Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information
For

Nickel-Catalyzed Reductive Monofluoroalkylation of Alkyl Tosylate with Bromofluoromethane to Primary Alkyl Fluoride

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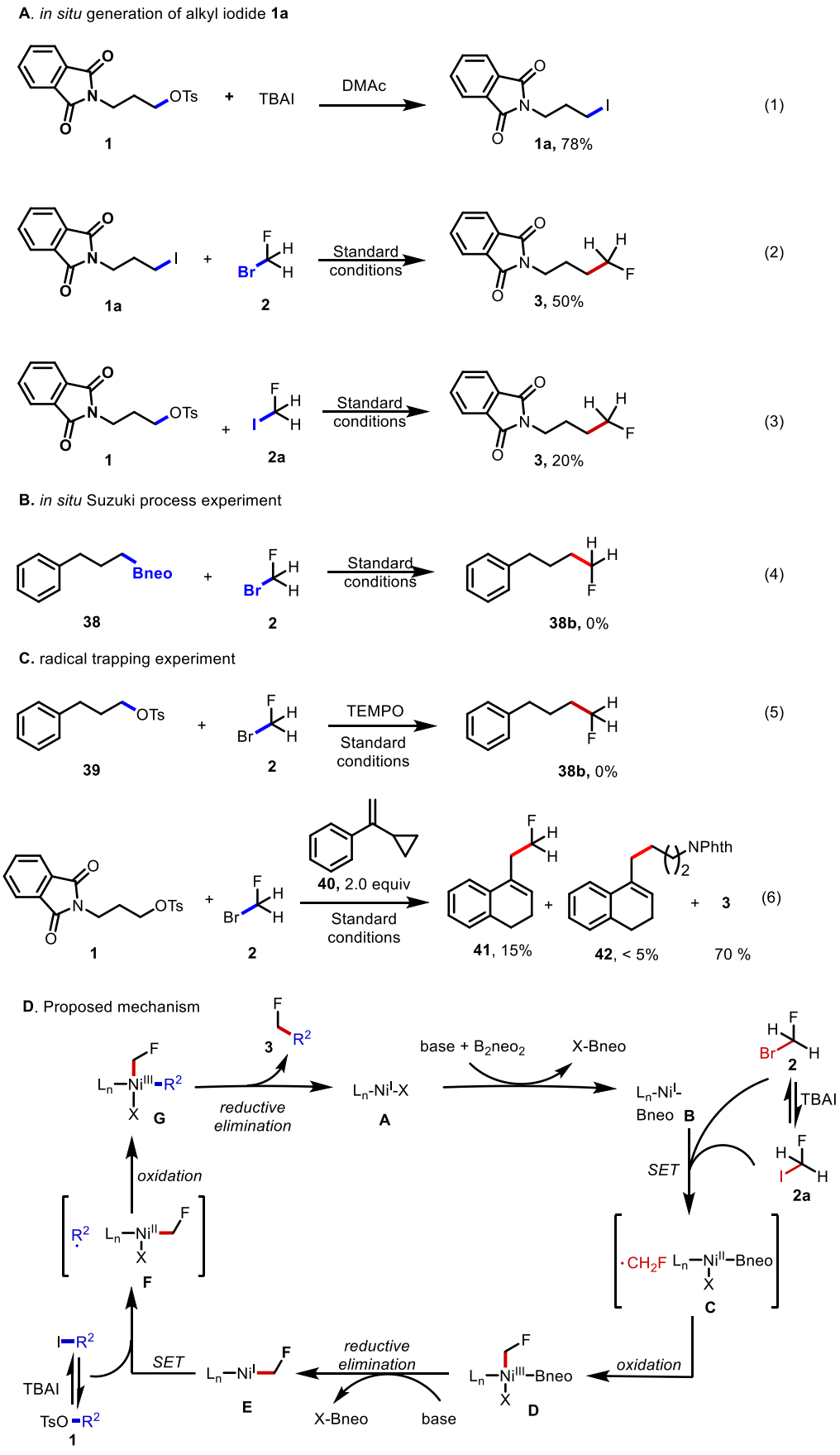
General Information:

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer(400 MHz for ^{1}H; 101 MHz for ^{13}C and 376 MHz for ^{19}F) or Bruker 500 MHz spectrometer(500 MHz for ^{1}H; 126 MHz for ^{13}C and 470 MHz for ^{19}F) in $CDCl_3$ unless otherwise noted. Signal positions were recorded in ppm with the abbreviations s, d, t, dd, dt, tt and m denoting singlet, doublet, triplet, doublet of doublets, doublet of triplets, triplets of triplets and multiplet respectively. All NMR chemical shifts were referenced to residual solvent peaks or to $Si(CH_3)_4$ as an internal standard. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm, $Si(CH_3)_4$ = δ 0 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm. High resolution mass spectra (HRMS) were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). GC-MS analysis was performed on an Aglient 7890 GC/MS gas chromatograph mass spectrometer. Organic solutions were concentrated under reduced pressure on Heidolph rotary evaporator. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λmax= 254 nm). Preparative TLC was performed on silica gel Xinnuo $HSGF_{254}$ preparative TLC plates. Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China.

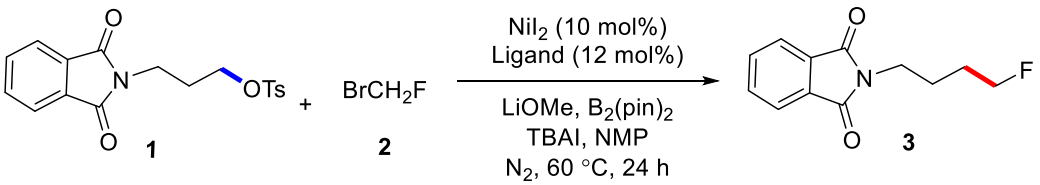
The following chemicals were purchased as follow: Bromofluoromethane (CAS: 373-52-4, Shangfluoro, 98%); nickel(II) chloride ethylene glycol dimethyl ether complex (CAS: 29046-78-4, Strem, 98%); anhydrous potassium carbonate (CAS: 584-08-7, Sinopharm, 99%); bis(neopentyl glycolato)diboron (CAS: 201733-56-4, TCI, 98%); Tetrabutylammonium iodide (CAS: 311-28-4, Sigma-Aldrich, 99%); *N*, *N*-Dimethylacetimide (CAS: 127-19-5, J&K, 99.5%, Water<0.005%). Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

Figure S1 Mechanistic study experiments and proposed mechanism.



Tables of the Optimization of Monofluoromethylation Reaction Conditions

Table S1. Ligands Screening[a]



Entry	Ligand (x mol%)	Yield (%)[b]
1	bpy (12)	8
2	dtbpy (12)	10
3	phen (12)	8
4	neocuprine (12)	10
5	dmbpy (12)	11
6	6-CN-bpy (12)	trace
7	dCF_3-bpy (12)	0
8	Py (24)	0
9	DMAP (24)	0
10	4-CN-Py (24)	0
11	PPh_3 (24)	trace
12	$\mathbf{L_1}$ (12)	23
13	$\mathbf{L_2}$ (12)	20
14	$\mathbf{L_3}$ (12)	15
15	$\mathbf{L_4}$ (12)	12
16	$\mathbf{L_5}$ (12)	16
17	$\mathbf{L_6}$ (12)	18
18	$\mathbf{L_7}$ (12)	11
19	$\mathbf{L_8}$ (12)	10

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), NiI_2 (10 mol%), Ligand (x mmol%), $B_2(pin)_2$ (0.4 mmol, 2 equiv), LiOMe (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), NMP (1.0 mL), 60 °C, 24 h.

[b]Yields determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

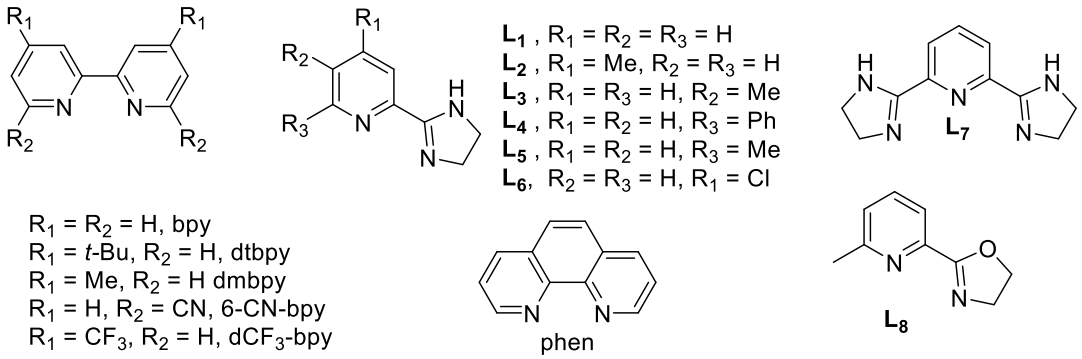
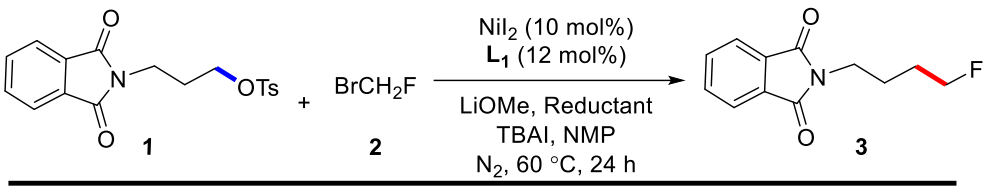


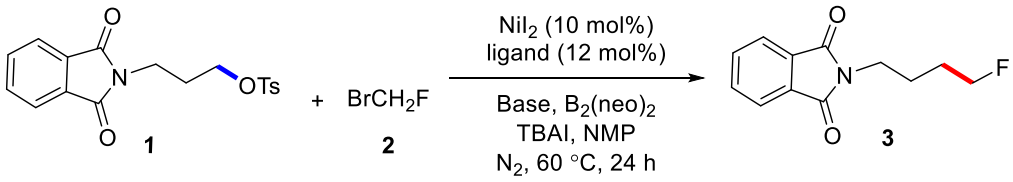
Table S2 Reductants Screening[a]



Entry	Reductant	Yield (%)[b]
1	Mn	0
2	Zn	0
3	Fe	0
4	$B_2(pin)_2$	21
5	$B_2(neo)_2$	30

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.),NiI_2 (10 mol%), $\mathbf{L_1}$ (12 mol%), reductant (0.4 mmol, 2 equiv), LiOMe (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), NMP (1.0 mL), 60 °C, 24 h.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

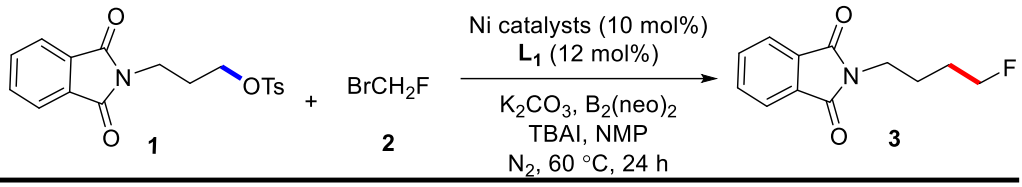
Table S3. Base Screening[a]



Entry	Base	Yield (%)	Entry	Base	Yield (%)[b]
1	$KHCO_3$	65	6	$NaHCO_3$	52
2	KF	trace	7	Na_2CO_3	65
3	K_3PO_4	20	8	LiOMe	32
4	Cs_2CO_3	32	9	LiOtBu	20
5	KOtBu	trace	10	K_2CO_3	68

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), NiI_2 (10 mol%), $\mathbf{L_1}$ (12 mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), Base (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), NMP (1.0 mL), 60 °C, 24 h.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

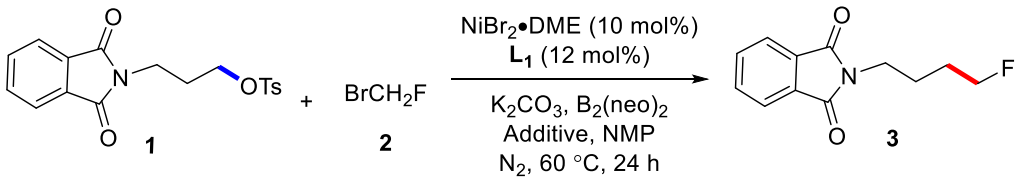
Table S4. Catalysts Screening[a]



Entry	[Ni]	Yield (%)[b]	Entry	[Ni]	Yield (%)[b]
1	No	0	6	$NiCl_2$(dtbpy)	18
2	$NiBr_2$	70	7	$NiBr_2$(dtbpy)	26
3	NiI_2	72	8	NiI_2(dtbpy)	20
4	$NiCl_2$	70	9	$Ni(NO_3)_2•6H_2O$	trace
5	$Ni(OAc)_2•4H_2O$	23	10	$NiBr_2$•(DME)	75

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), [Ni] (10 mol%), L_1 (12 mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), K_2CO_3 (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), NMP (1.0 mL), 60 °C, 24 h.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

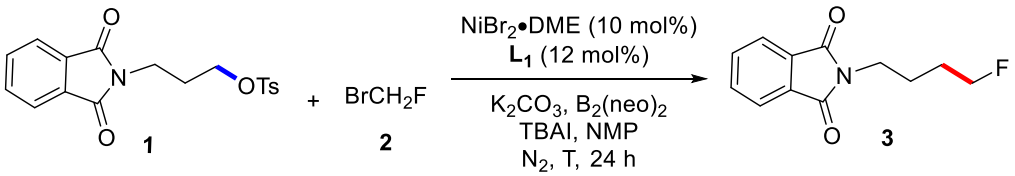
Table S5 Additive screening[a]



Entry	Additive	Yield (%)[b]
1	no	19
2	KI	65
3	NaI	65
4	TBAI	70
5	TBAC	50
6	TBAB	60

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.),$NiBr_2$•DME (10 mol%), L_1 (12 mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), K_2CO_3 (0.5 mmol, 2.5 equiv), Additive (0.4 mmol, 2 equiv), NMP (1.0 mL), 60 °C, 24 h; TBAI = Tetrabutylammonium iodide; TBAB = Tetrabutylammonium bromide ; TBAC = Tetrabutyl ammonium chloride.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

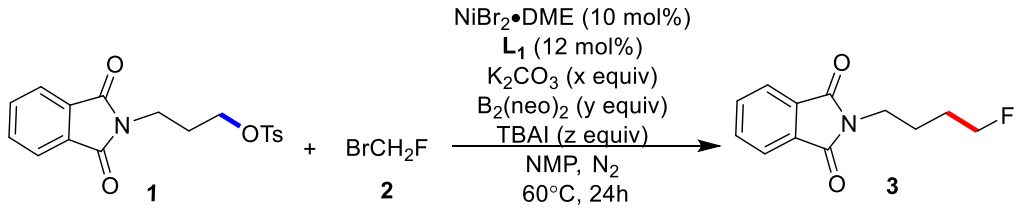
Table S6 Temperature Screening[a]



Entry	T/ °C	Yield (%)[b]
1	30	SM reserved
2	40	SM reserved
3	50	43
4	60	75
5	70	70
6	80	68

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.),$NiBr_2$•DME (10 mol%), $\mathbf{L_1}$ (12 mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), K_2CO_3 (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), NMP (1.0 mL), T °C, 24 h;
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

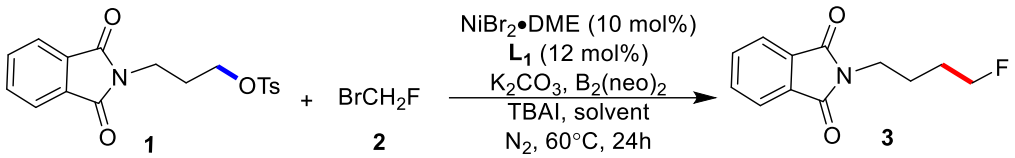
Table S7 Optimization the amount of reagents[a]



entry	x (equiv)	y (equiv)	z (equiv)	yield (%)[b]
1	2.0	2.0	2.0	65
2	2.5	2.0	2.0	75
3	3.0	2.0	2.0	74
4	2.5	1.5	2.0	48
5	2.5	2.5	2.0	68
6	2.5	2.0	1.0	40
7	2.5	2.0	1.5	61
8	2.5	2.0	2.5	70

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.),$NiBr_2$•DME (10 mol%), $\mathbf{L_1}$ (12 mol%), K_2CO_3 (x equiv), B_2neo_2 (y equiv), TBAI (z equiv), NMP (1.0 mL), 60 °C, 24 h.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.

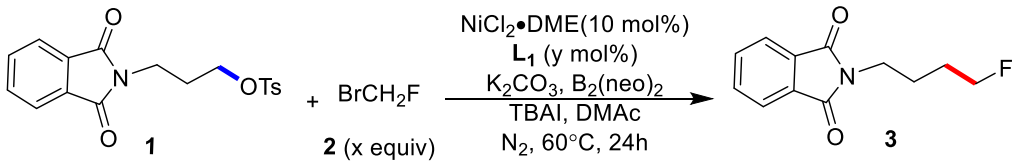
Table S8 Solvent Screening[a]



Entry	solvent	Yield (%)[b]	Entry	solvent	Yield (%)[b]
1	THF	31	8	NMP	73
2	dioxane	trace	9	DMF	38
3	DMSO	NR	10	DMAc	80
4	DCE	0	11	DMPU	36
5	MeCN	40	12	NMP/DMAc(1:1)	NR
6	NMP/THF(7:3)	73	13	NMP/DMAc(3:7)	60
7	NMP/THF(1:1)	52	14	$PhNO_2$	0

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (0.3 mmol, 1.5 equiv.),$NiBr_2$•DME (10 mol%), $\mathbf{L_1}$ (12 mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), K_2CO_3 (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), solvent (1.0 mL), 60 °C, 24 h.
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard

Table S9. Optimization the amount of bromofluoromethane[a]



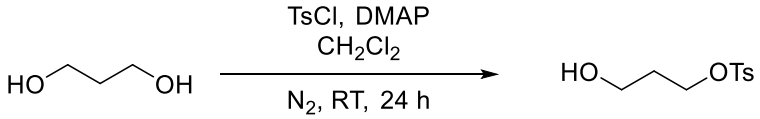
Entry	$BrCH_2F$ (x equiv)	$\mathbf{L_1}$ (y mol%)	Yield (%)[b]
1	1.0	$\mathbf{L_1}$ (12)	36
2	1.5	$\mathbf{L_1}$ (12)	63
3	2.0	$\mathbf{L_1}$ (12)	83
4	2.5	$\mathbf{L_1}$ (12)	72
5	2.0	$\mathbf{L_1}$ (10)	71
6[c]	2.0	$\mathbf{L_1}$ (13.5)	80
7	2.0	$\mathbf{L_1}$ (13.5)	87(85)

[a]Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), **2** (x equiv.),$NiCl_2$•DME (10 mol%), $\mathbf{L_1}$ (y mol%), $B_2(neo)_2$ (0.4 mmol, 2 equiv), K_2CO_3 (0.5 mmol, 2.5 equiv), TBAI (0.4 mmol, 2 equiv), DMAc (1.0 mL), 60 °C, 24 h;
[b]Yield was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard; numbers in parentheses were yields of isolated products.[c]$NiBr_2$•DME.

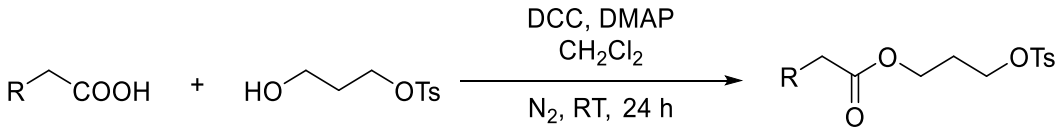
Preparation of Substrates:

Unless otherwise noted, all the alkyl alcohols were purchased from commercial sources and alkyl tosylates were prepared in the reported literature. Ligans **L_1-L_5** were synthesized using known method[1]、alkyl Bneo **38**[2]、alkene **40**[3] was synthesized according to the references. Compound **43**[4] was synthesized through known method.

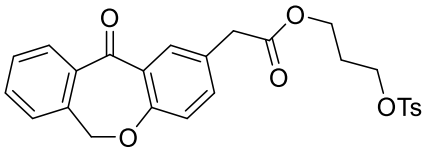
Preparation of Bioactive Molecule Alkyl tosylates.



To a flask equipped with a magnetic stir bar were added 1,3-diol (25 mmol, 1 equiv) and 4-(dimethylamino)pyridine (0.375 mmol, 1.5 mol %) dissolved in DCM (40 mL), triethylamine (27.5 mmol, 1.1 equiv) were added. The mixture was stirred for 15 min before *p*-toluenesulfonyl chloride (25 mmol, 1.0 equiv) in dichloromethane (8 mL) was added dropwise and stirred at 30 ℃ for another 4 hours. The reaction mixture was then filtrated, 100 ml of dichloromethane were added and the organic solution was washed with 1% HCl (2 × 40 mL), saturated sodium bicarbonate (2 × 40 mL), brine (2 × 40 mL), dried over magnesium sulfate and concentrated in vacuo. The product was purified by column chromatography on silica gel (silica gel, PE/EA 2:1) to afford the desired *mono*-tosylated alcohol.



To a solution of acid (5 mmol), 3-OTs-1-propanol (6 mmol) and DMAP (0.5 mmol) dissolved in 20 mL CH_2Cl_2, a solution of DCC (6 mmol) in DCM (10 mL) was slowly added under stirring and proceeded at room temperature overnight. The reaction mixture was then filtered and the solid was rinsed with DCM (2 x 10 mL). The combined filtrates were concentrated under vacuum and purified by column chromatography affording desired product.

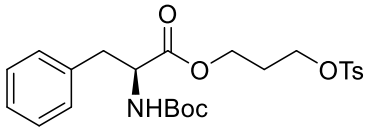


The 3-(tosyloxy)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate was purified with silica gel chromatography (PE/EA = 3:1) as a colorless solid (2.1 g, 89% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.57 (td, *J* = 7.4, 1.4 Hz, 1H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.19 (s, 2H), 4.13 (t, *J* = 6.1 Hz, 2H), 4.09 (t, *J* = 6.1 Hz, 2H), 3.57 (s, 2H), 2.44 (s, 3H), 1.98 (q, *J* = 6.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 190.91, 171.20, 160.64, 145.04, 140.52, 136.38, 135.67, 132.96, 132.95, 132.50, 130.02, 129.62, 129.40, 128.03, 127.96, 127.64, 125.25, 121.26, 73.77, 66.86, 60.78, 40.14, 28.30, 21.78.

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{26}H_{25}O_7S$: 481.1316, found: 481.1313.

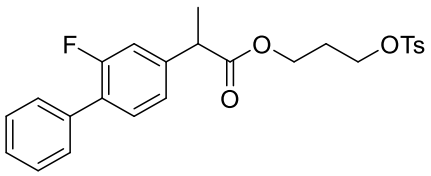


The Boc-L-phenylalanine alkyl tosylate was purified with silica gel chromatography (PE/EA = 8:1) as a colorless solid (1.8 g, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.75 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.17 (m, 3H), 7.15 – 7.04 (m, 2H), 5.05 (d, *J* = 8.3 Hz, 1H), 4.46 (d, *J* = 7.3 Hz, 1H), 4.10 (t, *J* = 6.1 Hz, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 2.99 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 1.89 (m, 2H),1.41(s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.61, 154.99, 144.94, 135.94, 132.75, 129.88, 129.15, 128.48, 127.80, 126.97, 79.82, 66.63, 60.83, 54.44, 38.28, 28.22, 28.06, 21.54.

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{24}H_{31}NO_7SNa$: 500.1713, found: 500.1720.

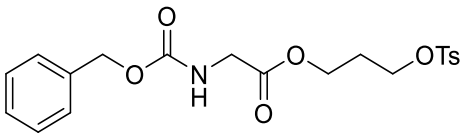


The 3-(tosyloxy) propyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl) propanoate was purified with silica gel chromatography (PE/EA = 6:1) as a colorless soild (2.0 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.03 (m, 2H), 4.14 (t, *J* = 6.1 Hz, 2H), 4.03 (t, *J* = 6.1 Hz, 2H), 3.69 (q, *J* = 7.1 Hz, 1H), 2.43 (s, 3H), 2.01 – 1.90 (m, 2H), 1.49 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.77, 159.79 (d, *J* = 248.5Hz), 145.02, 141.70 (d, *J* = 7.7Hz), 135.54, 133.03, 130.99 (d, *J* = 4.0 Hz), 130.01, 129.08 (d, *J* = 2.9 Hz), 128.59, 128.02 (d, *J* = 13.5Hz), 128.00, 127.84, 123.62 (d, *J* = 3.3 Hz), 115.30 (d, *J* = 23.6Hz), 66.80, 60.79, 45.03, 28.36, 21.77, 18.33.

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{25}H_{25}FO_5SNa$: 479.1299, found: 479.1302.

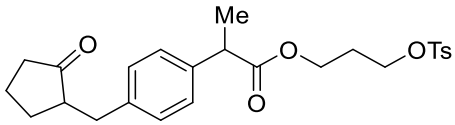


N-Carbobenzyloxyglycine alkyl tosylate was purified with silica gel chromatography (PE/EA = 8:1) as a colorless soild (1.7 g, 80% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.31 (m, 7H), 5.24 (t, *J* = 5.9 Hz, 1H), 5.13 (s, 2H), 4.19 (t, *J* = 6.1 Hz, 2H), 4.10 (t, *J* = 6.0 Hz, 2H), 3.90 (d, *J* = 5.6 Hz, 2H), 2.44 (s, 3H), 1.99 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 169.84, 156.35 145.15, 136.30, 132.89, 130.04, 128.67, 128.36, 128.25, 128.03, 67.26, 66.67, 61.23, 42.77, 28.19, 21.76.

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{20}H_{23}NO_7SNa$: 444.1087, found: 444.1088.

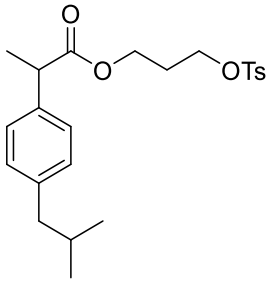


The 3-(tosyloxy)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate was purified with silica gel chromatography (PE/EA = 7:1) as a colorless solid (2.0 g, 87% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 4.00 (t, *J* = 6.2 Hz, 2H), 3.62 (q, *J* = 7.2 Hz, 1H), 3.11 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.45 (s, 3H), 2.39 – 2.29 (m, 2H), 2.20 – 2.04 (m, 2H), 2.01 – 1.86 (m, 2H), 1.84 – 1.64 (m, 1H), 1.62 – 1.48 (m, 1H), 1.43 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.12, 174.20, 144.90, 138.94, 138.09, 132.84, 129.88, 129.11, 127.82, 127.41, 77.48, 77.16, 76.84, 66.75, 60.26, 50.92, 44.92, 38.13, 35.13, 29.17, 28.15, 21.62, 20.49, 18.27.

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{25}H_{30}O_6SNa$: 481.1655., found: 481.1659.



The 3-(tosyloxy)propyl 2-(4-isobutylphenyl)propanoate was purified with silica gel chromatography (PE/EA = 7:1) as a colorless solid (1.8 g, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.70 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 3.99 (t, *J* = 6.2 Hz, 2H), 3.61 (q, *J* = 7.1 Hz, 1H), 2.45 (s, 3H), 1.90 (tt, *J* = 6.3, 3.1 Hz, 2H), 1.86 – 1.77 (m, 1H), 1.44 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.47, 144.93, 140.69, 137.58, 133.00, 129.96, 129.42, 127.96, 127.15, 66.85, 60.32, 45.10, 45.08, 30.27, 28.30, 22.47, 21.74, 18.39.

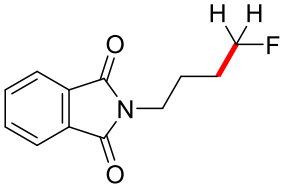
HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{23}H_{30}O_5SNa$: 441.1706, found: 441.1710.

Preparation of $BrCFH_2$ Stock Solution

Anhydrous DMAc (~23 mL) was added to a Schlenk graduated cylinder under nitrogen. The vessel and solvent were weighed. Next, $BrCFH_2$ was bubbled through the DMAc solution using a long needle until the total volume of the solution reached approximately 25 mL. The vessel was sealed weighed again. The concentration of the $BrCFH_2$ stock solution was calculated based on the mass of $BrCFH_2$ added and the total volume of the solution (~2.0 mol/L).

General Procedure for Nickel-catalyzed Cross-Coupling between Alkyl tosylates and Bromofluoromethane

In glove box, alkyl tosylate **1** (if solid, 1.0 equiv, 0.2 mmol), $NiCl_2$•DME (10 mol %, 0.02 mmol, 4.4 mg), **L$_1$** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) and Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl tosylate **1** (if liquid, 1.0 equiv, 0.2 mmol), Bromofluoromethane **2** (2.0 equiv, 0.4 mmol dissolved in DMAc) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired product as a colorless solid or oil.



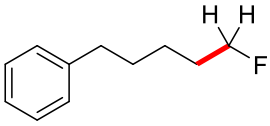
The product **3** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless solid (37.6 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.48 (dt, *J* = 47.6, 5.7 Hz, 2H), 3.75 (t, *J* = 6.8 Hz, 2H), 1.88 – 1.67 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 168.55, 134.11, 132.21, 123.39, 83.51 (d, *J* = 165.3 Hz), 37.60, 27.91 (d, *J* = 20.0 Hz), 24.74 (d, *J* = 4.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.82 (tt, *J* = 46.9, 25.0 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}FNO_2$: 222.0925, found: 222.0915.



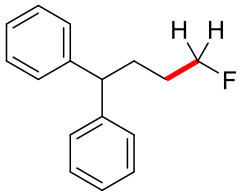
The product **4** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil (18.9 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 2H), 7.21 – 7.15 (m, 3H), 4.44 (dt, *J* = 47.3, 6.1 Hz, 2H), 2.65 – 2.60 (m, 2H), 1.78 – 1.62 (m, 4H), 1.50 – 1.40 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 142.52, 128.51, 128.42, 125.84, 84.24 (d, *J* = 164.1 Hz), 35.95, 31.26, 30.42 (d, *J* = 19.4 Hz), 24.99 (d, *J* = 5.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.06 (tt, *J* = 47.1, 24.9 Hz).

HRMS EI (m/z): $[M]^+$ calcd. for $C_{11}H_{15}F$: 166.1158, found: 166.1151.



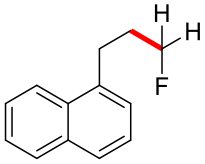
The product **5** was purified with silica gel chromatography (PE/EA = 75:1) as a colorless oil (29.7 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.22 (m, 8H), 7.20 – 7.14 (m, 2H), 4.43 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.92 (t, *J* = 7.9 Hz, 1H), 2.23 – 2.12 (m, 2H), 1.75 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.75, 128.64, 127.94, 126.38, 84.13 (d, *J* = 164.8 Hz), 51.06, 31.41 (d, *J* = 4.6 Hz), 29.16 (d, *J* = 19.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.47 (tt, *J* = 47.5, 26.0 Hz).

HRMS EI (m/z): $[M]^+$ calcd. for $C_{16}H_{17}F$: 228.1309, found: 228.1304.



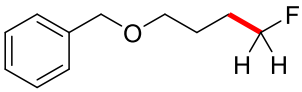
The product **6** was purified with silica gel chromatography (PE/EA = 50:1) as a colorless oil (23 mg, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 4.44 (dt, *J* = 47.2, 5.8 Hz, 2H), 3.19 – 3.10 (m, 2H), 2.15 – 1.99 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 137.28, 134.04, 131.86, 128.96, 127.03, 126.39, 126.06, 125.67, 123.75, 83.51 (d, *J* = 164.9 Hz), 31.50 (d, *J* = 19.8 Hz), 28.62 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -219.85 (tt, *J* = 47.2, 26.4 Hz).

HRMS EI (m/z): [M]+ calcd. for $C_{13}H_{13}F$: 188.1001, found: 188.0994.



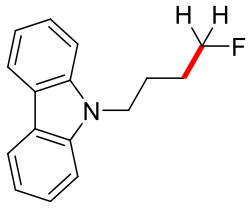
The product **7** was purified with silica gel chromatography (PE/EA = 80:1) as a colorless oil (17.5 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 4.51 (s, 2H), 4.47 (dt, *J* = 47.3, 5.8 Hz, 2H), 3.52 (t, *J* = 6.3 Hz, 2H), 1.88 – 1.68 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.60, 128.51, 127.74, 127.70, 84.10 (d, *J* = 164.2 Hz), 73.03, 69.82, 27.48 (d, *J* = 19.8 Hz), 25.70 (d, *J* = 5.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.25 (tt, *J* = 47.7, 25.6 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{11}H_{15}FONa$: 205.0999, found: 205.1013.



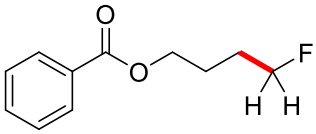
The product **8** was purified with silica gel chromatography (PE/EA = 6:1) as a colorless oil (41.0 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.37 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.11 (m, 2H), 4.31 (dt, *J* = 47.3, 5.8 Hz, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.71 – 1.54 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 140.39, 125.78, 122.94, 120.50, 118.99, 108.68, 83.85 (d, *J* = 165.2 Hz), 42.59, 28.21 (d, *J* = 19.8 Hz), 25.23 (d, *J* = 4.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.47 (tt, *J* = 47.4, 26.3 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{16}H_{17}FN$: 242.1340, found: 242.1339.



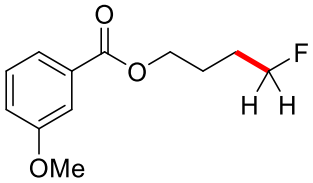
The product **9** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (22.8 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 7.97 (m, 2H), 7.62 – 7.51 (m, 1H), 7.50 – 7.40 (m, 2H), 4.53 (dt, *J* = 47.3, 5.7 Hz, 2H), 4.38 (t, *J* = 6.3 Hz, 2H), 2.01 – 1.76 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.70, 133.08, 130.37, 129.66, 128.50, 83.67 (d, *J* = 165.1 Hz), 64.52, 27.33 (d, *J* = 20.1 Hz), 24.91 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.83 (tt, *J* = 46.8, 25.3 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{11}H_{14}FO_2$: 197.0972, found: 197.0967.



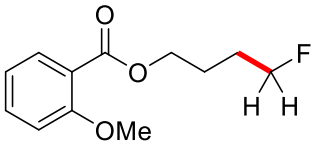
The product **10** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (32.6 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.56 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.10 (ddd, *J* = 8.3, 2.7, 1.1 Hz, 1H), 4.52 (dt, *J* = 47.1, 5.6 Hz, 2H), 4.37 (t, *J* = 6.2 Hz, 2H), 3.85 (s, 3H), 2.01 – 1.76 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.56, 159.69, 131.70, 129.53, 122.05, 119.47, 114.25, 83.64 (d, *J* = 165.1 Hz), 64.62, 55.57, 27.33 (d, *J* = 20.0 Hz), 24.91 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.88 (tt, *J* = 47.2, 25.4 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{12}H_{16}FO_3$: 227.1078, found: 227.1081.



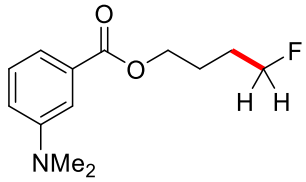
The product **11** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (36.2 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ7.79 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.55 – 7.40 (m, 1H), 7.06 – 6.91 (m, 2H), 4.52 (dt, *J* = 47.6, 5.5 Hz, 2H), 4.35 (t, *J* = 5.9 Hz, 2H), 3.90 (s, 3H), 2.02 – 1.80 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.38 , 159.26 , 133.62 , 131.66 , 120.24 , 112.13 , 83.71 (d, *J* = 164.8 Hz), 64.34 , 56.04 , 27.33 (d, *J* = 20.0 Hz), 24.81 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.71 (tt, *J* = 46.4, 25.9Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{12}H_{16}FO_3$: 227.1078, found: 227.1085.



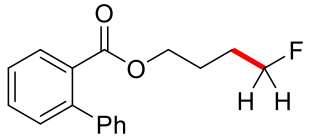
The product **12** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (28.7 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.35 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.8 Hz, 1H), 4.52 (dt, *J* = 47.3, 5.7 Hz, 2H), 4.36 (t, *J* = 6.2 Hz, 2H), 2.99 (s, 6H), 1.83 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.36, 150.49, 130.96, 129.11, 117.58, 116.91, 113.30, 83.71 (d, *J* = 165.0 Hz), 64.38, 40.69, 27.32 (d, *J* = 19.9 Hz), 24.86 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.79 (tt, *J* = 47.6, 26.0 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{13}H_{19}FNO_2$: 240.1394, found: 240.1399.



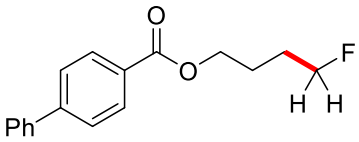
The product **13** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (35.4 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.79 (m, 1H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1H), 7.45 – 7.30 (m, 7H), 4.28 (dt, *J* = 47.5, 5.9 Hz, 2H), 4.07 (t, *J* = 6.1 Hz, 2H), 1.53 – 1.30 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.13, 142.32, 141.69, 131.33, 131.24, 130.78, 129.91, 128.45, 128.21, 127.33, 127.30, 83.53 (d, *J* = 164.8 Hz), 64.50, 26.81 (d, *J* = 19.8 Hz), 24.25 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): -219.01 (tt, *J* = 47.6, 26.0 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{17}H_{17}FO_2Na$: 295.1105, found: 295.1109.



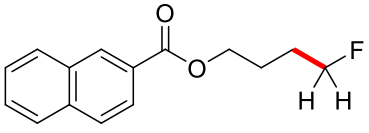
The product **14** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (40.8 mg, 75% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.31 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 4.44 (dt, *J* = 47.6, 5.7 Hz, 2H), 4.30 (t, *J* = 6.2 Hz, 2H), 1.89 – 1.69 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.54, 145.77, 140.08, 130.17, 129.09, 129.04, 128.26, 127.37, 127.16, 83.64 (d, *J* = 165.2 Hz), 64.51, 27.32 (d, *J* = 19.9 Hz), 24.93 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.78 (tt, *J* = 47.4, 25.7 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{17}H_{17}FO_2Na$: 295.1105, found: 295.1113.



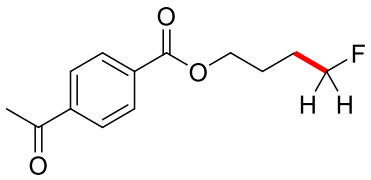
The product **15** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (42.8 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (d, *J* = 8.7 Hz, 1H), 8.19 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.63 (m, 1H), 7.58 – 7.46 (m, 2H), 4.56 (dt, *J* = 47.6, 5.6 Hz, 2H), 4.44 (t, *J* = 6.1 Hz, 2H), 2.04 – 1.85 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): 166.88, 135.66, 132.61, 131.14, 129.49, 128.40, 128.31, 127.91, 127.62, 126.80, 125.32, 83.71 (d, *J* = 165.1 Hz), 64.69, 27.38 (d, *J* = 20.1 Hz), 24.99 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.79 (tt, *J* = 47.5, 26.1 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{15}H_{15}FO_2Na$: 269.0954, found: 269.0951.



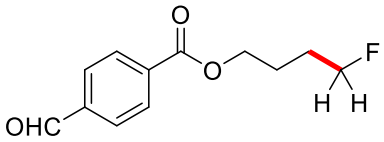
The product **16** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (35.7 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 4.54 (dt, *J* = 47.5, 5.6 Hz, 2H), 4.41 (t, *J* = 6.2 Hz, 2H), 2.65 (s, 3H), 2.01 – 1.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.64, 165.79, 140.35, 134.11, 129.90, 128.33, 83.58 (d, *J* = 165.2 Hz), 64.99, 27.26 (d, *J* = 20.1 Hz), 27.00, 24.88 (d, *J* = 4.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.91 (tt, *J* = 46.8, 25.4 Hz).

HRMS ESI (m/z): $[M+H]^+$calcd. for $C_{13}H_{16}FO_3$: 239.1078, found: 239.1074.



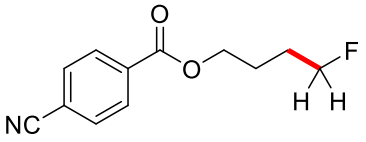
The product **17** was purified with silica gel chromatography (PE/EA = 6:1) as a colorless oil (30.5 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.27 – 8.15 (m, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 4.54 (dt, *J* = 47.6, 5.7 Hz, 2H), 4.42 (t, *J* = 6.3 Hz, 2H), 2.04 – 1.75 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 191.81, 165.68, 139.30, 135.35, 130.30, 129.68, 83.59 (d, *J* = 165.3 Hz), 65.19, 27.28 (d, *J* = 20.2 Hz), 24.91 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.89 (tt, *J* = 51.1, 25.9Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{12}H_{14}FO_3$: 225.0921, found: 225.0925.



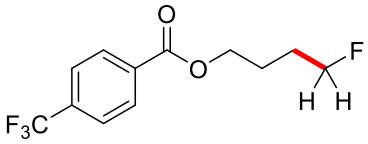
The product **18** was purified with silica gel chromatography (PE/EA = 6:1) as a colorless oil (31.0 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 4.53 (dt, *J* = 47.5, 5.6 Hz, 2H), 4.42 (t, *J* = 6.2 Hz, 2H), 1.99 – 1.80 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.03, 134.19, 132.38, 130.20, 118.10, 116.57, 83.53 (d, *J* = 165.5 Hz), 65.39, 27.25 (d, *J* = 20.2 Hz), 24.91 (d, *J* = 4.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -219.00 (tt, *J* = 47.2, 26.0 Hz).

HRMS ESI (m/z): $[M+Na]^+$calcd. for $C_{12}H_{12}FO_2NNa$:244.0744, found: 244.0737.



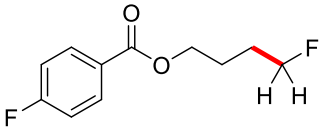
The product **19** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (38.6 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 4.53 (dt, *J* = 47.6, 5.7 Hz, 2H), 4.41 (t, *J* = 6.2 Hz, 2H), 2.01 – 1.82 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.47, 134.58 (q, *J* = 32.7 Hz), 133.58, 130.09, 125.56 (q, *J* = 3.7 Hz), 123.76 (q, *J* = 272.6 Hz), 83.59 (d, *J* = 165.3 Hz), 65.12, 27.28 (d, *J* = 20.1 Hz), 24.91 (d, *J* = 4.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.11 (s, 3F), -218.98 (tt, *J* = 47.4, 25.5 Hz, 1F).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}F_4O_2$: 265.0846, found: 265.0840.



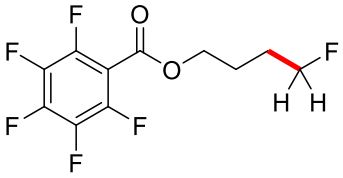
The product **20** was purified with silica gel chromatography (PE/EA = 12:1) as a colorless oil (31.3 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 – 7.65 (m, 2H), 7.17 – 7.04 (m, 2H), 4.52 (dt, *J* = 47.4, 5.6 Hz, 2H), 4.37 (t, *J* = 6.3 Hz, 2H), 1.98 – 1.78 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.91 (d, *J* = 253.8 Hz), 165.73, 132.22 (d, *J* = 9.4 Hz), 126.64 (d, *J* = 2.9 Hz), 115.67 (d, *J* = 22.0 Hz), 83.62 (d, *J* = 165.3 Hz), 64.67, 27.31 (d, *J* = 20.1 Hz), 24.93 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -105.71 (tt, *J* = 8.4, 5.5 Hz, 1F), -218.87 (dt, *J* = 47.3, 25.7 Hz, 1F)

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{11}H_{12}F_2O_2Na$: 237.0698, found: 237.0687.



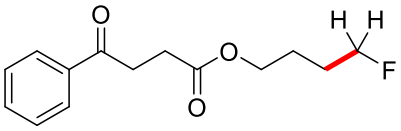
The product **21** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (34.3 mg, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.57 (t, *J* = 5.5 Hz, 1H), 4.45 (td, *J* = 6.1, 5.9, 4.6 Hz, 3H), 1.97 – 1.75 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.18, 83.46 (d, *J* = 165.3 Hz), 66.41, 27.06 (d, *J* = 20.2 Hz), 24.74 (d, *J* = 4.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -136.25 – -141.78 (m, 2F), -148.55 (tt, *J* = 21.0, 4.8Hz, 1F), -160.20 – -160.48 (m, 2F), -219.30 (tt, *J* = 47.2, 26.4 Hz, 1F).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{11}H_9F_6O_2$: 287.0501, found: 287.0512.



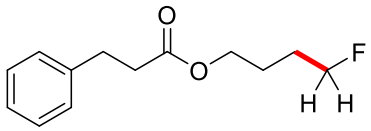
The product **22** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (37.8 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.93 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.39 (m, 2H), 4.47 (dt, *J* = 47.2, 5.7 Hz, 2H), 4.16 (t, *J* = 6.2 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 2.77 (t, *J* = 6.6 Hz, 2H), 1.83 – 1.67 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.23, 173.05, 136.65, 133.40, 128.77, 128.17, 83.67 (d, *J* = 164.8 Hz), 64.25, 33.49, 28.35, 27.17 (d, *J* = 20.0 Hz), 24.77 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.89 (tt, *J* = 47.4, 26.3 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{17}FO_3Na$: 275.1054, found: 275.1065.



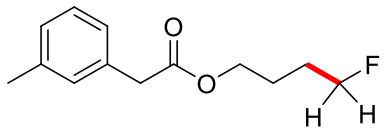
The product **23** was purified with silica gel chromatography (PE/EA = 20:1) as a colorless oil (43.5 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.44 (dt, *J* = 47.6, 5.2 Hz, 2H), 4.11 (t, *J* = 6.1 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.83 – 1.62 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.05, 140.56, 128.62, 128.41, 126.39, 83.63 (d, *J* = 165.0 Hz), 64.00, 35.99, 31.09, 27.11 (d, *J* = 20.0 Hz), 24.74 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.86 (tt, *J* = 47.8, 26.1 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{13}H_{17}FO_2Na$: 247.1105 found: 247.1108.



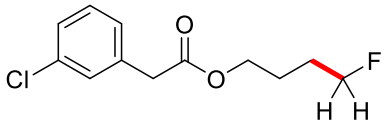
The product **24** was purified with silica gel chromatography (PE/EA = 12:1) as a colorless oil (29.2 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 1H), 7.18 (m, 3H), 4.42 (dt, *J* = 47.5, 5.4 Hz, 2H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.64 (s, 2H), 2.32 (s, 3H), 1.94 – 1.62 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.64, 136.88, 132.86, 130.45, 130.23, 127.52, 126.25, 83.60 (d, *J* = 165.0 Hz), 64.37, 39.34, 27.09 (d, *J* = 20.0 Hz), 24.70 (d, *J* = 5.1 Hz), 19.74.

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.83 (tt, *J* = 47.3, 25.7 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{13}H_{17}FO_2Na$: 247.1105, found: 247.1103.



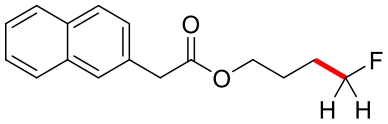
The product **25** was purified with silica gel chromatography (PE/EA = 10:1) as a colorless oil (34.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.25 (d, *J* = 1.3 Hz, 1H), 7.16 (m, 1H), 4.44 (dt, *J* = 47.3, 5.6 Hz, 2H), 4.15 (t, *J* = 6.2 Hz, 2H), 3.60 (s, 2H), 1.81 – 1.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.06, 135.92, 134.39, 129.91, 129.54, 127.60, 127.47, 83.57 (d, *J* = 165.0 Hz), 64.64, 41.03, 27.07 (d, *J* = 20.1 Hz), 24.70 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.89 (tt, *J* = 47.5, 26.1 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{12}H_{14}ClFO_2Na$: 267.0559, found: 267.0557.



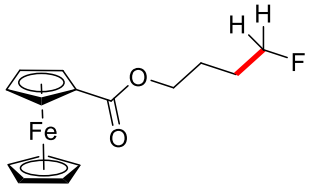
The product **26** was purified with silica gelchromatography (PE/EA = 10:1) as a colorless oil (33.8 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.6, 2.1 Hz, 1H), 7.58 – 7.44 (m, 2H), 7.47 – 7.37 (m, 2H), 4.33 (dt, *J* = 47.5, 5.8 Hz, 2H), 4.12 (t, *J* = 6.3 Hz, 2H), 4.07 (s, 2H), 1.76 – 1.50 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.69, 133.89, 132.15, 130.67, 128.85, 128.18, 128.10, 126.44, 125.90, 125.60, 123.86, 83.51 (d, *J* = 165.0 Hz), 64.46, 39.39, 26.99 (d, *J* = 20.0 Hz), 24.63 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.88 (tt, *J* = 47.5, 25.7 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}FO_2$: 261.1285, found: 261.1288.



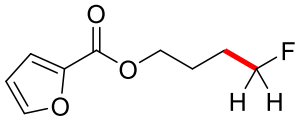
The product **27** was purified with silica gel chromatography (PE/EA = 3:1) as a red oil (47.4 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.81 (t, *J* = 1.9 Hz, 2H), 4.54 (dt, *J* = 47.0, 5.2 Hz, 2H), 4.43 – 4.36 (m, 2H), 4.27 (t, *J* = 5.9 Hz, 2H), 4.20 (s, 5H), 1.95 – 1.76 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): 171.84, 83.72 (d, *J* = 165.1 Hz), 71.30, 71.43, 70.25, 69.87, 63.77, 27.39 (d, *J* = 20.1 Hz), 25.09 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.60 (tt, J = 47.2, 25.9 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{15}H_{17}FO_2FeNa$: 327.0454, found: 327.0455.



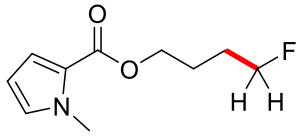
The product **28** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless oil (20.5 mg, 55% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.17 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.50 (dt, *J* = 47.3, 5.7 Hz, 2H), 4.35 (t, *J* = 6.3 Hz, 2H), 1.94 – 1.77 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.86, 146.46, 144.79, 118.03, 111.97, 83.60 (d, *J* = 165.1 Hz), 64.47, 27.19 (d, *J* = 20.1 Hz), 24.89 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.88 (tt, *J* = 47.2, 25.2 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_9H_{11}FO_3Na$: 209.0584, found: 209.0589.



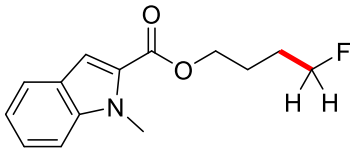
The product **29** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless oil (27.9 mg, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94 (dd, *J* = 3.8, 1.6 Hz, 1H), 6.78 (t, *J* = 2.2 Hz, 1H), 6.11 (dd, *J* = 3.6, 2.7 Hz, 1H), 4.51 (dt, *J* = 47.2, 5.6 Hz, 2H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.92 (s, 3H), 1.92 – 1.76 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.42, 129.68, 122.62, 117.91, 107.98, 83.73 (d, *J* = 165.0 Hz), 63.32, 36.95, 27.38 (d, *J* = 20.2 Hz), 25.01 (d, *J* = 5.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.74 (tt, *J* = 46.7, 25.7 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{10}H_{14}FNO_2$: 200.1081, found: 200.1085.



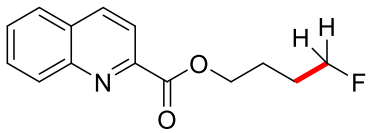
The product **30** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (31.4 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.15 (m, 1H), 4.53 (dt, *J* = 47.3, 5.6 Hz, 2H), 4.36 (t, *J* = 6.2 Hz,2H), 4.07 (s, 3H), 2.02 – 1.82 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.30, 139.75, 127.79, 125.90, 125.13, 122.67, 120.69, 110.37, 110.27, 83.69 (d, *J* = 165.0 Hz), 64.05, 31.74, 27.33 (d, *J* = 20.1 Hz), 24.91 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.77 (tt, *J* = 47.5, 25.7Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{14}H_{17}FNO_2$: 250.1238, found: 250.1243.



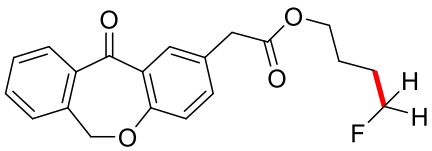
The product **31** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless oil (29.7 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (m, 2H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.83 – 7.72 (m, 1H), 7.69 – 7.60 (m, 1H), 4.55 (dt, *J* = 47.4, 5.9 Hz, 2H), 4.55 (t, *J* = 6.5 Hz, 2H), 2.12 – 1.82 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.47, 148.15, 147.75, 137.39, 130.92, 130.37, 129.41, 128.73, 127.64, 121.09, 83.64 (d, *J* = 165.3 Hz), 65.67, 27.21 (d, *J* = 20.0 Hz), 24.91 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.73 (tt, *J* = 47.1, 25.4 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{14}H_{15}FNO_2$: 248.1081, found: 248.1078.



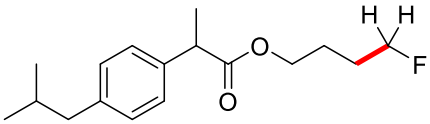
The product **32** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless oil (47.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.3 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.55 (td, *J* = 7.4, 1.3 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.44 (dt, *J* = 47.4, 5.5 Hz, 2H), 4.14 (t, *J* = 6.2 Hz, 2H), 3.64 (s, 2H), 1.81 – 1.66 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.89, 171.47, 160.56, 140.51, 136.39, 135.64, 132.87, 132.50, 129.55, 129.34, 127.90, 127.89, 125.22, 121.14, 83.52 (d, *J* = 165.1 Hz), 73.70, 64.50, 40.31, 27.08 (d, *J* = 20.0 Hz), 24.69 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.81 (tt, *J* = 47.3, 25.7 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{20}H_{19}FO_4Na$: 365.1165, found: 365.1160.



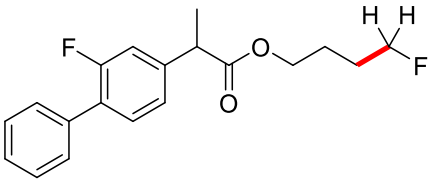
The product **33** was purified with silica gel chromatography (PE/EA = 5:1) as a colorless oil (39.2 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.37 (dt, *J* = 47.5, 5.8 Hz, 2H), 4.10 (m, 2H), 3.68 (d, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.90-1.78 (m, 1H), 1.74 – 1.57 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.84, 140.66, 137.90, 129.43, 127.25, 83.53 (d, *J* = 165.0 Hz), 64.14, 45.29, 45.14, 30.31, 27.03 (d, *J* = 20.0 Hz), 24.68 (d, *J* = 5.2 Hz), 22.47, 18.47.

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.87 (tt, *J* = 47.2, 25.7 Hz).

HRMS ESI (m/z): $[M+H]^+$ calcd. for $C_{17}H_{26}FO_2$: 281.1911, found: 281.1913.



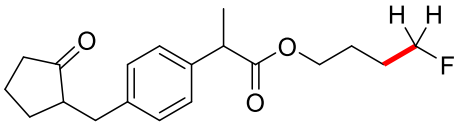
The product **34** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (42.7 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.50 (m, 2H), 7.48 – 7.34 (m, 4H), 7.21 – 7.08 (m, 2H), 4.43 (dt, *J* = 47.4, 5.6 Hz, 2H), 4.16 (t, *J* = 6.3 Hz, 2H), 3.77 (q, *J* = 7.1 Hz, 1H), 1.82 – 1.71 (m, 3H), 1.69 – 1.63 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.07, 159.77 (d, *J* = 248.5 Hz), 141.93 (d, *J* = 7.7 Hz), 135.57, 130.91 (d, *J* = 4.0 Hz), 129.05 (d, *J* = 2.8 Hz), 128.57, 127.92 (d, *J* = 13.7 Hz), 127.79, 123.64 (d, *J* = 3.5 Hz), 115.32 (d, *J* = 23.8 Hz), 83.53 (d, *J* = 165.2 Hz), 64.52, 45.15 (d, *J* = 1.6 Hz), 27.05 (d, *J* = 19.9 Hz), 24.69 (d, *J* = 5.0 Hz), 18.40.

^{19}F NMR (376 MHz, $CDCl_3$): δ -117.63 – -117.73 (m), -218.84 (tt, *J* = 47.4, 25.9 Hz)..

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{20}F_2O_2Na$: 341.1324 found:341.1331.



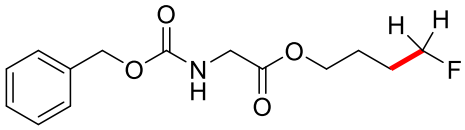
The product **35** was purified with silica gel chromatography (PE/EA = 6:1) as a colorless oil (46.8 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.38 (dt, *J* = 47.5, 5.7 Hz, 2H), 4.10 (t, *J* = 6.2 Hz, 2H), 3.69 (q, *J* = 7.1 Hz, 1H), 3.12 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.51 (dd, *J* = 13.9, 9.5 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.16 – 2.01 (m, 2H), 1.99 – 1.92 (m, 1H), 1.76 – 1.65 (m, 4H), 1.65 – 1.58 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 220.34, 174.74, 139.02, 138.51, 129.25, 127.64, 83.56 (d, *J* = 165.2 Hz), 64.25, 51.11, 45.29, 38.32, 35.32, 29.34, 27.07 (d, *J* = 20.2 Hz), 24.69 (d, *J* = 5.3 Hz), 20.67, 18.51.

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.75 (tt, *J* = 47.5, 25.6 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{25}FO_3Na$: 343.1680, found: 343.1689.



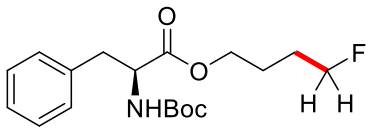
The product **36** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (46.5 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.29 (m, 5H), 5.34 (s, 1H), 5.12 (s, 2H), 4.46 (dt, *J* = 47.2, 5.5 Hz, 2H), 4.19 (t, *J* = 6.1 Hz, 2H), 3.97 (d, *J* = 5.6 Hz, 2H), 1.97 – 1.62 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.12, 156.37, 136.29, 128.62, 128.30, 128.21, 83.48 (d, *J* = 165.2 Hz), 67.18, 64.97, 42.81, 26.98 (d, *J* = 20.0 Hz), 24.68 (d, *J* = 4.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -218.96 (tt, *J* = 47.0, 26.8 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{18}FNO_4Na$: 306.1112, found: 306.1111.

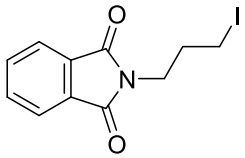


The product **37** was purified with silica gel chromatography (PE/EA = 8:1) as a colorless oil (50.2 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.57 (dd, *J* = 14.1, 6.4 Hz, 1H), 4.42 (dt, *J* = 47.4, 5.6 Hz, 2H), 4.19 – 4.06 (m, 2H), 3.15 – 3.00 (m, 2H), 1.81 – 1.58 (m, 4H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.10, 155.19, 136.16, 129.41, 128.67, 127.13, 83.48 (d, *J* = 165.3 Hz), 80.04, 64.83, 54.64, 38.62, 28.41, 27.00 (d, *J* = 20.1 Hz), 24.66 (d, *J* = 5.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -219.01 (tt, *J* = 47.1, 25.6 Hz).

