Supplementary Information for

Chiral *gem*-Difluoroalkyl Reagent: *gem*-Difluoroalkyl Propargylic Boron and *gem*-Difluoroalkyl α-Allenols

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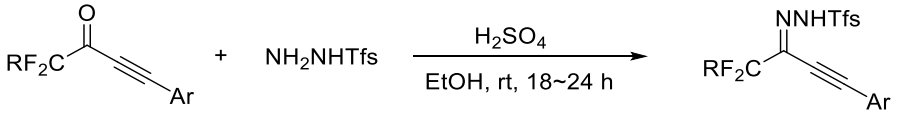
1. General Information

All reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified and dried using standard procedures.[1] All chiral dirhodium complexes were purchased from Strem or TCI and used as received. The borane adducts **2a** were purchased from J&K and used as received. The other borane adducts **2** were synthesized according to literature procedures.[2]

NMR spectra were recorded with a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 151 MHz (^{13}C NMR), 128 MHz (^{11}B NMR), 376 MHz (^{19}F NMR). Chemical shifts (δ values) were reported in ppm down field from internal Me_4Si (^{1}H and ^{13}C NMR). High Resolution Mass Spectra (HRMS) were recorded on an IonSpec FT-ICR mass spectrometer with Electron Spray Ionization (ESI) resource. Melting points were measured on a RY−I apparatus and uncorrected. Enantioselectivities were recorded on Agilent HPLC, using chiral stationary phase columns. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. As for the absolute structure, it was assigned by different methods including X-ray diffraction and circular dichroism. Circular dichroism spectra were measured on a circular dichroism spectrometer (MOS-500).

2. Preparation and Analytical Data of Substrates

2.1 Synthesis of *gem*-difluoroalkyl alkynyl *N*-triftosylhydrazones



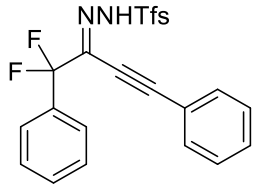
R = Aryl, Methyl

All *gem*-difluoroalkyl alkynyl *N*-triftosylhydrazones were prepared according to the literature.[3]

A 50 mL Schlenk bottle equipped with a magnetic stir bar was charged with 2-(trifluoromethyl)benzenesulfonic acid hydrazide (NH_2NHTfs, 1.1 equiv) and anhydrous ethanol (4 mL/mmol). Then, concentrated H_2SO_4 (0.2 mL) was added dropwise into the reaction system. After stirring at room temperature for additional 5 min, the solution became clear and then an ethanol solution (3–5 mL) of alkynyl ketone (1.0 equiv) was injected into the Schlenk bottle. The pale-yellow slurry was stirred at room temperature for 18–24 hours. The solid was isolated by suction filtration and washed with cold water and enthanol and then the white product was obtained.

2.2 Analytical data of *gem*-difluoroalkyl alkynyl *N*-triftosylhydrazones

N'-(1,1-difluoro-1,4-diphenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1a)



Serial number: zhn-6-38, 59% yield (1.14 g), white solid, melting point: 119–121 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.78 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.31 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.1, 134.1 (t, *J* = 36.4 Hz), 133.9 (t, *J* = 25.2 Hz), 133.7, 133.6, 132.4, 132.4, 131.0, 130.4 (t, *J* = 1.8 Hz), 128.8, 128.3 (q, *J* = 7.1 Hz), 128.2, 127.7 (q, *J* = 33.3 Hz), 125.8 (t, *J* = 5.9 Hz), 124.1 (t, *J* = 274.7 Hz), 119.4, 116.5 (t, *J* = 245.4 Hz), 107.1, 74.4.

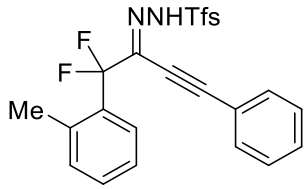
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.14, -95.51.

HRMS (ESI)

Calcd for $[C_{23}H_{16}F_5N_2O_2S, M + H]^+$: 479.0847, found: 479.0839.

N'-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1b)



Serial number: zjw-1-65, 92% yield (16.82 g), white solid, melting point: 132–134 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.82 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.38 (m, 6H), 7.35 – 7.29 (m, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.4 (t, *J* = 3.0 Hz), 136.1, 133.8 (t, *J* = 36.4 Hz) , 133.6, 132.5, 132.4, 132.0 (t, *J* = 23.2 Hz), 131.5, 131.0, 130.3, 128.8, 128.2 (q, *J* = 6.3 Hz), 127.6 (q, *J*

= 33.3 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 274.7 Hz), 119.5, 117.5 (t, *J* = 245.4 Hz), 107.0, 74.4, 19.7 (t, *J* = 2.7 Hz).

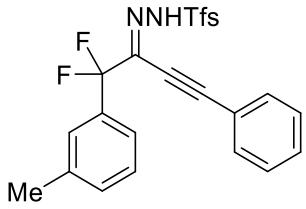
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.14, -93.57.

HRMS (ESI)

Calcd for $[C_{24}H_{18}F_5N_2O_2S, M + H]^+$: 493.1004, found: 493.0995.

_N_'-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1c)



Serial number: zhn-6-52, 54% yield (1.34 g), white solid, melting point: 97–99 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.80 (s, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.70 (dt, *J* = 28.3, 7.7 Hz, 2H), 7.58 – 7.35 (m, 5H), 7.28 – 7.11 (m, 4H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.0, 136.2, 134.0 (q, *J* = 31.1 Hz), 133.7, 133.5, 132.4, 132.4, 131.2, 131.0, 128.8, 128.3 (q, *J* = 6.6 Hz), 128.1, 127.7 (q, *J* = 33.3 Hz), 126.3 (t, *J* = 5.7 Hz), 123.0 (t, *J* = 5.9 Hz), 122.7 (q, *J* = 272.7 Hz), 119.5, 116.5 (t, *J* = 245.4 Hz), 107.0, 74.5, 21.4.

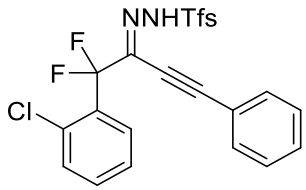
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.10, -95.50.

HRMS (ESI)

Calcd for $[C_{24}H_{18}F_5N_2O_2S, M + H]^+$: 493.1004, found: 493.0995.

_N_'-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1d)



Serial number: hml-1-41, 45% yield (0.69 g), white solid, melting point: 124–127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.88 (s, 1H), 7.89 (dd, *J* = 18.5, 7.9 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.65 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.60 – 7.28 (m, 8H), 7.14 (d, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.3, 133.7, 133.5, 133.5 (t, *J* = 35.4 Hz), 132.5, 132.4, 132.4, 131.9 (t, *J* = 24.8 Hz), 131.5, 131.0, 130.5, 128.8, 128.3 (q, *J* = 6.1 Hz), 128.1 (t, *J* = 8.1 Hz), 127.8 (q, *J* = 32.3 Hz), 126.5, 122.8 (q, *J* = 274.7 Hz), 119.5, 116.0 (t, *J* = 243.5 Hz), 107.1, 74.2.

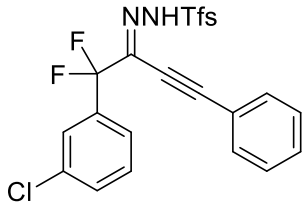
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.18, -93.87.

HRMS (ESI)

Calcd for $[C_{23}H_{15}ClF_5N_2O_2S, M + H]^+$: 513.0457, found: 513.0452.

_N_'-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1e)



Serial number: zjw-1-88, 37% yield (0.58 g), white solid, melting point: 109–110 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.80 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.57 – 7.40 (m, 6H), 7.35 – 7.27 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.0, 135.7 (t, *J* = 27.3Hz), 134.2, 133.8, 133.5, 133.5, 133.1, 132.5, 132.4, 131.1, 130.6, 129.6, 128.8, 128.3 (q, *J* = 6.4 Hz), 127.7 (q, *J* = 33.5 Hz), 126.2 (t, *J* = 6.0 Hz), 124.2 (t, *J* = 5.6 Hz), 122.7 (q, *J* = 273.7 Hz), 119.3, 116.0 (t, *J* = 245.2 Hz), 107.4, 74.1.

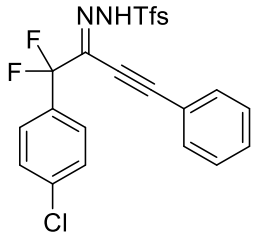
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.15, -95.30.

HRMS (ESI)

Calcd for $[C_{23}H_{15}ClF_5N_2O_2S, M + H]^+$: 513.0457, found: 513.0450.

_N_'-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1f)



Serial number: hml-1-43, 54% yield (0.84 g), white solid, melting point: 118–121 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.76 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.68 (t, *J* = 6.9 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.30 (m, 5H), 7.28 – 7.18 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.6, 136.0, 133.8, 133.6 (t, *J* = 37.4 Hz), 133.5, 132.5 (t, *J* = 27.3 Hz), 132.4, 131.1, 128.8, 128.5, 128.3 (q, *J* = 6.1 Hz), 127.7 (q, *J* = 32.3 Hz), 127.4 (t, *J* = 5.9 Hz), 122.7 (q, *J* = 274.7 Hz), 119.3, 116.3 (t, *J* = 246.4 Hz), 107.4, 74.1.

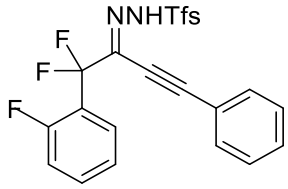
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.14, -95.22.

HRMS (ESI)

Calcd for $[C_{23}H_{15}ClF_5N_2O_2S, M + H]^+$: 513.0457, found: 513.0452.

_N_'-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1g)



Serial number: zhn-6-84, 34% yield (510 mg), white solid, melting point: 95–97 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.85 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.66 – 7.35 (m, 8H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 10.5, 8.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 159.7 (dt, *J* = 253.0, 4.2 Hz), 136.0 (d, *J* = 1.4 Hz), 133.7, 133.4, 133.2 (t, *J* = 36.7 Hz), 132.6 (dt, *J* = 8.2, 1.5 Hz), 132.4, 132.3, 131.0, 128.8, 128.3 (q, *J* = 6.3 Hz), 127.7 (q, 32.3 Hz), 127.5 (td, *J* = 6.9, 2.1 Hz), 123.8 (d, *J* = 3.6 Hz),

122.7 (q, *J* = 274.7 Hz), 121.5 (td, *J* = 38.4, 12.1 Hz), 119.5, 116.0, 115.8, 115.7 (td, *J* = 242.9, 1.4 Hz), 107.0, 74.0.

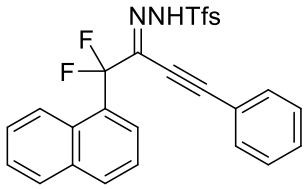
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.21, -93.57 (d, *J* = 10.2 Hz), -112.38 (t, *J* = 10.2 Hz).

HRMS (ESI)

Calcd for $[C_{23}H_{15}F_6N_2O_2S, M + H]^+$: 497.0753, found: 497.0754.

_N_'-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1h)



Serial number: zjw-1-94, 73% yield (1.13 g), white solid, melting point: 157–159 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.83 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.80 (dd, *J* = 13.0, 7.8 Hz, 2H), 7.72 – 7.65 (m, 3H), 7.56 – 7.36 (m, 8H), 7.27 (t, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 135.7, 134.0 (t, *J* = 36.4 Hz), 133.7, 133.5, 133.1, 132.4, 132.0, 131.5, 131.0, 129.5 (t, *J* = 23.6 Hz), 129.5 (t, *J* = 2.3 Hz), 128.8, 128.6, 127.9 (q, *J* = 6.4 Hz), 127.3 (q, *J* = 32.9 Hz), 126.7, 125.8, 125.3 (t, *J* = 8.8 Hz), 124.7 (t, *J* = 3.0 Hz), 124.4, 122.7 (q, *J* = 273.9 Hz), 119.5, 117.5 (t, *J* = 245.2 Hz), 107.3, 74.5.

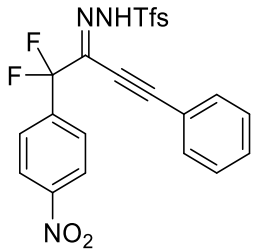
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.19, -91.51.

HRMS (ESI)

Calcd for $[C_{27}H_{18}F_5N_2O_2S, M + H]^+$: 529.1004, found: 529.1002.

_N_'-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1i)



Serial number: zhn-6-39, 66% yield (347 mg), white solid, melting point: 151–152 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.84 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.65 (td, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.49 (m, 5H), 7.46 – 7.42 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 149.1, 140.1 (t, *J* = 26.5 Hz), 136.0, 133.9, 133.3, 132.8 (t, *J* = 36.4 Hz), 132.4, 132.4, 131.3, 128.9, 128.5 (q, *J* = 6.4 Hz), 127.8 (q, *J* = 33.3 Hz), 127.3 (t, *J* = 5.8 Hz), 123.3, 122.6 (q, *J* = 274.7 Hz), 119.1, 115.9 (t, *J* = 246.4 Hz), 107.8, 73.7.

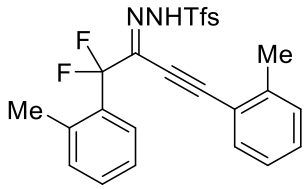
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.20, -95.65.

HRMS (ESI)

Calcd for $[C_{23}H_{15}F_5N_3O_4S, M + H]^+$: 524. 0698, found: 524. 0691.

_N_'-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1j)



Serial number: zhn-6-145, 94% yield (2.01 g), white solid, melting point: 156–157 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.78 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.40 – 7.30 (m, 2H), 7.28 – 7.18 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H), 2.40 (s, 3H), 1.96 (t, *J* = 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 141.3, 136.4 (t, *J* = 3.2 Hz), 136.2, 133.9 (t, *J* = 36.1 Hz), 133.7, 133.6, 132.9, 132.5, 132.1 (t, *J* = 23.7 Hz), 131.5, 131.1, 130.3, 129.9, 128.2 (q, *J* = 6.3 Hz), 127.7 (q, *J* = 33.3 Hz), 126.4 (t, *J* = 8.5 Hz), 126.1, 125.5, 122.7 (q, *J* = 273.9 Hz), 119.4, 117.4 (t, *J* = 244.4 Hz), 106.1, 78.3, 20.6, 19.6 (t, *J* = 2.6 Hz).

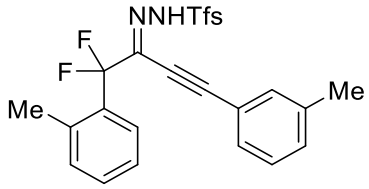
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.14, -93.87.

HRMS (ESI)

Calcd for $[C_{25}H_{20}F_5N_2O_2S, M + H]^+$: 507.1160, found: 507.1160.

***N*'-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1k)**



Serial number: zhn-6-82, 79% yield (1.40 g), white solid, melting point: 146–148 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.80 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 2.37 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.7, 136.5 (t, *J* = 3.1 Hz), 136.2, 133.9 (t, *J* = 30.3 Hz), 133.7, 133.6, 132.9, 132.5, 132.1(t, *J* = 23.6 Hz), 131.9, 131.4, 130.3, 129.6, 128.7, 128.2 (q, *J* = 6.3 Hz), 127.7 (q, *J* = 33.0 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 274.0 Hz), 119.3, 117.5 (t, *J* = 244.0 Hz), 107.3, 74.1, 21.2, 19.7 (t, *J* = 2.5 Hz).

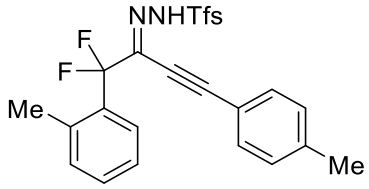
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.18, -93.57.

HRMS (ESI)

Calcd for $[C_{25}H_{20}F_5N_2O_2S, M + H]^+$: 507.1160, found: 507.1162.

***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1l)**



Serial number: zhn-6-83, 92% yield (1.63 g), white solid, melting point: 164–166 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.79 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.37 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 2.40 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 141.7, 136.5 (t, *J* = 3.0 Hz), 136.2, 134.0 (t, *J* = 36.5 Hz), 133.7, 133.5, 132.5, 132.4, 132.1 (t, *J* = 23.7 Hz), 131.4, 130.2, 129.6, 128.1 (q, *J* = 6.4 Hz), 127.7 (q, *J* = 33.3 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 273.9 Hz), 117.5 (t, *J* = 233.3 Hz), 116.4, 107.5, 74.1, 21.8, 19.7 (t, *J* = 2.7 Hz).

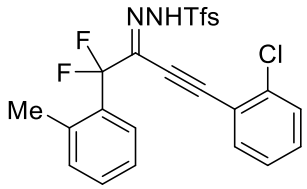
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.18, -93.60.

HRMS (ESI)

Calcd for $[C_{25}H_{20}F_5N_2O_2S, M + H]^+$: 507.1160, found: 507.1165.

_N_'-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1m)



Serial number: zhn-6-89, 89% yield (1.41 g), white solid, melting point: 150–152 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 9.14 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.72 (t, *J* = 6.8 Hz, 1H), 7.62 – 7.27 (m, 7H), 7.25 – 7.16 (m, 1H), 7.08 (d, *J* = 6.8 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.8, 136.5 (t, *J* = 2.3 Hz), 136.2, 133.7, 133.6, 132.7 (t, *J* = 36.7 Hz), 132.4, 132.0, 131.9 (t, *J* = 23.6 Hz), 131.5, 130.3, 129.6, 128.1 (q, *J* = 6.0 Hz), 127.8 (q, *J* = 33.4 Hz), 126.9, 126.4 (t, *J* = 8.6 Hz), 125.5, 122.6 (q, *J* = 273.9 Hz), 120.0, 117.5 (t, *J* = 244.0 Hz), 103.3, 79.6, 19.7.

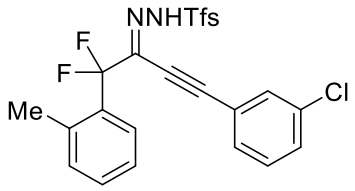
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.05, -93.37.

HRMS (ESI)

Calcd for $[C_{24}H_{17}ClF_5N_2O_2S, M + H]^+$: 527.0614, found: 527.0611.

_N_'-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1n)



Serial number: zhn-6-88, 87% yield (1.17 g), white solid, melting point: 147–150 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.82 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 1.8 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.41 – 7.32 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.4 (t, *J* = 3.1 Hz), 136.0, 134.8, 133.7, 133.7, 133.1 (t, *J* = 36.7 Hz), 132.5, 132.1, 131.9 (t, *J* = 23.6 Hz), 131.5, 131.2, 130.5, 130.4, 130.1, 128.2 (q, *J* = 6.2 Hz), 127.7 (q, *J* = 33.3 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 274.1 Hz), 121.1, 117.5 (t, *J* = 243.9 Hz), 104.9, 75.1, 19.7 (t, *J* = 2.7 Hz).

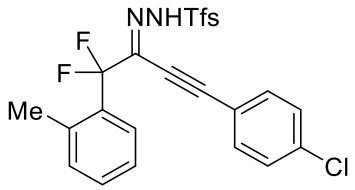
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.17, -93.48.

HRMS (ESI)

Calcd for $[C_{24}H_{17}ClF_5N_2O_2S, M + H]^+$: 527.0614, found: 527.0610.

_N_'-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1o)



Serial number: zhn-6-87, 92% yield (1.46 g), white solid, melting point: 187–189 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.78 (s, 1H), 8.03 – 7.29 (m, 10H), 7.28 – 7.00 (m, 2H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 137.4, 136.5, 136.1, 133.7, 133.6, 133.6, 133.4 (t, *J* = 36.6 Hz), 132.5, 131.9 (t, *J* = 24.1 Hz), 131.5, 130.3, 129.3, 128.2 (q, *J* = 6.9 Hz), 127.7 (q, *J* = 32.8 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 275.1 Hz), 117.9, 117.5 (t, *J* = 243.1 Hz), 105.5, 75.2, 19.7.

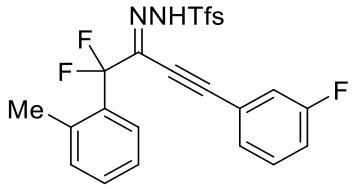
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.17, -93.48.

HRMS (ESI)

Calcd for $[C_{24}H_{17}ClF_5N_2O_2S, M + H]^+$: 527.0614, found: 527.0610.

_N_'-1,1-difluoro-4-(3-fluorophenyl)-1-(_o_-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1p)



Serial number: zhn-6-191, 82% yield (1.45 g), white solid, melting point: 146–148 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.80 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.30 (m, 4H), 7.25 – 7.15 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 163.5, 161.0, 136.4 (t, *J* = 2.8 Hz), 136.0, 133.7, 133.2 (t, *J* = 36.8 Hz), 132.5, 131.9 (t, *J* = 23.6 Hz), 131.5, 130.6 (d, *J* = 8.5 Hz), 130.4, 128.4, 128.4, 128.2 (q, *J* = 6.1 Hz), 127.7 (q, *J* = 33.2 Hz), 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 274.2 Hz), 121.2 (d, *J* = 9.2 Hz), 119.1 (d, *J* = 23.6 Hz), 118.5 (d, *J* = 21.0 Hz), 117.5 (t, *J* = 243.7 Hz), 105.0 (d, *J* = 3.6 Hz), 74.9, 19.7.

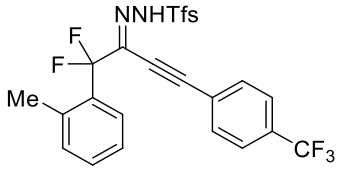
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.18, -93.52, -111.24.

HRMS (ESI)

Calcd for $[C_{24}H_{17}F_6N_2O_2S, M + H]^+$: 511.0909, found: 511.0907.

_N_'-(1,1-difluoro-1-(_o_-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazide (1q)



Serial number: zhn-8-45, 88% yield (702 mg), white solid, melting point: 179–182 ℃.

^{1}H NMR (400 MHz, THF-d_8)

δ 11.24 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.87 – 7.79 (m, 6H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (151 MHz, THF-d_8)

δ 136.9, 136.5 (t, *J* = 3.2 Hz), 133.6, 133.5, 132.7, 132.5, 132.4 (t, *J* = 23.5 Hz), 131.5 (t, *J* = 30.2 Hz), 131.4, 130.1, 130.0 (t, *J* = 36.9 Hz), 127.9 (q, *J* = 6.4 Hz), 127.3 (q, *J* = 33.3 Hz), 126.0 (t, *J* = 8.4 Hz), 125.5 (q, *J* = 3.7 Hz), 125.3, 124.6, 123.9 (q, *J* = 271.8 Hz), 122.8 (q, *J* = 286.9 Hz), 118.3 (t, *J* = 242.7 Hz), 102.0, 77.3, 19.1 (t, *J* = 2.5 Hz).

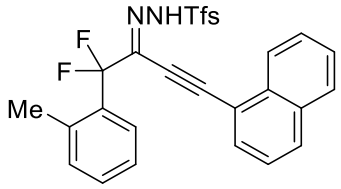
^{19}F NMR (376 MHz, THF-d_8)

δ -60.40, -65.71, -95.34.

HRMS (ESI)

Calcd for $[C_{25}H_{17}F_8N_2O_2S, M + H]^+$: 561.0878, found: 561.0876.

_N_'-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1r)



Serial number: zhn-6-189, 85% yield (2.01 g), white solid, melting point: 201–203 ℃.

^{1}H NMR (400 MHz, THF-d_6)

δ 11.10 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.06 – 7.84 (m, 5H), 7.79 (t, *J* = 7.9 Hz, 1H), 7.69 – 7.47 (m, 5H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, THF-d_6)

135.3,134.7 (t, *J* = 3.2 Hz), 131.7, 131.5, 131.3, 131.1, 130.7 (q, *J* = 23.2 Hz), 130.6, 130.3, 129.6, 129.2, 128.2, 126.5, 126.0 (q, *J* = 6.4 Hz), 125.6, 125.5 (q, *J* = 33.3 Hz), 124.9, 124.2 (t, *J* = 8.6 Hz), 123.5, 123.5, 123.2, 121.0 (q, *J* = 273.9 Hz), 116.4 (t, *J* = 243.4 Hz), 116.0, 100.7, 78.4, 17.2 (t, *J* = 2.5 Hz).

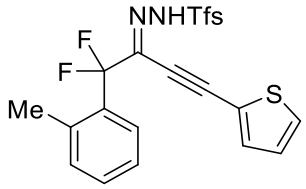
^{19}F NMR (376 MHz, THF-d_6)

δ -60.34, -95.55.

HRMS (ESI)

Calcd for $[C_{28}H_{20}F_5N_2O_2S, M + H]^+$: 543.1160, found: 543.1159.

_N_'-(1,1-difluoro-4-(thiophen-2-yl)-1-(_o_-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1s)



Serial number: zhn-6-90, 78% yield (1.17 g), white solid, melting point: 129–131 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.78 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.24 – 7.15 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.5 (t, *J* = 3.0 Hz), 136.1, 133.8 (t, *J* = 36.7 Hz), 133.7, 133.6, 133.1, 132.5, 132.0 (t, *J* = 23.6 Hz), 131.4, 130.3, 129.7, 128.2 (q, *J* = 6.5 Hz), 127.6 (q, *J* = 33.2 Hz), 126.6, 126.4 (t, *J* = 8.5 Hz), 125.5, 122.7 (q, *J* = 273.9 Hz), 118.6, 117.5 (t, *J* = 244.1 Hz), 102.1, 74.5, 19.7 (t, *J* = 2.5 Hz).

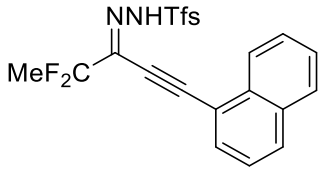
^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.15, -93.44.

HRMS (ESI)

Calcd for $[C_{22}H_{16}F_5N_2O_2S_2, M + H]^+$: 499.0568, found: 499.0564.

_N_'-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1t)



Serial number: zhn-7-123, 82% yield (306 mg), yellow solid, melting point: 106–108 ℃.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.94 (s, 1H), 8.42 – 8.36 (m, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.87 – 7.74 (m, 3H), 7.69 – 7.48 (m, 3H), 1.83 (t, *J* = 18.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.4, 133.9, 133.8 (t, *J* = 35.8 Hz), 133.2, 133.1, 132.9, 132.6, 132.5, 131.8, 128.7, 128.6 (q, *J* = 6.3 Hz), 128.0, 127.9 (q, *J* = 33.2 Hz), 127.1, 125.4, 125.2, 122.8 (q, *J* = 274.0 Hz), 118.6 (t, *J* = 238.0 Hz), 117.1, 105.2, 78.6, 21.4 (t, *J* = 25.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

δ -58.07, -89.13.

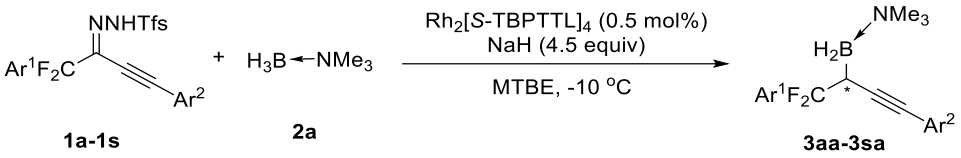
HRMS (ESI)

Calcd for $[C_{22}H_{15}F_5N_2O_2SNa, M+Na]^+$: 489.0667, found: 489.0667.

3. Procedures for B−H Bond Insertion Reaction

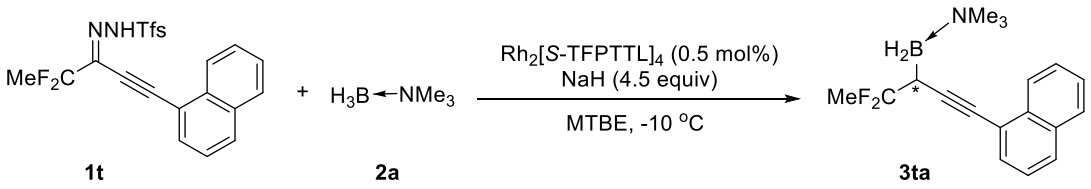
3.1 Typical procedures

Procedure A:



gem-Difluoroalkyl alkynyl *N*-triftosylhydrazones **1a** (71.7 mg, 0.15 mmol, 1.5 equiv), trimethylamine borane adduct **2a** (7.3 mg, 0.1 mmol), Rh_2(*S*-TBPTTL)$_4$ (**4d**, 1.3 mg, 0.0005 mmol, 0.5 mol%), and NaH (10.8 mg, 0.45 mmol, 4.5 equiv) were charged into a 25 mL Schlenk tube under argon atmosphere. After the mixture was cooled to −10 ℃, 2.5 mL dry MTBE was injected into the tube. At this temperature, the reaction was kept stirring for 24 h. Then the reaction system was concentrated and purified by a flash chromatography on silica gel to give **3aa** as light yellow oil (30.9 mg, 99% yield, 93% ee). Serial number: zhn-6-36.

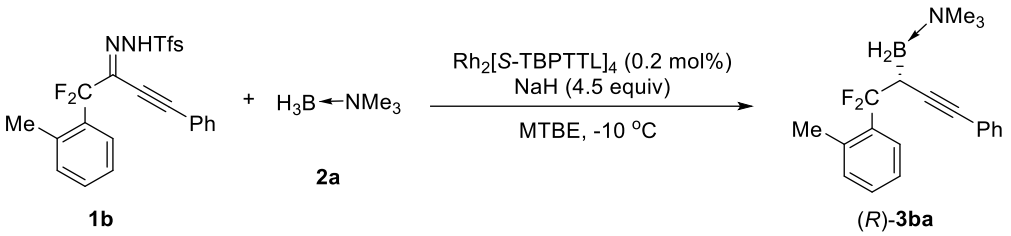
Procedure B:



gem-Difluoroalkyl alkynyl *N*-triftosylhydrazones **1t** (69.9 mg, 0.15 mmol, 1.5 equiv), trimethylamine borane adduct **2a** (7.3 mg, 0.1 mmol), Rh_2(*S*-TFPTTL)$_4$ (**4b**, 0.8 mg, 0.0005 mmol, 0.5 mol%), and NaH (10.8 mg, 0.45 mmol, 4.5 equiv) were charged into a 25 mL Schlenk tube under argon atmosphere. After the mixture was cooled to −10 ℃, 2.5 mL dry MTBE was injected into the tube. At this temperature, the reaction

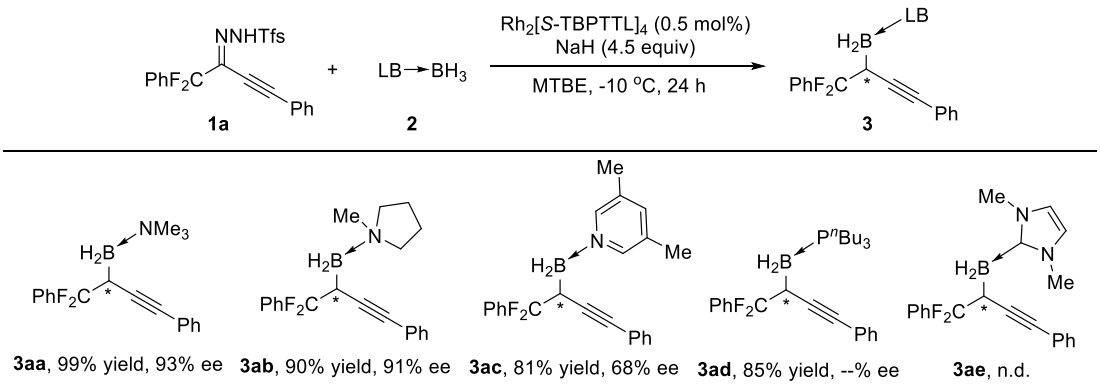
was kept stirring for 24 h. Then the reaction system was concentrated and purified by a flash chromatography on silica gel to give **3ta** as yellow oil (26.0 mg, 86% yield, 73% ee). Serial number: zhn-7-129.

3.2 Gram-scale experiment



gem-Difluoroalkyl alkynyl *N*-triftosylhydrazones **1b** (2.58 g, 5.24 mmol, 1.5 equiv), trimethylamine borane adduct **2a** (256 mg, 3.50 mmol, 1.0 equiv), and NaH (378 mg, 15.75 mmol, 4.5 equiv) were charged into an oven-dried 200 mL Schlenk tube under argon atmosphere. After the mixture was cooled to -10 °C, 75 mL dry MTBE was injected into the Schlenk tube by syringe. Rh_2(*S*-TBPTTL)$_4$ (**4d**, 18.7 mg, 0.007 mmol, 0.2 mol%) dissolved in 5 mL dry MTBE were injected into the Schlenk tube by a syringe. At this temperature, the reaction was kept stirring for 40 h. Then the reaction system was concentrated and purified by a flash chromatography on silica gel to give (*R*)-**3ba** as light yellow soild (0.87 g, 76% yield, 96% ee). Serial number: zhn-6-155.

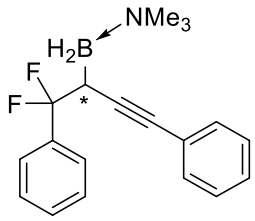
4. Scope of Borane Adducts



Note: due to the small polarity of **3ad**, the ee value is difficult to measure.

5. Analytical Data of B-H Bond Insertion Products

(-)-Trimethylamine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3aa)



Serial number: zhn-6-36, Light yellow oil, 99% yield (30.9 mg), 93% ee. $[\alpha]_D^{24}$ -41.6 (*c* 1.0, $CHCl_3$). TLC R_f = 0.50 (PE/EA = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.68 – 7.59 (m, 2H), 7.43 – 7.29 (m, 5H), 7.29 – 7.16 (m, 3H), 2.80 – 2.54 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.1 (t, *J* = 27.4 Hz), 131.2, 128.8, 128.1, 127.4, 127.1, 126.1 (t, *J* = 6.2 Hz), 124.7, 124.2 (t, *J* = 245.8 Hz), 93.5 (dd, *J* = 10.9, 5.5 Hz), 82.7, 52.7.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.98.

^{19}F NMR (376 MHz, $CDCl_3$)

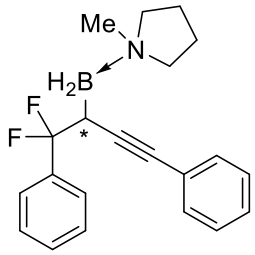
δ -86.63 (d, *J* = 231.7 Hz), -89.72 (d, *J* = 231.6 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{22}BF_2NK, M+K]^+$: 352.1445, found: 352.1449.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.22 min (major) and t_R = 7.56 min (minor).

(-)-1-methylpyrrolidine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ab)



Serial number: zhn-6-58, Colorless oil, 90% yield (30.7 mg), 91% ee. $[\alpha]_D^{24}$ -40.0 (*c* 0.5, $CHCl_3$). TLC R_f = 0.28 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.68 – 7.58 (m, 2H), 7.41 – 7.31 (m, 5H) 7.29 – 7.19 (m, 3H), 3.42 – 3.35 (m, 1H), 3.27 – 3.20 (m, 1H), 2.95 – 2.81 (m, 2H), 2.79 – 2.74 (m, 1H), 2.67 (s, 3H), 2.10 – 1.86 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.3 (t, *J* = 27.4 Hz), 131.2, 128.8 (t, *J* = 1.4 Hz), 128.1, 127.4, 127.0, 126.1 (t, *J* = 6.2 Hz), 124.9, 124.4 (t, *J* = 246.0 Hz), 82.5, 62.3, 61.8, 48.3, 22.7, 22.2.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -5.03 (t, *J* = 106.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

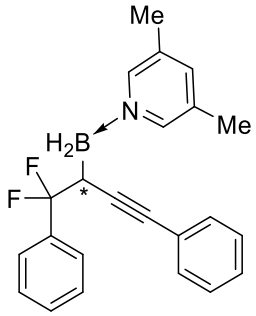
δ -87.22 (d, *J* = 231.8 Hz), -89.48 (d, *J* = 231.5 Hz).

HRMS (ESI)

Calcd for $[C_{21}H_{24}BF_2NK, M+K]^+$: 378.1601, found: 378.1605.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 7.61 min (major) and t_R = 9.23 min (minor).

(+)-3,5-dimethylpyridine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ac)



Serial number: hml-1-65, Light yellow oil, 81% yield (29.2 mg), 68% ee. $[\alpha]_D^{26}$ +4.0 (*c* 0.5, $CHCl_3$). TLC R_f = 0.70 (PE/EA = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.25 (s, 2H), 7.64 – 7.58 (m, 2H), 7.54 (s, 1H), 7.41 – 7.34 (m, 3H), 7.21 (s, 5H), 2.96 – 2.83 (m, 1H), 2.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 145.4, 141.3, 138.7 (t, *J* = 27.5 Hz), 134.7, 131.1, 128.9, 128.0, 127.6, 127.0, 125.8 (t, *J* = 6.2 Hz), 124.7, 124.5 (t, *J* = 245.0 Hz), 92.3 (dd, *J* = 8.0 Hz), 83.8, 18.3.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -6.54.

^{19}F NMR (376 MHz, $CDCl_3$)

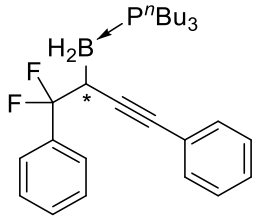
δ -58.24, -89.67.

HRMS (ESI)

Calcd for $[C_{23}H_{22}BF_2NK, M+K]^+$: 400.1445, found: 400.1447.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.64 min (minor) and t_R = 9.20 min (major).

(-)-tributylphosphane-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ad)



Serial number: zhn-6-61, Light yellow oil, 85% yield (38.9 mg), --% ee. $[\alpha]_D^{24}$ -55.0 (*c* 1.0, $CHCl_3$). TLC R_f = 0.65 (PE/EA = 50:1, v/v). Note: due to the small polarity of **3ad**, the ee value is difficult to measure.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.56 – 7.54 (m, 2H), 7.31 – 7.29 (m, 3H), 7.23 – 7.21 (m, 2H), 7.17 – 7.13 (m, 3H), 2.77 – 2.63 (m, 1H), 1.61 – 1.55 (m, 6H), 1.40 – 1.30 (m, 6H), 1.28 – 1.18 (m, 6H), 0.79 (t, *J* = 7.2 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.1 (t, *J* = 27.6 Hz), 131.1, 128.8, 128.1, 127.4, 127.0, 126.2 (t, *J* = 6.2 Hz), 124.7, 124.5 (t, *J* = 229.3 Hz), 93.6 – 93.3 (m), 82.1, 24.5, 24.5, 24.5, 24.4, 21.2, 20.8, 13.6.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -29.27 (t, *J* = 89.2 Hz).

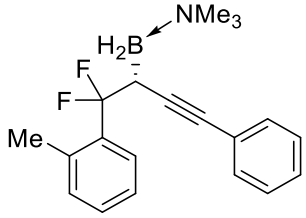
^{19}F NMR (376 MHz, $CDCl_3$)

-90.51, 90.56.

HRMS (ESI)

Calcd for $[C_{28}H_{40}BF_2PK, M+K]^+$: 495.2560, found: 495.2563.

(+)-(*R*)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ba)



Serial number: zhn-6-67, Yellow oil, 99% yield (32.4 mg), 99% ee. $[\alpha]_D^{25}$ +18.0 (*c* 1.0, $CHCl_3$). TLC R_f = 0.29 (PE/EA = 5:1, v/v). The absolute configuration of (*R*)-**3ba** was inferred from (*R*)-**3fa**.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.62 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.27 – 7.14 (m, 6H), 2.84 – 2.71 (m, 1H), 2.68 (s, 9H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.5 (t, *J* = 25.7 Hz), 135.5, 131.5, 131.3, 128.8, 128.1, 127.7 (t, *J* = 8.3 Hz), 127.1, 125.5 (t, *J* = 252.5 Hz), 124.8, 93.5 (t, *J* = 7.0 Hz), 82.6, 52.7, 20.9 (t, *J* = 4.0 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -4.12.

^{19}F NMR (376 MHz, $CDCl_3$)

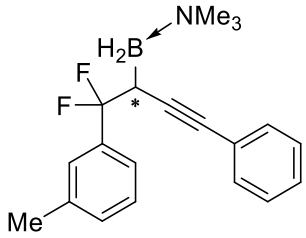
δ -85.27 (d, *J* = 240.3 Hz), -88.31 (d, *J* = 240.3 Hz).

HRMS (ESI)

Calcd for $[C_{20}H_{24}BF_2NK, M+K]^+$: 366.1601, found: 366.1604.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.30 min (major) and t_R = 7.09 min (minor).

(-)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-yl)borane (3ca)



Serial number: zhn-6-66, Yellow oil, 99% yield (32.5 mg), 89% ee. $[\alpha]_D^{25}$ -30.1 (*c* 1.0, $CHCl_3$). TLC R_f = 0.29 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.47 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.21 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.67 (s, 9H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 138.1 (t, *J* = 27.2 Hz), 136.9, 131.2, 129.6, 128.1, 127.3, 127.1, 126.8 (t, *J* = 6.2 Hz), 124.8, 124.3 (t, *J* = 242.4 Hz), 123.2 (t, *J* = 6.2 Hz), 93.7 (dd, *J* = 10.2, 6.0 Hz), 82.8, 52.8, 21.6.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.68 (t, J = 105.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

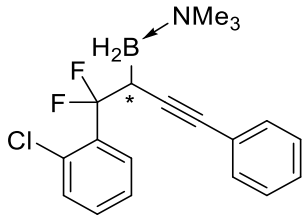
δ -86.56 (d, J = 231.4 Hz), -89.56 (d, J = 231.1 Hz).

HRMS (ESI)

Calcd for $[C_{20}H_{24}BF_2NNa, M+Na]^+$: 350.1862, found: 350.1871.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.24 min (major) and t_R = 7.10 min (minor).

(+)-Trimethylamine-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3da)



Serial number: zhn-6-71, Yellow oil, 74% yield (25.6 mg), 92% ee. $[\alpha]_D^{25}$ +24.0 (*c* 0.5 $CHCl_3$). TLC R_f = 0.31 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.73 – 7.66 (m, 1H), 7.41 – 7.39 (m, 1H), 7.31 – 7.29 (m, 4H), 7.25 – 7.19 (m, 4H), 3.32 – 3.16 (m, 1H), 2.69 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 135.0 (t, J = 27.1 Hz), 130.3, 129.7, 129.1, 128.0 (t, J = 9.3 Hz), 127.0, 126.0, 125.0, 123.7, 122.4 (t, J = 247.3 Hz), 92.0 (dd, J = 7.6, 3.2 Hz), 81.5, 51.6.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.86.

^{19}F NMR (376 MHz, $CDCl_3$)

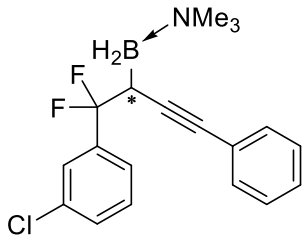
δ -87.70 (d, J = 240.5 Hz), -94.87 (d, J = 240.5 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{21}BClF_2NK, M+K]^+$: 386.1055, found: 386.1060.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 7.15 min (major) and t_R = 7,97 min (minor).

(-)-Trimethylamine-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3ea)



Serial number: zhn-6-74, Light yellow oil, 83% yield (28.7 mg), 87% ee. $[\alpha]_D^{25}$ -4.0 (*c* 0.5, $CHCl_3$). TLC R_f = 0.32 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.58 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.16 (m, 7H), 2.68 – 2.64 (m, 1H), 2.61 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 139.9 (t, *J* = 27.9 Hz), 133.4, 131.2, 129.0, 128.7, 128.1, 127.2, 126.7 (t, *J* = 6.4 Hz), 124.5, 124.4 (t, *J* = 6.2 Hz), 123.5 (t, *J* = 246.3 Hz), 93.0 (dd, *J* = 11.1, 5.6 Hz), 83.1, 52.8.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.85 (t, *J* = 109.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

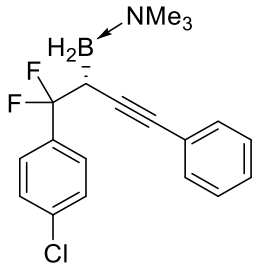
δ -85.67 (d, *J* = 231.7 Hz), -91.31 (d, *J* = 232.2 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{21}BClF_2NK, M+K]^+$: 386.1055, found: 386.1063.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.64 min (major) and t_R = 6.72 min (minor).

(-)-(*R*)-Trimethylamine-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3fa)



Serial number: zhn-6-72, White solid, melting point: 111–113 °C, 97% yield (33.8 mg), 90% ee. $[\alpha]_D^{25}$ -57.8 (*c* 1.0, $CHCl_3$). TLC R_f = 0.32 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.52 – 7.48 (m, 2H), 7.29 – 7.23 (m, 4H), 7.19 – 7.16 (m, 3H), 7.71 – 2.55 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.6 (t, *J* = 28.2 Hz), 134.9, 131.2, 128.2, 127.7 (t, *J* = 6.2 Hz), 127.6, 127.3, 124.6, 123.9 (t, *J* = 246.3 Hz), 93.1 (dd, *J* = 12.1, 5.1 Hz), 82.9, 52.8.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.70.

^{19}F NMR (376 MHz, $CDCl_3$)

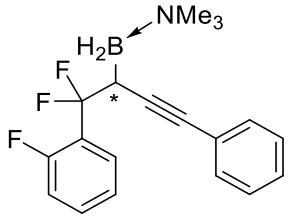
δ -85.04 (d, *J* = 232.0 Hz), -90.59 (d, *J* = 231.6 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{21}BClF_2NK, M+K]^+$: 386.1055, found: 386.1062.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.04 min (major) and t_R = 7.14 min (minor).

(+)-Trimethylamine-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-yl)borane (3ga)



Serial number: zhn-6-99, White solid, melting point: 92–94 ºC, 98% yield (32.4 mg), 95% ee. $[\alpha]_D^{26}$ +22.4 (*c* 1.0, $CHCl_3$). TLC R_f = 0.30 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.61 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.20 (m, 6H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 11.2, 8.3 Hz, 1H), 3.01 – 2.86 (m, 1H), 2.67 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 159.3 (dt, *J* = 249.9, 4.2 Hz), 131.3, 130.9 (d, *J* = 8.5 Hz), 128.5 – 128.3 (m), 128.0, 127.1, 126.1 (td, *J* = 28.2, 11.4 Hz), 124.7, 123.3 (d, *J* = 3.4 Hz), 123.0 (td, *J* = 245.9, 2.9 Hz), 115.9 (d, *J* = 22.3 Hz), 93.0 – 92.8 (m), 82.6, 52.7.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.79.

^{19}F NMR (376 MHz, $CDCl_3$)

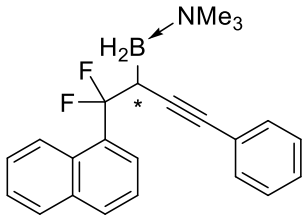
δ -85.78 (dd, *J* = 242.1, 11.4 Hz), -94.11 (dd, *J* = 241.5, 12.7 Hz), -114.63 (t, *J* = 12.1 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{21}BF_3NNa, M+Na]^+$: 354.1611, found: 354.1608.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.61 min (major) and t_R = 7.63 min (minor).

(+)-Trimethylamine-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-yl)borane (3ha)



Serial number: zhn-6-96, Light yellow oil, 99% yield (36.0 mg), 97% ee. $[\alpha]_D^{26}$ +130.6 (*c* 1.0, $CHCl_3$). TLC R_f = 0.45 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.42 (d, *J* = 8.5 Hz, 1H), 7.87 – 7.84 (m, 3H), 7.54 – 7.45 (m, 3H), 7.34 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 3.13 – 2.98 (m, 1H), 2.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 134.1, 133.8 (t, *J* = 25.1 Hz), 131.3, 130.1, 129.8, 128.8, 128.0, 127.1, 126.2, 125.8 (t, *J* = 9.1 Hz), 125.5 (t, *J* = 4.7 Hz), 125.3 (t, *J* = 247.5 Hz), 125.3, 124.8, 124.3, 93.5 (dd, *J* = 6.5, 6.5 Hz), 83.0, 52.6.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.70.

^{19}F NMR (376 MHz, $CDCl_3$)

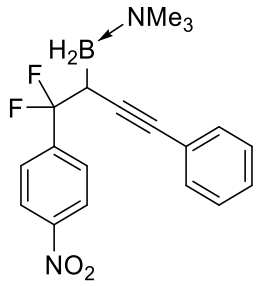
δ -82.71 (d, *J* = 240.2 Hz), -88.88 (d, *J* = 240.8 Hz).

HRMS (ESI)

Calcd for $[C_{23}H_{24}BF_2NNa, M+Na]^+$: 386.1862, found: 386.1866.

HPLC condition: Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 11.35 min (major) and t_R = 19.75 min (minor).

(-)-Trimethylamine-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-yl)borane (3ia)



Serial number: zhn-6-68, Light yellow oil, 80% yield (28.6 mg), 82% ee. $[\alpha]_D^{26}$ -77.2 (*c* 1.0, $CHCl_3$). TLC R_f = 0.25 (PE/EA = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.14 (m, 5H), 2.73 – 2.65 (m, 1H), 2.61 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 148.2, 144.3 (t, *J* = 28.1 Hz), 131.2, 128.3, 127.6, 127.6, 127.5, 124.2, 123.3 (t, *J* = 252.5 Hz), 122.6, 92.4 (dd, *J* = 12.5, 5.3 Hz), 83.3 (d, *J* = 1.8 Hz), 52.8.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -4.22.

^{19}F NMR (376 MHz, $CDCl_3$)

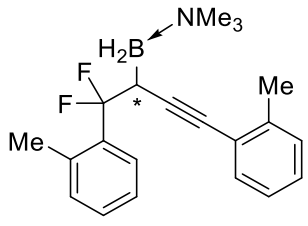
δ -85.31 (d, *J* = 232.7 Hz), -92.57 (d, *J* = 232.9 Hz).

HRMS (ESI)

Calcd for $[C_{19}H_{21}BF_2N_2O_2Na, M+Na]^+$: 381.1556, found: 381.1557.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 10.28 min (major) and t_R = 12.67 min (minor).

(+)-Trimethylamine-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-yl)borane (3ja)



Serial number: zhn-6-151, Light yellow oil, 94% yield (32.0 mg), 98% ee. $[\alpha]_D^{27}$ +5.2 (*c* 1.0, $CHCl_3$). TLC R_f = 0.39 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.19 – 6.95 (m, 7H), 2.78 – 2.67 (m, 1H), 2.59 (s, 9H), 2.45 (t, *J* = 2.6 Hz, 3H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 140.0, 136.5 (t, *J* = 25.8 Hz), 135.5 (t, *J* = 2.3 Hz), 131.5, 131.5, 129.2, 128.9, 127.8 (t, *J* = 8.2 Hz), 127.1, 125.5 (t, *J* = 242.4 Hz), 125.3, 124.9, 124.6, 97.5 (t, *J* = 7.3 Hz), 81.4, 52.7, 20.9 (t, *J* = 4.1 Hz), 20.8.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.58 (t, *J* = 105.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

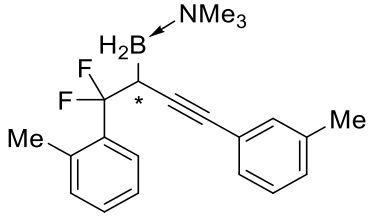
δ -85.51 (d, *J* = 241.6 Hz), -87.95 (d, *J* = 241.5 Hz).

HRMS (ESI)

Calcd for $[C_{21}H_{26}BF_2NNa, M+Na]^+$: 364.2019, found: 364.2027.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 10.42 min (major) and t_R = 11.16 min (minor).

(+)-Trimethylamine-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ka)



Serial number: zhn-6-97, Yellow oil, 82% yield (27.9 mg), 98% ee. $[\alpha]_D^{25}$ +18.2 (*c* 1.0, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.27 – 7.08 (m, 6H), 7.04 – 7.01 (m, 1H), 2.86 – 2.74 (m, 1H), 2.68 (s, 9H), 2.54 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 137.7, 136.5 (t, *J* = 25.8 Hz), 135.5, 131.9, 131.4, 128.8, 128.3, 128.0, 127.7 (t, *J* = 8.6 Hz), 125.5 (t, *J* = 252.5 Hz), 124.8, 124.6 (t, *J* = 246.44 Hz), 93.1 – 93.0 (m), 82.8, 52.8, 21.2, 20.9 (t, *J* = 4.1 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -4.00.

^{19}F NMR (376 MHz, $CDCl_3$)

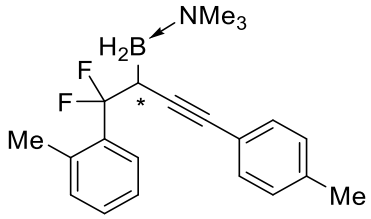
δ -85.10 (d, J = 240.1 Hz), -88.35 (d, J = 240.2 Hz).

HRMS (ESI)

Calcd for $[C_{21}H_{26}BF_2NNa, M+Na]^+$: 364.2019, found: 364.2026.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.07 min (major) and t_R = 5.46 min (minor).

(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-yl)borane (3la)



Serial number: zhn-6-98, Yellow oil, 80% yield (27.4 mg), 98% ee. $[\alpha]_D^{21}$ +15.5 (*c* 0.5, $CHCl_3$). TLC R_f = 0.33 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.61 (d, J = 7.7 Hz, 1H), 7.25 – 7.15 (m, 5H), 7.04 (d, J = 7.8 Hz, 2H), 2.86 – 2.73 (m, 1H), 2.68 (s, 9H), 2.53 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 137.0, 136.6 (t, J = 25.7 Hz), 135.5 (t, J = 2.5 Hz), 131.4, 131.2, 128.8, 128.8, 127.7 (t, J = 8.7 Hz), 125.5 (t, J = 242.4 Hz), 124.8, 121.7, 92.6 (t, J = 7.1 Hz), 82.7, 52.8, 21.4, 20.9 (t, J = 4.1 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.93.

^{19}F NMR (376 MHz, $CDCl_3$)

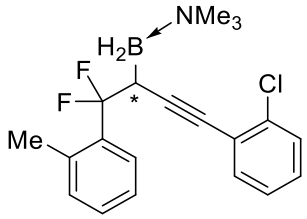
δ -85.35 (d, J = 239.9 Hz), -88.32 (d, J = 239.8 Hz).

HRMS (ESI)

Calcd for $[C_{21}H_{26}BF_2NNa, M+Na]^+$: 364.2019, found: 364.2026.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.20 min (major) and t_R = 6.84 min (minor).

(+)-Trimethylamine-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ma)



Serial number: zhn-6-104, Colorless oil, 97% yield (34.9 mg), 98% ee. $[\alpha]_D^{27}$ +19.6 (*c* 1.0, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.01 (m, 7H), 2.83 – 2.70 (m, 1H), 2.63 (s, 9H), 2.47 – 2.46 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.4, 135.5, 135.3, 133.3, 131.5, 128.9, 128.9, 128.0, 127.7 (t, *J* = 8.5 Hz), 126.3, 125.3 (t, *J* = 252.5 Hz), 124.9, 124.5, 99.3 (t, *J* = 7.2 Hz), 79.7, 52.8, 20.9.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.56.

^{19}F NMR (376 MHz, $CDCl_3$)

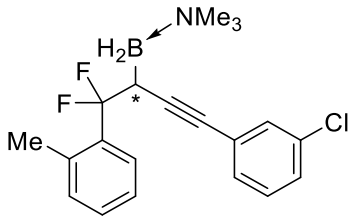
δ -85.26 (d, *J* = 241.3 Hz), -88.02 (d, *J* = 241.4 Hz).

HRMS (ESI)

Calcd for $[C_{20}H_{23}BClF_2NNa, M+Na]^+$: 384.1472, found: 384.1469.

HPLC condition: Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 12.42 min (major) and t_R = 14.63 min (minor).

(+)-Trimethylamine-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3na)



Serial number: zhn-6-103, Colorless oil, 98% yield (35.2 mg), 98% ee. $[\alpha]_D^{27}$ +18.6 (*c* 1.0, $CHCl_3$). TLC R_f = 0.35 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.10 (m, 7H), 2.83 – 2.73 (m, 1H), 2.67 (s, 9H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.3 (t, *J* = 25.7 Hz), 135.4, 133.8, 131.5, 131.1, 129.4, 129.3, 129.0, 127.6 (t, *J* = 8.5 Hz), 127.3, 126.5, 125.3 (t, *J* = 246.4 Hz), 124.9, 95.2 (t, *J* = 6.8, 6.8 Hz), 81.3, 52.7, 20.9.

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.95.

^{19}F NMR (376 MHz, $CDCl_3$)

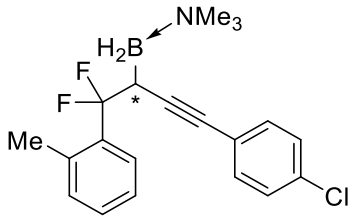
δ -84.99 (d, *J* = 241.0 Hz), -88.43 (d, *J* = 240.8 Hz).

HRMS (ESI)

Calcd for $[C_{20}H_{23}BClF_2NNa, M+Na]^+$: 384.1472, found: 384.1472.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.43 min (major) and t_R = 6.28 min (minor).

(+)-Trimethylamine-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3oa)



Serial number: zhn-6-102, Light yellow oil, 95% yield (34.3 mg), 99% ee. $[\alpha]_D^{27}$ +17.1 (*c* 1.0, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.52 (d, J = 7.8 Hz, 1H), 7.25 – 7.92 (m, 7H), 2.77 – 2.66 (m, 1H), 2.60 (s, 9H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.4 (t, *J* = 26.1 Hz), 135.4, 132.9, 132.5, 131.5, 128.9, 128.3, 127.6 (t, *J* = 8.6 Hz), 125.4 (t, *J* = 252.5 Hz), 124.8, 123.3, 94.7 (t, *J* = 7.1 Hz), 81.5, 52.7, 20.9 (t, *J* = 4.0 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.94.

^{19}F NMR (376 MHz, $CDCl_3$)

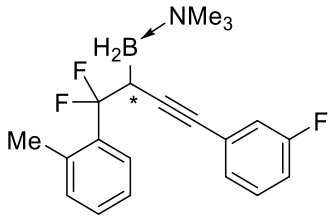
δ -85.01 (d, *J* = 240.2 Hz), -88.50 (d, *J* = 240.3 Hz).

HRMS (ESI)

Calcd for $[C_{20}H_{23}BClF_2NK, M+K]^+$: 400.1212, found: 400.1206.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.37 min (minor) and t_R = 7.20 min (major).

(+)-Trimethylamine-(1,1-difluoro-4-(3-fluorophenyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3pa)



Serial number: zhn-6-201, Light yellow oil, 98% yield (33.8 mg), 97% ee. $[\alpha]_D^{24}$ +16.6 (*c* 1.0, $CHCl_3$). TLC R_f = 0.31 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.07 (m, 4H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.93 – 6.89 (m, 1H), 6.87 – 6.82 (m, 1H), 2.80 – 2.66 (m, 1H), 2.61 (s, 9H), 2.46 (t, *J* = 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 162.3 (d, *J* = 245.3 Hz), 136.4 (t, *J* = 25.8 Hz), 135.4, 131.5, 131.1, 129.6 (d, *J* = 8.8 Hz), 128.9, 127.6 (t, *J* = 8.4 Hz), 127.1 (d, *J* = 2.4 Hz), 126.6 (d, *J* = 9.7 Hz), 125.3 (t, *J* = 246.4 Hz), 124.9, 118.0 (d, *J* = 21.9 Hz), 114.3 (d, *J* = 21.1 Hz), 95.0 – 94.8 (m), 81.5 (d, *J* = 3.2 Hz), 52.7, 20.9 (t, *J* = 3.8 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -4.03.

^{19}F NMR (376 MHz, $CDCl_3$)

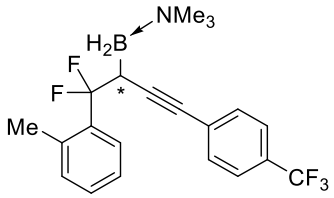
δ -85.11 (d, *J* = 240.7 Hz), -88.39 (d, *J* = 241.0 Hz), -113.74.

HRMS (ESI)

Calcd for $[C_{20}H_{23}BF_3NK, M+K]^+$: 384.1507, found: 384.1505.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.41 min (major) and t_R = 6.37 min (minor).

(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)borane (3qa)



Serial number: zhn-8-51, Light yellow oil, 97% yield (38.3 mg), 99% ee. $[\alpha]_D^{27}$ +15.4 (*c* 1.0, $CHCl_3$). TLC R_f = 0.35 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.18 (m, 3H), 2.90 – 2.77 (m, 1H), 2.71 (s, 9H), 2.57 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.3 (t, *J* = 25.7 Hz), 135.4 (t, *J* = 2.6 Hz), 131.6, 131.4, 129.0, 128.8 (q, *J* = 45.3 Hz), 128.6, 127.6 (t, *J* = 8.5 Hz), 127.6 (t, *J* = 8.4 Hz), 125.3 (t, *J* = 252.5 Hz), 125.0 (q, *J* = 3.9 Hz), 124.9, 124.2 (t, *J* = 272.7 Hz), 96.8 (t, *J* = 6.8 Hz), 81.5, 52.7, 20.9 (t, *J* = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

δ -62.62, -84.97 (d, *J* = 241.0 Hz), -88.40 (d, *J* = 241.1 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

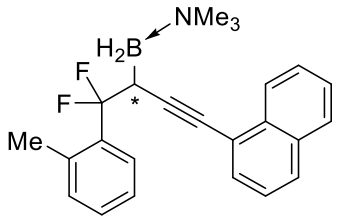
δ -3.68.

HRMS (ESI)

Calcd for $[C_{21}H_{23}BF_5NNa, M + Na]^+$: 418.1736, found: 418.1735.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 7.05 min (major) and t_R = 8.29 min (minor).

(-)-Trimethylamine-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ra)



Serial number: zhn-7-3, Light yellow oil, 94% yield (38.2 mg), 99% ee. $[\alpha]_D^{21}$ -3.2 (*c* 1.0, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.19 (d, *J* = 7.3 Hz, 1H), 7.82 – 7.62 (m, 3H), 7.56 – 7.11 (m, 7H), 2.99 – 2.84 (m, 1H), 2.69 (s, 9H), 2.56 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.6 (t, *J* = 25.8 Hz), 135.6 (t, *J* = 2.4 Hz), 133.7, 133.2, 131.6, 131.2, 129.4, 128.9, 128.0, 127.7 (t, *J* = 8.5 Hz), 127.5, 126.7, 126.4, 126.1, 125.5 (t, *J* = 238.4 Hz), 125.2, 125.0, 122.5, 98.7 – 98.6 (m), 80.6, 52.8, 21.0 (t, *J* = 3.9 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.56.

^{19}F NMR (376 MHz, $CDCl_3$)

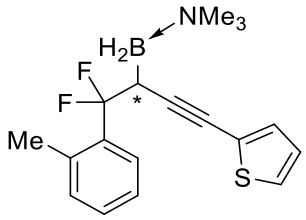
δ -85.44 (d, *J* = 241.3 Hz), -87.83 (d, *J* = 240.6 Hz).

HRMS (ESI)

Calcd for $[C_{24}H_{26}BF_2NNa, M+Na]^+$: 400.2019, found: 400.2024.

HPLC condition: Chiralcel IC-3 column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.87 min (major) and t_R = 7.29 min (minor).

(+)-Trimethylamine-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3sa)



Serial number: zhn-6-105, Yellow oil, 82% yield (27.5 mg), 96% ee. $[\alpha]_D^{27}$ +7.4 (*c* 1.0, $CHCl_3$). TLC R_f = 0.32 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.06 (m, 5H), 6.92 (d, *J* = 4.9 Hz, 1H), 2.73 – 2.67 (m, 1H), 2.60 (s, 9H), 2.46 (t, *J* = 2.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 136.5 (t, *J* = 25.5 Hz), 135.5 (t, *J* = 2.3 Hz), 131.5, 130.0, 128.9, 127.7 (t, *J* = 8.5 Hz), 126.8, 125.4 (t, *J* = 246.4 Hz), 124.8, 124.7, 123.7, 92.9 – 92.6 (m), 77.6, 52.7, 20.9 (t, *J* = 4.0 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -4.08.

^{19}F NMR (376 MHz, $CDCl_3$)

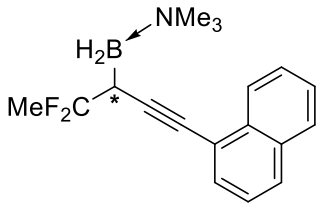
δ -84.68 (d, *J* = 239.7 Hz), -88.64 (d, *J* = 240.0 Hz).

HRMS (ESI)

Calcd for $[C_{18}H_{22}BF_2NSNa, M+Na]^+$: 356.1426, found: 356.1433.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.67 min (major) and t_R = 7.19 min (minor).

(-)-Trimethylamine-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-yl) borane (3ta)



Serial number: zhn-7-129, Light yellow oil, 86% yield (26.0 mg), 73% ee. $[\alpha]_D^{27}$ -4.0 (*c* 0.5, $CHCl_3$). TLC R_f = 0.32 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.36 (m, 3H), 7.29 (t, *J* = 7.7 Hz, 1H), 2.65 (s, 9H), 2.54 – 2.40 (m, 1H), 1.70 (t, *J* = 18.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 133.8, 133.2, 129.5, 128.1, 127.5, 126.9 (t, *J* = 242.4 Hz), 126.5, 126.5, 126.2, 125.2, 122.5, 99.4 (dd, *J* = 14.5, 3.4 Hz), 79.8 (d, *J* = 2.2 Hz), 52.8, 22.1 (t, *J* = 27.7 Hz).

^{11}B NMR (128 MHz, $CDCl_3$)

δ -3.16 (t, *J* = 103.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

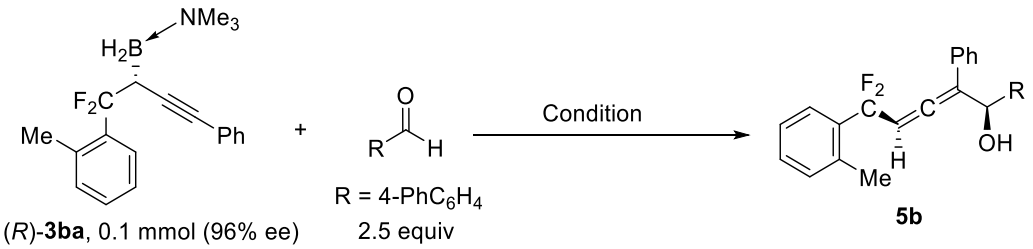
δ -78.86 (d, *J* = 224.8 Hz), -87.46 (d, *J* = 223.4 Hz).

HRMS (ESI)

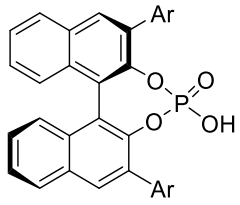
Calcd for $[C_{18}H_{22}BF_2NNa, M + Na]^+$: 324.1706, found: 324.1710.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.88 min (major) and t_R = 6.34 min (minor).

6. The Optimization of the Addition Reaction of Aldehydes with Chiral *gem*-Difluoroalkyl Propargylic Boron (*R*)-3ba

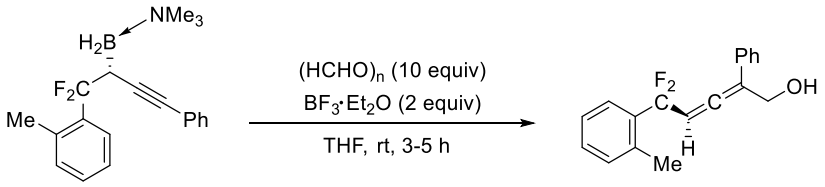


(*R*)-**3ba**, 0.1 mmol (96% ee)

Condition A:	 , 5 Å MS, toluene, rt, 24 h	No Conv.
	Ar = 2,4,6-triPh, (*R*) (5 mol%)	
Condition B:	CuBr (1 equiv), THF, rt, 24 h	No Conv.
Condition C:	Et_2Zn (1.2 equiv, 1 M in toluene), toluene, rt, 24 h	No Conv.
Condition D:	BF_3•Et_2O (2 equiv), rt, 3 h	75% yield, 95% ee

7. Procedures for Addition Reaction of Aldehydes with Chiral *gem*-Difluoroalkyl Propargylic Boron (*R*)-3ba

7.1 Procedure A

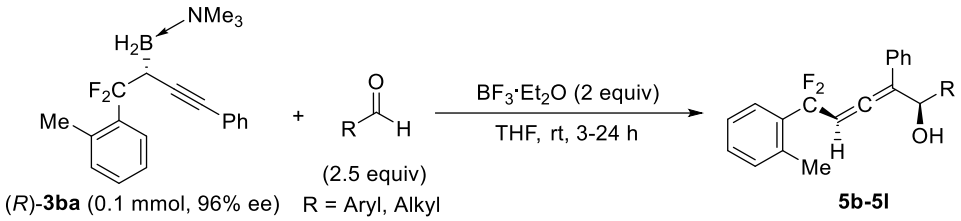


(*R*)-**3ba**, 0.1 mmol, 96% ee

A 25 mL Schlenk tube was charged with $(HCHO)_n$ (30.0 mg, 1.0 mmol). Then 1.2 mL dry THF was injected under nitrogen atmosphere. The reaction mixture was heated to 70 ºC for 2 h. To another 25 mL Schlenk tube was charged with (*R*)-**3ba** (32.7 mg, 0.1 mmol). Then 0.7 mL dry THF was injected under nitrogen atmosphere. After cooling to room temperature, transfer the latter mixture into the former Shlenck tube with a syringe. Then, BF_3•Et_2O (28.4 mg, 0.2 mmol) was added dropwise into the reaction system with a syringe. At room temperature, the reaction was kept stirring for

3 h, then TLC indicated that the substrate (*R*)-**3ba** was consumed completely. The reaction mixture was diluted with EtOAc (8 mL), and washed with brine (3 x 4 mL). The organic extract was dried over anhydrous $NaSO_4$, filtered, and concentrated to give crude product. The crude product was purified by a flash chromatography on silica gel (eluting with petroleum ether/EtOAc/NEt_3 = 100:10:1, v/v) to afford **5a** as colorless oil (21.9 mg, 77% yield, 95% ee, 99% es).

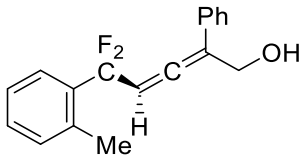
7.2 Procedure B



A 25 mL Schlenk tube was charged with (*R*)-**3ba** (32.7 mg, 0.1 mmol) and RCHO (0.25 mmol). Then 2.0 mL dry THF was injected under nitrogen atmosphere. Then, BF_3•Et_2O (28.4 mg, 0.2 mmol) was added dropwise into the reaction system with a syringe. At room temperature, the reaction was kept stirring for 3-24 h, then TLC indicated that the substrate (*R*)-**3ba** was consumed completely. The reaction mixture was diluted with EtOAc (8 mL), and washed with brine (3 x 4 mL). The organic extract was dried over anhydrous $NaSO_4$, filtered, and concentrated to give crude product. The crude product was purified by a flash chromatography on silica gel (eluting with petroleum ether/EtOAc/NEt_3 = 100:x:1, v/v) to afford **5b-5l**.

8. Analytical Data of Chiral *gem*-Difluoroalkyl α-Allenols

(-)-(*S*)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5a)



Serial number: zhn-7-31, 77% yield (21.9 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{22}$ -233.6 (*c* 0.5, $CHCl_3$). TLC R_f = 0.39 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.07 (m, 8H), 6.14 – 6.00 (m, 1H), 4.43 – 4.27 (m, 2H), 2.34 (d, *J* = 2.4 Hz, 3H), 1.12 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.9, 136.0 (t, *J* = 2.5 Hz), 134.8 (t, *J* = 25.3 Hz), 132.2 (t, *J* = 2.0 Hz), 131.7, 130.0, 128.7, 128.1, 126.5, 125.7 (t, *J* = 7.8 Hz), 125.6, 120.1, 112.1, 96.9 (t, *J* = 35.6 Hz), 61.6 (t, *J* = 2.4 Hz), 20.3 (t, *J* = 3.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

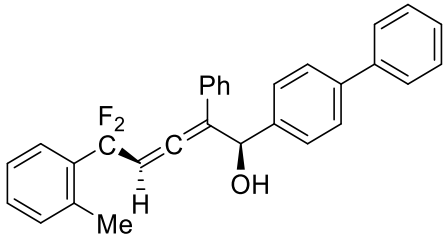
δ -85.22.

HRMS (ESI)

Calcd for $[C_{18}H_{16}F_2ONa, M + Na]^+$: 309.1061, found: 309.1065.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.69 min (minor) and t_R = 7.81 min (major).

(-)-(1*R*,3*S*)-1-([1,1'-biphenyl]-4-yl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5b)



Serial number: zhn-7-29, 75% yield (33.0 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{23}$ -234.0 (*c* 1.0, $CHCl_3$). TLC R_f = 0.37 (PE/EA = 5:1, v/v). Note: we confirmed absolute configurations of (*R*, *S*)-**5b** by ECD spectra (experimental and computed ECD spectra).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.60 – 7.49 (m, 3H), 7.44 – 7.40 (m, 4H), 7.36 – 7.32 (m, 2H), 7.29 – 7.14 (m, 7H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.32 (td, *J* = 6.1, 2.6 Hz, 1H), 5.61 (s, 1H), 2.39 (s, 3H), 1.96 (d, *J* = 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.4 (t, *J* = 10.0 Hz), 141.0, 140.6, 139.6, 136.4, 134.8 (t, *J* = 25.3 Hz), 132.6, 131.9, 130.0, 128.8, 128.6, 128.0, 127.6, 127.4, 127.3, 127.3, 127.1, 126.0 (t, *J* = 7.9 Hz), 125.7, 120.3, 115.8, 98.4 (t, *J* = 35.9 Hz), 72.7, 20.4 .

^{19}F NMR (376 MHz, $CDCl_3$)

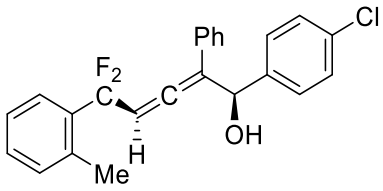
δ -84.05, -84.16.

HRMS (ESI)

Calcd for $[C_{30}H_{24}F_2ONa, M + Na]^+$: 461.1687, found: 461.1678.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 23.34 min (minor) and t_R = 32.00 min (major).

(-)-(1*R*,3*S*)-1-(4-chlorophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5c)



Serial number: zhn-7-81, 69% yield (27.4 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{26}$ -244.8 (*c* 1.0, $CHCl_3$). TLC R_f = 0.39 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.10 (m, 9H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.31 (td, *J* = 6.4, 2.6 Hz, 1H), 5.57 (s, 1H), 2.40 (s, 3H), 2.01 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 203.3 (t, *J* = 10.0 Hz), 138.0, 135.3, 133.7 (t, *J* = 25.1 Hz), 132.8, 131.2, 130.9, 129.0, 127.7, 127.5, 127.4, 127.1, 126.2, 124.9 (t, *J* = 7.9 Hz), 124.6, 119.1 (t, *J* = 242.4 Hz), 114.6, 97.3 (t, *J* = 36.1 Hz), 71.3, 19.3 (t, *J* = 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

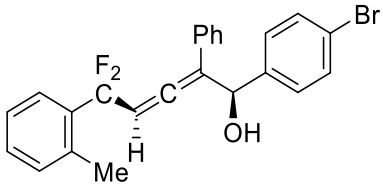
δ -84.13, -84.27.

HRMS (ESI)

Calcd for $[C_{24}H_{19}Cl_2F_2O, M + Cl]^-$: 431.0787, found: 431.0785.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 9.40 min (minor) and t_R = 14.36 min (major).

(-)-(1*R*,3*S*)-1-(4-bromophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5d)



Serial number: zhn-7-79, 73% yield (32.0 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{26}$ -202.1 (*c* 1.0, $CHCl_3$). TLC R_f = 0.38 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.54 (t, *J* = 6.0 Hz, 1H), 7.47 – 7.08 (m, 10H), 6.93 (t, *J* = 5.8 Hz, 2H), 6.31 (s, 1H), 5.55 (s, 1H), 2.40 (s, 3H), 2.02 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.3 (t, *J* = 10.0 Hz), 139.6, 136.4, 134.7 (t, *J* = 25.0 Hz), 132.3, 131.9, 131.6, 130.1, 128.8, 128.6, 128.1, 127.2, 126.0 (t, *J* = 7.9 Hz), 125.7, 122.1, 120.1 (t, *J* = 241.4 Hz), 115.6, 98.4 (t, *J* = 35.8 Hz), 72.4, 20.3.

^{19}F NMR (376 MHz, $CDCl_3$)

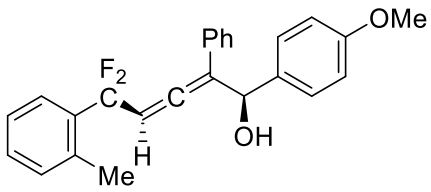
δ -84.15, -84.27.

HRMS (ESI)

Calcd for $[C_{24}H_{19}BrF_2OCl, M + Cl]^-$: 475.0281, found: 475.0280.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 10.09 min (minor) and t_R = 14.89 min (major).

(-)-(1*R*,3*S*)-5,5-difluoro-1-(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5e)



Serial number: zhn-7-83, 54% yield (21.2 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{25}$ -198.8 (*c* 0.5, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.11 (m, 7H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.33 (td, *J* = 6.5, 2.9 Hz, 1H), 5.55 (dd, *J* = 5.1, 2.9 Hz, 1H), 3.79 (s, 3H), 2.43 (s, 3H), 1.88 (d, *J* = 5.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.1 (t, *J* = 9.1 Hz), 159.4, 136.4, 134.8, 132.8, 132.6, 131.9, 130.0, 128.5, 128.5, 127.9, 127.2, 126.0 (t, *J* = 7.9 Hz), 125.6, 120.4 (t, *J* = 288.9 Hz), 116.0, 113.9, 98.3 (t, *J* = 36.4 Hz), 72.5, 55.2, 20.4 (t, *J* = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

δ -84.06, -84.21.

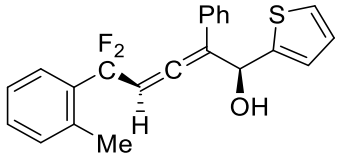
HRMS (ESI)

Calcd for $[C_{25}H_{22}F_2O_2K, M + K]^+$: 431.1219, found: 431.1225.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 15.19 min (minor) and t_R = 26.85 min

(major).

(-)-(1*S*,3*S*)-5,5-difluoro-2-phenyl-1-(thiophen-2-yl)-5-(*o*-tolyl)penta-2,3-dien-1-ol (5f)



Serial number: zhn-7-95, 62% yield (22.7 mg), 94% ee, 98% es, colorless oil, $[\alpha]_D^{25}$ -241.2 (*c* 0.5, $CHCl_3$). TLC R_f = 0.37 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.16 (m, 9H), 6.81 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.60 (d, *J* = 3.5 Hz, 1H), 6.31 (td, *J* = 6.9, 2.5 Hz, 1H), 5.79 (s, 1H), 2.38 (s, 3H), 2.07 (d, *J* = 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.0 (t, *J* = 9.8 Hz), 144.5, 136.3, 134.7, 132.3, 131.9, 130.0, 128.6, 128.1, 127.2, 126.8, 125.9 (t, *J* = 8.2 Hz), 125.9, 125.8, 125.7, 120.03 (t, *J* = 242.4 Hz), 116.0, 98.7 (t, *J* = 35.5 Hz), 68.5, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$)

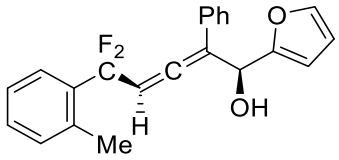
δ -84.56.

HRMS (ESI)

Calcd for $[C_{22}H_{18}F_2OSNa, M + Na]^+$: 391.0939, found: 391.0930.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 9.95 min (minor) and t_R = 22.70 min (major).

(-)-(1*S*,3*S*)-5,5-difluoro-1-(furan-2-yl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5g)



Serial number: zhn-7-91, 66% yield (23.2 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{26}$ -131.2 (*c* 0.25, $CHCl_3$). TLC R_f = 0.35 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.3 – 7.12 (m, 9H), 6.31 (td, *J* = 6.9, 2.6 Hz, 1H), 6.19 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.79 (d, *J* = 3.3 Hz, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 2.38 (s, 3H), 2.11 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 203.3 (t, *J* = 9.9 Hz), 152.4, 141.5, 135.2, 133.6 (t, *J* = 25.3 Hz), 131.3 (t, *J* = 1.8 Hz), 130.8, 128.9, 127.5, 127.0, 125.8, 124.9 (t, *J* = 7.9 Hz), 124.6, 119.0 (t, *J* = 242.4 Hz), 113.1, 109.4, 107.2, 97.7 (t, *J* = 35.8 Hz), 65.3, 19.3.

^{19}F NMR (376 MHz, $CDCl_3$)

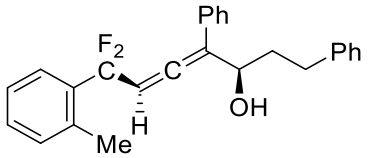
δ -84.65.

HRMS (ESI)

Calcd for $[C_{22}H_{18}F_2O_2Na, M + Na]^+$: 375.1167, found: 375.1163.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 10.99 min (minor) and t_R = 14.68 min (major).

(-)-(3*R*,5*S*)-7,7-difluoro-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-3-ol (5h)



Serial number: zhn-7-39, 70% yield (27.2 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{26}$ -19.2 (*c* 1.0, $CHCl_3$). TLC R_f = 0.42 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.37 – 6.94 (m, 13H), 6.18 (t, *J* = 6.4 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 1H), 2.69 – 2.49 (m, 2H), 2.35 (s, 3H), 1.81 – 1.54 (m, 2H), 1.48 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.1 (t, *J* = 9.8 Hz), 141.5, 136.2 (t, *J* = 2.6 Hz), 134.9 (t, *J* = 24.9 Hz), 133.0 (t, *J* = 2.0 Hz), 131.8, 130.0, 128.7, 128.5, 128.3, 128.1, 127.1, 125.9, 125.8 (t, *J* = 8.0 Hz), 125.6, 120.3 (t, *J* = 242.4 Hz) , 116.4, 97.5 (t, *J* = 35.8 Hz), 69.9, 37.1, 31.6, 20.4 (t, *J* = 2.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

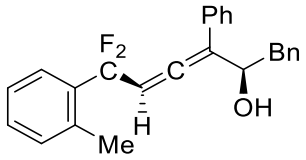
δ -84.14 (d, *J* = 261.7 Hz), -85.22 (d, *J* = 260.8 Hz).

HRMS (ESI)

Calcd for $[C_{26}H_{24}F_2ONa, M + Na]^+$: 413.1687, found: 413.1676.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 8.14 min (minor) and t_R = 11.67 min (major).

(-)-(2*R*,4*S*)-6,6-difluoro-1,3-diphenyl-6-(*o*-tolyl)hexa-3,4-dien-2-ol (5i)



Serial number: zhn-7-73, 71% yield (26.8 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{24}$ -86.4 (*c* 1.0, $CHCl_3$). TLC R_f = 0.48 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.57 – 7.52 (m, 1H), 7.36 – 7.17 (m, 11H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.18 (t, *J* = 8.0 Hz, 1H), 4.67 (d, *J* = 9.0 Hz, 1H), 2.77 – 2.72 (m, 1H), 2.50 – 2.43 (m, 1H), 2.40 (s, 3H), 1.61 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.5 (t, *J* = 9.5 Hz), 137.9, 136.3, 135.0 (t, *J* = 25.2 Hz), 133.1 (t, *J* = 2.0 Hz), 131.8, 130.0, 129.3, 128.7, 128.6, 128.1, 127.2, 126.7, 125.8 (t, *J* = 7.9 Hz), 125.6, 120.3 (t, *J* = 242.4 Hz), 115.9, 97.6 (t, *J* = 35.4 Hz), 71.4, 42.3, 20.4 (t, *J* = 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

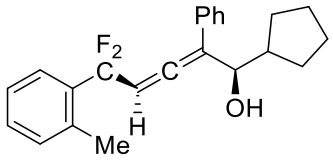
δ -84.25 (d, *J* = 261.2 Hz), -85.20 (d, *J* = 261.0 Hz).

HRMS (ESI)

Calcd for $[C_{25}H_{22}F_2ONa, M + Na]^+$: 399.1531, found: 399.1530.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 8.63 min (minor) and t_R = 10.55 min (major).

(-)-(1*R*,3*S*)-1-cyclopentyl-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5j)



Serial number: zhn-7-93, 73% yield (25.7 mg), 95% ee, 99% es, colorless oil, $[\alpha]_D^{26}$ -127.6 (*c* 0.5, $CHCl_3$). TLC R_f = 0.51 (PE/EA = 5:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.04 (m, 8H), 6.04 (t, *J* = 6.7 Hz, 1H), 4.18 (d, *J* = 7.6 Hz, 1H), 2.26 (s, 3H), 1.86 (q, *J* = 7.9 Hz, 1H), 1.58 – 1.39 (m, 5H), 1.27 – 0.96 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.7 (t, *J* = 9.7 Hz), 136.4 (t, *J* = 2.4 Hz), 134.9 (t, *J* = 25.1 Hz), 133.6, 131.8, 130.0, 128.5, 127.9, 127.5, 125.8 (t, *J* = 7.9 Hz), 125.5, 120.3 (t, *J* = 240.4 Hz), 116.2, 96.2 (t, *J* = 35.5 Hz), 75.5, 44.0, 29.2, 28.2, 25.7, 20.3 (t, *J* = 2.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

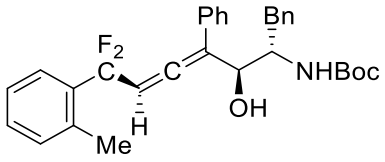
δ -84.15 (d, *J* = 261.7 Hz), -85.37 (d, *J* = 261.2 Hz).

HRMS (ESI)

Calcd for $[C_{23}H_{24}F_2ONa, M + Na]^+$: 377.1687, found: 377.1688.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 5.88 min (minor) and t_R = 10.25 min (major).

(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5k)



Serial number: zhn-7-77, 83% yield (41.8 mg), d.r. > 20:1, colorless oil, $[\alpha]_D^{24}$ -79.4 (*c* 1.0, $CHCl_3$). TLC R_f = 0.36 (PE/EA = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.14 (m, 11H), 6.98 (s, 2H), 6.15 (t, *J* = 7.6 Hz, 1H), 4.76 (s, 1H), 4.57 (s, 1H), 3.85 – 3.71 (m, 1H), 2.89 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.36 (s, 9H), 1.18 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 203.4 (t, *J* = 8.7 Hz), 155.9, 138.1, 136.1, 133.0, 131.8, 130.0, 129.4, 128.7, 128.5, 128.5 (t, *J* = 23.7 Hz), 128.2, 127.1, 126.5, 125.8 (t, *J* = 8.1 Hz), 125.7, 119.49 (t, *J* = 242.4 Hz), 115.2, 97.7 (t, *J* = 35.4 Hz), 79.4, 70.0, 54.6, 38.0, 28.2, 20.3 (t, *J* = 3.0 Hz).

