Supporting Information for

Access to Difluoromethylated Arenes by Pd-Catalyzed Reaction of Arylboronic Acids with Bromodifluoroacetate

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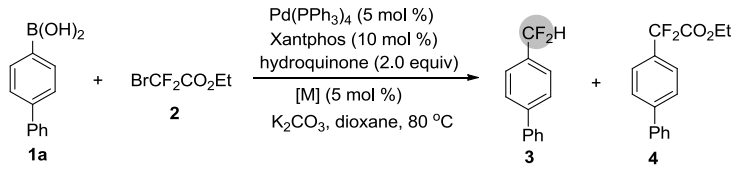
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 and AM500 spectrometer. ^{19}F NMR was recorded on a Bruker AM400 spectrometer ($CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are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

Materials: All reagents were used as received from commercial sources, unless specified otherwise. Anhydrous K_2CO_3 was purchased from Alfa. DMF, DMSO, and DCE were distilled under reduced pressure from CaH_2. 1,4-Dioxane and xylene were distilled from sodium and benzophenone immediately before use.

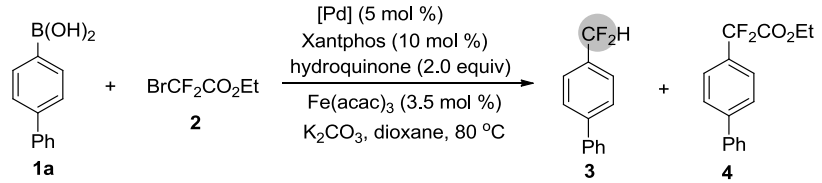
Table S1. Pd-Catalyzed Reaction of Arylboronic Acid 1a with Bromodifluoroacetate 2 in the Presence of Different Oxidants.[a]



entry	oxidant	**3**/**4** yield (%)[b]
1	$Cu(OTf)_2$	Trace/79
2	$Cu(acac)_2$	17/43
3	$Cu(OAc)_2$	6/61
4	$Co(acac)_3$	32/12
5	$Fe(acac)_3$	39/43
6 [c]	**$Fe(acac)_3$**	**48/46**

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), dioxane (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. [c]$Fe(acac)_3$ (3.5 mol %).

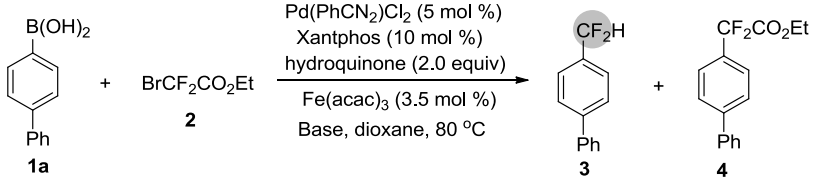
Table S2. Screening of Palladium Sources.[a]



entry	[Pd](mol %)	ligand (y)	**3**/**4** yield (%)[b]
1	$Pd(PPh_3)_4$ (5)	10	48/46
2	$Pd_2(dba)_3$ (2.5)	10	20/ trace
3	$Pd(OAc)_2$ (5)	10	38/trace
4	$PdCl_2$ (5)	10	30/4
5	**$PdCl_2(PPh_3)_2$ (5)**	**10**	**58/13**
6	$PdCl_2$(dppf) (5)	10	18/12
7	$PdCl_2(MeCN)_2$ (5)	10	55/9
8	$[PdCl(C_3H_5)]_2$ (2.5)	10	35/5
9	**$PdCl_2(PhCN)_2$ (5)**	**10**	**62/3**
10	$Pd(acac)_2$ (5)	10	36/1

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), dioxane (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

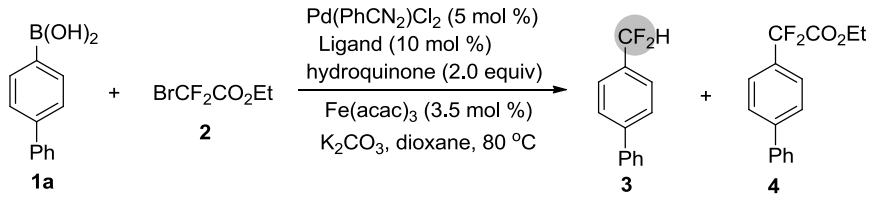
Table S3. Screening of Bases.[a]

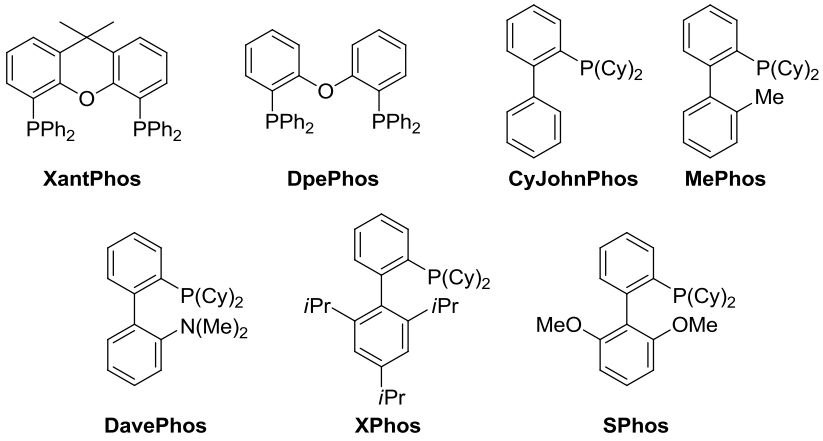


entry	base (equiv)	**3a**/**4a** yield (%)[b]
1	K_2CO_3 (4.0)	62/3
2	K_3PO_4 (4.0)	16/11
3	KOAc (4.0)	Trace/4
4	C_SOAc (4.0)	Trace/1
5	NaOAc (4.0)	nd/2
6	Na_2CO_3 (4.0)	nd/17
7	K_2CO_3 (3.5)	50/6
8	K_2CO_3 (3.0)	49/7
9	K_2CO_3 (2.5)	46/10
12	K_2CO_3 (2.0)	10/23
13	K_2CO_3 (1.5)	Trace/3

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), dioxane (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

Table S4. Screening of Ligands.[a]

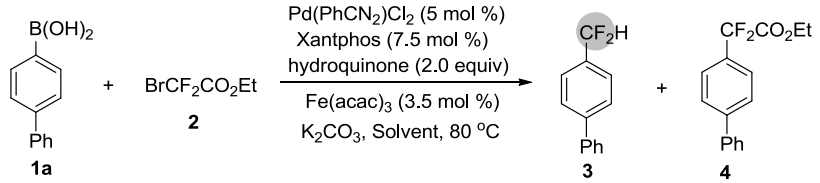




entry	ligand	**3a**/**4a** yield (%)[b]
1	Xantphos	62/3
2	DpePhos	32/nd
3	dppe	nd/nd
4	dppp	nd/nd
5	dppb	nd/nd
6	dppf	nd/nd
7	BINAP	nd/3
8	CyJohnPhos	trace/trace
9	MePhos	nd/nd
10	DavePhos	nd/nd
11	XPhos	nd/nd
12	SPhos	nd/nd
13[c]	Xantphos	45/2
14[d]	**Xantphos**	**63/2**

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), dioxane (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard. [c]Xantphos (5 mol %). [d]Xantphos (7.5 mol %).

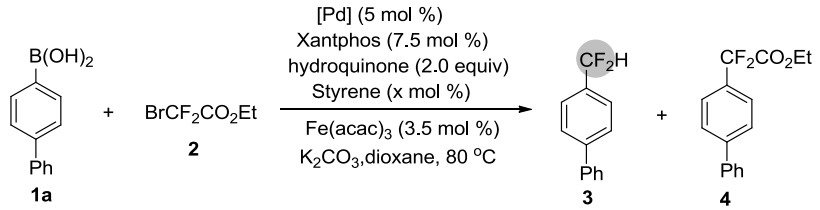
Table S5. Screening of Solvents.[a]



entry	solvent	**3a**/**4a** yield (%)[b]
1	**dioxane**	**63/1**
2	DMSO	nd/nd
3	Dimethoxyethane	3/nd
4	DMF	nd/nd
5	Xylene	nd/40
6	DCE	trace/nd
7	Diglyme	2/nd

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), solvent (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

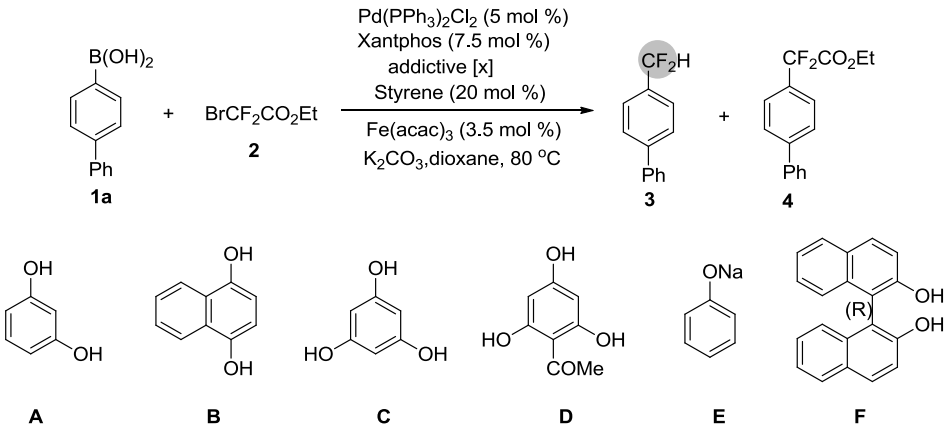
Table S6. Screening of Different Amount of Styrene.[a]



entry	styrene (x)	[Pd]	**3a**/**4a** yield (%)[b]
1	10	$Pd(PhCN)_2Cl_2$	49/3
2	20	$Pd(PhCN)_2Cl_2$	61/trace
3	40	$Pd(PhCN)_2Cl_2$	61/1
4	10	$Pd(PPh_3)_4$	60/30
5	20	$Pd(PPh_3)_4$	79/15
6	40	$Pd(PPh_3)_4$	5/3
7	10	$Pd(MeCN)_2Cl_2$	52/2
8	20	$Pd(MeCN)_2Cl_2$	60/2
9	40	$Pd(MeCN)_2Cl_2$	61/4
10	10	$Pd(PPh_3)_2Cl_2$	81/15
11	**20**	**$Pd(PPh_3)_2Cl_2$**	**82/12**
12	40	$Pd(PPh_3)_2Cl_2$	81/8
13[c]	**20**	**$Pd(PPh_3)_2Cl_2$**	**92(85)/7**

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), [Pd] (5 mol %), K_2CO_3 (4.0 equiv), dioxane (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard and number in parenthesis is isolated yield.. [c]2.5 mL of dioxane was used.

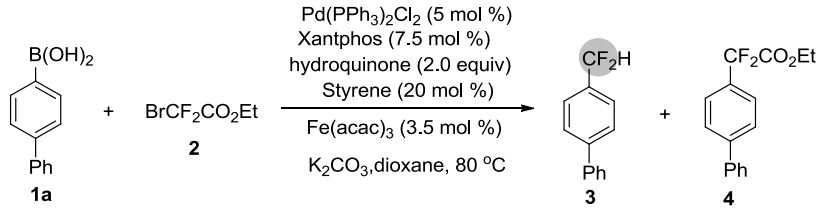
Table S7. Screening of Phenols.[a]



entry	additive	[x equiv]	**3a**/**4a** yield (%)[b]
1	**A**	(2.0 equiv)	nd/nd
2	**B**	(2.0 equiv)	18/trace
3	**C**	(2.0 equiv)	2/nd
4	**D**	(2.0 equiv)	3/trace
5	**E**	(2.0 equiv)	10/9
6	**F**	(2.0 equiv)	10/trace
7	**Hydroquinone**	**(2.0 equiv)**	**92/7**
8	Hydroquinone	(1.5 equiv)	54/16
9	hydroquinone	(1.0 equiv)	42/20
10	hydroquinone	(0.5 equiv)	25/36

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), dioxane (2.5 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

Table S8. Control Experiments of Pd-Catalyzed Reaction of Arylboronic Acid 1a with Bromodifluoroacetate.[a]

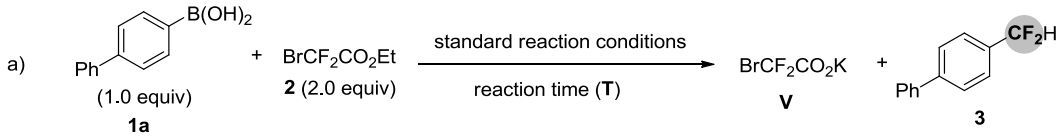


entry	[Fe]	[Pd]	ligand	additive	alkene	**3**/**4** yield (%)[b]
1	none	none	none	hydroquinone	styrene	nd/nd
2	$Fe(acac)_3$	none	none	hydroquinone	styrene	nd/nd
3	none	$Pd(PPh_3)_2Cl_2$	none	hydroquinone	styrene	nd/7
4	none	none	Xantphos	hydroquinone	styrene	nd/nd
5	$Fe(acac)_3$	none	Xantphos	hydroquinone	styrene	nd/nd
6	$Fe(acac)_3$	$Pd(PPh_3)_2Cl_2$	none	hydroquinone	styrene	nd/6%
7	none	$Pd(PPh_3)_2Cl_2$	Xantphos	hydroquinone	styrene	45/trace
8	none	$Pd(PPh_3)_2Cl_2$	Xantphos	hydroquinone	none	65/trace
9	$Fe(acac)_3$	$Pd(PPh_3)_2Cl_2$	Xantphos	hydroquinone	none	45/39
10	$Fe(acac)_3$	$Pd(PPh_3)_2Cl_2$	Xantphos	none	styrene	nd/33%
11	**$Fe(acac)_3$**	**$Pd(PPh_3)_2Cl_2$**	**Xantphos**	**hydroquinone**	**styrene**	**92/7**

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2** (2.0 equiv), K_2CO_3 (4.0 equiv), dioxane (2.5 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

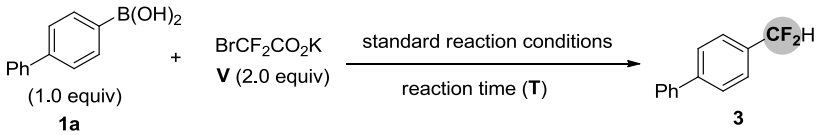
Mechanistic Studies

Scheme S1. Kinetic Studies of the Reaction of 1a with 2 or V.

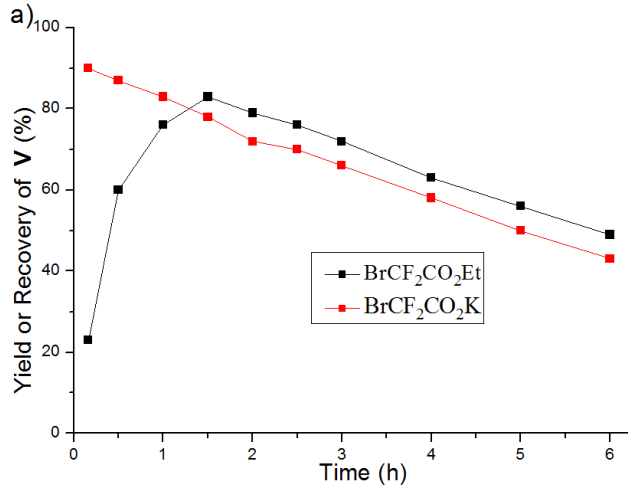


Entry	Time	**2** (Conversion)	**V** (Yield)	**3** (Yield)
1	10 min	29%	23%	0%
2	30 min	64%	60%	1%
3	1.0 h	80%	76%	3%
4	1.5 h	99%	83%	13%
5	2.0 h	99%	79%	20%
6	2.5 h	99%	76%	25%
7	3.0 h	99%	72%	26%
8	4.0 h	100%	63%	32%
9	5.0 h	100%	56%	39%
10	6.0 h	100%	49%	49%

b)



Entry	Time	**V**(Recovery)	**3** (Yield)
1	10 min	90%	0%
2	30 min	87%	3%
3	1.0 h	83%	7%
4	1.5 h	78%	10%
5	2.0 h	72%	15%
6	2.5 h	70%	17%
7	3.0 h	66%	22%
8	4.0 h	58%	27%
9	5.0 h	50%	33%
10	6.0 h	43%	44%



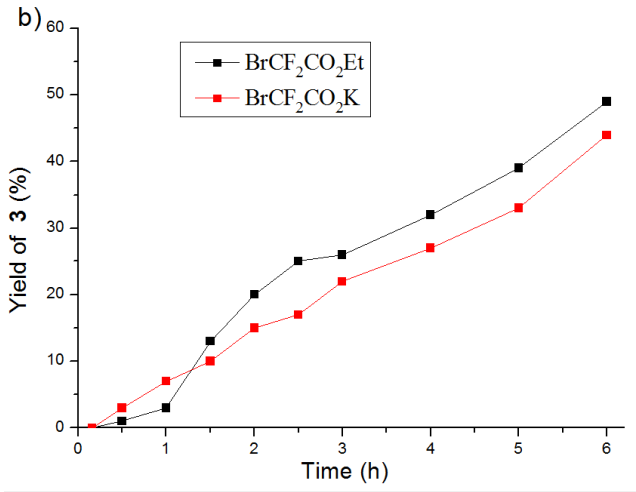
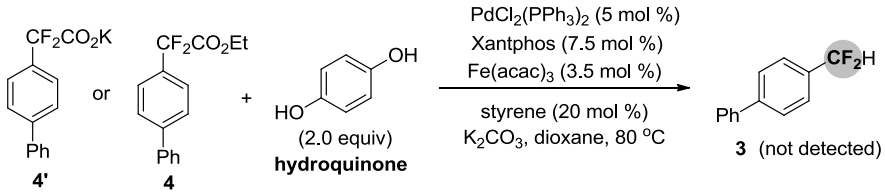


Figure S1. a) Yield (black line) or Recovery (red line) of **V** and **b)** Yield of **3** with $BrCF_2CO_2Et$ (black line) or $BrCF_2CO_2K$ (red line) as a Starting Material.

Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), styrene (20 mol %), ethyl bromodifluoroacetate **2** (2.0 equiv) or $BrCF_2CO_2K$ (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 °C (oil bath). The reaction was monitored by ^{19}F NMR using fluorobenzene as an internal standard.

Note: Attempt to isolation of pure **V** failed. The structure of **V** was characterized by ^{19}F NMR, ^{13}C NMR, IR, and MS from a mixture of **V** and hydroquinone. All of these data are consistence with the data of $BrCF_2CO_2K$. It also should be mentioned that the ^{1}H NMR spectroscopy of the mixture of **V** and hydroquinone only showed the spectrum of hydroquinone. Therefore, compound **V** was assigned to be $BrCF_2CO_2K$. Compound **V**: ^{19}F NMR (376 MHz, DMSO) δ -52.5 (s, 2 F); ^{13}C NMR (100 MHz, DMSO) δ 160.9 (t, J = 22.9 Hz), 117.2 (t, J = 325.2 Hz). IR (thin film) ν_{max} 1687, 1385, 1143 cm^{-1}; MS (ESI): *m/z* (%), 172.8 (M^+-K^+), 174.9 (M^+-K^+).

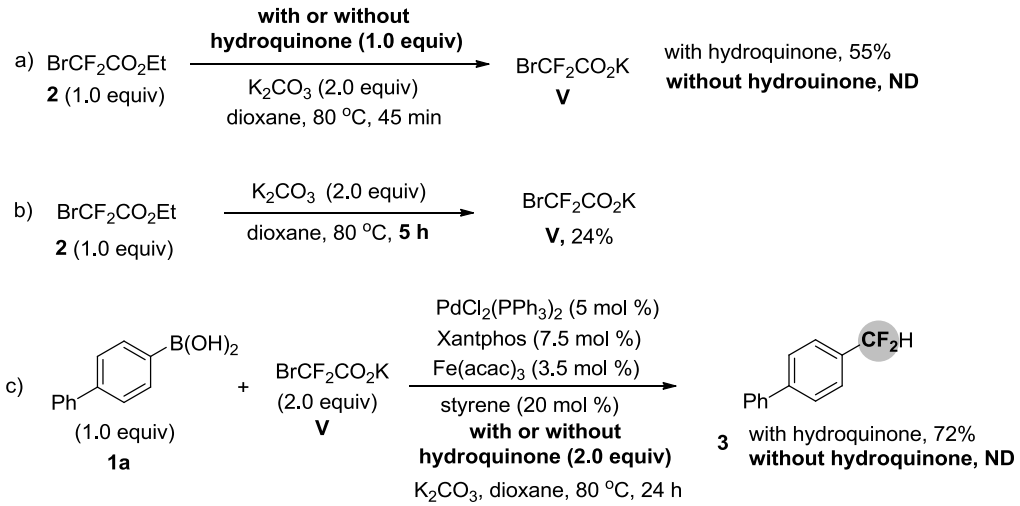
Scheme S2. Reaction of Compound 4 or 4' with Hydroquinone under Standard Reaction Conditions



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), compound **4** or **4'** (0.3 mmol, 1.0 equiv), styrene (20 mol %) and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 °C (oil bath). After stirring for 24 h, the reaction was cooled to room temperature. ^{19}F NMR spectroscopy showed no compound **3** was formed.

The Role of Hydroquinone for the Reaction

Scheme S3. The Roles of Hydroquinone for the Reaction

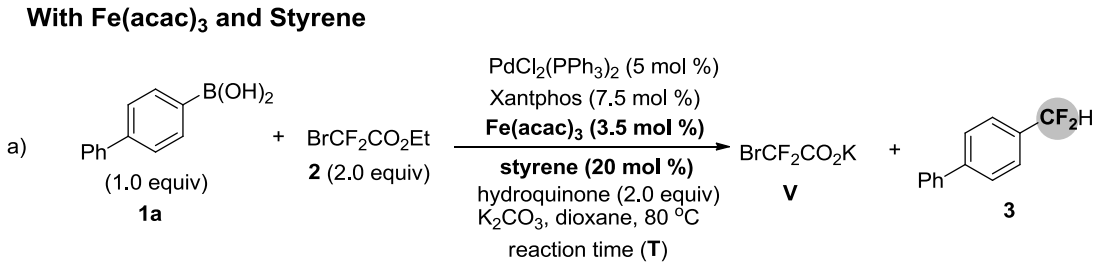


Procedure for the reaction of bromodifluoroacetate 2 with K_2CO_3 in the presence of hydroquinone: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 2.0 equiv), hydroquinone (1.0 equiv), ethyl bromodifluoroacetate **2** (1.0 equiv, 0.6 mmol) and fresh distilled dioxane (2.5 mL) under N_2. The reaction mixture was heated to 80 °C (oil bath). The reaction was monitored by ^{19}F NMR using fluorobenzene as an internal standard.

The Role of $Fe(acac)_3$ for the Reaction

The comparsions of reaction of **1a** with **2** or **V** in the presence of hydroquinone with or without $Fe(acac)_3$ and styrene (Scheme S5-S6 and Figure S2-S3) revealed that the iron species could facilitate the transformation of **V** into final product **3**.

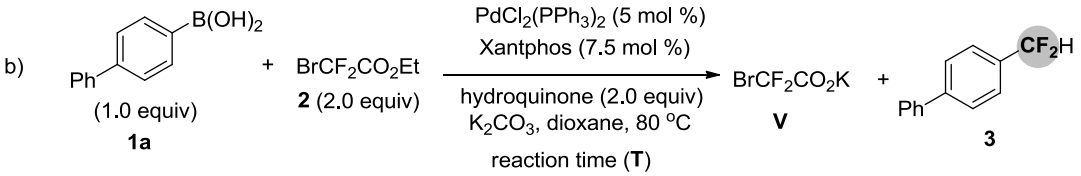
Scheme S4. Cross-Coupling Reaction between Arylboronic Acid 1a and Bromodifluoroacetate 2 with or without $Fe(acac)_3$ and Styrene.



Entry	Time	**2** (Conversion)	**V** (Yield)	**3** (Yield)
1	10 min	29%	23%	0%
2	30 min	64%	60%	1%
3	1.0 h	80%	76%	3%
4	1.5 h	99%	83%	13%
5	2.0 h	99%	79%	20%
6	2.5 h	99%	76%	25%
7	3.0 h	99%	72%	26%
8	4.0 h	100%	63%	32%
9	5.0 h	100%	56%	39%
10	6.0 h	100%	49%	49%

Without $Fe(acac)_3$ and Styrene

b)



Entry	Time	**2** (Conversion)	**V** (Yield)	**3** (Yield)
1	10 min	40%	60%	0%
2	30 min	93%	91%	0%
3	1.0 h	98%	93%	2%
4	1.5 h	100%	92%	10%
5	2.0 h	100%	70%	14%
6	2.5 h	100%	68%	18%
7	3.0 h	100%	67%	20%
8	4.0 h	100%	60%	25%
9	5.0 h	100%	58%	32%
10	6.0 h	100%	55%	34%

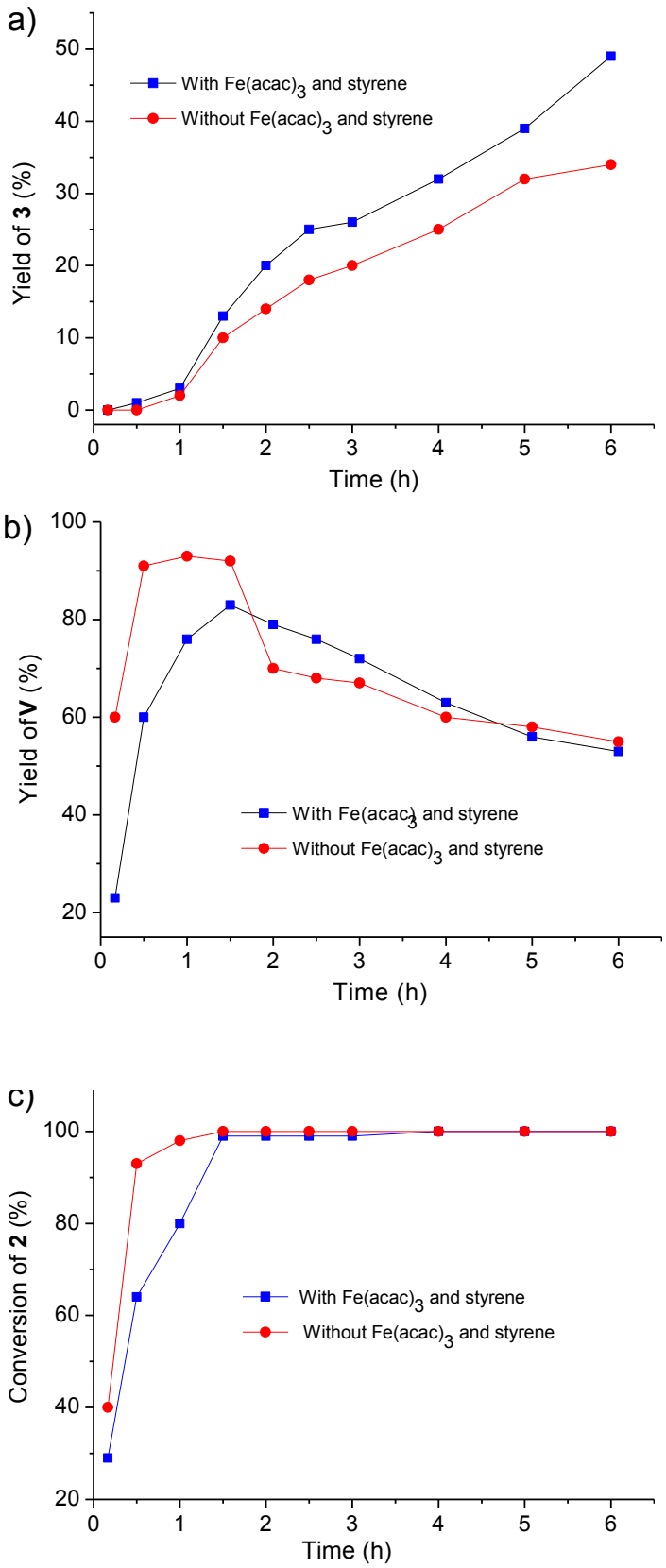
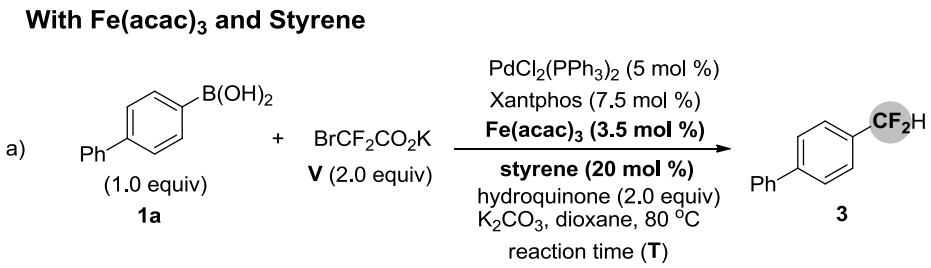


Figure S2. a) Yield of **3**; b) Yield of **V**; c) Conversion of **2**

Procedure (with $Fe(acac)_3$ and styrene): To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), styrene (20 mol %), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 ^oC (oil bath). The reaction was monitored by ^{19}F NMR using fluorobenzene as an internal standard.

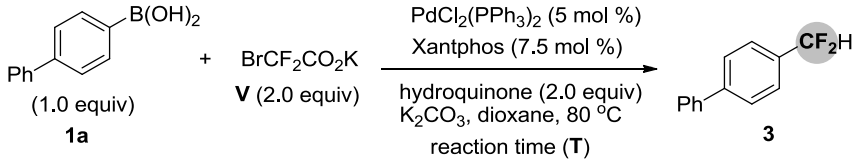
Scheme S5. Cross-Coupling Reaction between Arylboronic Acid 1a and $BrCF_2CO_2K$ V with or without $Fe(acac)_3$ and Styrene.



Entry	Time	**V**(Recovery)	**3** (Yield)
1	10 min	90%	0%
2	30 min	87%	3%
3	1.0 h	83%	7%
4	1.5 h	78%	10%
5	2.0 h	72%	15%
6	2.5 h	70%	17%
7	3.0 h	66%	22%
8	4.0 h	58%	27%
9	5.0 h	50%	33%
10	6.0 h	43%	44%

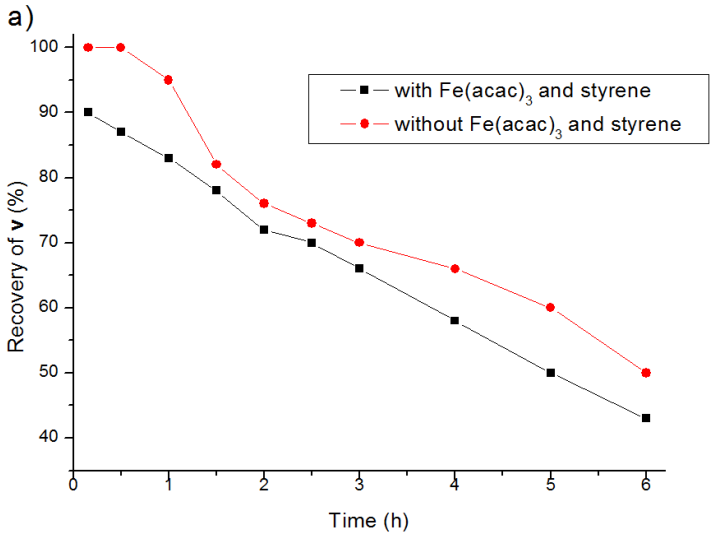
Without $Fe(acac)_3$ and Styrene

b)



Entry	Time	**V**(Recovery)	**3** (Yield)
1	10 min	100%	0%
2	30 min	100%	0%
3	1.0 h	95%	1%
4	1.5 h	82%	2%
5	2.0 h	76%	7%
6	2.5 h	73%	8%
7	3.0 h	70%	10%
8	4.0 h	66%	15%
9	5.0 h	60%	19%
10	6.0 h	50%	27%

a)



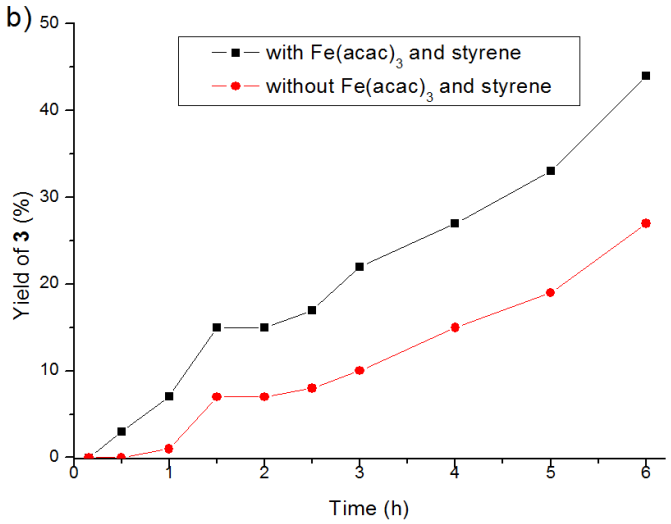
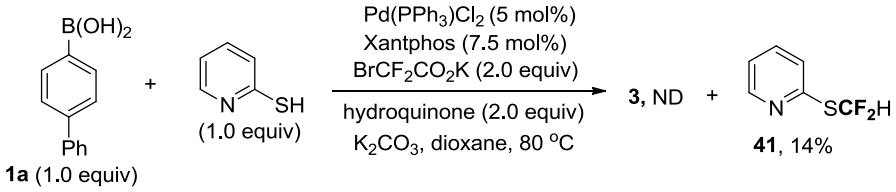


Figure S3. a) Recovery of **V**; **b)** Yield of **3**.

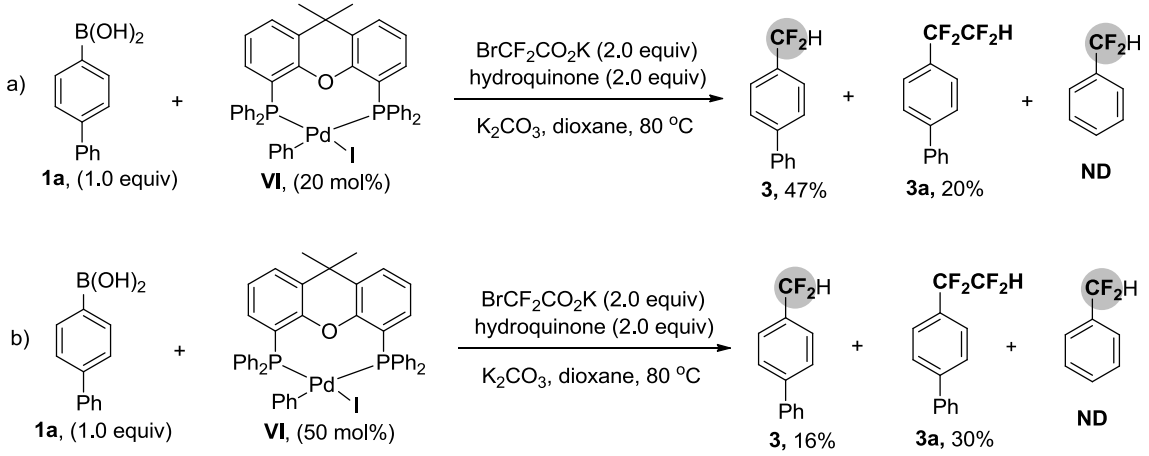
Identification of Difluorocarbene

Scheme S6. Reaction of 1a with V under Standard Reaction Conditions in the Presence of Pyridine-2-thiol



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), hydroquinone (2.0 equiv), 2-mercaptopyridine, $BrCF_2CO_2K$ **V** (0.6 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), and fresh distilled dioxane (2.5 mL) under N_2. The reaction mixture was heated to 80 ^oC (oil bath) for 24 h and provided **41** in 14% yield (determined by ^{19}F NMR using fluorobenzene as an internal standard). Compound **41:** This compound is known.[1] ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.3 (d, J = 56.1 Hz, 2 F). MS (EI): *m/z* (%) 161 (M^+).

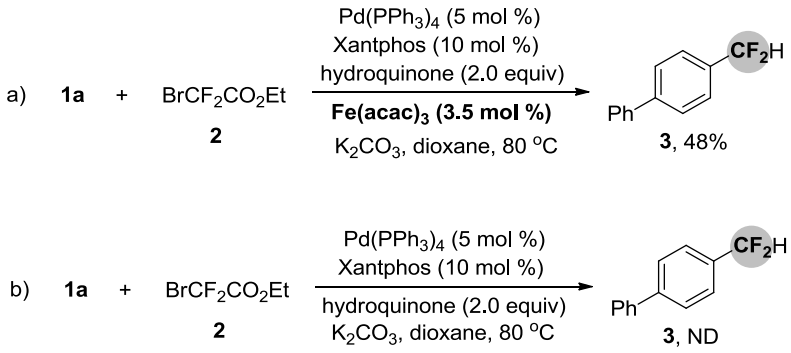
Scheme S7. Reaction of 1a with V in the Presence of Palladium Complex VI.



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), hydroquinone (2.0 equiv), $BrCF_2CO_2K$ **V** (0.6 mmol), $[PhPd(Xantphos)I]^2$ (20 mol% or 50 mol%), aryl boronic acid **1a** (0.3 mmol), and fresh distilled dioxane (2.5 mL) under N_2. The reaction mixture was heated to 80 °C (oil bath) for 24 h and provided compound **3** and 4-(1,1,2,2-tetrafluoroethyl)-1,1'-biphenyl **3a** (the yields were determined by ^{19}F NMR using fluorobenzene as an internal standard).

4-(1,1,2,2-tetrafluoroethyl)-1,1'-biphenyl (3a). This compound is known.[3] ^1H NMR (400 MHz, $CDCl_3$) δ7.12-7.69 (m, 2 H), 7.64-7.59 (m, 4 H), 7.49-7.45 (m, 2 H), 7.43-7.38 (m, 1 H), 5.96 (tt, *J* = 54.4 Hz, *J* = 2.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4 (m，2 F), -134.1 (dt, *J* = 54.4 Hz, *J* = 3.8 Hz, 2 F). MS (EI): *m/z* (%) 254 (M^+), 203 (100). HRMS calcd. for $C_{14}H_{10}F_4$ (M^+): 254.0719; Found: 254.0718.

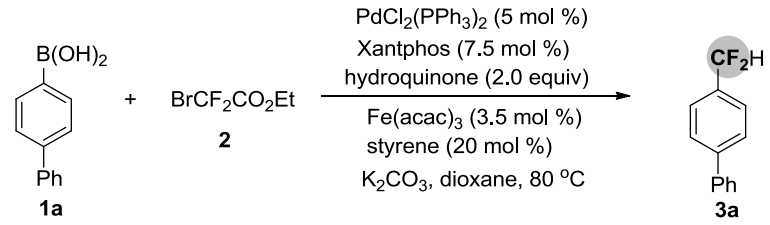
Scheme S8. Cross-Coupling Reaction between 1a and 2 in the Presence of $Pd(PPh_3)_4$ with or without $Fe(acac)_3$.



Procedure (with $Fe(acac)_3$): To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv) and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $Pd(PPh_3)_4$ (5 mol %), Xantphos (10 mol %), aryl boronic acid **1a** (0.3 mmol), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.0 mL). The reaction mixture was heated to 80 ^oC (oil bath). The reaction was monitored by ^{19}F NMR using fluorobenzene as an internal standard.

X-Ray Photoelectron Spectroscopy (XPS) Analysis of the Reaction

Scheme S9a. X-Ray Photoelectron Spectroscopy (XPS) Analysis of Reaction of 1a with 2 under Standard Reaction Conditions



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), styrene (20 mol %), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 ^oC (oil bath). After stirring for 24 h, the reaction was cooled to room temperature and concentrated under N_2. The resulting mixture was analyzed by X-ray photoelectron spectroscopy (XPS) (**Note:** all the experiments were carried out under N_2). The XPS showed that peak corresponding to Pd^{II} $3d_{5/2}$ was observed with the binding energy at 336.65 ev, which was negatively shifted by 0.85 ev compared with free $Pd(PPh_3)_2Cl_2$ (Pd^{II} $3d_{5/2}$ at 337.5 ev).[4]

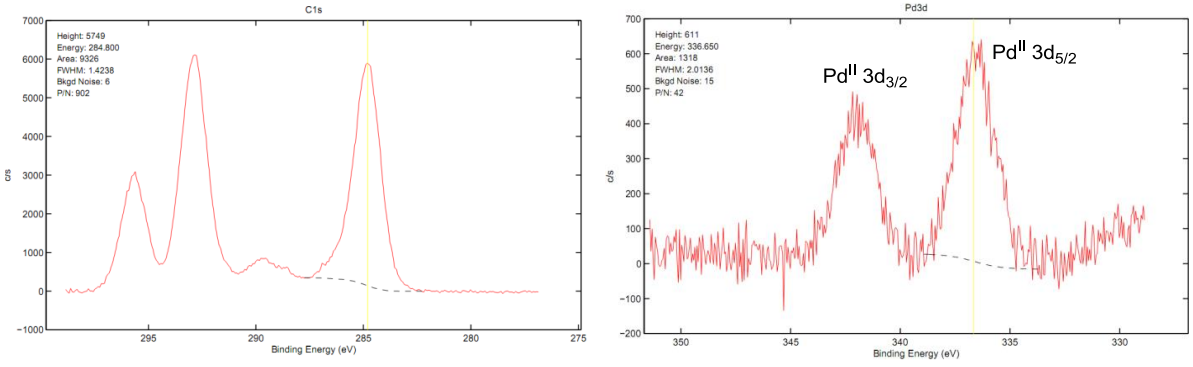
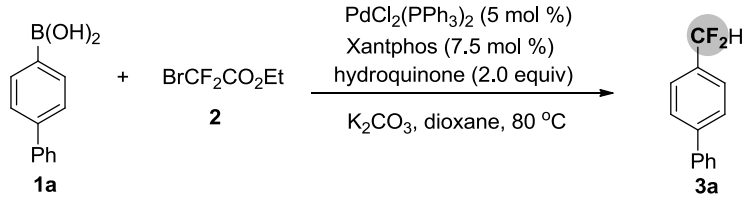


Figure S4a. XPS Analysis of Reaction of **1a** with **2** under Standard Reaction Conditions

Scheme S9b. X-Ray Photoelectron Spectroscopy (XPS) Analysis of Reaction of 1a with 2 in the Absence of $Fe(acac)_3$ and Styrene.



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 °C (oil bath). After stirring for 24 h, the reaction was cooled to room temperature and concentrated under N_2. The resulting mixture was analyzed by X-ray photoelectron spectroscopy (XPS) (**Note:** all the experiments were carried out under N_2). The XPS showed that peak corresponding to Pd^{II} $3d_{5/2}$ was observed with the binding energy at 336.85 ev, which was negatively shifted by 0.65 ev compared with free $Pd(PPh_3)_2Cl_2$ (Pd^{II} $3d_{5/2}$ at 337.5ev).[4]

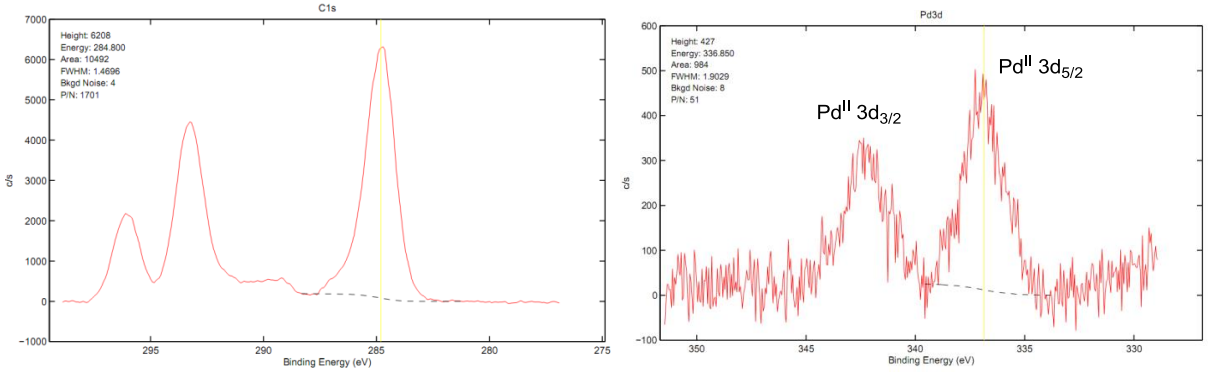
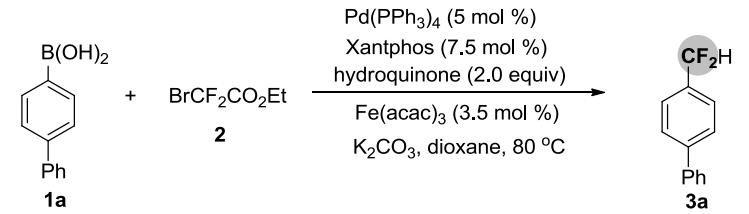


Figure S4b. XPS Analysis of Reaction of **1a** with **2** in the Absence of $Fe(acac)_3$ and Styrene

Scheme S10c. X-Ray Photoelectron Spectroscopy (XPS) Analysis of Reaction of 1a with 2 in the Presence of $Pd(PPh_3)_4$ and $Fe(acac)_3$.



Procedure: To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $Pd(PPh_3)_4$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1a** (0.3 mmol), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 °C (oil bath). After stirring for 24 h, the reaction was cooled to room temperature. After stirring for 24 h, the reaction was cooled to

room temperature and concentrated under N_2. The resulting mixture was analyzed by X-ray photoelectron spectroscopy (XPS) (**Note:** all the experiments were carried out under N_2). The XPS showed that peak corresponding to Pd^{II} $3d_{5/2}$ was observed with the binding energy at 336.80 ev, which was negatively shifted by 0.70 ev compared with free $Pd(PPh_3)_2Cl_2$ (Pd^{II} $3d_{5/2}$ at 337.5 ev).[4]

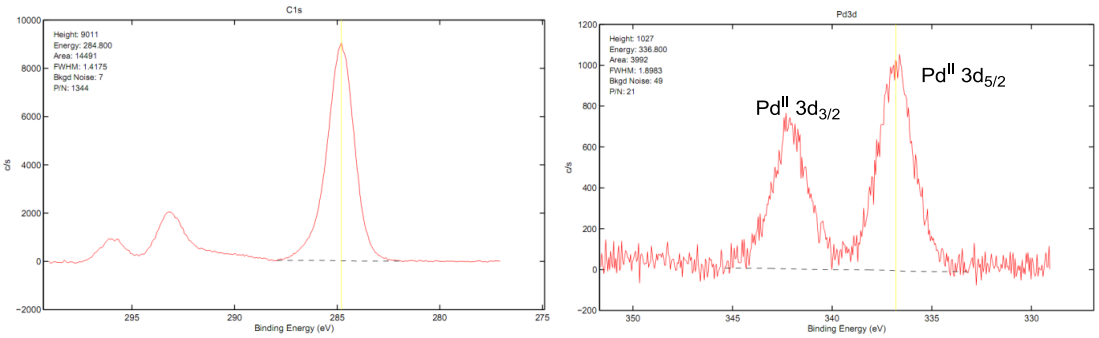
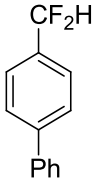


Figure S4c. XPS Analysis of Reaction of **1a** with **2** in the Presence of $Pd(PPh_3)_4$ and $Fe(acac)_3$

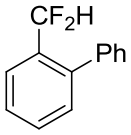
General Procedure for Pd-Catalyzed Difluoromethylation of Arylboronic Acids with Bromodifluoroacetate

To a 25 mL of Schlenk tube were added anhydrous K_2CO_3 (powder, 4.0 equiv), and hydroquinone (2.0 equiv) in glove box, followed by $Fe(acac)_3$ (3.5 mol %), $PdCl_2(PPh_3)_2$ (5 mol %), Xantphos (7.5 mol %), aryl boronic acid **1** (0.3 mmol), styrene (20 mol %), ethyl bromodifluoroacetate **2** (2.0 equiv), and fresh distilled dioxane (2.5 mL). The reaction mixture was heated to 80 ^oC (oil bath). After stirring for 24 h, the reaction was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography to give product.

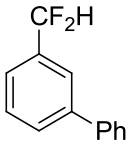


4-(Difluoromethyl)-1,1'-biphenyl (3). The product (52 mg, 85% yield) as a white solid (m.p. 78-82 ^oC) was purified with silica gel chromatography (Petroleum ether). This compound is known.[5] ^1H NMR (300 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2 H), 7.62-7.58 (m, 4 H), 7.49-7.45 (m, 2 H), 7.41-7.37 (m, 1 H), 6.71 (t, J = 56.4 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.7 (d, J = 56.4 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.7 (t, J = 2.0 Hz), 140.2, 133.2 (t, J = 22.4 Hz), 128.9, 127.9, 127.4, 127.2, 126.0 (t, J = 6.0 Hz), 114.7 (t, J = 238.3 Hz). MS (EI): *m/z* (%) 204 (M^+), 204 (100). HRMS calcd. for

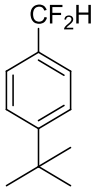
$C_{13}H_{10}F_2$ (M^+): 204.0751; Found: 204.0753.



2-(Difluoromethyl)-1,1'-biphenyl (5). The product (39 mg, 64% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 1 H), 7.54-7.48 (m, 2 H), 7.47-7.41 (m, 3 H), 7.36-7.34 (m, 3 H), 6.54 (t, *J* = 54.8 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.4 (d, *J* = 54.8 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4 (t, *J* = 6.6 Hz), 138.6, 131.7 (t, *J* = 22.2 Hz), 130.5 (t, *J* = 1.8 Hz), 130.2, 129.4, 128.4, 127.9, 127.8, 125.6 (t, *J* = 5.2 Hz), 113.1 (t, *J* = 234.6 Hz). MS (EI): *m/z* (%) 204 (M^+), 183, 154, 58 (100). HRMS calcd. for $C_{13}H_{10}F_2$ (M^+): 204.0751; Found: 204.0753.

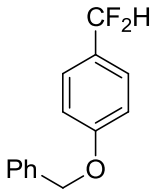


3-(Difluoromethyl)-1,1'-biphenyl (6). The product (54 mg, 89% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1 H), 7.73-7.71 (m, 1 H), 7.63-7.62 (m, 1 H), 7.61-7.60 (m, 1 H), 7.55 (t, *J* = 7.2 Hz, 1 H), 7.52-7.46 (m, 3 H), 7.40 (tt, *J* = 7.2 Hz, 1 H), *J* = 1.2 Hz, 1 H), 6.72 (t, *J* = 56.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.6 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.2, 134.9 (t, *J* = 22.0 Hz), 129.5 (t, *J* = 1.9 Hz), 129.2, 128.9, 127.8, 127.2, 124.4 (t, *J* = 5.9 Hz), 124.3 (t, *J* = 5.9 Hz), 114.8 (t, *J* = 237.6 Hz). MS (EI): *m/z* (%) 204 (M^+), 204 (100). HRMS calcd. for $C_{13}H_{10}F_2$ (M^+): 204.0751; Found: 204.0754.

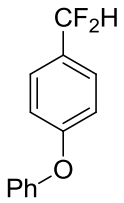


1-(Tert-butyl)-4-(difluoromethyl)benzene (7). The product (33 mg, 60% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 8.8 Hz, 2 H), 6.64 (t, *J* = 56.8 Hz, 1 H), 1.35 (s,

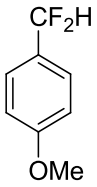
9 H). ^{19}F NMR (375 MHz, $CDCl_3$) δ -109.9 (d, *J* = 56.8 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 153.9 (t, *J* = 2.0 Hz), 131.6 (t, *J* = 22.4 Hz), 125.6, 125.3 (t, *J* = 5.8 Hz), 114.9 (t, *J* = 237.9 Hz), 34.8, 31.2. MS (EI): *m/z* (%) 184 (M^+), 169 (100). HRMS calcd. for $C_{11}H_{14}F_2$ (M^+): 184.1064; Found:184.1063.