HRMS ESI (m/z): $[M+Na]^+$ calcd. for $C_{18}H_{26}FNO_4Na$: 362.1738, found: 362.1743.



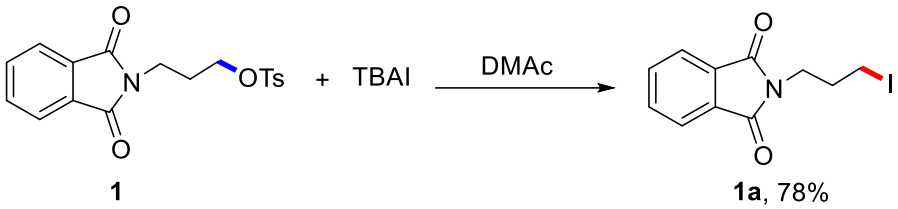
The product was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (49.2 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.78 (t, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.30 – 2.22 (m, 2H).

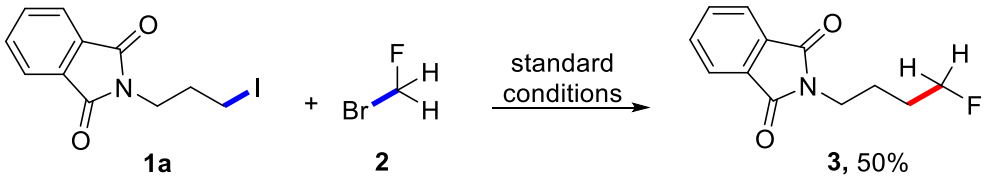
^{13}C NMR (126 MHz, $CDCl_3$): δ 168.35, 134.18, 132.09, 123.45, 38.76, 32.68, 1.33.

Mechanistic Studies

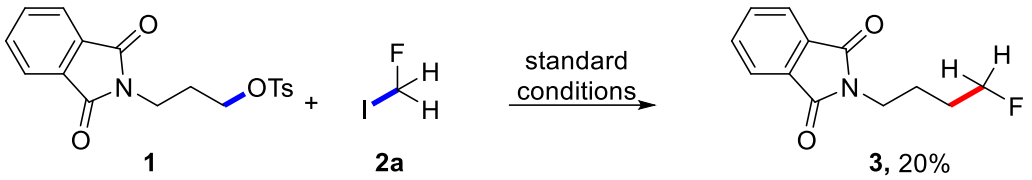
In-situ generation of 1a



In glove box, alkyl tosylate 1 (1.0 equiv, 0.2 mmol, 72 mg), Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL). The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give product **1a** in 78% yield.

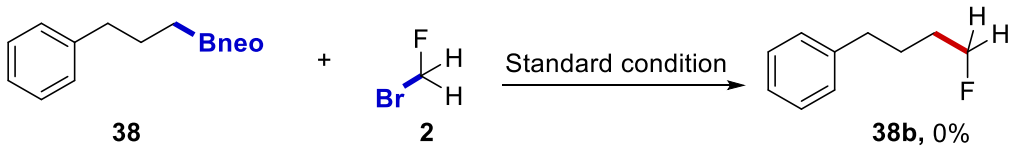


In glove box, $NiCl_2$•DME (10 mol %, 0.02 mmol, 4.4 mg), $\mathbf{L_1}$ (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl idioine **1a** (1.0 equiv, 0.2 mmol), **2** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give product **3** in 50% yield.



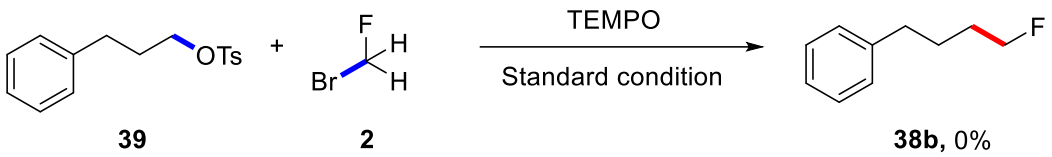
In glove box, $NiCl_2$•DME (10 mol%, 0.02 mmol, 4.4 mg), **L_1** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69.0 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl tosylate **1** (1.0 equiv, 0.2 mmol), **2a** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give product **3** in 20% yield.

In-situ Suzuki process



In glove box, $NiCl_2$•DME (10 mol%, 0.02 mmol, 4.4 mg), **L_1** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) and Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl-Bneo **38** (1.0 equiv, 0.2 mmol), **2** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature. No product **38b** was detected by crude ^{19}F NMR.

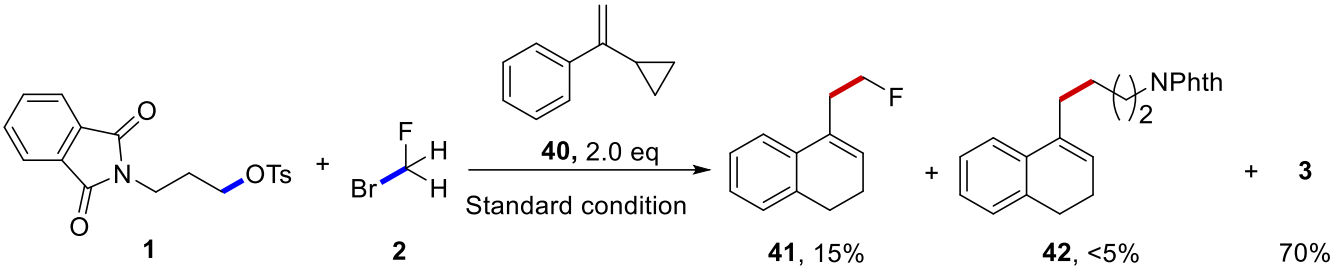
Radical Trapping Experiment with TEMPO.



39 **2** **38b**, 0%

In glove box, $NiCl_2$•DME (10 mol%, 0.02 mmol, 4.4 mg), **L1** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) and K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), radical inhibitors (TEMPO, 2.0 equiv, 0.4 mmol), alkyl tosylate **39** (1.0 equiv, 0.2 mmol), **2** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature. No product **38b** was detected by crude ^{19}F NMR.

Radical Clock Experiment:



1 **2** **41**, 15% **42**, <5% 70%

In glove box, $NiCl_2$•DME (10 mol%, 0.02 mmol, 4.4 mg), **L1** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) and Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl tosylate **1** (1.0 equiv, 0.2 mmol), **2** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give product **3** in 70% yield. The yield of product **41** was determined by crude ^{19}F NMR. Note: The structures of **41** and **42** were

determined by GC-MS and HRMS. Compound **41**: HRMS ESI (m/z): $[M+H]^+$calcd. for $C_{12}H_{14}F$: 177.1074, found: 177.1113. Compound **42**: HRMS ESI (m/z): $[M+H]^+$calcd. for $C_{22}H_{21}NNaO_2^+$: 354.1465, found: 354.1471.

Large scale reaction:

In glove box, $NiCl_2$•DME (10 mol%, 0.5 mmol, 110 mg), **L1** (13.5 mol%, 0.675 mmol, 99 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 10 mmol, 2.3 g), K_2CO_3 (2.5 equiv, 12.5 mmol, 1.7 g) and Tetrabutylammonium iodide (2.0 equiv, 10 mmol, 3.7 g) were combined in a 100 mL round-bottom flask. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and alkyl tosylate **1** (1.0 equiv, 5 mmol), Bromofluoromethane **2** (2.0 equiv, 10 mmol dissolved in DMAc) and *N*, *N*-Dimethylacetamide (30 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (2×20 mL) and extracted with EtOAc (2×25 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give desired product **3** as a colorless solid.

Monofluoroalkylation of Alkyl Tosylate:

4' **43** **44**, 34%

In glove box, $NiCl_2$•DME (10 mol%, 0.02 mmol, 4.4 mg), **L1** (13.5 mol%, 0.027 mmol, 4.0 mg), Bis(neopentyl glycolato)diboron (2.0 equiv, 0.4 mmol, 90.4 mg), K_2CO_3 (2.5 equiv, 0.5 mmol, 69 mg) and Tetrabutylammonium iodide (2.0 equiv, 0.4 mmol, 148 mg) were combined in a 5 mL oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), and 4-phenylbutyl 4-methylbenzenesulfonate **4'** (1.0 equiv, 0.2 mmol), (2-bromo-2-fluoroethyl) benzene **43** (2.0 equiv, 0.4 mmol) and *N*, *N*-Dimethylacetamide (1.0 mL) were then added via syringe. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 60 ℃ for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (20 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na_2SO_4, filtrated and concentrated under vacuum. The product **44** was purified with silica gel chromatography (PE/EA = 100:1) as a colorless oil. (17.4mg, 34% yield). Note: The structures of

44[5] was known. Compound **44**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34– 7.25 (m, 5H), 7.23– 7.12 (m, 5H), 4.78– 4.54 (m, 1H), 3.03– 2.74 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.71–1.61 (m, 3H), 1.58–1.49 (m, 2H), 1.48–1.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.56, 137.52 (d, *J* = 4.8 Hz), 129.50, 128.56, 128.52, 128.43, 126.66, 125.84, 94.62 (d, *J* = 170.9 Hz), 41.80 (d, *J* = 21.6 Hz), 35.96, 34.64 (d, *J* = 20.8 Hz), 31.38, 24.94 (d, *J*= 4.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -178.38– -178.76 (m).

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2. A. Joshi-Pangu, X. Ma, M. Diane, S. Iqbal, R. J. Kribs, R. Huang, C.-Y. Wang and M. R. Biscoe, *J. Org. Chem.* **2012**, *77*, 6629-6633.
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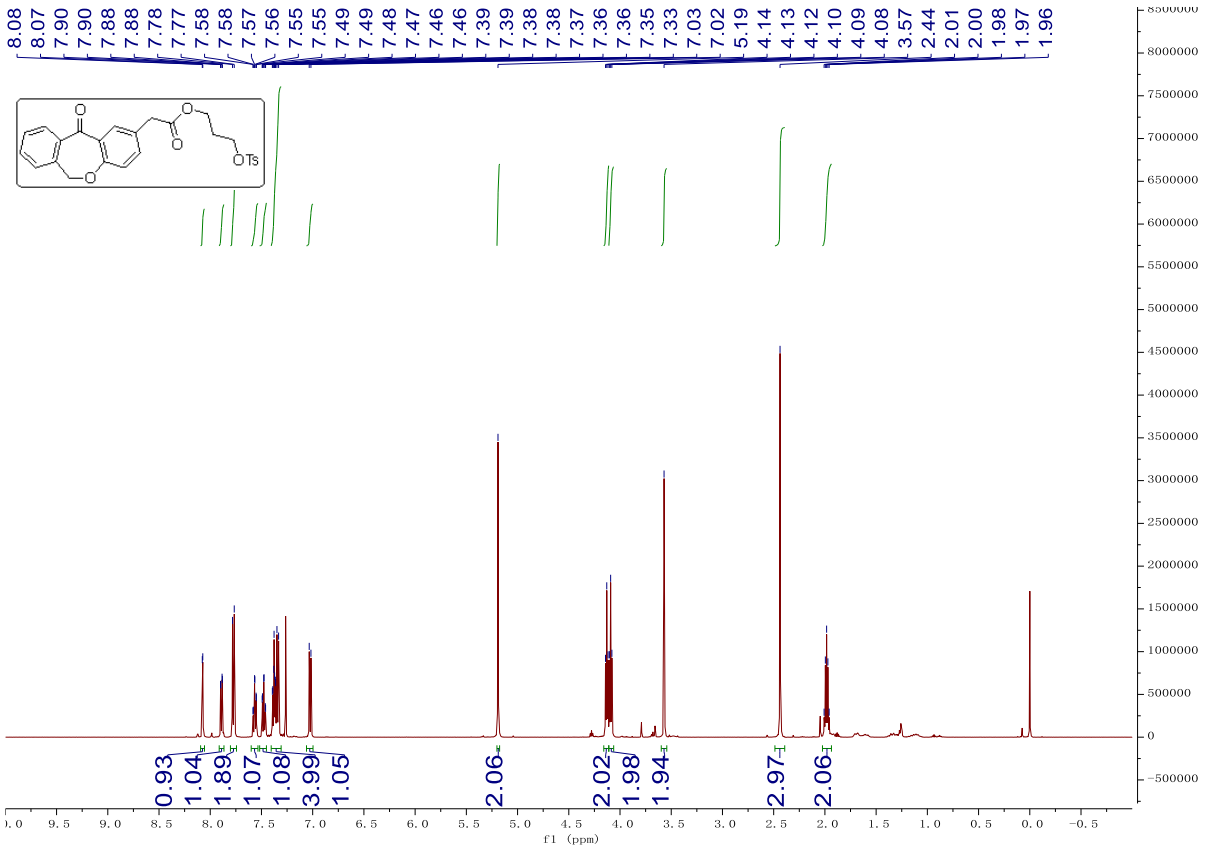
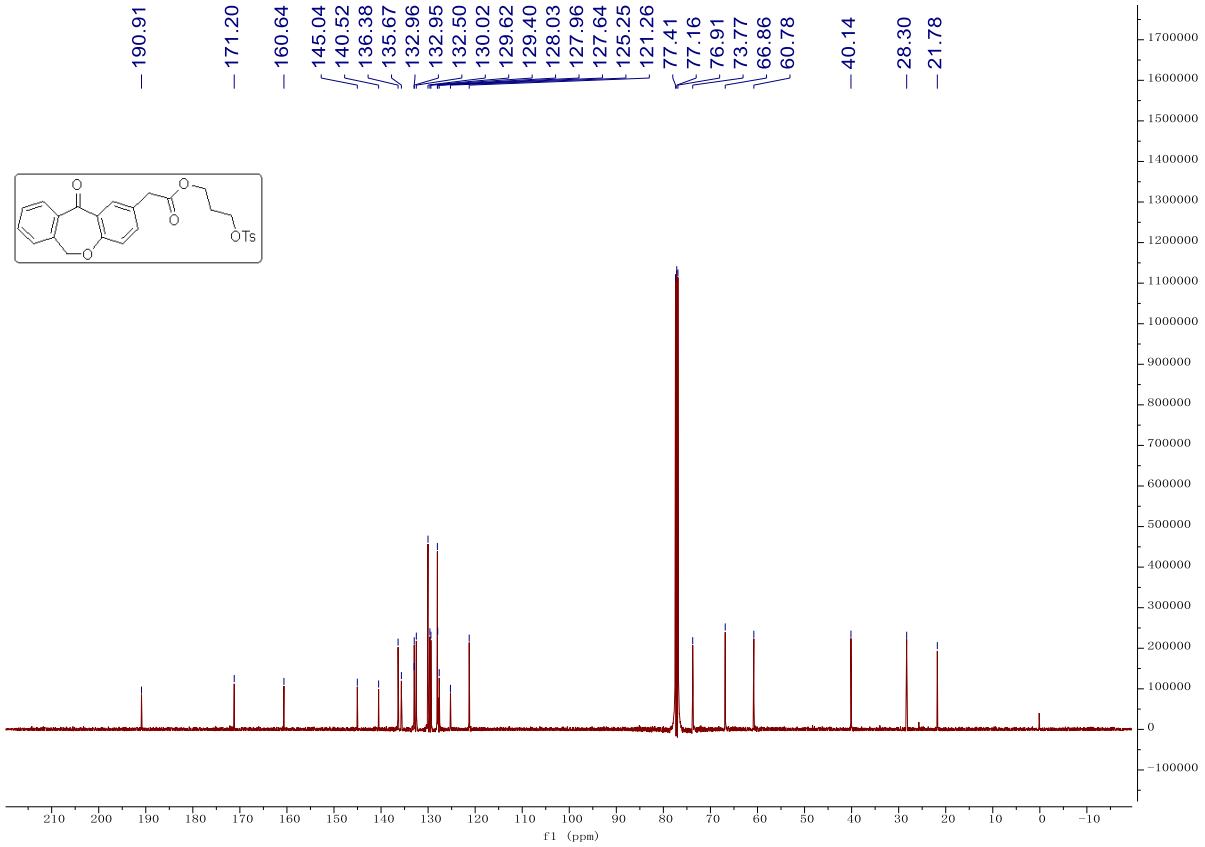
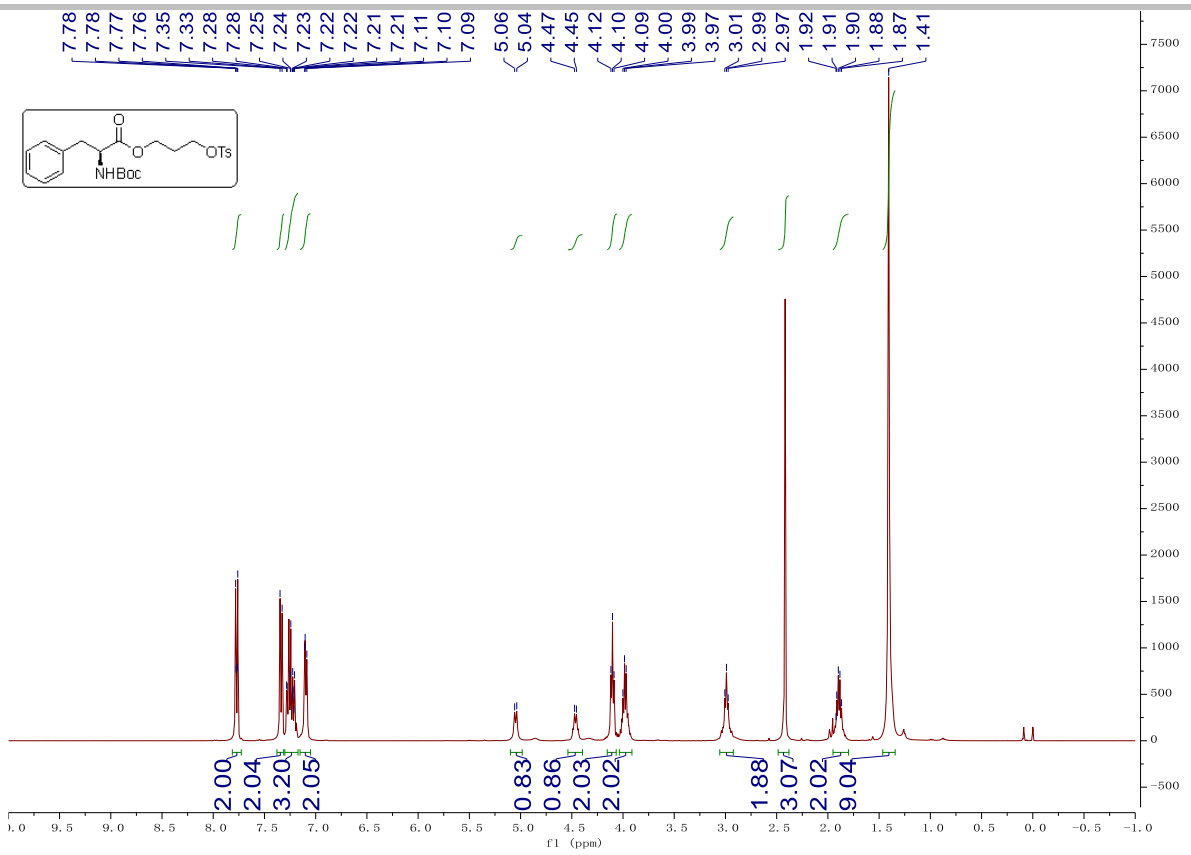
NMR Spectra of Substrates (^{1}H NMR, ^{19}F NMR, ^{13}C NMR)



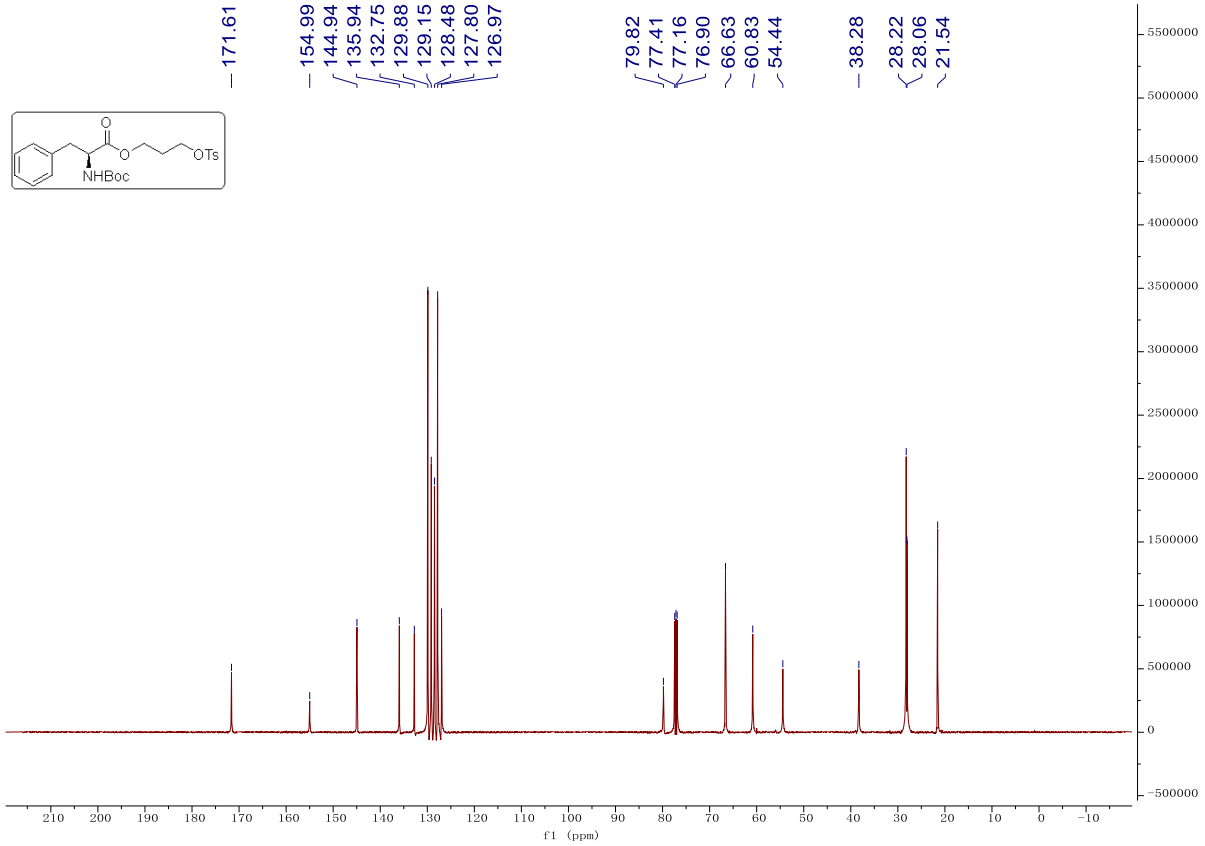
^{1}H NMR Spectrum of **3-(tosyloxy)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate** ($CDCl_3$, 500 MHz)



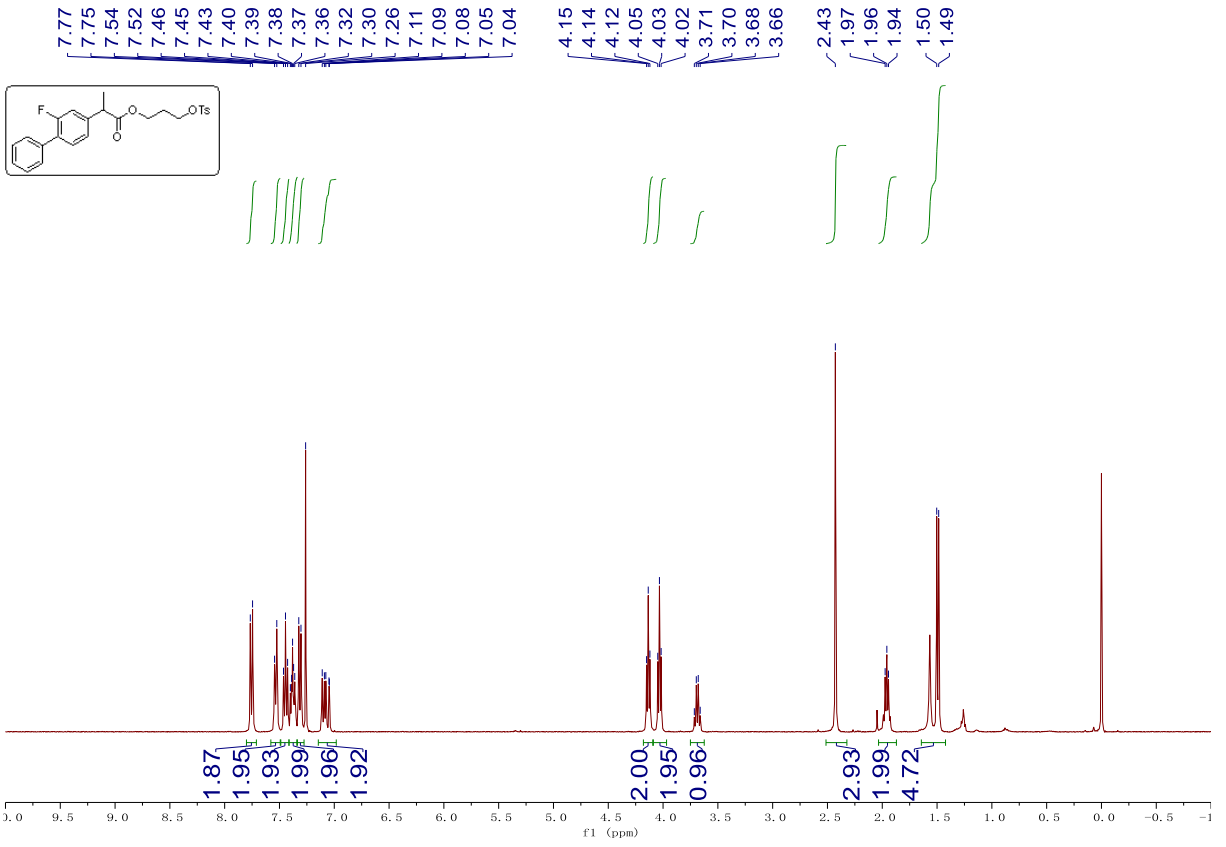
^{13}C NMR Spectrum of **3-(tosyloxy)propyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate** ($CDCl_3$, 126 MHz)



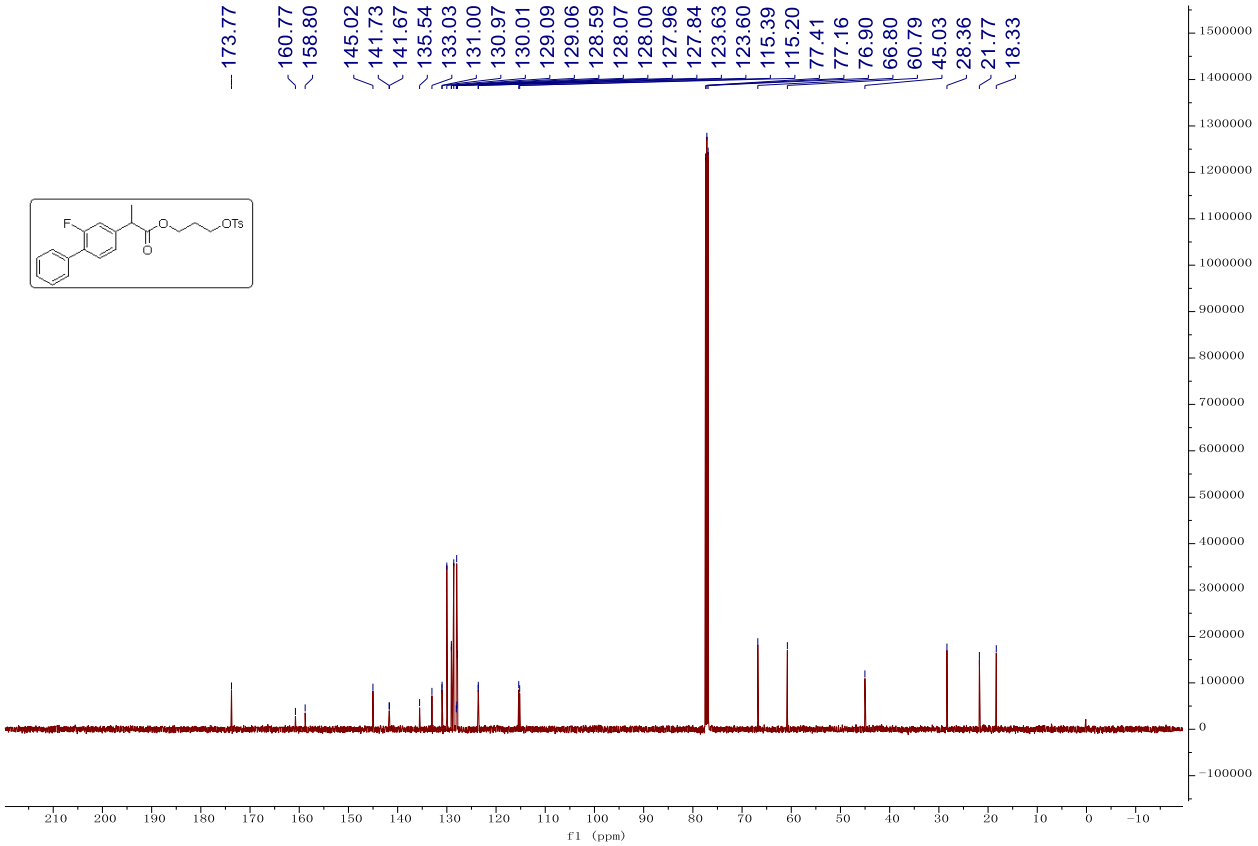
^{1}H NMR Spectrum of **Boc-L-phenylalanine alkyl tosylate** ($CDCl_3$, 400 MHz)



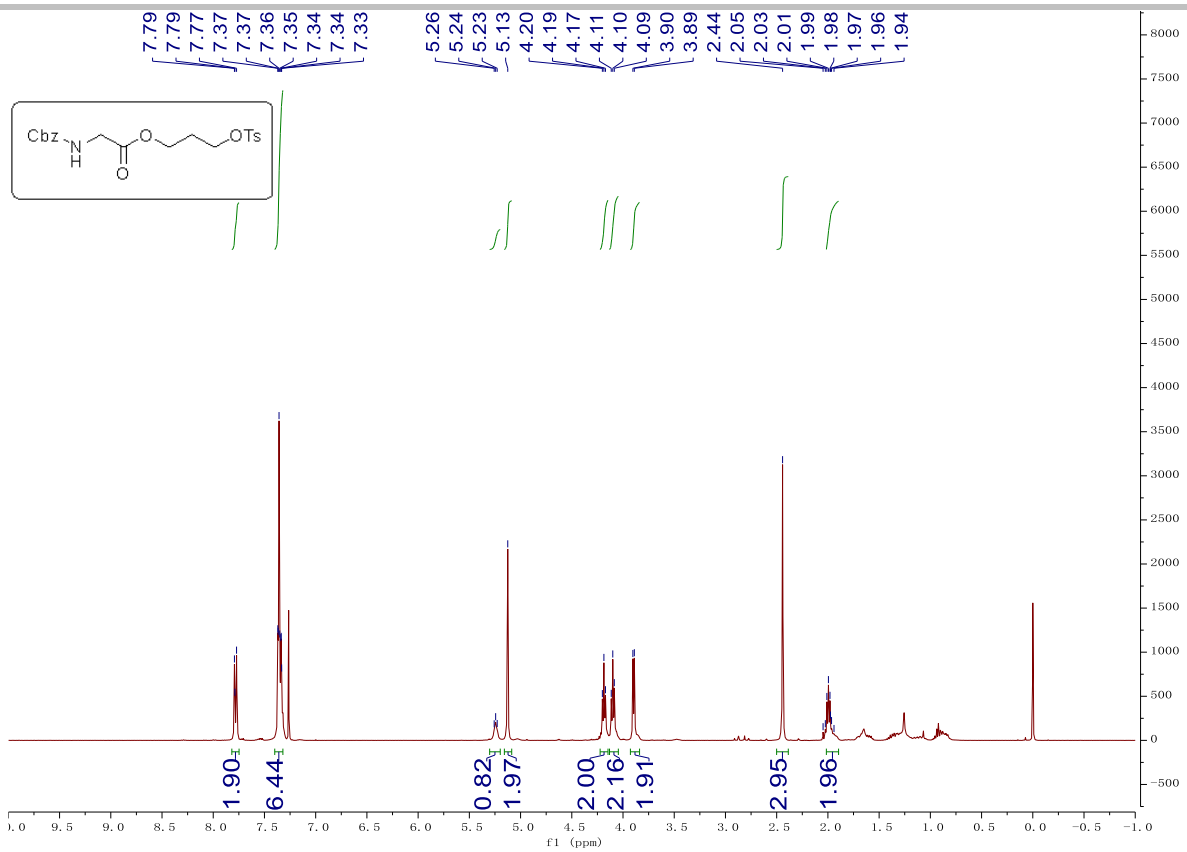
^{13}C NMR Spectrum of **Boc-L-phenylalanine alkyl tosylate** ($CDCl_3$, 126 MHz)



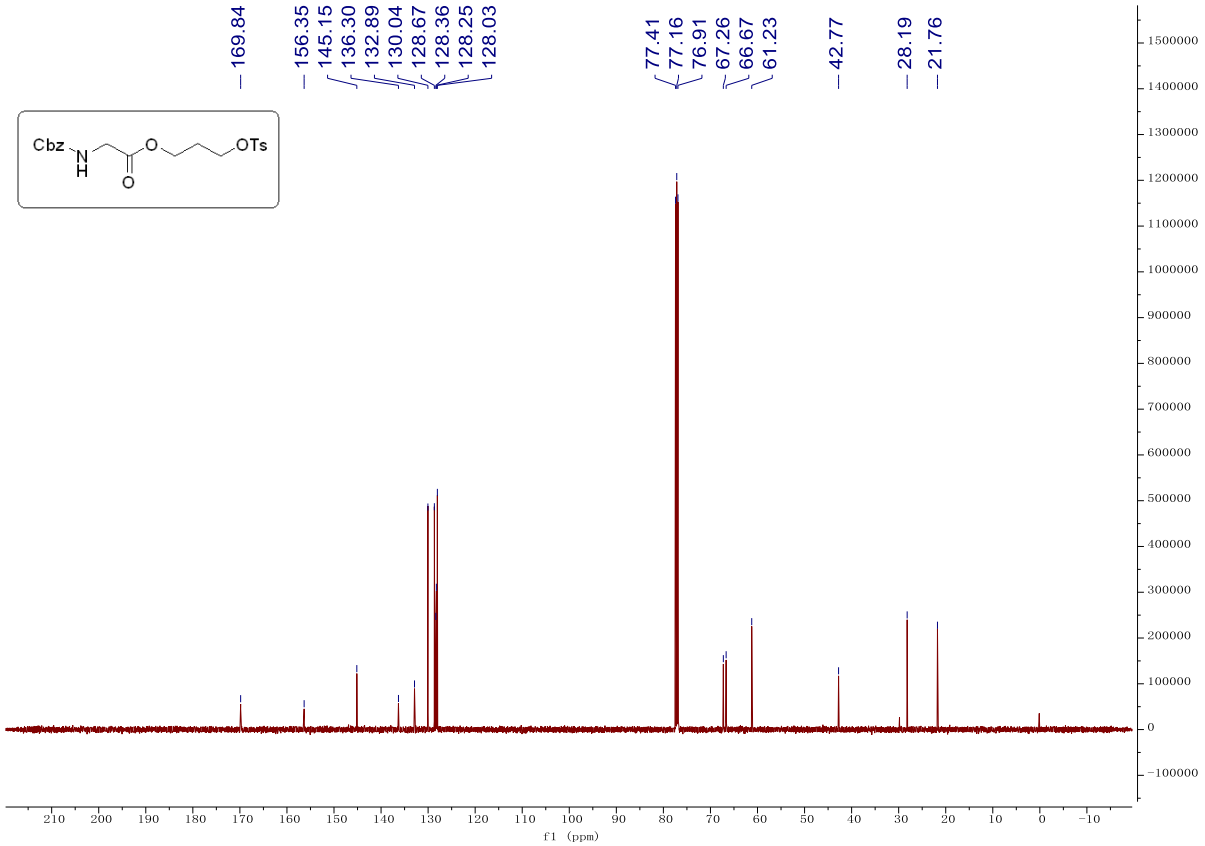
^{1}H NMR Spectrum of **3-(tosyloxy) propyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl) propanoate**($CDCl_3$, 400 MHz)



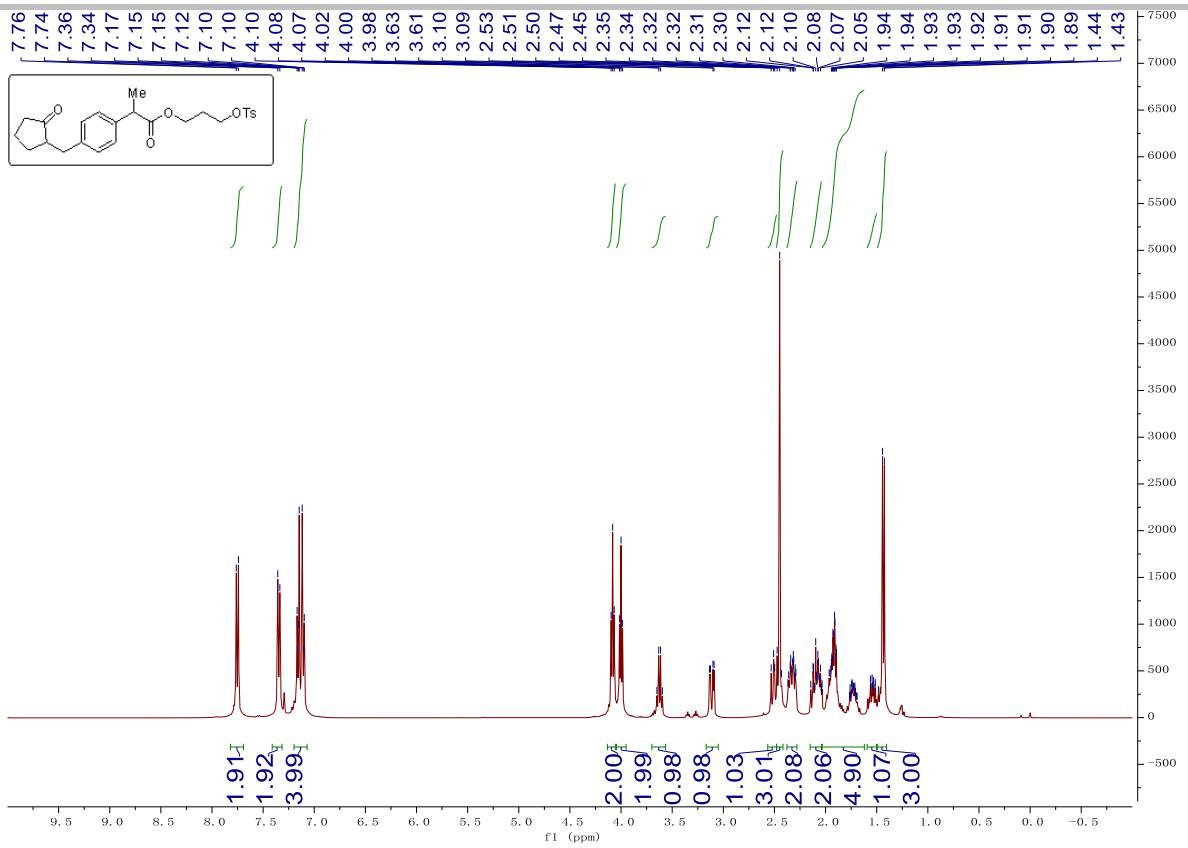
^{13}C NMR Spectrum of **3-(tosyloxy) propyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl) propanoate** ($CDCl_3$, 126 MHz)



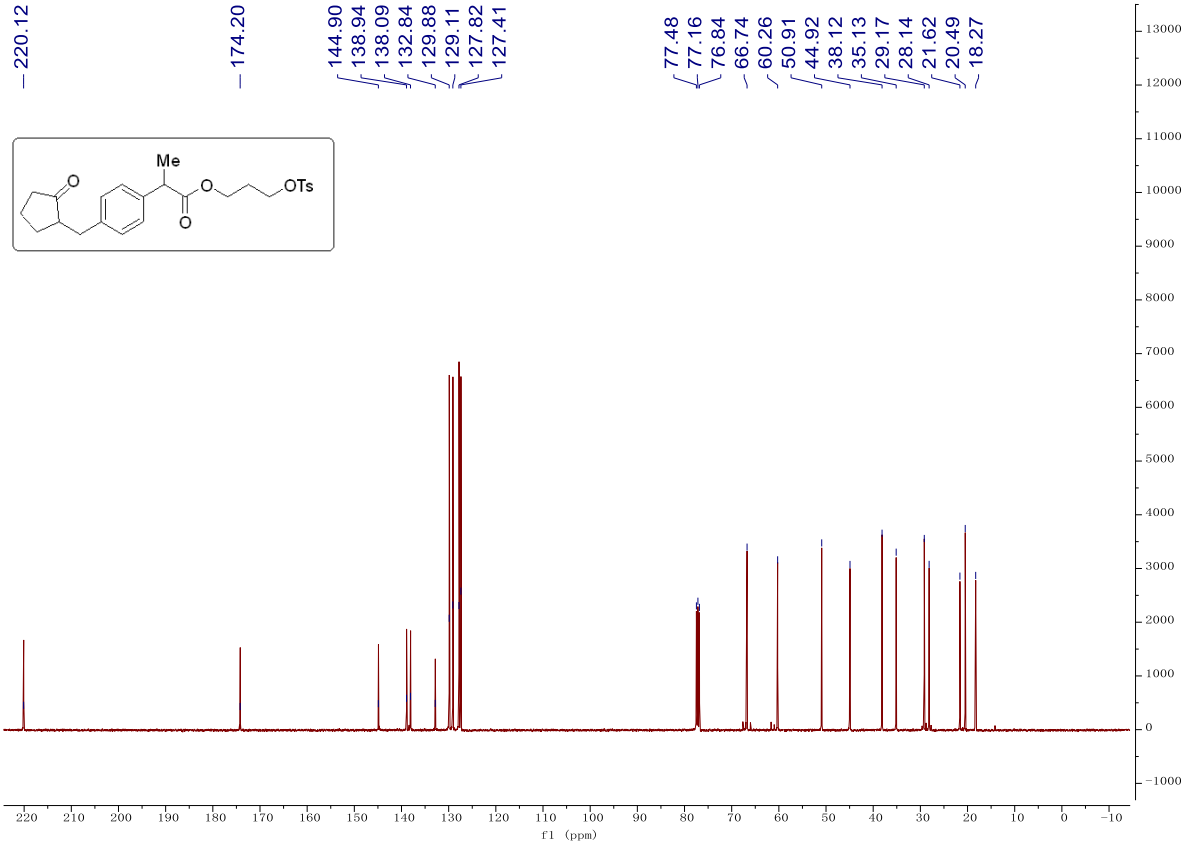
^{1}H NMR Spectrum of ***N*-Carbobenzyloxyglycine alkyl tosylate** ($CDCl_3$, 400 MHz)



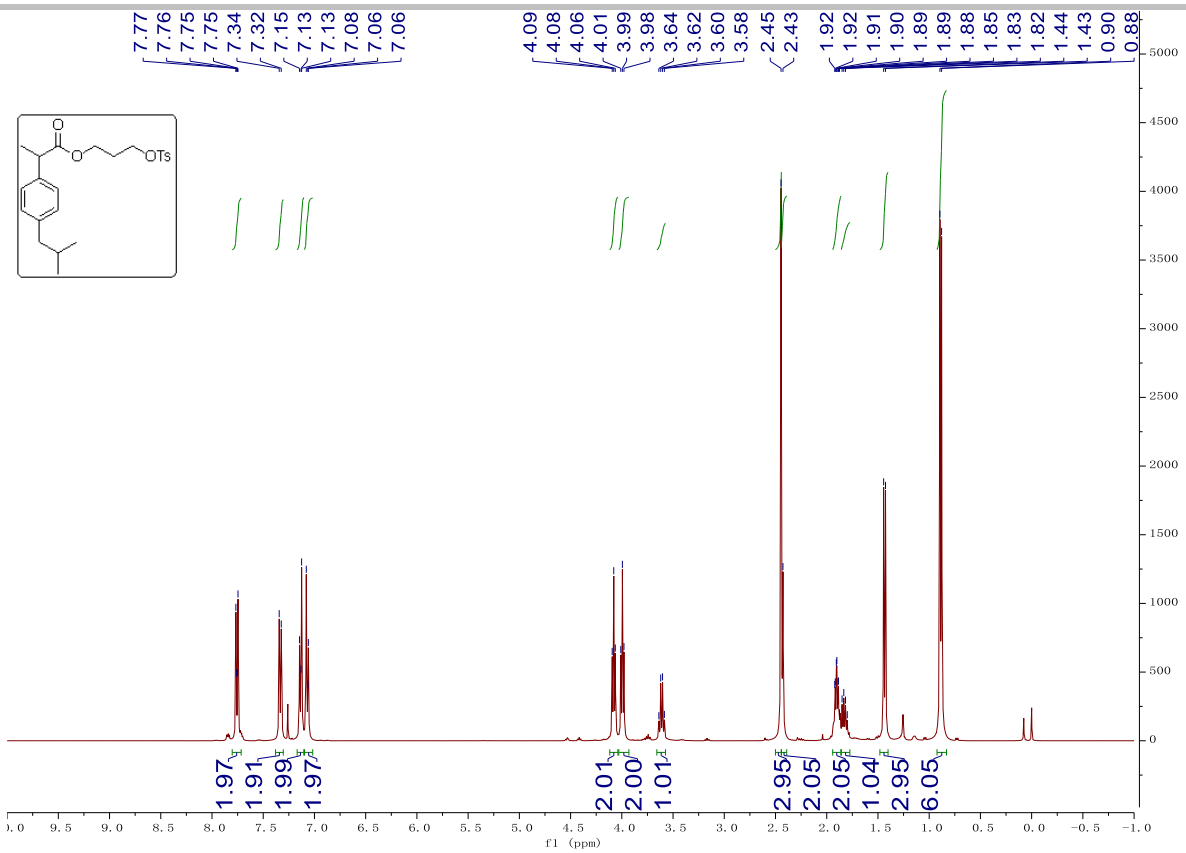
^{13}C NMR Spectrum of ***N*-Carbobenzyloxyglycine alkyl tosylate** ($CDCl_3$, 126 MHz)



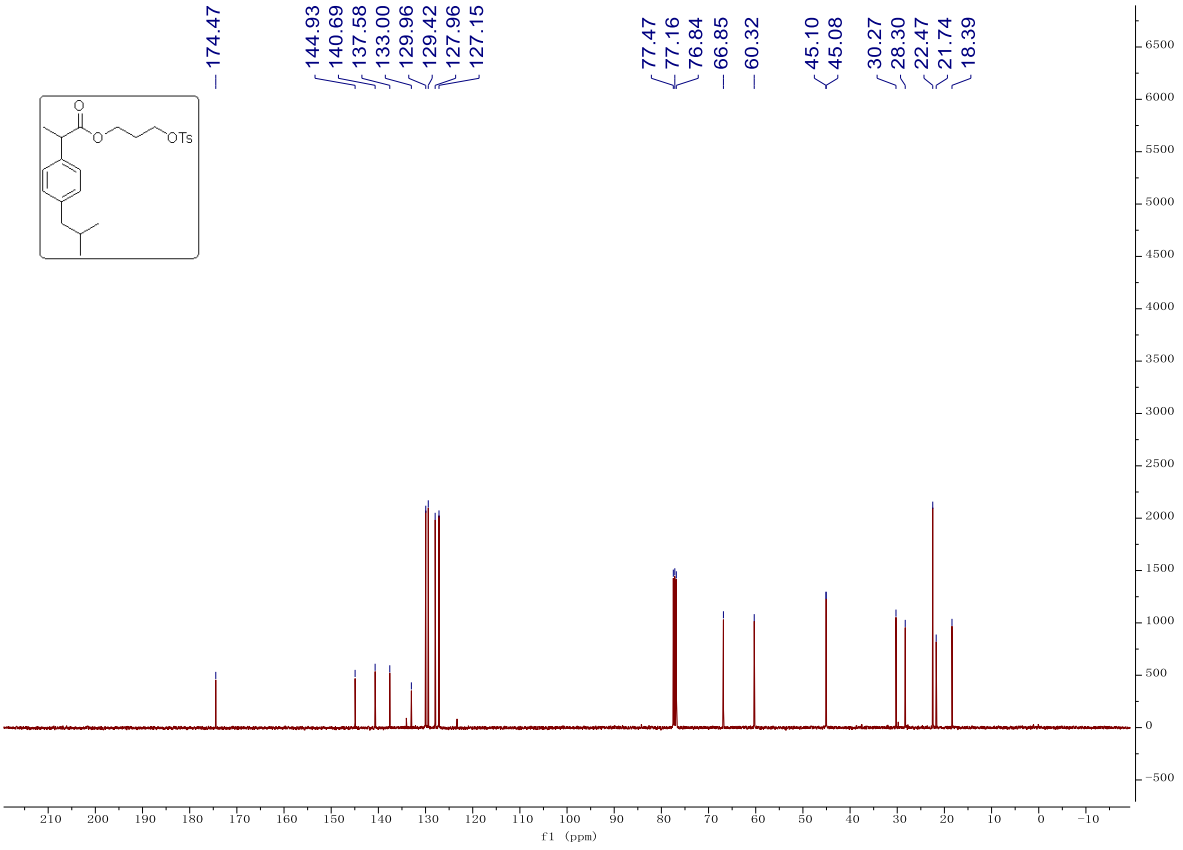
^{1}H NMR Spectrum of **3-(tosyloxy)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **3-(tosyloxy)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate** ($CDCl_3$, 126 MHz)

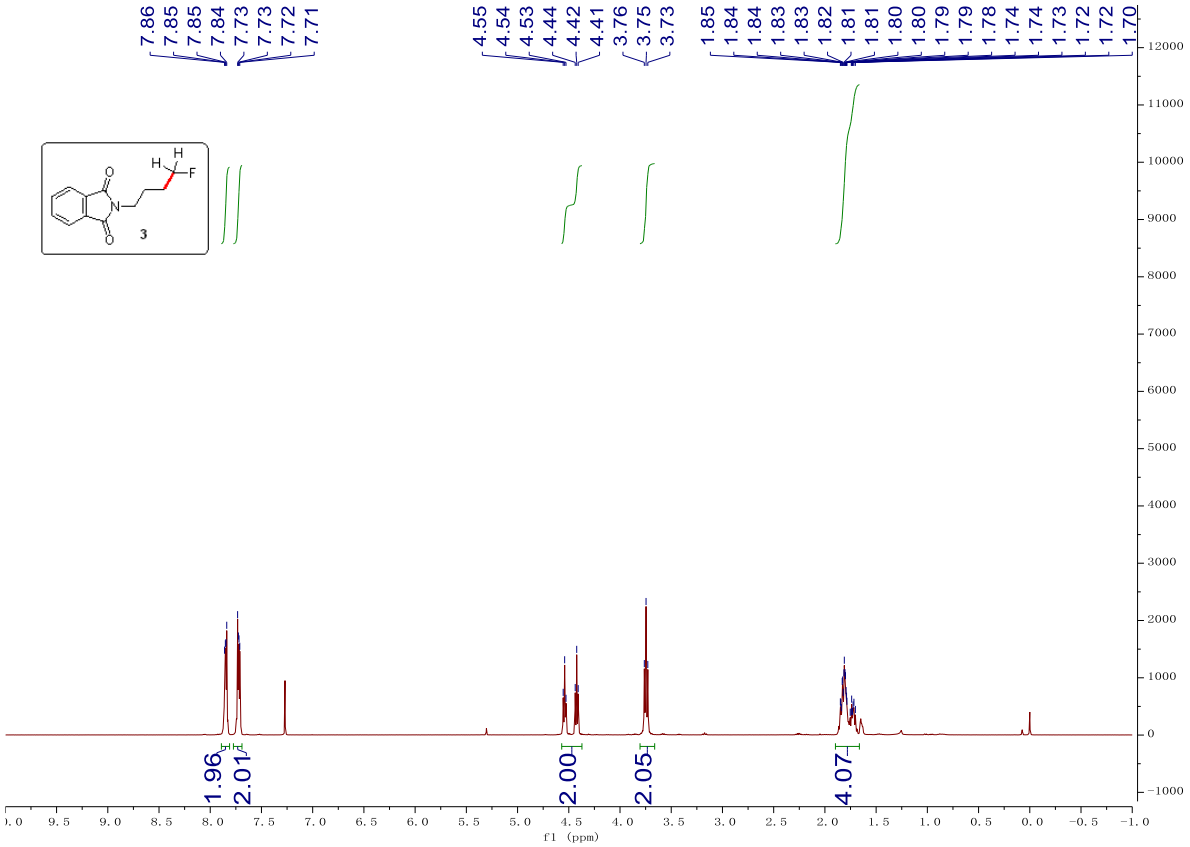


^{1}H NMR Spectrum of **3-(tosyloxy)propyl 2-(4-isobutylphenyl)propanoate**($CDCl_3$, 400 MHz)

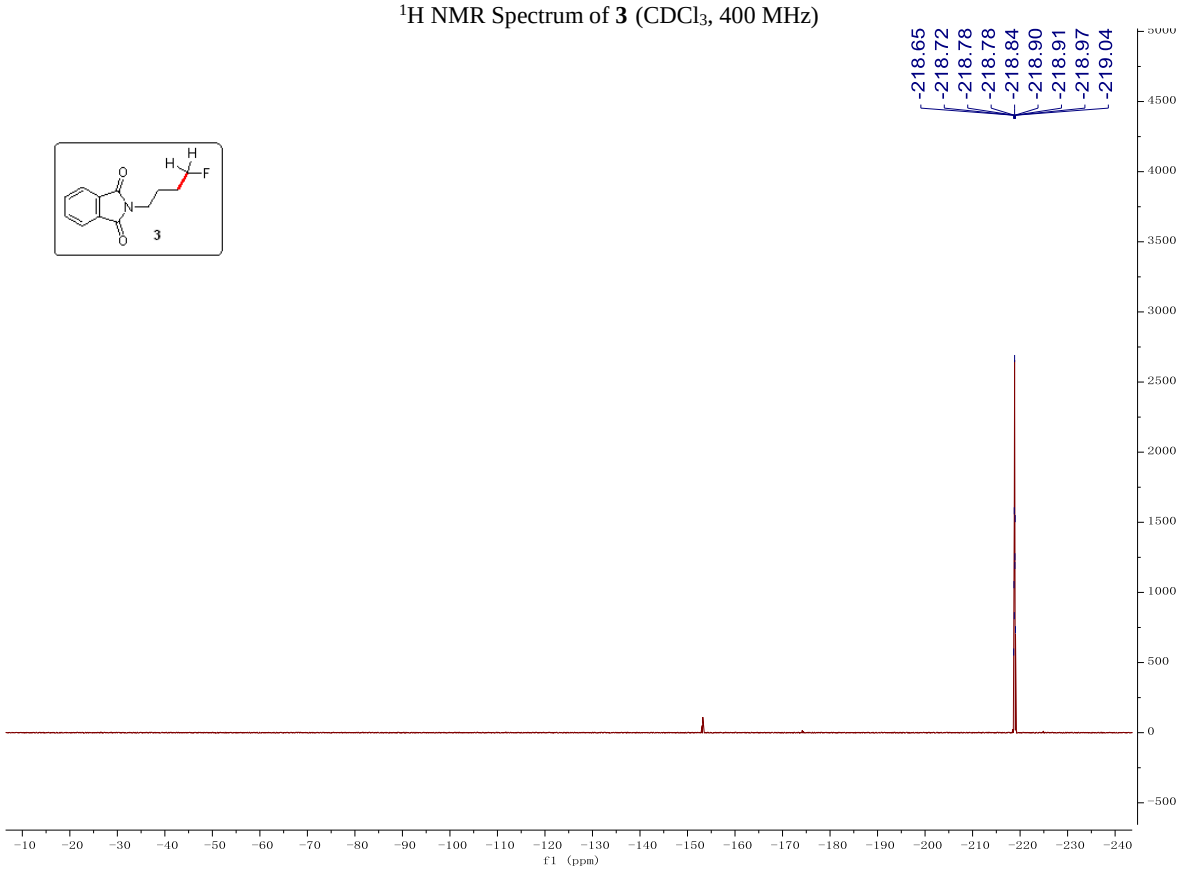


^{13}C NMR Spectrum of **3-(tosyloxy)propyl 2-(4-isobutylphenyl)propanoate** ($CDCl_3$, 126 MHz)

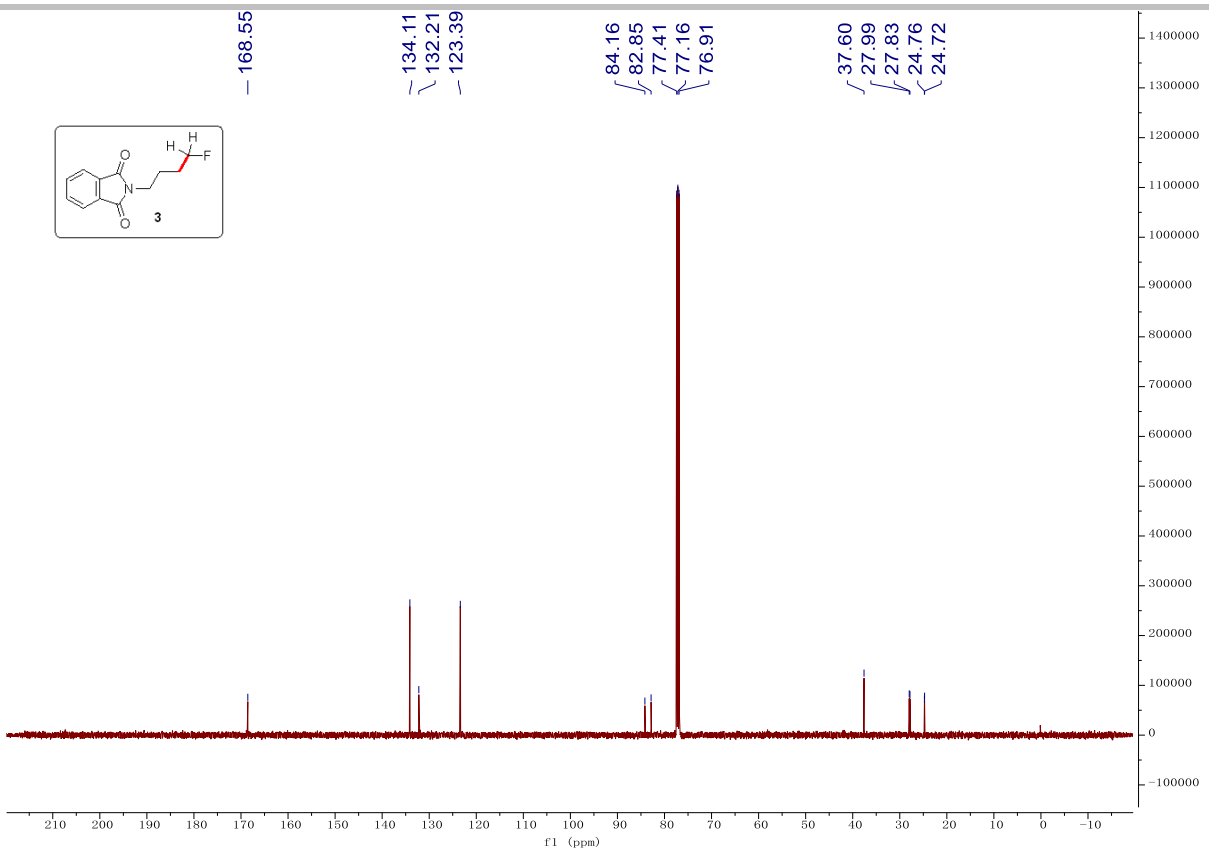
NMR Spectra of Products (^{1}H NMR, ^{19}F NMR, ^{13}C NMR)



