Supporting Online Material for

Transition-Metal-Free Oxidative Aliphatic C-H Fluorination

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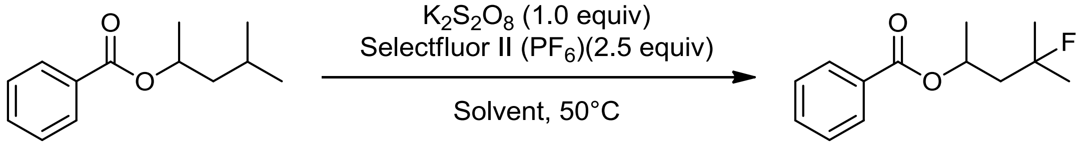
Materials and Methods

All reactions were performed under air condition without further degas procedure except as indicated otherwise. CH_3CN, DMF and DCM were dried by distillation over CaH_2. Toluene was dried by distillation over sodium/benzophenone. H_2O and acetone were distilled. $K_2S_2O_8$ was purchased from Alfa, Aesar and Aladdin. Selectfluor II, $CDCl_3$ and CD_3CN were purchased from Sigma-Aldrich. 5-Methylhexan-2-ol[4], butyl benzoate (**1a**)[4], isobutyl benzoate (**1d**)[4], isopentyl benzoate (**1e**)[4], 4-methylhexan-2-ylbenzoate (**1f**)[4], 5-methylhexan-2-yl benzoate (**1g**)[4] 1,4-dimethylpentyl 4-(trifluoromethyl)benzoate (**1h**)[4], 1,4-dimethylpentyl 4-cyanobenzoate (**1i**)[4], 1,4-dimethylpentyl 4-(*tert*-butyl)benzoate (**1j**)[4], 1,4-dimethylpentyl 2-bromobenzoate (**1k**)[4], 1,4-dimethylpentyl 2-chlorobenzoate (**1l**)[4], 4-methyl-1-phenyl-1-pentanone (**1m**)[4], 1,4-dimethylpentyl picolinate (**1n**)[4], *N*-phthaloyl-*L*-leucine methyl ester (**1o**)[4], methyl 4-methylpentanoate (**1p**)[4], 4-methylpentanamide (**1q**)[4], 2-adamant-1-ylisoindole-1,3-dione (**1r**)[4], 7-*O*-acetyl-13-*O*-(4-methylpentanoyl) baccatine III (**1y**)[4] were prepared as corresponding reference reported. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Bruker AVANCE AV 400 (400MHz, 101MHz and 376MHz). Signal positions were recorded in ppm with the abbreviations s, d, t and m denoting singlet, doublet, triplet, and multiplet respectively. All NMR chemical shifts were reported with the solvent resonance as internal standard. For ^1H NMR: $CDCl_3 = \delta$ 7.26 ppm, $CD_3CN = \delta$ 1.94 ppm. For ^{13}C NMR: $CDCl_3 = \delta$ 77.16 ppm, $CD_3CN = \delta$ 118.26 ppm. Mass spectra were acquired on Agilent 6520 Q-TOF LC/MS, Varian 7.0T FTMS and Aligent 7890/5975C-GS/MSD. ICP-AES experments were performed on Thermo Elemental IRIS Intrepid II XSP. EPR Spectras were acquired on Bruker EMX-6/1.

Experimental Data

Experimental Procedures and Compound Characterization

Effect of solvents on the reaction



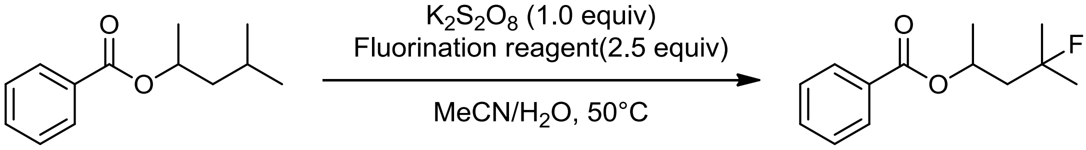
1f **2f**

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) were added solvent (0.5 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S1.

Table S1: Effect of solvents on the reaction

Solvent	Yield [%] (^{19}FNMR)	Solvent 3:2 (v/v)	Yield [%] (^{19}FNMR)
MeCN	0	MeCN/H_2O	70
DMF	0	DMF/H_2O	0
DCM	0	DCM/H_2O	0
Acetone	0	Acetone/H_2O	51
Toluene	0	Toluene/H_2O	0
H_2O	0		

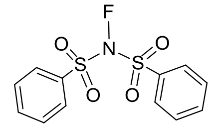
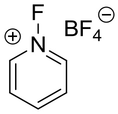
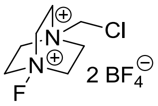
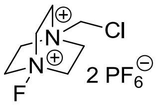
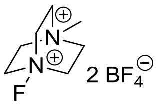
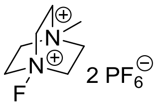
Effect of fluorinating reagents on the reaction



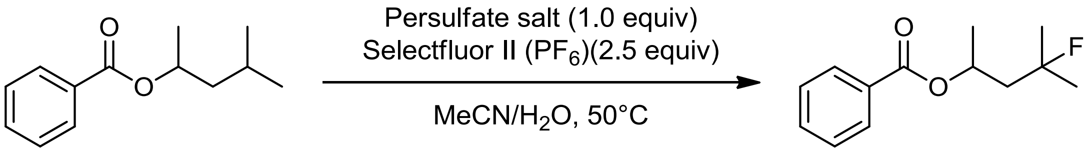
1f **2f**

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and fluorinating reagent (0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 µL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S2.

Table S2: Effect of fluorinating reagentson the reaction

Fluorinating reagent	Yield [%] (^{19}FNMR)
	0
	0
	17
	37
	67
	70

Effect of persulfate salts on the reaction



1f **2f**

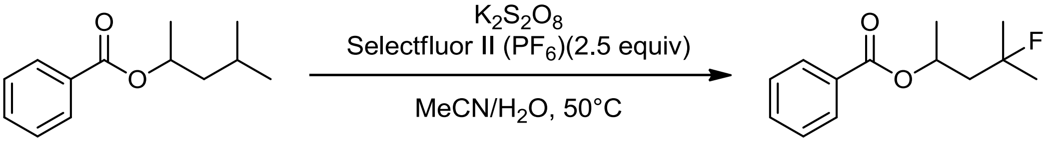
To persulfate salt (0.100 mmol, 1.00 equiv) and

4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S3.

Table S3: Effect of persulfate salts on the reaction

Persulfate salts	Yield [%] (^{19}FNMR)
-	0
$Na_2S_2O_8$	57
$K_2S_2O_8$	70
$(NH_4)_2S_2O_8$	55

Effect of persulfate salt amount on the reaction



1f **2f**

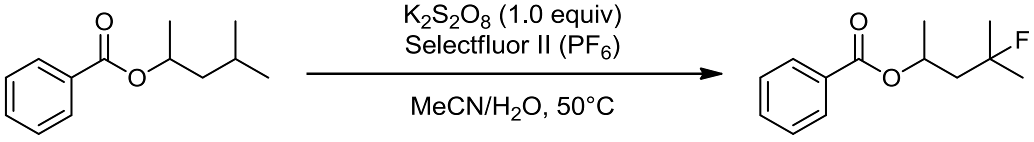
To potassium persulfate and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S4.

Table S4: Effect of persulfate salt amount on the reaction

Amount of persulfate salts (equiv)	Yield [%] (^{19}FNMR)
0.2	0

0.6	38
1.0	70
1.5	65
2.0	65

Effect of fluorinating reagent amount on the reaction



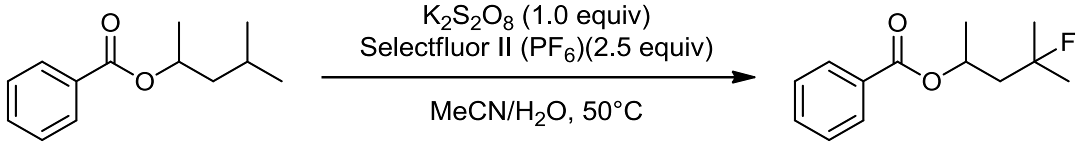
1f **2f**

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) in H_2O (0.2 mL) were added MeCN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 ^{o}C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S5.

Table S5: Effect of fluorinating reagent amount on the reaction

Amount of fluorination reagent (equiv)	Yield [%] (^{19}FNMR)
1.2	57
1.5	66
2.0	67
2.5	70
3.0	69

Effect of persulfate salt purity on the reaction



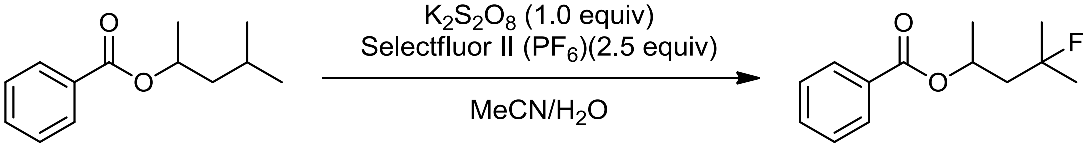
1f **2f**

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added MeCN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S6.

Table S6: Effect of persulfate salt purity on the reaction

Persulfate salt purity	Yield [%] (^{19}FNMR)
99.5% Potassium peroxydisufate	68
Recrystallized 99.5% potassium peroxydisufate	71
Alfa Aesar 99.99%(metals basis) potassium peroxydisufate	69
Recrystallized Alfa Aesar 99.99%(metals basis) potassium peroxydisufate	70

Effect of temperature on the reaction



1f **2f**

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added MeCN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred and heated for 10 hr in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S7.

Table S7: Effect of temperature on the reaction

Temperature	Yield [%] (^{19}FNMR)
40 ^{o}C	0
50 ^{o}C	70
60 ^{o}C	20

ICP data of potassium persulfate and selectfluor II (PF_6) used in experiments

The potassium persulfate and selectfluor II (PF_6) used in experiments were examined by ICP-AES for possible critical transition metals including Fe, Co, Ni, and Cu. The results are reported in Table S8.

Table S8: ICP data of potassium persulfate and selectfluor II (PF6) used in experiments

Element	$K_2S_2O_8$	Selectfluor II(PF_6)
Fe	6.3	4.0
Co	ND	ND
Ni	1.7	1.4
Cu	ND	ND

Unit: μg/g (ppm), ND: Not detected.

Effect of oxygen amount on the reaction

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in corresponding sealed vial were degased and charged with corresponding gas, then added H_2O (0.2 mL), MeCN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred and heated at 50 ^{o}C for 10 hr.

After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methyl-2-pentyl benzoate (**2f**) (-135.68 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). Yields are reported in Table S9.

Table S9: Effect of oxygen amount on the reaction

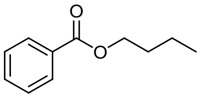
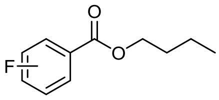
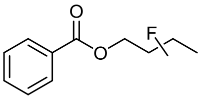
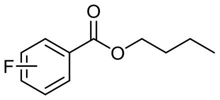
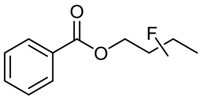
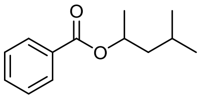
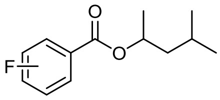
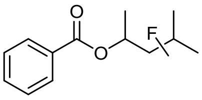
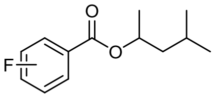
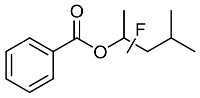
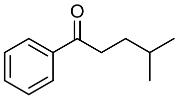
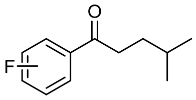
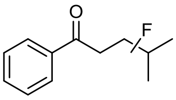
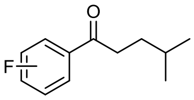
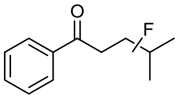
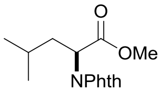
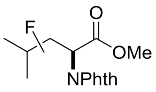
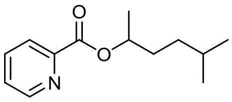
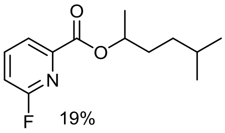
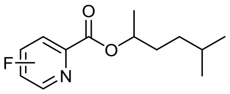
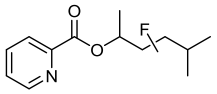
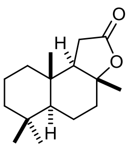
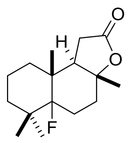
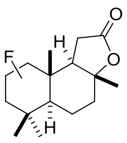
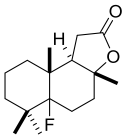
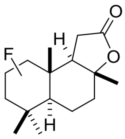
Entry	Atmosphere	Yield [%] (^{19}FNMR) In 2.00 mL sealed vial	Yield [%] (^{19}FNMR) In 20.0 mL sealed schlenk
1	Air	70	3
2	N_2	70	73
3	O_2	0	0

Fluorination of selected substrates with elemental fluorine

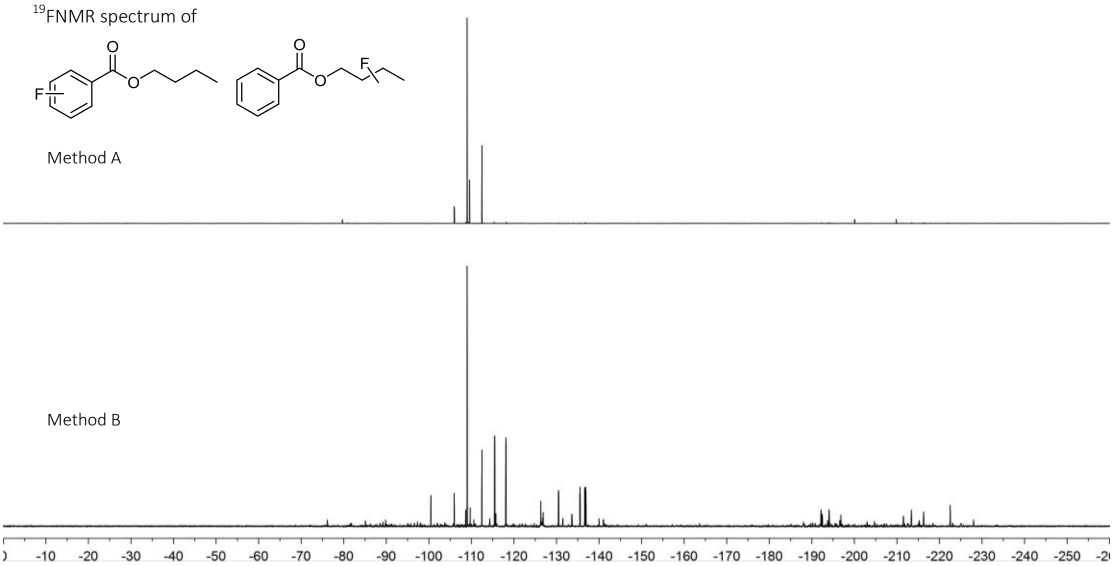
Method A: Elemental fluorine diluted in N_2 (v/v 10%, 1.00 mmol) was passed through the mixture of substrate (0.50 mmol, 1 equiv) and MeCN (2.5 mL) in an 8 mL sealed vial at 0 °C. Then the reaction mixture was poured into water (3 mL), neutralized with $NaHCO_3$ and extracted 3 times with EtOAc (5 mL). The combined organic layer was concentrated *in vacuo* to give the crude product. The crude product was dissolved in $CDCl_3$ and added 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol). The yield was determined by comparing the integration of the ^{19}F NMR resonance of the crude product with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). The results ^{19}F NMR resonance reported on Table S10.

Method B: Elemental fluorine diluted in N_2 (v/v 10%) was passed at *ca.* 50 mL/min through the mixture of substrate (0.50 mmol, 1 equiv) and MeCN (2.5 mL) in an 8 mL sealed vial at 0 °C. The reaction was monitored by GC. When the reaction was finished, the reaction mixture was poured into water (3 mL), neutralized with $NaHCO_3$ and extracted 3 times with EtOAc (5 mL). The combined organic layer was concentrated *in vacuo* to give the crude product. The crude product was dissolved in $CDCl_3$ and added 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol). The yield was determined by comparing the integration of the ^{19}F NMR resonance of the crude product with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). The results ^{19}F NMR resonance reported on Table S10.

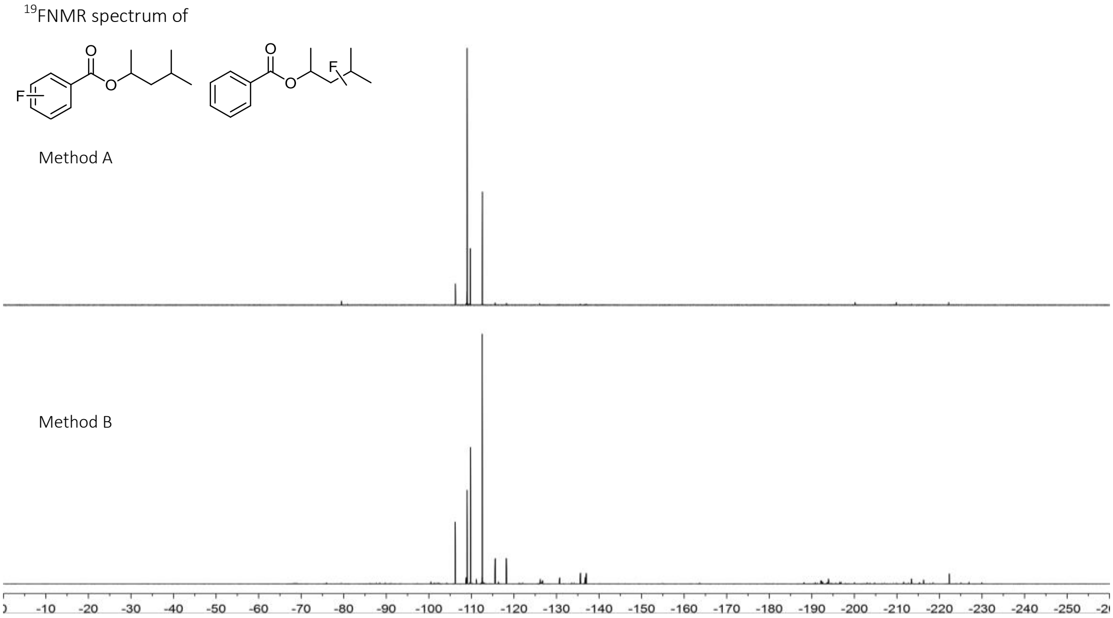
Table S10: Fluorination of selected substrates with elemental fluorine

Substante	Method A		Method B	
 **1a**	 8.4 % *o* : *m* : *p* = 2.3 : 1.4 : 1	 0 %	 3.1 % *o* : *m* : *p* = 1.8 : 0 : 1 conversion: 100%	 25.5 %
 **1f**	 8.7 % *o* : *m* : *p* = 4.8 : 2.9 : 1	 0 %	 29.3 % *o* : *m* : *p* = 5 : 2.8 : 1 conversion: 100%	 23.4 %
 **1m**	 5.0 % *o* : *m* : *p* = 5.4 : 3.6 : 1	 0 %	 0 % conversion: 100%	 36.5 %
 **1o**	ND		 20.3% conversion: 100%	
 **1n**	 19%		 9.6 % *o* : *m* : *p* = 1 : 4.6 : 1.8 conversion: 100%	 35.0 %
 **1w**	 17.9 %	 8.1 %	 15.4 % conversion: 100%	 23.5 % Other position: 41.4%

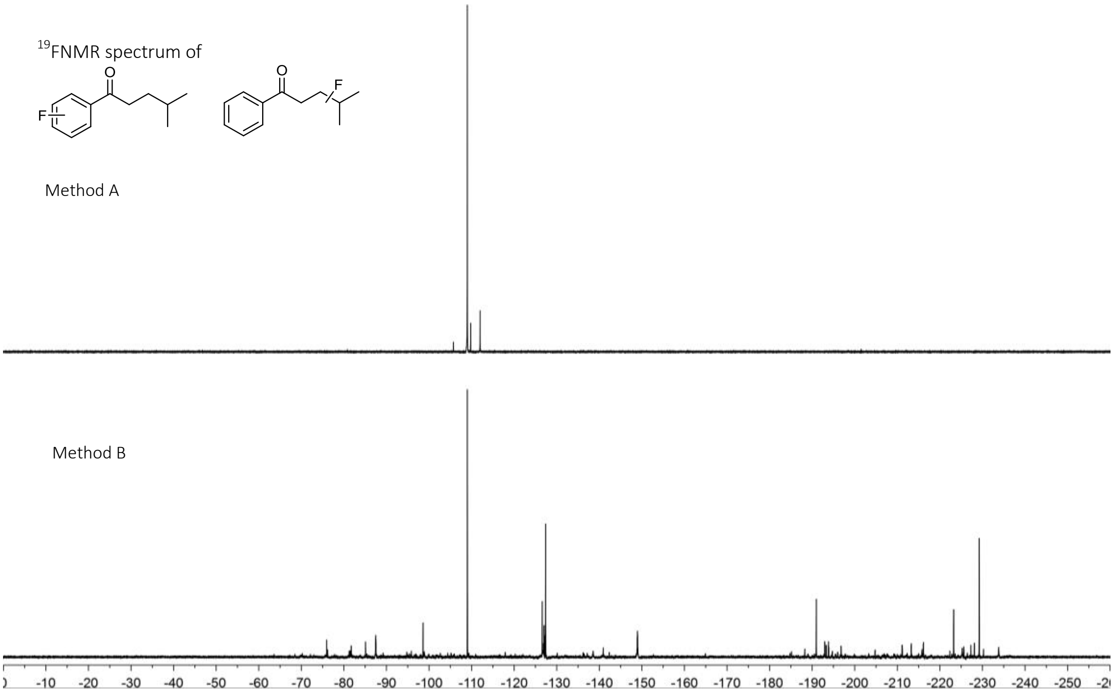
ND: Not detected.



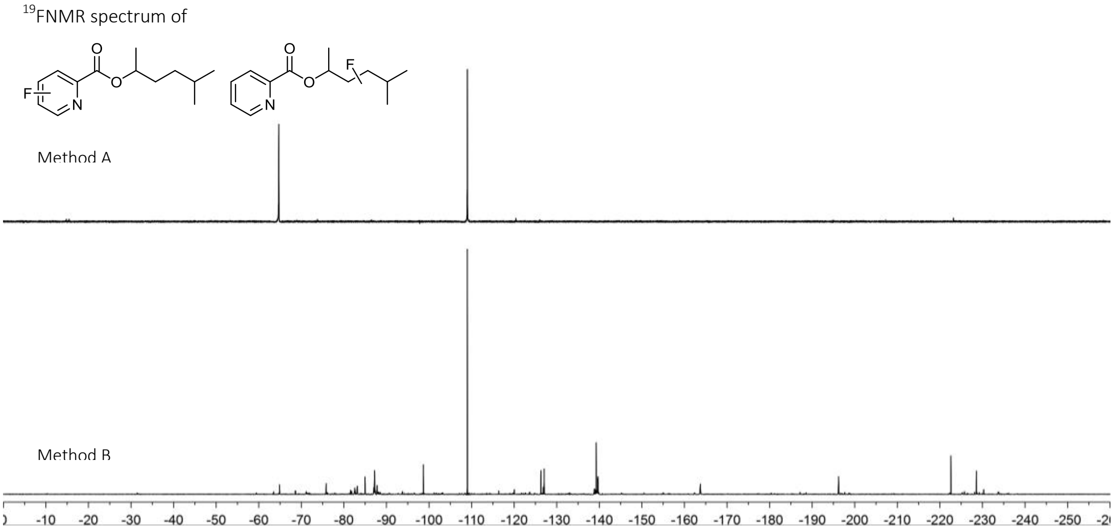
^{19}F NMR spectrum of strustrate **1a** with elemental fluorine.



