Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2024

Supporting Information

YlideFluor-CF_2Cl: A Shelf-Stable, Versatile electrophilic or Radical Chlorodifluoromethylating Reagent

Tian Zhang,[a] Yuhan Zhang,[a] Zimeng Li,[b] Botao Wu [b] and Qilong Shen[a,b,*]

[a]*Henan Institute of Advanced Technology, Zhengzhou University, 97 Wenhua Lu, Zhengzhou, Henan Province, 450003, PR China*

[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai, 200032, PR China*

Email: shenql@sioc.ac.cn

Table of Contents

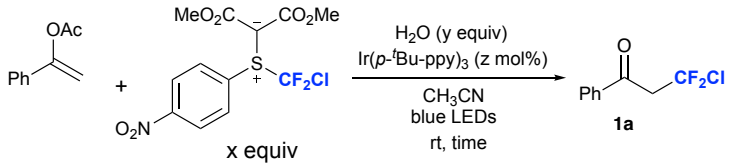
General Information

All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using.

^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz, 125 MHz, 100 MHz, 375 MHz spectrometer (400 MHz for ^{1} H; 100 MHz or 125 MHz for ^{13}C; 375 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300–400 mesh silica gel at medium pressure.

Optimization

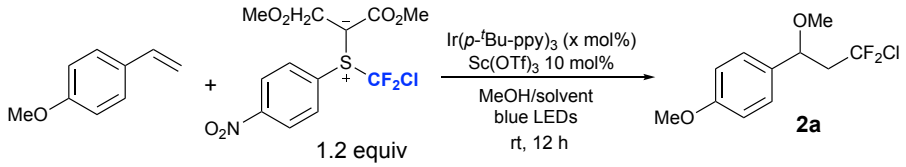
Table S1. Optimization of the reaction conditions for chlorodifluoromethylation of acetoxystyrene derivatives with **YlideFluor-CF_2Cl**.[a,b]



entry	solvent	x	y	z	t (h)	yield (%)
1	CH_3CN	1.0	1.0	1.5	4	66
2	toluene	1.0	1.0	1.5	4	20
3	CH_2Cl_2	1.0	1.0	1.5	4	15
4	THF	1.0	0.0	1.5	4	16
5	DMF	1.0	2.0	1.5	4	53
6	DMSO	1.0	3.0	1.5	4	44
7	CH_3CN	1.0	4.0	1.0	4	57
8	CH_3CN	1.0	1.0	2.0	4	76
9	CH_3CN	1.0	1.0	3.0	4	75
10	CH_3CN	1.2	1.0	2.0	4	77
11	CH_3CN	1.5	1.0	2.0	4	76
12	CH_3CN	1.8	1.0	2.0	4	74
13	CH_3CN	2.0	1.0	2.0	4	77
14	CH_3CN	1.0	0	2.0	4	42
15	CH_3CN	1.0	1.0	2.0	6	90
16	CH_3CN	1.0	1.0	2.0	8	89
17	CH_3CN	1.0	1.0	2.0	12	78
18	CH_3CN	1.0	1.0	2.0	24	72

[a]Reaction conditions: acetoxystyrene (0.1 mmol), **YlideFluor-CF_2Cl** (x equiv.), H_2O (y equiv), catalyst (z mol%), blue LEDs, in solvent (1.0 mL) at room temperature for t h; [b]Yields were determined by ^{19}F NMR spectroscopy with 1-fluoronaphthalene as an internal standard.

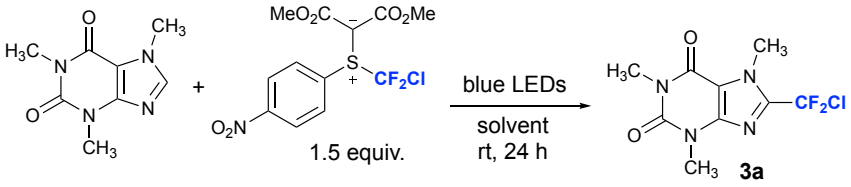
Table S2. Optimization of the reaction conditions for visible-light-promoted chlorodifluoromethylative difunctionalization of styrene derivatives with **YlideFluor-CF_2Cl**.[a,b]



entry	solvent	x	variation	yield (%)
1	DMSO	1	-	34
2	DMF	1	-	65
3	THF	1	-	69
4	CH_2Cl_2	1	-	99
5	CH_3CN	1	-	72
6	CH_2Cl_2	1	6 h	80
7	CH_2Cl_2	0.5	-	79
8	CH_2Cl_2	1	in air	ND
9	CH_2Cl_2	1	no BLEDs	ND
10	CH_2Cl_2	1	no $Sc(OTf)_3$	46

[a]Reaction conditions: 4-methoxystyrene (0.1 mmol), **YlideFluor-CF_2Cl** (0.12 mmol), Ir(*p*-^{t}Bu-ppy)$_3$ (x mol%), $Sc(OTf)_3$ (10 mol%) and methanol (0.2 mL) in solvent (2.0 mL) at room temperature react for 12 h; [b]Yields were determined by ^{19}F NMR spectroscopy with benzotrifluoride as an internal standard.

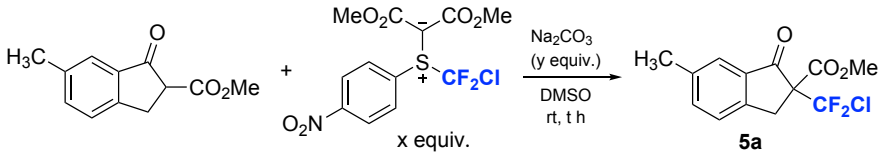
Table S3. Optimization of the reaction conditions for chlorodifluoromethylation of (hetero)cycles with **YlideFluor-CF_2Cl**.[a,b]



entry	solvent	cat.(2 mol%)	yield (%)
1	CH_3CN	$Ir(ppy)_3$	55
2	CH_2Cl_2	$Ir(ppy)_3$	29
3	CH_3CN	-	40
4	DMSO	$Ir(ppy)_3$	68
5	DMF	$Ir(ppy)_3$	23
6	DMSO	Ir(*p*-^{t}Bu-ppy)$_3$	72

[a]Reaction conditions: caffeine (0.1 mmol), **YlideFluor-CF_2Cl** (0.15 mmol) and [Ir] catalyst (2 mol%) in solvent (1.0 mL) at room temperature react for 24 h under blue LEDs; [b]Yields were determined by ^{19}F NMR spectroscopy with benzotrifluoride as an internal standard.

Table S4. Optimization of the reaction conditions for chlorodifluoromethylation of β-ketoesters.[a,b]

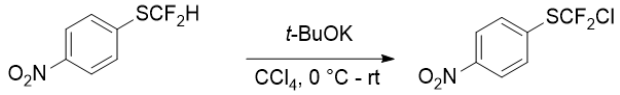


entry	x	y	t (h)	yield (%)
1	1.0	2.0	10	70
2	1.2	2.0	10	79
3	1.5	2.0	10	74
4	2.0	2.0	10	74
5	1.2	0.5	10	62
6	1.2	1.5	10	63
7	1.2	1.5	10	85
8	1.2	1.5	4	36
9	1.2	1.5	6	65
10	1.2	1.5	8	80
11	1.2	1.5	12	92

[a]Reaction conditoins: β-ketoesters (0.1 mmol), **YlideFluor-CF_2Cl** (x equiv.) and Na_2CO_3 (y equiv.) in DMSO (1.0 mL) react for t h; [b]Yields were determined by ^{19}F NMR spectroscopy with 1-fluoronaphthalene as an internal standard.

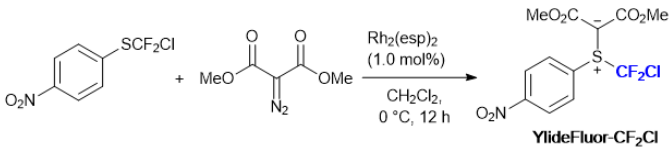
General procedures

General Procedure for Preparation of (Difluoromethyl)(4-nitrophenyl)thioether



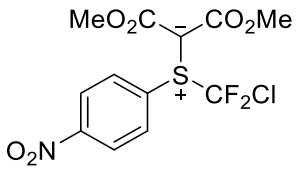
A mixture of (difluoromethyl)(4-nitrophenyl)thioether (10.3 g, 50.0 mmol) and ^{t}BuOK (28.1 g, 250 mmol) in CCl_4 (200 mL) was stirred at 0 ºC for 0.5 h and then was allowed to warm to room temperature for 12 h. Upon completion, Water (100 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was washed with brine (100 mL × 3) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography to give the pure desired product (chlorodifluoromethyl)(4-nitrophenyl)thioether (8.6 g, 72%).

General Procedure for Preparation of (Chlorodifluoromethyl)(4-nitrophenyl) bis(carbomethoxy)methylide (YlideFluor-CF_2Cl)



To an oven-dried 350-mL Schlenk tube was added $Rh_2(esp)_2$ (152 mg, 1.0 mol%), dichloromethane (50 mL) and (chlorodifluoromethyl)(4-nitrophenyl)thioether (4.78 g, 20.0 mmol) under an atmosphere of argon. The mixture was cooled to 0 ºC and dimethyl 2-diazomalonate (4.74 g, 30.0 mmol) was added dropwise. The mixture was stirred at 0 ºC for 12 h and then was allowed to warm to room temperature. The solvent was removed under vacuum. The residue was purified by chromatography to give YlideFluor-CF_2Cl (5.8 g, 78%).

(Chlorodifluoromethyl)(4-nitrophenyl)bis(carbomethoxy)methylide (YlideFluor-CF_2Cl)



Yellow solid(5.8 g, 78%). **m.p.**: 77-79 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.0 Hz, 2 H), 7.97 (d, *J* = 8.6 Hz, 2 H), 3.76 (s, 6 H);

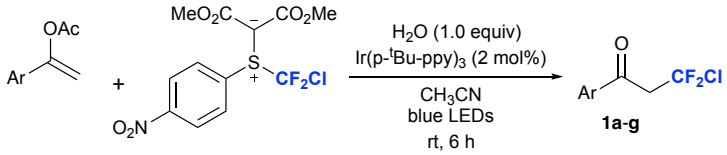
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 150.0, 131.1, 131.0 (t, *J* = 352.7 Hz), 130.0, 124.9, 57.23 (d, *J* = 2.0 Hz), 51.9;

^{19}F NMR (471 MHz, $CDCl_3$) δ -33.27 (d, *J* = 110.9 Hz), -35.80 (d, *J* = 110.8 Hz) ppm.

HRMS (DART POS) for $C_{12}H_{11}ClF_2NO_6S$ ($M+H^+$) Calcd: 369.9958; Found: 369.9958.

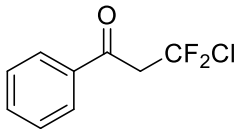
IR (KBr) ν_{max} = 3101, 2952, 1702, 1659, 1530, 1310, 1240, 1107, 855, 772 cm^{-1}.

General Procedure for Visible-light-promoted Chlorodifluoromethylation of Acetoxystyrene Derivatives



To a 25 mL Schlenk tube equipped with a magnetic stirring bar was added reagent YlideFluor-CF_2Cl (180 mg, 0.500 mmol), Ir(*p*-^{t}Bu-ppy)$_3$ (8.2 mg, 2.0 mol%), 1-phenylvinyl acetate (81 mg, 0.50 mmol), H_2O (10 mg, 0.50 mmol) and MeCN (5.0 mL) under argon atmosphere. The mixture was stirred at room temperature under blue LEDs irradiation for 6 h. Water was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer were washed with brine (10 mL × 3) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography to give 3-chloro-3,3-difluoro-1-phenylpropan-1-one **1a**.

3-Chloro-3,3-difluoro-1-phenylpropan-1-one 1a



Yellow oil (86 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 4.00 (t, *J* = 12.3 Hz, 2 H);

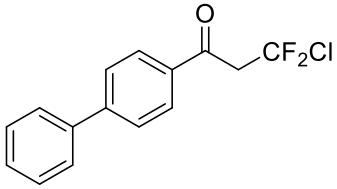
^{13}C NMR (151 MHz, $CDCl_3$) δ 190.0, 135.9, 134.2, 128.9, 128.4, 125.8 (t, *J* = 292.9 Hz), 48.9 (t, *J* = 24.0 Hz);

^{19}F NMR (565 MHz, $CDCl_3$) δ -48.35 (t, *J* = 12.1 Hz, 2 F) ppm.

HRMS (EI) for $C_9H_7ClF_2O$ (M^+) Calcd: 204.0148; Found: 204.0147.

IR (KBr): ν_{max} = 3065, 2930, 1701, 1598, 1361, 1252, 1022, 758, 687, 571 cm^{-1}.

1-([1,1'-Biphenyl]-4-yl)-3-chloro-3,3-difluoropropan-1-one 1b



White solid (118 mg, 84%), **m.p.**: 106-108 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.64 (d, *J* = 7.0 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 4.03 (t, *J* = 12.3 Hz, 2 H);

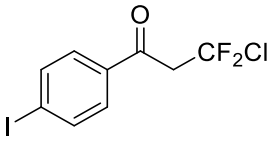
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 146.8, 139.4, 134.5, 129.1, 129.0, 128.5, 127.5, 127.3, 125.7 (t, *J* = 293.5 Hz), 48.9 (t, *J* = 23.8 Hz);

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.17 (t, *J* = 12.2 Hz, 2 F) ppm.

HRMS (EI) for $C_{15}H_{11}ClF_2O$ (M^+) Calcd: 280.0461; Found: 280.0463.

IR (KBr): ν_{max} = 3354, 2961, 1936, 1686, 1360, 1192, 952, 766, 695, 571 cm^{-1}.

3-Chloro-3,3-difluoro-1-(4-iodophenyl)propan-1-one 1c



White solid (113 mg, 69%), **m.p.**: 74-76 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 10.0 Hz, 2 H), 7.64 (d, *J* = 10.0 Hz, 2 H), 3.95 (t, *J* = 12.5 Hz, 2 H);

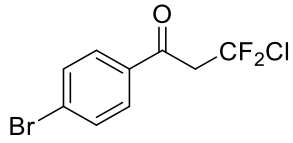
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.1, 138.0, 134.8, 127.5, 125.2 (t, *J* = 293.6 Hz), 102.3, 48.5 (t, *J* = 23.9 Hz);

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.32 (t, *J* = 14.1 Hz, 2 F) ppm.

HRMS (EI) for $C_9H_6OClF_2I$ (M^+) Calcd: 329.9114; Found: 229.9118.

IR (KBr): ν_{max} = 3083, 2929, 1694, 1581, 1364, 1186, 1098, 1020, 959, 812 cm^{-1}.

1-(4-Bromophenyl)-3-chloro-3,3-difluoropropan-1-one 1d



Yellow oil (76 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 12.0 Hz, 2 H), 3.96 (t, *J* = 12.0 Hz, 2 H);

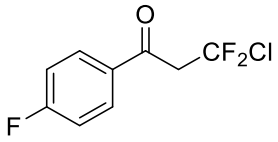
^{13}C NMR (126 MHz, $CDCl_3$) δ 188.8, 140.9, 134.2, 129.8, 129.3, 125.5 (t, *J* = 242.6 Hz), 48.9 (t, *J* = 20.2 Hz);

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.31 (t, *J* = 11.8 Hz, 2 F) ppm.

HRMS (EI) for $C_9H_6BrClF_2O$ (M^+) Calcd: 281.9253; Found: 281.9256.

IR (KBr): ν_{max} = 3377, 2933, 1695, 1585, 1409, 1367, 1249, 1186, 1099, 1021 cm^{-1}.

3-Chloro-3,3-difluoro-1-(4-fluorophenyl)propan-1-one 1e



Yellow oil (79 mg, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2 H), 7.18 (t, *J* = 7.5 Hz, 2 H), 3.97 (t, *J* = 12.5 Hz, 2 H);

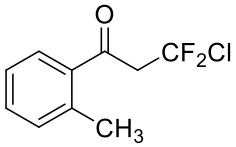
^{13}C NMR (126 MHz, $CDCl_3$) δ 188.40, 166.3 (d, *J* = 258.3 Hz), 132.3, 131.2 (d, *J* = 8.8 Hz), 125.54 (t, *J* = 293.6 Hz), 116.2 (d, *J* = 22.7 Hz), 48.9 (t, *J* = 23.9 Hz);

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.32 (t, *J* = 11.8 Hz, 2 F), -102.87 (m, 1 F) ppm.

HRMS (EI) for $C_9H_6ClF_3O$ (M^+) Calcd: 222.0054; Found: 222.0048.

IR (KBr): ν_{max} = 3079, 2933, 1701, 1600, 1508, 1414, 1362, 1230, 1160, 1089 cm^{-1}.

3-Chloro-3,3-difluoro-1-(o-tolyl)propan-1-one 1f



Yellow oil (84 mg, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 10.0 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 3.95 (t, *J* = 12.5 Hz, 2 H), 2.54 (s, 3 H);

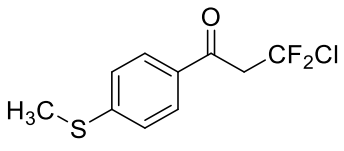
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 139.5, 136.1, 132.5, 132.4, 128.8, 125.9, 125.7 (t, *J* = 293.9 Hz), 51.2 (t, *J* = 23.3 Hz), 21.5;

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.22 (t, *J* = 11.8 Hz, 2 F) ppm.

HRMS (EI) for $C_{10}H_9ClF_2O$ (M^+) Calcd: 218.0309; Found: 218.0307.

IR (KBr): ν_{max} = 3367, 2973, 1699, 1602, 1354, 1222, 1088, 955, 757, 582 cm^{-1}.

3-Chloro-3,3-difluoro-1-(4-(methylthio)phenyl)propan-1-one 1g.



White solid (66 mg, 53%), **m.p.**: 68-70 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 10.0 Hz, 2 H), 7.29 (d, *J* = 10.0 Hz, 2 H), 3.95 (t, *J* = 12.5 Hz, 2 H), 2.53 (s, 3 H);

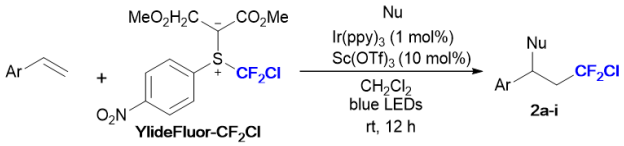
^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 147.7, 132.1, 128.8, 125.7 (t, *J* = 291.9 Hz), 125.0, 48.7 (t, *J* = 23.8 Hz), 14.6;

^{19}F NMR (471 MHz, $CDCl_3$) δ -48.14 (t, *J* = 11.8 Hz, 2 F) ppm.

HRMS (ESI) for $C_{10}H_9ClF_2SO$ ($M+H^+$) Calcd: 250.0025; Found: 250.0023.

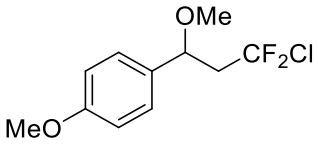
IR (KBr): ν_{max} = 3067, 2921, 1921, 1683, 1588, 1356, 1190, 1081, 986 cm^{-1}.

General Procedure for Visible-light-promoted Chlorodifluoromethylative Difunctionalization of Styrene Derivatives



To a 25 mL Schlenk tube equipped with a magnetic stirring bar was added reagent YlideFluor-CF_2Cl (222 mg, 0.600 mmol), $Ir(ppy)_3$ (3.3 mg, 1.0 mol%), $Sc(OTf)_3$(25 mg, 10 mol%), 4-methoxystyrene (67 mg, 0.50 mmol), MeOH (1.0 mL) and dichloromethane (10 mL) under argon atmosphere. The mixture was stirred at room temperature under blue LEDs irradiation for 12 h. The solvent was removed under vacuum and the residue was purified by chromatography to give 3-chloro-3,3-difluoro-1-(4-methoxyphenyl)propan-1-ol **2a**.

1-(3-Chloro-3,3-difluoro-1-methoxypropyl)-4-methoxybenzene2a



Yellow oil (120 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2 H), 6.91 (d, *J* = 8.7 Hz, 2 H), 4.47 (dd, *J* = 8.2, 3.9 Hz, 1 H), 3.81 (s, 3 H), 3.20 (s, 3 H), 2.94 – 2.78 (m, 1 H), 2.63 – 2.47 (m, 1 H);

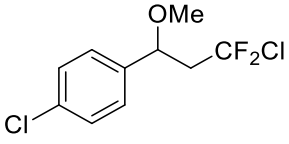
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.62, 132.00, 128.22 (t, *J* = 293.58 Hz), 127.85, 114.11, 78.29 (t, *J* = 3.0 Hz), 56.43, 55.30, 49.72 (t, *J* = 22.9 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -48.01 (ddd, *J* = 160.8, 14.0, 10.4 Hz, 1 F), -49.27 (dt, *J* = 161.2, 13.9 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{11}H_{13}O_2ClF_2$: 250.0567 (M^+), Found: 250.0571.

IR (KBr): ν_{max} = 2937, 2837, 1889, 1613, 1587, 1513, 1465, 1370, 1304, 1251, 1181 cm^{-1}

1-Chloro-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2b



Yellow oil (70 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 4.49 (dd, *J* = 8.1, 4.0 Hz, 1 H), 3.21 (s, 3 H), 2.92 – 2.75 (m, 1 H), 2.62 – 2.45 (m, 1 H);

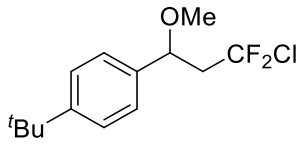
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.59, 134.16, 129.02, 127.97 (t, *J* = 293.58 Hz), 127.97, 78.16 (t, *J* = 2.9 Hz), 56.78, 49.66 (t, *J* = 23.1 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -48.16 (ddd, *J* = 161.5, 13.9, 10.6 Hz, 1 F), -49.32 (dt, *J* = 161.2, 13.6 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{10}H_{10}OCl_2F_2$: 254.0071(M^+), Found: 254.0076.

IR (KBr): ν_{max} = 2936, 2827, 1599, 1490, 1464, 1370, 1210, 1090, 1026, 937 cm^{-1}

1-(*tert*-Butyl)-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2c



Yellow oil (121 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.5 Hz, 2 H), 7.24 (d, *J* = 6.4 Hz, 2 H), 4.50 (dd, *J* = 8.9, 2.7 Hz, 1 H), 3.23 (s, 3 H), 2.94 – 2.77 (m, 1 H), 2.64 – 2.47 (m, 1 H), 1.32 (s, 9 H);

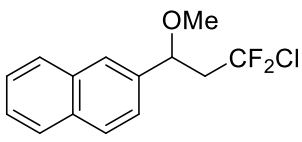
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.34, 136.99, 128.32 (t, *J* = 293.58 Hz), 126.21, 125.66, 78.52 (t, *J* = 2.9 Hz), 56.73, 49.79 (t, *J* = 22.8 Hz), 34.61, 31.35;

^{19}F NMR (376 MHz, $CDCl_3$) δ -47.98 (ddd, *J* = 160.8, 14.4, 10.0 Hz, 1 F), -49.48 (dt, *J* = 160.8, 14.1 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{14}H_{19}OClF_2$: 276.1087(M^+), Found: 276.1084.

IR (KBr): ν_{max} = 2964, 2872, 1614, 1511, 1464, 1364, 1316, 1260, 1214, 1108, 1023, 935, 834 cm^{-1}

2-(3-Chloro-3,3-difluoro-1-methoxypropyl)naphthalene 2d



Yellow oil (102 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 3 H), 7.81 (s, 1 H), 7.57 – 7.49 (m, 2

H), 7.47 (dd, *J* = 8.5, 1.7 Hz, 1 H), 4.72 (dd, *J* = 8.3, 3.9 Hz, 1 H), 3.29 (s, 3 H), 3.06 – 2.92 (m, 1 H), 2.75 – 2.61 (m, 1 H);

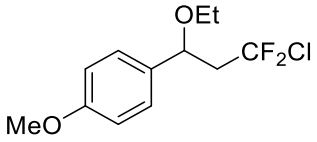
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.41, 133.40, 133.24, 128.94, 128.27 (t, *J* = 293.3 Hz), 127.98, 127.83, 126.50, 126.34, 126.09, 123.87, 78.97 (t, *J* = 2.9 Hz), 56.83, 49.72 (t, *J* = 23.0 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -47.99 (ddd, *J* = 161.4, 14.4, 10.6 Hz, 1 F), -49.27 (dt, *J* = 161.1, 13.8 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{14}H_{13}OClF_2$: 270.0618 (M^+), Found: 270.0619.

IR (KBr): ν_{max} = 3057, 2934, 1602, 1508, 1464, 1364, 1335, 1254, 1208, 1104, 1025, 938, 858 cm^{-1}

1-(3-Chloro-1-ethoxy-3,3-difluoropropyl)-4-methoxybenzene 2e



Yellow oil (105 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.1 Hz, 2 H), 6.89 (d, *J* = 7.1 Hz, 2 H), 4.58 (dd, *J* = 8.5, 4.0 Hz, 1 H), 3.81 (s, 3 H), 3.43 – 3.26 (m, 2 H), 2.94 – 2.77 (m, 1 H), 2.61 – 2.47 (m, 1 H), 1.16 (t, *J* = 6.3 Hz, 3 H);

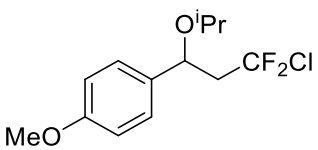
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.49, 132.81, 128.30 (t, *J* = 293.3 Hz), 127.70, 114.04, 76.36 (t, *J* = 3.0 Hz), 64.15, 55.29, 49.88 (t, *J* = 22.7 Hz), 15.11;

^{19}F NMR (376 MHz, $CDCl_3$) δ -47.95 (ddd, *J* = 160.7, 14.4, 10.8 Hz, 1 F), -49.11 (dt, *J* = 160.7, 13.7 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{12}H_{15}O_2ClF_2$: 264.0723 (M^+), Found: 264.0719.

IR (KBr): ν_{max} = 2976, 2876, 1612, 1587, 1512, 1464, 1343, 1251, 1101, 1036, 951, 832 cm^{-1}

1-(3-Chloro-3,3-difluoro-1-isopropoxypropyl)-4-methoxybenzene 2f



Yellow oil (105 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 4.71 (dd, *J* = 8.5, 3.6 Hz, 1 H), 3.80 (s, 3 H), 3.55 – 3.41 (m, 1 H), 2.88 – 2.74 (m, 1 H), 2.56 – 2.43 (m，1 H), 1.16 (d, *J* = 6.1 Hz, 3 H), 1.05 (d, *J* = 6.2 Hz, 3 H);

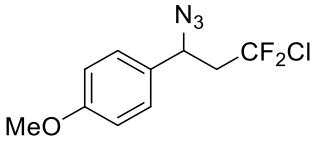
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.38, 133.63, 128.36 (t, *J* = 293.58 Hz), 127.63, 113.98, 73.70 (t, *J* = 2.9 Hz), 69.22, 55.26, 50.26 (t, *J* = 22.3 Hz), 23.33, 20.95;

^{19}F NMR (376 MHz, $CDCl_3$) δ -47.67 (ddd, *J* = 160.1, 14.0, 10.0 Hz, 1 F), -49.19 (dt, *J* = 160.2, 13.9 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{13}H_{17}O_2ClF_2$: 278.0880 (M^+), Found: 278.0882.

IR (KBr): ν_{max} = 2973, 2838, 1612, 1587, 1511, 1465, 1420, 1335, 1251, 1098, 1037, 942, 873 cm^{-1}

1-(1-Azido-3-chloro-3,3-difluoropropyl)-4-methoxybenzene 2g



Yellow oil (68 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.9 Hz, 2 H), 6.93 (d, *J* = 8.7 Hz, 2 H), 4.80 (dd, *J* = 8.1, 5.2 Hz, 1 H), 3.82 (s, 3 H), 2.75 – 2.87 (m, 1 H), 2.61 – 2.73 (m, 1 H);

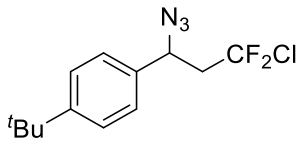
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.01, 129.71, 128.14, 127.70 (t, *J* = 292.8 Hz), 114.48, 60.48, 55.35, 47.78 (t, *J* = 23.6 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.24 (ddd, *J* = 165.44, 14.2, 11.3 Hz, 1 F), -49.92 (dt, *J* = 163.3, 13.0 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{10}H_{10}ON_3ClClF_2$: 261.0475 (M^+), Found: 261.0477.

IR (KBr): ν_{max} = 3335, 2960, 2839, 2486, 2150, 1889, 1612, 1586, 1514, 1442, 1370, 1370, 1251, 1097, 1033, 970 cm^{-1}

1-(1-Azido-3-chloro-3,3-difluoropropyl)-4-(tert-butyl)benzene 2h



Yellow oil (90 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.3 Hz, 2 H), 4.82

(dd, J = 8.7, 4.4 Hz, 1 H), 2.91 – 2.74 (m, 1 H), 2.76 – 2.60 (m, 1 H), 1.32 (s, 9 H);

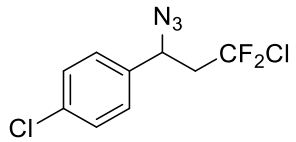
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.10, 134.85, 127.78 (t, J = 293.58 Hz), 126.41, 126.09, 60.64, 47.76 (t, J = 22.68 Hz), 34.69, 31.26;

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.17 (ddd, J = 162.9, 14.0, 10.3 Hz, 1 F), -50.20 (dt, J = 162.8, 13.2 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_{13}H_{16}N_3ClF_2$: 287.0995 (M^+), Found: 287.1001.

IR (KBr): ν_{max} = 3329, 2965, 2486, 2111, 1910, 1613, 1509, 1465, 1419, 1244, 1205, 1100, 1018, 951, 834 cm^{-1}

1-(1-Azido-3-chloro-3,3-difluoropropyl)-4-chlorobenzene 2i



Yellow oil (34 mg, 26%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 6.4 Hz, 2 H), 7.27 (d, J = 6.5 Hz, 2 H), 4.83 (t, J = 5.7 Hz, 1 H), 2.73 – 2.86 (m, 1 H), 2.59 – 2.72 (m, 1 H);

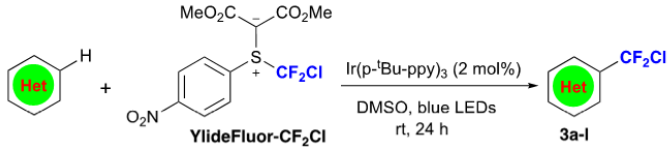
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.31, 134.98, 129.44, 128.18, 127.45 (t, J = 293.58 Hz), 60.32 (t, J = 2.9 Hz), 47.86 (t, J = 23.9 Hz);

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.29 (dt, J = 163.3, 12.2 Hz, 1 F), -50.00 (dt, J = 163.5, 12.9 Hz, 1 F) ppm.

HRMS (EI): Calcd for $C_9H_7N_3Cl_2F_2$: 264.9980 (M^+), Found: 264.9982.

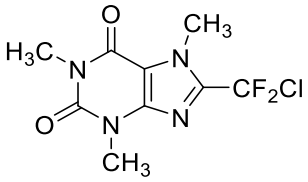
IR (KBr): ν_{max} = 3330, 2923, 2481, 2105, 1903, 1654, 1597, 1493, 1364, 1242, 1094, 1015, 973, 830 cm^{-1}

General procedure for Visible-light-promoted chlorodifluoromethylation of (hetero)cycles



To a 25 mL Schlenk tube equipped with a magnetic stirring bar was added reagent YlideFluor-CF_2Cl (275 mg, 0.750 mmol), Ir(*p*-^{t}Bu-ppy)$_3$ (8.2 mg, 2.0 mol%), caffeine (85 mg, 0.50 mmol) and DMSO (5.0 mL) under argon atmosphere. The mixture was stirred at room temperature under blue LEDs irradiation for 24 h. Water was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (10 mL × 3) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography to give **3a**.

8-(Chlorodifluoromethyl)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3a



White solid (88 mg, 63%), **m.p.**: 91-93 °C.

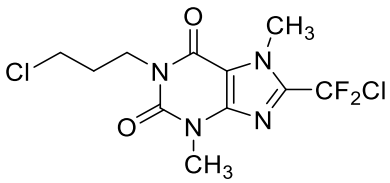
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (s, 3 H), 3.58 (s, 3 H), 3.40 (s, 3 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.54, 151.35, 146.33, 142.53 (t, J = 32.9 Hz), 119.68 (t, J = 288.1 Hz), 109.62, 33.46, 29.92, 28.20;

^{19}F NMR (376 MHz, $CDCl_3$) δ -51.14 ppm.

This compound has been reported by *Org. Lett.* **2017**, *19*, *19*, 5126 – 5129

8-(Chlorodifluoromethyl)-1-(3-chloropropyl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3b



White solid (110 mg, 66%), **m.p.**: 72-73 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.18 (t, *J* = 5.0 Hz, 2 H), 4.16 (s, 3 H), 3.61 (t, *J* = 6.6 Hz, 2 H), 3.59 (s, 3 H), 2.13 – 2.19 (m, 2 H);

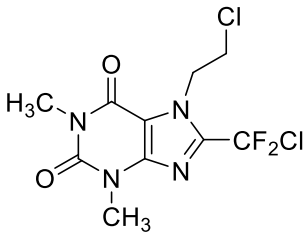
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.35, 151.10, 146.48, 142.70 (t, *J* = 33.0 Hz), 119.64 (t, *J* = 288.3 Hz), 109.60, 42.43, 39.53, 33.50 (t, *J* = 2.6 Hz), 31.02, 29.89;

^{19}F NMR (470 MHz, $CDCl_3$) δ -51.05 ppm.

HRMS (EI): Calcd for $C_{11}H_{12}O_2N_4Cl_2F_2$: 341.0378 ($M^+$+$H^+$), Found: 341.0380.

IR (KBr): ν_{max} = 2961, 2928, 1708, 1666, 1607, 1544, 1503, 1446, 1334, 1366, 1334, 1288, 1231, 1136, 1087, 1000, 870 cm^{-1}

8-(Chlorodifluoromethyl)-7-(2-chloroethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3c



Yellow solid (61 mg, 37%), **m.p.**: 77-78 °C.

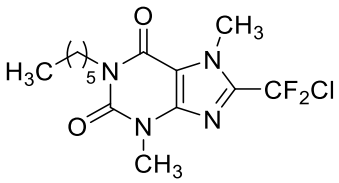
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (t, *J* = 6.8 Hz, 2 H), 3.95 (t, *J* = 6.8 Hz, 2 H), 3.63 (s, 3 H), 3.45 (s, 3 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.17, 151.23, 146.86, 142.78 (t, *J* = 33.0 Hz), 119.77 (t, *J* = 288.3 Hz), 108.98, 47.84 (t, *J* = 2.8 Hz), 41.37, 30.02, 28.34;

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.43 ppm.

This compound has been reported by *Eur. J. Org. Chem.* **2022**, e202200607.

8-(Chlorodifluoromethyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3d



Yellow solid (68 mg, 39%) , **m.p.**: 70-72 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 3 H), 4.02 – 3.98 (m, 2 H), 3.58 (s, 3 H), 1.68 – 1.60 (m, 2 H), 1.29 – 1.40 (m, 6 H), 0.87 – 0.90 (m, 3 H);

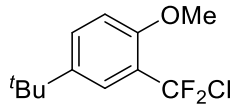
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.43, 151.11, 146.33, 142.45 (t, *J* = 33.0 Hz), 119.71 (t, *J* = 288.2 Hz), 109.70, 41.79, 33.45, 31.51, 29.83, 27.92, 26.63, 22.56, 14.05;

^{19}F NMR (376 MHz, $CDCl_3$) δ -51.10 ppm.

HRMS (EI): Calcd for $C_{14}H_{20}O_2N_4Cl_2F_2$: 349.1237 ($M^+$+$H^+$), Found: 349.1237.

IR (KBr): ν_{max} = 2958, 2856, 1712, 1663, 1607, 1544, 1451, 1383, 1332, 1286, 1230, 1132, 1091, 1002, 916 cm^{-1}

4-(*tert*-Butyl)-2-(chlorodifluoromethyl)-1-methoxybenzene 3e



Colorless oil (66 mg, 53%).

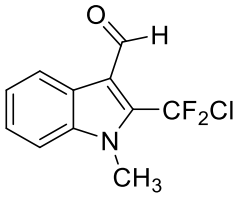
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.5 Hz, 1 H), 7.47 (dd, *J* = 8.7, 2.5 Hz, 1 H), 6.94 (d, *J* = 8.7 Hz, 1 H), 3.91 (s, 3 H), 1.31 (s, 9 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.44 (t, *J* = 2.8 Hz), 142.89, 129.62, 125.32 (t, *J* = 289.9 Hz), 123.57 (t, *J* = 24.6 Hz), 122.46, 112.02, 56.05, 34.27, 31.37;

^{19}F NMR (376 MHz, $CDCl_3$) δ -49.01 ppm.

This compound has been reported by *Org. Lett.* **2018**, *20*, *12*, 3491–3495

2-(Chlorodifluoromethyl)-1-methyl-1*H*-indole-3-carbaldehyde 3f



Yellow solid (67 mg, 55%), **m.p.**: 72-74 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1 H), 8.55 (d, *J* = 8.1 Hz, 1 H), 7.51 – 7.44 (m, 2 H), 7.41 (ddd, *J* = 8.1, 6.6, 1.5 Hz, 1 H), 4.00 (s, 3 H);

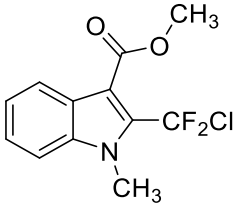
^{13}C NMR (126 MHz, $CDCl_3$) δ 185.93 (t, *J* = 7.8 Hz), 137.64, 136.36 (t, *J* = 33.5 Hz), 126.11, 124.35, 124.21, 124.01, 122.28 (t, *J* = 288.8 Hz), 115.70, 109.93, 31.81;

^{19}F NMR (376 MHz, $CDCl_3$) δ -44.56 ppm.

HRMS (EI): Calcd for $C_{11}H_8ONClF_2$: 243.0257 (M^+), Found: 243.0255.

IR (KBr): ν_{max} = 3060, 2879, 1654, 1577, 1524, 1474, 1400, 1366, 1351, 1223, 1169, 1088, 1029, 946, 810 cm^{-1}

Methyl 2-(chlorodifluoromethyl)-1-methyl-1*H*-indole-3-carboxylate 3g



Yellow solid (79 mg, 58%), **m.p.**: 88-90 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1 H), 7.43 (d, *J* = 3.3 Hz, 2 H), 7.33 (dt, *J* = 8.1, 4.0 Hz, 1 H), 4.00 (s, 3 H), 3.97 (t, *J* = 1.9 Hz, 3 H);

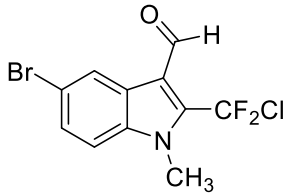
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.03, 136.94, 132.99 (t, *J* = 30.9 Hz), 125.29, 125.25, 122.73, 122.51, 121.80 (t, *J* = 288.9 Hz), 110.08, 108.01, 51.90, 32.19;

^{19}F NMR (376 MHz, $CDCl_3$) δ -44.50 ppm.

HRMS (EI): Calcd for $C_{12}H_{10}O_2NClF_2$: 273.0363 (M^+), Found:273.0358.

IR (KBr): νmax = 3077, 2950, 1716, 1576, 1543, 1471, 1436, 1404, 1335, 1274, 1236, 1201, 1112, 1076, 1019, 922 cm^{-1}

5-Bromo-2-(chlorodifluoromethyl)-1-methyl-1*H*-indole-3-carbaldehyde 3h



Yellow solid (60 mg, 37%), **m.p.**: 134-136 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (s, 1 H), 8.69 (d, *J* = 1.9 Hz, 1 H), 7.54 (dd, *J* = 8.9, 2.0 Hz, 1 H), 7.30 (d, *J* = 8.8 Hz, 1 H), 3.96 (s, 3 H);

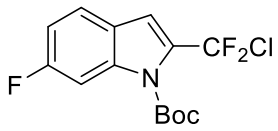
^{13}C NMR (126 MHz, $CDCl_3$) δ 185.52 (t, *J* = 7.9 Hz), 136.92 (t, *J* = 33.7 Hz), 136.29, 129.29, 126.50, 125.58, 121.92 (t, *J* = 289.0 Hz), 117.93, 114.98, 111.44, 32.03;

^{19}F NMR (376 MHz, $CDCl_3$) δ -45.13 ppm.

HRMS (EI): Calcd for $C_{11}H_7ONBrClF_2$: 320.9362 (M^+), Found: 320.9359.

IR (KBr): ν_{max} = 3069, 2901, 1654, 1606, 1572, 1522, 1471, 1397, 1342, 1224, 1141, 1087, 1051, 953 cm^{-1}

***tert*-Butyl 2-(chlorodifluoromethyl)-6-fluoro-1*H*-indole-1-carboxylate 3i**



Yellow oil (100 mg, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 10.6, 2.4 Hz, 1 H), 7.48 (dd, *J* = 8.6, 5.5 Hz, 1 H), 7.01 (d, *J* = 0.8 Hz, 1 H), 6.99 (td, *J* = 8.9, 2.4 Hz, 1 H), 1.63 (s, 9 H);

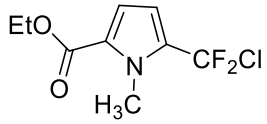
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.33 (d, *J* = 243.3 Hz), 148.44, 138.26, 132.17 (t, *J* = 34.0 Hz), 123.05 (d, *J* = 10.2 Hz), 122.60, 121.62 (t, *J* = 285.3 Hz), 112.43 (d, *J* = 24.8 Hz), 112.22 (t, *J* = 6.1 Hz), 103.40 (d, *J* = 29.4 Hz), 86.22, 27.92;

^{19}F NMR (376 MHz, $CDCl_3$) δ -44.53, -112.93 ppm.

HRMS (EI): Calcd for $C_9H_5NClF_3$: 319.0057 (M^+), Found: 319.0060.

IR (KBr): ν_{max} = 3130, 2986, 1745, 1632, 1556, 1488, 1435, 1373, 1329, 1297, 1260, 1175, 1141, 1047, 1000, 857 cm^{-1}

Ethyl 5-(chlorodifluoromethyl)-1-methyl-1*H*-pyrrole-2-carboxylate 3j



Yellow oil (94 mg, 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, *J* = 4.2 Hz, 1 H), 6.53 (d, *J* = 4.2 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 4.09 (s, 3 H), 1.39 (t, *J* = 7.1 Hz, 3H);

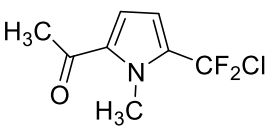
^{13}C NMR (151 MHz, $CDCl_3$) δ 160.88, 131.59 (t, *J* = 32.3 Hz), 126.78, 121.80 (t,*J* = 285.39 Hz), 115.79, 109.72 (t, *J* = 4.2 Hz), 60.50, 33.81, 14.32;

^{19}F NMR (376 MHz, $CDCl_3$) δ -46.44 ppm.

HRMS (EI): Calcd for $C_9H_{10}O2NClF_2$: 237.0363 (M^+), Found: 237.0364

IR (KBr): ν_{max} = 2984, 1803, 1717, 1539, 1488, 1397, 1247, 1107, 1035 cm^{-1}

1-(5-(Chlorodifluoromethyl)-1-methyl-1*H*-pyrrol-2-yl)ethan-1-one 3k



Yellow oil (80 mg, 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88 (d, *J* = 4.3 Hz, 1 H), 6.52 (d, *J* = 4.3 Hz, 1 H), 4.06

(s, 3 H), 2.48 (s, 3 H);

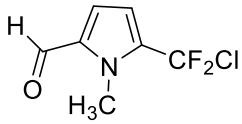
^{13}C NMR (151 MHz, $CDCl_3$) δ 189.83, 133.75, 132.59 (t, *J* = 32.2 Hz), 121.77 (t, *J* = 285.39 Hz), 117.40, 109.58 (t, *J* = 4.2 Hz), 34.46, 27.95;

^{19}F NMR (376 MHz, $CDCl_3$) δ -46.46 ppm.

HRMS (EI): Calcd for $C_8H_8ClF_2NO$: 207.0257 (M^+), Found: 207.0255

IR (KBr): ν_{max} = 3137, 2965, 1801, 1671, 1535, 1487, 1382, 1341, 1242, 1069 cm^{-1}

5-(Chlorodifluoromethyl)-1-methyl-1*H*-pyrrole-2-carbaldehyde 3l



Yellow oil(75 mg, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.68 (s, 1 H), 6.87 (d, *J* = 4.2 Hz, 1 H), 6.60 (d, *J* = 4.2 Hz, 1 H), 4.10 (s, 3 H);

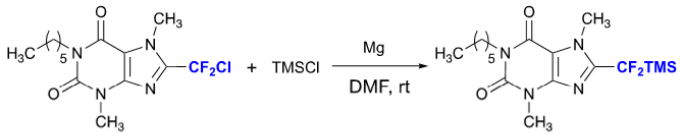
^{13}C NMR (151 MHz, $CDCl_3$) δ 181.13, 134.48, 133.93 (t, *J* = 32.2 Hz), 121.90, 121.54 (t, *J* = 285.8 Hz), 110.64 (t, *J* = 4.0 Hz), 33.81;

^{19}F NMR (376 MHz, $CDCl_3$) δ -46.95 ppm.

HRMS (EI): Calcd for $C_7H_6ClF_2NO$: 193.0100 (M^+), Found: 193.0097

IR (KBr): ν_{max} = 3139, 2960, 2255, 1682, 1534, 1470, 1390, 1337,1220, 1114, cm^{-1}

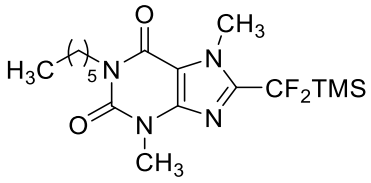
General procedure for preparation of 8-(difluoro(trimethylsilyl)methyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 4



3d **4**, 60%

To anhydous DMF (0.2 mL) were added magnesium powder (4.8 mg, 0.2 mmol) and chlorotrimethylsilane (25 μL, 0.4 mmol) under an atmosphere of argon. Then **3d** (35 mg, 0.10 mmol) was added dropwise. The reaction was exothermic and the mixture was stirred until it turned brown. The mixture was extracted with Et_2O (2.0 mL × 3). The organic layer washed with H_2O (2.0 mL × 3), dried over $MgSO_4$ and then purified by flash chromatography to afford compound **4** (23 mg, 60%) as a colourless liquid.

8-(Difluoro(trimethylsilyl)methyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 4



Yellow solid (23 mg, 60%), **m.p.**: 78-80 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (s, 3 H), 4.05 – 3.97 (m, 2 H), 3.55 (s, 3 H), 1.70 – 1.60 (m, 2 H), 1.42 – 1.31 (m, 6 H), 0.94 – 0.87 (m, 3 H), 0.37 (s, 9 H);

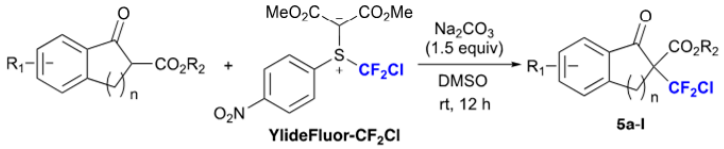
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.59, 151.32, 146.59, 146.13 (t, J = 26.3 Hz), 124.14 (t, J = 254.9 Hz), 109.01, 41.58, 33.16, 31.54, 29.57, 28.00, 26.66, 22.58, 14.07, -3.95;

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.42 ppm.

HRMS (EI): Calcd for $C_{17}H_{28}O_2N_4F_2Si$: 386.1944 (M^+), Found: 386.1942.

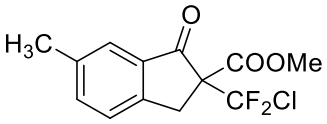
IR (KBr): ν_{max} = 2959, 2857, 1718, 1655, 1607, 1547, 1442, 1290, 1086, 966 cm^{-1}

General Procedure for Chlorodifluoromethylation of β-Ketoesters



To a 25 mL Schlenk tube equipped with a magnetic stirring bar was added reagent YlideFluor-CF_2Cl (221 mg, 0.600 mmol), β-ketoesters (102 mg, 0.500 mmol), Na_2CO_3 (79 mg, 0.75 mmol) and DMSO (5.0 mL) under argon atmosphere. The mixture was stirred at room temperature for 12 h. Water was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer were washed with brine (10 mL × 3) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by chromatography to give **5a**.

Methyl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5a



Yellow oil (129 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 7.49 (d, *J* = 7.8 Hz, 1 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 3.76 (s, 3 H), 3.75 (d, *J* = 18.4 Hz, 1 H),3.58 (d, *J* = 17.7 Hz, 1 H), 2.40 (s, 3 H);

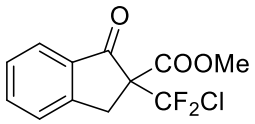
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 165.7, 148.9, 138.6, 137.5, 134.7, 126.8 (t, *J* = 299.9 Hz), 125.9, 125.2, 67.5 (t, *J* = 21.4 Hz), 53.4, 35.4, 20.9;

^{19}F NMR (470 MHz, $CDCl_3$) δ -55.25 (d, *J* = 166.4 Hz, 1 F), δ -56.67 (d, *J* = 166.4 Hz, 1 F) ppm.

HRMS (EI) for $C_{13}H_{11}ClF_2O_3$ (M^+) Calcd: 288.0359; Found: 288.0358.

IR (KBr): ν_{max} = 2958, 1759, 1618, 1587, 1497, 1283, 1222, 1154, 970 cm^{-1}.

Methyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5b



Yellow oil (129 mg, 94%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 6.0 Hz, 1 H), 7.70 (t, *J* = 6.0 Hz, 1 H), 7.55 (d, *J* = 6.0 Hz, 1 H), 7.46 (t, *J* = 9.0 Hz, 1 H), 3.82 (d, *J* = 18.0 Hz, 1 H), 3.77 (s, 3 H), 3.67 (d, *J* = 18.0 Hz, 1 H);

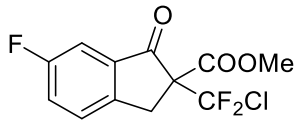
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 165.7, 151.4, 136.2, 134.5, 128.4, 126.7 (t, *J* = 300.1 Hz), 126.2, 125.5, 67.3 (t, *J* = 21.4 Hz), 53.5, 35.7;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.05 (d, *J* = 166.6 Hz, 1 F), δ -56.34 (d, *J* = 166.6 Hz, 1 F) ppm.

HRMS (EI) for $C_{12}H_9ClF_2O_3$ (M^+) Calcd: 274.0203; Found: 274.0208.

IR (KBr): ν_{max} = 3439, 2958, 2846, 1756, 1607, 1592, 1435, 1275, 1193, 1087 cm^{-1}.

Methyl 2-(chlorodifluoromethyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5c



Yellow liquid (143 mg, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.3, 4.1 Hz, 1 H), 7.43 – 7.37 (m, 2 H), 3.77 – 3.73 (m, 4 H), 3.60 (d, *J* = 17.7 Hz, 1 H);

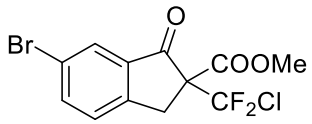
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 165.3 (d, *J* = 3.5 Hz), 162.6 (d, *J* = 250.1 Hz), 146.9, 136.2, 127.8 (d, *J* = 8.1 Hz), 126.5 (t, *J* = 301.1 Hz), 124.1 (d, *J* = 24.1 Hz), 111.1 (d, *J* = 22.6 Hz), 68.0 (t, *J* = 22.1 Hz), 53.7, 35.5;

^{19}F NMR (470 MHz, $CDCl_3$) δ -55.50 (d, *J* = 167.1 Hz, 1 F), δ -56.77 (d, *J* = 166.9 Hz, 1 F), -112.54 (s, 1 F) ppm.

HRMS (EI) for $C_{12}H_8ClF_3O_3$ (M^+) Calcd: 292.0109; Found: 292.0112.

IR (KBr): ν_{max} = 3072, 2960, 1760, 1492, 1437, 1269, 1224, 1190, 1156, 1056 cm^{-1}.

Methyl 6-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5d



Yellow solid (151 mg, 86%), **m.p.**: 72-74 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.6 Hz, 1 H), 7.78 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.42 (d, *J* = 8.2 Hz, 1 H), 3.78 (s, 3 H), 3.75 (d, *J* = 17.9 Hz, 1 H), 3.59 (d, *J* = 17.9 Hz, 1 H);

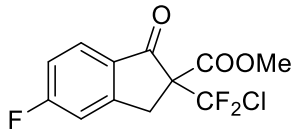
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 165.2 (d, *J* = 4.1 Hz), 149.9, 139.0, 136.3, 128.3, 127.8, 126.5 (t, *J* = 299.9 Hz), 122.6, 67.8 (t, *J* = 22.1 Hz), 53.7, 35.4;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.39 (d, *J* = 167.1 Hz, 1 F), δ -56.62 (d, *J* = 167.1 Hz, 1 F) ppm.

HRMS (EI) for $C_{12}H_8BrClF_2O_3$ (M^+) Calcd: 351.9313; Found: 351.9308.

IR (KBr): ν_{max} = 3033, 2838, 1763, 1599, 1432, 1292, 1204, 1114, 1040, 974 cm^{-1}.

Methyl 2-(chlorodifluoromethyl)-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5e



Yellow solid (114 mg, 78%), **m.p.**: 64-96 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 5.2 Hz, 1 H), 7.22 – 7.13 (m, 2 H), 3.79 – 3.82 (m, 4 H), 3.63 (d, *J* = 18.0 Hz, 1 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 167.9 (d, *J* = 250.7 Hz), 165.4 (d, *J* = 3.6 Hz), 154.4, 130.9, 128.0 (d, *J* = 11.1 Hz), 126.6 (t, *J* = 300.1 Hz), 117.0 (d, *J* = 24.3 Hz), 113.1 (d, *J* = 22.9 Hz), 67.6 (t, *J* = 22.1 Hz), 53.7, 35.5;

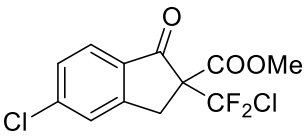
^{19}F NMR (470 MHz, $CDCl_3$) δ -55.51 (d, *J* = 166.8 Hz, 1 F), δ -56.77 (d, *J* = 166.8 Hz, 1 F), -99.2 (s, 1 F) ppm.

HRMS (EI) for $C_{12}H_8ClF_3O_3$ (M^+) Calcd: 292.0109; Found: 292.0106.

IR (KBr): ν_{max} = 3077, 2963, 1754, 1616, 1481, 1341, 1262, 1151, 1066, 937 cm^{-1}.

