Supporting Information

Ni-Catalyzed Defluorination for the Synthesis of *gem*-Difluoro-1,3-dienes and Their [4+2] Cycloaddition Reaction

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1. General Information and Materials.

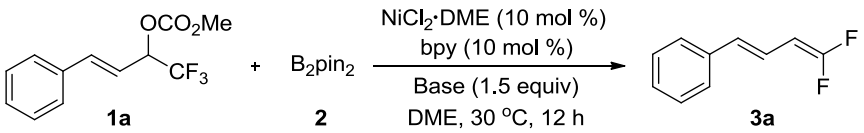
General Information: ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AM 400 spectrometer and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR; 77.6 ppm ^{13}C NMR; $CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless otherwise specified, or prepared as described in the literature. B_2pin_2 was purchased from Adamas and used as received. $NiCl_2$·DME was purchased from Strem Chemicals and used as received. 4,4'-Dimethoxy-2,2'-bipyridine was purchased from TCI and used as received. NaOMe was purchased from J&K and used as received. DME was purchased from Strem Chemicals and used as received.

2. Optimization of Ni-Catalyzed Defluorination of Methyl (1,1,1-trifluoro-4-phenylbut -3-en-2-yl) carbonate 1a with B_2pin_2 2 (Tables S1-S4)

To a 25 mL of Schlenk tube were added B_2pin_2 **2** (1.5 equiv), [Ni]-catalyst (10 mol %), *N*-ligand (10 mol %) and base (1.5 equiv) under argon atmosphere, followed by addition of solvent (1 mL). The reaction mixture was stirred for 10 min at room temperature, then a solution of compound **1a** (0.3 mmol, 1.0 equiv) in corresponding solvent (1 mL) was added. The tube was screw-capped and heated to 30-80 ℃ (oil bath). After stirring for 2-24 h, the reaction mixture was cooled to room temperature and fluorobenzene (1.0 equiv) was added. The yield was determined by ^{19}F NMR before working up. Then, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated. The residue was purified with silica gel chromatography (petroleum) to afford **3a** as a colorless oil.

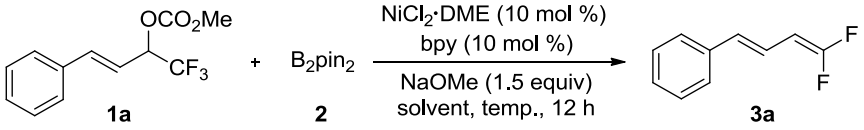
Table S1. Base Effect on Ni-Catalyzed Defluorination of **1a** with **2**[a]



Entry	Base	Yield of **3a**[b]
1	K_2CO_3	nr
2	K_3PO_4	nr
3	Na_2CO_3	nr
4	Cs_2CO_3	nr
5	NaOAc	nr
6	*t*-BuOK	12%
7	*t*-BuONa	33%
8	*t*-BuLi	14%
9	LiOMe	34%
10	NaOMe	40%
11	KOMe	15%

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), base (1.5 equiv), DME (2 mL), 30 °C for 12 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nr = no reaction.

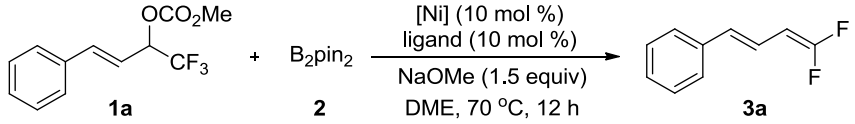
Table S2. Screening of Solvents and Reaction Temperatures for Ni-Catalyzed Defluorination of **1a** with **2**[a]



Entry	Solvent	Temp.	Yield of **3a**[b]
1	DME	30 °C	40%
2	DME	40 °C	43%
3	DME	50 °C	46%
4	DME	60 °C	50%
5	DME	70 °C	54%
6	DME	80 °C	49%
7	DMF	70 °C	nr
8	CH_3CN	70 °C	nr
9	THF	70 °C	48%
10	Diglyme	70 °C	48%
11	Dioxane	70 °C	44%

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), solvents (2 mL), 12 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nr = no reaction.

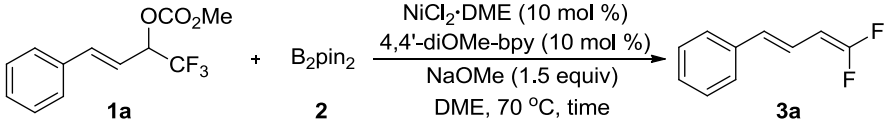
Table S3. Screening of Nickel Sources and Ligands for Ni-Catalyzed Defluorination of **1a** with **2**[a]



Entry	Nickel Sources	Ligands	Yield of **3a**[b]
1	$NiCl_2$·DME	bpy	54%
2	$NiCl_2$·DME	4,4′-diMe-bpy	55%
3	$NiCl_2$·DME	4,4′-di*t*Bu-bpy	34%
4	$NiCl_2$·DME	4,4′-diOMe-bpy	65%
5	$NiCl_2$·DME	6,6′-diMe-bpy	30%
6	$NiCl_2$·dppf	4,4′-diOMe-bpy	50%
7	$NiCl_2(PCy_3)_2$	4,4′-diOMe-bpy	54%
8	$NiBr_2$·DME	4,4′-diOMe-bpy	63%
9	$NiBr_2$·Diglyme	4,4′-diOMe-bpy	62%
10	$Ni(OTf)_2$	4,4′-diOMe-bpy	50%
11	$Ni(cod)_2$	4,4′-diOMe-bpy	37%

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), [Ni] (10 mol %), Ligand (10 mol %), DME (2 mL), 70 °C for 12 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

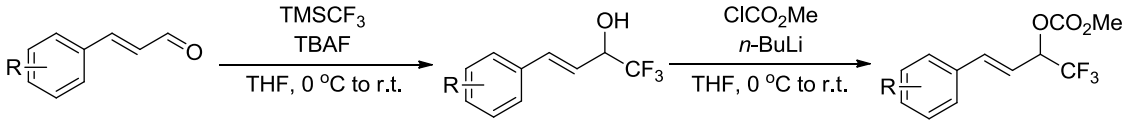
Table S4. Screening of Reaction Time and Control Experiments for Ni-Catalyzed Defluorination of **1a** with **2**[a]



Entry	[Ni]	Ligand	Base	Time	Yield of **3a**[b]
1	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	2 h	45%
2	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	3 h	53%
3	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	4 h	60%
4	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	5 h	68%
5	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	6 h	82%
6	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	7 h	70%
7	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	12 h	65%
8	$NiCl_2$·DME	4,4′-diOMe-bpy	NaOMe	24 h	56%
9	none	4,4′-diOMe-bpy	NaOMe	6 h	nr
10	$NiCl_2$·DME	none	NaOMe	6 h	nd
11	$NiCl_2$·DME	4,4′-diOMe-bpy	none	6 h	nr

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (0.45 mmol, 1.5 equiv), $NiCl_2$·DME (10 mol %), 4,4′-diOMe-bpy (10 mol %), NaOMe (1.5 equiv), DME (2 mL), 70 °C. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. nr = no reaction. nd = not detected.

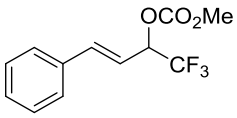
3. Preparation of Compounds 1



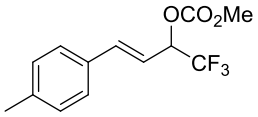
TBAF in THF (1.0 M, 0.1 equiv) was slowly dropped into the solution of *α, β*-unsaturated aldehyde (1.0 equiv) and $TMSCF_3$ (1.2 equiv) in anhydrous THF at 0 ℃ under argon. After stirring overnight at room temperature, the yellow mixture was quenched by addition of 1.0 M HCl (1.0 equiv). The reaction mixture was separated and the aqueous phase was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and concentrated. The resulting alcohol was purified by flash column chromatography with ethyl acetate/petroleum ether solvent system.

n-BuLi (1.1 equiv) was slowly added into the solution of alcohol (1.0 equiv) in THF at 0 °C under argon atmosphere. After the reaction mixture was stirred for 0.5 h at 0 °C, $ClCO_2Me$ (1.5 equiv) was added and the resulting mixture was stirred for 12 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl and then extracted twice with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography with ethyl acetate/petroleum ether solvent system.

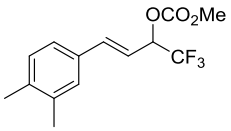
4. Data for Compounds 1



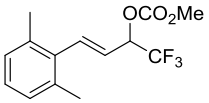
(*E*)-Methyl (1,1,1-trifluoro-4-phenylbut-3-en-2-yl) carbonate (1a). [Known compound[1]]: The reaction was carried out on 10 mmol-scale from alcohol. Compound **1a** (2.39 g, 92% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1). m.p. 53-55 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9 Hz, 7.9 Hz, 1H), 5.69 – 5.61 (m, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 139.9, 135.4, 129.8, 129.3, 127.7, 123.4 (q, *J* = 281.9 Hz), 117.2, 75.6 (q, *J* = 34.0 Hz), 56.2.



(*E*)-Methyl (1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl) carbonate (1b). The reaction was carried out on 5 mmol-scale from alcohol. Compound **1b** (1.14 g, 83% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1), m.p. 65-68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9 Hz, 7.9 Hz, 1H), 5.69 – 5.61 (m, 1H), 3.87 (s, 3H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 139.91, 139.88, 132.6, 130.0, 127.6, 123.5 (q, *J* = 280.6 Hz), 116.0, 75.7 (q, *J* = 33.9 Hz), 56.1, 21.8. IR (thin film) ν_{max} 2970, 1758, 1257 cm^{-1}. MS (EI): m/z (%) 274 (M^+), 129 (100). HRMS: Calcd. for $C_{13}H_{13}O_3F_3$: 274.0817; Found: 274.0816.

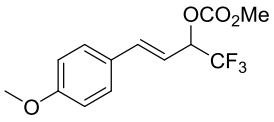


(*E*)-4-(3,4-Dimethylphenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1c). The reaction was carried out on 3 mmol-scale from alcohol. Compound **1c** (582.7 mg, 67% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 30: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0 Hz, 8.0 Hz, 1H), 5.67 – 5.58 (m, 1H), 3.86 (s, 3H), 2.27 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 140.1, 138.6, 137.5, 133.1, 130.6, 128.8, 125.2, 123.5 (q, *J* = 281.8 Hz), 115.8, 75.8 (q, *J* = 34.0 Hz), 56.1, 20.3, 20.2. MS (EI): m/z (%) 288 (M^+), 143 (100). HRMS: Calcd. for $C_{14}H_{15}O_3F_3$: 288.0973; Found: 288.0966.

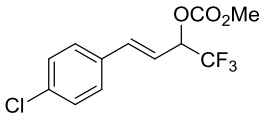


(*E*)-4-(2,6-Dimethylphenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1d). The reaction was carried out on 5 mmol-scale from alcohol. Compound **1d** (1.19 g, 83% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 30: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 15.2 Hz, 1H), 5.80 – 5.67 (m, 2H), 3.94 (s, 3H), 2.34 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 6.0 Hz, 3F). ^{13}C NMR (101

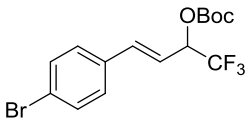
MHz, $CDCl_3$) δ 154.7, 138.2, 136.4, 135.3, 128.4, 128.2, 123.4 (q, *J* = 281.8 Hz), 123.1, 75.6 (q, *J* = 33.9 Hz), 56.1, 21.1. MS (EI): m/z (%) 288 (M^+), 143 (100). HRMS: Calcd. for $C_{14}H_{15}O_3F_3$: 288.0973; Found: 288.0970.



(*E*)-Methyl (1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl) carbonate (1e). The reaction was carried out on 5 mmol-scale from alcohol. Compound **1e** (1.09 g, 75% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 15: 1), m.p. 47-49 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.90 – 6.82 (m, 3H), 6.00 (dd, *J* = 15.9 Hz, 8.1 Hz, 1H), 5.65 – 5.56 (m, 1H), 3.85 (s, 3H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 154.8, 139.6, 129.1, 128.1, 123.5 (q, *J* = 281.9 Hz), 114.7, 75.9 (q, *J* = 34.1 Hz), 56.1, 55.9. IR (thin film) ν_{max} 2967, 1770, 1248 cm^{-1}. MS (EI): m/z (%) 290 (M^+), 145 (100). HRMS: Calcd. for $C_{13}H_{13}O_4F_3$: 290.0766; Found: 290.0768.

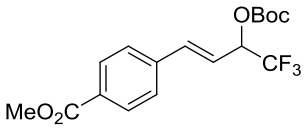


(*E*)-Methyl (1,1,1-trifluoro-4-(4-chlorophenyl)but-3-en-2-yl) carbonate (1f). The reaction was carried out on 10 mmol-scale from alcohol. Compound **1f** (1.97 g, 67% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1), m.p. 84-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 15.9 Hz, 7.7 Hz, 1H), 5.66 – 5.58 (m, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.7 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 138.5, 135.6, 133.9, 129.5, 128.9, 123.3 (q, *J* = 282.2 Hz), 117.8, 75.3 (q, *J* = 34.1 Hz), 56.2. IR (thin film) ν_{max} 2970, 1759, 1257 cm^{-1}. MS (EI): m/z (%) 294 (M^+), 129 (100). HRMS: Calcd. for $C_{12}H_{10}O_3F_3Cl$: 294.0271; Found: 294.0264.

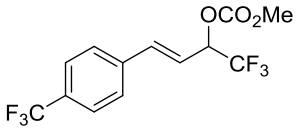


(*E*)-*tert*-Butyl (1,1,1-trifluoro-4-(4-bromophenyl)but-3-en-2-yl) carbonate (1g). The reaction was carried out on 0.86 mmol-scale from alcohol. Compound **1g** (266.1 mg, 81% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1). ^{1}H NMR (400

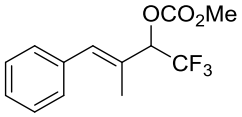
MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H), 5.65 – 5.56 (m, 1H), 1.49 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.6 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 137.8, 134.4, 132.4, 129.0, 123.512, 123.511 (q, *J* = 280.7 Hz), 118.5, 84.5, 74.1 (q, *J* = 33.8 Hz), 28.0. IR (thin film) ν_{max} 2360, 1759, 1256 cm^{-1}. MS (EI): m/z (%) 380 (M^+), 115 (100). HRMS: Calcd. for $C_{15}H_{16}O_3F_3Br$: 380.0235; Found: 380.0233.



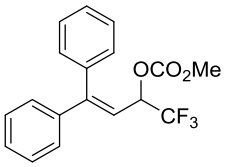
Methyl (*E*)-4-(3-((*tert*-butoxycarbonyl)oxy)-4,4,4-trifluorobut-1-en-1-yl)benzoate (1h). The reaction was carried out on 0.6 mmol-scale from alcohol. Compound **1h** (213.6 mg, 98% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 15: 1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0 Hz, 7.2 Hz, 1H), 5.66 – 5.57 (m, 1H), 3.92 (s, 3H), 1.49 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.6 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 152.2, 139.9, 137.9, 131.0, 130.6, 127.5, 123.5 (q, *J* = 280.7 Hz), 120.3, 84.8, 74.1 (q, *J* = 33.8 Hz), 52.8, 28.2.



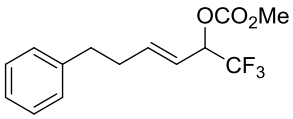
(*E*)-Methyl (1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl) carbonate (1i). The reaction was carried out on 5 mmol-scale from alcohol. Compound **1i** (717.9 mg, 44% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 30: 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0 Hz, 7.6 Hz, 1H), 5.73 – 5.65 (m, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F), -76.9 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 138.9 (q, *J* = 1.0 Hz), 138.0, 131.5 (q, *J* = 32.8 Hz), 127.8, 126.3 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 271.9 Hz), 123.4 (q, *J* = 280.5 Hz), 120.0, 75.1 (q, *J* = 34.2 Hz), 56.2. IR (thin film) ν_{max} 1766, 1328, 1131 cm^{-1}. MS (EI): m/z (%) 328 (M^+), 59 (100). HRMS: Calcd. for $C_{13}H_{10}O_3F_6$: 328.0534; Found: 328.0538.



(*E*)-Methyl (1,1,1-trifluoro-3-methyl-4-phenylbut-3-en-2-yl) carbonate (1j). The reaction was carried out on 10 mmol-scale from alcohol. Compound **1j** (2.14 g, 78% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 6.80 (s, 1H), 5.58 (q, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.02 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.9 (d, *J* = 7.1 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ154.8, 136.3, 134.8, 129.7, 128.9, 128.23, 128.20, 123.7 (q, *J* = 283.3 Hz), 79.3 (q, *J* = 33.1 Hz), 56.2, 14.6. IR (thin film) ν_{max} 2962, 1763, 1287 cm^{-1}. MS (EI): m/z (%) 274 (M^+), 129 (100). HRMS: Calcd. for $C_{13}H_{13}O_3F_3$: 274.0817; Found: 274.0809.

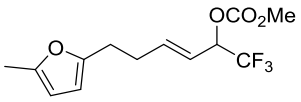


Methyl (1,1,1-trifluoro-4,4-diphenylbut-3-en-2-yl) carbonate (1k). The reaction was carried out on 2 mmol-scale from alcohol. Compound **1k** (436.2 mg, 65% yield) as a white solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40: 1), m.p. 69-72 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 3H), 7.32 – 7.21 (m, 7H), 6.06 (d, *J* = 9.6 Hz, 1H), 5.61 – 5.52 (m, 1H), 3.78 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.2 (d, *J* = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 152.8, 140.7, 138.1, 130.0, 129.5, 129.1, 129.0, 128.9, 128.2, 123.7 (q, *J* = 282.1 Hz), 116.1, 73.1 (q, *J* = 33.8 Hz), 56.0. IR (thin film) ν_{max} 2962, 2357, 1751, 1259 cm^{-1}. MS (EI): m/z (%) 336 (M^+), 55 (100). HRMS: Calcd. for $C_{18}H_{15}O_3F_3$: 336.0973; Found: 336.0974.

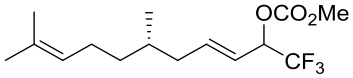


(*E*)-Methyl (1,1,1-trifluoro-6-phenylhex-3-en-2-yl) carbonate (1l). The reaction was carried out on 2 mmol-scale from alcohol. Compound **1l** (415.6 mg, 72% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.16 – 6.07 (m, 1H), 5.53 – 5.38 (m, 2H), 3.83 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.47 – 2.40 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

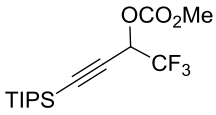
77.1 (d, J = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (s), 141.6 (s), 141.4 (s), 128.96, 128.94, 126.6, 123.4 (q, J = 281.7 Hz), 119.5, 75.4 (q, J = 33.8 Hz), 56.0, 35.3, 34.6. IR (thin film) ν_{max} 1763, 1258 cm^{-1}. MS (EI): m/z (%) 288 (M^+), 91 (100). HRMS: Calcd. for $C_{14}H_{15}O_3F_3$: 288.0973; Found: 288.0971.



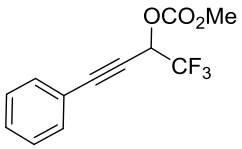
(*E*)-Methyl (1,1,1-trifluoro-6-(5-methylfuran-2-yl)hex-3-en-2-yl) carbonate (1m). The reaction was carried out on 2 mmol-scale from alcohol. Compound **1m** (581.7 mg, 98% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 20: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 – 6.06 (m, 1H), 5.86 – 5.81 (m, 2H), 5.55 – 5.39 (m, 2H), 3.80 (s, 3H), 2.68 (t, J = 7.2 Hz, 2H), 2.46 – 2.39 (m, 2H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.4 (d, J = 6.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 153.1, 150.9, 141.2, 123.4 (q, J = 281.6 Hz), 119.6 (q, J = 1.4 Hz), 106.4, 106.3, 75.2 (q, J = 33.7 Hz), 55.7, 31.4, 27.4, 13.6. IR (thin film) ν_{max} 2960, 1763, 1444, 1257 cm^{-1}. MS (EI): m/z (%) 292 (M^+), 95 (100). HRMS: Calcd. for $C_{13}H_{15}O_4F_3$: 292.0922; Found: 292.0915.



Methyl ((6*S*,*E*)-1,1,1-trifluoro-6,10-dimethylundeca-3,9-dien-2-yl) carbonate (1n). The reaction was carried out on 2 mmol-scale from alcohol. Compound **1n** (516.3 mg, 91% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 60: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (dt, J = 14.7 Hz, 7.3 Hz, 1H), 5.49 – 5.35 (m, 2H), 5.06 (t, J = 7.1 Hz, 1H), 3.81 (s, 3H), 2.18 – 2.07 (m, 1H), 2.03 – 1.88 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.56 – 1.49 (m, 1H), 1.33 – 1.28 (m, 1H), 1.19 – 1.11 (m, 1H), 0.86 (d, J = 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.25 (d, J = 5.6 Hz, 1.5F), -77.27 (d, J = 5.6 Hz, 1.5F, diastereoisomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 141.6, 141.5 (diastereoisomer), 131.9, 125.0, 123.5 (q, J = 281.7 Hz), 120.0, 75.55 (q, J = 33.7 Hz), 75.52 (q, J = 33.7 Hz, diastereoisomer), 55.9, 40.2, 37.1 (q, J = 5.3 Hz), 32.6, 26.2, 26.0, 19.8, 18.1. IR (thin film) ν_{max} 2962, 1764, 1258 cm^{-1}. MS (EI): m/z (%) 308 (M^+), 69 (100). HRMS: Calcd. for $C_{15}H_{23}O_3F_3$: 308.1599; Found: 308.1600.



Methyl (1,1,1-trifluoro-4-(triisopropylsilyl)but-3-yn-2-yl) carbonate (1o). The reaction was carried out on 2 mmol-scale from alcohol. Compound **1o** (343.3 mg, 51% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 100: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (q, *J* = 5.6 Hz, 1H), 3.87 (s, 3H), 1.08 – 1.05 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.1 (d, *J* = 5.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 122.0 (q, *J* = 282.1 Hz), 94.9, 93.6, 66.0 (q, *J* = 37.8 Hz), 56.4, 18.9, 11.5. IR (thin film) ν_{max} 2947, 1770, 1258 cm^{-1}. MS (EI): m/z (%) 338 (M^+), 93 (100). HRMS: Calcd. for $C_{15}H_{25}O_3F_3Si$: 338.1525; Found: 338.1528.

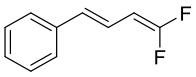


Methyl (1,1,1-trifluoro-4-phenylbut-3-yn-2-yl) carbonate (1p). The reaction was carried out on 30 mmol-scale from alcohol. Compound **1p** (3.94 g, 51% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.42 – 7.32 (m, 3H), 5.96 (q, *J* = 5.6 Hz, 1H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 5.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 132.8, 130.3, 129.0, 122.1 (q, *J* = 282.3 Hz), 121.1, 89.7, 77.5 (q, *J* = 2.1 Hz), 66.3 (q, *J* = 38.1 Hz), 56.5. IR (thin film) ν_{max} 2962, 2242, 1770, 1444, 1260 cm^{-1}. MS (EI): m/z (%) 258 (M^+), 182 (100). HRMS: Calcd. for $C_{12}H_9O_3F_3$: 258.0504; Found: 258.0509.

5. General Procedure for Ni-Catalyzed Defluorination of Compounds 1 with B_2pin_2 2.

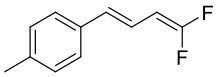
To a septum capped 25 mL of Schlenck tube were added B_2pin_2 **2** (228.6 mg, 1.5 equiv), $NiCl_2$·DME (13.2 mg, 10 mol %), 4,4′-dimethoxy-2,2′-bipyridine (13.0 mg, 10 mol %) and NaOMe (48.6 mg, 1.5 equiv) under argon, followed by addition of DME (2 mL). After stirring for 10 min at room temperature, a solution of compound **1** (0.6 mmol, 1.0 equiv) in DME (2 mL) was added to the reaction mixture. The tube was screw capped and put into an oil bath (preheated to 70 °C). After stirring for 6 h, the reaction mixture was cooled to room temperature, diluted with DCM, filtered through a pad of Celite and concentrated. The residue was purified with silica gel chromatography to give product **3**.

6. Data for Compounds 3

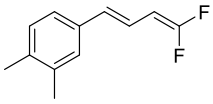


(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)benzene (3a). [Known compound[2]]: Compound **3a** (55.8 mg, 56% yield; 82% yield, determined by ^{19}F NMR) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.76 (dd, *J* = 16.0 Hz, 10.8 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 5.20 (dd, *J* = 24.0 Hz, 10.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.3 (dd, *J* = 26.7 Hz, 25.7 Hz, 1F), -87.1 (d, *J* = 26.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (dd, *J* = 297.1 Hz, 291.5 Hz), 137.5, 131.7 (dd, *J* = 11.5 Hz, 3.2 Hz), 129.2, 128.2, 126.7, 118.3 (dd, *J* = 4.2 Hz, 2.4 Hz), 83.4 (dd, *J* = 27.9 Hz, 17.1Hz).

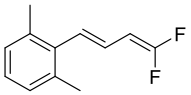
1-mmol Scale Synthesis of Compound 3a: To a septum capped 25 mL of Schlenck tube were added B_2pin_2 **2** (457.1 mg, 1.5 equiv), $NiCl_2$·DME (26.4 mg, 10 mol %), 4,4′-dimethoxy-2,2′-bipyridine (26.0 mg, 10 mol %) and NaOMe (97.2 mg, 1.5 equiv) under argon, followed by addition of DME (4 mL). After stirring for 30 min at room temperature, a solution of compound **1a** (312.3 mg, 1.2 mmol, 1.0 equiv) in DME (4 mL) was added to the reaction mixture. The tube was screw capped and put into an oil bath (preheated to 70 °C). After stirring for 6 h, the reaction mixture was cooled to room temperature, diluted with DCM, filtered through a pad of Celite and concentrated. The residue was purified with silica gel chromatography (Petroleum ether) to give product **3a** (123.6 mg, 62% yield; 69% yield, determined by ^{19}F NMR) as a colorless oil.



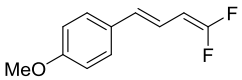
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-methylbenzene (3b). [Known compound[2]]: Compound **3b** (87.5 mg, 81% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.63 (dd, *J* = 16.0 Hz, 11.2 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.13 (dd, *J* = 24.1 Hz, 11.2 Hz, 1H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.8 (dd, *J* = 27.3 Hz, 26.3 Hz, 1F), -87.6 (d, *J* = 27.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (dd, *J* = 296.9 Hz, 291.2 Hz), 138.1, 134.7, 131.6 (dd, *J* = 11.6 Hz, 3.2 Hz), 129.9, 126.7, 117.4 (dd, *J* = 4.1 Hz, 2.4 Hz), 83.5 (dd, *J* = 27.7 Hz, 17.0 Hz), 21.8.



(*E*)-4-(4,4-Difluorobuta-1,3-dien-1-yl)-1,2-dimethylbenzene (3c). Compound **3c** (68.7 mg, 59% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 16.0 Hz, 11.2 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.14 (dd, *J* = 24.4 Hz, 11.2 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.9 (dd, *J* = 27.8 Hz, 24.4 Hz, 1F), -87.7 (d, *J* = 27.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (dd, *J* = 298.2 Hz, 292.5 Hz), 137.3, 136.9, 135.2, 131.8 (dd, *J* = 11.6 Hz, 3.3 Hz), 130.5, 128.0, 124.3, 117.2 (dd, *J* = 3.7 Hz, 2.3 Hz), 83.5 (dd, *J* = 27.7 Hz, 17.2 Hz), 20.3, 20.1. MS (EI): m/z (%) 194 (M^+, 100). HRMS: Calcd. for $C_{12}H_{12}F_2$: 194.0907; Found: 194.0910.

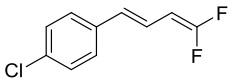


(*E*)-2-(4,4-Difluorobuta-1,3-dien-1-yl)-1,3-dimethylbenzene (3d). Compound **3d** (75.7 mg, 65% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 3H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0 Hz, 10.8 Hz, 1H), 5.22 (dd, *J* = 24.4 Hz, 10.8 Hz, 1H), 2.37 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.1 (dd, *J* = 28.6 Hz, 24.4 Hz, 1F), -87.7 (d, *J* = 28.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (dd, *J* = 297.7 Hz, 292.1 Hz), 137.0, 136.6, 129.8 (dd, *J* = 11.4 Hz, 3.2 Hz), 128.5, 127.4, 123.7 (dd, *J* = 4.2 Hz, 1.9 Hz), 83.4 (dd, *J* = 27.1 Hz, 17.0 Hz), 21.6. MS (EI): m/z (%) 194 (M^+, 100). HRMS: Calcd. for $C_{12}H_{12}F_2$: 194.0907; Found: 194.0912.

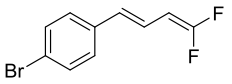


(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-methoxylbenzene (3e). [Known compound[3]]: Compound **3e** (64.7 mg, 55% yield) as acolorless oil was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40: 1)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.53 (dd, *J* = 16.0 Hz, 10.0 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.11 (ddd, *J* = 24.4 Hz, 10.0 Hz, 1.2 Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) -86.3 (t, *J* = 26.7 Hz, 1F), -88.1 (d, *J* = 29.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 157.2 (dd, *J* = 296.5 Hz, 290.6 Hz), 131.2 (dd, *J* = 11.7

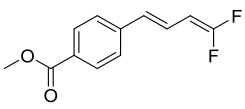
Hz, 3.3 Hz), 130.3, 128.0, 116.3 (dd, *J* = 3.9 Hz, 2.4 Hz), 114.7, 83.5 (dd, *J* = 27.7 Hz, 17.1 Hz), 55.8.



(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-chlorobenzene (3f). The reaction runs for 7 h. Compound **3f** (75.8 mg, 63% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 4H), 6.60 (dd, *J* = 16.0 Hz, 11.2 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 5.09 (dd, *J* = 24.0 Hz, 11.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.8 (t, *J* = 24.7 Hz, 1F), -88.4 (d, *J* = 24.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (dd, *J* = 297.6 Hz, 292.1 Hz), 136.0, 133.8, 130.3 (dd, *J* = 11.6 Hz, 3.3 Hz), 129.4, 127.9, 119.0 (dd, *J* = 3.6 Hz, 2.2 Hz), 83.3 (dd, *J* = 27.9 Hz, 16.9 Hz). IR (thin film) ν_{max} 3066, 1700, 1491, 1091 cm^{-1}. MS (EI): m/z (%) 200 (M^+), 165 (100). HRMS: Calcd. for $C_{10}H_7ClF_2$: 200.0204; Found: 200.0200.

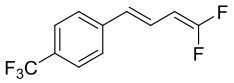


(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-bromobenzene (3g). *t*-Butyl carbonate was used as a substrate. Compound **3g** (61.8 mg, 42% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.64 (dd, *J* = 16.0 Hz, 10.8 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 5.12 (dd, *J* = 24.0 Hz, 10.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (t, *J* = 24.4 Hz, 1F), -86.3 (d, *J* = 24.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (dd, *J* = 297.8 Hz, 292.2 Hz), 136.4, 132.3, 130.4 (dd, *J* = 11.7 Hz, 3.4 Hz), 128.2, 121.9, 119.1 (dd, *J* = 4.3 Hz, 2.4 Hz), 83.3 (dd, *J* = 27.9 Hz, 16.8 Hz). IR (thin film) ν_{max} 3064, 1701, 1488, 1072 cm^{-1}. MS (EI): m/z (%) 244 (M^+), 165 (100). HRMS: Calcd. for $C_{10}H_7F_2Br$: 243.9699; Found: 243.9698.

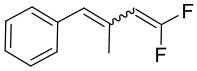


Methyl (*E*)-4-(4,4-difluorobuta-1,3-dien-1-yl)benzoate (3h). *t*-Butyl carbonate was used as a substrate. Compound **3h** (71.3 mg, 53% yield) as a light yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40: 1), m.p. 53-55 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.97 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 16.0 Hz, 10.8 Hz, 1H), 6.47 (d, *J* =

16.0 Hz, 1H), 5.14 (dd, *J* = 24.0 Hz, 10.8 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.8 (t, *J* = 22.9 Hz, 1F), -85.3 (d, *J* = 22.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 157.7 (dd, *J* = 298.5 Hz, 293.0 Hz), 141.8, 130.7– 130.5 (m, 2C), 129.5, 126.5, 120.9 (dd, *J* = 4.4 Hz, 2.4 Hz), 83.4 (dd, *J* = 28.0 Hz, 16.7 Hz), 52.6. IR (thin film) ν_{max} 3470, 1705, 1282 cm^{-1}. MS (EI): m/z (%) 224 (M^+), 164 (100). HRMS: Calcd. for $C_{12}H_{10}O_2F_2$: 224.0649; Found: 224.0645.

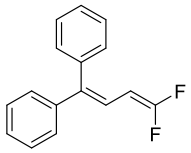


(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-trifluoromethylbenzene (3i). [Known compound[3]]: Compound **3i** (70.3 mg, 50% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.8 Hz, 2H), 7.46 (d, *J* = 6.8 Hz, 2H), 6.81 – 6.71 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 5.16 (d, *J* = 24.0 Hz, 11.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.4 (s, 3F), -88.7 (t, *J* = 22.9 Hz, 1F), -90.2 (d, *J* = 22.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 (dd, *J* = 298.4 Hz, 293.0 Hz), 140.9, 130.1 (dd, *J* = 11.6 Hz, 3.4 Hz), 130.4 – 129.4 (m, 1C), 126.8, 126.2 (q, *J* = 3.8 Hz), 126.0 – 118.0 (m, 1C), 121.0 (dd, *J* = 4.4 Hz, 2.3 Hz), 83.3 (dd, *J* = 28.1 Hz, 16.8 Hz).

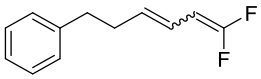


(4,4-Difluoro-2-methylbuta-1,3-dien-1-yl)benzene (3j). [Known compound[4]]: Compound **3j** (*E*/*Z* = 1.3:1, determined by ^{19}F NMR from the crude reaction mixture, 50.8 mg, 47% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 5H), 6.51 (s, 0.51H, *E*-isomer), 6.44 (s, 0.43H, *Z*-isomer), 5.46 (dd, *J* = 27.6 Hz, 4.9 Hz, 0.44H, *Z*-isomer), 5.13 (dd, *J* = 26.1 Hz, 5.0 Hz, 0.51H, *E*-isomer), 2.20 (dd, *J* = 3.7 Hz, 1.1 Hz, 1.53H, *Z*-isomer), 2.18 – 2.13 (m, 1.64H, *E*-isomer). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.4 – -80.5 (m, 0.46F, *Z*-isomer), -82.7 – -83.0 (m, 0.52F, *E*-isomer), -83.6 (dd, *J* = 31.6 Hz, 4.5 Hz, 0.46F, *Z*-isomer), -85.4 (dd, *J* = 36.1 Hz, 4.9 Hz, 0.53F, *E*-isomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (dd, *J* = 302.4 Hz, 289.7 Hz, *Z*-isomer), 156.5 (dd, *J* = 301.6 Hz, 288.5 Hz, *E*-isomer), 138.0 (*Z*-isomer), 137.9 (*E*-isomer), 130.4 – 130.1 (m), 129.6 (*E*-isomer), 129.5 (*Z*-isomer), 129.1 – 128.9 (m), 128.85 (*Z*-isomer), 128.7 (*E*-isomer), 128.0 – 127.8 (m), 127.4 (*Z*-isomer), 127.2 (*E*-isomer), 87.4 (dd, *J* = 28.4 Hz, 11.8 Hz, *E*-

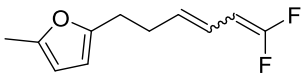
isomer), 81.7 (dd, *J* = 29.6 Hz, 12.2 Hz, *Z*-isomer), 23.2 (d, *J* = 6.3 Hz, *Z*-isomer), 16.7 (d, *J* = 6.2 Hz, *E*-isomer).



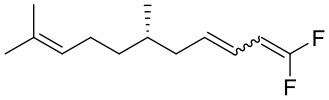
(4,4-Difluorobuta-1,3-diene-1,1-diyl)dibenzene (3k). [Known compound[5]]: Compound **3k** (103.2 mg, 71% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.30 (m, 10H), 6.76 (d, *J* = 11.6 Hz, 1H), 5.22 (ddd, *J* = 24.3 Hz, 11.2 Hz, 1.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (t, *J* = 23.7 Hz, 1F), -85.4 (d, *J* = 23.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (dd, *J* = 298.5 Hz, 291.8 Hz), 143.0 (d, *J* = 11.9 Hz, 3.5 Hz), 142.3, 139.7, 130.7, 129.0, 128.8, 128.2, 128.1, 128.0, 116.9 (dd, *J* = 3.3 Hz, 2.9 Hz), 81.6 (dd, *J* = 28.4 Hz, 14.9 Hz).



(6,6-Difluorohexa-3,5-dien-1-yl)benzene (3l). Compound **3l** (*E*/*Z* = 3.2:1, determined by ^{19}F NMR from the crude reaction mixture, 93.2 mg, 80% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 5H), 6.08 – 5.98 (m, 1H), 5.75 – 5.66 (m, 0.79H, *E*-isomer), 5.60 – 5.52 (m, 0.29H, *Z*-isomer), 5.22 – 5.11 (m, 0.28H, *Z*-isomer), 4.97 (dd, *J* = 24.4 Hz, 10.4 Hz, 0.72H, *E*-isomer), 2.81 – 2.75 (m, 2H), 2.52 – 2.45 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.4 (t, *J* = 27.8 Hz, 0.25F, *Z*-isomer), -87.3 (d, *J* = 27.8 Hz, 0.25F, *Z*-isomer), -87.5 (dd, *J* = 34.2 Hz, 24.8 Hz, 0.74F, *E*-isomer), -90.1 (d, *J* = 34.2 Hz, 0.76F, *E*-isomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (dd, *J* = 297.7 Hz, 291.5 Hz, *Z*-isomer), 156.5 (dd, *J* = 296.0 Hz, 290.4 Hz, *E*-isomer), 142.1 (*E*-isomer), 142.0 (*Z*-isomer), 131.1 (dd, *J* = 11.3 Hz, 3.2 Hz, *Z*-isomer), 133.0 (dd, *J* = 11.1 Hz, 3.0 Hz, *E*-isomer), 129.0 – 128.9 (m), 126.6 (*Z*-isomer), 126.5 (*E*-isomer), 119.8 (dd, *J* = 4.2 Hz, 1.2 Hz, *E*-isomer), 118.3 (dd, *J* = 3.9 Hz, 1.1 Hz, *Z*-isomer), 82.5 (dd, *J* = 26.8 Hz, 17.2 Hz, *E*-isomer), 78.6 (dd, *J* = 26.7 Hz, 16.6 Hz, *Z*-isomer), 36.2 (*E*-isomer), 36.1 (*Z*-isomer), 35.2 (*E*-isomer), 30.1(*Z*-isomer). MS (EI): m/z (%) 194 (M^+), 91 (100). HRMS: Calcd. for $C_{12}H_{12}F_2$: 194.0907; Found: 194.0905.

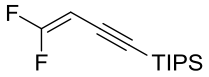


2-(6,6-Difluorohexa-3,5-dien-1-yl)-5-methylfuran (3m). Compound **3m** (*E*/*Z* = 2.4:1, determined by ^{19}F NMR from the crude reaction mixture, 61.8 mg, 52% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 – 5.94 (m, 1H), 5.89 – 5.85 (m, 2H), 5.70 – 5.60 (m, 0.71H, *E*-isomer), 5.53 – 5.44 (m, 0.29H, *Z*-isomer), 5.21 – 5.10 (m, 0.30H, *Z*-isomer), 4.92 (dd, *J* = 24.4 Hz, 10.8 Hz, 0.70H, *E*-isomer), 2.71 – 2.65 (m, 2H), 2.46 – 2.41 (m, 2H), 2.27 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.4 (t, *J* = 27.8 Hz, 0.29F, *Z*-isomer), -87.4 (d, *J* = 27.8 Hz, 0.28F, *Z*-isomer), -88.0 (dd, *J* = 35.0 Hz, 24.4 Hz, 0.72F, *E*-isomer), -90.8 (d, *J* = 35.0 Hz, 0.72F, *E*-isomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6 (dd, *J* = 298.3 Hz, 291.5 Hz, *Z*-isomer), 156.6 (dd, *J* = 296.2 Hz, 290.4 Hz, *E*-isomer), 154.0 (*E*-isomer), 153.8 (*Z*-isomer), 151.05 (*Z*-isomer), 150.96 (*E*-isomer), 132.6 (dd, *J* = 11.2 Hz, 3.0 Hz, *E*-isomer), 130.7 (dd, *J* = 11.4 Hz, 3.3 Hz, *Z*-isomer), 120.0 (d, *J* = 4.3 Hz, 1.4 Hz, *E*-isomer), 118.5 (d, *J* = 4.0 Hz, 1.3 Hz, *Z*-isomer), 106.44 (*Z*-isomer), 106.42 (*Z*-isomer), 106.39 (*E*-isomer), 106.2 (*E*-isomer), 82.5 (dd, *J* = 26.8 Hz, 17.2 Hz, *E*-isomer), 78.6 (dd, *J* = 26.8 Hz, 16.6 Hz, *Z*-isomer), 32.0 (*Z*-isomer), 28.5 (*Z*-isomer), 28.4 (*E*-isomer), 27.0 (*E*-isomer), 14.0. MS (EI): m/z (%) 198 (M^+), 95 (100). HRMS: Calcd. for $C_{11}H_{12}F_2O$: 198.0856; Found: 198.0850.

