Deaminative defluoroalkylation of α-trifluoromethyl alkenes enabled by photoredox catalysis

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1.General Information

Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on an Agilent DD2 400 MHz or Bruker 600 MHz spectrometers. The chemical shifts in ^{1}H NMR spectra were recorded relative to $CDCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.0). High-resolution mass spectrometry (HRMS) data were conducted at Bruker Dalton MAXIS. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography as performed over silica gel (200-300 mesh). Blue LED (40 W, λmax = 450-465 nm) purchased from GeAo chemical was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature (about 30℃).

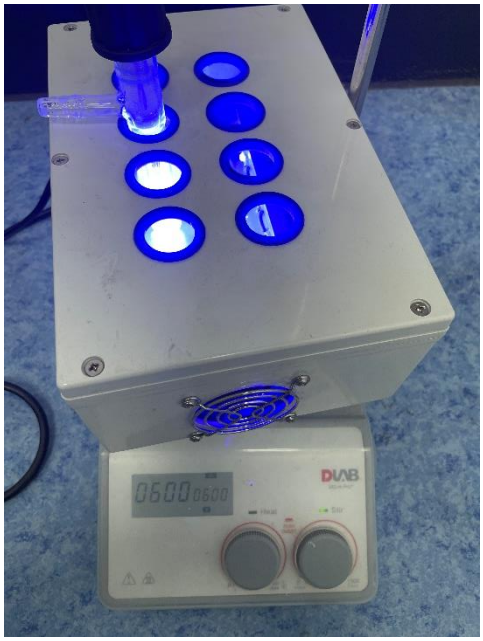


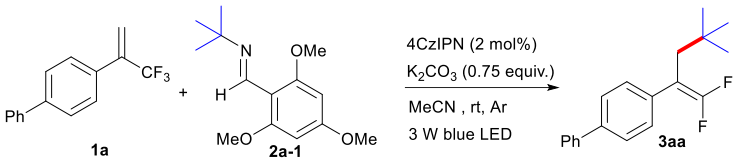
Figure S1 Photograph of the photocatalytic reactor used for reactions conducted under blue LED irradiation.

Preparation of Starting Materials.

α-Trifluoromethyl alkenes were synthesized according to literature.[1, 2, 3] Imines were synthesized according to literature report.[4, 5] The spectral data of the photocatalyst is consistent with the literature data.

Mechanistic Studies

Light/dark experiment



Six 10 mL schlenk tubes were charged with 4 CzIPN (1.6 mg, 0.002 mmol, 2 mol %), **1a** (25.0 mg 0.1 mmol, 1.0 equiv.), **2a-1** (30.0 mg, 0.12 mmol, 1.2 equiv.), K_2CO_3 (10.35 mg, 0.075 mmol), MeCN (1 mL), rt, Ar atmosphere. The mixtures were then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature. After 30 min, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining four vials were stirred in the absence of light for an additional 30 min. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 1 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 1 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining two reaction mixtures. After 1 h, the Blue LED was turned off, and one vial was removed for analysis. The last vials were stirred in the absence of light for an additional 1h, and then it was analyzed. The yield was determined by GC spectroscopy using tetradecane as an internal standard.

Time/h	0.5	1	2	3	4	5
Yield/%	19	18	46	47	62	62

Fluorescence quenching experiments

Emission intensities were recorded using an F-4600 FL Spectrophotometer. First, the emission intensity of 4CzIPN solutions was observed at 550 nm. The solutions were irradiated at 378 nm (Maximum absorption wavelength of 4CzIPN) and fluorescence was measured from 390 nm to 800 nm.

In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of 4CzIPN with different concentrations of **1a**, and **2a-1** in degassed anhydrous CH_3CN in 10 mm path length quartz cuvette was collected.

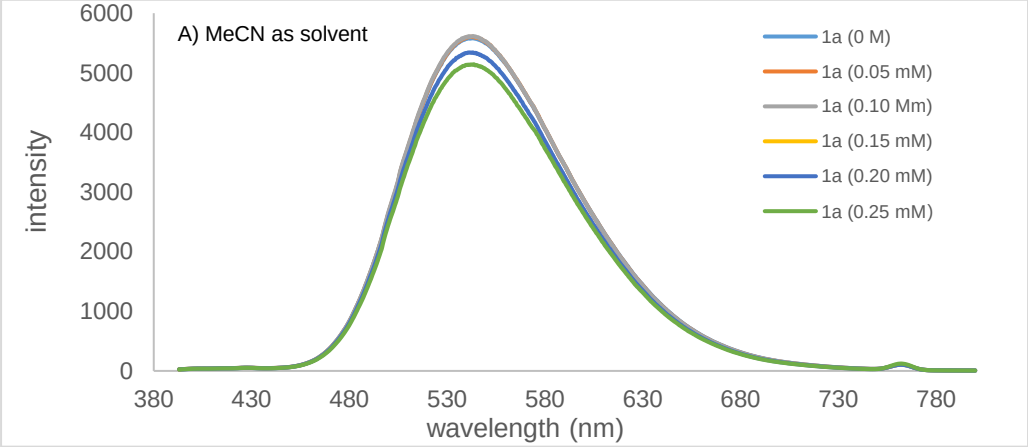


Figure S2 The emission spectra of $5 \times 10_{-5}$ M solutions of 4CzIPN with different concentrations of **1a** in degassed anhydrous CH_3CN.

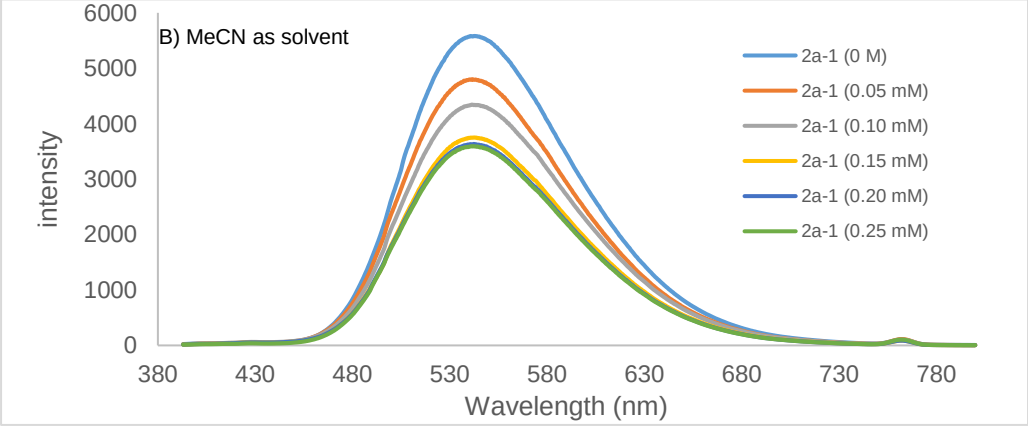


Figure S3 The emission spectra of 5×10^{-5} M solutions of 4CzIPN with different concentrations of **2a-1** in degassed anhydrous CH_3CN.

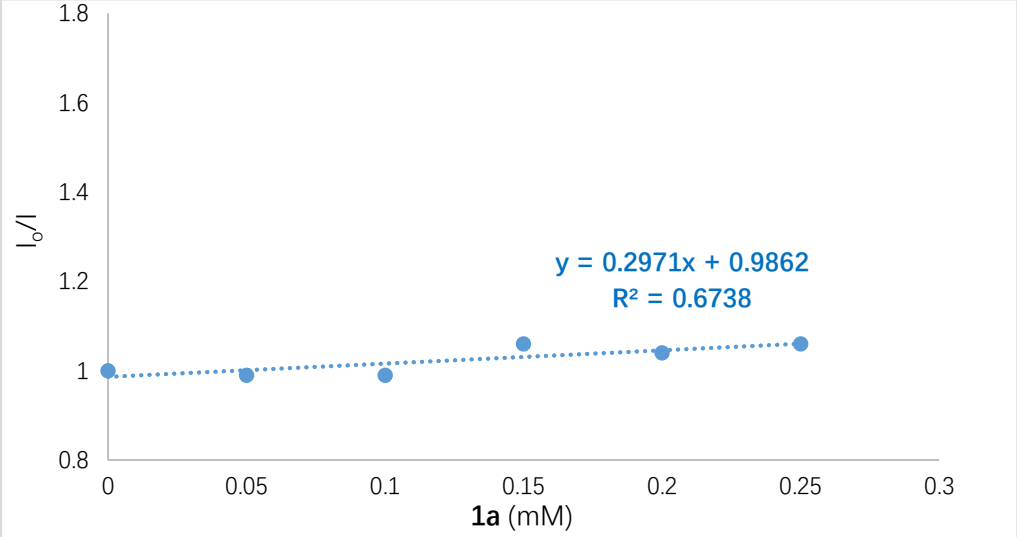


Figure S4 The linear relationship between I_0/I and the increasing concentration of **1a**.

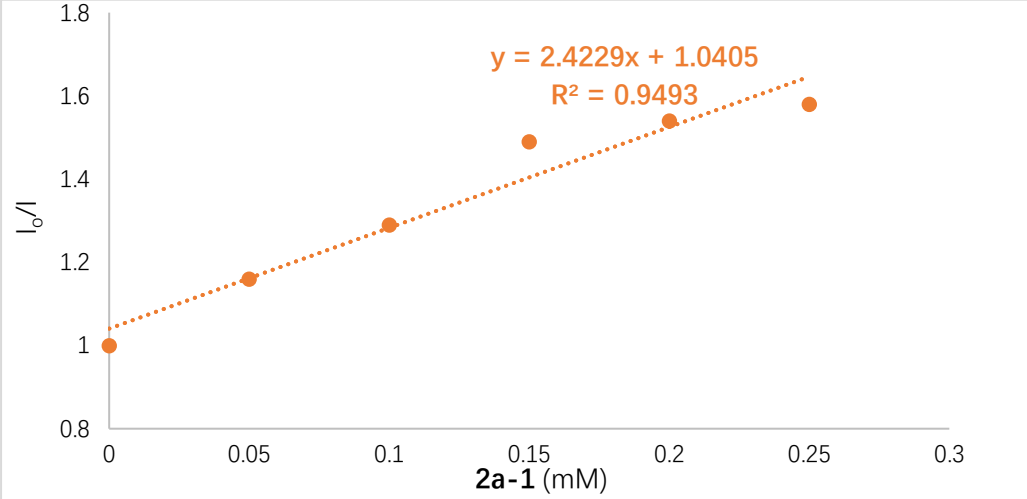


Figure S5 The linear relationship between I_0/I and the increasing concentration of **2a-1**.

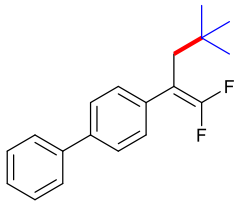
Synthesis and Characterization of the Corresponding Products

General Procedure for the deaminative defluoroallylation.

Two 10 mL glass vial was charged 4 CzIPN (1.6 mg, 0.002 mmol, 2 mol %), **1** (0.1 mmol), **2** (0.12 mmol, 1.2 equiv.), K_2CO_3 (10.5 mg, 0.075 mmol), MeCN (1 mL), rt, Ar atmosphere. The mixture was then stirred rapidly and irradiated with a 3 W Blue LED (approximately 1-2 cm away from the light source) at room temperature for 24 h. After the reactions were complete, these two mixtures were combined, brine (10 mL) was added and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography to yield the corresponding product.

Characterisation of products

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3aa）



According to the *general procedure*.

Yellow oil (52 mg, 90%).

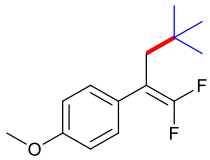
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 14.1, 8.1 Hz, 4H), 7.40 (ddt, *J* = 23.3, 14.7, 7.4 Hz, 5H), 2.39 (s, 2H), 0.85 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.5 (dd, J_{CF} = 288.4, 291.4 Hz), 140.5, 139.7, 134.5 (dd, J_{CF} = 3.0, 4.5 Hz), 128.8 (t, J_{CF} = 3.0 Hz), 128.8, 127.3, 127.0, 126.9, 90.8 (dd, J_{CF} = 12.1, 21.9 Hz), 41.00, 32.8 (t, J_{CF} = 2.3 Hz), 29.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.3 (d, *J* = 41.4 Hz, 1F), - 92.0 (d, *J* = 41.4 Hz, 1F) ppm.

The data are consistent with the reported literature.[6]

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-methoxybenzene（3ba）



According to the *general procedure*.

Yellow oil (35 mg, 72%).

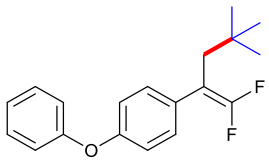
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.19 (m, 2H), 6.92 – 6.84 (m, 2H), 3.80 (s, 3H), 2.35 – 2.25 (m, 2H), 0.80 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.4, 154.3 (dd, J_{CF} = 287.9, 289.9 Hz), 129.5 (t, J_{CF} = 2.0 Hz), 127.7 (d, J_{CF} = 20.2 Hz), 113.7, 90.5 (dd, J_{CF} = 8.1, 21.2 Hz), 55.2, 41.2, 32.6 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.8 (d, *J* = 41.4 Hz, 1F), - 93.3 (d, *J* = 41.4 Hz, 1F) ppm.

The data are consistent with the reported literature.[6]

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-phenoxybenzene（3ca）



According to the *general procedure*.

Yellow oil (55 mg, 92%).

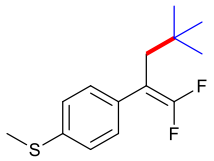
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 4H), 7.18 – 7.11 (m, 1H), 7.02 (ddt, *J* = 20.7, 9.5, 2.0 Hz, 4H), 2.41 – 2.28 (m, 2H), 0.85 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.9, 155.1, 153.3 (dd, J_{CF} = 287.9, 289.9 Hz), 150.5, 129.3 (dd, J_{CF} = 3.0, 5.1 Hz), 128.8, 128.7, 122.4, 118.0, 117.5, 89.5 (dd, J_{CF} = 13.1, 22.2 Hz), 40.2, 31.7 (t, J_{CF} = 3.0 Hz), 28.7 ppm

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.1 (d, *J* = 41.4 Hz, 1F), - 92.6 (d, *J* = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{19}H_{20}F_2O$ $(M + H)^+$ 303.1555, found 303.1543.

(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)penyl)(methyl)sulfane（3da）



According to the *general procedure*.

Yellow oil (35 mg, 68%).

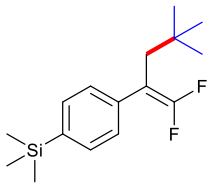
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 4H), 2.48 (s, 3H), 2.34 – 2.29 (m, 2H), 0.80 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4 (dd, J_{CF} = 288.9, 290.9 Hz), 137.1, 129.5, 128.8 (t, J_{CF} = 3.0 Hz), 126.3, 90.4 (dd, J_{CF} = 4.0, 8.1 Hz), 41.0, 32.7 (t, J_{CF} = 3.0 Hz), 29.7, 15.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.6 (d, *J* = 41.4 Hz, 1F), - 92.2 (d, *J* = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{14}H_{18}F_2S$ $(M + H)^+$ 257.1170, found 257.1168.

(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)trimethylsilane（3ea）



According to the *general procedure*.

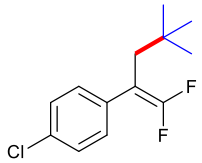
Yellow oil (46 mg, 81%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 6.9 Hz, 2H), 2.36 (s, 2H), 0.83 (s, 9H), 0.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.5 (dd, J_{CF} = 287.9, 290.9 Hz), 140.2, 137.0 (dd, J_{CF} = 3.0, 5.1 Hz), 134.3, 128.7 (t, J_{CF} = 3.0 Hz), 92.2 (dd, J_{CF} = 8.1, 14.1 Hz), 42.1, 33.8 (t, J_{CF} = 3.0 Hz), 30.9, 0.0 ppm.

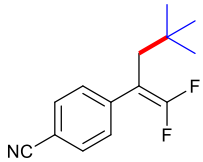
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.5 (d, J = 41.4 Hz, 1F), - 92.2 (d, J = 41.4 Hz, 1F) ppm.
HRMS m/z (ESI): calcd for $C_{16}H_{24}F_2Si$ $(M + Na)^+$ 305.1508, found 305.1547.

1-chloro-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene（3fa）



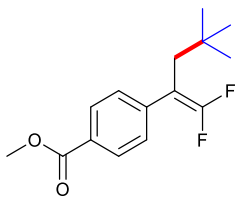
According to the *general procedure*.
Yellow oil (44 mg, 90%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 4H), 2.33 – 2.29 (m, 2H), 0.80 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4 (dd, J_{CF} = 289.9, 291.9 Hz), 134.1 (dd, J_{CF} = 3.0, 5.1 Hz), 132.8, 129.7 (t, J_{CF} = 3.0 Hz), 128.5, 90.3 (dd, J_{CF} = 13.1, 22.2 Hz), 41.1, 32.7 (t, J_{CF} = 3.0 Hz), 29.7 ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.0 (d, J = 41.4 Hz, 1F), - 91.7 (d, J = 37.6 Hz, 1F) ppm.
The data are consistent with the reported literature.[6]

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzonitrile（3ga）



According to the *general procedure*.
Yellow oil (36 mg, 76%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 2.38 – 2.33 (m, 2H), 0.80 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.6 (dd, J_{CF} = 289.9, 292.9 Hz), 140.7 (dd, J_{CF} = 3.0, 4.5 Hz), 132.1, 129.0 (t, J_{CF} = 3.0 Hz), 118.6, 110.7, 90.5 (dd, J_{CF} = 12.1, 24.2 Hz), 40.7, 32.8 (t, J_{CF} = 3.0 Hz), 29.6 ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 86.5 (d, J = 41.4 Hz, 1F), - 89.5 (d, J = 41.4 Hz, 1F) ppm.
HRMS m/z (APCI): calcd for $C_{14}H_{15}F_2N$ $(M + H)^+$ 236.1245, found 236.1210.

methyl 4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzoate（3ha）



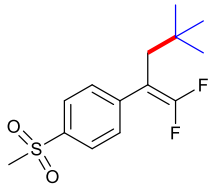
According to the *general procedure*.
Yellow oil (32.2 mg, 60%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.95 (m, 2H), 7.39 (dd, J = 8.5, 1.5 Hz, 2H), 3.91 (s, 3H), 2.40 – 2.30 (m, 2H), 0.79 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 154.5 (dd, J_{CF} = 289.9, 292.3 Hz), 151.7, 140.5 (dd, J_{CF} = 3.0, 5.0 Hz), 129.6, 128.4 (t, J_{CF} = 2.0 Hz), 90.9 (dd, J_{CF} = 12.1, 22.2 Hz), 52.1, 40.9, 32.8 (t, J_{CF}

= 3.0 Hz), 29.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 87.6 (d, J = 41.4 Hz, 1F), - 90.5 (d, J = 37.6 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{15}H_{18}F_2O_2$ $(M + H)^+$ 269.1348, found 269.1312.

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-(methylsulfonyl)benzene（3ia）



According to the *general procedure*.

Yellow oil (47.8 mg, 83%).

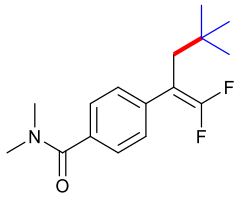
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.83 (m, 2H), 7.58 – 7.42 (m, 2H), 3.12 – 2.93 (m, 3H), 2.38 (s, 2H), 0.80 (d, J = 3.5 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5 (dd, J_{CF} = 290.9, 293.9 Hz), 141.7 (dd, J_{CF} = 3.0, 5.0 Hz), 129.3 (t, J_{CF} = 3.0 Hz), 127.4, 90.5 (dd, J_{CF} = 12.1, 23.3Hz), 44.5, 41.0, 32.9 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

^{19}F NMR (376MHz, $CDCl_3$): δ = - 86.5 (d, J = 41.4 Hz, 1F), - 89.7 (d, J = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{14}H_{18}F_2O_2S$ $(M + H)^+$ 289.1068, found 289.1037.

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-N,N-dimethylbenzamide（3ja）



According to the *general procedure*.

Yellow oil (50.6 mg, 92%).

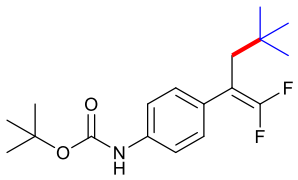
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 4H), 3.04 (d, J = 46.2 Hz, 6H), 2.34 (s, 2H), 0.79 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 154.5 (dd, J_{CF} = 288.9, 292.9 Hz), 137.1 (dd, J_{CF} = 3.0, 5.0 Hz), 134.8, 128.3 (t, J_{CF} = 3.0 Hz), 127.2, 90.8 (dd, J_{CF} = 12.1, 22.2Hz), 41.0, 39.6, 35.4, 32.8 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

^{19}F NMR (376MHz, $CDCl_3$): δ = - 88.6 (d, J = 37.6 Hz, 1F), - 91.4 (d, J = 37.6 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{16}H_{21}F_2NO$ $(M + H)^+$ 282.1664, found 282.1629.

tert-butyl (4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)carbamate（3ka）



According to the *general procedure*.

Yellow oil (40 mg, 61%).

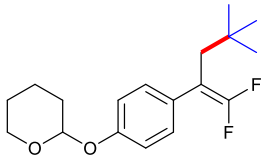
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 6.50 (s, 1H), 2.33 – 2.25 (m, 2H), 1.51 (s, 9H), 0.79 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4 (dd, J_{CF} = 287.9, 290.9 Hz), 152.7, 137.1, 130.1 (dd, J_{CF} = 3.0, 5.0 Hz), 129.0 (t, J_{CF} = 3.0 Hz), 118.2, 90.5 (dd, J_{CF} = 13.1, 21.2 Hz), 80.6, 41.0, 32.7 (t, J_{CF} = 3.0 Hz), 29.7, 28.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.2 (d, J = 41.4 Hz, 1F), - 92.7 (d, J = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{18}H_{25}F_2NO_2$ $(M + H)^+$ 326.1926, found 326.1970.

2-(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenoxy)tetrahydro-2H-pyran（3la）



According to the *general procedure*.

Yellow oil (46.5 mg, 75%).

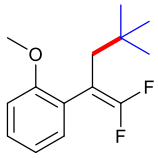
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.15 (m, 2H), 7.07 – 6.95 (m, 2H), 5.40 (s, 1H), 3.92 (t, *J* = 10.6 Hz, 1H), 3.61 (d, *J* = 11.6 Hz, 1H), 2.29 (s, 2H), 2.00 (td, *J* = 14.3, 13.3, 8.0 Hz, 1H), 1.85 (d, *J* = 3.8 Hz, 2H), 1.78 – 1.50 (m, 4H), 0.80 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.0, 154.3 (dd, J_{CF} = 286.9, 288.4 Hz), 129.4 (t, J_{CF} = 3.0 Hz), 128.6 (dd, J_{CF} = 3.0, 4.5 Hz), 116.1, 96.4, 90.6 (dd, J_{CF} = 13.6, 21.1 Hz), 62.1, 41.2, 32.6 (t, J_{CF} = 3.0 Hz), 30.4, 29.7, 25.2, 18.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.8 (d, J = 41.4 Hz, 1F), - 93.3 (d, J = 41.4 Hz, 1F) ppm.

HRMS m/z (ESI): calcd for $C_{18}H_{24}F_2O_2$ $(M + Na)^+$ 333.1637, found 333.1601.

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-2-methoxybenzene（3ma）



According to the *general procedure*.

Yellow oil (30.2 mg, 63%).

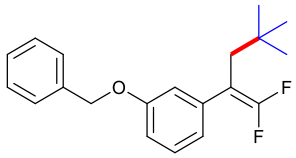
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 1H), 6.94 – 6.89 (m, 1H), 6.87 (dt, *J* = 2.6, 1.4 Hz, 1H), 6.82 – 6.77 (m, 1H), 3.81 (s, 3H), 2.36 – 2.29 (m, 2H), 0.82 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.4, 154.4 (dd, J_{CF} = 286.9, 289.9 Hz), 137.0 (dd, J_{CF} = 1.5, 4.5 Hz), 129.2, 121.0 (t, J_{CF} = 3.0 Hz), 114.5 (t, J_{CF} = 3.0 Hz), 112.1, 91.0 (dd, J_{CF} = 12.1, 21.1 Hz), 55.2, 41.2, 32.7 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

HRMS m/z (ESI): calcd for $C_{14}H_{18}F_2O$ $(M + Na)^+$ 263.1218, found 263.1249.

The data are consistent with the reported literature.[6]

1-(benzyloxy)-3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene（3na）



According to the *general procedure*.

Yellow oil (54 mg, 85%).

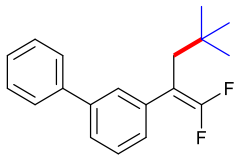
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 7.24 (dd, *J* = 8.9, 1.5 Hz, 2H), 6.99 – 6.93 (m, 2H), 5.06 (s, 2H), 2.34 – 2.27 (m, 2H), 0.81 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.7, 154.3 (dd, J_{CF} = 287.9, 289.9 Hz), 136.9, 129.5 (t, J_{CF} = 3.0 Hz), 128.6, 128.0, 127.5, 114.6, 90.5 (dd, J_{CF} = 13.1, 21.0 Hz), 70.0, 41.2, 32.7 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.7 (d, *J* = 45.1 Hz, 1F), - 93.2 (d, *J* = 45.1 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{20}H_{22}F_2O$ $(M + H)^+$ 317.1711, found 317.1703.

3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3oa）



According to the *general procedure*.

Yellow oil (47mg, 82%).

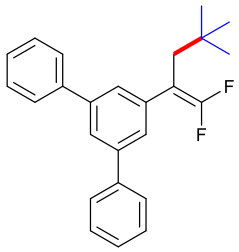
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 2H), 7.56 – 7.52 (m, 1H), 7.52 – 7.33 (m, 5H), 7.33 – 7.28 (m, 1H), 2.43 – 2.36 (m, 2H), 0.84 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5 (dd, J_{CF} = 287.9, 290.9 Hz), 141.3, 141.0, 136.1 (dd, J_{CF} = 3.0, 5.0 Hz), 128.8, 128.7, 127.4, 127.3 (t, J_{CF} = 3.0 Hz), 127.2, 125.9, 91.1 (dd, J_{CF} = 13.1, 21.2 Hz), 41.3, 32.8 (t, J_{CF} = 3.0 Hz), 29.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.6 (d, *J* = 37.6 Hz, 1F), - 92.0 (d, *J* = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{19}H_{20}F_2$ $(M + H)^+$ 287.1606, found 287.1595

5'-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1':3',1''-terphenyl（3pa）



According to the *general procedure*.

Yellow oil (61 mg, 84%).

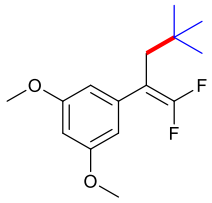
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (t, *J* = 1.6 Hz, 1H), 7.73 – 7.67 (m, 4H), 7.58 (t, *J* = 1.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.47 – 7.39 (m, 2H), 2.53 – 2.46 (m, 2H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.6 (dd, J_{CF} = 288.9, 290.9 Hz), 141.8, 141.0, 136.6 (dd, J_{CF} = 3.0, 5.0 Hz), 128.8, 127.5, 127.3, 126.3 (t, J_{CF} = 3.0 Hz), 124.9, 91.2 (dd, J_{CF} = 13.1, 22.2 Hz), 41.3, 32.8 (t, J_{CF} = 3.0 Hz), 29.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.2 (d, *J* = 37.6 Hz, 1F), - 91.4 (d, *J* = 37.6 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{25}H_{24}F_2$ $(M + H)^+$ 363.1919, found 363.1928.

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-3,5-dimethoxybenzene（3qa）



According to the *general procedure*.

Yellow oil (46 mg, 85%).

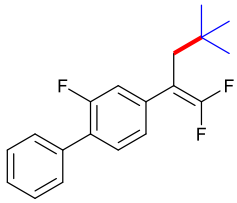
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.52 – 6.46 (m, 2H), 6.38 (t, *J* = 2.2 Hz, 1H), 3.81 (s, 6H), 2.34 – 2.26 (m, 2H), 0.84 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.6, 154.4 (dd, J_{CF} = 287.9, 291.9 Hz), 137.6 (dd, J_{CF} = 3.0, 5.0 Hz), 106.9 (t, J_{CF} = 3.0 Hz), 98.8, 91.2 (dd, J_{CF} = 13.1, 21.2 Hz), 55.3, 41.2, 32.4 (t, J_{CF} = 3.0 Hz), 29.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.4 (d, *J* = 37.6 Hz, 1F), - 91.0 (d, *J* = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{15}H_{20}F_2O_2$ $(M + H)^+$ 271.1504, found 271.1465.

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-2-fluoro-1,1'-biphenyl（3ra）



According to the *general procedure*.

Yellow oil (50.5 mg, 83%).

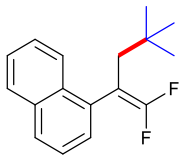
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dt, *J* = 8.1, 1.4 Hz, 2H), 7.50 – 7.36 (m, 4H), 7.23 – 7.13 (m, 2H), 2.41 – 2.36 (m, 2H), 0.88 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.5 (d, J_{CF} = 248.5 Hz), 154.6 (dd, J_{CF} = 288.9, 290.9 Hz), 151.7, 136.7 (m), 135.4 (d, J_{CF} =1 .0 Hz), 130.4 (d, J_{CF} = 4.0 Hz), 128.9 (d, J_{CF} =3.0 Hz), 128.5, 127.7, 127.5 (d, J_{CF} = 13.3 Hz), 124.4 (q, J_{CF} = 3.0 Hz), 116.1 (dt, J_{CF} = 3.0, 24.2 Hz), 90.3 (ddd, J_{CF} = 1.0, 12.1, 22.2 Hz), 40.9, 32.8 (t, J_{CF} = 3.0 Hz), 29.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 88.1 (d, *J* = 37.6 Hz, 1F), - 90.6 (d, *J* = 37.6 Hz, 1F), -118.1 ppm.

HRMS m/z (APCI): calcd for $C_{19}H_{19}F_3$ $(M + H)^+$ 305.1512, found 305.1549.

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)naphthalene（3sa）



According to the *general procedure*.

Yellow oil (40 mg, 77%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 1H), 7.91 – 7.86 (m, 1H), 7.81 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 2.58 – 2.45 (m, 2H), 0.85 (s, 9H).

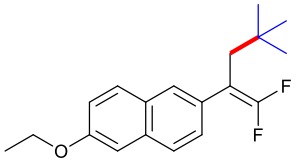
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9 (dd, J_{CF} = 290.9, 293.9 Hz), 132.7, 128.5, 127.0, 126.4 (dd, J_{CF} = 2.0, 3.0 Hz), 125.1, 124.7, 124.3, 124.3, 124.1, 87.9 (dd, J_{CF} = 6.1, 20.2 Hz), 42.5, 31.9

(t, J_{CF} = 3.0 Hz), 28.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 86.6 (d, J = 37.6 Hz, 1F), - 90.0 (d, J = 37.6 Hz, 1F) ppm.

The data are consistent with the reported literature.[6]

2-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-6-ethoxynaphthalene（3ta）



According to the *general procedure*.

Yellow oil (28.6 mg, 47%).

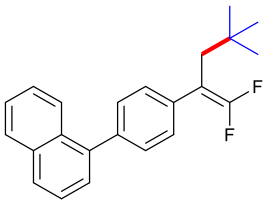
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (t, J = 7.6 Hz, 3H), 7.40 (d, J = 8.6 Hz, 1H), 7.18 – 7.08 (m, 2H), 4.15 (q, J = 7.0 Hz, 2H), 2.46 – 2.41 (m, 2H), 1.49 (t, J = 7.0 Hz, 3H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.1, 153.5 (dd, J_{CF} = 289.9, 290.9 Hz), 132.5, 129.6 (dd, J_{CF} = 3.0, 5.0 Hz), 128.3, 127.6, 126.1 (t, J_{CF} = 3.0 Hz), 125.9 (t, J_{CF} = 3.0 Hz), 125.6, 118.3, 105.3, 90.5 (dd, J_{CF} = 13.4, 22.2 Hz), 62.5, 40.2, 31.7 (t, J_{CF} = 3.0 Hz), 28.7, 13.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.8 (d, J = 41.4 Hz, 1F), - 92.6 (d, J = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{19}H_{22}F_2O$ $(M + Na)^+$ 305.1711, found 305.1684.

1-(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)naphthalene（3ua）



According to the *general procedure*.

Yellow oil (52 mg, 77%).

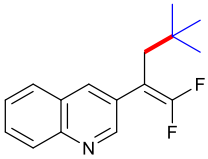
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.67 (m, 3H), 7.69 – 7.32 (m, 8H), 2.46 (s, 2H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.6 (dd, J_{CF} = 287.9, 289.9 Hz), 139.8, 139.4, 134.6 (dd, J_{CF} = 3.0, 5.0 Hz), 133.9, 131.6, 128.3 (t, J_{CF} = 3.0 Hz), 127.7, 127.0, 126.1, 126.0, 125.8, 125.4, 90.5 (dd, J_{CF} = 12.1, 21.2 Hz), 41.2, 32.9 (t, J_{CF} = 3.0 Hz), 29.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.7 (d, J = 41.4 Hz, 1F), - 91.9 (d, J = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{23}H_{22}F_2$ $(M + H)^+$ 337.1762, found 337.1784.

3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)quinoline（3va）



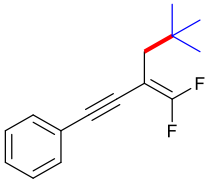
According to the *general procedure*.

Yellow oil (26.6 mg, 51%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 8.13 – 8.04 (m, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.70 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.59 – 7.50 (m, 1H), 2.49 – 2.43 (m, 2H), 0.82 (s, 9H).

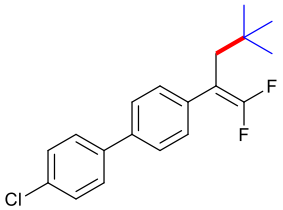
^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.0 (dd, J_{CF} = 290.9, 292.9 Hz), 150.5 (t, J_{CF} = 3.0 Hz), 146.9, 134.8 (t, J_{CF} = 3.0 Hz), 129.5, 129.2, 128.9 (t, J_{CF} = 3.0 Hz), 127.7, 127.6, 127.0, 88.6 (dd, J_{CF} = 13.1, 23.2 Hz), 41.0, 32.9 (t, J_{CF} = 3.0 Hz), 29.8 ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 87.2 (d, J = 41.4 Hz, 1F), - 90.7 (d, J = 41.4 Hz, 1F) ppm.
HRMS m/z (APCI): calcd for $C_{16}H_{17}F_2N$ $(M + H)^+$ 262.1402, found 262.1367

(3-(difluoromethylene)-5,5-dimethylhex-1-yn-1-yl)benzene（3wa）



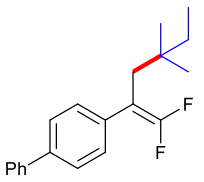
According to the *general procedure*.
Yellow oil (35 mg, 48%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 0H), 7.46 – 7.39 (m, 2H), 7.34 – 7.29 (m, 3H), 2.08 (t, J = 2.3 Hz, 2H), 1.04 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.7 (dd, J_{CF} = 295.9, 298.0 Hz), 131.2, 128.3, 128.2, 123.2, 93.2 (t, J_{CF} = 6.1 Hz), 83.1 (dd, J_{CF} = 5.1, 9.1 Hz), 60.4, 41.2, 32.4 (t, J_{CF} = 3.0 Hz), 29.3 ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 79.2 (d, J = 11.3 Hz, 1F), - 83.3 (d, J = 15.0 Hz, 1F) ppm.
HRMS m/z (APCI): calcd for $C_{15}H_{16}F_2$ $(M + H)^+$ 235.1293, found 235.1283.