Methyl 5-chloro-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-

carboxylate 5f



Yellow solid (150 mg, 97%), **m.p.**: 96-98 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.0 Hz, 1 H), 7.53 (s, 1 H), 7.44 (d, *J* = 6.0 Hz, 1 H), 3.78 (d, *J* = 18.0 Hz, 1 H), 3.78 (s, 3 H), 3.63 (d, *J* = 18.0 Hz, 1 H);

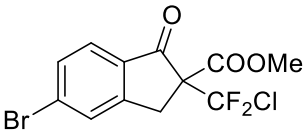
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 165.3, 152.8, 143.0, 133.0, 129.4, 126.6, 126.5, 126.5 (t, *J* = 300.1 Hz), 67.5 (t, *J* = 22.1 Hz), 53.7, 35.4;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.43 (d, *J* = 163.9 Hz, 1 F), δ -56.65 (d, *J* = 163.9 Hz, 1 F) ppm.

HRMS (EI) for $C_{12}H_8Cl_2F_2O_3$ (M^+) Calcd: 307.9813; Found: 307.9820.

IR (KBr): ν_{max} = 3431, 2963, 1755, 1598, 1445, 1325, 1281, 1146, 1052, 965 cm^{-1}.

Methyl 5-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5g



Yellow solid (160 mg, 91%), **m.p.**: 96-98 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.60 (d, *J* = 8.2 Hz, 1 H), 3.80 – 3.78 (m, 4 H), 3.63 (d, *J* = 17.9 Hz, 1 H);

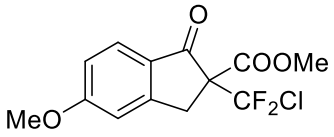
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 165.3 (d, *J* = 3.5 Hz), 152.8, 133.4, 132.2, 131.9, 129.6, 126.6, 126.5 (t, *J* = 300.5 Hz), 67.4 (t, *J* = 22.1 Hz), 53.7, 35.3;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.41 (d, *J* = 167.1 Hz, 1 F), δ -56.64 (d, *J* = 166.9 Hz, 1 F) ppm.

HRMS (EI) for $C_{12}H_8BrClF_2O_3$ (M^+) Calcd: 351.9308; Found: 351.9315.

IR (KBr): ν_{max} = 2963, 1755, 1594, 1437, 1323, 1221, 1053, 946, 837, 750 cm^{-1}.

Methyl 2-(chlorodifluoromethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5h



Yellow oil (123 mg, 81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 1 H), 7.28 (dd, *J* = 8.4, 2.5 Hz, 1 H), 7.24 (d, *J* = 2.4 Hz, 1 H), 3.85 (s, 3 H), 3.78 (s, 3 H), 3.71 (d, *J* = 17.5 Hz, 1 H), 3.58 (d, *J* = 17.5 Hz, 1 H);

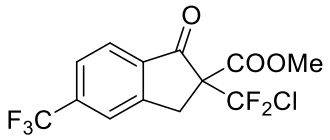
^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 165.7, 160.0, 144.4, 135.8, 126.9, 126.7 (t, *J* = 299.9 Hz), 125.8, 106.2, 67.9 (t, *J* = 22.4 Hz), 55.6, 53.5, 35.1;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.23 (d, *J* = 166.6 Hz, 1 F), δ -56.61 (d, *J* = 166.6 Hz, 1 F) ppm.

HRMS (EI) for $C_{13}H_{11}ClF_2O_4$ (M^+) Calcd: 304.0308; Found: 304.0314.

IR (KBr): ν_{max} = 3010, 2958, 1759, 1618, 1496, 1435, 1281, 1166, 1055, 971 cm^{-1}.

Methyl 2-(chlorodifluoromethyl)-1-oxo-5-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 5i



Yellow oil (135 mg, 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 7.93 (d, *J* = 8.1 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 3.88 (d, *J* = 18.2 Hz, 1 H), 3.78 (s, 3 H), 3.72 (d, *J* = 18.2 Hz, 1 H);

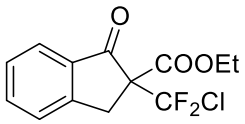
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.82, 165.11, 154.51, 135.02, 132.67 (q, *J* = 3.4 Hz), 131.42 (q, *J* = 33.4 Hz), 127.21, 126.46 (t, *J* = 300.0 Hz), 123.36 (q, *J* = 272.6 Hz), 122.76 (q, *J* = 3.9 Hz), 67.64 (t, *J* = 21.4 Hz), 53.80, 35.83;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.53 (d, *J* = 167.5 Hz, 1 F), δ -56.70 (d, *J* = 167.2 Hz, 1 F), -62.74 (s, 3 F) ppm.

HRMS (EI) for $C_{13}H_8ClF_5O_3$ (M^+) Calcd: 342.0077; Found: 342.0073.

IR (KBr): ν_{max} = 2961, 1763, 1627, 1438, 1332, 1256, 1171, 1131, 1058, 972 cm^{-1}.

Ethyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5j



Yellow oil (138 mg, 96%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 6.0 Hz, 1 H), 7.67 (t, *J* = 9.0 Hz, 1 H), 7.52 (d, *J* = 12.0 Hz, 1 H), 7.43 (t, *J* = 6.0 Hz, 1 H), 4.27 – 4.17 (m, 2 H)., 3.80 (d, *J* = 18.0 Hz, 1 H), 3.64 (d, *J* = 18.0 Hz, 1 H), 1.21 (t, *J* = 6.0 Hz, 3 H);

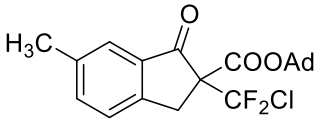
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 165.1, 151.4, 136.1, 134.5, 128.3, 126.8 (t, *J* = 300.0 Hz), 126.2, 125.4, 67.4 (t, *J* = 22.1 Hz), 62.7, 35.7, 13.7;

^{19}F NMR (565 MHz, $CDCl_3$) δ -55.17 (d, *J* = 163.9 Hz, 1 F), δ -56.31 (d, *J* = 169.5 Hz, 1 F) ppm.

HRMS (EI) for $C_{13}H_{11}ClF_2O_3$ (M^+) Calcd: 288.0359; Found: 288.0355.

IR (KBr): ν_{max} = 2985, 1756, 1608, 1466, 1276, 1215, 1049, 937, 887, cm^{-1}.

(3s,5s,7s)-Adamantan-1-yl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5k



Yellow oil (114 mg, 56%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 7.47 (d, *J* = 7.8 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 1 H), 3.68 (d, *J* = 17.6 Hz, 1 H), 3.55 (d, *J* = 17.6 Hz, 1 H), 2.41 (s, 3 H), 2.15 – 2.12 (m, 3 H), 2.05 (d, *J* = 3.0 Hz, 6 H), 1.61 (q, *J* = 4.8, 3.9 Hz, 6 H);

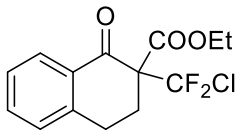
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 163.8, 148.9, 138.4, 137.2, 135.1, 127.0 (t, *J* = 300.5 Hz), 125.8, 125.2, 84.21, 68.5 (t, *J* = 20.8 Hz), 40.8, 35.9, 35.6, 30.8, 21.0;

^{19}F NMR (470 MHz, $CDCl_3$) δ -55.07 (d, *J* = 166.1 Hz, 1 F), δ -56.95 (d, *J* = 165.9 Hz, 1 F) ppm.

HRMS (EI) for $C_{22}H_{23}ClF_2O_3$ (M^+) Calcd: 408.1298; Found: 408.1300.

IR (KBr): ν_{max} = 3431, 2913, 1724, 1618, 1496, 1258, 1104, 1049, 933 cm^{-1}.

2,2-Dimethyl-3,4-dihydronaphthalen-1(2*H*)-one 5l



Yellow oil (75 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.0 Hz, 1 H), 7.51 (t, *J* = 9.0 Hz, 1 H), 7.35 (t, *J* = 9.0 Hz, 1 H), 7.24 (d, *J* = 6.0 Hz, 1 H), 4.26 – 4.20 (m, 2 H), 3.03 (s, 2 H), 2.89 (d, *J* = 18.0 Hz, 1 H), 2.57 – 2.50 (m, 1 H), 1.19 – 1.15 (m, 3 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 165.2, 141.9, 134.1, 131.7, 128.6, 128.4, 127.5 (t, *J* = 300.7 Hz), 127.2, 66.0 (t, *J* = 20.2 Hz), 62.9, 28.7, 25.3, 13.8;

^{19}F NMR (565 MHz, $CDCl_3$) δ -53.59 (d, *J* = 169.5 Hz, 1 F), δ -55.30 (d, *J* = 169.5 Hz, 1 F) ppm.

HRMS (FI) for $C_{14}H_{13}O_3ClF_2$ (M^+) Calcd: 302.0516; Found: 302.0522.

IR (KBr): ν_{max} = 2984, 1740, 1602, 1456, 1305, 1207, 1105, 1002, 960 cm^{-1}.

Electroanalysis

Alumina powders, polishing pads, glassy carbon working electrodes, and silver wire reference electrodes were procured from CH Instruments Inc., and platinum counter electrodes were purchased from Gaoss Union. Cyclic voltammetric experiments were recorded on a CHI610E workstation at room temperature within a nitrogen-filled glovebox. The reference electrode was composed of a silver wire electrode and $AgNO_3$ solution in acetonitrile. It was calibrated using 2 mmol/L of Fc^+/Fc before conducting cyclic voltammetric tests.

Test data were analyzed and graphed using OriginPro learning edition. Anodic peak potentials (E_{pa}) and cathodic peak potentials (E_{pc}) were both identified and marked on the plots. For the quasi-reversible Fc^+/Fc redox couple, the estimation of the reduction potential (E_{red}) was based on the calculation of the half-wave potential ($E_{1/2}$), which are averages between the E_{pa} and the E_{pc}. For the irreversible **YlideFluor-CF$_2$Cl**/[**YlideFluor-CF$_2$Cl**]$^{-\bullet}$ redox couple, the inflection-point potential (E_i) was employed to estimate the E_{red}, defined as the potentials where the second derivative of the current with respect to the potential is zero while the first derivative is not ($\partial^2 i/\partial E^2 = 0$ and $\partial i/\partial E \neq 0$)

Reference: E. M. Espinoza, J. A. Clark, J. Soliman, J. B. Derr, M. Morales and V. I. Vullev, *J. Electrochem. Soc.* **2019**, *166*, H3175..

Building on our prior studies, we postulated that the first cathodic peak corresponds to the reduction of **YlideFluor-CF$_2$Cl** to [**YlideFluor-CF$_2$Cl**]$^{-\bullet}$, and the second cathodic peak signifies the reduction of $CF_2Cl^\bullet$ to CF_2Cl^-. Additionally, the third cathodic peak along with the neighboring anodic peak is associated with the redox process of the nitro group within [4-NO_2-C_6H_4-S-$C(CO_2Me)_2$]$^-$.

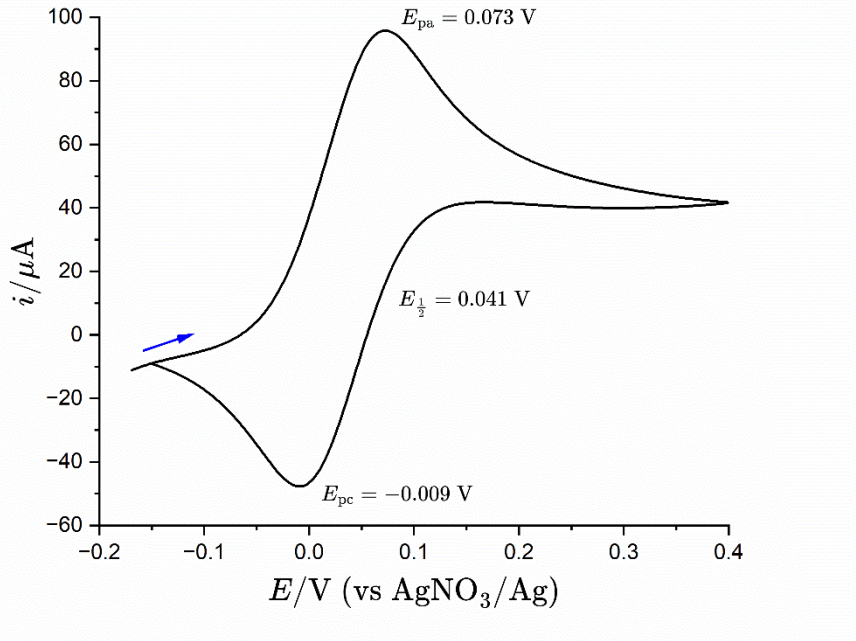


Figure S1. Calibration of the $AgNO_3$/Ag reference electrode. The scan rate was 20 mV/s. Ferrocene (2 mmol/L), $TBAPF_6$ (100 mmol/L), and acetonitrile (10 mL). The solution resistance of 53.6 Ω was fully compensated.

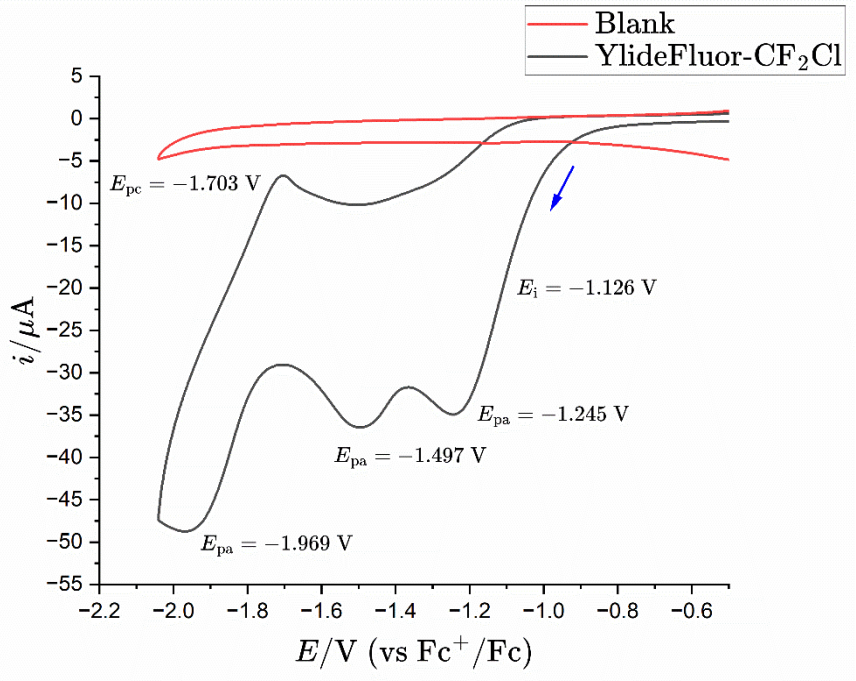


Figure S2. Scan rates were 100 mV/s. The red curve: $TBAPF_6$ (100 mmol/L) and acetonitrile (10 mL). The solution resistance of 52.4 Ω was fully compensated. The black curve: **YlideFluor-CF_2Cl** (20 mmol/L), $TBAPF_6$ (100 mmol/L), and acetonitrile (10 mL). The solution resistance of 53.6 Ω was fully compensated.

UV–Vis Spectrum of YlideFluor-CF_2Cl

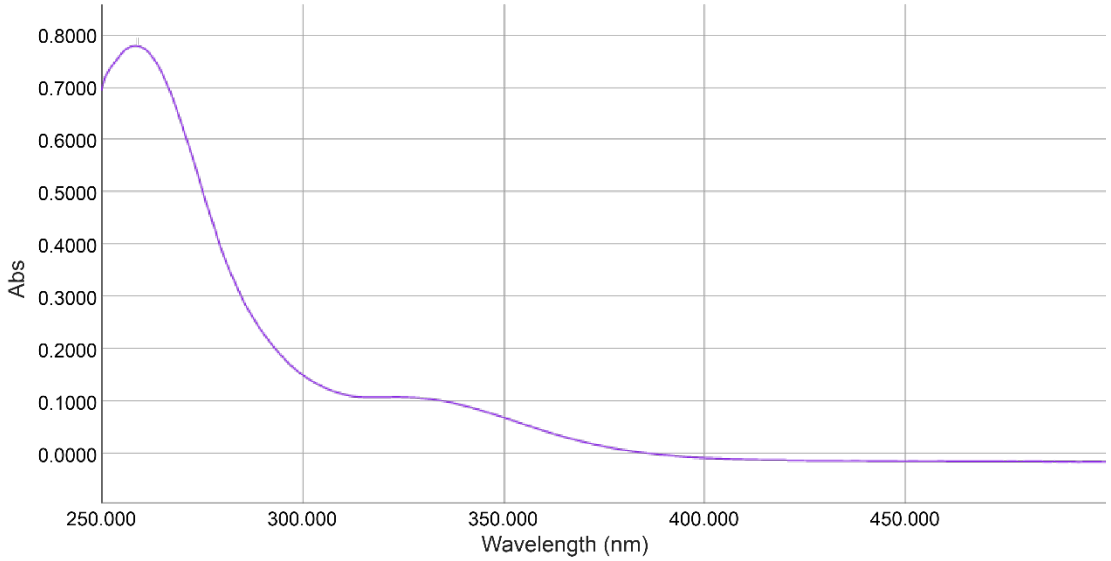
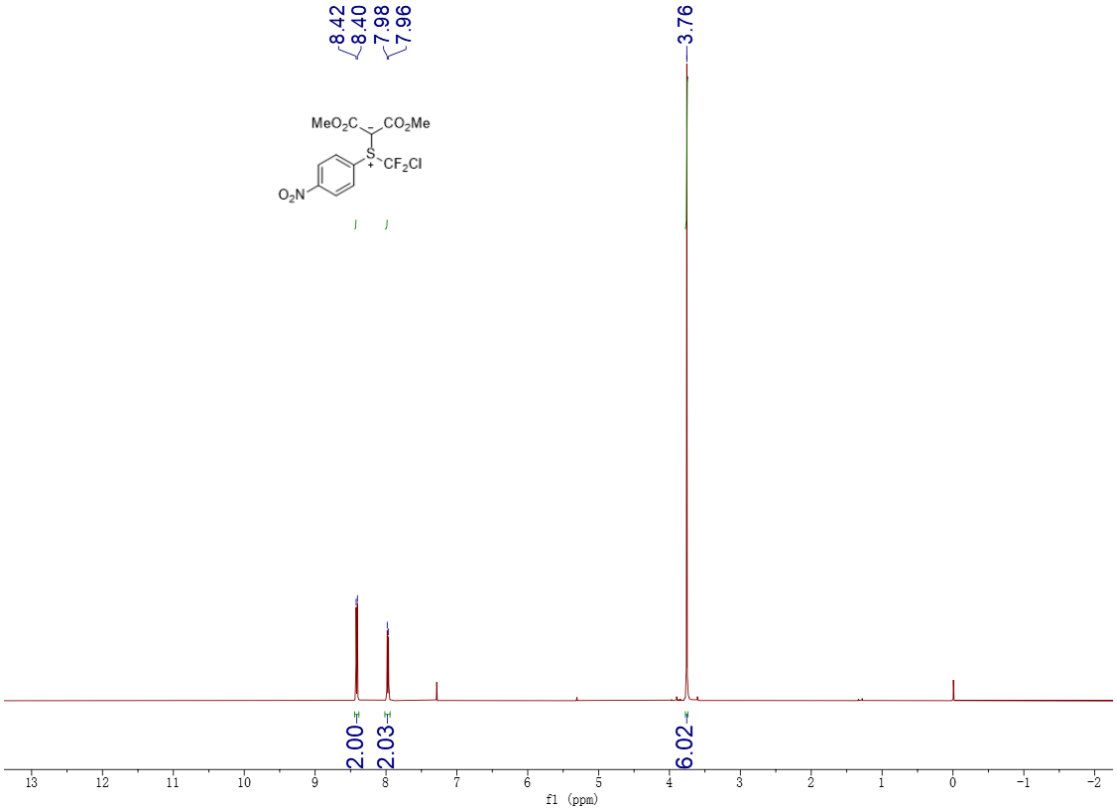


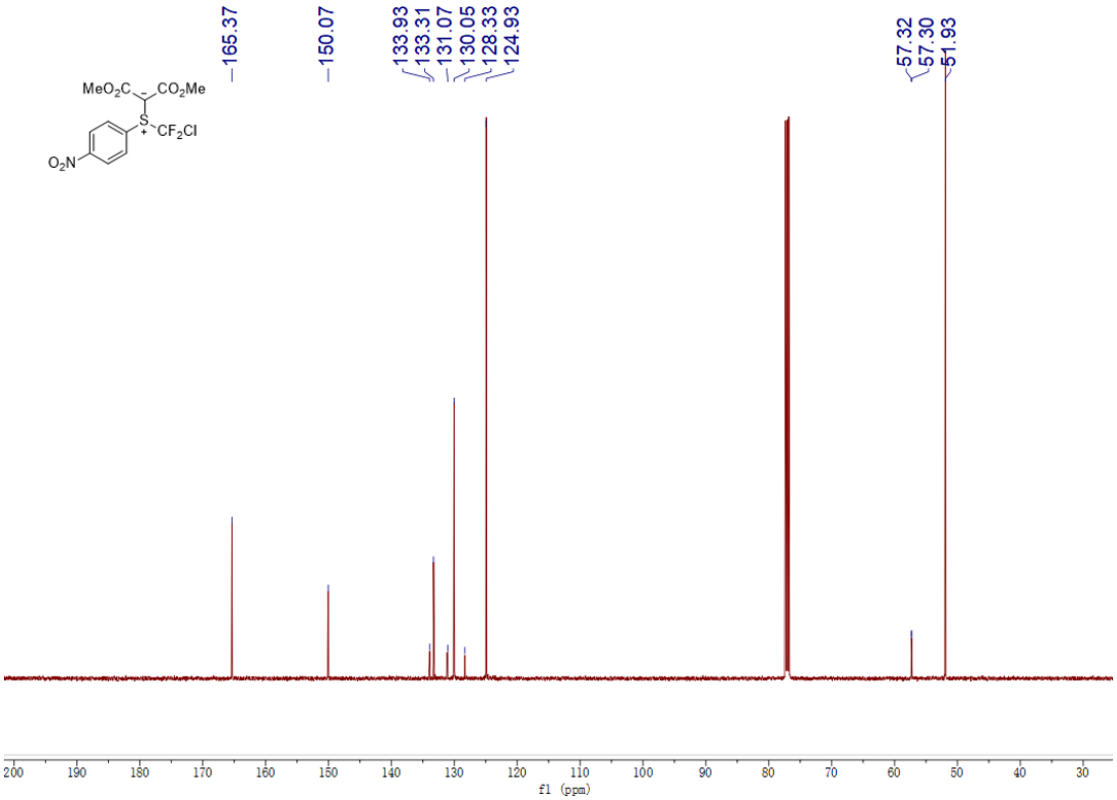
Figure S3. UV–Vis spectrum of **YlideFluor-CF_2Cl**.

^{1}H, ^{13}C, and ^{19}F NMR Spectra

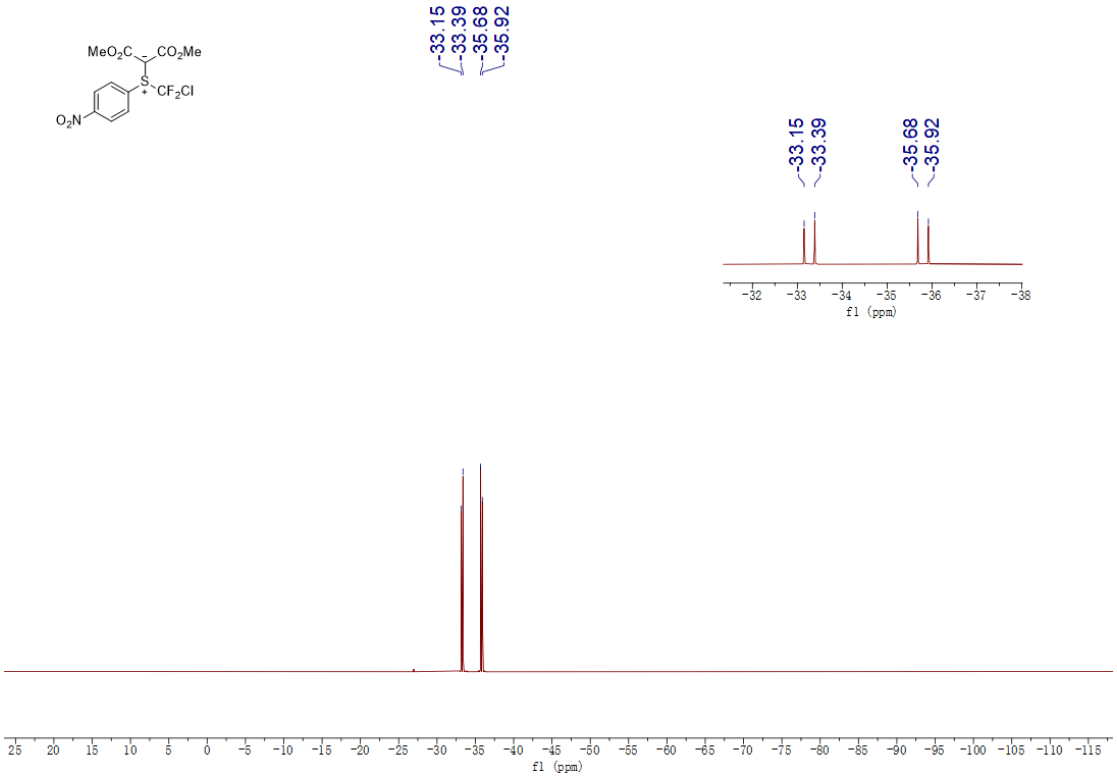
^{1}H NMR spectrum of YlideFluor-CF_2Cl



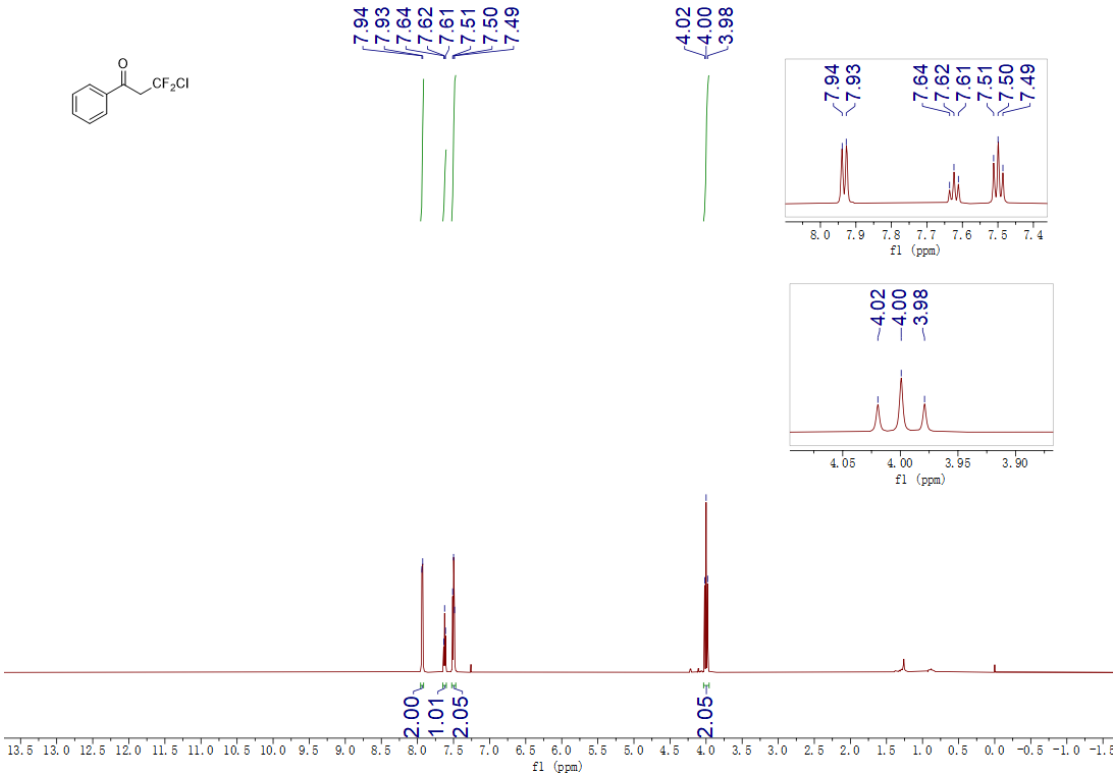
^{13}C NMR spectrum of YlideFluor-CF_2Cl



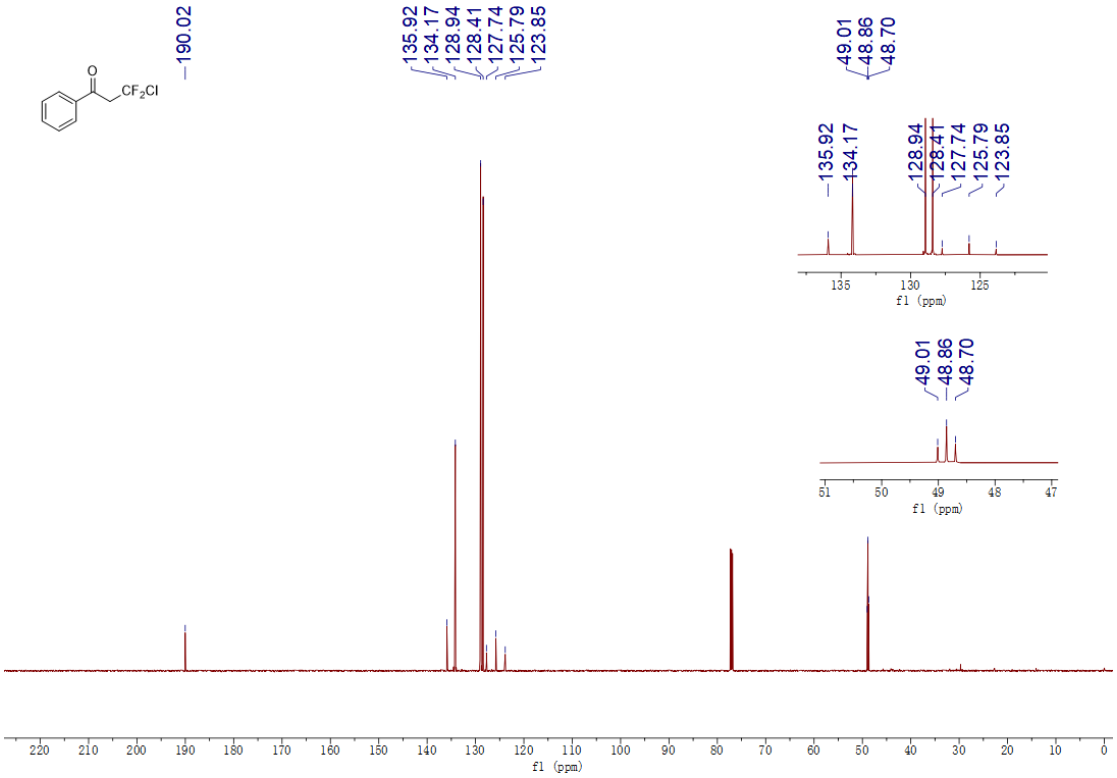
^{19}F NMR spectrum of YlideFluor-CF_2Cl



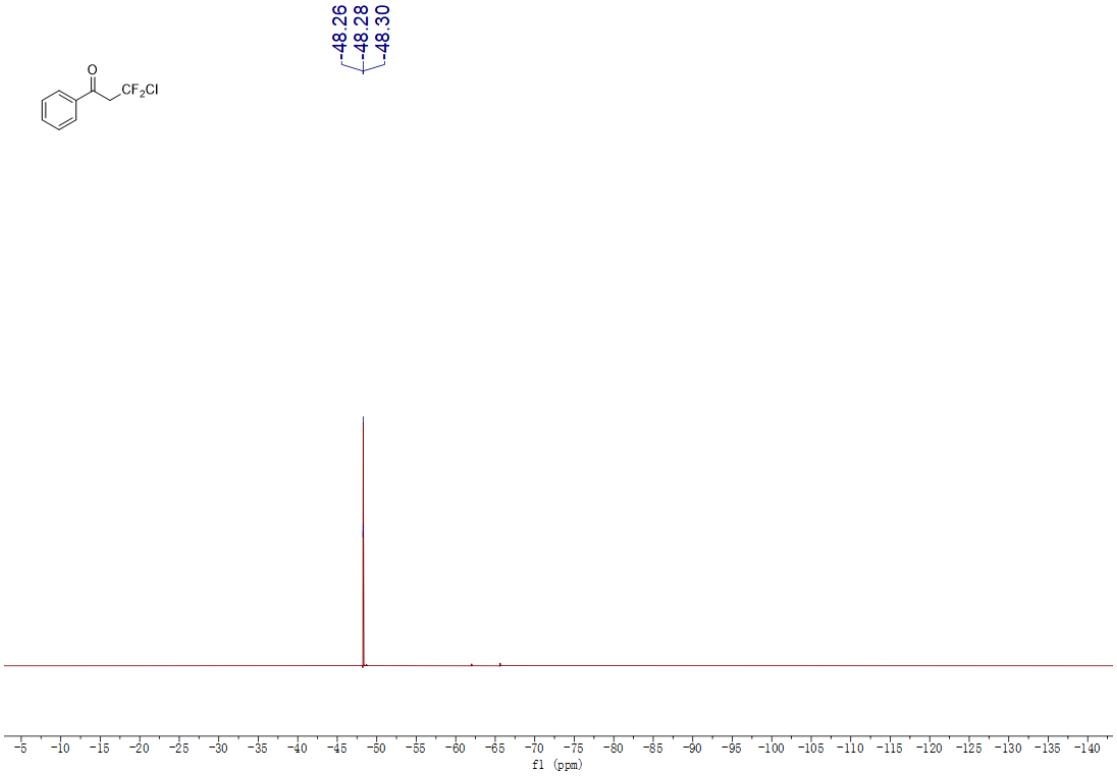
^{1}H NMR spectrum of 3-Chloro-3,3-difluoro-1-phenylpropan-1-one 1a



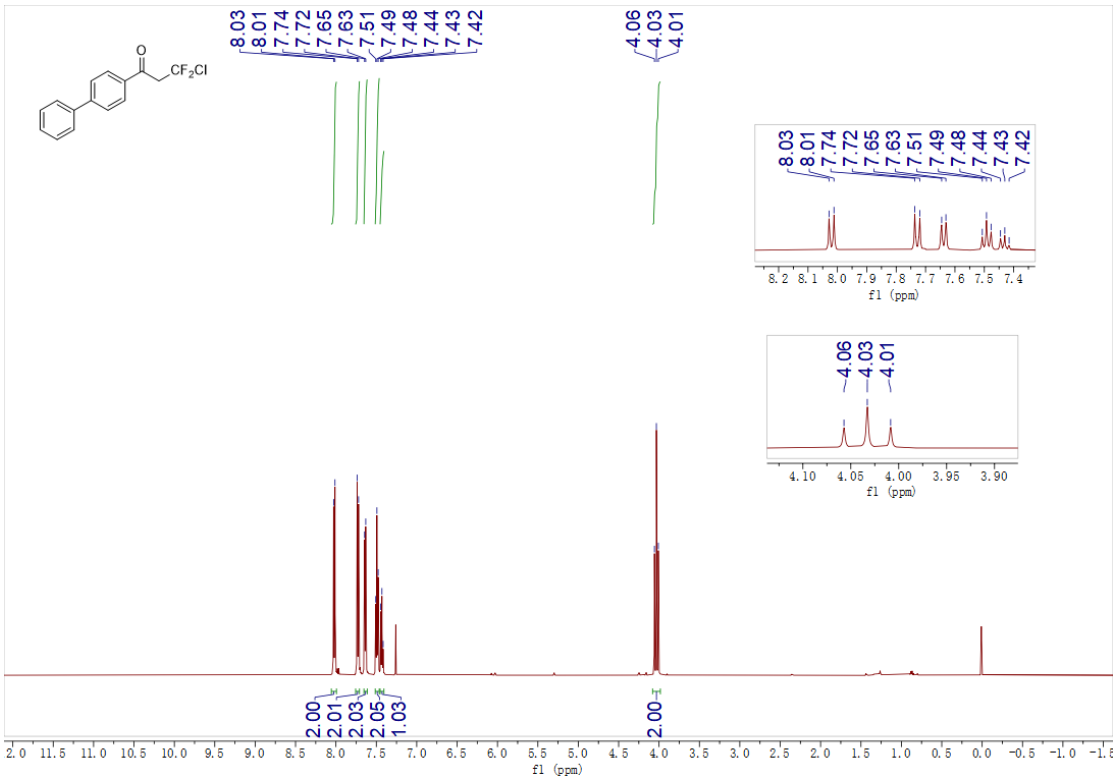
^{13}C NMR spectrum of 3-Chloro-3,3-difluoro-1-phenylpropan-1-one 1a



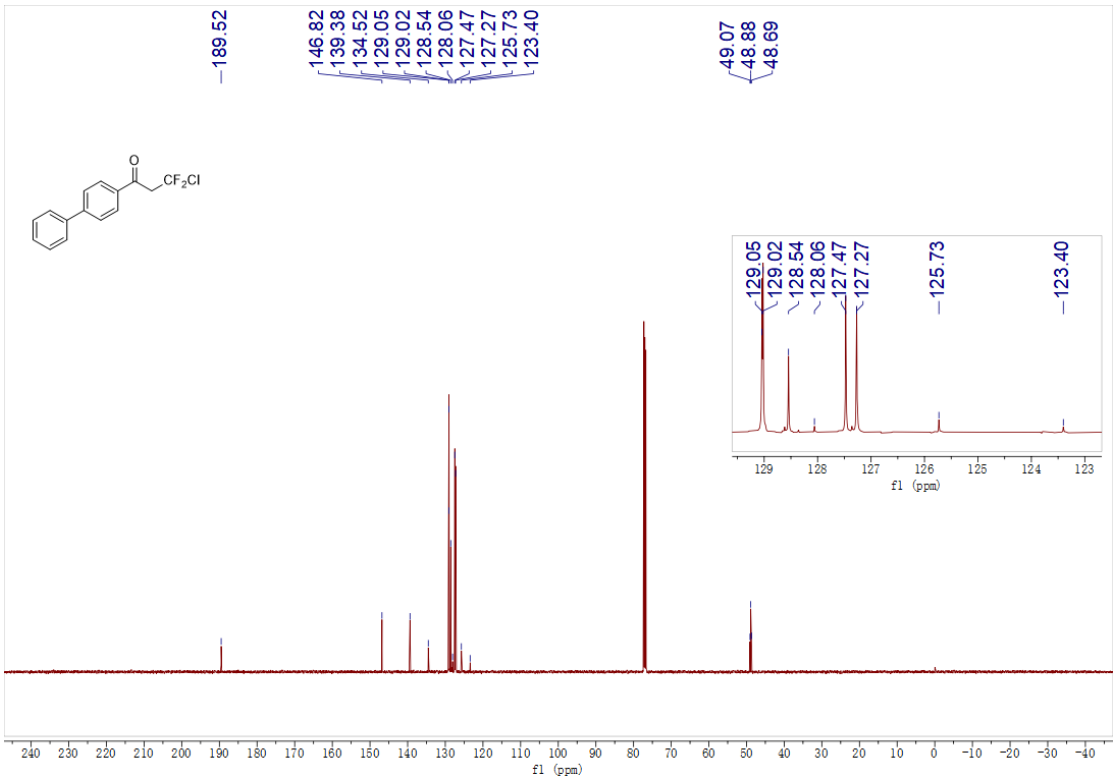
^{19}F NMR spectrum of 3-Chloro-3,3-difluoro-1-phenylpropan-1-one 1a



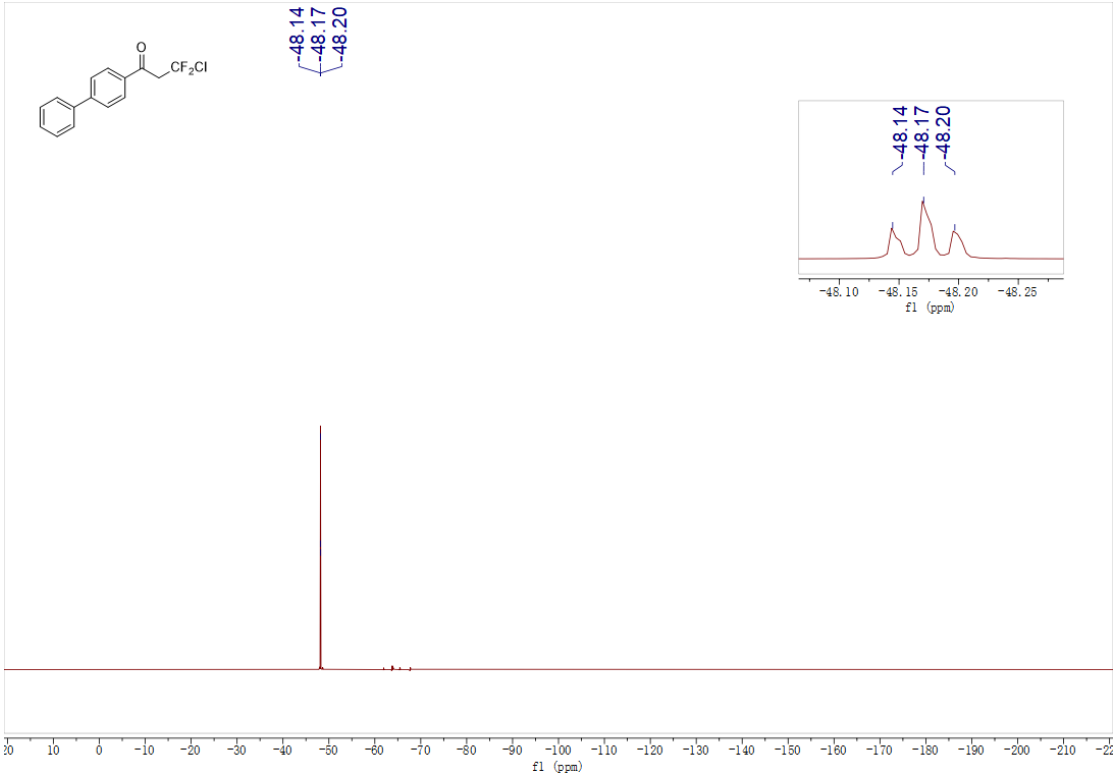
^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl) -3-chloro-3,3-difluoropropan-1-one 1b



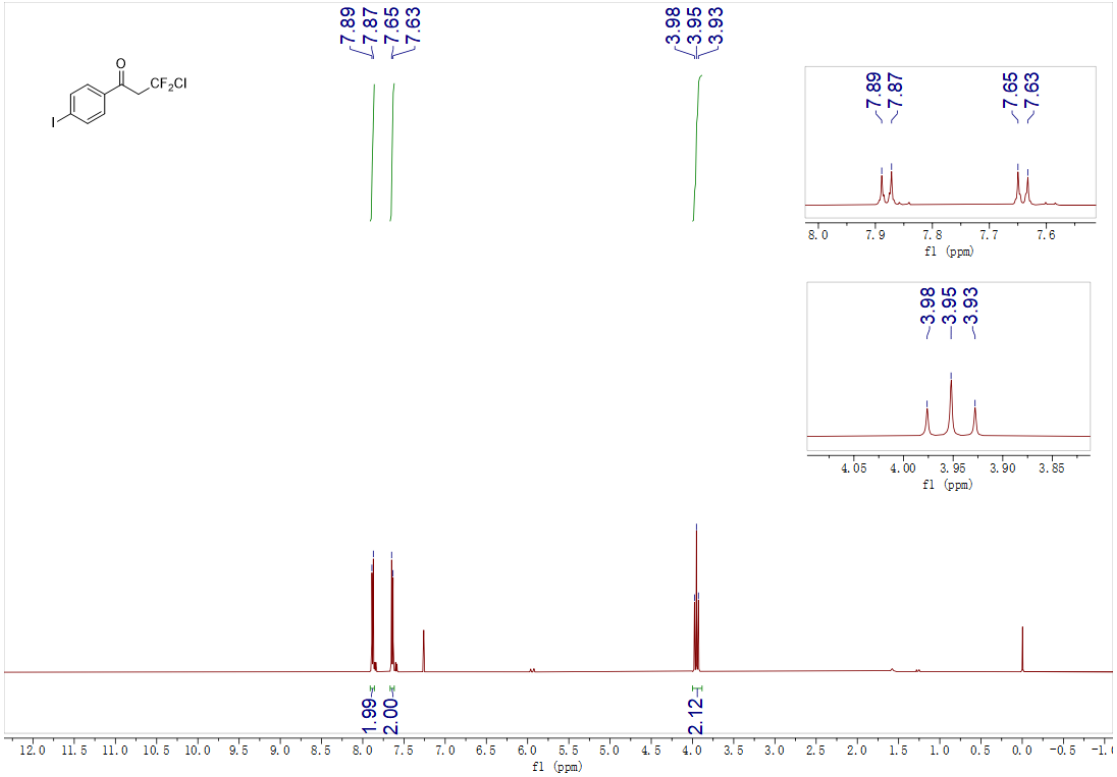
^{13}C NMR spectrum of 1-([1,1'-biphenyl]-4-yl) -3-chloro-3,3-difluoropropan-1-one 1b



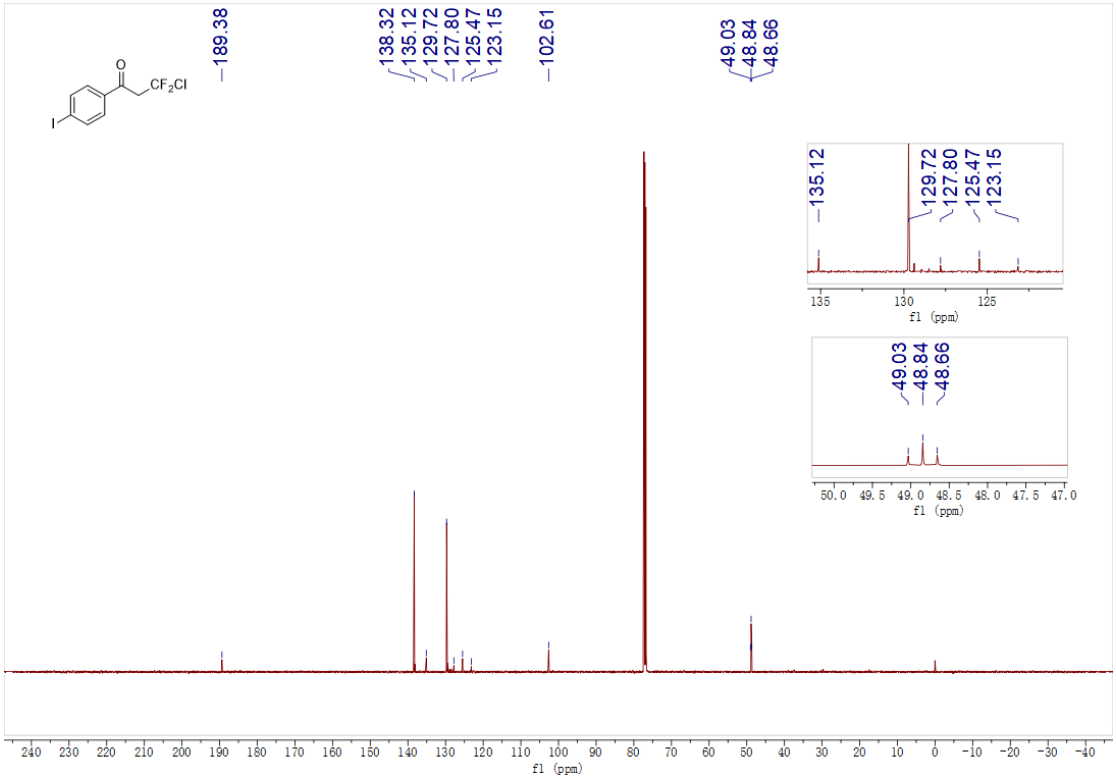
^{19}F NMR spectrum of 1-([1,1'-biphenyl]-4-yl) -3-chloro-3,3-difluoropropan-1-one 1b



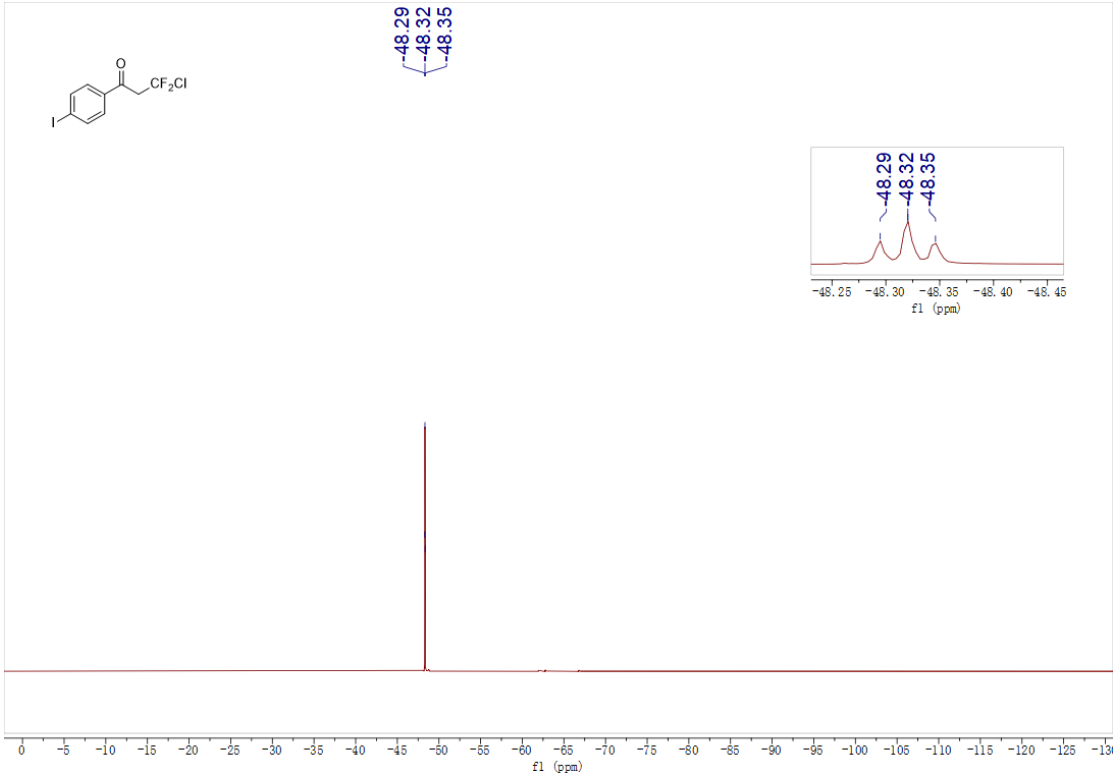
^{1}H NMR spectrum of 3-chloro-3,3-difluoro-1-(4-iodophenyl)propan-1-one 1c



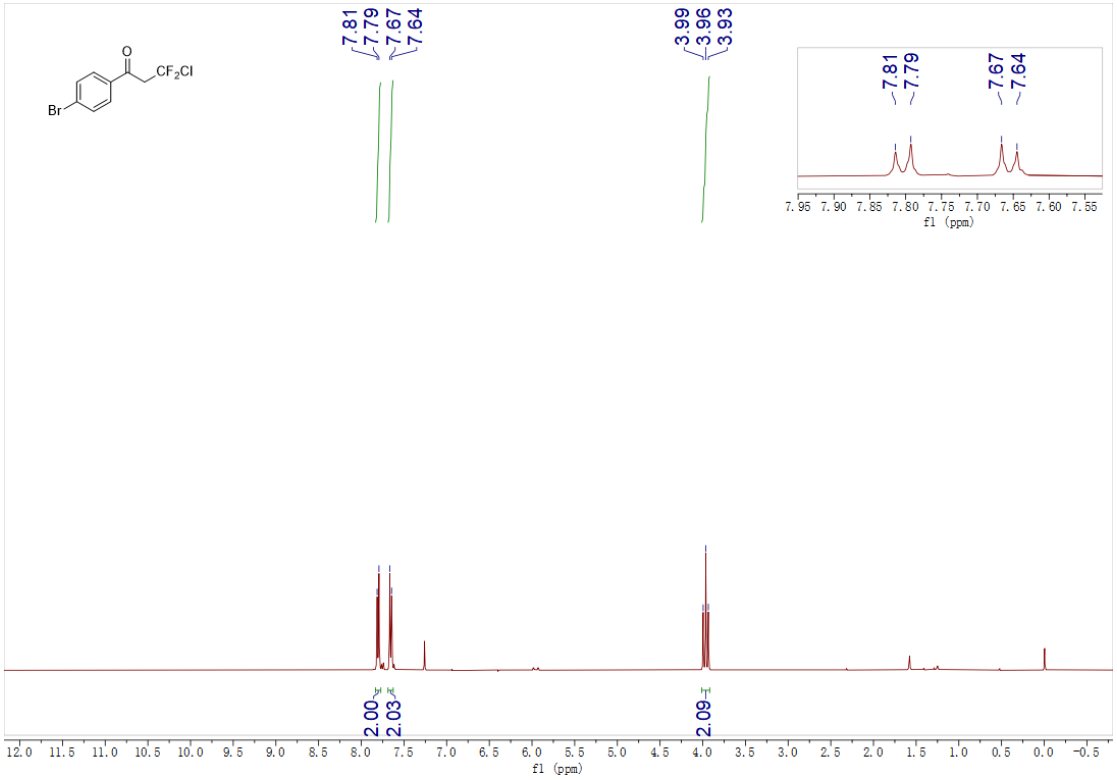
^{13}C NMR spectrum of 3-chloro-3,3-difluoro-1-(4-iodophenyl)propan-1-one 1c