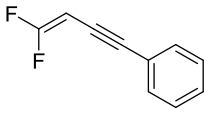


(*S*)-1,1-Difluoro-6,10-dimethylundeca-1,3,9-triene (3n). Compound **3n** (*E*/*Z* = 4.4:1, determined by ^{19}F NMR from the crude reaction mixture, 77.1 mg, 60% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 – 5.84 (m, 1H), 5.63 – 5.54 (m, 0.78H, *E*-isomer), 5.52 – 5.42 (m, 0.27H, *Z*-isomer), 5.20 – 5.07 (m, 1.27H), 4.91 (dd, *J* = 24.8 Hz, 10.8 Hz, 0.74H, *E*-isomer), 2.14 – 2.04 (m, 1H), 2.02 – 1.89 (m, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.55 – 1.48 (m, 1H), 1.40 – 1.30 (m, 1H), 1.20 – 1.10 (m, 1H), 0.90 – 0.86 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.9 (dd, *J* = 29.0 Hz, 24.8 Hz, 0.22F, *Z*-isomer), -87.8 (d, *J* = 29.0 Hz, 0.24F, *Z*-isomer), -88.0 (dd, *J* = 35.0 Hz, 24.4 Hz, 0.76F, *E*-isomer), -90.8 (d, *J* = 35.0 Hz, 0.77F, *E*-isomer). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (dd, *J* = 297.5 Hz, 291.0 Hz, *Z*-isomer), 156.5 (dd, *J* = 295.8 Hz, 290.0 Hz, *E*-isomer), 132.8 (dd, *J* = 11.2 Hz, 3.0 Hz, *E*-isomer), 131.9 (*Z*-isomer), 131.8 (*E*-isomer), 131.1 (dd, *J* = 11.3 Hz, 3.3 Hz, *Z*-isomer), 125.32 (*E*-isomer), 125.26 (*Z*-isomer), 120.3 (dd, *J* = 4.1

Hz, 1.4 Hz, *E*-isomer), 118.4 (dd, *J* = 3.8 Hz, 1.2 Hz, *Z*-isomer), 82.6 (dd, *J* = 26.6 Hz, 17.3 Hz, *E*-isomer), 78.8 (dd, *J* = 26.5 Hz, 16.7 Hz, *Z*-isomer), 40.9 (*E*-isomer), 37.3 (*Z*-isomer), 37.2 (*E*-isomer), 35.5 (*Z*-isomer), 33.5 (*Z*-isomer), 33.4 (*E*-isomer), 26.3 (*E*-isomer), 26.23 (*Z*-isomer), 26.18 (*E*-isomer), 20.02 (*Z*-isomer), 19.97 (*E*-isomer), 18.2 (*E*-isomer). MS (EI): m/z (%) 214 (M^+), 69 (100). HRMS: Calcd. for $C_{13}H_{20}F_2$: 214.1533; Found: 214.1537.

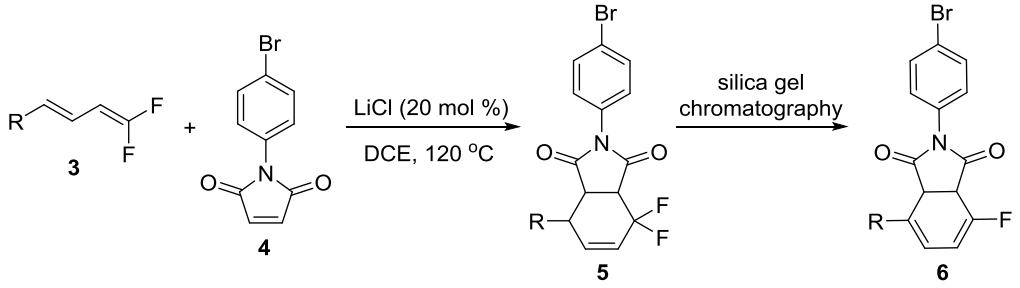


(4,4-Difluorobut-3-en-1-yn-1-yl)triisopropylsilane (3o). Compound **3o** (105.5 mg, 72% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, *J* = 23.2 Hz, 1H), 1.12 – 1.07 (m, 21H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.4 (dd, *J* = 22.9 Hz, 4.1 Hz, 1F), -80.3 (d, *J* = 4.1 Hz, 1F).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (dd, *J* = 300.4 Hz, 294.6 Hz), 96.4 (dd, *J* = 7.7 Hz, 3.5 Hz), 95.2 (dd, *J* = 10.8 Hz, 4.2 Hz), 66.5 (dd, *J* = 41.0 Hz, 19.2 Hz), 19.1, 11.8. IR (thin film) ν_{max} 2946, 2152, 1716, 1222 cm^{-1}. MS (EI): m/z (%) 244 (M^+), 91 (100). HRMS: Calcd. for $C_{13}H_{22}F_2Si$: 244.1459; Found: 244.1463.

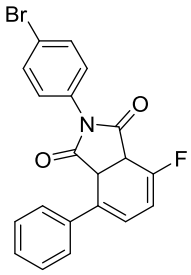


(4,4-Difluorobut-3-en-1-yn-1-yl)benzene (3p). [Known compound[6]]: Compound **3p** (42.3 mg, 43% yield) as a yellow oil was purified with silica gel chromatography (Petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.34 – 7.29 (m, 3H), 4.80 (d, *J* = 22.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.6 (dd, *J* = 23.3 Hz, 4.9 Hz, 1F), -79.9 (d, *J* = 4.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 300.6 Hz, 294.5 Hz), 132.0, 129.1, 128.9, 123.4, 93.8 (dd, *J* = 8.7 Hz, 3.7 Hz), 78.1 (dd, *J* = 11.9 Hz, 4.4 Hz), 66.3 (dd, *J* = 42.2 Hz, 18.8 Hz).

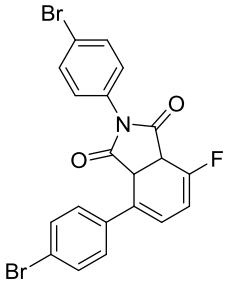
7. Synthesis of Compounds 6



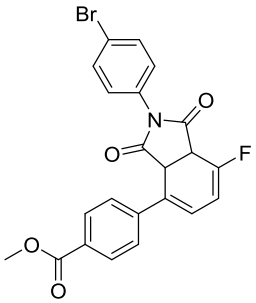
To a 25 mL of Schlenk tube were added *N*-(4-bromophenyl)maleimide **4** (1.2 equiv), compound **3** (0.3 mmol, 1.0 equiv) and LiCl (20 mol %) under argon atmosphere, followed by addition of DCE (2 mL). The reaction mixture was stirred for 2 days at 120 ^{0}C (oil bath). Then, the reaction mixture was cooled to room temperature and fluorobenzene (1.0 equiv) was added. The yield was determined by ^{19}F NMR before working up. Then, the reaction mixture was diluted with dichloromethane, filtered through a pad of Celite and concentrated. The residue was purified with silica gelchromatography (Ethyl acetate/Petroleum ether) to afford compound **6**.



2-(4-Bromophenyl)-4-fluoro-7-phenyl-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione (6a). Compound **6a** (87.0 mg, 73% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 5: 1), m.p. 171-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.22 (m, 5H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.60 – 6.53 (m, 1H), 6.35 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 4.27 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H), 4.23 – 4.16 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.3 – -99.5 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 163.5, 158.2 (d, *J* = 284.0 Hz), 143.0 (d, *J* = 9.1 Hz), 132.8, 132.6, 130.9, 129.4, 129.3, 129.0, 128.4, 122.8, 122.2 (d, *J* = 30.8 Hz), 100.3 (d, *J* = 7.3 Hz), 45.6 (d, *J* = 1.9 Hz), 39.8. IR (thin film) ν_{max} 1709, 1376 cm^{-1}. MS (EI): m/z (%) 397 (M^+), 172 (100). HRMS: Calcd. for $C_{20}H_{13}NO_2BrF$: 397.0114; Found: 397.0111.

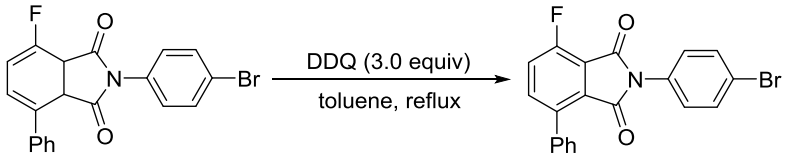


2,4-Bis(4-bromophenyl)-7-fluoro-3a,7a-dihydro-1H-isoindole-1,3(2*H*)-dione (6b). Compound **6b** (78.0 mg, 55% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 5: 1), m.p. 194-195 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.59 – 6.52 (m, 1H), 6.39 (dd, *J* = 10.0 Hz, 6.0 Hz, 1H), 4.31 (dd, *J* = 9.2 Hz, 4.0 Hz, 1H), 4.19 (dd, *J* = 9.2 Hz, 5.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.2 (dd, *J* = 4.5 Hz, 9.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 163.4, 158.0 (d, *J* = 284.6 Hz), 142.3 (d, *J* = 9.2 Hz), 132.8, 132.6, 131.9, 131.2, 130.8, 128.4, 123.2, 123.0, 122.8 (d, *J* = 31.0 Hz), 100.3 (d, *J* = 7.3 Hz), 45.5 (d, *J* = 2.1 Hz), 39.1. MS (EI): m/z (%) 472 (M^+), 84 (100). HRMS: Calcd. for $C_{20}H_{10}NO_2Br_2F$: 472.9062; Found: 472.9065.



Methyl4-(2-(4-bromophenyl)-7-fluoro-1,3-dioxo-2,3,3a,7a-tetrahydro-1*H*-isoindol-4-yl)benzoate (6c). Compound **6c** (84.6 mg, 62% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 3: 1), m.p. 184-187 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.60 – 6.53 (m, 1H), 6.41 (dd, *J* = 9.6 Hz, 5.6 Hz, 1H), 4.33 (dd, *J* = 9.6 Hz, 4.0 Hz, 1H), 4.27 (dd, *J* = 9.6 Hz, 5.6 Hz, 1H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.2 (dd, *J* = 9.8 Hz, 4.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 167.0, 163.3, 158.0 (d, *J* = 284.6 Hz), 142.1 (d, *J* = 9.0 Hz), 138.2, 132.7, 130.84, 130.80, 130.6, 129.6, 128.3, 122.95, 122.94 (d, *J* = 31.1 Hz), 100.4 (d, *J* = 7.2 Hz), 52.8, 45.5 (d, *J* = 2.0 Hz), 39.5. MS (EI): m/z (%) 455 (M^+), 199 (100). HRMS: Calcd. for $C_{22}H_{15}NO_4BrF$: 455.0168; Found: 455.0175.

8. Synthesis of Compound 7



2-(4-Bromophenyl)-4-fluoro-7-phenylisoindoline-1,3-dione (7). To a 50 mL round bottom flask equipped with a magnetic bar were added toluene (10 mL), compound **6a** (0.2 mmol, 1.0 equiv) and DDQ (0.6 mmol, 3.0 equiv). The resulting mixture was stirred reflux for 12 h. Then the reaction mixture was concentrated and subjected to flash column chromatography. The product was eluted with ethyl acetate/petroleum ether = 10: 1 to afford compound **7** (60.0 mg, 76% yield) as a yellow solid. m.p. 195-197 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.44 (m, 6H), 7.31 (d, *J* = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8 (dd, *J* = 8.3 Hz, 4.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.8, 157.9 (d, *J* = 267.9 Hz), 139.8 (d, *J* = 7.5 Hz), 138.7 (d, *J* = 4.0 Hz), 135.7, 132.8, 130.8, 129.9, 129.5, 129.0, 128.8, 128.6, 123.5 (d, *J* = 19.8 Hz), 122.6. MS (EI): m/z (%) 394 (M^+), 397 (100). HRMS: Calcd. for $C_{20}H_{11}NO_2BrF$: 394.9957; Found: 394.9960.

9. References

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2) Fujino, T.; Satoh, T. *Org. Lett.* **2005**, *7*, 721.

3) Ichitsuka, T.; Ichikawa, J. *J. Fluorine Chem.* **2015**, *170*, 29.

4) Hu, J.; Shi, Z. *Angew. Chem., Int. Ed.* **2017**, *56*, 13342.

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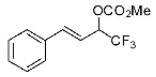
6) Fujino,T.; Satoh,T. *Org. Lett.* **2016**, *18*, 5688.

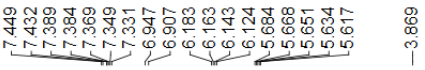
7) Elsheimer, S.; Foti, C. J.; Bartberger, M. D. *J. Org. Chem.* **1996**, *61*, 6252.

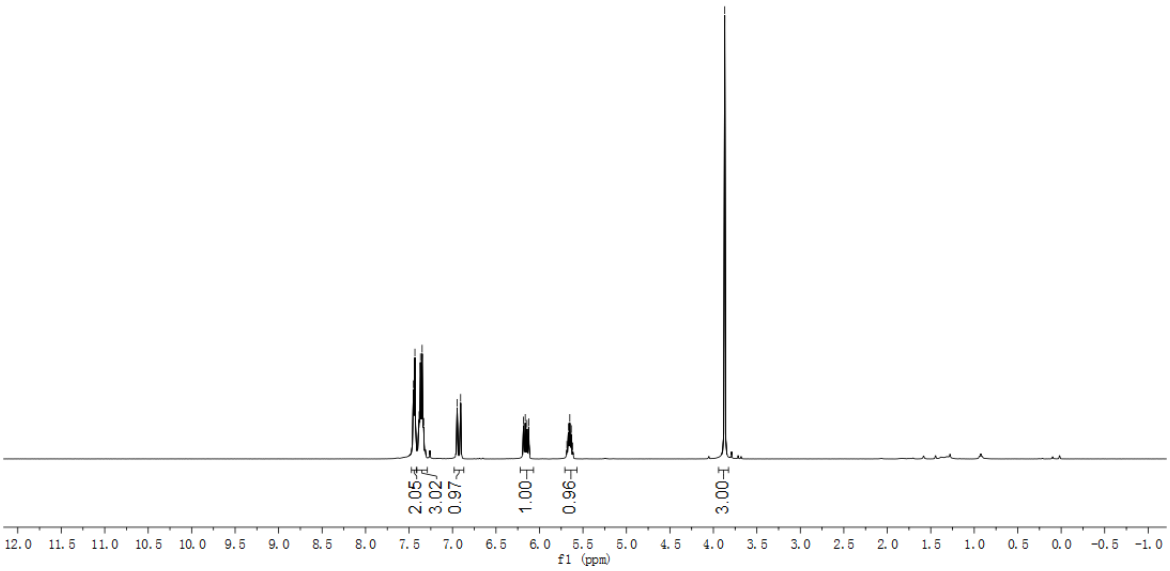
10. Copies of ^{1}HNMR, ^{13}C NMR, and ^{19}F NMR Spectra of Compounds

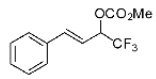
(*E*)-Methyl (1,1,1-trifluoro-4-phenylbut-3-en-2-yl) carbonate (1a).



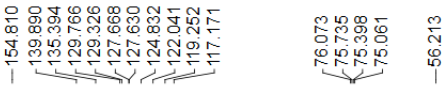
Chemical Formula: $C_{12}H_{11}F_3O_3$
Exact Mass: 260.0660

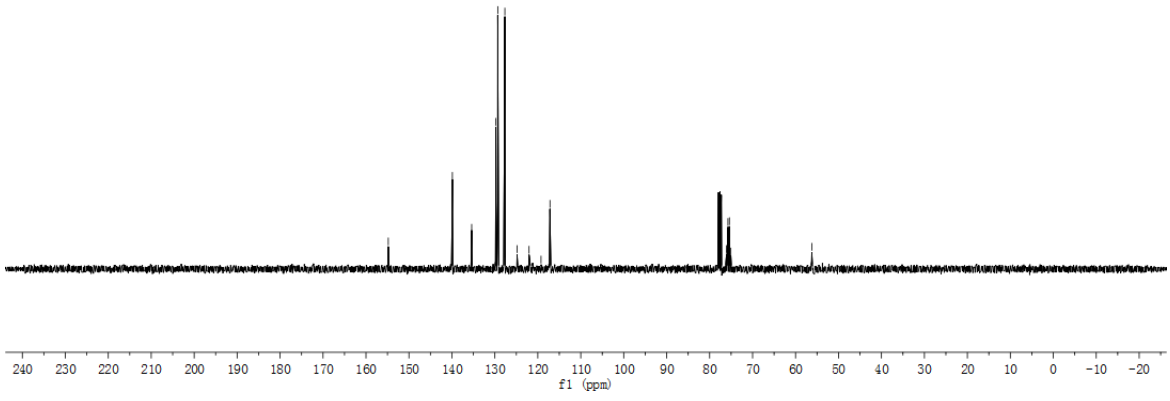


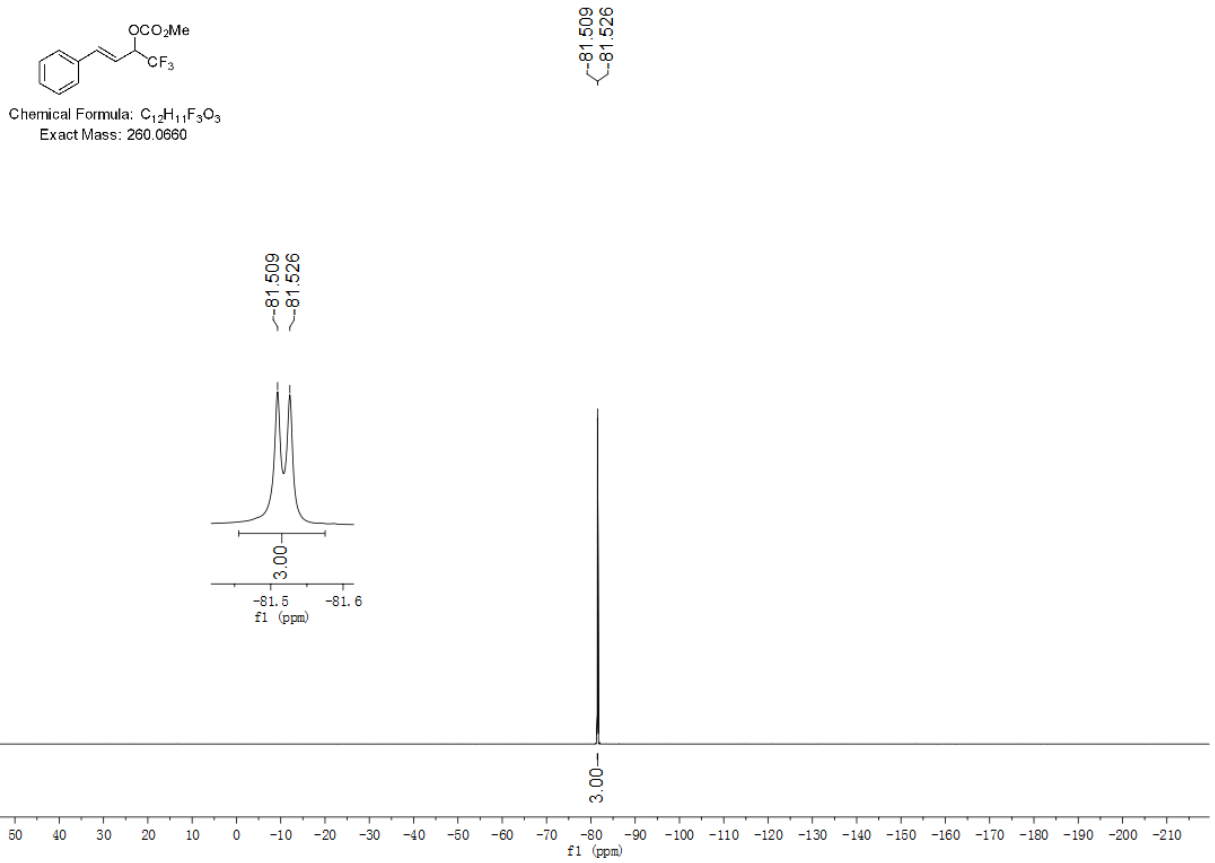




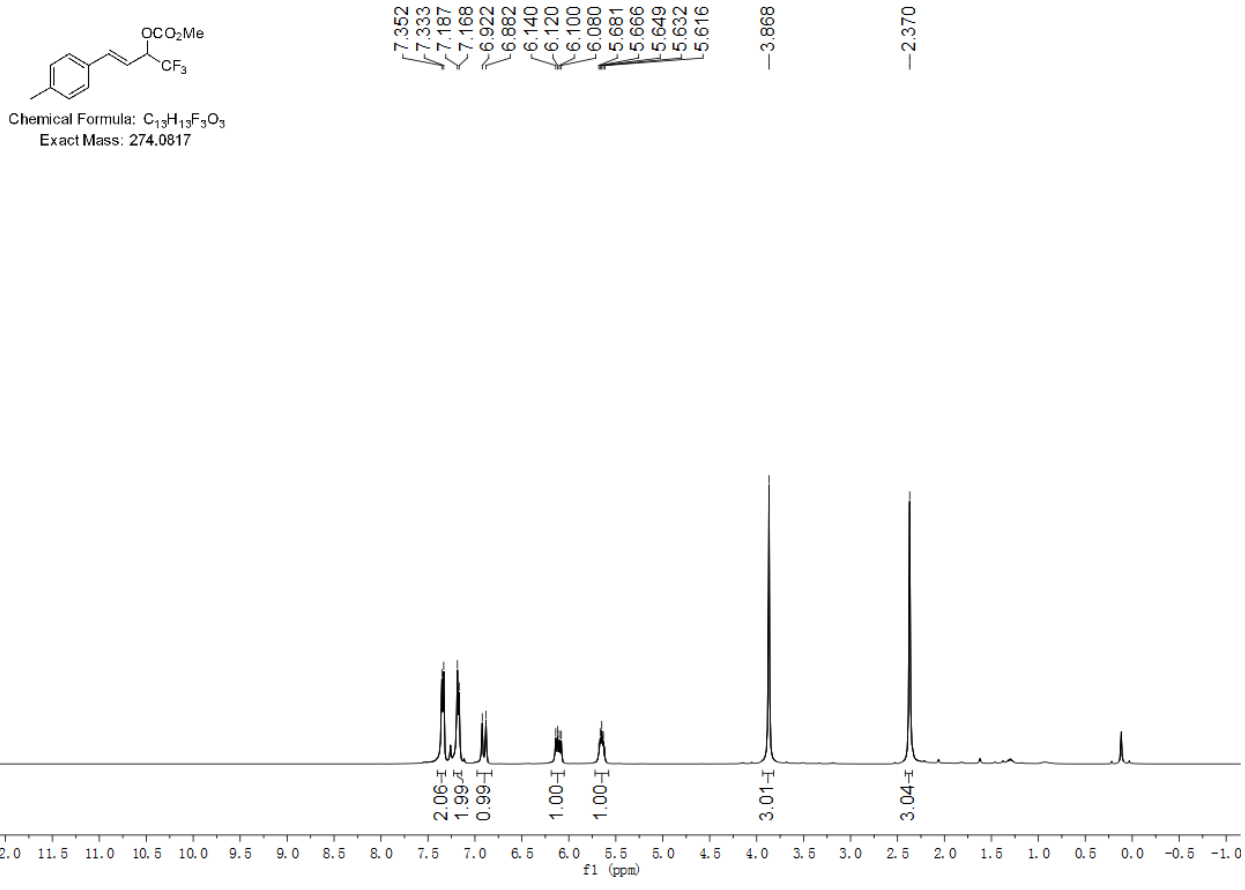
Chemical Formula: $C_{12}H_{11}F_3O_3$
Exact Mass: 260.0660

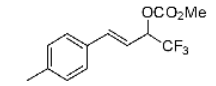






(*E*)-Methyl (1,1,1-trifluoro-4-(*p*-tolyl)but-3-en-2-yl) carbonate (1b).





Chemical Formula: $C_{13}H_{13}F_3O_3$
Exact Mass: 274.0817

154.823
139.911
139.878
132.642
129.999
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127.591
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122.090
119.300
116.029
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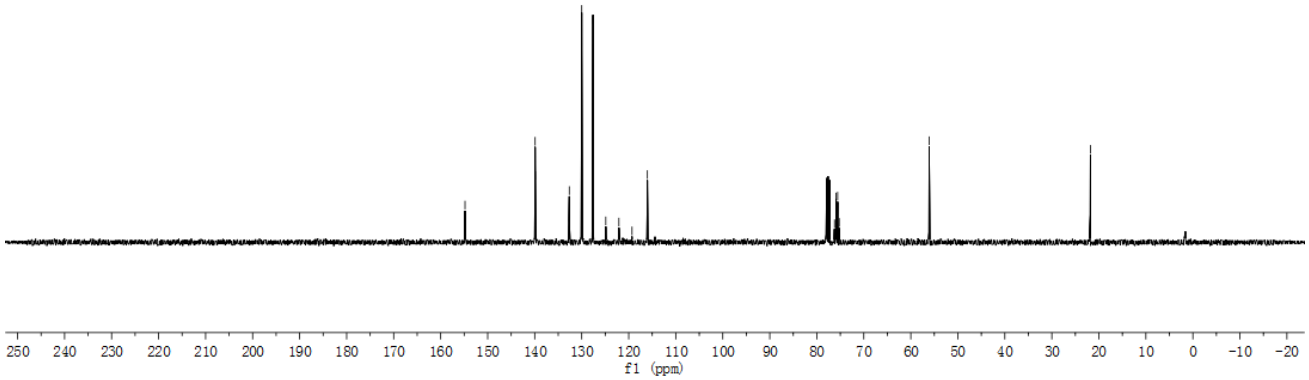
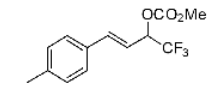
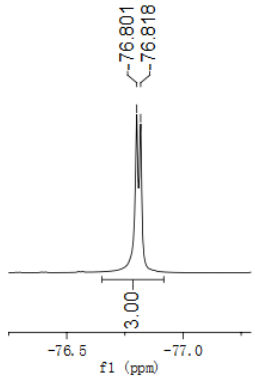
75.895
75.559
75.221
56.093
21.802

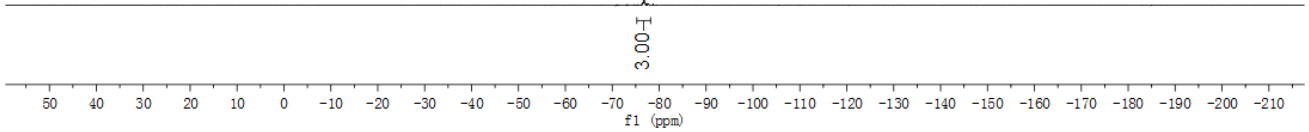




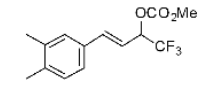
Chemical Formula: $C_{13}H_{13}F_3O_3$
Exact Mass: 274.0817

76.801
76.818

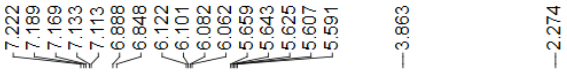


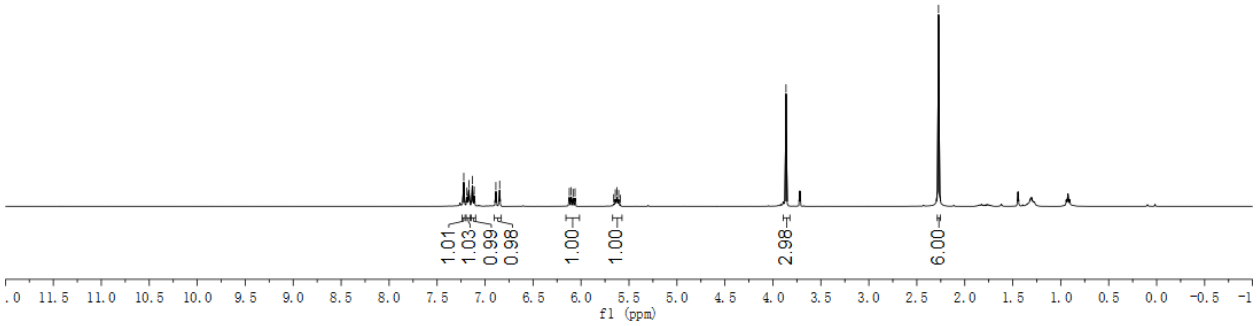


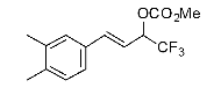
(*E*)-4-(3,4-Dimethylphenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1c).



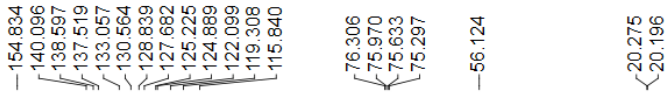
Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

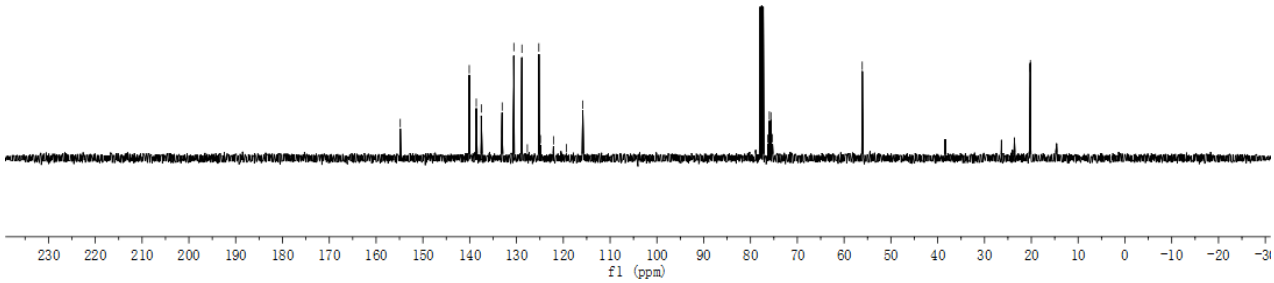


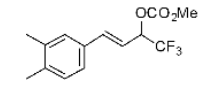




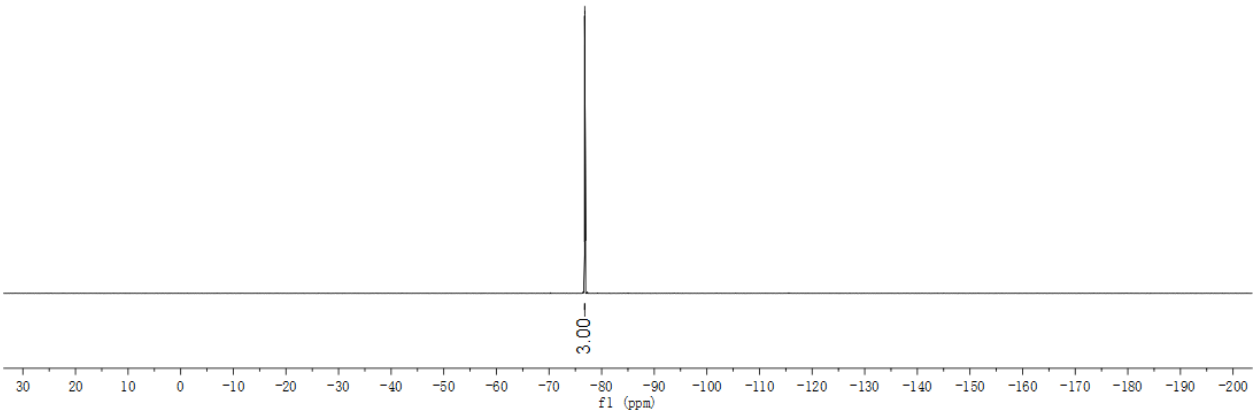
Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973



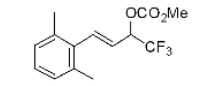




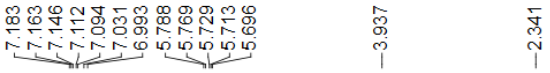
Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

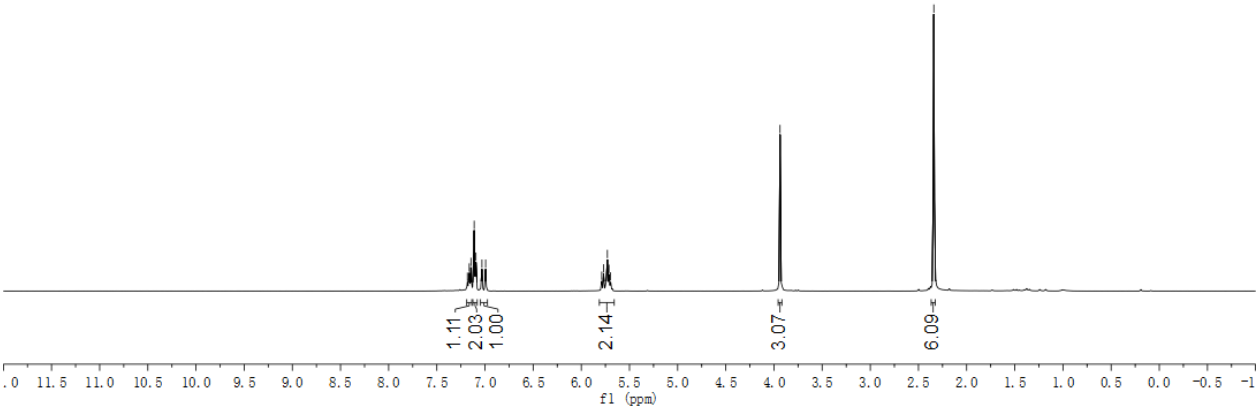


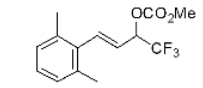
(*E*)-4-(2,6-Dimethylphenyl)-1,1,1-trifluorobut-3-en-2-yl methyl carbonate (1d).



Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973







Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

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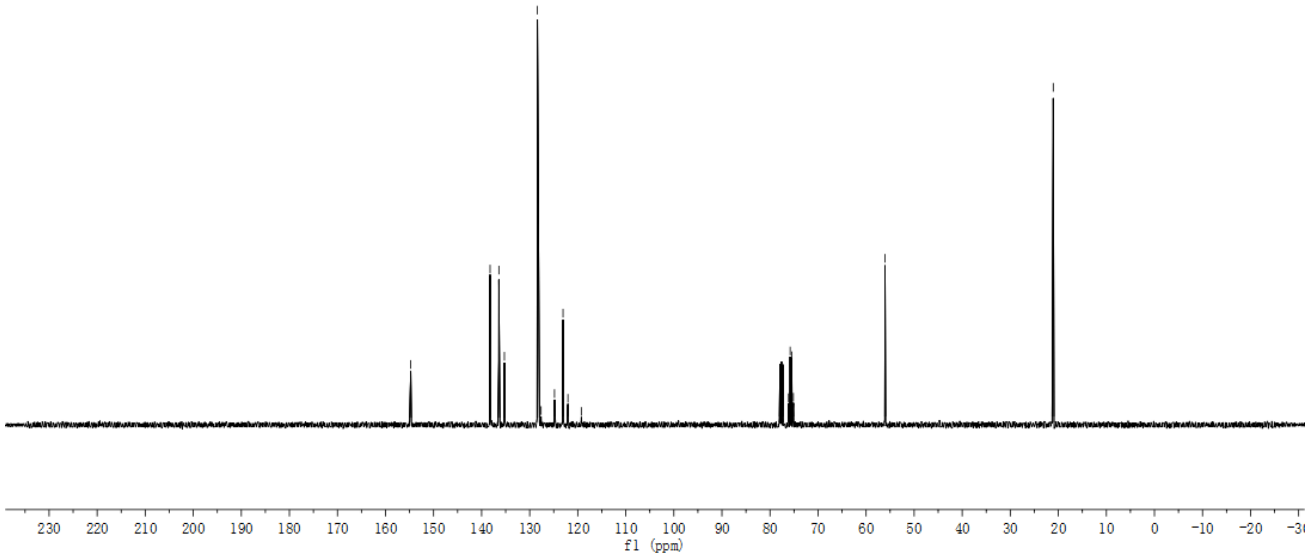
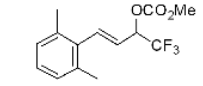
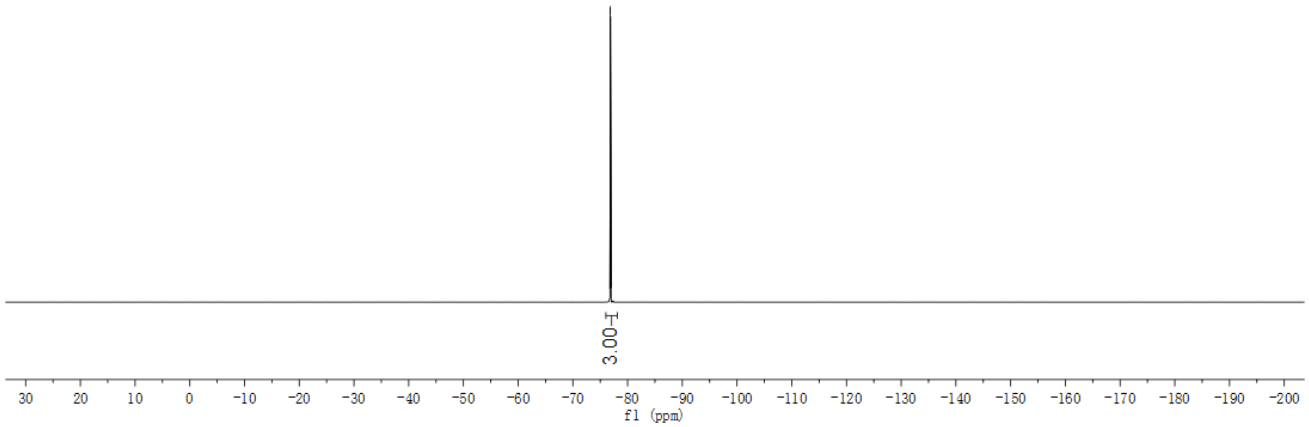
56.053
21.057



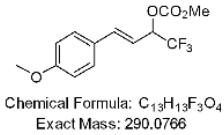


Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

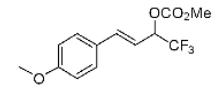
76.836
76.852



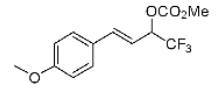
(*E*)-Methyl (1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl) carbonate (1e).