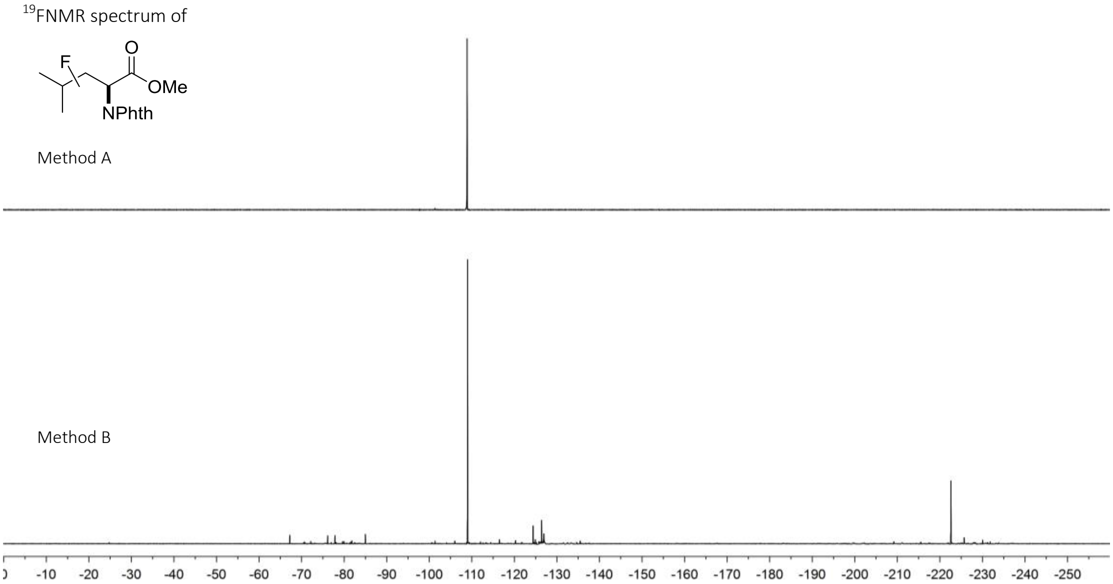
^{19}F NMR spectrum of strustrate **1f** with elemental fluorine.



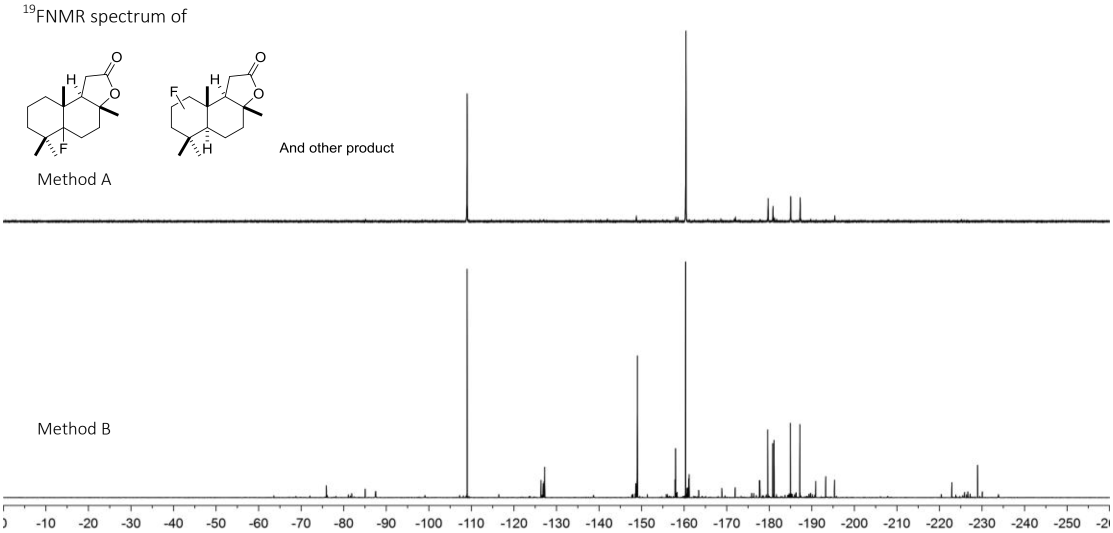
^{19}F NMR spectrum of strustrate **1m** with elemental fluorine.



^{19}F NMR spectrum of strustrate **1n** with elemental fluorine.



^{19}F NMR spectrum of strustrate **1o** with elemental fluorine.



^{19}F NMR spectrum of strustrate **1w** with elemental fluorine.

EPR Spectra

Typical spectrometer parameters were: Receiver Gain = 2.00*10^{5}; Phase = 0 deg; Harmonic= 1; Mod. Frequency = 100 kHz; Mod. Amplitude = 1G; Center Field = 3510; Sweep width = 120; Resolution = 1024; Conversion = 163.84 ms; Time const = 40.96 m; Sweep time = 167.77s; power= 1 mw. DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) was employed as the radical trapper.

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added MeCN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 1 hr at 50 °C in a 2 mL sealed vial.

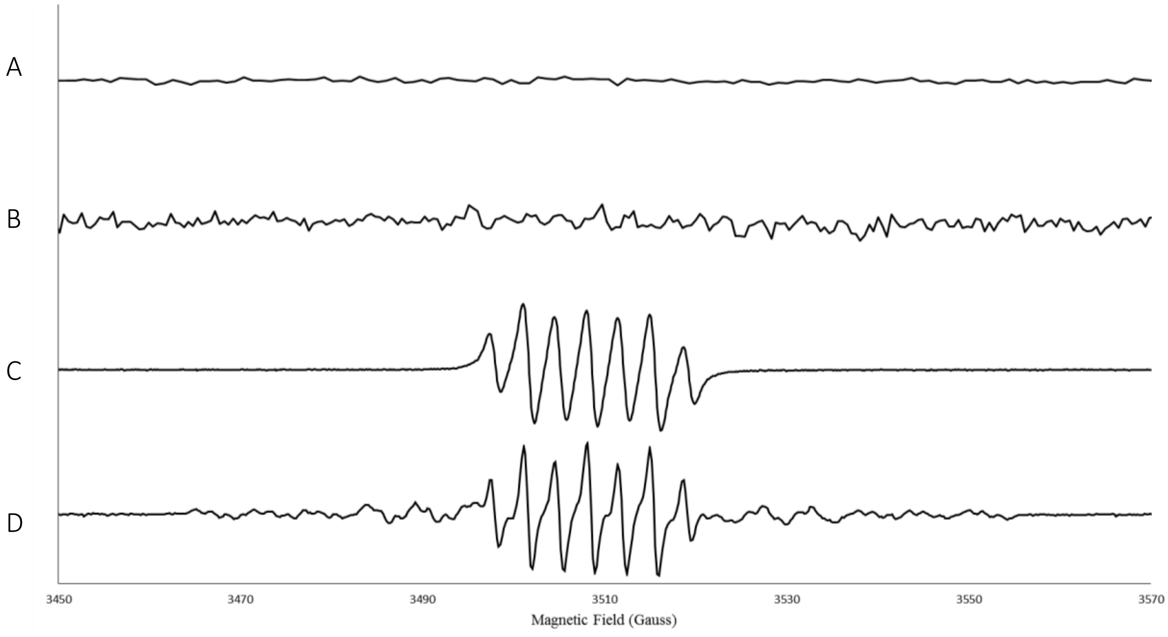
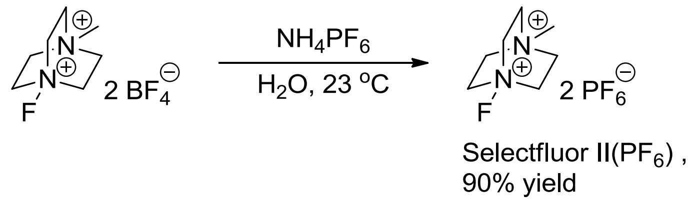


Figure 1: EPR spectra of condition A: reaction mixture without DMPO; condition B: **1f** (0.100 mmol) in a 1 mL tube was added 100 μL DMPO (0.05 mol/L in MeCN); condition C: 10.0 μL reaction mixture in a 1 mL tube was added 100 μL DMPO (0.05 mol/L in MeCN) under air; condition D: 10.0 μL reaction mixture in a 1 mL tube was added 100 μL DMPO (0.05 mol/L in MeCN) under N_2

Selectfluor II (PF_6)

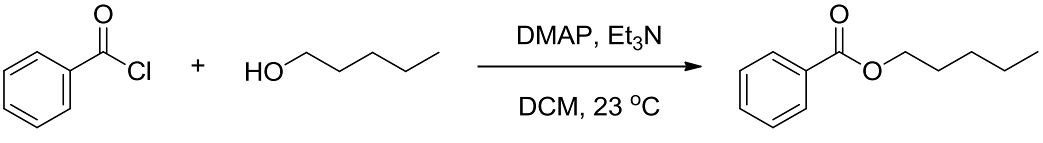


To 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (0.957 g, 3.00 mmol, 1.00 equiv) in H_2O (9.0 mL) was added ammonium hexafluorophosphate (2.93 g, 18.0 mmol, 6.00 equiv) and stirred for 1 hr at 23 °C. The suspension was filtered and washed 3 times with H_2O (15.0 mL) and Et_2O (10.0 mL) to afford 1.17g Selectfluor II (PF_6) (4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate))[1] as a white solid (90% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, CD_3CN) δ 4.63 (dd, *J* = 15.1, 7.4 Hz, 6H), 4.25 – 4.08 (m, 6H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 58.3 (d, *J* = 14.7 Hz), 57.6, 53.5.

^{19}F NMR (376 MHz, CD_3CN) δ 52.11 (s, 1F), -67.45 (d, *J* = 706.6 Hz, 12F).

Pentyl benzoate (1b)

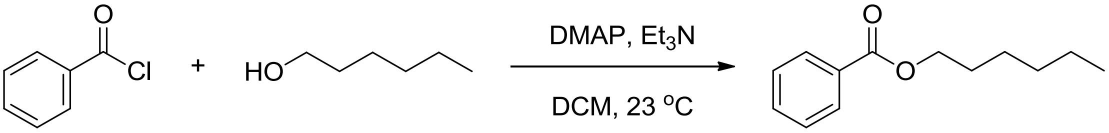


1b, 90% yield

To a solution of pentan-1-ol (0.880 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (24.4 mg, 2.00 mmol, 0.200 equiv) and Et_3N (2.00 mL, 15.0 mmol, 1.50 equiv) in CH_2Cl_2 (50.0 mL) at 0 °C was added benzoyl chloride (1.68 g, 12.0 mmol, 1.20 equiv). The reaction mixture was warmed to 23 °C and stirred for 6 hr before quenched with H_2O (10.0 mL) and extracted 2 times with CH_2Cl_2 (20.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 1.73 g pentyl benzoate (**1b**)[2] as a colourless liquid (90% yield).

R_f = 0.50 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.92 – 1.68 (m, 2H), 1.51 – 1.31 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.9, 130.7, 129.7, 128.5, 65.3, 28.6, 28.3, 22.5, 14.1.

Hexyl benzoate (1c)

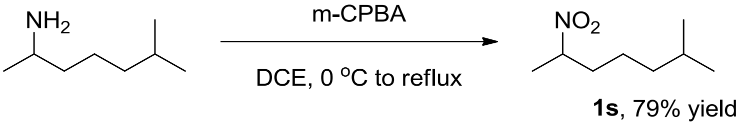


1c, 86% yield

To a solution of hexan-1-ol (1.02 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (24.4 mg, 2.00 mmol, 0.200 equiv) and Et_3N (2.00 mL, 15.0 mmol, 1.50 equiv) in CH_2Cl_2 (50.0 mL) at 0 °C was added benzoyl chloride (1.68 g, 12.0 mmol, 1.20 equiv). The reaction mixture was warmed to 23 °C and stirred for 6 hr before quenched with H_2O (10.0 mL) and extracted 2 times with CH_2Cl_2 (20.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 1.77 g hexyl benzoate (**1c**)[3] as a colourless liquid (86% yield).

R_f = 0.50 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.52 – 1.40 (m, 2H), 1.39 – 1.28 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.9, 130.7, 129.7, 128.5, 65.3, 31.6, 28.8, 25.9, 22.7, 14.2.

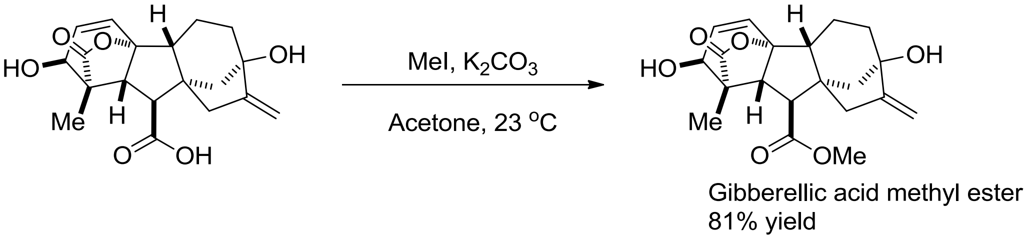
2-Methyl-6-nitroheptane (1s)



To a solution of 6-methylheptan-2-amine (1.29 g, 10.0 mmol, 1.00 equiv) in DCE (100 mL) was added m-CPBA (3-chloroperbenzoic acid, 6.00 g, 30.0 mmol, 3.00 equiv) at 0 °C. The reaction mixture was stirred and refluxed for 3 hr before cooling down to 23 °C and washed 3 times with aqueous NaOH (10%, 10.0 mL). The organic layer was washed with saturated brine then dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v), to afford 1.26 g 2-methyl-6-nitroheptane (**1s**) as a yellow liquid (79% yield).

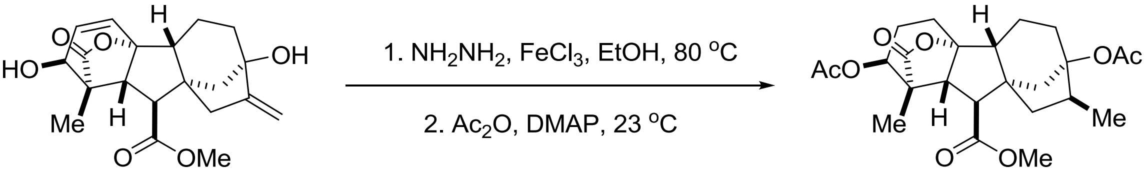
R_f = 0.6 (hexanes/EtOAc 1:20 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 – 4.42 (m, 1H), 2.06 – 1.93 (m, 1H), 1.78 – 1.61 (m, 1H), 1.60 – 1.47 (m, 4H), 1.41 – 1.27 (m, 2H), 1.26 – 1.14 (m, 2H), 0.88 (d, J = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.7, 38.3, 35.5, 27.8, 23.6, 22.6, 22.5, 19.4. Spectrometry: MS-EI (m/z): calcd for $C_8H_{16}NO_2$ [M - H] 158.1, found 158.1.

16*β*-Tetrahydrogibberellate diacetate methyl ester (1x)



To a solution of gibberellic acid (1.04 g, 3.00 mmol, 1.00 equiv) and K_2CO_3 (0.800 g, 6.00 mmol, 2.00 equiv) in acetone (30.0 mL) was added MeI (0.380 mL, 6.00 mmol, 2.00 eqiuiv). The reaction was stirred at 23 °C for 10 hr before quenched with H_2O (5.0 mL), then concentrated *in vacuo* and extracted 3 times with CH_2Cl_2 (10.0 mL). The combined organic layer was washed with saturated brine then dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 1:1 (v/v), to afford 0.875 g gibberellic acid methyl ester[5] as a white solid (81% yield).

R_f = 0.2 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (d, J = 9.3 Hz, 1H), 5.91 (dd, J = 9.3, 3.7 Hz, 1H), 5.28 (s, 1H), 4.97 (s, 1H), 4.16 (s, 1H), 3.73 (d, J = 8.3 Hz, 3H), 3.21 (d, J = 10.8 Hz, 1H), 2.79 (d, J = 10.7 Hz, 1H), 2.28 – 1.53 (m, 11H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 172.7, 157.0, 133.1, 132.5, 107.8, 90.5, 78.3, 70.0, 53.6, 52.9, 52.4, 51.2, 50.7, 50.6, 44.9, 43.2, 38.4, 17.2, 14.6.

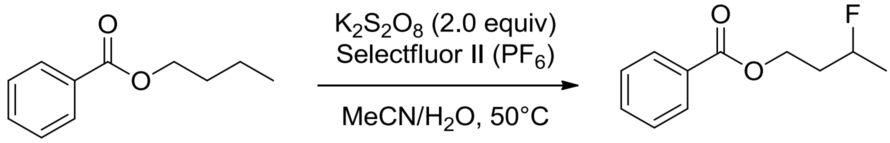


1x, 71% yield

To a solution of gibberellic acid methyl ester (720 mg, 2.00 mmol, 1.00 equiv) and $FeCl_3$ (16.2 mg, 0.100 mmol, 0.0500 equiv) in ethanol (30.0 mL) was added aqueous hydrazine (5.00 mL). The reaction mixture was stirred at 80 °C for 6 hr before quenched with H_2O (20.0 mL) at 23 °C, then concentrated *in vacuo* and extracted 3 times with CH_2Cl_2 (10.0 mL). The combined organic layer was washed with saturated brine then dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford the crude product.[6] This crude product was used in next step without further purification. To the crude product dissolved in CH_2Cl_2 (20.0 mL) were added DMAP (244 mg, 2.00 mmol, 1.00 equiv) and acetic anhydride (5.00 ml, 45.0 mmol, 22.5 equiv). The reaction mixture was stirred at 23 °C for 10 hr before quenched with H_2O (5.0 mL), then extracted 3 times with CH_2Cl_2 (10.0 mL). The combined organic layer was washed with saturated brine then dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v), to afford 0.636 g 16*β*-tetrahydrogibberellate diacetate methyl ester (**1x**)[5] as a white solid (71% yield for two steps).

R_f= 0.30 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H), 3.73 (s, 3H), 3.14 (d, *J* = 10.7 Hz, 1H), 2.63 (t, *J* = 8.5 Hz, 1H), 2.58 (dd, *J* = 10.9, 1.9 Hz, 1H), 2.05 – 1.68 (m, 13H), 2.13 (s, 3H), 1.98 (s, 3H), 1.57 (s, 3H), 1.04 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 173.1, 170.4, 170.4, 93.1, 85.7, 71.5, 56.5, 53.4, 52.6, 52.3, 52.2, 50. 9, 42.8, 42.3, 40.8, 27.7, 26.0, 25.5, 22.1, 21.3, 17.0, 15.7, 14.6.

3-Fluorobutyl benzoate (2a)



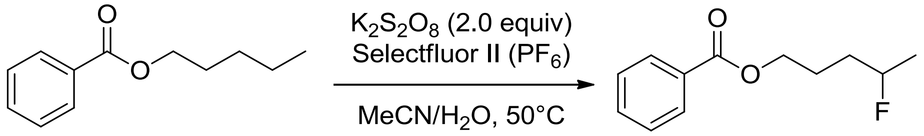
1a

2a, 65% yield

To potassium persulfate (54.0 mg, 0.200 mmol, 2.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.4 mL) were added CH_3CN (0.6 mL) and butyl benzoate (**1a**) (17.8 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/toluene 20:1 (v/v), to afford 12.8 mg 3-fluorobutyl benzoate (**2a**) as a colorless liquid (65% yield).

R$_f$ = 0.30 (hexanes/ Toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 8.04 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 4.90 (dm, *J* = 47.9 Hz, 1H), *δ* 4.50 – 4.41 (m, 2H), 2.21 – 1.86 (m, 2H), 1.40 (dd, *J* = 27.3, 13.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.6, 133.1, 130.3, 129.7, 128.5, 88.0 (d, *J* = 165.5 Hz), 61.2, 36.2 (d, *J* = 21.0 Hz), 21.2 (d, *J* = 22.5 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) *δ* -175.27 – -175.83 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{13}FO_2Na$ [M +Na], 219.0797. Found, 219.0787.

4-Fluoropentyl benzoate (2b)

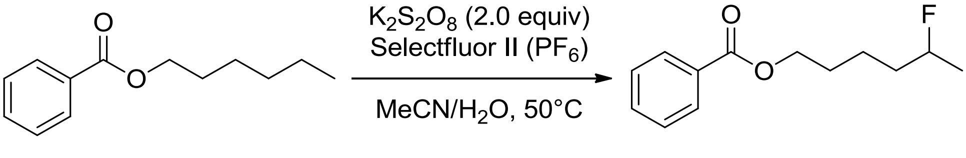


1b **2b**, 71% yield

To potassium persulfate (54.0 mg, 0.200 mmol, 2.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in added H_2O (0.4 mL) were added CH_3CN (0.6 mL) and pentyl benzoate (**1b**) (19.2 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/toluene 4:1 (v/v), to afford 15.0 mg 4-fluoropentyl benzoate (**2b**) as a colorless liquid (71% yield).

R$_f$ = 0.30 (hexanes/toluene 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.74 (dm, *J* = 53.8 Hz, 1H), 4.40 – 4.33 (m, 2H), 2.02 – 1.50 (m, 4H), 1.36 (dd, *J* = 23.9, 6.1 Hz, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 166.6, 132.9, 130.3, 129.6, 128.4, 90.4 (d, *J* = 165.0 Hz), 64.6, 33.5 (d, *J* = 21.2 Hz), 24.6 (d, *J* = 4.6 Hz), 21.0 (d, *J* = 22.7 Hz). ^{19}F NMR (376 MHz, CDCl$_3$) *δ* -173.05 – -173.81 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{15}FO_2Na$ [M +Na],233.0954. Found, 233.0944.

5-Fluorohexyl benzoate (2c)

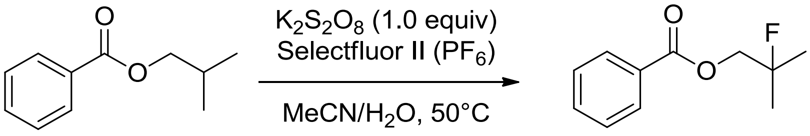


1c **2c**, 46% ^{19}FNMR yield

To potassium persulfate (54.0 mg, 0.200 mmol, 2.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.4 mL) were added CH_3CN (0.6 mL) and hexyl benzoate (**1c**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 5-fluorohexyl benzoate (**2c**) was determined by comparing the integration of the ^{19}F NMR resonance of 5-fluorohexyl benzoate (**2c**)[7] (-172.92 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm) (46% ^{19}F NMR yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.51 – -173.21 (m, 1F).

