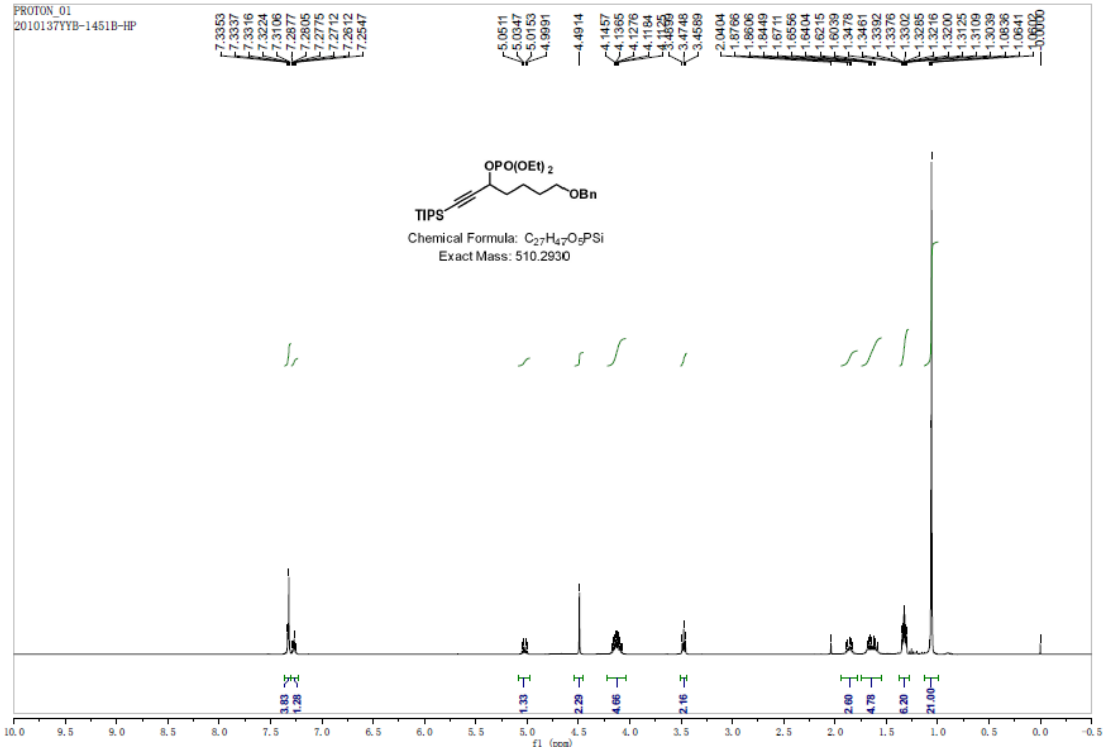


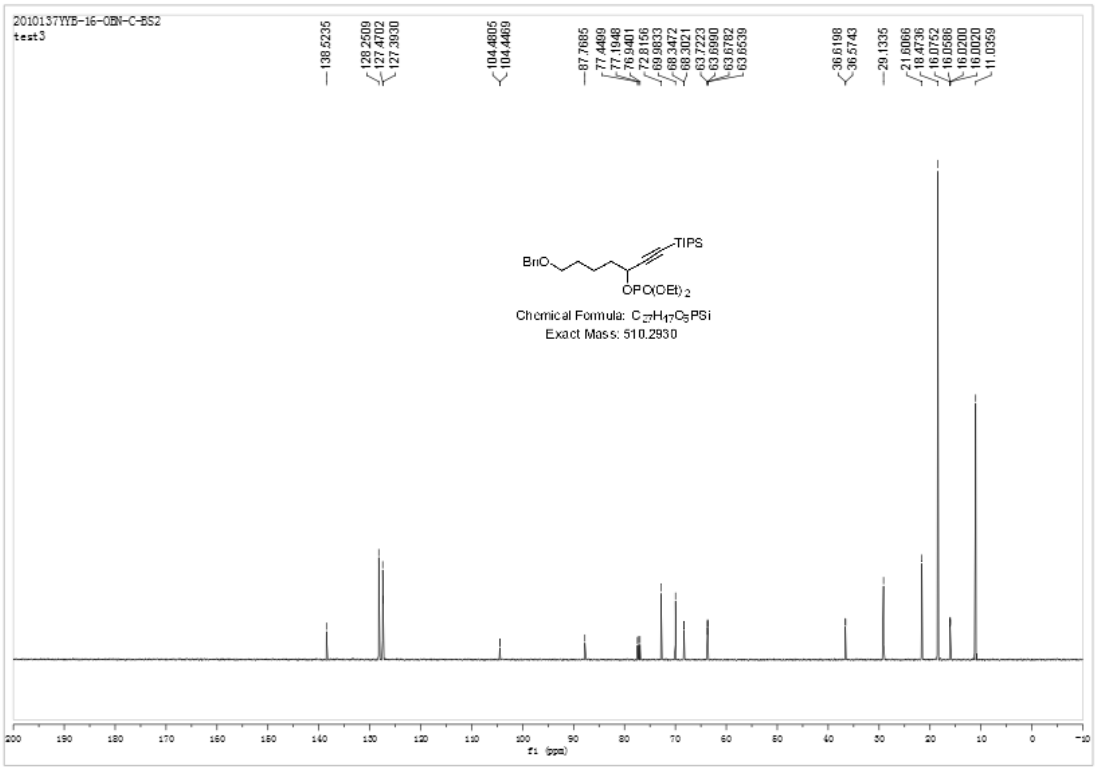
7-((*tert*-Butyldimethylsilyl)oxy)-1-(triisopropylsilyl)hept-1-yn-3-yl diethyl phosphate (2g)



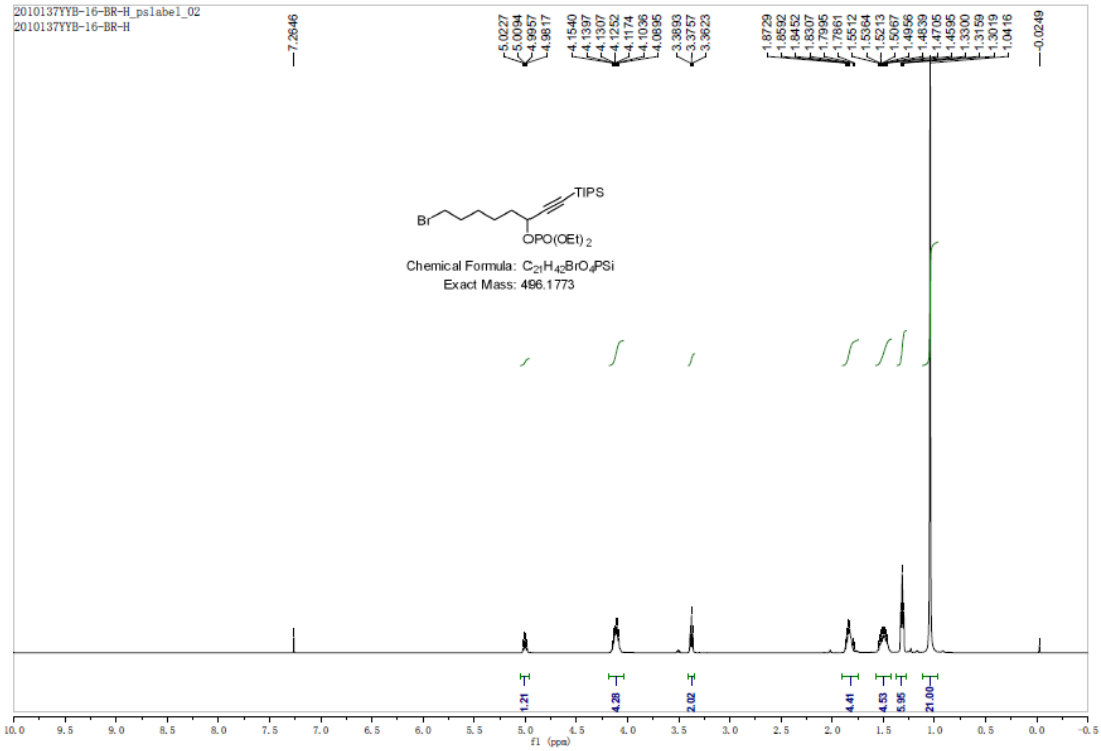


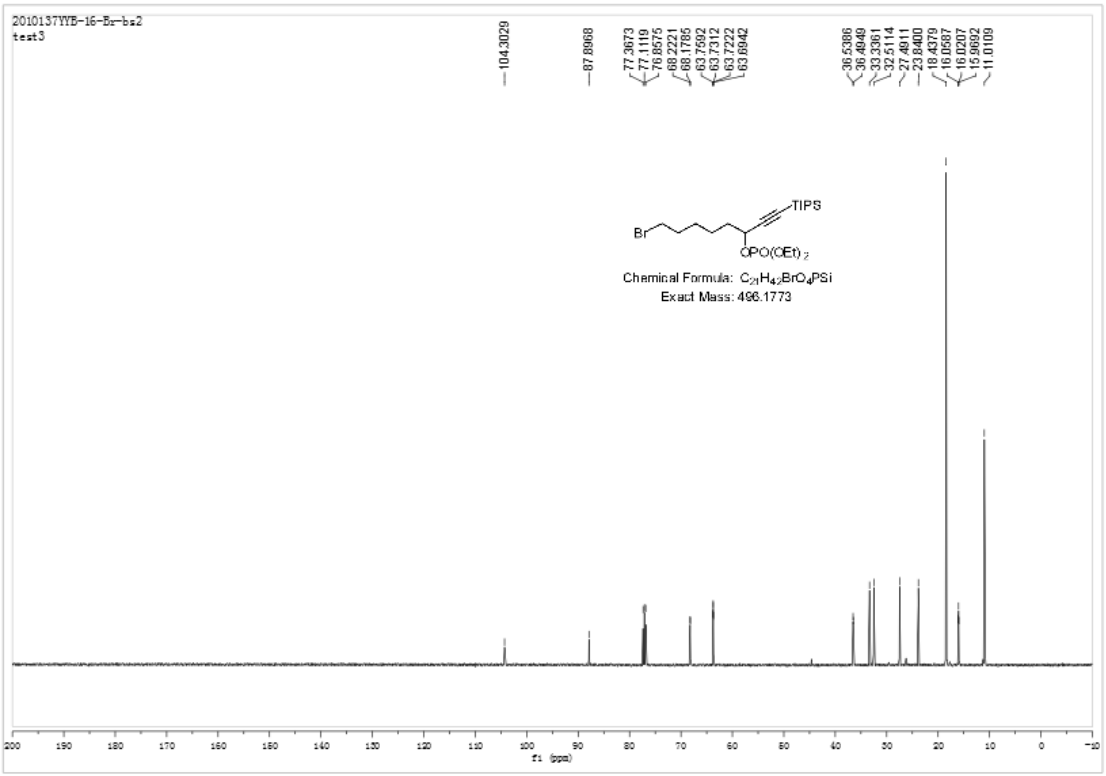
7-(Benzyloxy)-1-(triisopropylsilyl)hept-1-yn-3-yl diethyl phosphate (2h)



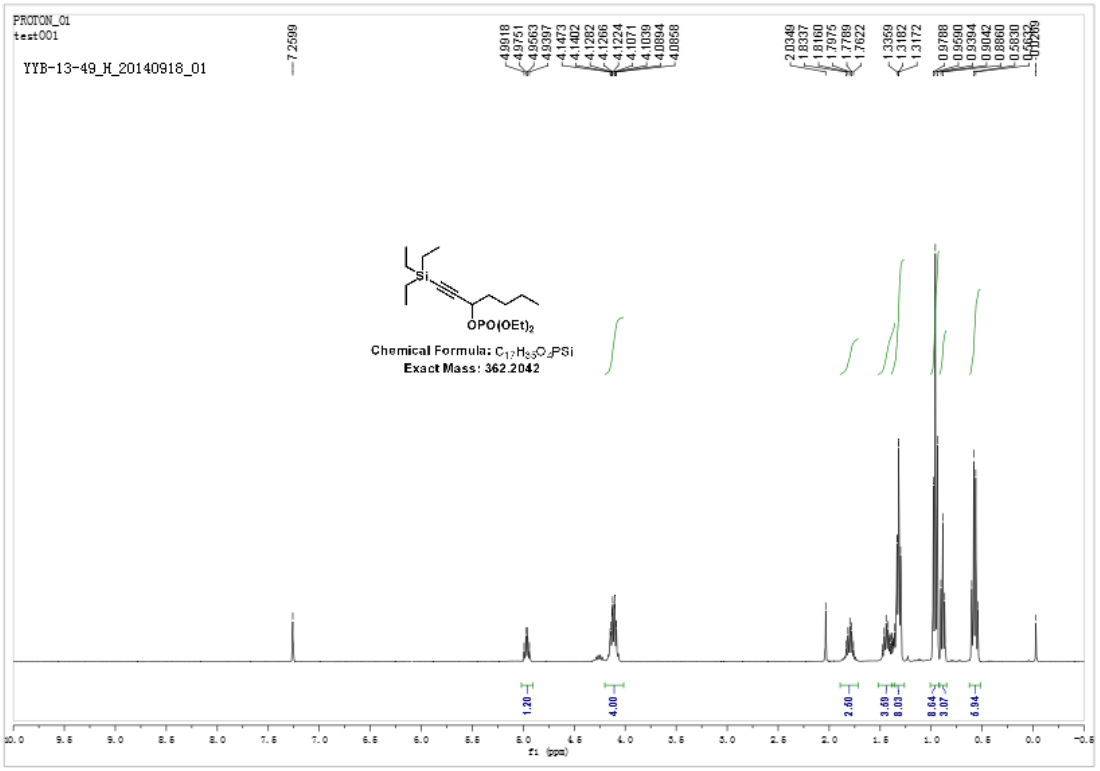


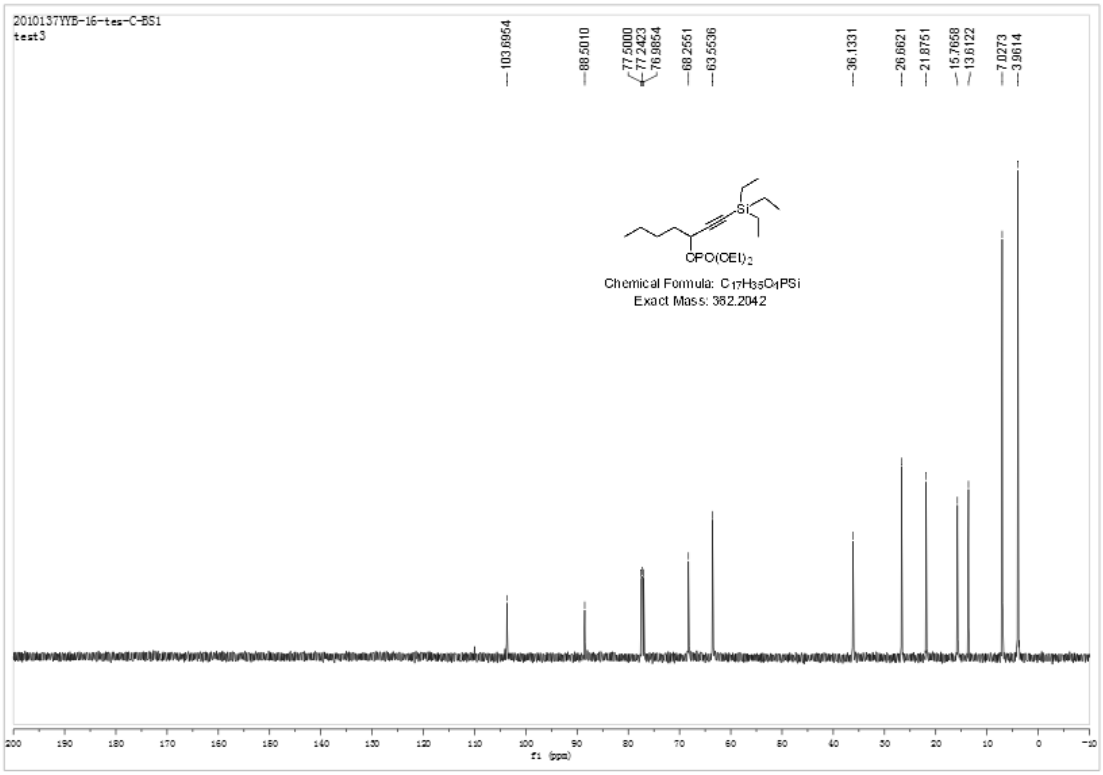
8-Bromo-1-(triisopropylsilyl)oct-1-yn-3-yl diethyl phosphate (2i)



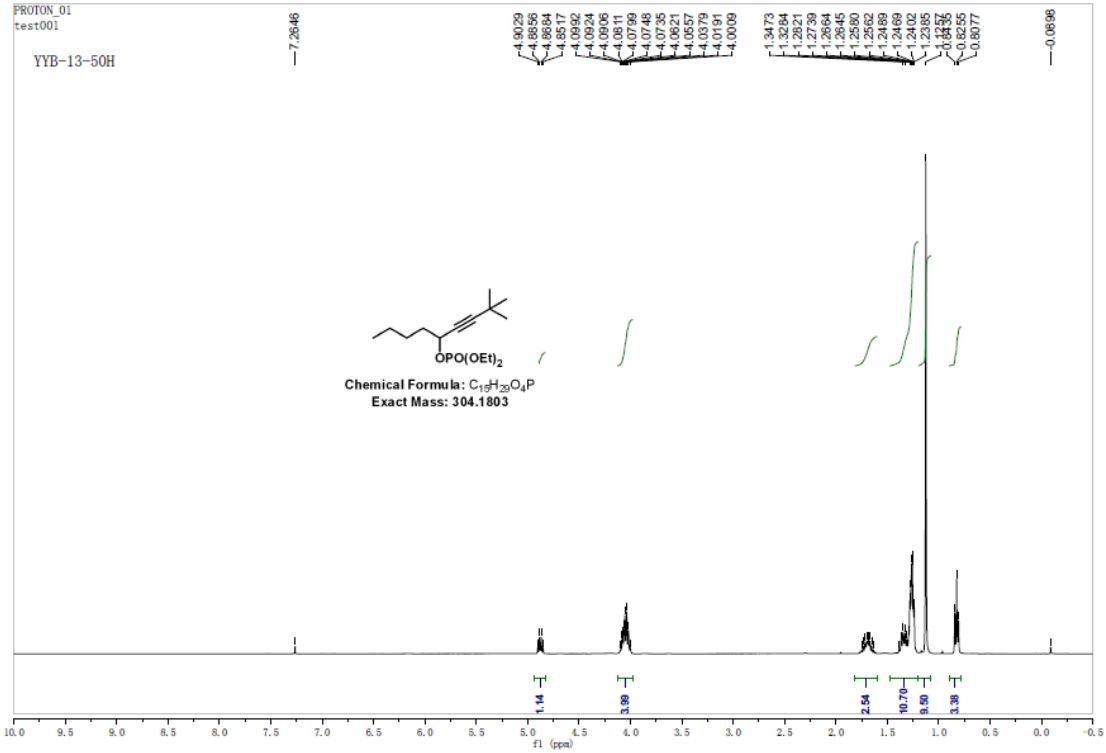


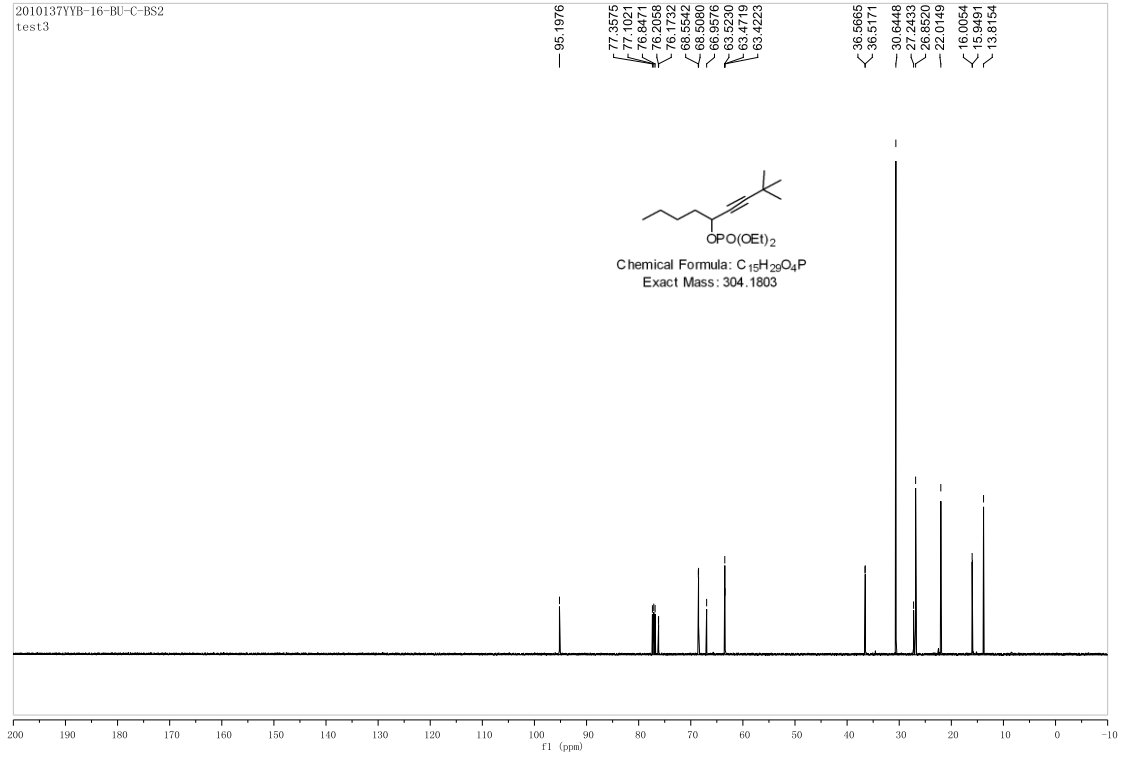
Diethyl (1-(triethylsilyl)hept-1-yn-3-yl) phosphate (2j)



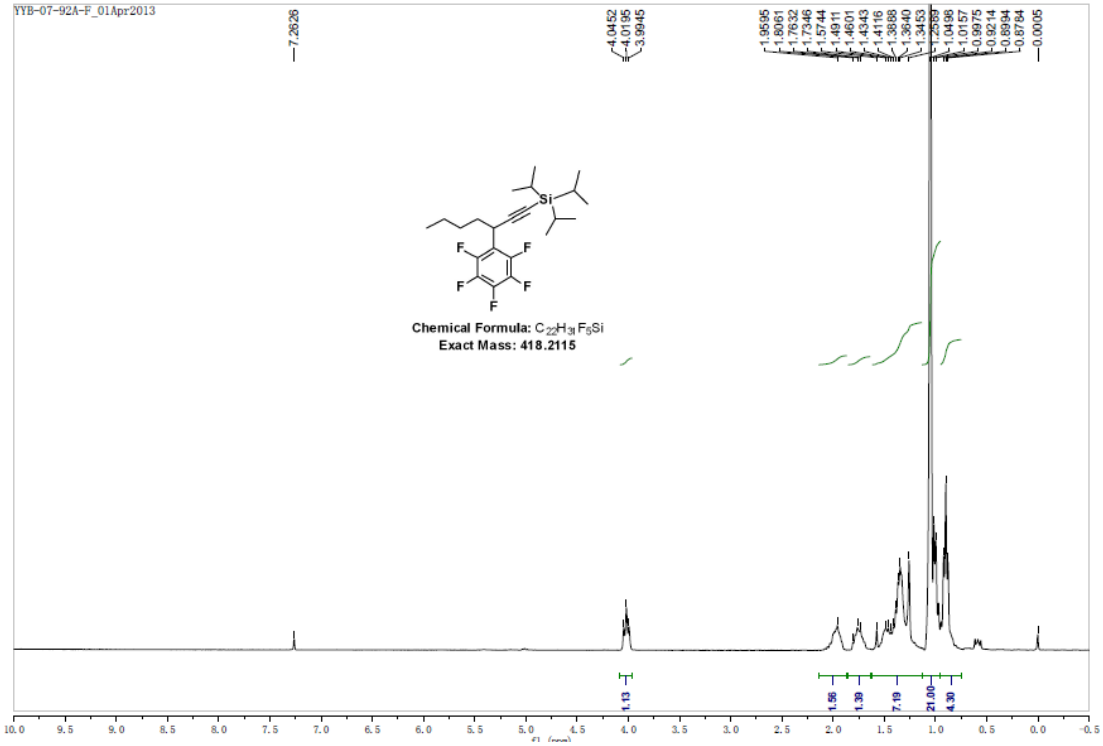


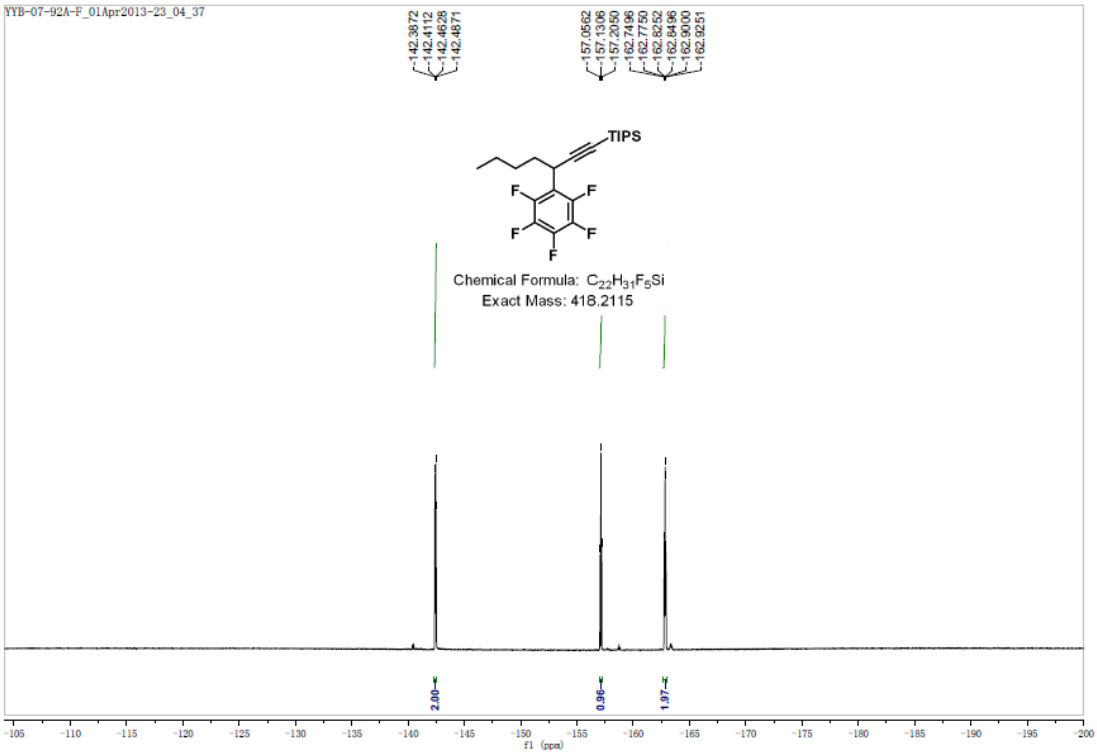
2,2-Dimethylnon-3-yn-5-yl diethyl phosphate (2k)

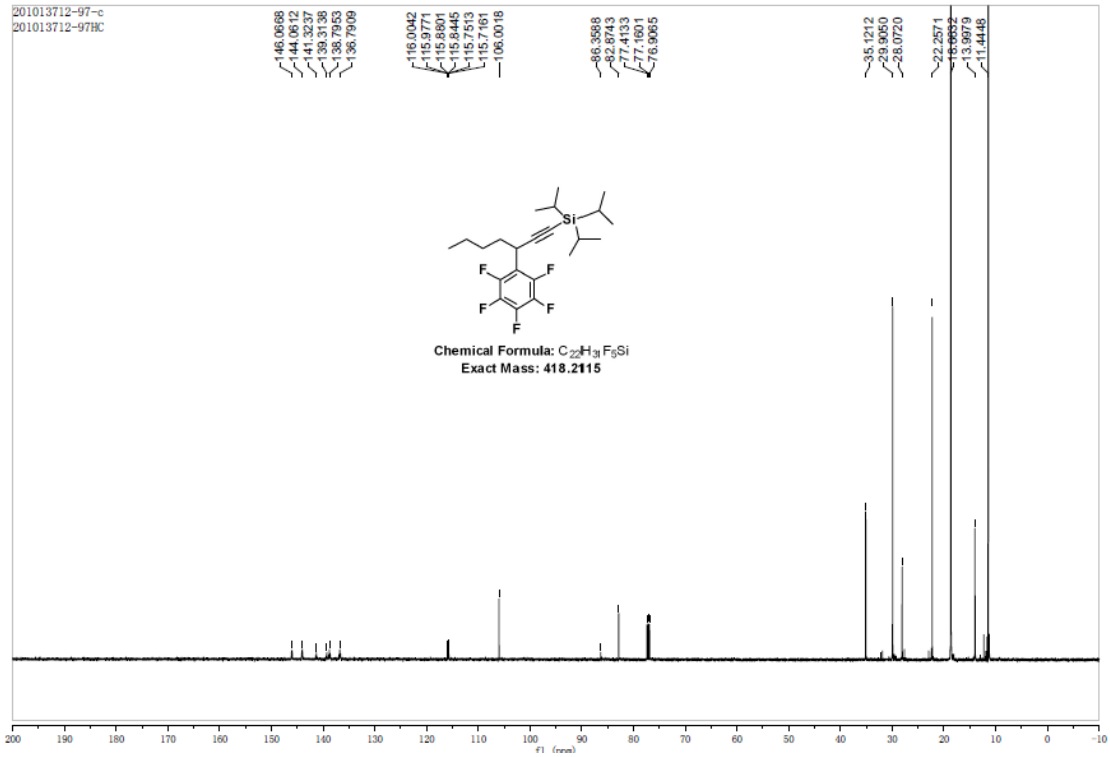




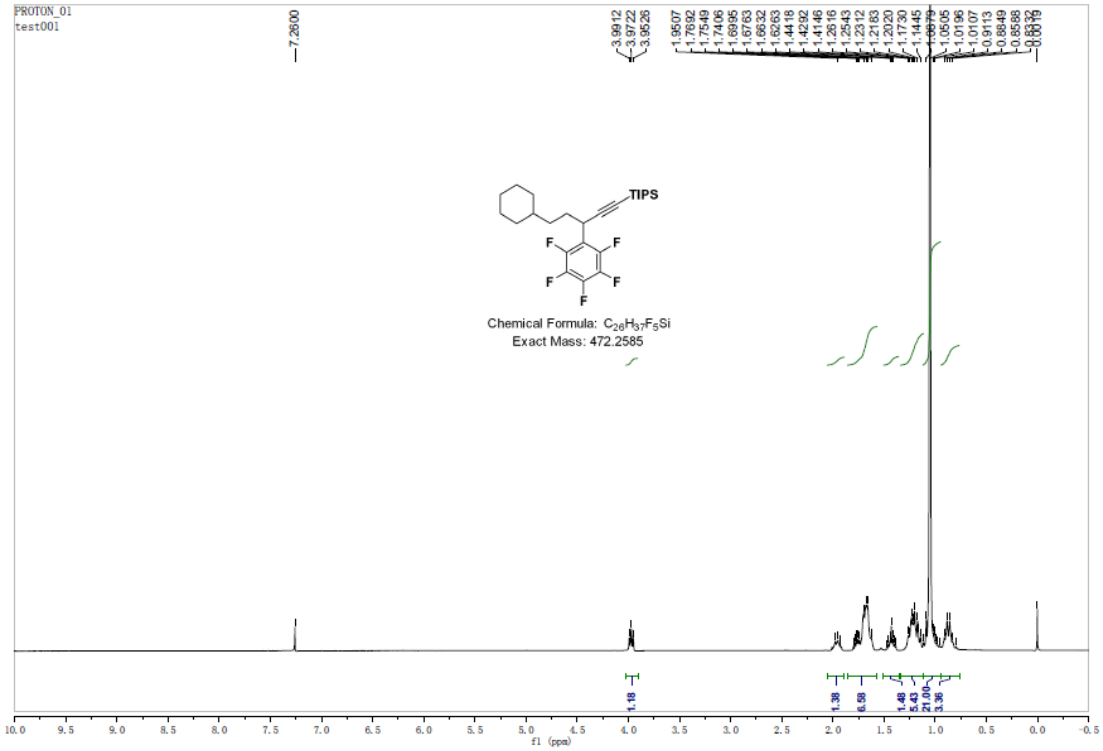
Triisopropyl(3-(perfluorophenyl)hept-1-yn-1-yl)silane (3a)

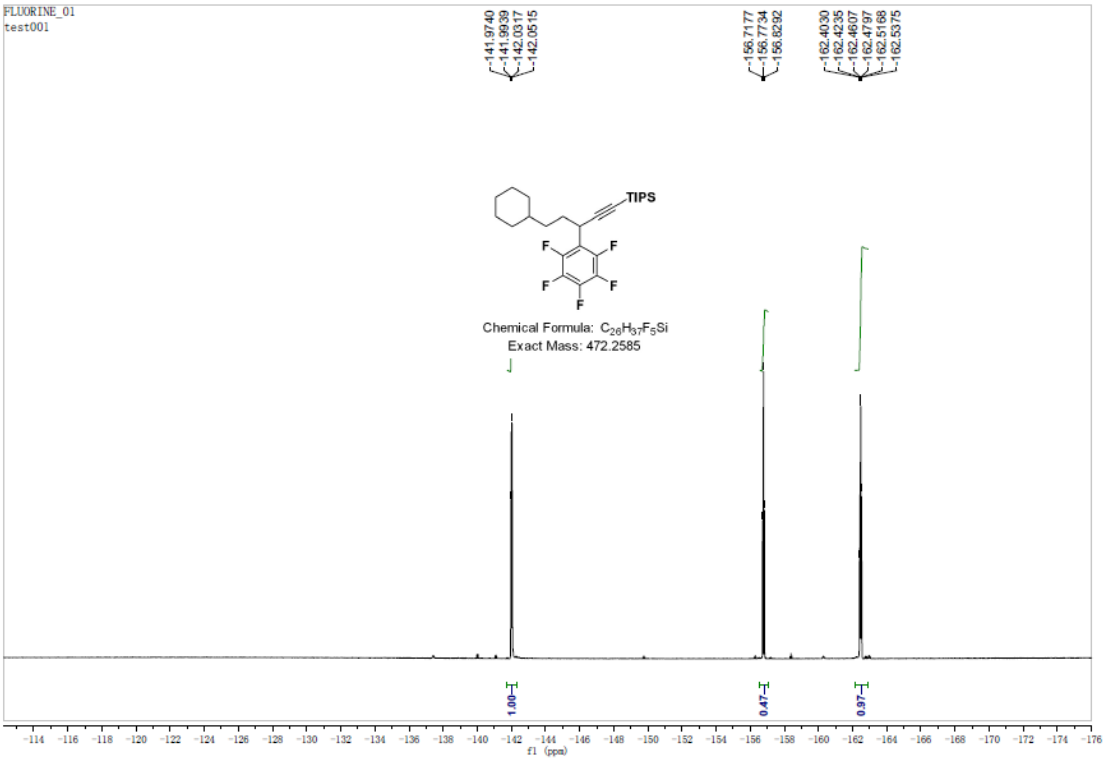


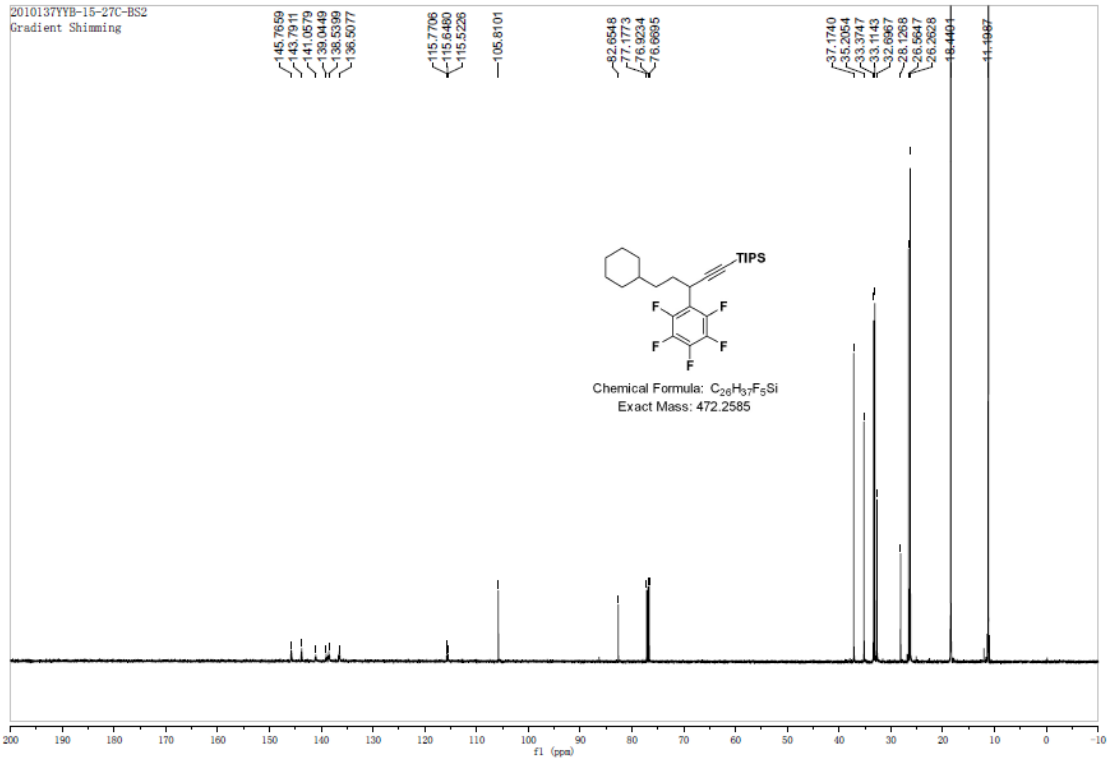




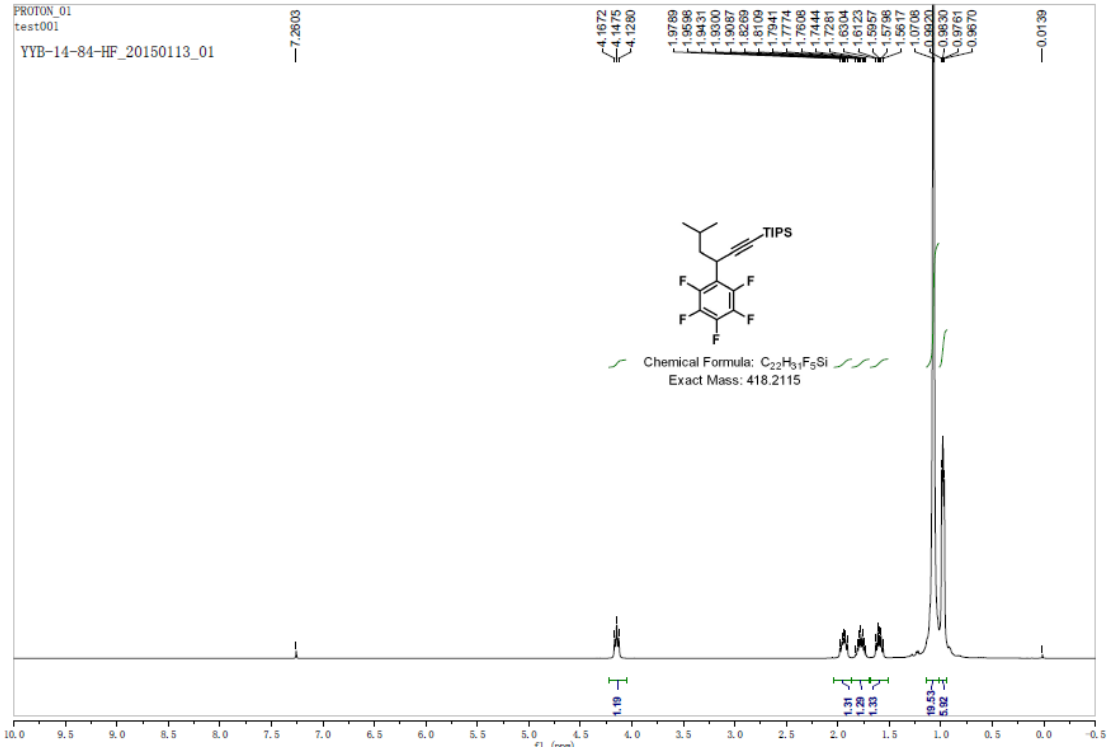
(5-Cyclohexyl-3-(perfluorophenyl)pent-1-yn-1-yl)triisopropylsilane (3b)