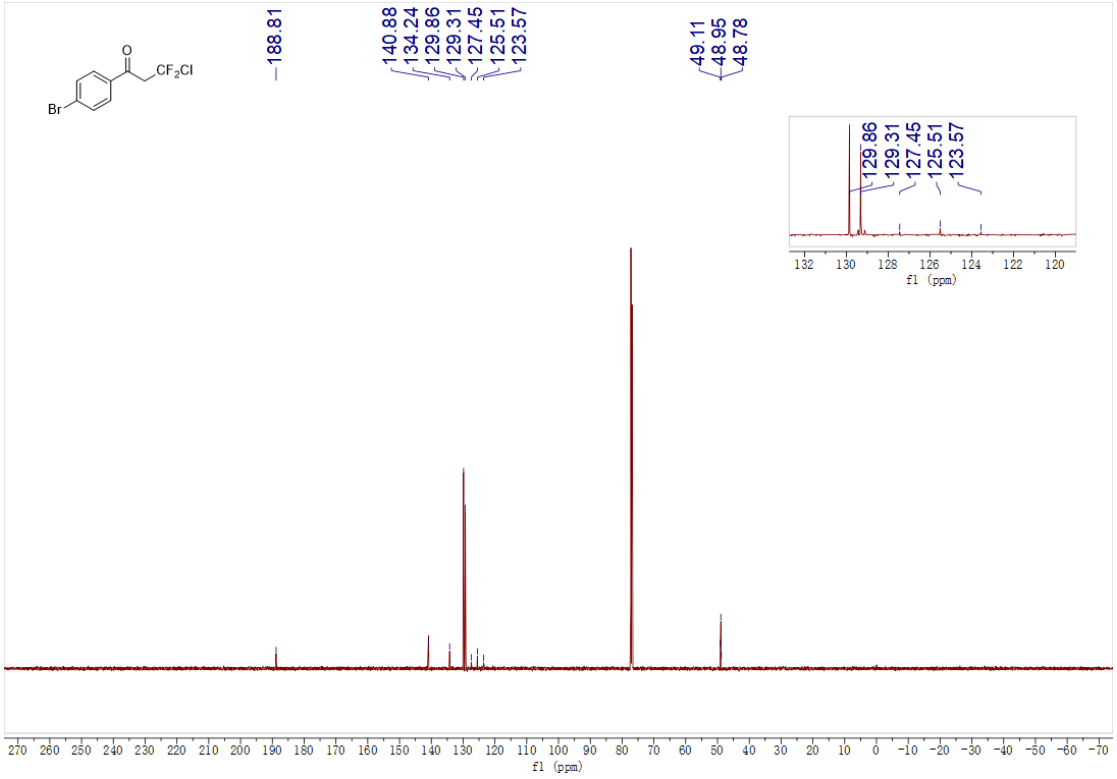
^{19}F NMR spectrum of 3-chloro-3,3-difluoro-1-(4-iodophenyl)propan-1-one 1c



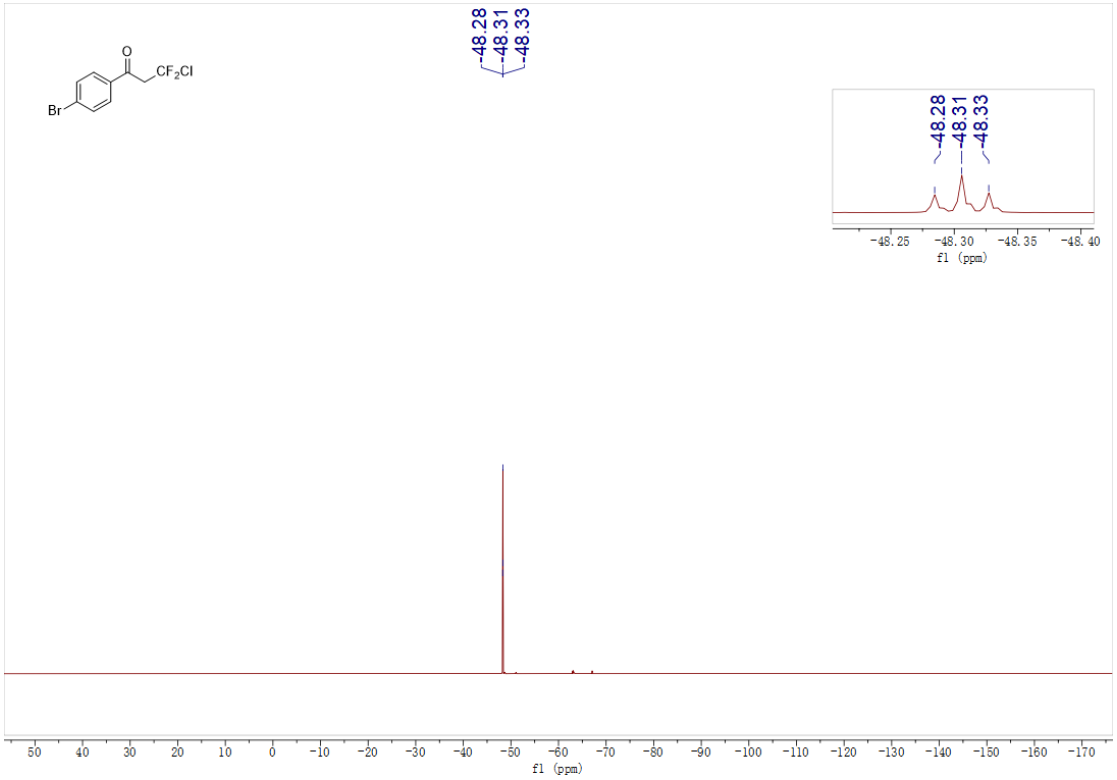
^{1}H NMR spectrum of 1-(4-bromophenyl)-3-chloro-3,3-difluoropropan-1-one 1d



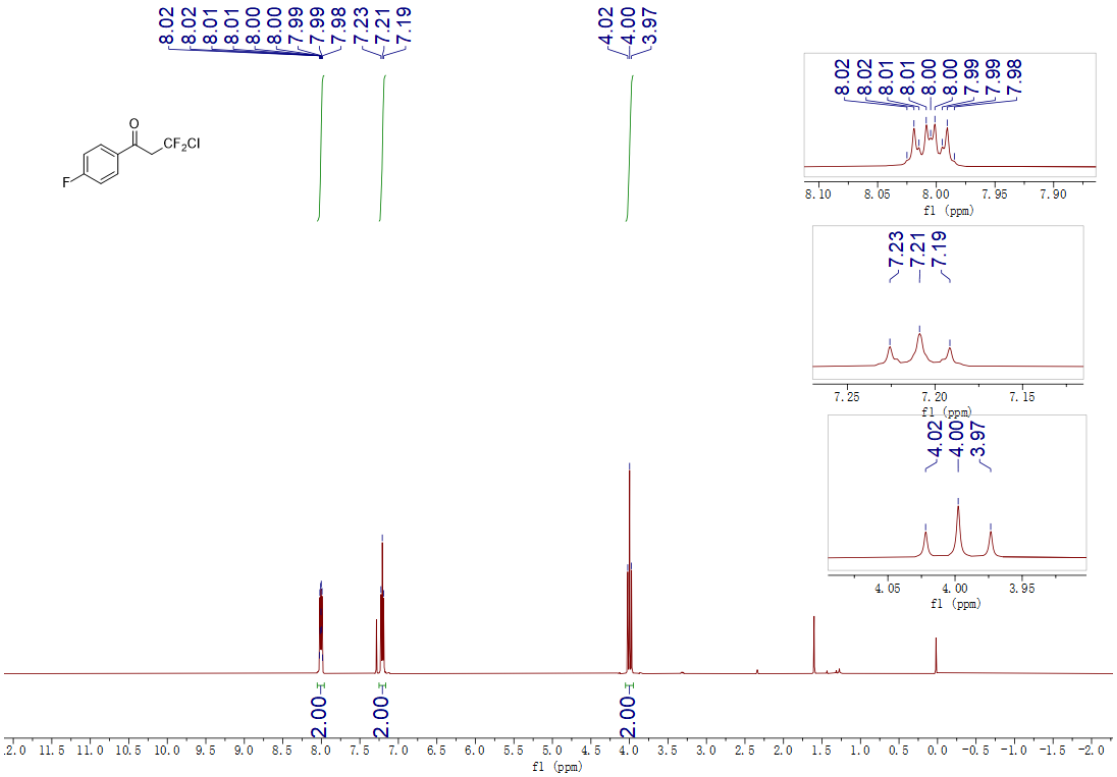
^{13}C NMR spectrum of 1-(4-bromophenyl)-3-chloro-3,3-difluoropropan-1-one 1d



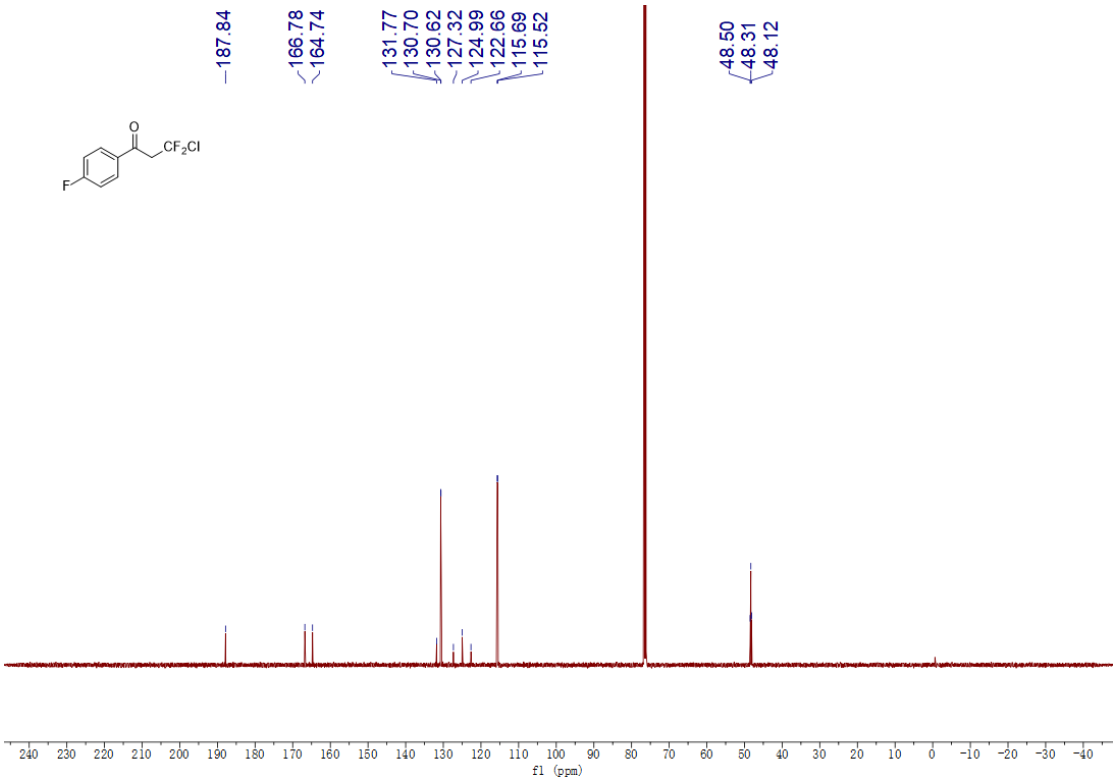
^{19}F NMR spectrum of 1-(4-bromophenyl)-3-chloro-3,3-difluoropropan-1-one 1d



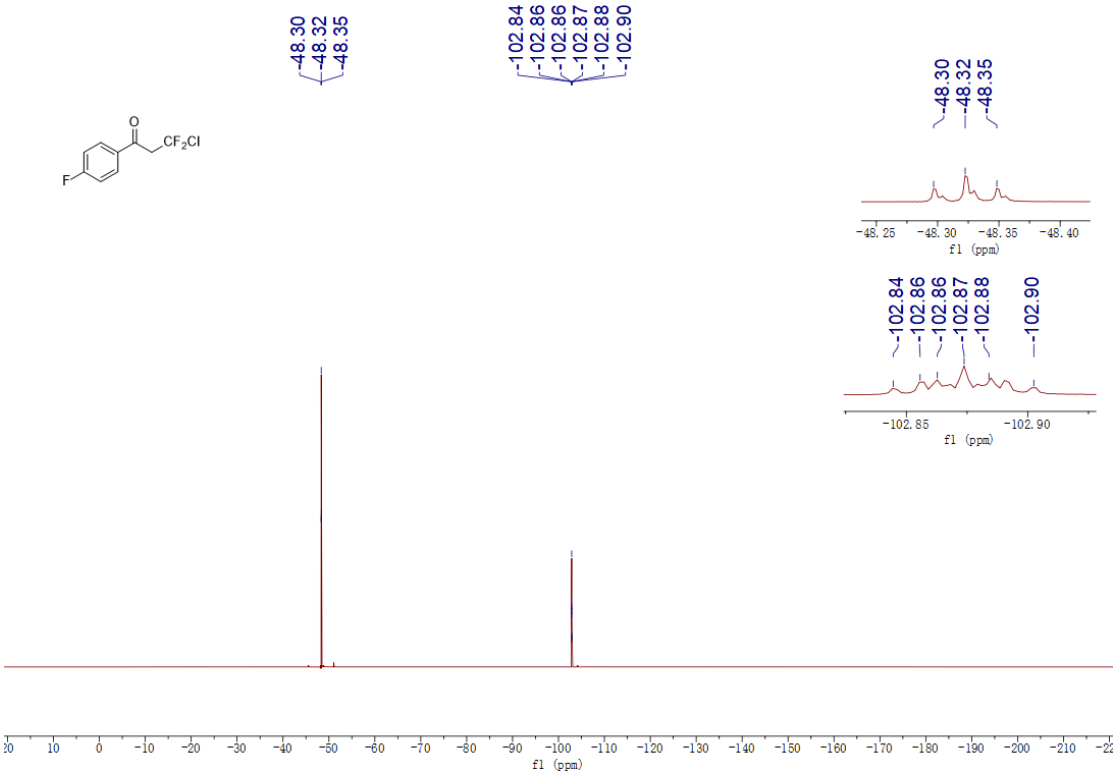
^{1}H NMR spectrum of 3-chloro-3,3-difluoro-1-(4-fluorophenyl)propan-1-one 1e



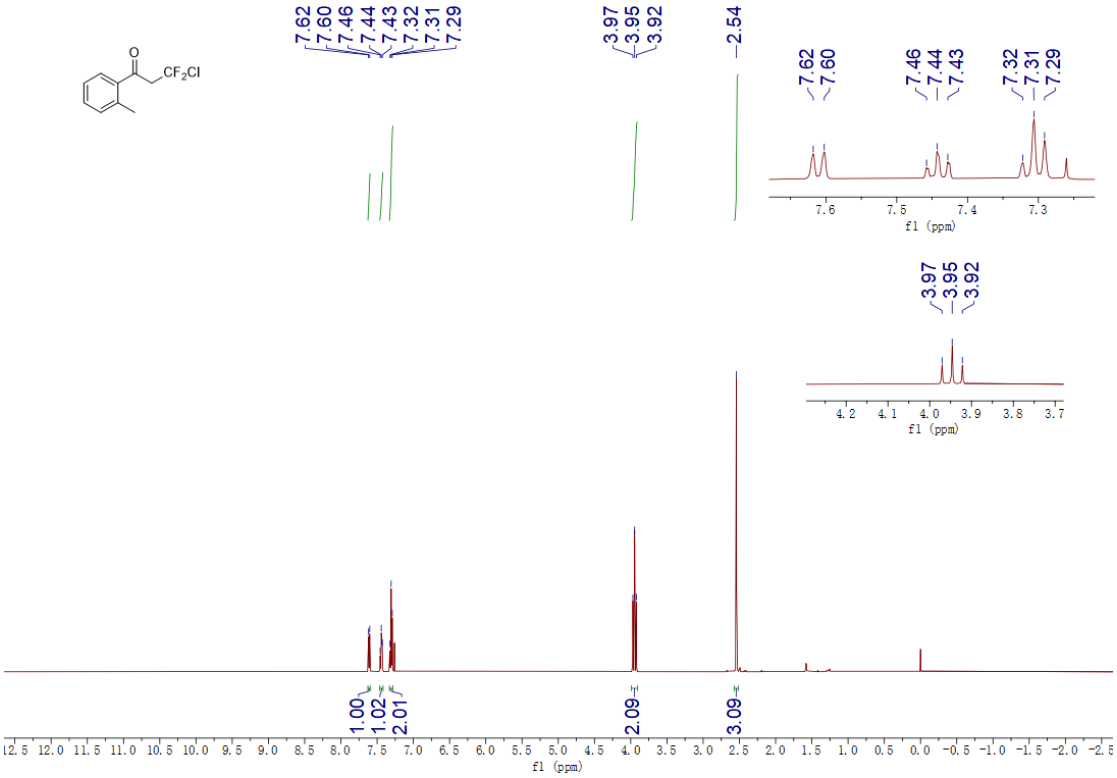
^{13}C NMR spectrum of 3-chloro-3,3-difluoro-1-(4-fluorophenyl)propan-1-one 1e



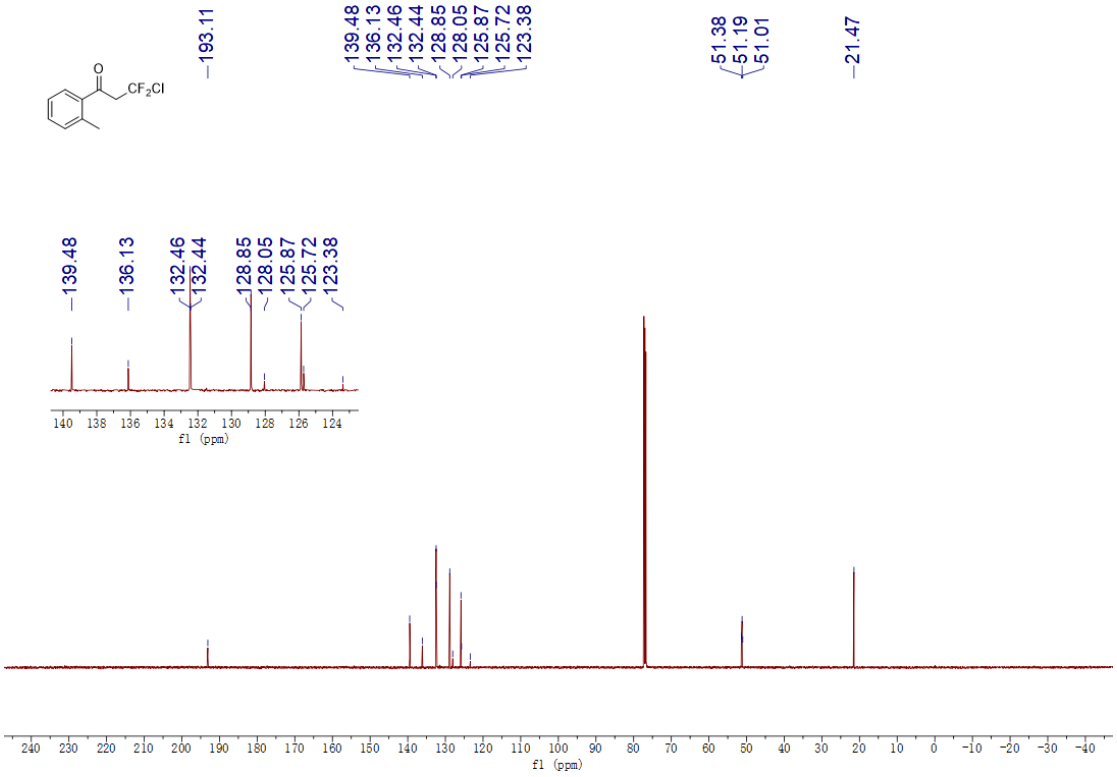
^{19}F NMR spectrum of 3-chloro-3,3-difluoro-1-(4-fluorophenyl)propan-1-one 1e



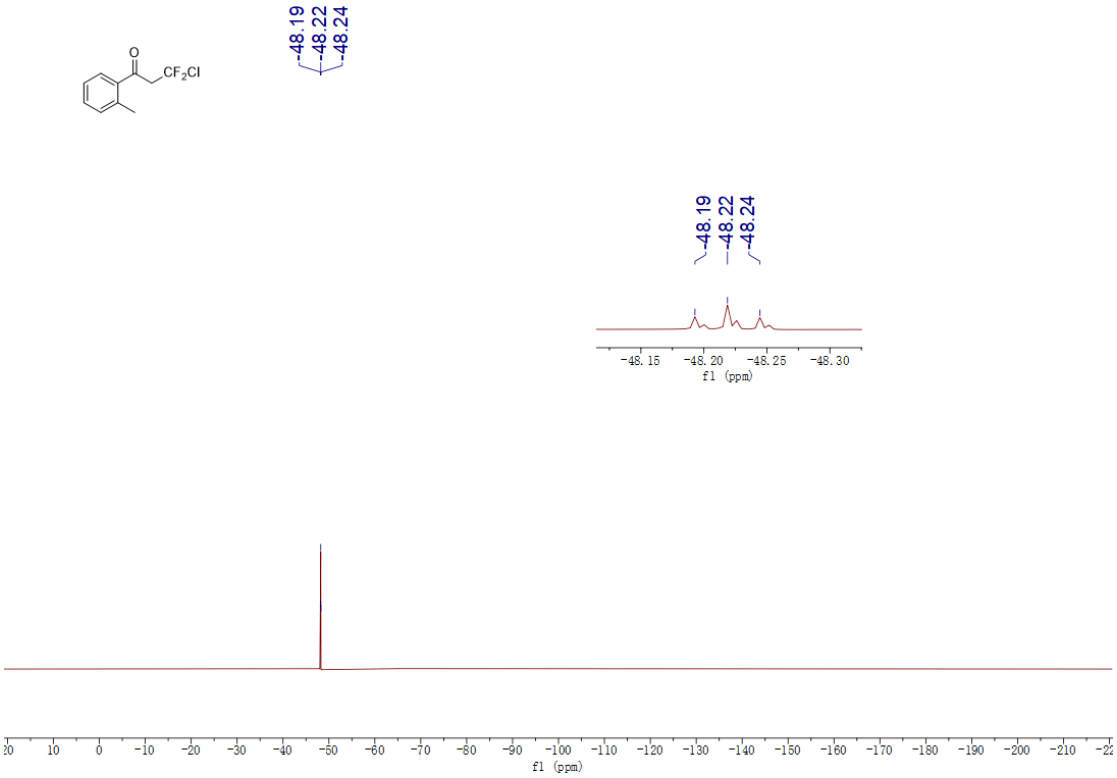
^{1}H NMR spectrum of 3-chloro-3,3-difluoro-1-(o-tolyl)propan-1-one 1f



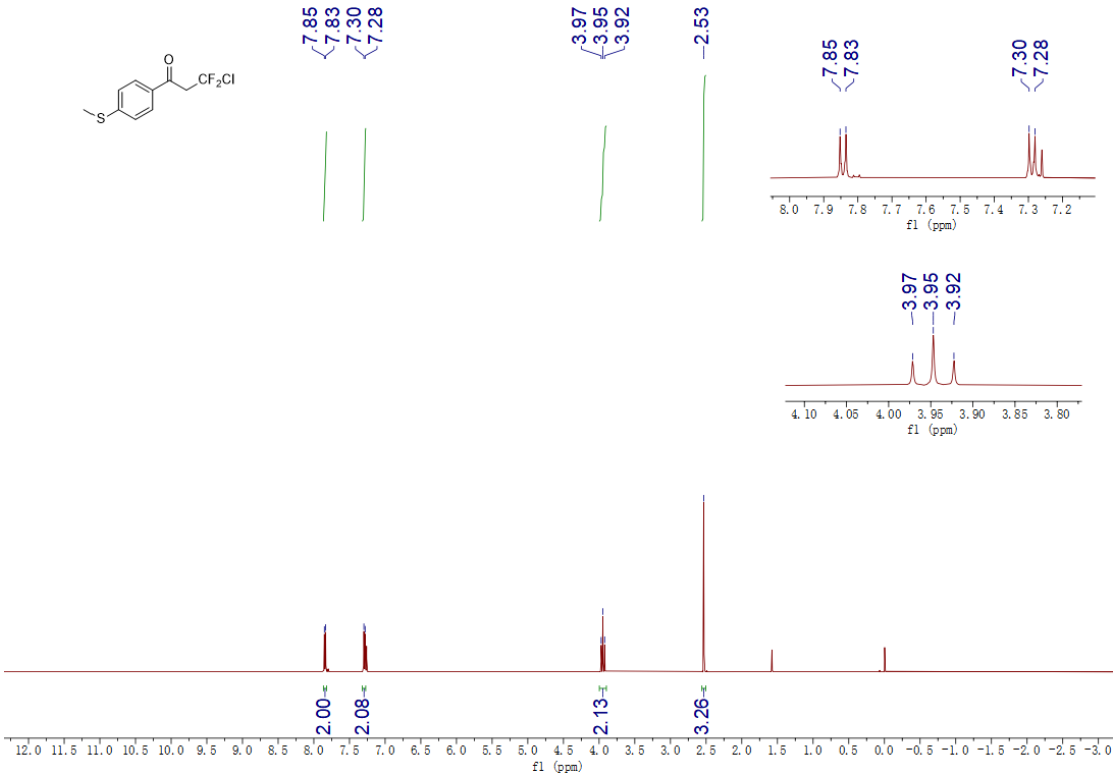
^{13}C NMR spectrum of 3-chloro-3,3-difluoro-1-(o-tolyl)propan-1-one 1f



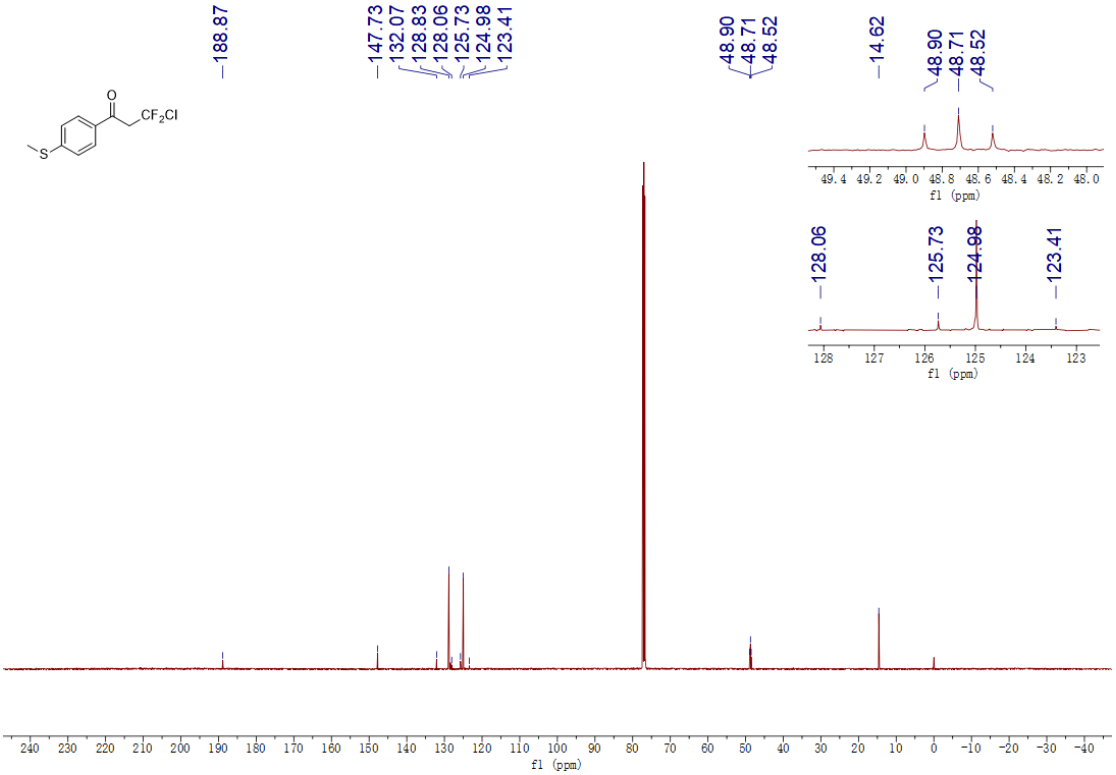
^{19}F NMR spectrum of 3-chloro-3,3-difluoro-1-(o-tolyl)propan-1-one 1f



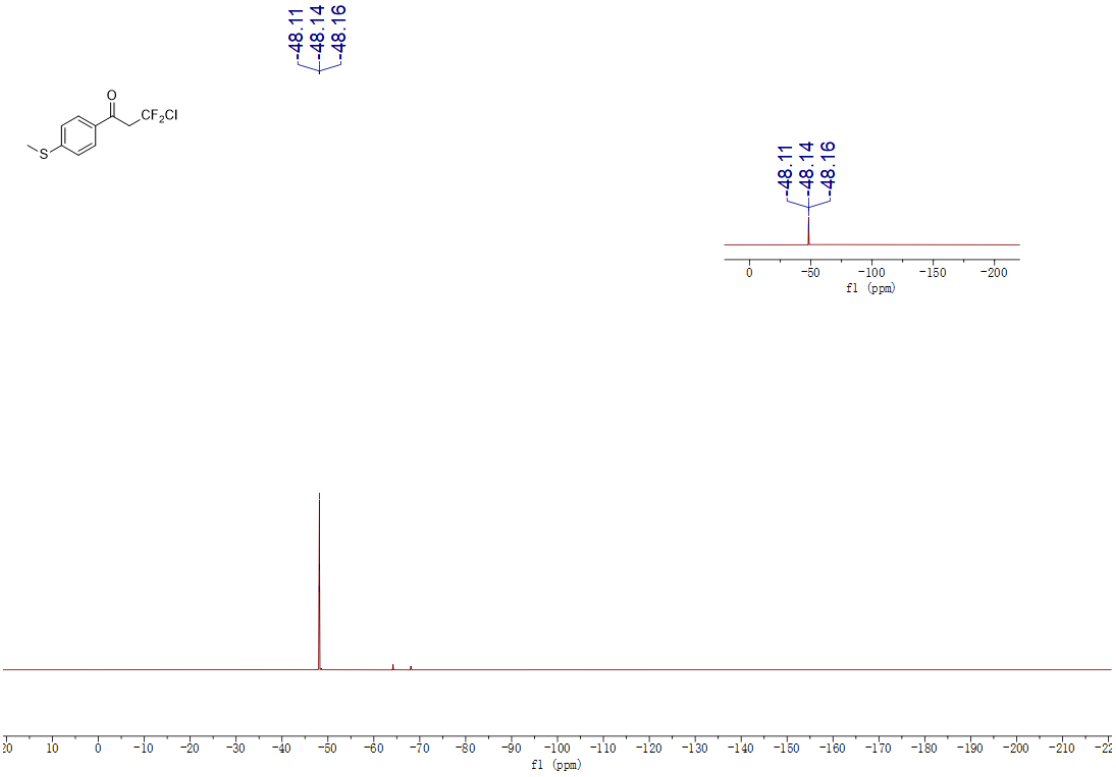
^{1}H NMR spectrum of 3-chloro-3,3-difluoro-1-(4-(methylthio) phenyl)propan-1-one 1g



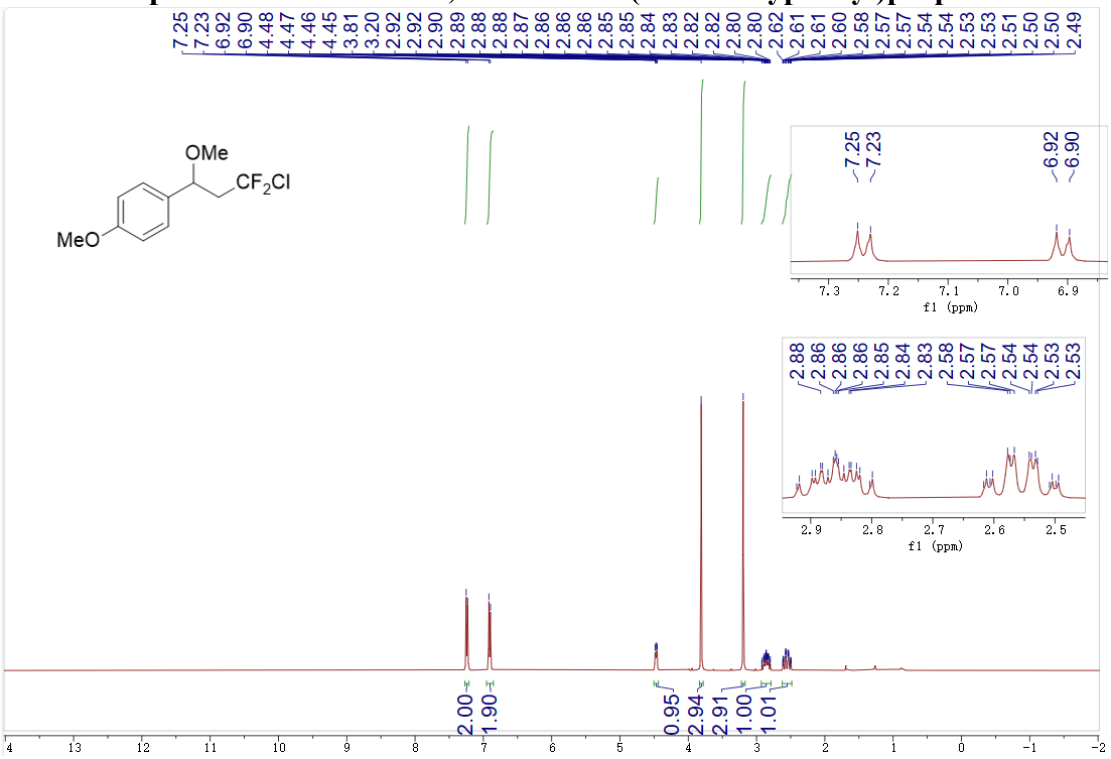
^{13}C NMR spectrum of 3-chloro-3,3-difluoro-1-(4-(methylthio) phenyl)propan-1-one 1g



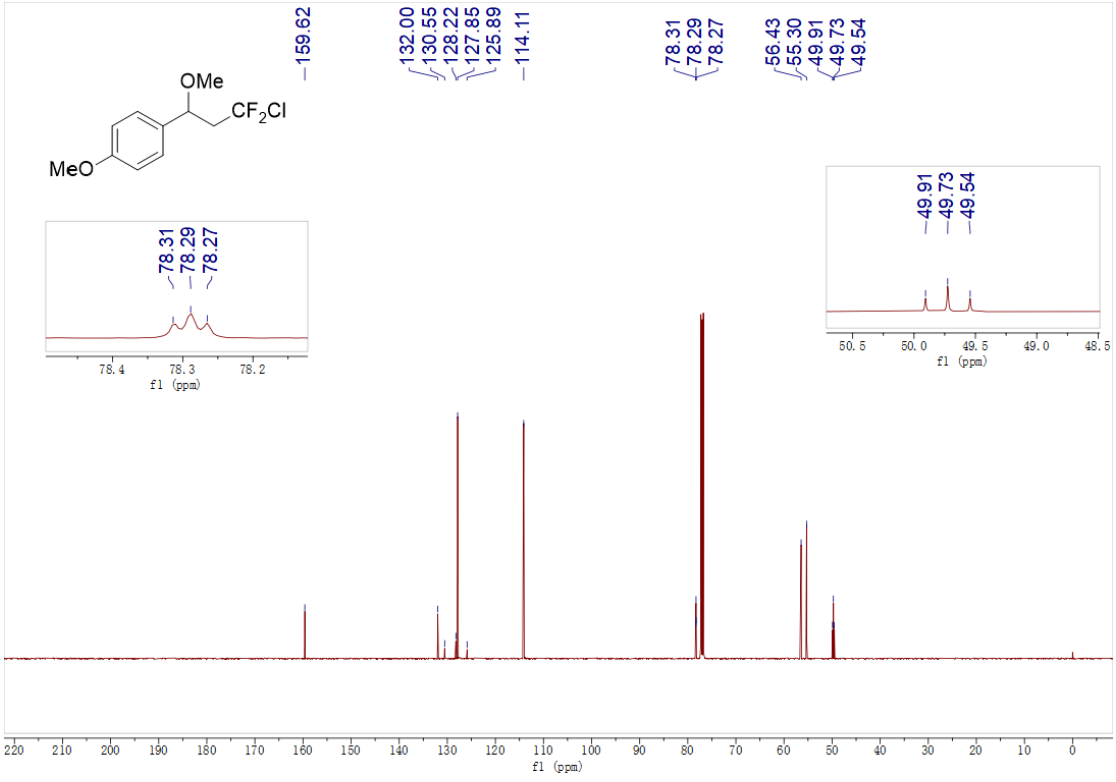
^{19}F NMR spectrum of 3-chloro-3,3-difluoro-1-(4-(methylthio) phenyl)propan-1-one 1g



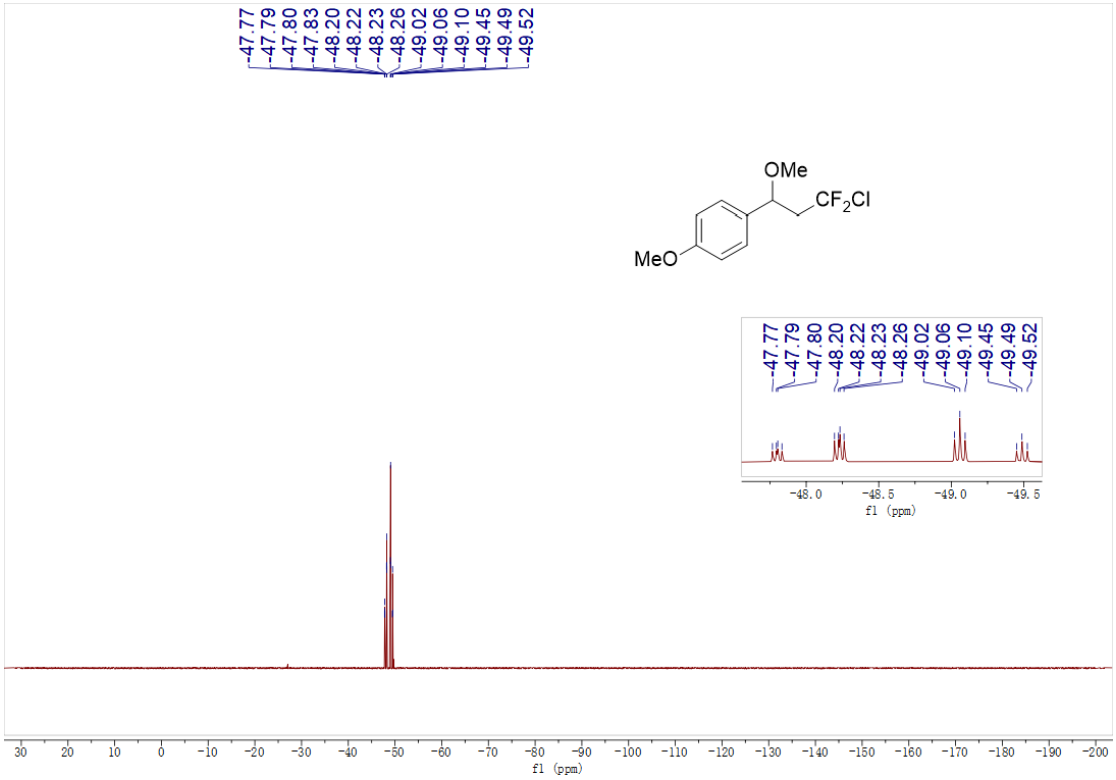
^{1}H NMR spectrum of 3-chloro-3,3-difluoro-1-(4-methoxyphenyl)propan-1-ol 2a



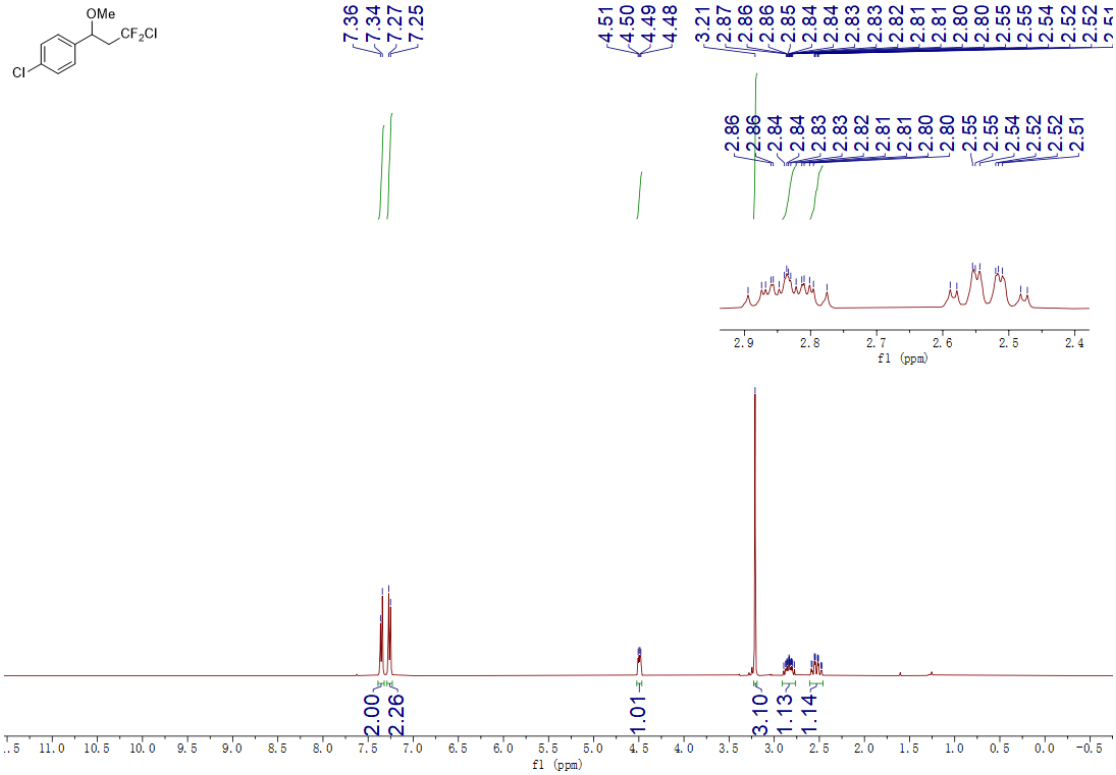
^{13}C NMR spectrum of 3-chloro-3,3-difluoro-1-(4-methoxyphenyl)propan-1-ol 2a



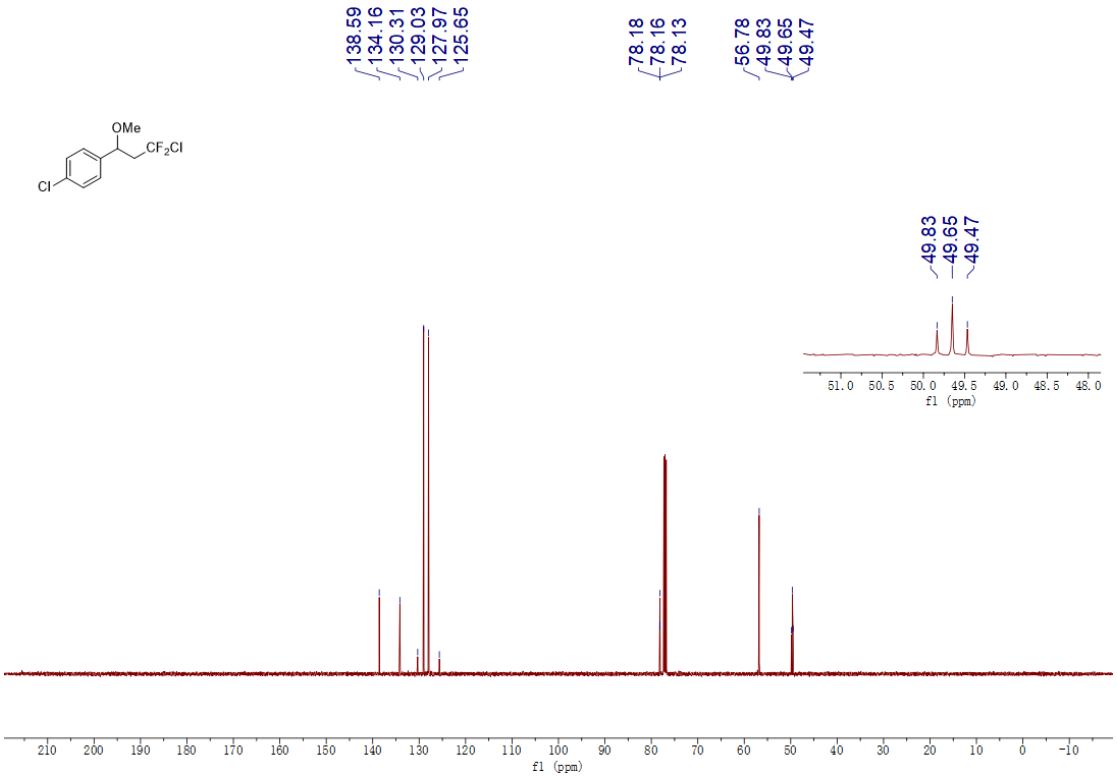
^{19}F NMR spectrum of 3-chloro-3,3-difluoro-1-(4-methoxyphenyl)propan-1-ol 2a



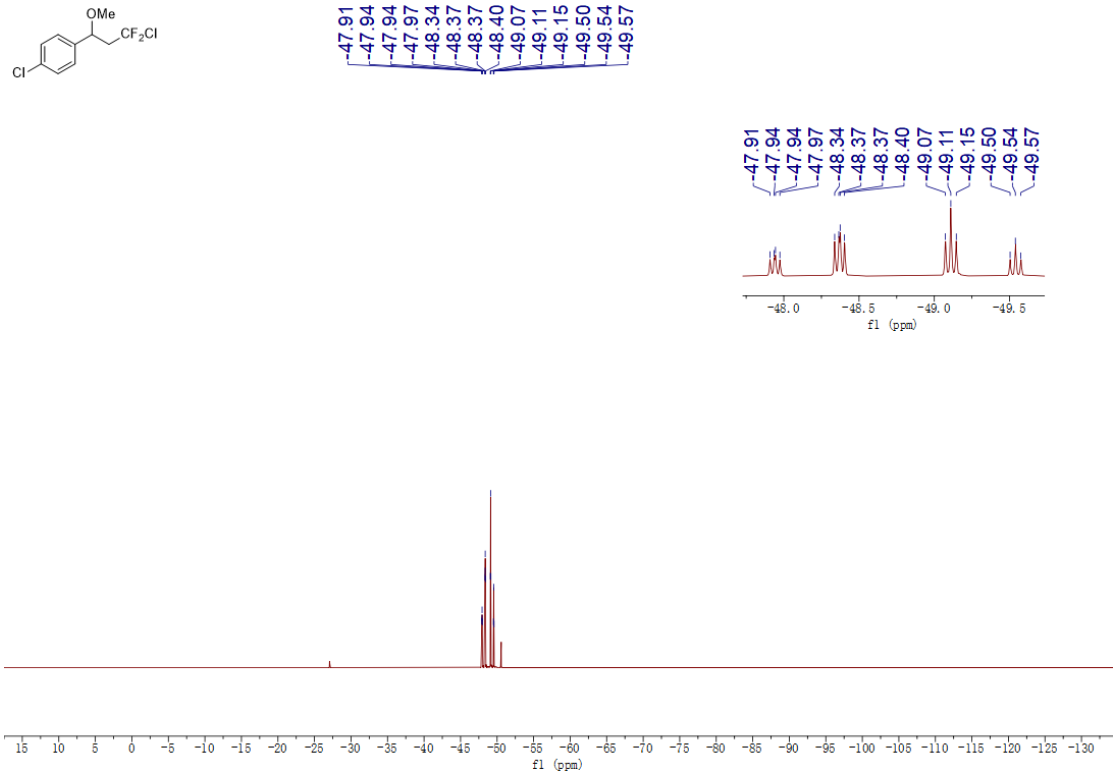
^{1}H NMR spectrum of 1-chloro-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2b



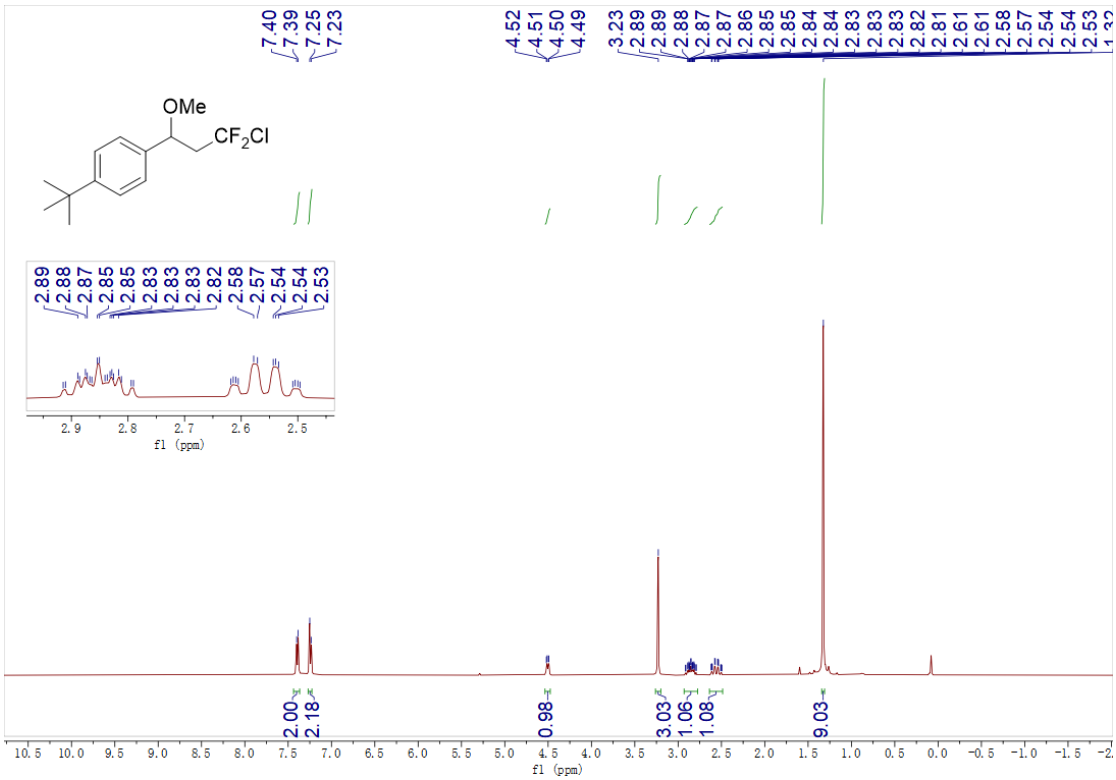
^{13}C NMR spectrum of 1-chloro-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2b



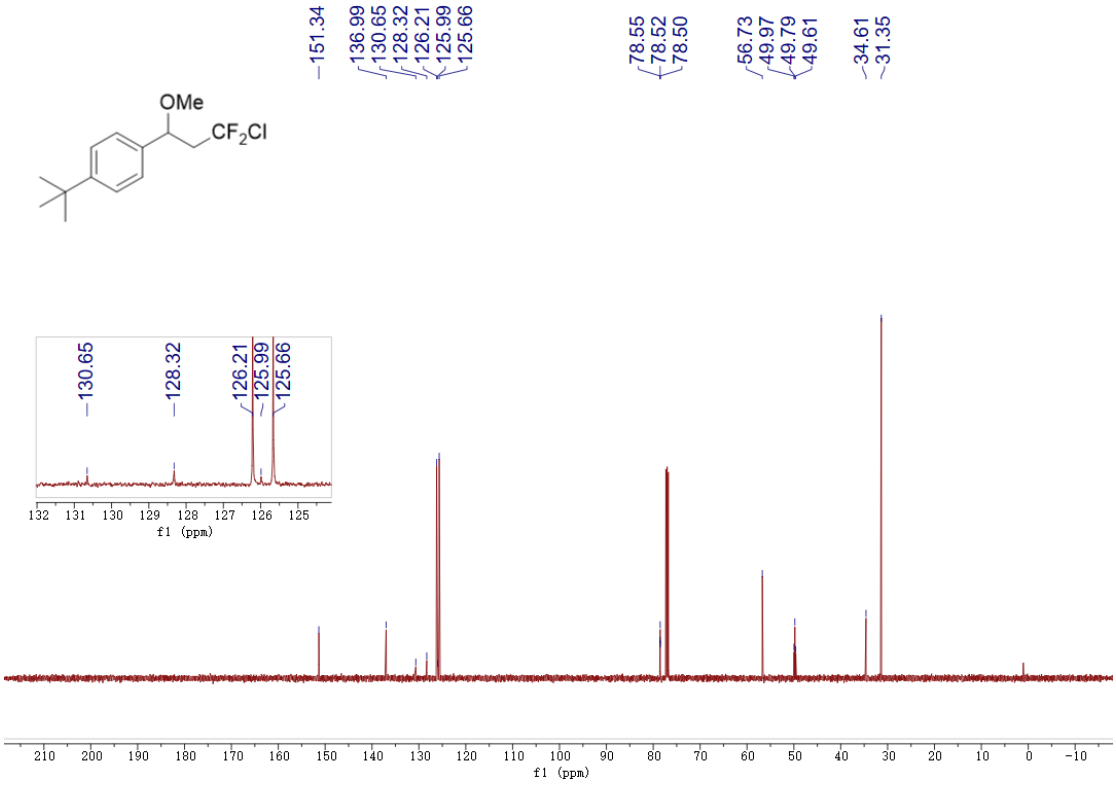
^{19}F NMR spectrum of 1-chloro-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2b



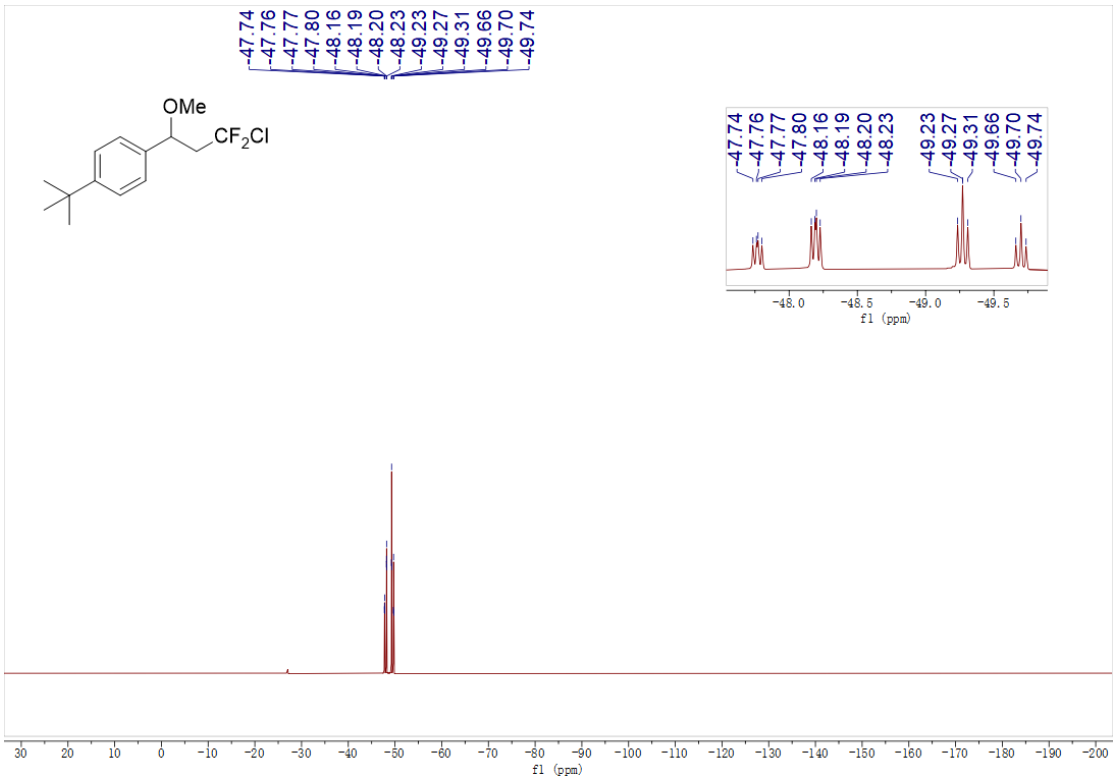
^{1}H NMR spectrum of 1-(tert-butyl)-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2c