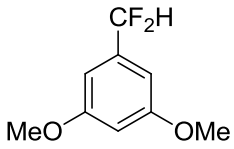
1-(Benzyloxy)-4-(difluoromethyl)benzene (8). The product (47 mg, 67% yield) as a wihte solid (m.p. 78-80 ºC) was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1). This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 4 H), 7.42-7.38 (m, 2 H), 7.36-7.32 (m, 1 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.61 (t, *J* = 56.8 Hz, 1 H), 5.11 (s, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 (d, *J* = 56.8 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (t, *J* = 1.4 Hz), 136.5, 128.7, 128.2, 127.5, 127.2 (t, *J* = 6.0 Hz), 127.0, 114.9, 114.8 (t, *J* = 236.0 Hz), 70.1. MS (EI): *m/z* (%) 234 (M^+), 91 (100). HRMS calcd. for $C_{14}H_{12}OF_2$ (M^+): 234.0856; Found: 234.0859. IR (thin film) ν_{max} 3032, 2940, 1615, 1598 cm^{-1}.



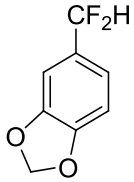
1-(Difluoromethyl)-4-phenoxybenzene (9). The product (41 mg, 62% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2 H), 7.39-7.35 (m, 2 H), 7.17 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1 H), 7.06 (m, 2 H), 7.03 (s, 2 H), 6.63 (t, *J* = 56.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (t, *J* = 2.0 Hz), 156.2, 129.9, 128.9 (t, *J* = 22.6 Hz), 127.3 (t, *J* = 6.0 Hz), 124.1, 119.6, 118.3, 114.6 (t, *J* = 236.8 Hz). MS (EI): *m/z* (%) 220 (M^+), 220 (100). HRMS calcd. for $C_{13}H_{10}OF_2$ (M^+): 220.0700; Found: 220.0698. IR (thin film) ν_{max} 3041, 2963, 1765, 1590 cm^{-1}.



1-(Difluoromethyl)-4-methoxybenzene (10). The product (33 mg, 70% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1). This compound is known.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 6.60 (t, *J* = 56.8 Hz, 1 H), 3.84 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 161.4, 127.1 (t, *J* = 6.0 Hz), 126.8 (t, *J* = 22.8 Hz), 114.9 (t, *J* = 237.3 Hz), 113.9, 55.3. MS (EI): *m/z* (%) 158 (M^+), 158 (100). HRMS calcd. for $C_8H_8OF_2$ (M^+): 158.0543; Found: 158.0541.

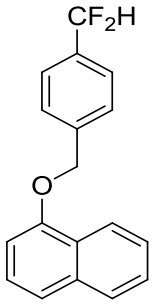


1-(Difluoromethyl)-3,5-dimethoxybenzene (11). The product (41 mg, 73% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (m, 2 H), 6.54 (m, 1 H), 6.56 (t, *J* = 56.4 Hz, 1 H), 3.82 (s, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 136.4 (t, *J* = 22.0 Hz), 114.5 (t, *J* = 238.1 Hz), 103.4 (t, *J* = 6.2 Hz), 102.7 (t, *J* = 1.4 Hz), 55.5. MS (EI): *m/z* (%) 188 (M^+), 188 (100). HRMS calcd. for $C_9H_{10}O_2F_2$ (M^+): 188.0649; Found: 188.0651.

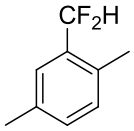


5-(Difluoromethyl)benzo[*d*][1,3]dioxole (12). The product (34 mg, 65% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1). This compound is known.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99-6.96 (m, 2 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 6.55 (t, *J* = 56.4 Hz, 1 H), 6.02 (s, 2 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.3 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6 (t, *J* = 1.4 Hz), 148.1, 128.3 (t, *J* = 22.6 Hz), 120.1 (t, *J* = 7.2 Hz), 114.6 (t, *J* = 236.6 Hz), 108.2, 105.8 (t, *J* = 5.4 Hz), 101.6. MS (EI): *m/z* (%) 172 (M^+), 171 (100). HRMS calcd. for $C_8H_6O_2F_2$ (M^+):

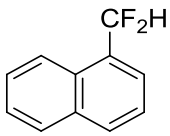
172.0336; Found: 172.0337.



1-((4-(Difluoromethyl)benzyl)oxy)naphthalene (13). The product (55 mg, 65% yield) as a solid (m.p. 76-80 ^{o}C) was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1 H), 7.84-7.82 (m, 1 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.54-7.50 (m, 2 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.37 (t, *J* = 8.4 Hz, 1 H), 6.87 (d, *J* = 7.6 Hz, 1 H), 6.69 (t, *J* = 56.4 Hz, 1 H), 5.30 (s, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.7 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 140.0 (t, *J* = 2.0 Hz), 134.6, 133.9 (t, *J* = 22.3 Hz), 127.6, 127.4, 126.6, 125.9 (t, *J* = 5.9 Hz), 125.8 (t, *J* = 7.9 Hz), 125.4, 122.1, 120.8, 114.7 (t, *J* = 237.1 Hz), 105.2, 69.4. MS (EI): *m/z* (%) 284 (M^+), 141 (100). HRMS calcd. for $C_{18}H_{14}OF_2$ (M^+): 284.1013; Found: 284.1010

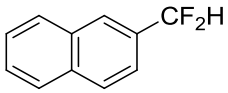


2-(Difluoromethyl)-1,4-dimethylbenzene (14). The product (19 mg, 41% yield; ^{19}F NMR yield 71%) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 7.11 (d, *J* = 7.8 Hz, 1 H), 6.73 (t, *J* = 55.5 Hz, 1 H), 2.39 (s, 3 H), 2.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.3 (d, *J* = 55.5 Hz, 2 F). MS (EI): *m/z* (%) 156 (M^+), 141, 105 (100). HRMS calcd. for $C_9H_{10}F_2$ (M^+): 156.0751; Found:156.0747.

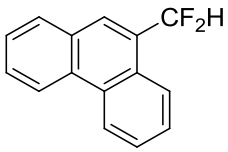


1-(Difluoromethyl)naphthalene (15). The product (45 mg, 84% yield) as a colorless oil was purified

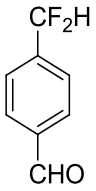
with silica gel chromatography (Petroleum ether). This compound is known.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 6.8 Hz, 1 H), 7.60-7.52 (m, 2 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.12 (t, *J* = 55.2 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (d, *J* = 55.2 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 131.5 (t, *J* = 1.6 Hz), 129.7 (t, *J* = 2.8 Hz), 129.5 (t, *J* = 20.6 Hz), 128.8, 127.2, 126.4, 124.8 (t, *J* = 8.6 Hz), 124.7, 123.6, 115.4 (t, *J* = 237.0 Hz). MS (EI): *m/z* (%) 178 (M^+), 178 (100). HRMS calcd. for $C_{11}H_8F_2$ (M^+): 178.0594; Found: 178.0590.



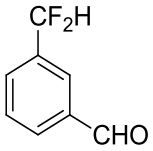
2-(Difluoromethyl)naphthalene (16). The product (41 mg, 77% yield) as a white solid was purified with silica gel chromatography (Petroleum ether). This compound is known.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1 H), , 7.95-7.89 (m, 3 H), 7.62 (d, *J* = 9.2 Hz, 1 H), 7.59-7.54 (m, 2 H), 6.82 (t, *J* = 56.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 134.3 (t, *J* = 1.3 Hz), 132.6, 131.6 (t, *J* = 22.2 Hz), 128.9, 128.5, 127.9, 127.4, 126.8, 125.9 (t, *J* = 7.7 Hz), 122.0 (t, *J* = 4.8 Hz), 115.1 (t, *J* = 238.4 Hz). MS (EI): *m/z* (%) 178 (M^+), 178 (100). HRMS calcd. for $C_{11}H_8F_2$ (M^+): 178.0594; Found: 178.0596.



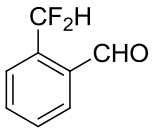
9-(Difluoromethyl)phenanthrene (17). The product (49 mg, 72% yield) as a white solid (m.p. 116-118 ^{o}C) was purified with silica gel chromatography (Petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ8.70 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1 H), 8.64 (d, *J* = 8.4 Hz, 1 H), 8.20-8.18 (m, 1 H), 7.93 (s, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.72-7.58 (m, 4 H), 7.12 (t, *J* = 55.2 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7 (d, *J* = 55.2 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.4, 130.9, 130.2, 129.5, 128.3, 128.0 (t, *J* = 20.5 Hz), 127.9 (t, *J* = 1.8 Hz), 127.2, 127.15, 127.13, 126.8 (t, *J* = 9.4 Hz), 124.5 (t, *J* = 1.6 Hz), 123.3, 122.7, 115.7 (t, *J* = 237.1 Hz). MS (EI): *m/z* (%) 228 (M^+), 228 (100). HRMS calcd. for $C_{15}H_{10}F_2$ (M^+): 228.0751; Found: 228.0753.



4-(Difluoromethyl)benzaldehyde (18). The product (27 mg, 57% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (s, 1 H), 7.98 (d, *J* = 7.8 Hz, 2 H), 7.69 (d, *J* = 7.8 Hz, 2 H), 6.72 (t, *J* = 56.1 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.9 (d, *J* = 56.1 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 139.8 (t, *J* = 22.3 Hz), 137.9, 129.9, 126.3 (t, *J* = 6.1 Hz), 113.8 (t, *J* = 238.6 Hz). MS (EI): *m/z* (%) 156 (M^+), 156 (100). HRMS calcd. for $C_8H_6OF_2$ (M^+): 156.0387; Found: 156.0384.

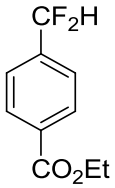


3-(Difluoromethyl)benzaldehyde (19). The product (26 mg, 55% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1 H), 8.02 (s, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 6.65 (t, *J* = 7.6 Hz, 1 H), 6.72 (t, *J* = 56.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 136.6, 135.5 (t, *J* = 23.1 Hz), 131.8 (t, *J* = 1.4 Hz), 131.3 (t, *J* = 5.7 Hz), 129.6, 126.8 (t, *J* = 6.3 Hz), 113.8 (t, *J* = 238.4 Hz). MS (EI): *m/z* (%) 156 (M^+), 155 (100). HRMS calcd. for $C_8H_6OF_2$ (M^+): 156.0387; Found: 156.0390.

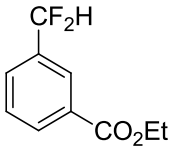


2-(Difluoromethyl)benzaldehyde (20). The product (25 mg, 52% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1 H), 7.95-7.93 (m, 1 H), 7.83-7.81 (m, 1 H), 7.75-7.70 (m, 2 H), 7.43 (t, *J* = 54.9 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.1 (d, *J* = 54.9 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 191.7, 134.6, 134.1, 133.4, 131.1 (t, *J* = 1.9 Hz), 128.9, 126.5 (t, *J* = 8.3 Hz), 111.9 (t,

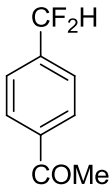
J = 238.2 Hz). IR (thin film) ν_{max} 2959, 2926, 1732, 1715 cm^{-1}. MS (EI): *m/z* (%) 156 (M^+), 155 (100). HRMS calcd. for $C_8H_6OF_2$ (M^+): 156.0387; Found: 156.0385.



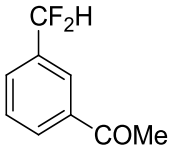
Ethyl 4-(difluoromethyl)benzoate (21). The product (48 mg, 80% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[6] ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 8.4 Hz, 2 H), 6.69 (t, J = 56.1 Hz, 1 H), 4.39 (q, J = 7.2 Hz, 2 H), 1.40 (t, J = 7.2 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2 (d, J = 56.1 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.3 (t, J = 22.3 Hz), 132.6, 129.9, 125.6 (t, J = 5.9 Hz), 114.0 (t, J = 238.4 Hz), 61.4, 14.3. IR (thin film) ν_{max} 2983, 2930, 1767, 1723 cm^{-1}. MS (EI): *m/z* (%) 200 (M^+), 199, 172, 155 (100). HRMS calcd. for $C_{10}H_{10}O_2F_2$ (M^+): 200.0649; Found: 200.0648.



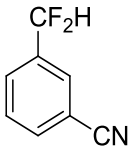
Ethyl 3-(difluoromethyl)benzoate (22). The product (45 mg, 75% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 2 H), 7.71 (d, J = 7.6 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 6.69 (t, J = 56.0 Hz, 1 H), 4.41 (q, J = 6.8 Hz, 2 H), 1.41 (t, J = 6.8 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.1 (d, J = 56.0 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 134.7 (t, J = 22.5 Hz), 131.7 (t, J = 1.3 Hz), 131.1, 129.7 (t, J = 5.6 Hz), 128.9, 126.9 (t, J = 6.1 Hz), 114.2 (t, J = 238.1 Hz), 61.4, 14.3. IR (thin film) ν_{max} 2983, 1766, 1615 cm^{-1}. MS (EI): *m/z* (%) 200 (M^+), 193, 172, 155 (100). HRMS calcd. for $C_{10}H_{10}O_2F_2$ (M^+): 200.0649; Found: 200.0652.



1-(4-(Difluoromethyl)phenyl)ethanone (23). The product (28 mg, 55% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2 H), 7.59 (d, *J* = 8.1 Hz, 2 H), 6.68 (t, *J* = 56.1 Hz, 1 H), 2.62 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.7 (d, *J* = 56.1 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 138.8, 138.5 (t, *J* = 22.1 Hz), 128.6, 125.9 (t, *J* = 6.0 Hz), 113.9 (t, *J* = 238.2 Hz), 26.8. IR (thin film) ν_{max} 3064, 2967, 1767, 1689 cm^{-1}. MS (EI): *m/z* (%) 170 (M^+), 155 (100). HRMS calcd. for $C_9H_8OF_2$ (M^+): 170.0543; Found: 170.0542.

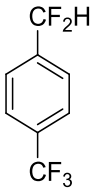


1-(3-(Difluoromethyl)phenyl)ethanone (24). The product (37 mg, 73% yield) was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 8.04 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 6.68 (t, *J* = 56.0 Hz, 1 H), 2.61 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2 (d, *J* = 56.0 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 137.5, 134.9 (t, *J* = 22.8 Hz), 130.5, 129.9 (t, *J* = 5.8 Hz), 129.2, 125.5 (t, *J* = 6.3 Hz), 114.1 (t, *J* = 238.0 Hz), 26.7. MS (EI): *m/z* (%) 170 (M^+), 155 (100). HRMS calcd. for $C_9H_8OF_2$ (M^+): 170.0543; Found:170.0542.

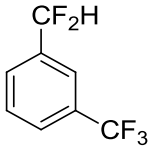


3-(Difluoromethyl)benzonitrile (25). The reaction was conducted in 0.6 mmol scale. The product (41 mg, 45% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1). This compound is known.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1 H), 7.77 (t, *J* = 8.0 Hz, 2 H), 7.60 (t, *J* = 8.0 Hz, 1 H), 6.68 (t, *J* = 56.1 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 (d, *J* = 56.1 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 134.2 (t, *J* = 1.5 Hz), 129.9 (t, *J* = 5.9 Hz), 129.8, 129.3

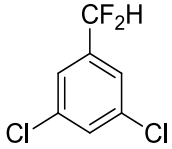
(t, J = 6.2 Hz), 117.8 (t, J = 12.7 Hz), 113.2, 113.1 (t, J = 240.3 Hz), 109.9. IR (thin film) ν_{max} 2924, 2234, 1766 cm^{-1}. MS (EI): *m/z* (%) 153 (M^+), 152 (100). HRMS calcd. for $C_8H_5NF_2$ (M^+): 153.0390; Found: 153.0388.



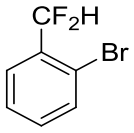
1-(Difluoromethyl)-4-(trifluoromethyl)benzene (26). Due to the low biol point of the product, the yield (84%) was determined by ^{19}F NMR using fluorobenzene as an internal standard. This compound is known.[6] The product was characterized by ^{19}F NMR and GC-MS analysis.



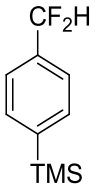
1-(Difluoromethyl)-3-(trifluoromethyl)benzene (27). Due to the low biol point of the product, the yield (78% yield) was determined by ^{19}F NMR using fluorobenzene as an internal standard. The product was characterized by ^{19}F NMR and GC-MS analysis.



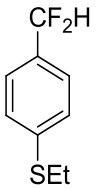
1,3-dichloro-5-(difluoromethyl)benzene (28). The product (26 mg, 43% yield; ^{19}F NMR yield 54%) was purified with silica gel chromatography (Petroleum ether). This compound is known.[9] ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 1 H), 7.39 (s, 2 H), 6.58 (t, J = 56.1 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.7 (d, J = 56.1 Hz, 2 F). MS (EI): *m/z* (%) 195 (M^+), 186, 177, 161 (100). HRMS calcd. for $C_7H_4Cl_2F_2$ (M^+): 195.9658; Found:195.9653.



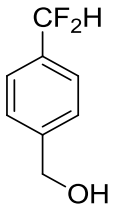
1-Bromo-2-(difluoromethyl)benzene (29). The product (20 mg, 33% yield; ^{19}F NMR yield 38%) as a colorless oil was purified with silica gel chromatography (Petroleum ether). This compound is known.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1 H), 7.62-7.60 (m, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 6.92 (t, *J* = 54.8 Hz, 1 H). ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.6 (d, *J* = 54.8 Hz, 2 F). MS (EI): *m/z* (%) 206 (M^+), 206 (100). HRMS calcd. for $C_7H_5BrF_2$ (M^+): 205.9543; Found: 205.9540.



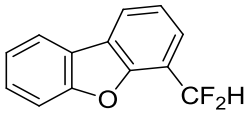
(4-(Difluoromethyl)phenyl)trimethylsilane (30). The product (43 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1). This compound is known.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2 H), 7.49 (d, *J* = 7.5 Hz, 2 H), 6.64 (t, *J* = 56.7 Hz, 1 H), 0.3 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.2 (d, *J* = 56.7 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 143.9, 134.6 (t, *J* = 22.2 Hz), 133.6, 124.7 (t, *J* = 6.0 Hz), 114.8 (t, *J* = 238.5 Hz), -1.3. MS (EI): *m/z* (%) 200 (M^+), 185 (100). HRMS calcd. for $C_{10}H_{14}SiF_2$ (M^+): 200.0833; Found: 200.0838.



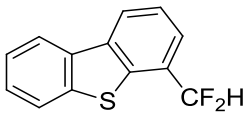
(4-(Difluoromethyl)phenyl)(ethyl)sulfane (31). The product (49 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 6.61 (t, *J* = 56.7 Hz, 1 H), 2.98 (q, *J* = 7.5 Hz, 2 H), 1.35 (t, *J* = 7.5 Hz, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.5 (d, *J* = 56.7 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 140.7 (t, *J* = 2.0 Hz), 131.3 (t, *J* = 22.4 Hz), 127.8, 125.9 (t, *J* = 5.9 Hz), 114.6 (t, *J* = 238.3 Hz), 26.8, 14.1. MS (EI): *m/z* (%) 188 (M^+), 160 (100). HRMS calcd. for $C_9H_{10}SF_2$ (M^+): 188.0471; Found: 188.0469.



(4-(Difluoromethyl)phenyl)methanol (32). The product (36 mg, 76% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). This compound is known.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 6.65 (t, *J* = 56.4 Hz, 1 H), 4.76 (s, 2 H), 1.76 s, 1 H) . ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4 (d, *J* = 56.4 Hz, 2 F). MS (EI): *m/z* (%) 158 (M^+), 127, 107 (100). IR (thin film) ν_{max} 3332, 1759, 1620, 1508 cm^{-1}. HRMS calcd. for $C_8H_8OF_2$ (M^+):158.0543; Found: 158.0540.

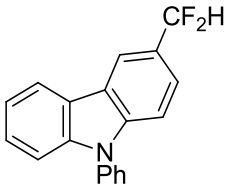


4-(Difluoromethyl)dibenzo[*b,d*]furan (33). The product (50 mg, 77% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1 H), 7.94 (d, *J* = 7.6 Hz, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.50 (td, *J* = 8.4 Hz, *J* = 1.2 Hz, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.23 (t, *J* = 55.2 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0 (d, *J* = 55.2 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 156.3, 127.8, 125.1, 123.7 (t, *J* = 5.8 Hz), 123.4, 123.2, 123.1 (t, *J* = 1.6 Hz), 122.7, 120.8, 118.5 (t, *J* = 24.0 Hz), 111.9, 111.8 (t, *J* = 237.4 Hz). MS (EI): *m/z* (%) 218 (M^+), 218 (100). HRMS calcd. for $C_{13}H_8OF_2$ (M^+): 218.0543; Found: 218.0538.

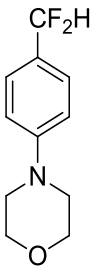


4-(Difluoromethyl)dibenzo[*b,d*]thiophene (34). The product (55 mg, 79% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23-8.20 (m, 1 H), 8.17-8.14 (m, 1 H), 7.89-7.86 (m, 1 H), 7.63-7.60 (m, 1 H), 7.53-7.47 (m, 3 H), 6.93 (t, *J* = 55.4 Hz, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.7 (d, *J* = 55.4 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 139.5 (t, *J* = 1.0 Hz), 136.9, 136.6 (t, *J* = 3.3 Hz), 134.6, 128.5 (t, *J* = 22.8 Hz), 127.3, 124.7, 124.4, 124.3 (t, *J* = 7.0 Hz), 123.7 (t, *J* = 1.8 Hz), 122.7, 121.7, 114.5 (t, *J* = 239.4 Hz). MS (EI): *m/z*

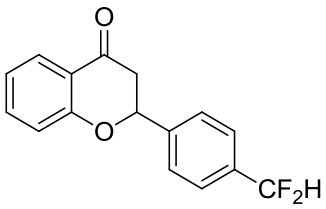
(%) 234 (M^+), 234 (100). HRMS calcd. for $C_{13}H_8SF_2$ (M^+): 234.0315; Found: 234.0320. IR (thin film) ν_{max} 3067, 2963, 1457 cm^{-1}.



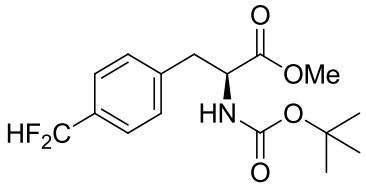
3-(Difluoromethyl)-9-phenyl-9*H*-carbazole (35). The product (49 mg, 56% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 8.18 (d, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 6.8 Hz, 2 H), 7.57-7.55 (m, 3 H), 7.52-7.42 (m, 4 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 6.88 (t, *J* = 56.8 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.3 (d, *J* = 56.8 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 142.0, 141.5, 137.2, 130.0, 127.9, 127.2, 126.6, 126.1 (t, *J* = 22.4 Hz), 123.2 (t, *J* = 5.7 Hz), 123.1, 122.9, 120.49, 120.48, 118.1 (t, *J* = 6.4 Hz), 115.8 (t, *J* = 237.3 Hz), 110.1, 109.9. MS (EI): *m/z* (%) 292 (M^+-H), 271 (100). HRMS calcd. for $C_{19}H_{13}NF_2$ (M^+): 293.1016; Found: 293.1017. IR (thin film) ν_{max} 3062, 1761, 1686 cm^{-1}.



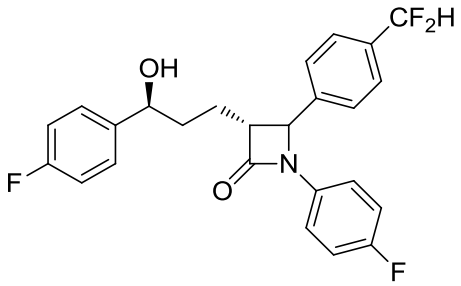
4-(4-(Difluoromethyl)phenyl)morpholine (36). The product (40 mg, 62% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.58 (t, *J* = 57.2 Hz, 1 H), 3.87 (t, *J* = 4.8 Hz, 4 H), 3.21 (t, *J* = 4.8 Hz, 4 H). ^{19}F NMR (375 MHz, $CDCl_3$) δ -108.1 (d, *J* = 57.2 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 152.9 (t, *J* = 1.5 Hz), 126.7 (t, *J* = 5.9 Hz), 125.3 (t, *J* = 22.9 Hz), 115.1 (t, *J* = 236.8 Hz), 114.8, 66.7, 48.5. MS (EI): *m/z* (%) 213 (M^+), 206, 191 (100). HRMS calcd. for $C_{11}H_{13}NOF_2$ (M^+): 213.0965; Found: 213.0970. IR (thin film) ν_{max} 2963, 2853, 1686, 1600cm^{-1}.



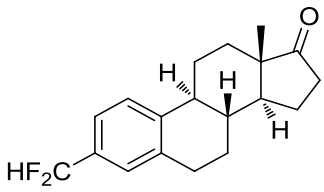
(2-(4-(Difluoromethyl)phenyl)chroman-4-one (37). The product (63 mg, 76% yield) as a white solid (m.p. 61-63 ^{o}C) was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1 H), 7.59 (s, 4 H), 7.52 (td, *J* = 8.4 Hz, *J* = 1.6 Hz, 1 H), 7.08-7.05 (m, 2 H), 6.67 (t, *J* = 56.4 Hz, 1 H), 5.53 (dd, *J* = 12.8 Hz, *J* = 2.8 Hz, 1 H), 3.06 (dd, *J* = 16.8 Hz, *J* = 13.2 Hz, 1 H), 2.90 (dd, *J* = 16.8 Hz, *J* = 2.8 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 191.4, 161.3, 141.5 (t, *J* = 1.9 Hz), 136.3, 134.7 (t, *J* = 22.6 Hz), 127.1, 126.4, 126.1 (t, *J* = 6.2 Hz), 121.9, 120.9, 118.1, 114.4 (t, *J* = 238.8 Hz), 79.0, 44.6. IR (thin film) ν_{max} 3066, 1763, 1690, 1606 cm^{-1}. MS (EI): *m/z* (%) 274 (M^+), 147, 120 (100). HRMS calcd. for $C_{16}H_{12}O_2F_2$: 274.0805; Found: 274.0806.



(*S*)-Methyl 2-((tert-butoxycarbonyl)amino)-3-(4-(difluoromethyl)phenyl)propanoate (38). The product (60 mg, 61% yield) as a white solid (m.p. 70-73 ^{o}C) was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 6.61 (t, *J* = 56.4 Hz, 1 H), 5.01 (d, *J* = 6.8 Hz, 1 H), 4.61 (dd, *J* = 13.2 Hz, *J* = 6.4 Hz, 1 H), 3.71 (s, 3 H), 3.17 (dd, *J* = 13.6 Hz, *J* = 5.6 Hz, 1 H), 3.06 (dd, *J* = 13.6 Hz, *J* = 5.6 Hz, 1 H), 1.40 (s, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5 (d, *J* = 56.4 Hz, 2 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 155.0, 139.0 (t, *J* = 2.0 Hz), 133.2 (t, *J* = 22.1 Hz), 129.7, 125.8 (t, *J* = 5.9 Hz), 114.6 (t, *J* = 237.1 Hz), 80.1, 54.3, 52.3, 38.2, 28.3. IR (thin film) ν_{max} 3372, 2978, 1748, 1714, 1508 cm^{-1}. MS (EI): *m/z* (%) 328 (M^+-H), 212, 88, 57 (100). HRMS calcd. for $C_{16}H_{21}NO_4F_2$: 329.1439; Found: 329.1436.



(3*R*)-4-(4-(Difluoromethyl)phenyl)-1-(4-fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)azetidin-2-one (39). The product (77 mg, 58% yield) as a white solid (m.p. 141-146 ^{o}C) was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 7.31-7.28 (m, 2 H), 7.23-7.19 (m, 2 H), 7.02 (t, *J* = 8.4 Hz, 2 H), 6.94 (t, *J* = 8.4 Hz, 2 H), 6.64 (t, *J* = 56.4 Hz, 1 H), 4.72 (m, 1 H), 4.67 (d, *J* = 2.4 Hz, 1 H), 3.08 (td, *J* = 6.8 Hz, *J* = 2.4 Hz, 1 H), 2.11 (d, *J* = 3.6 Hz, 1 H), 2.04-1.90 (m, 4 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (d, *J* = 56.4 Hz, 2 F), -114.7 (m, 1 F), -117.6 (m, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.2 (d, *J* = 244.3 Hz), 159.1 (d, *J* = 242.5 Hz), 140.4 (t, *J* = 2.0 Hz), 139.9 (d, *J* = 3.1 Hz), 134.8 (t, *J* = 22.5 Hz), 133.6 (d, *J* = 2.3 Hz), 127.3 (d, *J* = 8.0 Hz), 126.6 (t, *J* = 6.0 Hz), 126.2, 118.3 (d, *J* = 7.8 Hz), 115.9 (d, *J* = 22.8 Hz), 115.4 (d, *J* = 20.1 Hz), 114.2 (t, *J* = 237.7 Hz), 73.2, 60.9, 60.5, 36.6, 25.1. IR (thin film) ν_{max} 3432, 2928, 1739, 1714, 1507 cm^{-1}. MS (EI): *m/z* (%) 443 (M^+), 333, 292, 250 (100). HRMS calcd. for $C_{25}H_{21}NO_2F_4$: 443.1508; Found: 443.1512.



(8*R*,9*S*,13*S*,14*S*)-3-(Difluoromethyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (40). The product (69 mg, 76% yield) as a white solid (m.p. 59-62 ^{o}C) was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 7.24 (s, 1 H), 6.58 (t, *J* = 56.4 Hz, 1 H), 2.97-2.94 (m, 2 H), 2.51 (q, *J* = 8.8 Hz, 1 H), 2.47-2.42 (m, 1 H), 2.32 (t, *J* = 10.0 Hz, 1 H), 2.19-2.12 (m, 1 H), 2.10-2.03 (m, 2 H), 1.99-1.96 (m, 1 H), 1.67-1.42 (m, 6 H), 0.91 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9 (dd, *J* = 56.4 Hz, *J* = 5.3 Hz, 2 F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 220.6, 142.6 (t, *J* = 1.9 Hz), 137.1, 131.9 (t, *J* = 22.4 Hz), 126.1 (t, *J* = 5.9 Hz), 125.7, 122.8 (t, *J* = 16.6 Hz), 114.9 (t, *J* = 237.9 Hz), 50.5, 47.9, 44.4, 37.9, 35.8, 31.5, 29.3, 26.2, 25.6, 21.5, 13.8. IR (thin film)

ν_{max} 2984, 1734, 1616 cm^{-1}. MS (EI): *m/z* (%) 304 (M^+), 304 (100). HRMS calcd. for $C_{19}H_{22}OF_2$: 304.1639; Found: 304.1634.

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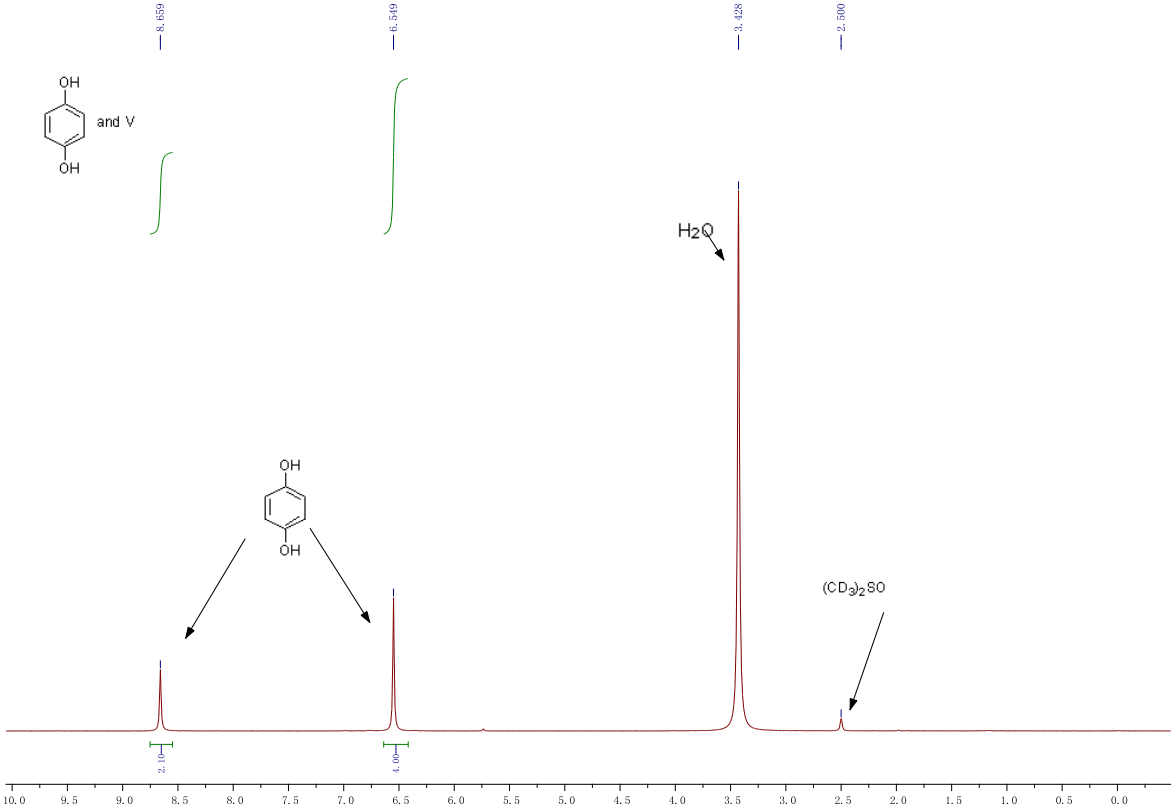
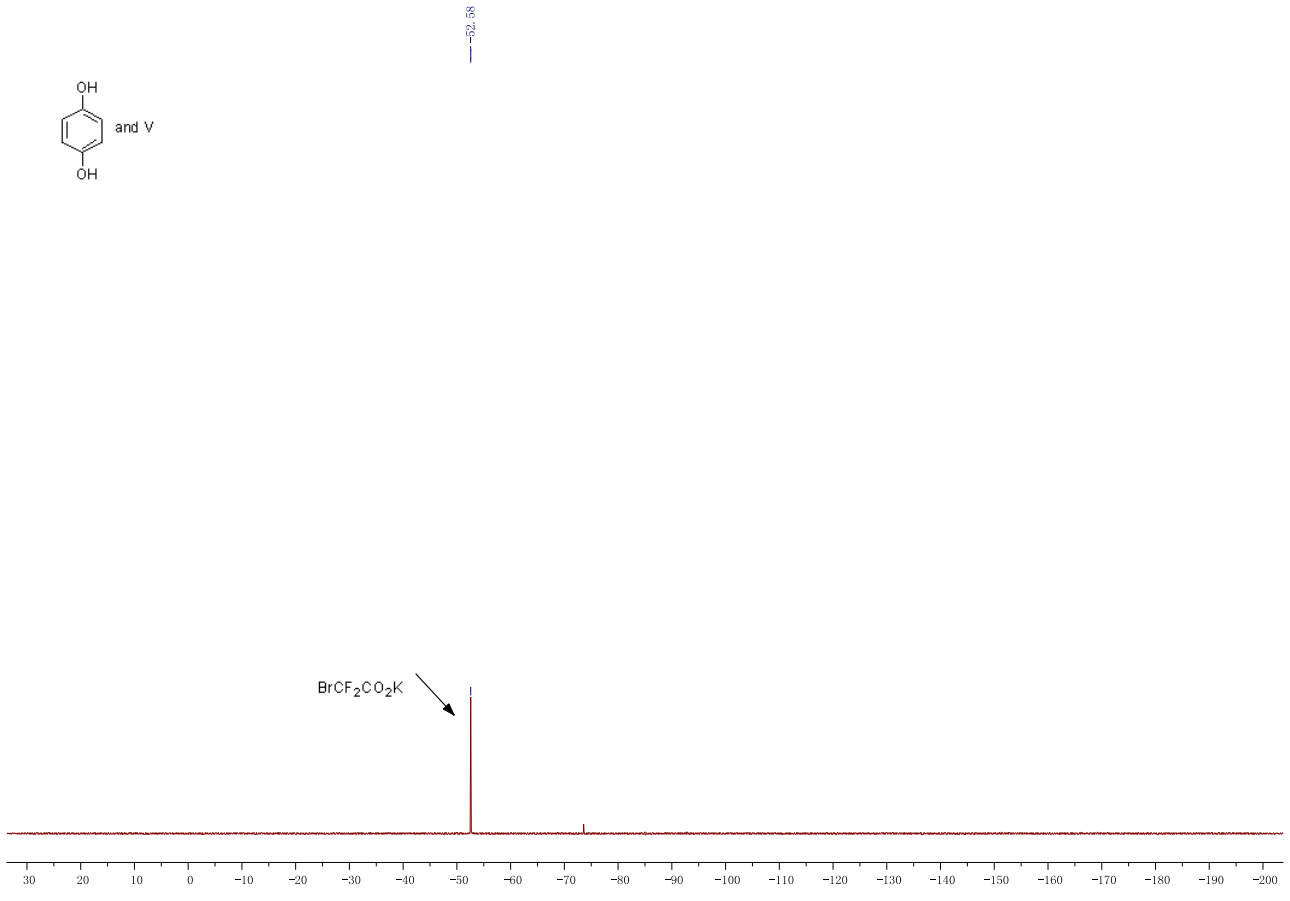
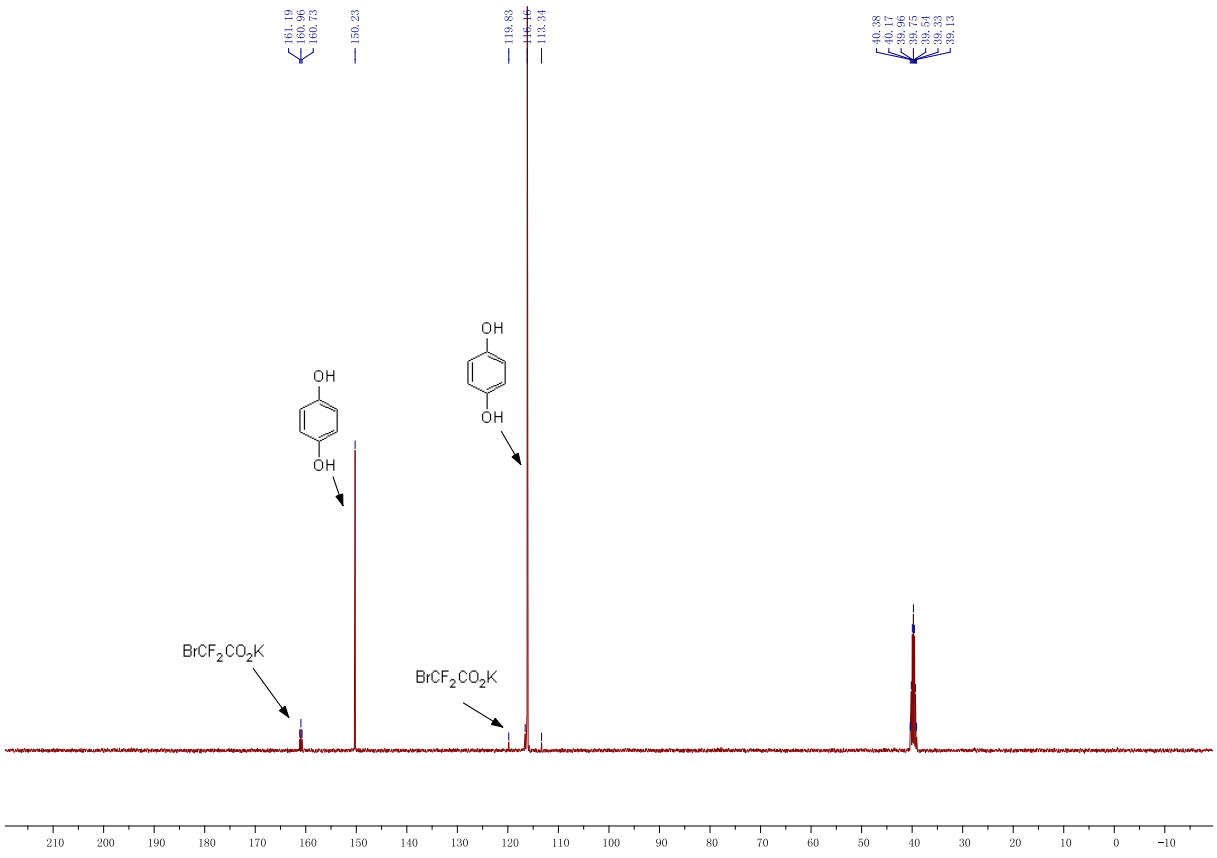
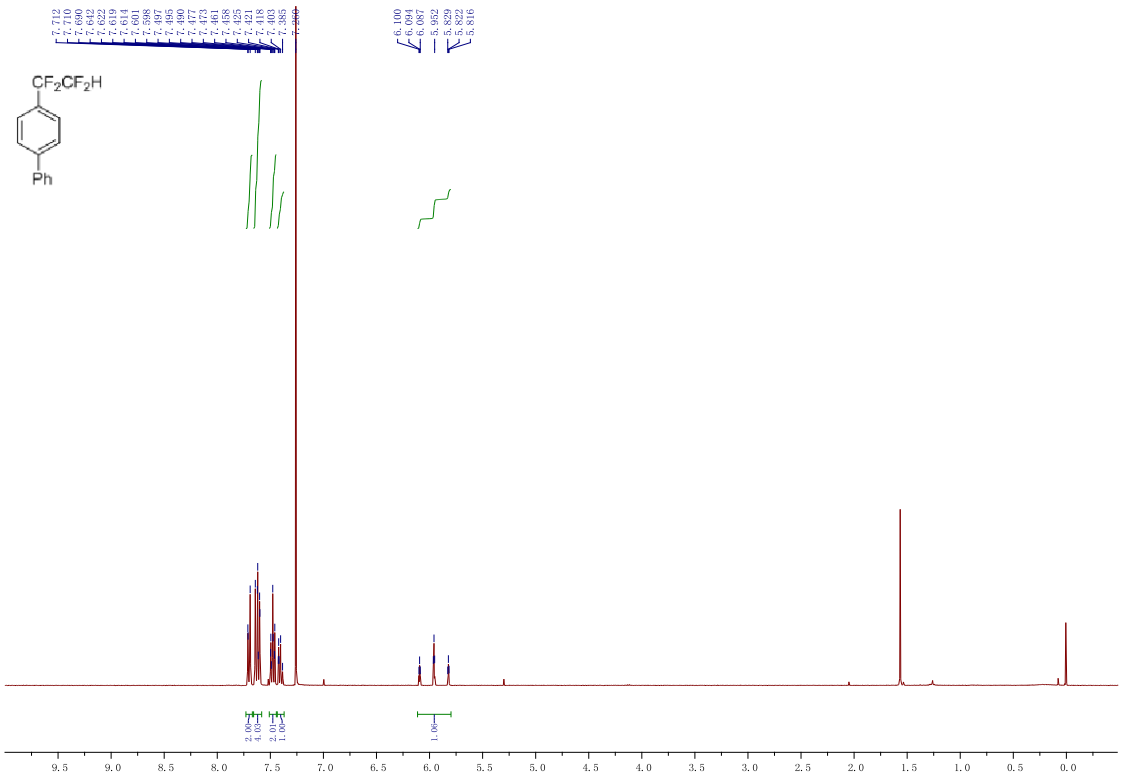
Compound $BrCF_2CO_2K$ V (determined from a mixture of V and hydroquinone)

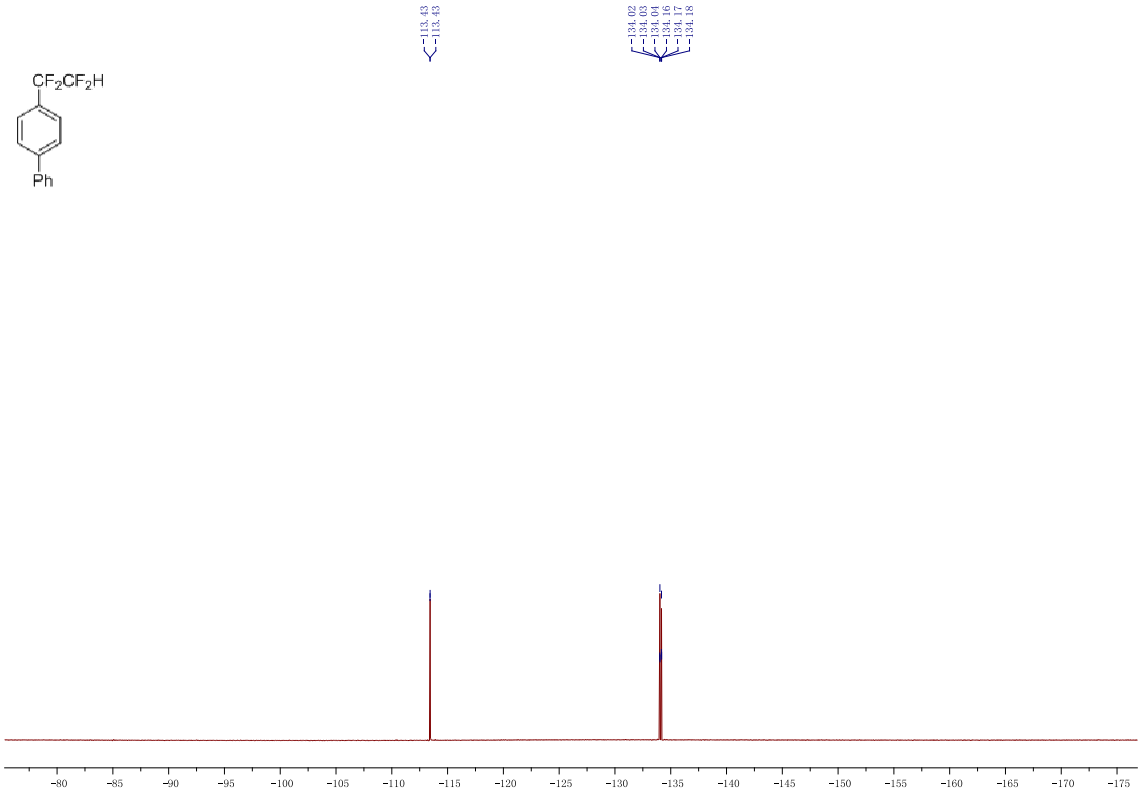






4-(1,1,2,2-Tetrafluoroethyl)-1,1'-biphenyl (3a)

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CF2CF2H
Ph
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-90
-95
-100
-105
-110
-115
-120
-125
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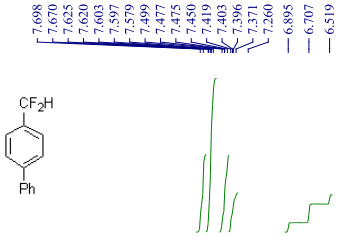
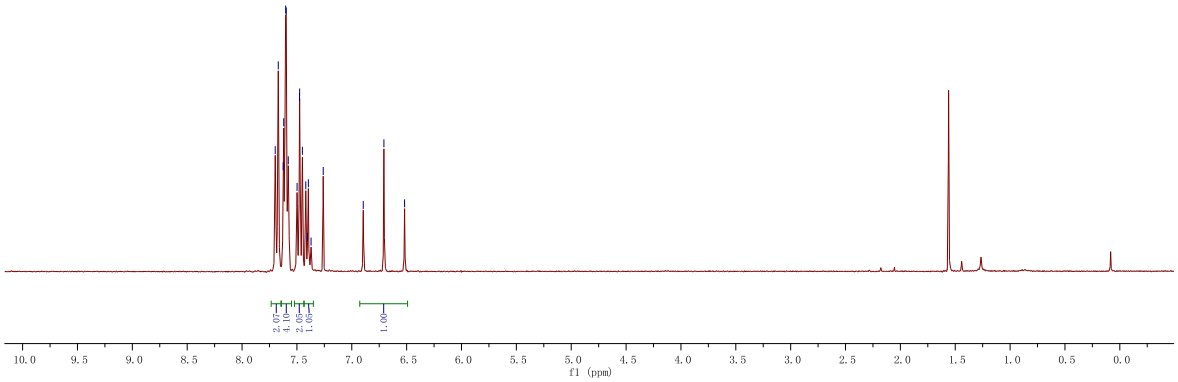
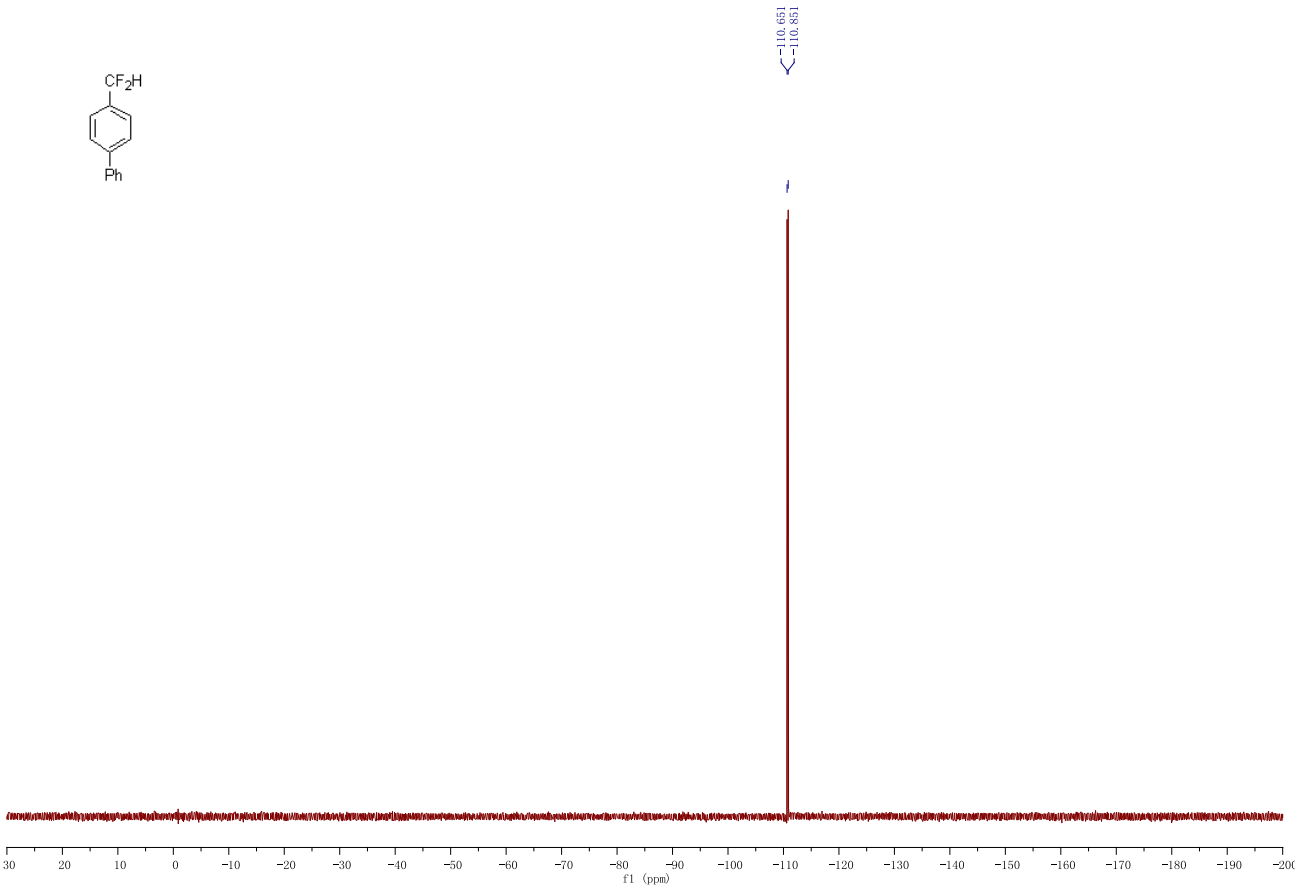
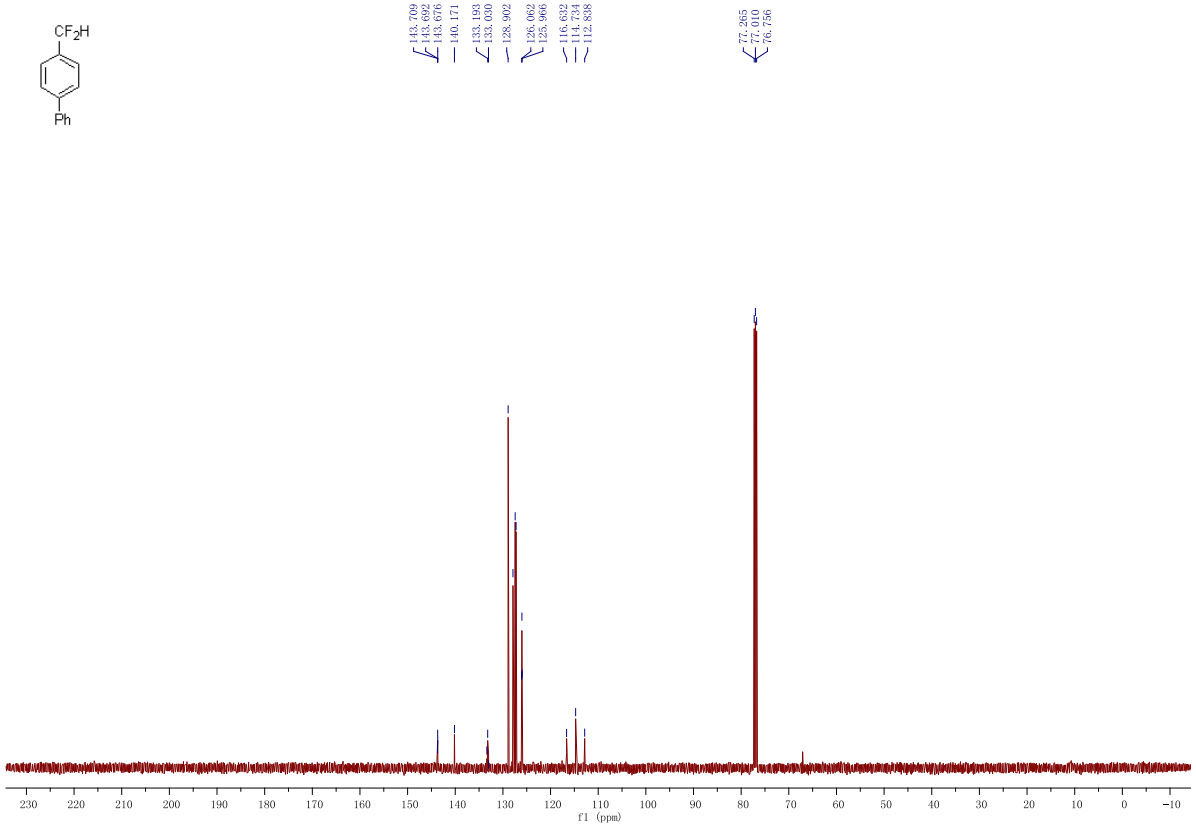
-165
-170
-175