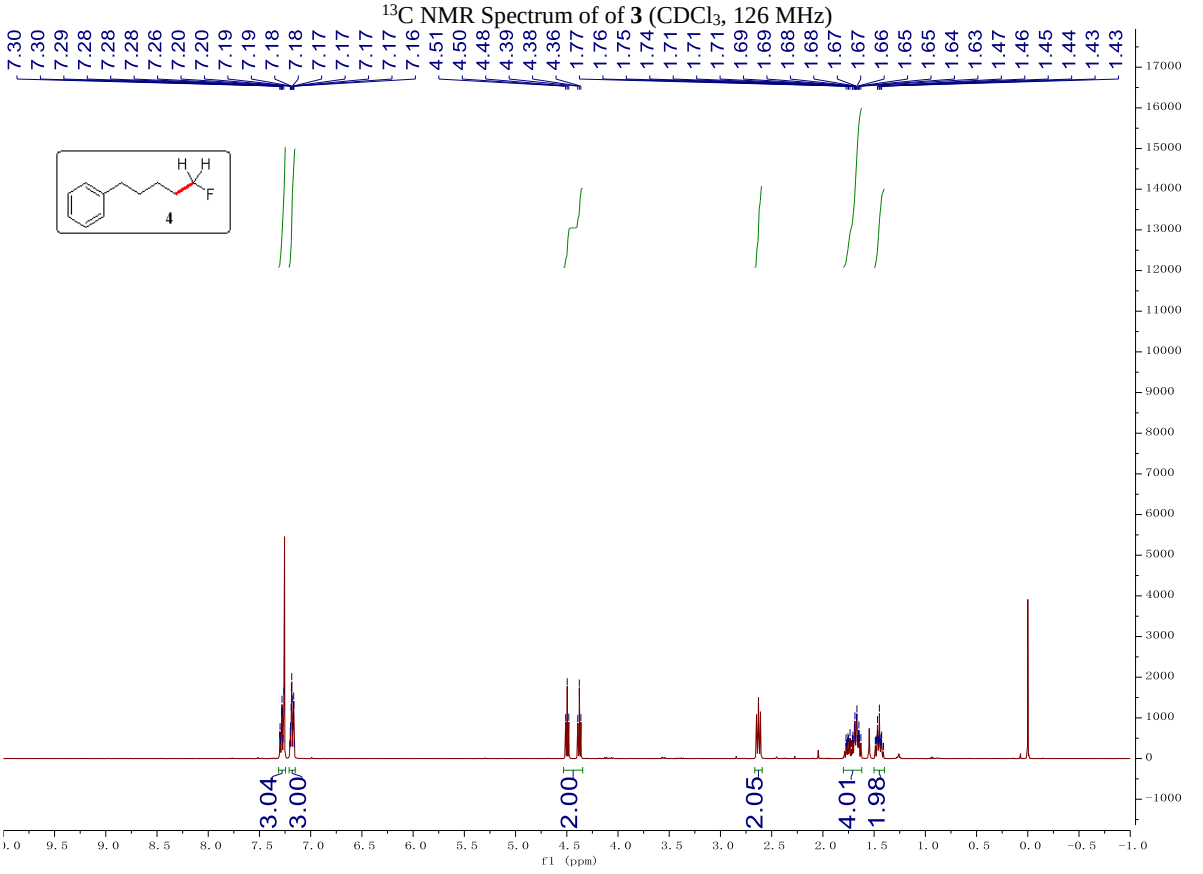
^{1}H NMR Spectrum of **3** ($CDCl_3$, 400 MHz)



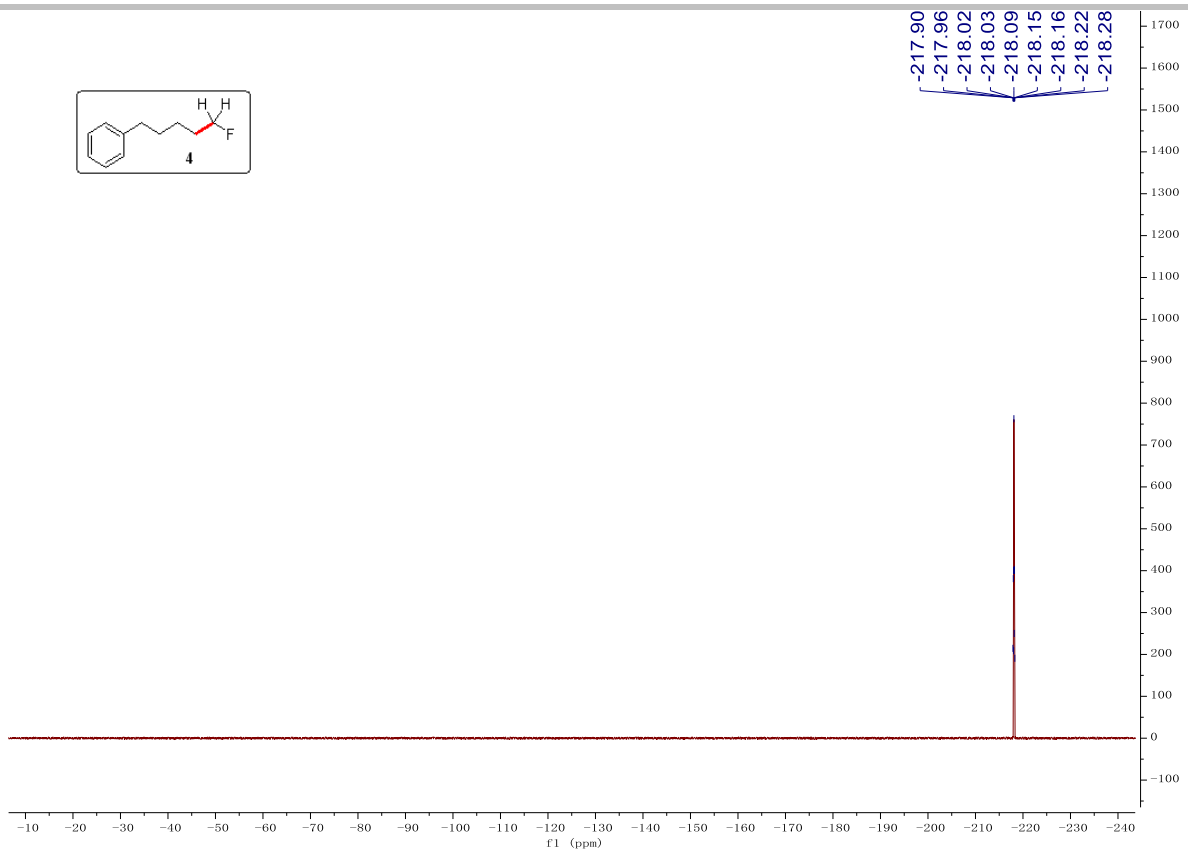
^{19}F NMR Spectrum of of **3** ($CDCl_3$, 376 MHz)



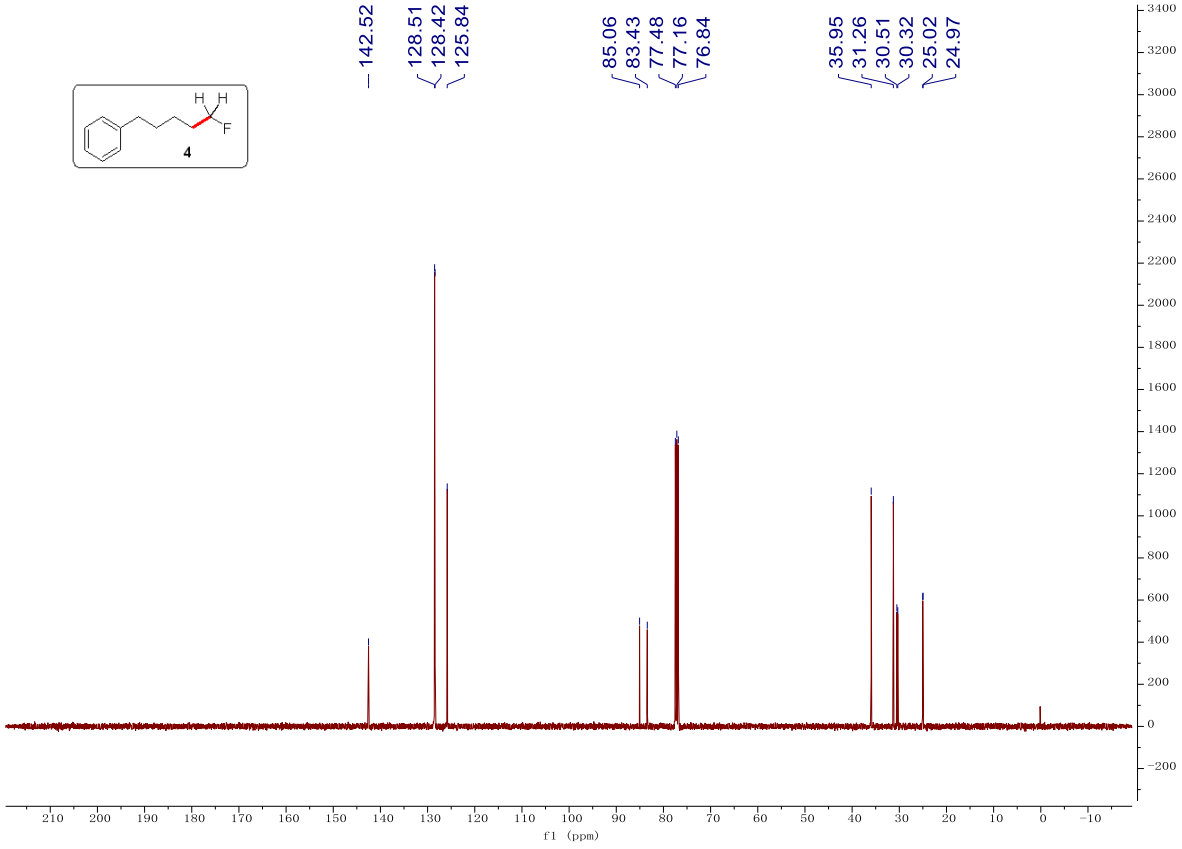
^{13}C NMR Spectrum of of **3** ($CDCl_3$, 126 MHz)



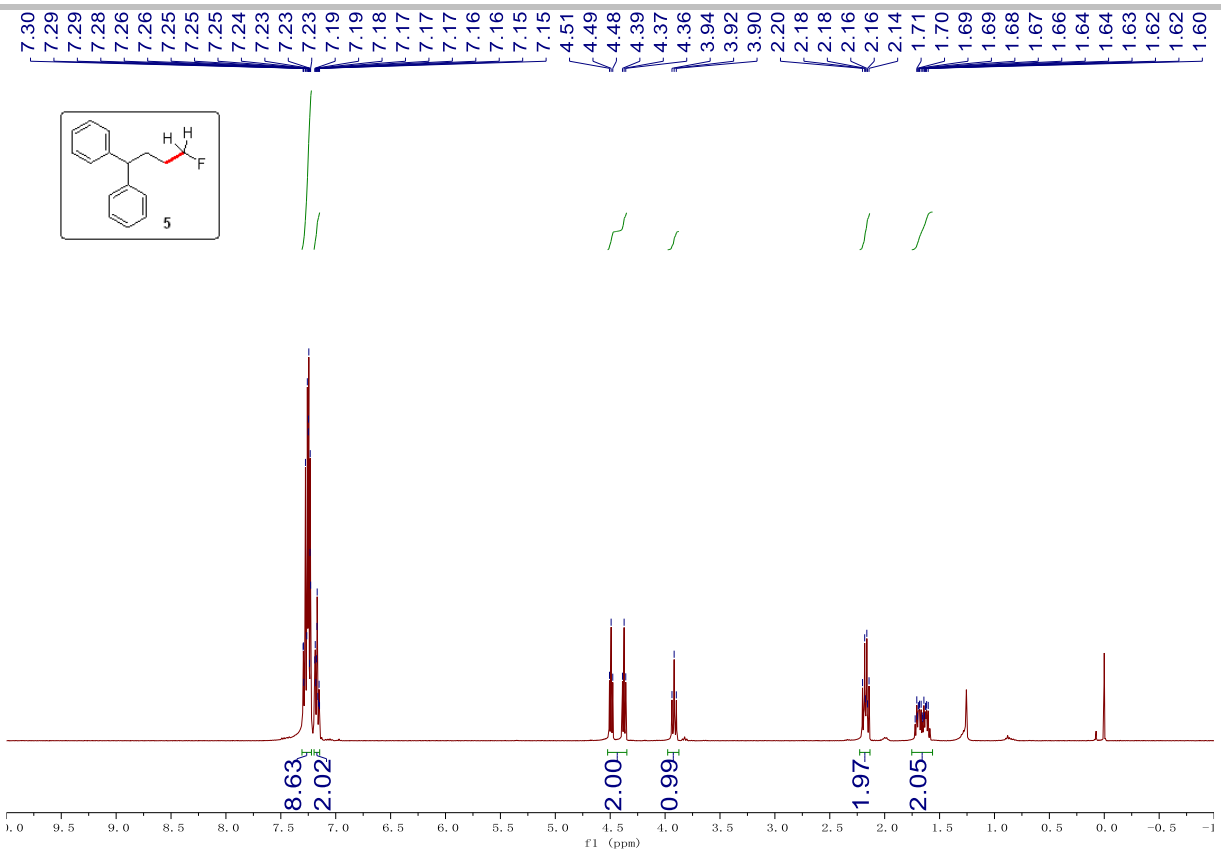
^{1}H NMR Spectrum of **4** ($CDCl_3$, 400 MHz)



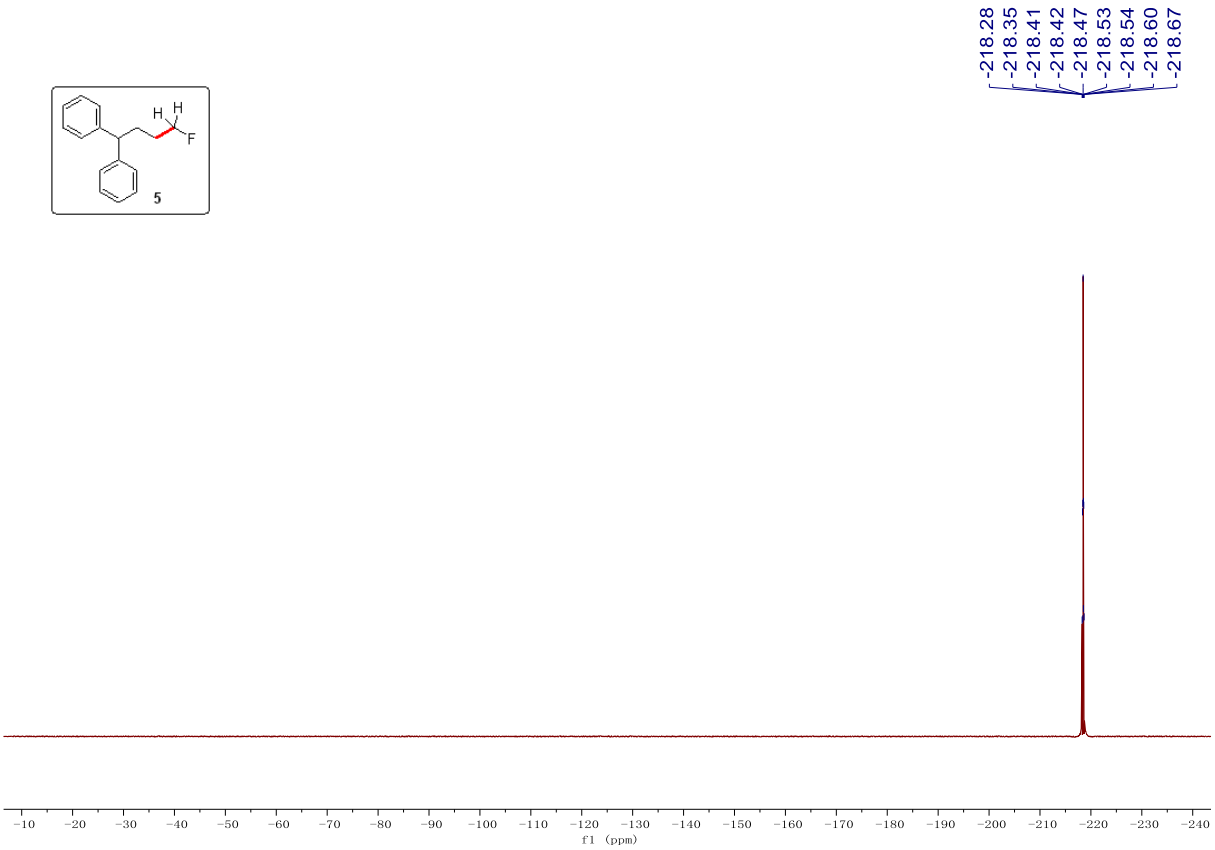
^{19}F NMR Spectrum of of **4** ($CDCl_3$, 376 MHz)



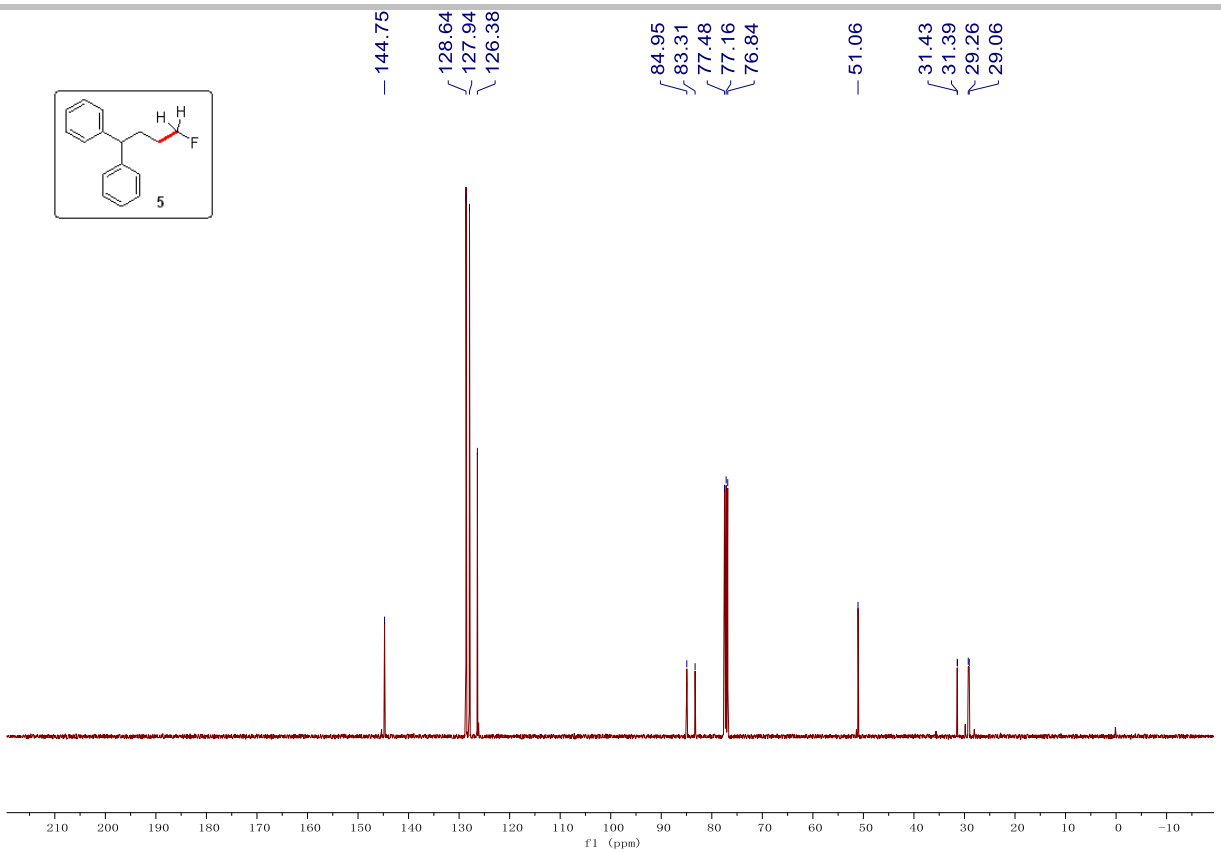
^{13}C NMR Spectrum of of **4** ($CDCl_3$, 126 MHz)



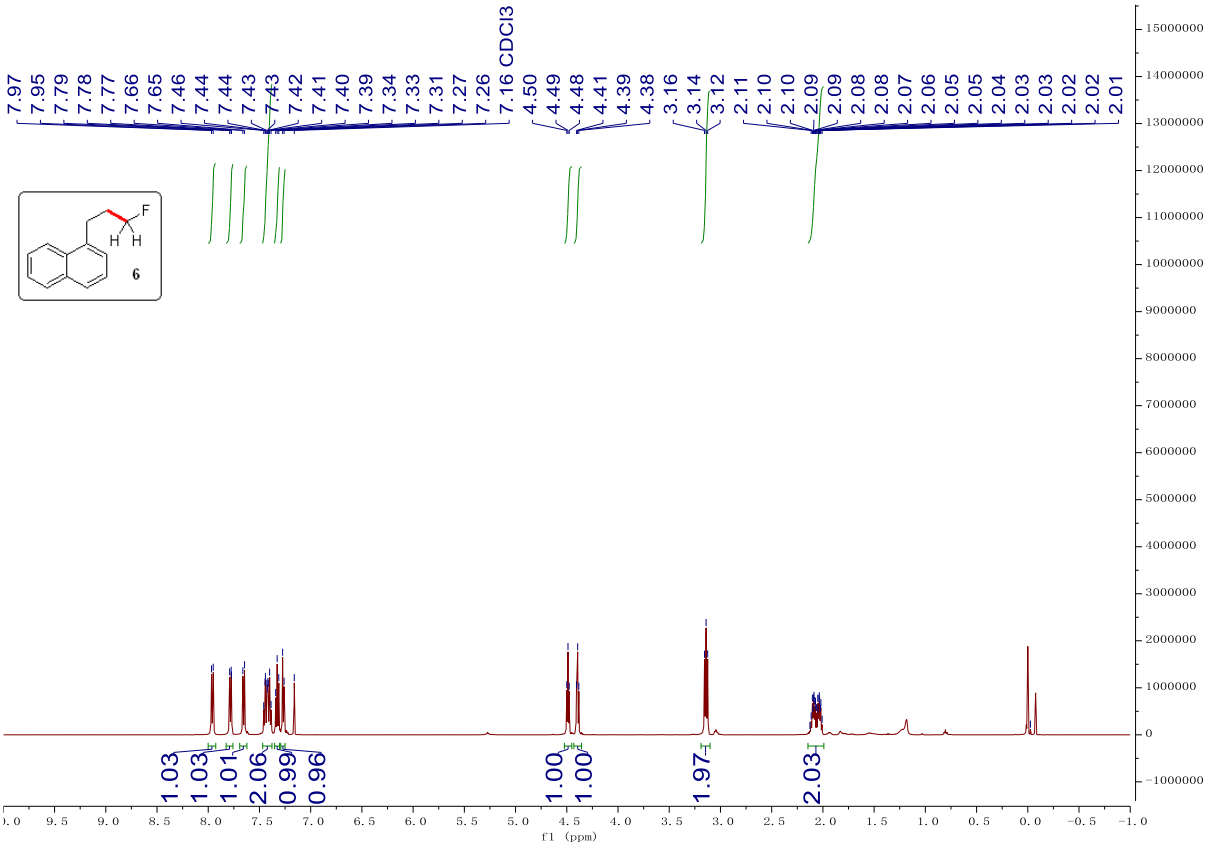
^{1}H NMR Spectrum of **5** ($CDCl_3$, 400 MHz)



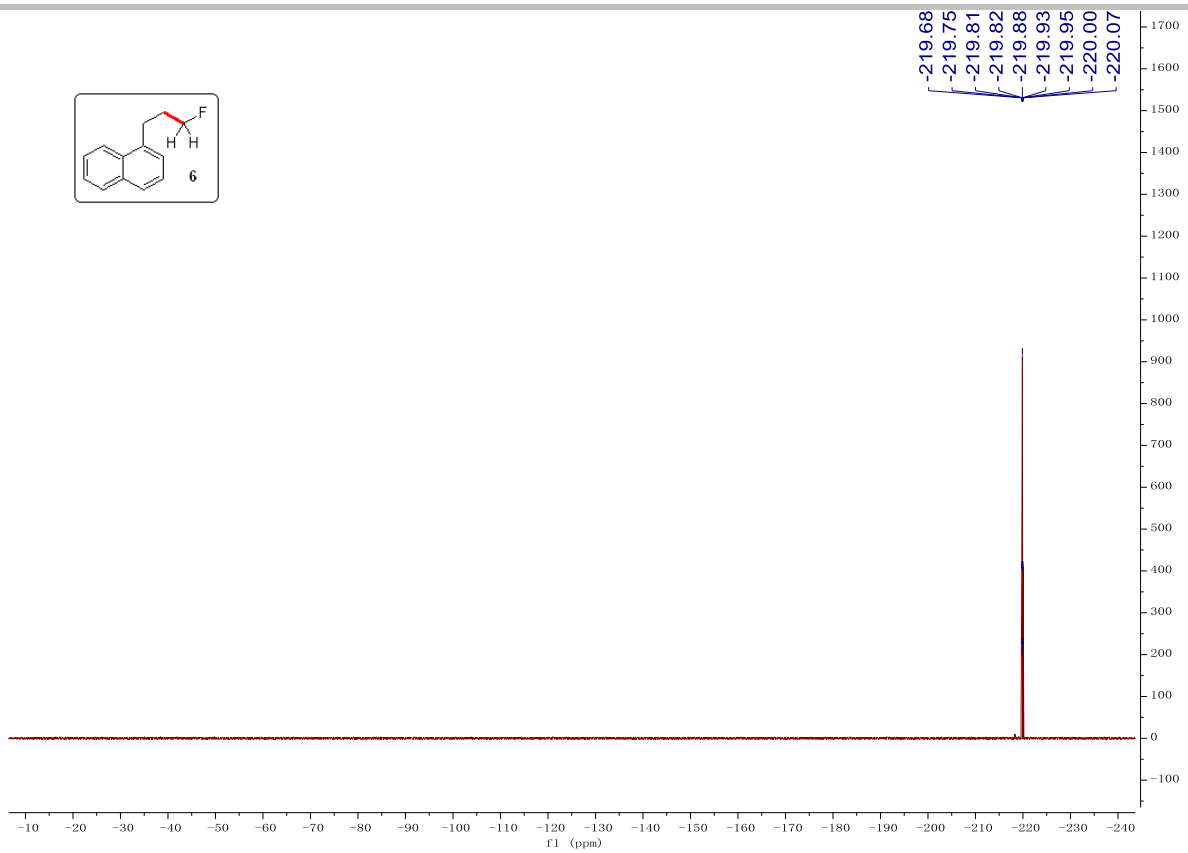
^{19}F NMR Spectrum of of **5** ($CDCl_3$, 376 MHz)



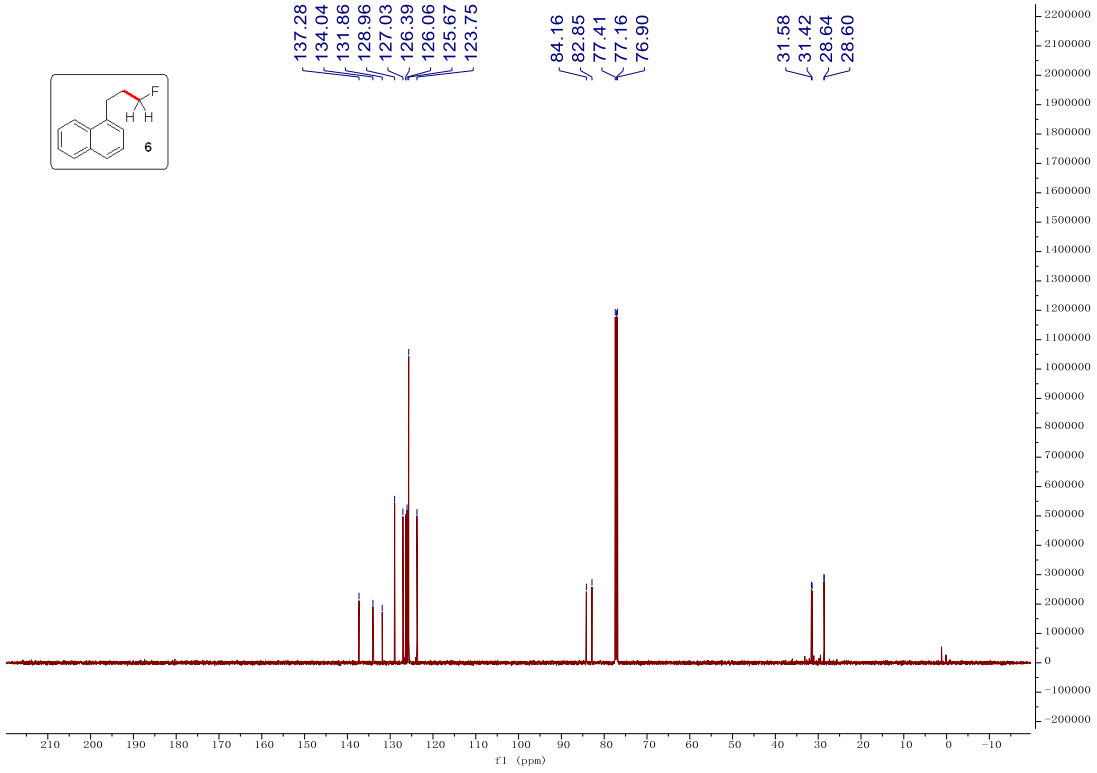
^{13}C NMR Spectrum of of **5** ($CDCl_3$, 101 MHz)



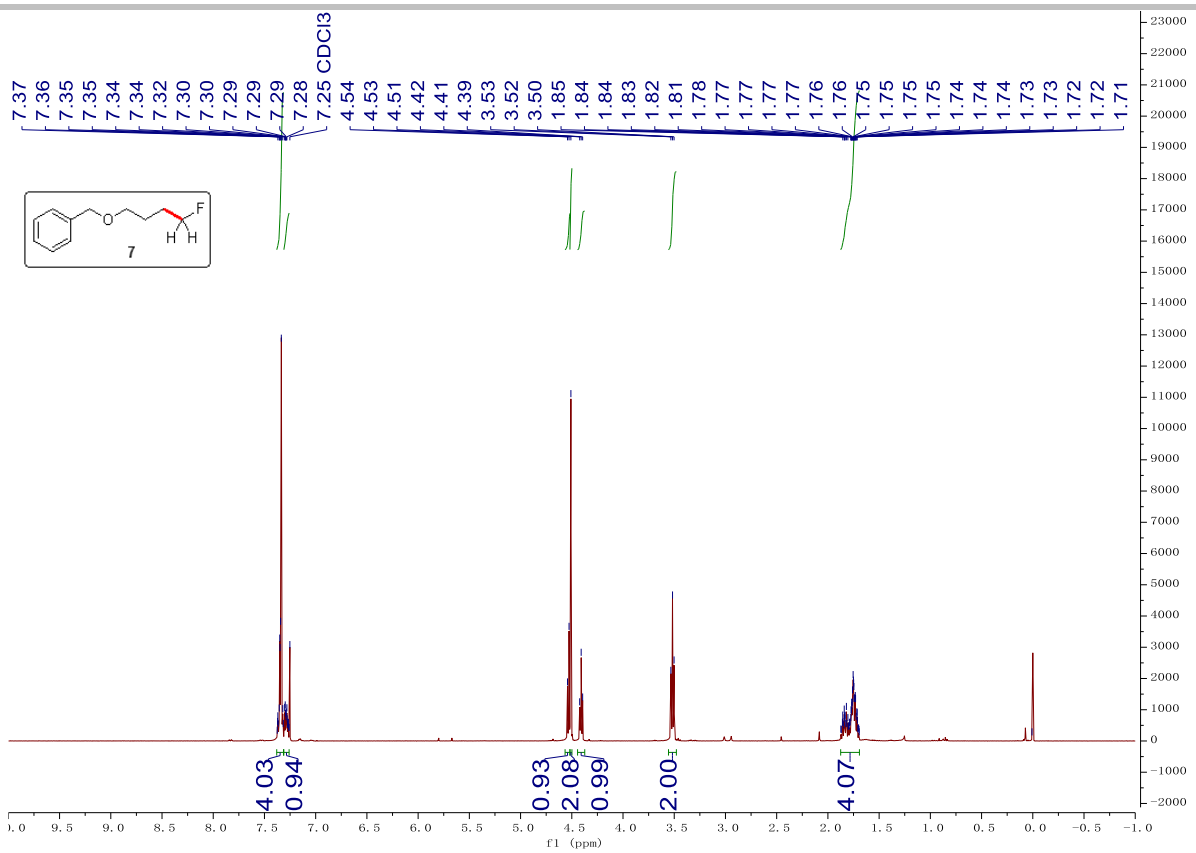
^{1}H NMR Spectrum of of **6** ($CDCl_3$, 500 MHz)



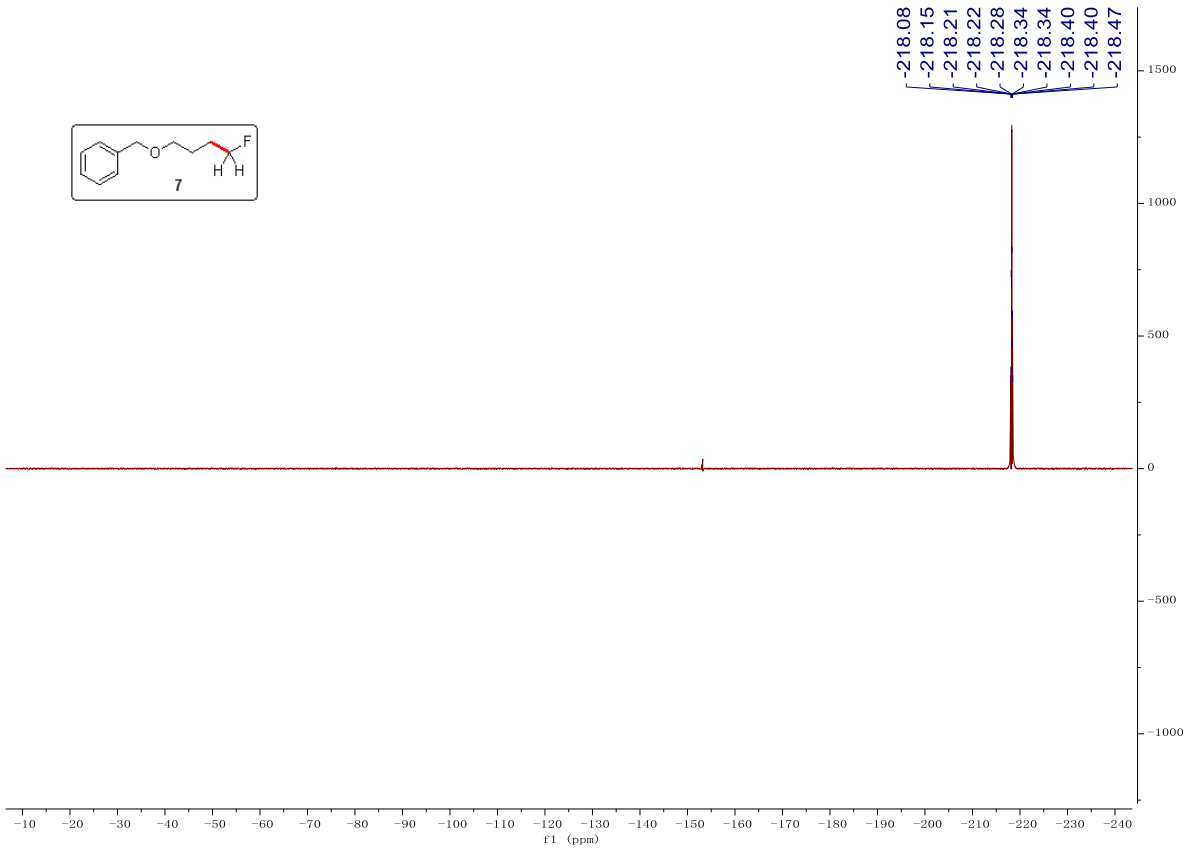
^{19}F NMR Spectrum of of **6** ($CDCl_3$, 376 MHz)



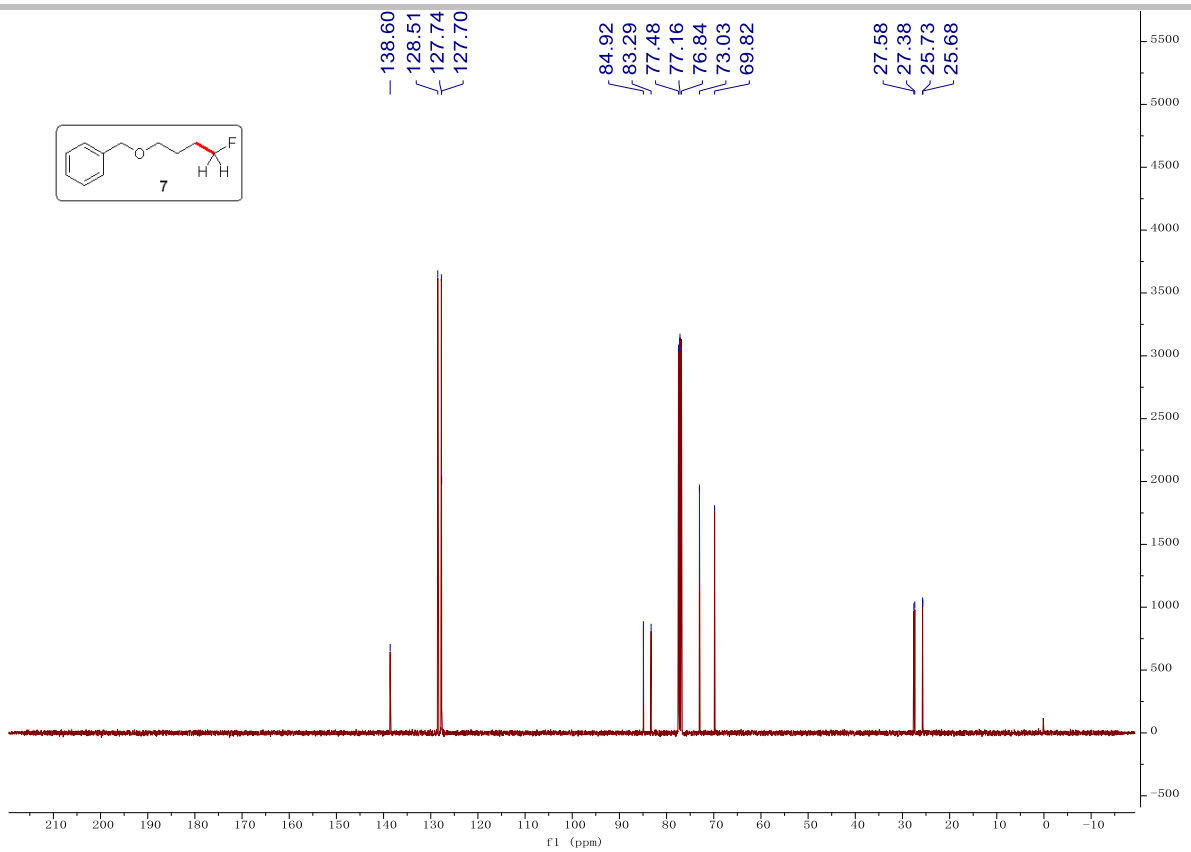
^{13}C NMR Spectrum of of **6** ($CDCl_3$, 126 MHz)



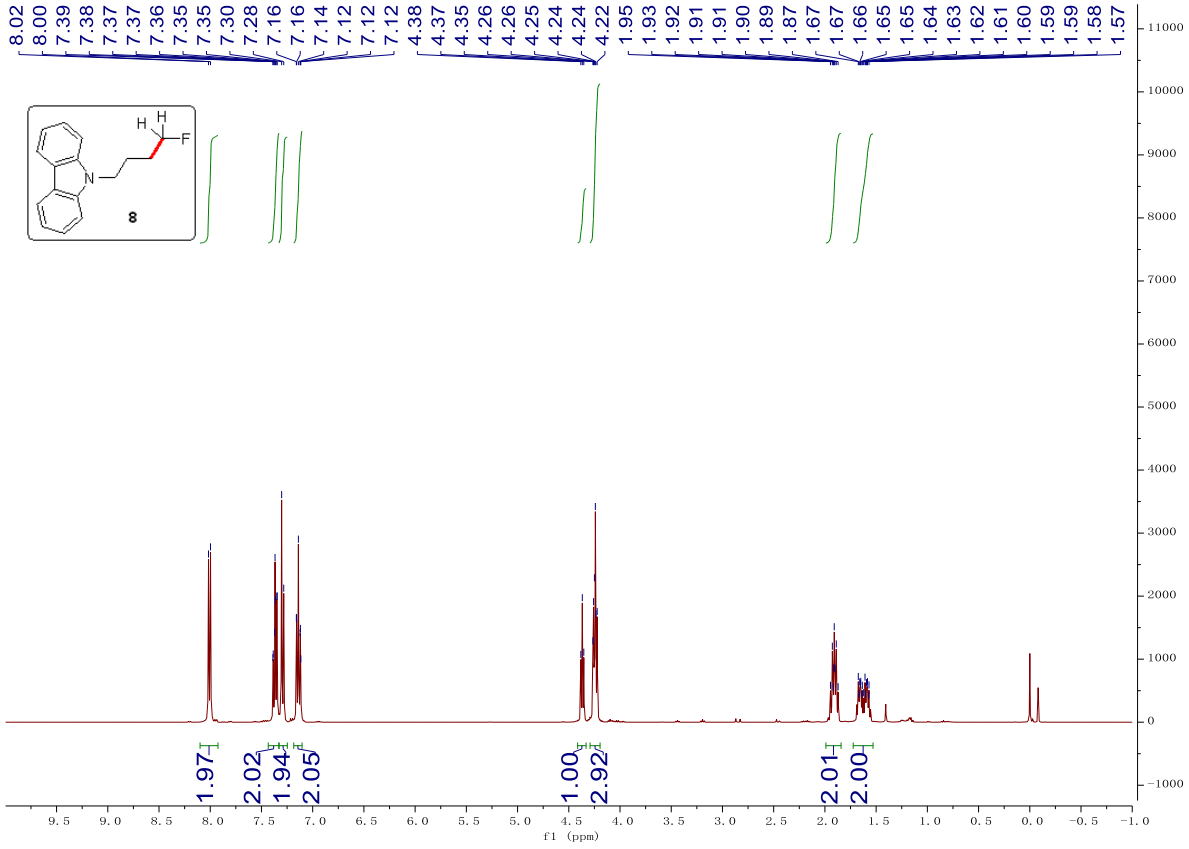
^{1}H NMR Spectrum of of **7** ($CDCl_3$, 400 MHz)



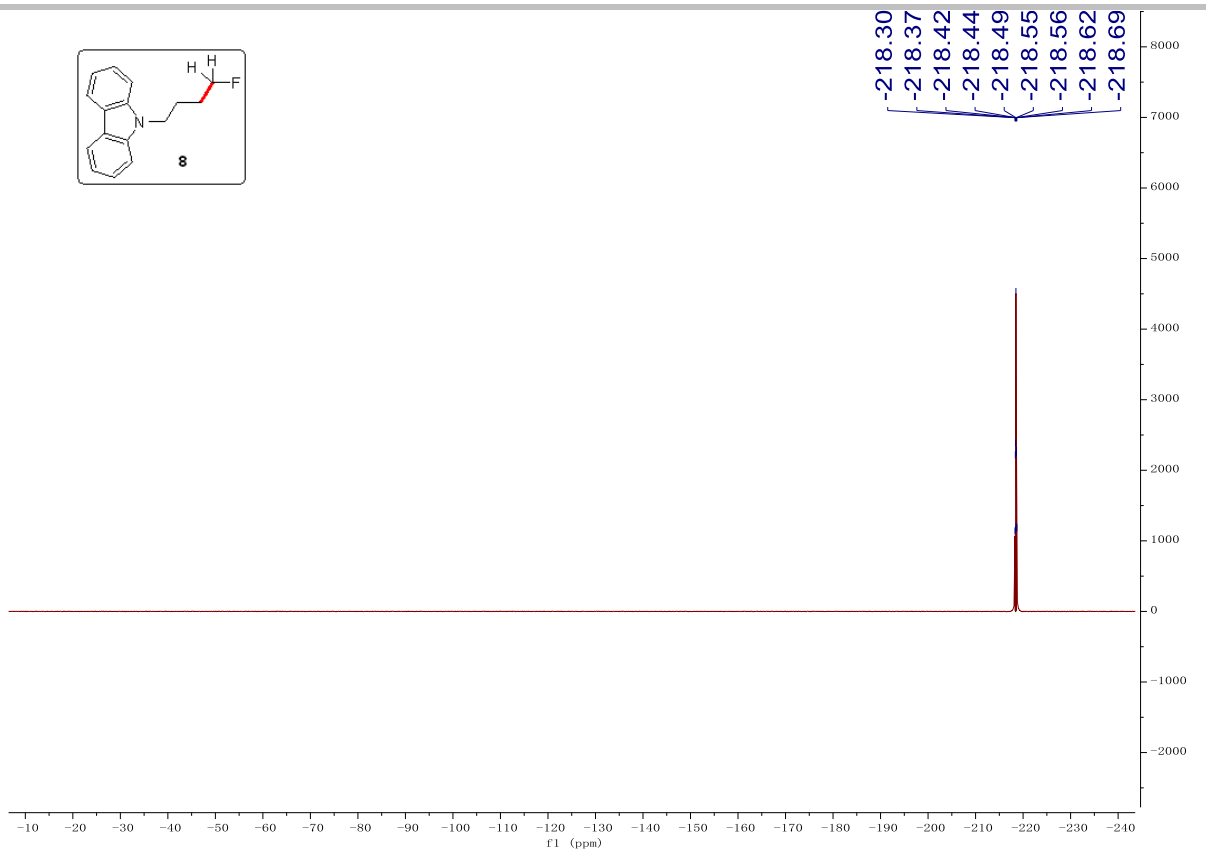
^{19}F NMR Spectrum of of **7** ($CDCl_3$, 376 MHz)



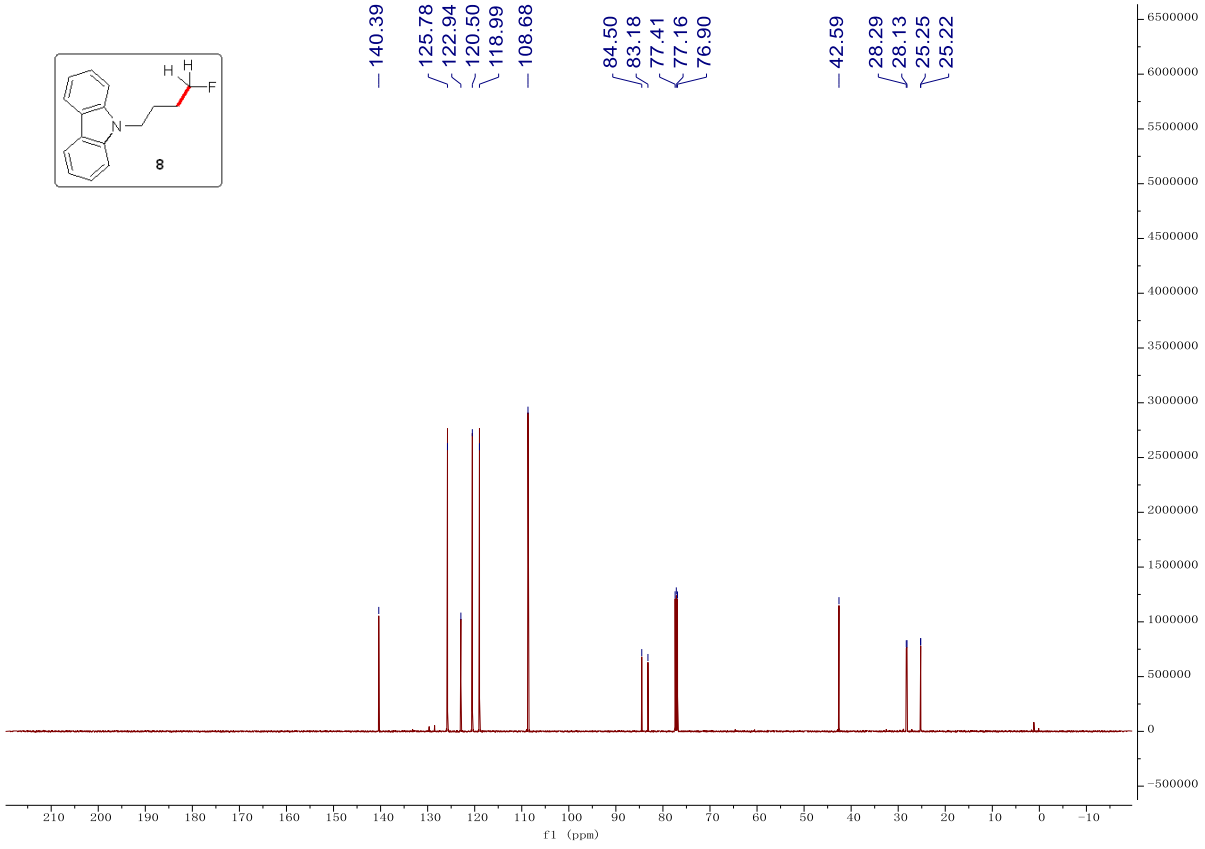
^{13}C NMR Spectrum of of **7** ($CDCl_3$, 101 MHz)



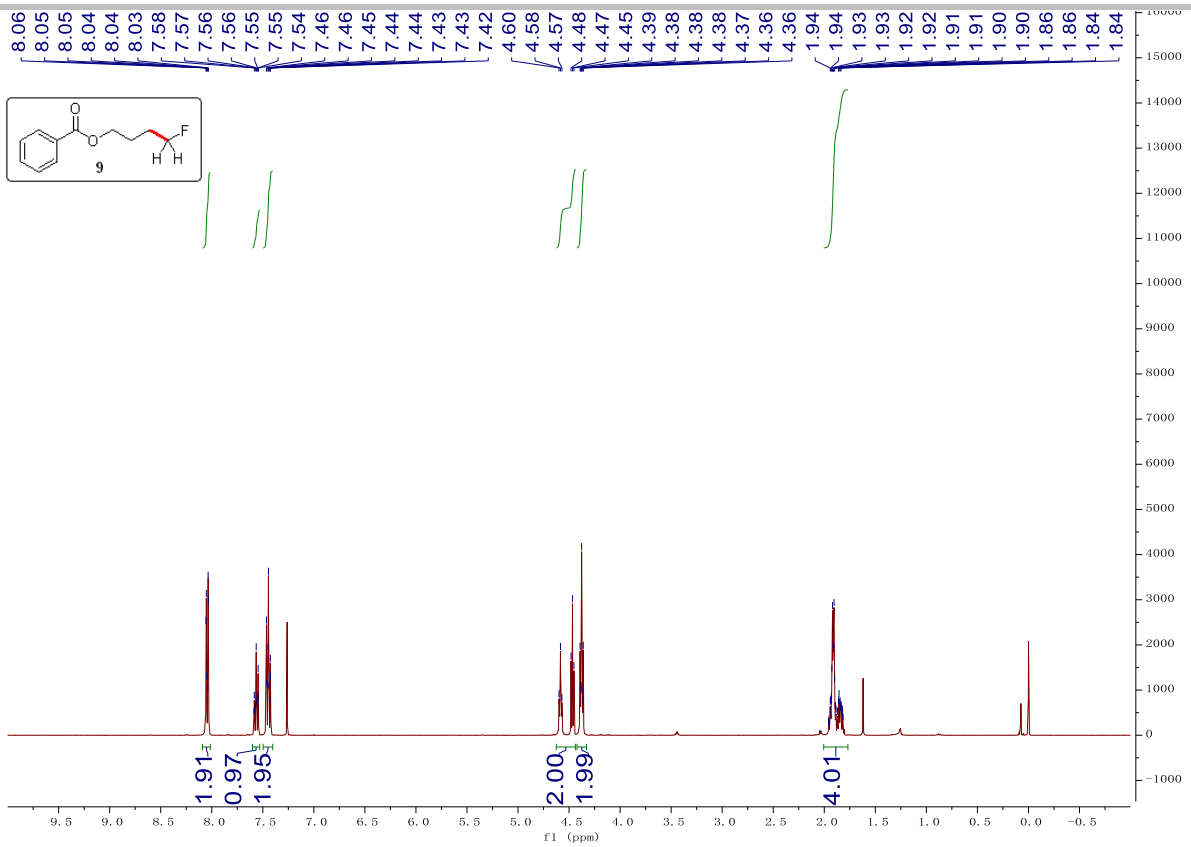
^{1}H NMR Spectrum of of **8** ($CDCl_3$, 400 MHz)



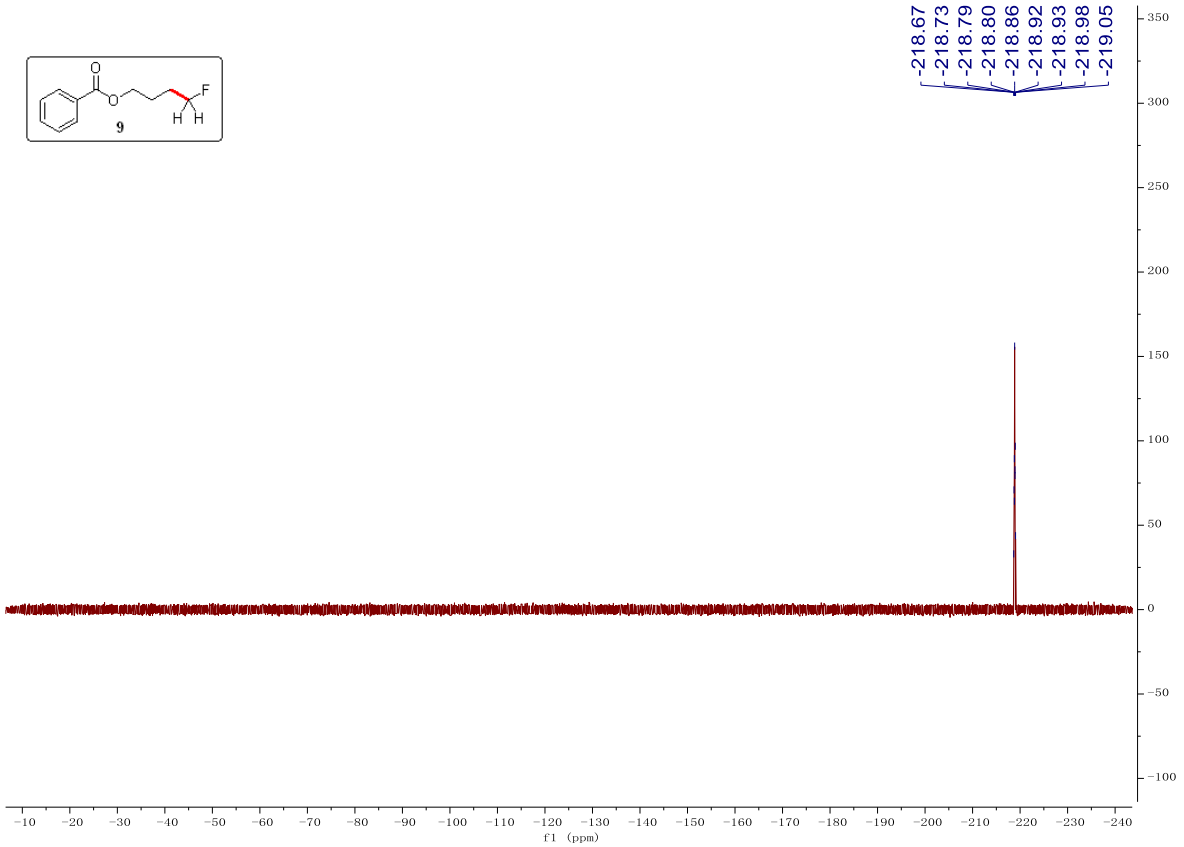
^{19}F NMR Spectrum of of **8** ($CDCl_3$, 376 MHz)



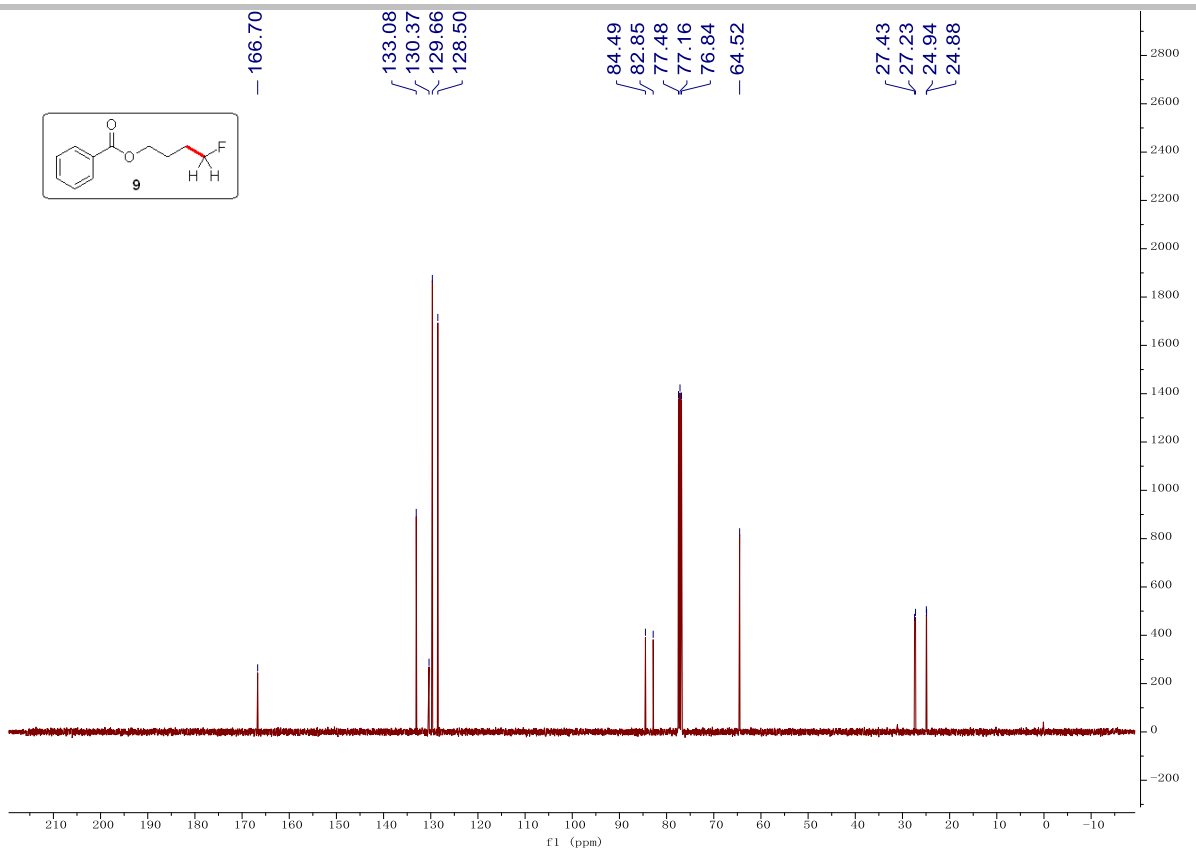
^{13}C NMR Spectrum of of **8** ($CDCl_3$, 126 MHz)



