

*Supporting Information*

## **Copper-Catalyzed Perfluoroalkylation of Alkynyl Bromides and Terminal Alkynes**

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**General information:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 600 MHz spectrometer in  $\text{CDCl}_3$ . Data for  $^1\text{H}$  NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra were obtained by ESI on a TOF mass analyzer.

**Materials:** All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air, and refilled with an inert atmosphere of  $\text{N}_2$  at room temperature. DMF, DMSO, DMPU were distilled under reduced pressure from  $\text{CaH}_2$ . Toluene, 1,4-Dioxane, THF, Diglyme, and DME were distilled from sodium and benzophenone immediately before use.

#### **Preparation of bis(heptafluoropropyl)zinc reagent $\text{Zn}(\text{C}_3\text{F}_7)_2(\text{DMPU})_2$**

To an oven-dried 100-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added Toluene (15 mL) and DMPU (2.4 mL, 20 mmol) under argon atmosphere. Heptafluoropropyl iodide (3.6 mL, 25 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 10 mL, 10 mmol) was then added dropwise at  $-41\text{ }^\circ\text{C}$ . After the reaction mixture was stirred at  $-5\text{ }^\circ\text{C}$  for 12 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (50 mL) three times and dried under vacuum to give  $\text{Zn}(\text{C}_3\text{F}_7)_2(\text{DMPU})_2$  as a white powder (6.0 g, 92% yield).

#### **Preparation of bis(Perfluorobutyl)zinc reagent $\text{Zn}(\text{C}_4\text{F}_9)_2(\text{DMPU})_2$**

To an oven-dried 100-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added Toluene (15 mL) and DMPU (2.4 mL, 20 mmol) under argon atmosphere. Perfluorobutyl iodide (4.3 mL, 25 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 10 mL, 10 mmol) was then added dropwise at  $-41\text{ }^\circ\text{C}$ . After the reaction mixture was stirred at  $-5\text{ }^\circ\text{C}$  for 12 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (50 mL) three times and dried under vacuum to give  $\text{Zn}(\text{C}_4\text{F}_9)_2(\text{DMPU})_2$  as a white powder (6.8 g, 88% yield).

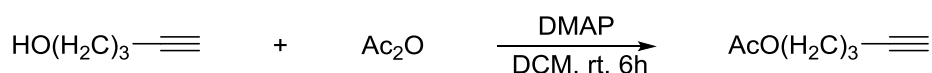
#### **Preparation of bis(tridecafluorohexyl)zinc reagent $\text{Zn}(\text{C}_6\text{F}_{13})_2(\text{DMPU})_2$**

To an oven-dried 100-mL two-neck round-bottomed flask equipped with a magnetic stir bar were added Toluene (15 mL) and DMPU (2.4 mL, 20 mmol) under argon atmosphere. Tridecafluorohexyl iodide (5.4 mL, 25 mmol) was added to the solution. Diethyl zinc solution (1.0 M in hexanes, 10 mL, 10 mmol) was then added dropwise at -41 °C. After the reaction mixture was stirred at -5 °C for 12 h, the precipitate was obtained. After removing the solution, the precipitate obtained was washed with hexane (50 mL) three times and dried under vacuum to give Zn(C<sub>6</sub>F<sub>13</sub>)<sub>2</sub>(DMPU)<sub>2</sub> as a white powder (8.3 g, 87% yield).

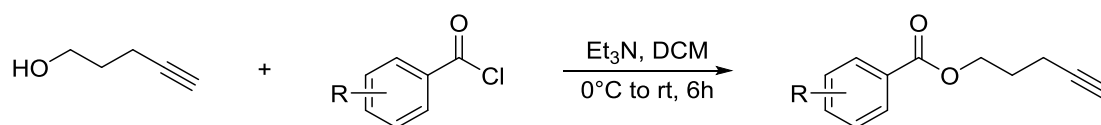
### Synthesis of aliphatic alkynyl derivatives



To a solution of pent-4-yn-1-ol (0.168 g, 2 mmol) in THF (15 mL) was added imidazole (0.34g, 5 mmol) followed by TBSCl (0.32g, 2.1 mmol) and the mixture stirred at room temperature overnight. Water (300 mL) was added and then the reaction mixture was extracted with Et<sub>2</sub>O (3 x 300 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure to leave a light yellow oil. The solvent was dissolved in petroleum ether and filtered through a short column of silica gel. Solvent was removed in vacuo to afford desired product.

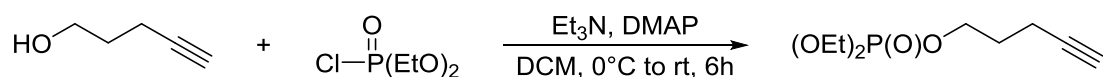


To a solution of pent-4-yn-1-ol (0.168 g, 2 mmol) and DMAP (0.489 g, 4 mmol) in 10 mL of methylene chloride were added acetic anhydride (0.856 g, 8.4 mmol). The solution was stirred at rt overnight and diluted with 10 mL of methylene chloride. The organic layer was washed with water, 2% of aqueous HCl solution, water again, and brine. Drying over Na<sub>2</sub>SO<sub>4</sub> was followed by filtration and concentration, and purification by silica gel column chromatography provided product 0.167 g. Yield 65%.

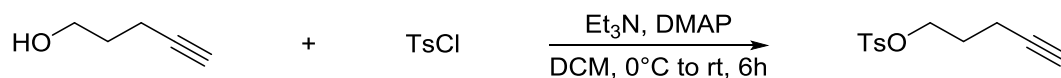


pent-4-yn-1-ol (0.168 g, 2 mmol) and Et<sub>3</sub>N (0.42 g, 4 mmol) were added to DCM (10 mL). Benzoyl chloride derivatives (3 mmol) was added at 0 °C, and the reaction mixture

was allowed to stir at r.t. for 6 h. The reaction was then quenched with water (20 mL), extracted with DCM (3 × 60 mL). The combined organic layers were washed with brine (60 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated in vacuo. The crude residue was purified by flash column chromatography to afford desired product.

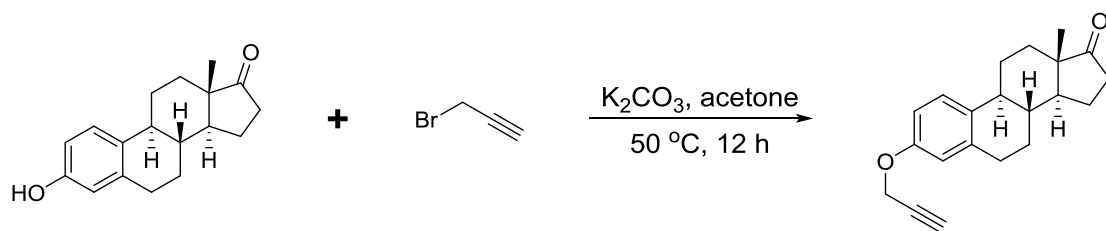


A flame-dried Schlenk flask is successively charged with the corresponding pent-4-yn-1-ol (0.168 g, 2.0 mmol), Et<sub>3</sub>N (0.303 g, 3.0 mmol), DMAP (0.061 g, 0.5 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The reaction mixture is cooled to 0 °C and diethyl chlorophosphate (1.5 equiv) is added dropwise to the solution. The resulting suspension is allowed to warm to room temperature and stirred for further 6h at this temperature. After completion (TLC monitoring), the reaction is carefully quenched with saturated aqueous NH<sub>4</sub>Cl solution, and the aqueous phase is extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic phases are washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.



A flame-dried Schlenk flask is successively charged with the corresponding pent-4-yn-1-ol (0.168 g, 2.0 mmol), Et<sub>3</sub>N (0.404 g, 4.0 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The reaction mixture is cooled to 0 °C and 4-methylbenzenesulfonyl chloride (1.05 equiv) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) is added dropwise to the solution. The resulting suspension is allowed to warm to room temperature and stirred for further 6h at this temperature. After completion (TLC monitoring), the reaction is carefully quenched with saturated aqueous NH<sub>4</sub>Cl solution, and the aqueous phase is extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic phases are washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

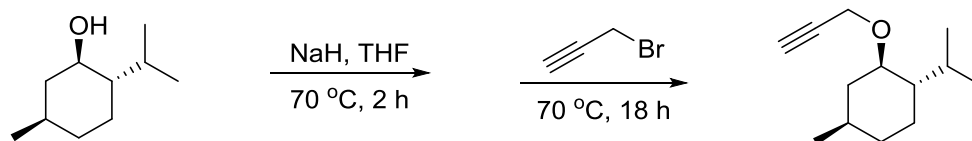
### Synthesis of alkynyl derivatives of Steroids



A flame-dried Schlenk flask is successively charged with the corresponding estrone (0.54 g, 2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (0.33 g, 2.4 mmol), and acetone (10 mL), a magnetic stir bar

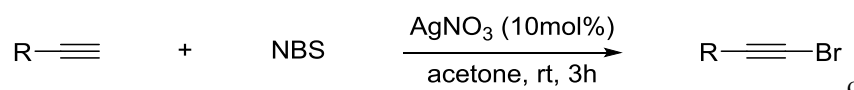
under an atmosphere of nitrogen for 10 min. Next, propargyl bromide (0.238 g, 2.0 mmol, 1.0 equiv) was slowly added at rt. The mixture was allowed to stir at 50 °C for 12 h. After completion (TLC monitoring), the reaction was concentrated in vacuo. The solid residue was taken up in ethyl acetate (100 ml) and washed twice with H<sub>2</sub>O (50 ml) and once with satd. aq NaCl (50 ml), before it was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, silica gel column chromatography (PE/ ethyl acetate = 10 : 1) gave zcg-02-01 (0.370 g, 60 %) as a white solid.

### Synthesis of (1S,2R,4R)-1-isopropyl-4-methyl-2-(prop-2-yn-1-yloxy)cyclohexane



The procedure for the preparation of zcg-02-40 was operated by a literature procedure with a slight modification.<sup>1</sup> A three-necked flask was charged with (L)-menthol (1.56 g, 10 mmol), tetrahydrofuran (30 mL, 0.33 M), and a magnetic stir bar under an atmosphere of nitrogen. Next, 60% NaH (0.8 g, 20 mmol, 2.0 equiv) was added in one portion at 0 °C. The resulting heterogenous mixture was stirred vigorously at 70 °C for 2 h, the reaction was allowed to cool to rt. Next, propargyl bromide (2.2 mL, 25 mmol, 2.5 equiv) was slowly added at rt. The mixture was allowed to stir at 70 °C for 18 h. After completion [R<sub>f</sub> = 0.3 (Petroleum ether (100%), stained with KMnO<sub>4</sub> in TLC monitoring], the reaction is carefully quenched with saturated aqueous NH<sub>4</sub>Cl solution (30 mL), and the aqueous phase is extracted with ethyl acetate (3 × 50 mL). The combined organic phases are washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product (528 mg, 27%) as a slightly yellow oil.

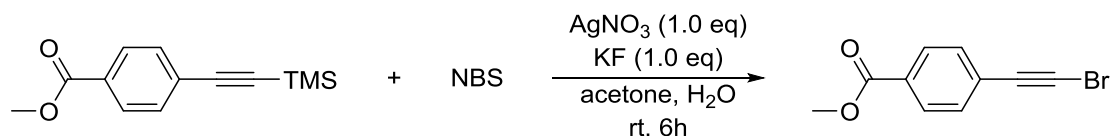
### Synthesis of alkynyl bromides (1a-1h, 1j, 1l-1r)



AgNO<sub>3</sub> (0.017 g, 0.1 mmol) was added to a solution of alkynyl derivatives (1 mmol) in acetone (5 mL). Then NBS (0.196 g, 1.1 mmol) was added in portion. The mixture was stirred for 3 h at room temperature, and then concentrated in vacuo. The solvent was

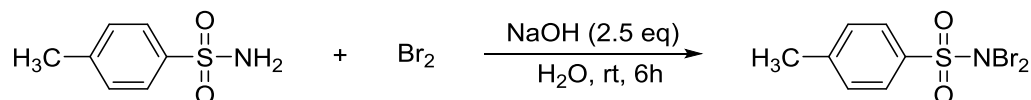
dissolved in petroleum ether and filtered through a short column of silica gel. Solvent was removed in vacuo to afford desired product.

### Synthesis of alkynyl bromides 1i

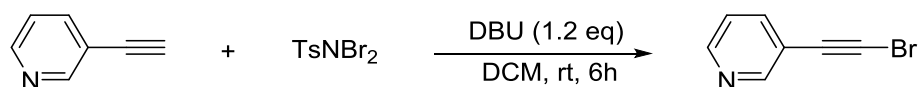


To the solution of methyl 4-((trimethylsilyl)ethynyl)benzoate (0.232 g, 1.0 mmol) in 6 mL of acetonitrile, water (36  $\mu\text{L}$ , 2 mmol) was added under  $\text{N}_2$ . Next  $\text{AgNO}_3$  (0.178 g, 1.0 mmol) and  $\text{KF}$  (0.058g, 1.0 mmol) and  $\text{NBS}$  (2.43 g, 10.4 mmol) were added. The reaction was stirred for 6 h at room temperature without an access of light. The solvent was removed under reduced pressure and the residue was purified by elution through silica gel ( $\text{CH}_2\text{Cl}_2$ ) yielding 227 mg (0.95 mmol, 95%) of white solid.

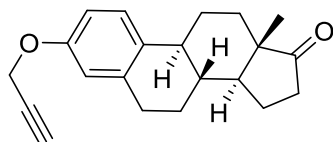
### Synthesis of alkynyl Bromides 1k



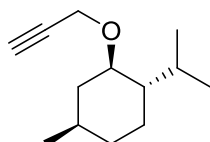
4-Methylbenzenesulphonamide (2.12 g, 12 mmol) was dissolved in a solution of  $\text{NaOH}$  (1.2 g, 30 mmol) in water (25 mL) at room temperature. Then bromine (2.17 mL) was added with vigorous stirring. The resulting precipitate of  $\text{N,N}$ -dibromo-4-methylbenzenesulphonamide was filtrated and washed with cold water. Recrystallization with ethanol afforded pure reagent in 80% yield.



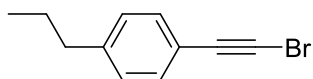
To a stirred solution of 3-ethynylpyridine (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 ml),  $\text{TsNBr}_2$  (1.2 mmol) and  $\text{DBU}$  (1.2 mmol) was added. The progress of the reaction was monitored by TLC. After the completion of the reaction sodium thiosulfate (200 mg) was added to the reaction mixture and further stirred for 5 mins. The reaction mixture was washed with water and extracted with ethylacetate. The organic layer was separated and dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The solvent was removed under reduced pressure and the residue was purified by elution through silica gel (Petroleum ether / Ethyl acetate =3:1) yielding 107 mg (yield 59%) of brown solid.



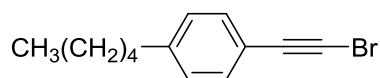
**3-O-Propagylestrone.** This compound is known.<sup>1</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 8.6 Hz, 1H), 6.79 (dd, *J* = 8.6 Hz, 2.8 Hz, 1H), 6.72 (d, 2.8 Hz, 1H), 4.66 (d, *J* = 2.4 Hz, 2H), 2.90 (m, 2H), 2.51 (m, 2H), 2.39 (m, 1H), 2.25 (m, 1H), 2.14 (m, 1H), 2.01 (m, 3H), 1.63 (m, 2H), 1.52 – 1.39 (m, 4H), 0.93 (s, 3H).



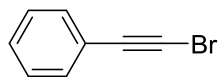
**(1S,2R,4R)-1-isopropyl-4-methyl-2-(prop-2-yn-1-yloxy)cyclohexane.** This compound is known.<sup>2</sup> <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 4.24 – 4.16 (m, 1H), 4.14 (dd, *J* = 15.9, 2.3 Hz, 1H), 3.25 (td, *J* = 10.6, 4.2 Hz, 1H), 2.36 (td, *J* = 2.4, 0.8 Hz, 1H), 2.21 (m, 1H), 2.09 (m, 1H), 1.63 (m, 2H), 1.35 (m, 1H), 1.21 (m, 1H), 0.99 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.4 (m, 2H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H).



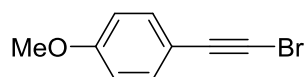
**(E)- 1-(Bromoethynyl)-4-propylbenzene (1a).** This compound is known.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 5.61 (dt, *J* = 14.4 Hz, 7.8 Hz, 2H), 0.93 (t, *J* = 7.8 Hz, 3H).



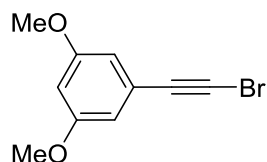
**1-(Bromoethynyl)-4-pentylbenzene (1b).** This compound is known.<sup>4</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.59 (dt, *J* = 15.0 Hz, 7.8 Hz, 2H), 1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).



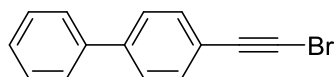
**(Bromoethynyl)benzene (1c).** This compound is known.<sup>5</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.35 (m, 3H).



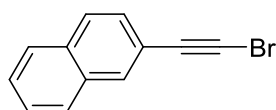
**Methyl 4-(bromoethynyl)benzoate (1d).** This compound is known.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H).



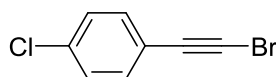
**1-(Bromoethynyl)-4-methoxybenzene (1e).** This compound is known.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.60 (d, *J* = 2.3 Hz, 2H), 6.46 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 6H).



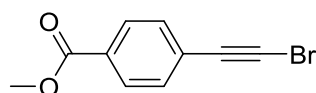
**4-(Bromoethynyl)-1,1'-biphenyl (1f).** This compound is known.<sup>4</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H).



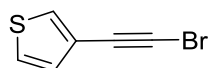
**2-(Bromoethynyl)naphthalene (1g).** This compound is known.<sup>6</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.99 (s, 3H), 7.79 (m, 1H), 7.49 (m, 3H).



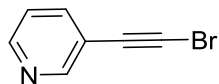
**1-(Bromoethynyl)-4-chlorobenzene (1h).** This compound is known.<sup>7</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H).



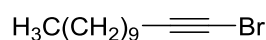
**methyl 4-(bromoethynyl)benzoate (1i).** This compound is known.<sup>7</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.60 (d, *J* = 2.4Hz, 1H), 6.46 (t, *J* = 2.4Hz, 1H), 3.77 (s, 6H).



**3-(Bromoethynyl)thiophene (1j).** This compound is known.<sup>7</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 3.0Hz, 1H), 7.25 (m, 1H), 7.12 (d, *J* = 4.8Hz, 1H).

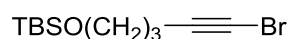


**3-(Bromoethynyl)pyridine (1k).** This compound is known.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.67 (s, 1H), 8.53 (d, *J* = 4.8Hz, 1H), 7.71 (d, *J* = 7.8Hz, 1H), 7.22 (m, 1H).

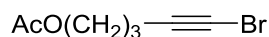


**1-Bromododec-1-yne (1l).** This compound is known.<sup>8</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.18 (t, *J* = 7.2Hz, 2H), 1.49 (dt, *J* = 15.0 Hz, 7.2Hz, 2H), 1.35 (m, 2H), 1.27 (m, 13H),

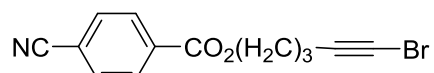
0.87(t,  $J = 6.6\text{Hz}$ , 3H).



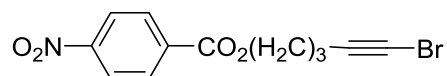
**((5-Bromopent-4-yn-1-yl)oxy)(tert-butyl)dimethylsilane (1m).** This compound is known.<sup>9</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.66 (t,  $J = 6.0\text{Hz}$ , 2H), 2.28 (t,  $J = 7.2\text{ Hz}$ , 2H), 1.69 (dt,  $J = 13.2\text{Hz}$ , 6.0Hz, 2H), 0.88 (s, 9H), 0.04(s, 6H).



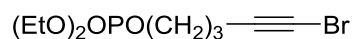
**5-Bromopent-4-yn-1-yl acetate (1n).** This compound is known.<sup>3</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.12 (m, 2H), 2.29(m, 2H), 2.03 (s, 3H), 1.83 (m, 2H).



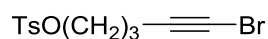
**5-Bromopent-4-yn-1-yl 4-cyanobenzoate (1o).** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.14 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.74 (d,  $J = 7.8\text{Hz}$ , 2H), 4.44 (t,  $J = 6.0\text{ Hz}$ , 2 H), 2.40 (t,  $J = 7.2\text{ Hz}$ , 2H), 2.00 (dt,  $J = 13.2\text{ Hz}$ ,  $J = 6.6\text{ Hz}$ , 2H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>) δ 164.8, 133.9, 132.2, 130.0, 117.9, 116.4, 78.6, 64.4, 39.1, 27.2, 16.7. IR (thin film):  $\nu_{\text{max}}$  2231, 1716, 761 cm<sup>-1</sup>. MS (EI) m/z: (%) 290 (M), 130, 65 (100). HRMS (EI) m/z: [M]<sup>+</sup> Calculated for C<sub>13</sub>H<sub>10</sub>BrNO<sub>2</sub>: 290.9859; Found: 290.9864.



**5-Bromopent-4-yn-1-yl 4-nitrobenzoate (1p).** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.27 (d,  $J = 8.4\text{ Hz}$ , 2H), 8.19 (d,  $J = 8.4\text{Hz}$ , 2H), 4.45 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.40 (t,  $J = 6.6\text{ Hz}$ , 2H), 2.00 (dt,  $J = 13.2\text{ Hz}$ ,  $J = 6.6\text{ Hz}$ , 2H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>) δ 164.6, 150.5, 135.5, 130.7, 123.5, 78.6, 64.5, 39.1, 27.3, 16.7. IR (thin film):  $\nu_{\text{max}}$  1714, 1248, 717 cm<sup>-1</sup>. MS (EI) m/z: (%) 310 (M), 150, 65 (100). HRMS (APCI-LTQ Orbitrap) m/z: [M+H]<sup>+</sup> Calculated for C<sub>12</sub>H<sub>11</sub>BrNO<sub>4</sub>: 311.9866; Found: 311.9867.

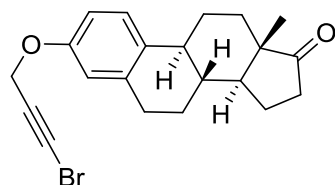


**5-Bromopent-4-yn-1-yl diethyl phosphate (1q).** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.08 (m, 6 H), 2.31 (t,  $J = 7.2\text{Hz}$ , 2 H), 1.83 (dt,  $J = 13.2\text{ Hz}$ ,  $J = 6.0\text{ Hz}$ , 2 H), 1.30 (t,  $J = 7.2\text{ Hz}$ , 6 H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>) δ 78.6, 65.7, 63.7, 38.8, 28.8, 16.1, 15.9. IR (thin film):  $\nu_{\text{max}}$  2982, 1269, 977 cm<sup>-1</sup>. MS (EI) m/z: (%) 298 (M), 99, 65 (100). HRMS (APCI-LTQ Orbitrap) m/z: [M+H]<sup>+</sup> Calculated for C<sub>9</sub>H<sub>17</sub>BrO<sub>4</sub>P: 299.0042; Found: 299.0042.



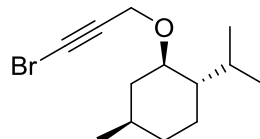
**5-Bromopent-4-yn-1-yl 4-methylbenzenesulfonate (1r).** This compound is known.<sup>10</sup>

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 7.8$  Hz, 2H), 4.09 (t,  $J = 6.0$  Hz, 2H), 2.43 (s, 3H), 2.24 (t,  $J = 7.2$  Hz, 2H), 1.81 (dt,  $J = 13.2$  Hz, 6.0 Hz, 2H).



**(8R,9S,13S,14S)-3-((3-bromoprop-2-yn-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1s).**

This compound is known.<sup>1</sup>  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 8.6$  Hz, 1H), 6.77 (dd,  $J = 8.6$  Hz, 2.8 Hz, 1H), 6.69 (d, 2.8 Hz, 1H), 4.67 (d,  $J = 2.4$  Hz, 2H), 2.90 (m, 2H), 2.51 (m, 1H), 2.38 (m, 1H), 2.25 (m, 1H), 2.16 (m, 1H), 2.04 (m, 3H), 1.62 (m, 2H), 1.52 – 1.39 (m, 4H), 0.91 (s, 3H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 155.5, 137.9, 133.0, 126.4, 114.9, 112.2, 75.2, 56.6, 50.4, 47.9, 47.3, 43.9, 38.2, 35.8, 31.5, 29.6, 26.5, 25.8, 21.5, 13.8. IR (thin film):  $\nu_{\text{max}}$  2928, 2874, 1040, 2360, 2223, 1726, 1604, 1197, 1230, 1009  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calculated for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{BrNa}^+$ : 409.0769; Found: 409.0774.



**(1S,2R,4R)-2-((3-bromoprop-2-yn-1-yl)oxy)-1-isopropyl-4-methylcyclohexane (1t).**

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.20 (d, dd,  $J = 15.8, 1.2$  Hz, 1H), 4.16 (d,  $J = 15.8, 1.2$  Hz, 1H), 3.23 (td,  $J = 10.6, 4.2$  Hz, 1H), 2.20 (m, 1H), 2.06 (m, 1H), 1.62 (ddq,  $J = 18.8, 13.3, 3.4$  Hz, 2H), 1.34 (tdd,  $J = 12.2, 6.5, 3.3$  Hz, 1H), 1.19 (m, 1H), 0.99 (m, 1H), 0.91 (d,  $J = 6.5$  Hz, 3H), 0.4 (m, 2H), 0.88 (d,  $J = 7.0$  Hz, 3H), 0.82 (m, 2H), 0.78 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  78.0, 77.2, 56.2, 48.1, 44.9, 39.7, 34.4, 31.4, 25.3, 23.2, 22.3, 21.0, 16.1. IR (thin film):  $\nu_{\text{max}}$  2924, 2342, 1685, 1631, 1604, 1559, 1384, 1083  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calculated for  $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Br}$ : 273.0849; Found: 273.0850.

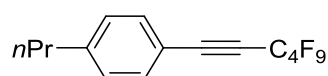
### Representative results for optimization of copper-catalyzed perfluoroalkylation of alkynyl bromides 1a

To a septum capped 25 mL of sealed tube were added Cu catalyst (0.01-10 mol%),

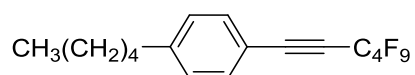
Zn(C<sub>4</sub>F<sub>9</sub>)<sub>2</sub>(DMPU)<sub>2</sub> (1.0 equiv) under N<sub>2</sub>, followed by solvent (2.0 mL) with stirring. **1a** (0.2 mmol) was then added subsequently. The sealed tube was screw capped and heated to 40-100 °C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature. The yield was determined by <sup>19</sup>F NMR before working up. If necessary, the reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product.

### General procedure for copper-catalyzed perfluoroalkylation of alkynyl bromides

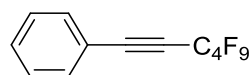
To a septum capped 25 mL of sealed tube were added CuI (0.5 mol%), Zn(R<sub>F</sub>)<sub>2</sub>(DMPU)<sub>2</sub> (0.2 mmol) under N<sub>2</sub>, followed by toluene (2.0 mL) with stirring. **1** (0.2 mmol) was then added subsequently. The sealed tube was screw capped and heated to 80 °C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.



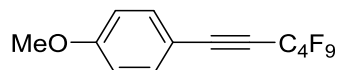
**1-(perfluorohex-1-yn-1-yl)-4-propylbenzene (6a)**. This compound is known.<sup>11</sup> The product (67 mg, 92% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.65 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.1 (t, *J* = 9.0 Hz, 3F), -97.1 (s, 2F), -123.8 (t, *J* = 5.6 Hz, 2F), -125.5 (q, *J* = 4.0 Hz, 2F).



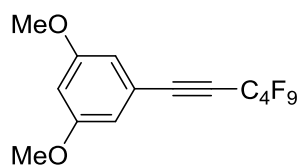
**1-pentyl-4-(perfluorohex-1-yn-1-yl)benzene (6b)**. This compound is known.<sup>11</sup> The product (69 mg, 88% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.62 (m, 2H), 1.32 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.1 (t, *J* = 9.6 Hz, 3F), -97.1 (d, *J* = 2.3 Hz, 2F), -123.5 (m, 2F), -125.5 (m, 2F).



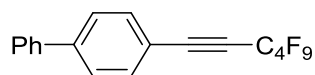
**(perfluorohex-1-yn-1-yl)benzene (6c).** This compound is known.<sup>11</sup> (53 mg, 83% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.7 (s, 3F), -98.0 (s, 2F), -124.1 (s, 2F), -126.1 (s, 2F).



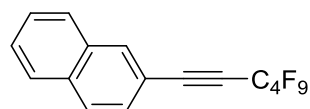
**1-methoxy-4-(perfluorohex-1-yn-1-yl)benzene (6d).** This compound is known.<sup>11</sup> The product (63 mg, 90% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.6 (t, *J* = 9.6 Hz, 3F), -97.4 (d, *J* = 5.6 Hz, 2F), -124.0 (s, 2F), -126.1 (d, *J* = 6.8 Hz, 2F).



**1,3-dimethoxy-5-(perfluorohex-1-yn-1-yl)benzene (6e).** This compound is known.<sup>11</sup> The product (57 mg, 75% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl ether = 40:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.69 (s, 2H), 6.58 (s, 2H), 3.80 (s, 6H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.1 (t, *J* = 9.0 Hz, 3F), -97.5 (s, 2F), -123.4 (t, *J* = 4.5 Hz, 2F), -125.5 (q, *J* = 4.5 Hz, 2F).

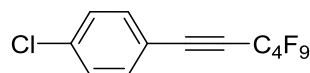


**4-(perfluorohex-1-yn-1-yl)-1,1'-biphenyl (6f).** This compound is known.<sup>11</sup> The product (68 mg, 86% yield) as a white solid was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.64 (s, *J* = 9.0 Hz, 4H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 3H), 7.42 (t, *J* = 7.8 Hz, 1H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.0 (d, *J* = 7.3 Hz, 3F), -97.3 (s, 2F), -123.4 (s, 2F), -125.5 (s, 2F).

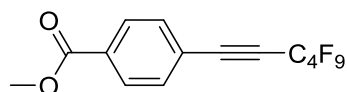


**3-(Perfluorohex-1-yn-1-yl)pyridine (6g).** This compound is known.<sup>11</sup> The product (55 mg, 85% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.13 (s, 3H), 7.85 (m, 3H),

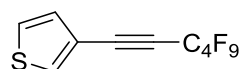
7.57 (m, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.0(m, 3F), -97.2 (s, 2F), -123.3(s, 2F), -125.4(s, 2F).



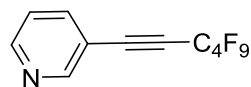
**1-chloro-4-(perfluorohex-1-yn-1-yl)benzene (6h).** This compound is known.<sup>11</sup> The product (52 mg, 73% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 8.4 Hz, 2H), 7.43 (d,  $J$  = 9.0 Hz, 2H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -76.8 (t,  $J$  = 9.6 Hz, 3F), -93.5 (s, 2F), -119.2 (s, 2F), -121.3 (s, 2F).



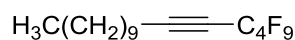
**Methyl 4-(perfluorohex-1-yn-1-yl)benzoate (6i).** This compound is known.<sup>11</sup> The product (68 mg, 90% yield) as a white solid was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =20:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J$  = 8.4Hz, 2H), 7.64 (d,  $J$  = 8.4 Hz, 2H), 3.95 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.0 (s, 3F), -98.0 (s, 2F), -123.4 (s, 2F), -125.5(s, 2F).



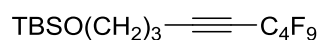
**3-(Perfluorohex-1-yn-1-yl)thiophene(6j).** This compound is known.<sup>11</sup> The product (56 mg, 87% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J$  = 1.8Hz, 1H), 7.34 (m, 1H), 7.20 (d,  $J$  = 4.8Hz, 1H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 3F), -97.3 (s, 2F), -123.4 (m, 2F), -125.5(m, 2F).



**3-(Perfluorohex-1-yn-1-yl)pyridine (6k).** The product (44 mg, 68% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (s, 1H), 8.68 (d,  $J$  = 4.8Hz, 1H), 7.84 (d,  $J$  = 7.8Hz, 1H), 7.33 (m, 1H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8 (t,  $J$  = 2.4 Hz), 151.2, 139.4, 132.1, 118.4-116.1 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 115.8 (t,  $J$  = 2.9 Hz), 110.2-105.4 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 88.7 (t,  $J$  = 6.3 Hz), 77.6 (t,  $J$  = 36.3 Hz).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -85.9 (m, 3F), -103.1 (s, 2F), -128.2 (s, 2F), -130.3(s, 2F). IR (thin film):  $\nu_{\text{max}}$  2925, 1237, 1135  $\text{cm}^{-1}$ . MS (EI) m/z: (%) 321 (M), 152 (100), 99. HRMS (APCI-LTQ Orbitrap) m/z:  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{11}\text{H}_5\text{F}_9\text{N}$ : 322.0273; Found: 322.0273.

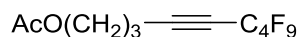


**1,1,1,2,2,3,3,4,4-Nonafluorohexadec-5-yne (6l).** This compound is known.<sup>11</sup> The product (54 mg, 71% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.35 (dt, *J* = 12.6Hz, 6.6Hz, 2H), 1.58 (dt, *J* = 15.0 Hz, 7.2Hz, 2H), 1.39 (m, 2H), 1.28 (m, 13H), 0.88 (t, *J* = 6.6Hz, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.2 (s, 3F), -96.5(s,2F), -123.6 (s, 2F), -125.5 (s,2F).

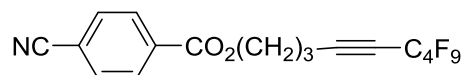


**tert-Butyldimethyl((6,6,7,7,8,8,9,9,9-nonafluoronon-4-yn-1-yl)oxy)silane (6m).**

The product (52 mg, 63% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 3.69 (t, *J* = 5.4Hz, 2H), 2.47 (dt, *J* = 12.6 Hz, 6.6Hz, 2H), 1.78 (dt, *J* = 12.6Hz, 6.0Hz, 2H), 0.89 (s, 9H), 0.05(s, 6H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>) δ 122.0-104.0 [m, -(CF<sub>2</sub>)CF<sub>3</sub>], 95.0 (t, *J* = 9.2 Hz), 67.3 (t, *J* = 53.7 Hz), 60.7, 30.2, 29.7, 25.7, 18.2, 14.8, 5.7. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.2 (S, 3F), -96.6 (s,2F), -123.6 (s, 2F), -125.6 (s,2F). IR (thin film): ν<sub>max</sub> 2982, 1269, 977 cm<sup>-1</sup>. MS (EI) m/z: (%) 416 (M), 146, 77 (100). HRMS (EI) m/z: [M]<sup>+</sup> Calculated for C<sub>15</sub>H<sub>21</sub>F<sub>9</sub>OSi: 416.1218; Found: 416.1215.

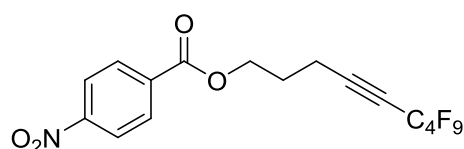


**6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl acetate (6n).** The product (54 mg, 79% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =20:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.15 (t, *J* = 6.6Hz, 2H), 2.48 (dt, *J* = 12.6 Hz, 6.0Hz, 2H), 2.06 (s, 3H), 1.93 (dt, *J* = 13.2Hz, 6.0Hz, 2H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>) δ 170.8, 118.2-104.8 [m, -(CF<sub>2</sub>)CF<sub>3</sub>], 93.7 (t, *J* = 6.0 Hz), 67.7 (t, *J* = 36.0 Hz), 62.4, 26.4, 20.6, 15.4. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.2 (s, 3F), -96.5 (s, 2F), -123.6 (s, 2F), -125.5 (s, 2F). IR (thin film): ν<sub>max</sub> 2360, 1239, 671 cm<sup>-1</sup>. MS (EI) m/z: (%) 344 (M), 155, 91 (100). HRMS (EI) m/z: [M]<sup>+</sup> Calculated for C<sub>11</sub>H<sub>9</sub>F<sub>9</sub>O<sub>2</sub>: 344.0459; Found: 344.0455.

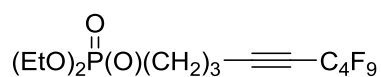


**6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-cyanobenzoate (6o).** The product (64 mg, 74% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =20:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 4.45 (t, *J* = 6.0 Hz, 2H), 2.57 (dt, *J* = 12.0 Hz, 6.6Hz,

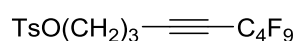
2H), 2.10 (dt,  $J = 13.2\text{Hz}$ ,  $6.6\text{Hz}$ , 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 133.6, 132.2, 130.1, 120.3-117.0 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 117.8, 116.6, 116.5-104.8 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 93.4 (t,  $J = 6.0\text{ Hz}$ ), 68.0 (t,  $J = 35.9\text{ Hz}$ ), 63.8, 26.4, 15.6 (t,  $J = 2.4\text{ Hz}$ ).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.2 (s, 3F), -97.1 (s, 2F), -123.5 (s, 2F), -125.5 (s, 2F). IR (thin film):  $\nu_{\text{max}}$  2258, 1735, 861  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 431 (M), 130 (100), 102. HRMS (APCI-LTQ Orbitrap)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{17}\text{H}_{11}\text{F}_9\text{NO}_2$ : 432.0641; Found: 432.0641.



**6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-nitrobenzoate (6p).** The product (62 mg, 68% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate = 15:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 8.4\text{ Hz}$ , 2H), 8.20 (d,  $J = 9.0\text{ Hz}$ , 2H), 4.47 (t,  $J = 6.6\text{ Hz}$ , 2H), 2.59 (dt,  $J = 12\text{ Hz}$ ,  $6.0\text{Hz}$ , 2H), 2.12 (dt,  $J = 12.6\text{Hz}$ ,  $6.6\text{Hz}$ , 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 150.6, 135.2, 130.7, 123.5, 118.4-105.1 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 93.3 (t,  $J = 6.0\text{ Hz}$ ), 68.0 (t,  $J = 35.9\text{ Hz}$ ), 63.8, 26.4, 15.6 (t,  $J = 2.4\text{ Hz}$ ).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (t,  $J = 9.0\text{Hz}$ , 3F), -97.1 (s, 2F), -123.5 (s, 2F), -125.5 (s, 2F). IR (thin film):  $\nu_{\text{max}}$  2258, 1533, 719  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 451 (M), 150 (100), 115. HRMS (APCI-LTQ Orbitrap)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{16}\text{H}_{11}\text{F}_9\text{NO}_4$ : 452.0539; Found: 452.0540.

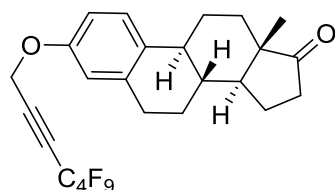


**Diethyl (6,6,7,7,8,8,9,9,9-nonafluoronon-4-yn-1-yl) phosphate (6q).** The product (70 mg, 80% yield) as a pale yellow oil was purified with silica gel chromatography (dichloromethane / methyl alcohol = 20:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.10 (dt,  $J = 14.4\text{ Hz}$ ,  $7.2\text{Hz}$ , 6H), 2.17 (dt,  $J = 12.6\text{ Hz}$ ,  $6.0\text{Hz}$ , 2H), 1.94 (dt,  $J = 13.2\text{ Hz}$ ,  $6.6\text{Hz}$ ), 2.06 (t,  $J = 7.2\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  119.1-106.4 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 93.7 (t,  $J = 8.9\text{ Hz}$ ), 68.0 (t,  $J = 53.8\text{ Hz}$ ), 65.4, 64.0, 28.1, 16.2, 15.0 (t,  $J = 3.6\text{ Hz}$ ).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (t,  $J = 9.6\text{Hz}$ , 3F), -96.9 (s, 2F), -123.5 (s, 2F), -125.5 (m, 2F). IR (thin film):  $\nu_{\text{max}}$  2988, 1239, 746  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 438 (M), 217, 99 (100). HRMS (APCI-LTQ Orbitrap)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{13}\text{H}_{17}\text{F}_9\text{O}_4\text{P}$ : 439.0715; Found: 439.0715.



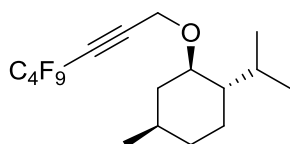
**6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-methylbenzenesulfonate (6r).** The

product (77 mg, 85% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =10:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.4$  Hz, 2H), 7.33 (d,  $J = 7.8$  Hz, 2H), 4.08 (t,  $J = 6.0$  Hz, 2H), 2.44 (m, 5H), 1.92 (dt,  $J = 12.6$ Hz, 6.6Hz, 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 132.6, 130.0, 127.8, 118.4-104.2 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 92.8 (t,  $J = 9.2$  Hz), 68.2 (t,  $J = 54.0$  Hz), 67.9, 26.8, 21.5, 14.8.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 3F), -97.2 (m, 2F), -123.5 (m, 2F), -125.5 (m, 2F). IR (thin film):  $\nu_{\text{max}}$  2262, 1242, 554  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 556 (M), 155, 91 (100). HRMS (EI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calculated for  $\text{C}_{16}\text{H}_{13}\text{F}_9\text{O}_3\text{SNa}$ : 479.0334; Found: 479.0336.



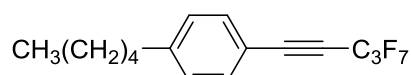
**(8R,9S,13S,14S)-13-methyl-3-((4,4,5,5,6,6,7,7,7-nonafluorohept-2-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (6s).**

The product (95 mg, 90% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =10:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J = 8.8, 1.0$  Hz, 1H), 6.76 (dd,  $J = 8.6, 2.9$  Hz, 1H), 6.70 (d,  $J = 2.8$  Hz, 1H), 4.79 (t,  $J = 4.5$  Hz, 2H), 2.96 – 2.85 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 – 2.35 (m, 1H), 2.26 (td,  $J = 10.8, 4.3$  Hz, 1H), 2.15 (dt,  $J = 19.1$ Hz, 9.0 Hz, 1H), 2.10 – 1.93 (m, 3H), 1.62 (m, 2H), 1.52 – 1.40 (m, 4H), 0.92 (s, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.09 (t,  $J = 9.7$  Hz, 3F), -98.56 – -98.87 (m, 2F), -123.41 (tq,  $J = 10.5$ Hz, 5.2 Hz, 2F), -125.40 – -125.71 (m, 2F).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 155.1, 138.1, 133.8, 126.5, 118.2, 116.3, 115.0, 114.4, 112.4, 108.3, 88.3, 72.9, 55.3, 50.4, 48.0, 44.0, 38.2, 35.8, 31.5, 29.6, 26.4, 25.8, 21.6, 13.8. IR (thin film):  $\nu_{\text{max}}$  2924, 2360, 1740, 1684, 1631, 1540, 1236, 1138, 1057  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calculated for  $\text{C}_{25}\text{H}_{23}\text{O}_2\text{F}_9\text{Na}$ : 549.1447; Found: 549.1445.

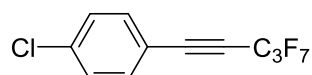


**(1S,2R,4R)-1-isopropyl-4-methyl-2-((4,4,5,5,6,6,7,7,7-nonafluorohept-2-yn-1-yl)oxy)cyclohexane (6t).** The product (75 mg, 91% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =100:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.33 (m, 2H), 3.24 (td,  $J = 10.6, 4.2$  Hz, 1H), 2.17 (pd,  $J = 7.0, 2.6$

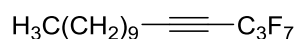
Hz, 1H), 2.11 (dtd,  $J = 12.2, 3.8, 1.9$  Hz, 1H), 1.65 (dddd,  $J = 16.5, 13.1, 6.2, 3.4$  Hz, 2H), 1.36 (tt,  $J = 15.0, 6.5, 3.2$  Hz, 1H), 1.23 (tt,  $J = 10.3, 3.0$  Hz, 1H), 1.05 – 0.97 (m, 1H), 0.89 (d,  $J = 6.5$  Hz, 3H), 0.86 (d,  $J = 7.0$  Hz, 3H), 0.88 – 0.80 (m, 2H), 0.78 (d,  $J = 6.9$  Hz, 3H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.21(t,  $J = 9.7$  Hz, 3F), -98.10(m, 2F), -123.41(tq,  $J = 10.5$ Hz, 5.2 Hz, 2F), -125.65 (m, 2F).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  118.0, 116.3, 108.4, 106.8, 48.1, 39.6, 34.3, 31.4, 25.4, 23.2, 22.1, 20.8, 16.0. IR (thin film):  $\nu_{\text{max}}$  2924, 2853, 2360, 1685, 1631, 1604, 1559, 1540, 1384, 1236, 1137, 865  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{17}\text{H}_{22}\text{OF}_9$ : 413.1522; Found: 413.1527.



**1-Pentyl-4-(perfluoropent-1-yn-1-yl)benzene (5b).** The product (54 mg, 80% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.4$ Hz, 2H), 7.20 (d,  $J = 7.8$ Hz, 2H), 2.63 (t,  $J = 7.8$ Hz, 2H), 1.60 (dt,  $J = 15.0$ Hz, 7.8Hz, 2H), 1.31 (m, 4H), 0.88 (t,  $J = 7.2$ Hz, 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 132.5 (t,  $J = 3.5$  Hz), 128.8, 122.0-116.0 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 115.6 (t,  $J = 4.4$  Hz), 113.8-104.5 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 92.8 (t,  $J = 9.6$  Hz), 74.0 (t,  $J = 52.2$  Hz), 36.1, 31.4, 30.8, 22.5, 14.0.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.2 (t,  $J = 8.5$ Hz, 3F), -97.9 (m, 2F), -126.9 (t,  $J = 6.2$ Hz, 2F). IR (thin film):  $\nu_{\text{max}}$  2928, 1569, 877  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 340 (M), 283 (100), 164. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calculated for  $\text{C}_{16}\text{H}_{15}\text{F}_7$ : 340.1062; Found: 340.1059.



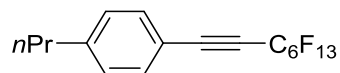
**1-Chloro-4-(perfluoropent-1-yn-1-yl)benzene (5h).** The product (40 mg, 66% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 9.0$ Hz, 2H), 7.38 (d,  $J = 8.4$ Hz, 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 133.7 (t,  $J = 2.3$  Hz), 129.1, 120.5-118.3 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 116.8 (t,  $J = 2.9$  Hz), 116.7-105.2 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 90.9 (t,  $J = 6.5$  Hz), 75.3 (t,  $J = 36.5$  Hz).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.1 (t,  $J = 7.9$ Hz, 3F), -98.5 (m, 2F), -126.9 (t,  $J = 5.6$ Hz, 2F). IR (thin film):  $\nu_{\text{max}}$  2925, 1050, 666  $\text{cm}^{-1}$ . MS (EI)  $m/z$ : (%) 303 (M), 185 (100), 151. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calculated for  $\text{C}_{11}\text{H}_4\text{ClF}_7$ : 303.9890; Found: 303.9884.