4-chloro-4'-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3xa）



According to the *general procedure*.
Yellow oil (56 mg, 88%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 4H), 7.41 (dt, J = 7.0, 2.1 Hz, 4H), 2.42 – 2.38 (m, 2H), 0.86 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5 (dd, J_{CF} = 289.9, 290.9 Hz), 139.0, 138.5, 135.0 (dd, J_{CF} = 3.0, 5.0 Hz), 133.4, 128.9, 128.9 (t, J_{CF} = 4.0 Hz), 128.2, 126.8, 90.8 (dd, J_{CF} = 13.1, 22.1 Hz), 41.2, 32.9 (t, J_{CF} = 3.0 Hz), 29.9 ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.0 (d, J = 41.4 Hz, 1F), - 91.8 (d, J = 41.4 Hz, 1F) ppm.
HRMS m/z (APCI): calcd for $C_{19}H_{19}ClF_2$ $(M + H)^+$ 321.1216, found 321.1194.

4-(1,1-difluoro-4,4-dimethylhex-1-en-2-yl)-1,1'-biphenyl（3ab）



According to the *general procedure*.

Yellow oil (36 mg, 60%).

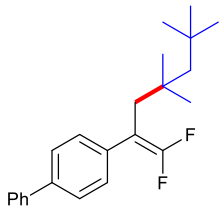
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (ddt, *J* = 14.7, 8.5, 1.7 Hz, 4H), 7.49 – 7.30 (m, 5H), 2.44 – 2.29 (m, 2H), 1.21 (q, *J* = 7.5 Hz, 2H), 0.83 – 0.72 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4 (dd, J_{CF} = 288.9, 291.9 Hz), 140.6, 139.7, 135.0 (dd, J_{CF} = 3.0, 5.0 Hz), 128.8 (t, J_{CF} = 3.0 Hz), 128.8, 127.3, 127.0, 126.9, 90.6 (dd, J_{CF} = 13.1, 21.1 Hz), 39.2, 35.3 (t, J_{CF} = 3.0 Hz), 34.7, 26.6, 8.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.3 (d, *J* = 41.4 Hz, 1F), - 91.8 (d, *J* = 41.4 Hz, 1F) ppm.

The data are consistent with the reported literature.[7]

4-(1,1-difluoro-4,4,6,6-tetramethylhept-1-en-2-yl)-1,1'-biphenyl（3ac）



According to the *general procedure*.

Yellow oil (45 mg, 66%).

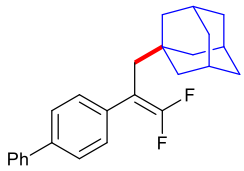
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 12.9, 8.1 Hz, 4H), 7.49 – 7.32 (m, 5H), 2.45 (s, 2H), 1.31 – 1.27 (m, 2H), 0.98 (s, 9H), 0.89 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5 (dd, J_{CF} = 288.9, 290.9 Hz), 140.6, 139.7, 134.9 (dd, J_{CF} = 3.0, 5.0 Hz), 128.9 (t, J_{CF} = 3.0 Hz), 128.8, 127.3, 127.0, 127.0, 90.7 (dd, J_{CF} = 13.1, 22.2 Hz), 55.6, 42.3, 37.3 (t, J_{CF} = 2.0 Hz), 32.3, 32.1, 28.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 89.0 (d, *J* = 37.6 Hz, 1F), - 91.7 (d, *J* = 33.8 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{23}H_{28}F_2$ $(M + H)^+$ 343.2232, found 343.2228.

(3r,5r,7r)-1-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)adamantane（3ad）



According to the *general procedure*.

Yellow oil (36.4 mg,50%).

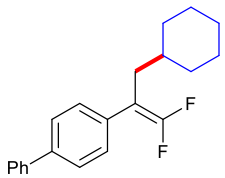
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.55 (m, 4H), 7.48 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 2.29 – 2.21 (m, 2H), 1.89 (s, 3H), 1.64 (d, *J* = 12.1 Hz, 3H), 1.56 (d, *J* = 11.2 Hz, 3H), 1.42 (d, *J* = 2.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4 (dd, J_{CF} = 287.9, 291.9 Hz), 140.6, 139.5, 134.9 (dd, J_{CF} = 3.0, 5.0 Hz), 128.8, 128.7 (t, J_{CF} = 3.0 Hz), 127.0, 126.9, 89.4 (dd, J_{CF} = 12.1, 22.1 Hz), 42.7, 41.8, 36.9, 34.7 (t, J_{CF} = 3.0 Hz), 28.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 88.5 (d, *J* = 41.4 Hz, 1F), - 91.6 (d, *J* = 41.4 Hz, 1F) ppm.

HRMS m/z (APCI): calcd for $C_{25}H_{26}F_2$ $(M + H)^+$ 365.2075, found 365.2027.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl（3ae）



According to the *general procedure*.

Yellow oil (18 mg, 33%).

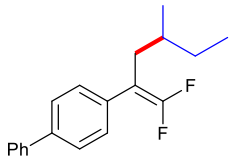
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (t, *J* = 8.5 Hz, 4H), 7.49 – 7.31 (m, 5H), 2.32 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.78 – 1.64 (m, 4H), 1.59 (d, *J* = 16.7 Hz, 2H), 1.32 (ddd, *J* = 15.4, 7.6, 3.9 Hz, 1H), 1.17 – 1.12 (m, 2H), 1.03 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, J_{CF} = 286.8, 291.9 Hz), 139.6, 138.8, 132.0 (dd, J_{CF} = 4.0, 7.1 Hz), 127.8, 127.6 (t, J_{CF} = 3.0 Hz), 126.0, 126.0, 91.2 (dd, J_{CF} = 12.1, 22.2 Hz), 34.7 (t, J_{CF} = 3.0 Hz), 34.1, 31.9, 25.4, 25.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 90.7 (d, *J* = 45.1 Hz, 1F), - 91.3 (d, *J* = 41.4 Hz, 1F) ppm.

The data are consistent with the reported literature.[8]

4-(1,1-difluoro-4-methylhex-1-en-2-yl)-1,1'-biphenyl（3af）



According to the *general procedure*.

Yellow oil (15 mg, 31%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 4H), 7.49 – 7.31 (m, 5H), 2.43 (ddt, *J* = 14.3, 5.9, 2.9 Hz, 1H), 2.27 – 2.19 (m, 1H), 1.45 – 1.36 (m, 2H), 1.19 – 1.12 (m, 1H), 0.89 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.1 (dd, J_{CF} = 290.9, 292.9 Hz), 140.6, 139.9, 128.8, 128.7 (t, J_{CF} = 3.0 Hz), 127.3, 127.0, 127.0, 91.2 (dd, J_{CF} = 11.1, 21.2 Hz), 34.5, 32.7 (t, J_{CF} = 3.0 Hz), 29.1, 18.6, 11.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = - 91.0 (d, *J* = 41.4 Hz, 1F), - 91.3 (d, *J* = 41.4 Hz, 1F) ppm.

The data are consistent with the reported literature.[8]

References

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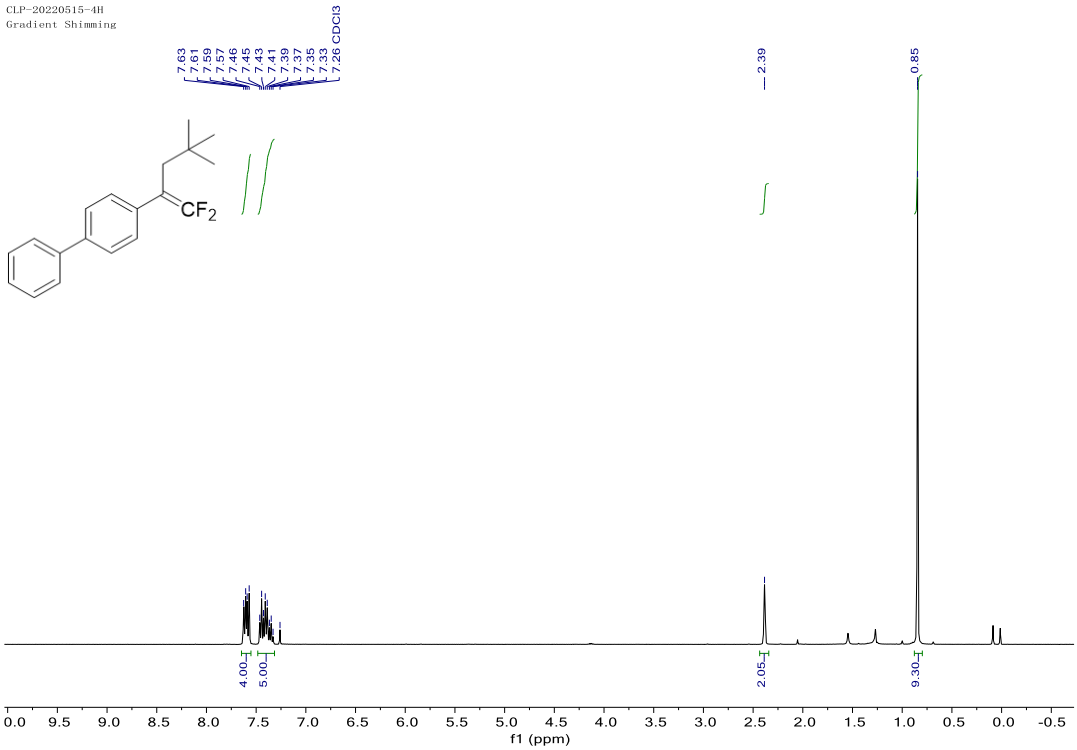
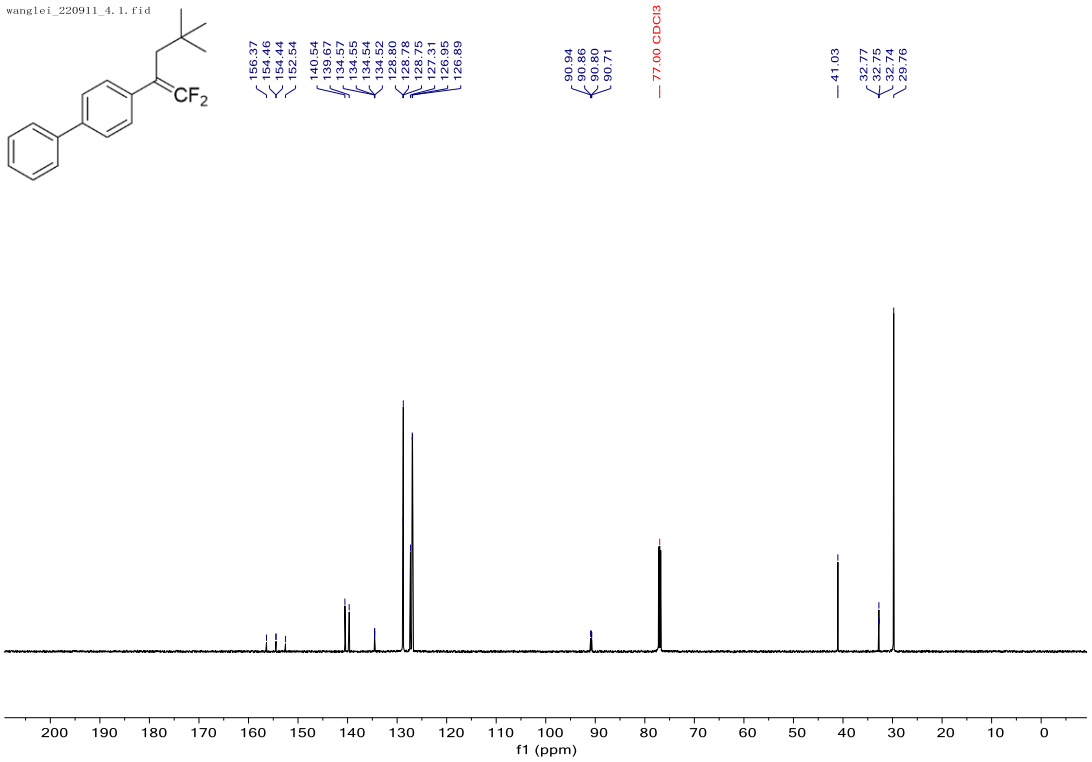
NMR spectra

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3aa）

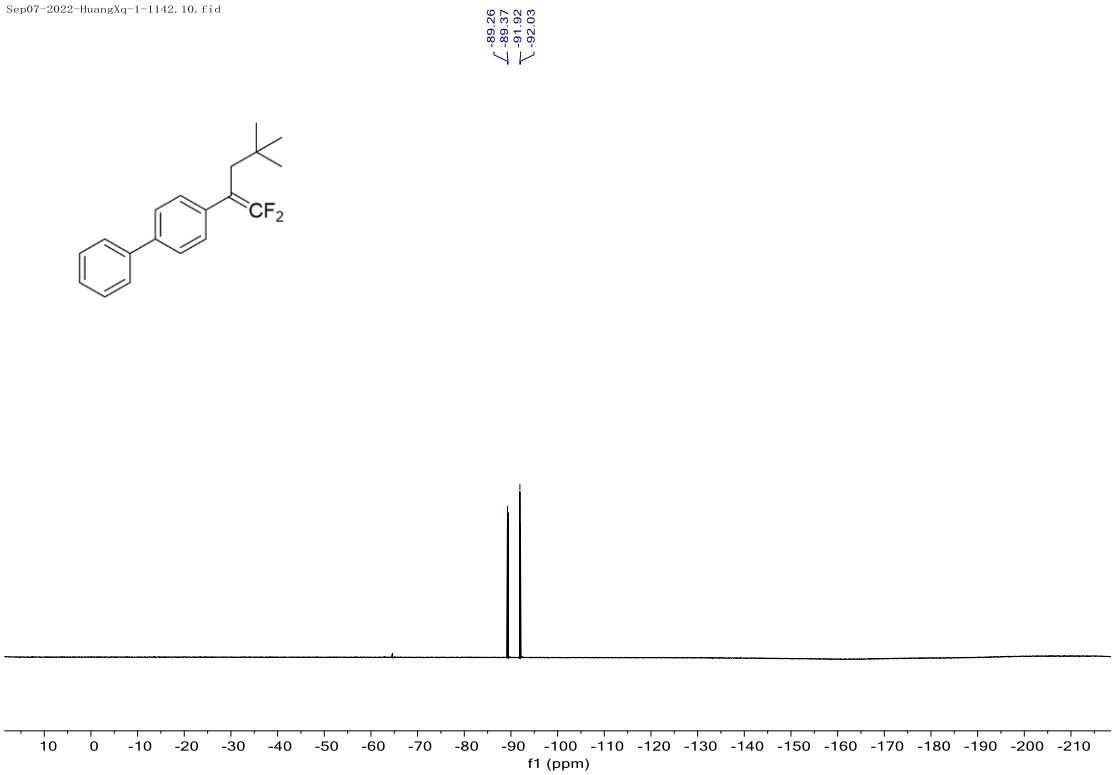
^{1}H NMR



^{13}C NMR

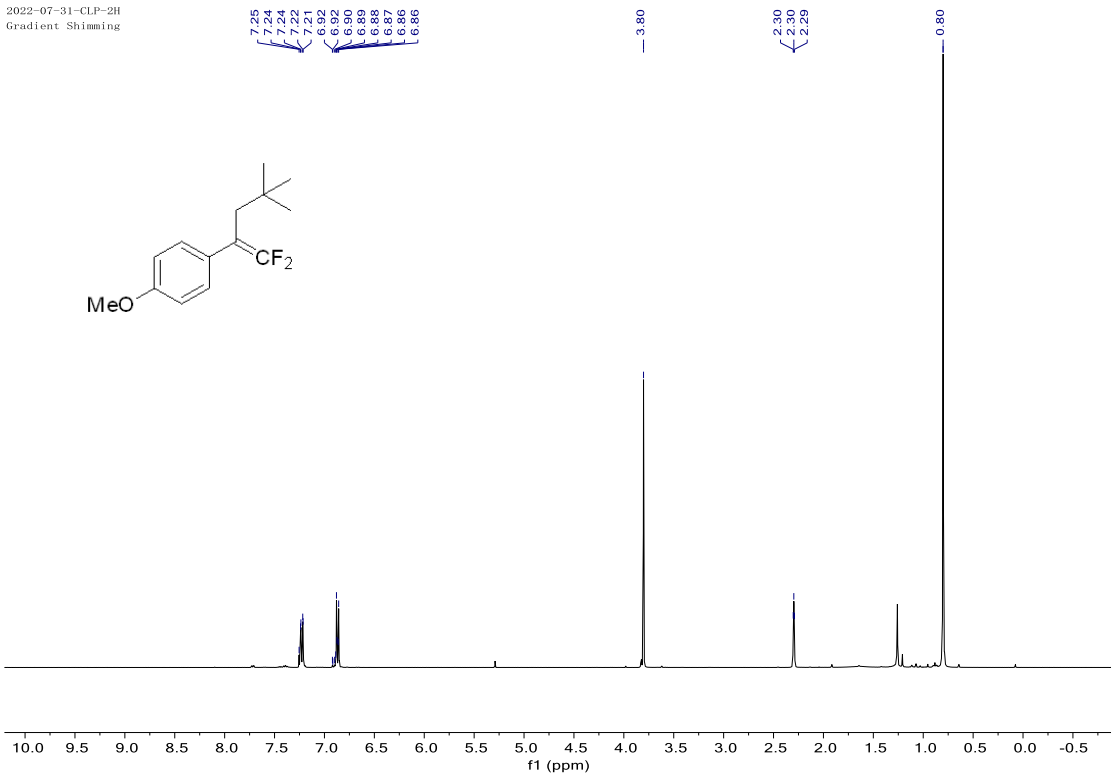


^{19}F NMR

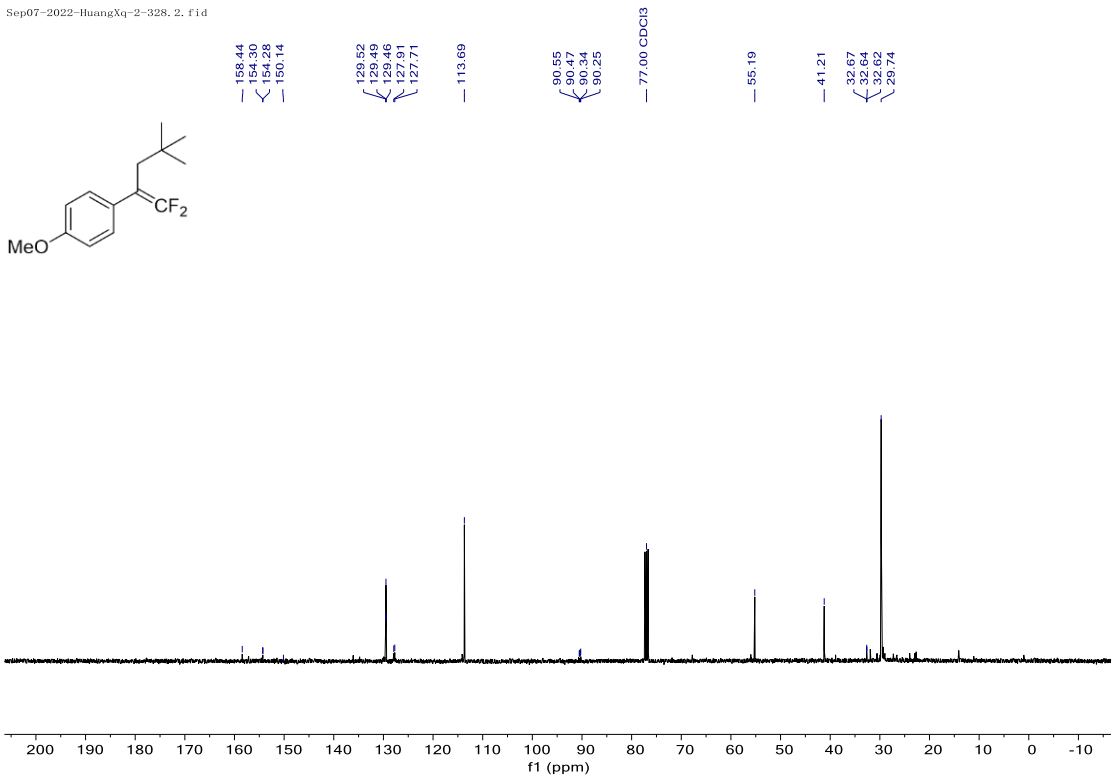

Sep07-2022-HuangXq-1-1142.10.fid
-89.26
-89.37
-91.92
-92.03
CF2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-methoxybenzene（3ba）

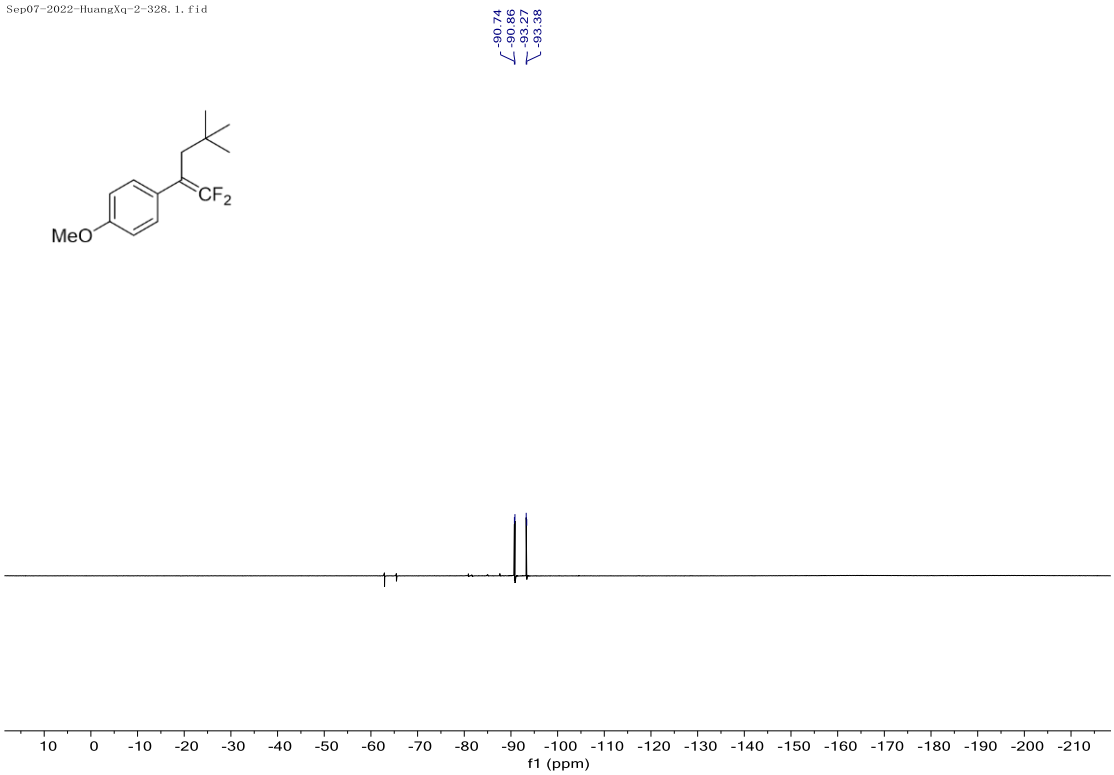
^{1}H NMR



^{13}C NMR

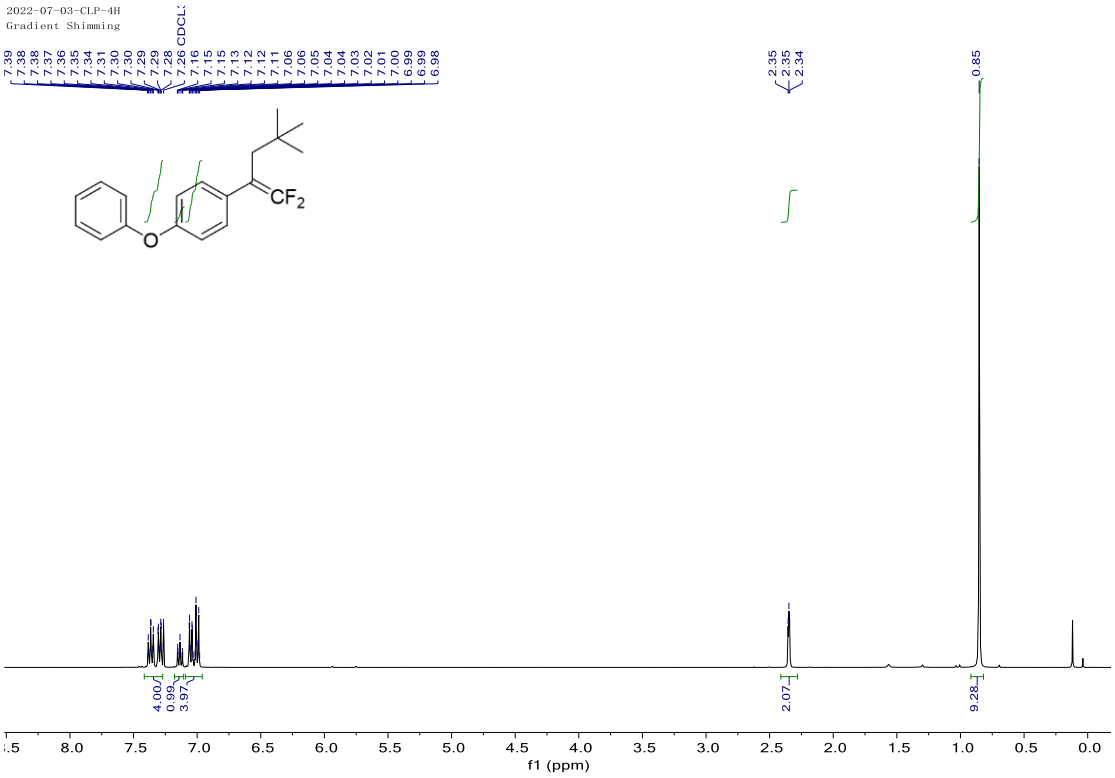


^{19}F NMR

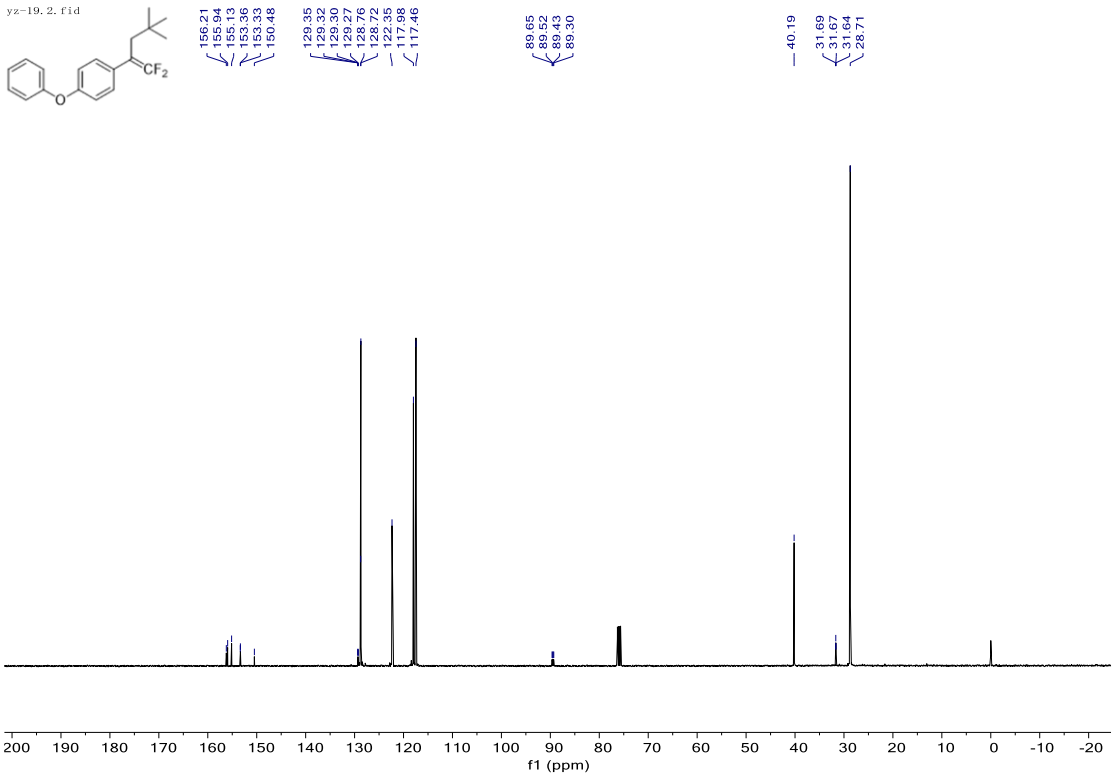

Sep07-2022-HuangXq-2-328.1.fid
-90.74
-90.86
-93.27
-93.38
CF2
MeO
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-phenoxybenzene（3ca）

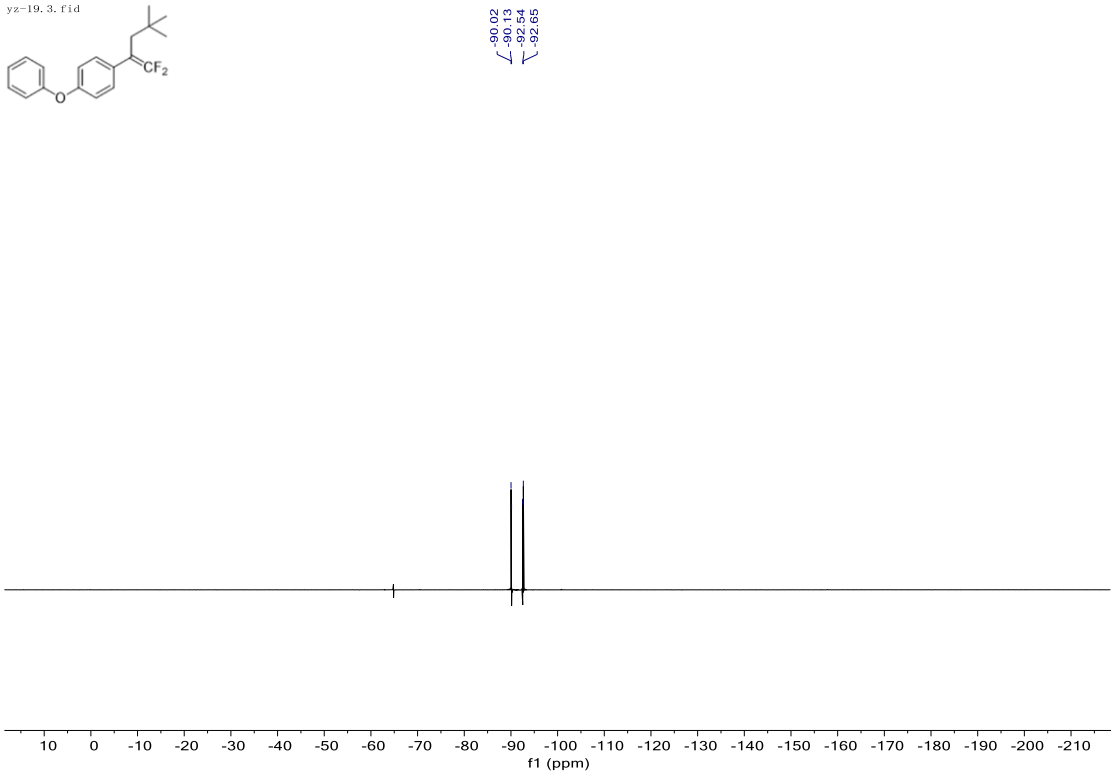
^{1}H NMR



^{13}C NMR

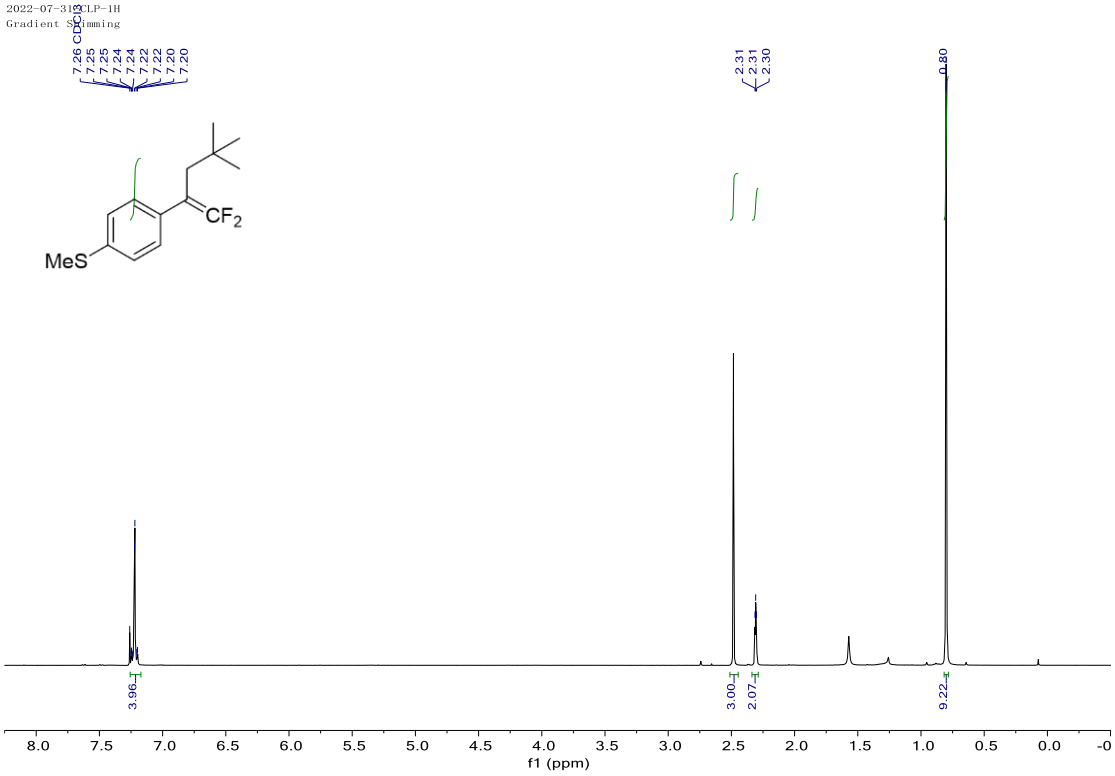


^{19}F NMR

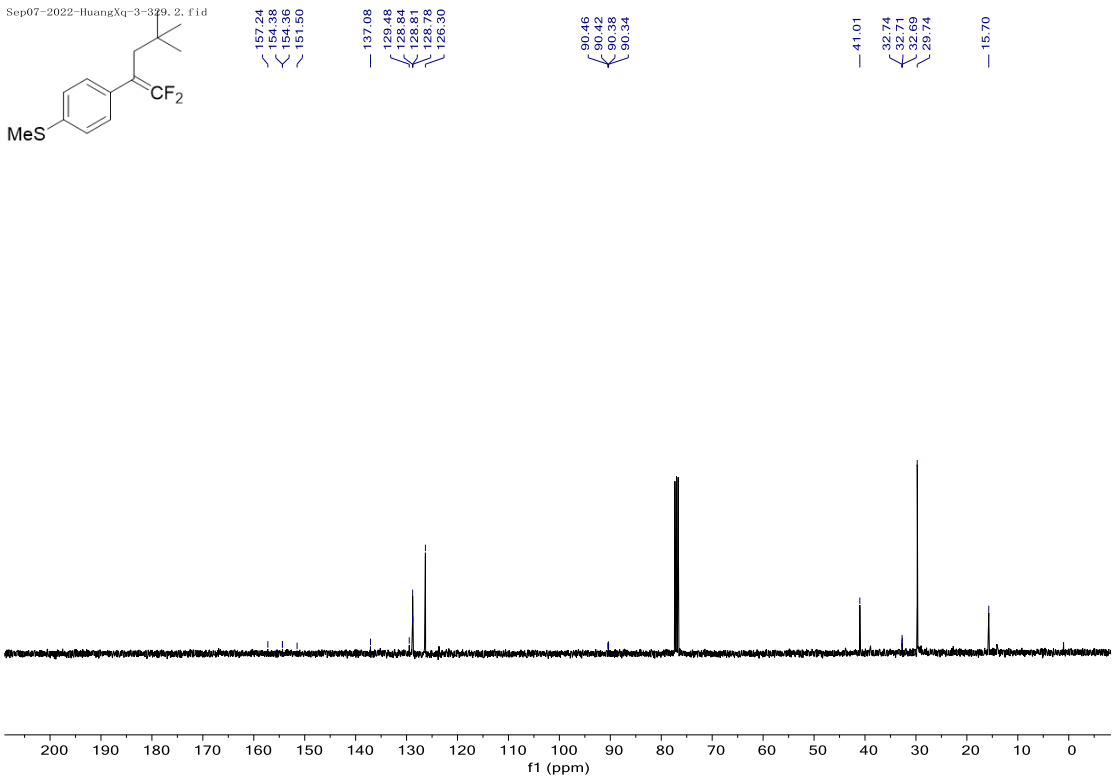

yz-19.3.fid
-90.02
-90.13
-92.54
-92.65
CF2
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)penyl)(methyl)sulfane（3da）