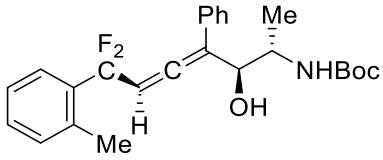
^{19}F NMR (376 MHz, $CDCl_3$)

δ -85.17 (d, *J* = 257.2 Hz), -86.08 (d, *J* = 256.6 Hz).

HRMS (ESI)

Calcd for $[C_{31}H_{34}F_2NO_3, M + H]^+$: 506.2501, found: 506.2494.

(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-4-phenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5l)



Serial number: zhn-7-89, 77% yield (33.1 mg), d.r. > 20:1, colorless oil, $[\alpha]_D^{23}$ -65.0 (*c* 1.0, $CHCl_3$). TLC R_f = 0.34 (PE/EA = 3:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.64 (d, *J* = 6.9 Hz, 1H), 7.39 – 7.18 (m, 8H), 6.20 (t, *J* = 8.2 Hz, 1H), 4.60 (s, 1H), 4.48 – 4.41 (m, 1H), 3.76 – 3.65 (m, 1H), 2.45 (s, 3H), 1.44 (d, *J* = 3.0 Hz, 9H), 1.29 (d, *J* = 3.1 Hz, 1H), 1.05 (dd, *J* = 7.1, 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.1 (t, *J* = 8.8 Hz), 156.3, 136.2, 135.0 (t, *J* = 25.4 Hz), 133.6, 131.9, 130.0, 128.7, 128.1, 127.3, 125.8 (t, *J* = 7.9 Hz), 125.7, 119.7 (t, *J* = 242.4 Hz), 114.7, 97.2 (t, *J* = 34.7 Hz), 79.7, 74.9, 50.2, 28.3, 20.3 (t, *J* = 3.1 Hz), 17.8.

^{19}F NMR (376 MHz, $CDCl_3$)

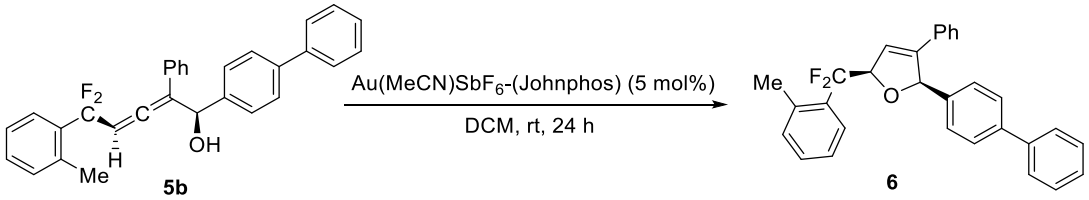
δ -85.04, -84.11.

HRMS (ESI)

Calcd for $[C_{25}H_{30}F_2NO_3, M + H]^+$: 430.2188, found: 430.2185.

9. Transformations of Chiral *gem*-Difluoroalkyl α-Allenols

9.1 Transformation of 5b to 6



0.1 mmol (95% ee, >20:1 d.r.)

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **5b** (43.8 mg, 0.1 mmol, 1.0 equiv), [Au(Johnphos)(CH_3CN)]SbF_6 (3.8 mg, 0.005 mmol, 5 mol%) in a glove box under Ar atmosphere. Anhydrous DCM (3.0 mL) was added via a syringe. The resulting reaction mixture was stirred at room temperature for 24 hours. After the volatiles were removed under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) to give the product **6** (35.9 mg, colorless oil, 82% yield, 94% ee, 99% es, > 20:1

d.r.). Serial number: zhn-7-107, $[\alpha]_D^{23}$ -146.8 (*c* 0.5, $CHCl_3$). TLC R_f = 0.39 (PE/EA = 20:1, v/v). Note: The relative configuration of the compound **6** was determined by ^{1}H-^{1}H Noesy.

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.63 – 6.98 (m, 18H), 6.41 (s, 1H), 6.18 (s, 1H), 5.44 (p, *J* = 5.3 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 144.2, 141.0, 140.7, 138.2, 137.0, 132.5 (t, *J* = 23.7 Hz), 132.1, 132.0, 129.9, 129.1, 128.8, 128.5, 128.4, 127.5 (t, *J* = 8.1 Hz), 127.4, 127.1, 127.1, 126.8, 125.5, 121.6, (t, *J* = 249.0 Hz), 120.1, 89.1, 88.11 (t, *J* = 33.3 Hz), 20.7 (t, *J* = 4.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

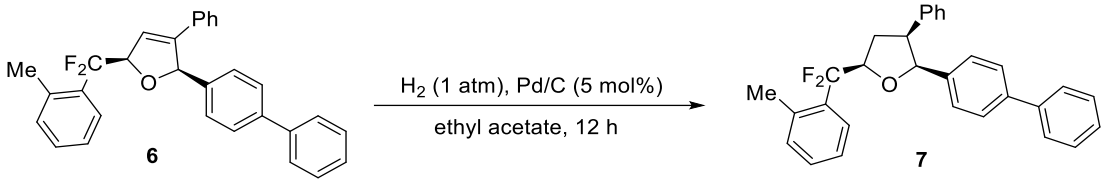
δ -99.38 (d, *J* = 256.1 Hz), -103.19 (d, *J* = 256.0 Hz).

HRMS (ESI)

Calcd for $[C_{30}H_{28}F_2NO, M+NH_4]^+$: 456.2134, found: 456.2128.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 6.71 min (minor) and t_R = 8.72 min (major).

9.2 Transformation of 6 to 7



0.07 mmol (94% ee, >20:1 d.r.)

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with **6** (30.7 mg, 0.07 mmol, 1.0 equiv) and EtOAc (3 mL). To the solution was added Pd/C (3.7 mg, 10% w/w). The resulting mixture was stirred for 12 hours at room temperature under H_2 atomosphere (a balloon). The black solids were filtered off and washed thoroughly with DCM. After the volatiles were removed under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to give product **7** (27.0 mg, colorless oil, 88% yield, 94% ee, 100% es, > 20:1 d.r.). Serial number: zhn-7-109. $[\alpha]_D^{23}$ +120.7 (*c* 0.5, $CHCl_3$). TLC R_f = 0.37 (PE/EA = 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.31 – 7.25 (m, 5H), 7.06 – 6.93 (m, 5H), 6.88 – 6.77 (m, 2H), 5.34 (d, *J* = 8.6 Hz, 1H), 4.72 – 4.63 (m, 1H), 3.92 – 3.85 (m, 1H), 2.60 (t, *J* = 2.7 Hz, 3H), 2.58 – 2.50 (m, 1H), 2.44 – 2.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)

δ 140.9, 139.5, 138.9, 138.5, 136.7, 133.0 (t, *J* = 24.1 Hz), 132.1, 130.12, 128.7, 128.6, 127.8, 127.3 (t, *J* = 8.8 Hz), 127.1, 127.0, 126.9, 126.5, 126.1, 125.7, 121.9 (dd, *J* = 249.0, 243.6 Hz), 84.8, 80.8 (dd, *J* = 35.0, 29.4 Hz), 49.8, 32.2, 20.9 (t, *J* = 4.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$)

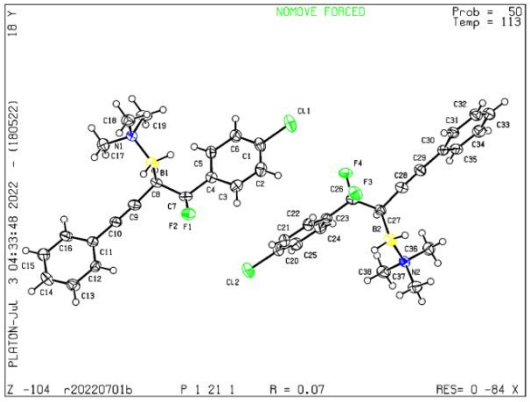
-99.63 (d, *J* = 257.5 Hz), -105.49 (d, *J* = 257.7 Hz).

HRMS (ESI)

Calcd for $[C_{30}H_{26}F_2NaO, M+Na]^+$: 463.1844, found: 463.1850.

HPLC condition: Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, 254 nm UV detector, t_R = 11.56 min (major) and t_R = 13.10 min (minor).

10. X-Ray Diffraction Analysis of (*R*)-3fa



CCDC number	2246187
Empirical formula	$C_{19}H_{21}BClF_2N$
Formula weight	347.63
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.2271(5)
b/Å	10.3968(7)
c/Å	21.4304(11)
α/°	90

β/°	96.909(6)
γ/°	90
Volume/Å^3	1819.75(19)
Z	4
ρ_{calcg}/cm^3	1.269
μ/mm^{-1}	0.228
F(000)	728.0
Crystal size/mm^3	0.23 × 0.2 × 0.17
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.828 to 65.884
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -32 ≤ l ≤ 31
Reflections collected	22992
Independent reflections	11704 [R_{int} = 0.0679, R_{sigma} = 0.1339]
Data/restraints/parameters	11704/7/456
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0677, wR_2 = 0.1228
Final R indexes [all data]	R_1 = 0.1428, wR_2 = 0.1648
Largest diff. peak/hole / e Å^{-3}	0.26/-0.26
Flack parameter	0.05(7)

11. Confirm Absolute Configurations of (*R*, *S*)-5b by ECD Spectra.

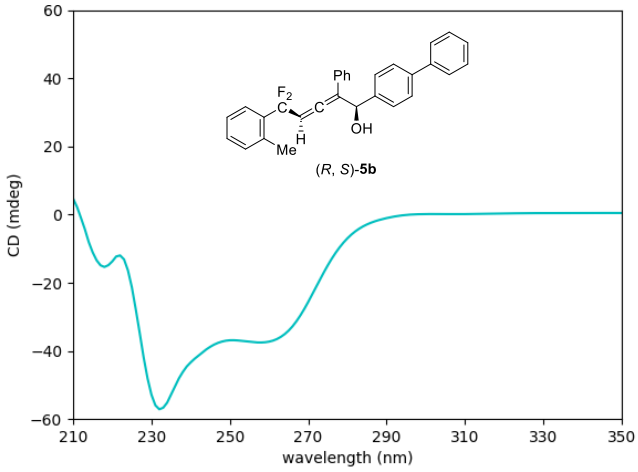


Figure 1. Experimental ECD spectrum of (-)-**5b**

(The experimental spectra were measured at a concentration of 0.2 mg/mL in $CHCl_3$ solvent and 0.1 cm path length.)

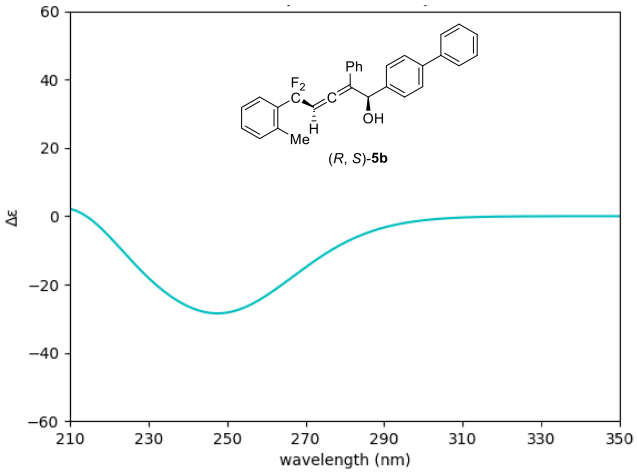
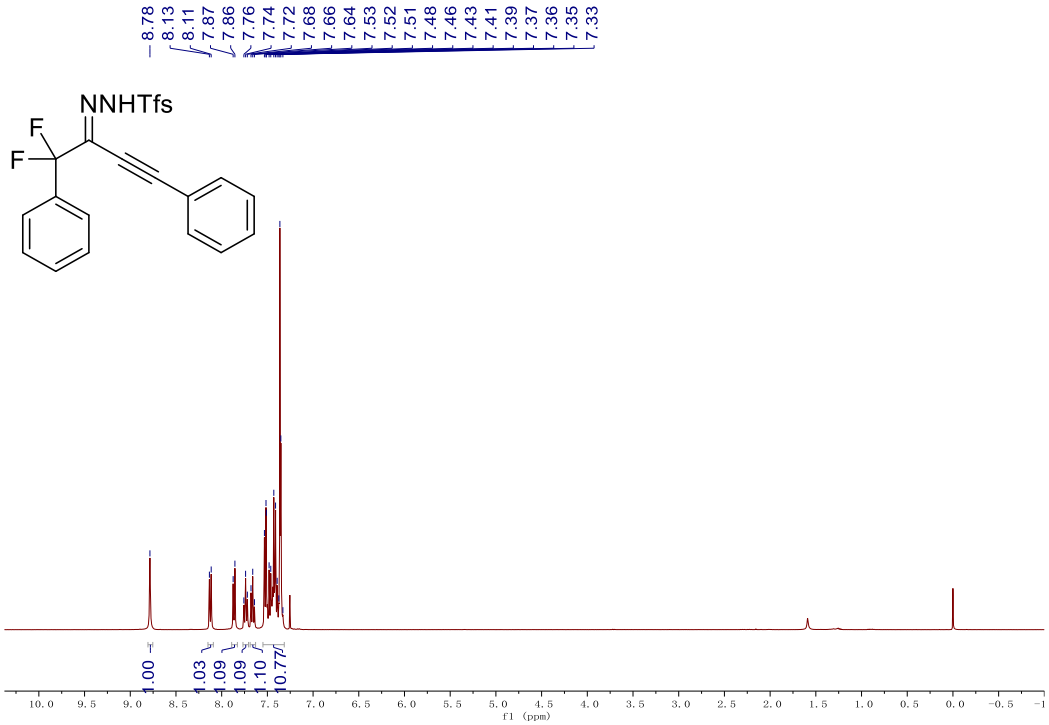


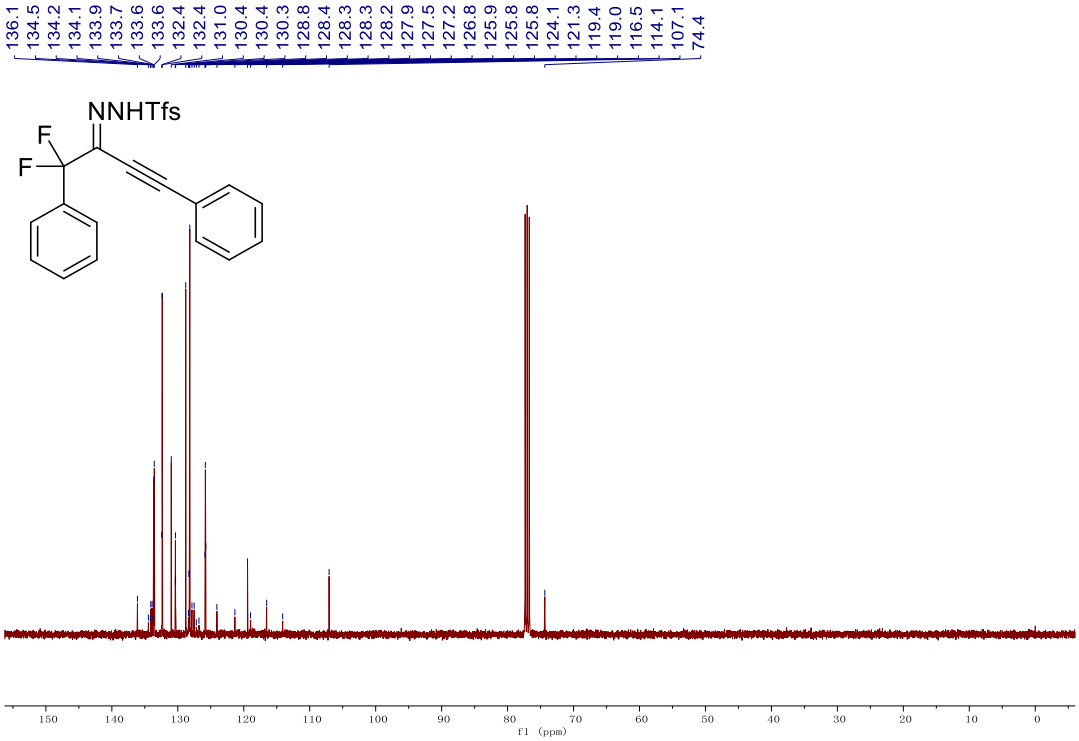
Figure 2. Computed ECD spectrum of (*R*, *S*)-**5b**

12. NMR Spectra for New Compounds

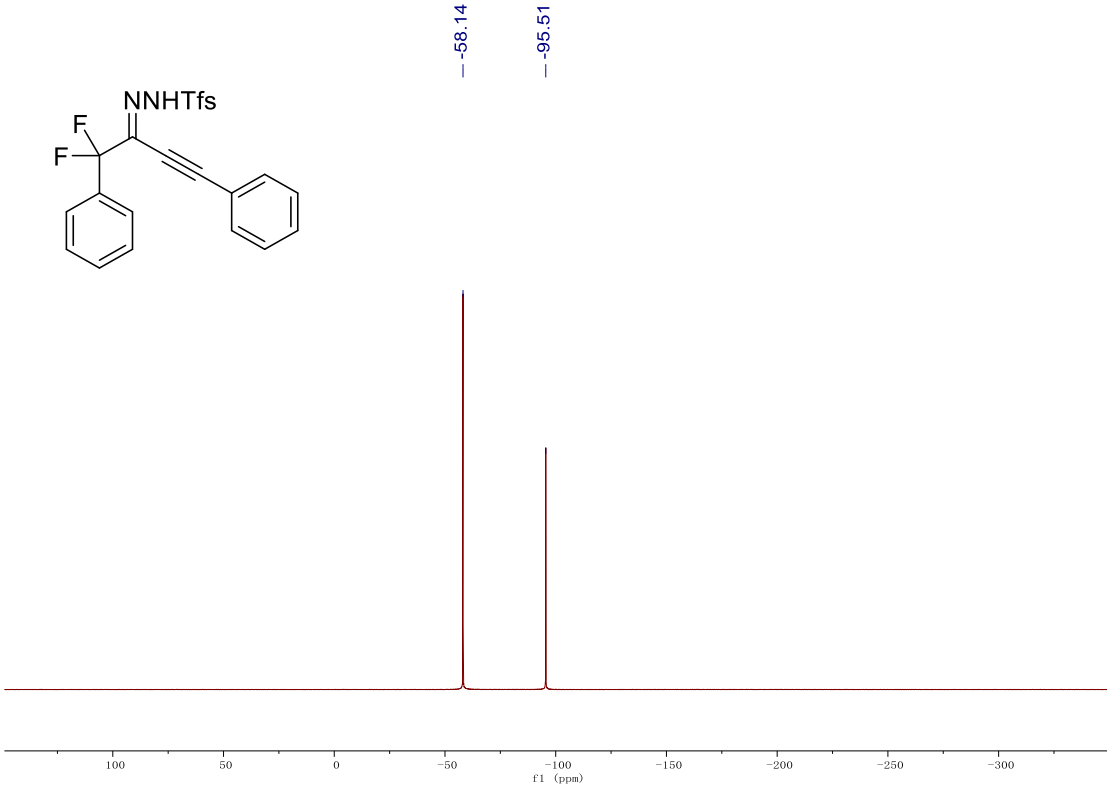
N'-(1,1-difluoro-1,4-diphenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1a): ^{1}H NMR (400 MHz, $CDCl_3$)



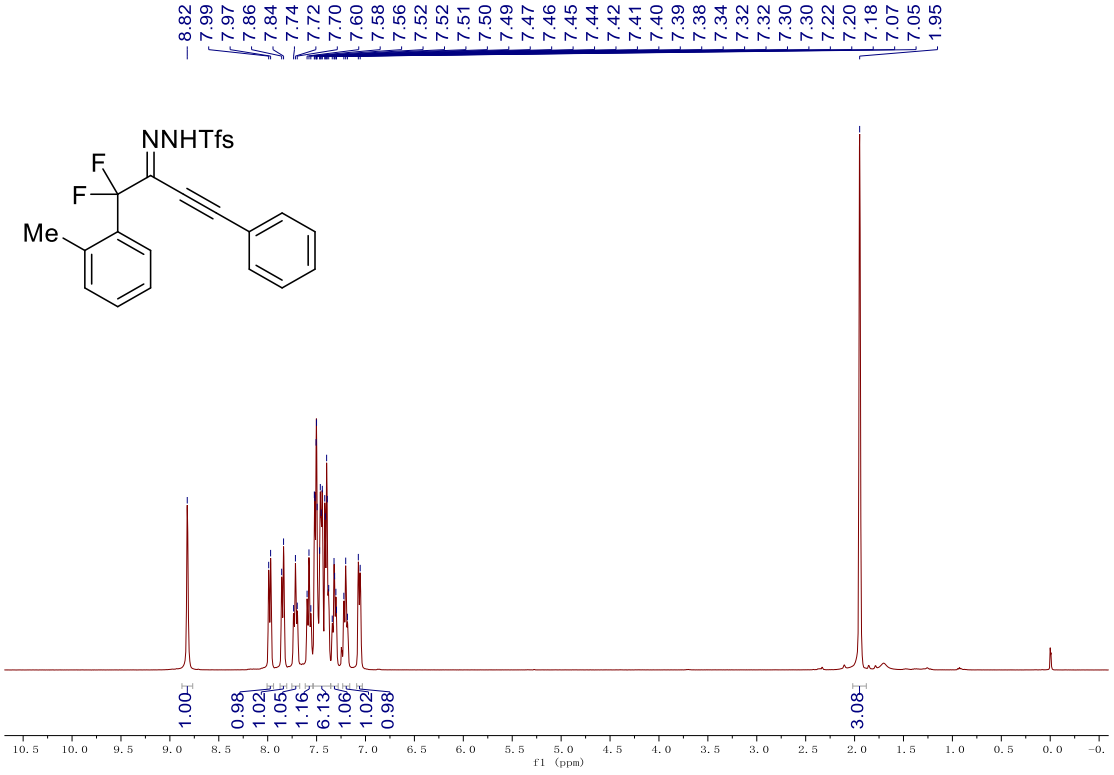
N'-(1,1-difluoro-1,4-diphenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1a): ^{13}C NMR (101 MHz, $CDCl_3$)



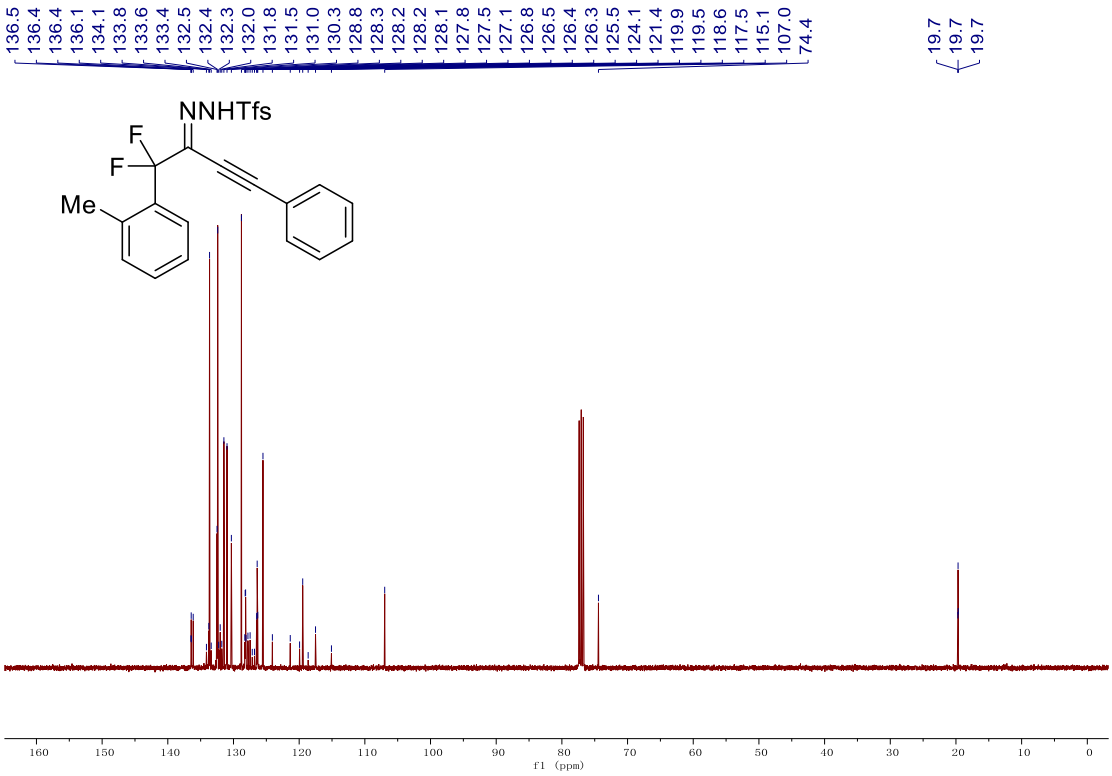
***N*'-(1,1-difluoro-1,4-diphenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1a): ^{19}F NMR (376 MHz, $CDCl_3$)**



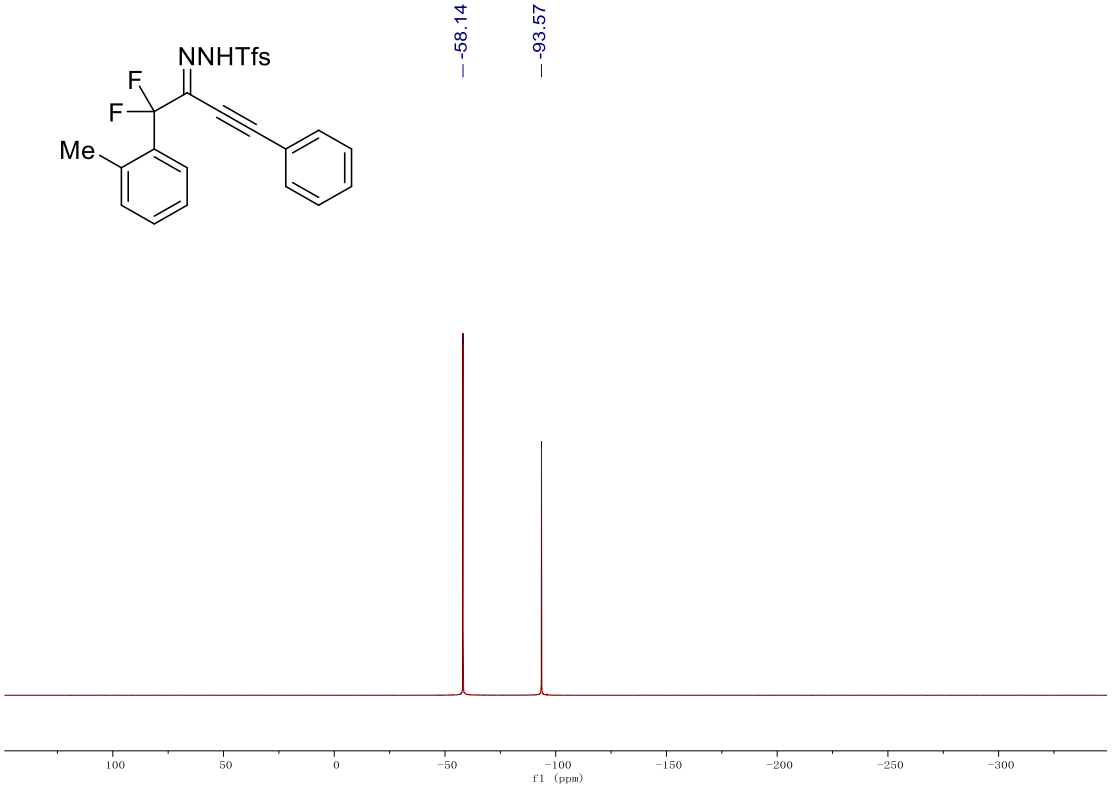
***N*'-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1b): ^{1}H NMR (400 MHz, $CDCl_3$)**



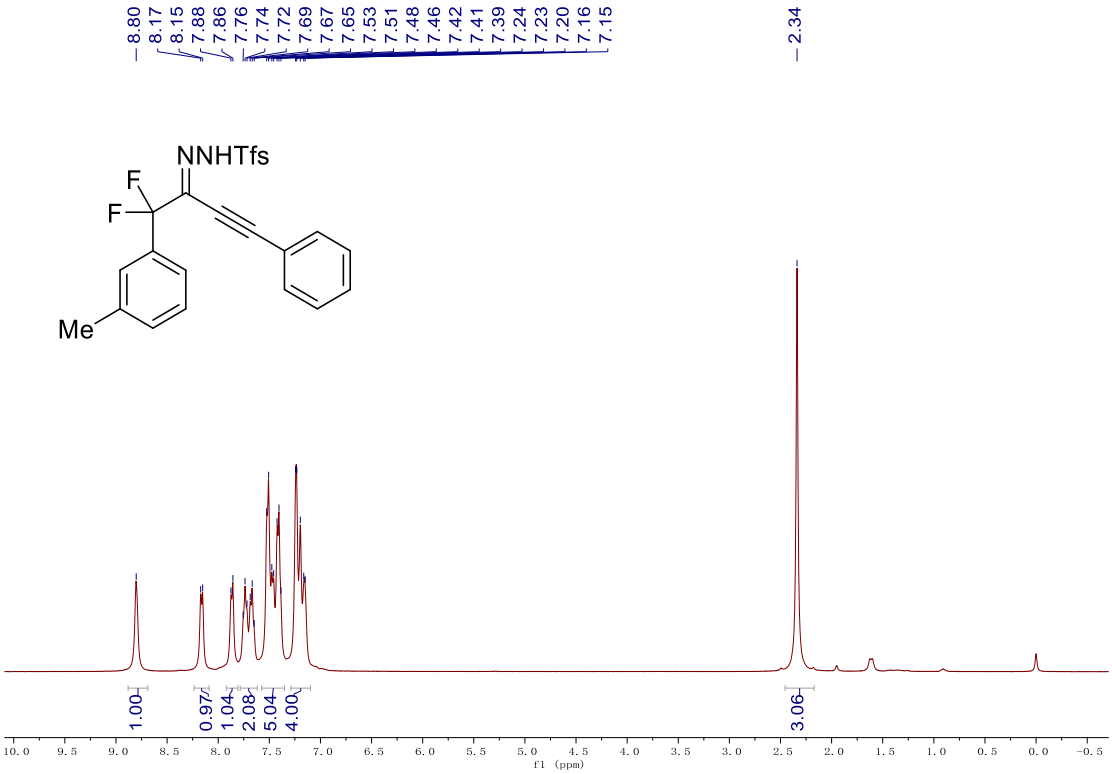
***N*'-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1b): ^{13}C NMR (101 MHz, $CDCl_3$)**



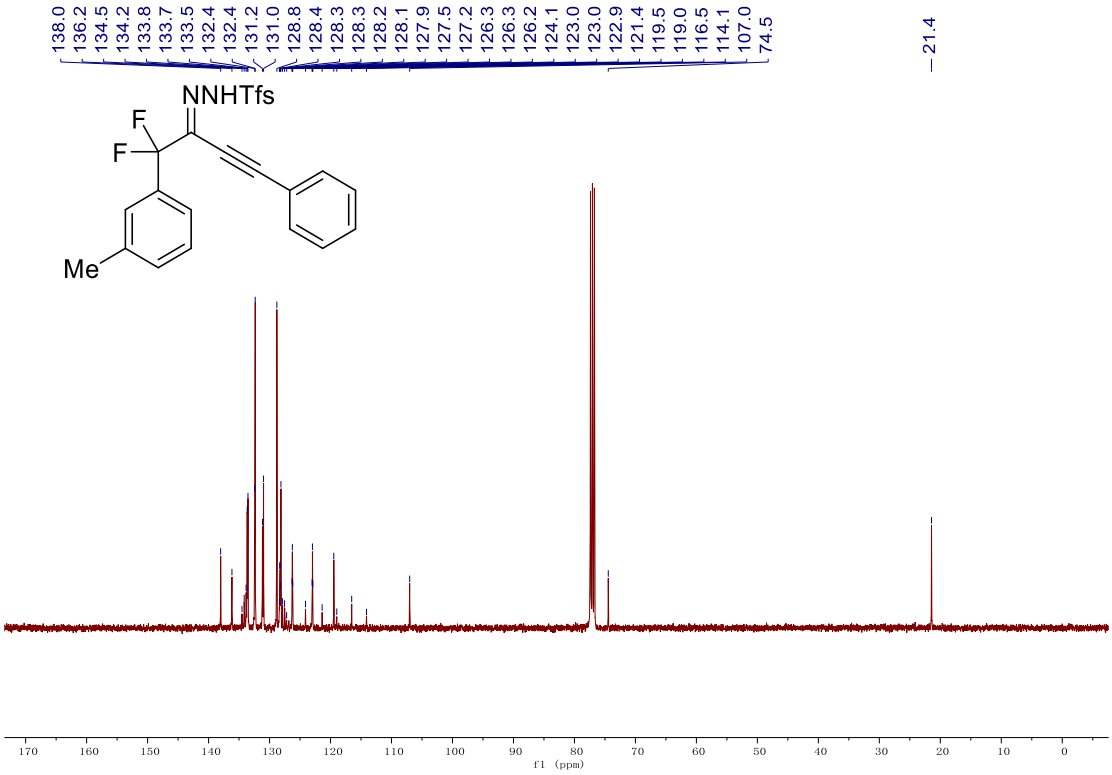
***N*'-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1b): ^{19}F NMR (376 MHz, $CDCl_3$)**



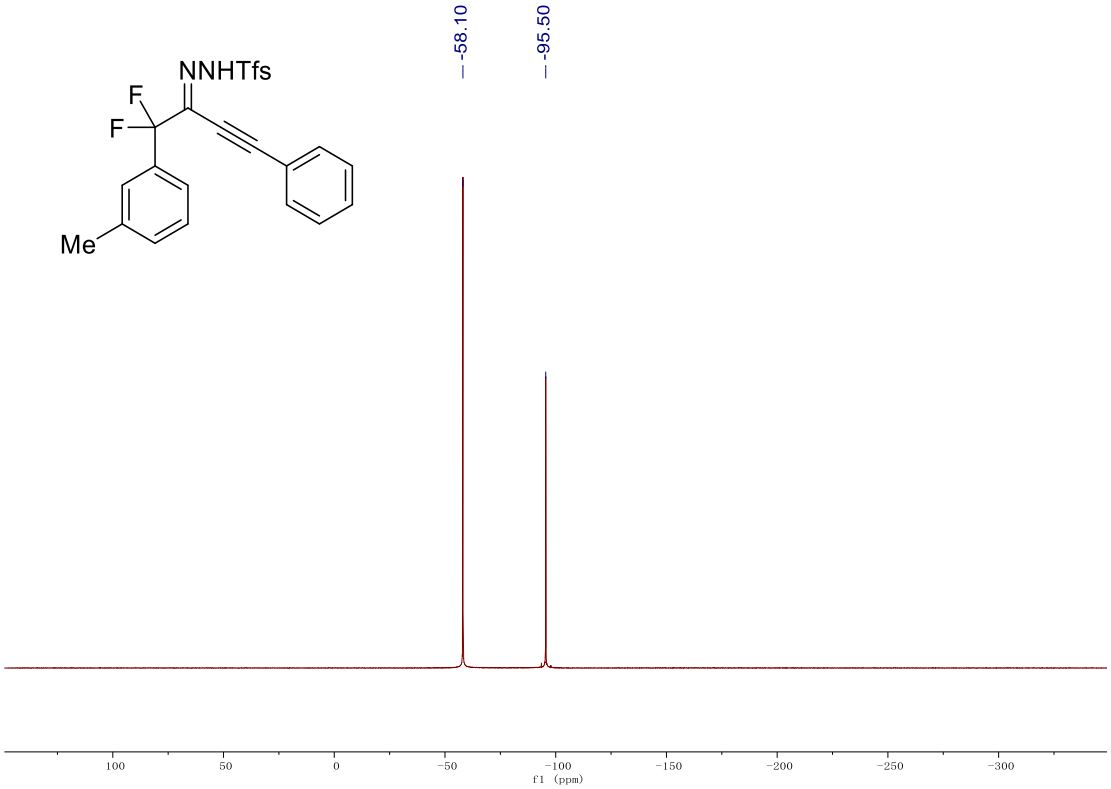
***N*'-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1c): ^{1}H NMR (400 MHz, $CDCl_3$)**



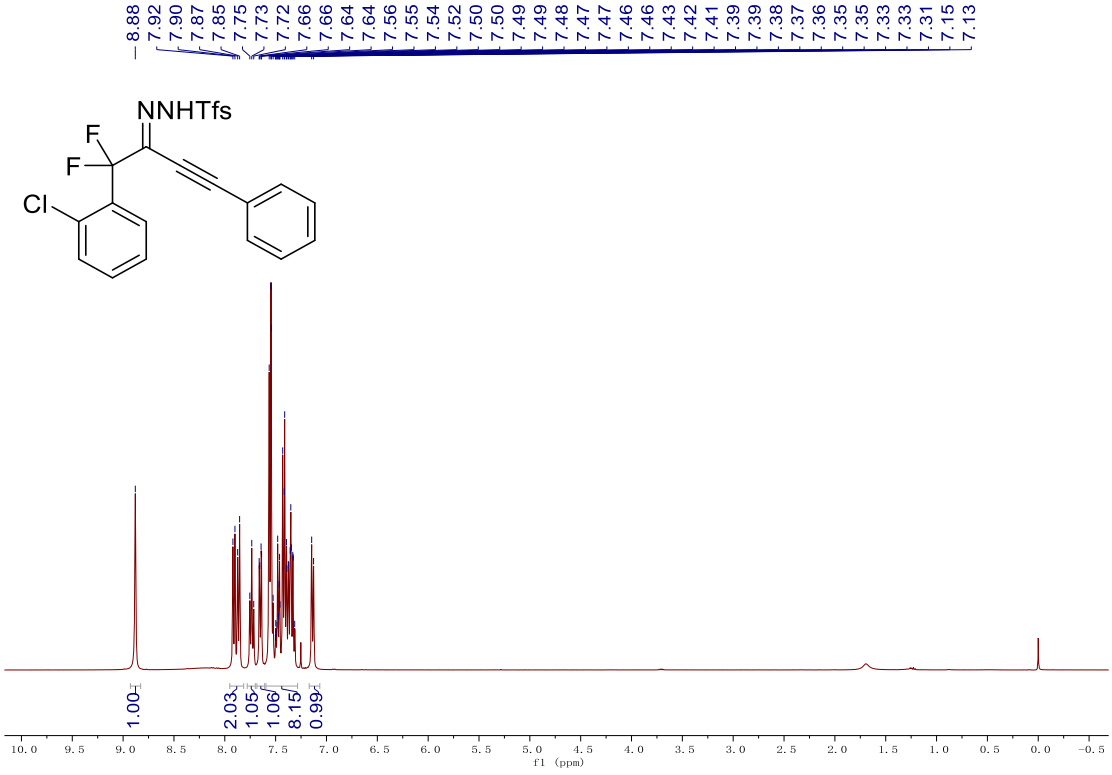
***N*'-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1c): ^{13}C NMR (101 MHz, $CDCl_3$)**



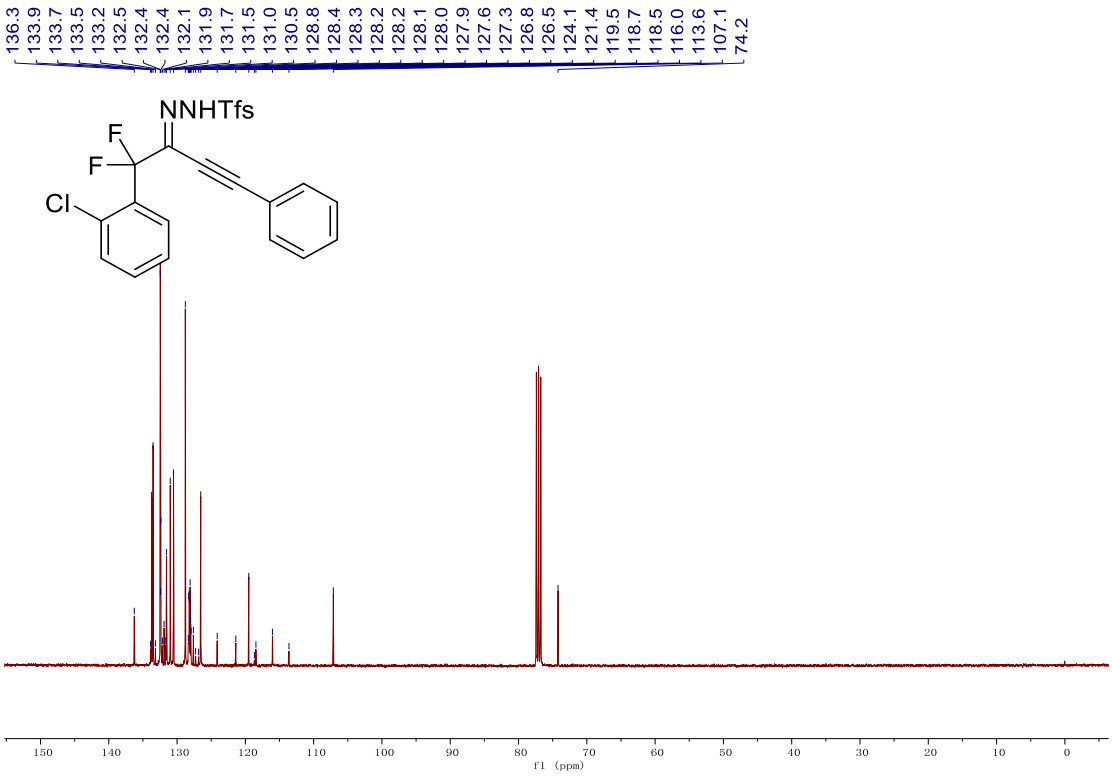
***N*'-(1,1-difluoro-4-phenyl-1-(m-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1c): ^{19}F NMR (376 MHz, $CDCl_3$)**



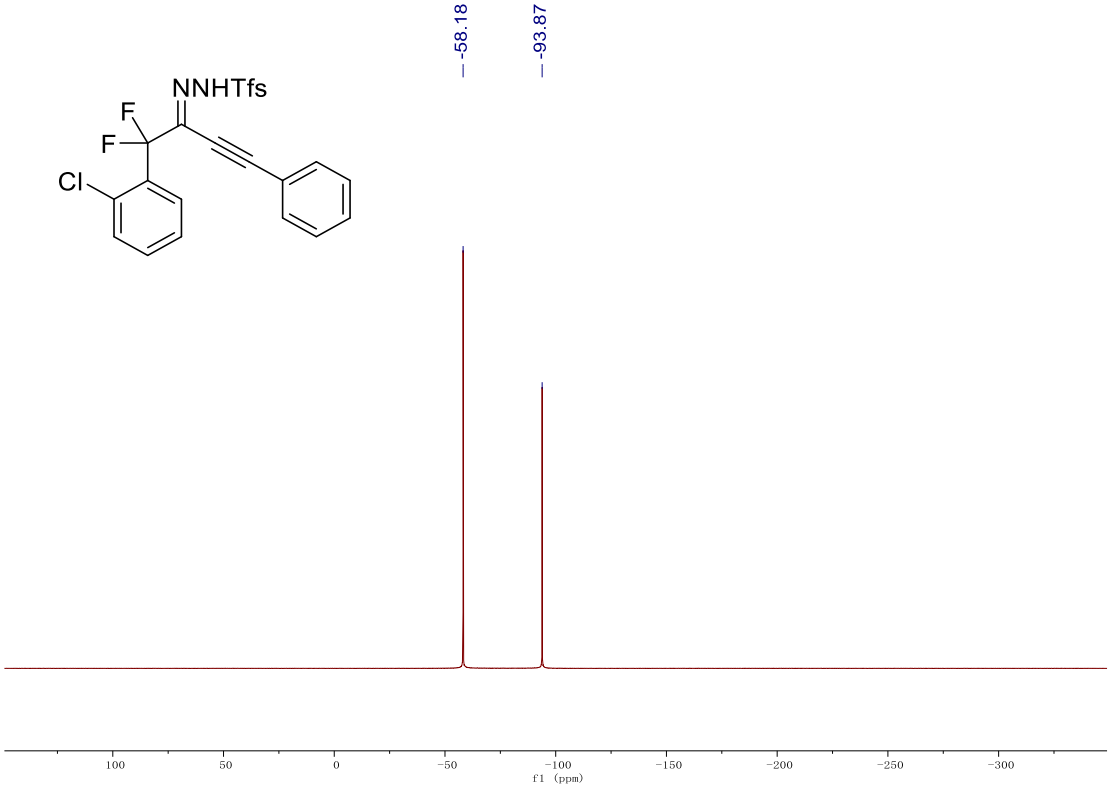
***N*'-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1d): ^{1}H NMR (400 MHz, $CDCl_3$)**



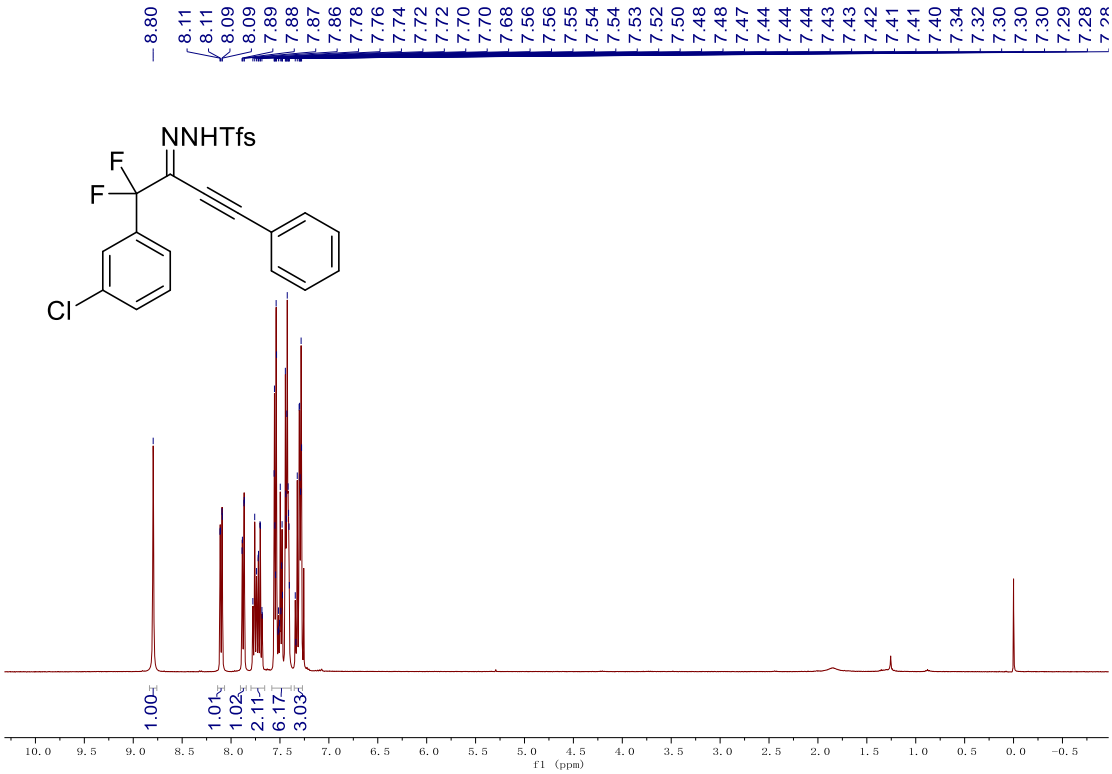
***N*'-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1d): ^{13}C NMR (101 MHz, $CDCl_3$)**



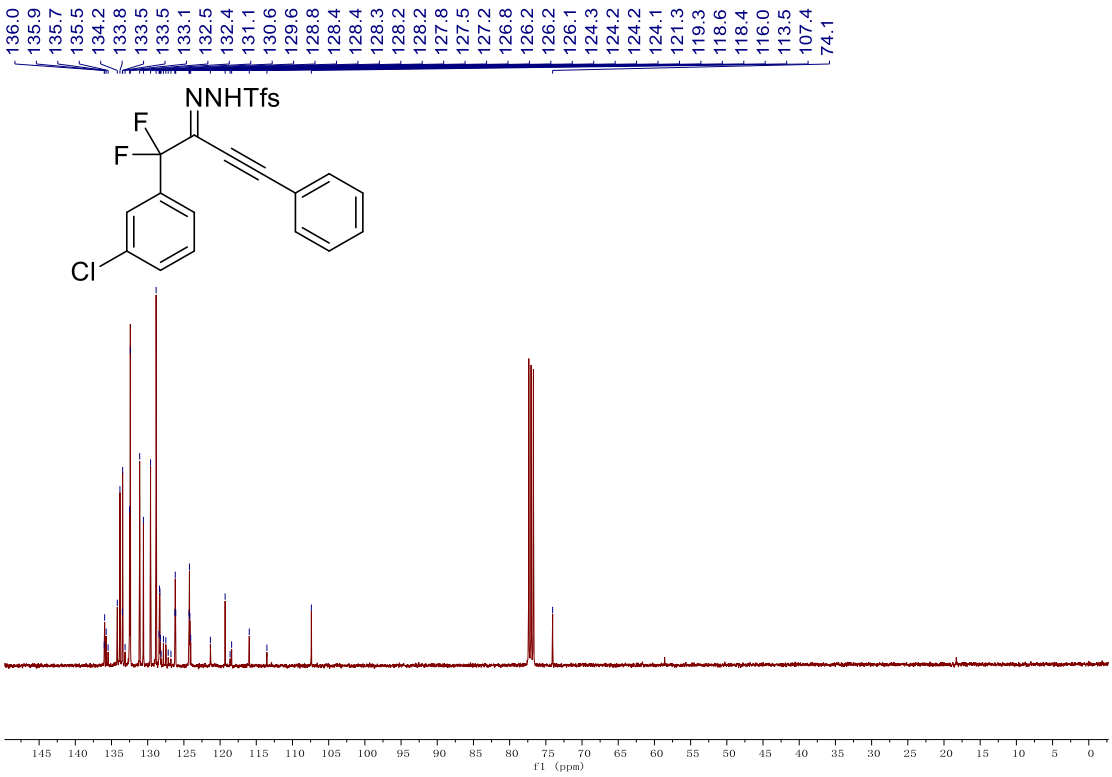
***N*'-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1d): ^{19}F NMR (376 MHz, $CDCl_3$)**



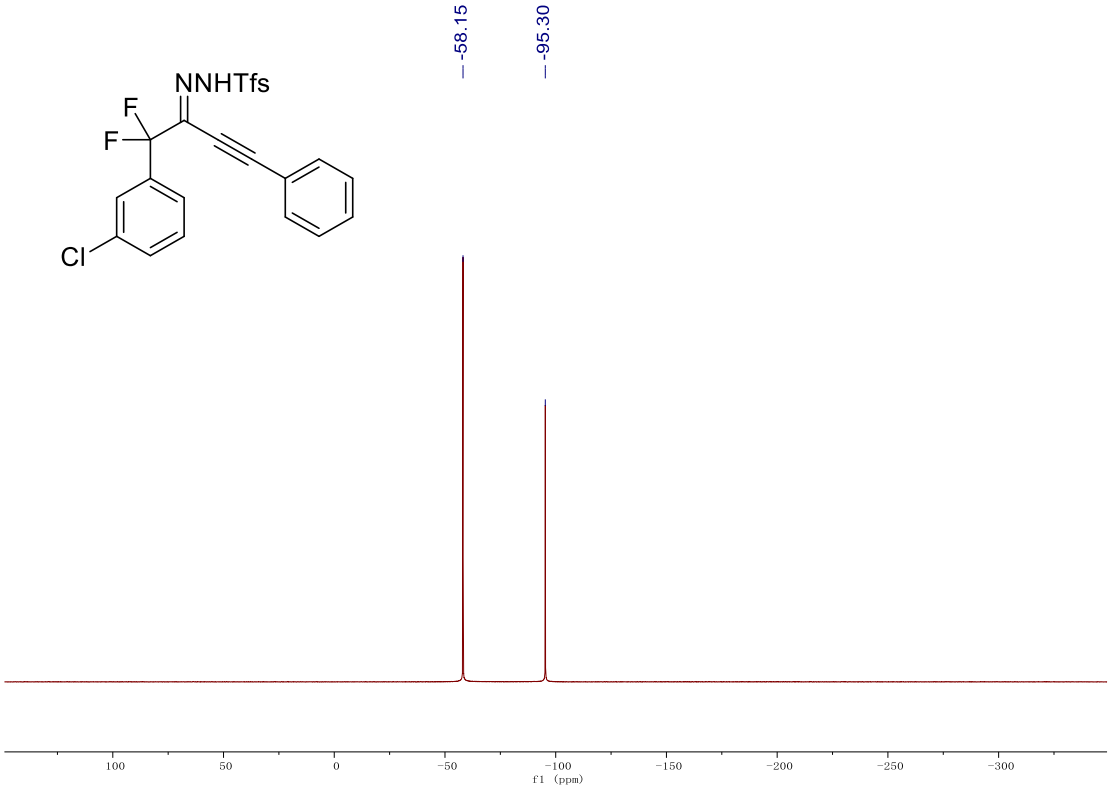
***N*'-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1e): ^{1}H NMR (400 MHz, $CDCl_3$)**



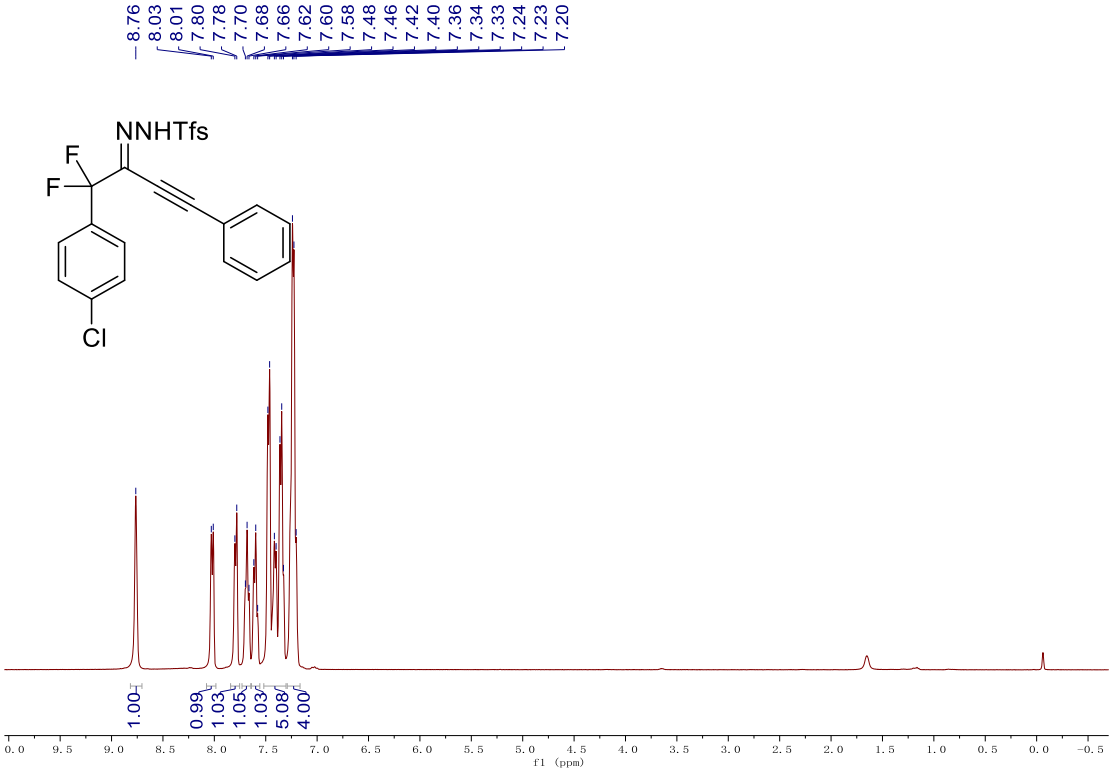
***N*'-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1e): ^{13}C NMR (101 MHz, $CDCl_3$)**



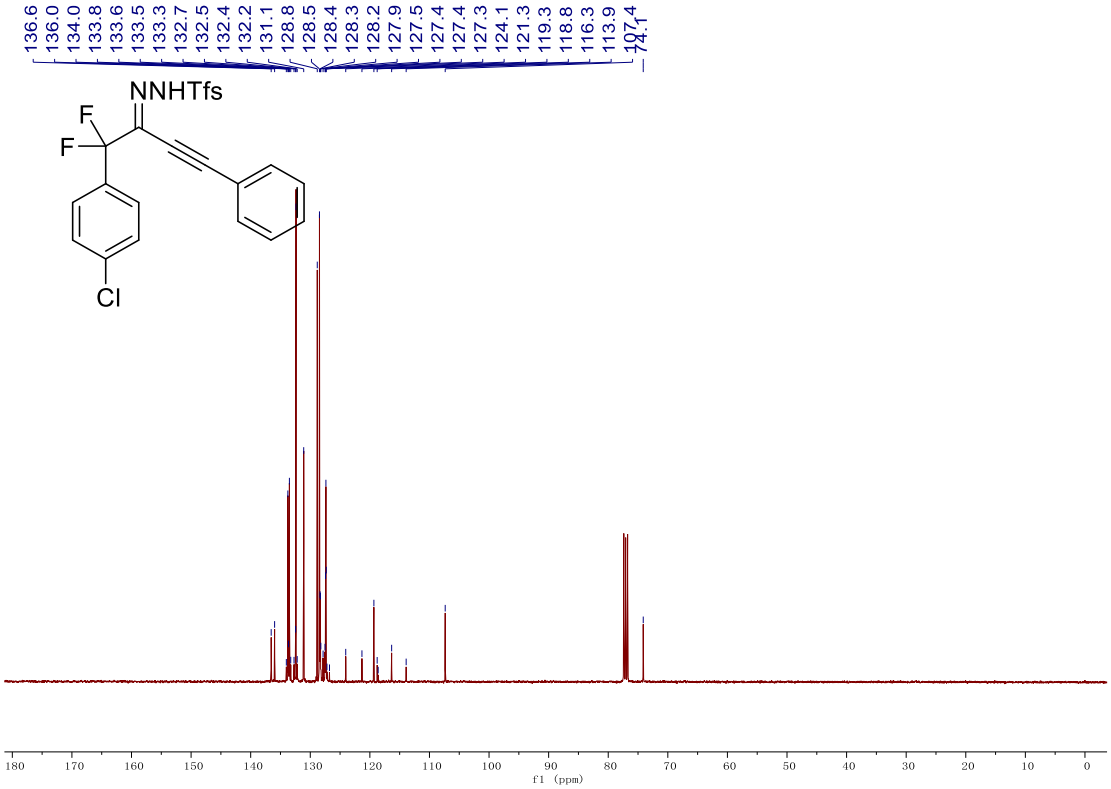
***N*'-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1e): ^{19}F NMR (376 MHz, $CDCl_3$)**



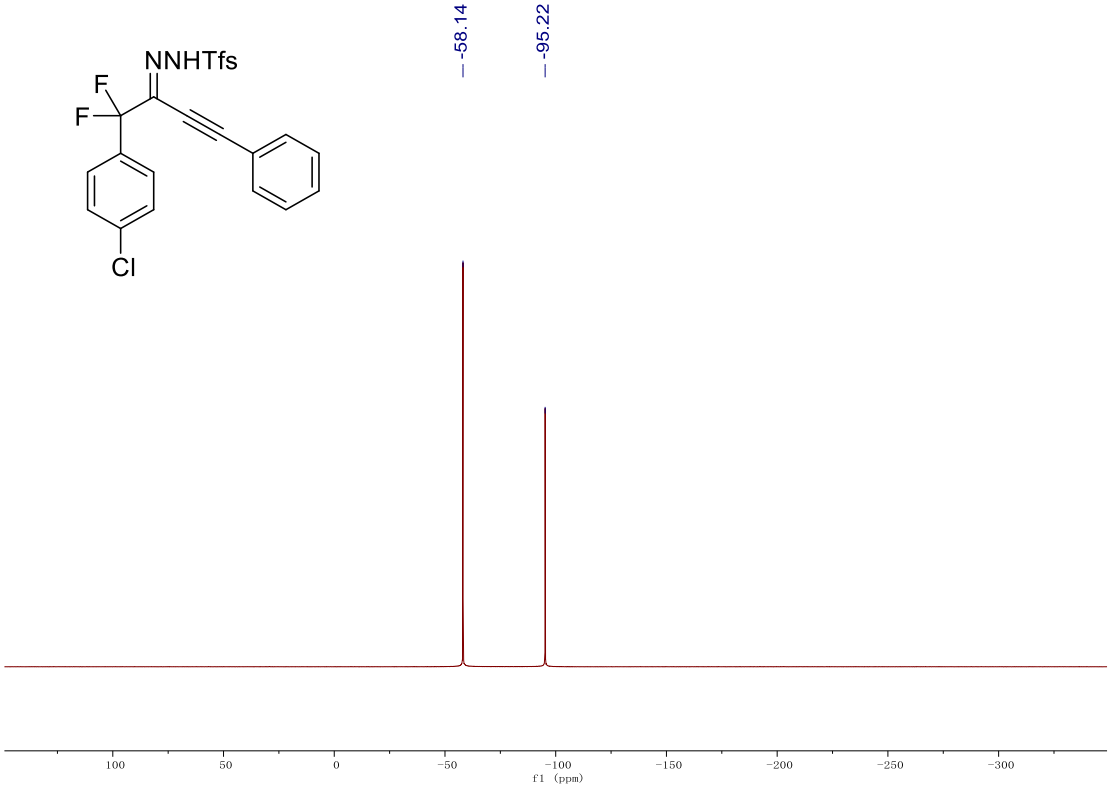
***N*'-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1f): ^{1}H NMR (400 MHz, $CDCl_3$)**



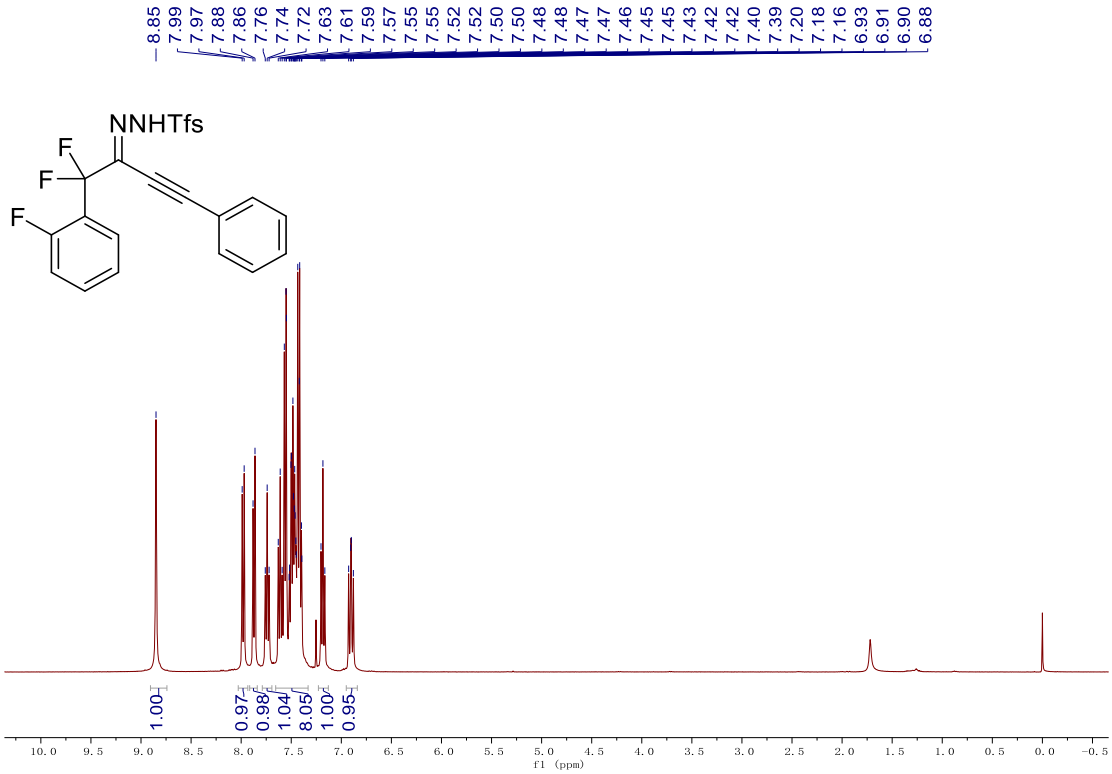
***N*'-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1f): ^{13}C NMR (101 MHz, $CDCl_3$)**



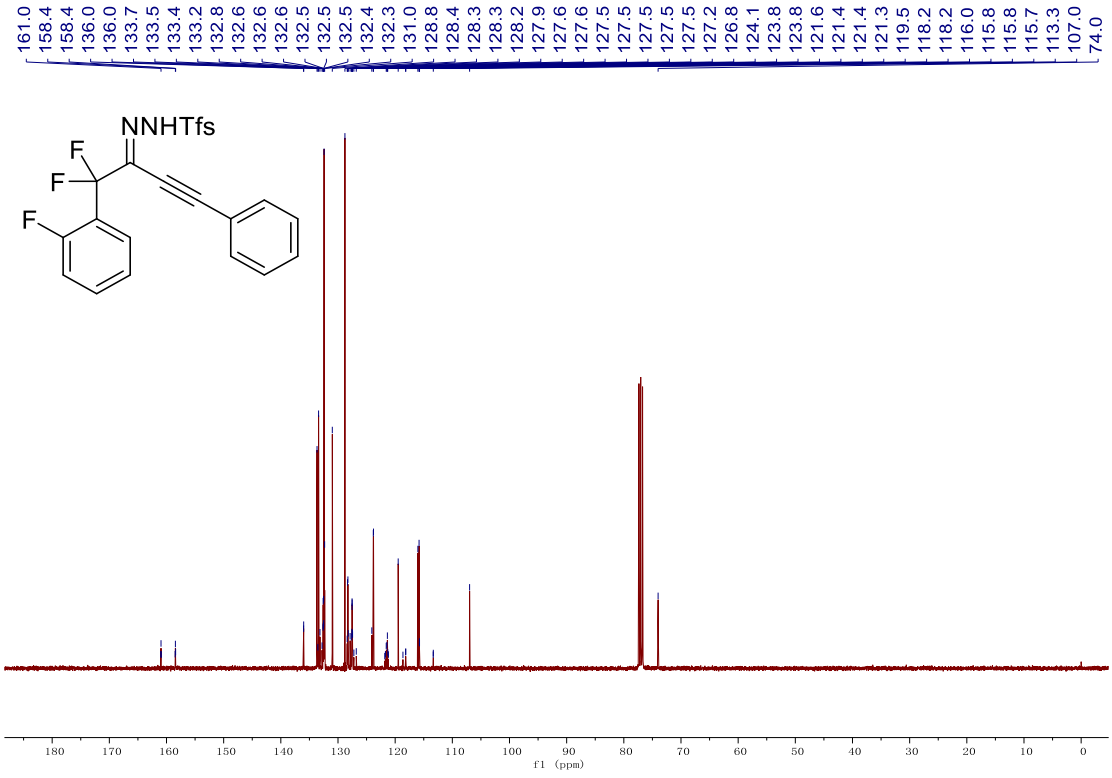
***N*'-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1f): ^{19}F NMR (376 MHz, $CDCl_3$)**



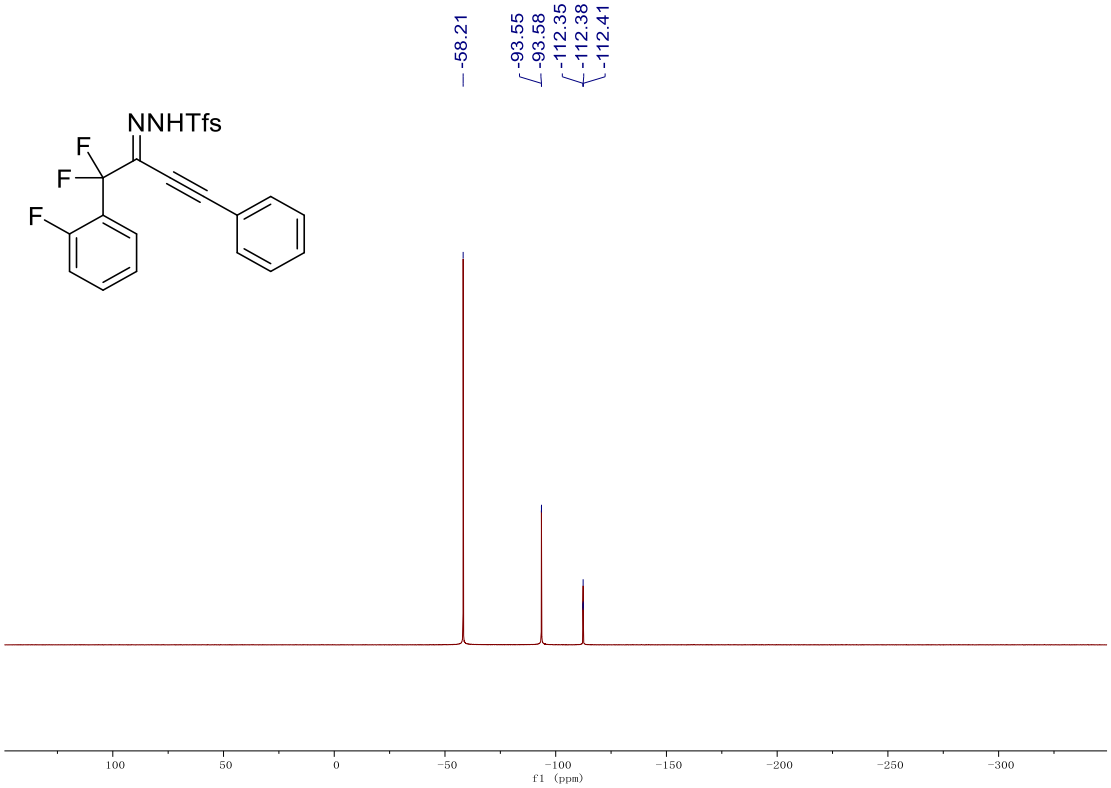
***N*'-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1g): ^{1}H NMR (400 MHz, $CDCl_3$)**



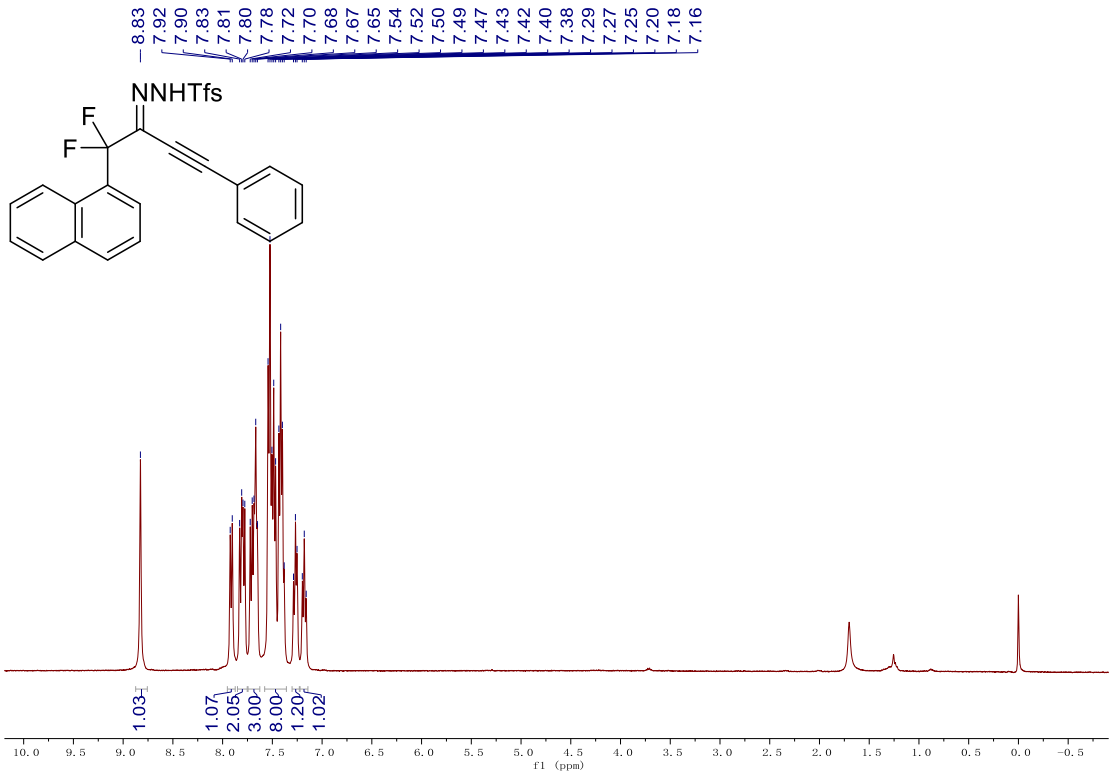
***N*'-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1g): ^{13}C NMR (101 MHz, $CDCl_3$)**



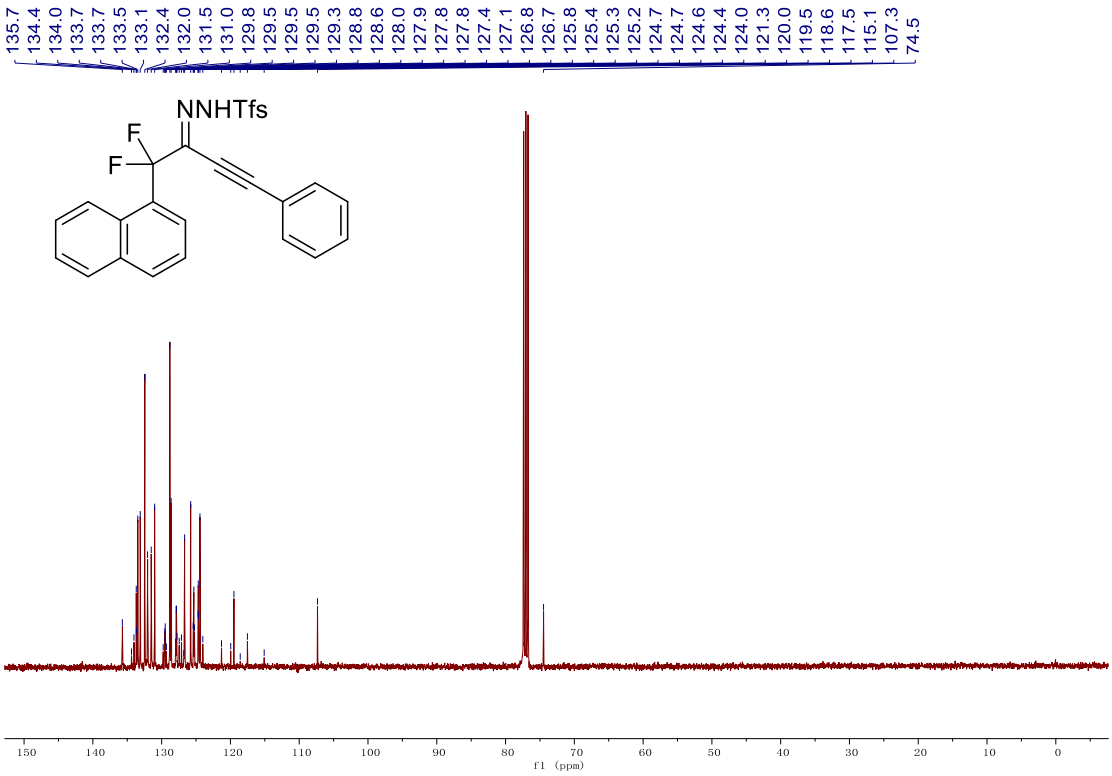
***N*'-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1g): ^{19}F NMR (376 MHz, $CDCl_3$)**



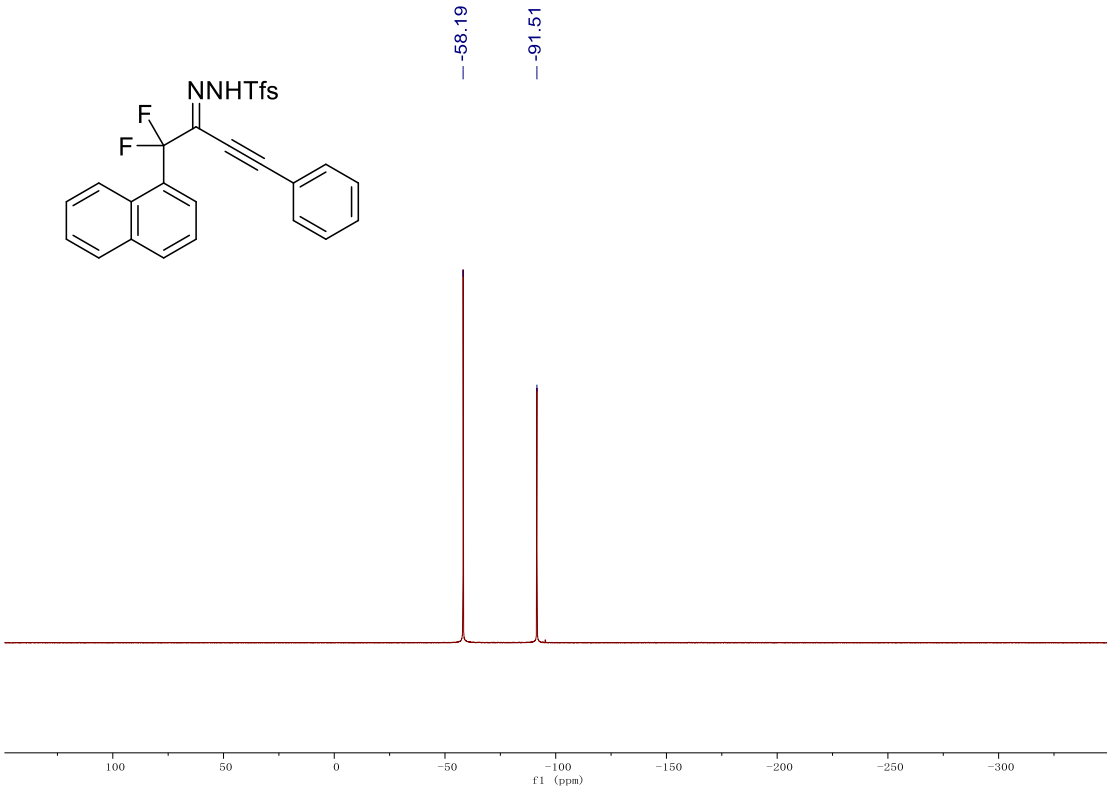
***N*'-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1h): ^{1}H NMR (400 MHz, $CDCl_3$)**



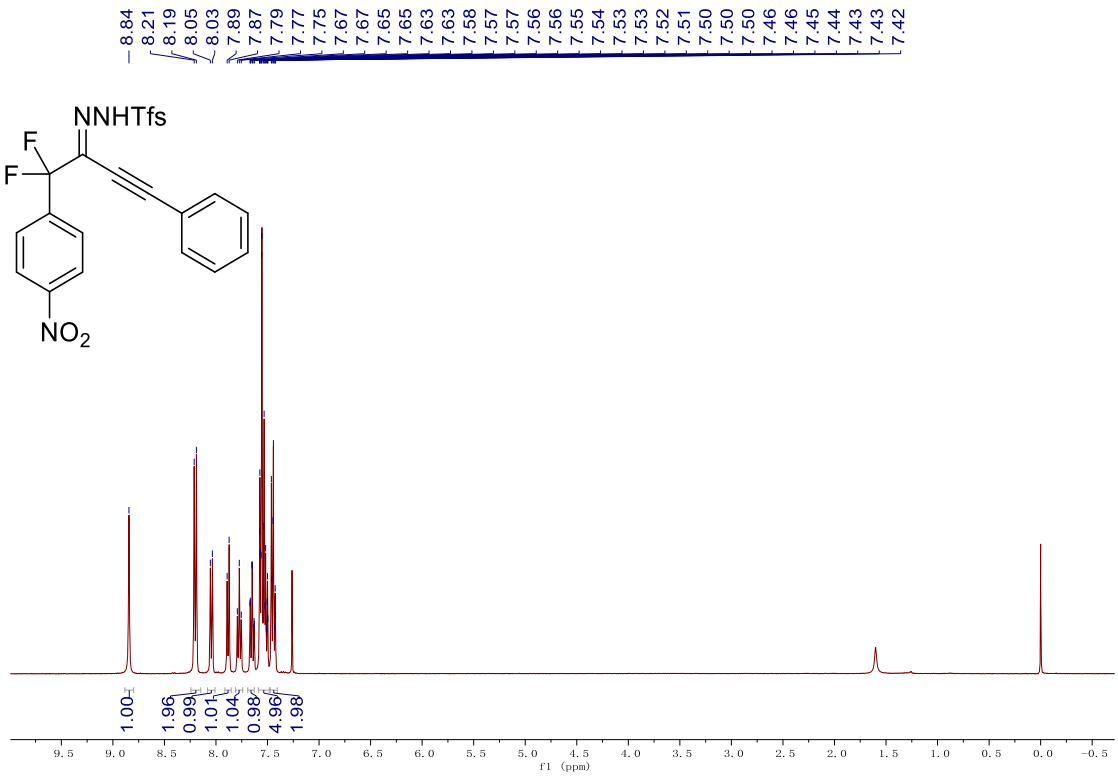
***N*'-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1h): ^{13}C NMR (101 MHz, $CDCl_3$)**



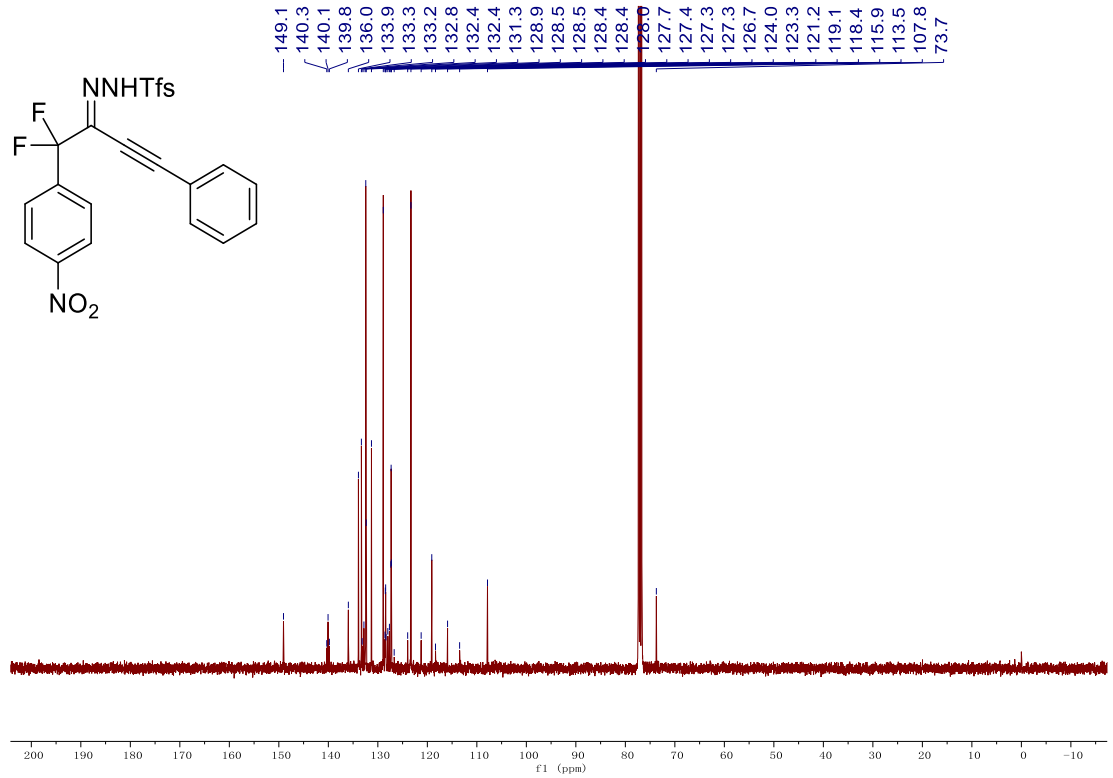
***N*'-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1h): ^{19}F NMR (376 MHz, $CDCl_3$)**



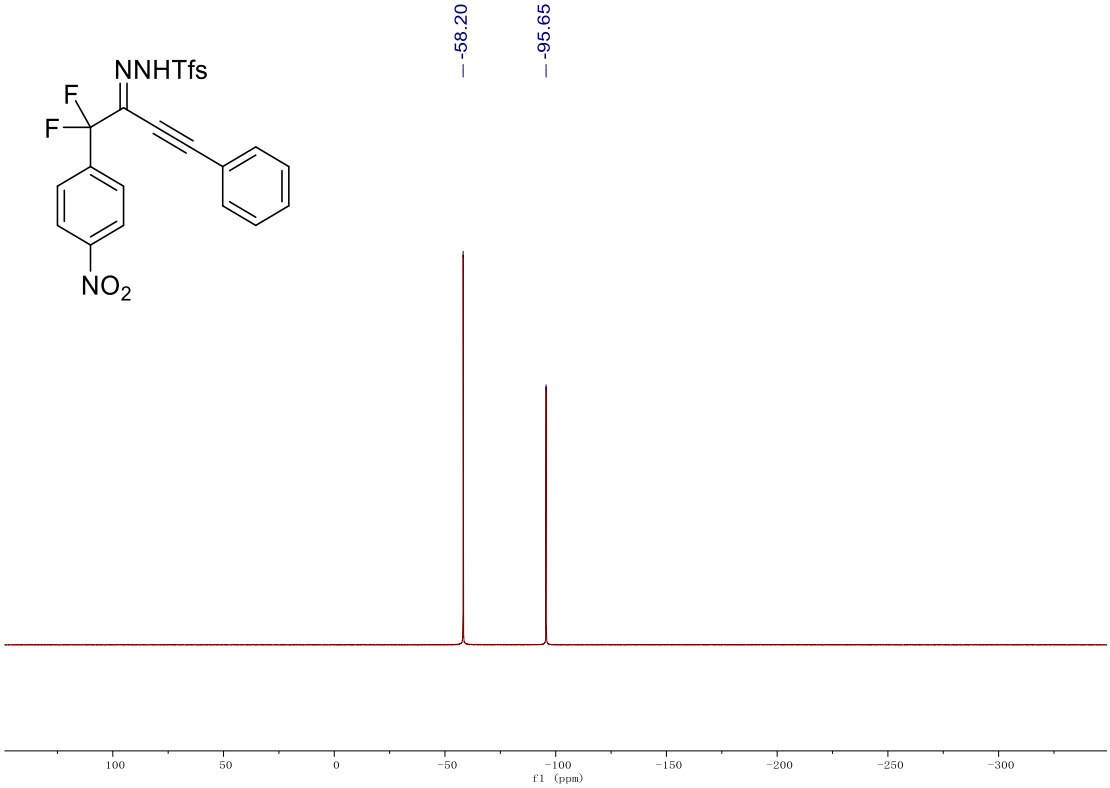
***N*'-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1i): ^{1}H NMR (400 MHz, $CDCl_3$)**