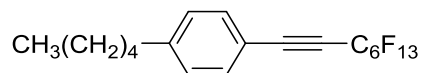
**1,1,1,2,2,3,3-Heptafluoropentadec-4-yne (5l).** The product (50 mg, 75% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%).  $^1\text{H}$

NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  2.35 (dt,  $J = 12.6\text{Hz}$ ,  $6.6\text{Hz}$ , 2H), 1.59 (dt,  $J = 15.0\text{ Hz}$ ,  $7.2\text{Hz}$ , 2H), 1.40 (m, 2H), 1.27 (m, 13H), 0.89 (t,  $J = 6.6\text{Hz}$ , 3H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)  $\delta$  120.5-104.8 [m, -(CF<sub>2</sub>)CF<sub>3</sub>], 95.3 (t,  $J = 6.2\text{ Hz}$ ), 67.1 (t,  $J = 35.7\text{ Hz}$ ), 31.8, 29.4, 29.3, 29.2, 28.8, 28.5, 27.1 (t,  $J = 1.8\text{ Hz}$ ), 22.6, 18.4 (t,  $J = 2.4\text{ Hz}$ ), 14.0. <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -80.3 (m, 3F), -97.4 (m, 2F), -127.1 (s, 2F). IR (thin film):  $\nu_{\text{max}}$  2928, 1369, 1020 cm<sup>-1</sup>. MS (EI) m/z: (%) 334 (M), 69 (100), 55. HRMS (EI) m/z: [M]<sup>+</sup> Calculated for C<sub>15</sub>H<sub>21</sub>F<sub>7</sub>: 334.1531; Found: 334.1531.

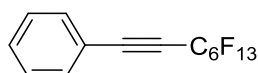
**6,6,7,7,8,8,8-Heptafluorooct-4-yn-1-yl acetate (5n).** The product (36 mg, 61% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate =20:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  4.13 (t,  $J = 6.6\text{Hz}$ , 2H), 2.45 (dt,  $J = 12.6\text{ Hz}$ ,  $6.0\text{Hz}$ , 2H), 2.04 (s, 3H), 1.91 (dt,  $J = 13.2\text{Hz}$ ,  $6.0\text{Hz}$ , 2H). <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)  $\delta$  170.8, 120.2-104.7 [m, -(CF<sub>2</sub>)CF<sub>3</sub>], 93.6 (t,  $J = 6.2\text{ Hz}$ ), 67.6 (t,  $J = 36.0\text{ Hz}$ ), 62.4, 26.4 (t,  $J = 2.0\text{ Hz}$ ), 20.7, 15.4 (t,  $J = 2.4\text{ Hz}$ ). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -80.2 (m, 3F), -97.7 (s, 2F), -120.7 (s, 2F). IR (thin film):  $\nu_{\text{max}}$  2925, 1742, 1147 cm<sup>-1</sup>. MS (EI) m/z: (%) 294 (M), 115, 61 (100). HRMS (APCI-LTQ Orbitrap) m/z: [M+H]<sup>+</sup> Calculated for C<sub>10</sub>H<sub>10</sub>F<sub>7</sub>O<sub>2</sub>: 295.0564; Found: 295.0564.



**1-(perfluorooct-1-yn-1-yl)-4-propylbenzene (7a).** This compound is known.<sup>11</sup> The product (79 mg, 86% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.21 (d,  $J = 8.4\text{ Hz}$ , 2H), 2.62 (t,  $J = 7.8\text{ Hz}$ , 2H), 1.65 (m, 2H), 0.94 (t,  $J = 7.2\text{ Hz}$ , 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -80.9 (t,  $J = 9.6\text{ Hz}$ , 3F), -96.8 (s, 2F), -121.4 (s, 2F), -122.6 (s, 2F), -122.9 (s, 2F), -126.2 (s, 2F).

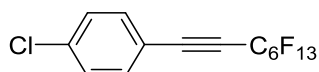


**1-pentyl-4-(perfluorooct-1-yn-1-yl)benzene (7b).** This compound is known.<sup>11</sup> The product (88 mg, 90% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.21 (d,  $J = 7.8\text{ Hz}$ , 2H), 2.64 (t,  $J = 7.8\text{ Hz}$ , 2H), 1.61 (m, 2H), 1.32 (m, 4H), 0.90 (t,  $J = 7.2\text{ Hz}$ , 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)  $\delta$  -80.9 (d,  $J = 8.5\text{ Hz}$ , 3F), -96.8 (s, 2F), -121.4 (s, 2F), -122.6 (s, 2F), -122.9 (s, 2F), -126.2 (s, 2F).

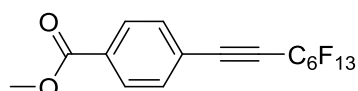


**(perfluorooct-1-yn-1-yl)benzene (7c).** This compound is known.<sup>11</sup> The product (75 mg, 89% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -80.9 (t, *J* = 9.6 Hz, 3F), -97.2 (s, 2F), -121.4 (s, 2F), -122.6 (s, 2F), -122.9 (s, 2F), -126.2 (t, *J* = 14.1 Hz, 2F).

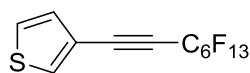
**1-methoxy-4-(perfluorooct-1-yn-1-yl)benzene (7d).** This compound is known.<sup>11</sup> The product (83 mg, 92% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -81.0 (d, *J* = 7.9 Hz, 3F), -96.6 (s, 2F), -121.4 (s, 2F), -122.6 (s, 2F), -122.9 (s, 2F), -126.3 (d, *J* = 7.9 Hz, 2F).



**1-chloro-4-(perfluorooct-1-yn-1-yl)benzene (7h).** This compound is known.<sup>11</sup> The product (75 mg, 83% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -80.9 (t, *J* = 9.6 Hz, 3F), -97.5 (s, 2F), -121.4 (s, 2F), -122.5 (s, 2F), -122.9 (s, 2F), -126.2 (d, *J* = 14.1 Hz, 2F).



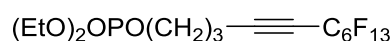
**Methyl 4-(perfluorooct-1-yn-1-yl)benzoate (7i).** This compound is known.<sup>11</sup> The product (83 mg, 86% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl ether =15:1). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H). <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -80.9 (t, *J* = 8.5 Hz, 3F), -97.8 (s, 2F), -121.38 (s, 2F), -122.5 (s, 2F), -122.9 (s, 2F), -126.2 (s, 2F).



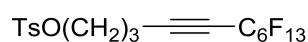
**3-(Perfluorooct-1-yn-1-yl)thiophene (7j).** The product (71 mg, 83% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether (100%)). <sup>1</sup>H



silica gel chromatography (Petroleum ether (100%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  3.67 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.45 (dt,  $J = 12.6\text{ Hz}$ , 6.6 Hz, 2H), 1.77 (dt,  $J = 12.6\text{ Hz}$ , 7.2 Hz, 2H), 0.88 (s, 9H), 0.04 (s, 6H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  121.3-104.3 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 95.0 (t,  $J = 5.9\text{ Hz}$ ), 67.3 (t,  $J = 35.7\text{ Hz}$ ), 60.7, 30.2, 29.7, 25.7, 18.2, 14.9, 5.7.  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.9 (t,  $J = 9.0\text{ Hz}$ , 3F), -96.3 (s, 2F), -121.4 (s, 2F), -122.7 (s, 2F), -123.0 (s, 2F), -126.2 (s, 2F). IR (thin film):  $\nu_{\text{max}}$  2258, 1364, 1147  $\text{cm}^{-1}$ . MS (EI) m/z: (%) 526 (M), 146, 77 (100). HRMS (EI) m/z:  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{17}\text{H}_{22}\text{F}_{13}\text{OSi}$ : 517.1227; Found: 517.1227.



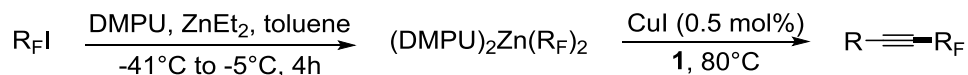
**Diethyl (6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundec-4-yn-1-yl) phosphate (7q).** The product (81 mg, 75% yield) as a pale yellow oil was purified with silica gel chromatography (dichloromethane / methyl alcohol = 20:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09 (m, 6H), 2.50 (dt,  $J = 12.0\text{ Hz}$ , 6.0 Hz, 2H), 1.93 (dt,  $J = 7.2\text{ Hz}$ , 6.0 Hz), 1.30 (t,  $J = 6.6\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  119.0-106.4 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 93.6 (t,  $J = 8.9\text{ Hz}$ ), 67.9 (t,  $J = 53.8\text{ Hz}$ ), 65.3, 63.9, 28.0, 16.1, 14.9 (t,  $J = 3.6\text{ Hz}$ ).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 3F), -96.7 (m, 2F), -121.5 (s, 2F), -122.7 (s, 2F), -123.0 (s, 2F), -126.3 (m, 2F). IR (thin film):  $\nu_{\text{max}}$  225, 1258, 1040  $\text{cm}^{-1}$ . MS (EI) m/z: (%) 538 (M), 127, 99 (100). HRMS (APCI-LTQ Orbitrap) m/z:  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{15}\text{H}_{17}\text{F}_{13}\text{O}_4\text{P}$ : 539.0651; Found: 539.0652.



**6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundec-4-yn-1-yl 4-methylbenzenesulfonate (7r).** The product (96 mg, 87% yield) as a pale yellow oil was purified with silica gel chromatography (Petroleum ether / Ethyl acetate = 10:1).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.35 (d,  $J = 8.4\text{ Hz}$ , 2H), 4.10 (t,  $J = 6.0\text{ Hz}$ , 2H), 2.46 (m, 5H), 1.94 (dt,  $J = 13.2\text{ Hz}$ , 6.0 Hz, 2H).  $^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 132.6, 129.9, 127.8, 119.7-105.1 [m,  $-(\text{CF}_2)\text{CF}_3$ ], 92.7 (t,  $J = 6.0\text{ Hz}$ ), 68.2 (t,  $J = 36.0\text{ Hz}$ ), 67.8, 26.7, 21.4, 14.8 (t,  $J = 2.4\text{ Hz}$ ).  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.9 (t,  $J = 10.2\text{ Hz}$ , 3F), -96.9 (s, 2F), -121.4 (s, 2F), -122.5 (s, 2F), -122.9 (s, 2F), -126.2 (m, 2F). IR (thin film):  $\nu_{\text{max}}$  2258, 1364, 1147  $\text{cm}^{-1}$ . MS (EI) m/z: (%) 556 (M), 155, 91 (100). HRMS (APCI-LTQ Orbitrap) m/z:  $[\text{M}+\text{H}]^+$  Calculated for  $\text{C}_{18}\text{H}_{14}\text{F}_{13}\text{O}_3\text{S}$ : 557.0451; Found: 557.0451.

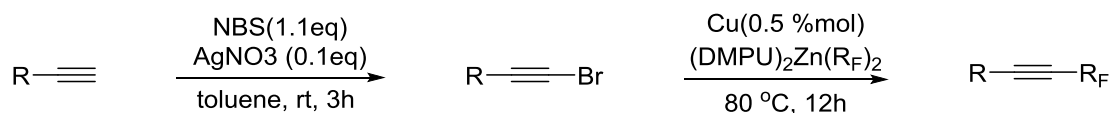
## One-pot synthesis of copper-catalyzed perfluoroalkylation reactions

Method A:



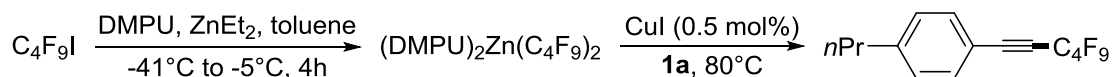
To a septum capped 25 mL of sealed tube were added DMPU (77 mg, 0.6 mmol), C<sub>4</sub>F<sub>9</sub>I (221 mg, 0.64 mmol) under N<sub>2</sub>, followed by toluene (2.0 mL) with stirring. The reaction mixture is cooled to -41 °C and ZnEt<sub>2</sub> (0.3 mmol, 1M in hexane) is added dropwise to the solution. After stirring at -5 °C for 4 h, the sealed tube were added CuI (0.5 mol%) and **1a** (0.2 mmol) under N<sub>2</sub> at room temperature and then heated to 80 °C (oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

Method B:



AgNO<sub>3</sub> (3.4 mg, 0.02 mmol) was added to a solution of alkynyl derivatives (0.2 mmol) in toluene (4 mL). Then NBS (39 mg, 0.22 mmol) was added in portion. The mixture was stirred for 3 h at room temperature, then CuI(0.5 mol %) and (DMPU)<sub>2</sub>Zn(R<sub>F</sub>)<sub>2</sub> (1.0 equiv) were added under N<sub>2</sub>, and heated to 80 °C (oil bath). After stirring for 12 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

### Gram-scale synthesis of copper-catalyzed perfluoroalkylation of alkynyl bromides



4.42 g, 12.8 mmol

**3**

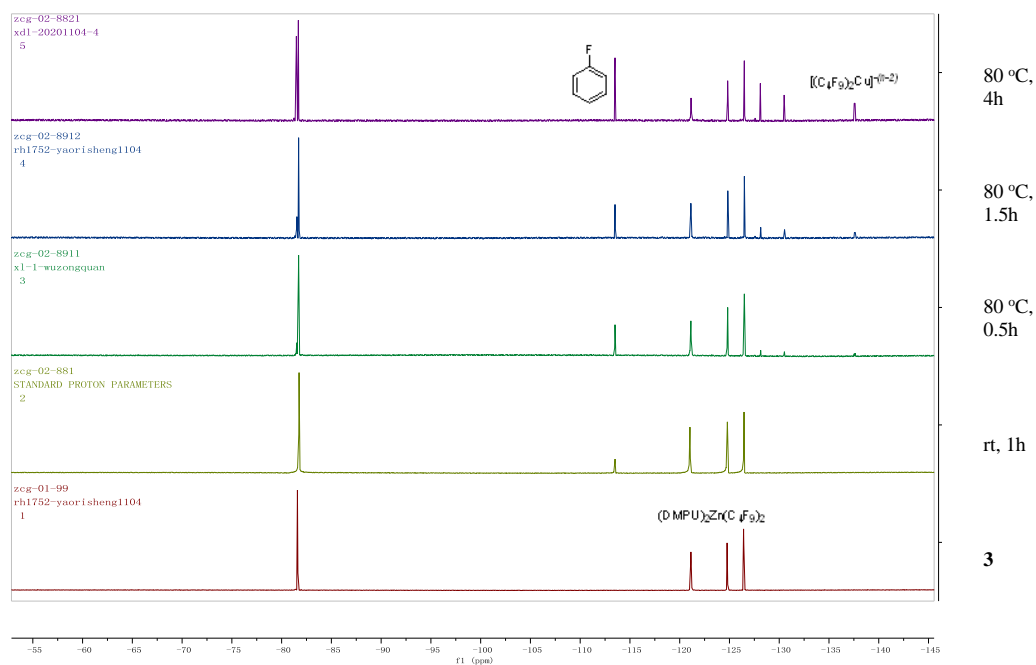
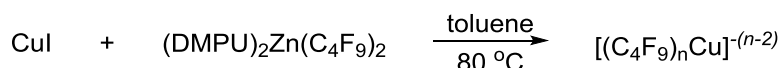
**6a**, 1.28 g (89%)

C<sub>4</sub>F<sub>9</sub>I (4.42 g, 12.8 mmol) and DMPU (1.54 g, 12 mmol) were added to by toluene (10 mL) under N<sub>2</sub>. ZnEt<sub>2</sub> (6 mmol, 1M in hexane) was added dropwise to the solution at -41 °C. After stirring at -5 °C for 4 h, the sealed tube were added CuI (0.5 mol%), **1a** (4.0 mmol) under N<sub>2</sub> at room temperature and heated to 100 °C (oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was

diluted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product (1.28 g, 89%).

### The NMR spectroscopic monitoring of copper species using (DMPU)<sub>2</sub>Zn(C<sub>4</sub>F<sub>9</sub>)<sub>2</sub> and CuI.

CuI (38.2 mg, 0.2 mmol) and (DMPU)<sub>2</sub>Zn(nC<sub>4</sub>F<sub>9</sub>)<sub>2</sub> (152 mg, 0.2 mmol) were added to a 25 ml Schlenk tube equipped with a magnetic stir bar. Then, toluene (2 ml, with 1% volume of fluorobenzene as internal standard) was added under N<sub>2</sub>. The mixture was stirred for 1 h at room temperature under. The reaction was monitored by <sup>19</sup>F NMR analysis and CDCl<sub>3</sub> was sealed capillary filled with CDCl<sub>3</sub> for signal lock. At room temperature, transmetallation reaction was not observed. The reaction mixture was heated to 80 °C, then monitored 0.5h, 1.5h and 4h after heating. A group of peaks [-81.53 (3F), -123.13 (2F), -130.52 (2F), -137.54 (2F)] can be observed clearly and increased with the reaction time.<sup>12</sup>



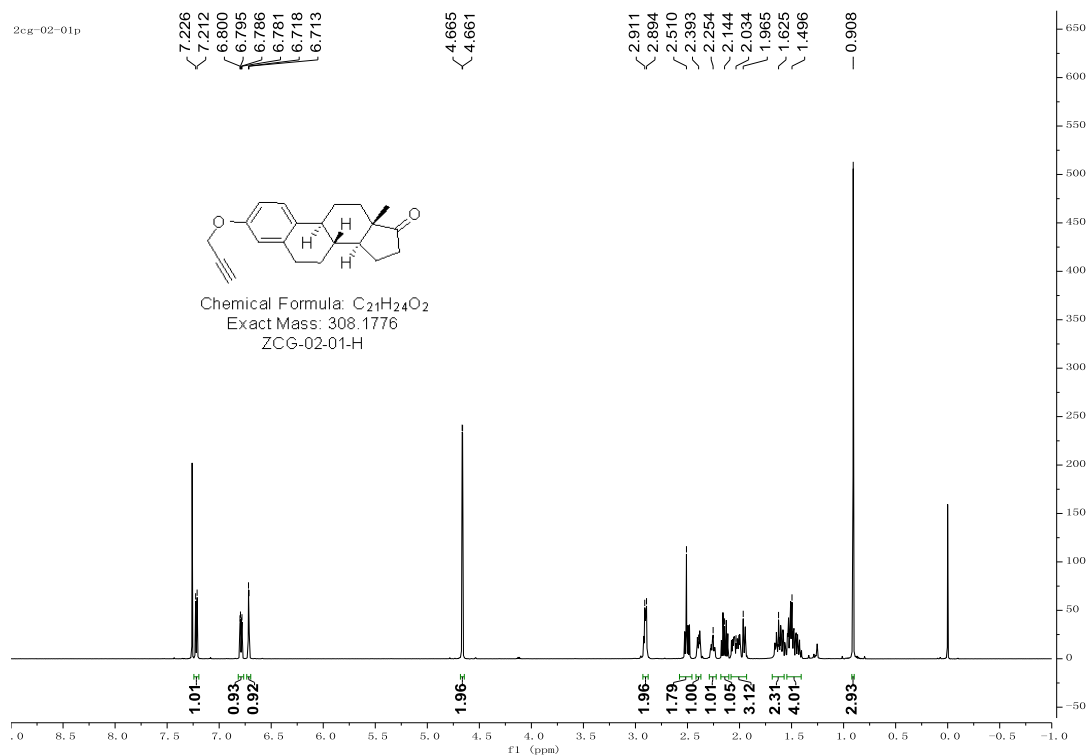
## Reference:

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# Copies of $^1\text{H}$ NMR, $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR spectra

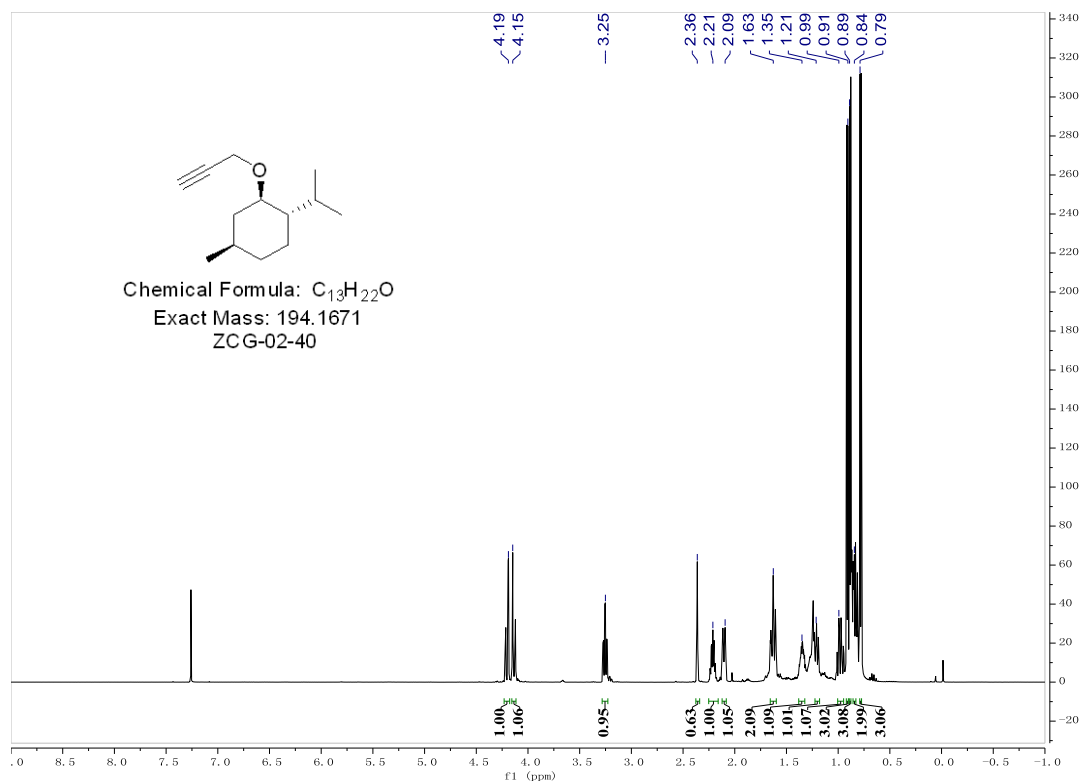
## 3-O-Propagylestrone

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



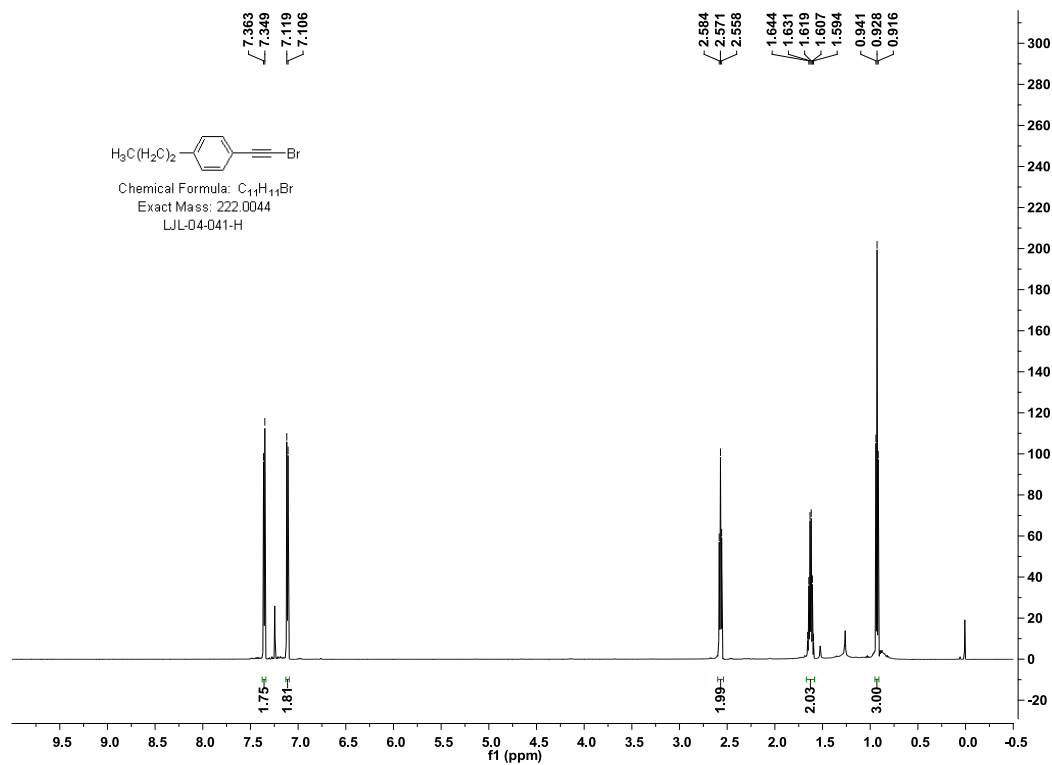
## L-Menthyl propargyl ether

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



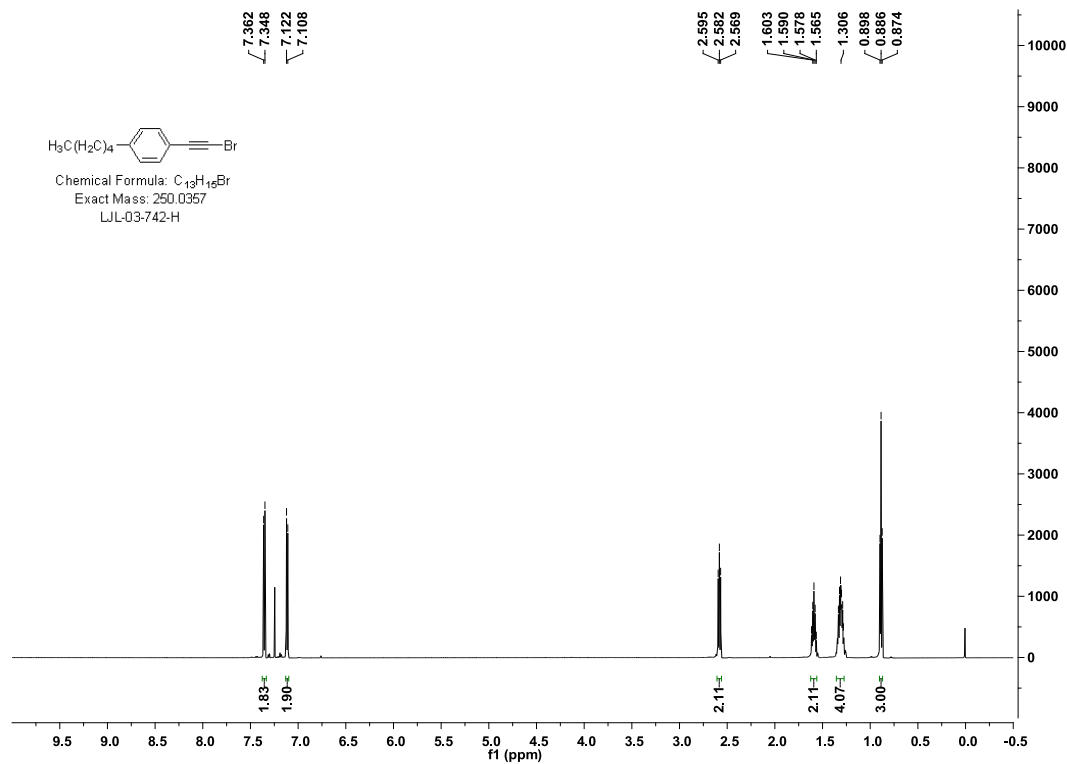
### (E)- 1-(Bromoethynyl)-4-propylbenzene (1a)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



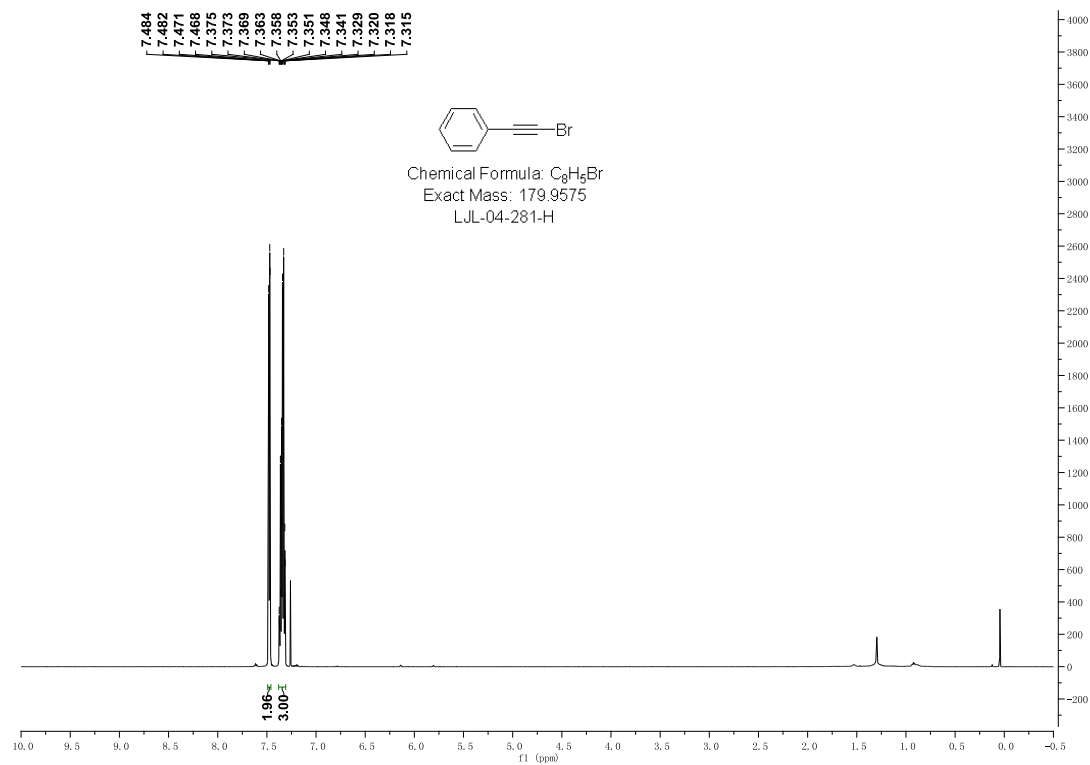
### (Bromoethynyl)-4-pentylbenzene (1b)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



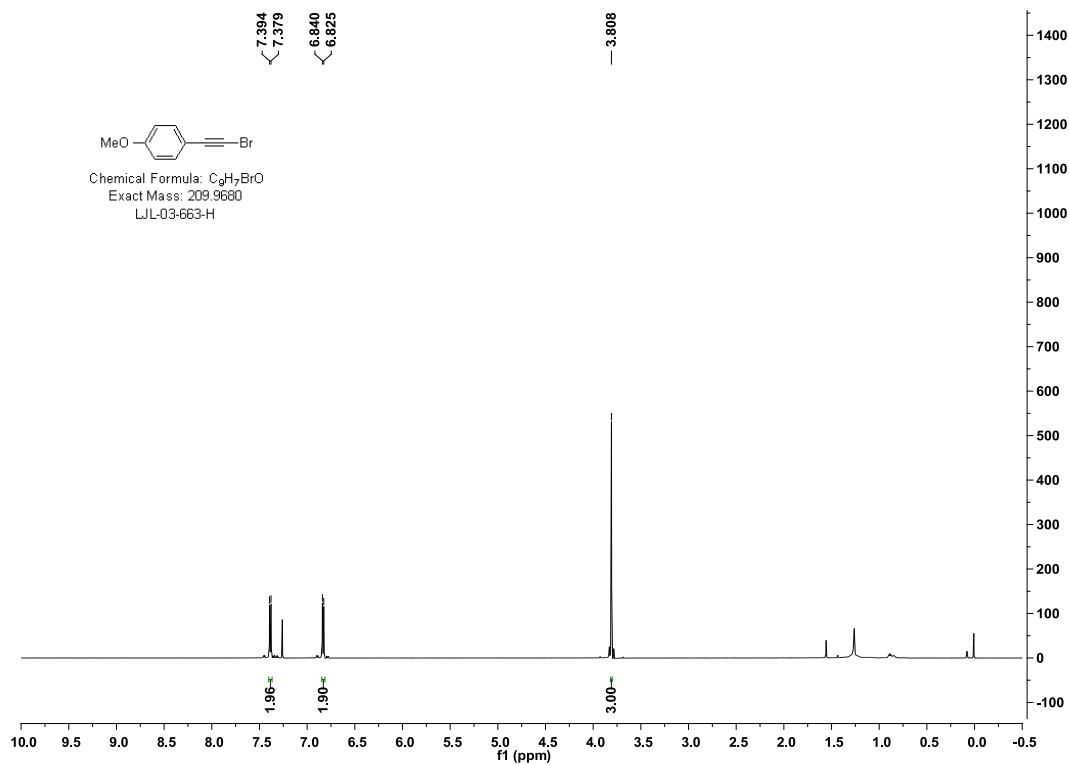
### (Bromoethynyl)benzene (1c)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



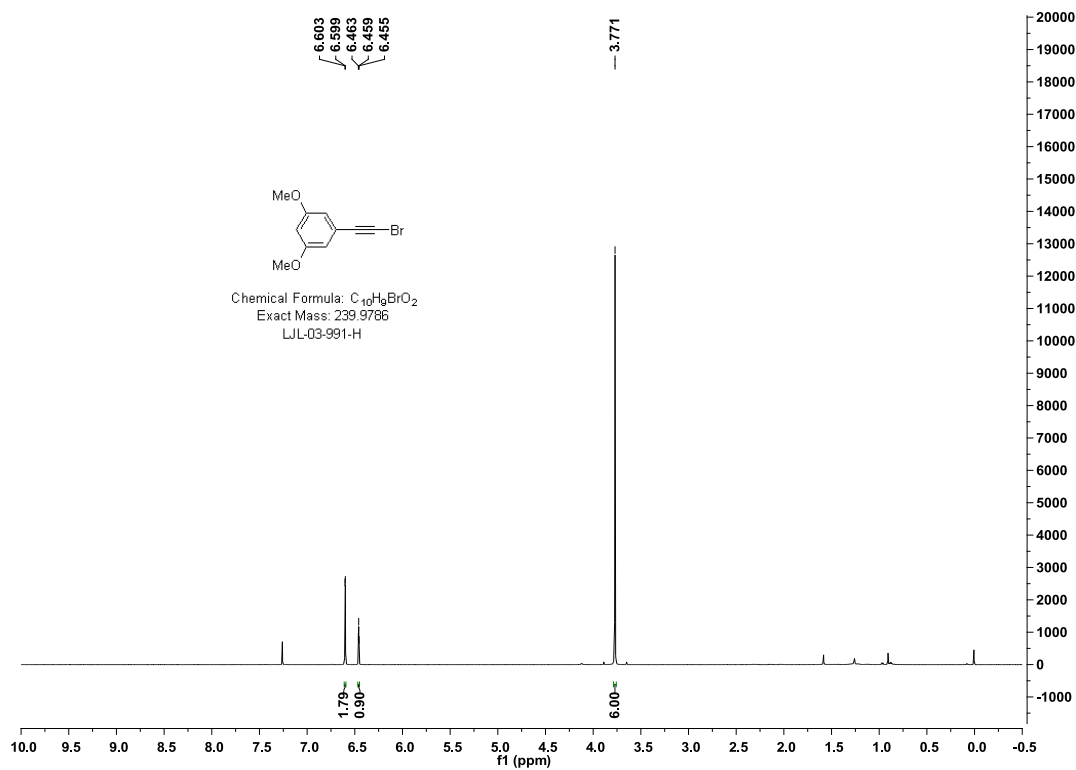
### 1-(Bromoethynyl)-4-methoxybenzene (1d)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



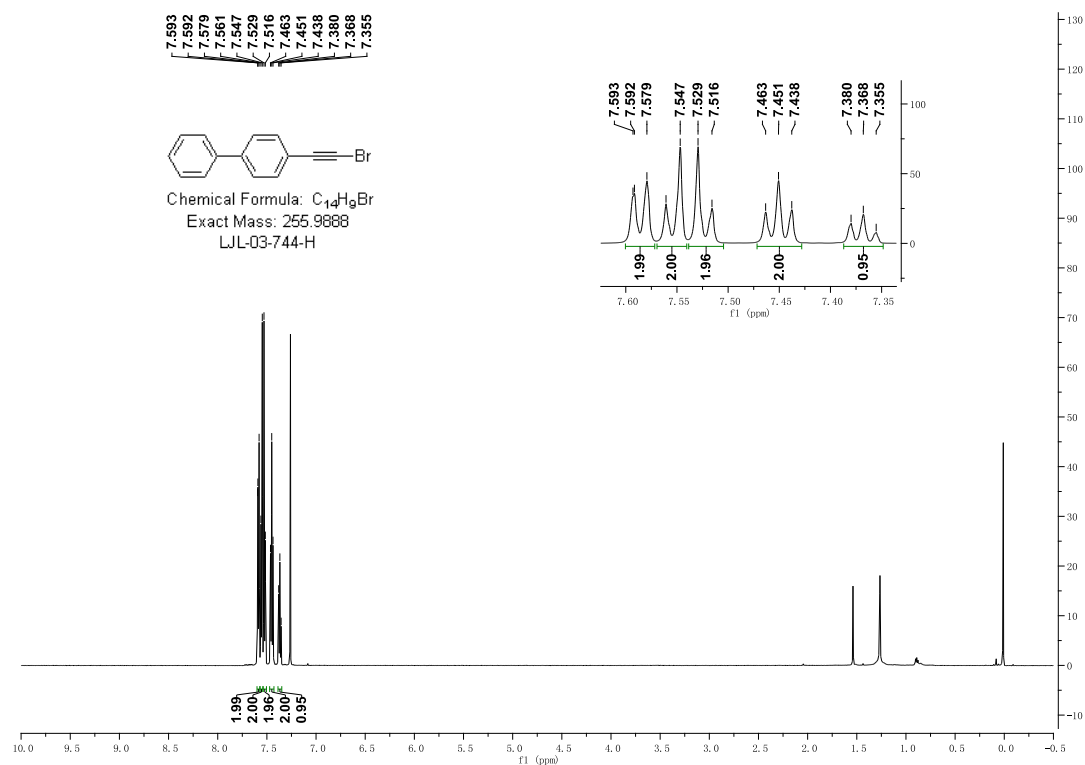
# 1-(Bromoethynyl)-3,5-dimethoxybenzene (1e)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



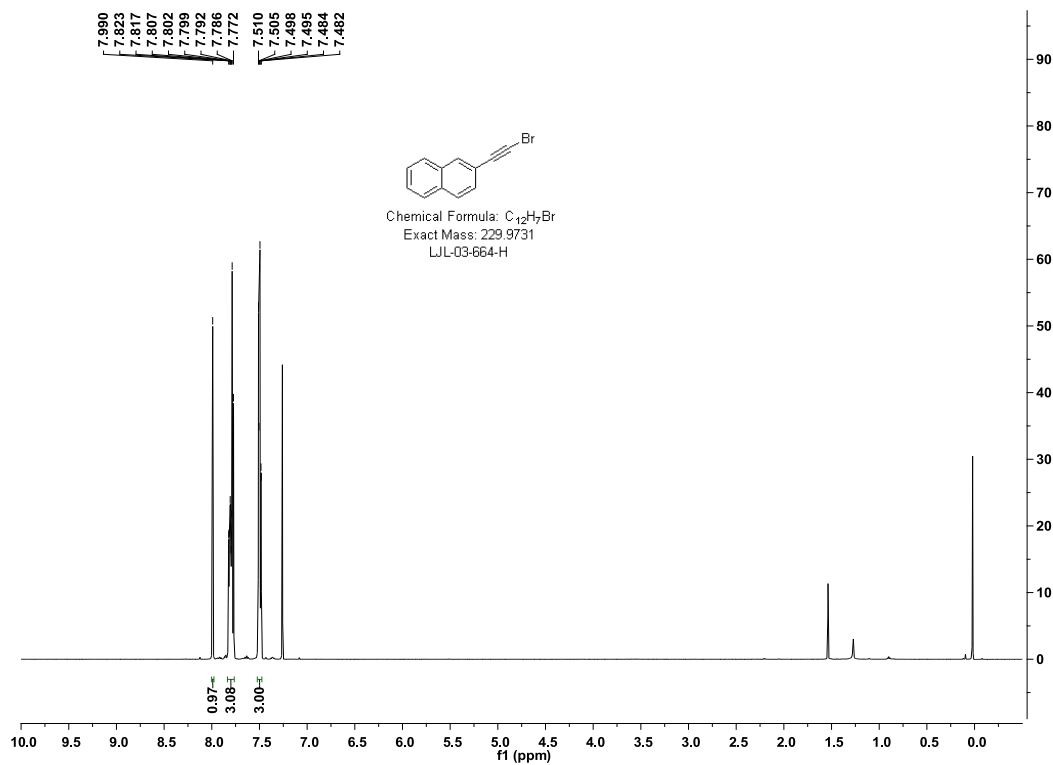
# 4-(Bromoethynyl)-1,1'-biphenyl (1f)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



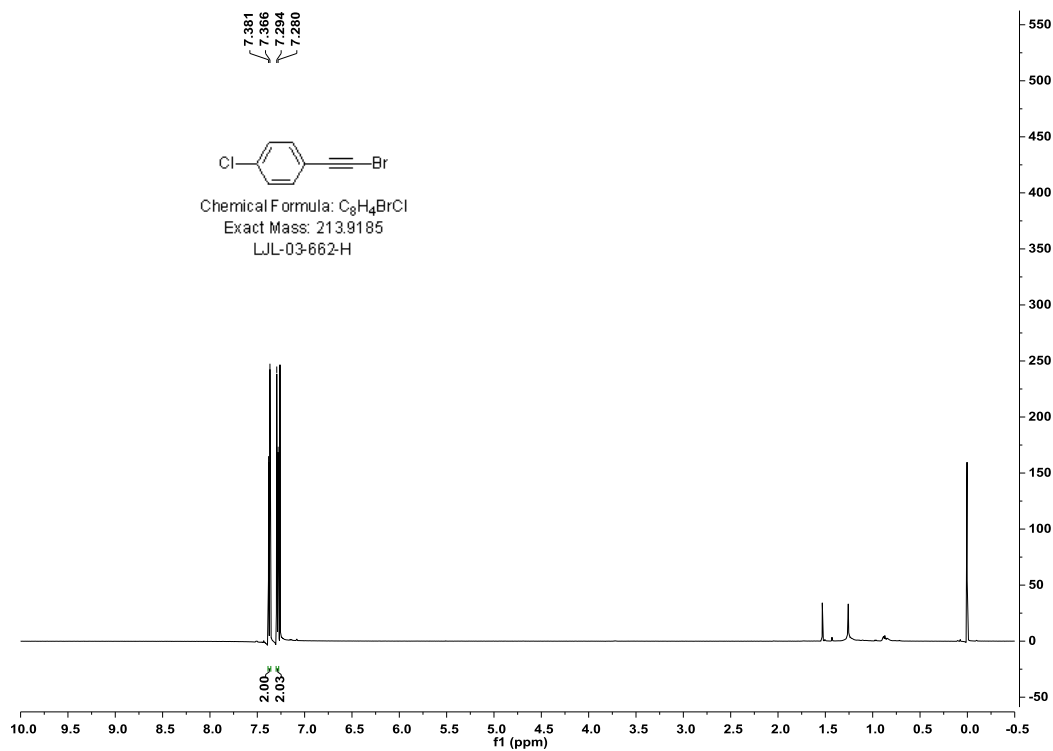
## 2-(Bromoethynyl)naphthalene (1g)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



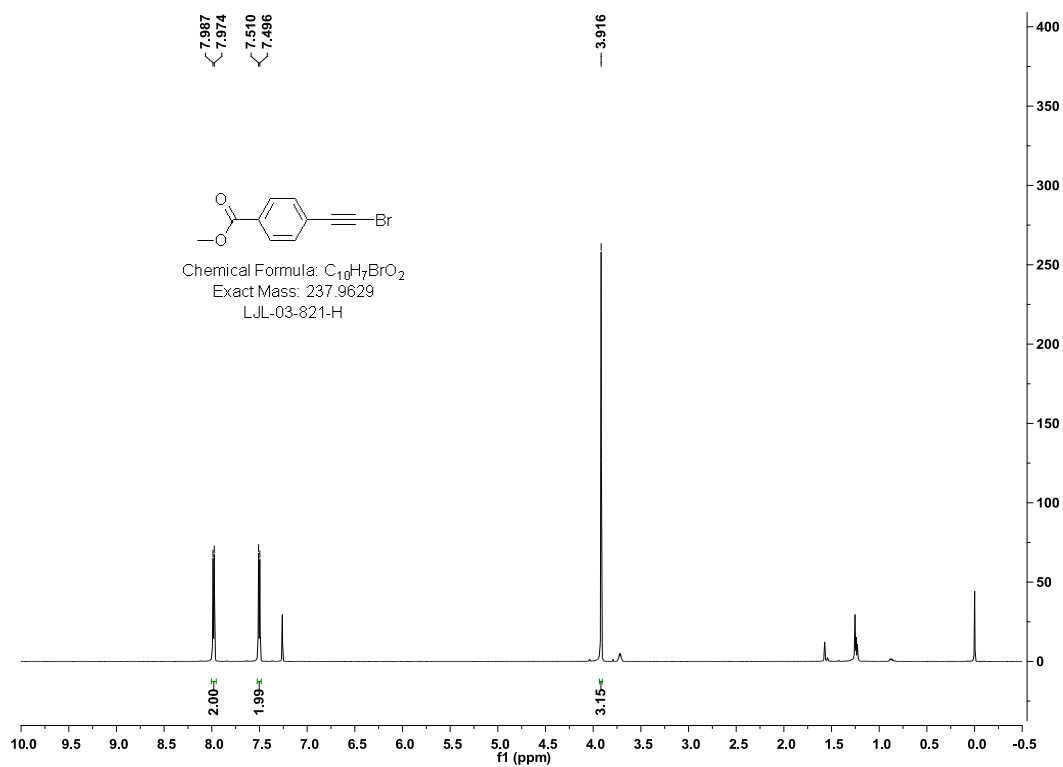
## 1-(Bromoethynyl)-4-chlorobenzene (1h)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