2-Fluoro-2-methylpropyl benzoate (2d)

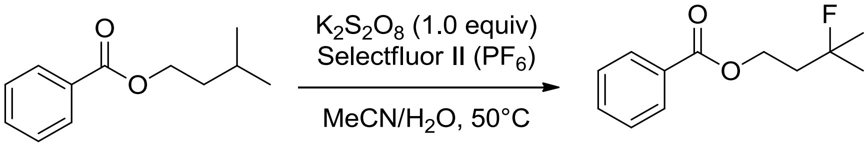


1d **2d**, 98% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and isobutyl benzoate (**1d**) (17.8 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 19.2 mg 2-fluoro-2-methylpropyl benzoate (**2d**) as a colorless liquid (98% yield).

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.33 (d, J = 12.0 Hz, 2H), 1.48 (d, J = 21.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 133.3, 130.0, 129.8, 128.5, 93.5 (d, J = 169.9 Hz), 69.6 (d, J = 25.1 Hz), 24.0 (d, J = 24.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.43 – -145.96 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{13}FO_2Na$ [M + Na], 219.0797, 219.0794.

3-Fluoro-3-methylbutyl benzoate (2e)

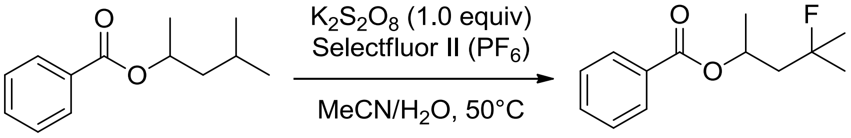


1e **2e**, 82% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and isopentyl benzoate (**1e**) (19.2 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 17.3 mg 3-fluoro-3-methylbutyl benzoate (**2e**) as a colorless liquid (82% yield).

R_f = 0.50 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 4.48 (t, J = 6.8 Hz, 2H), 2.13 (dt, J = 19.5, 6.8 Hz, 2H), 1.45 (d, J = 21.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 133.0, 130.2, 129.6, 128.4, 94.3 (d, J = 166.1 Hz), 61.0 (d, J = 6.1 Hz), 39.9 (d, J = 23.3 Hz), 27.1 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.83 – -138.37 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{15}FO_2Na$ [M + Na], 233.0954. Found, 233.0950.

4-Fluoro-4-methylpentan-2-yl benzoate (2f)



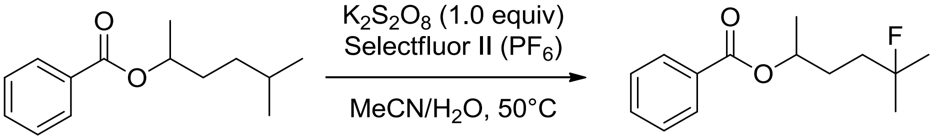
1f

2f, 65% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 4-methylpentan-2-yl benzoate (**1f**) (20.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 14.6 mg 4-fluoro-4-methylpentan-2-yl benzoate (**2f**) as a colorless liquid (65% yield).

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.46 – 5.35 (m, 1H), 2.26 – 2.07 (m, 1H), 1.94 (td, J = 15.7, 4.2 Hz, 1H), 1.41 (d, J = 21.5 Hz, 6H), 1.40 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 133.0, 130.8, 129.7, 128.5, 94.5 (d, J = 166.0 Hz), 68.6 (d, J = 4.4 Hz), 47.1 (d, J = 22.7 Hz), 28.1 (d, J = 24.6 Hz), 26.5 (d, J = 24.8 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.39 – -135.90 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{17}FO_2Na$ [M + Na], 247.1110. Found, 247.1095.

5-Fluoro-5-methylhexan-2-yl benzoate (2g)

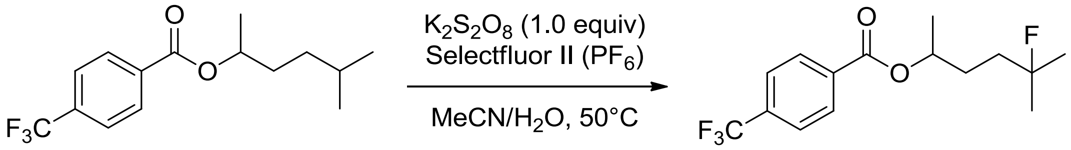


1g **2g**, 71% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 5-methylhexan-2-yl benzoate (**1g**) (22.0 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 16.9 mg 5-fluoro-5-methylhexan-2-yl benzoate (**2g**) as a colorless liquid (71% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 5.22 – 5.11 (m, 1H), 1.93 – 1.58 (m, 4H), 1.37 (d, J = 6.4 Hz, 3H), 1.36 (d, J = 21.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 132.9, 130.8, 129.6, 128.4, 95.3 (d, J = 165.6 Hz), 71.7, 37.2 (d, J = 23.2 Hz), 30.5 (d, J = 4.9 Hz), 26.9 (d, J = 24.8 Hz), 26.7 (d, J = 24.8 Hz), 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.75 – -139.21 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{20}FO_2$ [M+H], 239.1447. Found, 239.1442.

4-Fluoro-1,4-dimethylpentyl 4-(trifluoromethyl)benzoate (2h)

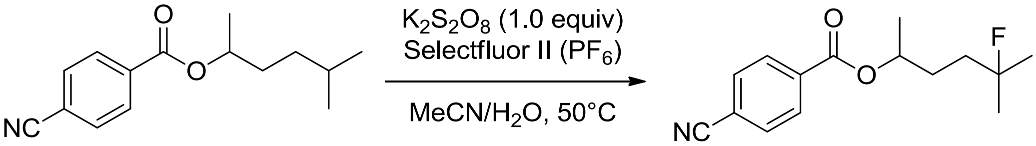


1h **2h**, 87% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl 4-(trifluoromethyl)benzoate (**1h**) (28.8 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 26.6 mg 4-fluoro-1,4-dimethylpentyl 4-(trifluoromethyl)benzoate (**2h**) as a colorless liquid (87% yield).

R$_f$ = 0.40 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.15 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 5.28 – 5.07 (m, 1H), 2.05 – 1.55 (m, 4H), 1.39 (s, 3H), 1.38 (d, *J* = 3.6 Hz, 3H), 1.33 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 134.3 (q, *J* = 32.6 Hz), 133.9, 129.9, 125.4 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 272.7 Hz), 95.1 (d, *J* = 165.9 Hz), 72.4, 37.0 (d, *J* = 23.3 Hz), 30.3 (d, *J* = 5.0 Hz), 26.7 (d, *J* = 24.8 Hz), 26.6 (d, *J* = 24.7 Hz), 20.0. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -63.10 (s, 3F), -138.98 – -139.49 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{18}F_4O_2Na$ [M + Na], 329.1141. Found, 329.1140.

4-Fluoro-1,4-dimethylpentyl 4-cyanobenzoate (2i)

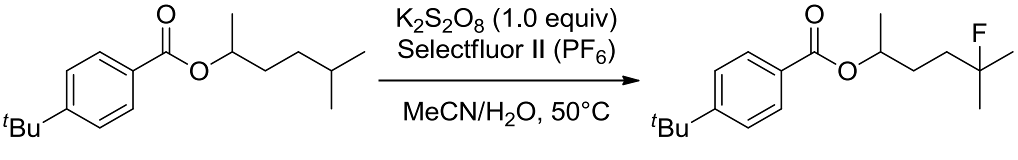


1i **2i**, 78% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl 4-cyanobenzoate (**1i**) (24.5 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v), to afford 20.5 mg 4-fluoro-1,4-dimethylpentyl 4-cyanobenzoate (**2i**) as a colorless liquid (78% yield).

R$_f$ = 0.30 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.13 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 5.18 (dd, *J* = 11.9, 5.6 Hz, 1H), 1.99 – 1.58 (m, 4H), 1.43 – 1.28 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 134.6, 132.4, 130.2, 118.2, 116.4, 95.2 (d, *J* = 165.6 Hz), 72.9, 37.1 (d, *J* = 23.2 Hz), 30.4 (d, *J* = 4.7 Hz), 26.9 (d, *J* = 25.0 Hz), 26.7 (d, *J* = 24.7 Hz), 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -139.02 – -139.62 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{22}FN_2O_2Na$ [M +NH_4],281.1665. Found, 281.1658.

4-Fluoro-1,4-dimethylpentyl 4-(*tert*-butyl) benzoate (2j)

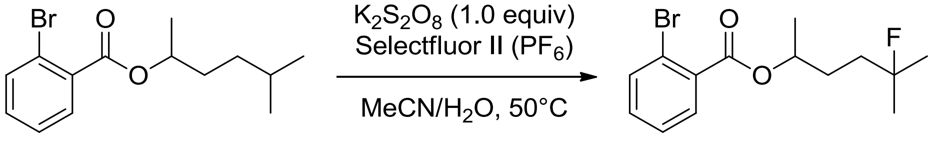


1j **2j**, 82% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl 4-(*tert*-butyl)benzoate (**1j**) (27.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 24.1 mg 4-fluoro-1,4-dimethylpentyl 4-(*tert*-butyl)benzoate (**2j**) as a colorless liquid (82% yield).

R_f = 0.40 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 5.20 – 5.10 (m, 1H), 1.94 – 1.60 (m, 4H), 1.43 – 1.29 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 156.6, 129.5, 128.0, 125.5, 95.4 (d, J = 165.5 Hz), 71.4, 37.2 (d, J = 23.2 Hz), 35.2, 31.3, 30.6 (d, J = 4.8 Hz), 26.9 (d, J = 22.9 Hz), 26.7 (d, J = 22.8 Hz), 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.66 – -139.53 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{28}FO_2$ [M +H], 295.2073. Found, 295.2066.

4-Fluoro-1,4-dimethylpentyl 2-bromobenzoate (2k)



1k

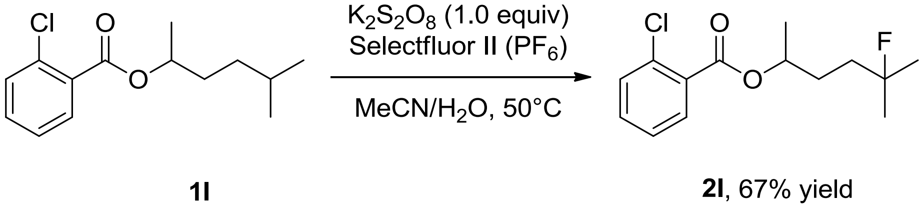
2k, 91% yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl 2-bromobenzoate (**1k**) (29.8 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 28.7 mg 4-fluoro-1,4-dimethylpentyl 2-bromobenzoate (**2k**) as a colorless liquid (91% yield).

R_f = 0.40 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.74 (dd, J = 7.5, 1.9 Hz, 1H), 7.65 (dd, J = 7.8, 1.1 Hz, 1H), 7.36 (dt, J = 7.6, 3.8 Hz, 1H), 7.32 (td, J = 7.6, 1.9 Hz, 1H), 5.25 – 5.14 (m, 1H), 1.91 – 1.64 (m, 4H), 1.38 (s, 3H), 1.40 (d, J = 3.7 Hz, 3H), 1.33 (d, J = 3.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 134.4, 133.1, 132.5, 131.2, 127.3, 121.5, 95.3 (d, J = 165.4 Hz), 72.8, 37.2 (d, J = 23.2 Hz), 30.4 (d, J = 5.0 Hz), 26.9 (d, J = 22.5 Hz), 26.7 (d, J = 22.5 Hz), 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.77

– -139.21 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}BrFO_2Na$ [M + Na], 339.0372. Found, 339.0366.

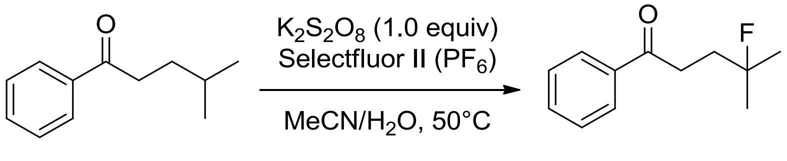
4-Fluoro-1,4-dimethylpentyl 2-chlorobenzoate (2l)



To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl 2-chlorobenzoate (**1l**) (25.4 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 18.2 mg 4-fluoro-1,4-dimethylpentyl 2-chlorobenzoate (**2l**) as a colorless liquid (67% yield).

R_f = 0.30 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.5, 1.8 Hz, 1H), 7.65 (dd, J = 7.8, 1.1 Hz, 1H), 7.37 (td, J = 7.5, 1.3 Hz, 1H), 7.32 (td, J = 7.6, 1.9 Hz, 1H), 5.27 – 5.13 (m, 1H), 1.93 – 1.62 (m, 4H), 1.38 (s, 3H), 1.36 (dd, J = 24.8, 3.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 134.4, 133.1, 132.5, 131.2, 127.3, 121.5, 95.3 (d, J = 165.6 Hz), 72.8, 37.2 (d, J = 23.1 Hz), 30.4 (d, J = 5.0 Hz), 26.9 (d, J = 22.7 Hz), 26.7 (d, J = 23.4 Hz), 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.68 – -139.33 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}ClFO_2Na$ [M + Na],295.0877. Found, 295.0868.

4-Fluoro-4-methyl-1-phenyl-1-pentanone (2m)

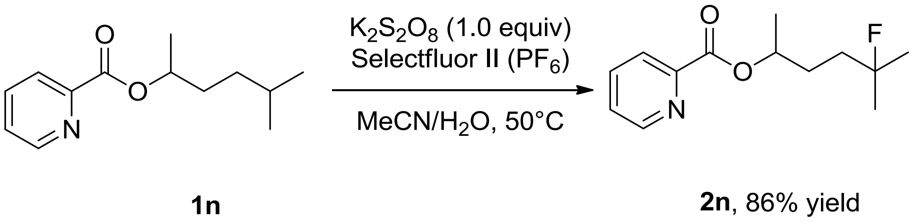


To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 4-methyl-1-phenyl-1-pentanone (**1m**) (17.6 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with

$NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 13.2 mg 4-fluoro-4-methyl-1-phenyl-1-pentanone (**2m**) as a colorless liquid (68% yield).

R_f = 0.40 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 2H), 7.67 – 7.39 (m, 3H), 3.13 (t, J = 7.6 Hz, 2H), 2.08 (dt, J = 21.0, 7.7 Hz, 2H), 1.45 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 137.0, 133.2, 128.8, 128.2, 95.2 (d, J = 166.2 Hz), 35.2 (d, J = 22.6 Hz), 33.2 (d, J = 3.5 Hz), 26.9 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.90 (dp, J = 42.6, 21.3 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{15}FONa$ [M + Na],217.1005. Found, 217.1003.

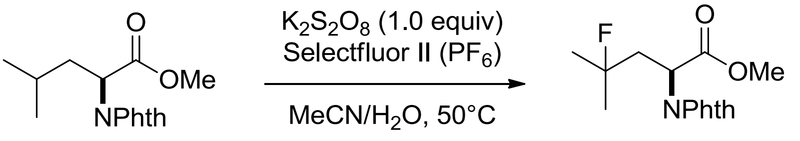
4-Fluoro-1,4-dimethylpentyl picolinate (2n)



To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1,4-dimethylpentyl picolinate (**1n**) (22.1 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v), to afford 20.6 mg 4-fluoro-1,4-dimethylpentyl picolinate (**2n**) as a colorless liquid (86% yield).

R_f = 0.20 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 4.0 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.84 (td, J = 7.7, 1.7 Hz, 1H), 7.47 (ddd, J = 7.6, 4.7, 1.1 Hz, 1H), 5.25 (dq, J = 12.4, 6.3 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.85 – 1.61 (m, 3H), 1.42 (d, J = 6.3 Hz, 3H), 1.35 (dd, J = 21.4, 2.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 150.1, 148.6, 137.1, 126.8, 125.2, 95.3 (d, J = 165.5 Hz), 72.9, 37.3 (d, J = 23.2 Hz), 30.5 (d, J = 4.9 Hz), 26.9 (d, J = 24.8 Hz), 26.6 (d, J = 24.7 Hz), 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.58 – -138.98 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{19}FNO_2$ [M +H],240.1400. Found, 240.1396.

N-phthaloyl-4-fluoro-*L*-leucine methyl ester (2o)



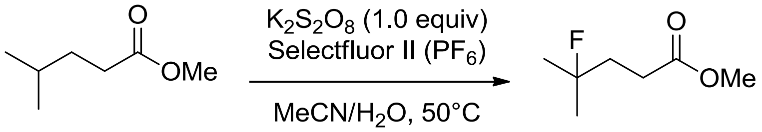
1o

2o, 71% yield

To *N*-phthaloyl-*L*-leucine methyl ester (**1o**) (27.5 mg, 0.100 mmol, 1.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) was added H_2O (0.2 mL) then CH_3CN (0.3 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v), to afford 20.8 mg *N*-phthaloyl-4-fluoro-*L*-leucine methyl ester (**2o**)[8] as a colourless liquid (71% yield).

R_f = 0.30 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 5.4, 3.1 Hz, 2H), 7.73 (dd, J = 5.5, 3.0 Hz, 2H), 5.15 (dd, J = 11.0, 2.7 Hz, 1H), 3.74 (s, 3H), 2.86 – 2.70 (m, 1H), 2.49 (ddd, J = 29.0, 15.5, 2.7 Hz, 1H), 1.40 (dd, J = 33.5, 21.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 167.7, 134.3, 132.1, 123.7, 94.7 (d, J = 167.1 Hz), 53.2, 48.4, 38.7 (d, J = 21.0 Hz), 28.1 (d, J = 24.4 Hz), 25.6 (d, J = 24.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.99 – -143.43 (m, 1F).

Methyl 4-fluoro-4-methylpentanoate (2p)



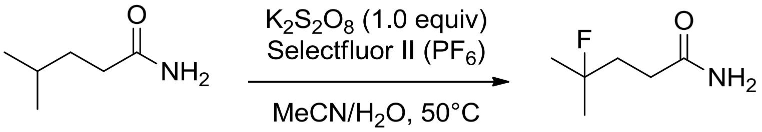
1p

2p, 65% ^{19}FNMR yield

To potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and methyl 4-methylpentanoate (**1p**) (13.1 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of methyl 4-fluoro-4-methylpentanoate (**2p**) was determined by comparing the integration of the ^{19}F NMR resonance of 4-fluoro-4-methylpentanoate (**2p**)[9] (-136.81 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm). (65% ^{19}F NMR yield)

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.61 – -137.01 (m, 1F).

4-Fluoro-4-methylpentanamide (2q)

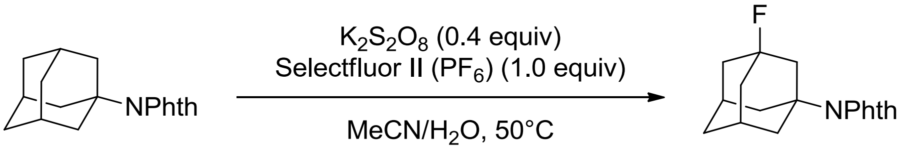


1q **2q**, 61% yield

To 4-methylpentanamide (**1q**) (11.5 mg, 0.100 mmol, 1.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) was added H_2O (0.2 mL) then CH_3CN (0.3 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 2:1 (v/v), to afford 8.10 mg 4-fluoro-4-methylpentanamide (**2q**) as a white solid (61% yield).

R_f = 0.30 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.44 (br, 2H), 2.41 – 2.30 (m, 2H), 2.03 – 1.91 (m, 2H), 1.36 (d, *J* = 21.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 175.1, 95.3 (d, *J* = 166.5 Hz), 36.3 (d, *J* = 23.2 Hz), 30.2 (d, *J* = 4.0 Hz), 26.6 (d, *J* = 24.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.02 (dt, *J* = 42.5, 21.1 Hz). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_6H_{12}FNONa$ [M + Na],156.0801. Found, 156.0796.

3-Fluoroadamantan-1-ylisoindoline-1,3-dione (2r)



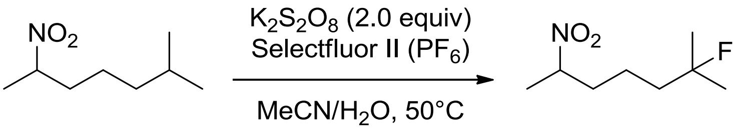
1r (5.0 equiv) **2r**, 71%

To 2-(adamantan-1-yl)isoindoline-1,3-dione (**1r**) (351 mg, 1.25 mmol, 5.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 0.40 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 1.00 equiv) was added H_2O (0.4 mL) then CH_3CN (0.6 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 40:1 (v/v), to afford 53.10 mg 3-fluoroadamantan-1-ylisoindoline-1,3-dione (**2r**) as a white solid (71% yield).

R_f = 0.30 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ

7.77 (d, *J* = 2.9 Hz, 2H), 7.69 (d, *J* = 2.8 Hz, 2H), 2.69 (d, *J* = 6.0 Hz, 2H), 2.56 – 2.32 (m, 6H), 1.94 (d, *J* = 25.8 Hz, 4H), 1.57 (d, *J* = 11.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 134.0, 131.9, 122.9, 92.5 (d, *J* = 184.2 Hz), 62.1 (d, *J* = 12.4 Hz), 45.4 (d, *J* = 20.4 Hz), 41.7 (d, *J* = 17.6 Hz), 38.9, 34.6, 31.3 (d, *J* = 10.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.67 – -130.83 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{19}FNO_2$ [M + H],300.1394. Found, 300.1393.

2-Fluoro-2-methyl-6-nitroheptane (2s)

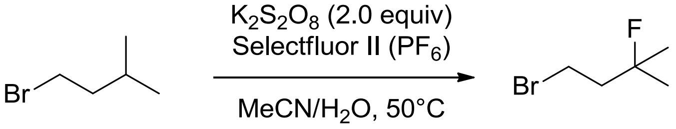


1s **2s**, 63% yield

To potassium persulfate (56.0 mg, 0.200 mmol, 2.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 2-methyl-6-nitroheptane (**1s**) (15.9 mg, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford the 11.2 mg 2-fluoro-2-methyl-6-nitroheptane (**2s**) as a colorless liquid (63% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.63 – 4.53 (m, 1H), 2.03 (dt, *J* = 15.5, 8.3 Hz, 1H), 1.85 – 1.38 (m, 5H), 1.54 (d, *J* = 6.7 Hz, 3H), 1.33 (d, *J* = 21.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 95.4 (d, *J* = 165.5 Hz), 83.5, 40.6 (d, *J* = 23.3 Hz), 35.4, 26.7 (d, *J* = 24.8 Hz), 20.4 (d, *J* = 4.7 Hz), 19.4. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -138.43 – -138.84 (m, 1F). Mass Spectrometry: MS-EI (m/z): calcd for $C_8H_{16}F$ [M – NO_2] 131.1, found 131.1.

1-Bromo-3-fluoro-3-methylbutane (2t)

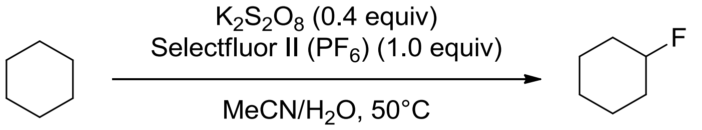


1t **2t**, 71% ^{19}FNMR yield

To potassium persulfate (54.0 mg, 0.200 mmol, 2.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and 1-bromo-3-methylbutane (**1t**) (12 μL, 0.100 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of 1-bromo-3-fluoro-3-methylbutane (**2t**) was determined by comparing the integration of the ^{19}F NMR resonance of 1-bromo-3-fluoro-3-methylbutane (**2t**) (-140.12 ppm) with that of 1-fluoro-3-nitrobenzene (-109.00 ppm) (71% ^{19}F NMR yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.92 – -140.31 (m, 1F). Mass Spectrometry: MS-EI (m/z): calcd for $C_5H_{10}BrF$ [M] 168.0, found 168.0.