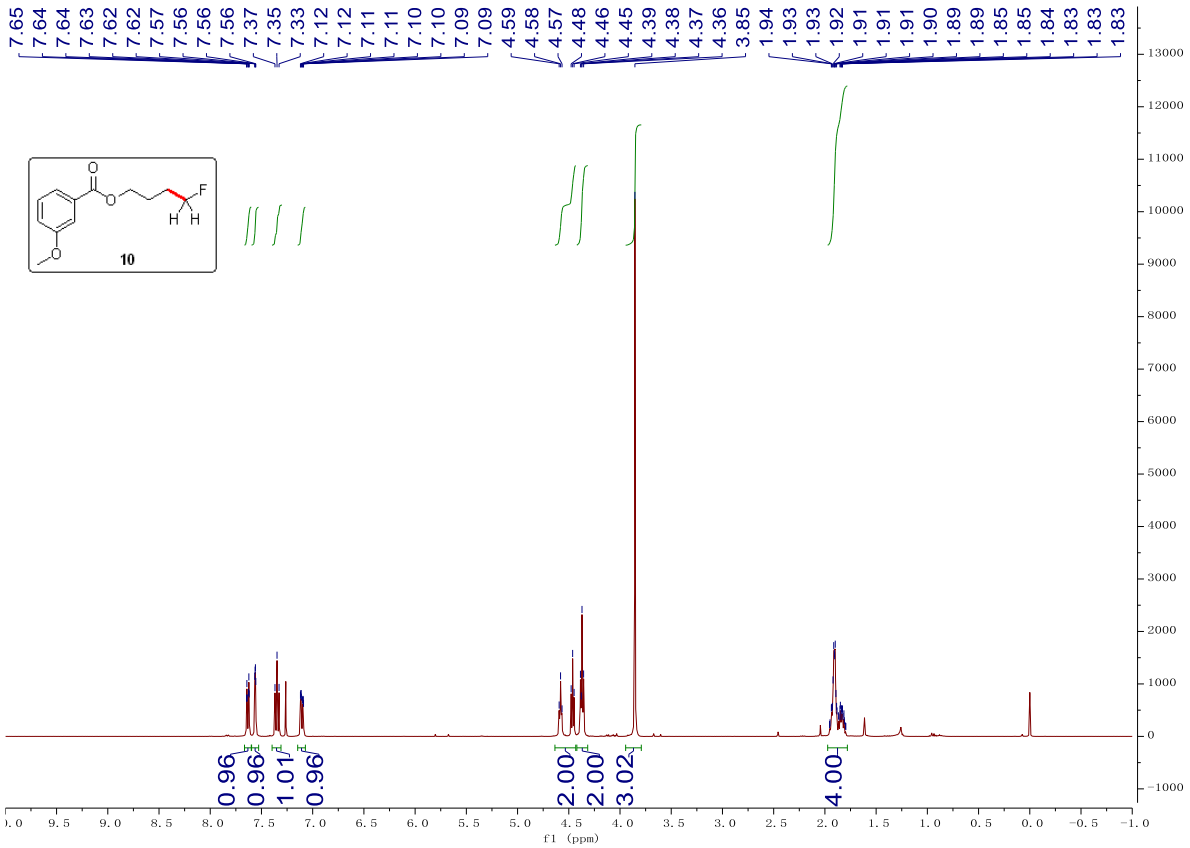
^{1}H NMR Spectrum of of **9** ($CDCl_3$, 400 MHz)



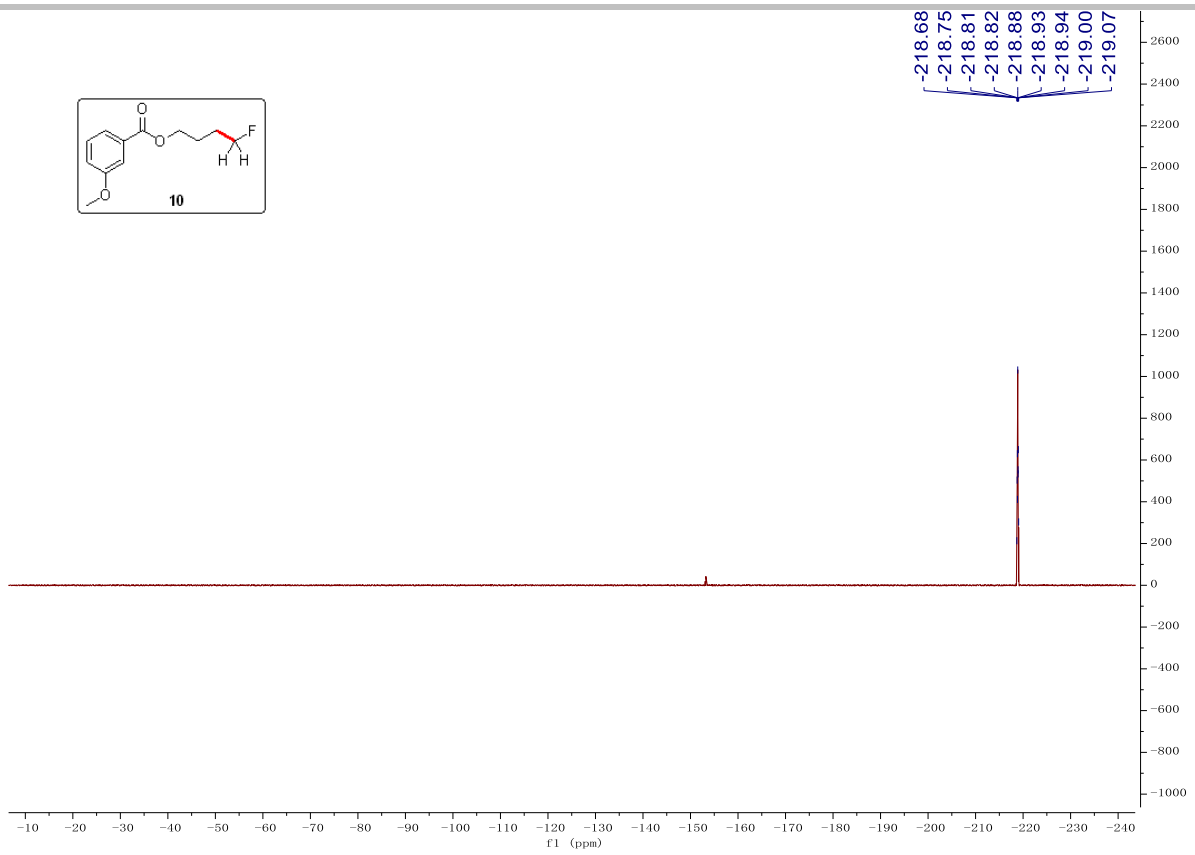
^{19}F NMR Spectrum of of **9** ($CDCl_3$, 376 MHz)



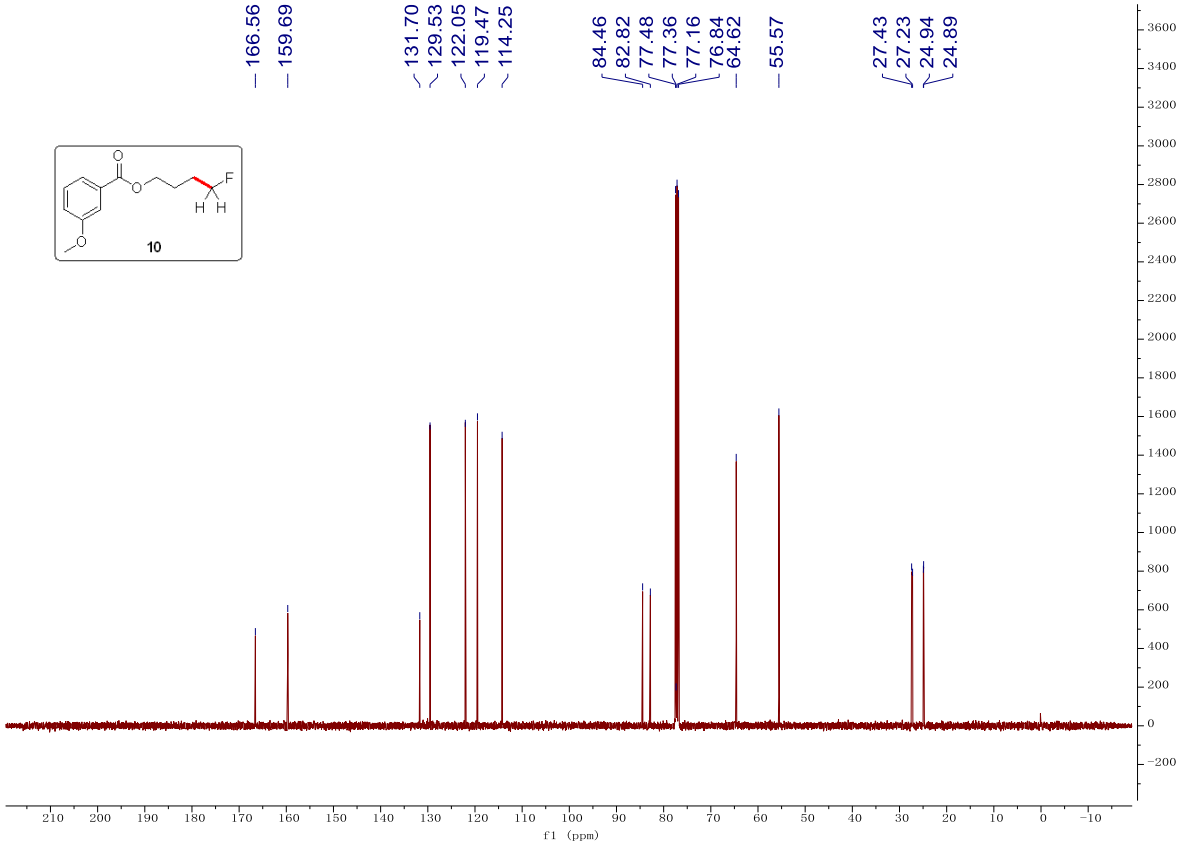
^{13}C NMR Spectrum of of **9** ($CDCl_3$, 101 MHz)



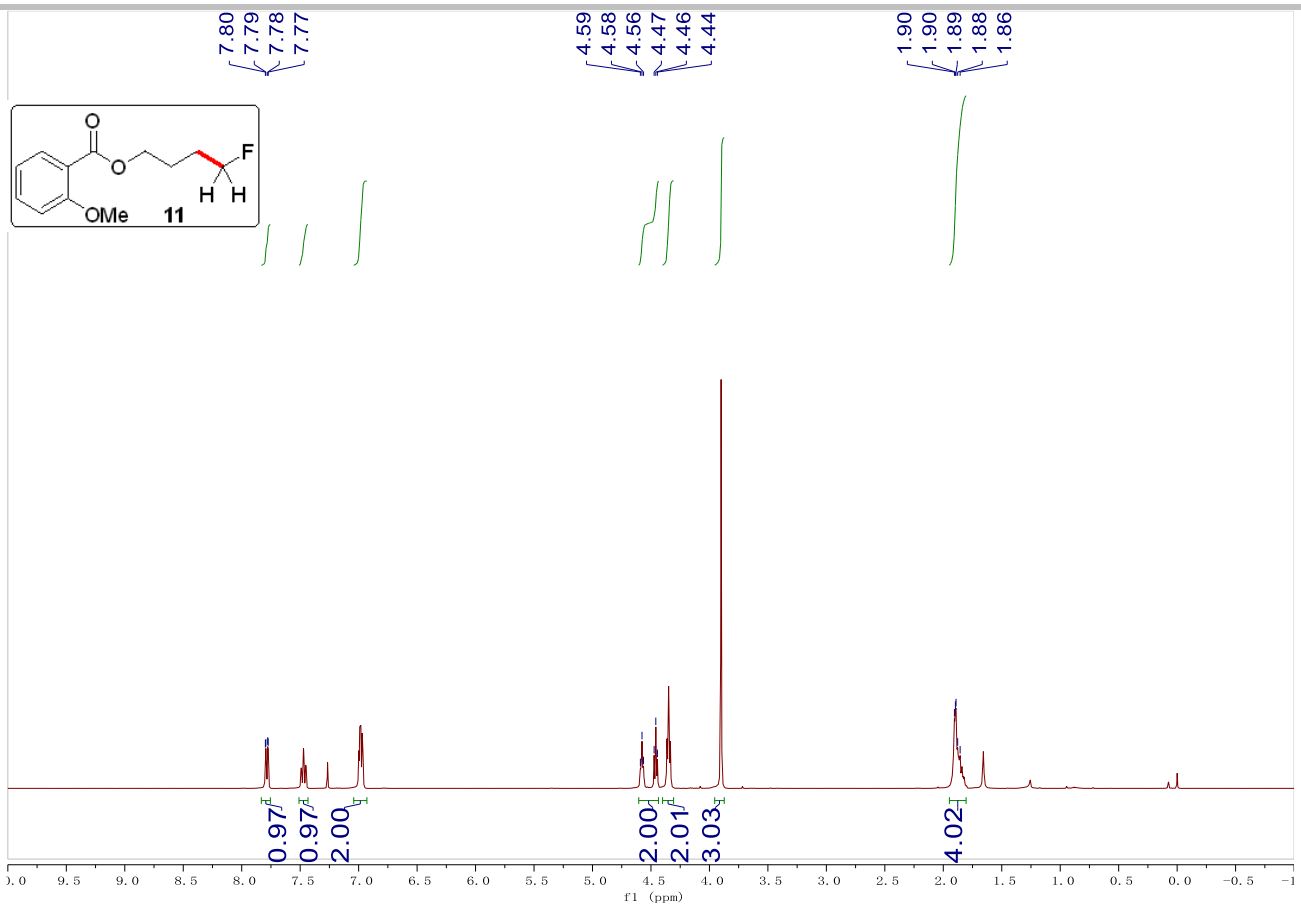
^{1}H NMR Spectrum of of **10** ($CDCl_3$, 400 MHz)



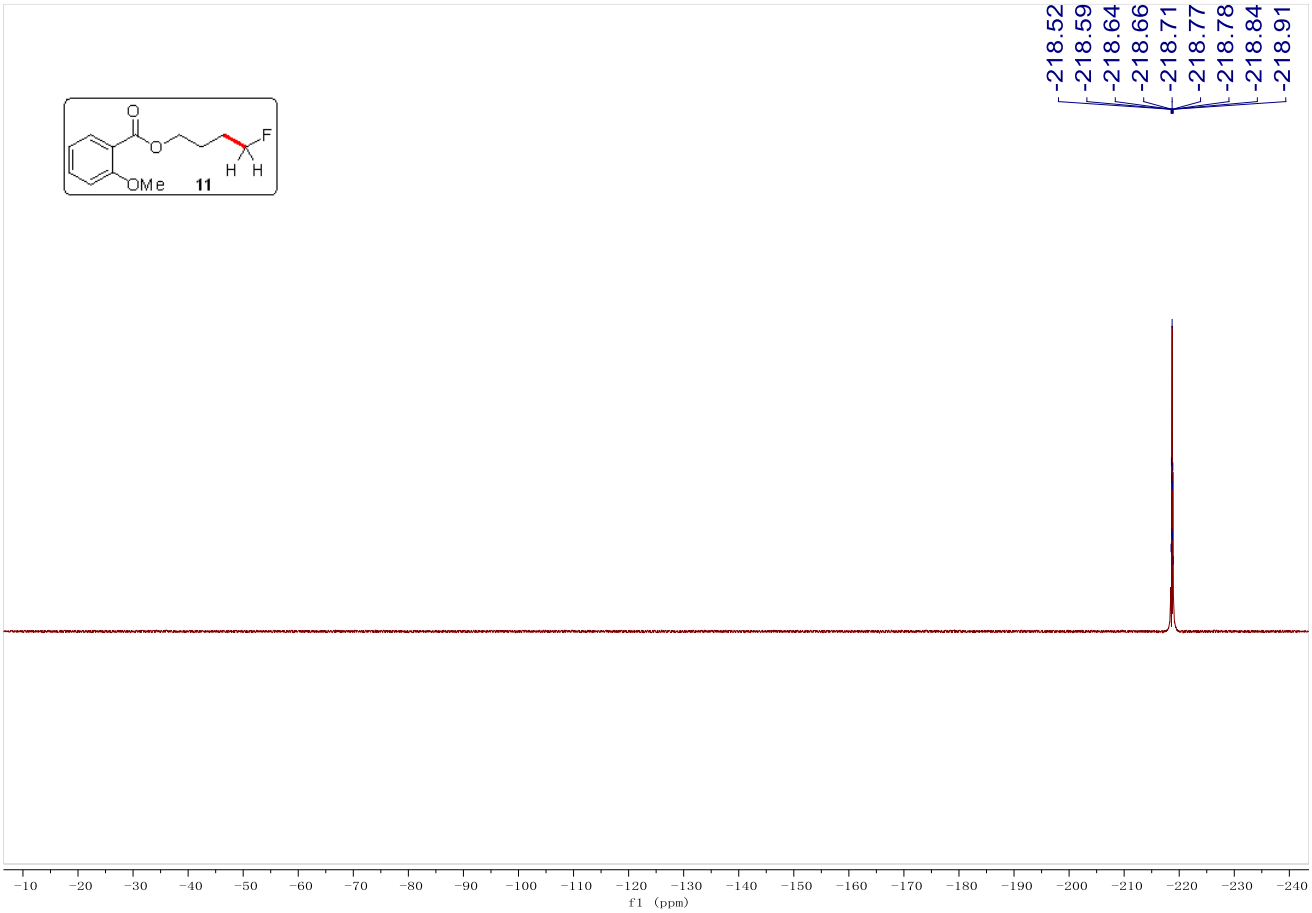
^{19}F NMR Spectrum of of **10** ($CDCl_3$, 376 MHz)



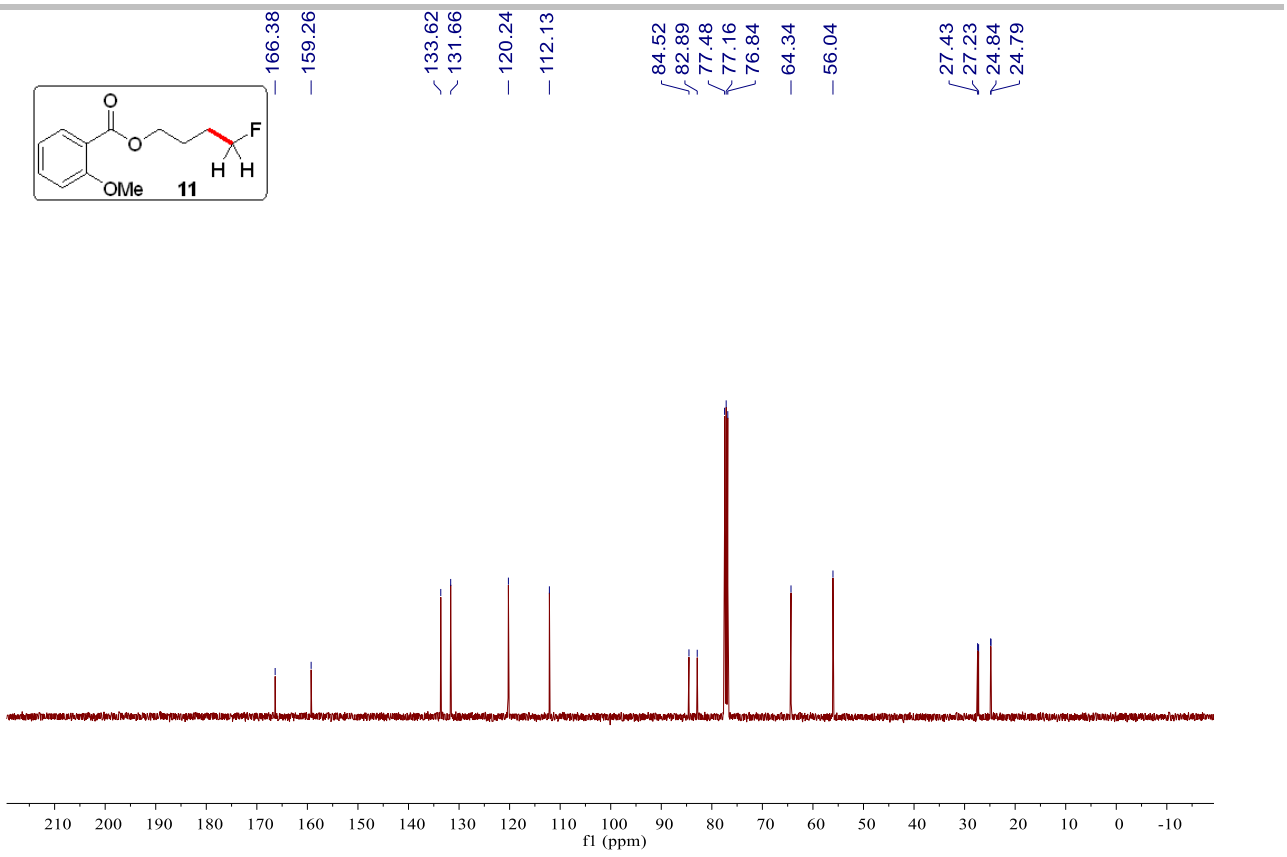
^{13}C NMR Spectrum of of **10** ($CDCl_3$, 101 MHz)



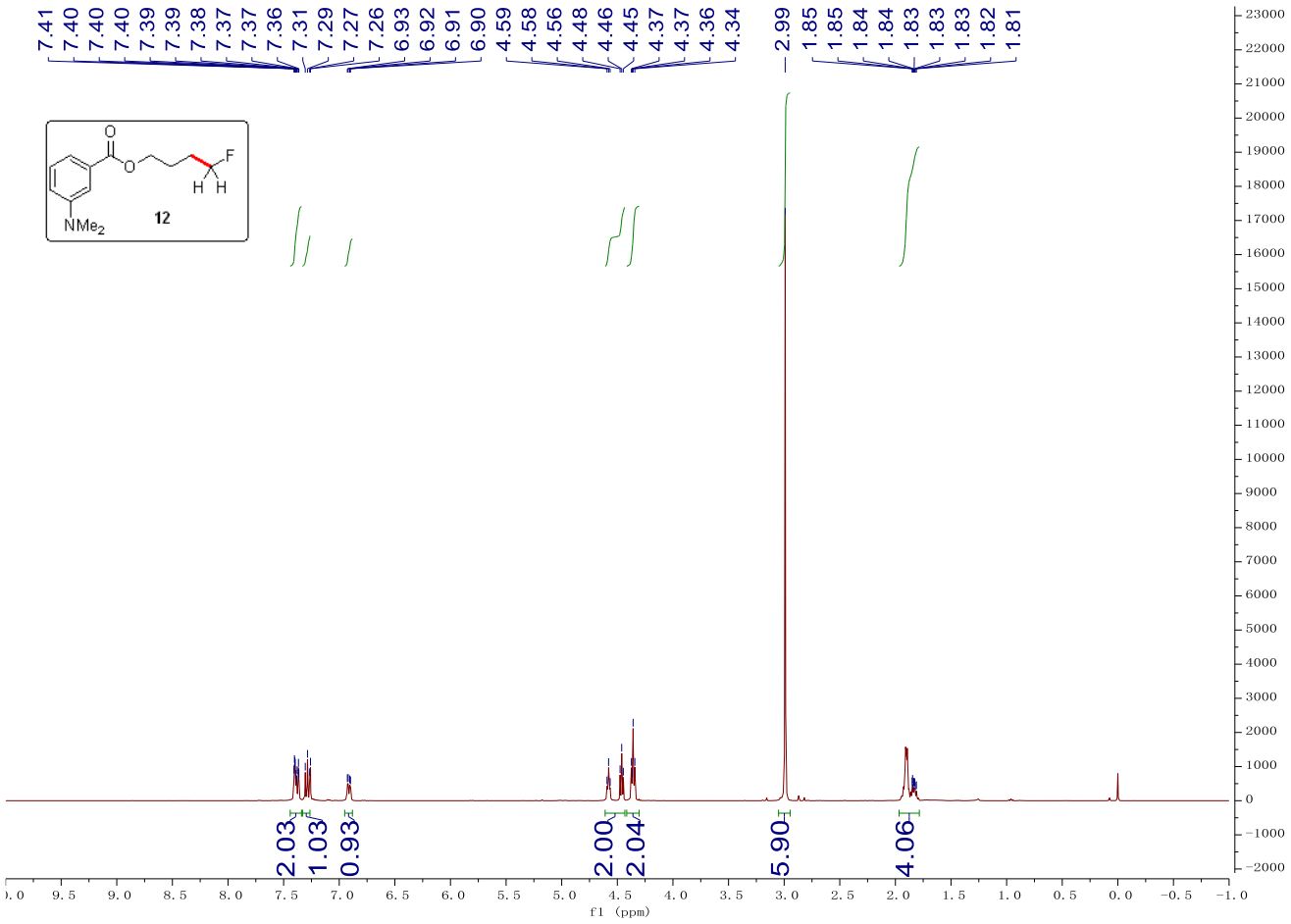
^{1}H NMR Spectrum of of **11** ($CDCl_3$, 400 MHz)



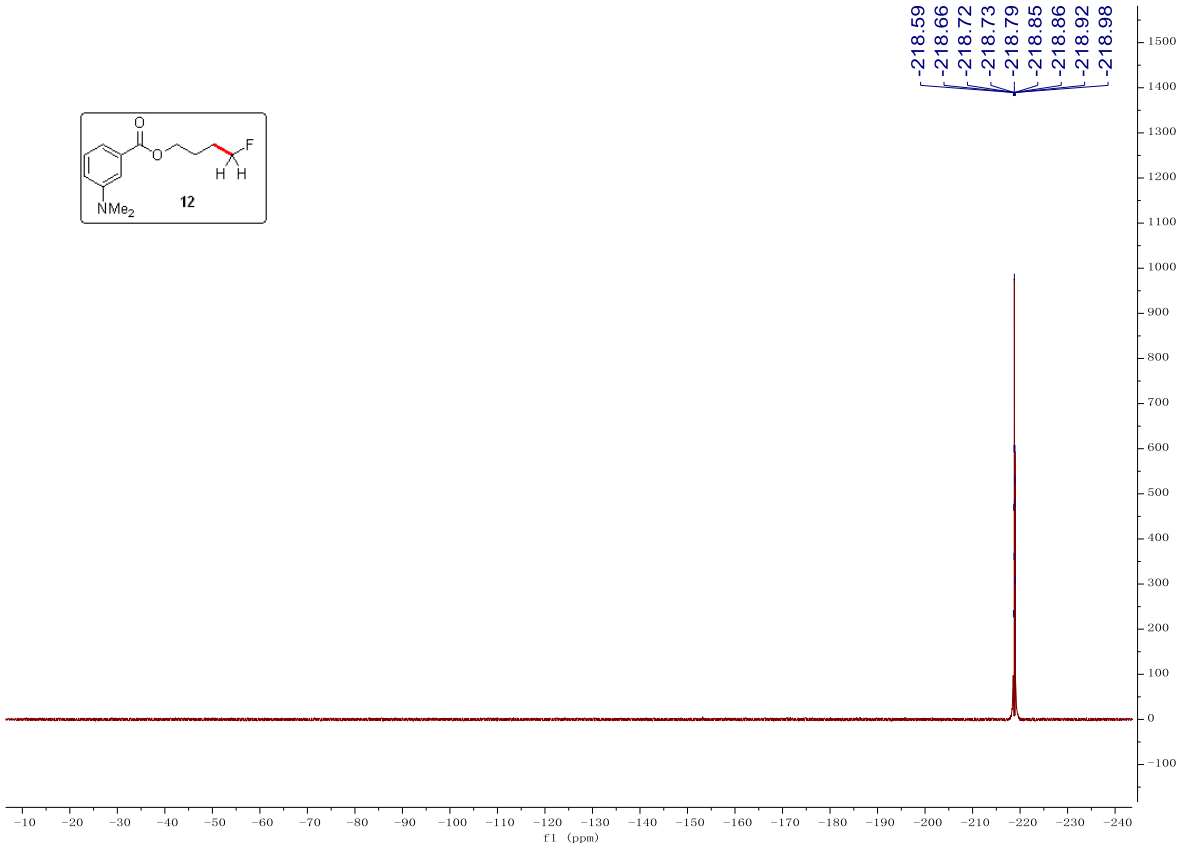
^{19}F NMR Spectrum of of **11** ($CDCl_3$, 376 MHz)



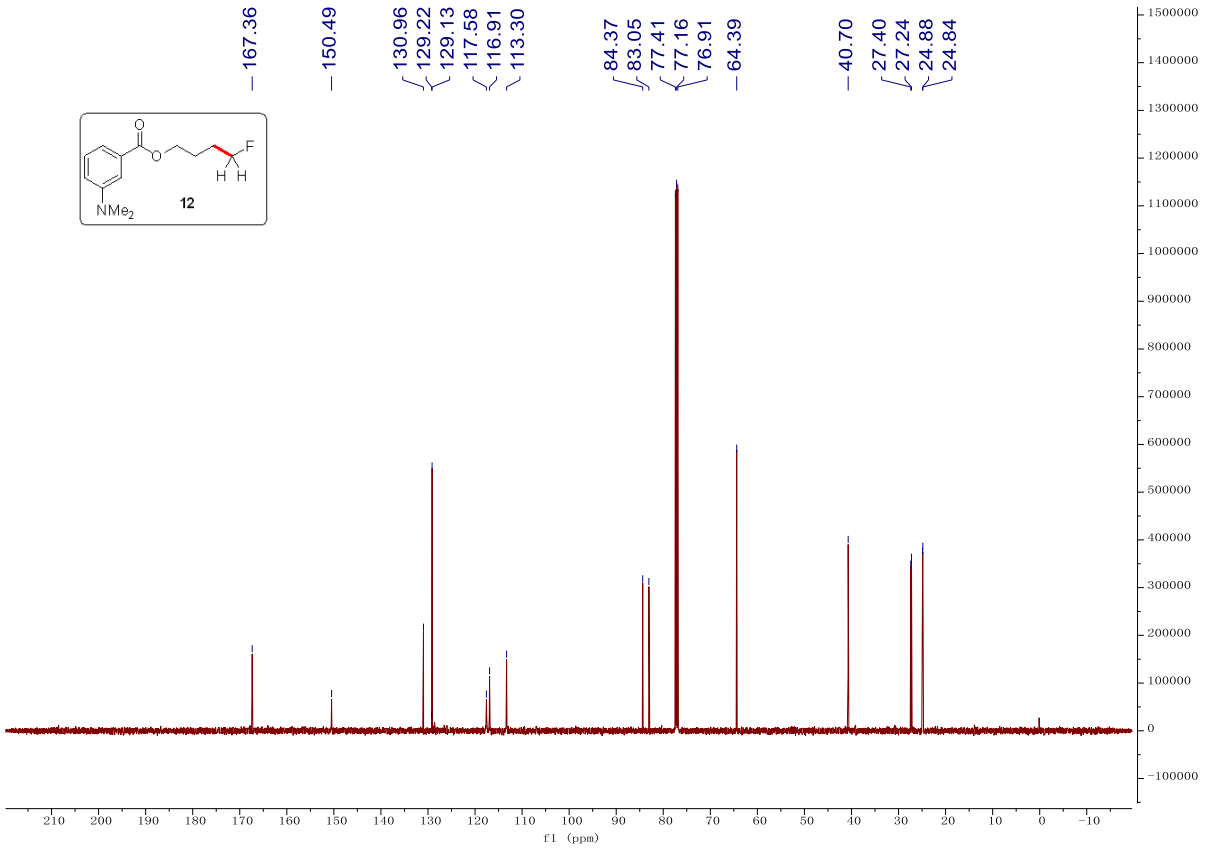
^{13}C NMR Spectrum of of **11** ($CDCl_3$, 101 MHz)



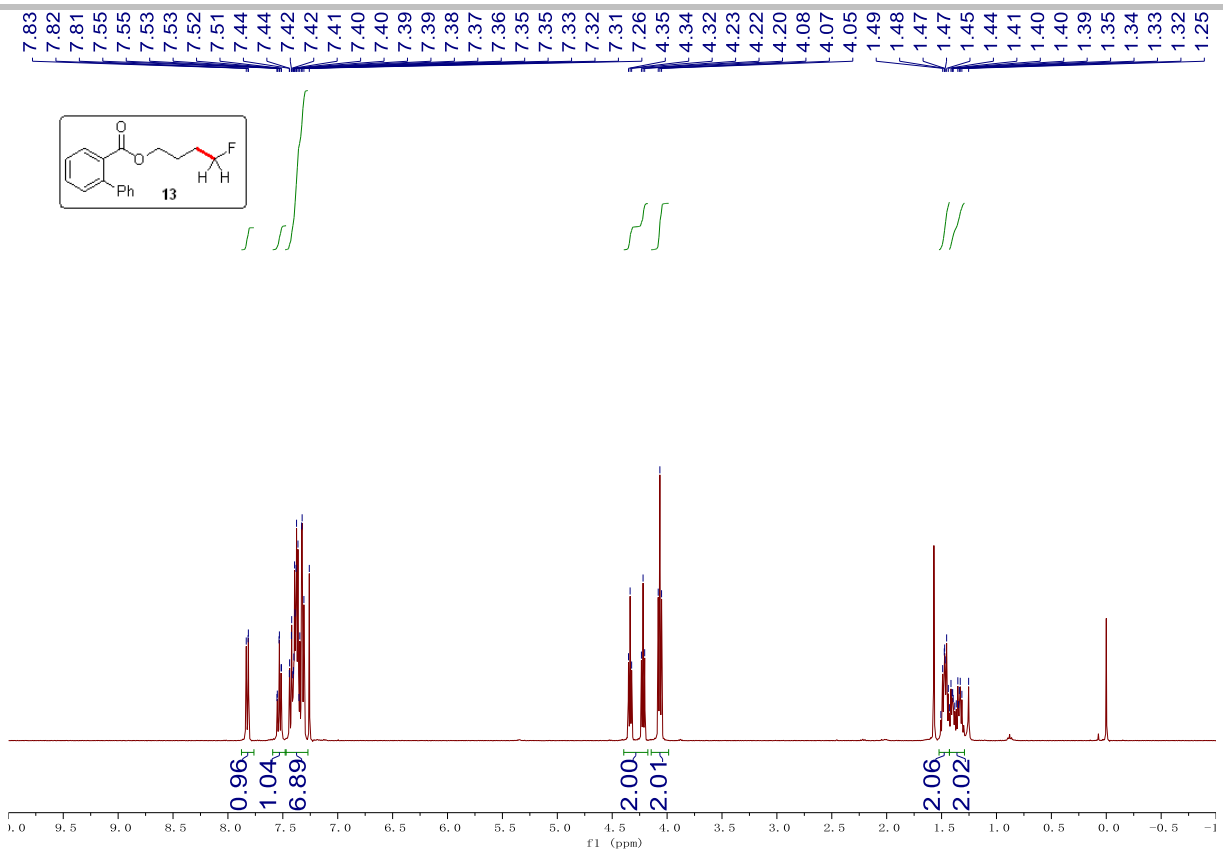
^{1}H NMR Spectrum of of **12** ($CDCl_3$, 400 MHz)



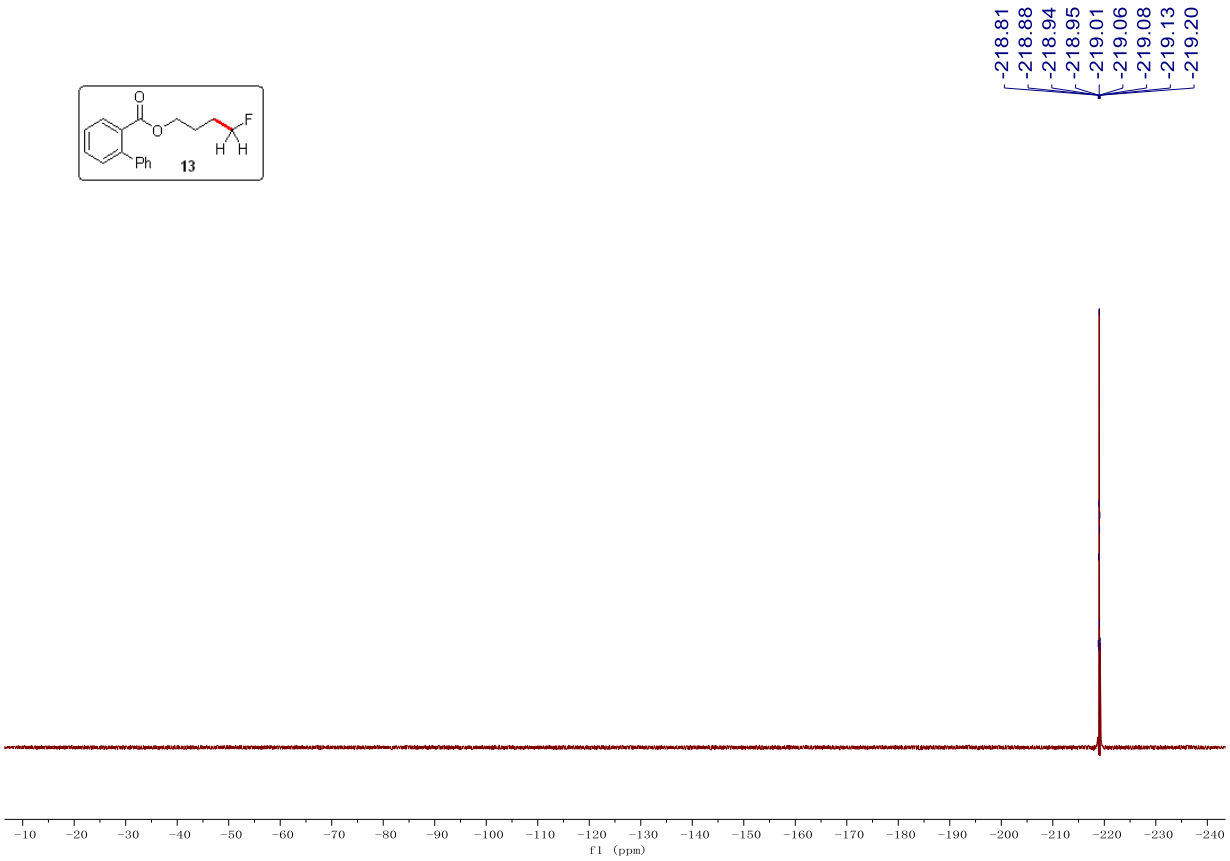
^{19}F NMR Spectrum of of **12** ($CDCl_3$, 376 MHz)



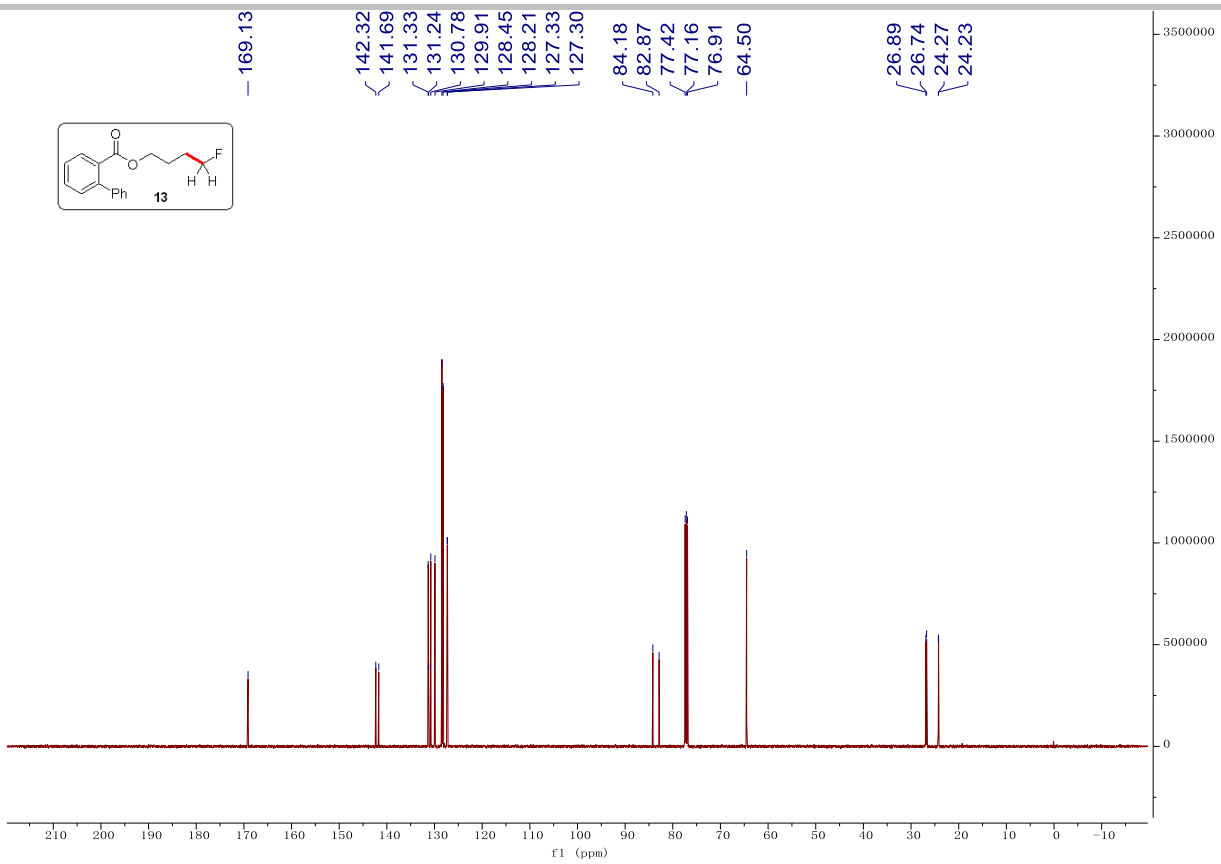
^{13}C NMR Spectrum of of **12** ($CDCl_3$, 126 MHz)



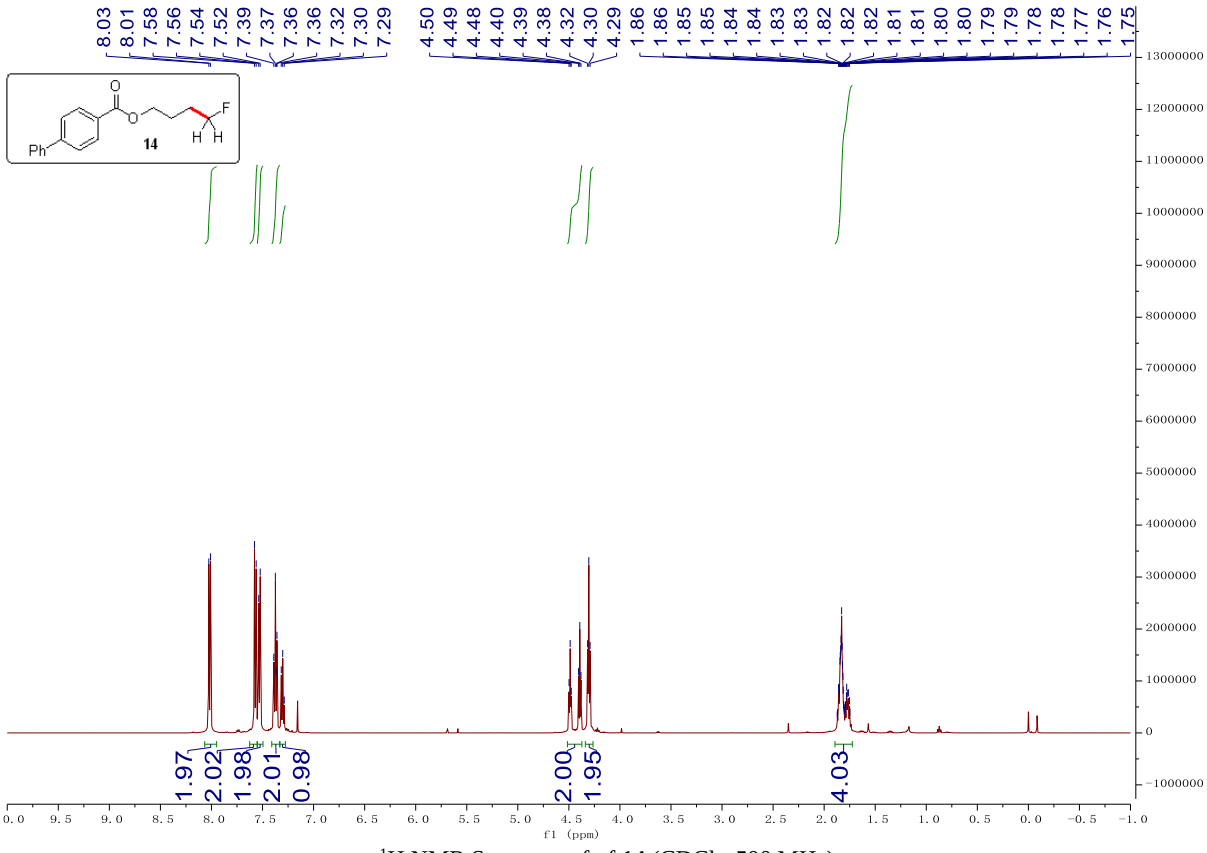
^{1}H NMR Spectrum of of **13** ($CDCl_3$, 400 MHz)



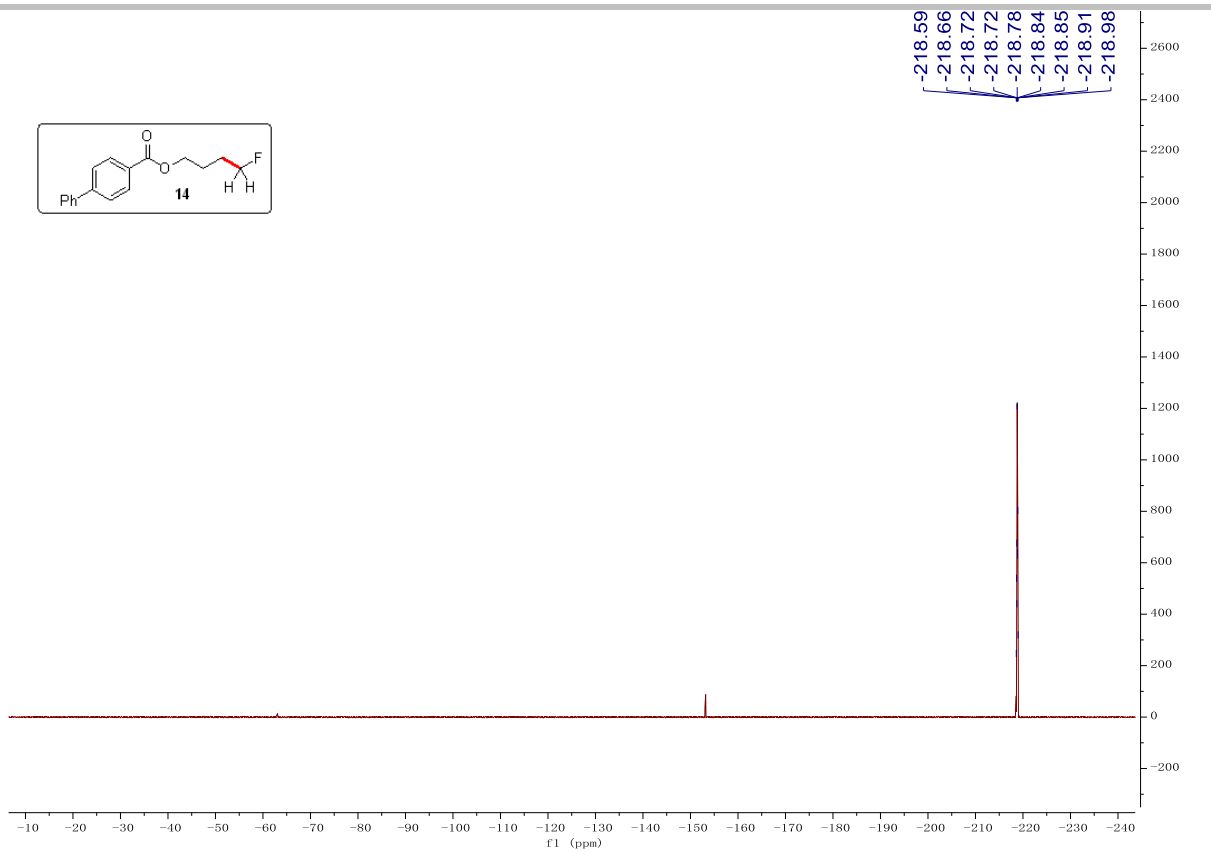
^{19}F NMR Spectrum of of **13** ($CDCl_3$, 376 MHz)



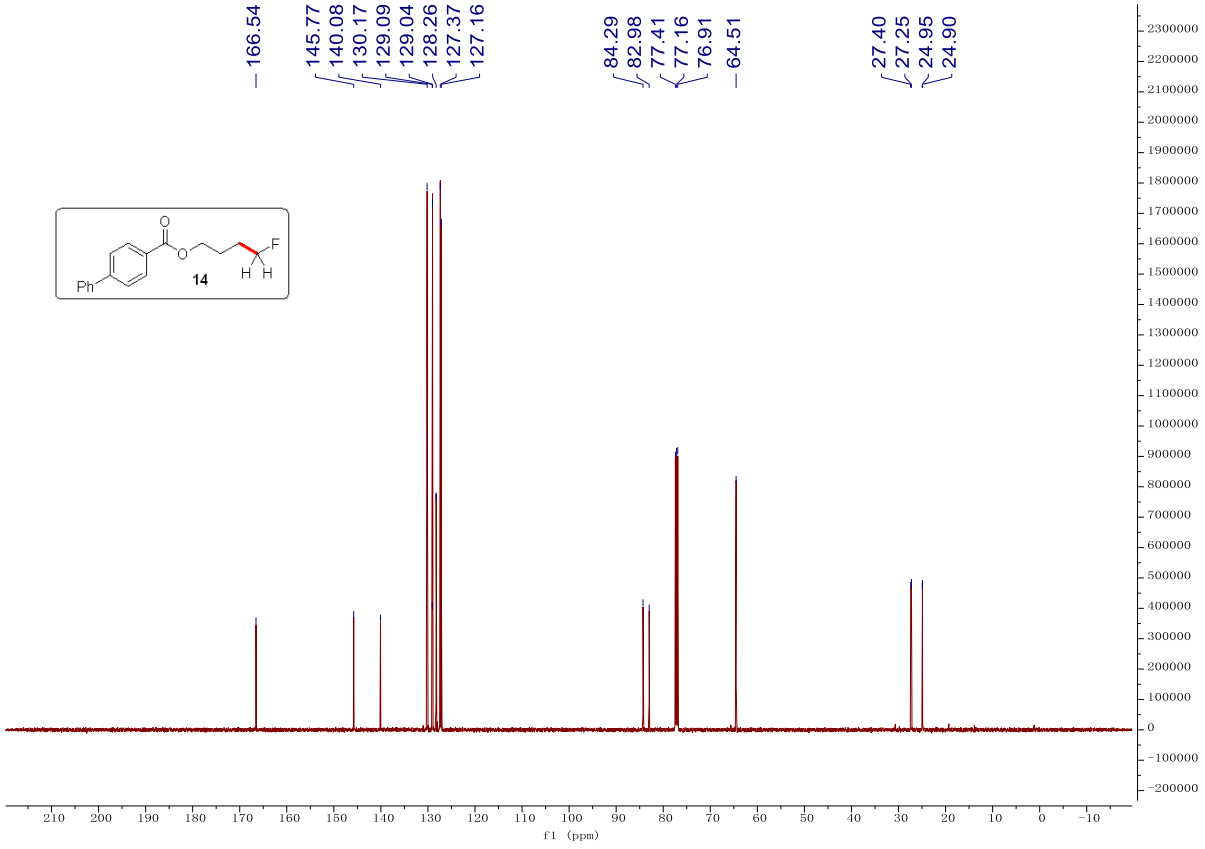
^{13}C NMR Spectrum of **13** ($CDCl_3$, 126 MHz)



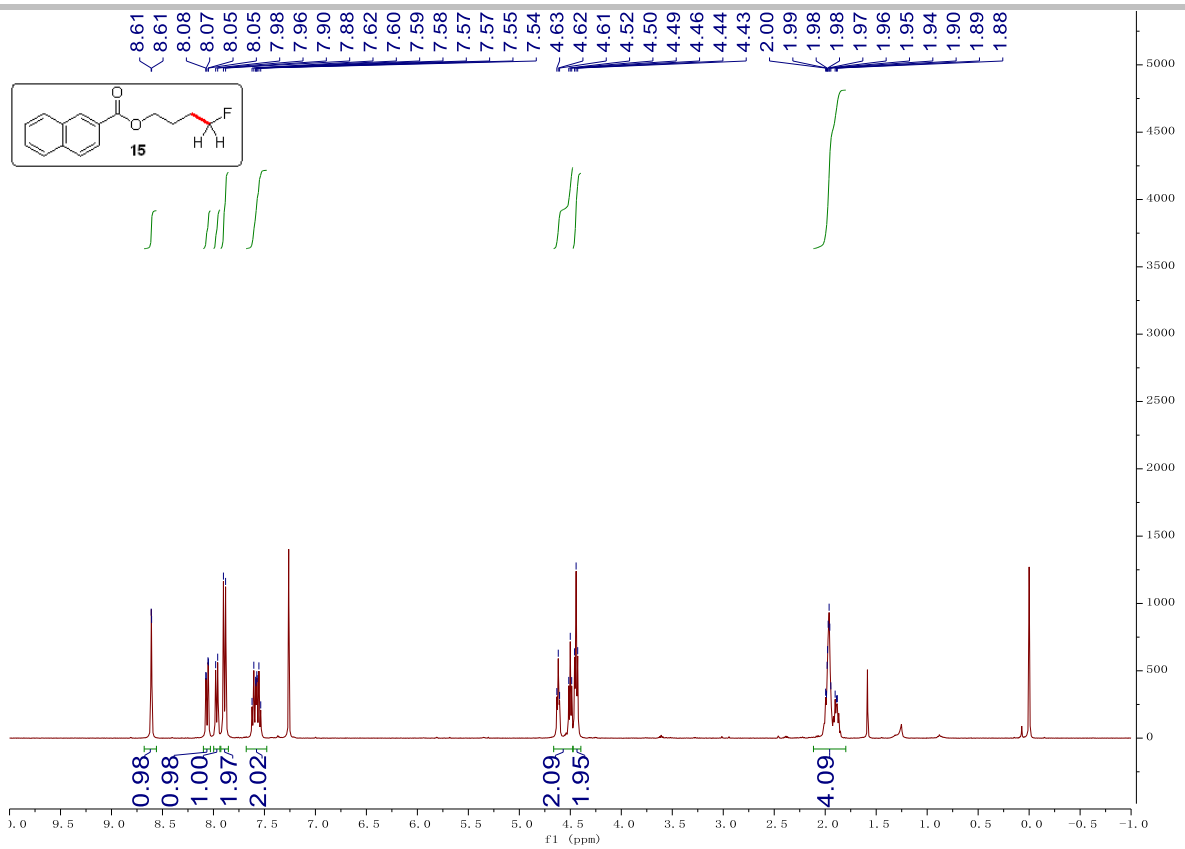
^{1}H NMR Spectrum of of **14** ($CDCl_3$, 500 MHz)



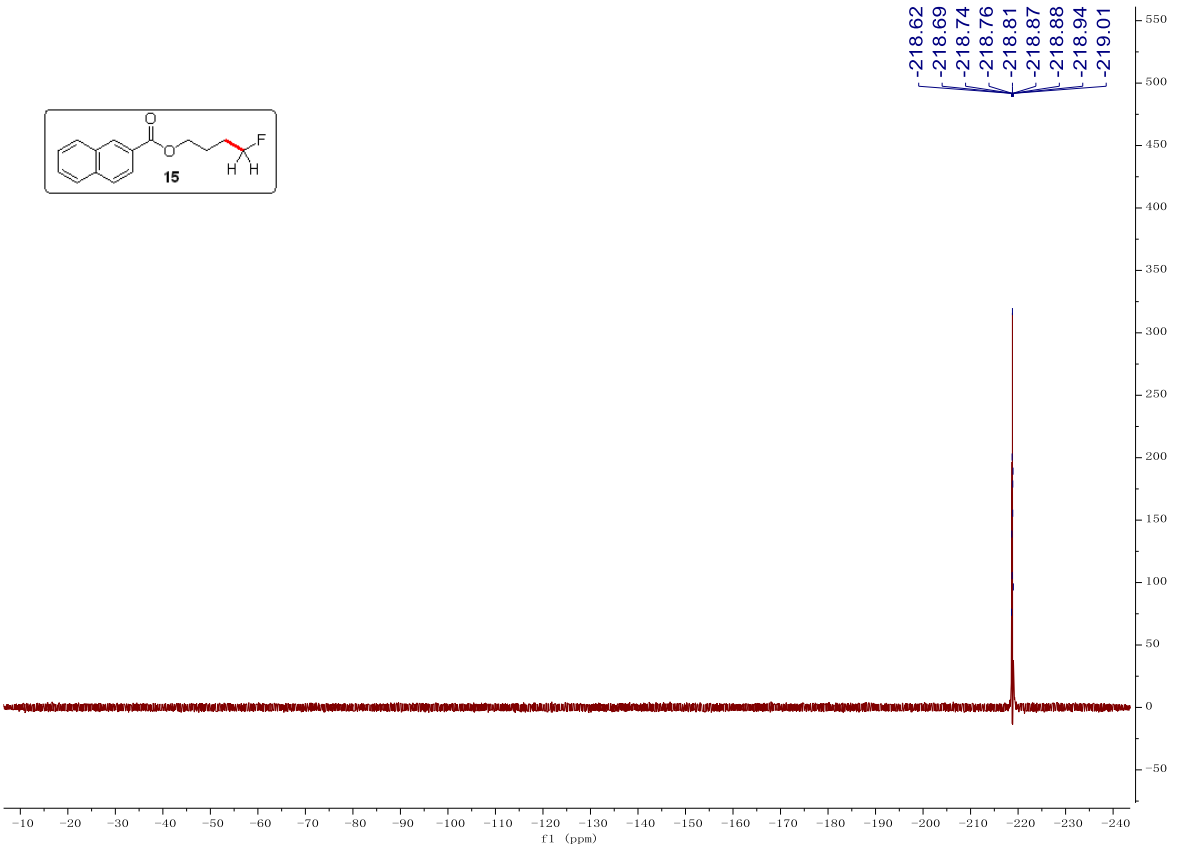
^{19}F NMR Spectrum of of **14** ($CDCl_3$, 376 MHz)