4-(Difluoromethyl)-1,1'-biphenyl (3)

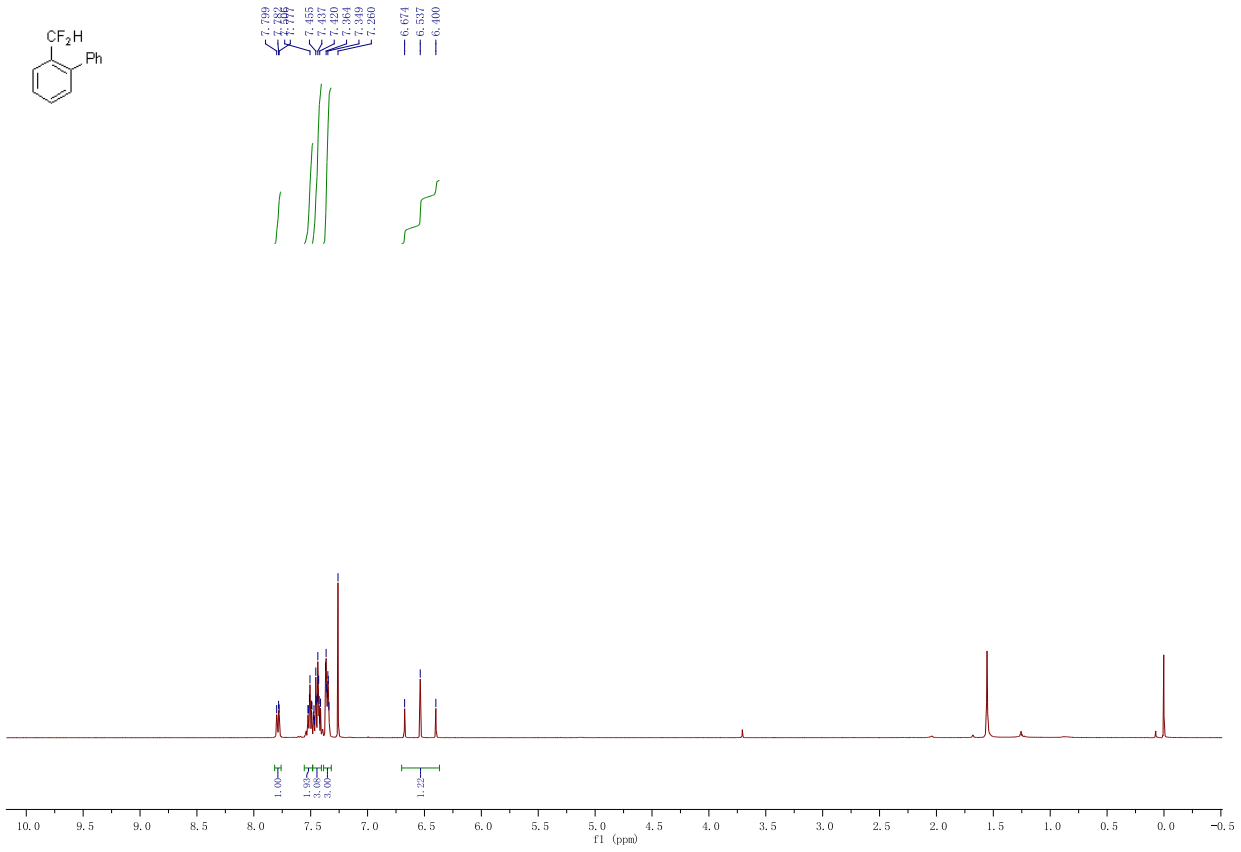


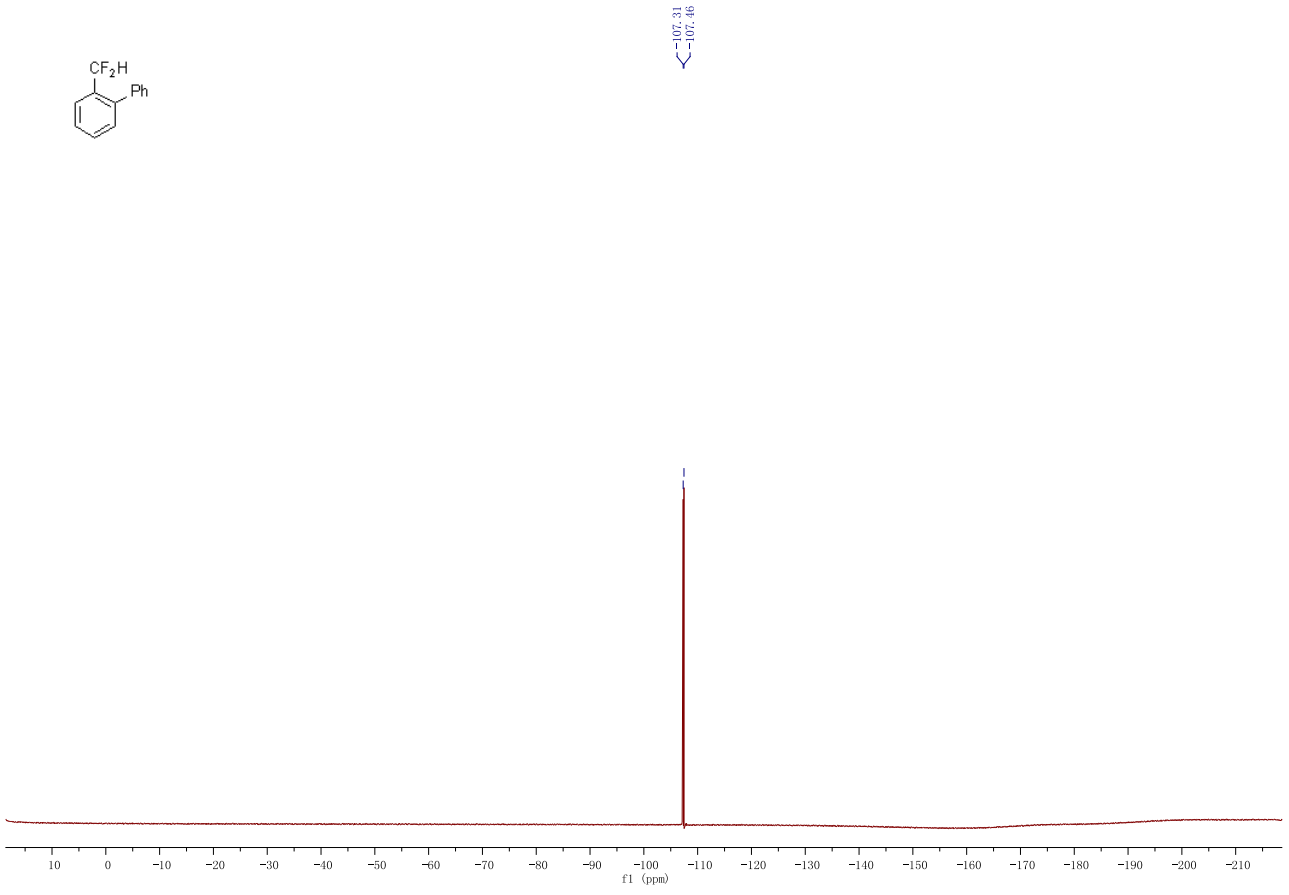


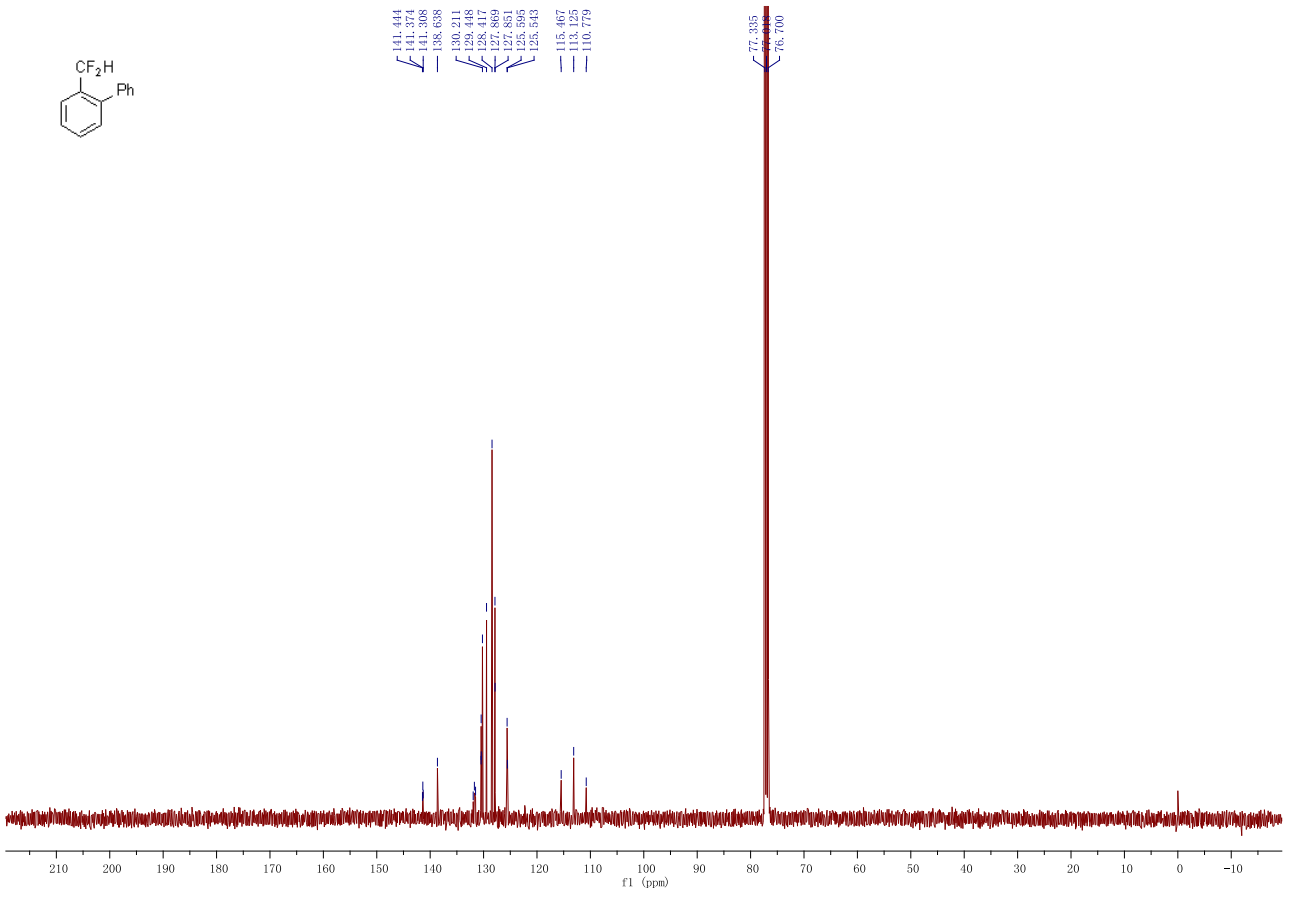




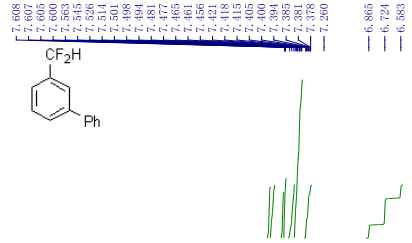
2-(Difluoromethyl)-1,1'-biphenyl (5).

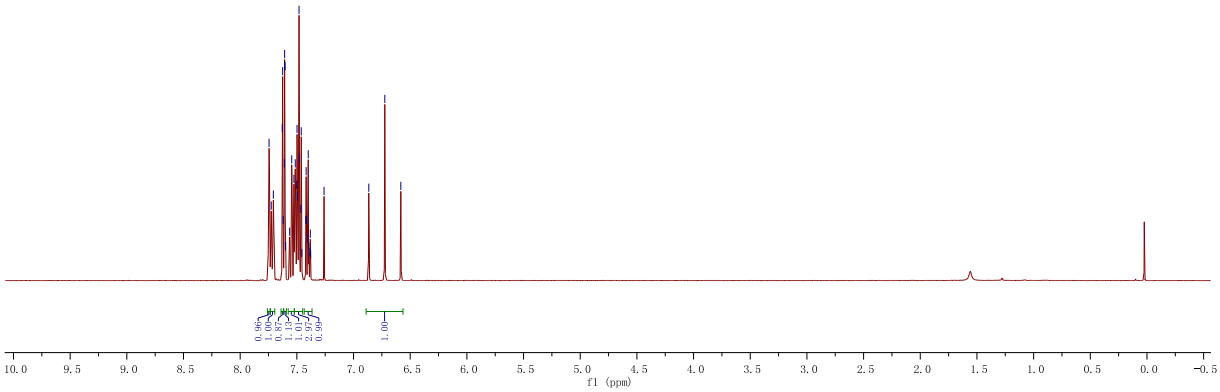


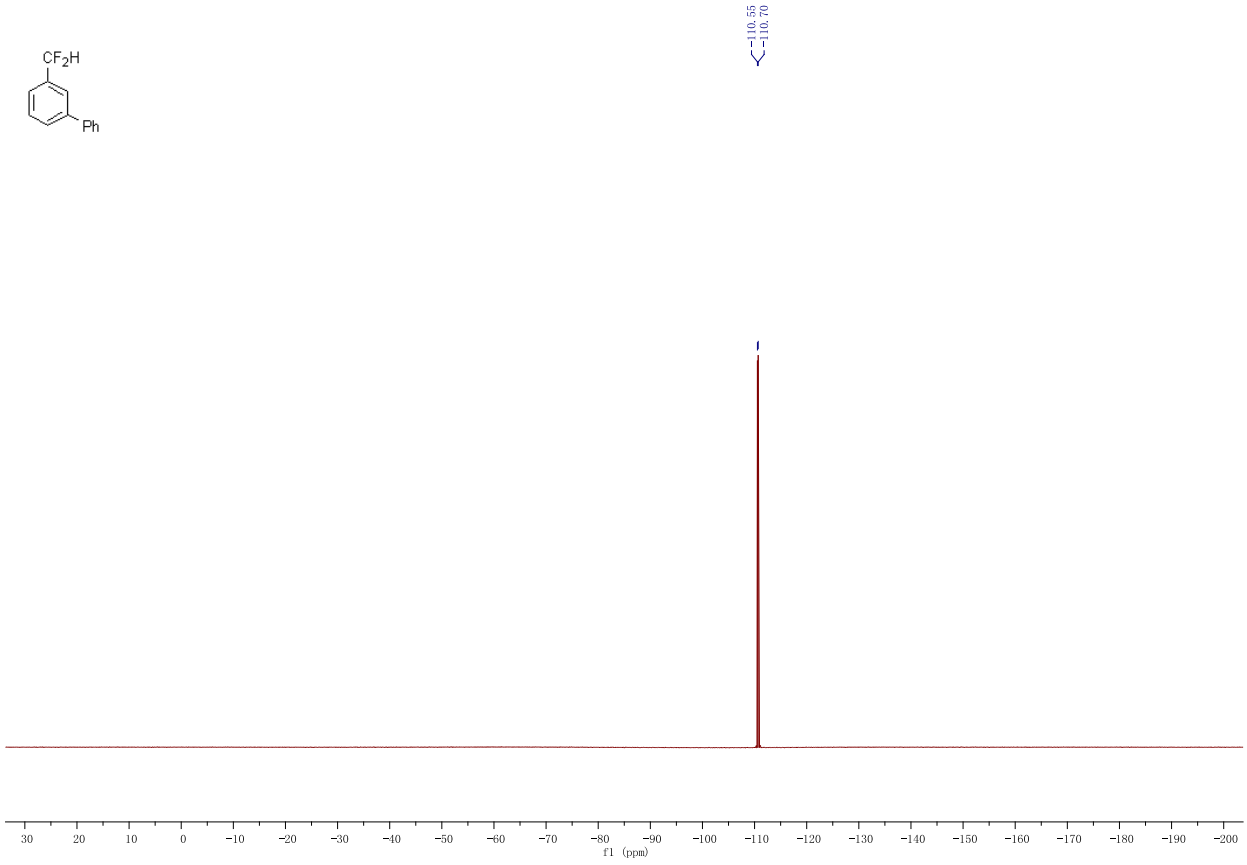

CF2H
Ph
-107.31
-107.46
f1 (ppm)

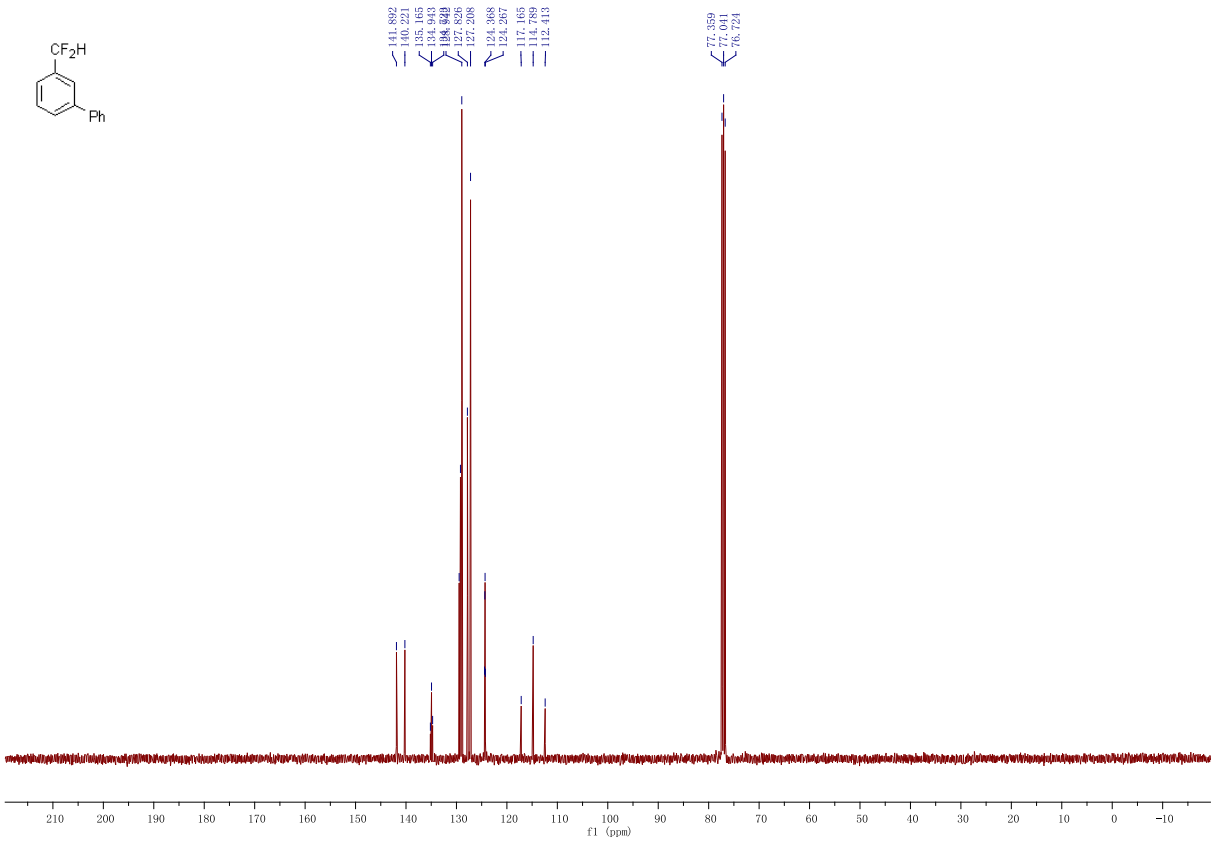

CF2H
Ph
141.444
141.374
141.308
138.638
130.211
129.448
128.417
127.869
127.651
125.895
125.543
115.467
113.125
110.779
77.335
77.018
76.700
f1 (ppm)

3-(Difluoromethyl)-1,1'-biphenyl (6).

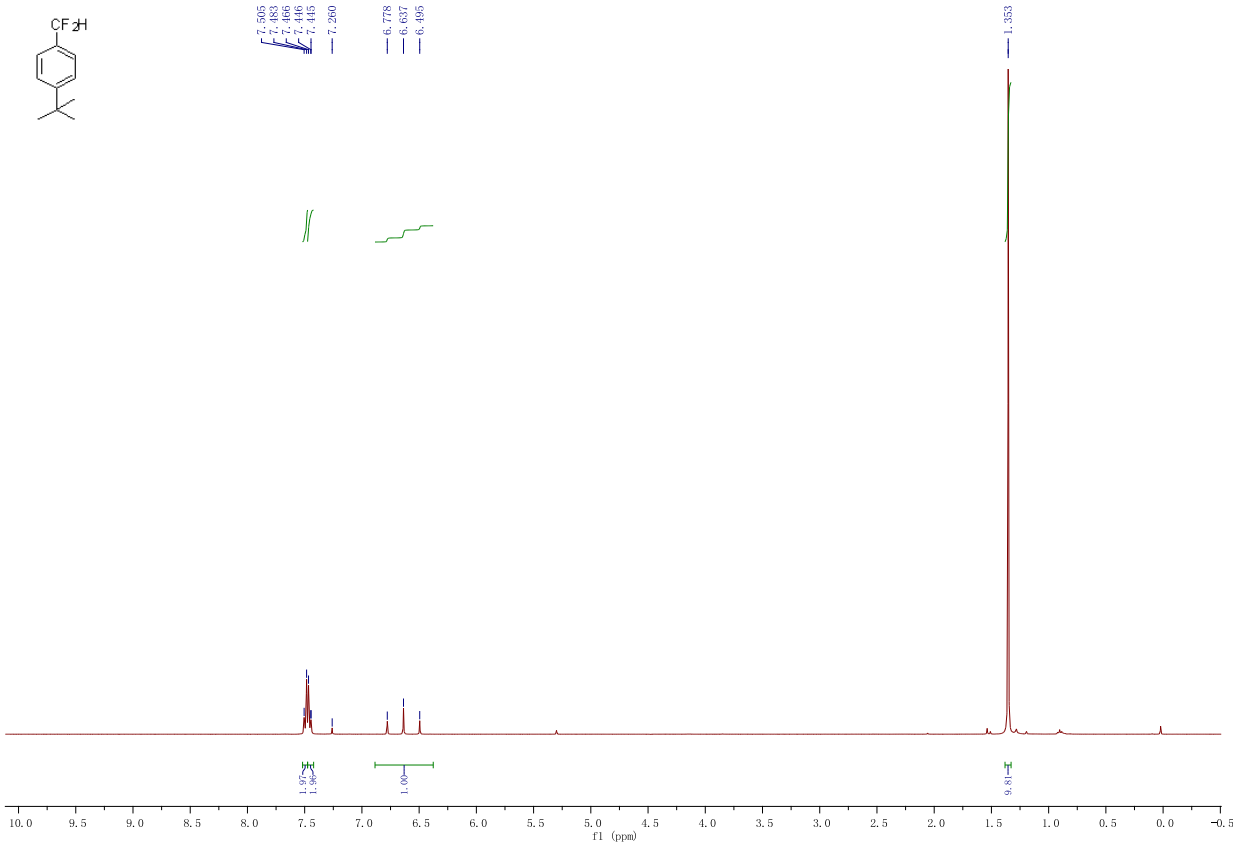


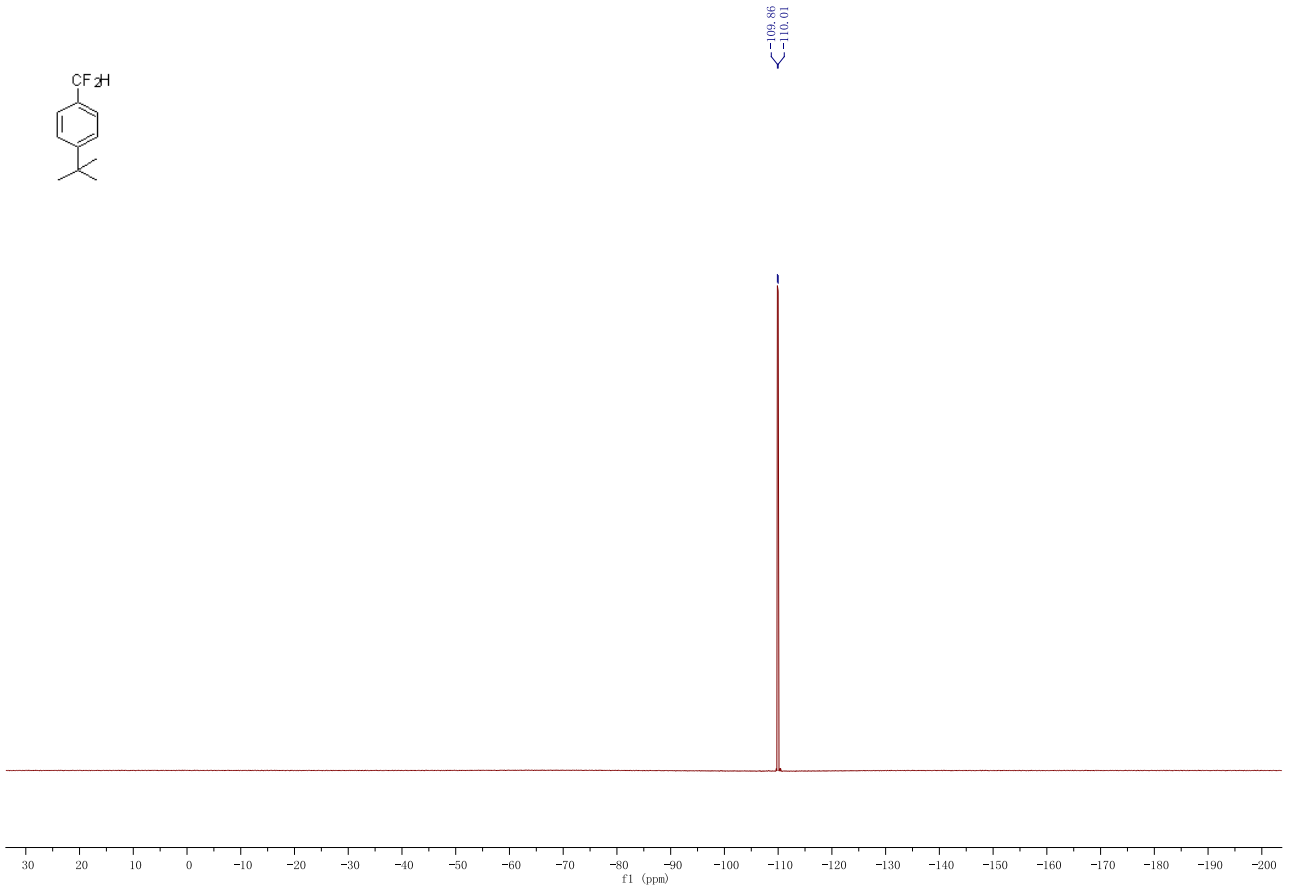


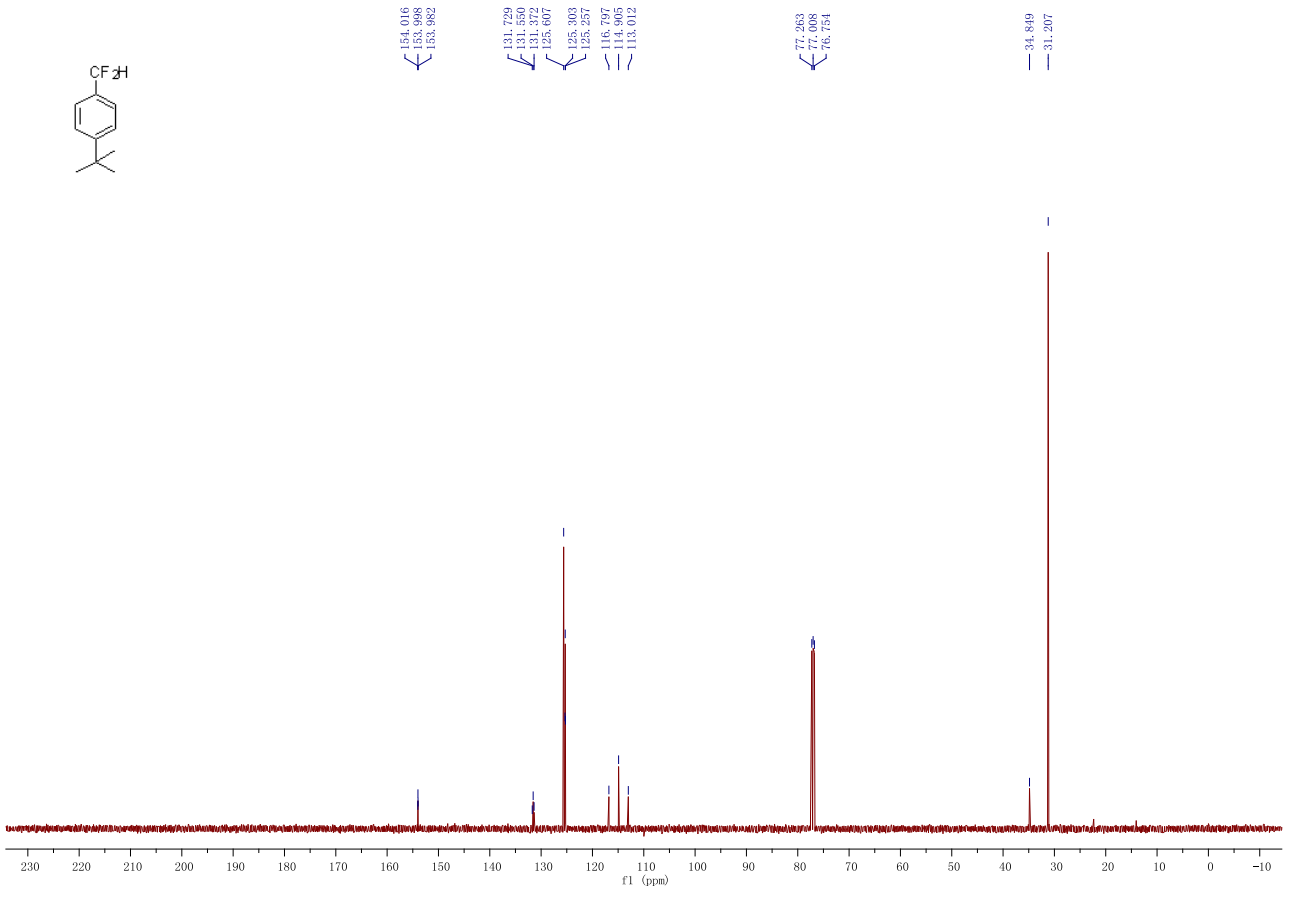




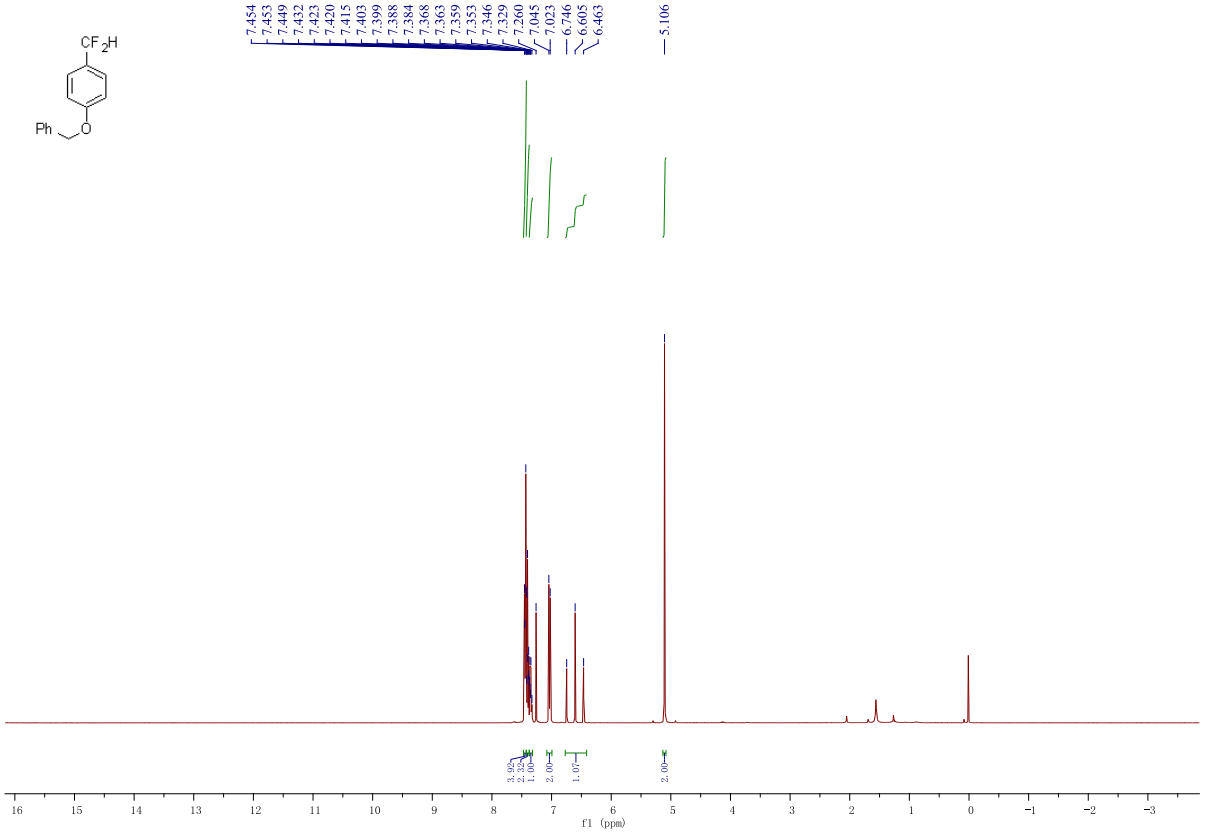
1-(Tert-butyl)-4-(difluoromethyl)benzene (7)

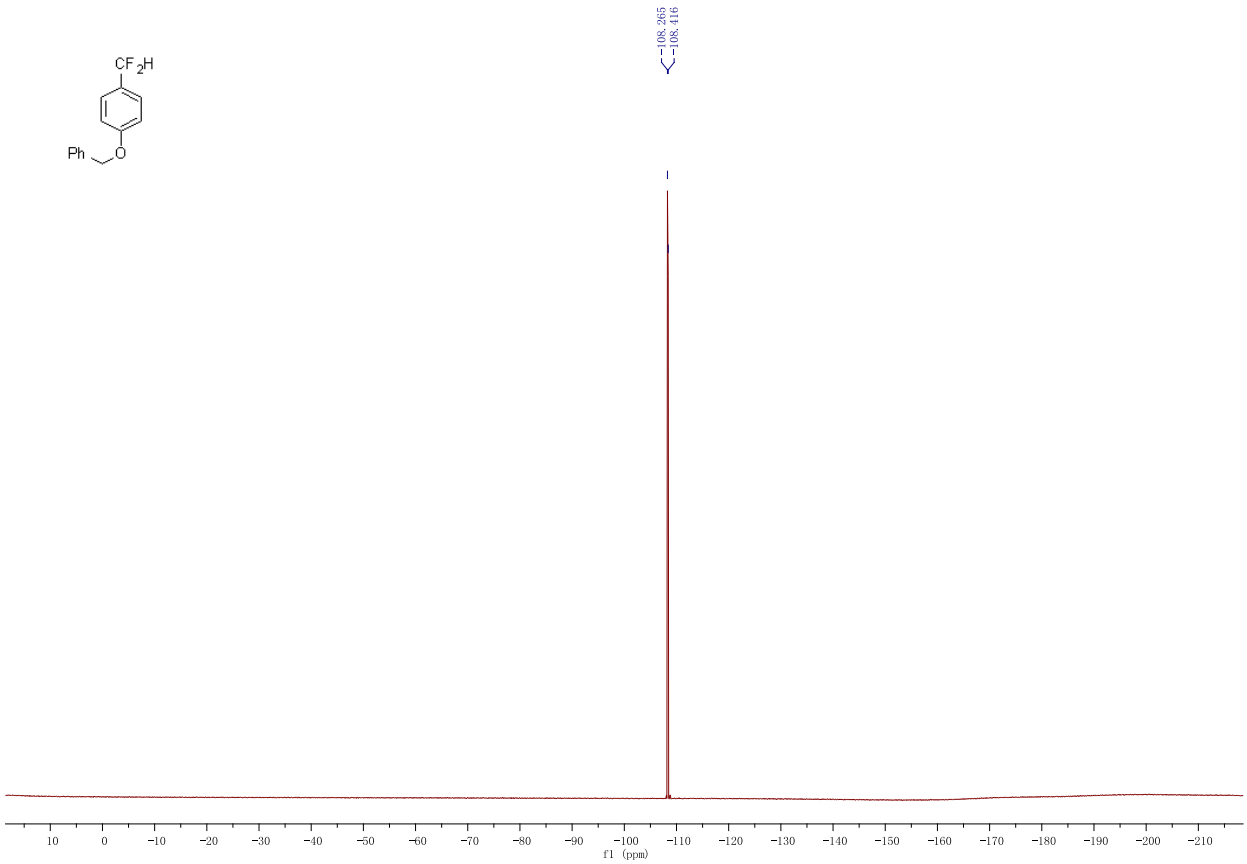


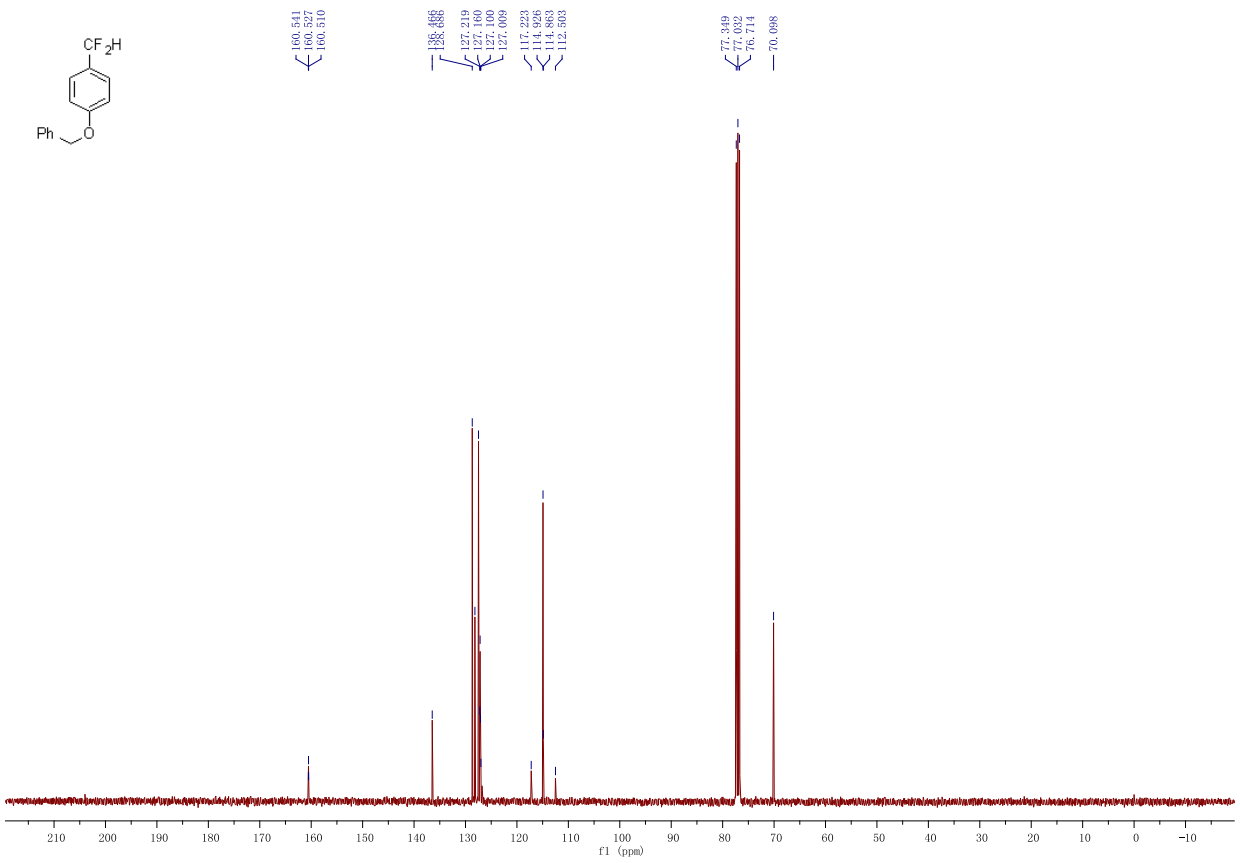

CF2H
-109.86
-110.01
f1 (ppm)


CF2H
154.016
153.998
153.982
131.729
131.550
131.372
125.607
125.303
125.257
116.797
114.905
113.012
77.263
77.008
76.754
34.849
31.207
f1 (ppm)

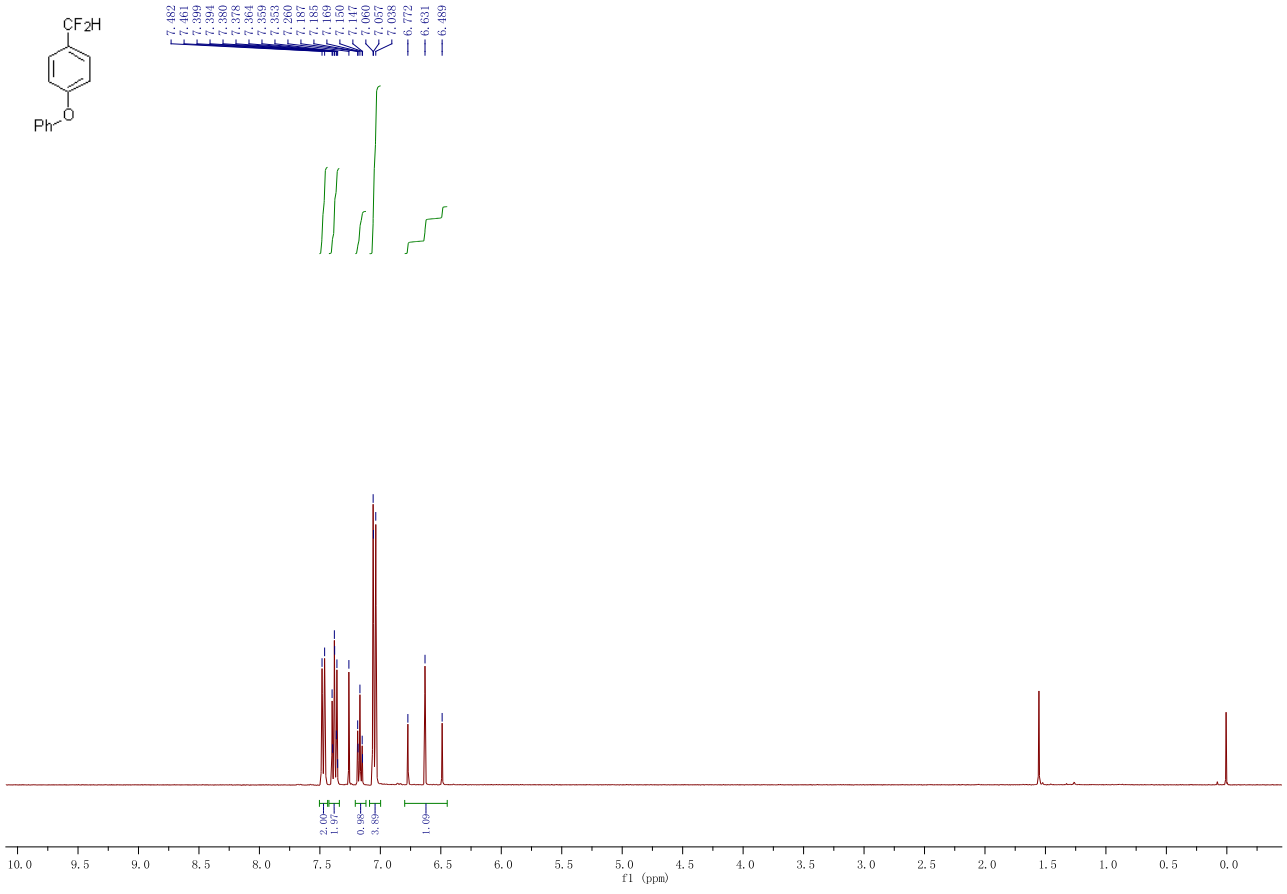
1-(Benzyloxy)-4-(difluoromethyl)benzene (8).