Chemical Formula: $C_{13}H_{13}F_3O_4$
Exact Mass: 290.0766

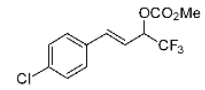


Chemical Formula: $C_{13}H_{13}F_3O_4$
Exact Mass: 290.0766

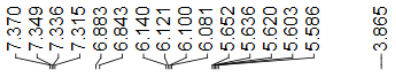


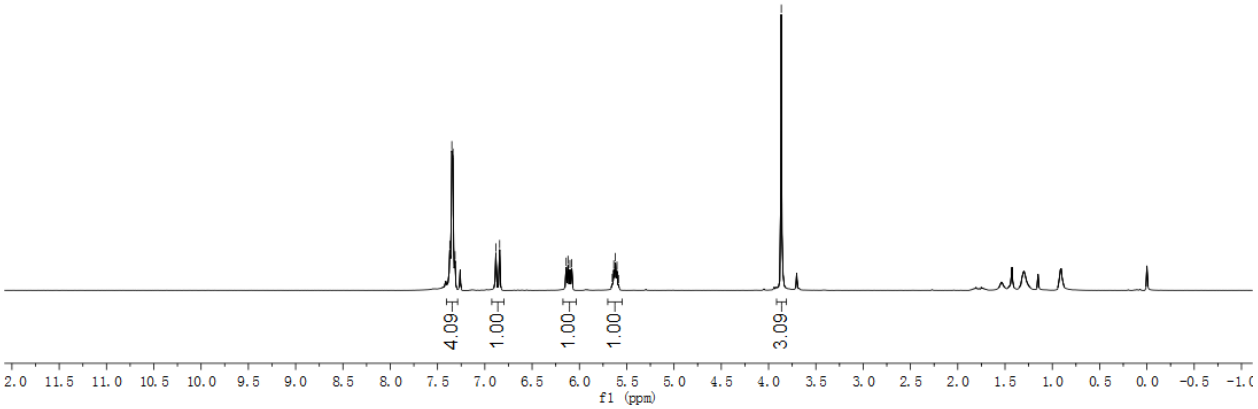
Chemical Formula: $C_{13}H_{13}F_3O_4$
Exact Mass: 290.0766

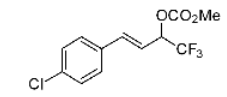
(*E*)-Methyl (1,1,1-trifluoro-4-(4-chlorophenyl)but-3-en-2-yl) carbonate (1f).



Chemical Formula: $C_{12}H_{10}ClF_3O_3$
Exact Mass: 294.0271

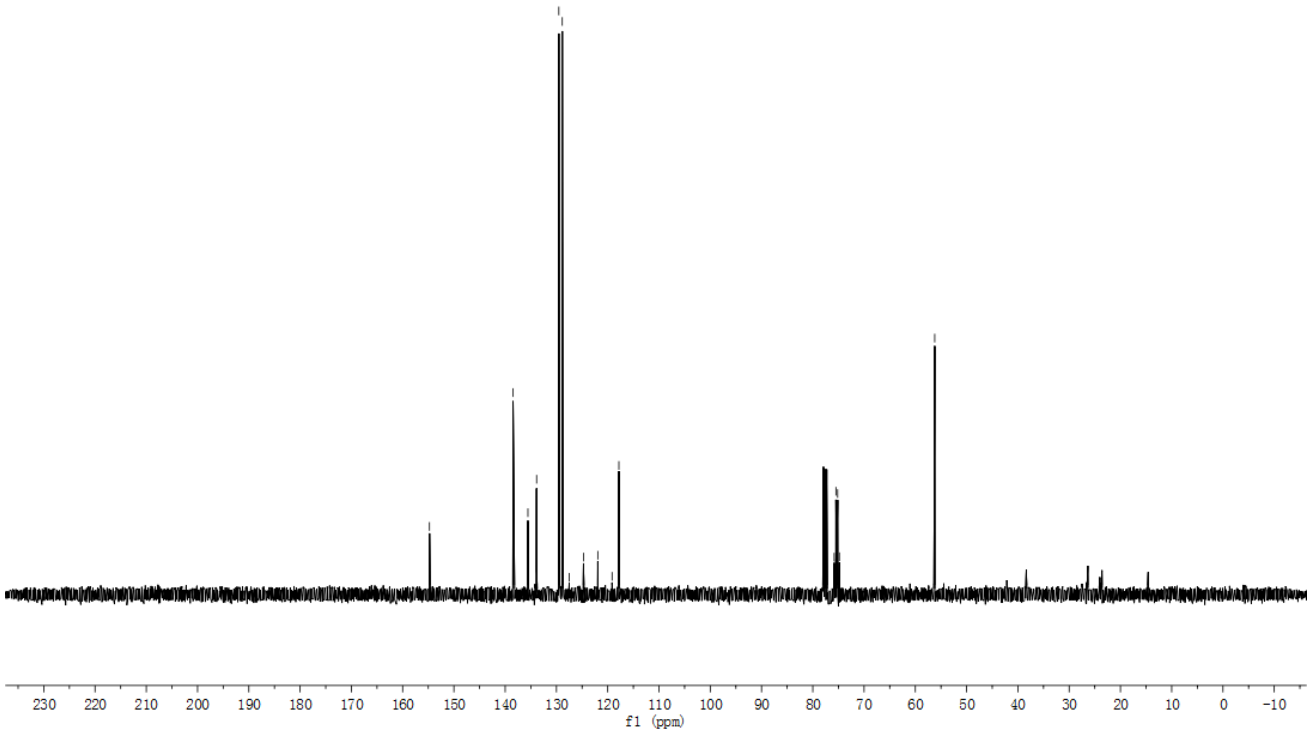




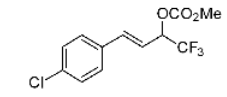


Chemical Formula: $C_{12}H_{10}ClF_3O_3$
Exact Mass: 294.0271

154.768
138.452
135.567
133.871
129.534
128.862
127.518
124.730
121.936
119.150
117.824
75.831
75.493
75.155
74.817
56.219

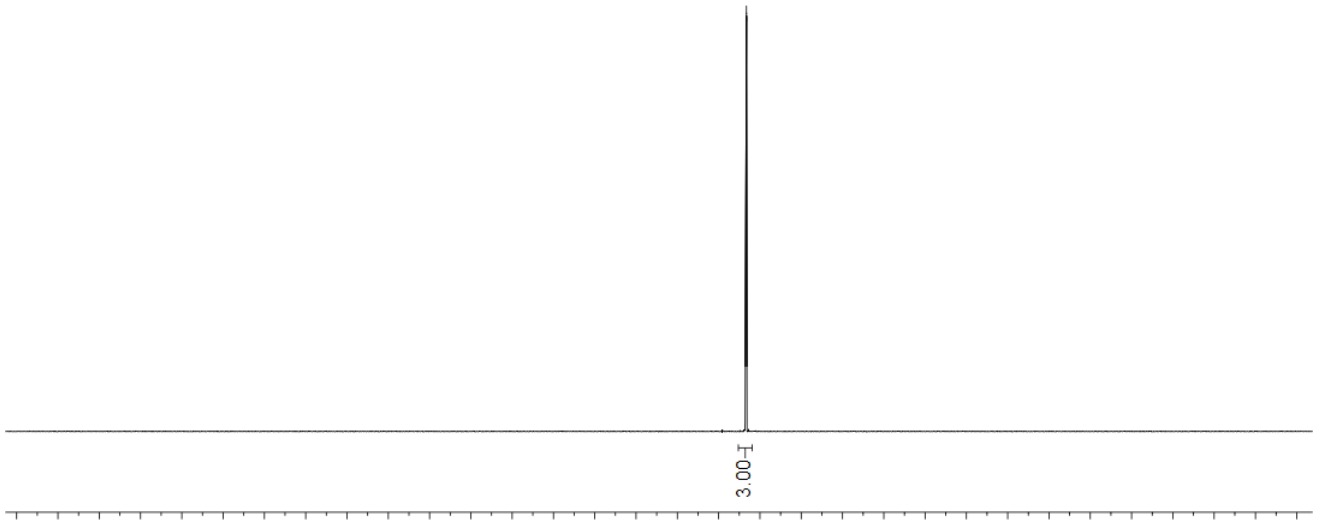


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



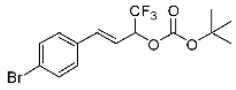
Chemical Formula: $C_{12}H_{10}ClF_3O_3$
Exact Mass: 294.0271

76.731
76.748

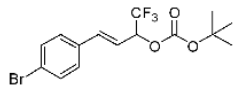


100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

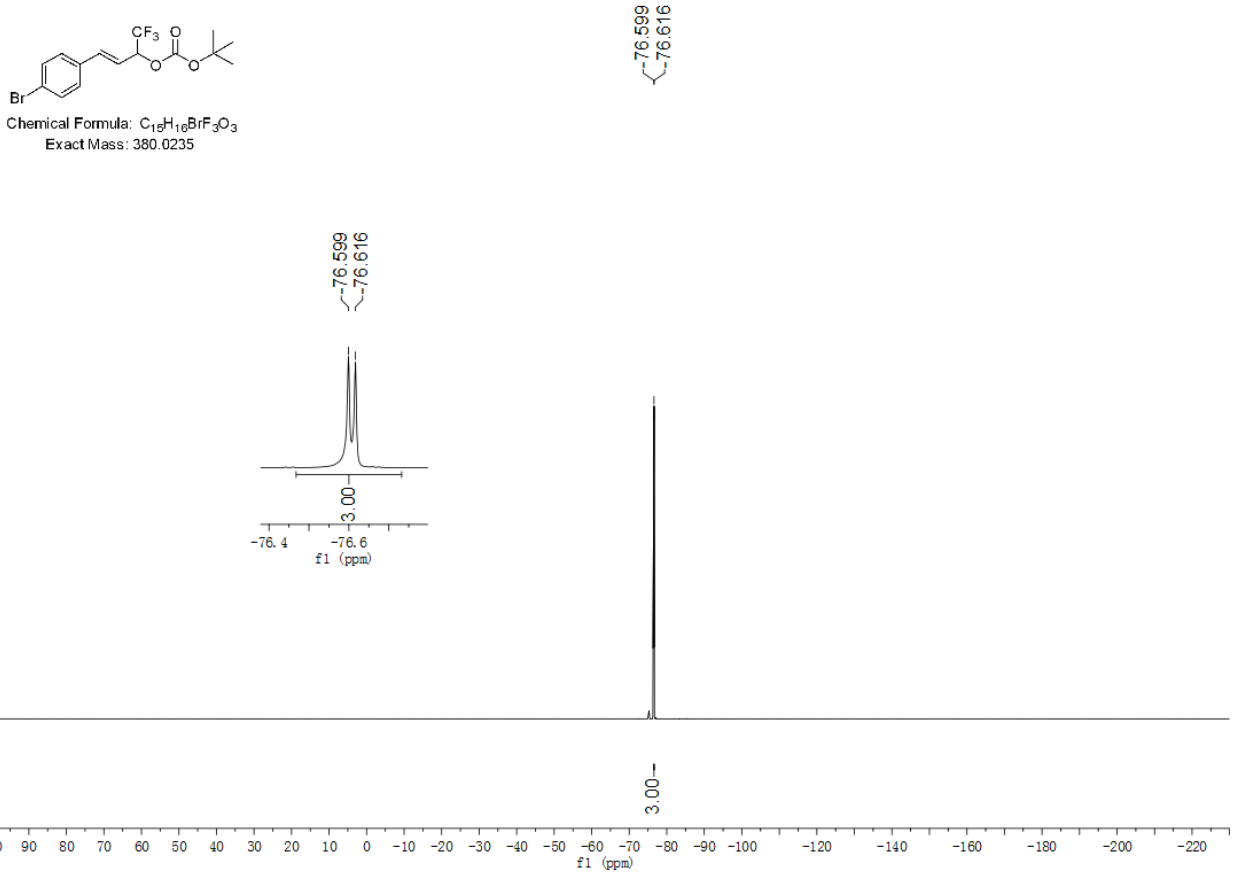
(*E*)-*tert*-Butyl (1,1,1-trifluoro-4-(4-bromophenyl)but-3-en-2-yl) carbonate (1g).



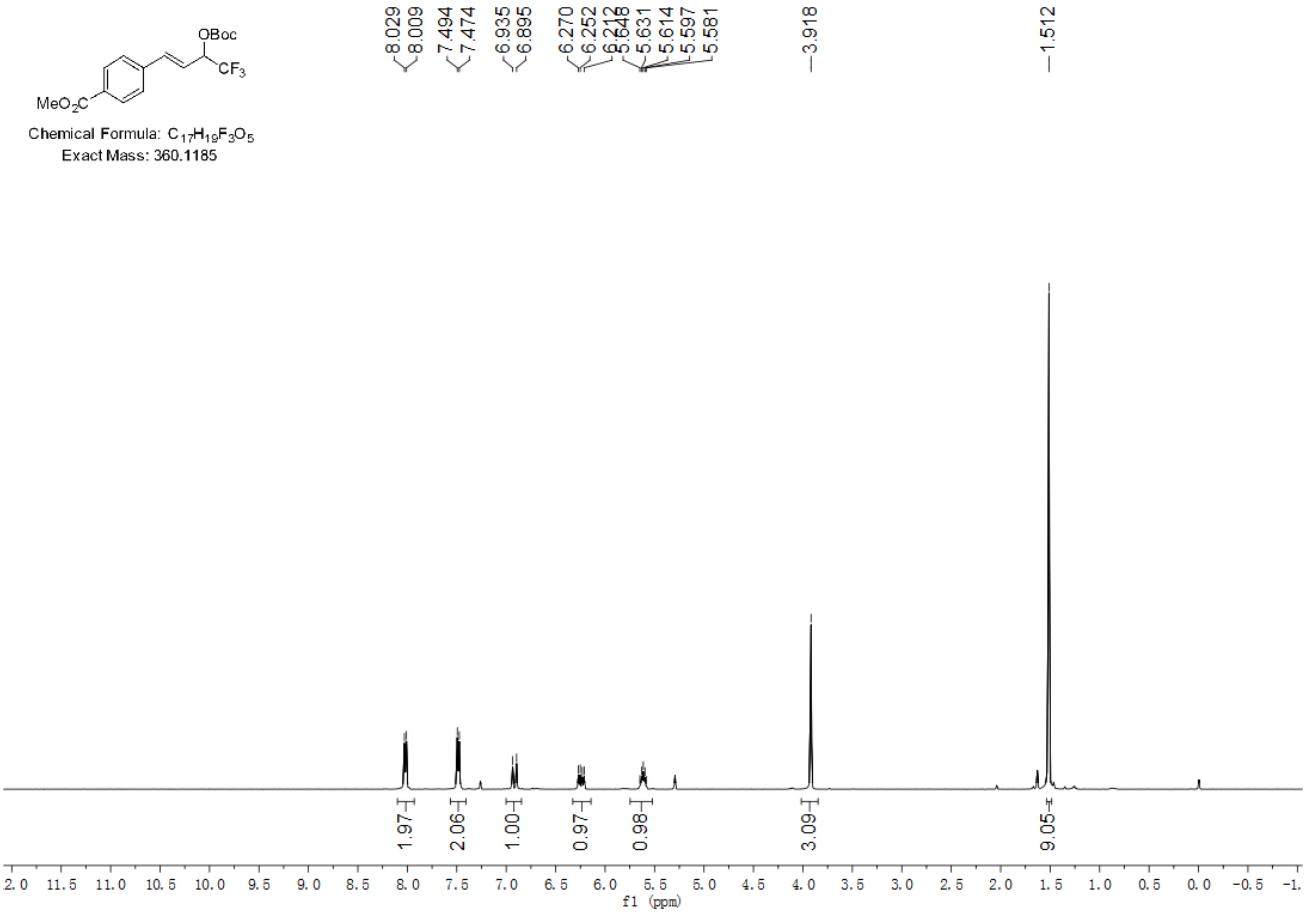
Chemical Formula: $C_{15}H_{16}BrF_3O_3$
Exact Mass: 380.0235

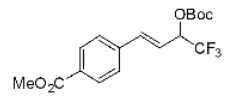


Chemical Formula: $C_{15}H_{16}BrF_3O_3$
Exact Mass: 380.0235



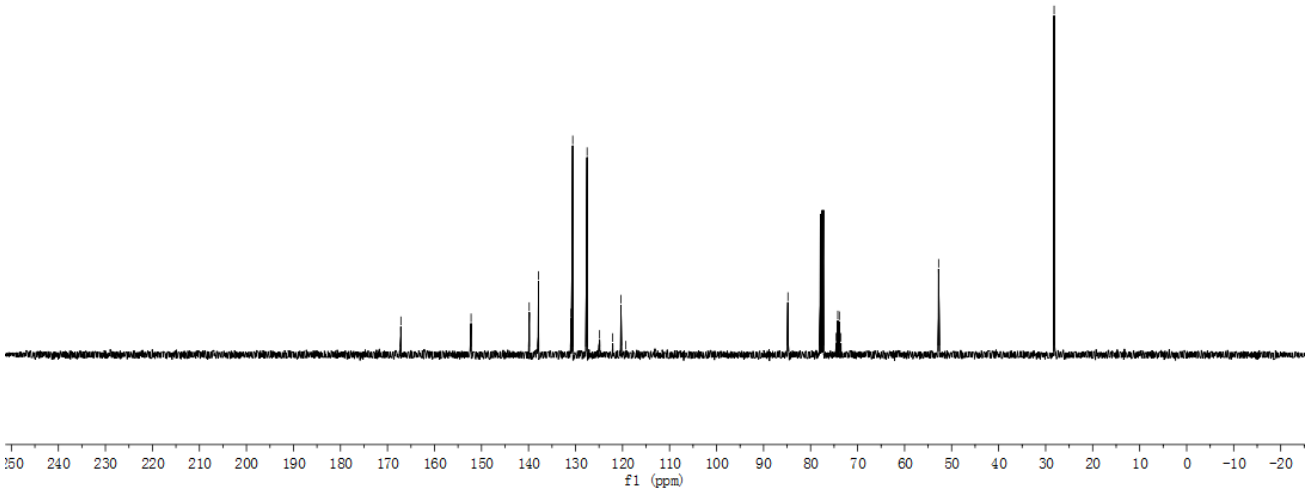
Methyl (*E*)-4-(3-((*tert*-butoxycarbonyl)oxy)-4,4,4-trifluorobut-1-en-1-yl)benzoate (1h).

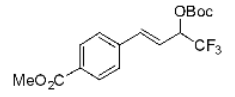




Chemical Formula: $C_{17}H_{19}F_3O_5$
Exact Mass: 360.1185

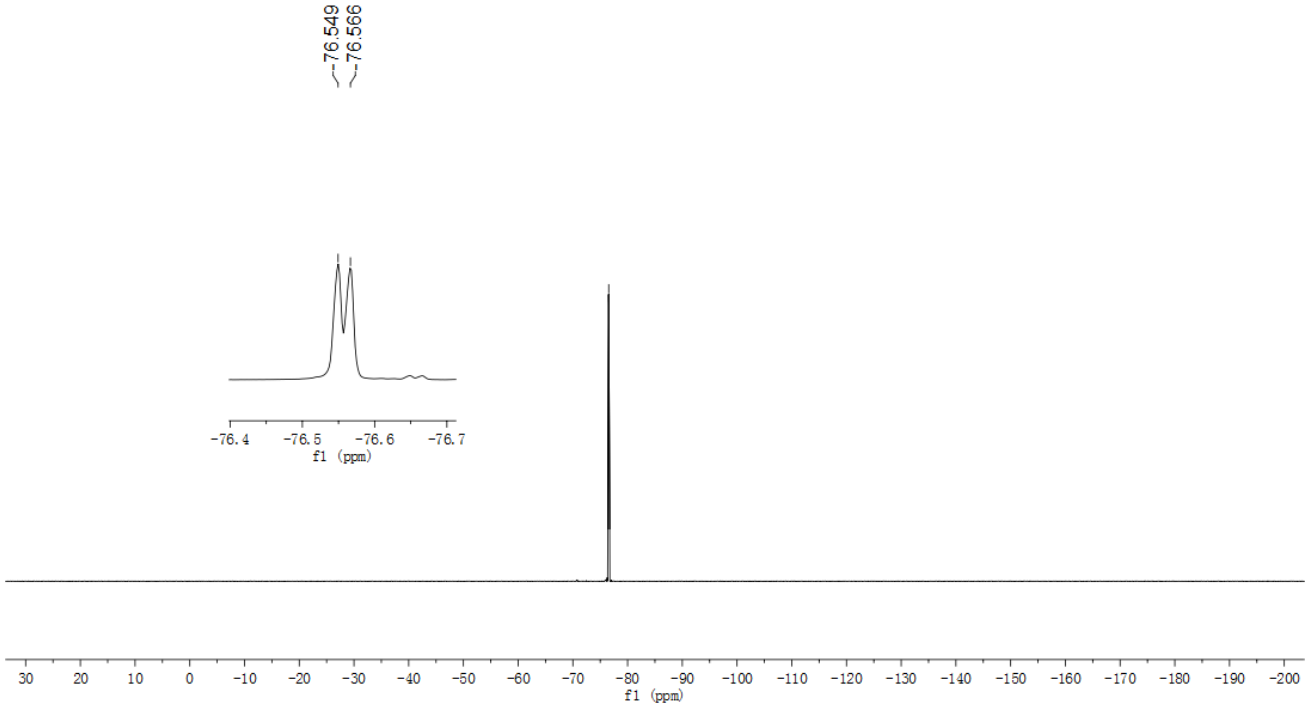
167.148
152.221
139.851
137.891
130.955
130.591
127.676
127.538
124.882
122.088
120.342
119.296
84.816
74.549
74.214
73.879
73.543
52.772
28.198



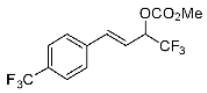


Chemical Formula: $C_{17}H_{19}F_3O_5$
Exact Mass: 360.1185

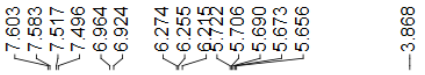
76.549
76.566

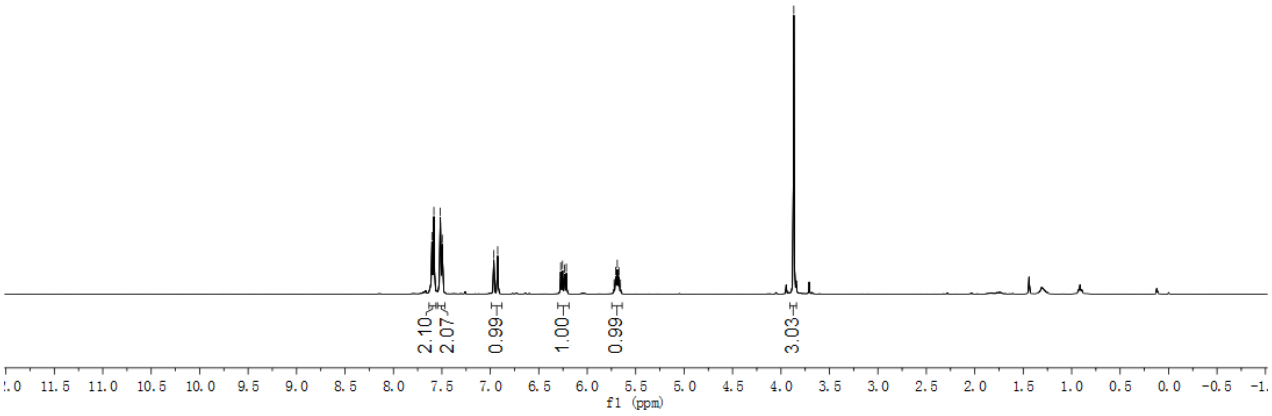


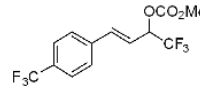
(*E*)-Methyl (1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl) carbonate (1i).



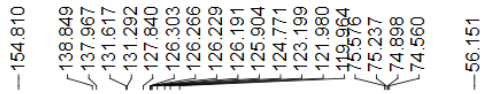
Chemical Formula: $C_{13}H_{10}F_6O_3$
Exact Mass: 328.0534

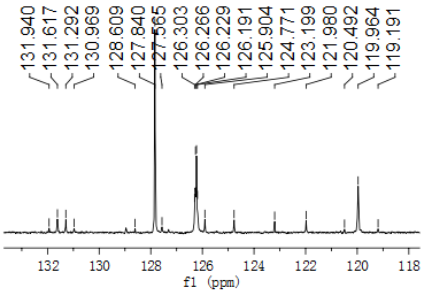


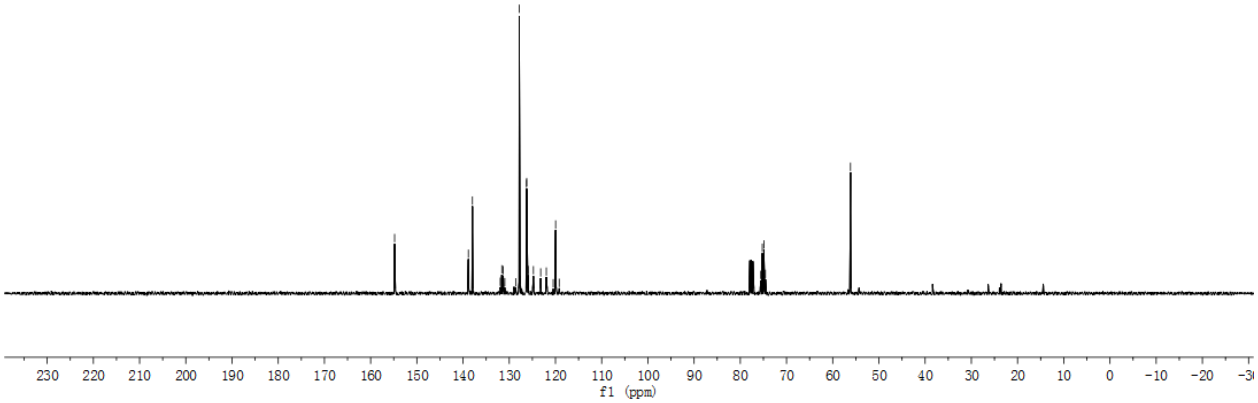


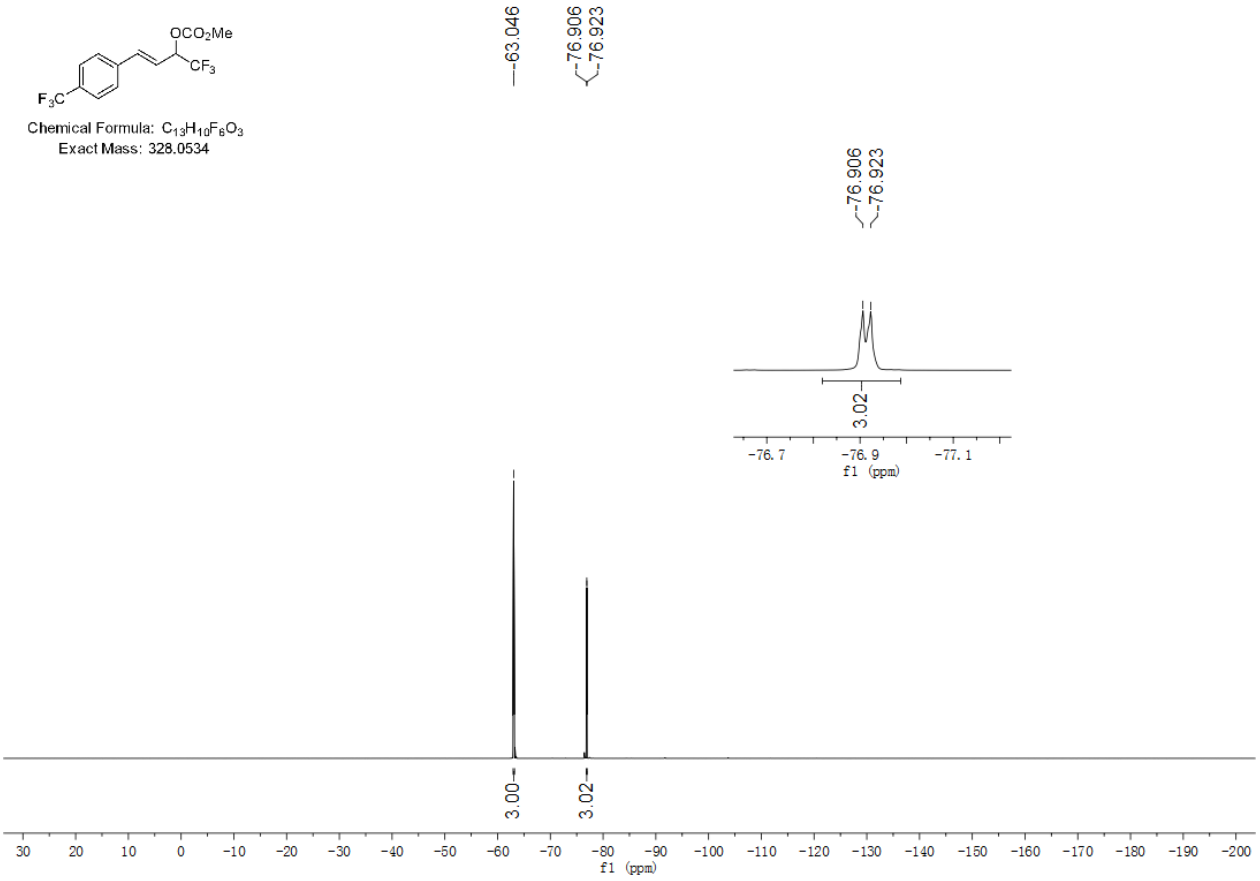


Chemical Formula: $C_{13}H_{10}F_6O_3$
Exact Mass: 328.0534

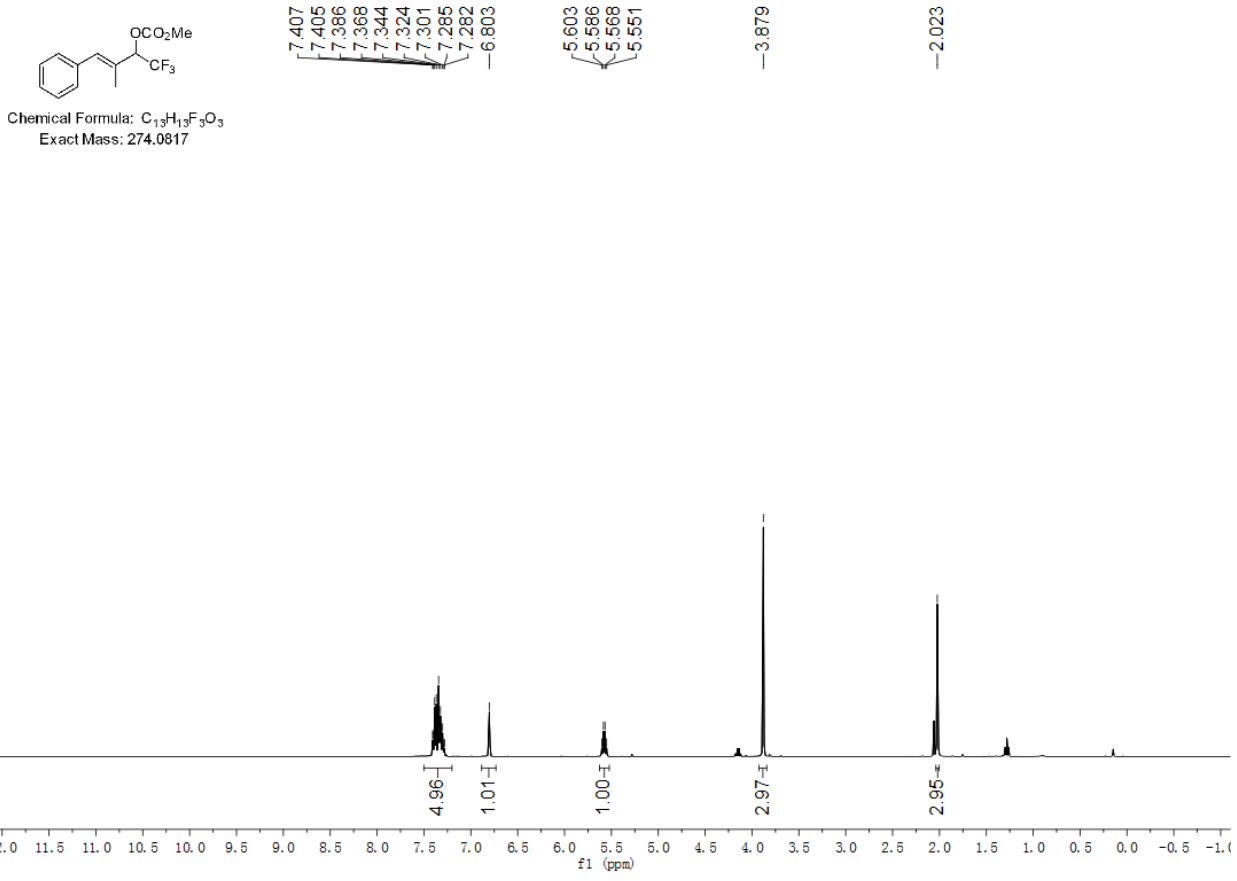


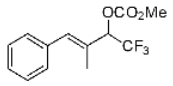






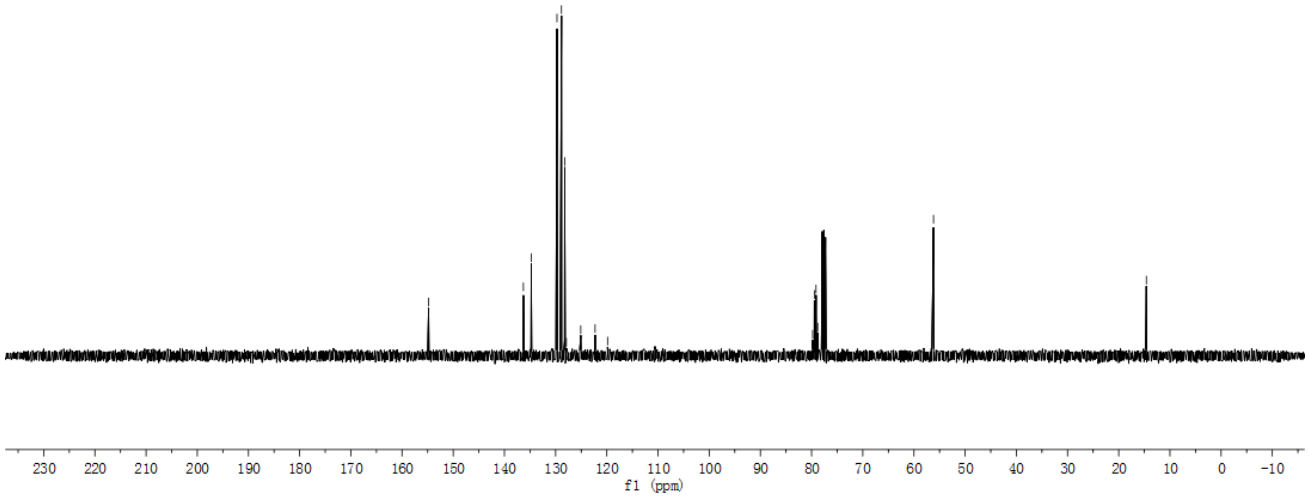
(*E*)-Methyl (1,1,1-trifluoro-3-methyl-4-phenylbut-3-en-2-yl) carbonate (1j).

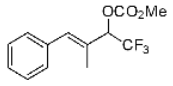




Chemical Formula: $C_{13}H_{13}F_3O_3$
Exact Mass: 274.0817

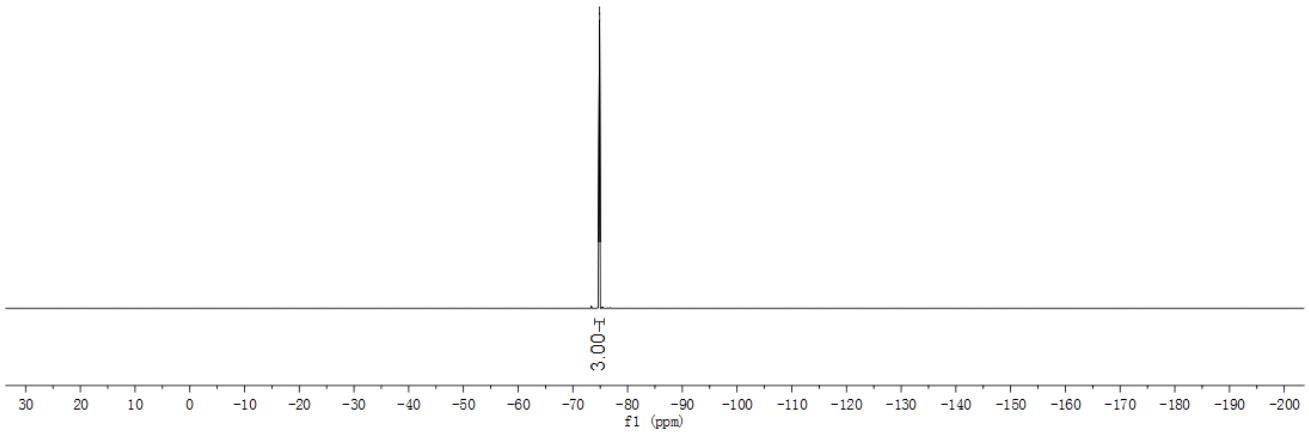
154.812
136.294
134.756
129.733
128.856
128.229
128.196
127.897
125.091
122.286
119.851
79.785
79.459
79.131
78.805
56.179
14.602



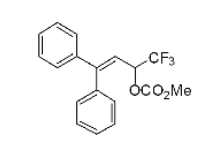


Chemical Formula: $C_{13}H_{13}F_3O_3$
Exact Mass: 274.0817

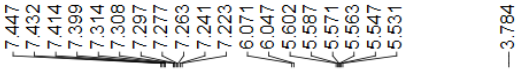
74.880
74.899

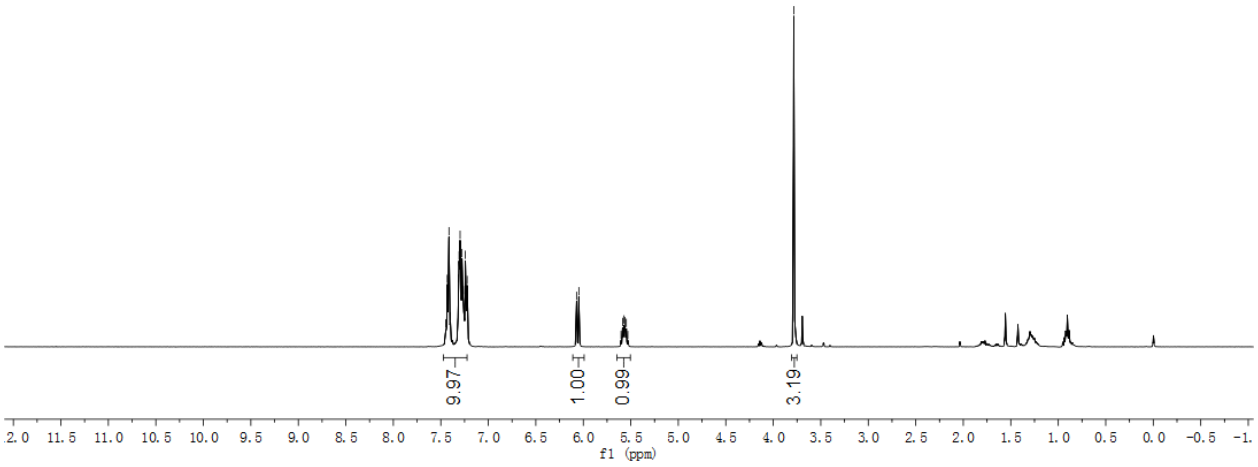


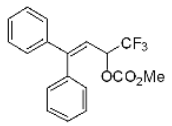
Methyl (1,1,1-trifluoro-4,4-diphenylbut-3-en-2-yl) carbonate (1k).