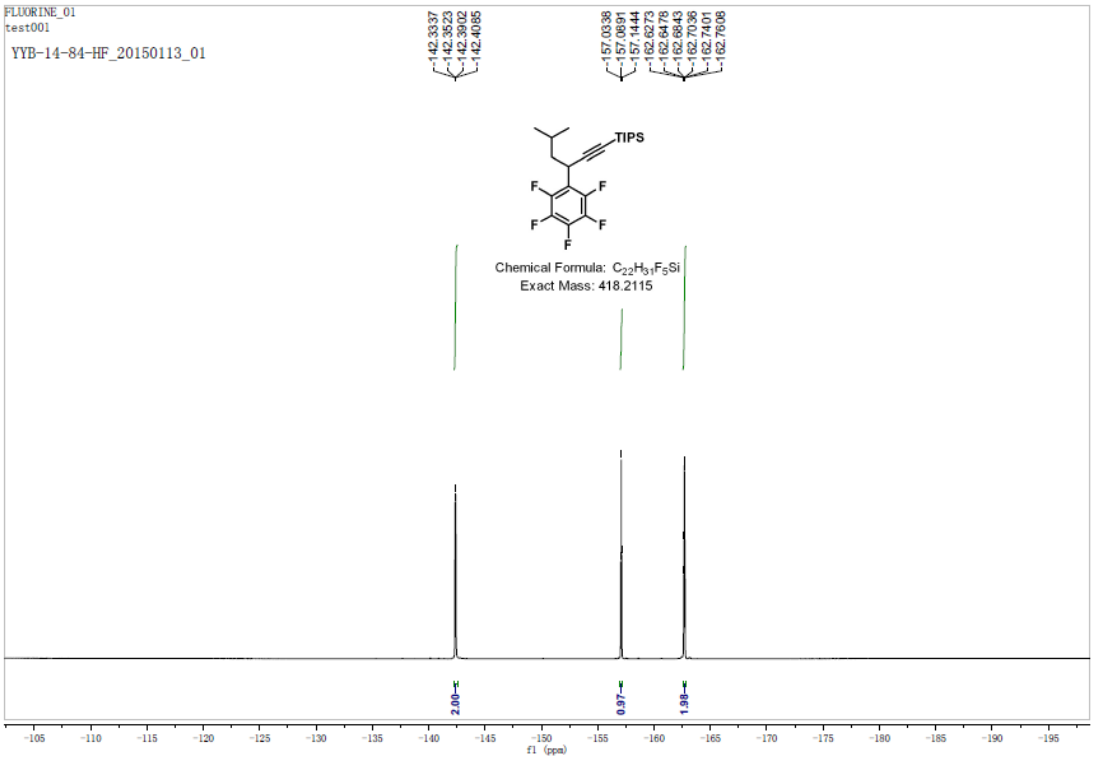


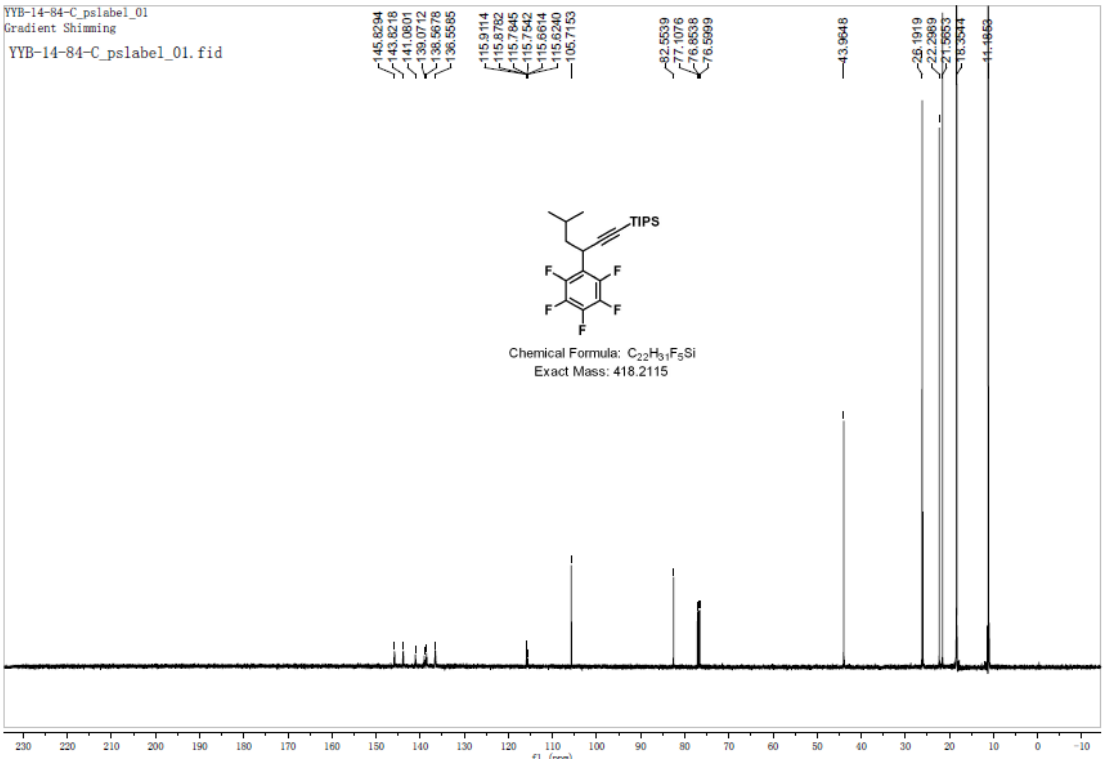

FLUORINE_01
test001
-141.9740
-141.9939
-142.0317
-142.0515
-156.7177
-156.7734
-156.8292
-162.4030
-162.4235
-162.4607
-162.4797
-162.5168
-162.5375
TIPS
F
F
F
F
F
Chemical Formula: C26H37F5Si
Exact Mass: 472.2585
1.00
0.47
0.97
f1 (ppm)


2010137YYB-15-27C-BS2
Gradient Shimming
145.7659
143.7911
141.0579
139.0449
136.5399
136.5077
115.7706
115.6460
115.5226
105.8101
82.6548
77.1773
76.9234
76.6895
37.1740
35.2054
33.3747
33.1143
32.6967
28.1268
26.5647
26.2828
18.4401
11.1987
TIPS
F
F
F
F
F
Chemical Formula: C26H37F5Si
Exact Mass: 472.2585
f1 (ppm)

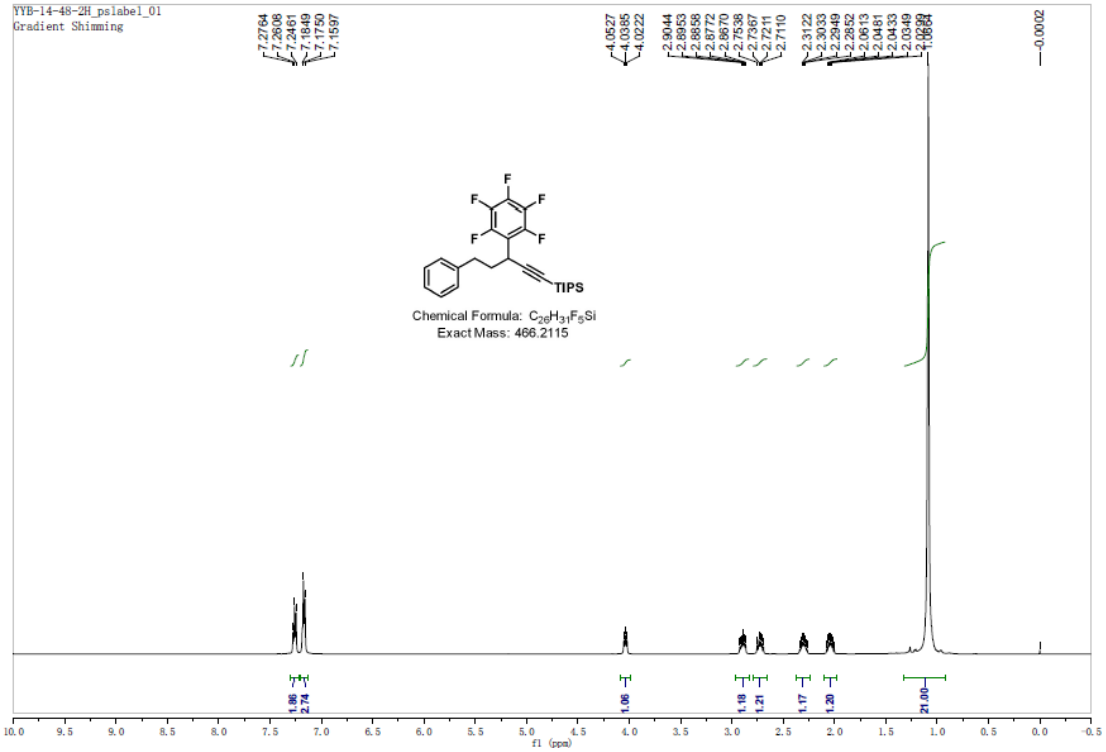
Triisopropyl(5-methyl-3-(perfluorophenyl)hex-1-yn-1-yl)silane (3c)

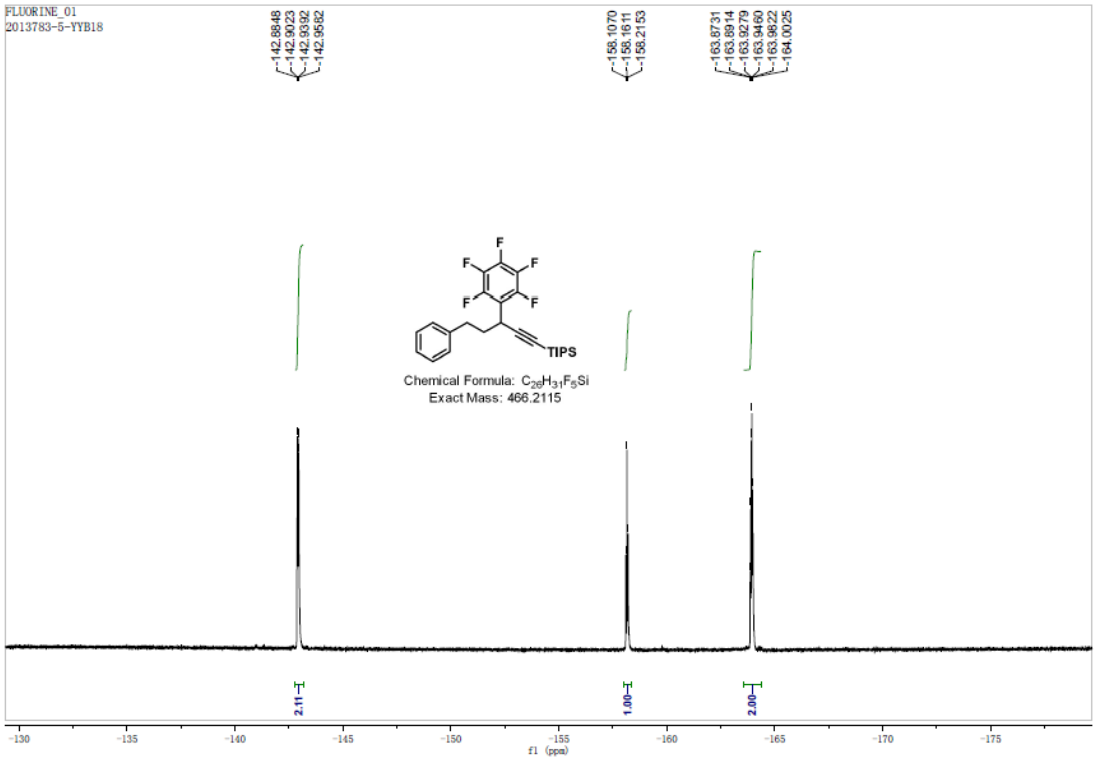


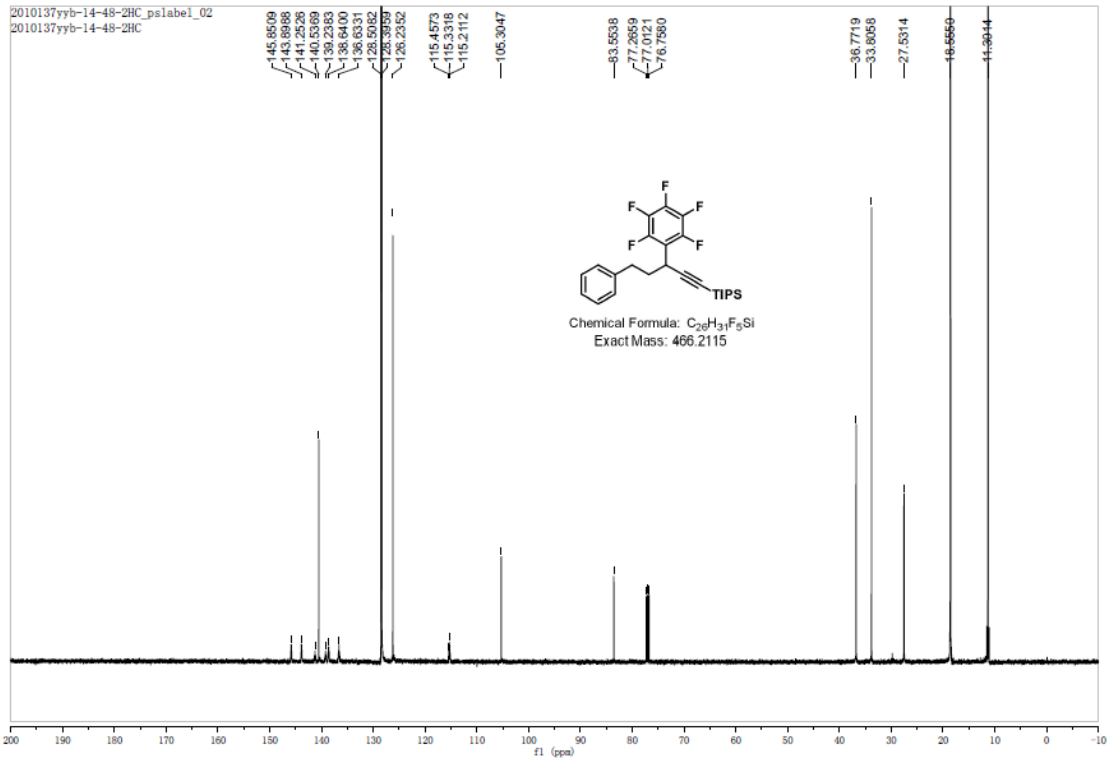




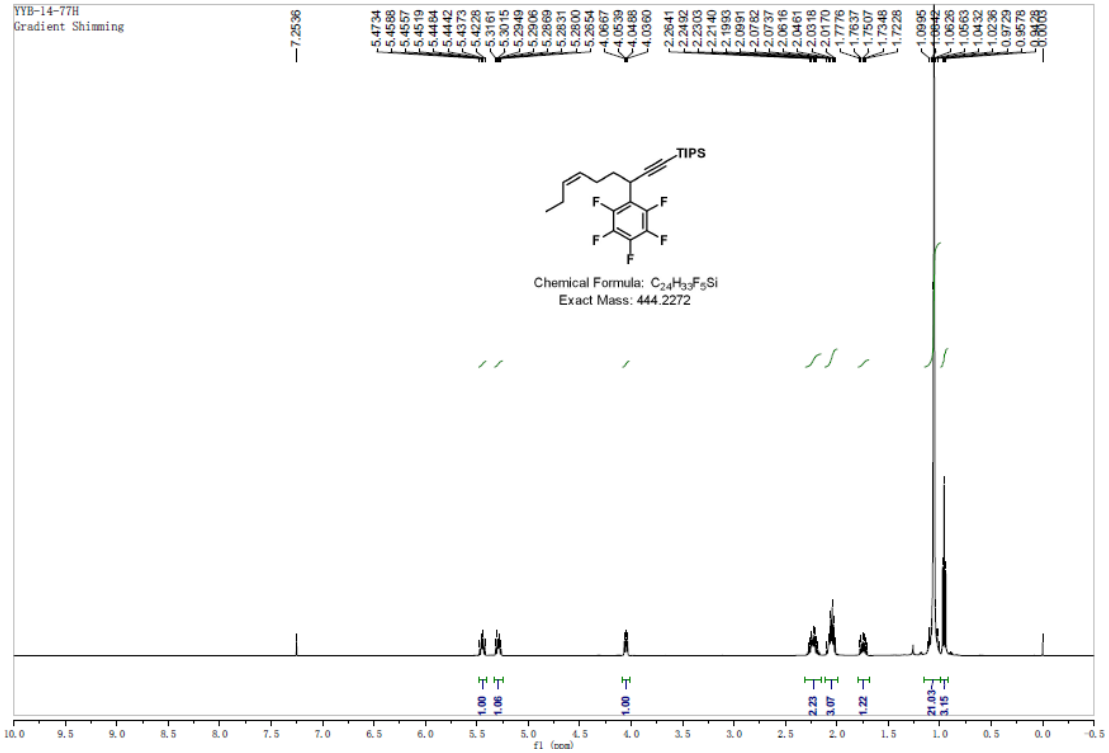
Triisopropyl(3-(perfluorophenyl)-5-phenylpent-1-yn-1-yl)silane (3d)

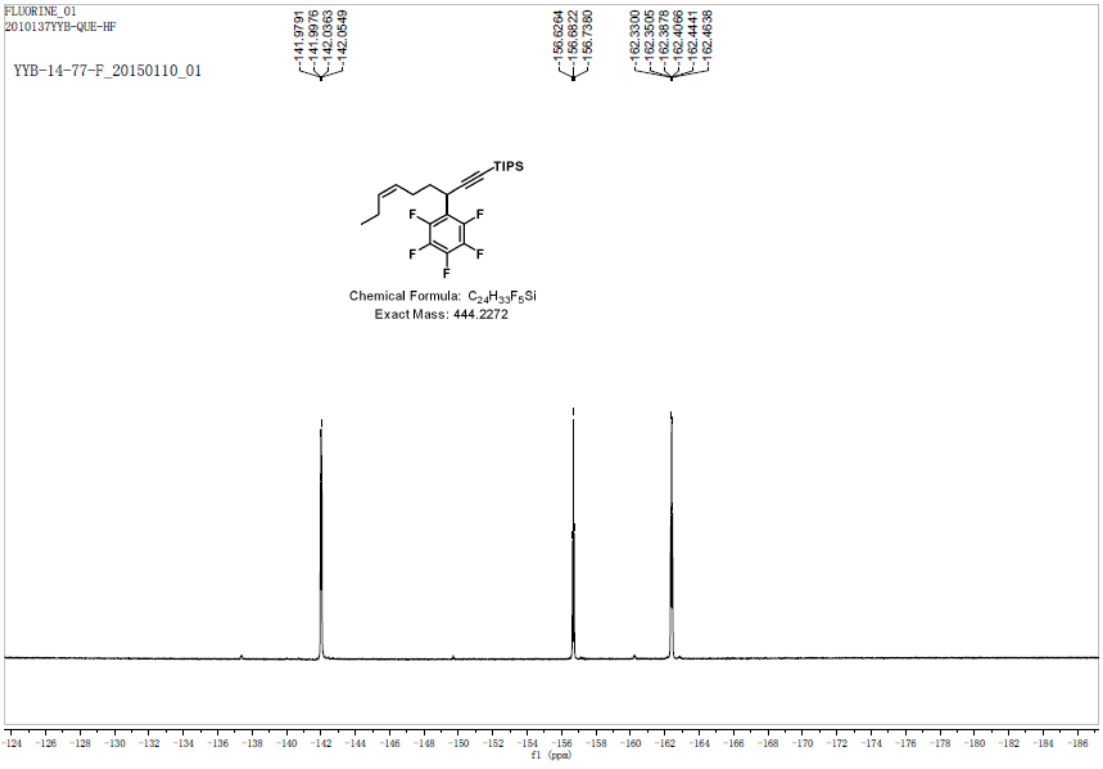


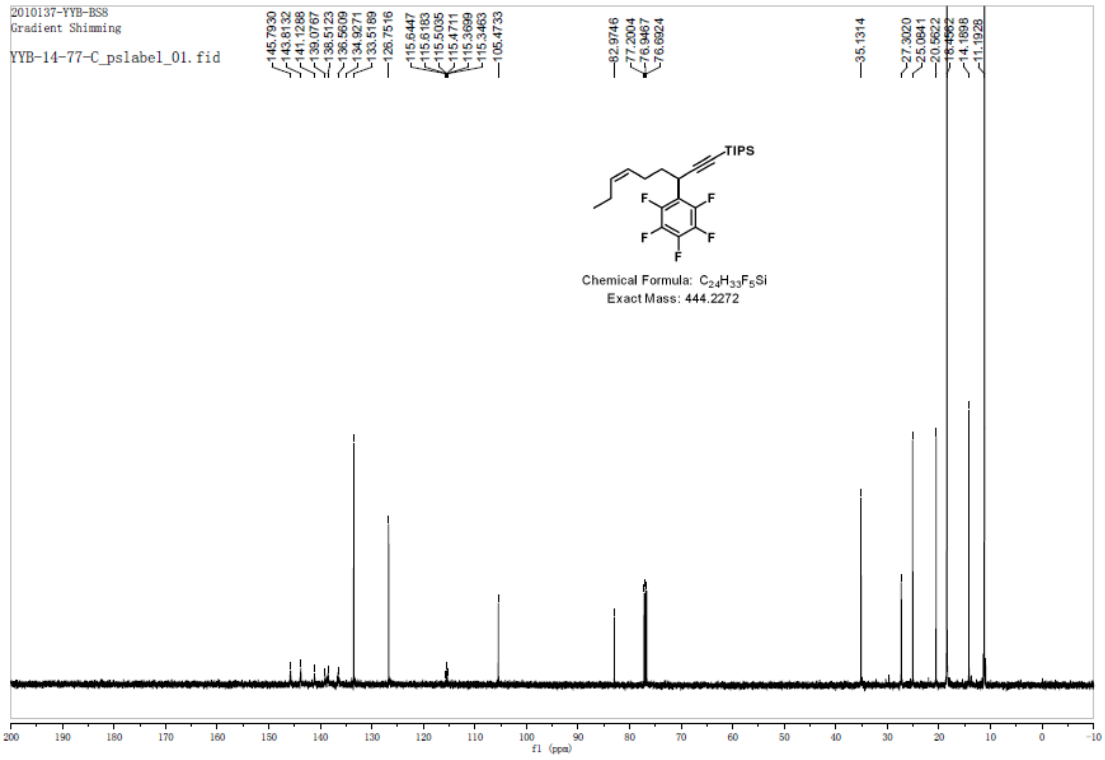

FLUORINE_01
2013783-5-YYB18
-142.8848
-142.9023
-142.9392
-142.9582
-158.1070
-158.1611
-158.2153
-163.8731
-163.8914
-163.9279
-163.9460
-163.9822
-164.0025
TIPS
Chemical Formula: C26H31F5Si
Exact Mass: 466.2115
2.11
1.00
2.00
f1 (ppm)


2010137yyb-14-48-2HC_pslabel_02
2010137yyb-14-48-2HC
145.8509
143.8988
141.2526
140.5369
139.2383
138.6400
136.6331
128.5082
126.3959
126.2352
115.4573
115.3318
115.2112
105.3047
83.5538
77.2659
77.0121
76.7580
36.7719
33.8058
27.5314
18.5560
11.3014
TIPS
Chemical Formula: C26H31F5Si
Exact Mass: 466.2115
f1 (ppm)

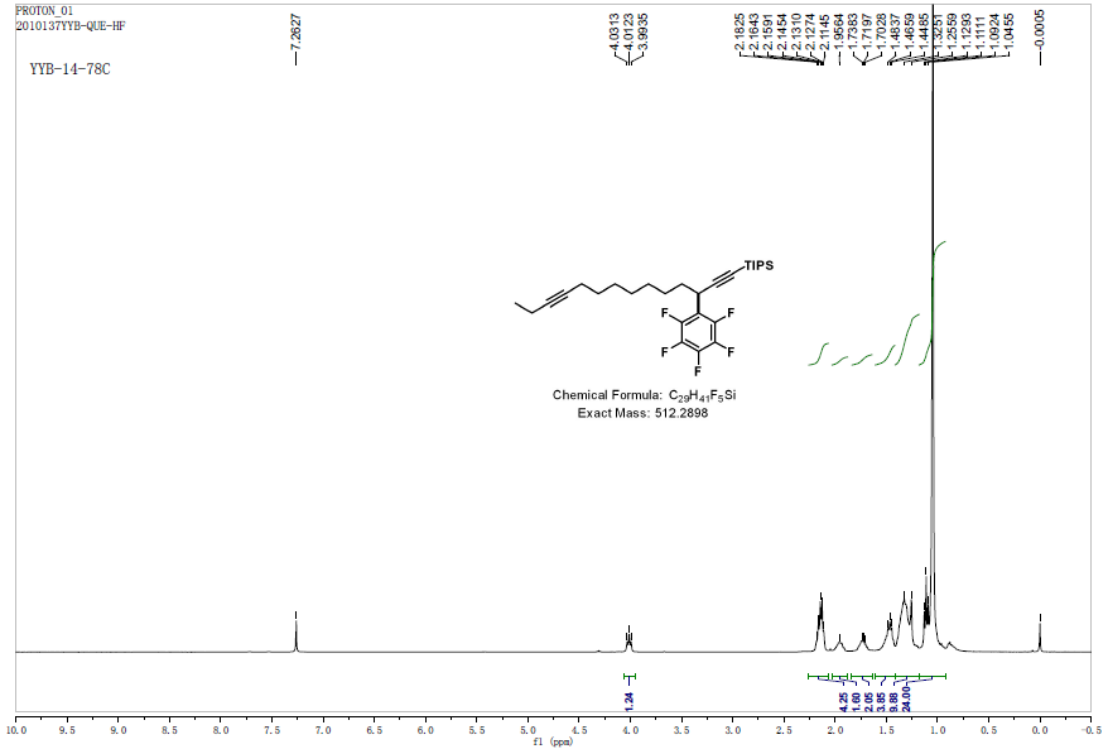
(*Z*)-Triisopropyl(3-(perfluorophenyl)non-6-en-1-yn-1-yl)silane (3e)

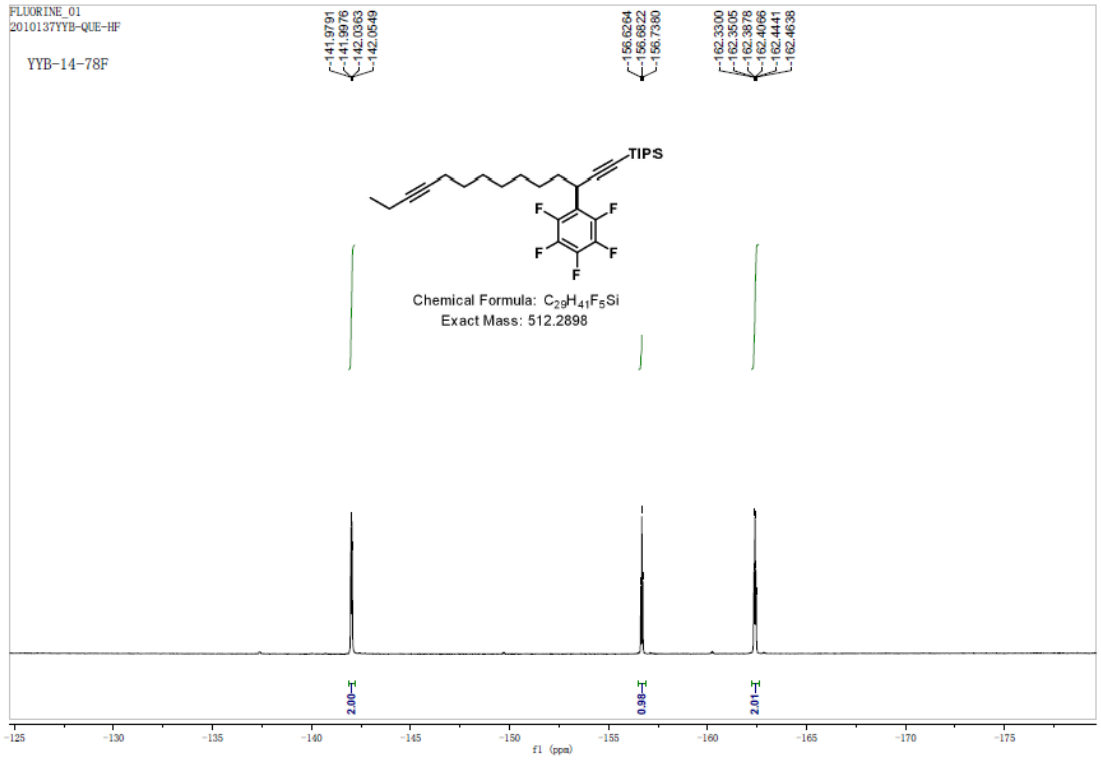


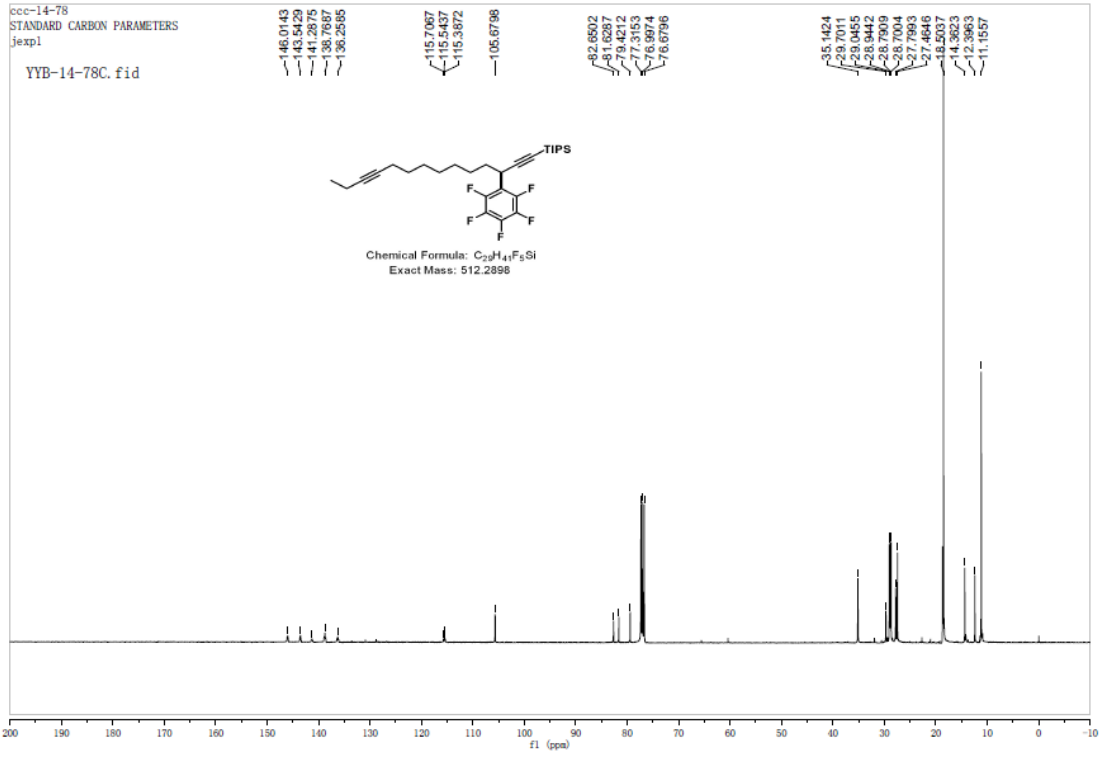




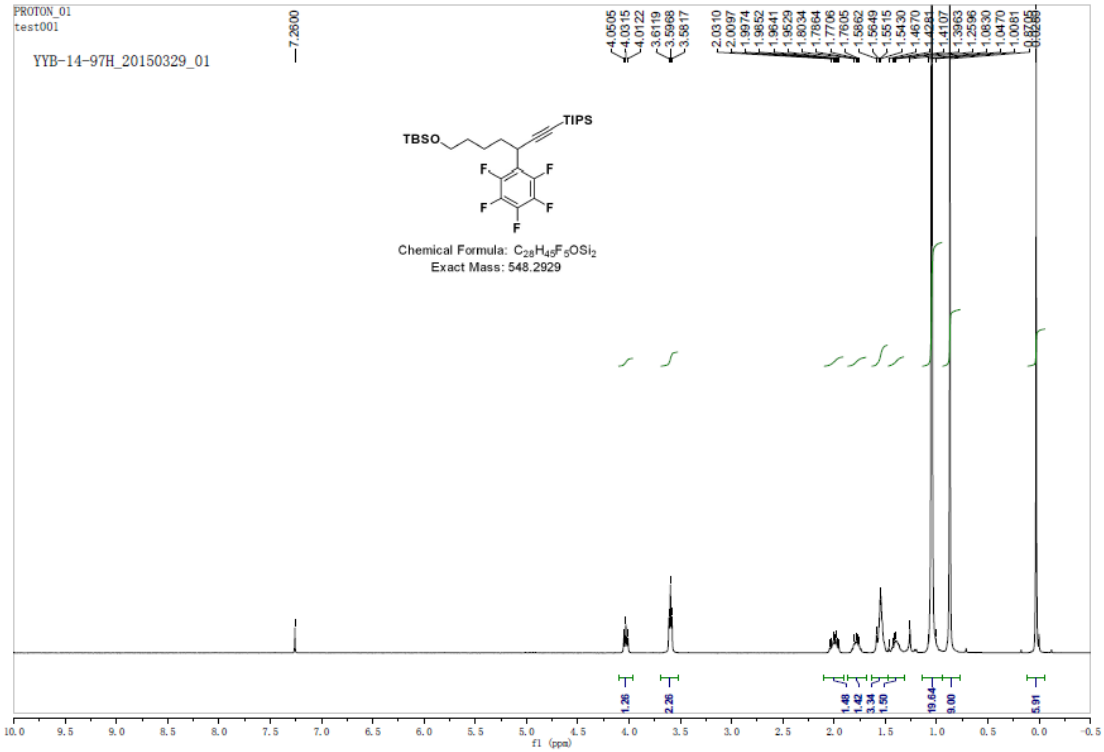
Triisopropyl(3-(perfluorophenyl)tetradeca-1,11-diyn-1-yl)silane (3f)

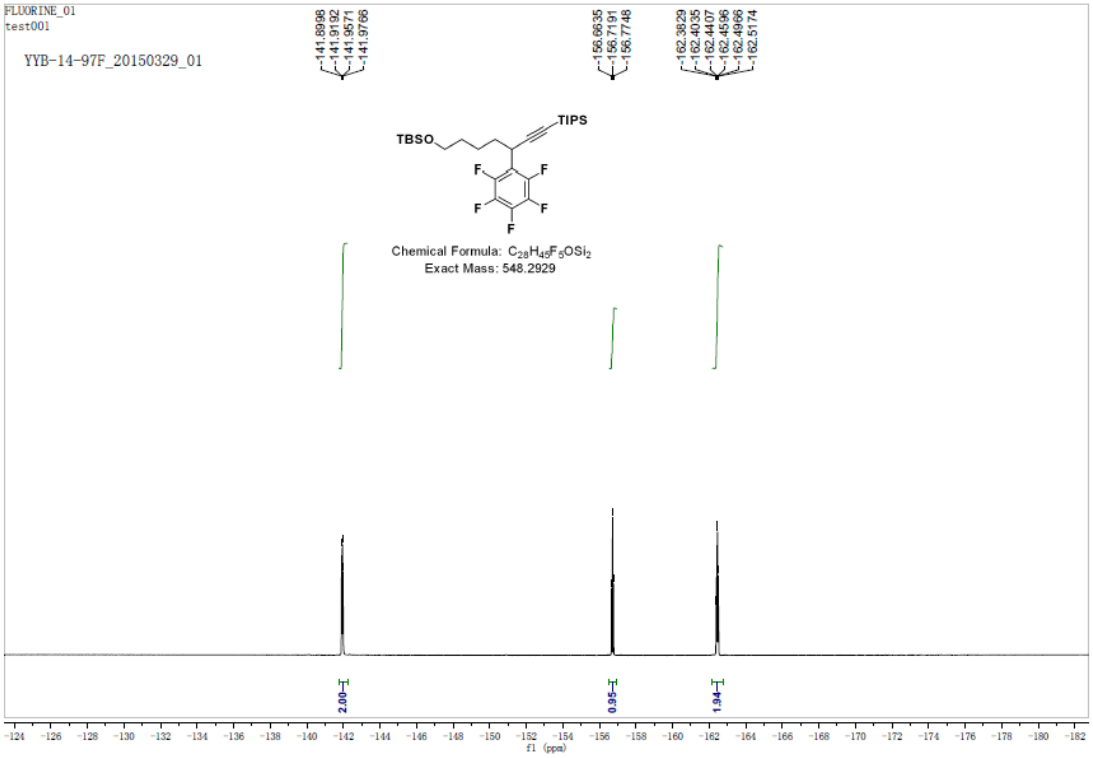


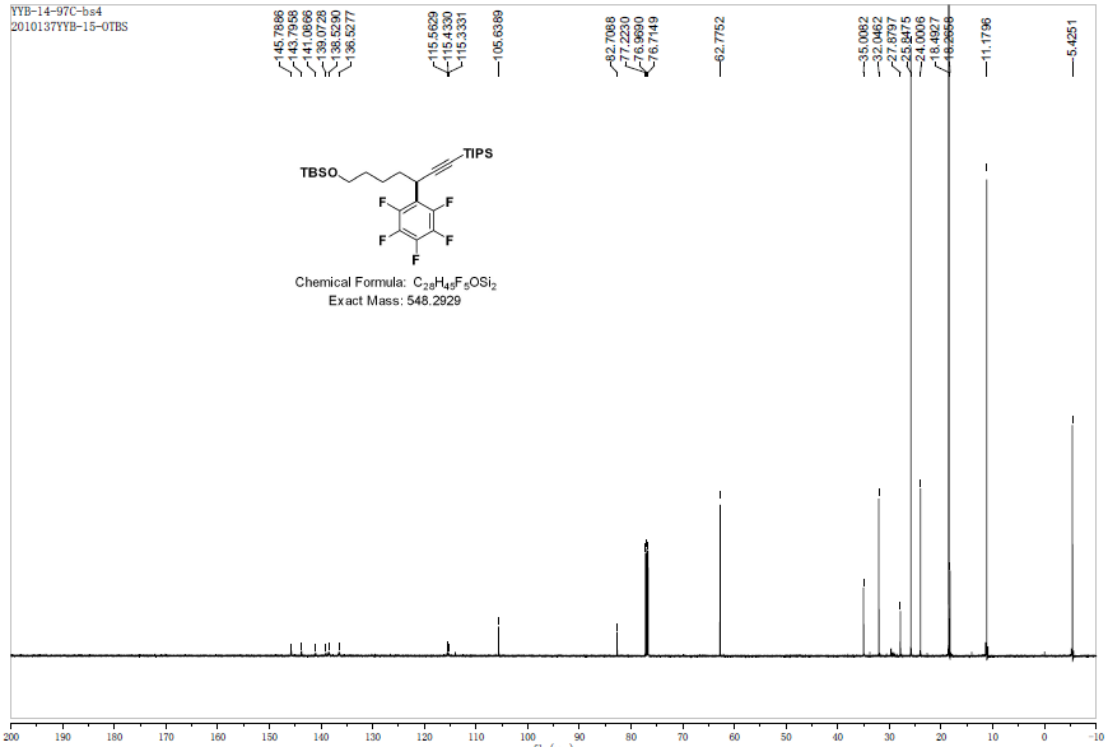

FLUORINE_01
20101137YYB-QUE-HF
YYB-14-78F
-141.9791
-141.9976
-142.0363
-142.0549
-156.6264
-156.6822
-156.7380
-162.3300
-162.3505
-162.3878
-162.4066
-162.4441
-162.4638
TIPS
F
F
F
F
F
Chemical Formula: C29H41F5Si
Exact Mass: 512.2898
2.00
0.98
2.01
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)


ccc-14-78
STANDARD CARBON PARAMETERS
jexp1
YYB-14-78C.fid
-146.0143
-143.5429
-141.2875
-138.7687
-136.2585
-115.7067
-115.5437
-115.3872
-105.6798
-82.6502
-81.6287
-79.4212
-77.3153
-76.9974
-76.6796
-35.1424
-29.7011
-29.0455
-28.9442
-28.7909
-28.7004
-27.7993
-27.4646
-18.5037
-14.3623
-12.3963
-11.1557
TIPS
F
F
F
F
F
Chemical Formula: C29H41F5Si
Exact Mass: 512.2898
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