Fluorocyclohexane (2u)



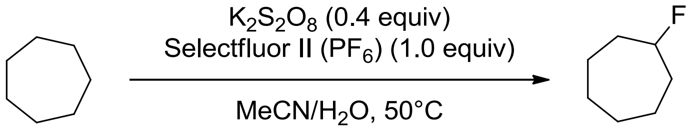
1u (5.0 equiv)

2u, 63% ^{1}HNMR yield

To potassium persulfate (27.0 mg, 0.100 mmol, 0.400 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 1.00 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and cyclohexane (**1u**) (135 μL, 1.25 mmol, 5.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) and CD_3CN (4.0 mL) was added to the reaction mixture. The yield of fluorocyclohexane (**2u**) was determined by comparing the integration of the ^{1}H NMR resonance of fluorocyclohexane (**2u**)[10] with that of 1-fluoro-3-nitrobenzene (63% ^{1}H NMR yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.76 – -171.34 (br, 1F).

Fluorocyclohexane (2v)



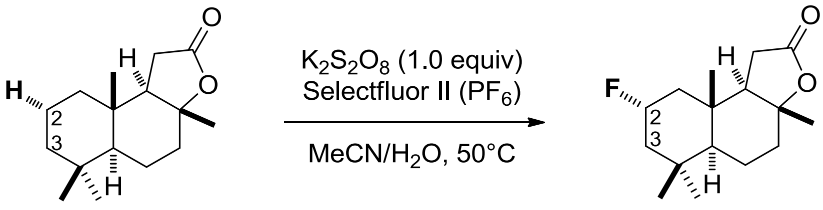
1v (5.0 equiv)

2v, 63% ^{19}FNMR yield

To potassium persulfate (27.0 mg, 0.100 mmol, 0.400 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 1.00 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL) and cycloheptane (**1v**) (151 μL, 1.250 mmol, 5.00 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, 1-fluoro-3-nitrobenzene (6.0 μL, 0.056 mmol) was added to the reaction mixture. The yield of fluorocycloheptane (**2v**) was determined by comparing the integration of the ^{19}F NMR resonance of fluorocycloheptane (**2v**) (-161.30 ppm)[11] with that of 1-fluoro-3-nitrobenzene (-109.00 ppm) (63% ^{19}F NMR yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -161.51 – -162.08 (m, 1F).

2*α*-Fluorosclareolide (2w)



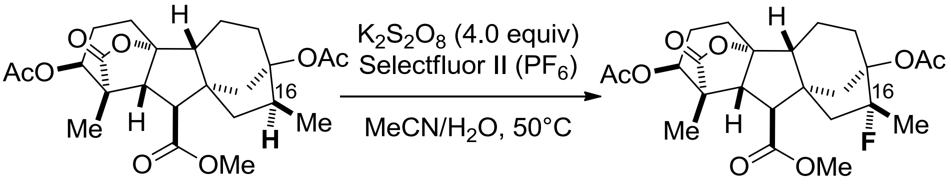
1w

2w, 69% yield

To sclareolide **(1w)** (25.0 mg, 0.100 mmol, 1.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) was added H_2O (0.2 mL) then CH_3CN (0.3 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 10:1 (v/v), to afford 18.6 mg 2*α*-fluorosclareolide (**2w**)[12] as a white solid (69% yield).

R_f = 0.20 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (dddd, *J* = 48.0, 16.1, 11.4, 4.8 Hz, 1H), 2.46 (dd, *J* = 16.1, 14.8 Hz, 1H), 2.28 (dd, *J* = 16.1, 6.5 Hz, 1H), 2.19 – 1.88 (m, 6H), 1.71 (td, *J* = 12.5, 4.3 Hz, 1H), 1.45 – 1.35 (m, 3H), 1.34 (s, 3H), 1.01 (d, *J* = 3.5 Hz, 3H), 0.97 (d, *J* = 5.9 Hz, 3H), 0.89 (d, *J* = 9.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 88.6, 86.5 (d, *J* = 96.5 Hz), 58.9, 56.2 (d, *J* = 1.7 Hz), 48.0 (d, *J* = 15.9 Hz), 45.4 (d, *J* = 17.4 Hz), 38.5, 37.6 (d, *J* = 15.5 Hz), 35.1 (d, *J* = 12.2 Hz), 33.4, 31.1, 29.8, 28.8, 21.8 (d, *J* = 18.0 Hz), 20.3, 16.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.87 (dm, *J* = 48.6 Hz, 1F).

16*β*-Fluorotetrahydrogibberellate diacetate methyl ester (2x)



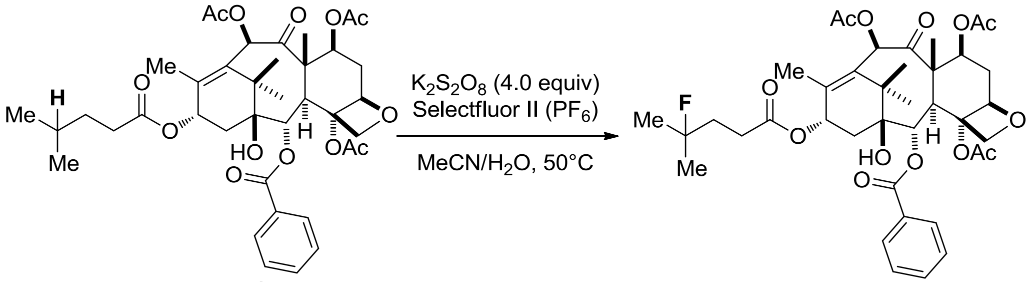
1x

2x, 42% yield

To 16*β*-tetrahydrogibberellate diacetate methyl ester (**1x**) (44.8 mg, 0.100 mmol, 1.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 2.50 equiv) was added CH_3CN (0.3 mL) and H_2O (0.2 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1 mL), then quenched with $NaHCO_3$ (16.8 mg, 0.200 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 3:1 (v/v), to afford 19.6 mg 16*β*-Fluorotetrahydrogibberellate diacetate methyl ester (**2x**) as a white solid (42% yield).

R_f = 0.30 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (s, 1H), 3.74 (s, 3H), 3.13 (d, *J* = 10.4 Hz, 1H), 2.70 (d, *J* = 11.4 Hz, 1H), 2.66 (d, *J* = 10.5 Hz, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 2.17 – 1.56 (m, 12H), 1.49 (d, *J* = 22.5 Hz, 3H), 1.05 (d, *J* = 12.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 173.1, 170.3, 170.3, 102.2 (d, *J* = 182.3 Hz), 92.8, 84.3 (d, *J* = 17.1 Hz), 71.5, 56.7, 53.4, 53.0, 52.6, 52.4, 50.2 (d, *J* = 23.3 Hz), 48.5, 37.6, 28.7, 27.4, 25.4, 21.9, 21.3, 19.4 (d, *J* = 28.6 Hz), 17.3, 14.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.03 – -136.57 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{24}H_{31}FO_8Na$ [M + Na],489.1901. Found, 489.1903.

7-*O*-Acetyl-13-*O*-(4-fluoro-4-methylpentanoyl) baccatine III (2y)

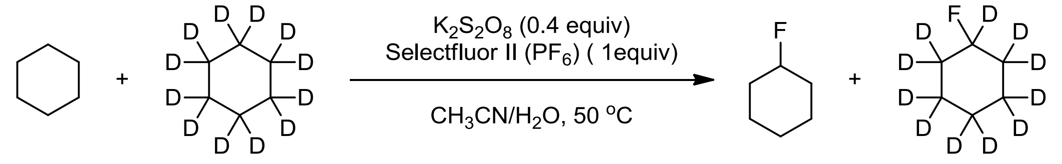


1y **2y**, 33% yield

To 7-*O*-Acetyl-13-*O*-(4-methylpentanoyl) baccatine III (**1y**) (18.0 mg, 0.025 mmol, 1.00 equiv), potassium persulfate (27.0 mg, 0.100 mmol, 4.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (27.0 mg, 0.063 mmol, 2.50 equiv) was added CH_3CN (0.3 mL) and H_2O (0.2 mL). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (2.0 mL) and H_2O (1.0 mL), then quenched with $NaHCO_3$ (4.20 mg, 0.050 mmol, 2.00 equiv) and extracted 2 times with EtOAc (5.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 4:1 (v/v), to afford 6.2 mg 7-*O*-acetyl-13-*O*-(4-fluoro-4-methylpentanoyl) baccatine III (**2y**) as a white solid (33% yield).

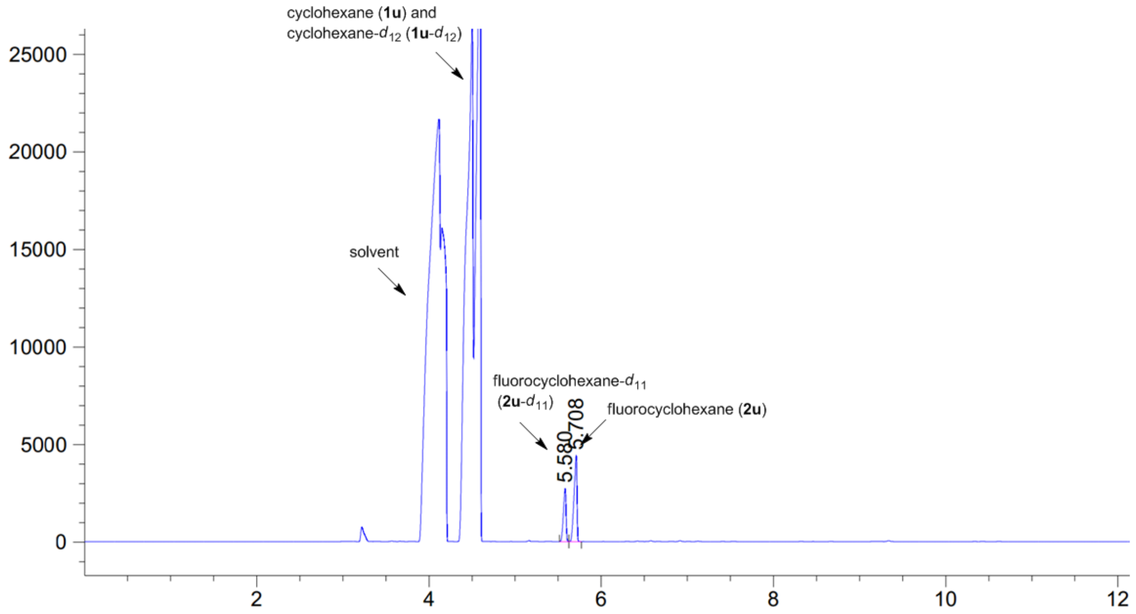
R_f = 0.30 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 6.26 (s, 1H), 6.19 (t, *J* = 8.9 Hz, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 5.59 (dd, *J* = 10.3, 7.2 Hz, 1H), 4.97 (d, *J* = 9.4 Hz, 1H), 4.33 (d, *J* = 8.6 Hz, 1H), 4.16 (d, *J* = 8.3 Hz, 1H), 3.96 (d, *J* = 6.8 Hz, 1H), 2.60 (dt, *J* = 16.0, 7.8 Hz, 2H), 2.35 (s, 3H), 2.25 (d, *J* = 8.1 Hz, 2H), 2.18 (d, *J* = 6.4 Hz, 3H), 2.04 (s, 3H), 1.96 (s, 3H), 1.90 – 1.81 (m, 1H), 1.81 (s, 3H), 1.65 (s, 1H), 1.43 (d, *J* = 3.0 Hz, 3H), 1.38 (d, *J* = 3.3 Hz, 3H), 1.25 (s, 3H), 1.22 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 173.1, 170.6, 169.8, 169.1, 167.1, 141.6, 133.9, 132.5, 130.2, 129.3, 128.8, 94.6 (d, *J* = 166.9 Hz), 84.1, 81.0, 78.9, 76.5, 75.5, 74.6, 71.6, 69.7, 56.2, 47.4, 43.3, 36.1 (d, *J* = 22.9 Hz), 35.7, 33.5, 29.3 (d, *J* = 4.3 Hz), 26.9 (d, *J* = 15.0 Hz), 26.7 (d, *J* = 14.9 Hz), 26.5, 22.6, 21.3, 20.9, 20.8, 15.0, 10.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -141.27 – -142.90 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{39}H_{49}FNaO_{13}$ [M + Na], 767.3055. Found, 767.3052.

The intermolecular kinetic isotope effect study



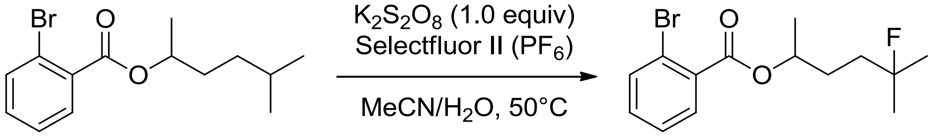
1u (10 equiv) **1u-*d*$_{12}$** (10 equiv) **2u** (1.8 :1) **2u-*d*$_{11}$**

To potassium persulfate (27.0 mg, 0.100 mmol, 0.400 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (109 mg, 0.250 mmol, 1.00 equiv) in H_2O (0.2 mL) were added CH_3CN (0.3 mL), cyclohexane (**1u**) (269 µL, 2.50 mmol, 10.0 equiv) and cyclohexane-*d*$_{12}$ (**1u-*d*$_{12}$**) (273 µL, 2.50 mmol, 10.0 equiv). The reaction mixture was stirred for 10 hr at 50 °C in a 2 mL sealed vial. The ratio of fluorocyclohexane (**2u**) and fluorocyclohexane (**2u-*d*$_{11}$**) was determined by GC to be 63.9:36.0 on Agilent 7890A GC system.



No. #	retention time [min]	type	peak width [min]	peak area [pA*s]	peak height [pA]	peak area %
1	5.580	BV	0.0339	5814.94189	2721.28735	36.04516
2	5.708	VB	0.0343	1.03174e4	4405.94775	63.95484

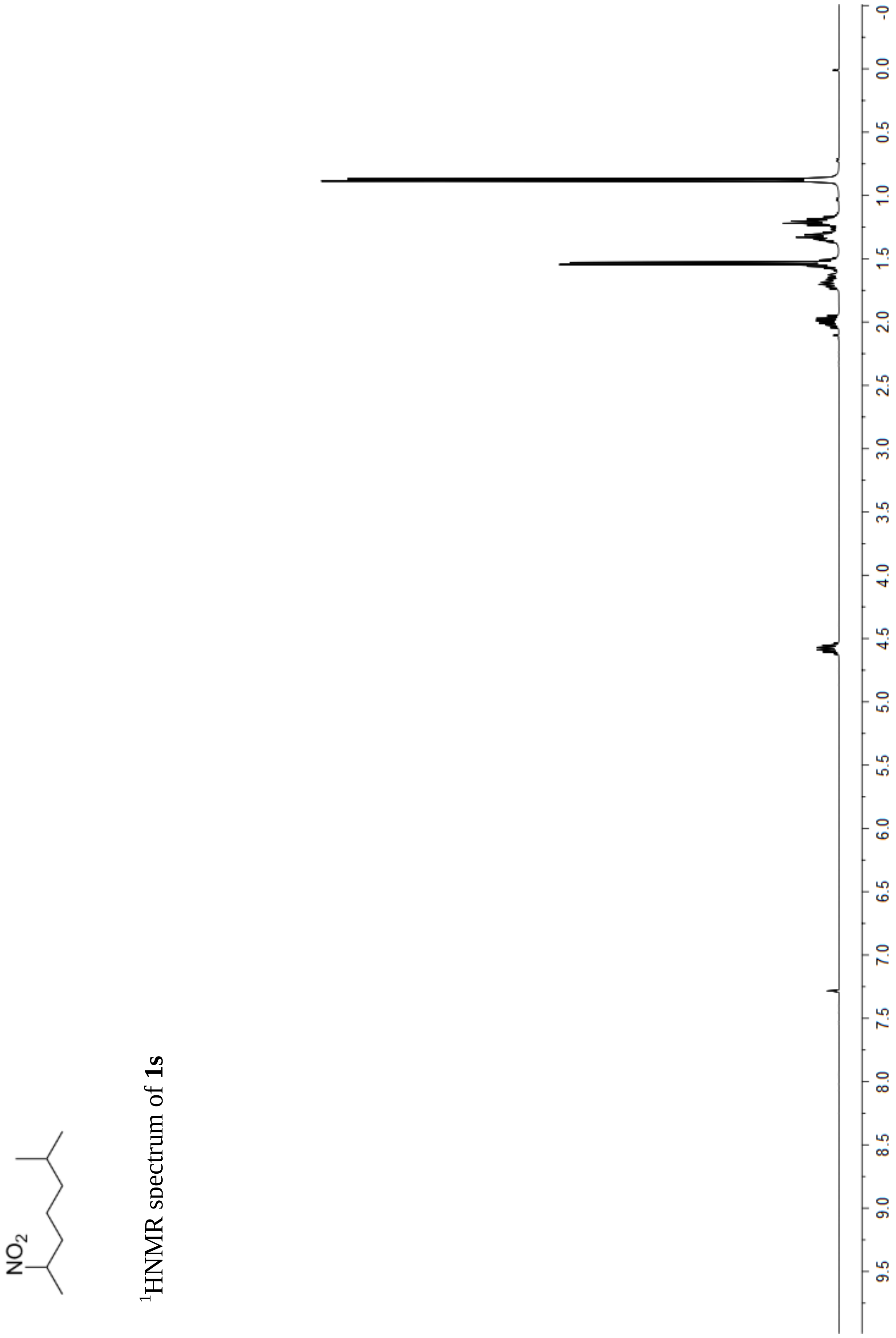
Gram-scale synthesis of 5-fluoro-1,4-dimethylpentyl 2-bromobenzoate (2k)



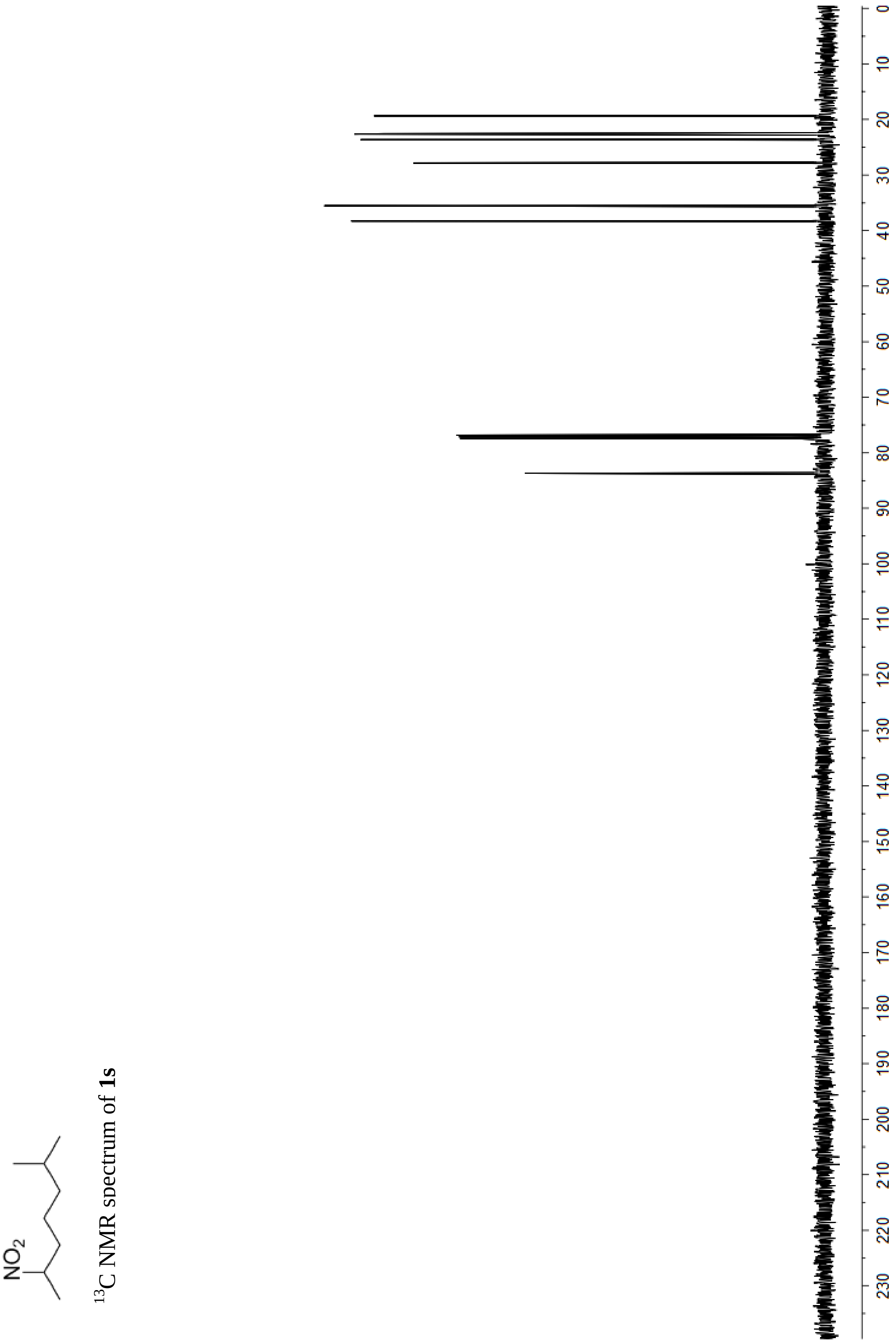
1k **2k**, 91% yield

To potassium persulfate (907 mg, 3.36 mmol, 1.00 equiv) and 4-fluoro-1-methyl-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (3.66 g, 8.40 mmol, 2.50 equiv) in a 25 mL sealed vial were added H_2O (6.7 mL), CH_3CN (10.0 mL) and 1,4-dimethylpentyl 2-bromobenzoate (**1k**) (1.00 g, 3.36 mmol, 1.00 equiv). The reaction mixture was stirred for 10 hr at 50 ^oC in a 25 mL sealed vial. After cooling to room temperature, the reaction was diluted with EtOAc (5.0 mL) and H_2O (2.0 mL), then quenched with $NaHCO_3$ (564 mg, 6.72 mmol, 2.00 equiv) and extracted 3 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 881 mg 5-fluoro-1,4-dimethylpentyl 2-bromobenzoate (**2k**) as a colorless liquid (83% yield).