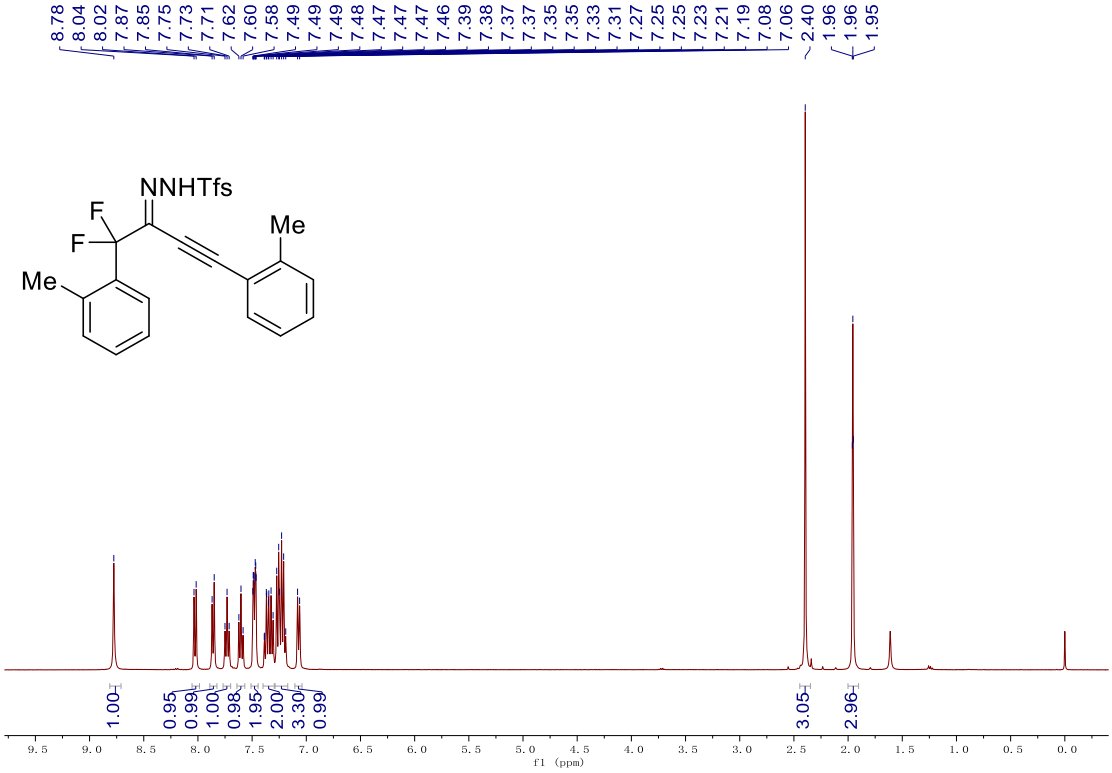
***N*'-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1i): ^{13}C NMR (101 MHz, $CDCl_3$)**



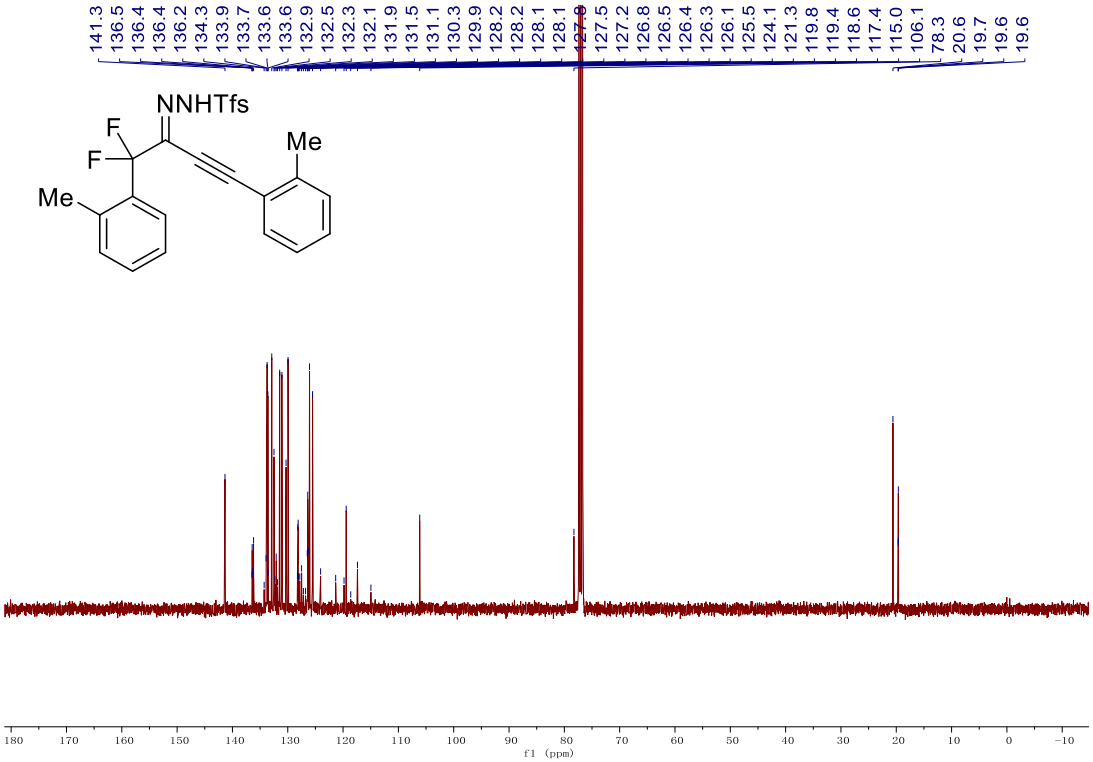
***N*'-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1i): ^{19}F NMR (376 MHz, $CDCl_3$)**



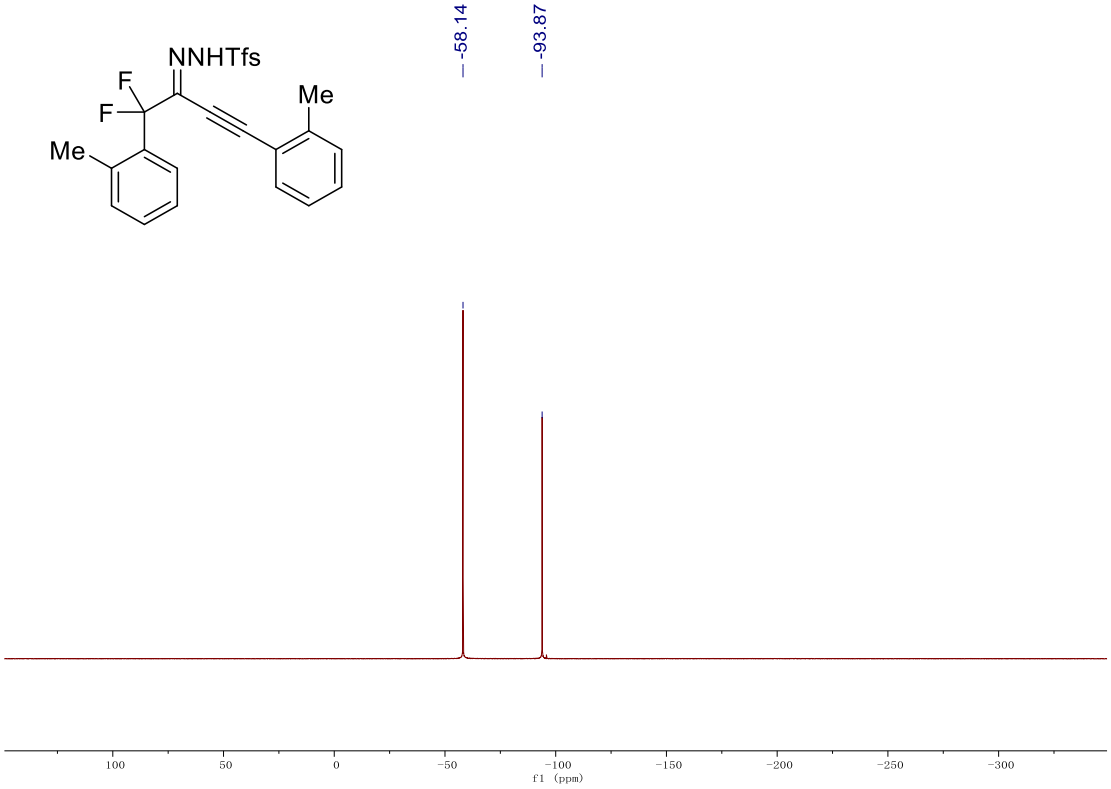
***N*'-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1j): ^{1}H NMR (400 MHz, $CDCl_3$)**



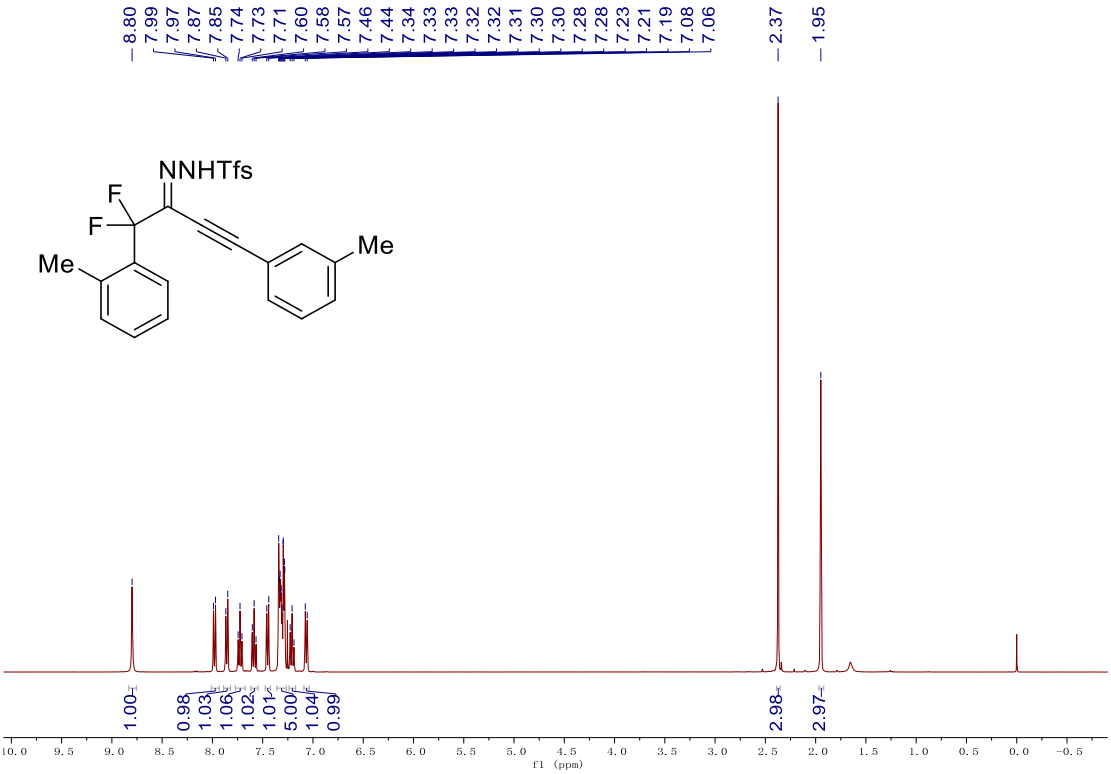
***N*'-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1j): ^{13}C NMR (101 MHz, $CDCl_3$)**



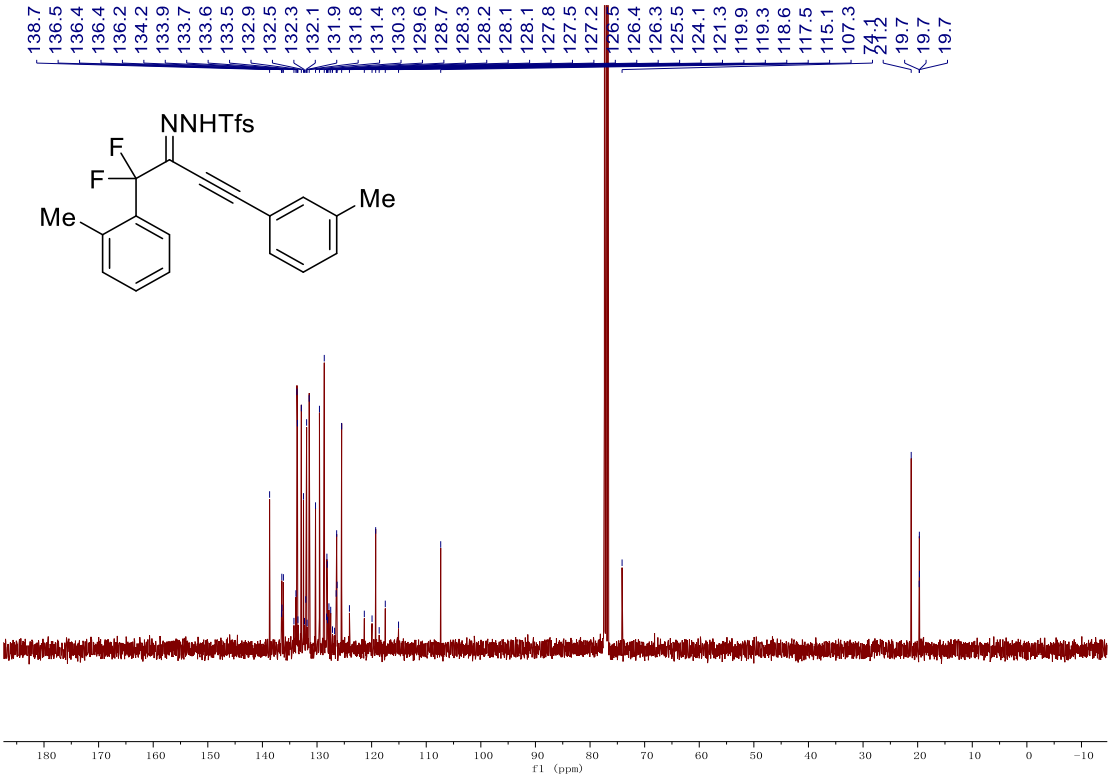
***N*'-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1j): ^{19}F NMR (376 MHz, $CDCl_3$)**



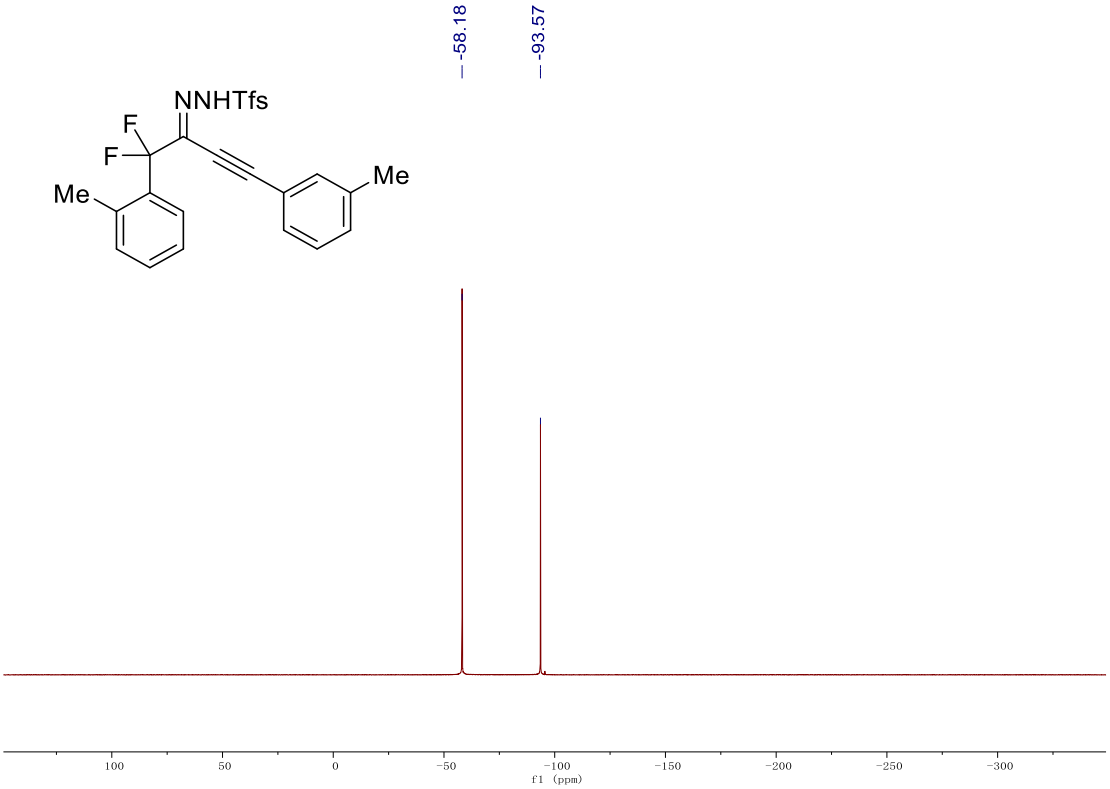
***N*'-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1k): ^{1}H NMR (400 MHz, $CDCl_3$)**



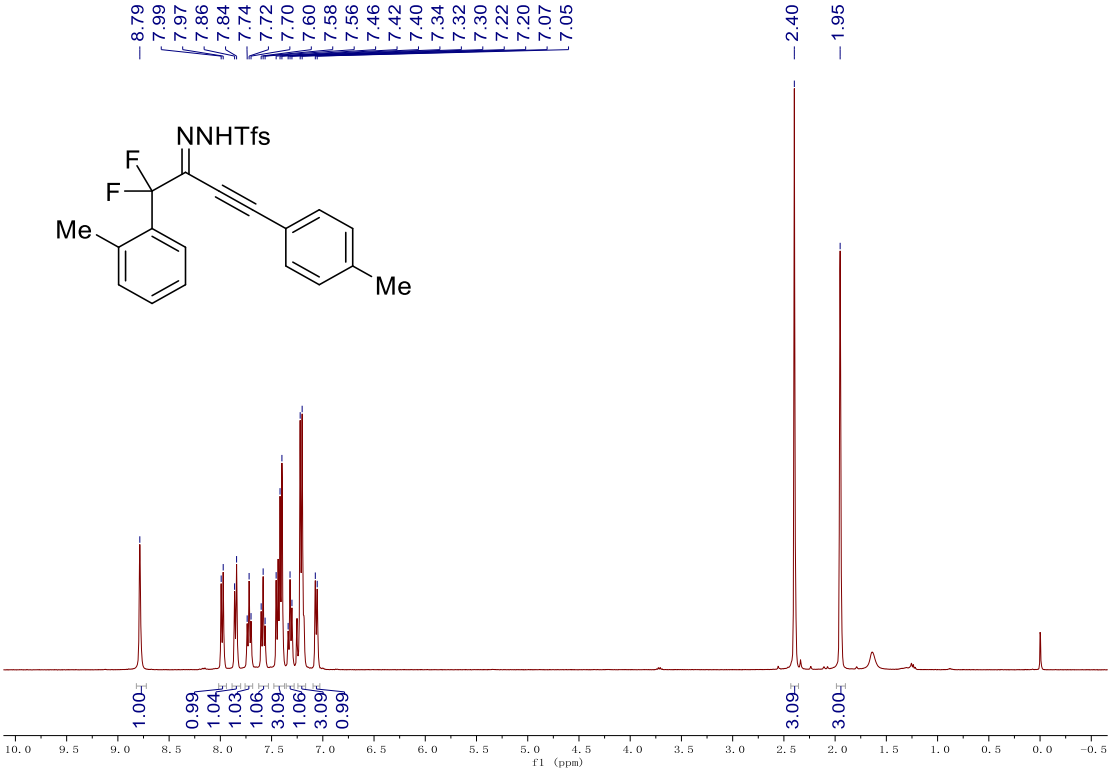
***N*'-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1k): ^{13}C NMR (101 MHz, $CDCl_3$)**



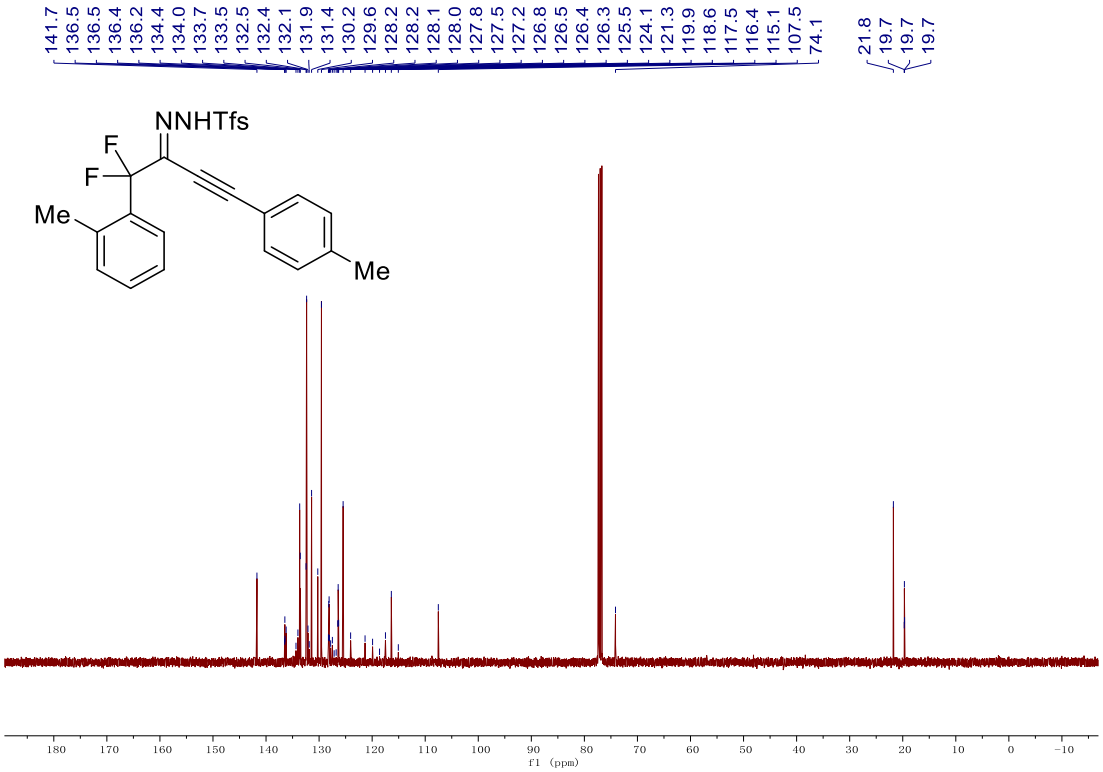
***N*'-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1k): ^{19}F NMR (376 MHz, $CDCl_3$)**



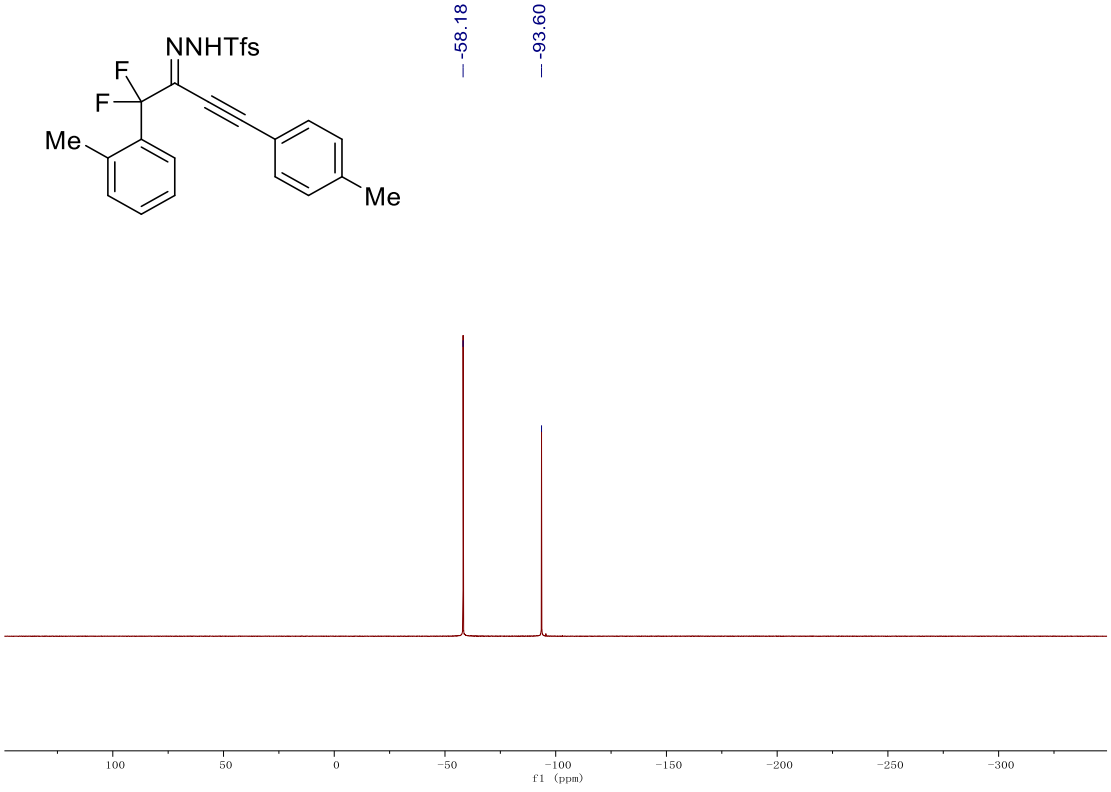
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1l): ^{1}H NMR (400 MHz, $CDCl_3$)**



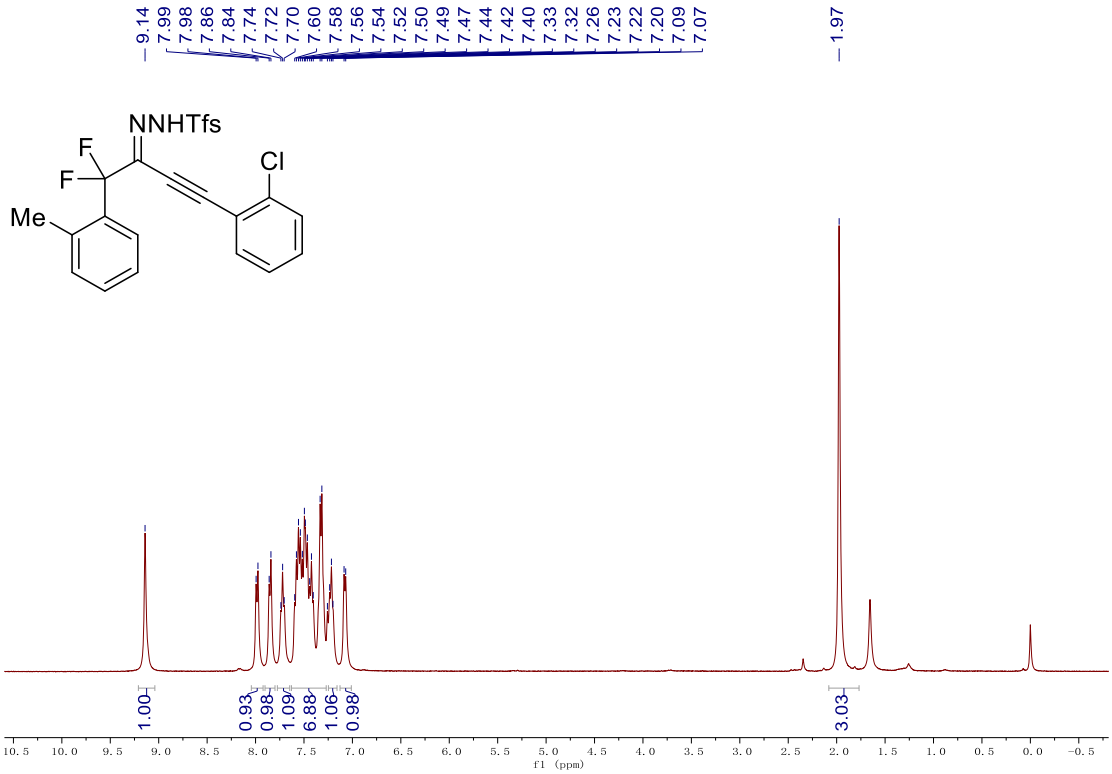
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1l): ^{13}C NMR (101 MHz, $CDCl_3$)**



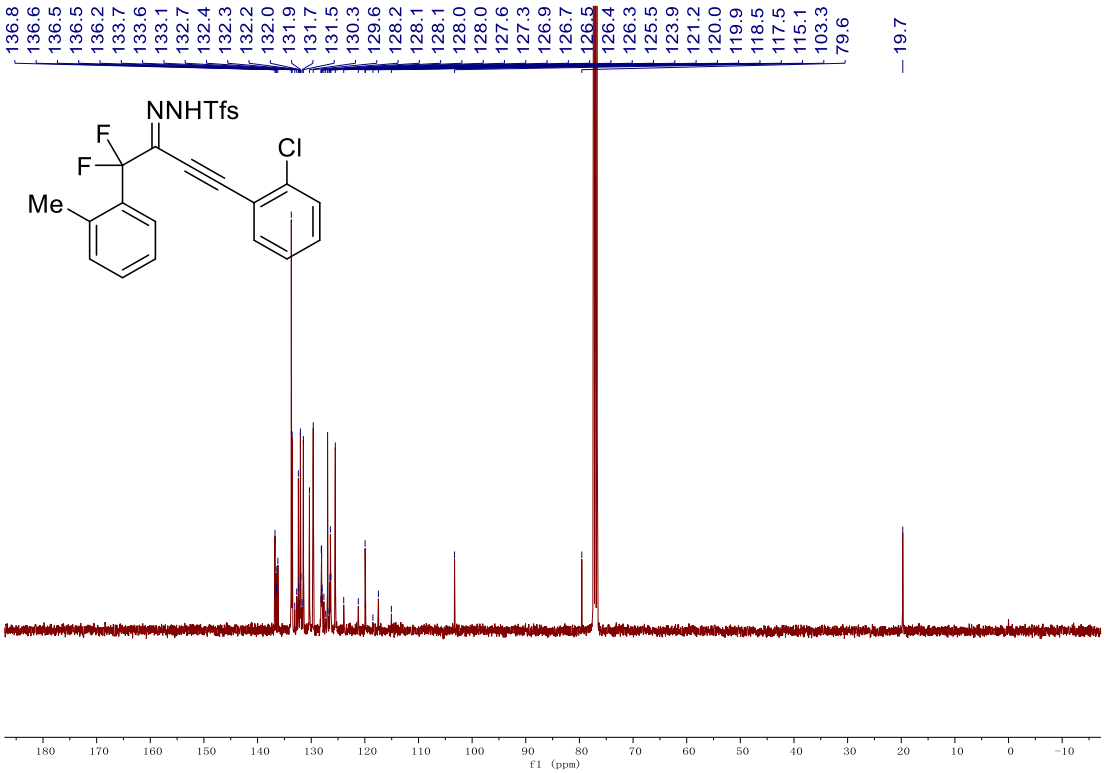
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1l): ^{19}F NMR (376 MHz, $CDCl_3$)**



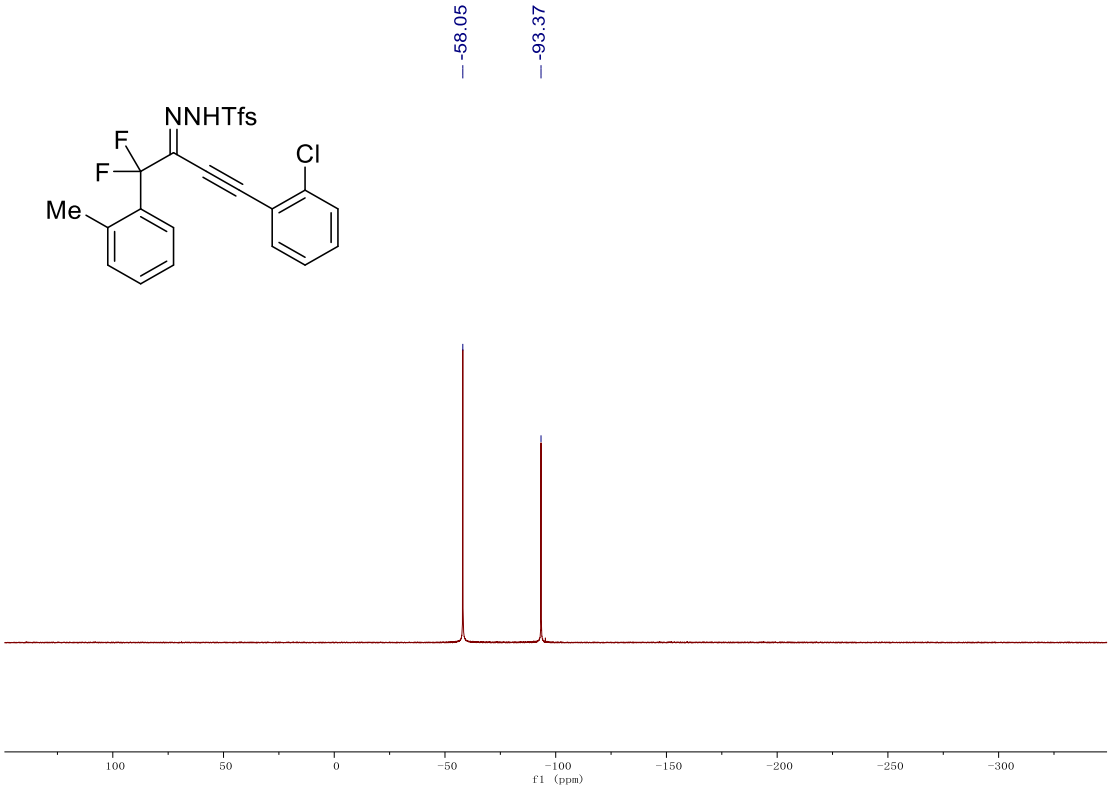
***N*'-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1m): ^{1}H NMR (400 MHz, $CDCl_3$)**



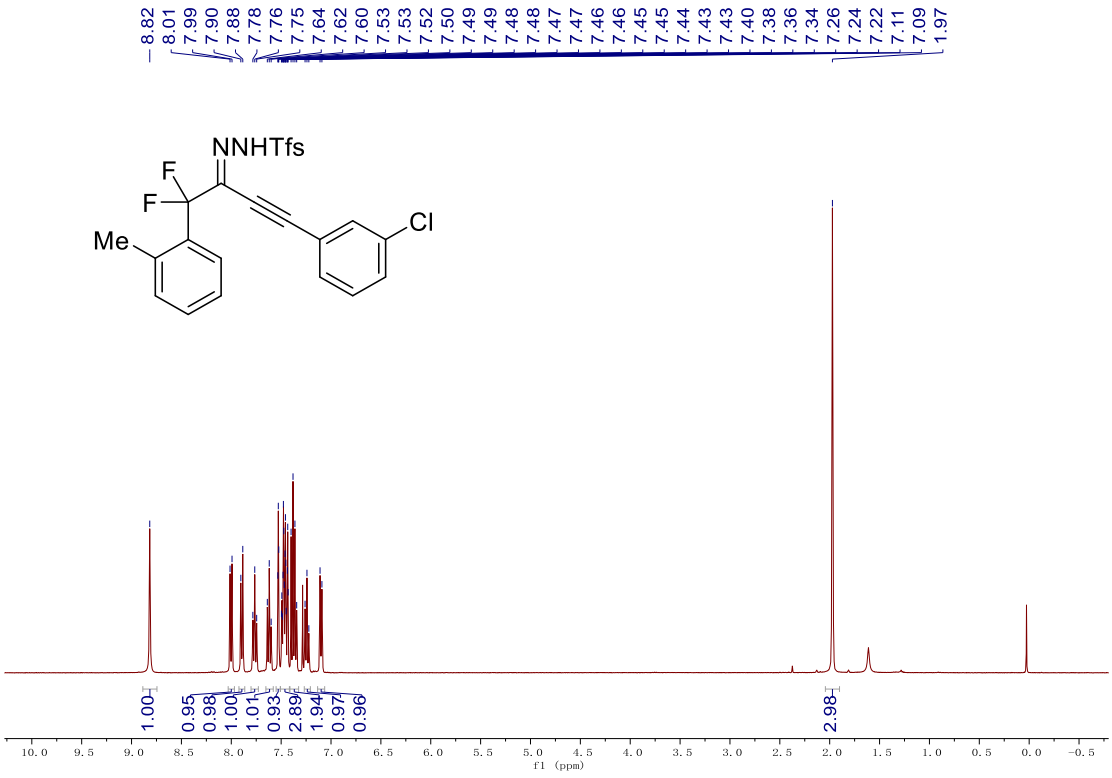
***N*'-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1m): ^{13}C NMR (101 MHz, $CDCl_3$)**



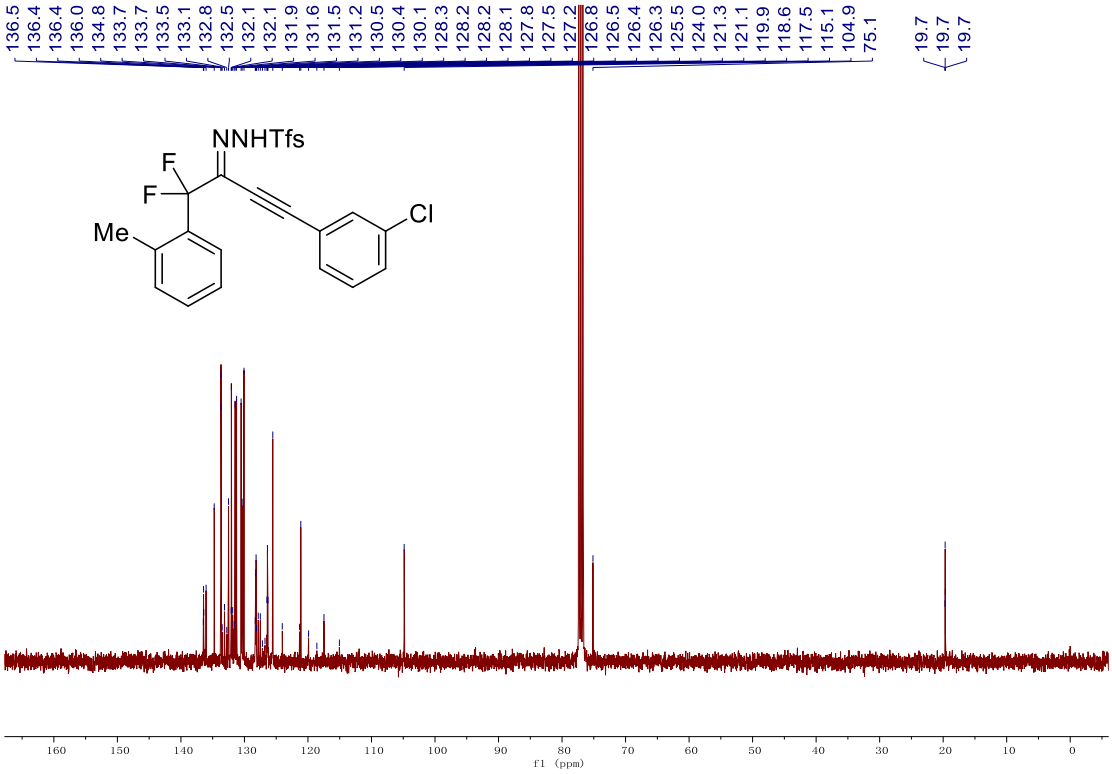
***N*'-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1m): ^{19}F NMR (376 MHz, $CDCl_3$)**



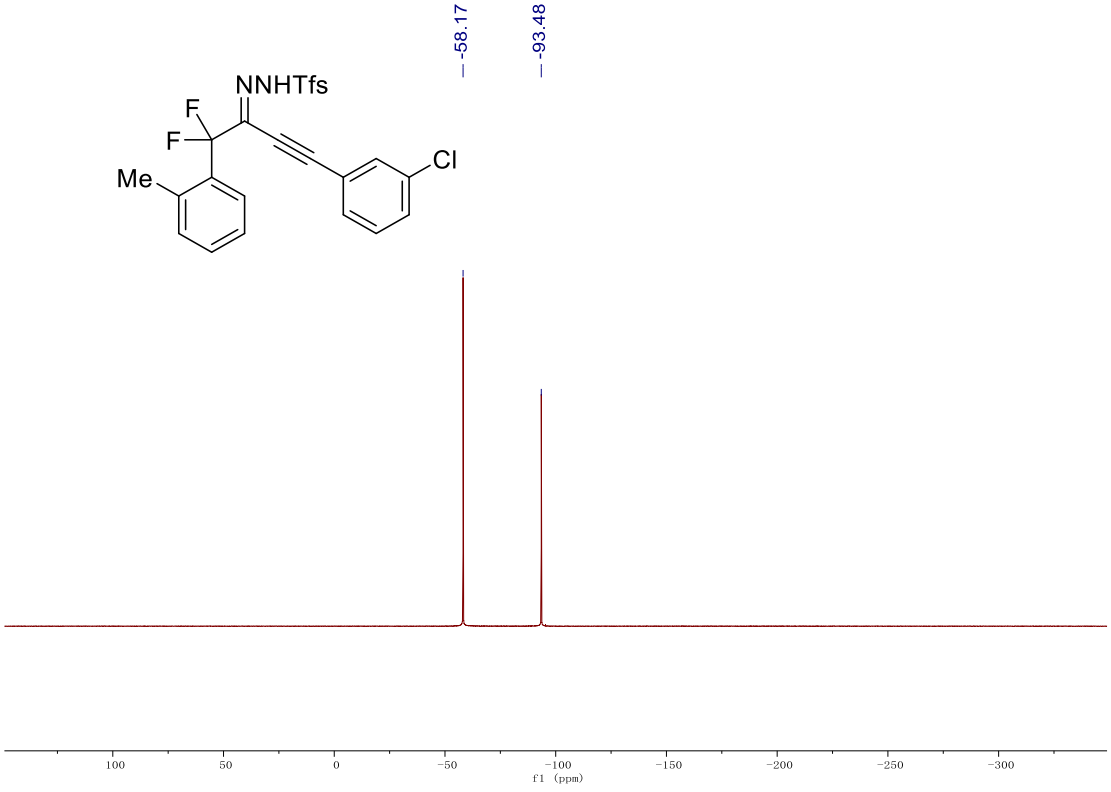
***N*'-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1n): ^{1}H NMR (400 MHz, $CDCl_3$)**



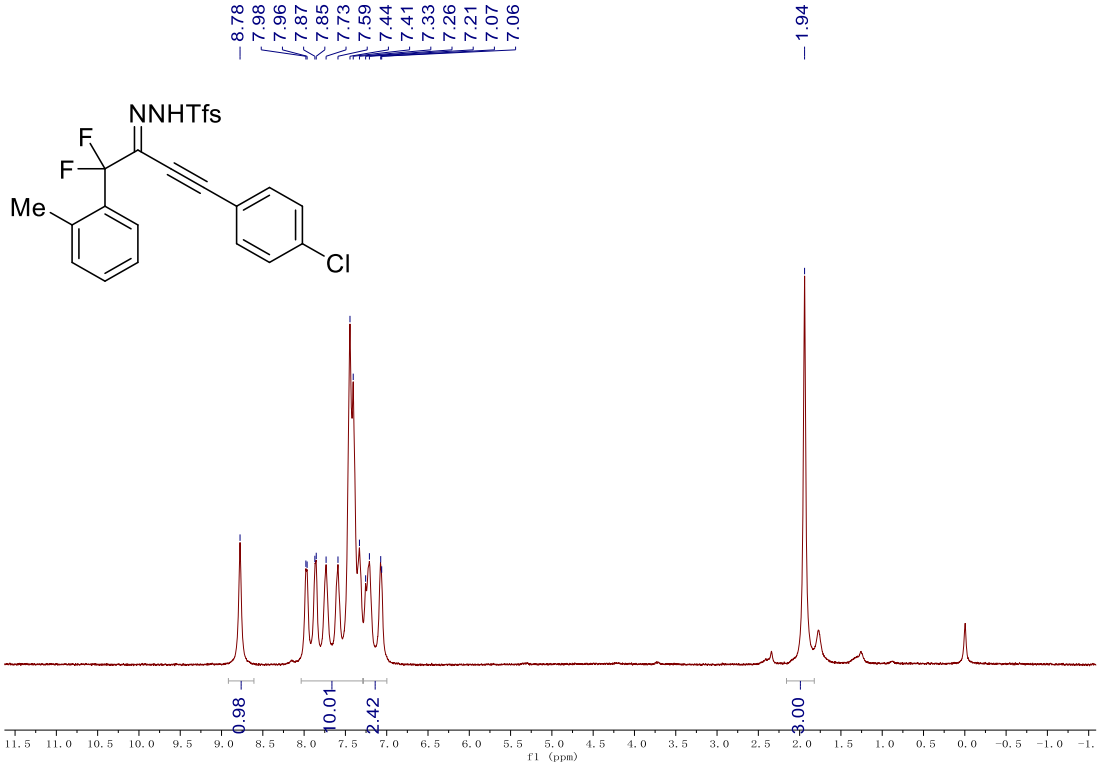
***N*'-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1n): ^{13}C NMR (101 MHz, $CDCl_3$)**



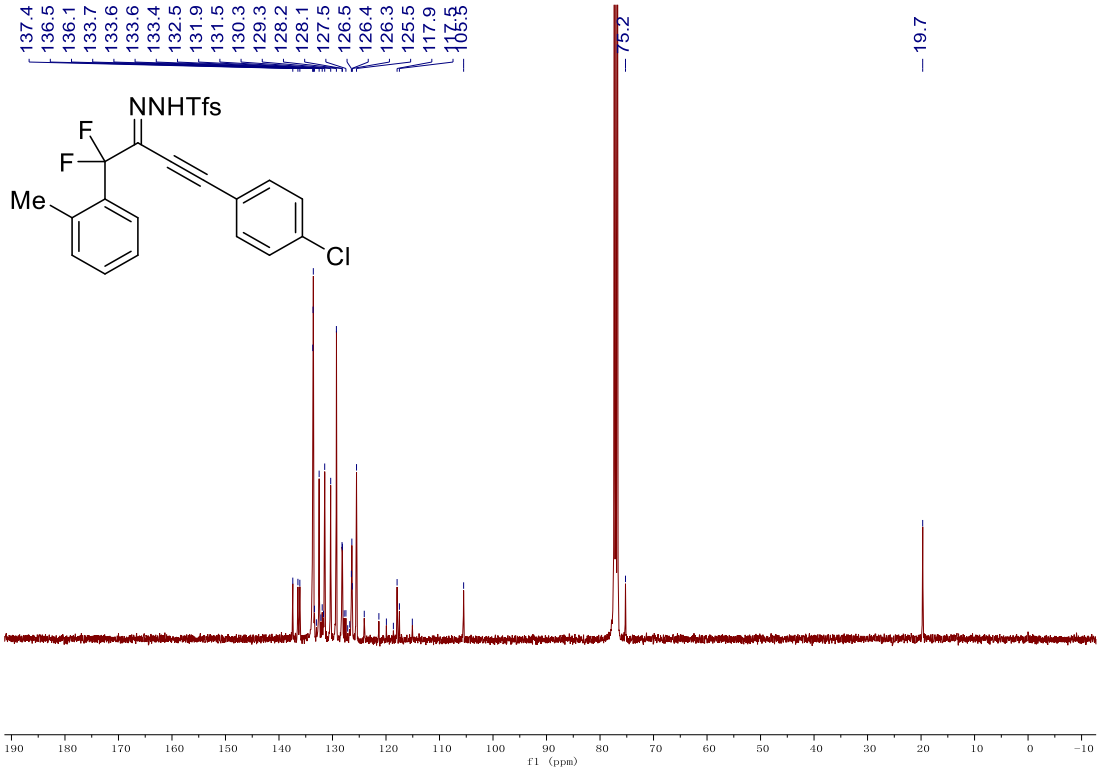
***N*'-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1n): ^{19}F NMR (376 MHz, $CDCl_3$)**



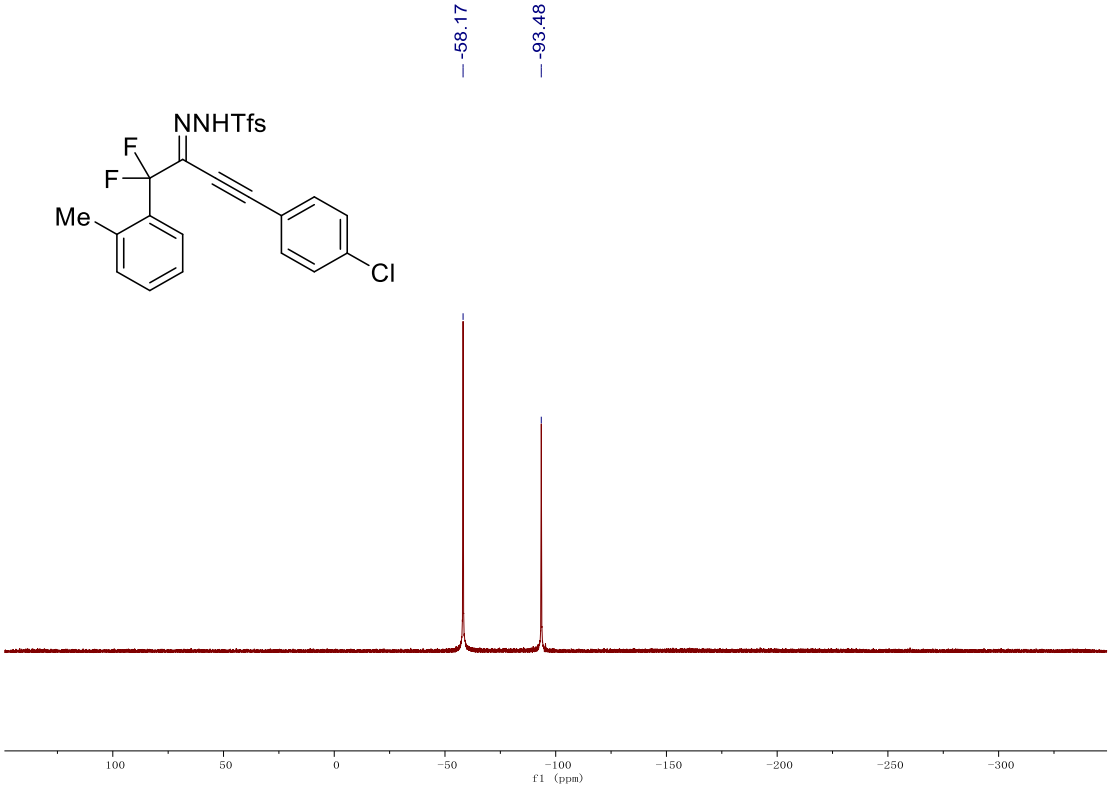
***N*'-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1o): ^{1}H NMR (400 MHz, $CDCl_3$)**



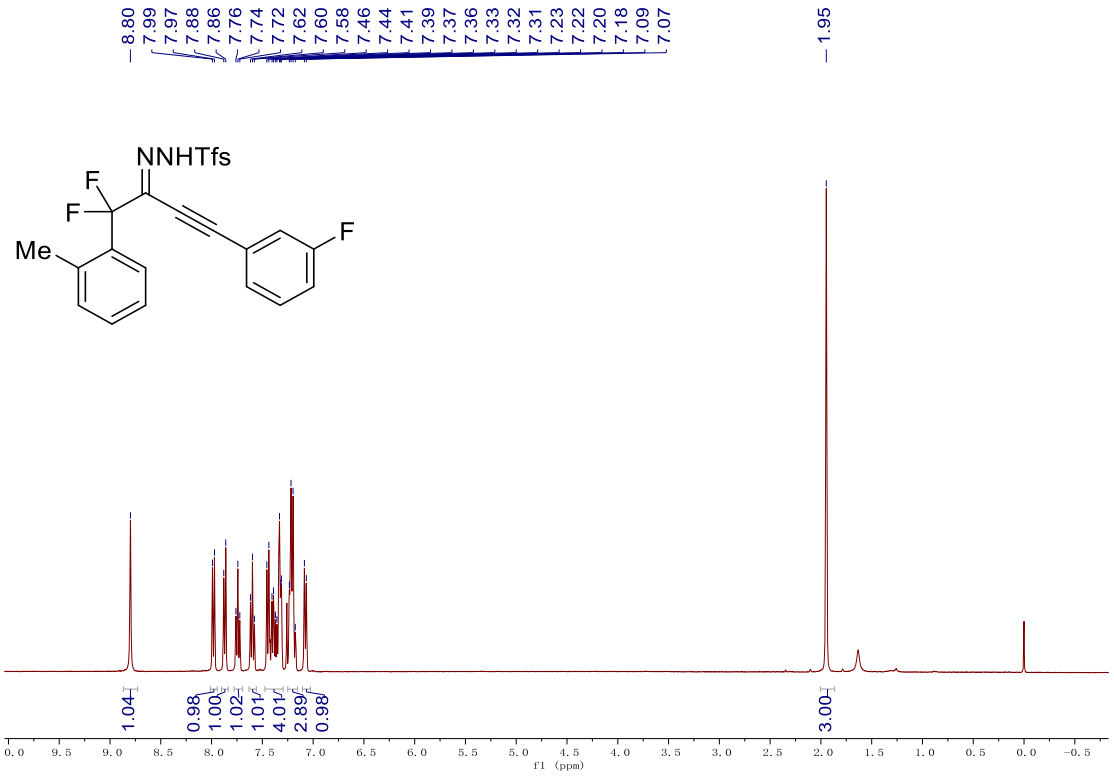
***N*'-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1o): ^{13}C NMR (101 MHz, $CDCl_3$)**



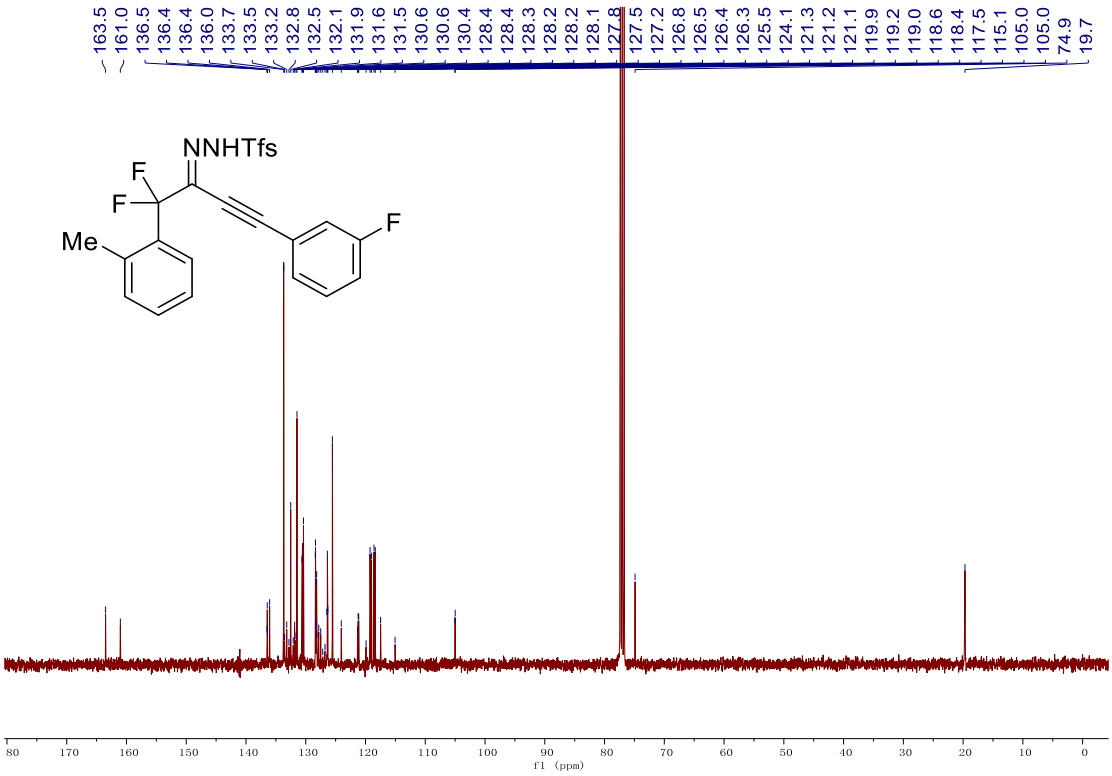
***N*'-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1o): ^{19}F NMR (376 MHz, $CDCl_3$)**



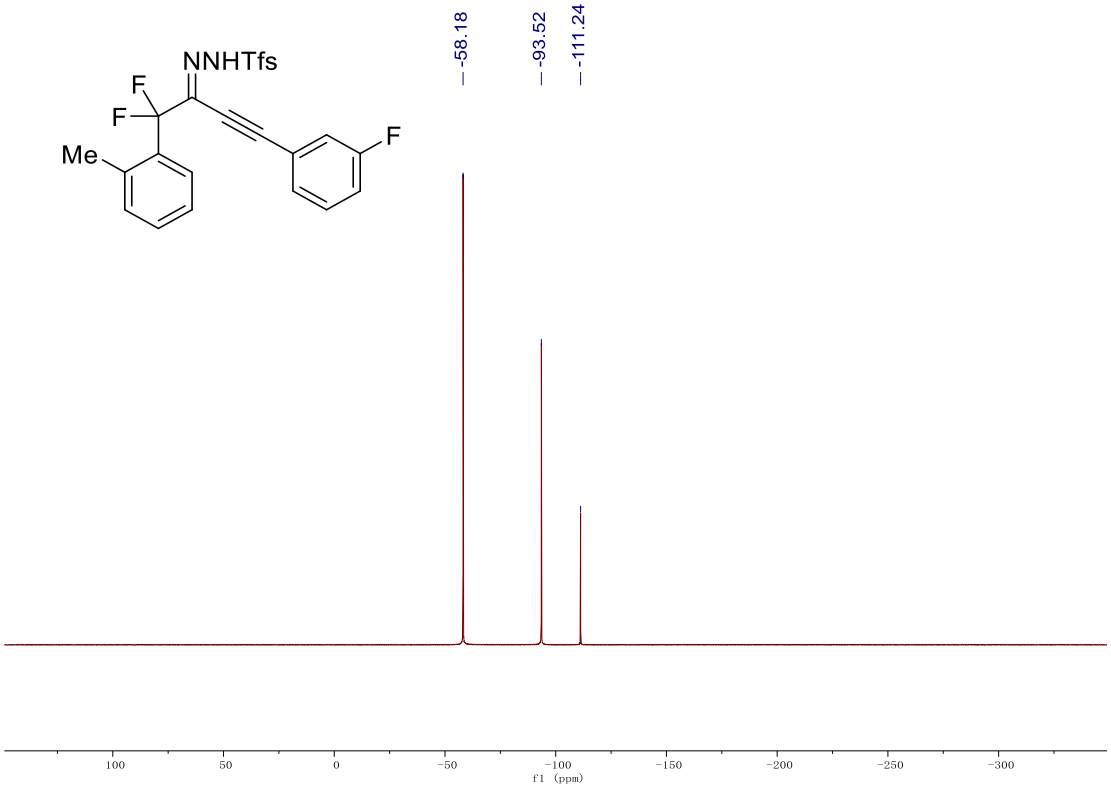
***N*'1,1-difluoro-(4-(3-chlorophenyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1p): ^{1}H NMR (400 MHz, $CDCl_3$)**



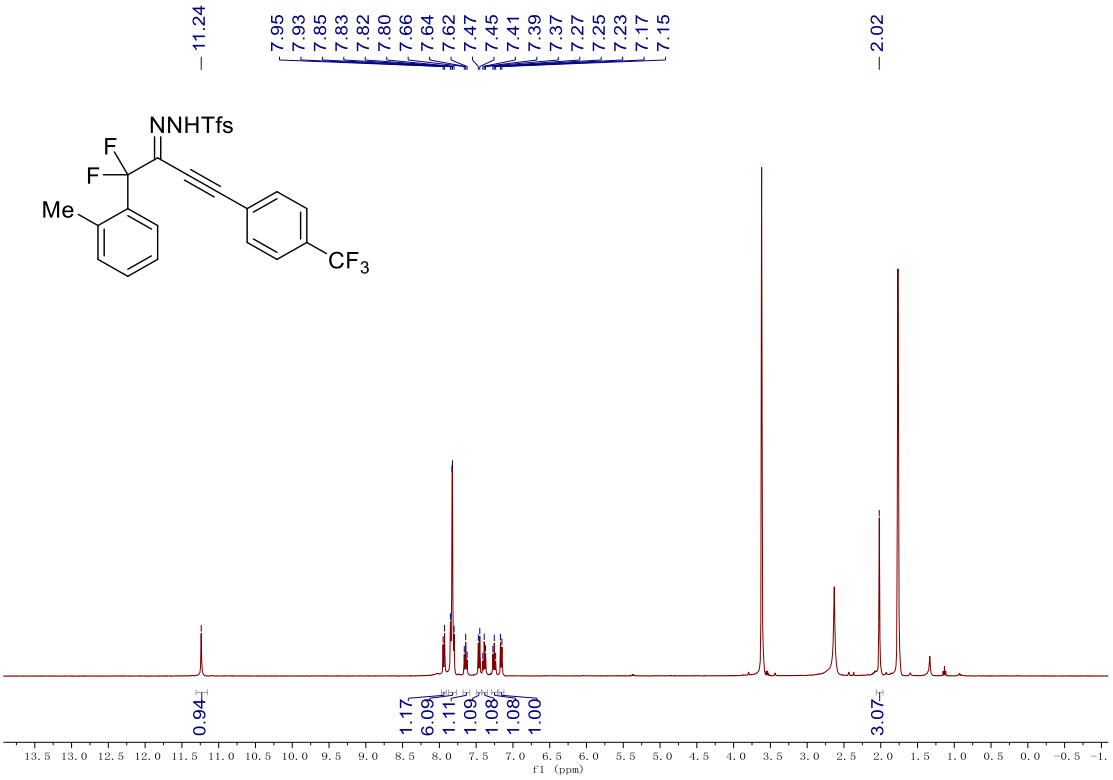
***N*'-(1,1-difluoro-4-(3-chlorophenyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1p): ^{13}C NMR (101 MHz, $CDCl_3$)**



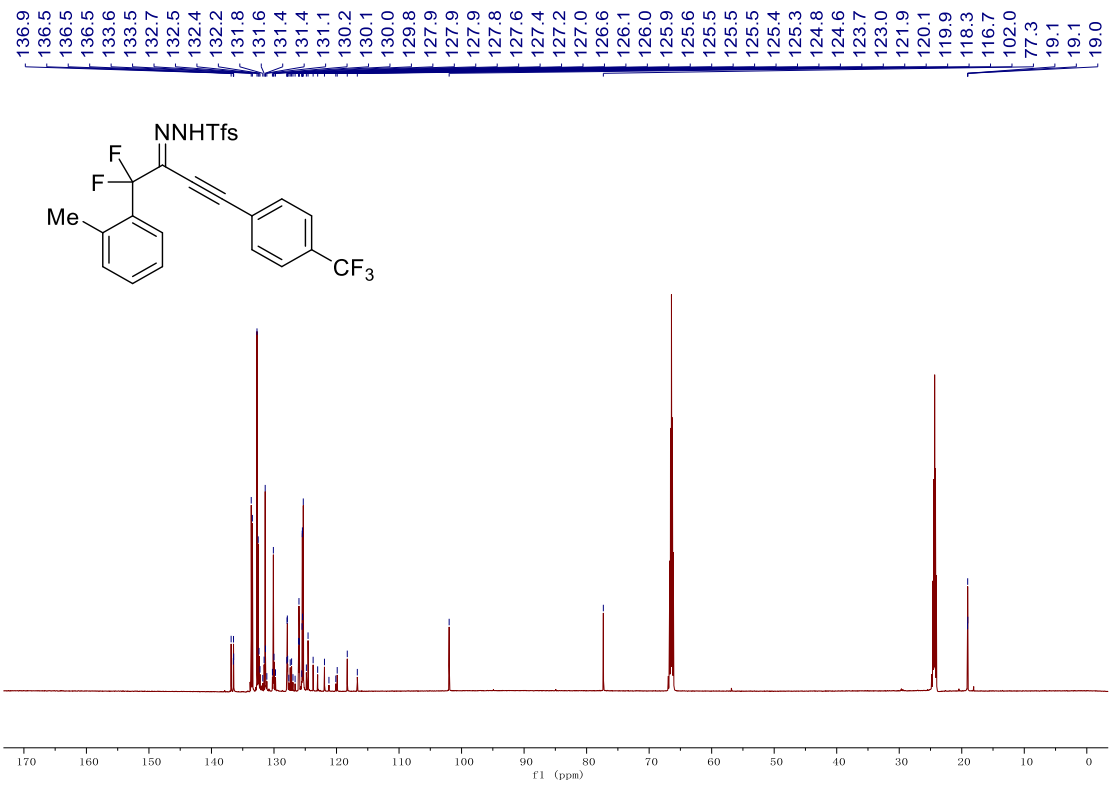
***N*'-1,1-difluoro-(4-(3-chlorophenyl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1p): ^{19}F NMR (376 MHz, $CDCl_3$)**



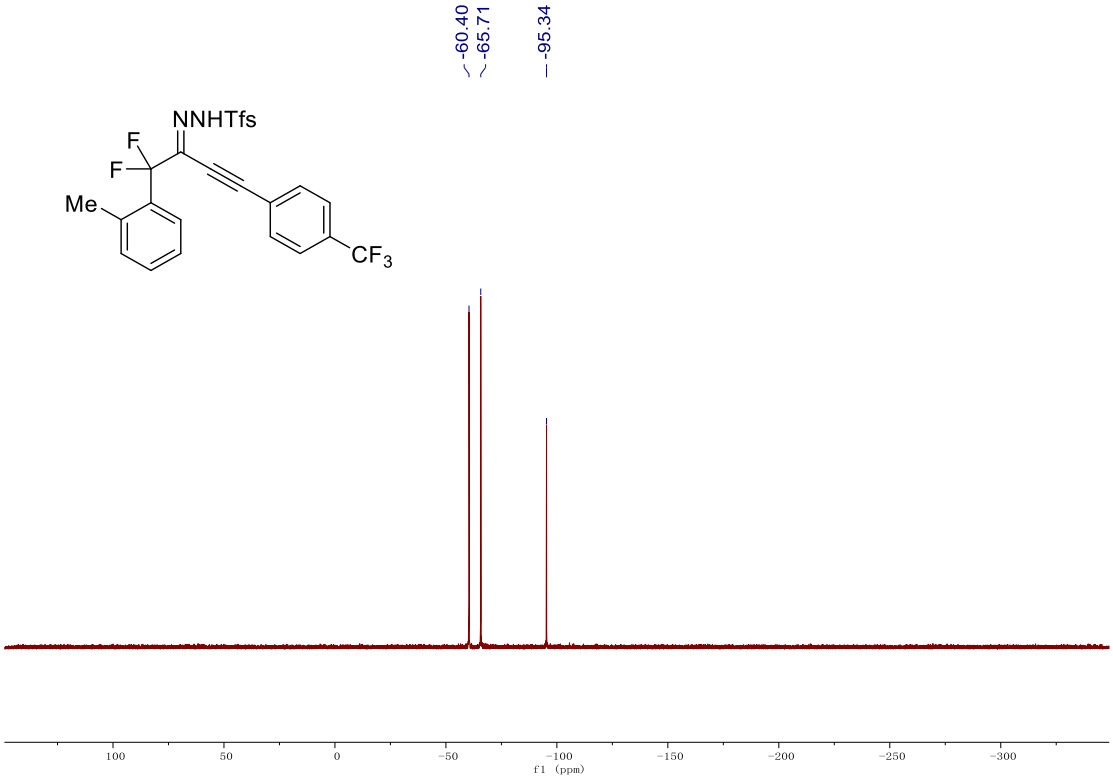
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazide (1q): ^{1}H NMR (400 MHz, THF-d$_8$)**



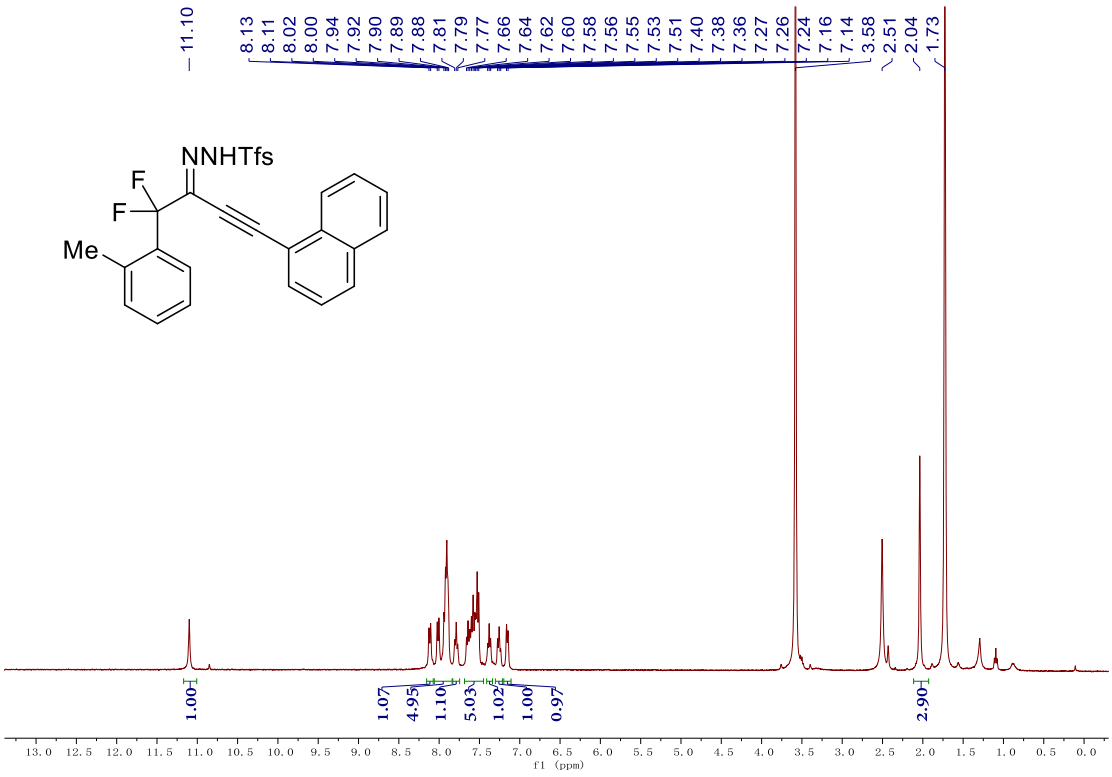
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazide (1q): ^{13}C NMR (151 MHz, THF-d$_8$)**



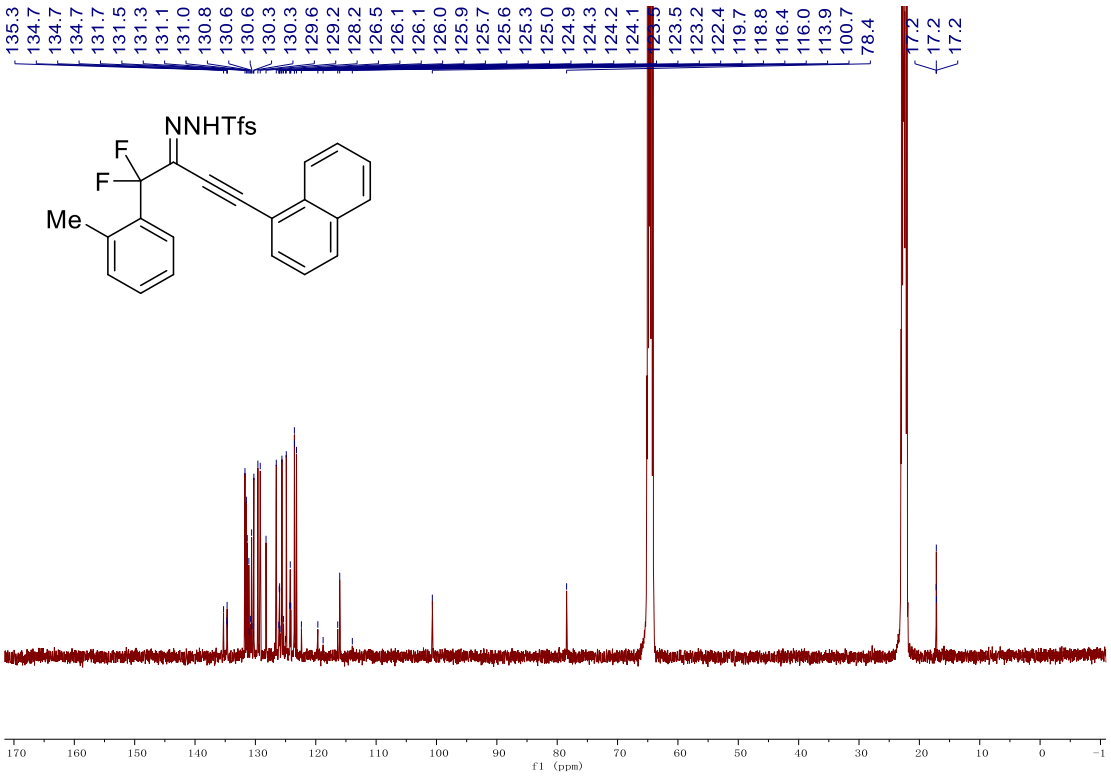
***N*'-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazide (1q): ^{19}F NMR (376 MHz, THF-d$_8$)**



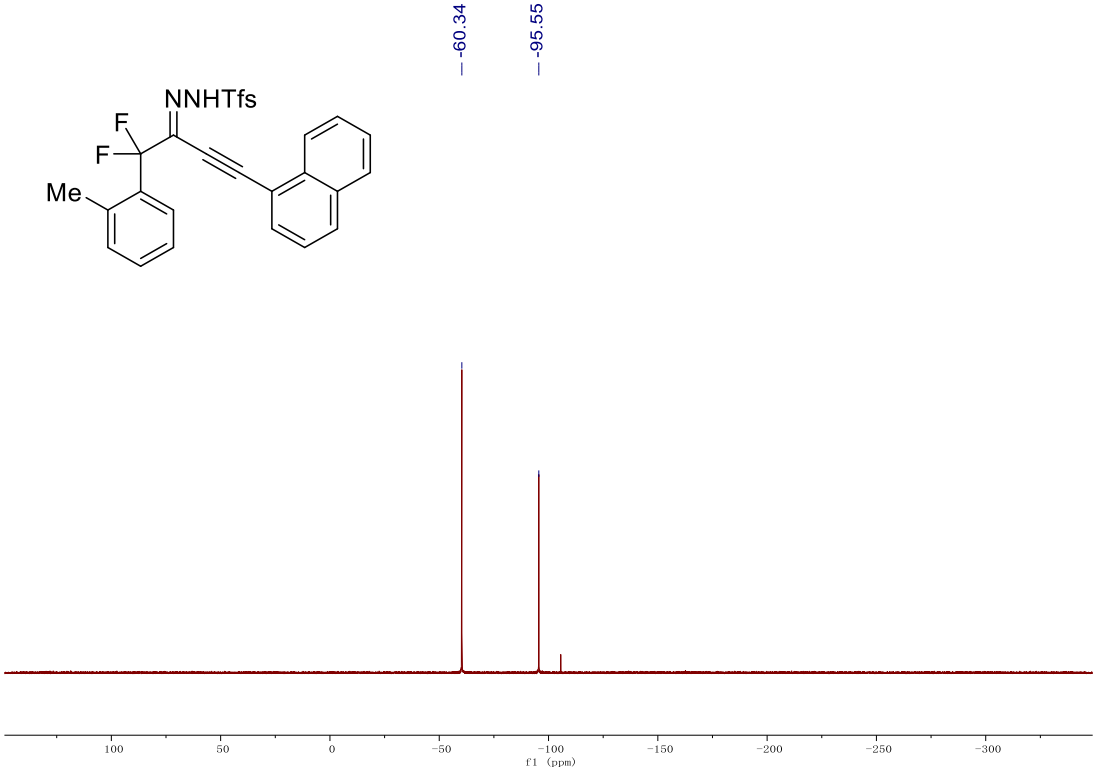
***N*'-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1r): ^{1}H NMR (400 MHz, THF-*d*$_6$)**



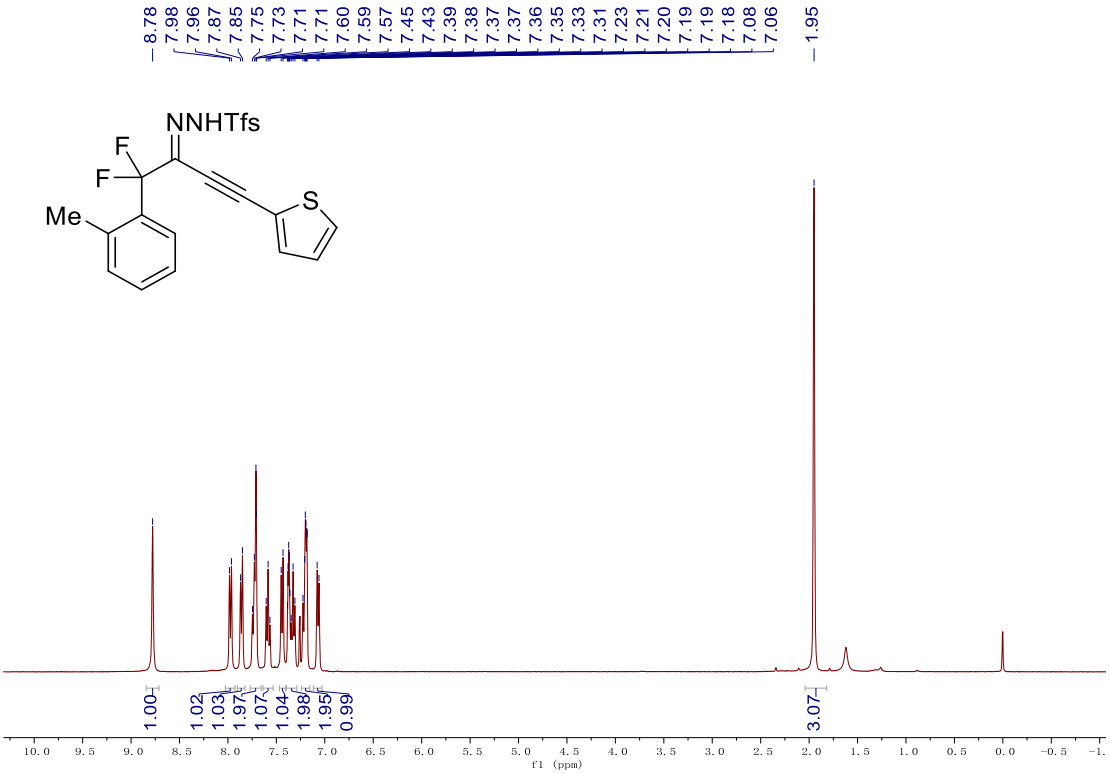
***N*'-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1r): ^{13}C NMR (101 MHz, THF-d_6)**



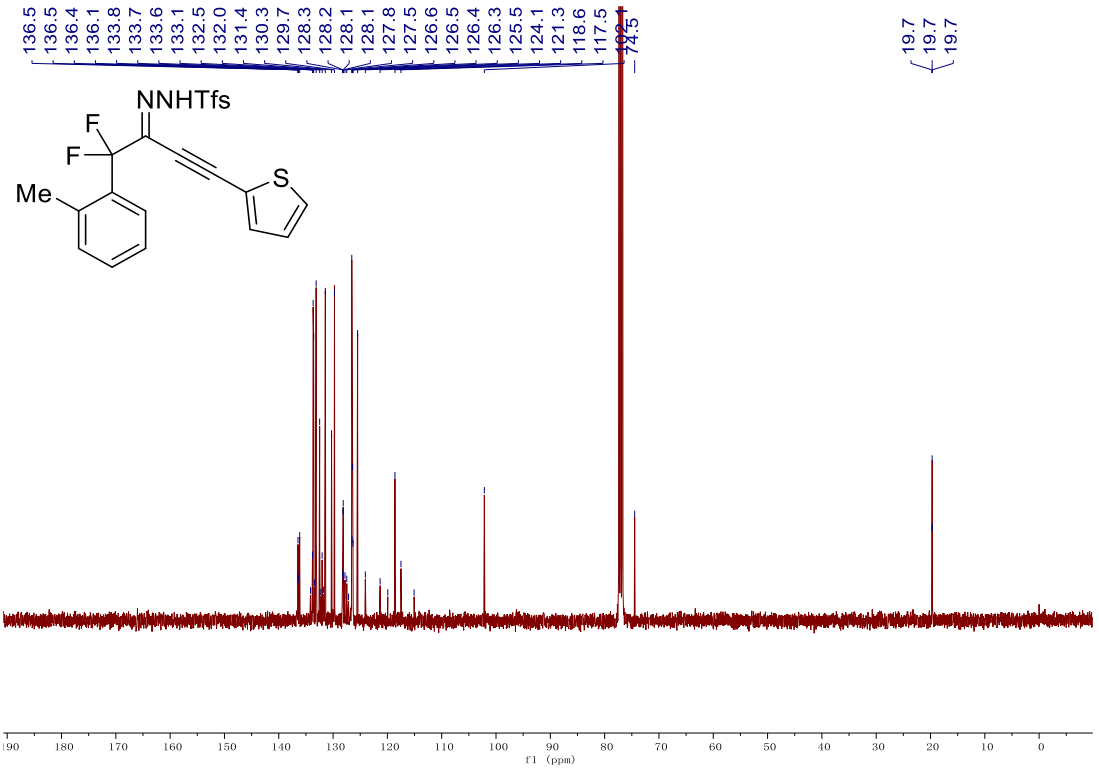
***N*'-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1r): ^{19}F NMR (376 MHz, THF-d_6)**



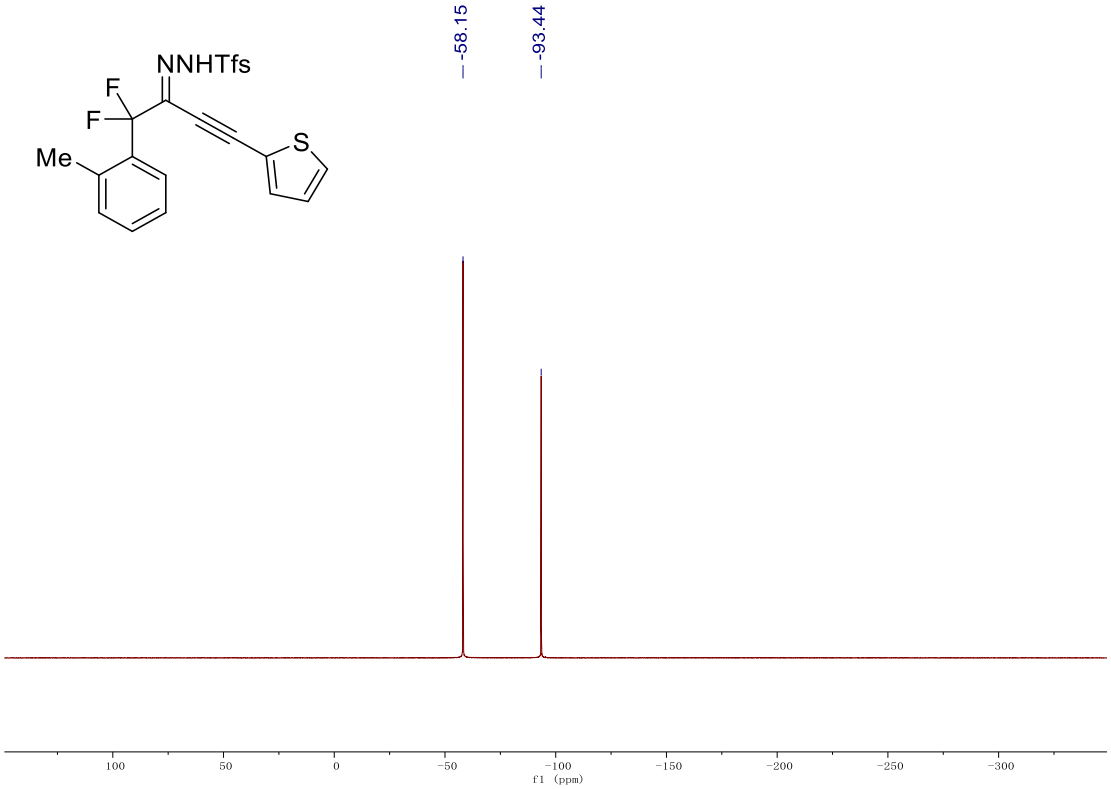
***N*'-(1,1-difluoro-4-(thiophen-2-yl)-1-(o-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1s): ^{1}H NMR (400 MHz, $CDCl_3$)**



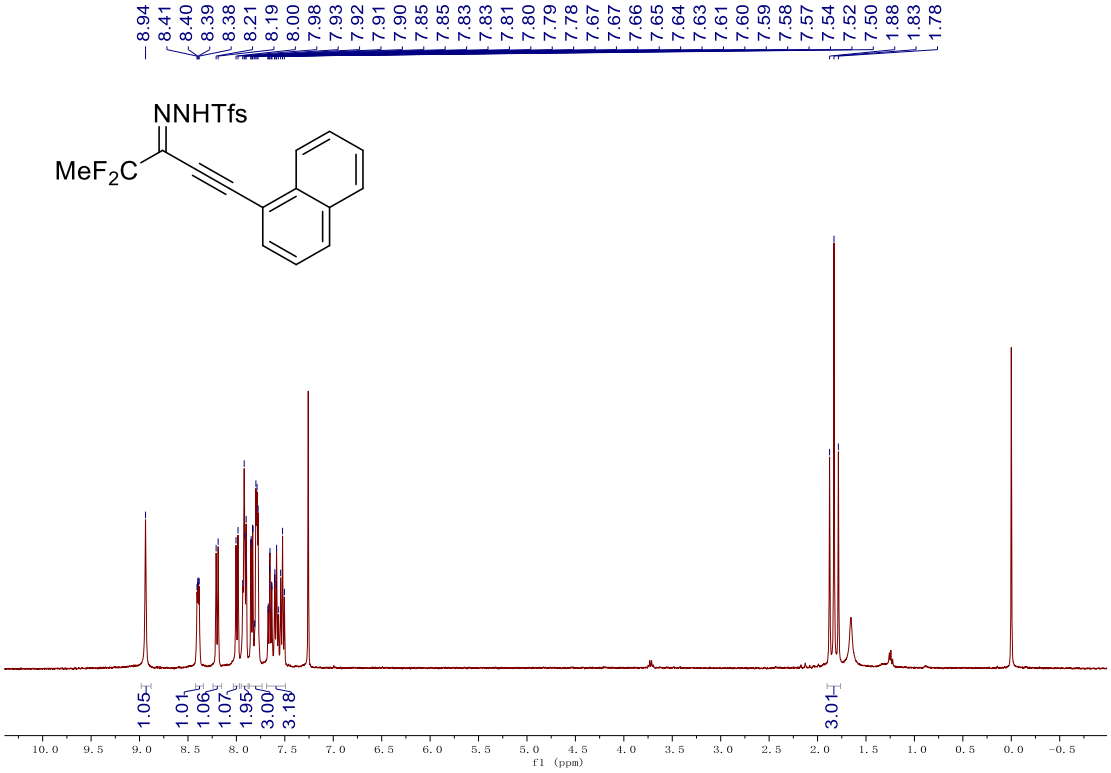
***N*'-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1s): ^{13}C NMR (101 MHz, $CDCl_3$)**