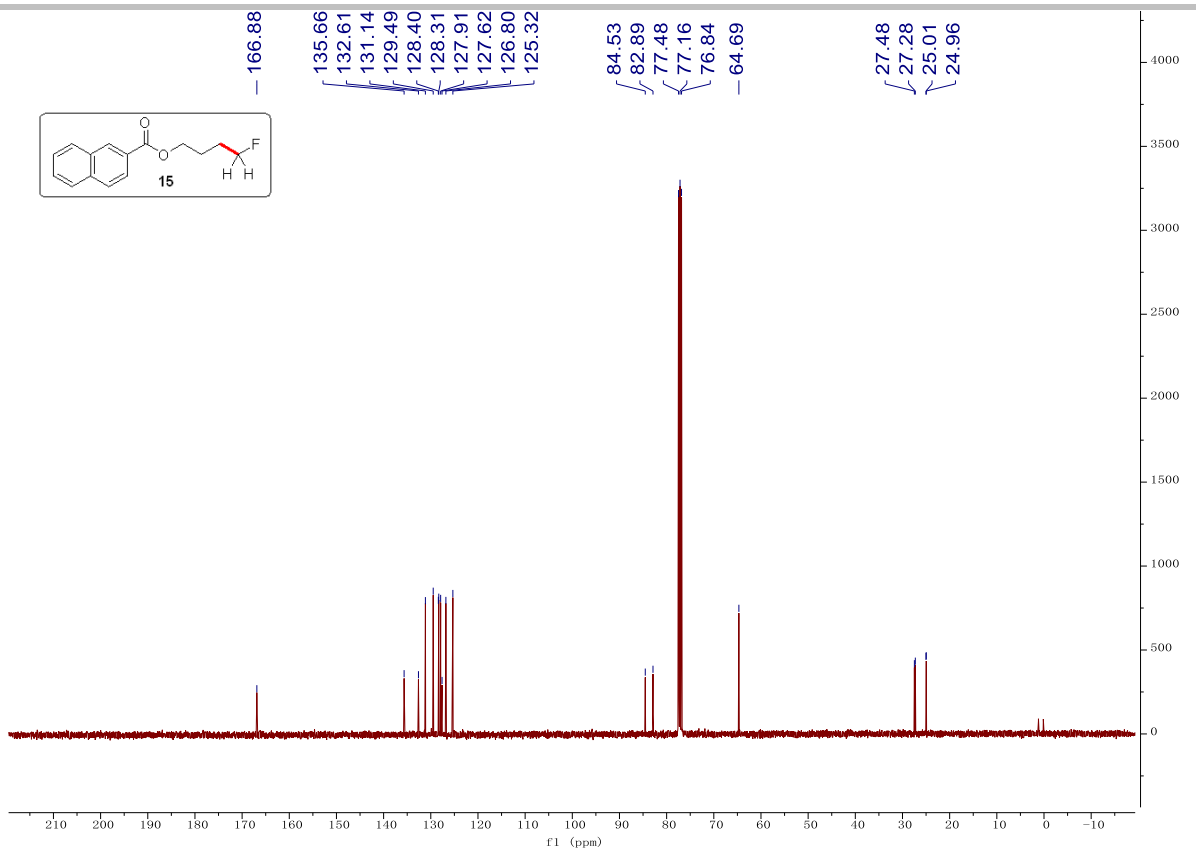
^{13}C NMR Spectrum of **14** ($CDCl_3$, 126 MHz)



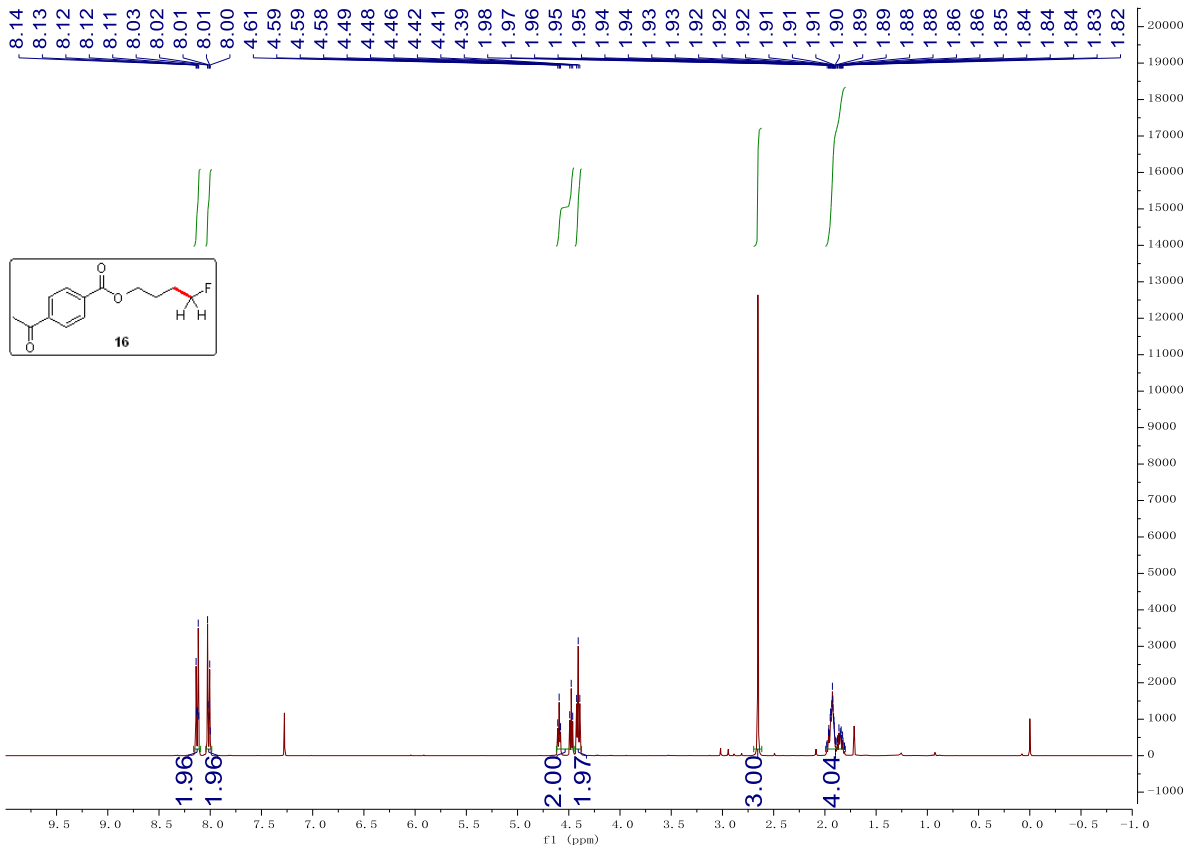
^{1}H NMR Spectrum of of **15** ($CDCl_3$, 500 MHz)



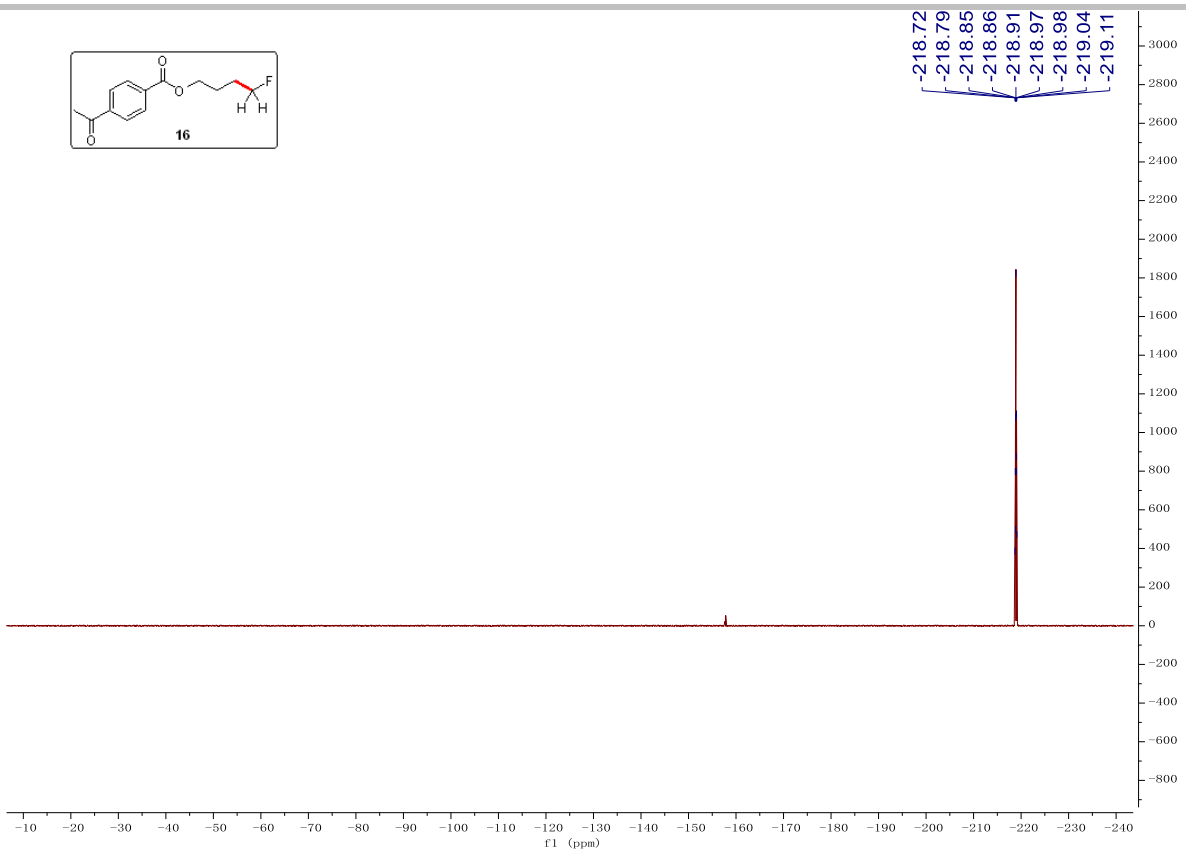
^{19}F NMR Spectrum of of **15** ($CDCl_3$, 376 MHz)



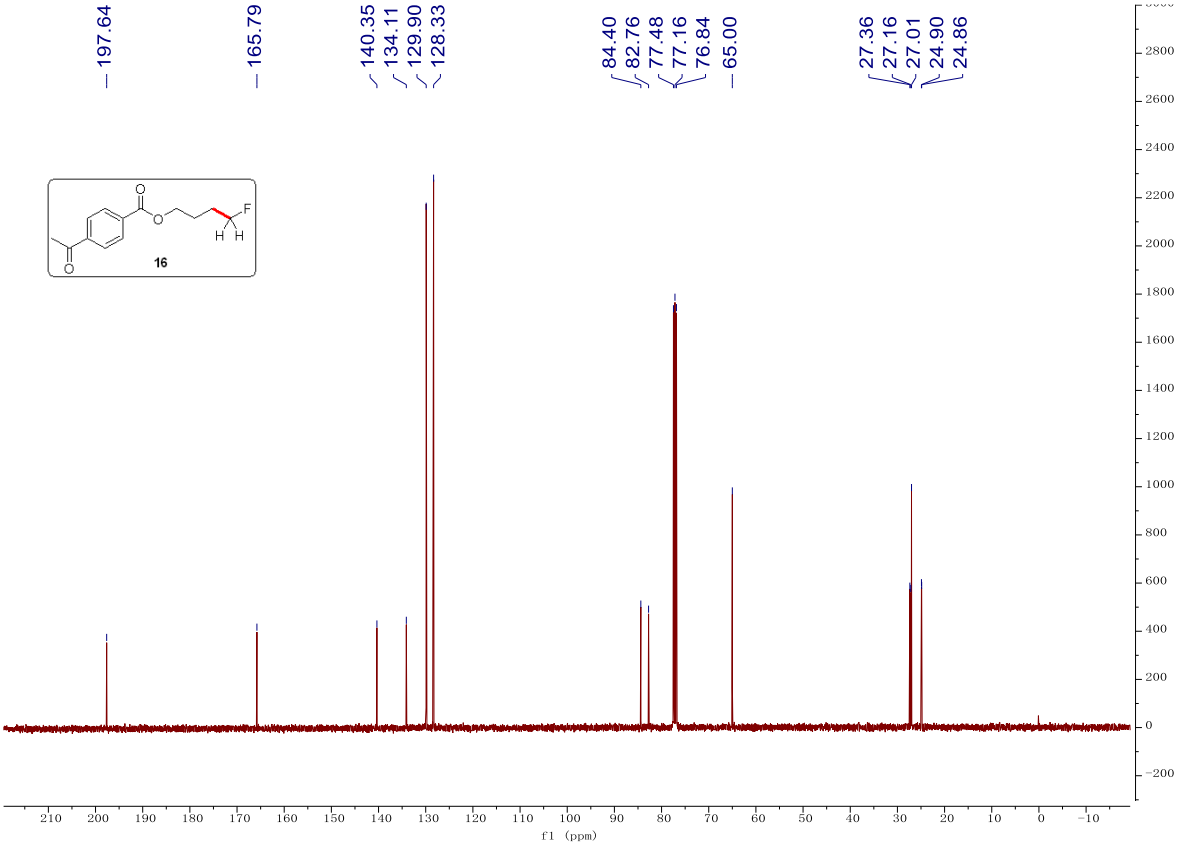
^{13}C NMR Spectrum of **15** ($CDCl_3$, 126 MHz)



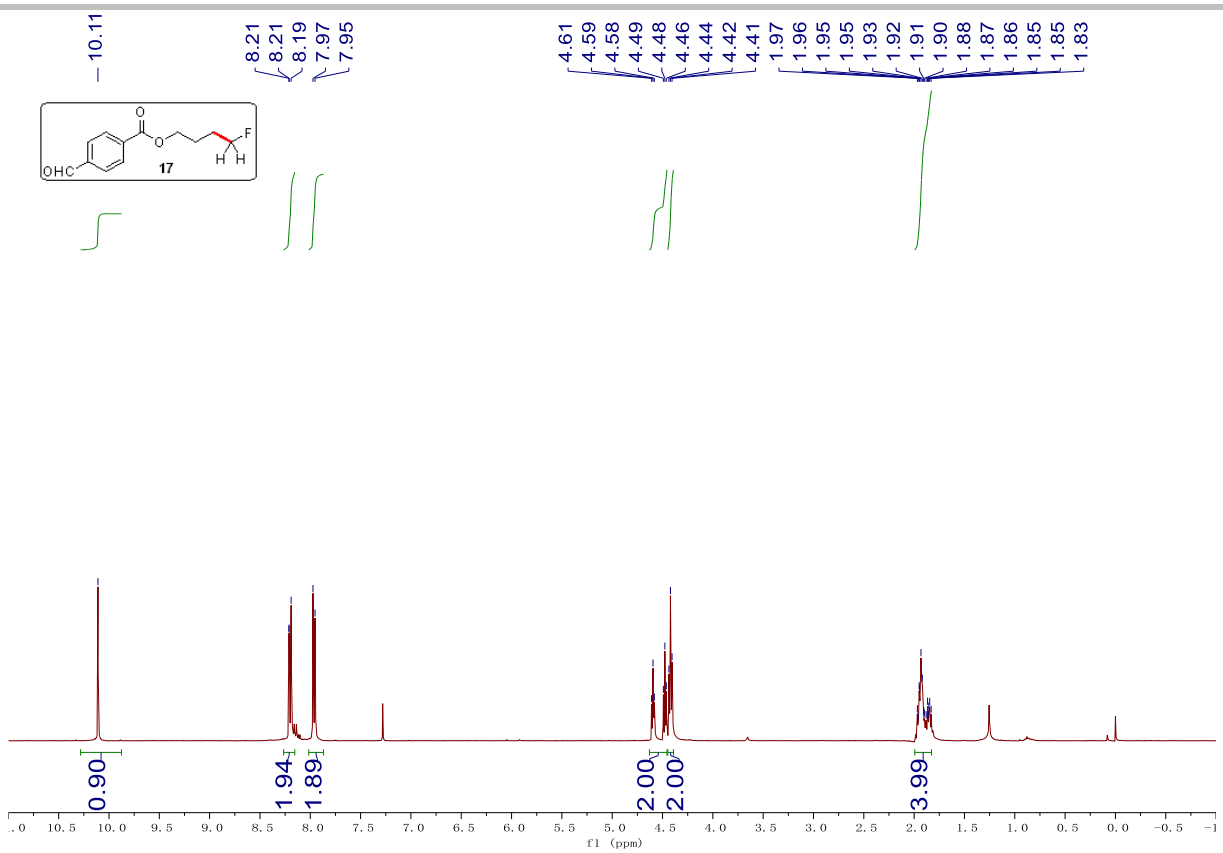
^{1}H NMR Spectrum of of **16** ($CDCl_3$, 400 MHz)



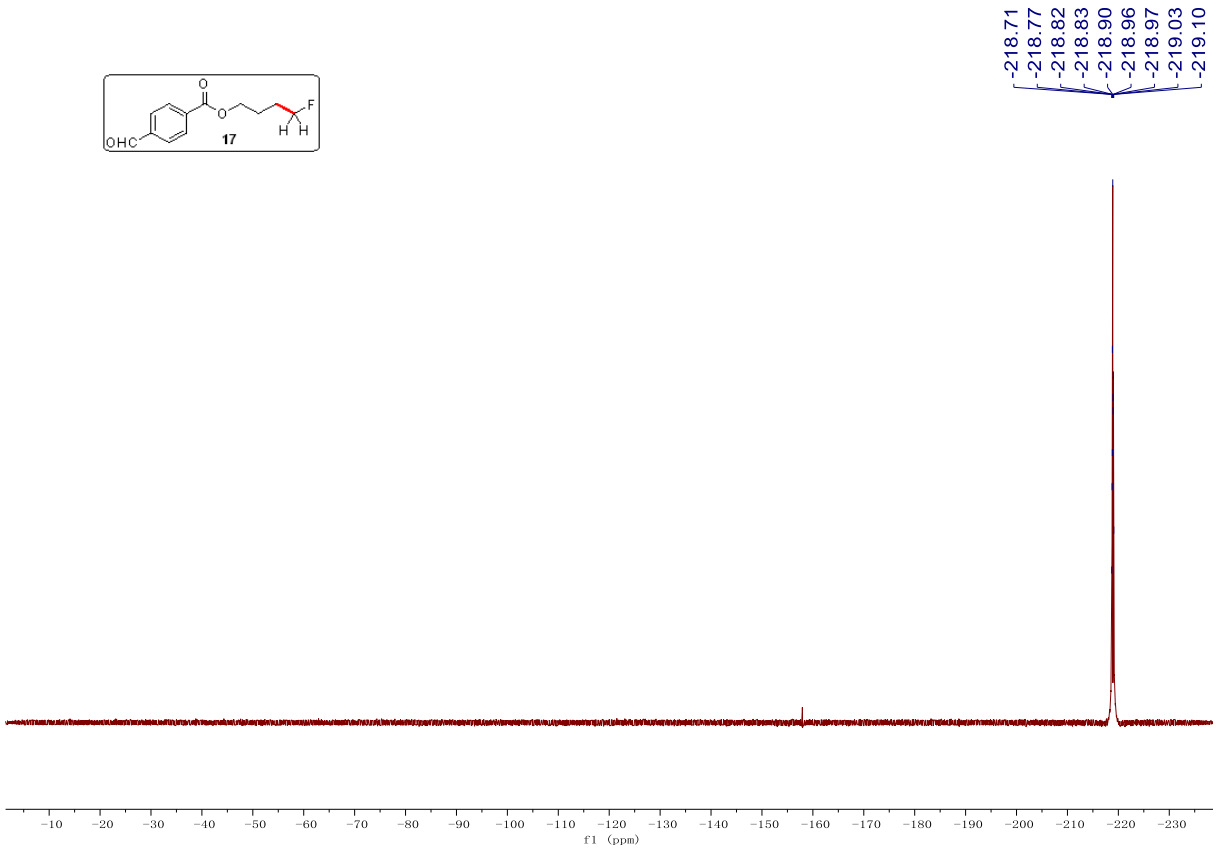
^{19}F NMR Spectrum of of **16** ($CDCl_3$, 376 MHz)



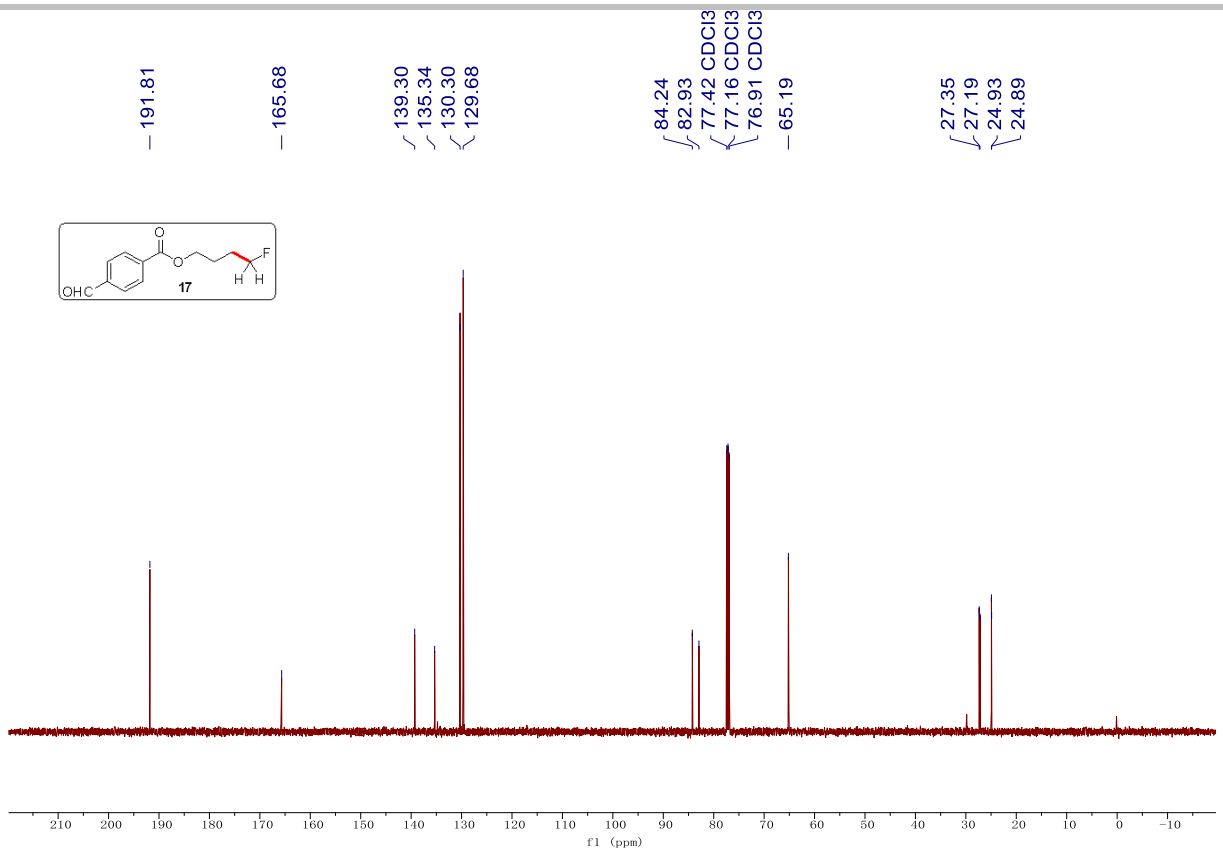
^{13}C NMR Spectrum of **16** ($CDCl_3$, 101 MHz)



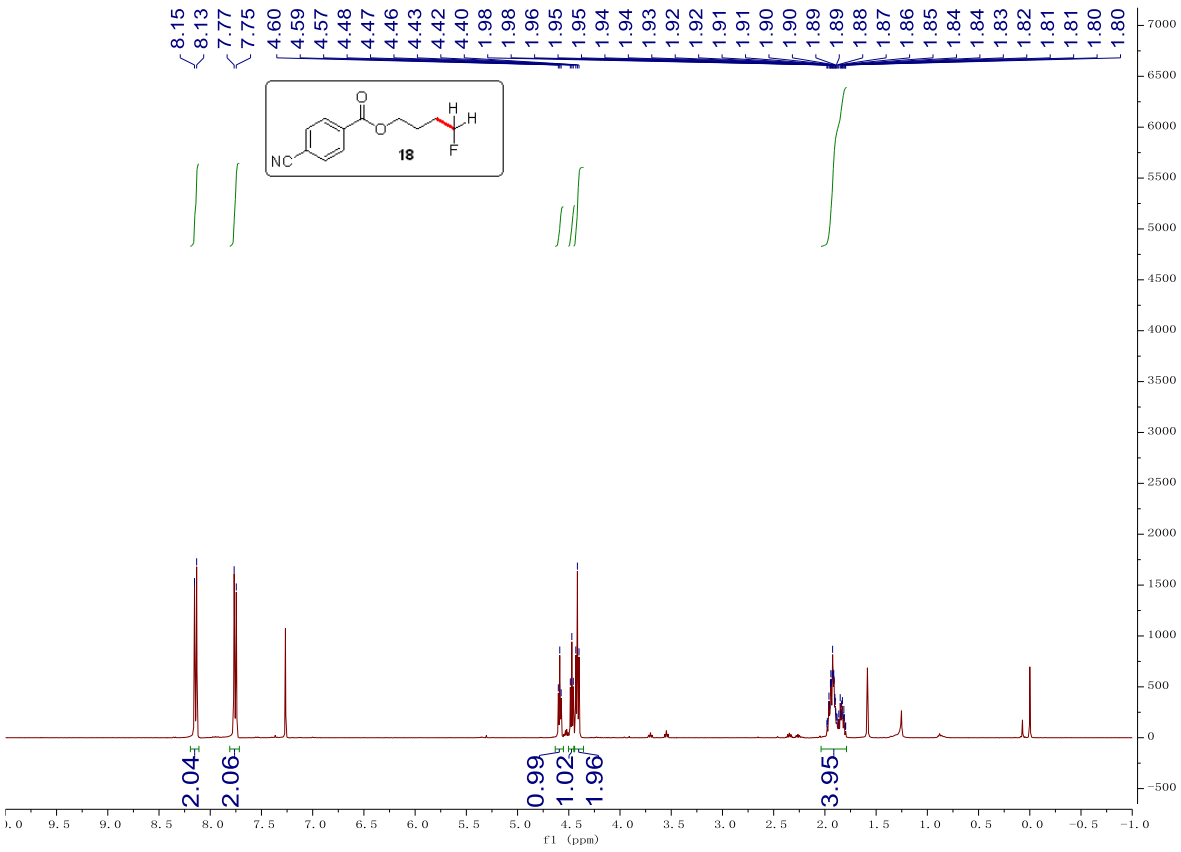
^{1}H NMR Spectrum of of **17** ($CDCl_3$, 400 MHz)



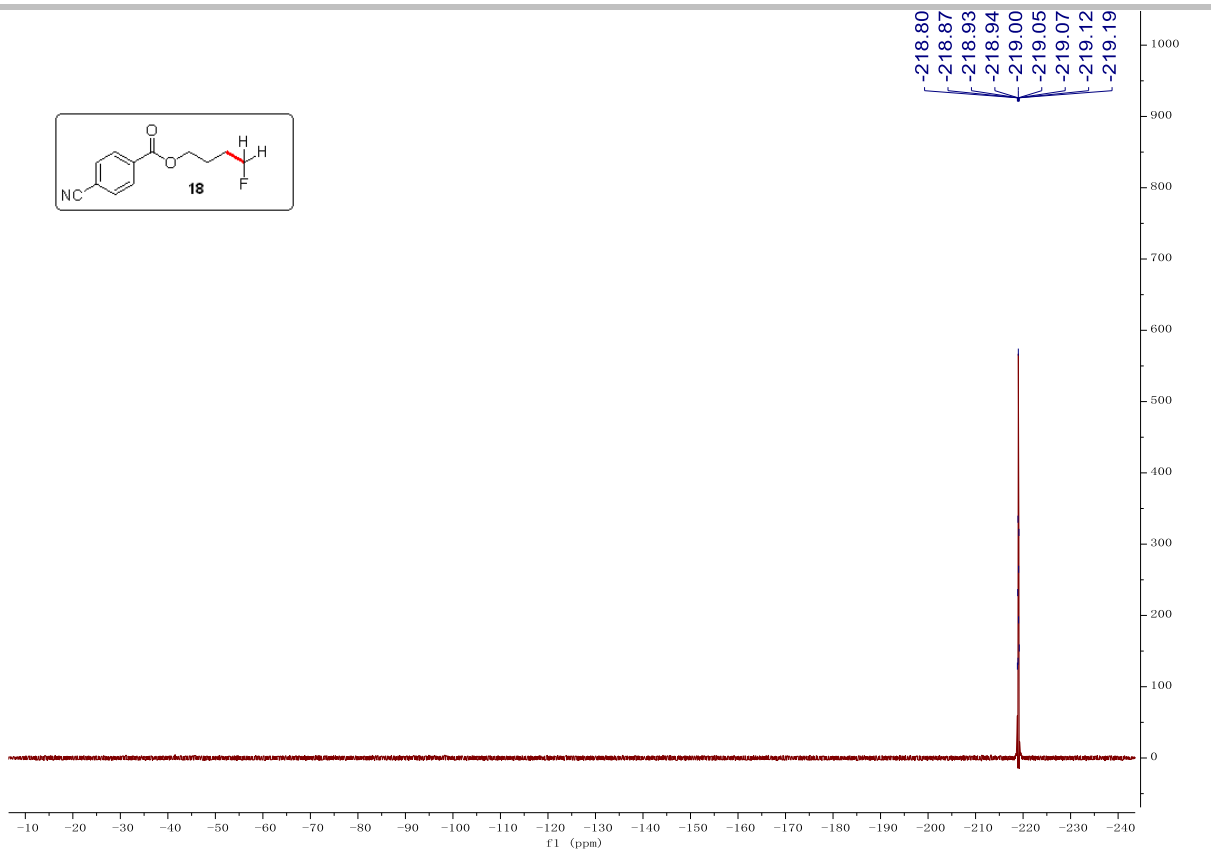
^{19}F NMR Spectrum of of **17** ($CDCl_3$, 376 MHz)



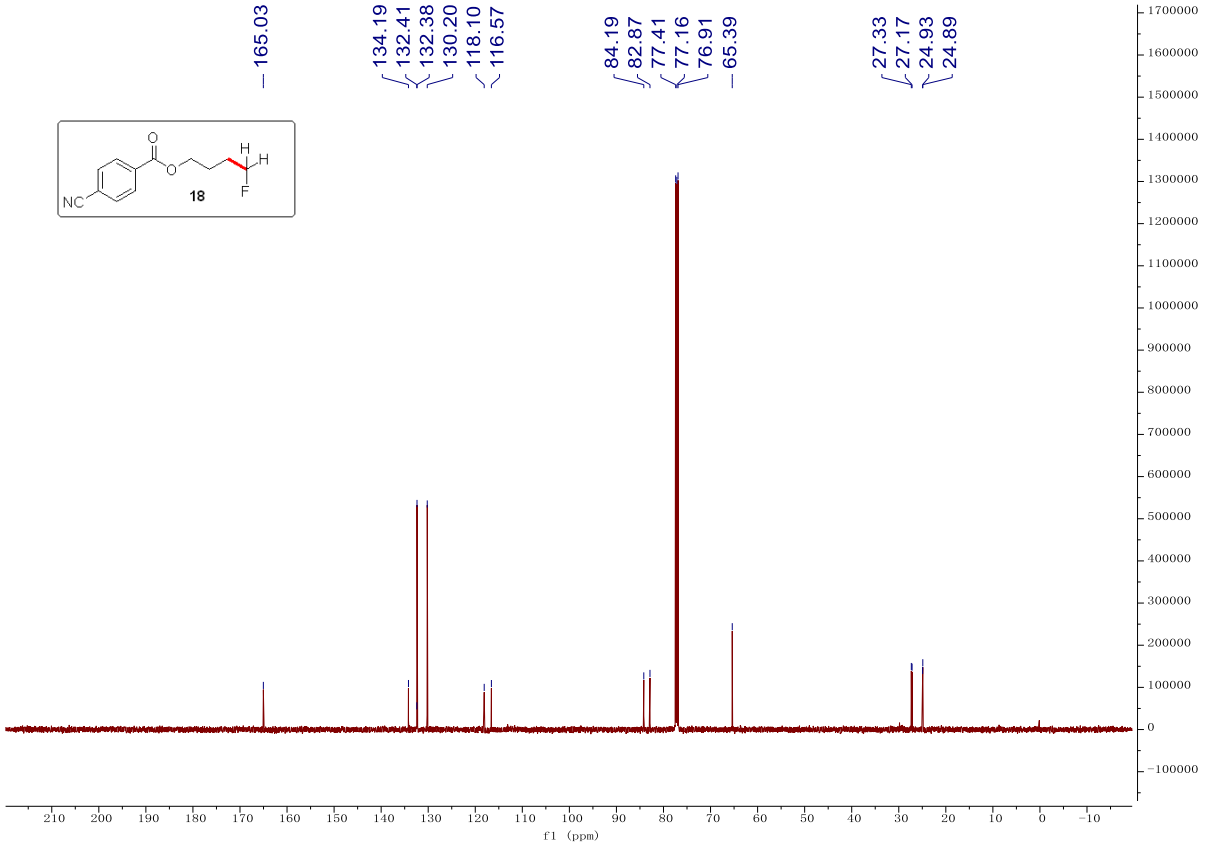
^{13}C NMR Spectrum of **17** ($CDCl_3$, 126 MHz)



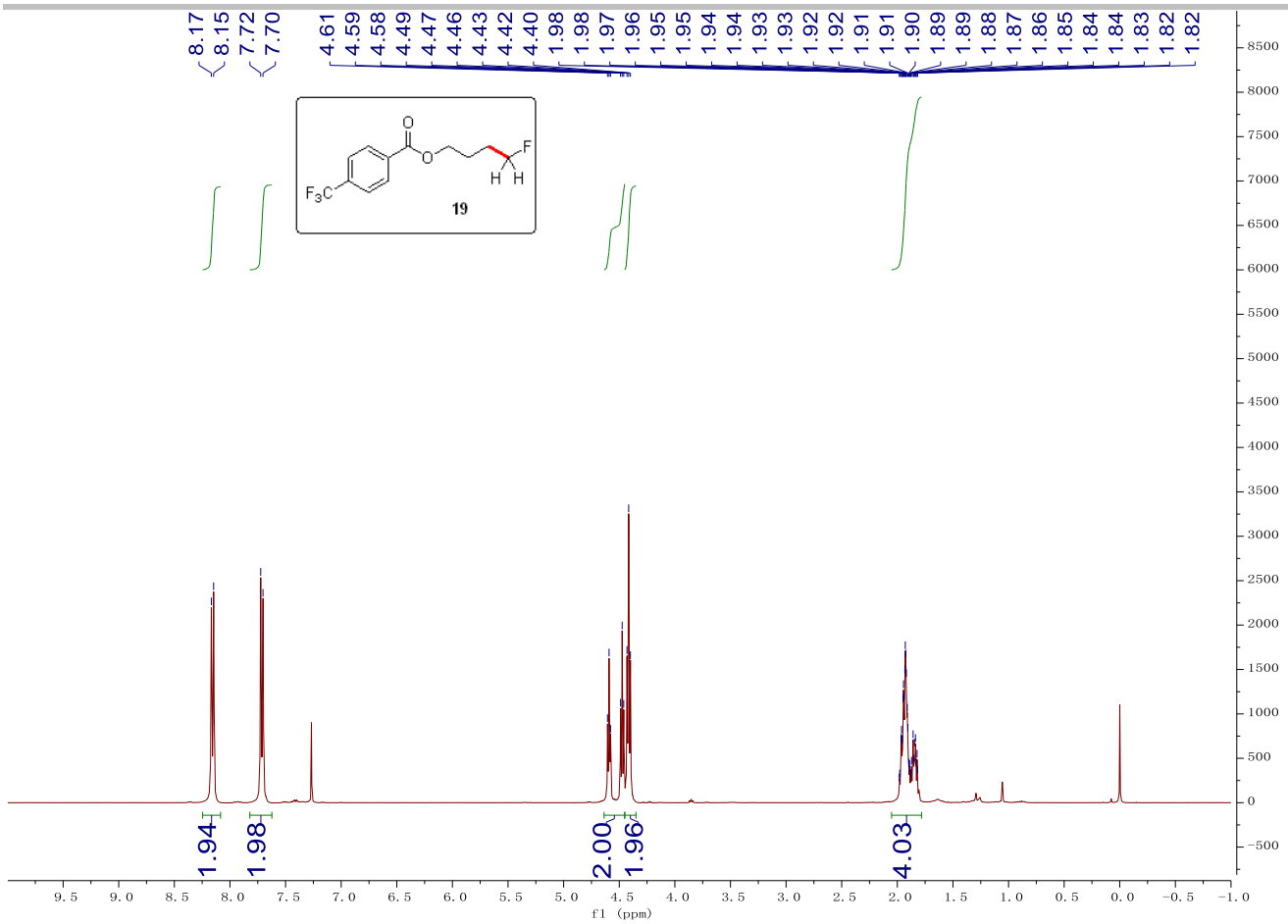
^{1}H NMR Spectrum of of **18** ($CDCl_3$, 400 MHz)



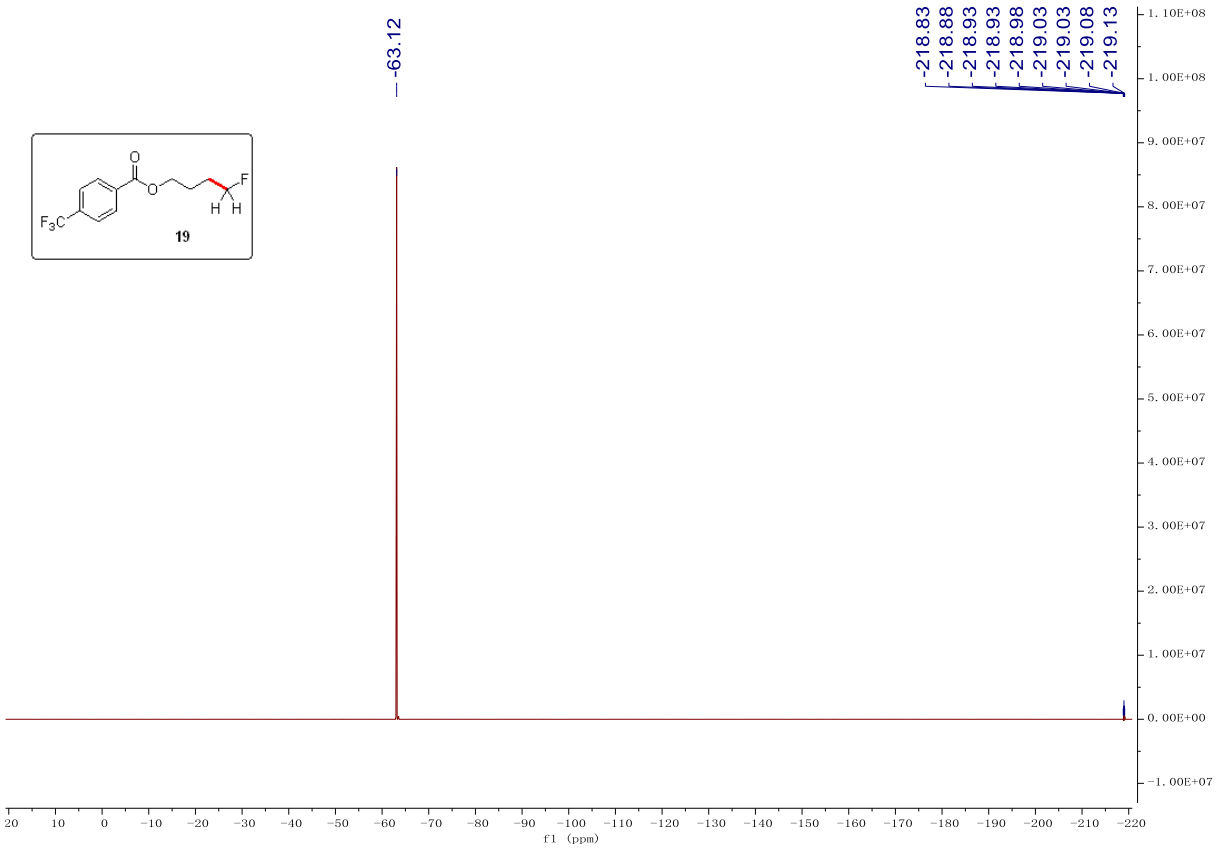
^{19}F NMR Spectrum of of **18** ($CDCl_3$, 376 MHz)



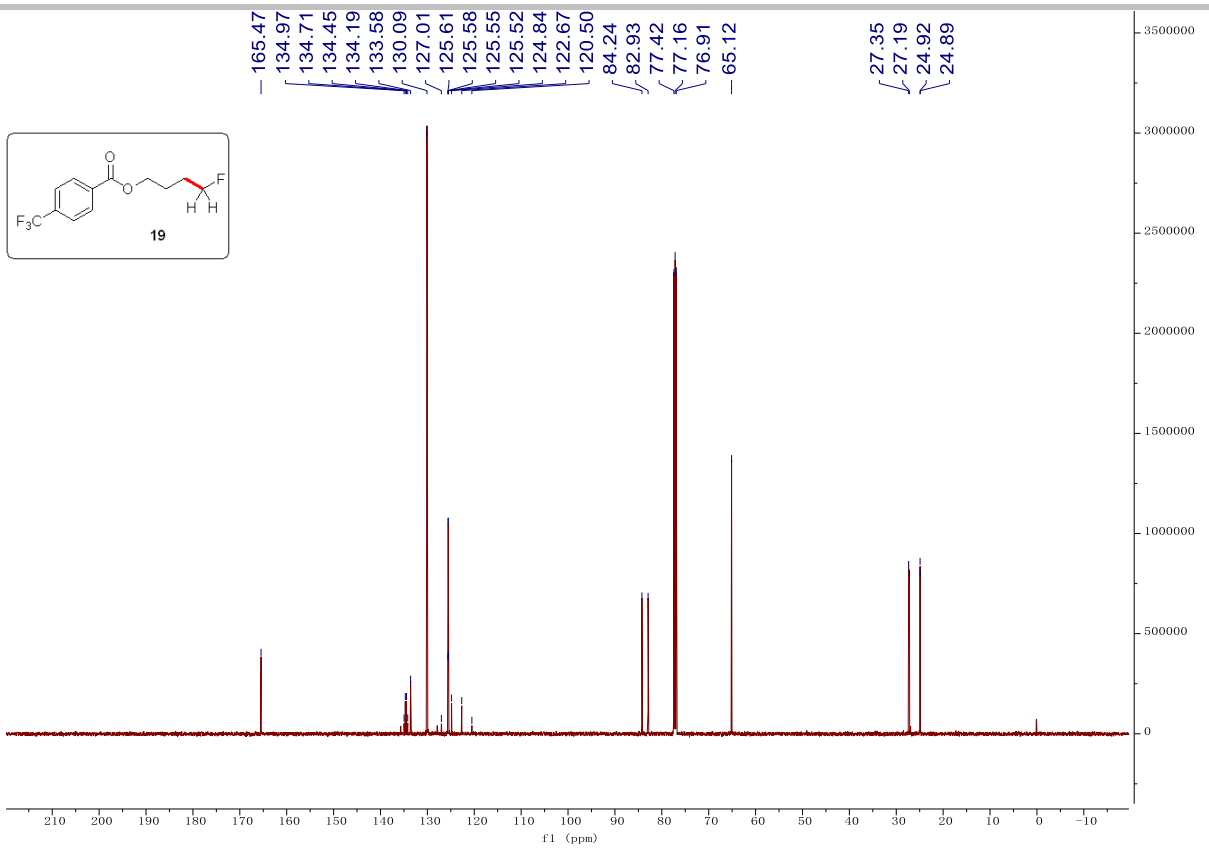
^{13}C NMR Spectrum of **18** ($CDCl_3$, 126 MHz)



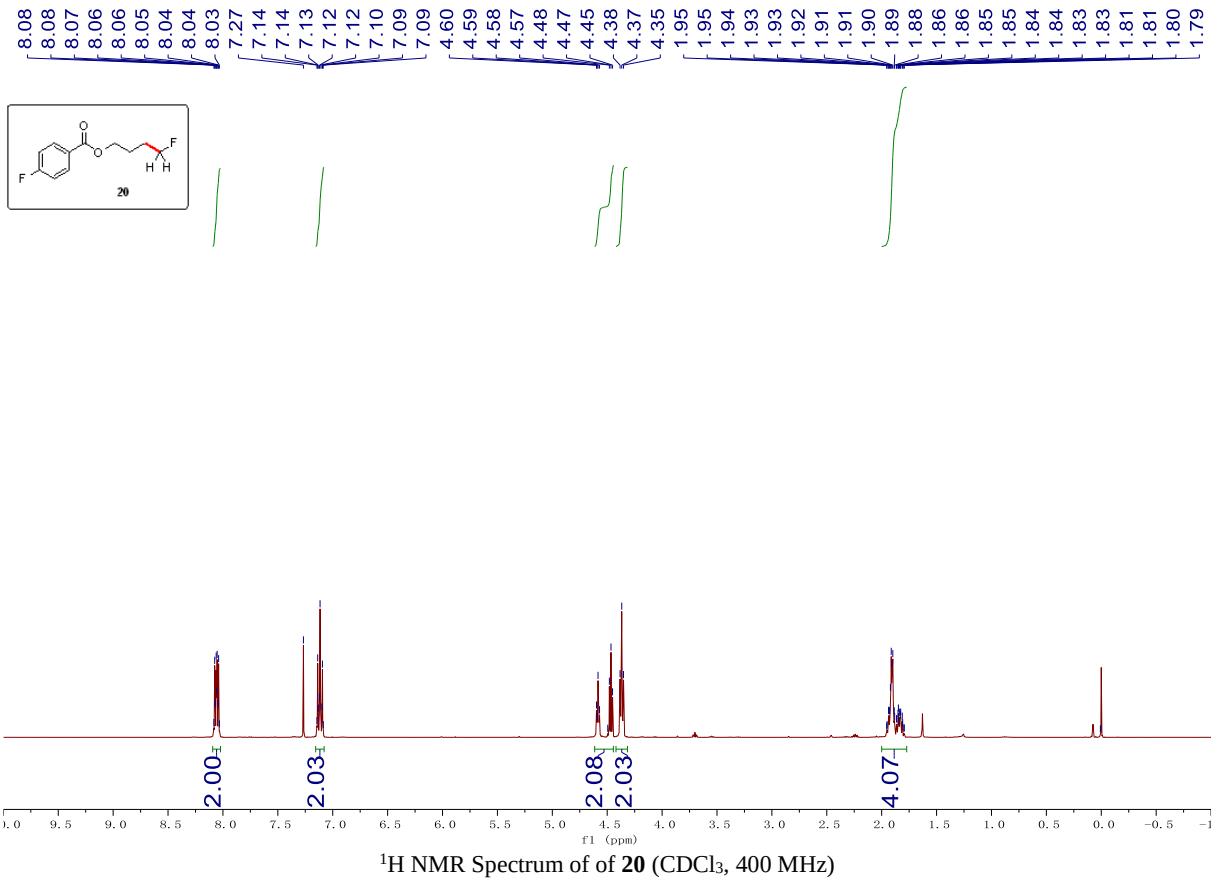
^{1}H NMR Spectrum of of **19** ($CDCl_3$, 400 MHz)



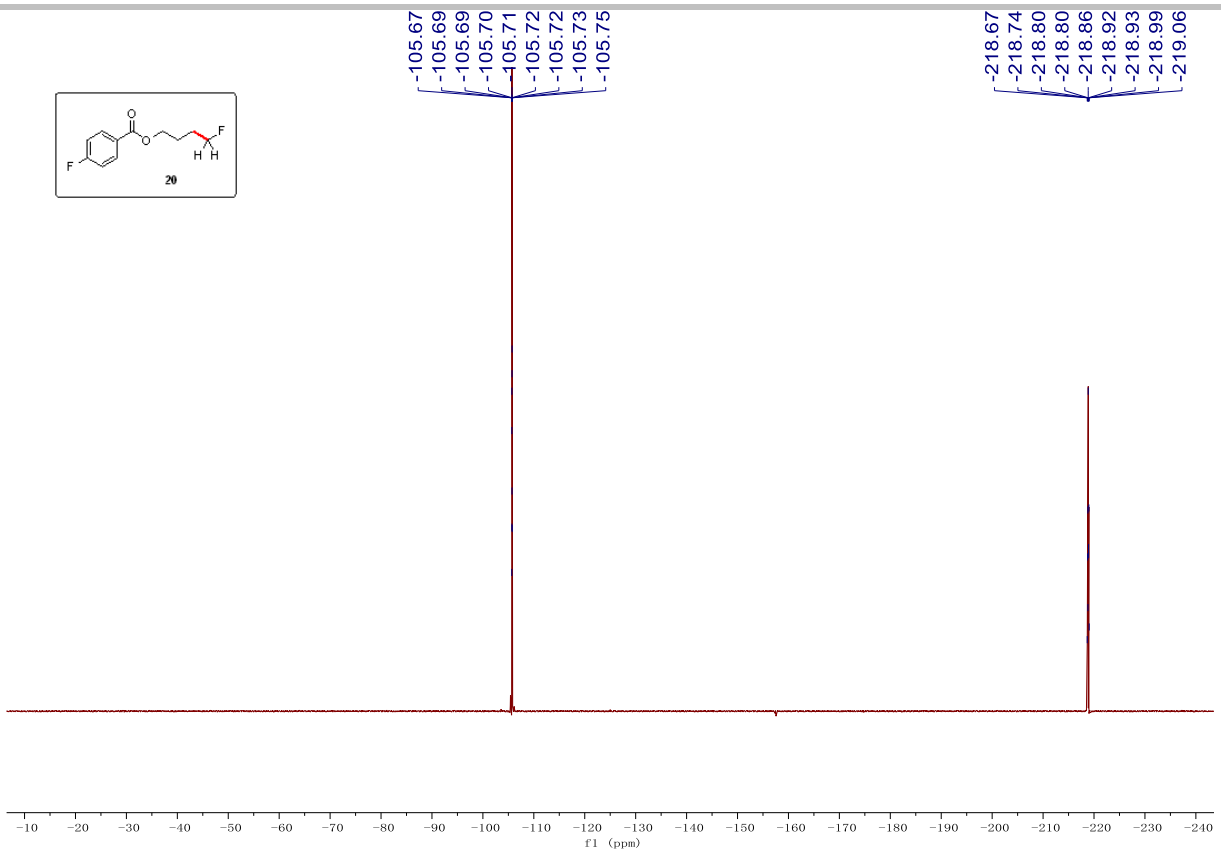
^{19}F NMR Spectrum of of **19** ($CDCl_3$, 376 MHz)



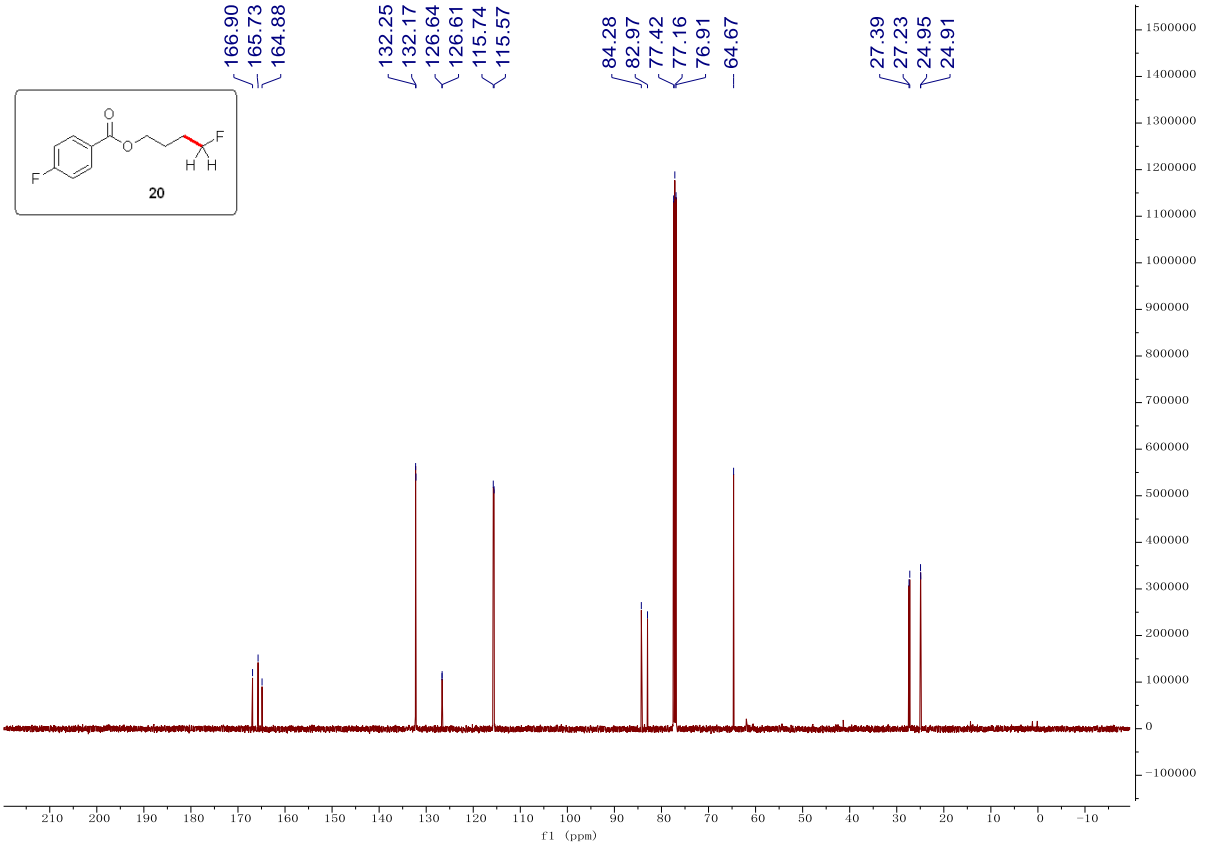
^{13}C NMR Spectrum of **19** ($CDCl_3$, 126 MHz)



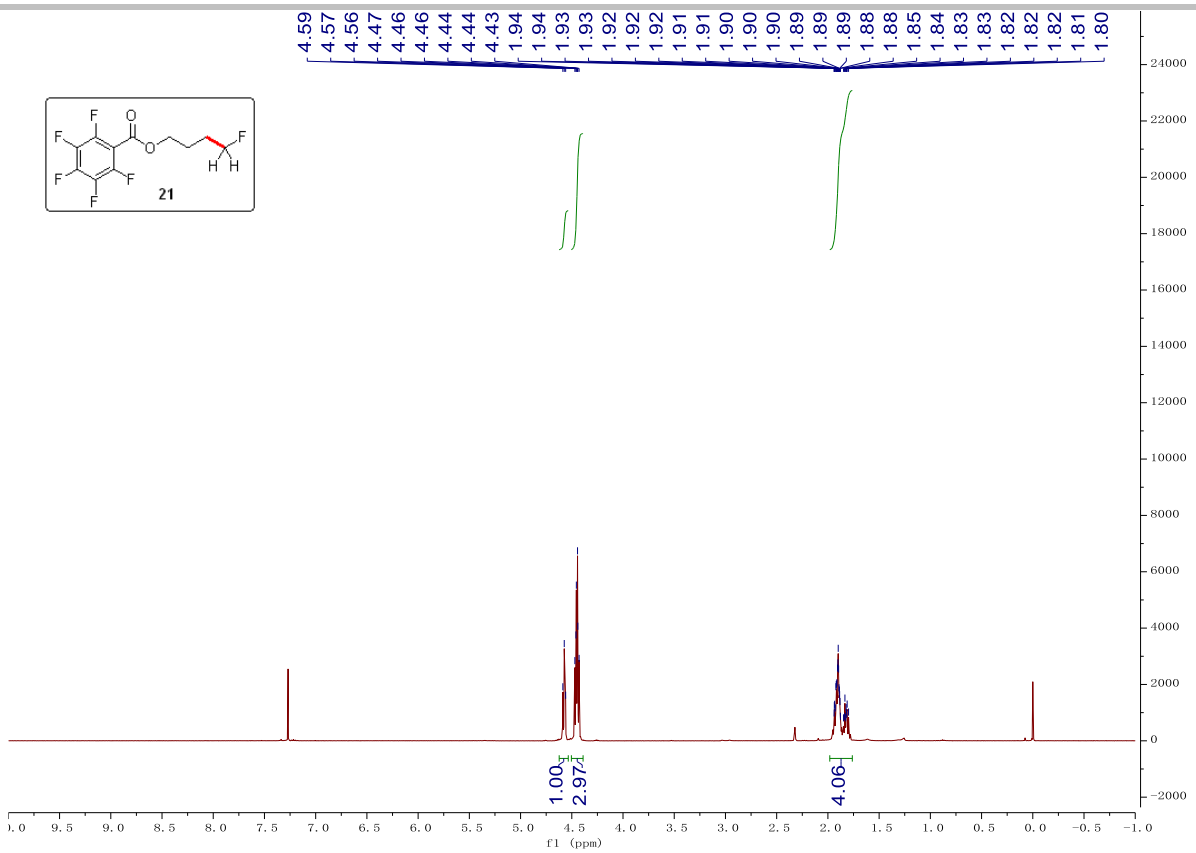
^{1}H NMR Spectrum of of **20** ($CDCl_3$, 400 MHz)