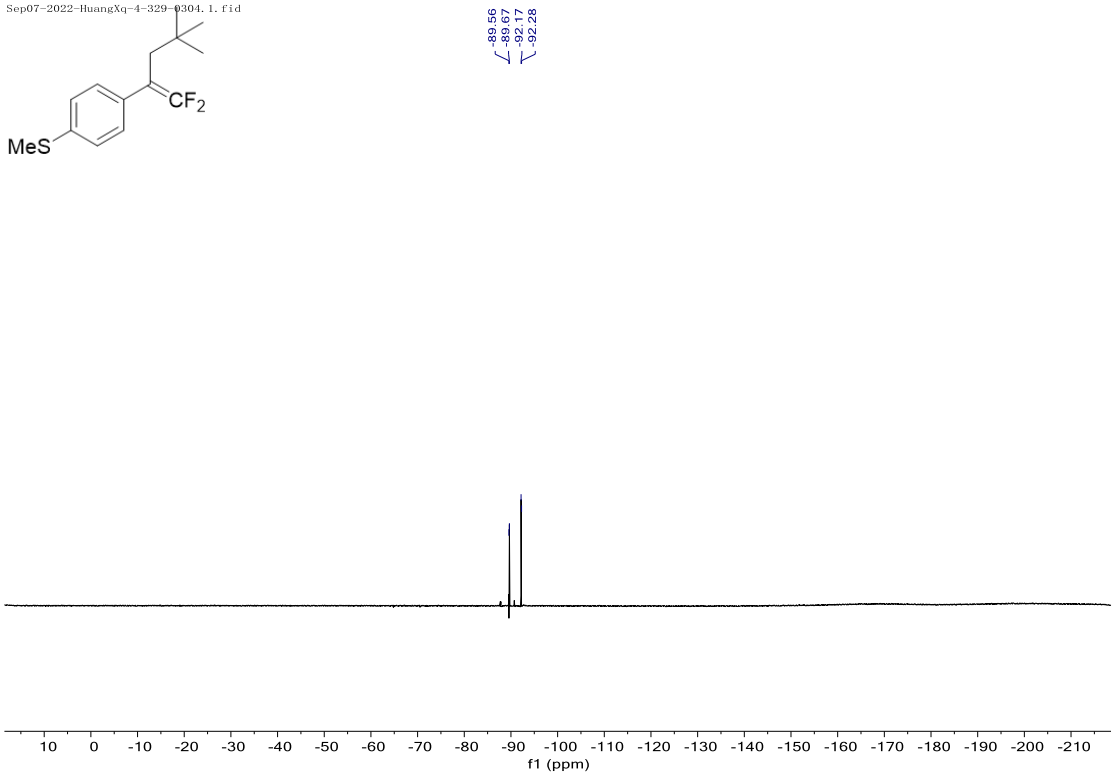
^{1}H NMR



^{13}C NMR

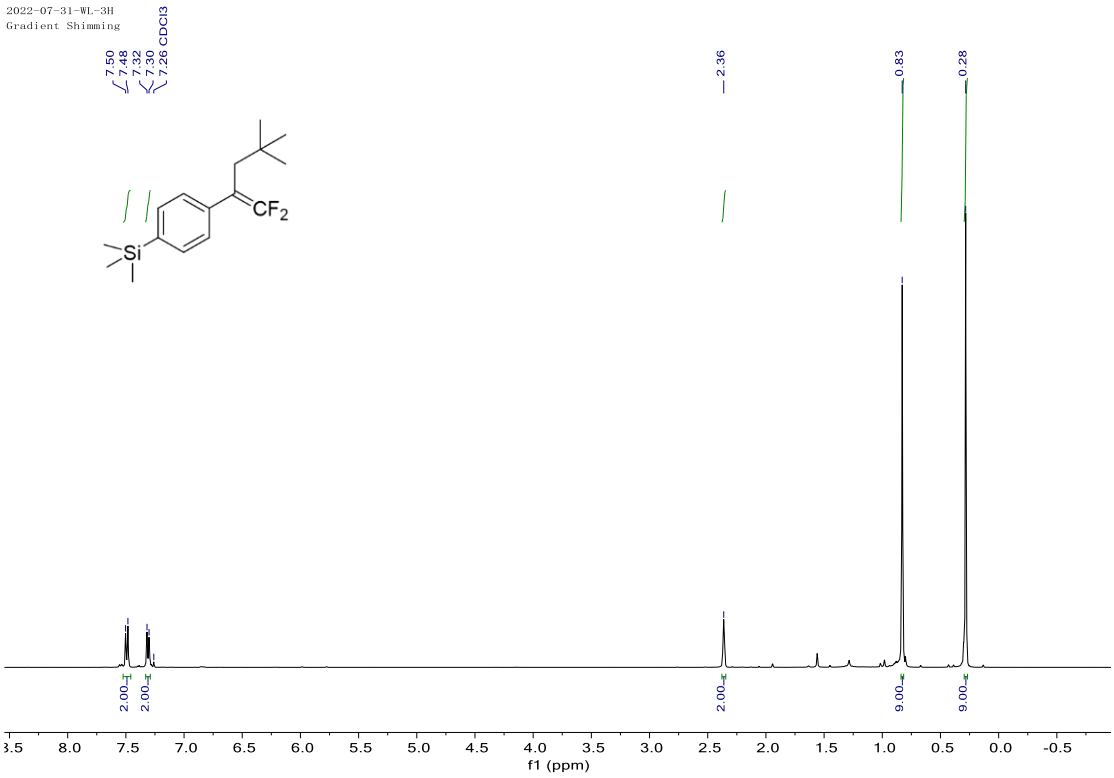


^{19}F NMR

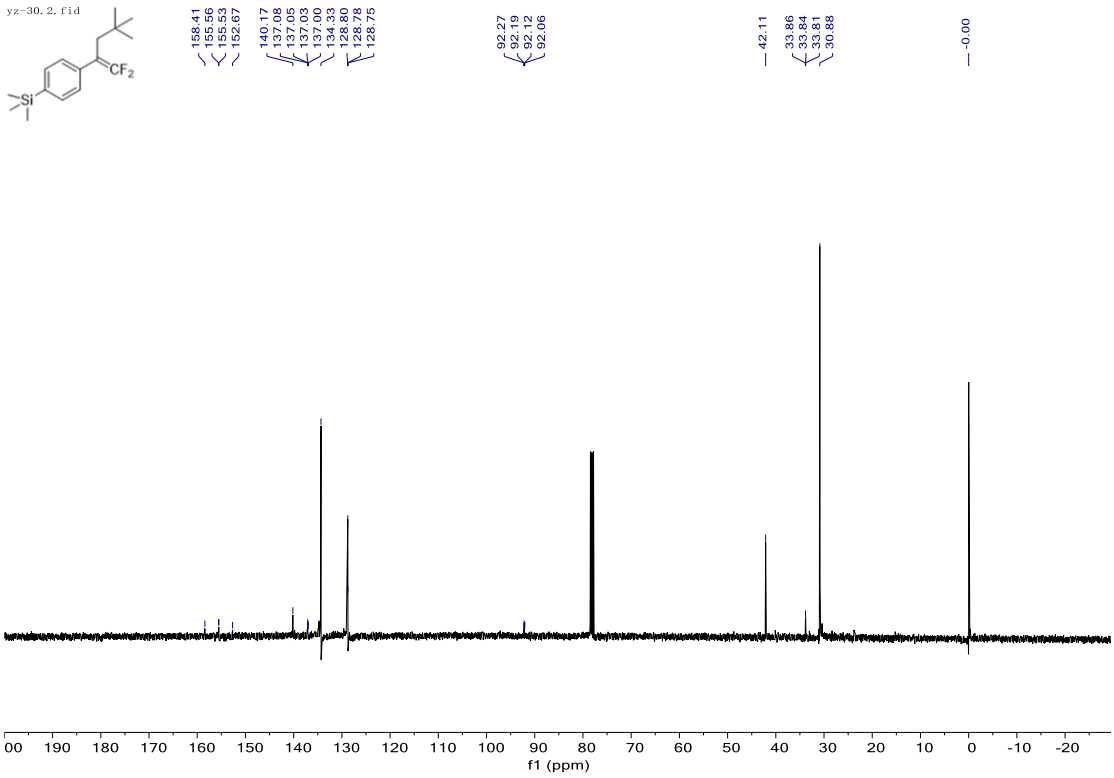

Sep07-2022-HuangXq-4-329-0304.1.fid
-89.56
-89.67
-92.17
-92.28
CF2
MeS
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)trimethylsilane（3ea）

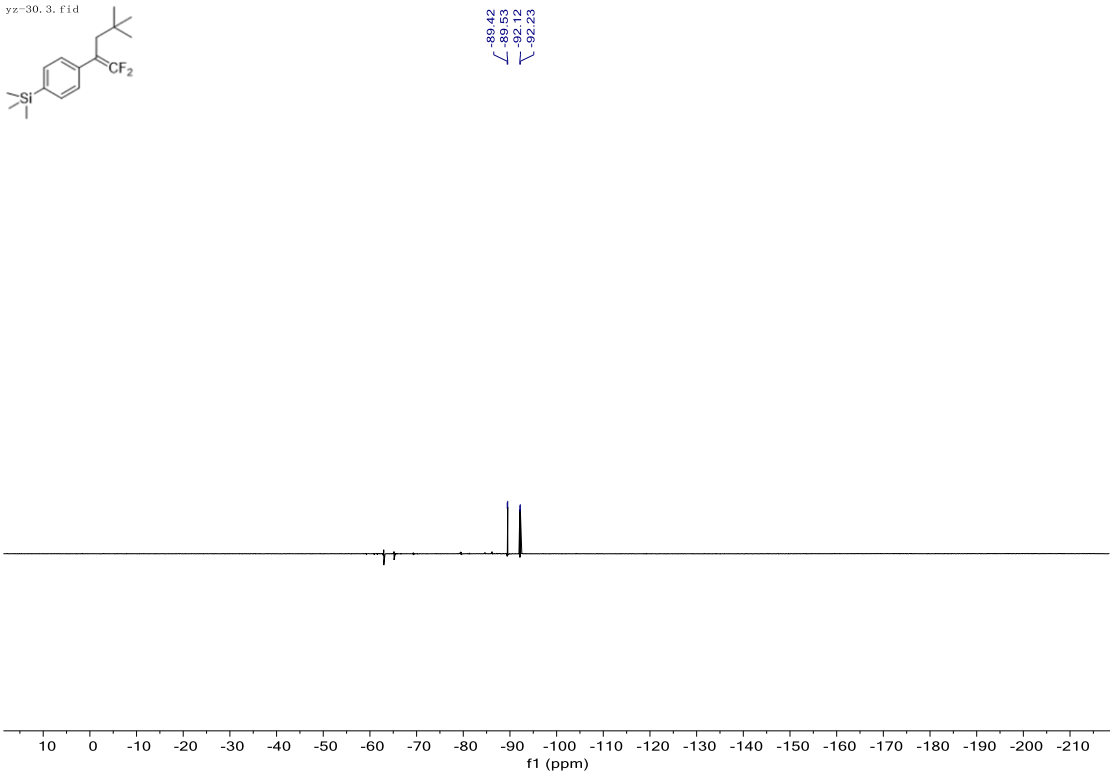
^{1}H NMR



^{13}C NMR

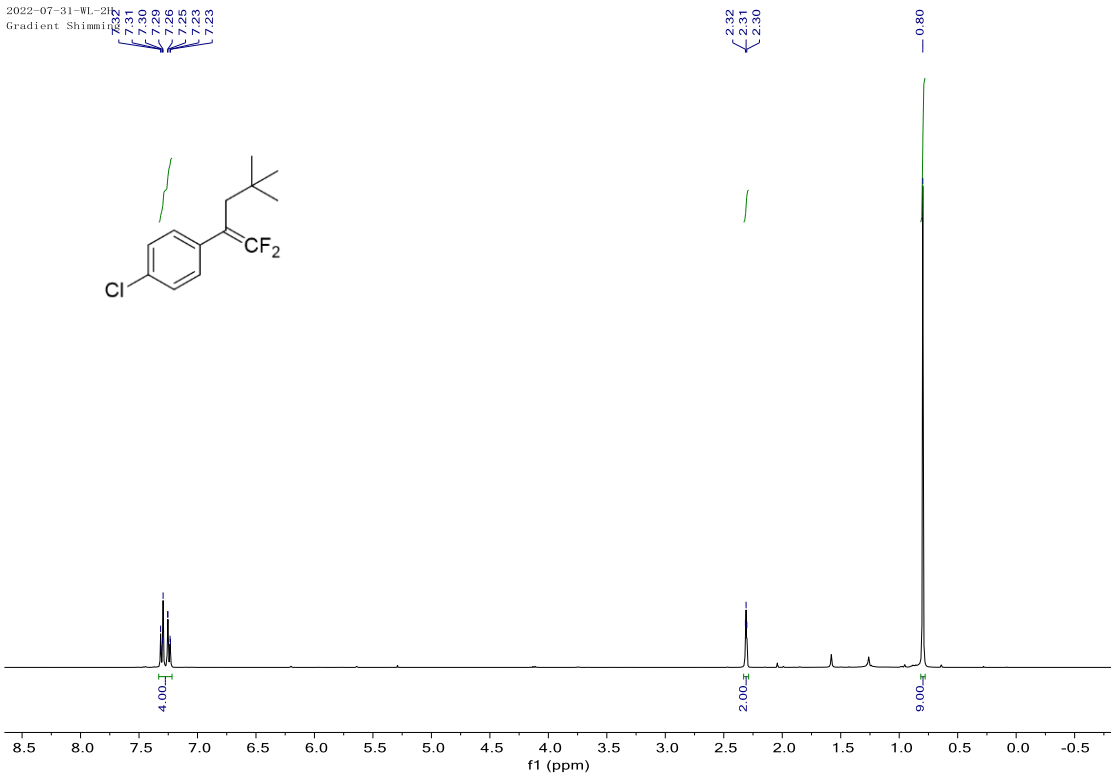


^{19}F NMR

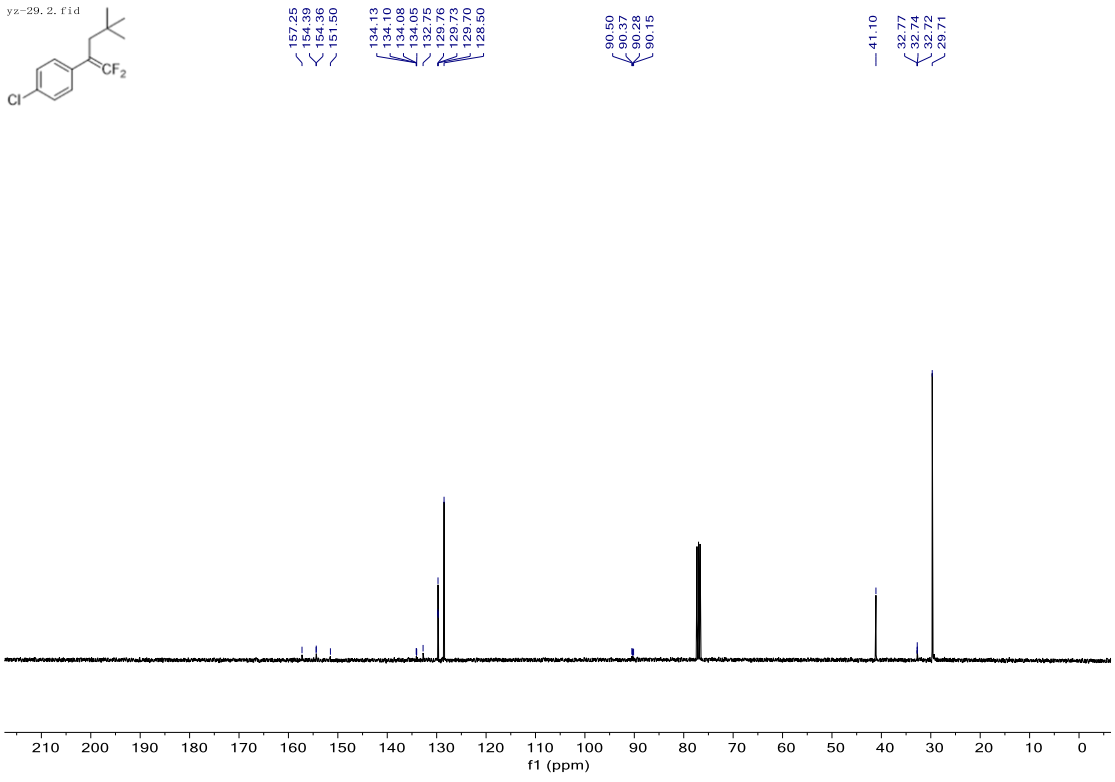

yz-30.3.fid
CF2
Si
-89.42
-89.53
-92.12
-92.23
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-chloro-4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (3fa)

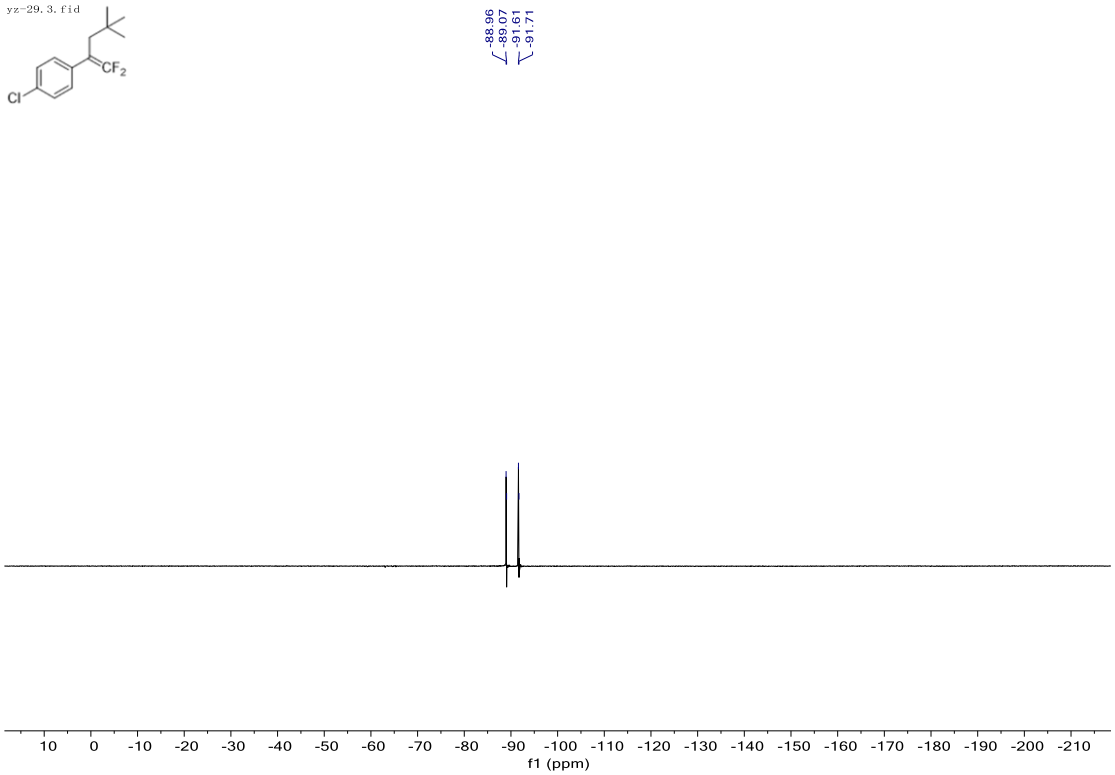
^{1}H NMR



^{13}C NMR



^{19}F NMR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Cl
CF2
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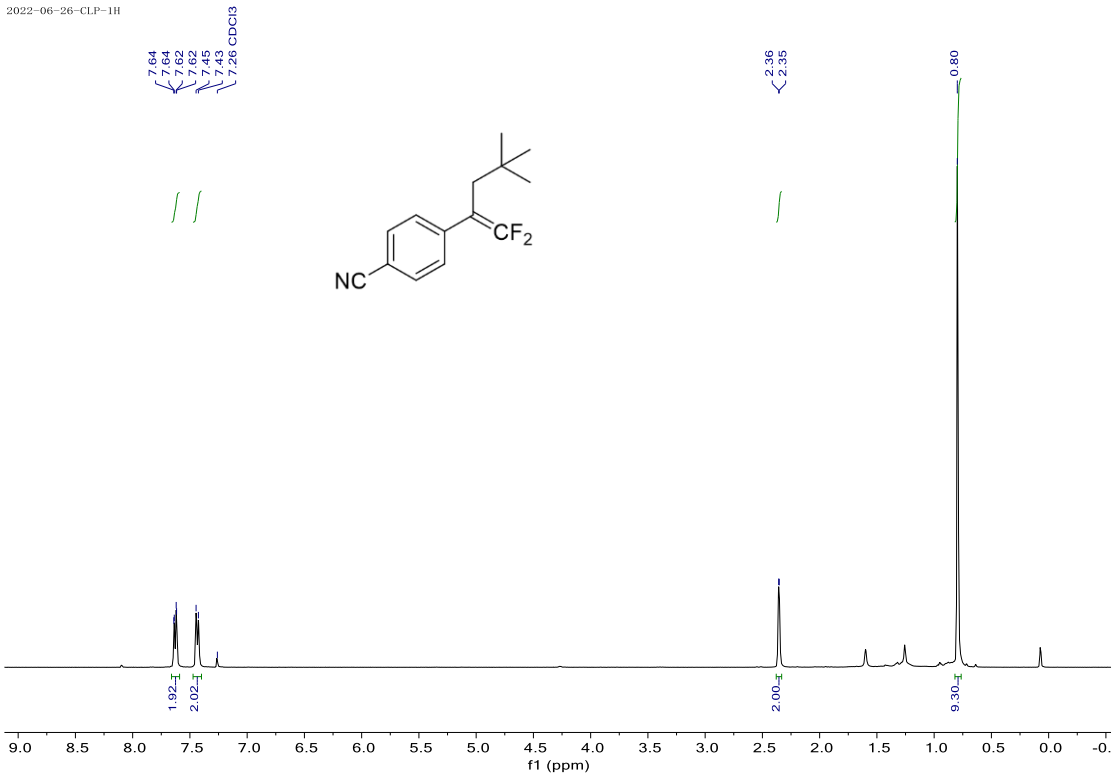
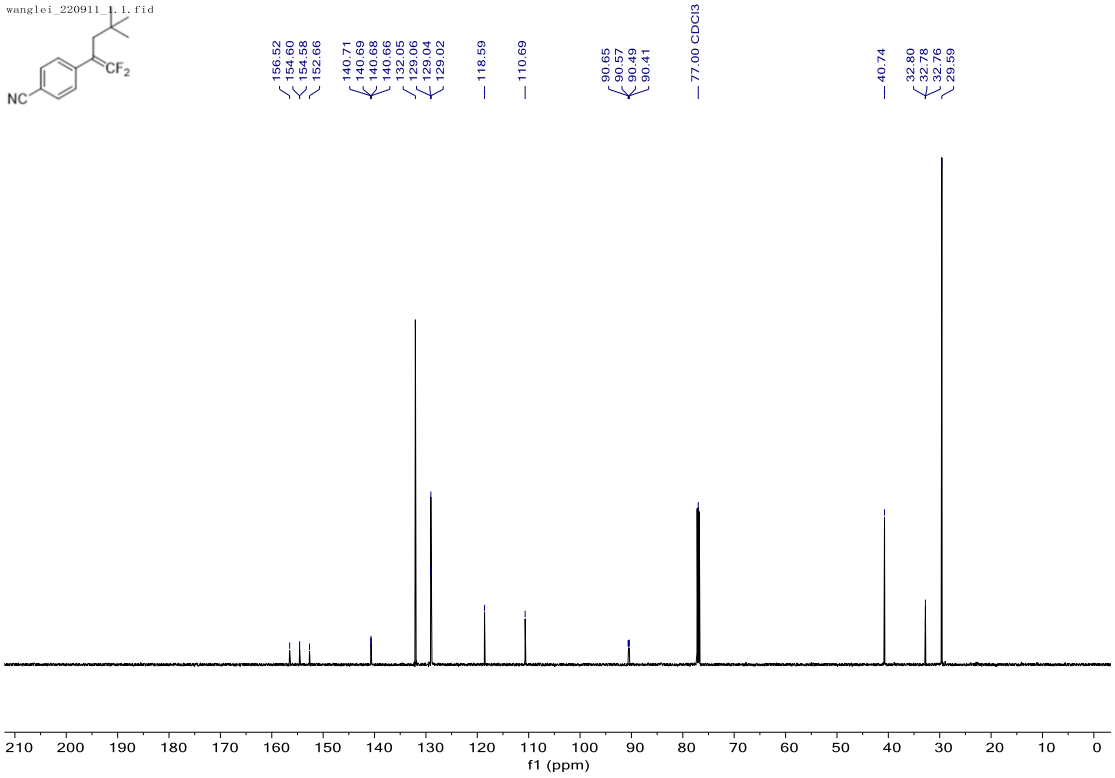
-89.07
-91.61
-91.71
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzonitrile（3ga）

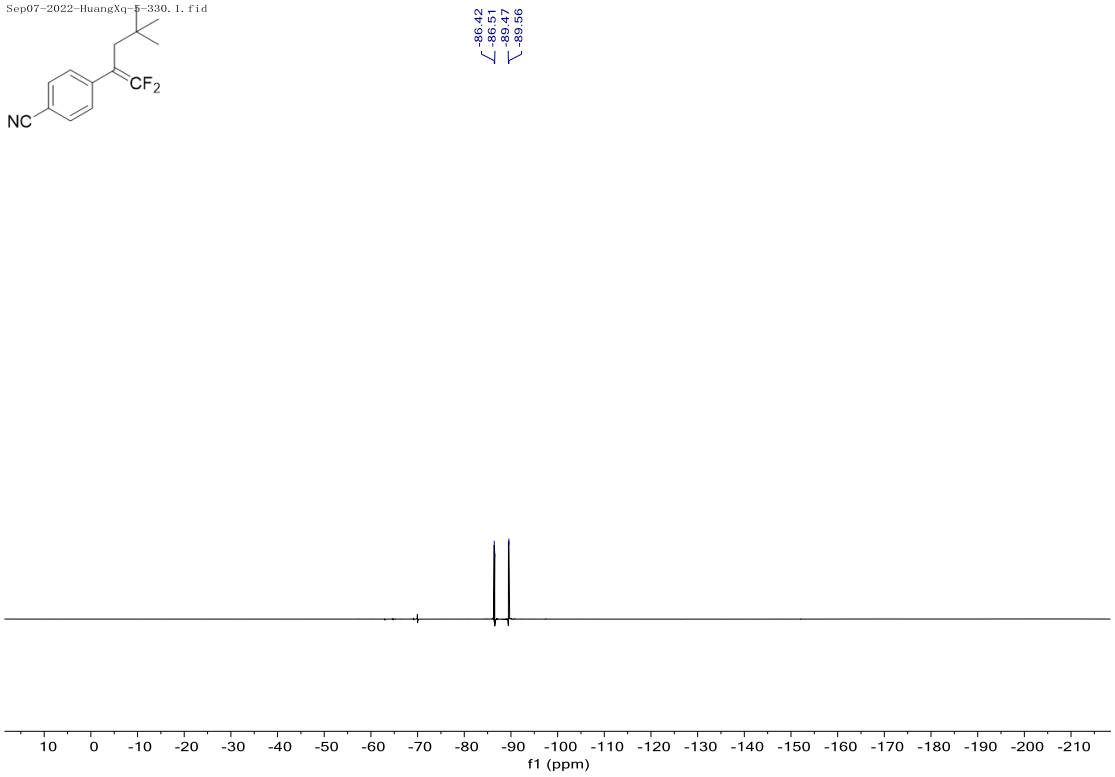
^{1}H NMR



^{13}C NMR



^{19}F NMR


Sep07-2022-HuangXq-5-330.1.fid
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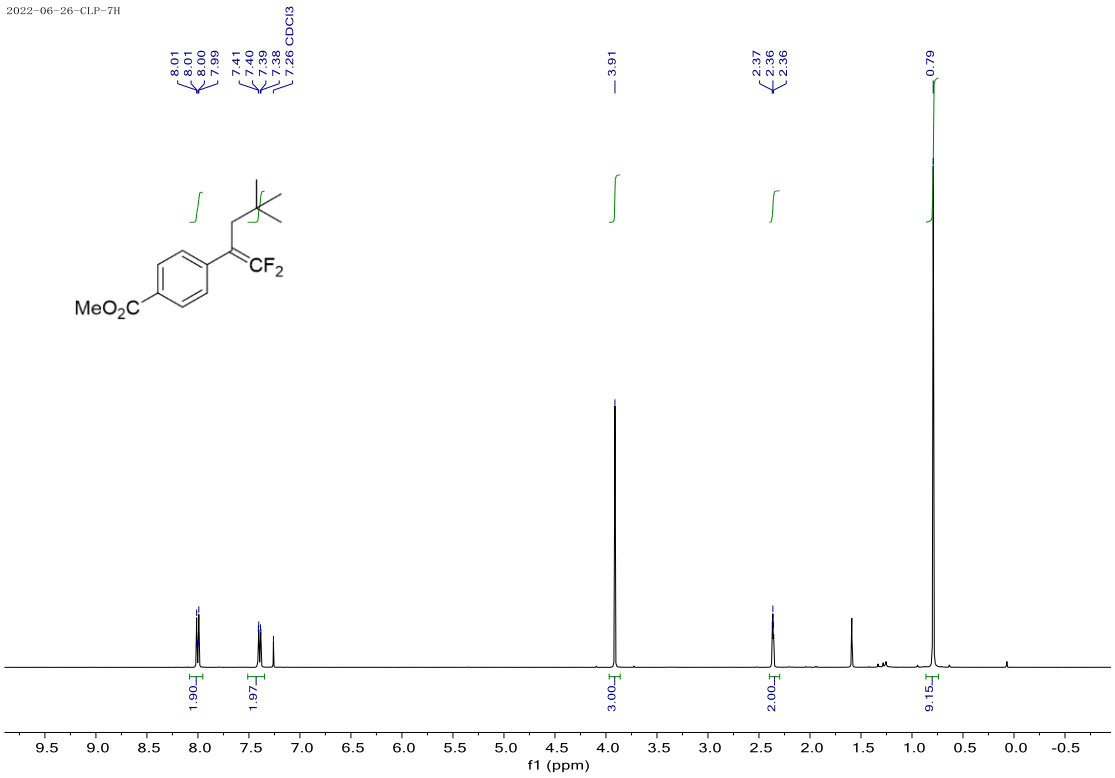
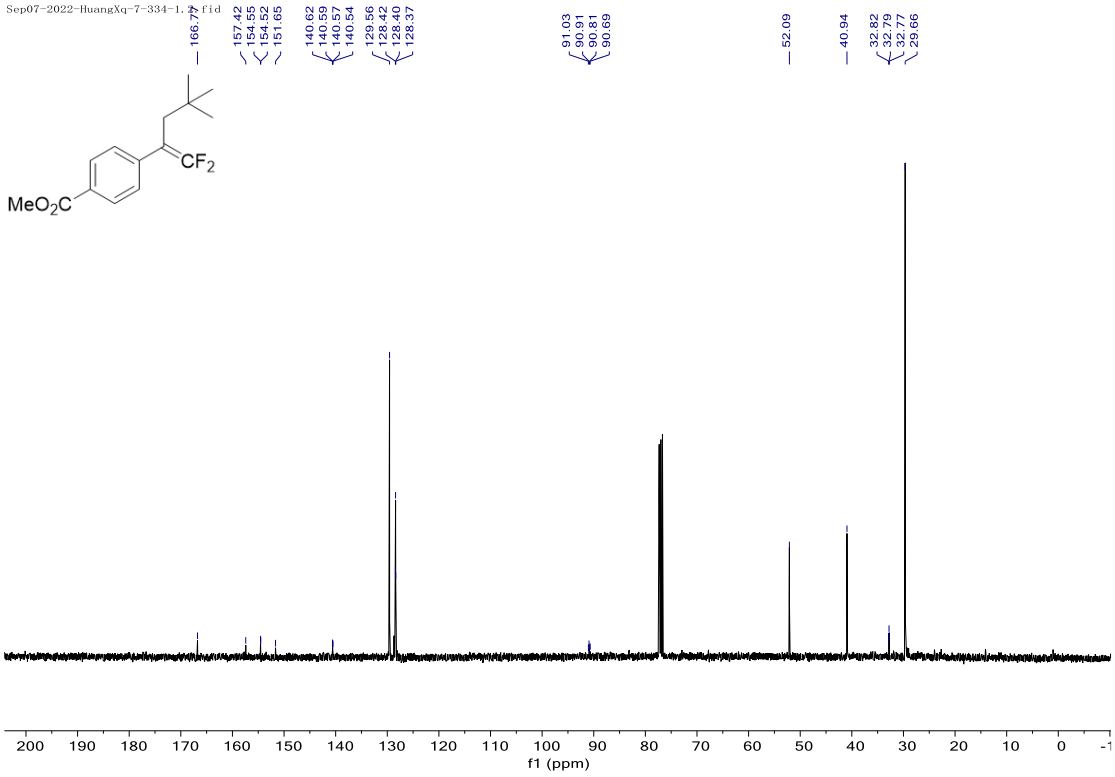
-89.47
-89.56
CF2
NC
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