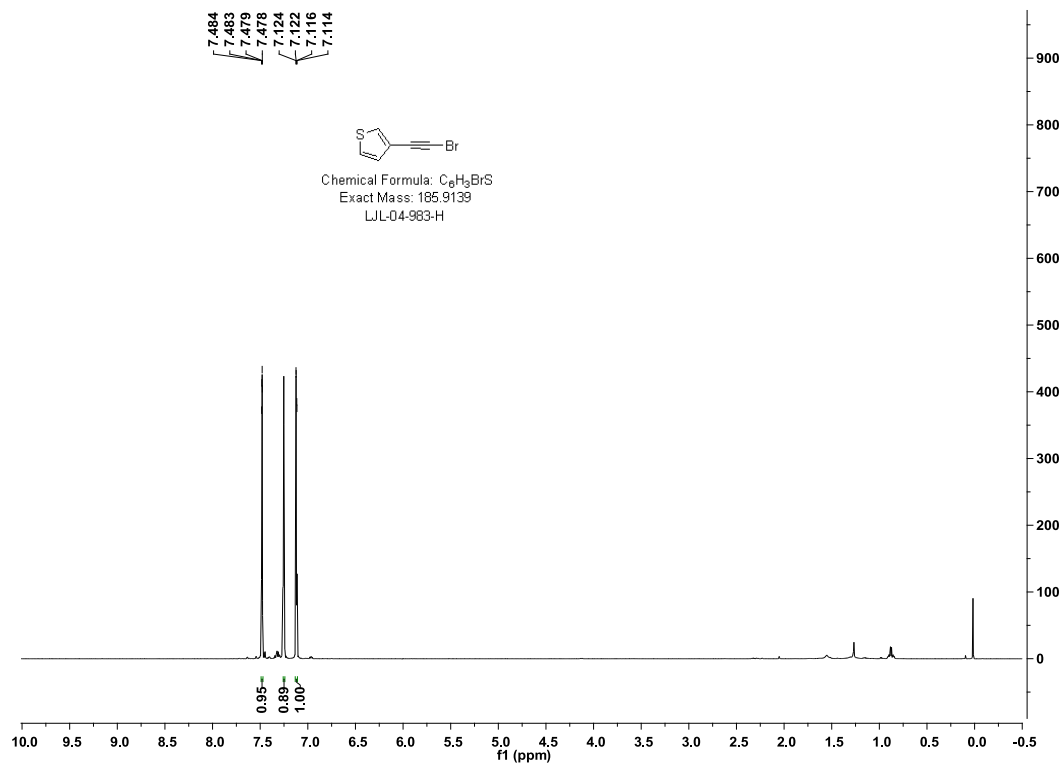
## Methyl 4-(bromoethynyl)benzoate (1i)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



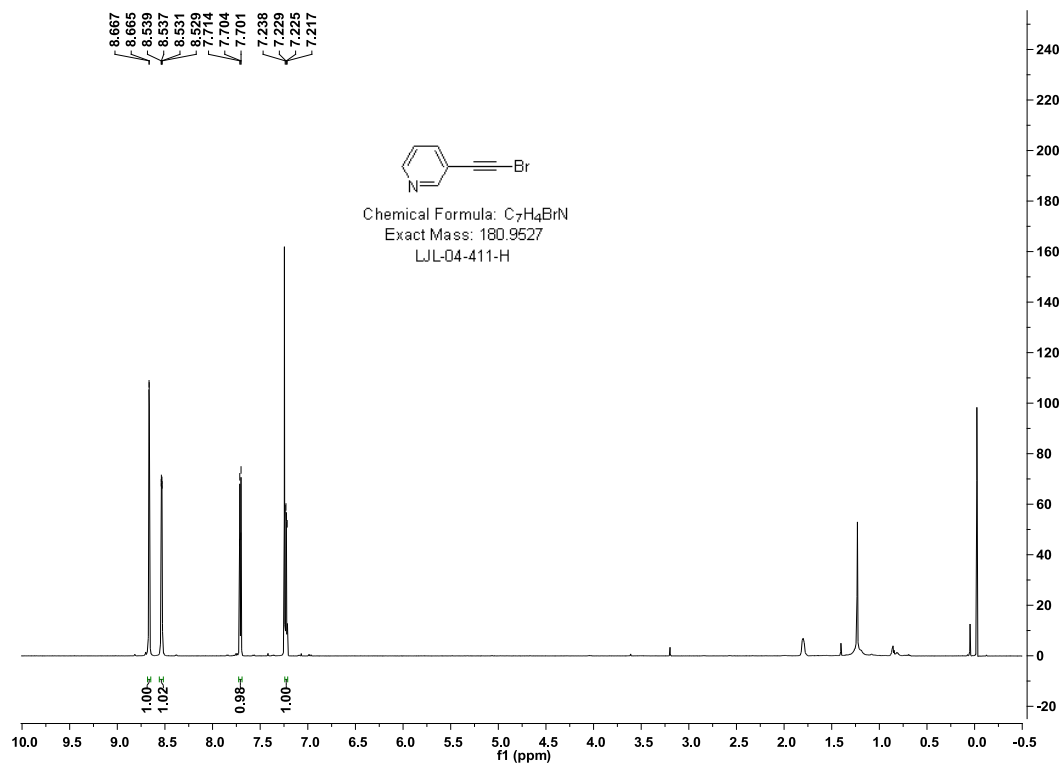
## 1-3-(Bromoethynyl)thiophene (1j)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



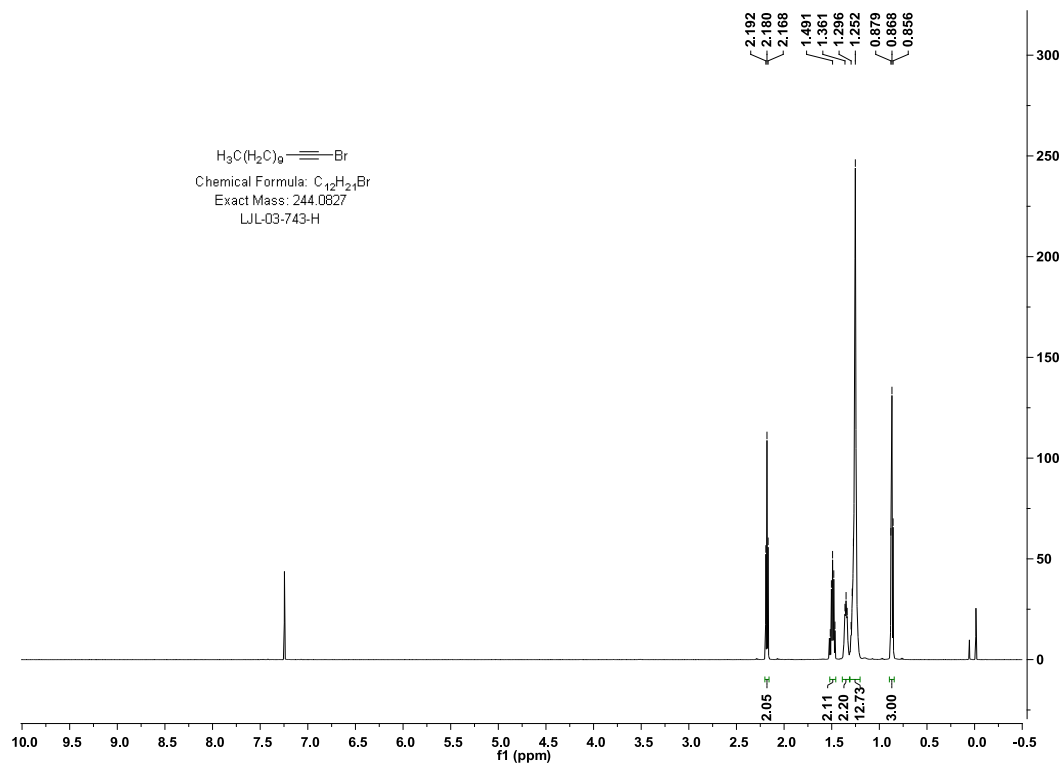
### 3-(Bromoethynyl)pyridine (1k)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



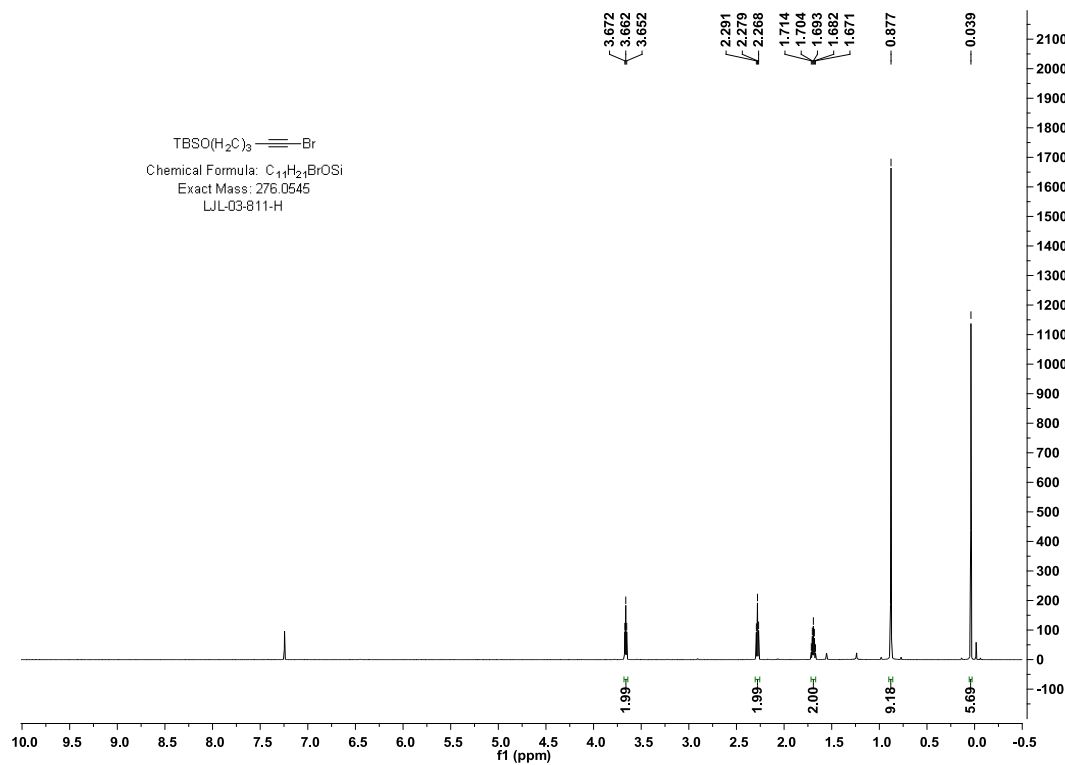
### 1-Bromododec-1-yne (1l)

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )



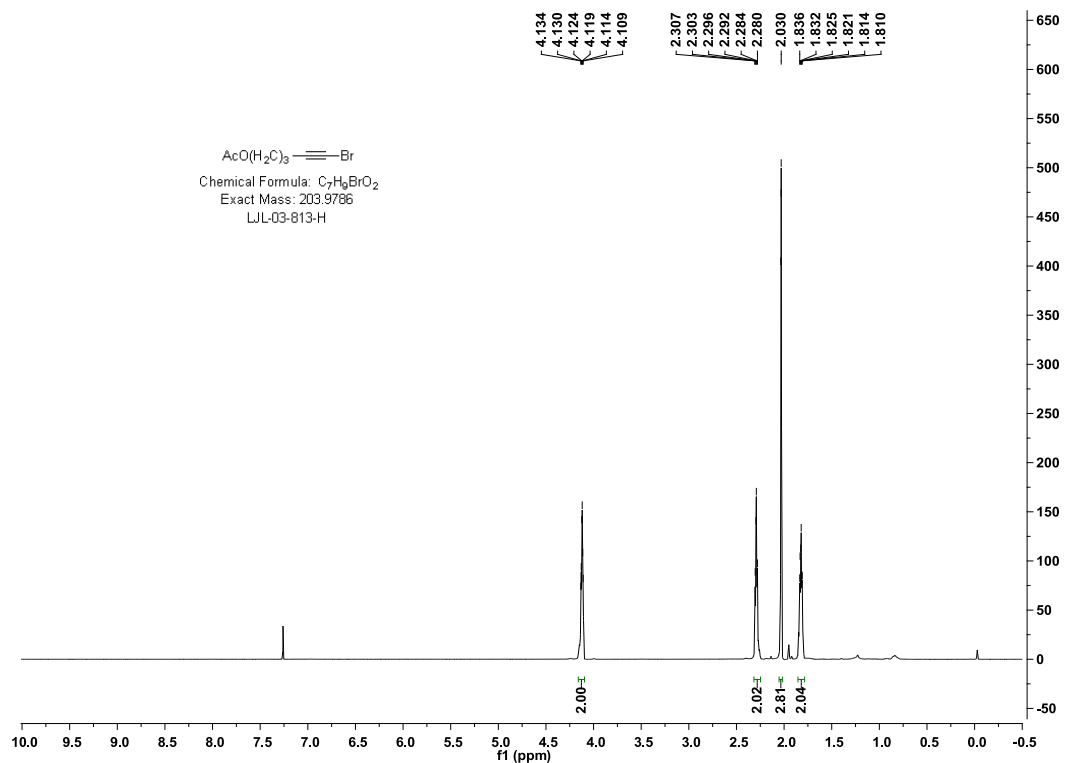
# ((5-Bromopent-4-yn-1-yl)oxy)(tert-butyl)dimethylsilane (1m)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



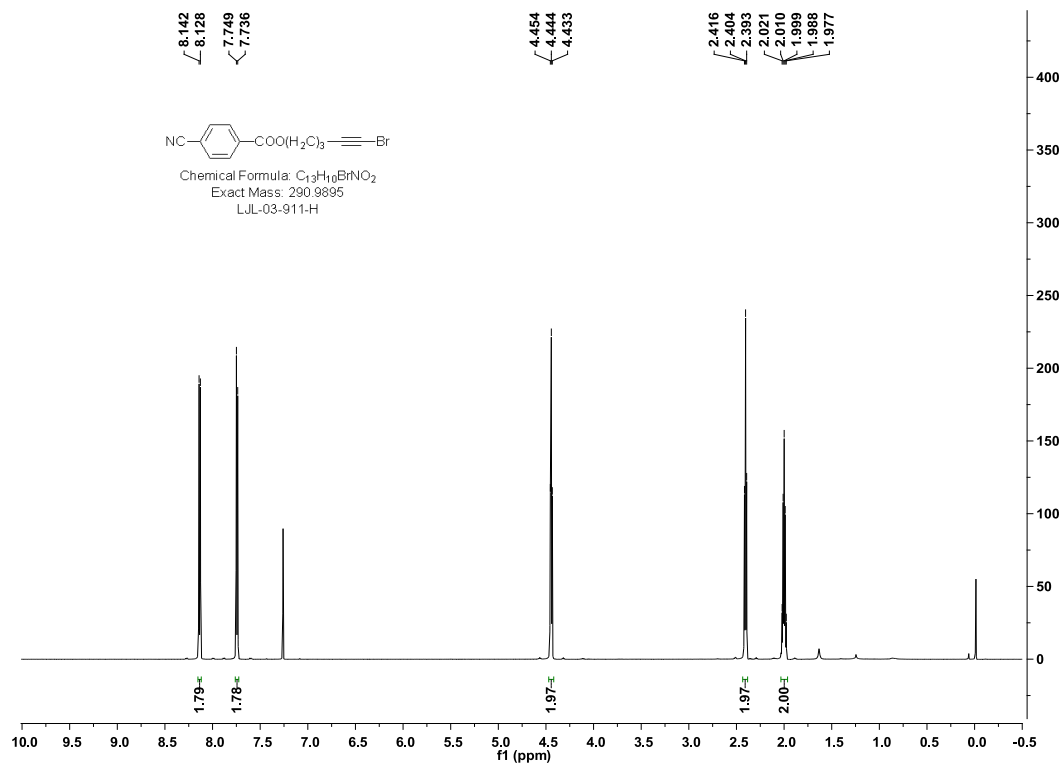
# 5-Bromopent-4-yn-1-yl acetate (1n)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

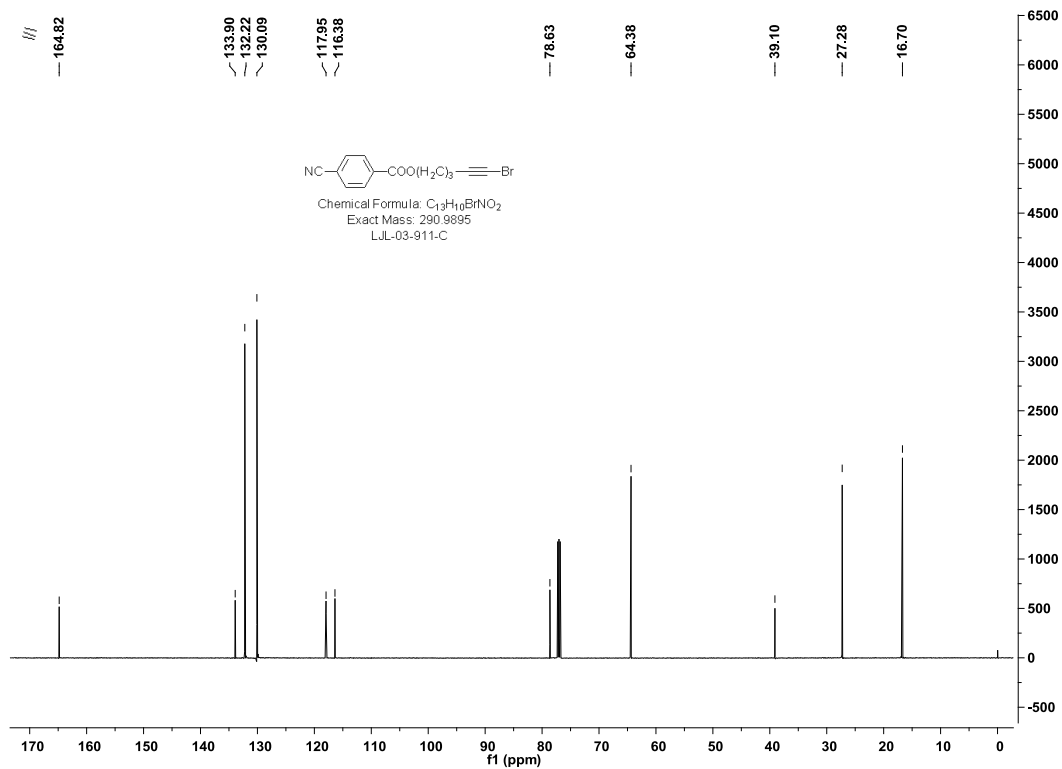


# 5-Bromopent-4-yn-1-yl 4-cyanobenzoate (1o)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

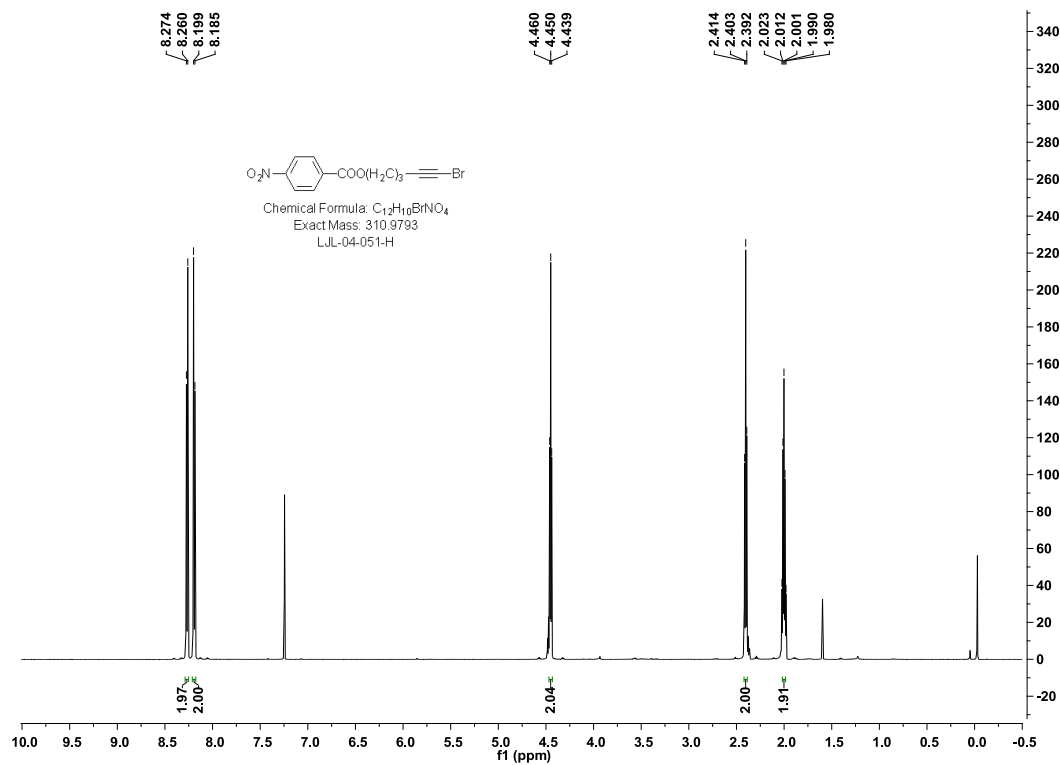


$^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )

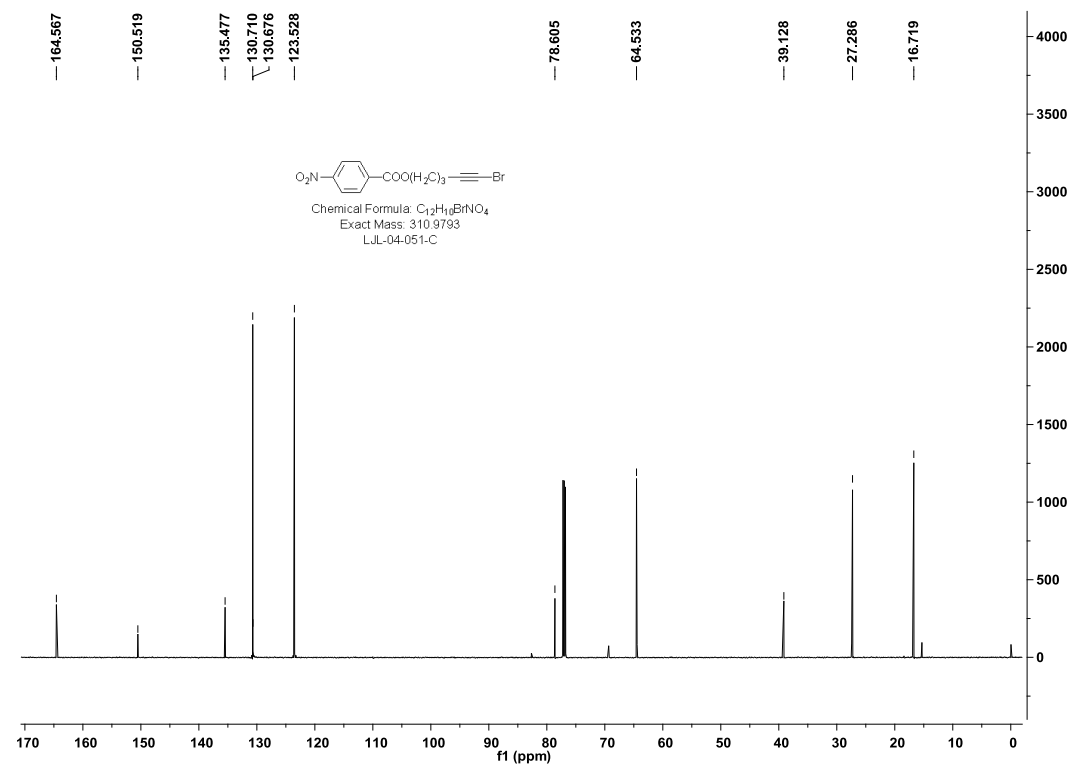


# 5-Bromopent-4-yn-1-yl 4-nitrobenzoate (1p)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

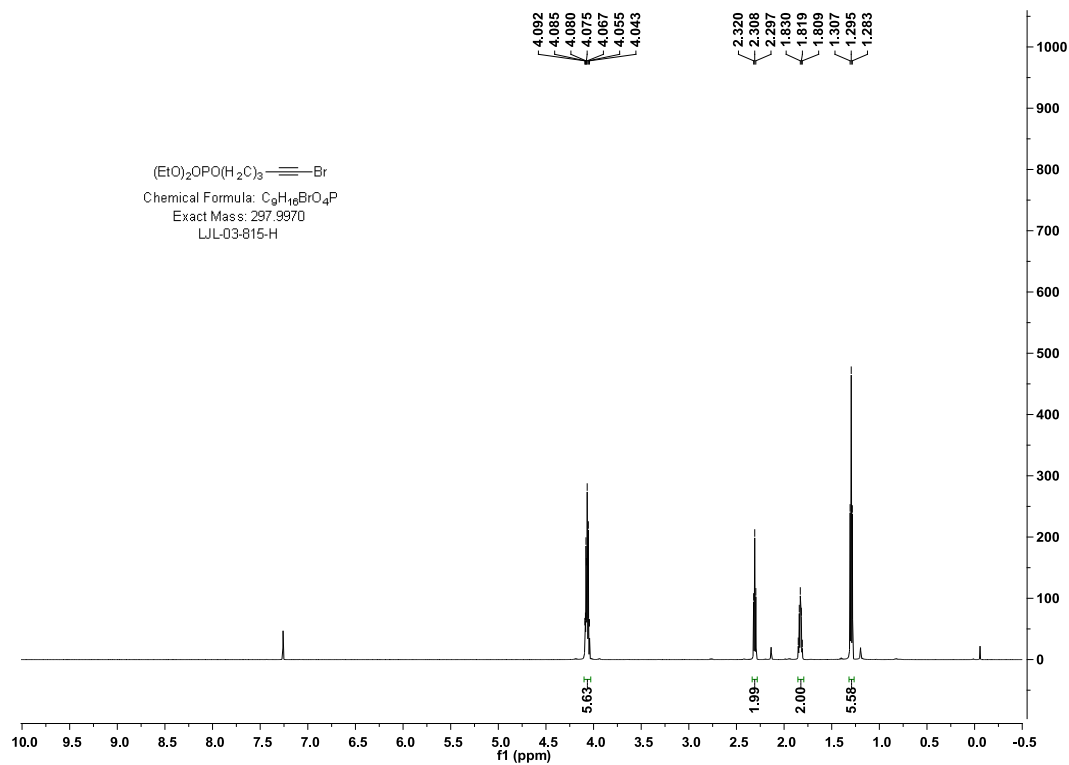


$^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )

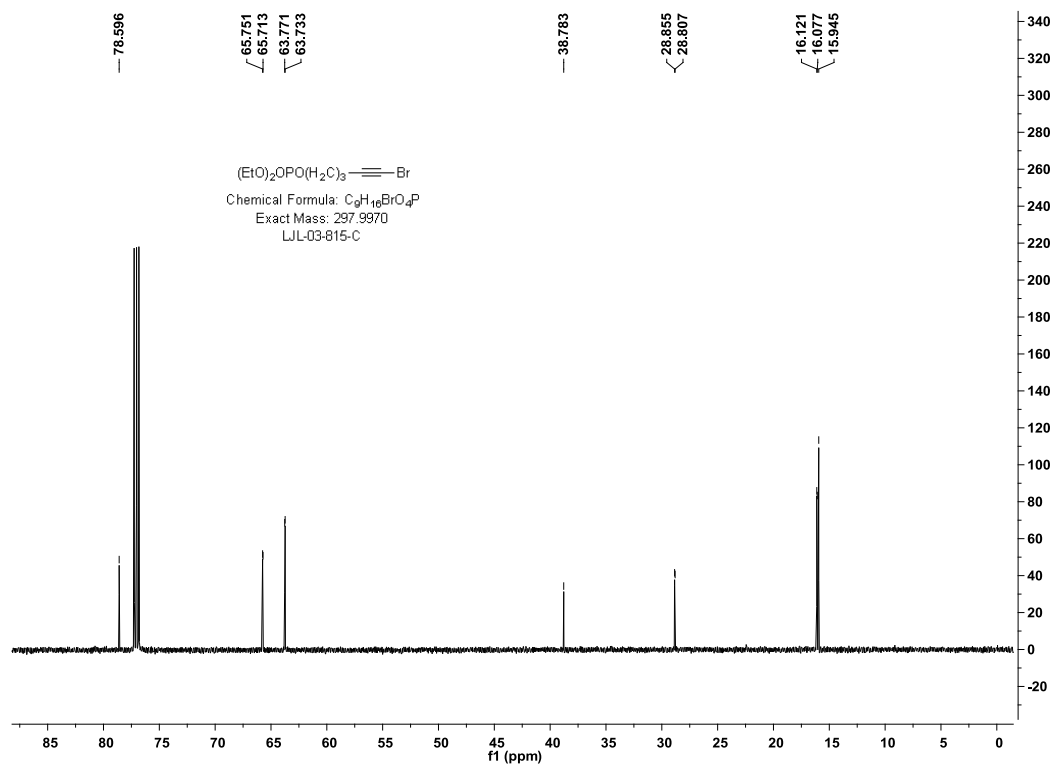


# 5-Bromopent-4-yn-1-yl diethyl phosphate (1q)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

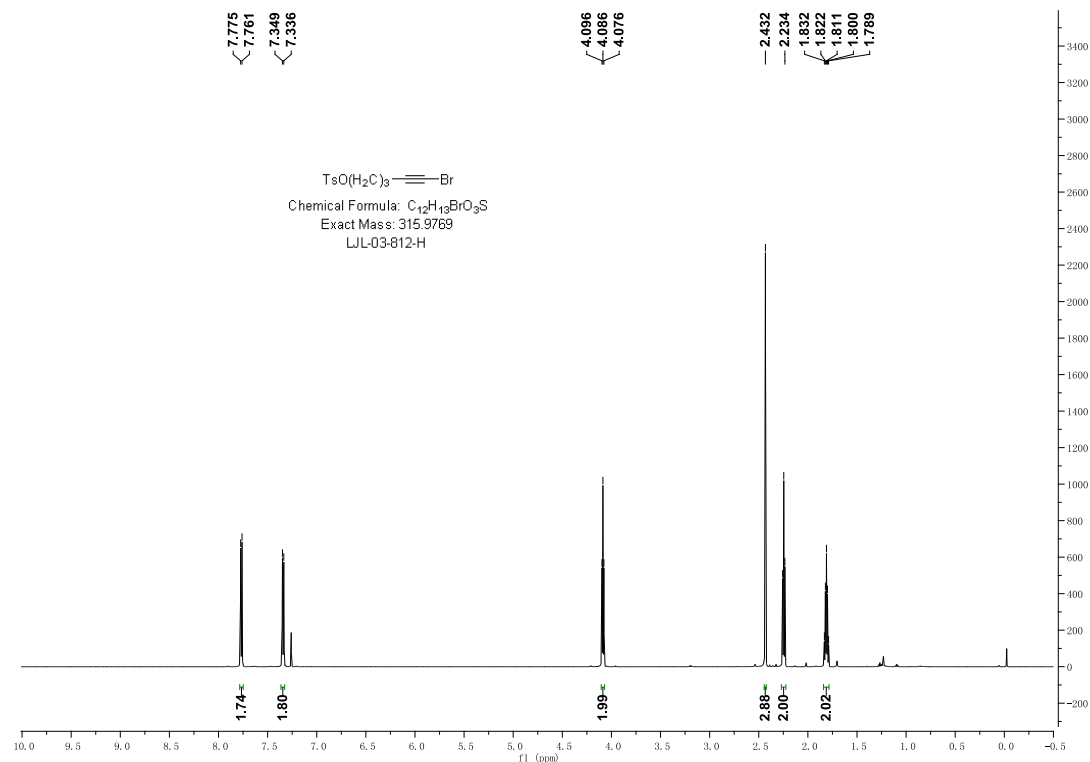


$^{13}\text{C}$  NMR (150.8 MHz,  $\text{CDCl}_3$ )



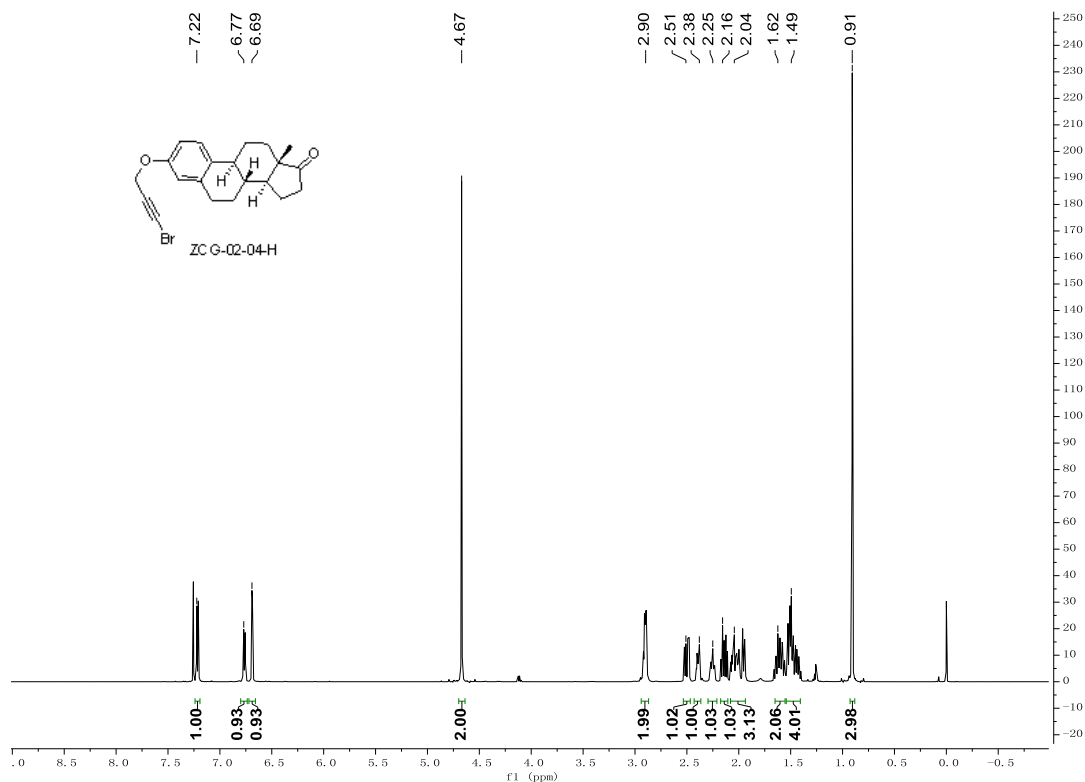
### 5-Bromopent-4-yn-1-yl 4-methylbenzenesulfonate (1r)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

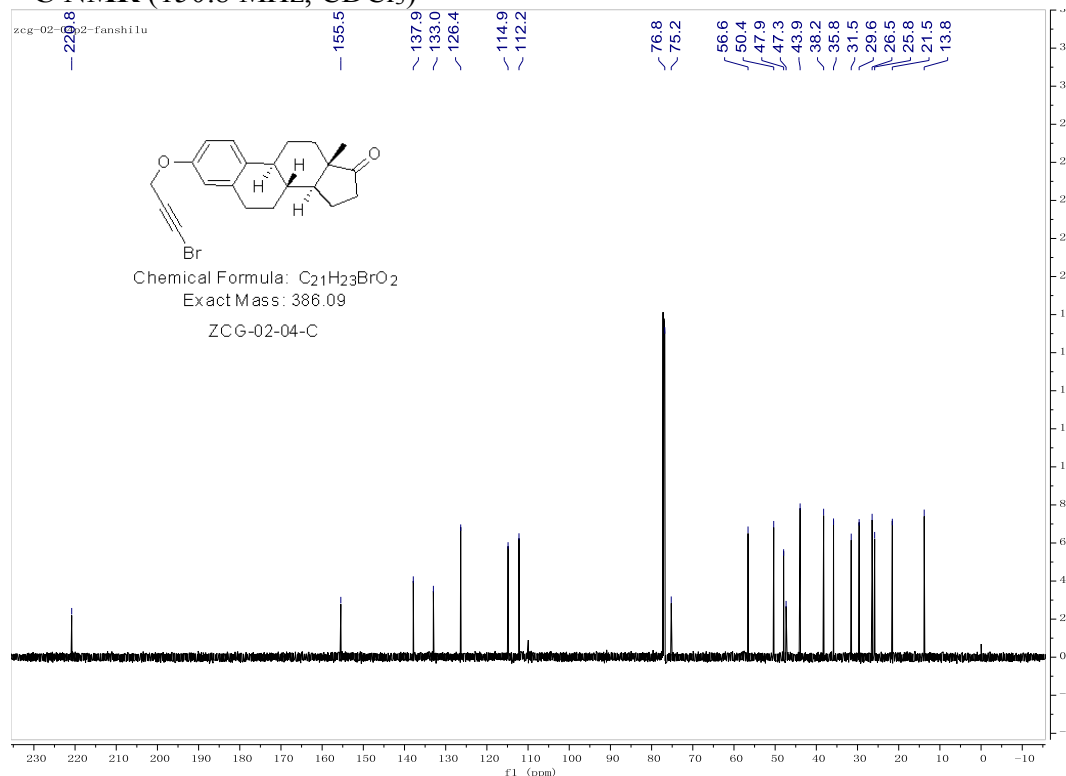


### (8R,9S,13S,14S)-3-((3-bromoprop-2-yn-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1s)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

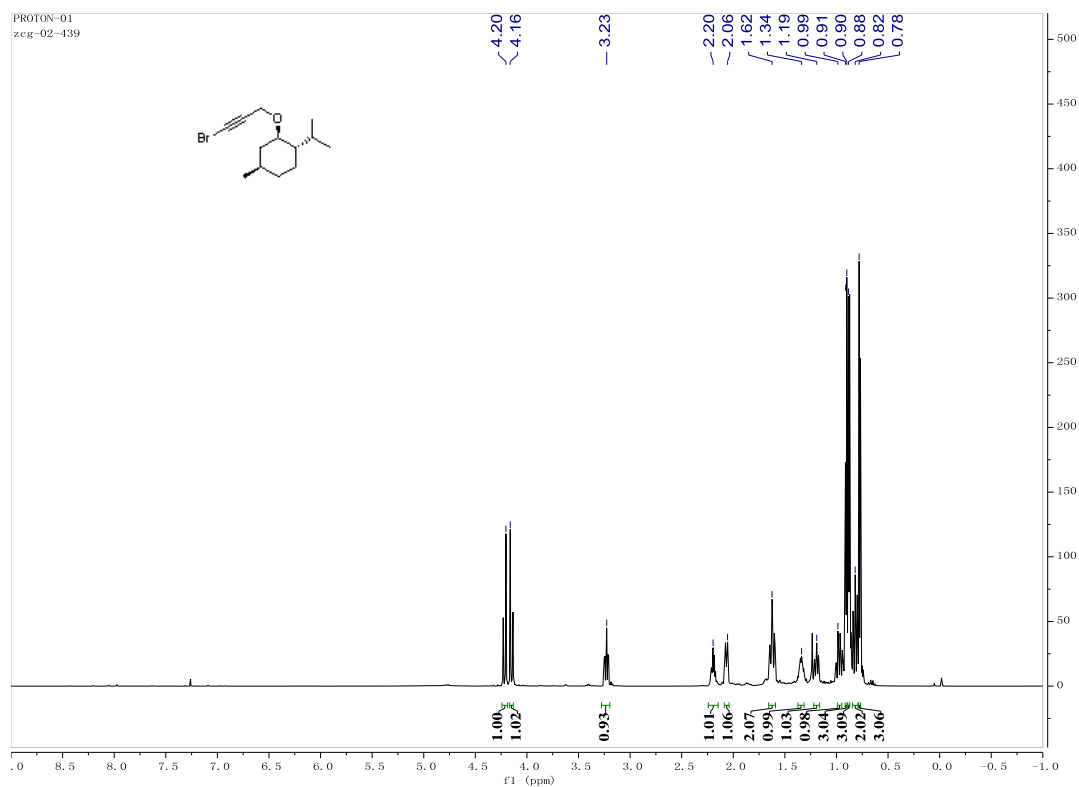


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )



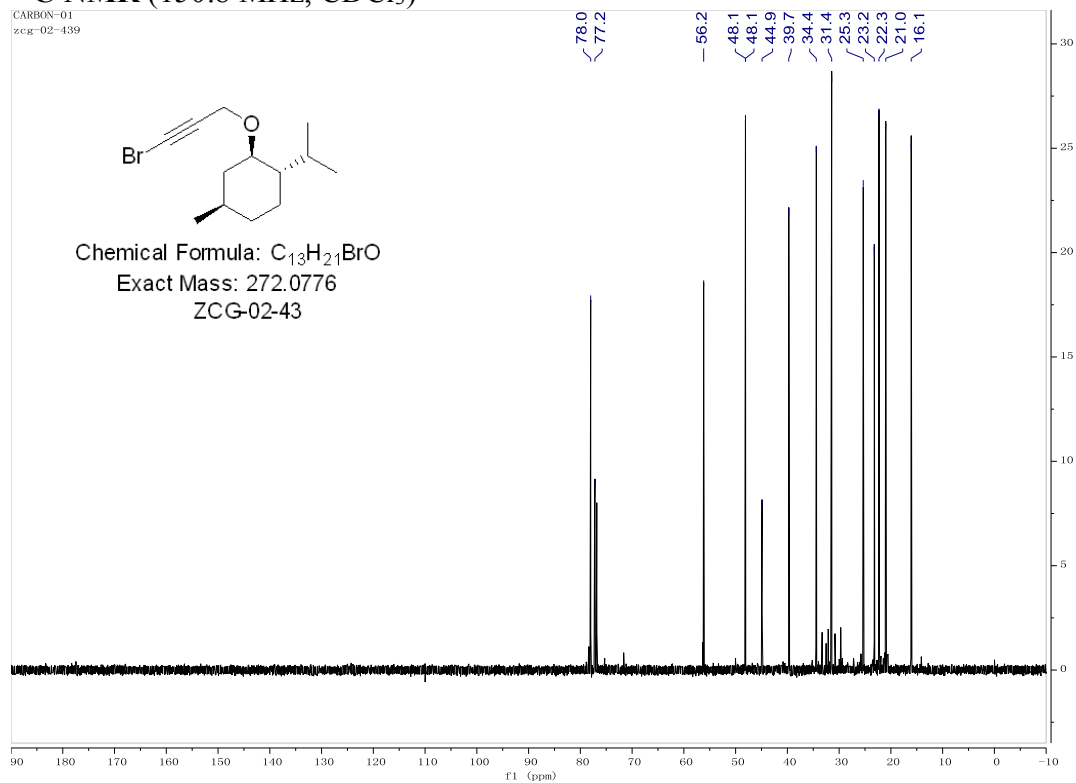
### (1S,2R,4R)-2-((3-bromoprop-2-yn-1-yl)oxy)-1-isopropyl-4-methylcyclohexane (1t)

### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



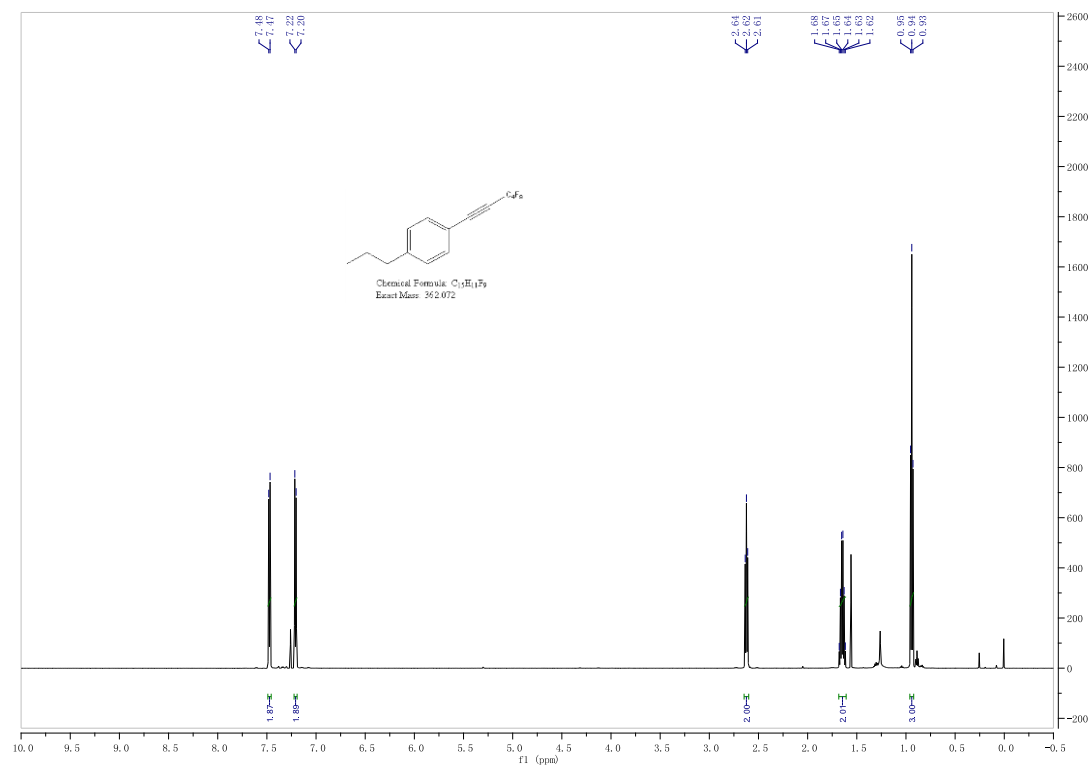
# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