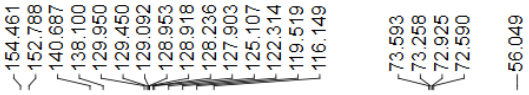
Chemical Formula: $C_{18}H_{15}F_3O_3$
Exact Mass: 336.0973

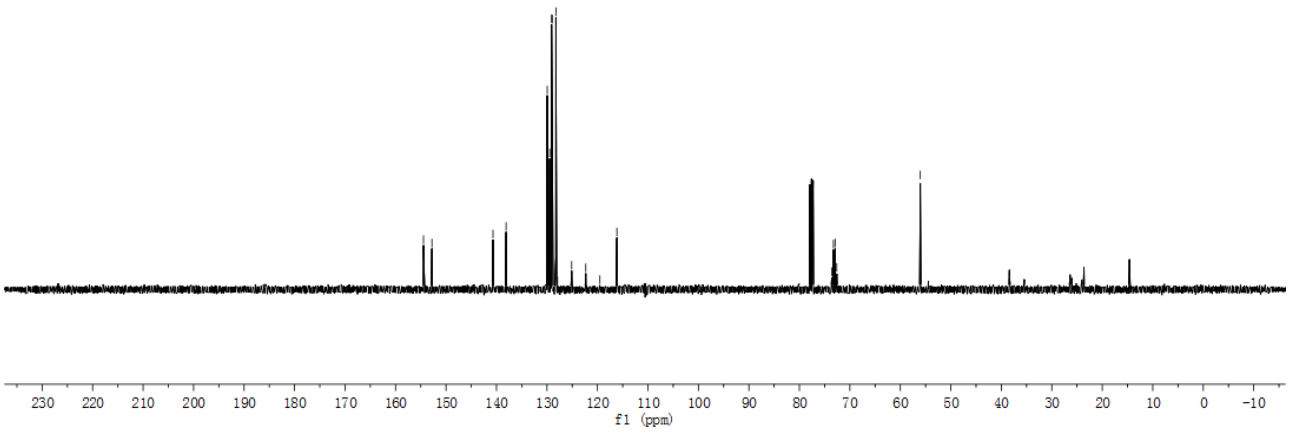


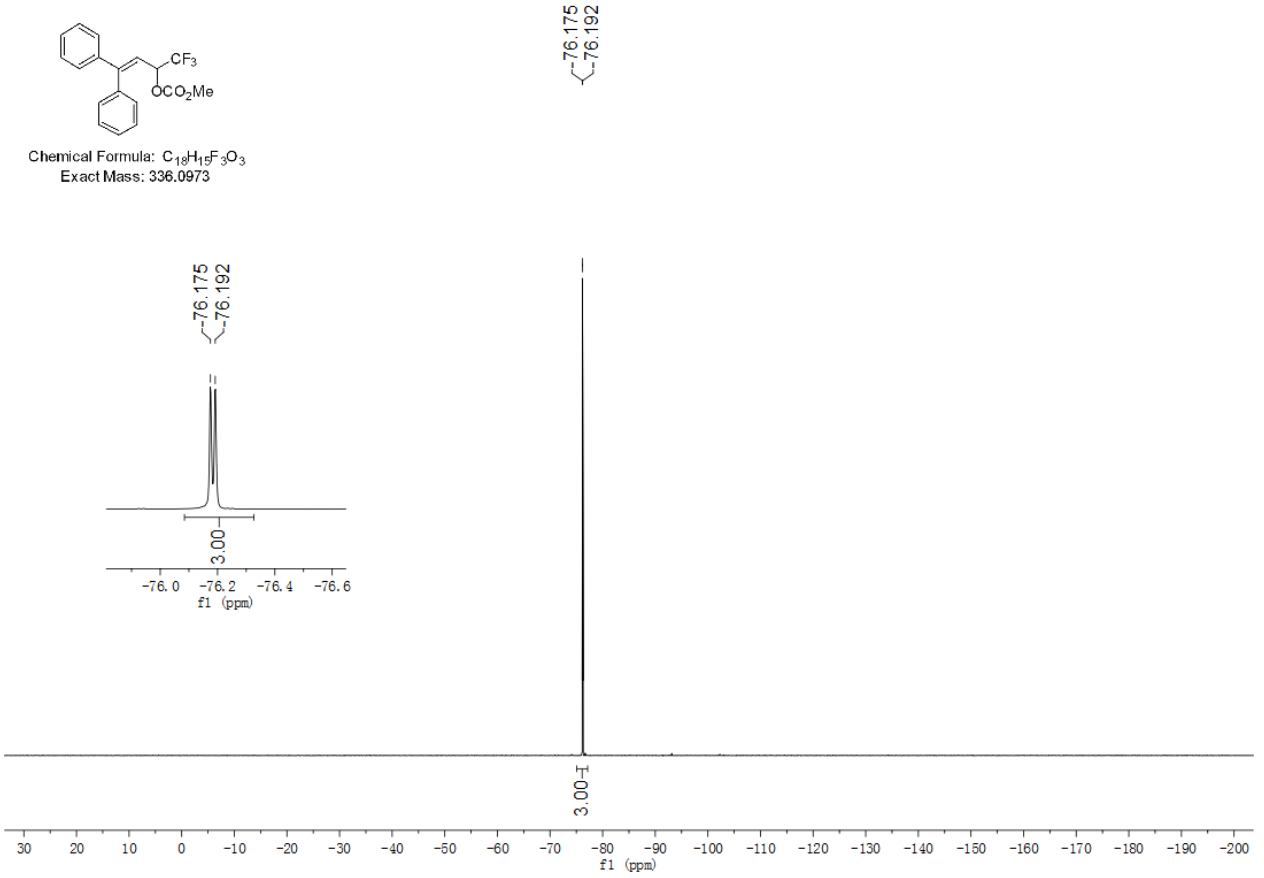




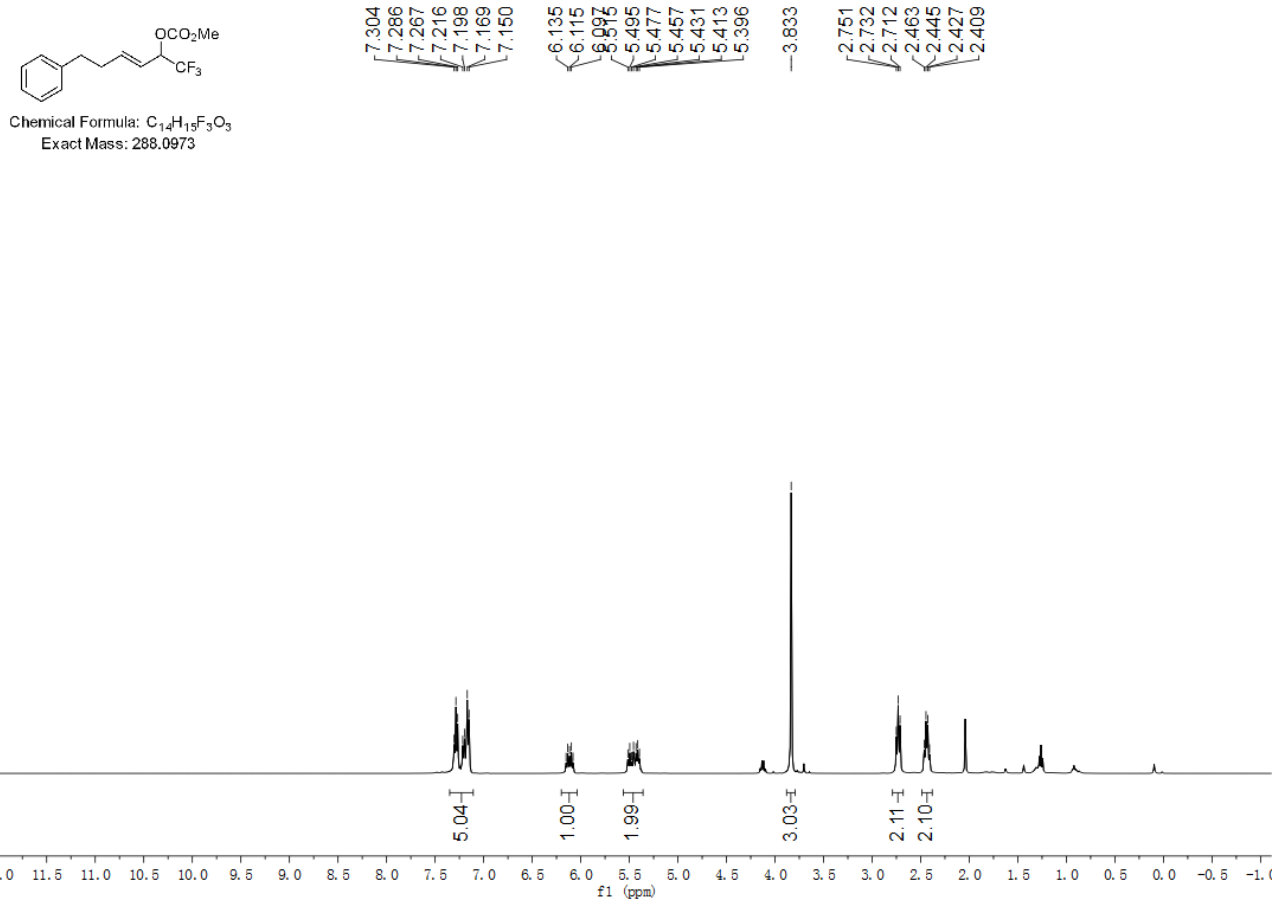
Chemical Formula: $C_{18}H_{15}F_3O_3$
Exact Mass: 336.0973

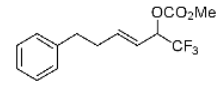






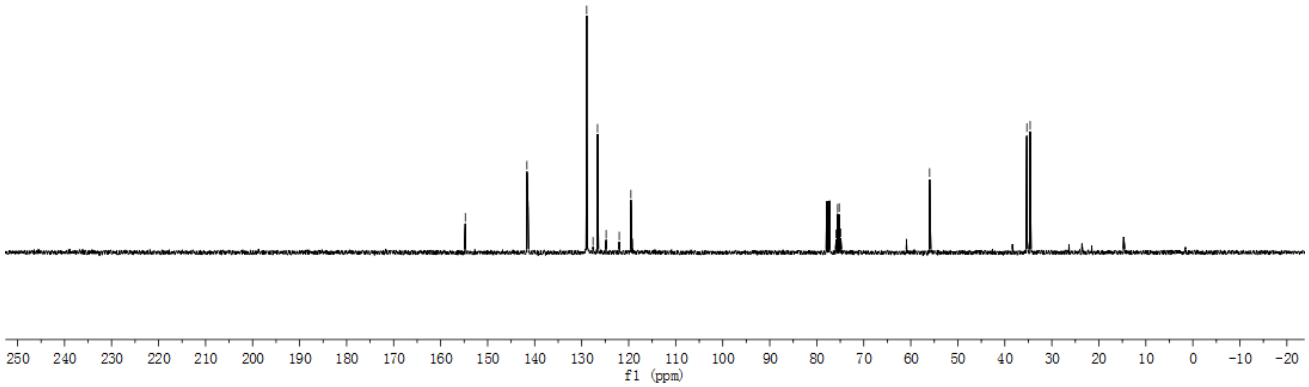
(*E*)-Methyl (1,1,1-trifluoro-6-phenylhex-3-en-2-yl) carbonate (1l).

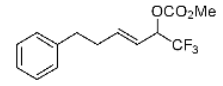




Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

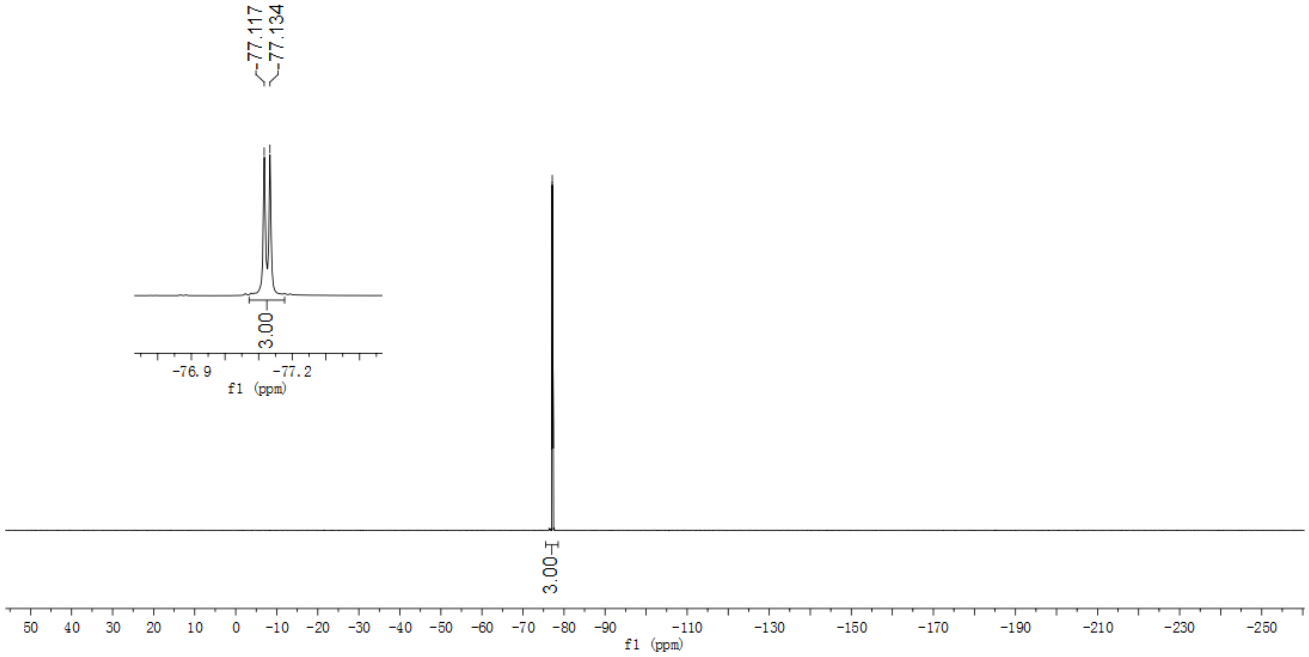
154.750
141.649
141.405
128.960
128.936
127.587
126.625
124.799
122.010
119.533
119.220
75.888
75.553
75.218
74.882
55.996
35.309
34.614



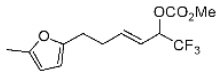


Chemical Formula: $C_{14}H_{15}F_3O_3$
Exact Mass: 288.0973

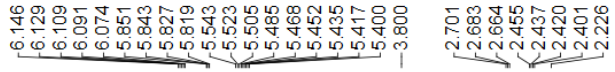
77.117
77.134

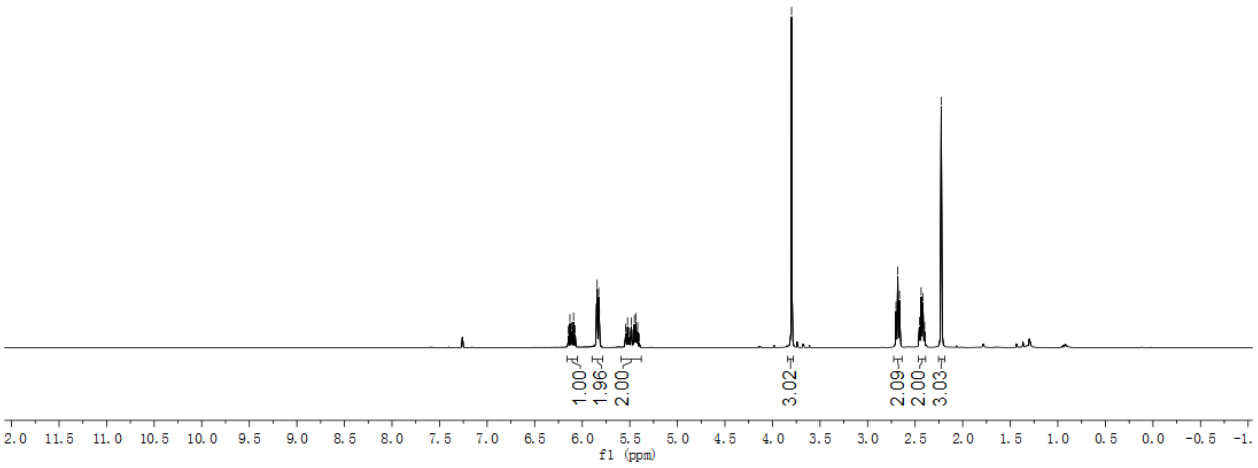


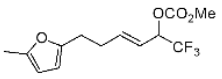
(*E*)-Methyl (1,1,1-trifluoro-6-(5-methylfuran-2-yl)hex-3-en-2-yl) carbonate (1m).



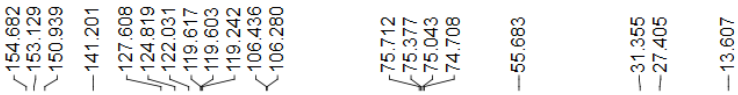
Chemical Formula: $C_{13}H_{15}F_3O_4$
Exact Mass: 292.0922

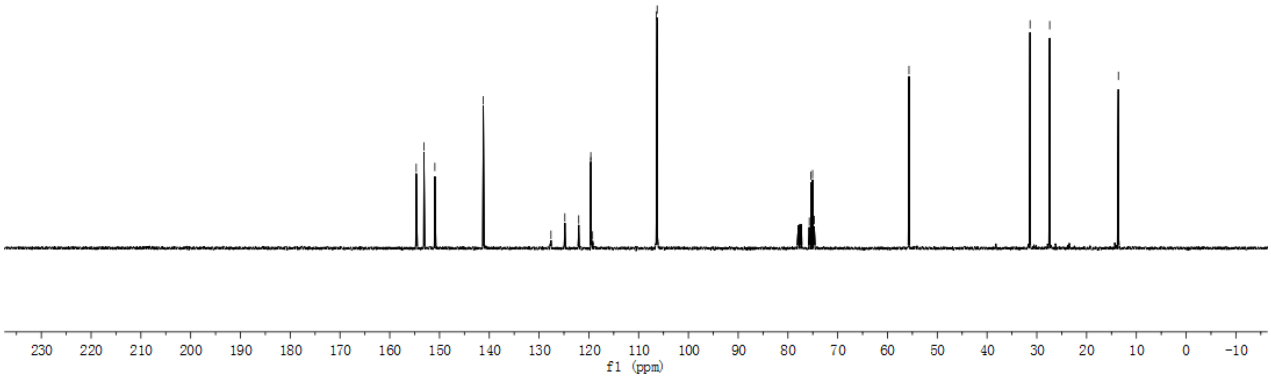


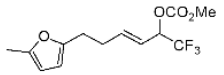




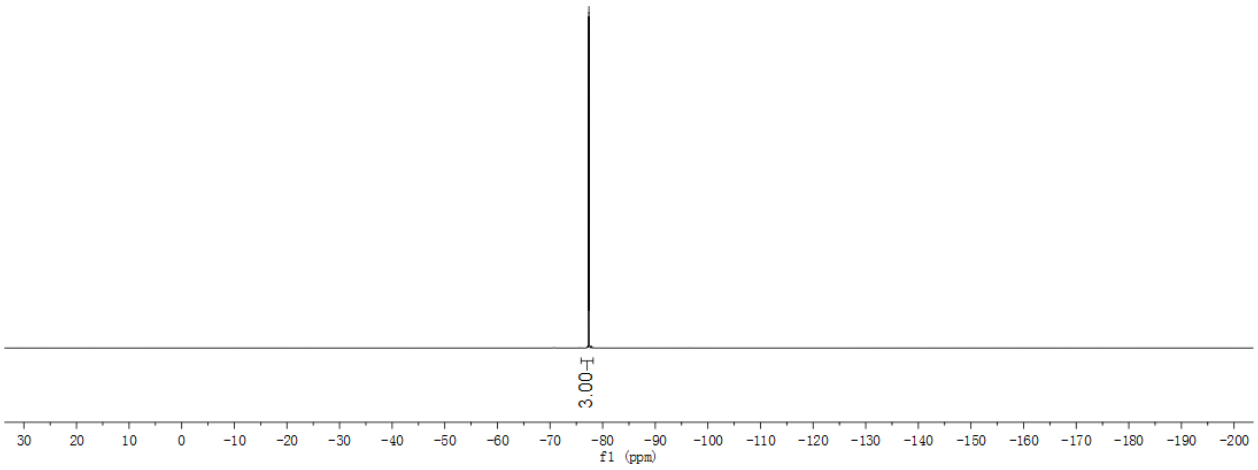
Chemical Formula: $C_{13}H_{15}F_3O_4$
Exact Mass: 292.0922



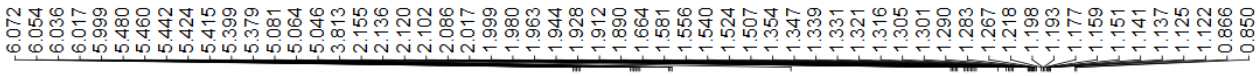


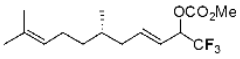


Chemical Formula: $C_{13}H_{15}F_3O_4$
Exact Mass: 292.0922

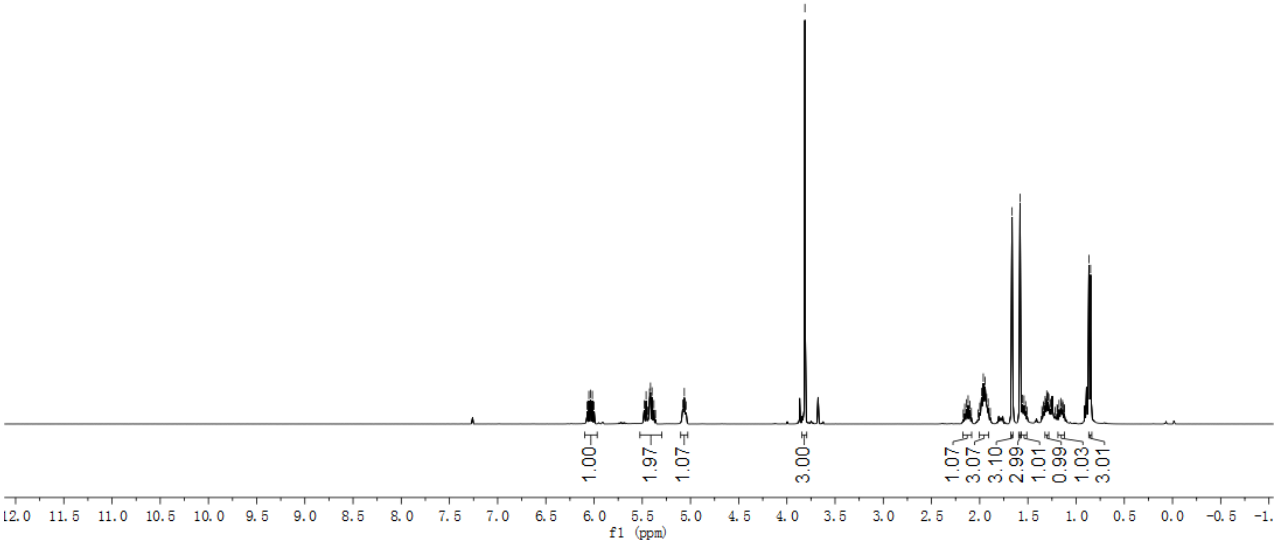


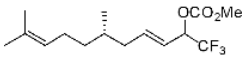
Methyl ((6*S*,*E*)-1,1,1-trifluoro-6,10-dimethylundeca-3,9-dien-2-yl) carbonate (1n).





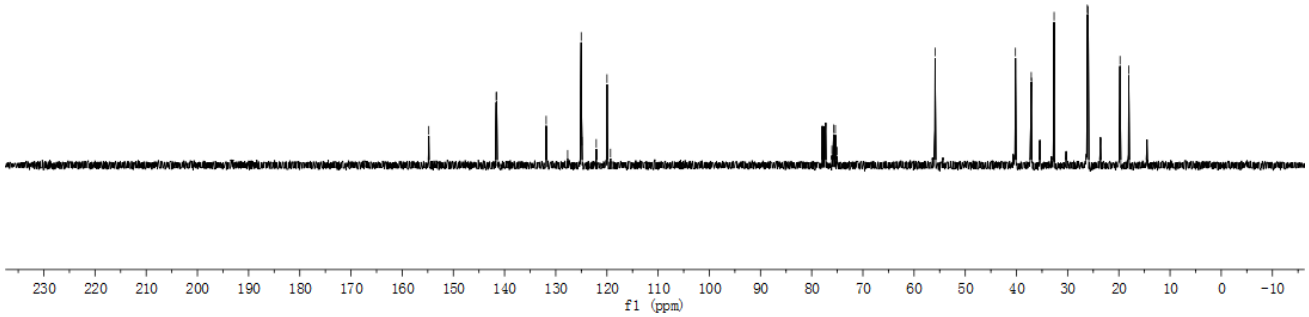
Chemical Formula: $C_{15}H_{23}F_3O_3$
Exact Mass: 308.1599

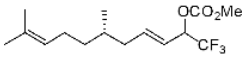




Chemical Formula: $C_{15}H_{23}F_3O_3$
Exact Mass: 308.1599

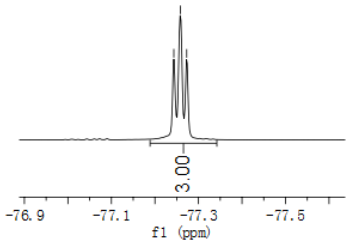
154.803
141.642
141.532
131.874
127.671
125.019
124.871
122.082
119.986
119.293
76.048
75.716
75.382
75.047
55.899
40.196
37.107
37.055
32.645
26.170
25.996
19.763
18.065



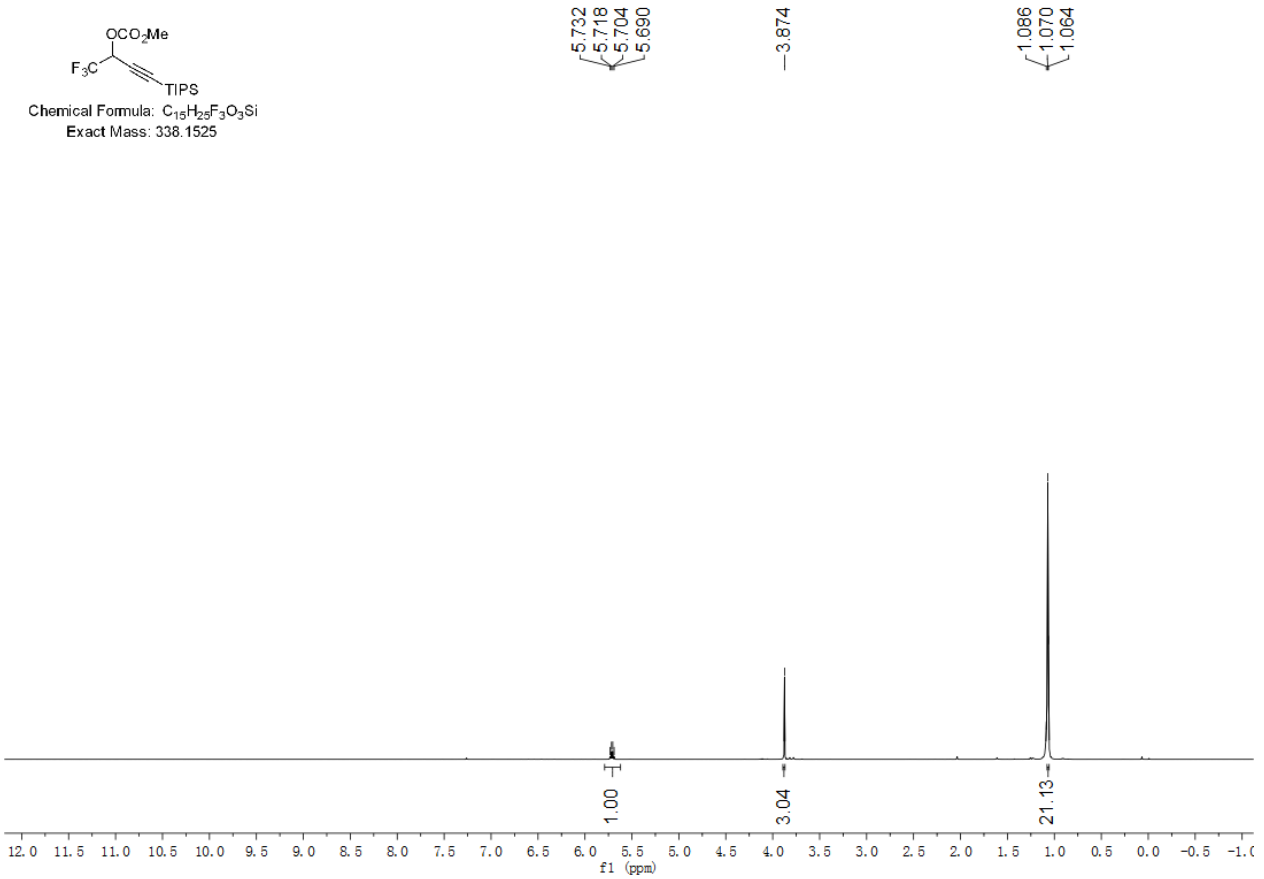


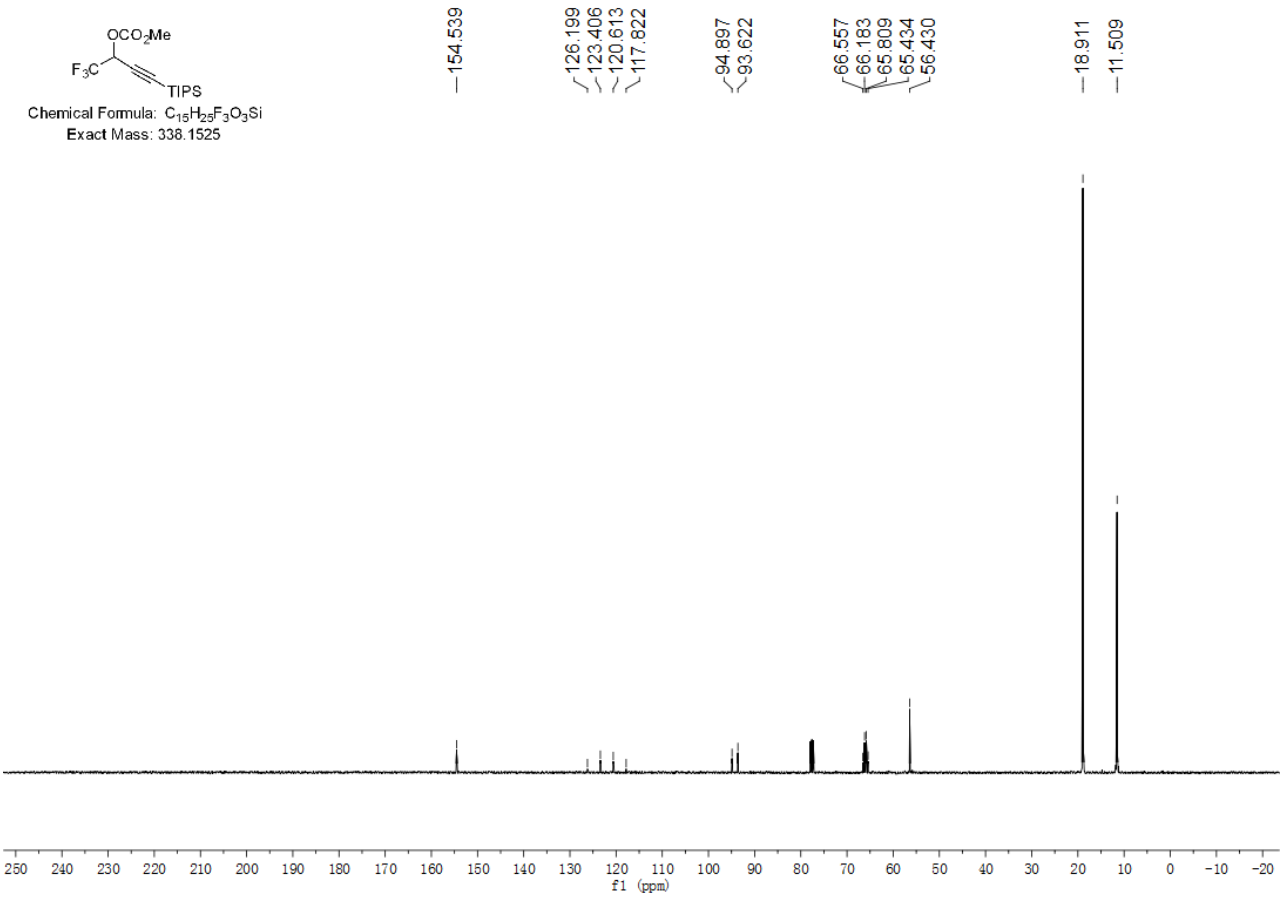
Chemical Formula: $C_{15}H_{23}F_3O_3$
Exact Mass: 308.1599

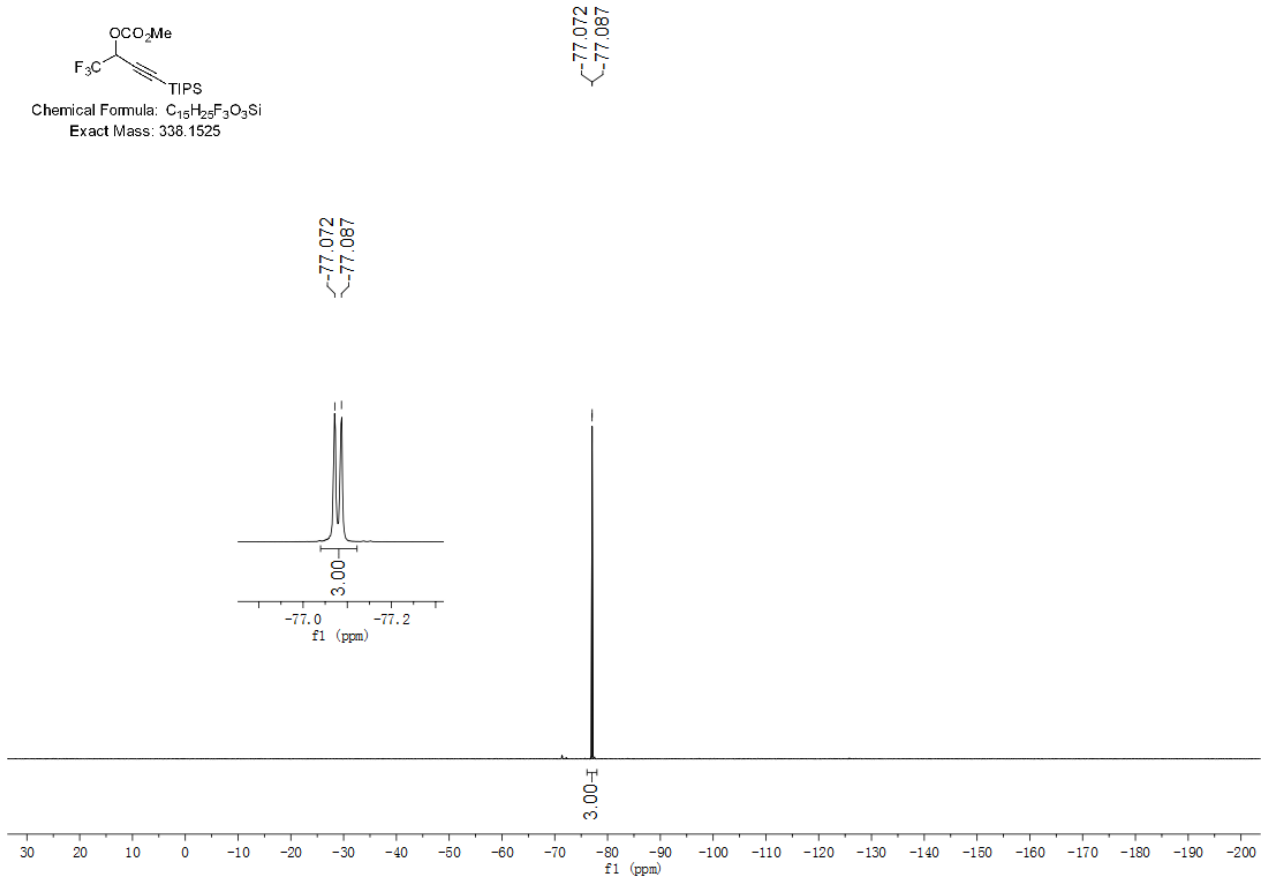
77.243
77.258
77.273



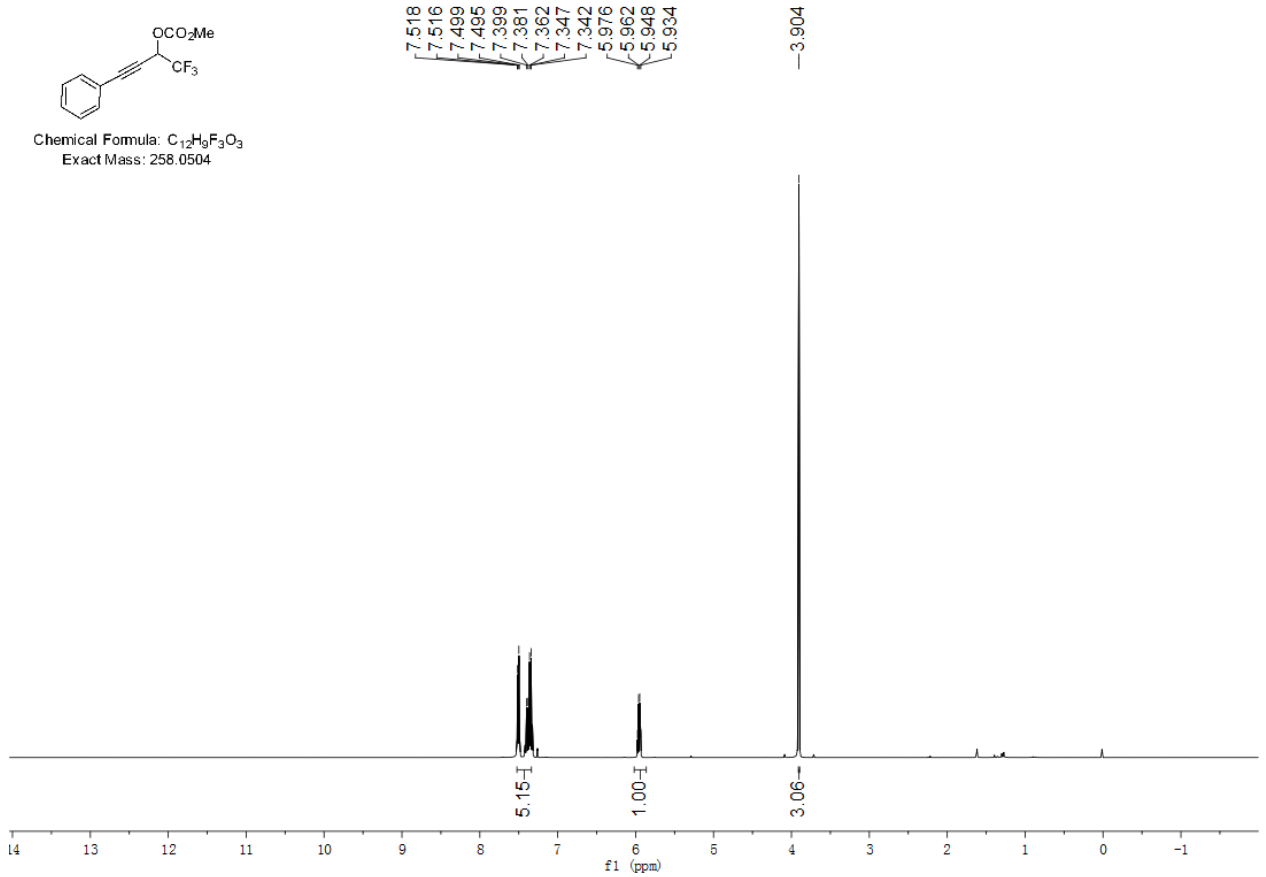
Methyl (1,1,1-trifluoro-4-(triisopropylsilyl)but-3-yn-2-yl) carbonate (1o).

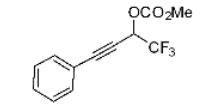




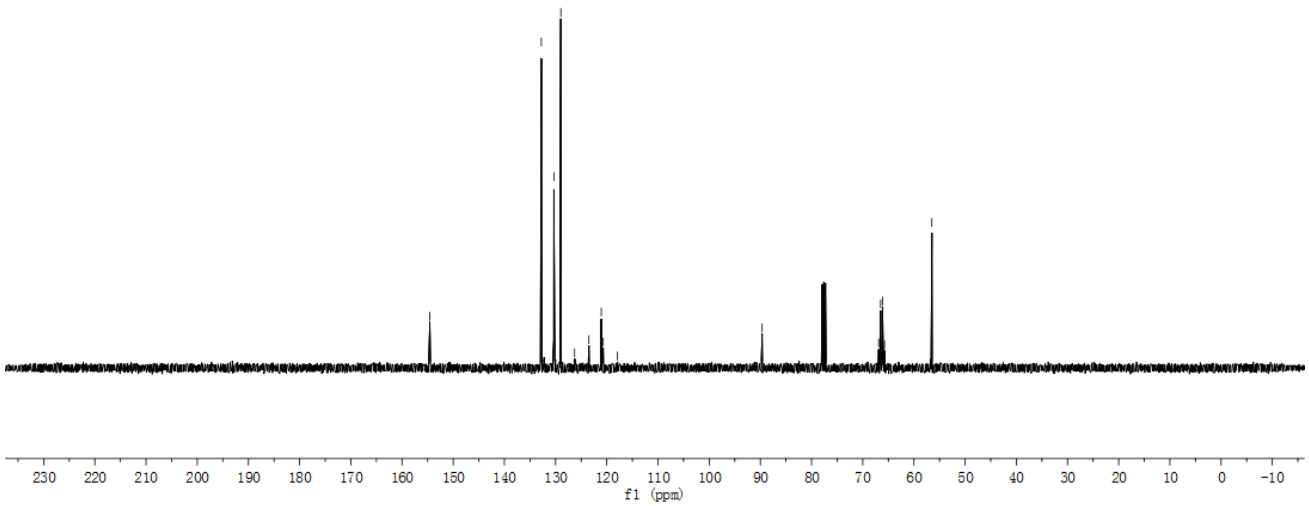


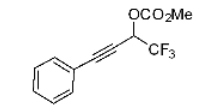
Methyl (1,1,1-trifluoro-4-phenylbut-3-yn-2-yl) carbonate (1p).