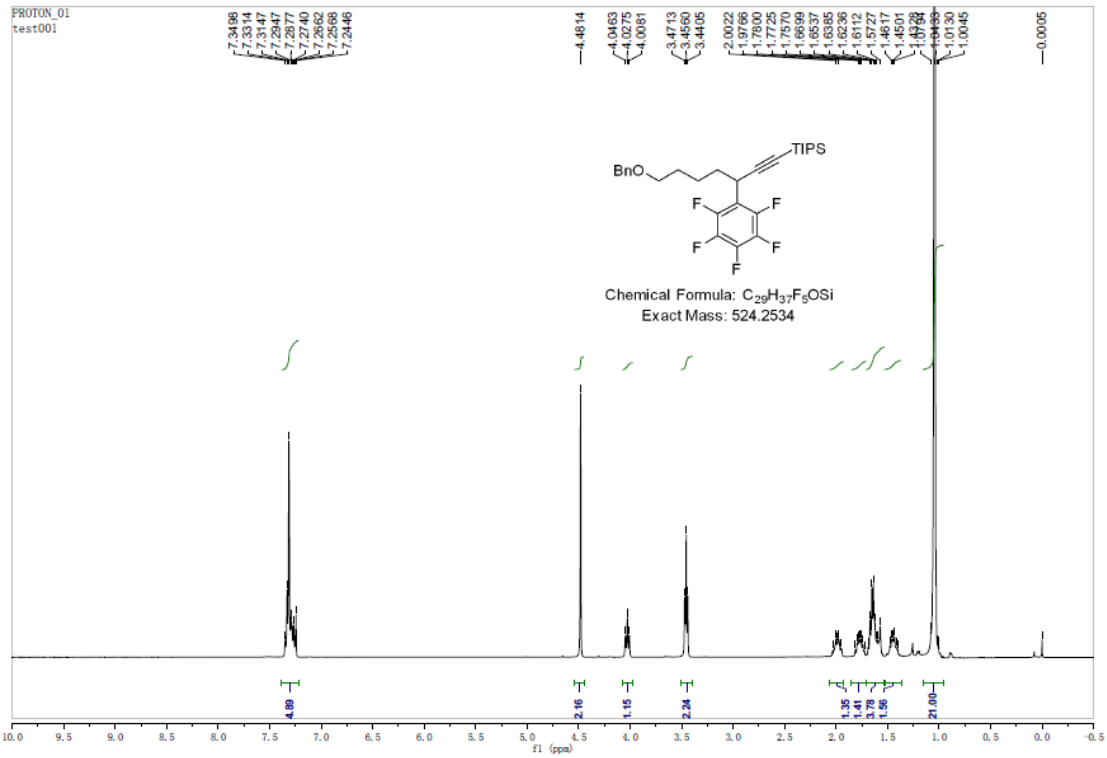
tert-Butyldimethyl((5-(perfluorophenyl)-7-(triisopropylsilyl)hept-6-yn-yl)oxy)silane (3g)

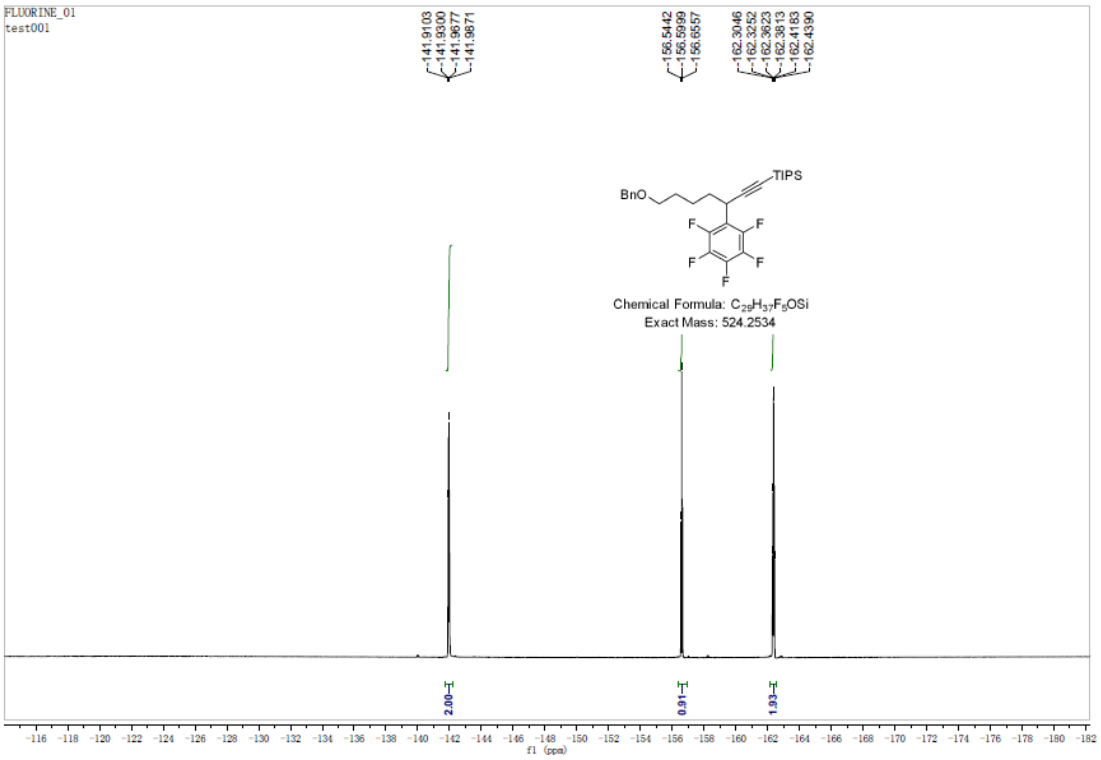


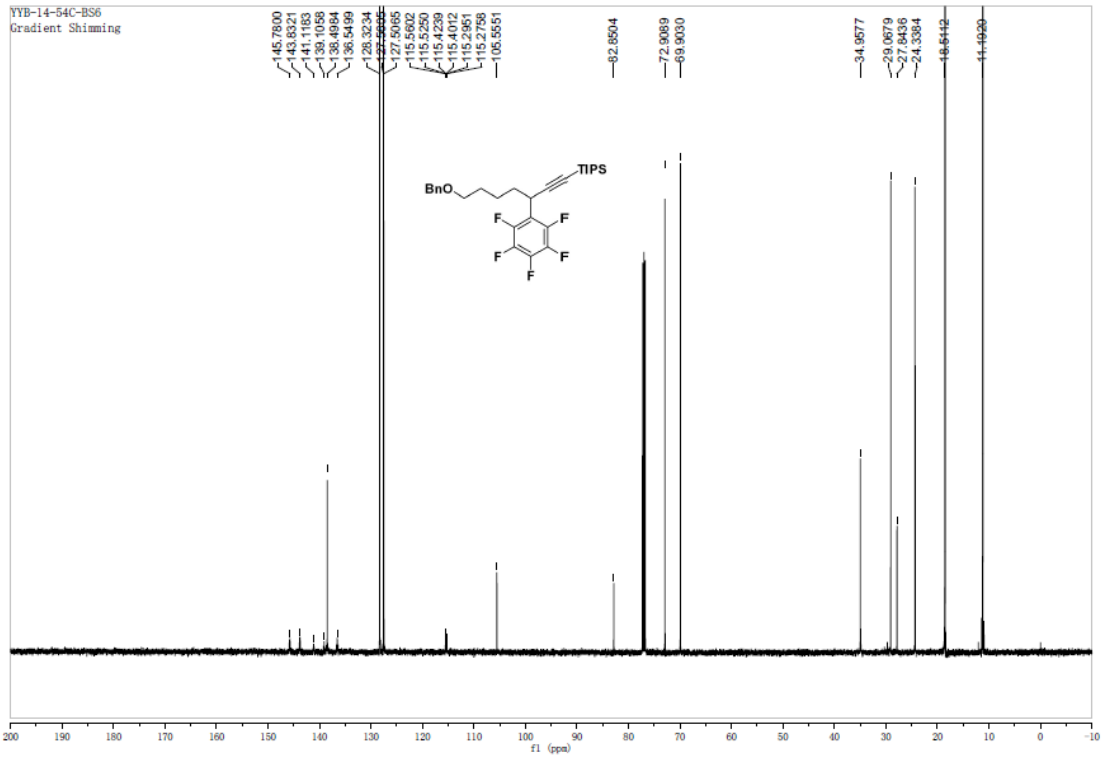




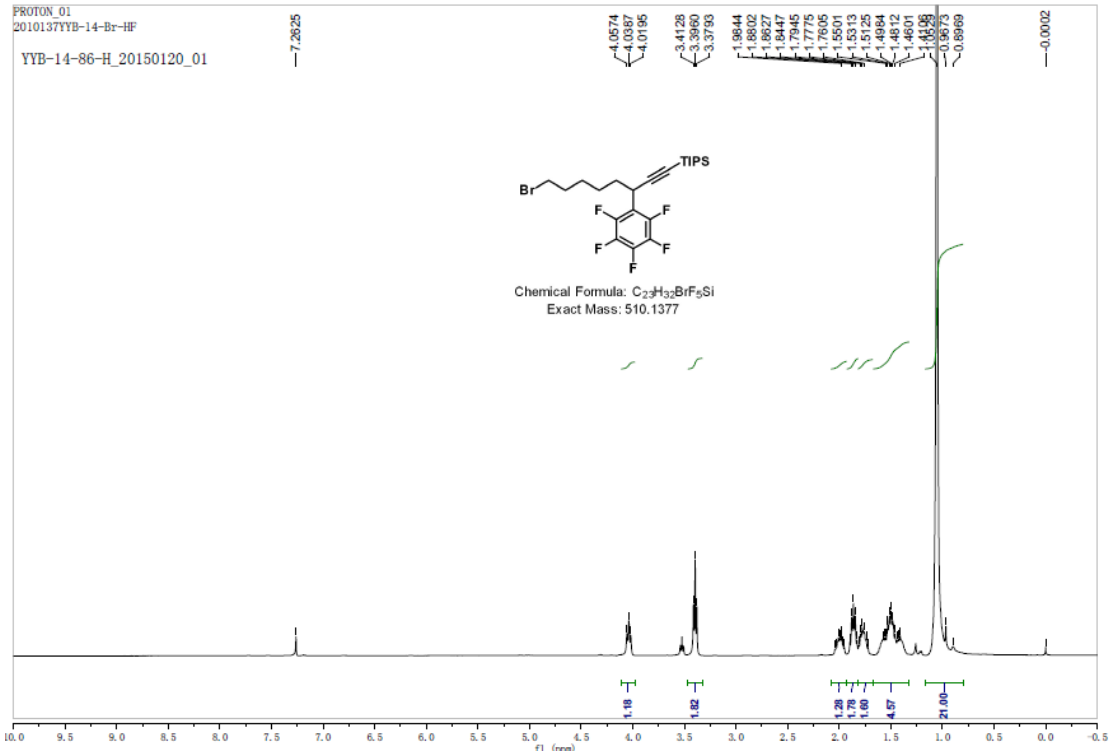
(7-(Benzyloxy)-3-(perfluorophenyl)hept-1-yn-1-yl)triisopropylsilane (3h)

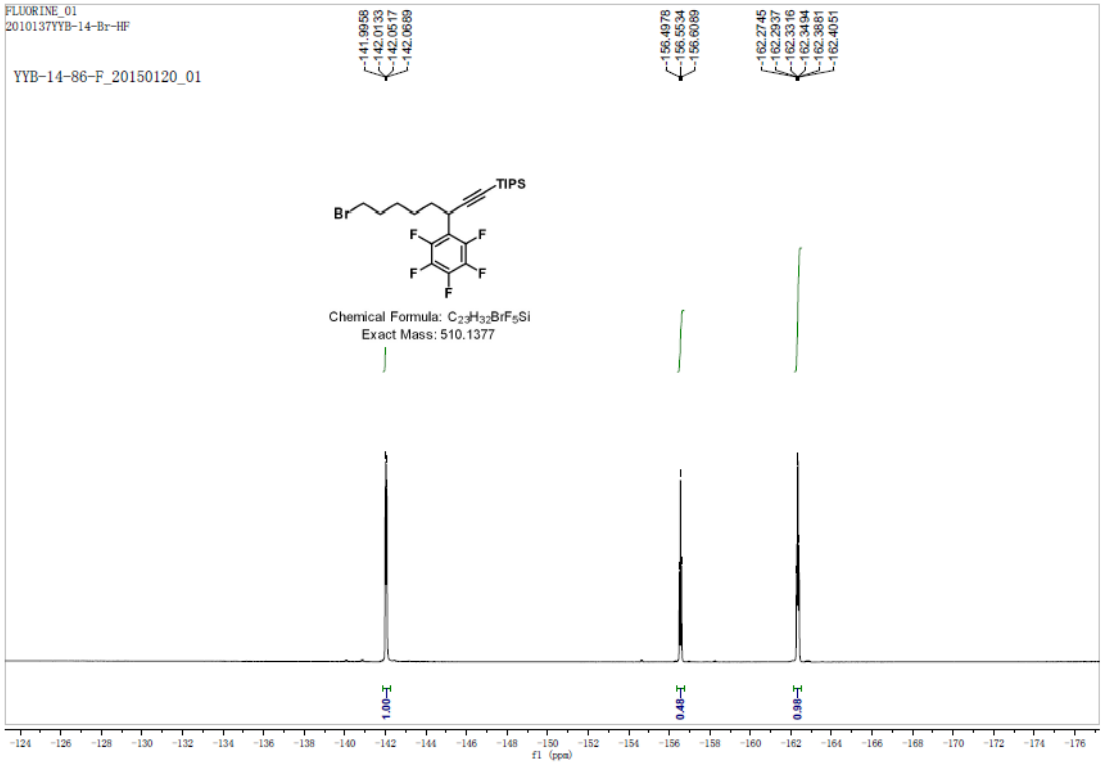


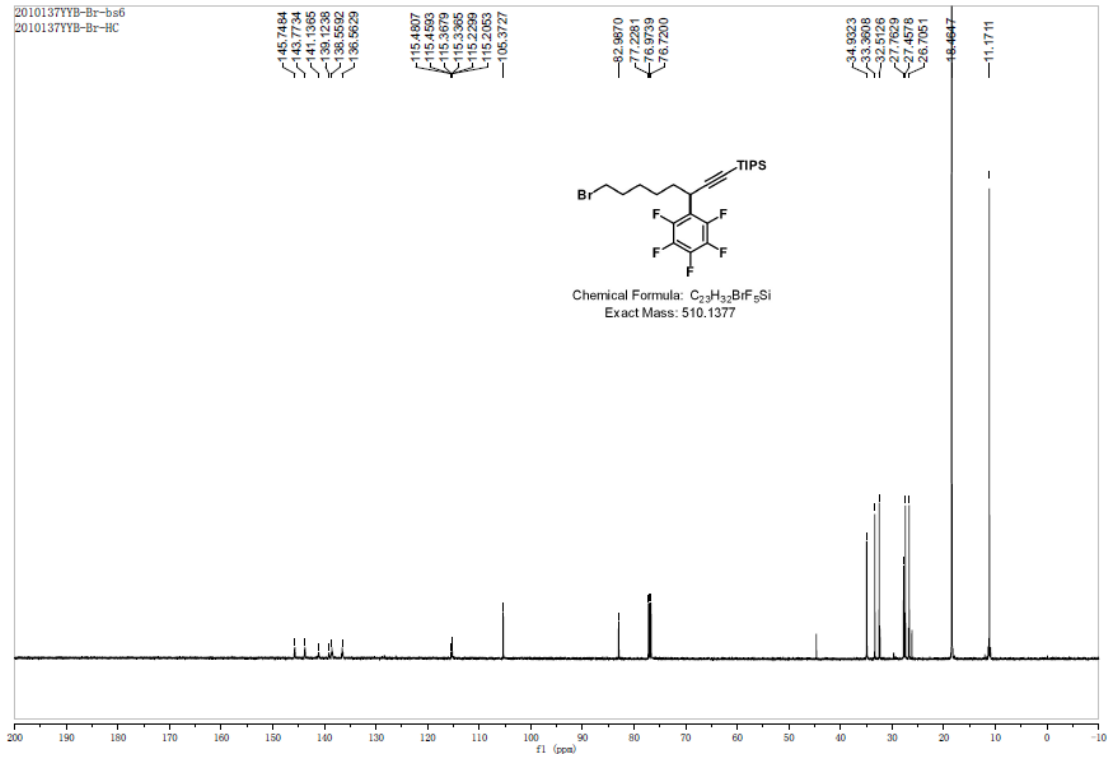

FLUORINE_01
test001
-141.9103
-141.9300
-141.9677
-141.9871
-156.5442
-156.5999
-156.6557
-162.3046
-162.3252
-162.3623
-162.3813
-162.4183
-162.4390
TIPS
BnO
F
F
F
F
F
Chemical Formula: C29H37F5OSi
Exact Mass: 524.2534
2.00
0.91
1.93
f1 (ppm)


YYB-14-54C-BS6
Gradient Shimming
145.7800
143.8321
141.1183
139.1058
138.4984
136.5499
128.3234
127.5065
115.5602
115.5250
115.4239
115.4012
115.2951
115.2756
105.5551
82.8504
72.9089
69.9030
34.9577
29.0679
27.8436
24.3384
18.6412
11.1920
TIPS
BnO
F
F
F
F
F
f1 (ppm)

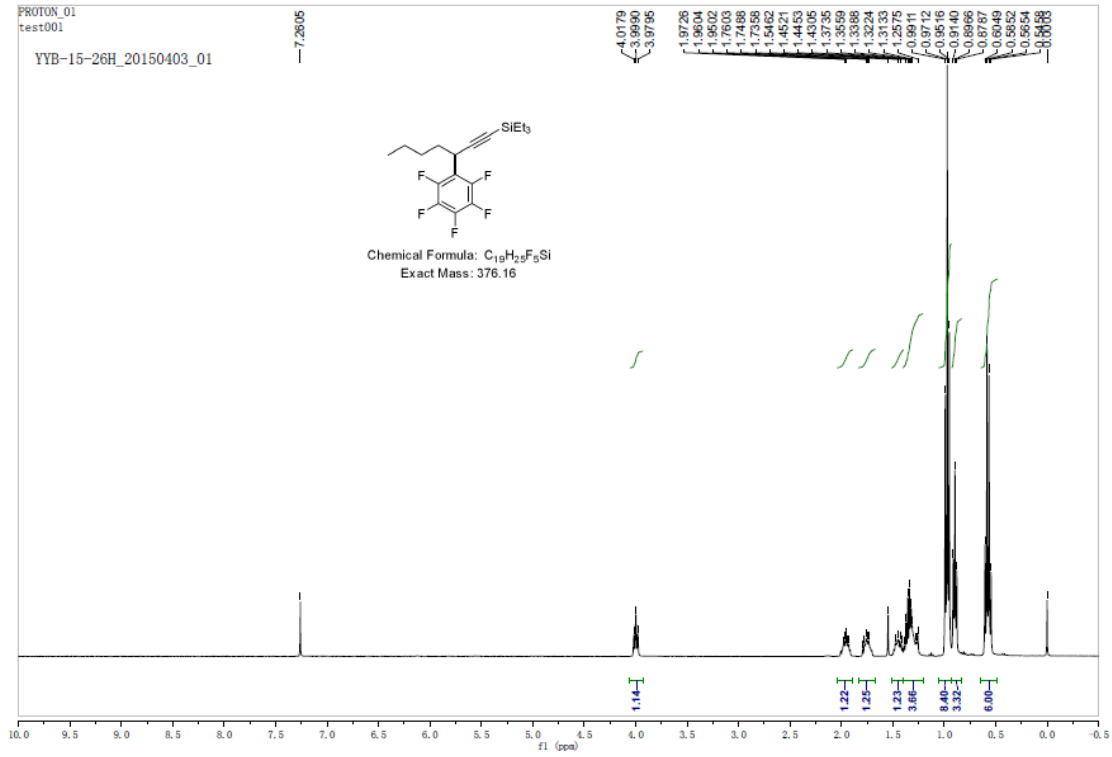
8-Bromo-3-(perfluorophenyl)oct-1-yn-1-yl)triisopropylsilane (3i)

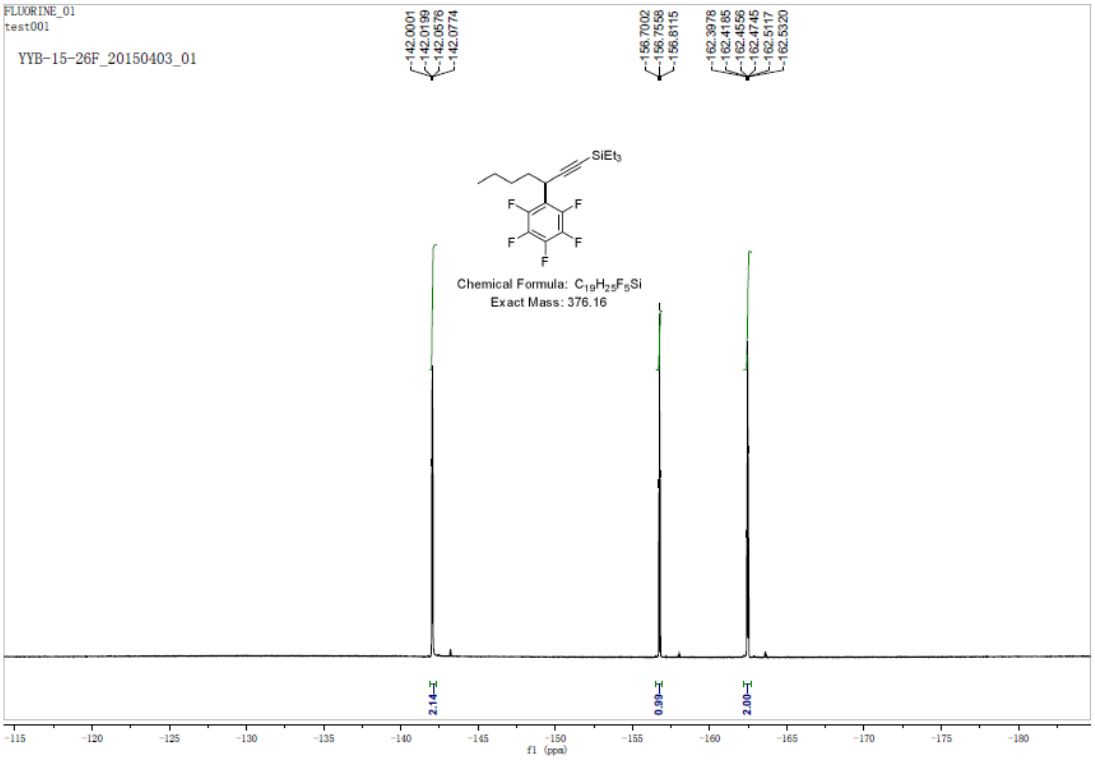


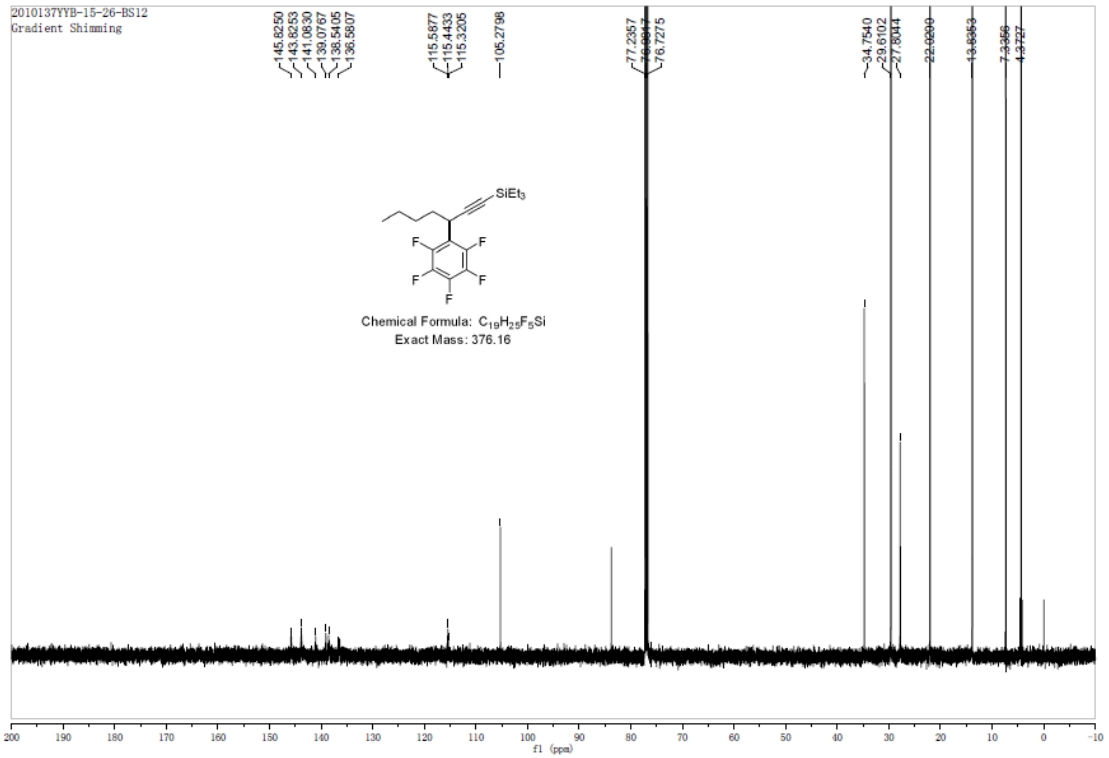




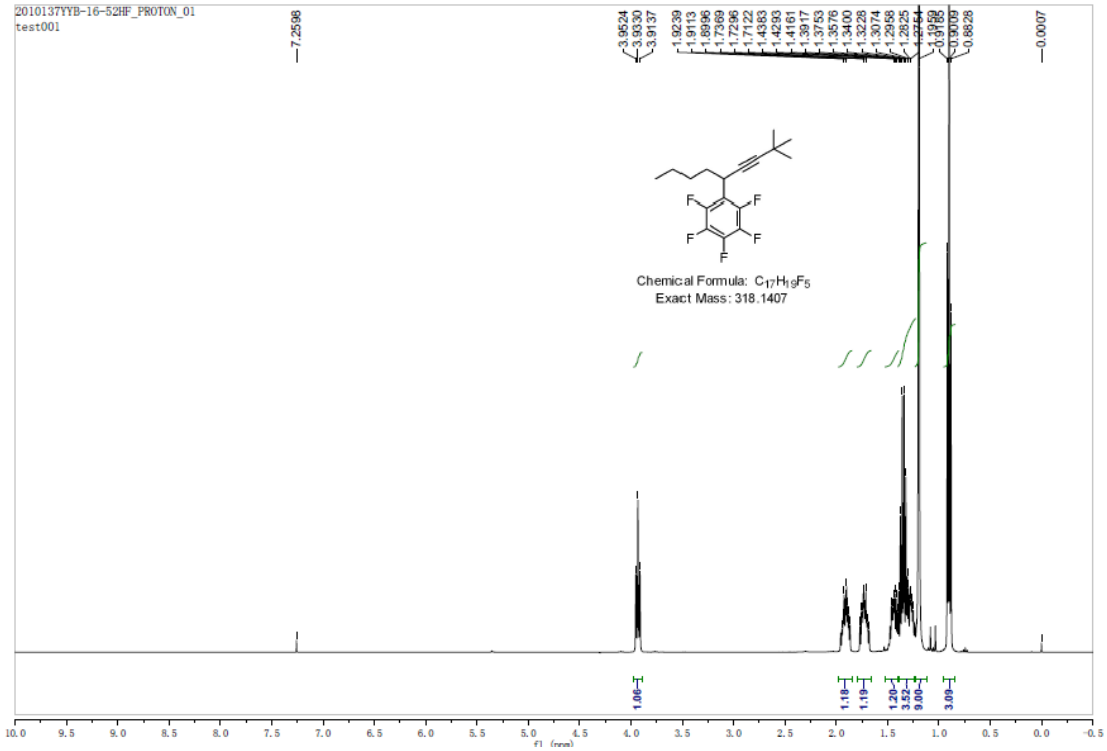
Triethyl(3-(perfluorophenyl)hept-1-yn-1-yl)silane (3j)

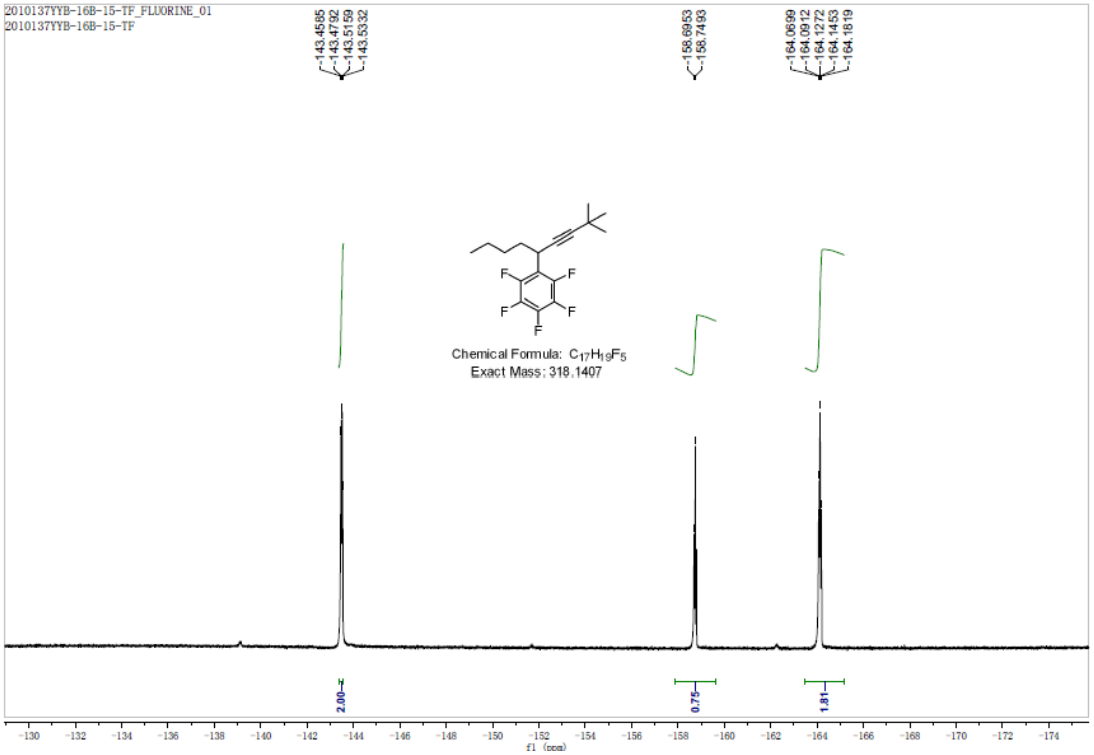


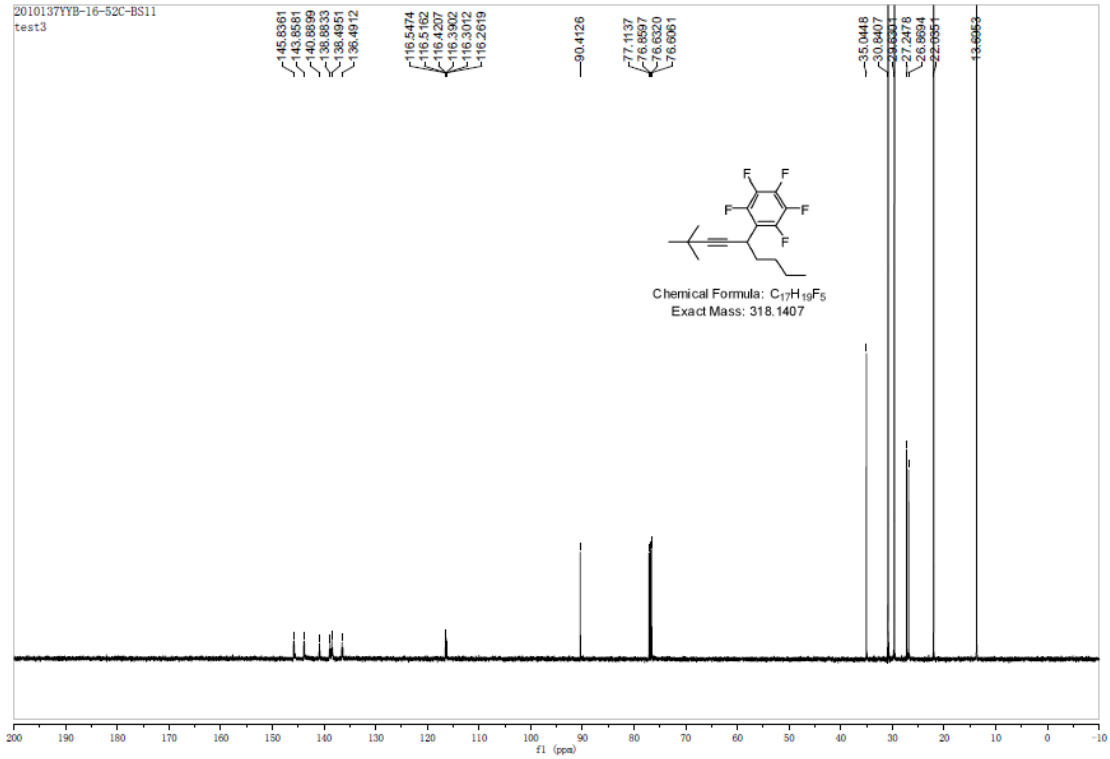

FLUORINE_01
test001
YYB-15-26F_20150403_01
-142.0001
-142.0199
-142.0576
-142.0774
-156.7002
-156.7558
-156.8115
-162.3978
-162.4185
-162.4556
-162.4745
-162.5117
-162.5320
SiEt3
F
F
F
F
F
Chemical Formula: C19H25F5Si
Exact Mass: 376.16
2.14
0.99
2.00
f1 (ppm)


2010137YYB-15-26-BS12
Gradient Shimming
145.8250
143.8253
141.8830
139.0767
138.5405
136.5807
115.5877
115.4433
115.3205
105.2796
77.2357
76.7275
34.7540
29.6102
27.8044
22.6090
13.8363
7.3956
4.3727
SiEt3
F
F
F
F
F
Chemical Formula: C19H25F5Si
Exact Mass: 376.16
f1 (ppm)

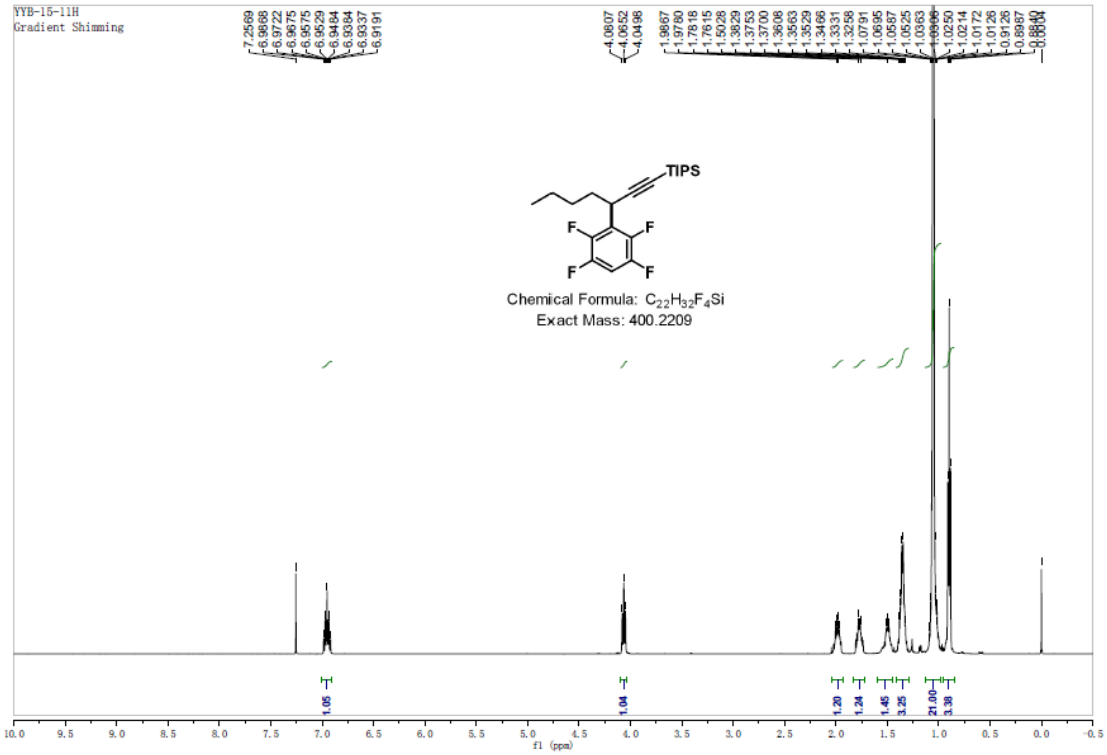
1-(2,2-Dimethylnon-3-yn-5-yl)-2,3,4,5,6-pentafluorobenzene (3k)