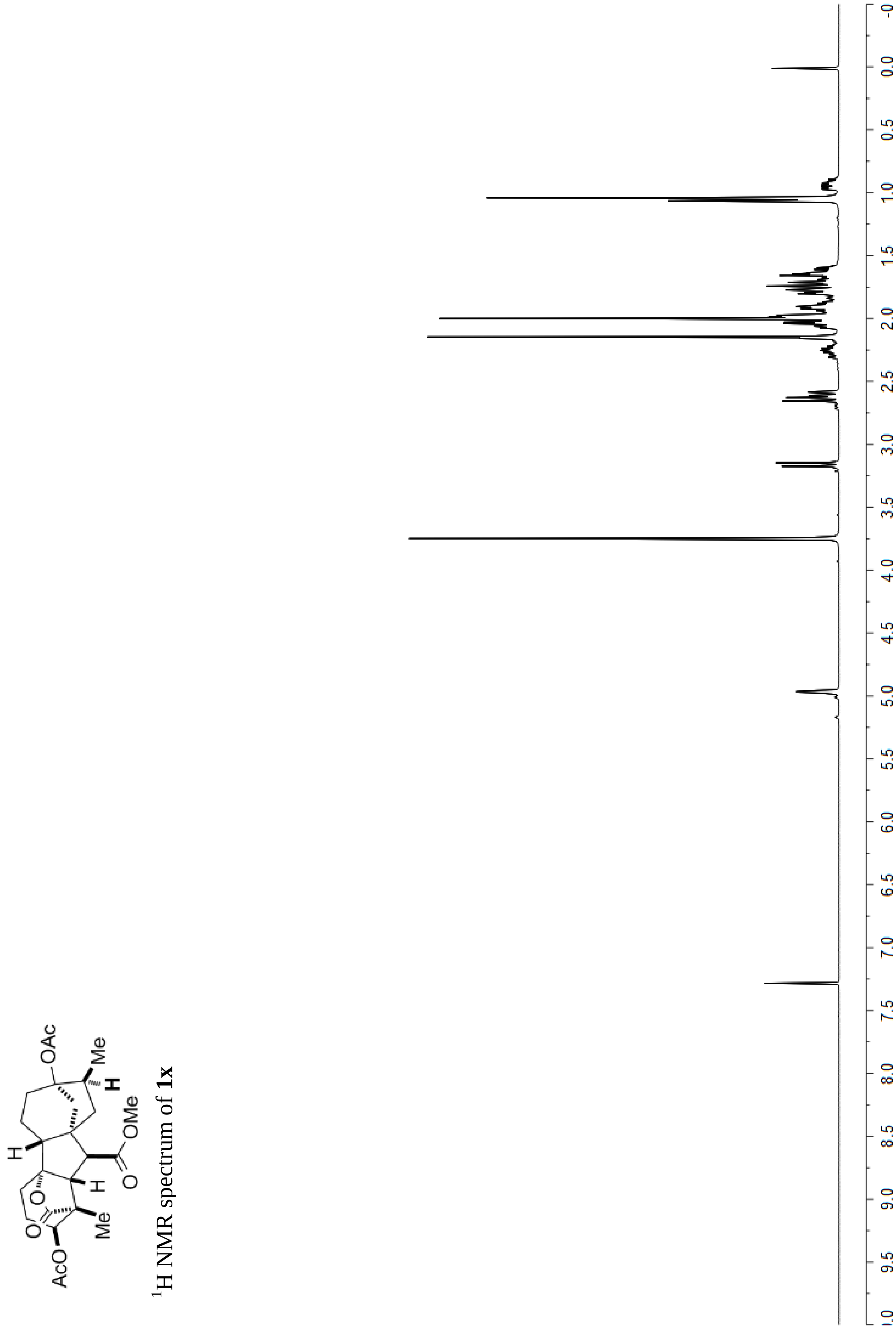
Spectroscopic Data



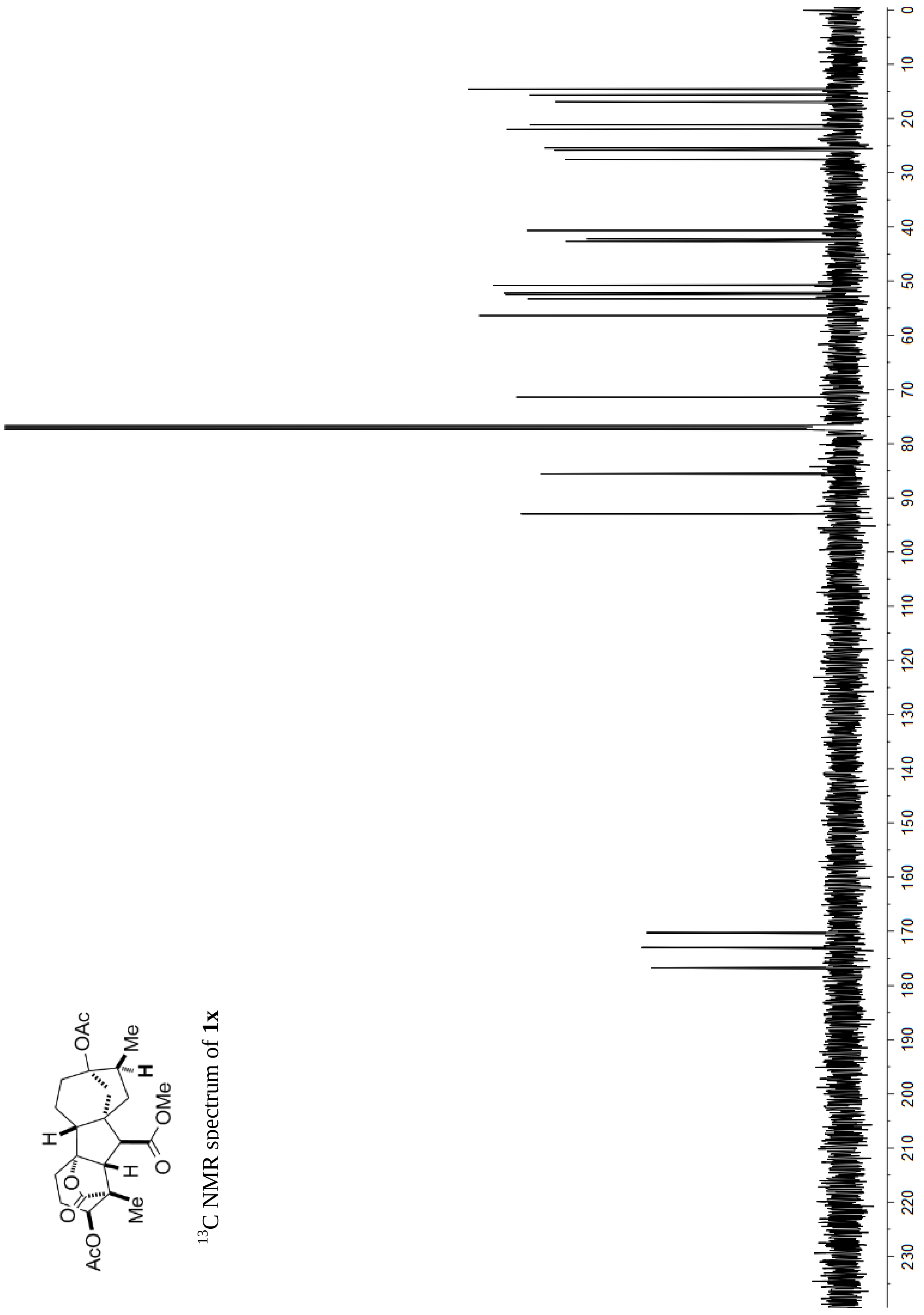
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **1s**



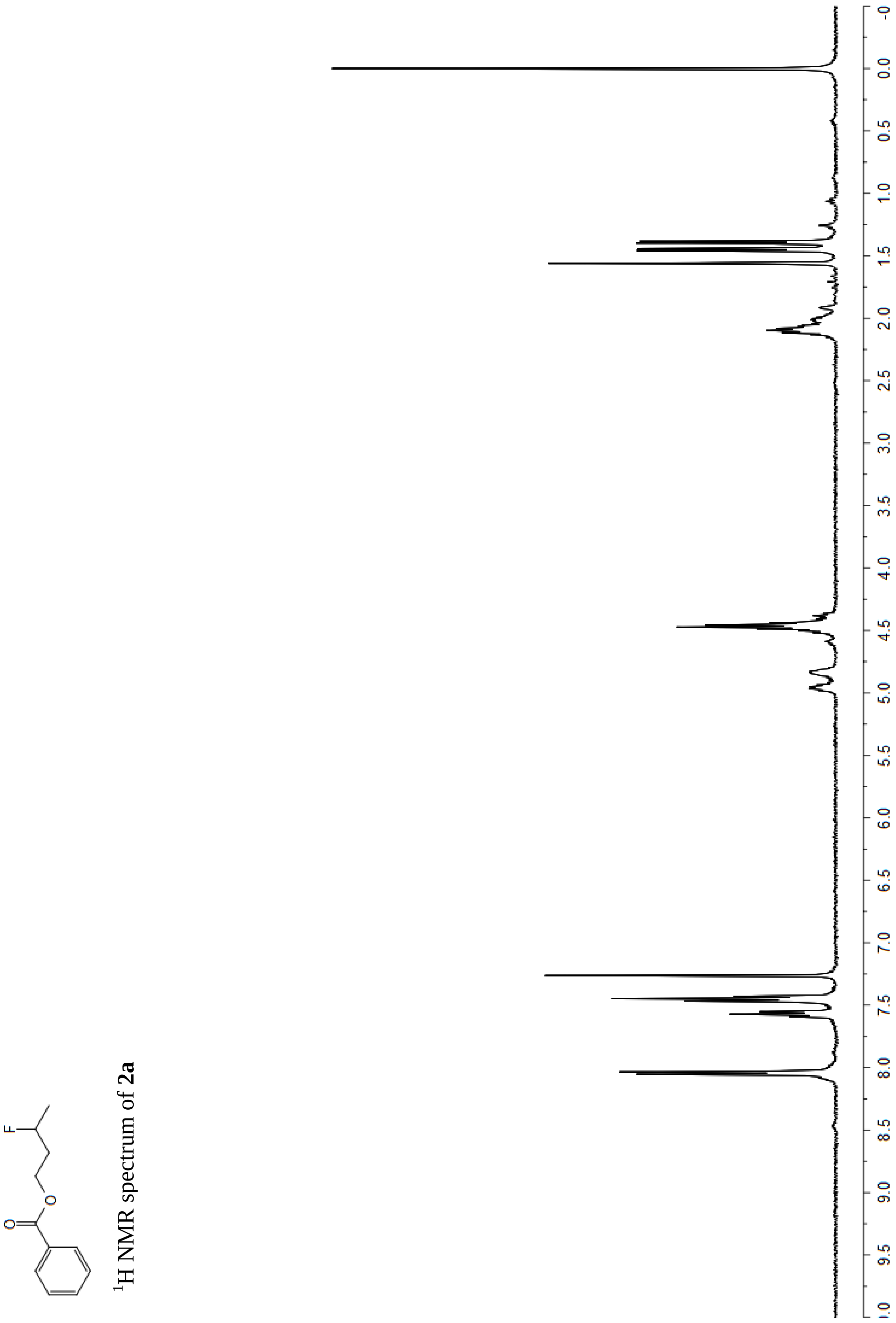
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **1s**



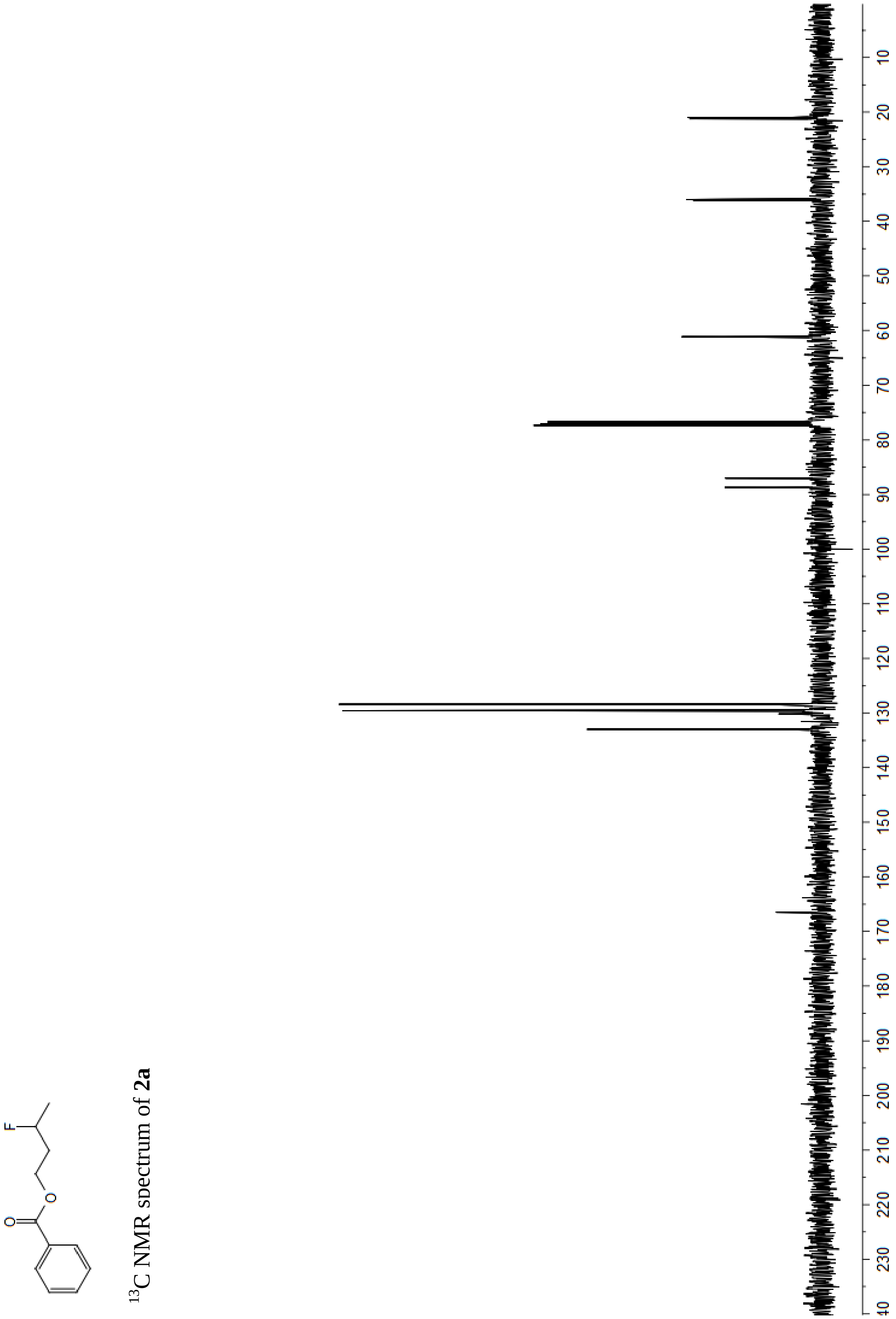
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ℃) of **1x**



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **1x**

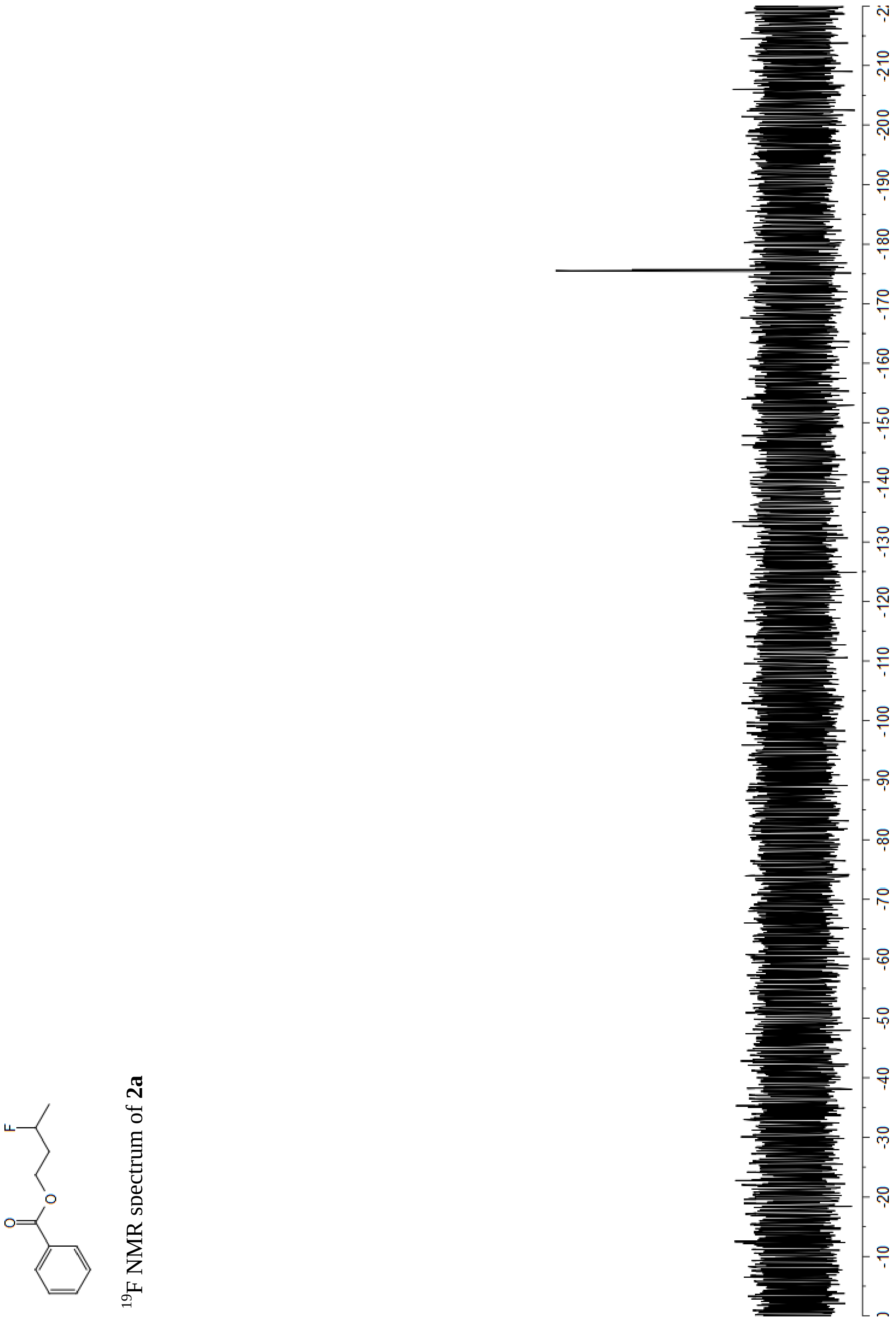


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2a**

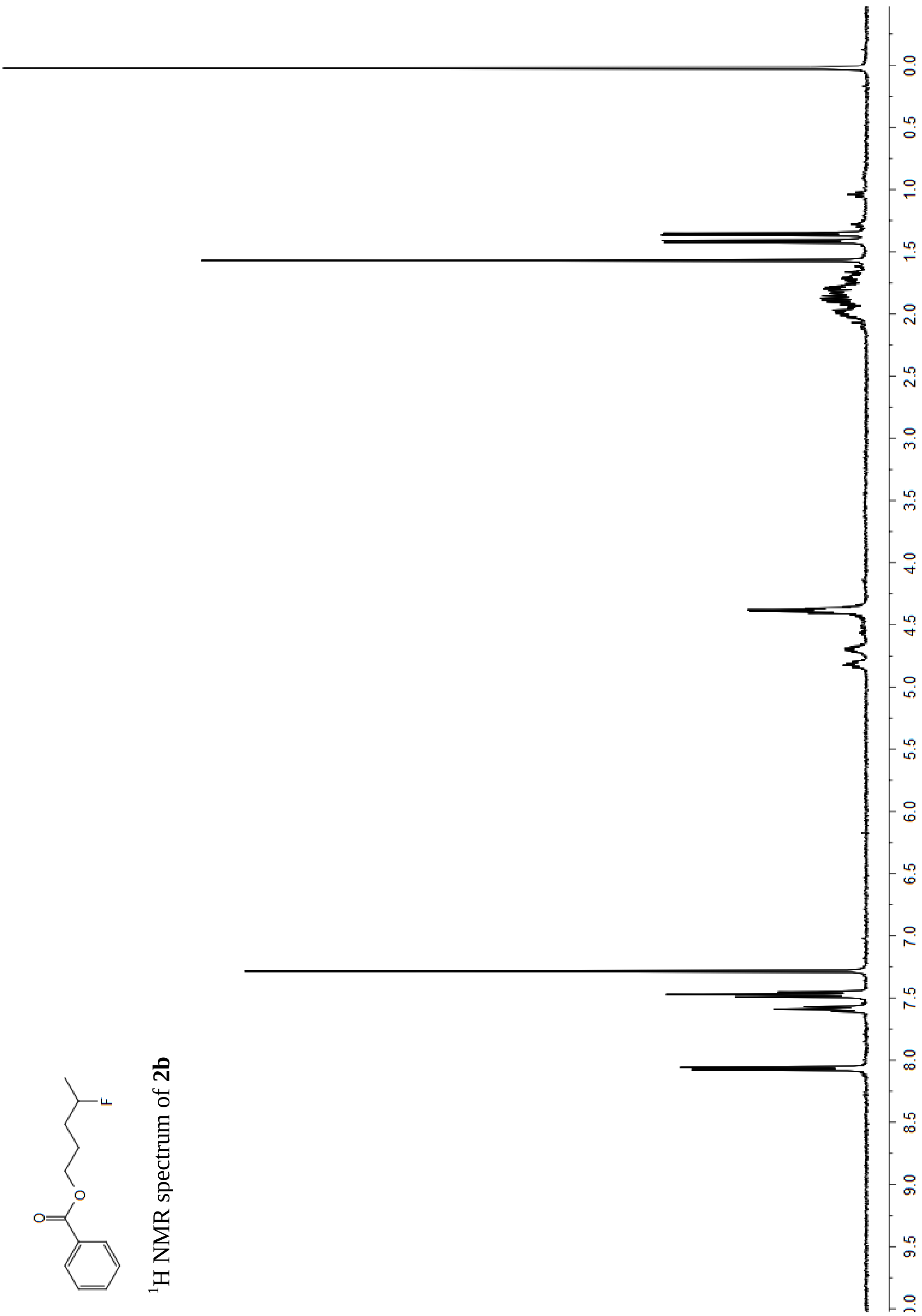


^{13}C NMR spectrum of **2a**

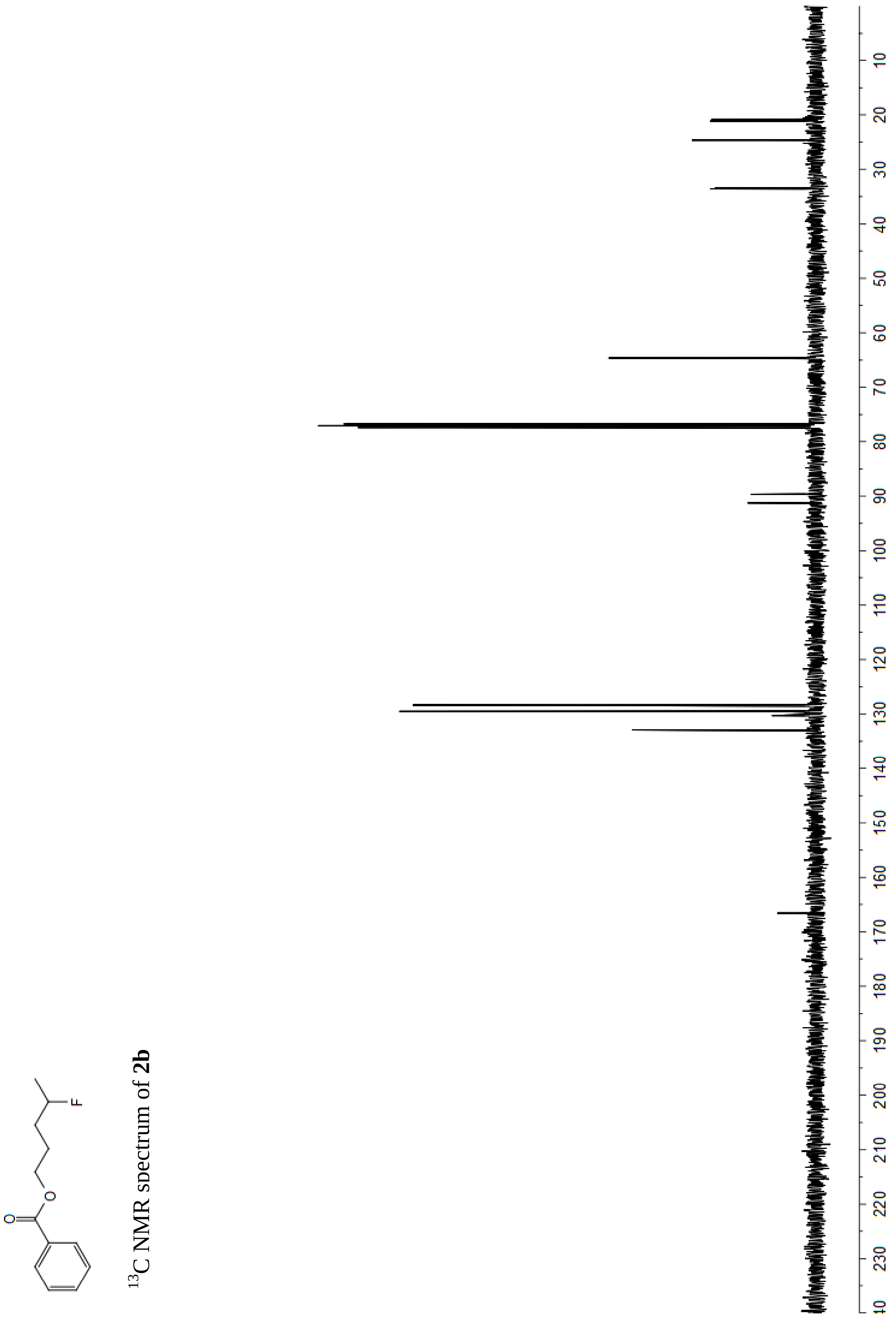
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2a**