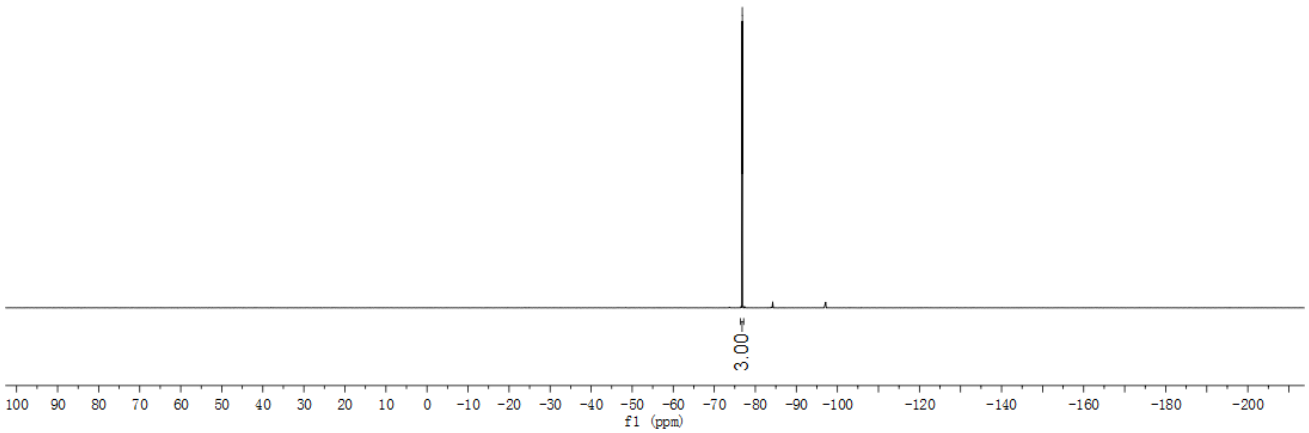


Chemical Formula: $C_{12}H_9F_3O_3$
Exact Mass: 258.0504

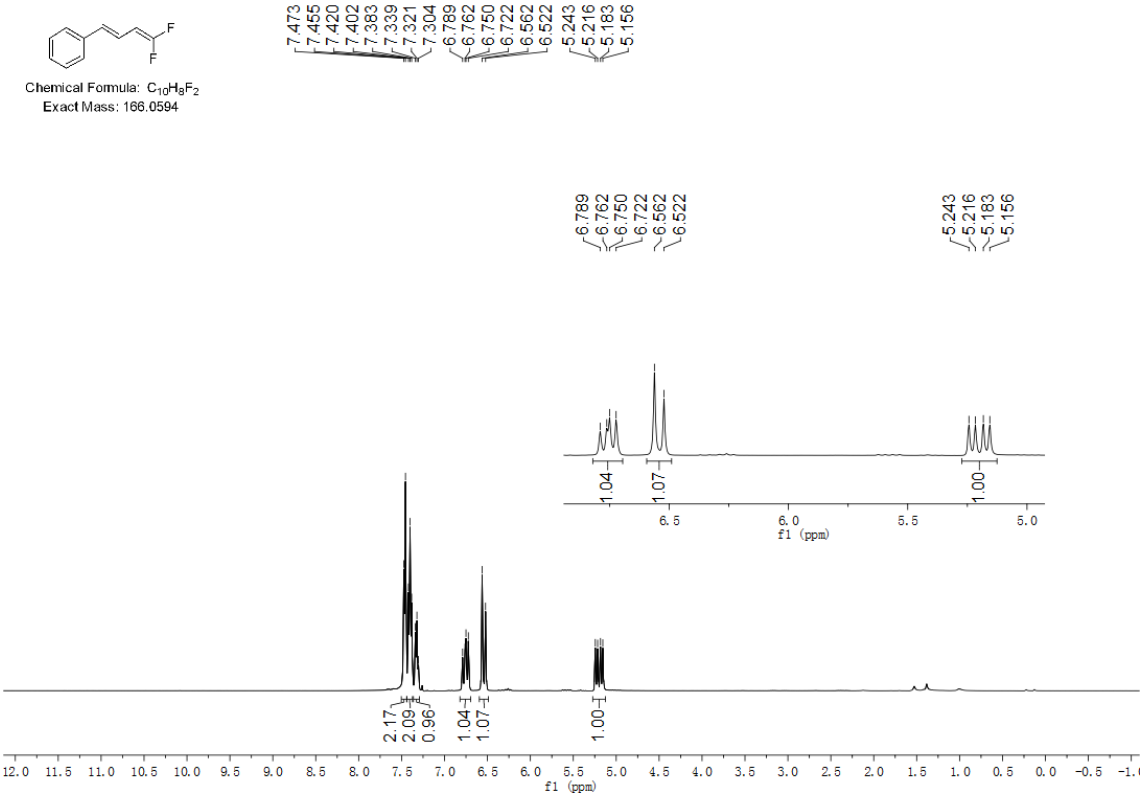


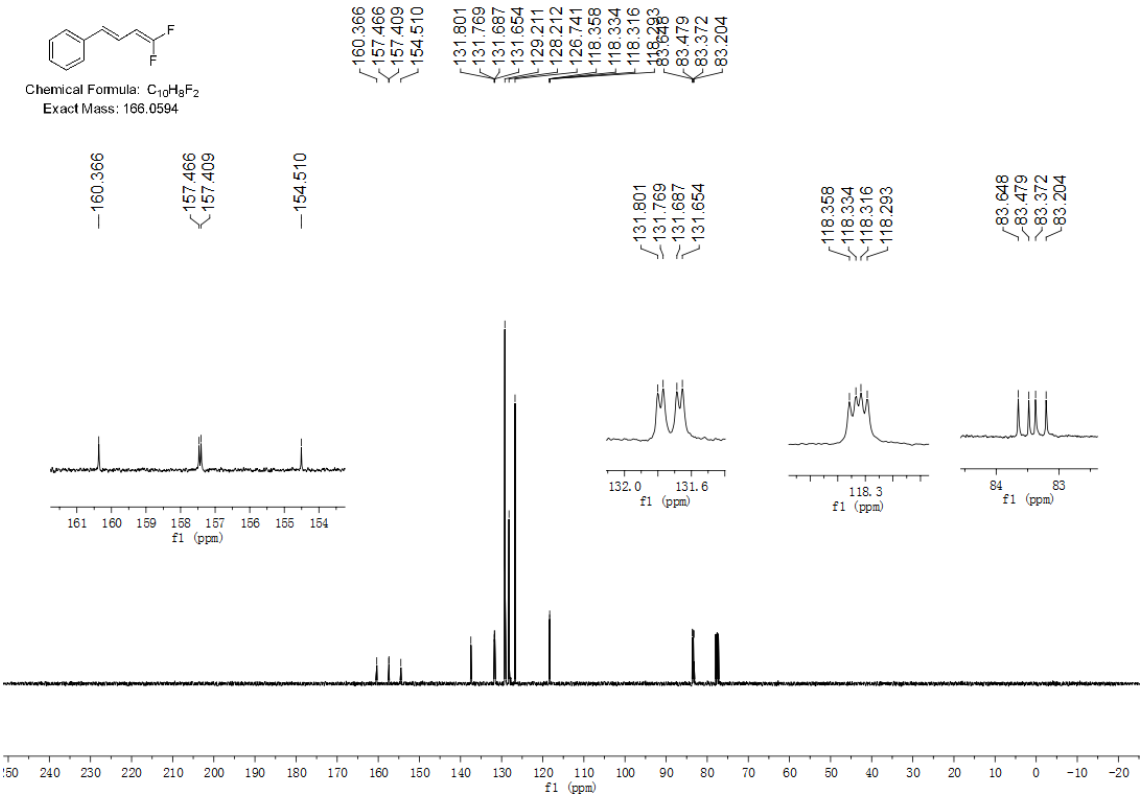


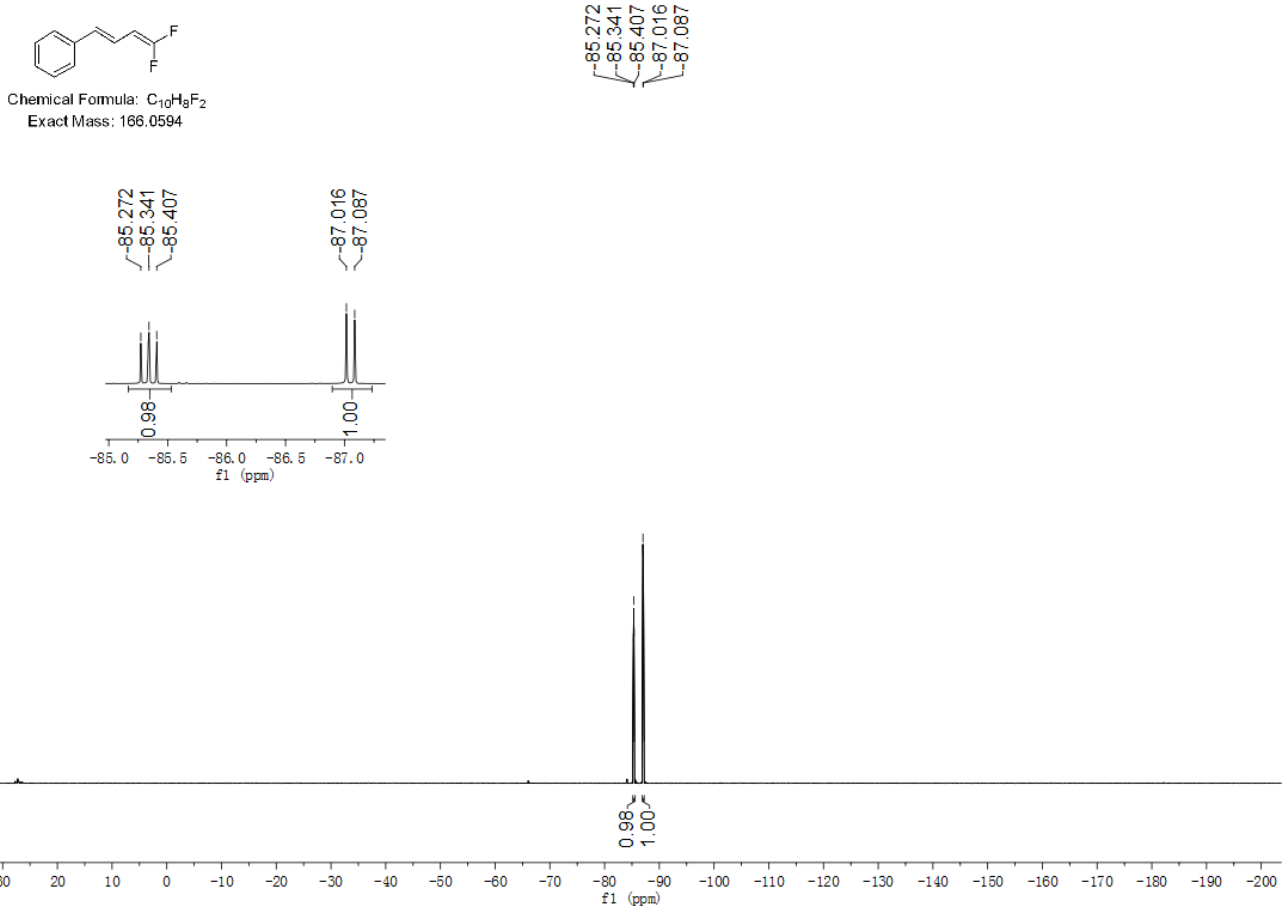
Chemical Formula: $C_{12}H_9F_3O_3$
Exact Mass: 258.0504



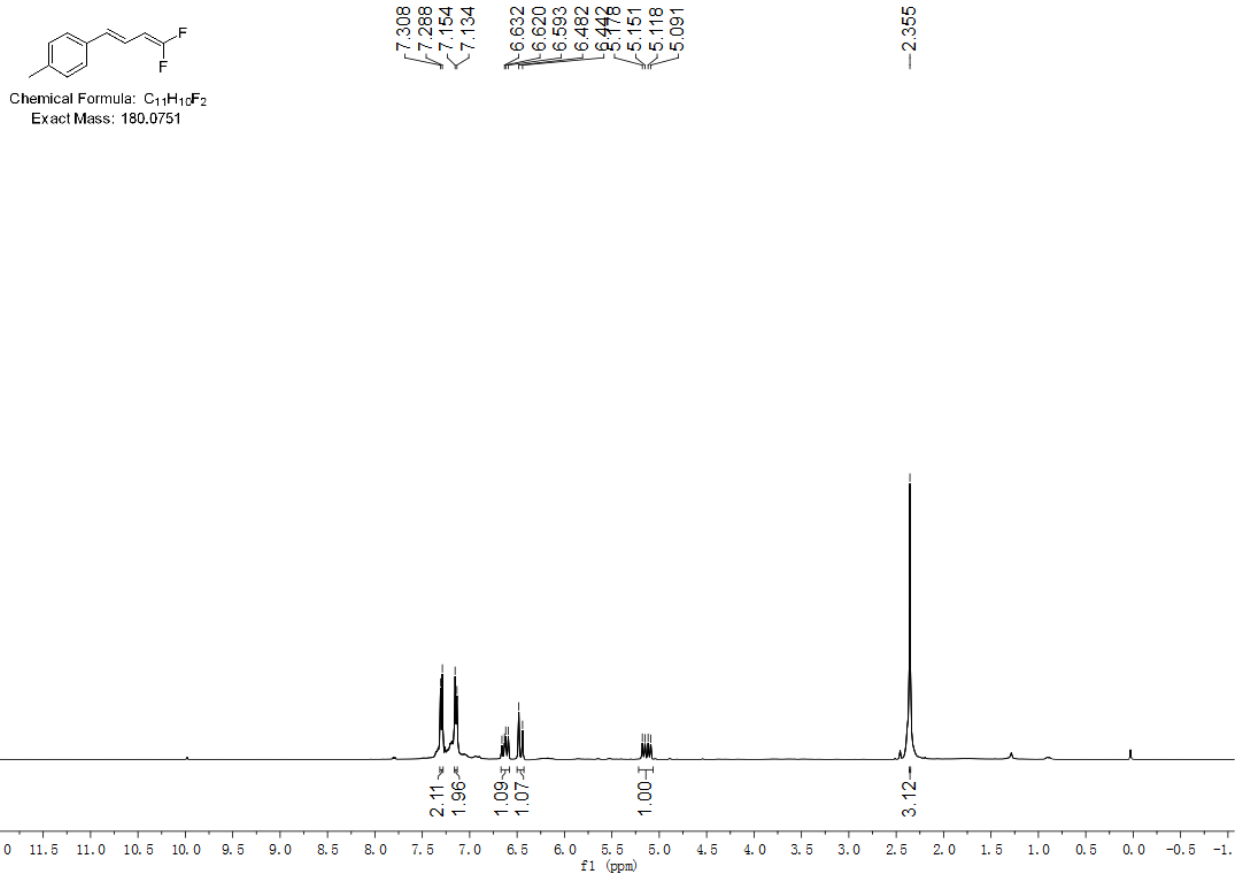
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)benzene (3a).

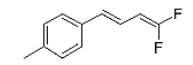




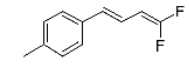


(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-methylbenzene (3b).



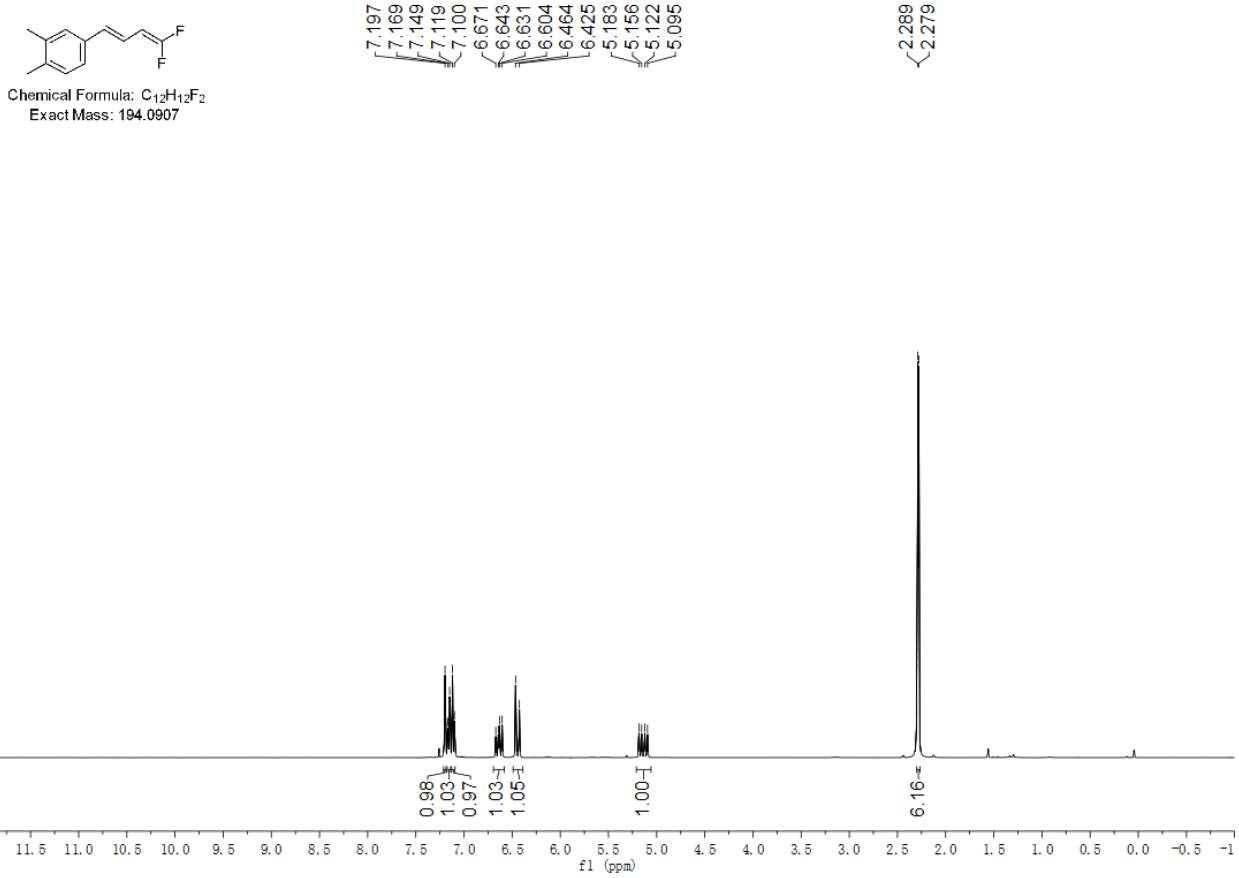


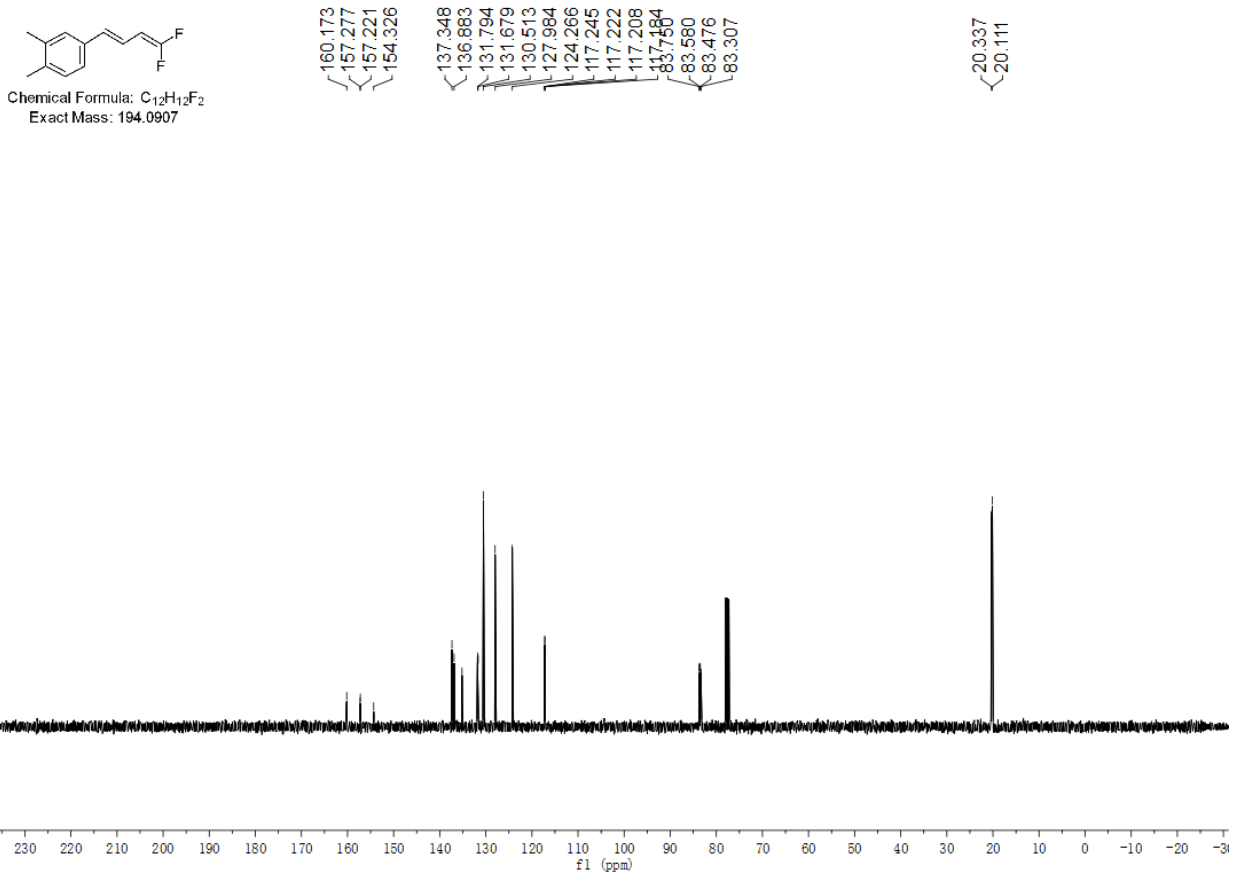
Chemical Formula: $C_{11}H_{10}F_2$
Exact Mass: 180.0751

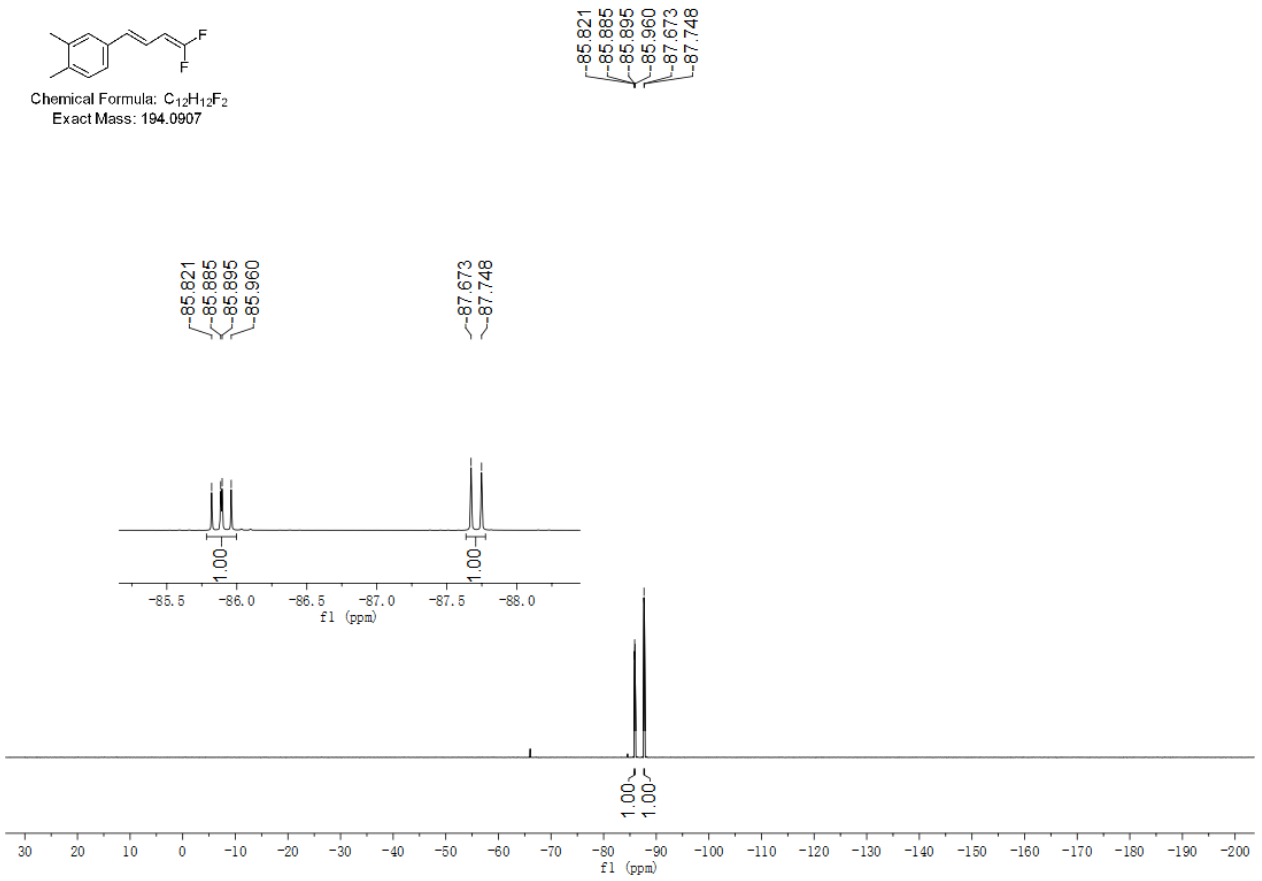


Chemical Formula: $C_{11}H_{10}F_2$
Exact Mass: 180.0751

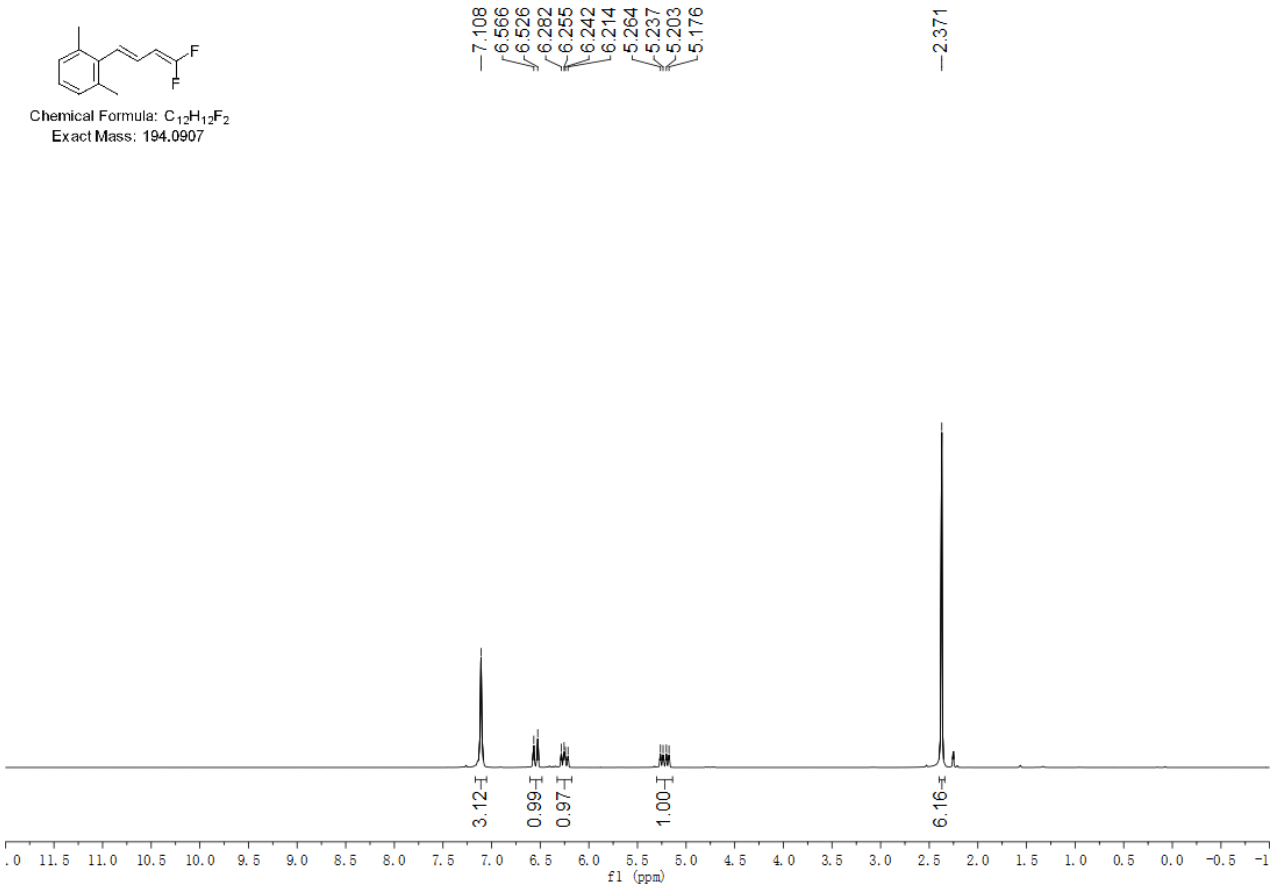
(*E*)-4-(4,4-Difluorobuta-1,3-dien-1-yl)-1,2-dimethylbenzene (3c).

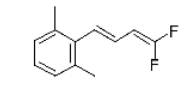






(*E*)-2-(4,4-Difluorobuta-1,3-dien-1-yl)-1,3-dimethylbenzene (3d).

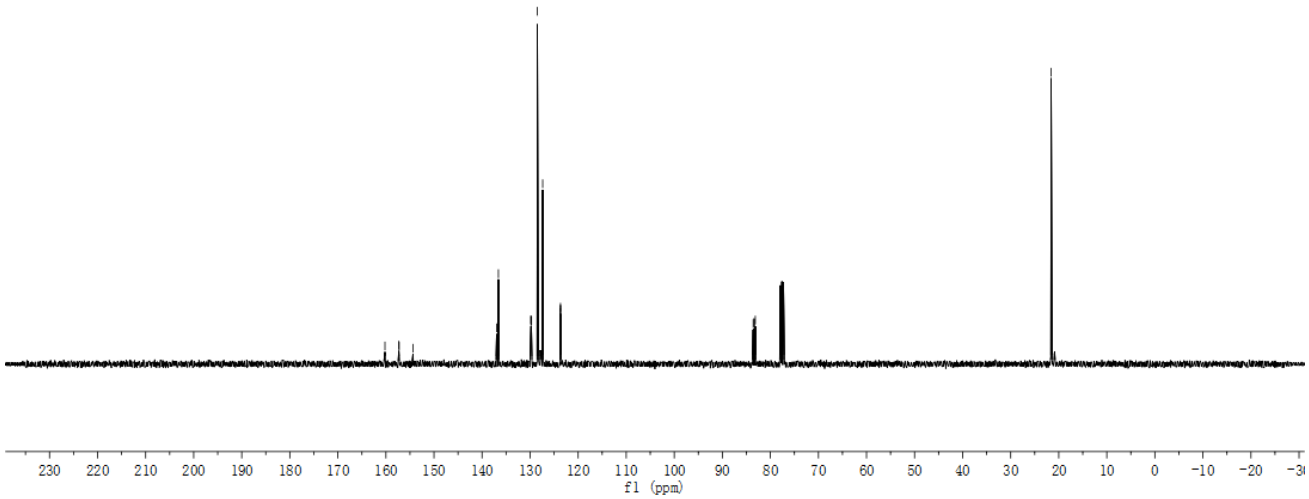




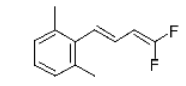
Chemical Formula: $C_{12}H_{12}F_2$
Exact Mass: 194.0907

160.200
157.308
157.252
154.358
136.967
136.598
129.851
129.819
129.738
129.705
128.486
127.378
123.718
123.699
123.676
123.658
83.578
83.410
83.310
83.142

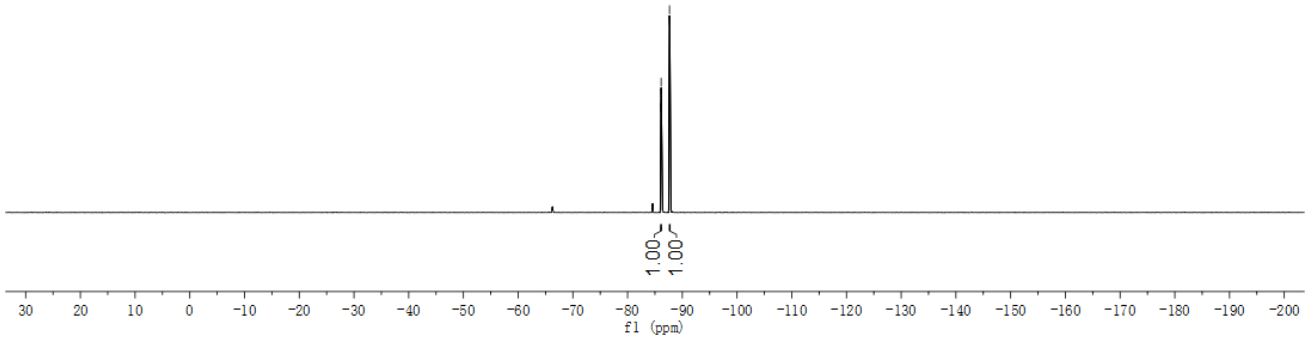
21.579



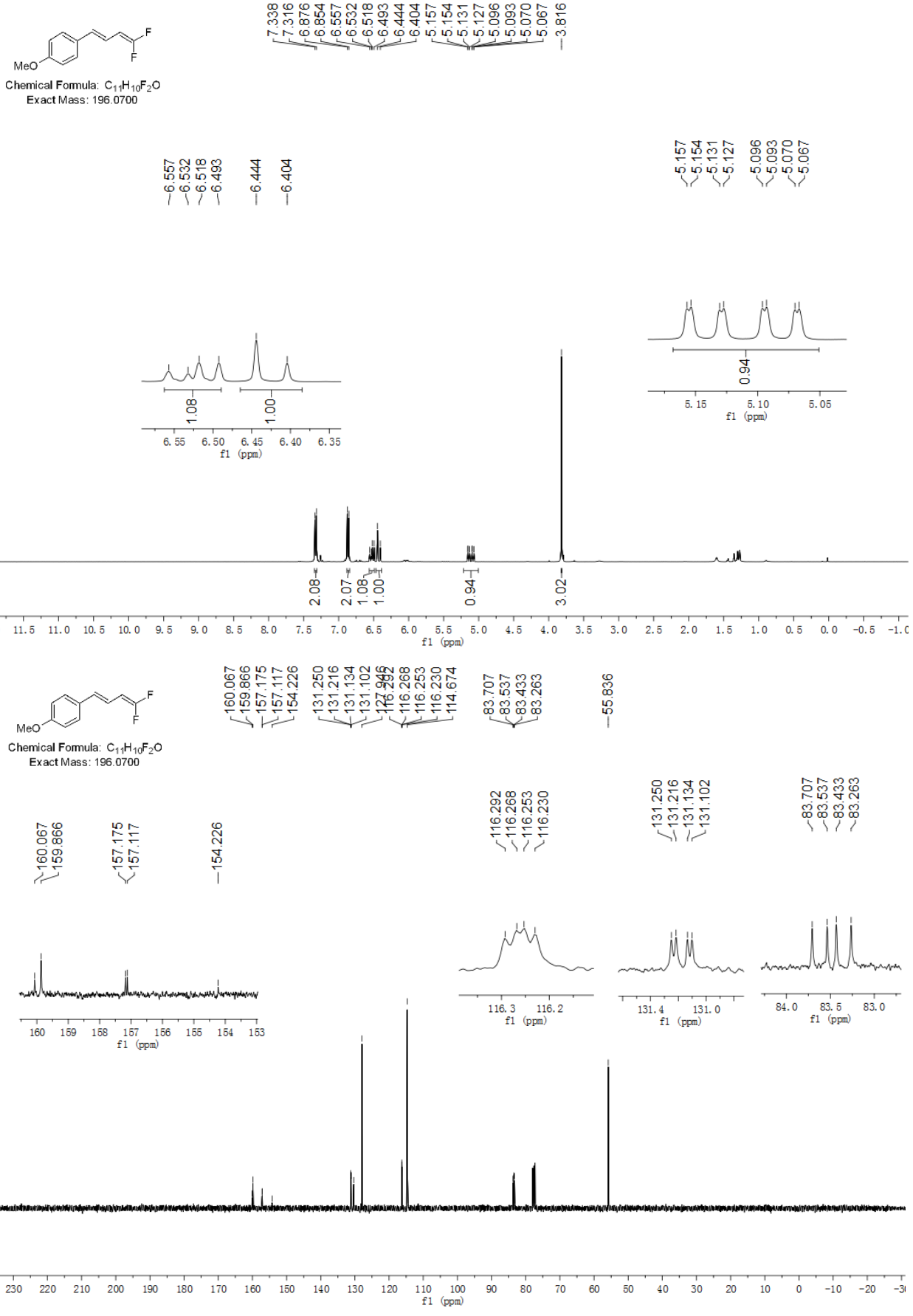
86.052
86.116
86.128
86.193
87.658
87.735