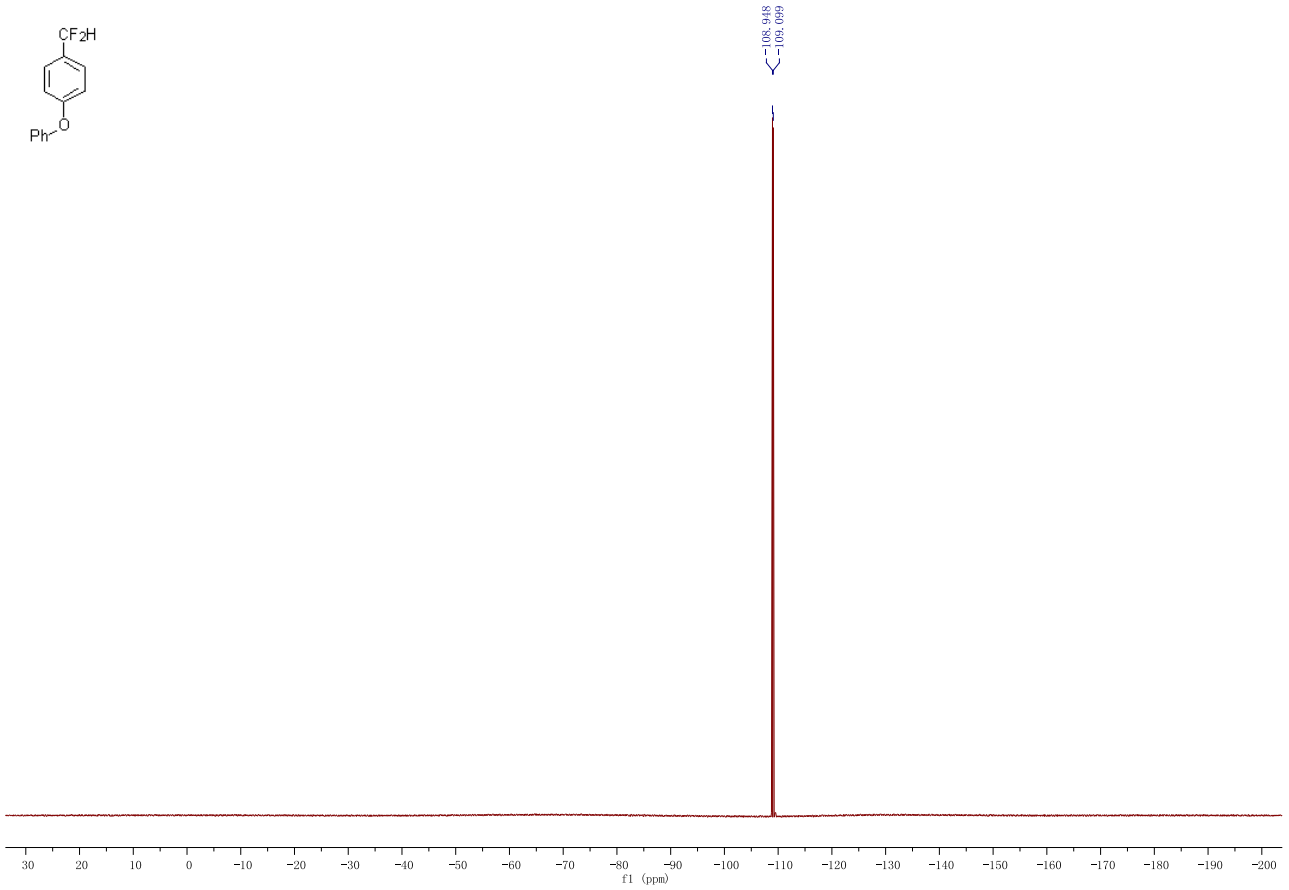


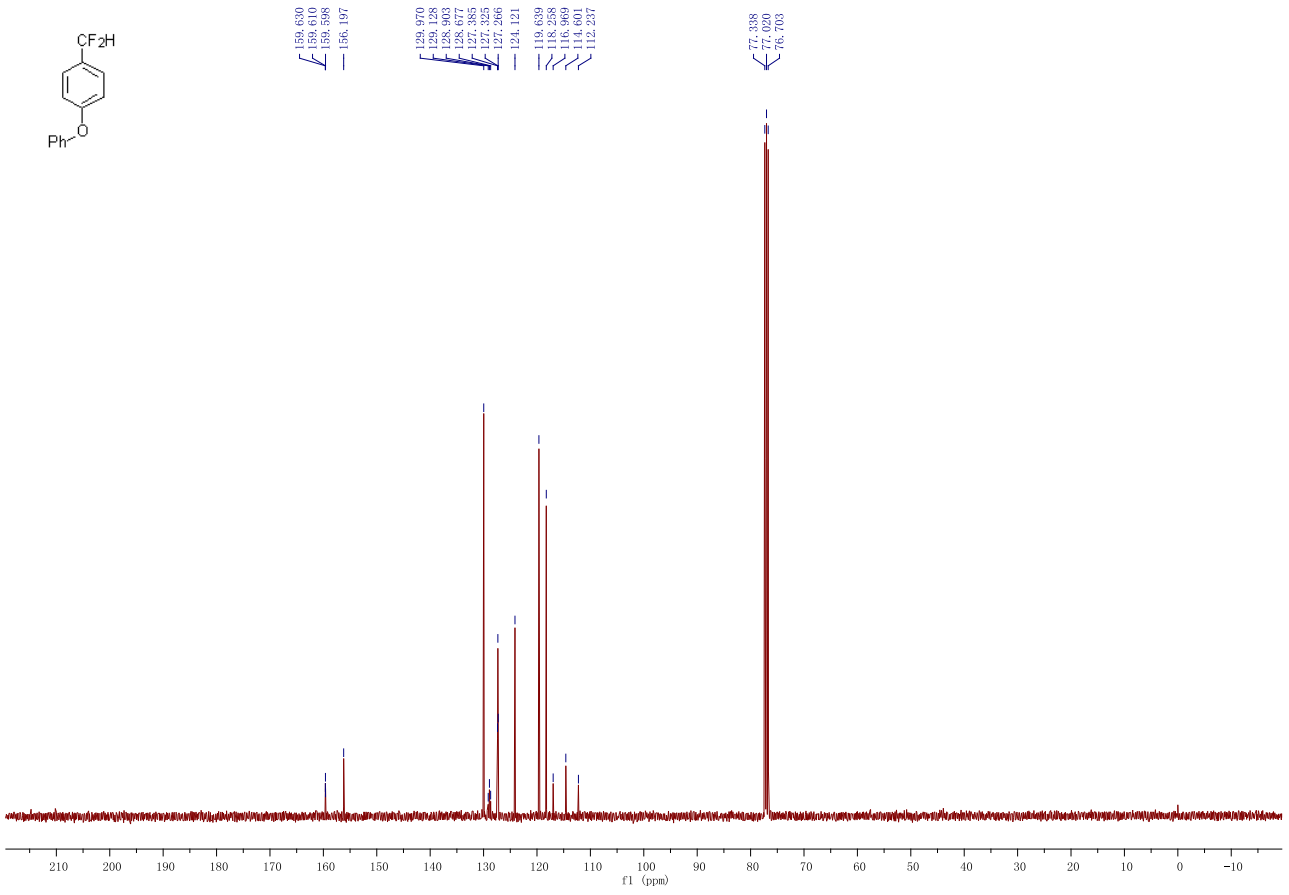




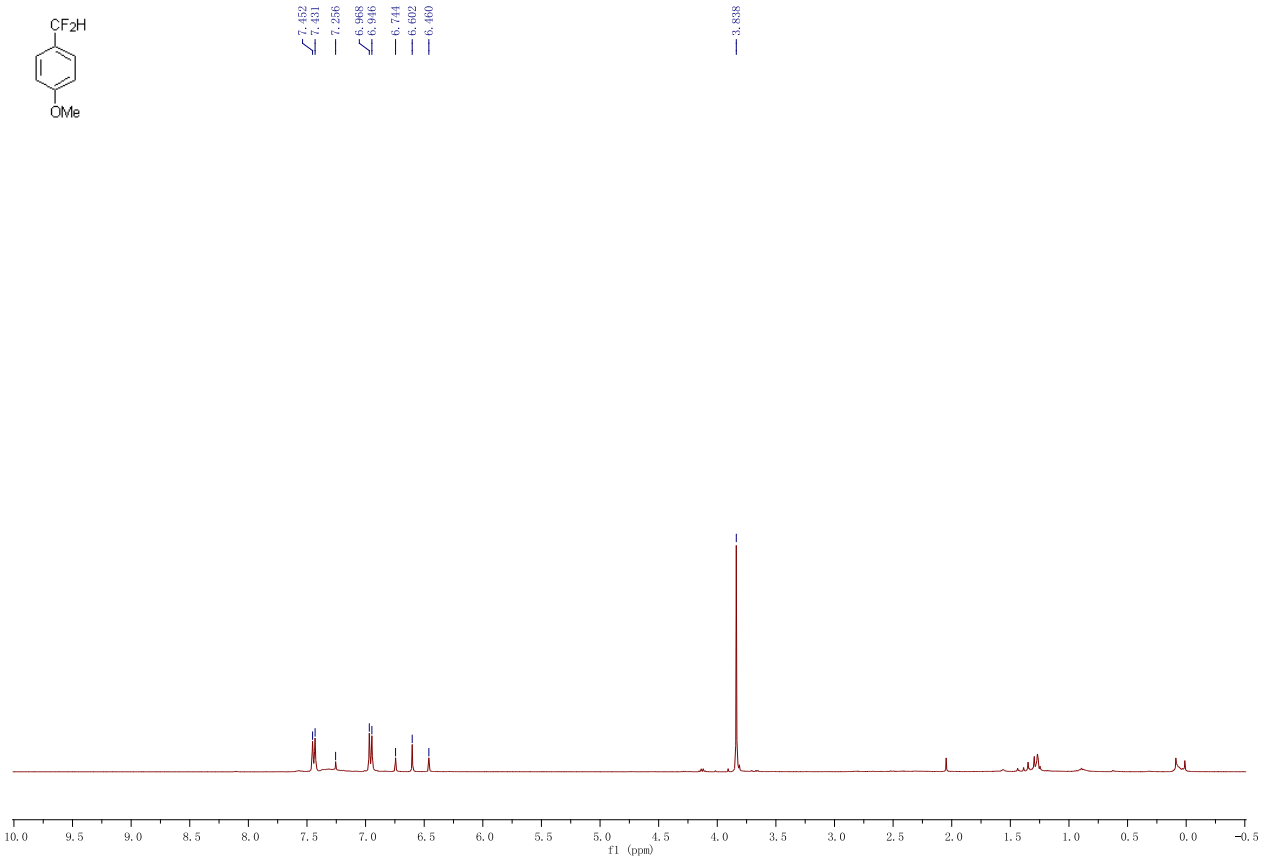
1-(Difluoromethyl)-4-phenoxybenzene (9).

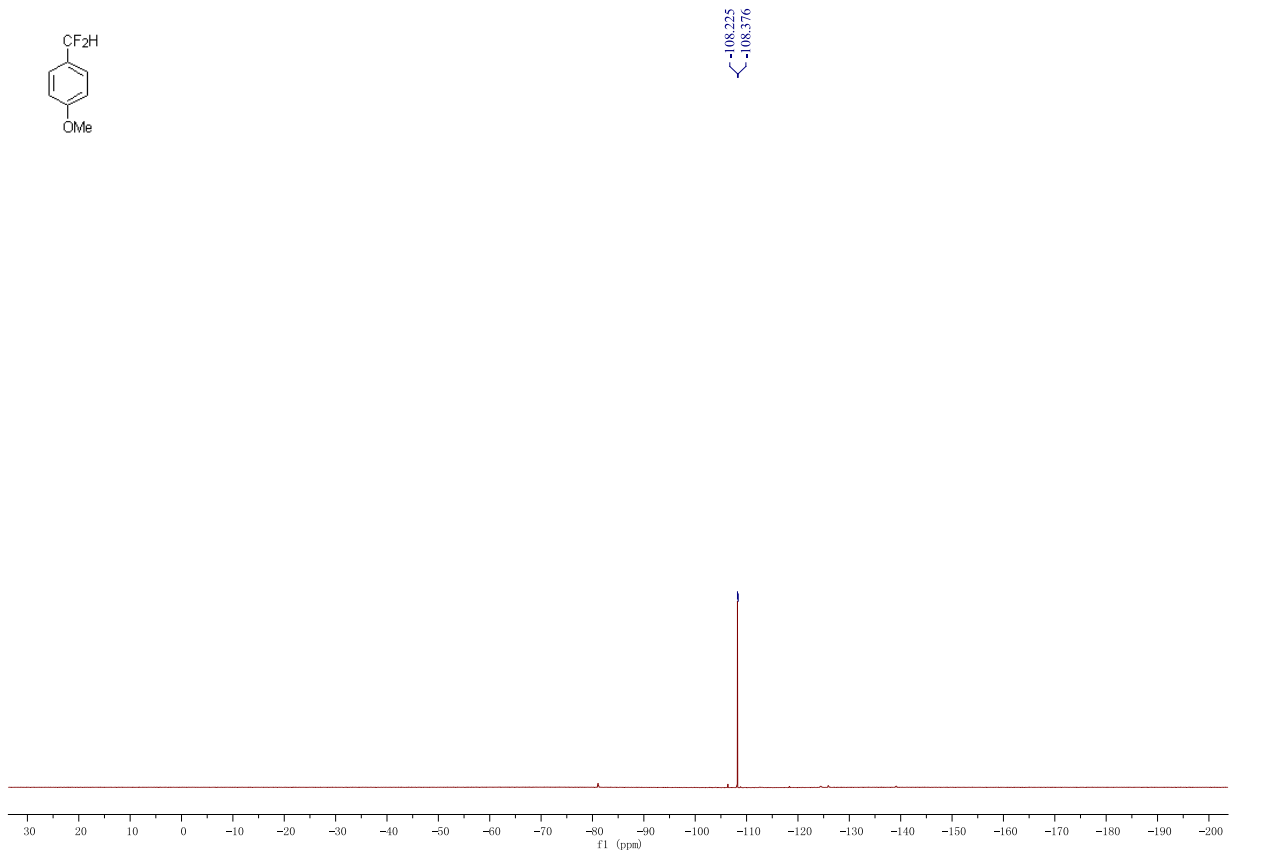


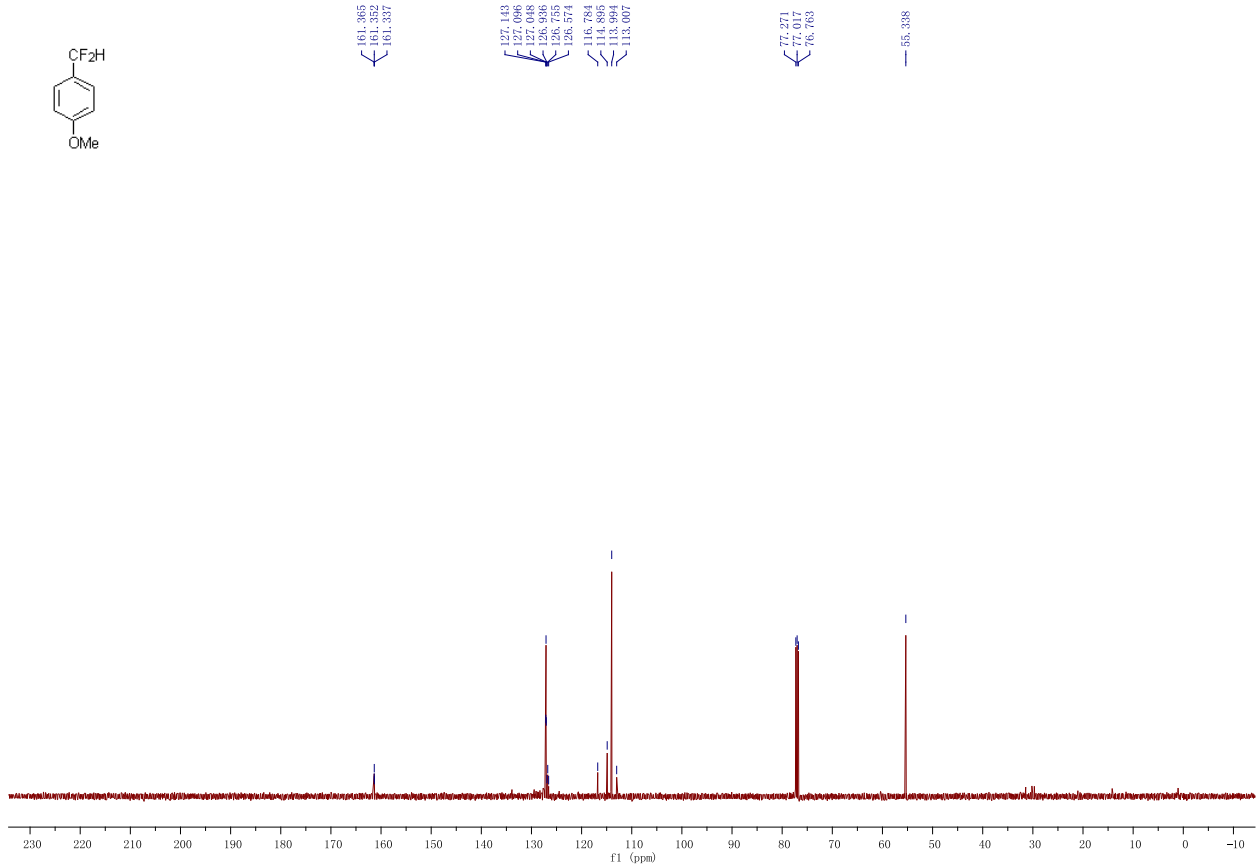

CF2H
Ph
O
-108.948
-109.099
f1 (ppm)


CF2H
Ph
O
159.630
159.610
159.598
156.197
129.970
129.128
128.903
128.677
127.385
127.325
127.266
124.121
119.639
118.258
116.969
114.601
112.237
77.338
77.020
76.703
f1 (ppm)

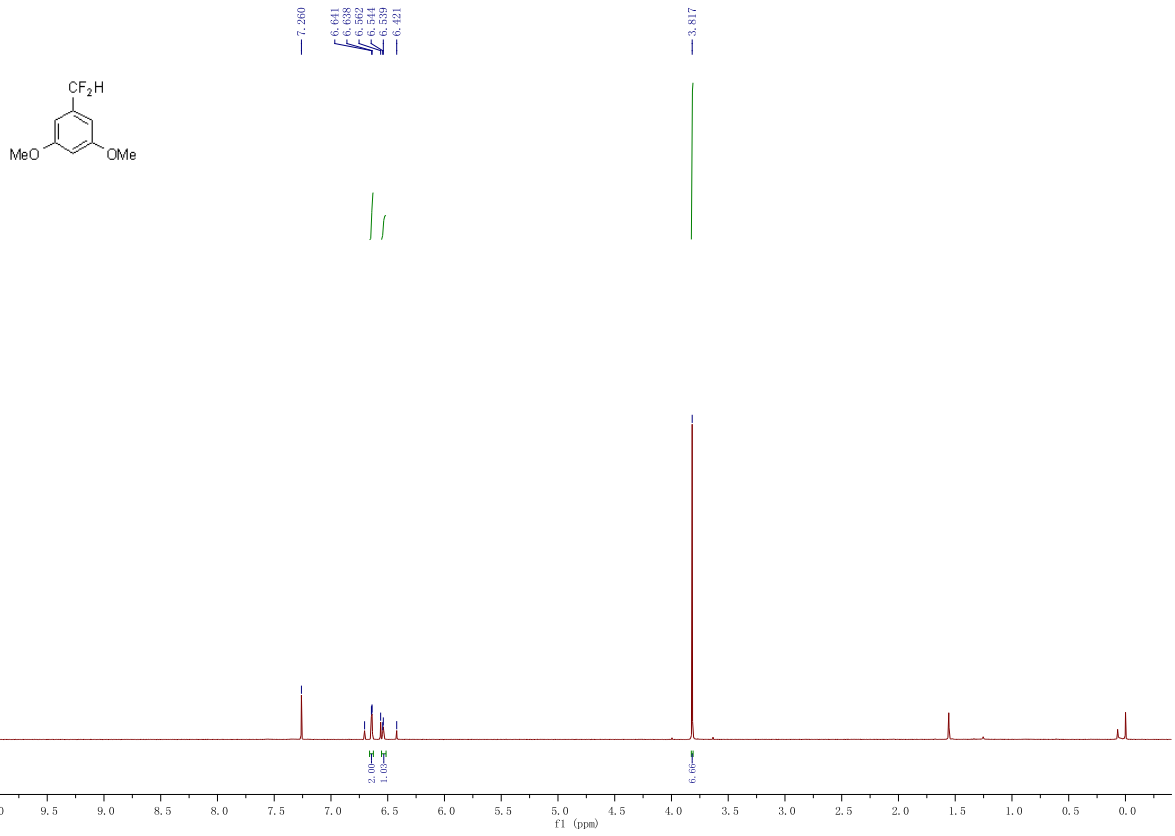
1-(Difluoromethyl)-4-methoxybenzene (10).

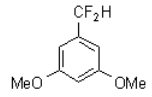




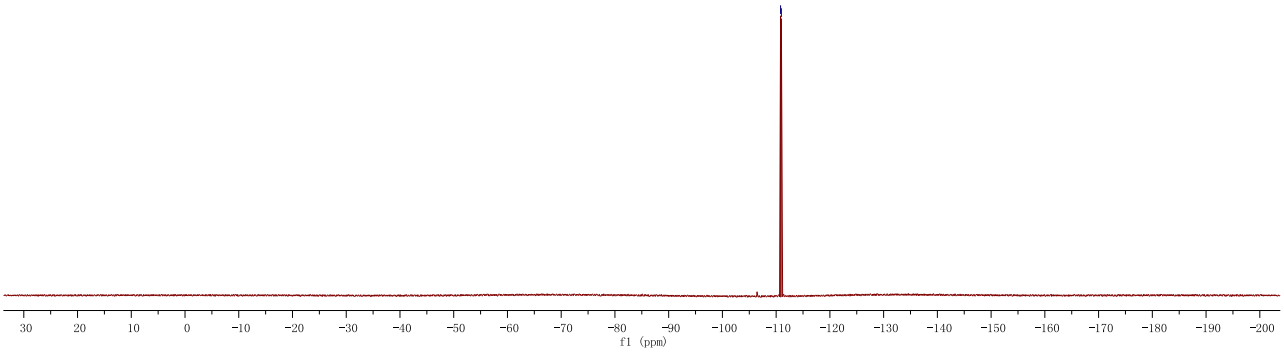


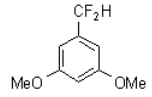
1-(Difluoromethyl)-3,5-dimethoxybenzene (11).



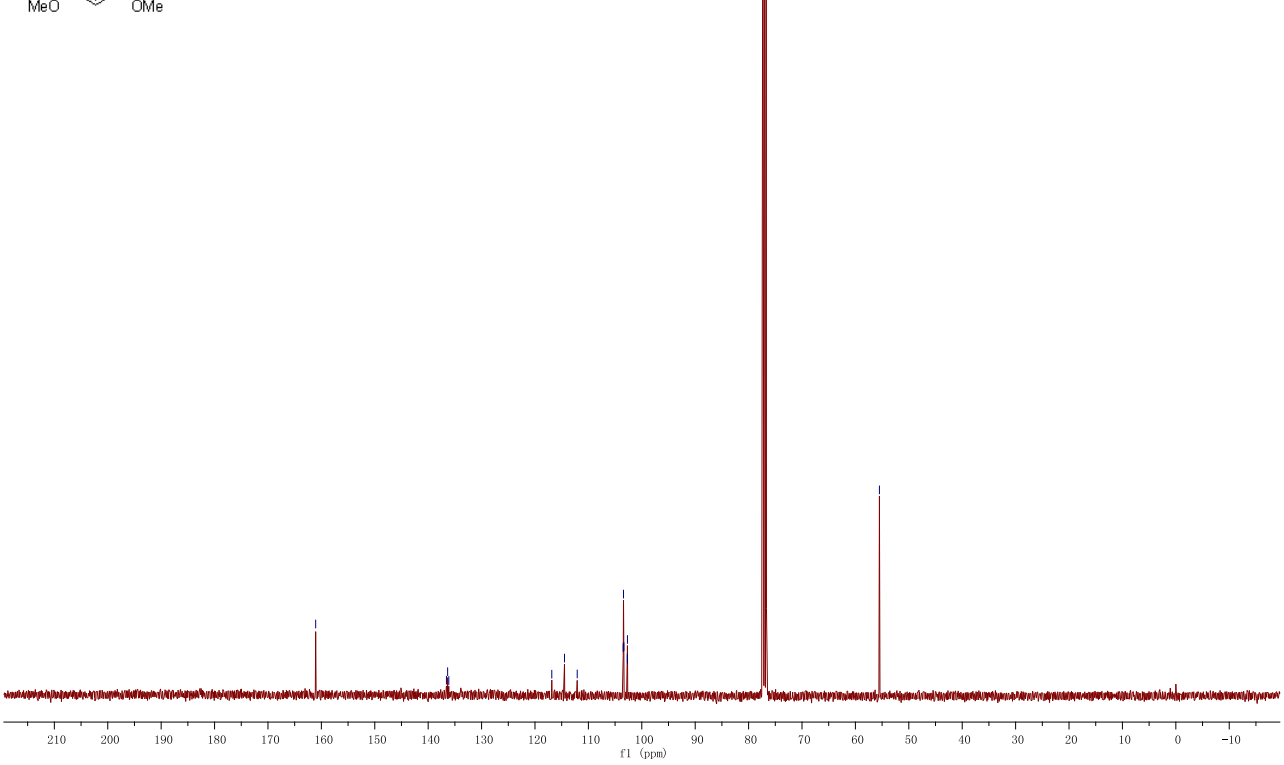

CF2H
MeO
OMe


-110.821
-110.971

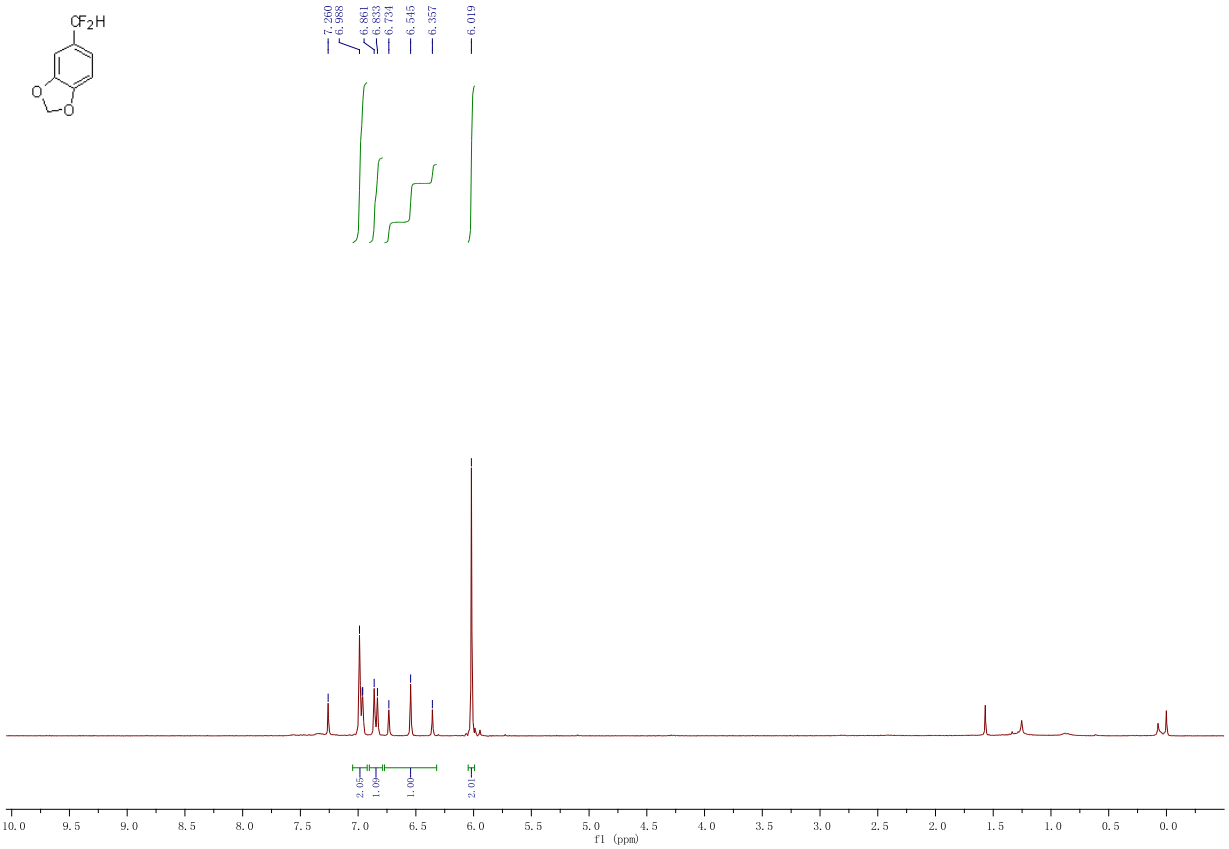

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

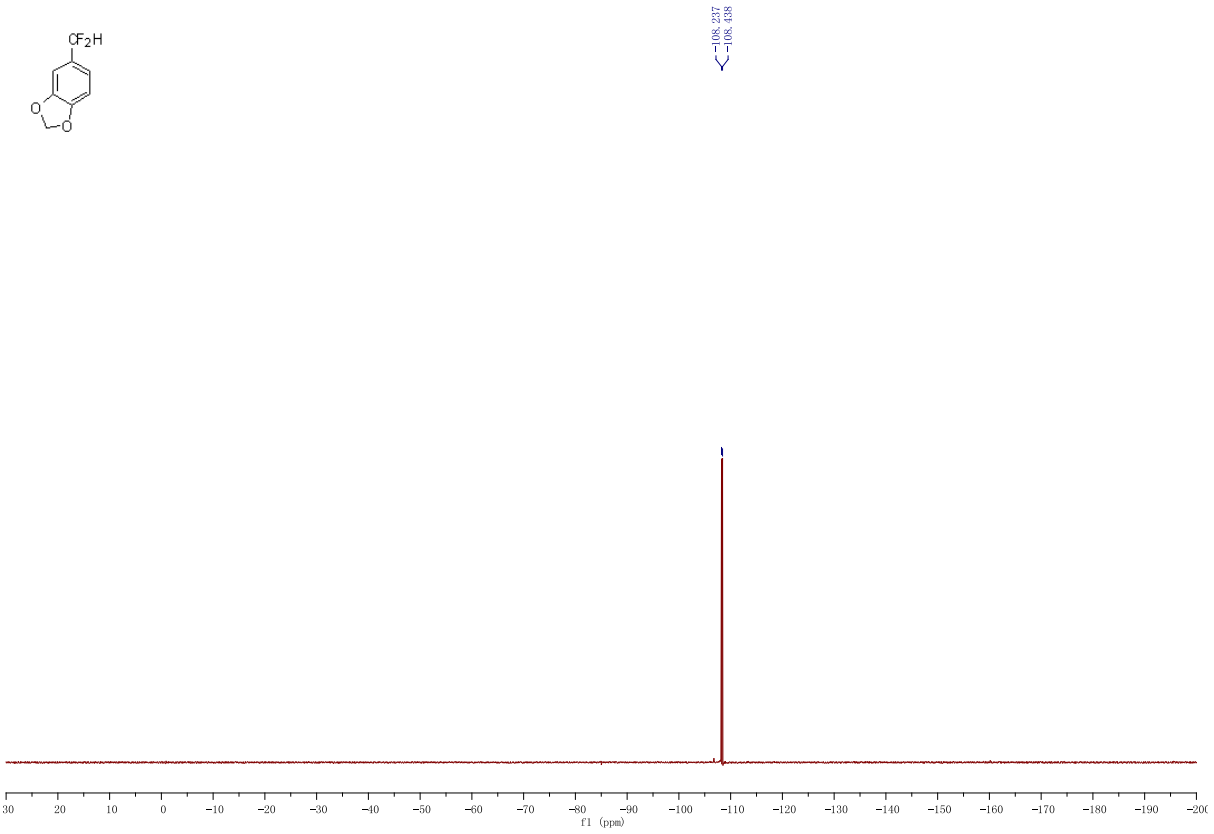

CF2H
MeO
OMe

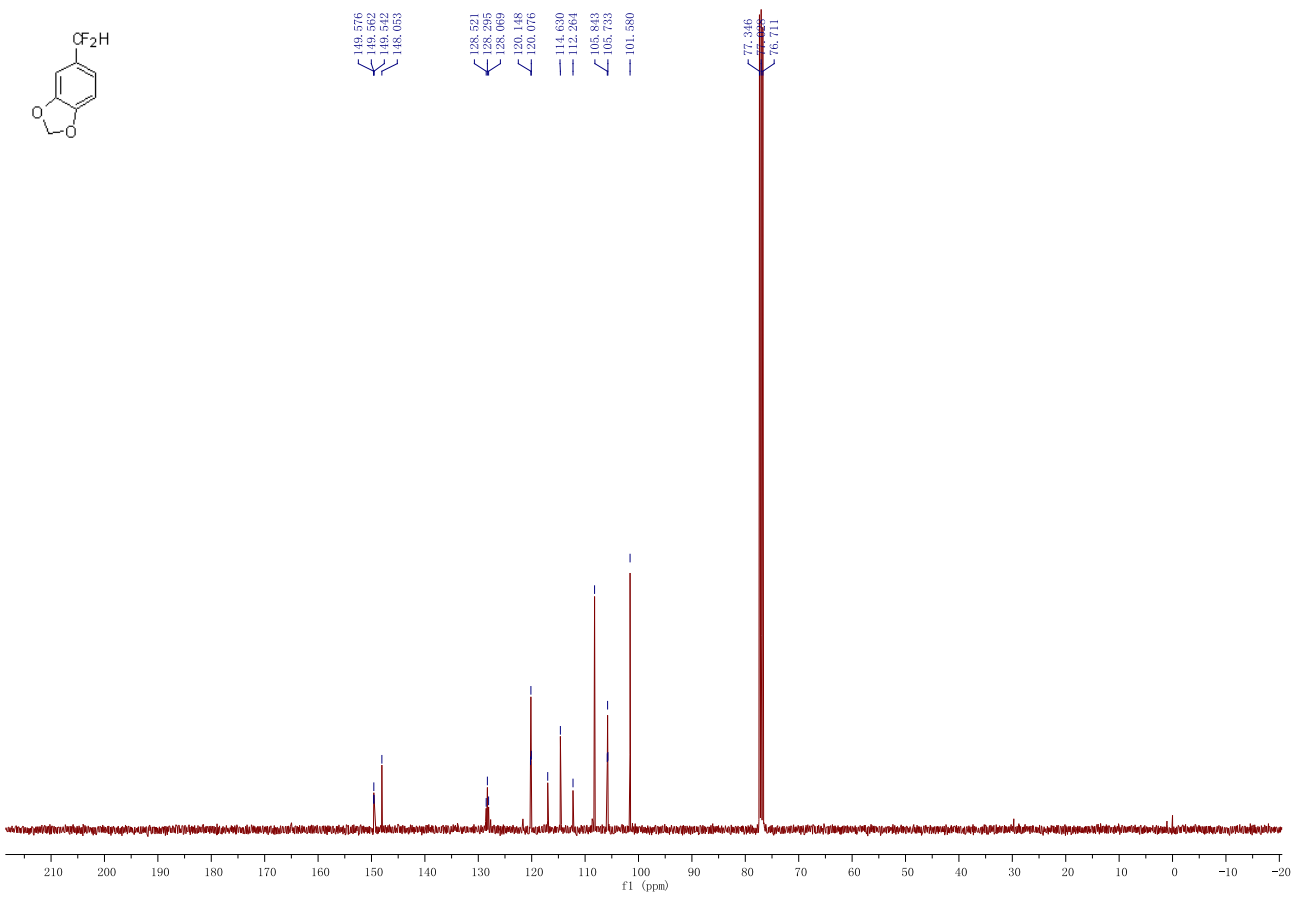

161.066
136.582
136.358
136.138
116.853
114.474
112.093
103.483
103.421
103.357
102.705
102.686
102.672
55.501


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)

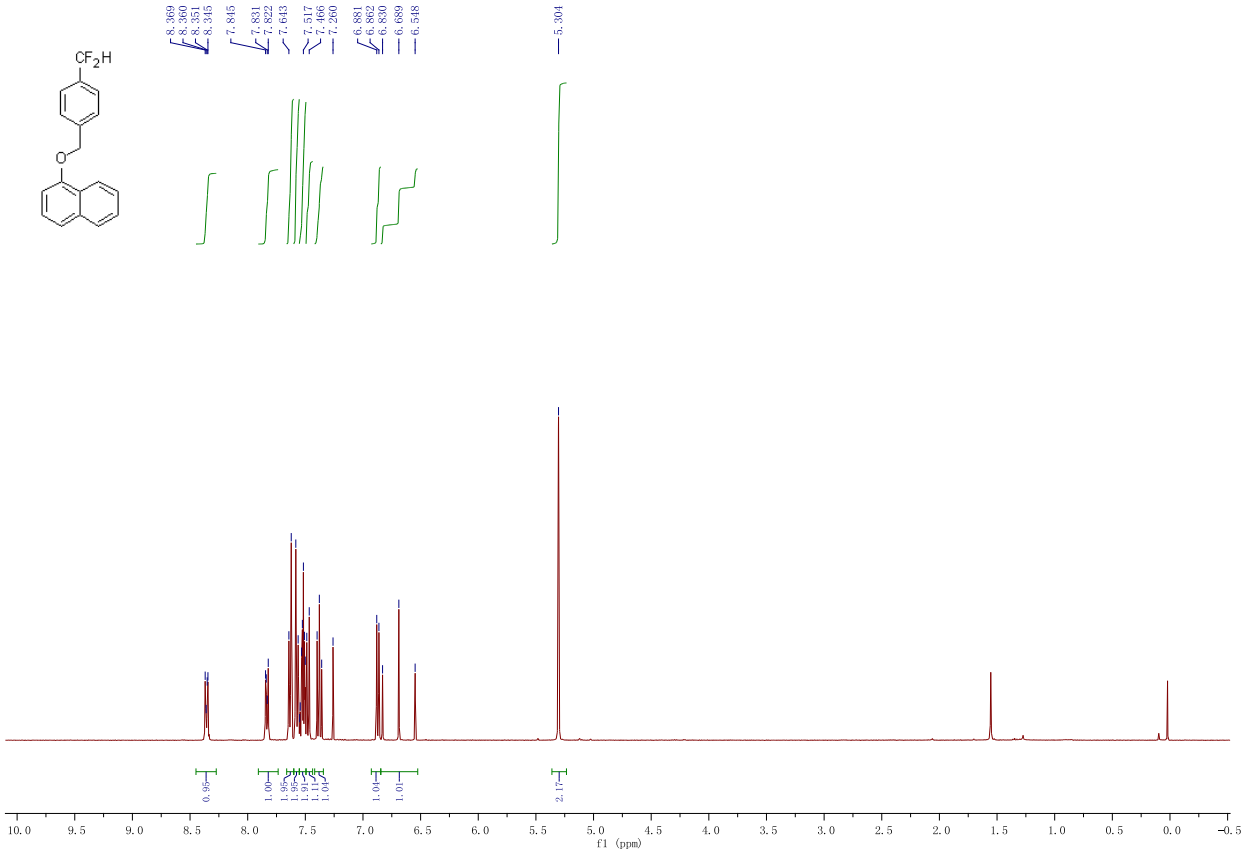
5-(Difluoromethyl)benzo[d][1,3]dioxole (12).

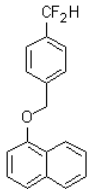




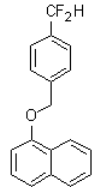


1-((4-(Difluoromethyl)benzyl)oxy)naphthalene (13).



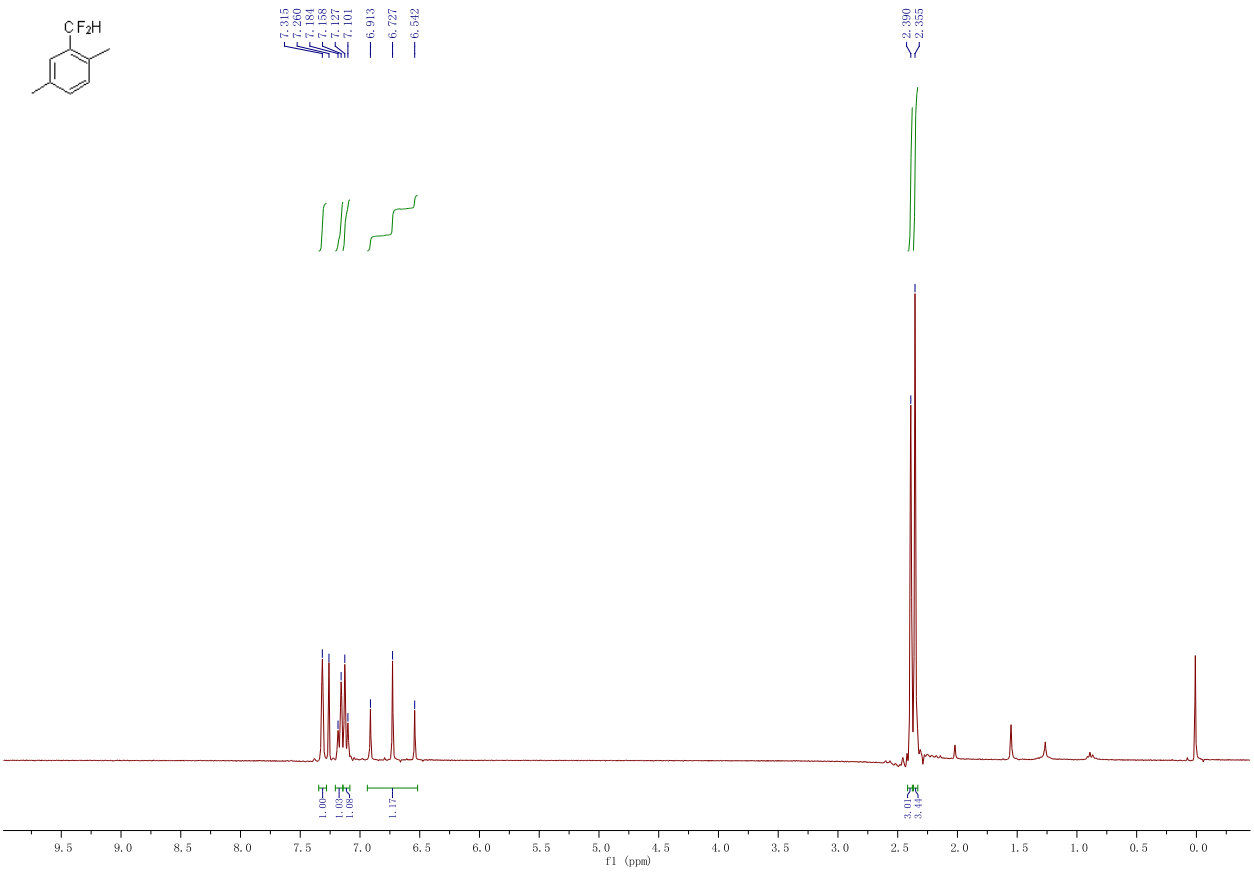

CF_2H
O

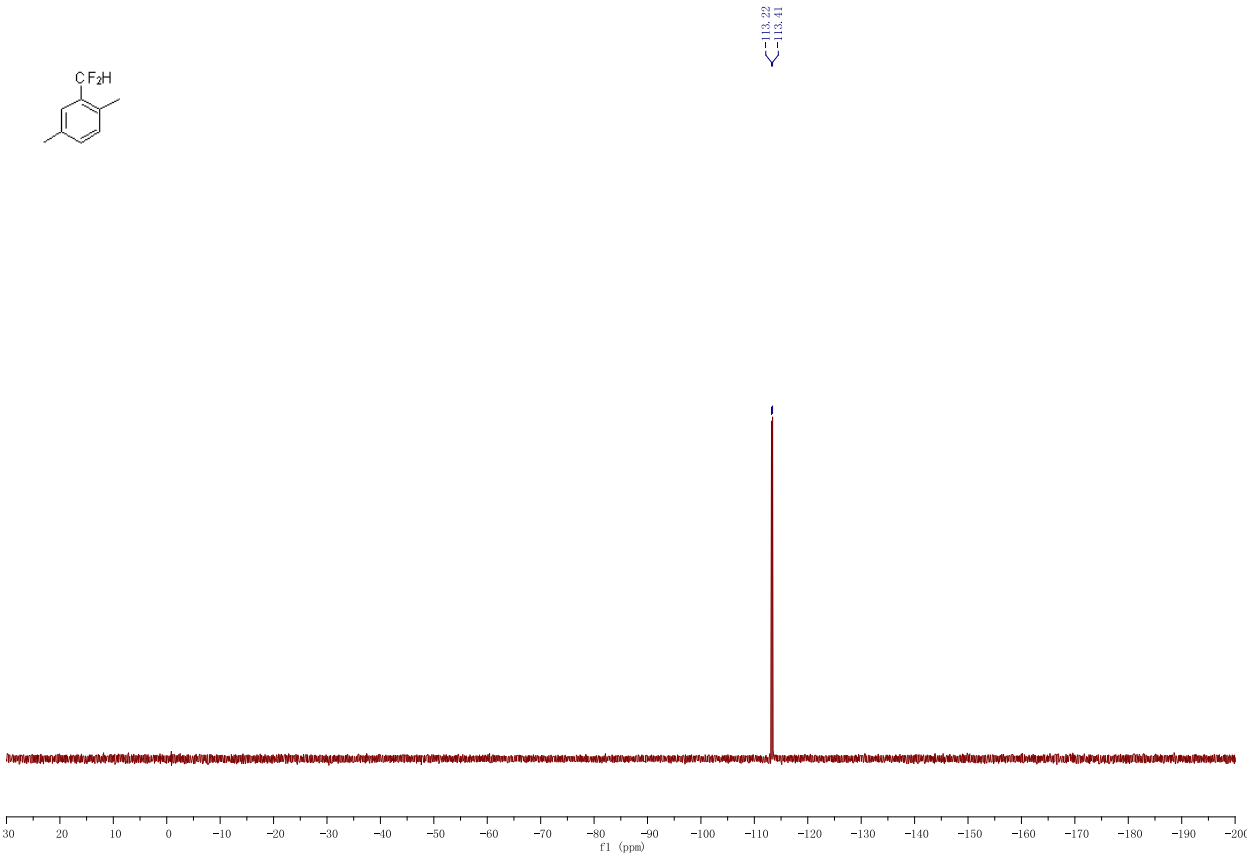
-110.425
-110.576
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


CF_2H
O

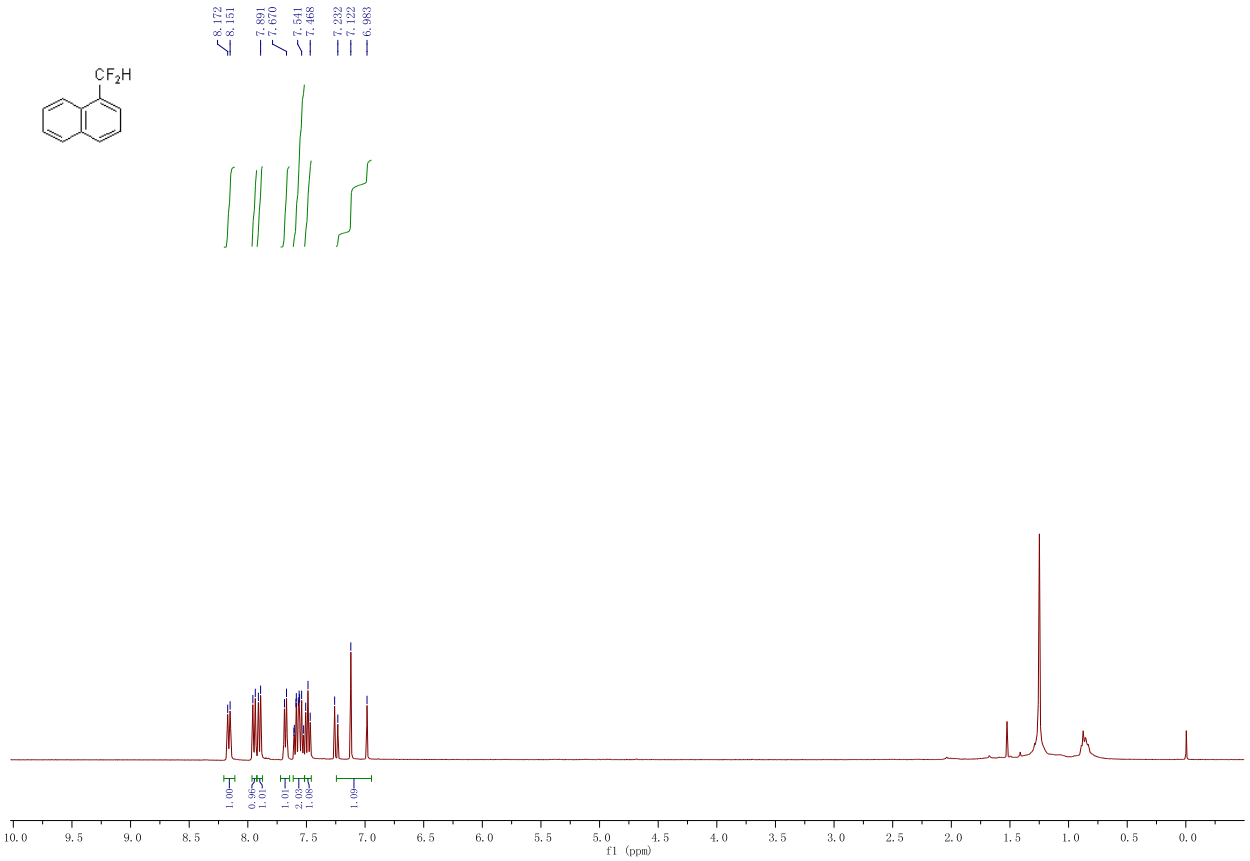
154.237
140.046
140.033
133.995
125.865
125.437
120.819
117.042
114.668
112.297
105.238
77.409
77.091
76.773
69.458
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

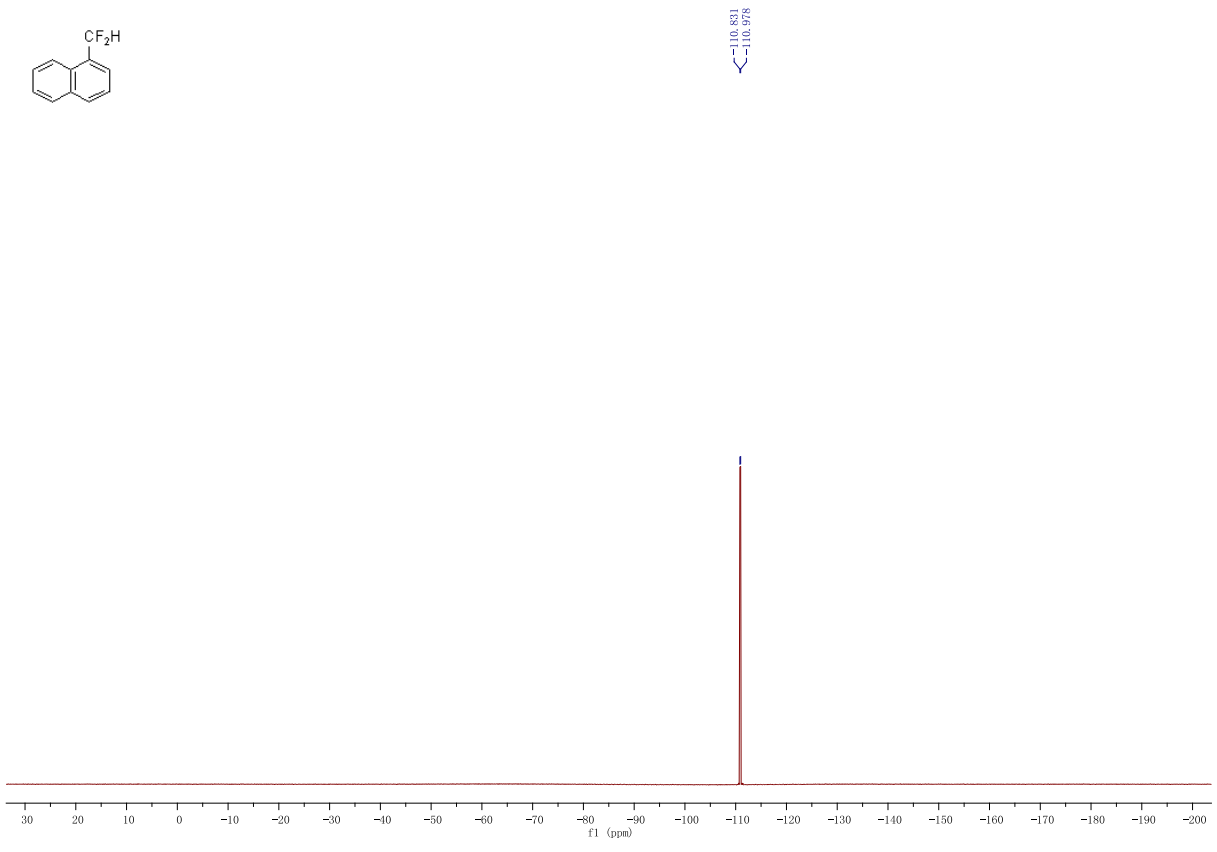
2-(Difluoromethyl)-1,4-dimethylbenzene (14).