methyl 4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzoate（3ha）

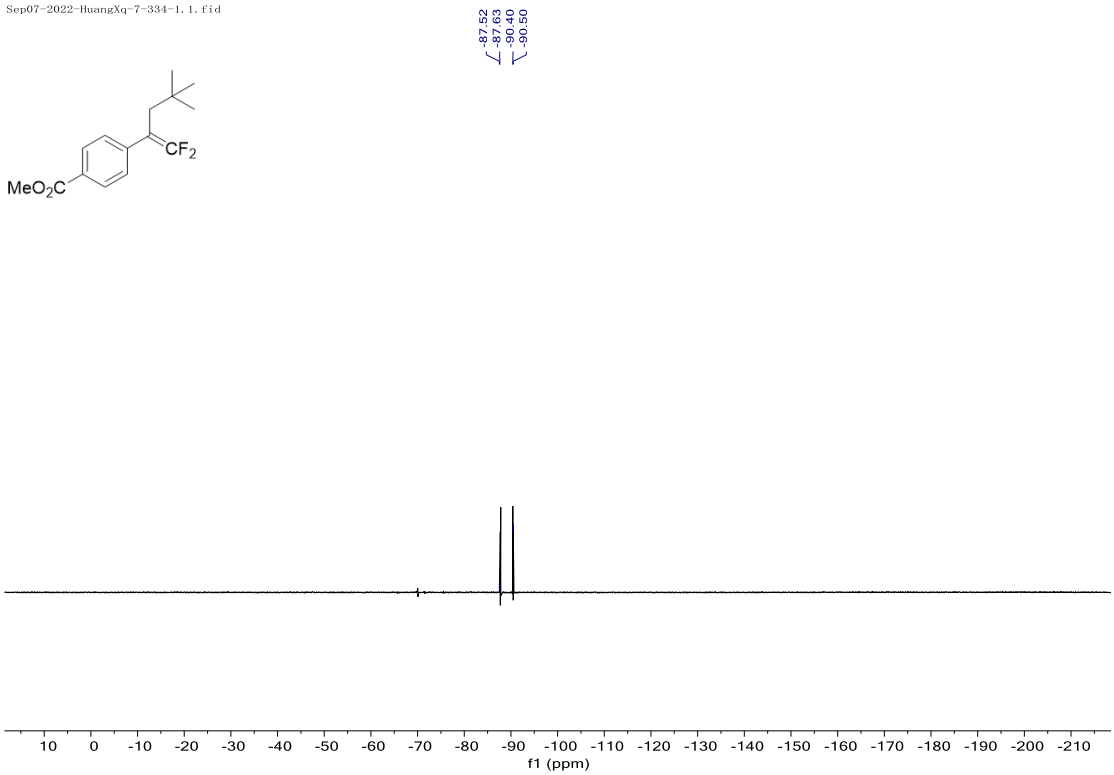
^{1}H NMR



^{13}C NMR



^{19}F NMR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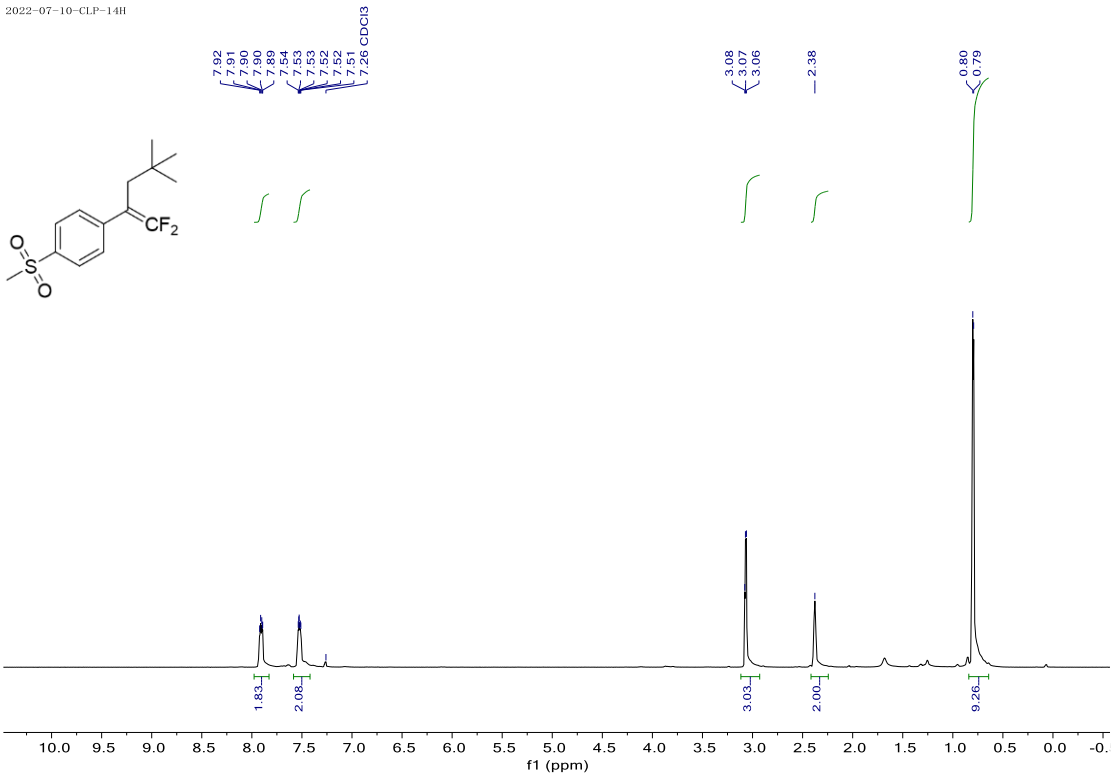
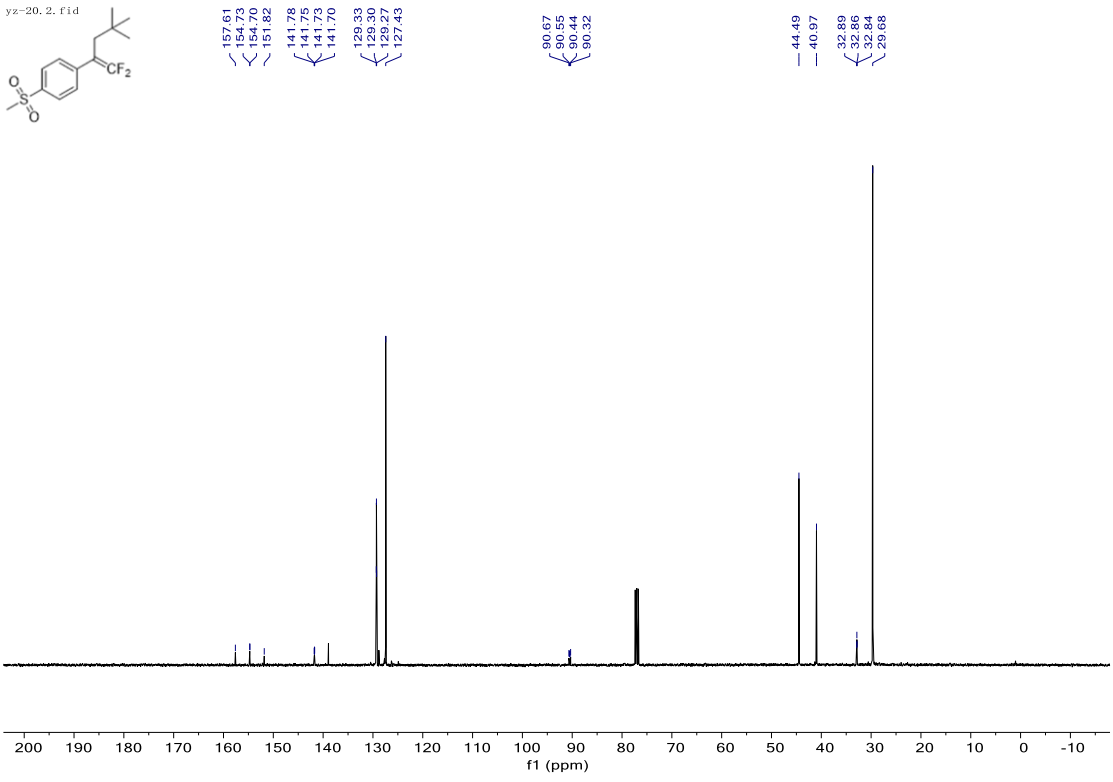
-87.52
-87.63
-90.40
-90.50
CF2
MeO2C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-4-(methylsulfonyl)benzene （3ia）

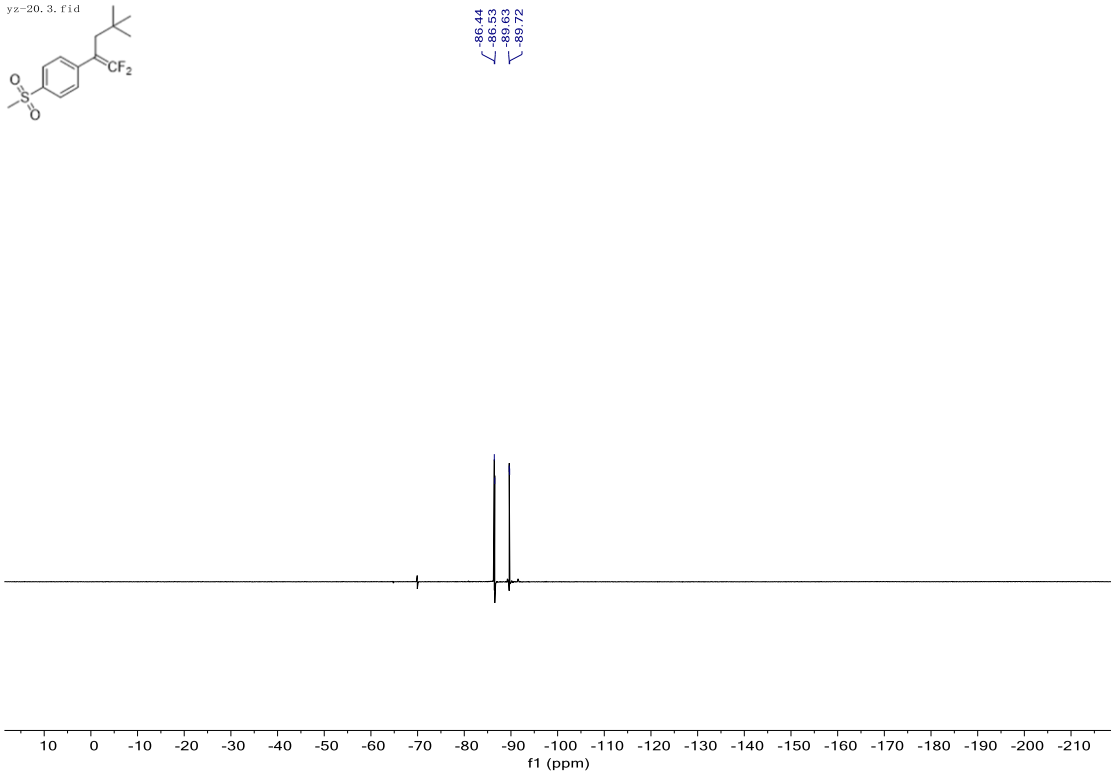
^{1}H NMR



^{13}C NMR

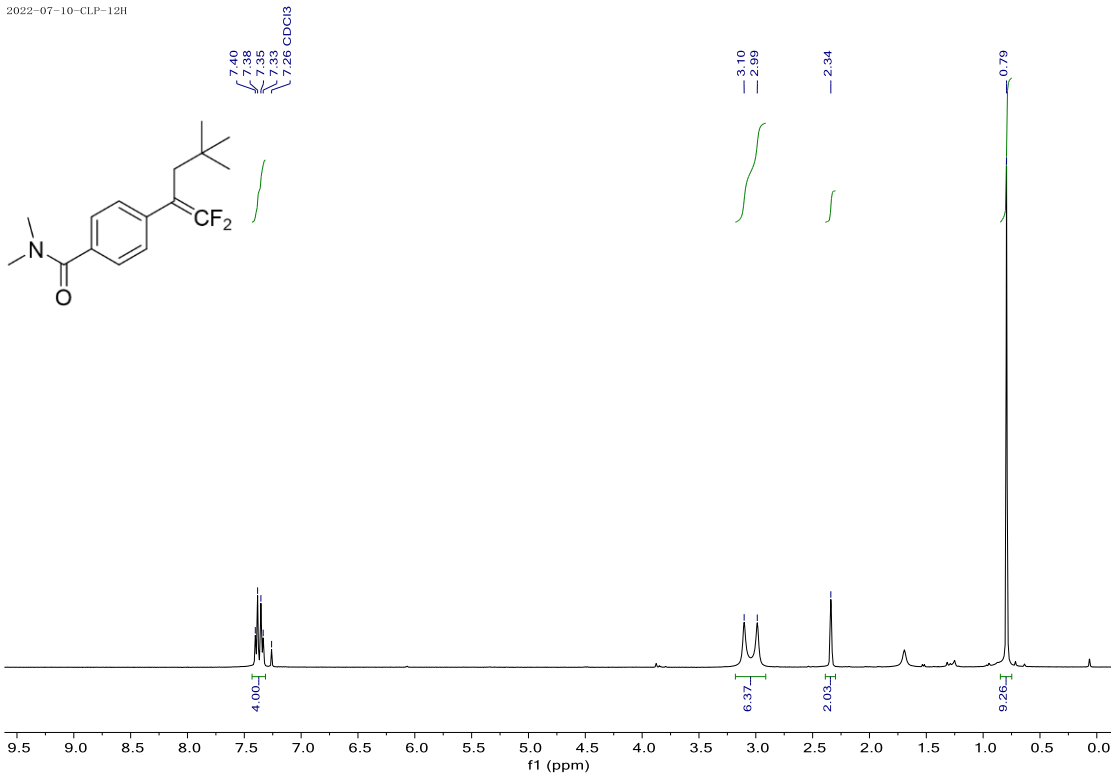


^{19}F NMR

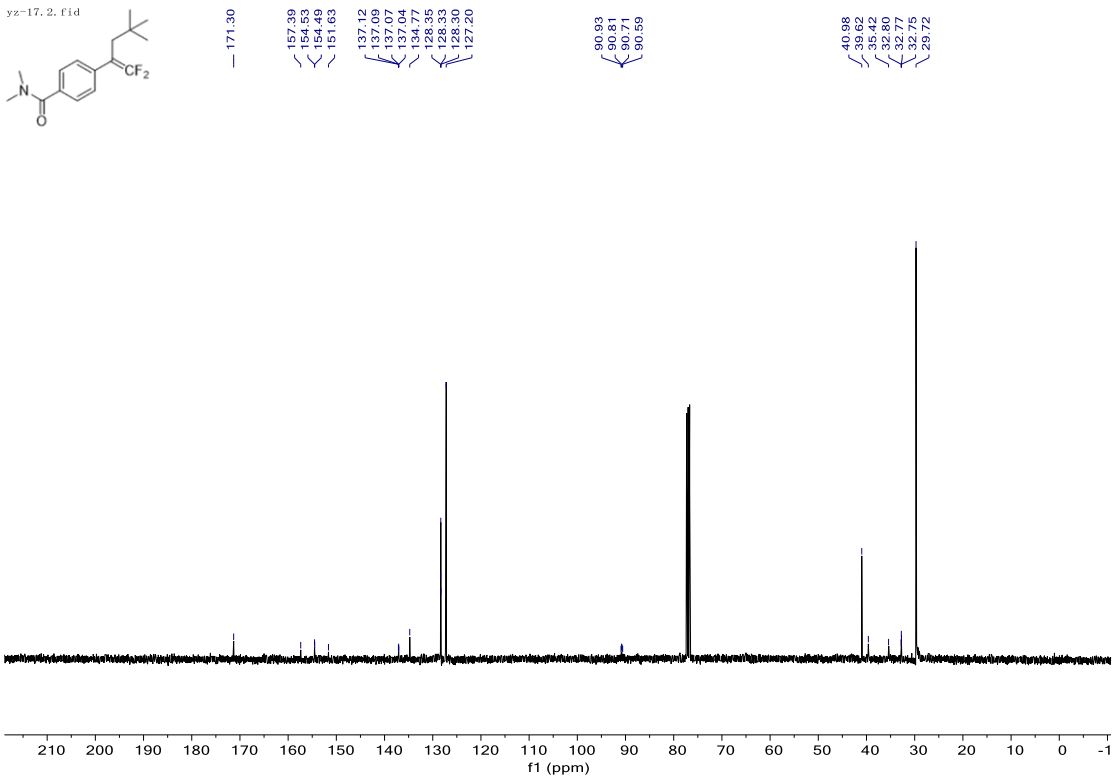

yz-20.3.fid
-86.44
-86.53
-89.63
-89.72
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-N,N-dimethylbenzamide (3ja)

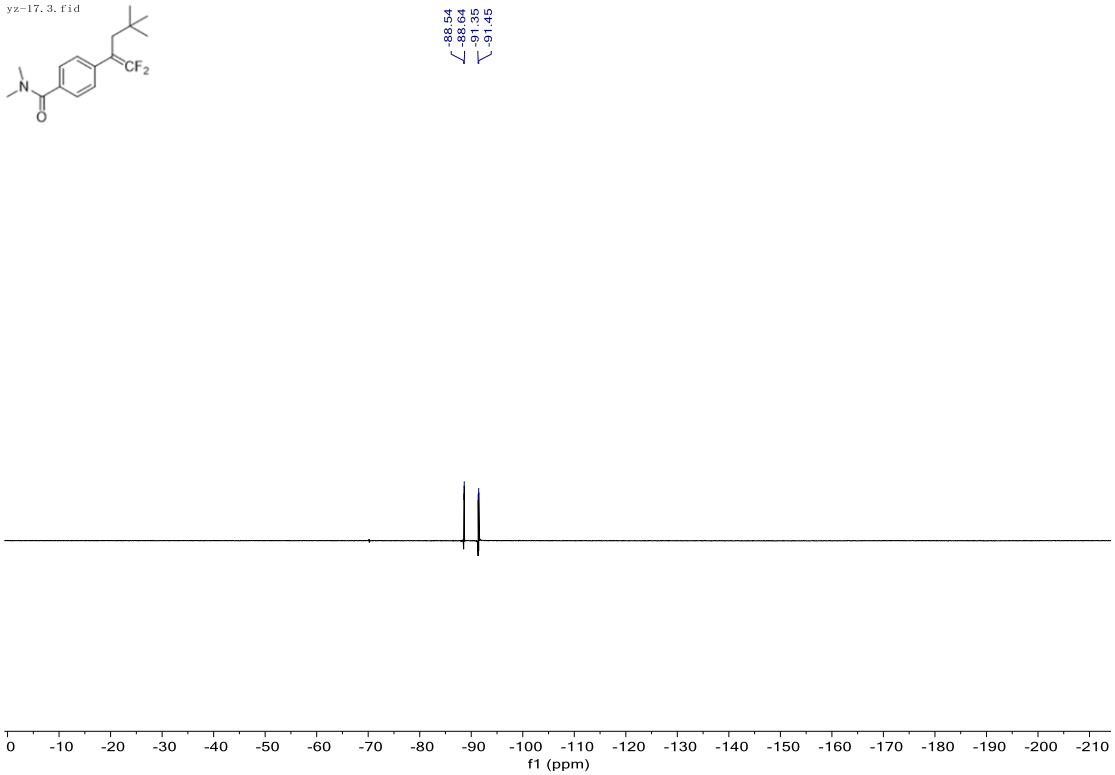
^{1}H NMR



^{13}C NMR

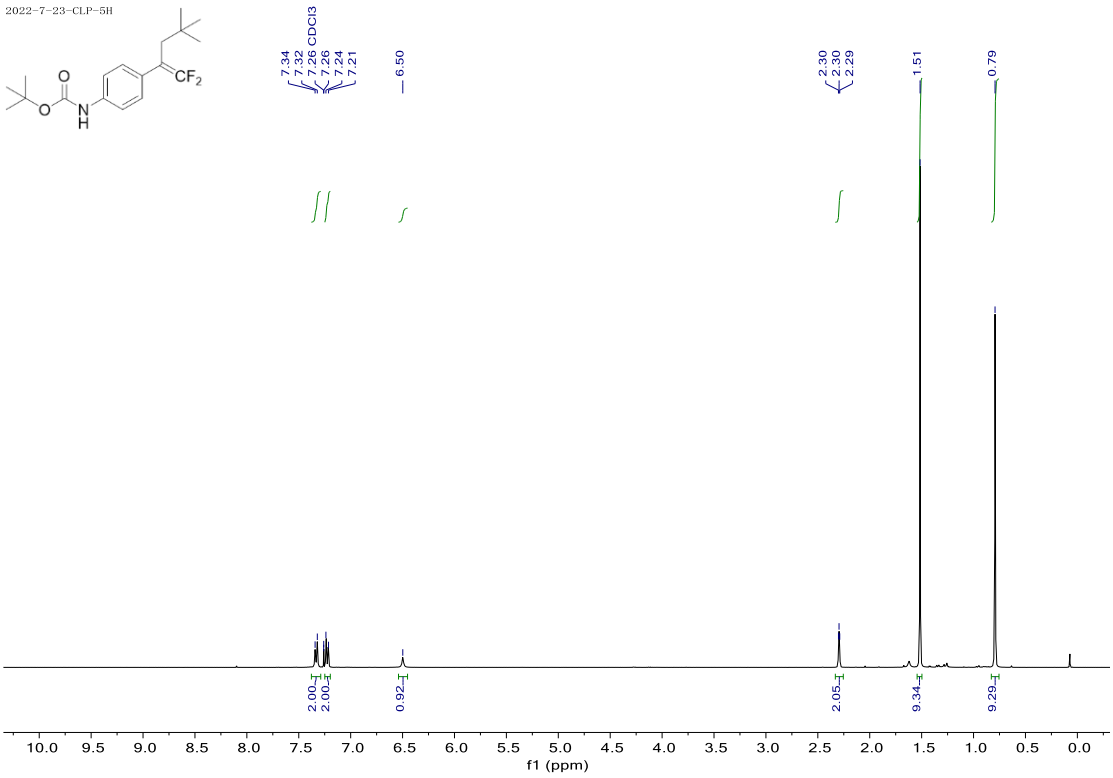


^{19}F NMR

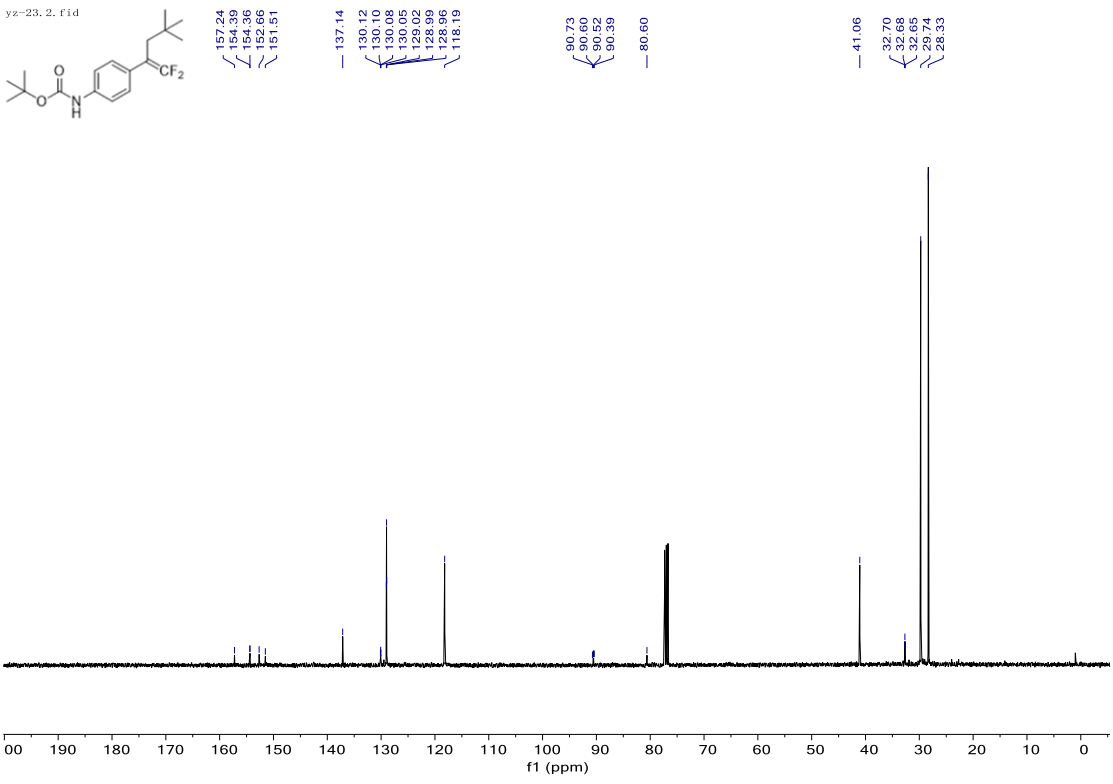

yz-17.3.fid
-88.54
-88.64
-91.35
-91.45
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

tert-butyl (4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)carbamate（3ka）

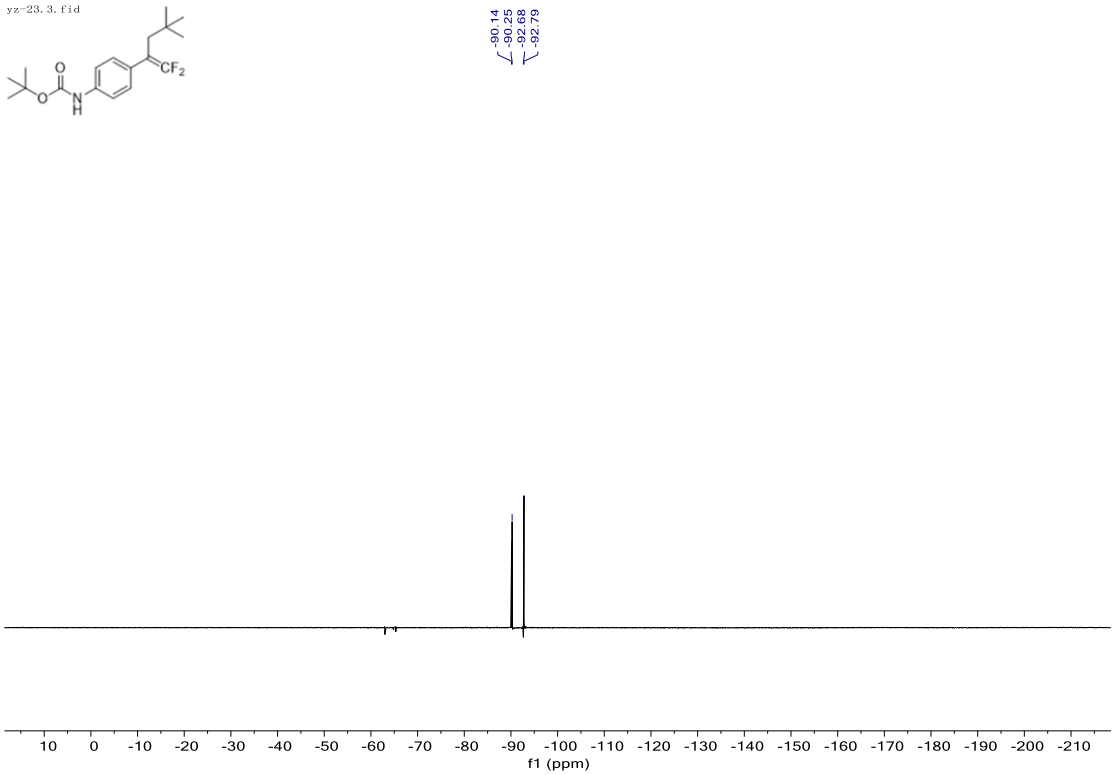
^{1}H NMR



^{13}C NMR



^{19}F NMR


yz-23.3.fid
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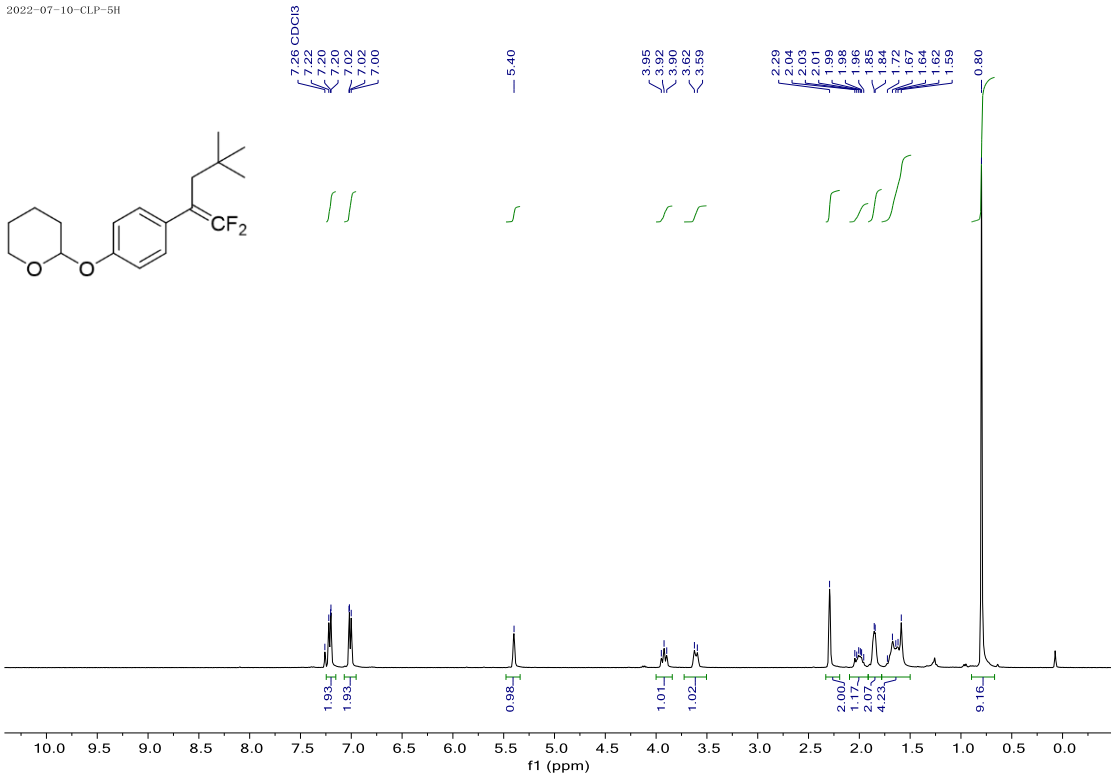
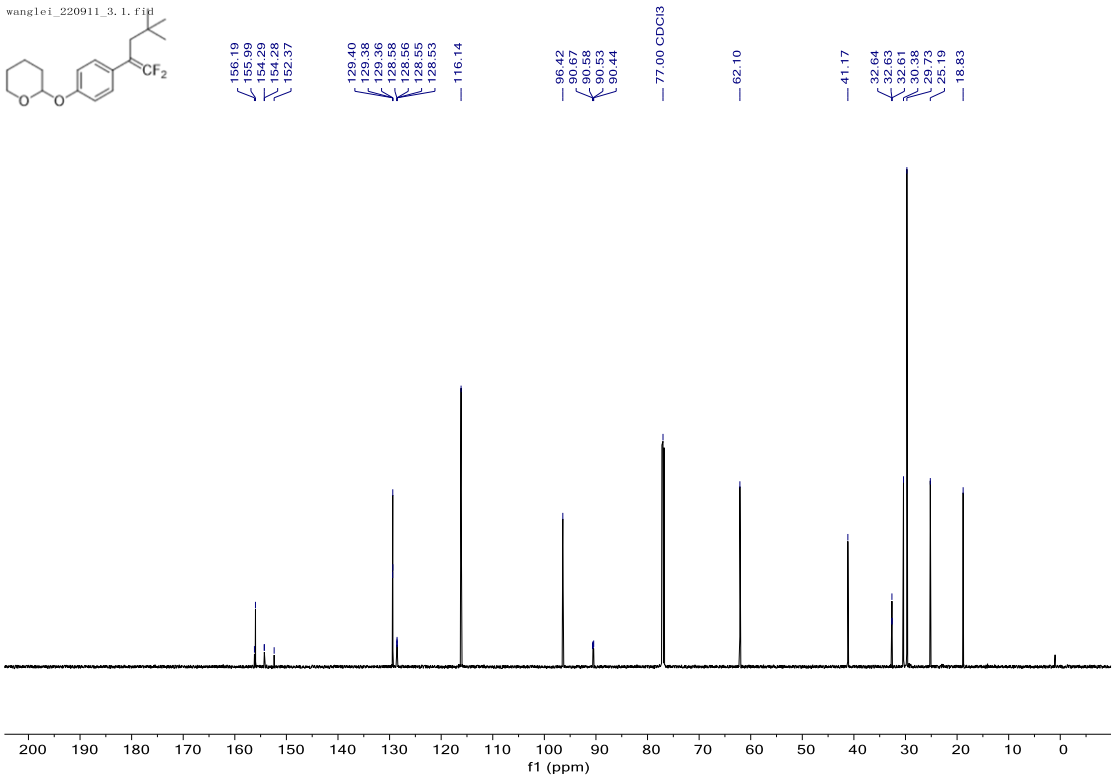
-90.25
-92.68
-92.79
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2-(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenoxy)tetrahydro-2H-pyran（3la）