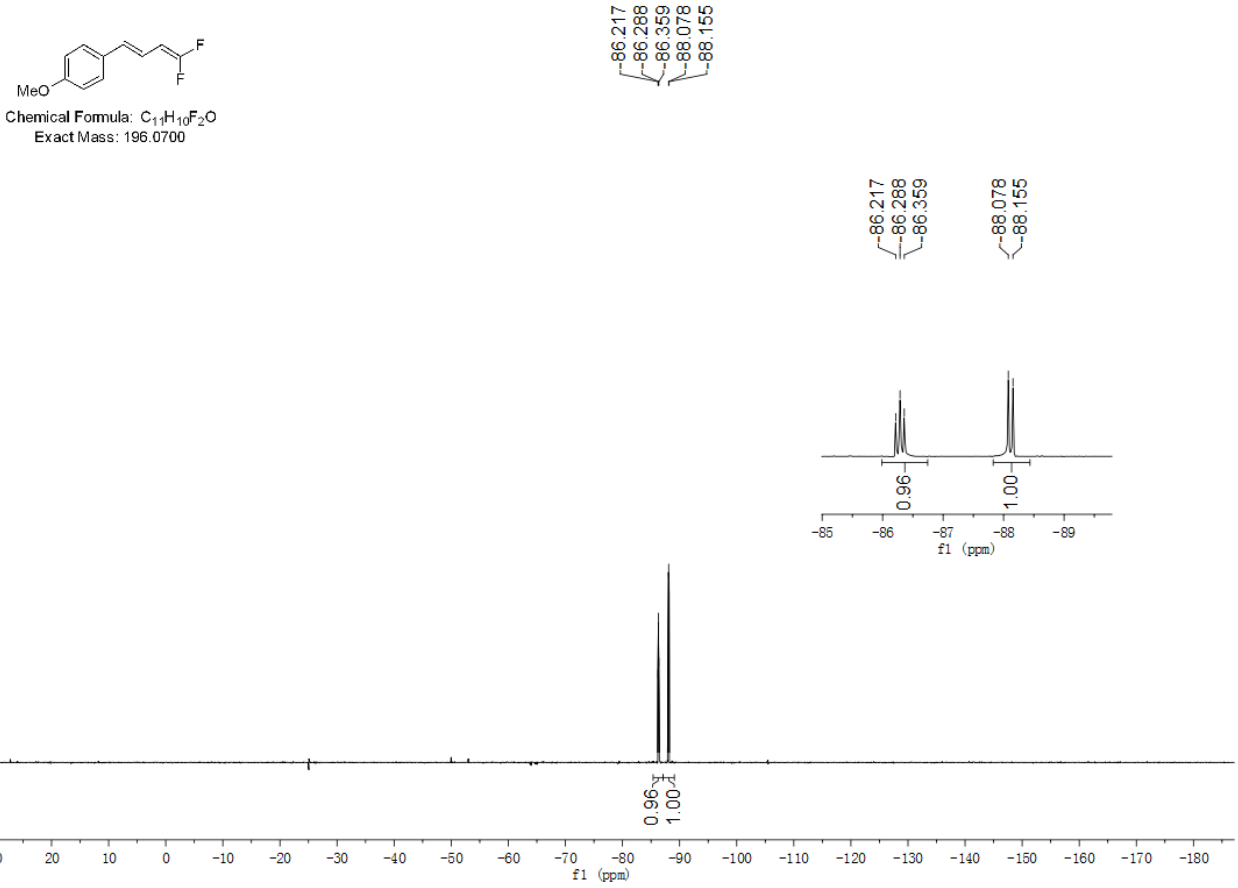


Chemical Formula: $C_{12}H_{12}F_2$
Exact Mass: 194.0907

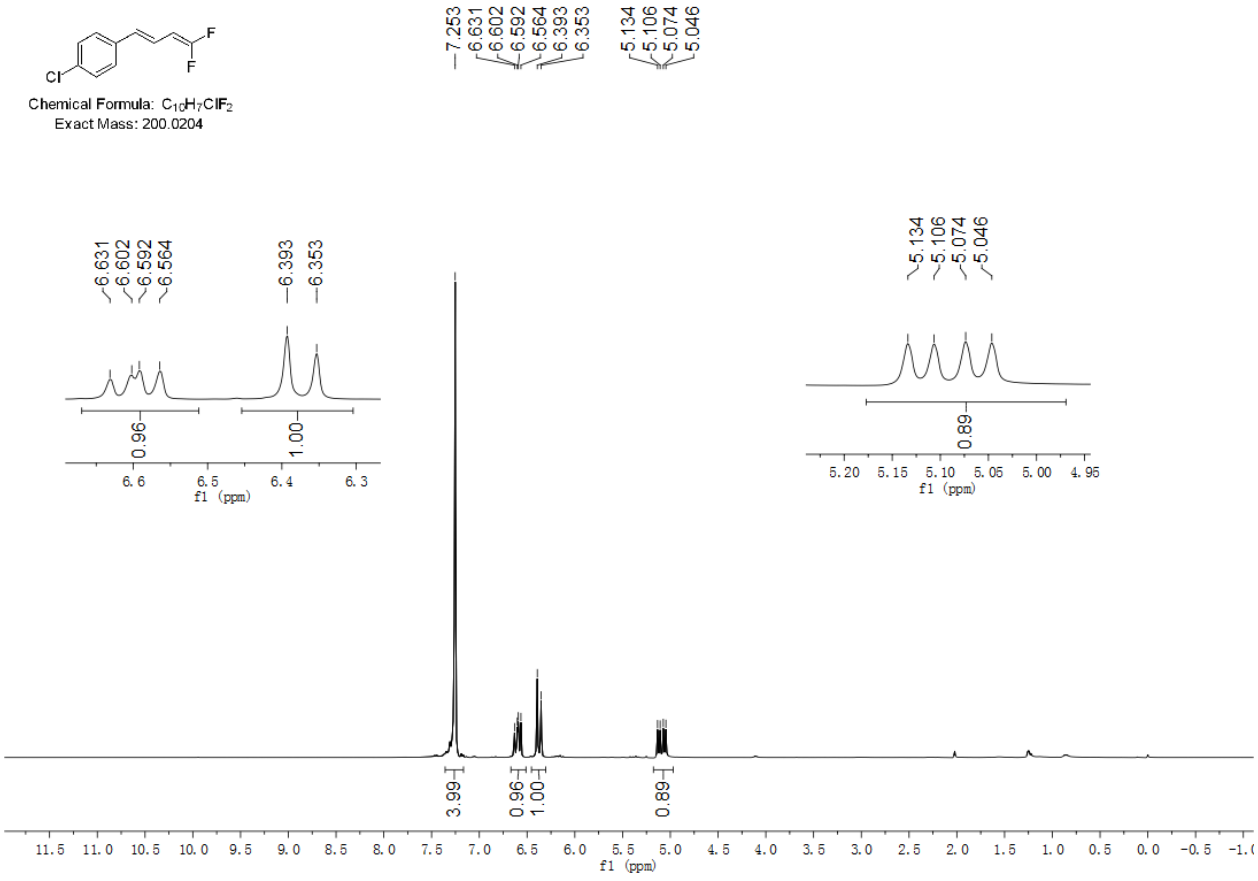


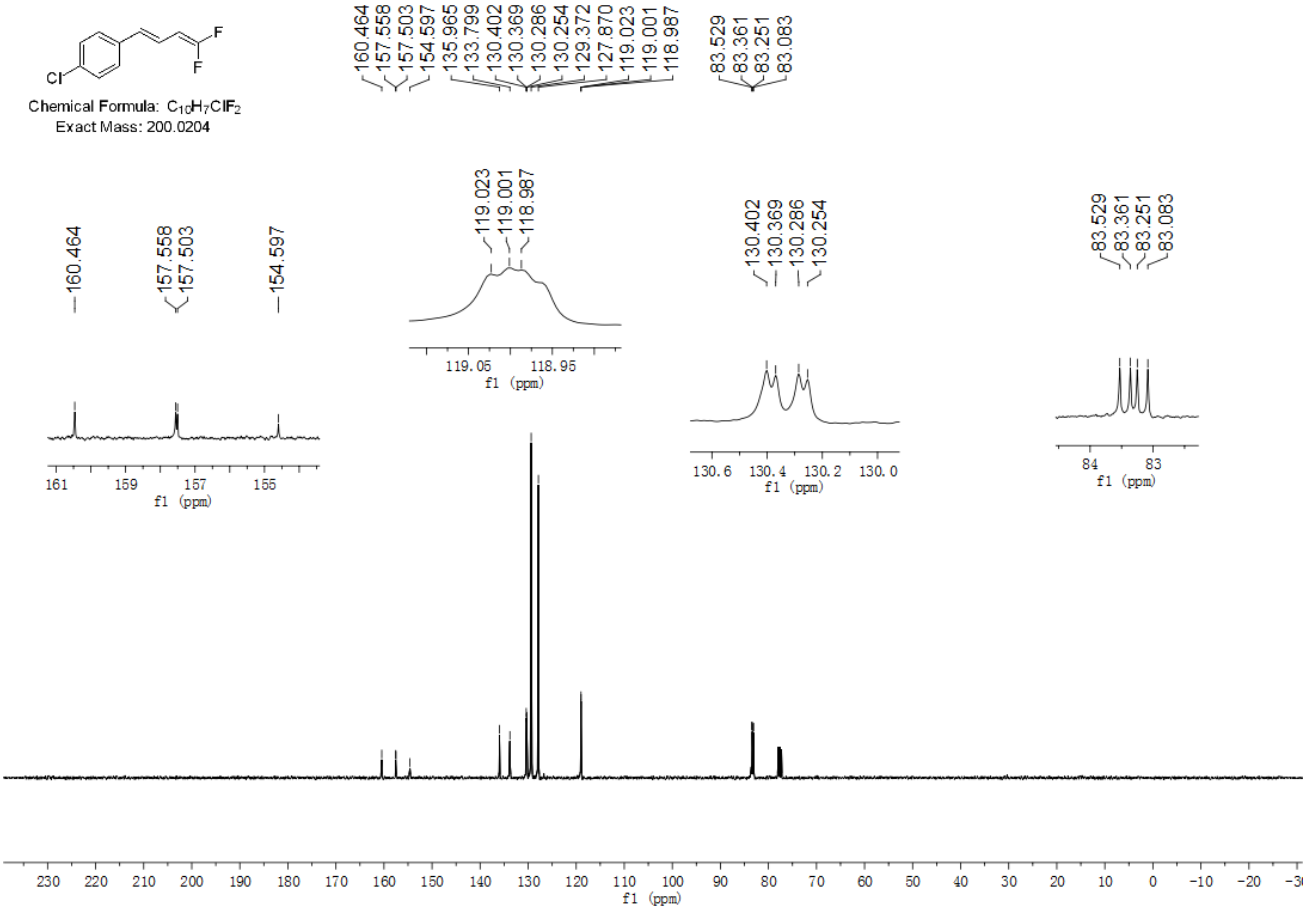
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-methoxylbenzene (3e).

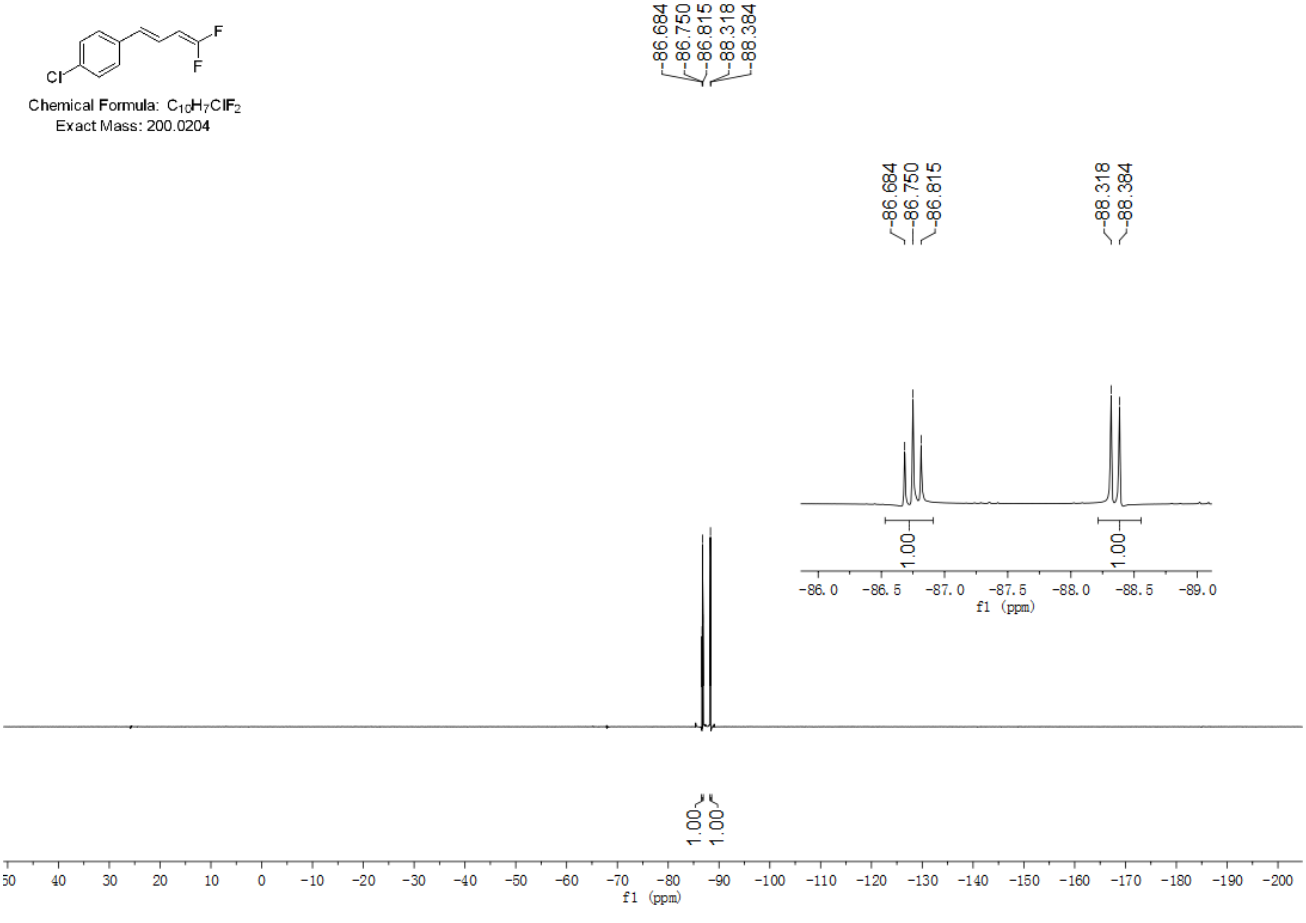




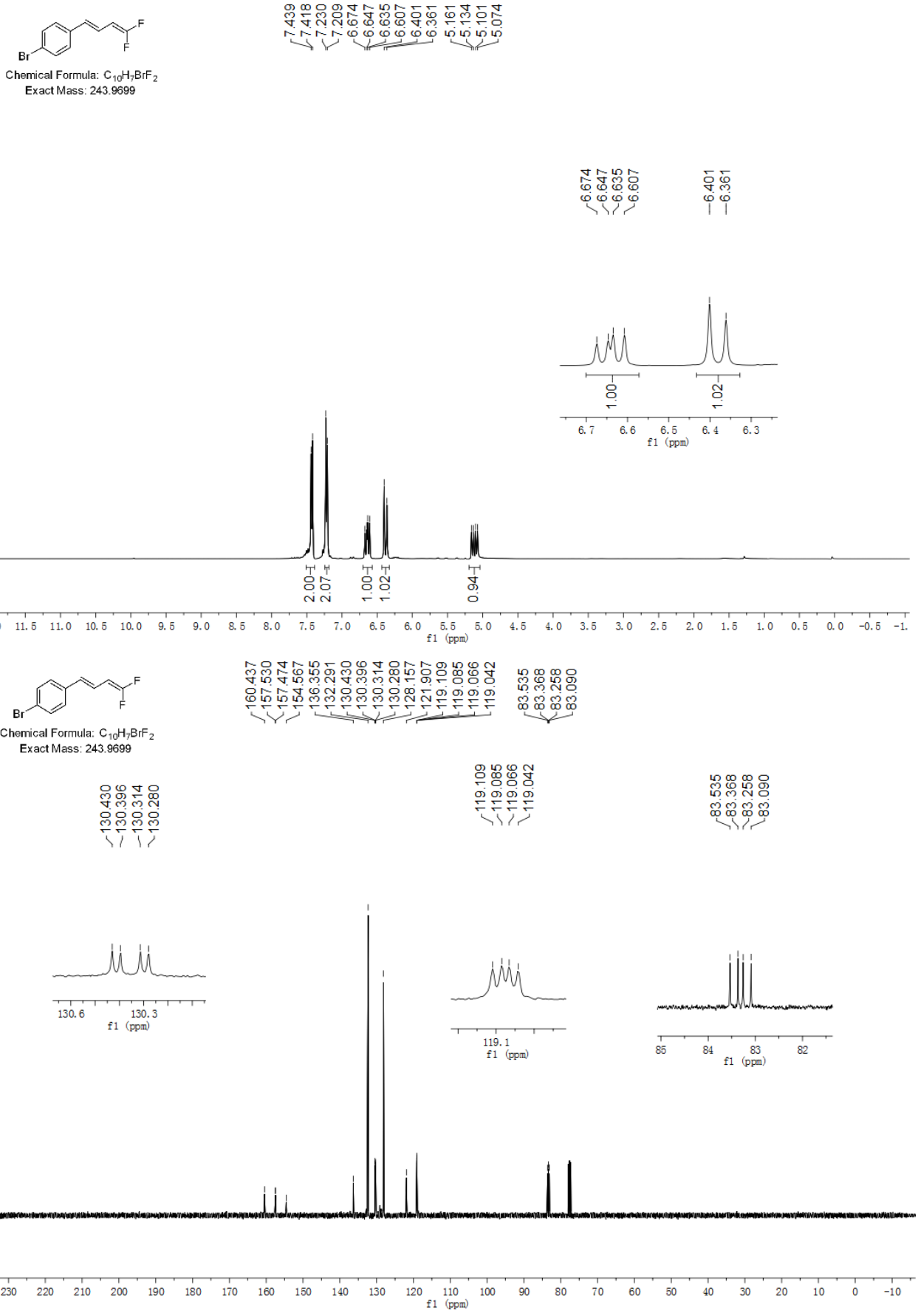
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-chlorobenzene (3f).

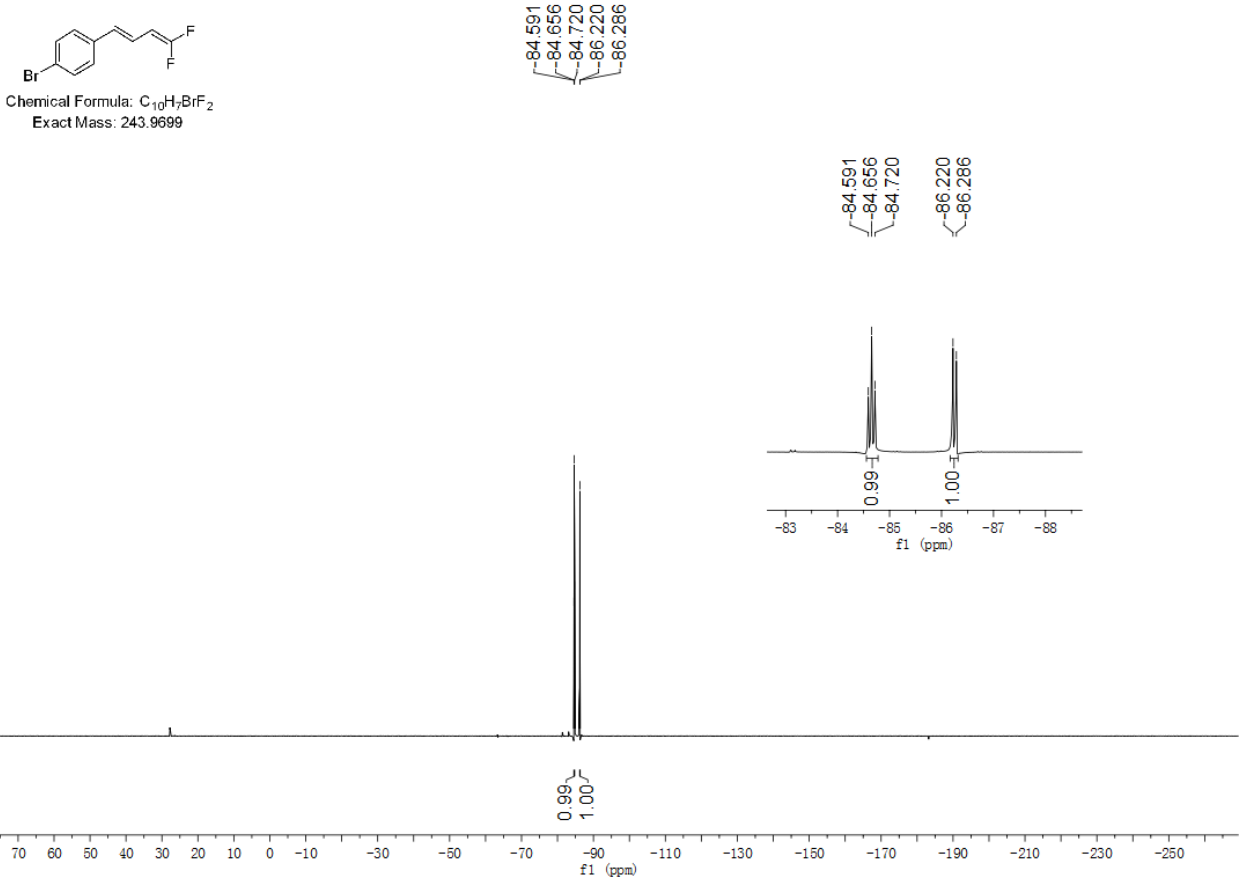



Chemical Formula: C10H7ClF2
Exact Mass: 200.0204
160.464
157.558
157.503
154.597
135.965
133.799
130.402
130.369
130.286
130.254
129.372
127.870
119.023
119.001
118.987
83.529
83.361
83.251
83.083
f1 (ppm)

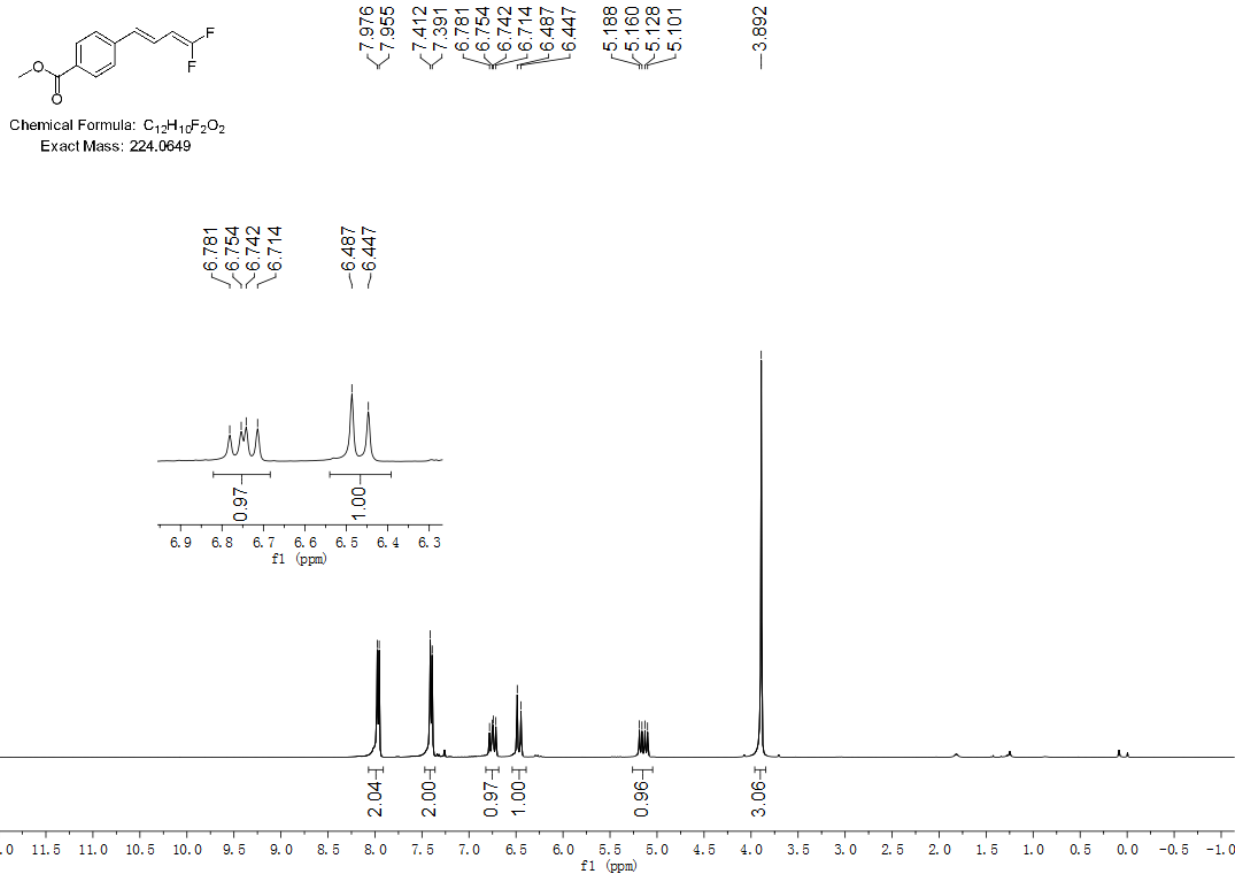

Chemical Formula: C10H7ClF2
Exact Mass: 200.0204
86.684
86.750
86.815
88.318
88.384
1.00
1.00
f1 (ppm)

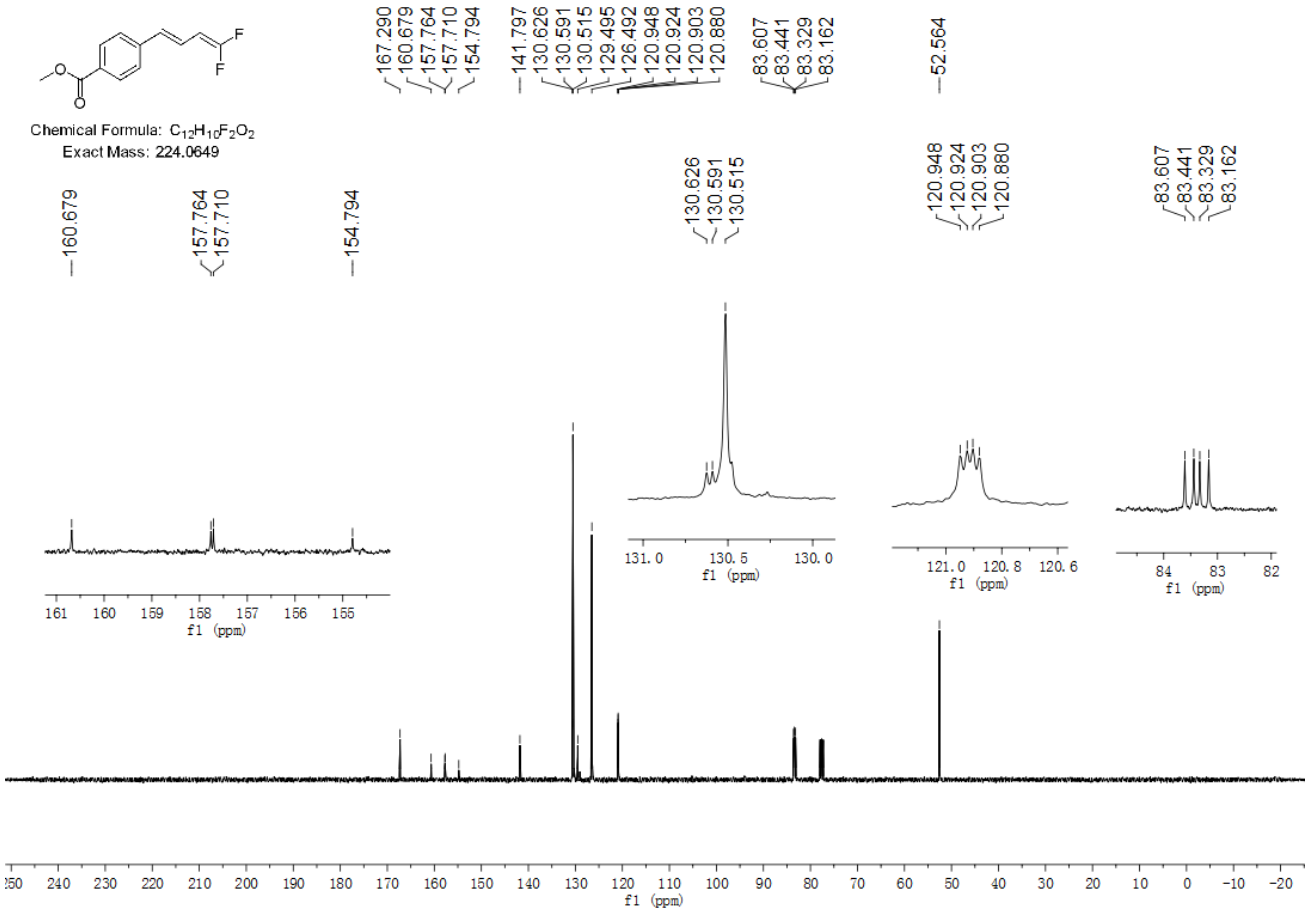
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-bromobenzene (3g).

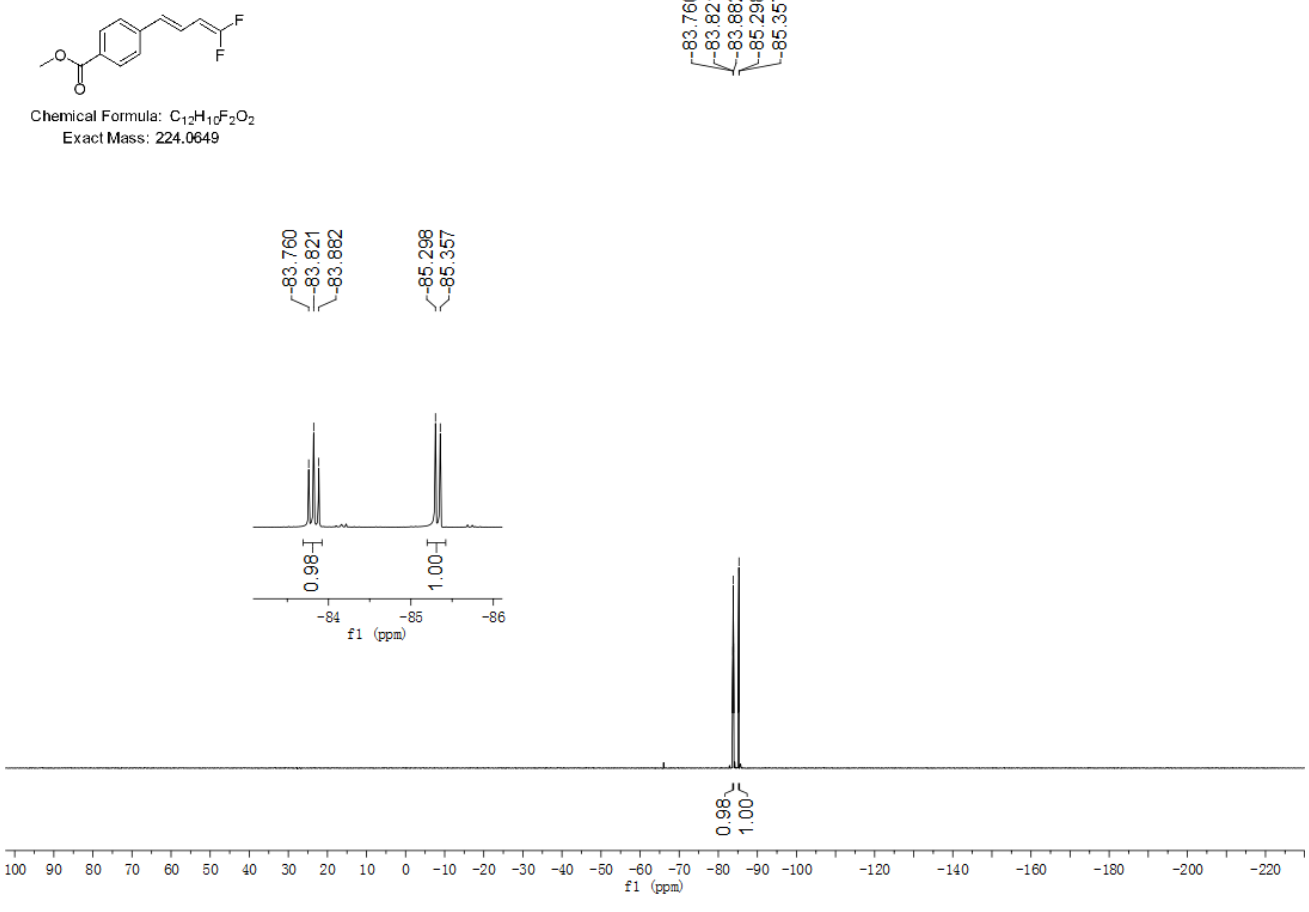




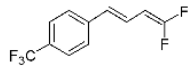
Methyl (*E*)-4-(4,4-difluorobuta-1,3-dien-1-yl)benzoate (3h).



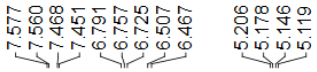

Chemical Formula: C12H10F2O2
Exact Mass: 224.0649
167.290
160.679
157.764
157.710
154.794
141.797
130.626
130.591
130.515
129.495
126.492
120.948
120.924
120.903
120.880
83.607
83.441
83.329
83.162
52.564
f1 (ppm)

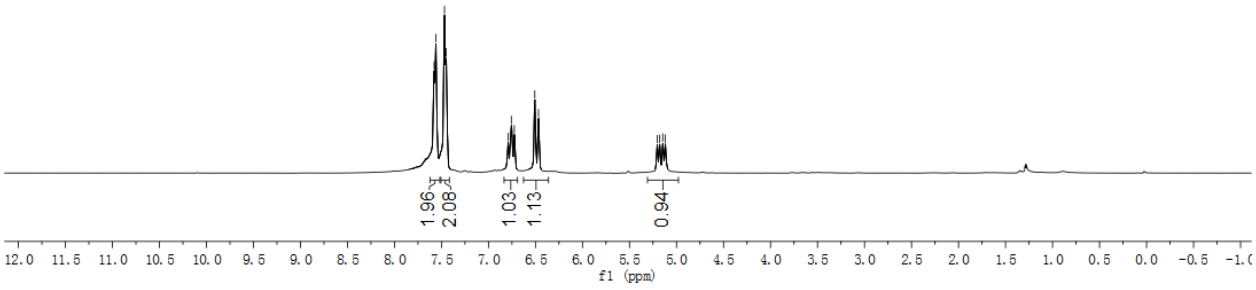

Chemical Formula: C12H10F2O2
Exact Mass: 224.0649
83.760
83.821
83.882
85.298
85.357
0.98
1.00
f1 (ppm)

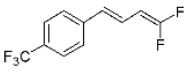
(*E*)-(4,4-Difluorobuta-1,3-dien-1-yl)-4-trifluoromethylbenzene (3i).



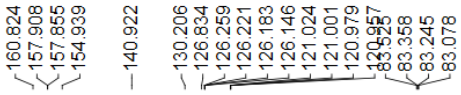
Chemical Formula: $C_{11}H_7F_5$
Exact Mass: 234.0468

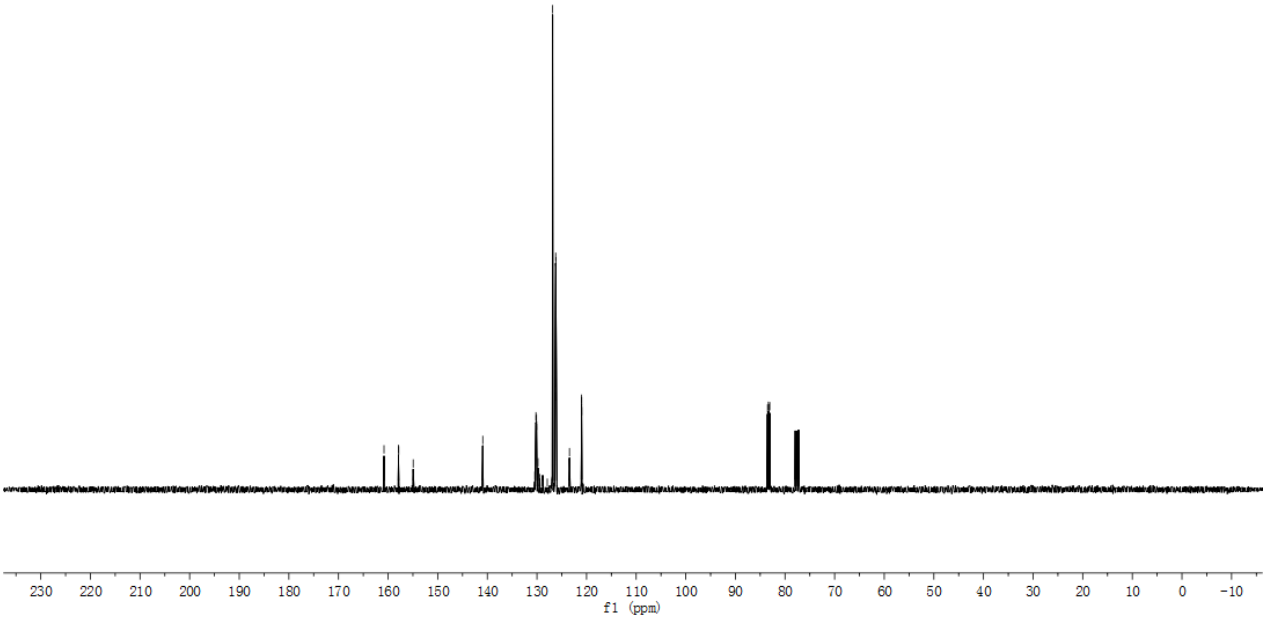


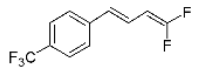




Chemical Formula: $C_{11}H_7F_5$
Exact Mass: 234.0468

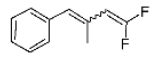




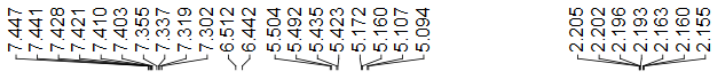


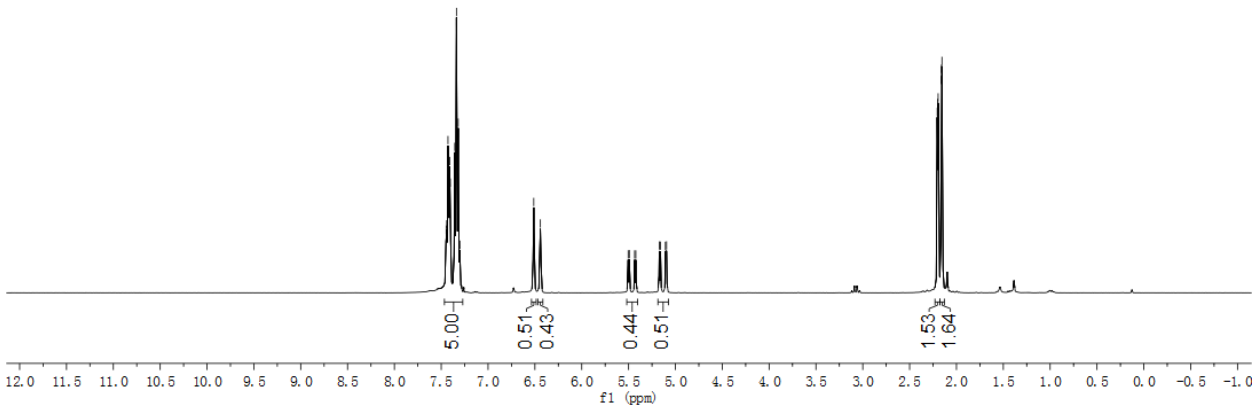
Chemical Formula: $C_{11}H_7F_5$
Exact Mass: 234.0468

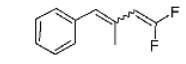
(4,4-Difluoro-2-methylbuta-1,3-dien-1-yl)benzene (3j).