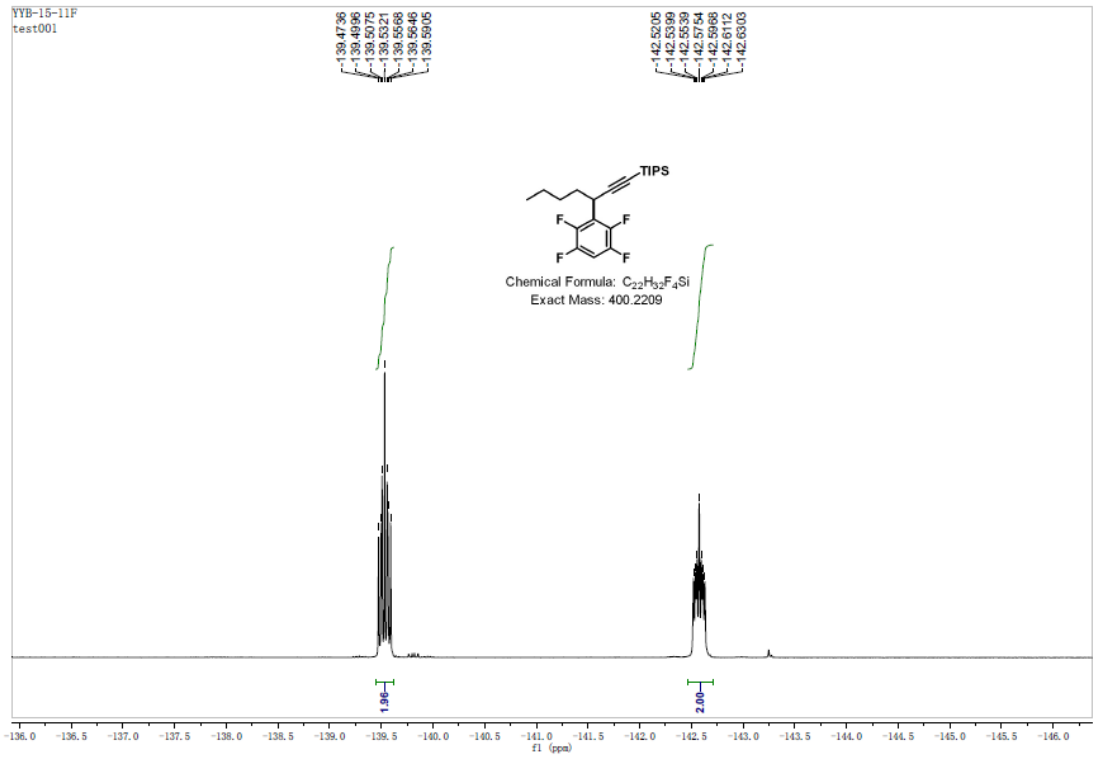


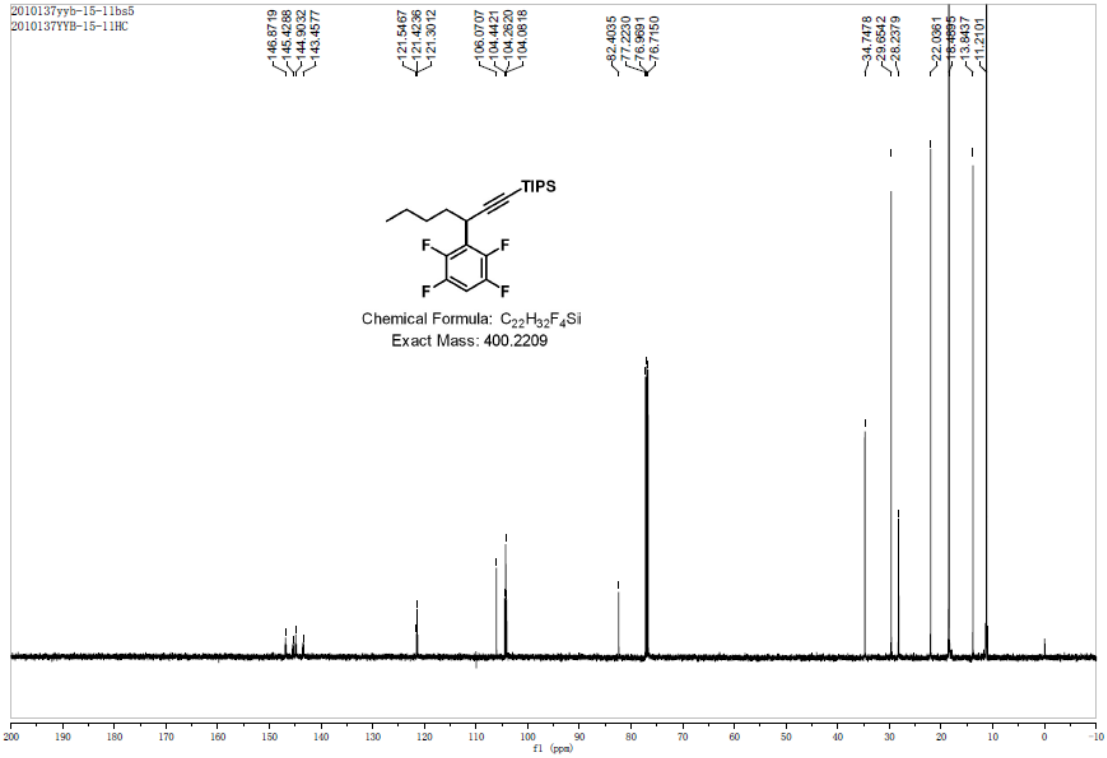




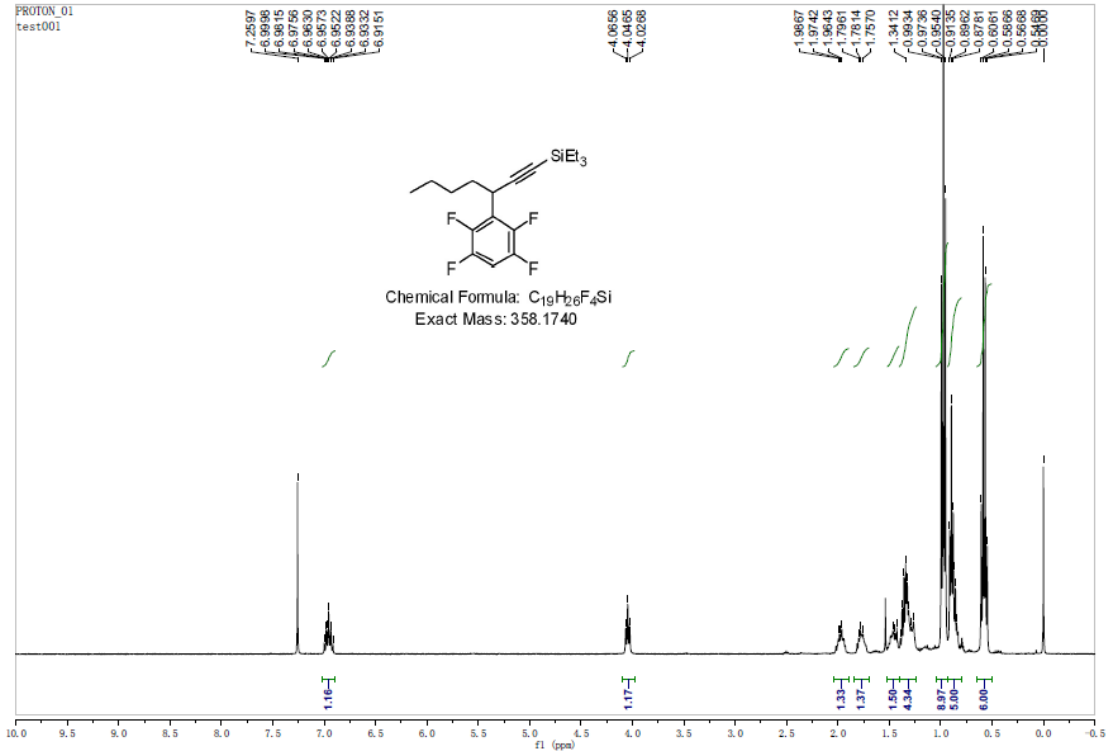
Triisopropyl(3-(2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4a)

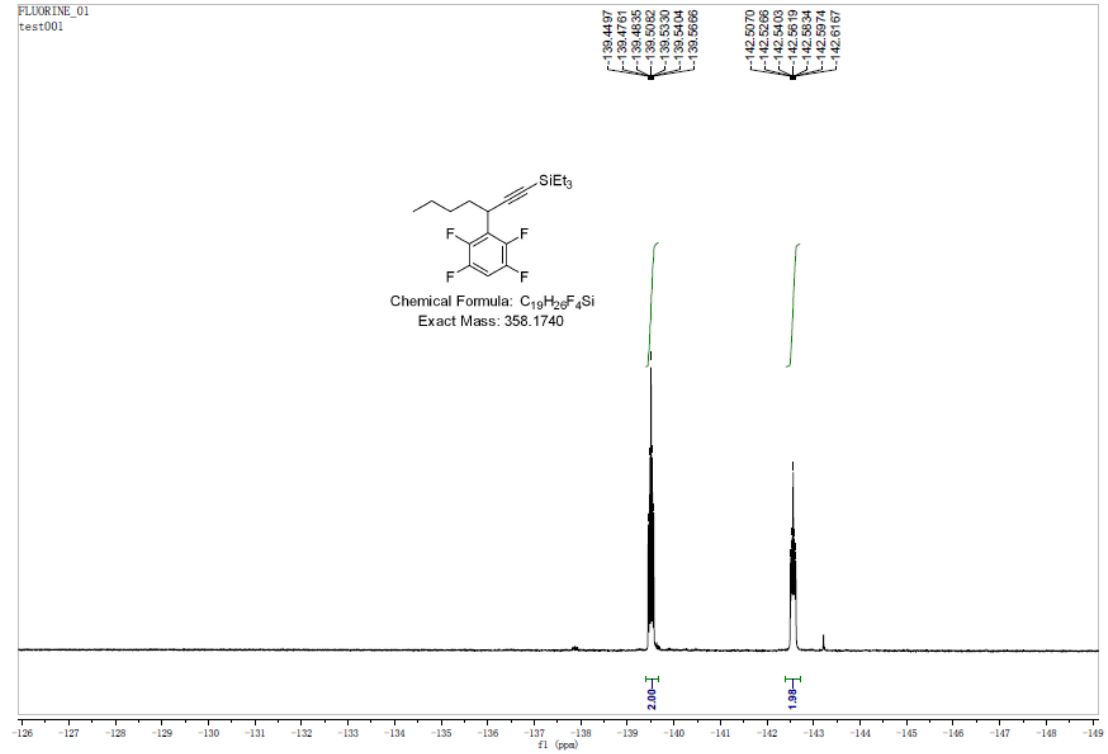


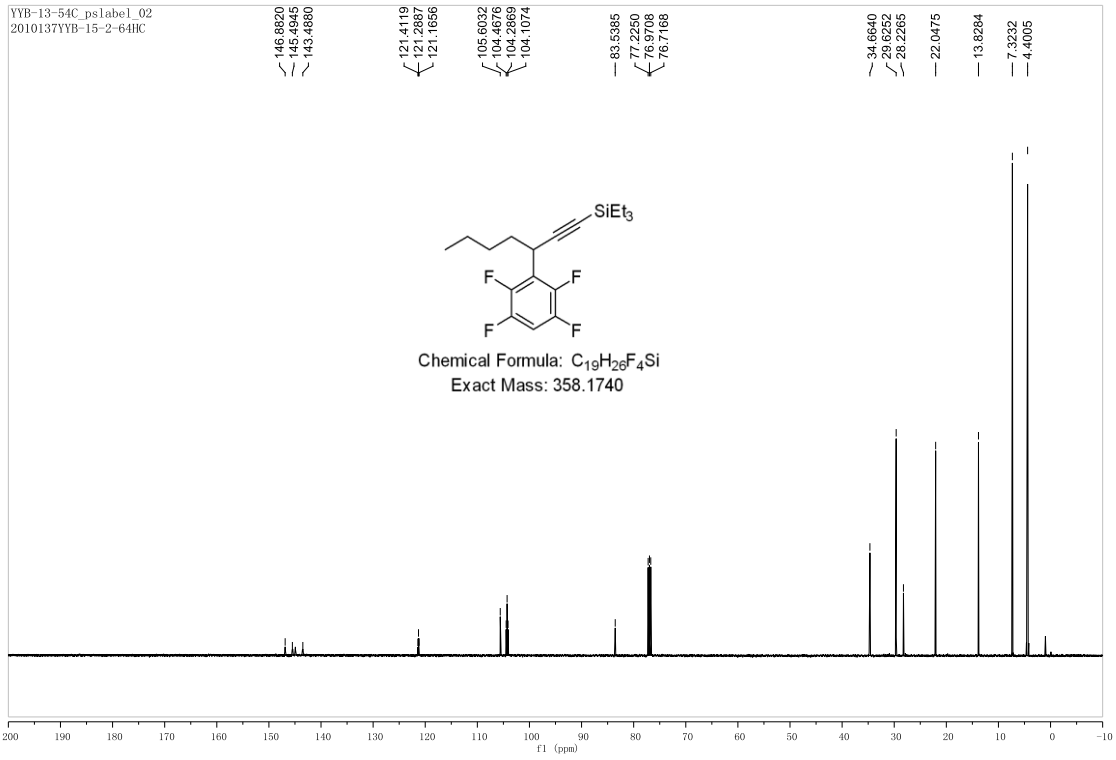

YYB-15-11F
test001
-139.4736
-139.4996
-139.5075
-139.5321
-139.5568
-139.5646
-139.5905
-142.5205
-142.5399
-142.5539
-142.5754
-142.5968
-142.6112
-142.6303
TIPS
F
F
F
F
Chemical Formula: C22H32F4Si
Exact Mass: 400.2209
1.00
2.00
f1 (ppm)


2010137yyb-15-11bs5
2010137YYB-15-11HC
146.8719
145.4288
144.9032
143.4577
121.5467
121.4236
121.3012
106.0707
104.4421
104.2820
104.0818
82.4035
77.2230
76.9661
76.7150
34.7478
29.6542
28.2379
22.0361
18.4895
13.8437
11.2101
TIPS
F
F
F
F
Chemical Formula: C22H32F4Si
Exact Mass: 400.2209
f1 (ppm)

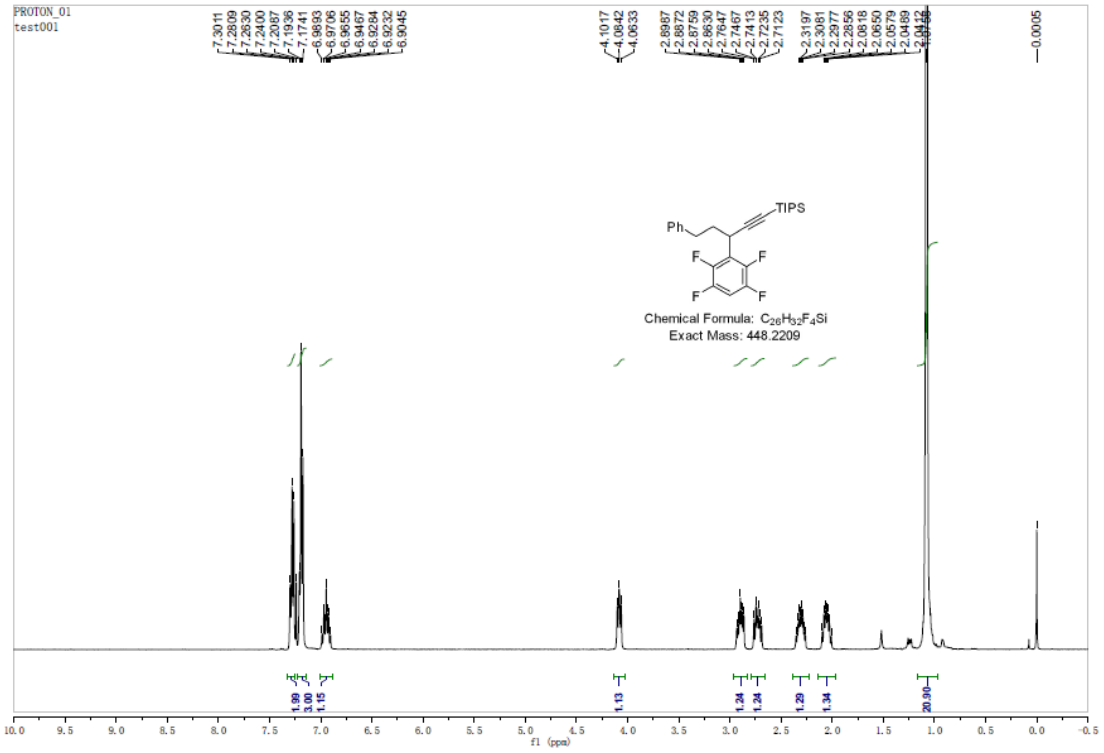
Triethyl(3-(2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4b)

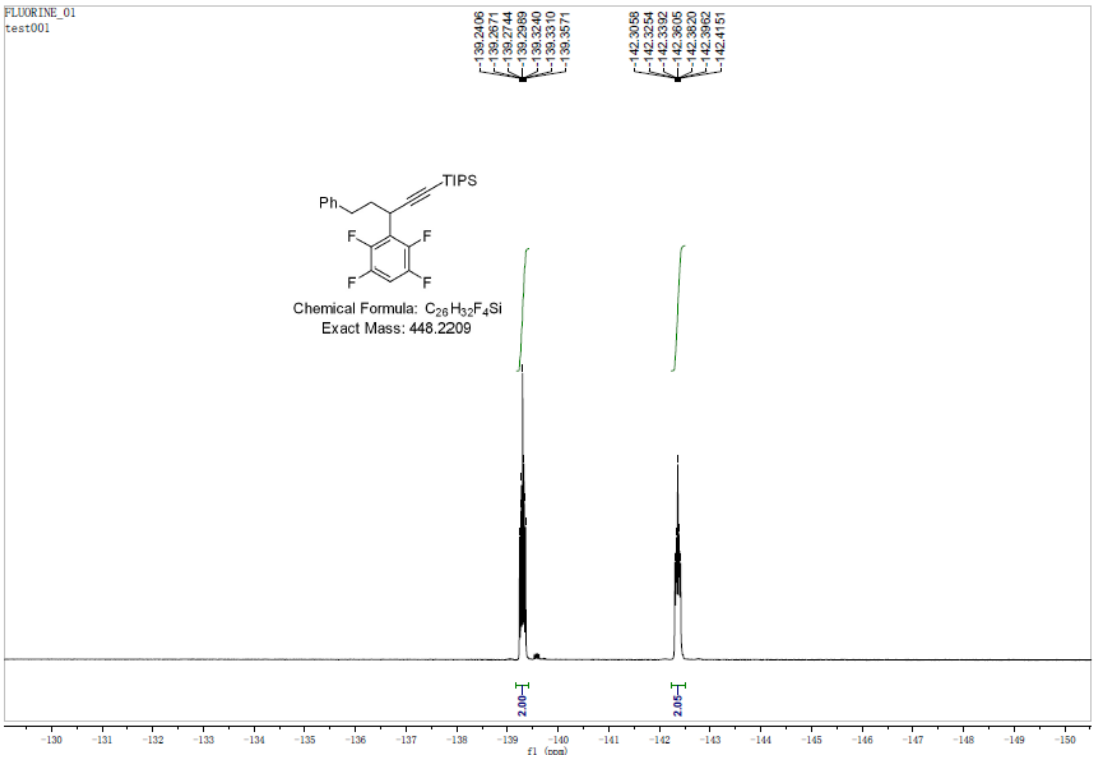


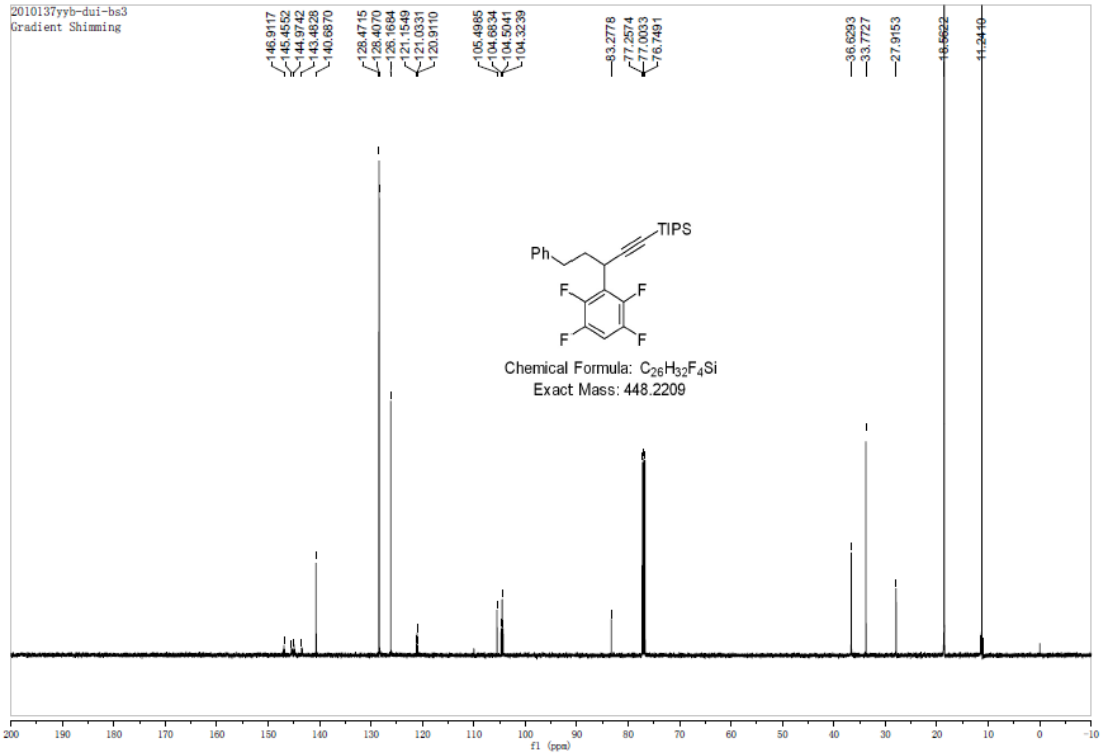




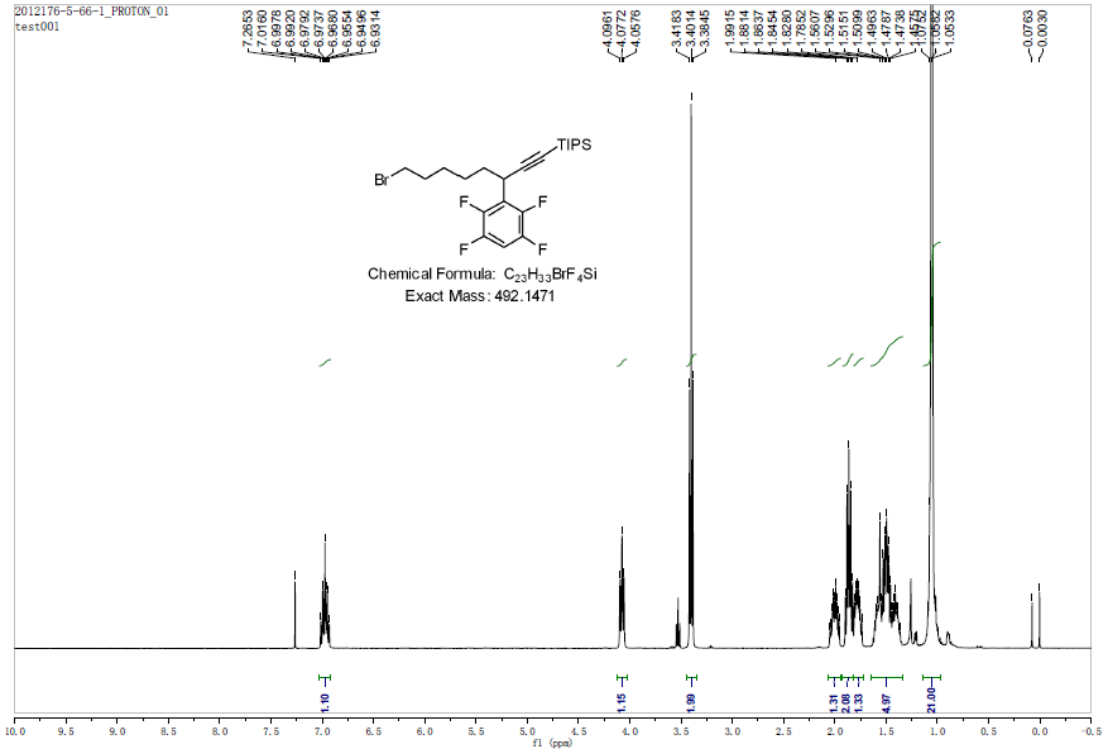
Triisopropyl(5-phenyl-3-(2,3,5,6-tetrafluorophenyl)pent-1-yn-1-yl)silane (4c)

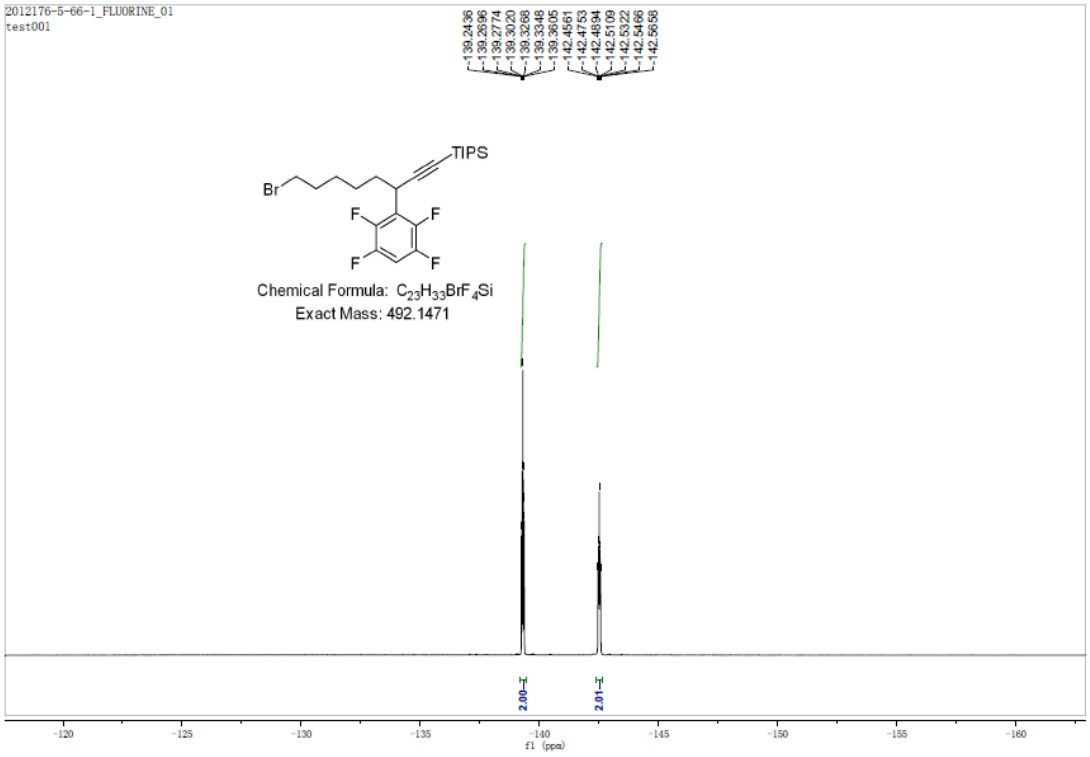


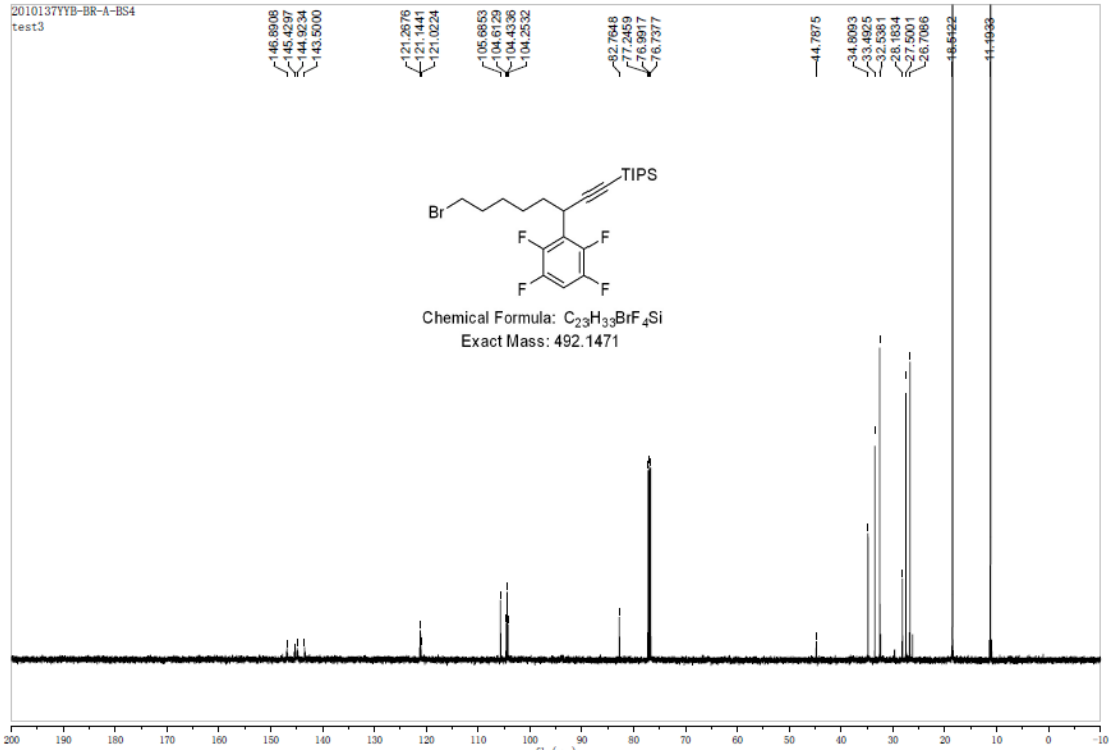

FLUORINE_01
test001
-139.2406
-139.2671
-139.2744
-139.2989
-139.3240
-139.3310
-139.3571
-142.3058
-142.3254
-142.3392
-142.3605
-142.3823
-142.3962
-142.4151
TIPS
Ph
F
F
F
F
Chemical Formula: C26H32F4Si
Exact Mass: 448.2209
2.00
2.05
f1 (ppm)


2010137yyb-dui-bs3
Gradient Shimming
146.9117
145.4552
144.9742
143.4828
140.6870
128.4715
128.4070
126.1684
121.1549
121.0331
120.9110
105.4965
104.6834
104.5041
104.3239
83.2778
77.2574
77.0033
76.7491
36.6293
33.7727
27.9153
18.5622
11.2410
TIPS
Ph
F
F
F
F
Chemical Formula: C26H32F4Si
Exact Mass: 448.2209
f1 (ppm)

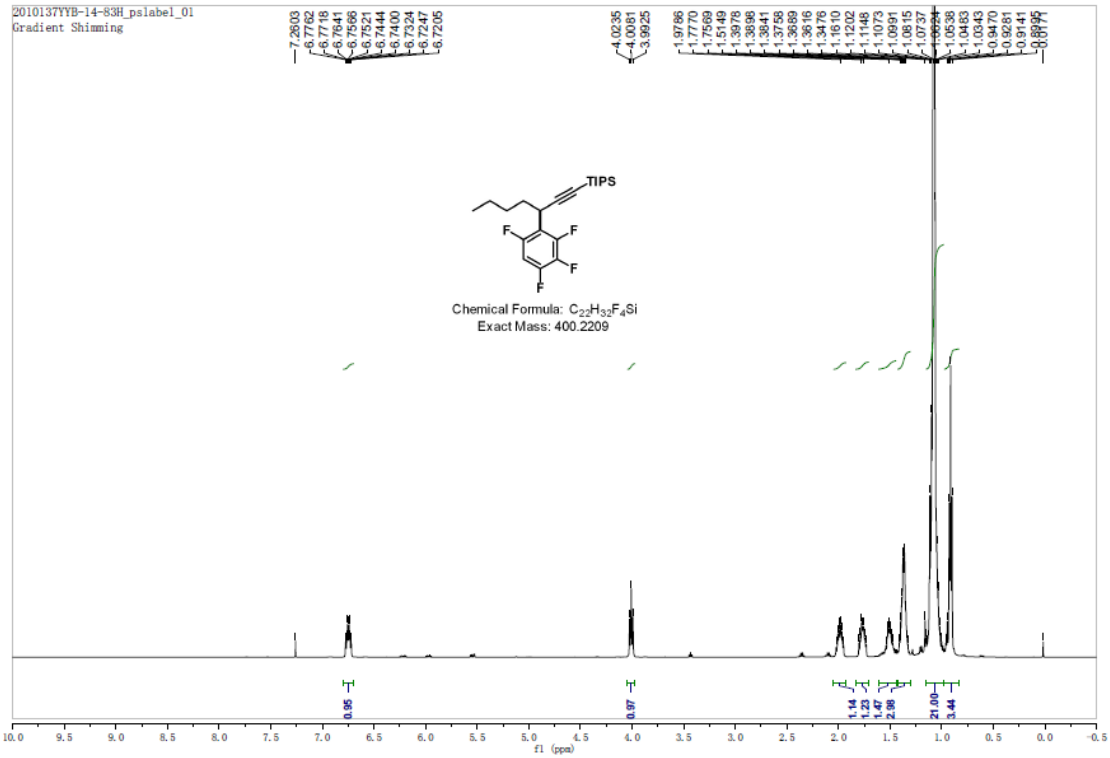
8-Bromo-3-(2,3,5,6-tetrafluorophenyl)oct-1-yn-1-yl)triisopropylsilane (4d)

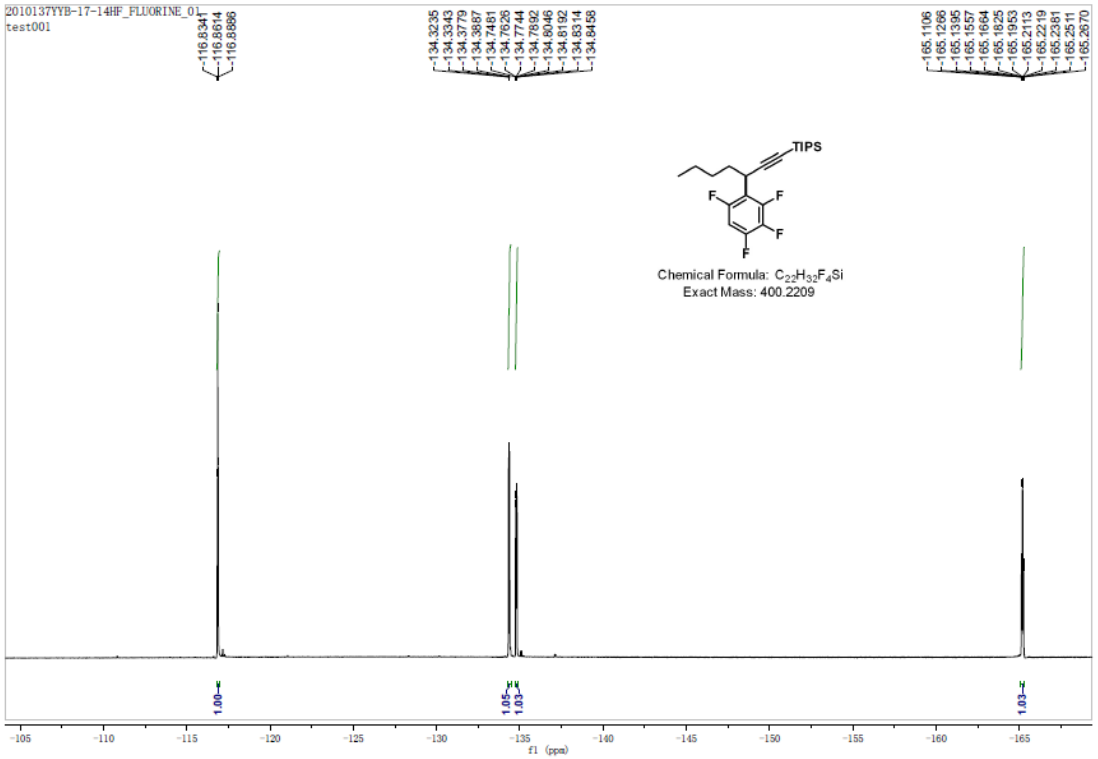


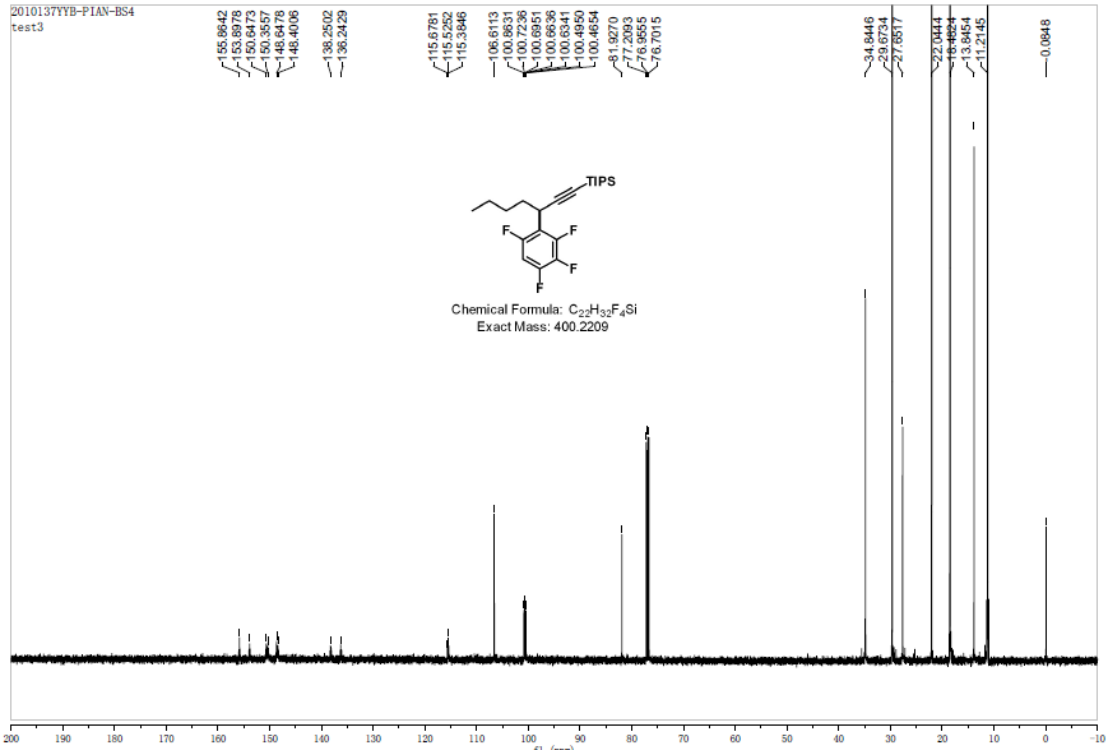




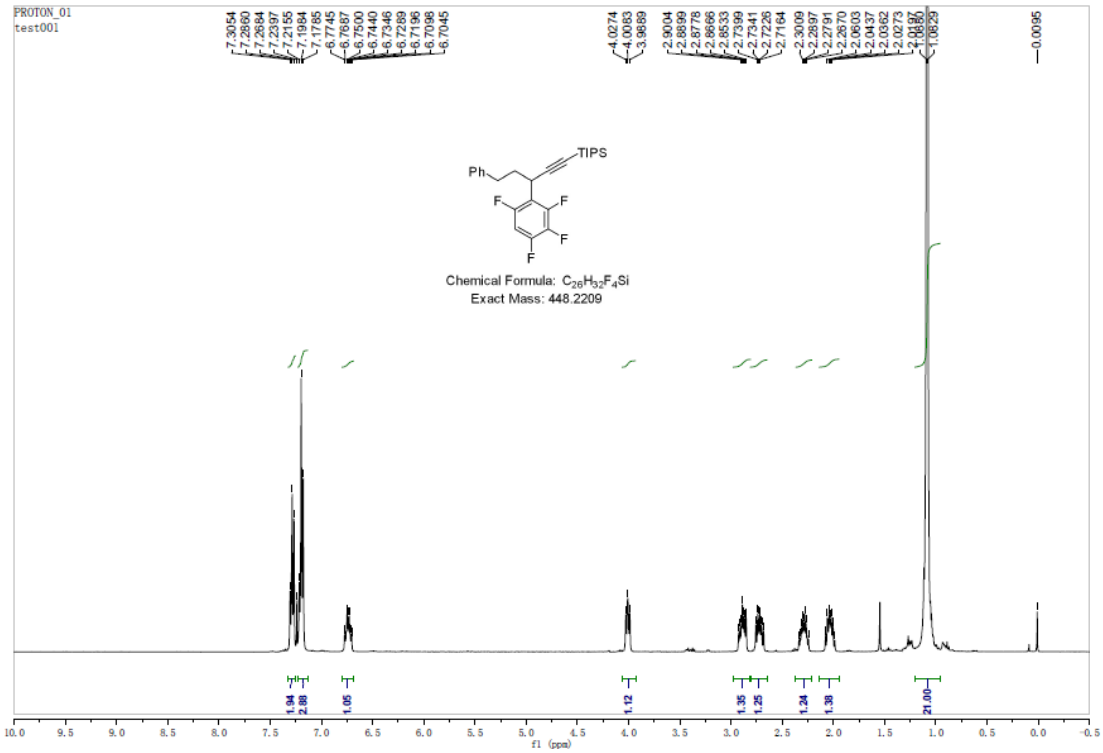
Triisopropyl(3-(2,3,4,6-tetrafluorophenyl)hept-1-yn-1-yl)silane (4e)