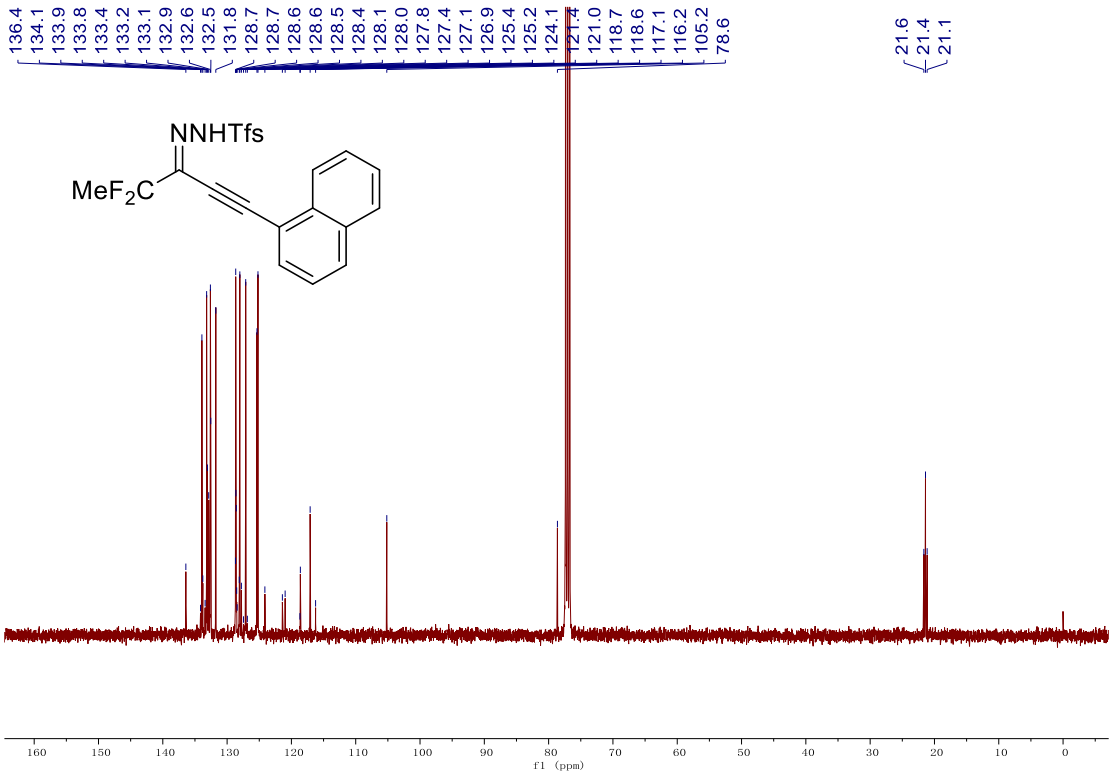
***N*'-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1s): ^{19}F NMR (376 MHz, $CDCl_3$)**



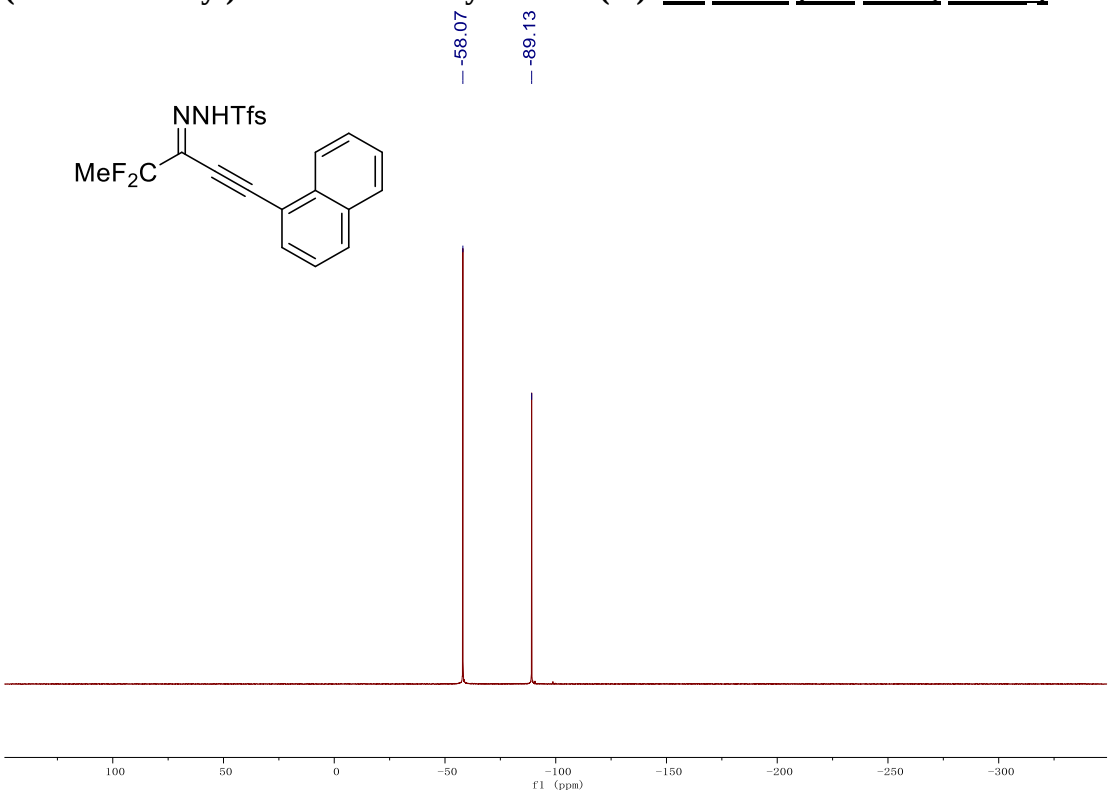
***N*'-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1t): ^{1}H NMR (400 MHz, $CDCl_3$)**



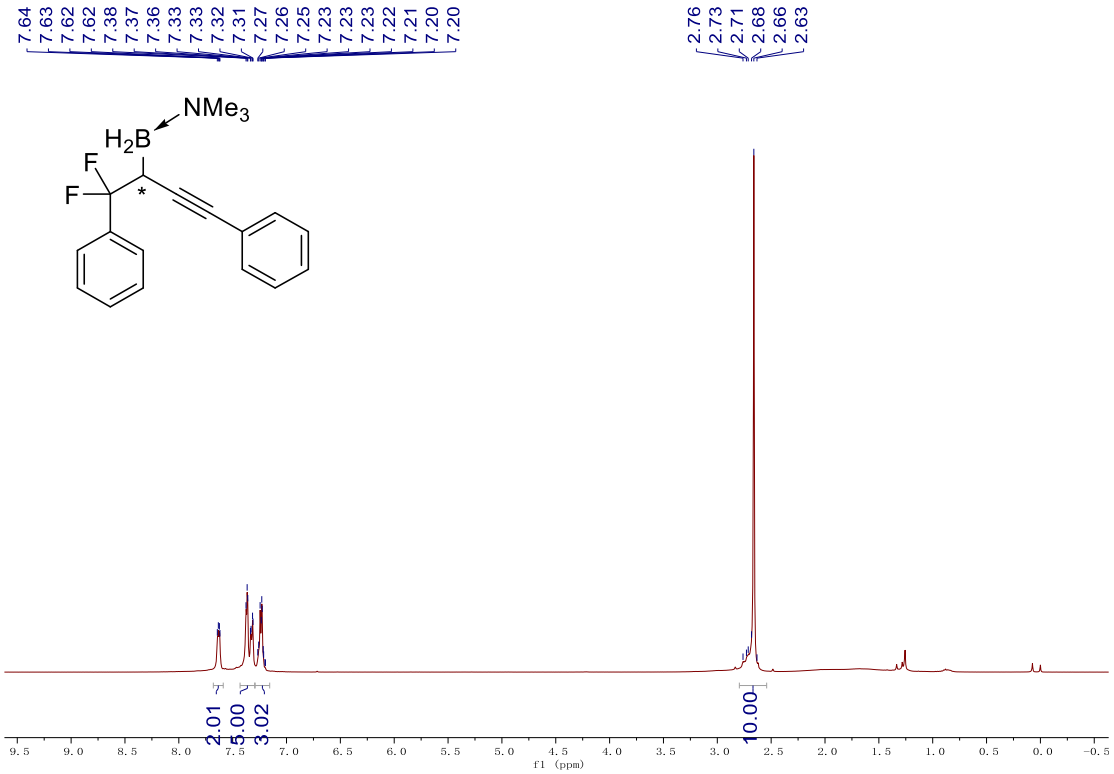
***N*'-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1t): ^{13}C NMR (101 MHz, $CDCl_3$)**



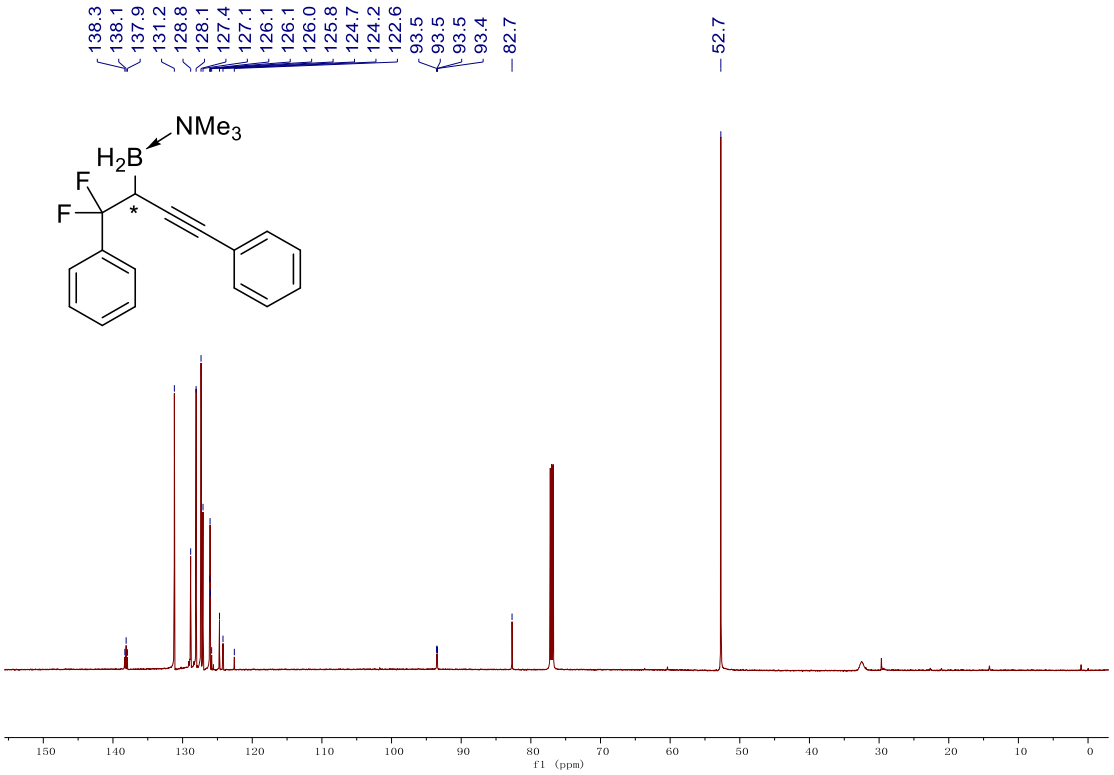
***N*'-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-ylidene)-2-(trifluoromethyl)benzenesulfonohydrazone (1t): ^{19}F NMR (376 MHz, $CDCl_3$)**



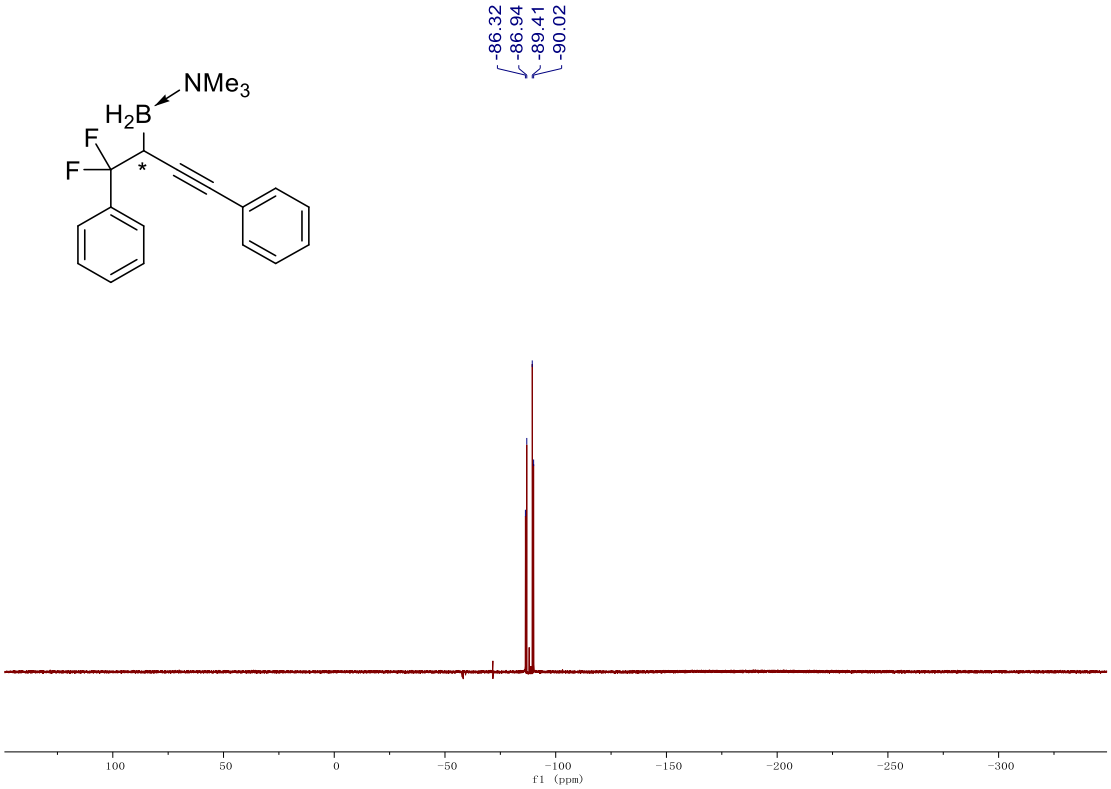
(-)-Trimethylamine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3aa): ^{1}H NMR (400 MHz, $CDCl_3$)



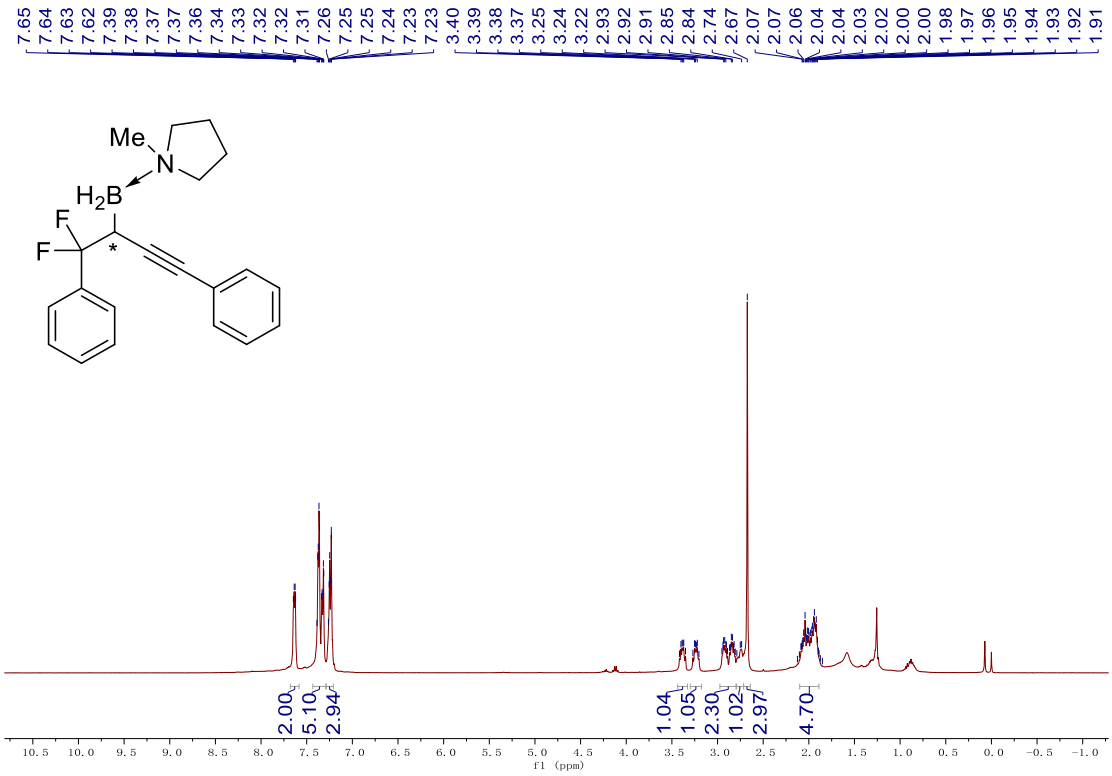
(-)-Trimethylamine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3aa): ^{13}C NMR (101 MHz, $CDCl_3$)



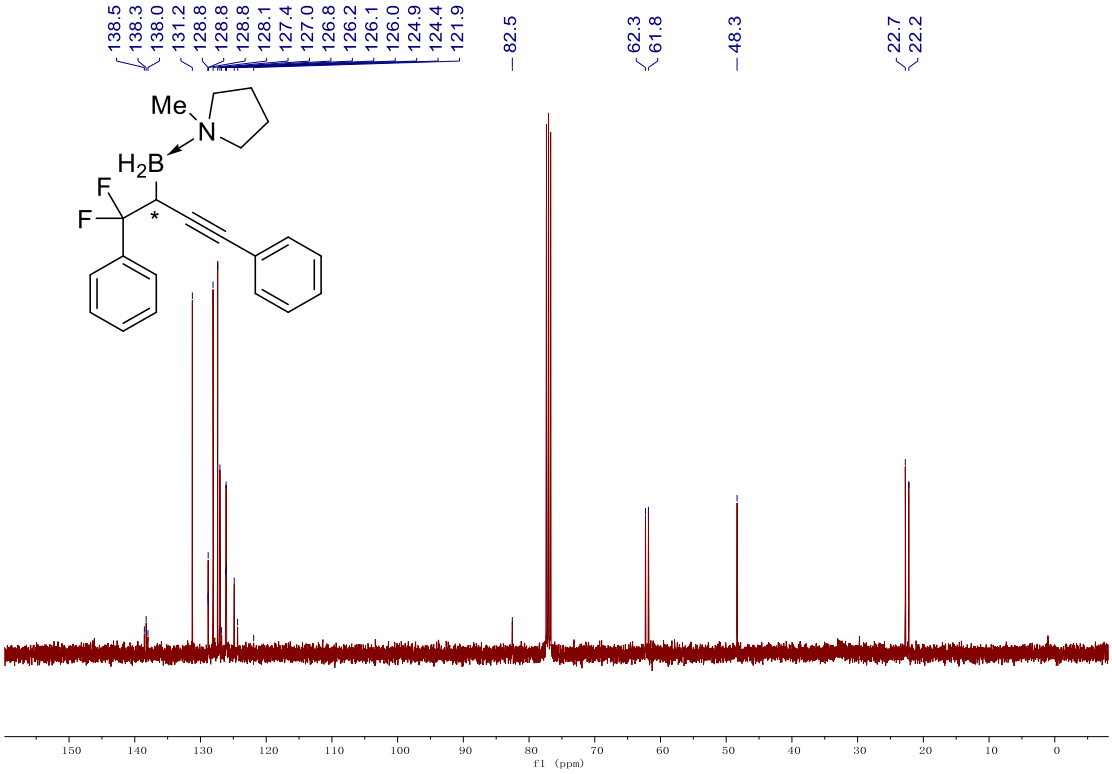
(-)-Trimethylamine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3aa): ^{19}F NMR (376 MHz, $CDCl_3$)



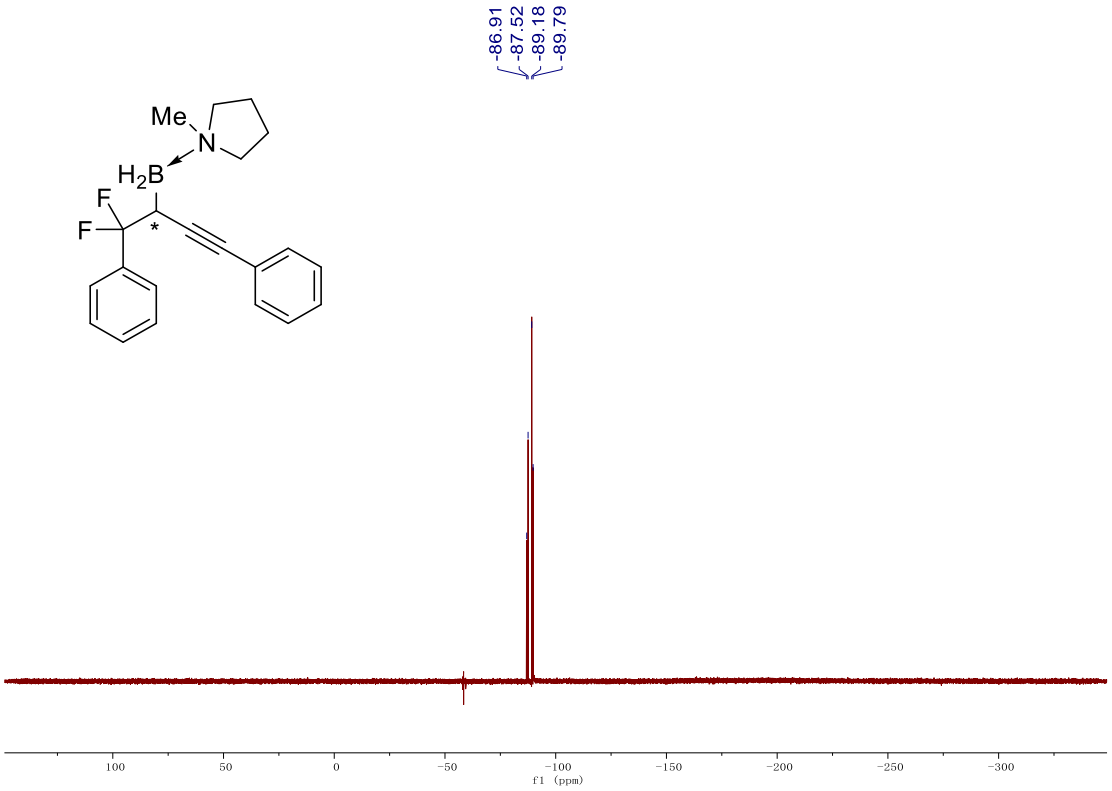
(-)-1-methylpyrrolidine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ab): ^{1}H NMR (400 MHz, $CDCl_3$)



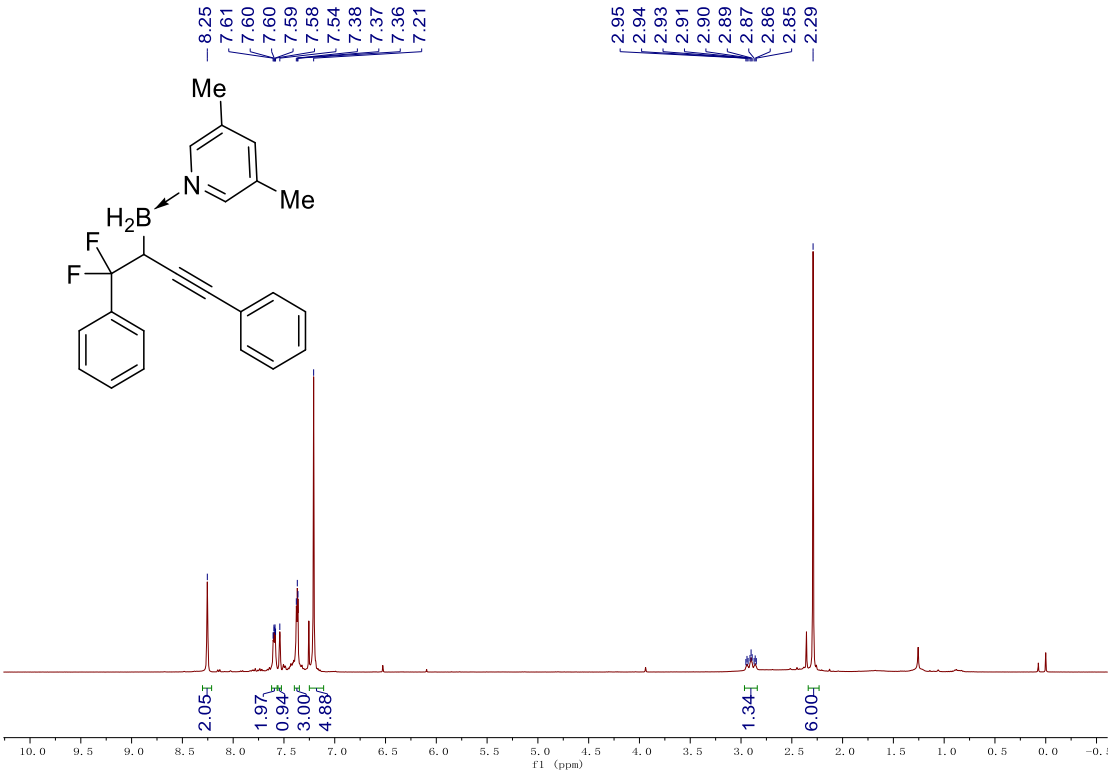
(-)-1-methylpyrrolidine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ab): ^{13}C NMR (101 MHz, $CDCl_3$)



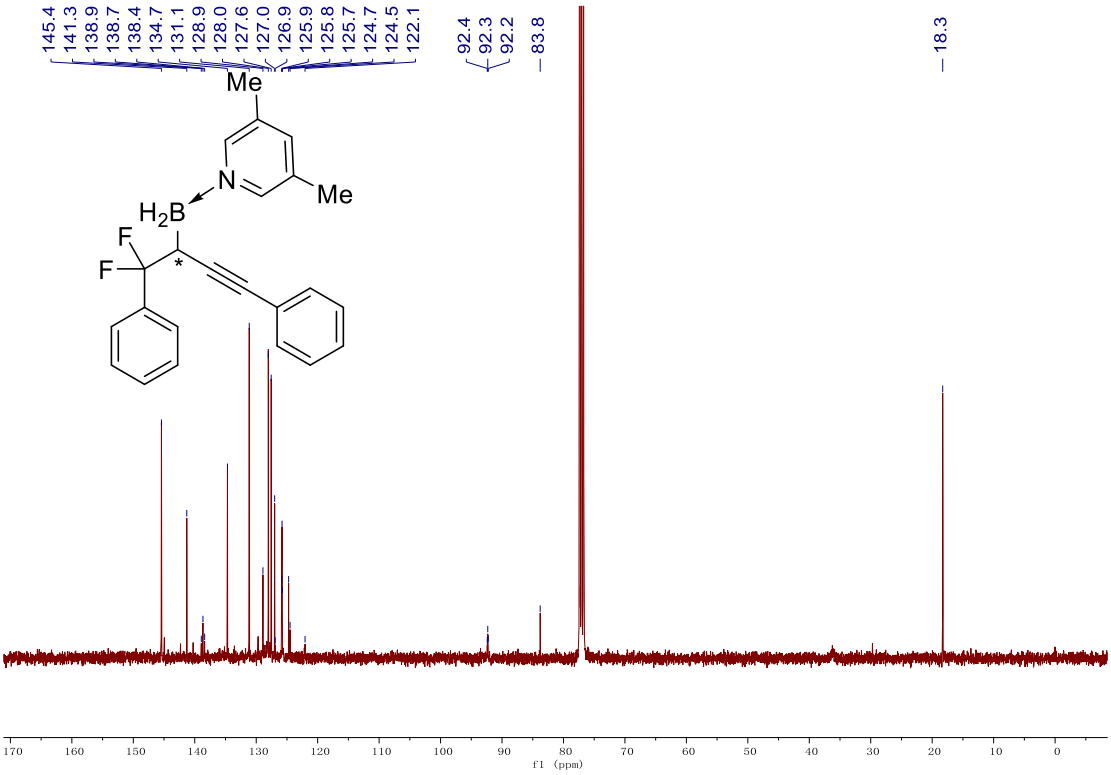
(-)-1-methylpyrrolidine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ab): ^{19}F NMR (376 MHz, $CDCl_3$)



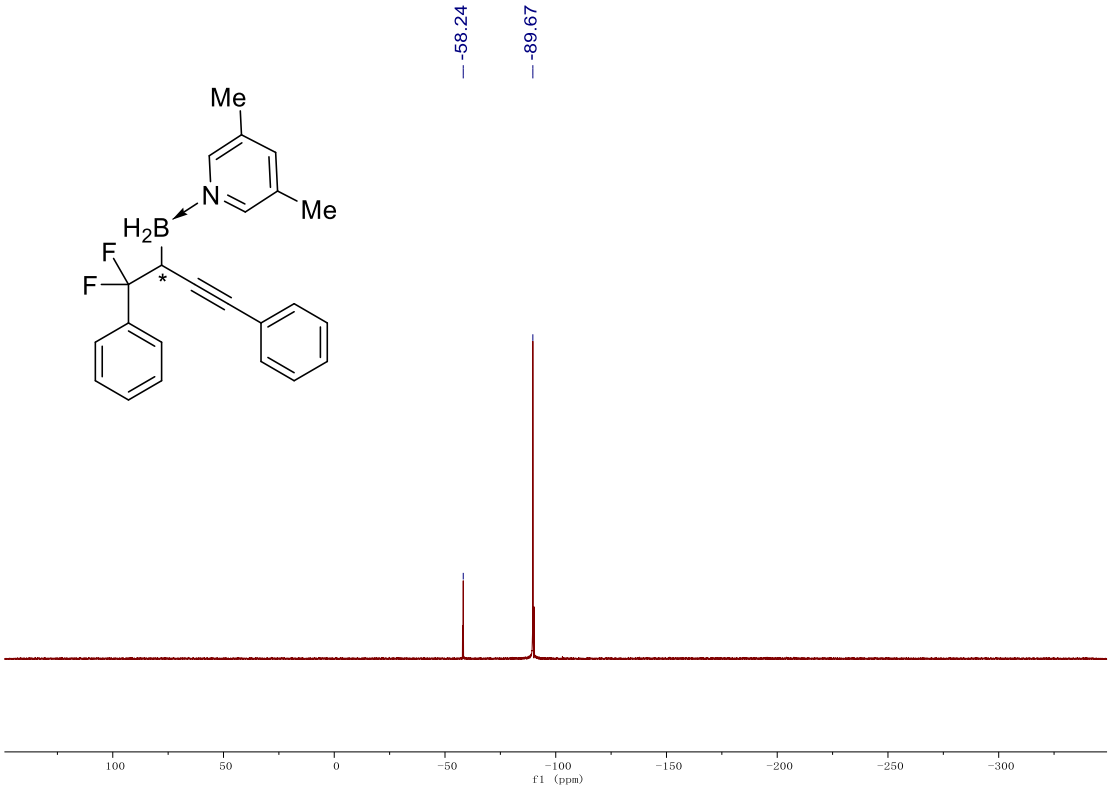
(+)-3,5-dimethylpyridine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ac): ^{1}H NMR (400 MHz, $CDCl_3$)



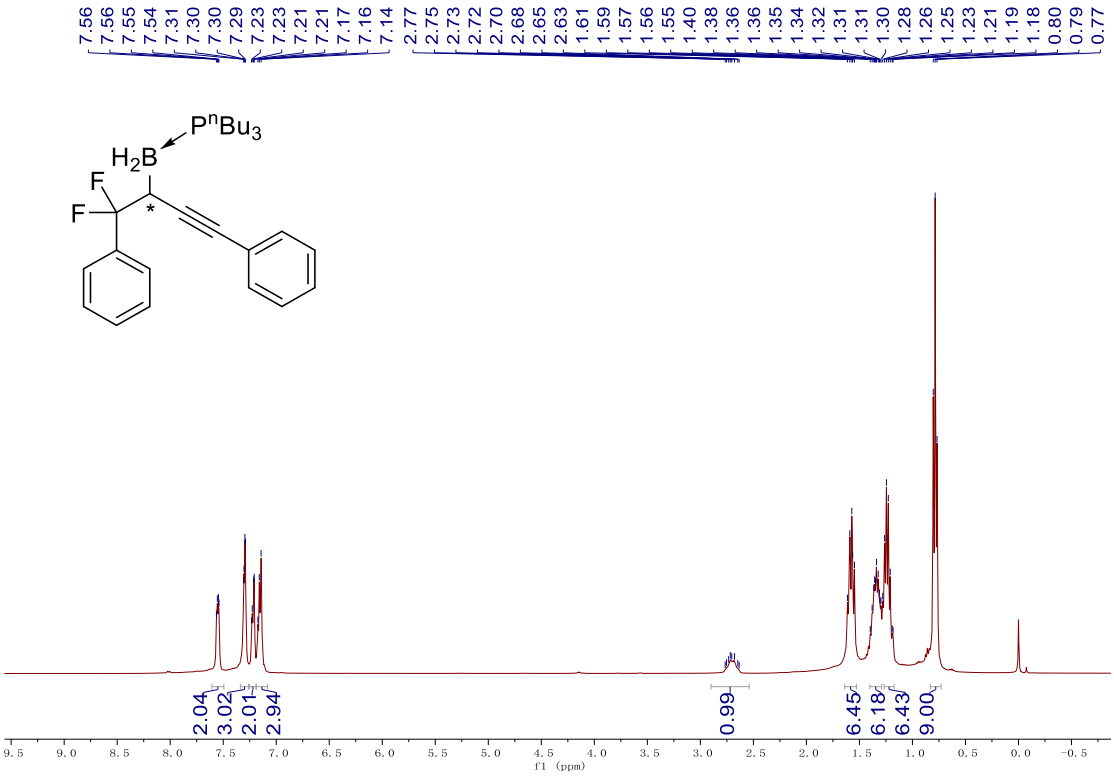
(+)-3,5-dimethylpyridine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ac): ^{13}C NMR (101 MHz, $CDCl_3$)



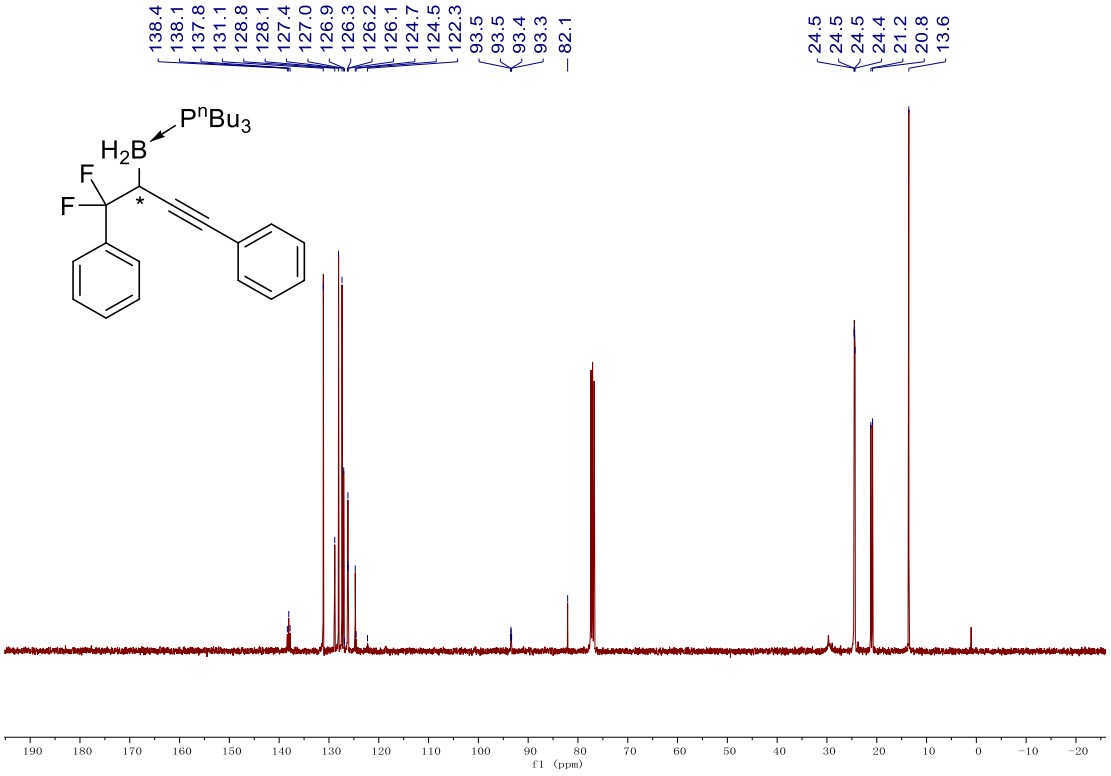
(+)-3,5-dimethylpyridine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ac): ^{19}F NMR (376 MHz, $CDCl_3$)



(-)-tributylphosphane-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ad): ^{1}H NMR (400 MHz, $CDCl_3$)

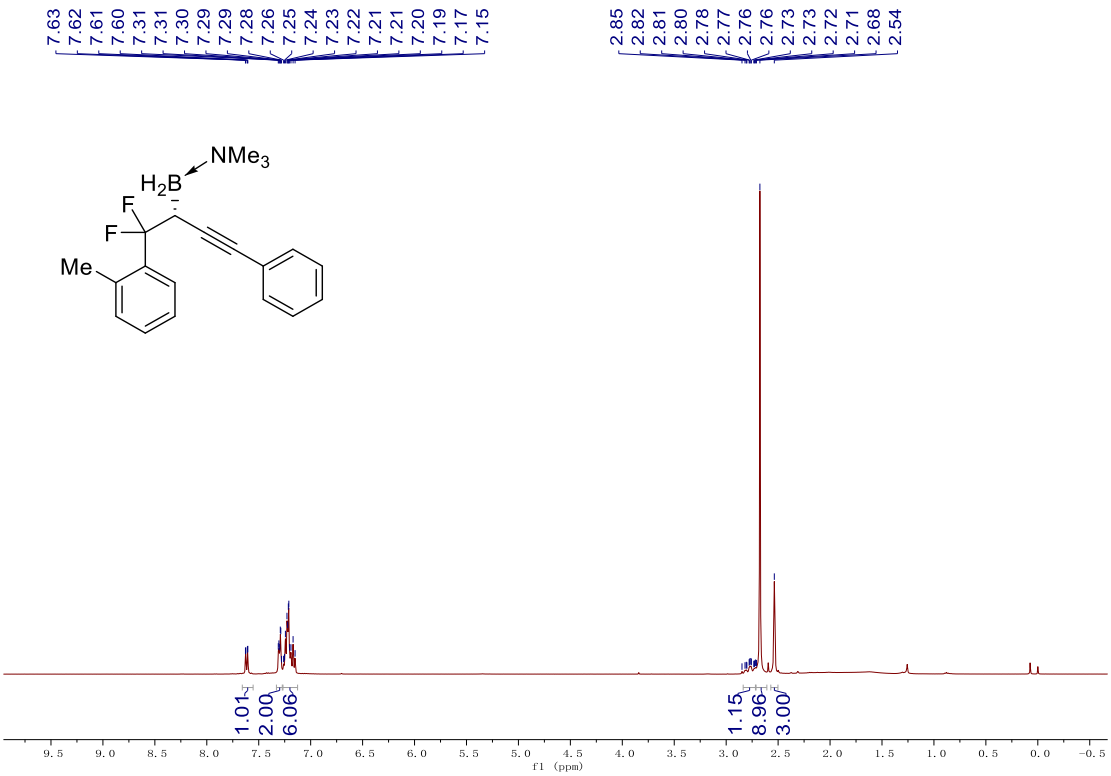


(-)-tributylphosphane-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ad): ^{13}C NMR (101 MHz, $CDCl_3$)

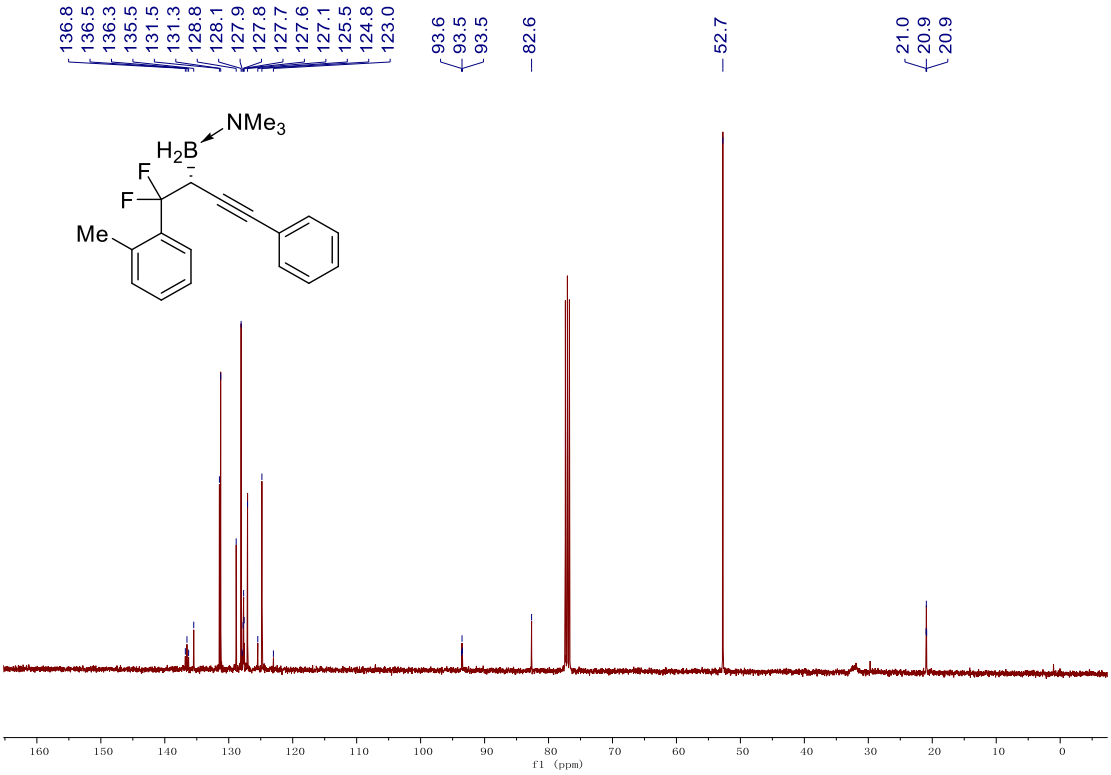


(-)-tributylphosphane-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ad): ^{19}F NMR (376 MHz, $CDCl_3$)

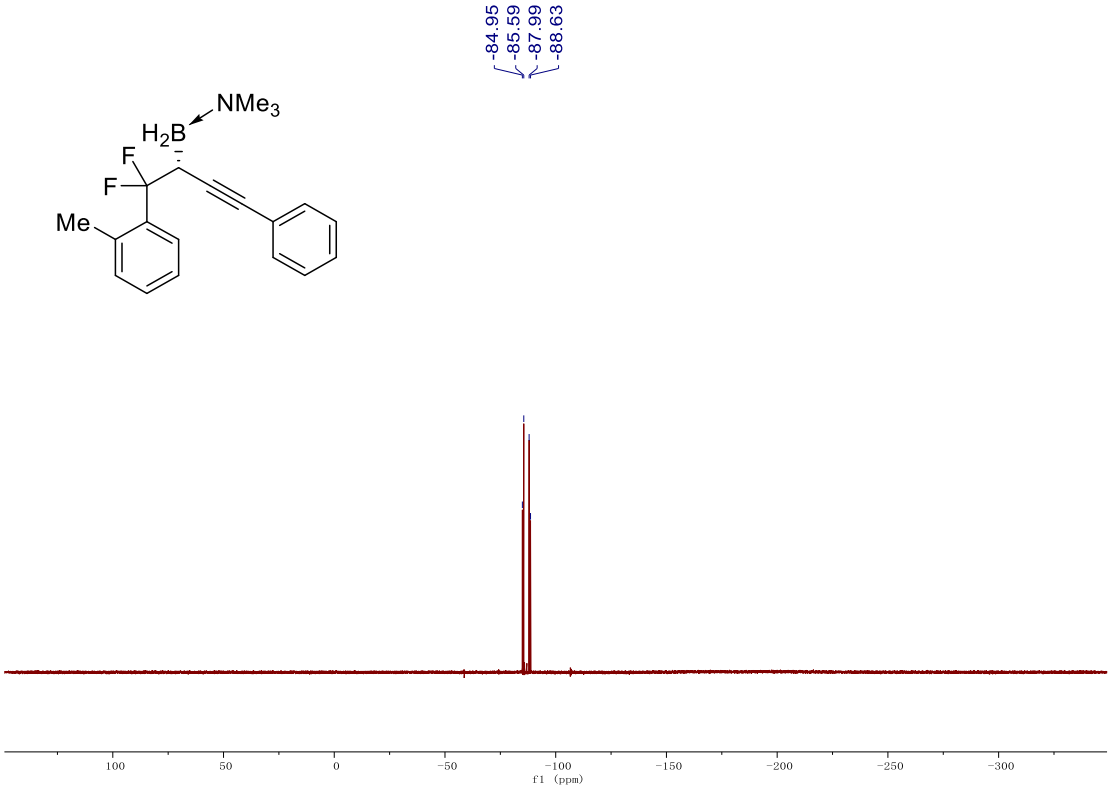
(+)-(*R*)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ba): ^{1}H NMR (400 MHz, $CDCl_3$)



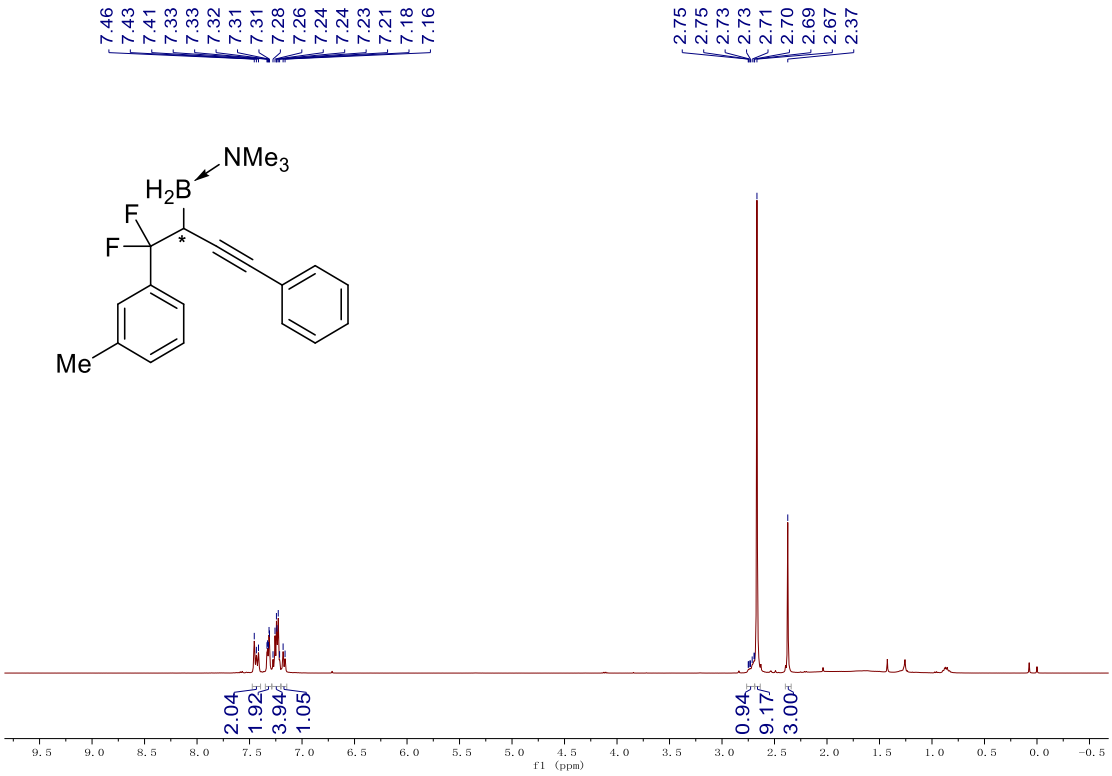
(+)-(*R*)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ba): ^{13}C NMR (101 MHz, $CDCl_3$)



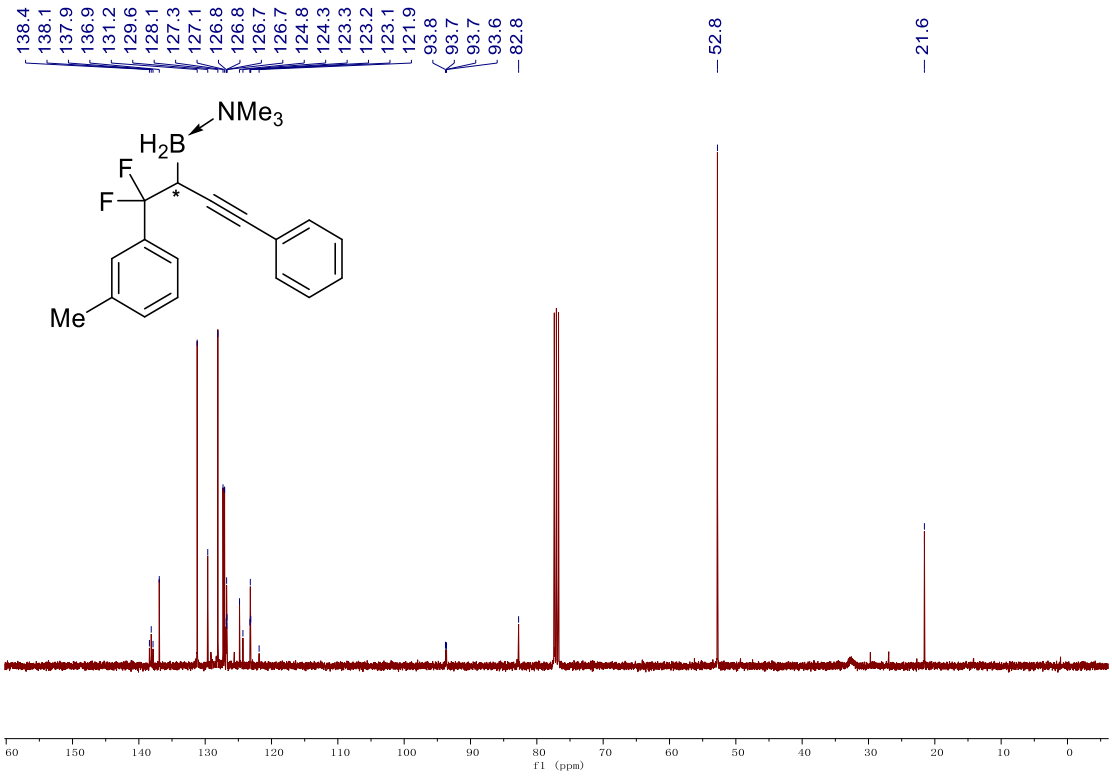
(+)-(*R*)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ba): ^{19}F NMR (376 MHz, $CDCl_3$)



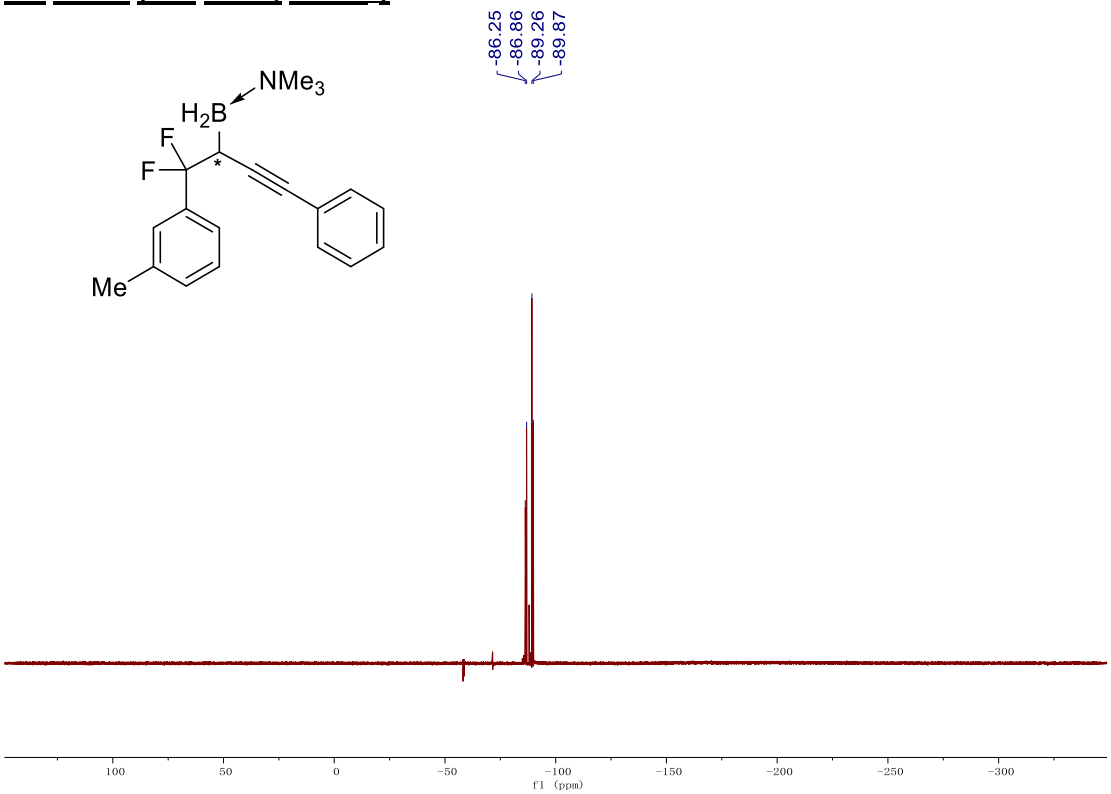
(-)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-yl)borane (3ca): ^{1}H NMR (400 MHz, $CDCl_3$)



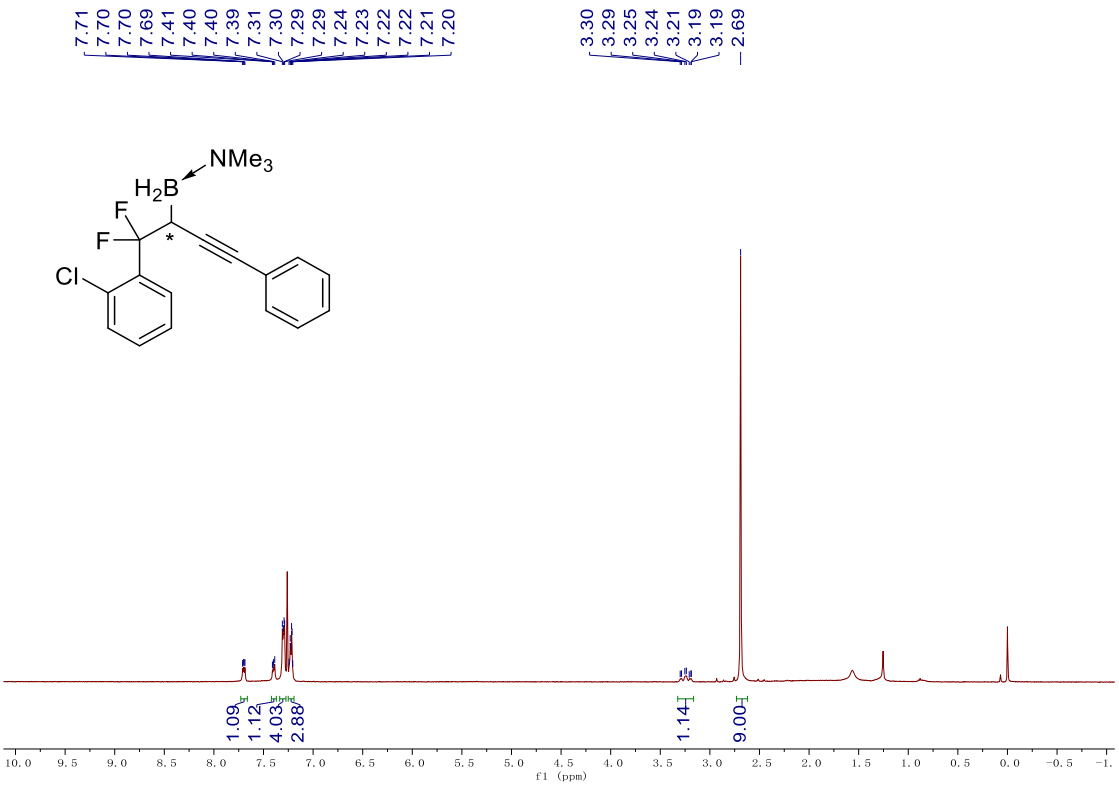
(-)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-yl)borane (3ca): ^{13}C NMR (101 MHz, $CDCl_3$)



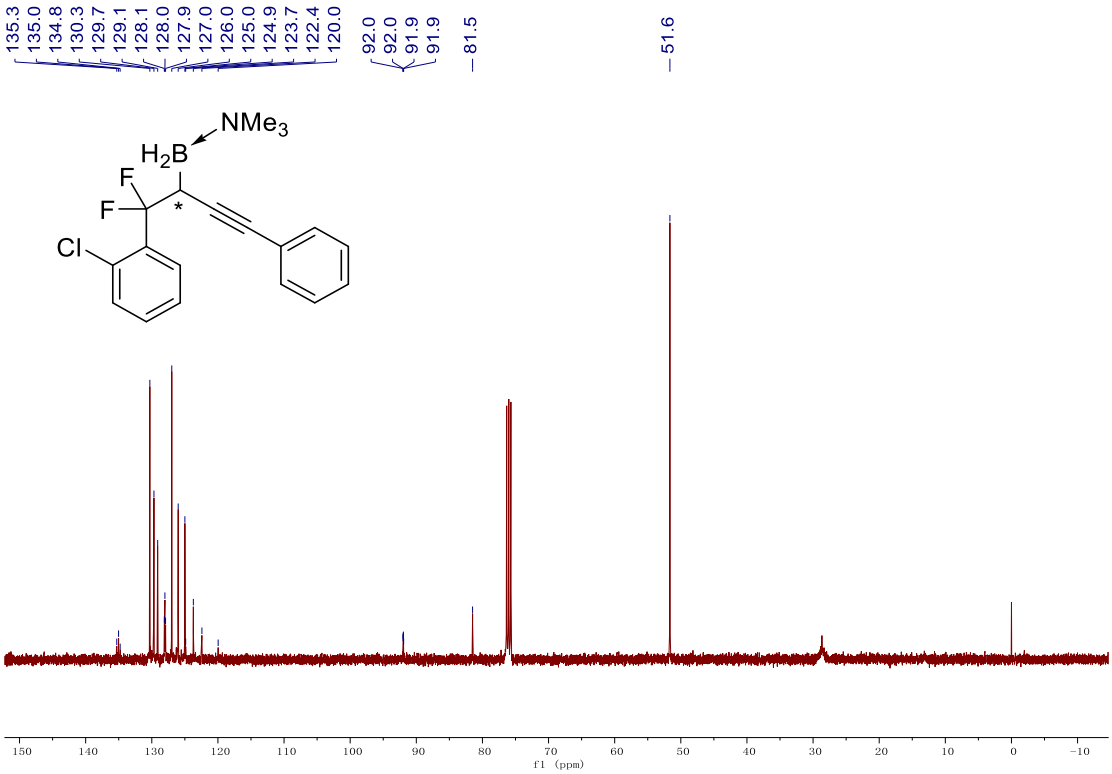
(-)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-yl)borane (3ca): ^{19}F NMR (376 MHz, $CDCl_3$)



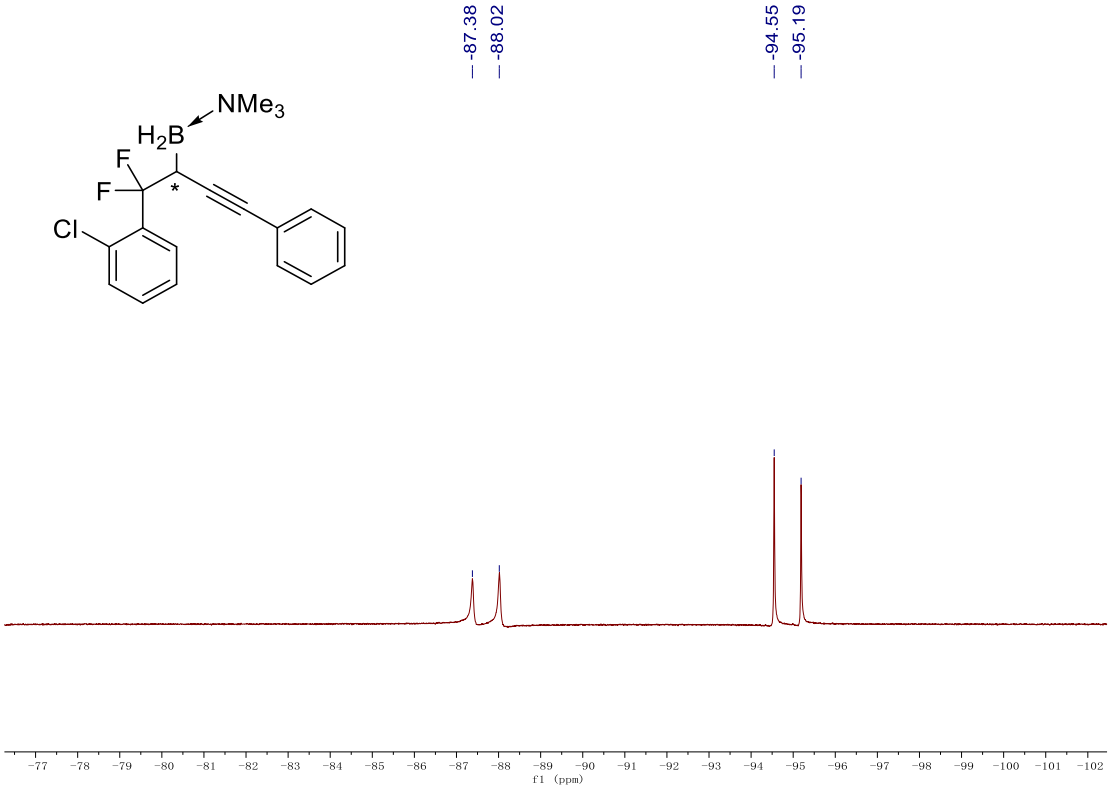
(+)-Trimethylamine-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3da): ^{1}H NMR (400 MHz, $CDCl_3$)



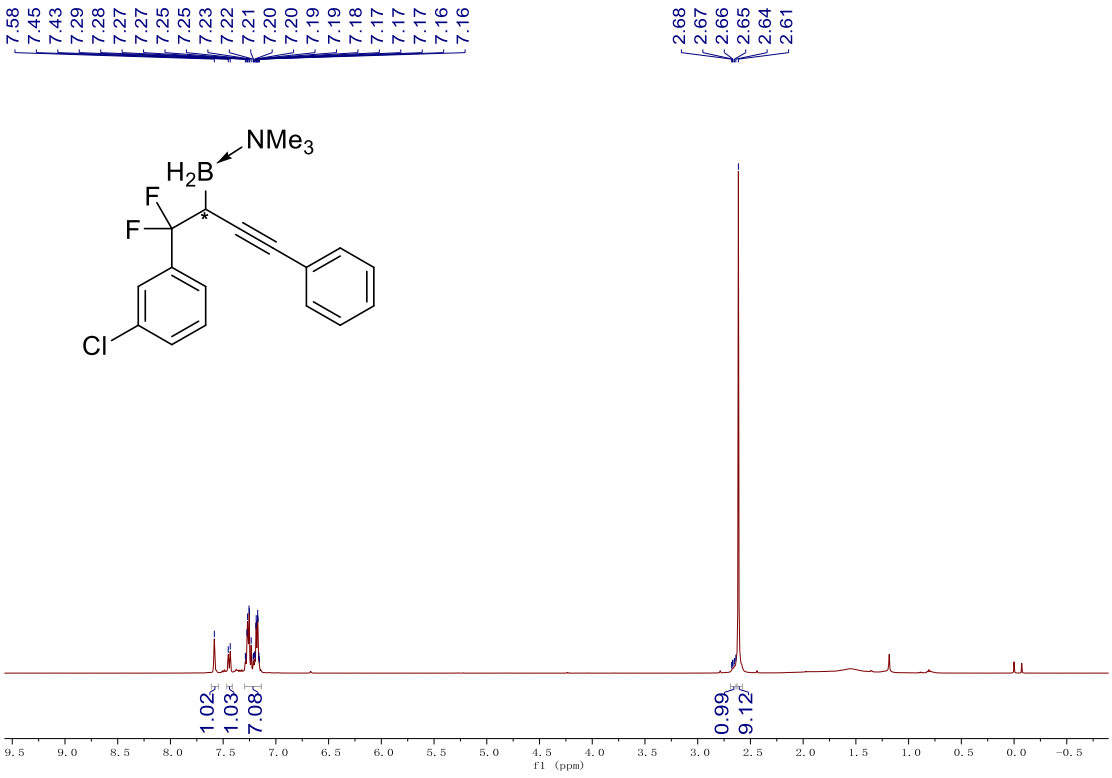
(+)-Trimethylamine-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3da): ^{13}C NMR (101 MHz, $CDCl_3$)



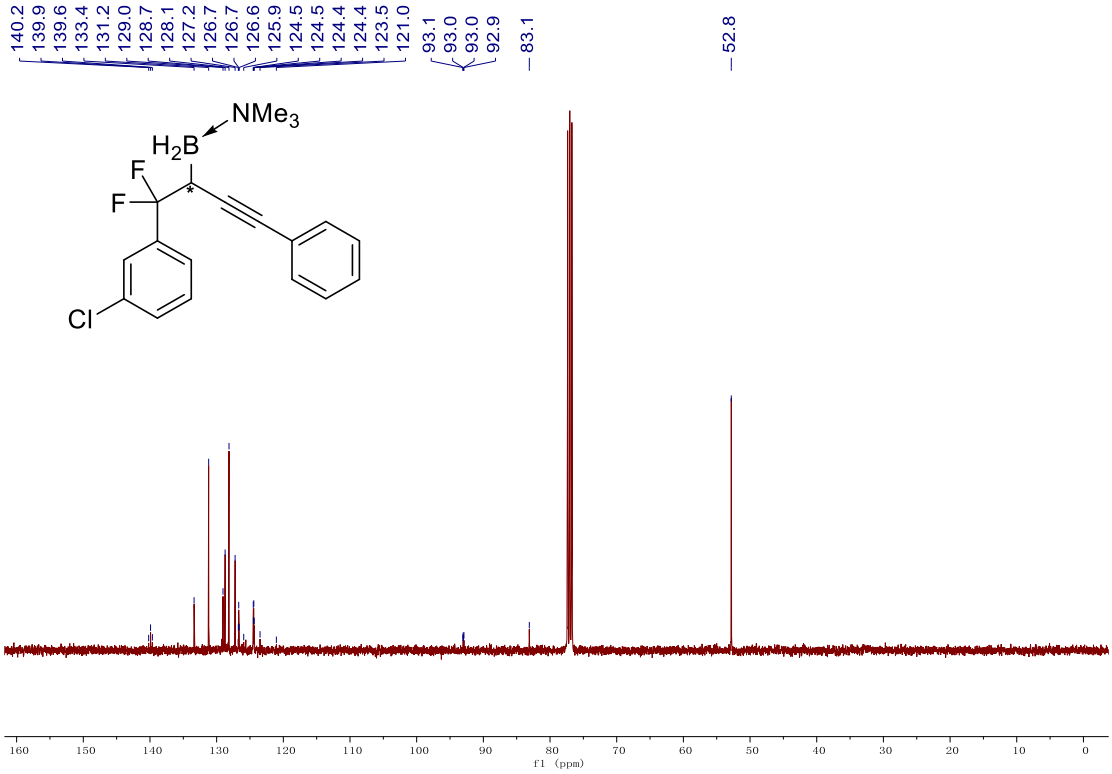
(+)-Trimethylamine-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3da): ^{19}F NMR (376 MHz, $CDCl_3$)



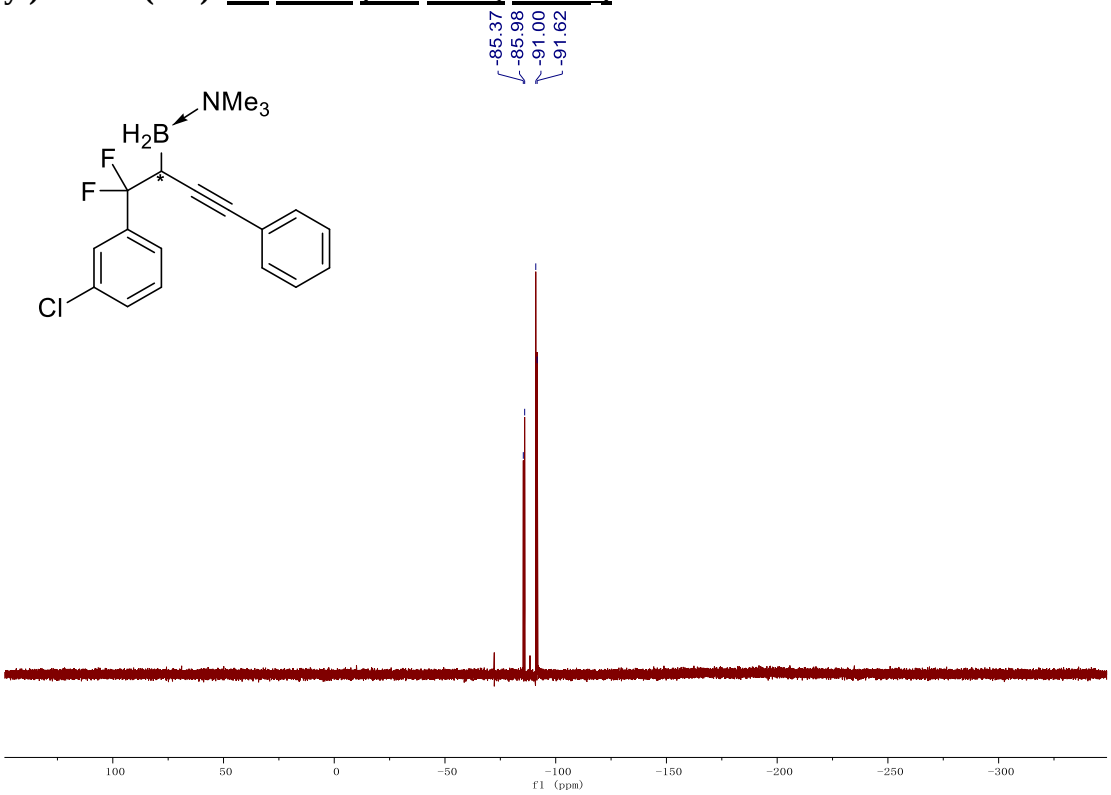
(-)-Trimethylamine-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3ea): ^{1}H NMR (400 MHz, $CDCl_3$)



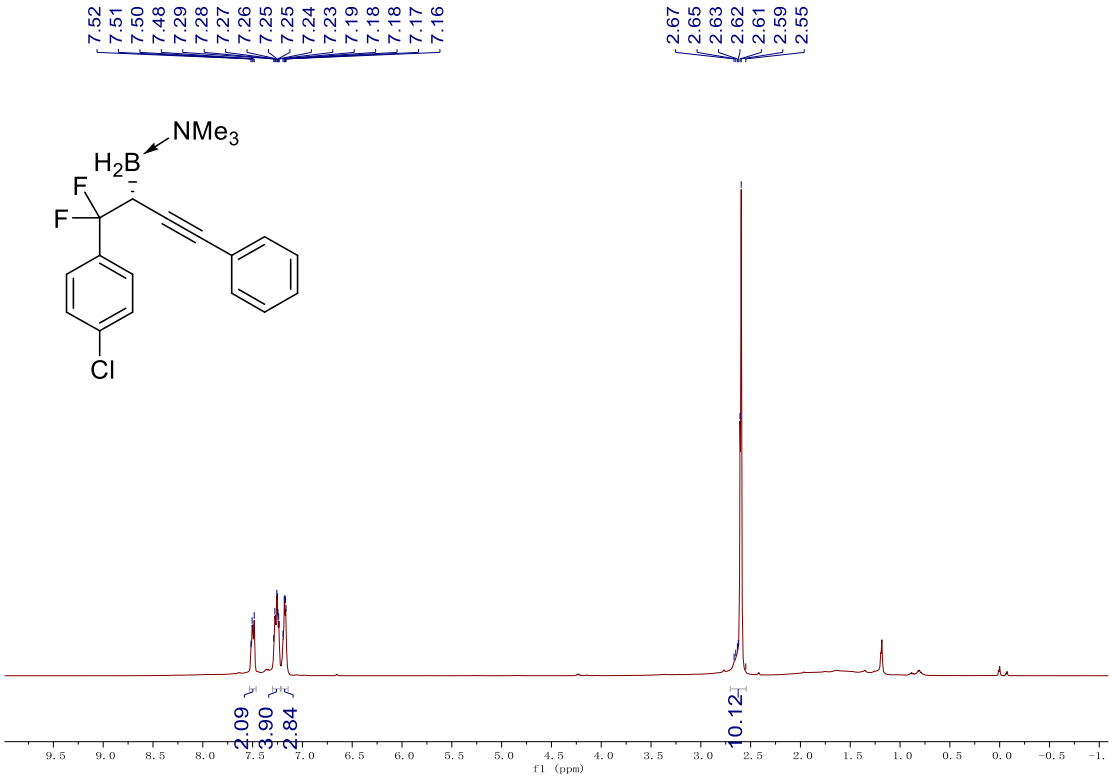
(-)-Trimethylamine-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3ea): ^{13}C NMR (101 MHz, $CDCl_3$)



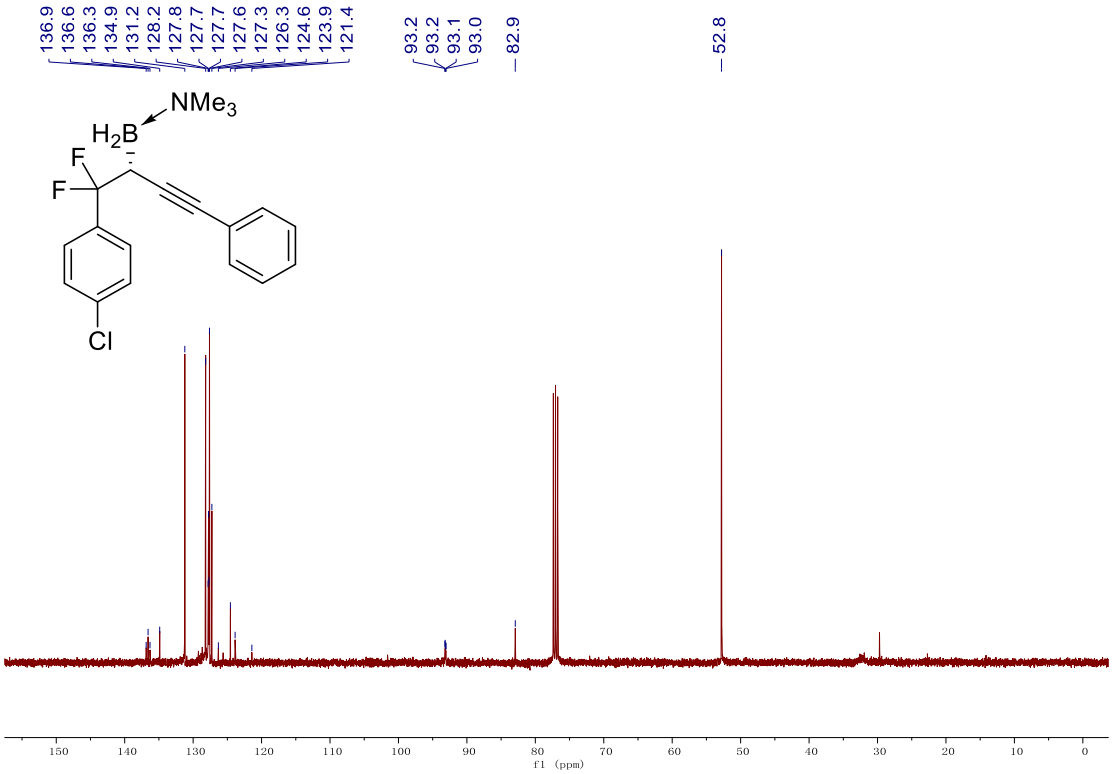
(-)-Trimethylamine-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3ea): ^{19}F NMR (376 MHz, $CDCl_3$)



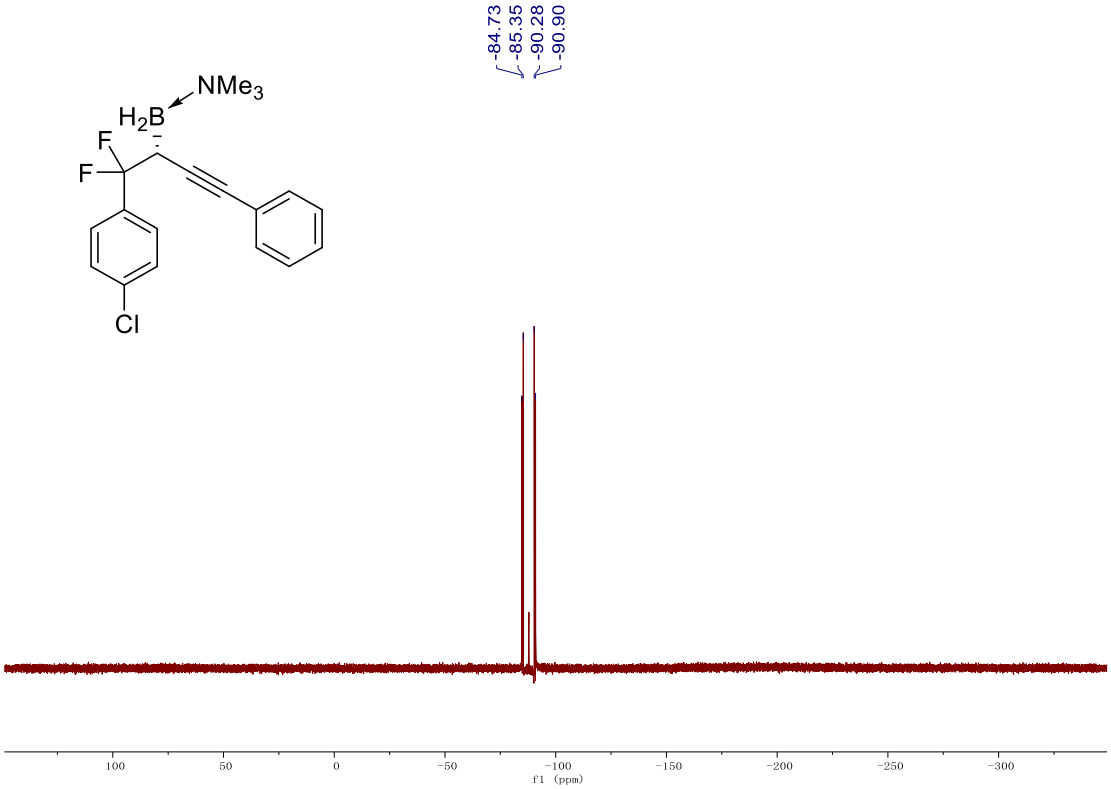
(-)-(*R*)-Trimethylamine-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3fa): ^{1}H NMR (400 MHz, $CDCl_3$)



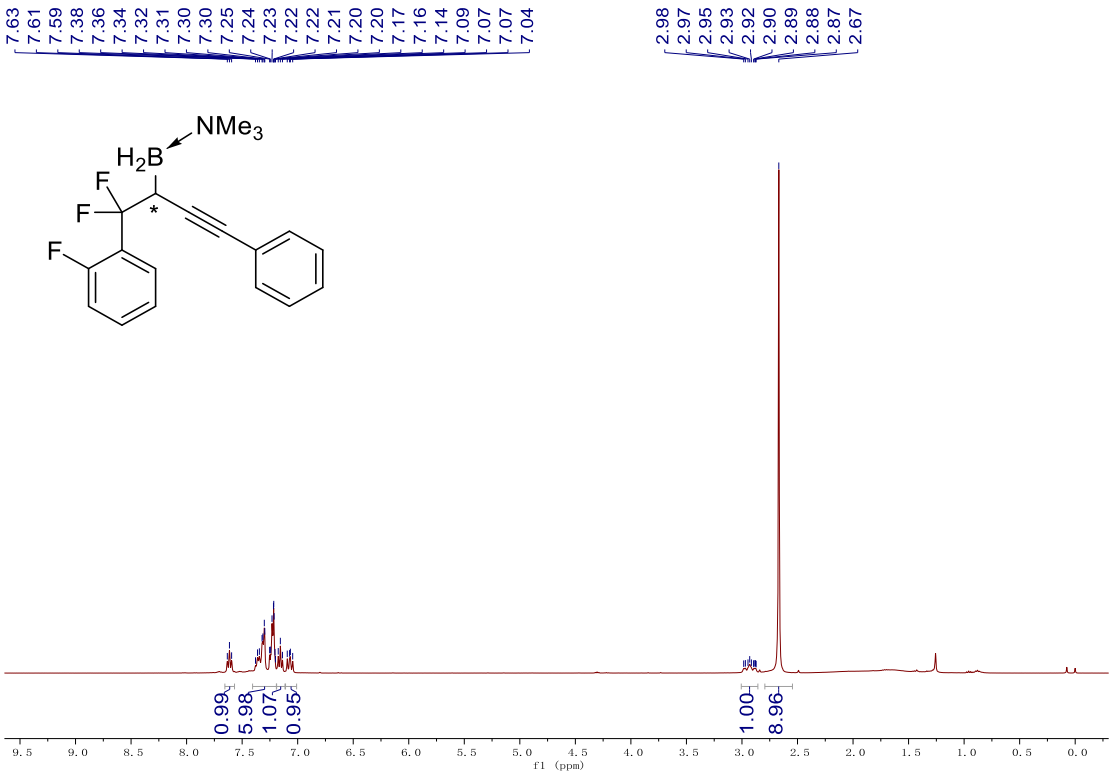
(-)-(*R*)-Trimethylamine-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3fa): ^{13}C NMR (101 MHz, $CDCl_3$)



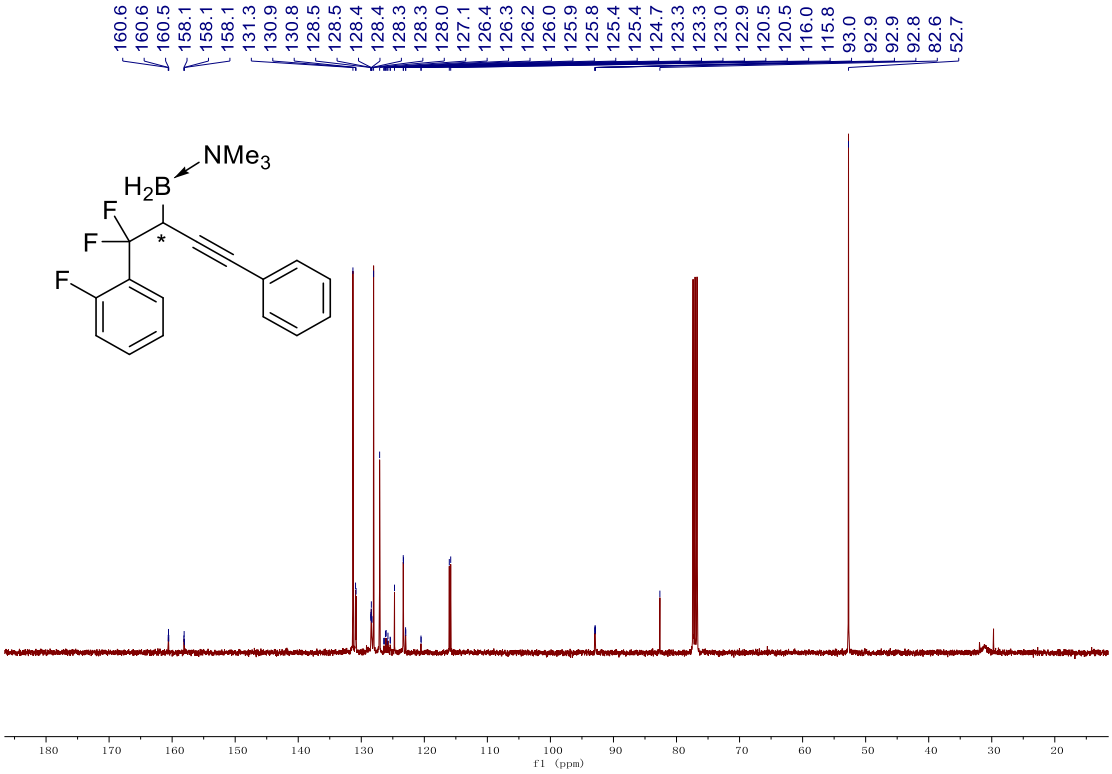
(-)-(*R*)-Trimethylamine-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3fa): ^{19}F NMR (376 MHz, $CDCl_3$)