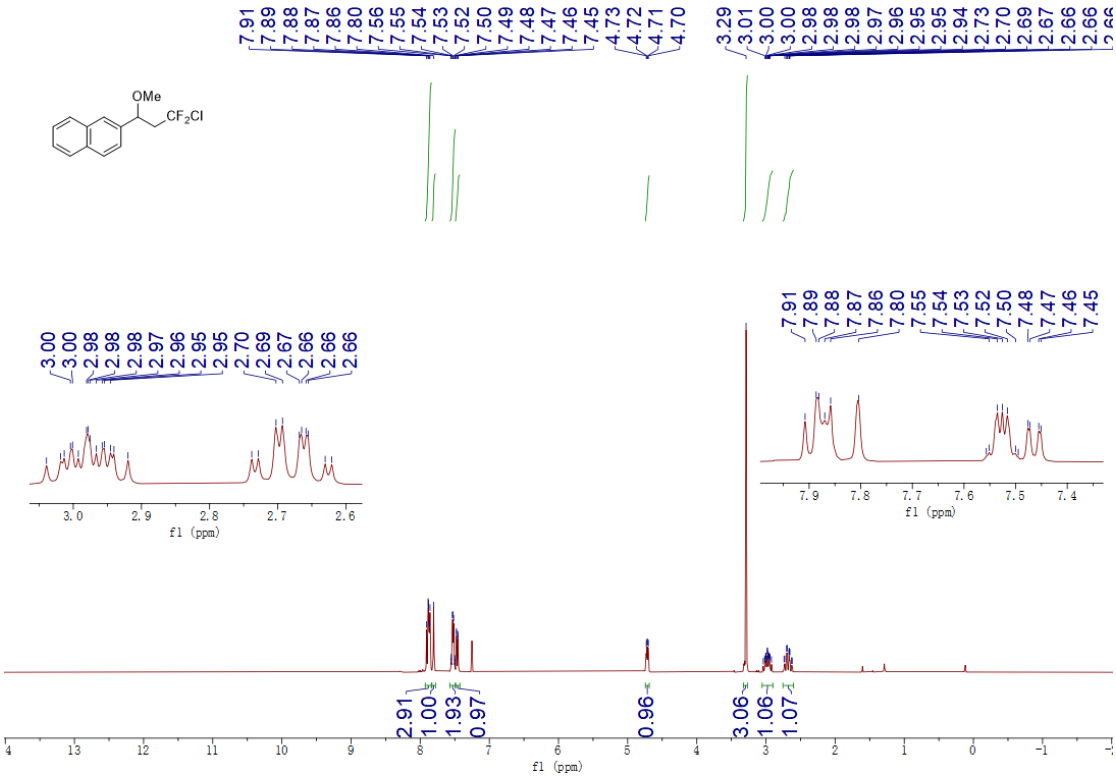
^{13}C NMR spectrum of 1-(tert-butyl)-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2c



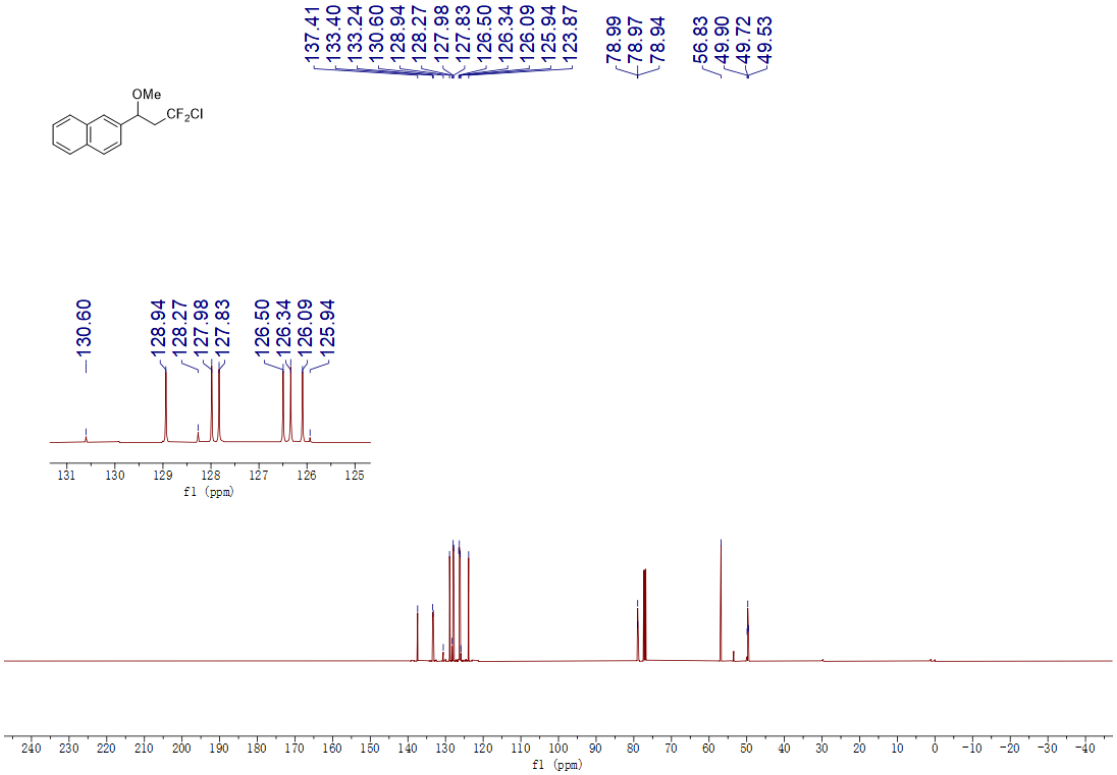
^{19}F NMR spectrum of 1-(tert-butyl)-4-(3-chloro-3,3-difluoro-1-methoxypropyl)benzene 2c



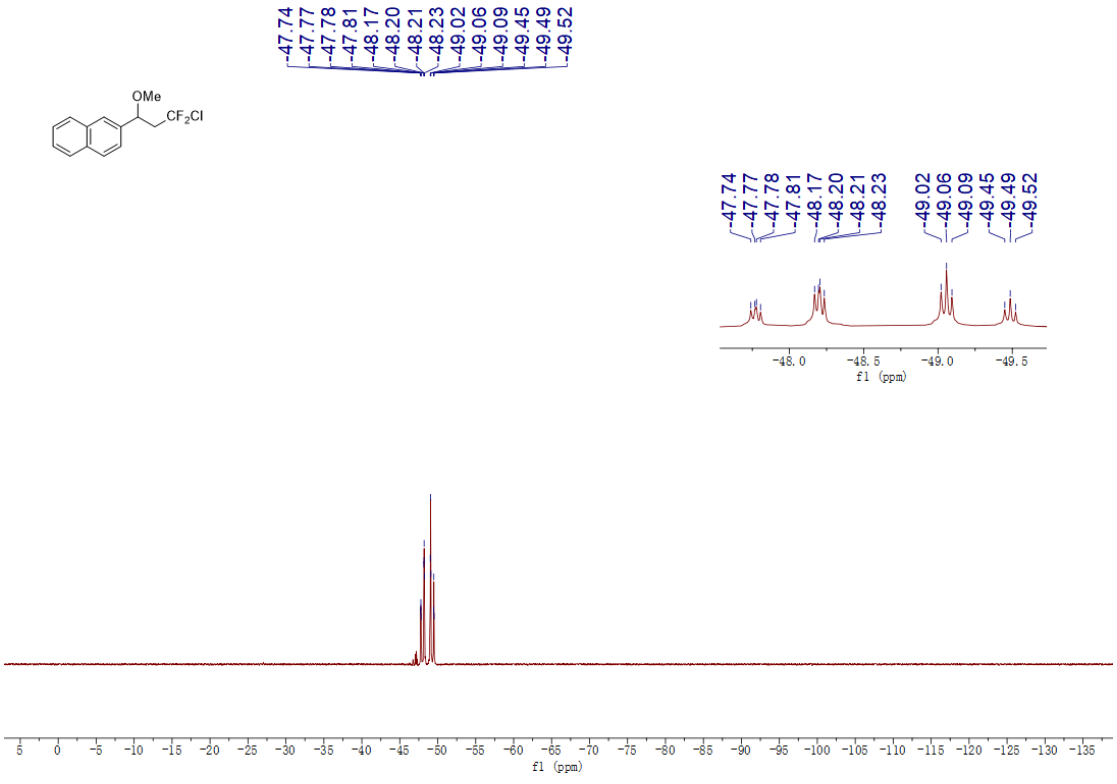
^{1}H NMR spectrum of 2-(3-chloro-3,3-difluoro-1-methoxypropyl)naphthalene 2d



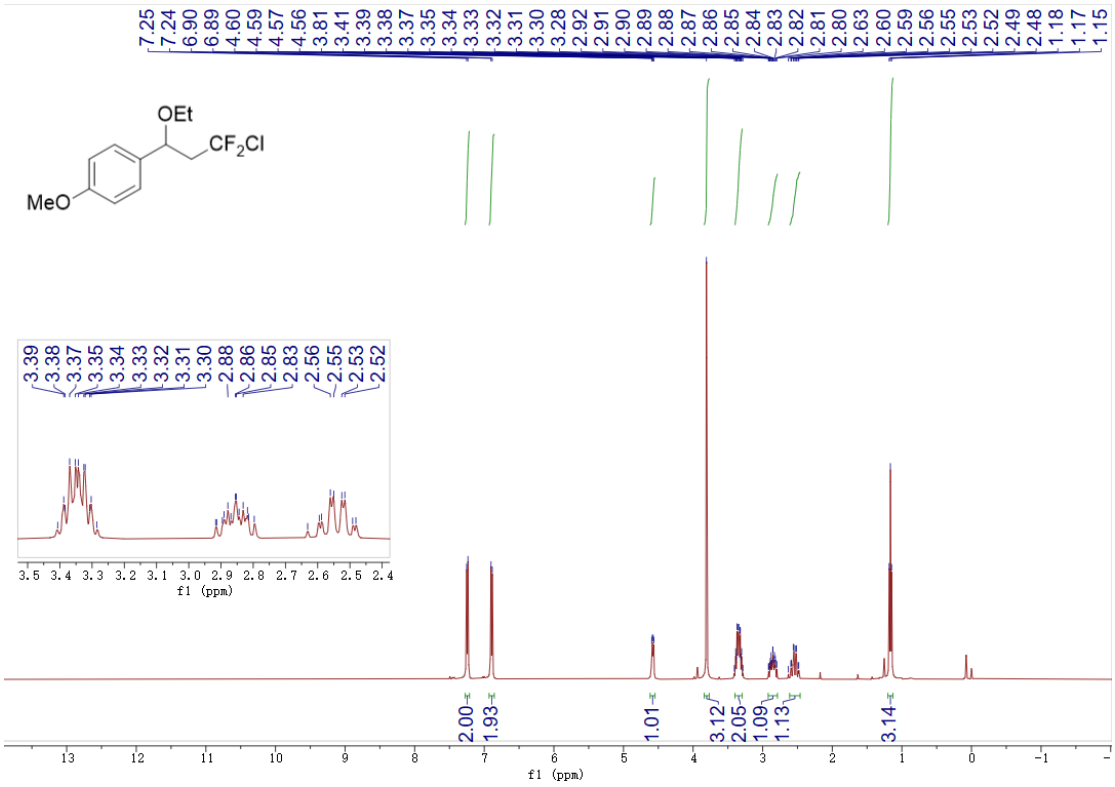
^{13}C NMR spectrum of 2-(3-chloro-3,3-difluoro -1-methoxypropyl)naphthalene 2d



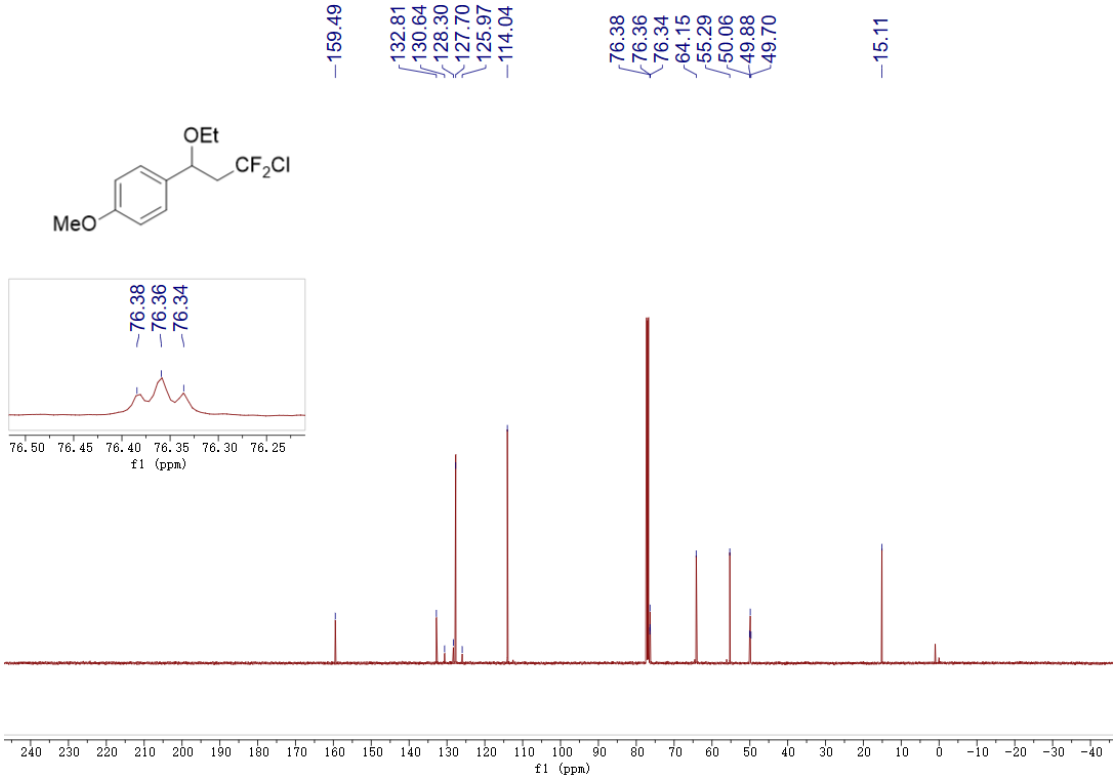
^{19}F NMR spectrum of 2-(3-chloro-3,3-difluoro -1-methoxypropyl)naphthalene 2d



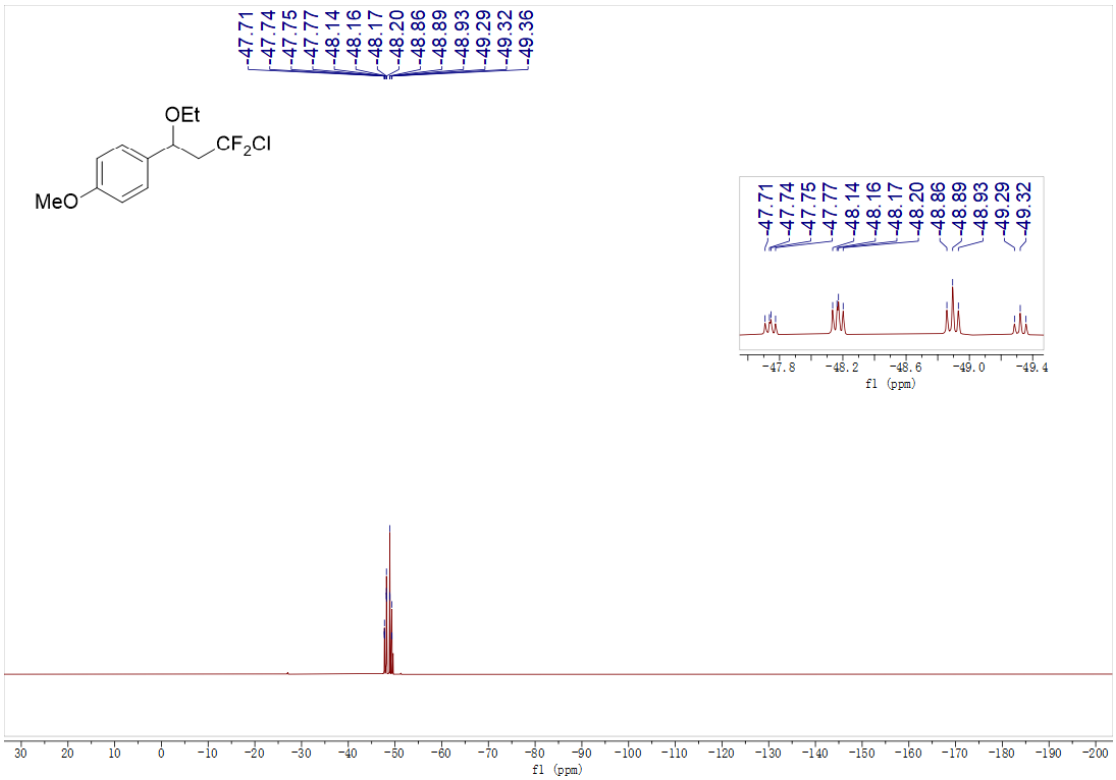
^{1}H NMR spectrum of 1-(3-chloro-1-ethoxy-3,3-difluoropropyl)-4-methoxybenzene 2e



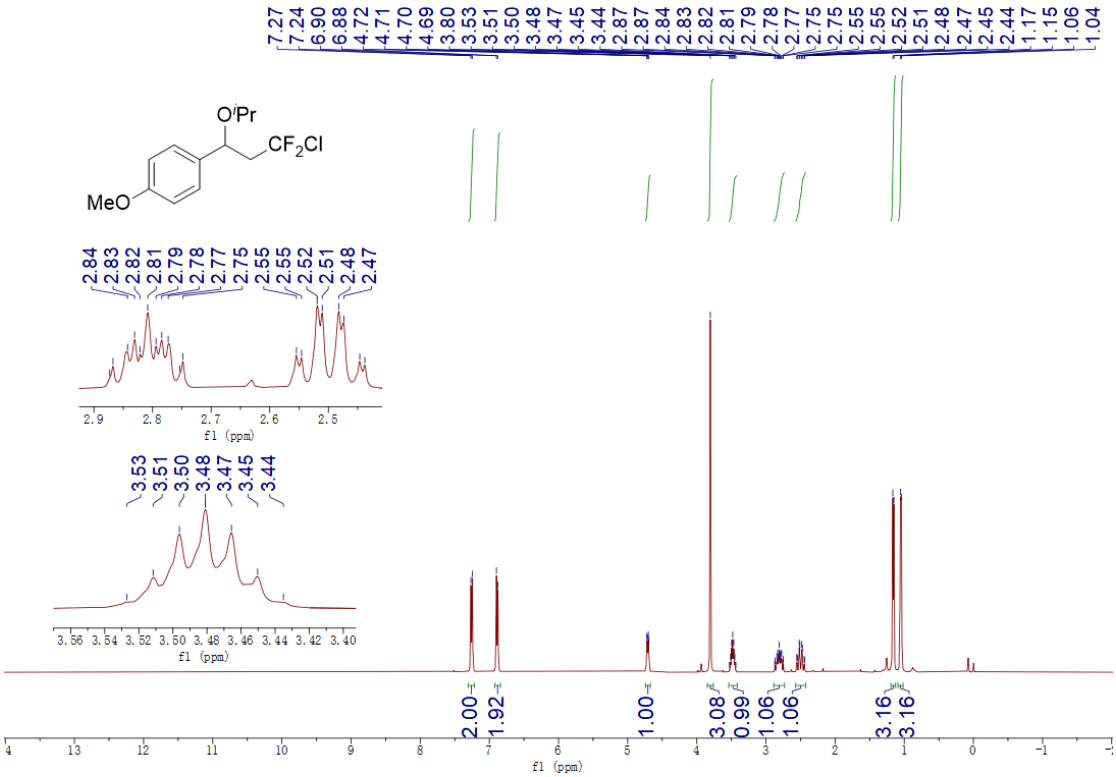
^{13}C NMR spectrum of 1-(3-chloro-1-ethoxy-3,3-difluoropropyl)-4-methoxybenzene 2e



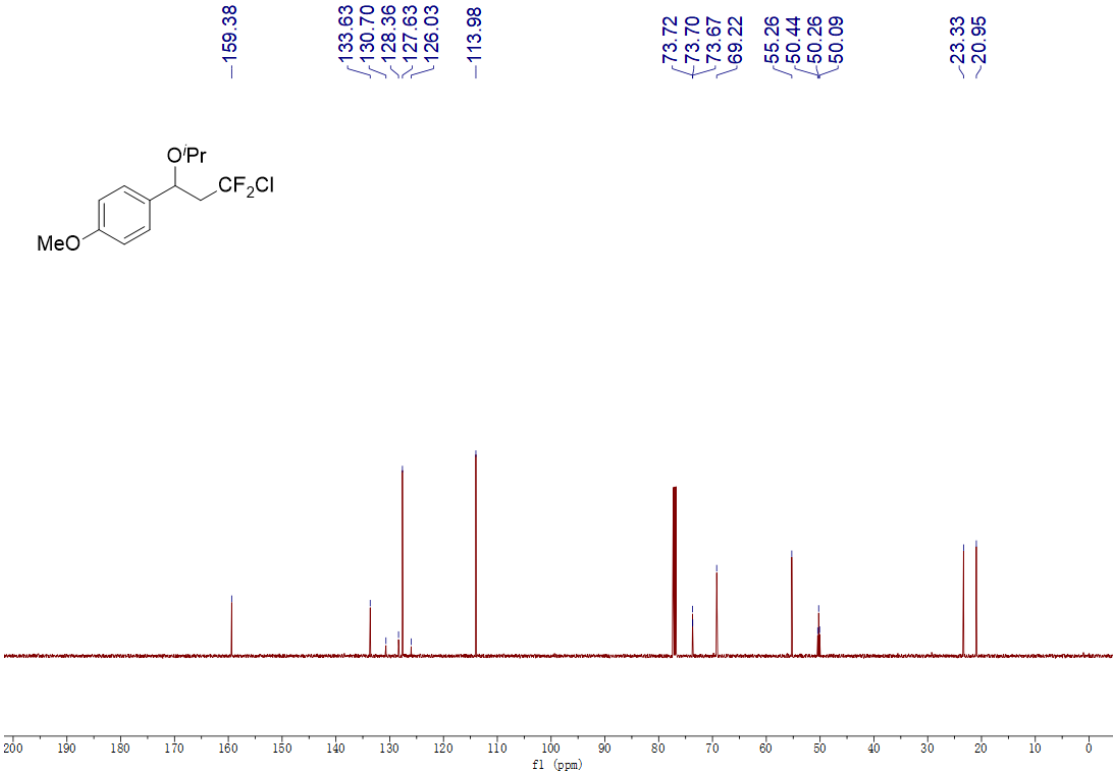
^{19}F NMR spectrum of 1-(3-chloro-1-ethoxy-3,3-difluoropropyl)-4-methoxybenzene 2e



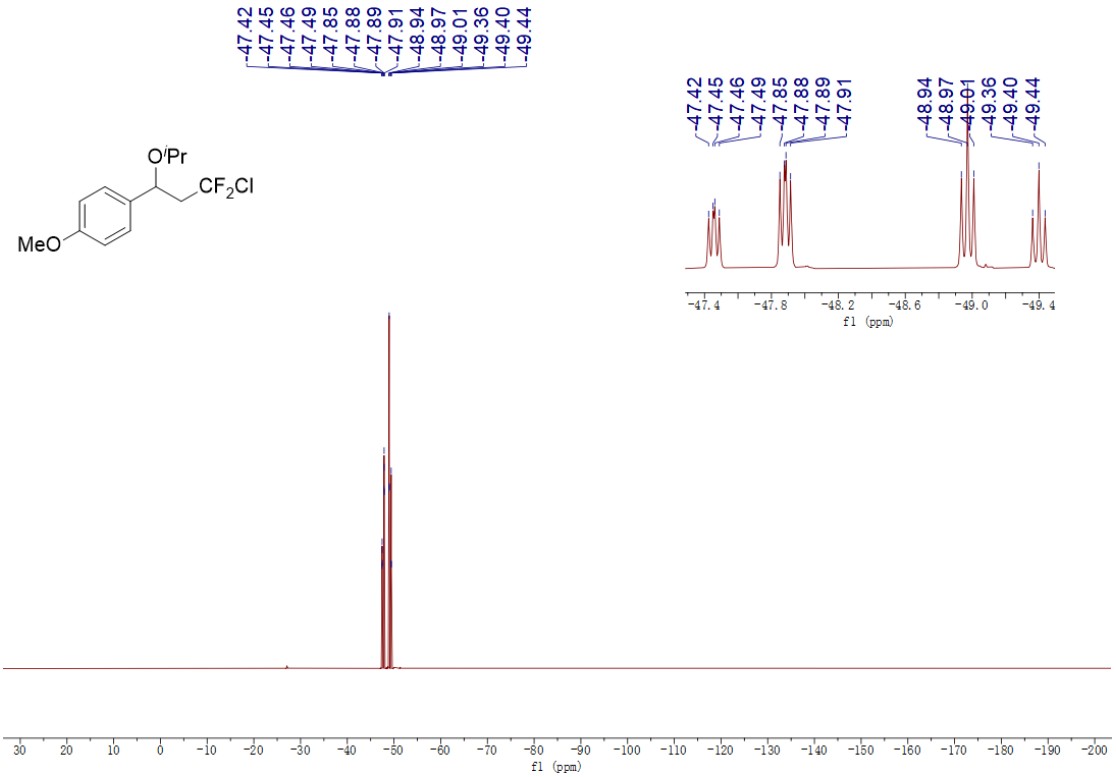
^{1}H NMR spectrum of 1-(3-chloro-3,3-difluoro-1-isopropoxypropyl)-4-methoxybenzene 2f



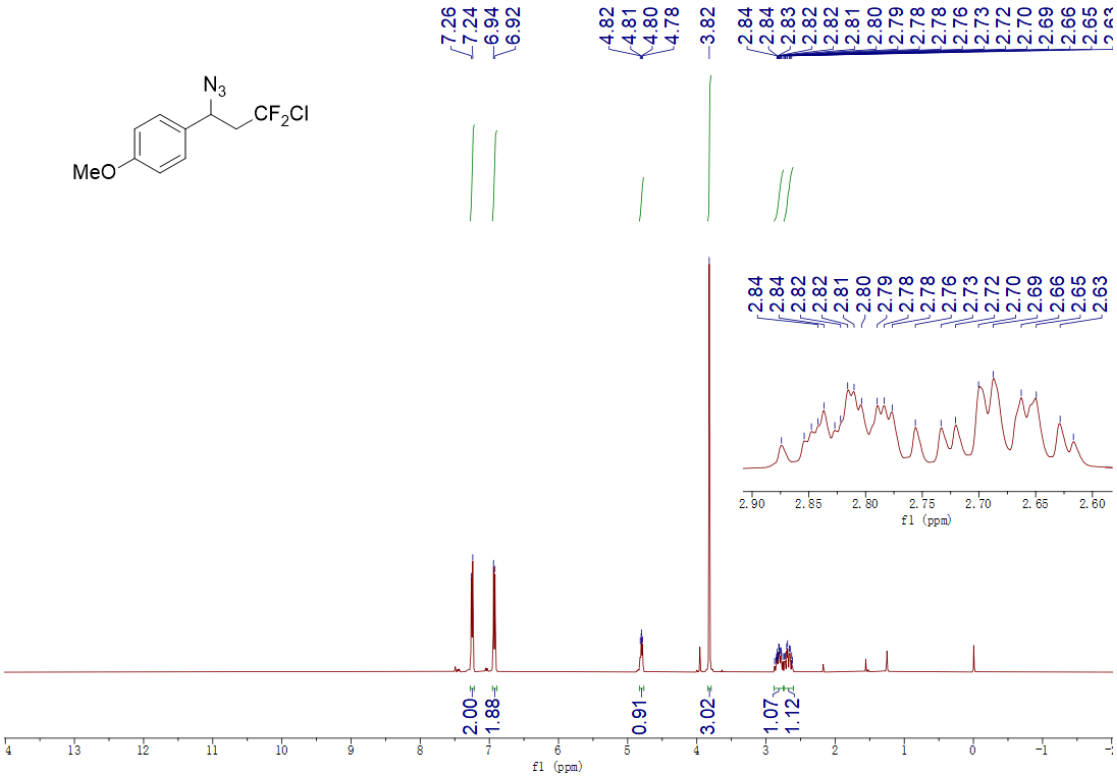
^{13}C NMR spectrum of 1-(3-chloro-3,3-difluoro-1-isopropoxypropyl)-4-methoxybenzene 2f



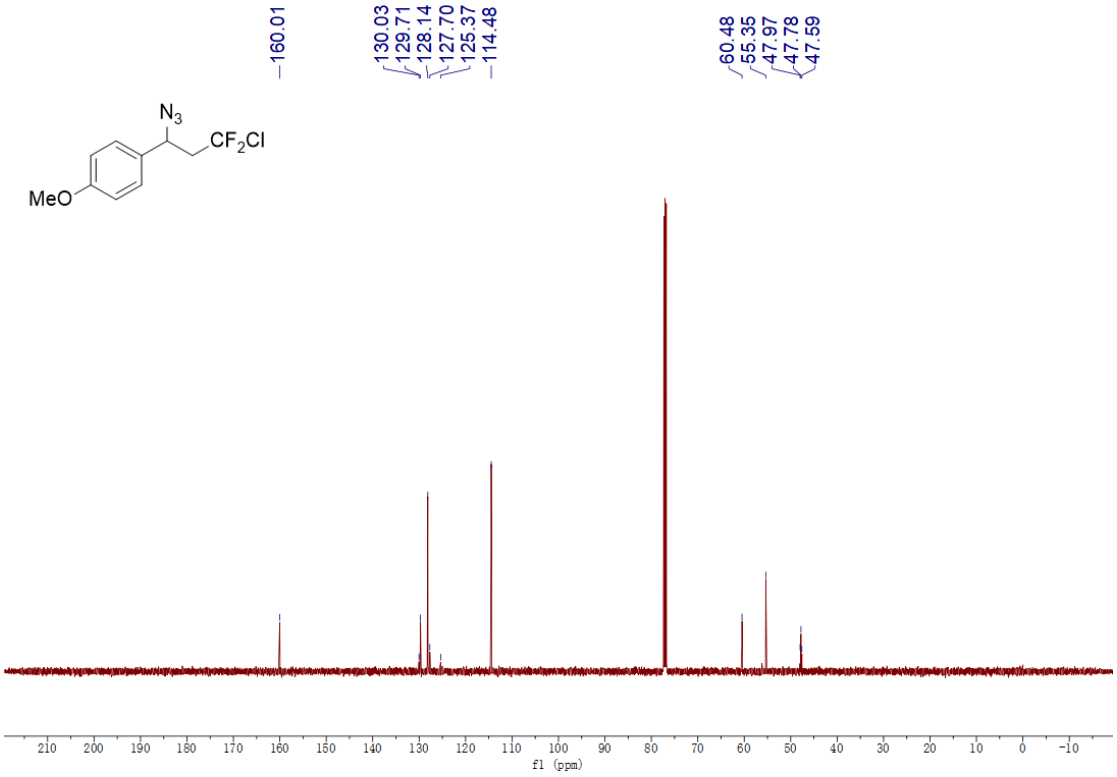
^{19}F NMR spectrum of 1-(3-chloro-3,3-difluoro-1-isopropoxypropyl)-4-methoxybenzene 2f



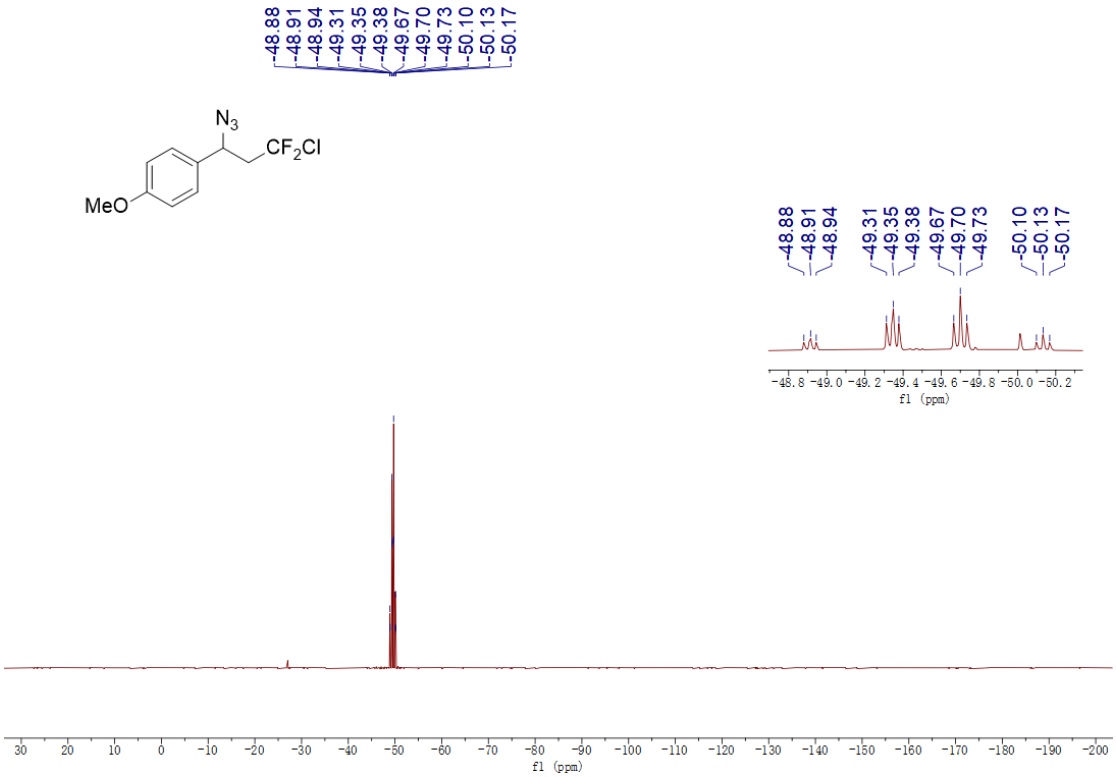
^{1}H NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-methoxybenzene 2g



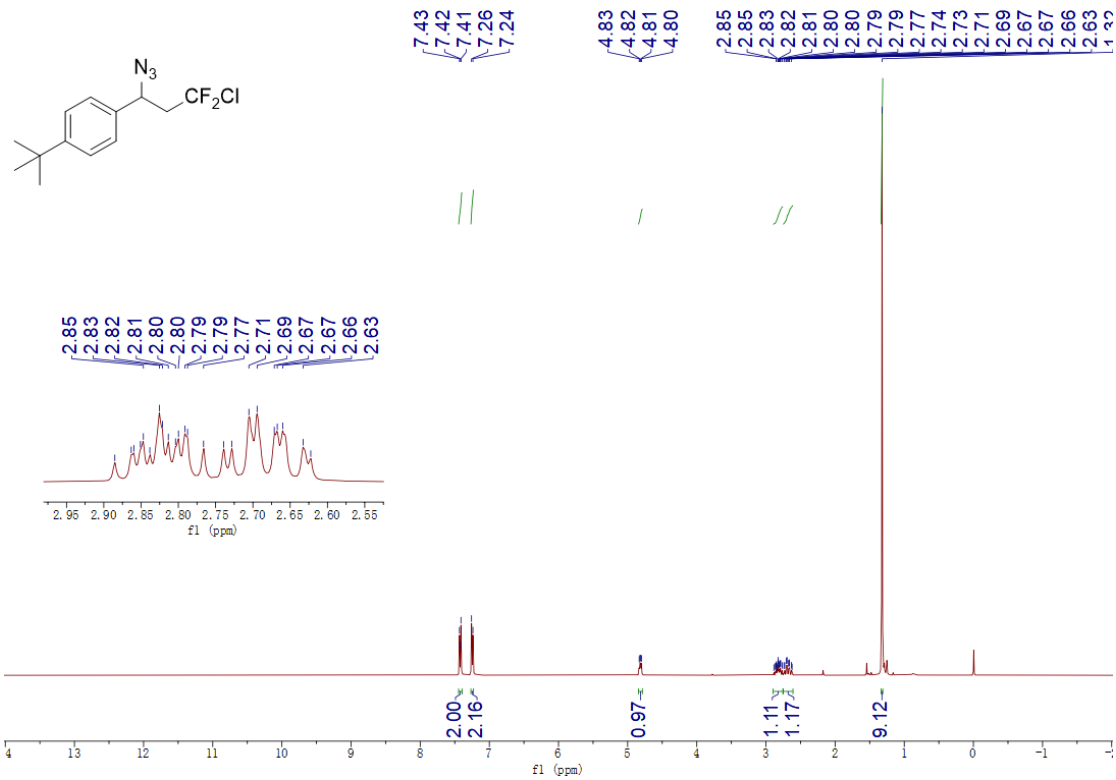
^{13}C NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-methoxybenzene 2g



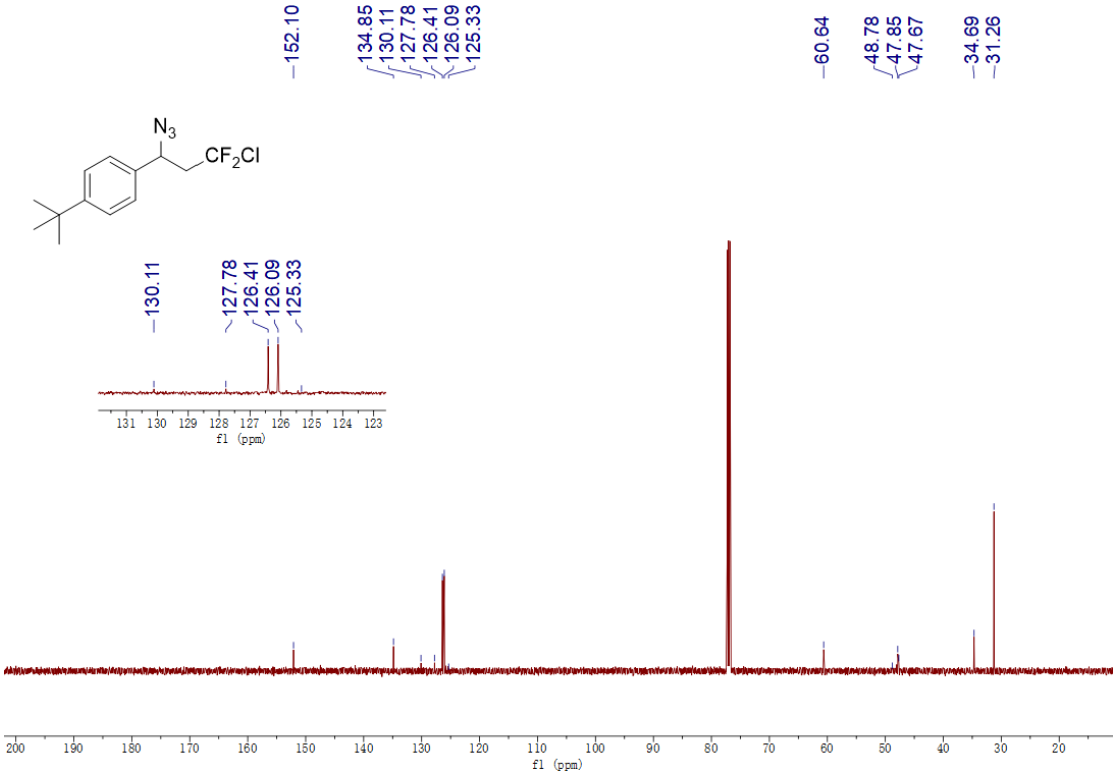
^{19}F NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-methoxybenzene 2g



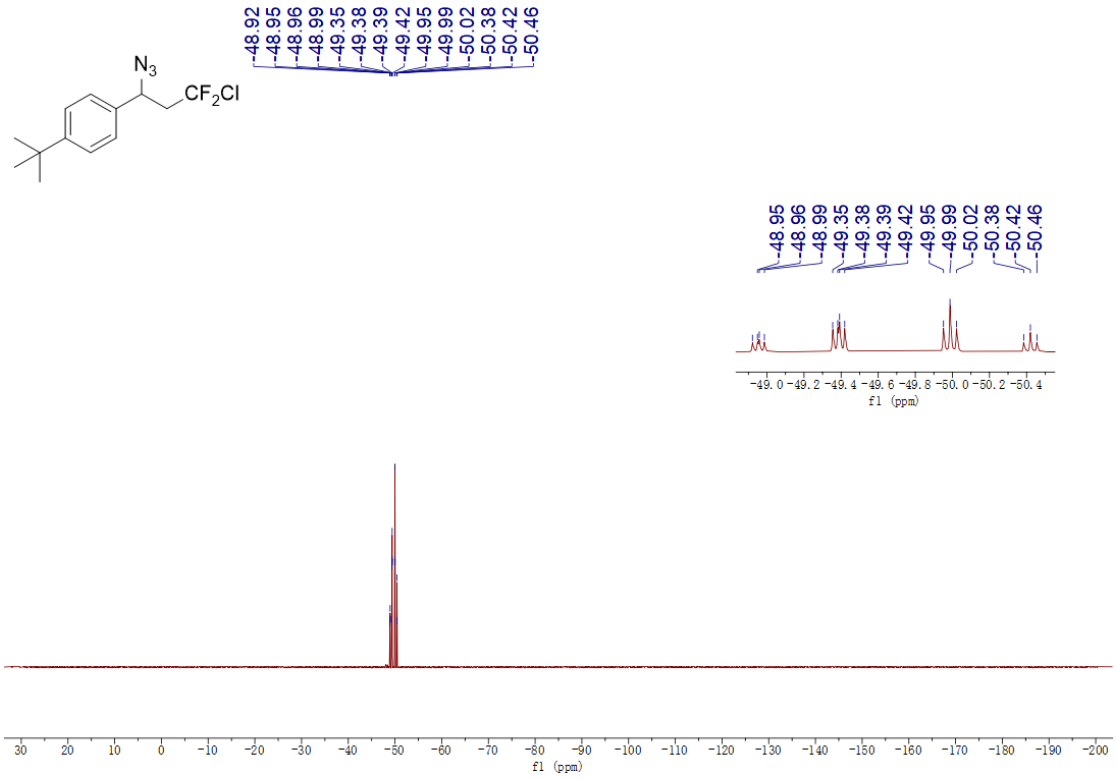
^{1}H NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-(tert-butyl)benzene 2h



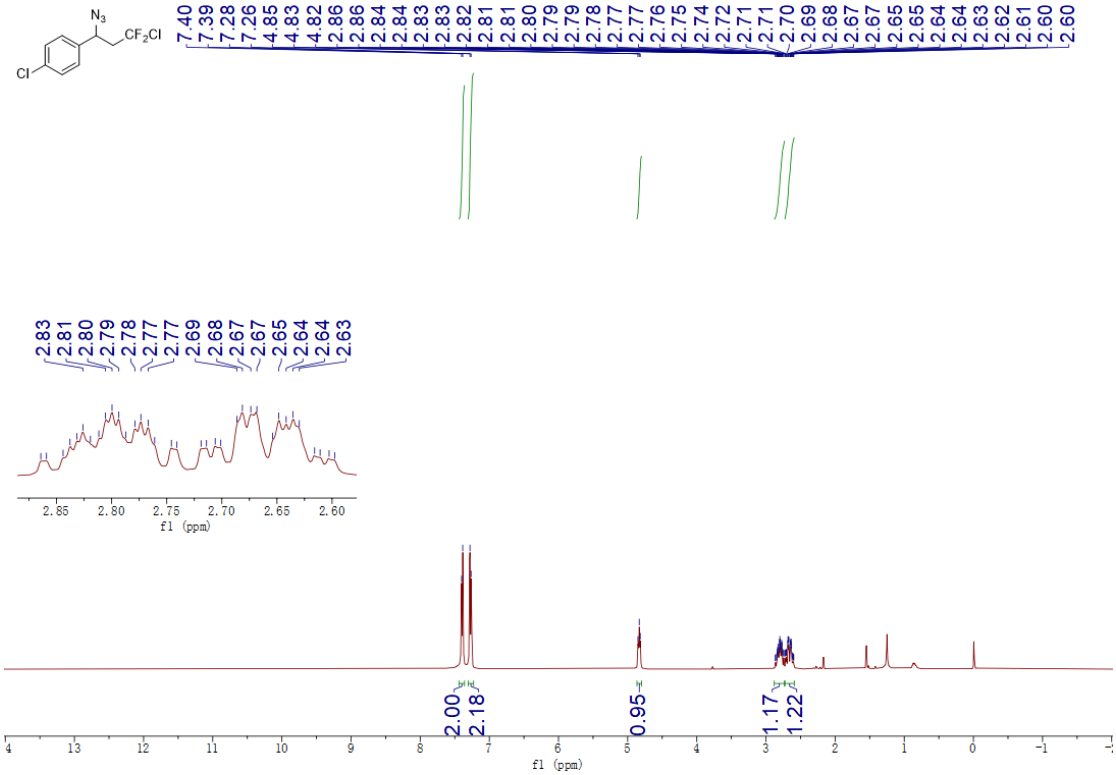
^{13}C NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-(tert-butyl)benzene 2h



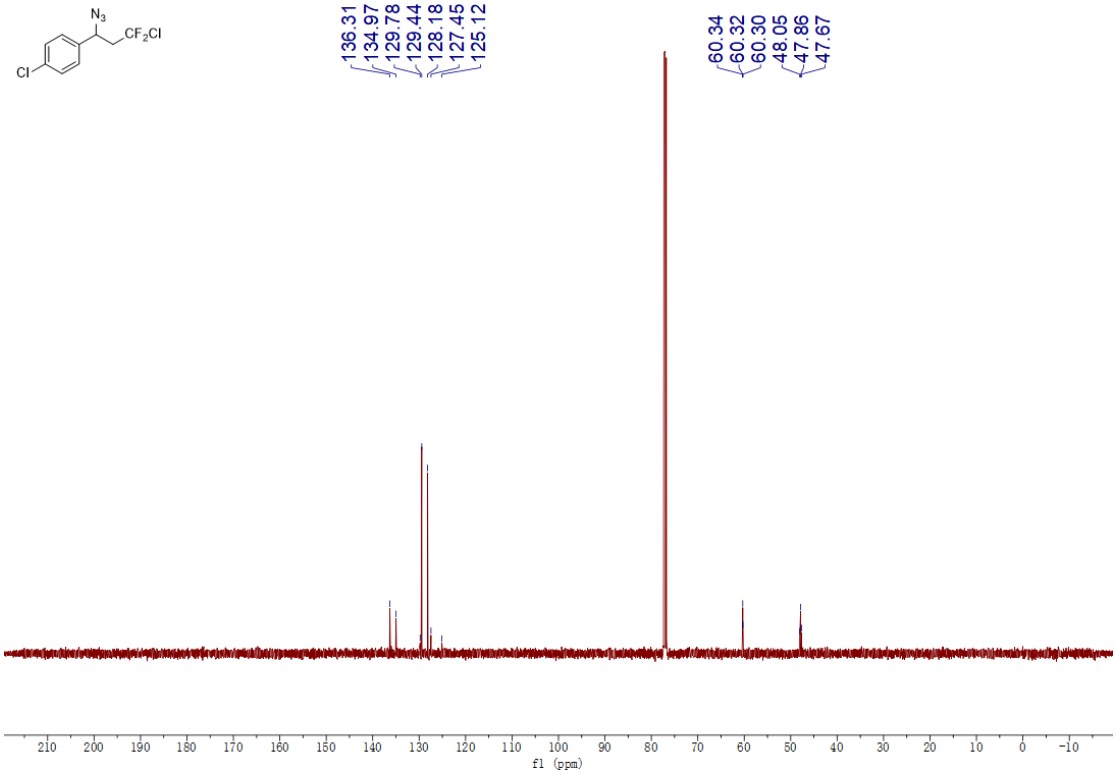
^{19}F NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl)-4-(tert-butyl)benzene 2h



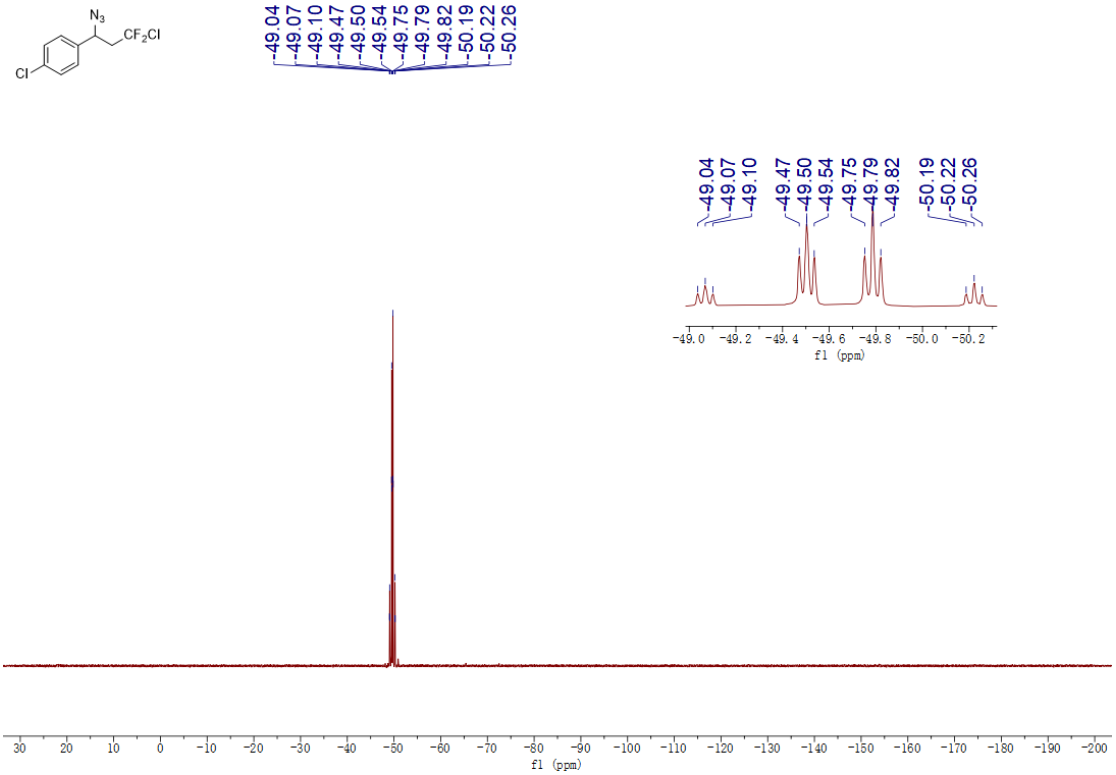
^{1}H NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl) -4-chlorobenzene 3i



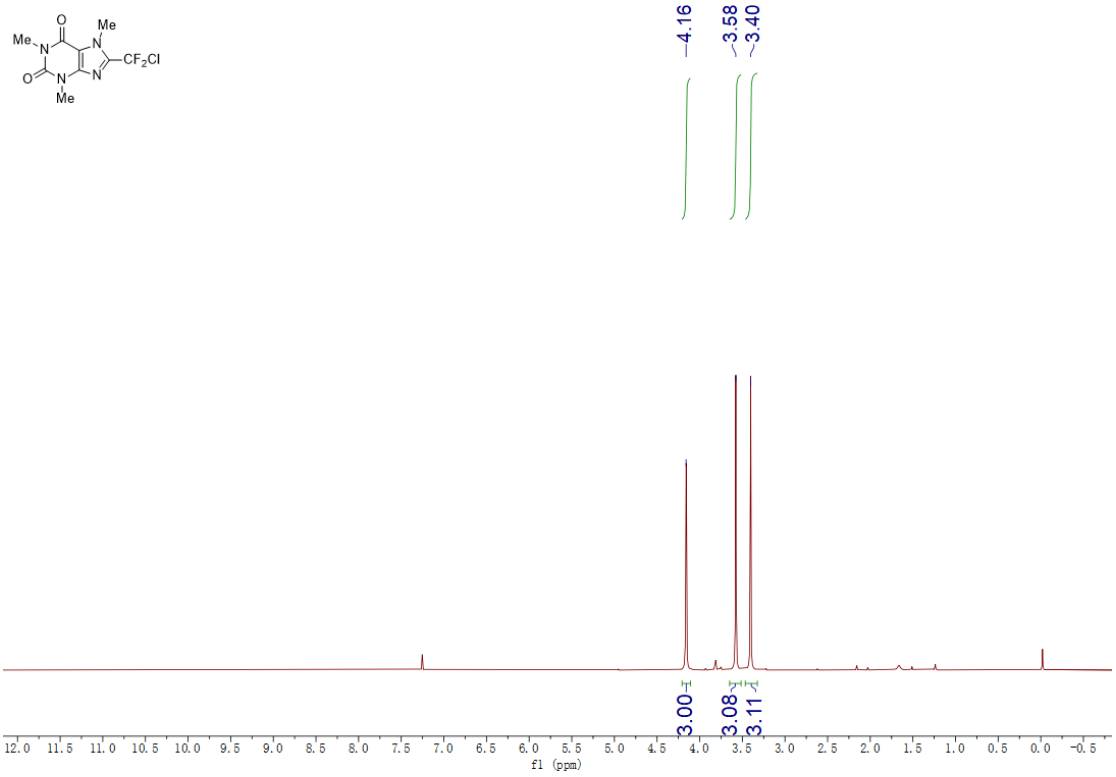
^{13}C NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl) -4-chlorobenzene 3i