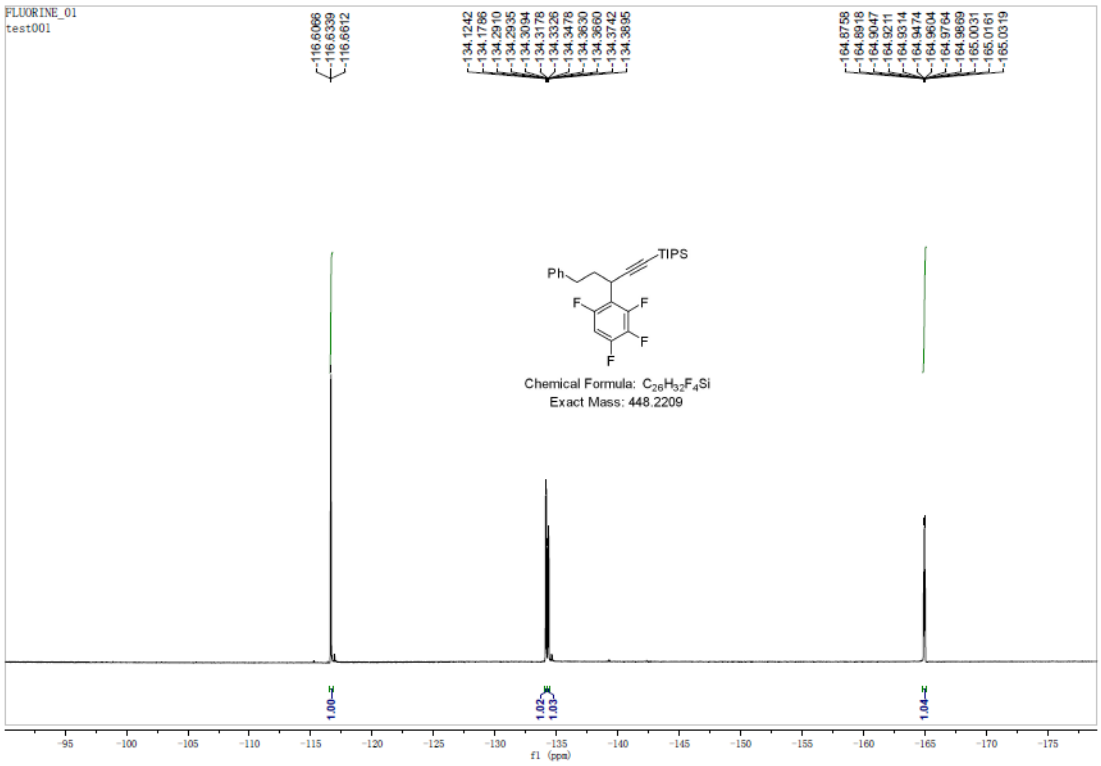


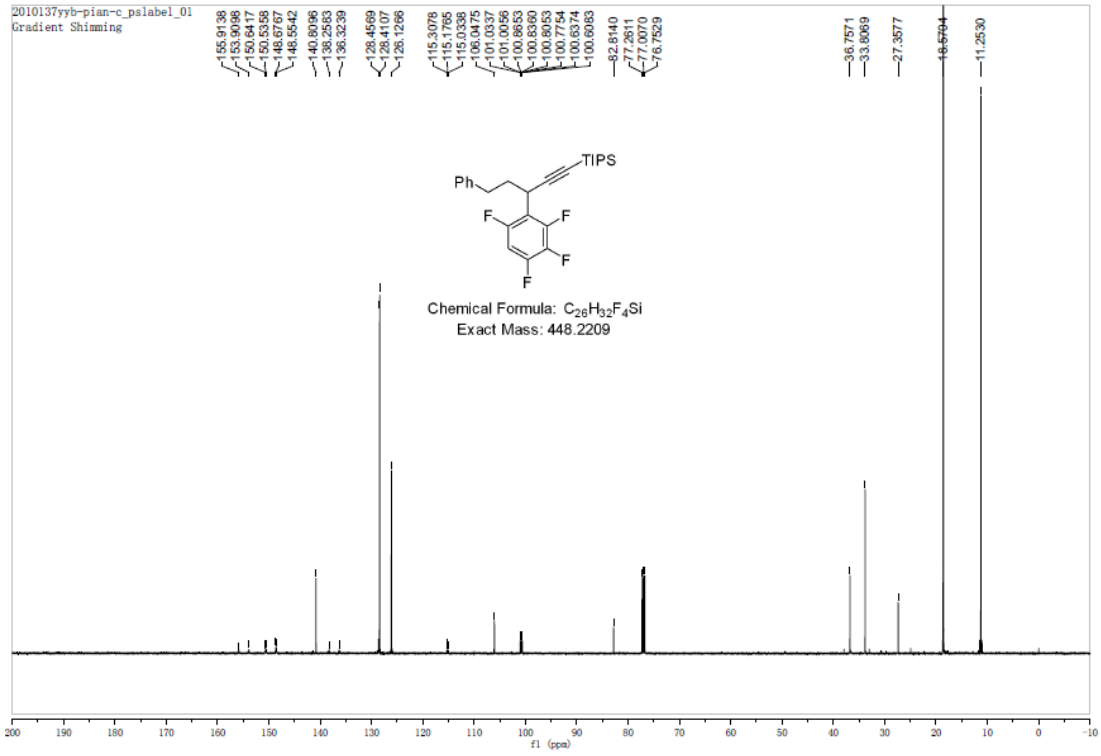

2010137YYB-17-14HF_FLUORINE_01
test001
-116.8341
-116.8614
-116.8886
-134.3235
-134.3343
-134.3779
-134.3867
-134.7481
-134.7626
-134.7744
-134.7892
-134.8046
-134.8192
-134.8314
-134.8458
-165.1106
-165.1266
-165.1395
-165.1557
-165.1664
-165.1825
-165.1953
-165.2113
-165.2219
-165.2381
-165.2511
-165.2670
TIPS
F
F
F
F
Chemical Formula: C22H32F4Si
Exact Mass: 400.2209
1.00
1.05
1.03
1.03
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)


2010137YYB-PIAN-BS4
test3
155.8642
153.8978
150.6473
150.3557
148.6478
148.4006
138.2502
136.2429
115.6781
115.5252
115.3846
106.6113
100.8631
100.7236
100.6951
100.6636
100.6341
100.4950
100.4654
81.9270
77.2093
76.9555
76.7015
34.8446
29.6734
27.8517
22.0444
18.4824
13.8454
11.2145
-0.0848
TIPS
F
F
F
F
Chemical Formula: C22H32F4Si
Exact Mass: 400.2209
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

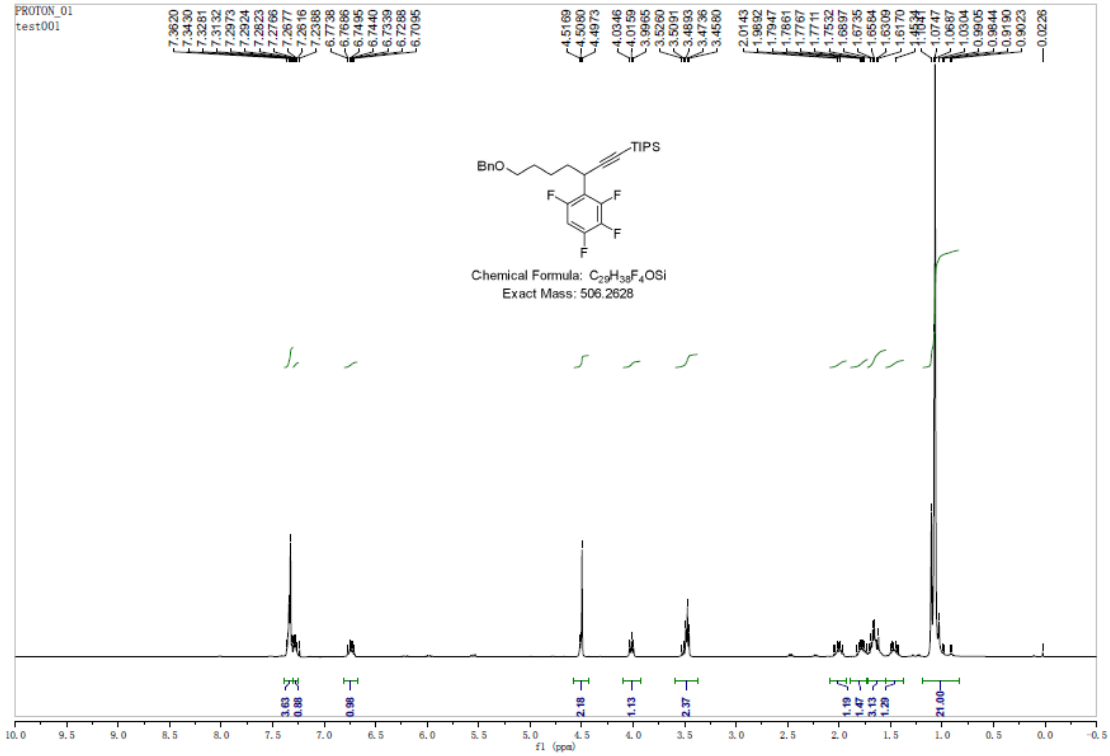
Triisopropyl(5-phenyl-3-(2,3,4,6-tetrafluorophenyl)pent-1-yn-1-yl)silane (4f)

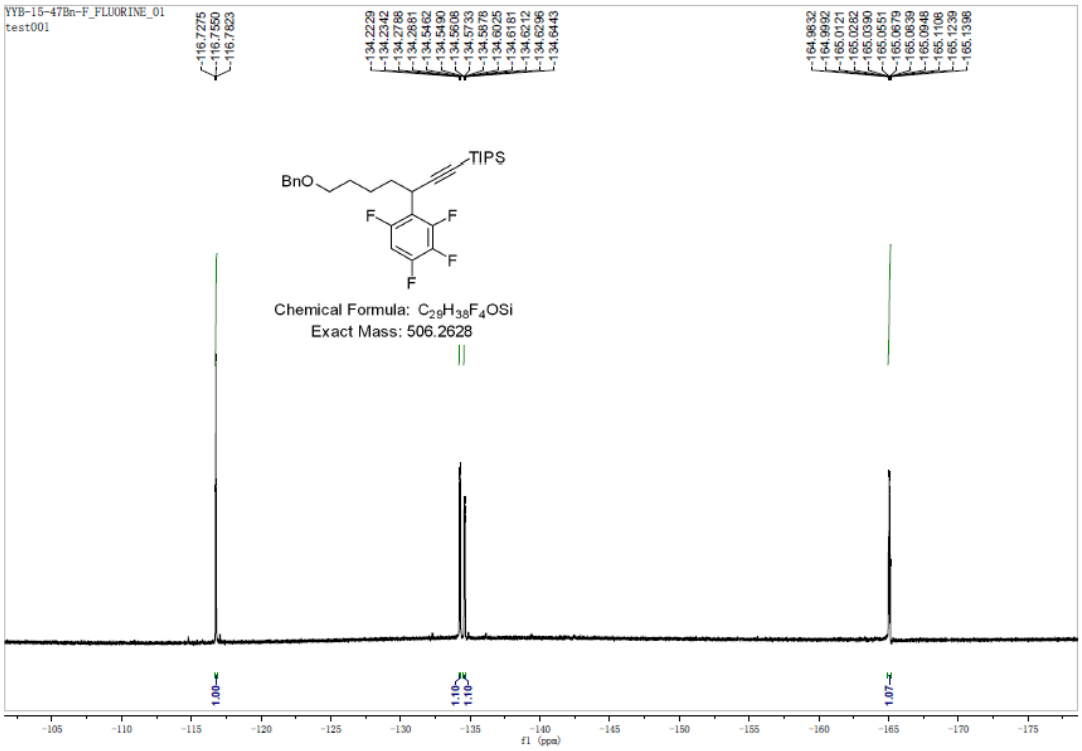


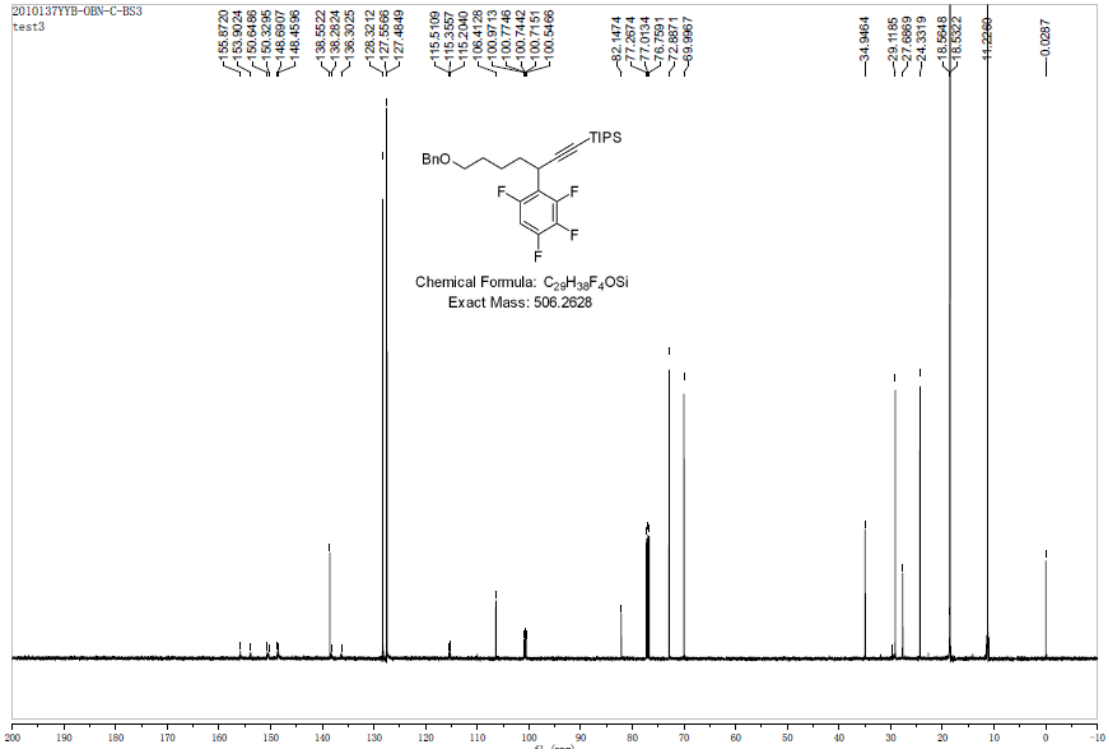




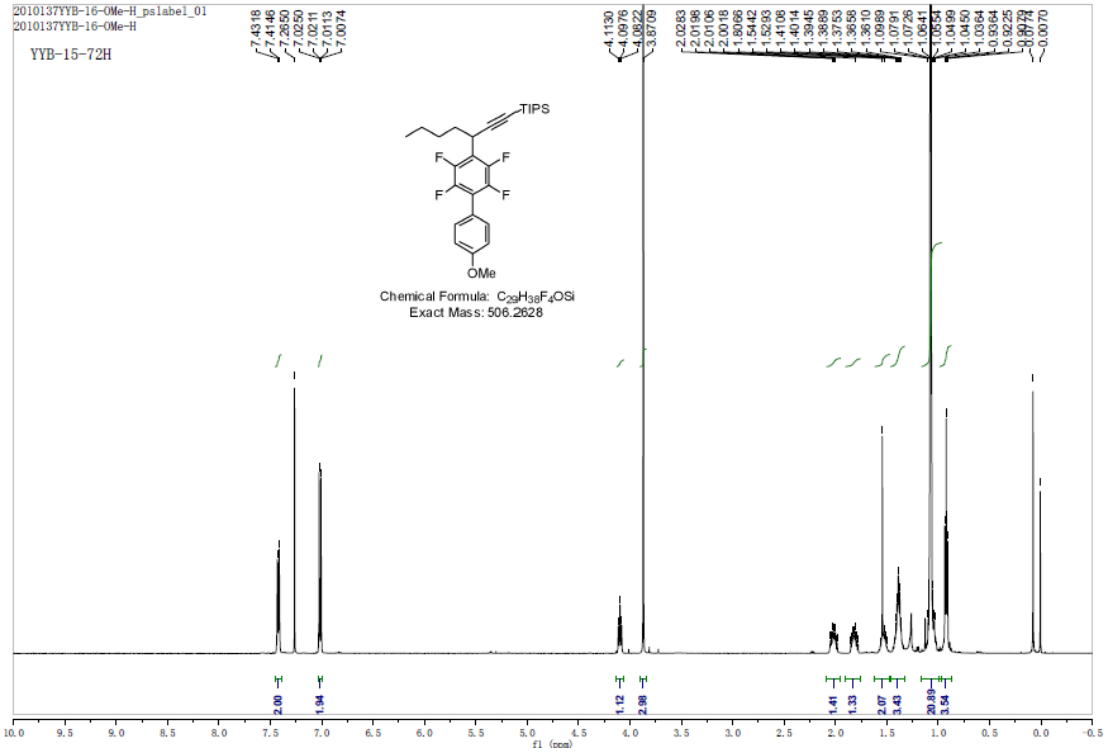
7-(Benzyloxy)-3-(2,3,4,6-tetrafluorophenyl)hept-1-yn-1-yl)triisopropylsilane (4g)

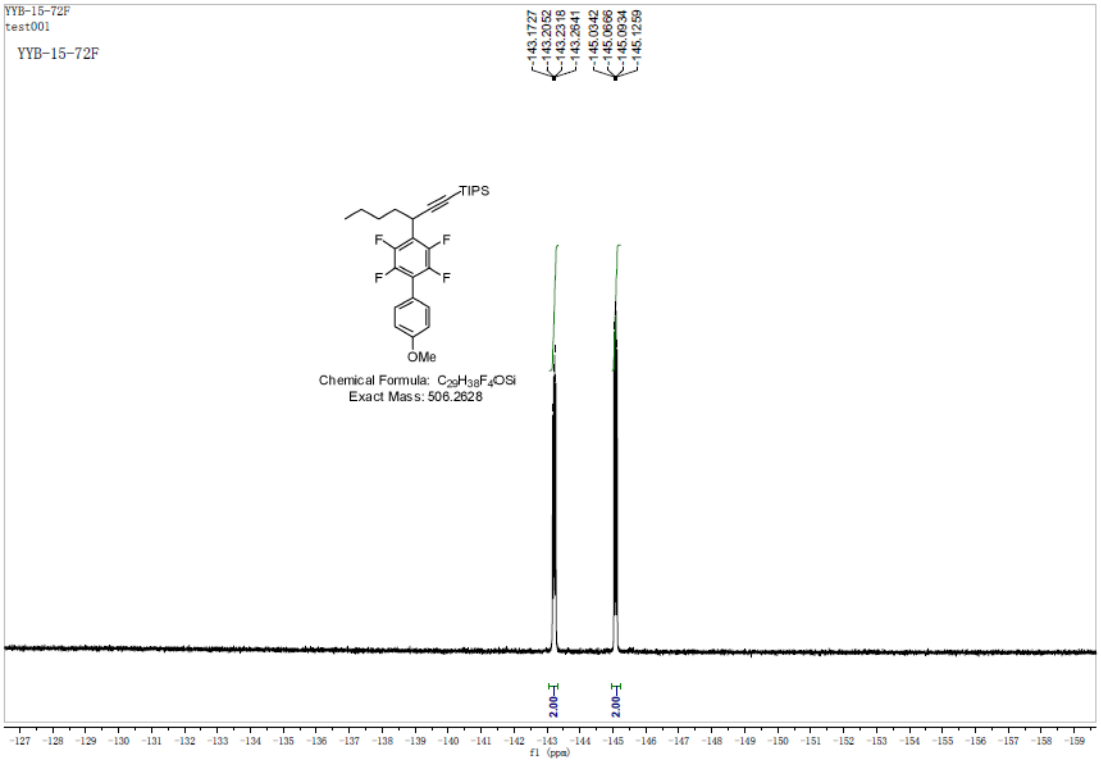


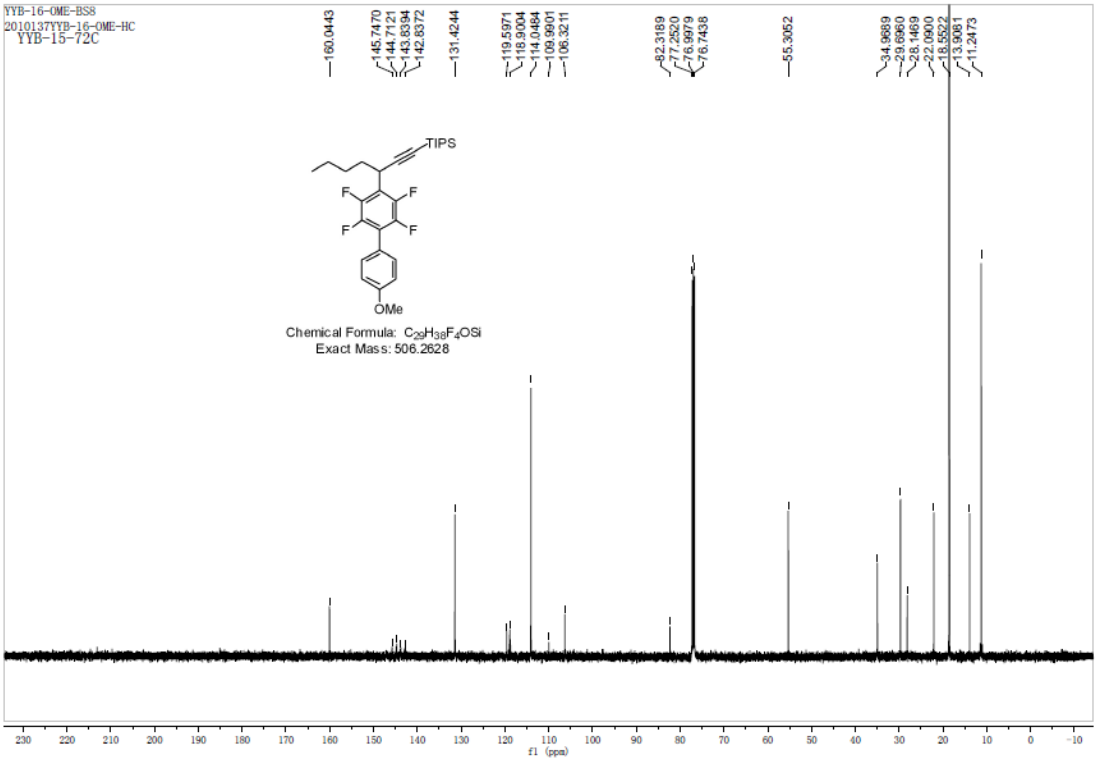

YYB-15-47Bn-F_FLUORINE_01
test001
-116.7275
-116.7550
-116.7823
-134.2229
-134.2342
-134.2788
-134.2881
-134.5462
-134.5490
-134.5608
-134.5733
-134.5878
-134.6025
-134.6181
-134.6212
-134.6296
-134.6443
-164.9832
-164.9992
-165.0121
-165.0282
-165.0390
-165.0551
-165.0679
-165.0839
-165.0948
-165.1106
-165.1239
-165.1398
TIPS
BnO
F
F
F
F
Chemical Formula: C29H38F4OSi
Exact Mass: 506.2628
1.00
1.10
1.10
1.07
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)


20101137YYB-OBN-C-BS3
test3
155.8720
153.9024
150.6486
150.3295
148.6907
148.4596
138.5522
138.2824
136.3025
128.3212
127.5566
127.4849
115.5109
115.3557
115.2040
106.4128
100.9713
100.7746
100.7442
100.7151
100.5466
82.1474
77.2674
77.0134
76.7591
72.8871
69.9967
34.9464
29.1185
27.6869
24.3319
18.5648
18.5322
14.2260
0.0257
TIPS
BnO
F
F
F
F
Chemical Formula: C29H38F4OSi
Exact Mass: 506.2628
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

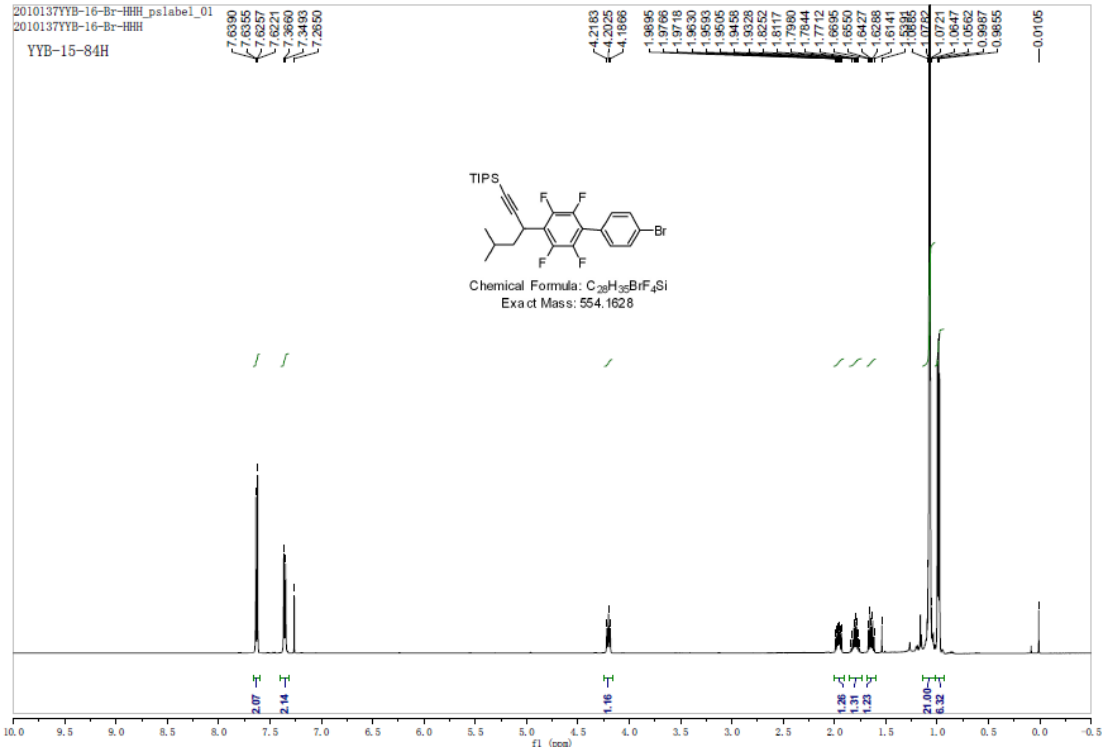
Triisopropyl(3-(2,3,5,6-tetrafluoro-4'-methoxy-[1,1'-biphenyl]-4-yl)hept-1-yn-1-yl)silane (4h)

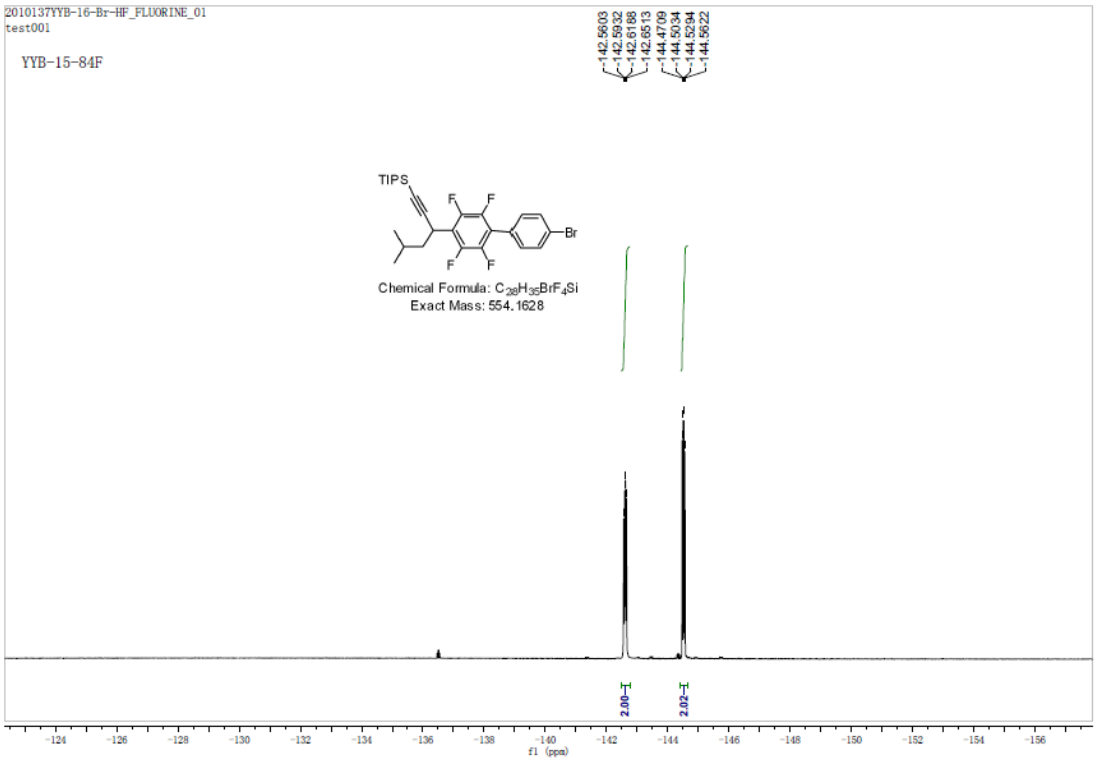


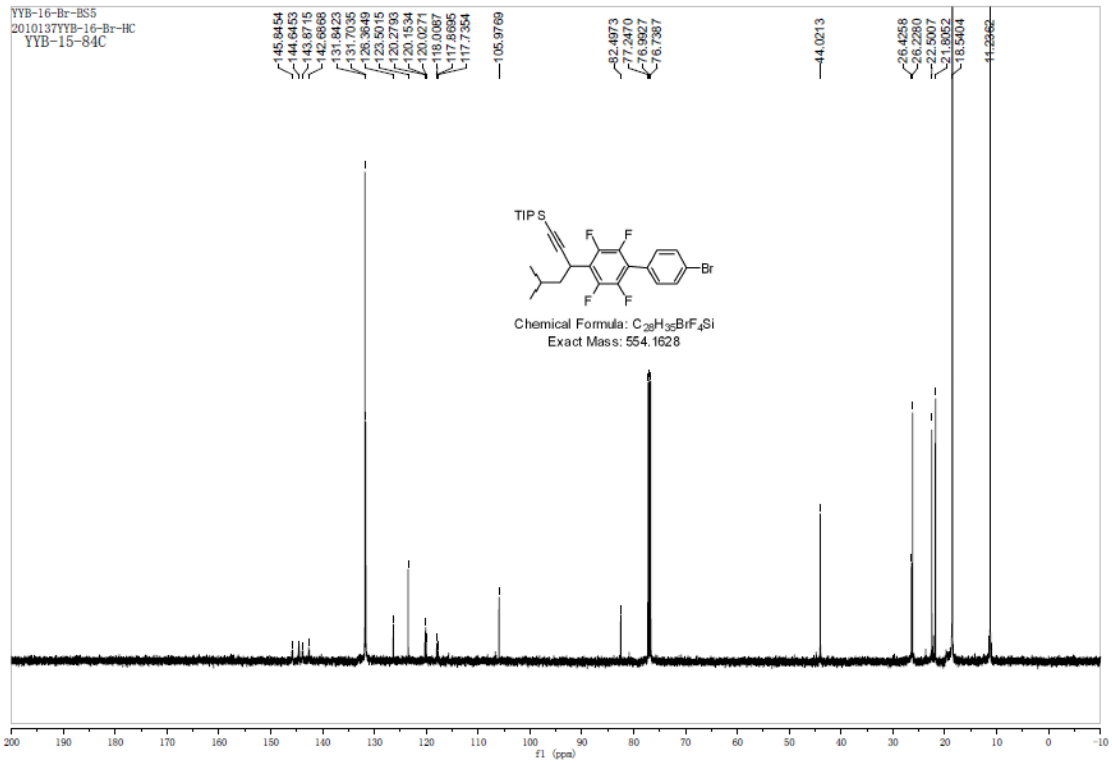




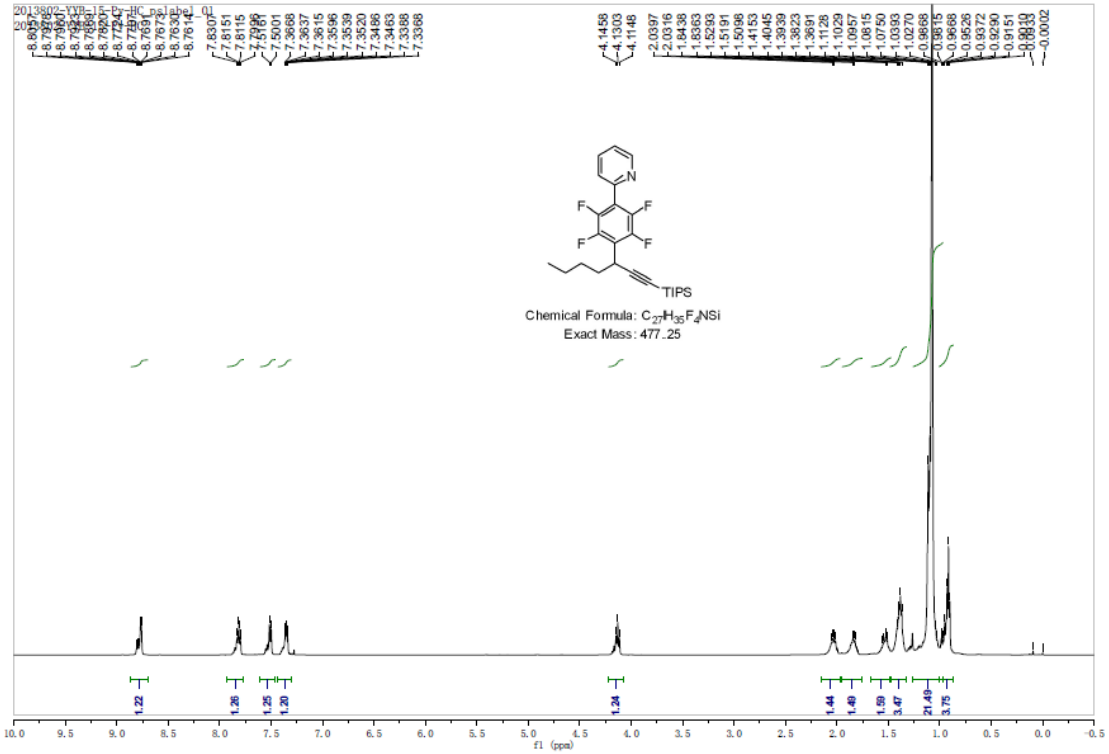
(3-(4'-Bromo-2,3,5,6-tetrafluoro-[1,1'-biphenyl]-4-yl)-5-methylhex-1-yn-1-yl)triisopropylsilane (4i)

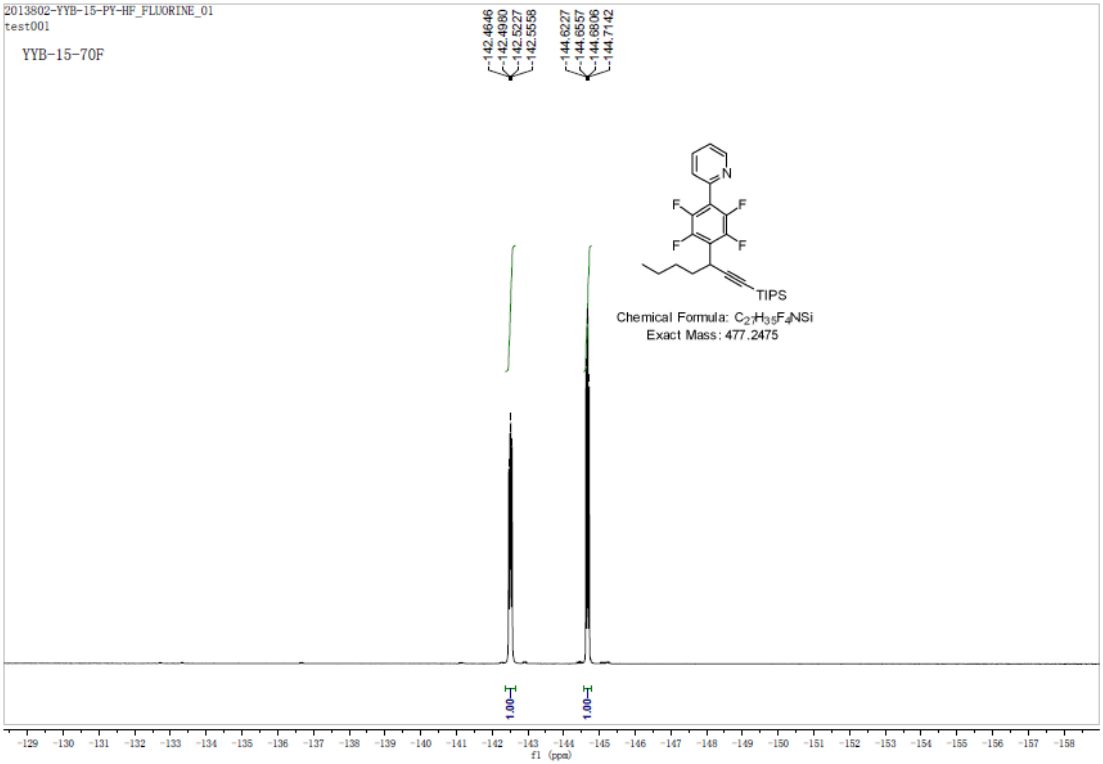


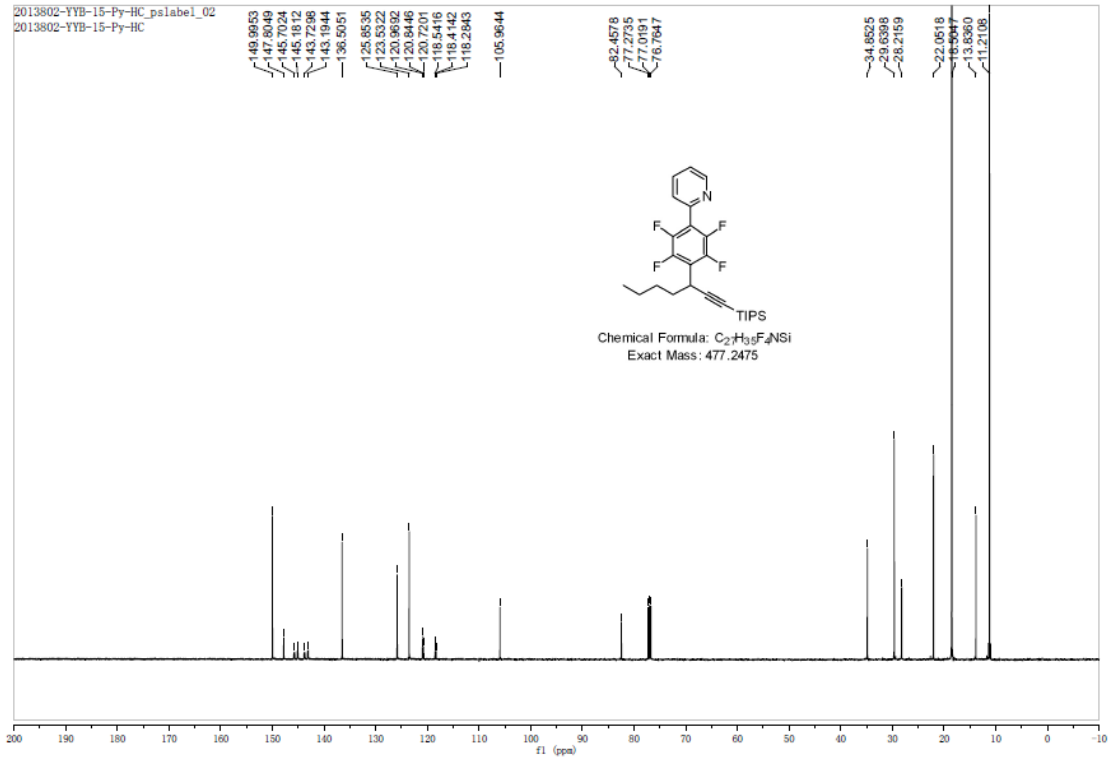

2010137YYB-16-Br-HF_FLUORINE_01
test001
YYB-15-84F
-142.5603
-142.5932
-142.6188
-142.6513
-144.4709
-144.5034
-144.5294
-144.5622
TIPS
F
F
Br
F
F
Chemical Formula: C28H35BrF4Si
Exact Mass: 554.1628
2.00
2.02
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
f1 (ppm)


YYB-16-Br-BS5
2010137YYB-16-Br-HC
YYB-15-84C
145.8454
144.6453
143.8715
142.6668
131.8423
131.7035
126.3649
123.5015
120.2793
120.1534
120.0271
118.0087
117.8695
117.7354
105.9769
82.4973
77.2470
76.9927
76.7387
44.0213
26.4258
26.2280
22.5007
21.8052
18.5404
11.2362
TIPS
F
F
Br
F
F
Chemical Formula: C28H35BrF4Si
Exact Mass: 554.1628
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

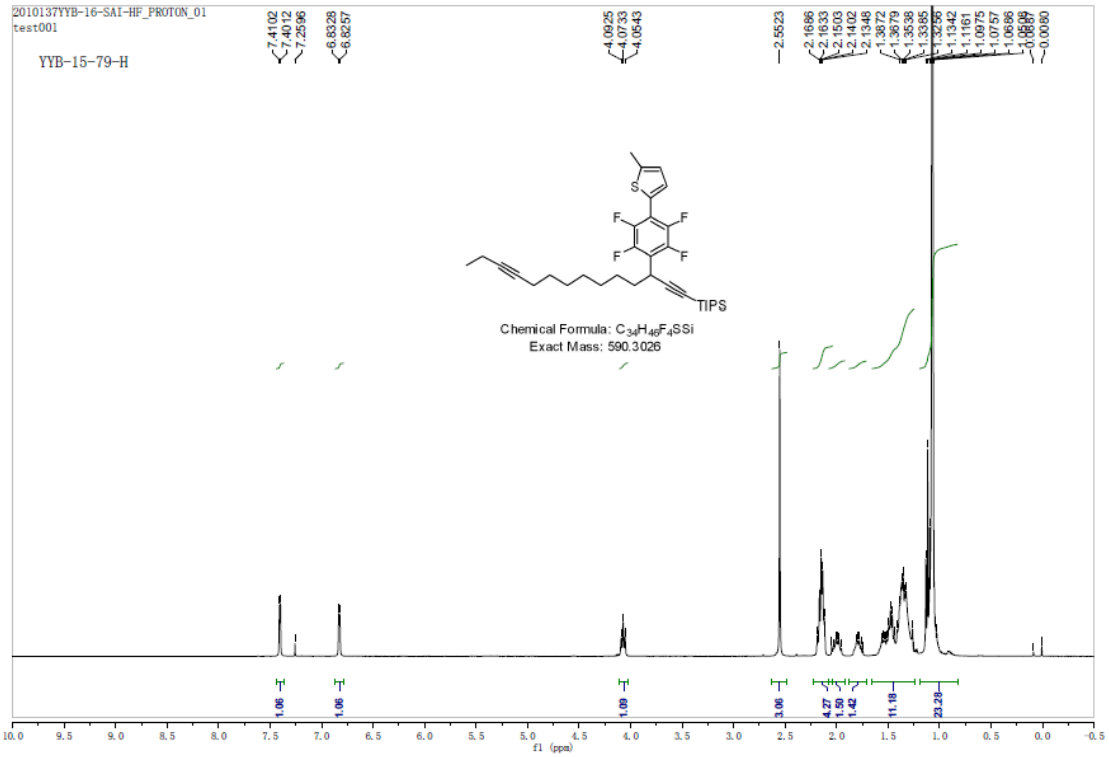
2-(2,3,5,6-Tetrafluoro-4-(1-(triisopropylsilyl)hept-1-yn-3-yl)phenyl)pyridine (4j)