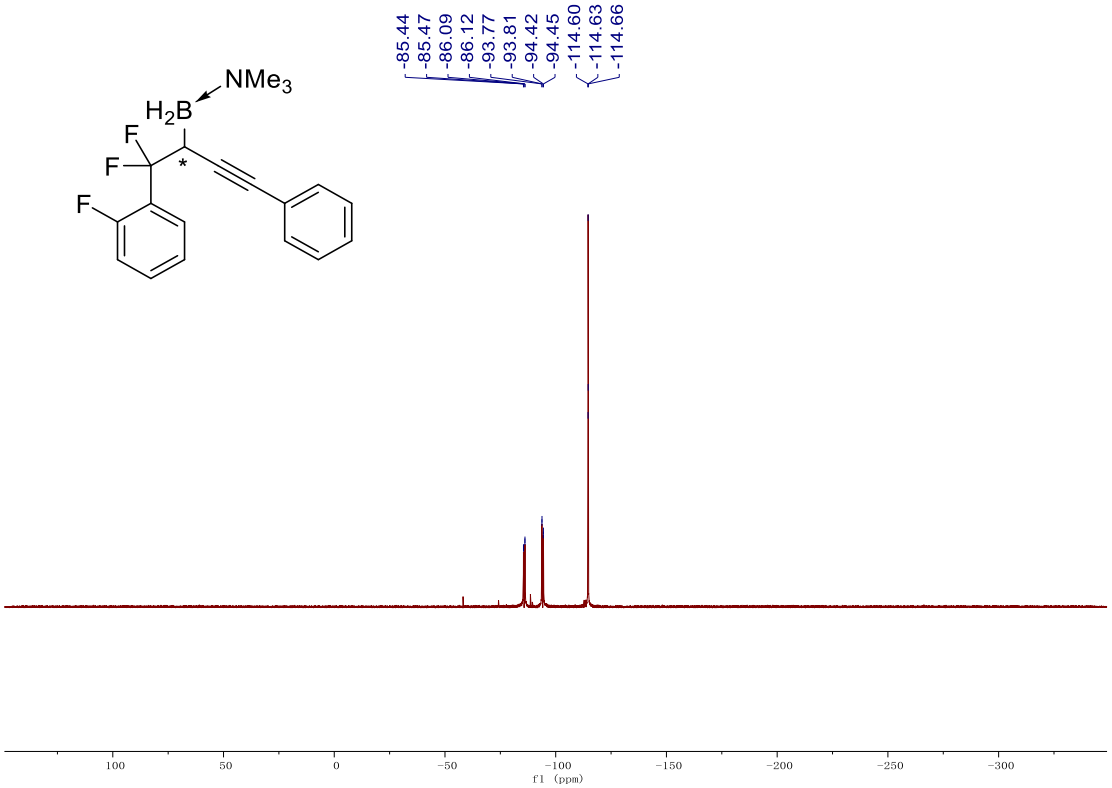
(+)-Trimethylamine-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-yl)borane (3ga): ^{1}H NMR (400 MHz, $CDCl_3$)



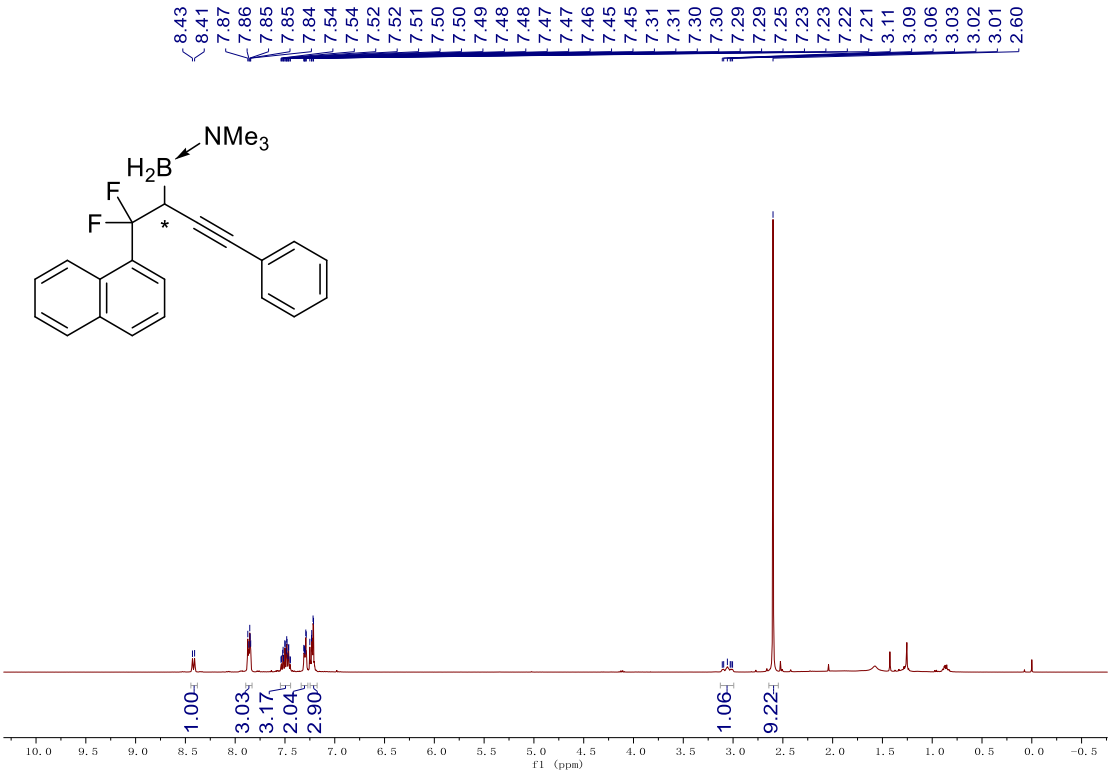
(+)-Trimethylamine-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-yl)borane (3ga): ^{13}C NMR (101 MHz, $CDCl_3$)



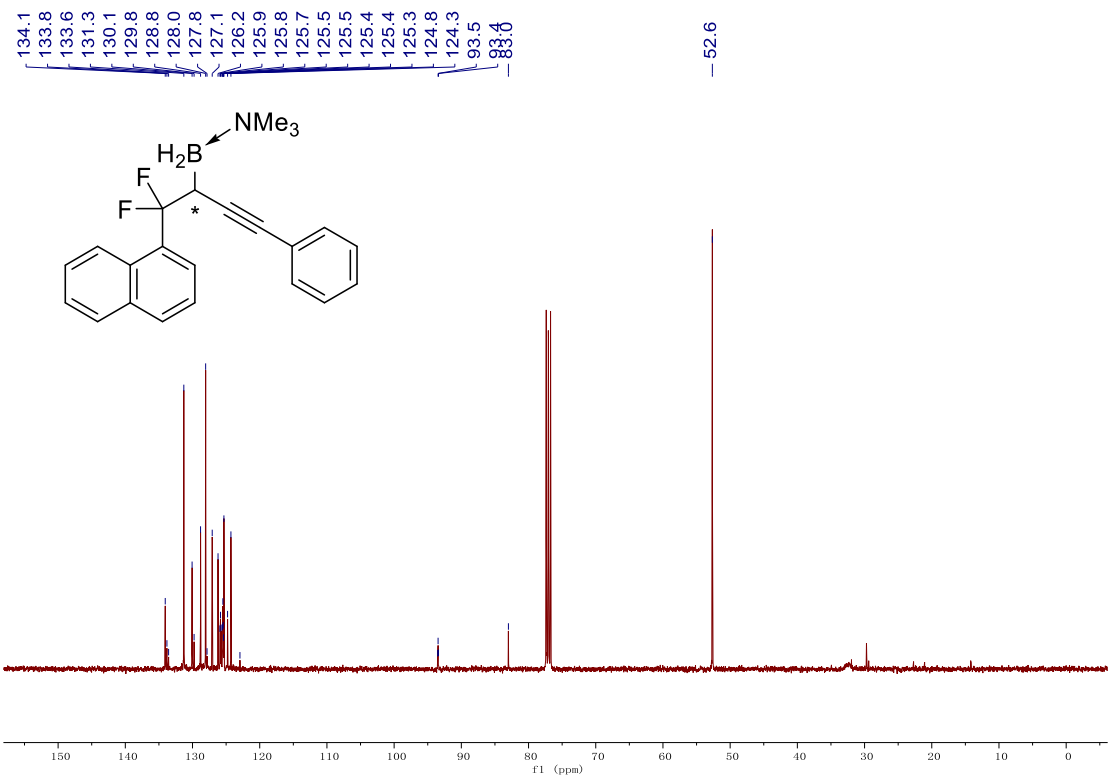
(+)-Trimethylamine-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-yl)borane (3ga): ^{19}F NMR (376 MHz, $CDCl_3$)



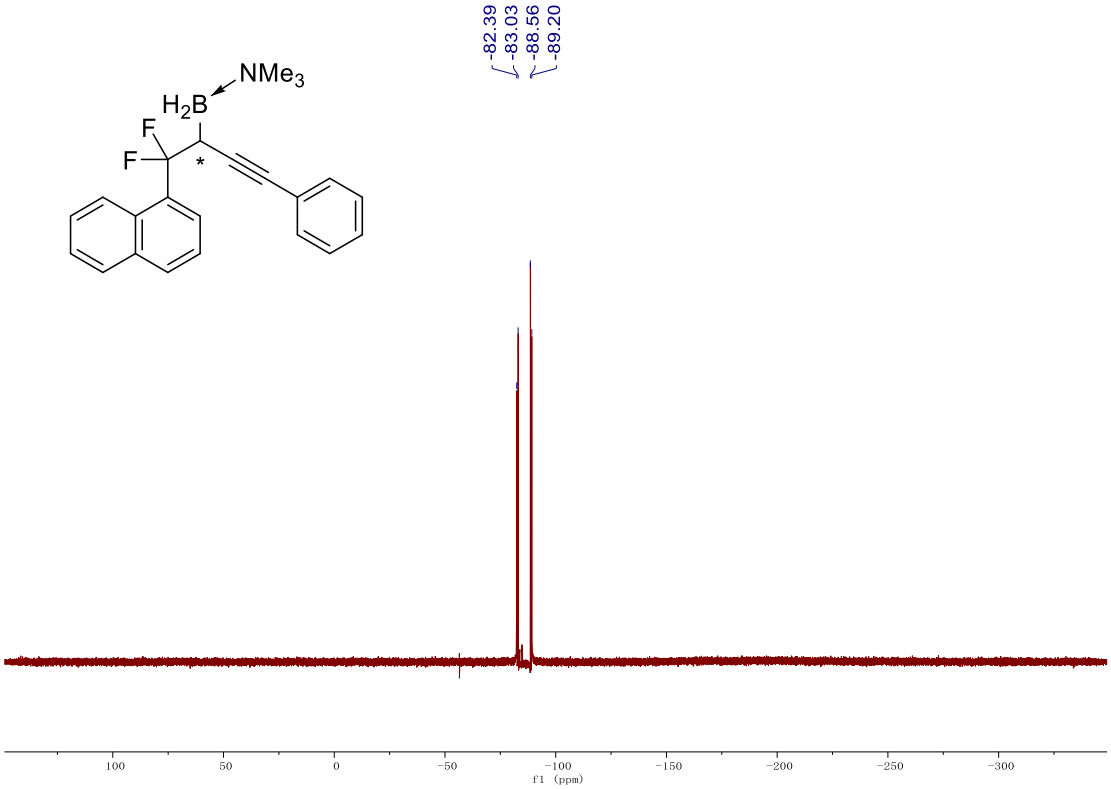
(+)-Trimethylamine-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-yl)borane (3ha): ^{1}H NMR (400 MHz, $CDCl_3$)



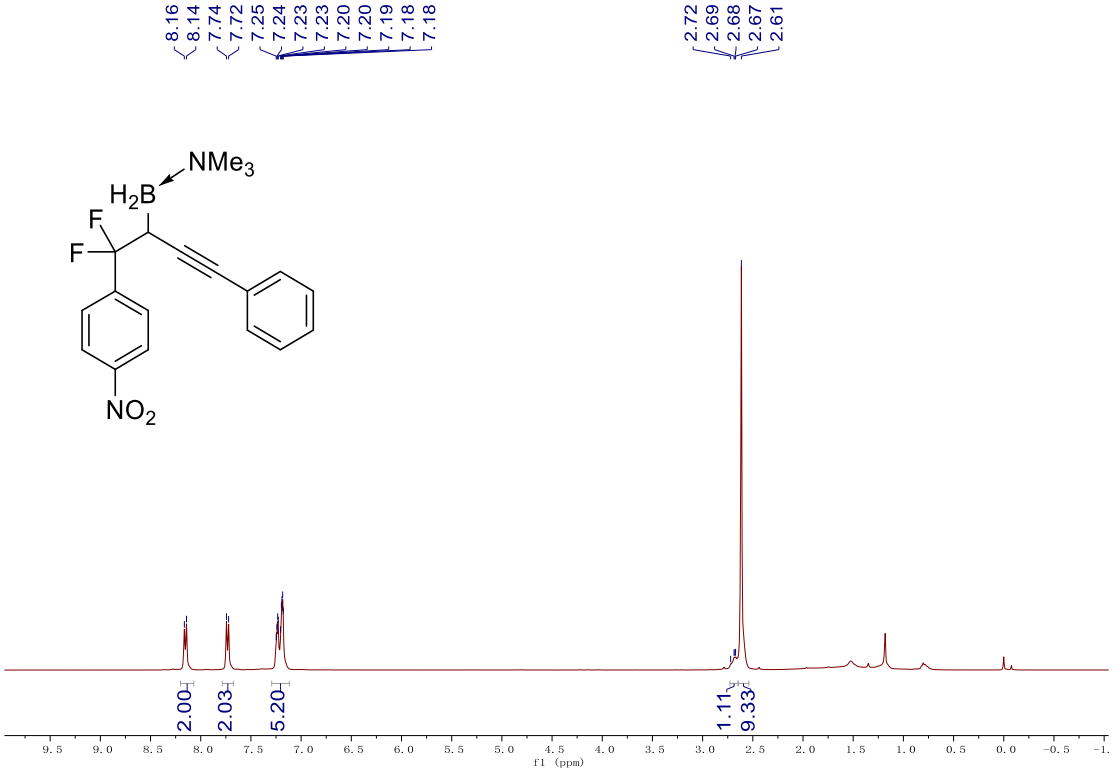
(+)-Trimethylamine-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-yl)borane (3ha): ^{13}C NMR (101 MHz, $CDCl_3$)



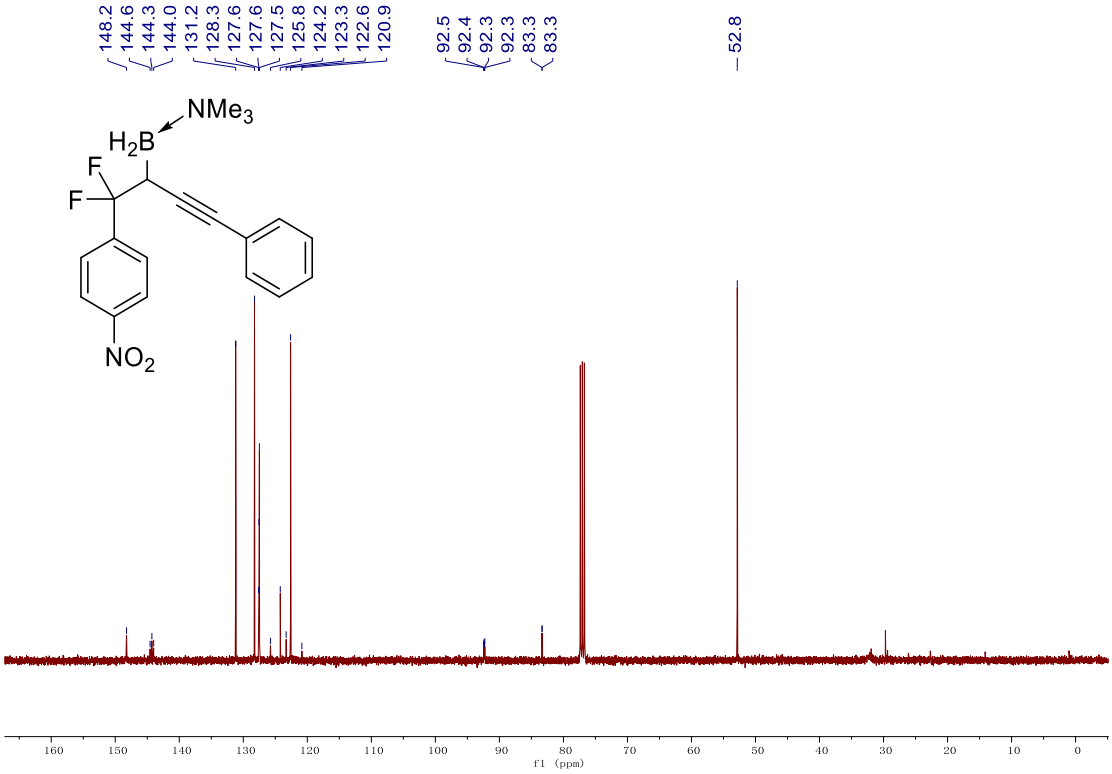
(+)-Trimethylamine-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-yl)borane (3ha): ^{19}F NMR (376 MHz, $CDCl_3$)



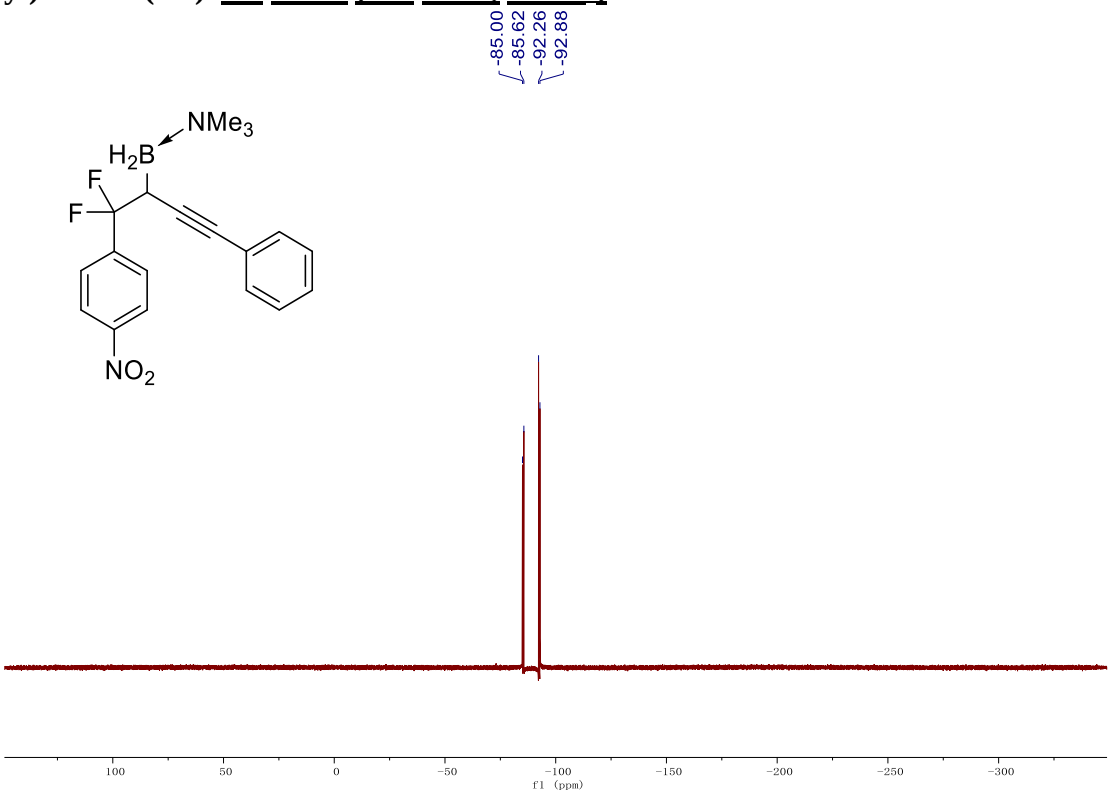
(-)-Trimethylamine-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-yl)borane (3ia): ^{1}H NMR (400 MHz, $CDCl_3$)



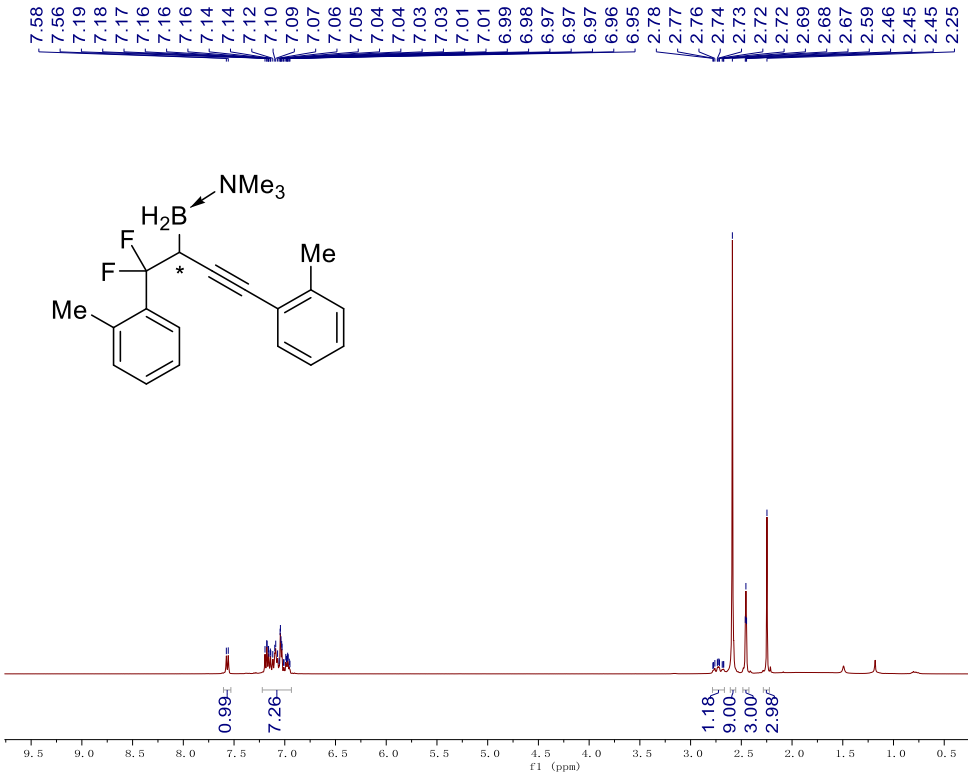
(-)-Trimethylamine-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-yl)borane (3ia): ^{13}C NMR (101 MHz, $CDCl_3$)



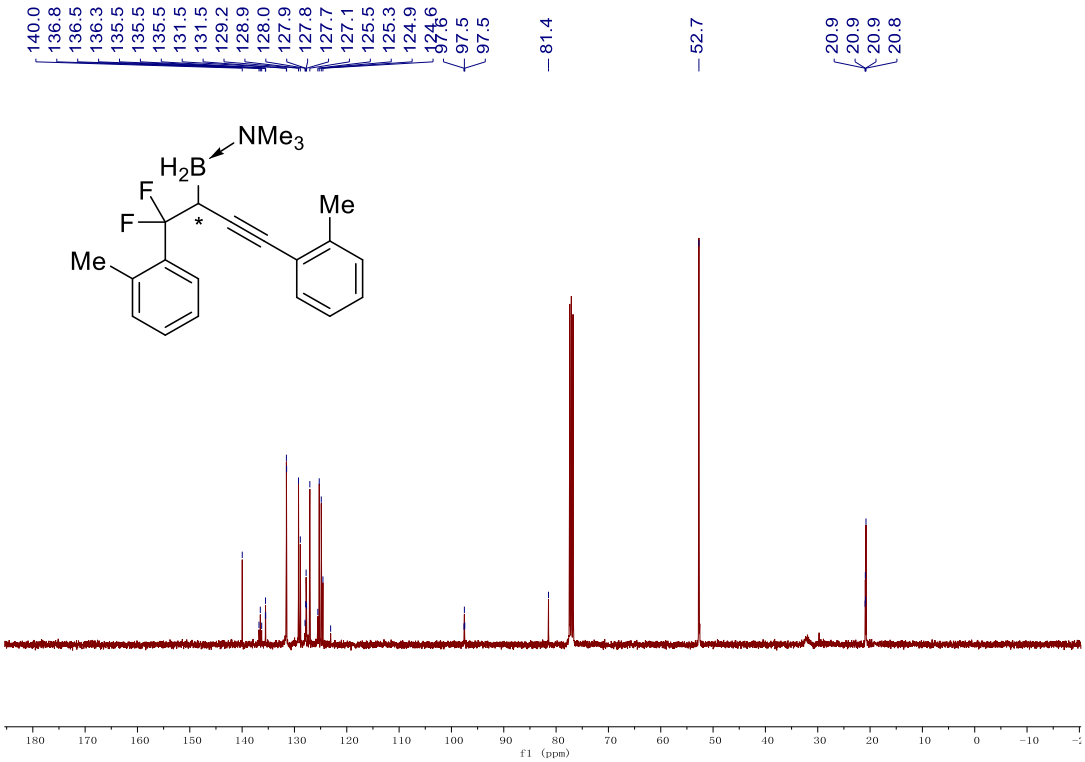
(-)-Trimethylamine-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-yl)borane (3ia): ^{19}F NMR (376 MHz, $CDCl_3$)



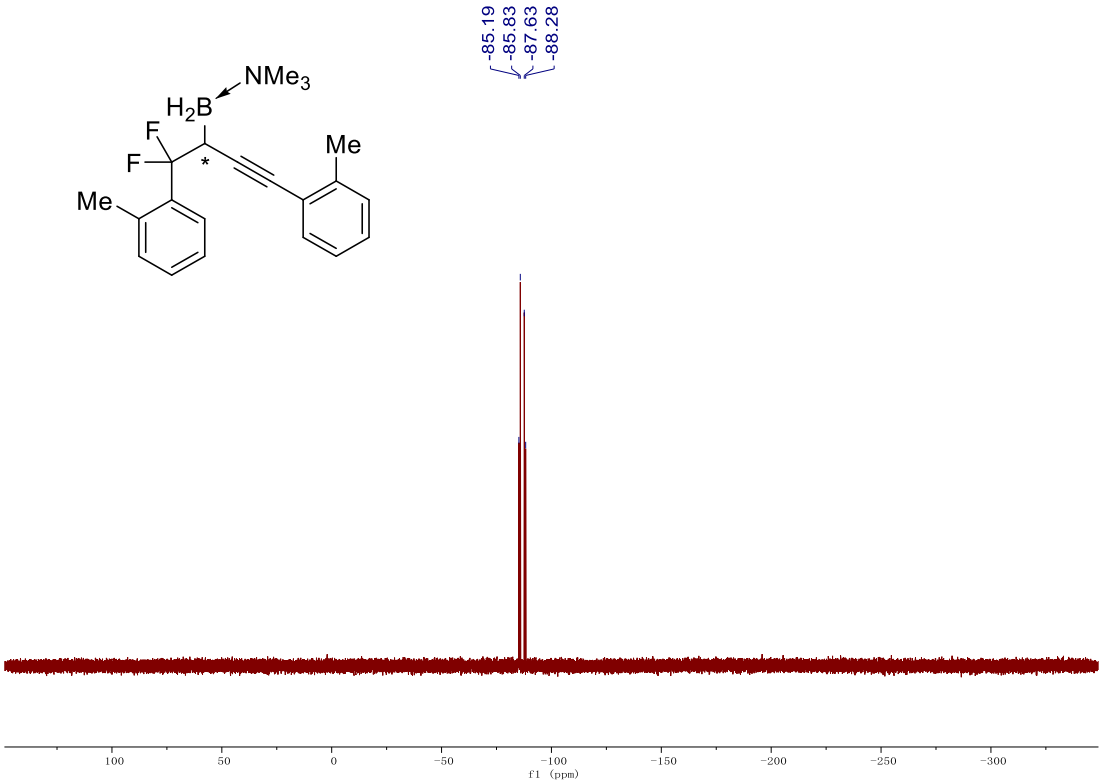
(+)-Trimethylamine-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-yl)borane (3ja): ^{1}H NMR (400 MHz, $CDCl_3$)



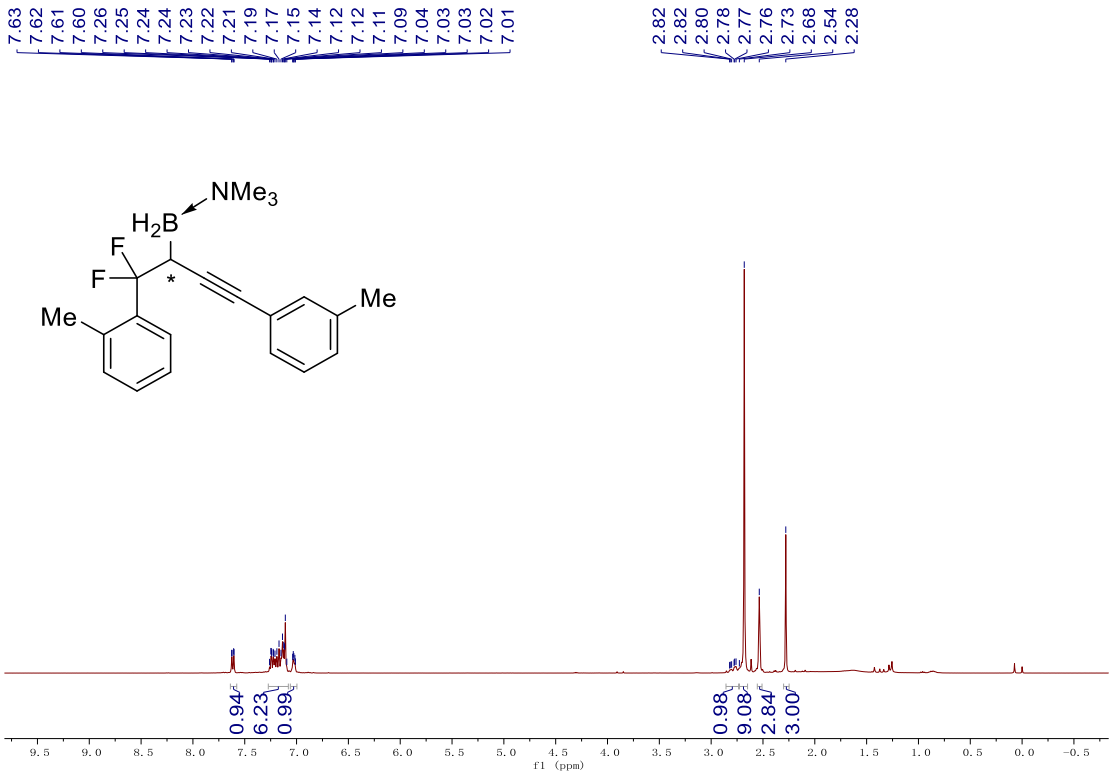
(+)-Trimethylamine-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-yl)borane (3ja): ^{13}C NMR (101 MHz, $CDCl_3$)



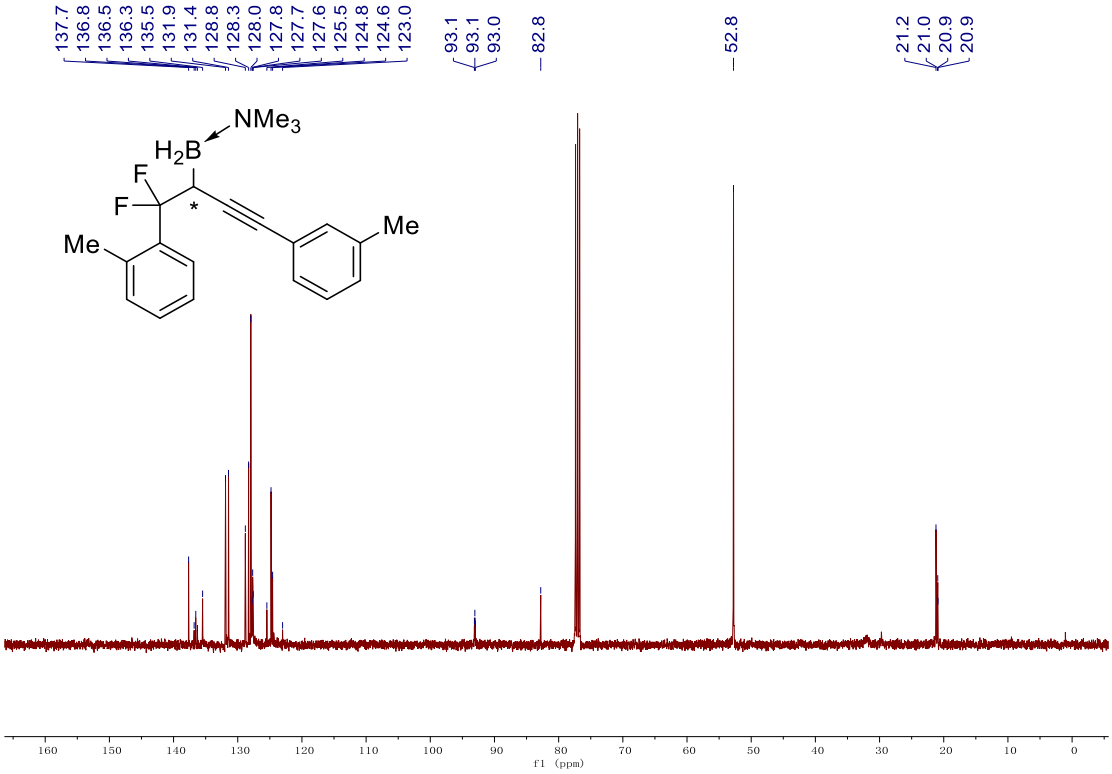
(+)-Trimethylamine-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-yl)borane (3ja): ^{19}F NMR (376 MHz, $CDCl_3$)



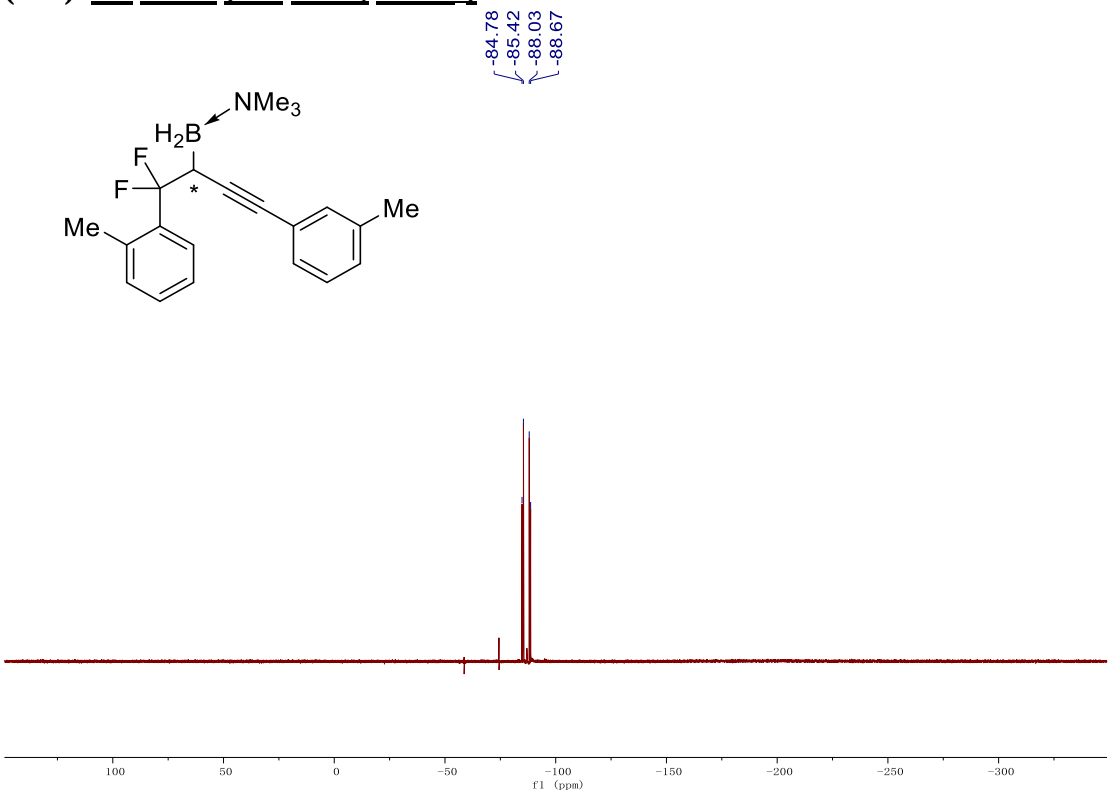
(+)-Trimethylamine-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ka): ^{1}H NMR (400 MHz, $CDCl_3$)



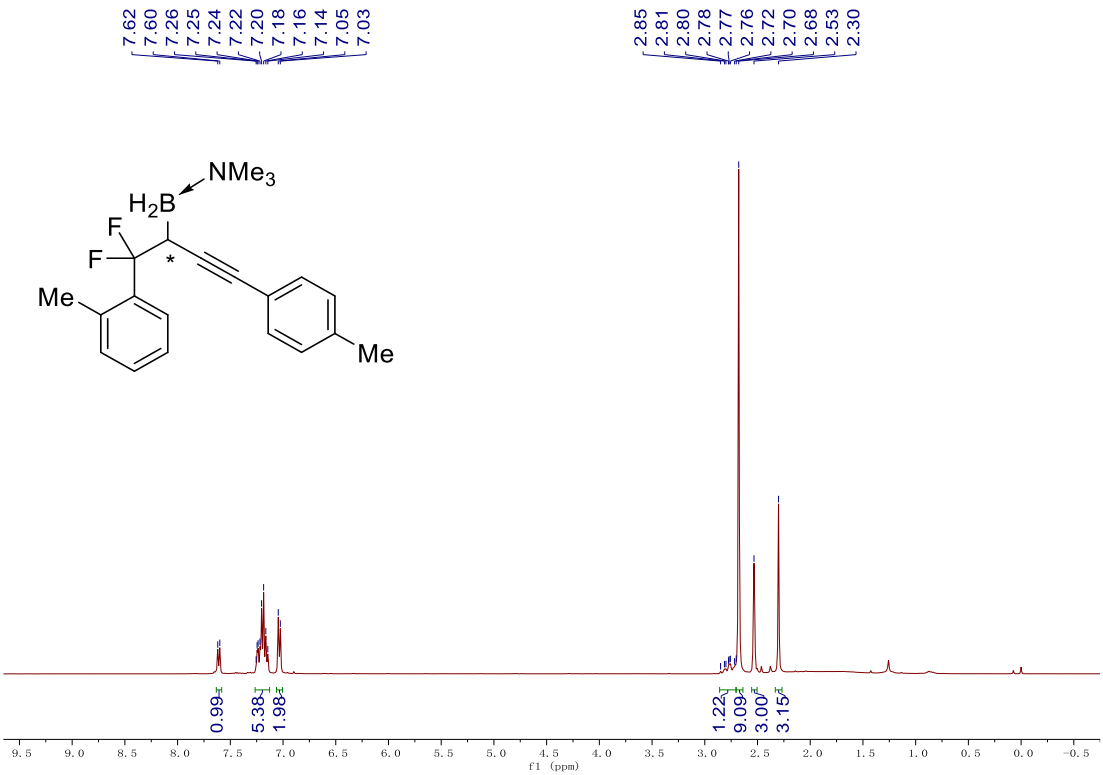
(+)-Trimethylamine-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ka): ^{13}C NMR (101 MHz, $CDCl_3$)



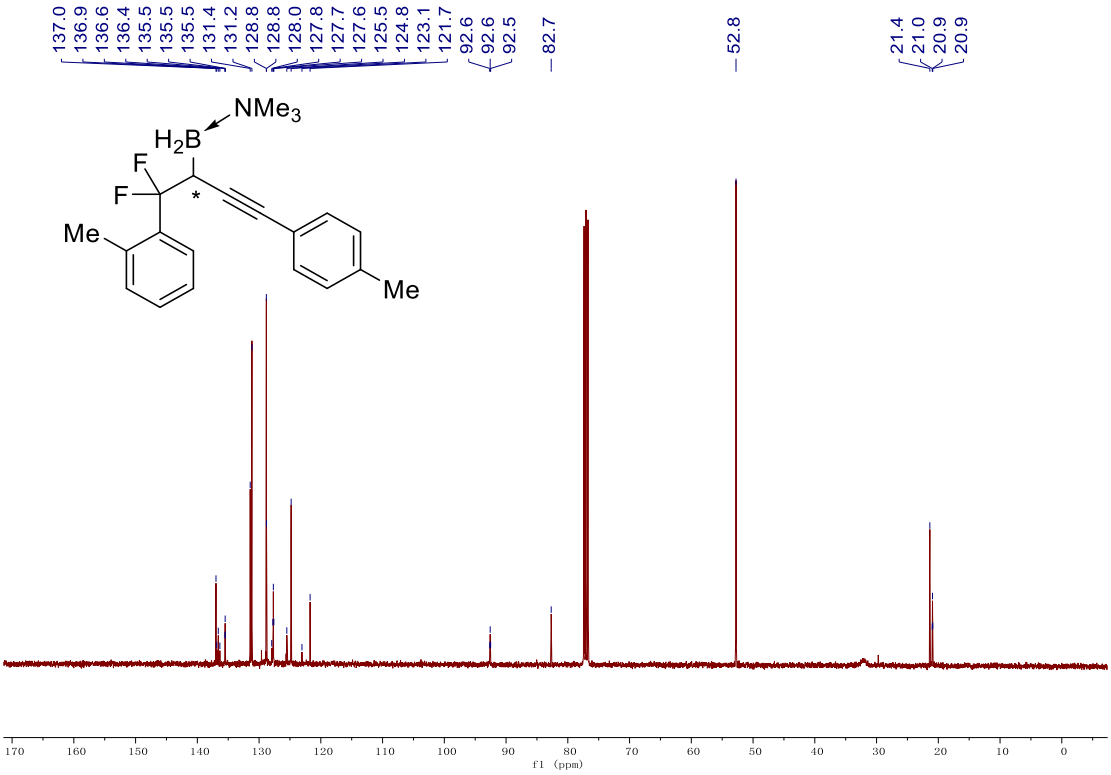
(+)-Trimethylamine-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ka): ^{19}F NMR (376 MHz, $CDCl_3$)



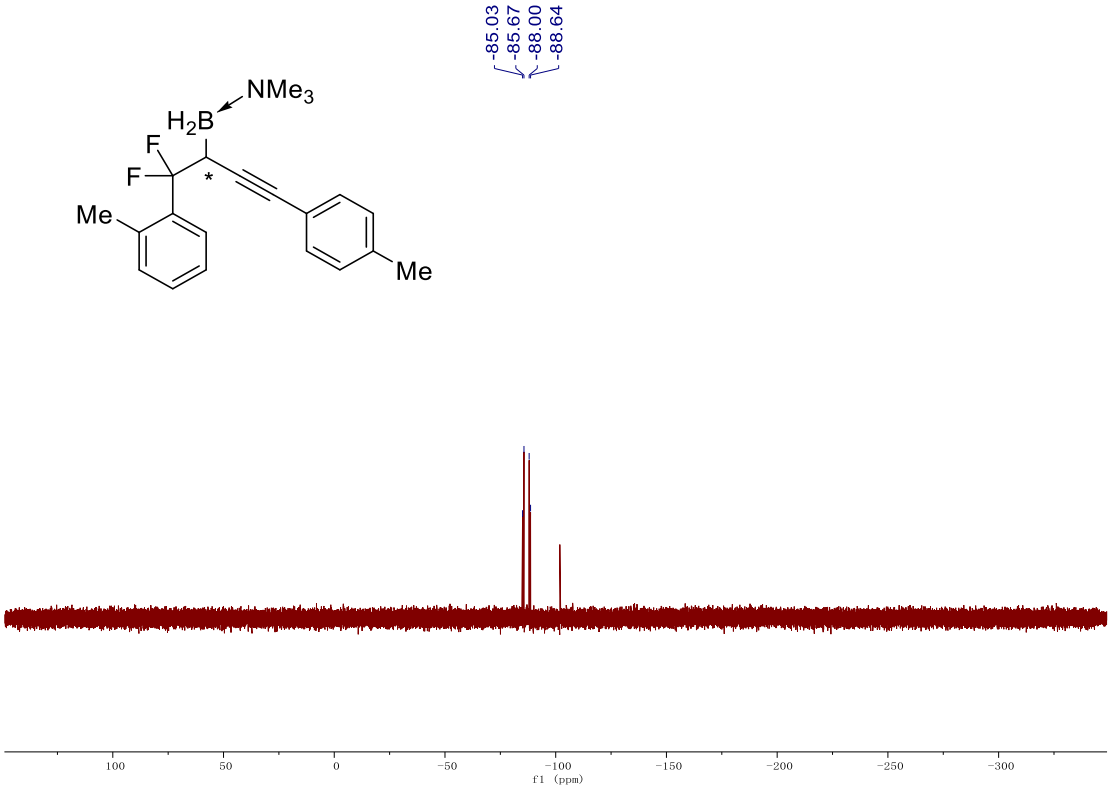
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-yl)borane (3la): ^{1}H NMR (400 MHz, $CDCl_3$)



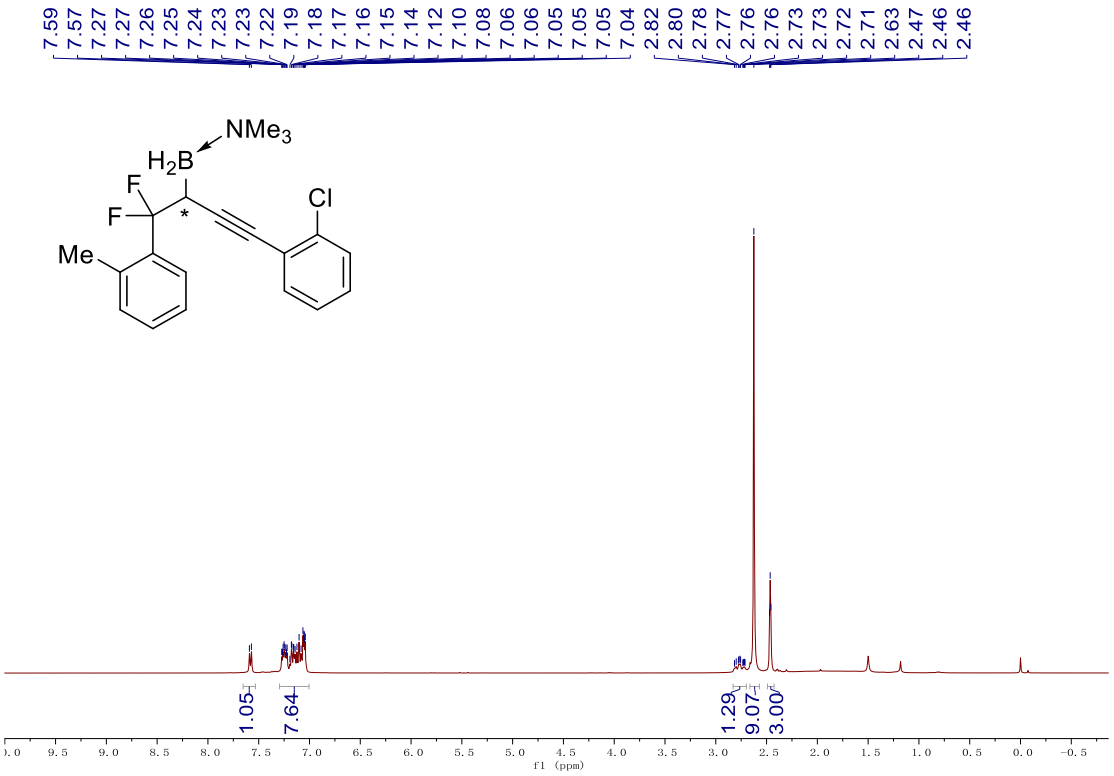
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-yl)borane (3la): ^{13}C NMR (101 MHz, $CDCl_3$)



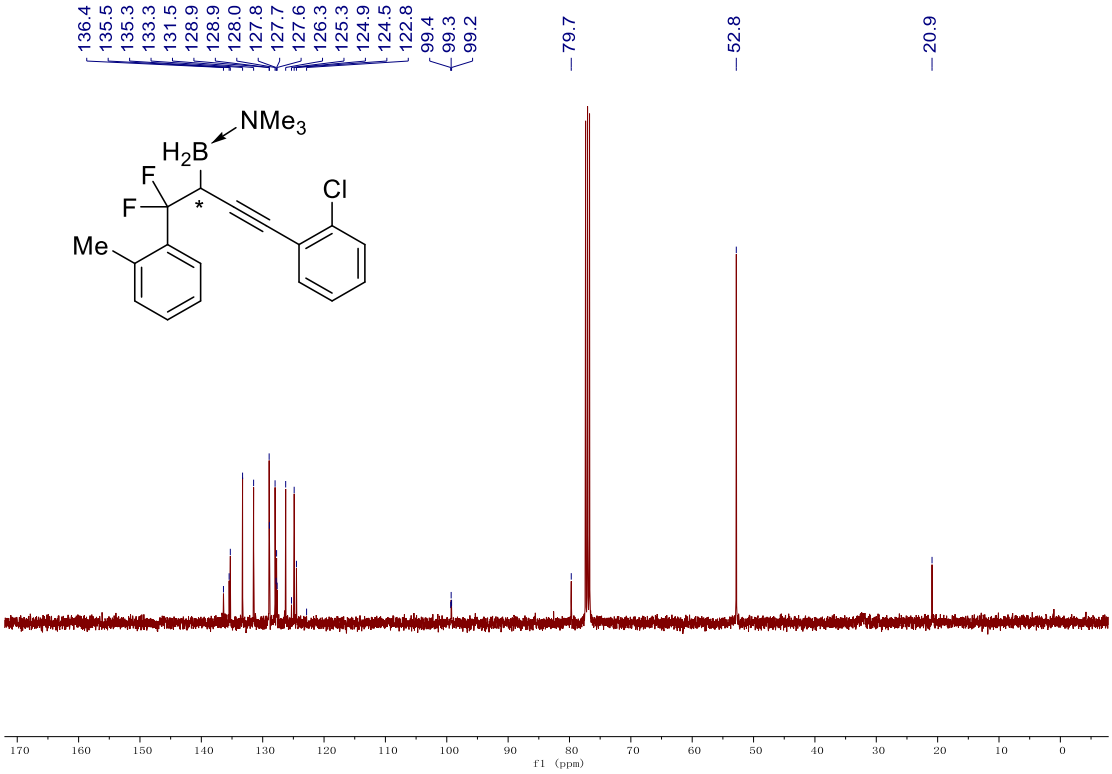
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-yl)borane (3la): ^{19}F NMR (376 MHz, $CDCl_3$)



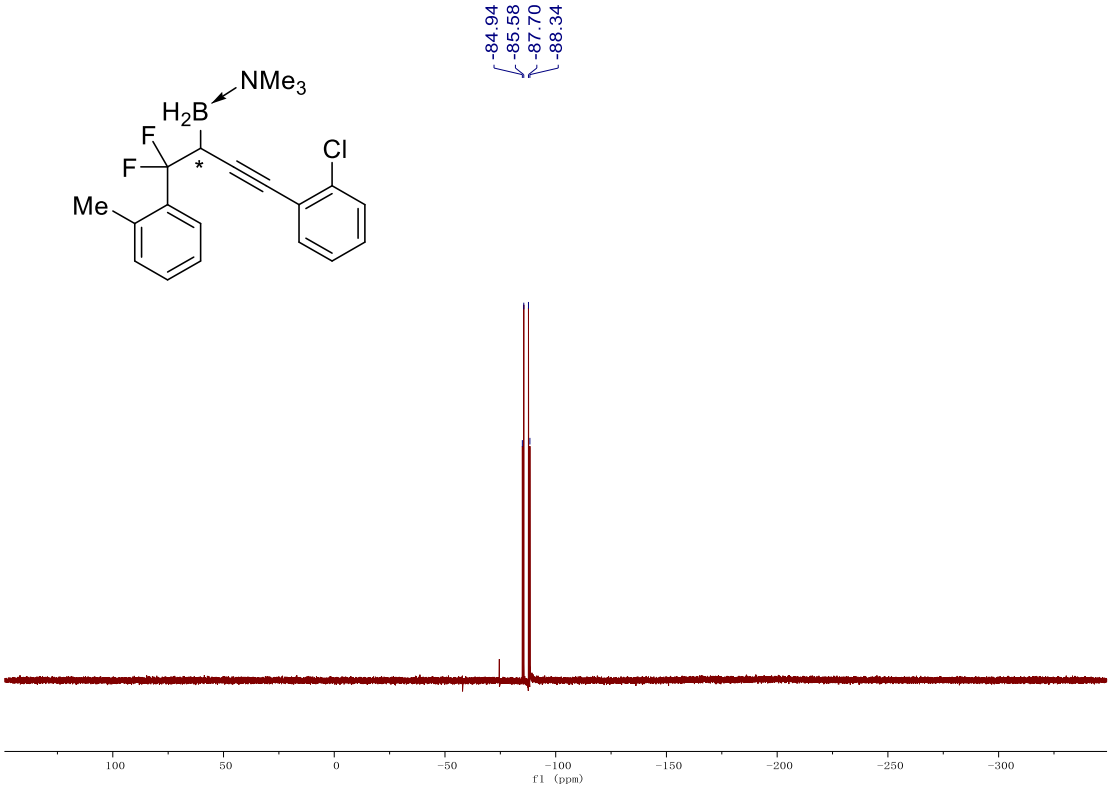
(+)-Trimethylamine-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ma): ^{1}H NMR (400 MHz, $CDCl_3$)



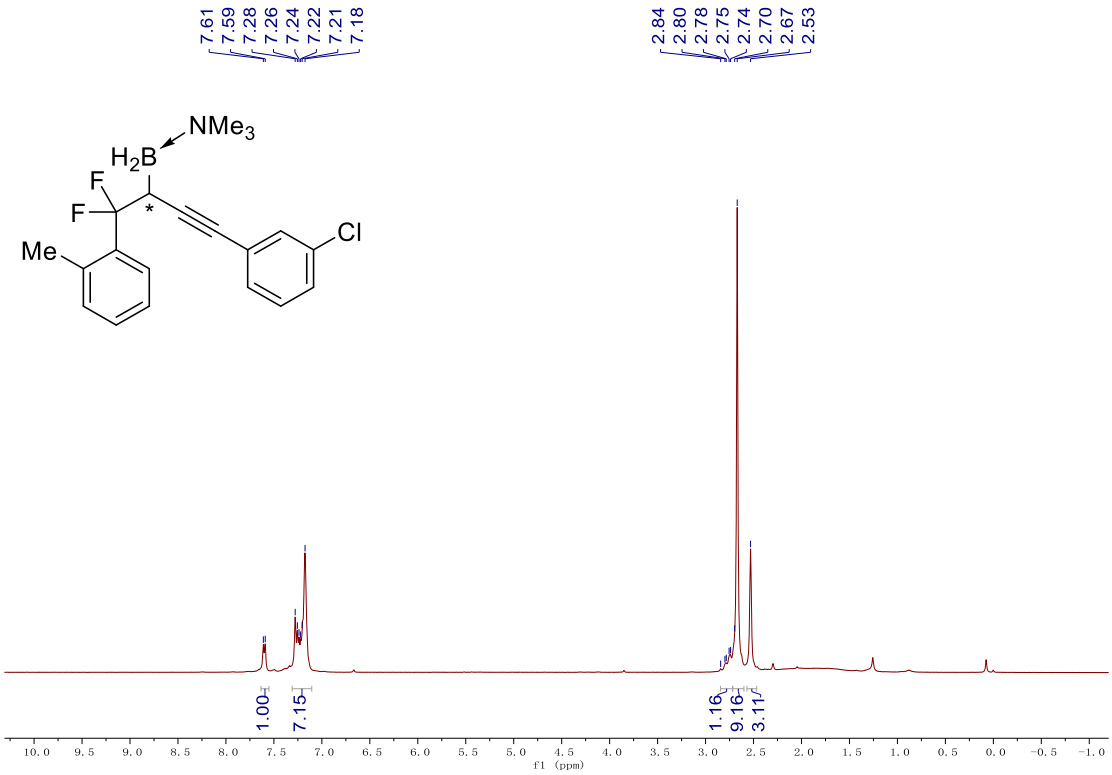
(+)-Trimethylamine-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ma): ^{13}C NMR (101 MHz, $CDCl_3$)



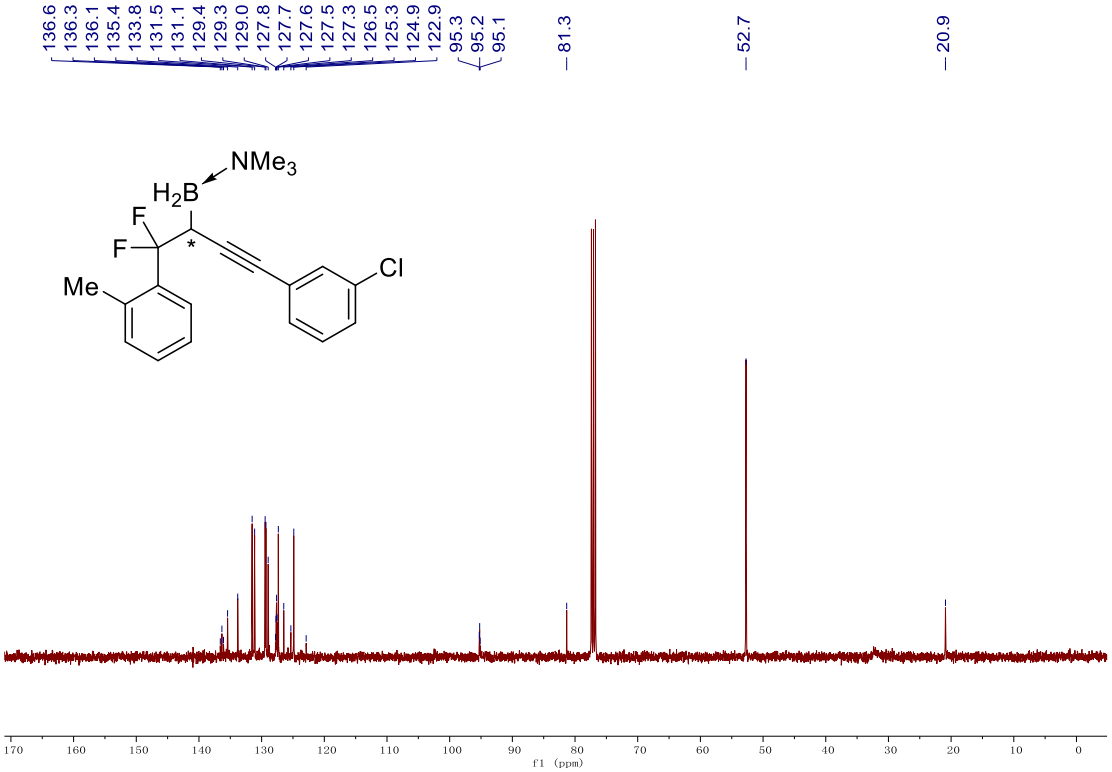
(+)-Trimethylamine-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ma): ^{19}F NMR (376 MHz, $CDCl_3$)



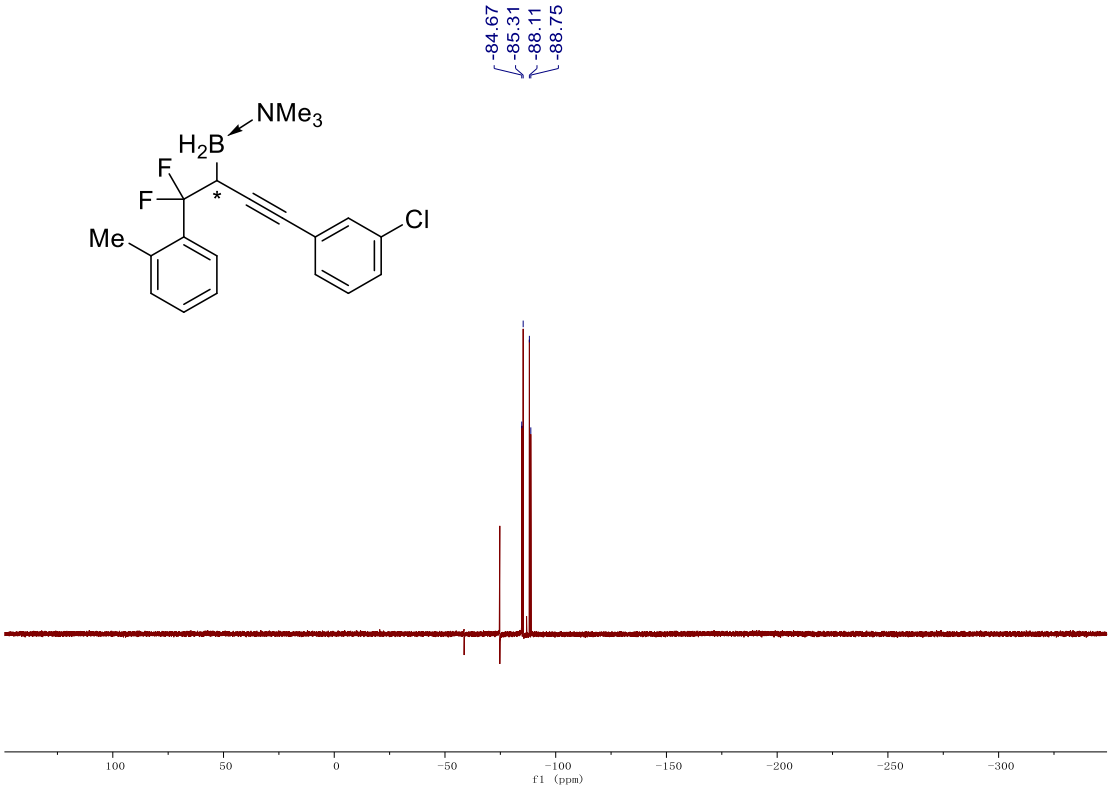
(+)-Trimethylamine-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3na): ^{1}H NMR (400 MHz, $CDCl_3$)



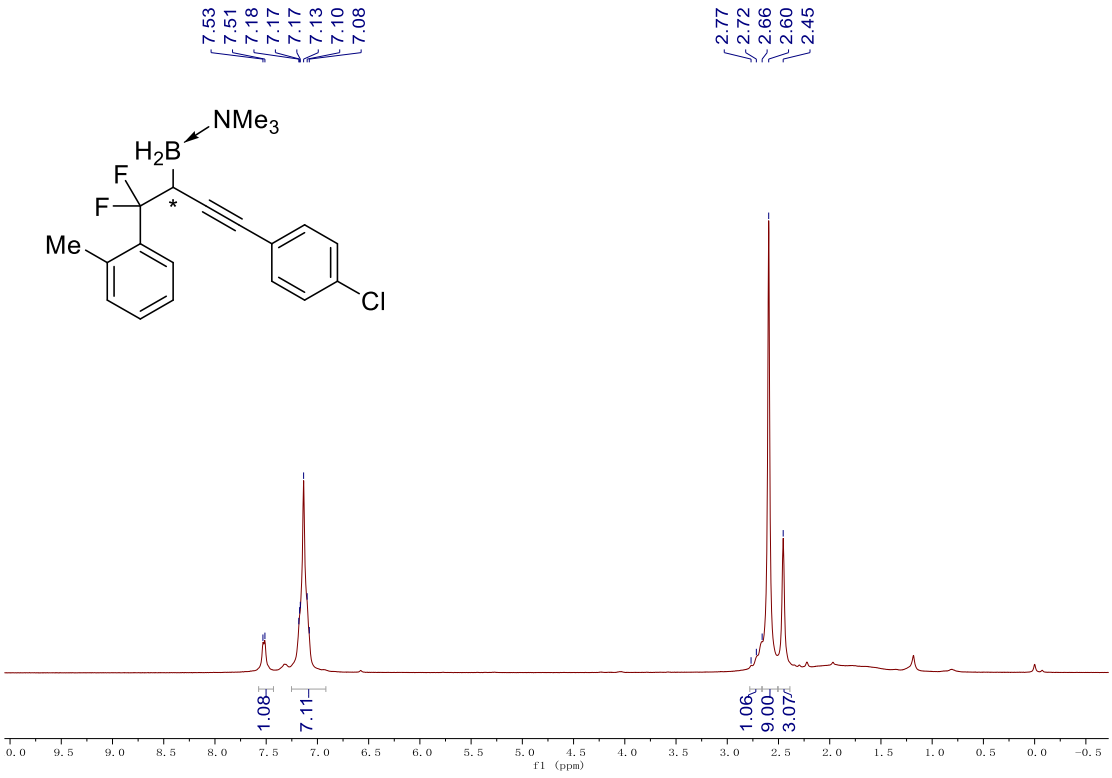
(+)-Trimethylamine-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3na): ^{13}C NMR (101 MHz, $CDCl_3$)



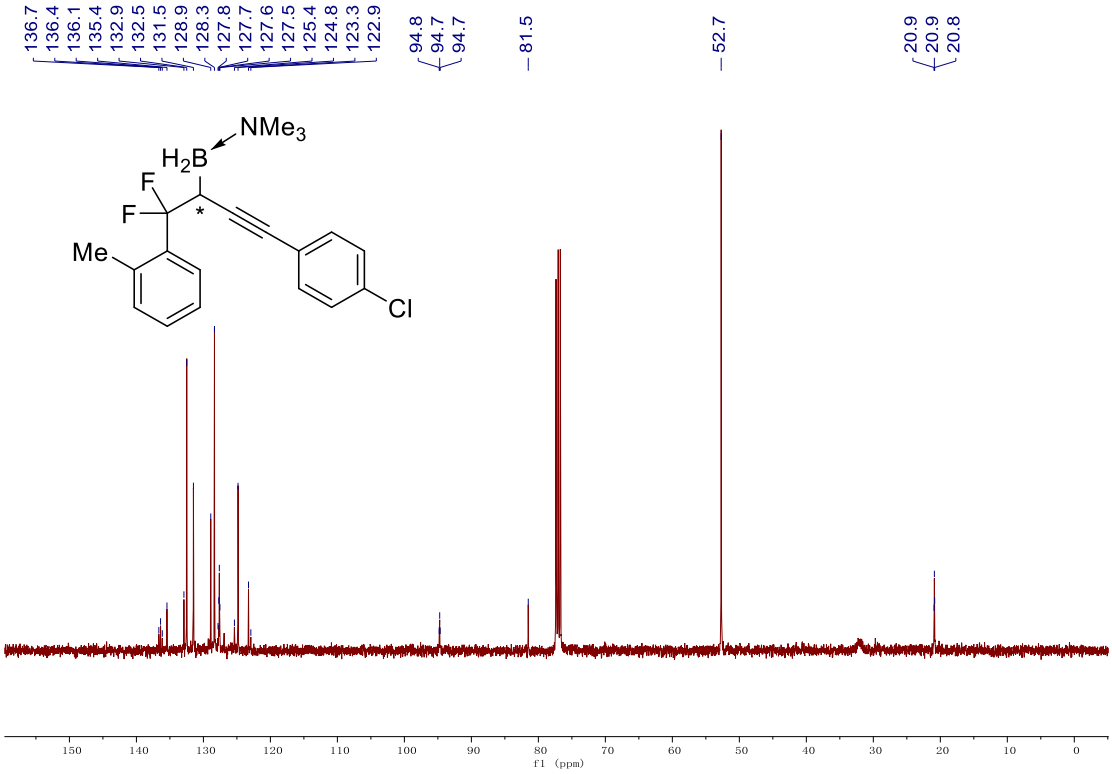
(+)-Trimethylamine-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3na): ^{19}F NMR (376 MHz, $CDCl_3$)



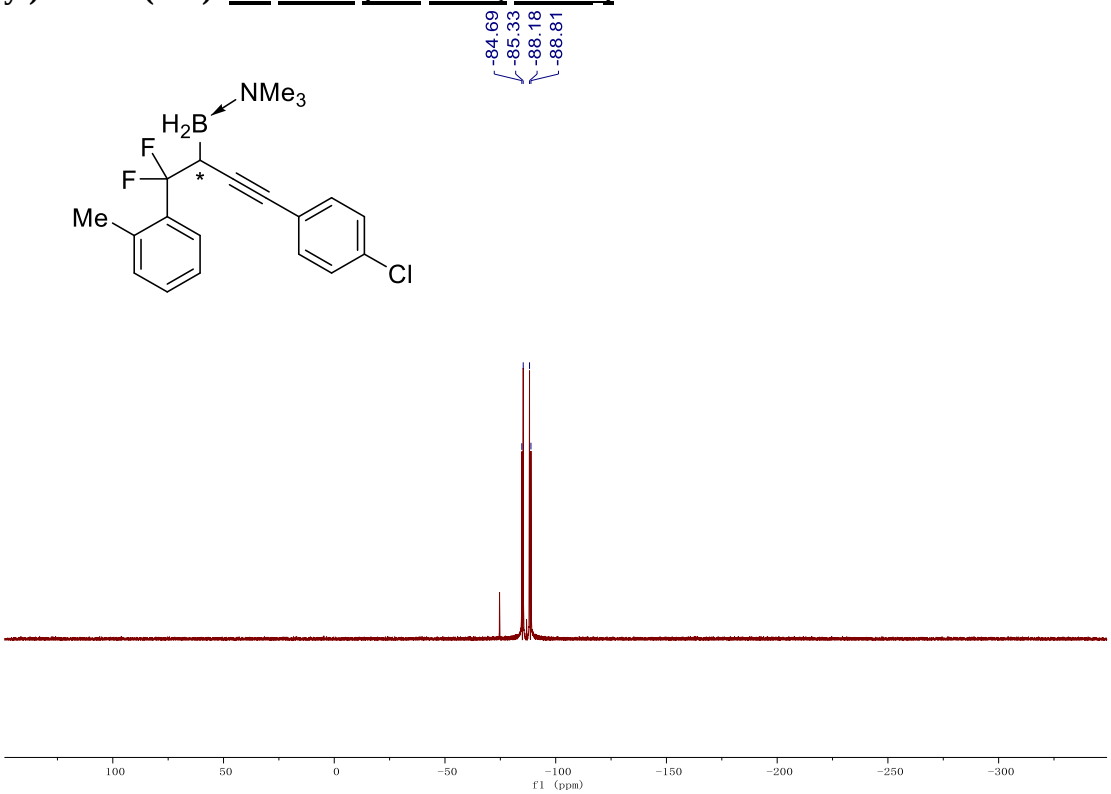
(+)-Trimethylamine-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3oa): ^{1}H NMR (400 MHz, $CDCl_3$)



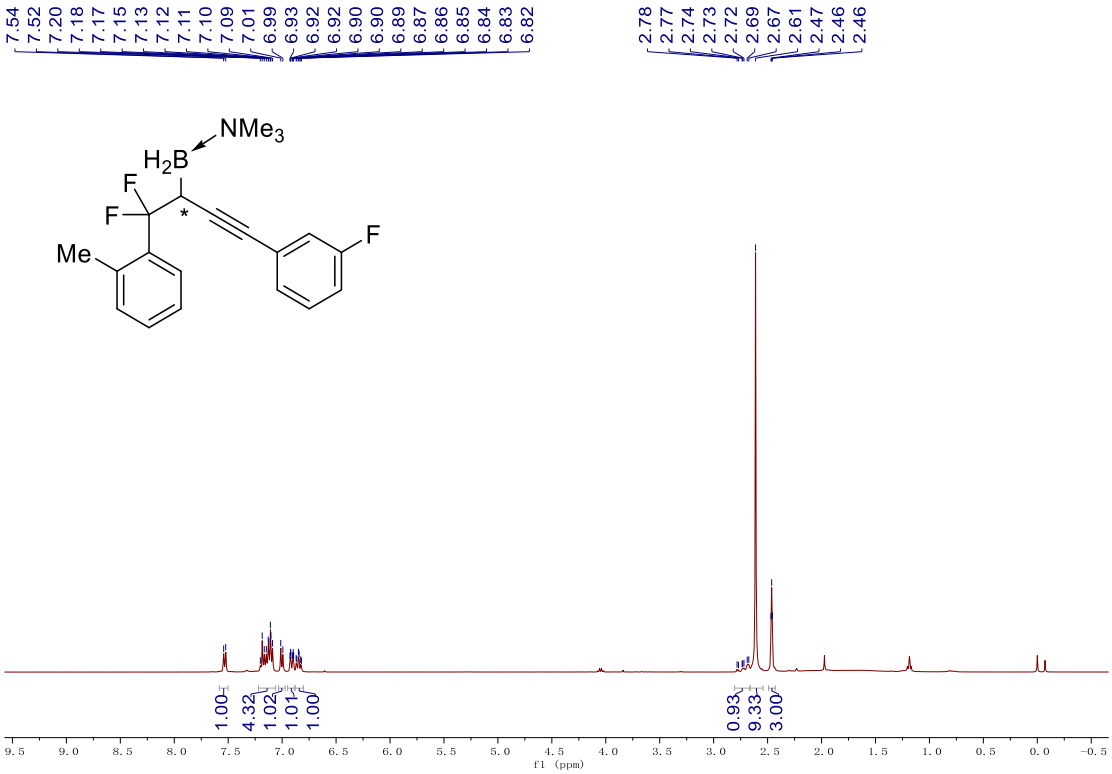
(+)-Trimethylamine-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3oa): ^{13}C NMR (101 MHz, $CDCl_3$)



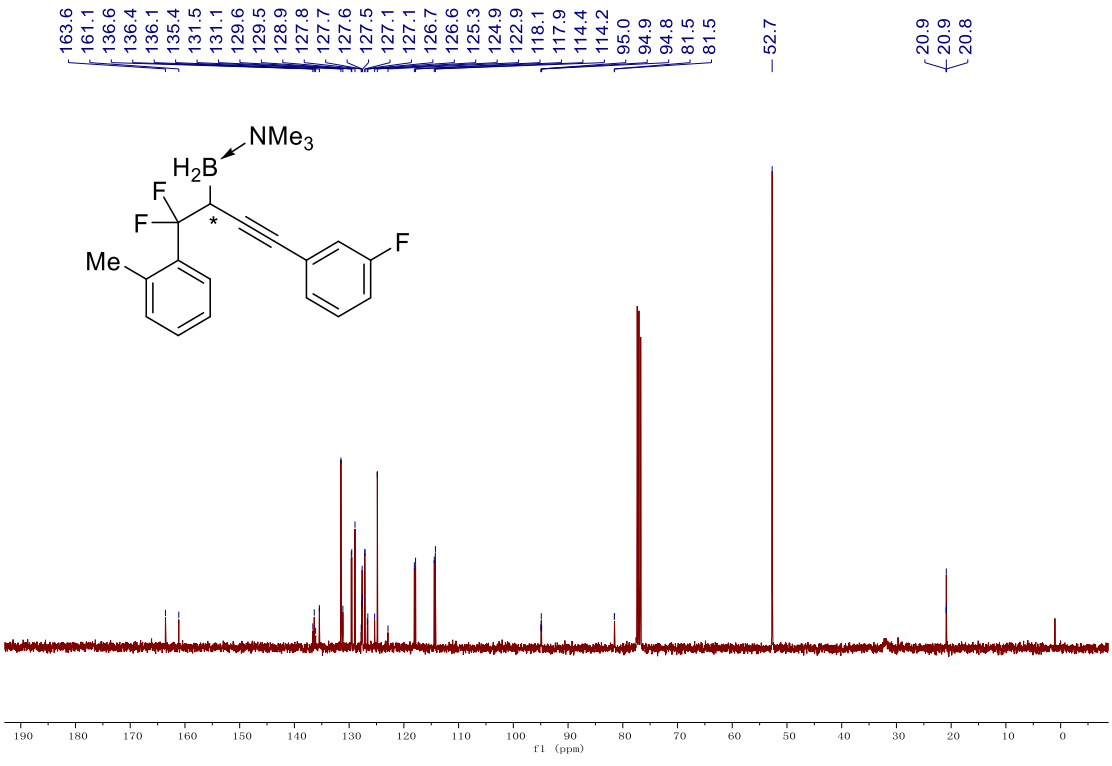
(+)-Trimethylamine-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3oa): ^{19}F NMR (376 MHz, $CDCl_3$)



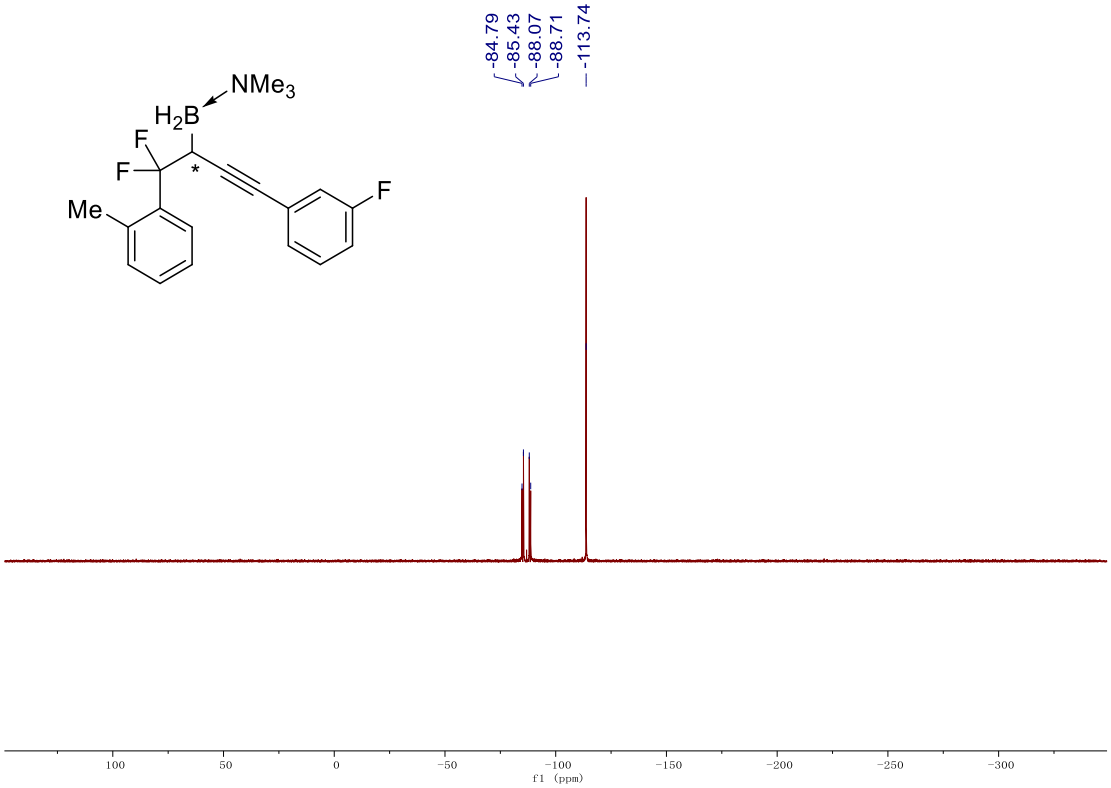
(+)-Trimethylamine-(1,1-difluoro-4-(3-fluorophenyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3pa): ^{1}H NMR (400 MHz, $CDCl_3$)



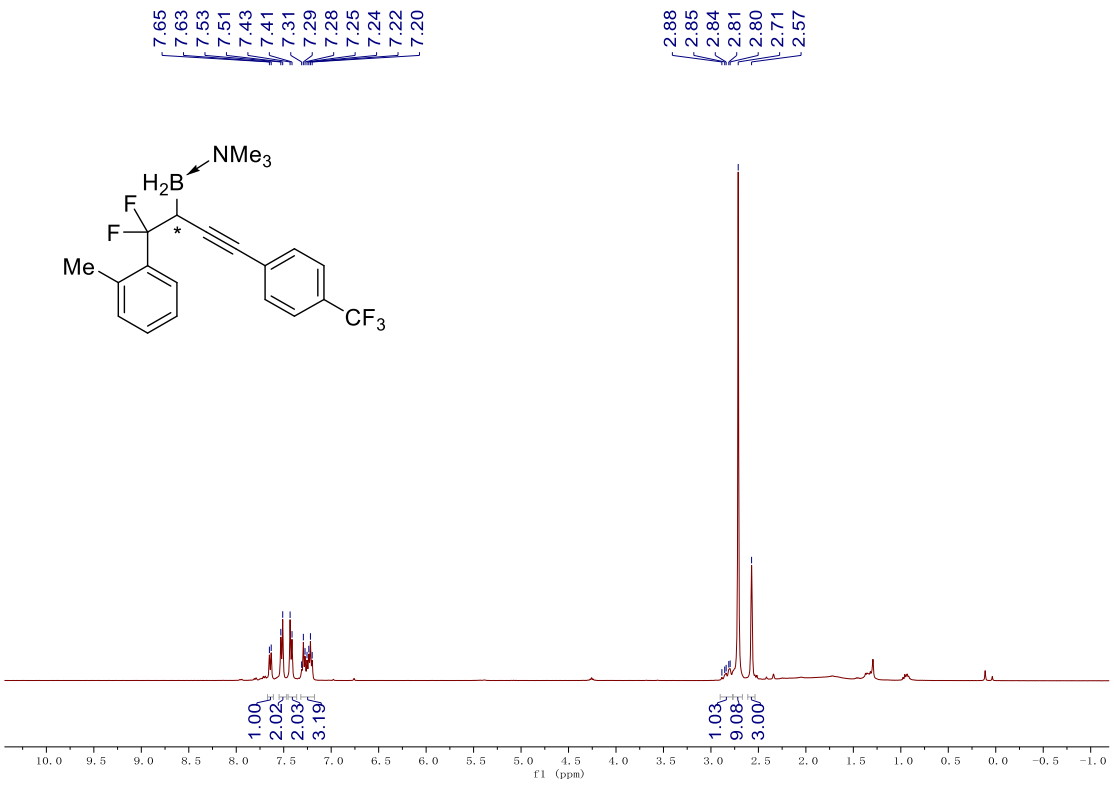
(+)-Trimethylamine-(1,1-difluoro-4-(3-fluorophenyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3pa): ^{13}C NMR (101 MHz, $CDCl_3$)



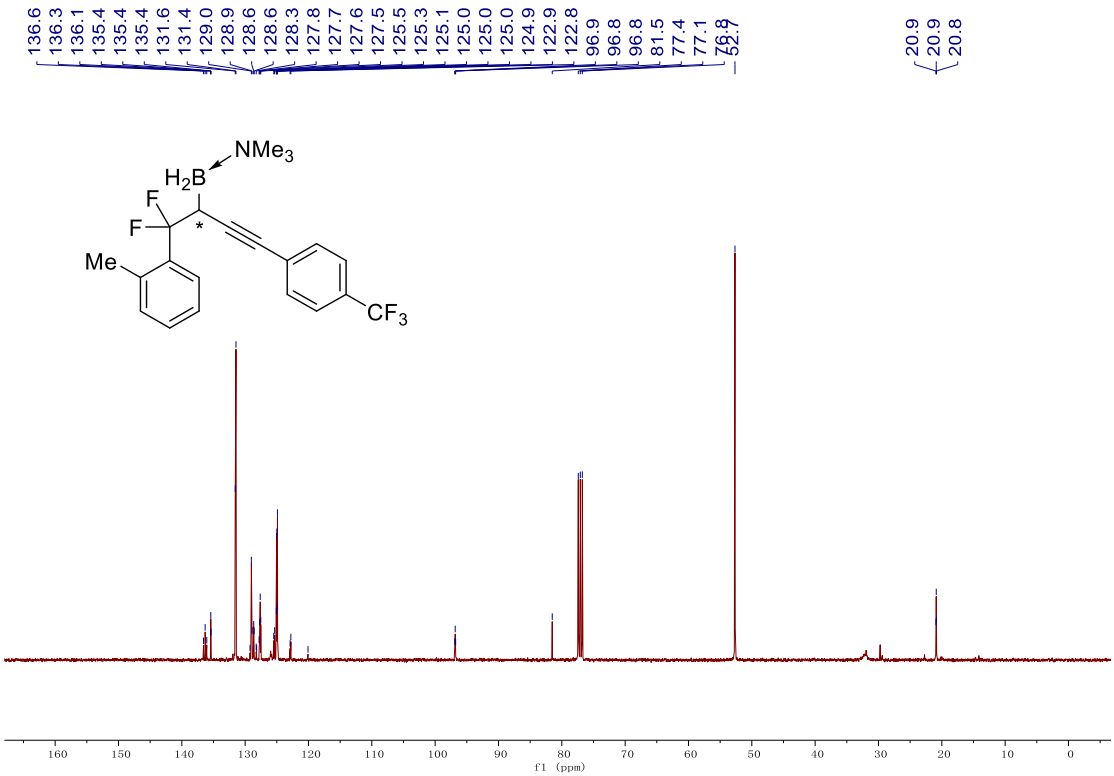
(+)-Trimethylamine-(1,1-difluoro-4-(3-fluorophenyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3pa): ^{19}F NMR (376 MHz, $CDCl_3$)



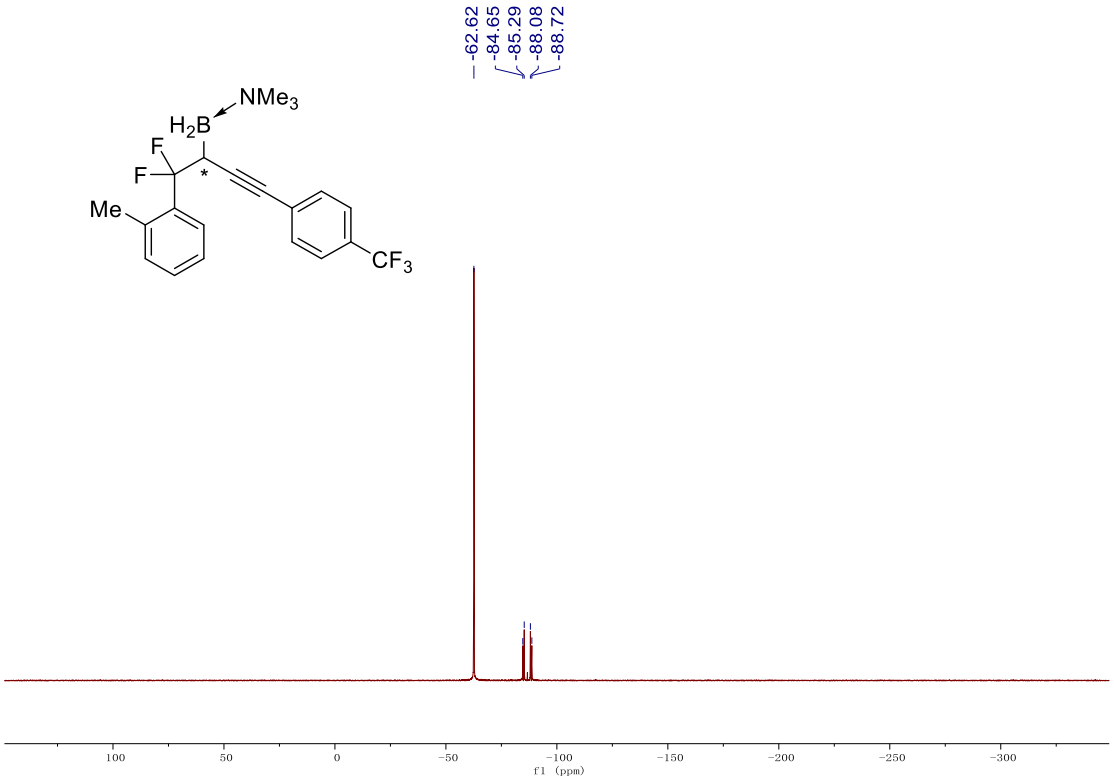
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)borane (3qa): ^{1}H NMR (400 MHz, $CDCl_3$)