CARBON-01  
zcg-02-439

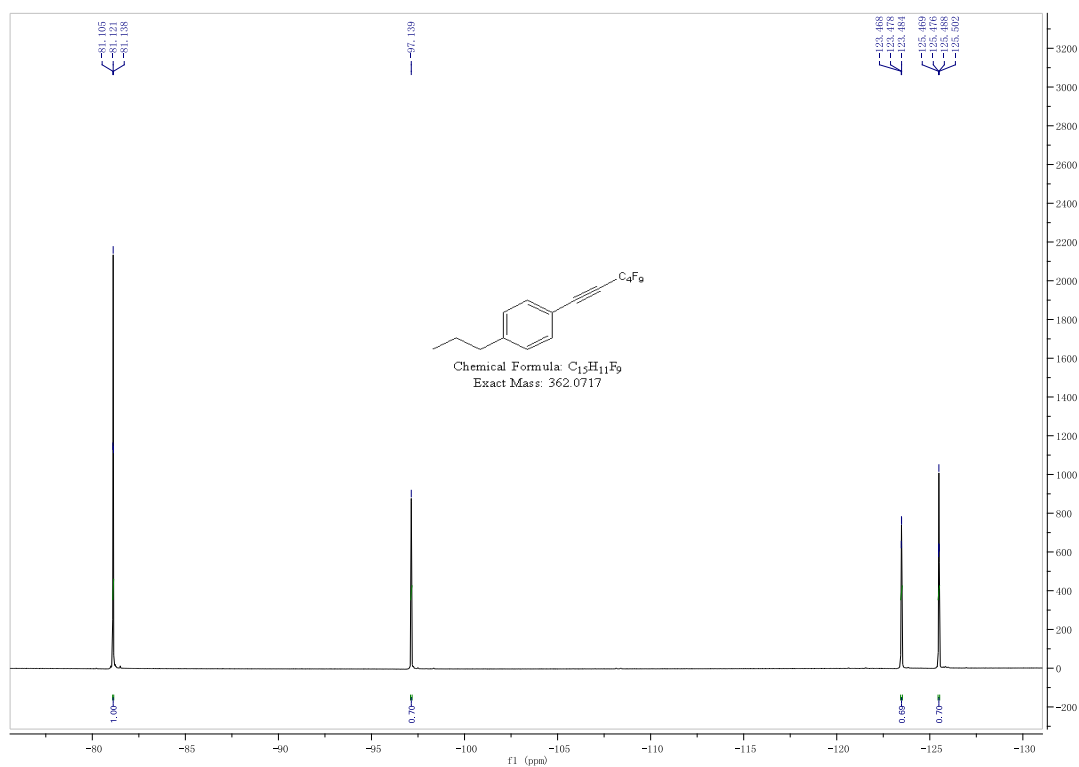


# 1-(perfluorohex-1-yn-1-yl)-4-propylbenzene (6a)

## <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

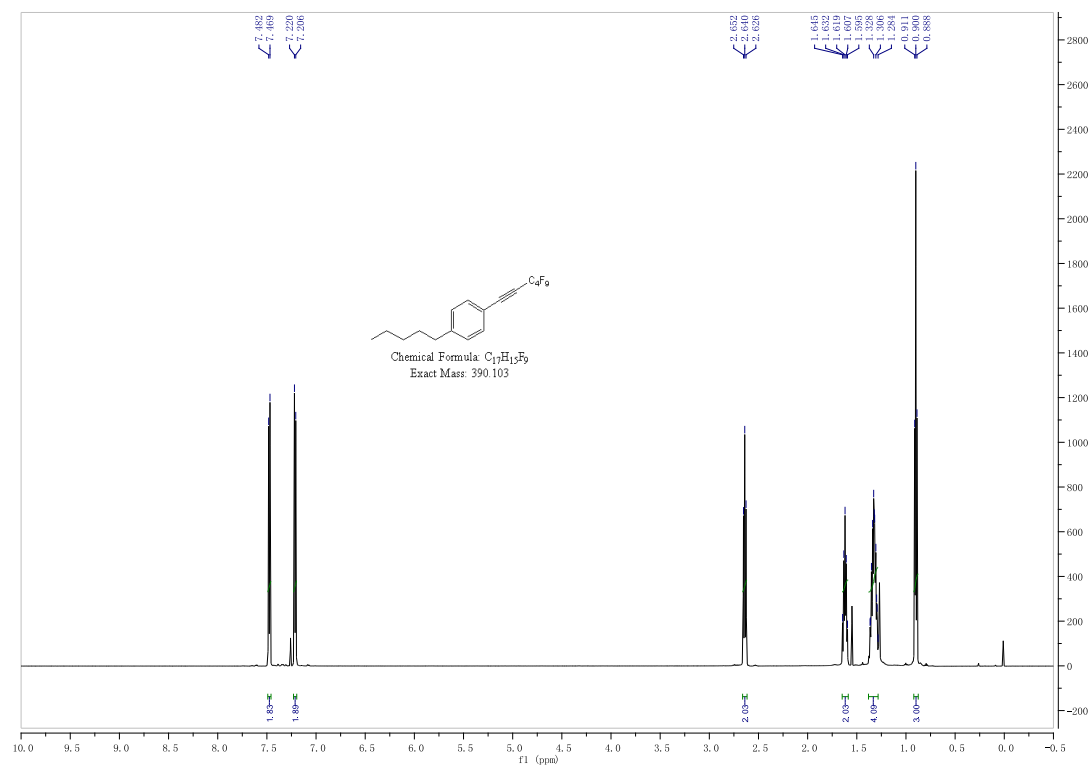


### $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

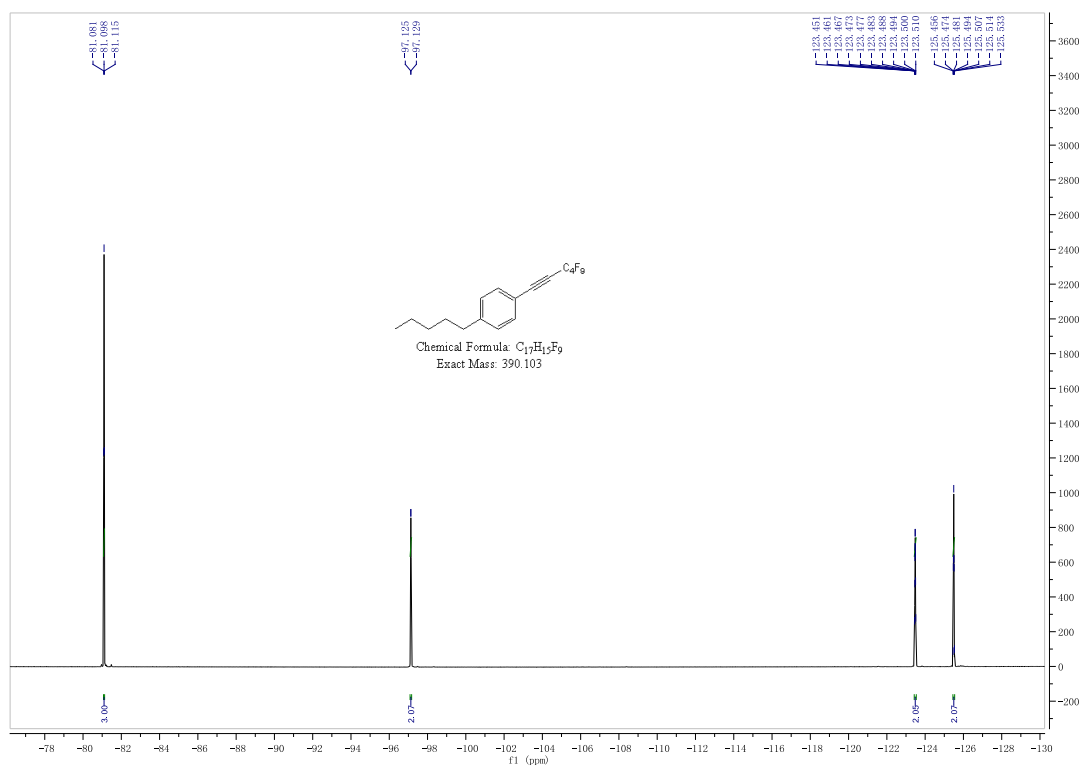


### 1-pentyl-4-(perfluorohex-1-yn-1-yl)benzene (6b)

### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

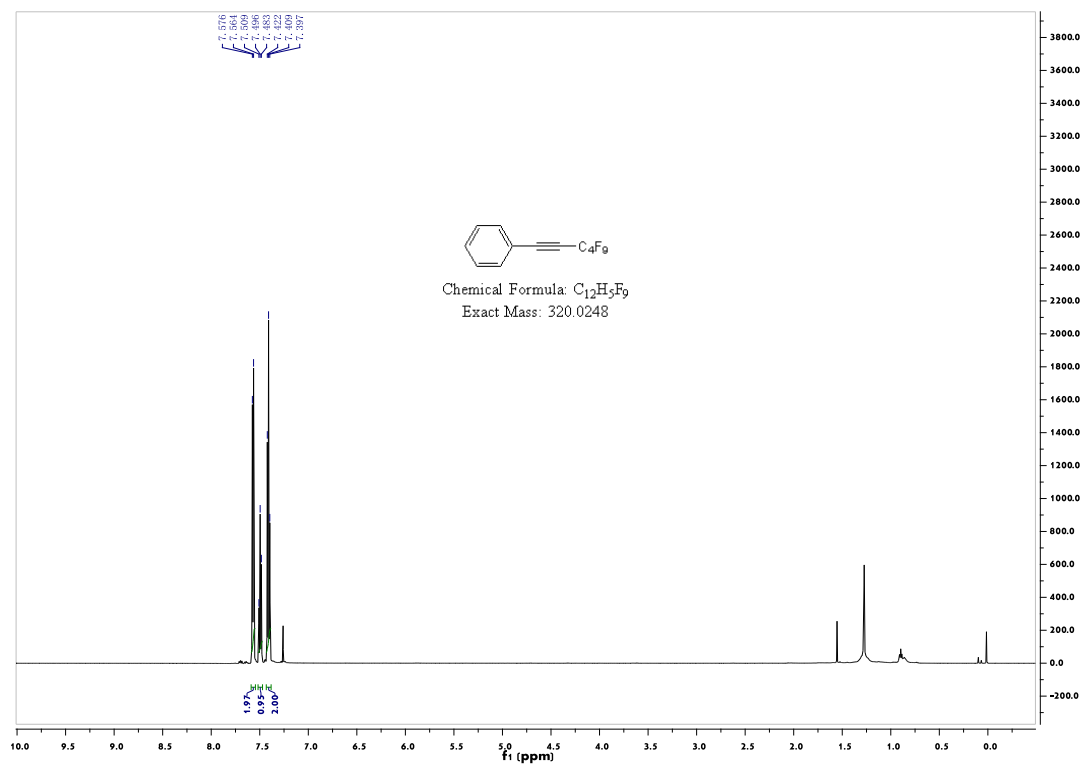


# $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

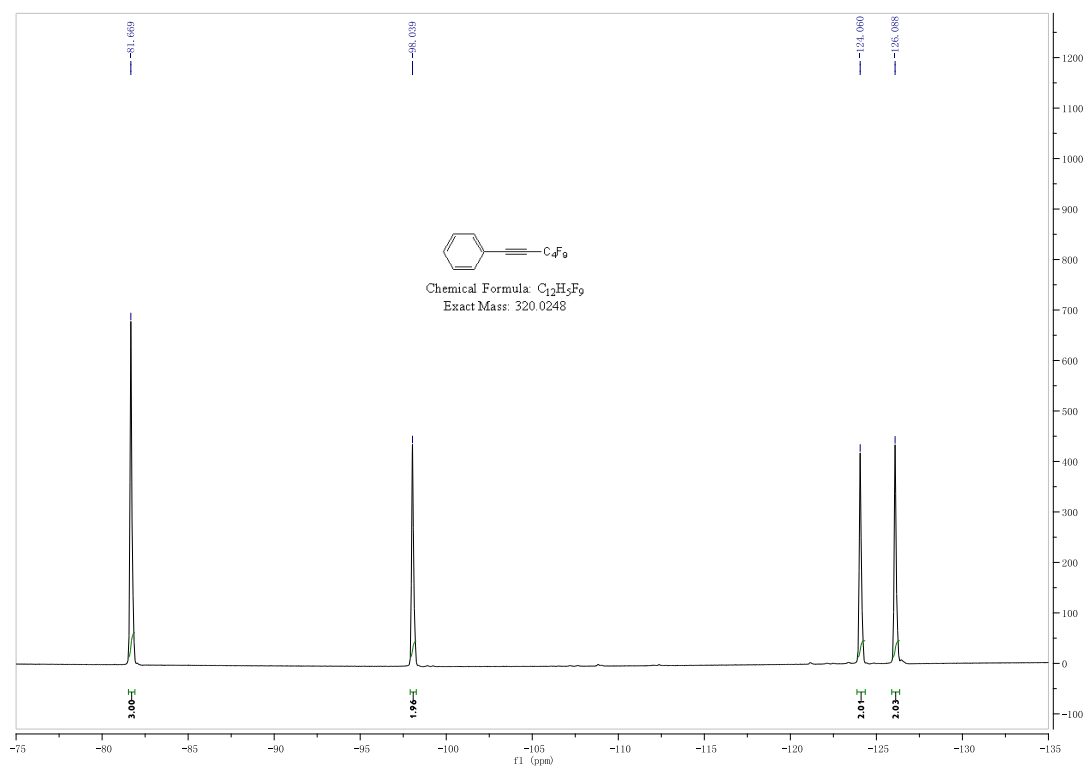


# (perfluorohex-1-yn-1-yl)benzene (6c)

## $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

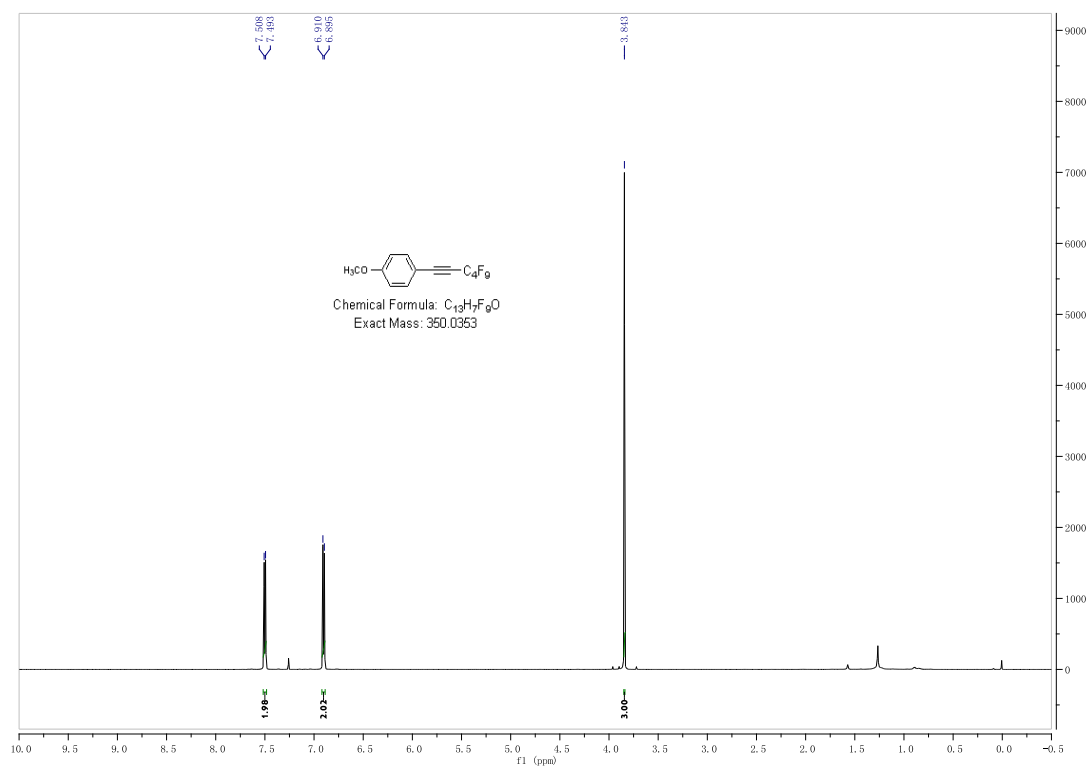


### $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

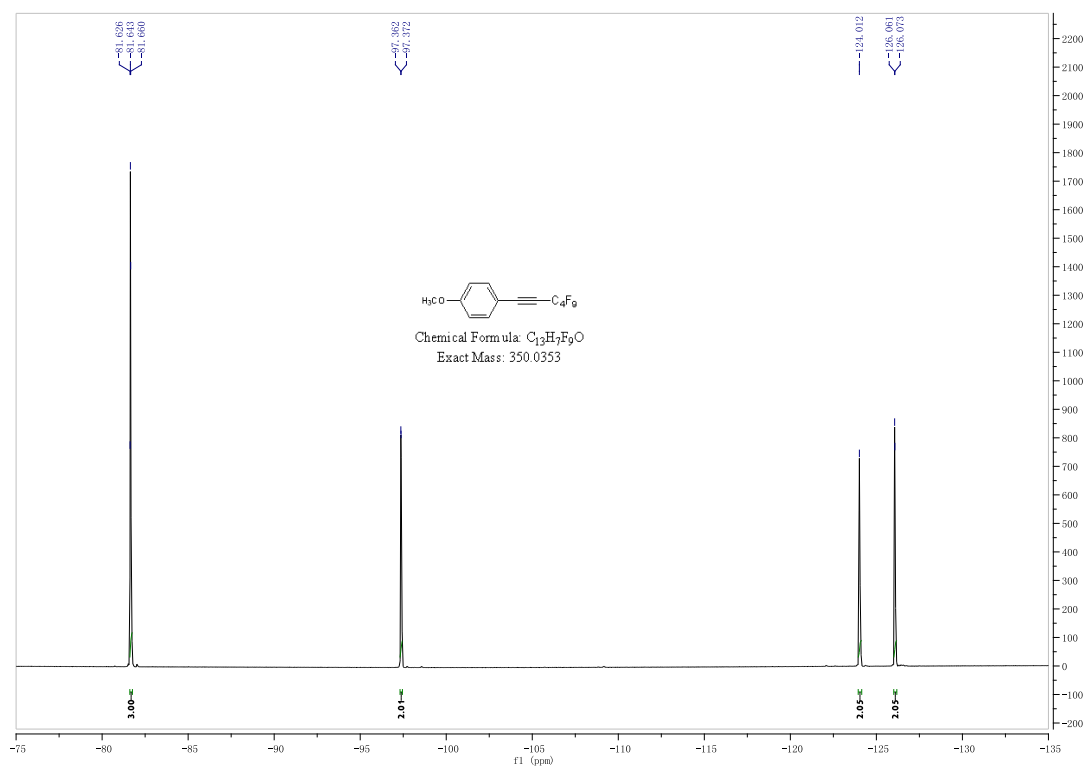


### 1-methoxy-4-(perfluorohex-1-yn-1-yl)benzene (6d)

#### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

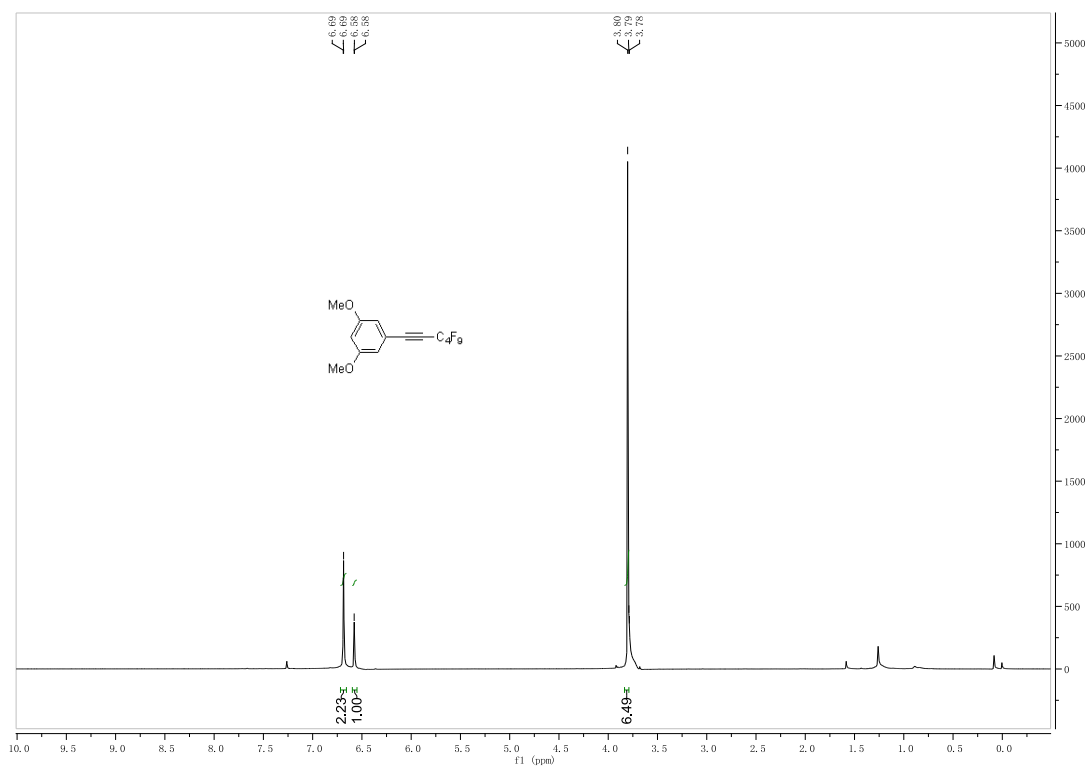


### $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

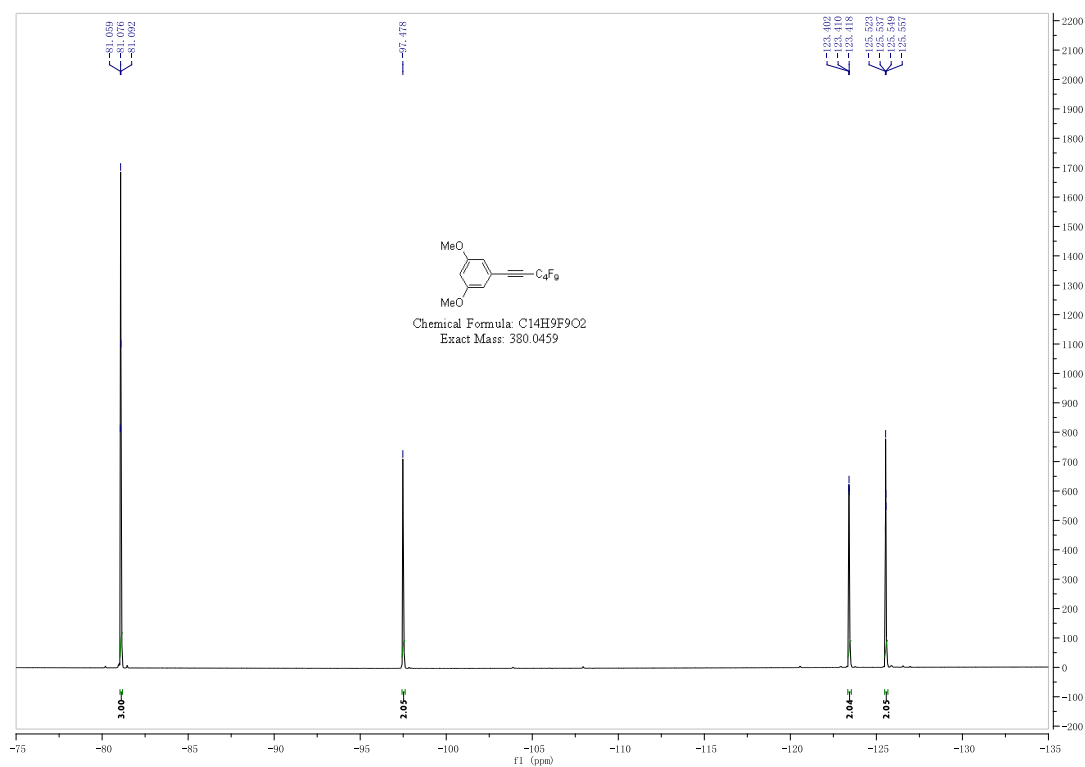


### 1,3-dimethoxy-5-(perfluorohex-1-yn-1-yl)benzene (6e)

### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

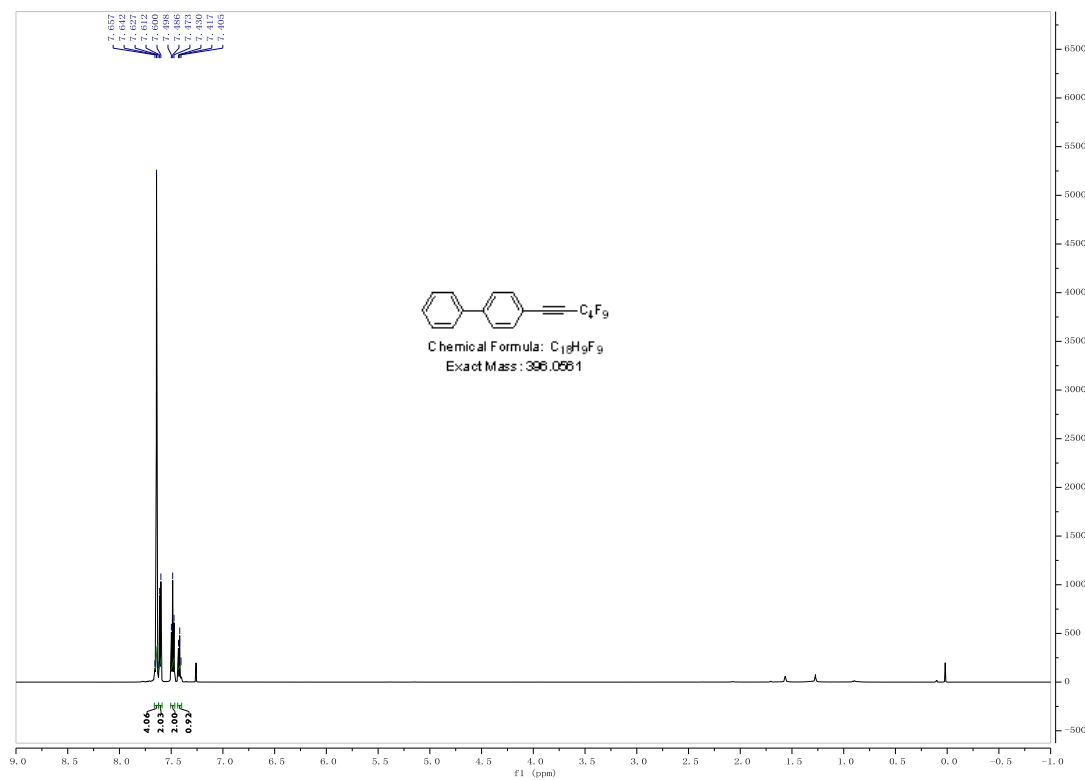


### $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

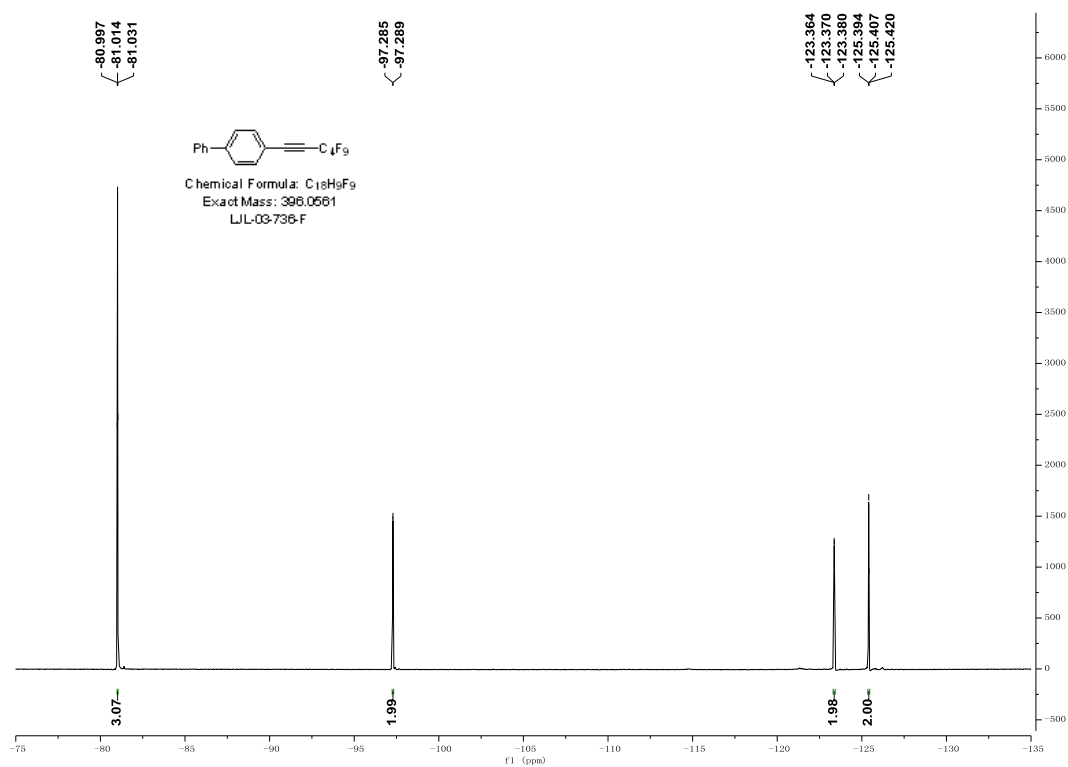


### 4-(perfluorohex-1-yn-1-yl)-1,1'-biphenyl (6f)

### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

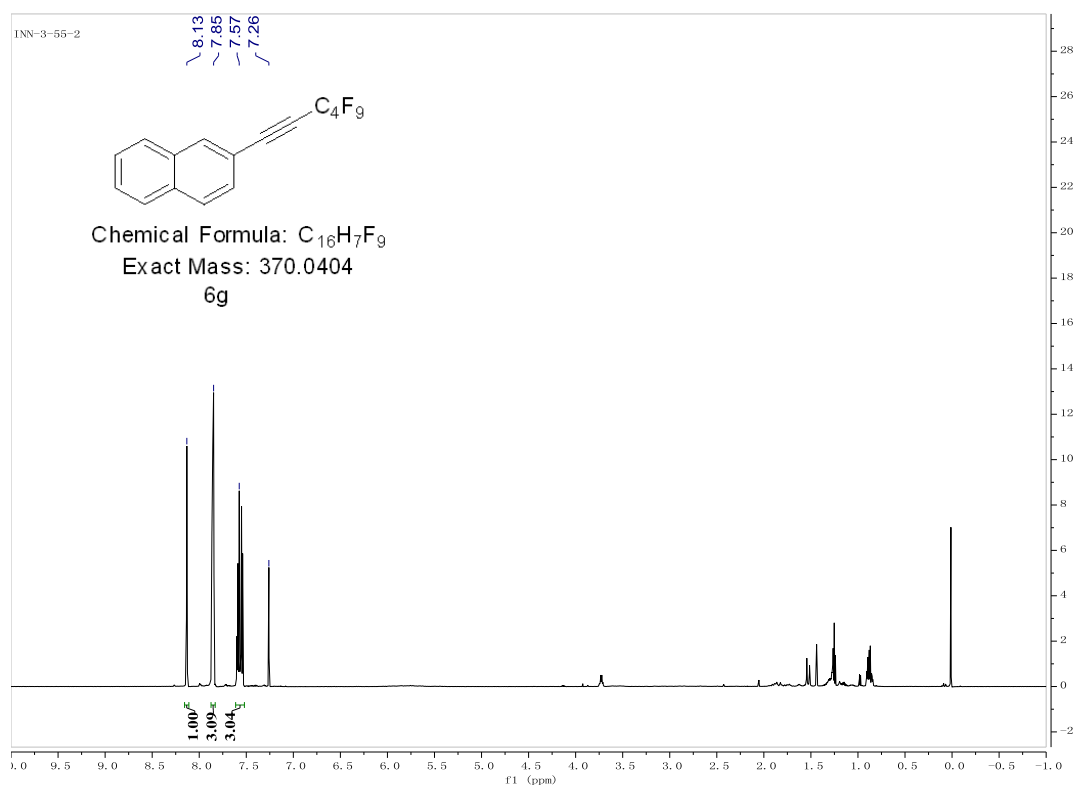


# $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )



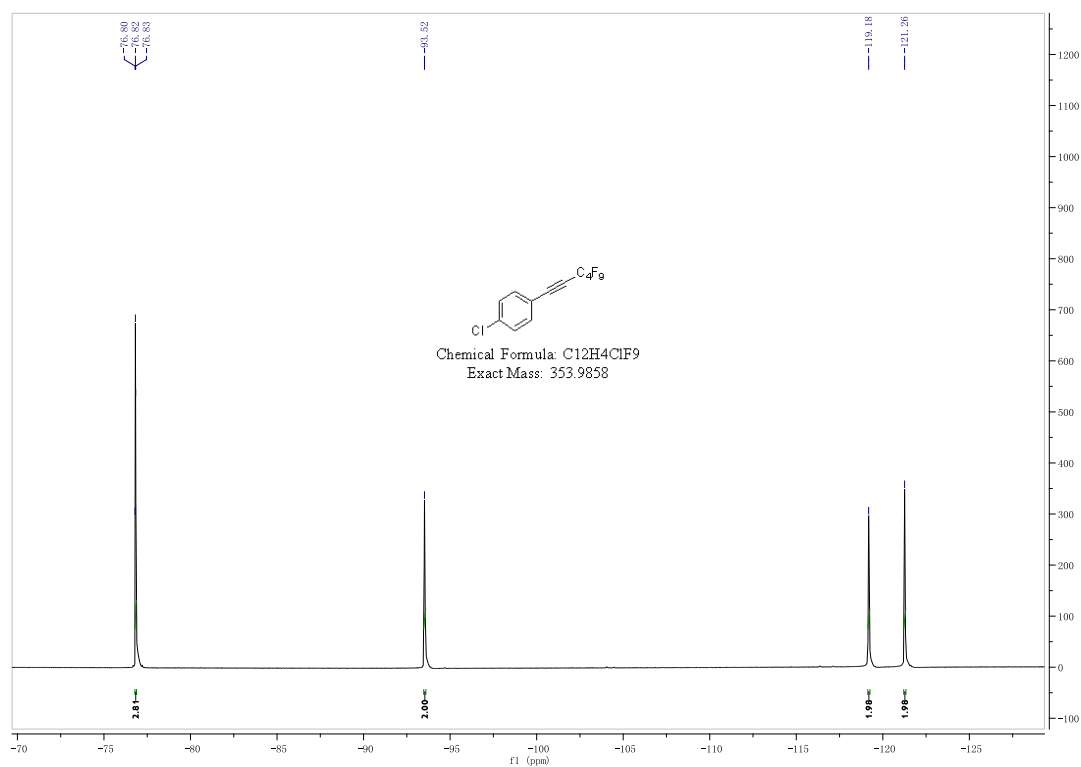
# Methyl 4-(perfluorohex-1-yn-1-yl)benzoate (6g)

## $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



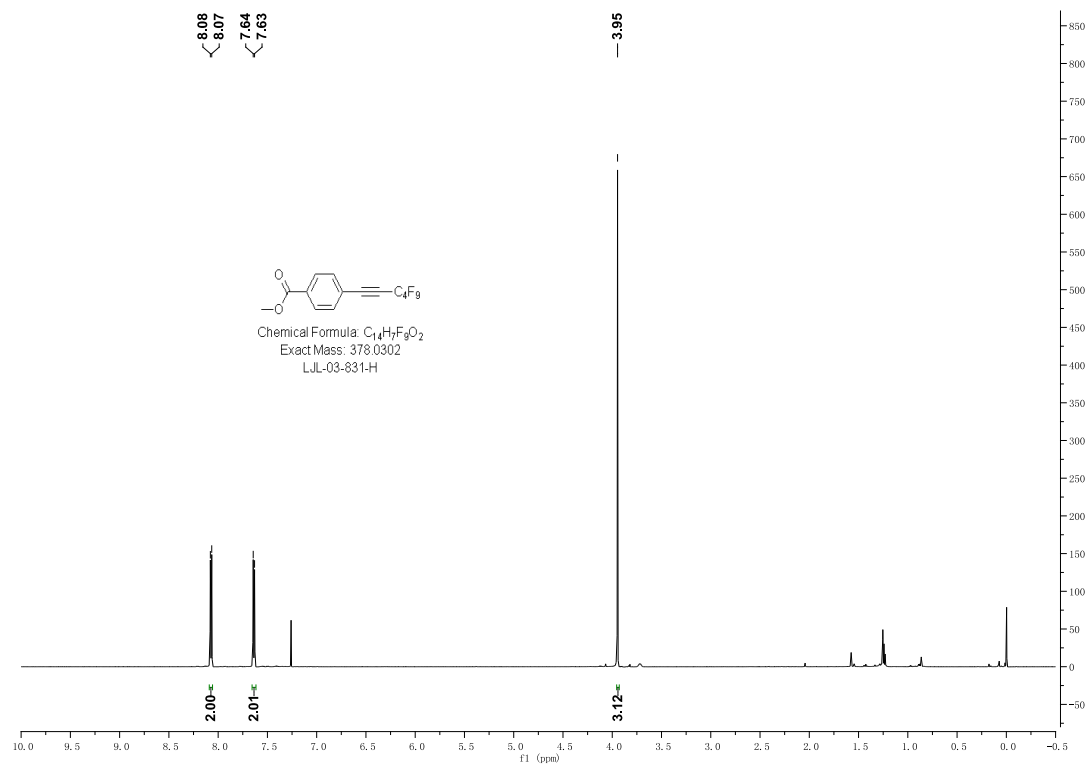


### $^{19}\text{F}$ NMR (564 MHz, $\text{CDCl}_3$ )

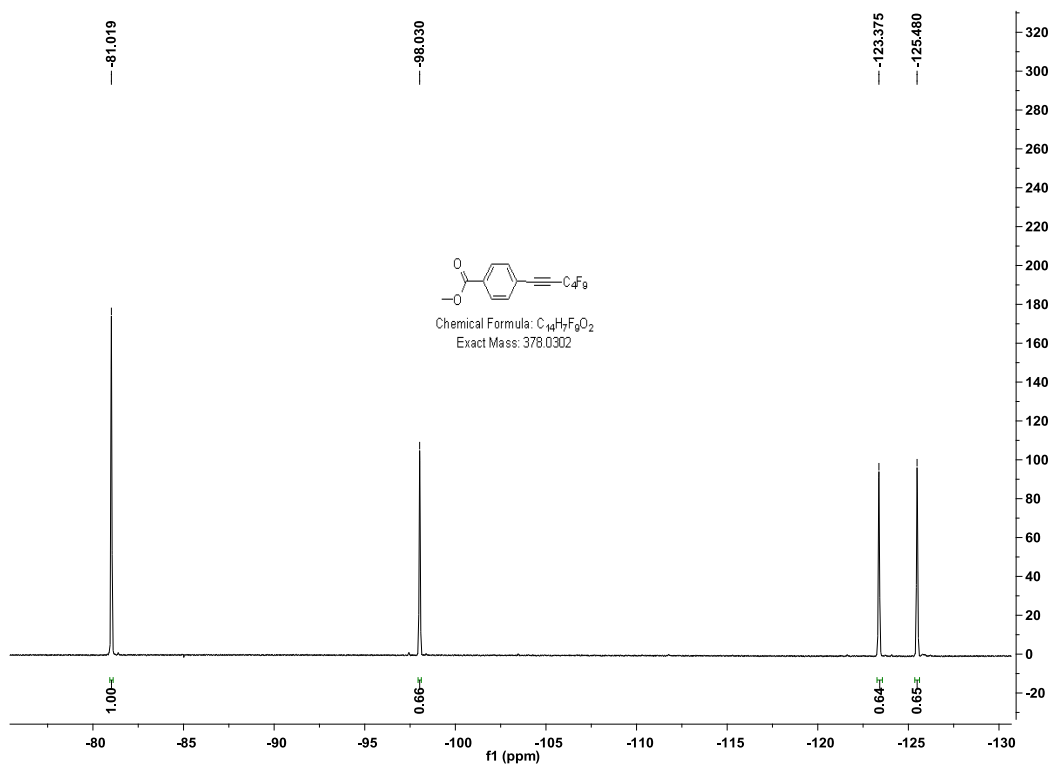


### Methyl 4-(perfluorohex-1-yn-1-yl)benzoate (6i)

#### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )

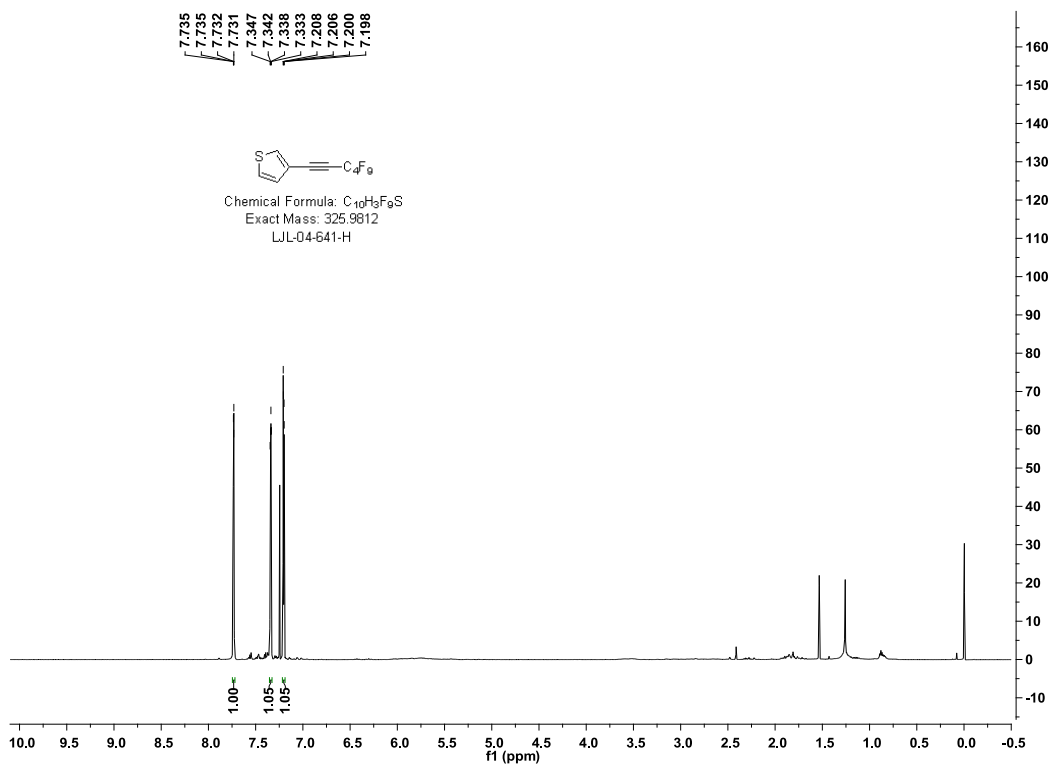


### <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

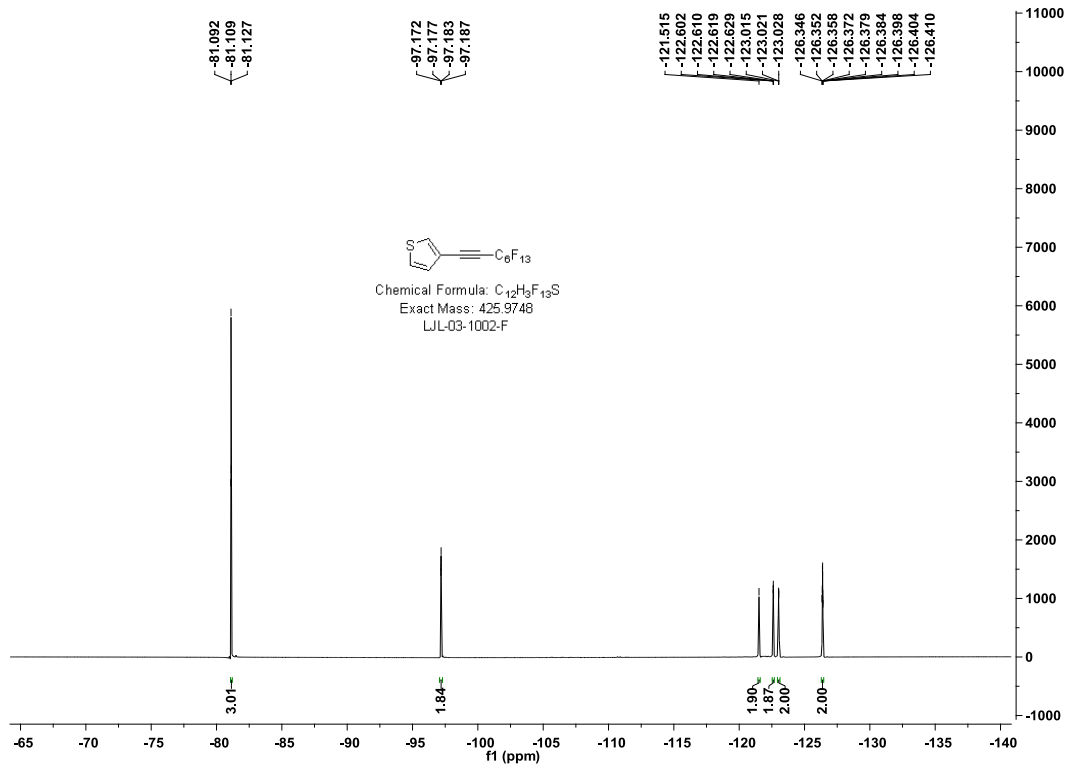


### 4-(Perfluorohex-1-yn-1-yl)thiophene(6j)

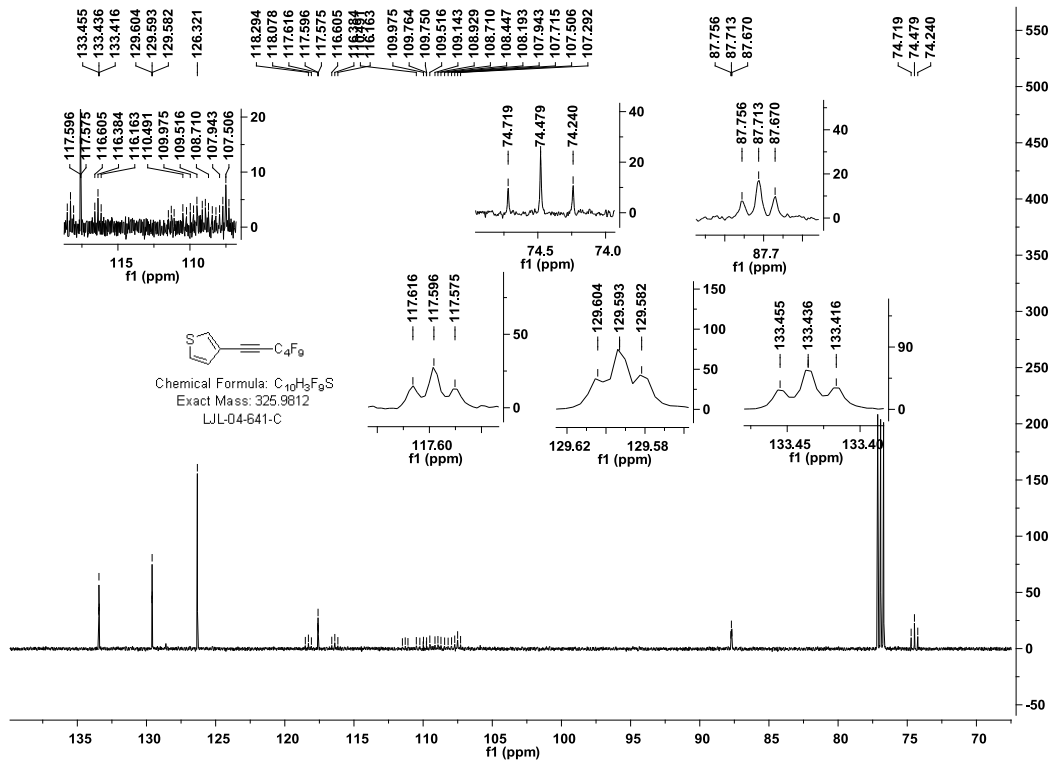
#### <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