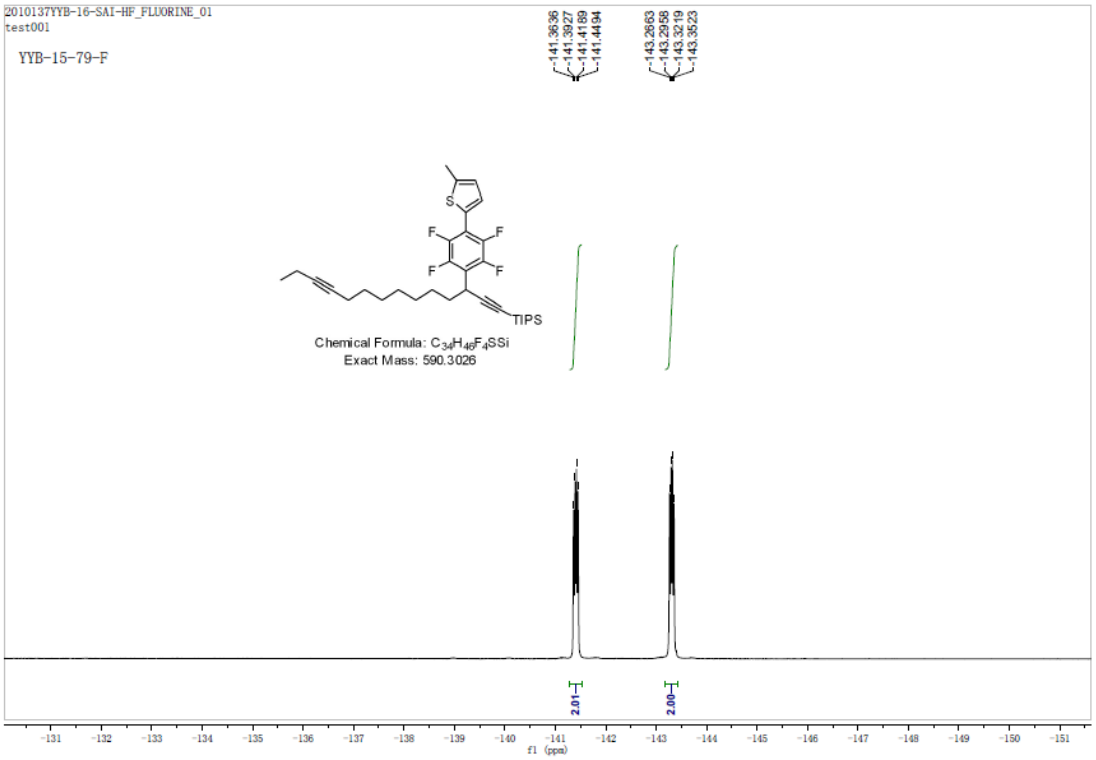


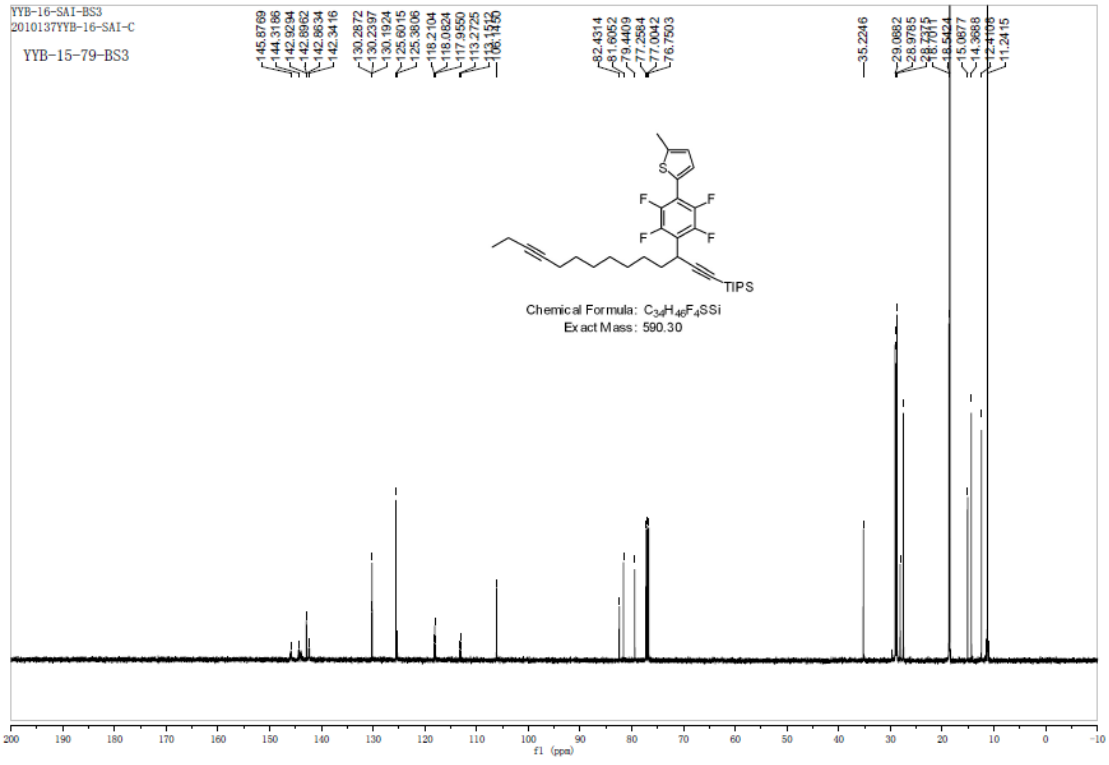




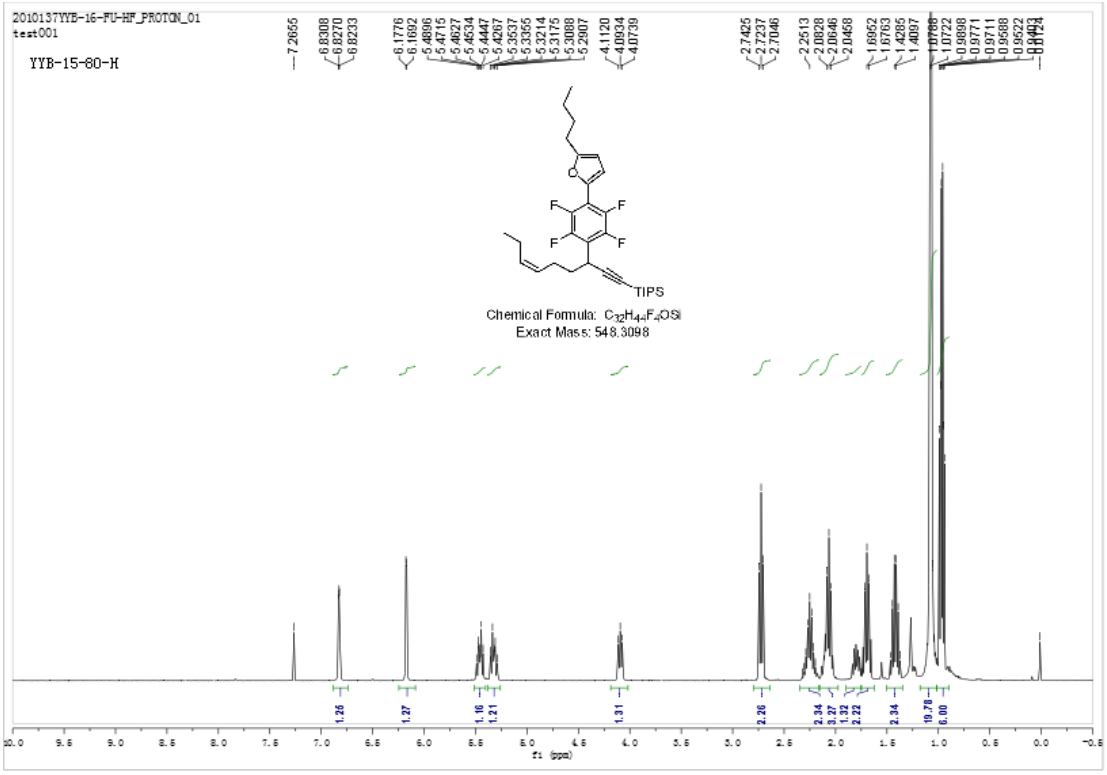
Triisopropyl(3-(2,3,5,6-tetrafluoro-4-(5-methylthiophen-2-yl)phenyl)tetradeca-1,11-diyn-1-yl)silane (4k)

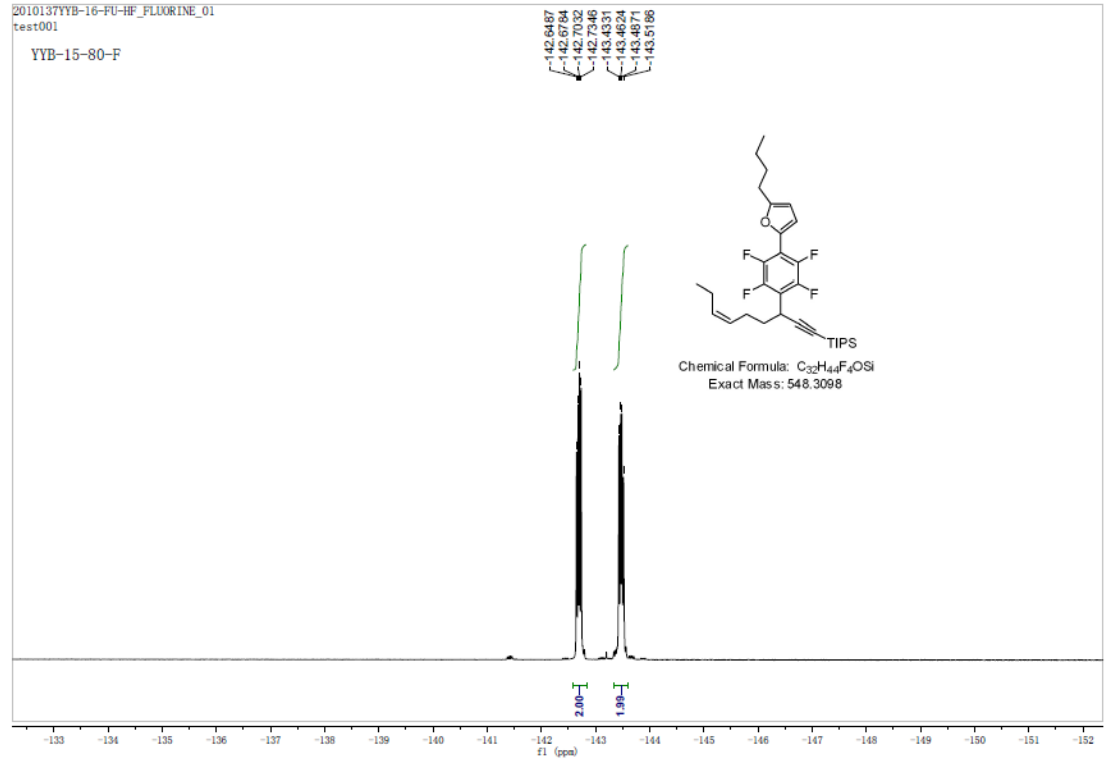


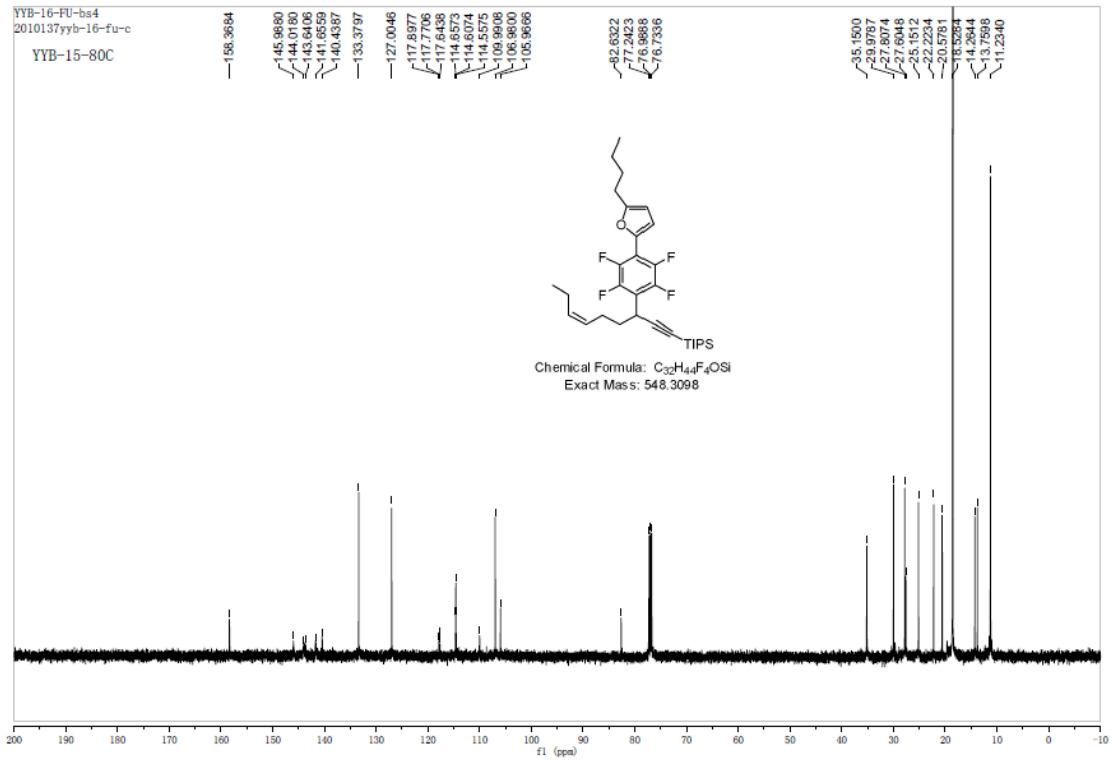

2010137YYB-16-SAI-HF_FLUORINE_01
test001
YYB-15-79-F
141.3636
141.3927
141.4189
141.4494
143.2663
143.2938
143.3219
143.3523
TIPS
Chemical Formula: C34H46F4SSi
Exact Mass: 590.3026
2.01
2.00
f1 (ppm)


YYB-16-SAI-BS3
2010137YYB-16-SAI-C
YYB-15-79-BS3
145.8769
144.3166
142.9234
142.8962
142.8634
142.3416
130.2872
130.2397
130.1924
125.6015
125.3806
118.2104
118.0624
117.9550
113.2725
82.4314
81.6052
79.4409
77.2984
77.0042
76.7503
35.2246
29.0682
28.9785
18.5424
15.0677
14.3668
12.4106
11.2415
TIPS
Chemical Formula: C34H46F4SSi
Exact Mass: 590.30
f1 (ppm)

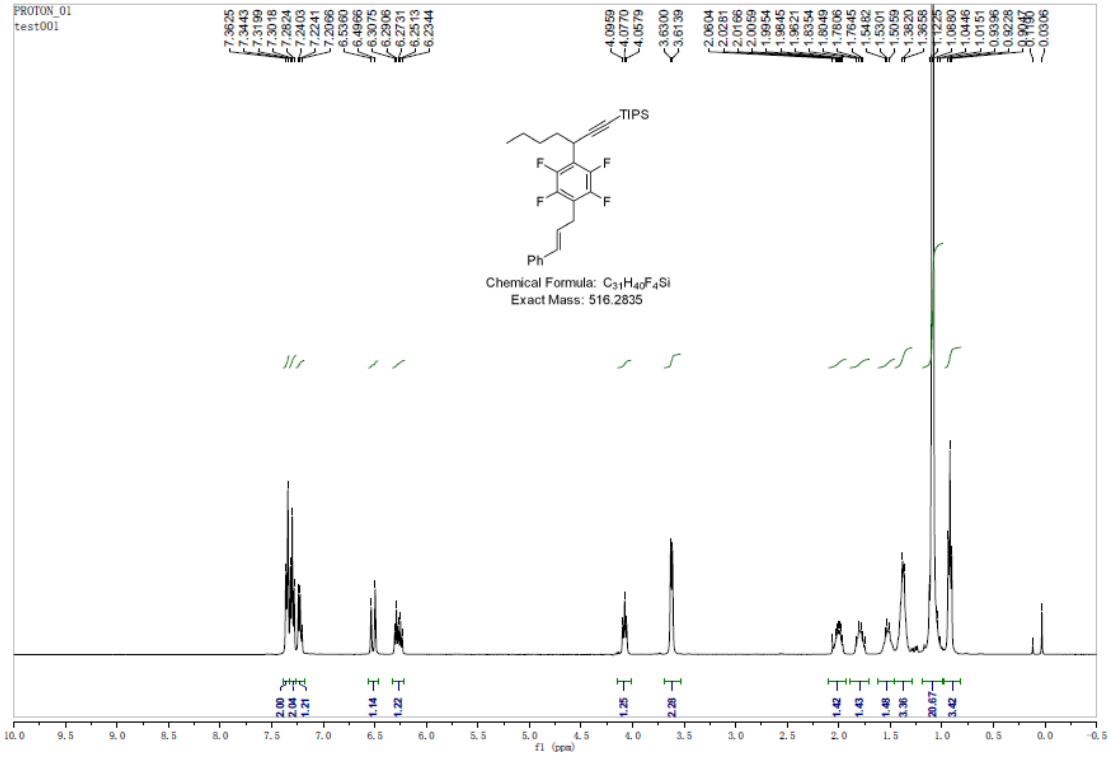
(*Z*)-(3-(4-(5-Butylfuran-2-yl)-2,3,5,6-tetrafluorophenyl)non-6-en-1-yn-1-yl)triisopropylsilane (4l)

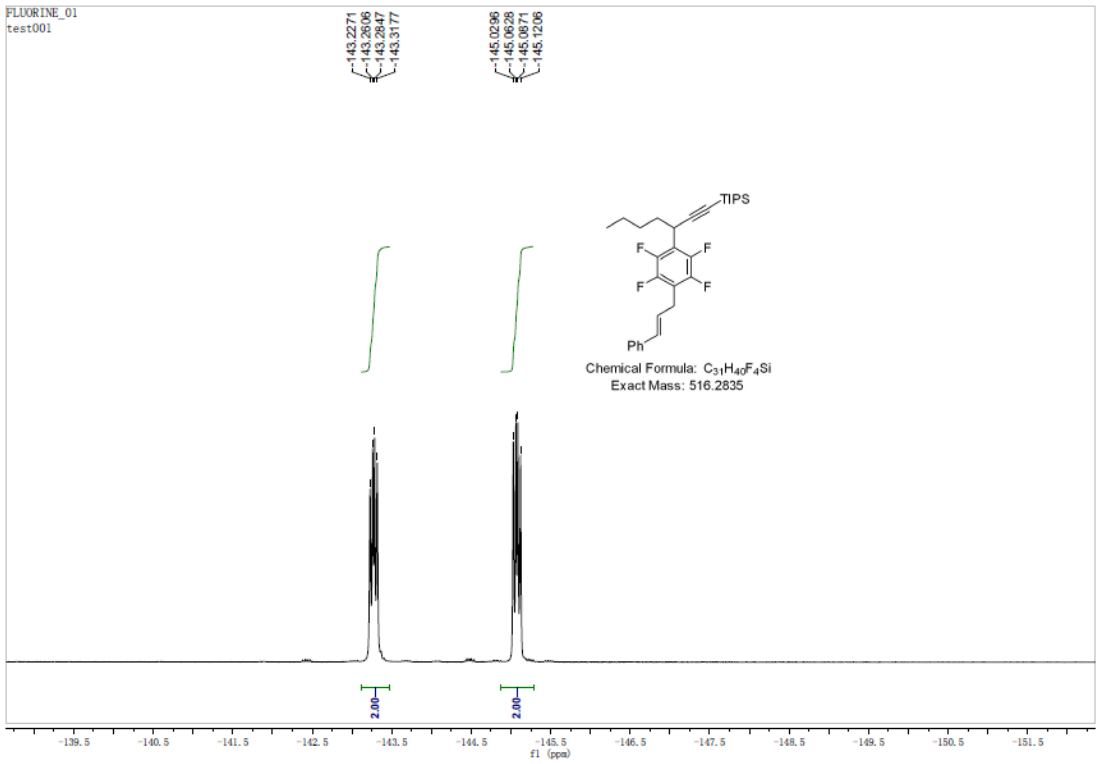


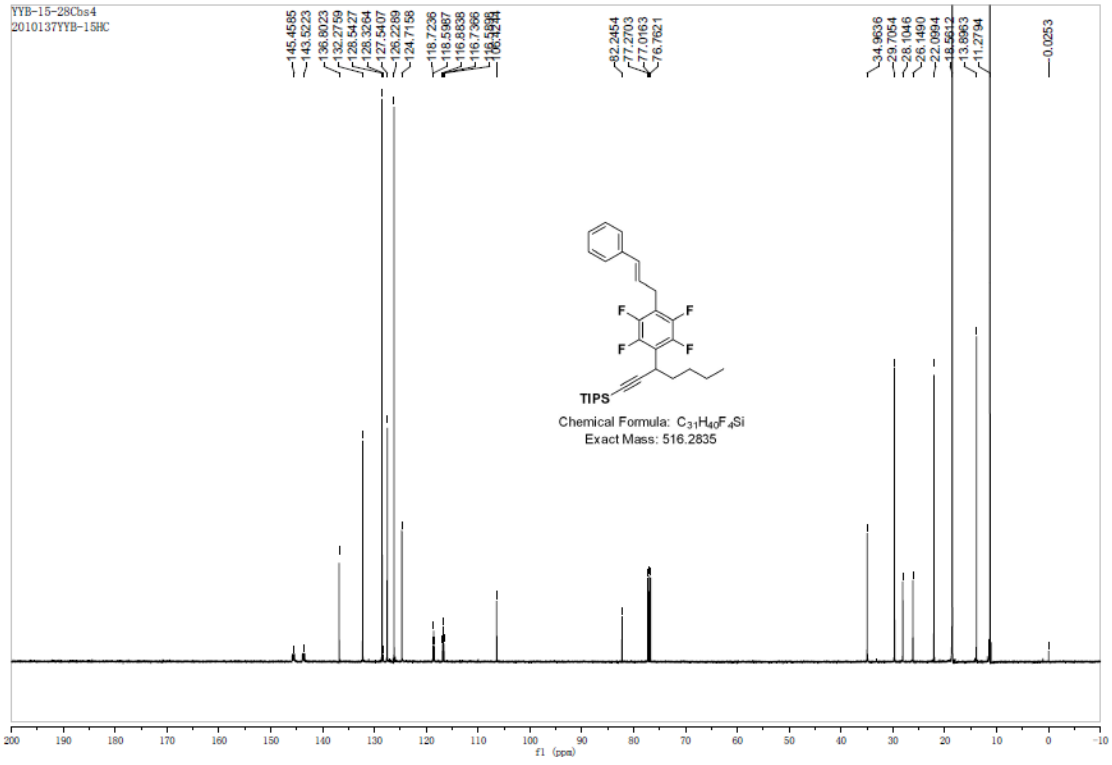




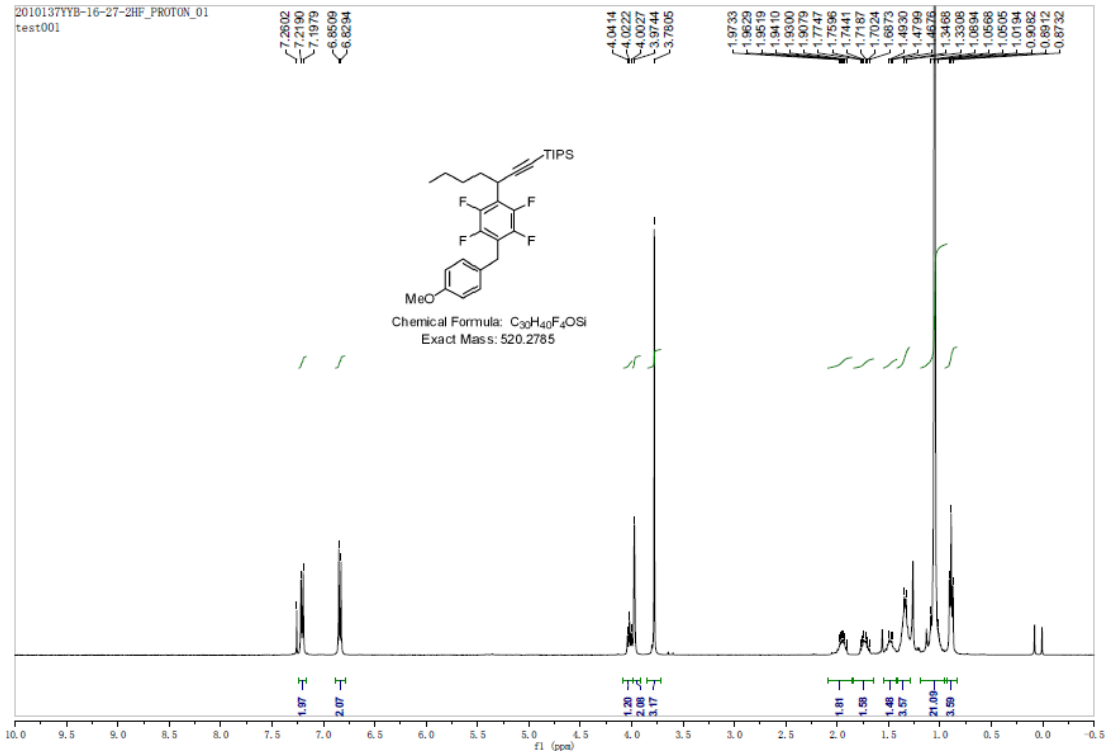
(3-(4-Cinnamyl-2,3,5,6-tetrafluorophenyl)hept-1-yn-1-yl)triisopropylsilane (6)

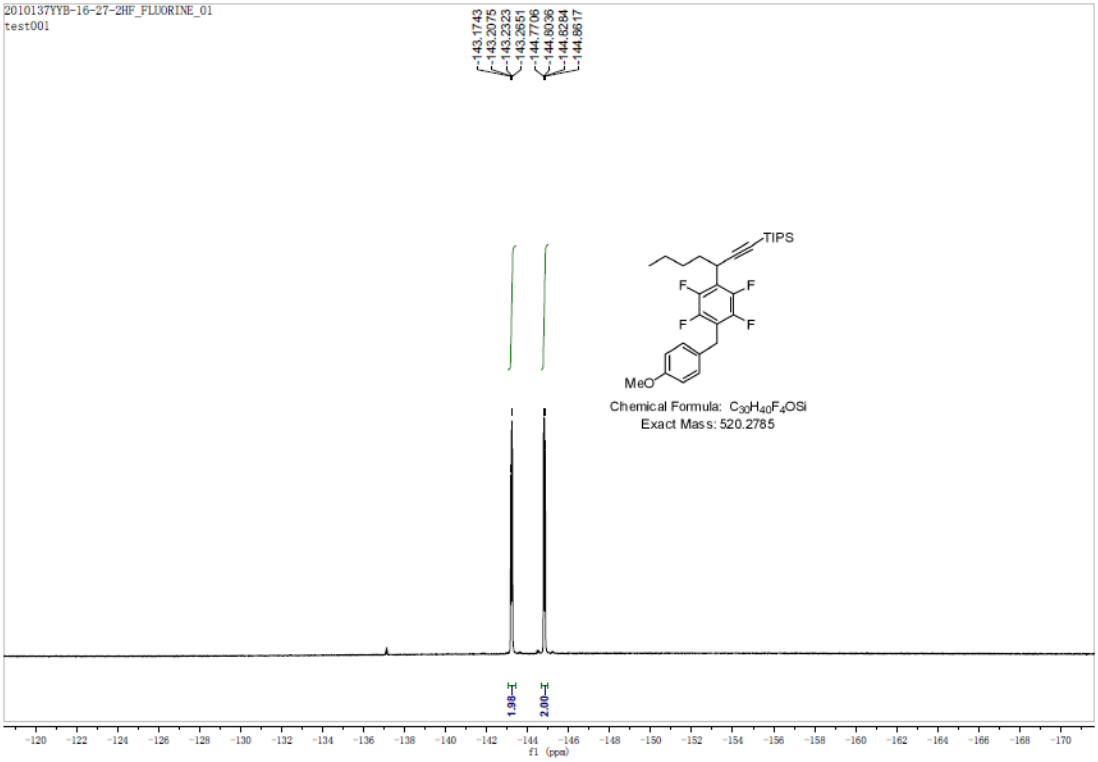


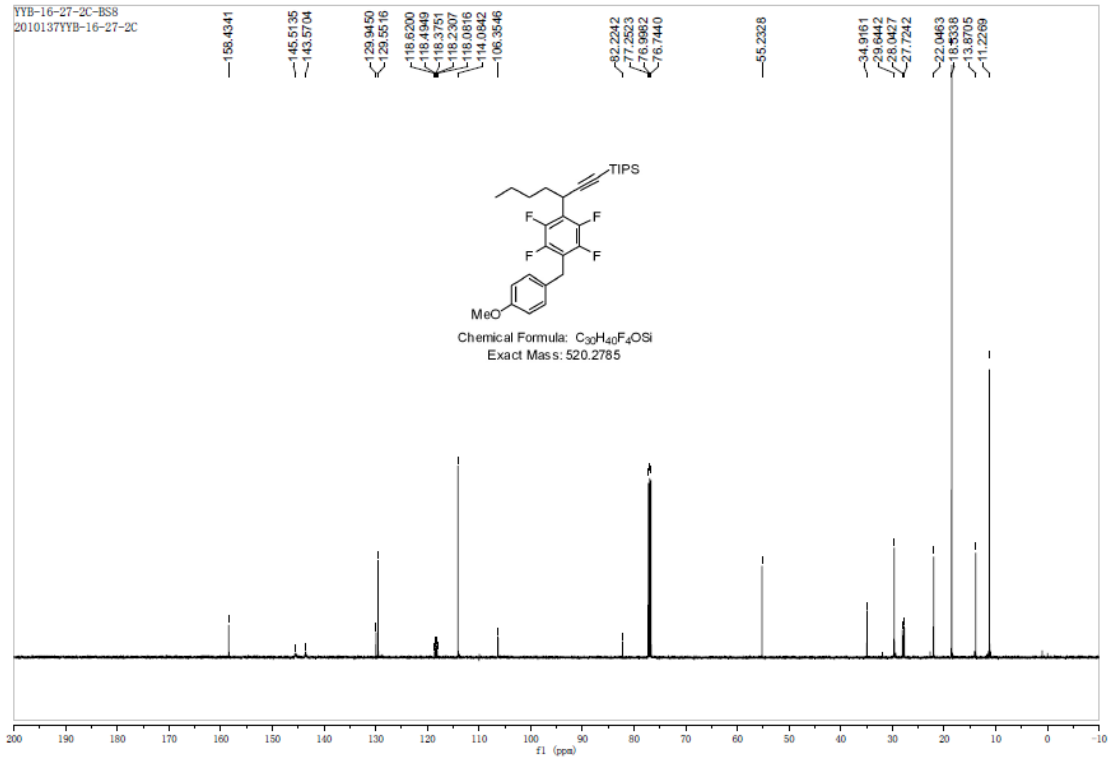

FLUORINE_01
test001
143.2271
143.2606
143.2847
143.3177
145.0296
145.0628
145.0871
145.1206
TIPS
F
F
F
F
Ph
Chemical Formula: C31H40F4Si
Exact Mass: 516.2835
2.00
2.00
f1 (ppm)


YYB-15-28Cbs4
2010137YYB-15HC
145.4585
143.5223
136.8023
132.2759
128.5427
128.3264
127.5407
126.2289
124.7158
118.7236
118.5967
116.8838
116.7366
82.2454
77.2703
77.0163
76.7621
34.9636
29.7054
28.1046
26.1490
22.0994
18.5612
13.8963
11.2794
0.0253
F
F
F
F
TIPS
Chemical Formula: C31H40F4Si
Exact Mass: 516.2835
f1 (ppm)

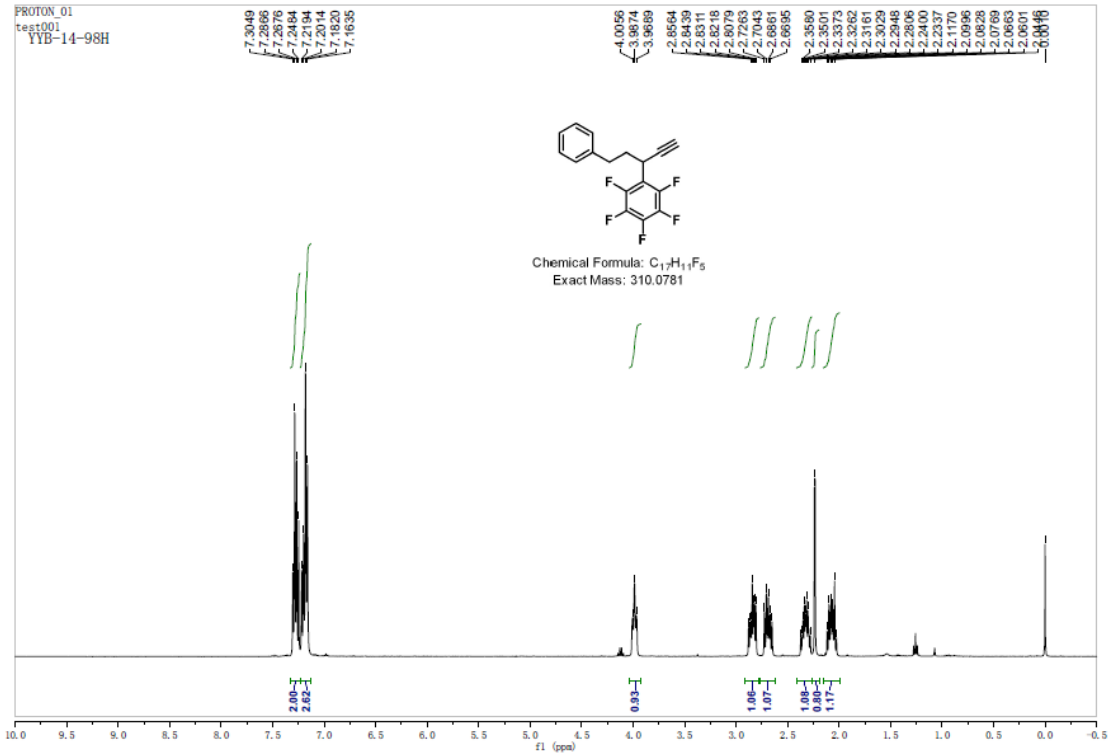
Triisopropyl(3-(2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)phenyl)hept-1-yn-1-yl)silane (8)

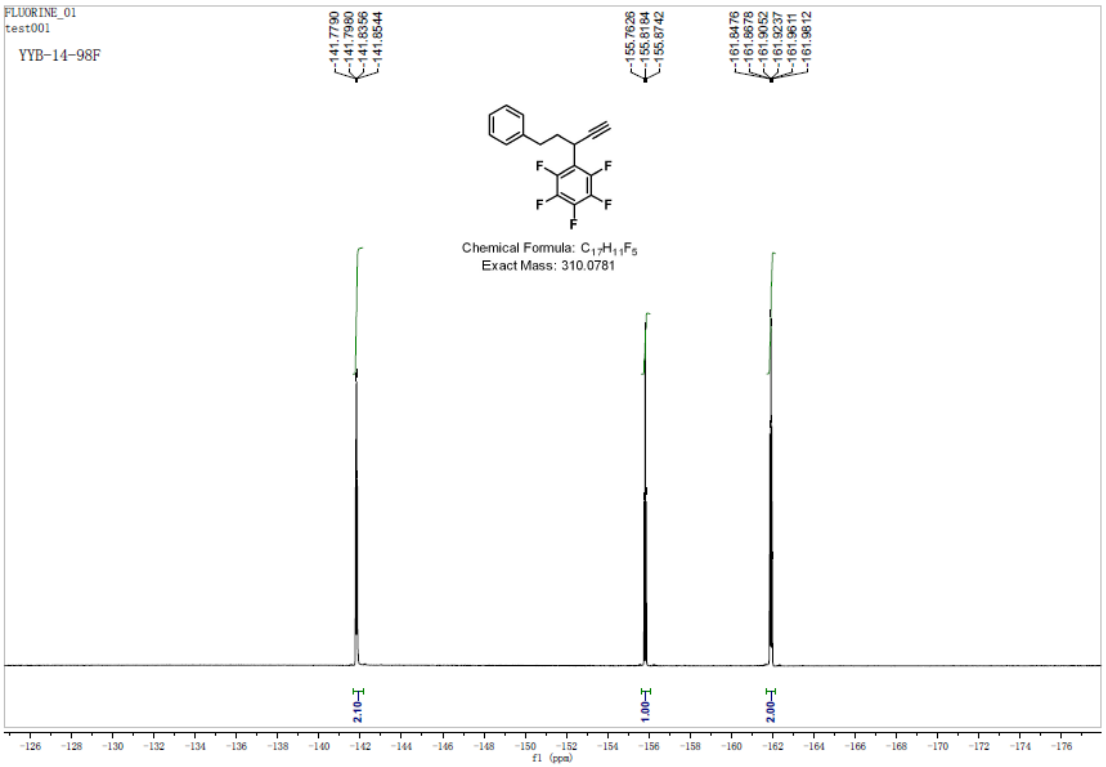


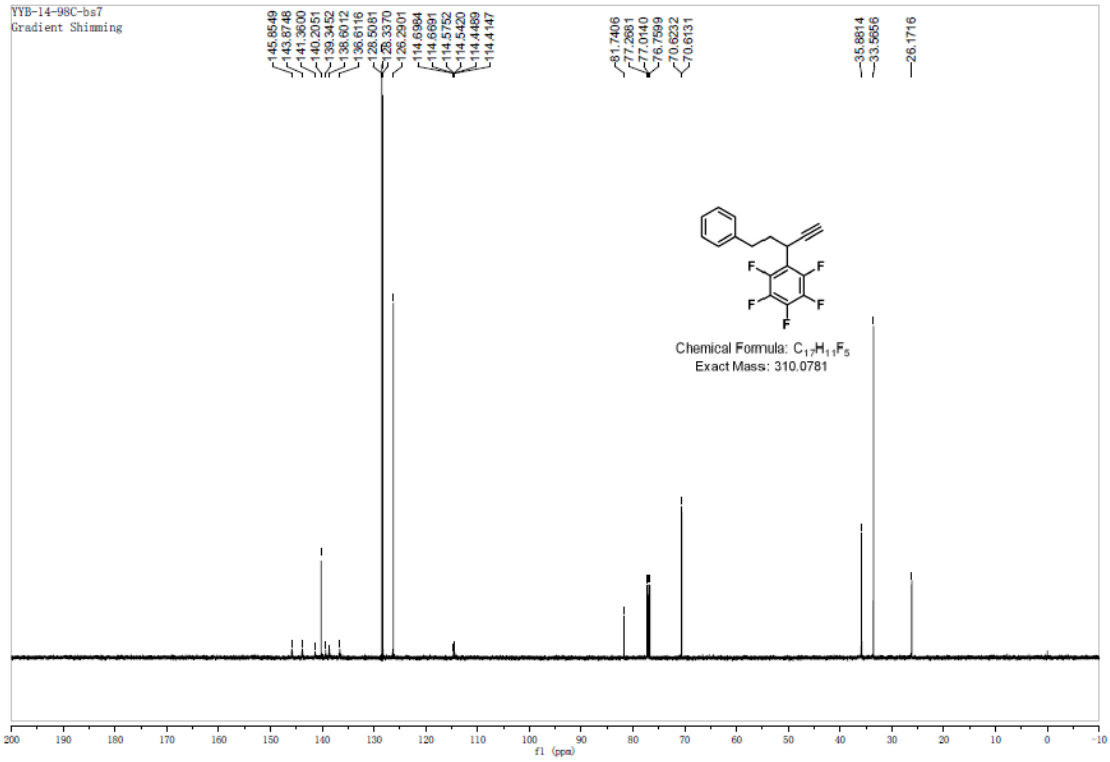




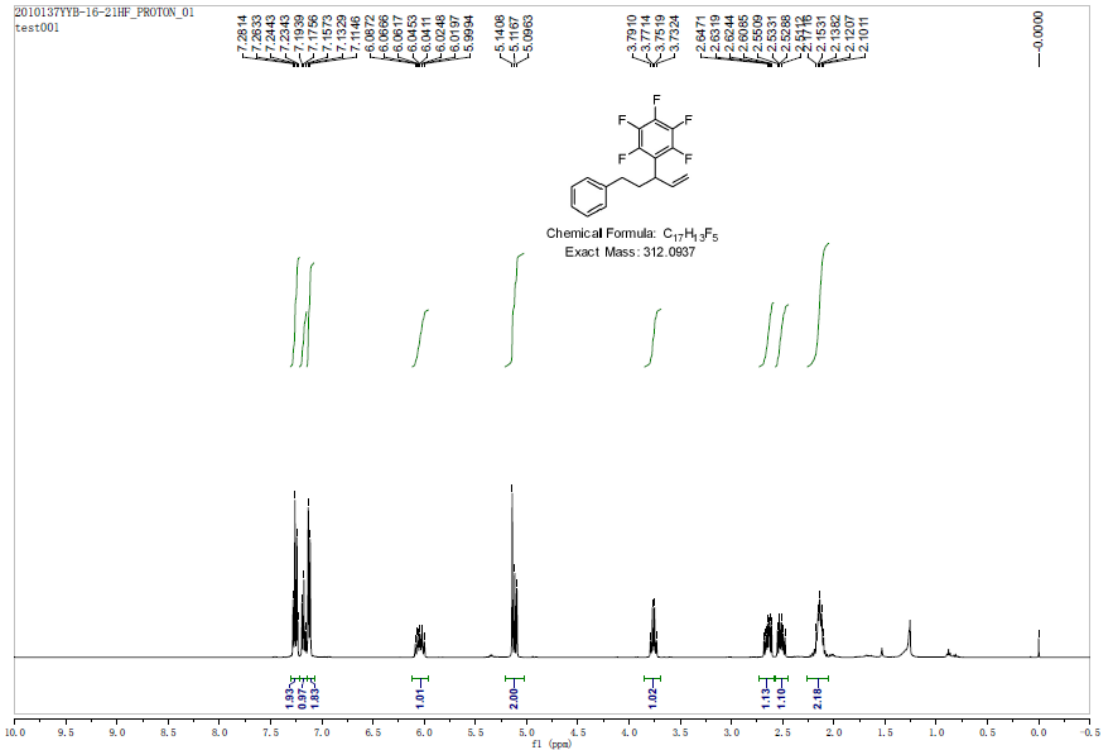
1,2,3,4,5-Pentafluoro-6-(5-phenylpent-1-yn-3-yl)benzene (9)