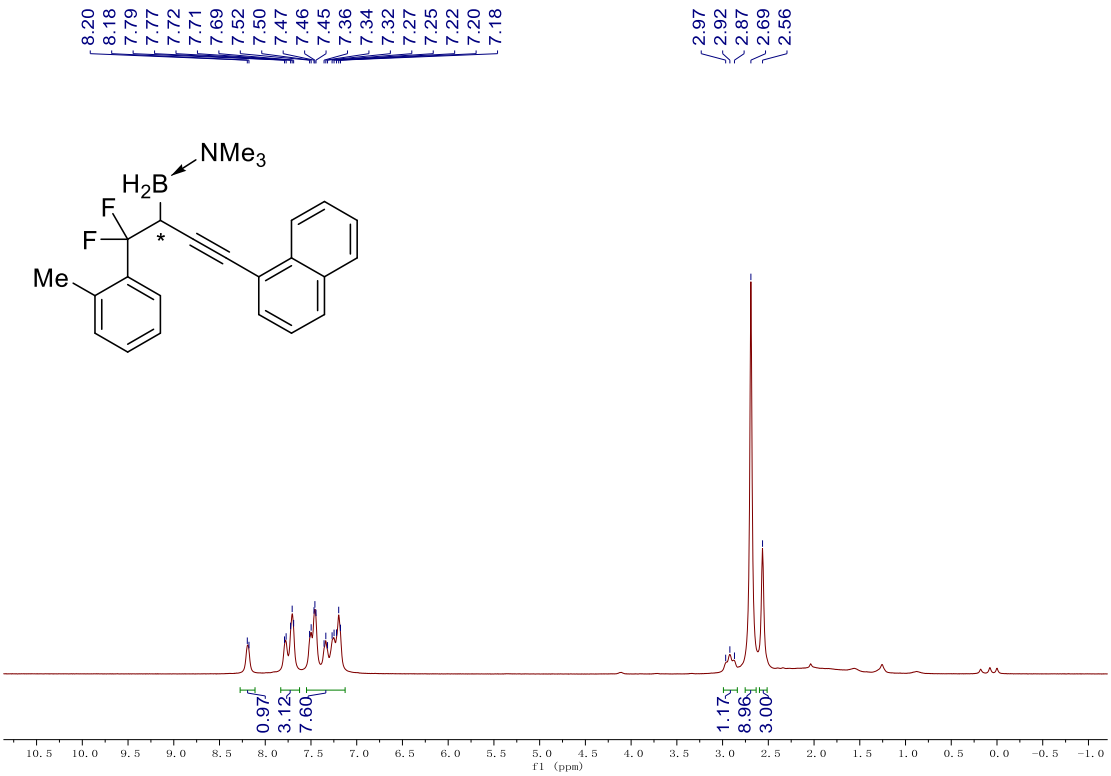
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)borane (3qa): ^{13}C NMR (101 MHz, $CDCl_3$)



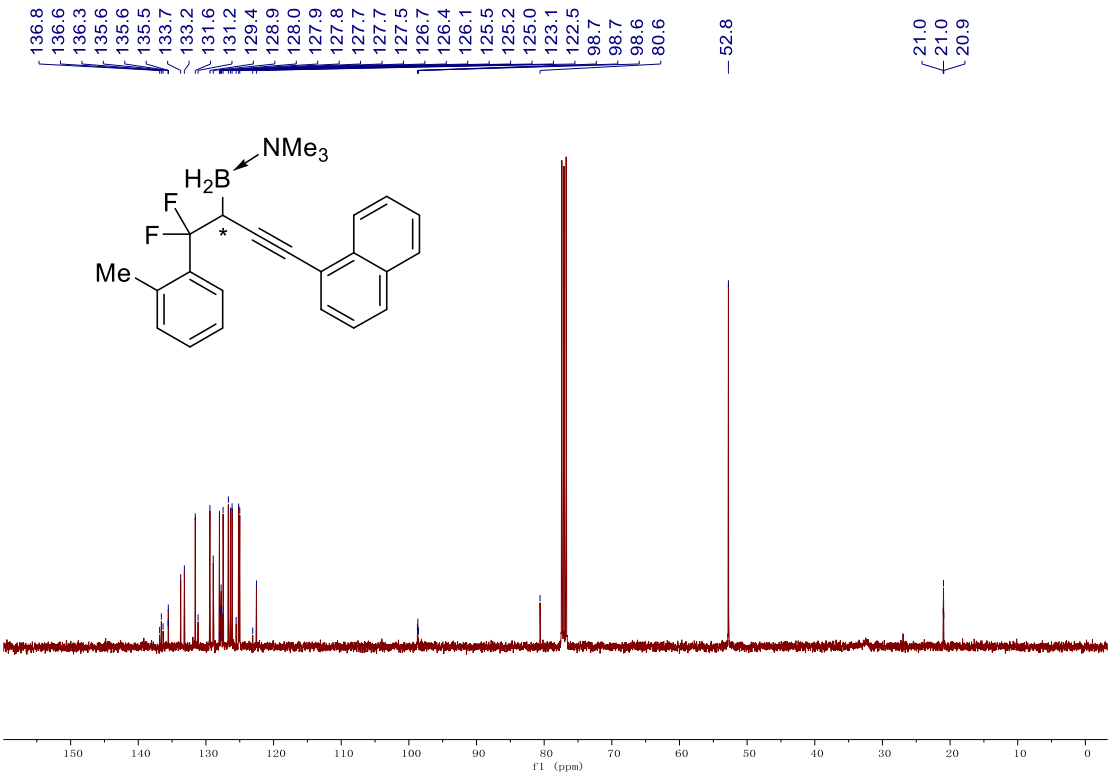
(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)borane (3qa): ^{19}F NMR (376 MHz, $CDCl_3$)



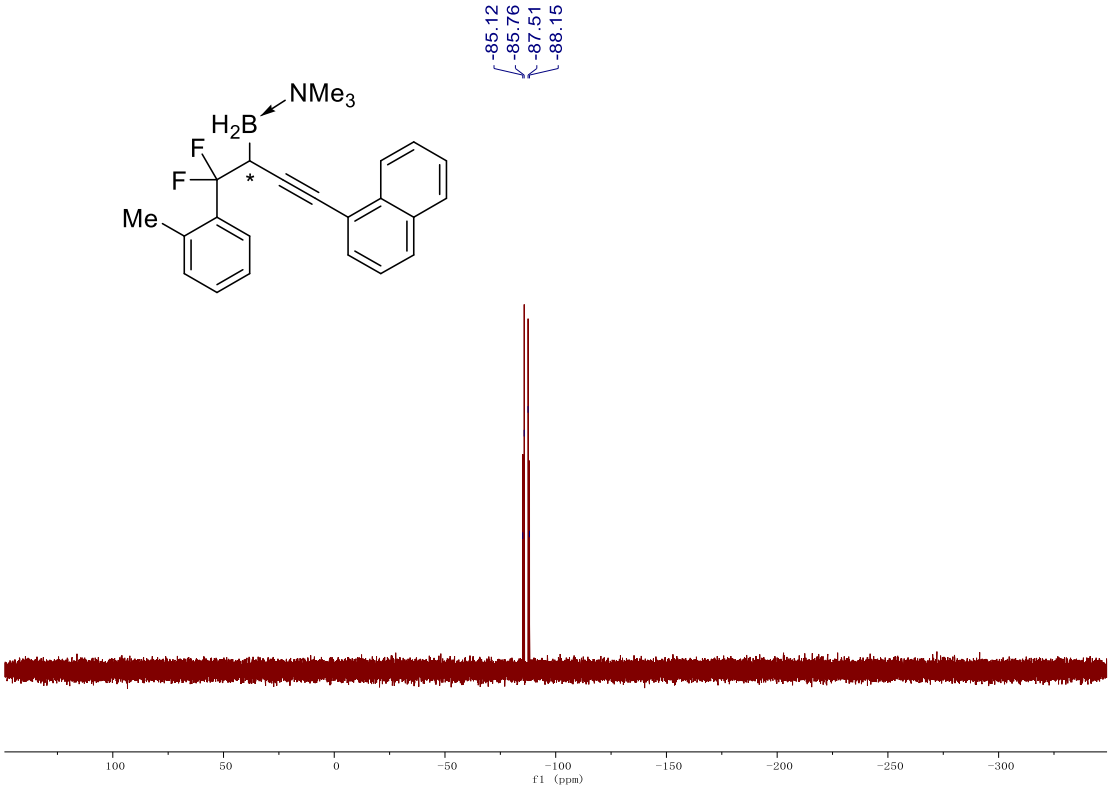
(-)-Trimethylamine-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ra): ^{1}H NMR (400 MHz, $CDCl_3$)



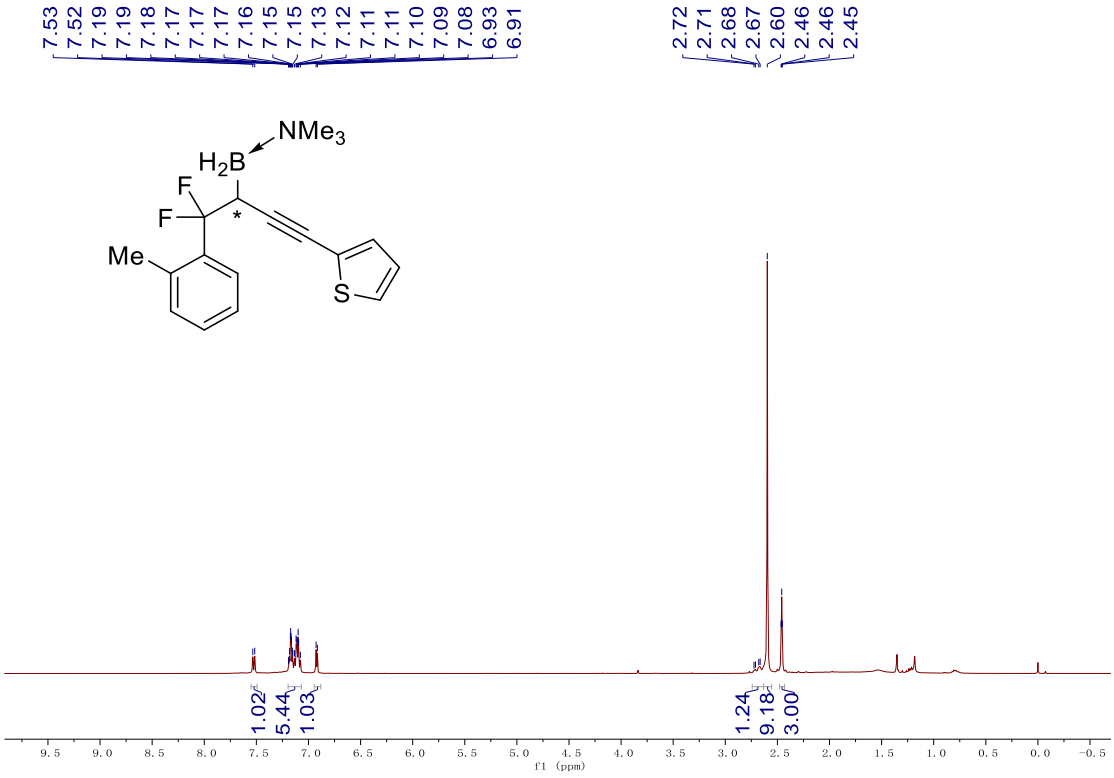
(-)-Trimethylamine-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ra): ^{13}C NMR (101 MHz, $CDCl_3$)



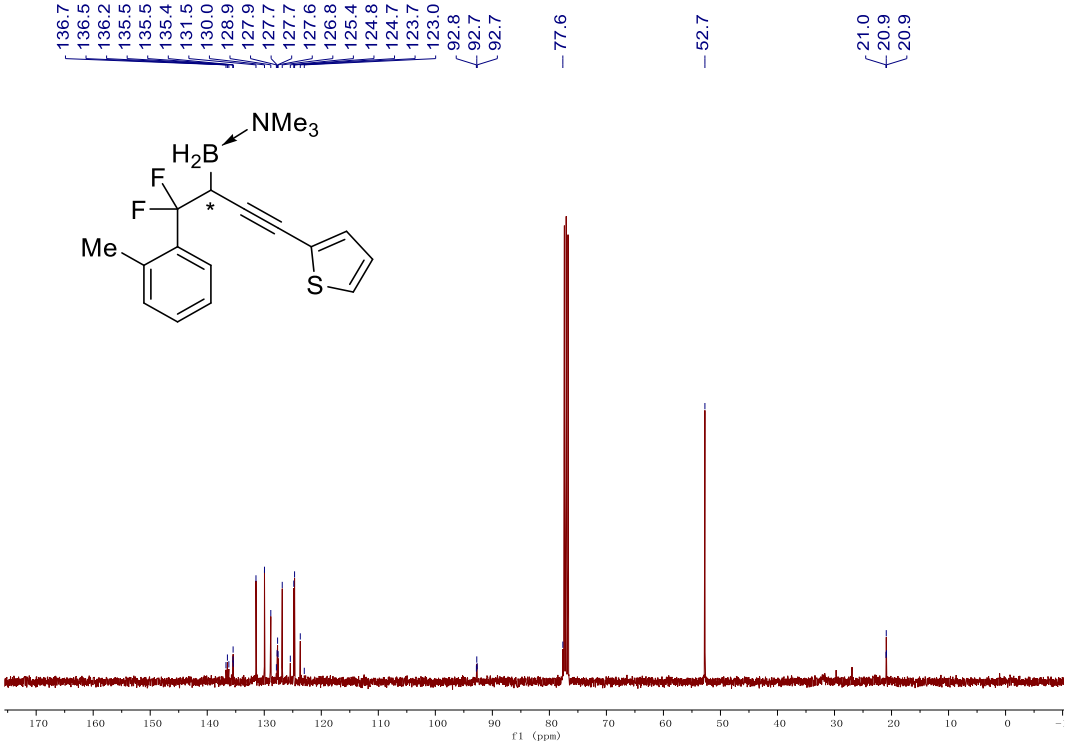
(-)-Trimethylamine-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ra): ^{19}F NMR (376 MHz, $CDCl_3$)



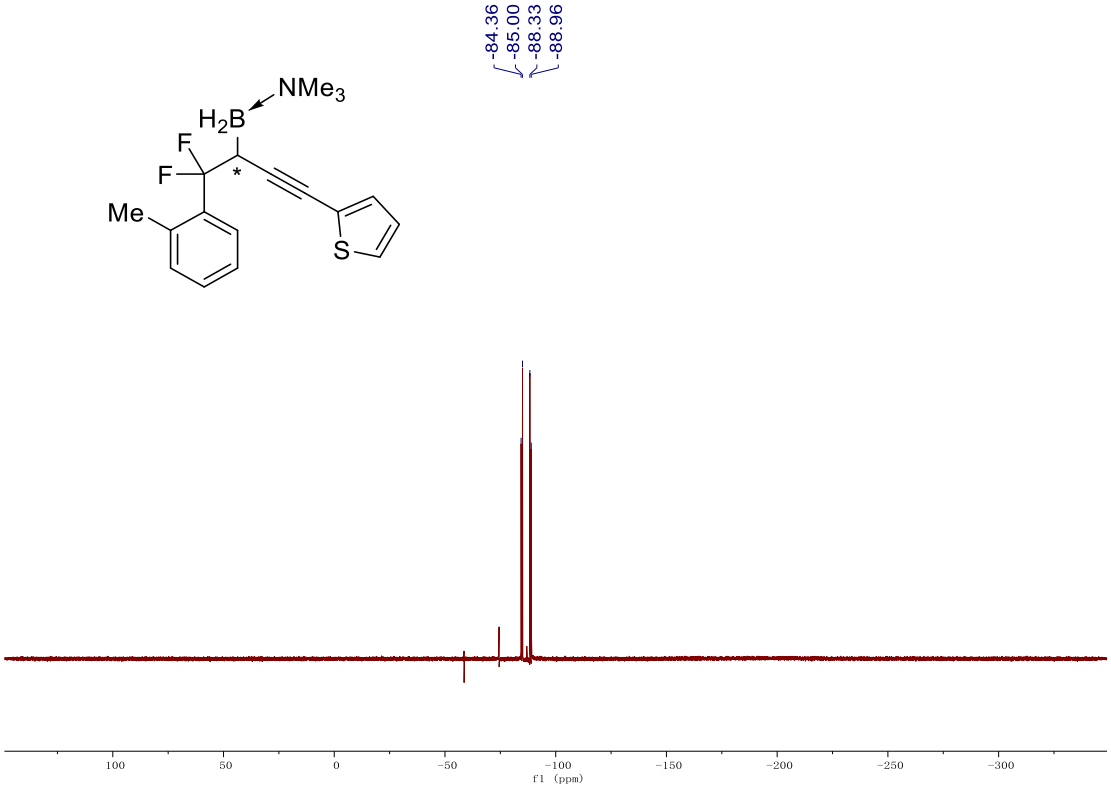
(+)-Trimethylamine-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3sa): ^{1}H NMR (400 MHz, $CDCl_3$)



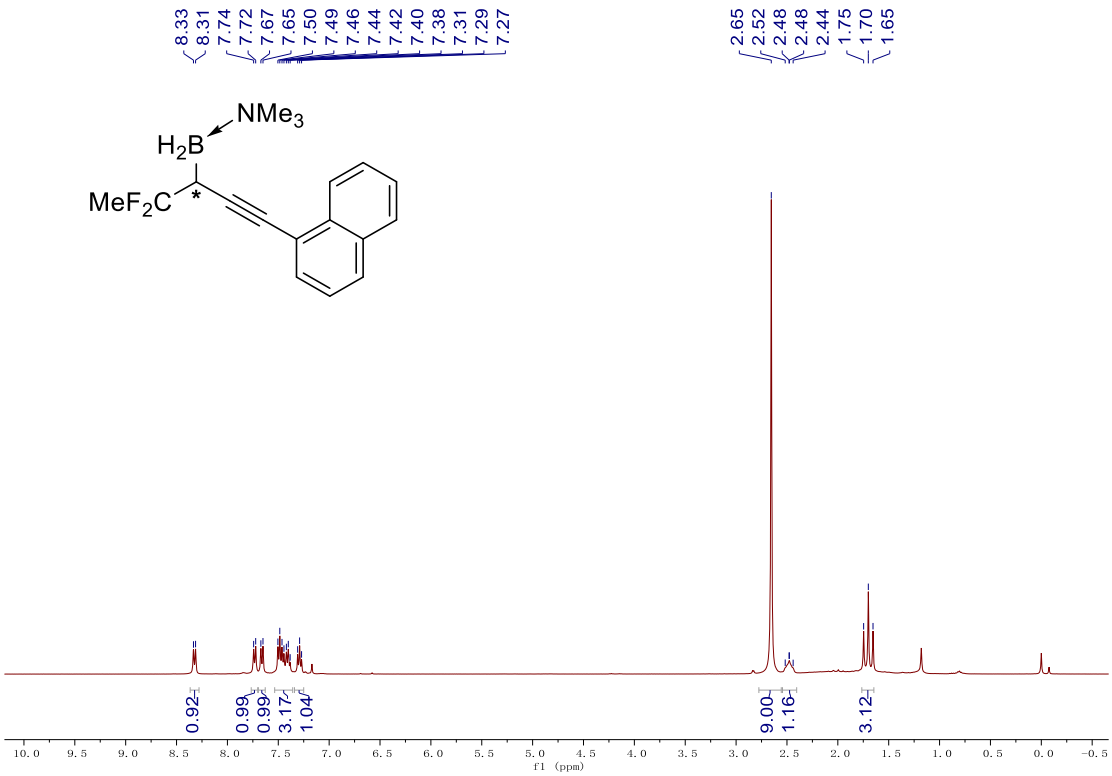
(+)-Trimethylamine-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3sa): ^{13}C NMR (101 MHz, $CDCl_3$)



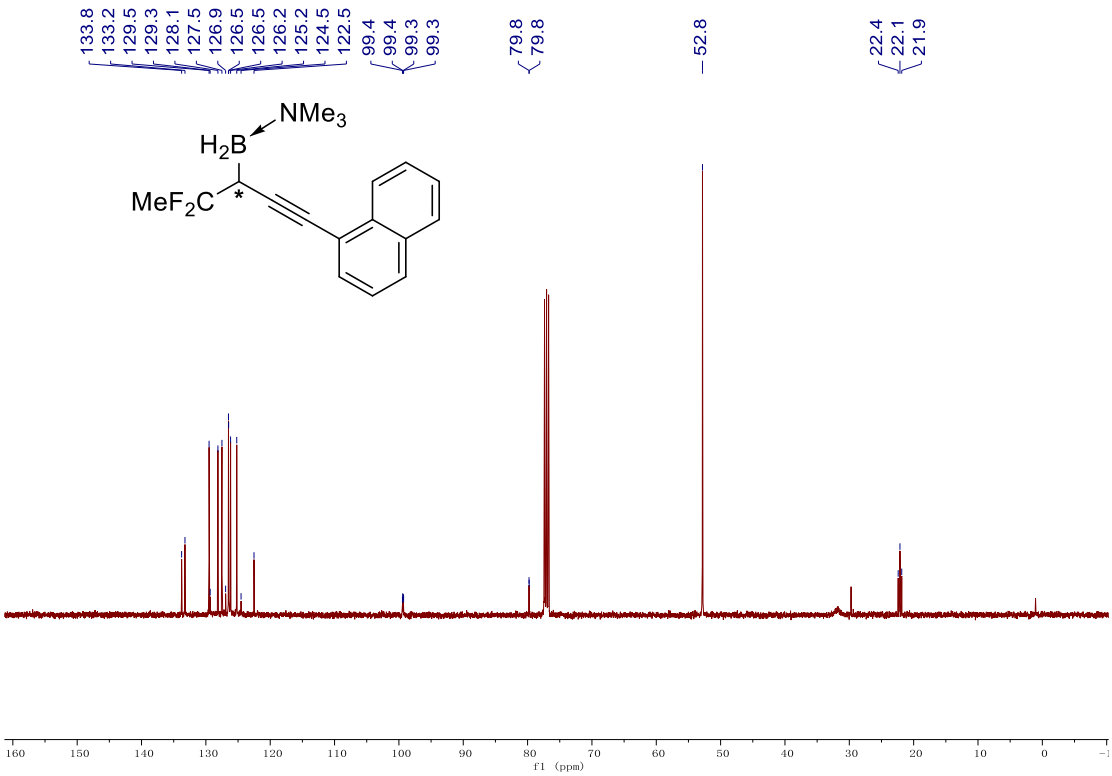
(+)-Trimethylamine-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3sa): ^{19}F NMR (376 MHz, $CDCl_3$)



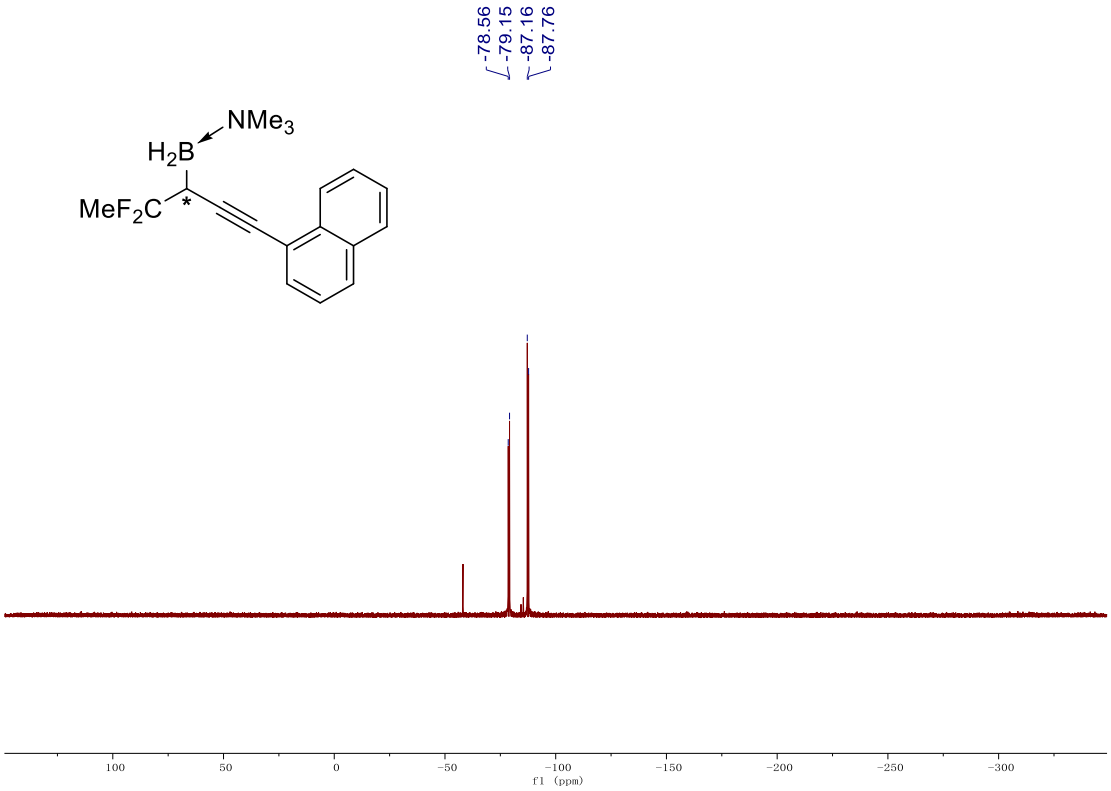
(-)-Trimethylamine-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-yl) borane (3ta): ^{1}H NMR (400 MHz, $CDCl_3$)



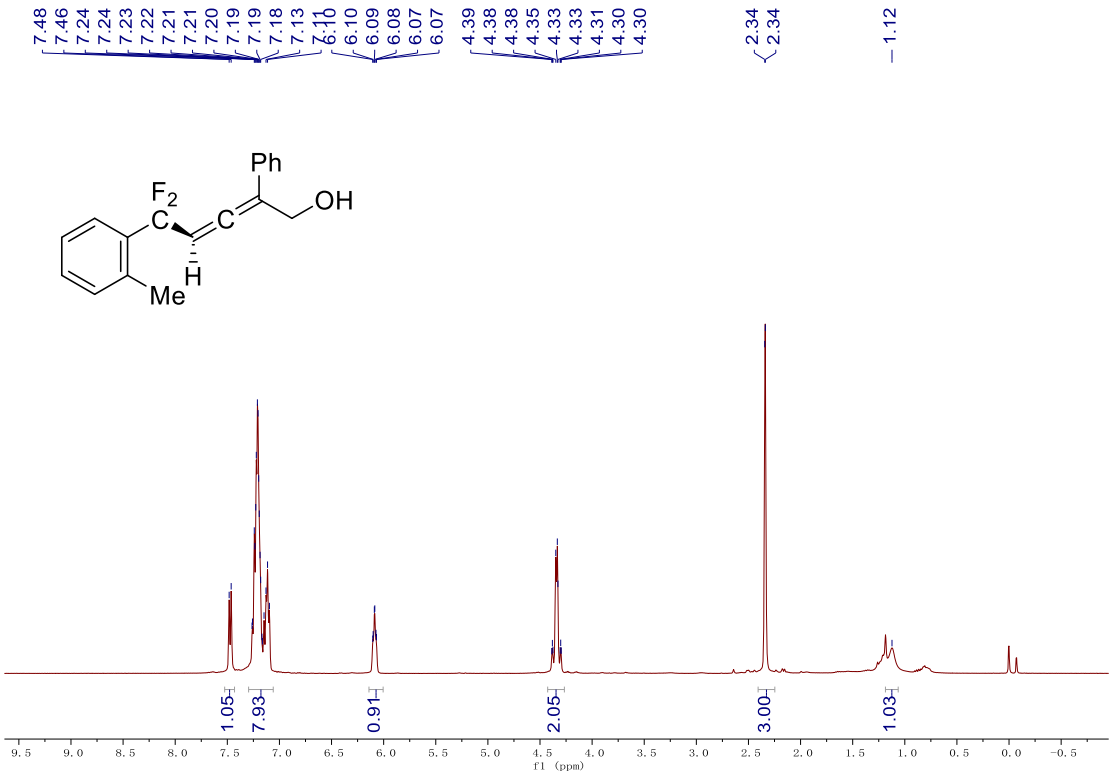
(-)-Trimethylamine-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-yl) borane (3ta): ^{13}C NMR (101 MHz, $CDCl_3$)



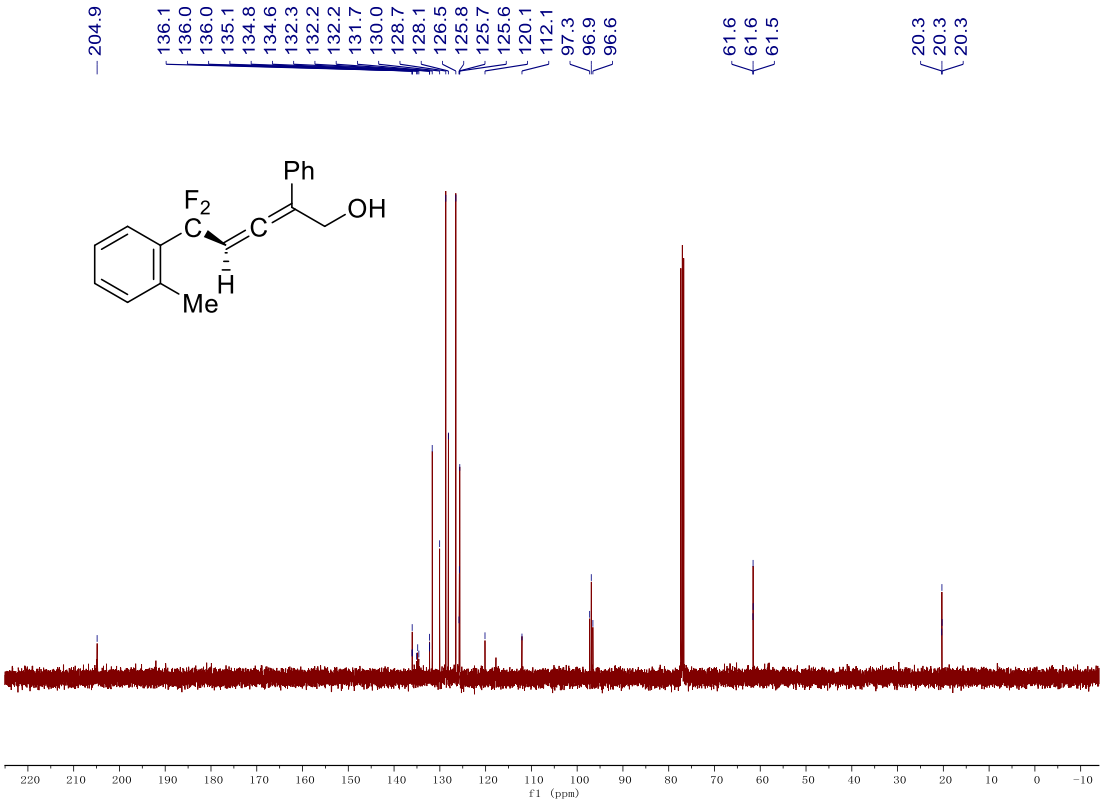
(-)-Trimethylamine-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-yl) borane (3ta): ^{19}F NMR (376 MHz, $CDCl_3$)



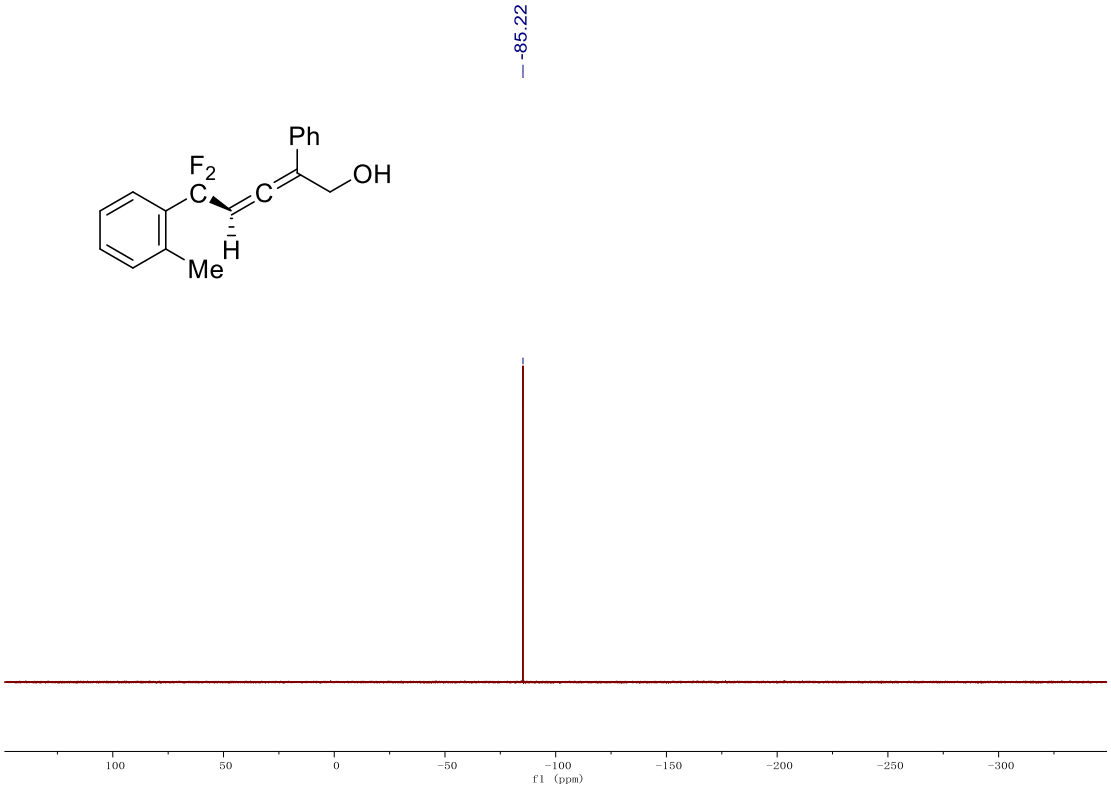
(-)-(*S*)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5a): ^{1}H NMR (400 MHz, $CDCl_3$)



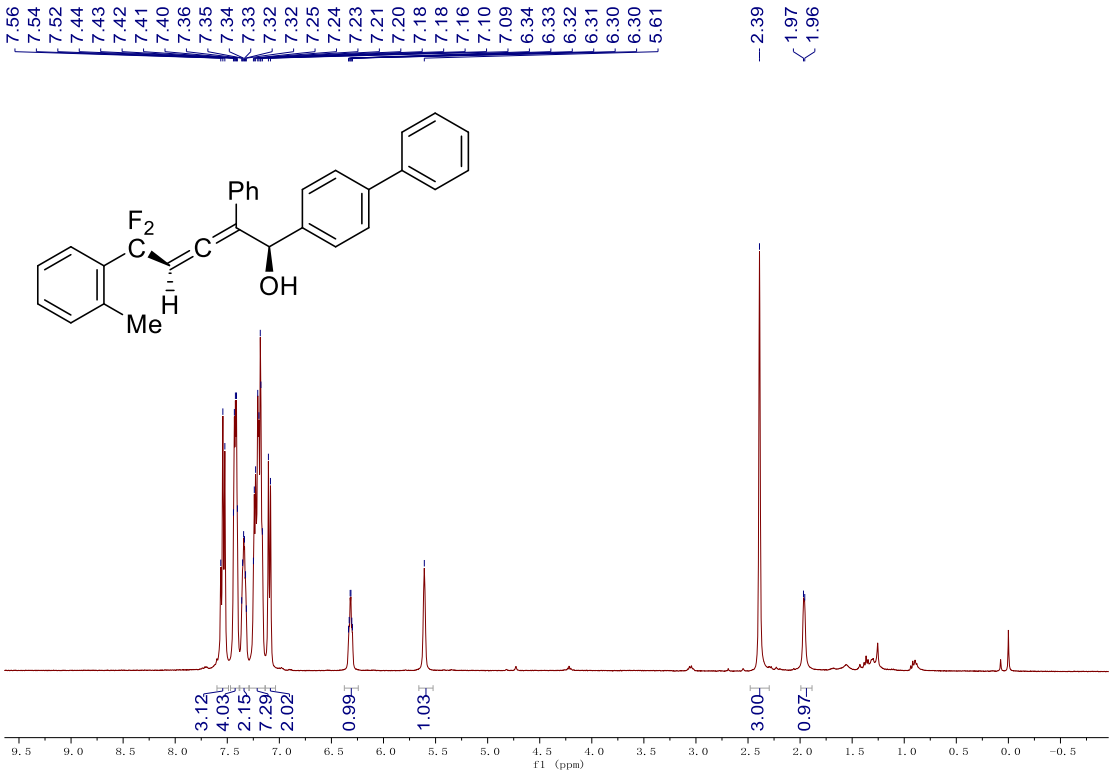
(-)-(*S*)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5a): ^{13}C NMR (101 MHz, $CDCl_3$)



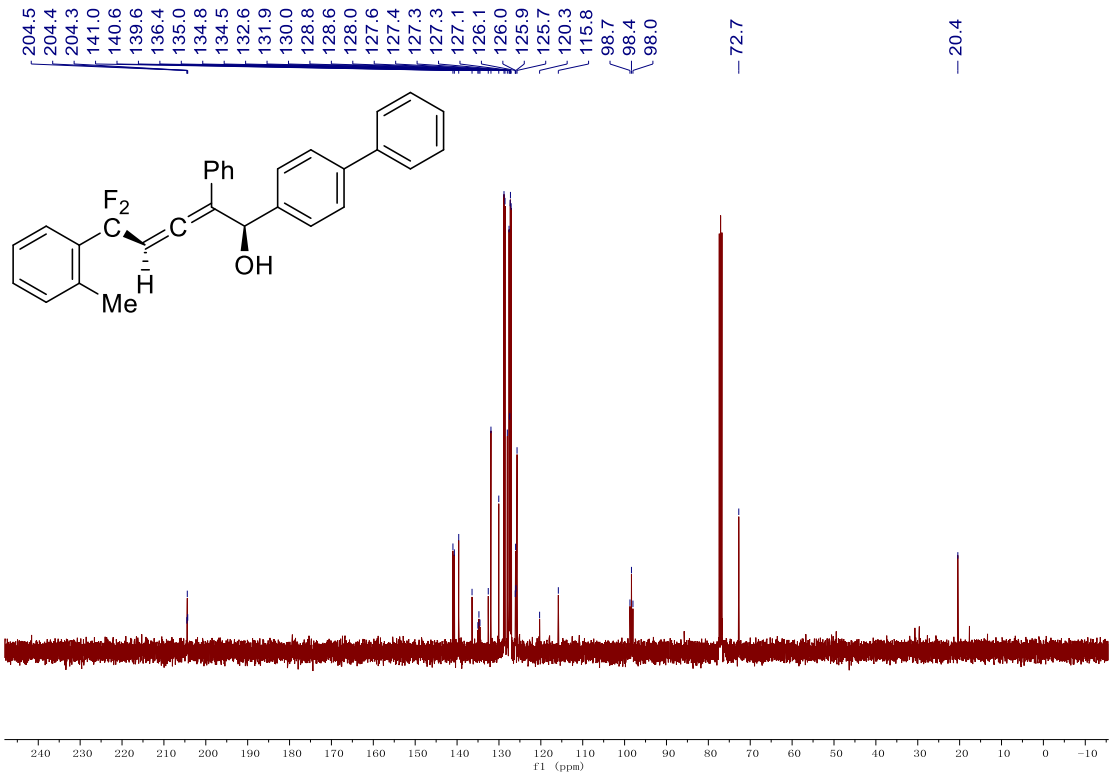
(-)-(*S*)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5a): ^{19}F NMR (376 MHz, $CDCl_3$)



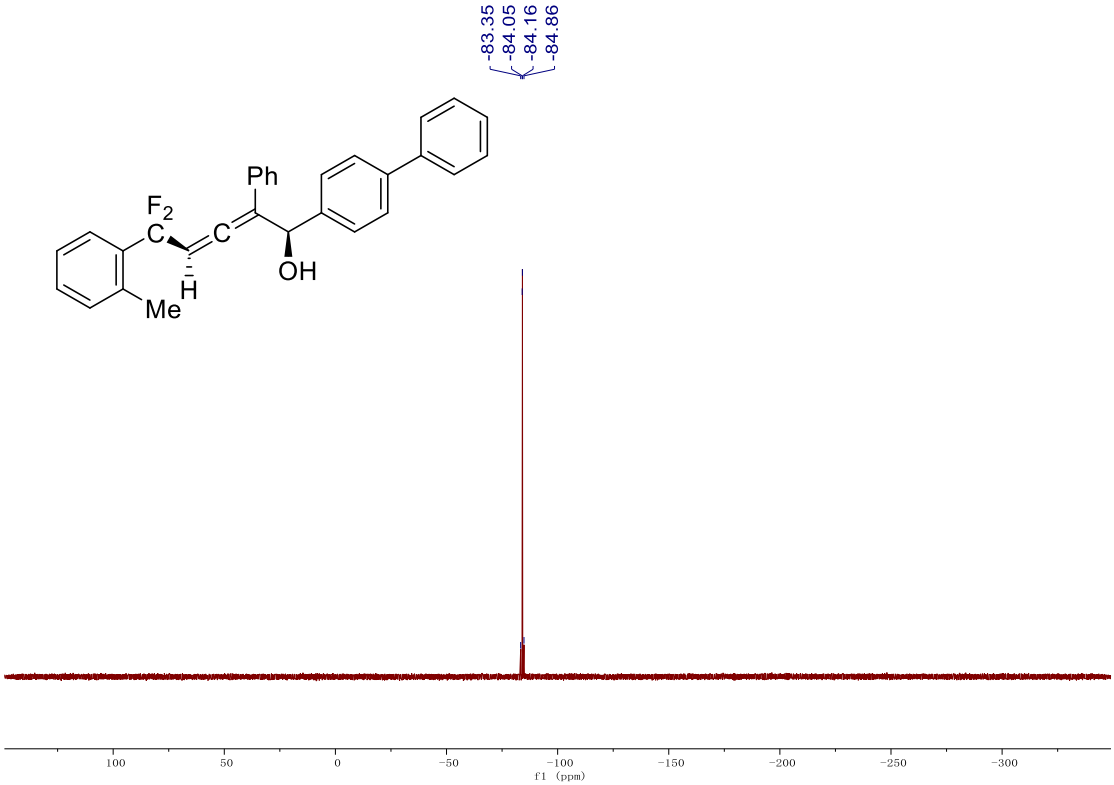
(-)-(1*R*,3*S*)-1-([1,1'-biphenyl]-4-yl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5b): ^{1}H NMR (400 MHz, $CDCl_3$)



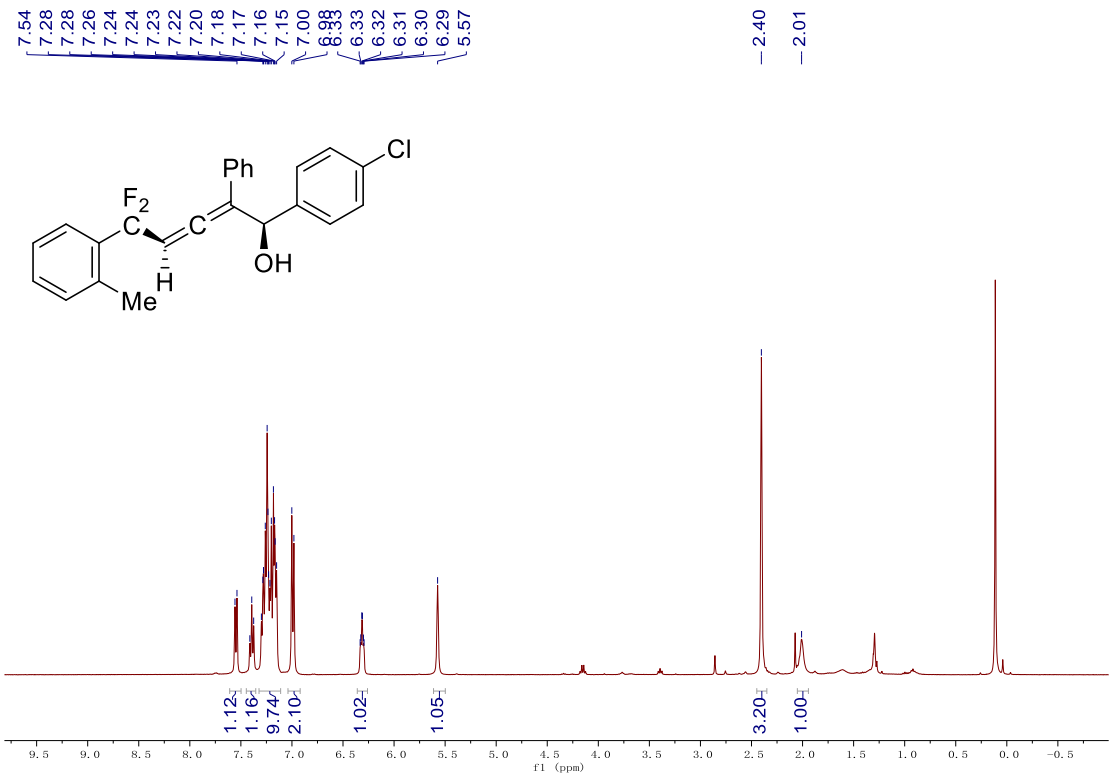
(-)-(1*R*,3*S*)-1-([1,1'-biphenyl]-4-yl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5b): ^{13}C NMR (101 MHz, $CDCl_3$)



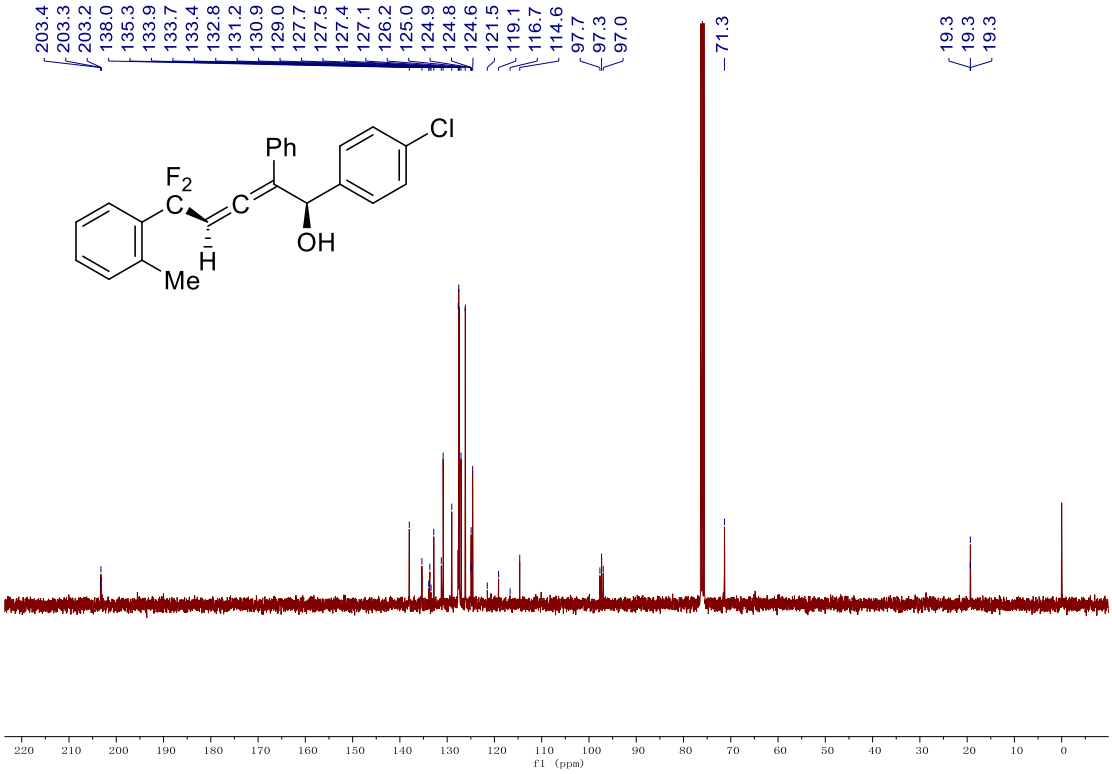
(-)-(1*R*,3*S*)-1-([1,1'-biphenyl]-4-yl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5b): ^{19}F NMR (376 MHz, $CDCl_3$)



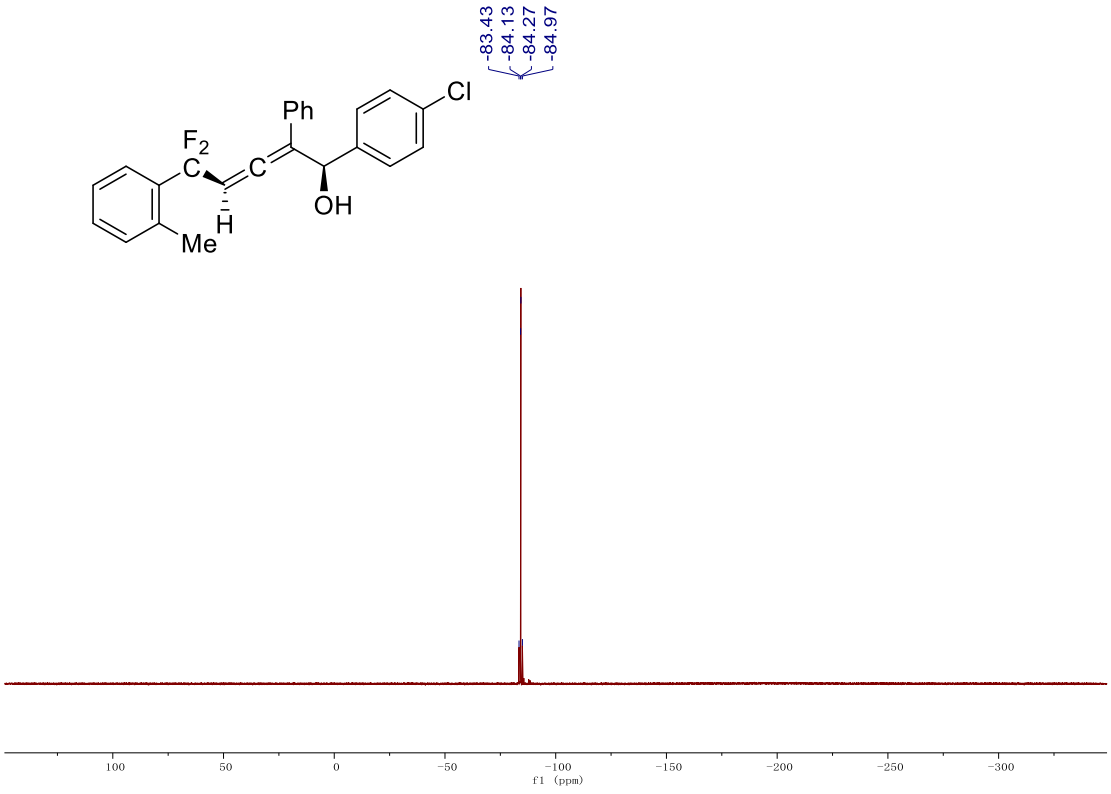
(-)-(1*R*,3*S*)-1-(4-chlorophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5c): ^{1}H NMR (400 MHz, $CDCl_3$)



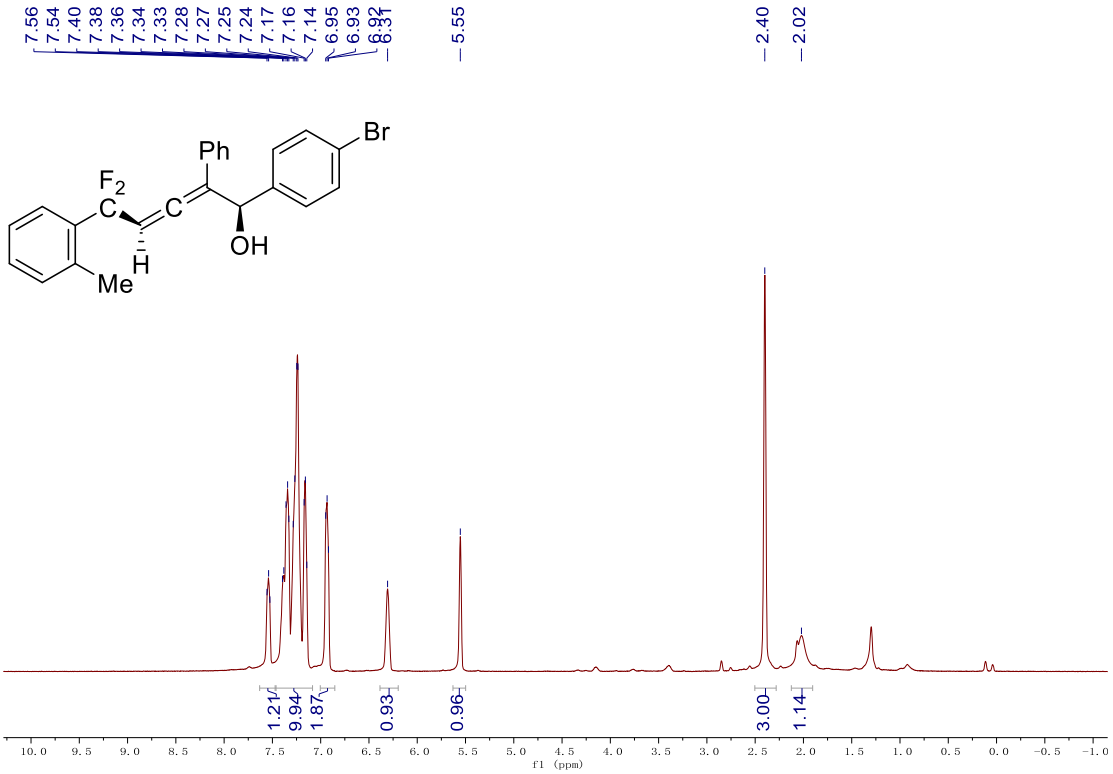
(-)-(1*R*,3*S*)-1-(4-chlorophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5c): ^{13}C NMR (101 MHz, $CDCl_3$)



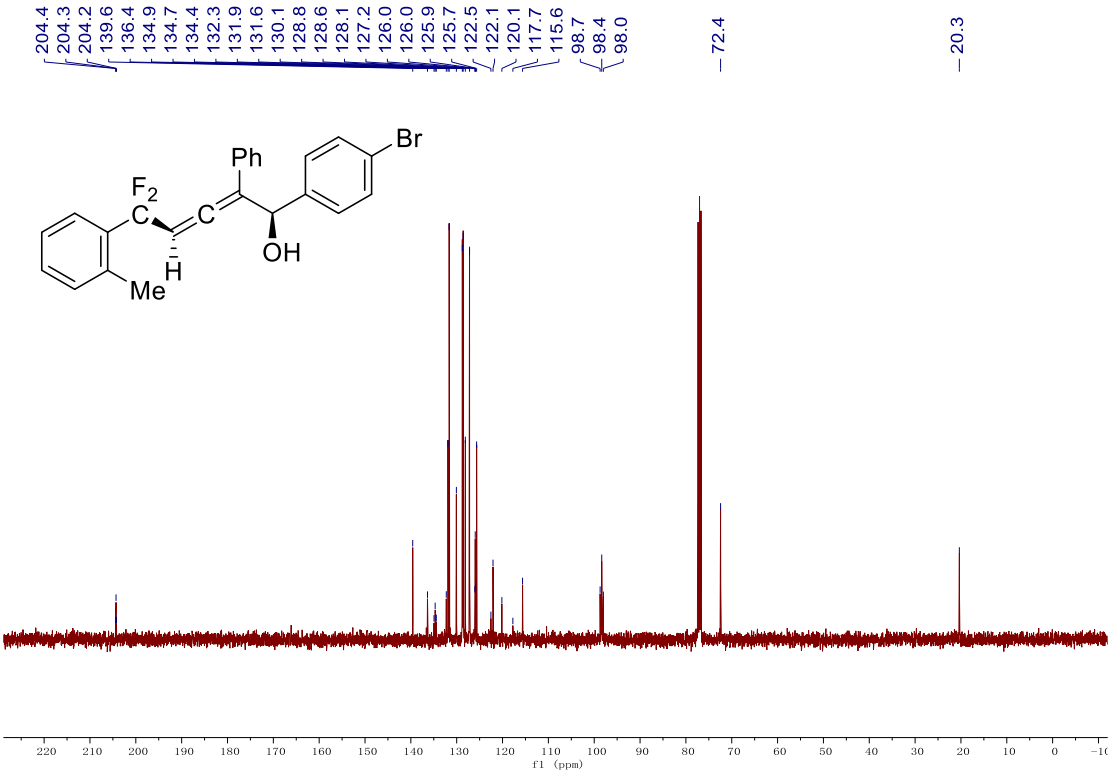
(-)-(1*R*,3*S*)-1-(4-chlorophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5c): ^{19}F NMR (376 MHz, $CDCl_3$)



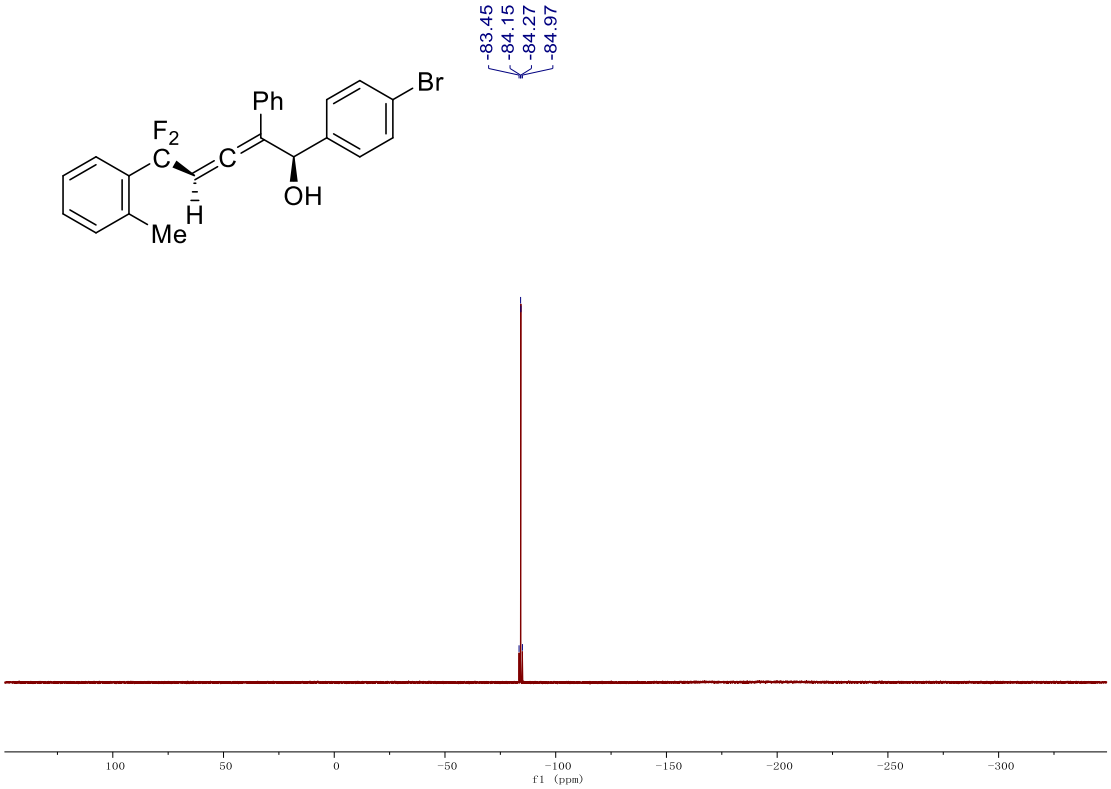
(-)-(1*R*,3*S*)-1-(4-bromophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5d): ^{1}H NMR (400 MHz, $CDCl_3$)



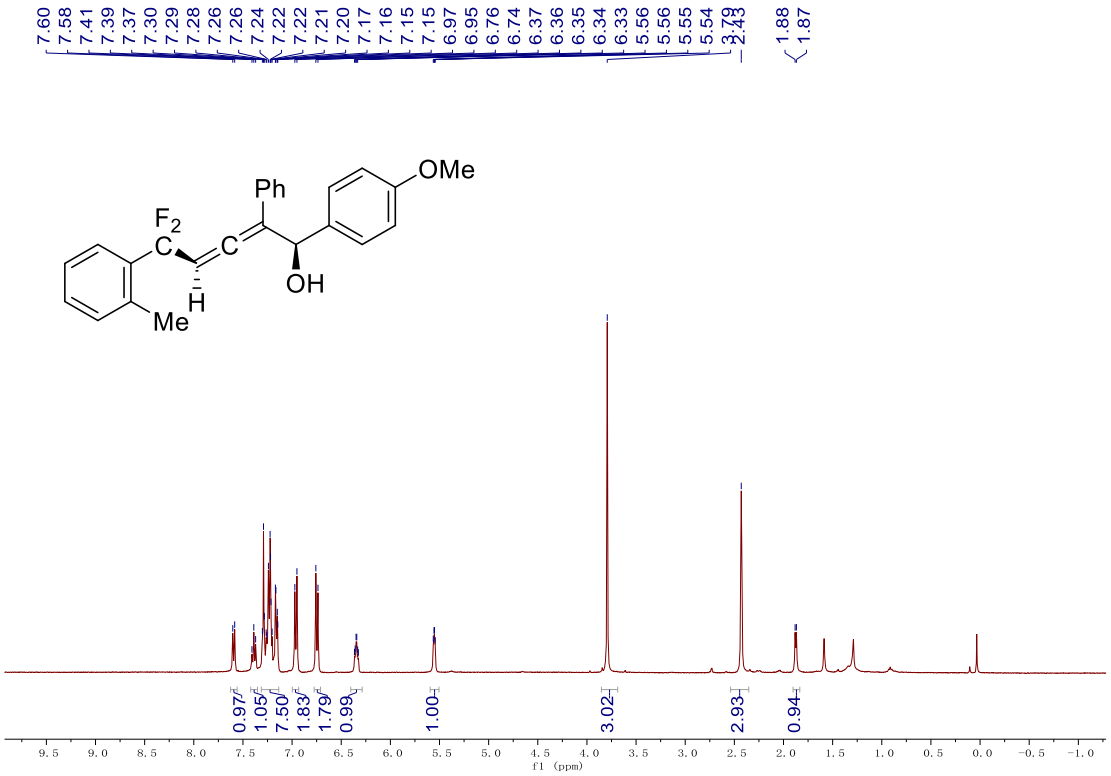
(-)-(1*R*,3*S*)-1-(4-bromophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5d): ^{13}C NMR (101 MHz, $CDCl_3$)



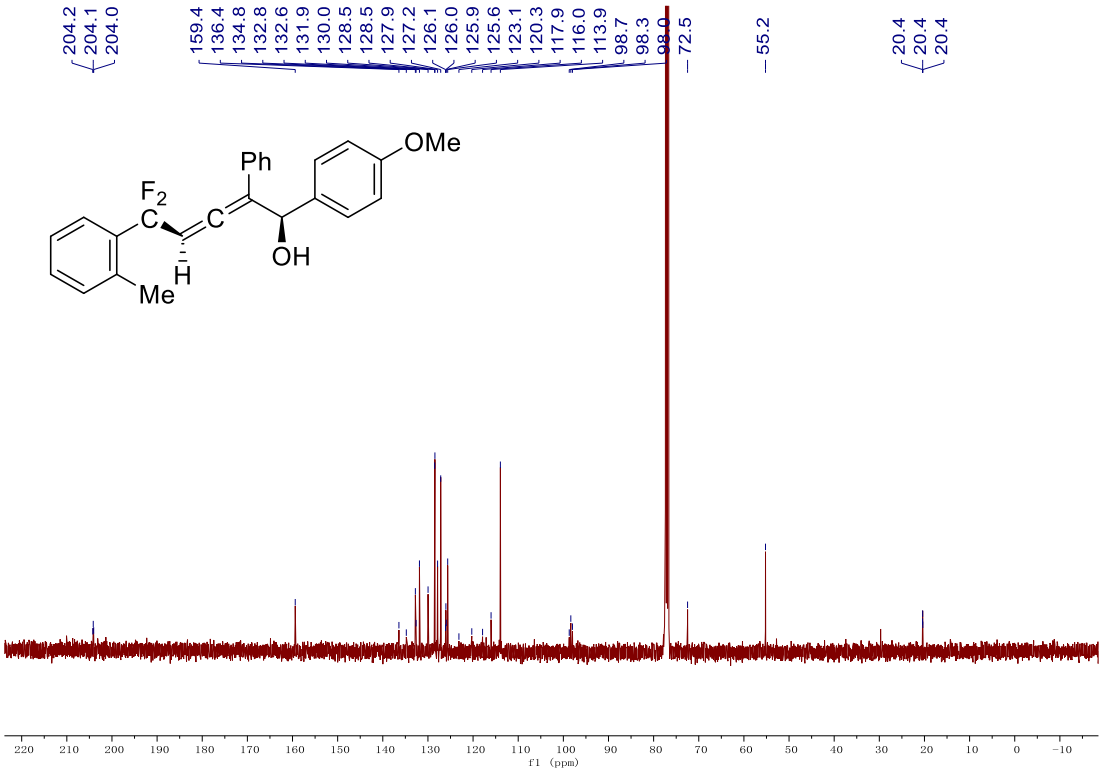
(-)-(1*R*,3*S*)-1-(4-bromophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5d): ^{19}F NMR (376 MHz, $CDCl_3$)



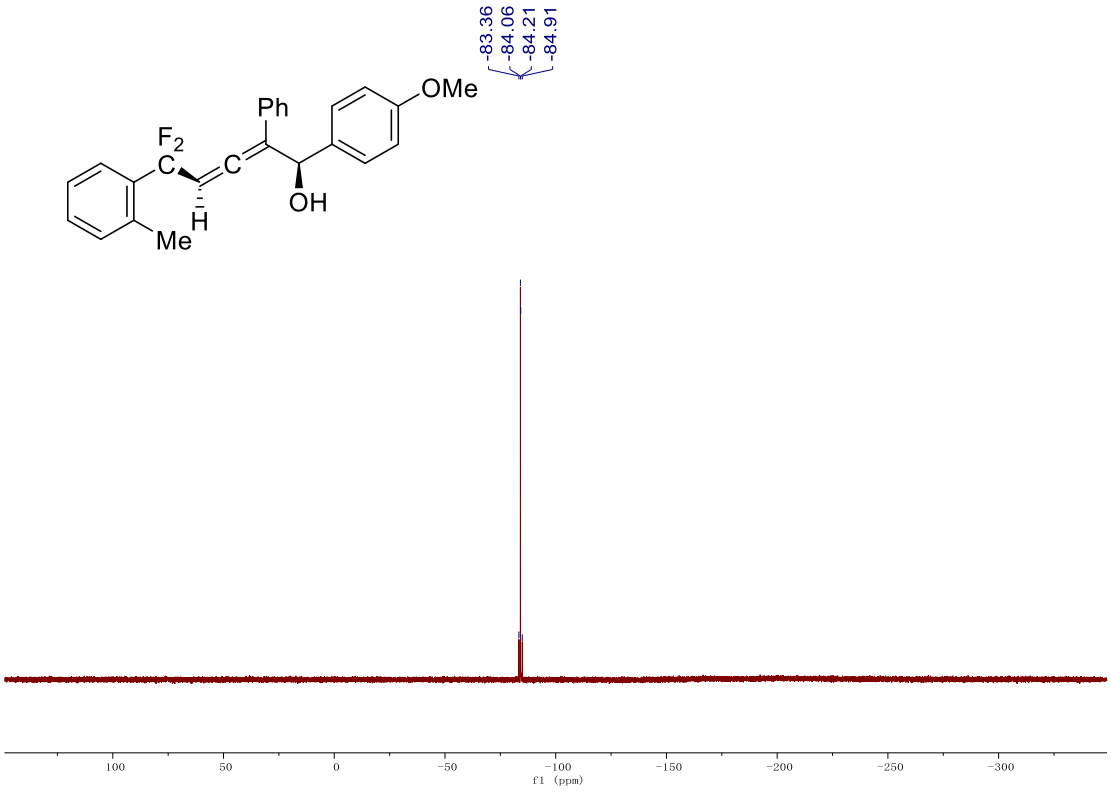
(-)-(1*R*,3*S*)-5,5-difluoro-1-(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5e): ^{1}H NMR (400 MHz, $CDCl_3$)



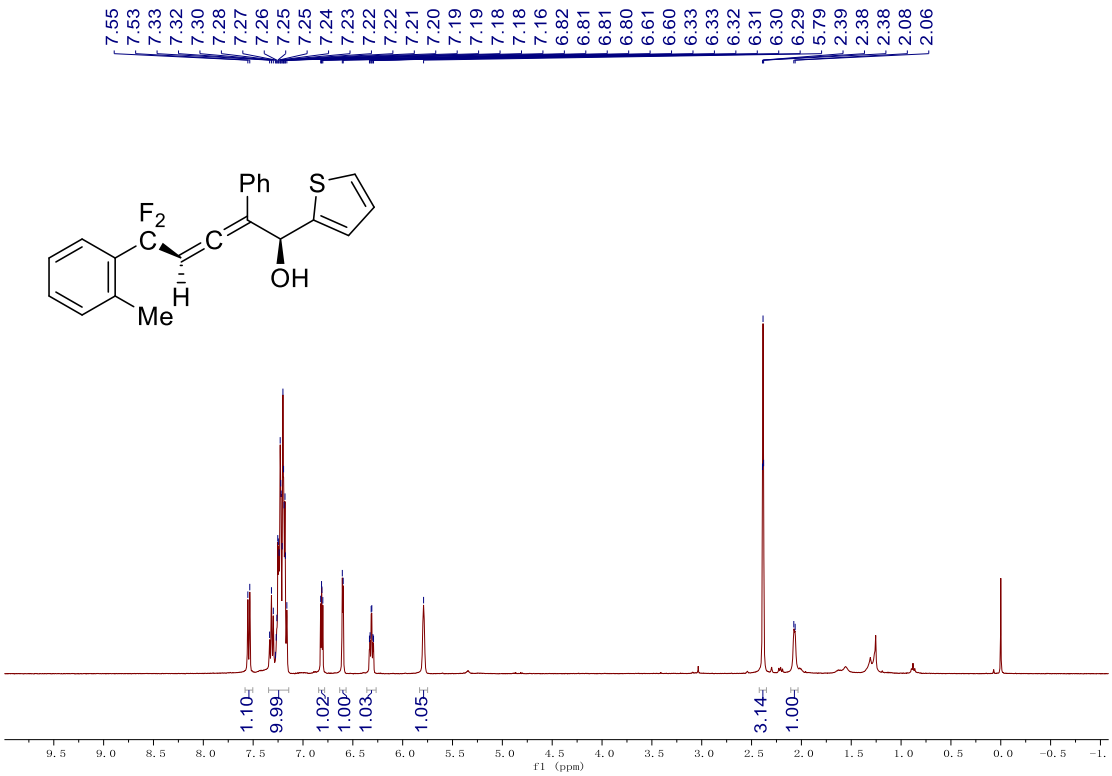
(-)-(1*R*,3*S*)-5,5-difluoro-1-(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5e): ^{13}C NMR (101 MHz, $CDCl_3$)



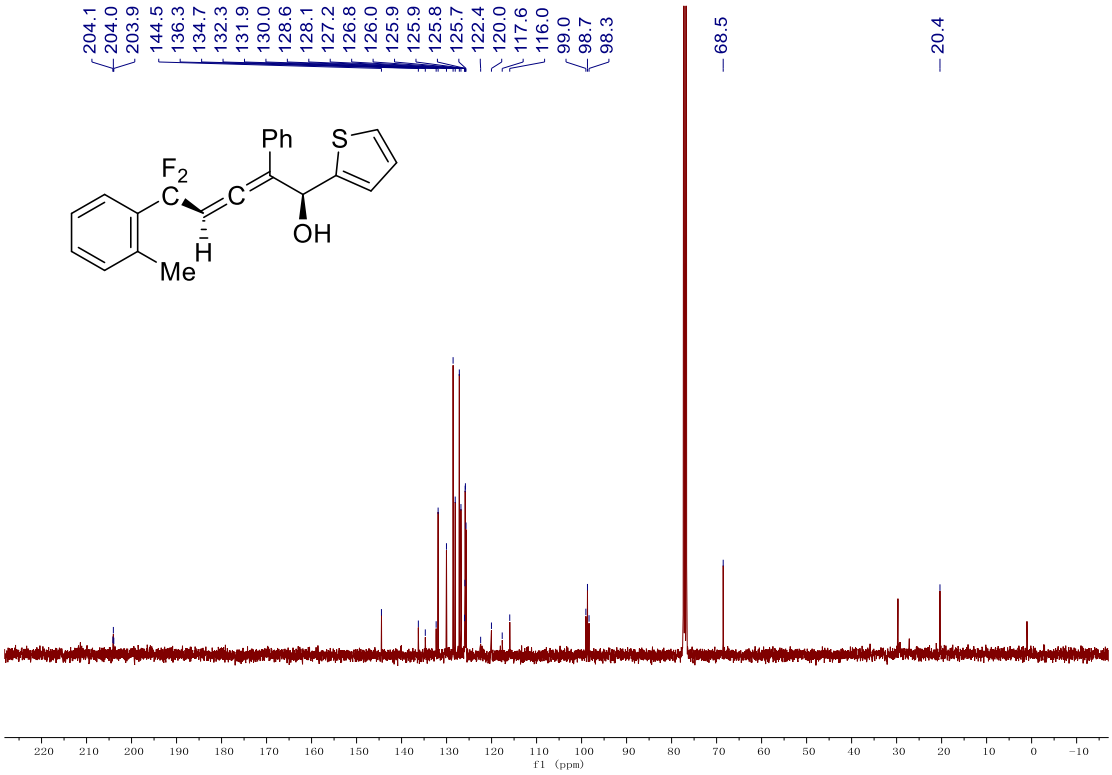
(-)-(1*R*,3*S*)-5,5-difluoro-1-(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5e): ^{19}F NMR (376 MHz, $CDCl_3$)



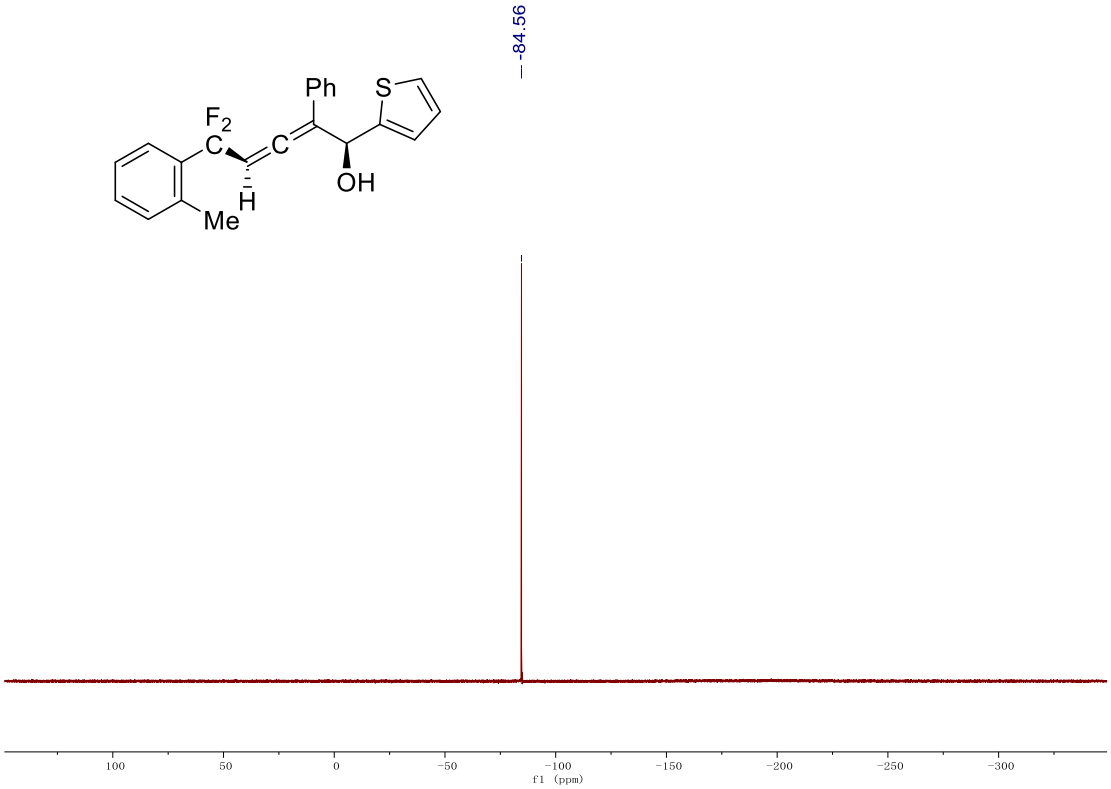
(-)-(1*S*,3*S*)-5,5-difluoro-2-phenyl-1-(thiophen-2-yl)-5-(*o*-tolyl)penta-2,3-dien-1-ol (5f): ^{1}H NMR (400 MHz, $CDCl_3$)



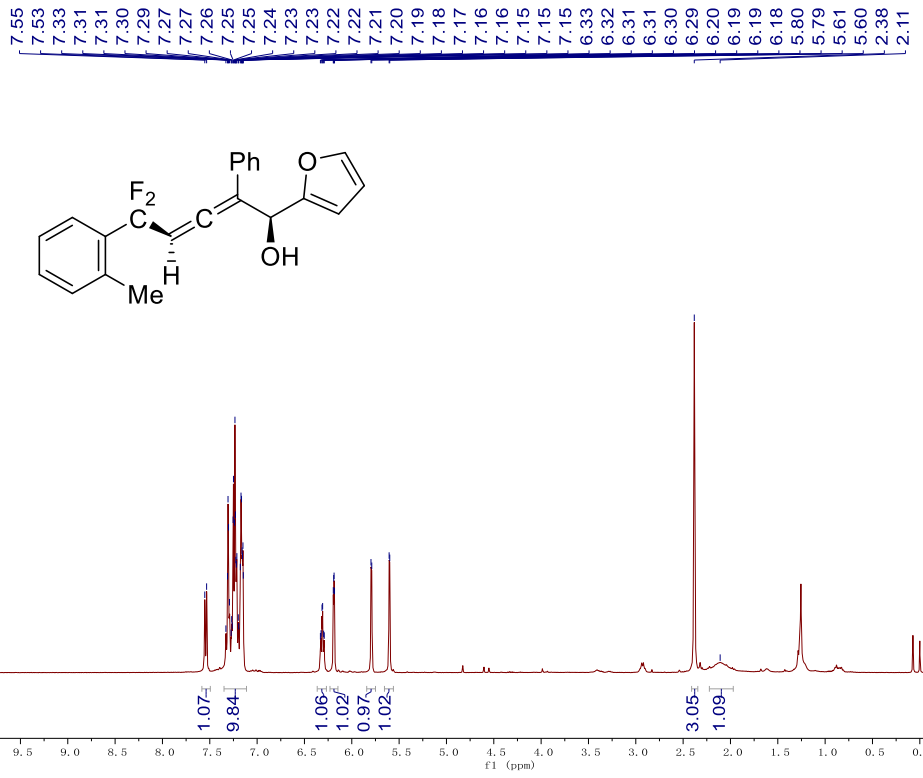
(-)-(1*S*,3*S*)-5,5-difluoro-2-phenyl-1-(thiophen-2-yl)-5-(*o*-tolyl)penta-2,3-dien-1-ol (5f): ^{13}C NMR (101 MHz, $CDCl_3$)



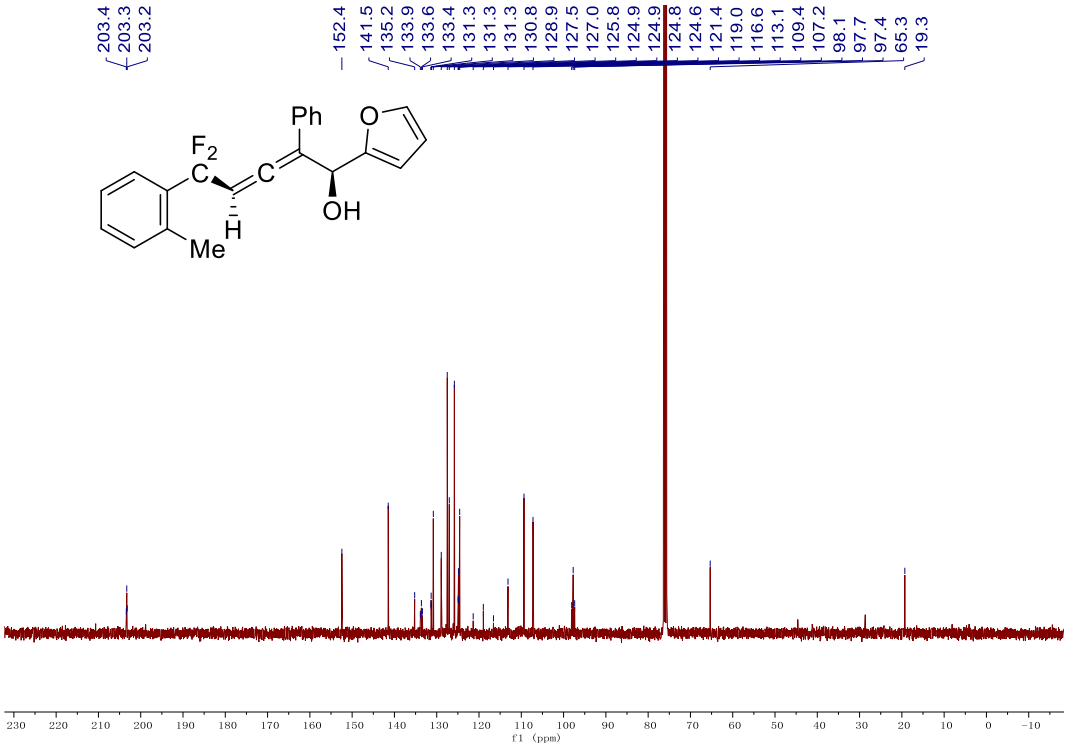
(-)-(1*S*,3*S*)-5,5-difluoro-2-phenyl-1-(thiophen-2-yl)-5-(*o*-tolyl)penta-2,3-dien-1-ol (5f): ^{19}F NMR (376 MHz, $CDCl_3$)



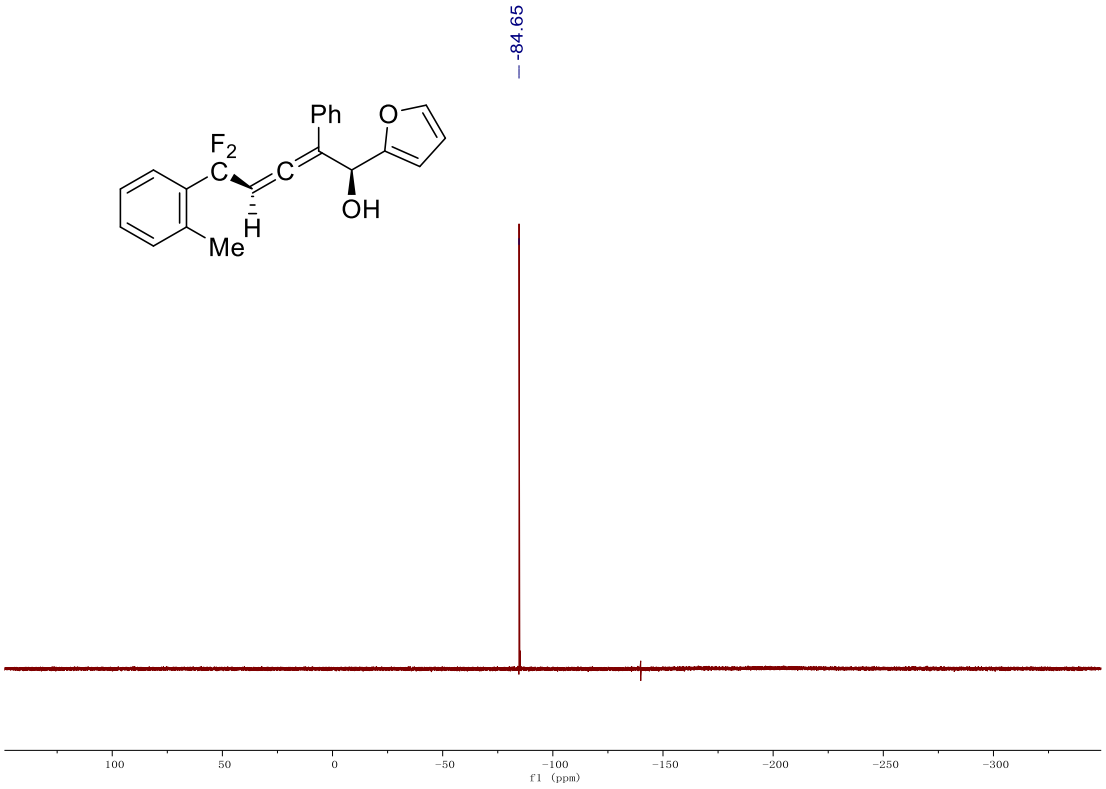
(-)-(1*S*,3*S*)-5,5-difluoro-1-(furan-2-yl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5g): ^{1}H NMR (400 MHz, $CDCl_3$)



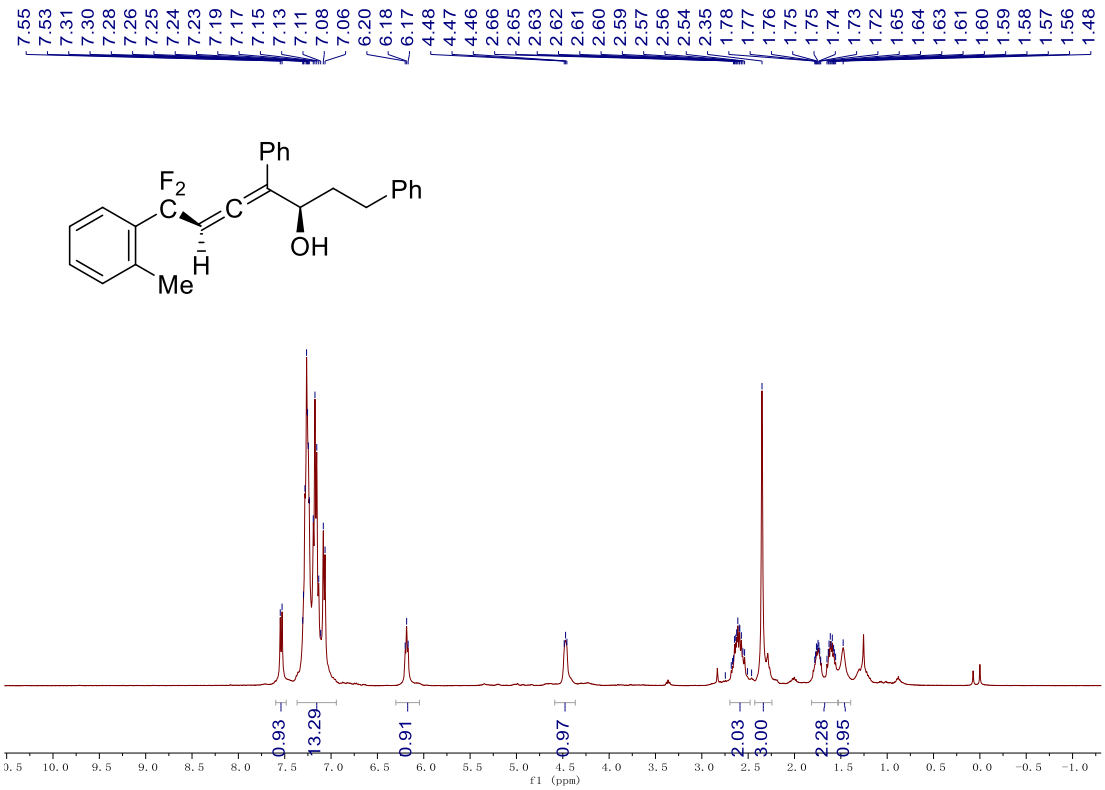
(-)-(1*S*,3*S*)-5,5-difluoro-1-(furan-2-yl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5g): ^{13}C NMR (101 MHz, $CDCl_3$)