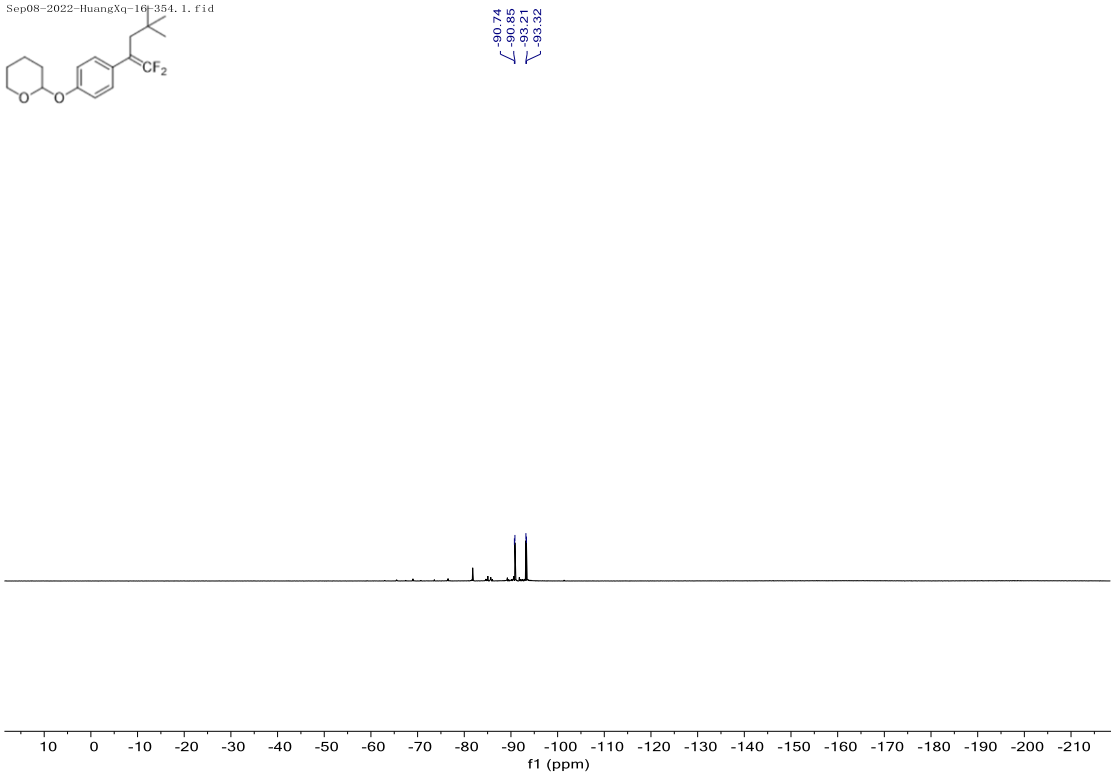
^{1}H NMR



^{13}C NMR

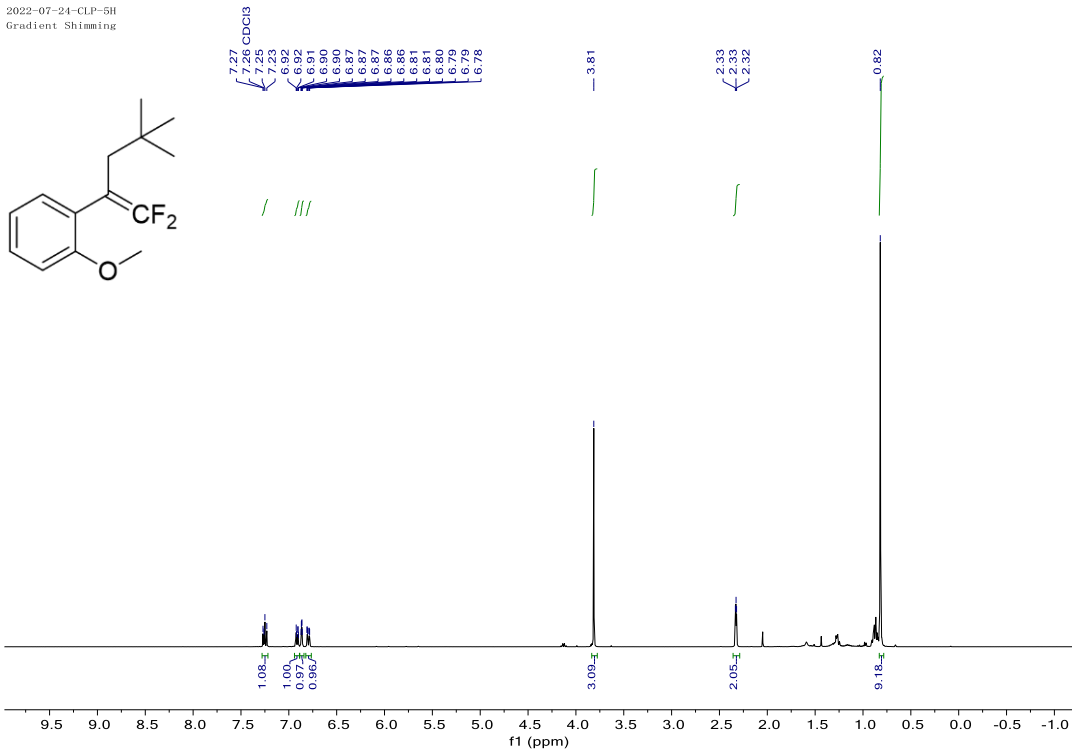


^{19}F NMR

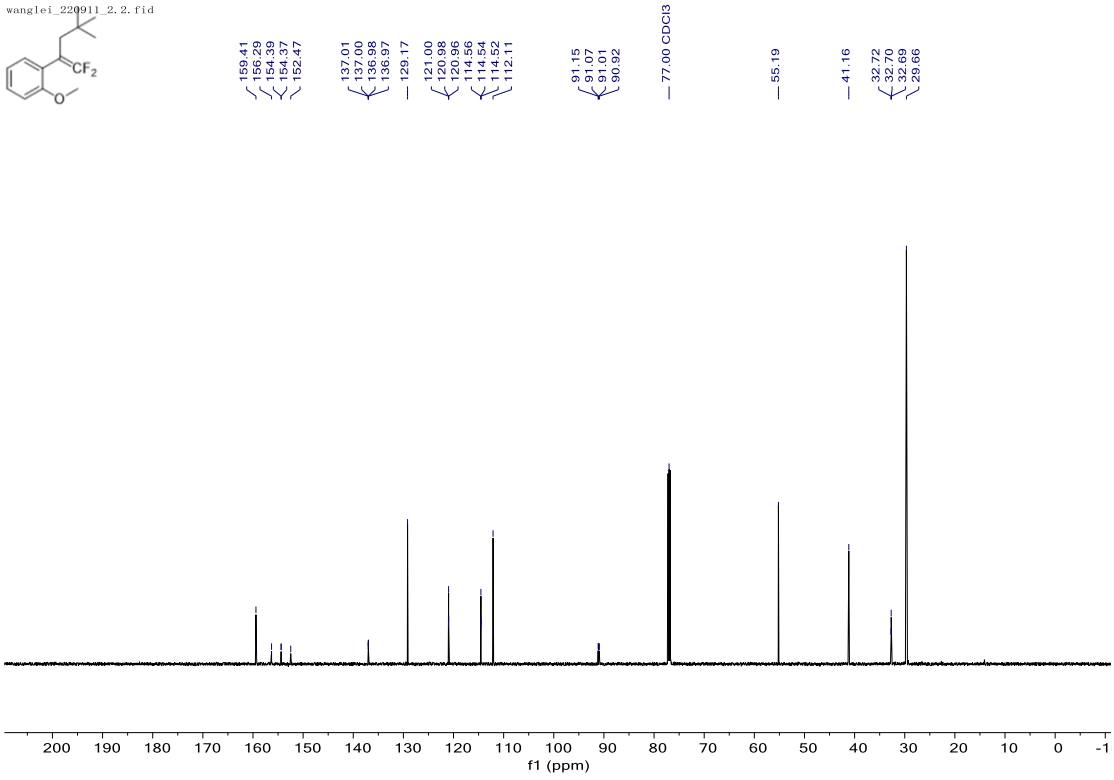

Sep08-2022-HuangXq-16-354.1.fid
-90.74
-90.85
-93.21
-93.32
CF2
O
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-2-methoxybenzene（3ma）

^{1}H NMR

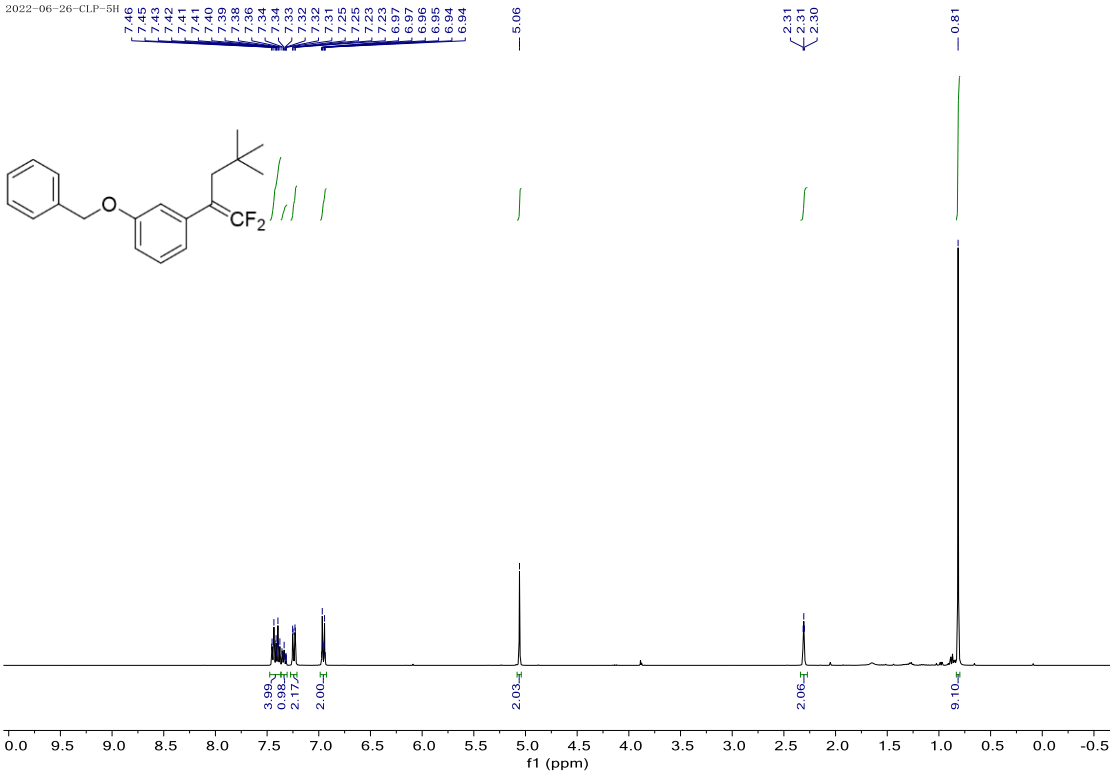


^{13}C NMR

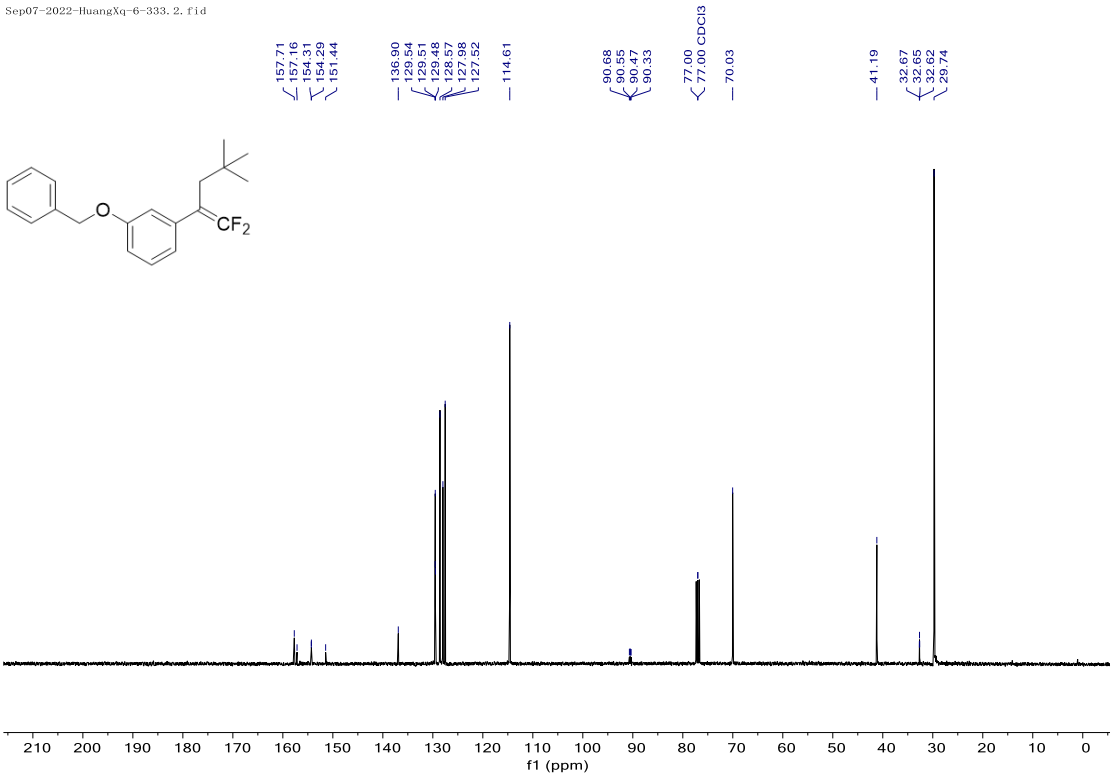


1-(benzyloxy)-3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)benzene (3na)

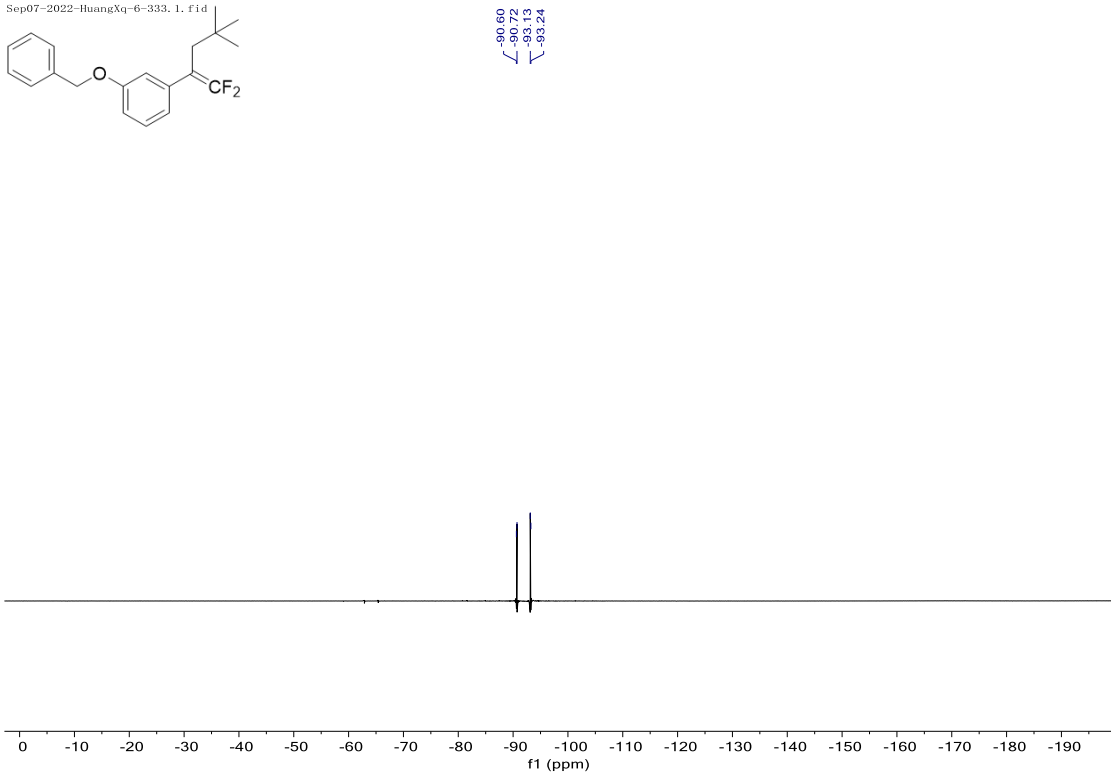
^{1}H NMR



^{13}C NMR

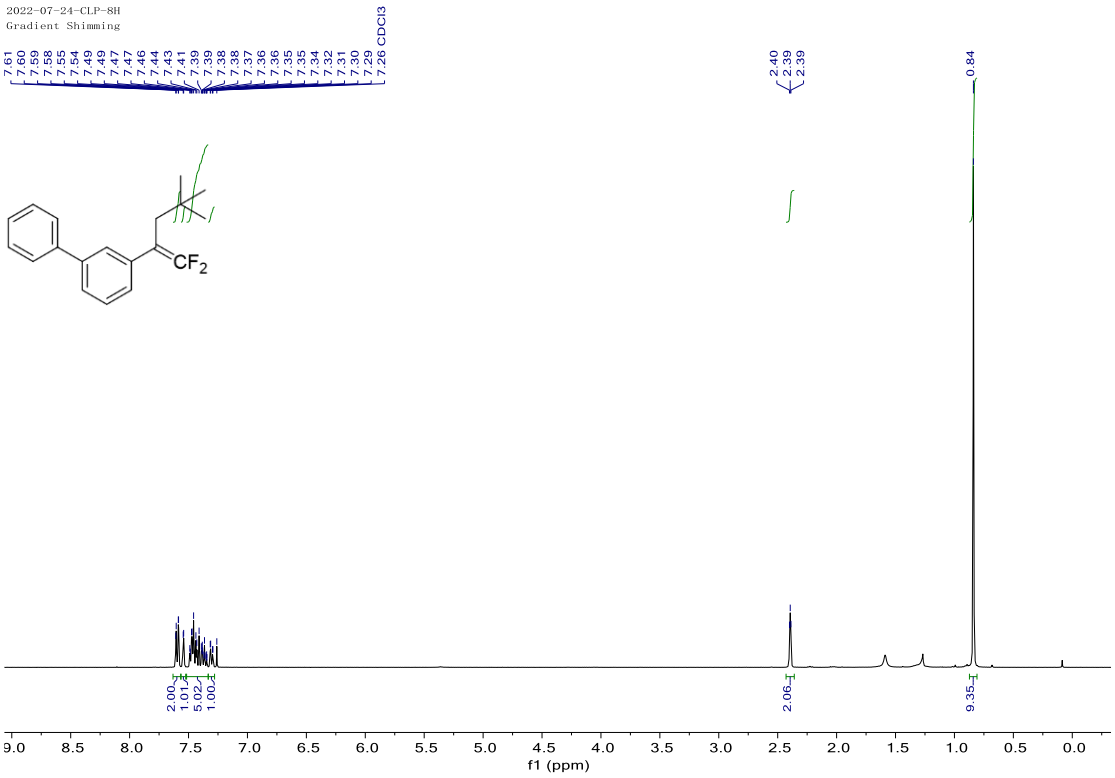


^{19}F NMR

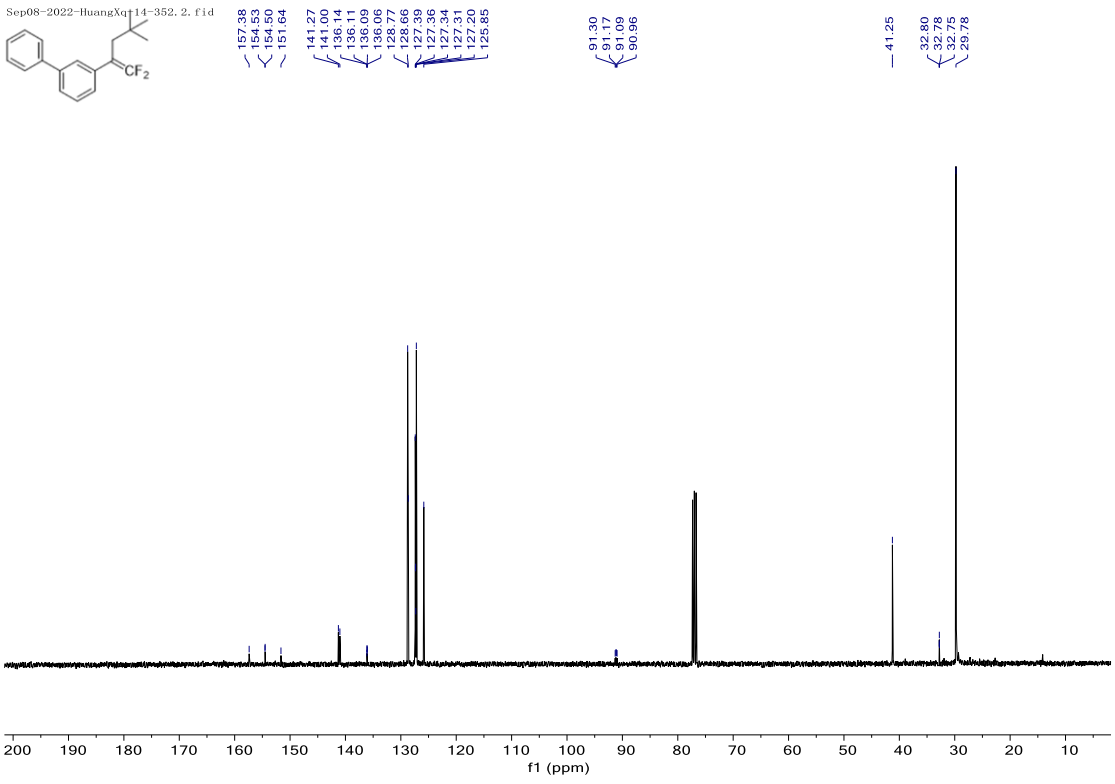

Sep07-2022-HuangXq-6-333.1.fid
-90.60
-90.72
-93.13
-93.24
O
CF2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3oa）

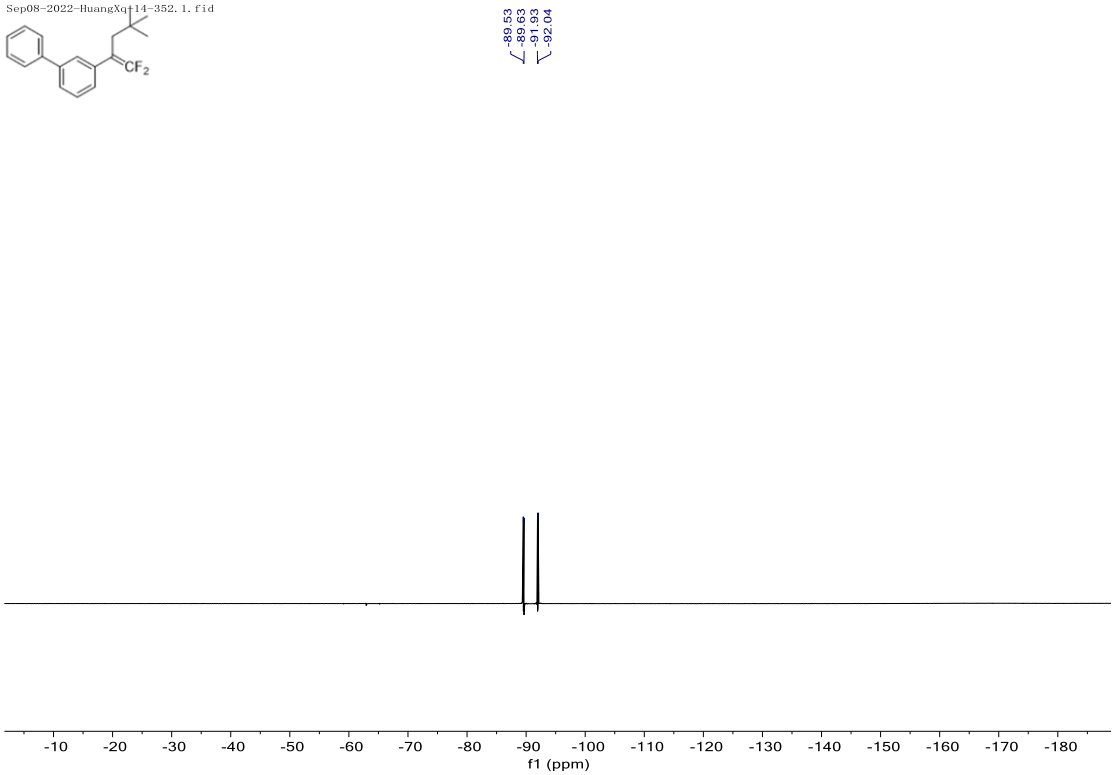
^{1}H NMR



^{13}C NMR

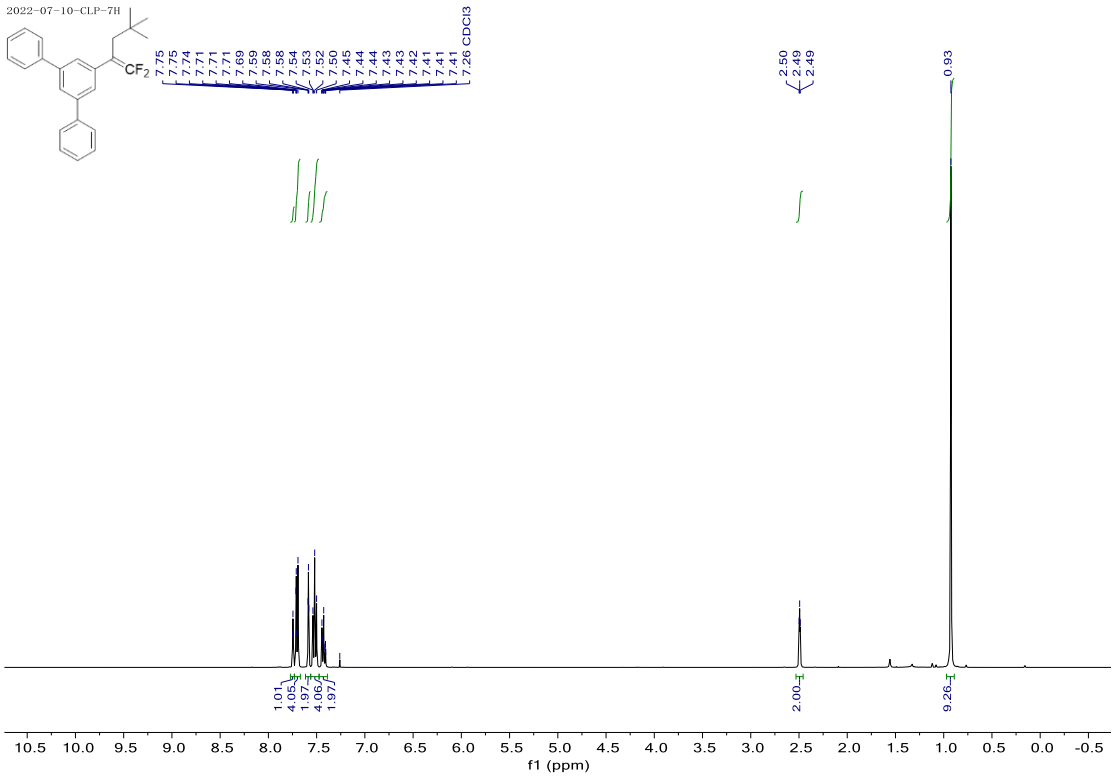


^{19}F NMR

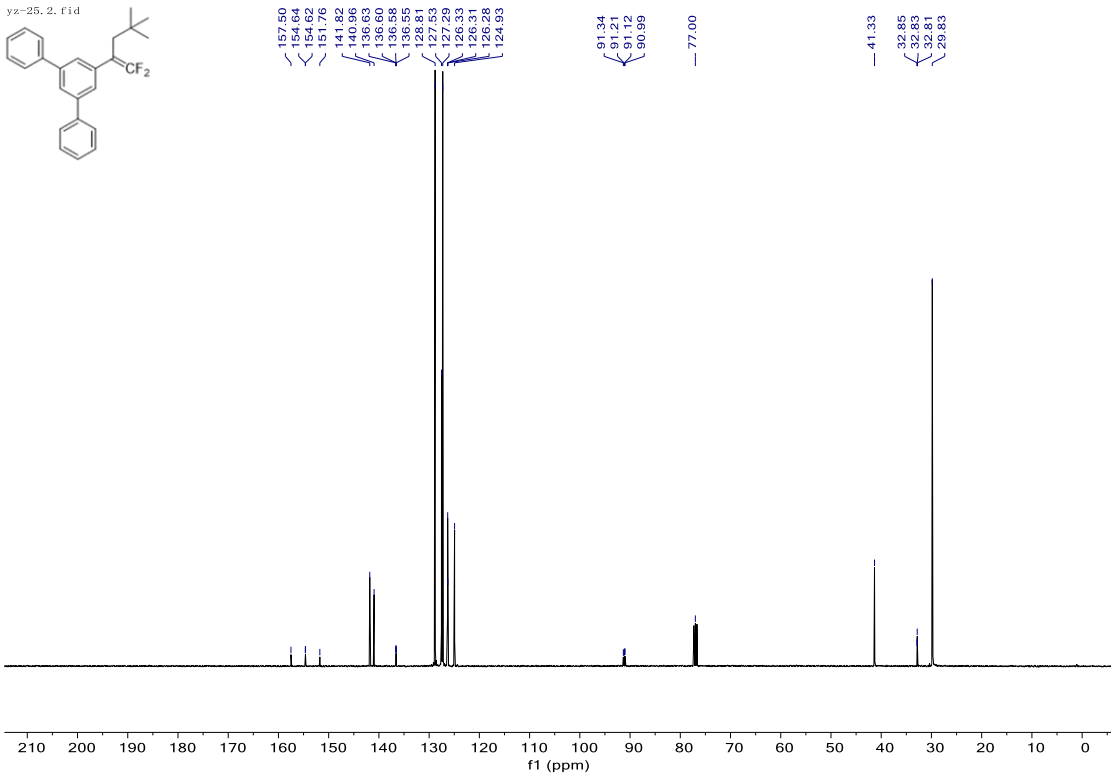

Sep08-2022-HuangXq-14-352.1.fid
CF2
-89.53
-89.63
-91.93
-92.04
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

5'-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1':3',1''-terphenyl（3pa）

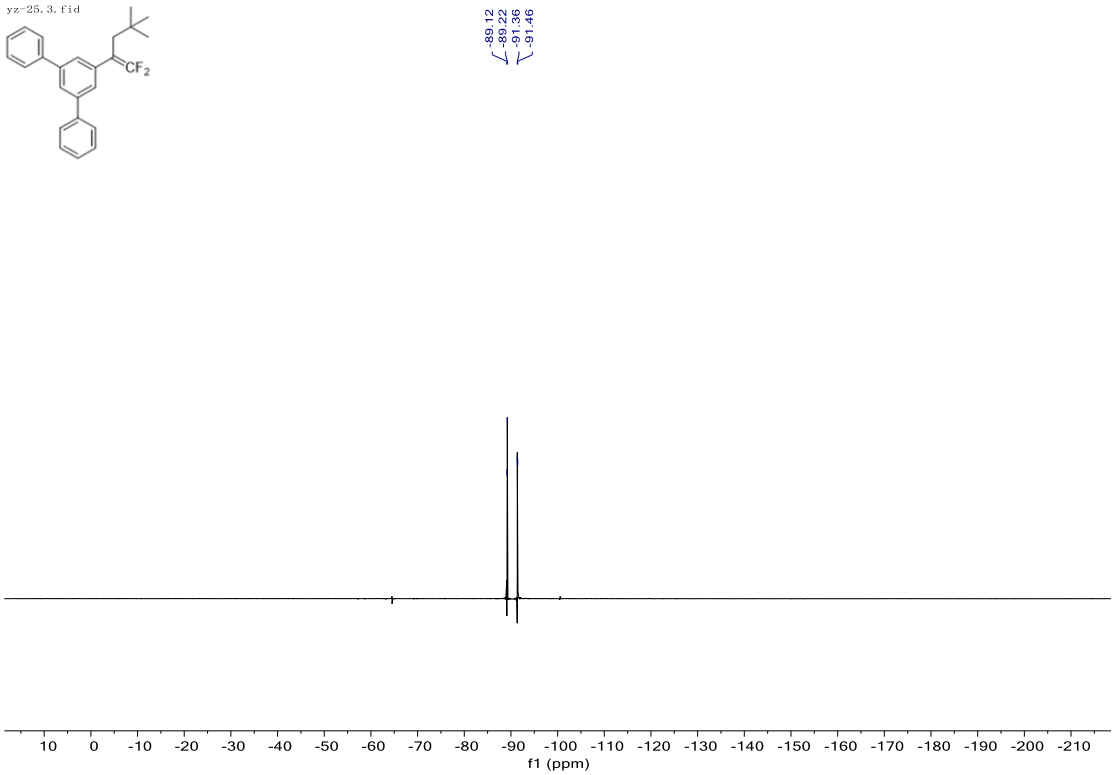
^{1}H NMR



^{13}C NMR

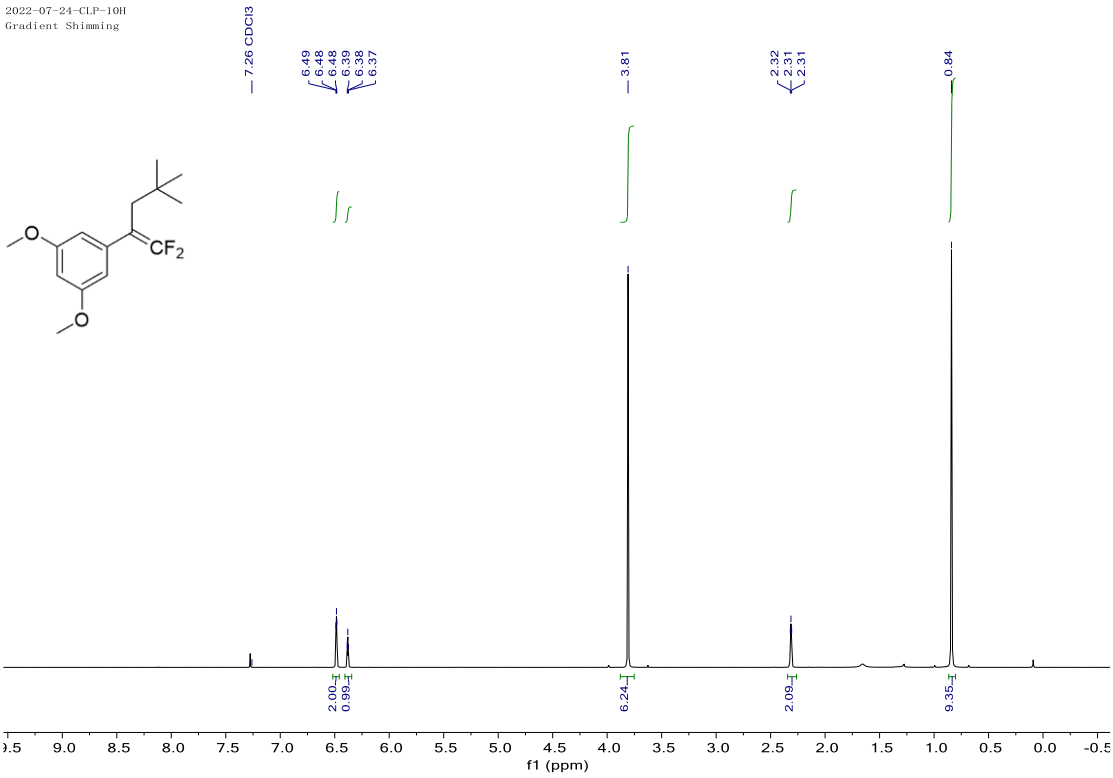


^{19}F NMR

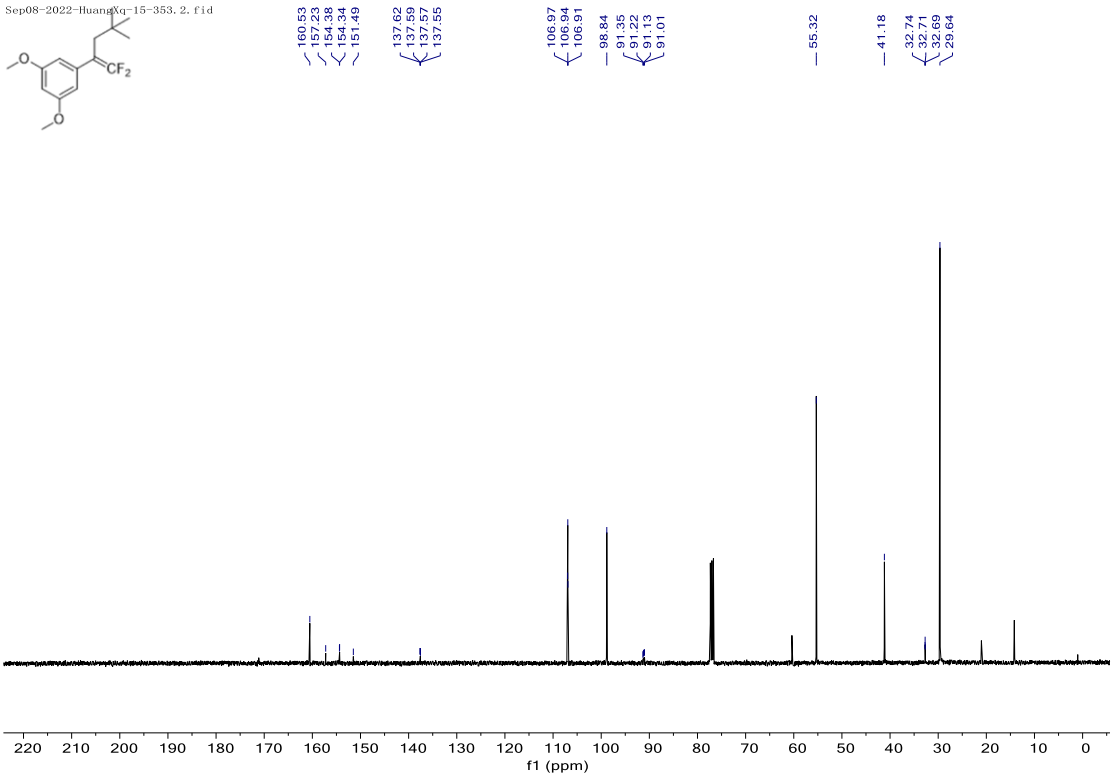

yz-25.3.fid
CF2
-89.12
-89.22
-91.36
-91.46
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-3,5-dimethoxybenzene（3qa）