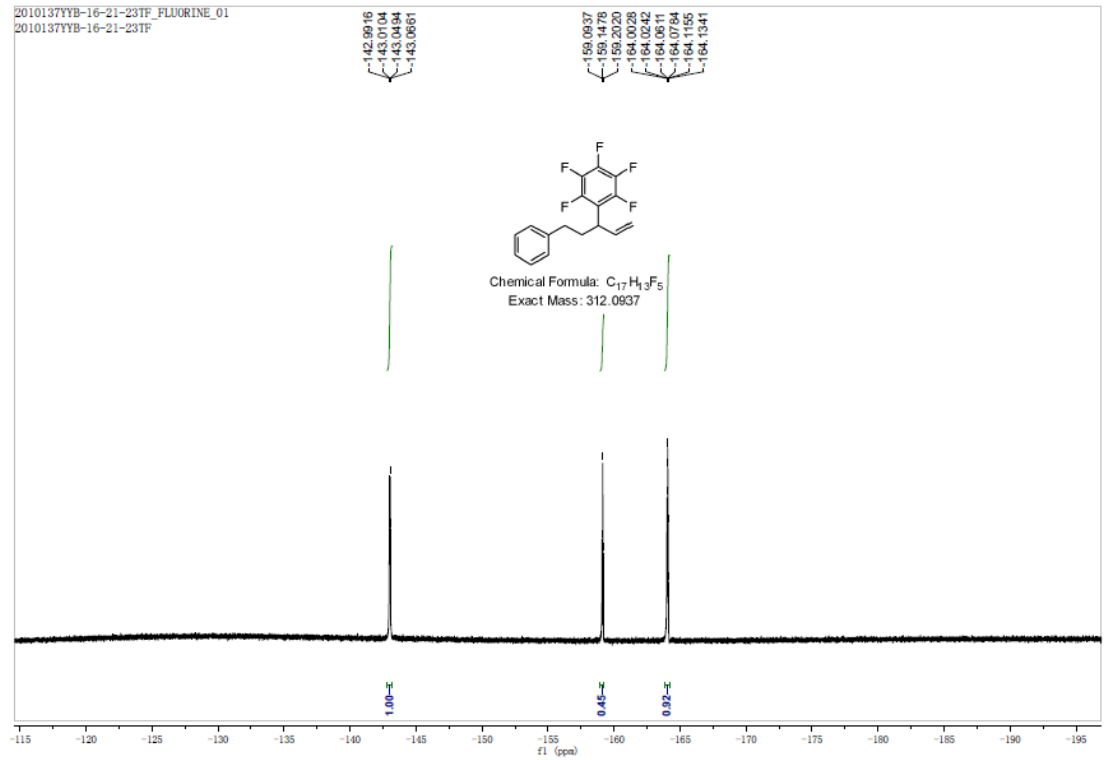


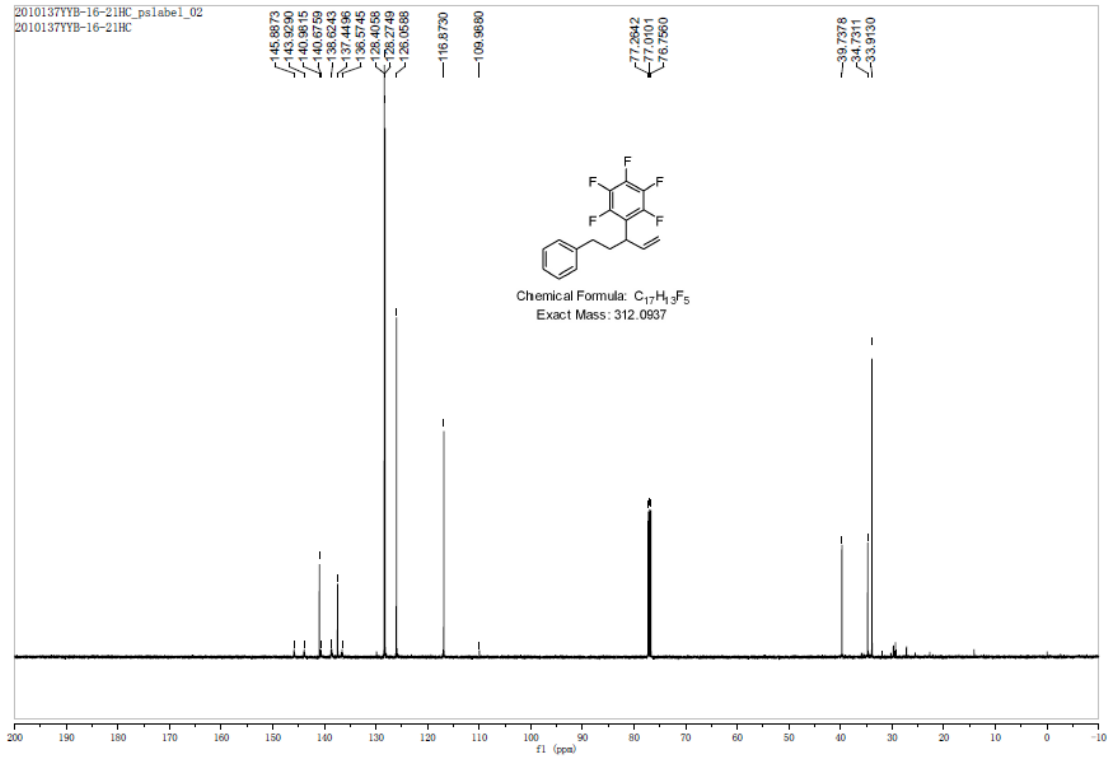

FLUORINE_01
test001
YYB-14-98F
141.7790
141.7980
141.8356
141.8544
155.7626
155.8184
155.8742
161.8476
161.8678
161.9052
161.9237
161.9611
161.9812
Chemical Formula: C17H11F5
Exact Mass: 310.0781
2.10
1.00
2.00
f1 (ppm)


YYB-14-98C-bs7
Gradient Shimming
145.6549
143.6748
141.3600
140.2051
139.3452
138.6012
136.6116
128.5081
128.3370
126.2901
114.6984
114.6691
114.5752
114.5420
114.4469
114.4147
81.7406
77.2881
77.0140
76.7599
70.6232
70.6131
35.8814
33.5656
26.1716
Chemical Formula: C17H11F5
Exact Mass: 310.0781
f1 (ppm)

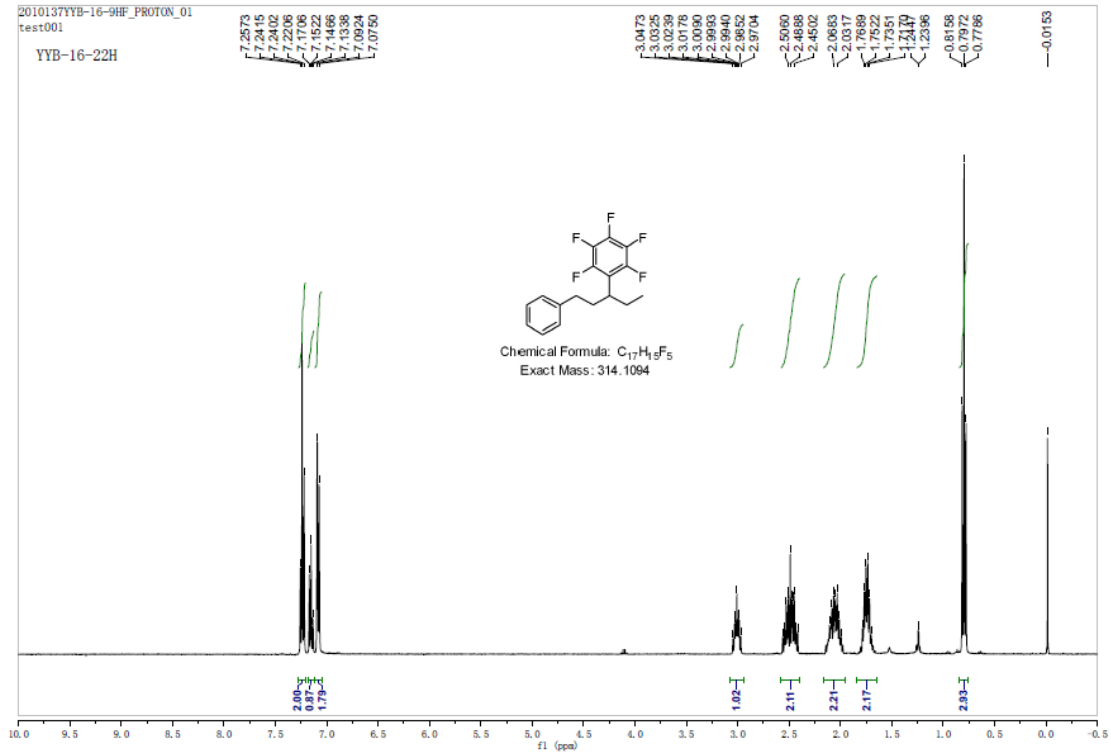
1,2,3,4,5-Pentafluoro-6-(5-phenylpent-1-en-3-yl)benzene (10a)

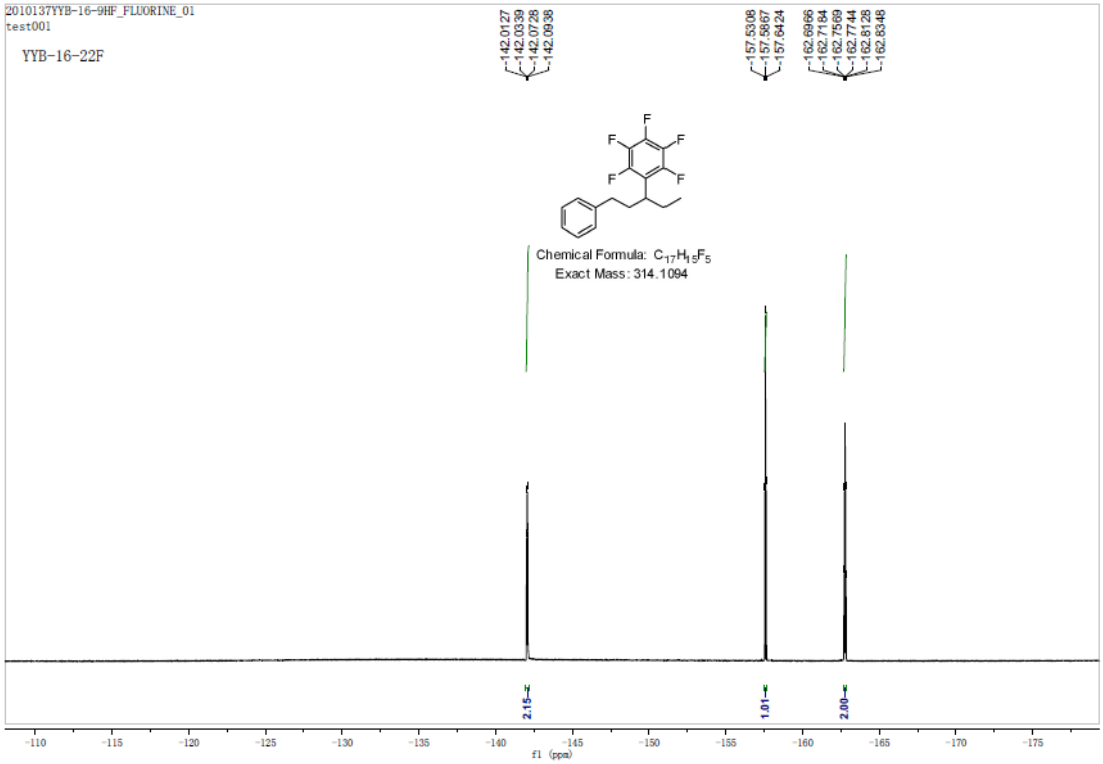


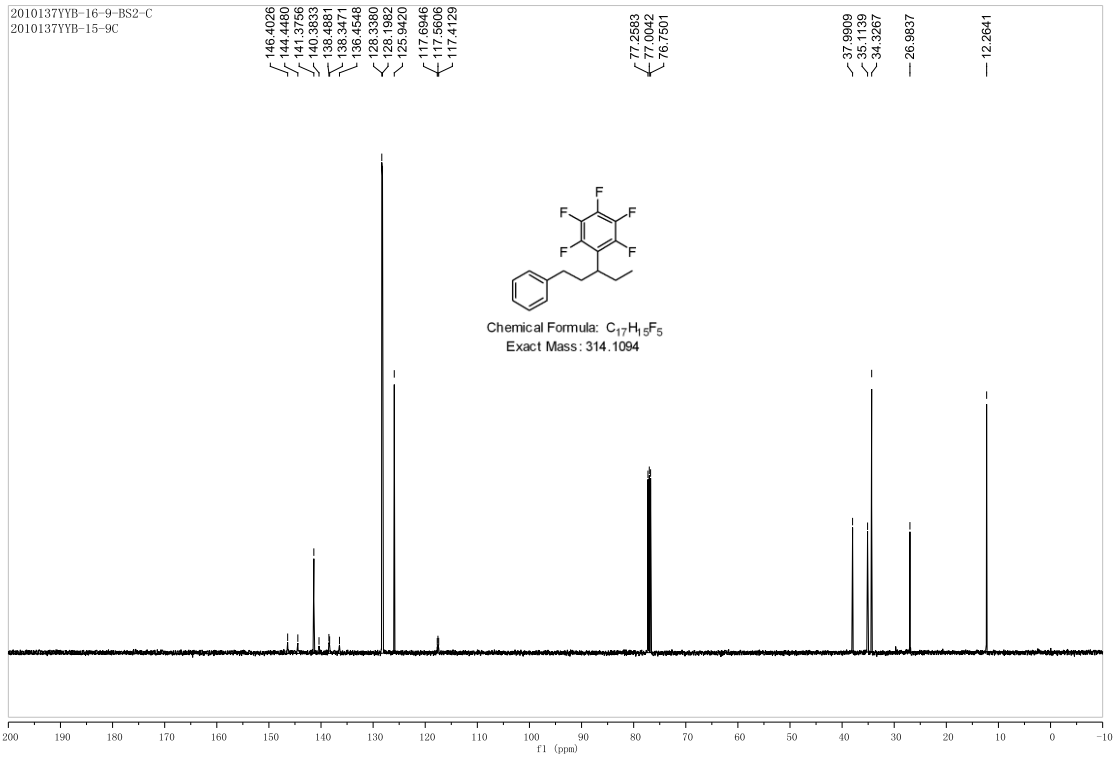




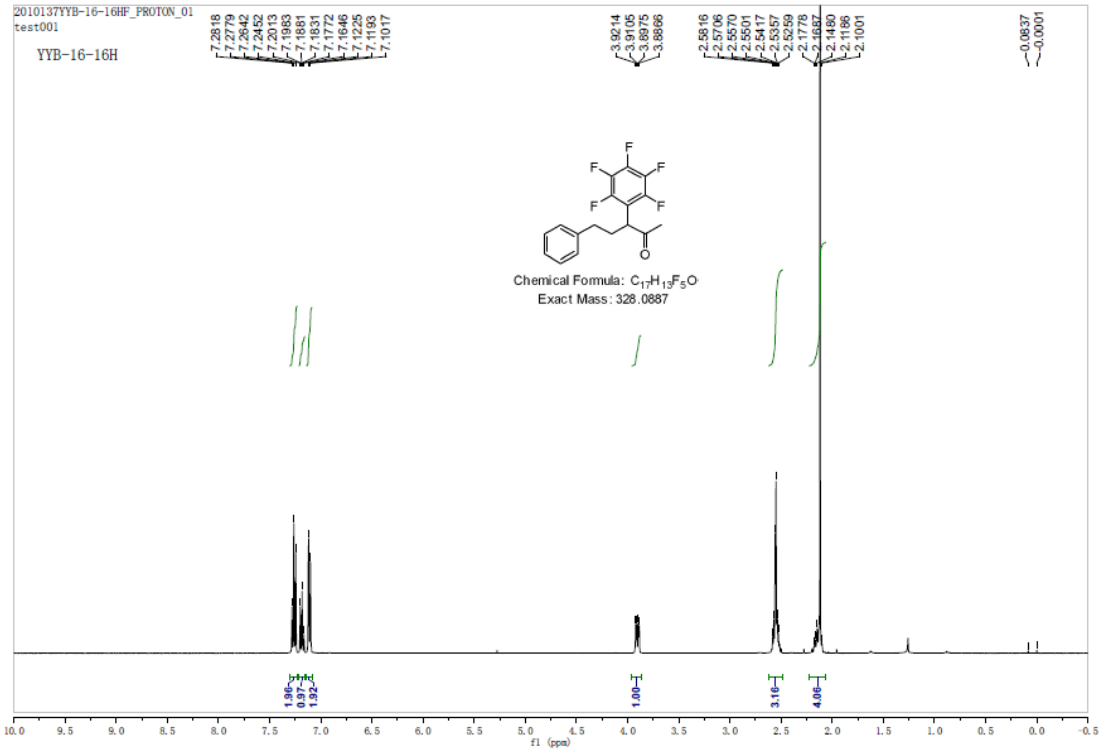
1,2,3,4,5-Pentafluoro-6-(1-phenylpentan-3-yl)benzene (10b)

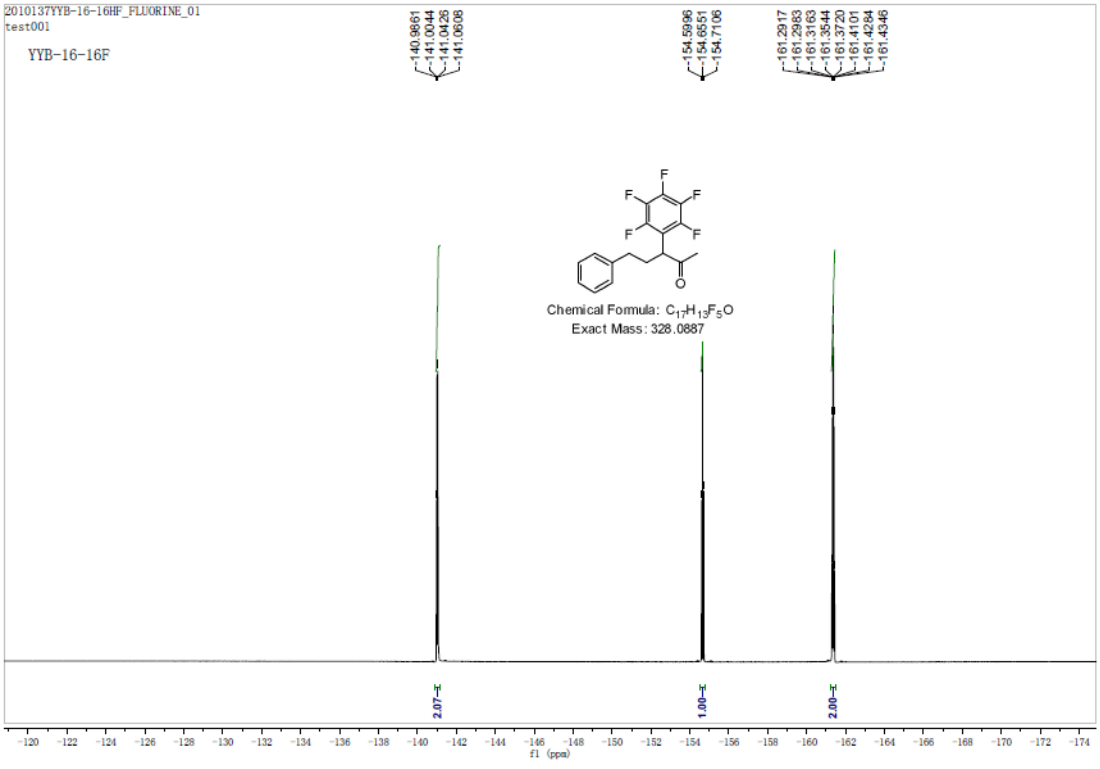


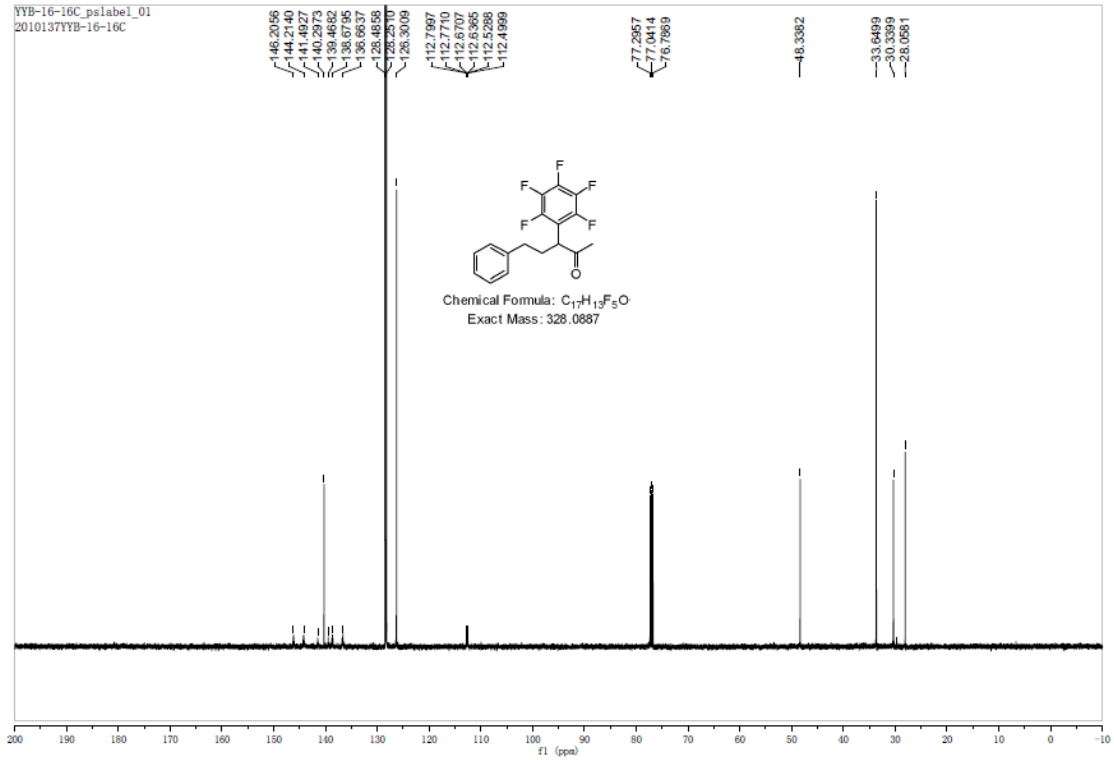

2010137YYB-16-9HF_FLUORINE_01
test001
YYB-16-22F
142.0127
142.0339
142.0728
142.0938
157.5306
157.5867
157.6424
162.6966
162.7164
162.7569
162.7744
162.8128
162.8348
Chemical Formula: C17H15F5
Exact Mass: 314.1094
2.15
1.01
2.00
f1 (ppm)


2010137YYB-16-9-BS2-C
2010137YYB-15-9C
146.4026
144.4480
141.3756
140.3833
138.4881
138.3471
136.4548
128.3380
128.1982
125.9420
117.6946
117.5606
117.4129
77.2583
77.0042
76.7501
37.9909
35.1139
34.3267
26.9837
12.2641
Chemical Formula: C17H15F5
Exact Mass: 314.1094
f1 (ppm)

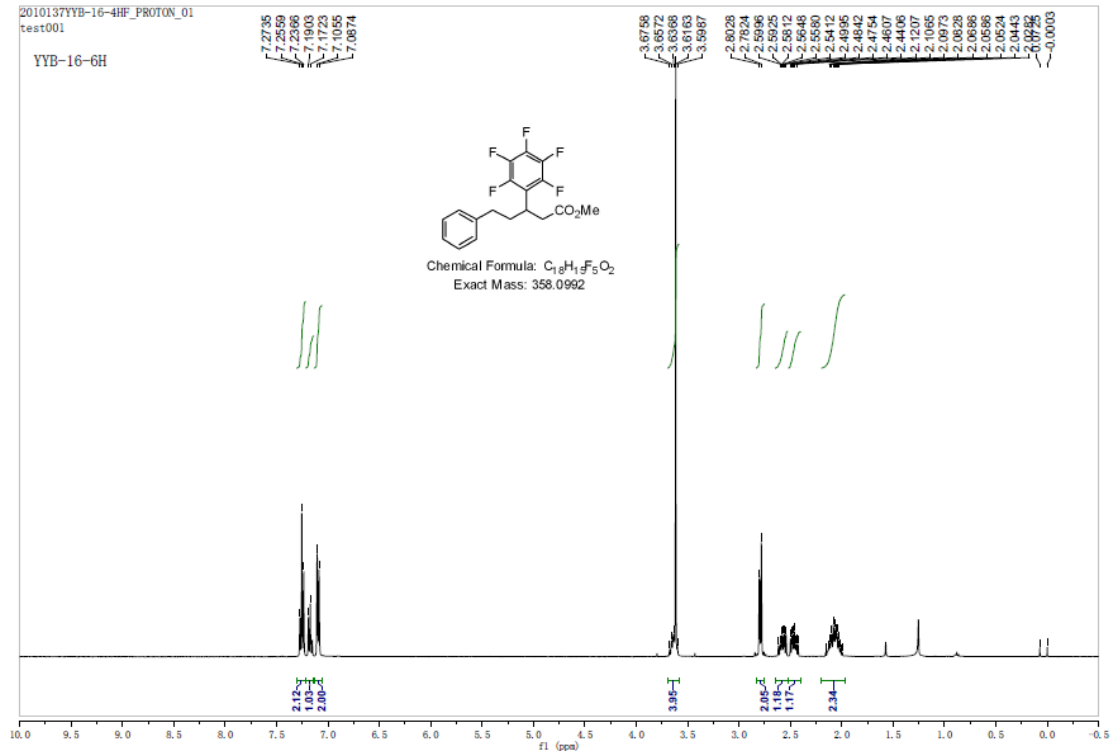
3-(Perfluorophenyl)-5-phenylpentan-2-one (10c)

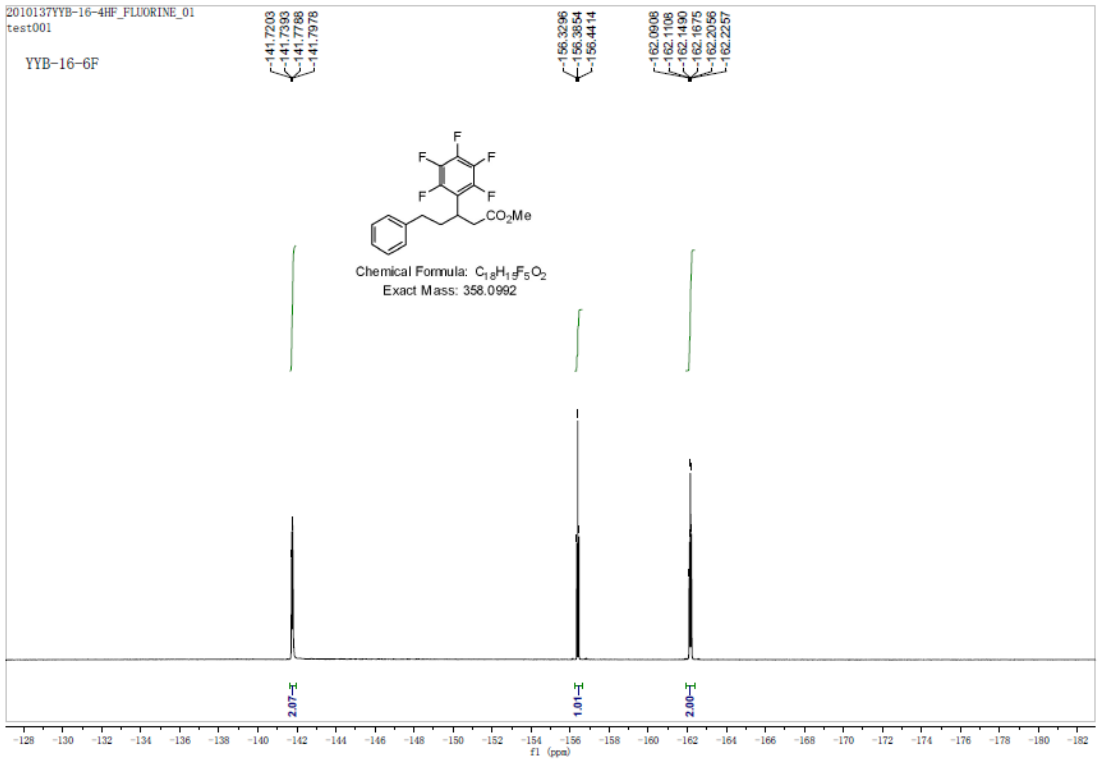


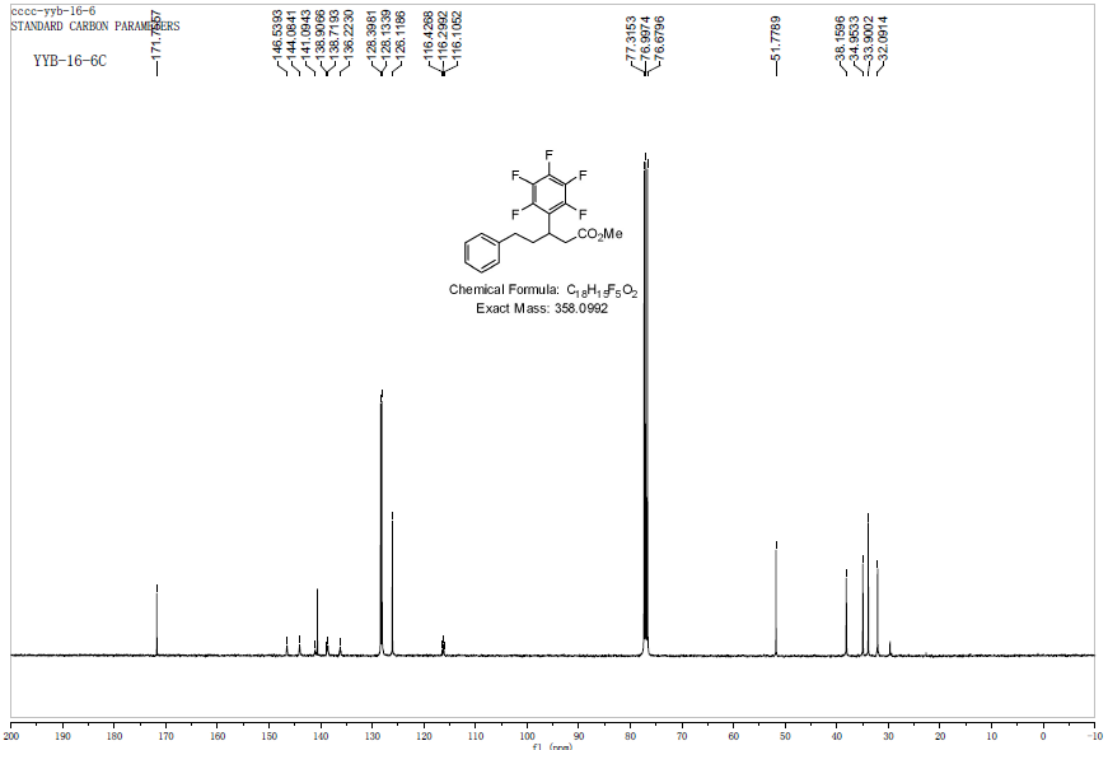




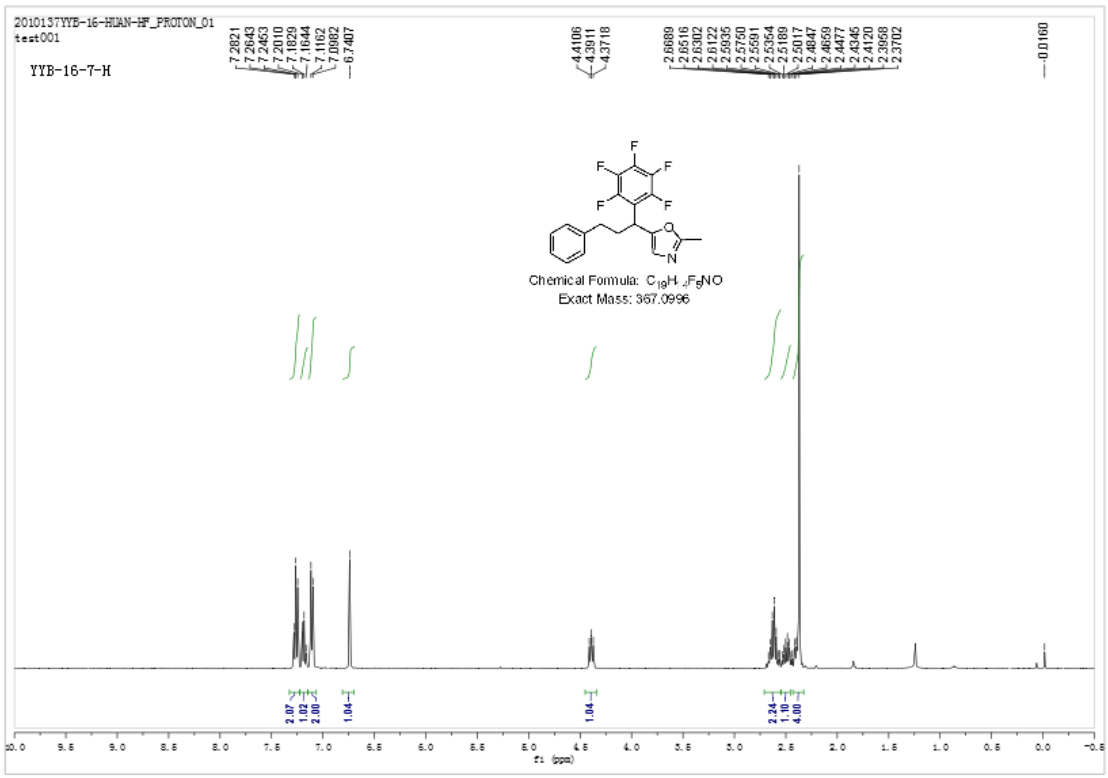
Methyl 3-(perfluorophenyl)-5-phenylpentanoate (10d)

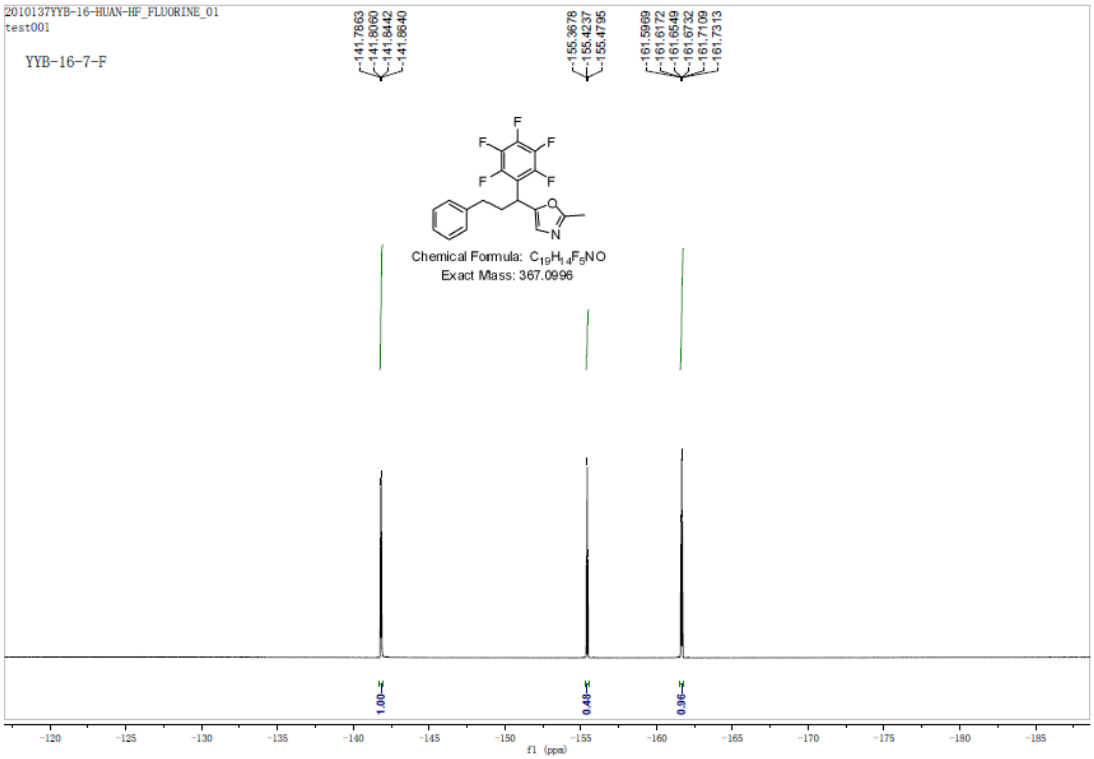


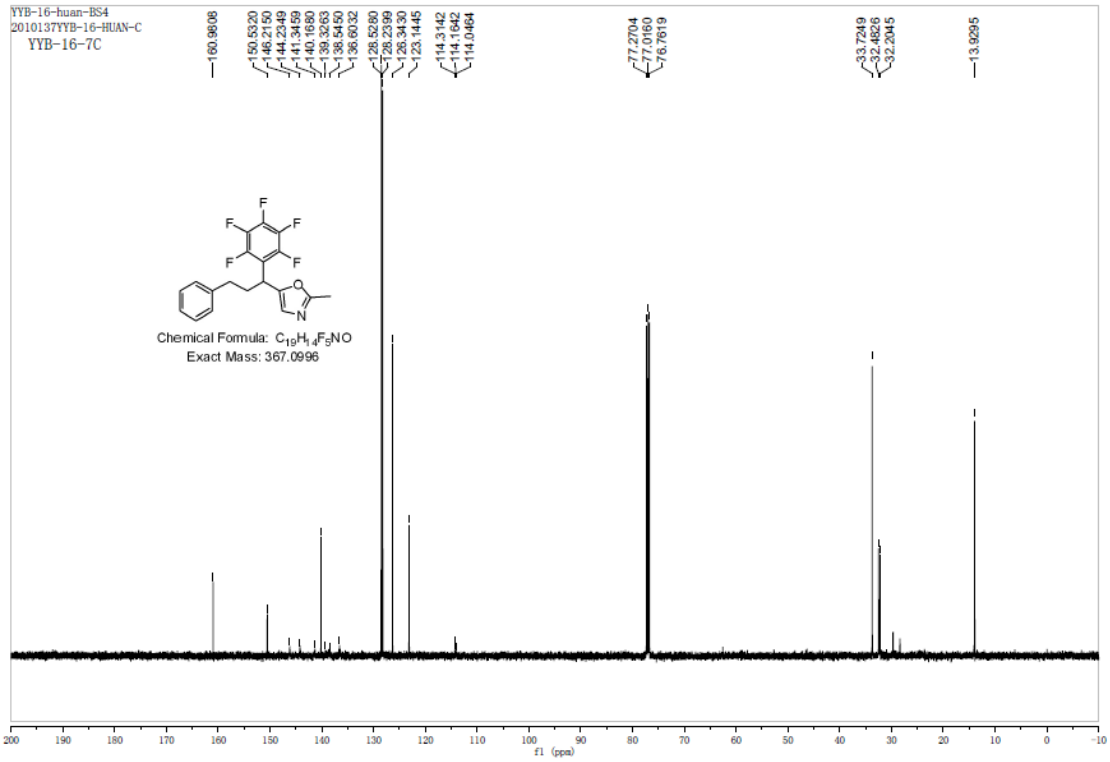

2010137YYB-16-4HF_FLUORINE_01
test001
YYB-16-6F
-141.7203
-141.7393
-141.7788
-141.7978
-156.3296
-156.3654
-156.4414
-162.0906
-162.1108
-162.1490
-162.1675
-162.2056
-162.2257
F
F
F
F
F
CO2Me
Chemical Formula: C18H13F5O2
Exact Mass: 358.0992
2.07
1.01
2.00
f1 (ppm)


cccc-yyb-16-6
STANDARD CARBON PARAMETERS
YYB-16-6C
171.7657
146.5393
144.0641
141.0943
138.9066
138.7193
136.2230
128.3981
128.1339
126.1186
116.4288
116.2992
116.1052
77.3153
76.9974
76.6796
51.7789
38.1596
34.9533
33.9002
32.0914
F
F
F
F
F
CO2Me
Chemical Formula: C18H13F5O2
Exact Mass: 358.0992
f1 (ppm)