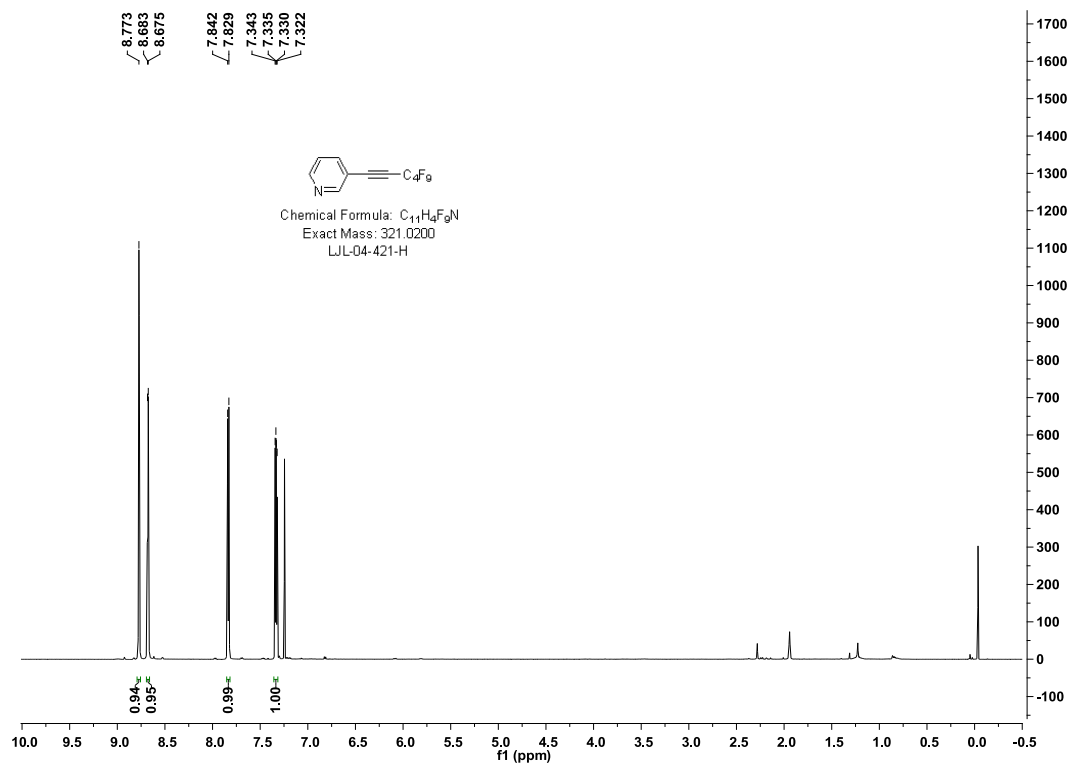


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

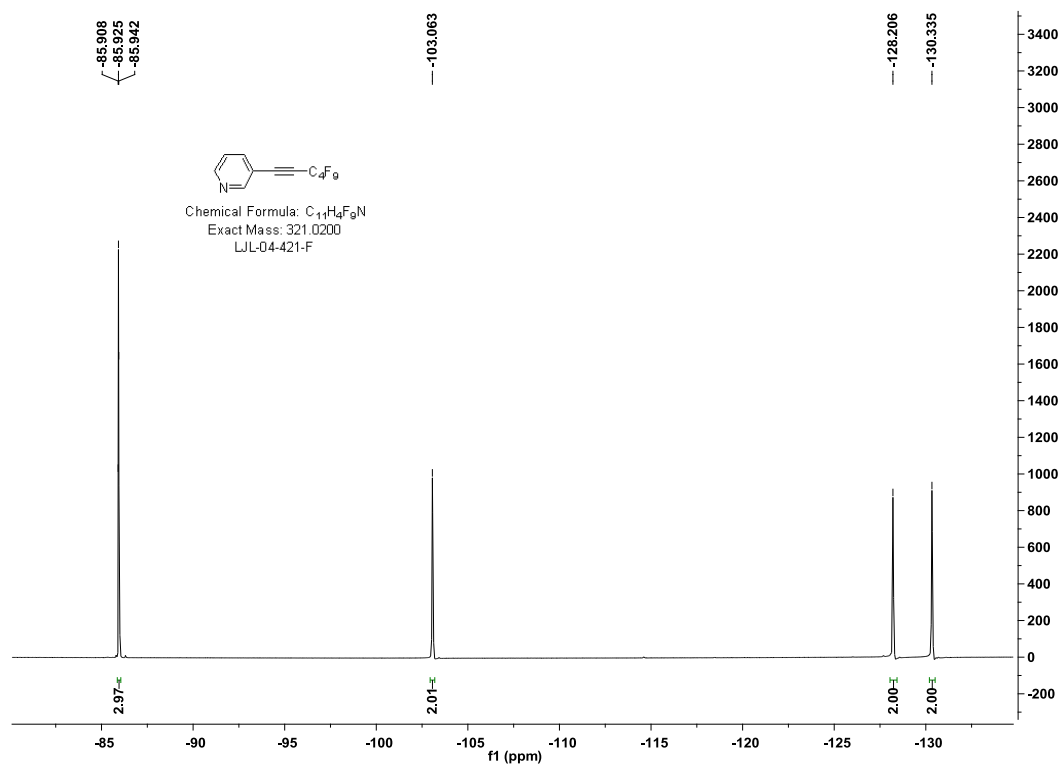


### 3-(Perfluorohex-1-yn-1-yl)pyridine(6k)

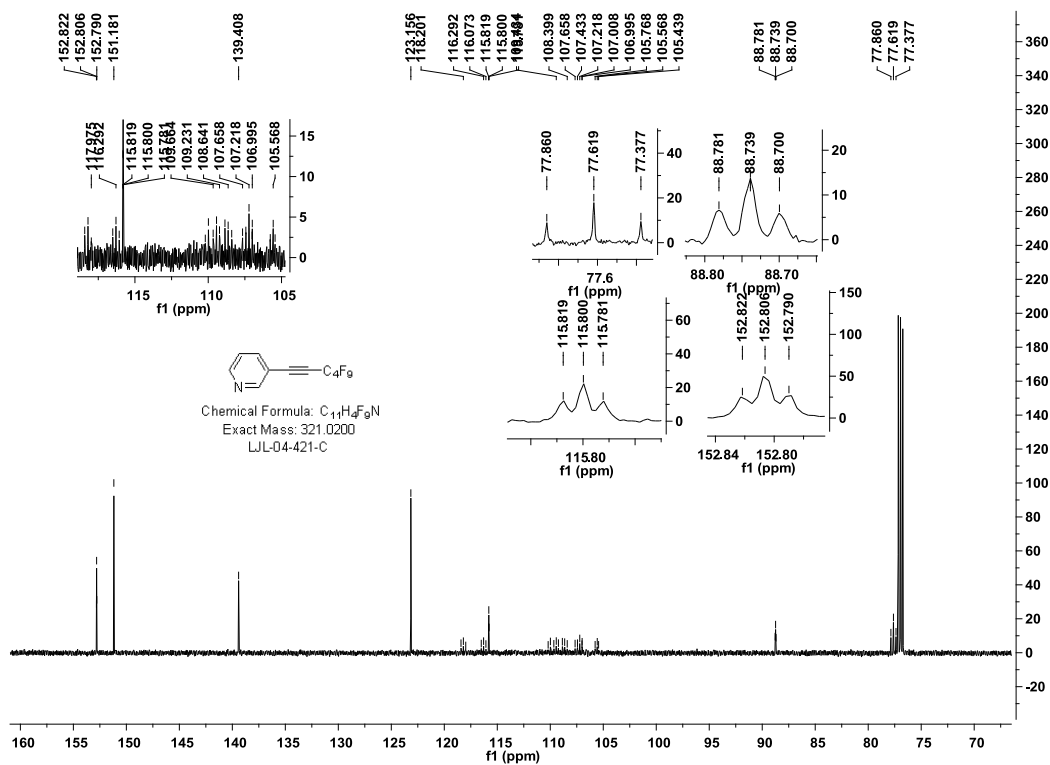
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

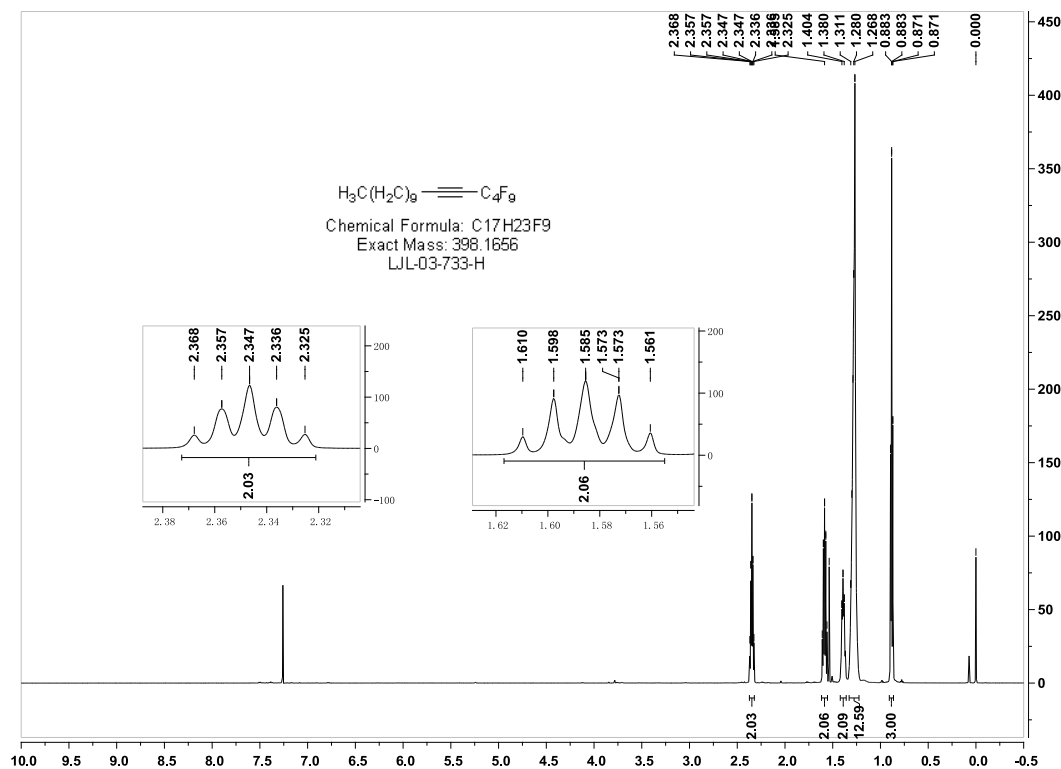


# $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

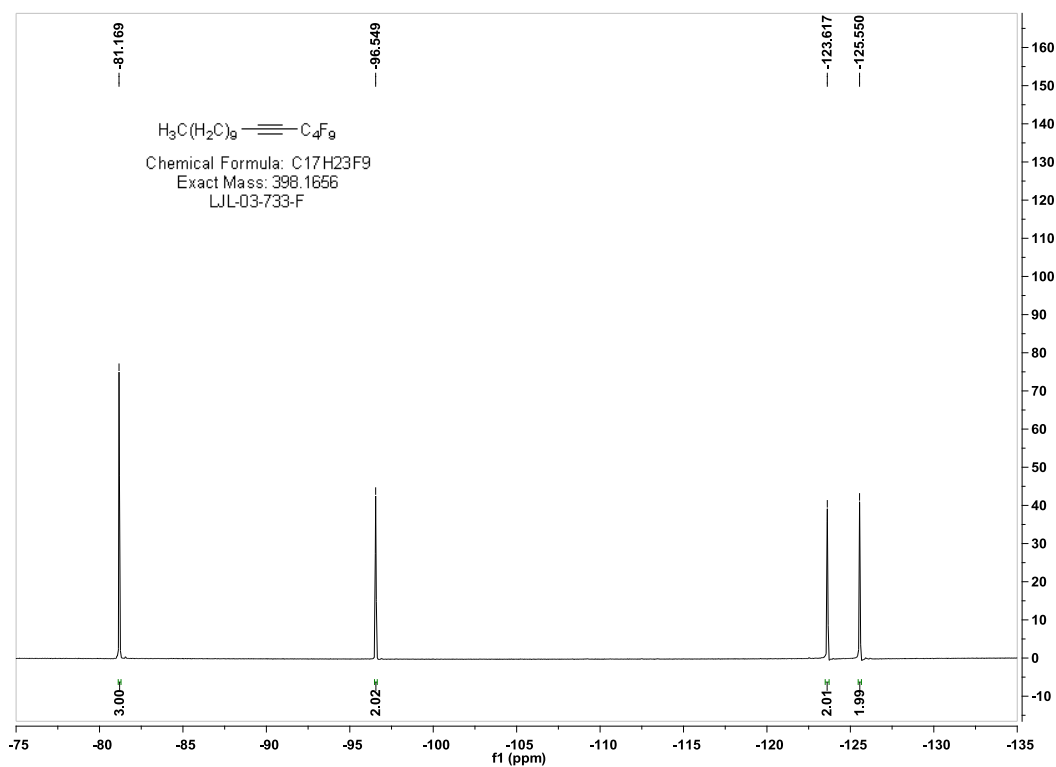


# 1,1,1,2,2,3,3,4,4-Nonafluorohexadec-5-yne(6l)

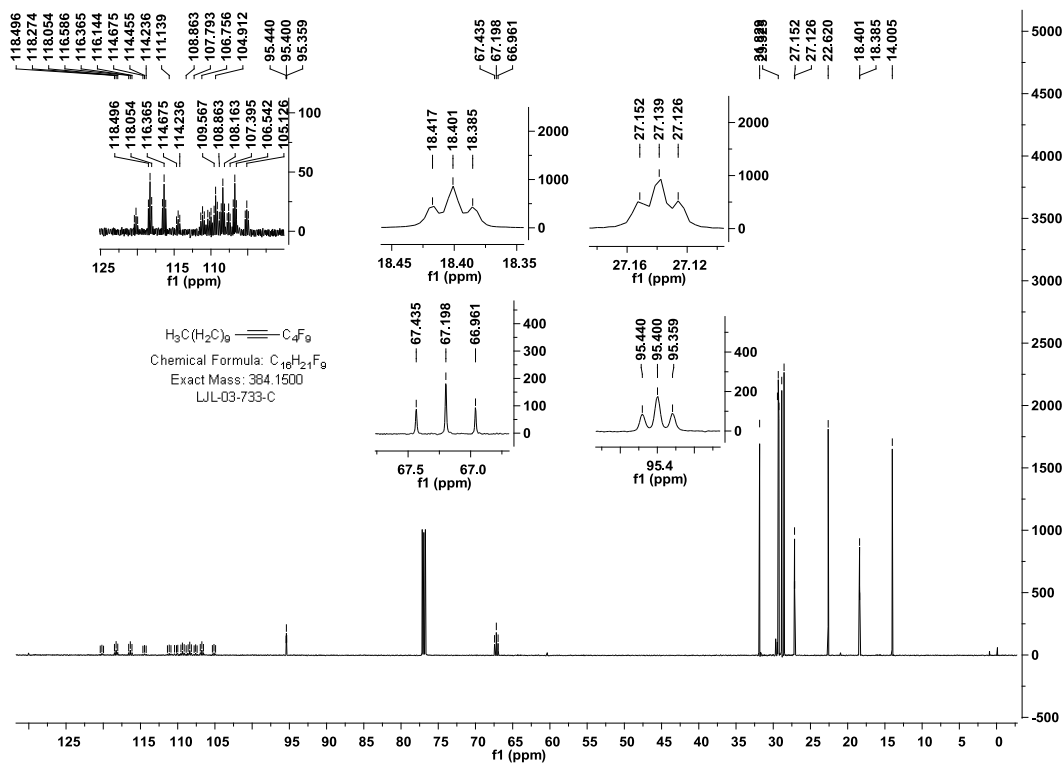
## $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

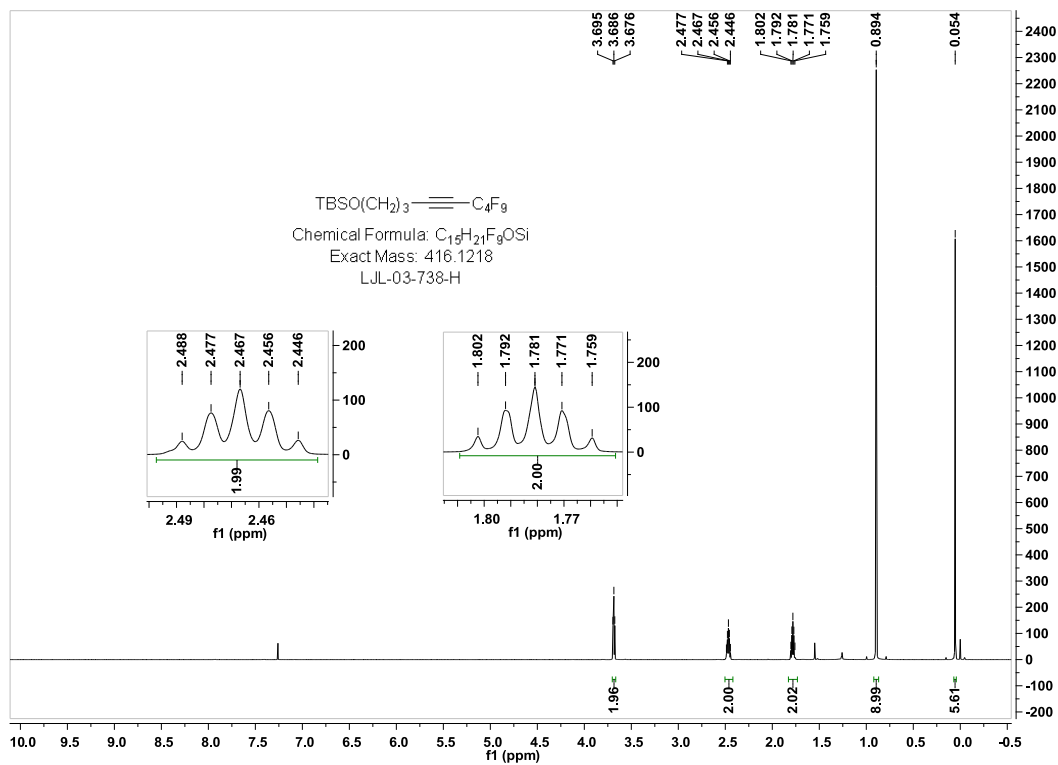


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

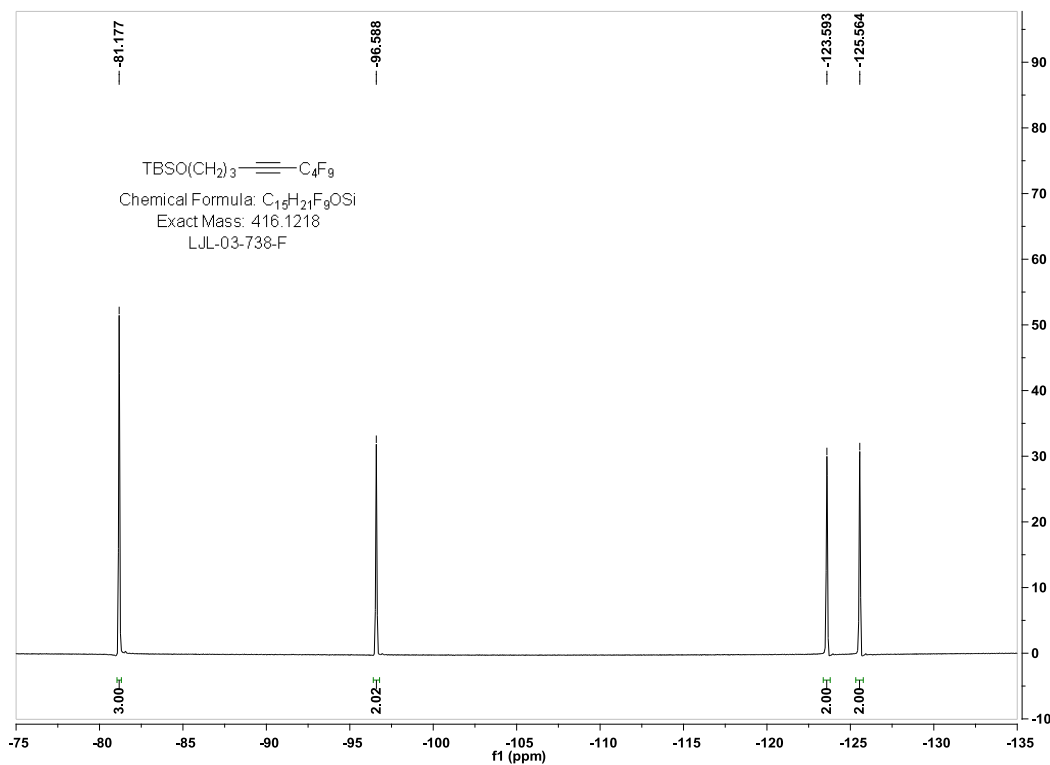


# tert-Butyldimethyl((6,6,7,7,8,8,9,9,9-nonafluoronon-4-yn-1-yl)oxy)silane (6m)

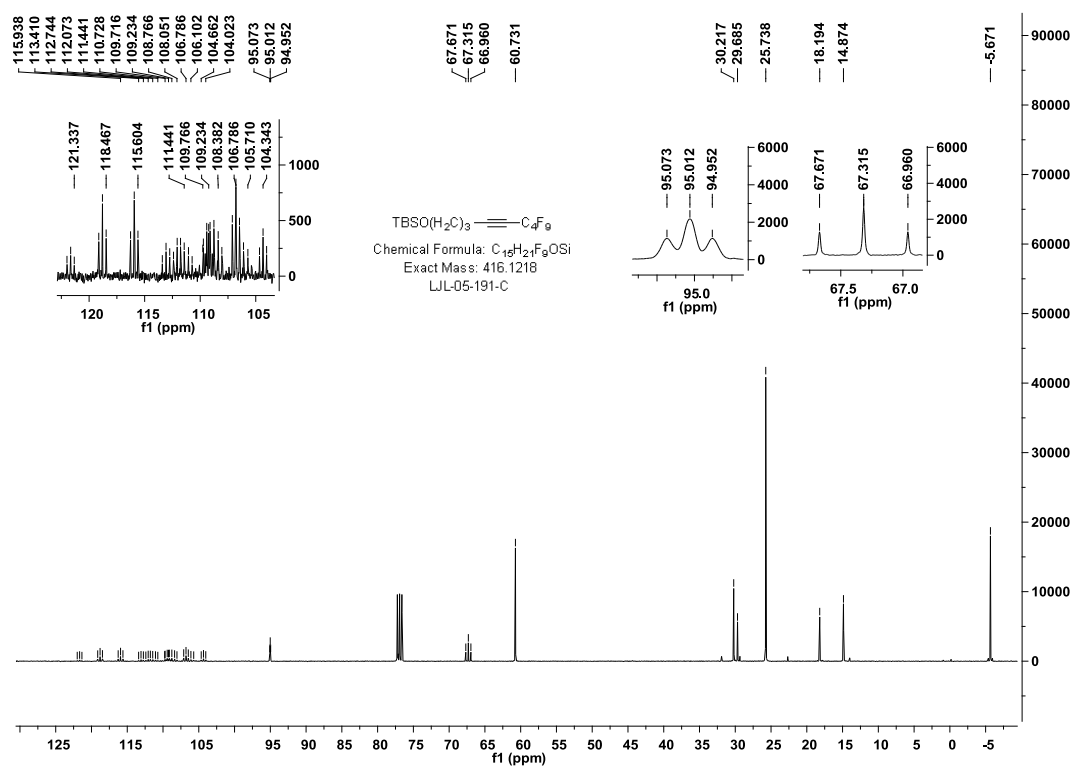
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

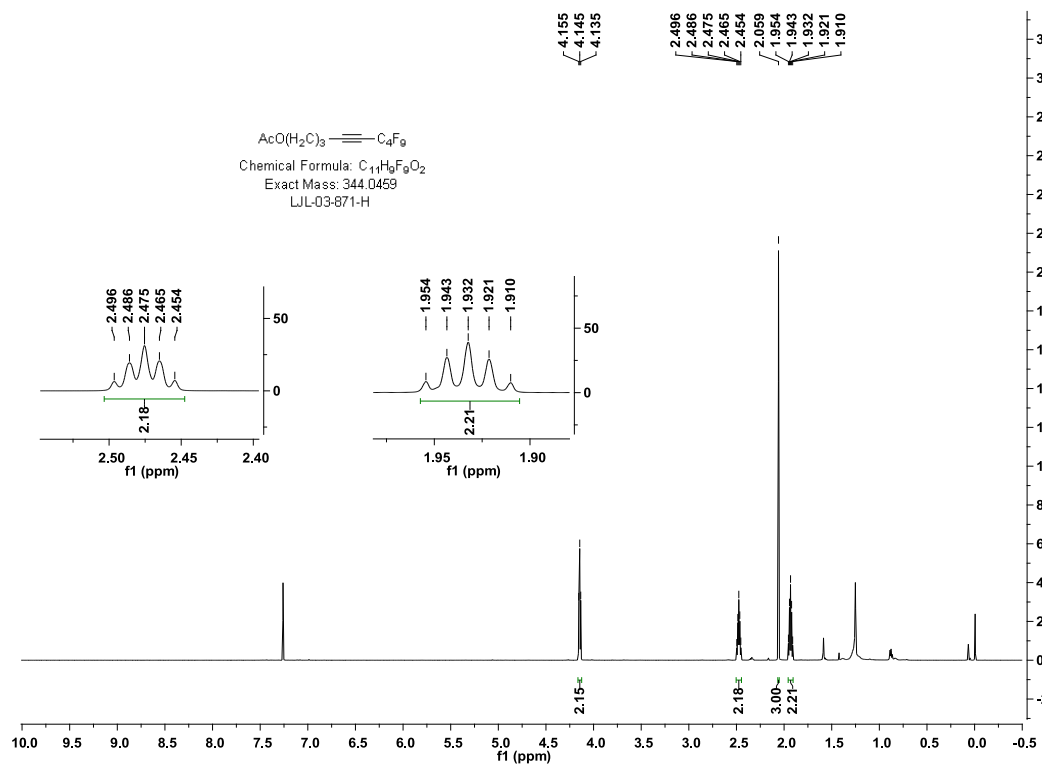


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

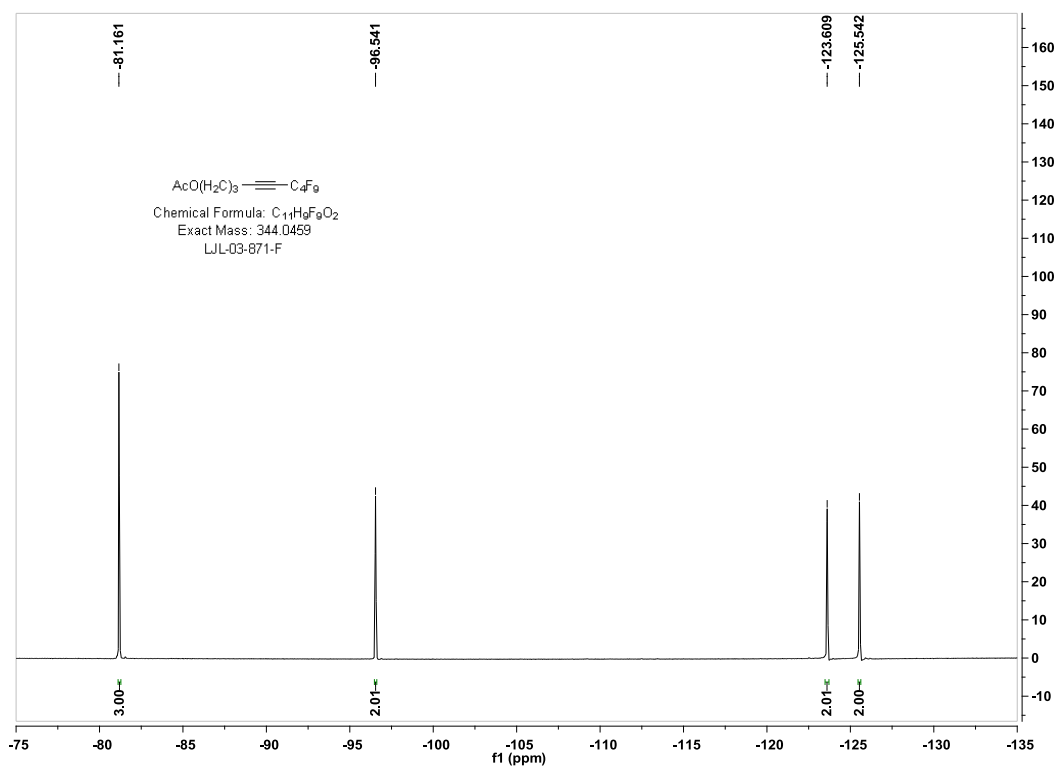


### 6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl acetate (6n)

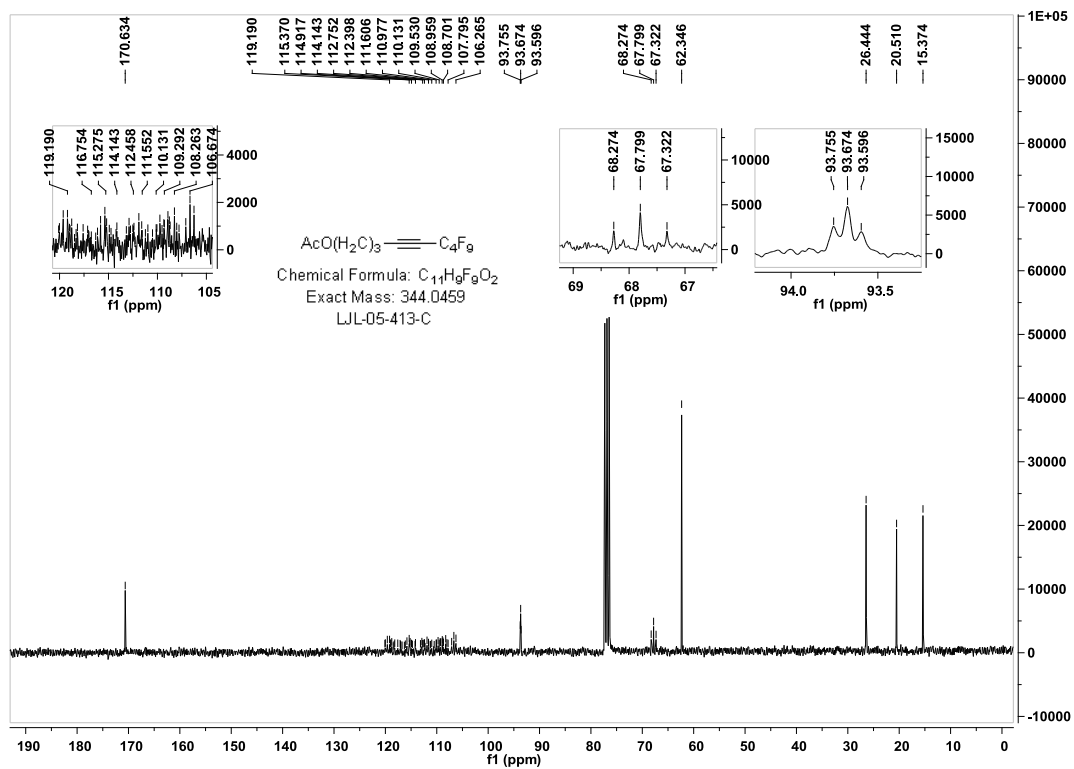
#### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

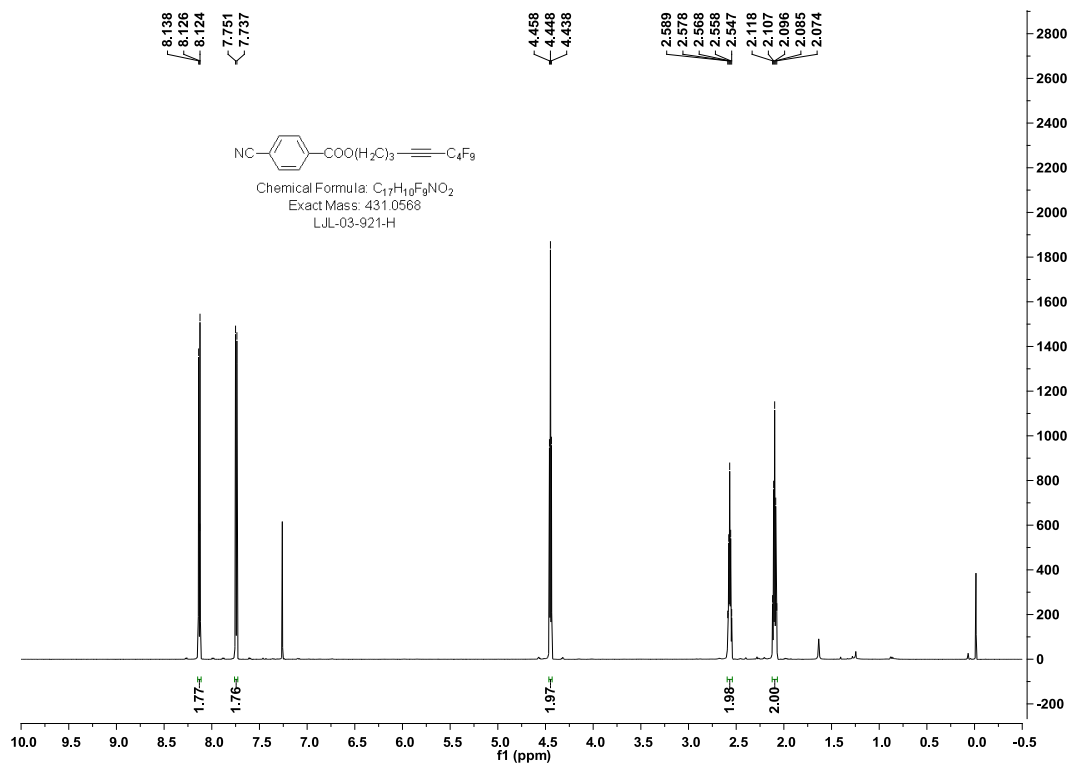


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

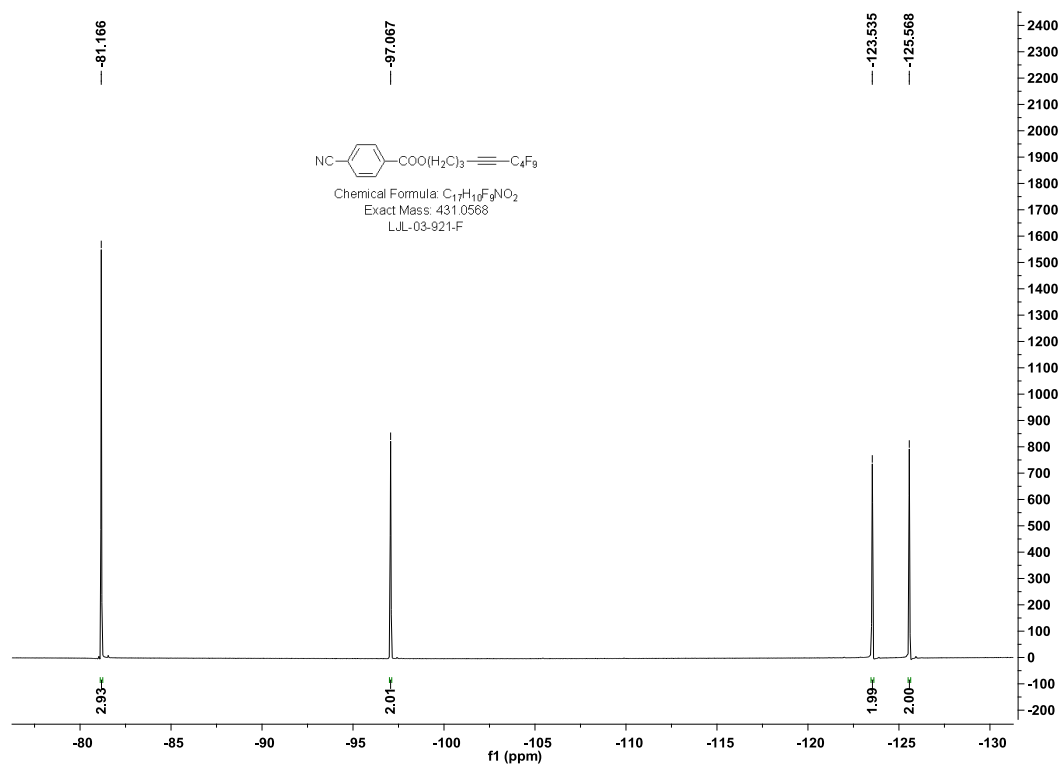


# 6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-cyanobenzoate (6o)

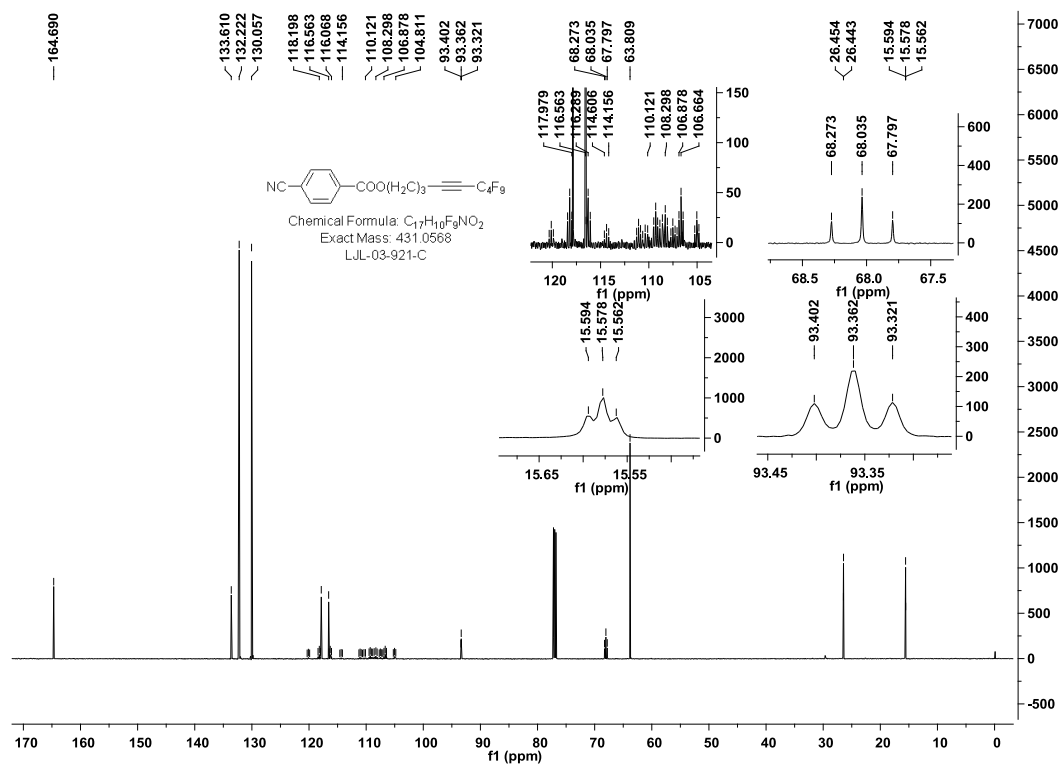
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

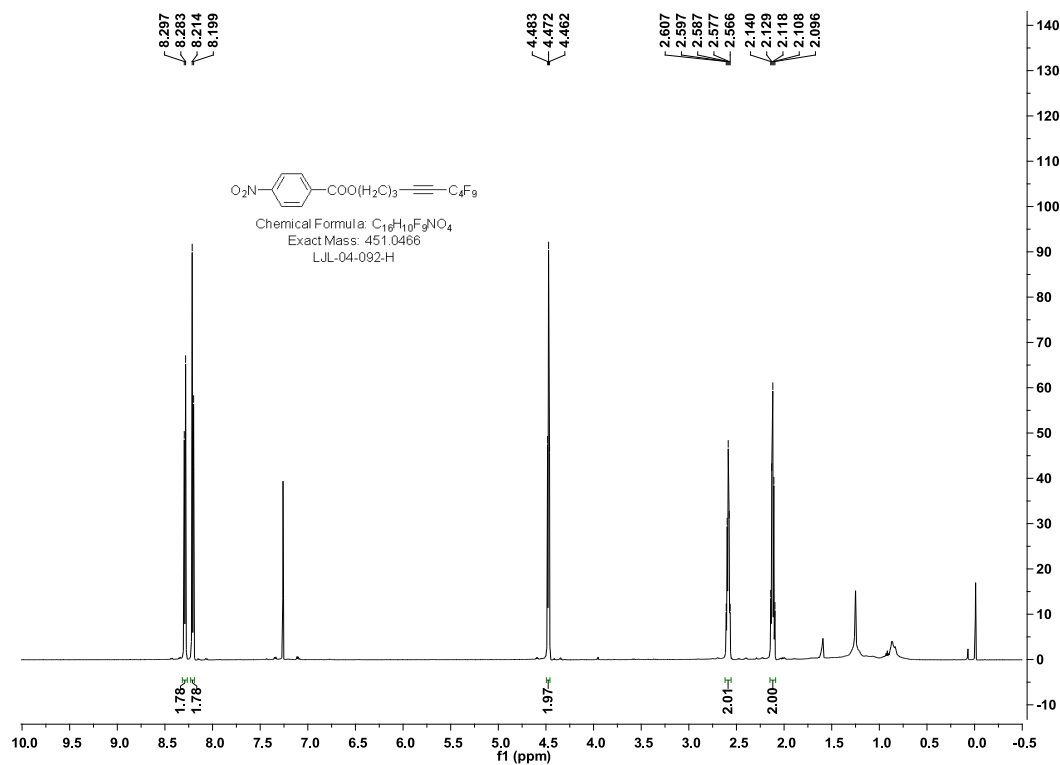


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

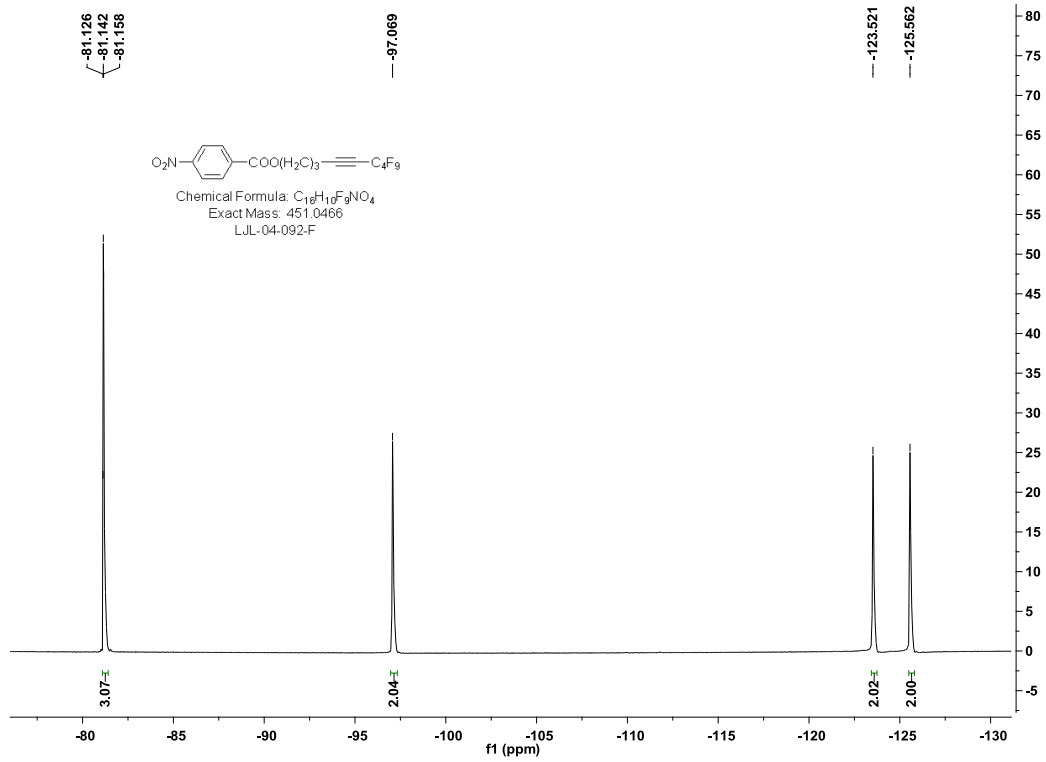


### 6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-nitrobenzoate (6p)

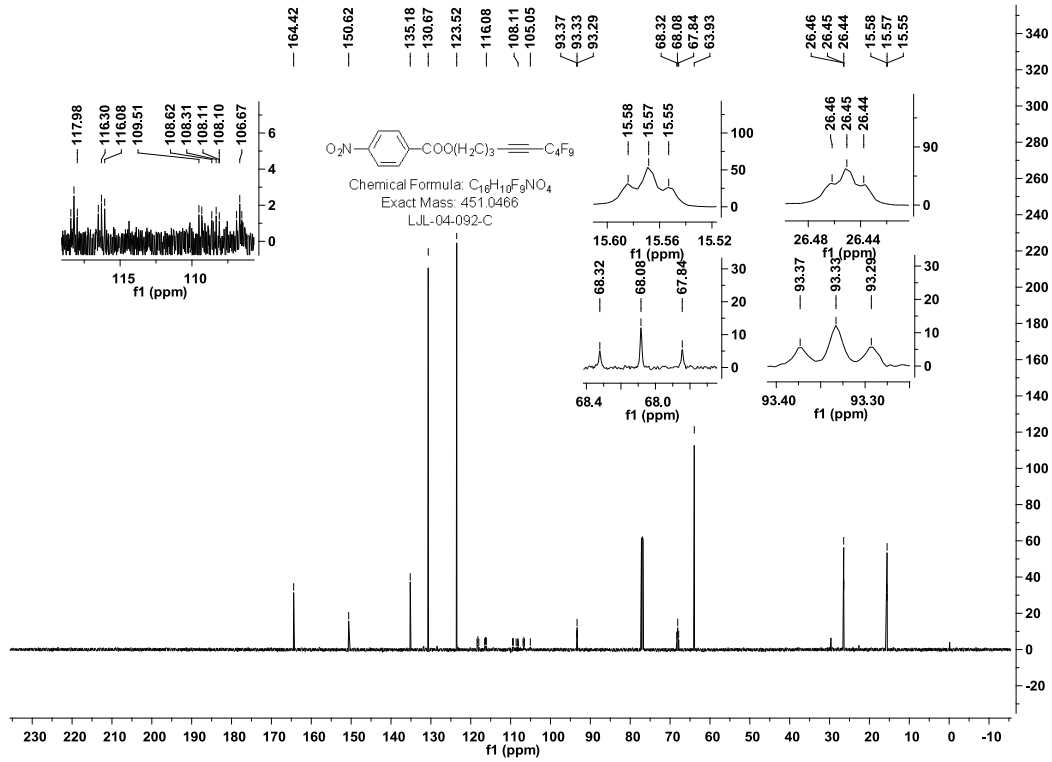
### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