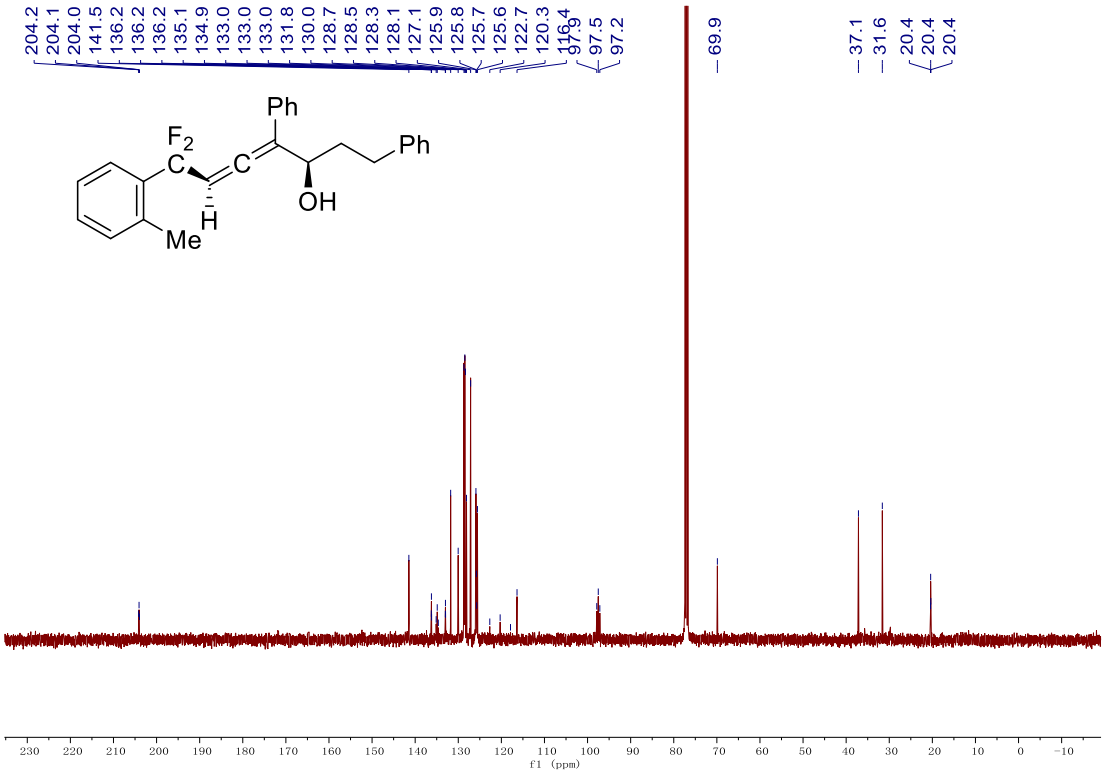
(-)-(1*S*,3*S*)-5,5-difluoro-1-(furan-2-yl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5g):



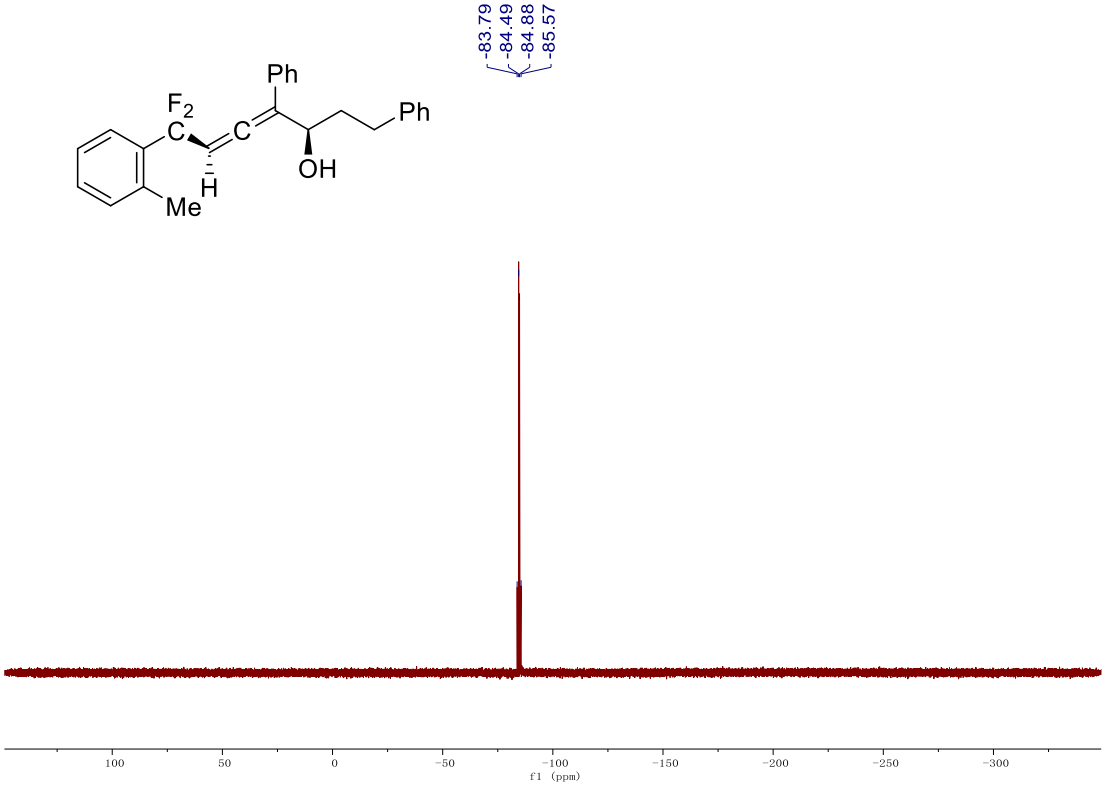
(-)-(3*R*,5*S*)-7,7-difluoro-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-3-ol (5h): ^{1}H NMR (400 MHz, $CDCl_3$)



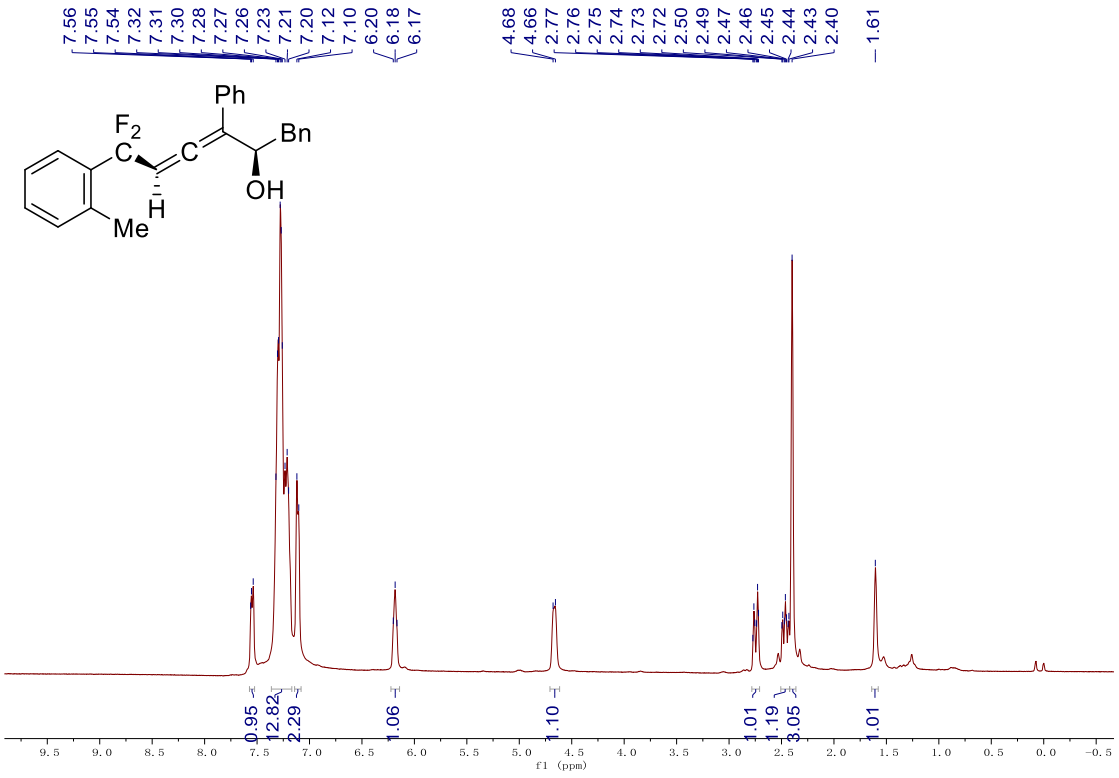
(-)-(3*R*,5*S*)-7,7-difluoro-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-3-ol (5h): ^{13}C NMR (101 MHz, $CDCl_3$)



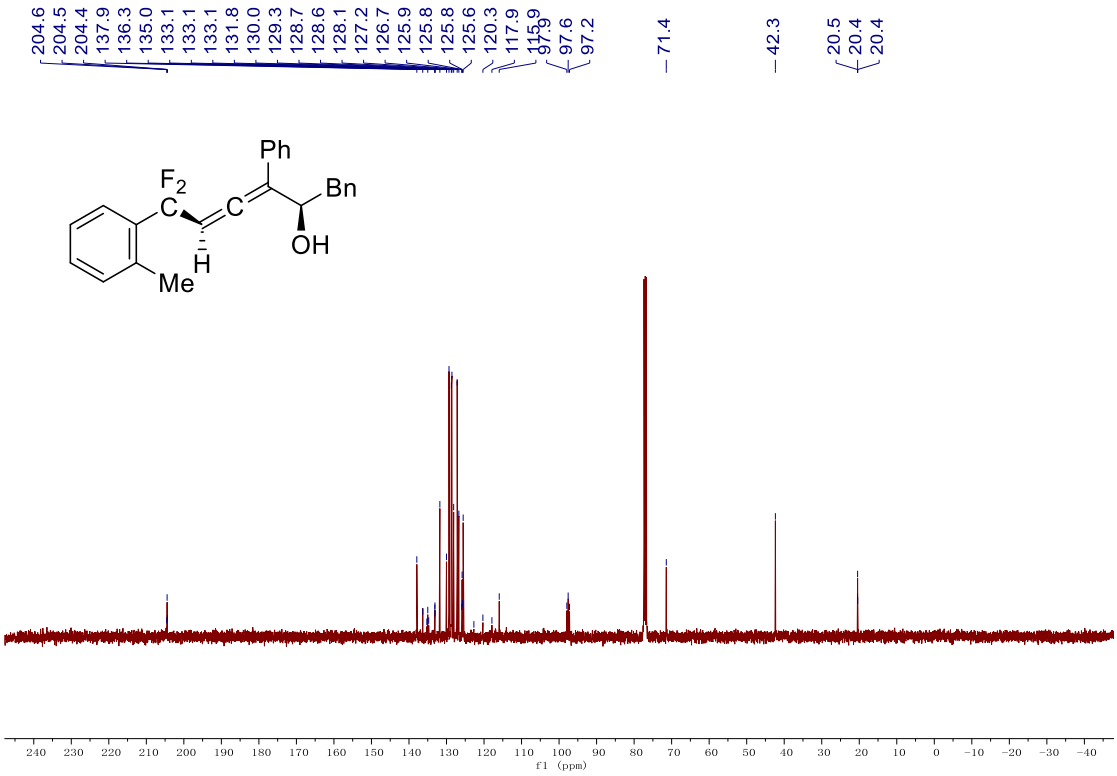
(-)-(3*R*,5*S*)-7,7-difluoro-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-3-ol (5h): ^{19}F NMR (376 MHz, $CDCl_3$)



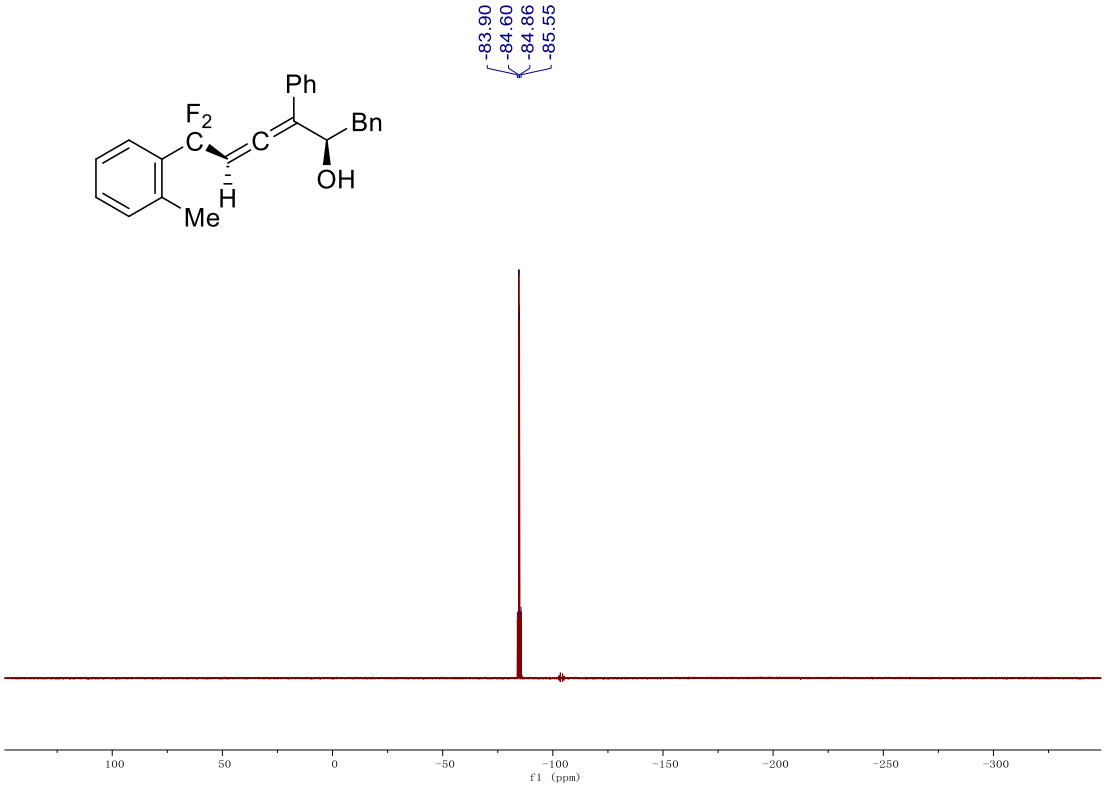
(-)-(2*R*,4*S*)-6,6-difluoro-1,3-diphenyl-6-(*o*-tolyl)hexa-3,4-dien-2-ol (5i): ^{1}H NMR (400 MHz, $CDCl_3$)



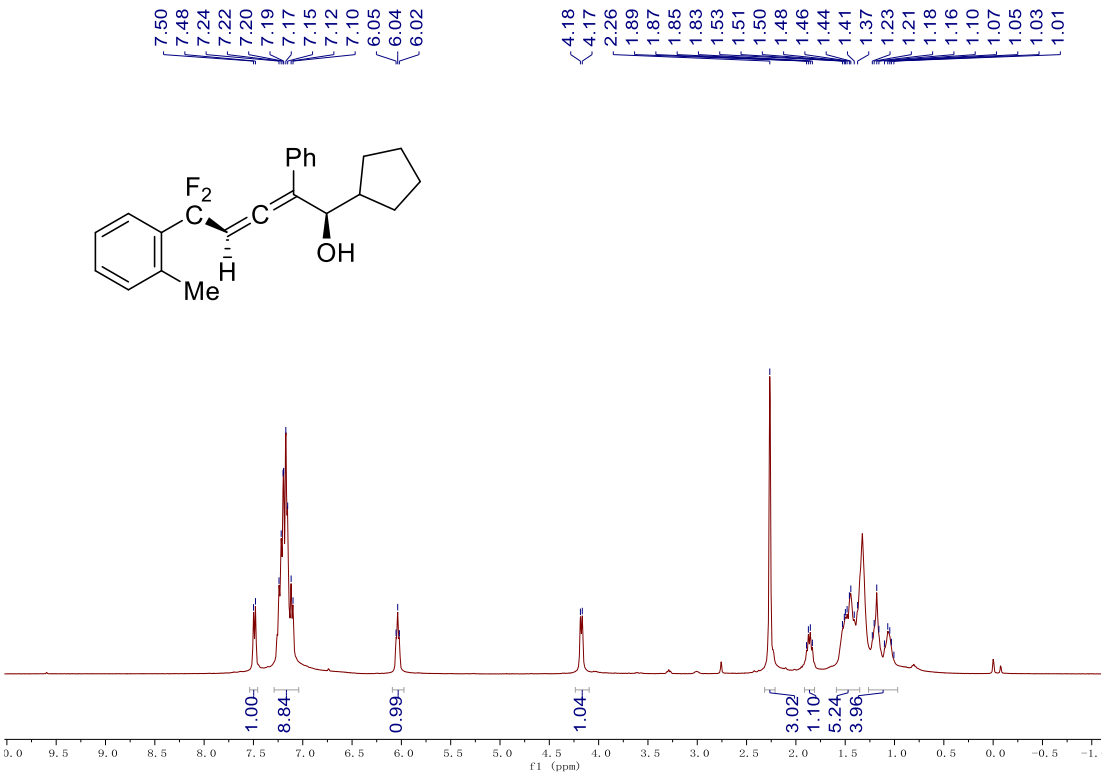
(-)-(2*R*,4*S*)-6,6-difluoro-1,3-diphenyl-6-(*o*-tolyl)hexa-3,4-dien-2-ol (5i): ^{13}C NMR (101 MHz, $CDCl_3$)



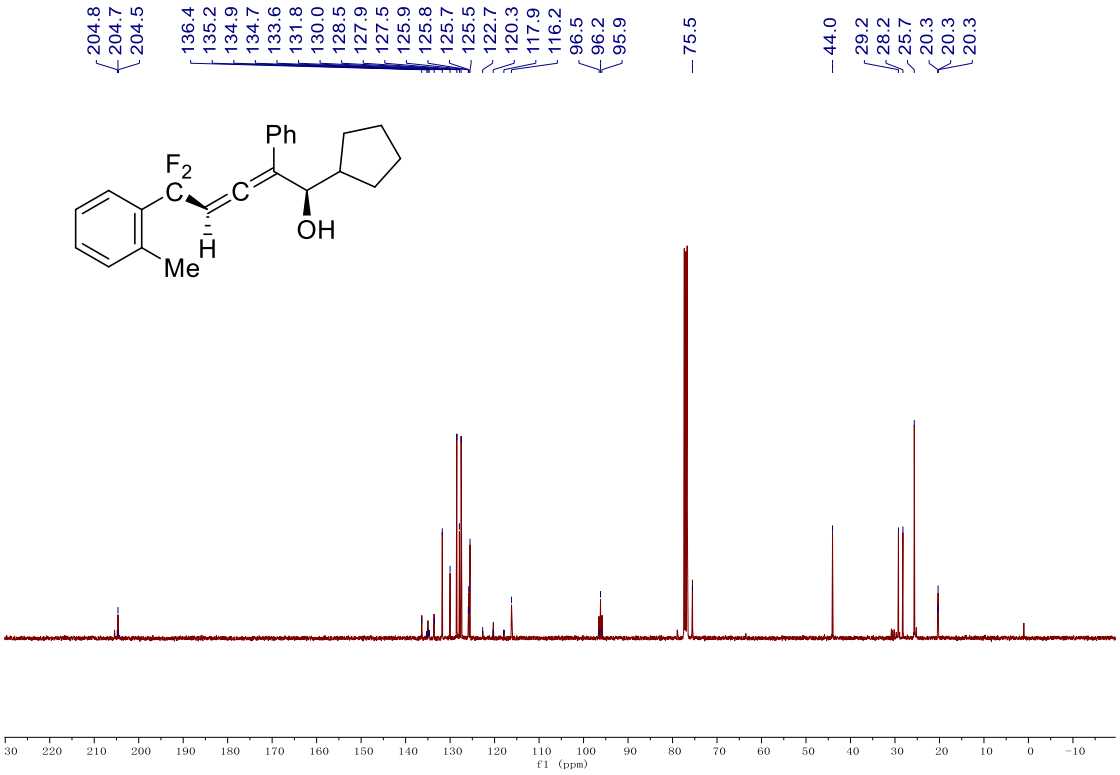
(-)-(2*R*,4*S*)-6,6-difluoro-1,3-diphenyl-6-(*o*-tolyl)hexa-3,4-dien-2-ol (5i): ^{19}F NMR (376 MHz, $CDCl_3$)



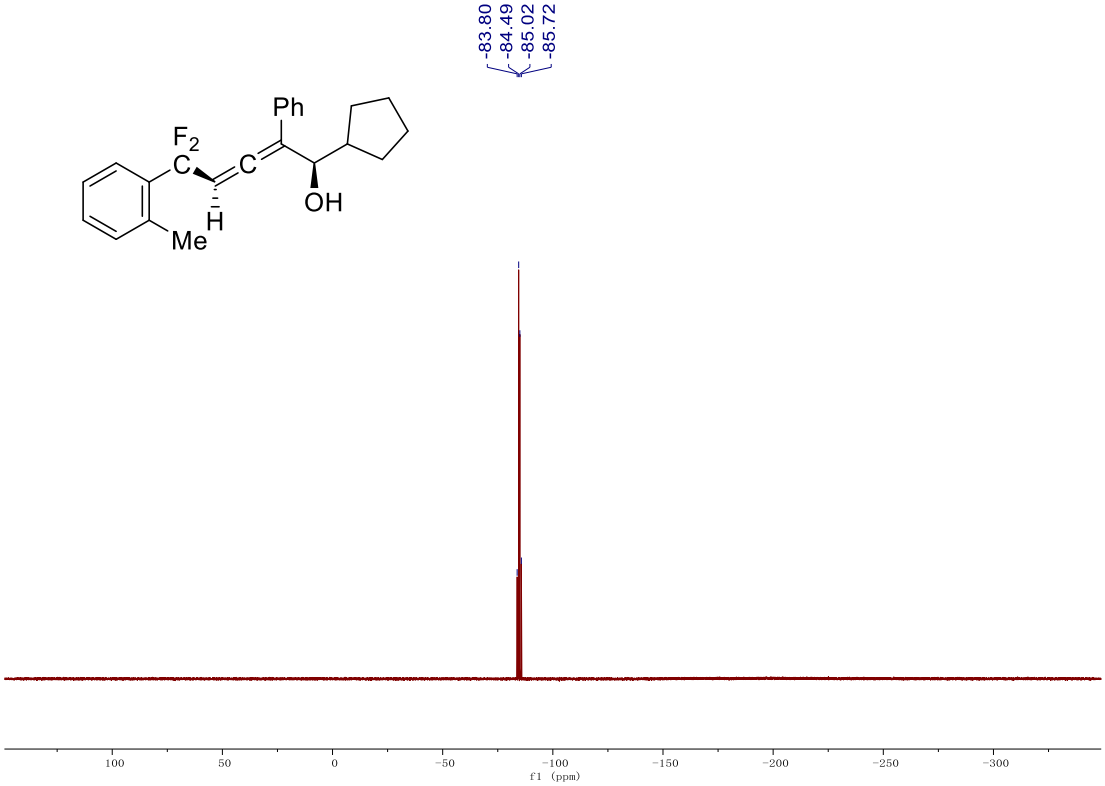
(-)-(1*R*,3*S*)-1-cyclopentyl-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5j): ^{1}H NMR (400 MHz, $CDCl_3$)



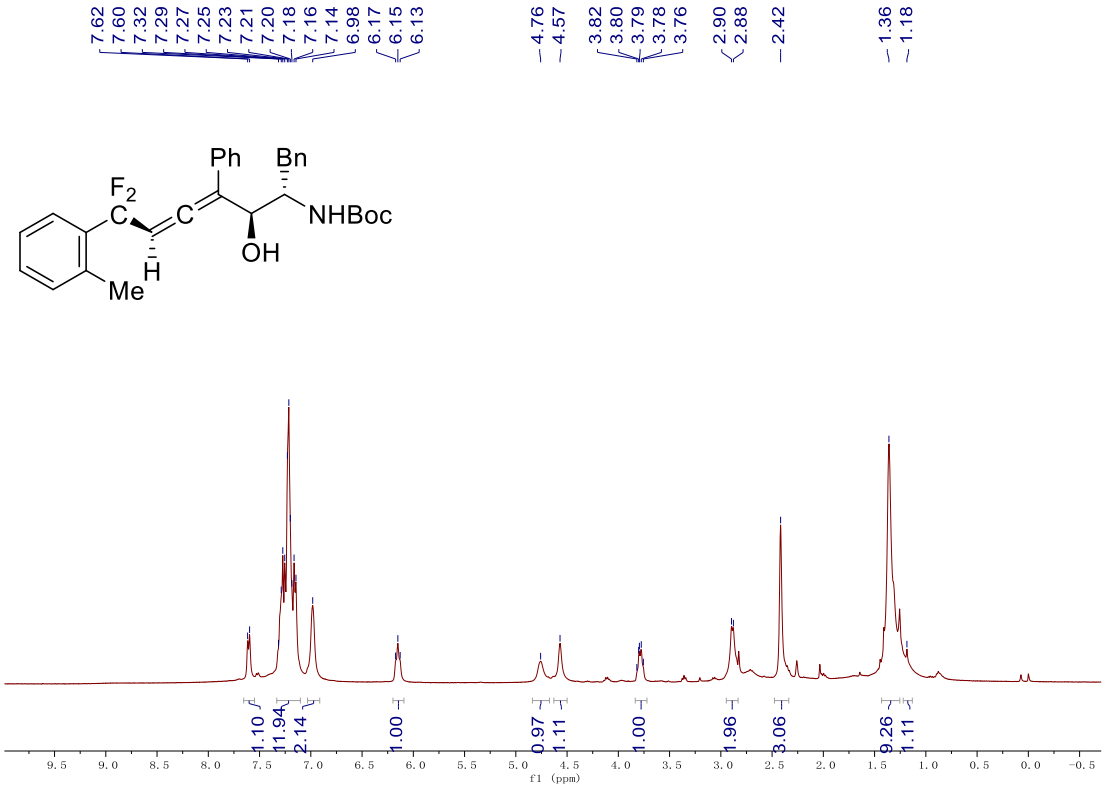
(-)-(1*R*,3*S*)-1-cyclopentyl-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5j): ^{13}C NMR (101 MHz, $CDCl_3$)



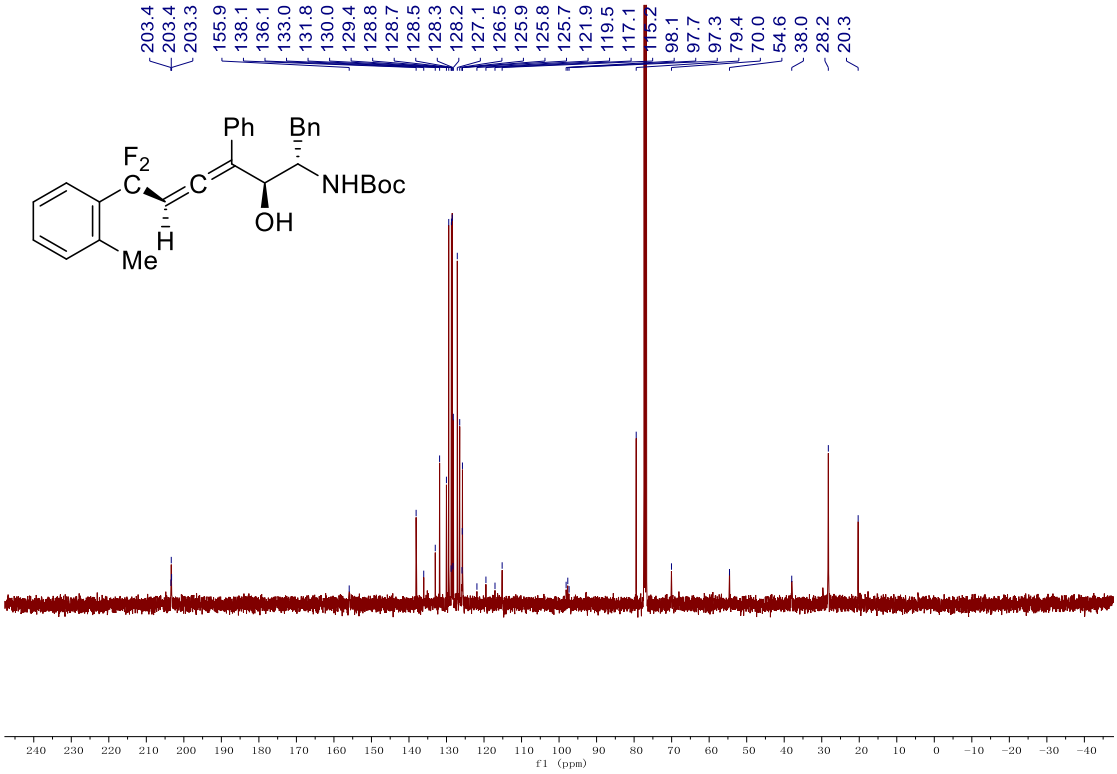
(-)-(1*R*,3*S*)-1-cyclopentyl-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5j): ^{19}F NMR (376 MHz, $CDCl_3$)



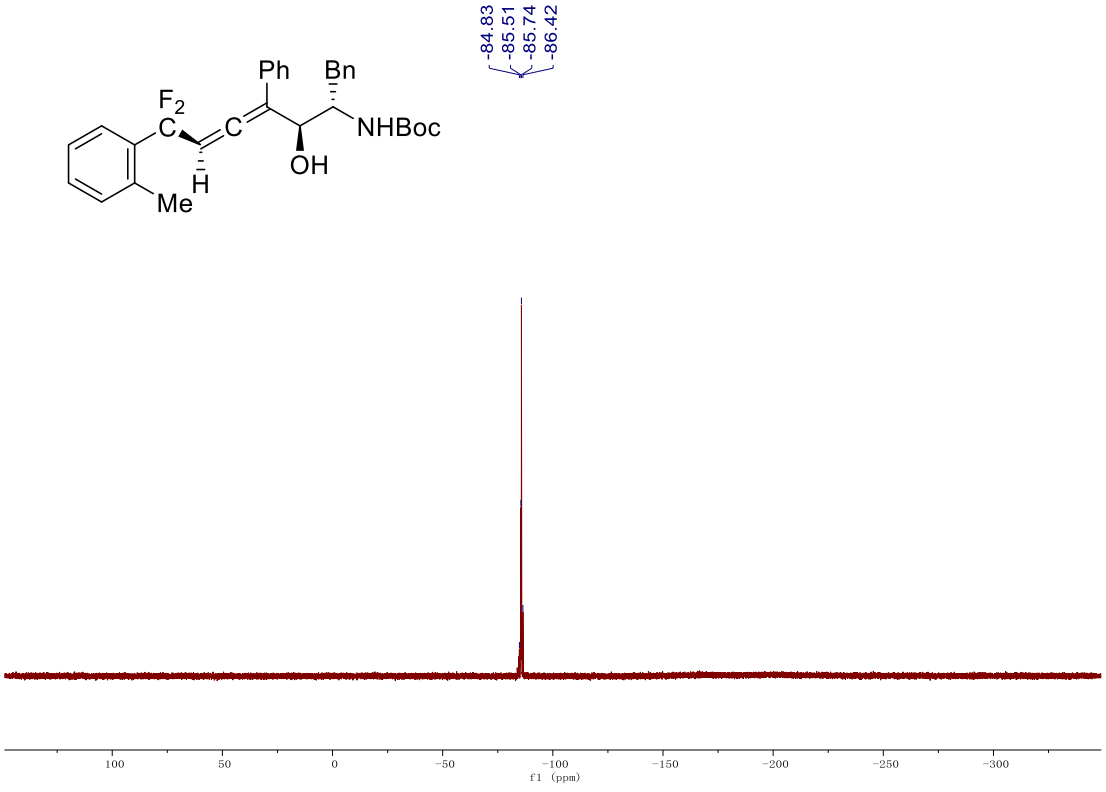
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5k): ^{1}H NMR (400 MHz, $CDCl_3$)



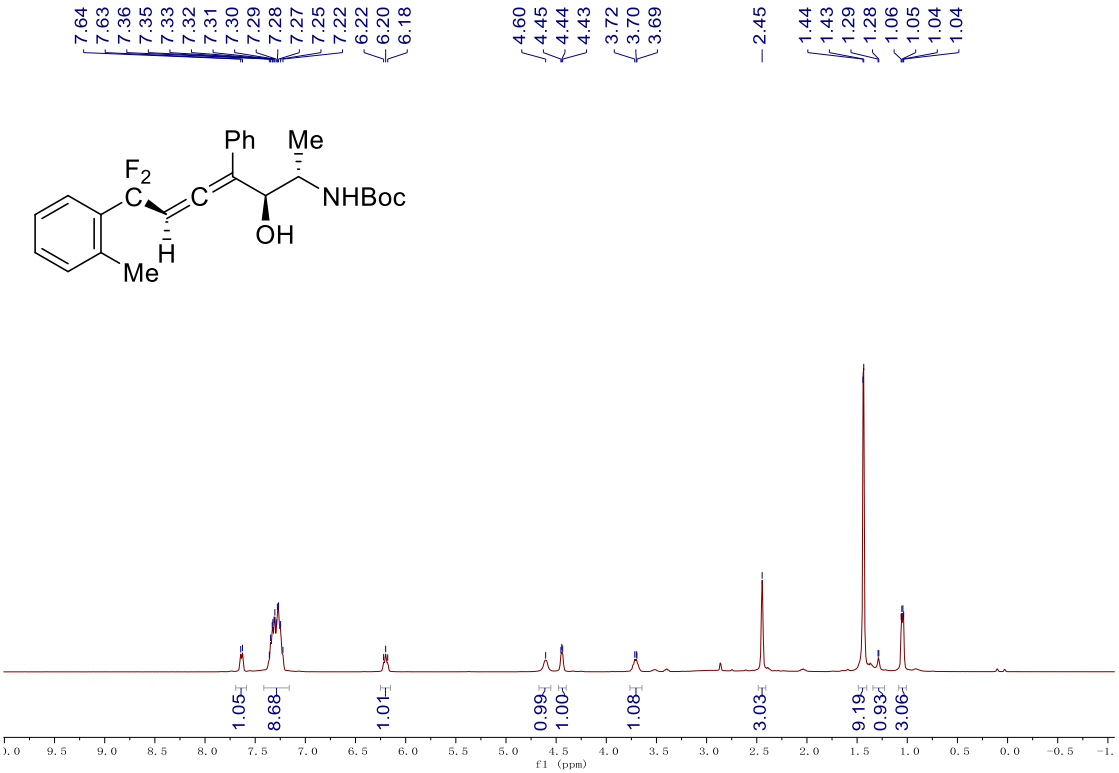
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5k): ^{13}C NMR (101 MHz, $CDCl_3$)



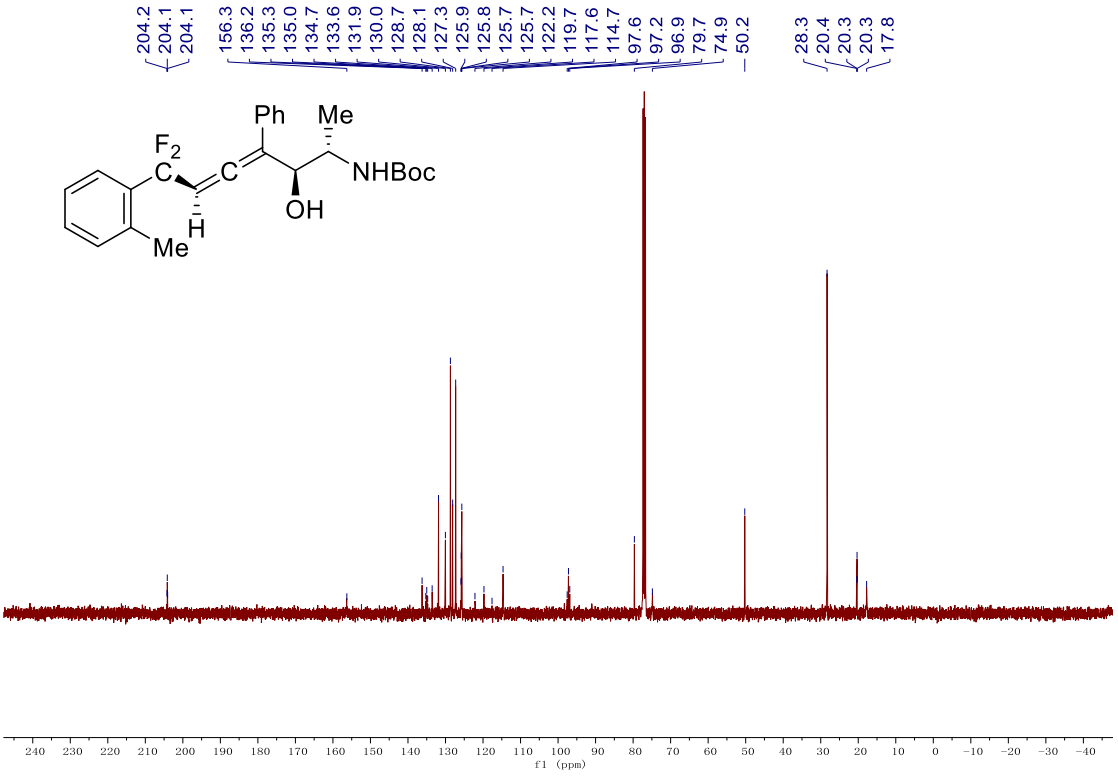
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5k): ^{19}F NMR (376 MHz, $CDCl_3$)



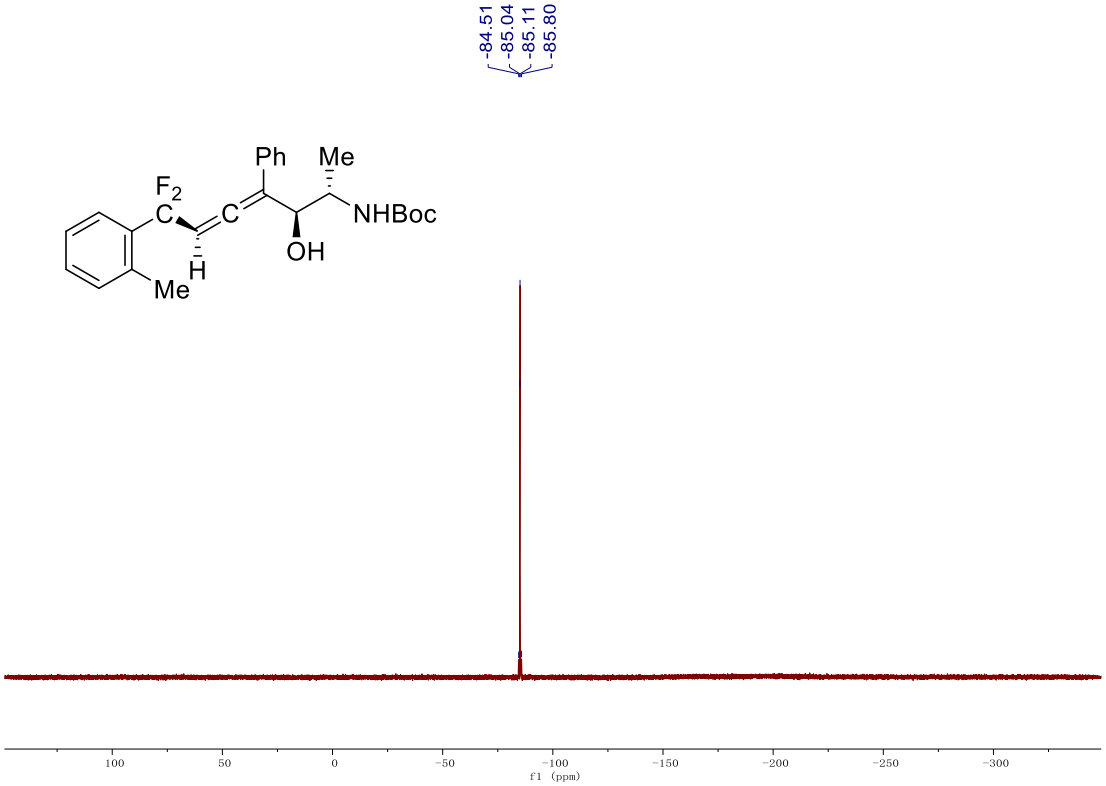
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-4-phenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5l): ^{1}H NMR (400 MHz, $CDCl_3$)



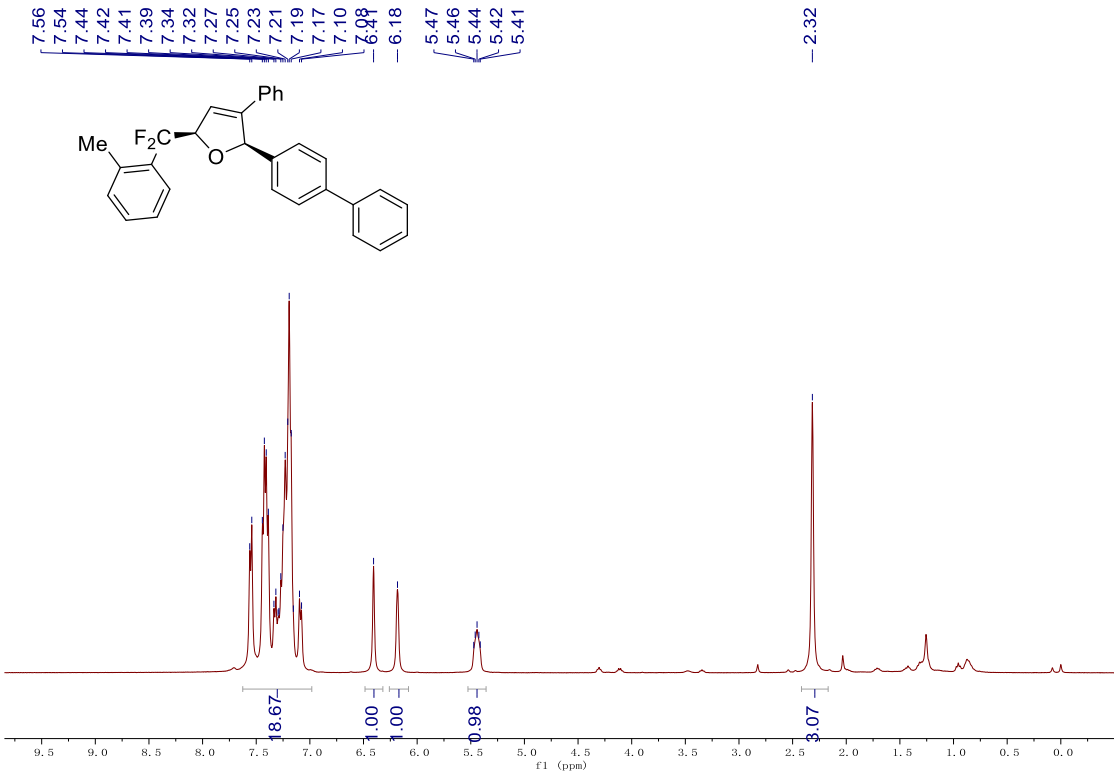
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-4-phenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5l): ^{13}C NMR (101 MHz, $CDCl_3$)



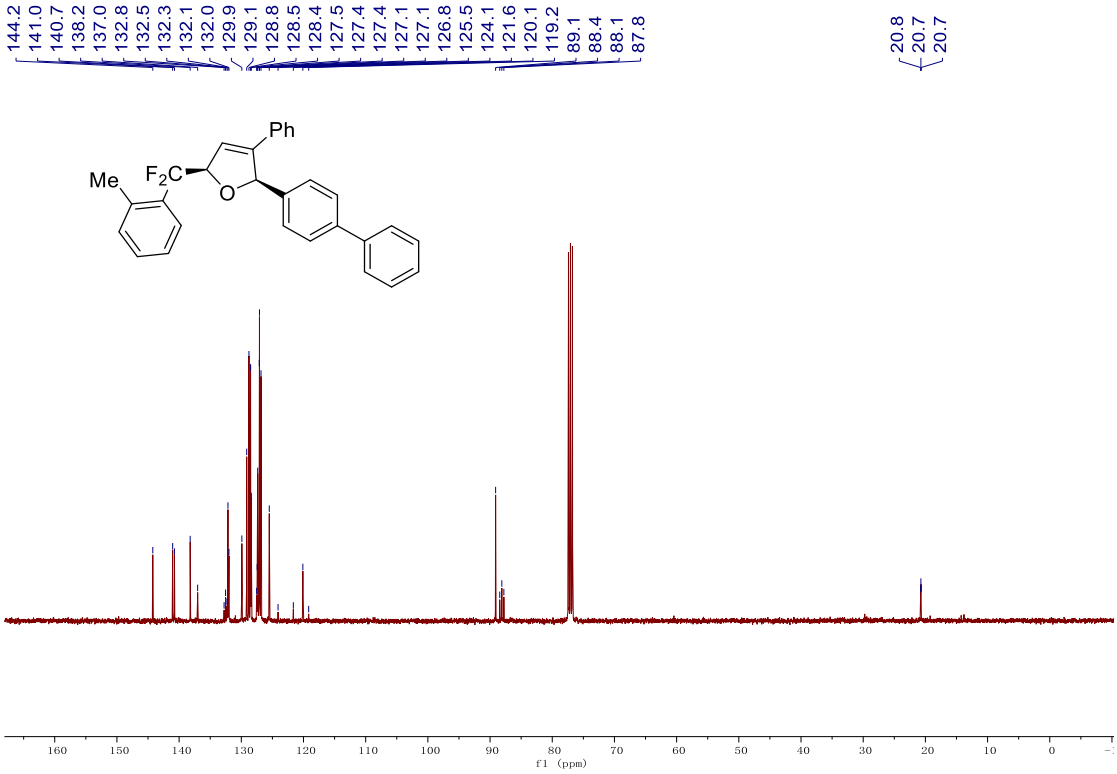
(-)-*tert*-butyl((2*S*,3*S*,5*S*)-7,7-difluoro-3-hydroxy-4-phenyl-7-(*o*-tolyl)hepta-4,5-dien-2-yl)carbamate (5l): ^{19}F NMR (376 MHz, $CDCl_3$)



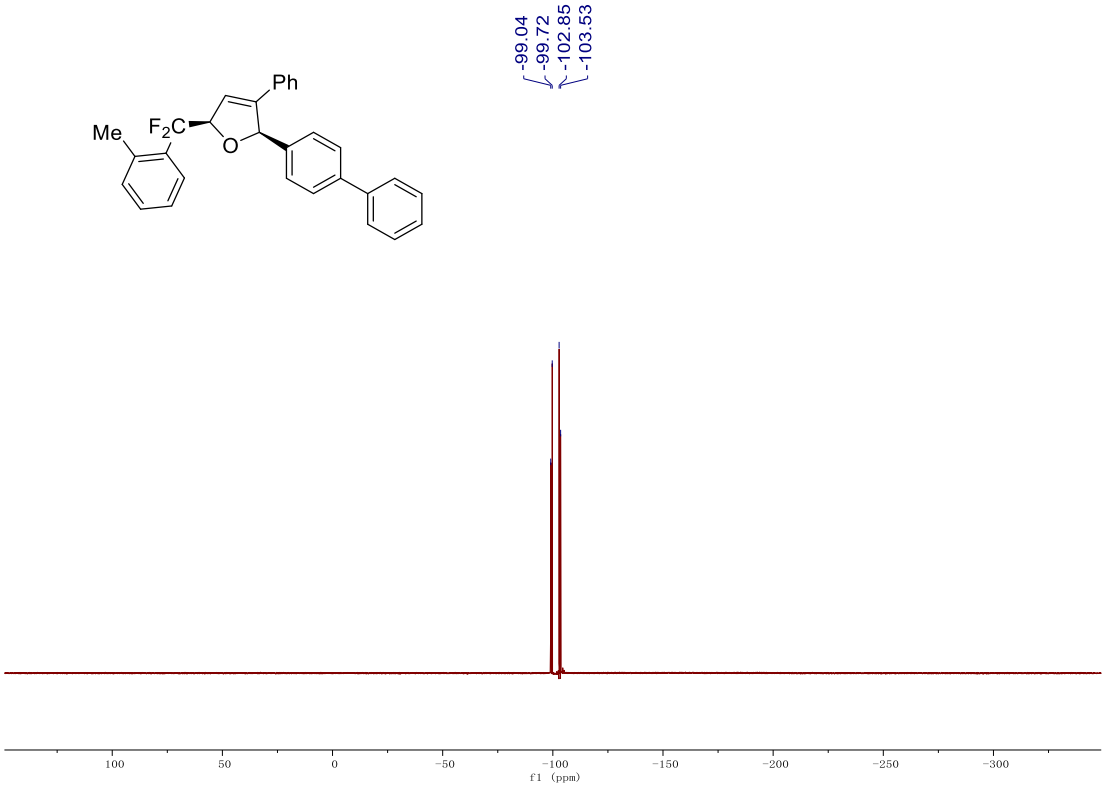
(-)-(2*R*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyl-2,5-dihydrofuran (6): ^{1}H NMR (400 MHz, $CDCl_3$)



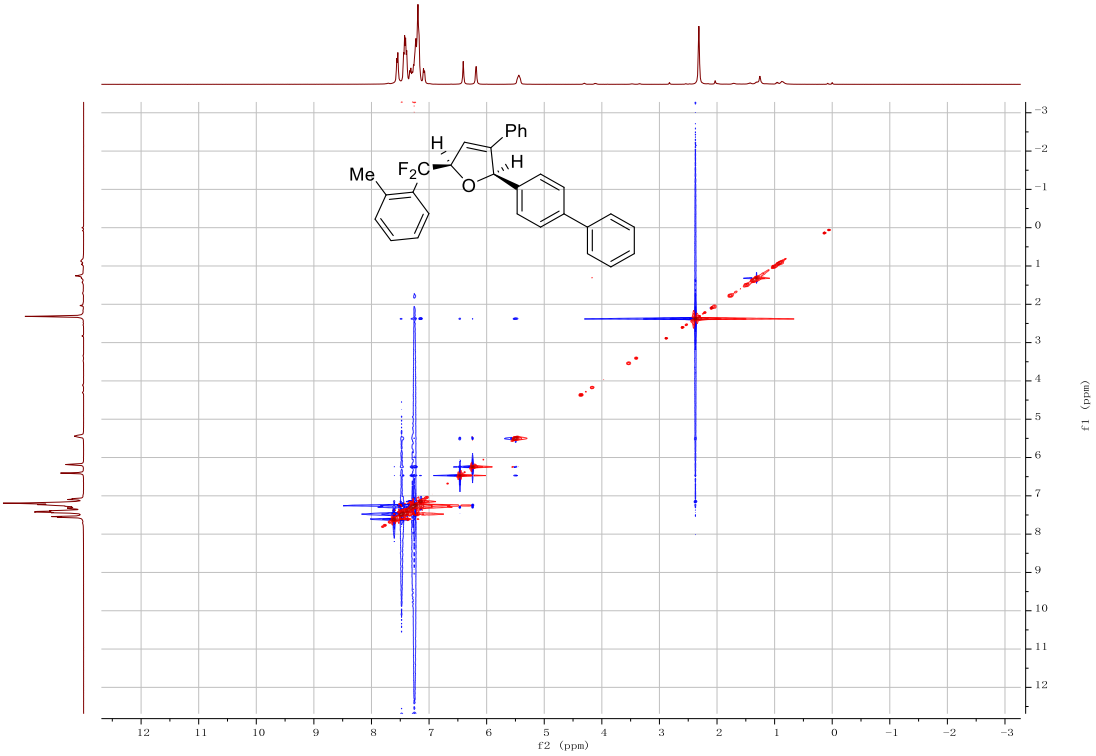
(-)-(2*R*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyl-2,5-dihydrofuran (6): ^{13}C NMR (101 MHz, $CDCl_3$)

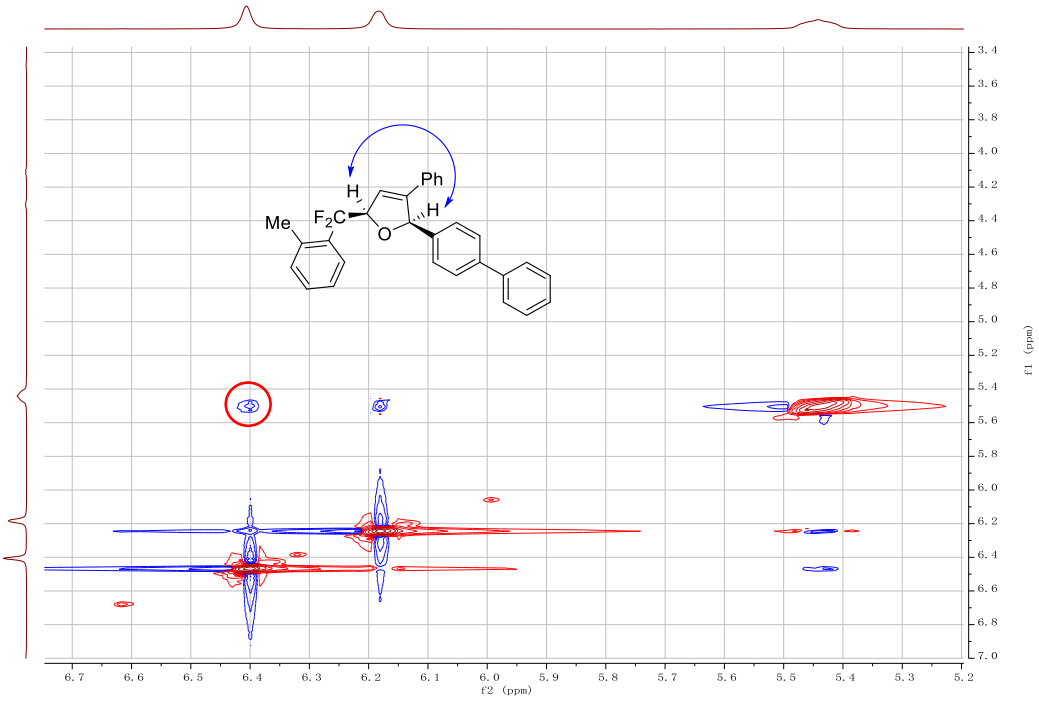


(-)-(2*R*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyl-2,5-dihydrofuran (6):

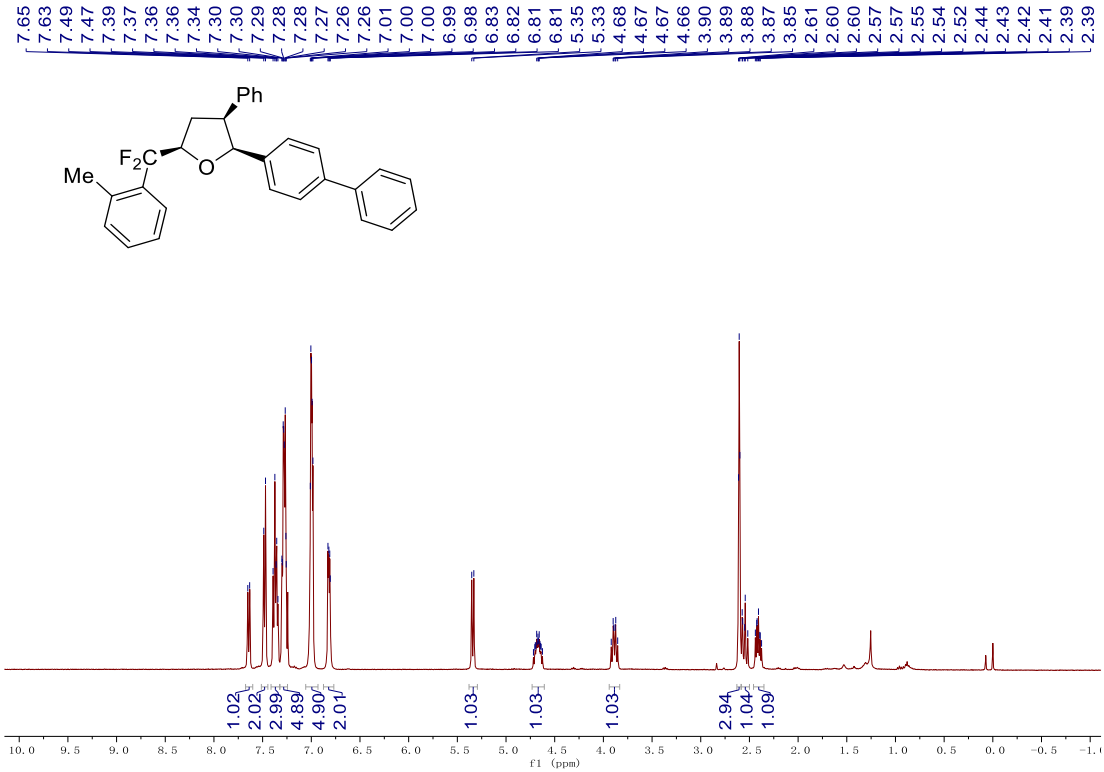


(-)-(2*R*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyl-2,5-dihydrofuran (6): ^{1}H-^{1}H Noesy (400 MHz, $CDCl_3$)

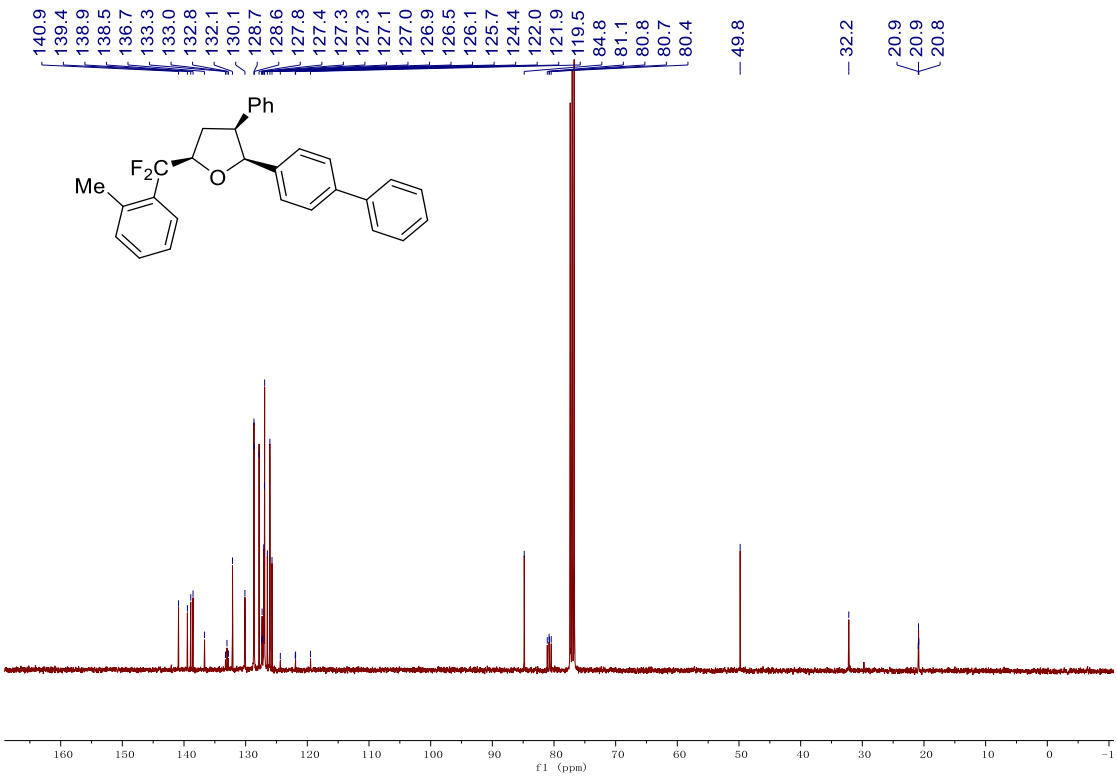




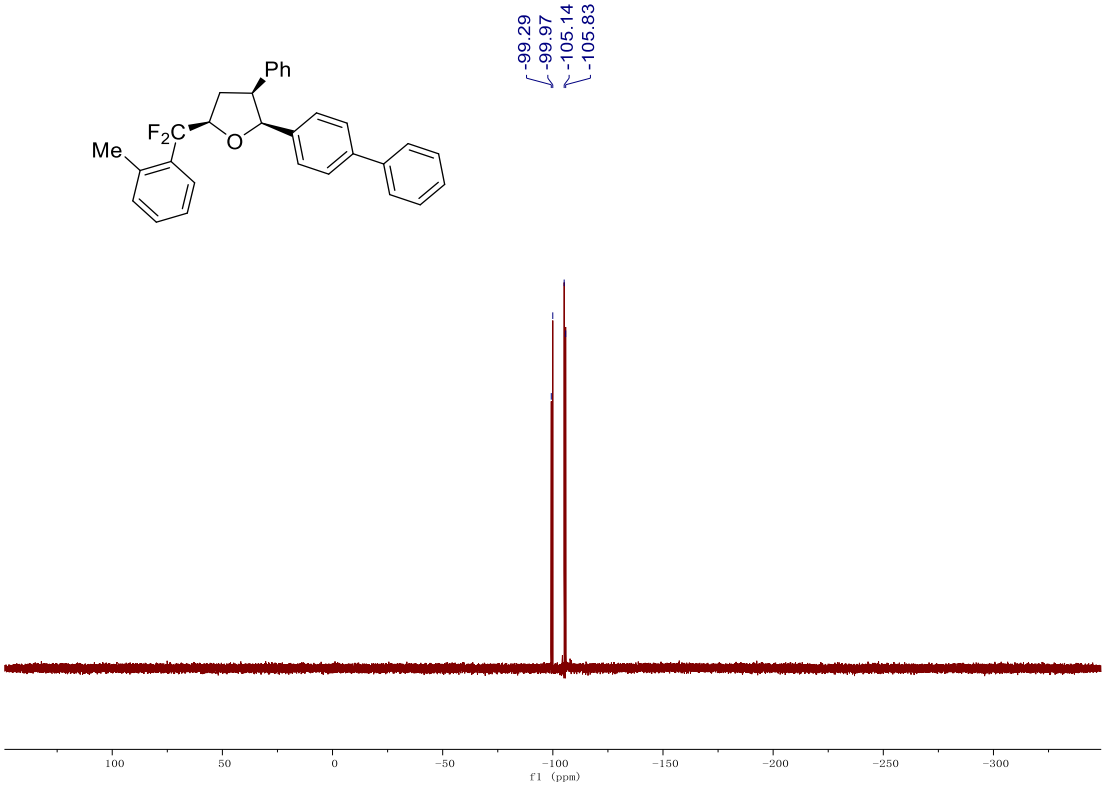
(-)-(2*S*,3*S*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyltetrahydrofuran (7) ^{1}H NMR (400 MHz, $CDCl_3$)



(-)-(2*S*,3*S*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyltetrahydrofuran (7): ^{13}C NMR (101 MHz, $CDCl_3$)

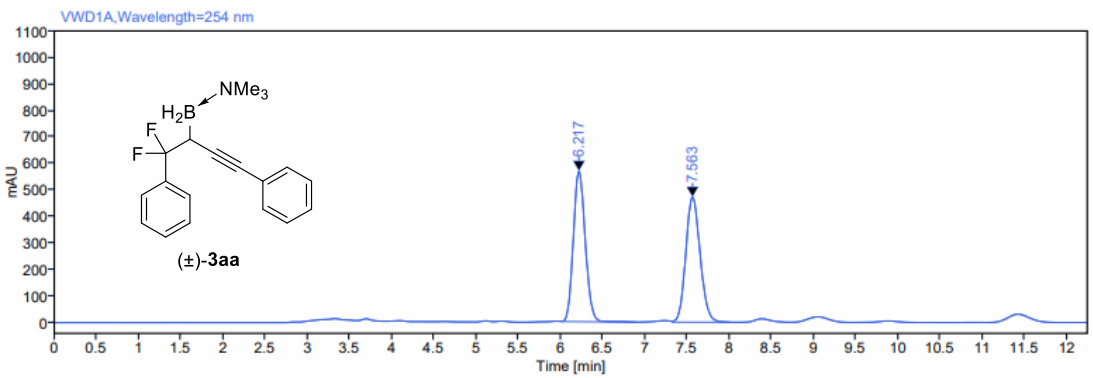


(-)-(2*S*,3*S*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyltetrahydrofuran (7): ^{19}F NMR (376 MHz, $CDCl_3$)

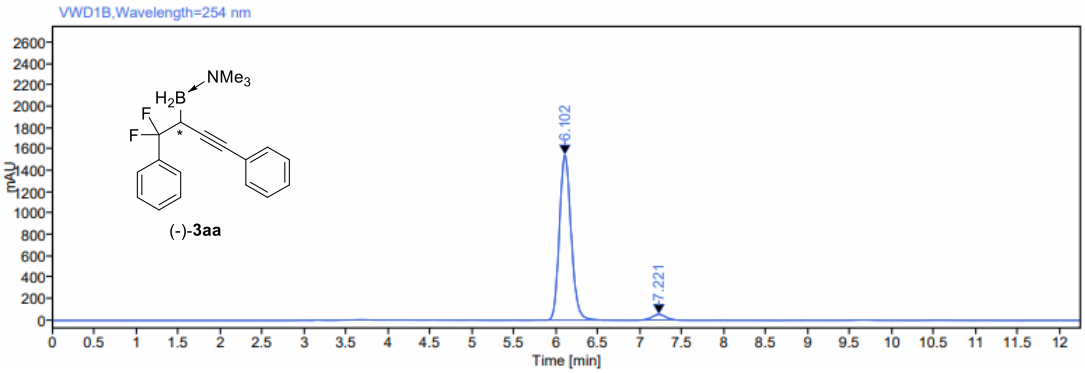


13. HPLC Charts

(-)-Trimethylamine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3aa)

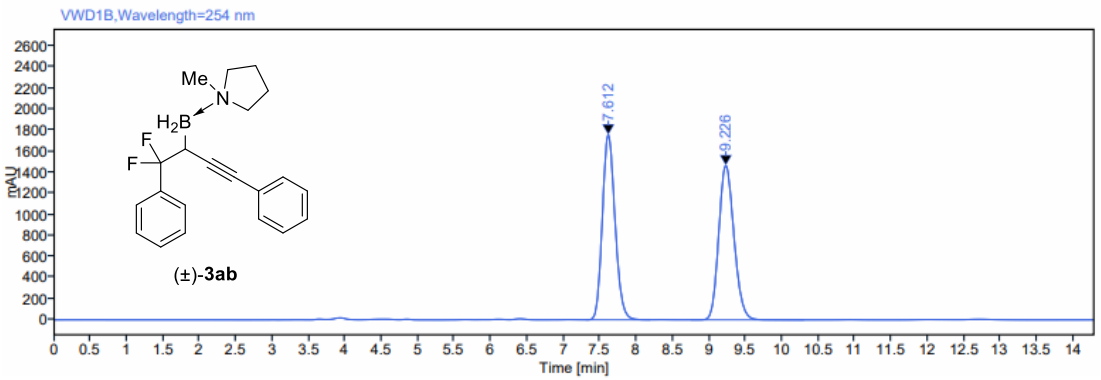


RT [min]	Type	Width [min]	Area	Height	Area%
6.217	VB	0.89	5588.72	568.97	49.96
7.563	VBA	0.69	5596.64	472.62	50.04
		Sum	11185.36		

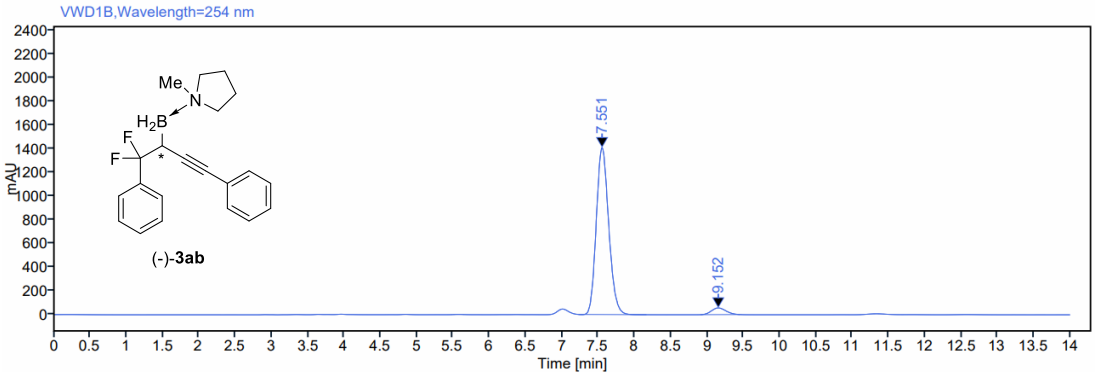


RT [min]	Type	Width [min]	Area	Height	Area%
6.102	MM m	0.15	14994.86	1545.98	96.42
7.221	MM m	0.17	556.17	50.56	3.58
		Sum	15551.03		

(-)-1-methylpyrrolidine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ab)

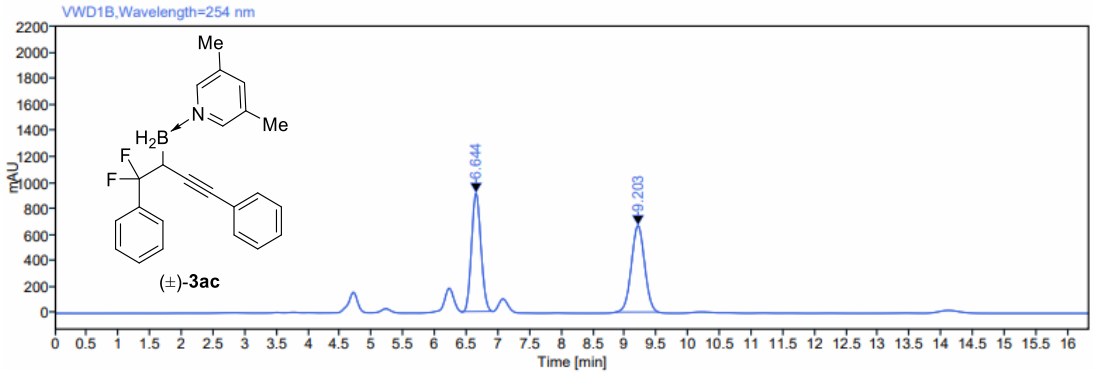


RT [min]	Type	Width [min]	Area	Height	Area%
7.612	BV	0.88	21292.58	1758.06	49.89
9.226	MB m	0.23	21387.76	1466.48	50.11
		Sum	42680.33		

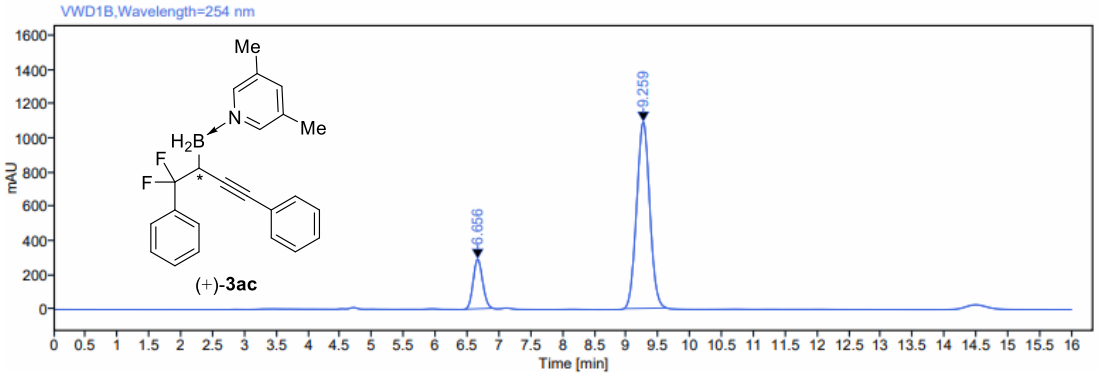


RT [min]	Type	Width [min]	Area	Height	Area%
7.551	MM m	0.19	16774.35	1406.40	95.56
9.152	MM m	0.22	780.06	56.41	4.44
		Sum	17554.40		

(+)-3,5-dimethylpyridine-(1,1-difluoro-1,4-diphenylbut-3-yn-2-yl)borane (3ac)

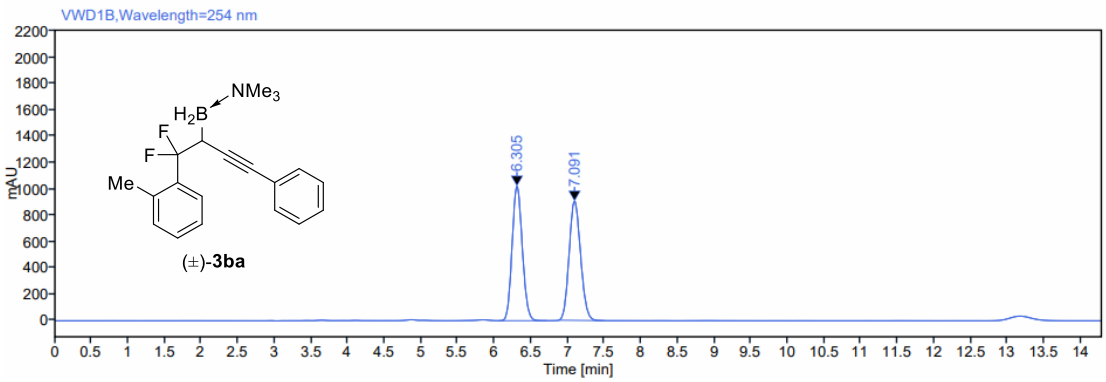


RT [min]	Type	Width [min]	Area	Height	Area%
6.644	MM m	0.16	9430.15	909.54	49.34
9.203	BM m	0.23	9683.80	664.84	50.66
		Sum	19113.95		

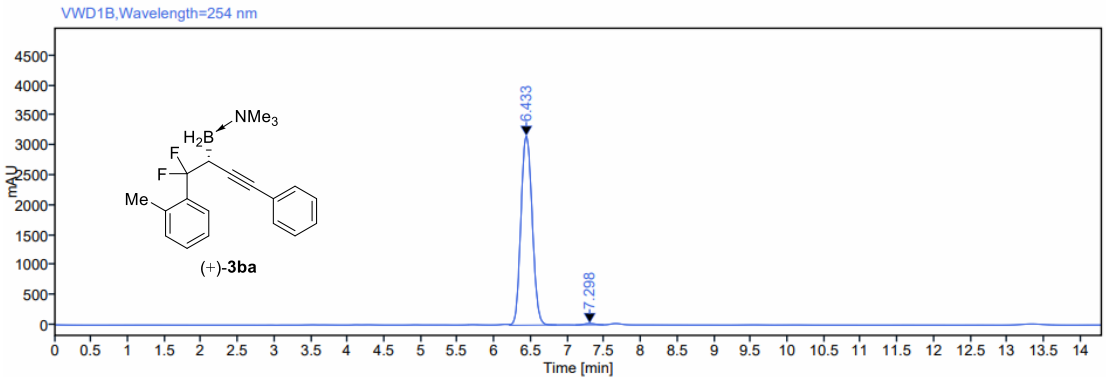


RT [min]	Type	Width [min]	Area	Height	Area%
6.656	BBA	0.44	2996.40	289.75	16.10
9.259	BBA	0.67	15609.20	1088.18	83.90
		Sum	18605.60		

(+)-(*R*)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ba)

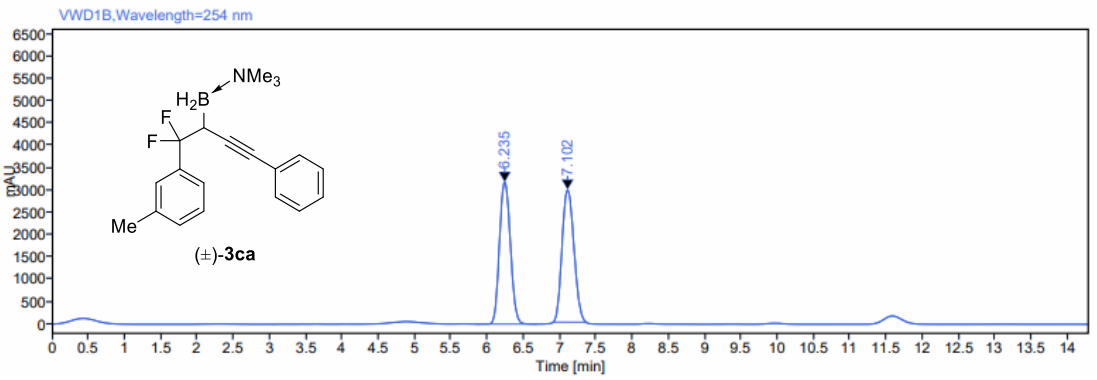


RT [min]	Type	Width [min]	Area	Height	Area%
6.305	BB	0.66	9909.79	1021.86	50.08
7.091	BBA	0.62	9878.35	904.93	49.92
		Sum	19788.14		

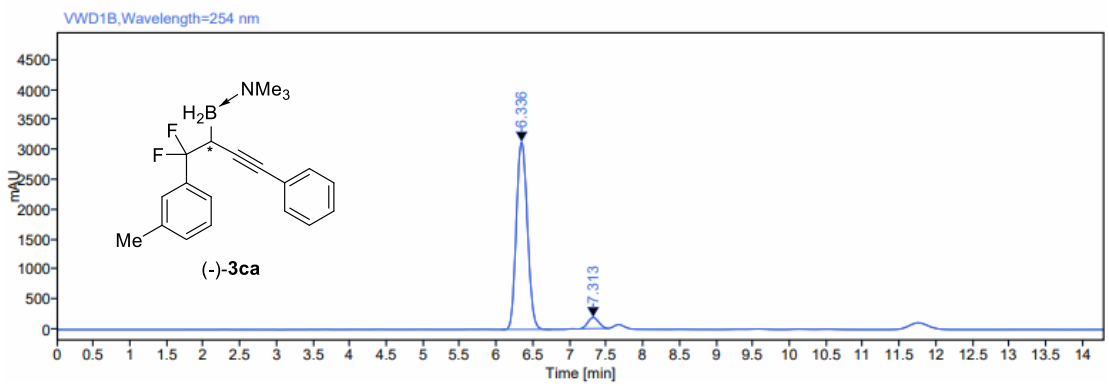


RT [min]	Type	Width [min]	Area	Height	Area%
6.433	MB m	0.17	33833.78	3154.37	99.30
7.298	BB	0.38	238.41	23.16	0.70
		Sum	34072.19		

(-)-Trimethylamine-(1,1-difluoro-4-phenyl-1-(*m*-tolyl)but-3-yn-2-yl)borane (3ca)

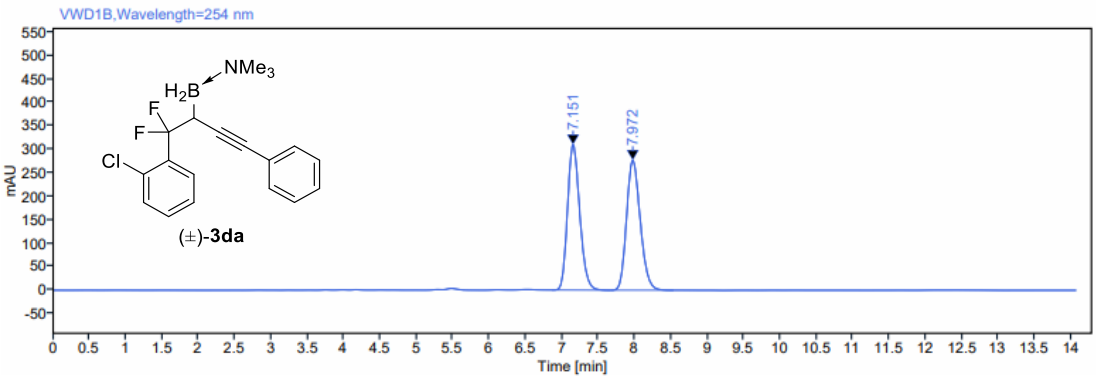


RT [min]	Type	Width [min]	Area	Height	Area%
6.235	MM m	0.17	33328.63	3176.45	49.64
7.102	MM m	0.18	33812.34	2963.18	50.36
		Sum	67140.97		

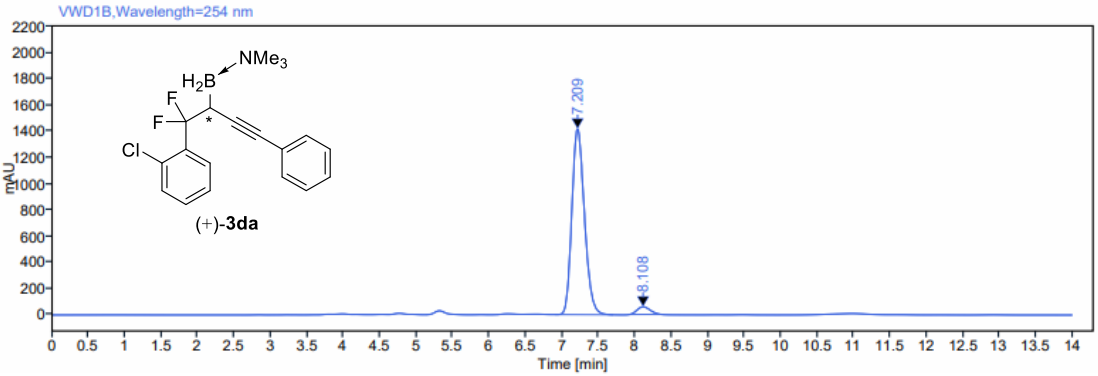


RT [min]	Type	Width [min]	Area	Height	Area%
6.336	BB	0.67	32946.03	3128.23	94.59
7.313	BBA	0.37	1885.97	183.38	5.41
		Sum	34832.00		

(+)-Trimethylamine-(1-(2-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3da)

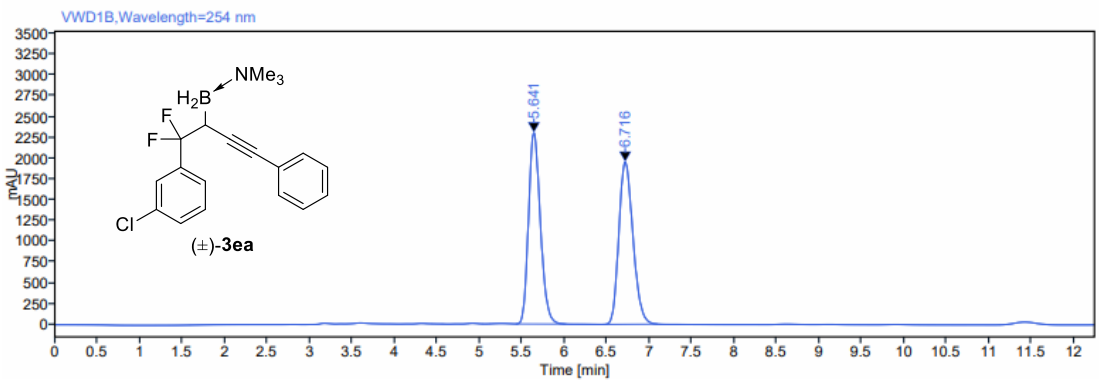


RT [min]	Type	Width [min]	Area	Height	Area%
7.151	BB	0.80	3621.56	309.35	49.94
7.972	BBA	0.87	3629.60	276.53	50.06
		Sum	7251.16		

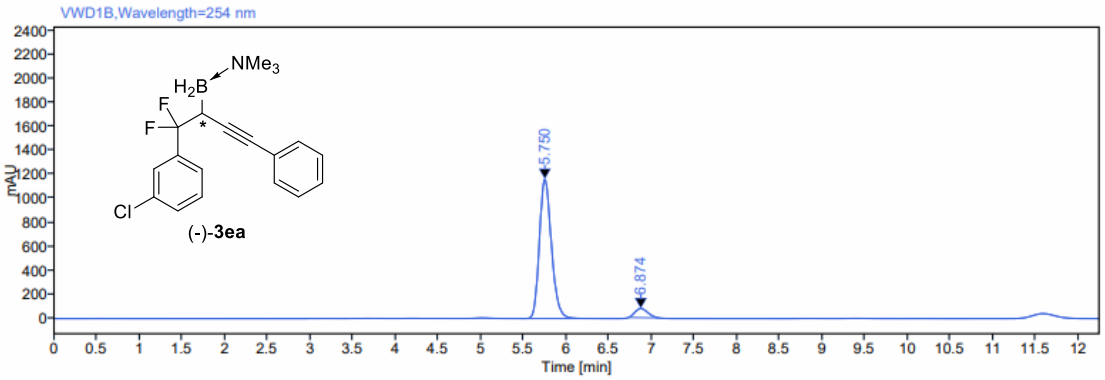


RT [min]	Type	Width [min]	Area	Height	Area%
7.209	BBA	0.79	17064.17	1418.28	95.90
8.108	BBA	0.44	729.32	58.70	4.10
		Sum	17793.49		

(-)-Trimethylamine-(1-(3-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3ea)

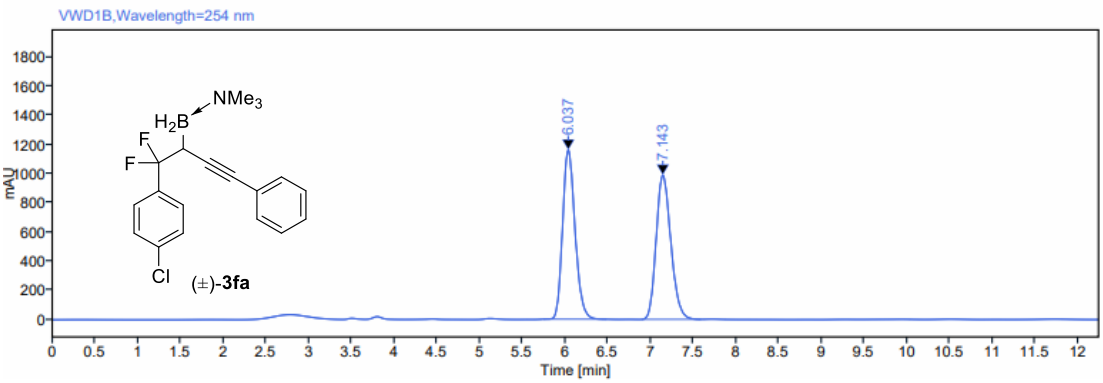


RT [min]	Type	Width [min]	Area	Height	Area%
5.641	BBA	0.59	22316.87	2299.53	49.70
6.716	BBA	0.65	22583.34	1951.50	50.30
		Sum	44900.21		