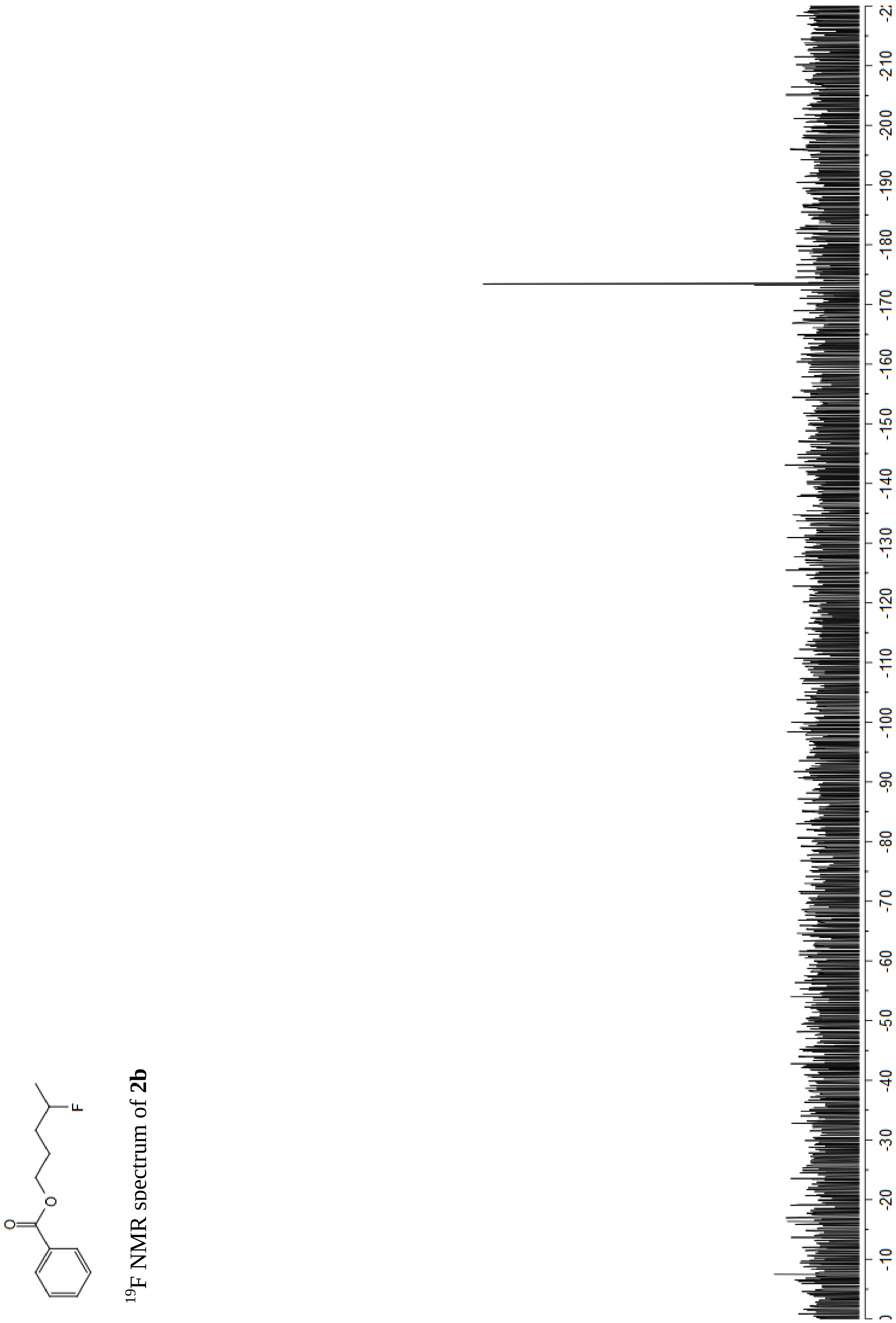
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2a**



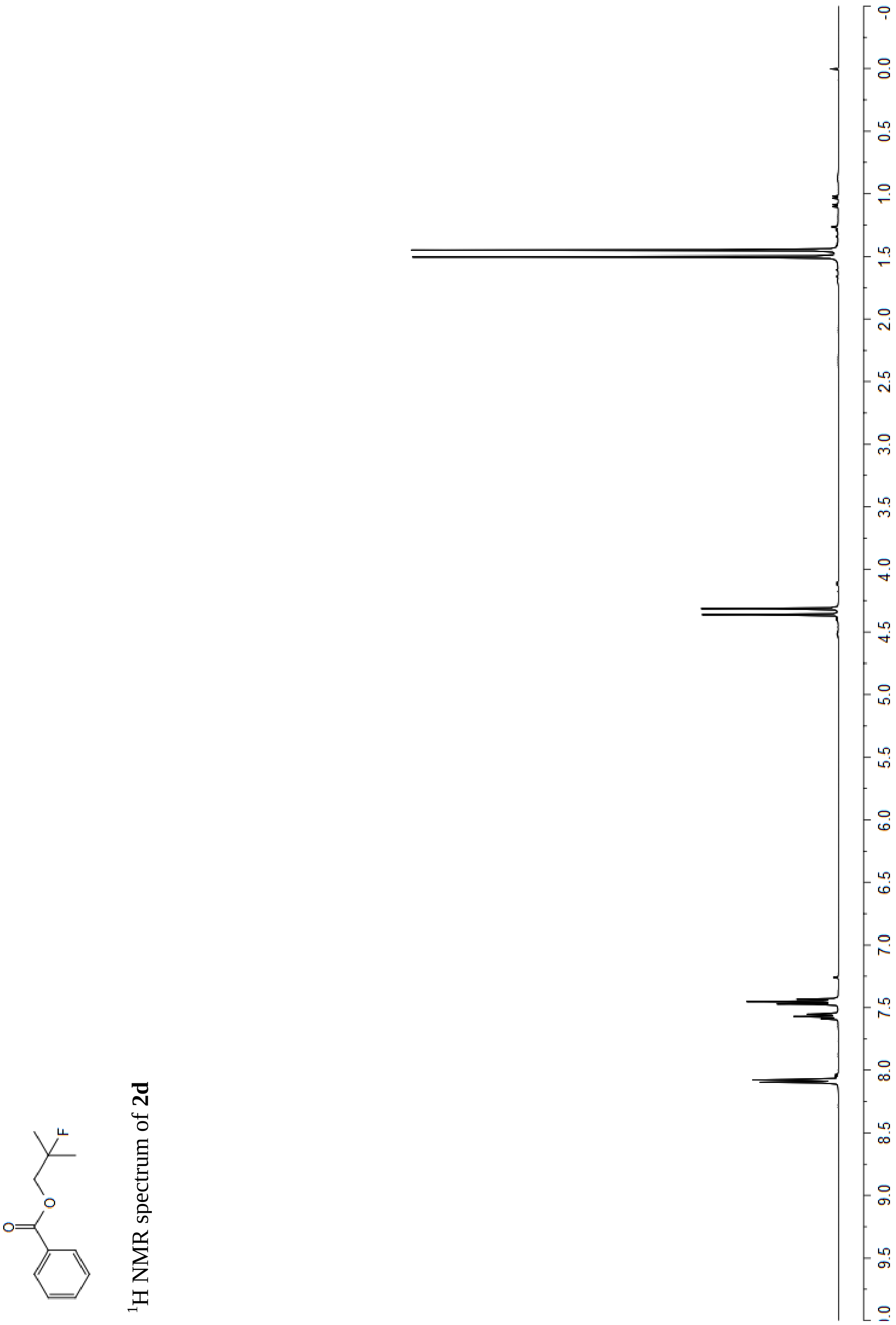
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 °C) of **2b**



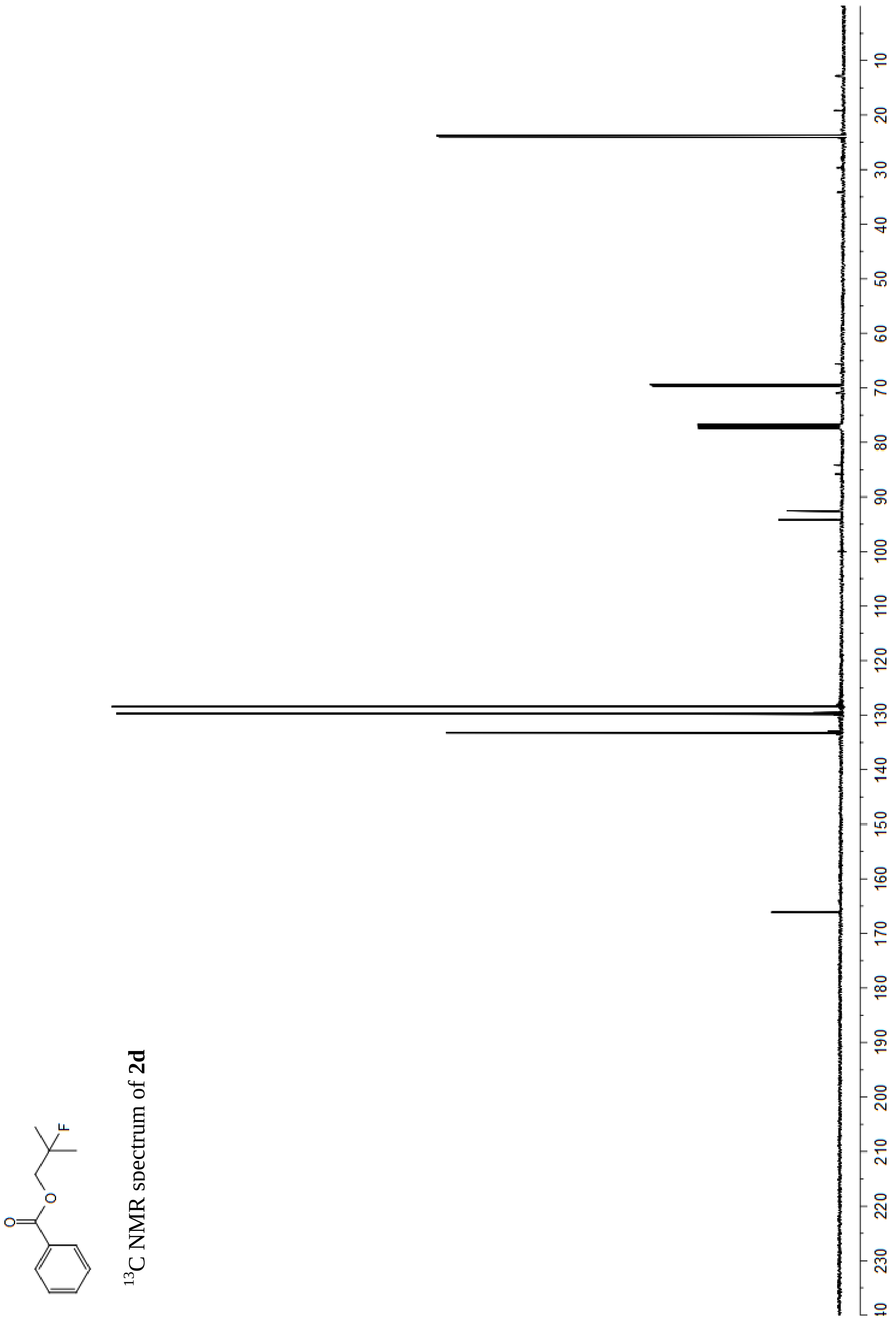
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2b**



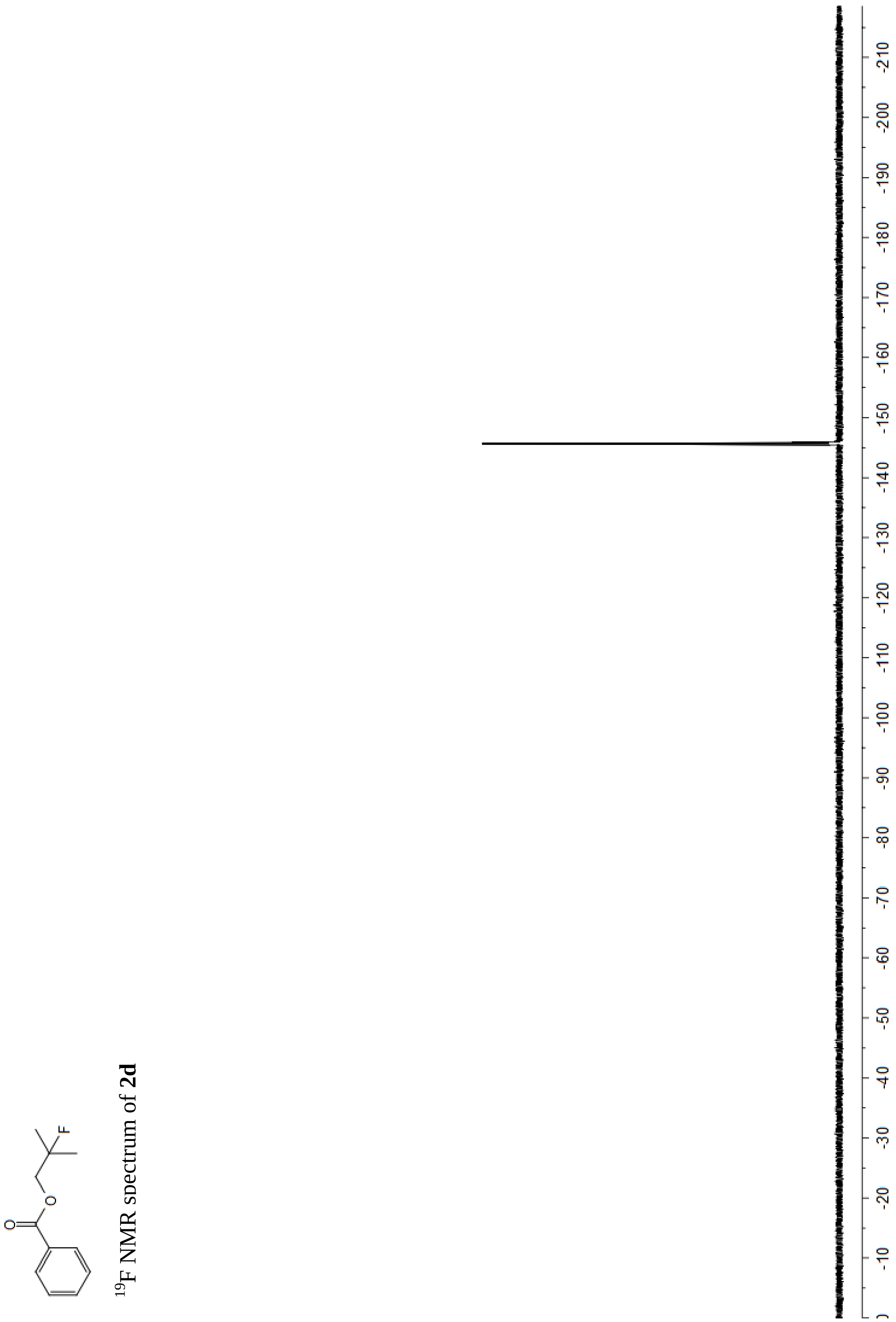
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 °C) of **2b**



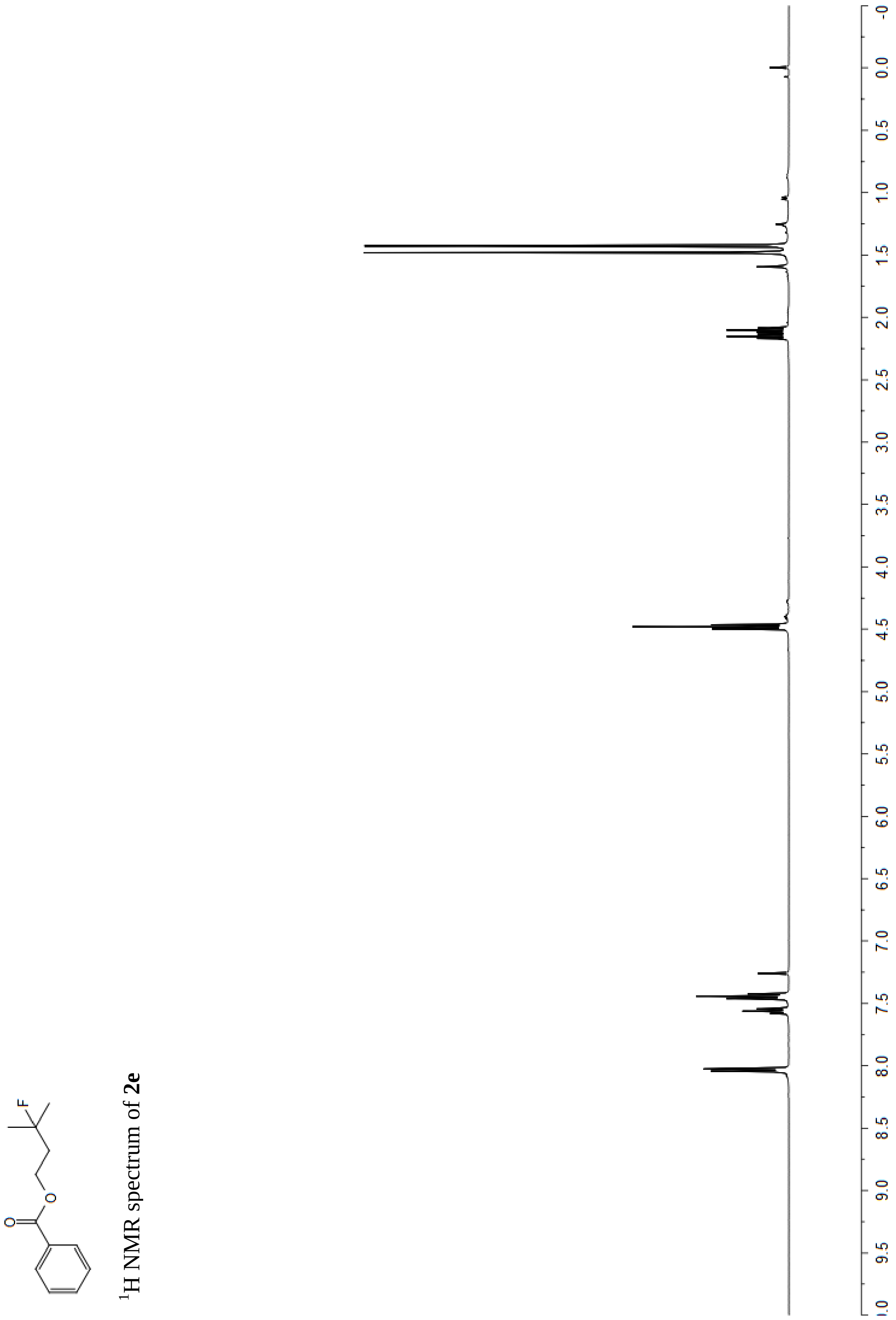
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 °C) of **2d**



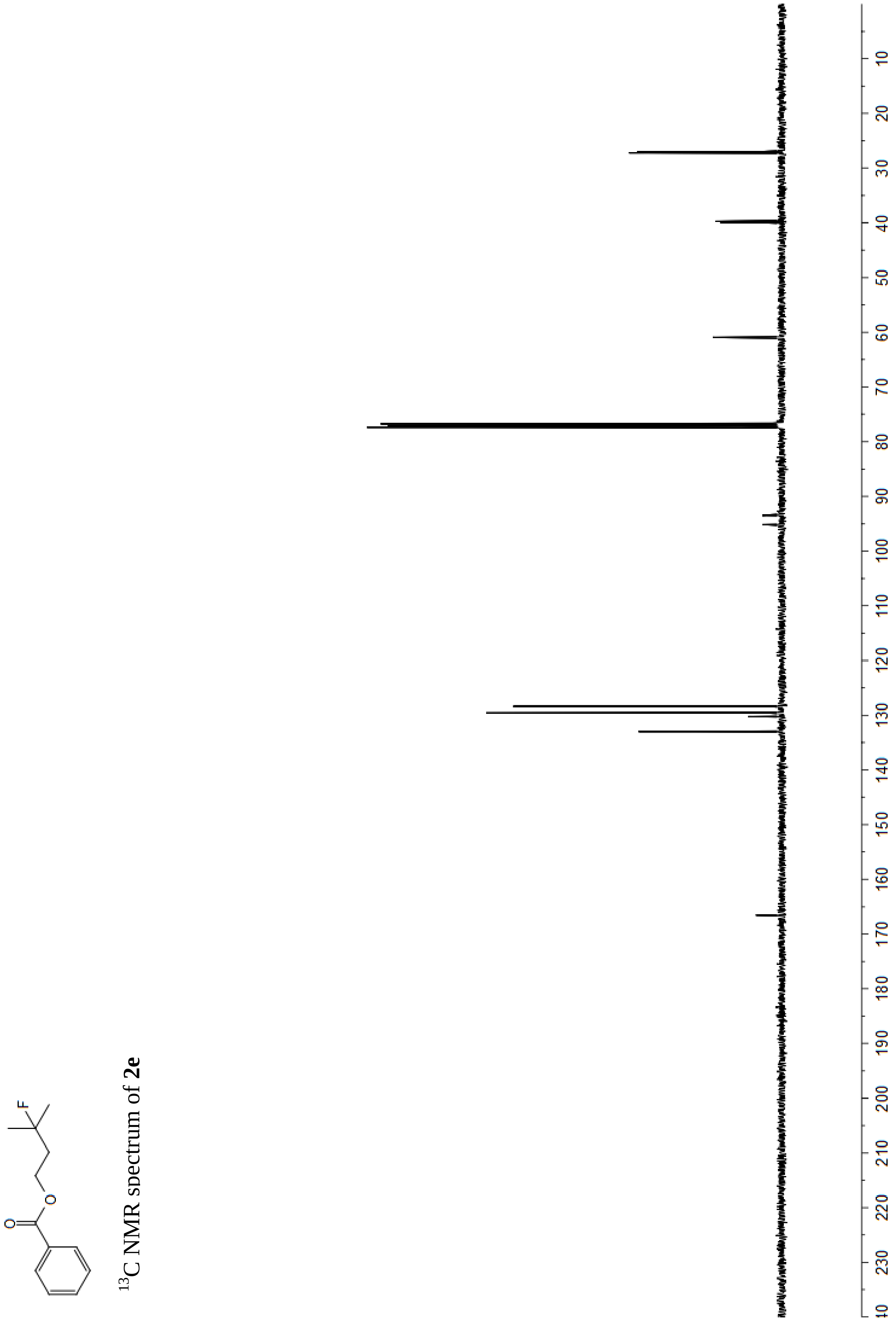
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2d**