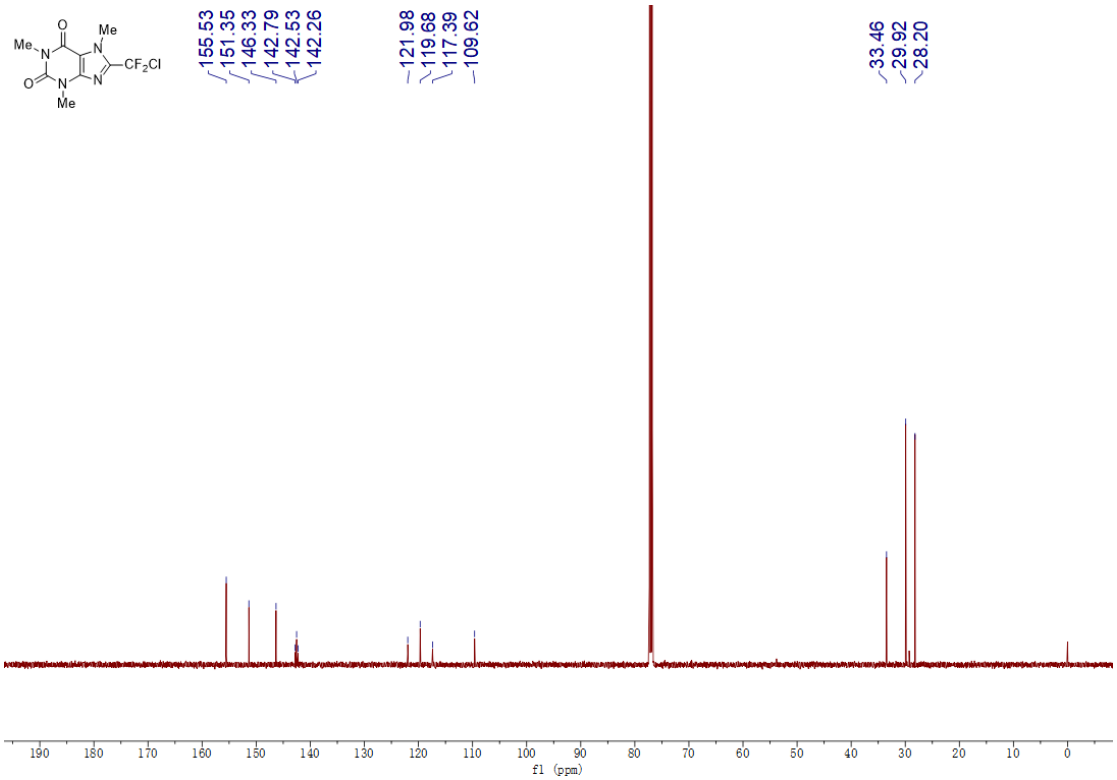
^{19}F NMR spectrum of 1-(1-azido-3-chloro-3,3-difluoropropyl) -4-chlorobenzene 3i



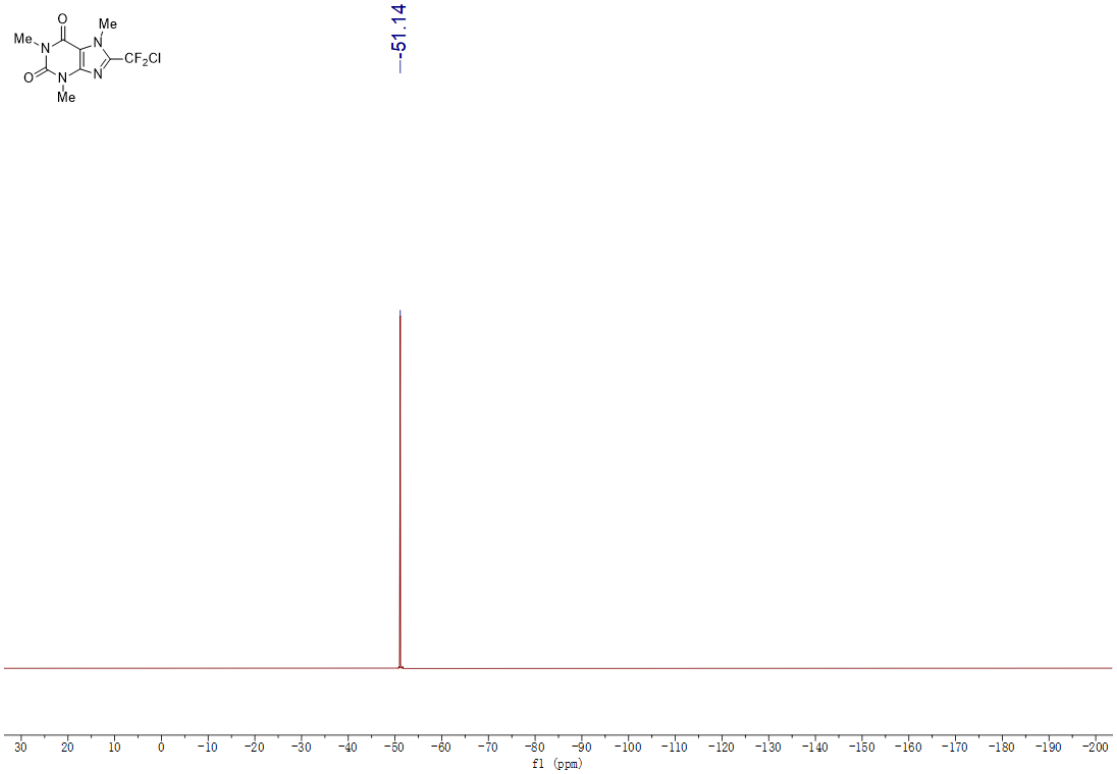
^{1}H NMR spectrum of 8-(chlorodifluoromethyl)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3a



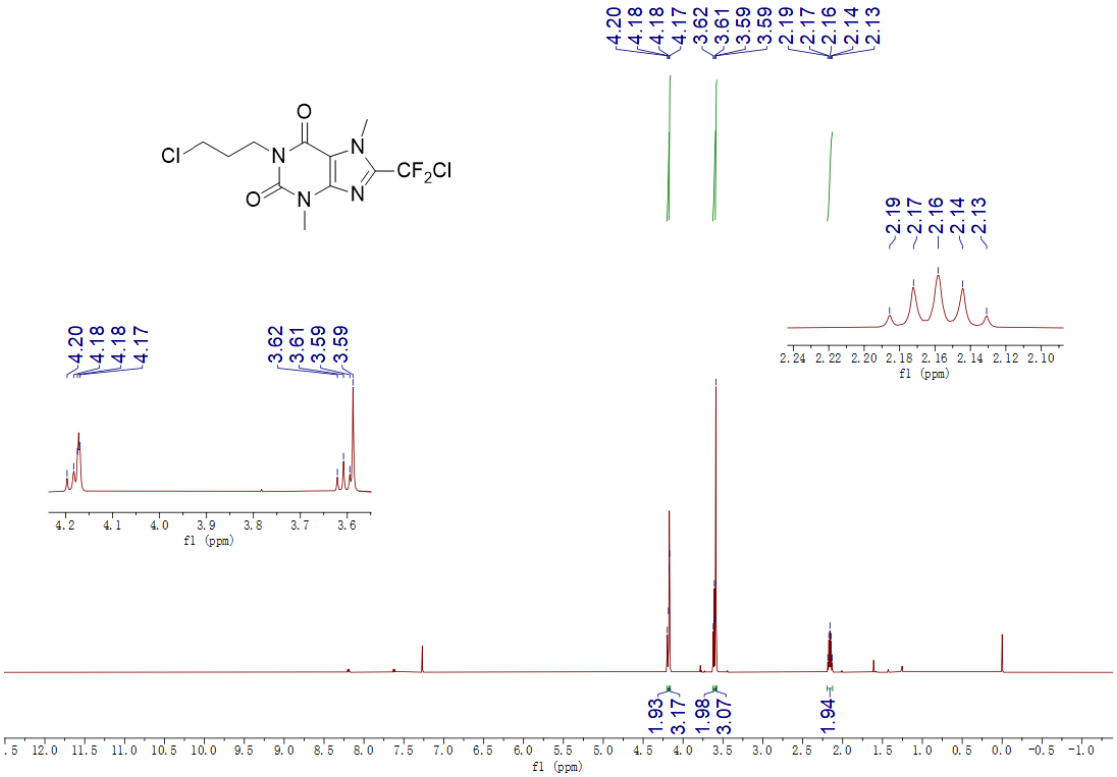
^{13}C NMR spectrum of 8-(chlorodifluoromethyl)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3a



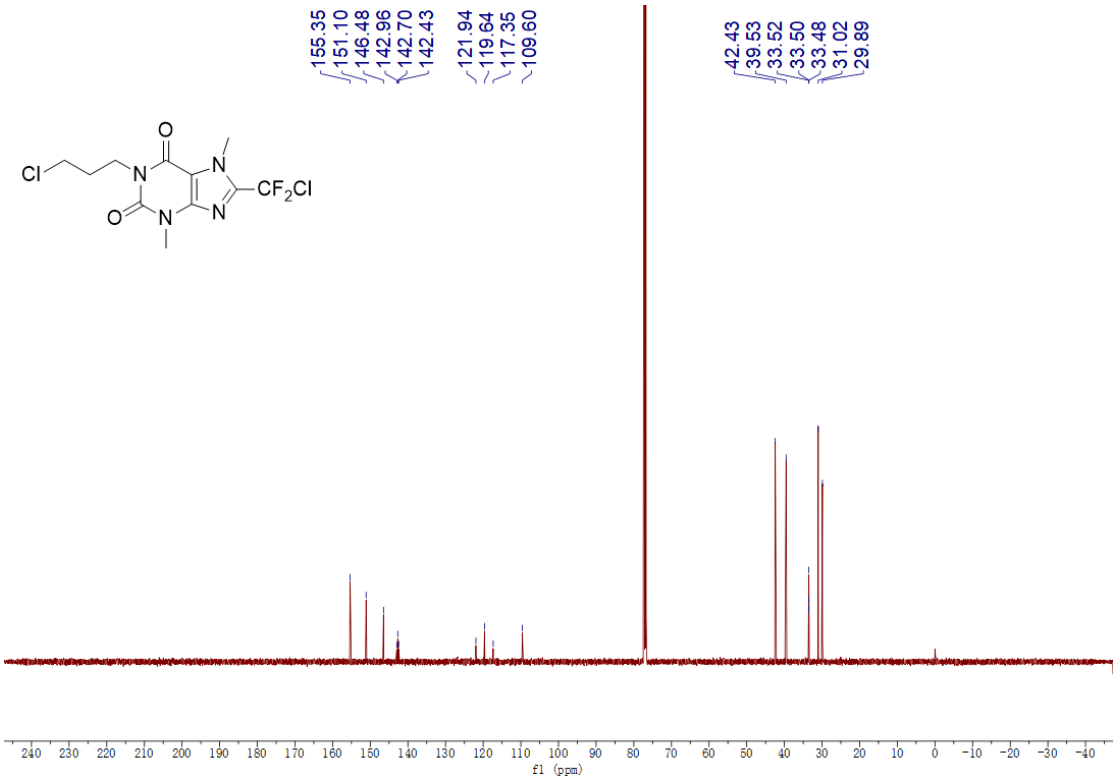
^{19}F NMR spectrum of 8-(chlorodifluoromethyl)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3a



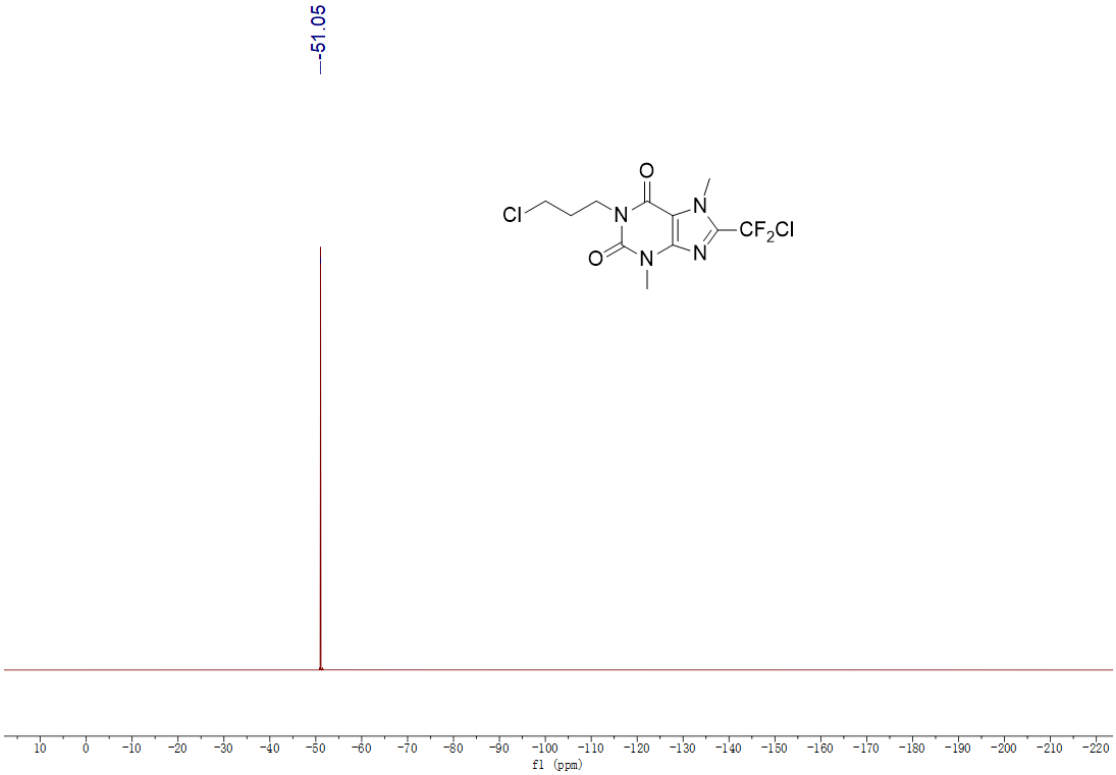
^{1}H NMR spectrum of 8-(chlorodifluoromethyl)-1-(3-chloropropyl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3b



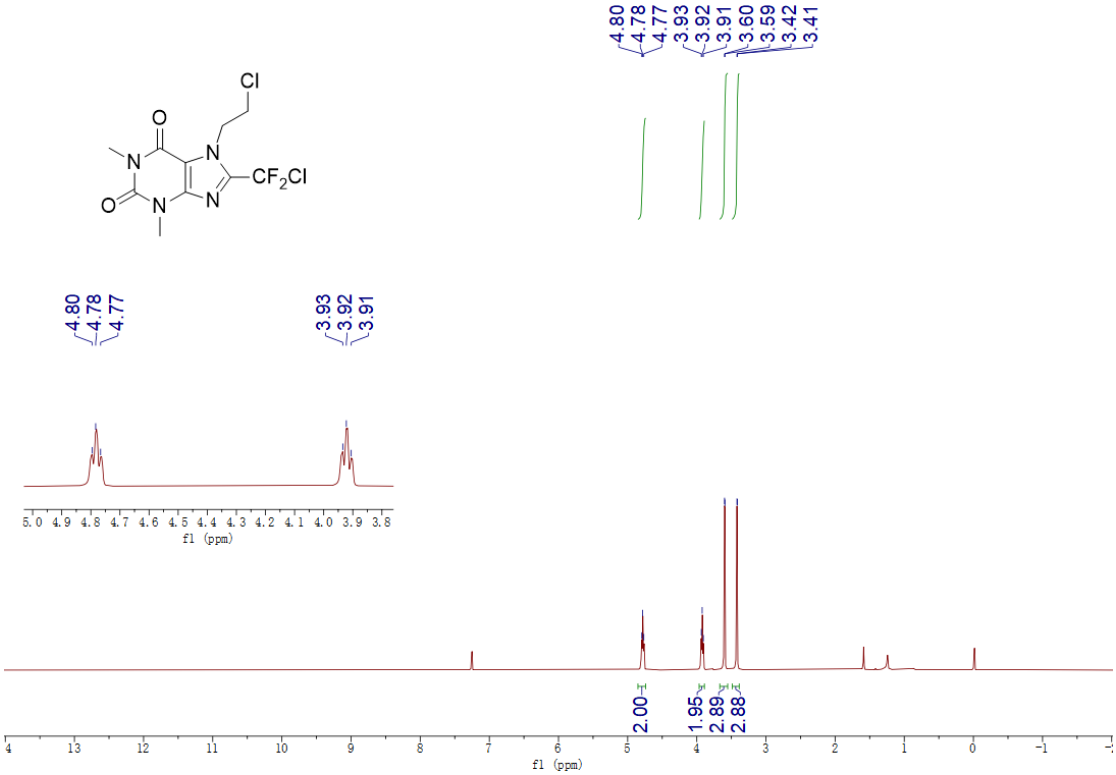
^{13}C NMR spectrum of 8-(chlorodifluoromethyl)-1-(3-chloropropyl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3b



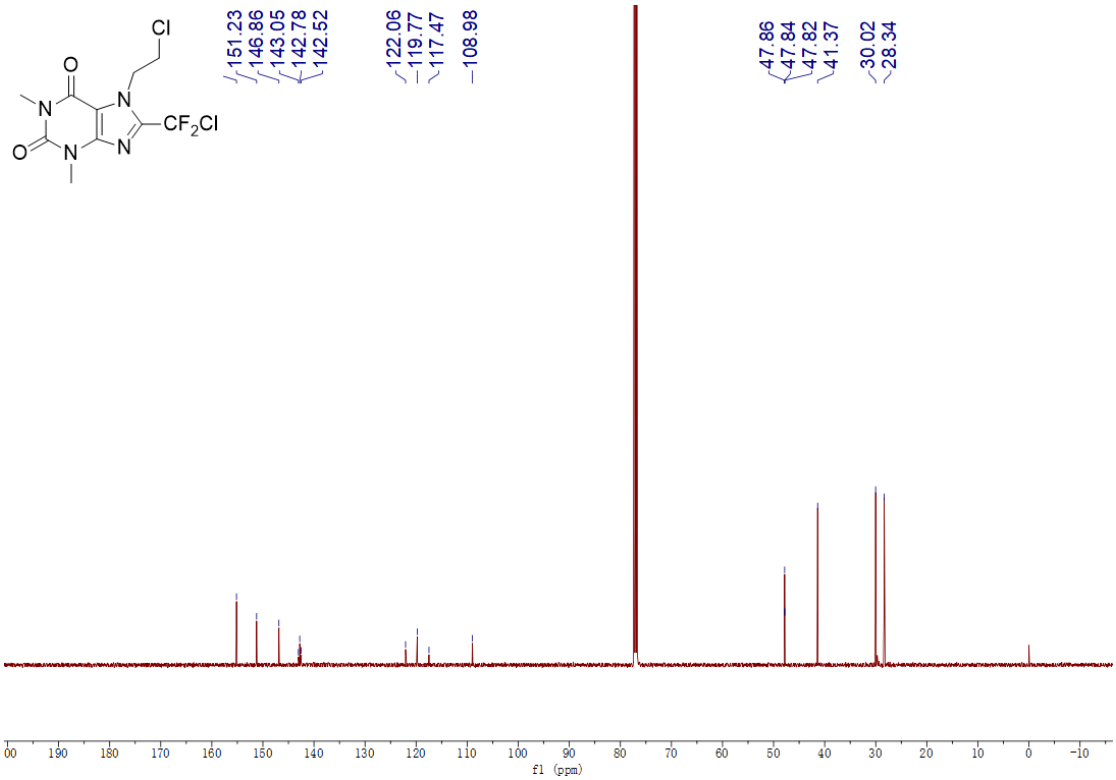
^{19}F NMR spectrum of 8-(chlorodifluoromethyl)-1-(3-chloropropyl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3b



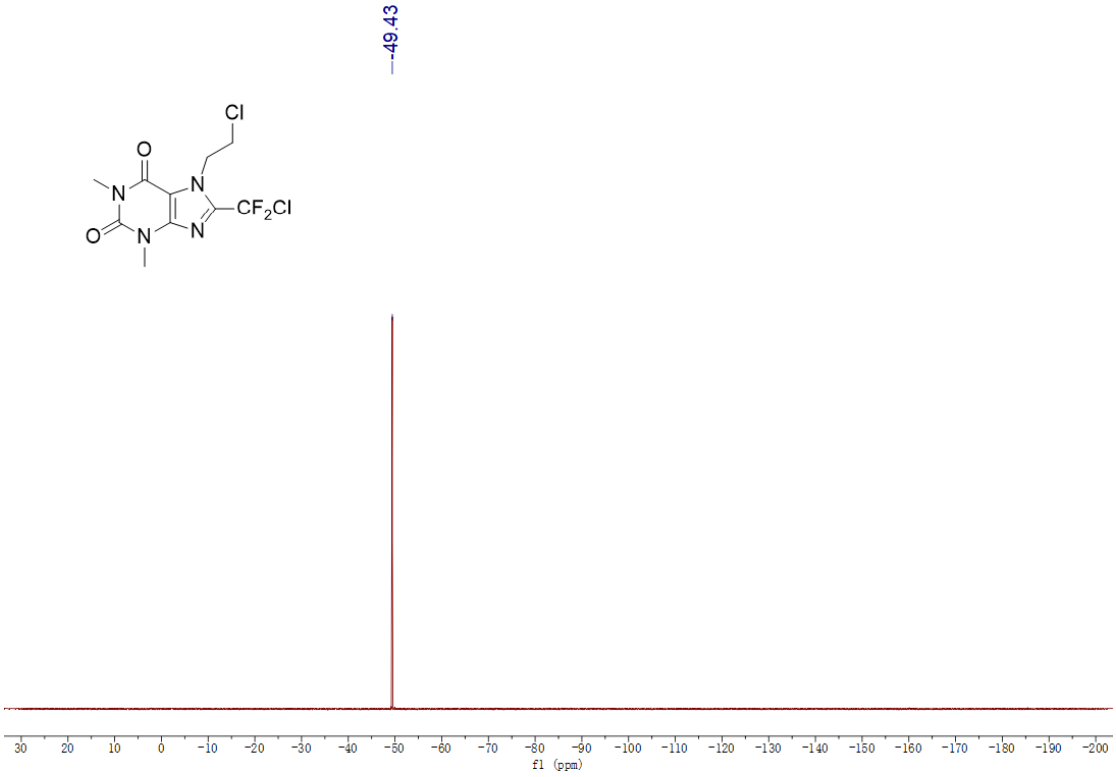
^{1}H NMR spectrum of 8-(chlorodifluoromethyl)-7-(2-chloroethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3c



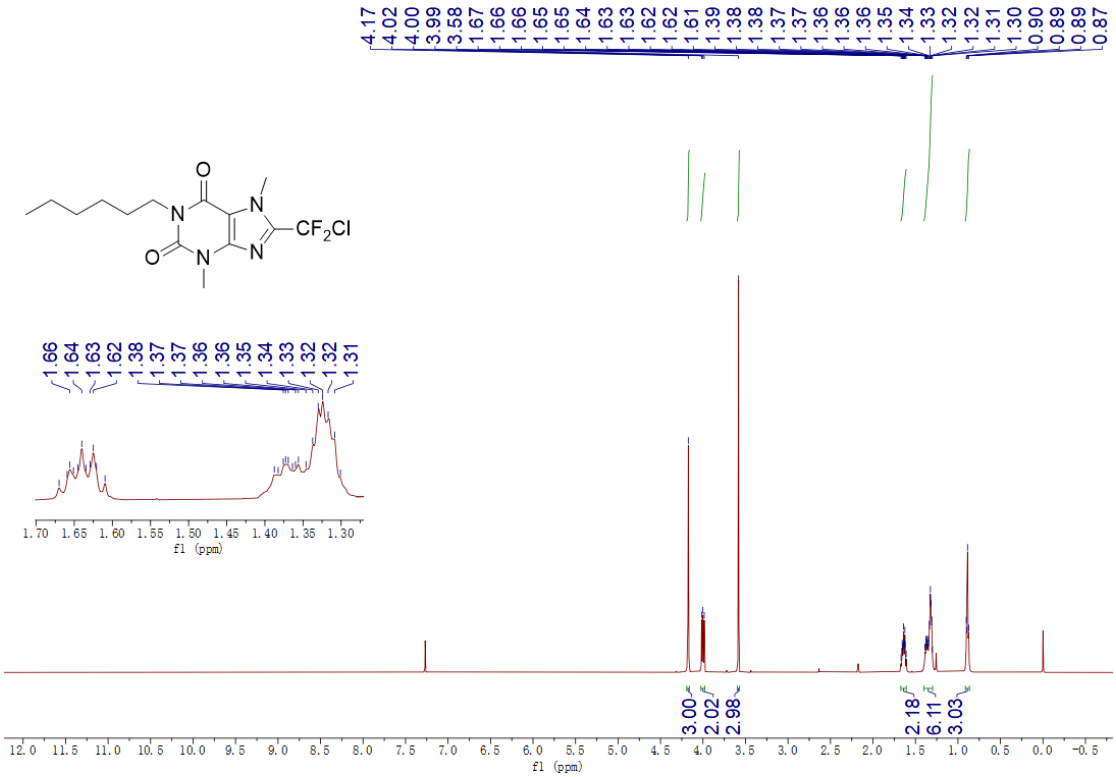
^{13}C NMR spectrum of 8-(chlorodifluoromethyl)-7-(2-chloroethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3c



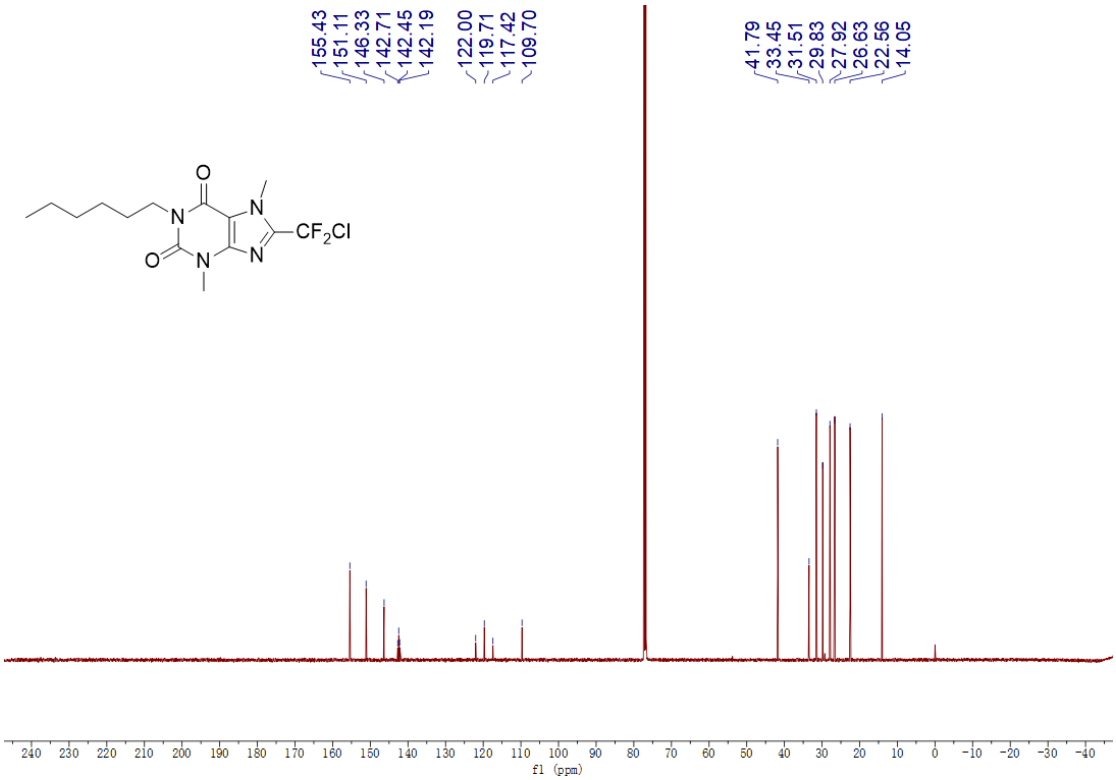
^{19}F NMR spectrum of 8-(chlorodifluoromethyl)-7-(2-chloroethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3c



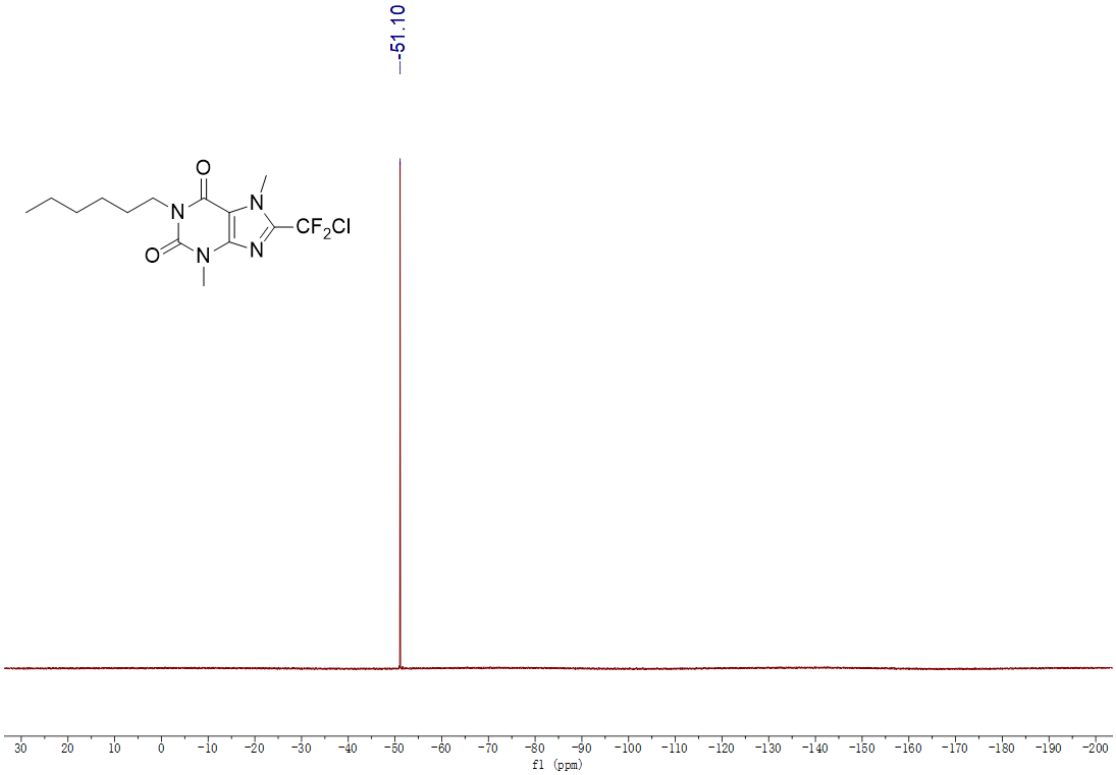
^{1}H NMR spectrum of 8-(chlorodifluoromethyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3d



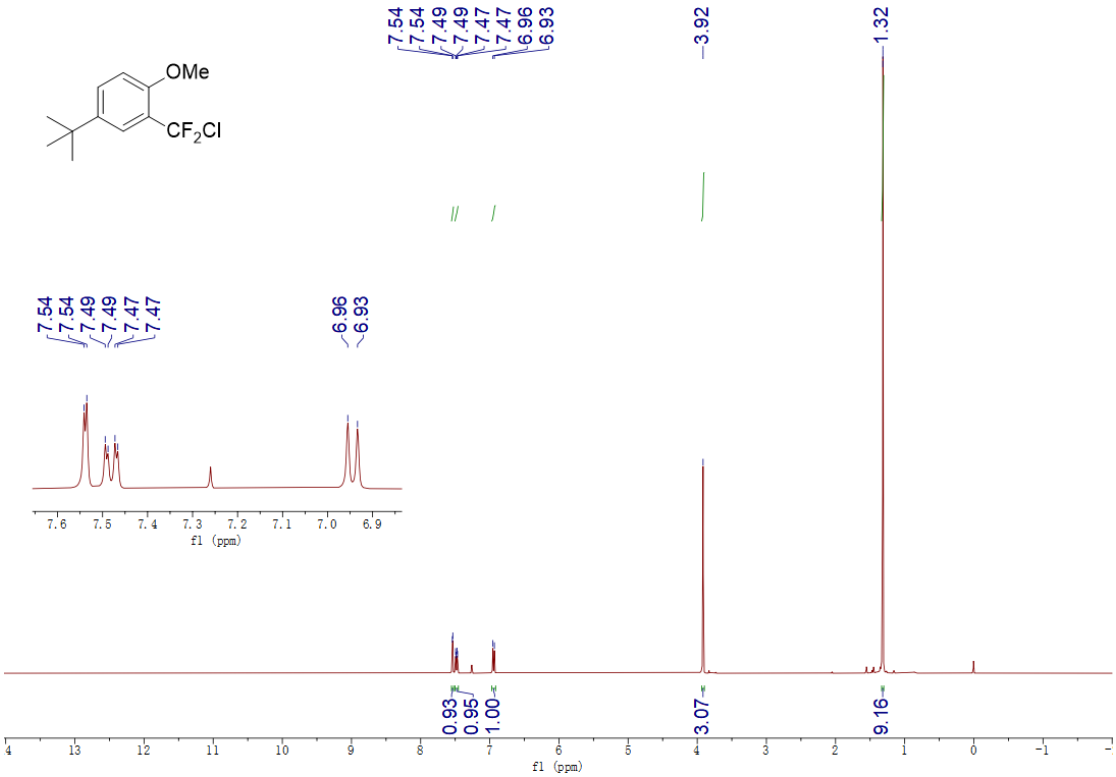
^{13}C NMR spectrum of 8-(chlorodifluoromethyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3d



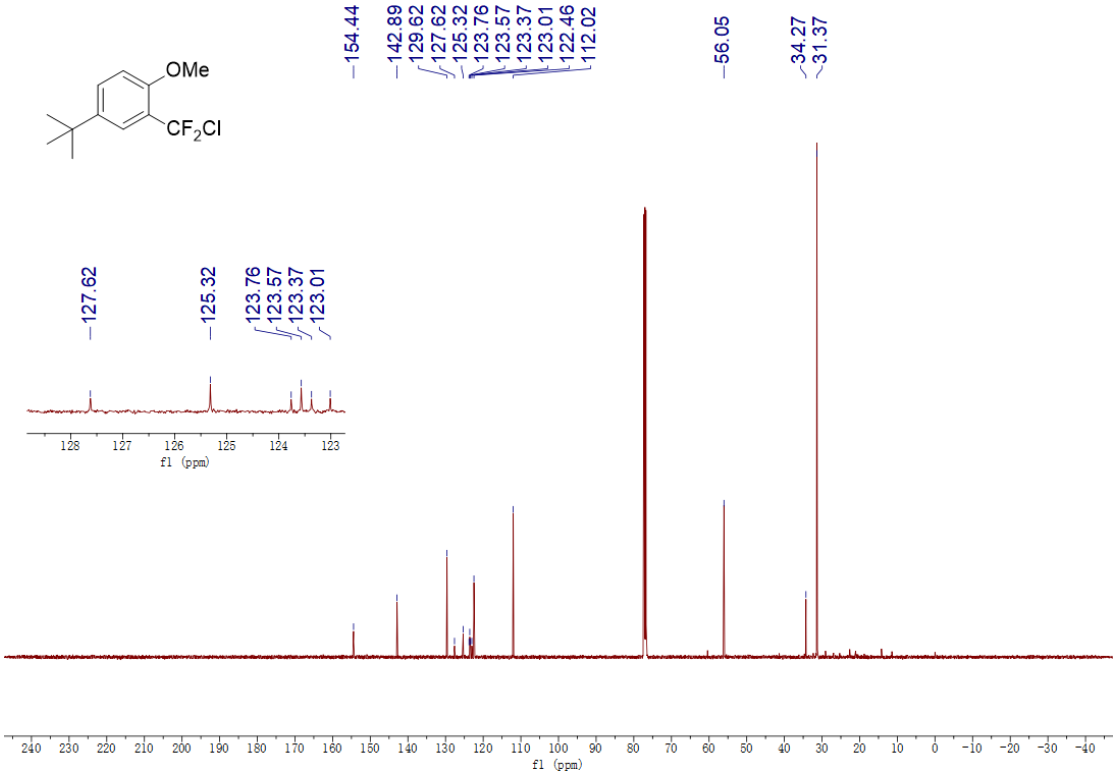
^{19}F NMR spectrum of 8-(chlorodifluoromethyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 3d



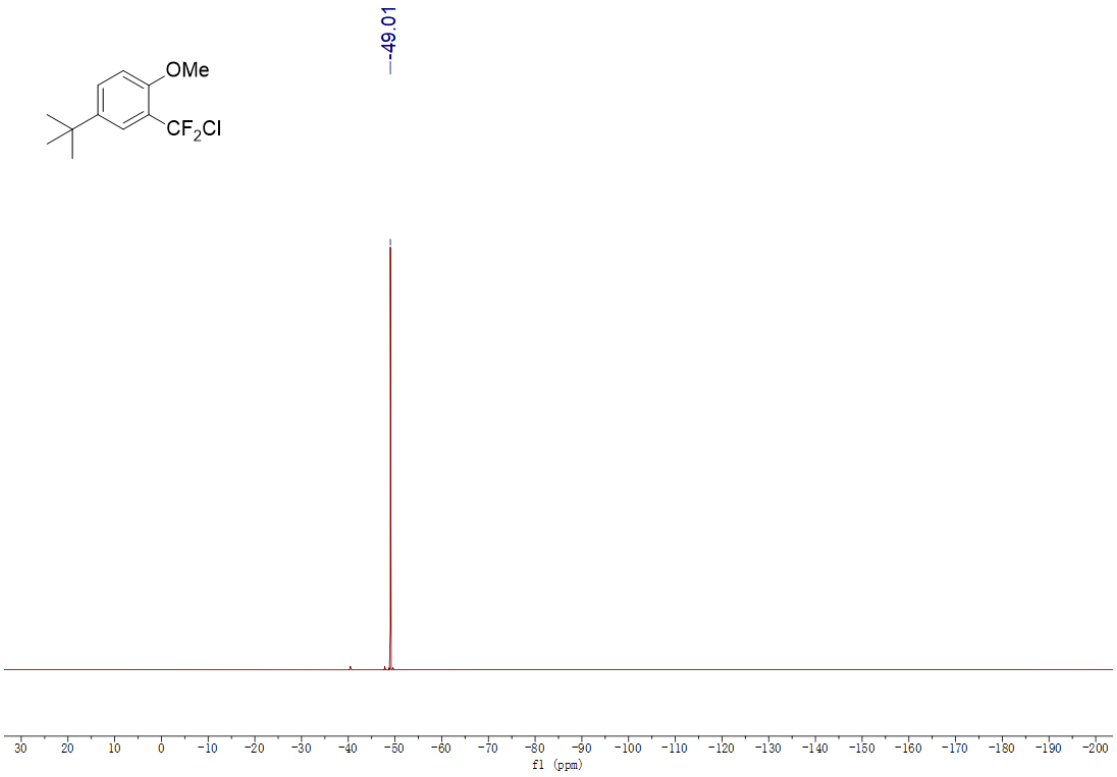
^{1}H NMR spectrum of 4-(*tert*-butyl)-2-(chlorodifluoromethyl)-1-methoxybenzene 3e



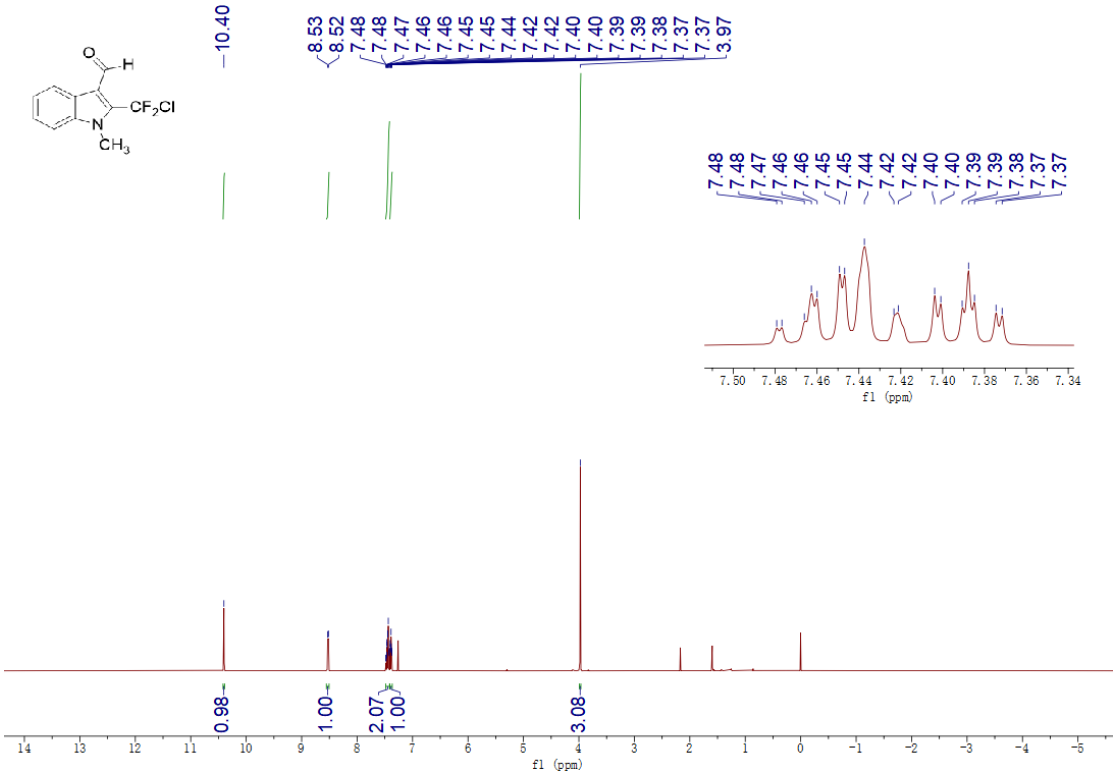
^{13}C NMR spectrum of 4-(*tert*-butyl)-2-(chlorodifluoromethyl)-1-methoxybenzene 3e



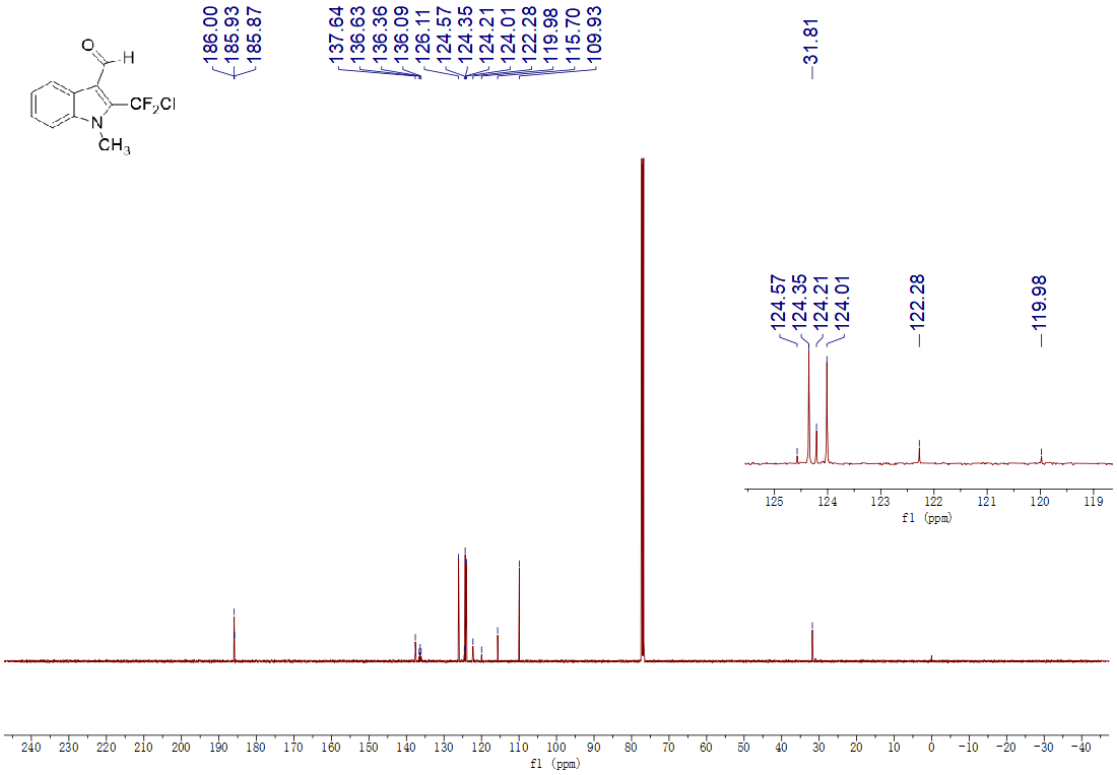
^{19}F NMR spectrum of 4-(tert-butyl)-2-(chlorodifluoromethyl)-1-methoxybenzene 3e



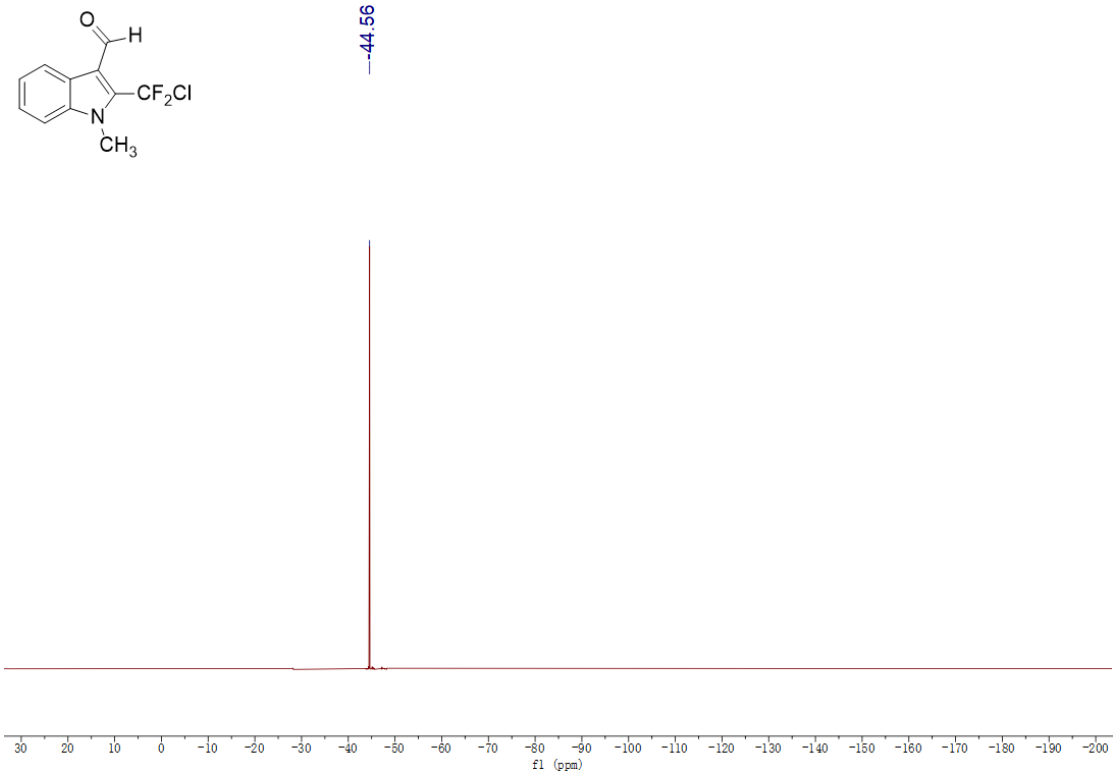
^{1}H NMR spectrum of 2-(chlorodifluoromethyl)-1-methyl-1*H*-indole-3-carbaldehyde 3f



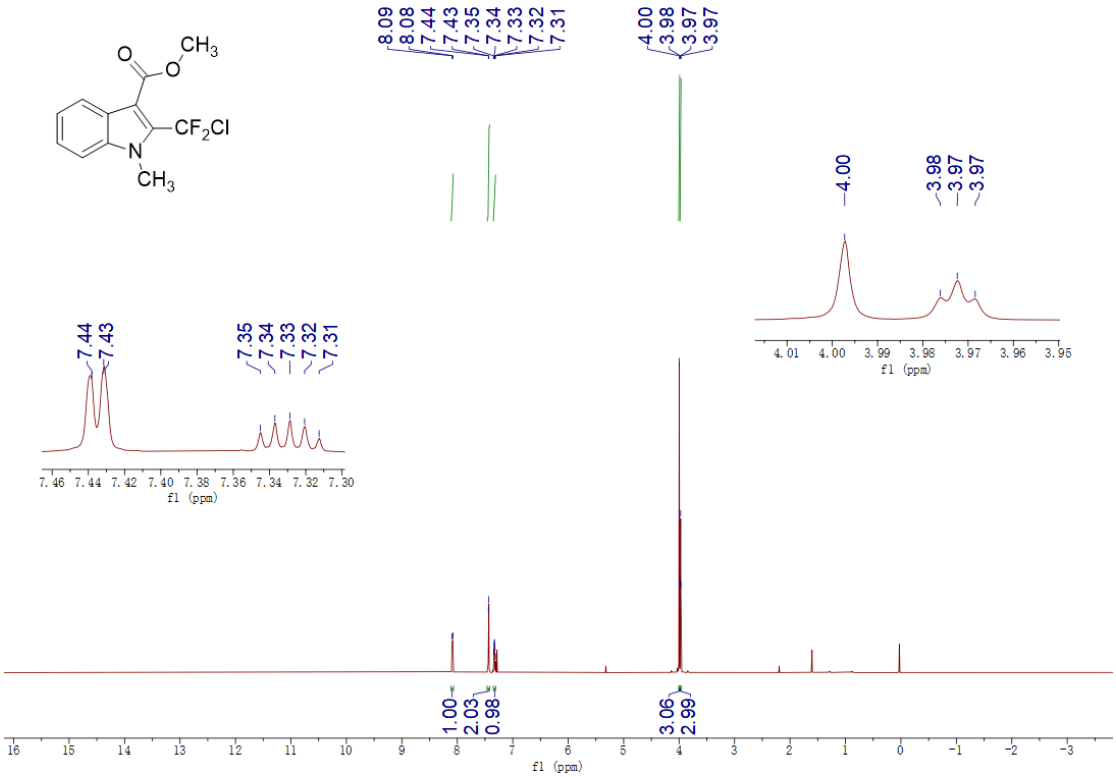
^{13}C NMR spectrum of 2-(chlorodifluoromethyl)-1-methyl-1*H*-indole-3-carbaldehyde 3f



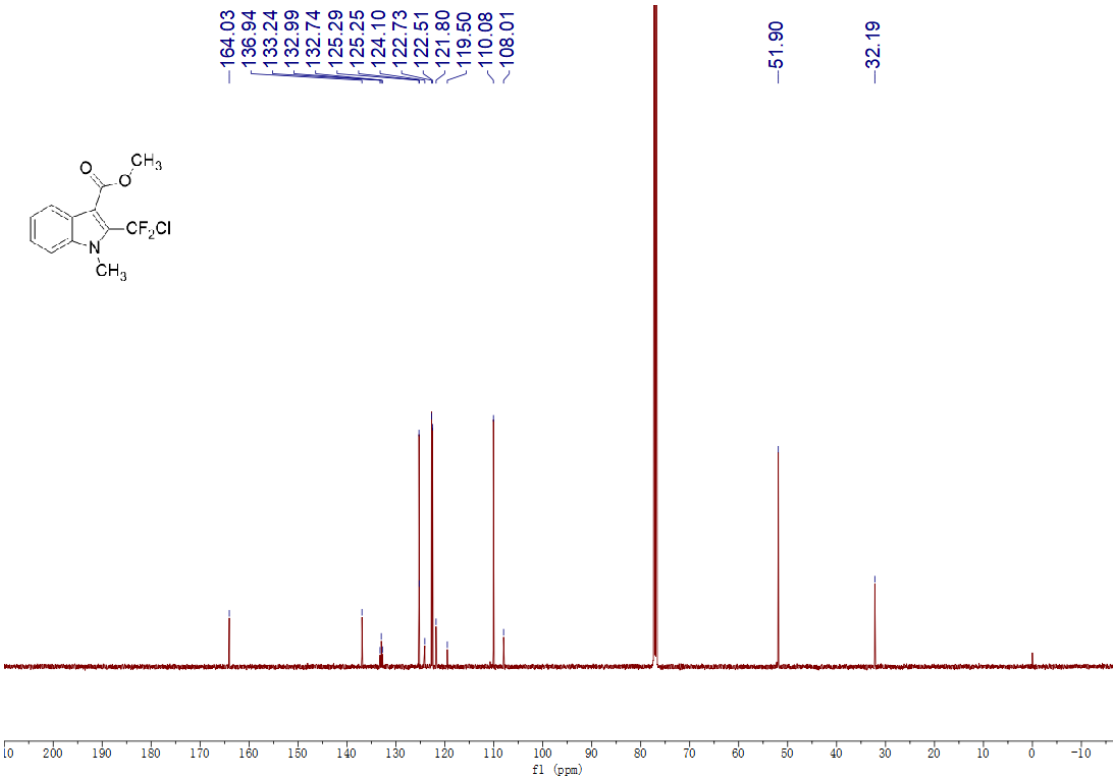
^{19}F NMR spectrum of 2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carbaldehyde 3f



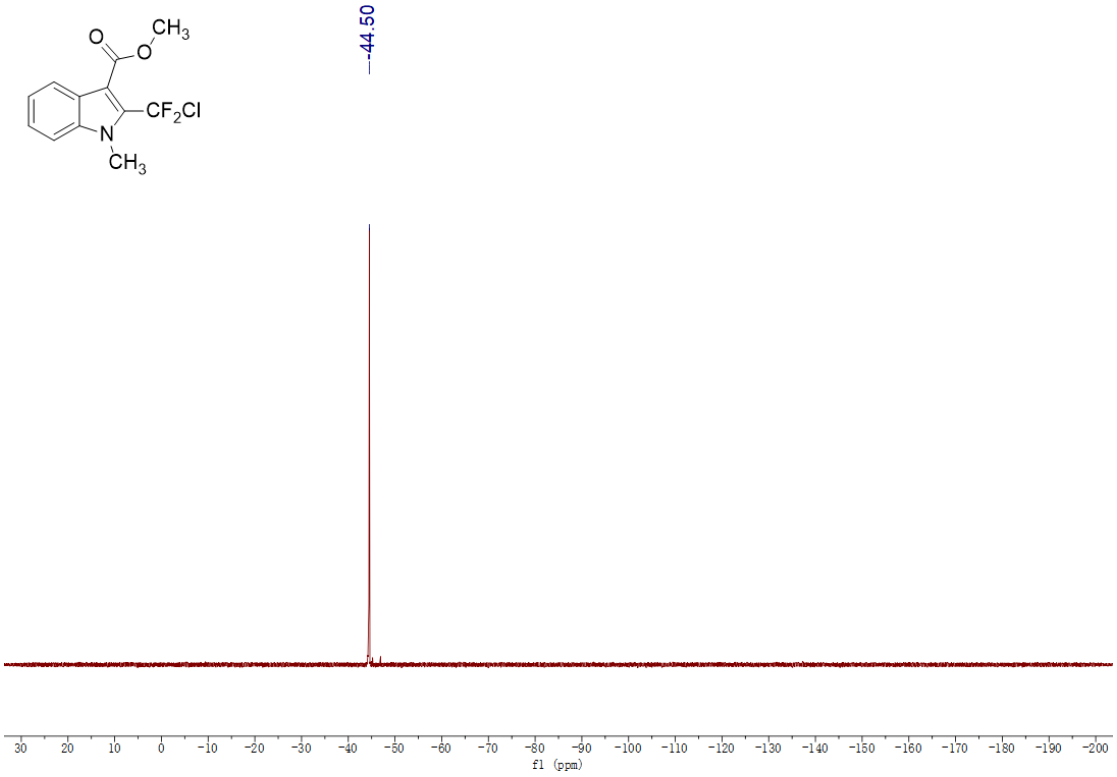
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carboxylate 3g