Chemical Formula: $C_{11}H_{10}F_2$
Exact Mass: 180.0751

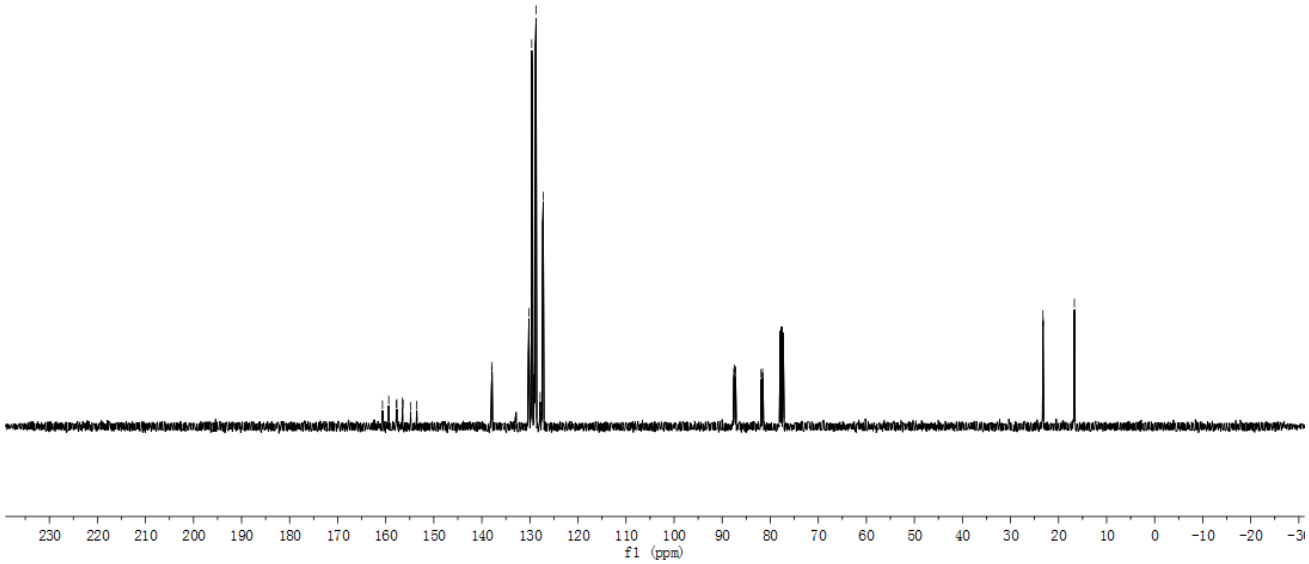


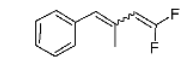




Chemical Formula: $C_{11}H_{10}F_2$
Exact Mass: 180.0751

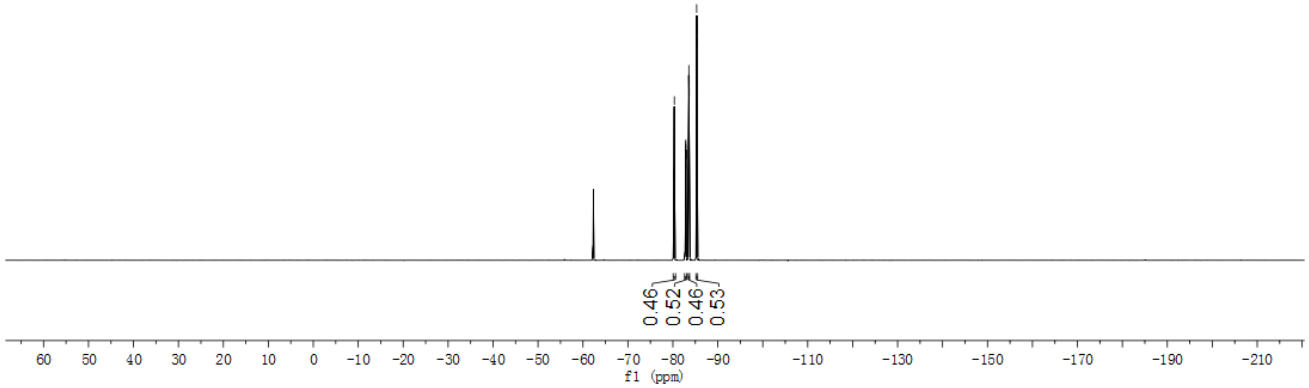
160.692
159.382
157.824
157.698
156.526
156.396
154.831
153.549
130.305
130.224
130.167
129.637
129.477
128.853
128.724
127.351
127.236
87.561
87.474
87.310
87.191
81.911
81.790
81.618
81.496
23.248
23.186
16.712
16.651



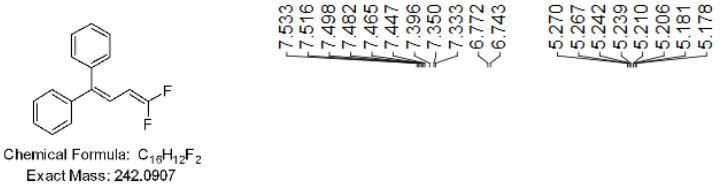


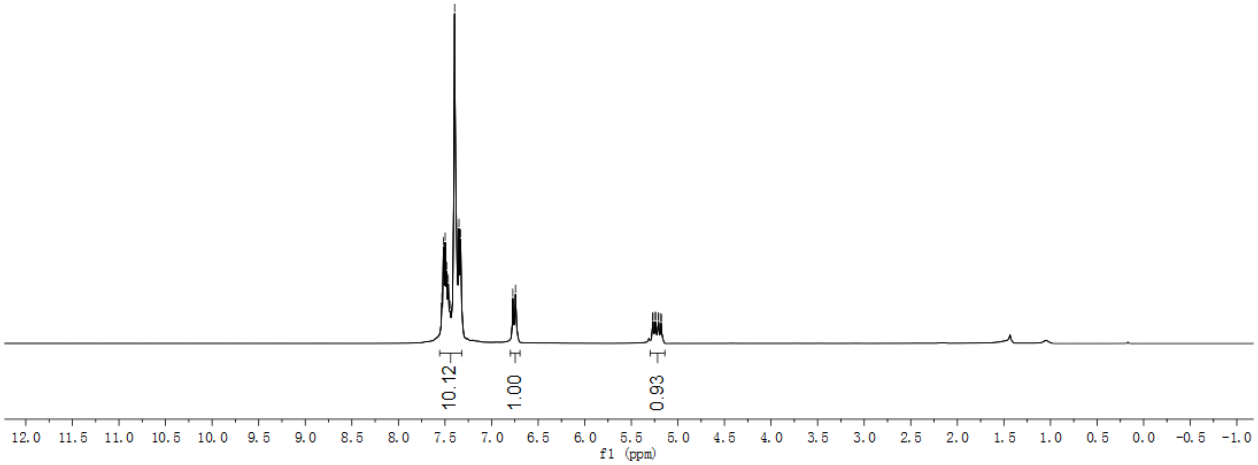
Chemical Formula: $C_{11}H_{10}F_2$
Exact Mass: 180.0751

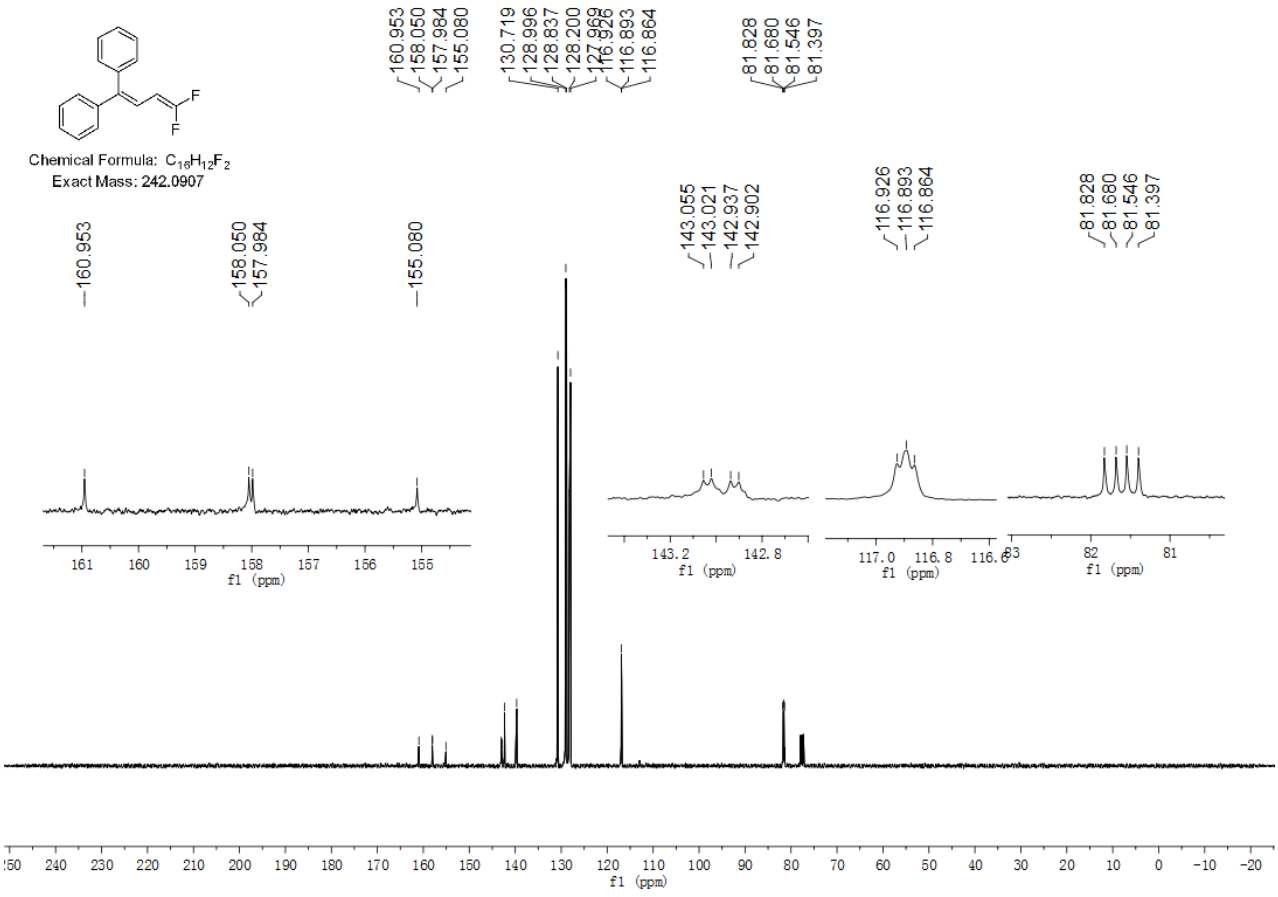
80.248
80.257
80.331
80.405
80.414
82.785
82.791
82.854
82.861
82.871
82.880
82.887
82.950
82.956
83.552
83.564
83.636
83.648
85.298
85.311
85.394
85.407

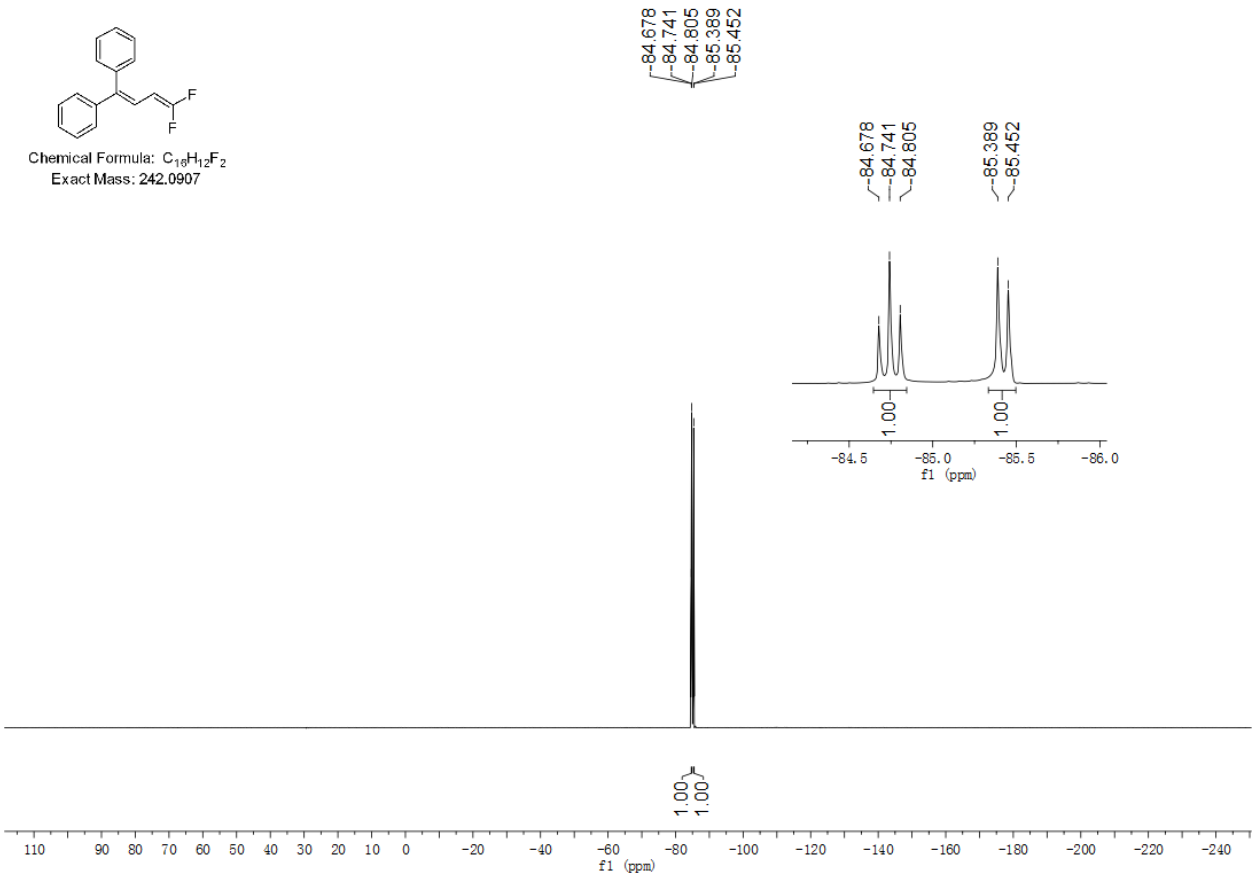


(4,4-Difluorobuta-1,3-diene-1,1-diyl)dibenzene (3k).

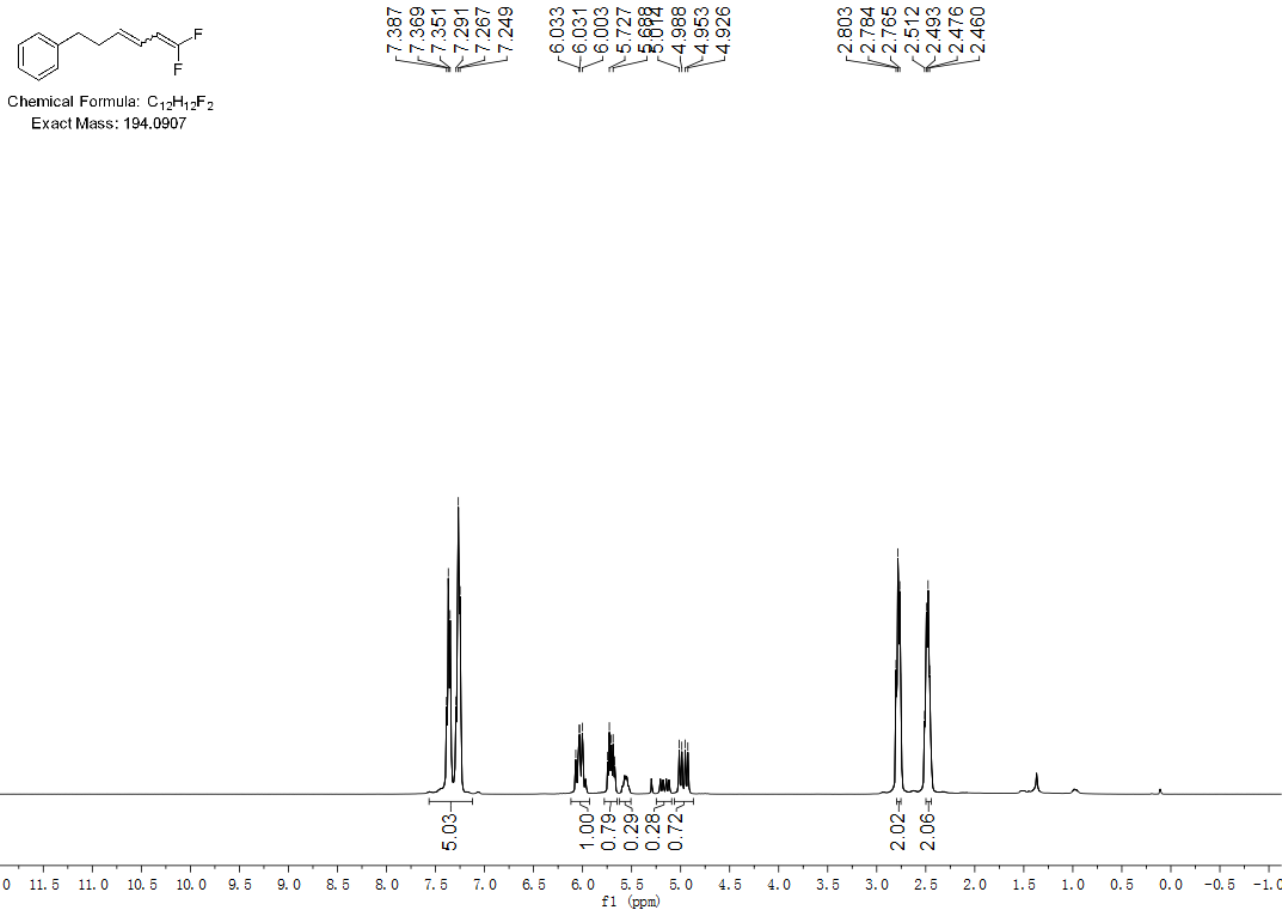


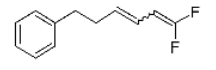






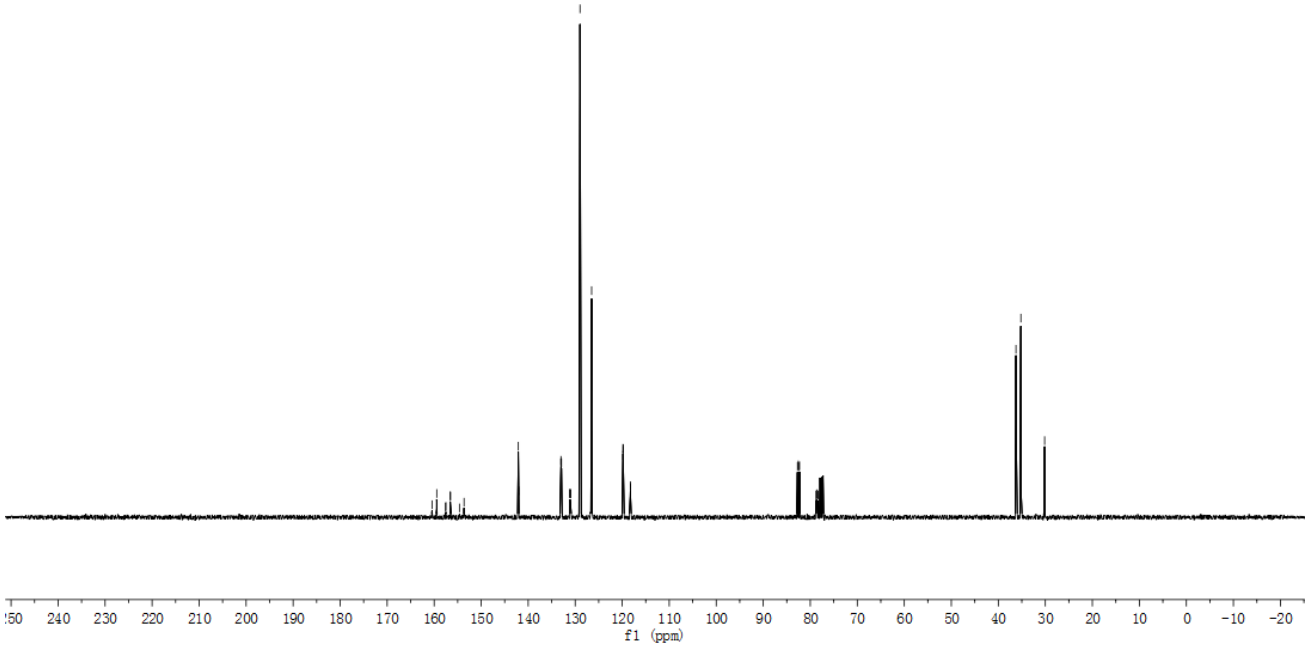
(6,6-Difluorohexa-3,5-dien-1-yl)benzene (3l).

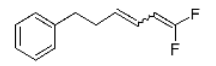




Chemical Formula: $C_{12}H_{12}F_2$
Exact Mass: 194.0907

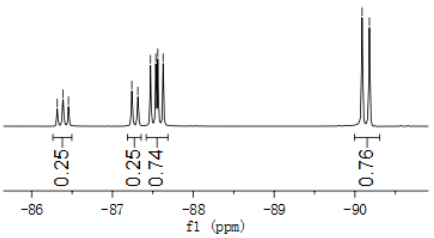
160.458
159.453
157.572
157.510
156.578
156.522
154.622
153.646
142.097
128.979
128.954
128.930
126.580
126.505
119.855
119.843
119.813
119.801
82.721
82.551
82.456
82.286
78.782
78.618
78.518
78.353
36.249
36.135
35.202
30.149

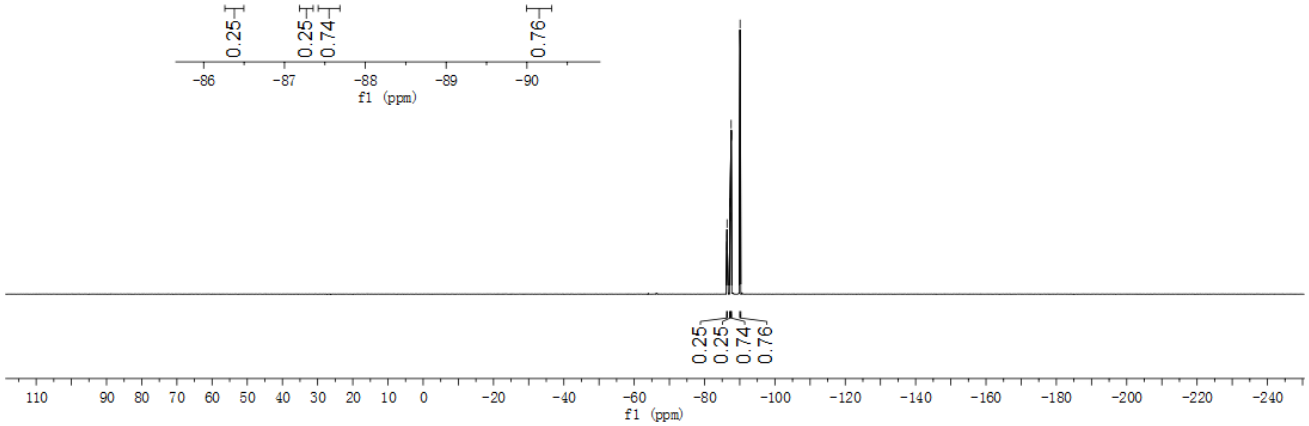




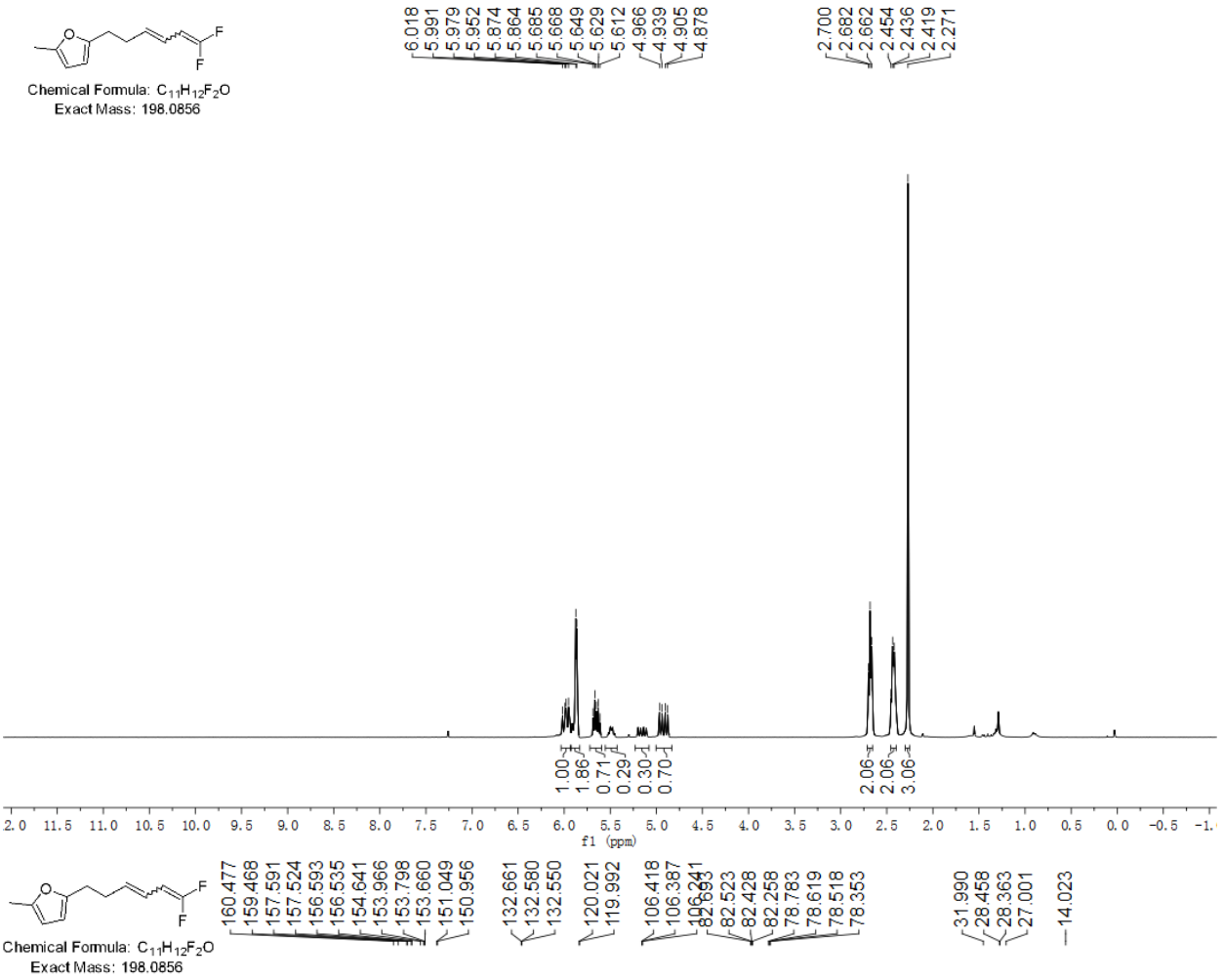
Chemical Formula: $C_{12}H_{12}F_2$
Exact Mass: 194.0907

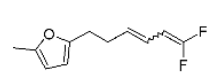
86.317
86.389
86.455
87.239
87.313
87.470
87.536
87.561
87.626
90.088
90.179



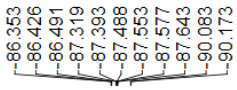


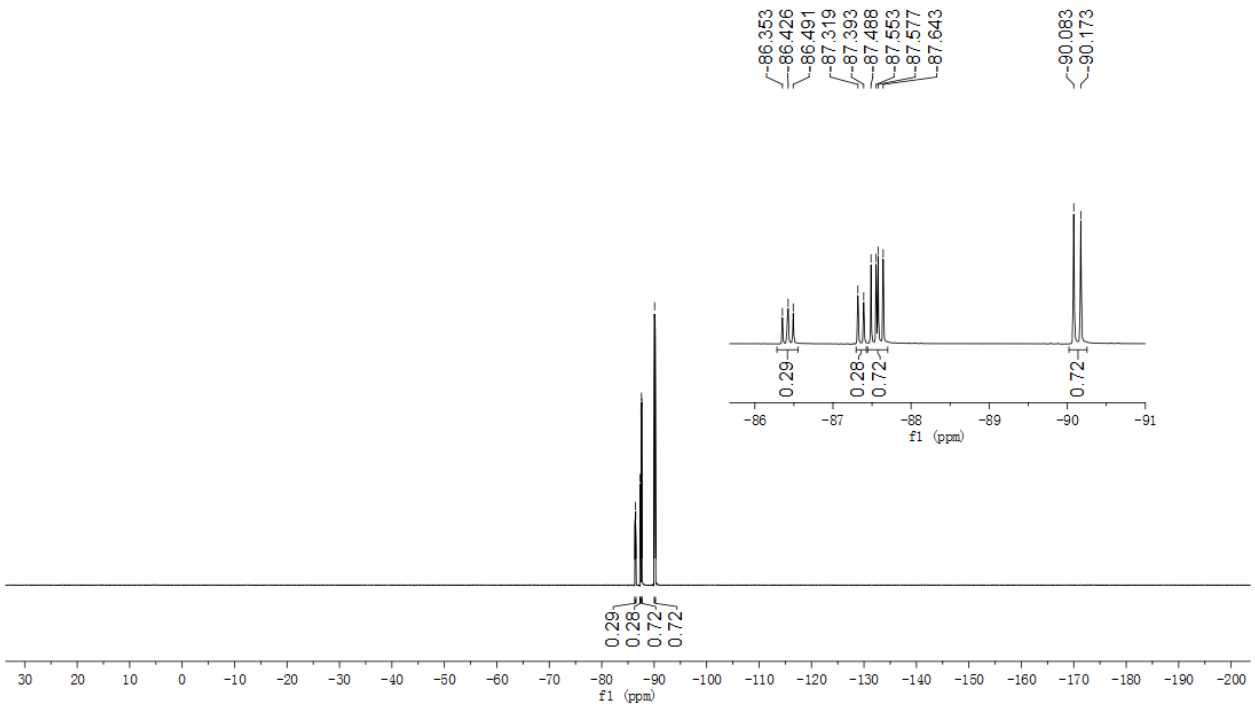
2-(6,6-Difluorohexa-3,5-dien-1-yl)-5-methylfuran (3m).



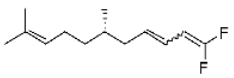


Chemical Formula: $C_{11}H_{12}F_2O$
Exact Mass: 198.0856

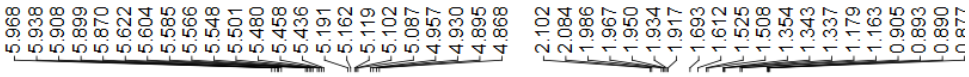


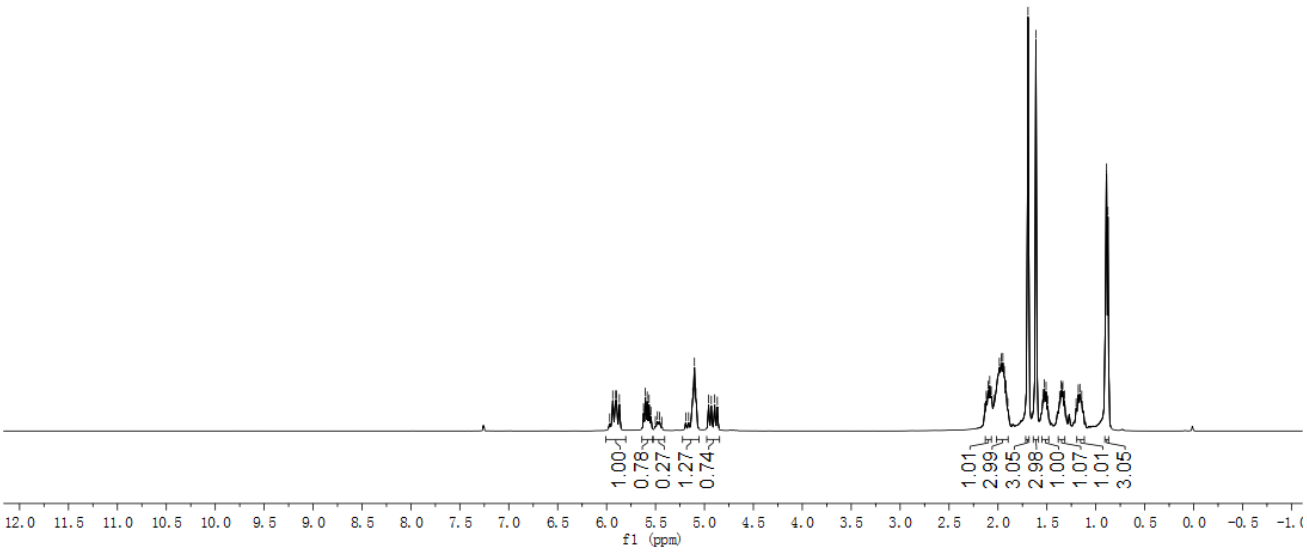


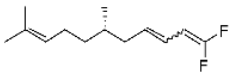
(*S*)-1,1-Difluoro-6,10-dimethylundeca-1,3,9-triene (3n).



Chemical Formula: $C_{13}H_{20}F_2$
Exact Mass: 214.1533

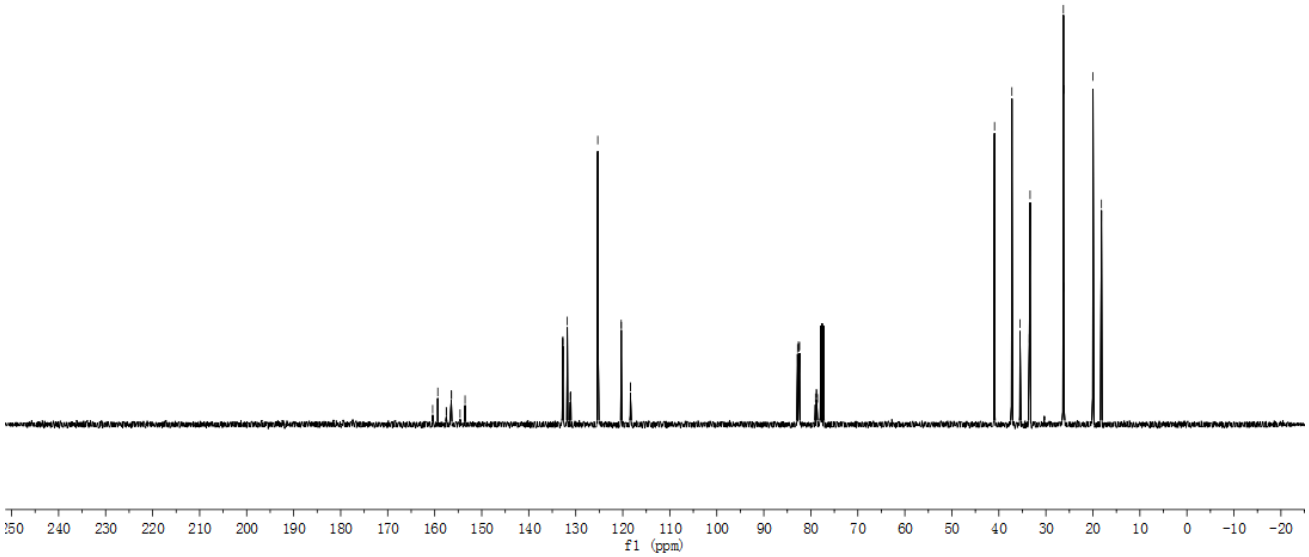




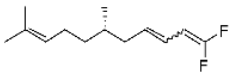


Chemical Formula: $C_{13}H_{20}F_2$
Exact Mass: 214.1533

160.437
159.347
157.556
157.491
156.476
156.418
154.610
153.546
132.845
132.815
132.734
132.705
131.799
125.316
125.262
120.329
120.302
82.823
82.652
82.560
82.389
79.012
78.847
78.750
78.585
40.921
37.295
37.229
35.506
33.521
33.358
26.277
26.226
26.182
20.021
19.971
18.176

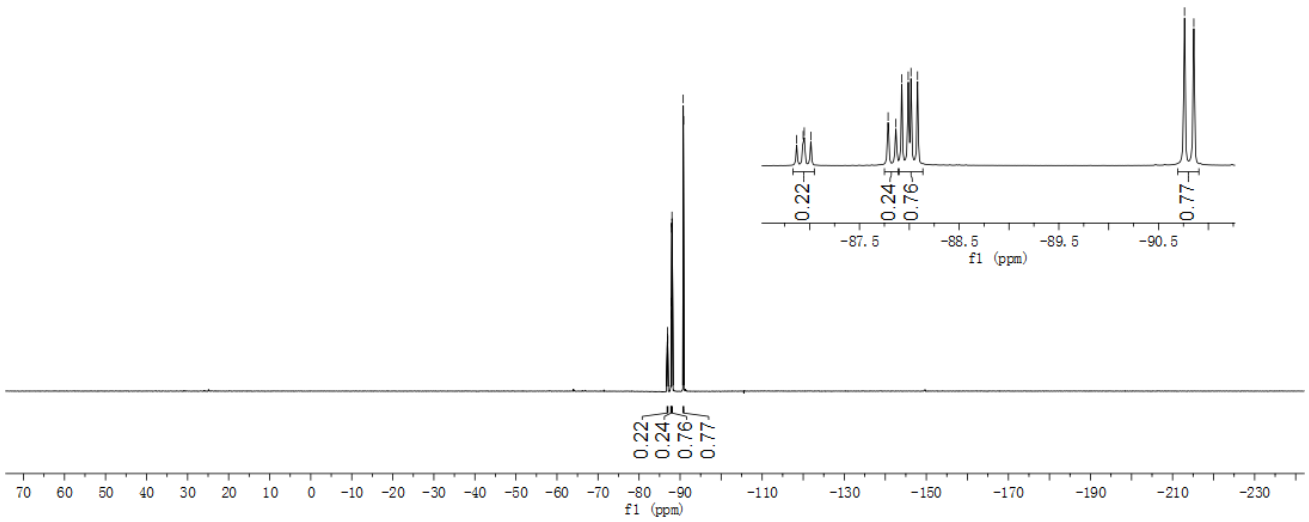


f1 (ppm)



Chemical Formula: $C_{13}H_{20}F_2$
Exact Mass: 214.1533

-86.869
-86.935
-86.946
-87.012
-87.787
-87.865
-87.924
-87.989
-88.017
-88.083
-90.761
-90.854