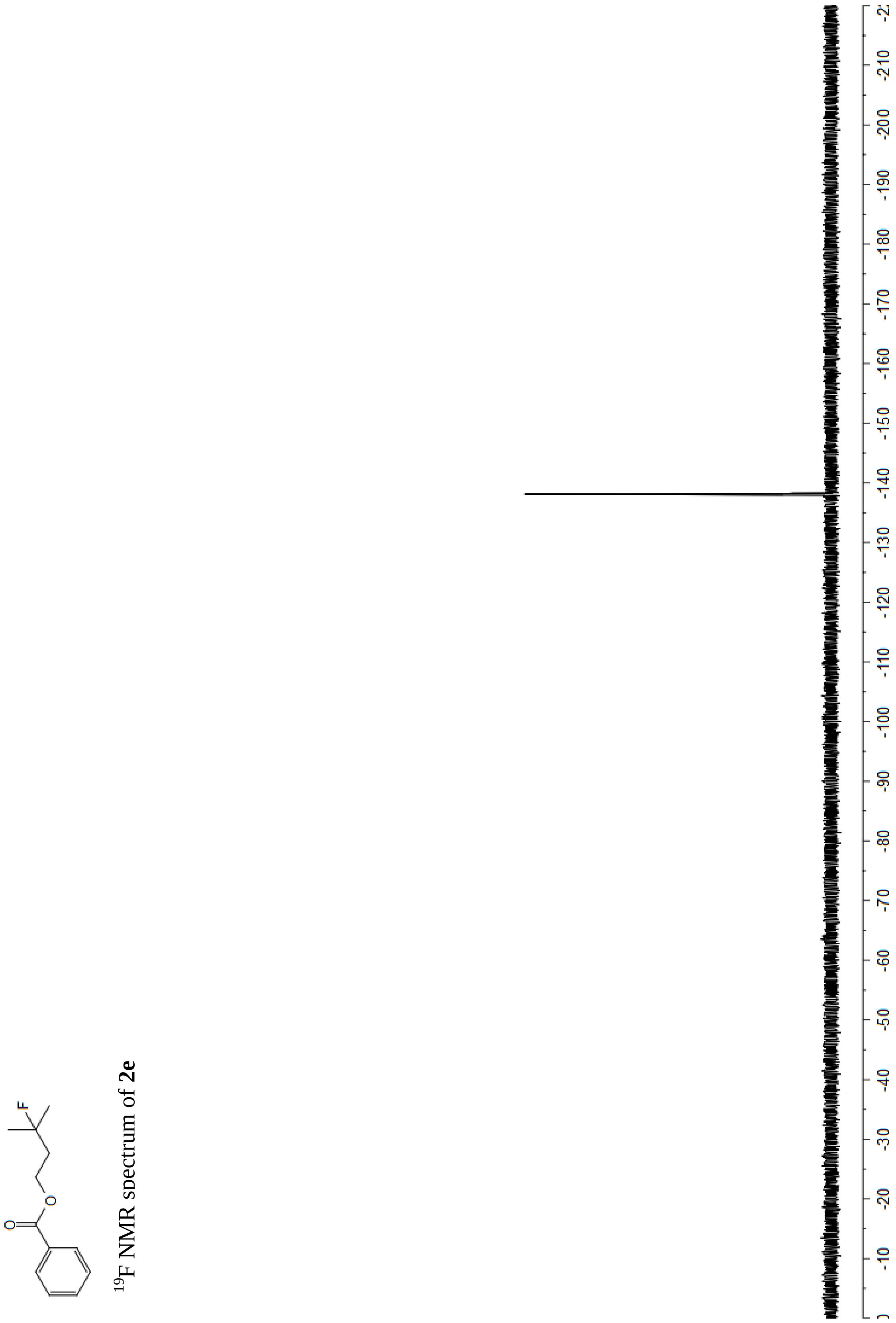
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2d**



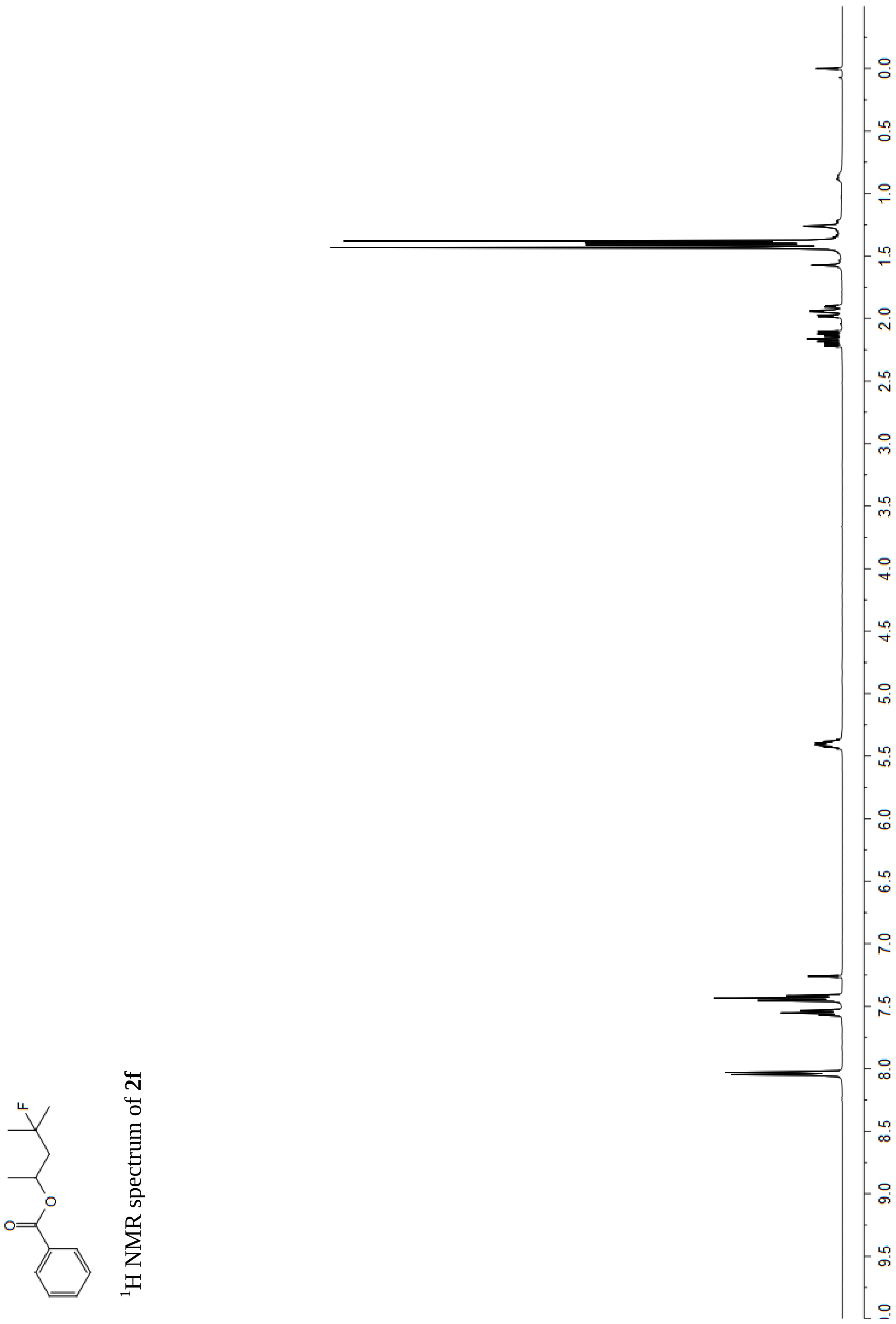
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of **2e**



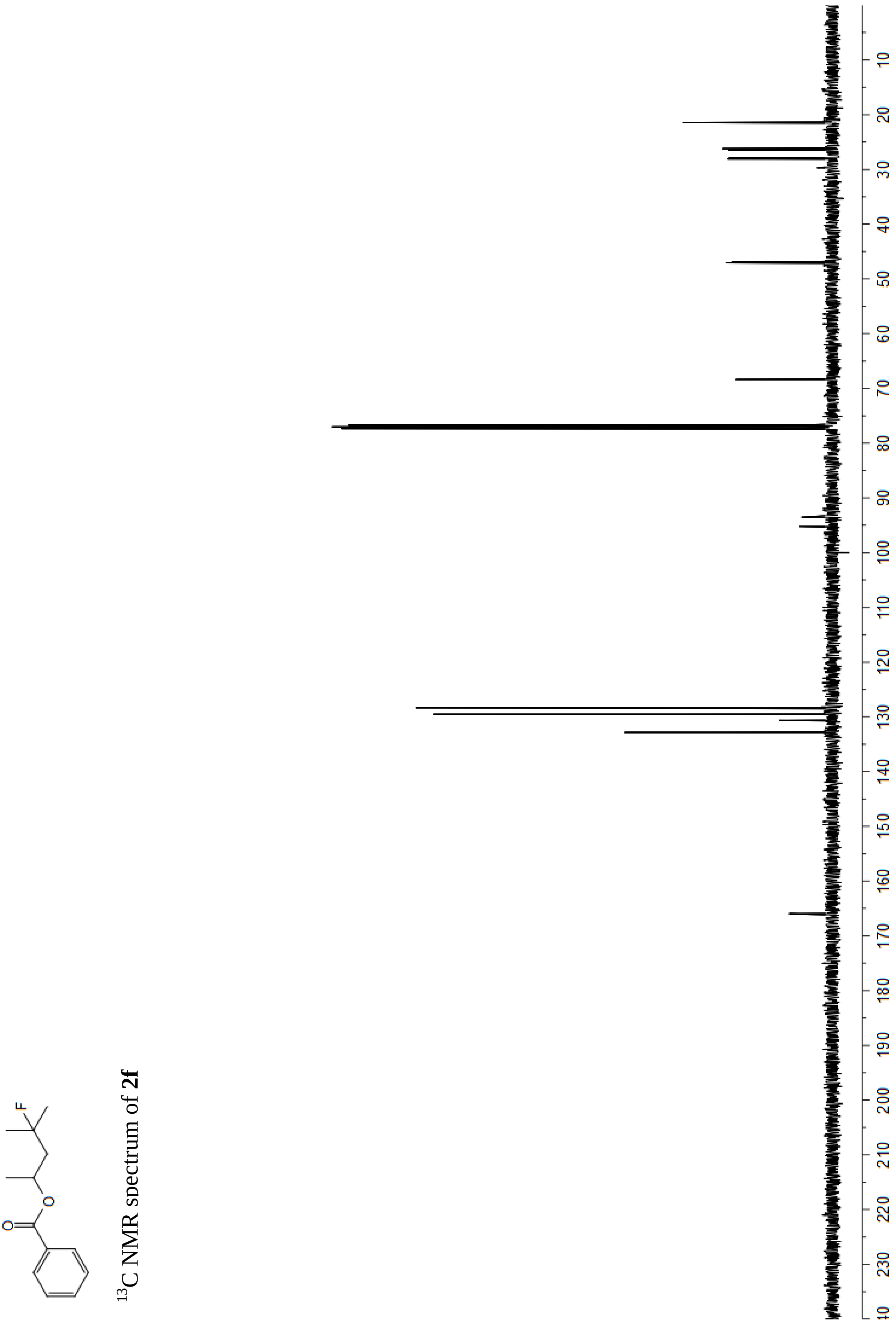
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2e**



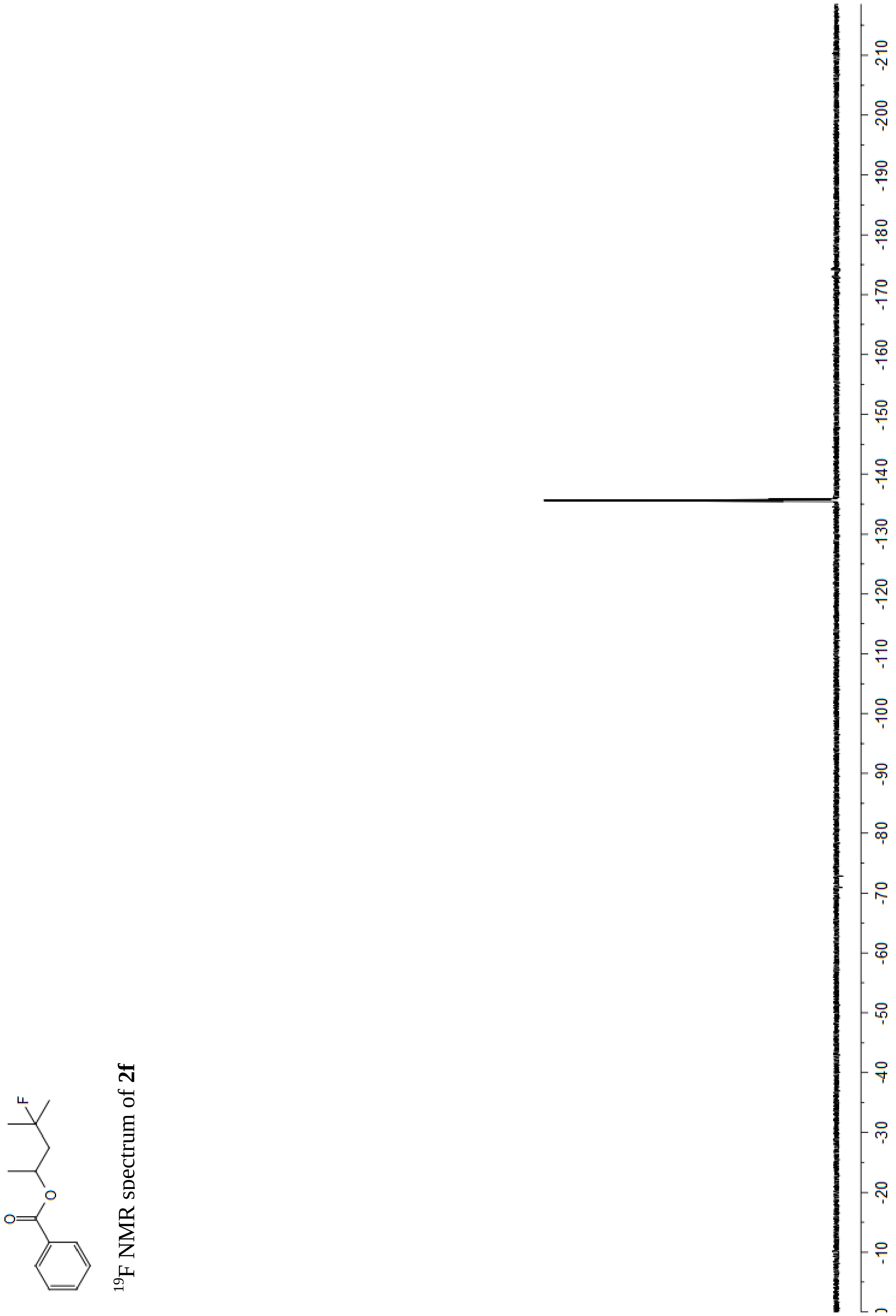
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2e**



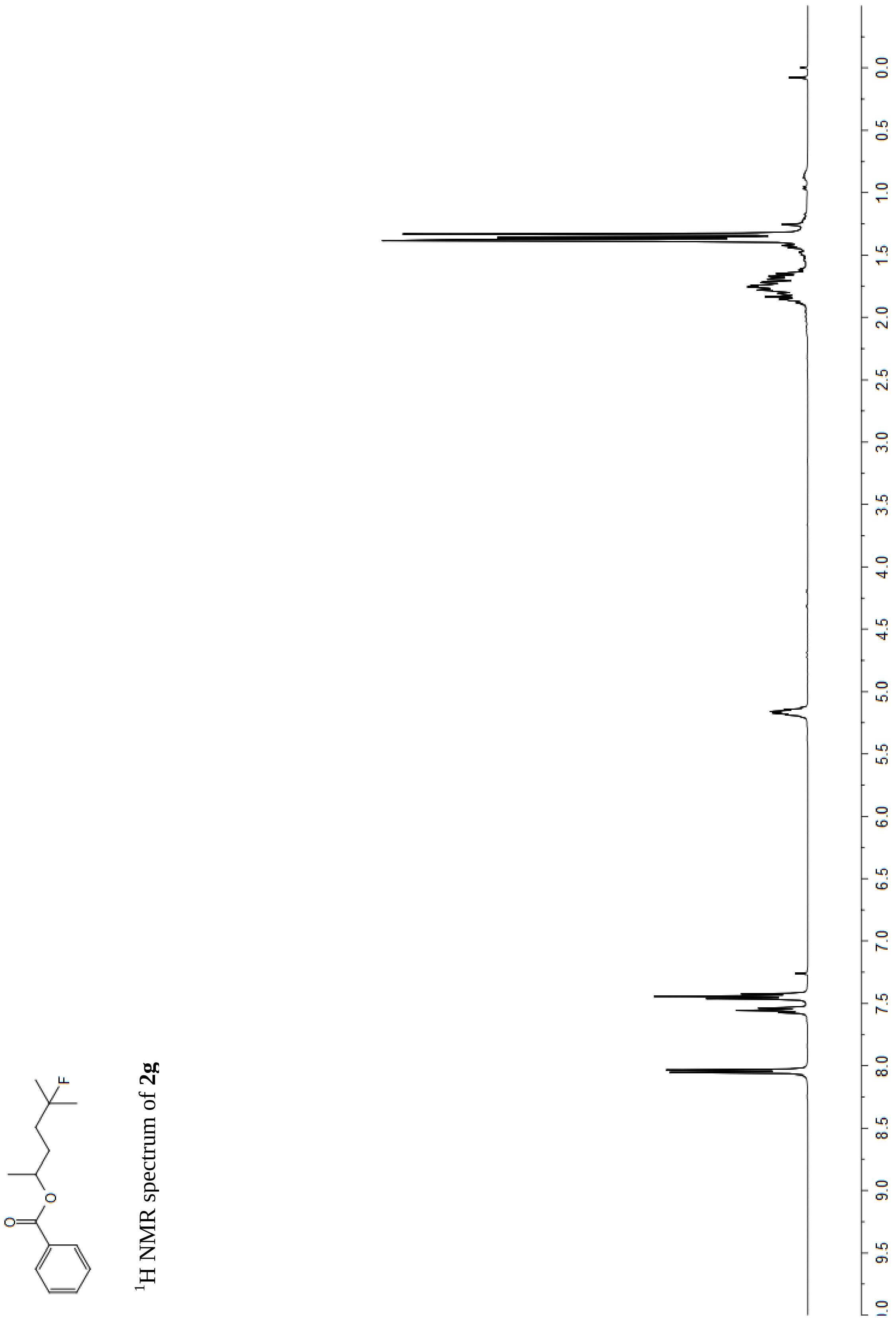
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2f**



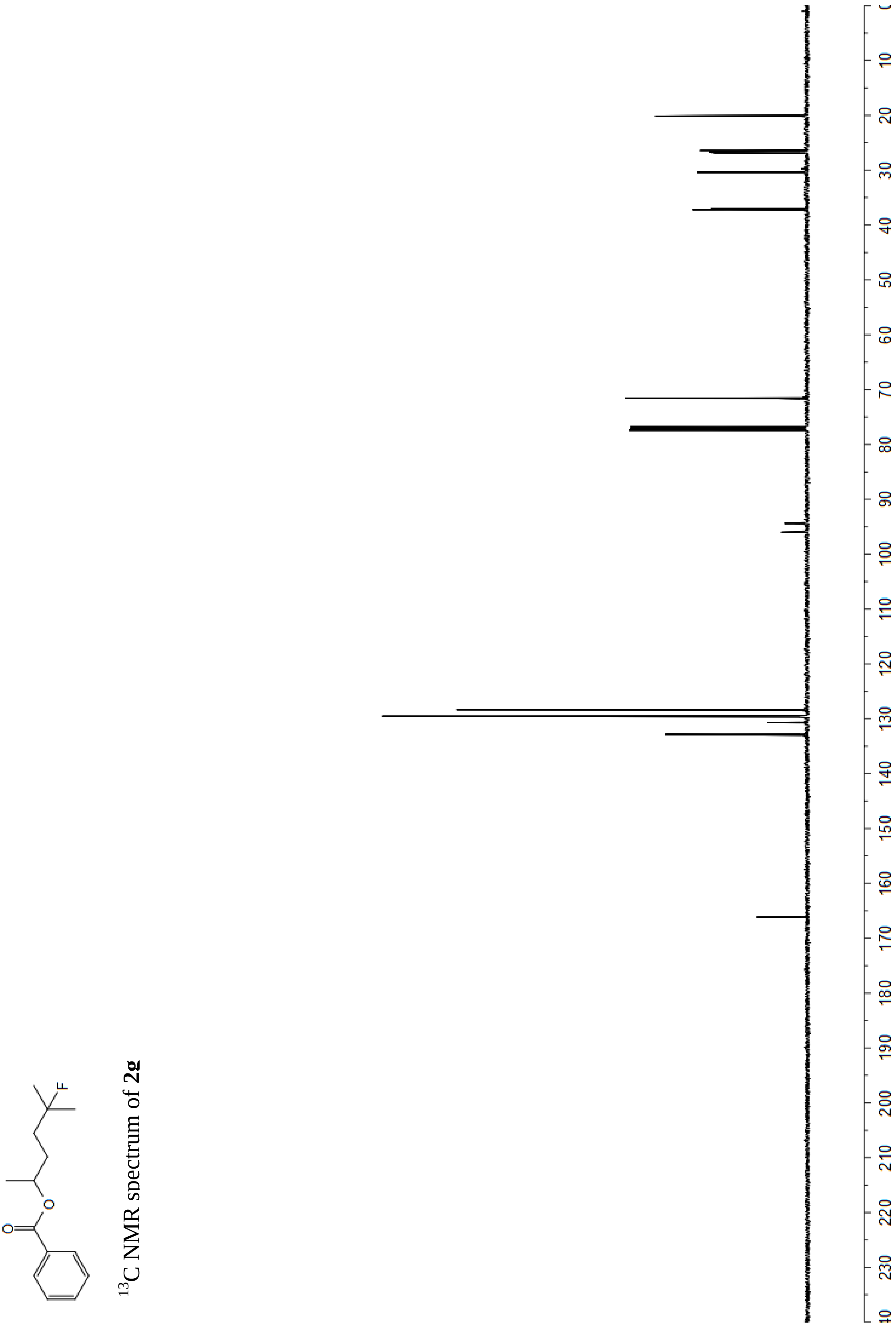
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2f**