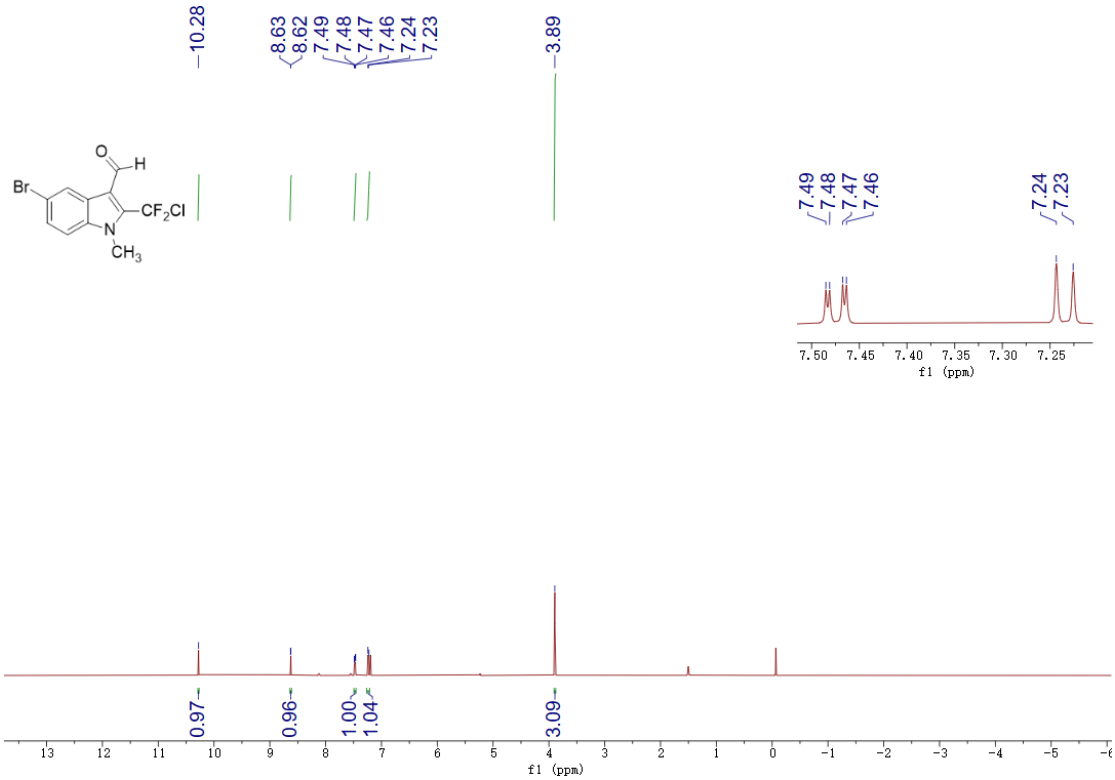
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carboxylate 3g



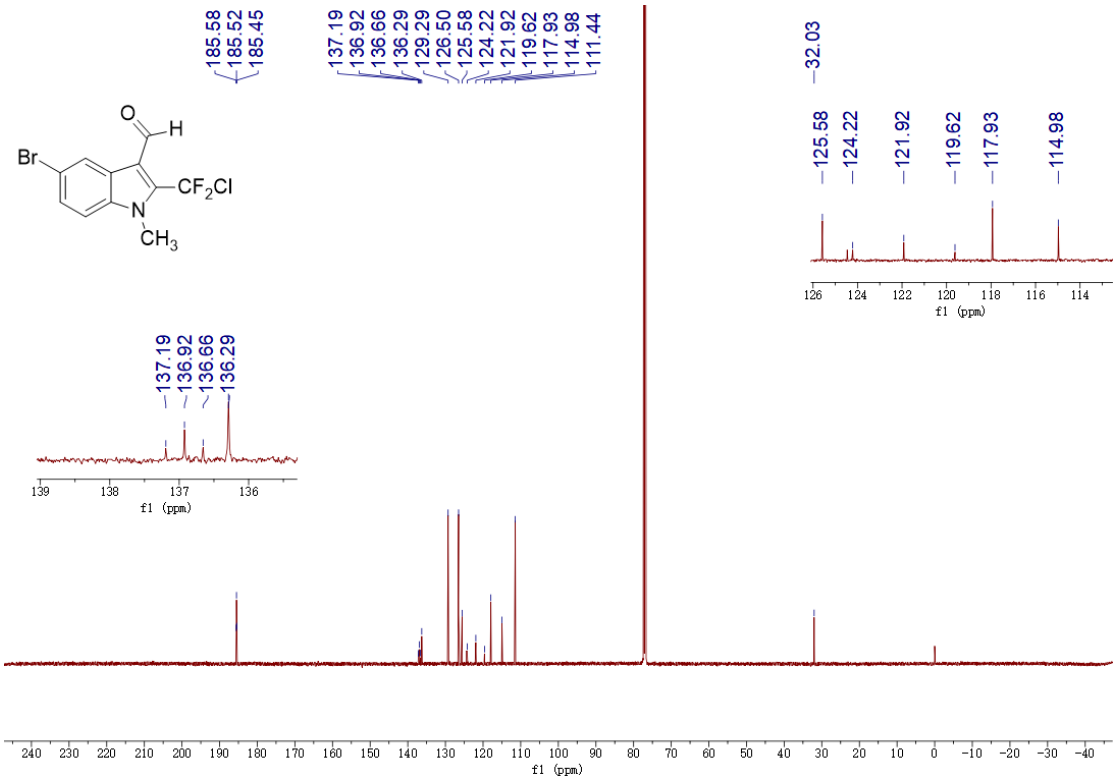
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carboxylate 3g



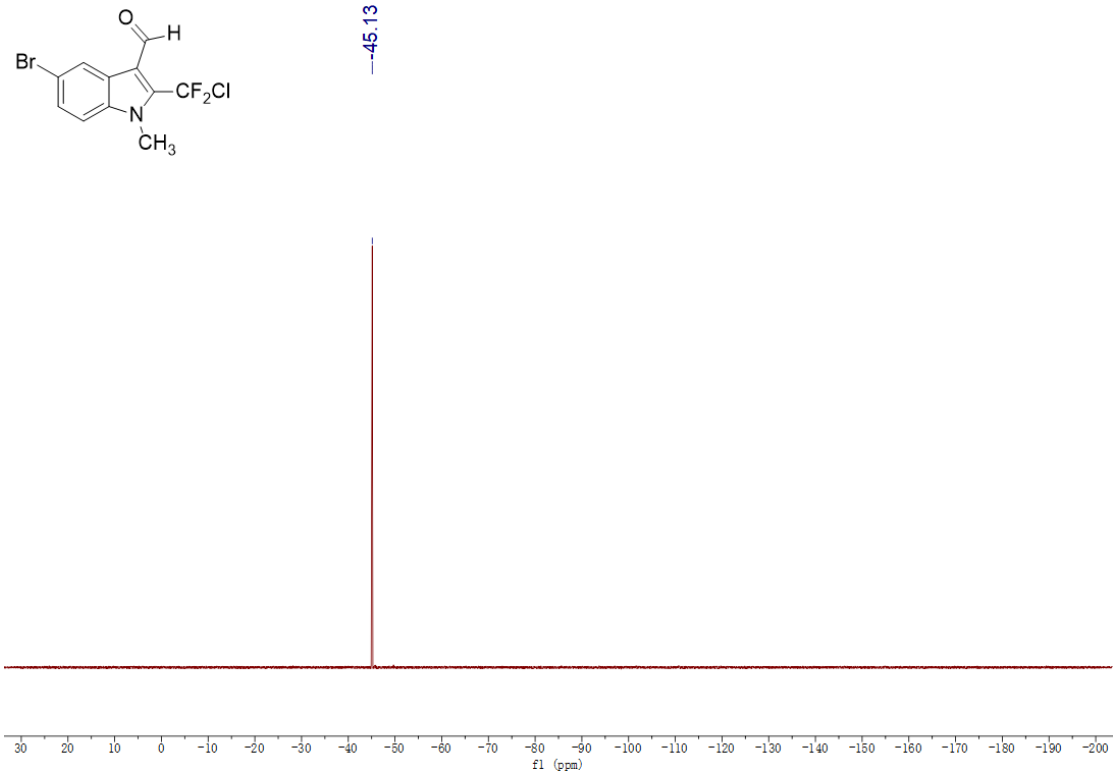
^{1}H NMR spectrum of 5-bromo-2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carbaldehyde 3h



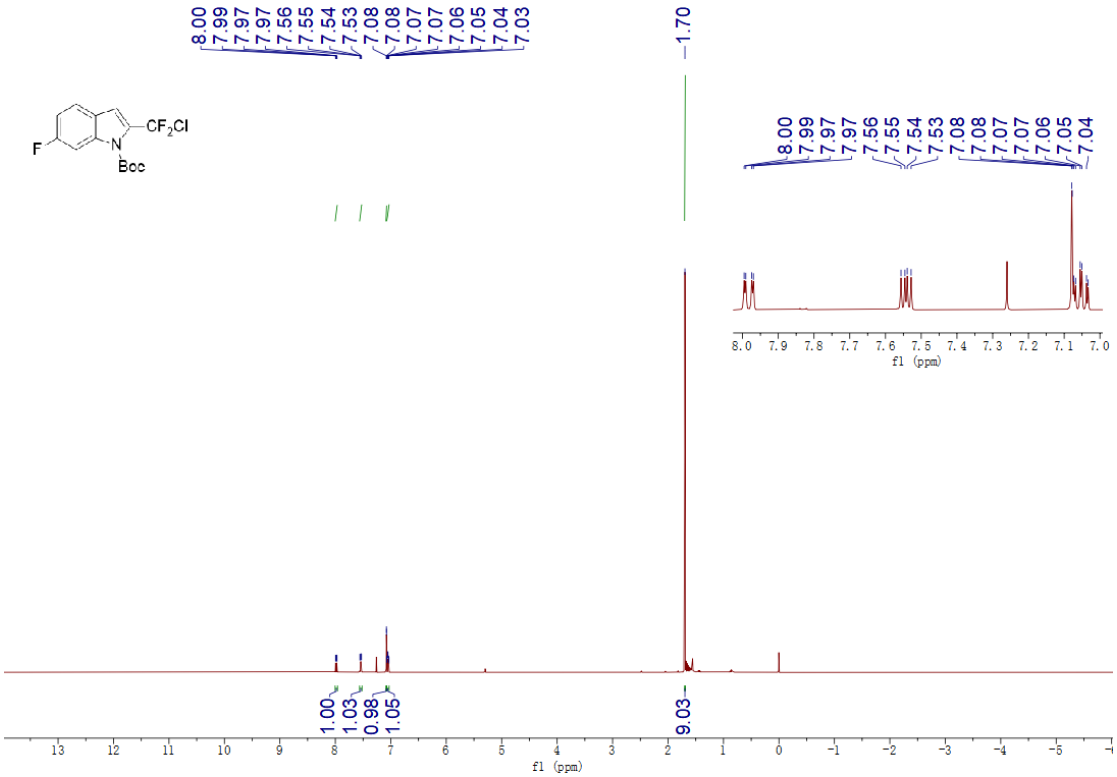
^{13}C NMR spectrum of 5-bromo-2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carbaldehyde 3h



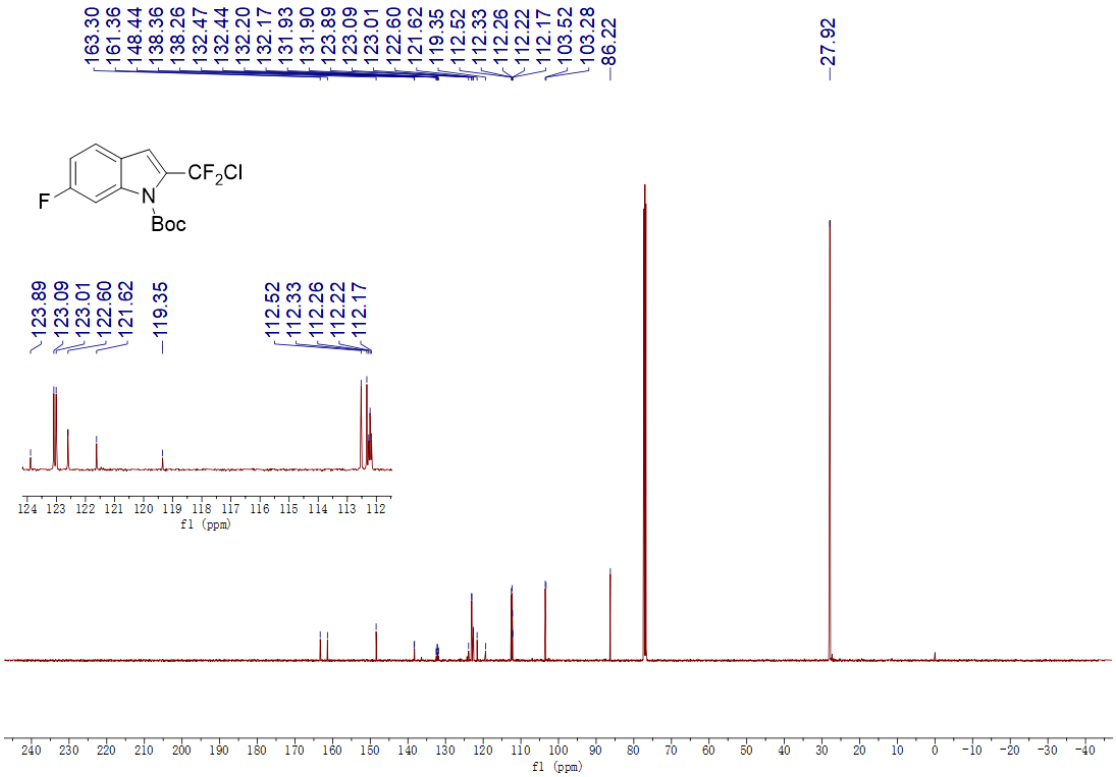
^{19}F NMR spectrum of 5-bromo-2-(chlorodifluoromethyl)-1-methyl -1*H*-indole-3-carbaldehyde 3h



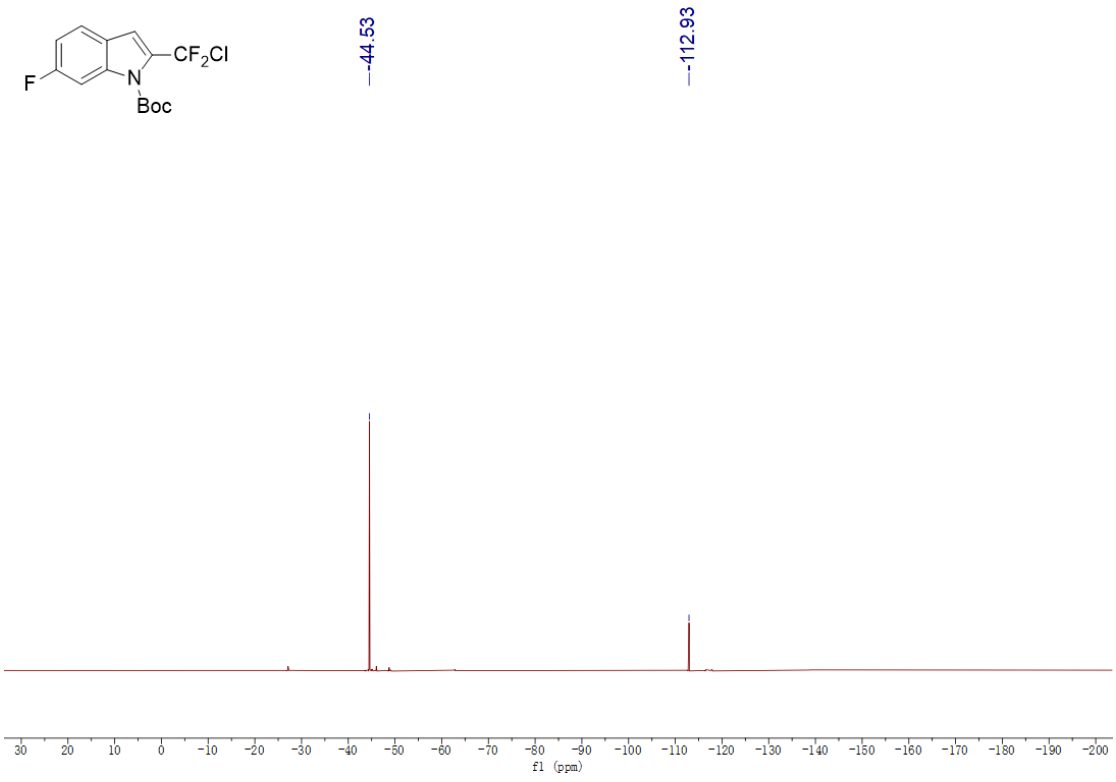
^{1}H NMR spectrum of *tert*-butyl 2-(chlorodifluoromethyl)-6-fluoro -1*H*-indole-1-carboxylate 3i



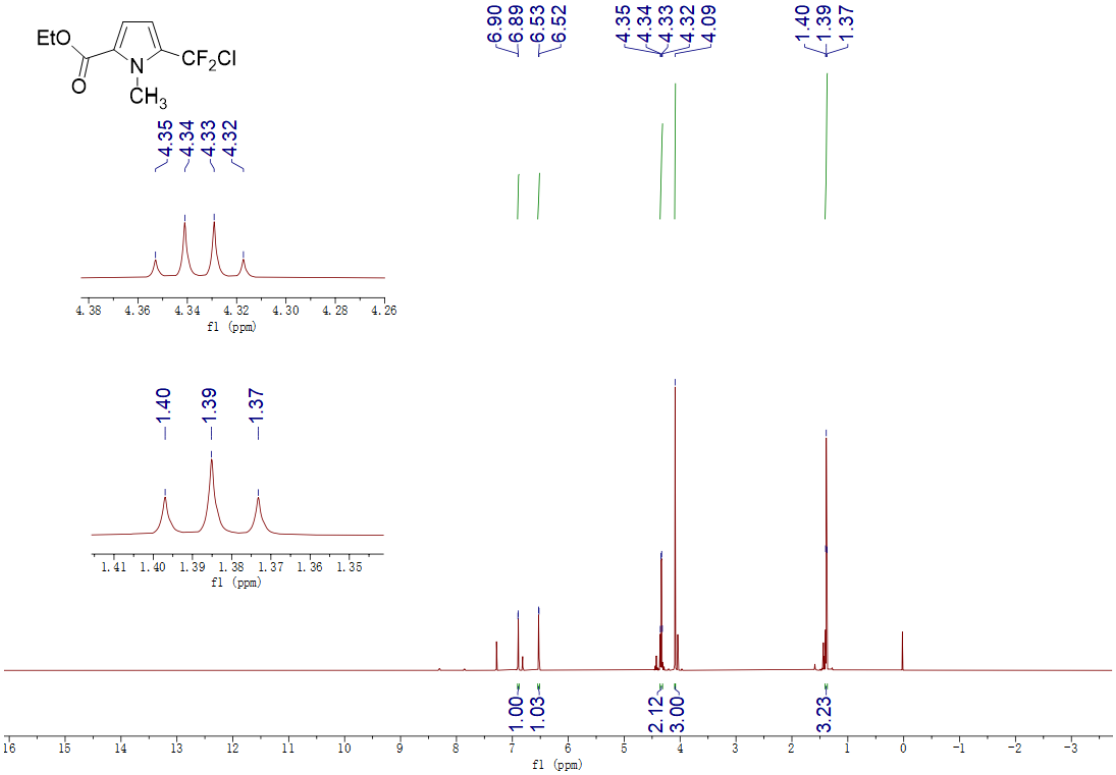
^{13}C NMR spectrum of *tert*-butyl 2-(chlorodifluoromethyl)-6-fluoro -1*H*-indole-1-carboxylate 3i



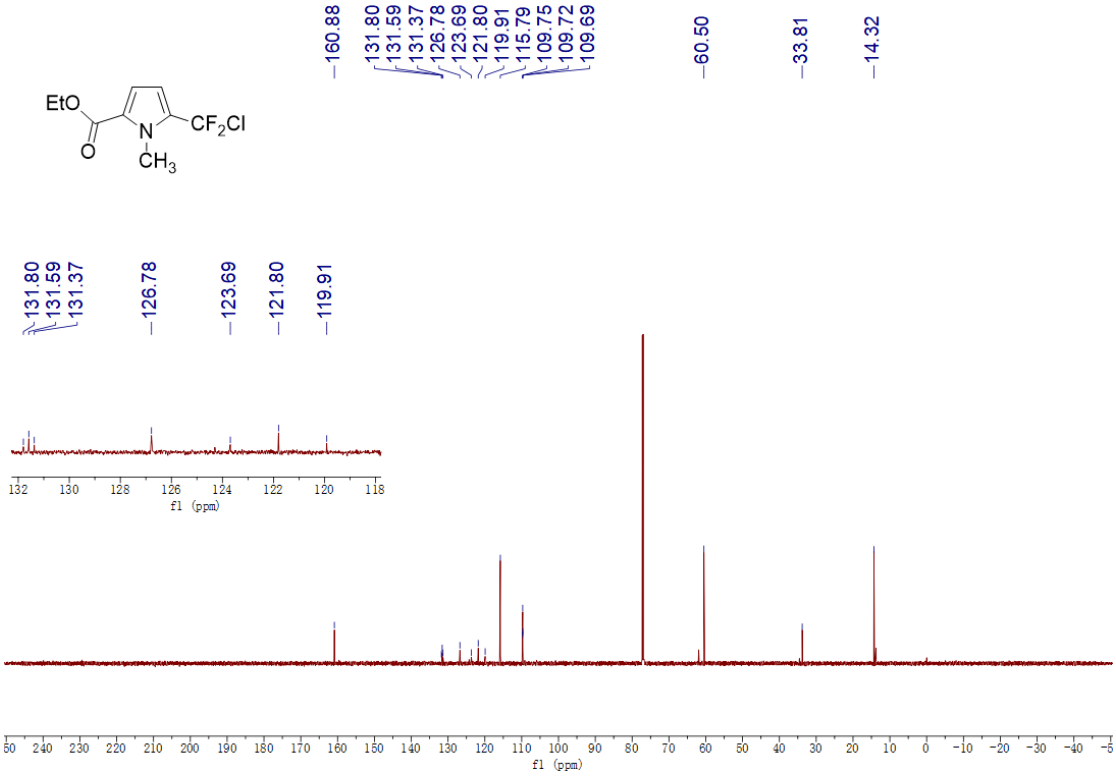
^{19}F NMR spectrum of *tert*-butyl 2-(chlorodifluoromethyl)-6-fluoro -1*H*-indole-1-carboxylate 3i



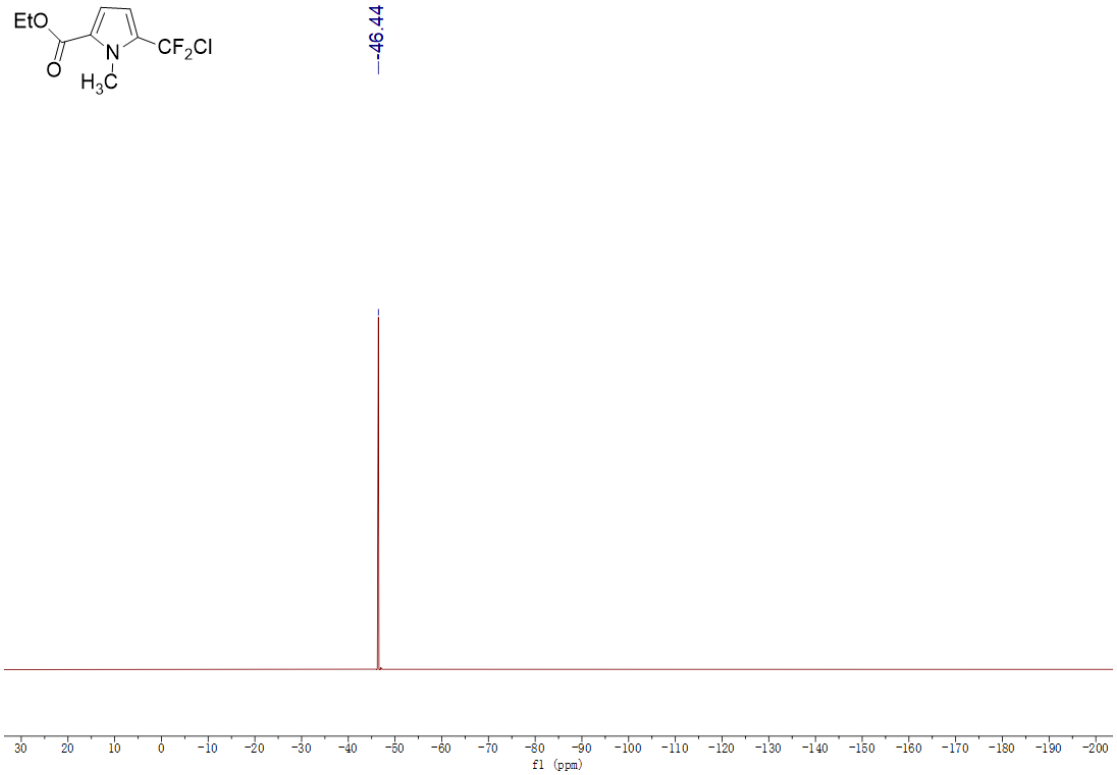
^{1}H NMR spectrum of ethyl 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carboxylate 3j



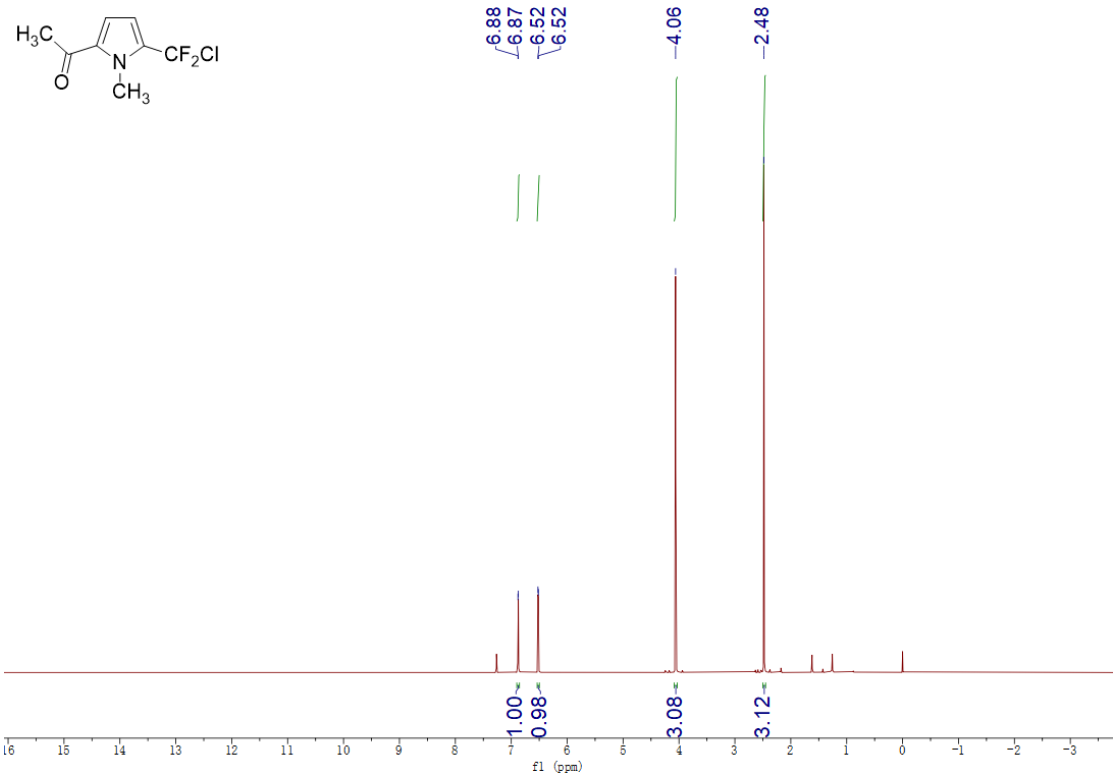
^{13}C NMR spectrum of ethyl 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carboxylate 3j



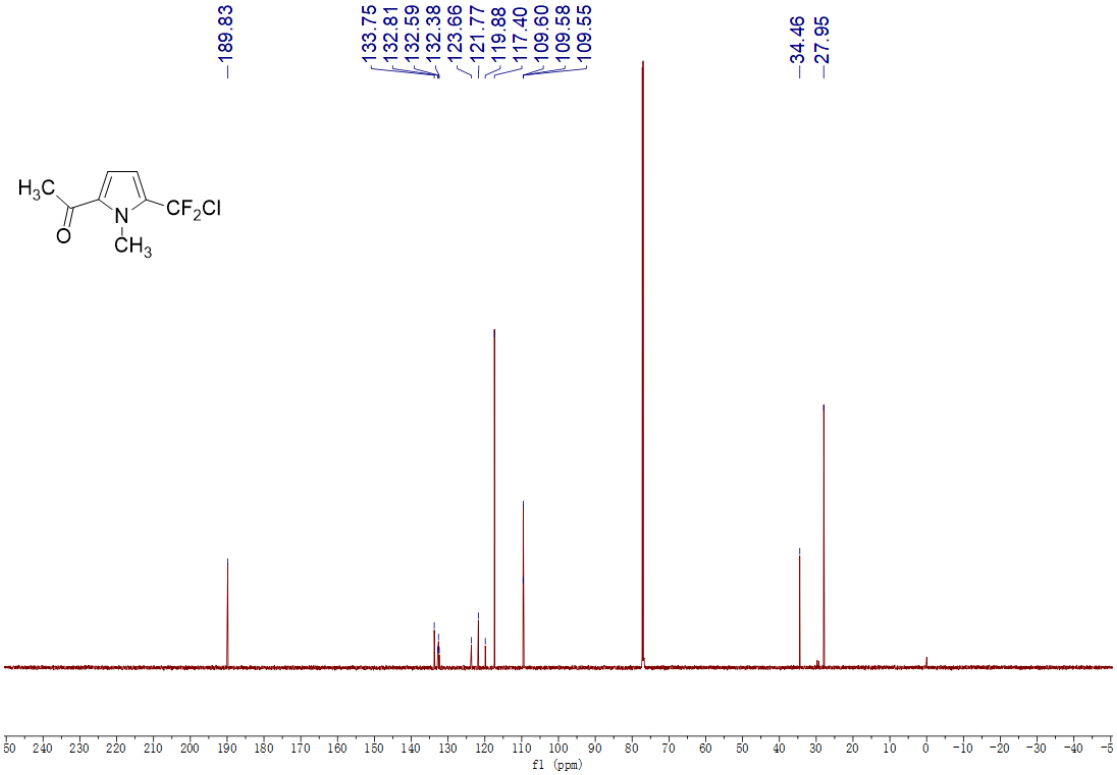
^{19}F NMR spectrum of ethyl 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carboxylate 3j



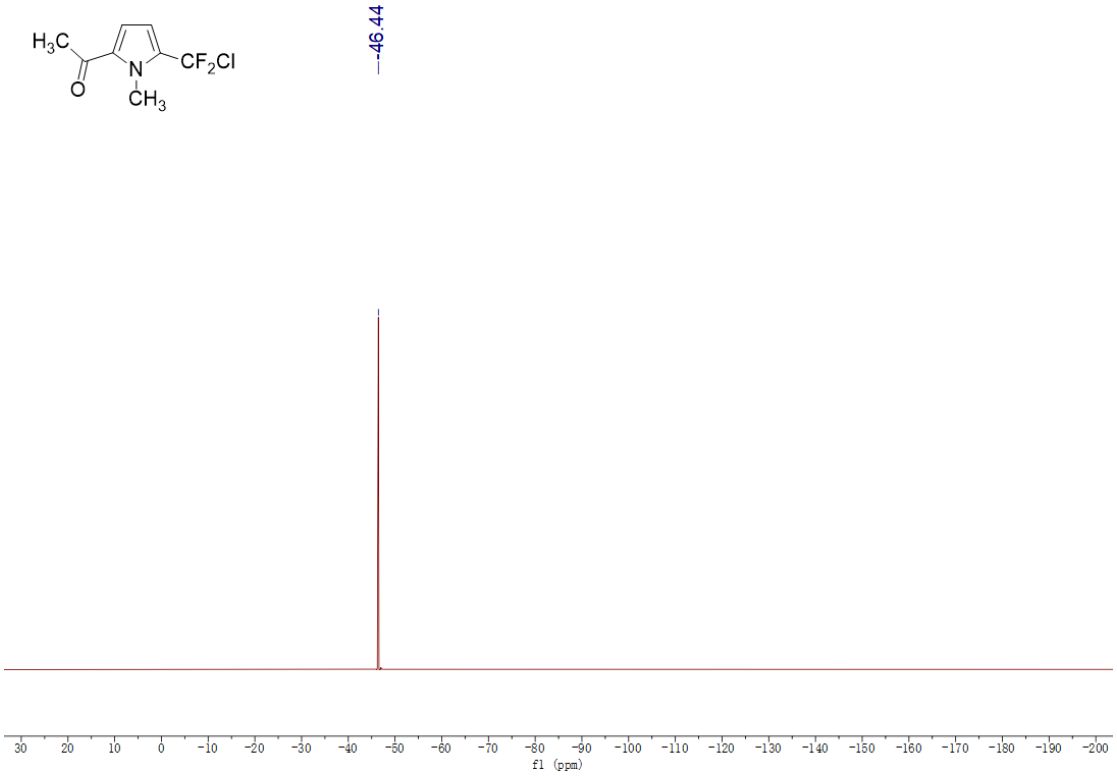
^{1}H NMR spectrum of 1-(5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrol-2-yl)ethan-1-one 3k



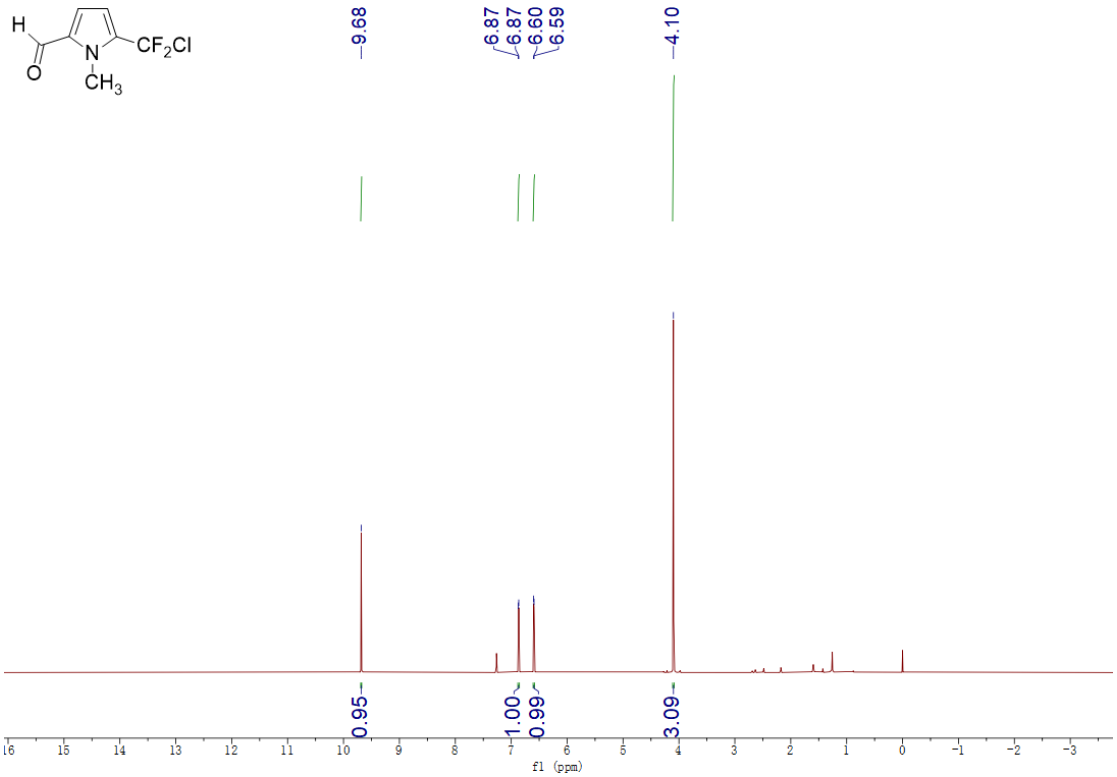
^{13}C NMR spectrum of 1-(5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrol-2-yl)ethan-1-one 3k



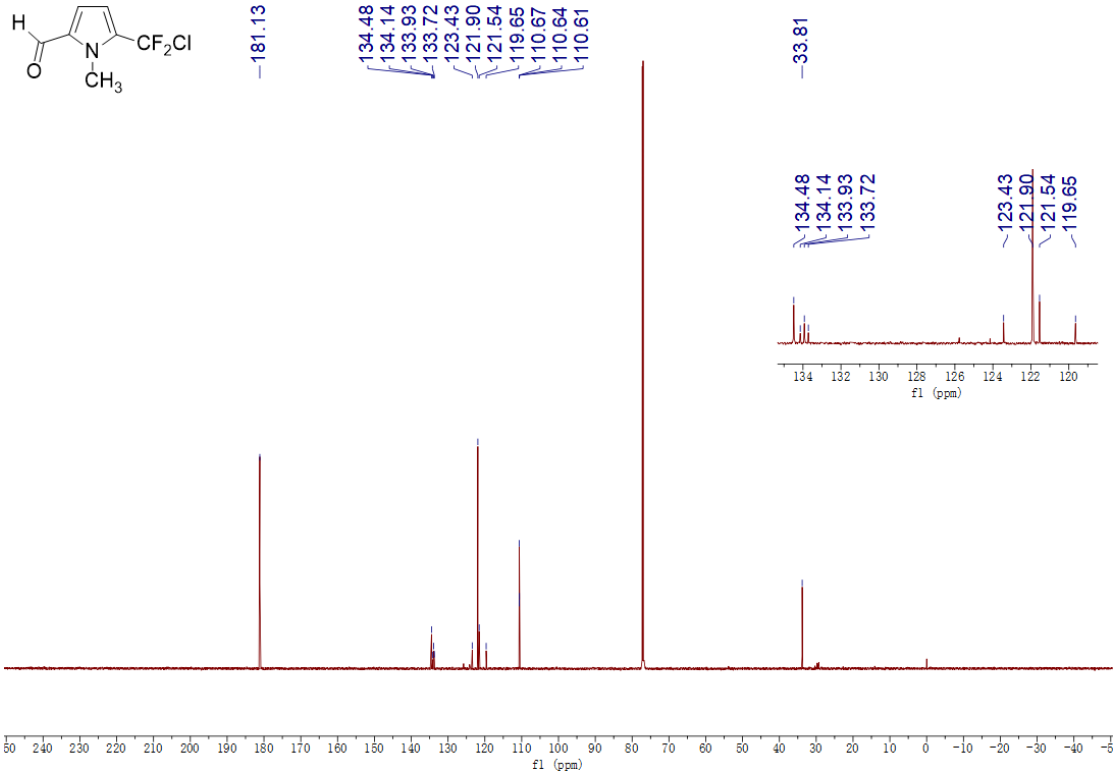
^{19}F NMR spectrum of 1-(5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrol-2-yl)ethan-1-one 3k



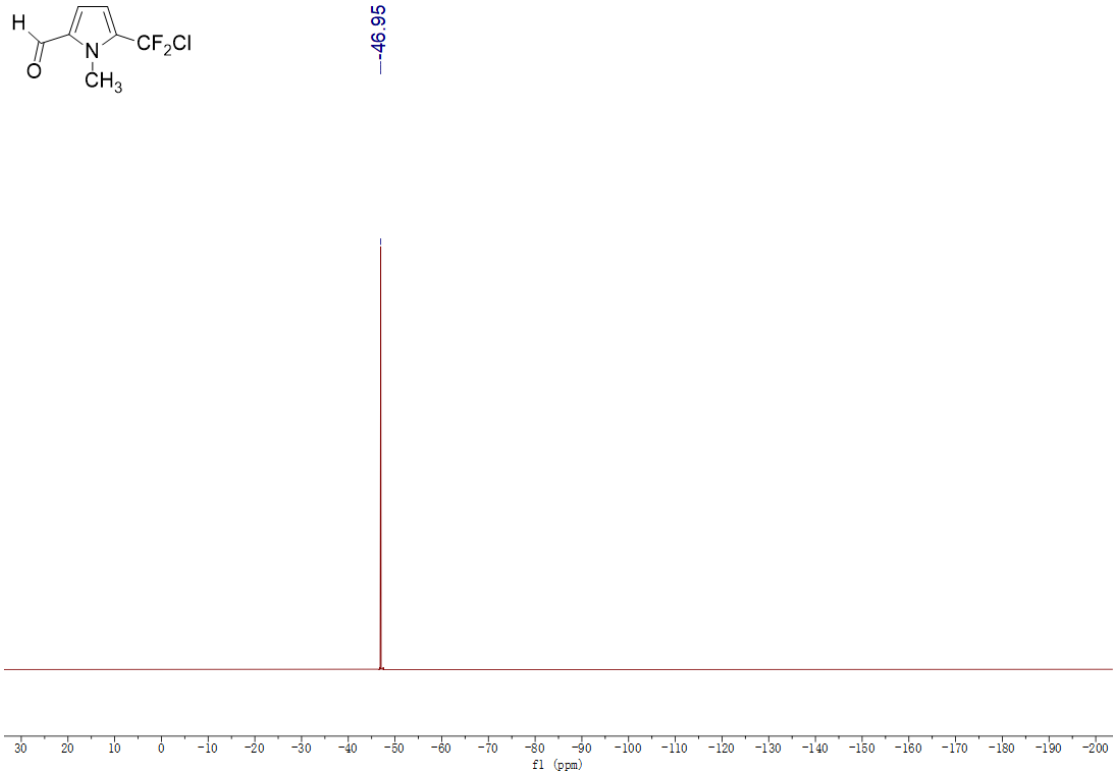
^{1}H NMR spectrum of 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carbaldehyde 3l



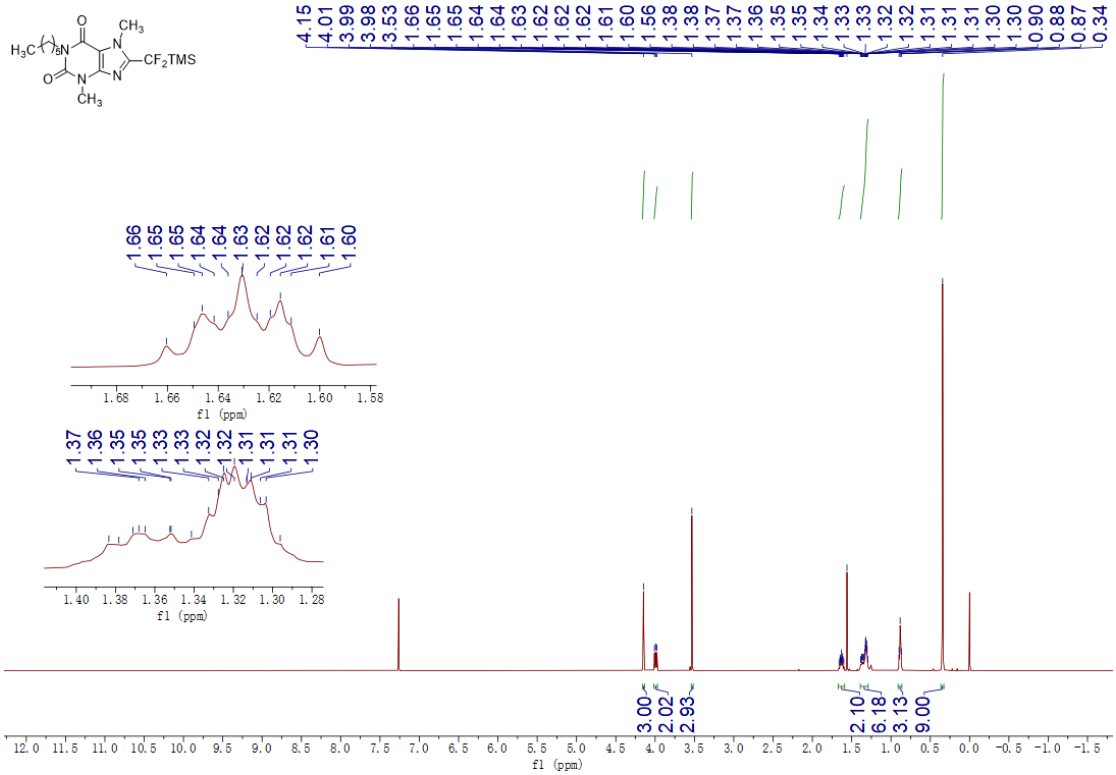
^{13}C NMR spectrum of 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carbaldehyde 3l



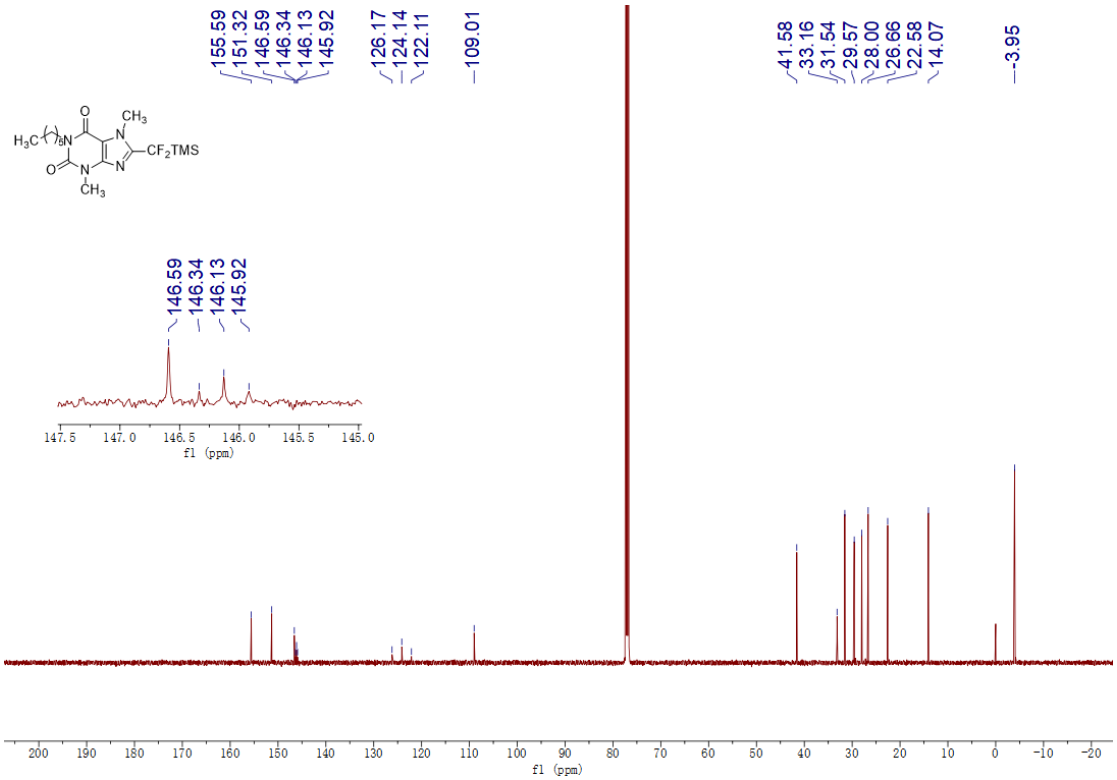
^{19}F NMR spectrum of 5-(chlorodifluoromethyl)-1-methyl -1*H*-pyrrole-2-carbaldehyde 3l



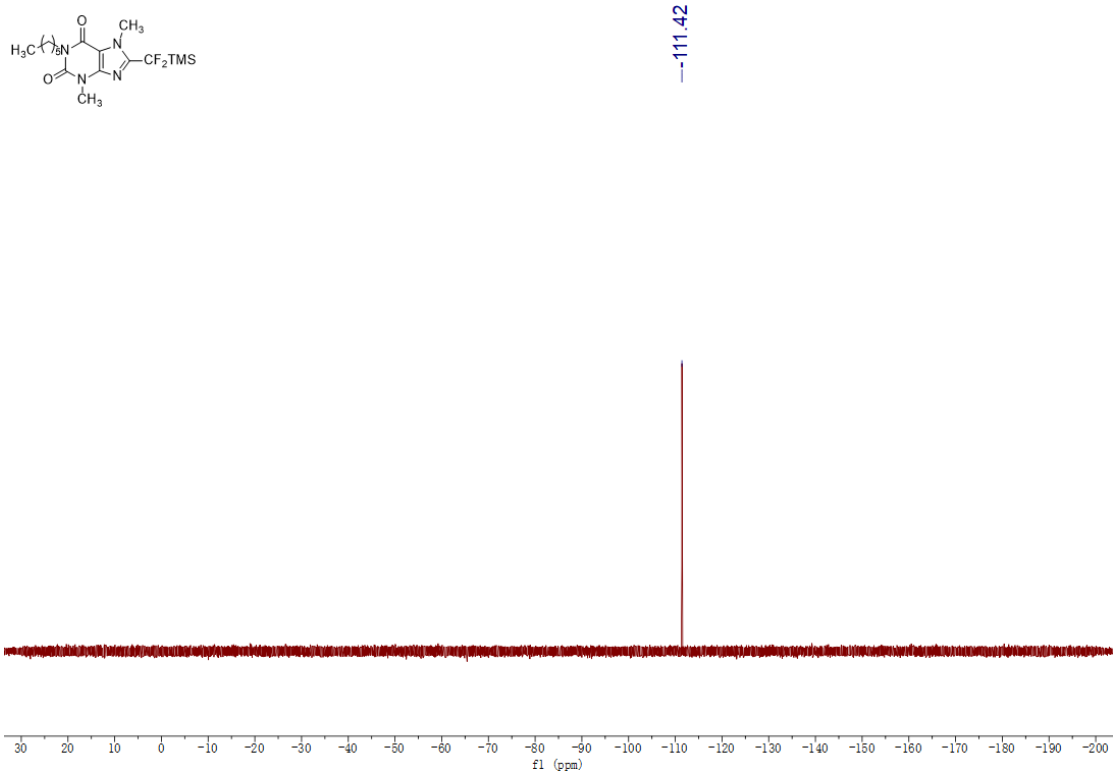
^{1}H NMR spectrum of 8-(difluoro(trimethylsilyl)methyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 4



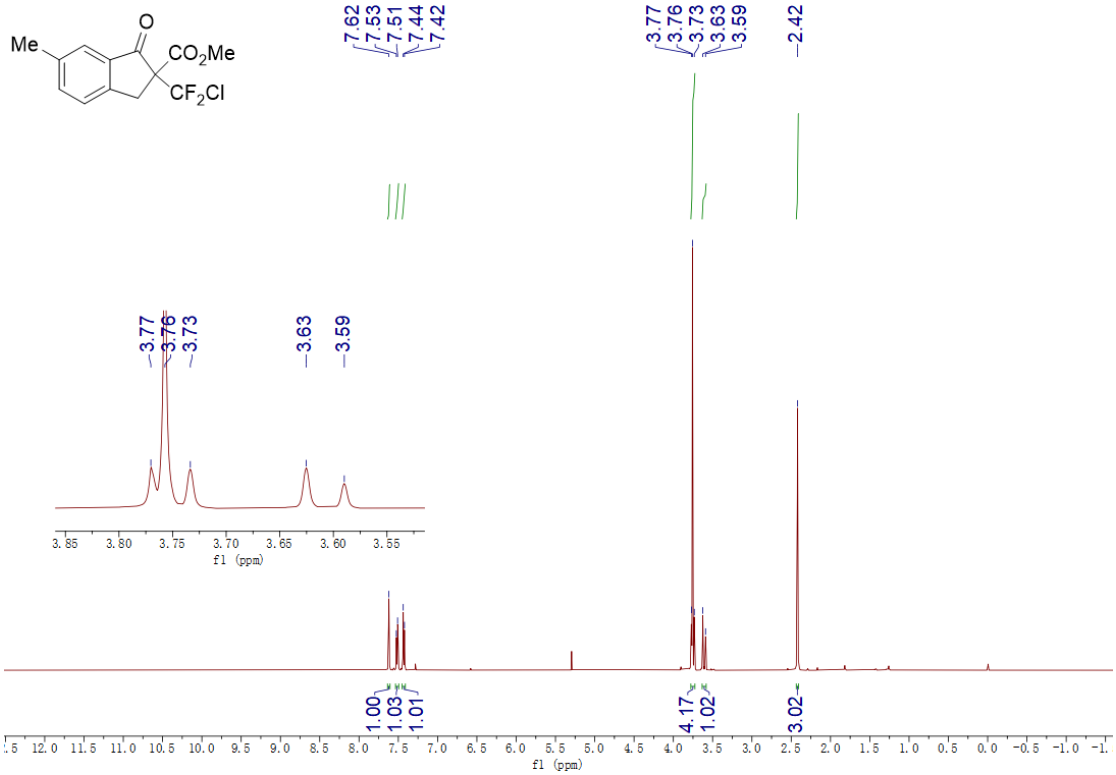
^{13}C NMR spectrum of 8-(difluoro(trimethylsilyl)methyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 4



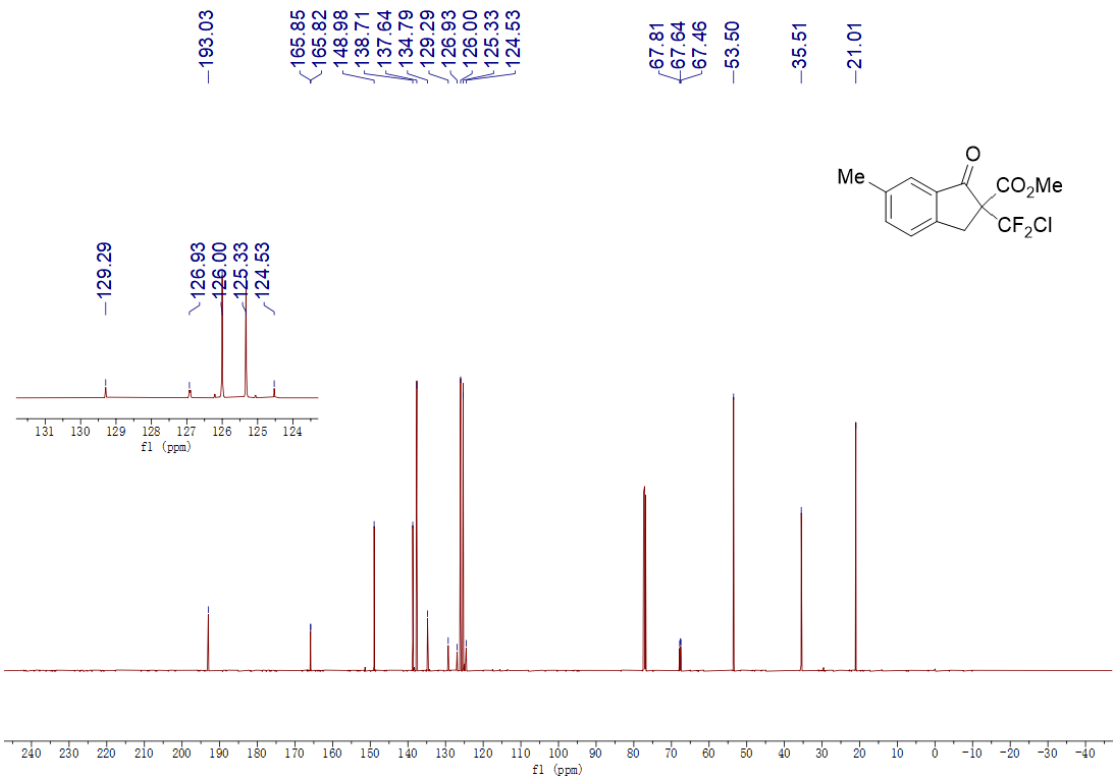
^{19}F NMR spectrum of 8-(difluoro(trimethylsilyl)methyl)-1-hexyl-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione 4