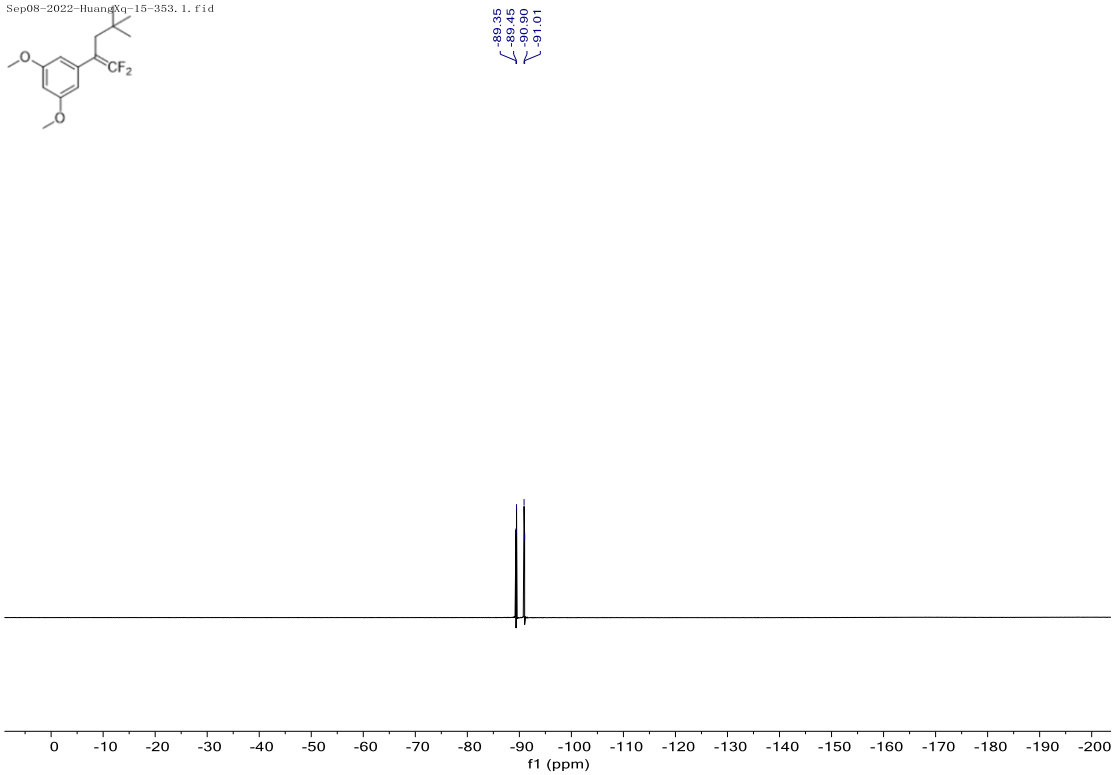
^{1}H NMR



^{13}C NMR

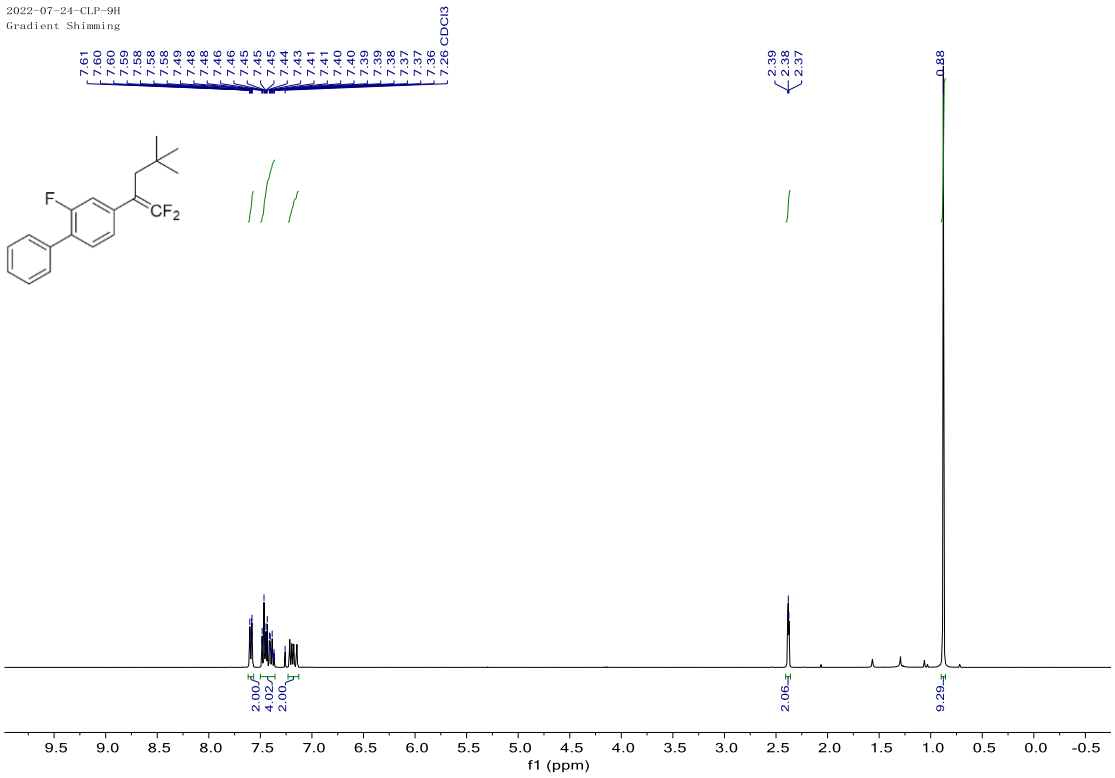


^{19}F NMR

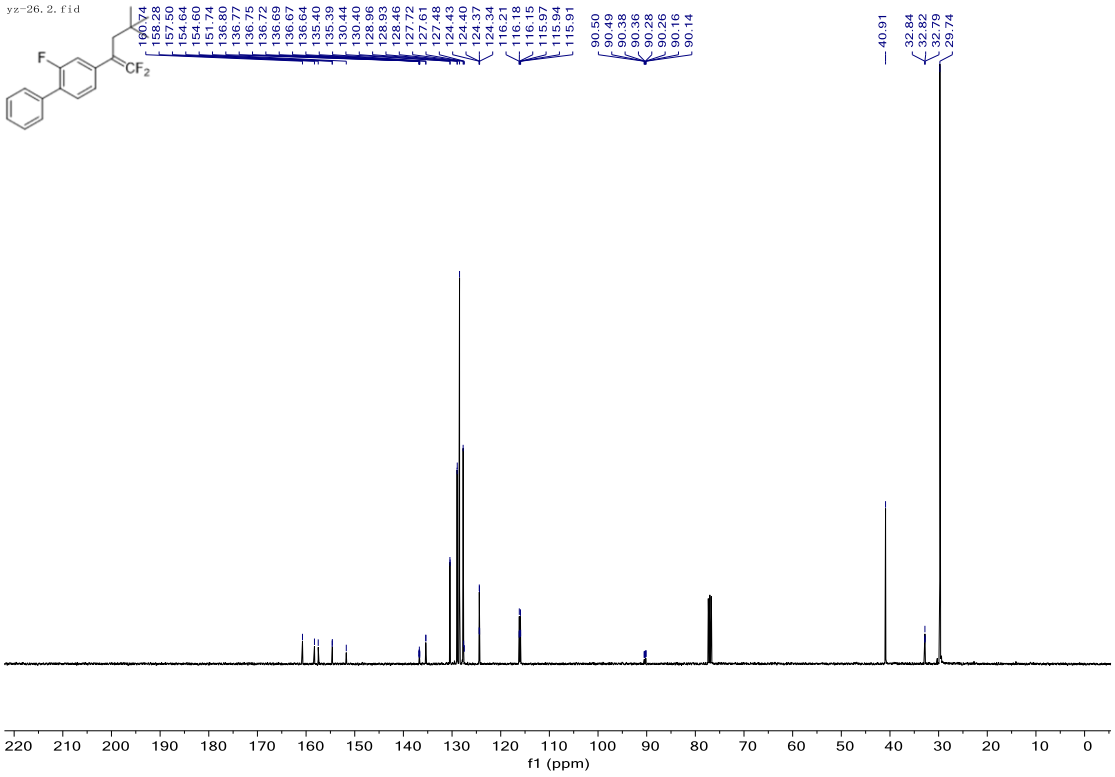

Sep08-2022-HuangXq-15-353.1.fid
-89.35
-89.45
-90.90
-91.01
O
O
CF2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-2-fluoro-1,1'-biphenyl（3ra）

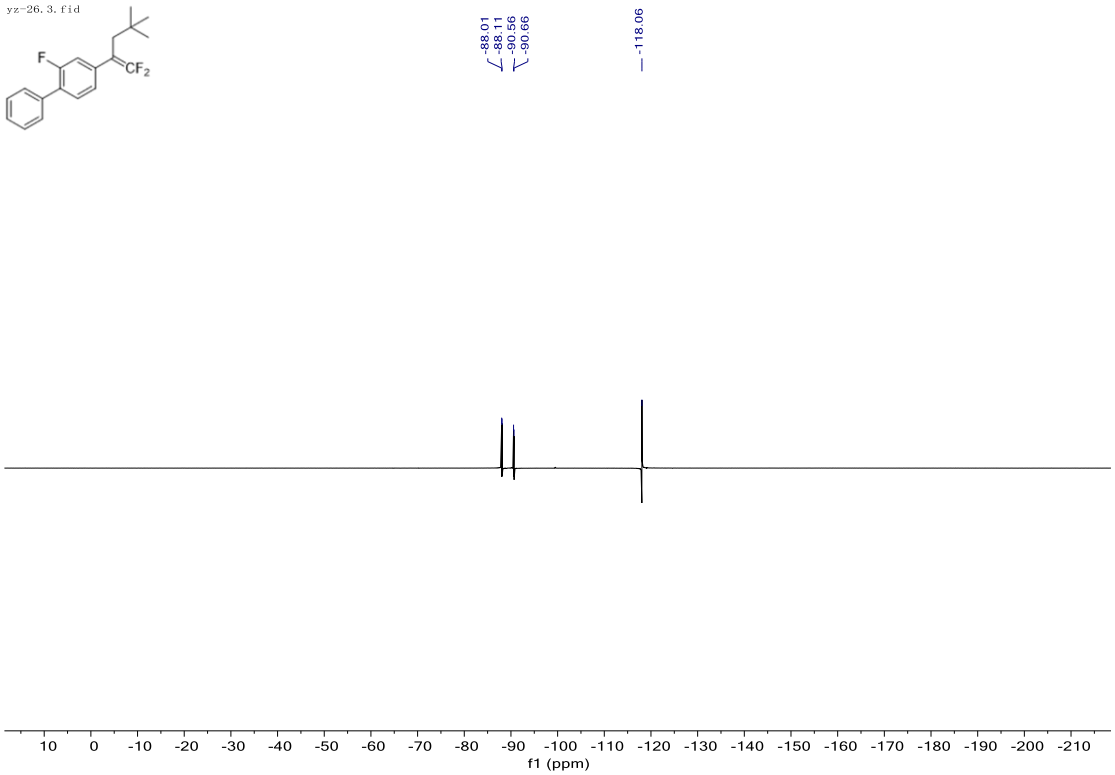
^{1}H NMR



^{13}C NMR

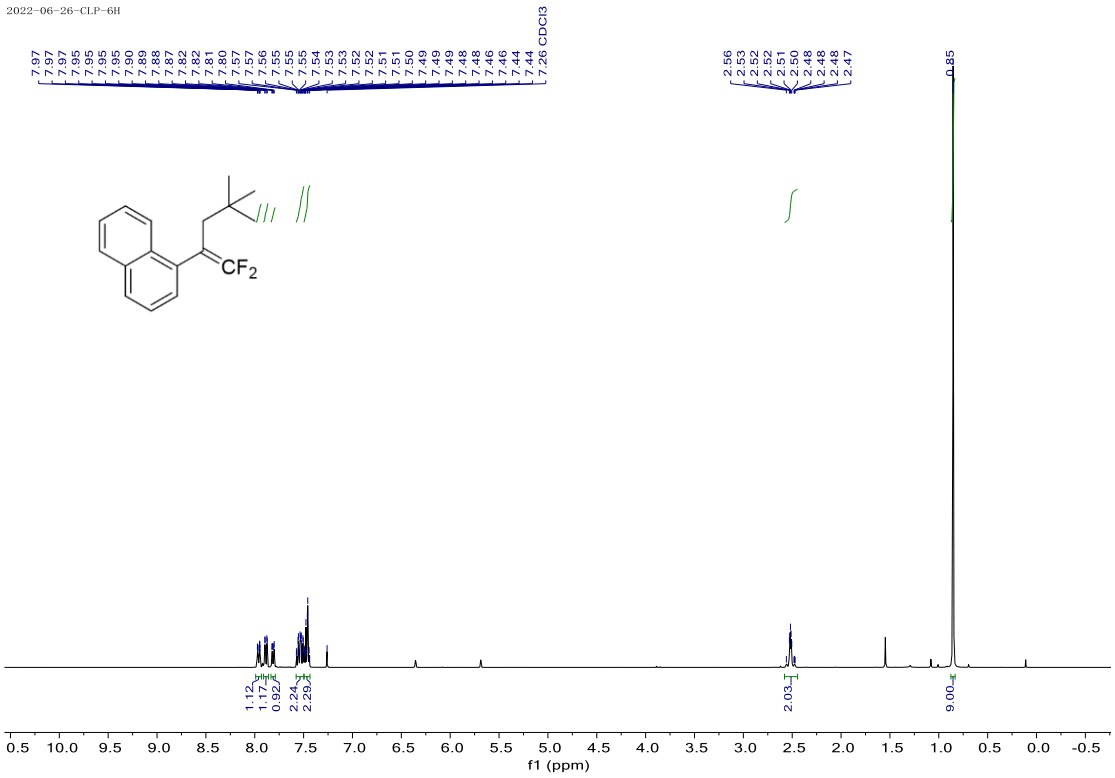


^{19}F NMR

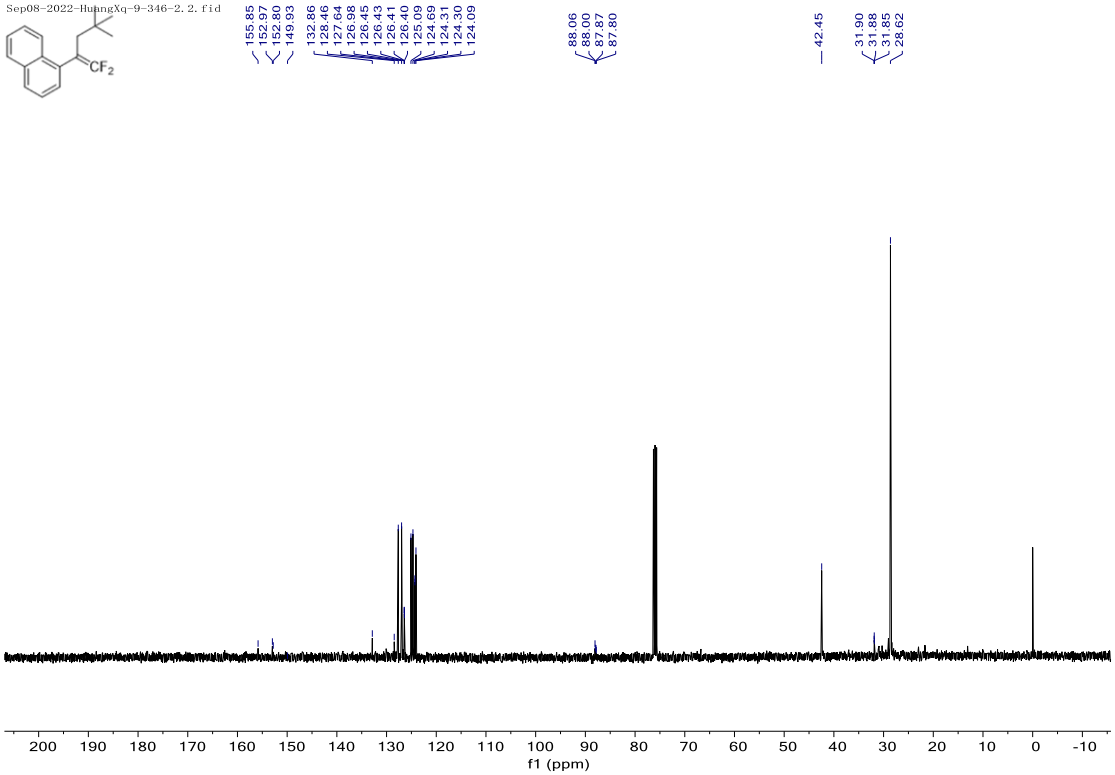

yz-26.3.fid
F
CF2
-88.01
-88.11
-90.56
-90.66
-118.06
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)naphthalene (3sa)

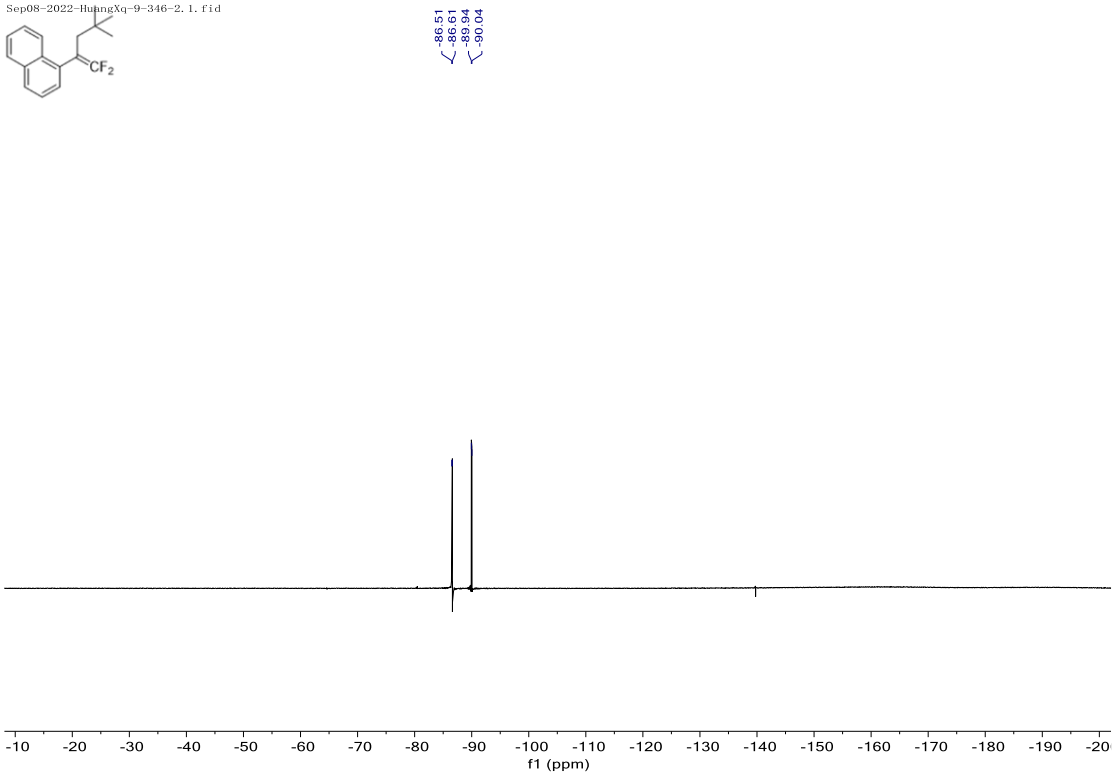
^{1}H NMR



^{13}C NMR

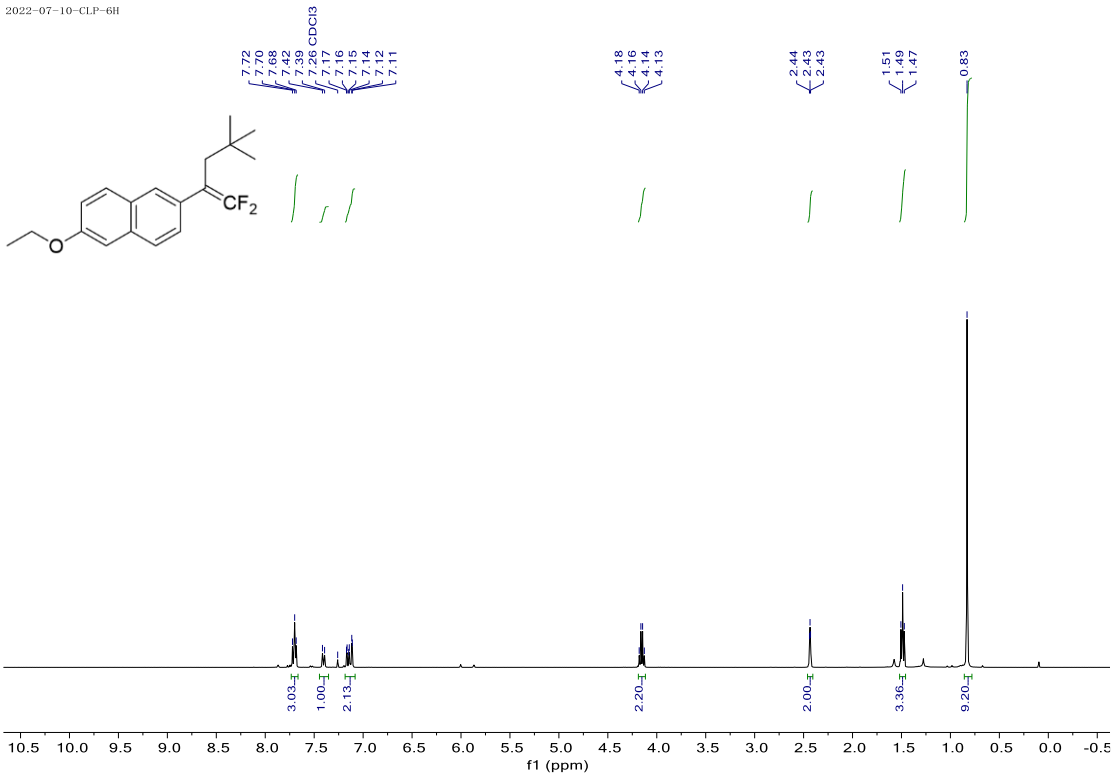


^{19}F NMR

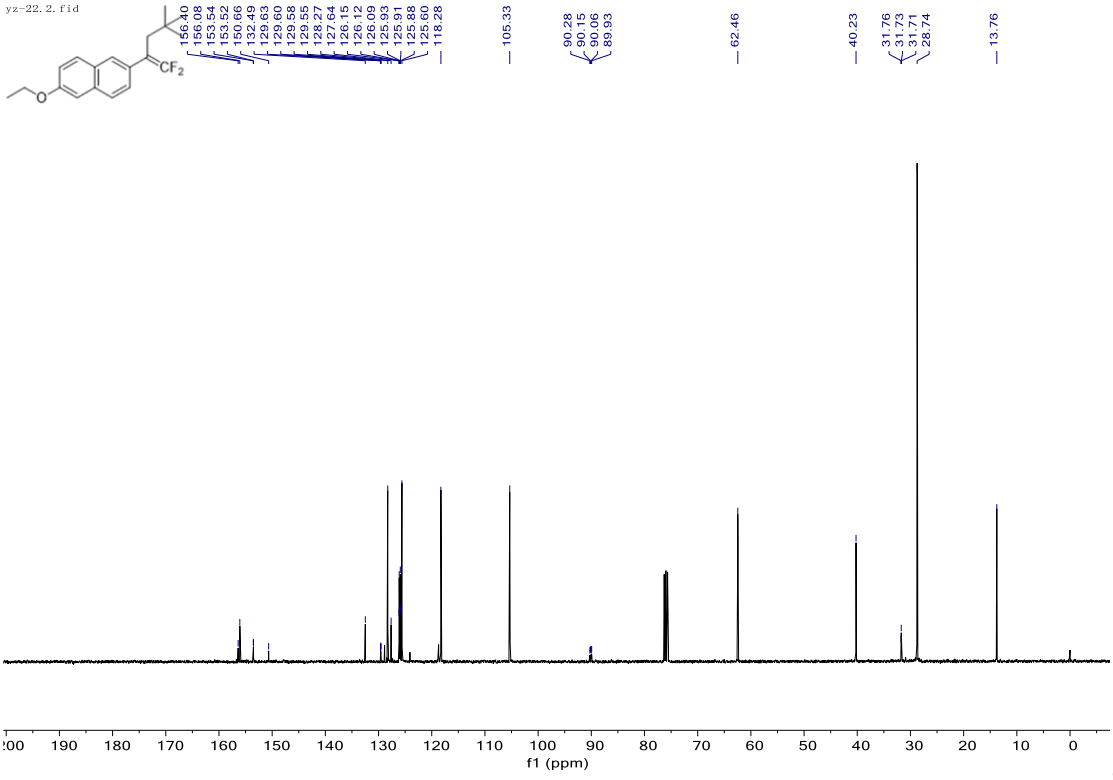

Sep08-2022-HuangXq-9-346-2.1.fid
-86.51
-86.61
-89.94
-90.04
CF2
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

2-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-6-ethoxynaphthalene（3ta）

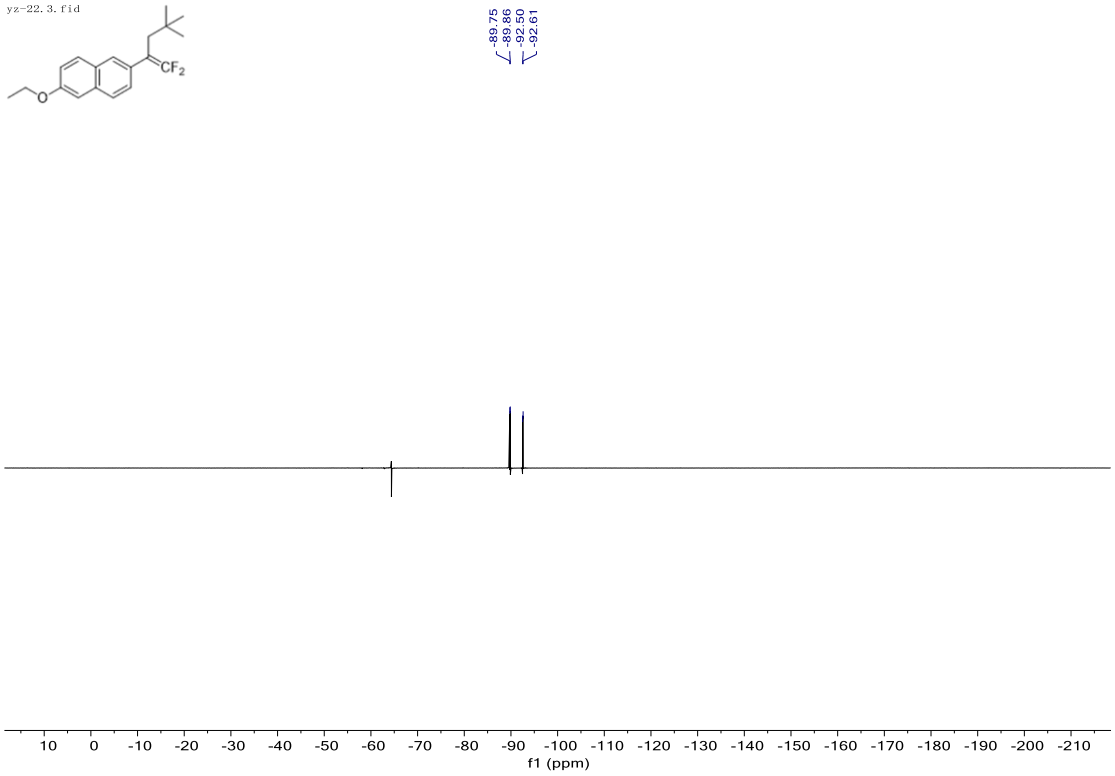
^{1}H NMR



^{13}C NMR

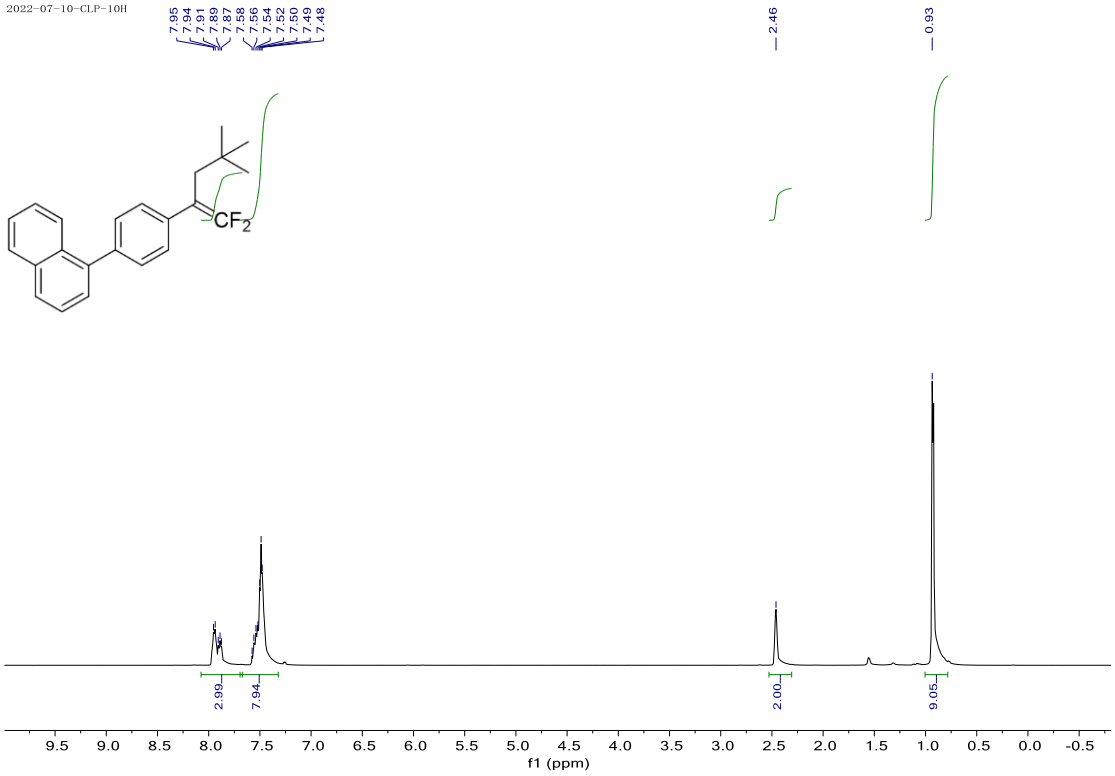


^{19}F NMR

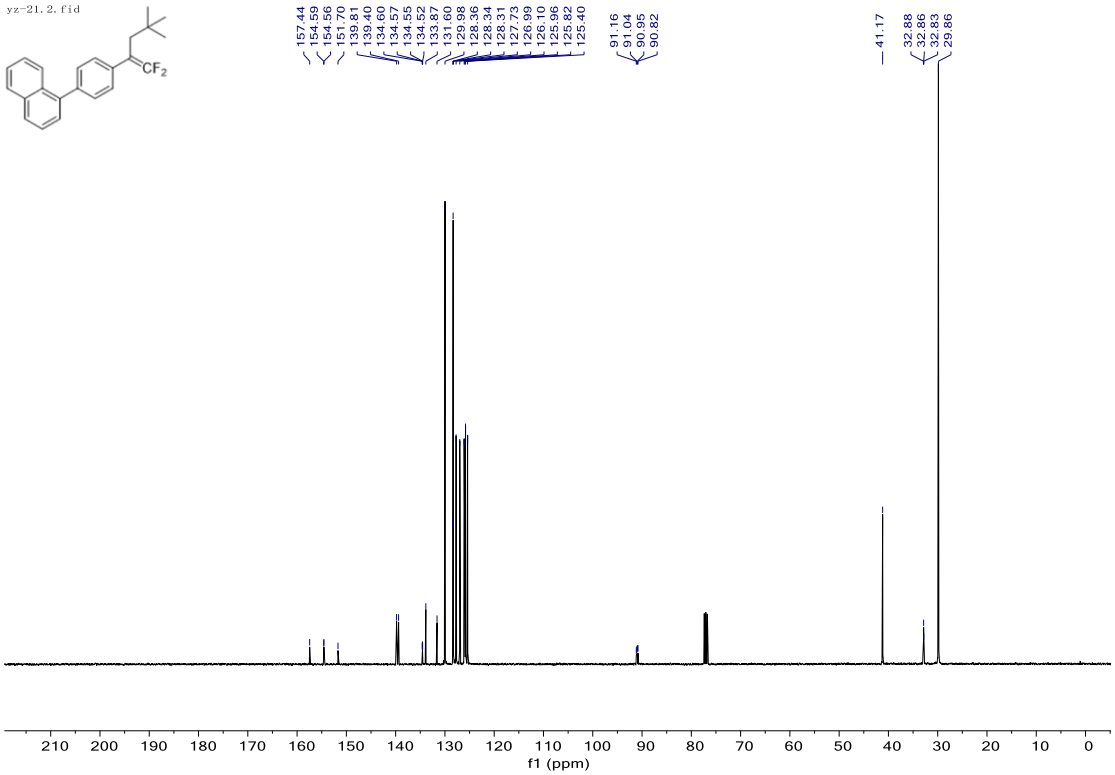

yz-22.3.fid
-89.75
-89.86
-92.50
-92.61
CF2
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)phenyl)naphthalene（3ua）