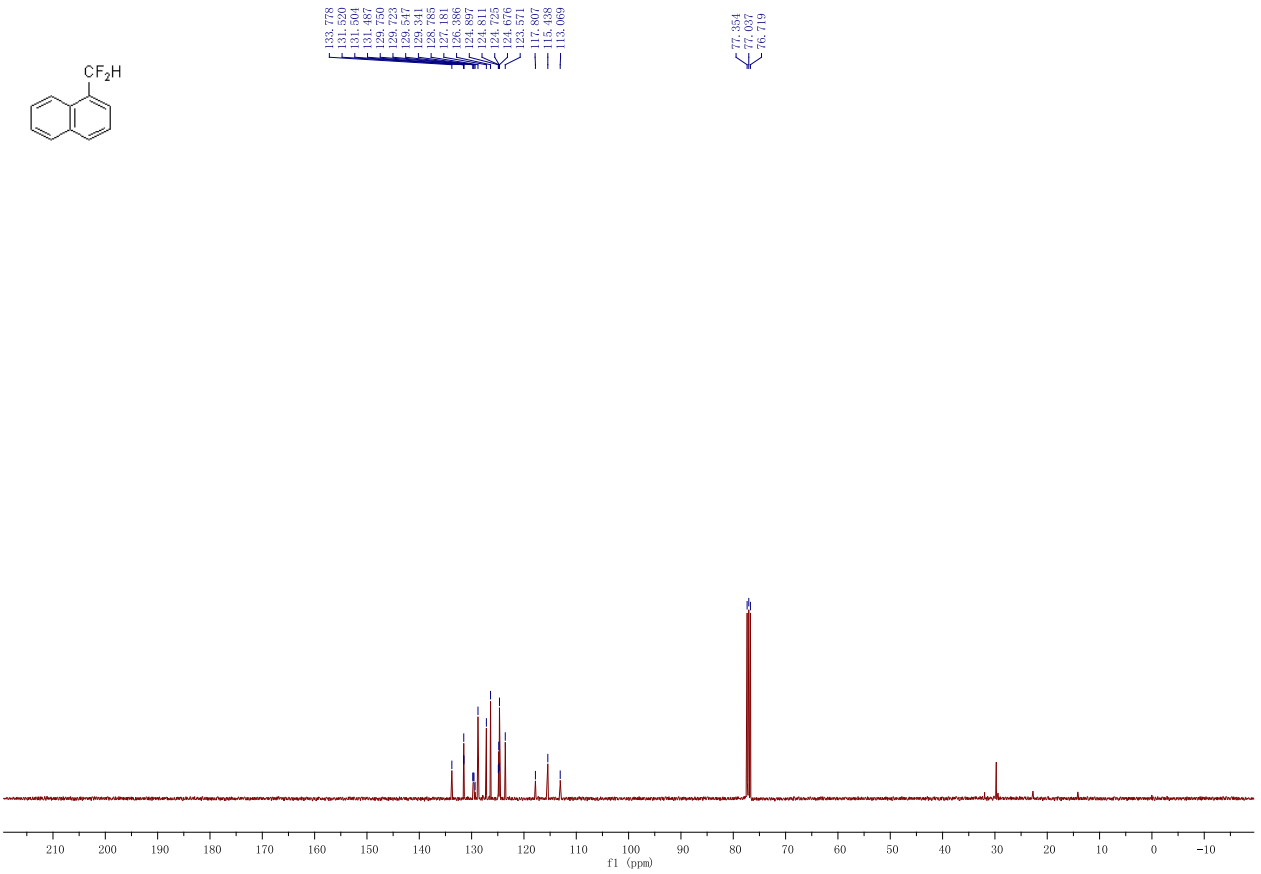




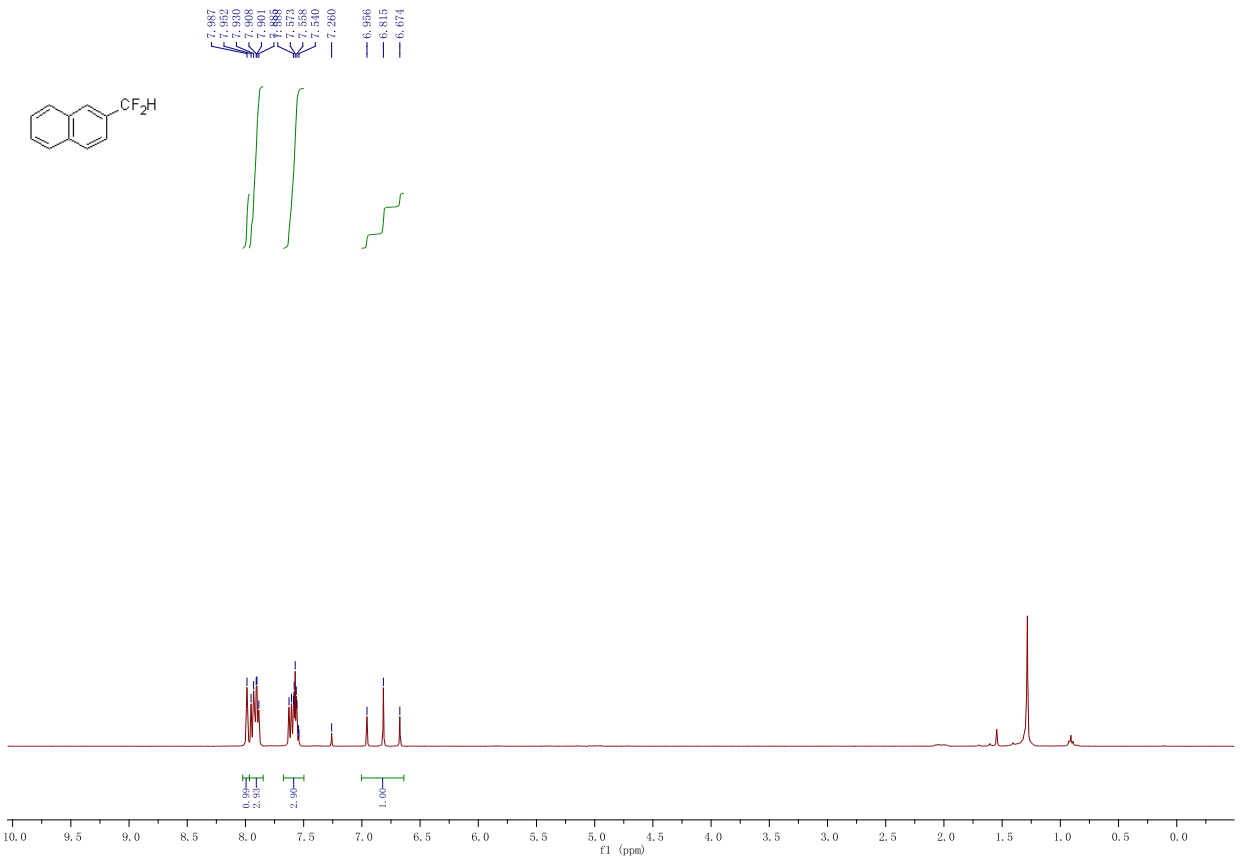
1-(Difluoromethyl)naphthalene (15).

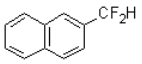




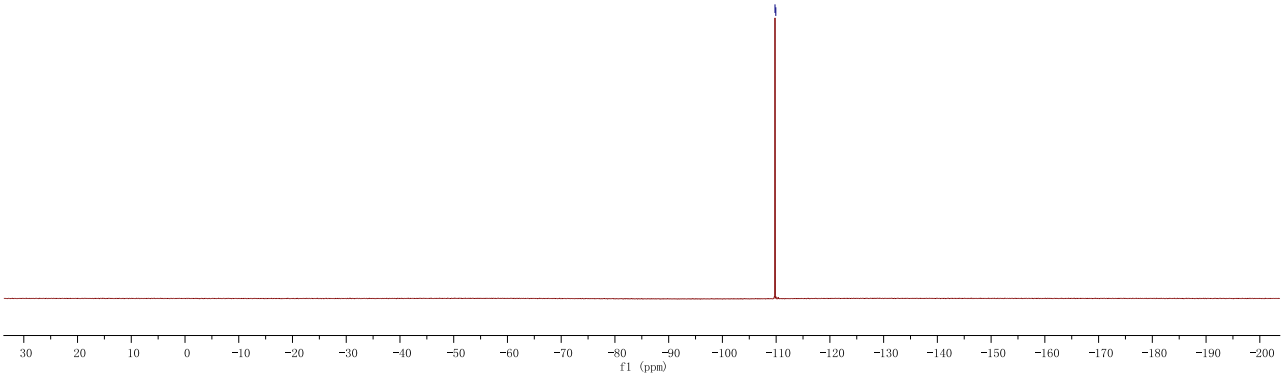


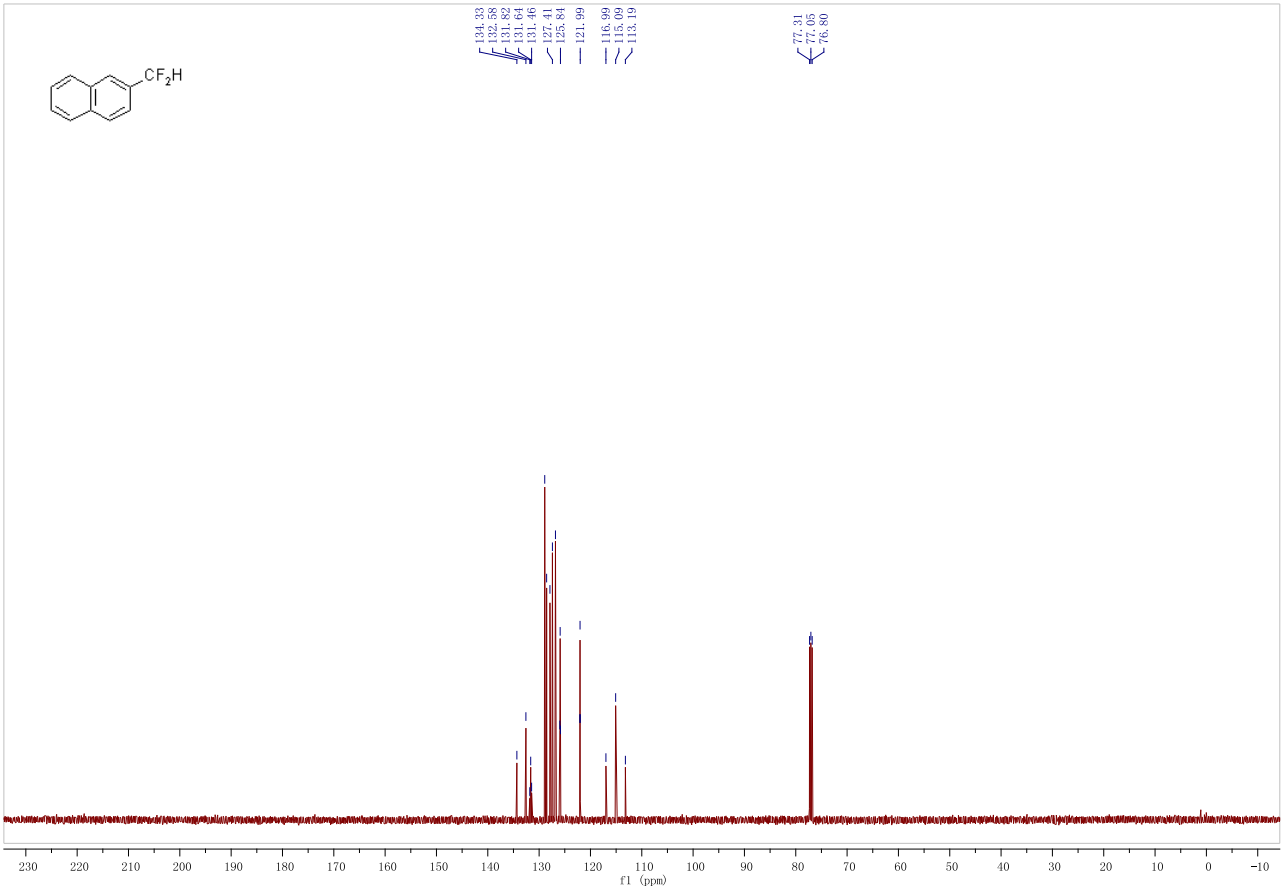
2-(Difluoromethyl)naphthalene (16).



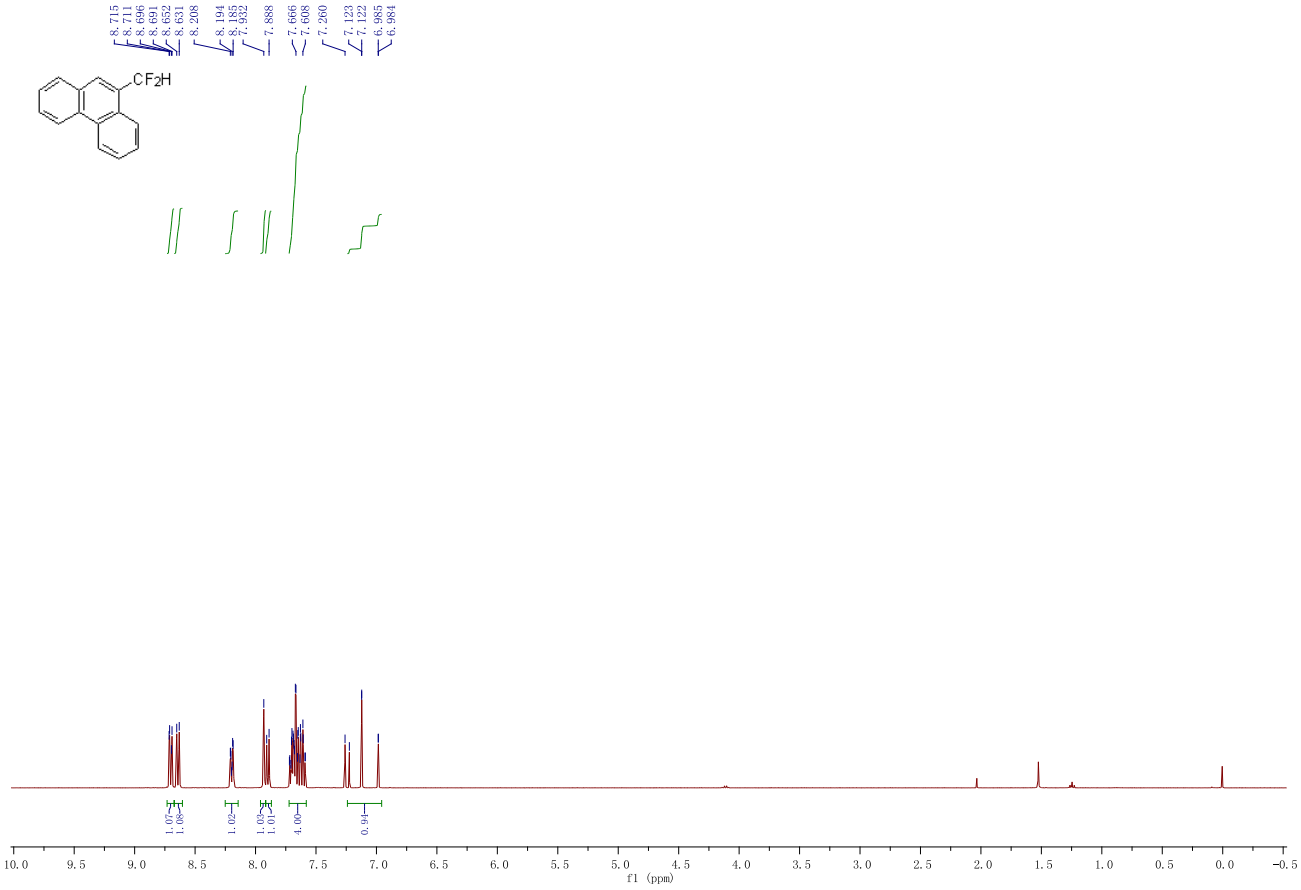

CF2H

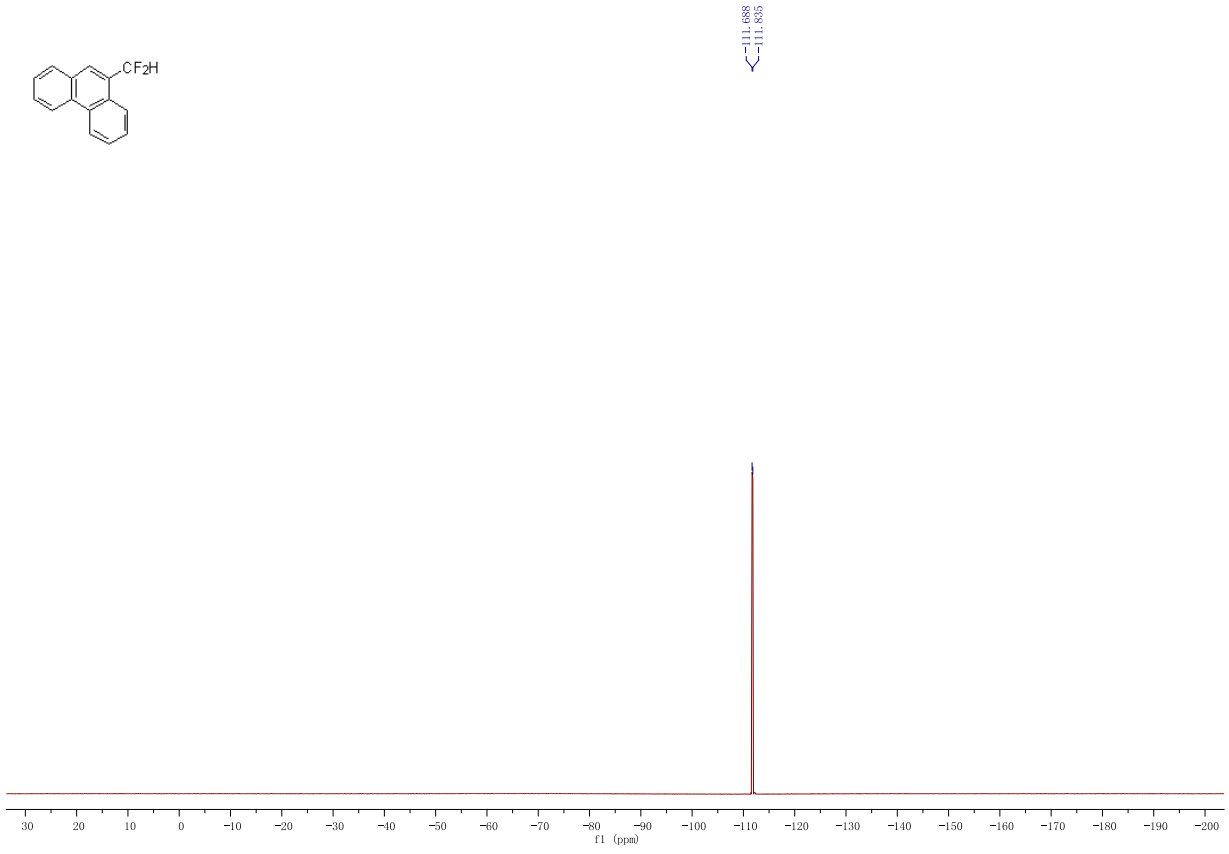

-109.79
-109.94

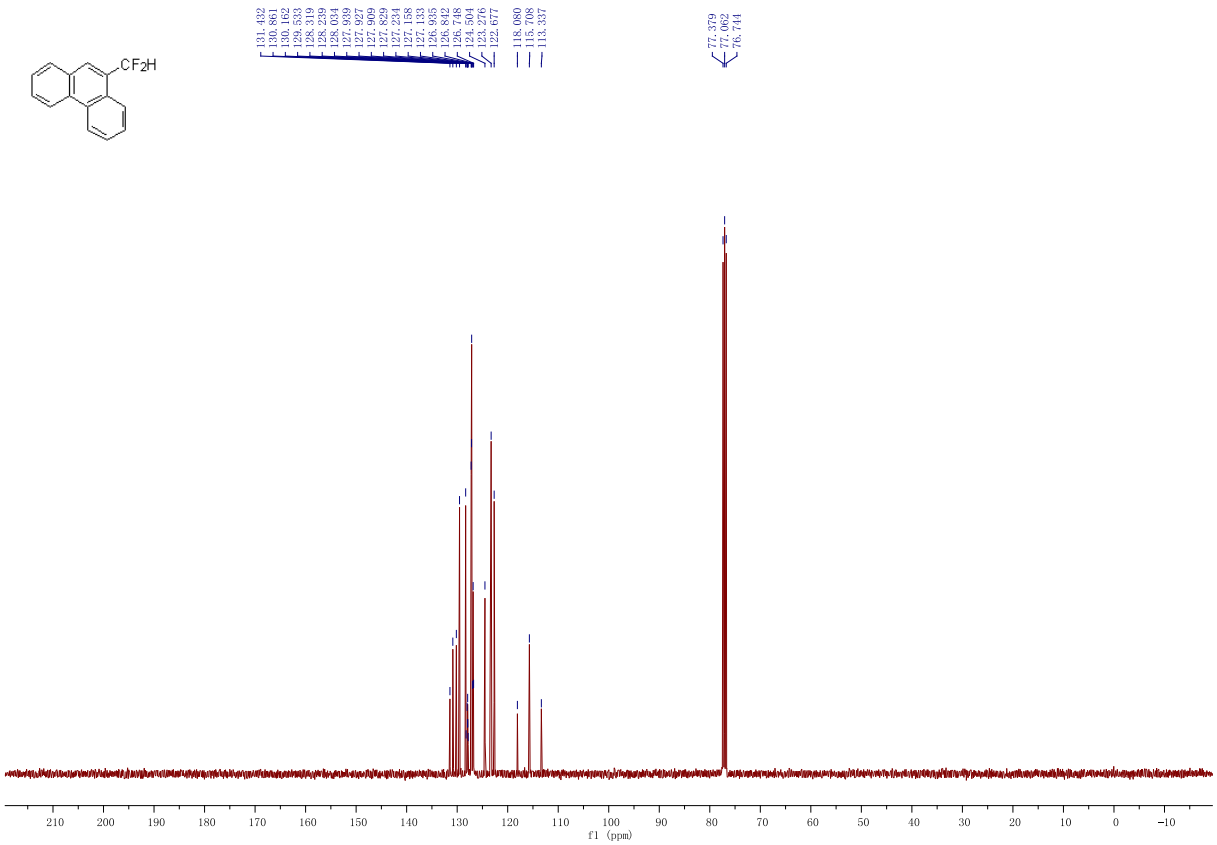

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


134.33
132.88
131.82
131.64
131.46
127.41
125.84
121.99
116.99
115.09
113.19
77.31
77.05
76.80
CF2H
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)

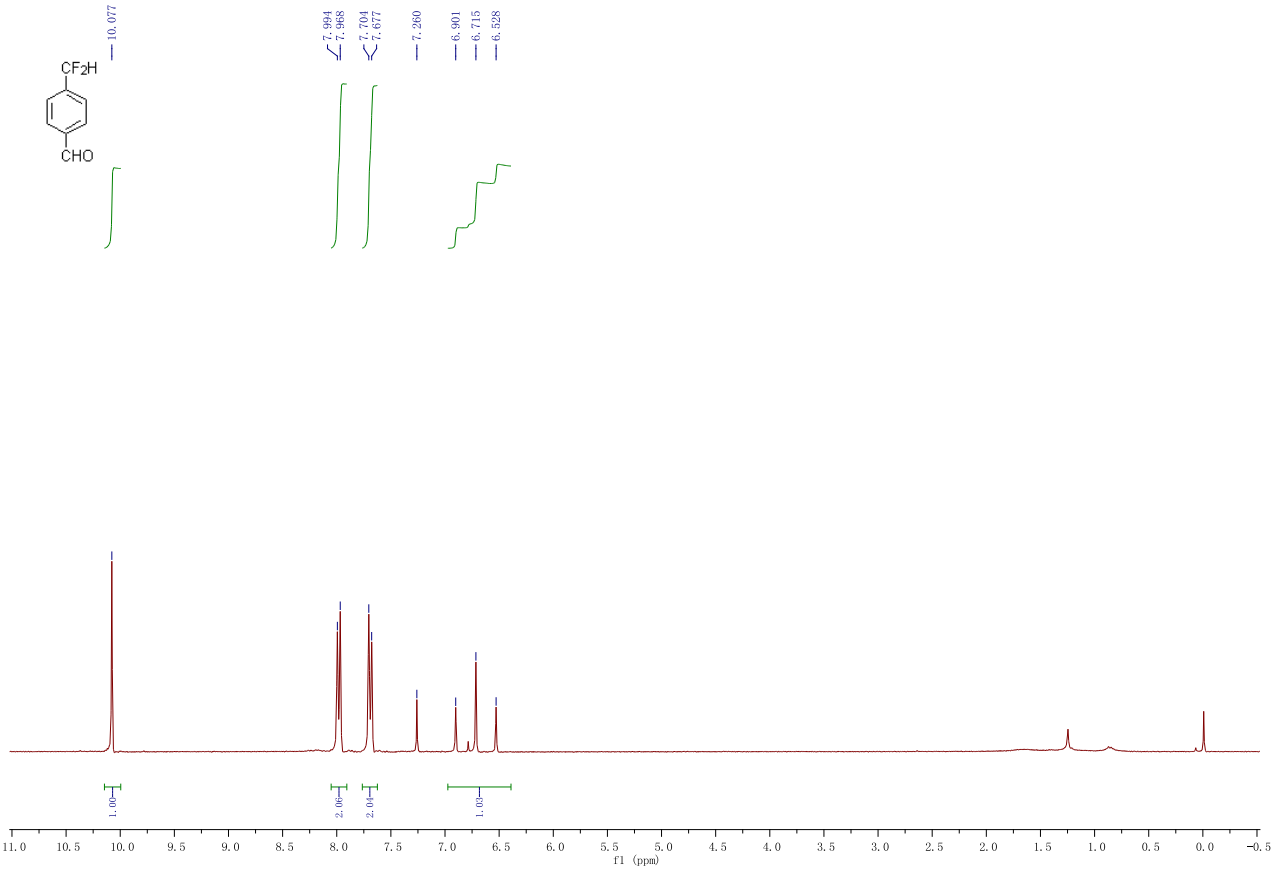
9-(Difluoromethyl)phenanthrene (17).

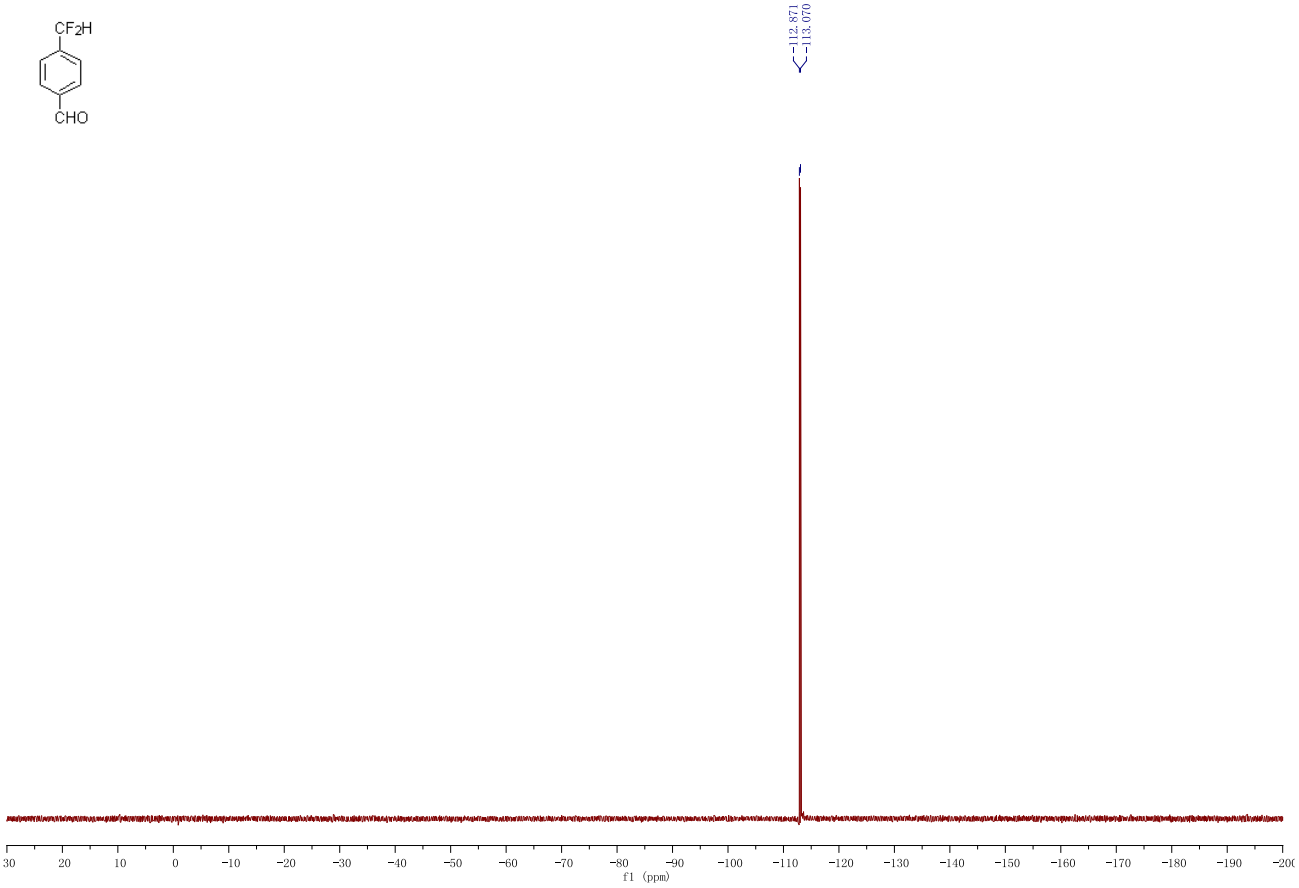


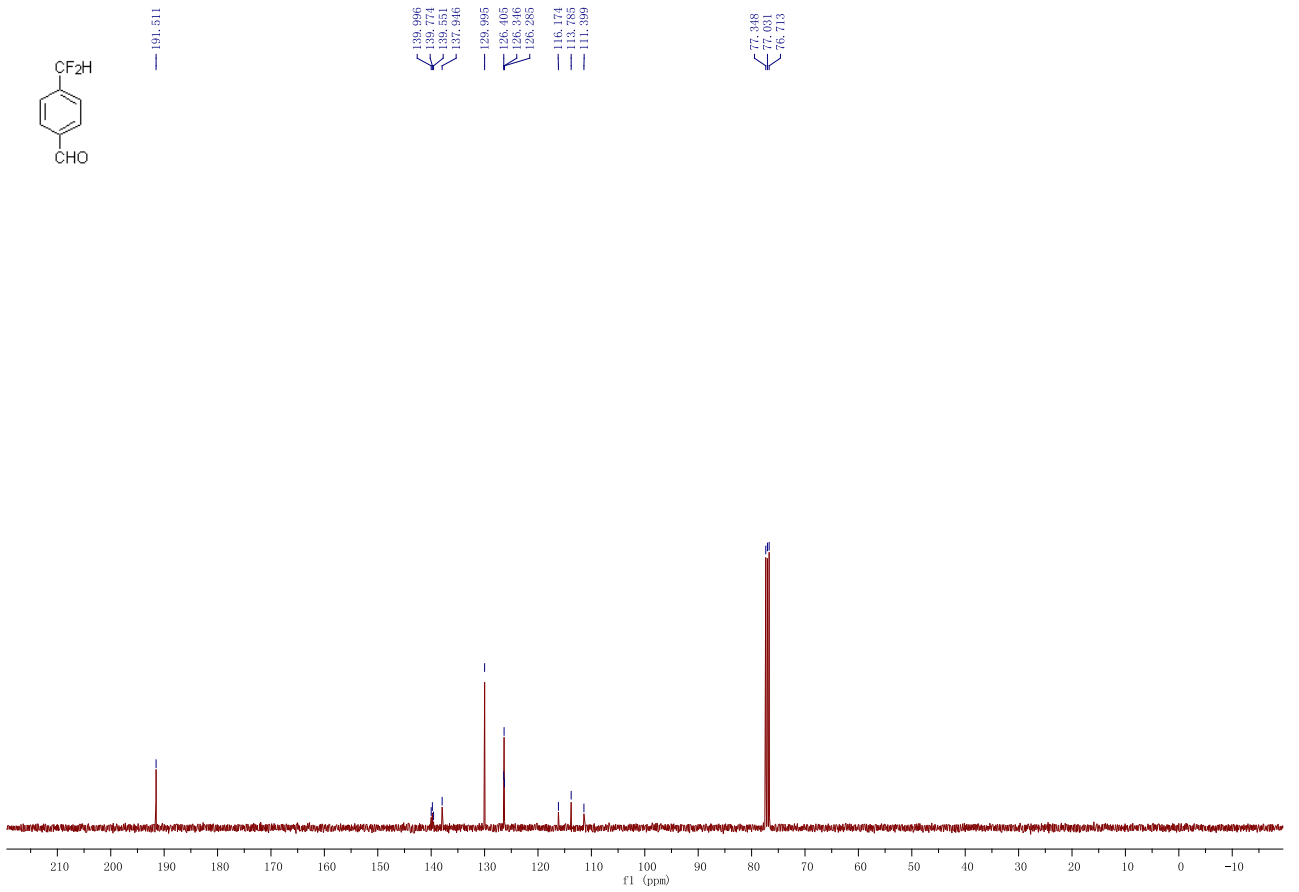




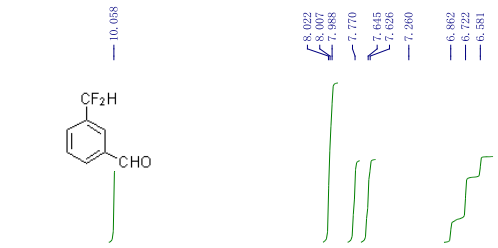
4-(Difluoromethyl)benzaldehyde (18).

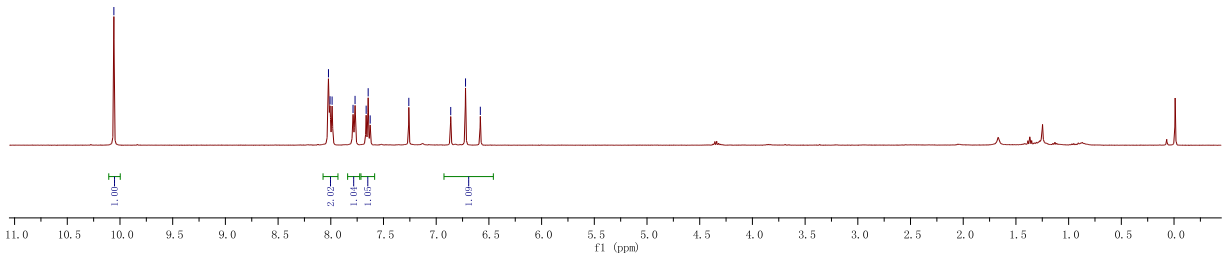


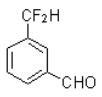

CF2H
CHO
-112.871
-113.070
f1 (ppm)

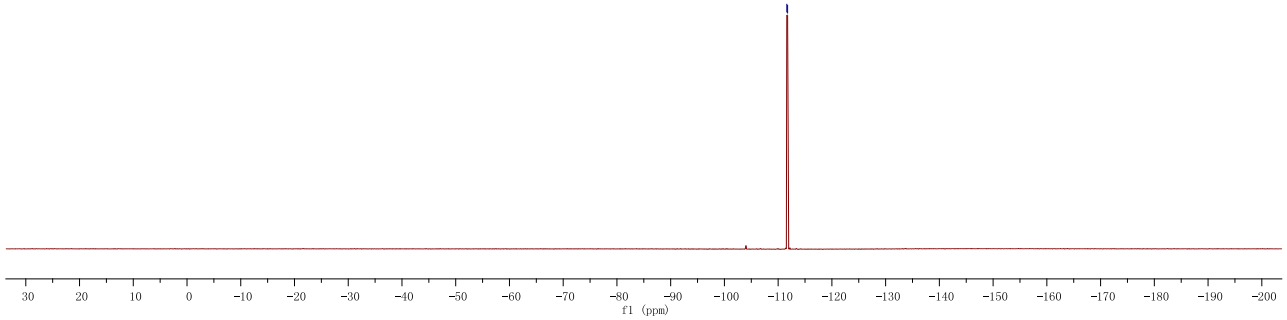

191.511
139.996
139.774
139.551
137.946
129.995
126.405
126.346
126.285
116.174
113.785
111.399
77.348
77.031
76.713
CF2H
CHO
f1 (ppm)

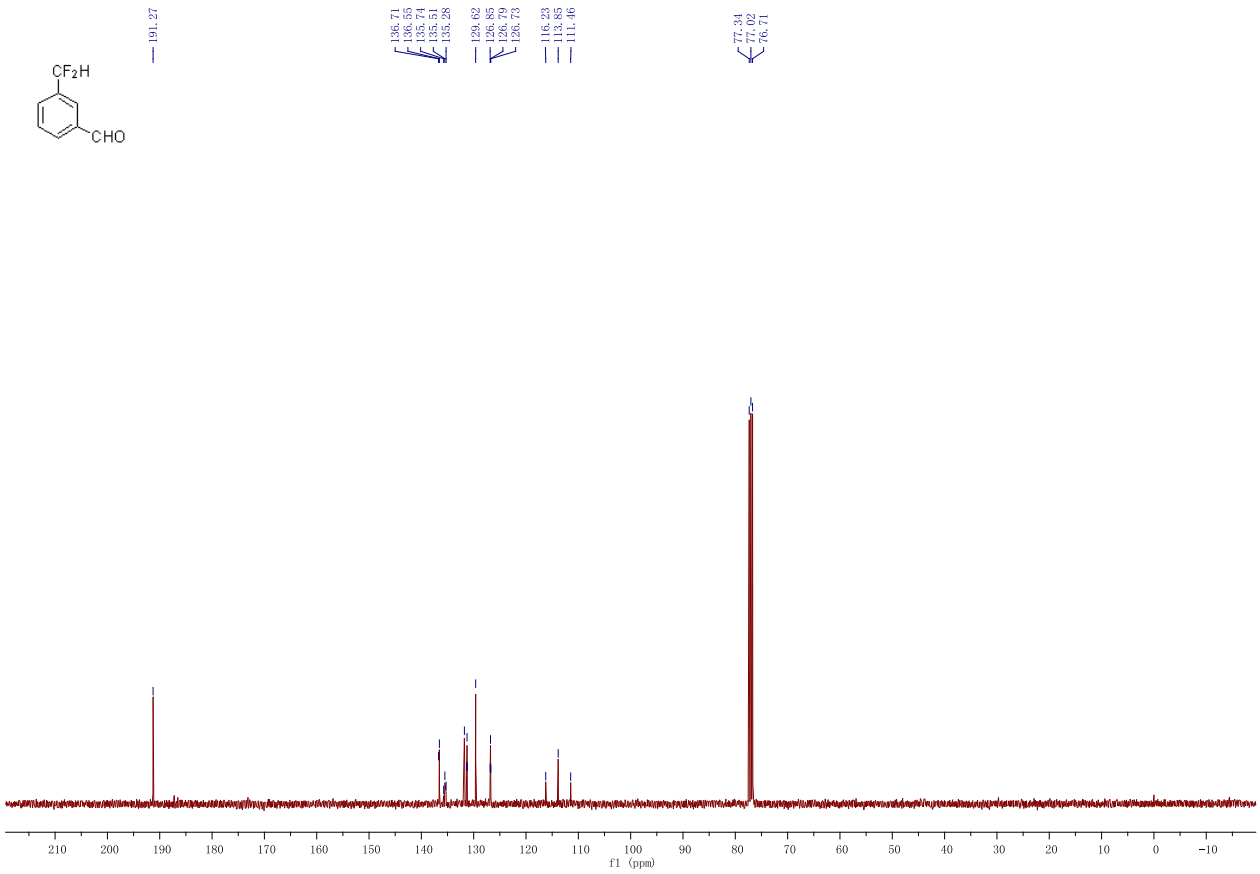
3-(Difluoromethyl)benzaldehyde (19).



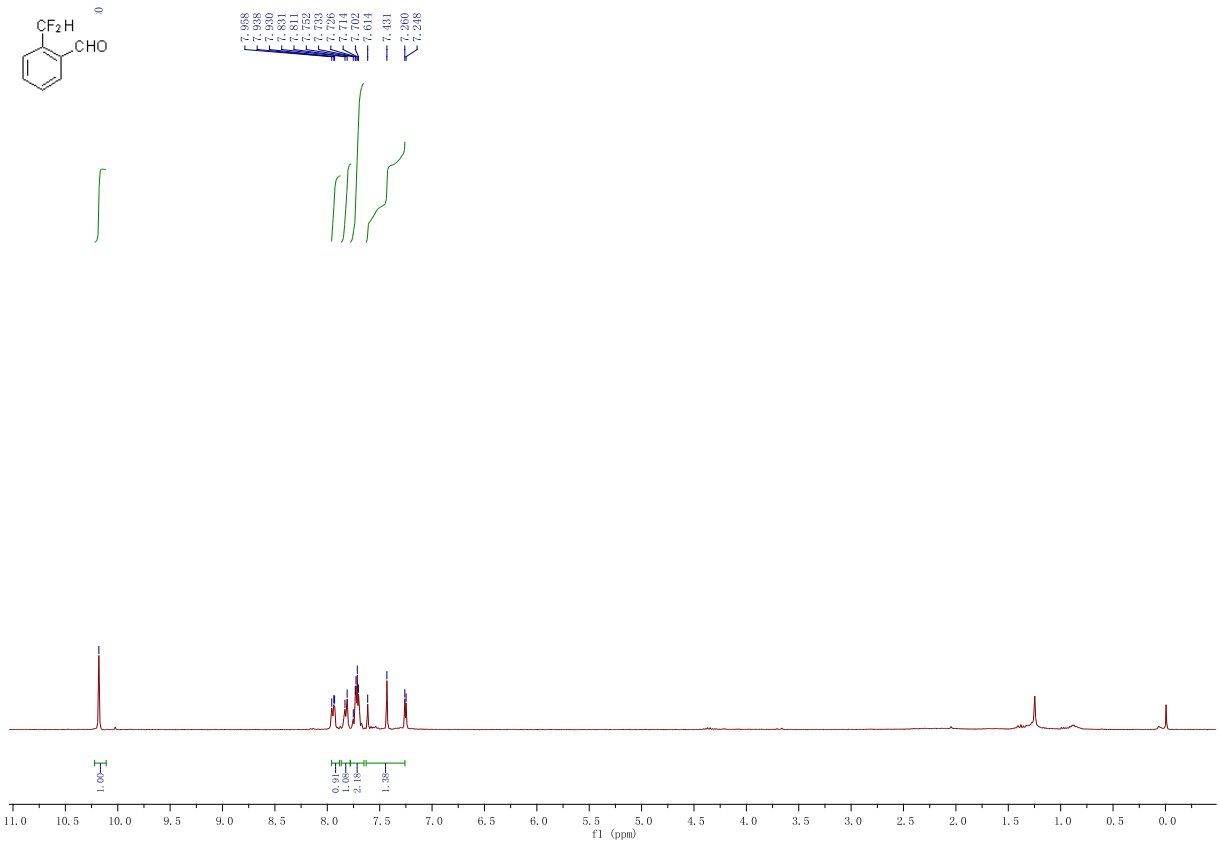


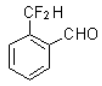






2-(Difluoromethyl)benzaldehyde (20).



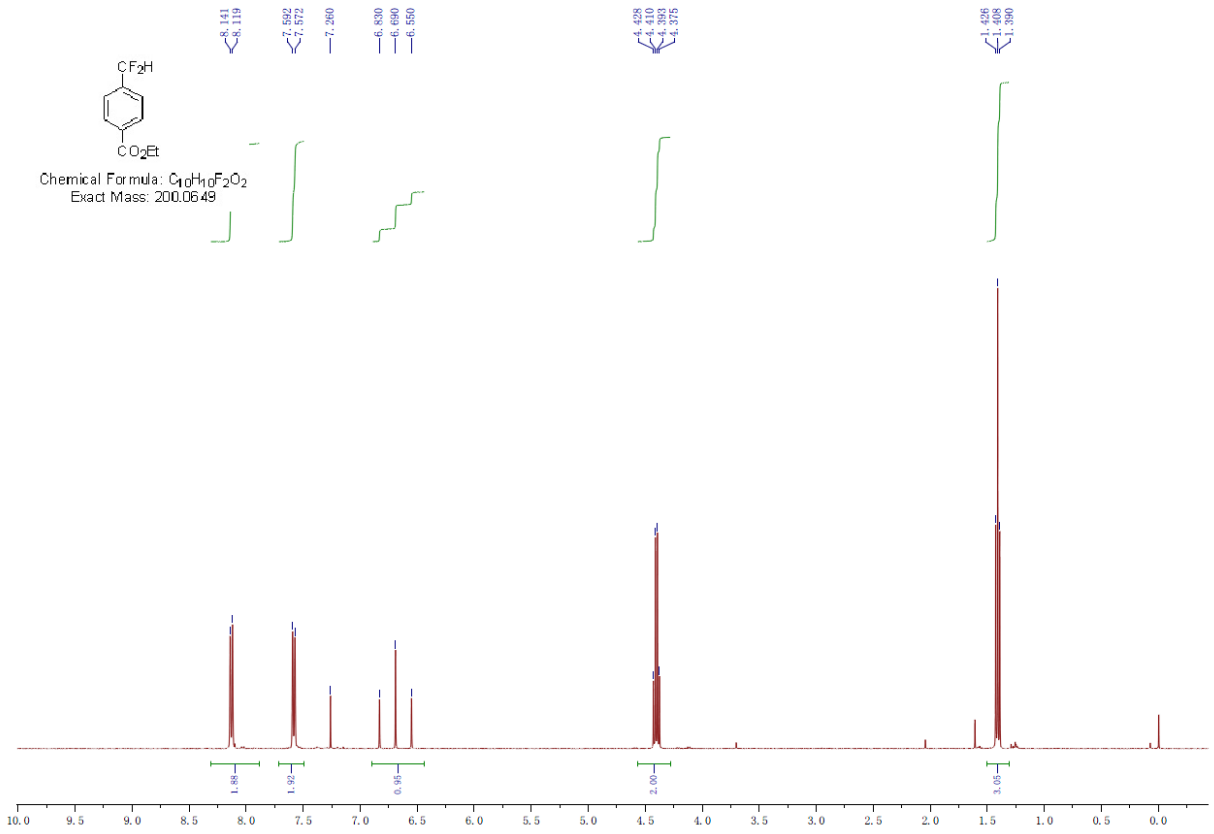

CF2H
CHO

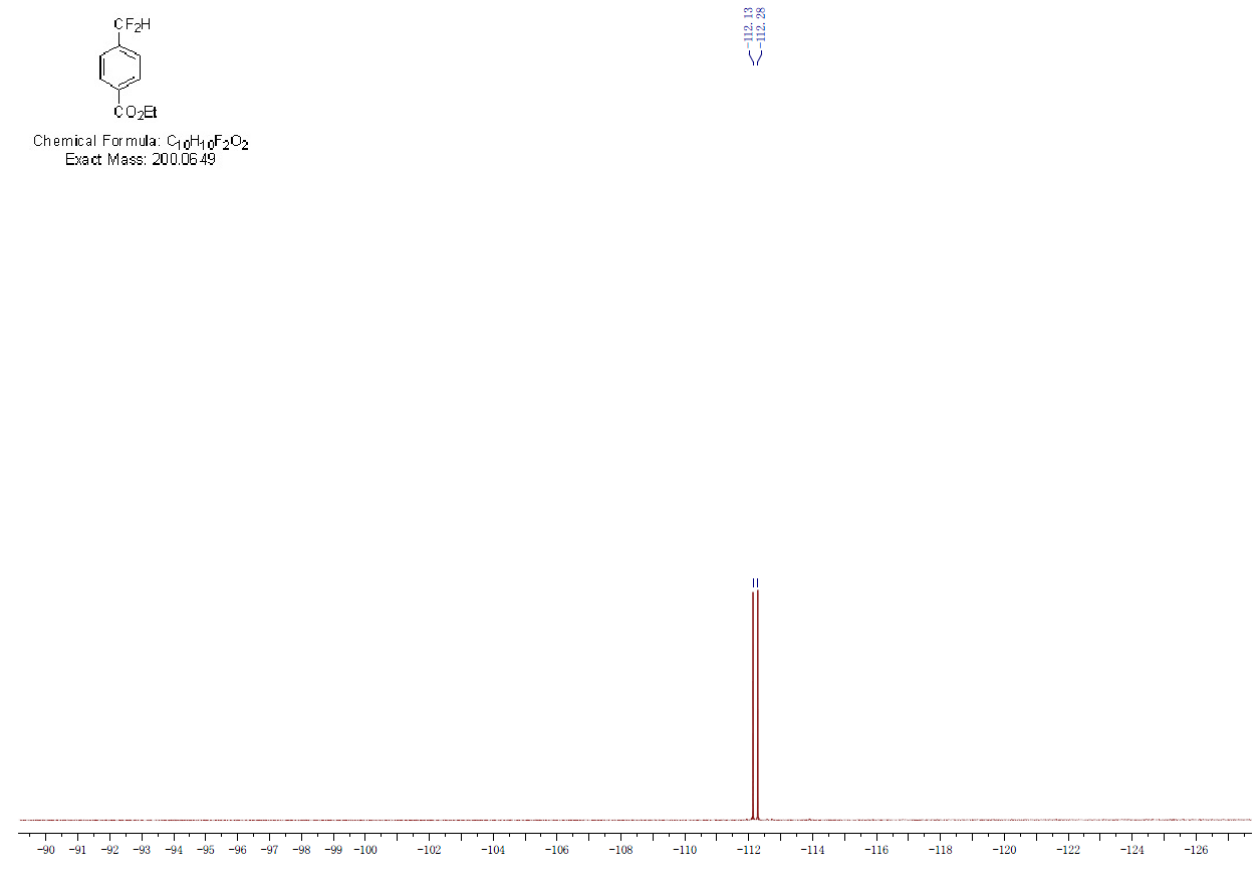
-112.034
-112.229
f1 (ppm)

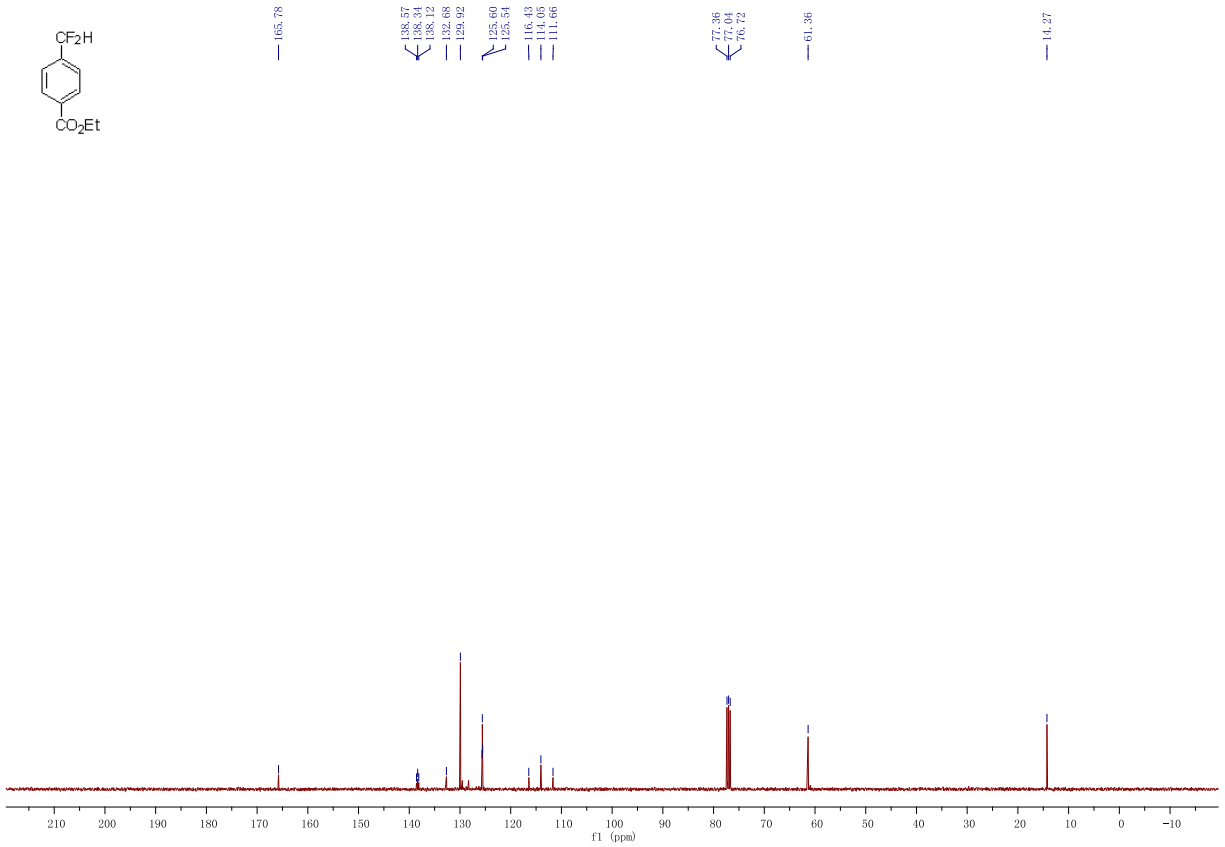

CF2H
CHO

191.714
134.588
134.046
133.447
131.109
131.094
131.079
128.990
126.896
126.523
126.457
113.890
111.995
110.100
77.263
77.009
76.755
f1 (ppm)

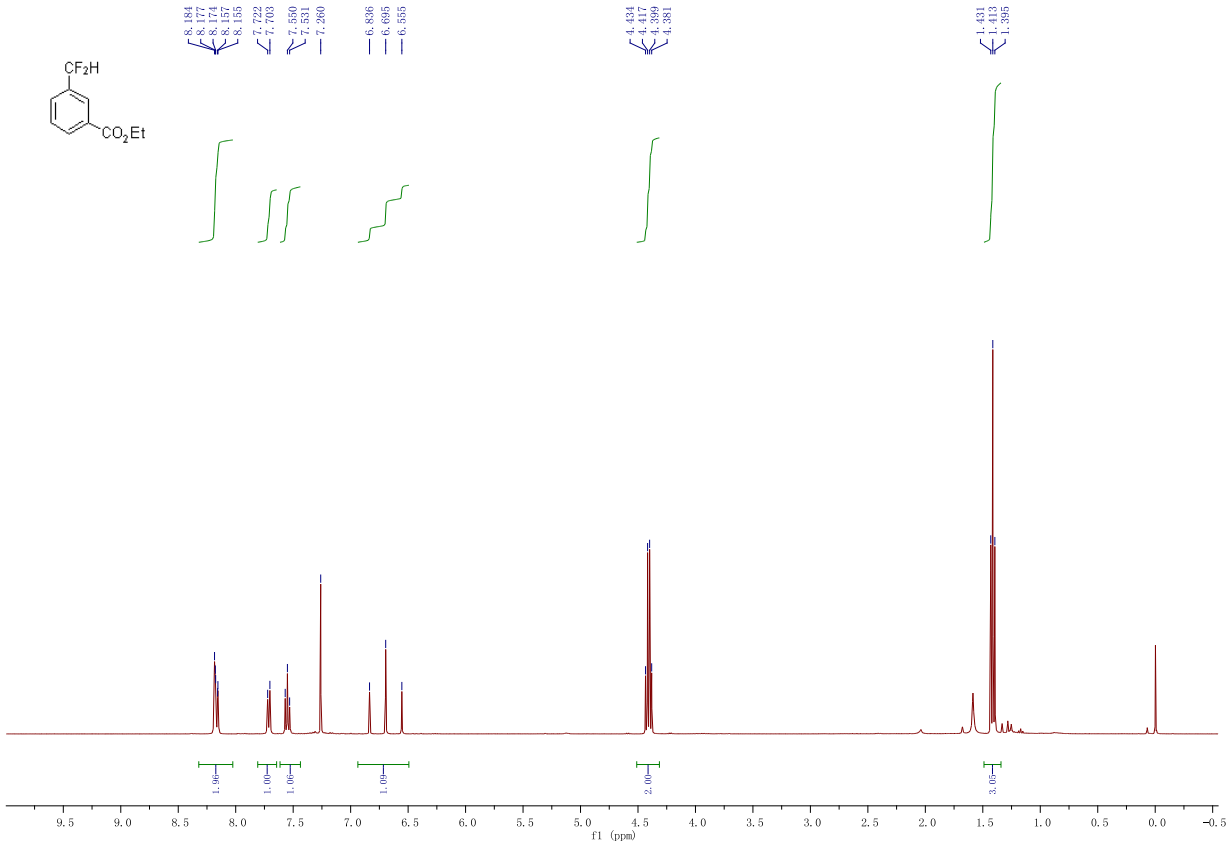
Ethyl 4-(difluoromethyl)benzoate (21).