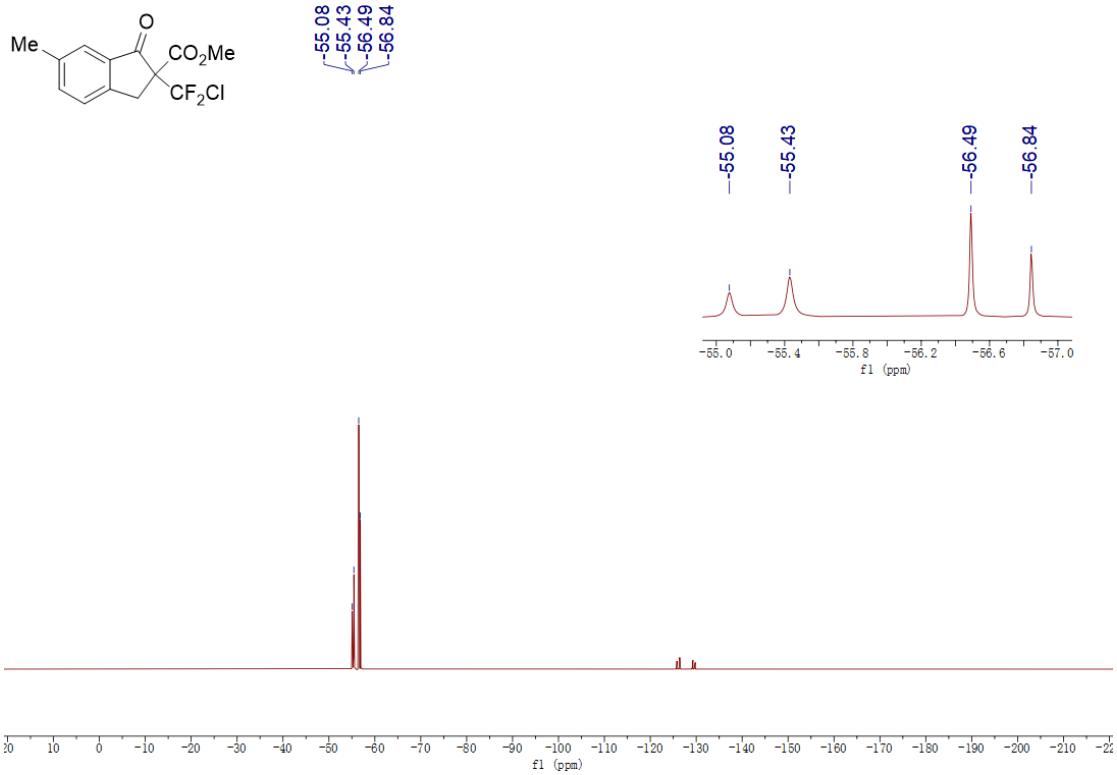
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5a



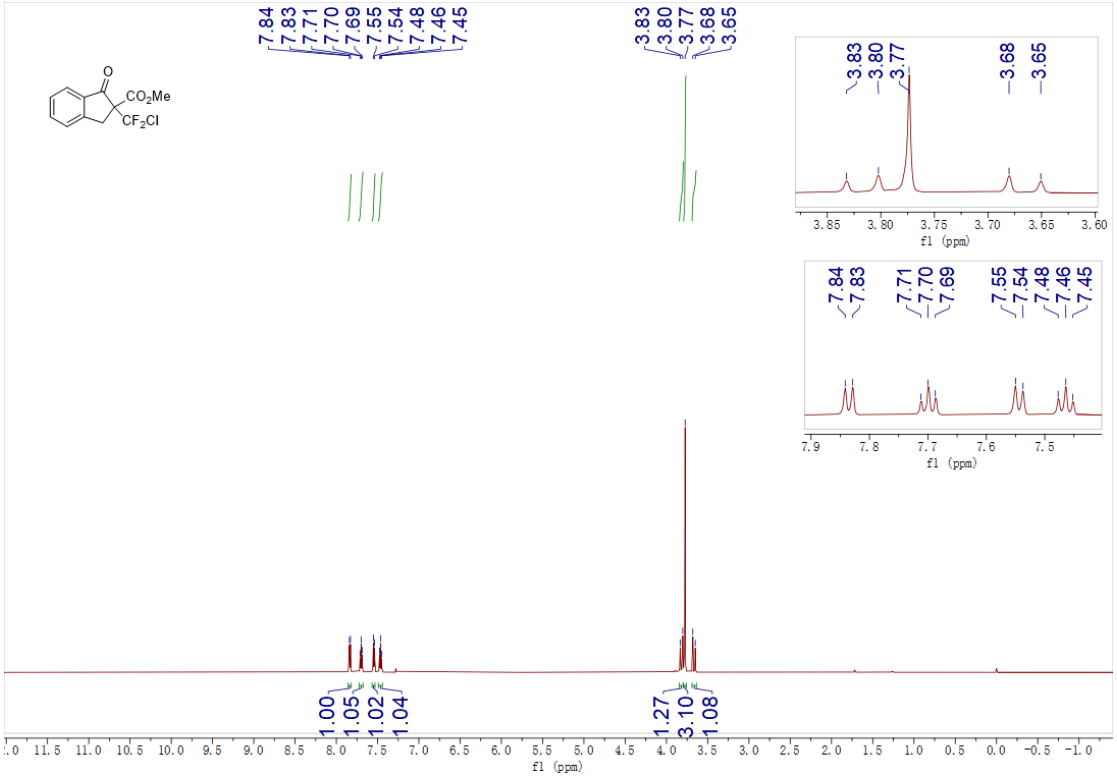
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5a



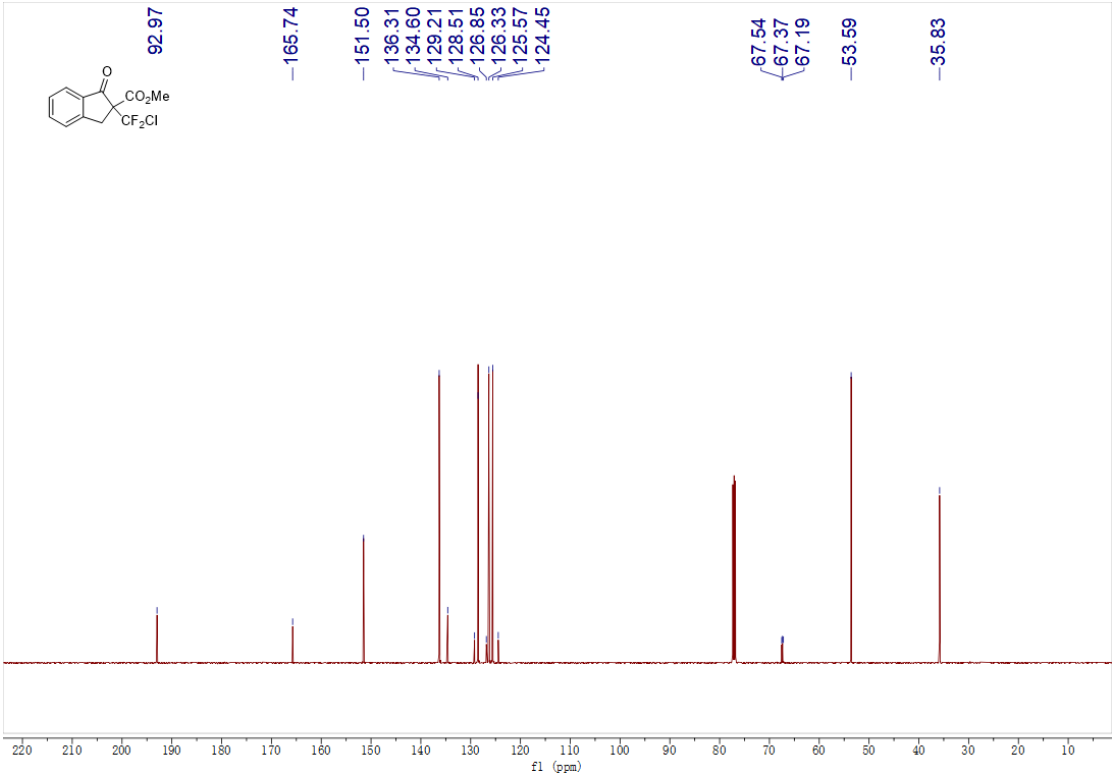
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5a



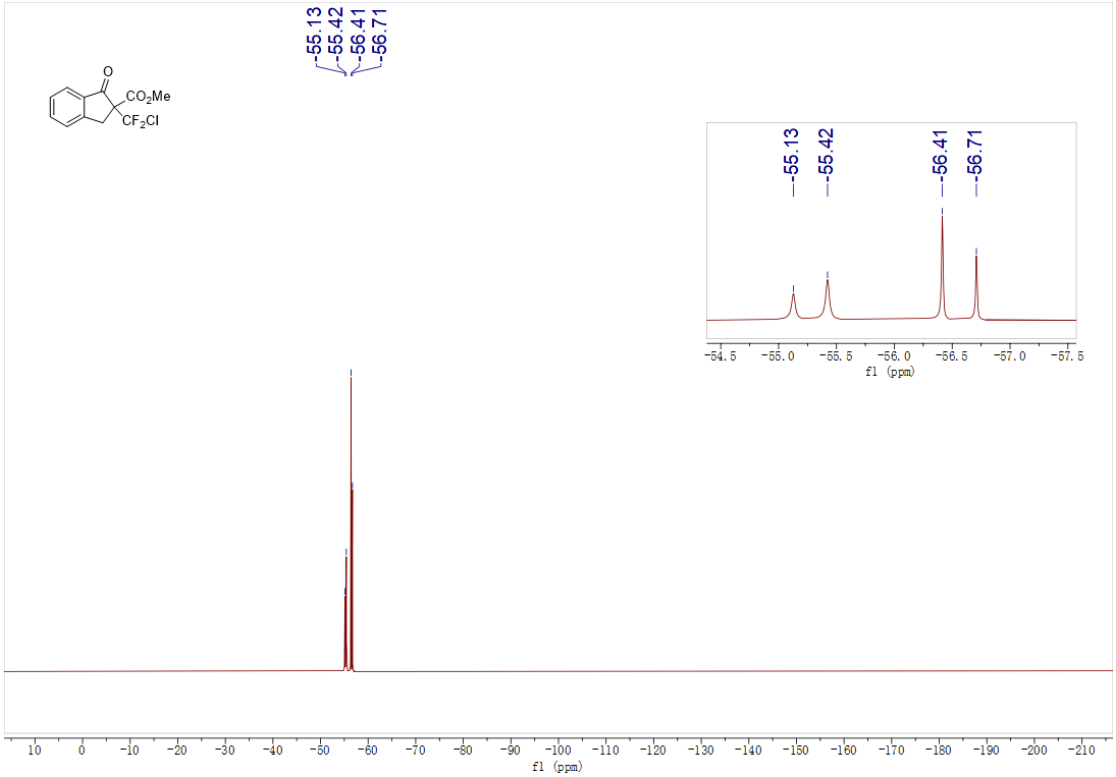
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5b



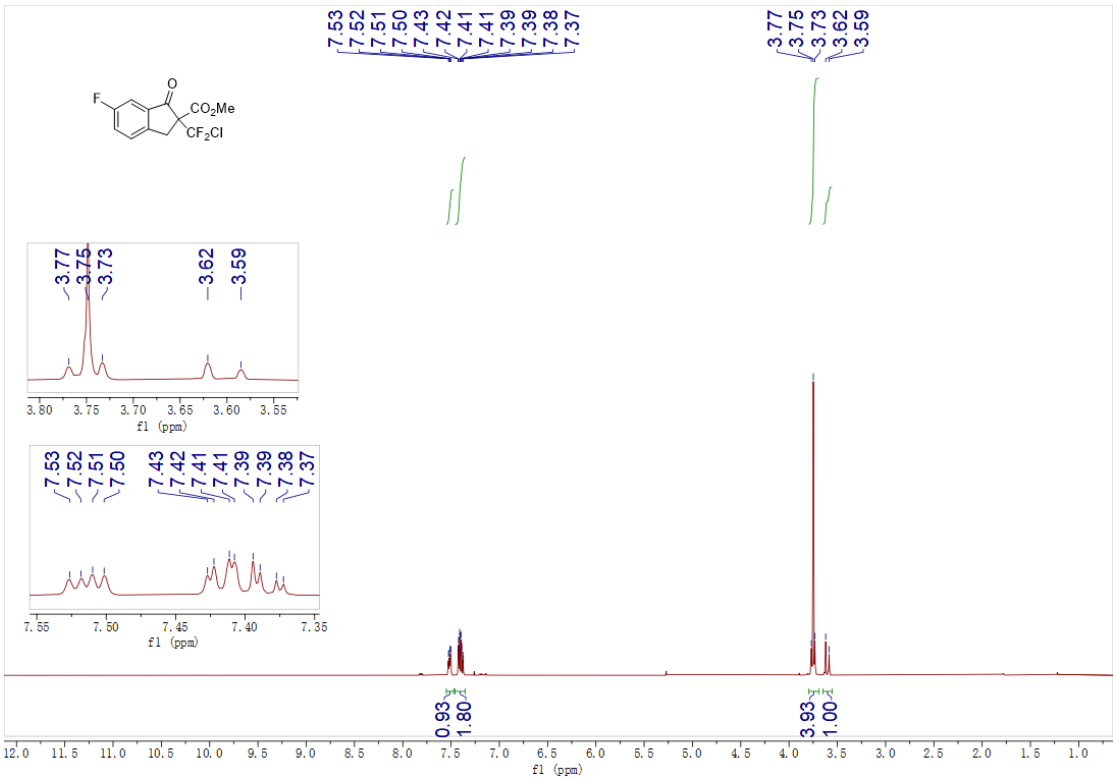
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5b



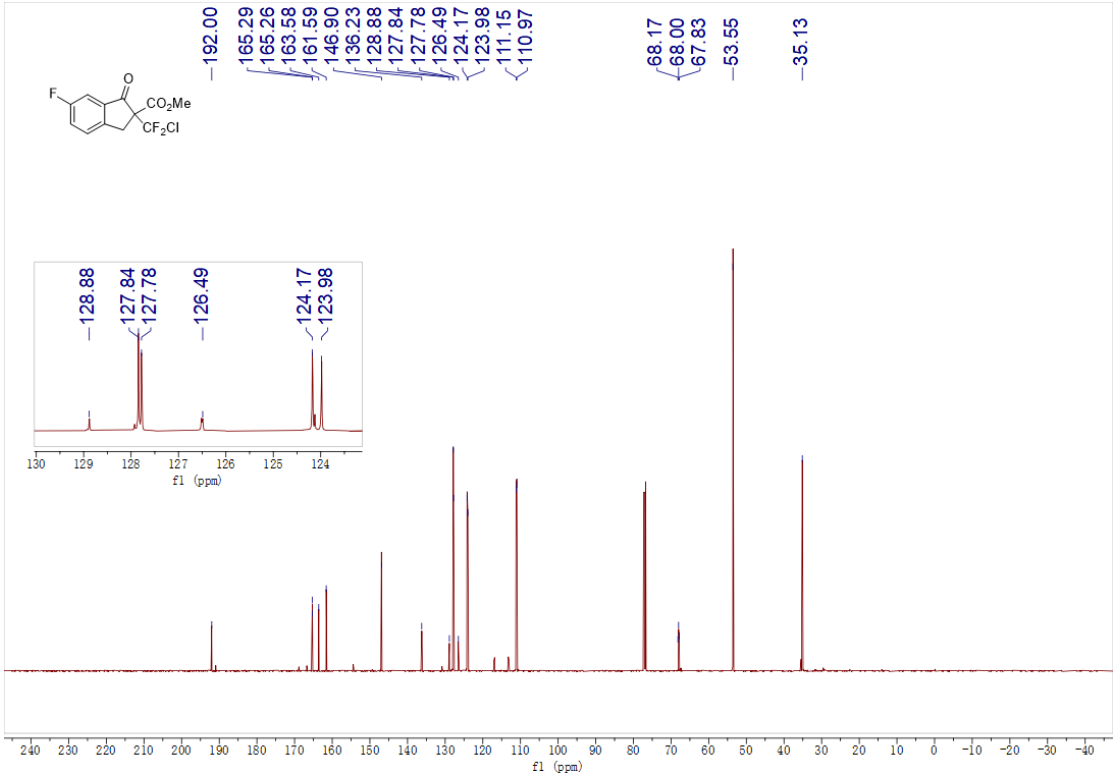
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5b



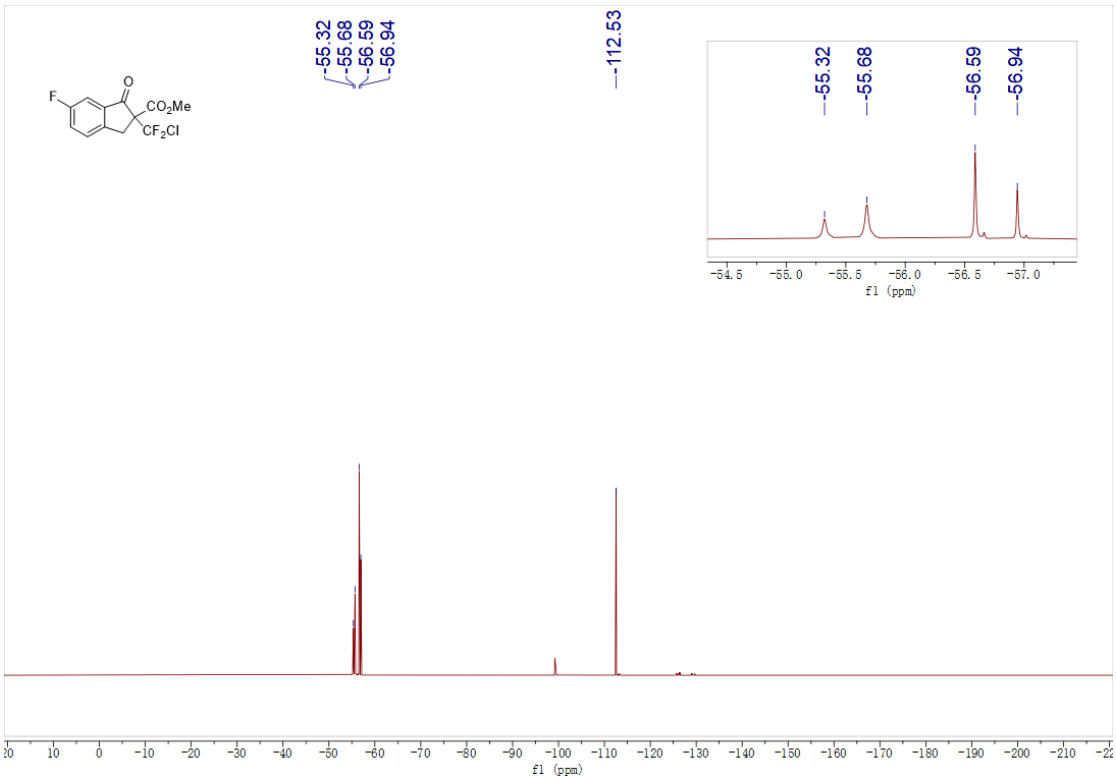
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5c



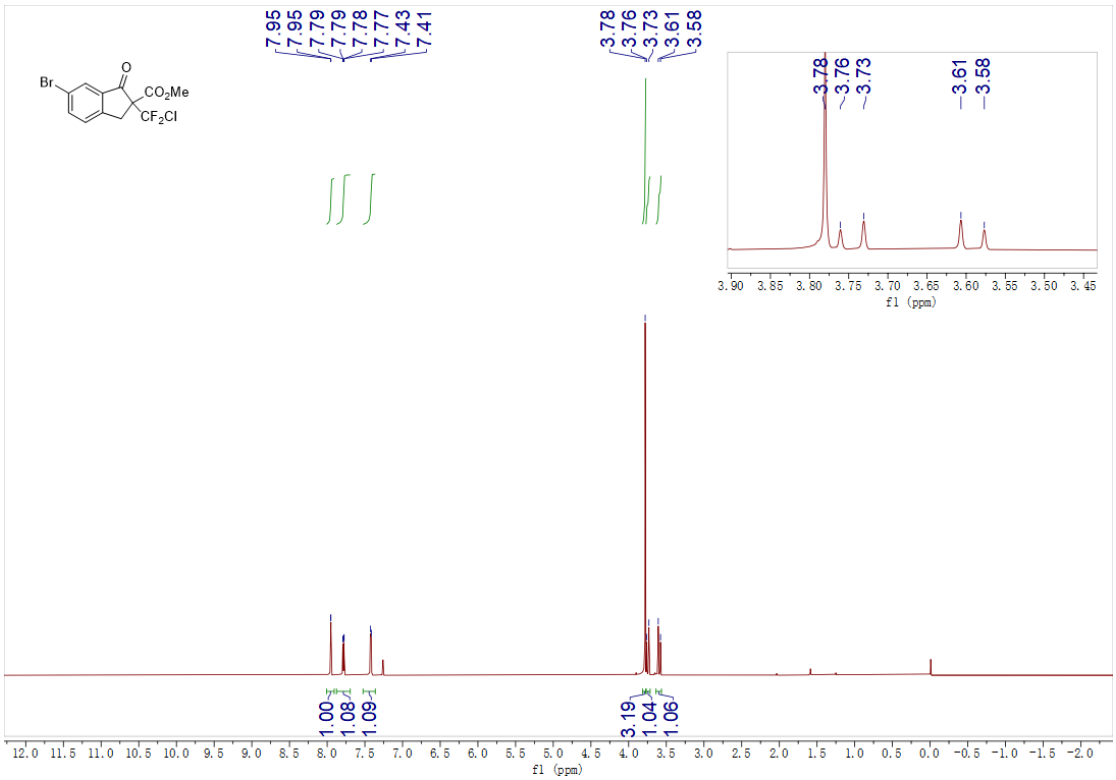
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5c



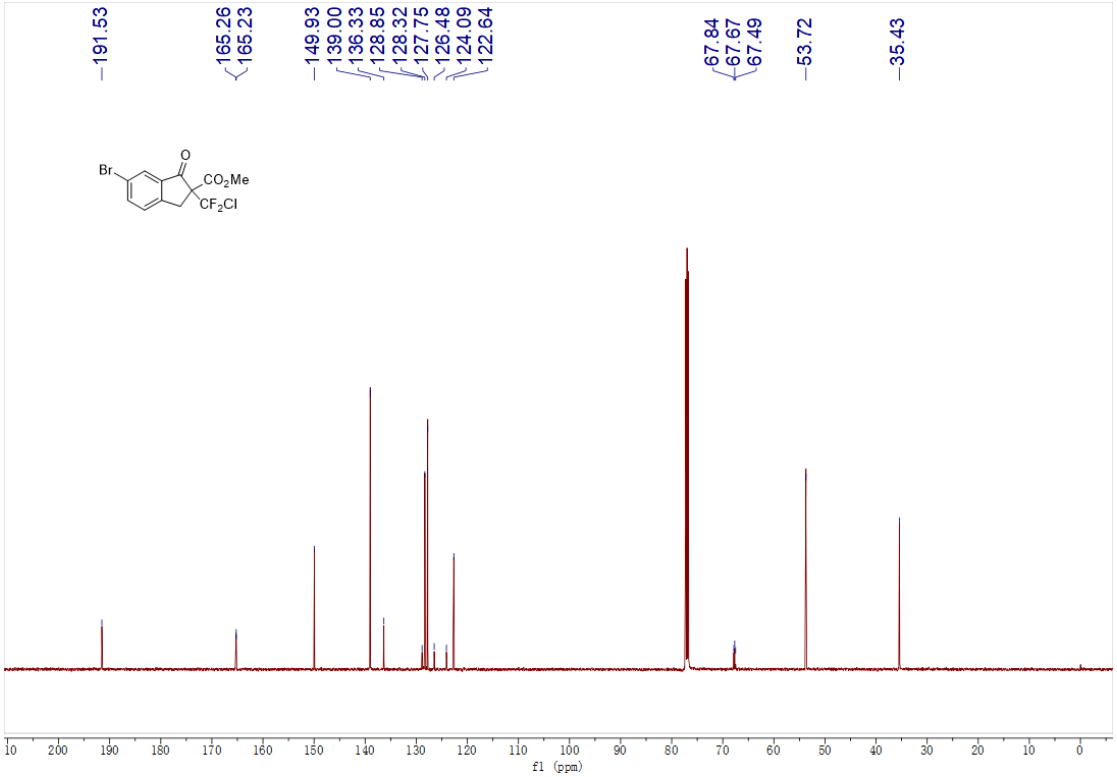
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5c



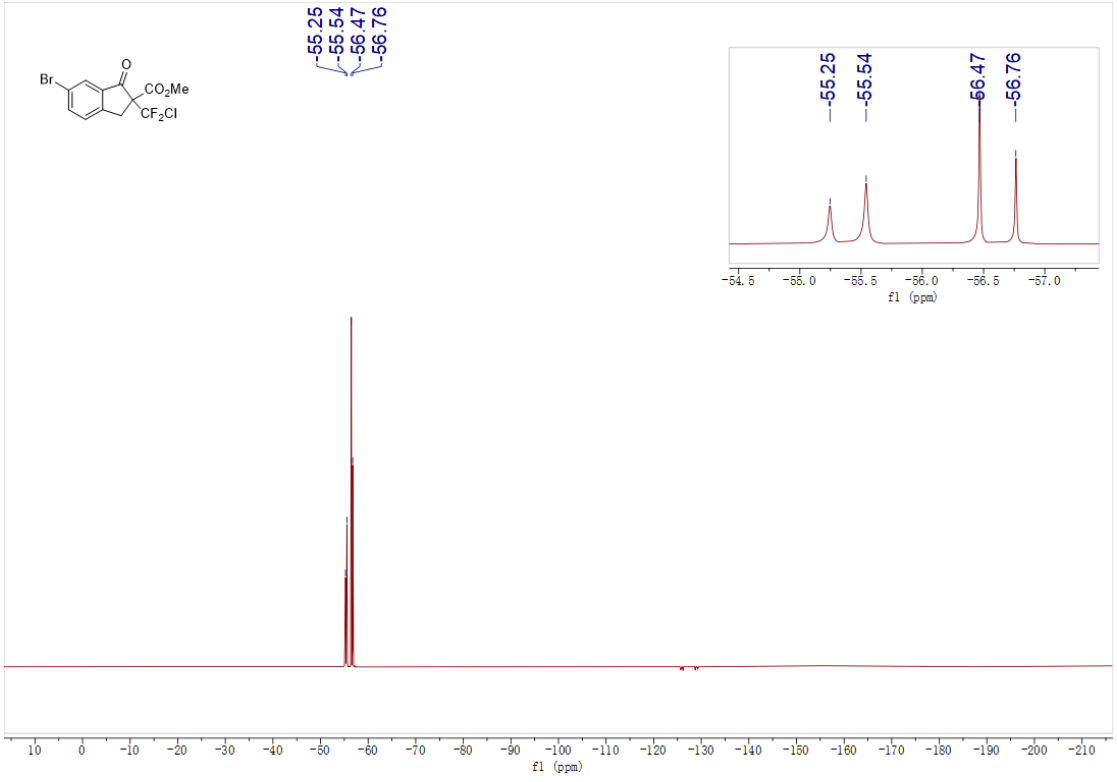
^{1}H NMR spectrum of methyl 6-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5d



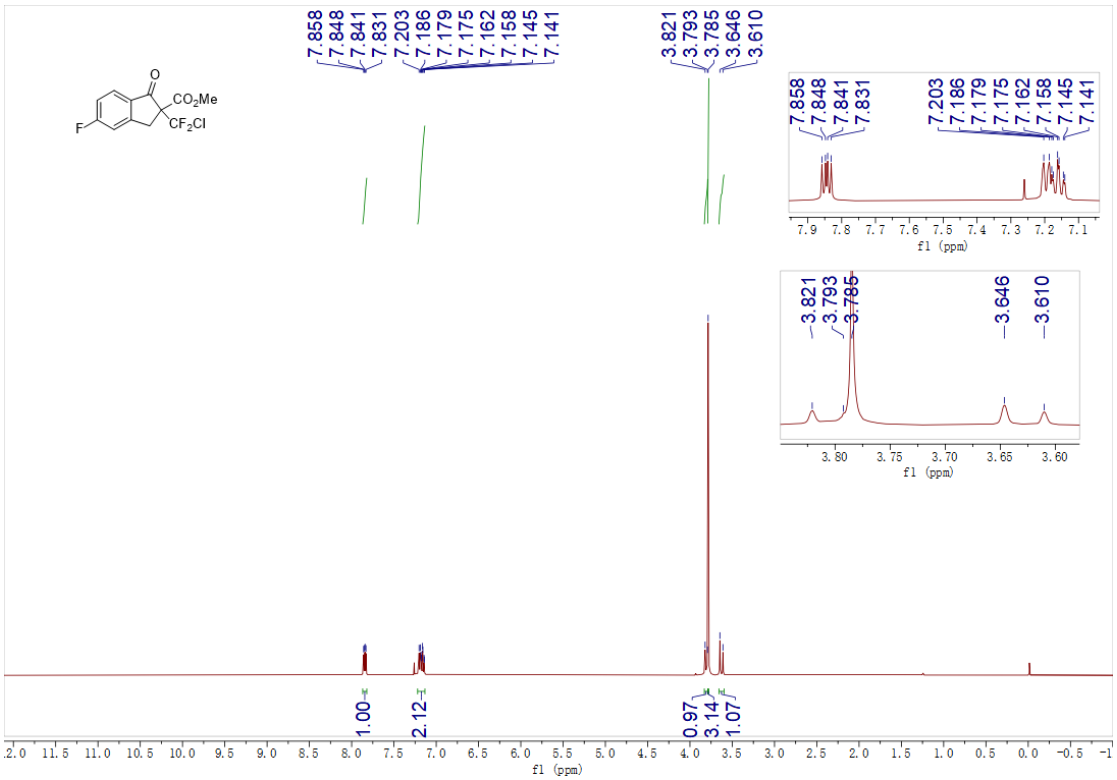
^{13}C NMR spectrum of methyl 6-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5d



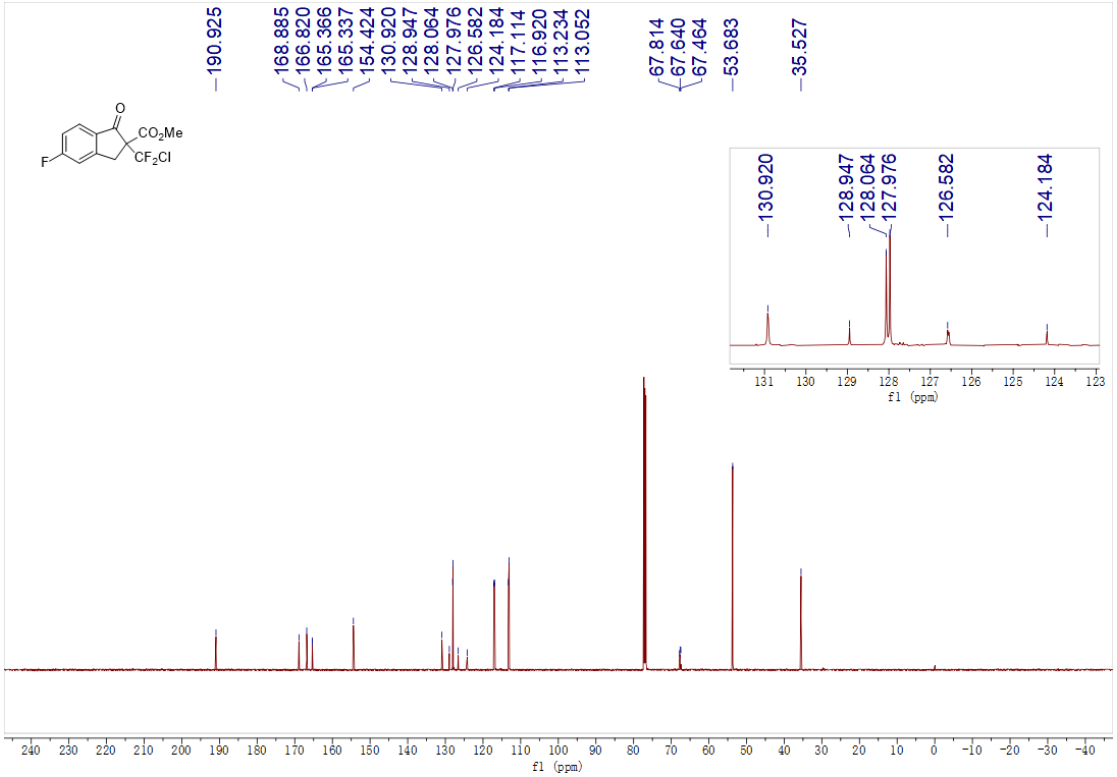
^{19}F NMR spectrum of methyl 6-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5d



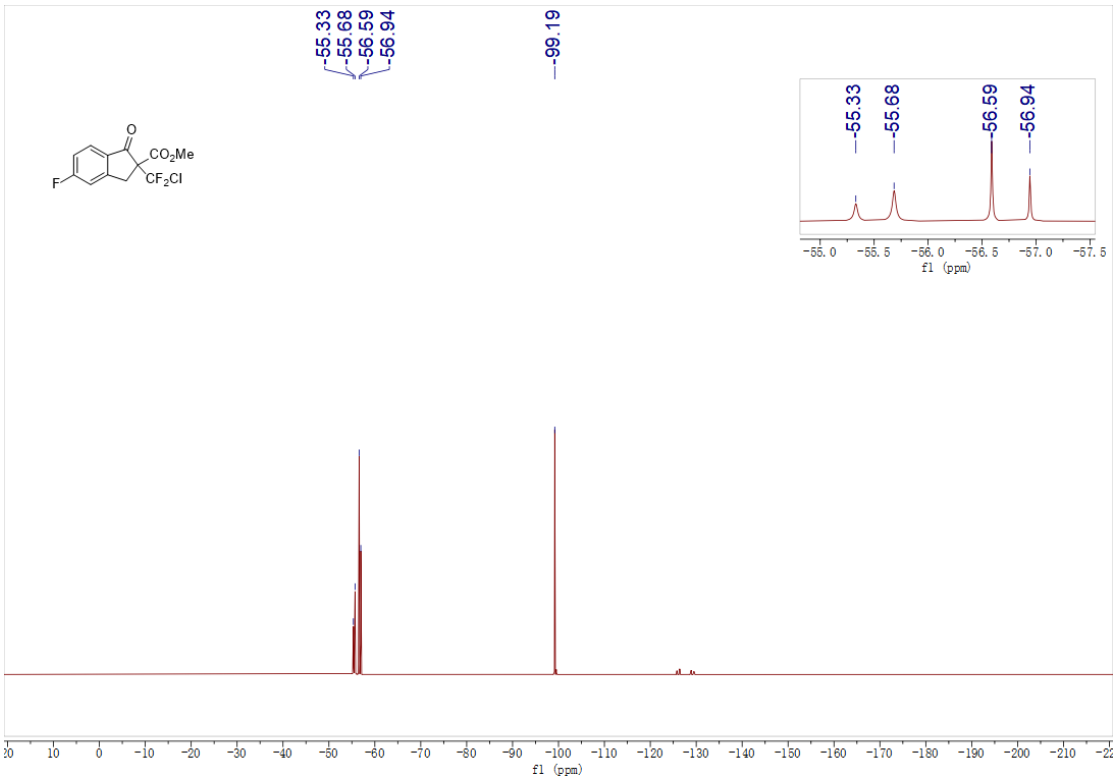
[1] H NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5e



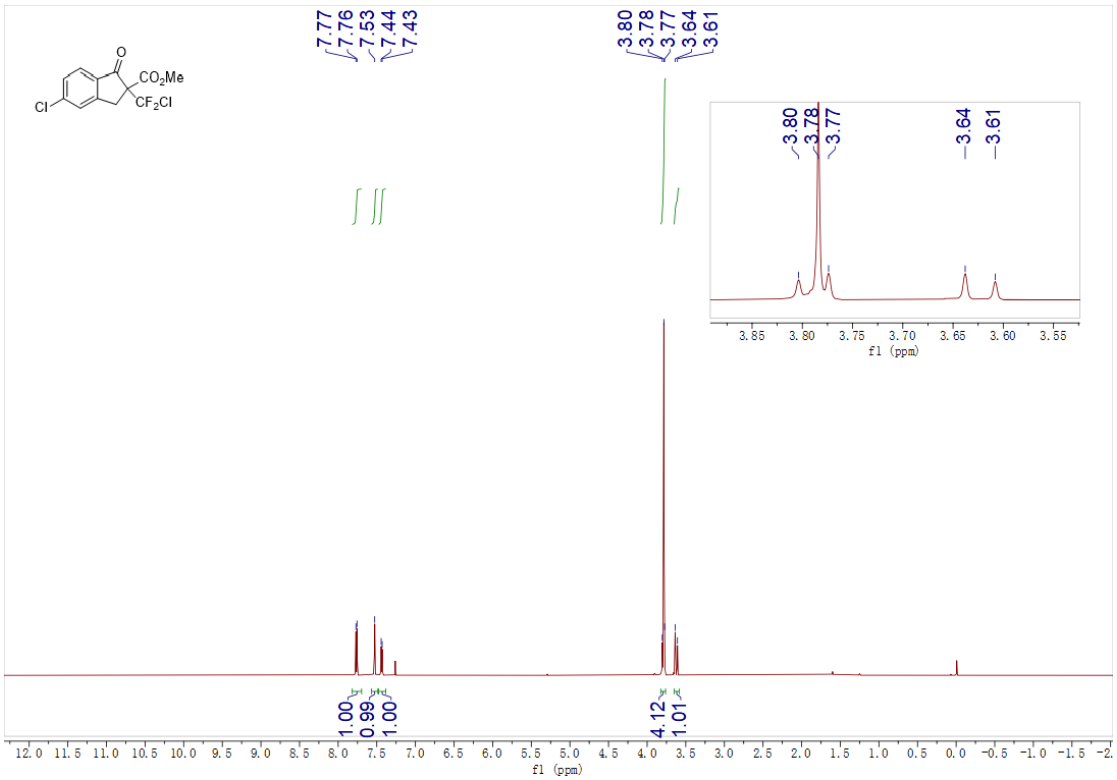
[13]C NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5e



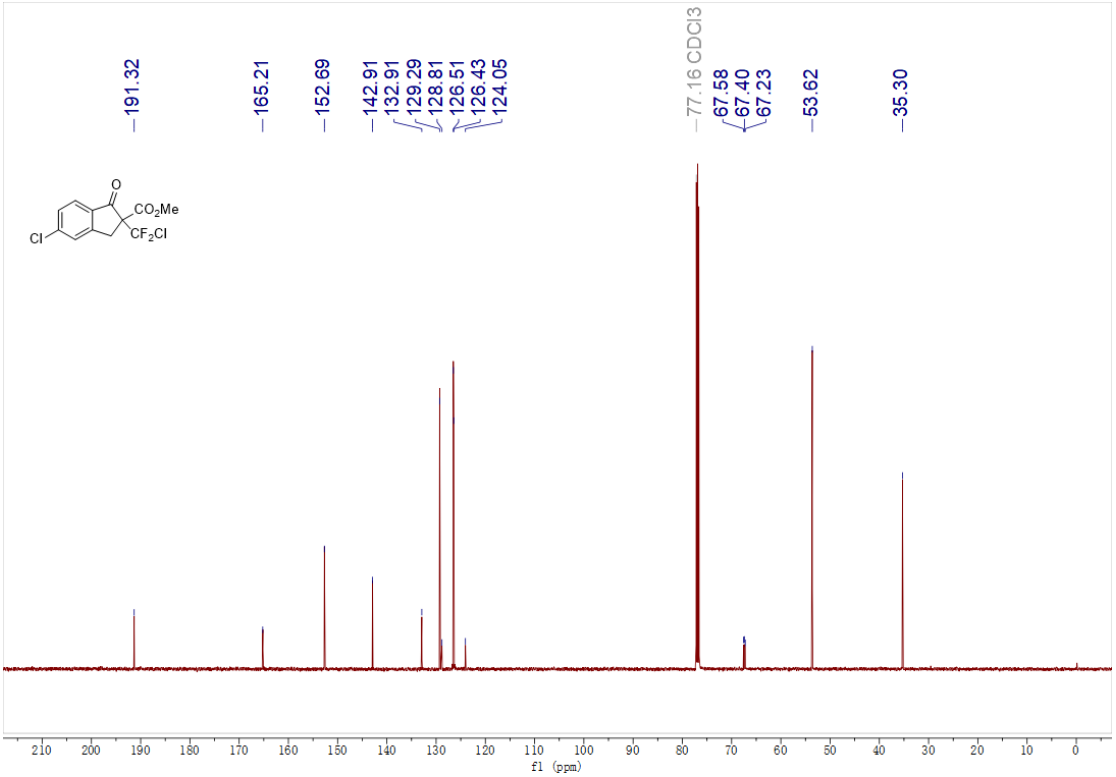
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 5e



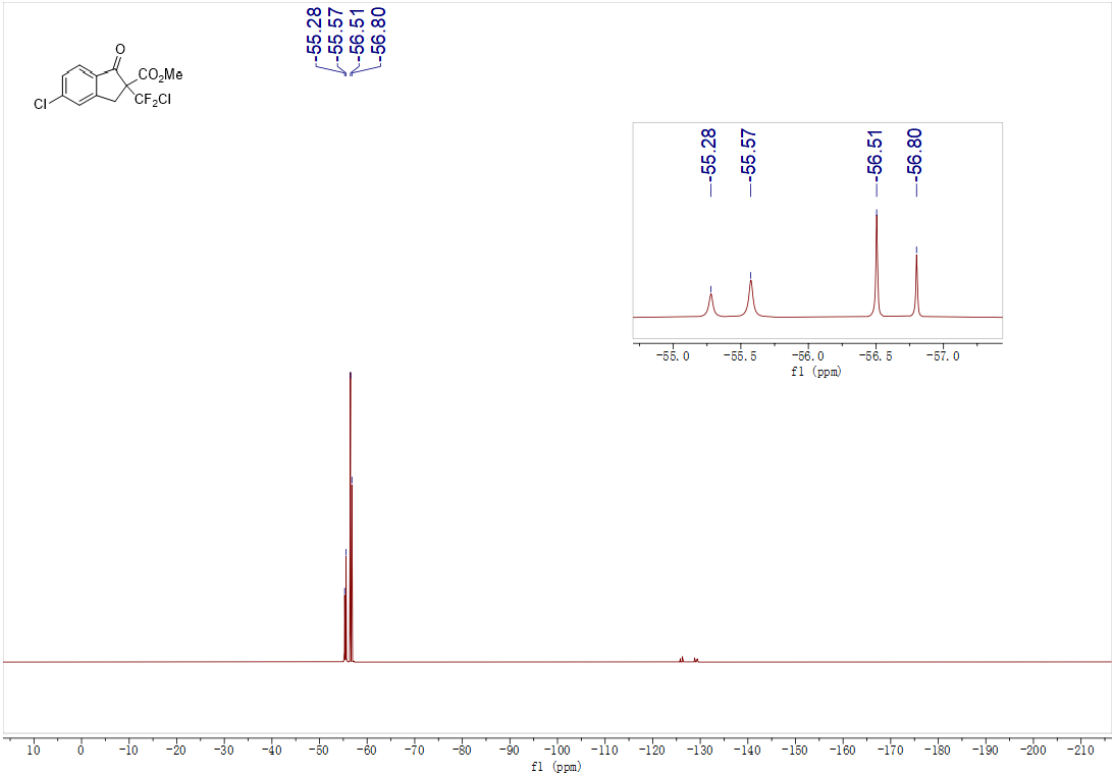
^{1}H NMR spectrum of methyl 5-chloro-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5f



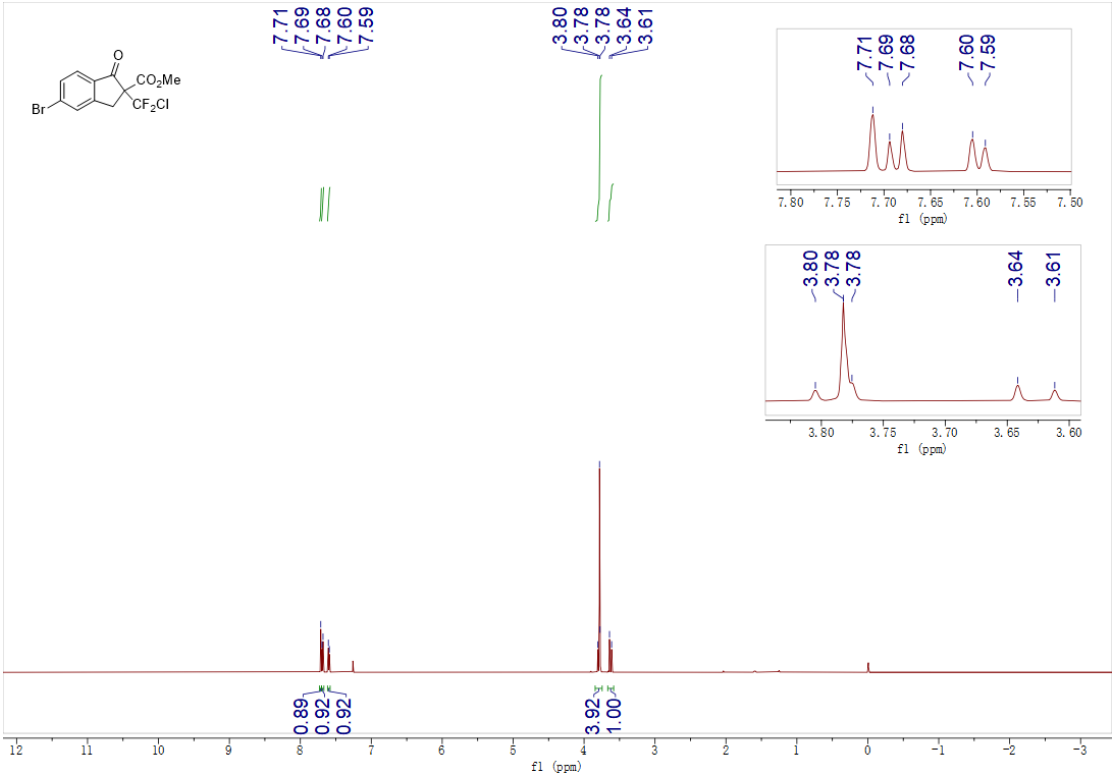
^{13}C NMR spectrum of methyl 5-chloro-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5f



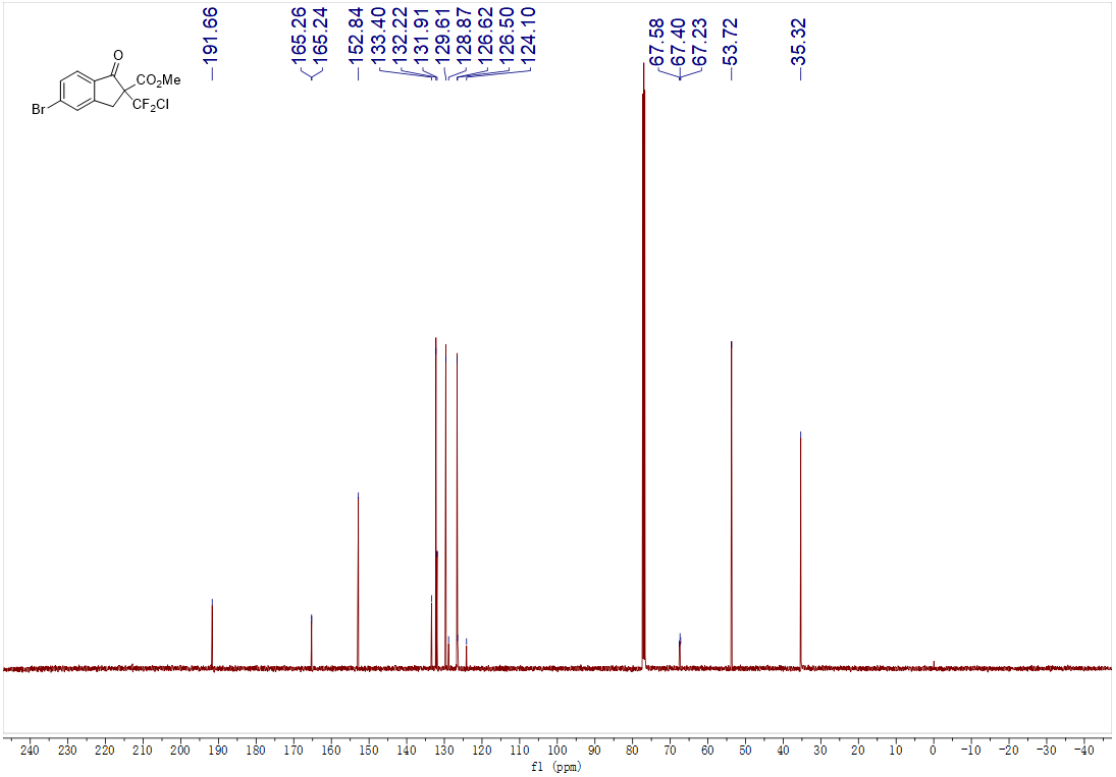
^{19}F NMR spectrum of methyl 5-chloro-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5f



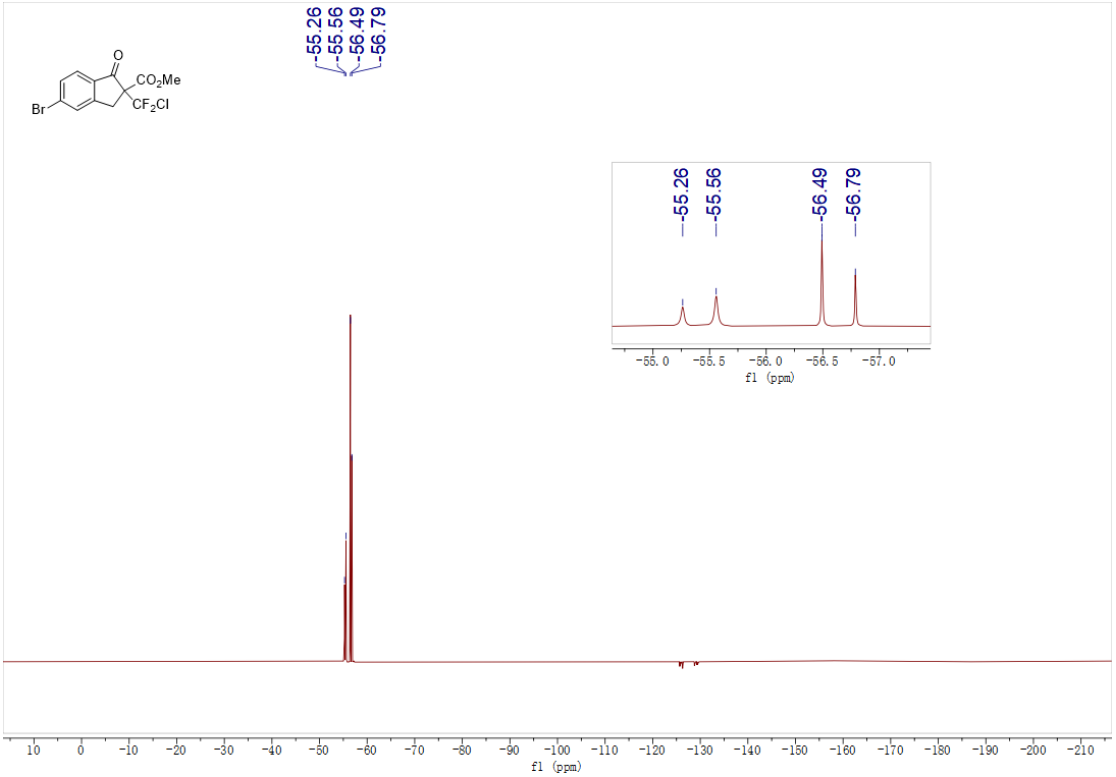
^{1}H NMR spectrum of methyl 5-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5g



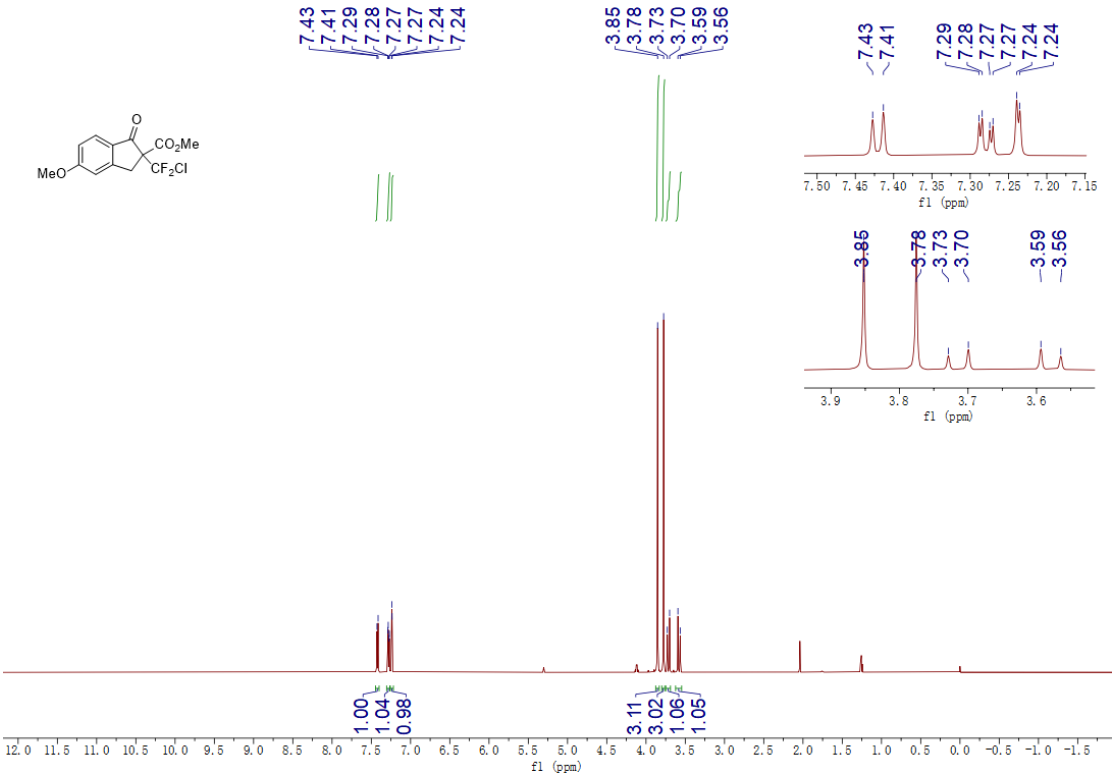
^{13}C NMR spectrum of methyl 5-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5g