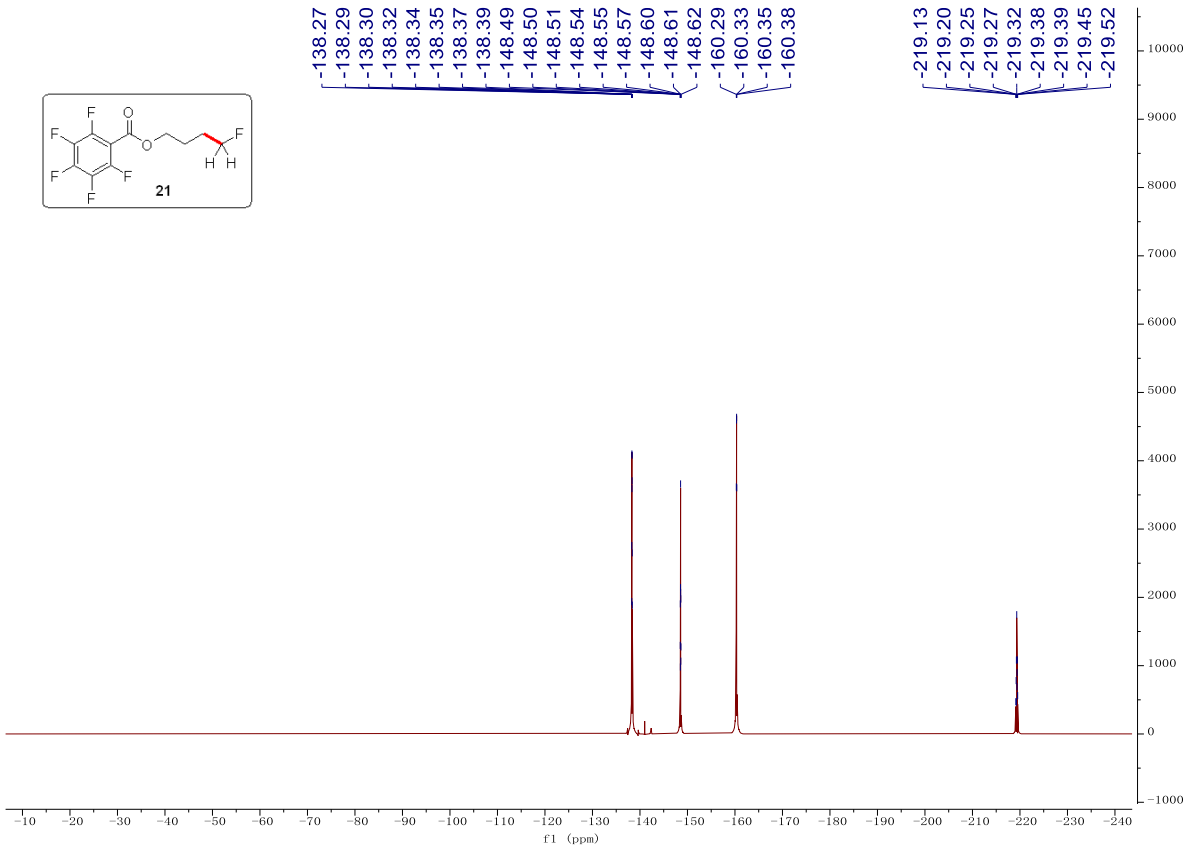
^{19}F NMR Spectrum of of **20** ($CDCl_3$, 376 MHz)



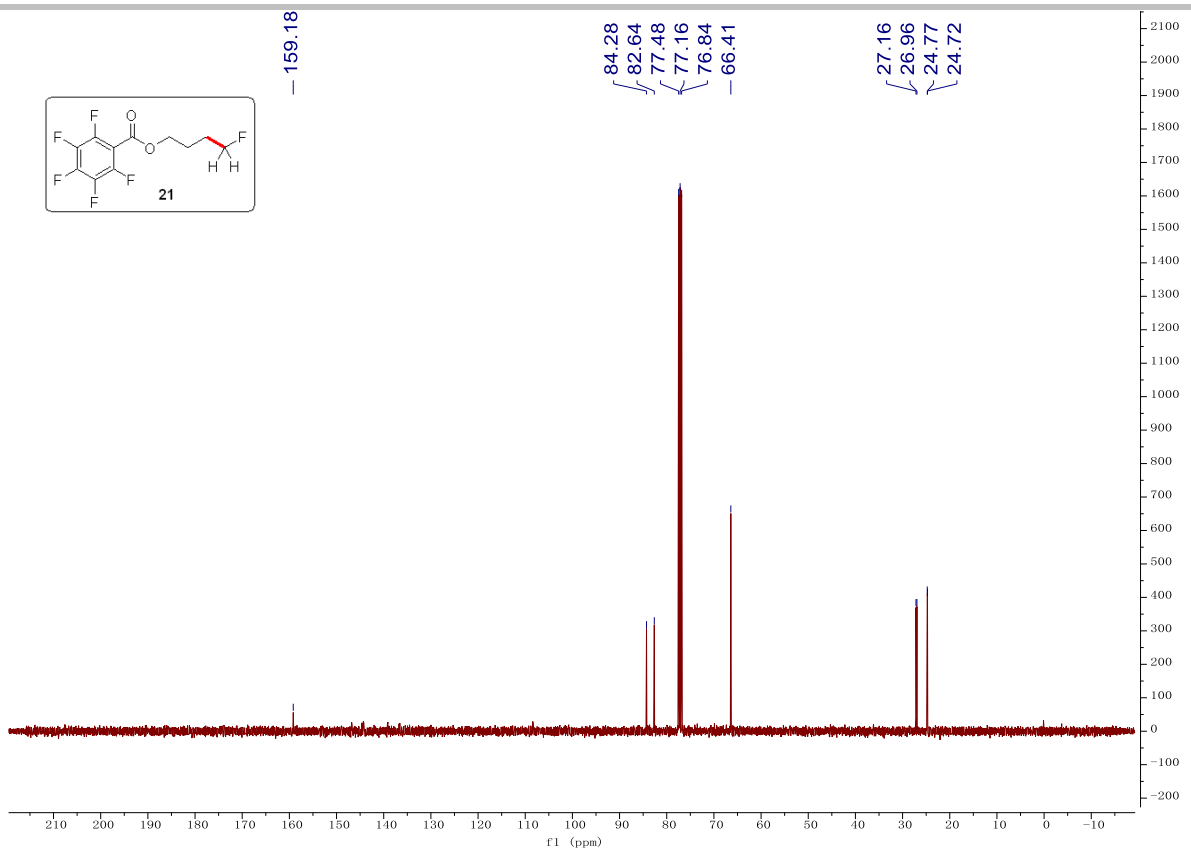
^{13}C NMR Spectrum of **20** ($CDCl_3$, 126 MHz)



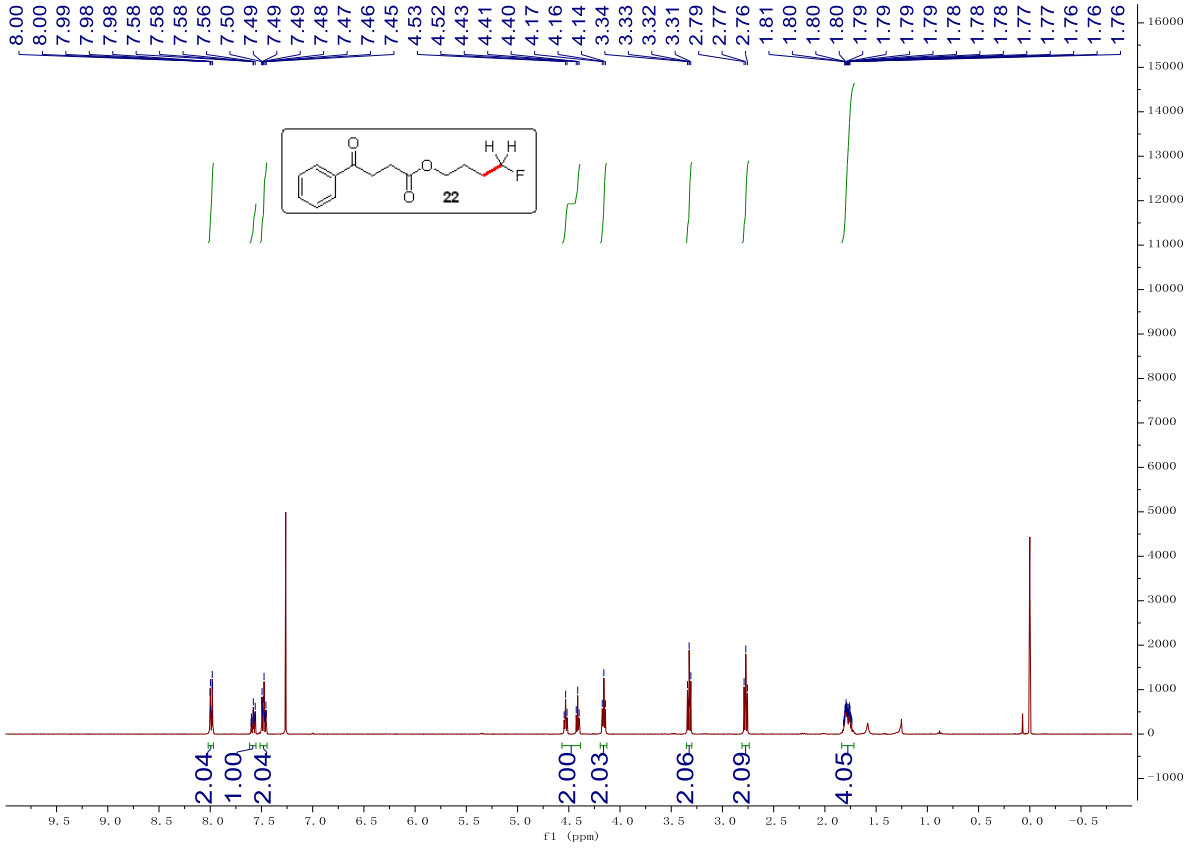
^{1}H NMR Spectrum of of **21** ($CDCl_3$, 400 MHz)



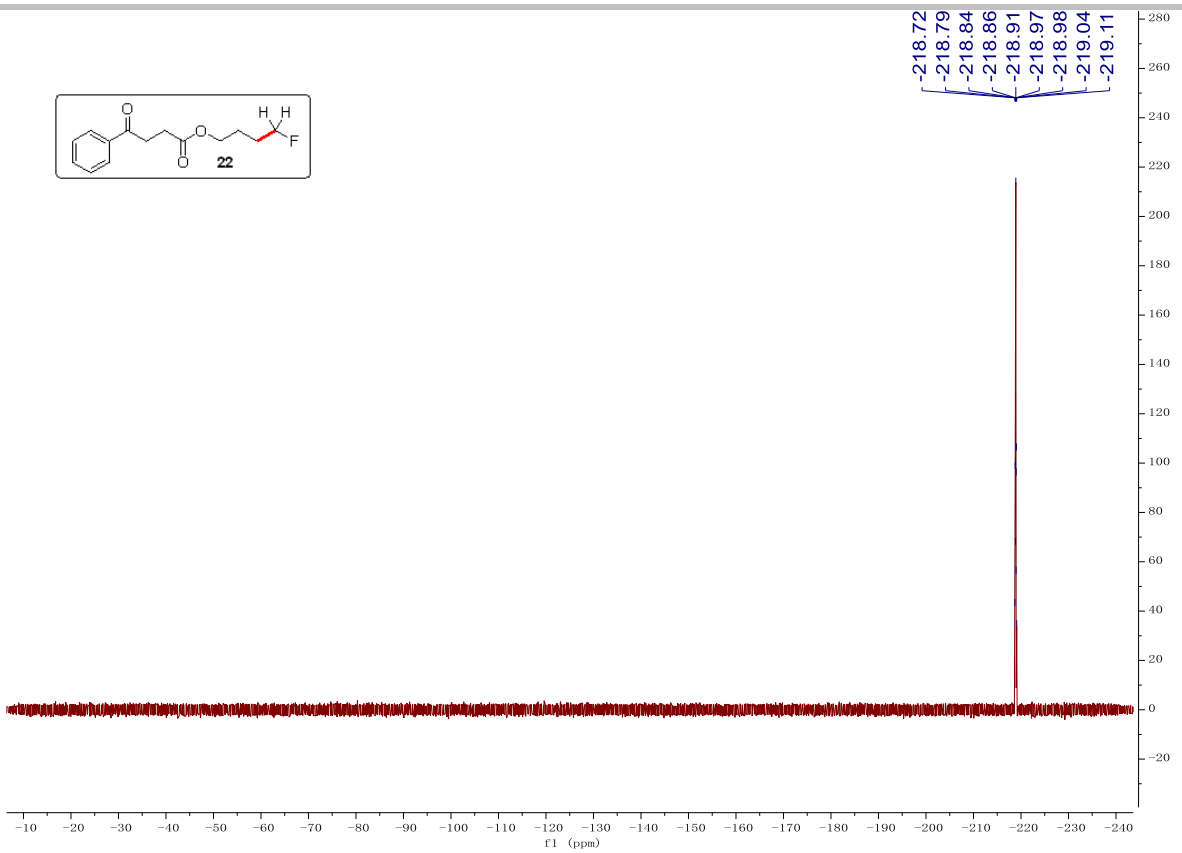
^{19}F NMR Spectrum of of **21** ($CDCl_3$, 376 MHz)



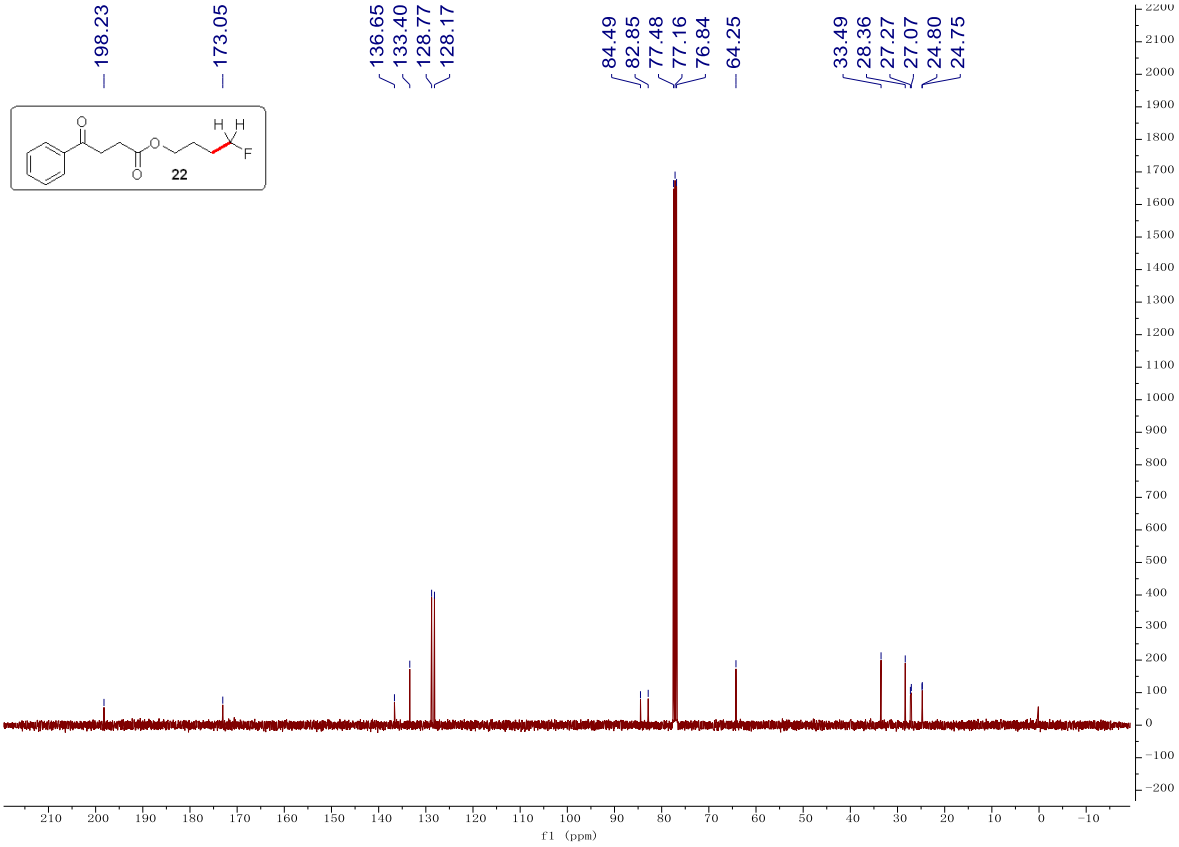
^{13}C NMR Spectrum of **21** ($CDCl_3$, 126 MHz)



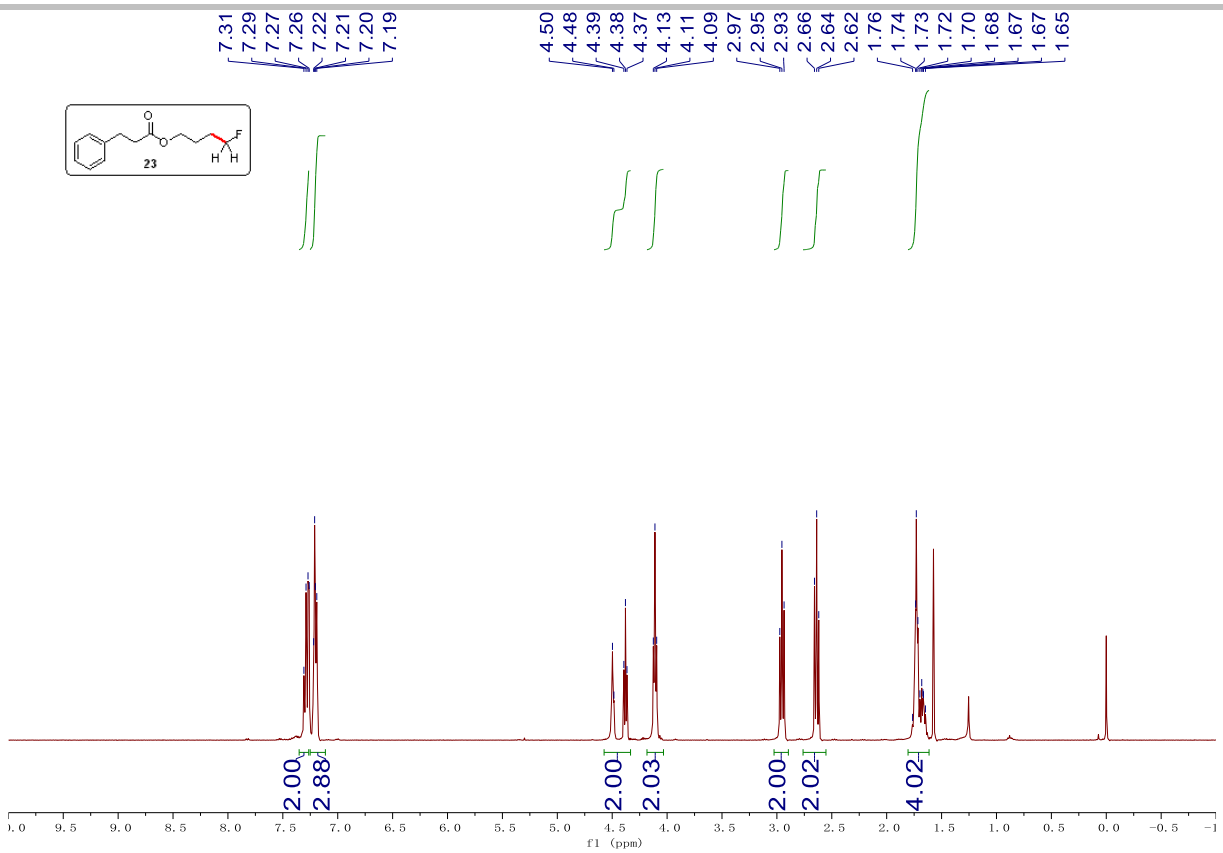
^{1}H NMR Spectrum of of **22** ($CDCl_3$, 400 MHz)



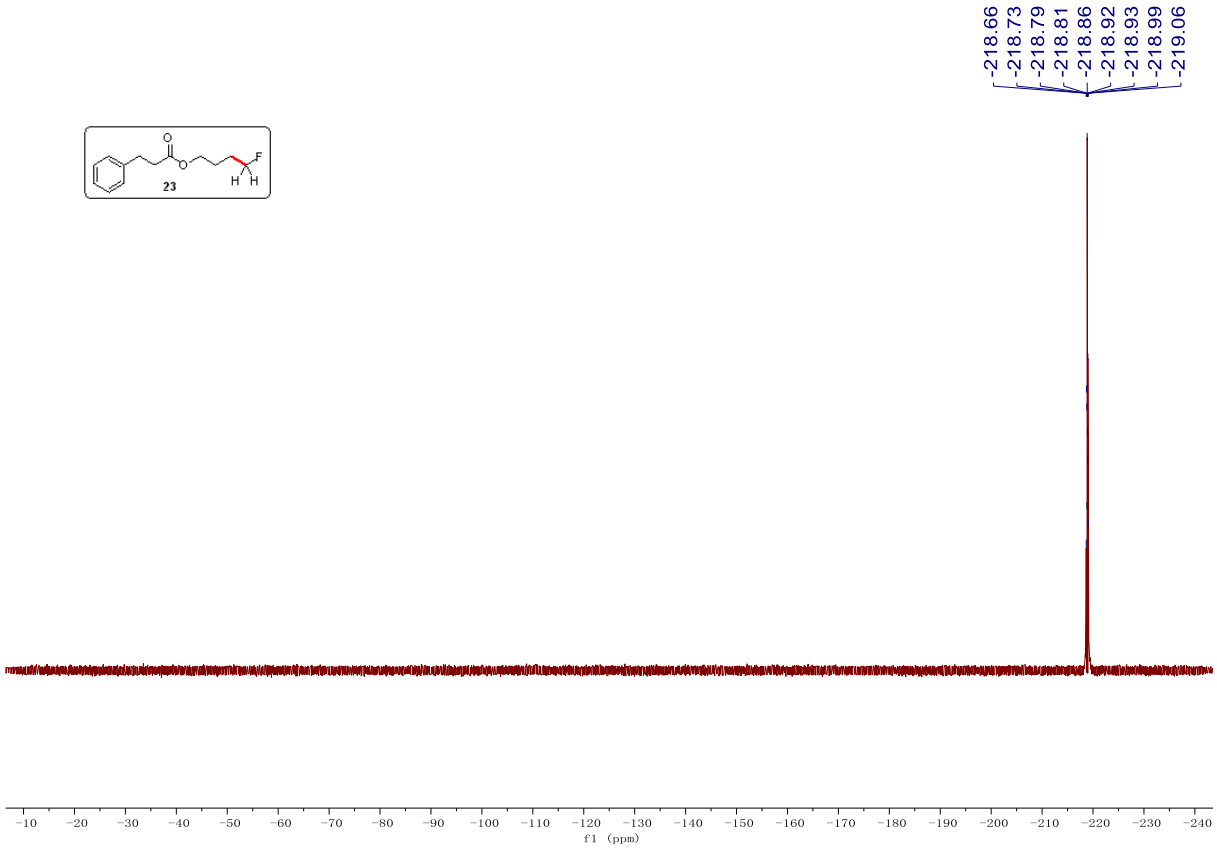
^{19}F NMR Spectrum of of **22** ($CDCl_3$, 376 MHz)



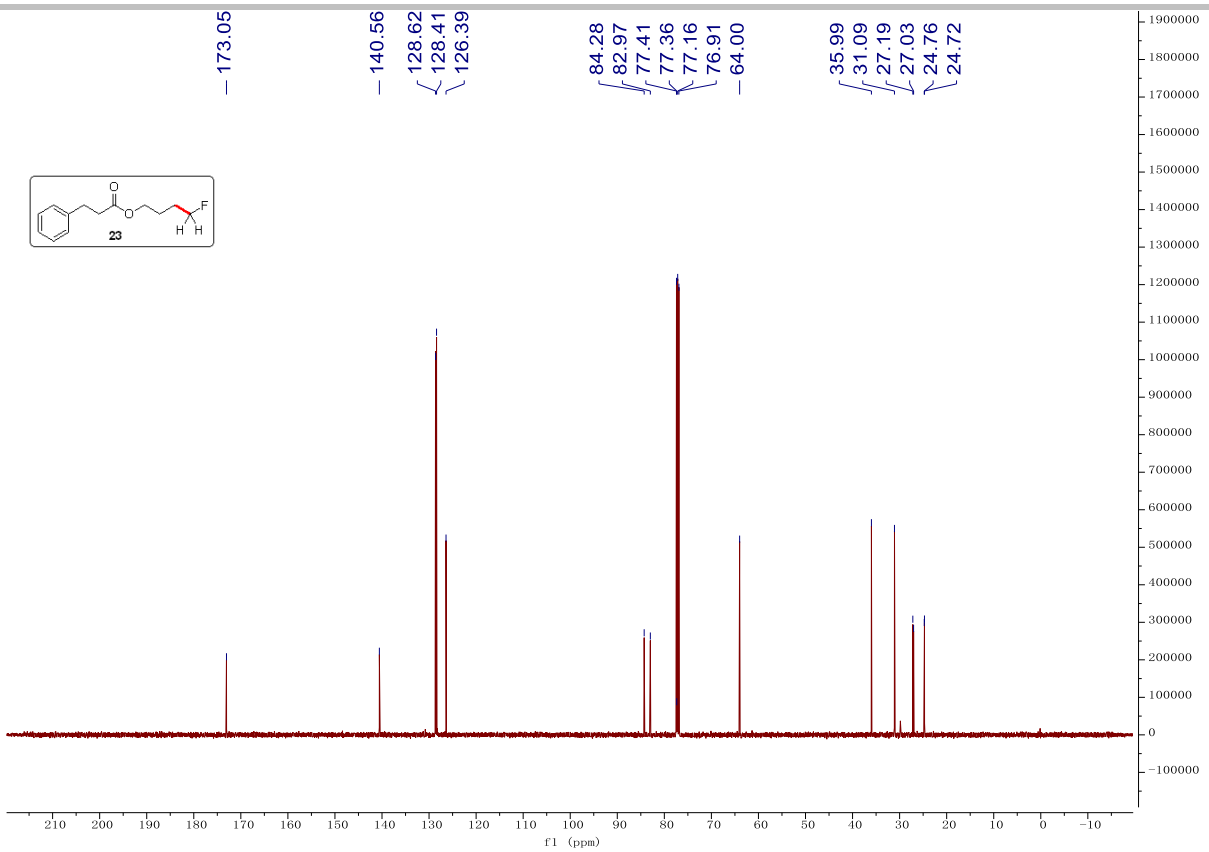
^{13}C NMR Spectrum of **22** ($CDCl_3$, 101 MHz)



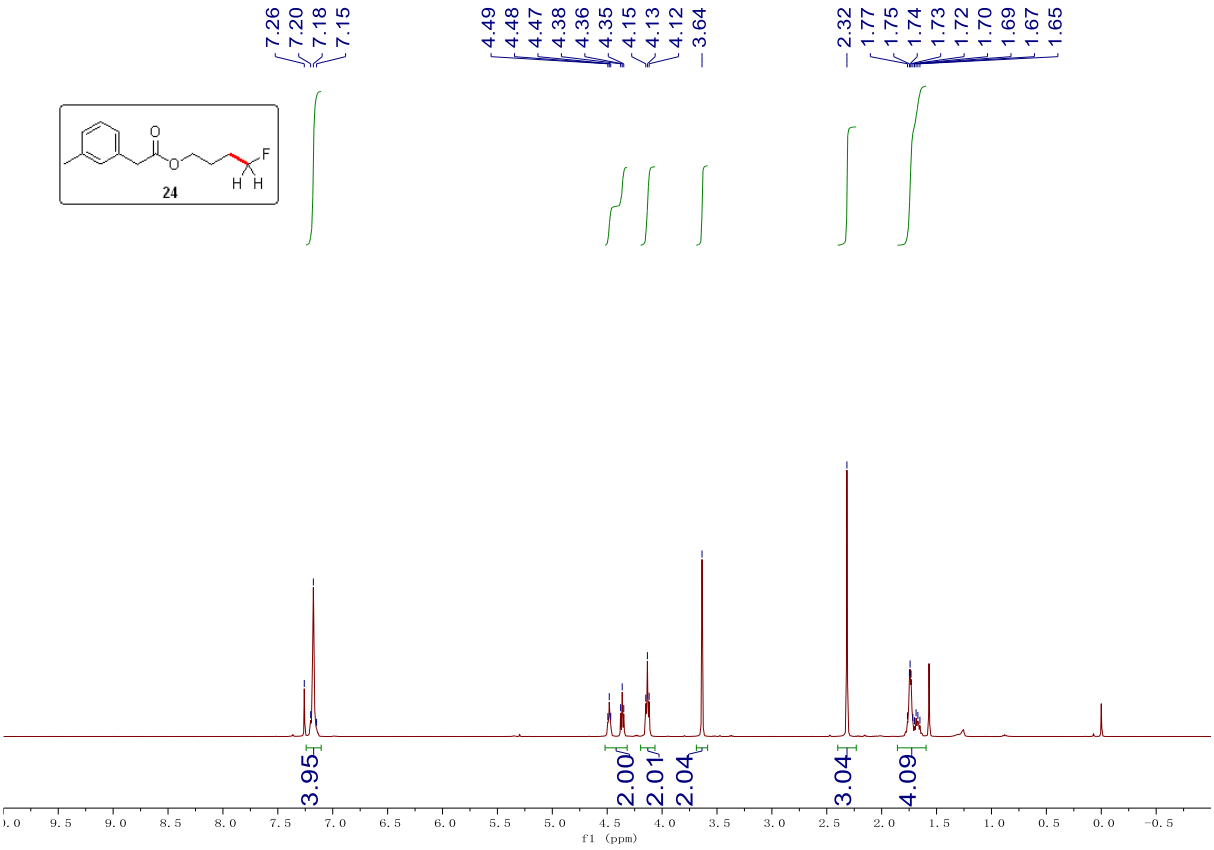
^{1}H NMR Spectrum of of **23** ($CDCl_3$, 400 MHz)



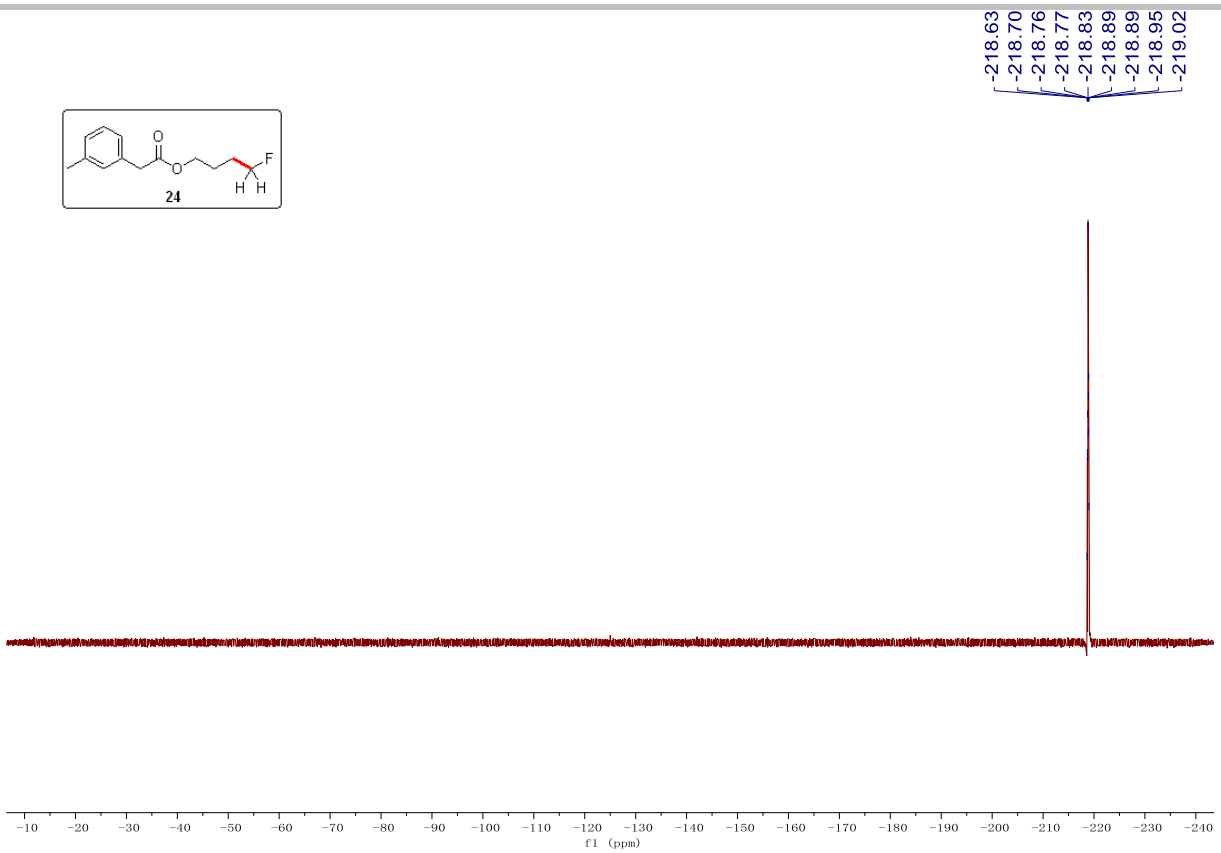
^{19}F NMR Spectrum of of **23** ($CDCl_3$, 376 MHz)



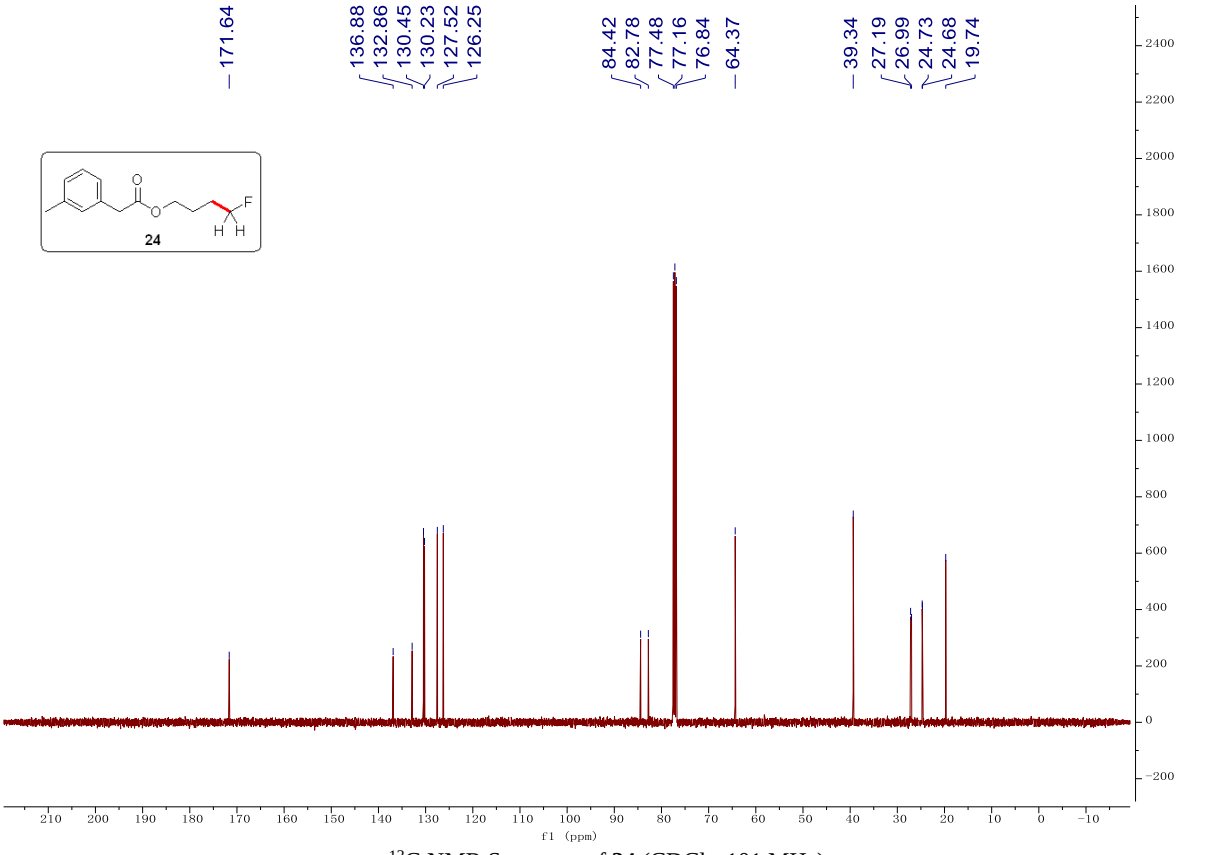
^{13}C NMR Spectrum of **23** ($CDCl_3$, 126 MHz)



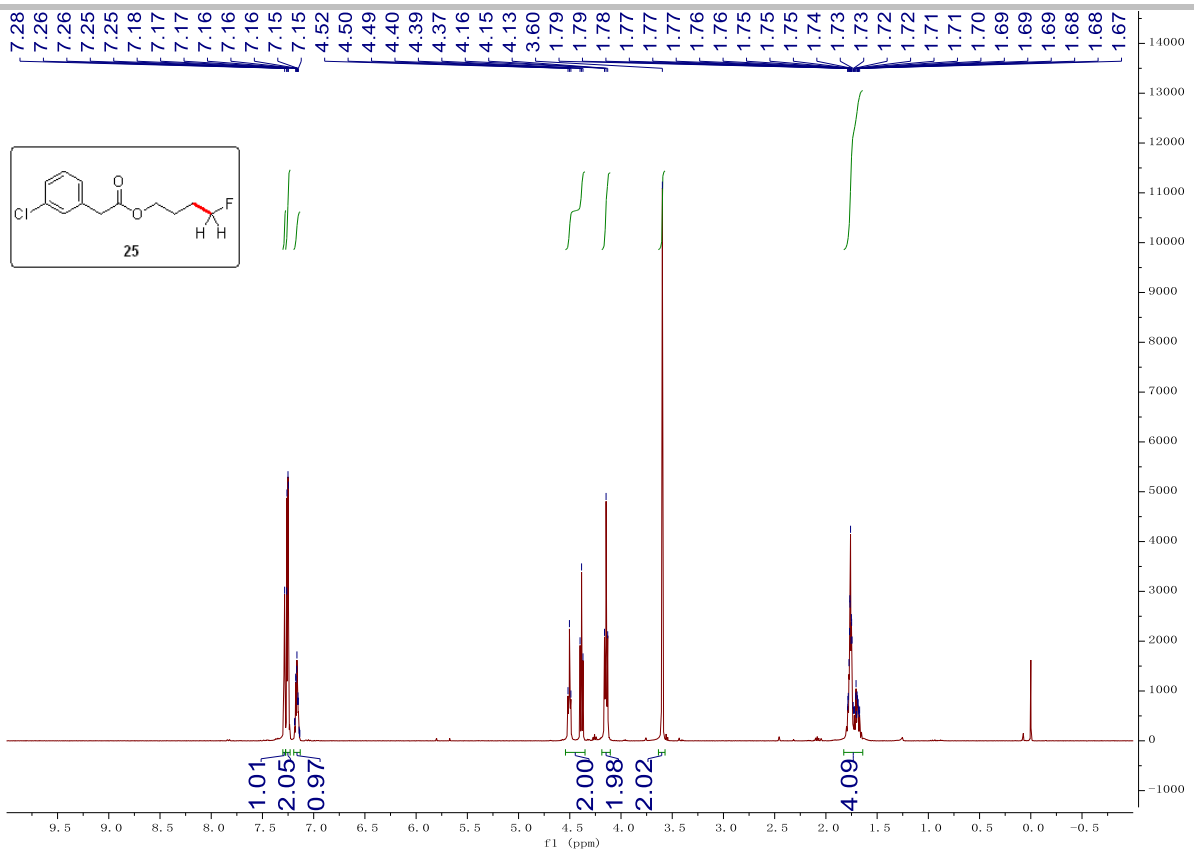
^{1}H NMR Spectrum of of **24** ($CDCl_3$, 400 MHz)



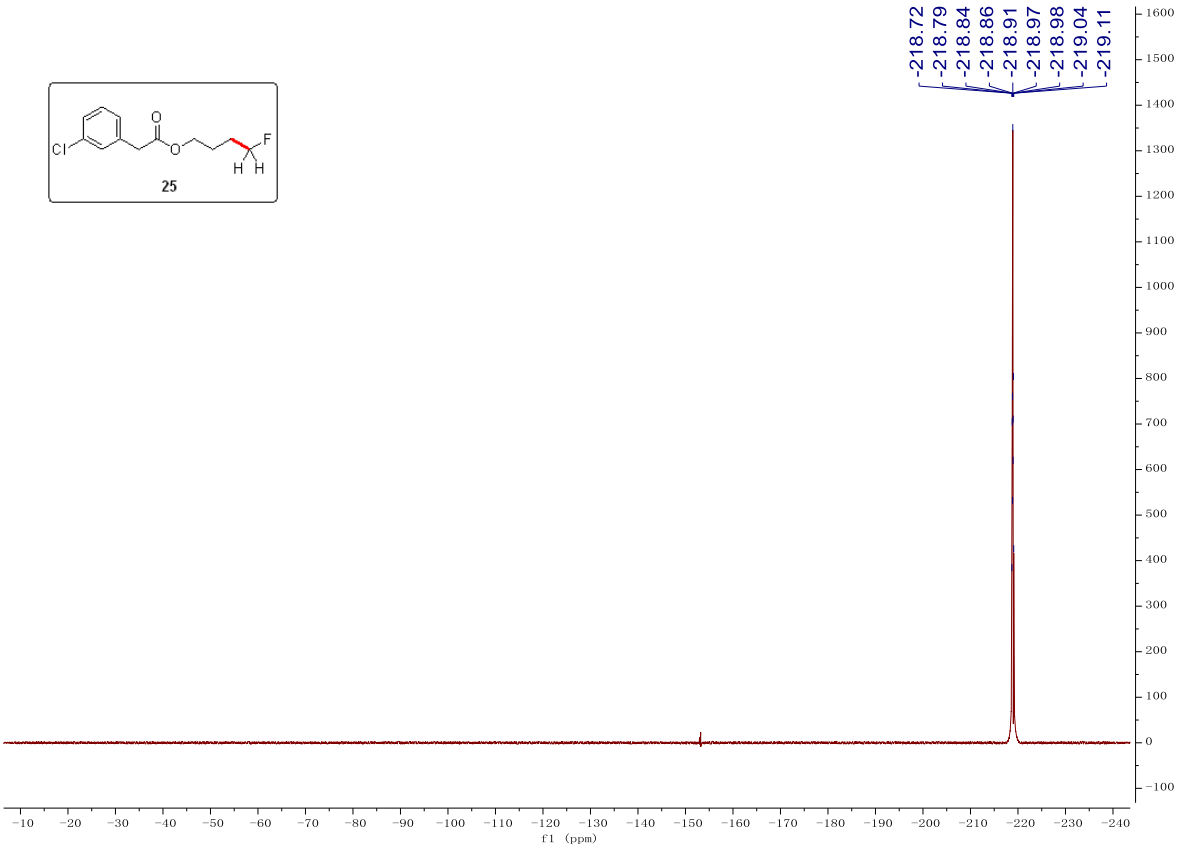
^{19}F NMR Spectrum of of **24** ($CDCl_3$, 376 MHz)



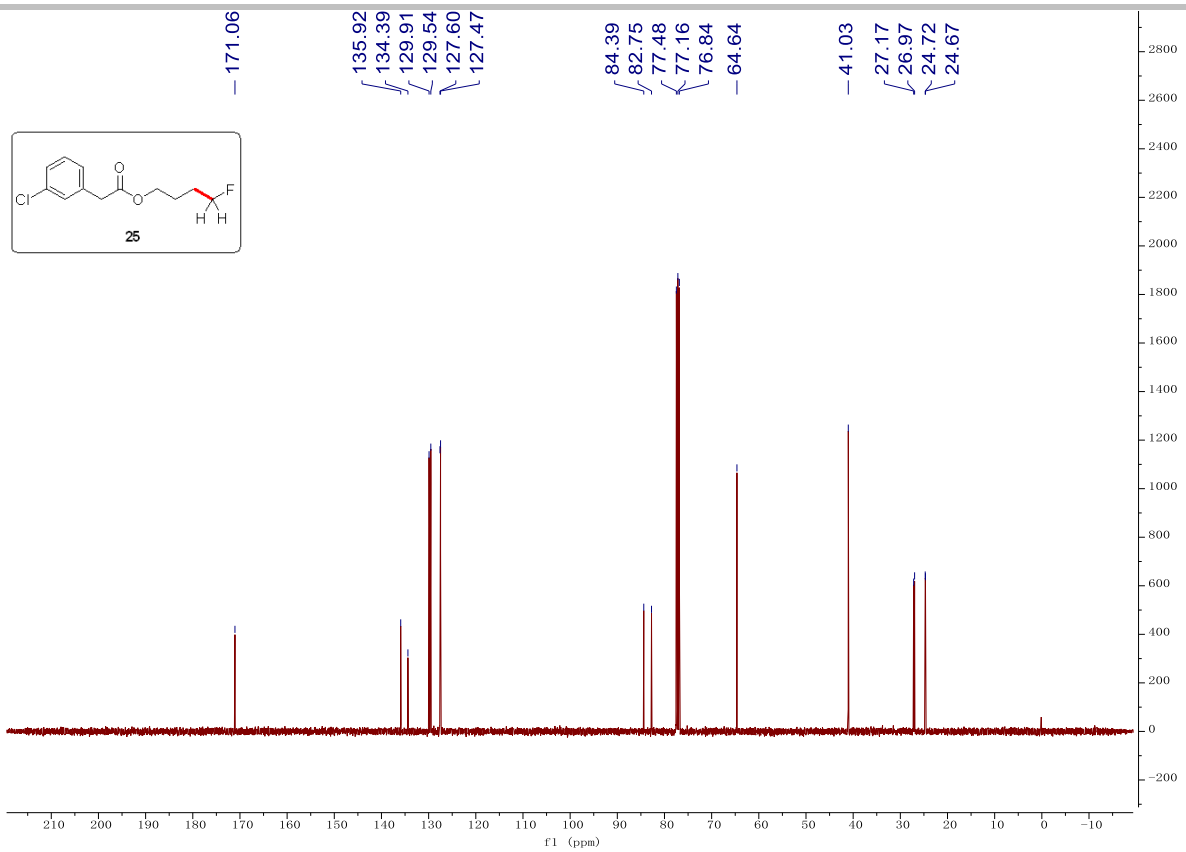
^{13}C NMR Spectrum of **24** ($CDCl_3$, 101 MHz)



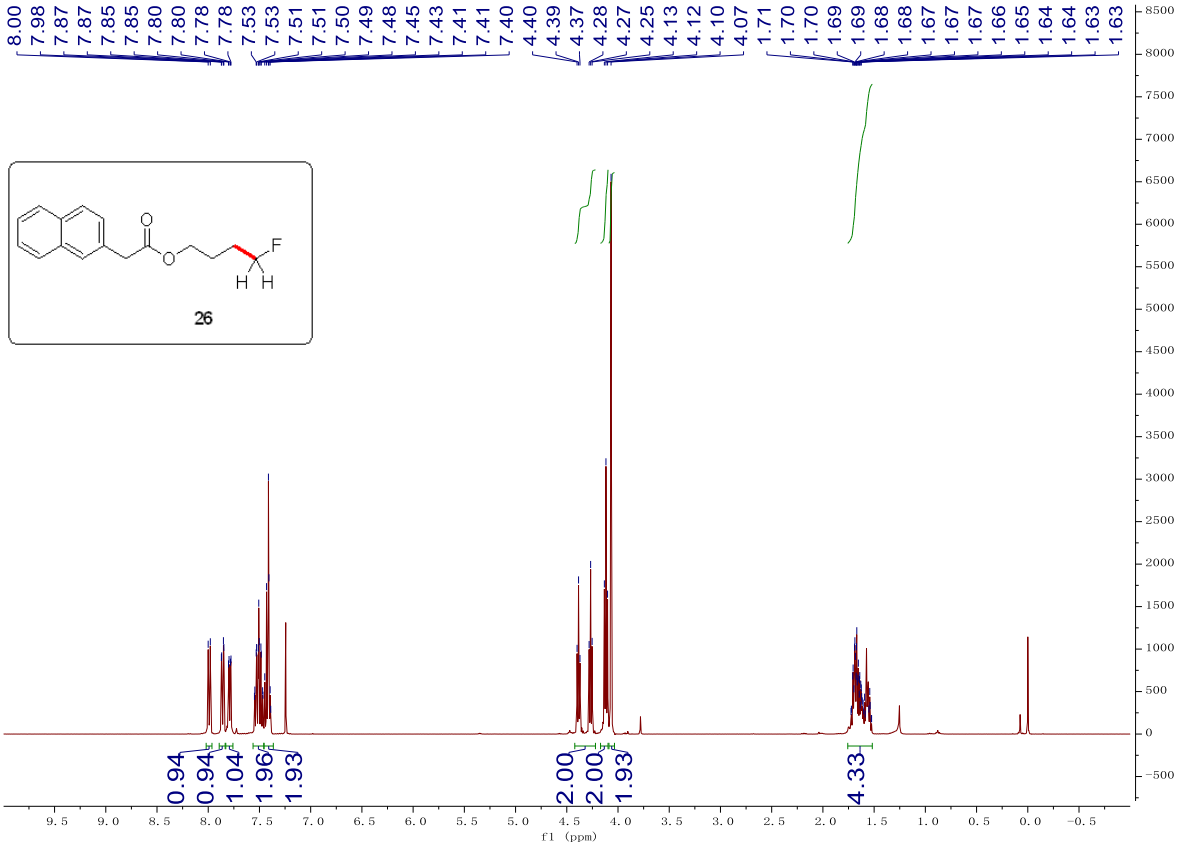
^{1}H NMR Spectrum of of **25** ($CDCl_3$, 400 MHz)



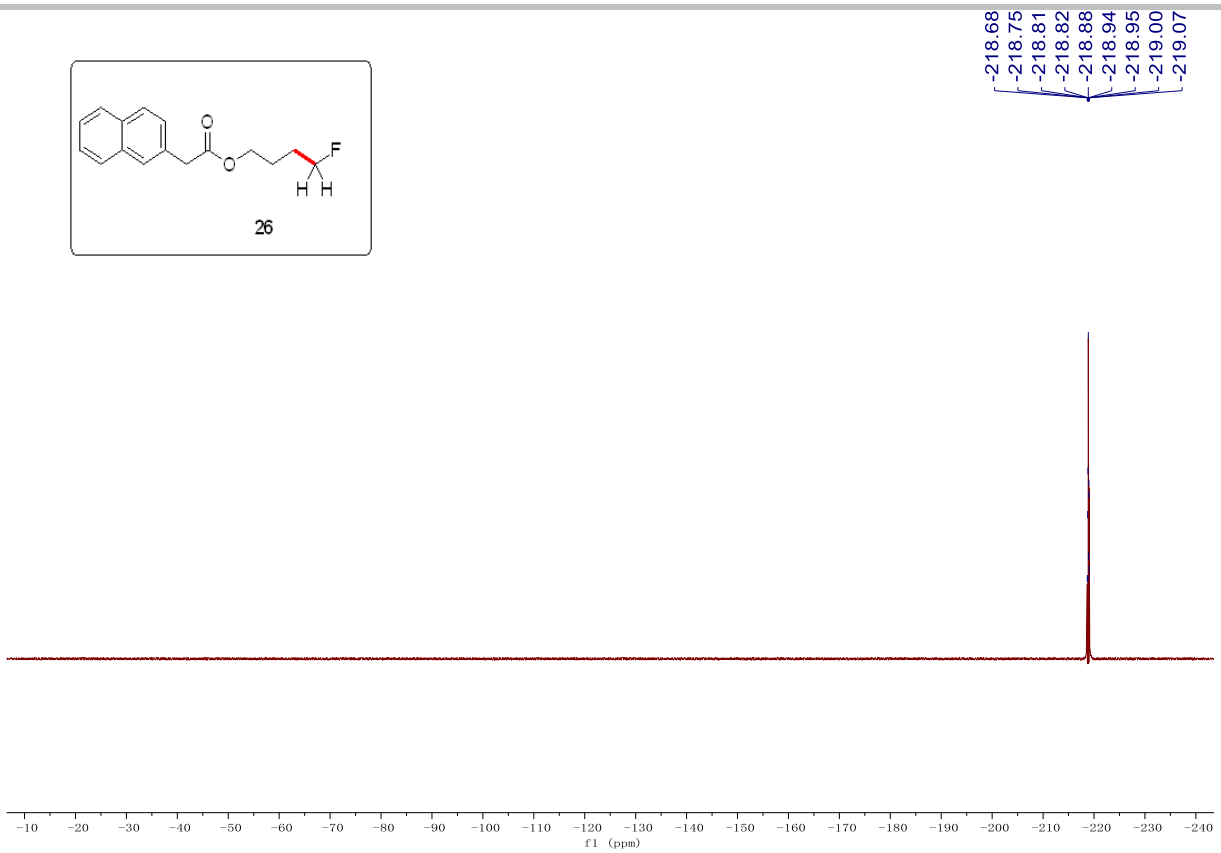
^{19}F NMR Spectrum of of **25** ($CDCl_3$, 376 MHz)



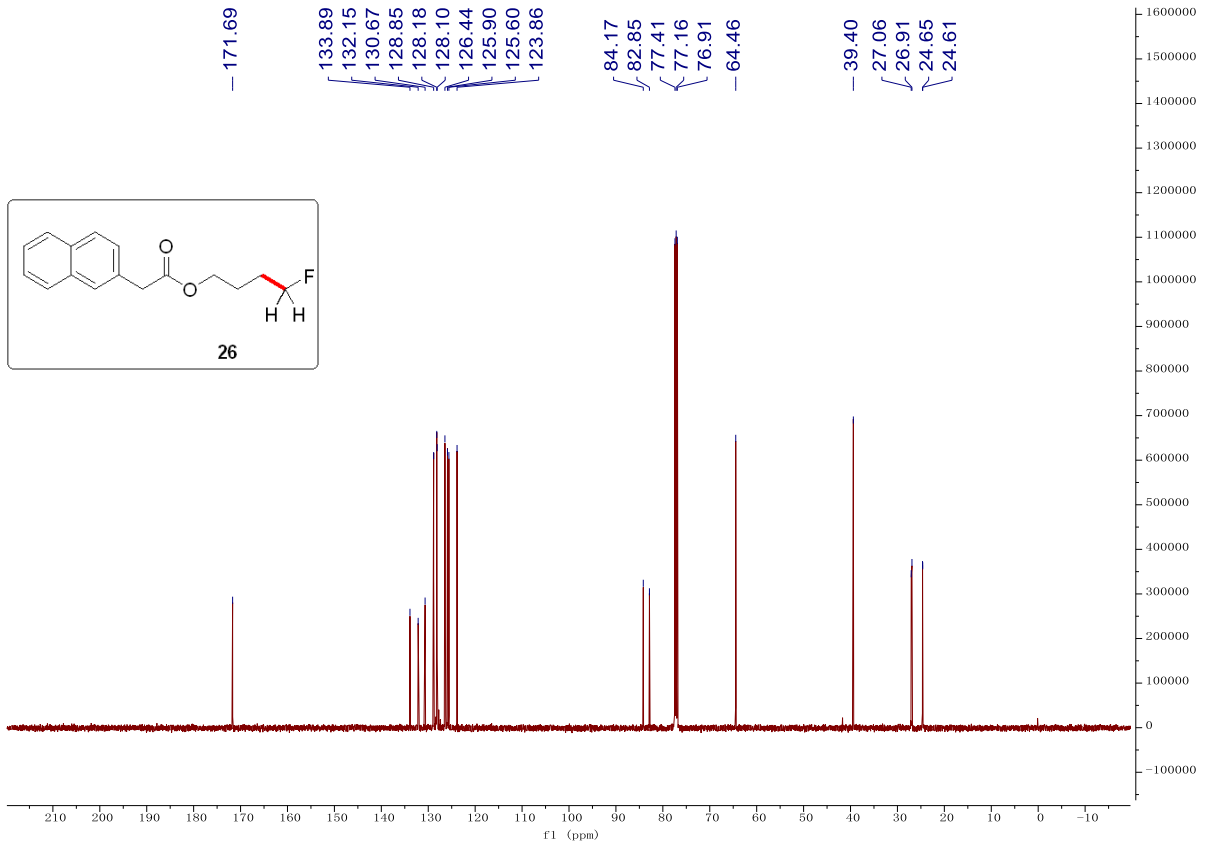
^{13}C NMR Spectrum of **25** ($CDCl_3$, 101 MHz)



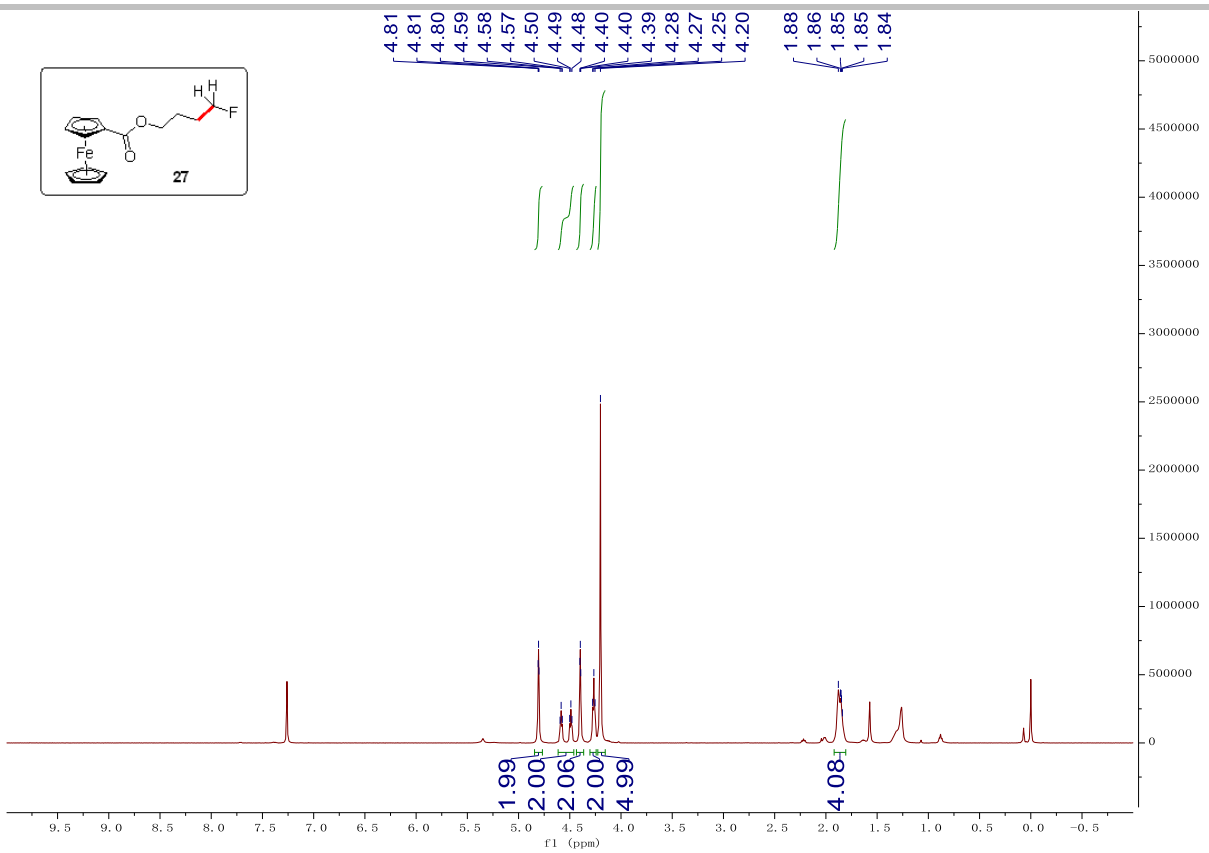
^{1}H NMR Spectrum of of **26** ($CDCl_3$, 400 MHz)