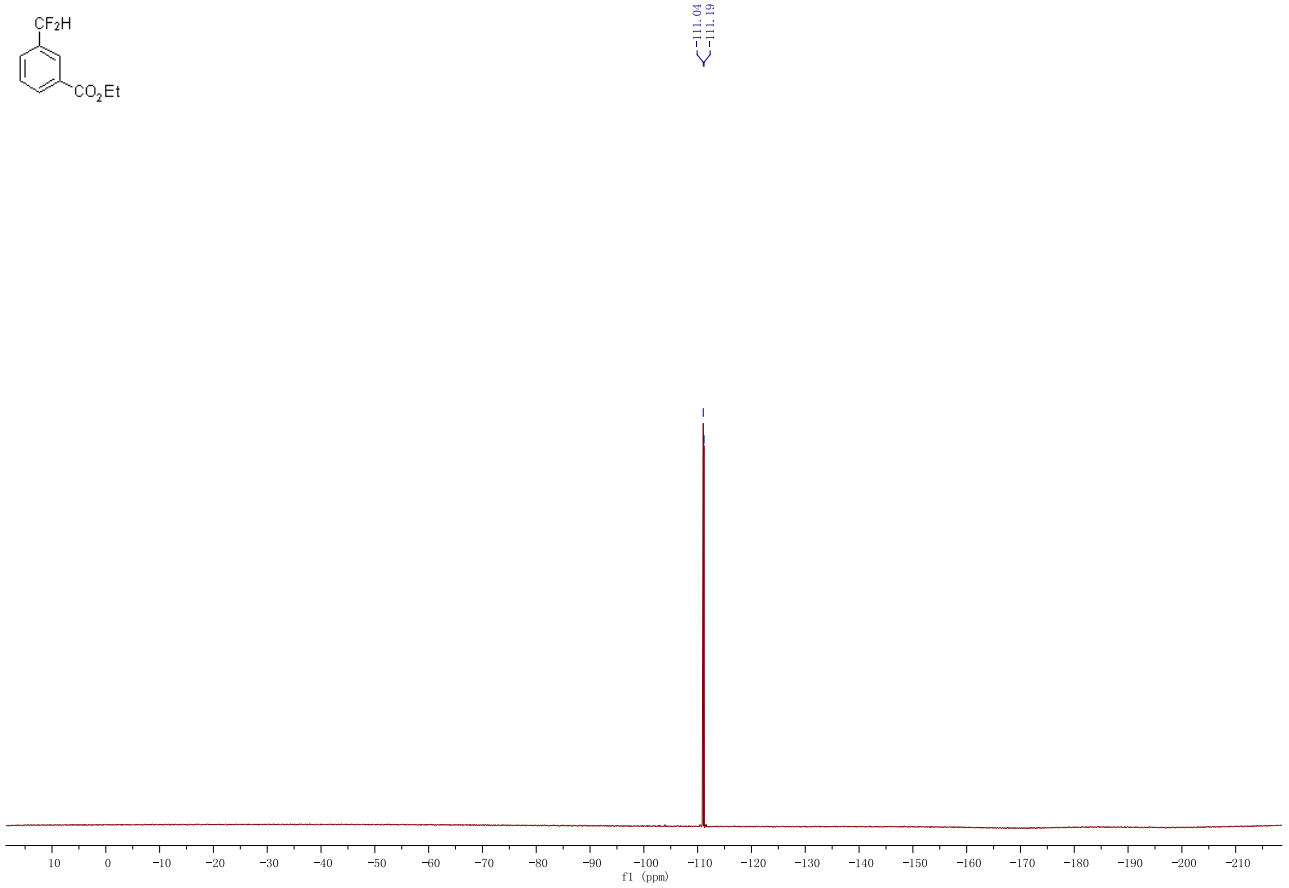


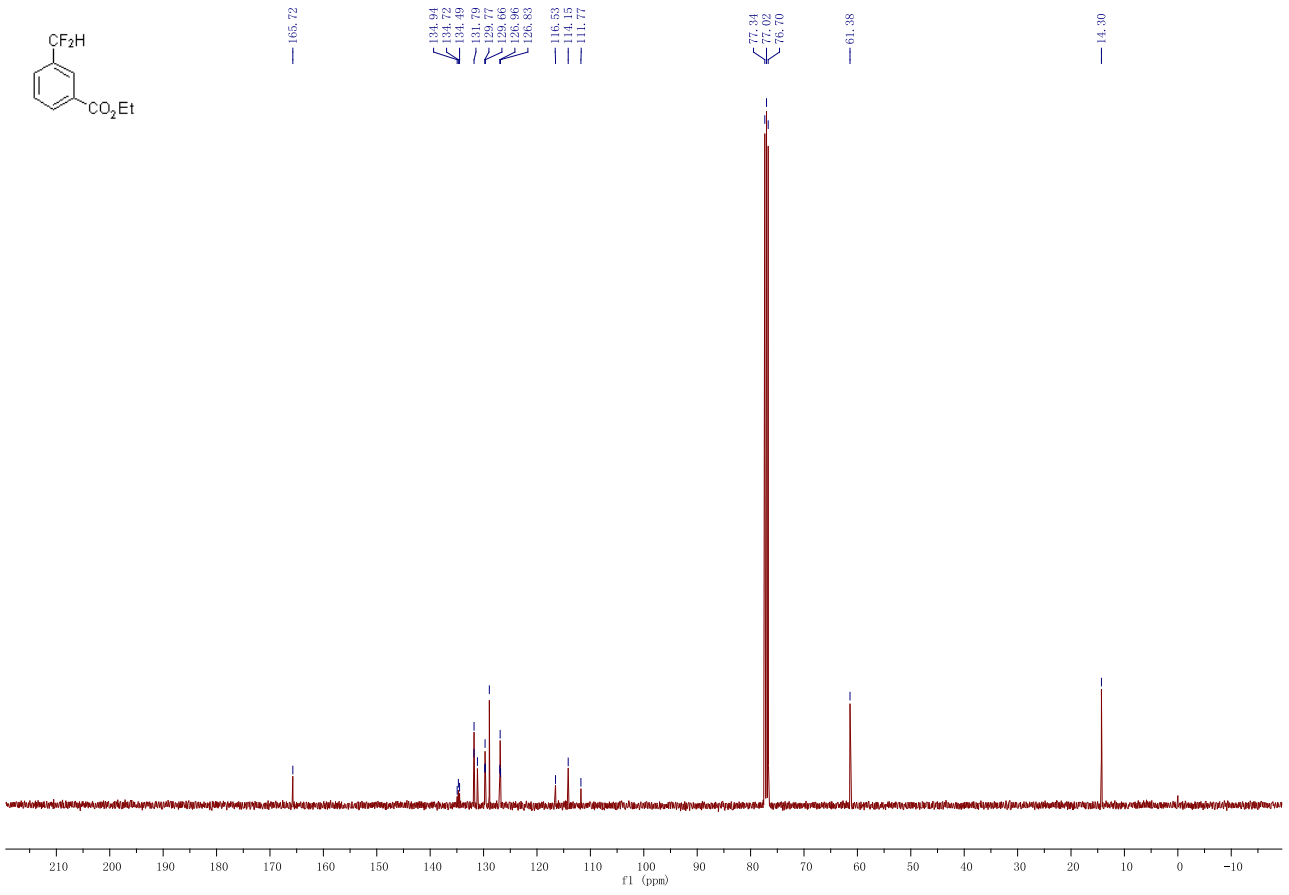




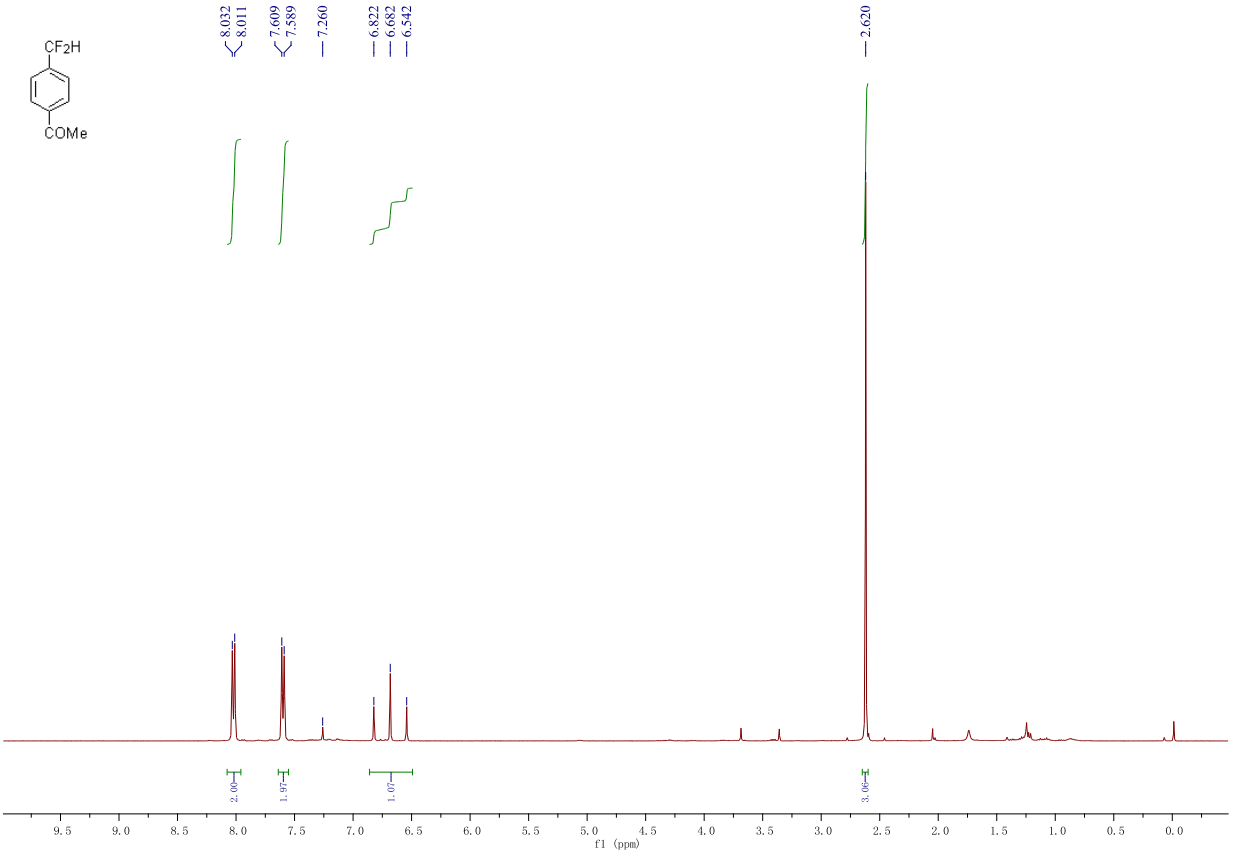
Ethyl 3-(difluoromethyl)benzoate (22).

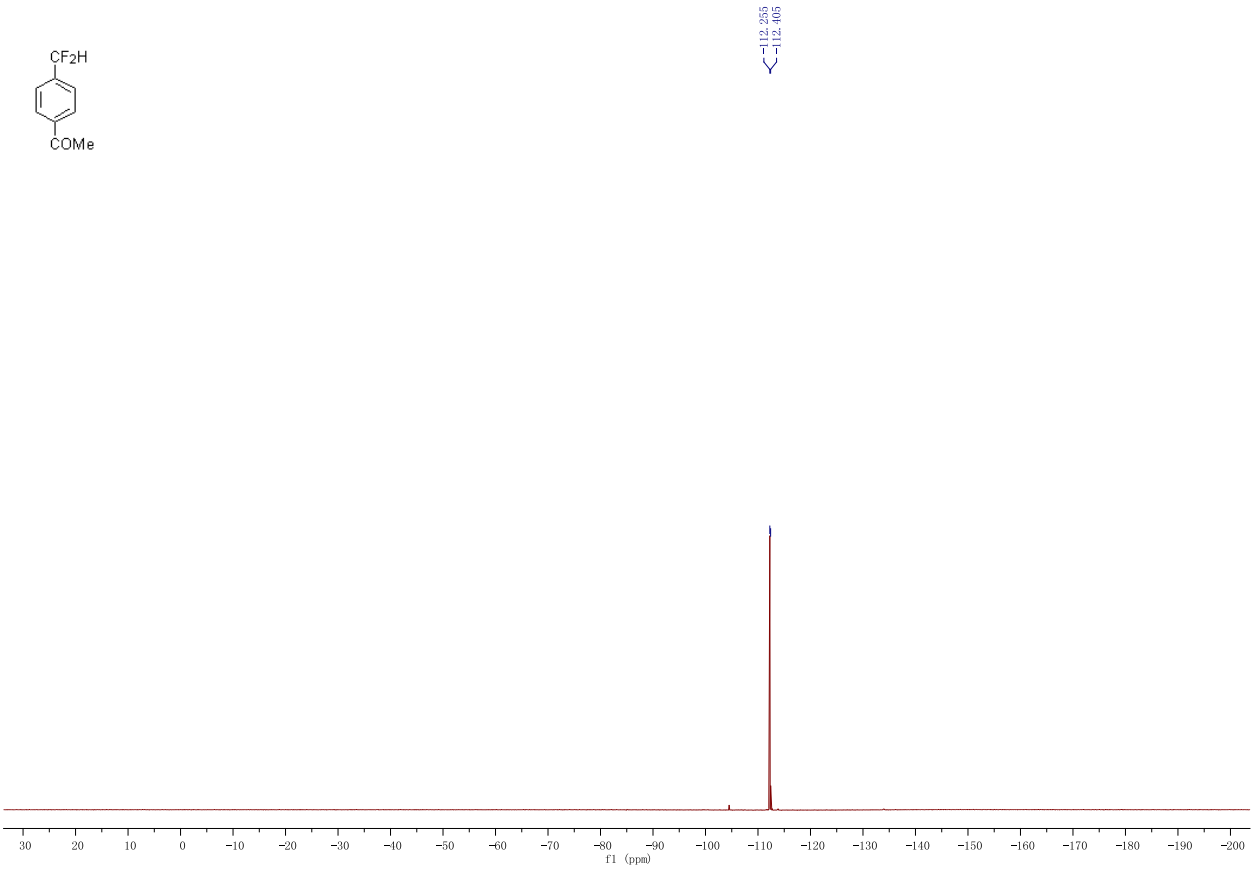


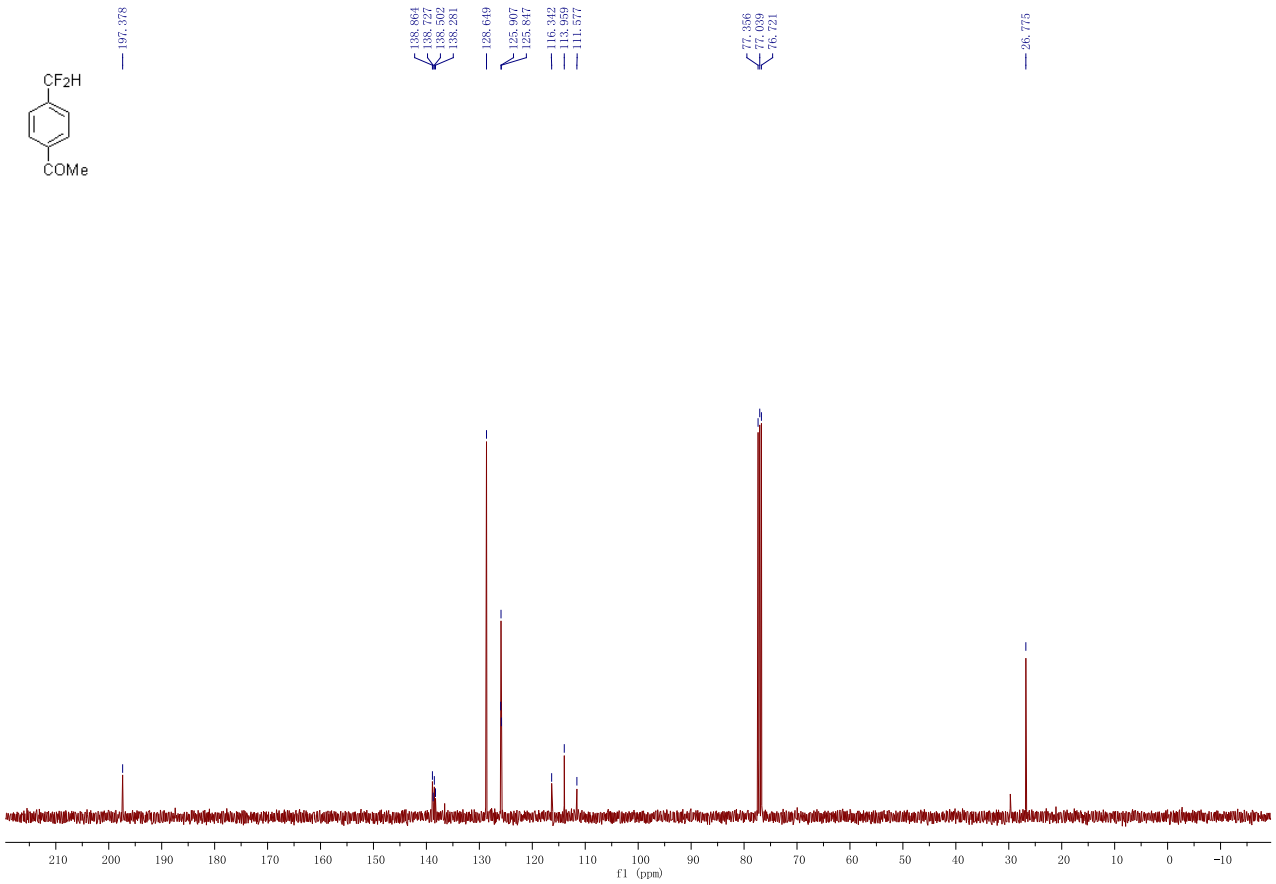

CF2H
CO2Et
-111.04
-111.19
f1 (ppm)


CF2H
CO2Et
165.72
134.94
134.72
134.49
131.79
129.77
129.66
126.96
126.83
116.53
114.15
111.77
77.34
77.02
76.70
61.38
14.30
f1 (ppm)

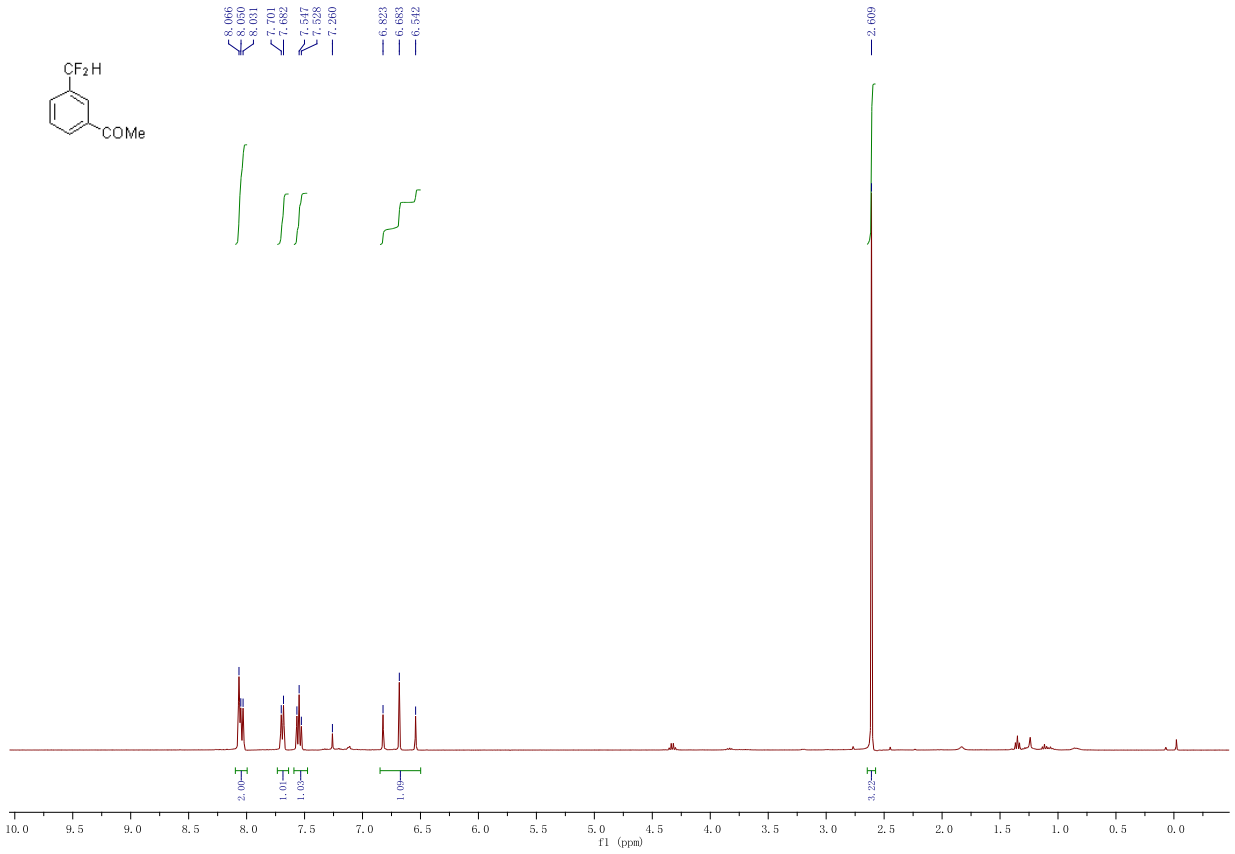
1-(4-(Difluoromethyl)phenyl)ethanone (23).

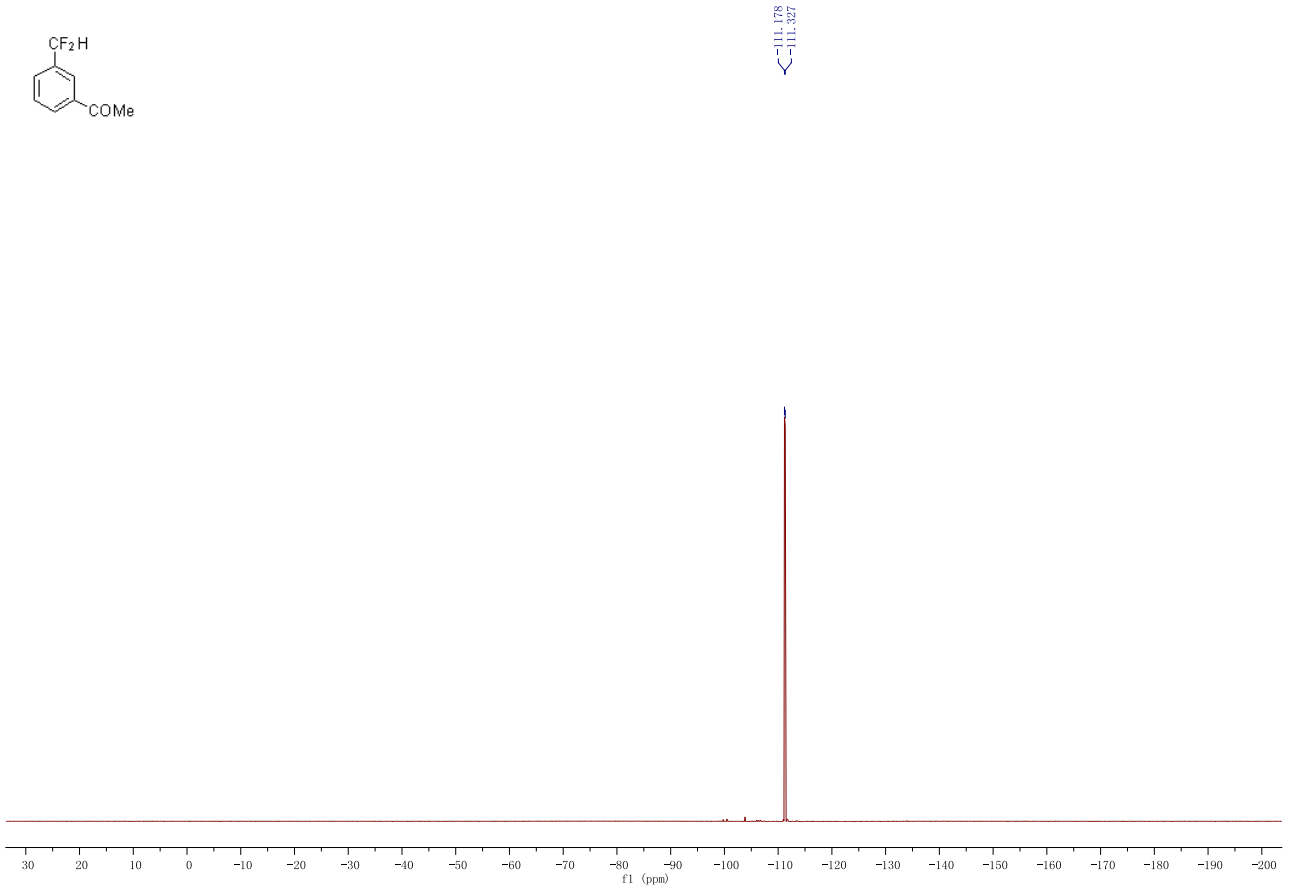


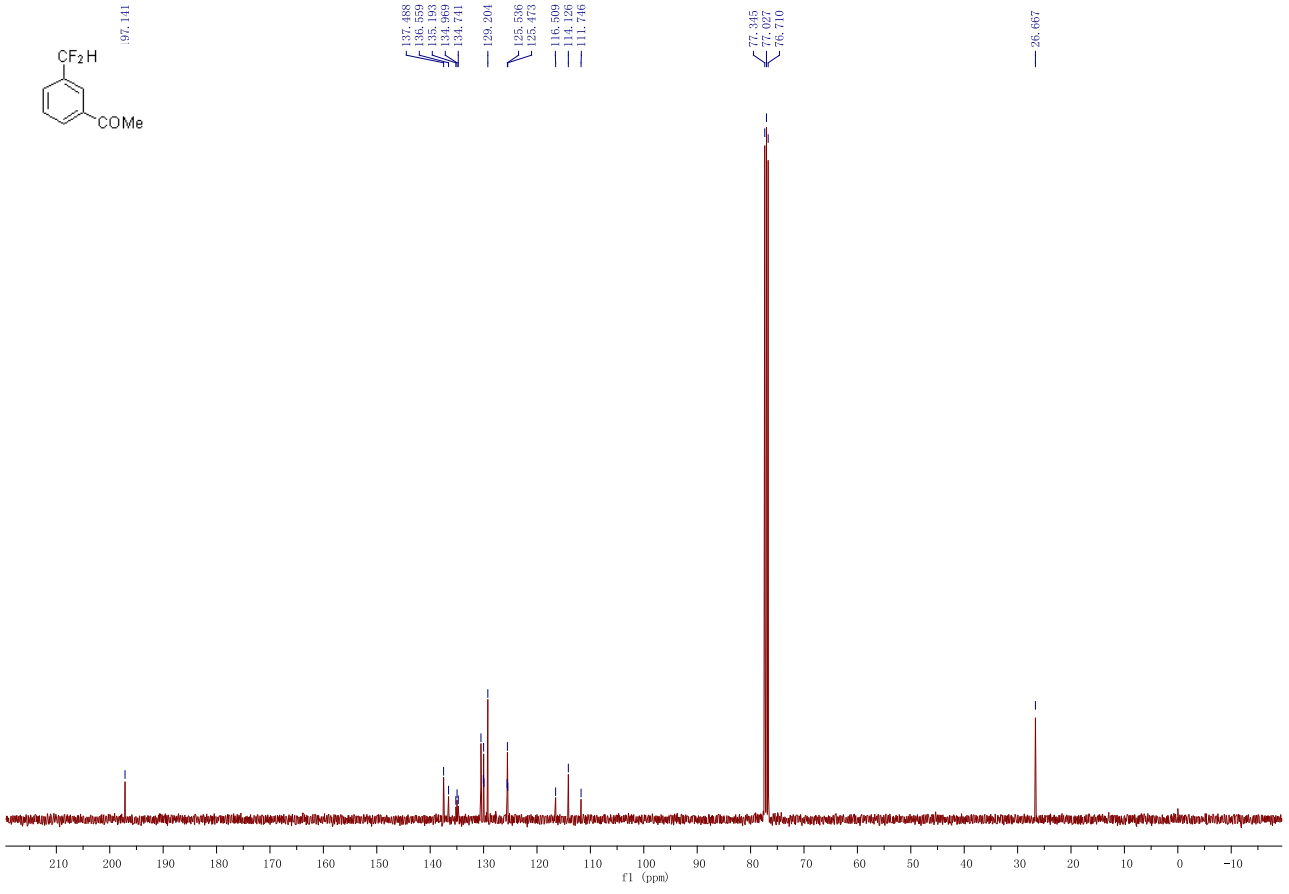




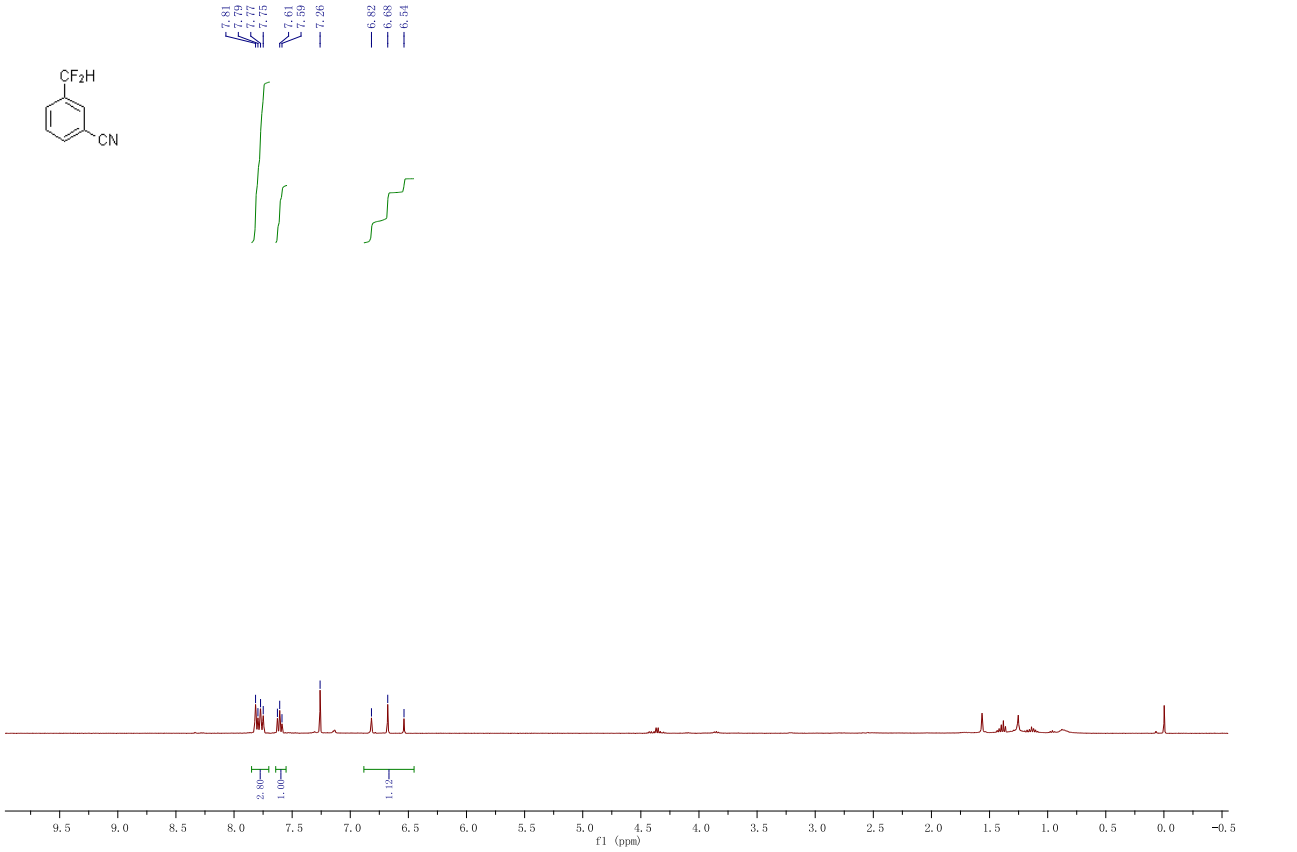
1-(3-(Difluoromethyl)phenyl)ethanone (24).

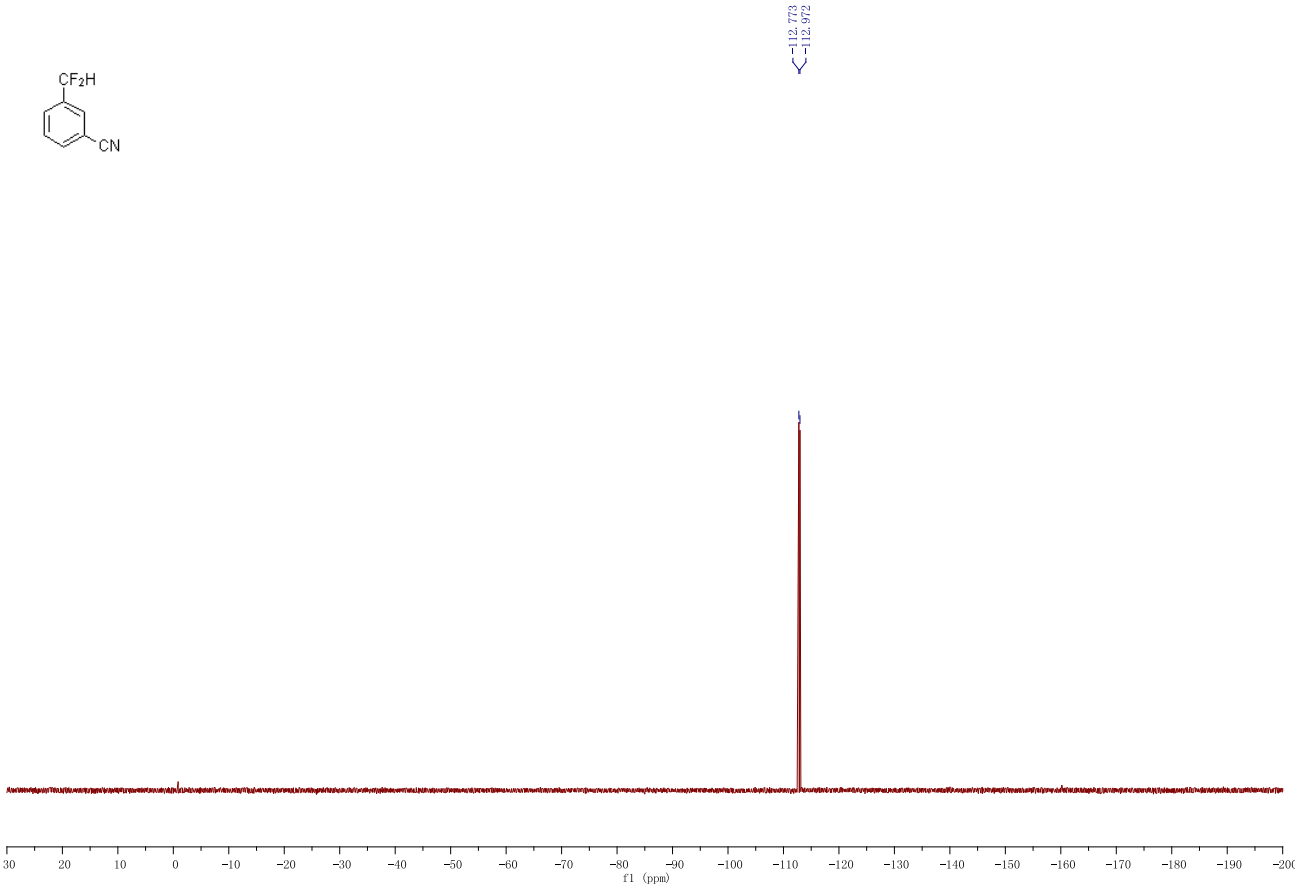



CF2H
COMe
-111.178
-111.327
f1 (ppm)

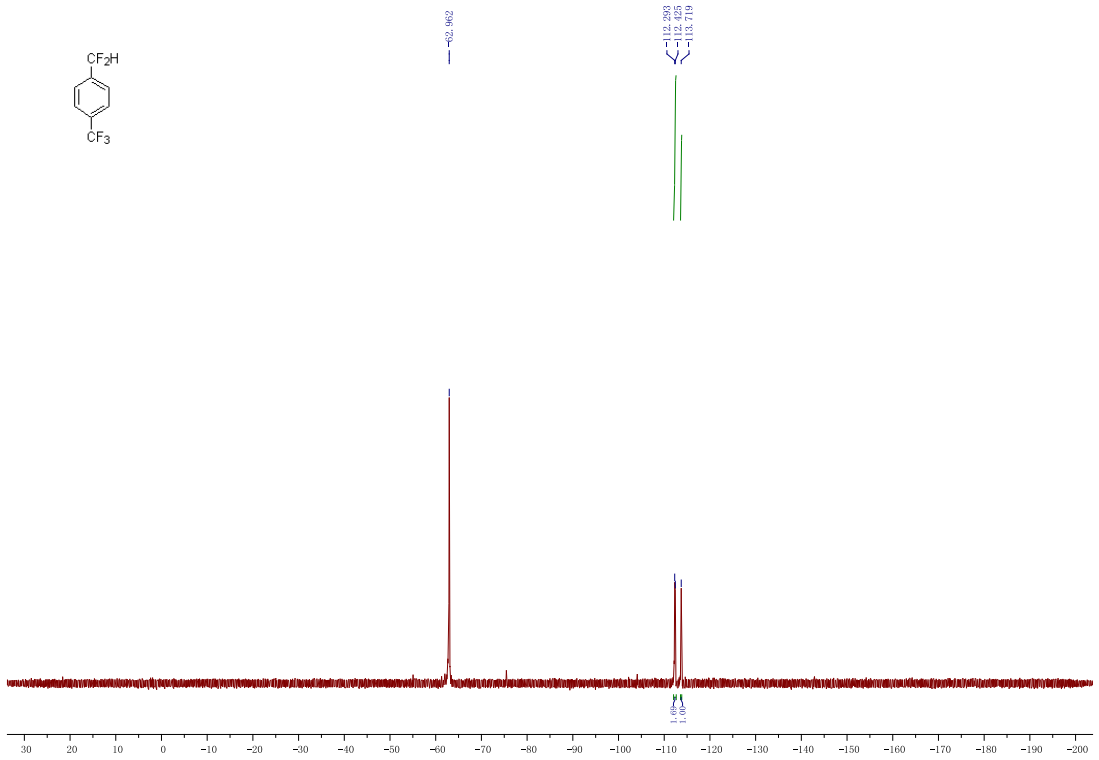

CF2H
COMe
197.141
137.488
136.559
135.193
134.969
134.741
129.204
125.536
125.473
116.509
114.126
111.746
77.345
77.027
76.710
26.667
f1 (ppm)

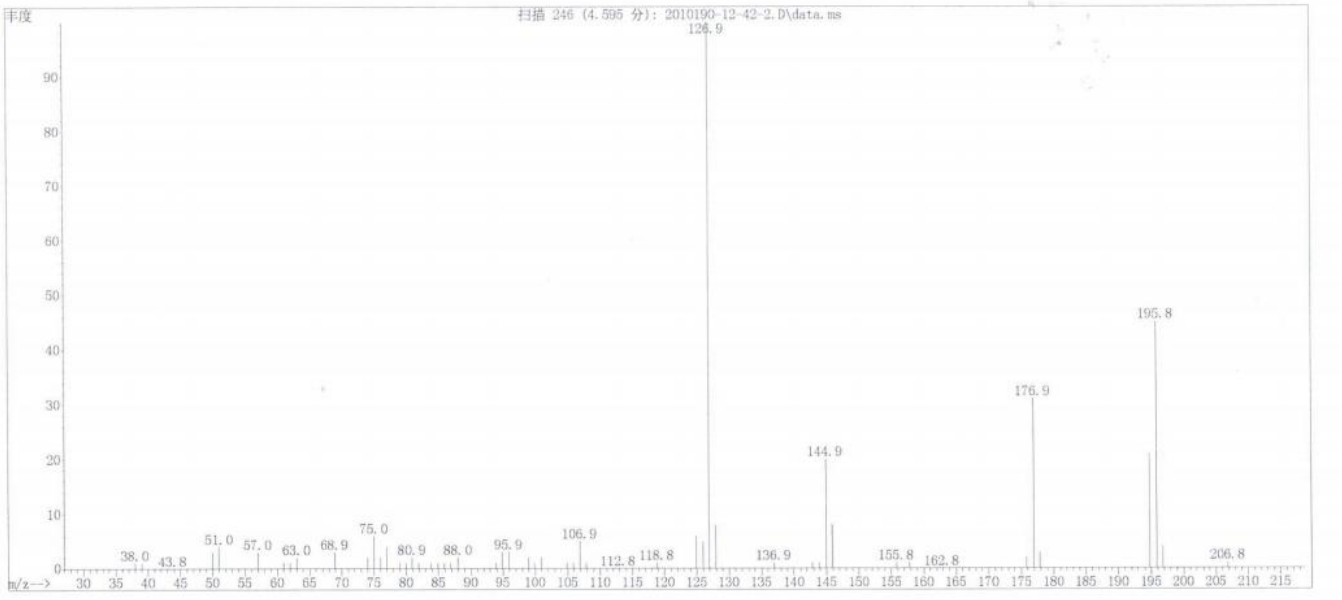
3-(Difluoromethyl)benzonitrile (25).



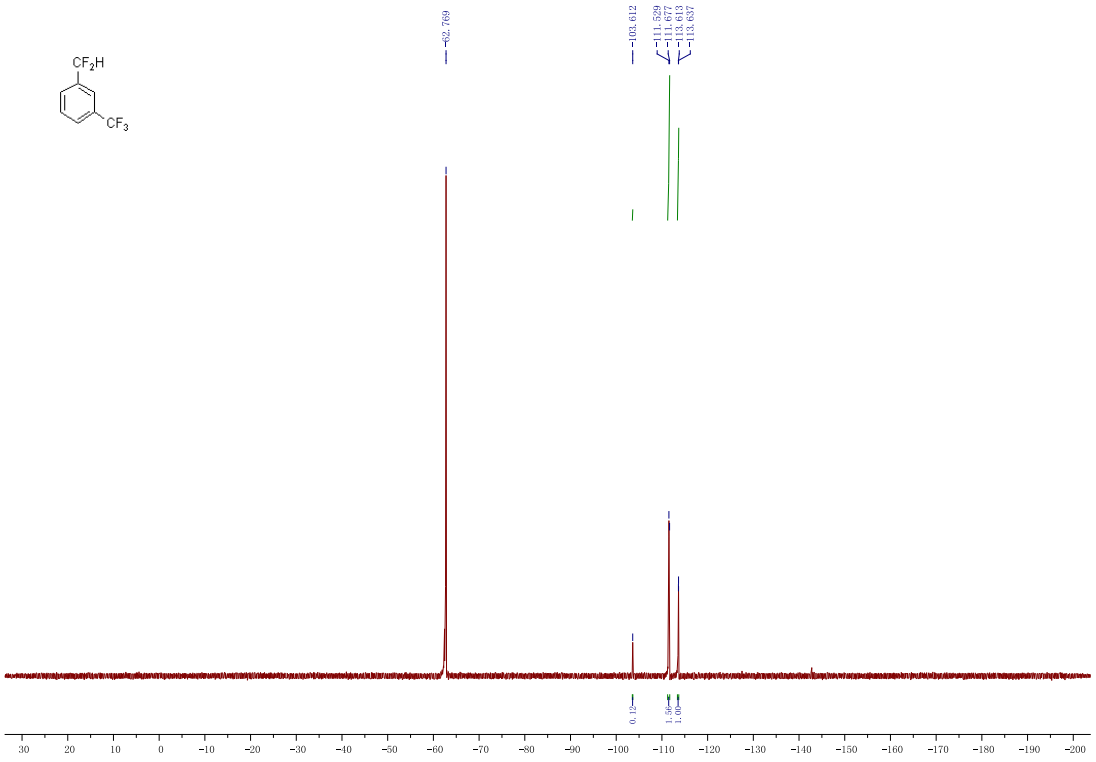


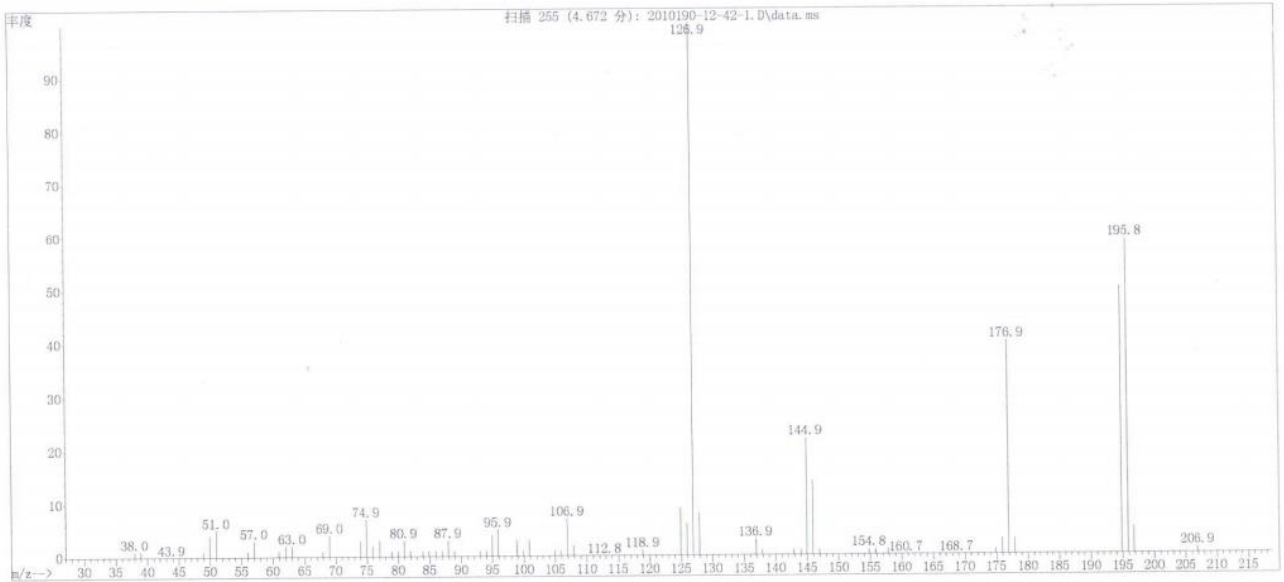
1-(Difluoromethyl)-4-(trifluoromethyl)benzene (26). (Due to the low boil point of 26, a crude ^{19}F NMR was provided)