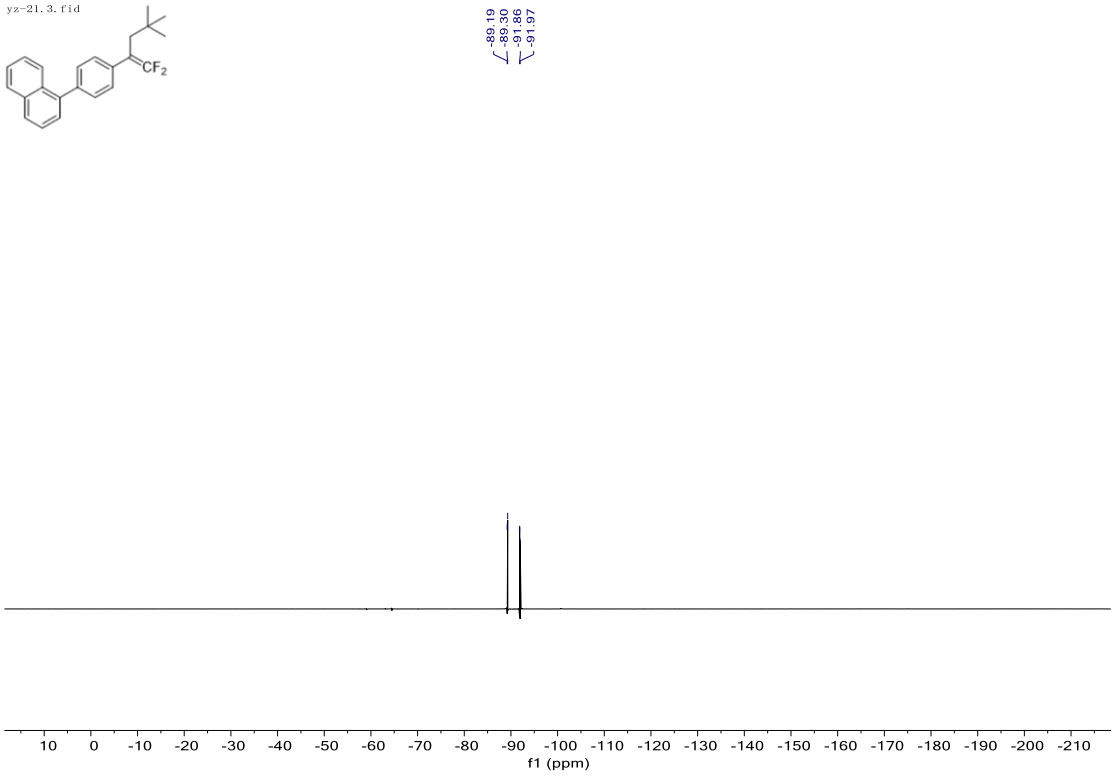
^{1}H NMR



^{13}C NMR

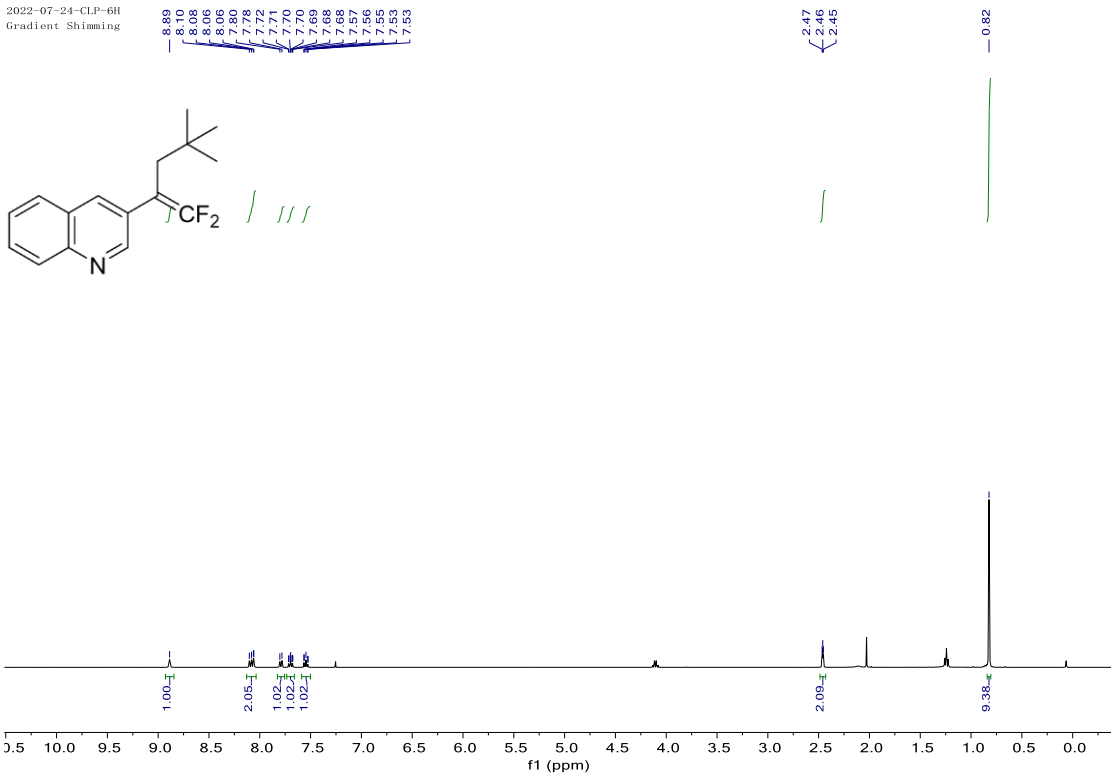


^{19}F NMR

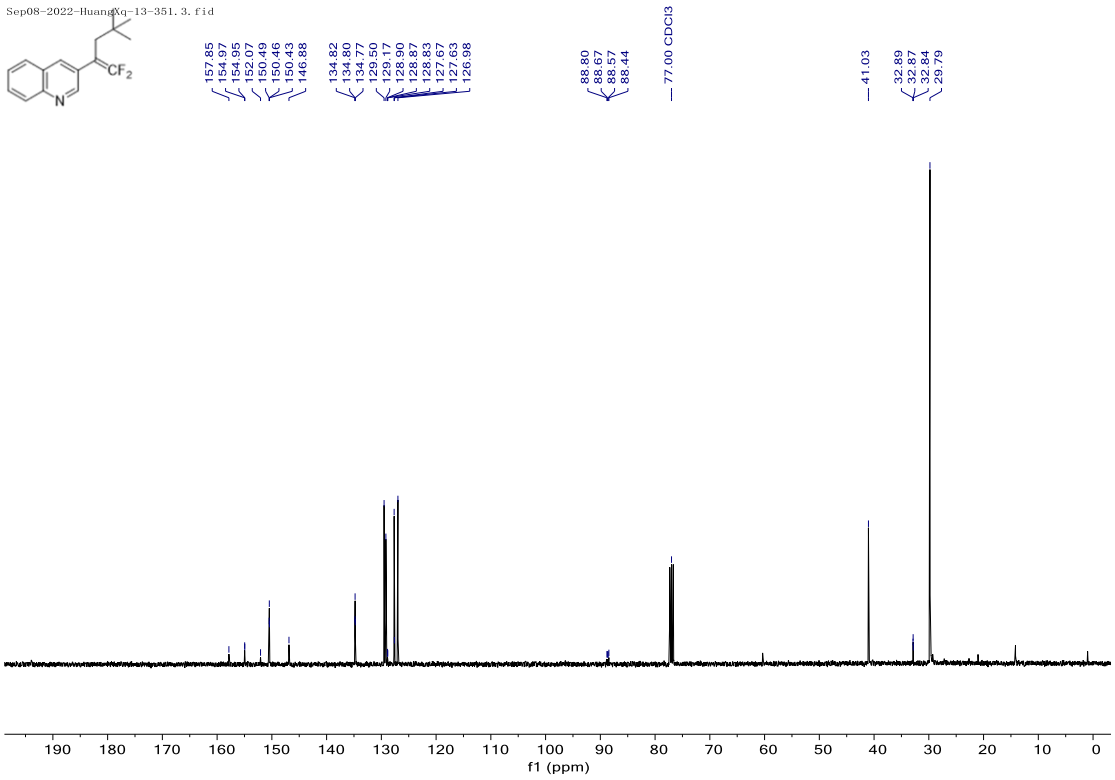

yz-21.3.fid
CF2
-89.19
-89.30
-91.86
-91.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)quinoline（3va）

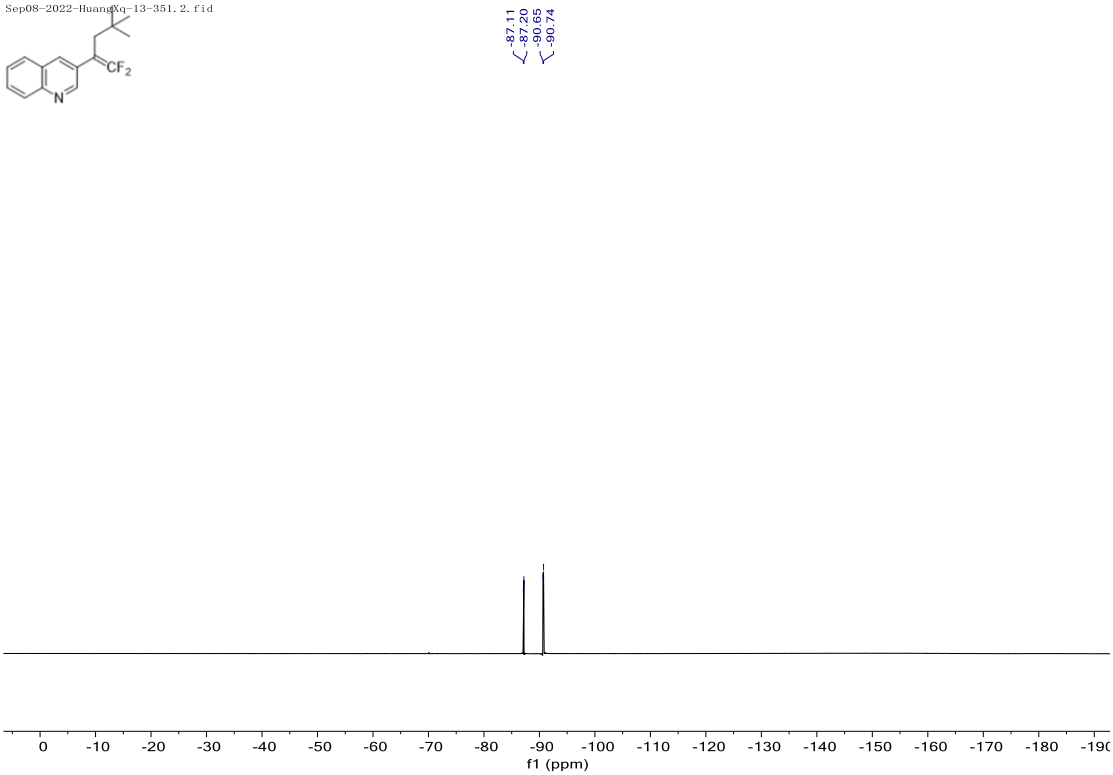
^{1}H NMR



^{13}C NMR

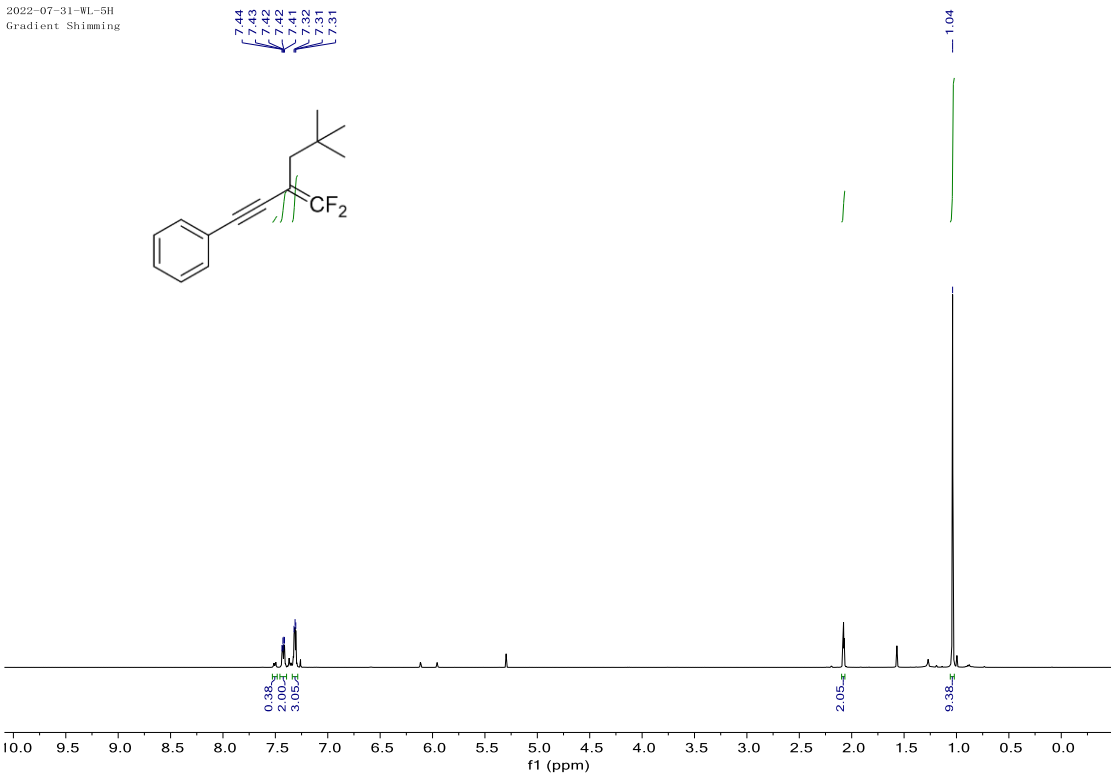


^{19}F NMR

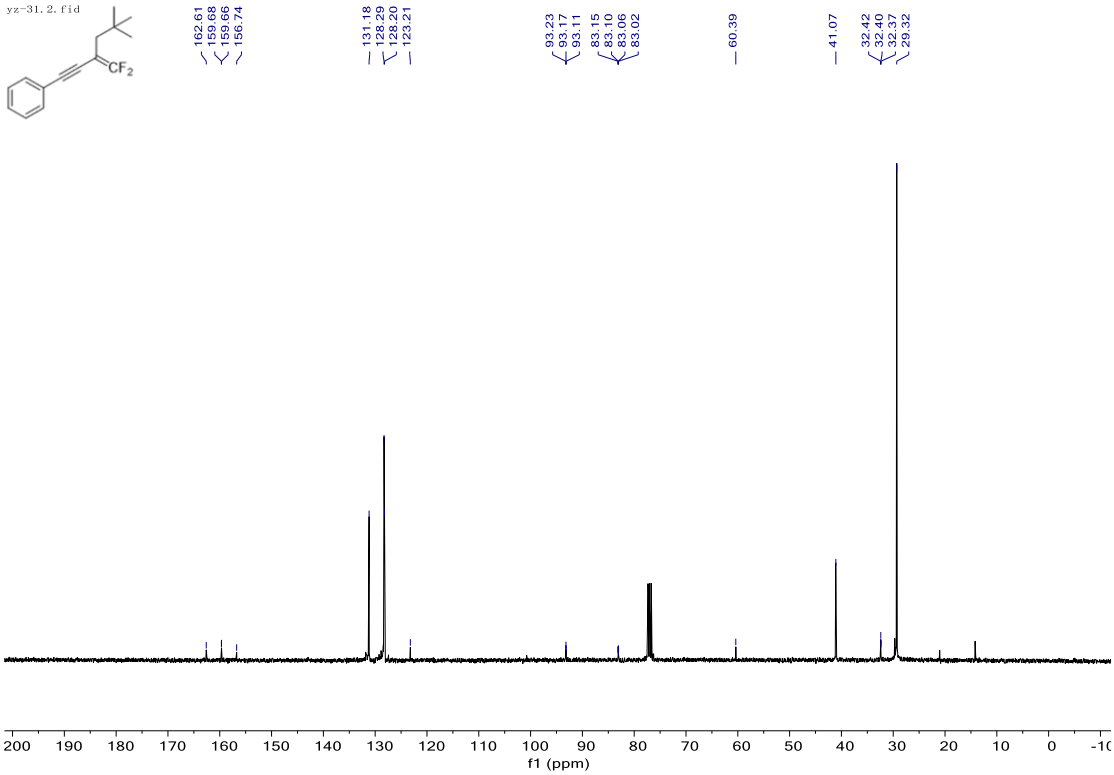

Sep08-2022-HuangXq-13-351.2.fid
-87.11
-87.20
-90.65
-90.74
CF2
N
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

(3-(difluoromethylene)-5,5-dimethylhex-1-yn-1-yl)benzene (3wa)

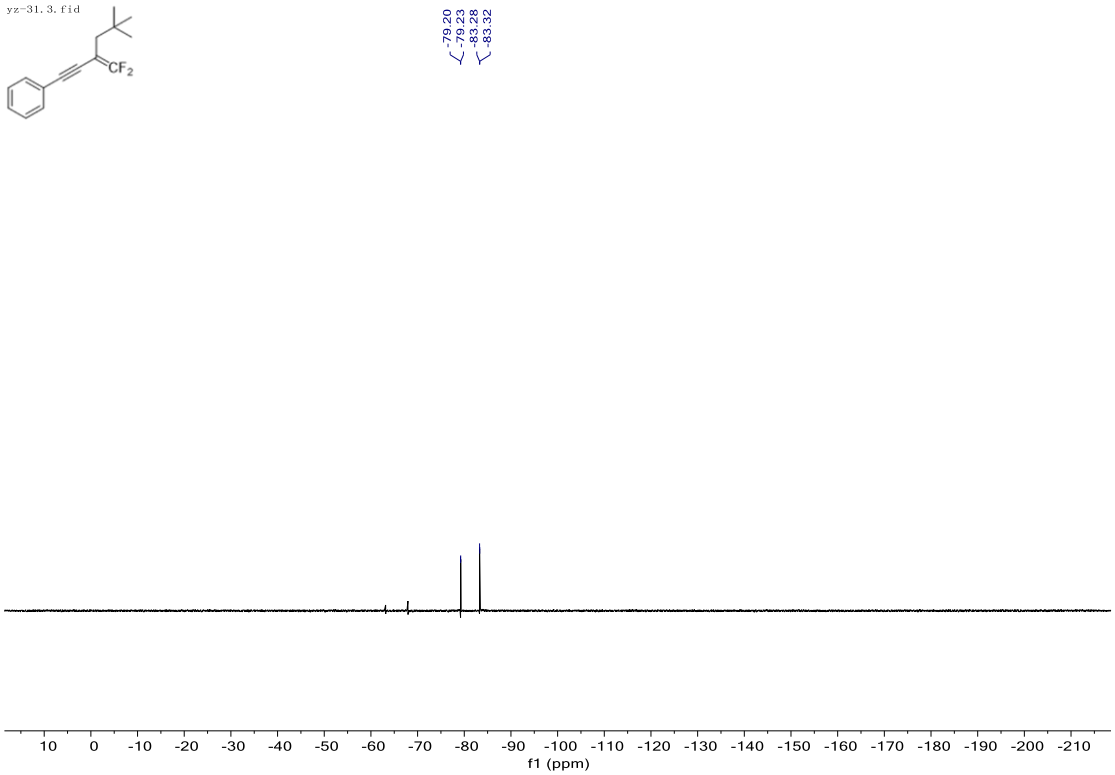
^{1}H NMR



^{13}C NMR

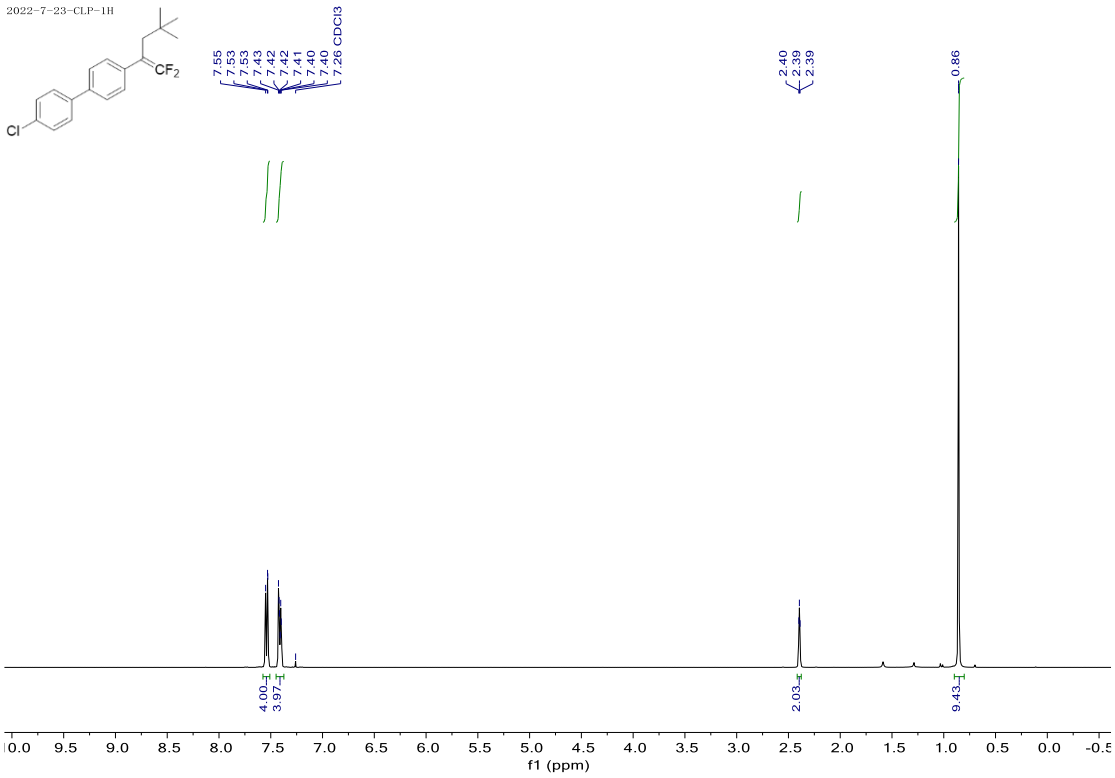


^{19}F NMR

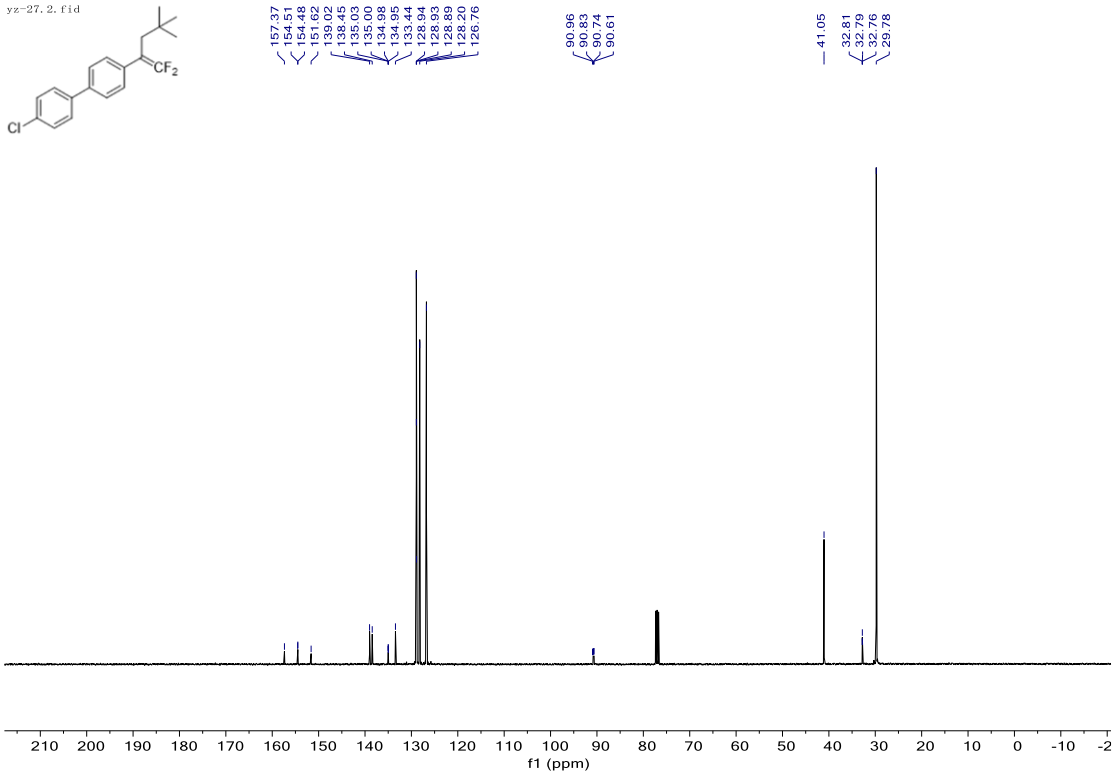

yz-31.3.fid
CF2
-79.20
-79.23
-83.28
-83.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-chloro-4'-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl（3xa）

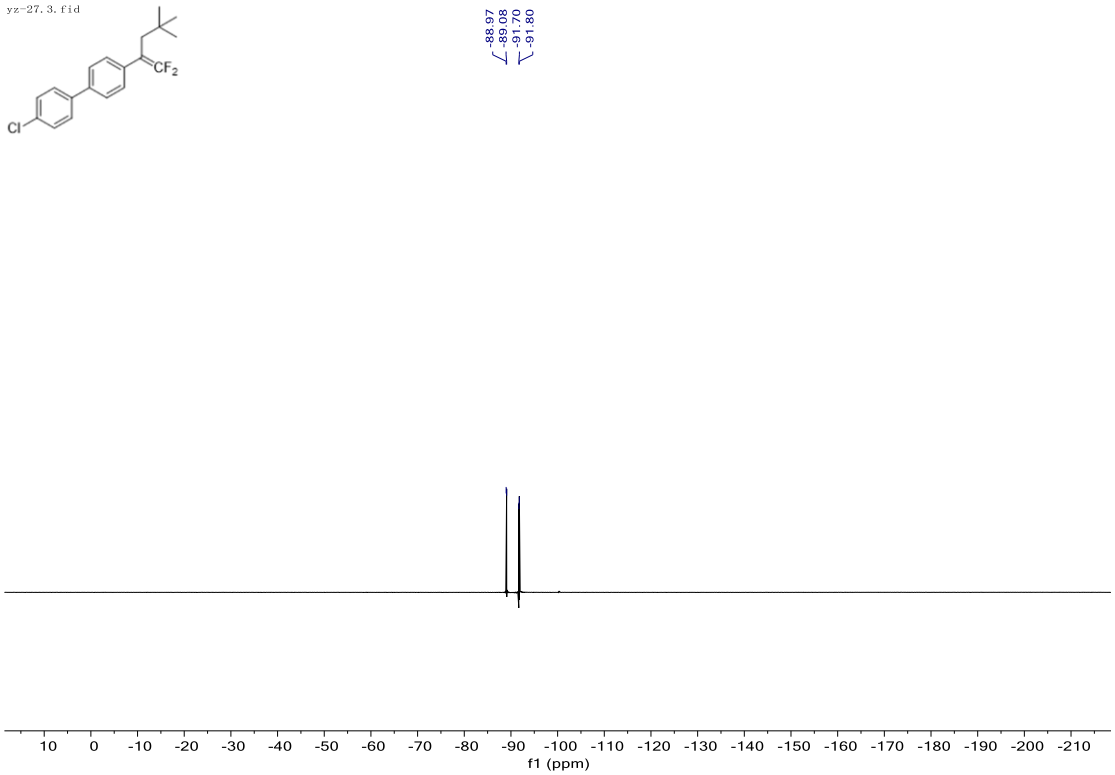
^{1}H NMR



^{13}C NMR

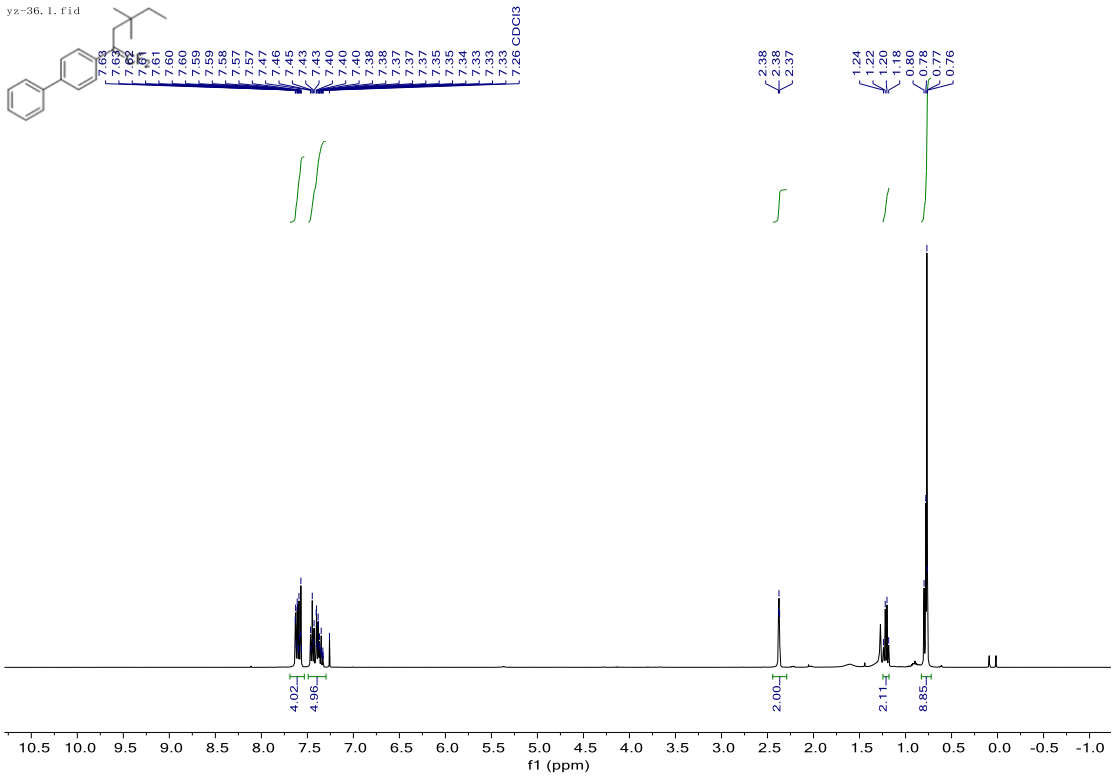


^{19}F NMR

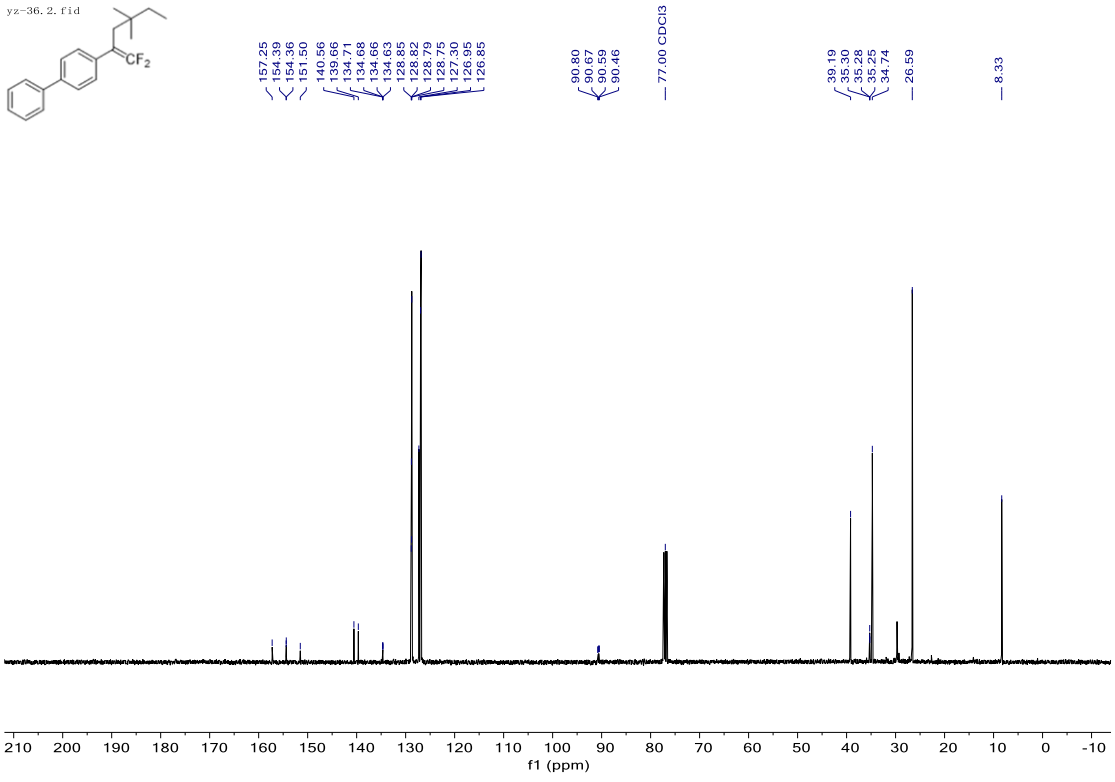

yz-27.3.fid
-88.97
-89.08
-91.70
-91.80
Cl
CF2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(1,1-difluoro-4,4-dimethylhex-1-en-2-yl)-1,1'-biphenyl (3ab)