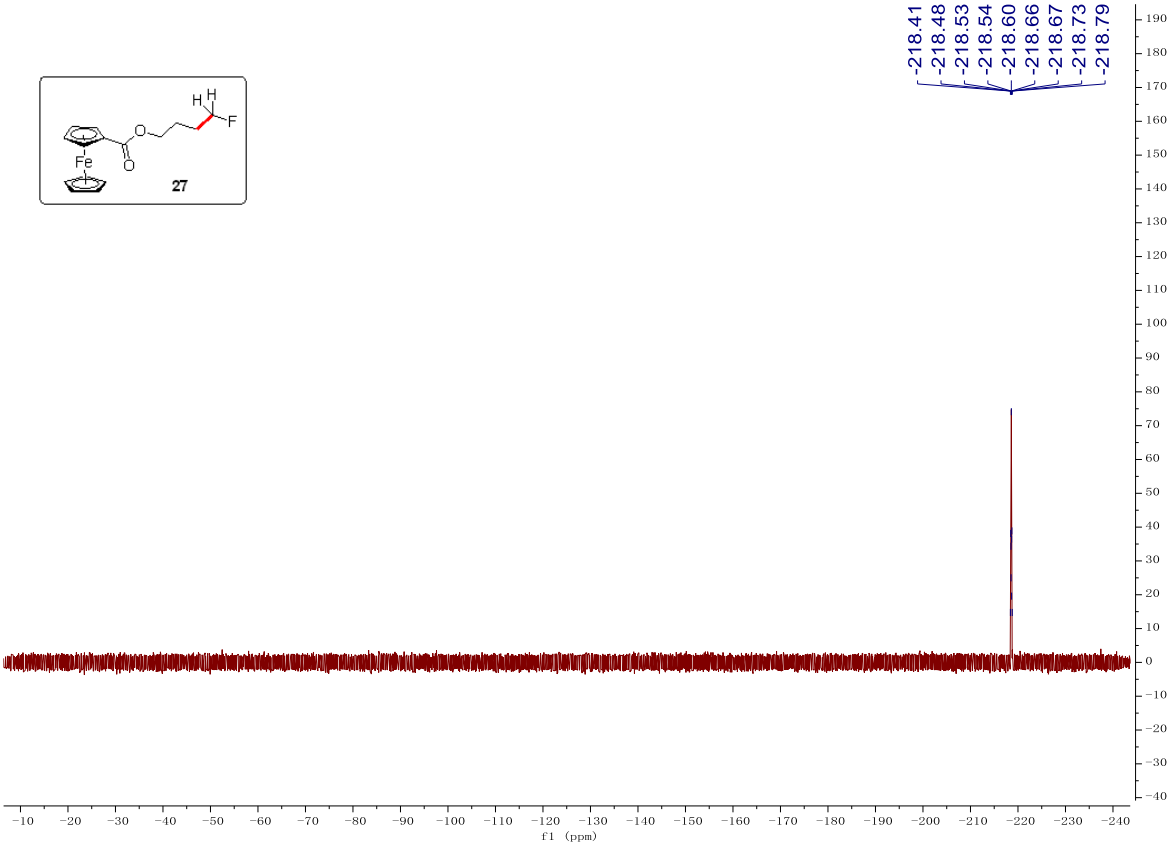
^{19}F NMR Spectrum of of **26** ($CDCl_3$, 376 MHz)



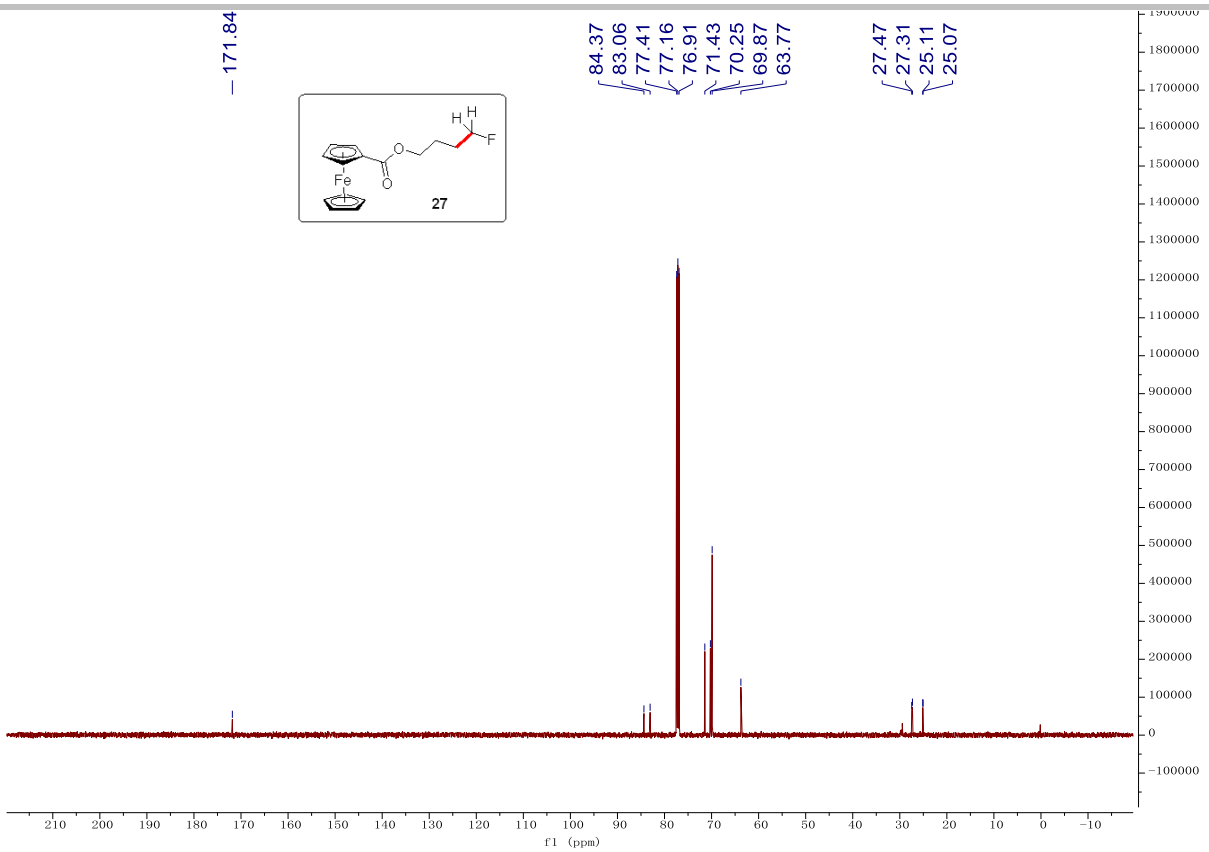
^{13}C NMR Spectrum of **26** ($CDCl_3$, 126 MHz)



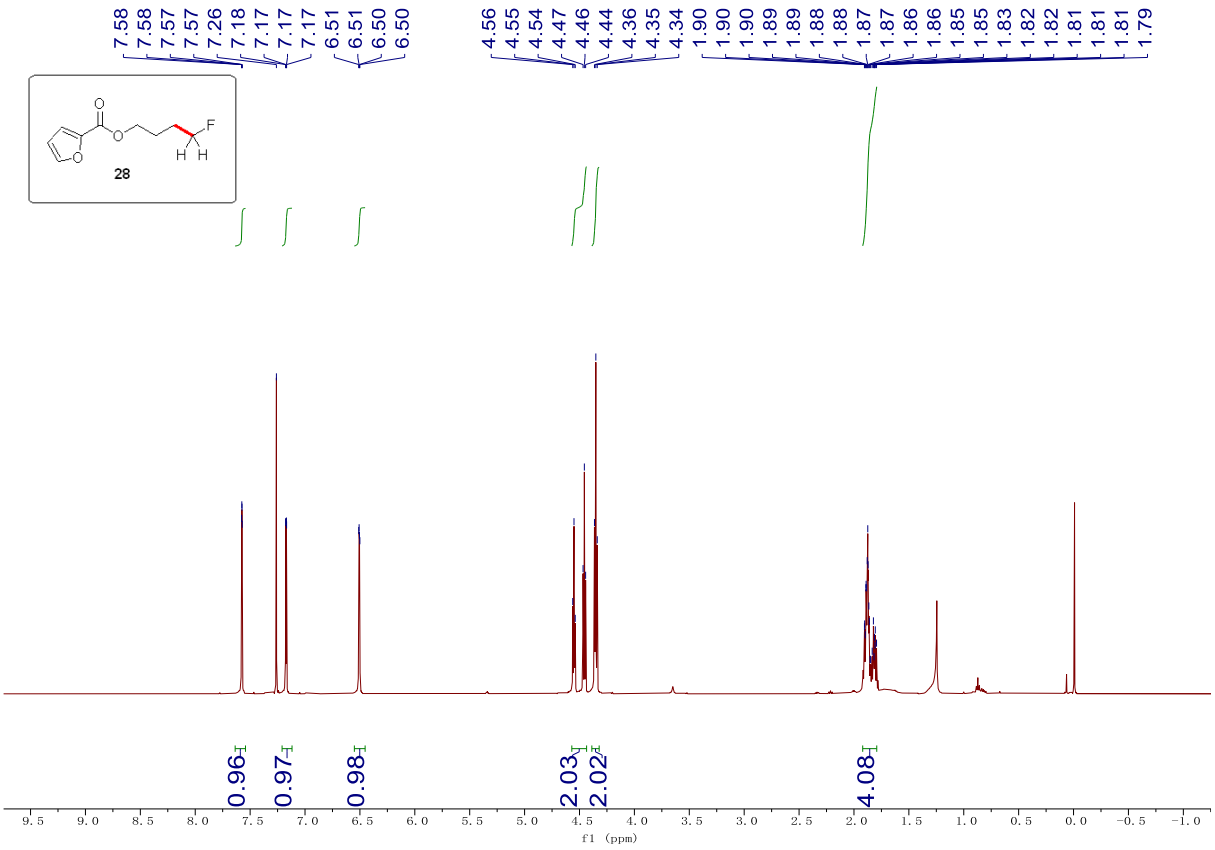
^{1}H NMR Spectrum of of **27** ($CDCl_3$, 500 MHz)



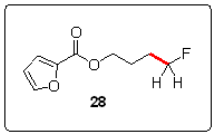
^{19}F NMR Spectrum of of **27** ($CDCl_3$, 376 MHz)



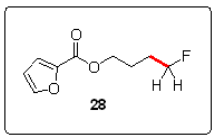
^{13}C NMR Spectrum of **27** ($CDCl_3$, 126 MHz)



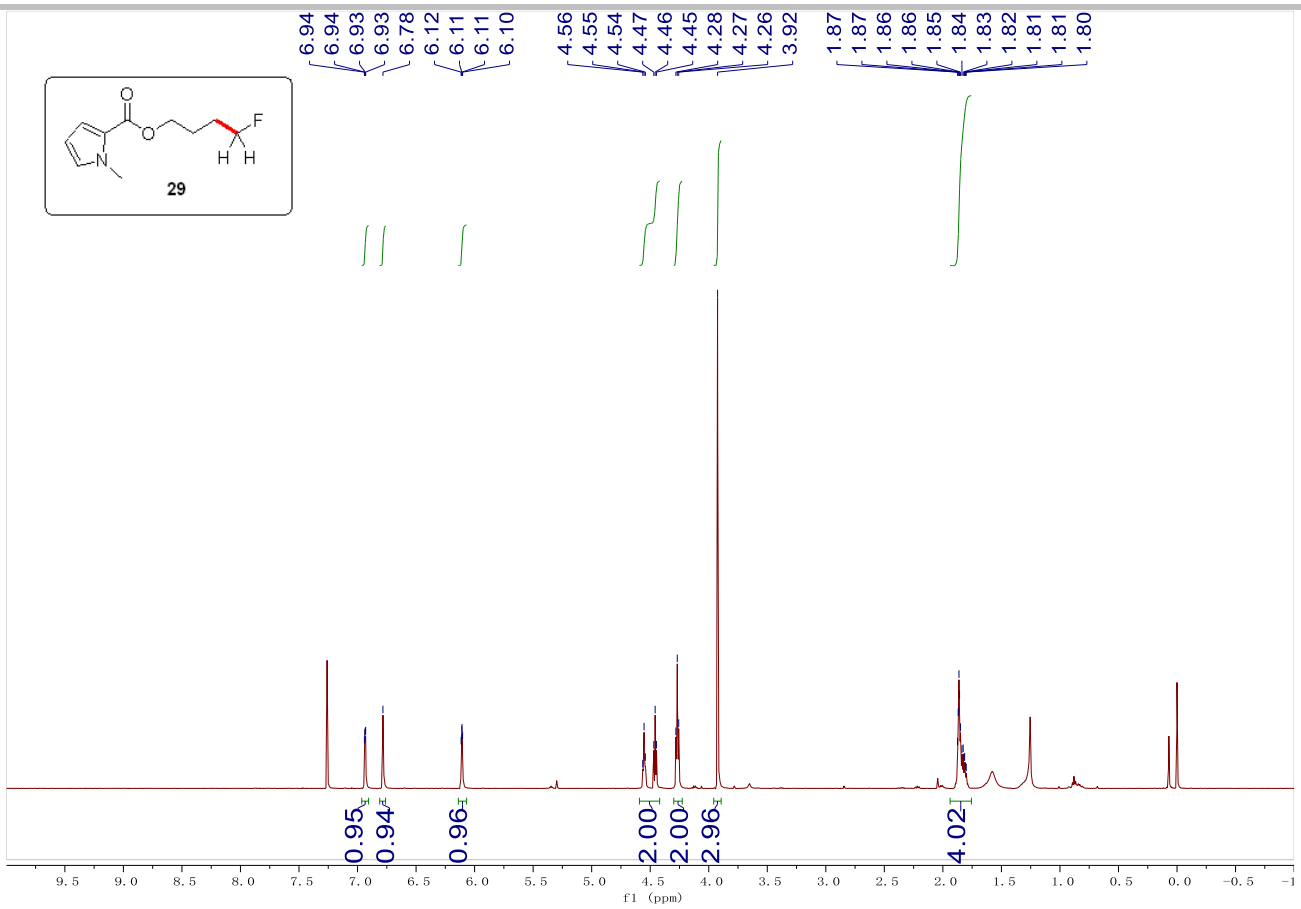
^{1}H NMR Spectrum of of **28** ($CDCl_3$, 500 MHz)



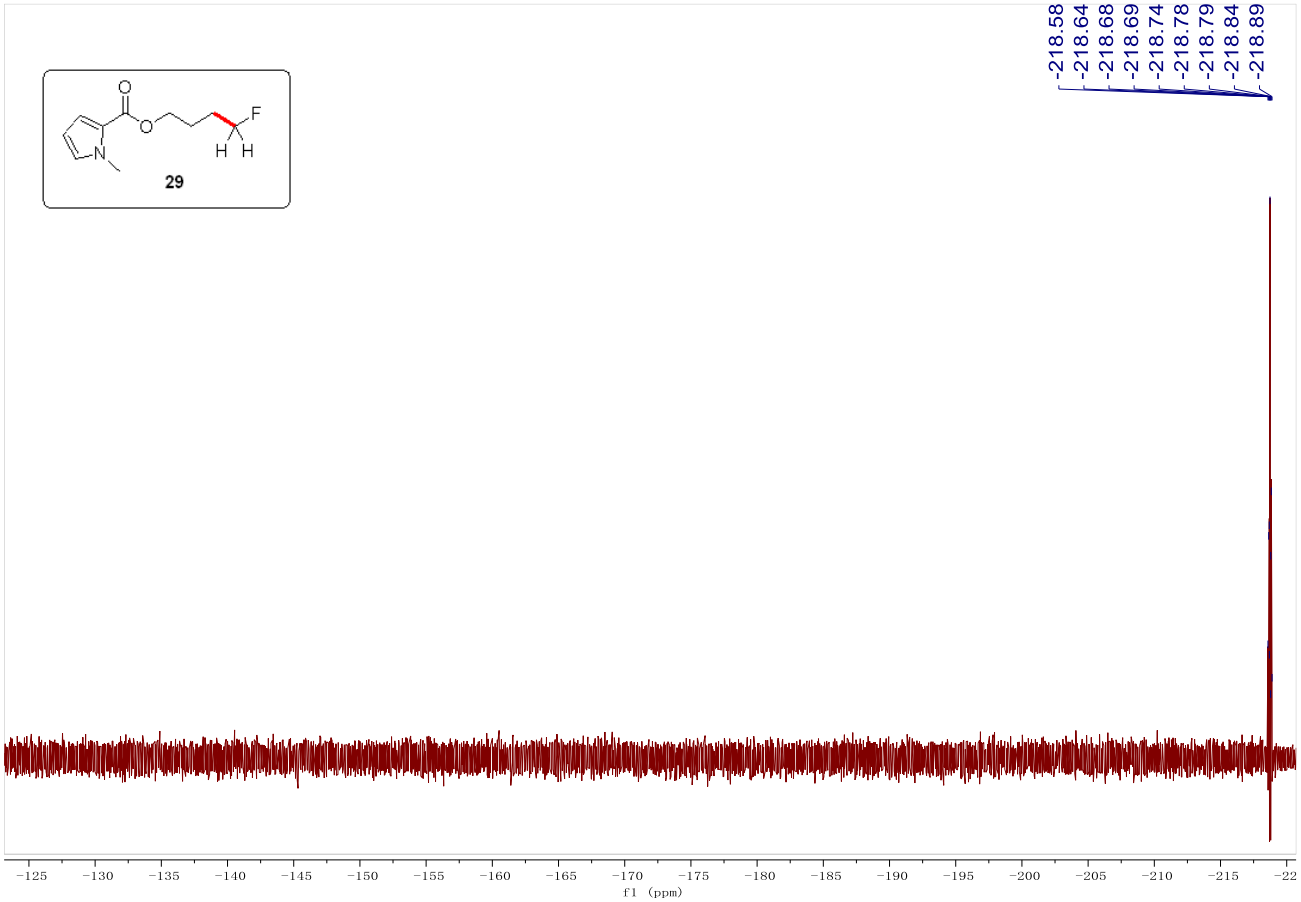
^{19}F NMR Spectrum of of **28** ($CDCl_3$, 376 MHz)



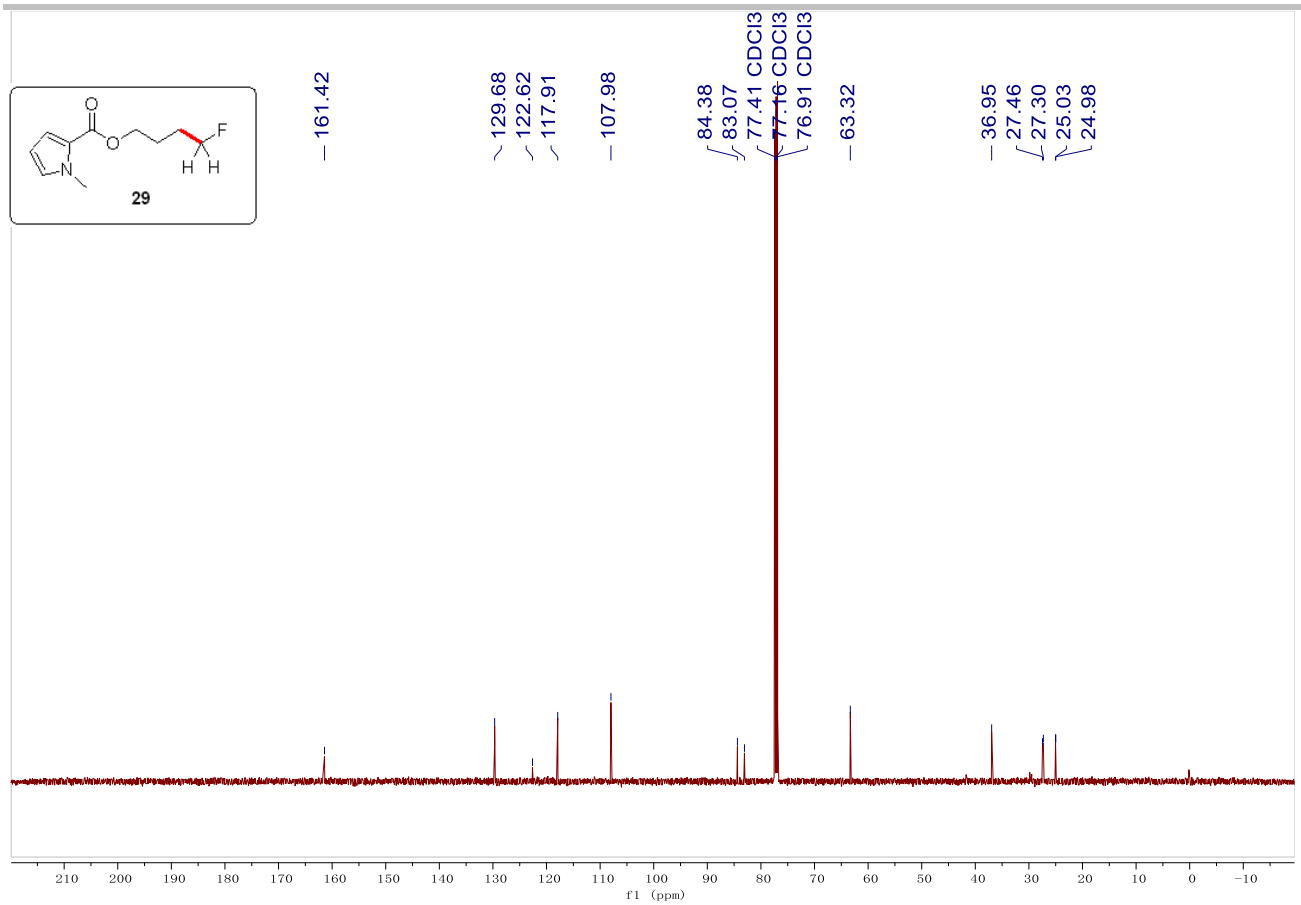
^{13}C NMR Spectrum of **28** ($CDCl_3$, 126 MHz)



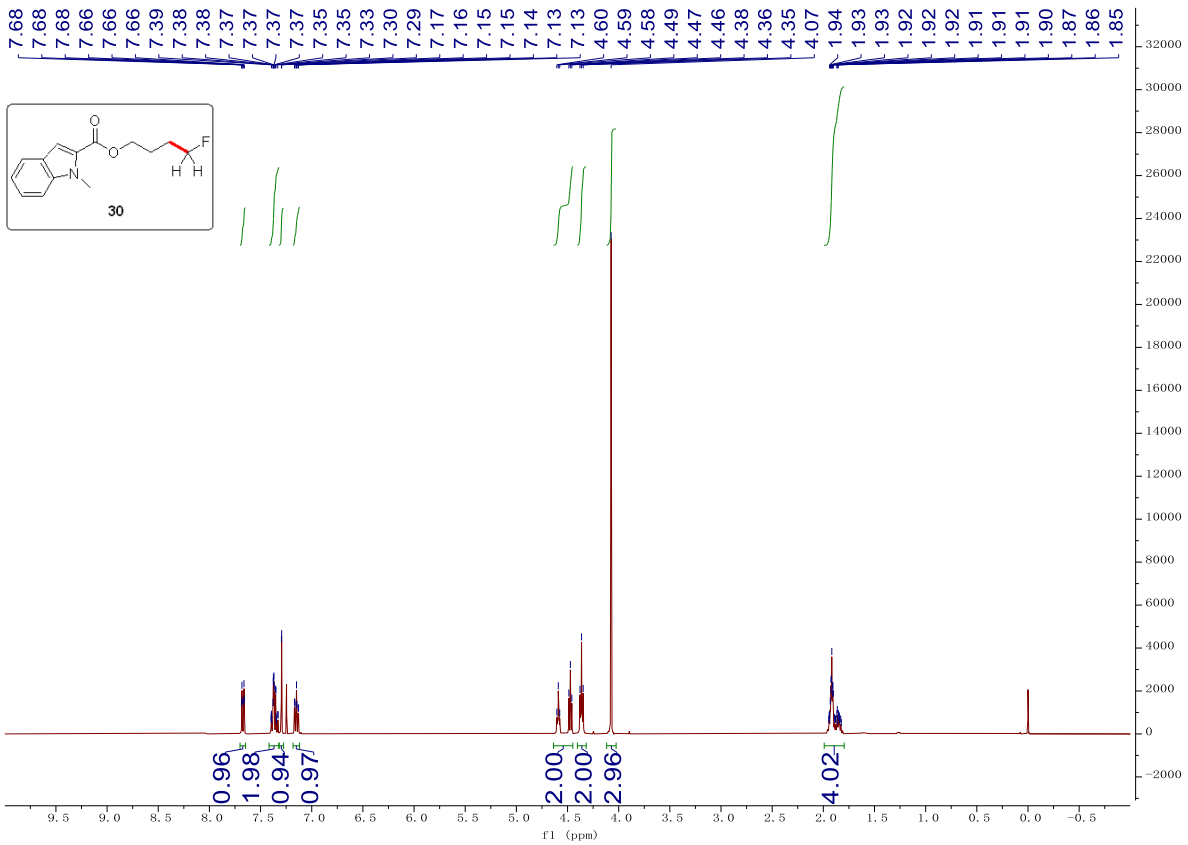
^{1}H NMR Spectrum of of **29** ($CDCl_3$, 500 MHz)



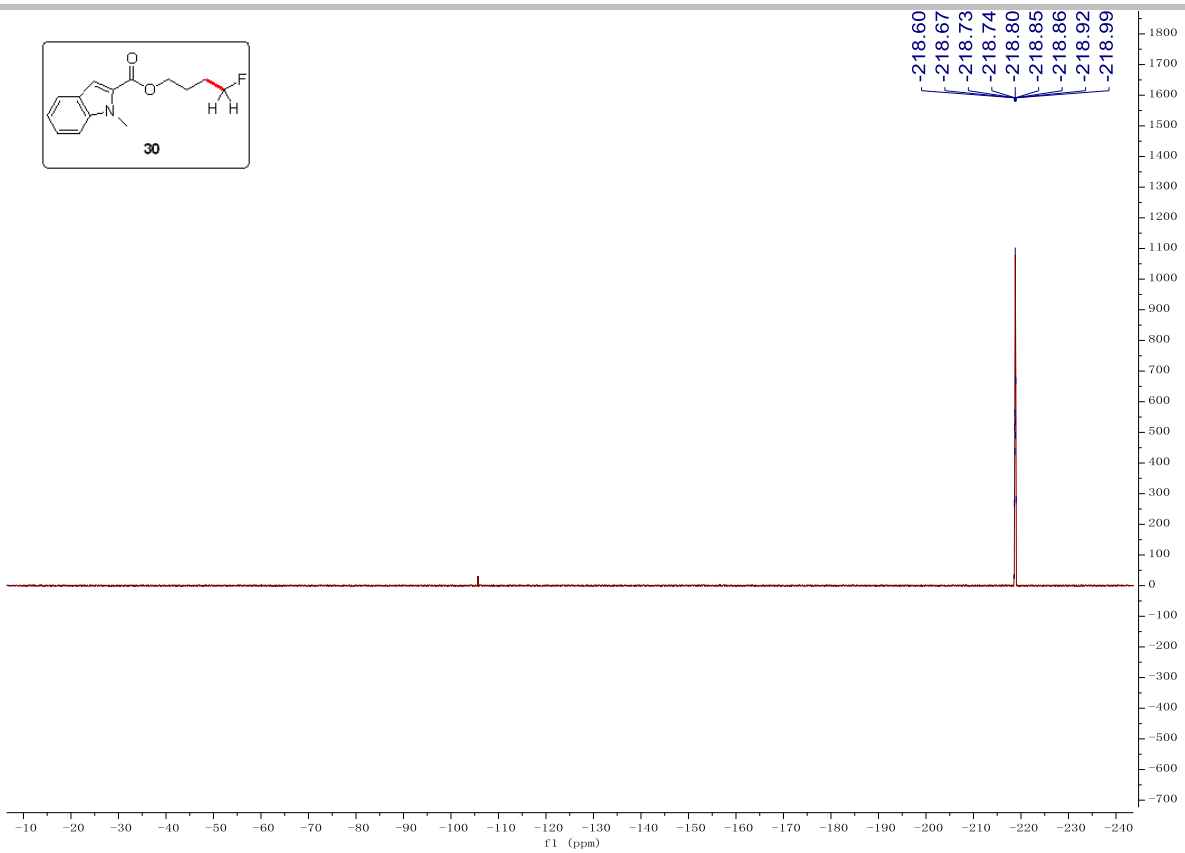
^{19}F NMR Spectrum of of **29** ($CDCl_3$, 376 MHz)



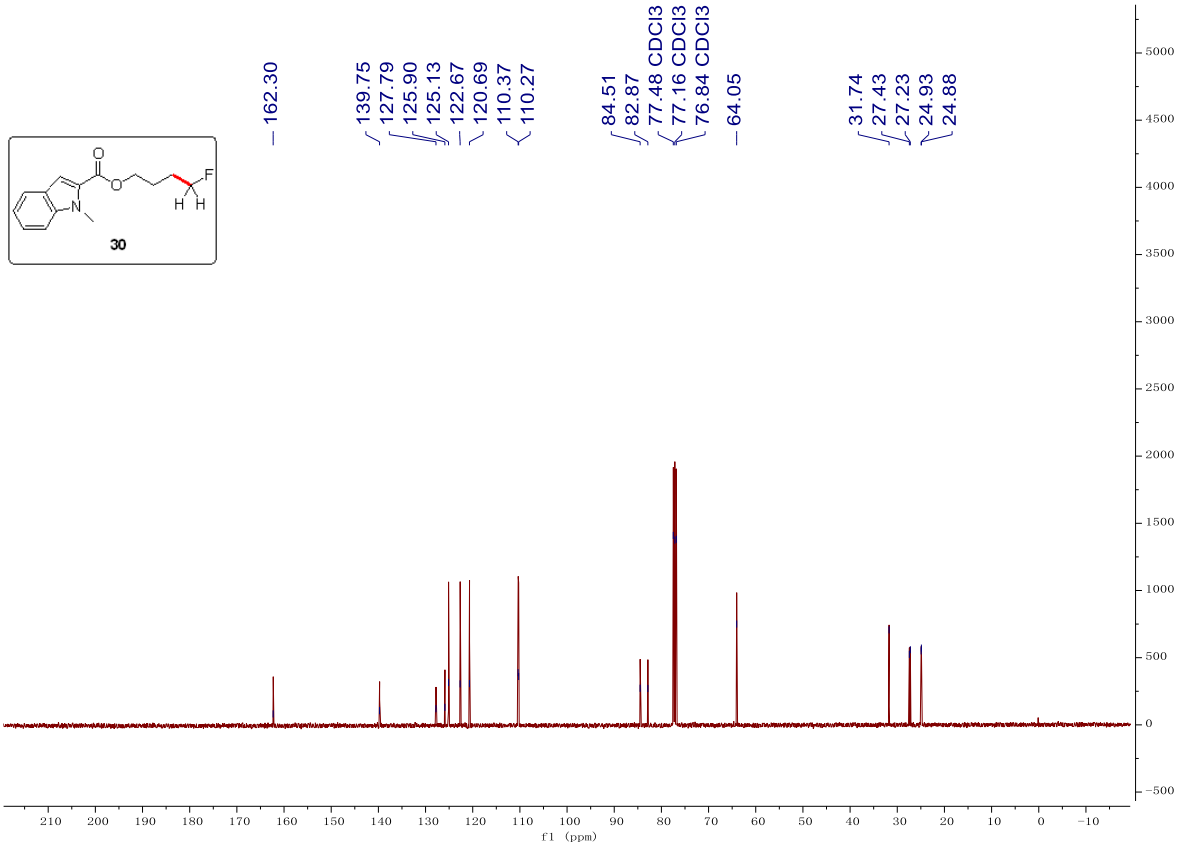
^{13}C NMR Spectrum of **29** ($CDCl_3$, 126 MHz)



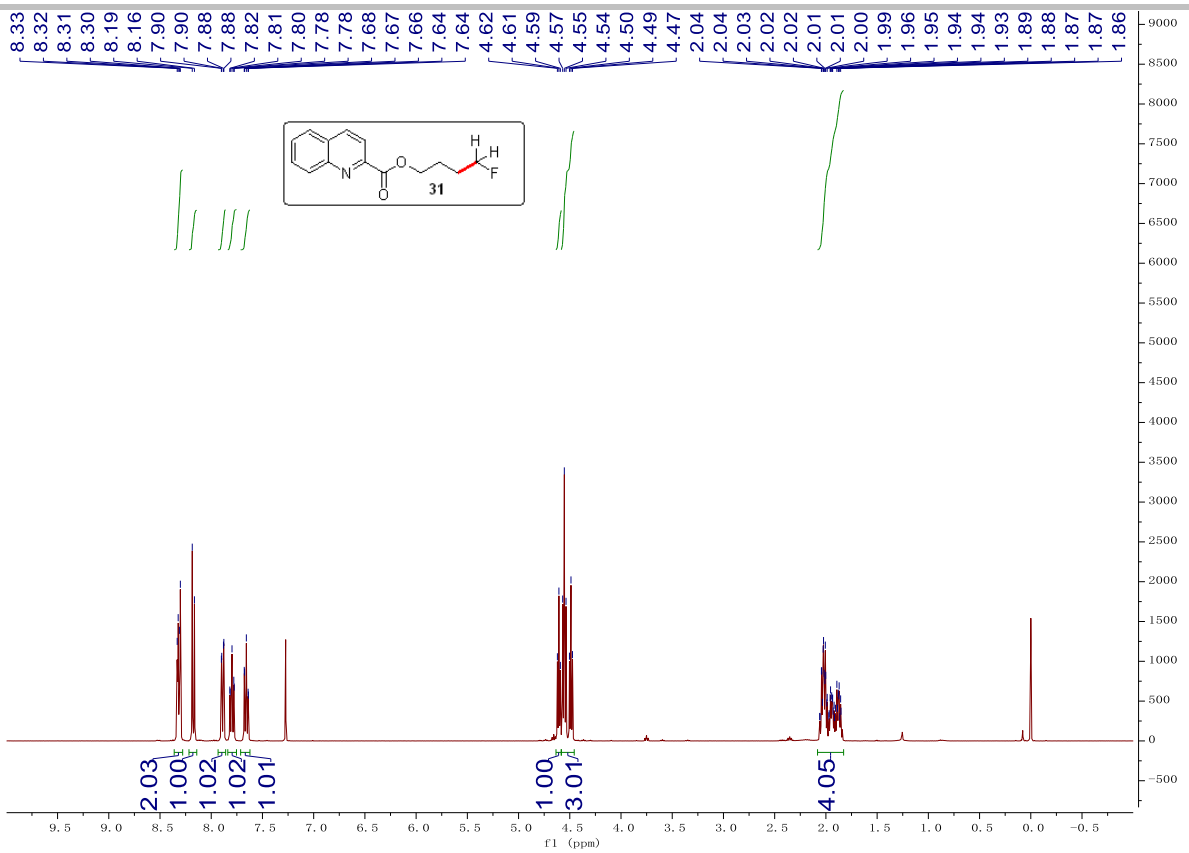
^{1}H NMR Spectrum of of **30** ($CDCl_3$, 400 MHz)



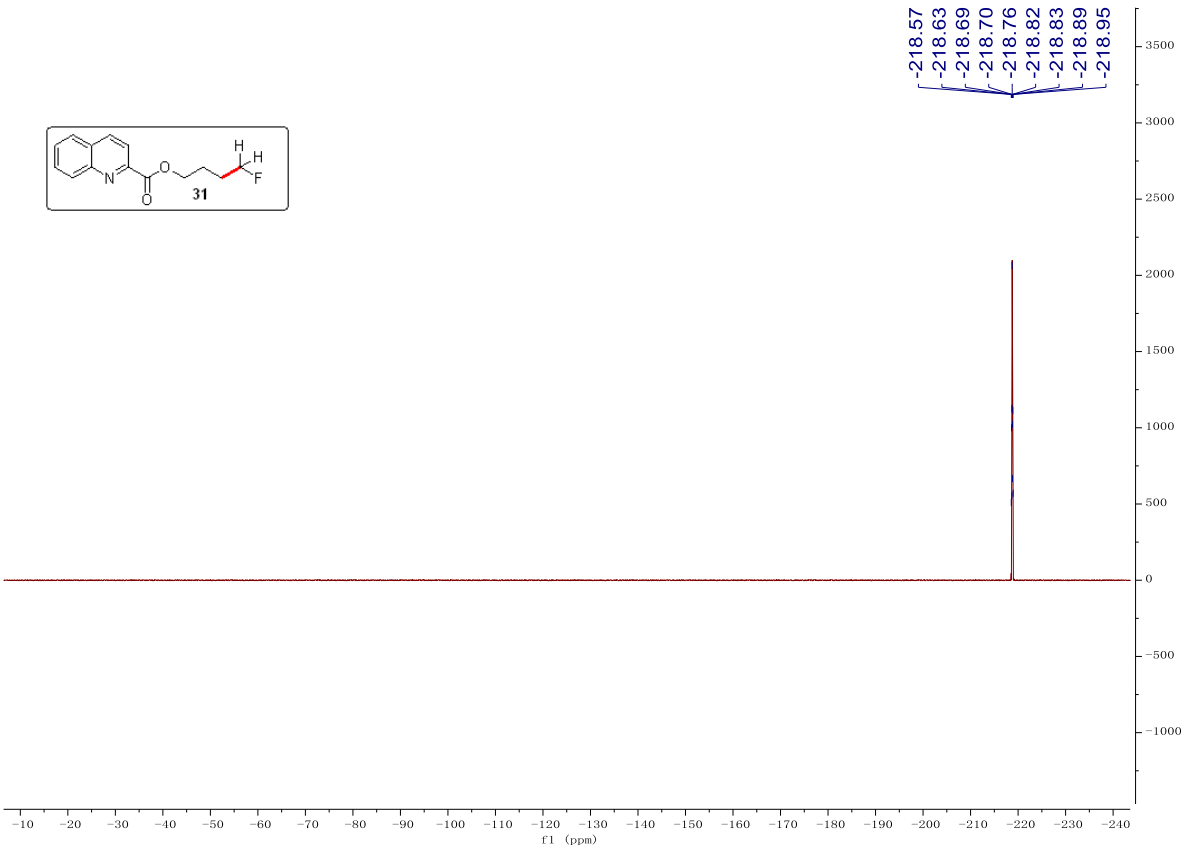
^{19}F NMR Spectrum of of **30** ($CDCl_3$, 376 MHz)



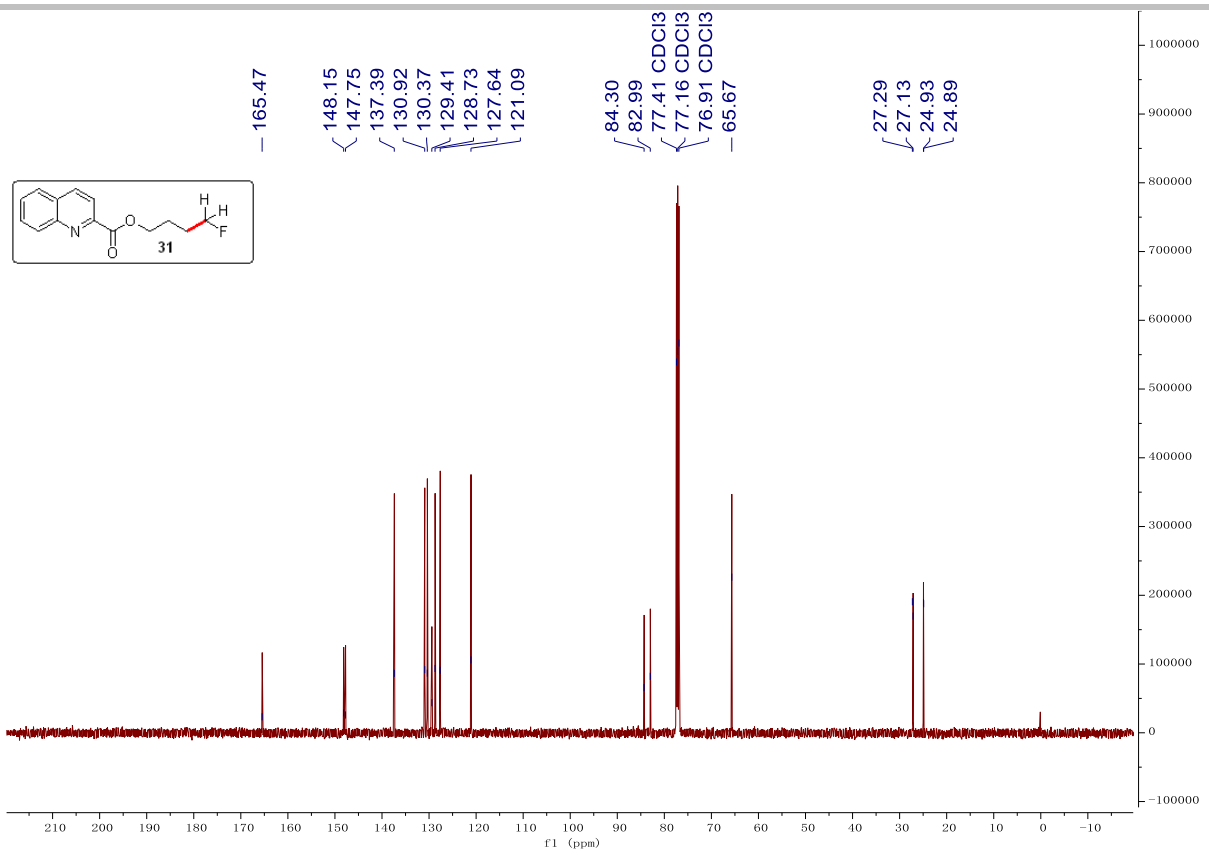
^{13}C NMR Spectrum of **30** ($CDCl_3$, 101 MHz)



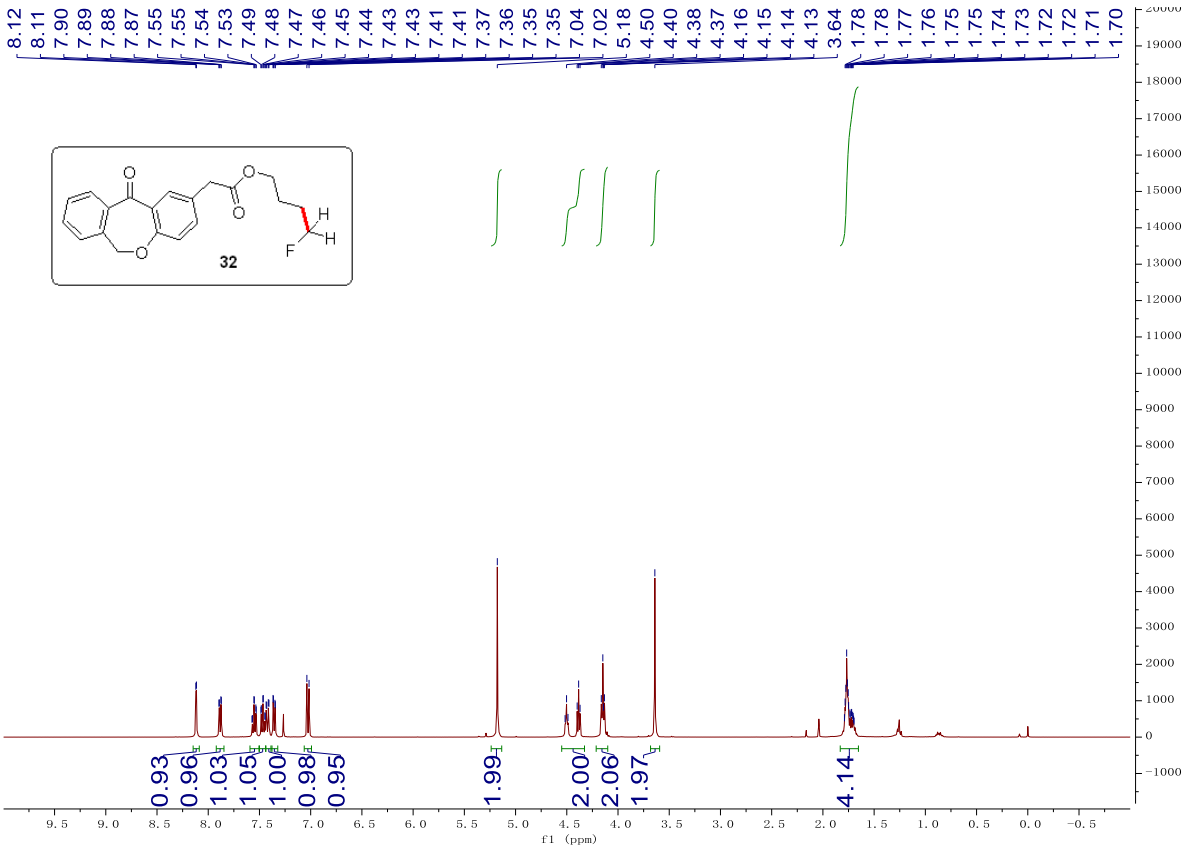
^{1}H NMR Spectrum of of **31** ($CDCl_3$, 400 MHz)



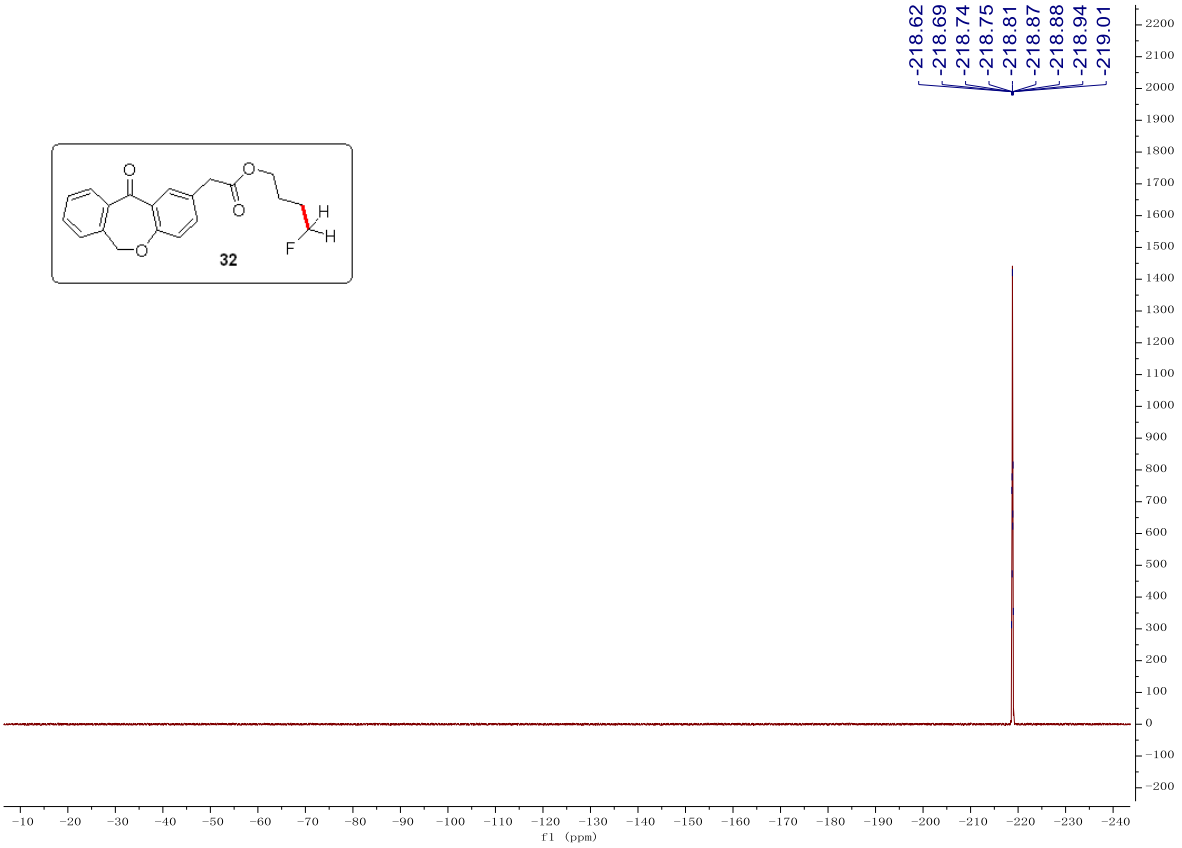
^{19}F NMR Spectrum of of **31** ($CDCl_3$, 376 MHz)



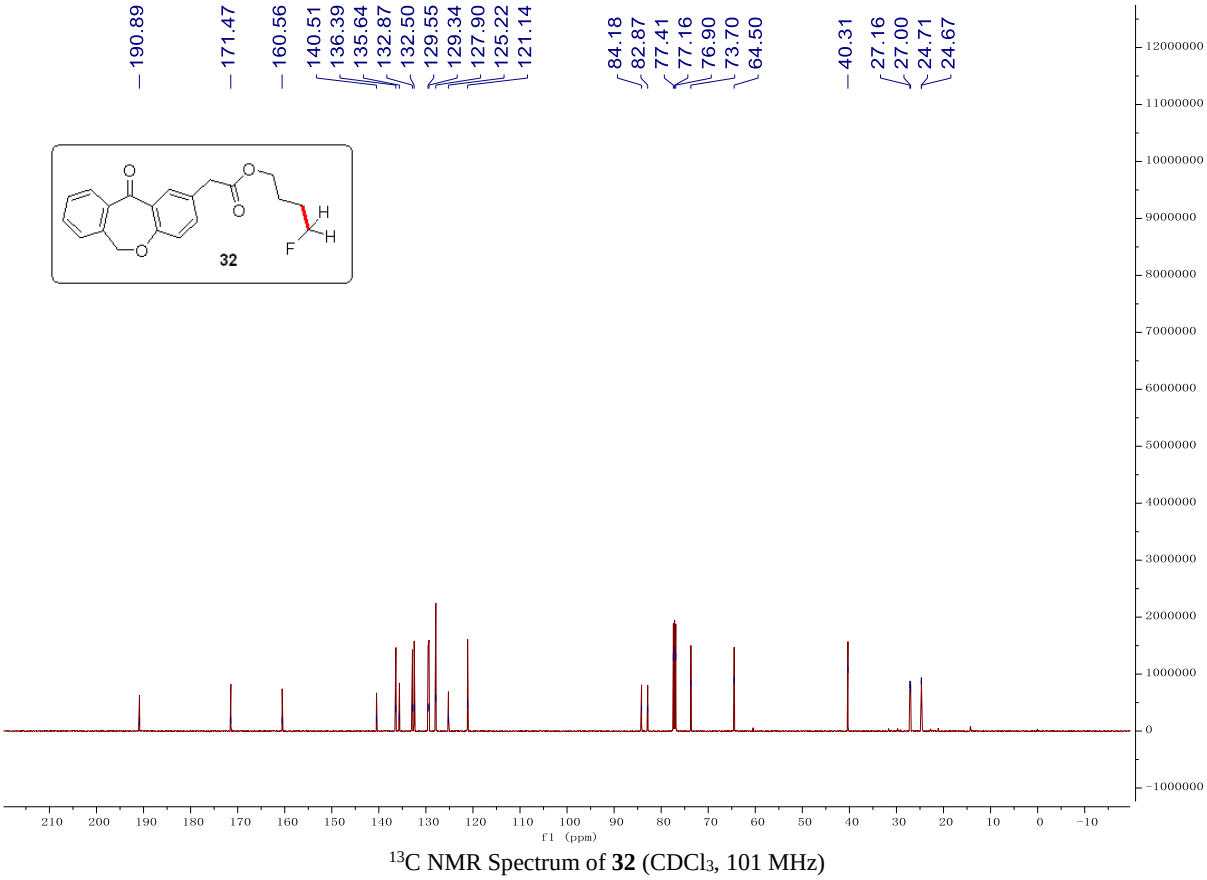
^{13}C NMR Spectrum of **31** ($CDCl_3$, 101 MHz)



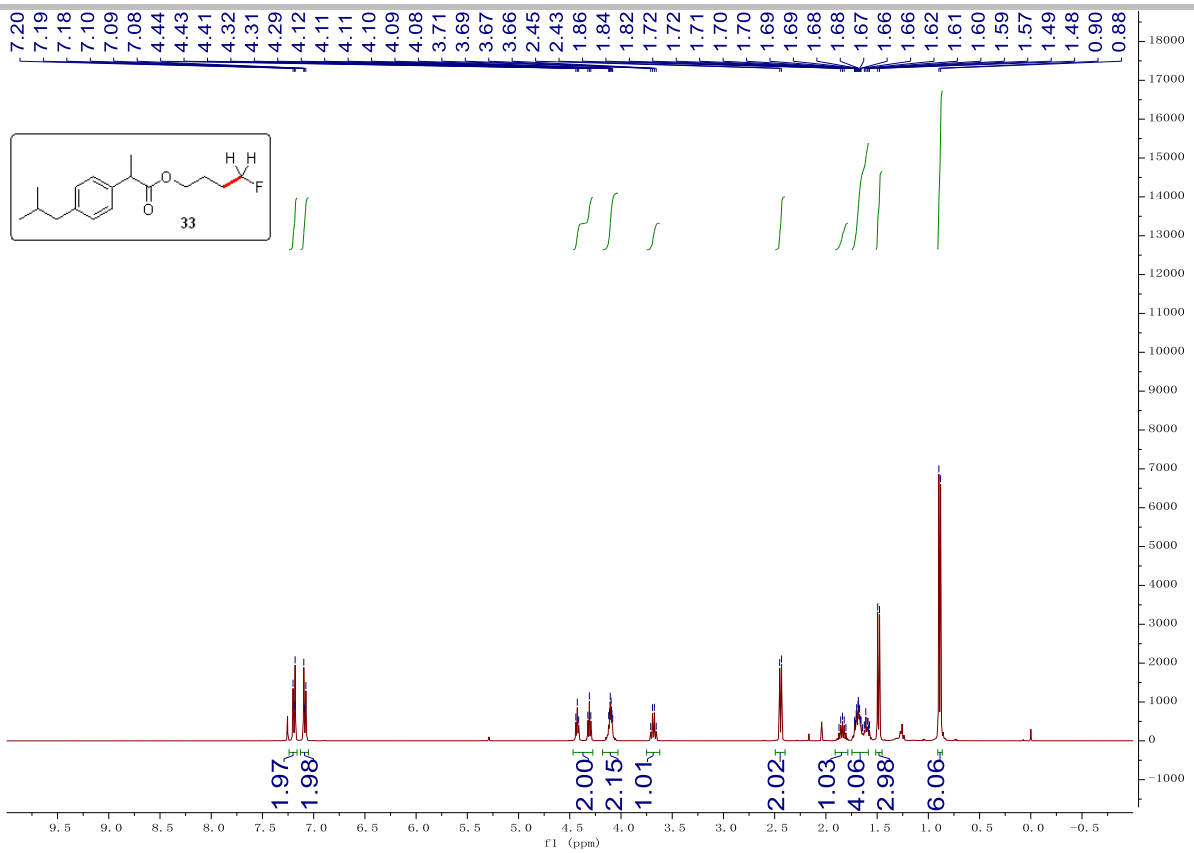
^{1}H NMR Spectrum of of **32** ($CDCl_3$, 400 MHz)



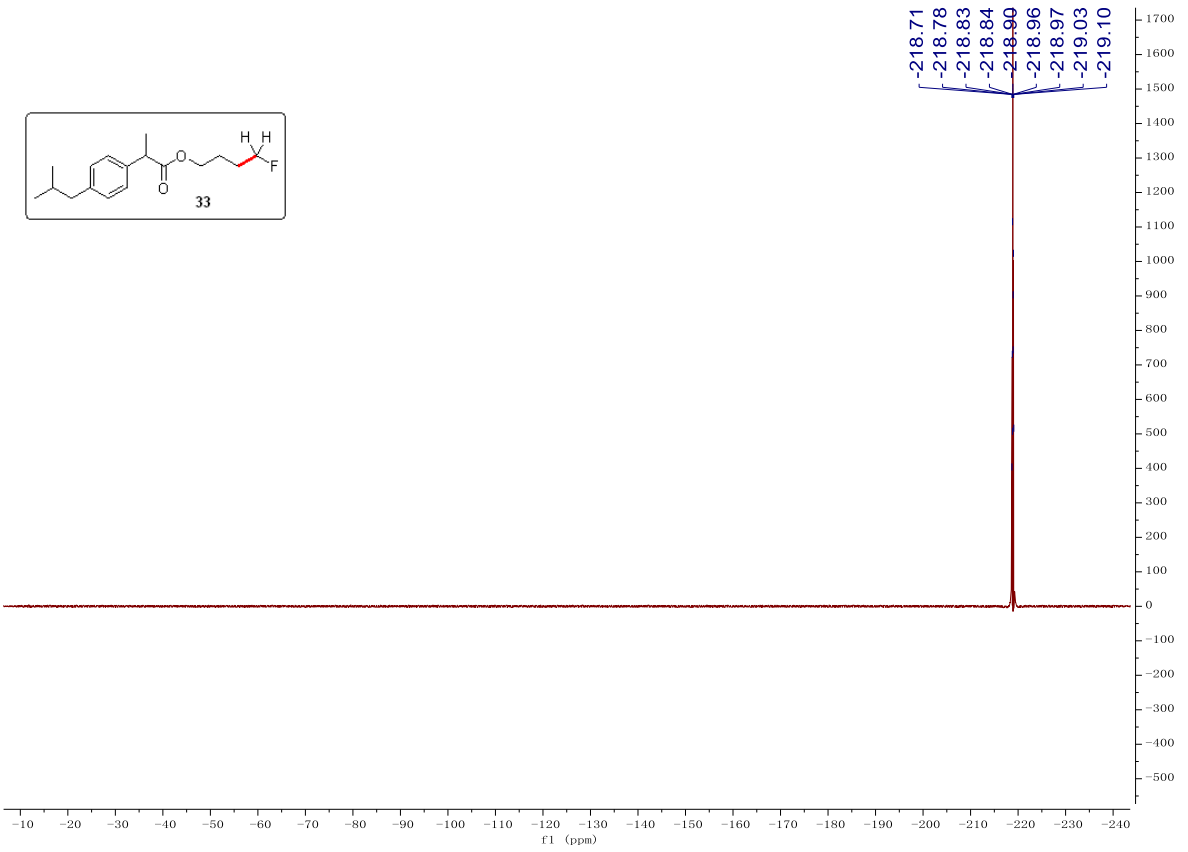
^{19}F NMR Spectrum of of **32** ($CDCl_3$, 376 MHz)