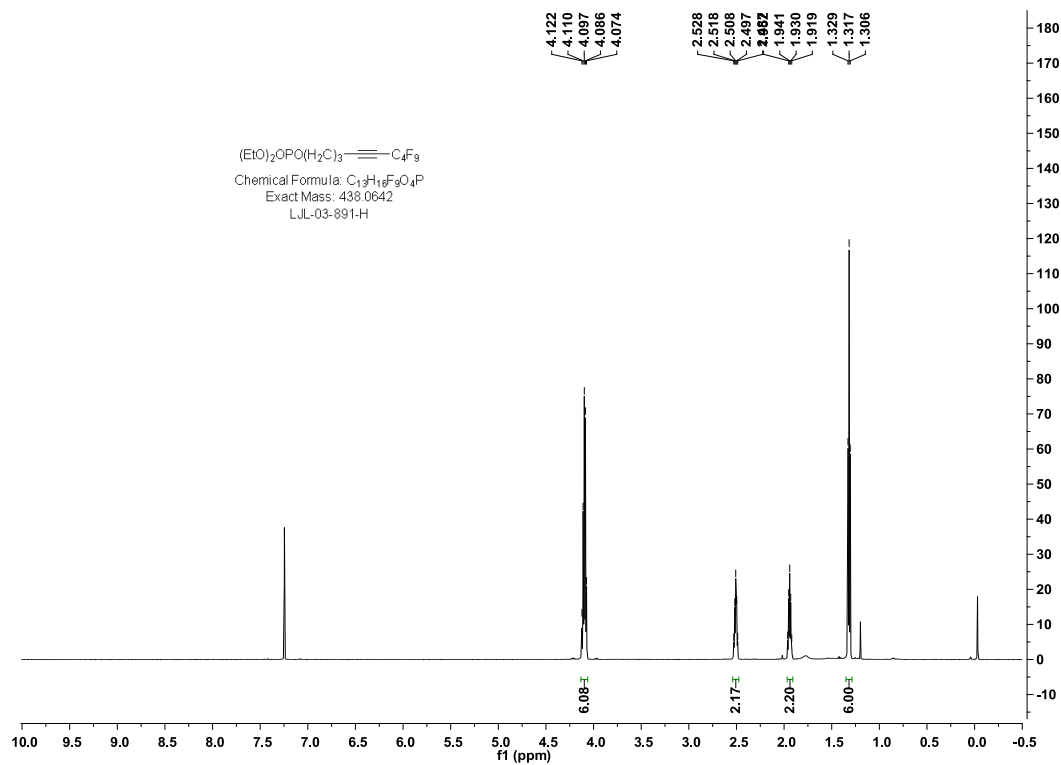


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

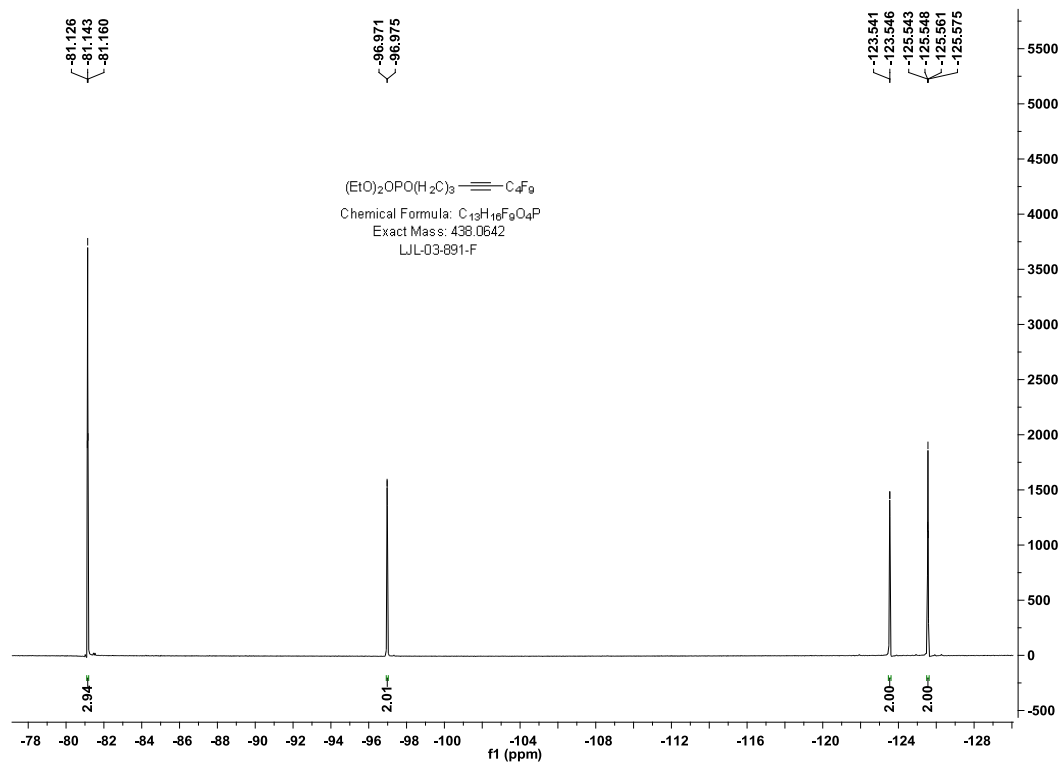


# Diethyl (6,6,7,7,8,8,9,9,9-nonafluoronon-4-yn-1-yl) phosphate (6q)

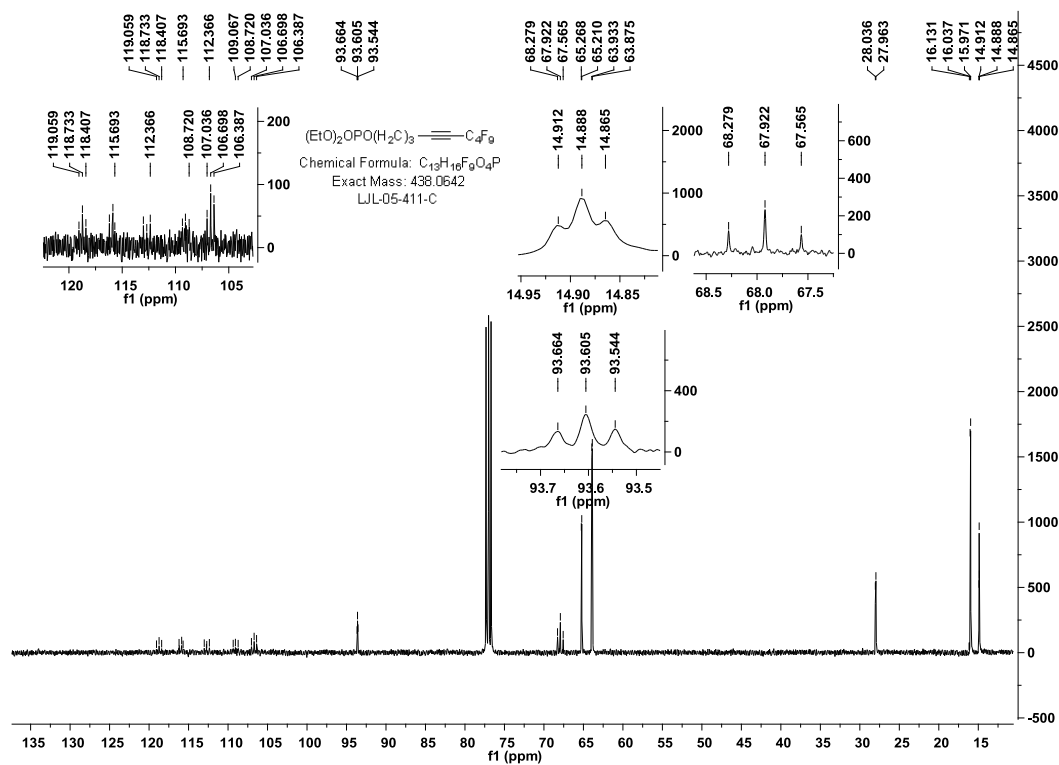
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

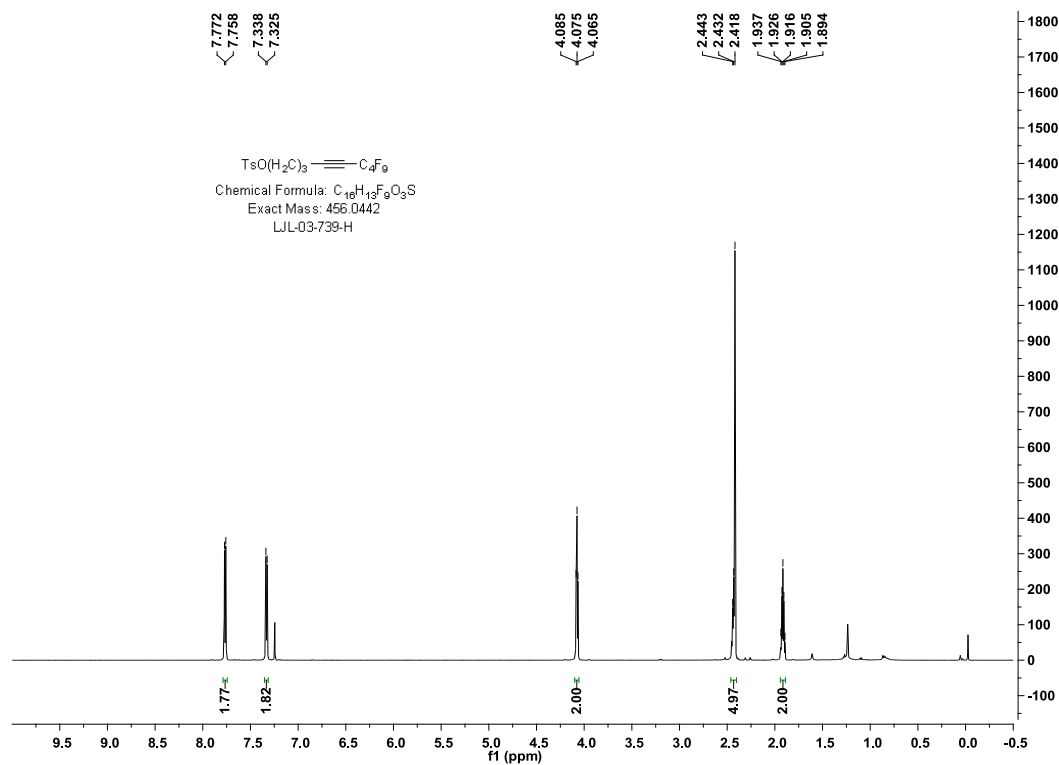


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

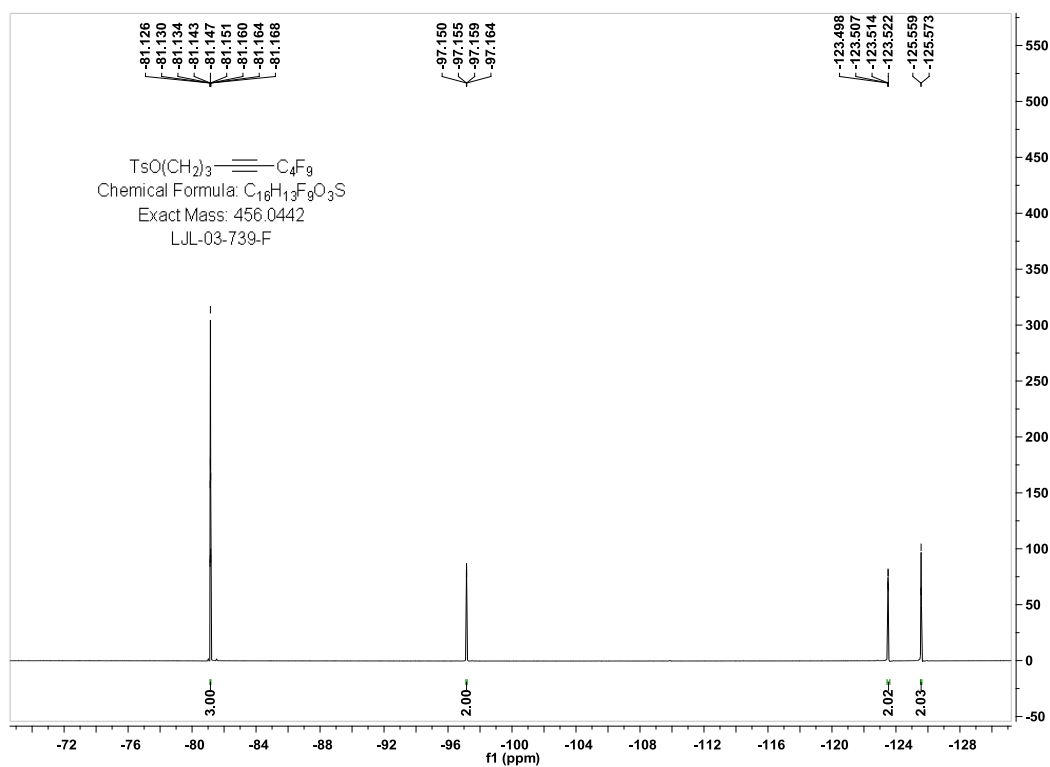


### 6,6,7,7,8,8,9,9,9-Nonafluoronon-4-yn-1-yl 4-methylbenzenesulfonate (6r)

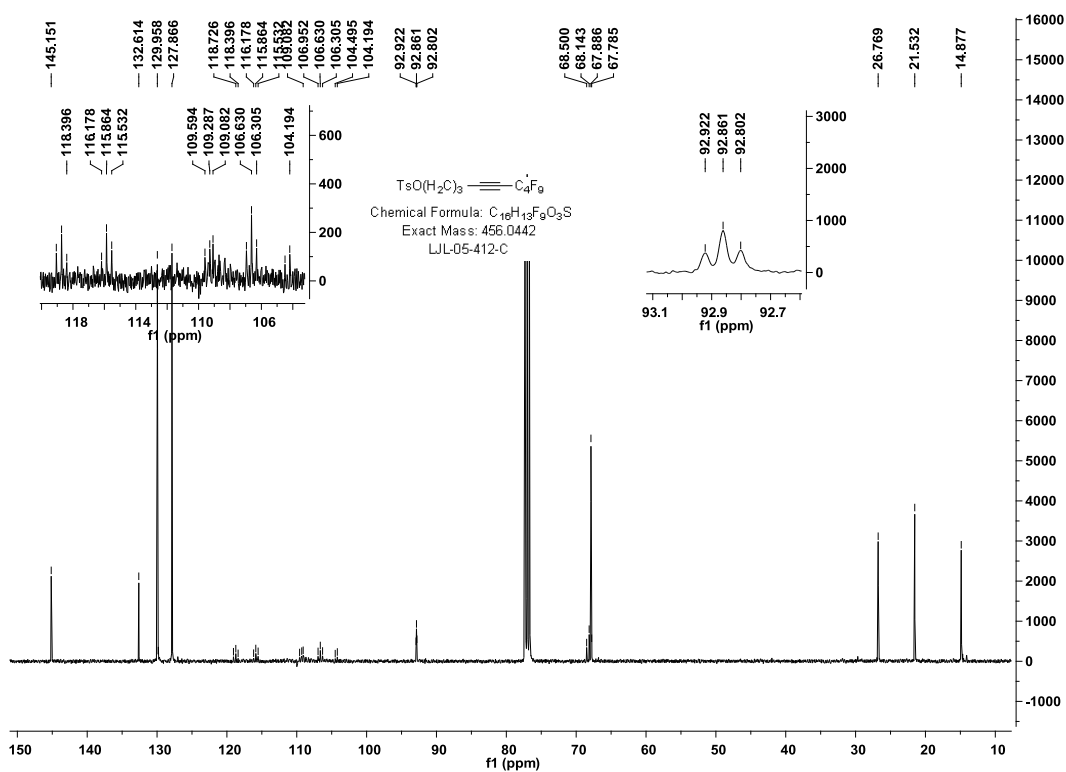
#### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

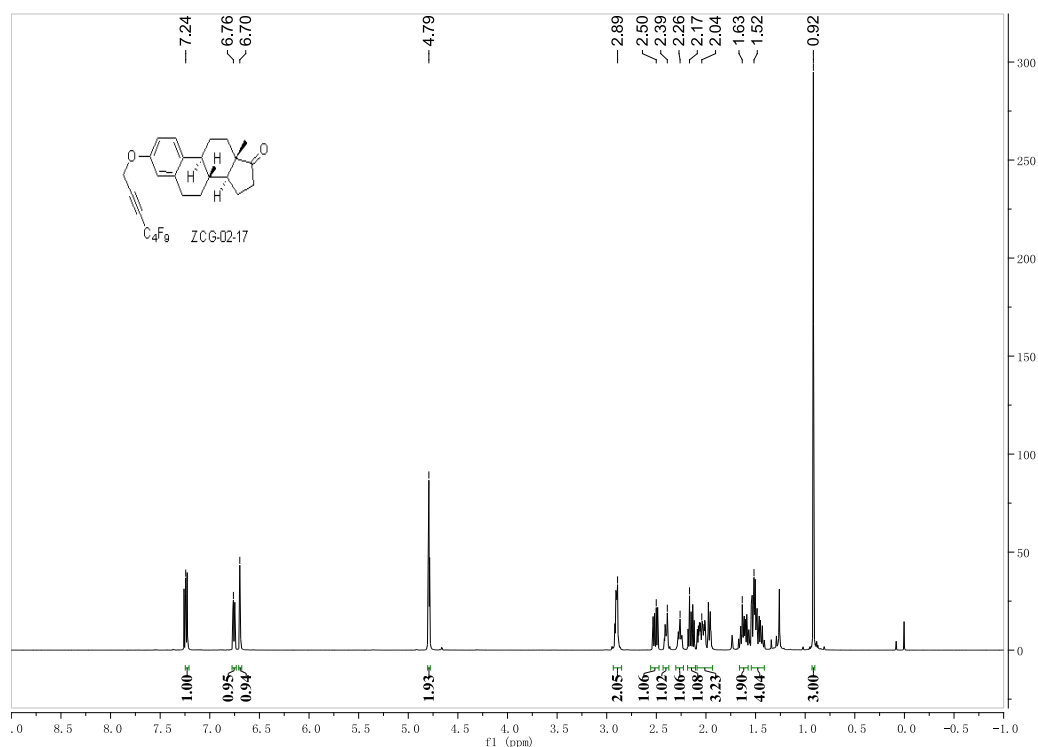


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

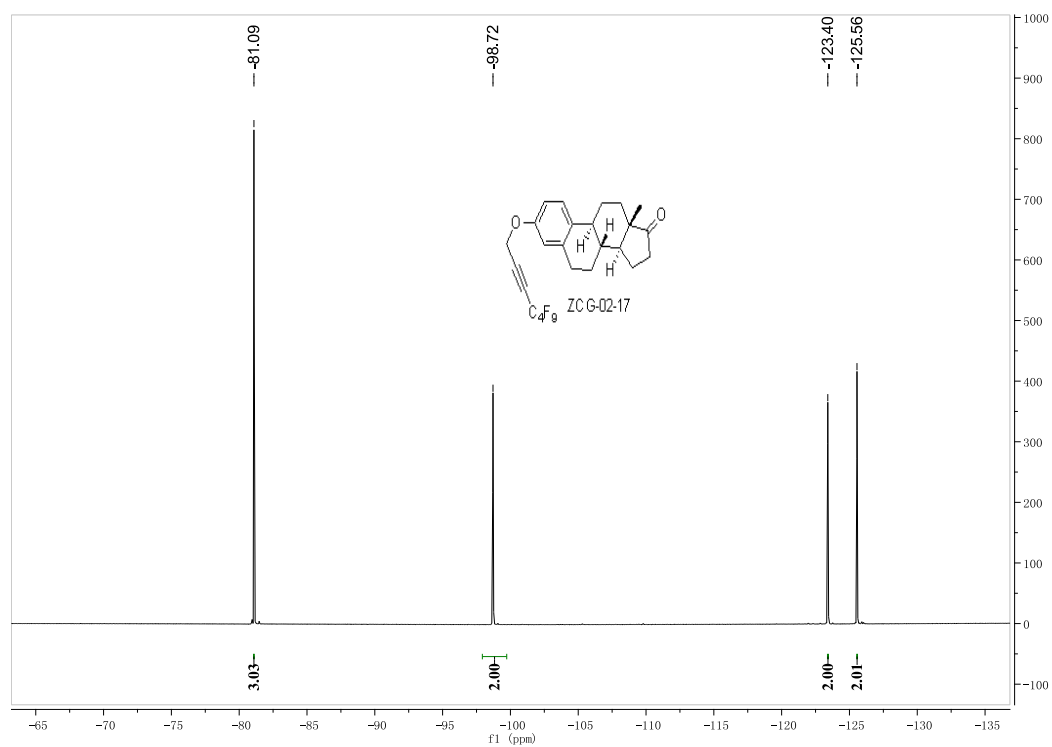


**(8R,9S,13S,14S)-13-methyl-3-((4,4,5,5,6,6,7,7,7-nonafluorohept-2-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (6 s)**

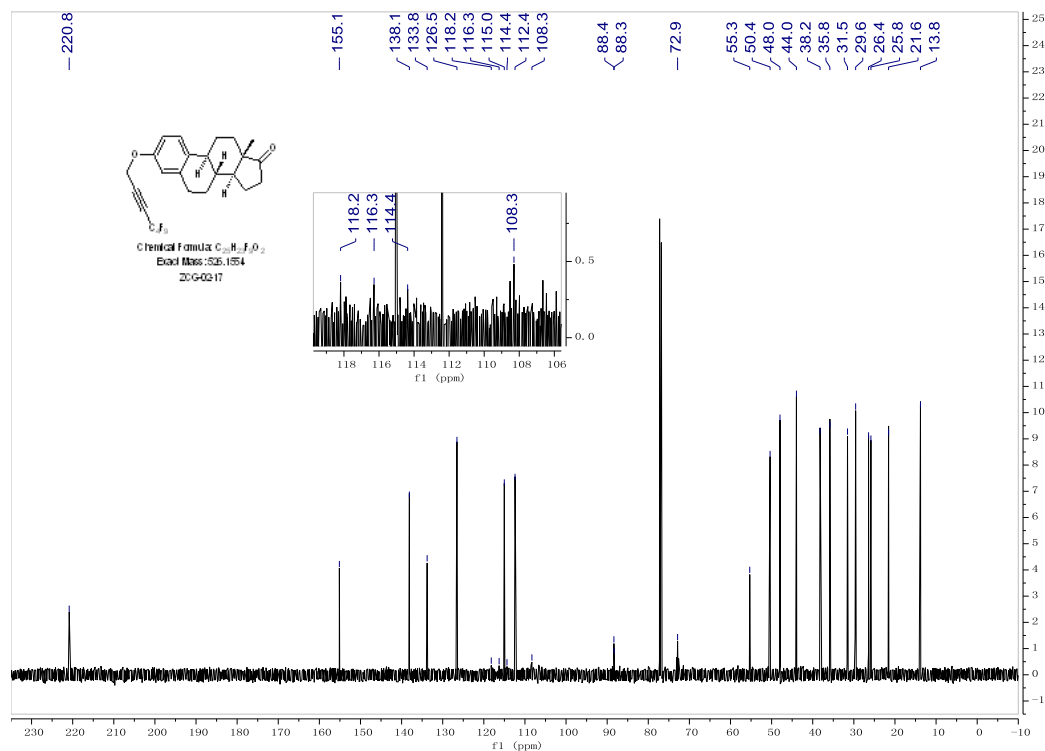
**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )**

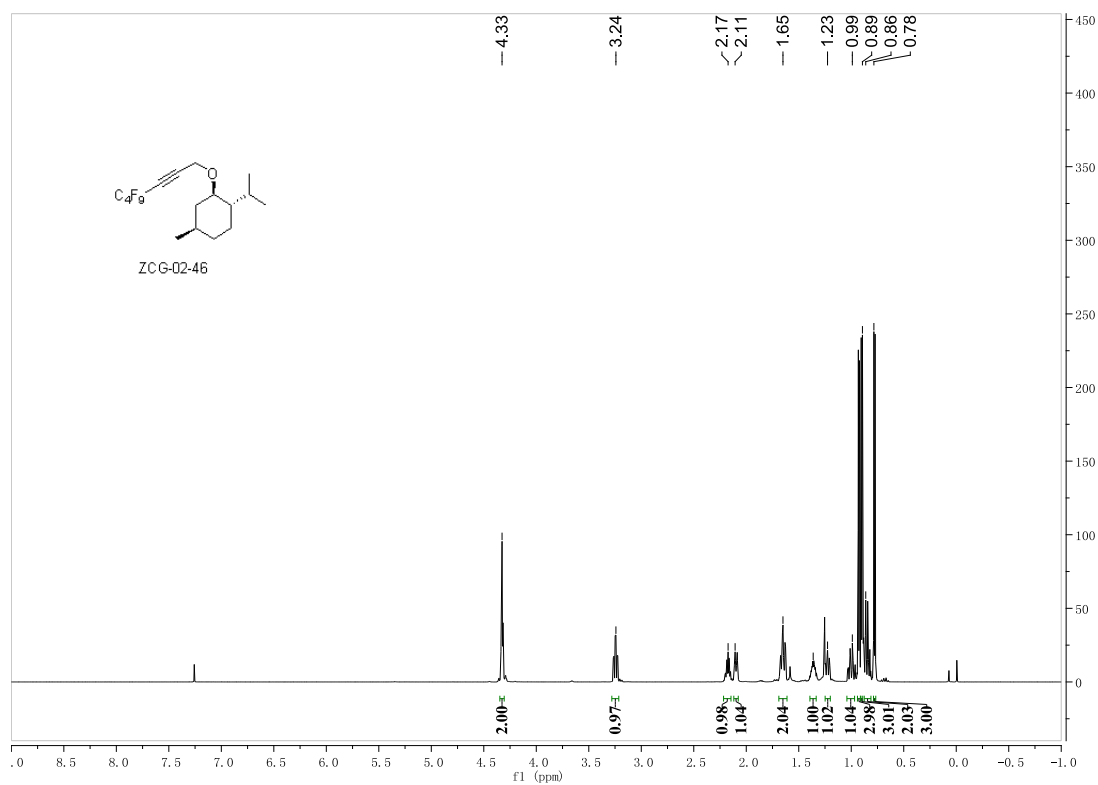


**<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)**

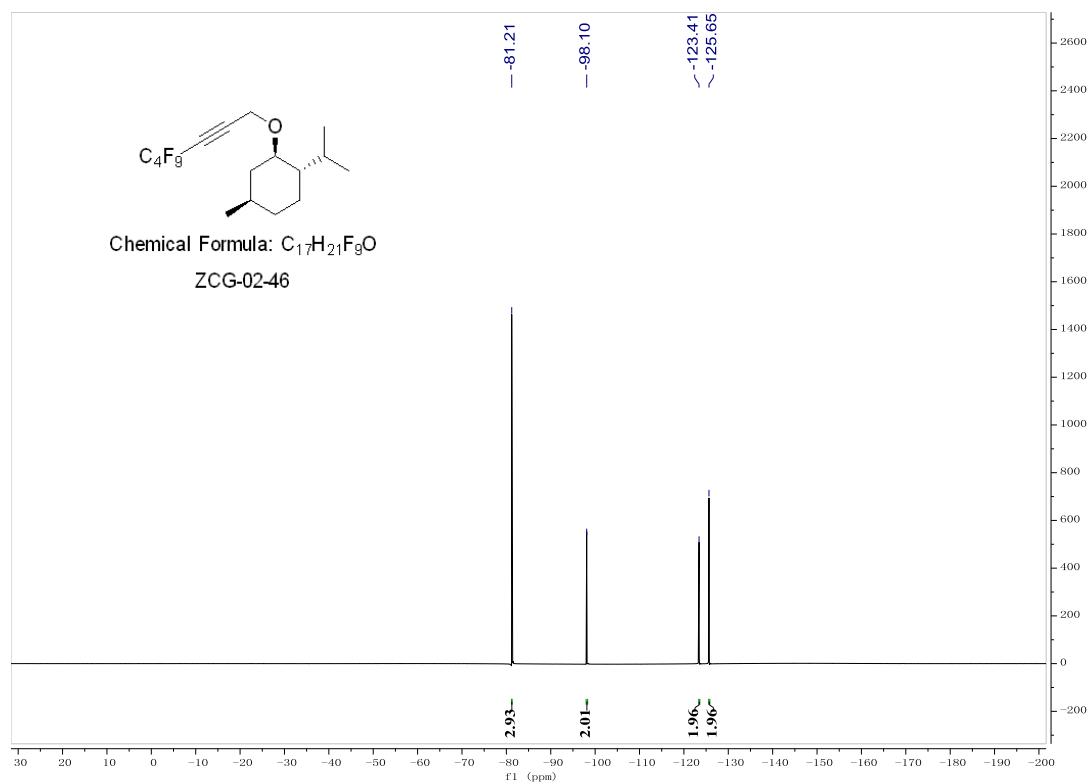


**(1S,2R,4R)-1-isopropyl-4-methyl-2-((4,4,5,5,6,6,7,7,7-nonafluorohept-2-yn-1-yl)oxy)cyclohexane (6t)**

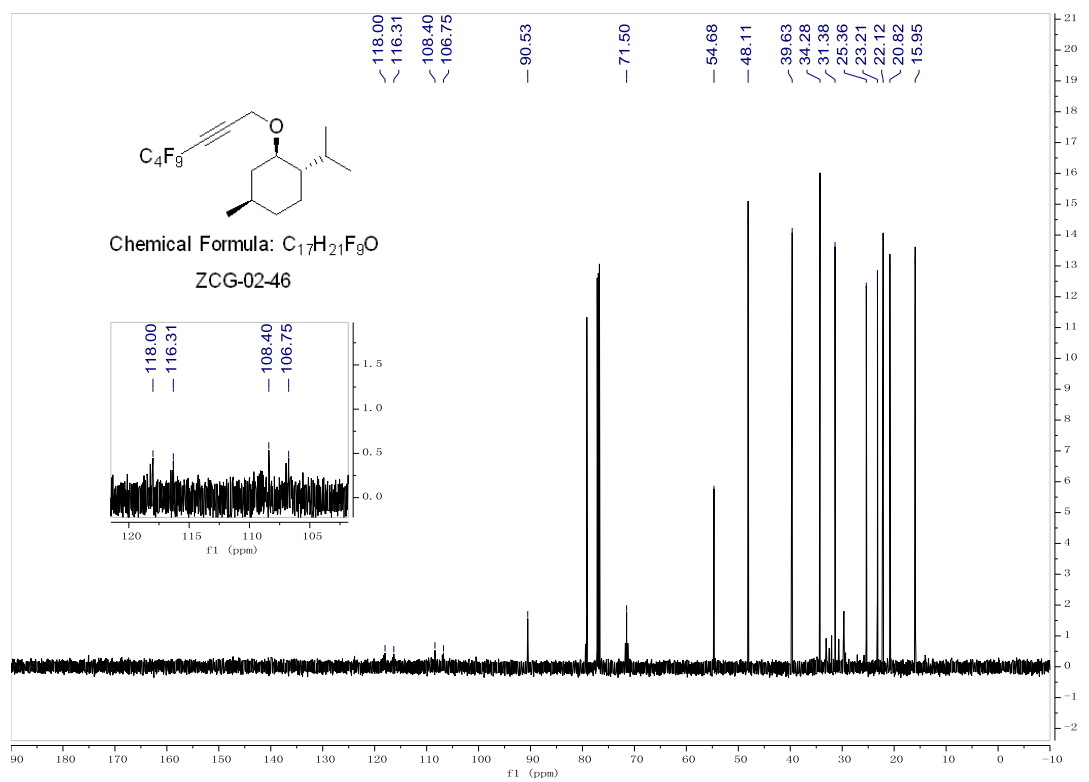
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**



**<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)**

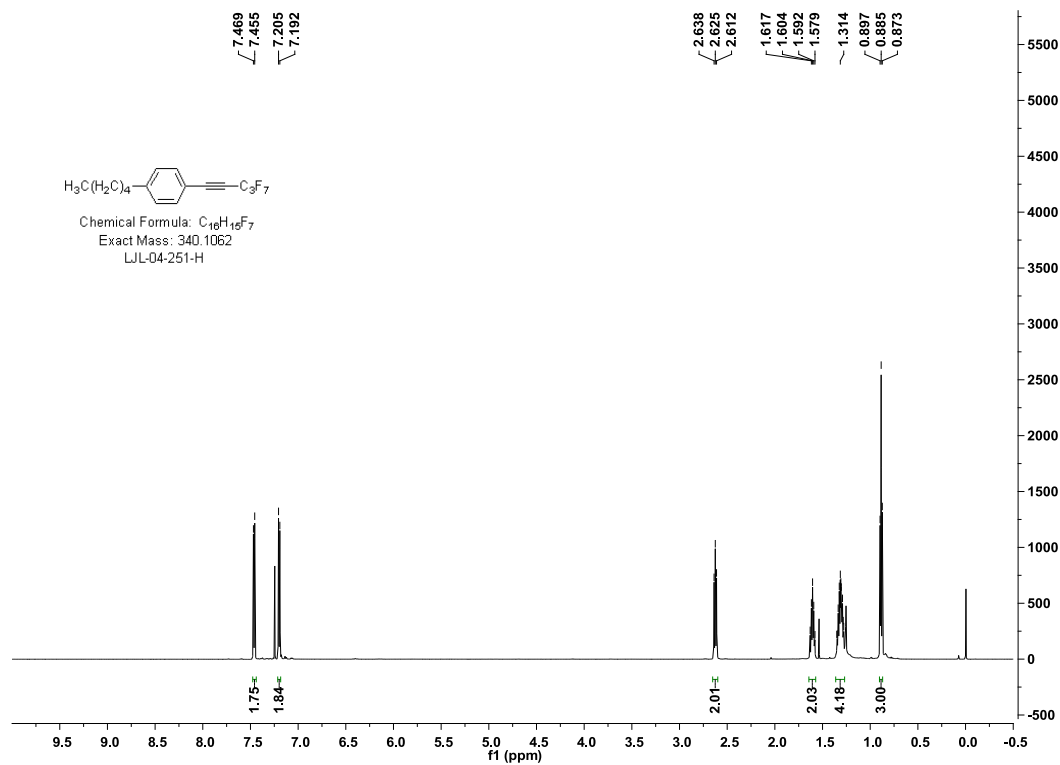


**<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)**

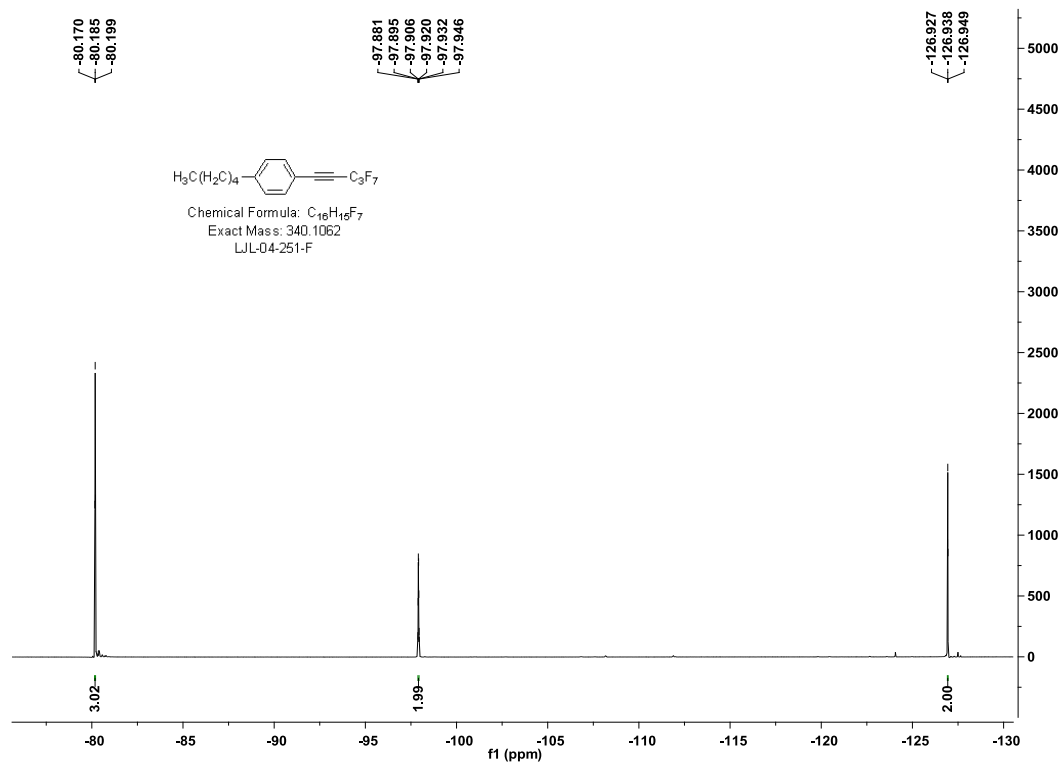


# 1-Pentyl-4-(perfluoropent-1-yn-1-yl)benzene (5b)

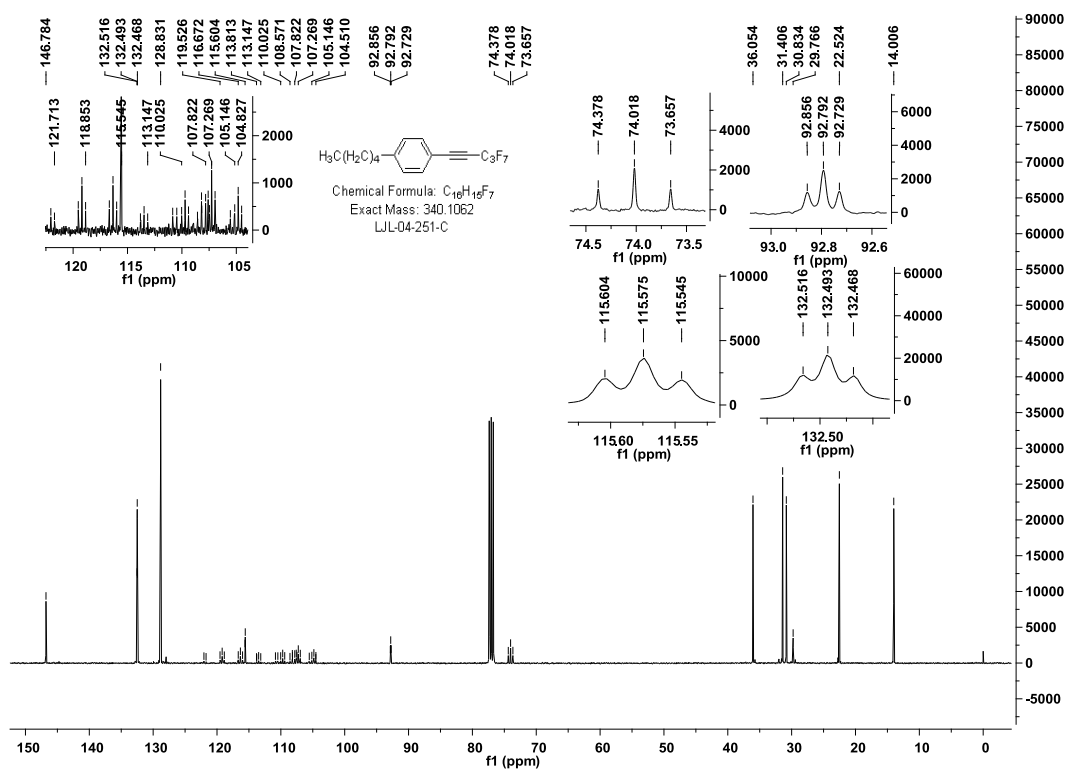
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

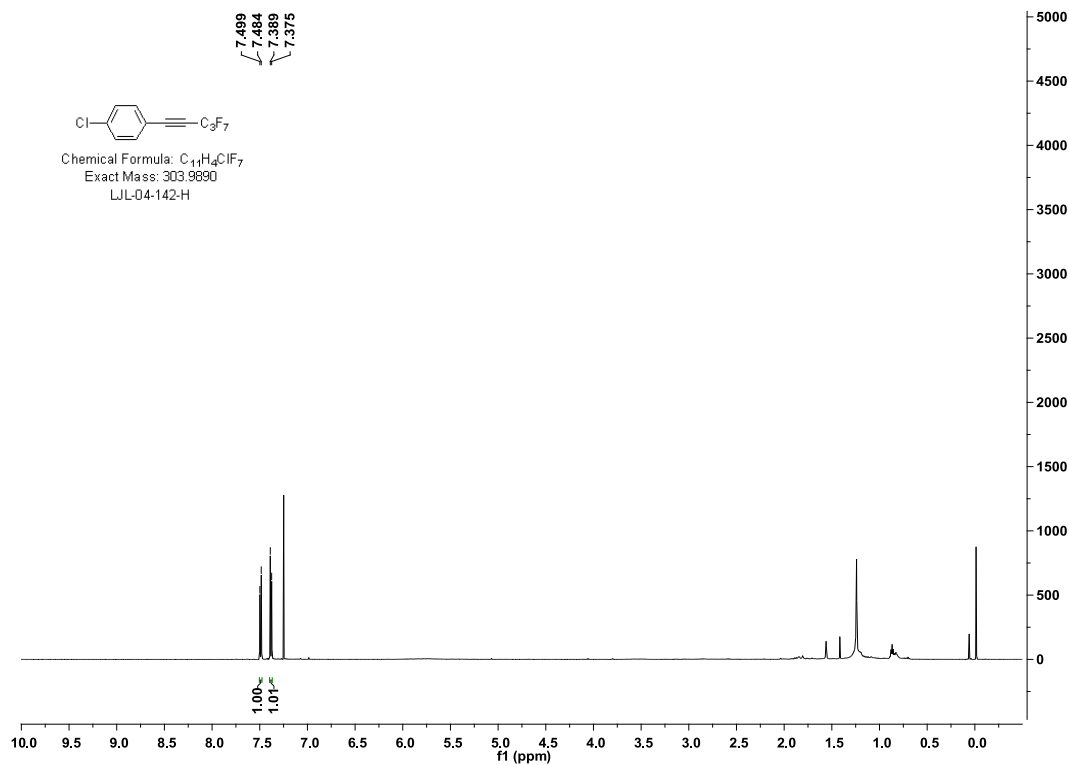


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

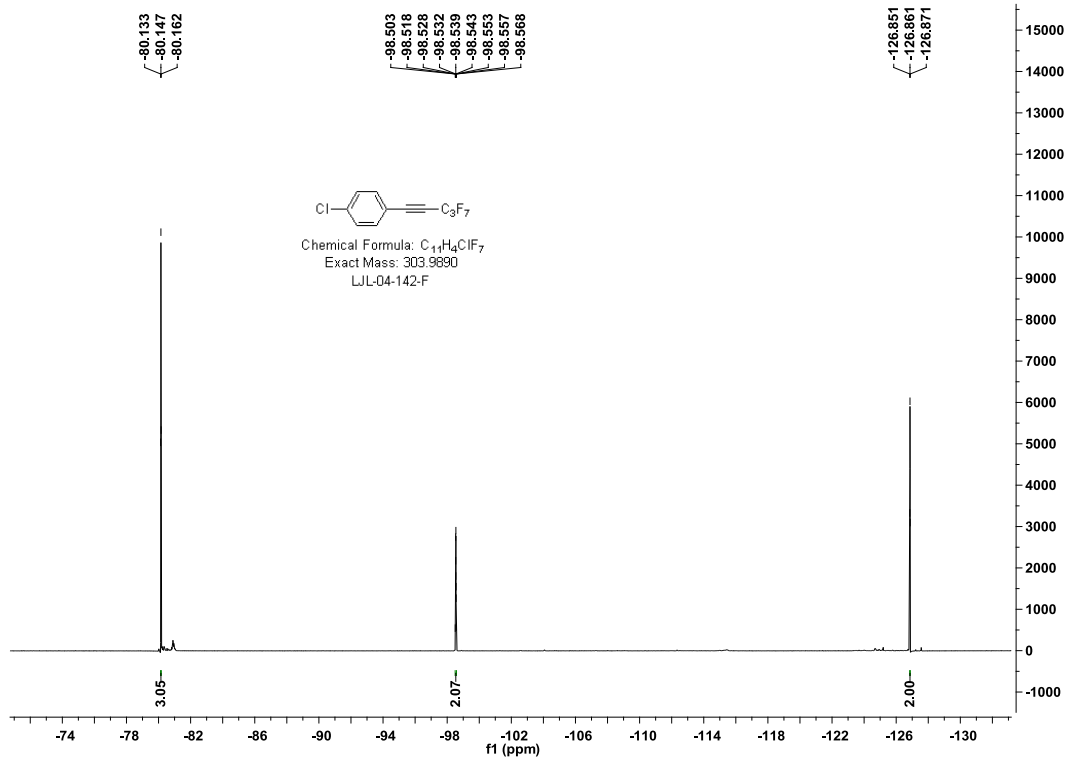


### 1-Chloro-4-(perfluoropent-1-yn-1-yl)benzene (5h)

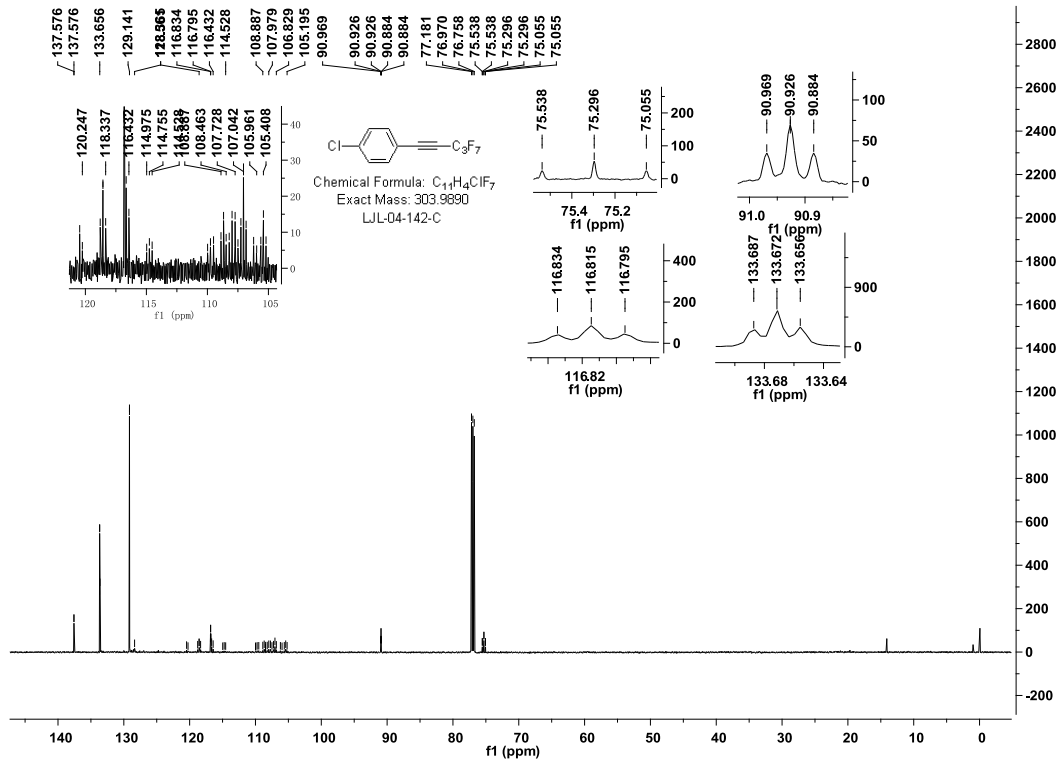
### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