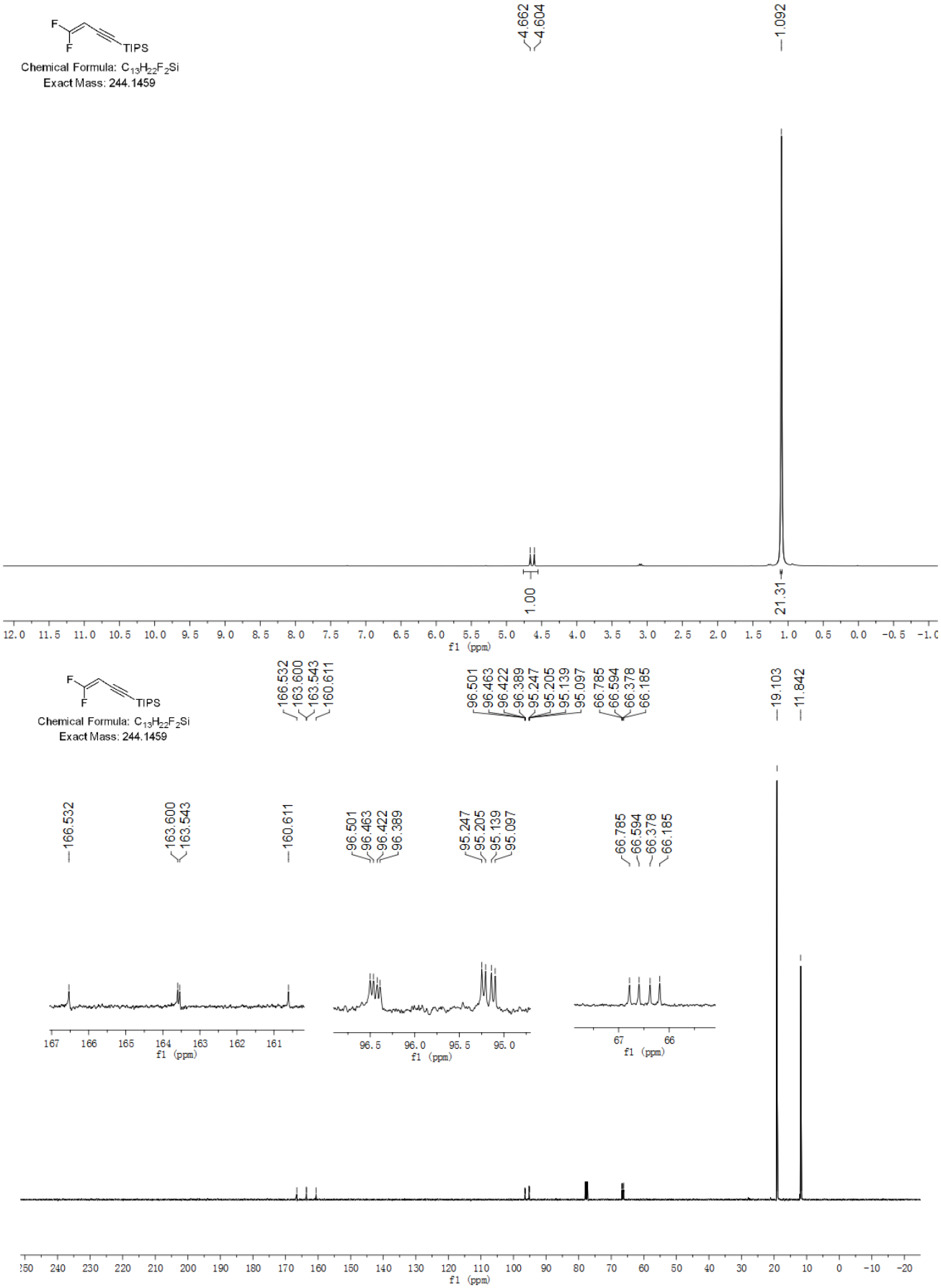
0.22
0.24
0.76
0.77

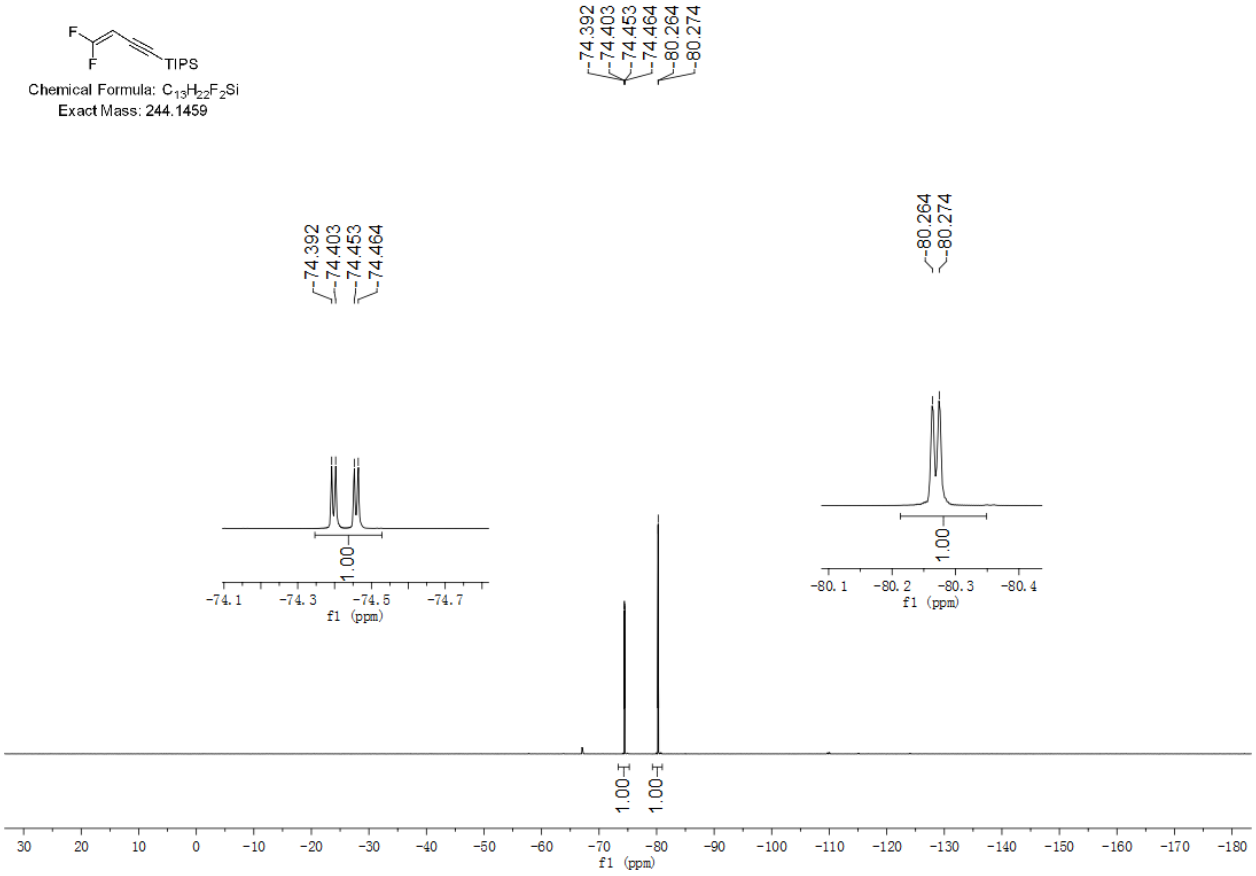
-87.5
-88.5
-89.5
-90.5
f1 (ppm)

0.22
0.24
0.76
0.77

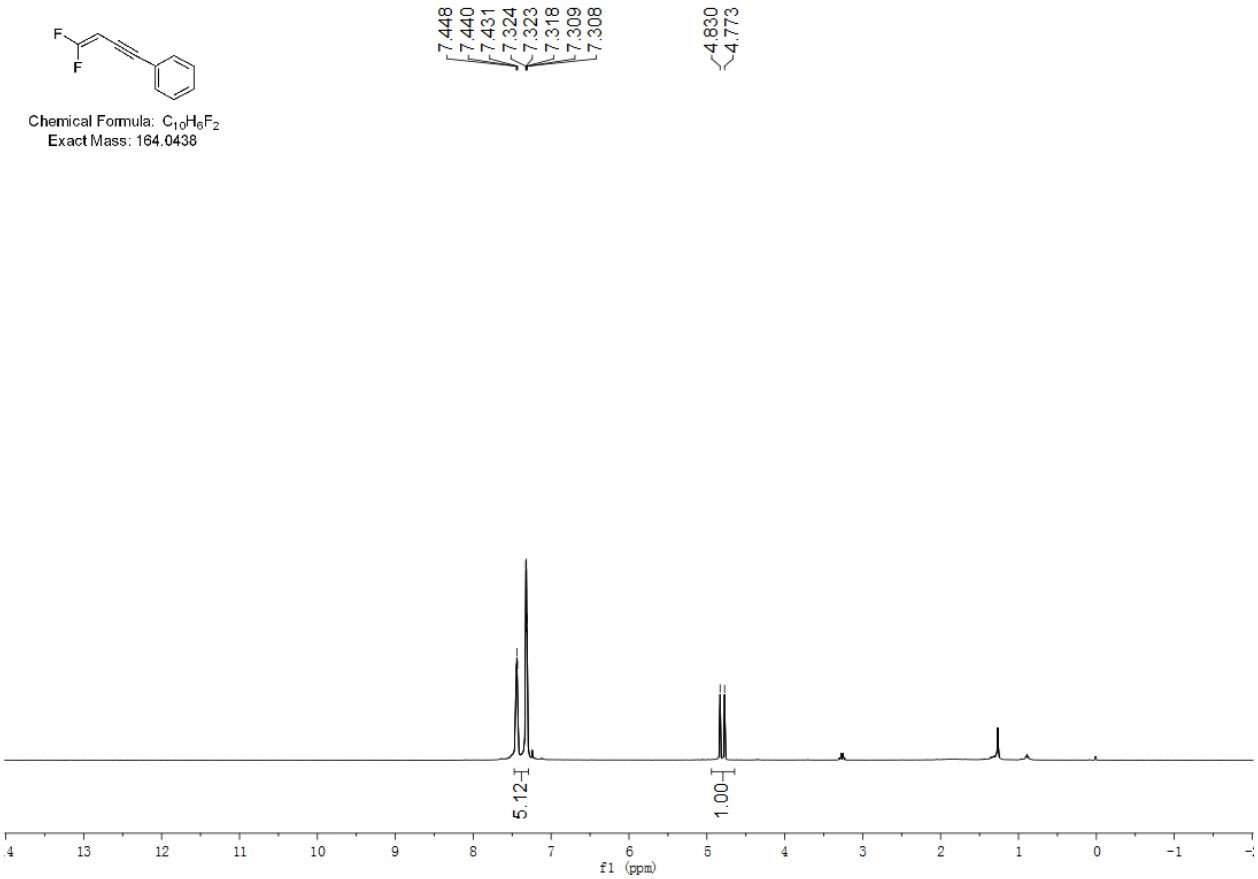
f1 (ppm)

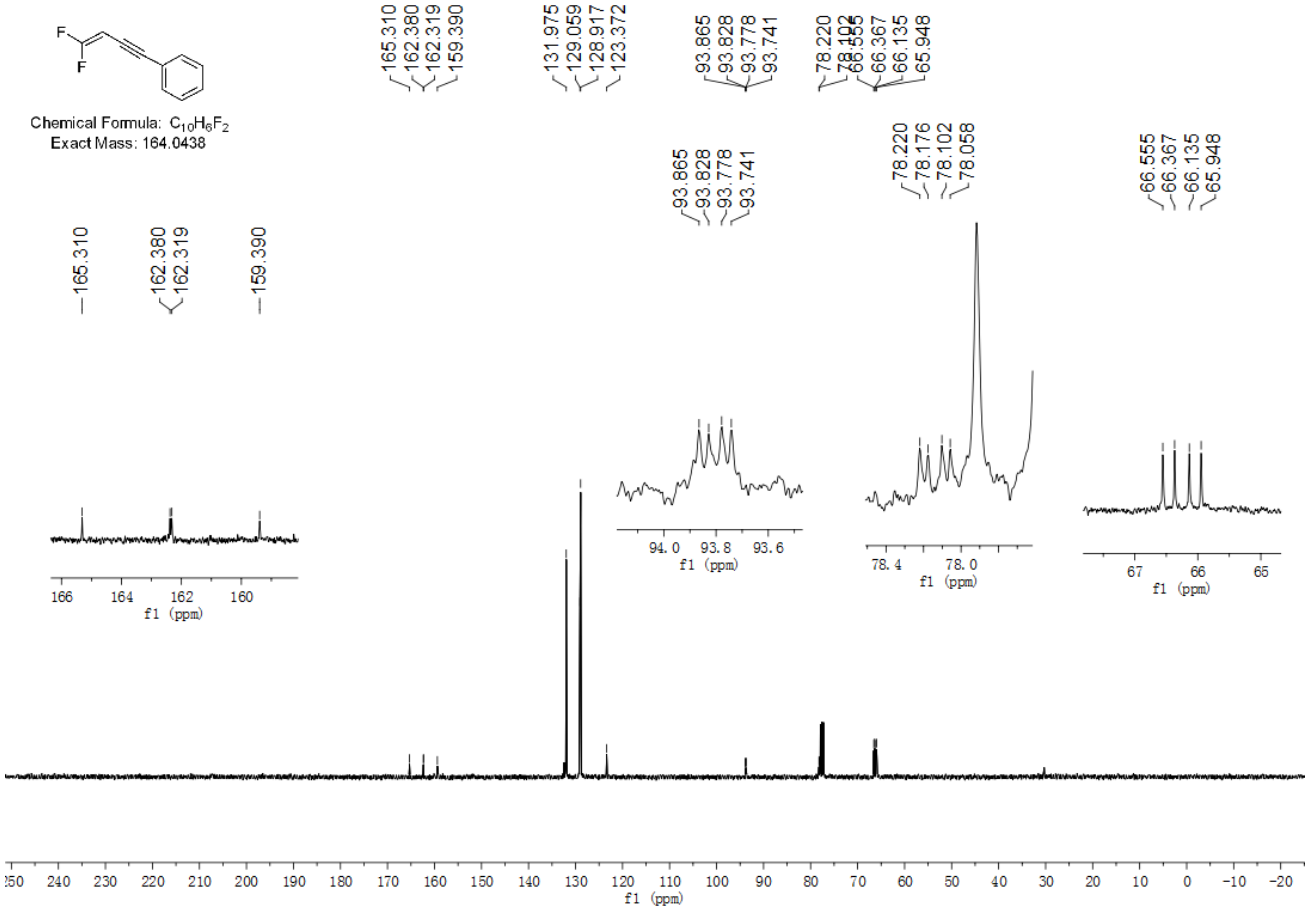
(4,4-Difluorobut-3-en-1-yn-1-yl)triisopropylsilane (3o).

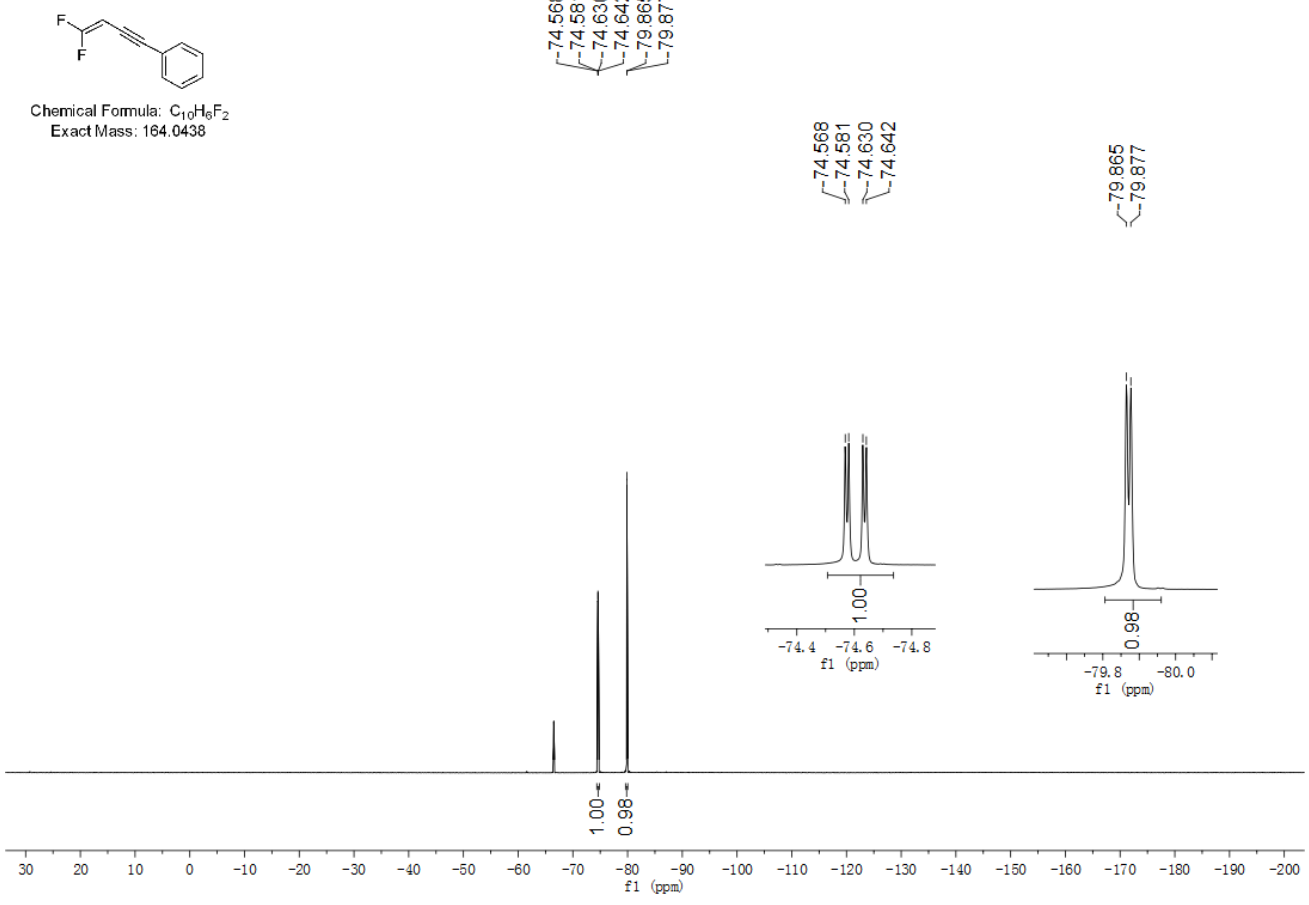




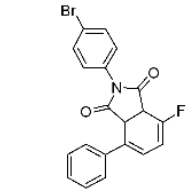
(4,4-Difluorobut-3-en-1-yn-1-yl)benzene (3p).



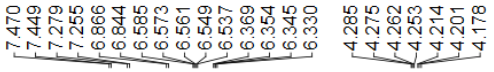

Chemical Formula: C10H6F2
Exact Mass: 164.0438
165.310
162.380
162.319
159.390
131.975
129.059
128.917
123.372
93.865
93.828
93.778
93.741
78.220
78.176
78.102
78.058
66.555
66.367
66.135
65.948
f1 (ppm)

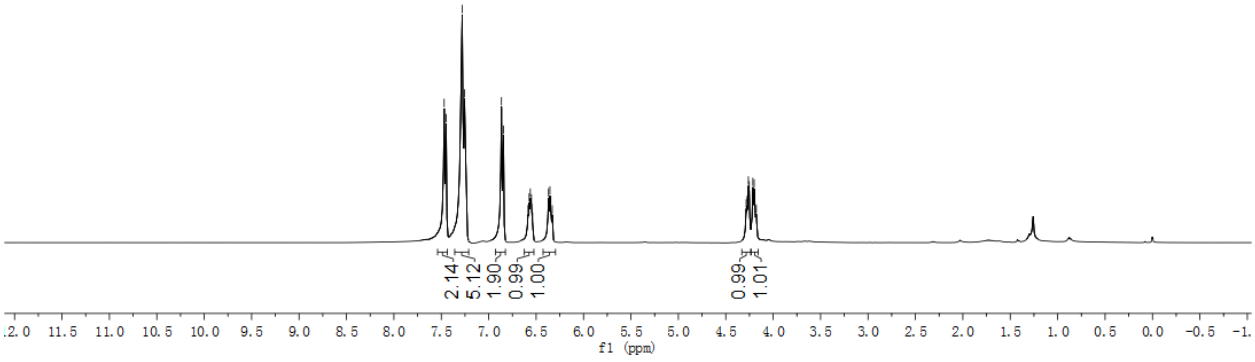

Chemical Formula: C10H6F2
Exact Mass: 164.0438
74.568
74.581
74.630
74.642
79.865
79.877
1.00
0.98
f1 (ppm)

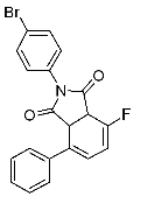
2-(4-Bromophenyl)-4-fluoro-7-phenyl-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione (6a)



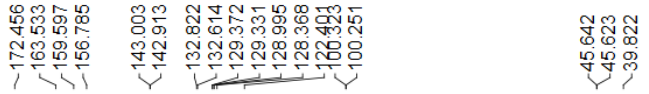
Chemical Formula: $C_{20}H_{13}BrFNO_2$
Exact Mass: 397.0114

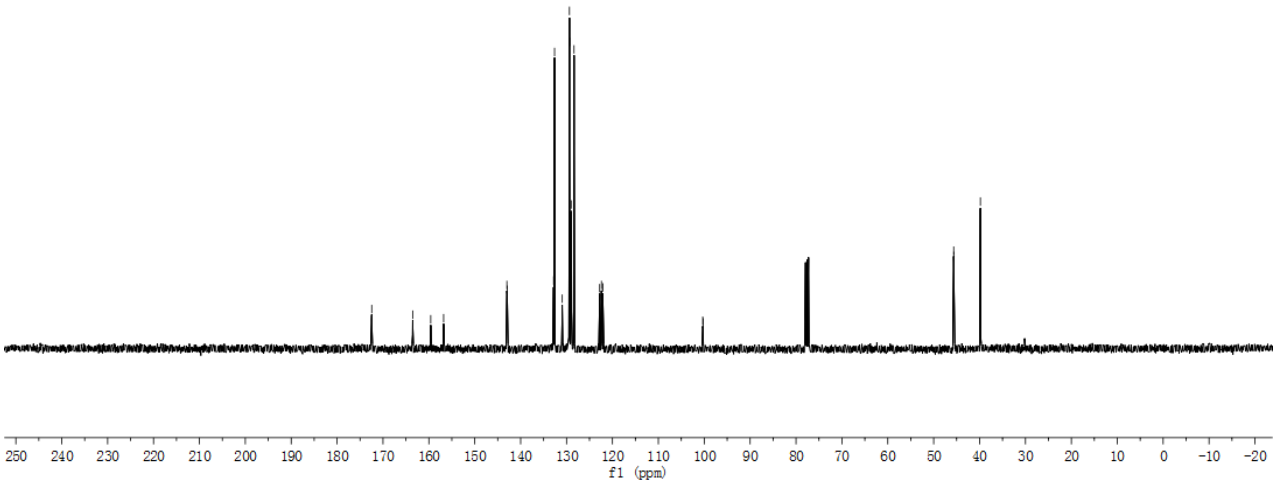


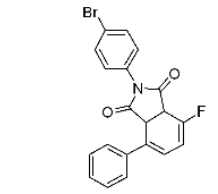




Chemical Formula: $C_{20}H_{13}BrFNO_2$
Exact Mass: 397.0114

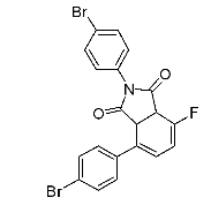




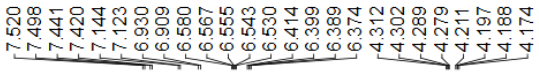


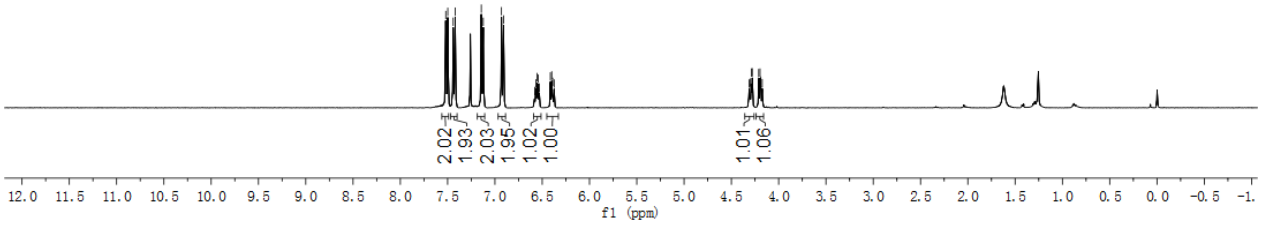
Chemical Formula: $C_{20}H_{13}BrFNO_2$
Exact Mass: 397.0114

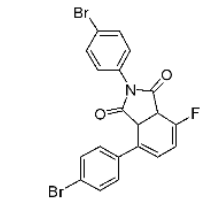
2,4-Bis(4-bromophenyl)-7-fluoro-3a,7a-dihydro-1*H*-isoindole-1,3(2*H*)-dione (6b)



Chemical Formula: $C_{20}H_{12}Br_2FNO_2$
Exact Mass: 474.9219

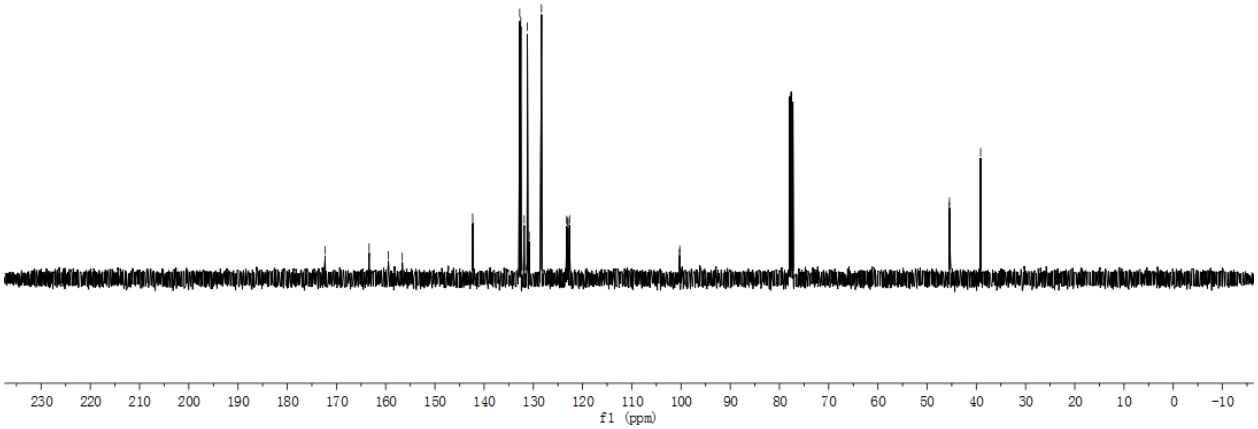


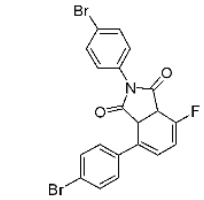




Chemical Formula: $C_{20}H_{12}Br_2FNO_2$
Exact Mass: **474**.9219

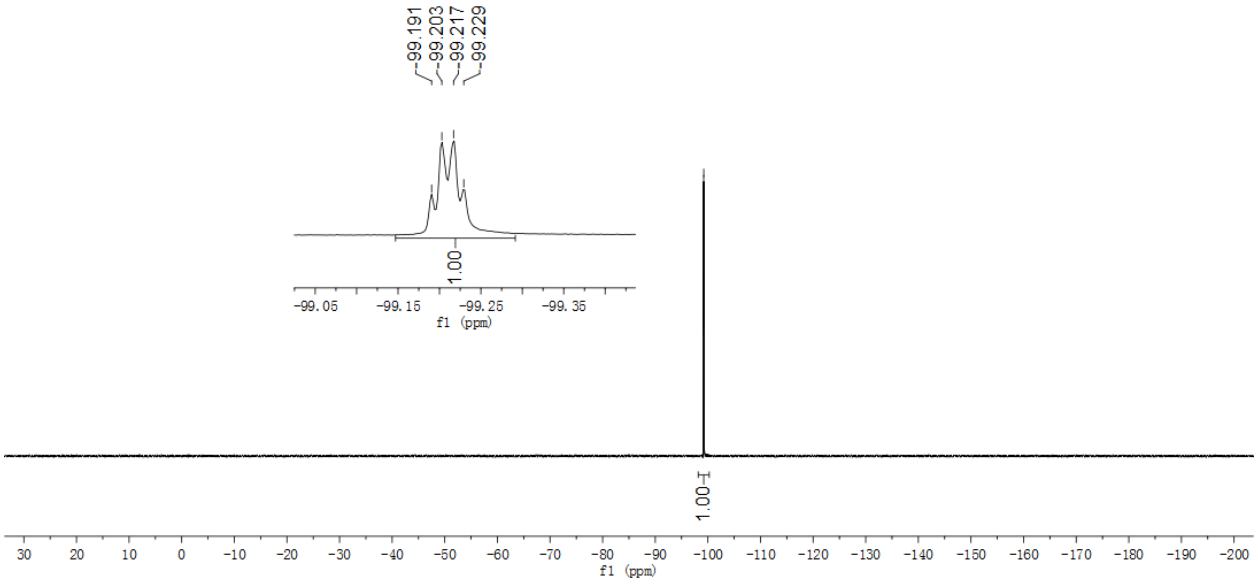
172.299
163.371
159.447
156.629
142.331
142.240
132.775
132.563
131.867
131.209
128.353
123.239
122.638
100.321
100.249
45.491
45.470
39.133



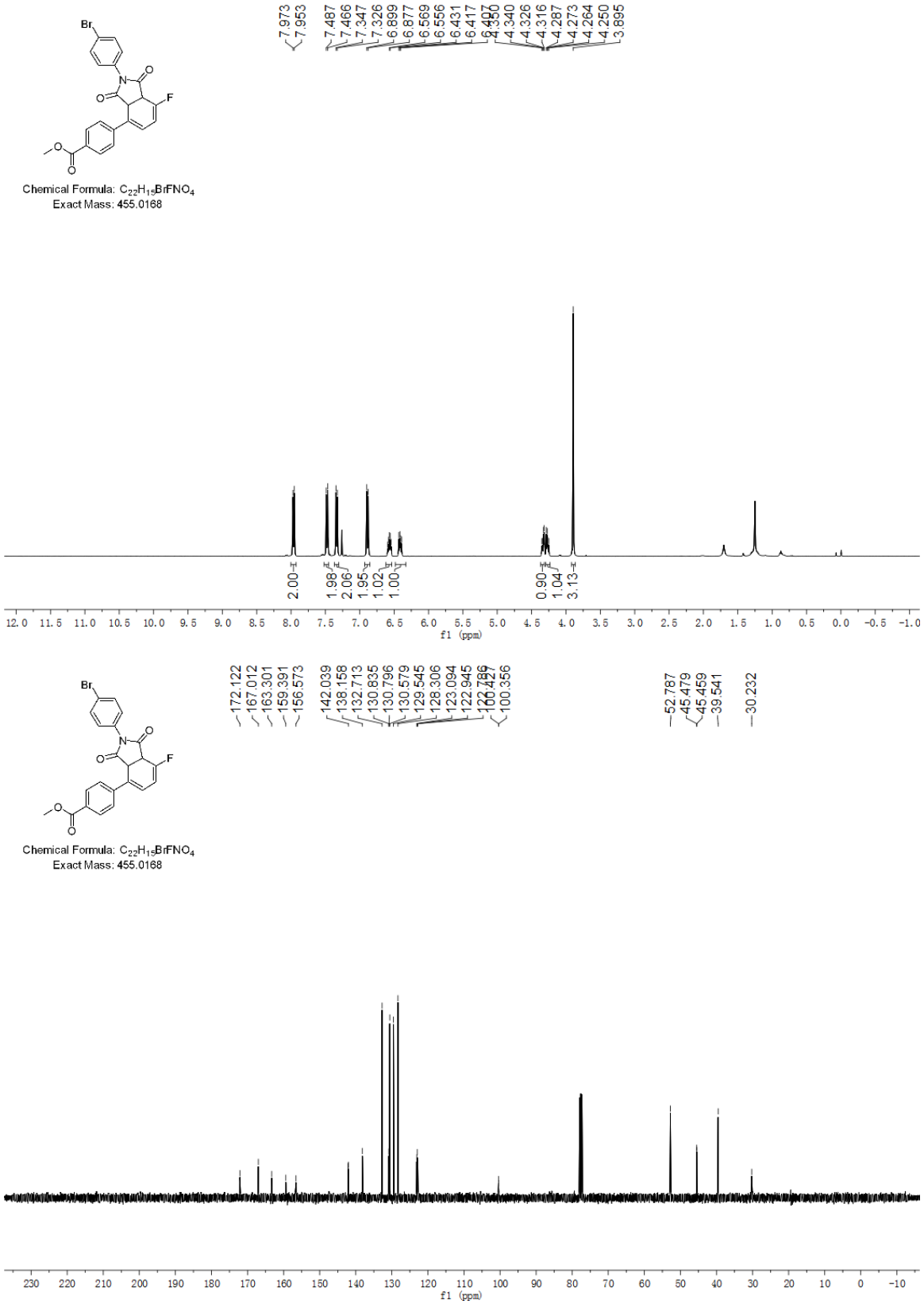


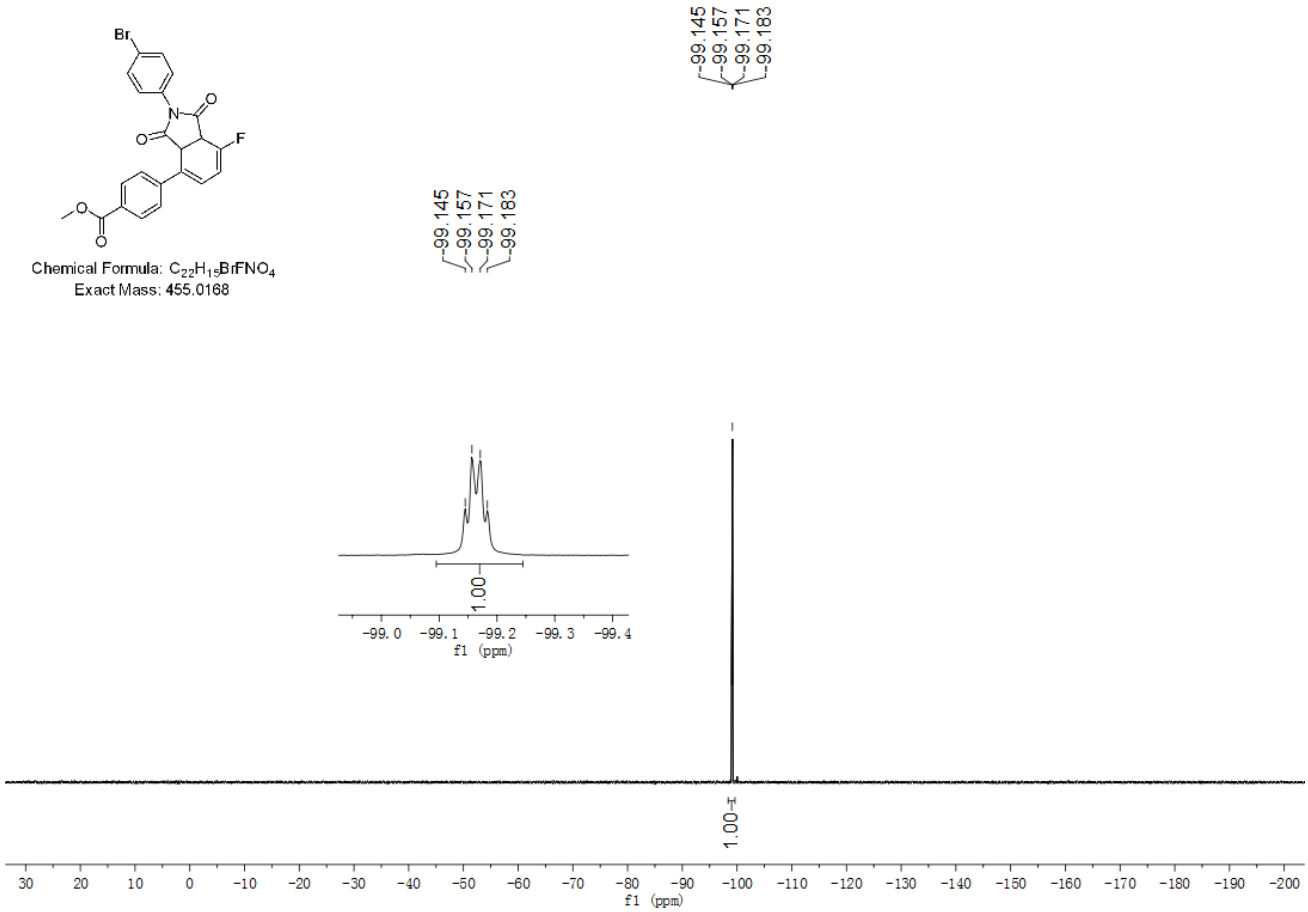
Chemical Formula: $C_{20}H_{12}Br_2FNO_2$
Exact Mass: **474**.9219

99.191
99.203
99.217
99.229

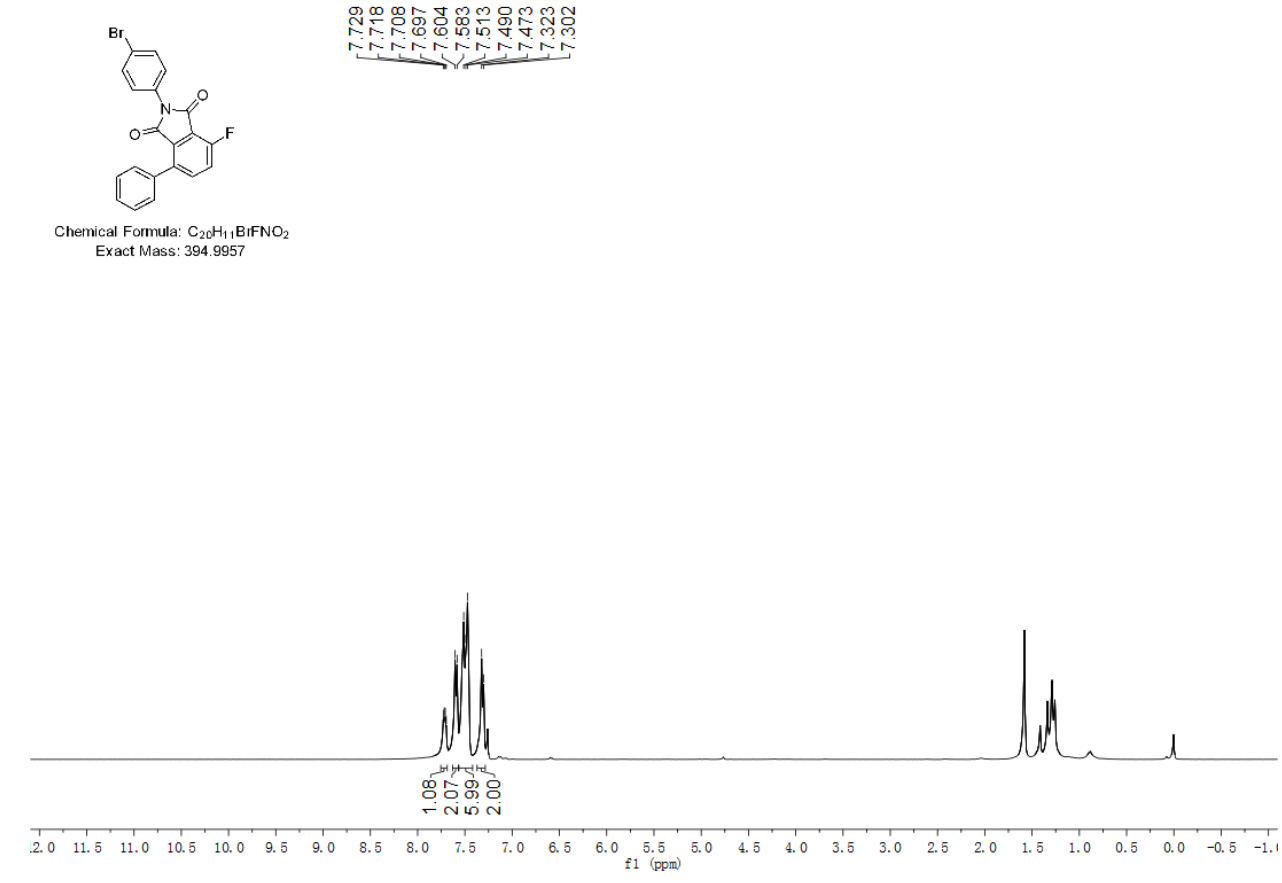


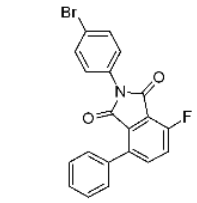
Methyl4-(2-(4-bromophenyl)-7-fluoro-1,3-dioxo-2,3,3a,7a-tetrahydro-1H-isoindol-4-yl)benzoate (6c)





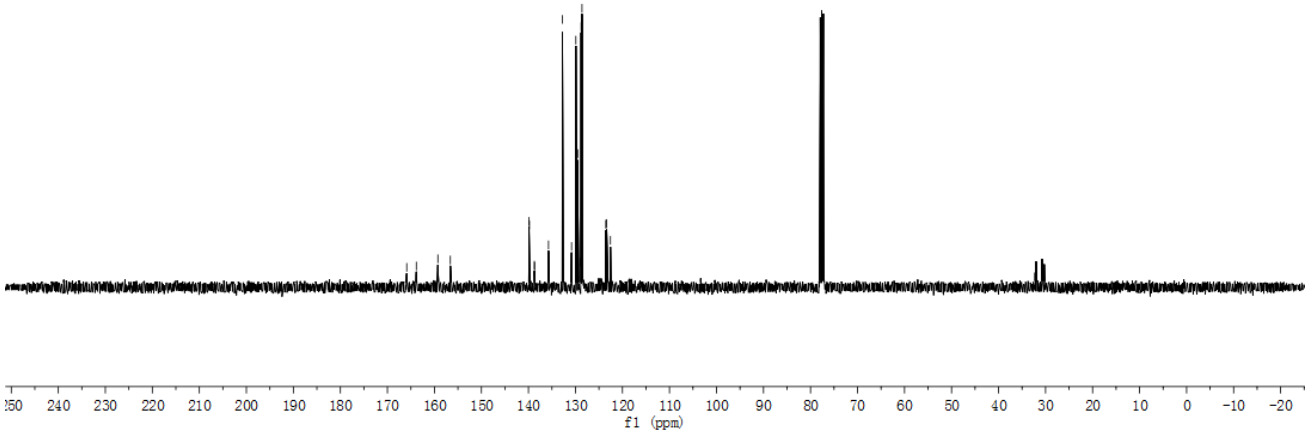
2-(4-Bromophenyl)-4-fluoro-7-phenylisoindoline-1,3-dione (7)

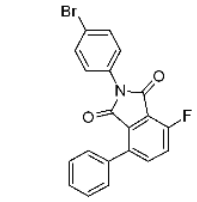




Chemical Formula: $C_{20}H_{11}BrFNO_2$
Exact Mass: 394.9957

165.888
163.841
159.262
156.610
139.867
139.793
138.741
138.701
135.731
132.768
130.831
129.911
129.524
128.996
128.793
128.608
123.548
123.352
122.555





Chemical Formula: $C_{20}H_{11}BrFNO_2$
Exact Mass: 394.9957

114.786
114.798
114.808
114.820

114.786
114.798
114.808
114.820