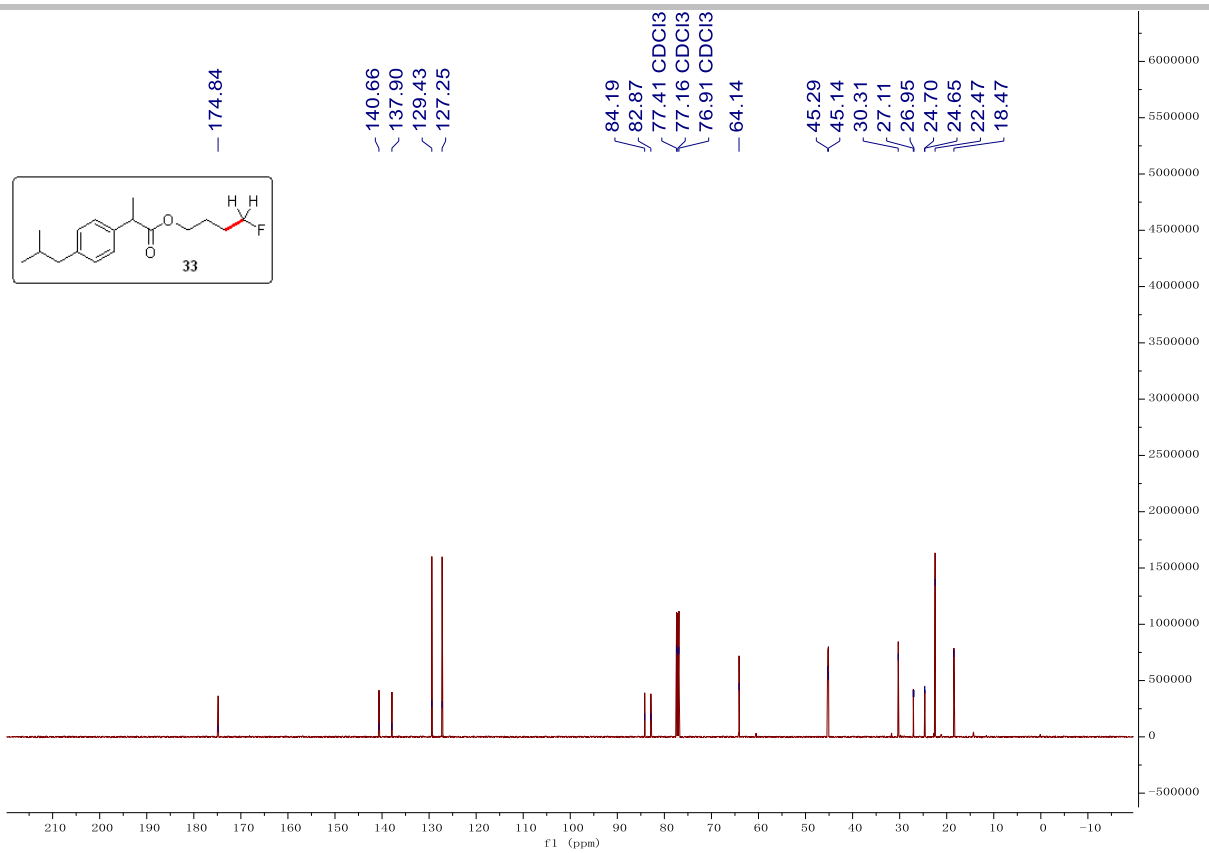
^{13}C NMR Spectrum of **32** ($CDCl_3$, 101 MHz)



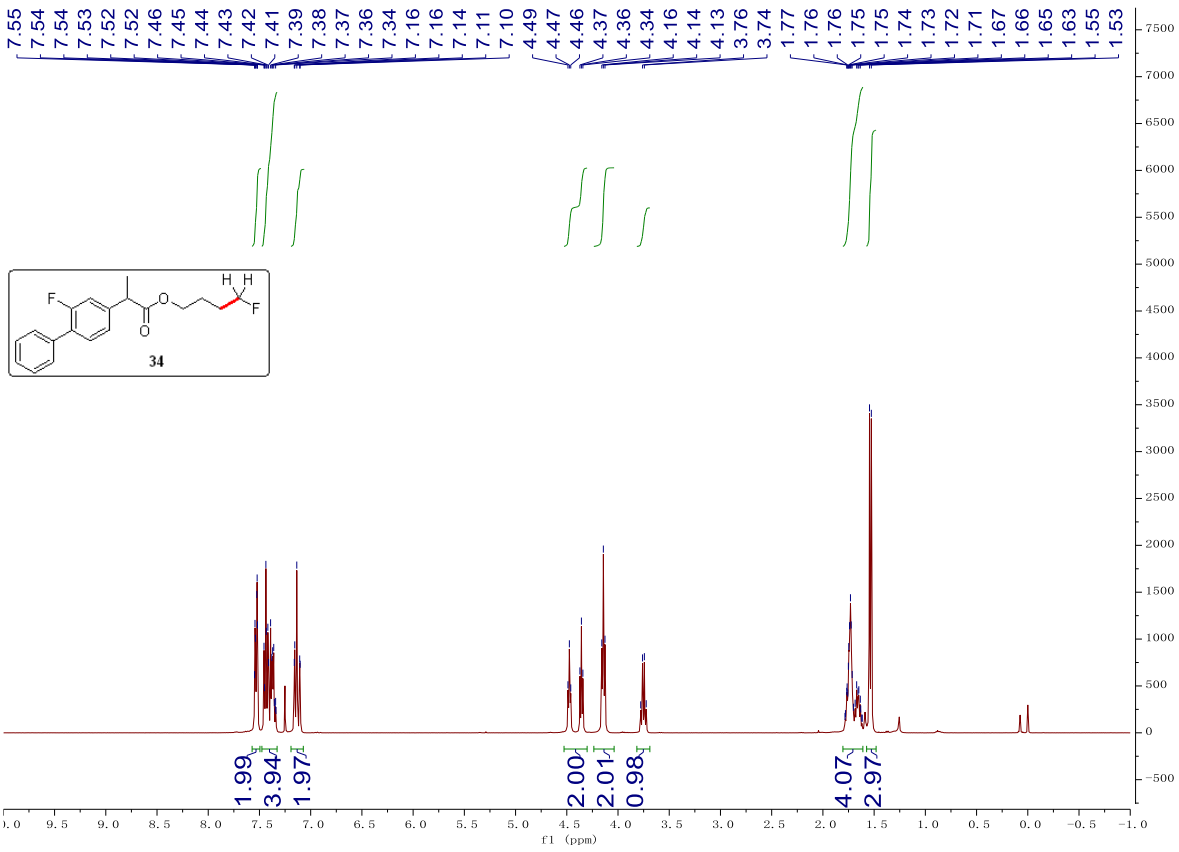
^{1}H NMR Spectrum of of **33** ($CDCl_3$, 400 MHz)



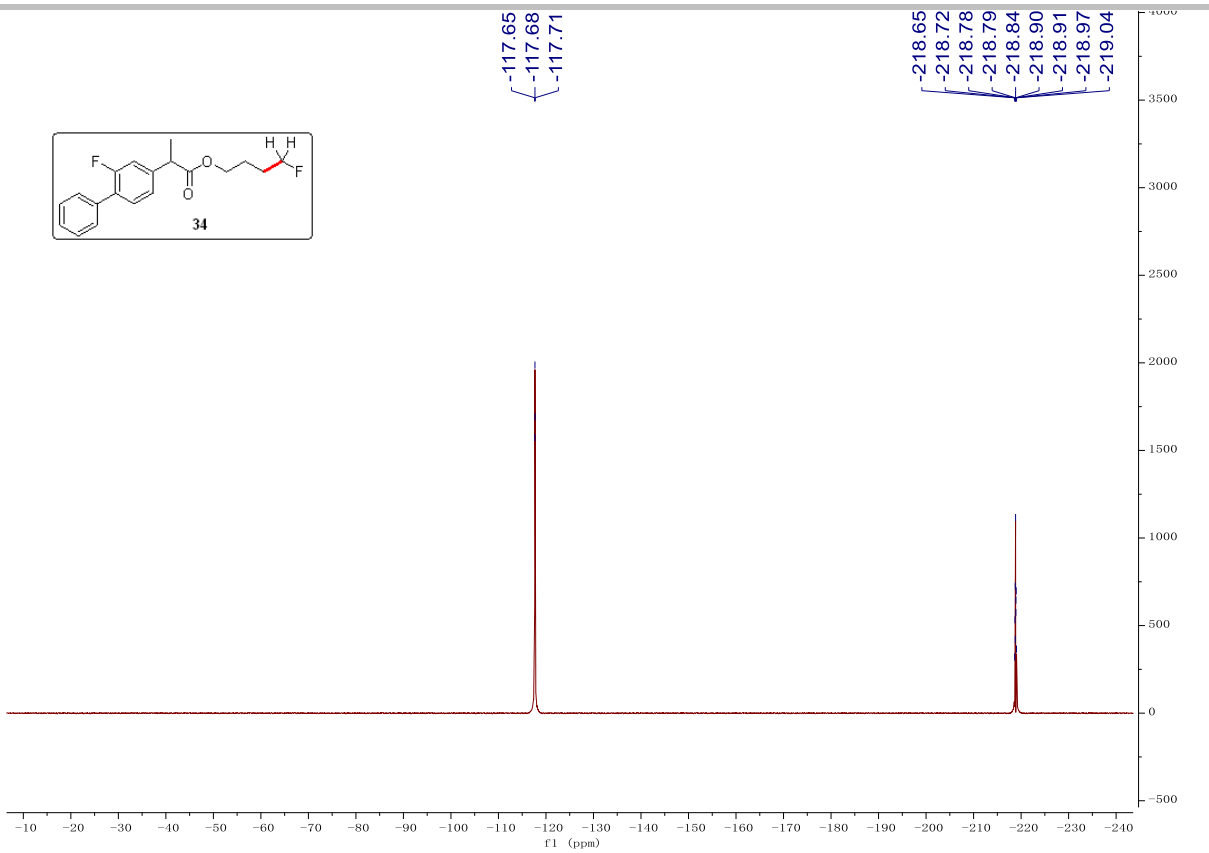
^{19}F NMR Spectrum of of **33** ($CDCl_3$, 376 MHz)



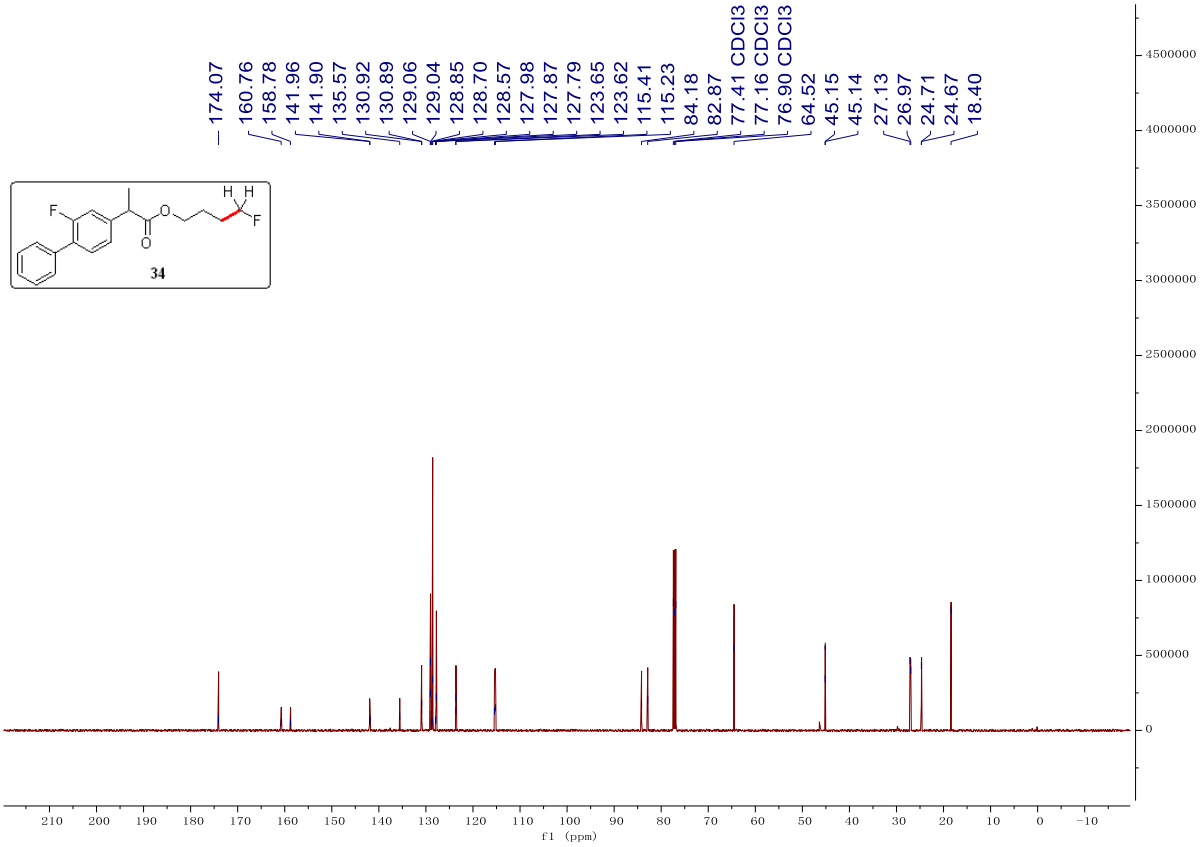
^{13}C NMR Spectrum of **33** ($CDCl_3$, 126 MHz)



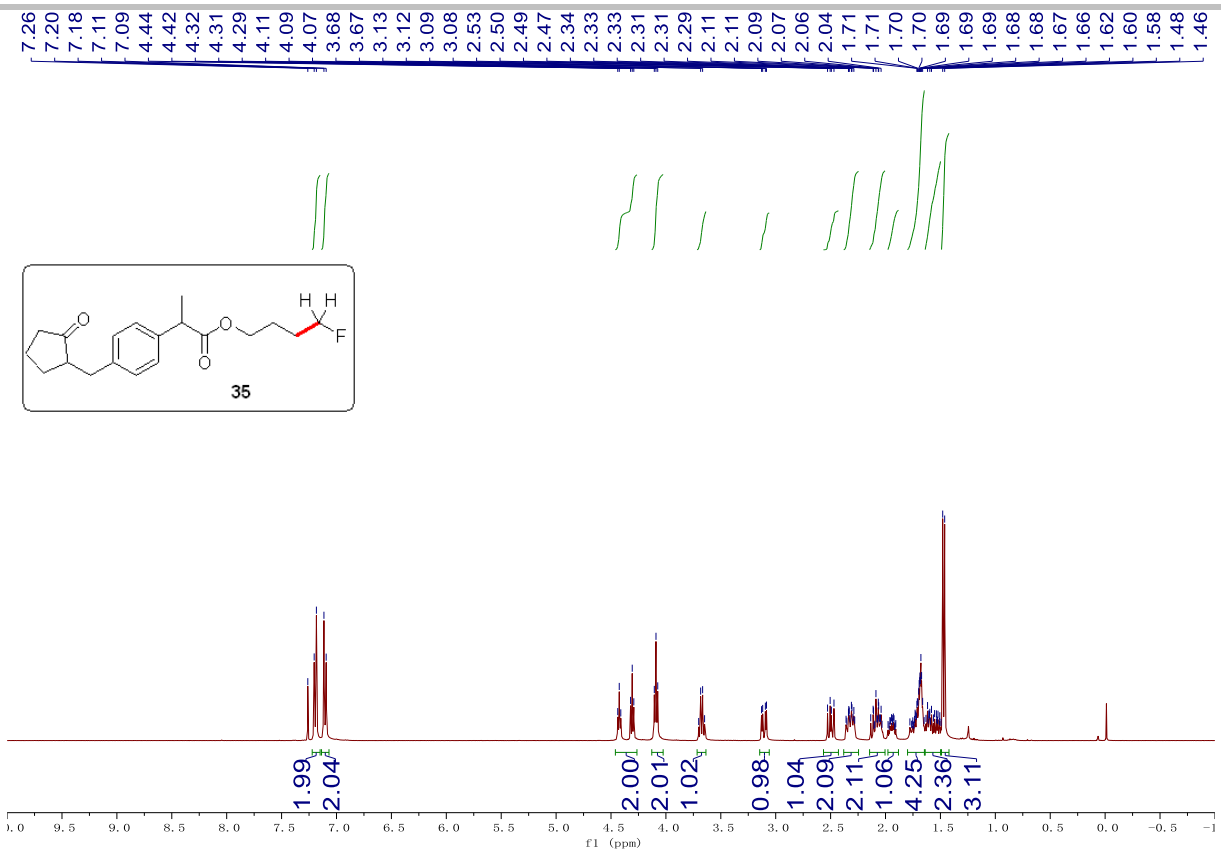
^{1}H NMR Spectrum of of **34** ($CDCl_3$, 400 MHz)



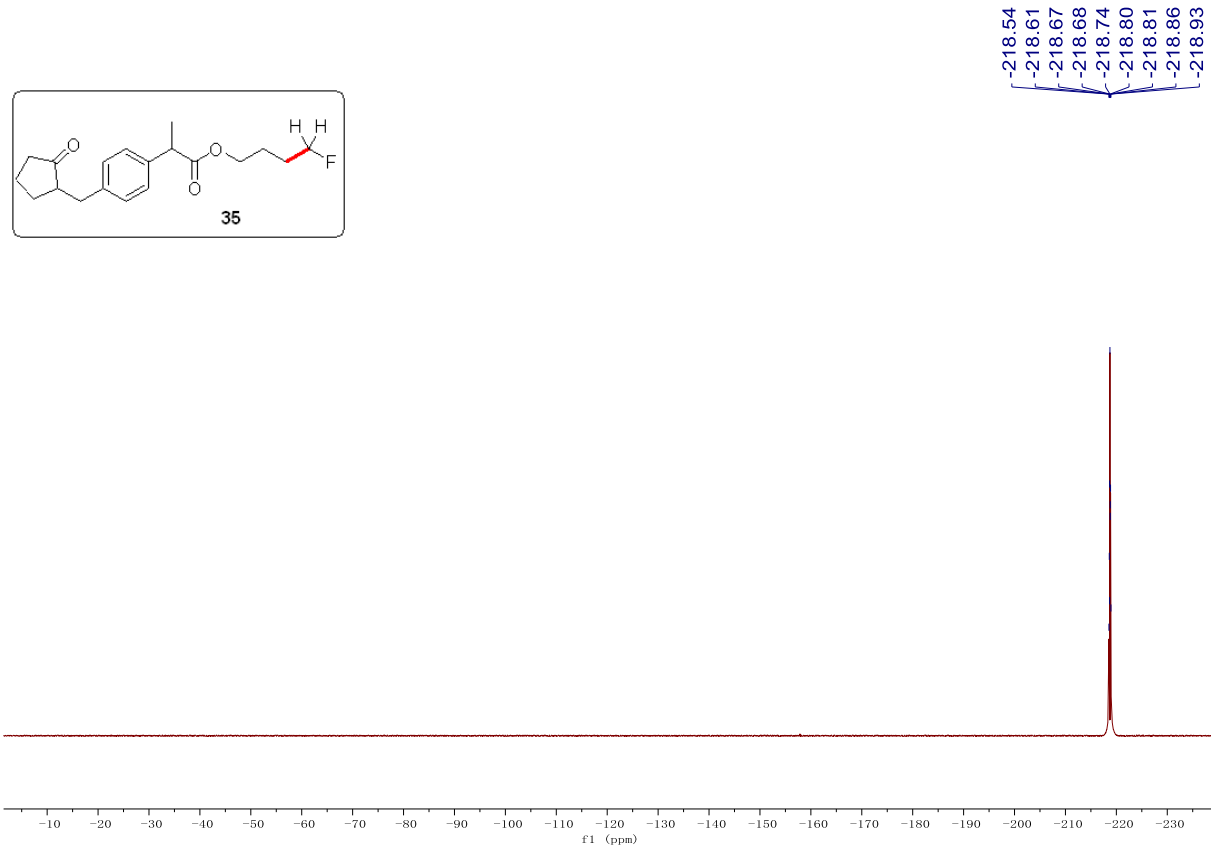
^{19}F NMR Spectrum of of **34** ($CDCl_3$, 376 MHz)



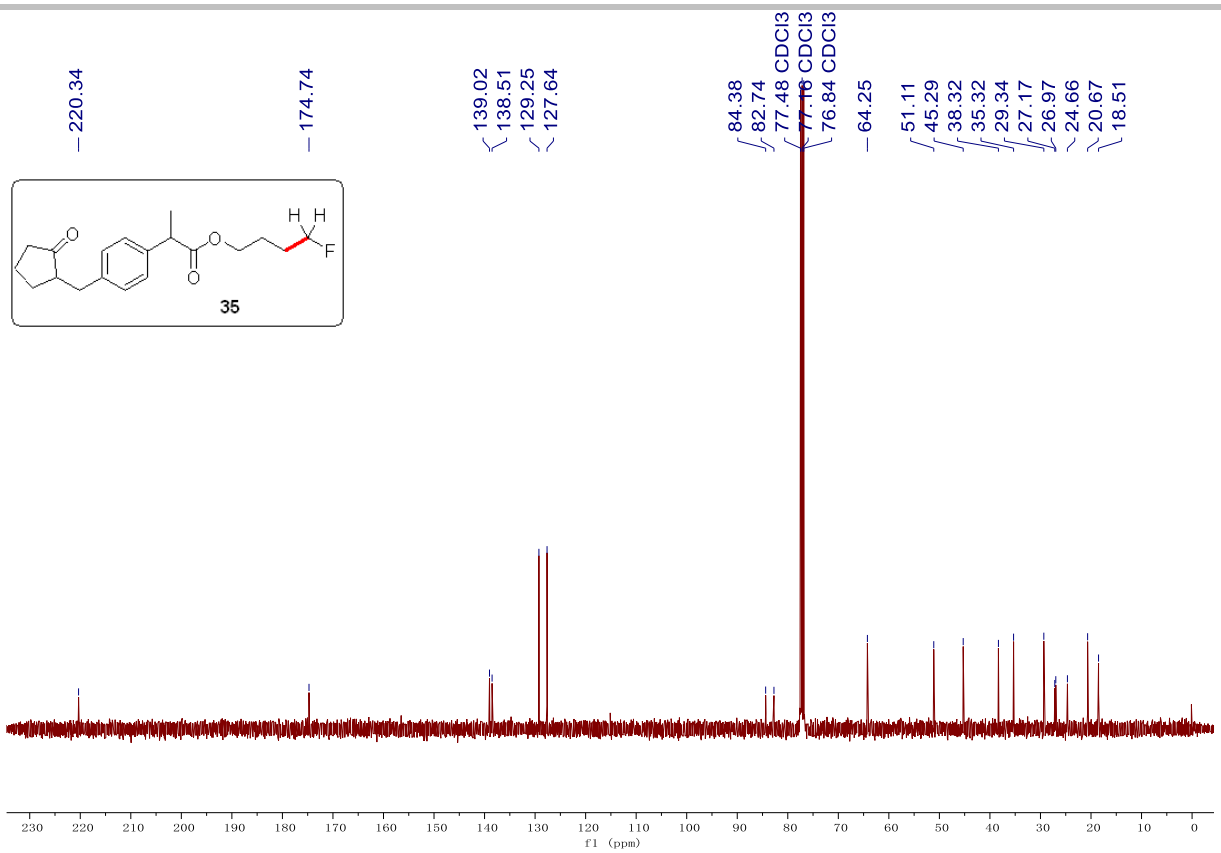
^{13}C NMR Spectrum of **34** ($CDCl_3$, 101 MHz)



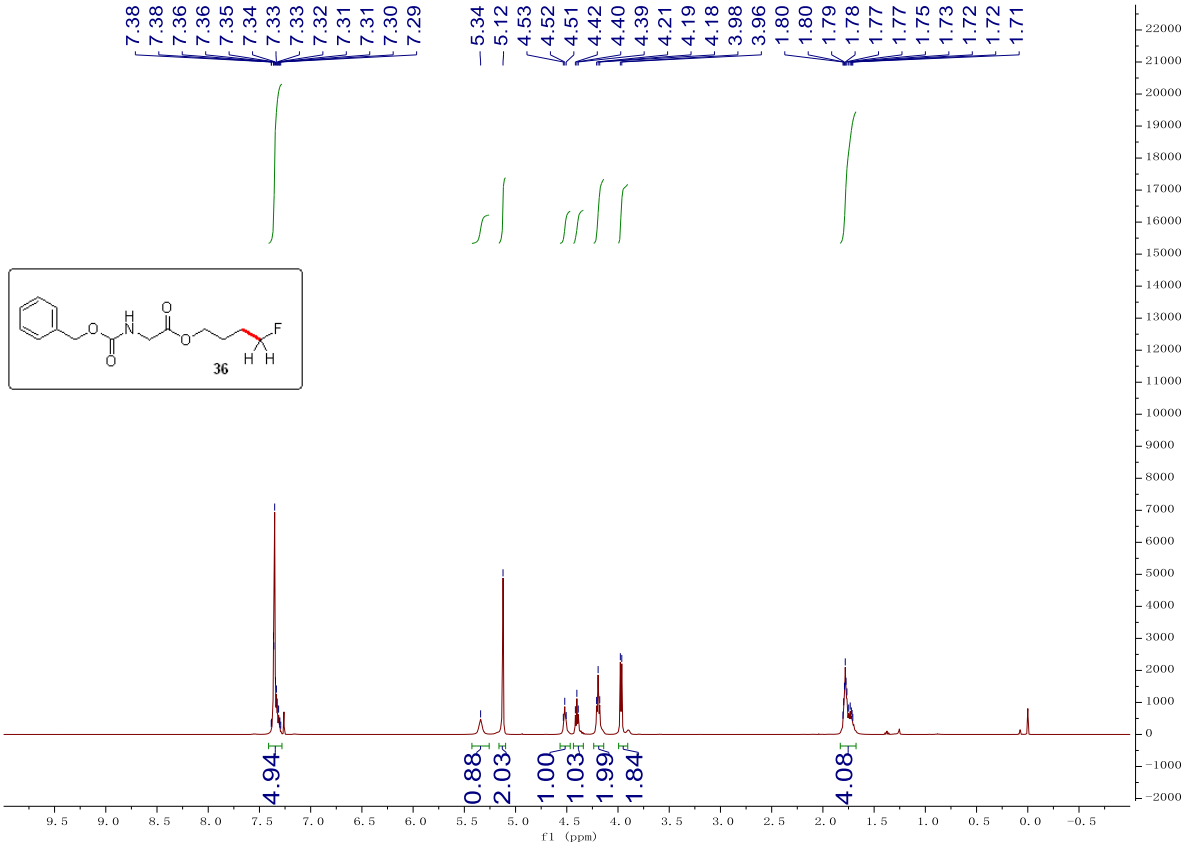
^{1}H NMR Spectrum of of **35** ($CDCl_3$, 400 MHz)



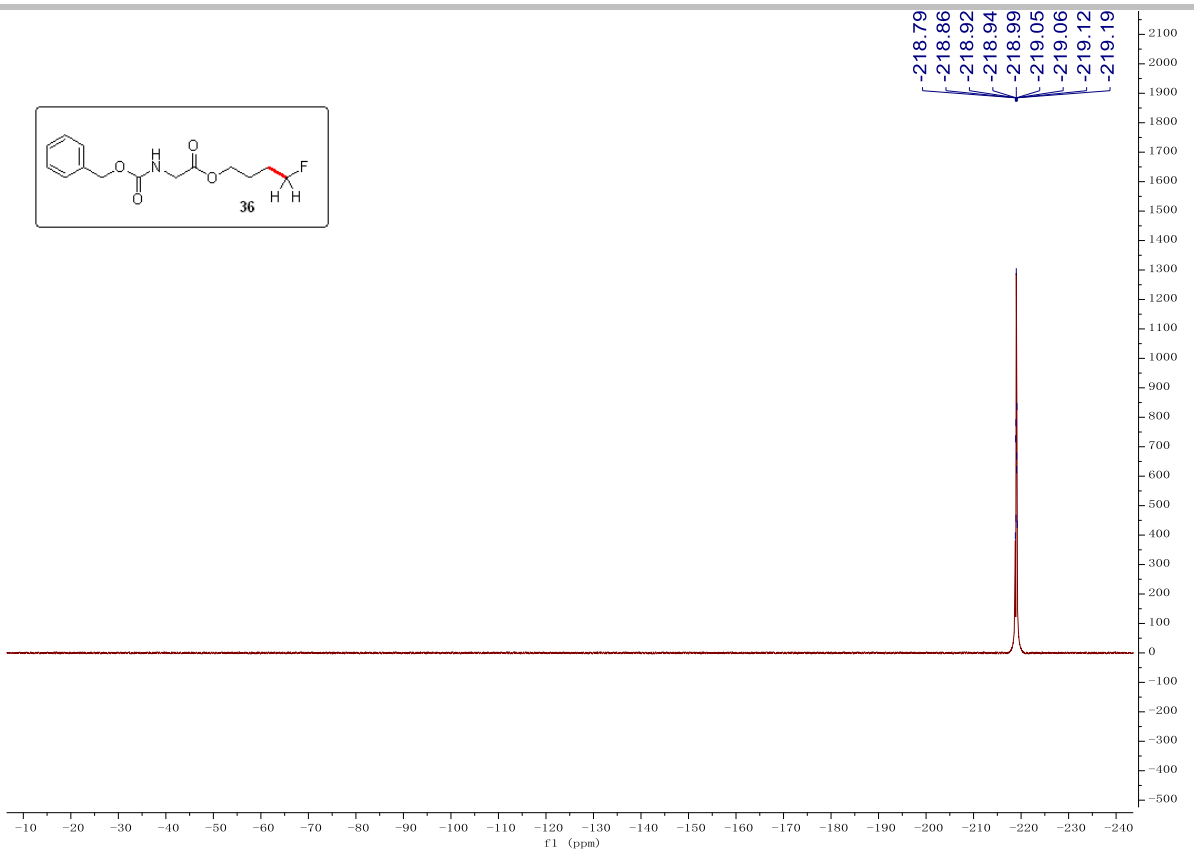
^{19}F NMR Spectrum of of **35** ($CDCl_3$, 376 MHz)



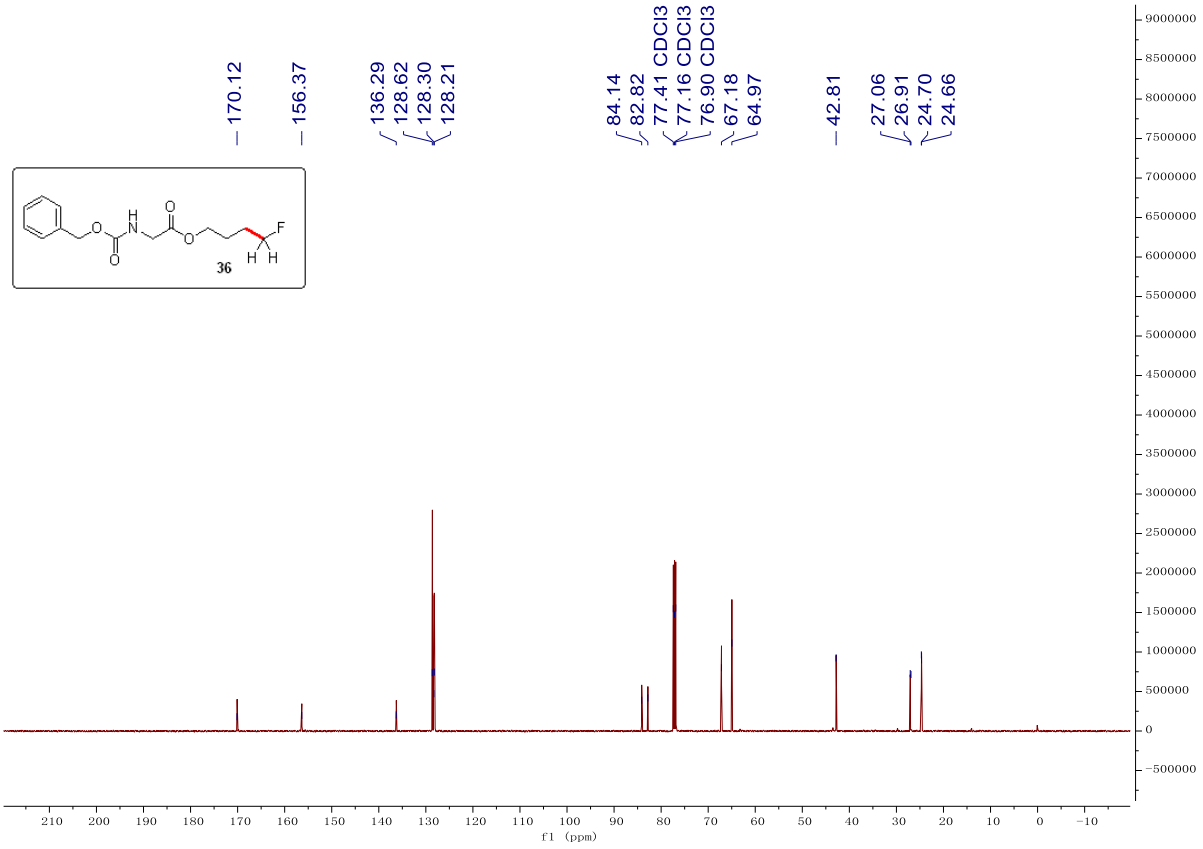
^{13}C NMR Spectrum of **35** ($CDCl_3$, 101 MHz)



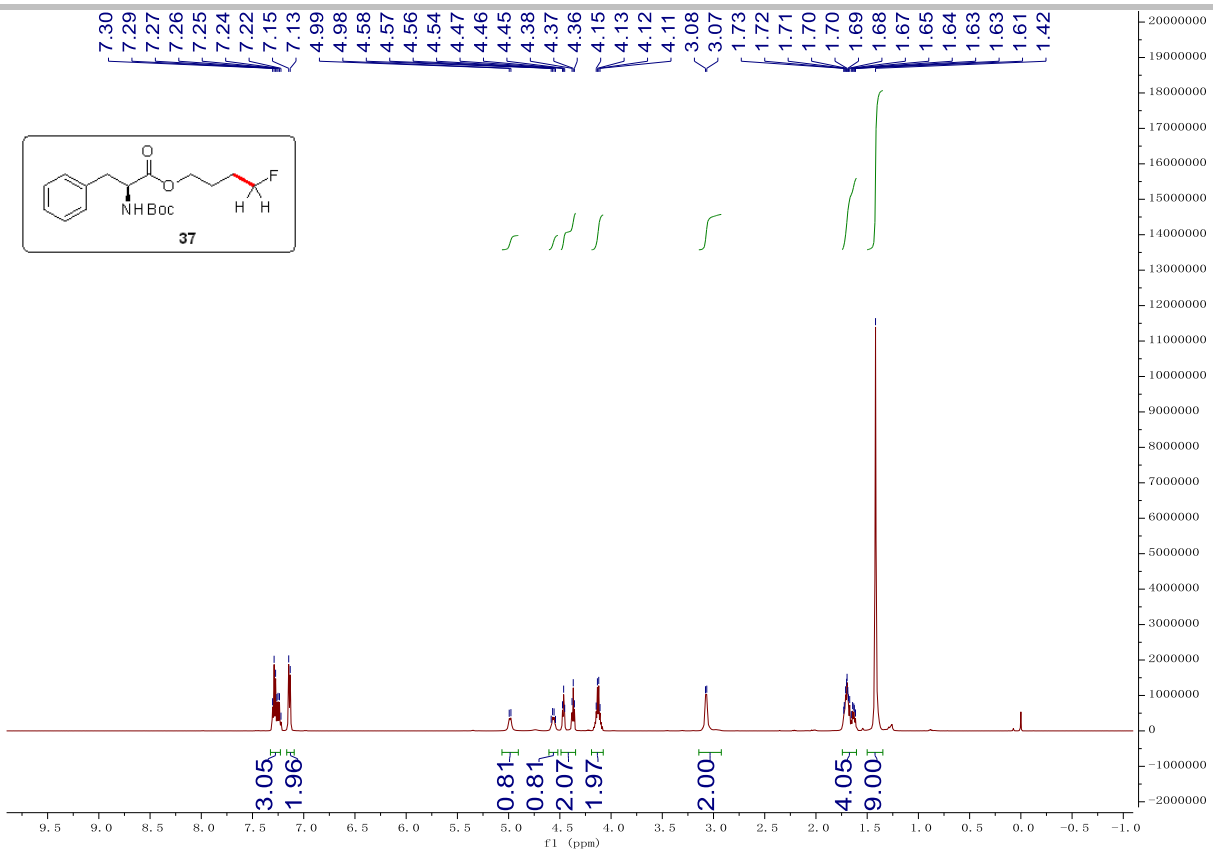
^{1}H NMR Spectrum of of **36** ($CDCl_3$, 400 MHz)



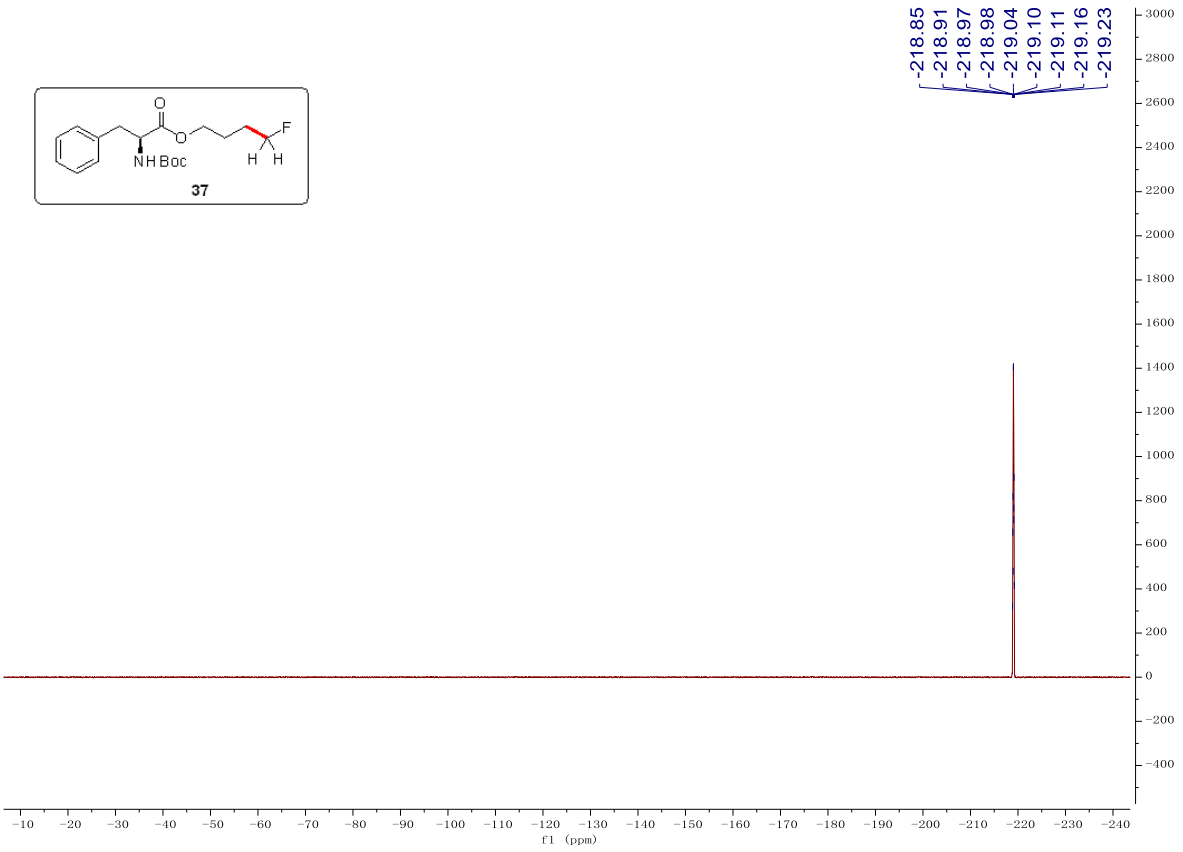
^{19}F NMR Spectrum of of **36** ($CDCl_3$, 376 MHz)



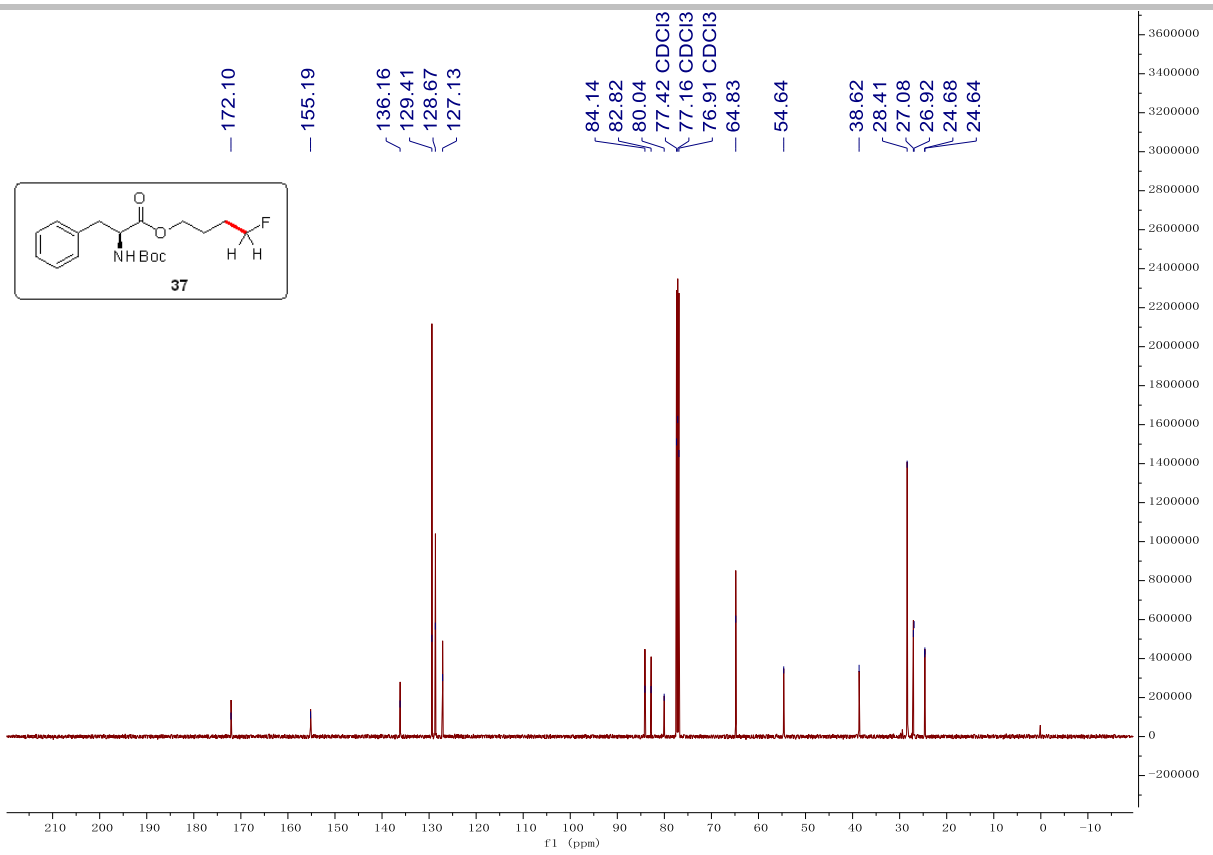
^{13}C NMR Spectrum of **36** ($CDCl_3$, 126 MHz)



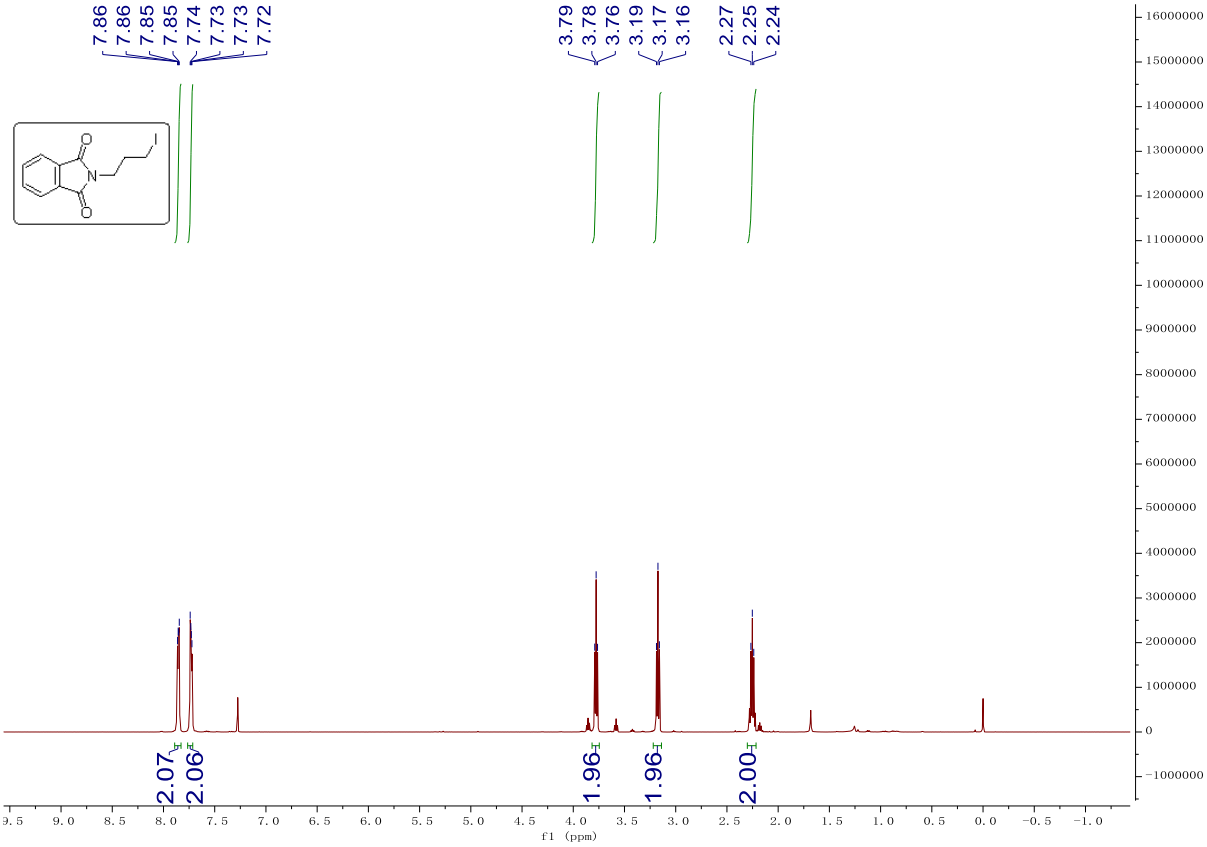
^{1}H NMR Spectrum of of **37** ($CDCl_3$, 500 MHz)



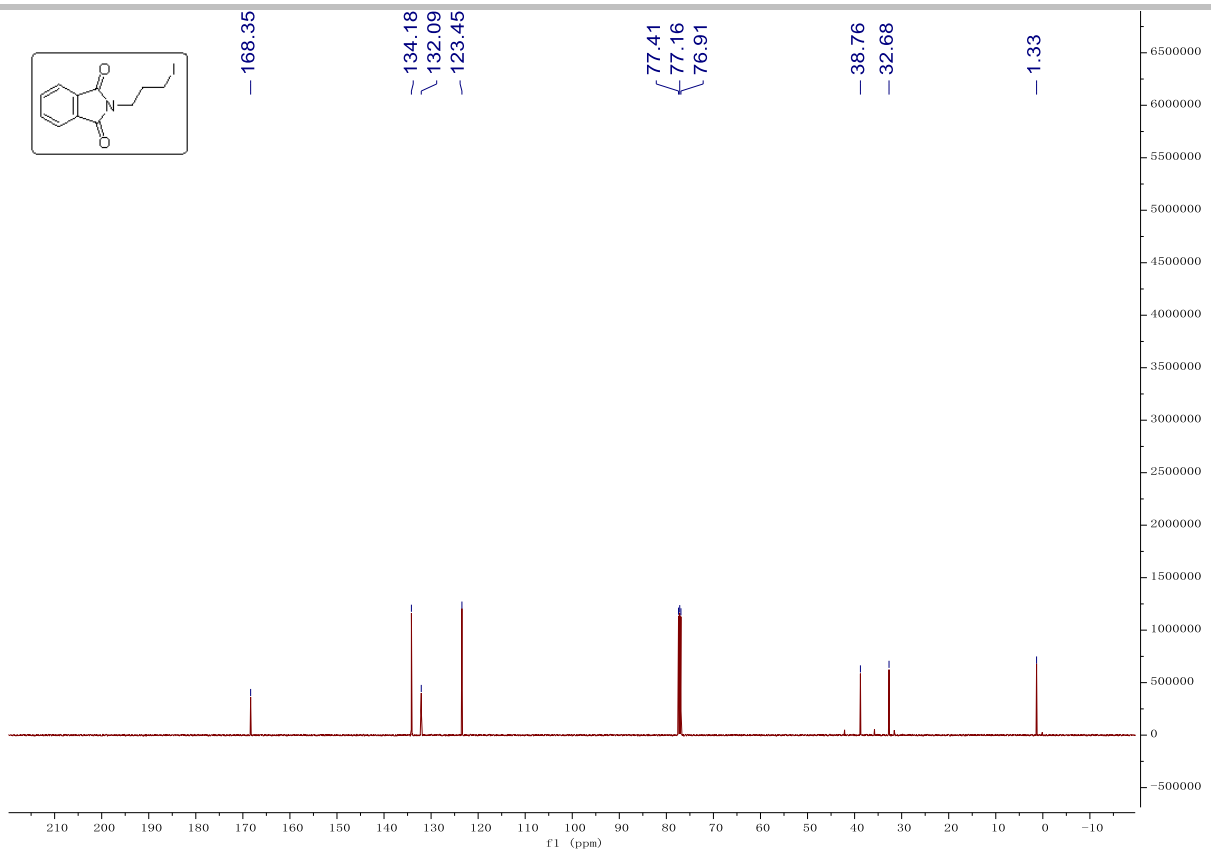
^{19}F NMR Spectrum of of **37** ($CDCl_3$, 376 MHz)



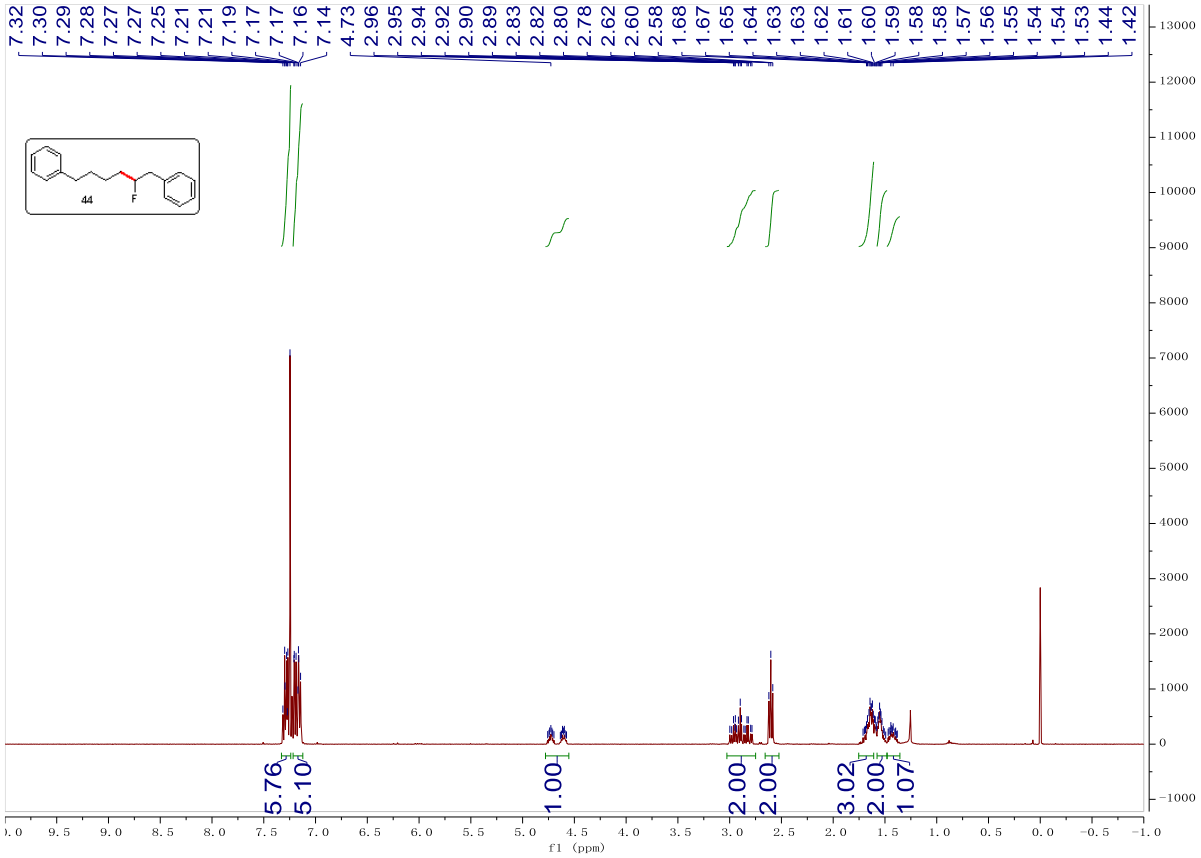
^{13}C NMR Spectrum of **37** ($CDCl_3$, 126 MHz)



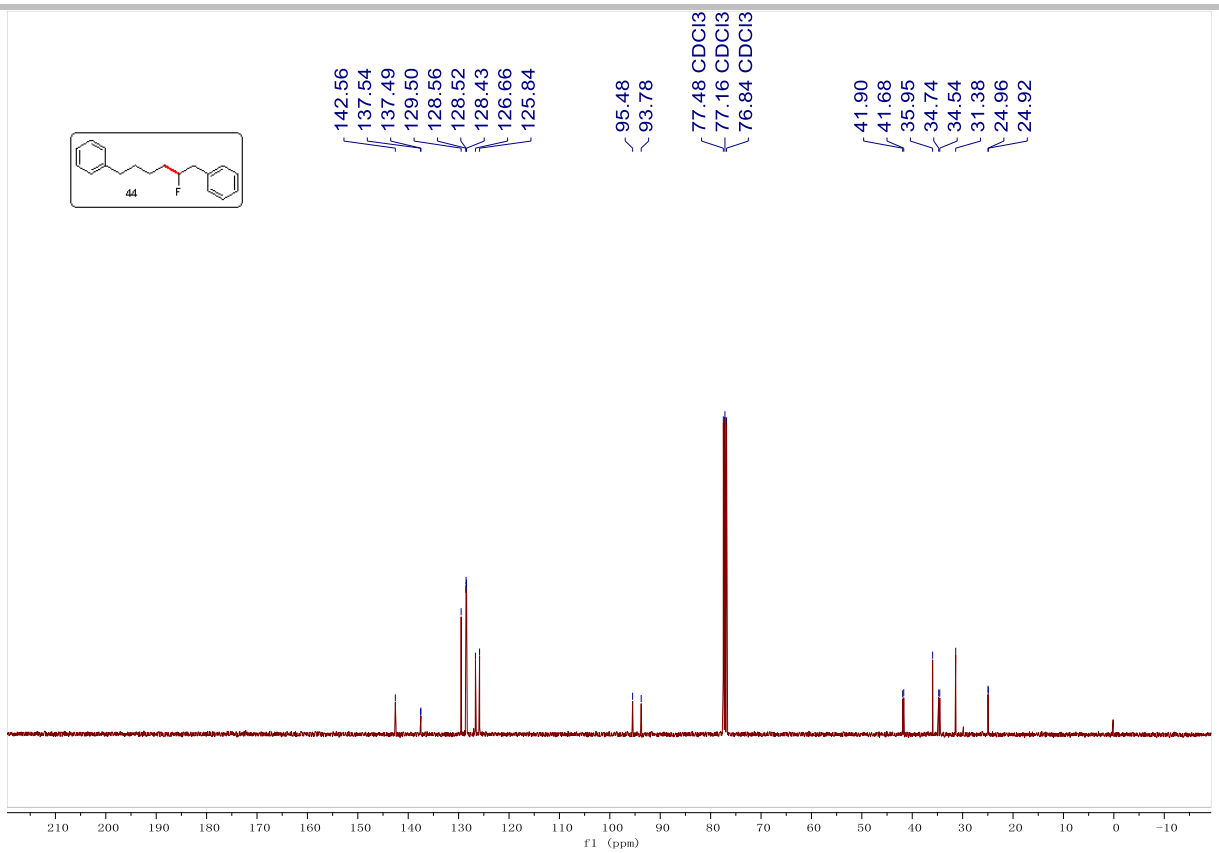
^{1}H NMR Spectrum of of 2-(3-iodopropyl)isoindoline-1,3-dione ($CDCl_3$, 500 MHz)



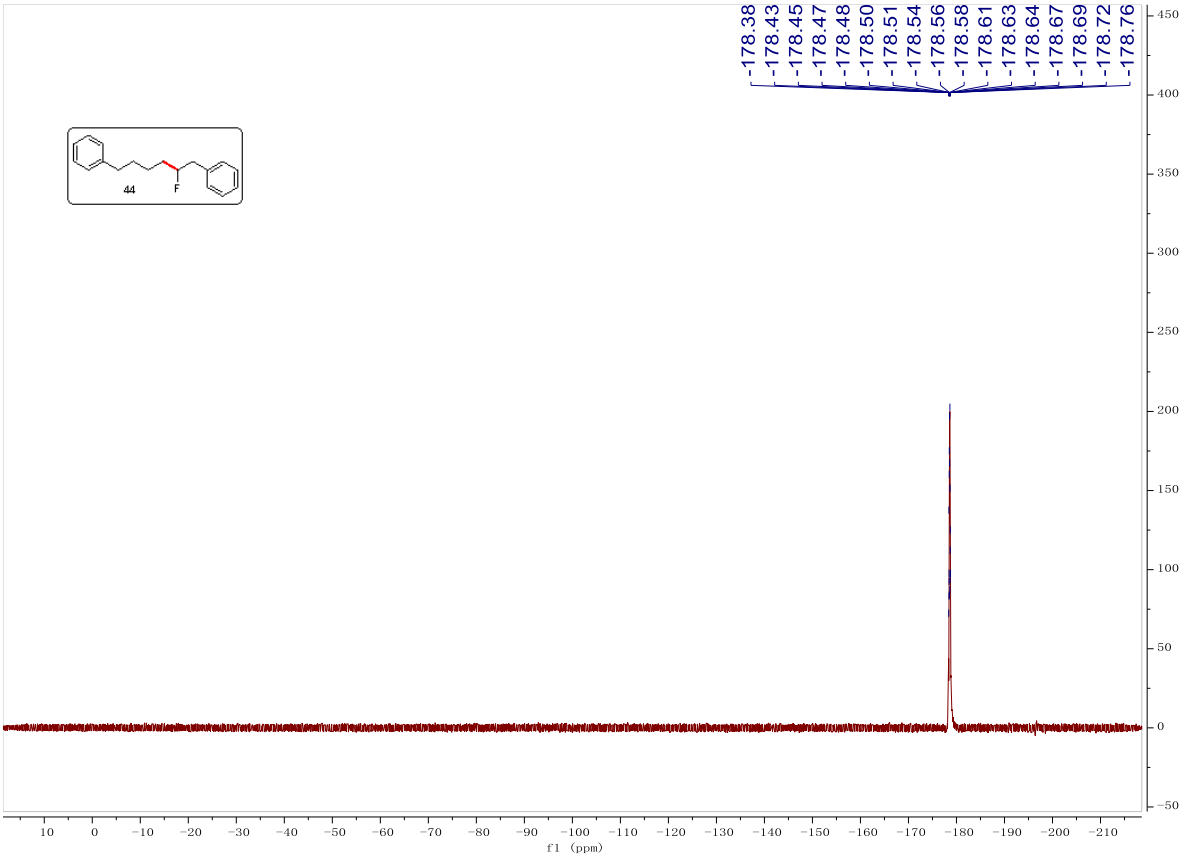
^{13}C NMR Spectrum of 2-(3-iodopropyl)isoindoline-1,3-dione ($CDCl_3$, 126 MHz)



^{1}H NMR Spectrum of compound **44** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **44** ($CDCl_3$, 101 MHz)



^{19}F NMR Spectrum of of **44** ($CDCl_3$, 376 MHz)