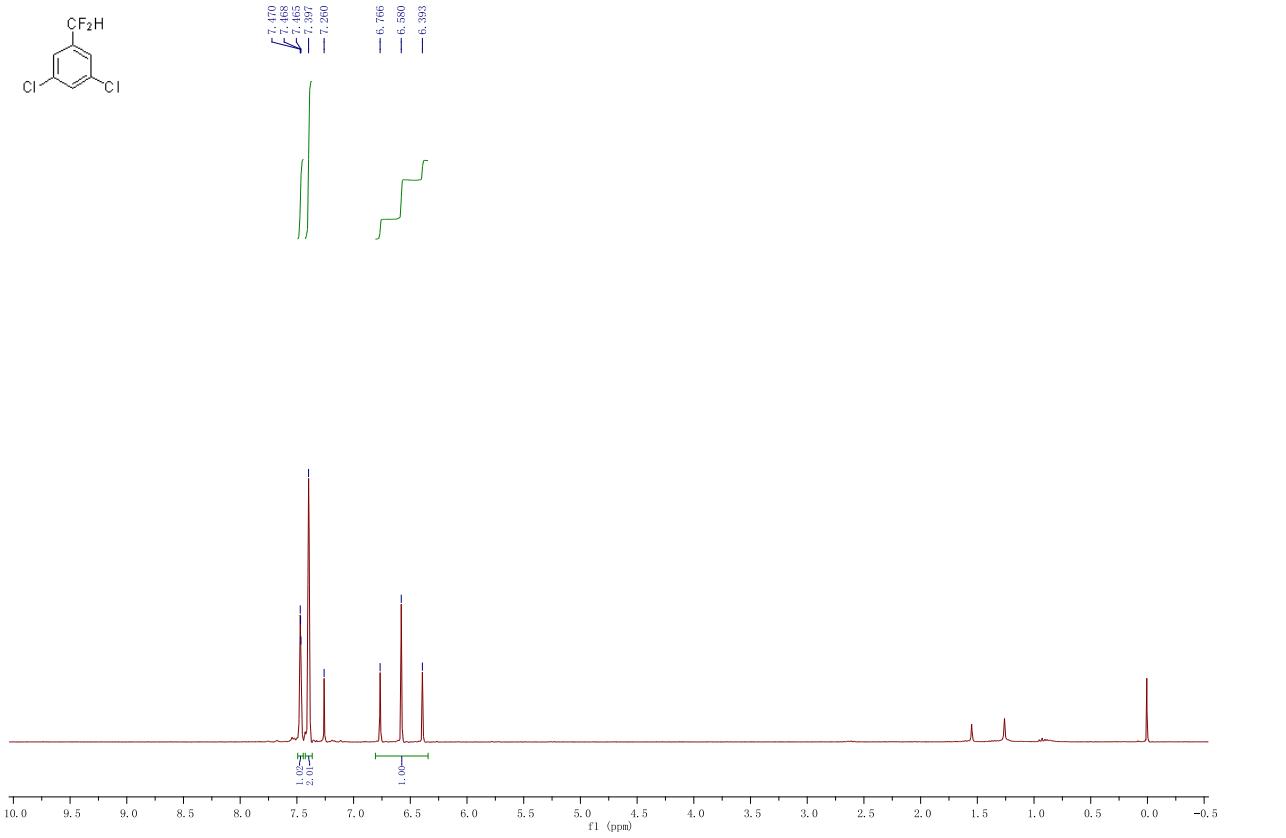


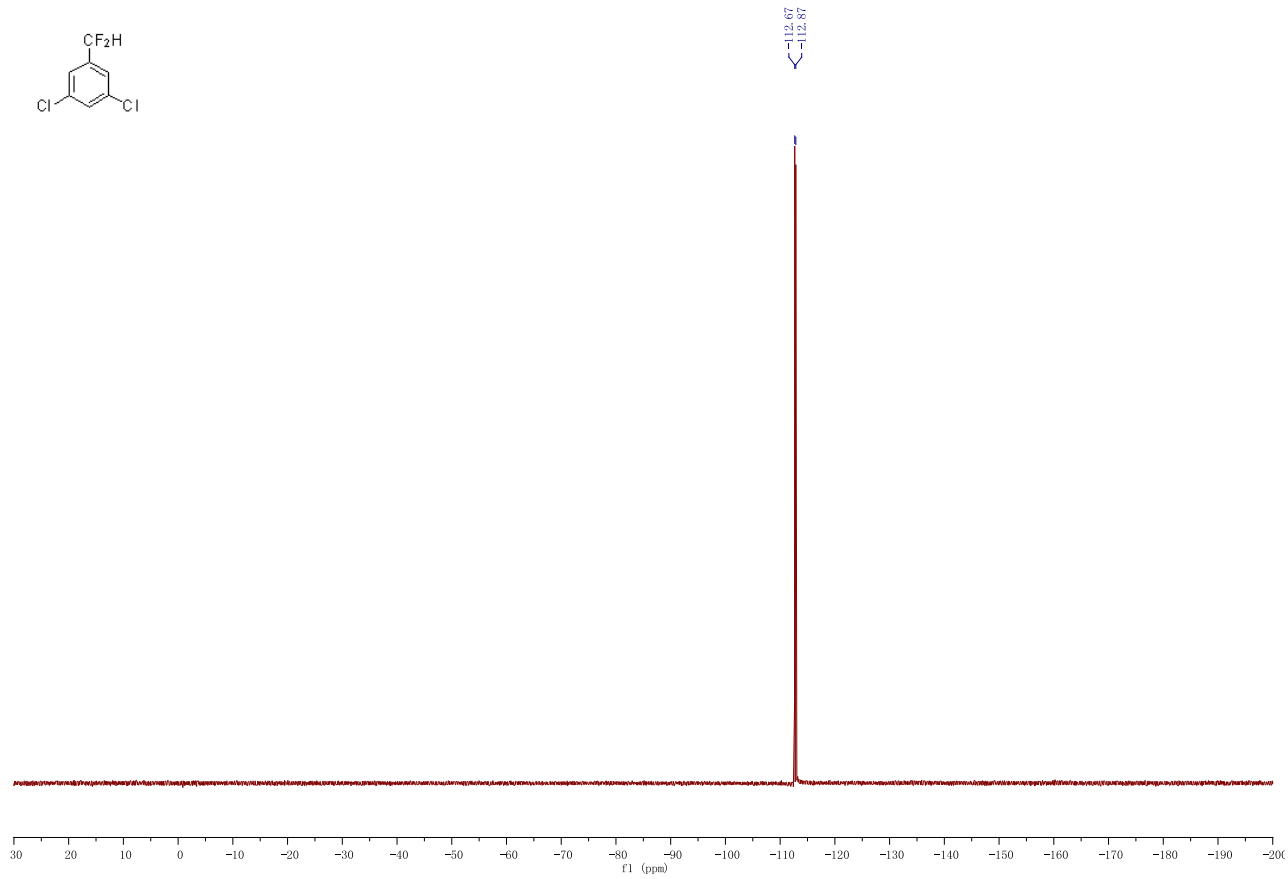
1-(Difluoromethyl)-3-(trifluoromethyl)benzene (27) (Due to the low boil point of 27, a crude ^{19}F NMR was provided)



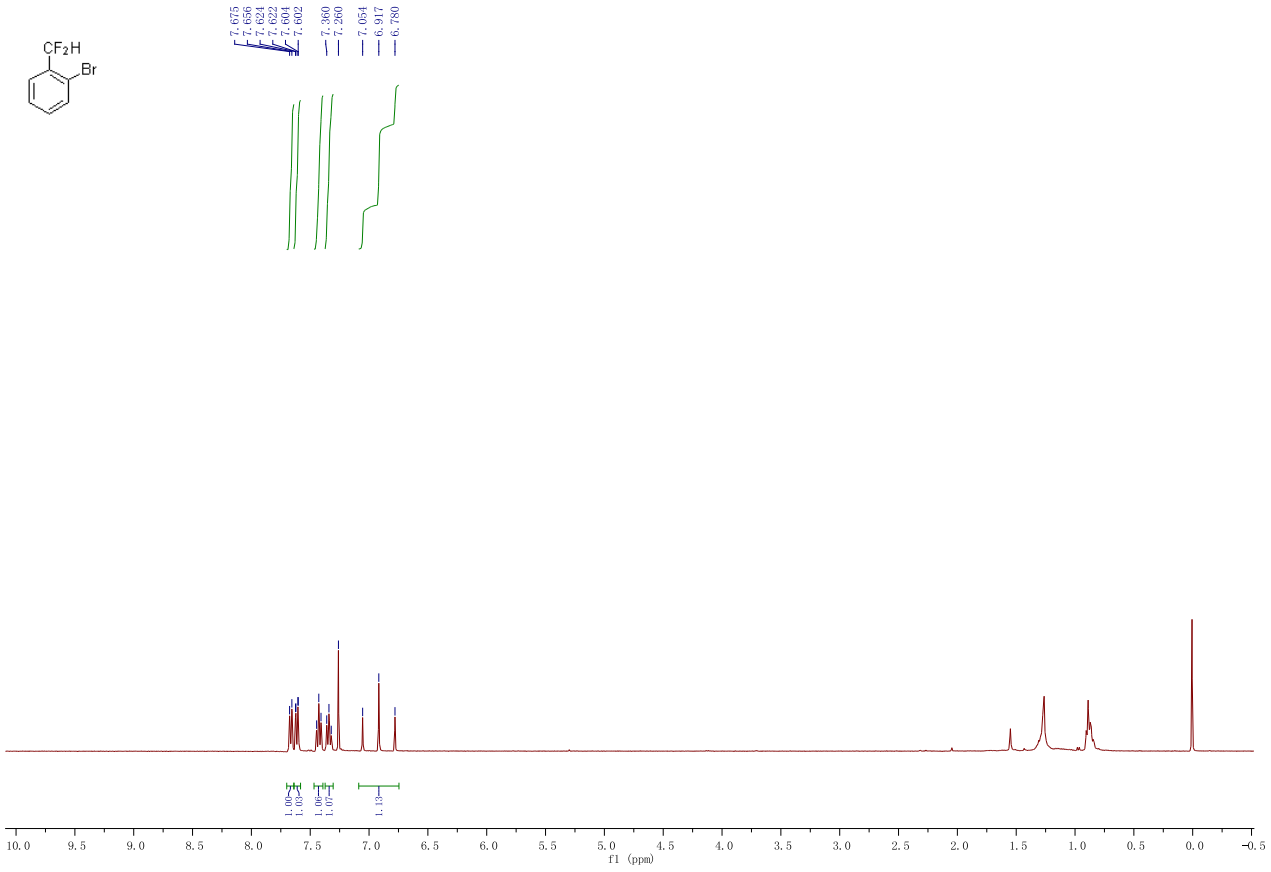


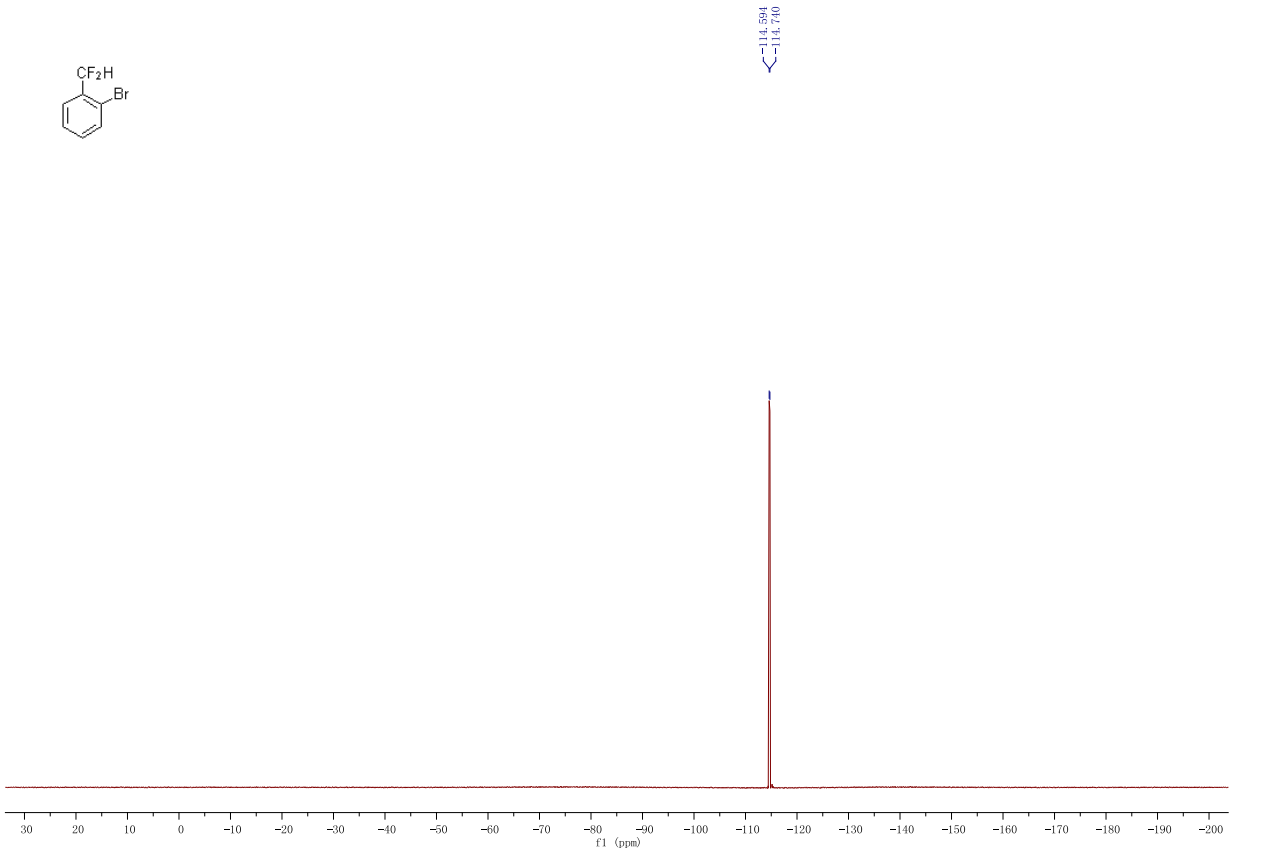
1,3-dichloro-5-(difluoromethyl)benzene (28).



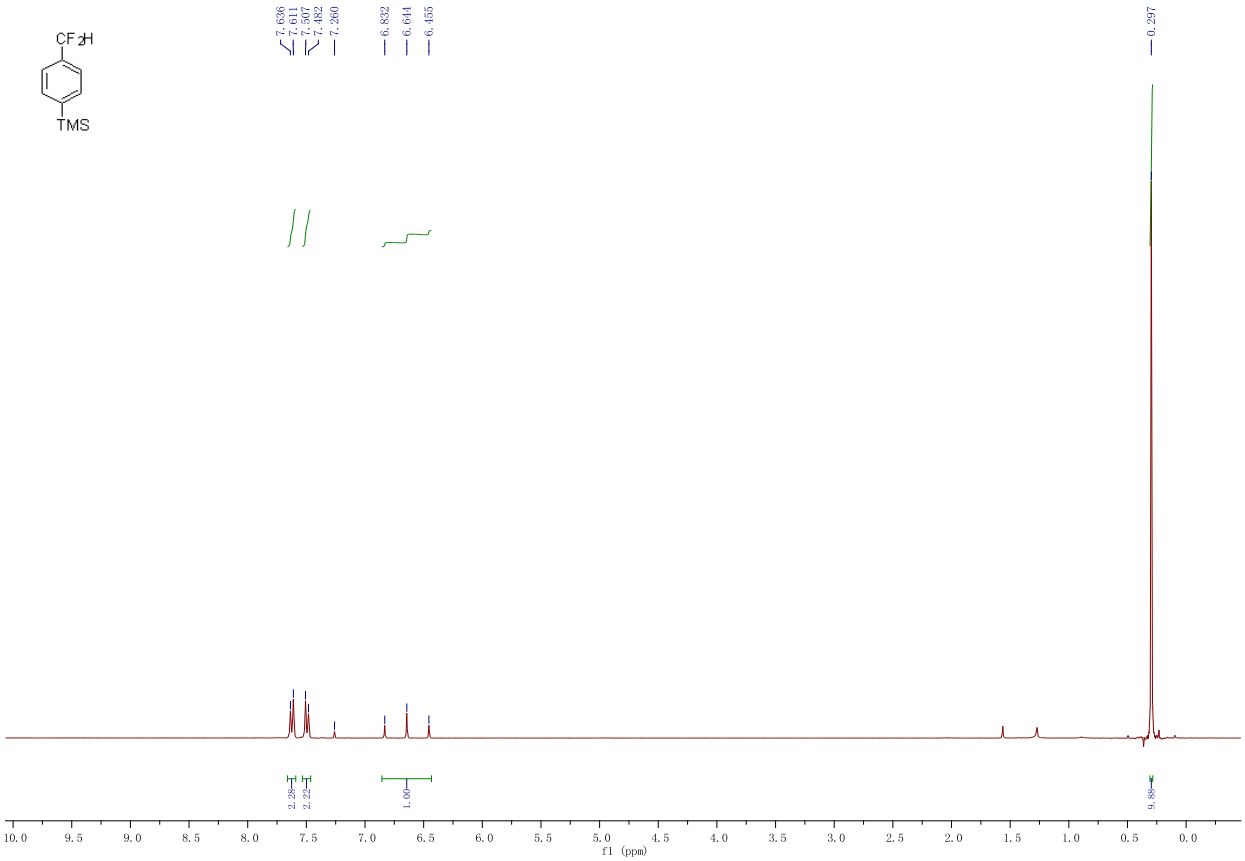


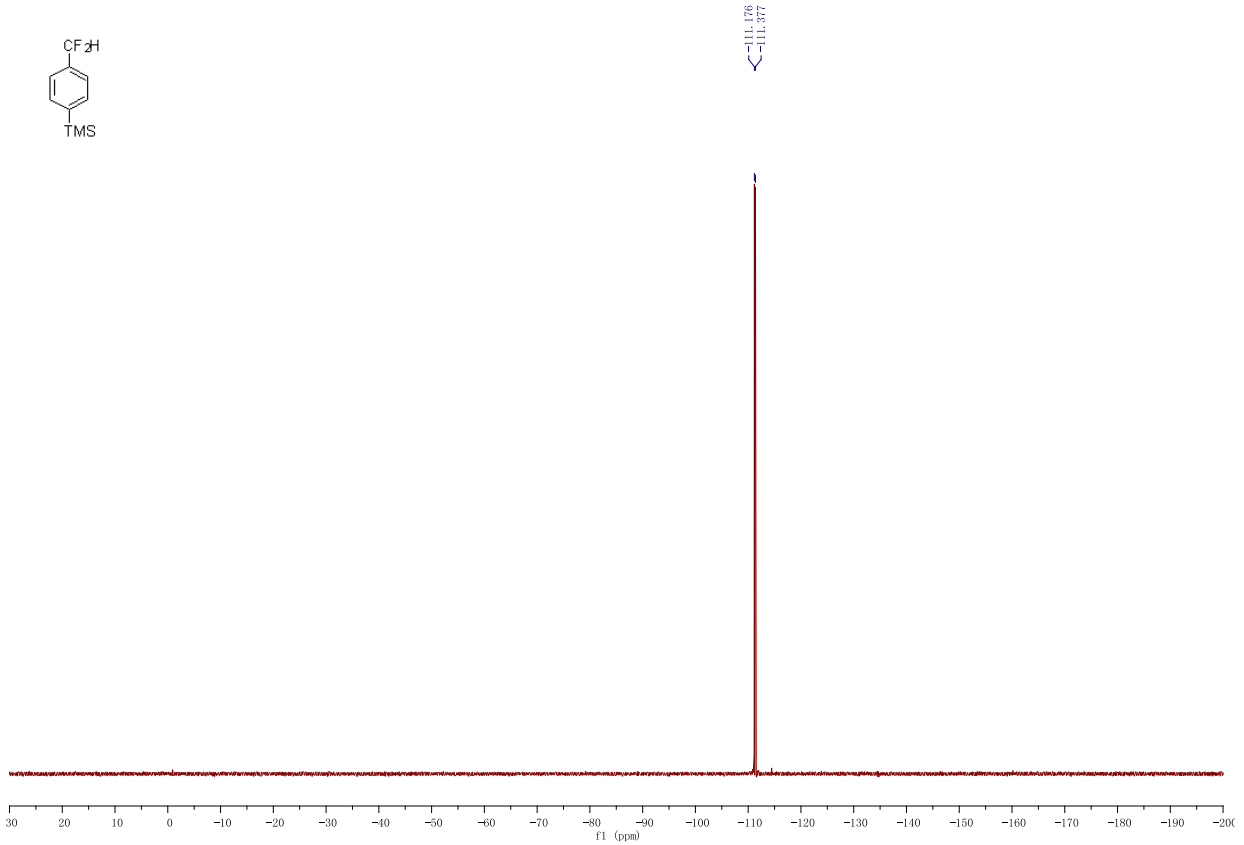
1-Bromo-2-(difluoromethyl)benzene (29).

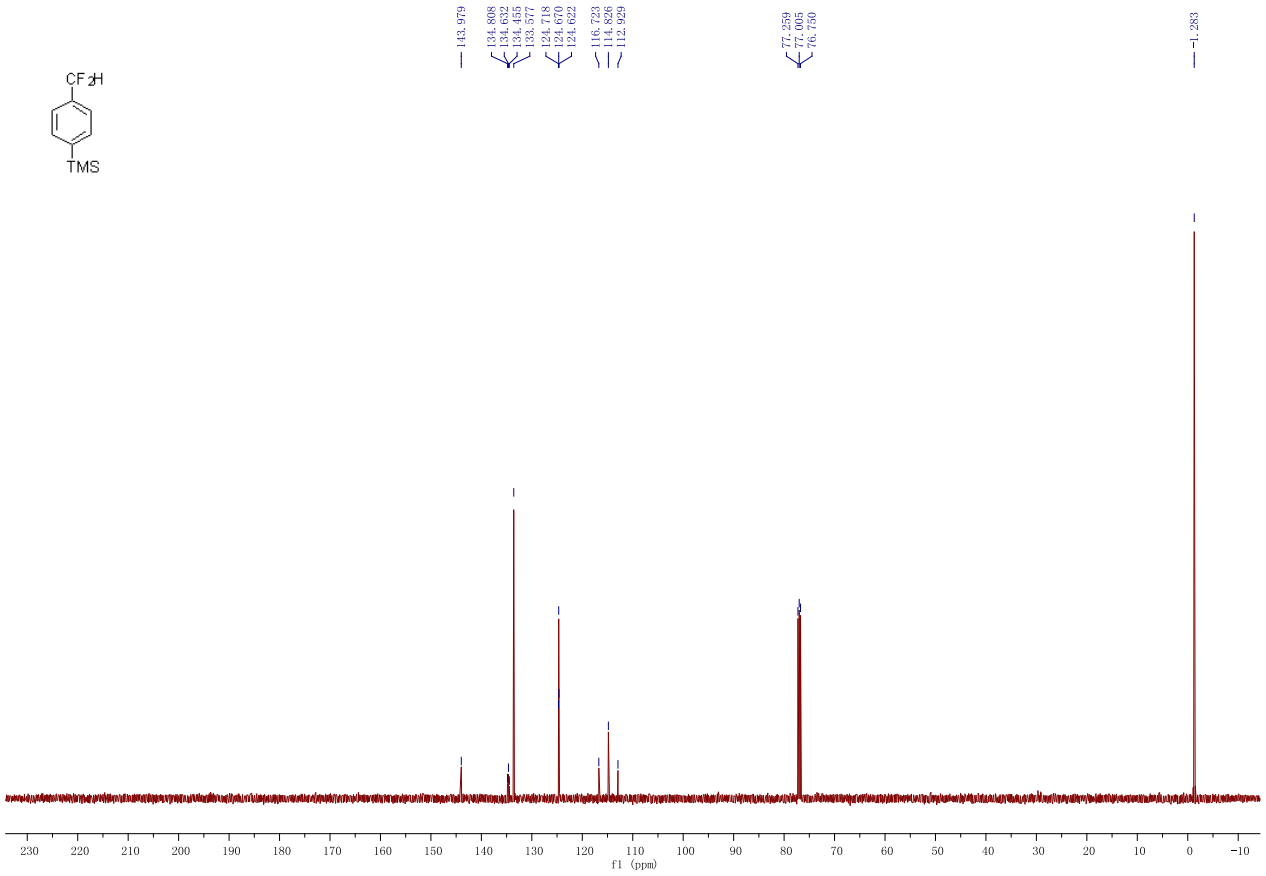




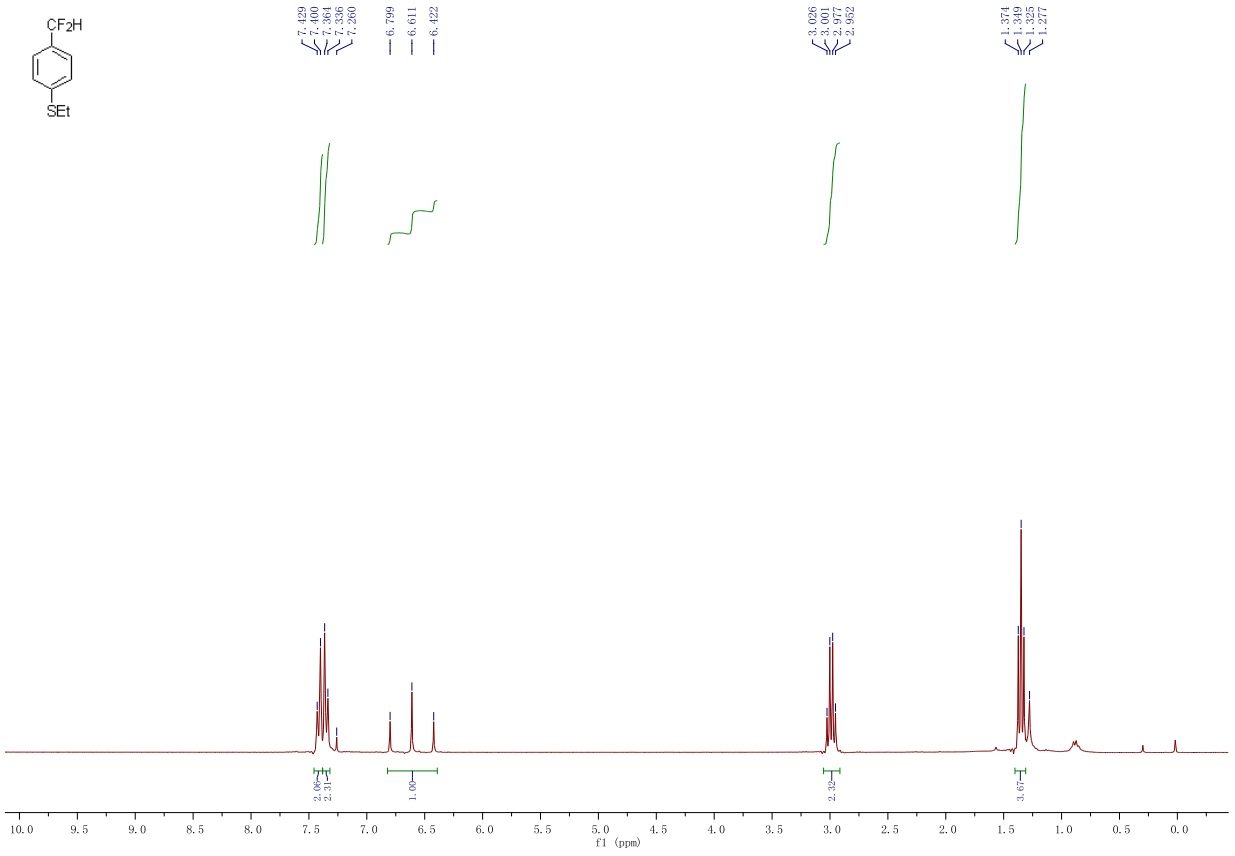
(4-(Difluoromethyl)phenyl)trimethylsilane (30).

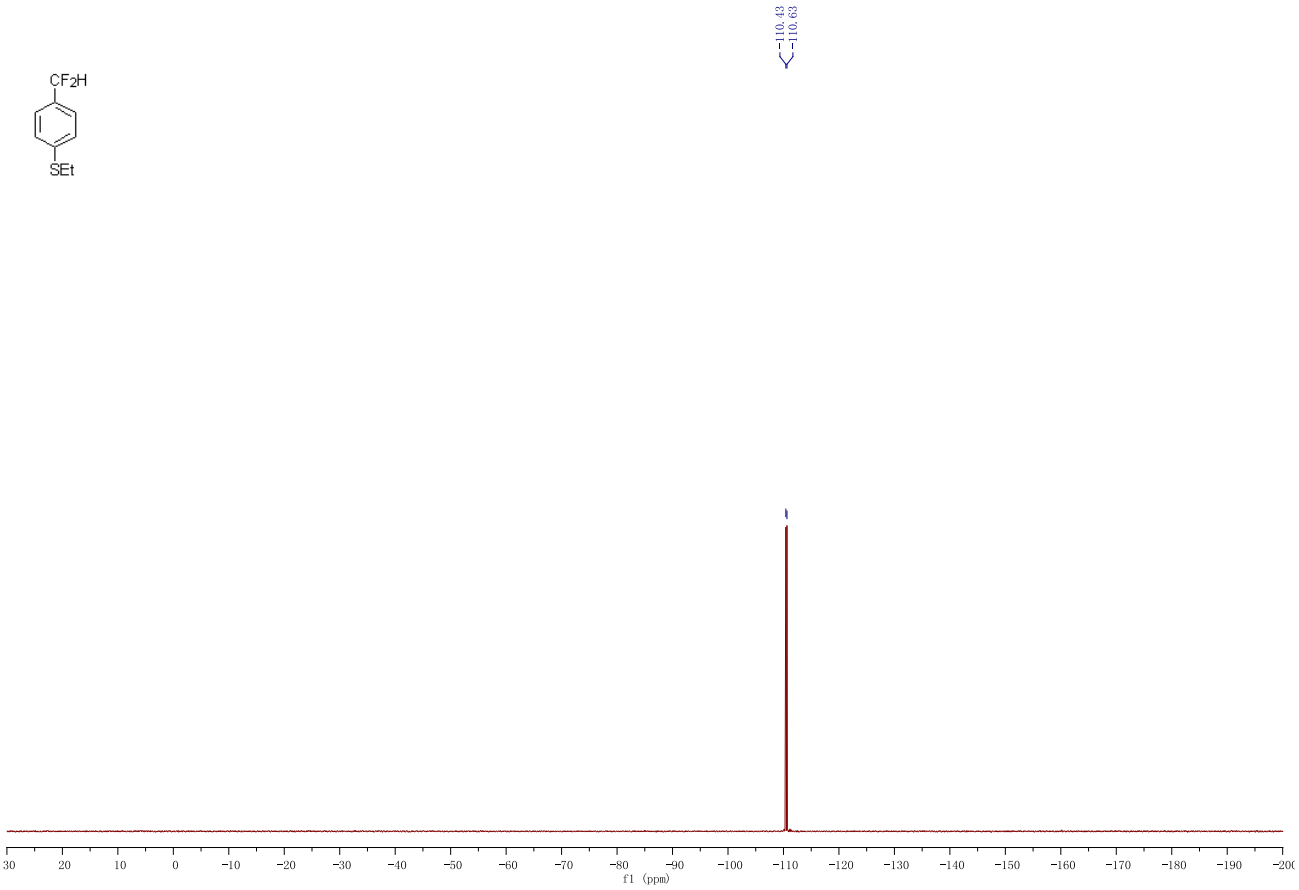


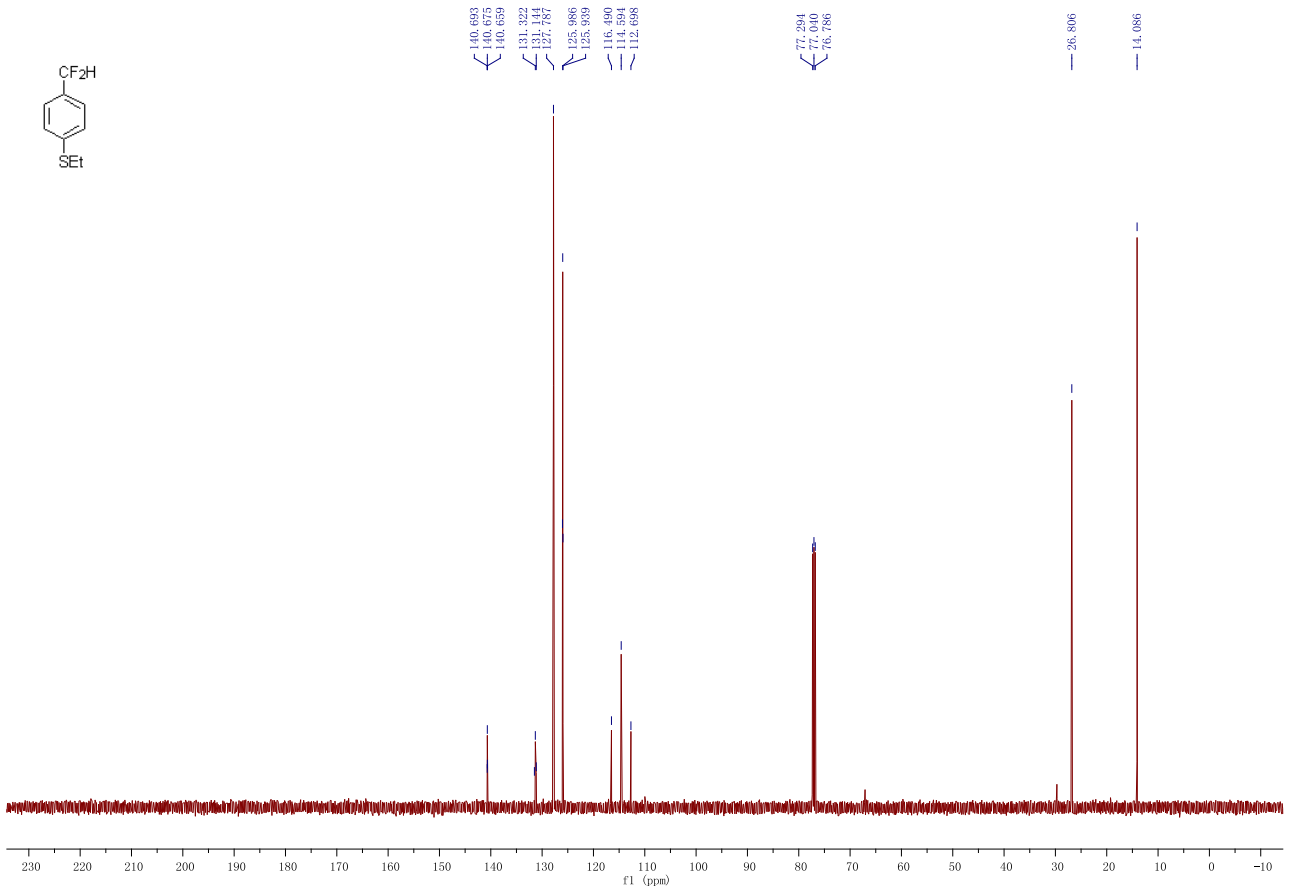




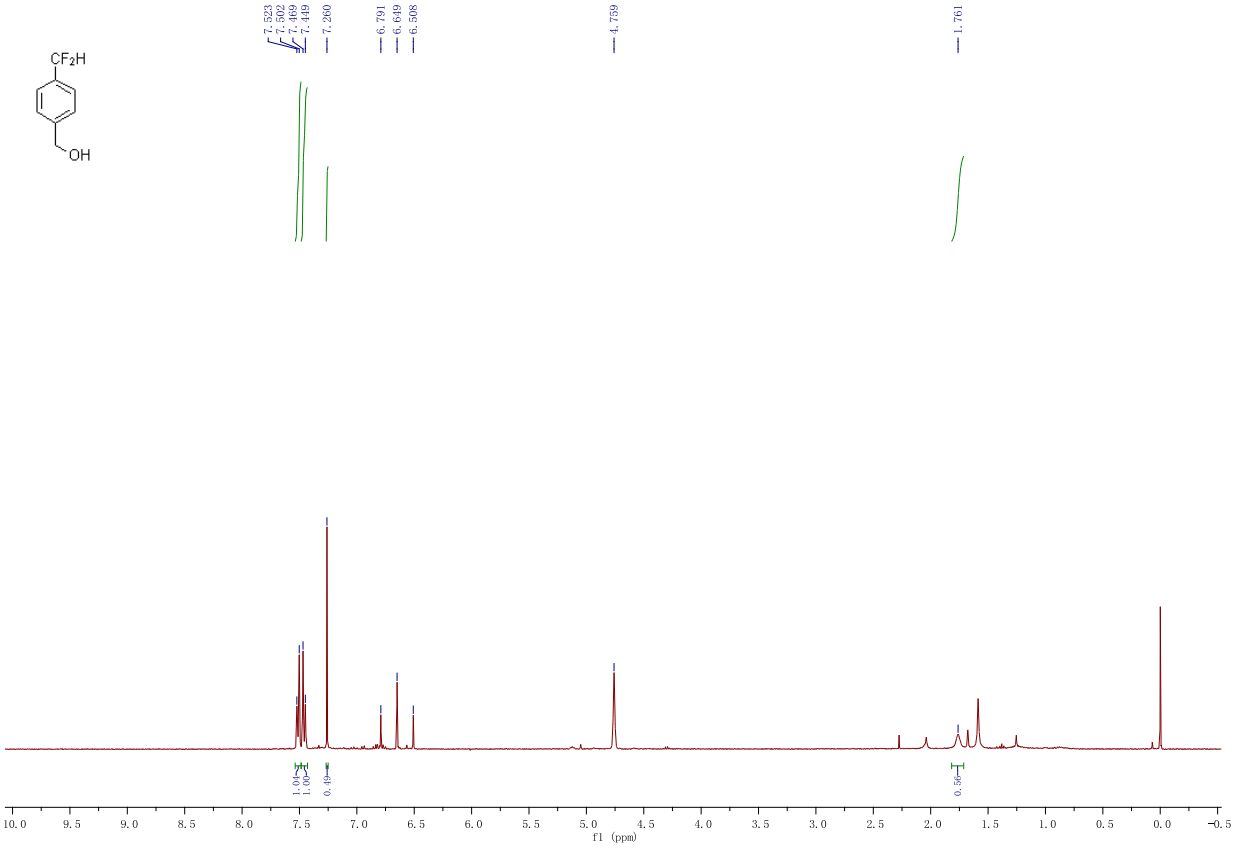
(4-(Difluoromethyl)phenyl)(ethyl)sulfane (31).

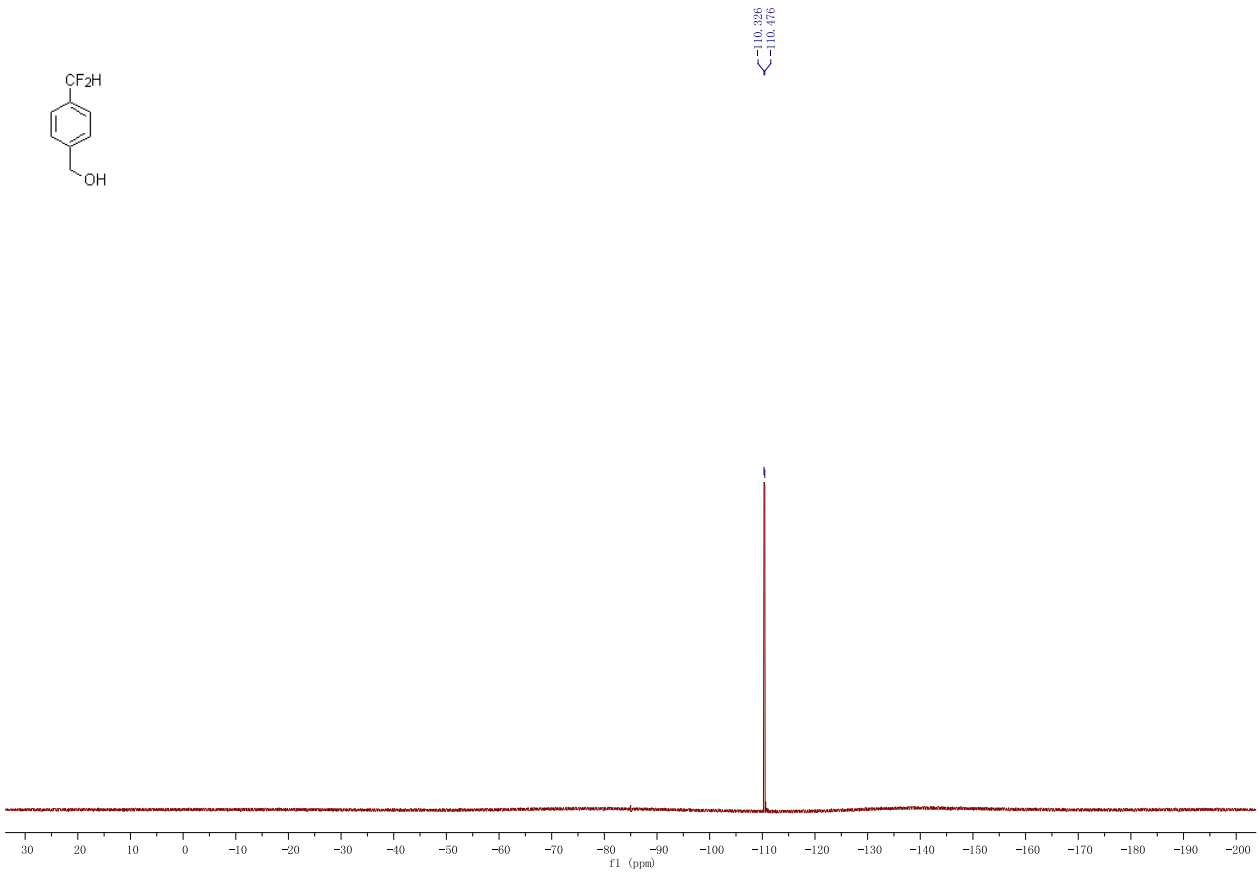



CF2H
SEt
-110.43
-110.63
f1 (ppm)

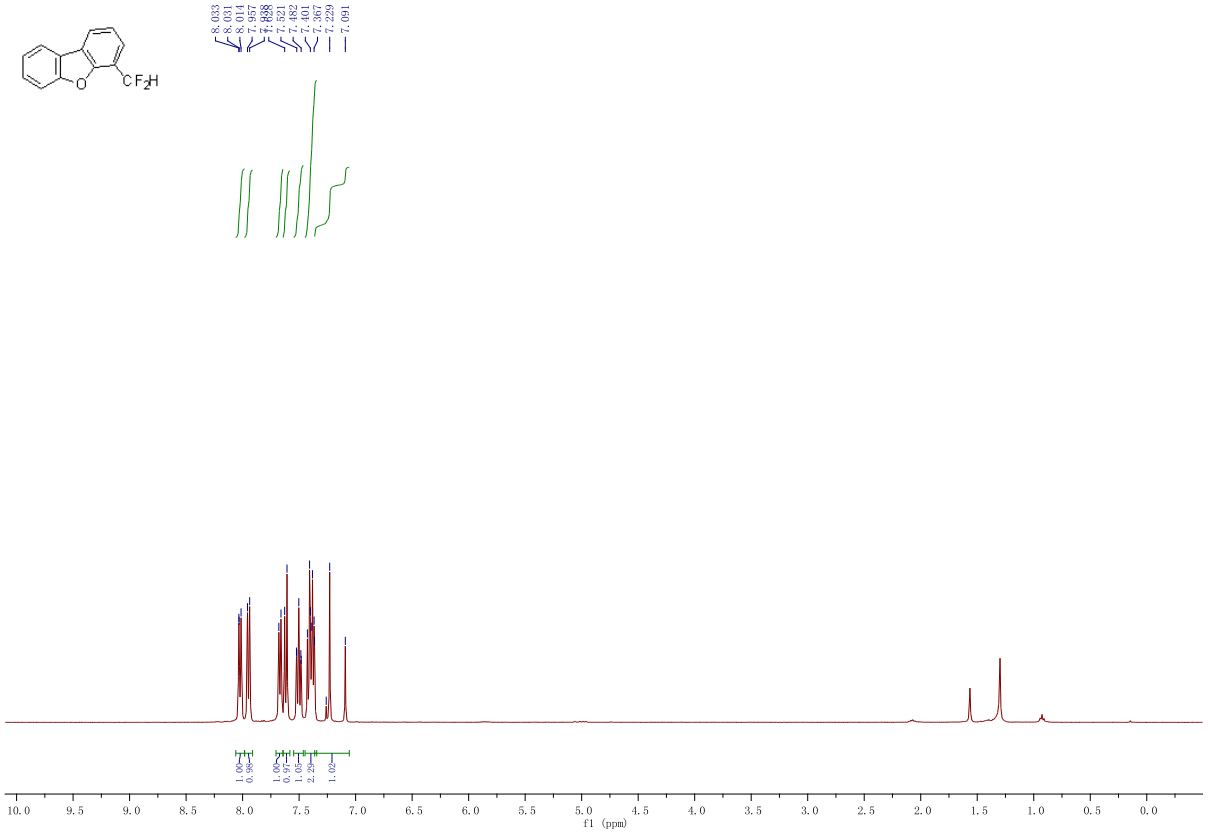

CF2H
SEt
140.693
140.675
140.659
131.322
131.144
127.787
125.986
125.939
116.490
114.594
112.698
77.294
77.040
76.786
26.806
14.086
f1 (ppm)

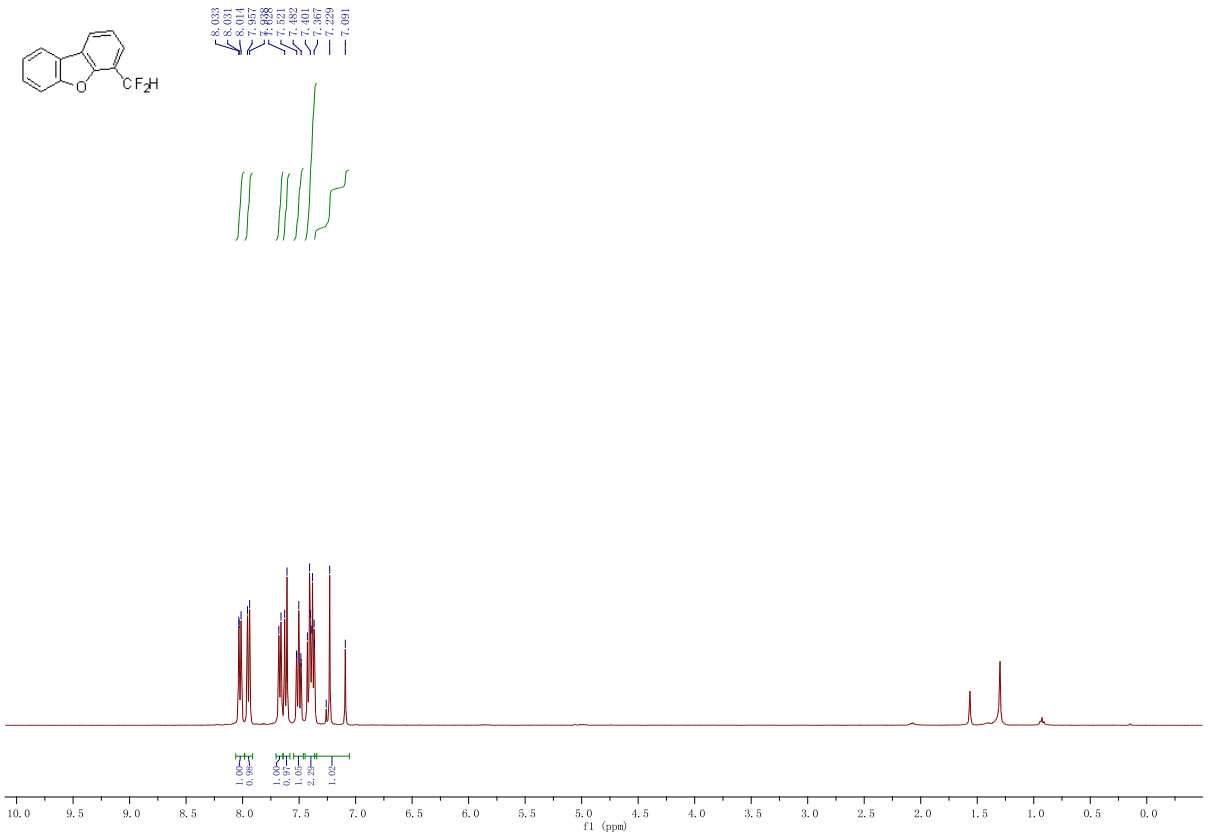
(4-(Difluoromethyl)phenyl)methanol (32).

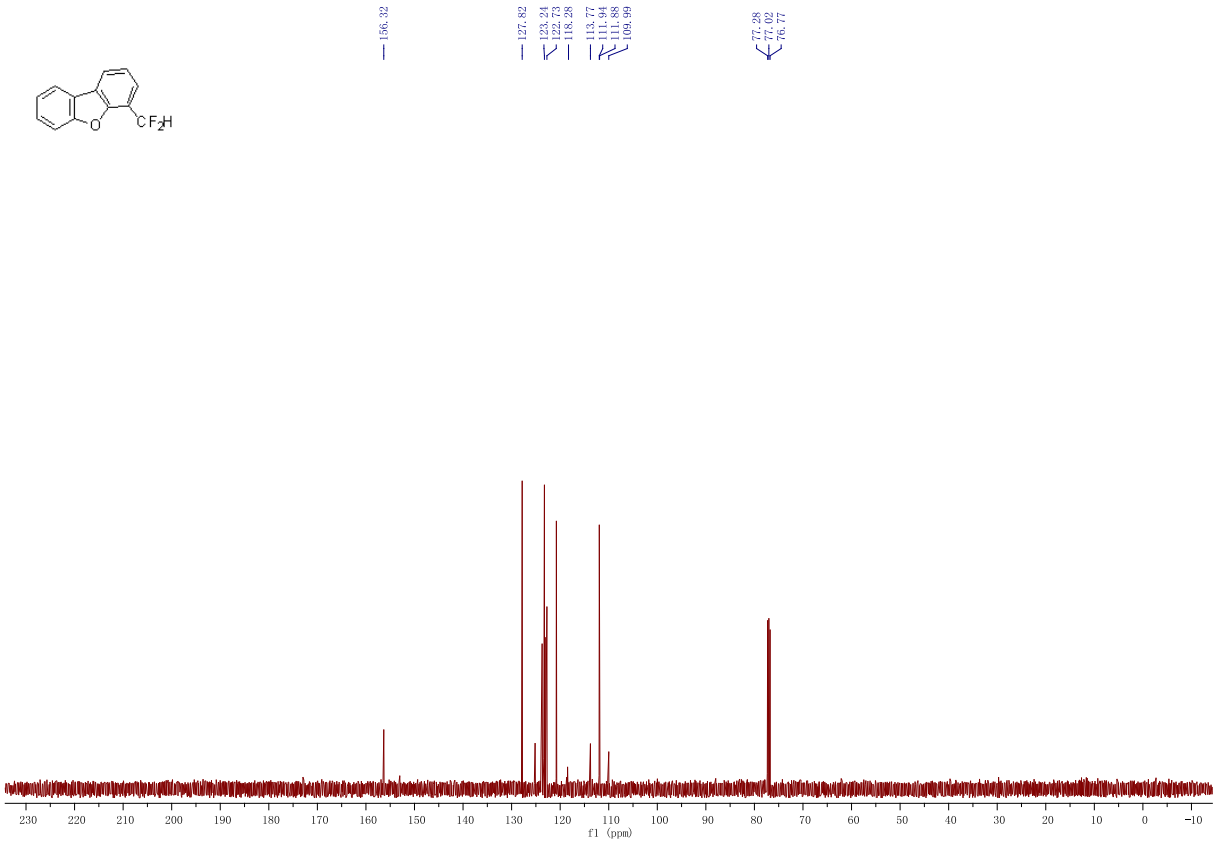




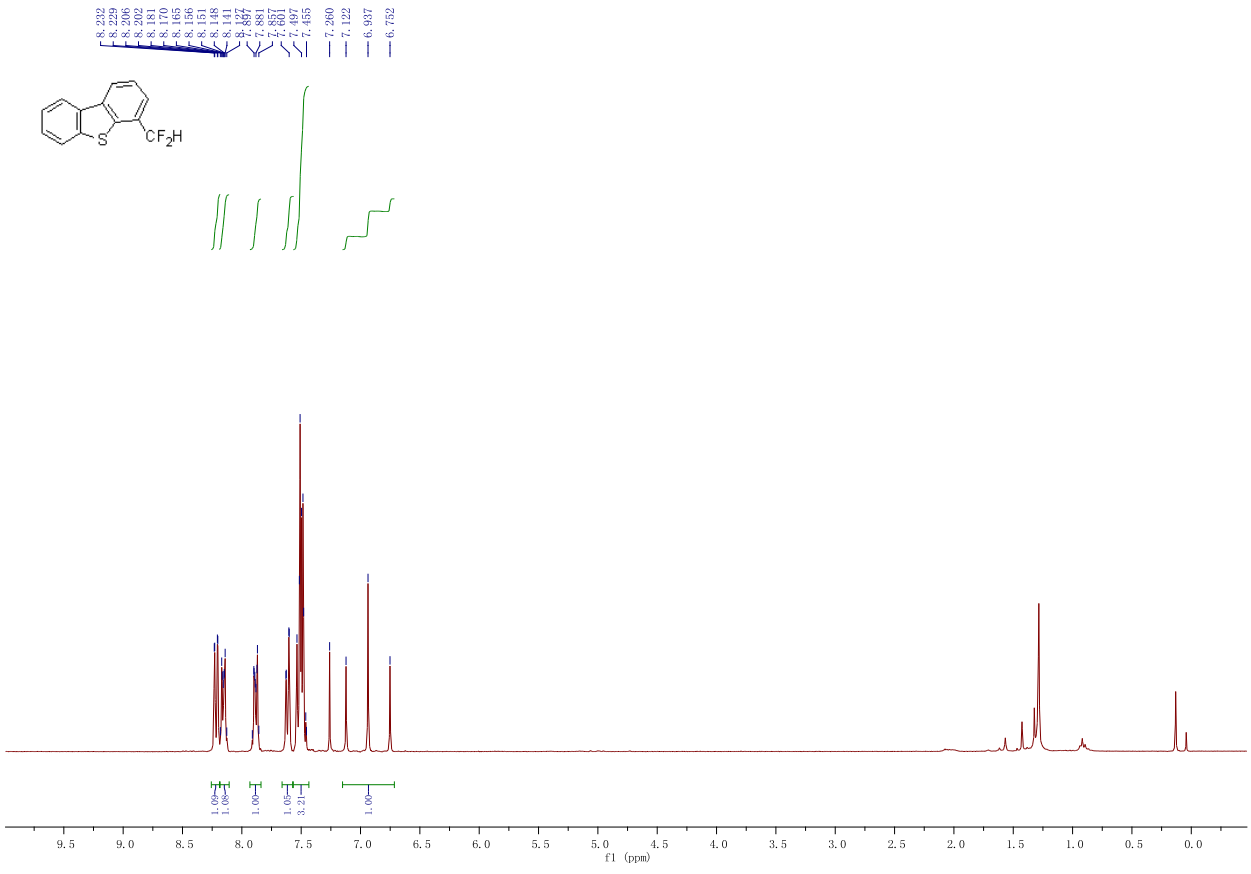
4-(Difluoromethyl)dibenzo[b,d]furan (33).