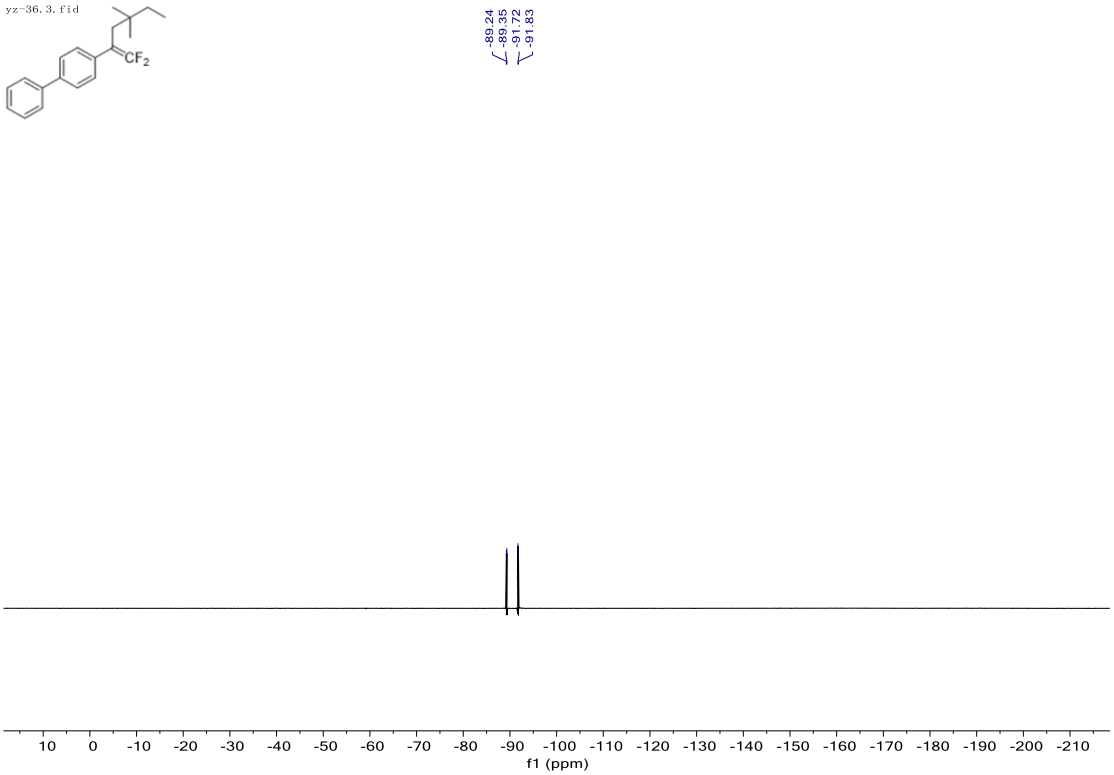
^{1}H NMR



^{13}C NMR

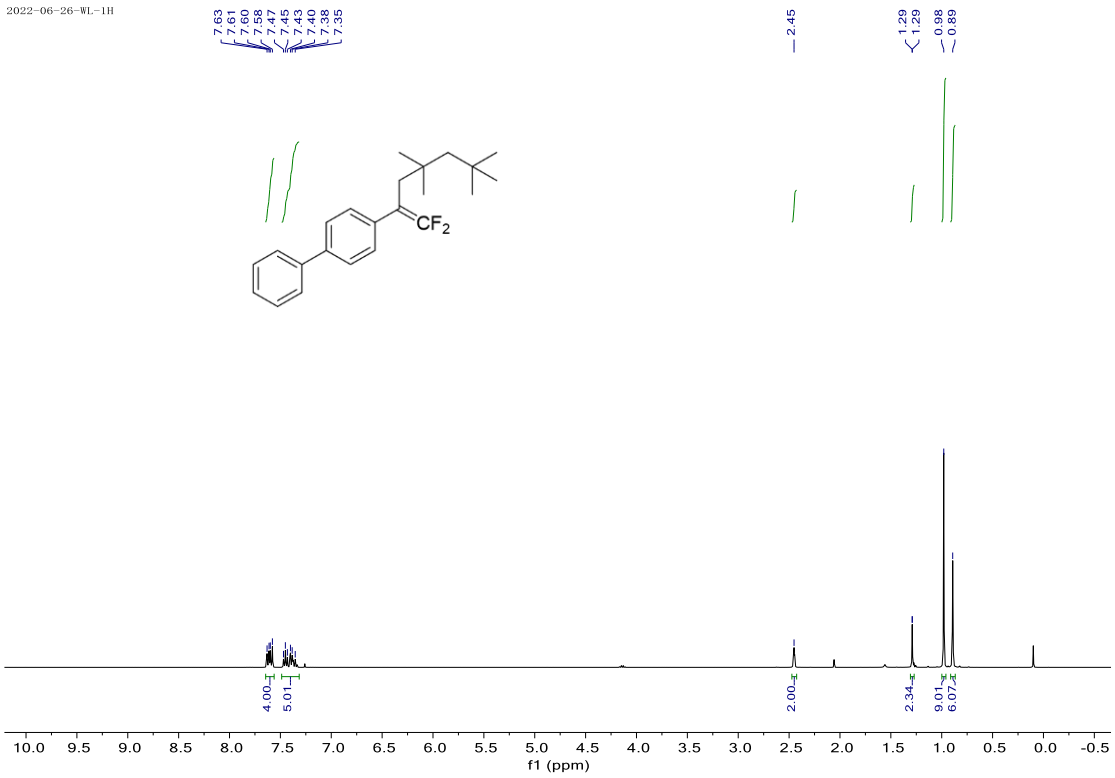


^{19}F NMR

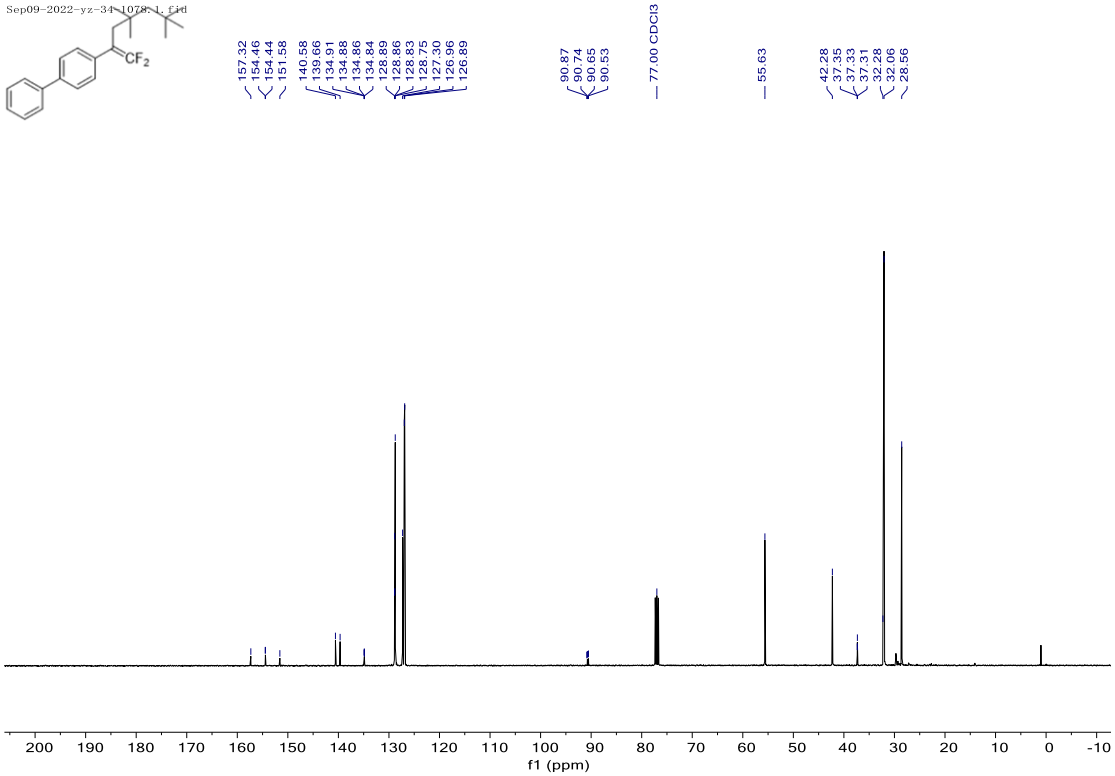

yz-36.3.fid
CF2
-89.24
-89.35
-91.72
-91.83
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(1,1-difluoro-4,4,6,6-tetramethylhept-1-en-2-yl)-1,1'-biphenyl (3ac)

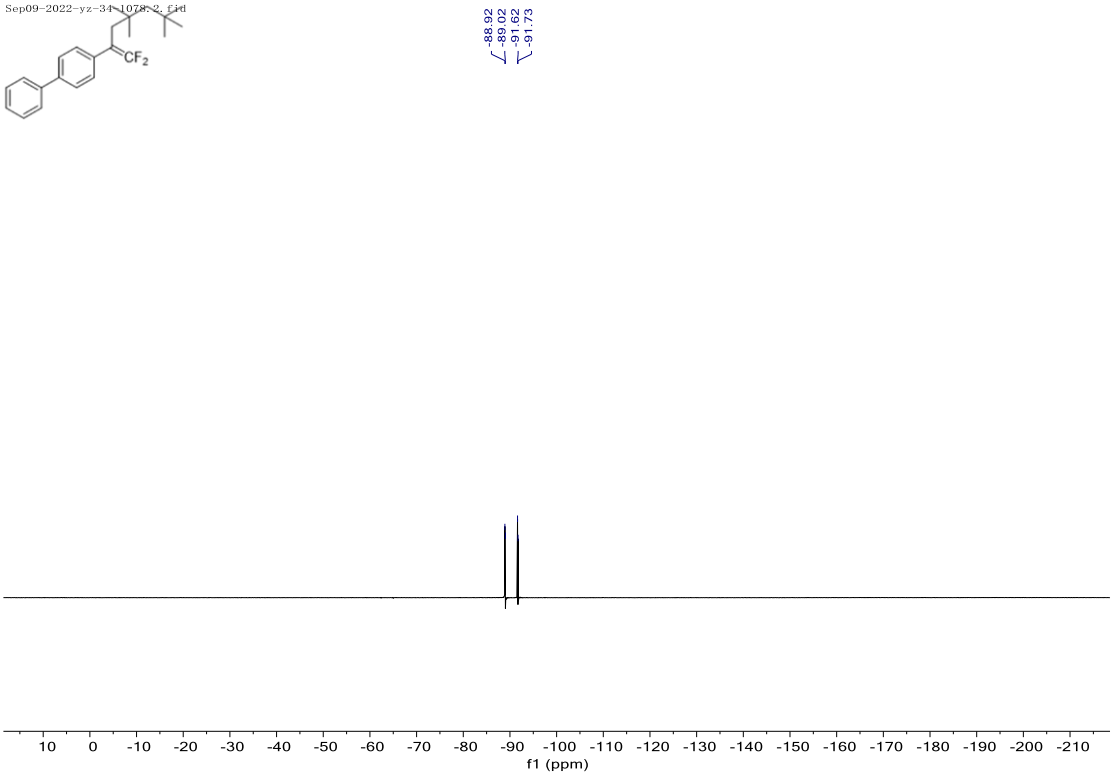
^{1}H NMR



^{13}C NMR

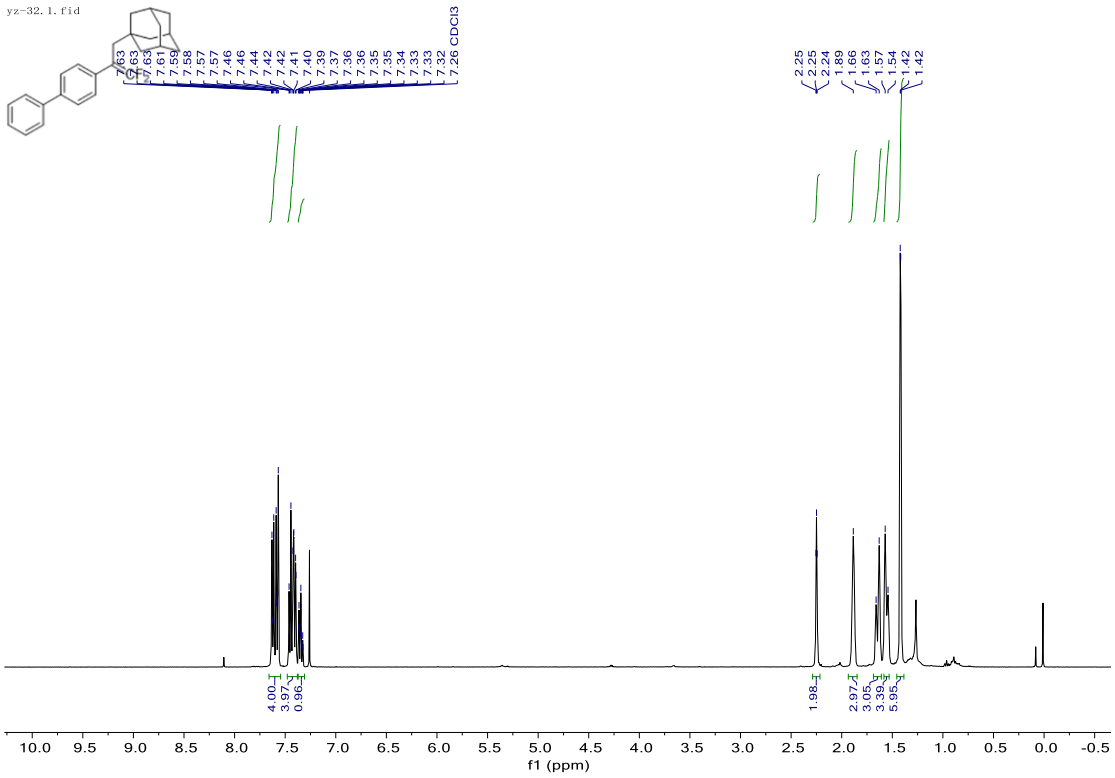


^{19}F NMR

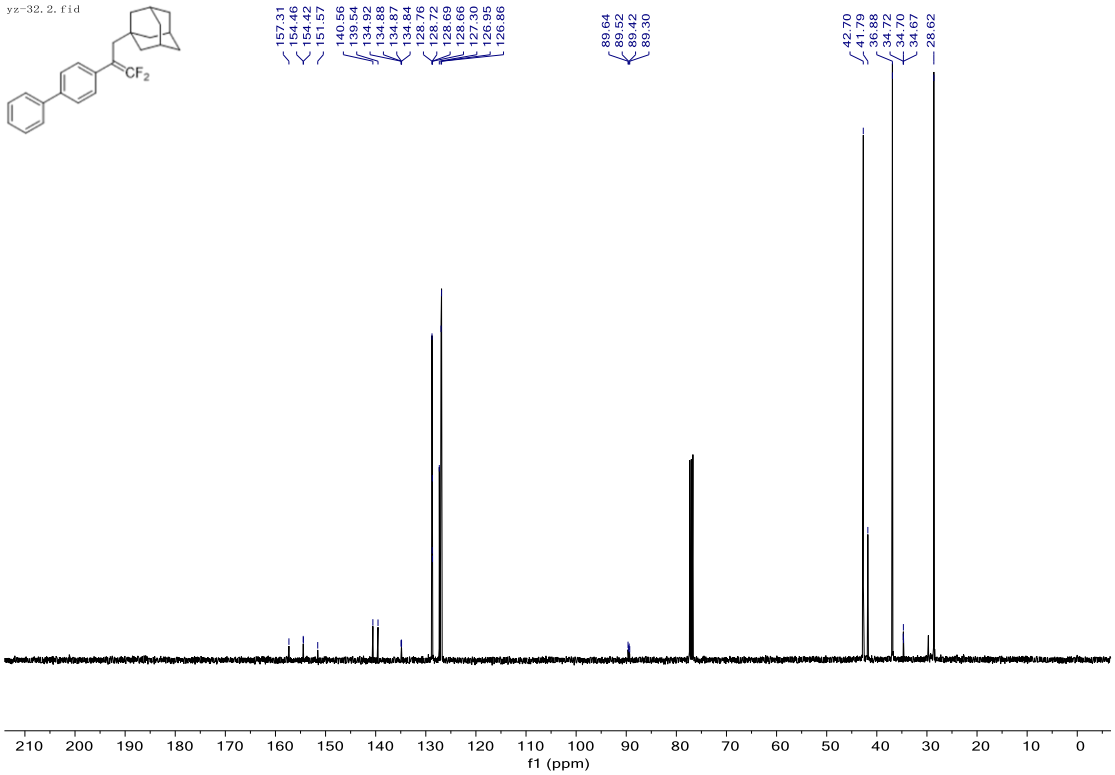

Sep09-2022-yz-34-1078-2. fid
CF2
-88.92
-89.02
-91.62
-91.73
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(3r,5r,7r)-1-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)adamantane（3ad）

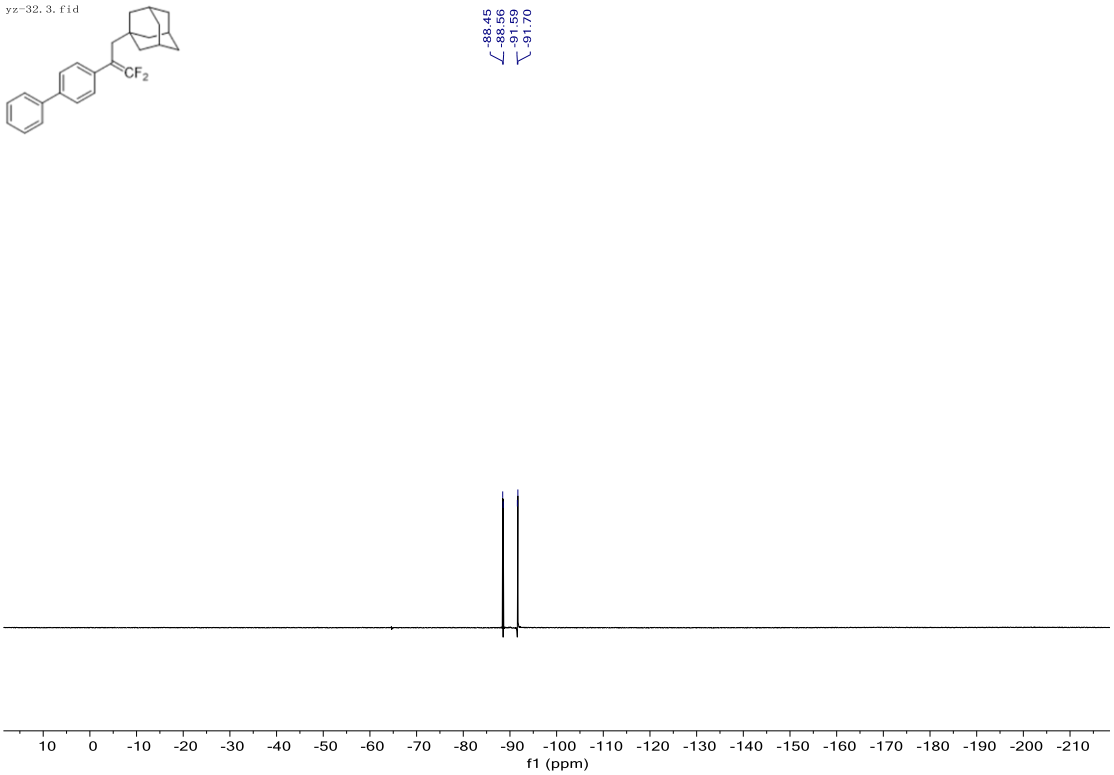
^{1}H NMR



^{13}C NMR

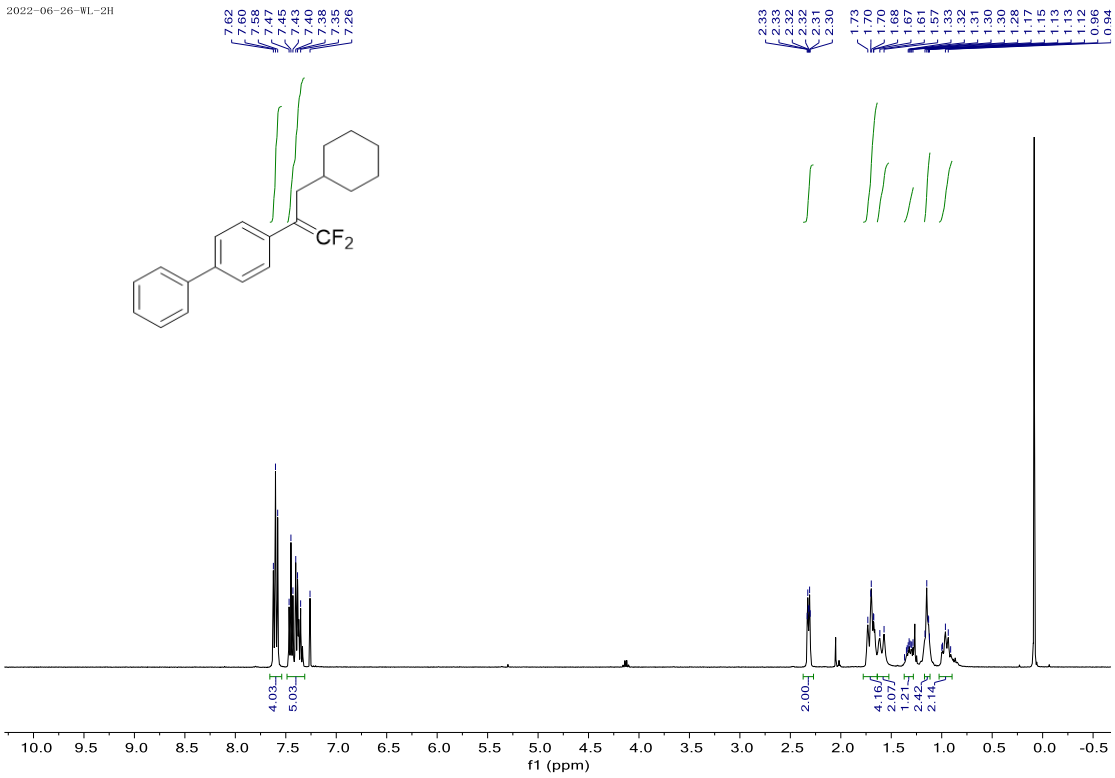


^{19}F NMR

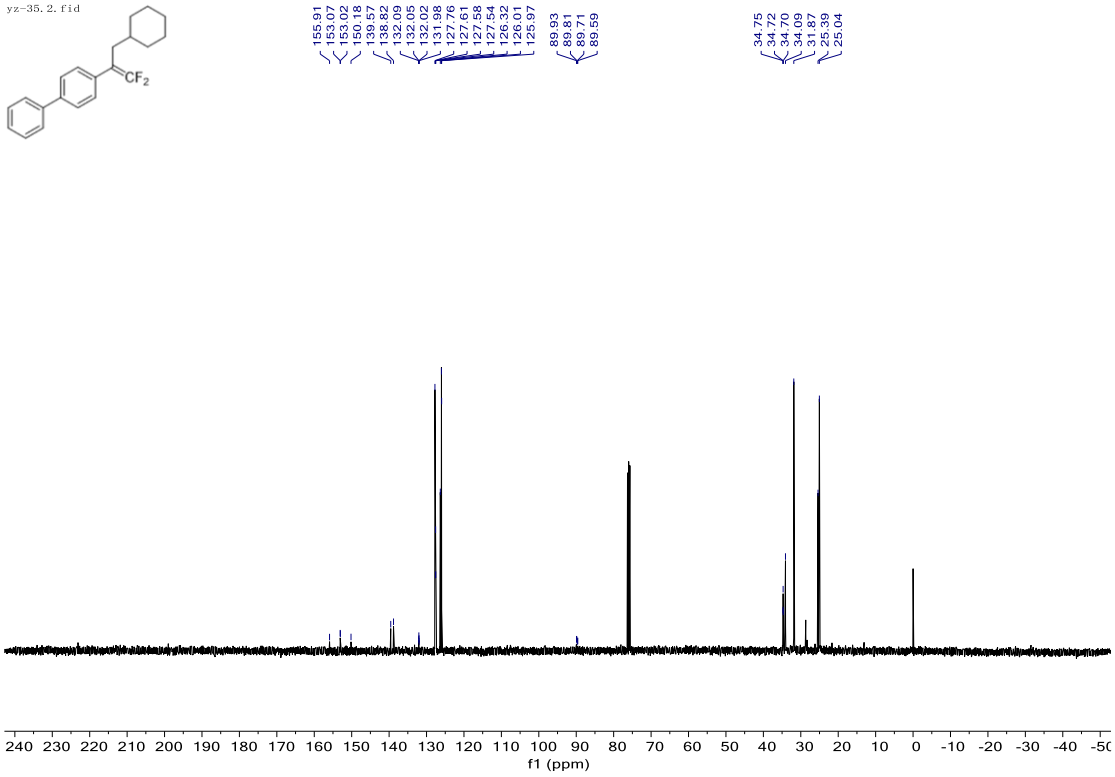

yz-32.3.fid
-88.45
-88.56
-91.59
-91.70
CF2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl（3ae）

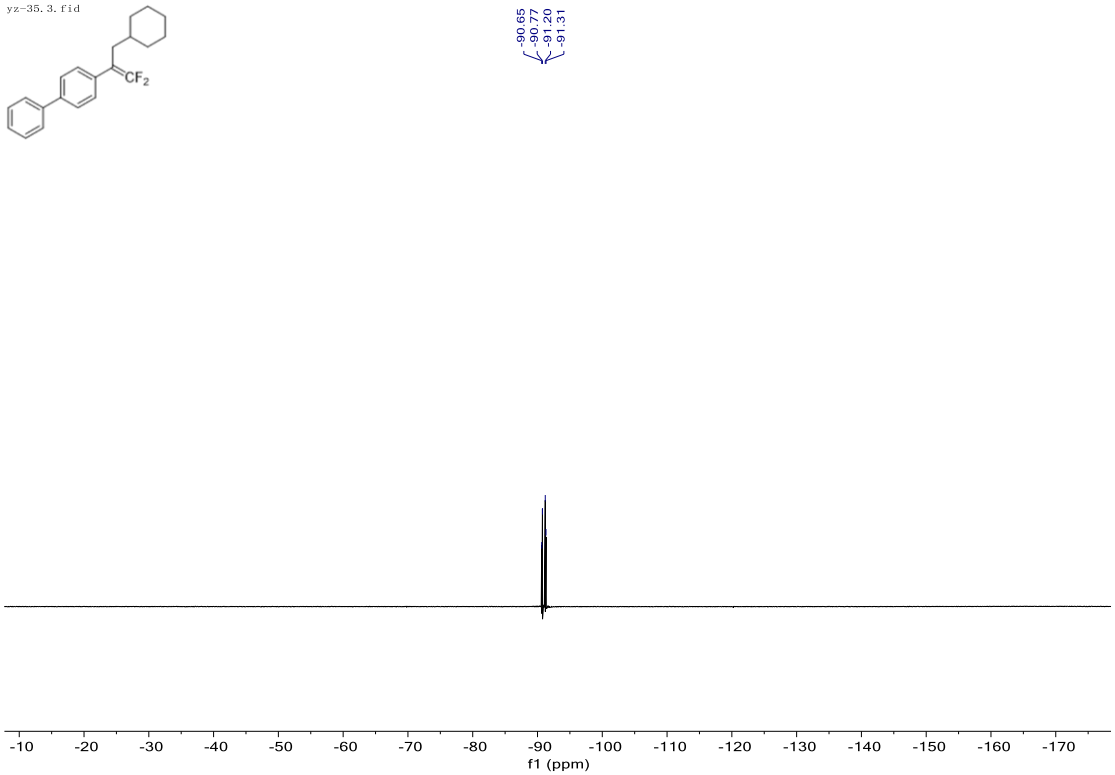
^{1}H NMR



^{13}C NMR

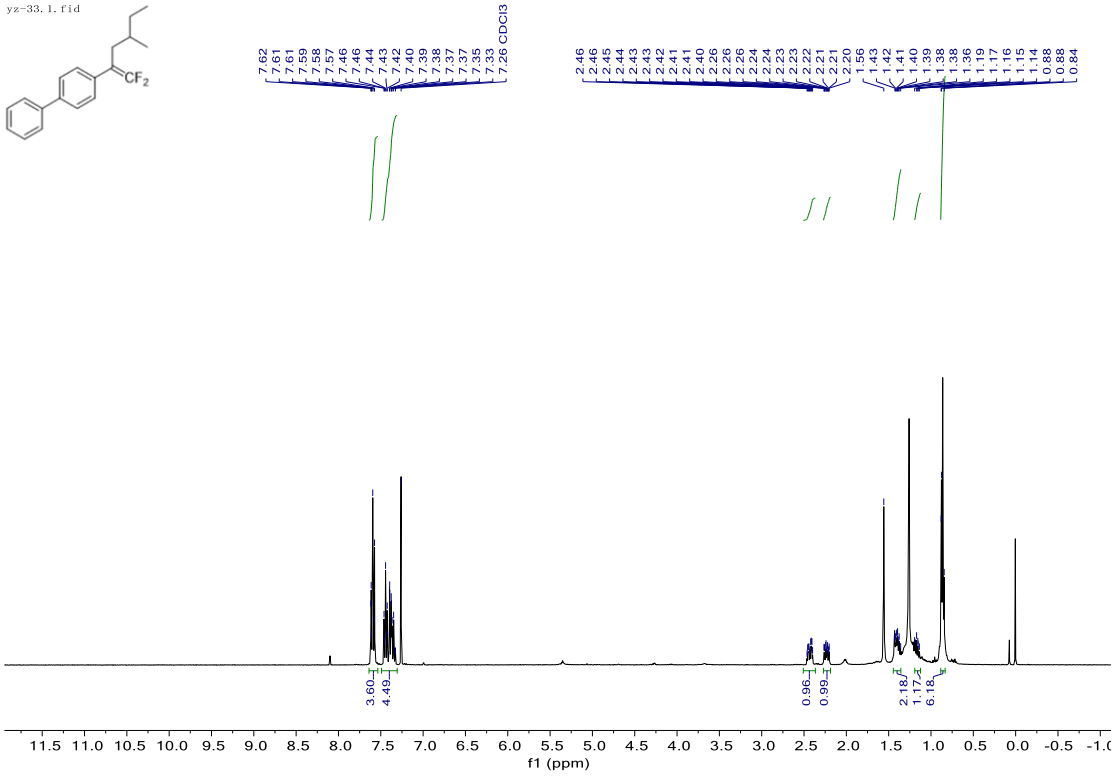


^{19}F NMR

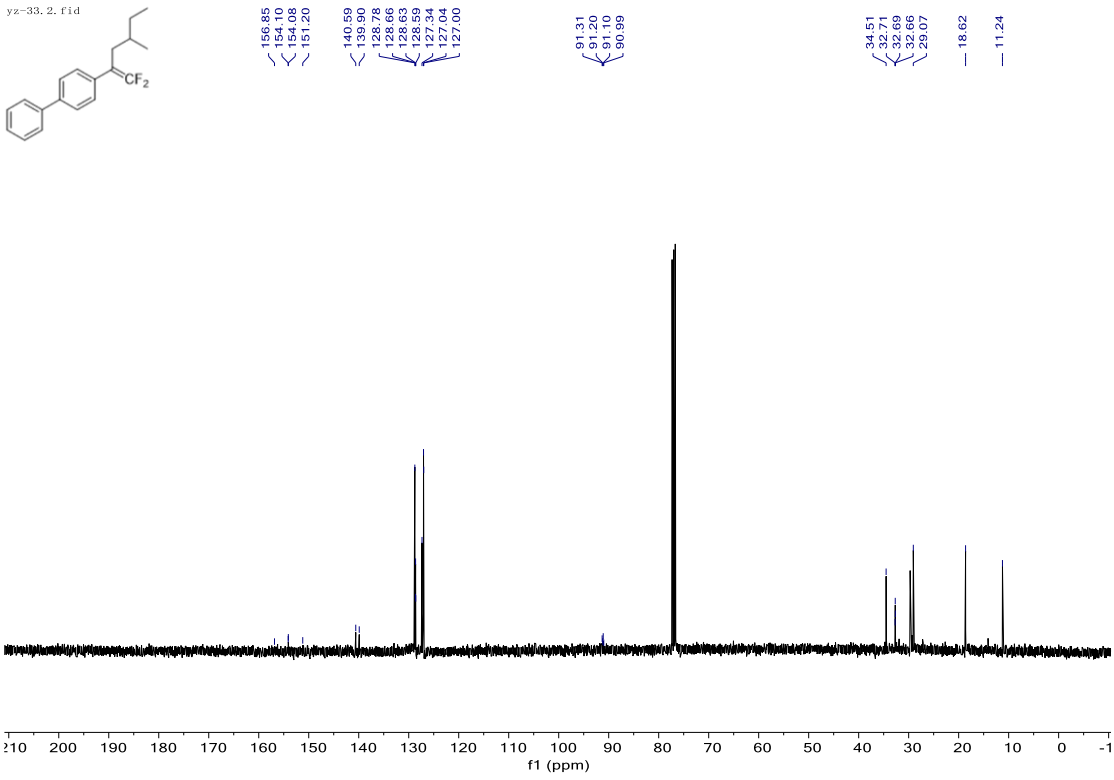

yz-35.3.fid
CF2
-90.65
-90.77
-91.20
-91.31
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

4-(1,1-difluoro-4-methylhex-1-en-2-yl)-1,1'-biphenyl（3af）

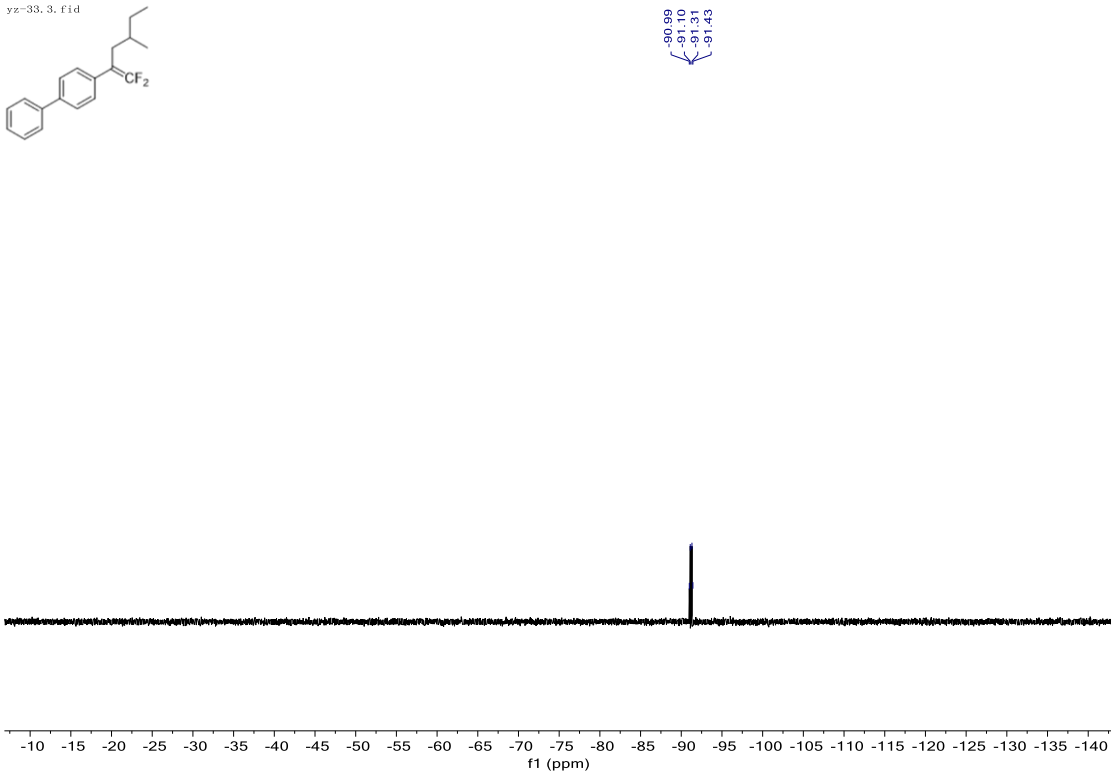
^{1}H NMR



^{13}C NMR



^{19}F NMR


yz-33.3.fid
CF2
-90.99
-91.10
-91.31
-91.43
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)