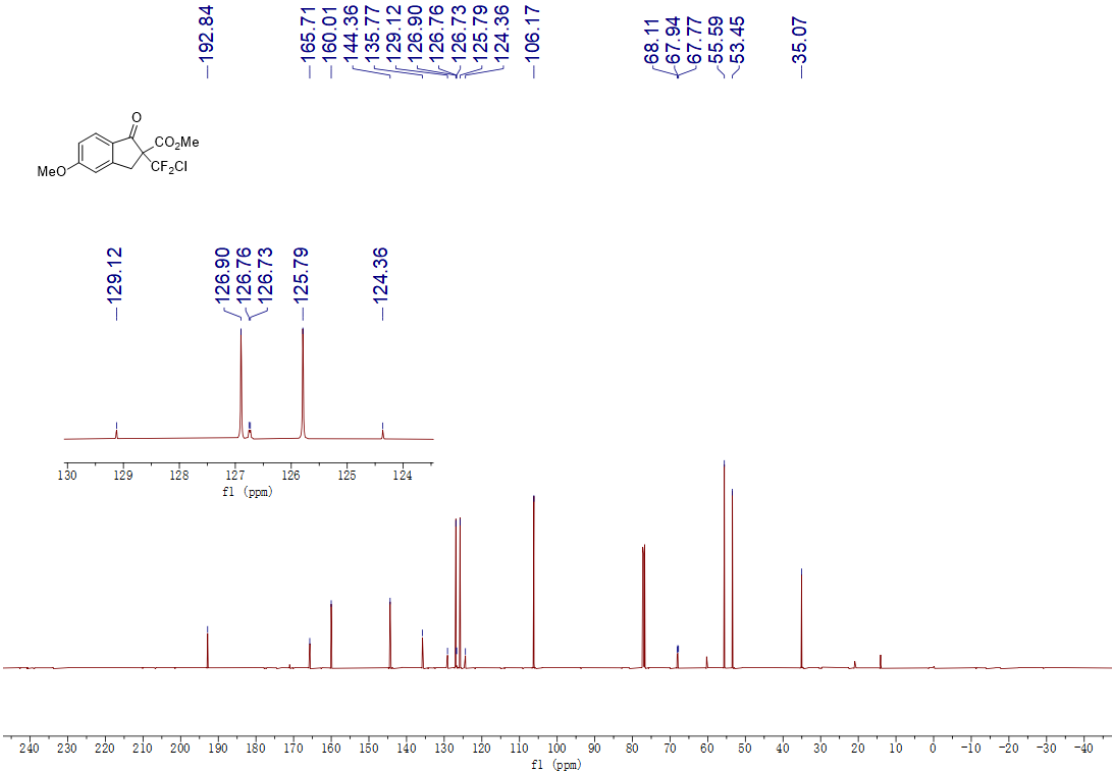
^{19}F NMR spectrum of methyl 5-bromo-2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5g



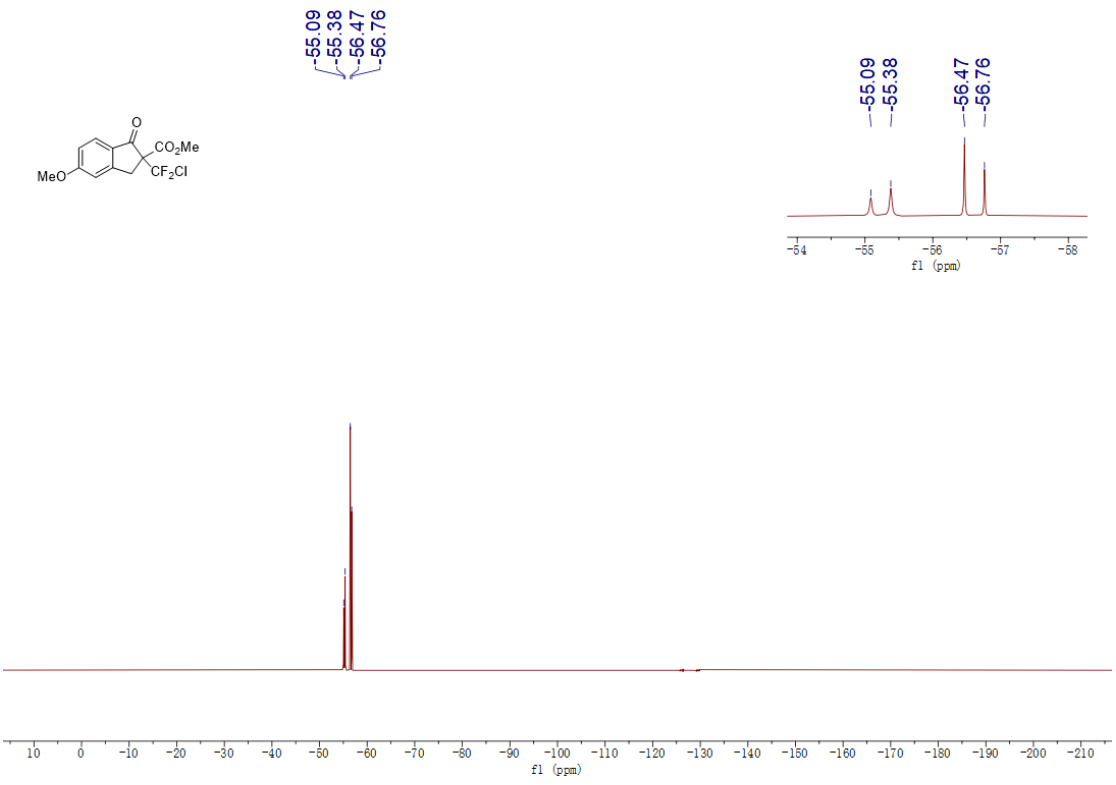
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5h



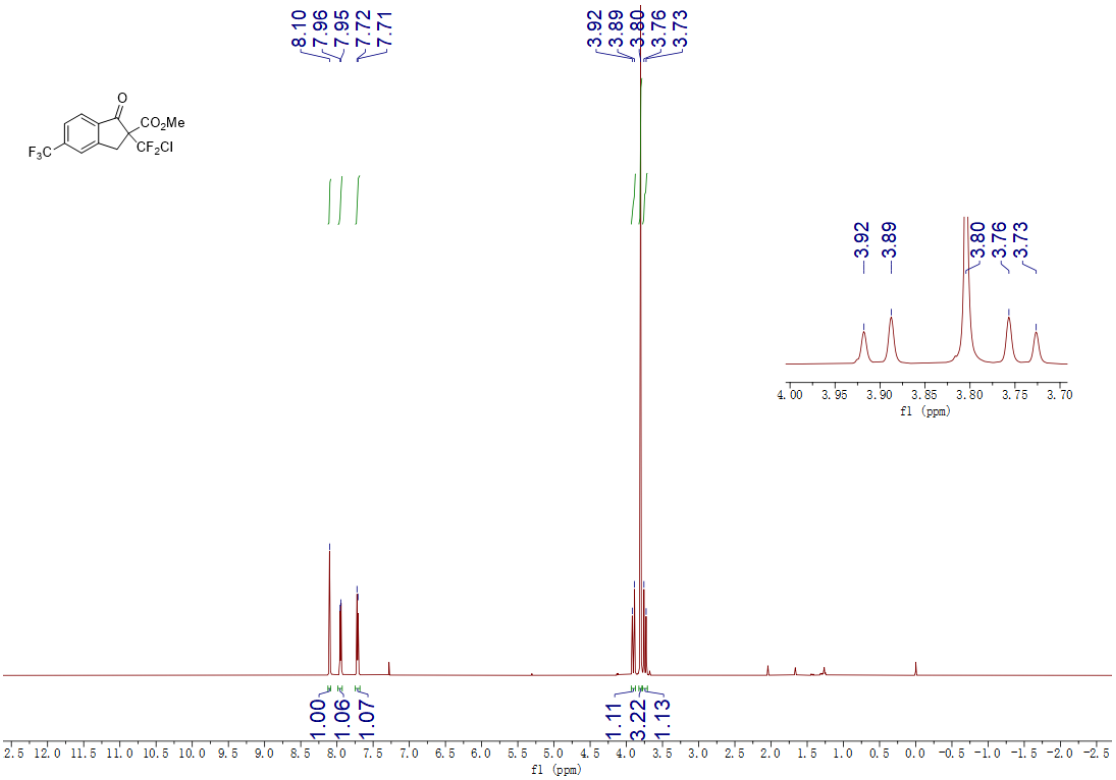
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5h



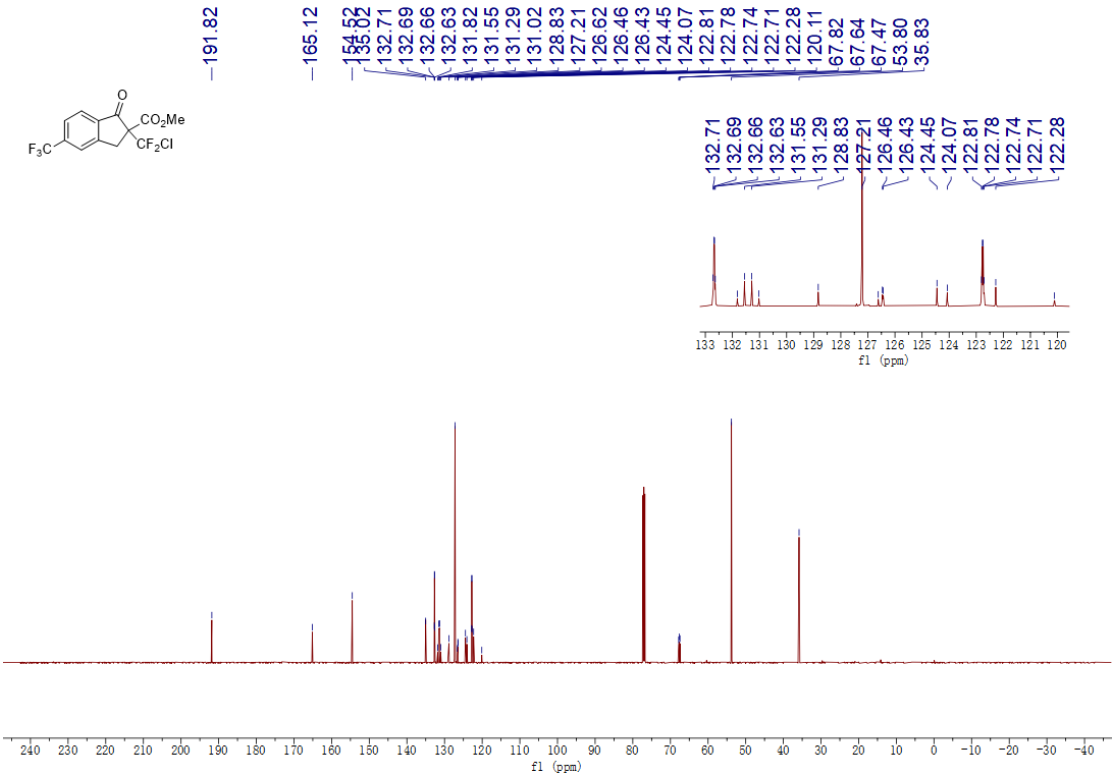
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5h



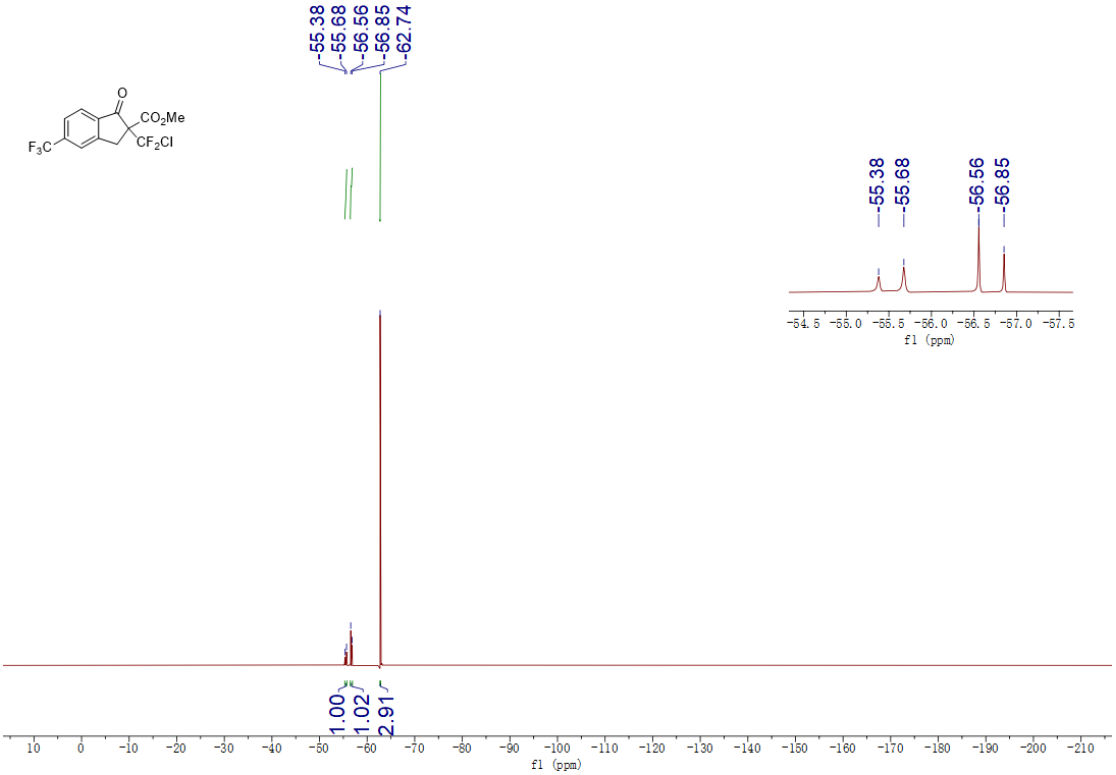
^{1}H NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-5-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 5i



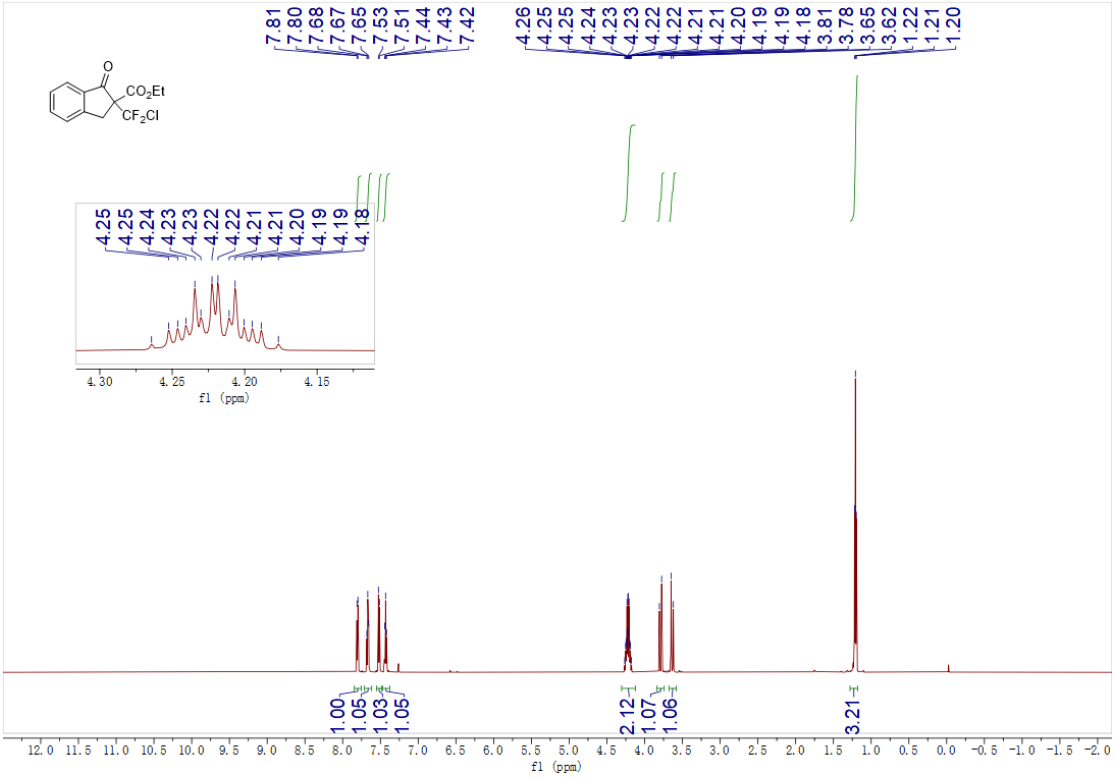
^{13}C NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-5-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 5i



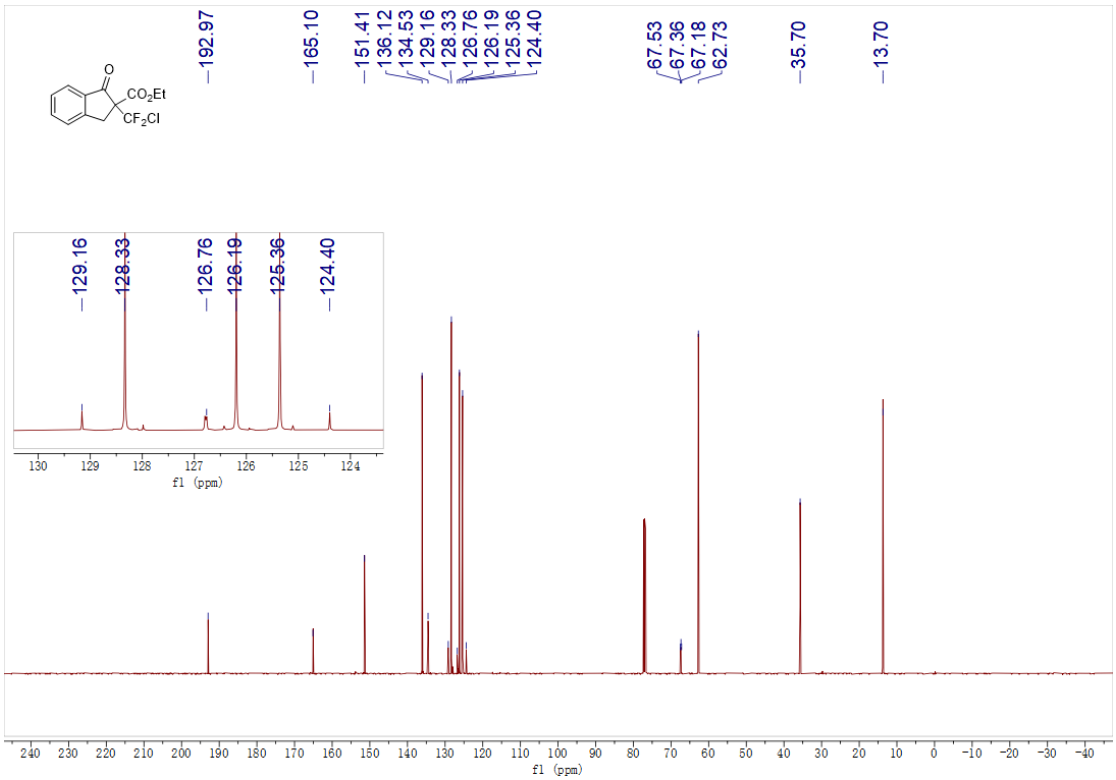
^{19}F NMR spectrum of methyl 2-(chlorodifluoromethyl)-1-oxo-5-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 5i



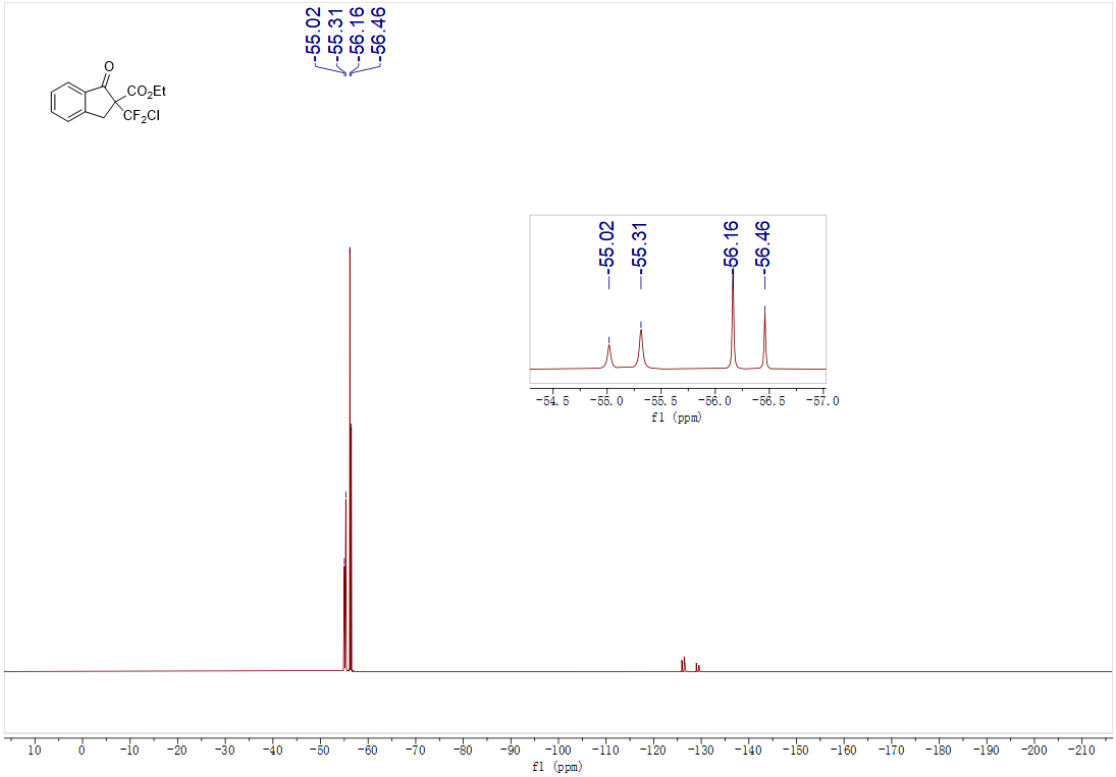
^{1}H NMR spectrum of ethyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5j



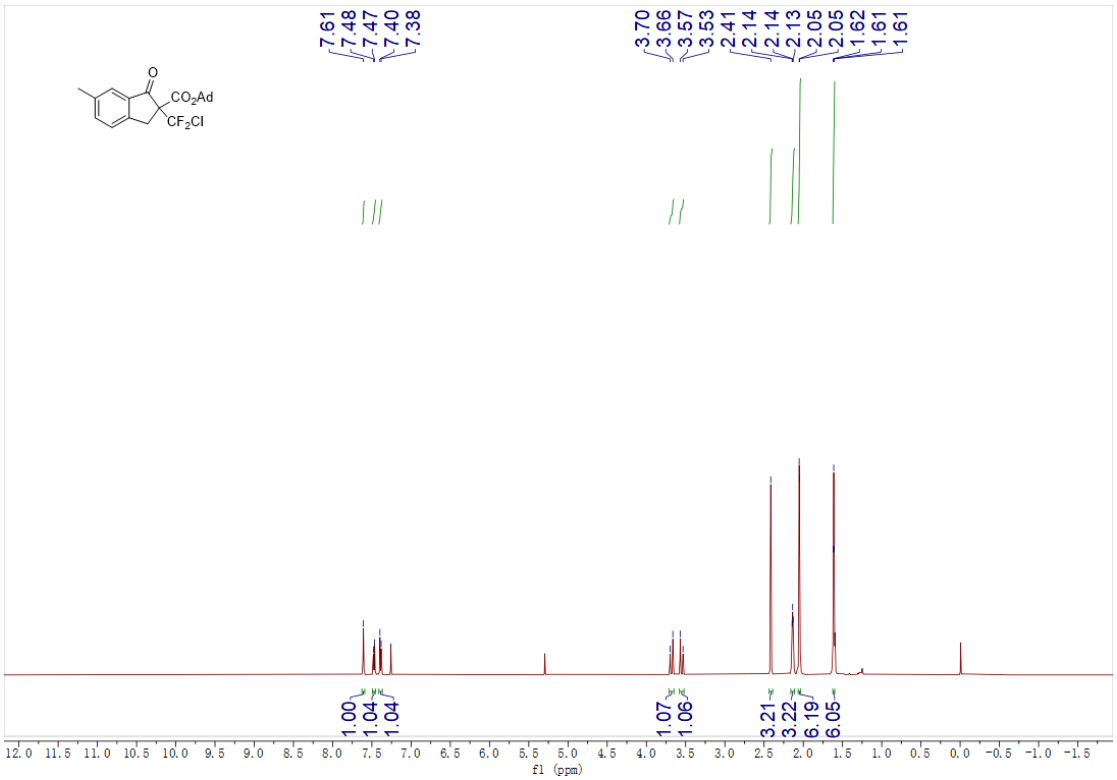
^{13}C NMR spectrum of ethyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5j



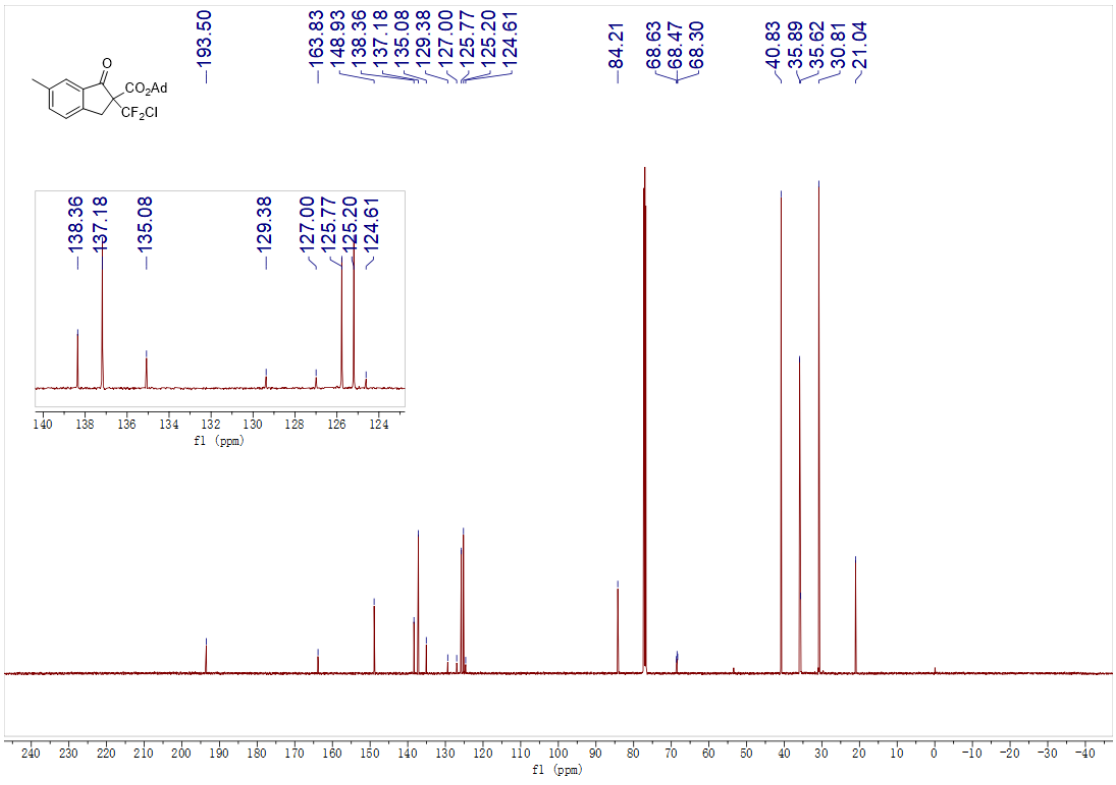
^{19}F NMR spectrum of ethyl 2-(chlorodifluoromethyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5j



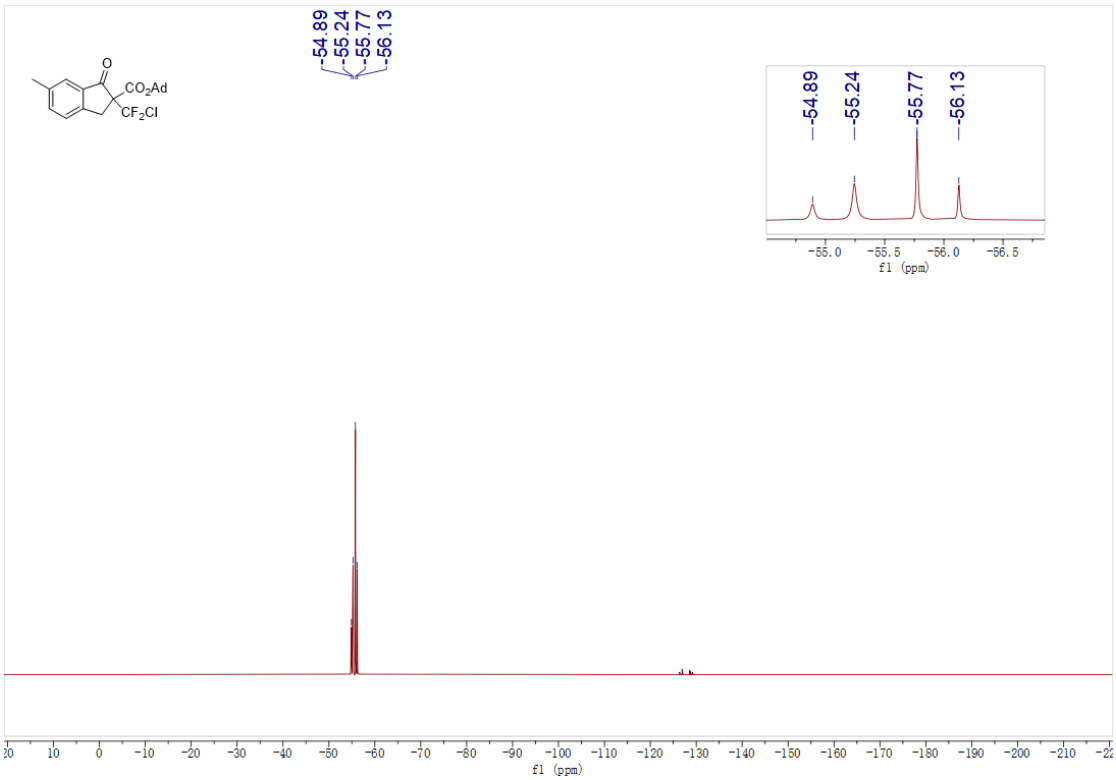
^{1}H NMR spectrum of (3s,5s,7s)-adamantan-1-yl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5k



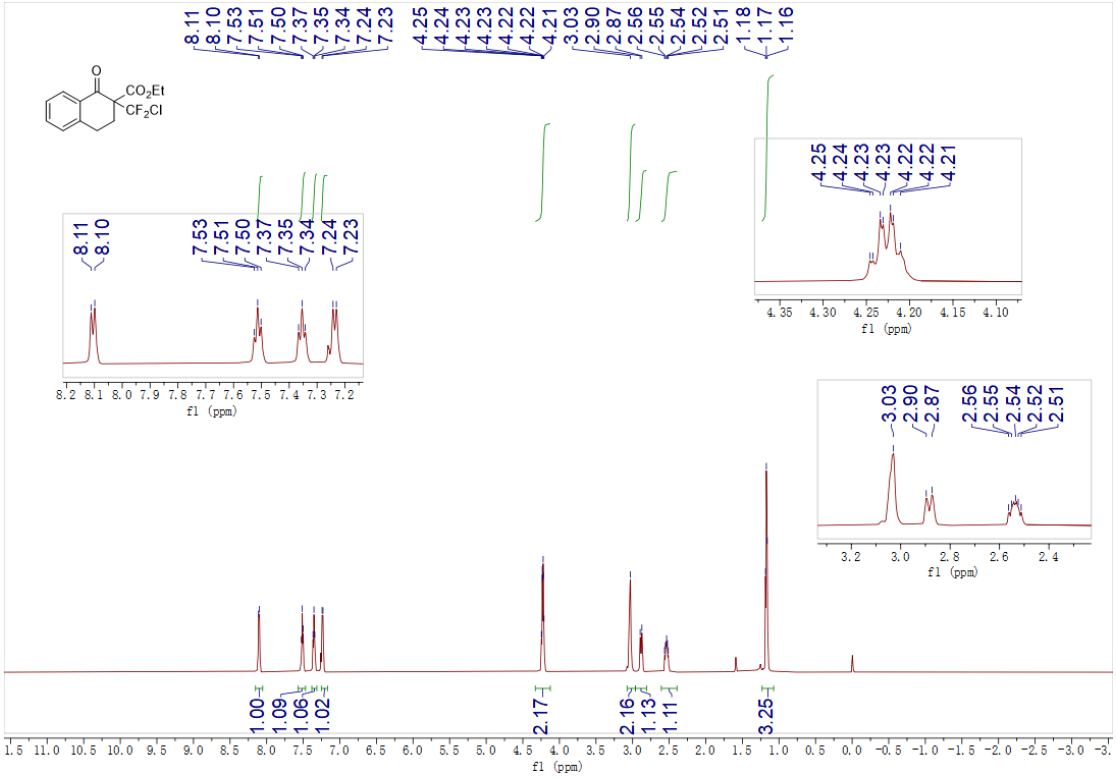
^{13}C NMR spectrum of (3s,5s,7s)-adamantan-1-yl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5k



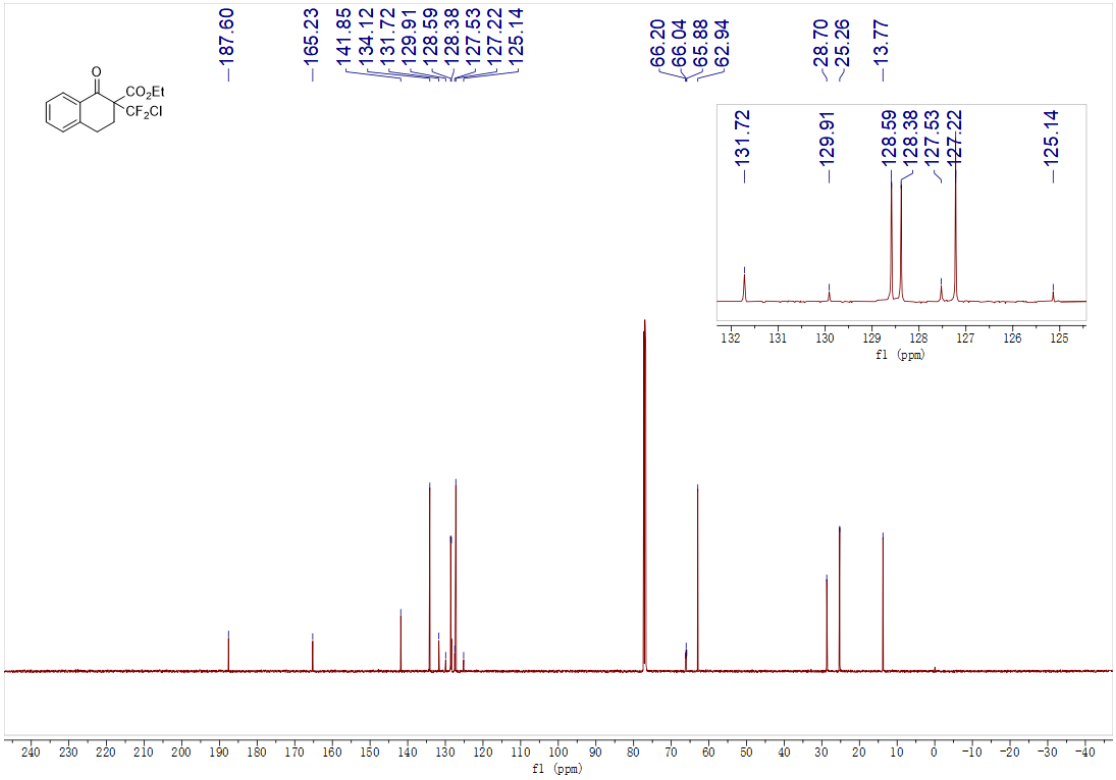
^{19}F NMR spectrum of (3s,5s,7s)-adamantan-1-yl 2-(chlorodifluoromethyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 5k



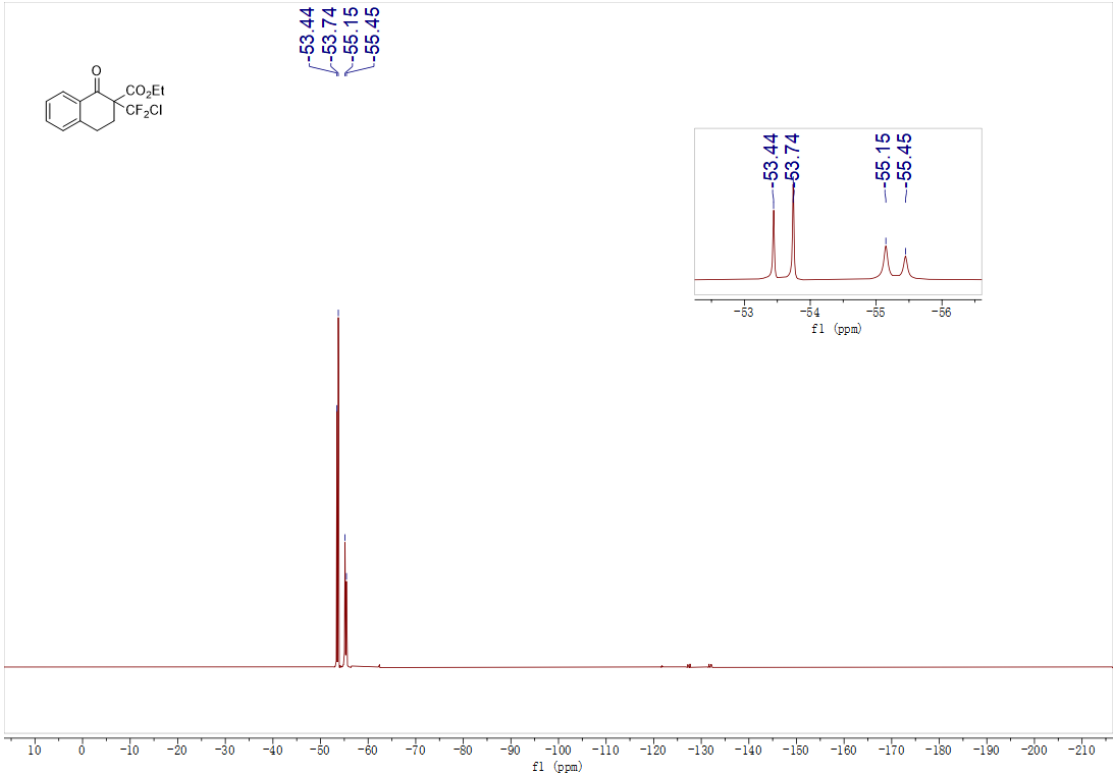
^{1}H NMR spectrum of 2,2-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one 5l



^{13}C NMR spectrum of 2,2-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one 5l



^{19}F NMR spectrum of 2,2-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one 5l



X-Ray Diffraction Data of YlideFluor-CF_2Cl

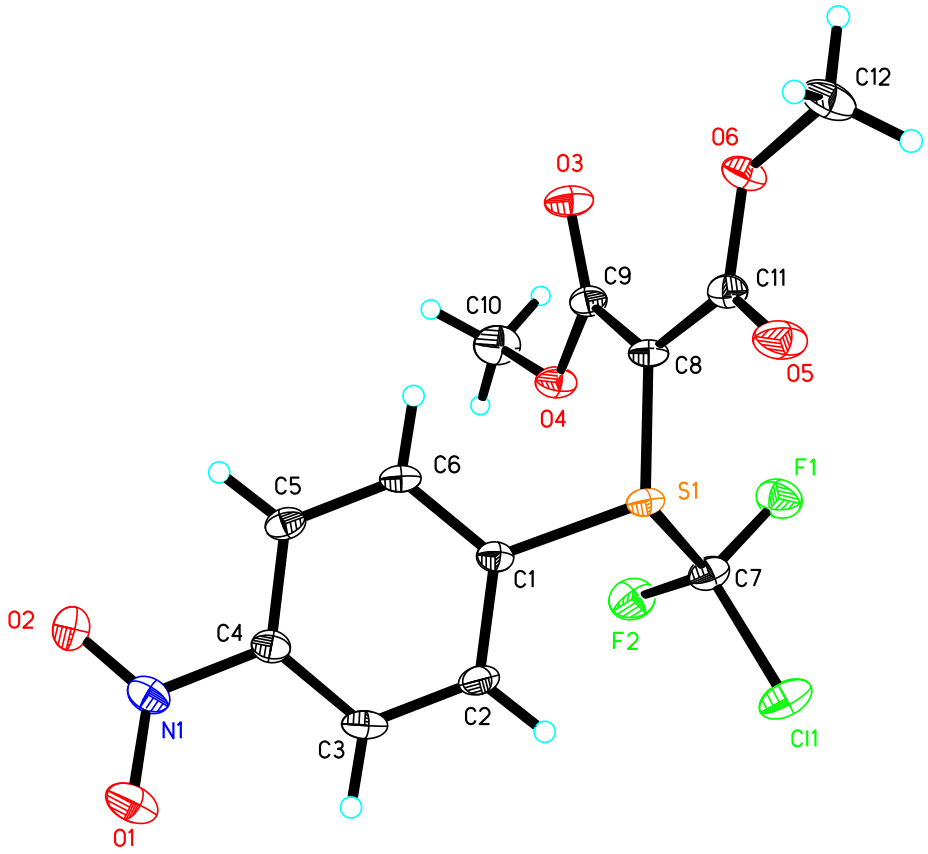


Figure S4. ORTEP diagrams of reagent **YlideFluor-CF_2Cl**. Ellipsoids are shown at the 30% level.

Table S5. Crystal data and structure refinement for mo_d8v23103_0m.

Identification code	mo_d8v23103_0m	
Empirical formula	C12 H10 Cl F2 N O6 S	
Formula weight	369.72	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 16.5250(5) Å	α = 90°.
	b = 12.9543(4) Å	β = 97.0120(10)°.
	c = 6.9523(2) Å	γ = 90°.
Volume	1477.15(8) $Å^3$	
Z	4	
Density (calculated)	1.662 Mg/m^3	
Absorption coefficient	0.453 mm^{-1}	
F(000)	752	
Crystal size	0.200 x 0.160 x 0.120 mm^3	
Theta range for data collection	4.009 to 25.494°.	
Index ranges	-18<=h<=20, -15<=k<=15, -8<=l<=8	
Reflections collected	10261	
Independent reflections	2503 [R(int) = 0.0573]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5049	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2503 / 2 / 211	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0777	
R indices (all data)	R1 = 0.0309, wR2 = 0.0786	
Absolute structure parameter	0.08(4)	
Extinction coefficient	0.013(3)	
Largest diff. peak and hole	0.248 and -0.163 $e.Å^{-3}$	

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v23103_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4091(1)	8542(1)	-164(2)	50(1)
S(1)	5090(1)	7004(1)	2228(1)	25(1)
F(1)	5549(1)	8865(2)	1280(4)	45(1)
F(2)	4646(1)	8943(2)	3288(3)	45(1)
O(1)	2332(2)	5864(2)	7997(4)	47(1)
O(2)	3400(2)	5801(2)	10147(4)	42(1)
O(3)	7186(2)	7135(2)	5450(4)	38(1)
O(4)	6025(2)	8055(2)	5313(4)	32(1)
O(5)	6089(2)	5791(2)	140(4)	44(1)
O(6)	7279(1)	6184(2)	1887(4)	33(1)
N(1)	3070(2)	5958(2)	8505(4)	33(1)
C(1)	4516(2)	6778(2)	4217(5)	25(1)
C(2)	3685(2)	7017(3)	3950(5)	31(1)
C(3)	3215(2)	6752(3)	5381(6)	32(1)
C(4)	3580(2)	6270(3)	7018(5)	27(1)
C(5)	4403(2)	6028(2)	7304(5)	28(1)
C(6)	4875(2)	6278(2)	5855(5)	27(1)
C(7)	4865(2)	8436(3)	1760(5)	33(1)
C(8)	6095(2)	6844(2)	2916(5)	26(1)
C(9)	6512(2)	7334(2)	4650(5)	26(1)
C(10)	6341(3)	8559(3)	7082(6)	45(1)
C(11)	6464(2)	6224(2)	1520(5)	28(1)
C(12)	7671(2)	5575(3)	520(6)	44(1)

Table S7. Bond lengths [Å] and angles [°] for mo_d8v23103_0m.

Cl(1)-C(7)	1.740(4)
S(1)-C(8)	1.684(3)
S(1)-C(1)	1.794(3)
S(1)-C(7)	1.912(3)
F(1)-C(7)	1.337(4)
F(2)-C(7)	1.336(4)
O(1)-N(1)	1.234(4)
O(2)-N(1)	1.221(4)
O(3)-C(9)	1.210(4)
O(4)-C(9)	1.351(4)
O(4)-C(10)	1.434(4)
O(5)-C(11)	1.214(4)
O(6)-C(11)	1.341(4)
O(6)-C(12)	1.448(4)
N(1)-C(4)	1.468(4)
C(1)-C(6)	1.380(5)
C(1)-C(2)	1.399(4)
C(2)-C(3)	1.378(5)
C(2)-H(2)	0.9400
C(3)-C(4)	1.372(5)
C(3)-H(3)	0.9400
C(4)-C(5)	1.387(5)
C(5)-C(6)	1.385(5)
C(5)-H(5)	0.9400
C(6)-H(6)	0.9400
C(8)-C(11)	1.450(5)
C(8)-C(9)	1.459(4)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(10)-H(10C)	0.9700
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(12)-H(12C)	0.9700
C(8)-S(1)-C(1)	110.89(16)
C(8)-S(1)-C(7)	109.39(16)
C(1)-S(1)-C(7)	100.33(15)

C(9)-O(4)-C(10)	116.0(3)
C(11)-O(6)-C(12)	114.6(3)
O(2)-N(1)-O(1)	124.4(3)
O(2)-N(1)-C(4)	118.4(3)
O(1)-N(1)-C(4)	117.2(3)
C(6)-C(1)-C(2)	122.0(3)
C(6)-C(1)-S(1)	119.9(2)
C(2)-C(1)-S(1)	117.7(3)
C(3)-C(2)-C(1)	118.7(3)
C(3)-C(2)-H(2)	120.7
C(1)-C(2)-H(2)	120.7
C(4)-C(3)-C(2)	118.9(3)
C(4)-C(3)-H(3)	120.6
C(2)-C(3)-H(3)	120.6
C(3)-C(4)-C(5)	123.1(3)
C(3)-C(4)-N(1)	118.5(3)
C(5)-C(4)-N(1)	118.3(3)
C(6)-C(5)-C(4)	118.2(3)
C(6)-C(5)-H(5)	120.9
C(4)-C(5)-H(5)	120.9
C(1)-C(6)-C(5)	119.1(3)
C(1)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
F(2)-C(7)-F(1)	108.3(3)
F(2)-C(7)-Cl(1)	109.1(2)
F(1)-C(7)-Cl(1)	109.9(3)
F(2)-C(7)-S(1)	114.0(3)
F(1)-C(7)-S(1)	107.0(2)
Cl(1)-C(7)-S(1)	108.43(19)
C(11)-C(8)-C(9)	126.8(3)
C(11)-C(8)-S(1)	111.0(2)
C(9)-C(8)-S(1)	122.1(2)
O(3)-C(9)-O(4)	122.9(3)
O(3)-C(9)-C(8)	127.1(3)
O(4)-C(9)-C(8)	110.0(3)
O(4)-C(10)-H(10A)	109.5
O(4)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5

O(4)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(5)-C(11)-O(6)	122.4(3)
O(5)-C(11)-C(8)	124.7(3)
O(6)-C(11)-C(8)	112.9(3)
O(6)-C(12)-H(12A)	109.5
O(6)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
O(6)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v23103_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	48(1)	45(1)	53(1)	5(1)	-14(1)	12(1)
S(1)	19(1)	27(1)	27(1)	-3(1)	-3(1)	4(1)
F(1)	36(1)	38(1)	60(2)	6(1)	8(1)	-3(1)
F(2)	50(2)	37(1)	48(1)	-7(1)	4(1)	13(1)
O(1)	29(1)	60(2)	55(2)	-12(1)	9(1)	-6(1)
O(2)	44(2)	43(2)	40(2)	11(1)	6(1)	0(1)
O(3)	25(1)	41(1)	46(2)	-8(1)	-9(1)	4(1)
O(4)	24(1)	35(1)	33(1)	-12(1)	-2(1)	1(1)
O(5)	29(1)	57(2)	42(2)	-19(1)	-4(1)	6(1)
O(6)	23(1)	38(1)	40(1)	-10(1)	7(1)	3(1)
N(1)	27(2)	30(1)	42(2)	-6(1)	8(1)	-3(1)
C(1)	20(2)	28(2)	28(2)	-3(1)	0(1)	0(1)
C(2)	23(2)	39(2)	30(2)	-1(1)	-4(1)	7(1)
C(3)	18(2)	36(2)	39(2)	-7(2)	-2(1)	4(1)
C(4)	23(2)	27(2)	31(2)	-4(1)	1(1)	-2(1)
C(5)	25(2)	25(2)	31(2)	-3(1)	-5(1)	-1(1)
C(6)	17(2)	29(2)	33(2)	-3(1)	-4(1)	3(1)
C(7)	32(2)	30(2)	36(2)	0(1)	-2(1)	6(1)
C(8)	16(2)	29(2)	33(2)	-2(1)	-2(1)	1(1)
C(9)	22(2)	26(2)	30(2)	-2(1)	-2(1)	-1(1)
C(10)	42(2)	50(2)	41(2)	-20(2)	-3(2)	2(2)
C(11)	24(2)	25(2)	34(2)	1(1)	2(1)	2(1)
C(12)	32(2)	46(2)	56(2)	-18(2)	12(2)	6(2)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 × 10^3) for mo_d8v23103_0m.

	x	y	z	U(eq)
H(2)	3451	7351	2817	37
H(3)	2653	6899	5238	38
H(5)	4635	5704	8450	33
H(6)	5432	6108	5986	32
H(10A)	6844	8913	6904	67
H(10B)	6447	8050	8105	67
H(10C)	5946	9057	7435	67
H(12A)	7522	5841	-779	66
H(12B)	7497	4862	577	66
H(12C)	8258	5614	847	66

Table S10. Torsion angles [°] for mo_d8v23103_0m.

C(8)-S(1)-C(1)-C(6)	-15.7(3)
C(7)-S(1)-C(1)-C(6)	-131.2(3)
C(8)-S(1)-C(1)-C(2)	171.5(3)
C(7)-S(1)-C(1)-C(2)	55.9(3)
C(6)-C(1)-C(2)-C(3)	0.7(5)
S(1)-C(1)-C(2)-C(3)	173.4(3)
C(1)-C(2)-C(3)-C(4)	0.4(5)
C(2)-C(3)-C(4)-C(5)	-0.4(5)
C(2)-C(3)-C(4)-N(1)	-177.9(3)
O(2)-N(1)-C(4)-C(3)	-159.9(3)
O(1)-N(1)-C(4)-C(3)	20.7(4)
O(2)-N(1)-C(4)-C(5)	22.5(4)
O(1)-N(1)-C(4)-C(5)	-156.9(3)
C(3)-C(4)-C(5)-C(6)	-0.6(5)
N(1)-C(4)-C(5)-C(6)	176.8(3)
C(2)-C(1)-C(6)-C(5)	-1.8(5)
S(1)-C(1)-C(6)-C(5)	-174.3(2)
C(4)-C(5)-C(6)-C(1)	1.7(5)
C(1)-S(1)-C(8)-C(11)	133.8(2)
C(7)-S(1)-C(8)-C(11)	-116.5(2)
C(1)-S(1)-C(8)-C(9)	-49.5(3)
C(7)-S(1)-C(8)-C(9)	60.3(3)
C(10)-O(4)-C(9)-O(3)	-2.0(5)
C(10)-O(4)-C(9)-C(8)	176.6(3)
C(11)-C(8)-C(9)-O(3)	-17.5(6)
S(1)-C(8)-C(9)-O(3)	166.3(3)
C(11)-C(8)-C(9)-O(4)	164.0(3)
S(1)-C(8)-C(9)-O(4)	-12.2(4)
C(12)-O(6)-C(11)-O(5)	-0.7(5)
C(12)-O(6)-C(11)-C(8)	-179.8(3)
C(9)-C(8)-C(11)-O(5)	176.5(3)
S(1)-C(8)-C(11)-O(5)	-6.9(4)
C(9)-C(8)-C(11)-O(6)	-4.3(5)
S(1)-C(8)-C(11)-O(6)	172.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S11. Hydrogen bonds for mo_d8v23103_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12)-H(12B)...O(3)#1	0.97	2.64	3.600(5)	172.2
C(5)-H(5)...O(5)#2	0.94	2.55	3.225(4)	129.4
C(2)-H(2)...O(3)#3	0.94	2.58	3.433(4)	150.5
C(2)-H(2)...Cl(1)	0.94	2.89	3.606(4)	134.4
C(12)-H(12B)...O(3)#1	0.97	2.64	3.600(5)	172.2
C(5)-H(5)...O(5)#2	0.94	2.55	3.225(4)	129.4
C(2)-H(2)...O(3)#3	0.94	2.58	3.433(4)	150.5
C(2)-H(2)...Cl(1)	0.94	2.89	3.606(4)	134.4
C(2)-H(2)...Cl(1)	0.94	2.89	3.606(4)	134.4
C(2)-H(2)...O(3)#3	0.94	2.58	3.433(4)	150.5
C(5)-H(5)...O(5)#2	0.94	2.55	3.225(4)	129.4
C(12)-H(12B)...O(3)#1	0.97	2.64	3.600(5)	172.2

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1,z-1/2 #2 x,y,z+1 #3 x-1/2,-y+3/2,z-1/2