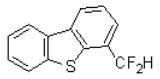




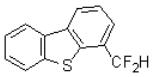


4-(Difluoromethyl)dibenzo[b,d]thiophene (34).



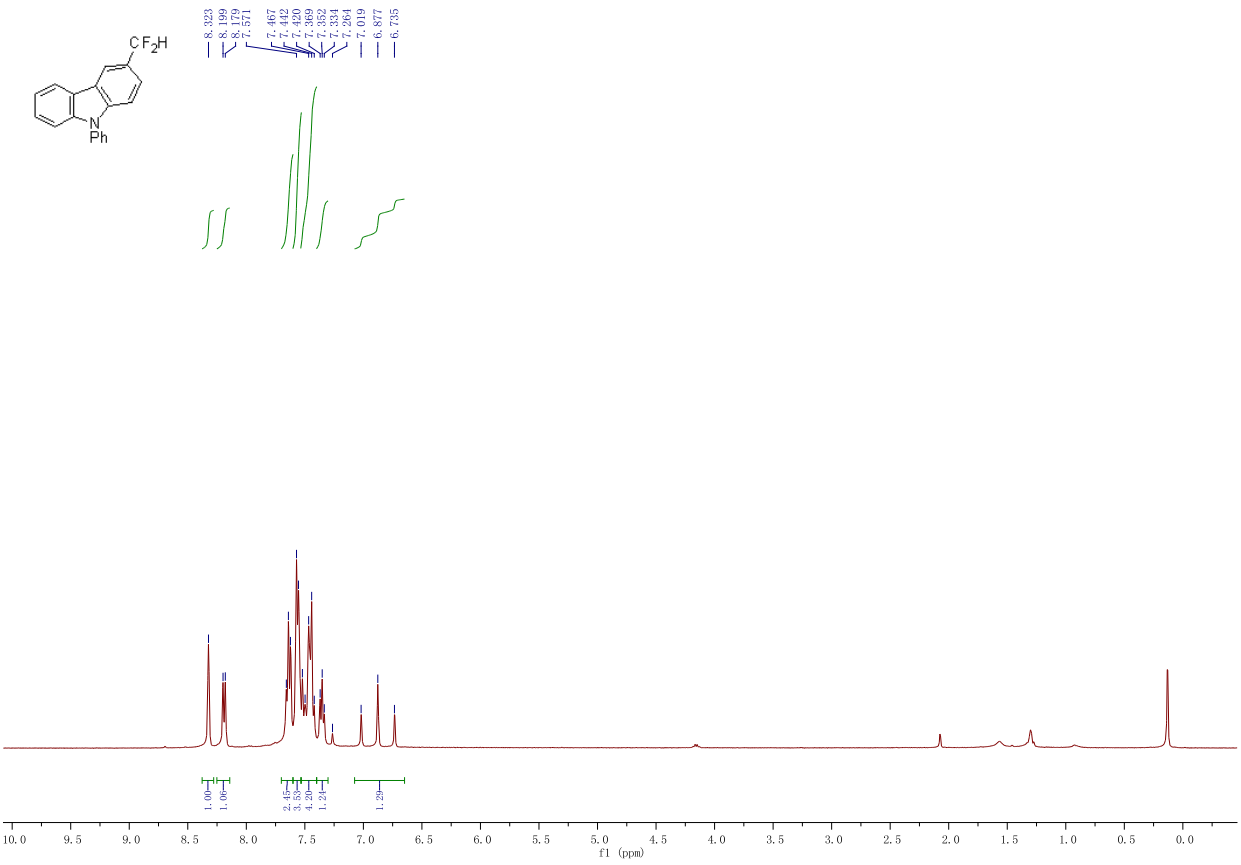

S
CF2H

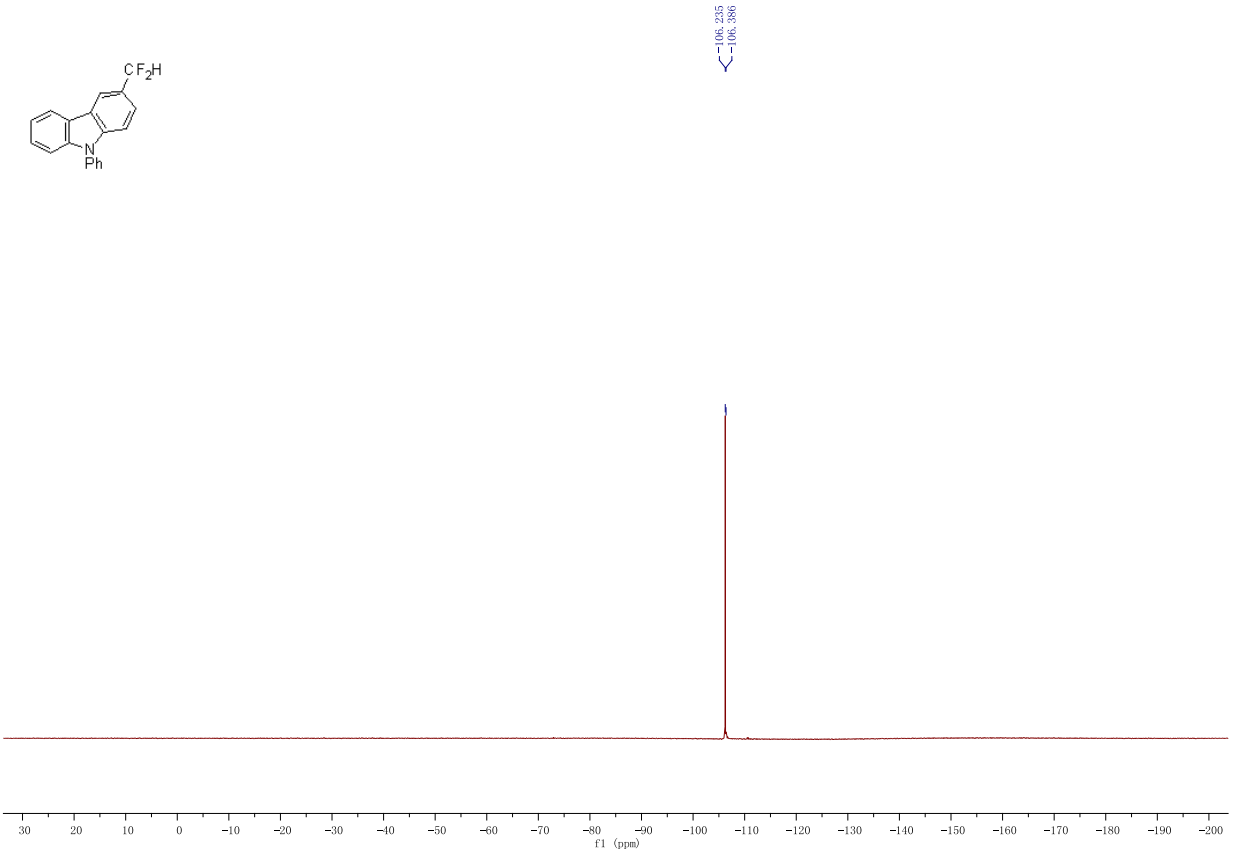
-113.597
-113.794
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

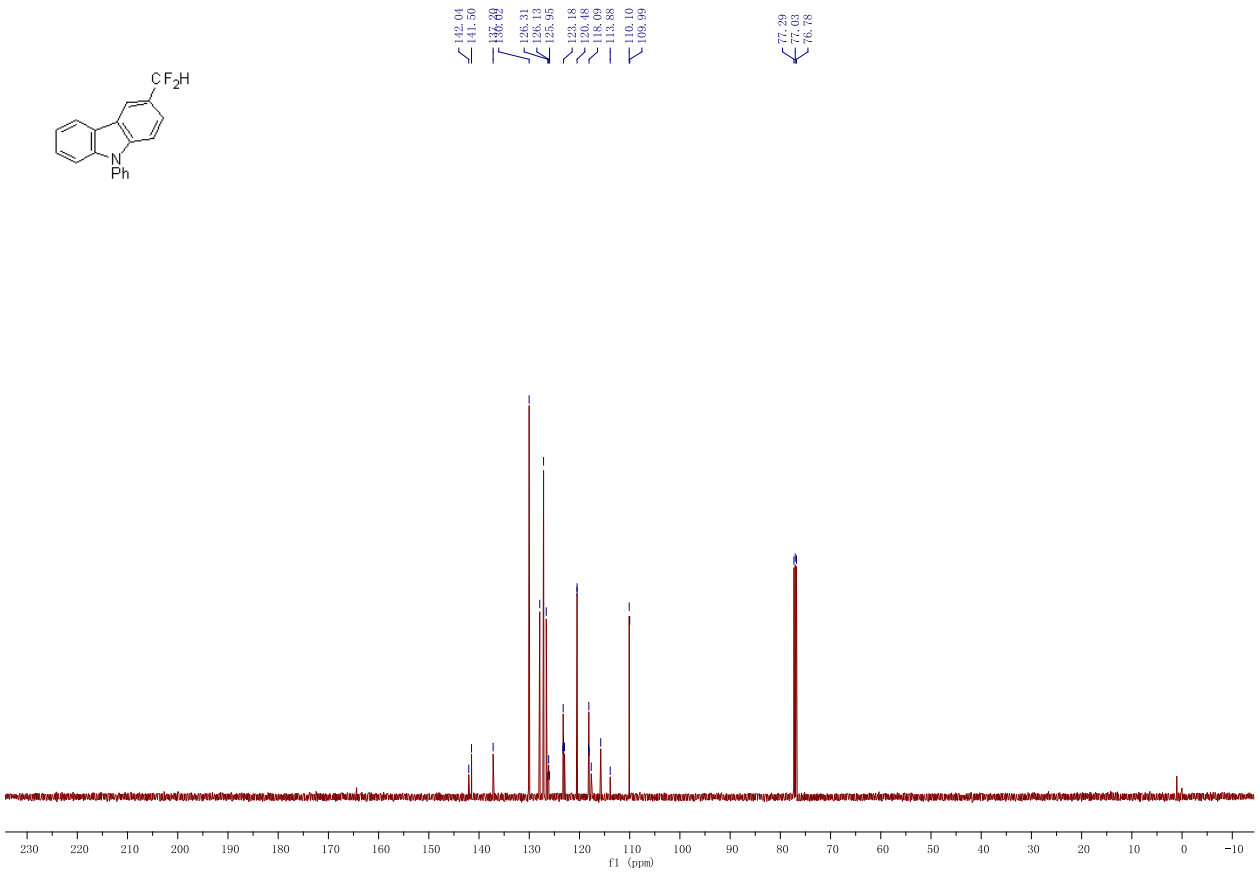

S
CF2H

139.468
139.460
139.451
136.963
136.636
136.610
134.601
128.485
121.677
116.388
114.981
112.576
77.311
77.057
76.803
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)

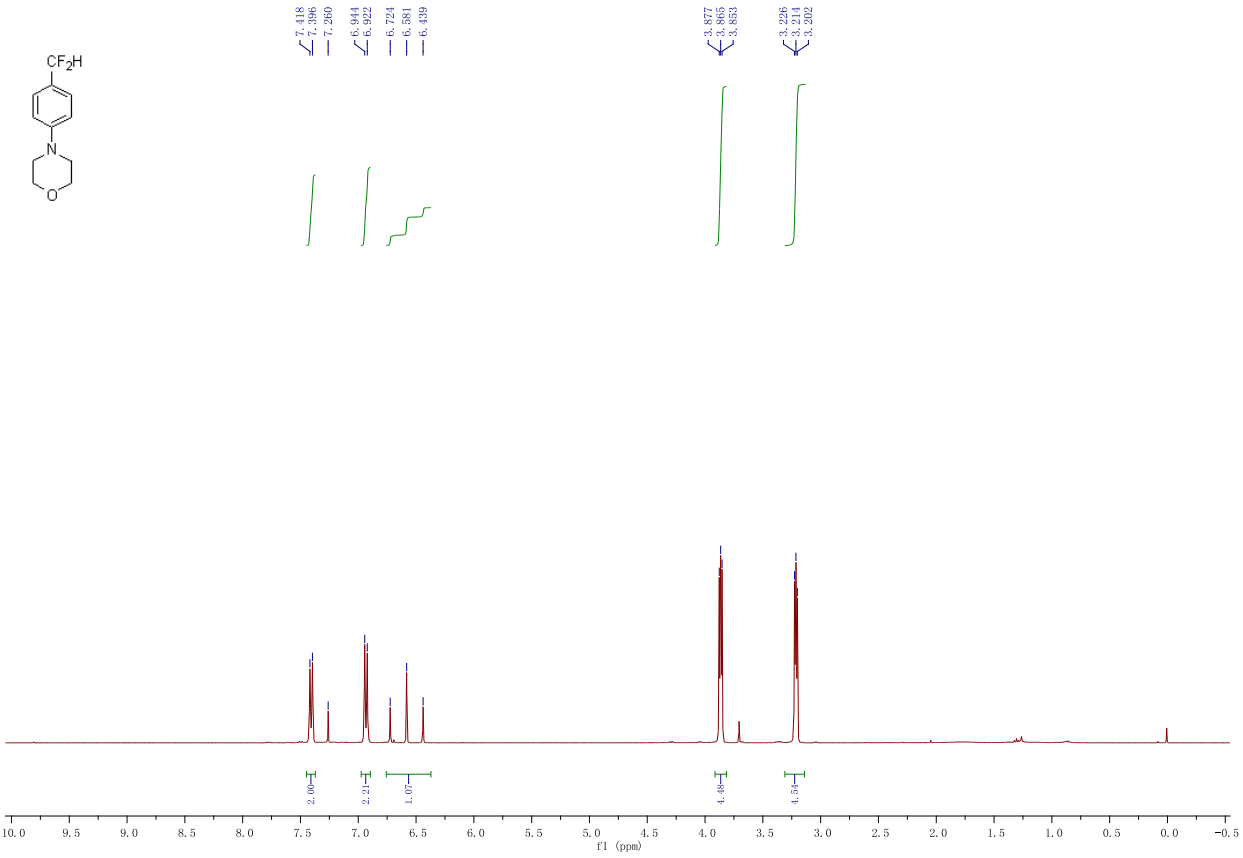
3-(Difluoromethyl)-9-phenyl-9H-carbazole (35).

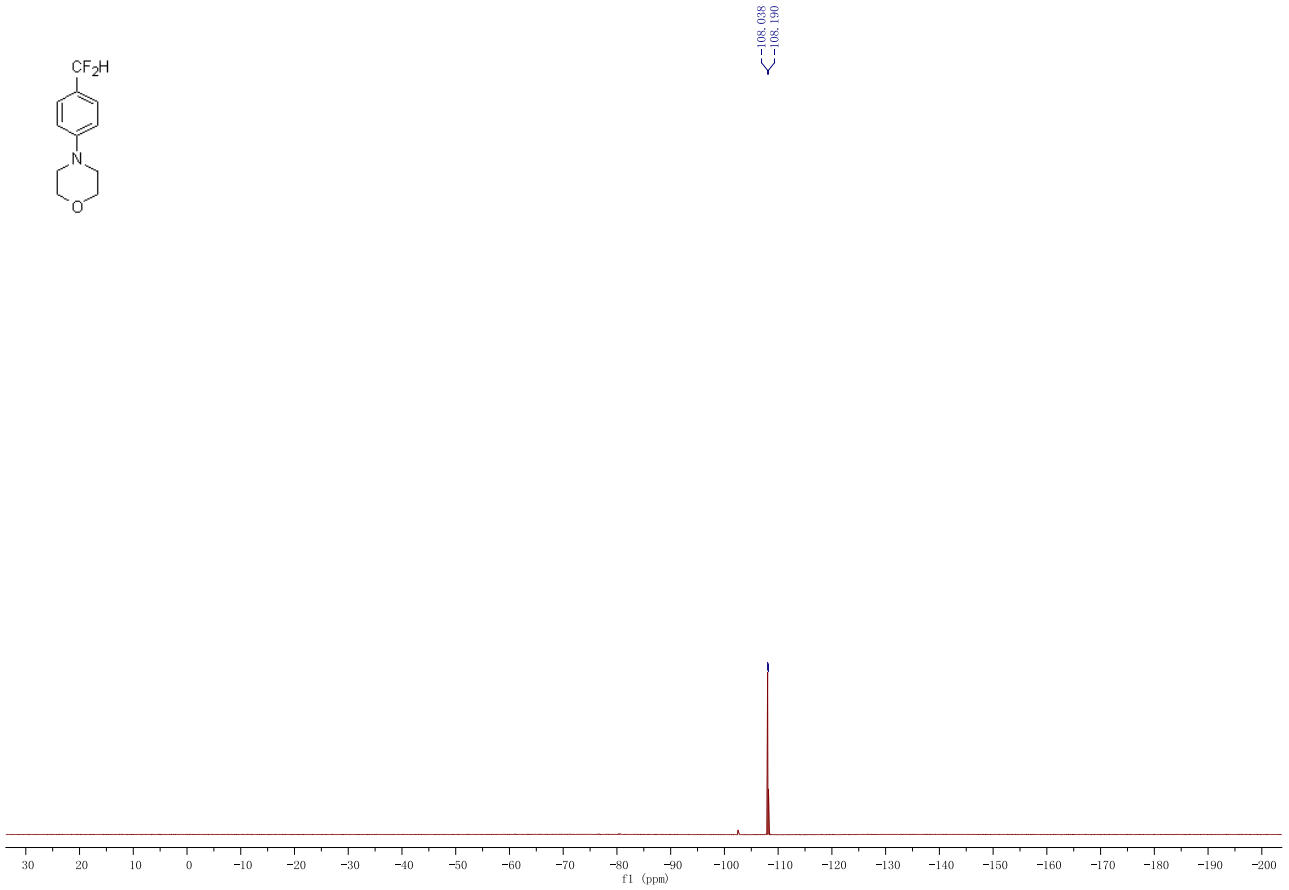


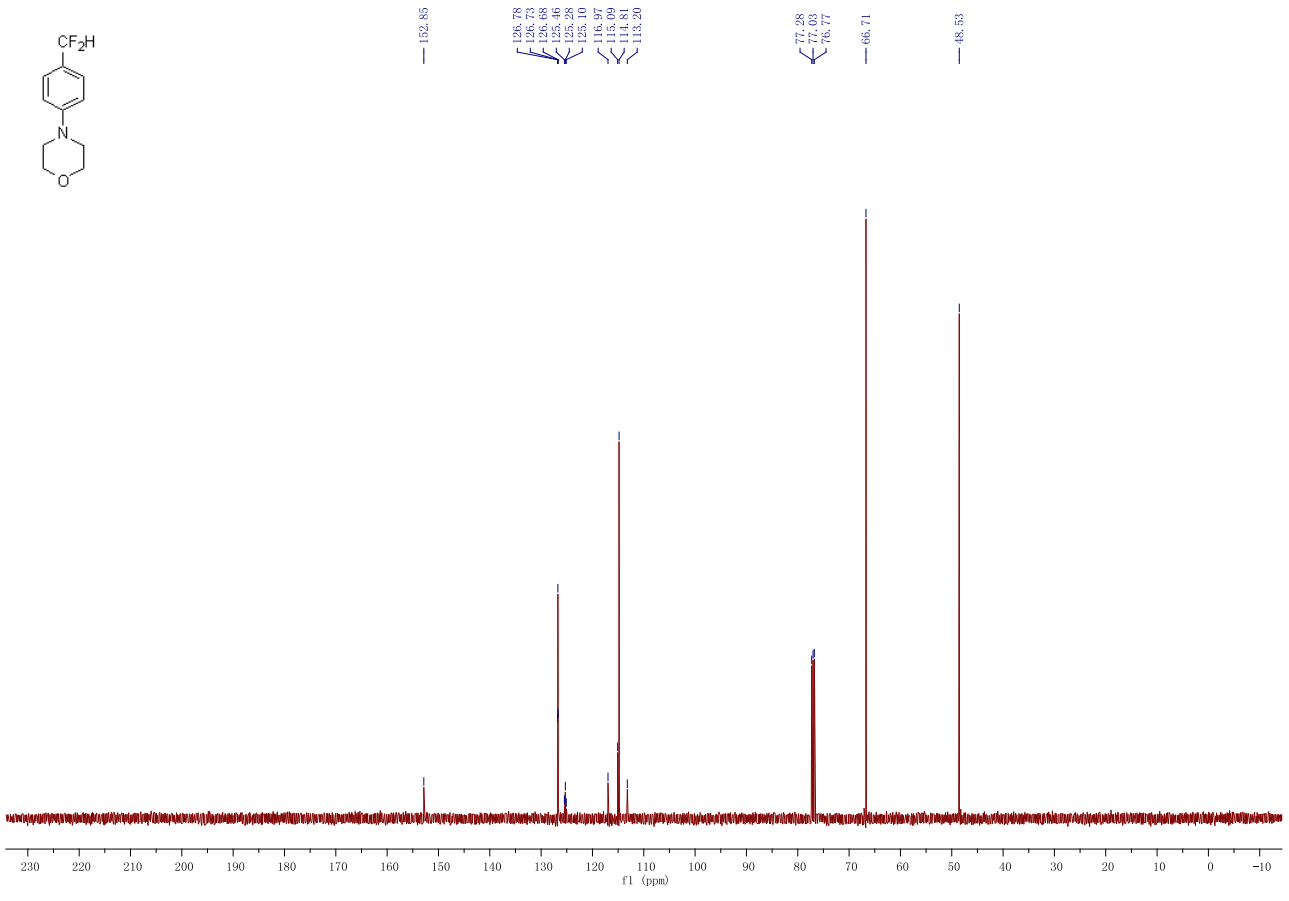




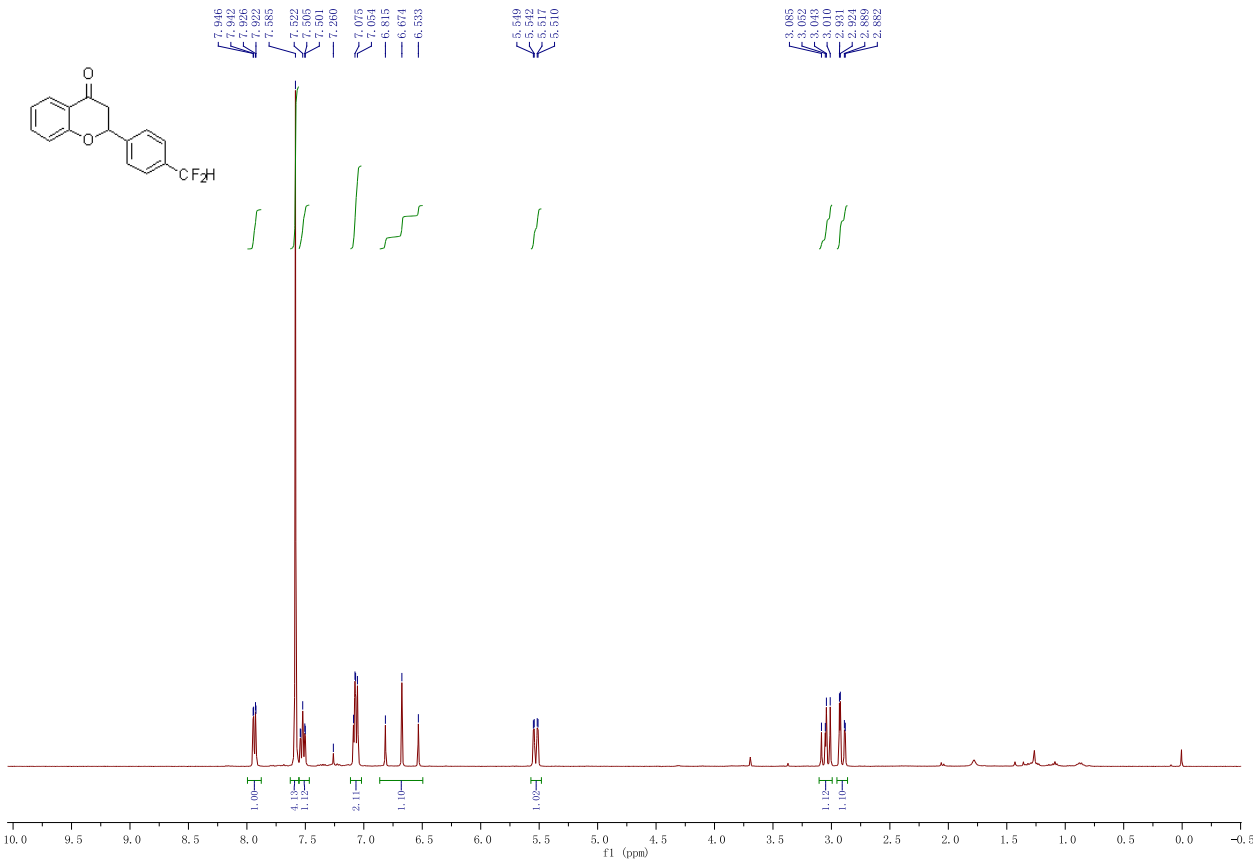
4-(4-(Difluoromethyl)phenyl)morpholine (36).

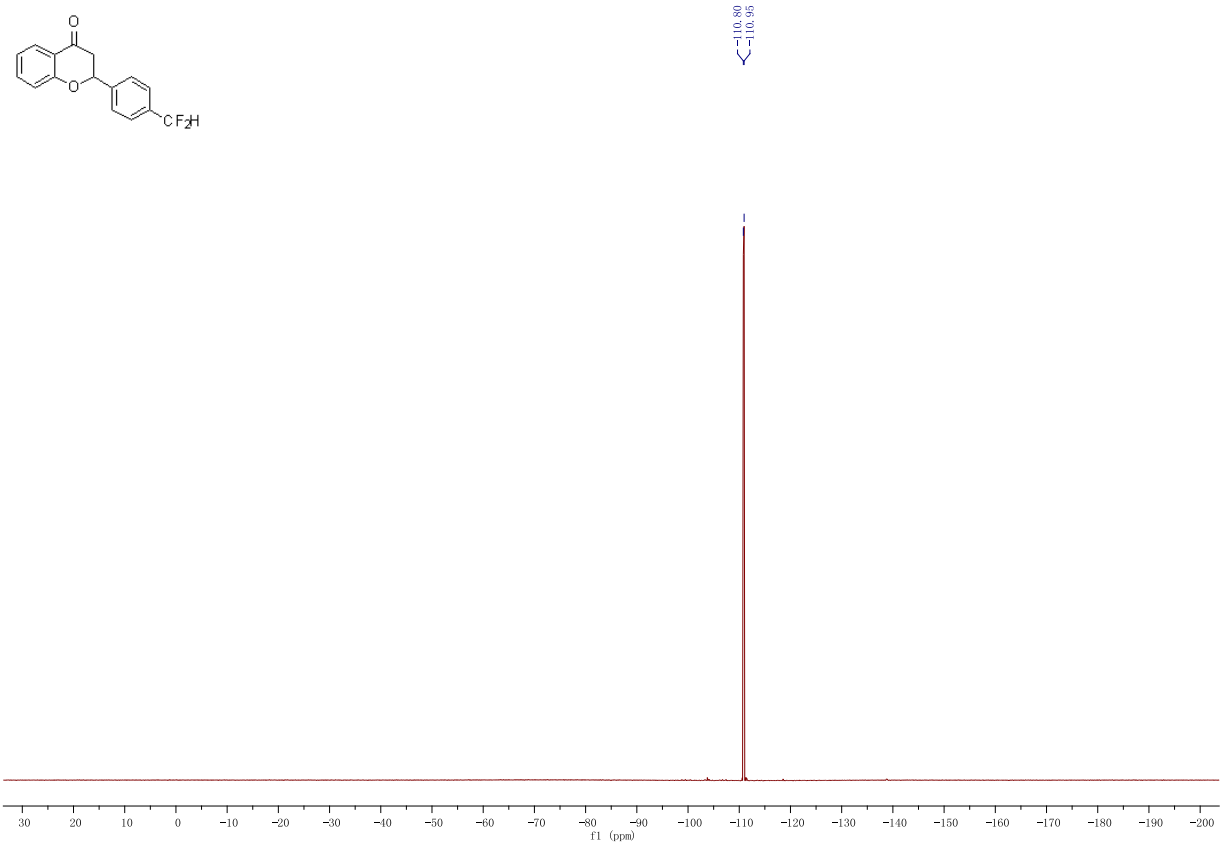


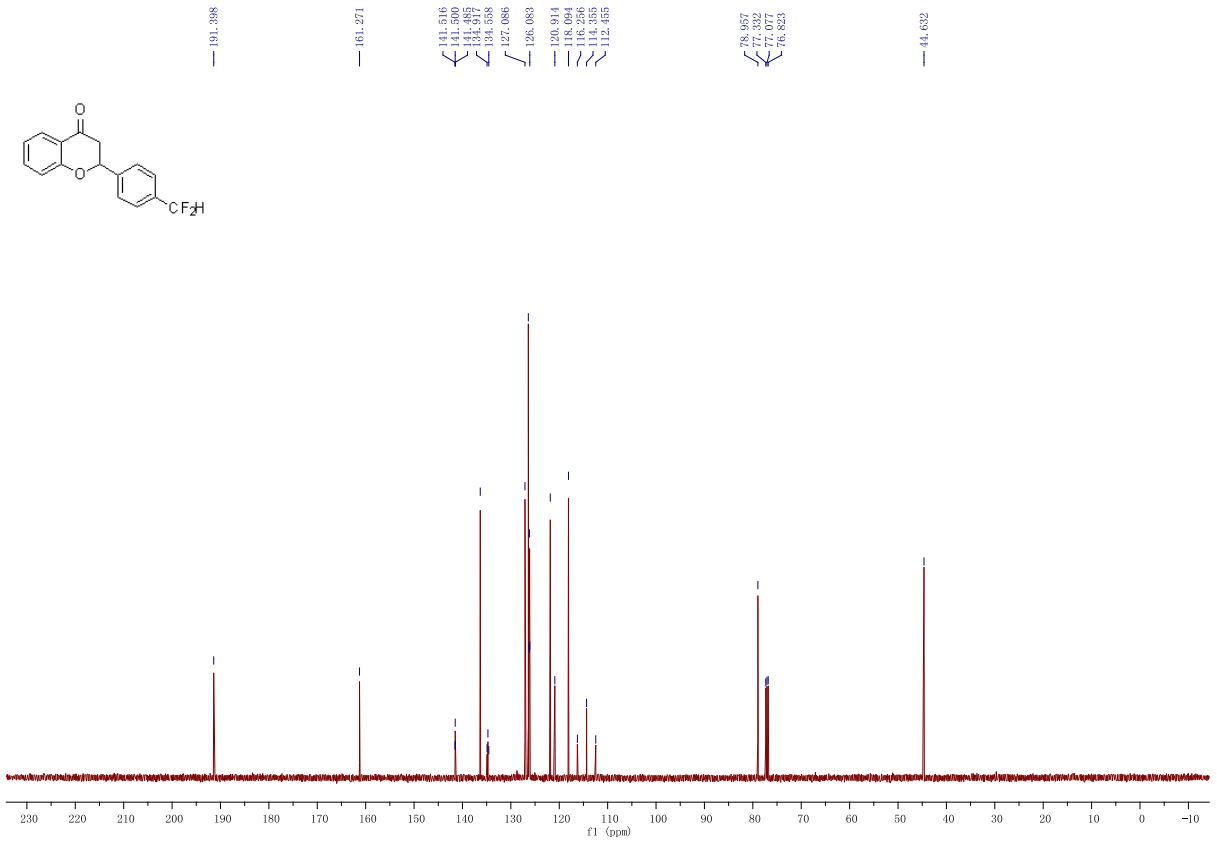

CF2H
N
O
-108.038
-108.190
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


CF2H
N
O
152.85
126.78
126.73
126.68
125.46
125.28
125.10
116.97
115.09
114.81
113.20
77.28
77.03
76.77
66.71
48.53
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)

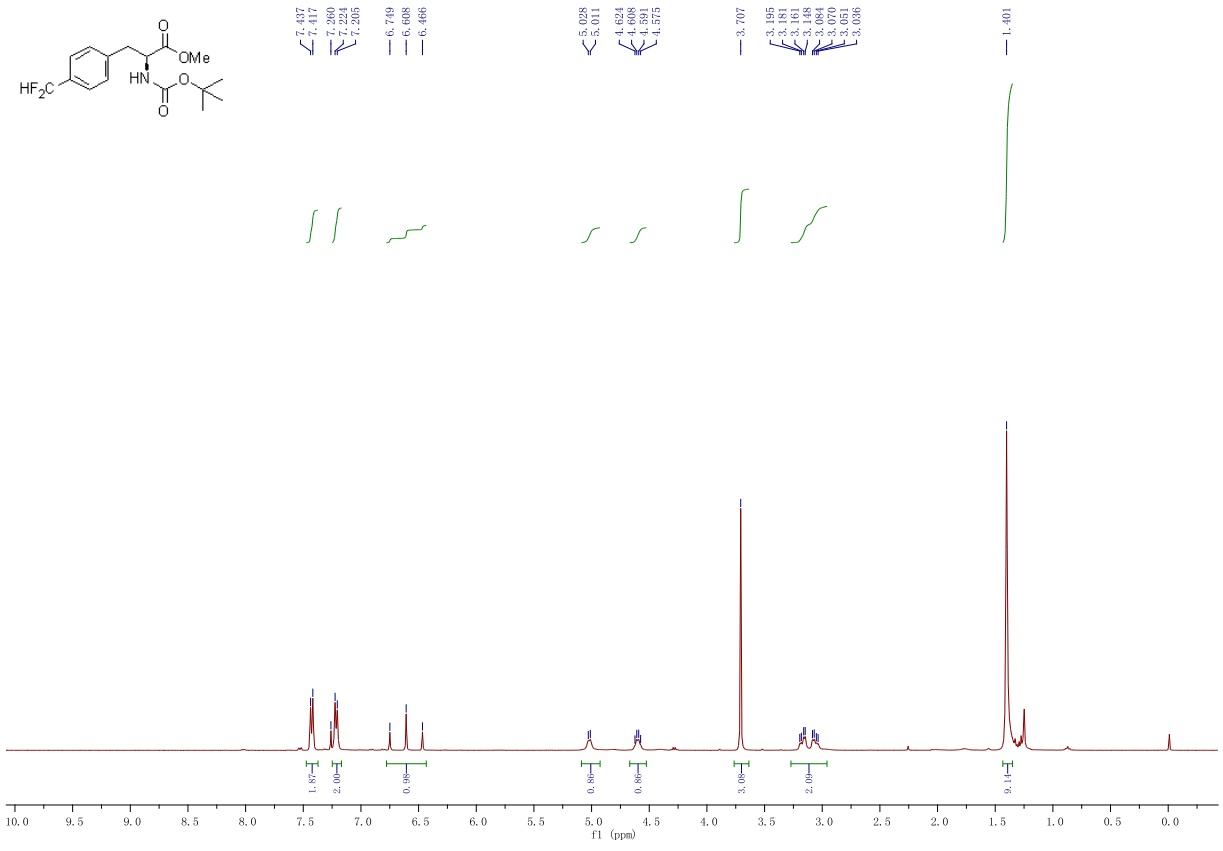
(2-(4-(Difluoromethyl)phenyl)chroman-4-one (37).

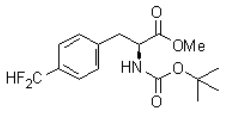




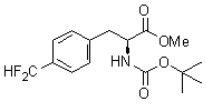


(S)-Methyl 2-((tert-butoxycarbonyl)amino)-3-(4-(difluoromethyl)phenyl)propanoate (38).



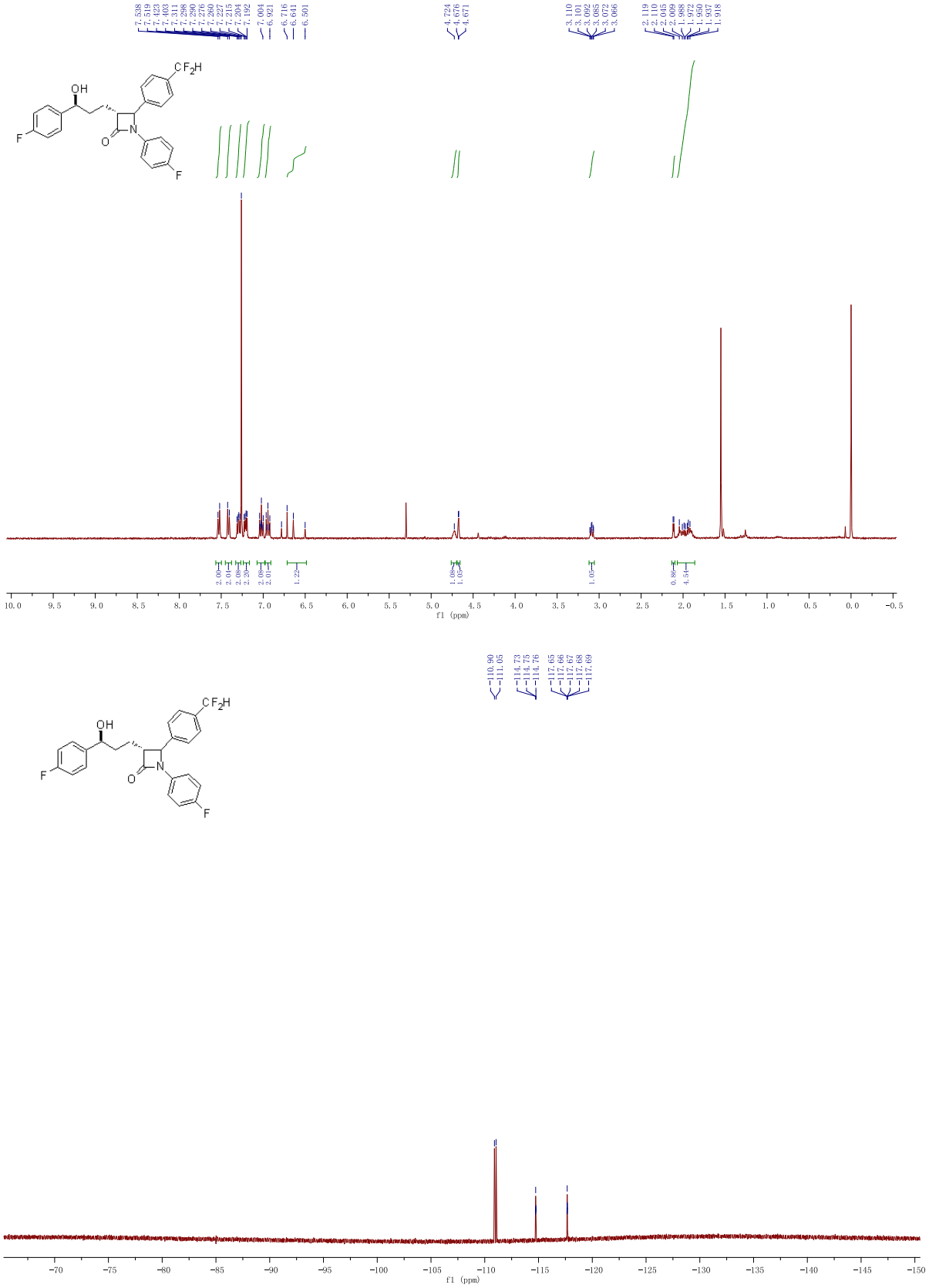

O
OMe
HN
O
O
HF_2C

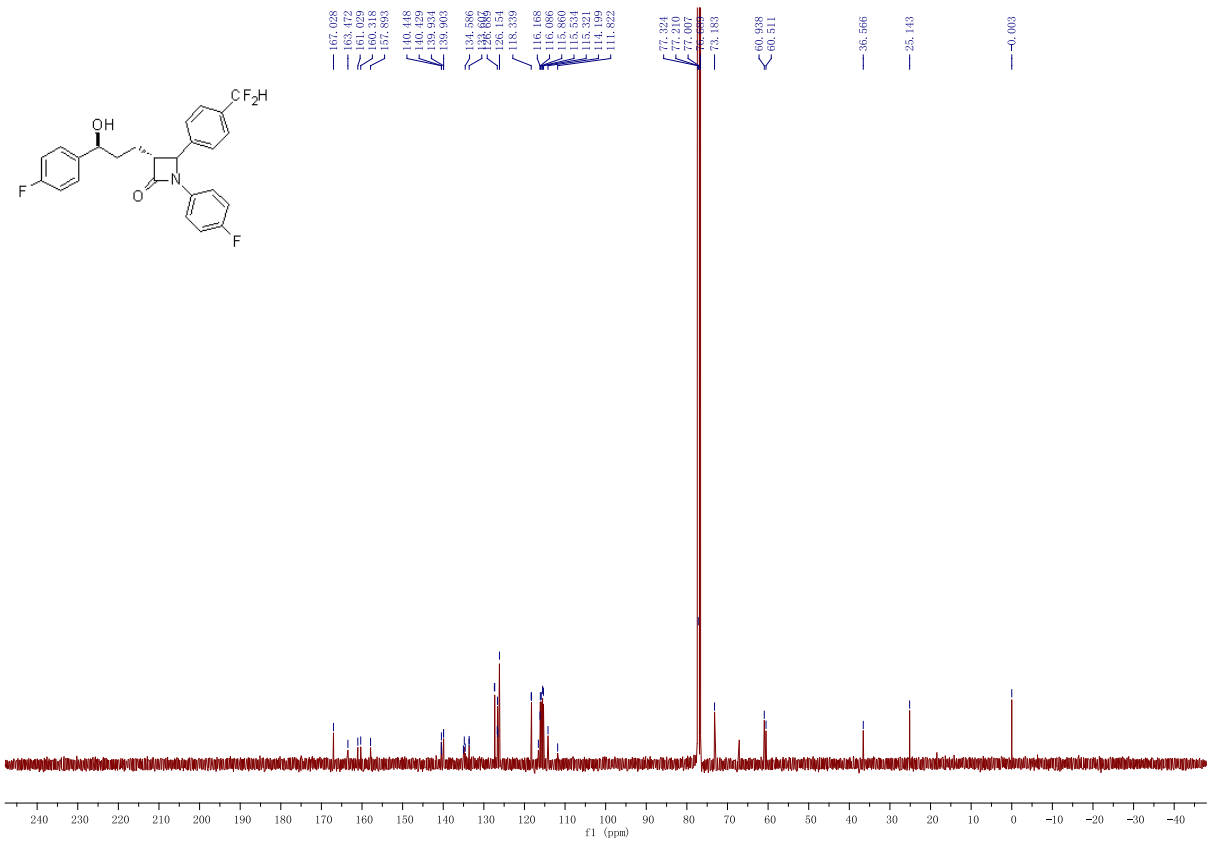
-110.460
-110.610
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


O
OMe
HN
O
O
HF_2C

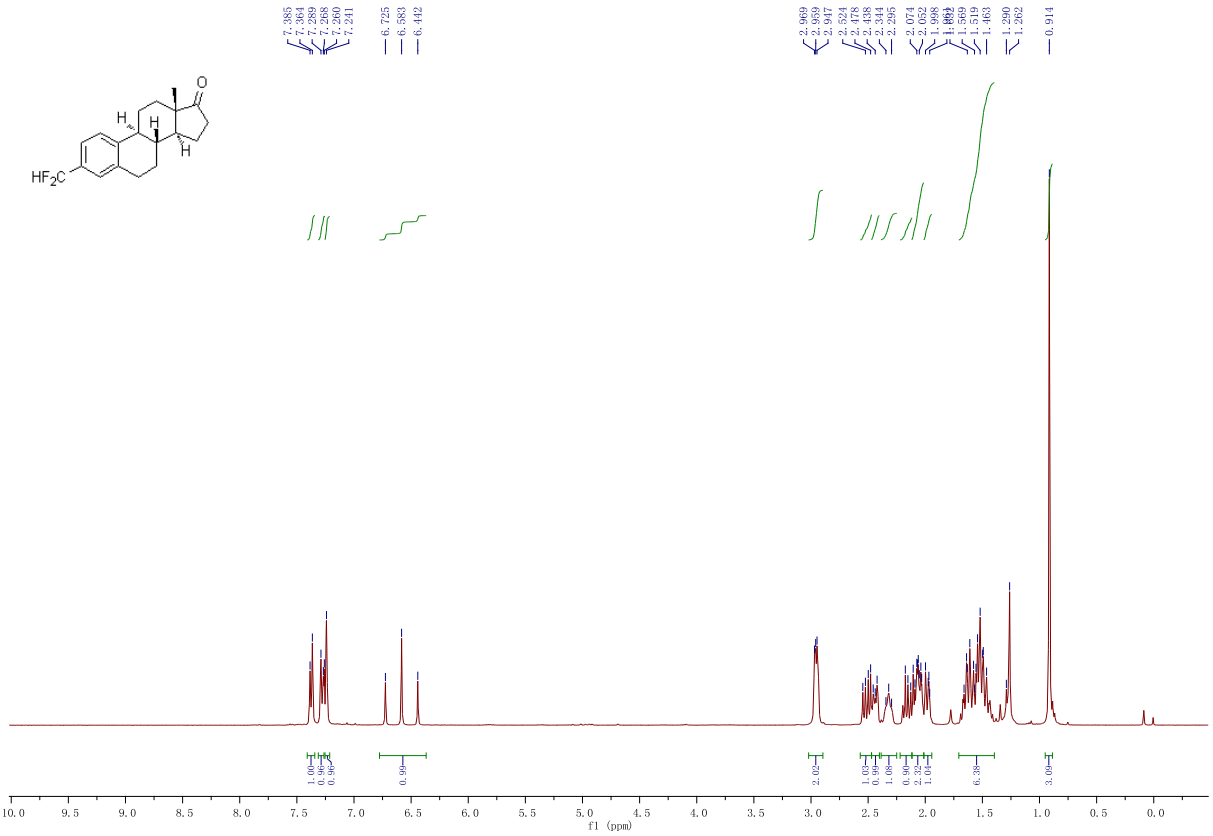
172.052
155.009
139.032
133.150
132.927
129.656
125.753
125.694
116.992
114.622
112.251
80.091
77.355
77.037
76.719
54.260
52.316
38.221
28.253
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

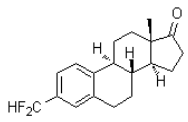
(3R)-4-(4-(Difluoromethyl)phenyl)-1-(4-fluorophenyl)-3-((S)-3-(4-fluorophenyl)-3-hydroxypropyl)azetidin-2-one (39).



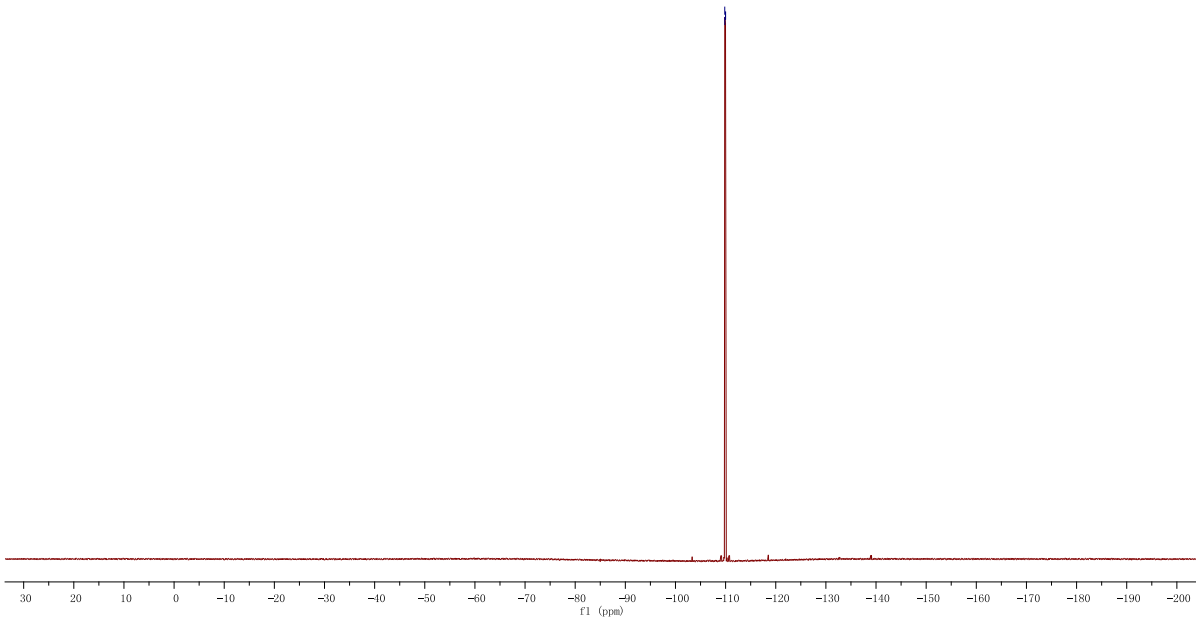


(8*R*,9*S*,13*S*,14*S*)-3-(Difluoromethyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one (40).

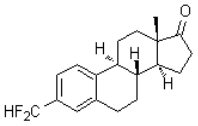


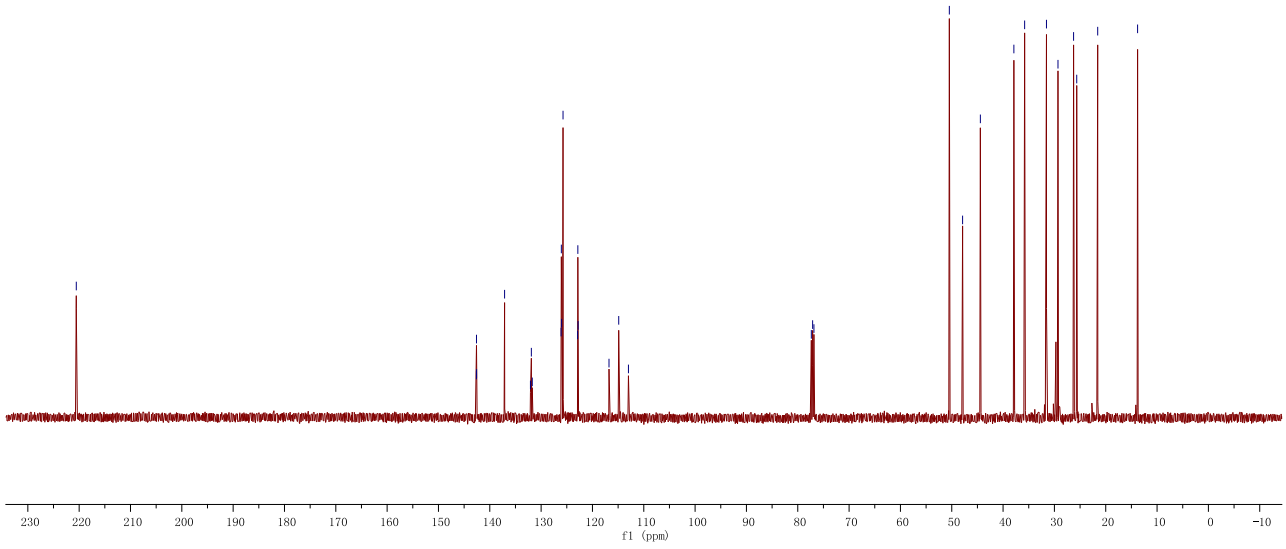

O
H
H
H
HF2C


109.831
109.845
109.981
109.996


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


220.559
142.605
142.590
142.575
137.116
131.902
126.730
122.844
122.796
116.775
114.881
112.988
77.359
77.104
76.850
50.470
47.887
44.426
37.896
35.802
29.305
25.651
21.565
13.796


O
H
H
H
HF2C


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)