**<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)**

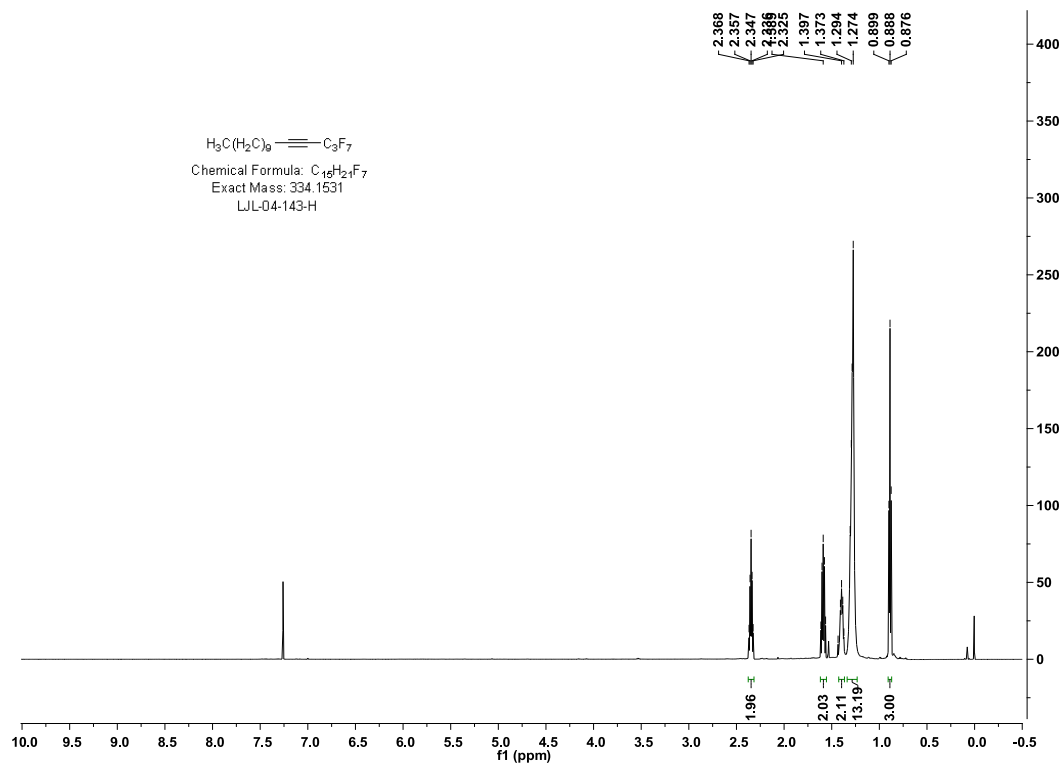


**<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)**

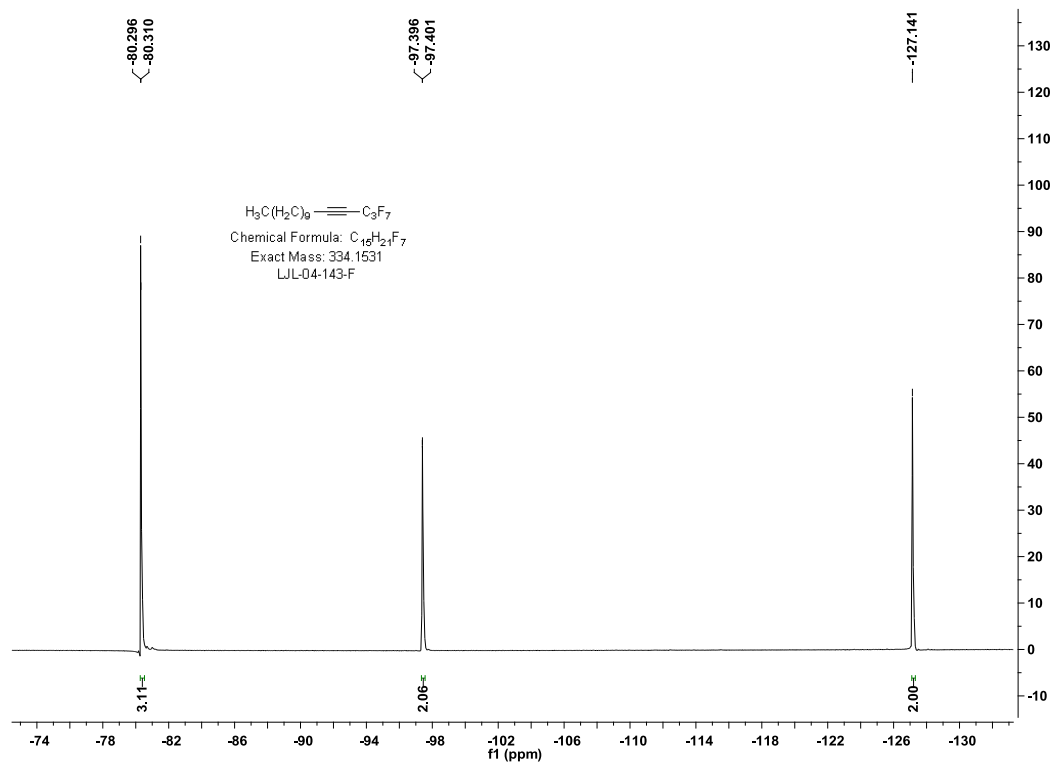


# 1,1,1,2,2,3,3-Heptafluoropentadec-4-yne (5I)

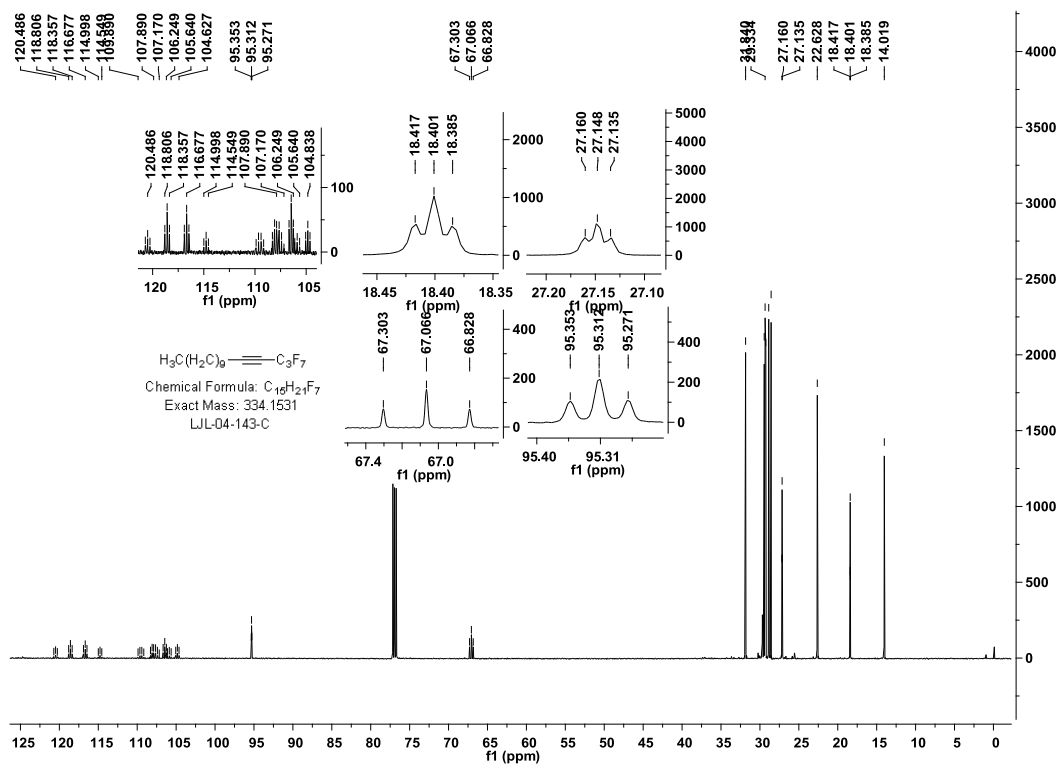
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

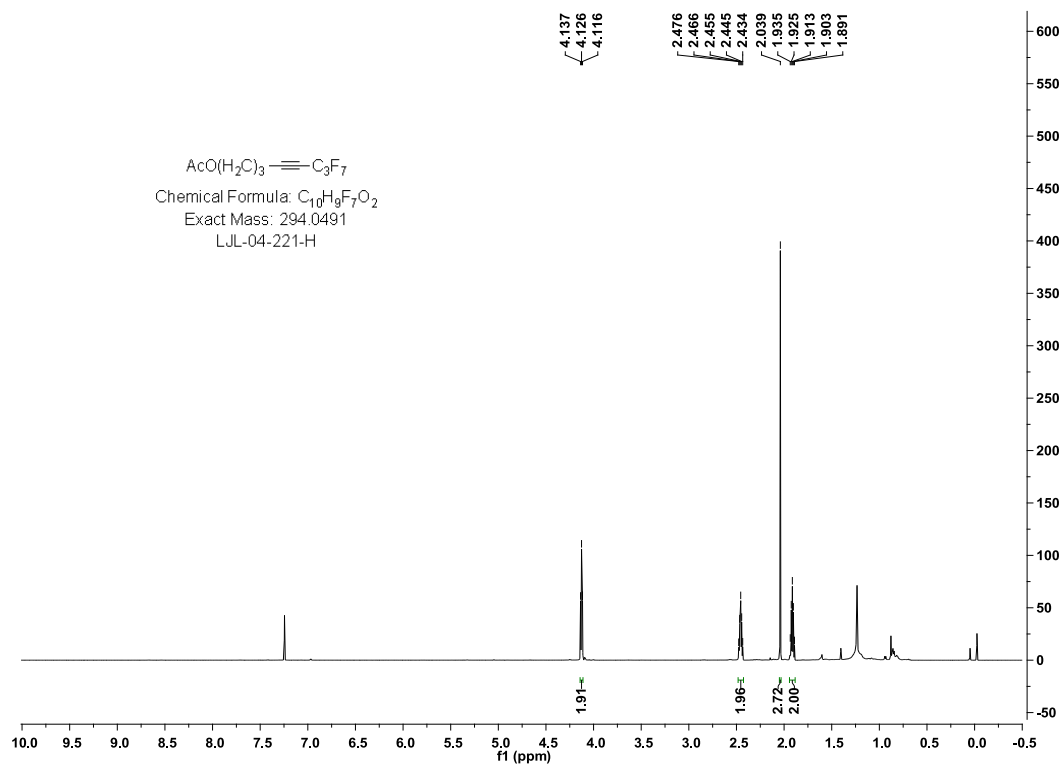


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

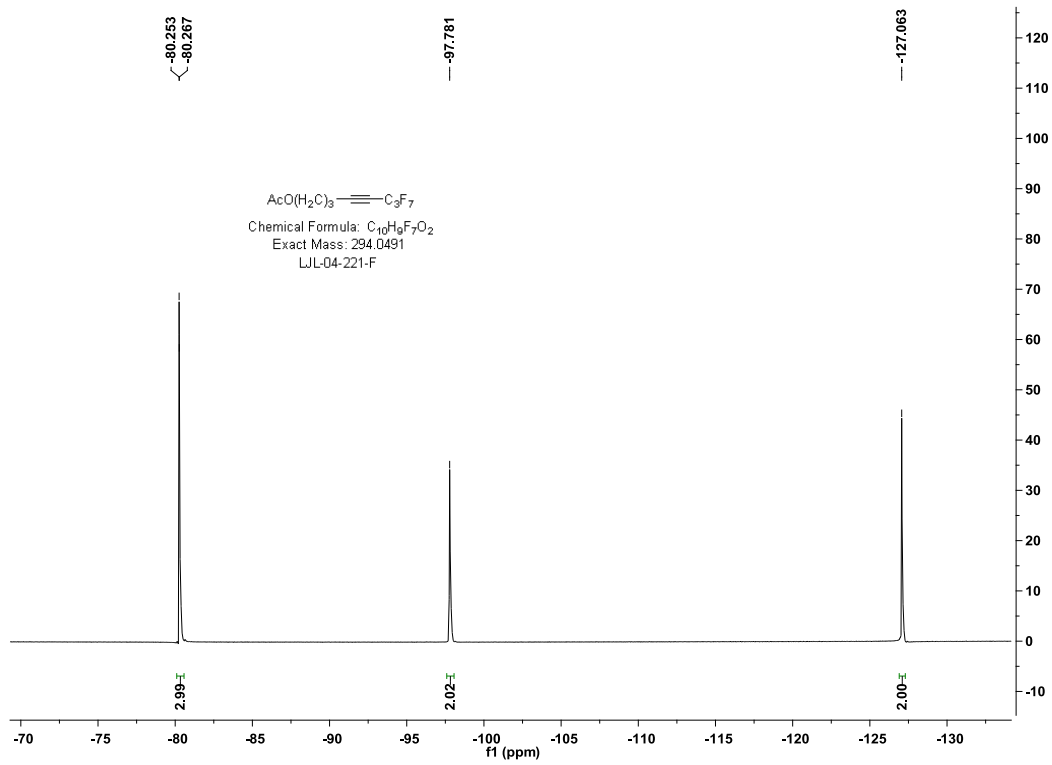


### 6,6,7,7,8,8,8-Heptafluorooct-4-yn-1-yl acetate (5n)

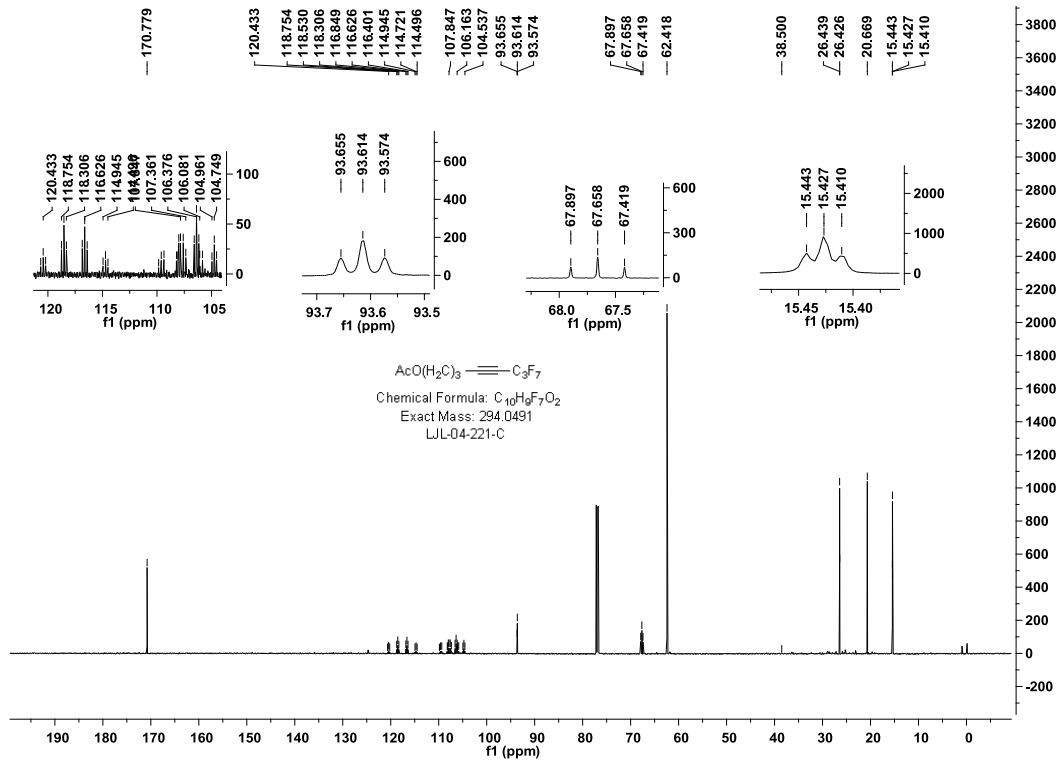
### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

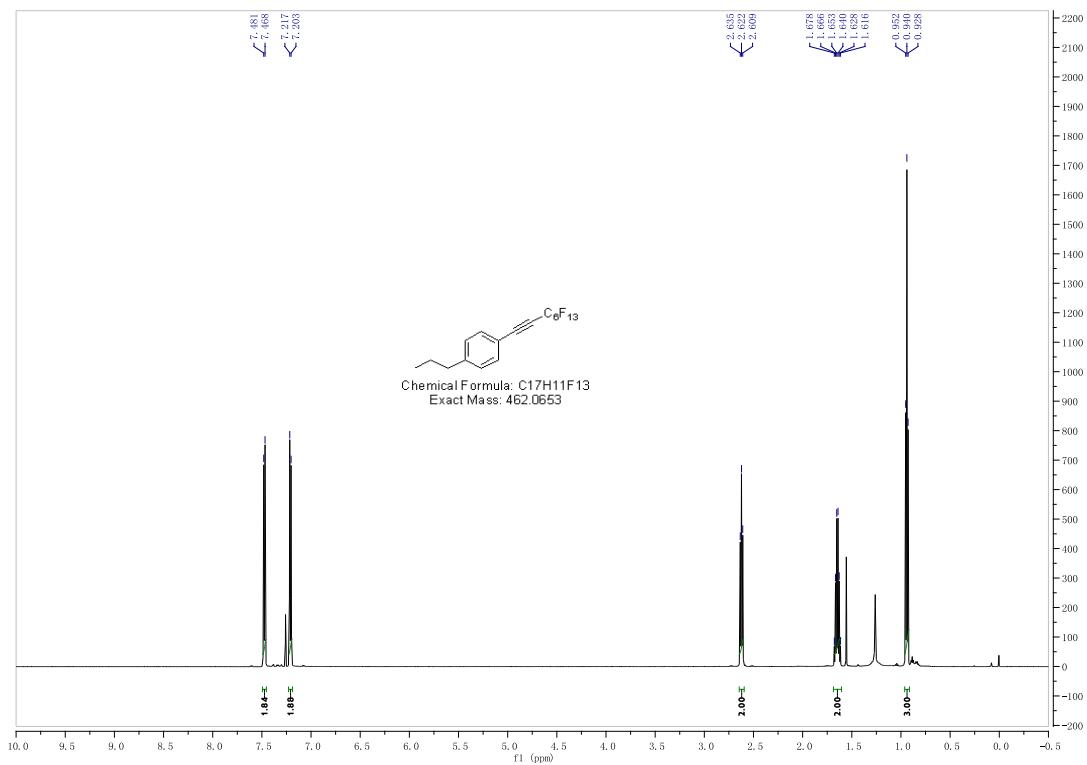


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

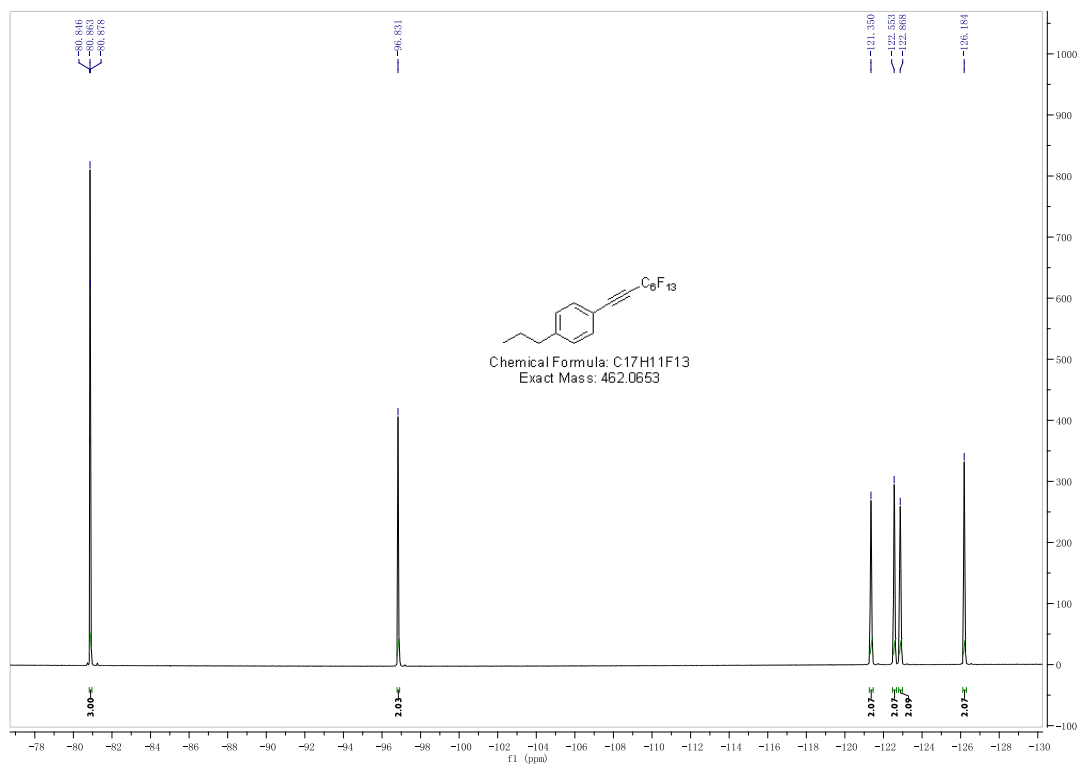


# 1-(perfluorooct-1-yn-1-yl)-4-propylbenzene (7a)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

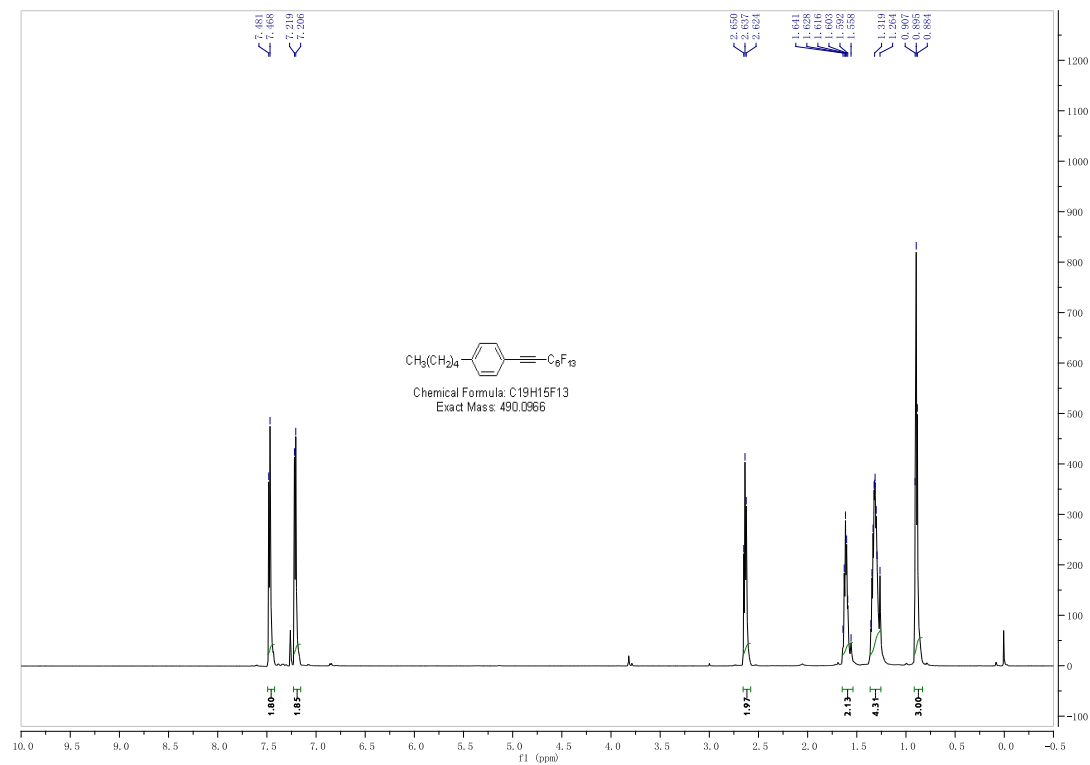


$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

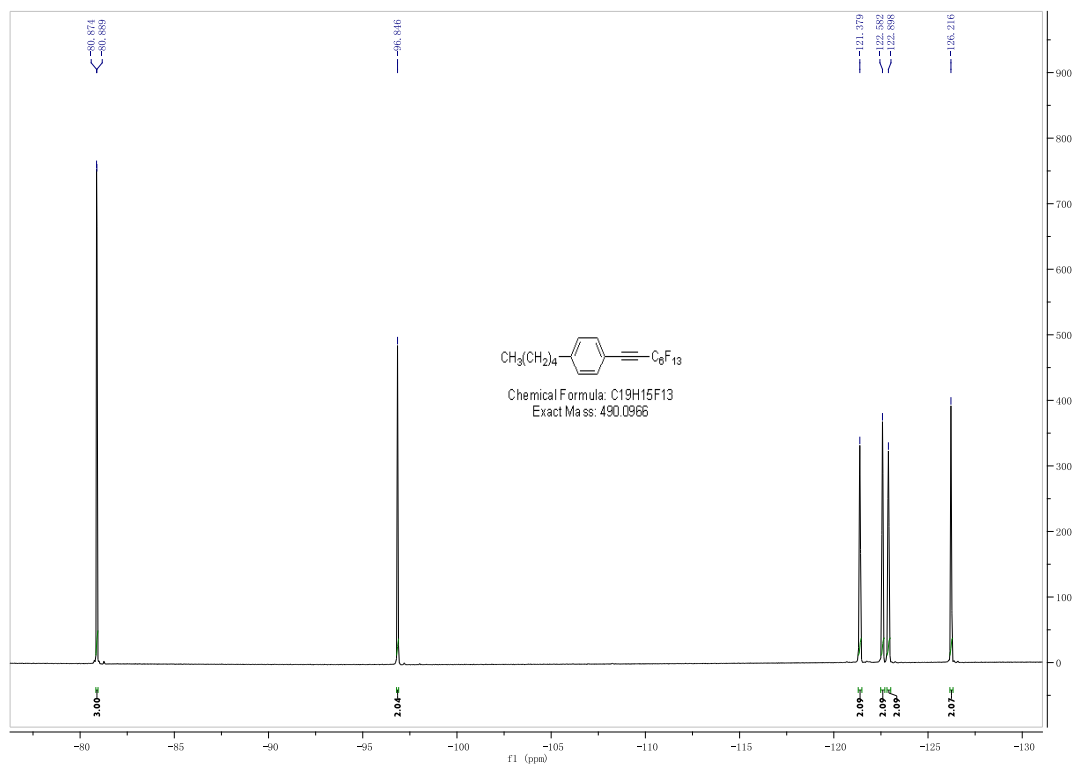


# 1-pentyl-4-(perfluorooct-1-yn-1-yl)benzene (7b)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

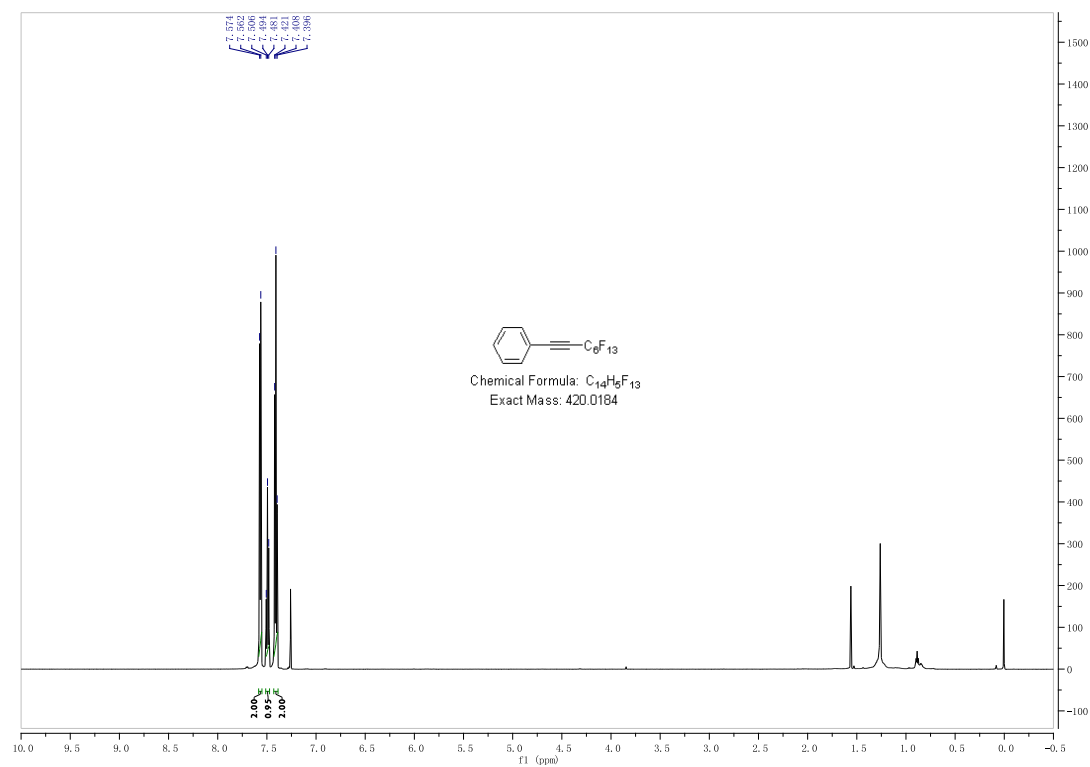


$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

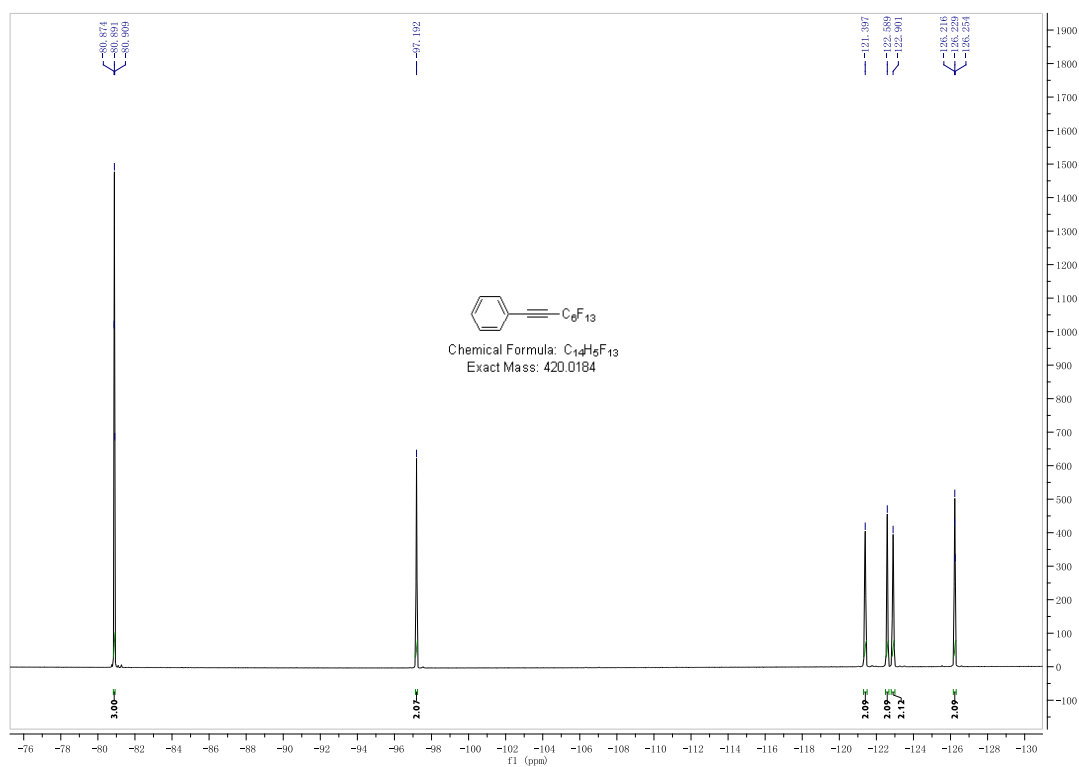


# (perfluorooct-1-yn-1-yl)benzene (7c)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

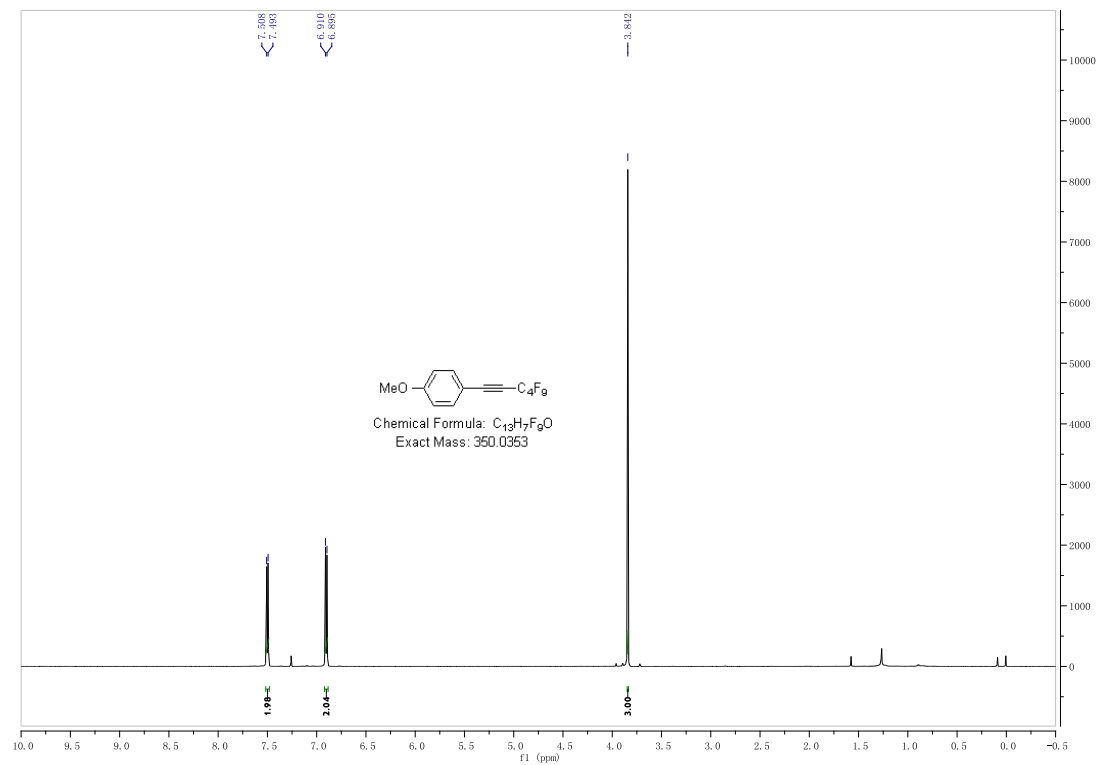


$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

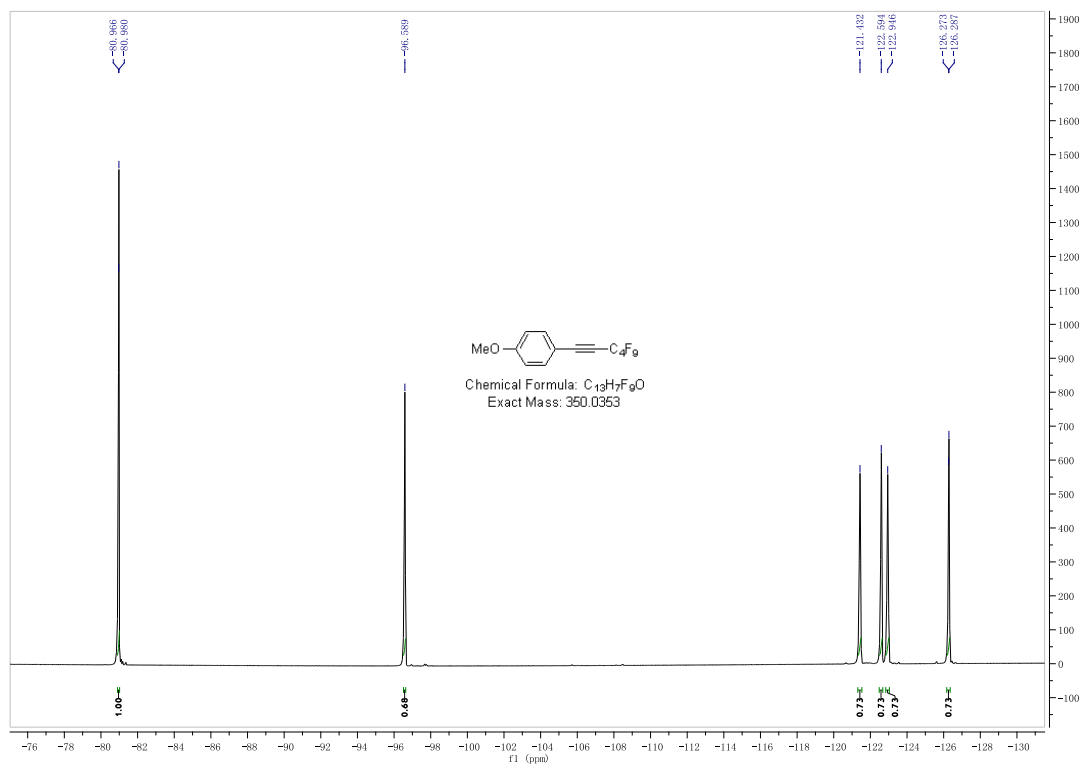


# 1-methoxy-4-(perfluorooct-1-yn-1-yl)benzene (7d)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

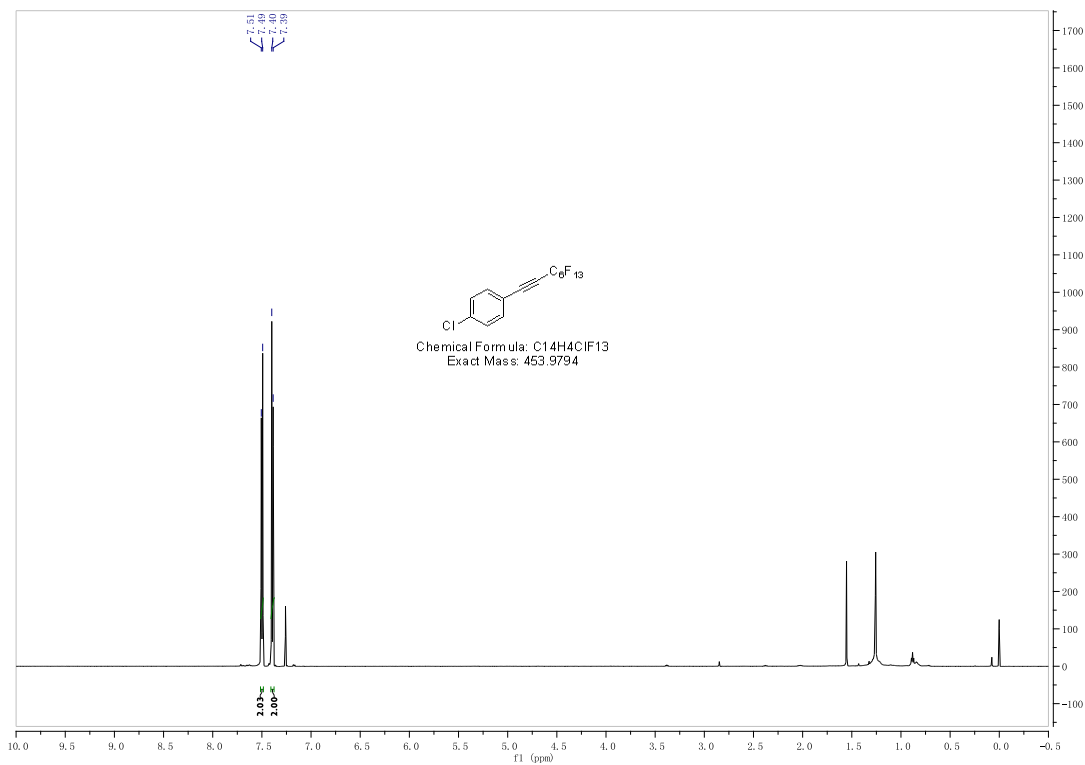


$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

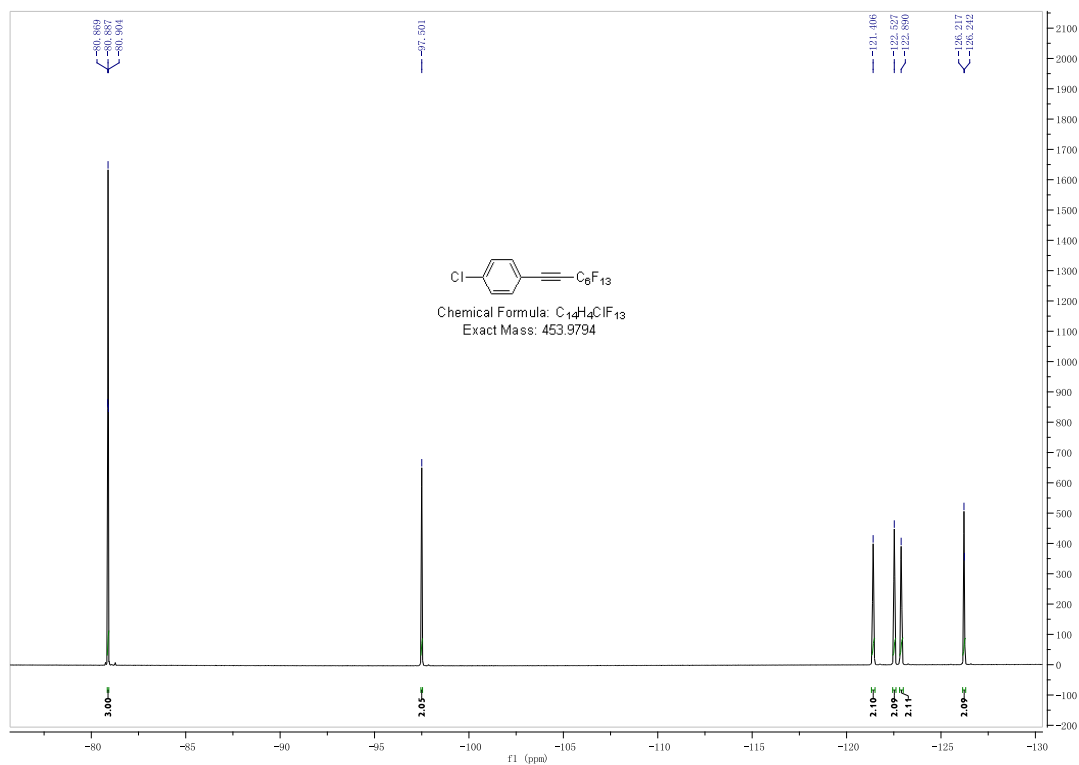


# 1-chloro-4-(perfluorooct-1-yn-1-yl)benzene (7h)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

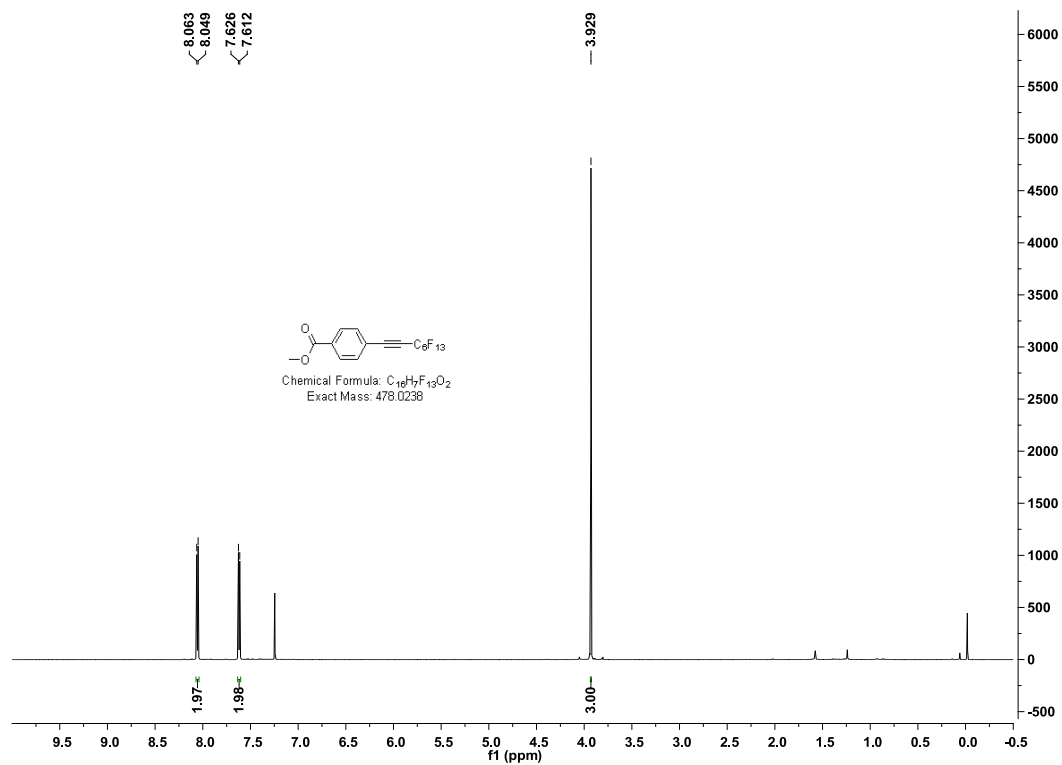


$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

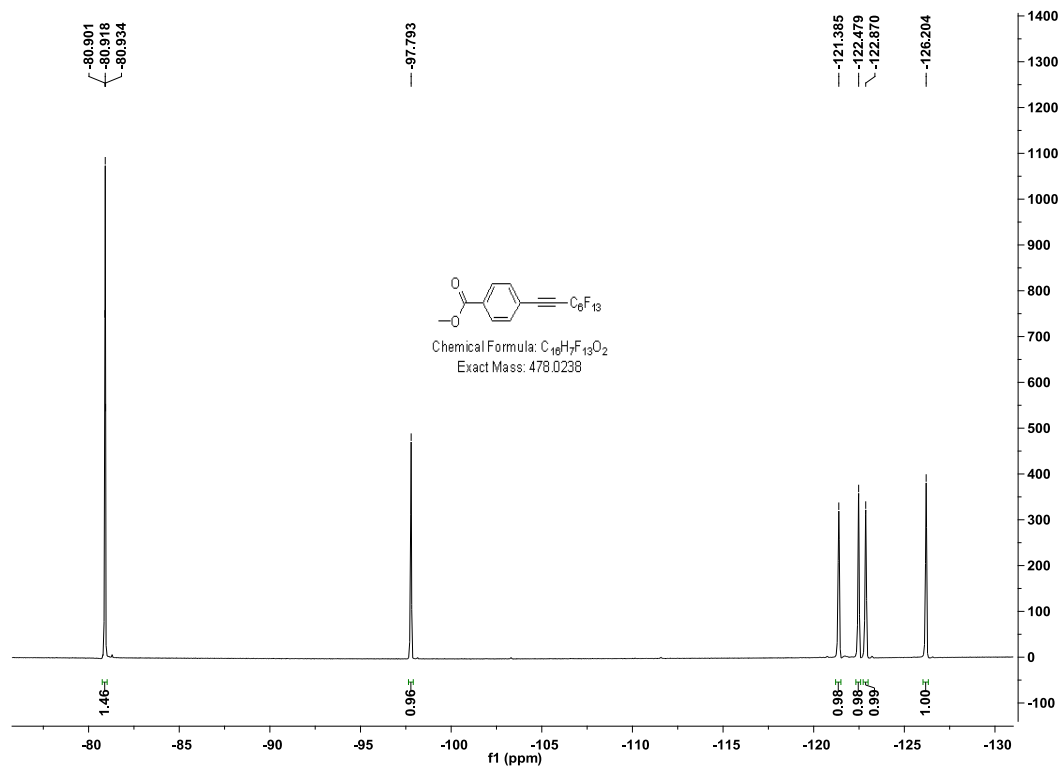


# Methyl 4-(perfluorooct-1-yn-1-yl)benzoate (7i)

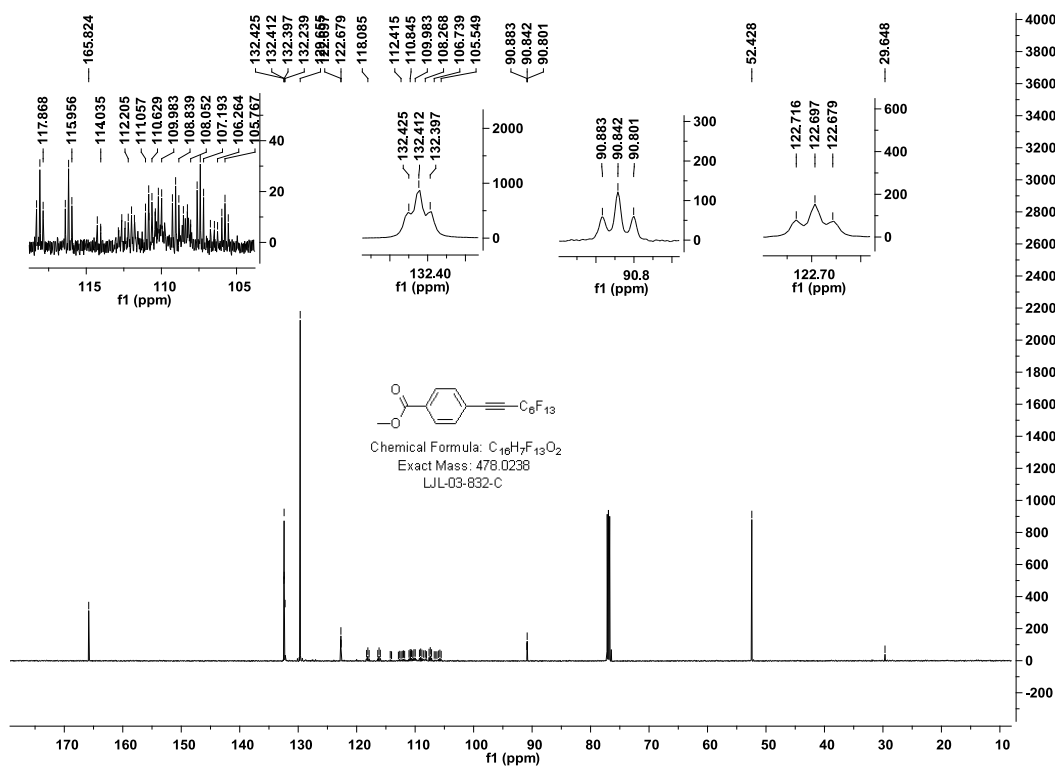
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