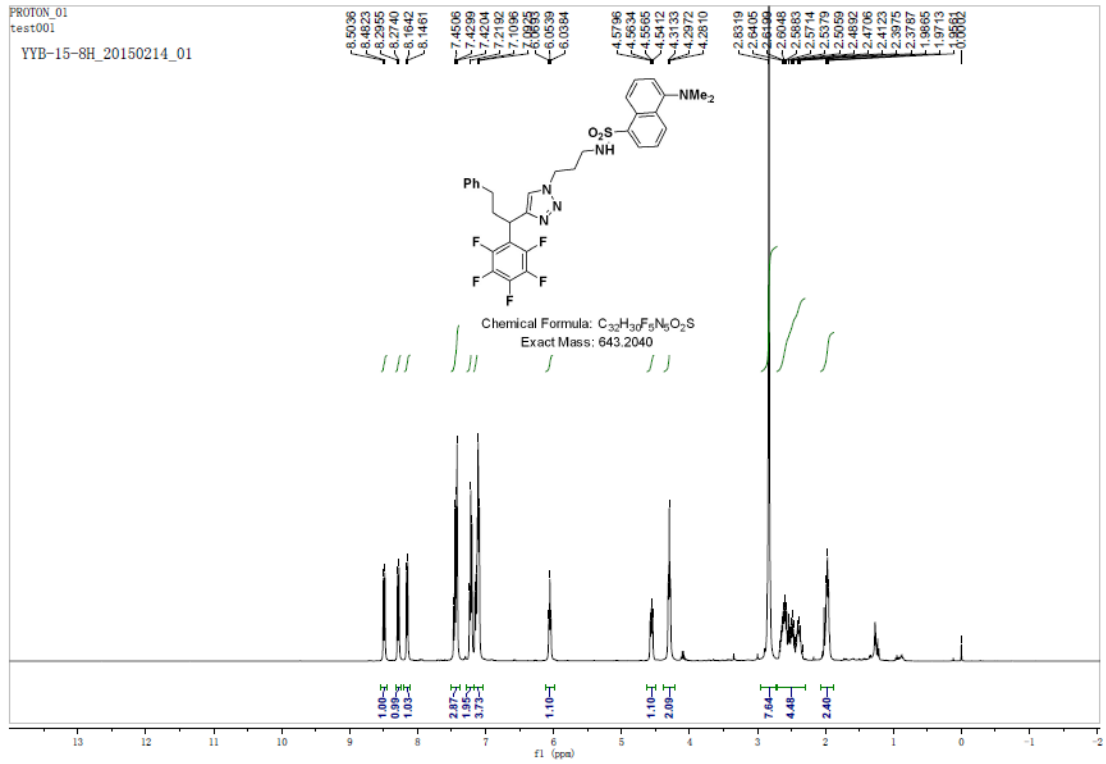
2-Methyl-5-(1-(perfluorophenyl)-3-phenylpropyl)oxazole (10e)

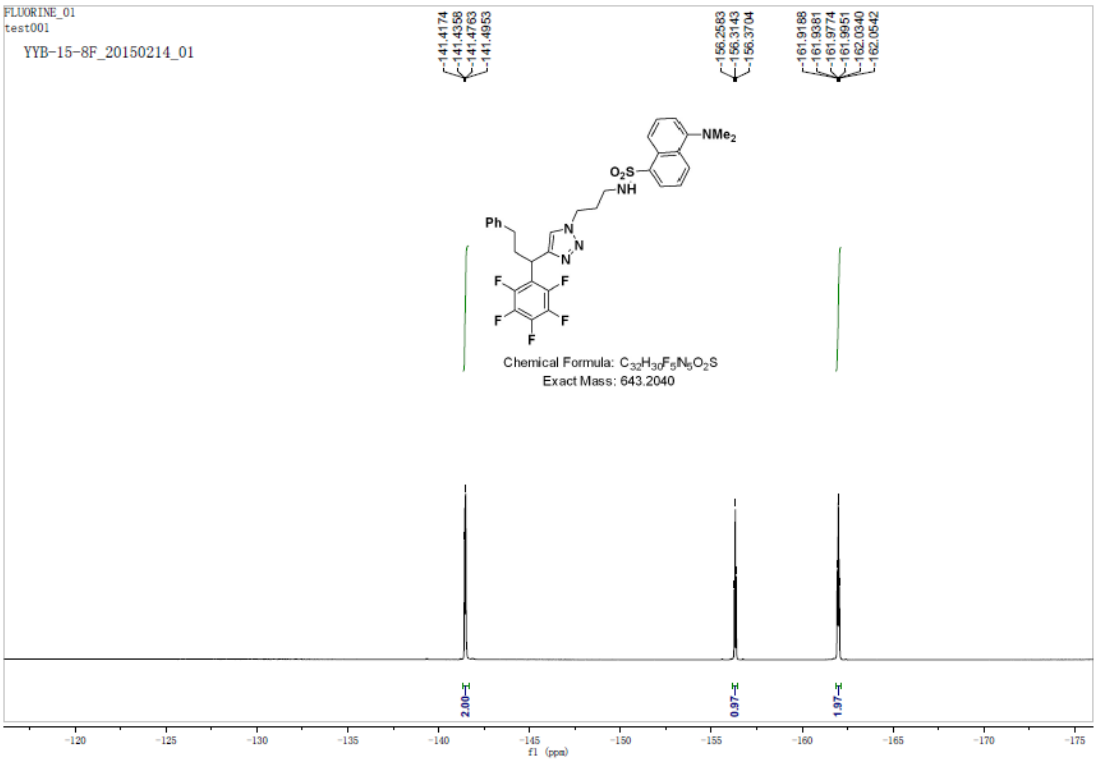


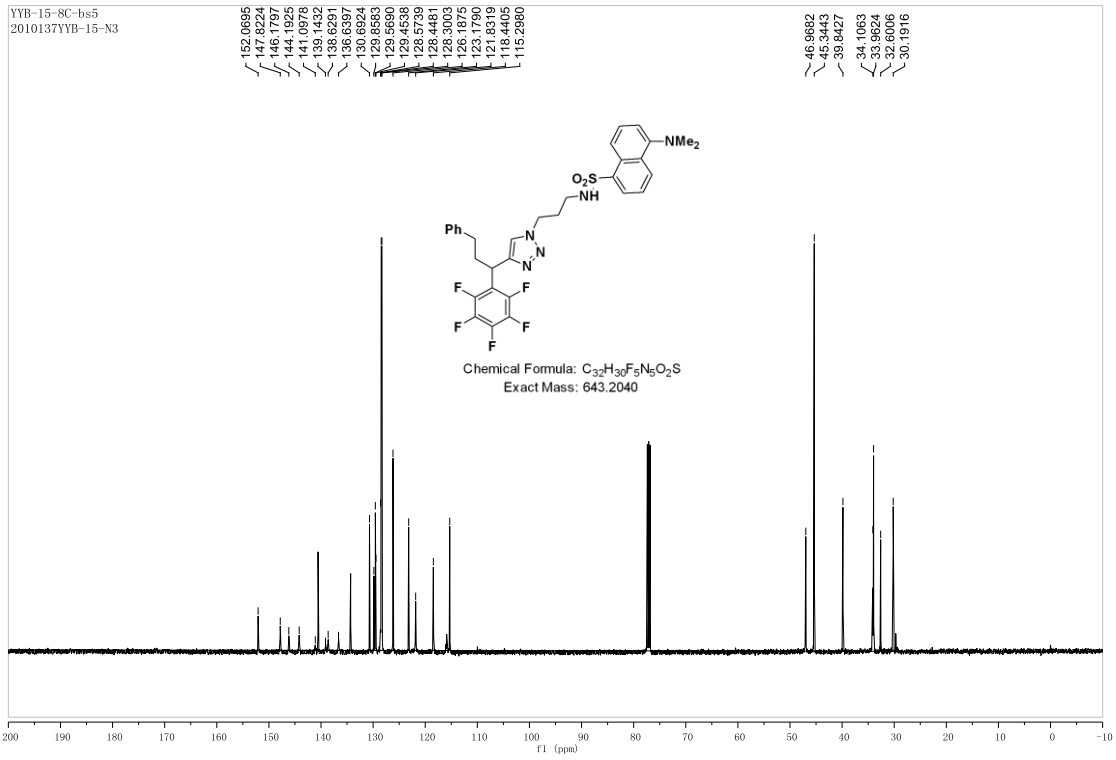




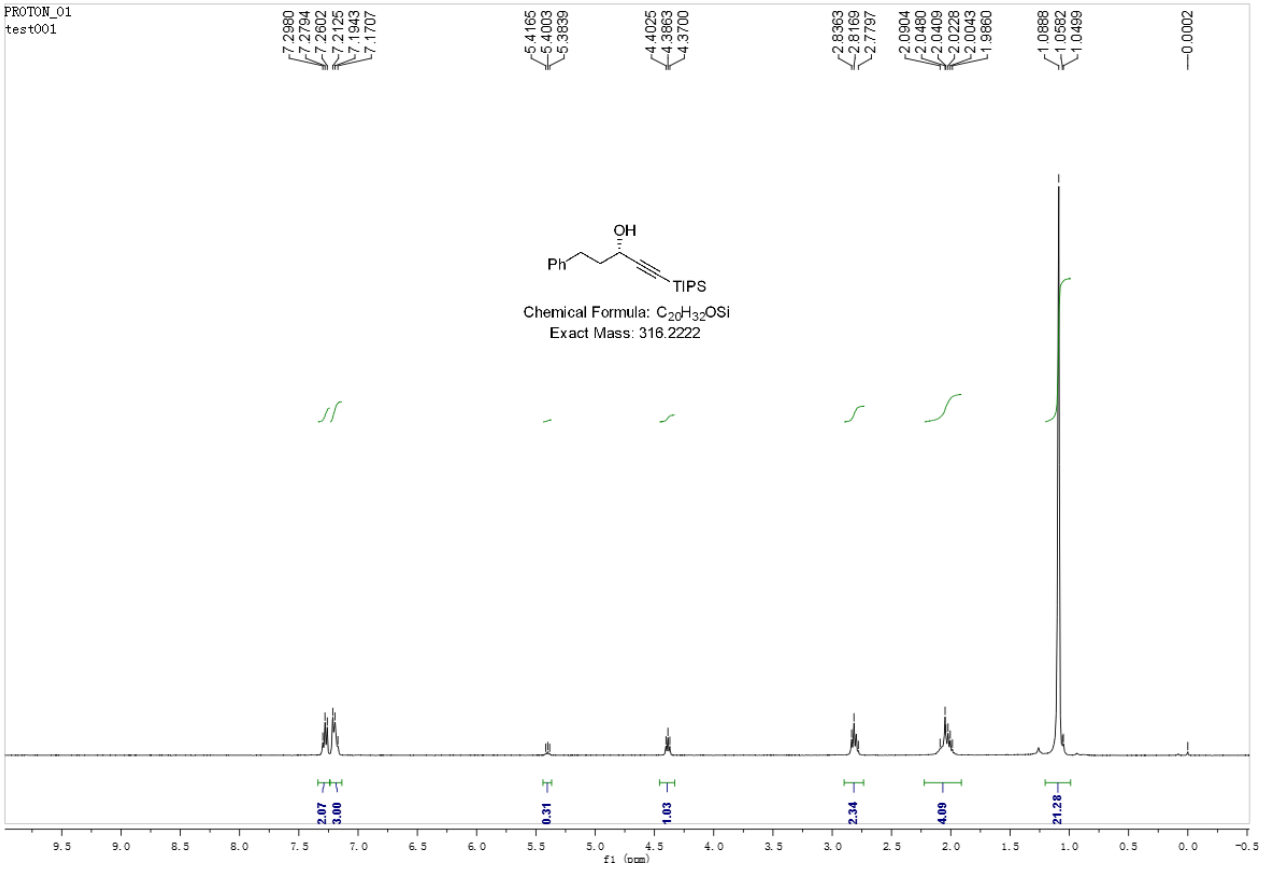
5-(Dimethylamino)-n-(3-(4-(1-(perfluorophenyl)-3-phenylpropyl)-1h-1,2,3-triazol-1-yl)propyl)naphthalene-1-sulfonamide (10f)

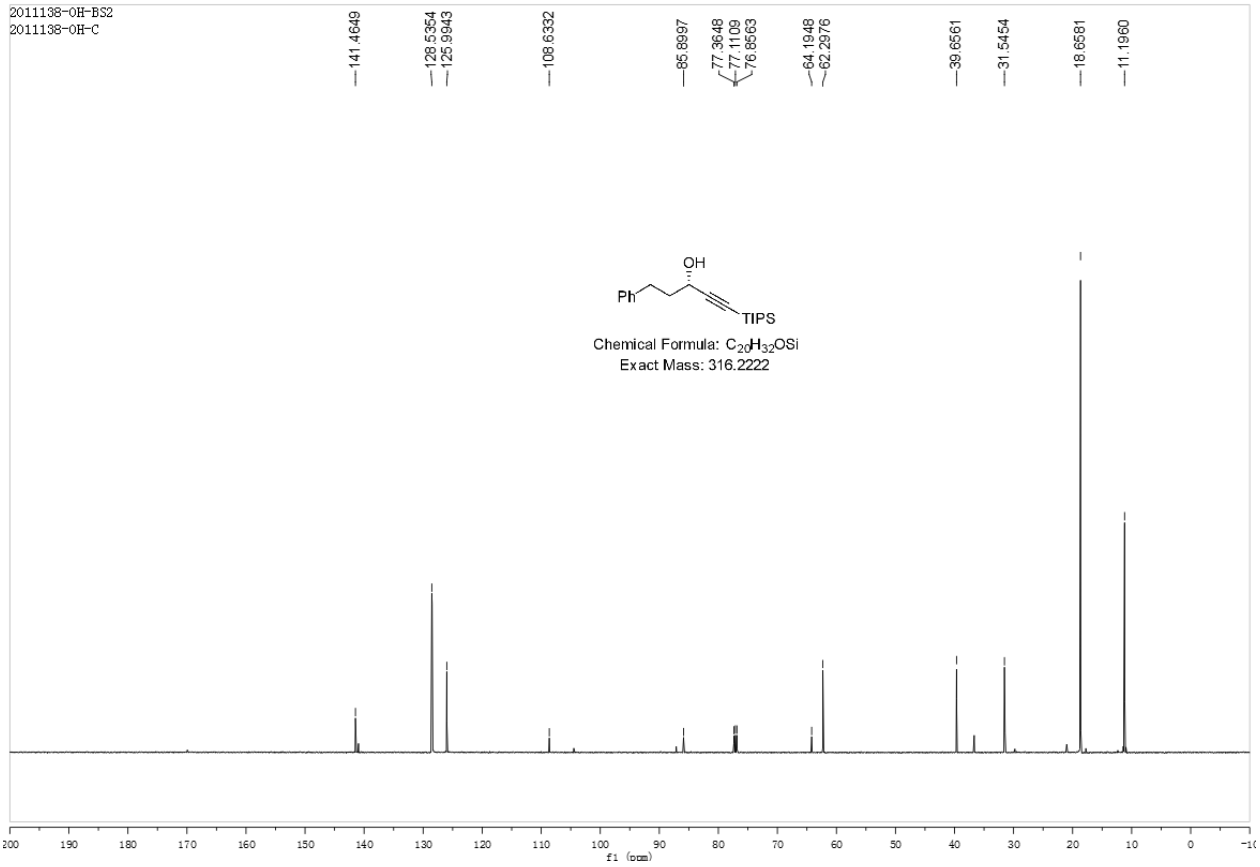


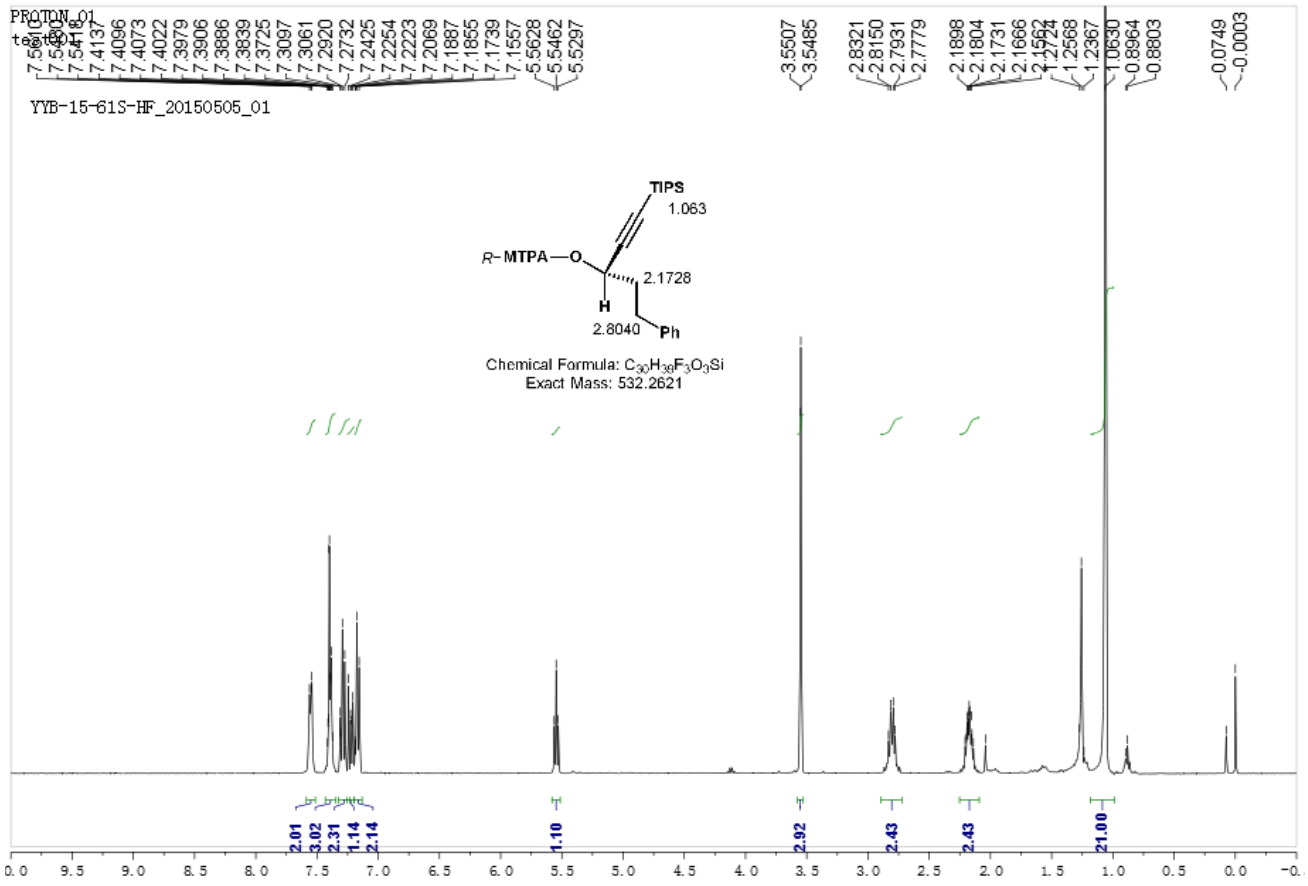

FLUORINE_01
test001
YYB-15-8F_20150214_01
-141.4174
-141.4358
-141.4763
-141.4953
-156.2563
-156.3143
-156.3704
-161.9188
-161.9381
-161.9774
-161.9951
-162.0340
-162.0542
NMe2
O2S
NH
Ph
N
N
N
F
F
F
F
F
Chemical Formula: C32H30F5N5O2S
Exact Mass: 643.2040
2.00
0.97
1.97
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)

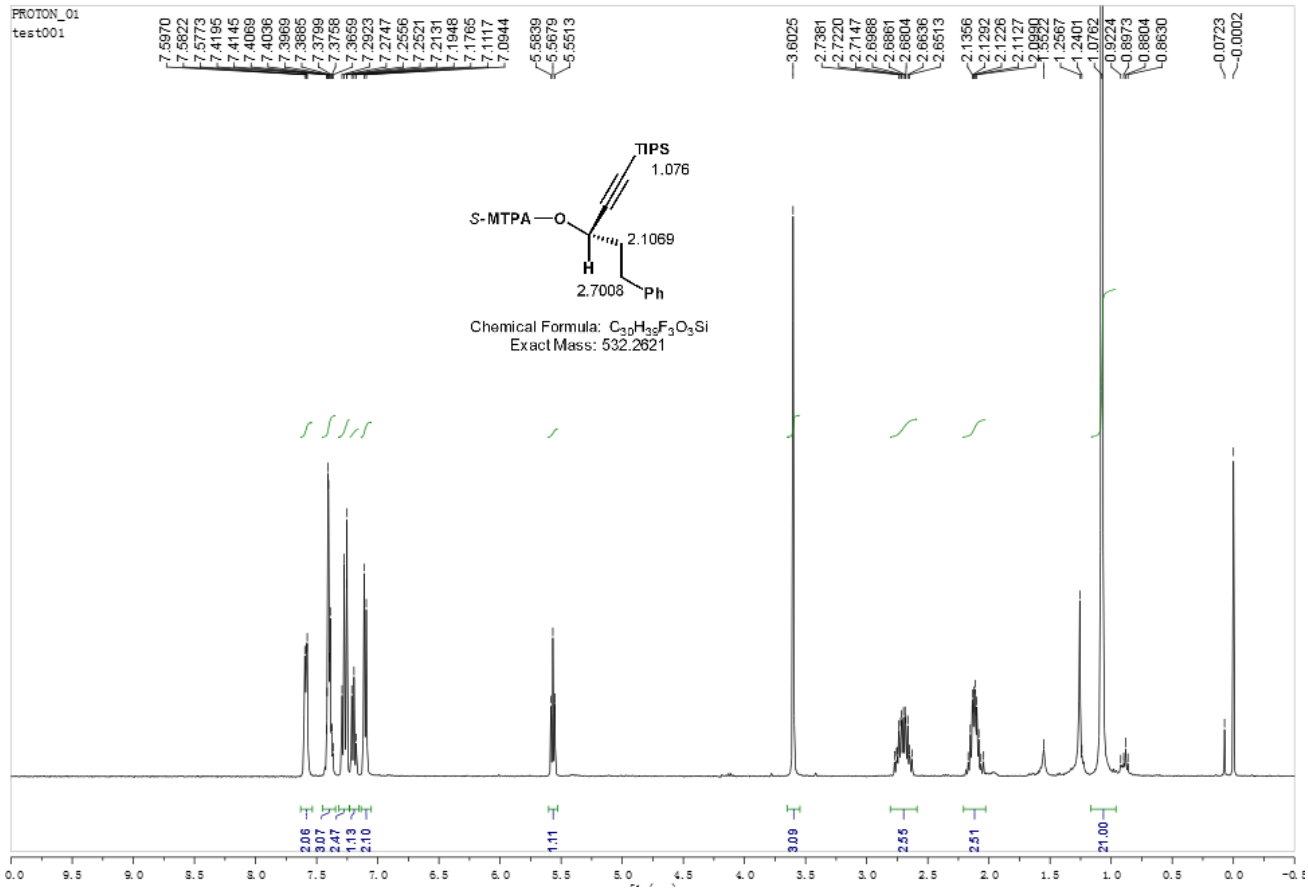

YYB-15-8C-bs5
2010137YYB-15-N3
152.0695
147.8224
146.1797
144.1925
141.0978
139.1432
138.6291
136.6397
130.6924
129.8583
129.5690
129.4538
128.5739
128.4481
128.3003
126.1875
123.1790
121.8319
118.4405
115.2980
46.9682
45.3443
39.8427
34.1063
33.9624
32.6006
30.1916
NMe2
O2S
NH
Ph
N
N
N
F
F
F
F
F
Chemical Formula: C32H30F5N5O2S
Exact Mass: 643.2040
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(*R*)-5-Phenyl-1-(triisopropylsilyl)pent-1-yn-3-ol (*S*-2da)

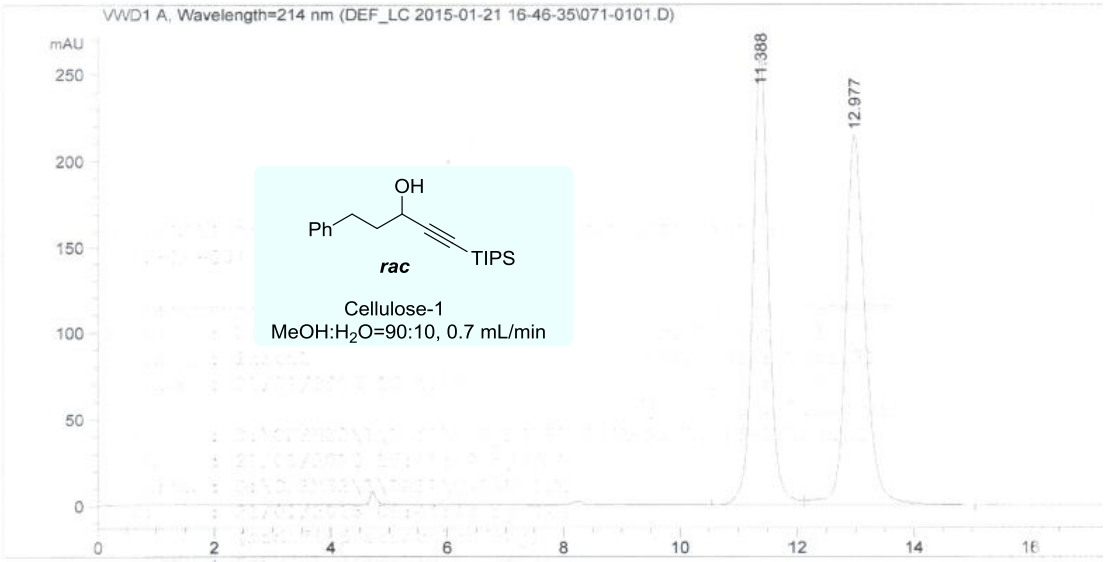





PROTON_01
test001
YYB-15-61S-HF_20150505_01
TIPS
1.063
R-MTPA—O
2.1728
H
2.8040
Ph
Chemical Formula: C30H39F3O3Si
Exact Mass: 532.2621
2.01
3.02
2.31
1.14
2.14
1.10
2.92
2.43
2.43
21.00


PROTON_01
test001
TIPS
1.076
S-MTPA—O
2.1069
H
2.7008
Ph
Chemical Formula: C30H39F3O3Si
Exact Mass: 532.2621
2.06
3.07
2.47
1.13
2.10
1.11
3.09
2.55
2.51
21.00

Copies of HPLC Analysis Spectra of Compounds *S*-**2da**, *S*-**2d**, and *S*-**3d**

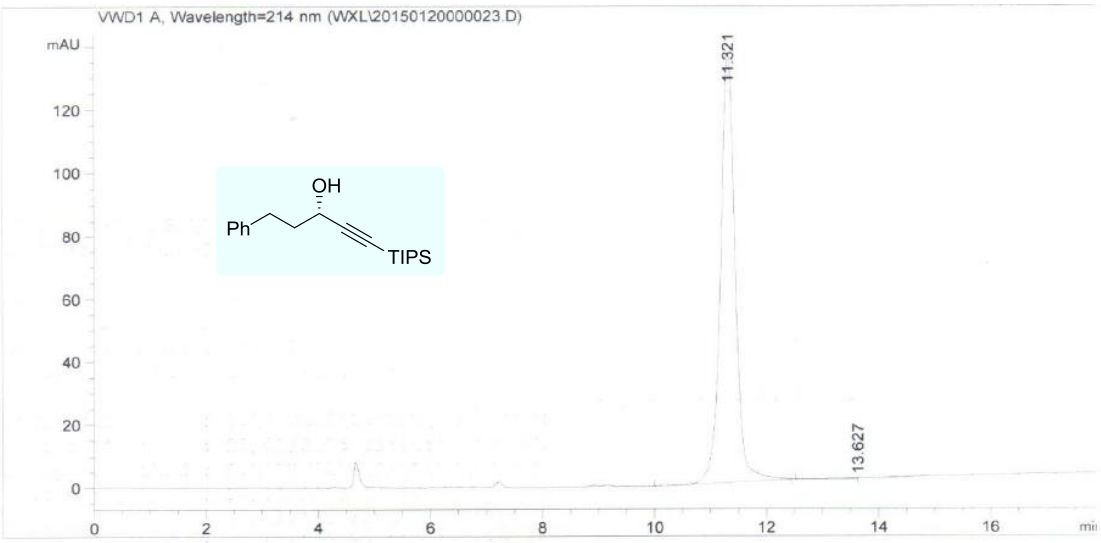


Area Percent Report with Performance

Signal 1: VWD1 A, Wavelength=214 nm

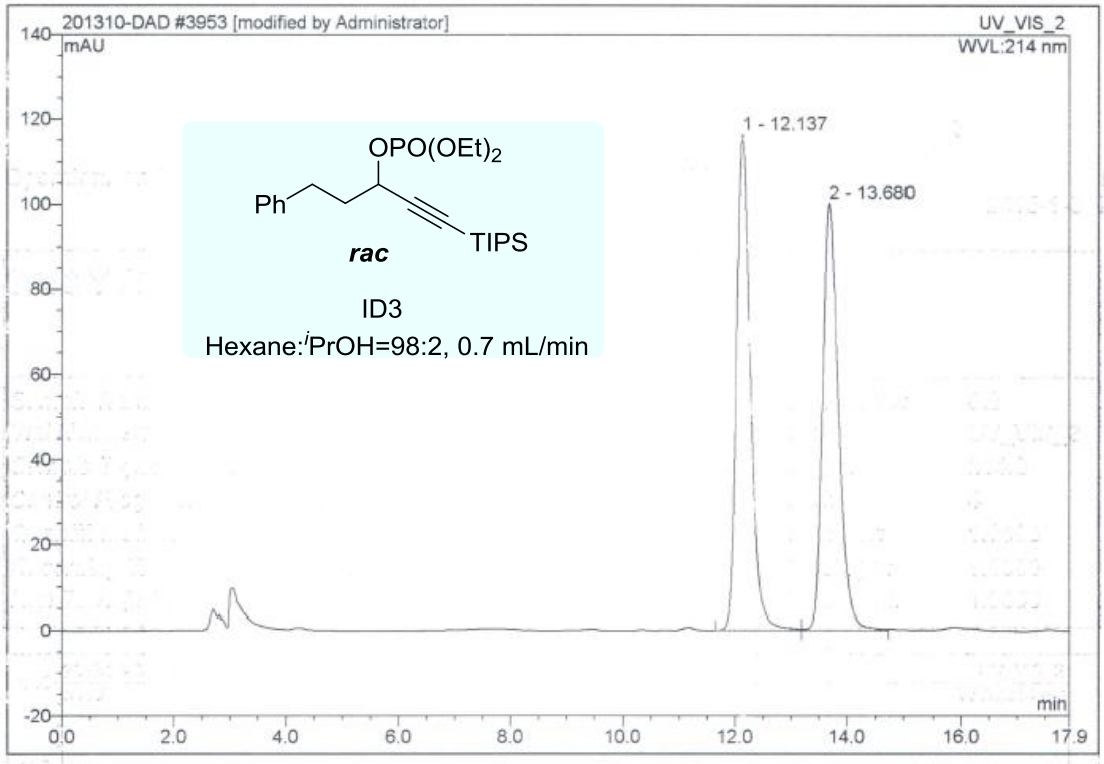
RetTime [min]	k'	Area [mAU*s]	Height [mAU]	Symm.	Width [min]	Plates	Resolution	Selectivity	
11.388	-	4927.50098	260.06110	0.92	0.2774	9342	-	-	49.6%
12.977	-	4998.58105	214.29591	0.77	0.3381	8161	3.03	1.14	50.4%

*** End of Report ***

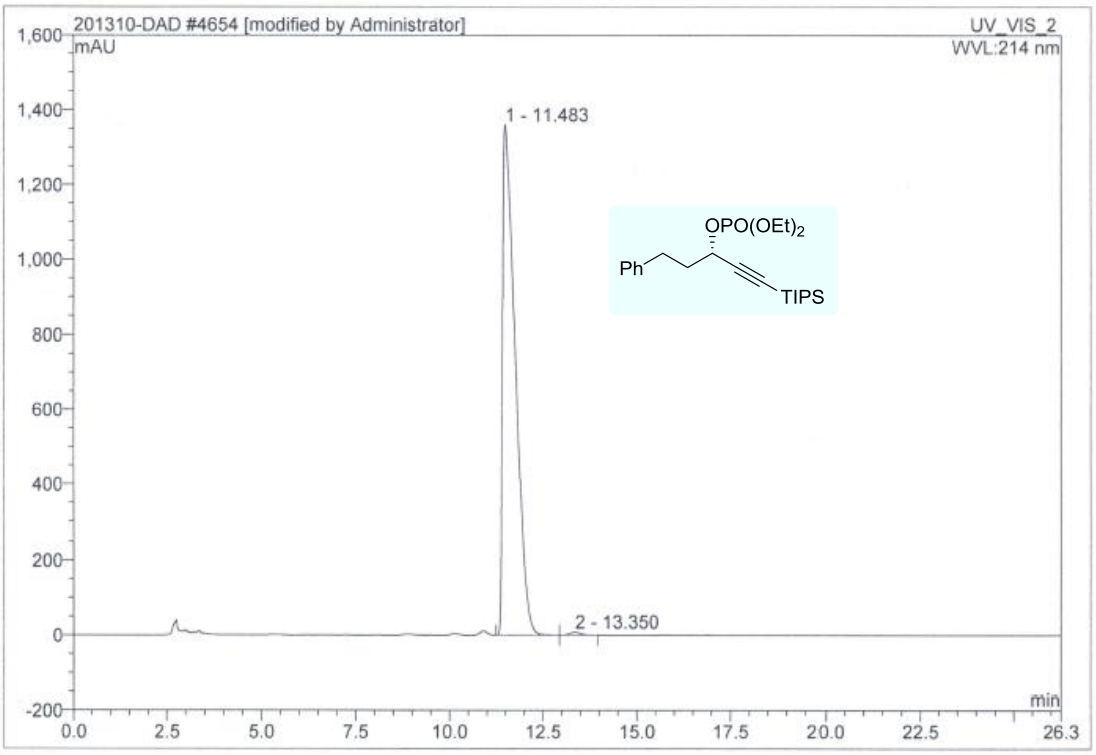


Signal 1: VWD1 A, Wavelength=214 nm

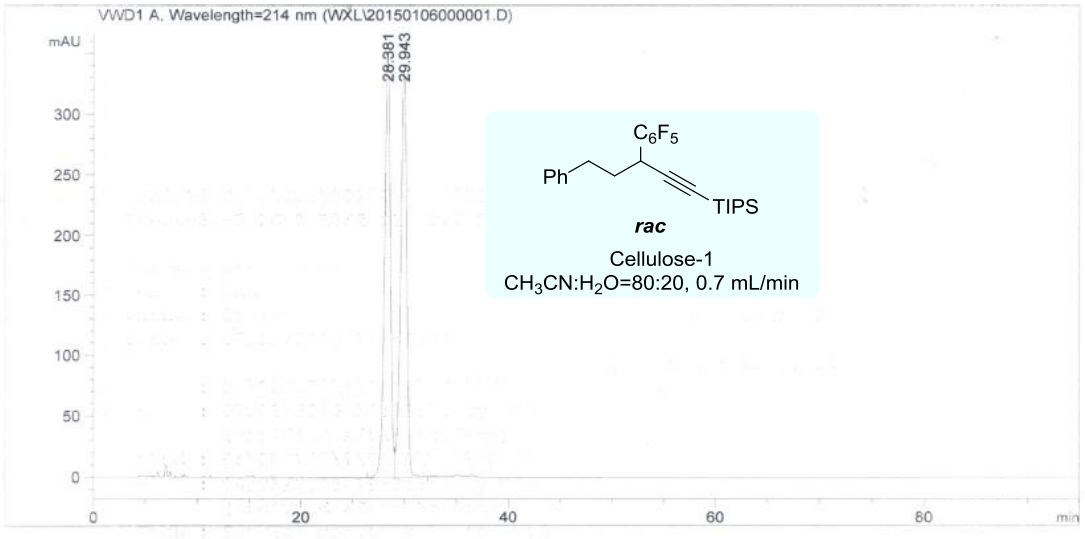
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.321	MM	0.3043	2478.39575	135.73846	99.8210
2	13.627	MM	0.4483	4.44363	1.65219e-1	0.1790
Totals :				2482.83939	135.90368	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.14	n.a.	116.376	33.618	50.35	n.a.	BM *
2	13.68	n.a.	100.220	33.148	49.65	n.a.	M *
Total:			216.596	66.765	100.00	0.000	



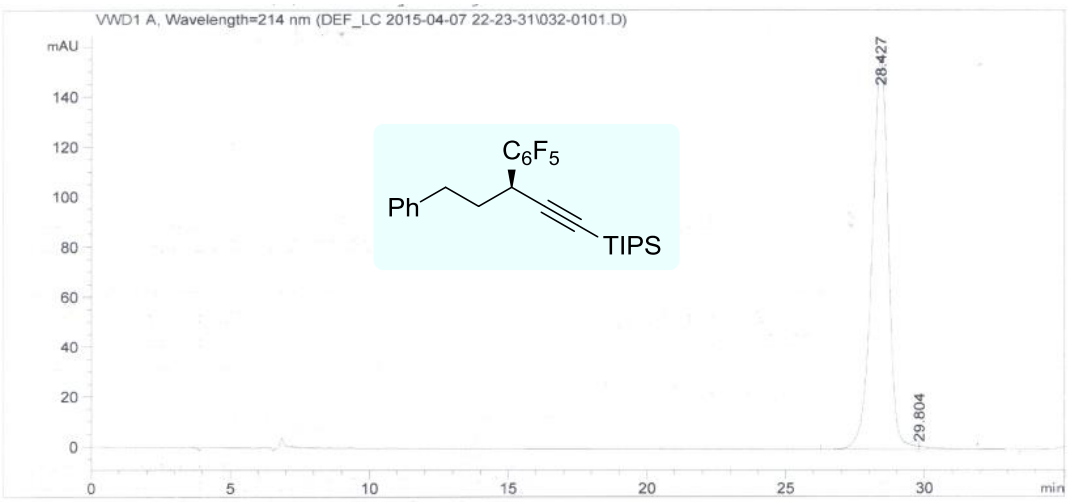
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.48	n.a.	1360.363	534.667	99.45	n.a.	BM *
2	13.35	n.a.	8.401	2.930	0.55	n.a.	MB*
Total:			1368.763	537.597	100.00	0.000	



Area Percent Report

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.381	MF	0.6637	1.39522e4	350.37167	50.0763
2	29.943	FM	0.6898	1.39097e4	336.06897	49.9237
Totals :				2.78619e4	686.44064	



Area Percent Report

Signal 1: VWD1 A, Wavelength=214 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.427	MF	0.6870	6488.23975	157.40114	99.1138
2	29.804	FM	0.8018	58.01460	1.20593	0.8862
Totals :				6546.25434	158.60707	