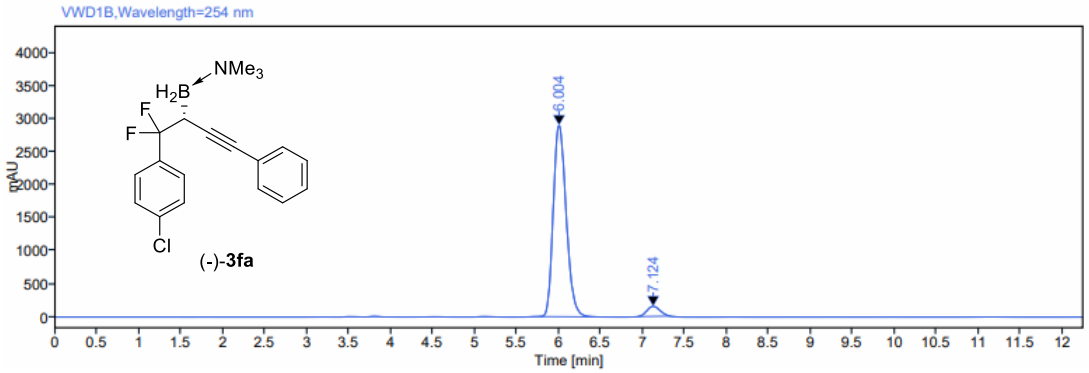


RT [min]	Type	Width [min]	Area	Height	Area%
5.750	BBA	0.84	11381.68	1161.01	93.55
6.874	BBA	0.35	785.08	75.61	6.45
		Sum	12166.76		

(-)-(*R*)-Trimethylamine-(1-(4-chlorophenyl)-1,1-difluoro-4-phenylbut-3-yn-2-yl)borane (3fa)

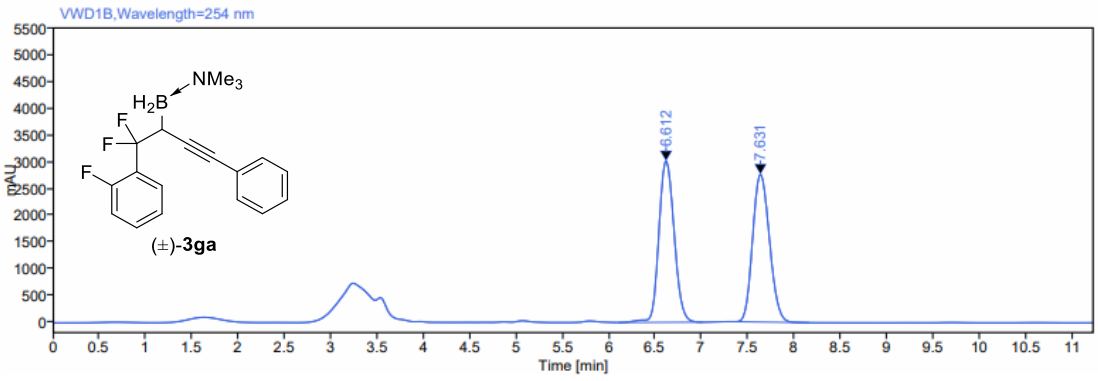


RT [min]	Type	Width [min]	Area	Height	Area%
6.037	BBA	0.73	11763.00	1160.40	49.88
7.143	BBA	0.69	11820.55	989.67	50.12
		Sum	23583.55		

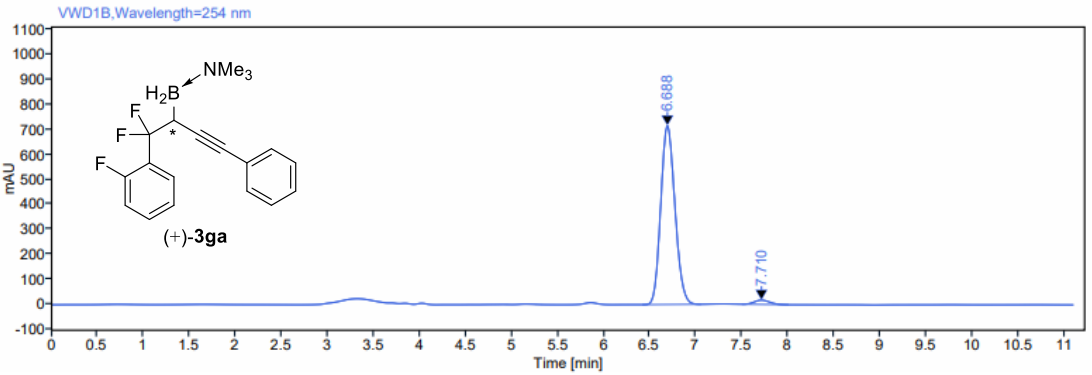


RT [min]	Type	Width [min]	Area	Height	Area%
6.004	BBA	0.71	31073.23	2899.40	94.96
7.124	BBA	0.38	1650.54	151.80	5.04
		Sum	32723.77		

(+)-Trimethylamine-(1,1-difluoro-1-(2-fluorophenyl)-4-phenylbut-3-yn-2-yl)borane (3ga)

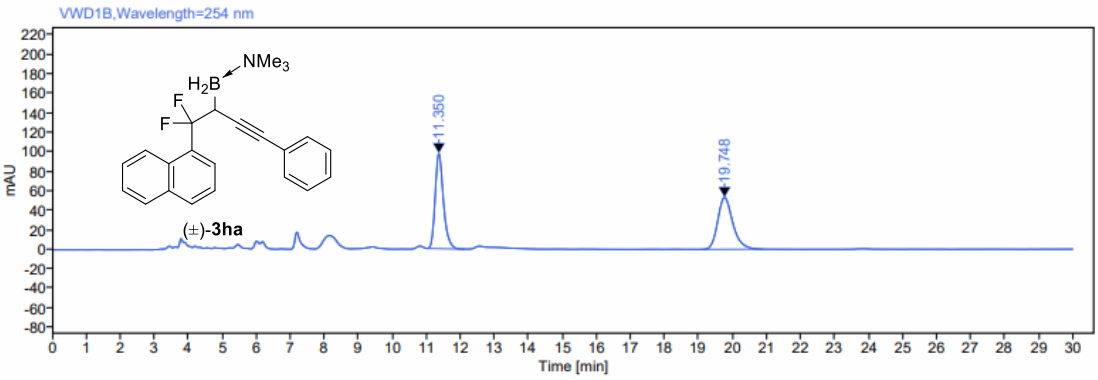


RT [min]	Type	Width [min]	Area	Height	Area%
6.612	BB	0.91	34650.28	3010.02	49.82
7.631	BBA	0.80	34900.50	2755.25	50.18
		Sum	69550.79		

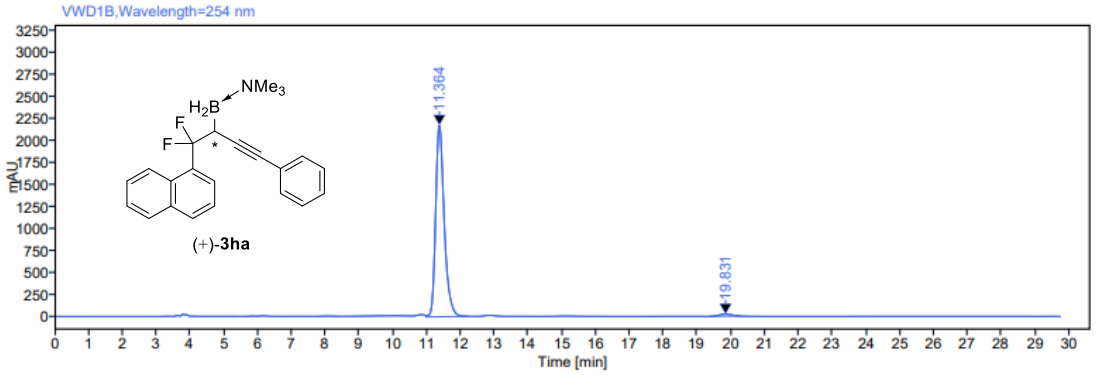


RT [min]	Type	Width [min]	Area	Height	Area%
6.688	BB	0.64	7654.25	712.94	97.47
7.710	BBA	0.51	198.89	17.04	2.53
		Sum	7853.14		

(+)-Trimethylamine-(1,1-difluoro-1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-yl)borane (3ha)

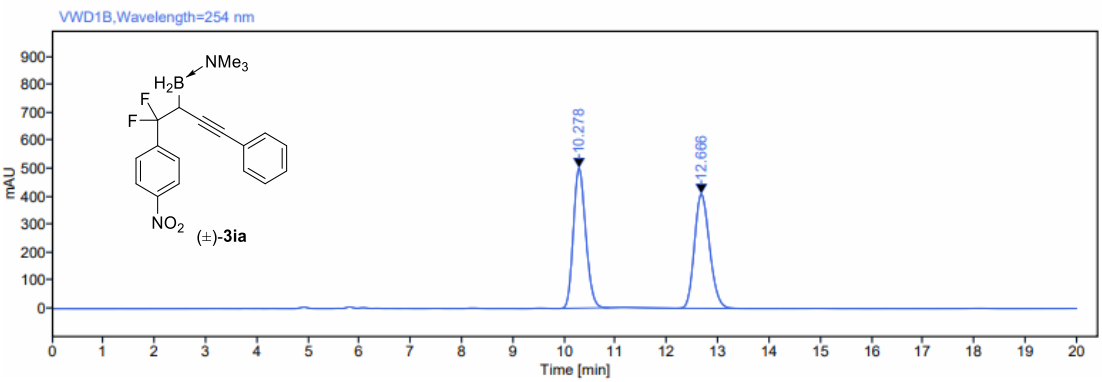


RT [min]	Type	Width [min]	Area	Height	Area%
11.350	BB	1.11	1649.34	97.62	50.15
19.748	BBA	1.84	1639.78	53.24	49.85
		Sum	3289.13		

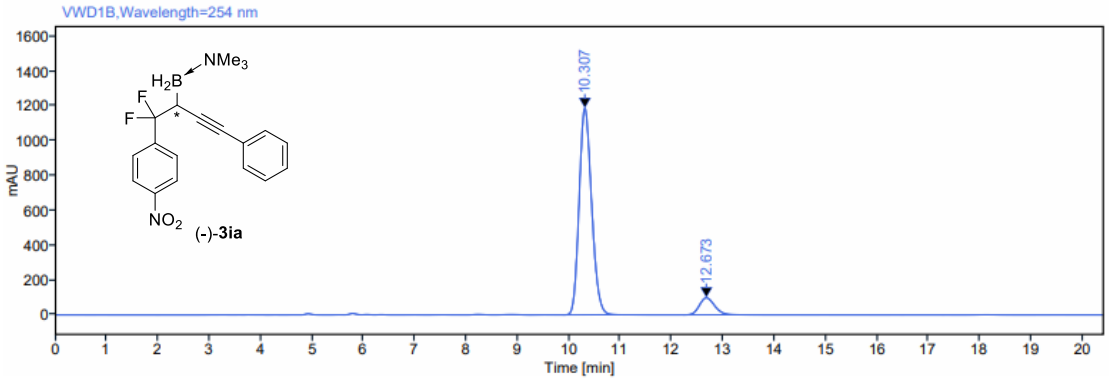


RT [min]	Type	Width [min]	Area	Height	Area%
11.364	MB m	0.27	38290.84	2176.05	98.39
19.831	BBA	0.89	627.71	23.99	1.61
		Sum	38918.55		

(-)-Trimethylamine-(1,1-difluoro-1-(4-nitrophenyl)-4-phenylbut-3-yn-2-yl)borane (3ia)

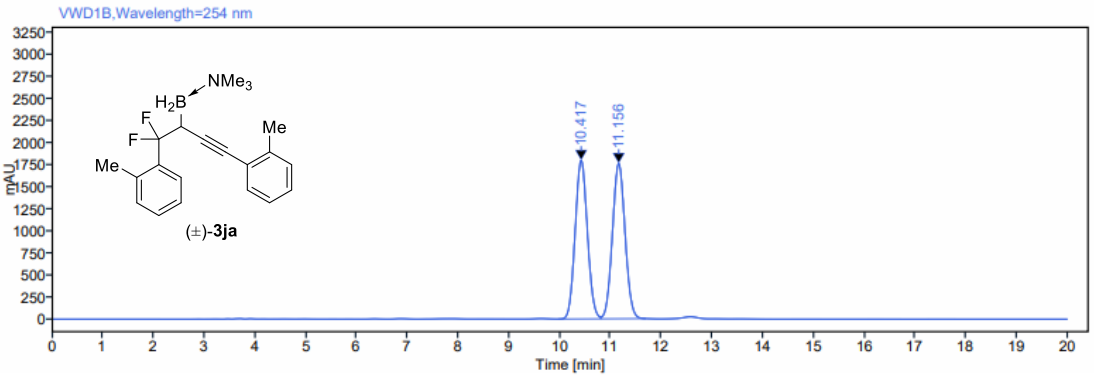


RT [min]	Type	Width [min]	Area	Height	Area%
10.278	BB	0.98	8389.13	500.06	49.92
12.666	BBA	1.23	8416.26	408.33	50.08
		Sum	16805.40		

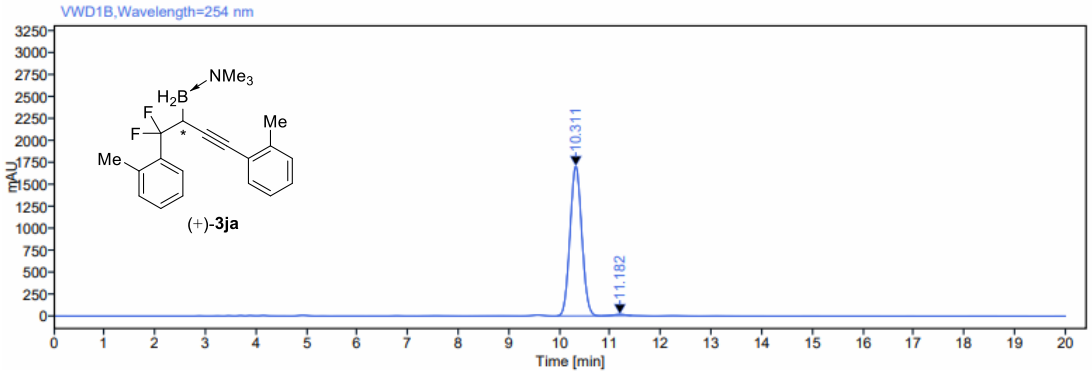


RT [min]	Type	Width [min]	Area	Height	Area%
10.307	BBA	1.05	20001.72	1186.89	90.90
12.673	BBA	1.07	2002.21	97.63	9.10
		Sum	22003.93		

(+)-Trimethylamine-(1,1-difluoro-1,4-di-*o*-tolylbut-3-yn-2-yl)borane (3ja)

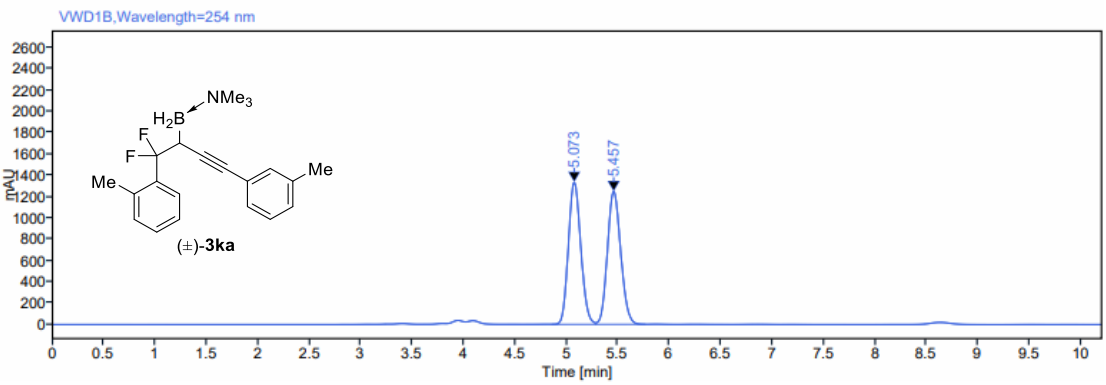


RT [min]	Type	Width [min]	Area	Height	Area%
10.417	BV	0.84	30116.20	1797.32	49.70
11.156	VBA	0.88	30473.81	1760.34	50.30
		Sum	60590.01		

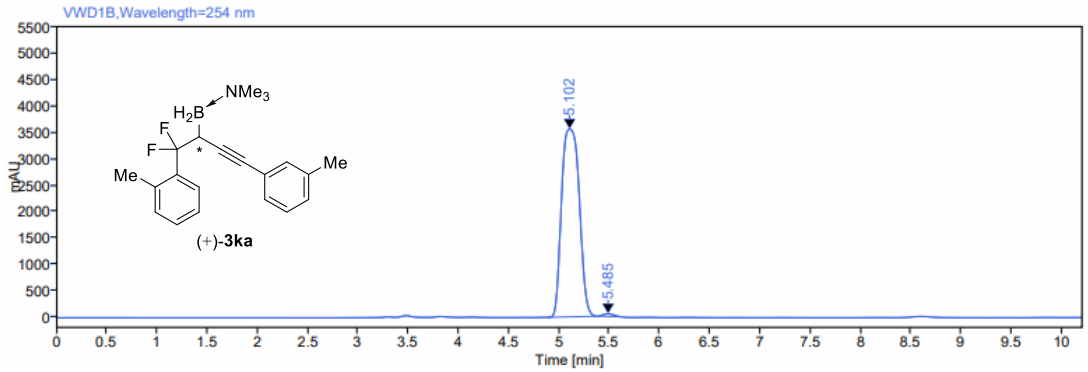


RT [min]	Type	Width [min]	Area	Height	Area%
10.311	BB	0.86	27571.40	1704.96	99.11
11.182	BBA	0.61	247.71	14.64	0.89
		Sum	27819.11		

(+)-Trimethylamine-(1,1-difluoro-4-(*m*-tolyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ka)

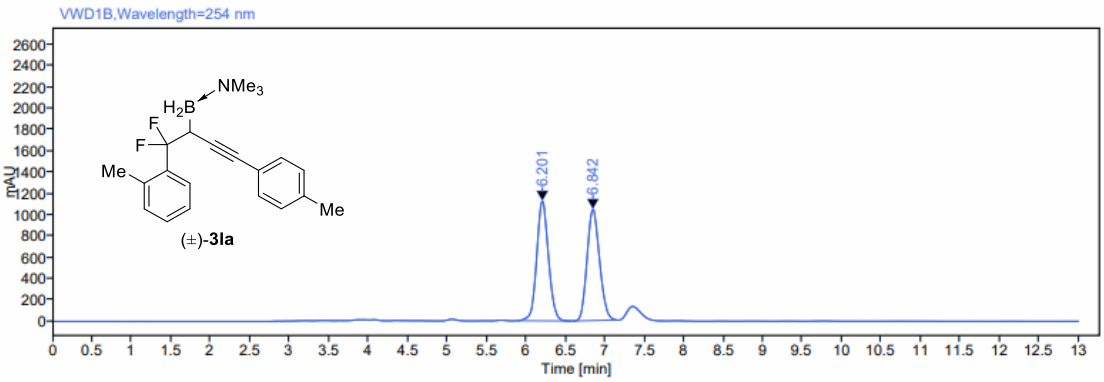


RT [min]	Type	Width [min]	Area	Height	Area%
5.073	VV	0.43	11201.26	1335.33	49.93
5.457	VB	0.48	11233.39	1248.33	50.07
		Sum	22434.64		

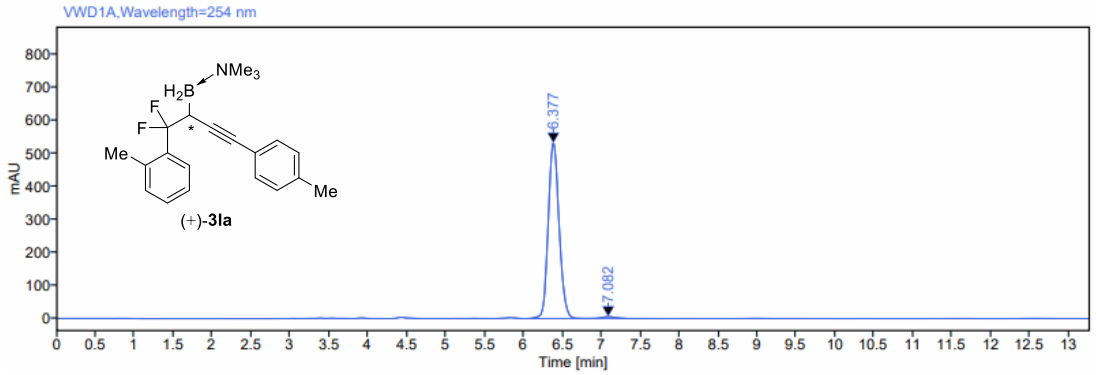


RT [min]	Type	Width [min]	Area	Height	Area%
5.102	BBA	0.49	43533.56	3549.70	99.18
5.485	BBA	0.22	358.80	49.35	0.82
		Sum	43892.36		

(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(*p*-tolyl)but-3-yn-2-yl)borane (3la)

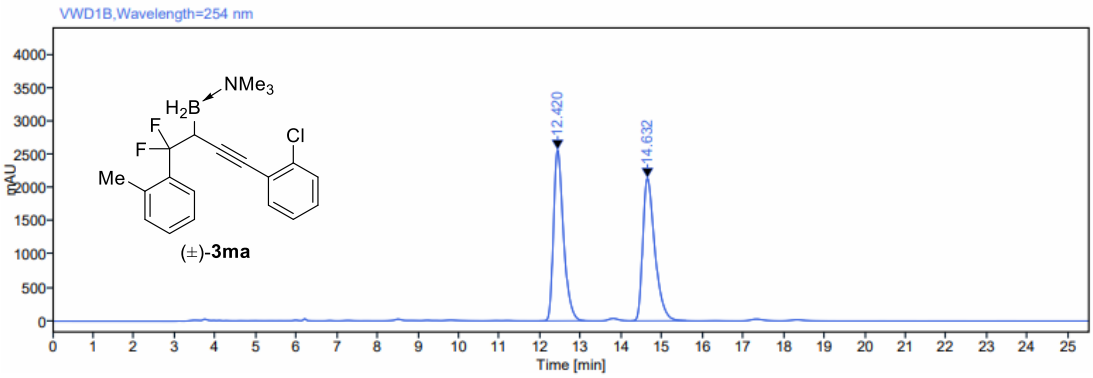


RT [min]	Type	Width [min]	Area	Height	Area%
6.201	BB	0.67	11665.13	1125.30	50.37
6.842	BBA	0.55	11492.75	1046.10	49.63
		Sum	23157.88		

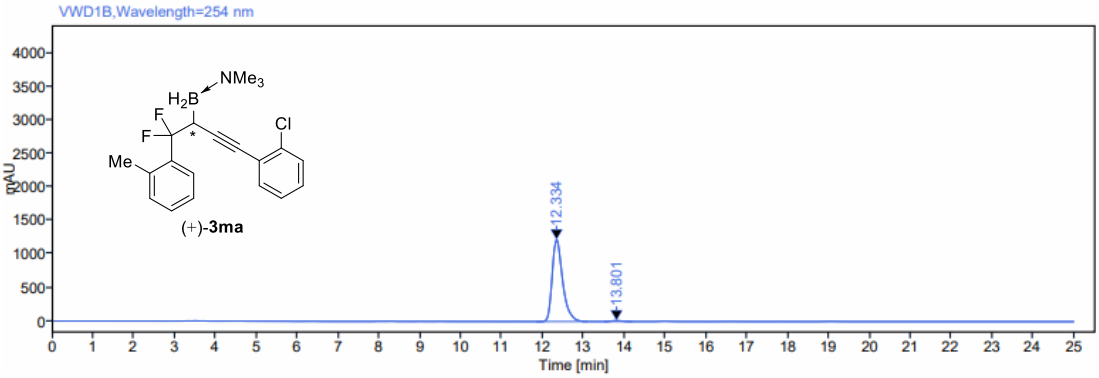


RT [min]	Type	Width [min]	Area	Height	Area%
6.377	BB	0.74	5143.07	531.15	98.96
7.082	BBA	0.38	54.05	5.23	1.04
		Sum	5197.12		

(+)-Trimethylamine-(4-(2-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ma)

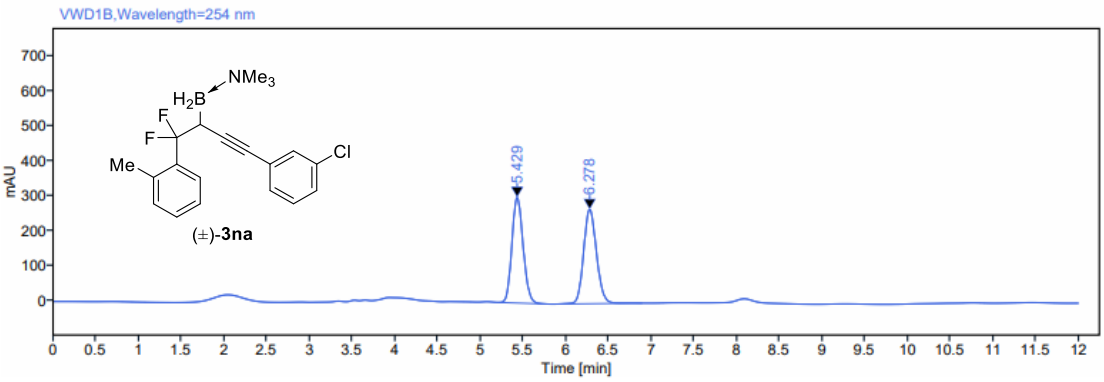


RT [min]	Type	Width [min]	Area	Height	Area%
12.420	BBA	1.12	43927.95	2566.23	49.81
14.632	BBA	1.36	44267.14	2141.89	50.19
		Sum	88195.10		

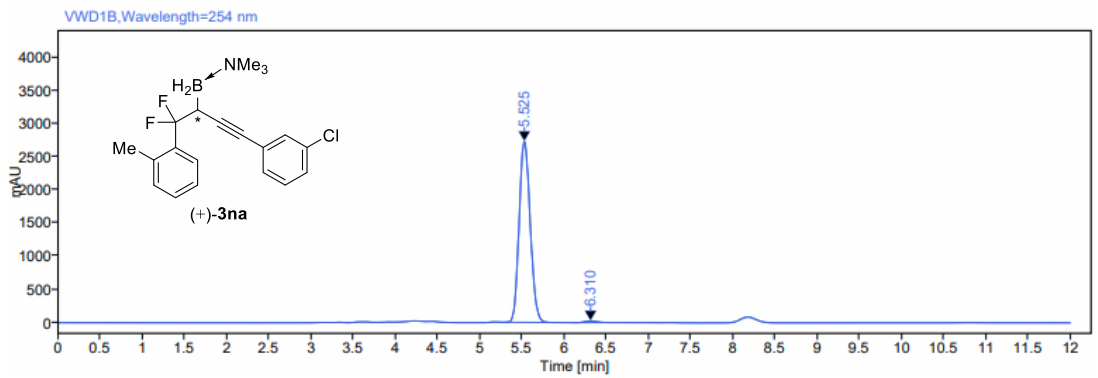


RT [min]	Type	Width [min]	Area	Height	Area%
12.334	BBA	1.25	21653.09	1219.80	98.97
13.801	BBA	0.68	226.12	12.89	1.03
		Sum	21879.21		

(+)-Trimethylamine-(4-(3-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3na)

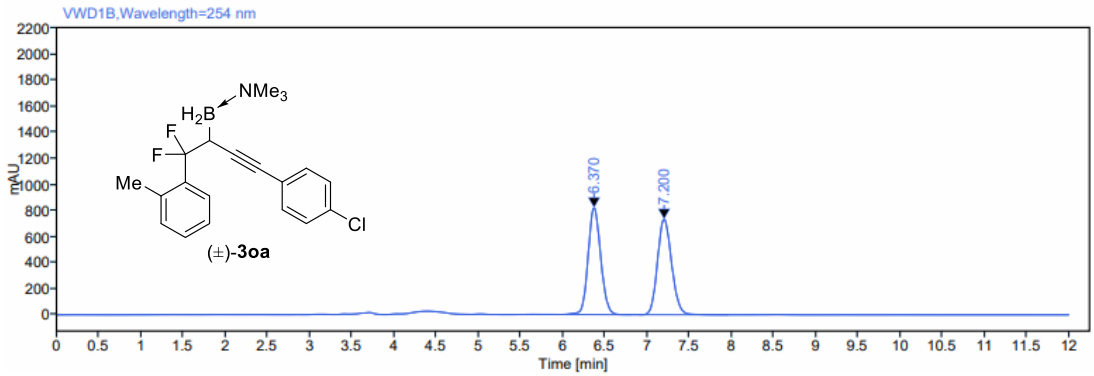


RT [min]	Type	Width [min]	Area	Height	Area%
5.429	BB	0.57	2755.97	301.34	49.35
6.278	BBA	1.03	2828.03	268.91	50.65
		Sum	5584.00		

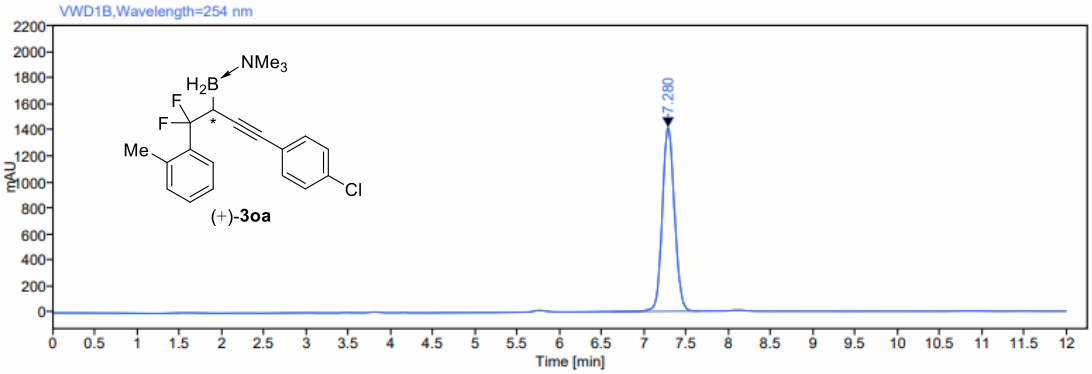


RT [min]	Type	Width [min]	Area	Height	Area%
5.525	BB	0.60	24904.59	2730.83	99.02
6.310	BB	0.44	246.78	25.40	0.98
		Sum	25151.37		

(+)-Trimethylamine-(4-(4-chlorophenyl)-1,1-difluoro-1-(*o*-tolyl)but-3-yn-2-yl)borane (3oa)

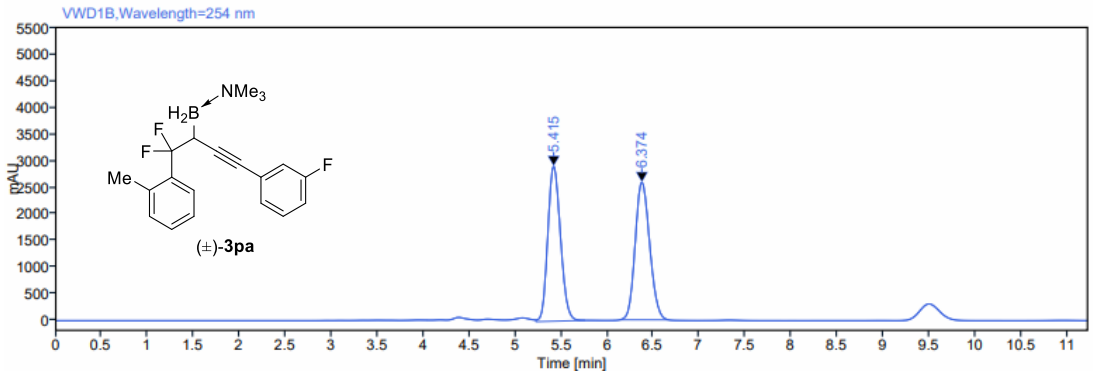


RT [min]	Type	Width [min]	Area	Height	Area%
6.370	BB	0.84	8505.86	819.66	49.91
7.200	BBA	1.06	8535.54	733.86	50.09
		Sum	17041.39		

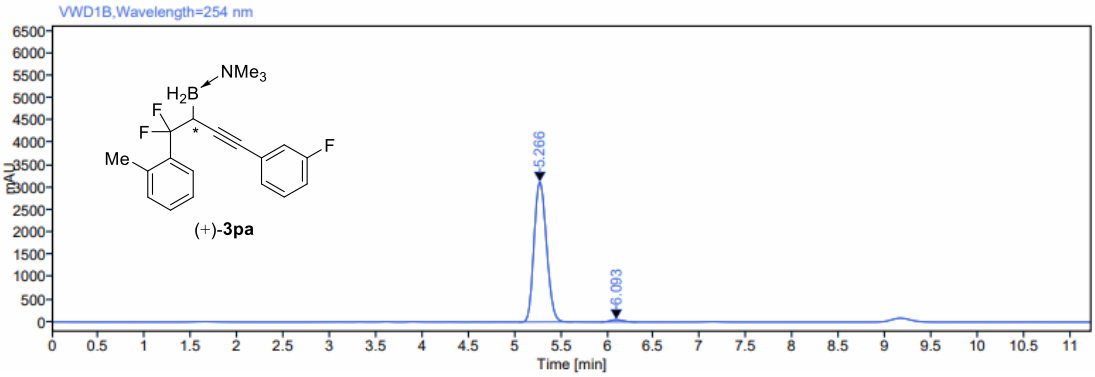


RT [min]	Type	Width [min]	Area	Height	Area%
7.280	VB	1.05	14228.36	1411.19	100.00
		Sum	14228.36		

(+)-Trimethylamine-(1,1-difluoro-4-(3-fluorophenyl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3pa)

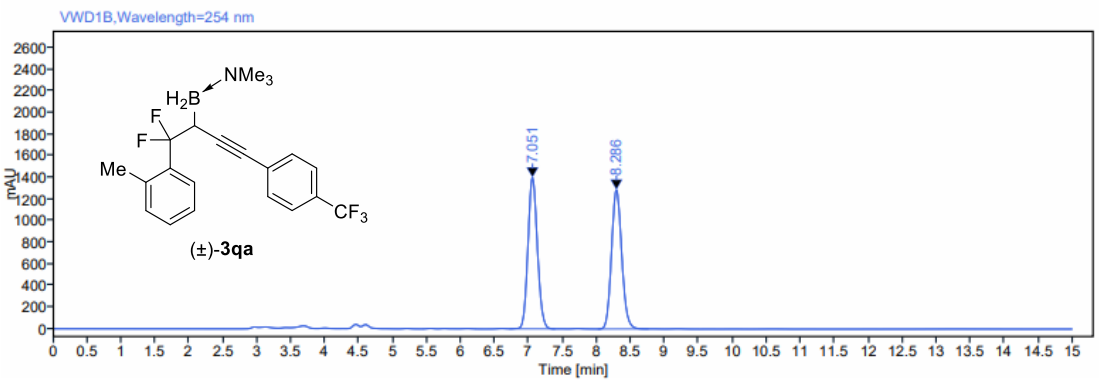


RT [min]	Type	Width [min]	Area	Height	Area%
5.415	MB m	0.15	27904.88	2910.89	49.58
6.374	BBA	0.53	28376.99	2583.50	50.42
		Sum	56281.87		

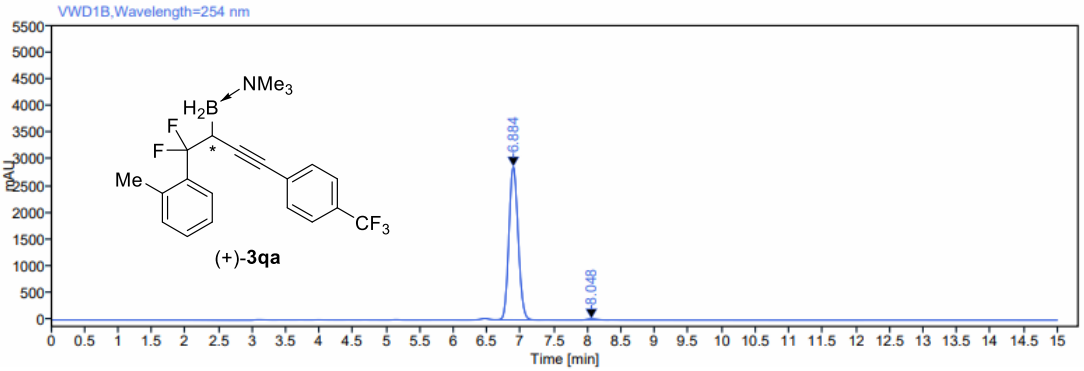


RT [min]	Type	Width [min]	Area	Height	Area%
5.266	BBA	0.58	29311.52	3120.41	98.33
6.093	BBA	0.39	498.65	51.61	1.67
		Sum	29810.17		

(+)-Trimethylamine-(1,1-difluoro-1-(*o*-tolyl)-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)borane (3qa)

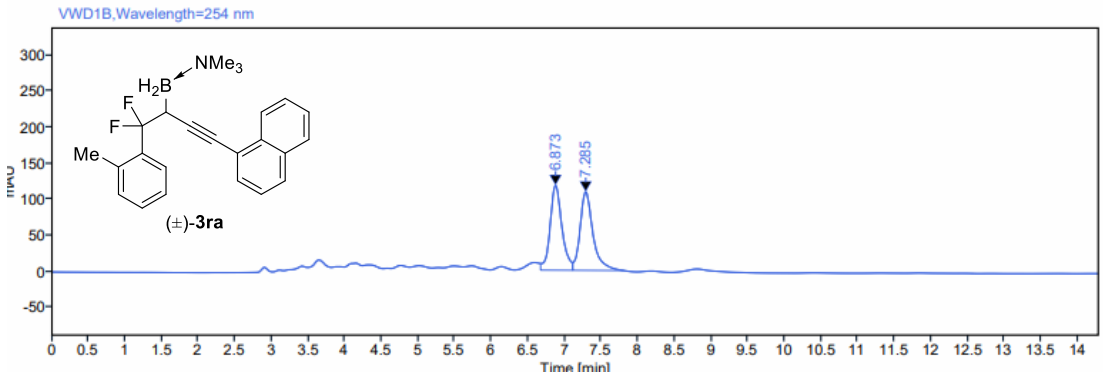


RT [min]	Type	Width [min]	Area	Height	Area%
7.051	BB	0.67	13517.74	1398.00	50.05
8.286	BB	0.75	13491.62	1286.21	49.95
		Sum	27009.35		

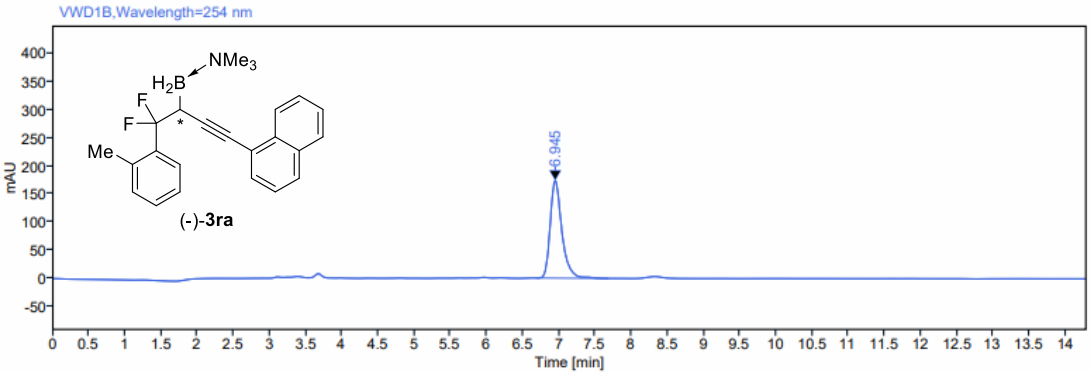


RT [min]	Type	Width [min]	Area	Height	Area%
6.884	BB	0.67	27378.80	2857.51	99.36
8.048	BBA	0.41	177.66	18.39	0.64
		Sum	27556.46		

(-)-Trimethylamine-(1,1-difluoro-4-(naphthalen-1-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3ra)

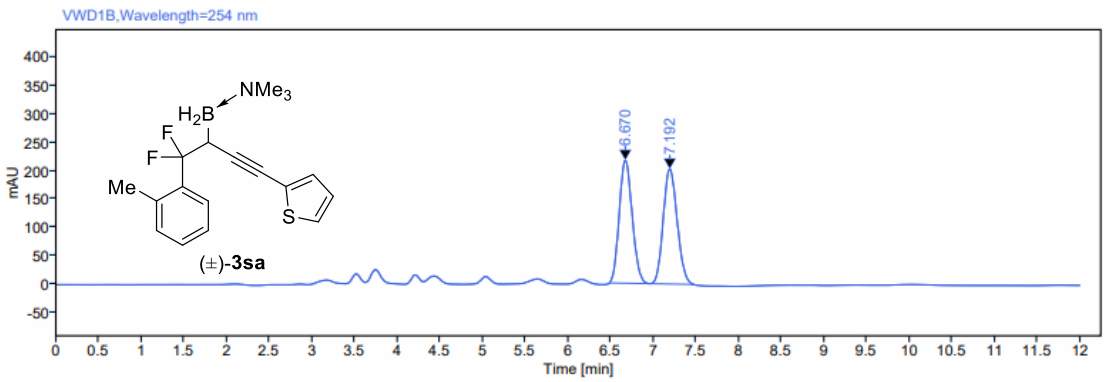


RT [min]	Type	Width [min]	Area	Height	Area%
6.873	MM m	0.17	1323.35	117.59	49.71
7.285	MB m	0.18	1338.76	108.83	50.29
		Sum	2662.11		

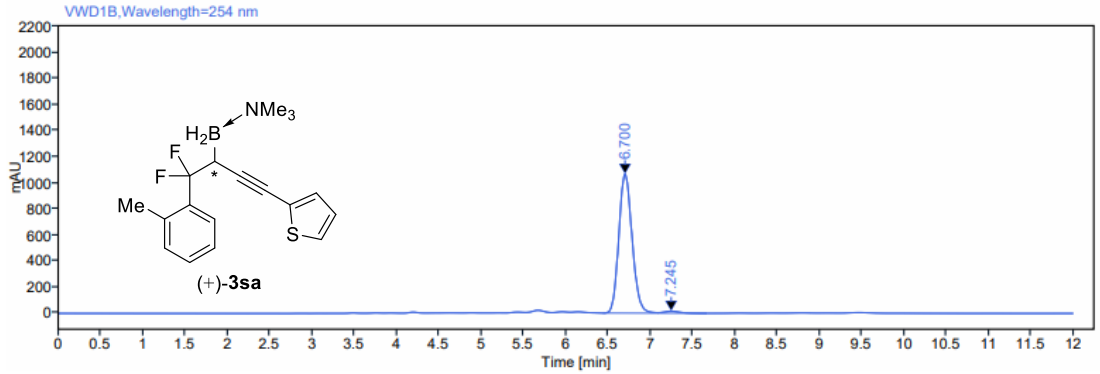


RT [min]	Type	Width [min]	Area	Height	Area%
6.945	BBA	1.00	1947.51	172.77	100.00
		Sum	1947.51		

(+)-Trimethylamine-(1,1-difluoro-4-(thiophen-2-yl)-1-(*o*-tolyl)but-3-yn-2-yl)borane (3sa)

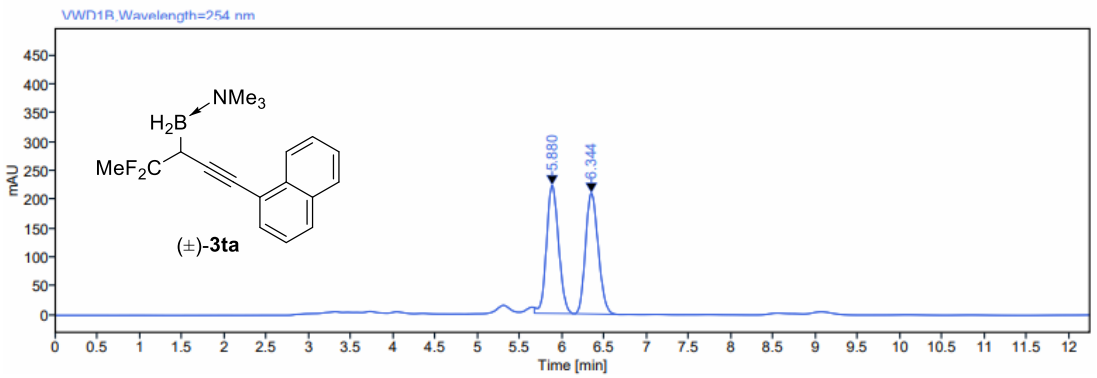


RT [min]	Type	Width [min]	Area	Height	Area%
6.670	BB	0.47	2278.90	215.97	49.85
7.192	BBA	0.51	2292.78	201.99	50.15
		Sum	4571.68		

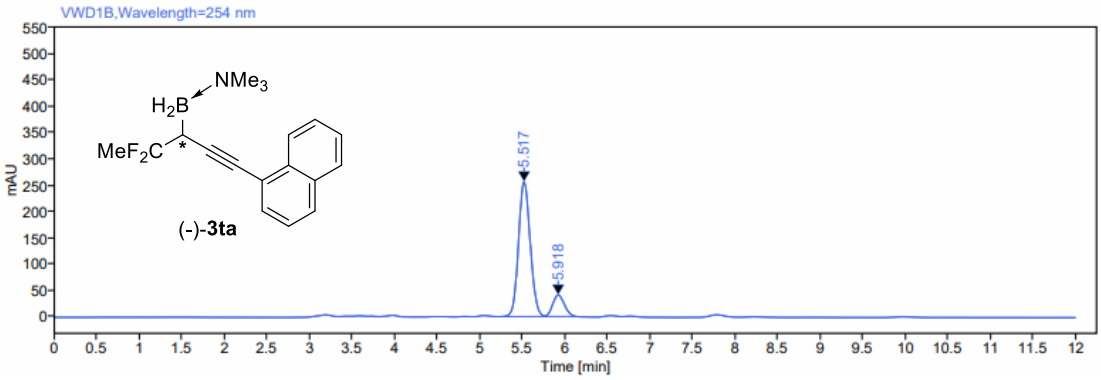


RT [min]	Type	Width [min]	Area	Height	Area%
6.700	BV	0.65	11661.58	1067.06	98.30
7.245	VB	0.58	202.02	15.91	1.70
		Sum	11863.60		

(-)-Trimethylamine-(4,4-difluoro-1-(naphthalen-1-yl)pent-1-yn-3-yl) borane (3ta)

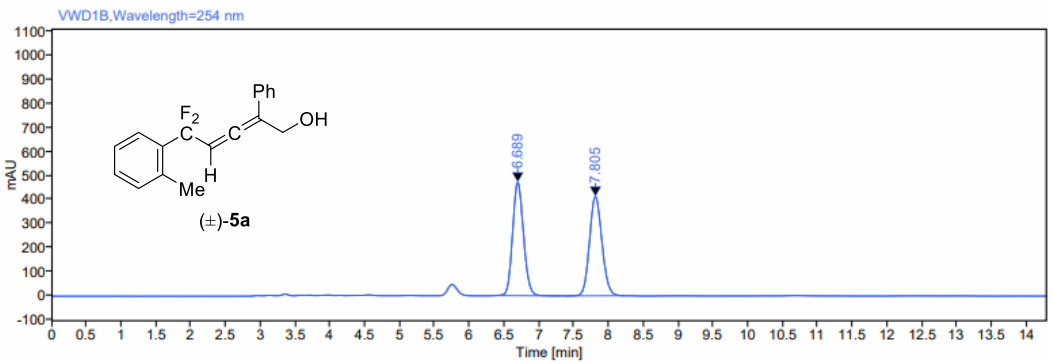


RT [min]	Type	Width [min]	Area	Height	Area%
5.880	MB m	0.16	2211.73	221.76	50.19
6.344	BBA	0.51	2195.18	209.39	49.81
		Sum	4406.92		

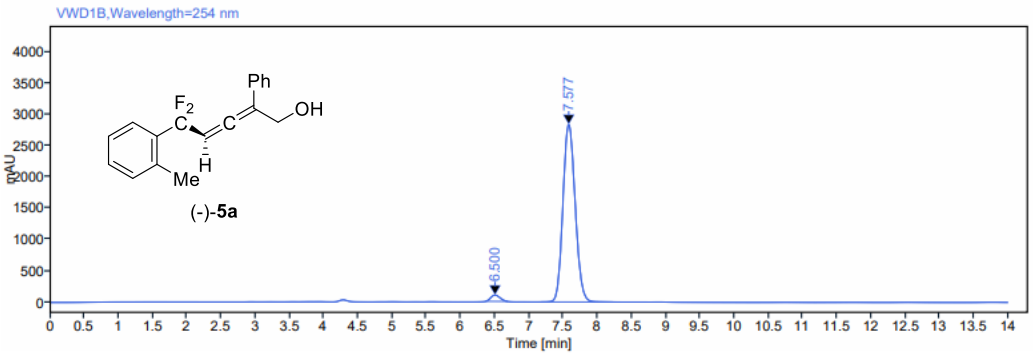


RT [min]	Type	Width [min]	Area	Height	Area%
5.517	BV	0.52	2455.30	256.16	86.34
5.918	VBA	0.37	388.59	40.79	13.66
		Sum	2843.90		

(-)-(*S*)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5a)

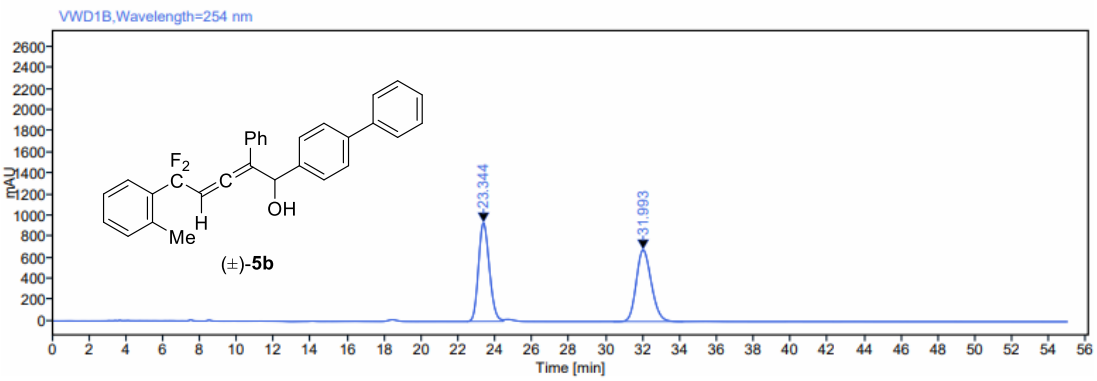


RT [min]	Type	Width [min]	Area	Height	Area%
6.689	BB	0.95	5129.04	470.22	50.08
7.805	BBA	0.87	5113.37	411.88	49.92
		Sum	10242.41		

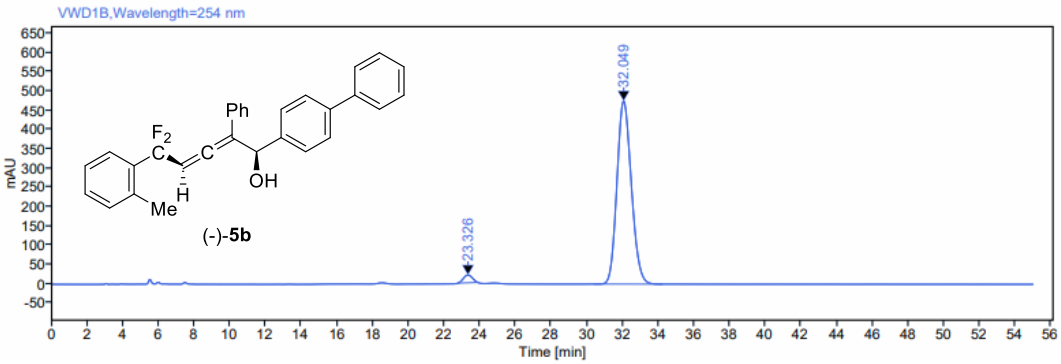


RT [min]	Type	Width [min]	Area	Height	Area%
6.500	BBA	0.32	946.34	100.92	2.60
7.577	BBA	1.05	35422.93	2838.73	97.40
		Sum	36369.27		

(-)-(1*R*,3*S*)-1-([1,1'-biphenyl]-4-yl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5b)

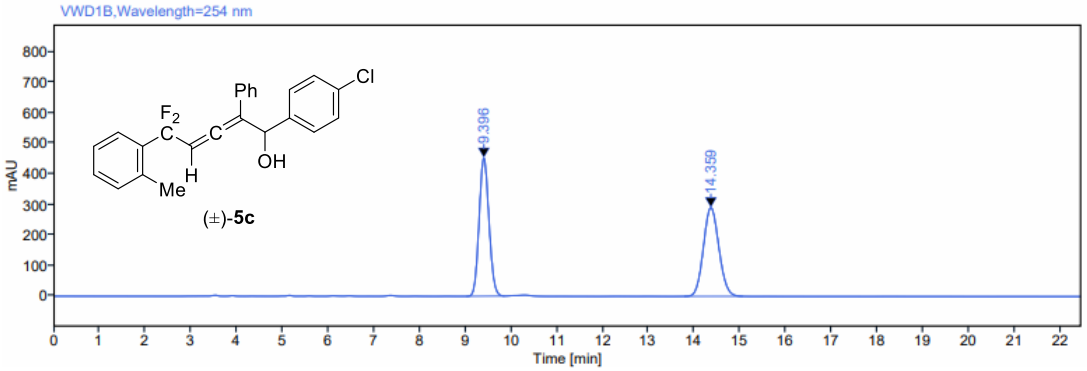


RT [min]	Type	Width [min]	Area	Height	Area%
23.344	BM m	0.64	38436.16	935.54	49.95
31.993	BB	3.79	38513.62	680.62	50.05
		Sum	76949.77		

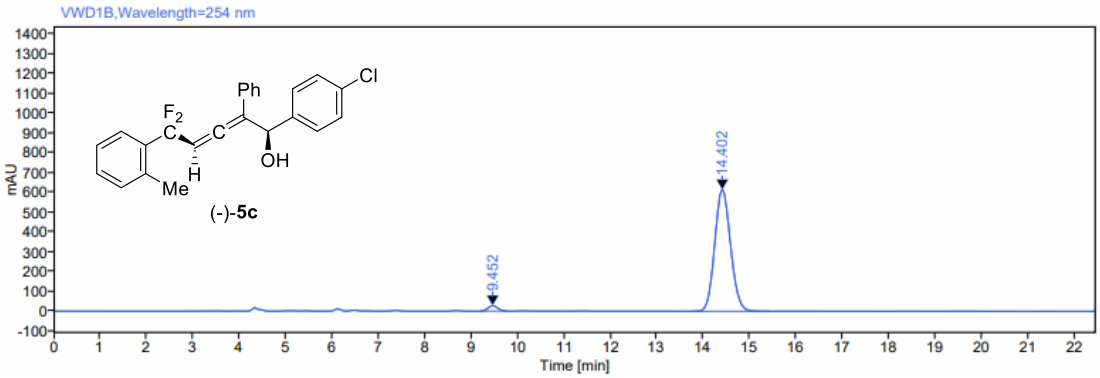


RT [min]	Type	Width [min]	Area	Height	Area%
23.326	BBA	1.11	698.50	20.14	2.55
32.049	BBA	3.85	26652.41	475.15	97.45
		Sum	27350.91		

(-)-(1*R*,3*S*)-1-(4-chlorophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5c)

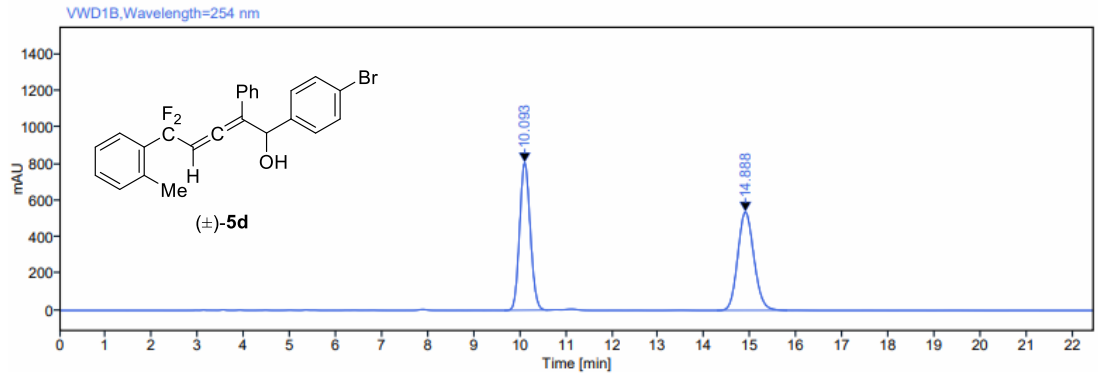


RT [min]	Type	Width [min]	Area	Height	Area%
9.396	BBA	0.83	6795.10	452.60	49.82
14.359	BBA	1.28	6844.58	290.57	50.18
		Sum	13639.69		

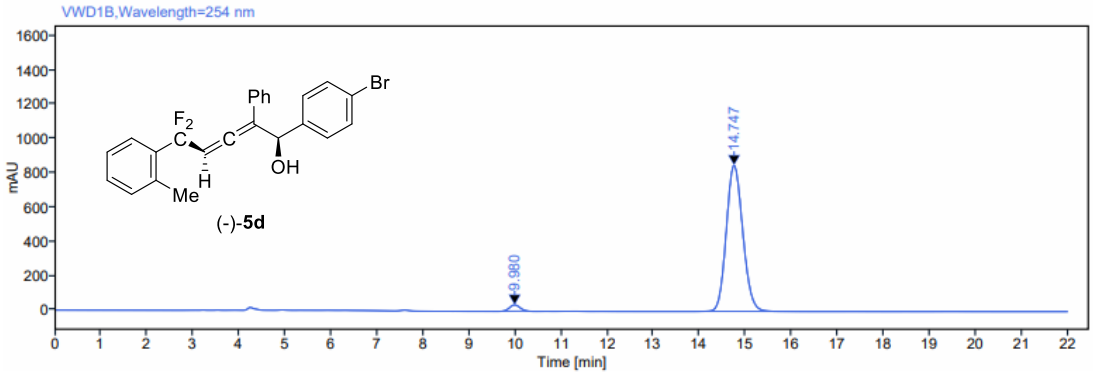


RT [min]	Type	Width [min]	Area	Height	Area%
9.452	BBA	0.57	394.85	26.99	2.63
14.402	BBA	1.69	14590.71	614.21	97.37
		Sum	14985.56		

(-)-(1*R*,3*S*)-1-(4-bromophenyl)-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5d)

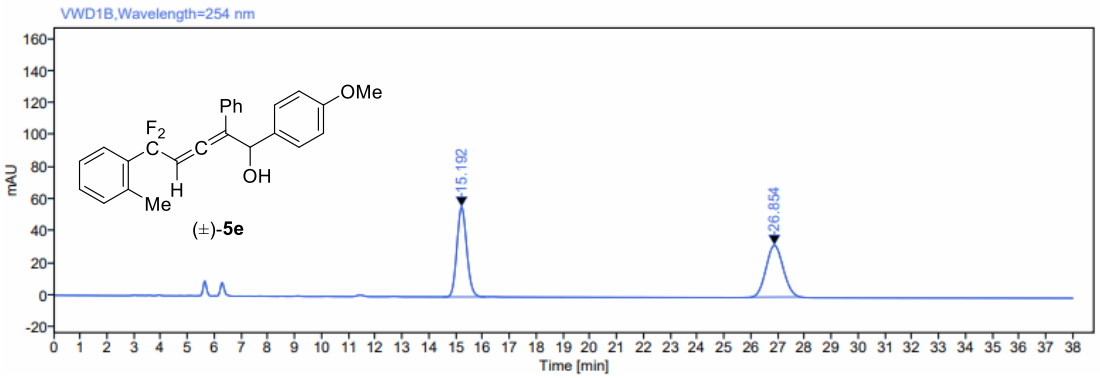


RT [min]	Type	Width [min]	Area	Height	Area%
10.093	BB	0.95	13004.32	805.40	49.72
14.888	BBA	1.53	13152.18	537.09	50.28
		Sum	26156.50		

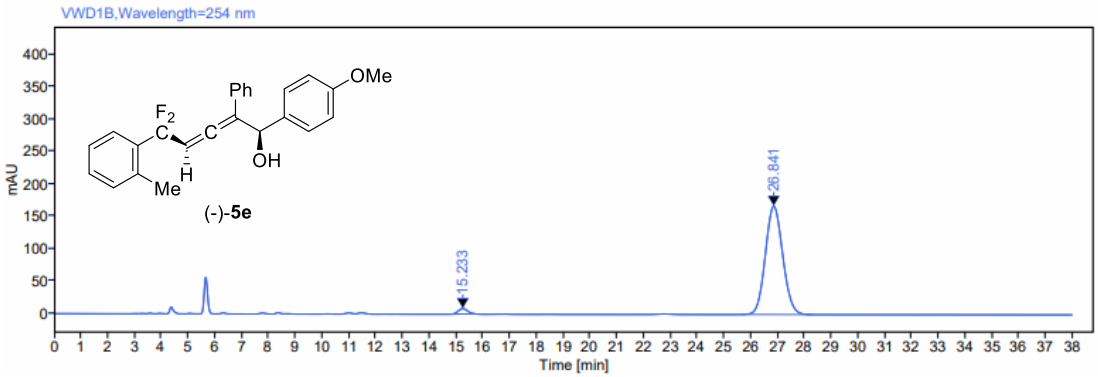


RT [min]	Type	Width [min]	Area	Height	Area%
9.980	BBA	0.57	564.01	36.23	2.59
14.747	BBA	1.57	21217.57	852.05	97.41
		Sum	21781.59		

(-)-(1*R*,3*S*)-5,5-difluoro-1-(4-methoxyphenyl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5e)

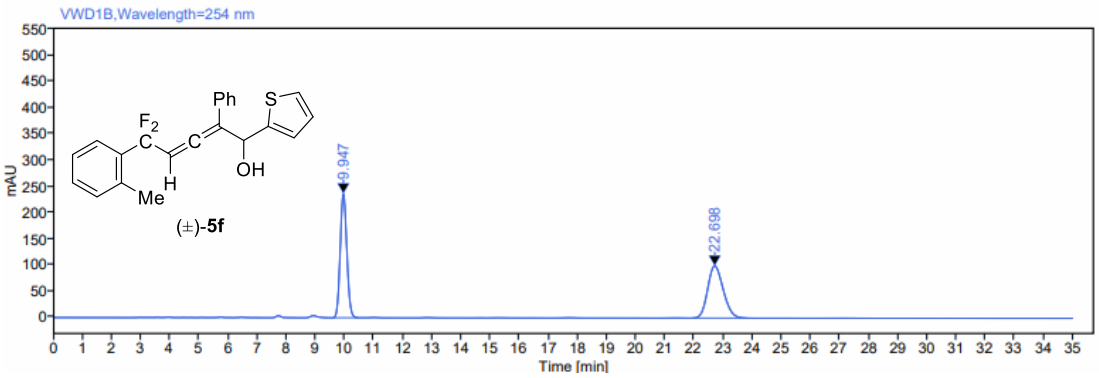


RT [min]	Type	Width [min]	Area	Height	Area%
15.192	BB	1.57	1435.43	56.13	49.98
26.854	BBA	1.85	1436.75	32.31	50.02
		Sum	2872.18		

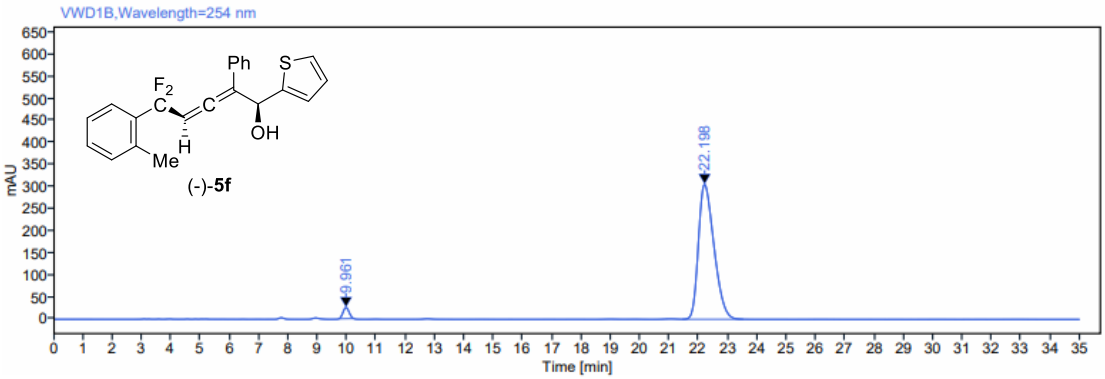


RT [min]	Type	Width [min]	Area	Height	Area%
15.233	BBA	0.87	196.45	8.28	2.54
26.841	BBA	2.64	7529.74	167.21	97.46
		Sum	7726.19		

(-)-(1*S*,3*S*)-5,5-difluoro-2-phenyl-1-(thiophen-2-yl)-5-(*o*-tolyl)penta-2,3-dien-1-ol (5f)

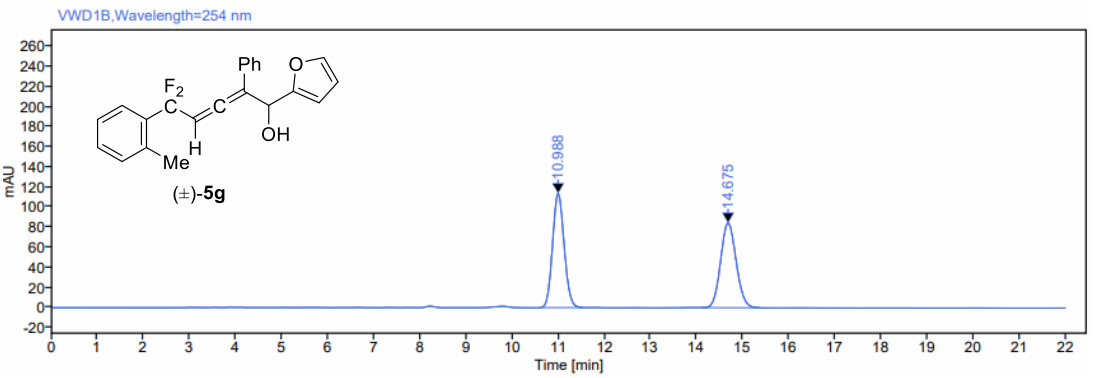


RT [min]	Type	Width [min]	Area	Height	Area%
9.947	BBA	0.85	3723.94	236.63	50.27
22.698	BBA	1.87	3683.75	99.49	49.73
		Sum	7407.68		

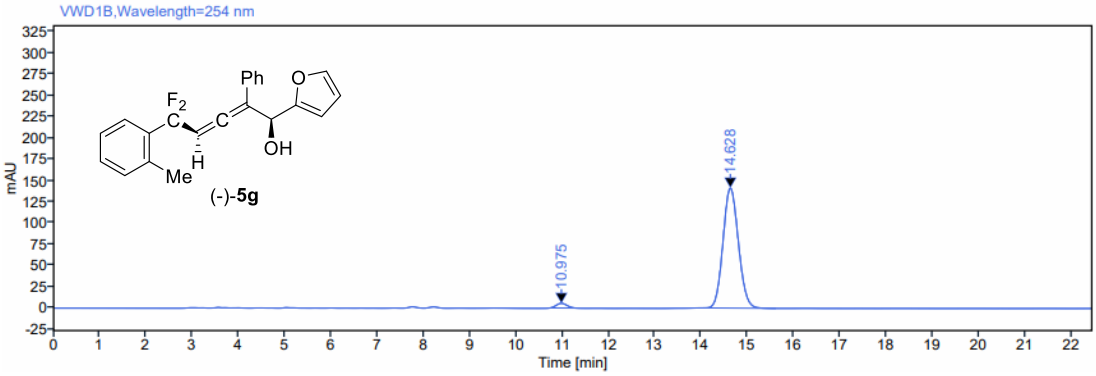


RT [min]	Type	Width [min]	Area	Height	Area%
9.961	BBA	0.51	364.43	25.31	3.13
22.198	BBA	2.07	11280.52	305.52	96.87
		Sum	11644.94		

(-)-(1*S*,3*S*)-5,5-difluoro-1-(furan-2-yl)-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5g)

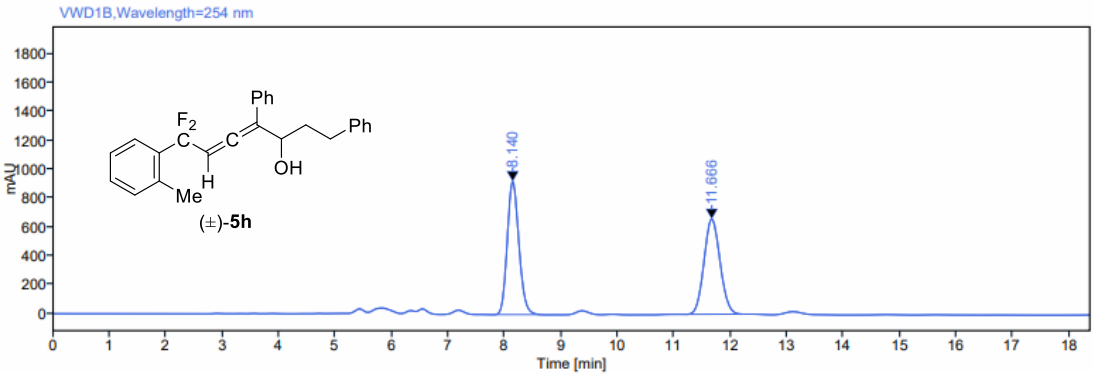


RT [min]	Type	Width [min]	Area	Height	Area%
10.988	BBA	0.92	1985.67	113.65	50.17
14.675	BBA	1.25	1972.03	84.39	49.83
		Sum	3957.70		

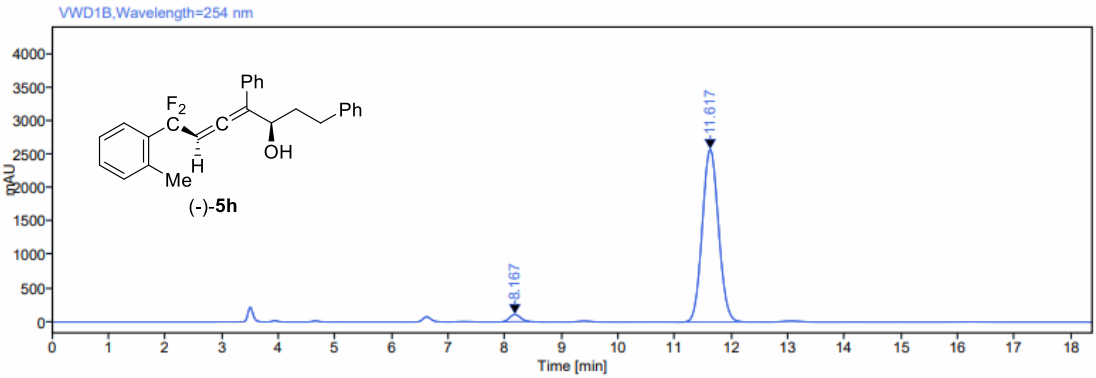


RT [min]	Type	Width [min]	Area	Height	Area%
10.975	BBA	0.56	87.49	5.49	2.61
14.628	BBA	1.57	3266.12	141.13	97.39
		Sum	3353.60		

(-)-(3*R*,5*S*)-7,7-difluoro-1,4-diphenyl-7-(*o*-tolyl)hepta-4,5-dien-3-ol (5h)

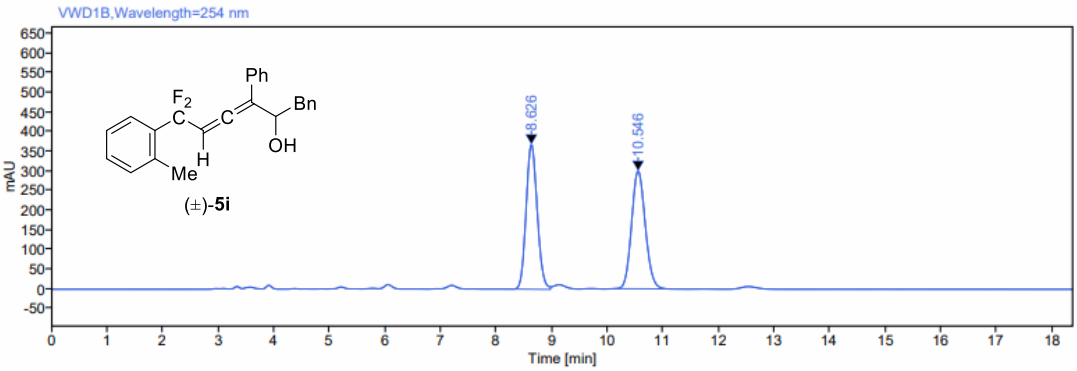


RT [min]	Type	Width [min]	Area	Height	Area%
8.140	BBA	0.79	13236.91	921.81	50.37
11.666	BBA	1.01	13042.38	658.58	49.63
		Sum	26279.29		

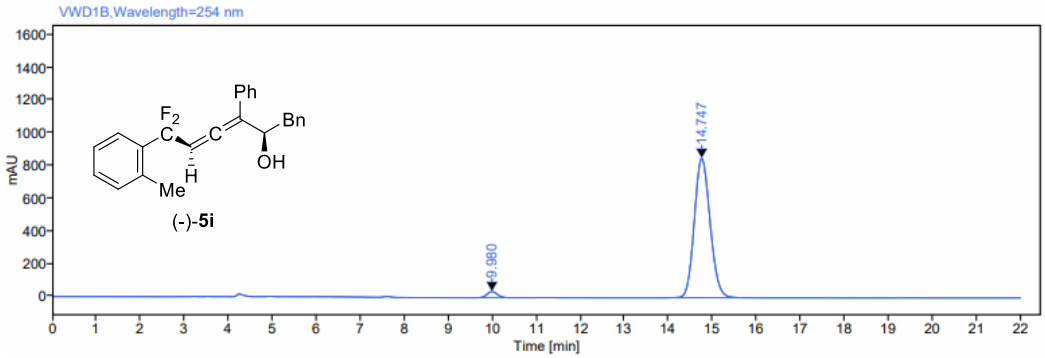


RT [min]	Type	Width [min]	Area	Height	Area%
8.167	BBA	0.51	1419.24	106.82	2.68
11.617	BBA	1.29	51573.75	2577.77	97.32
		Sum	52992.99		

(-)-(2*R*,4*S*)-6,6-difluoro-1,3-diphenyl-6-(*o*-tolyl)hexa-3,4-dien-2-ol (5i)

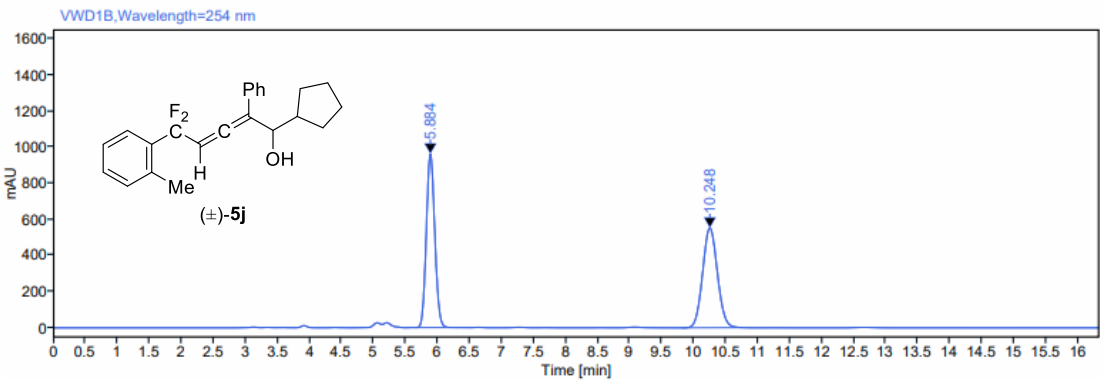


RT [min]	Type	Width [min]	Area	Height	Area%
8.626	BM m	0.22	5113.66	368.14	49.91
10.546	BBA	0.96	5133.08	299.73	50.09
		Sum	10246.74		

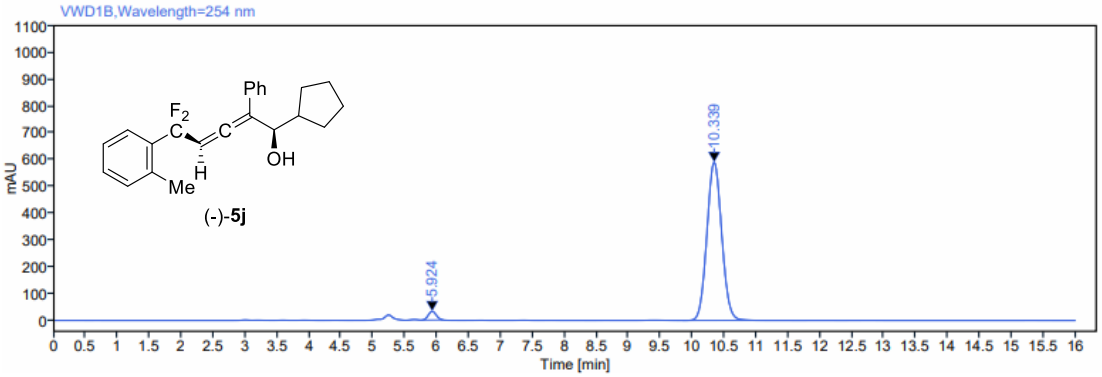


RT [min]	Type	Width [min]	Area	Height	Area%
9.980	BBA	0.57	564.01	36.23	2.59
14.747	BBA	1.57	21217.57	852.05	97.41
		Sum	21781.59		

(-)-(1*R*,3*S*)-1-cyclopentyl-5,5-difluoro-2-phenyl-5-(*o*-tolyl)penta-2,3-dien-1-ol (5j)

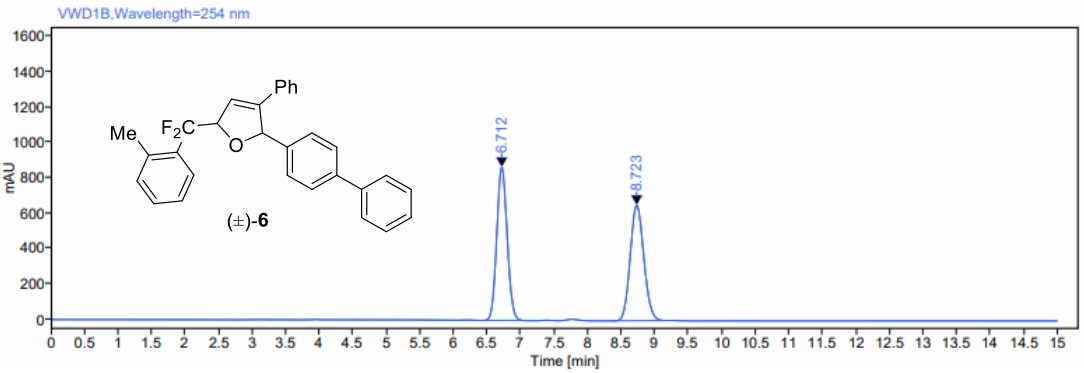


RT [min]	Type	Width [min]	Area	Height	Area%
5.884	BBA	0.67	8830.35	963.30	49.84
10.248	BBA	0.95	8886.85	553.62	50.16
		Sum	17717.19		

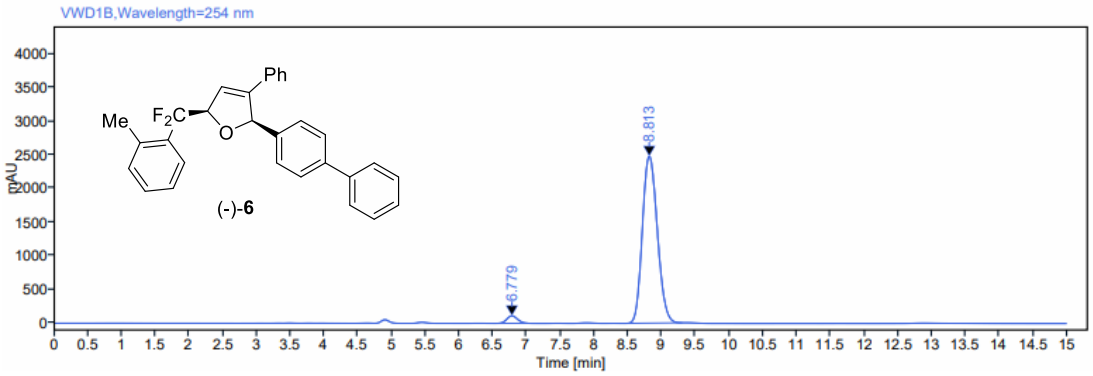


RT [min]	Type	Width [min]	Area	Height	Area%
5.924	BBA	0.33	280.47	32.18	2.86
10.339	BBA	1.17	9539.85	590.60	97.14
		Sum	9820.32		

(-)-(2*R*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyl-2,5-dihydrofuran (6)

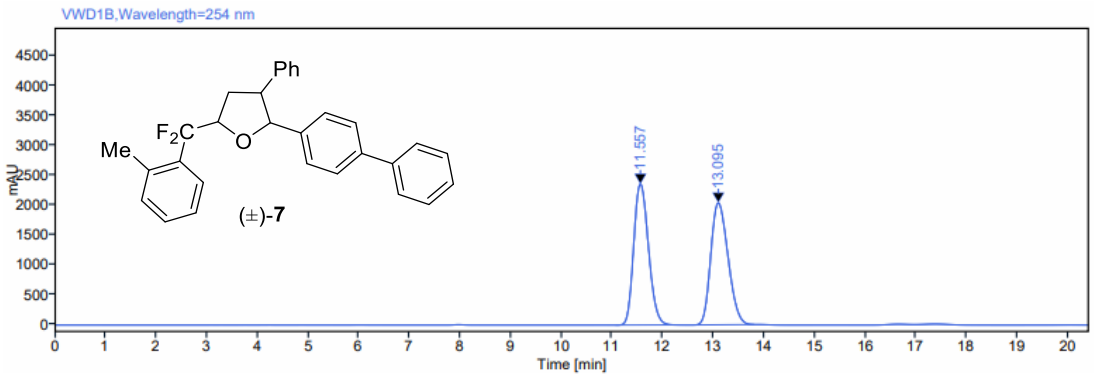


RT [min]	Type	Width [min]	Area	Height	Area%
6.712	BBA	0.57	9339.22	864.98	50.28
8.723	BV	0.80	9234.14	652.65	49.72
		Sum	18573.36		

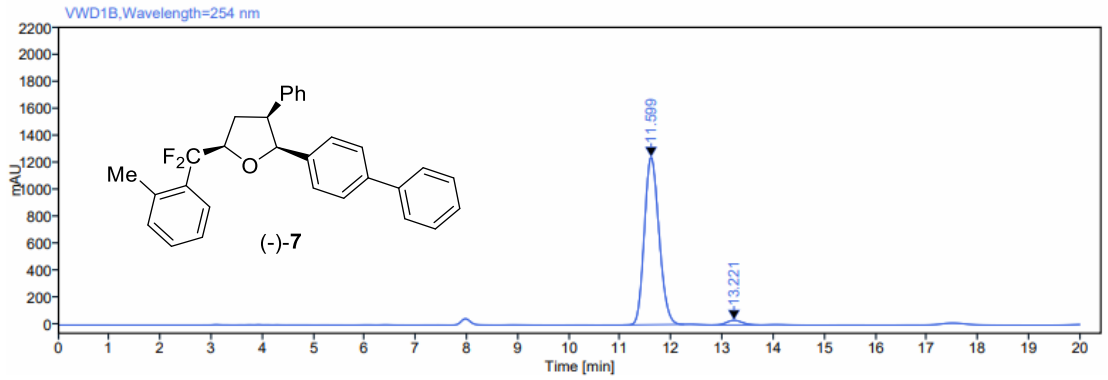


RT [min]	Type	Width [min]	Area	Height	Area%
6.779	BBA	0.45	1212.62	110.87	3.07
8.813	BB	0.85	38250.31	2480.41	96.93
		Sum	39462.93		

(-)-(2*S*,3*S*,5*R*)-2-([1,1'-biphenyl]-4-yl)-5-(difluoro(*o*-tolyl)methyl)-3-phenyltetrahydrofuran (7)



RT [min]	Type	Width [min]	Area	Height	Area%
11.557	BBA	1.17	47741.55	2353.87	49.71
13.095	BBA	1.16	48308.04	2035.45	50.29
		Sum	96049.59		



RT [min]	Type	Width [min]	Area	Height	Area%
11.599	BB	1.19	24807.84	1237.81	97.13
13.221	BBA	0.90	733.80	34.55	2.87
		Sum	25541.64		

14. ECD Graph Computation

The theoretical ECD graph was computed by the following method.

1. Draw one conformer of the molecule.
2. Run molecular dynamics with GFN0-xTB[4] method using xTB[5] software under temperature 400 K and total simulation time 100 ps. Save molecular structure to a file every 50 fs.
3. Optimize the structures generated by molecular dynamics using crest[6] software. The conformers were optimized by GFN0-xTB method using xTB at 298.15 K.
4. Remove duplicated optimized structures using Molclus[7] software with energy threshold 0.5 kcal/mol and distance threshold 0.5 angstroms, and save the conformers.
5. Run DFT calculations for the conformers. The optimization and frequency calculations were carried out with the restricted PBE0[8] functional with D3BJ[9] dispersion correction and def2-SVP[10] basis set involving the solvation effect of chloroform using the SMD solvent model[11] in Gaussian 16[12] under 298.15 K. The duplicated structures were removed again after DFT optimizations.
6. Run TDDFT calculation and retrieve the ECD graph. The TDDFT calculations were carried out under the same theory level with the optimization. The 30 lowest energy excited states were calculated for each different conformer. The ECD graph for each conformer were generated by GaussView[13] and exported to a text file.
7. Retrieve the final ECD graph. The final graph was calculated by the weighted average of graphs for each conformer. The weight was calculated by Boltzmann distribution with the Gibbs energy value from frequency calculations. The graph was generated by matplotlib[14] in python.

The optimized structures can be found in the supporting information as an xyz file.

15. References

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