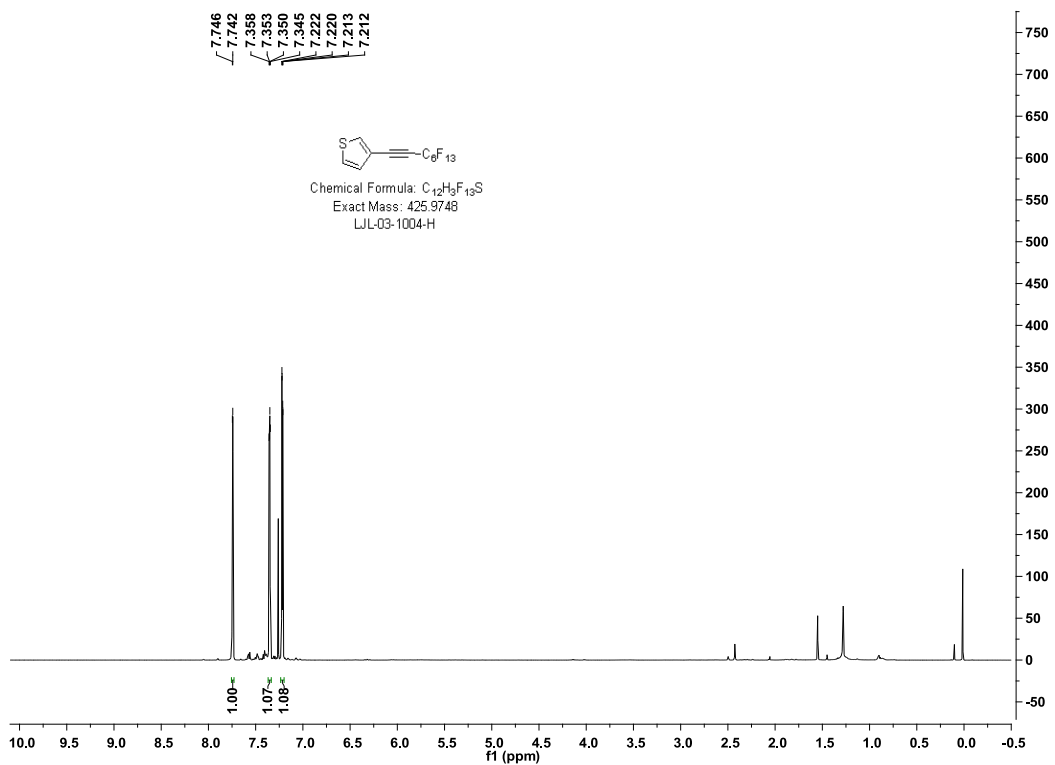


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

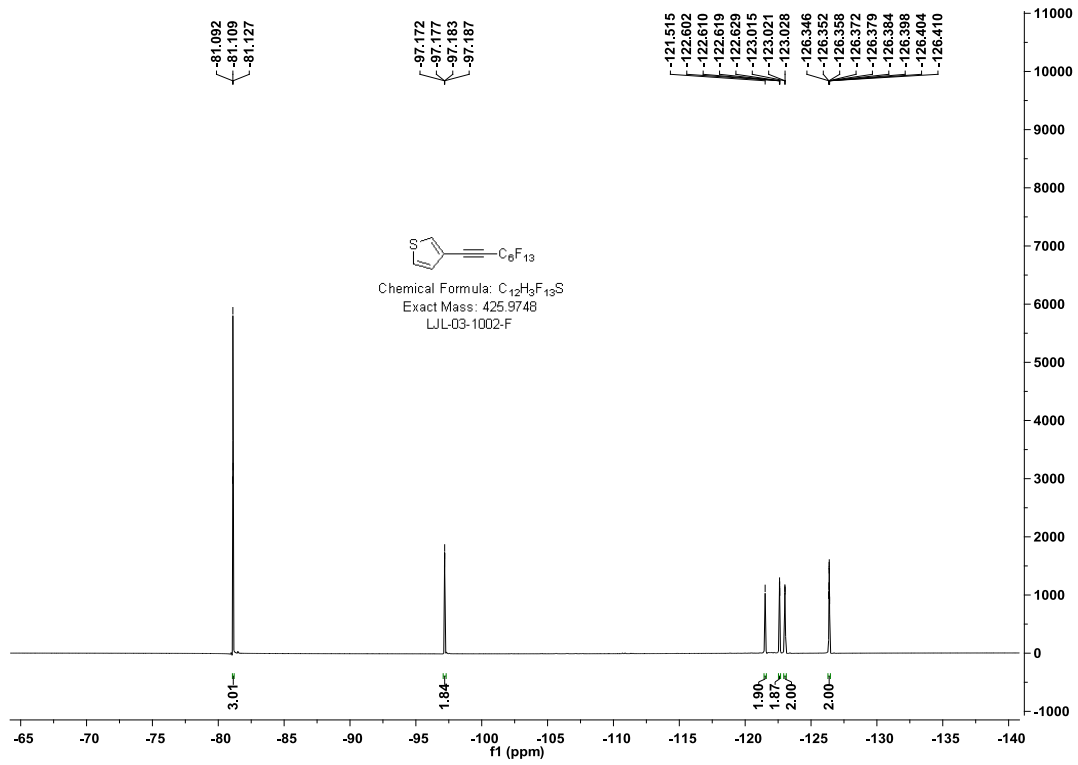


### 3-(Perfluorooct-1-yn-1-yl)thiophene (7j)

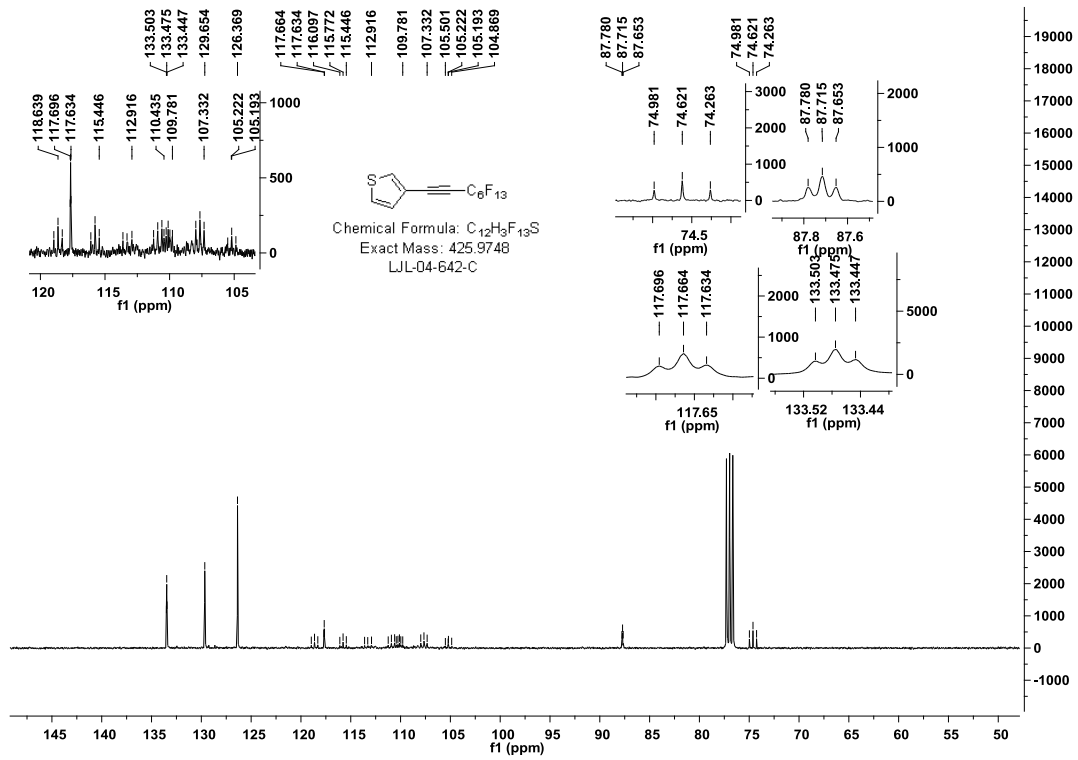
#### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)

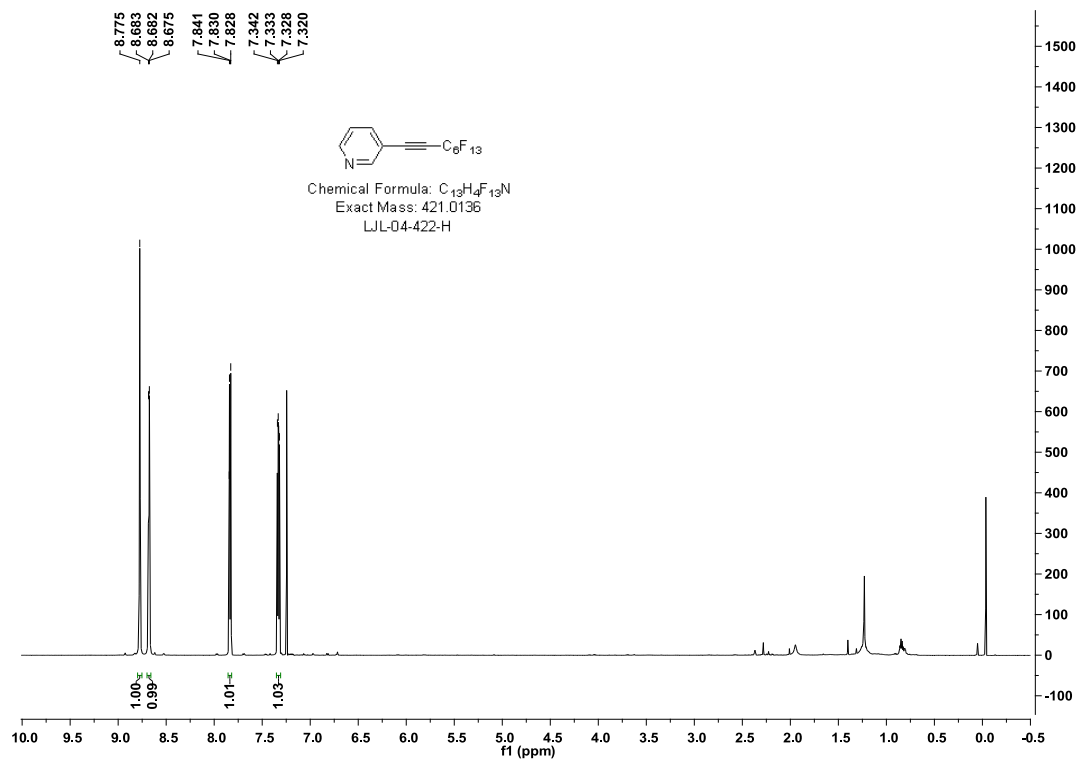


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

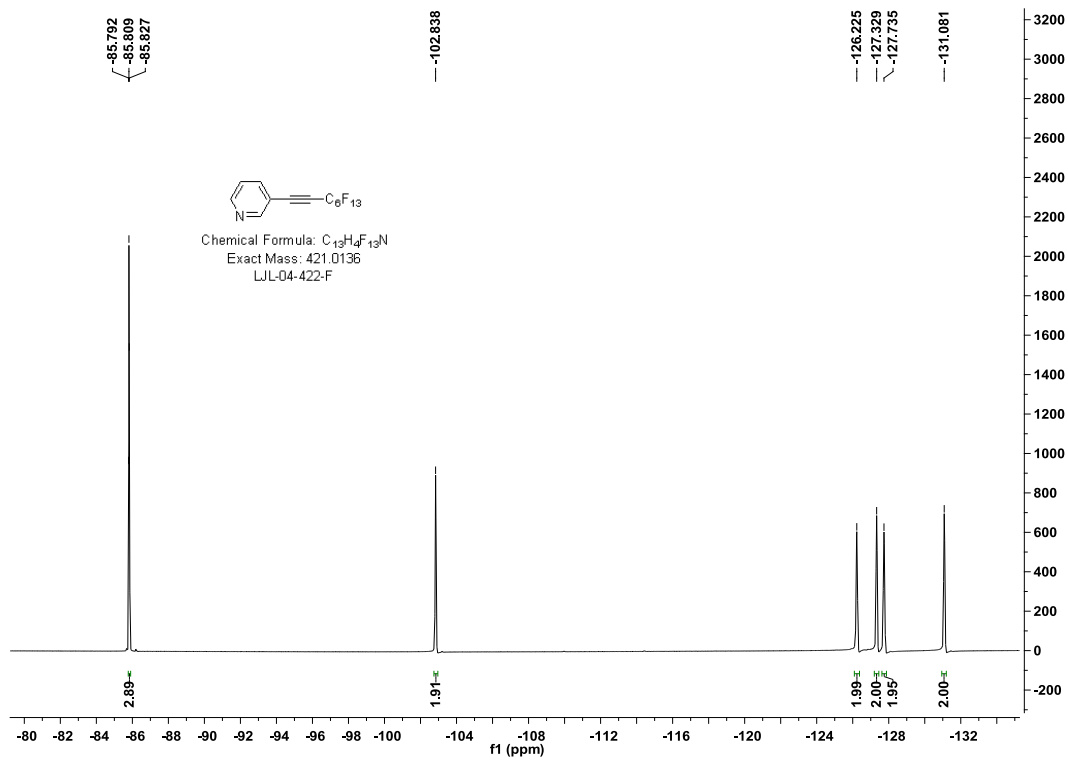


### 3-(Perfluorohex-1-yn-1-yl)pyridine (7k)

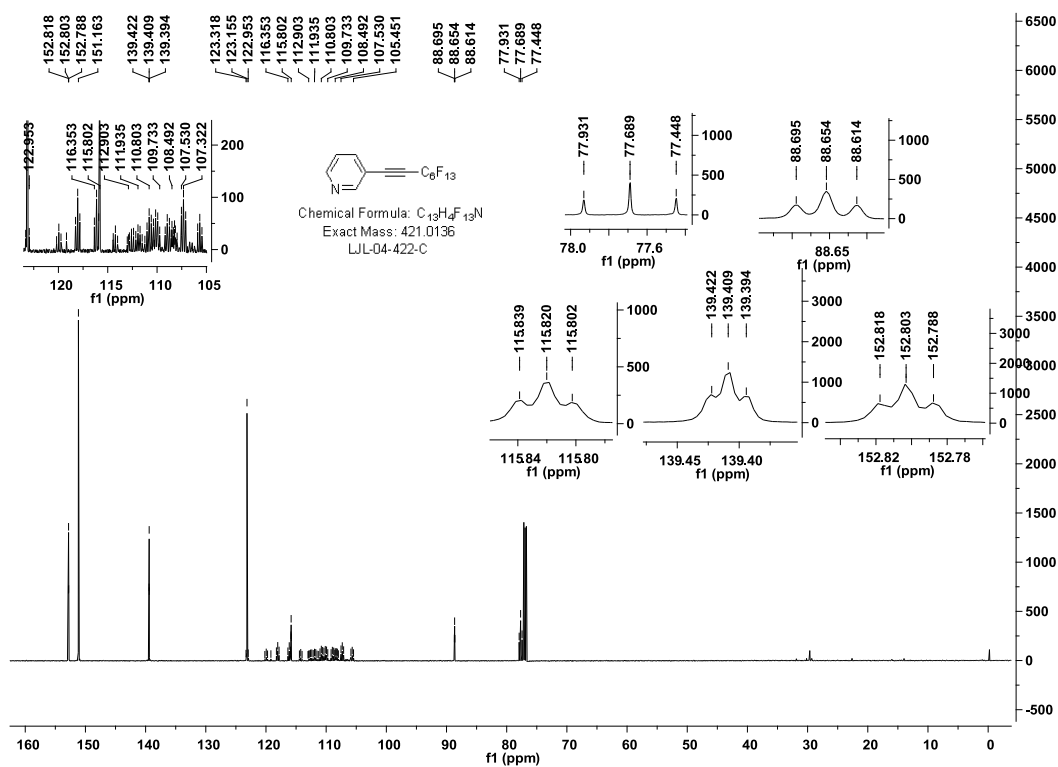
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )

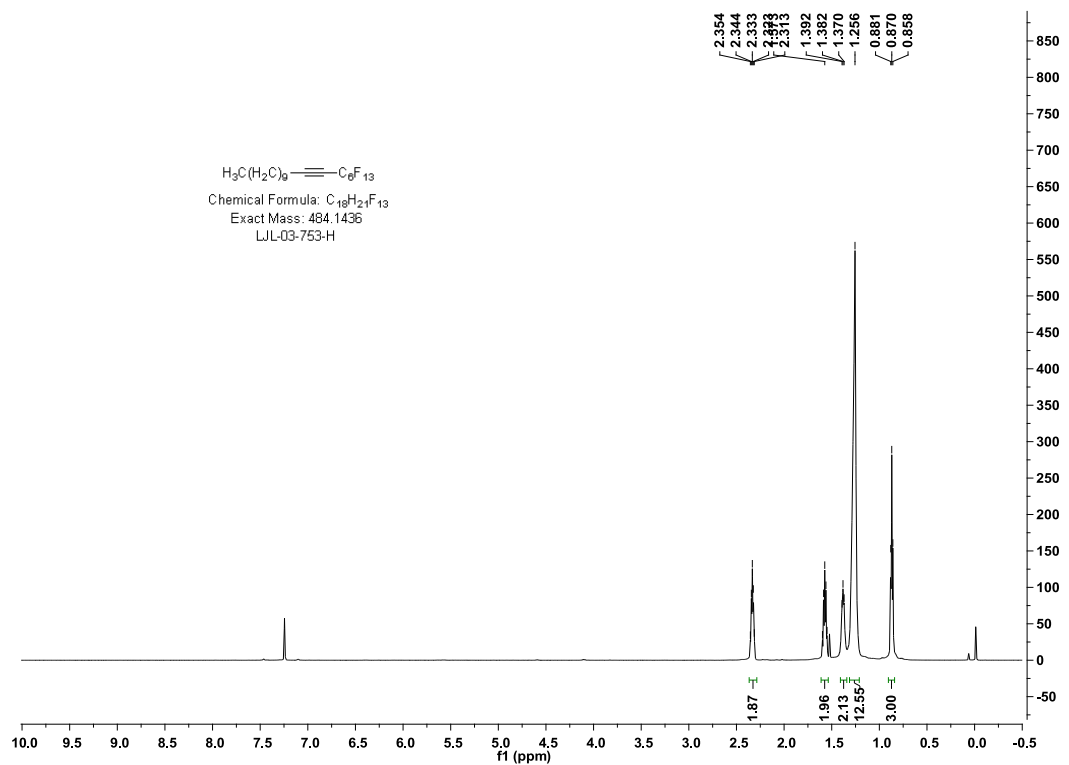


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

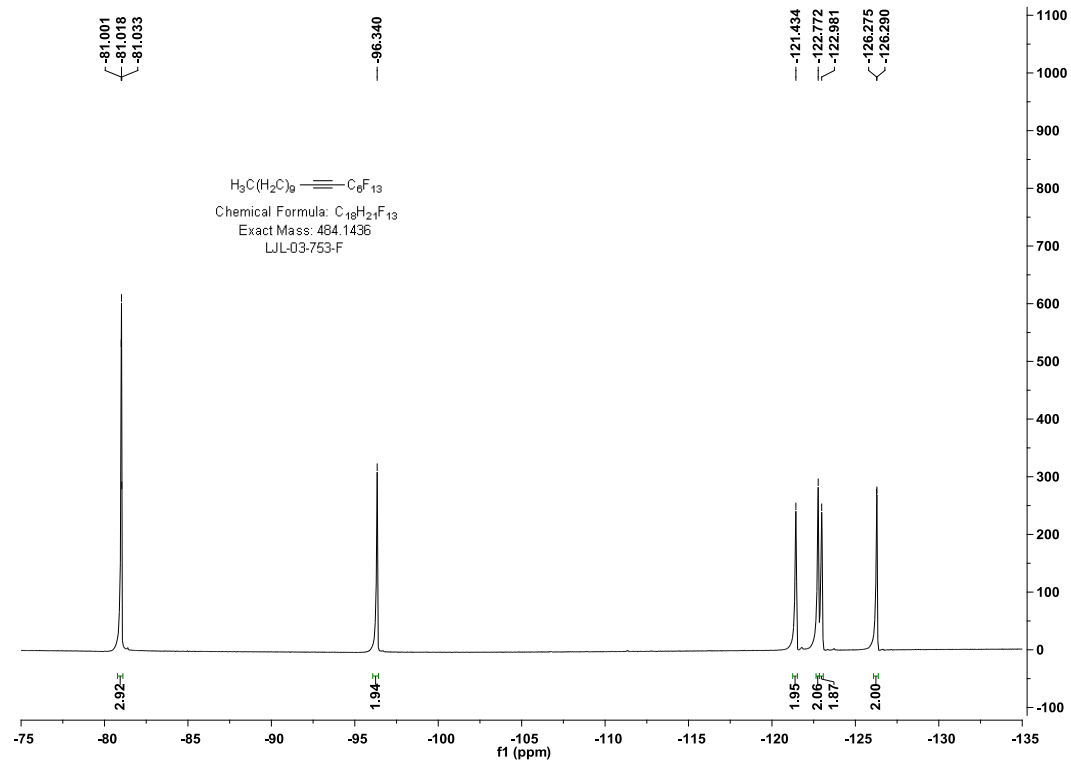


### 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorooct-7-yne (7I)

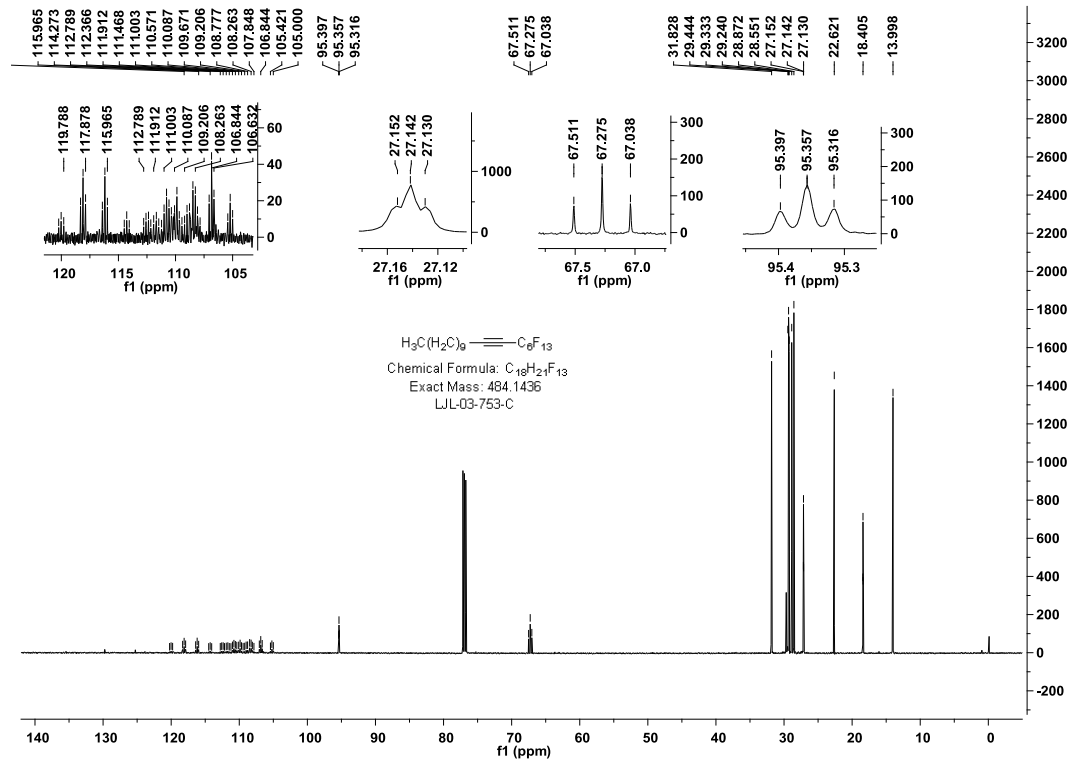
### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



**<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)**

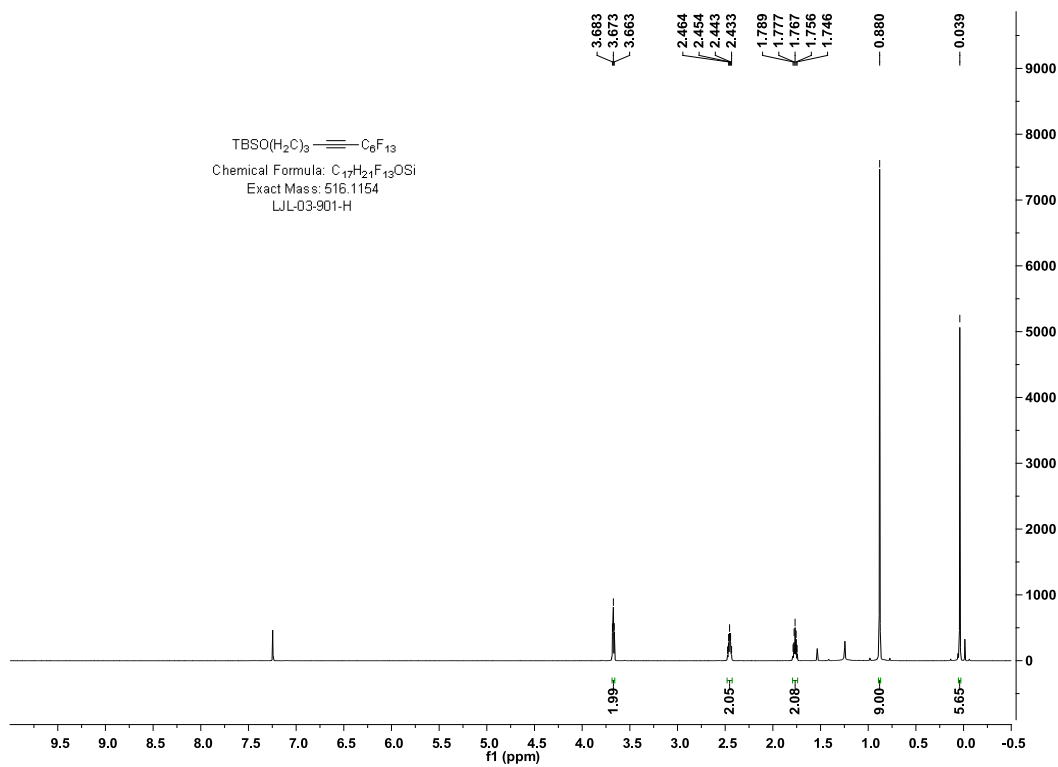


**<sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)**

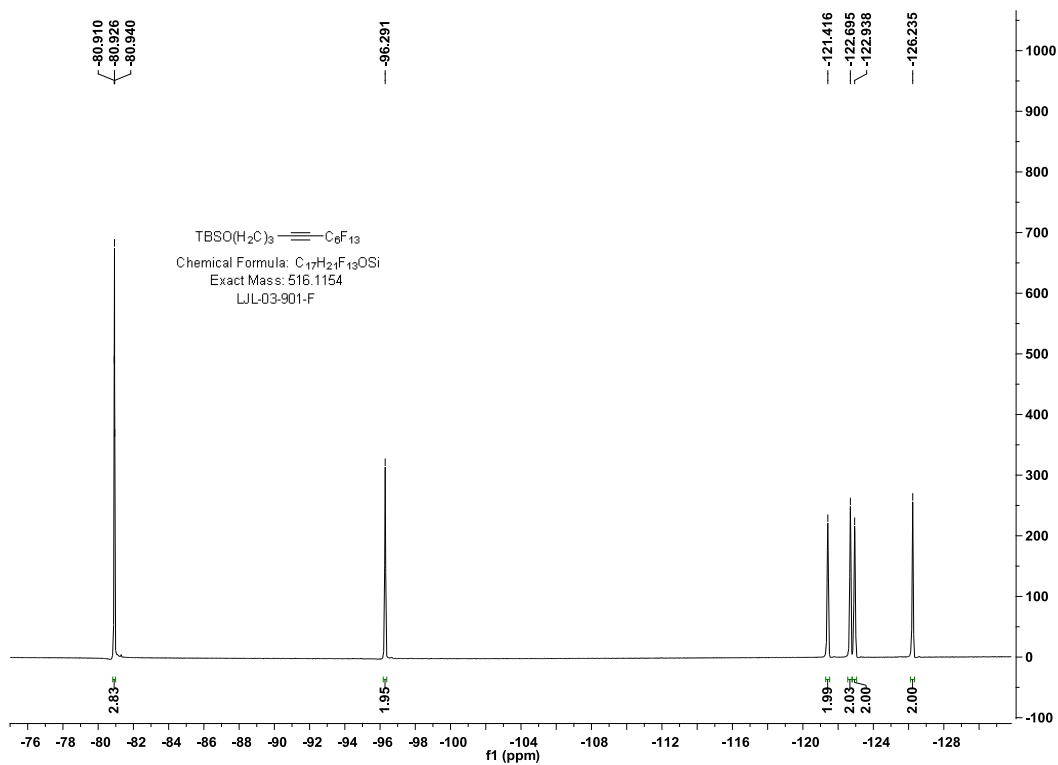


**tert-Butyldimethyl((6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundec-4-yn-1-yl)oxy)silane (7m)**

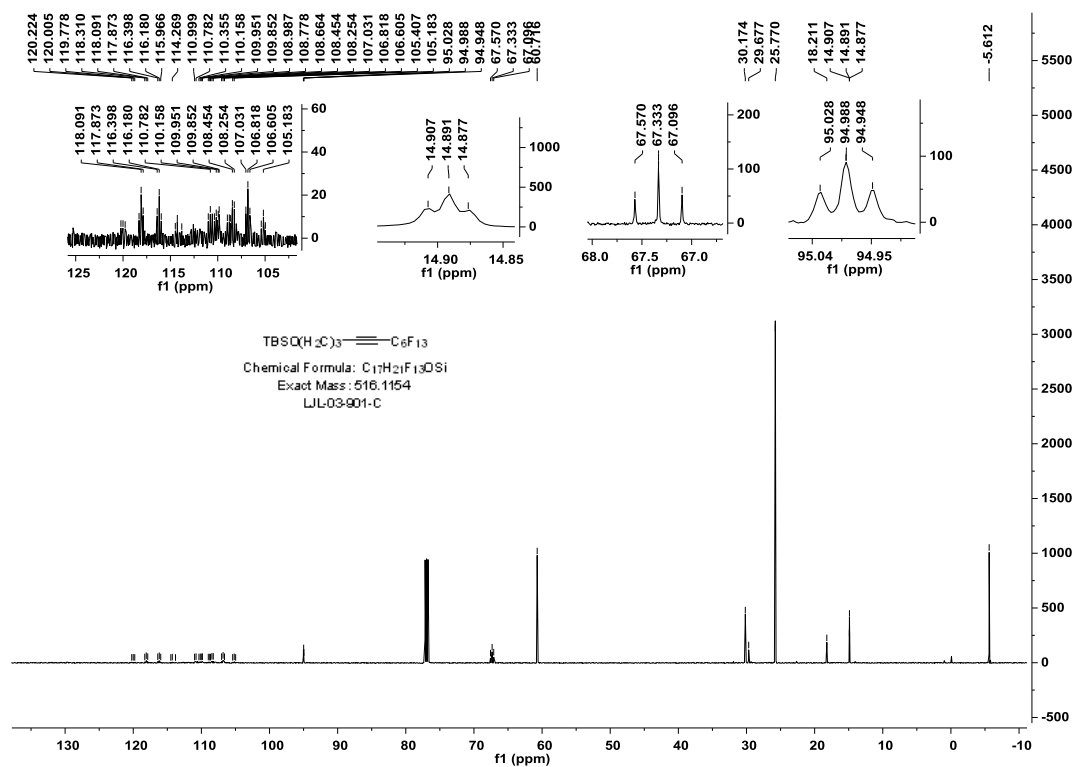
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**



**<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>)**

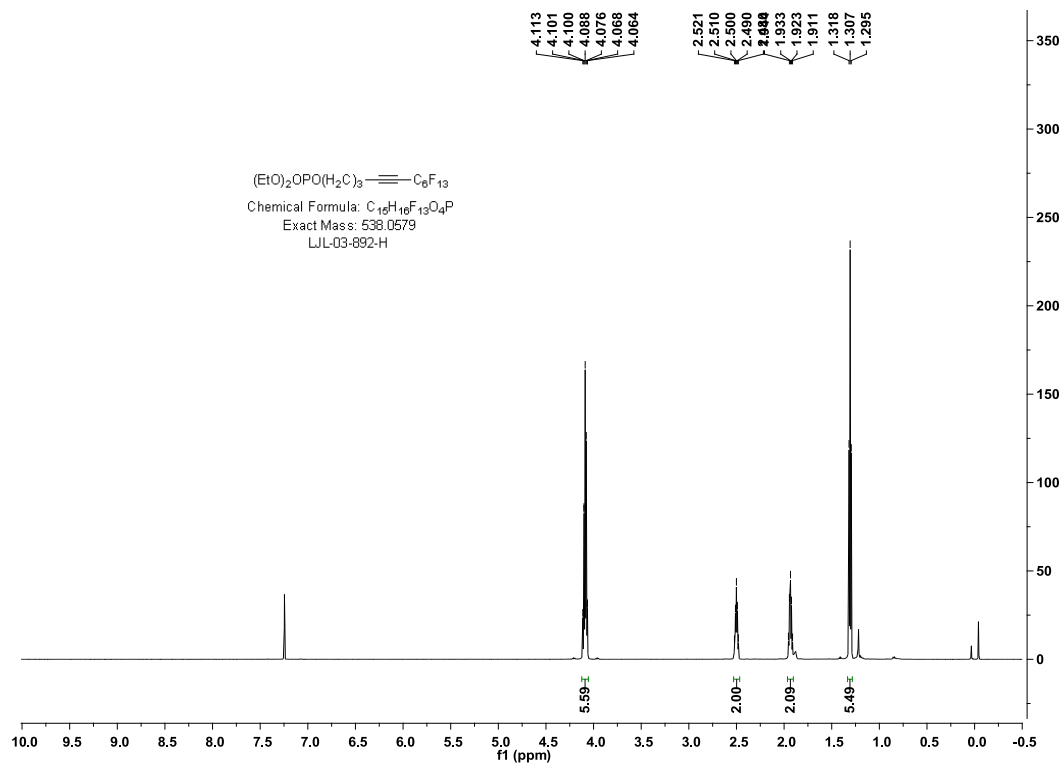


### $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

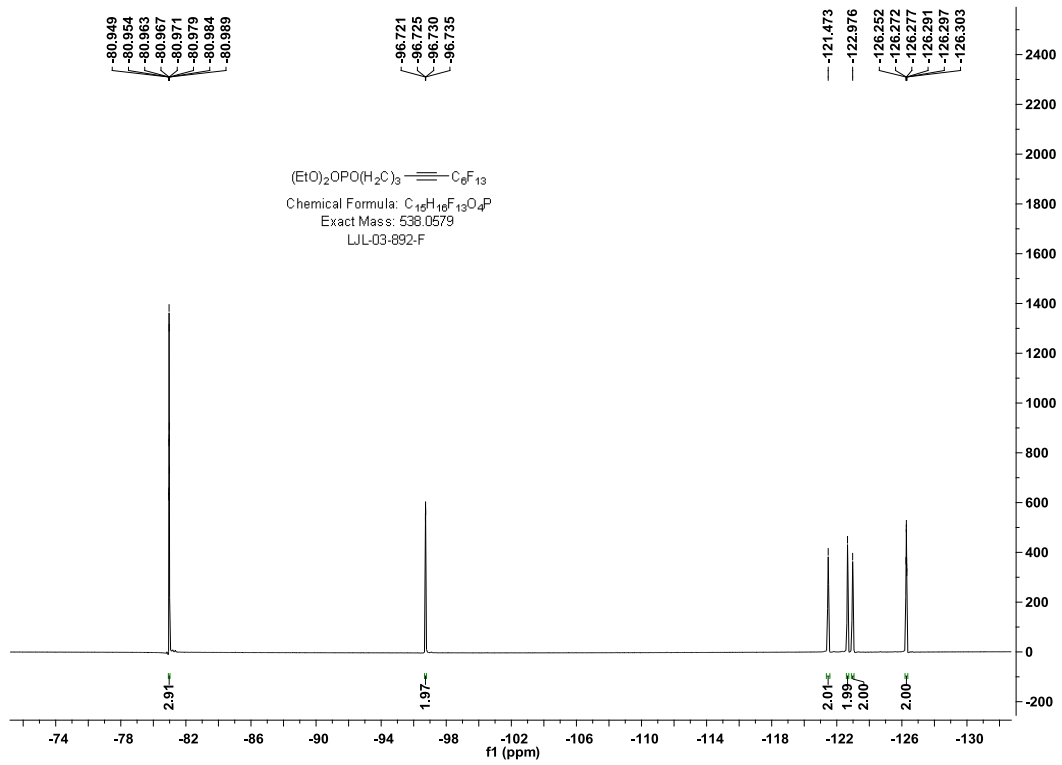


### Diethyl (6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoroundec-4-yn-1-yl) phosphate (7q)

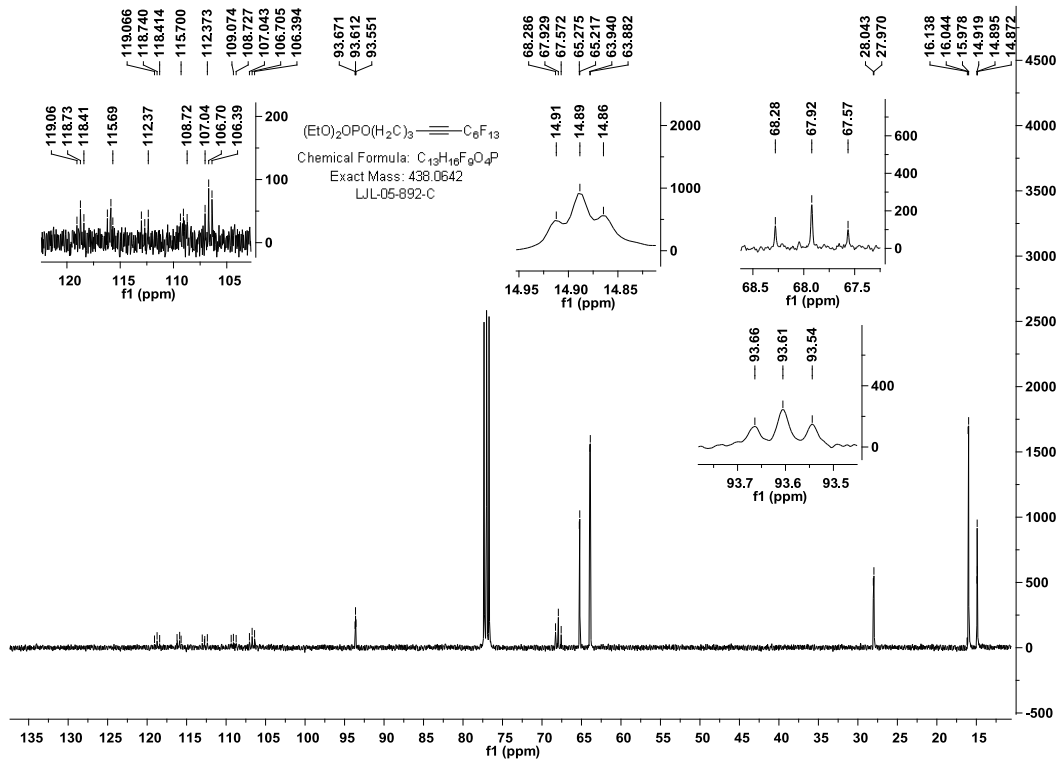
### $^1\text{H}$ NMR (600 MHz, $\text{CDCl}_3$ )



# <sup>19</sup>F NMR (150.8 MHz, CDCl<sub>3</sub>)

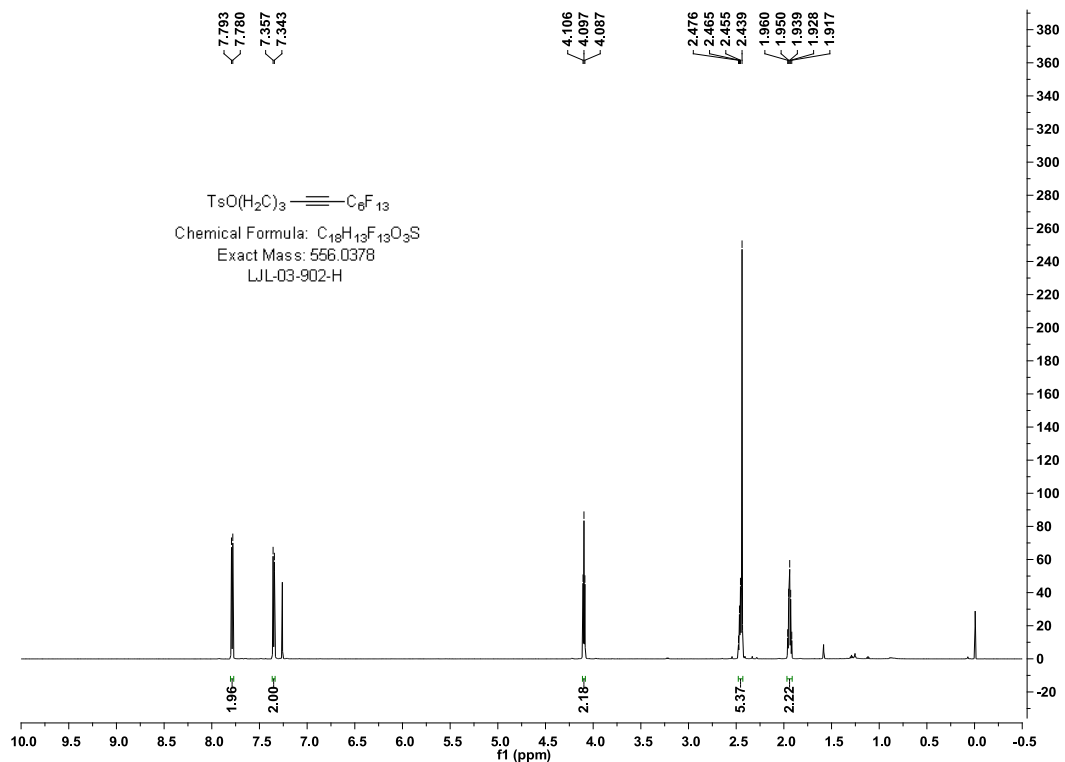


# <sup>13</sup>C NMR (150.8 MHz, CDCl<sub>3</sub>)

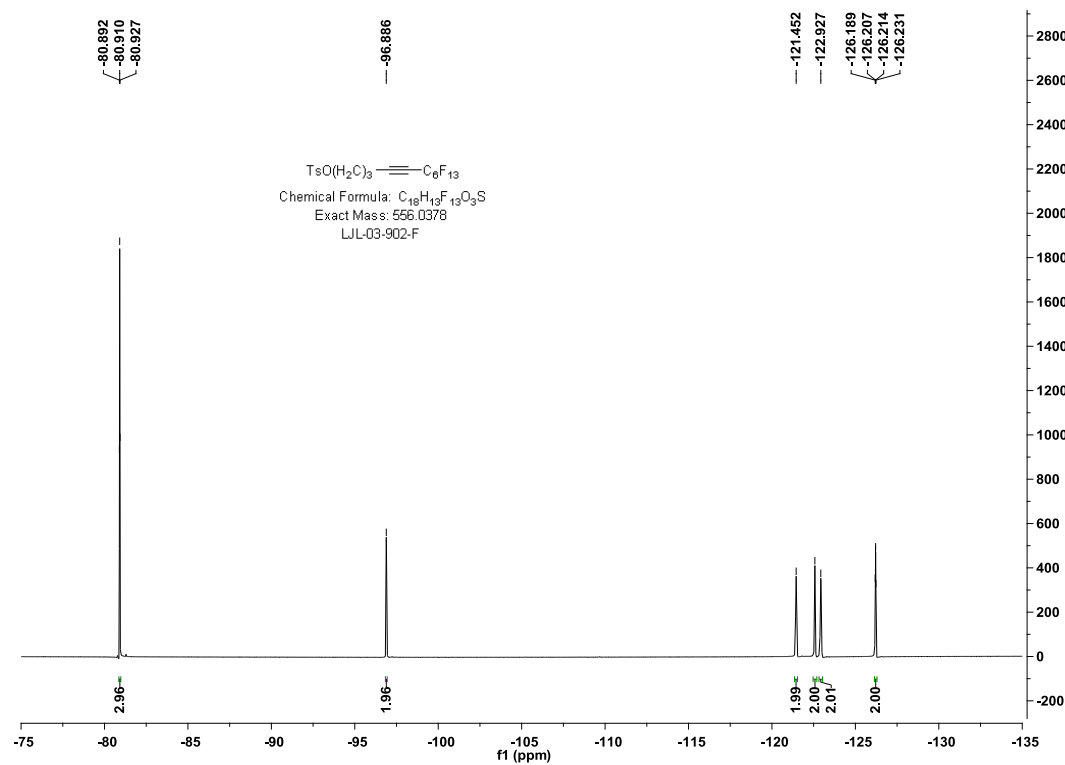


**6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundec-4-yn-1-yl-4-methylbenzenesulfonate (7r)**

**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )**



# $^{13}\text{C}$ NMR (150.8 MHz, $\text{CDCl}_3$ )