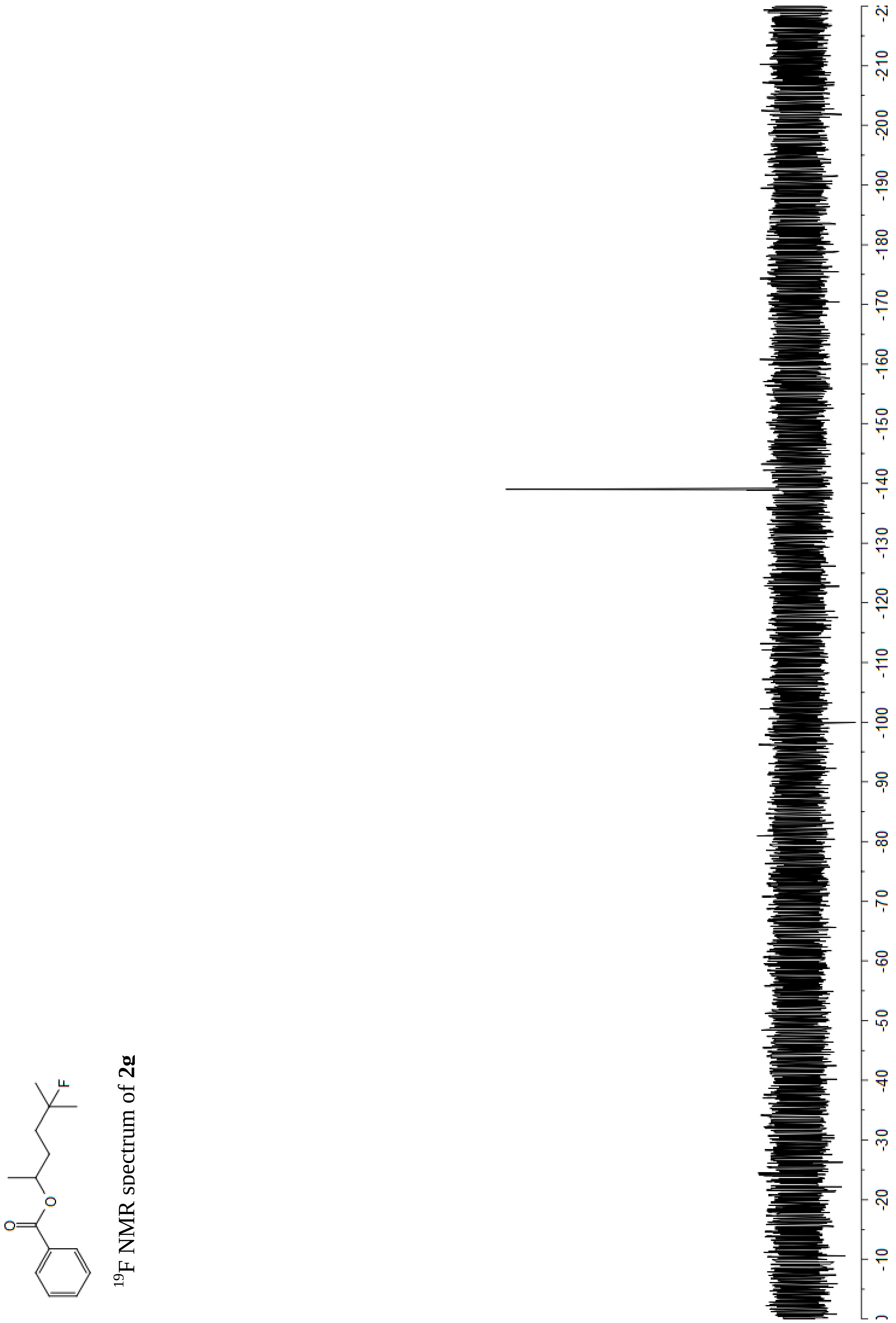
^{19}FNMR spectrum (375 MHz, CDCl$_3$, 23 ℃) of **2f**



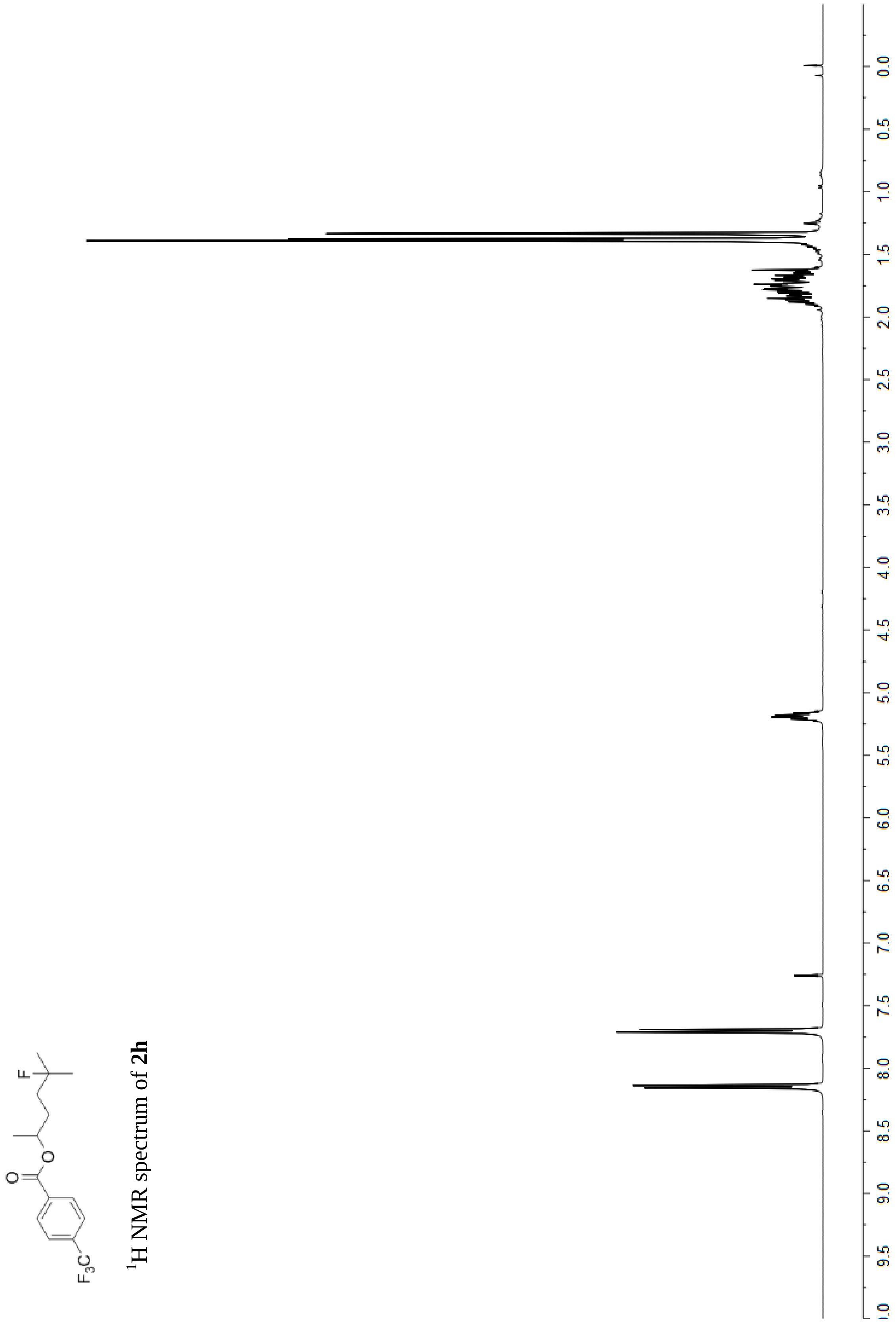
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ℃) of **2g**



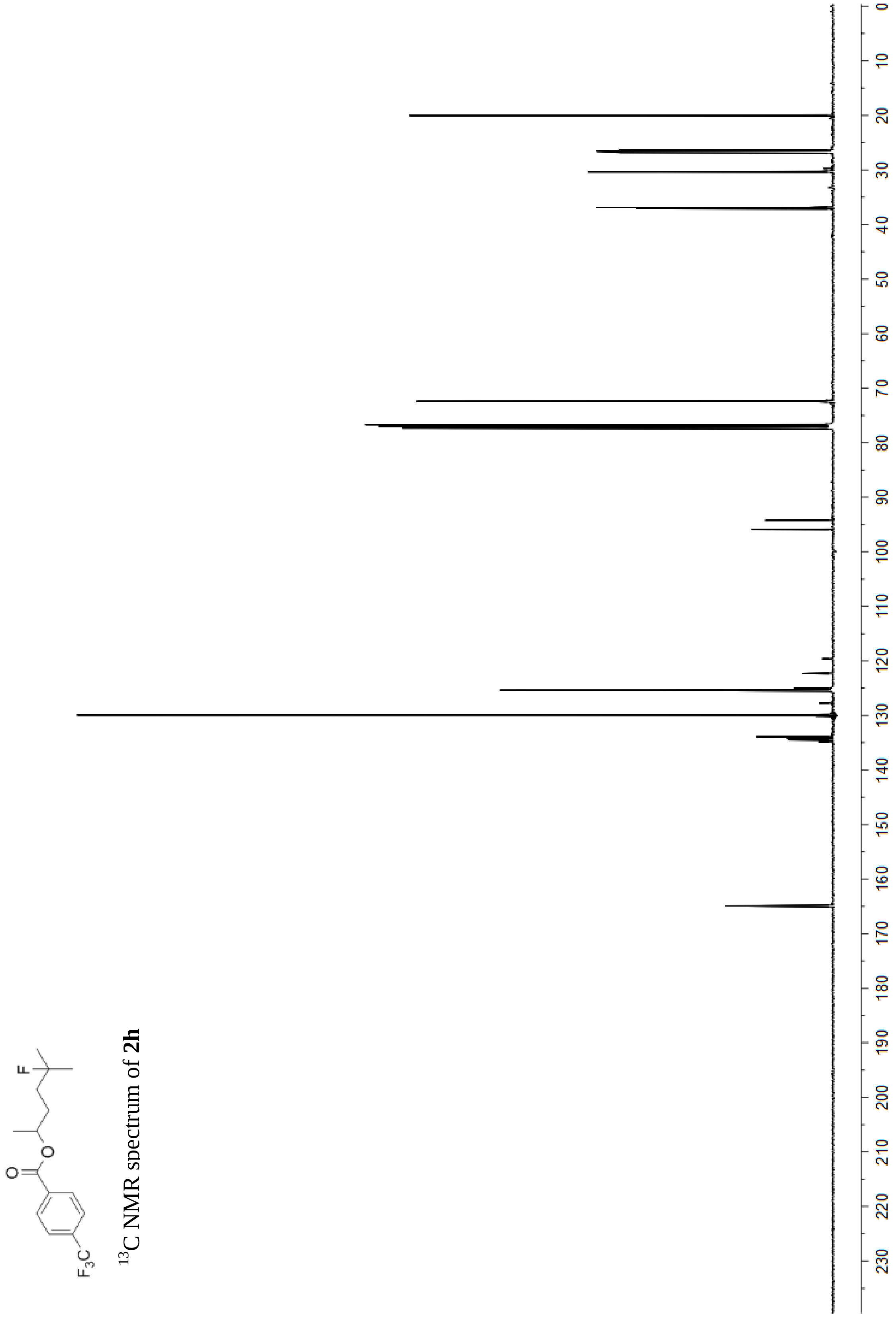
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2g**



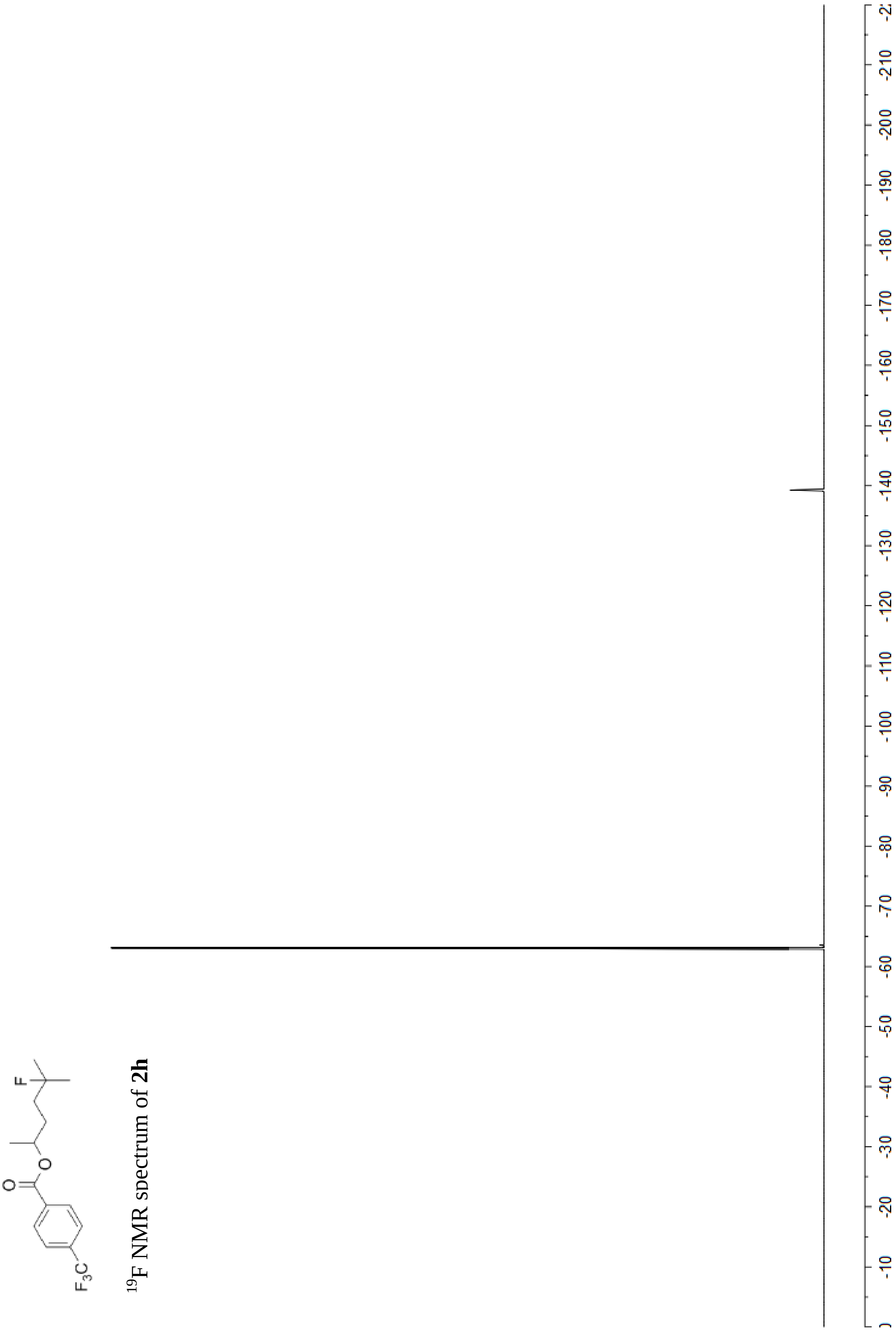
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2g**



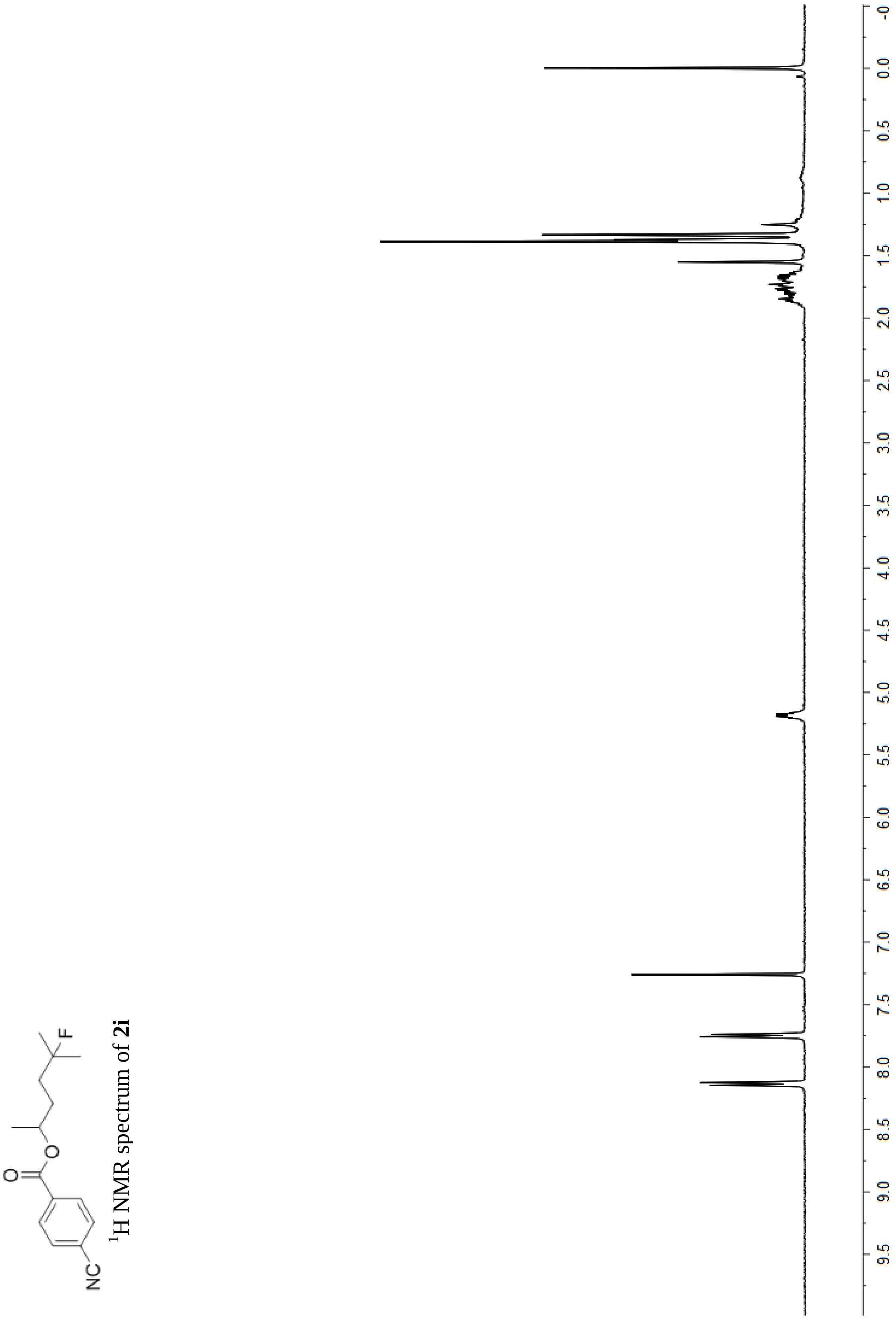
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2h**



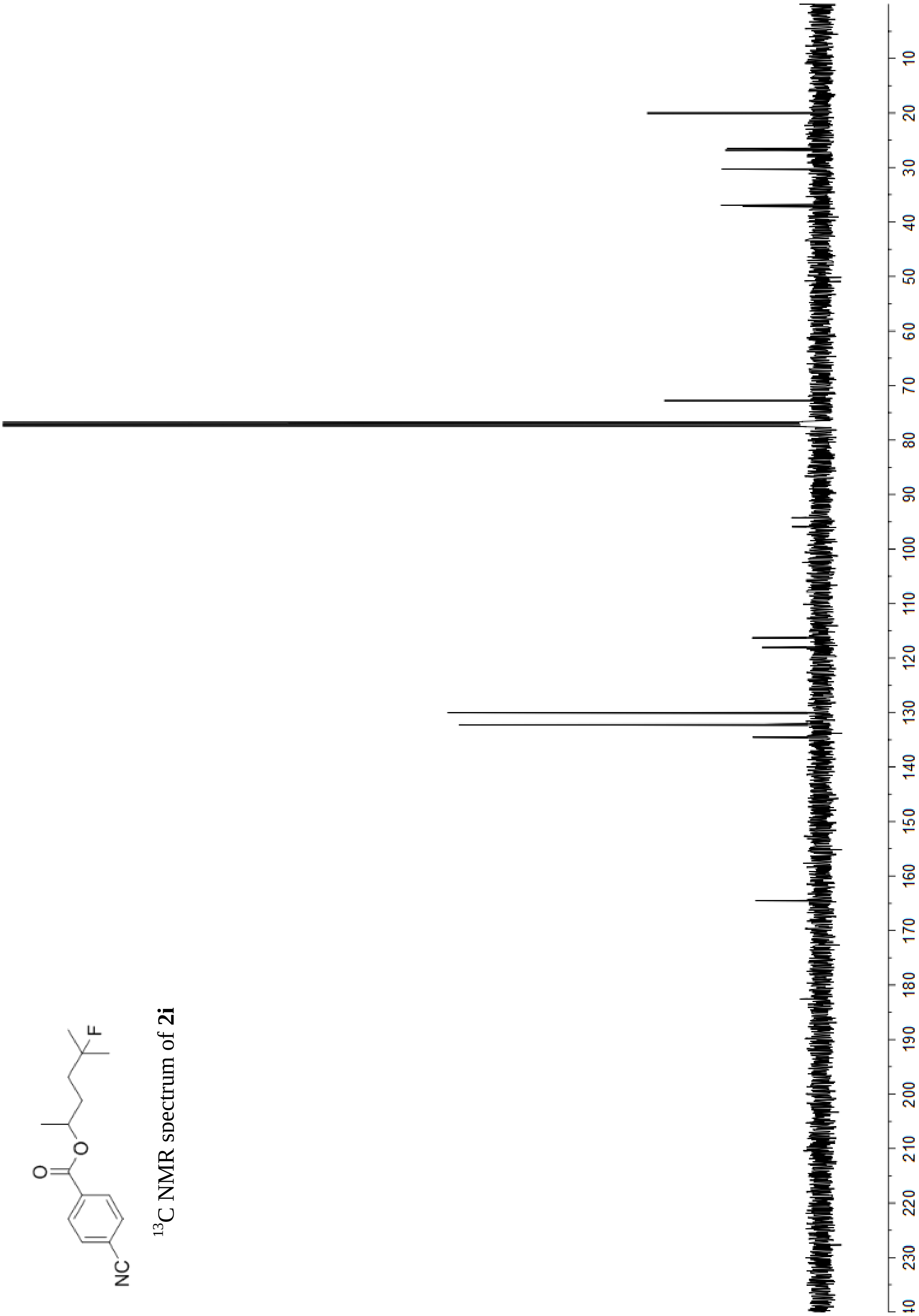
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2h**



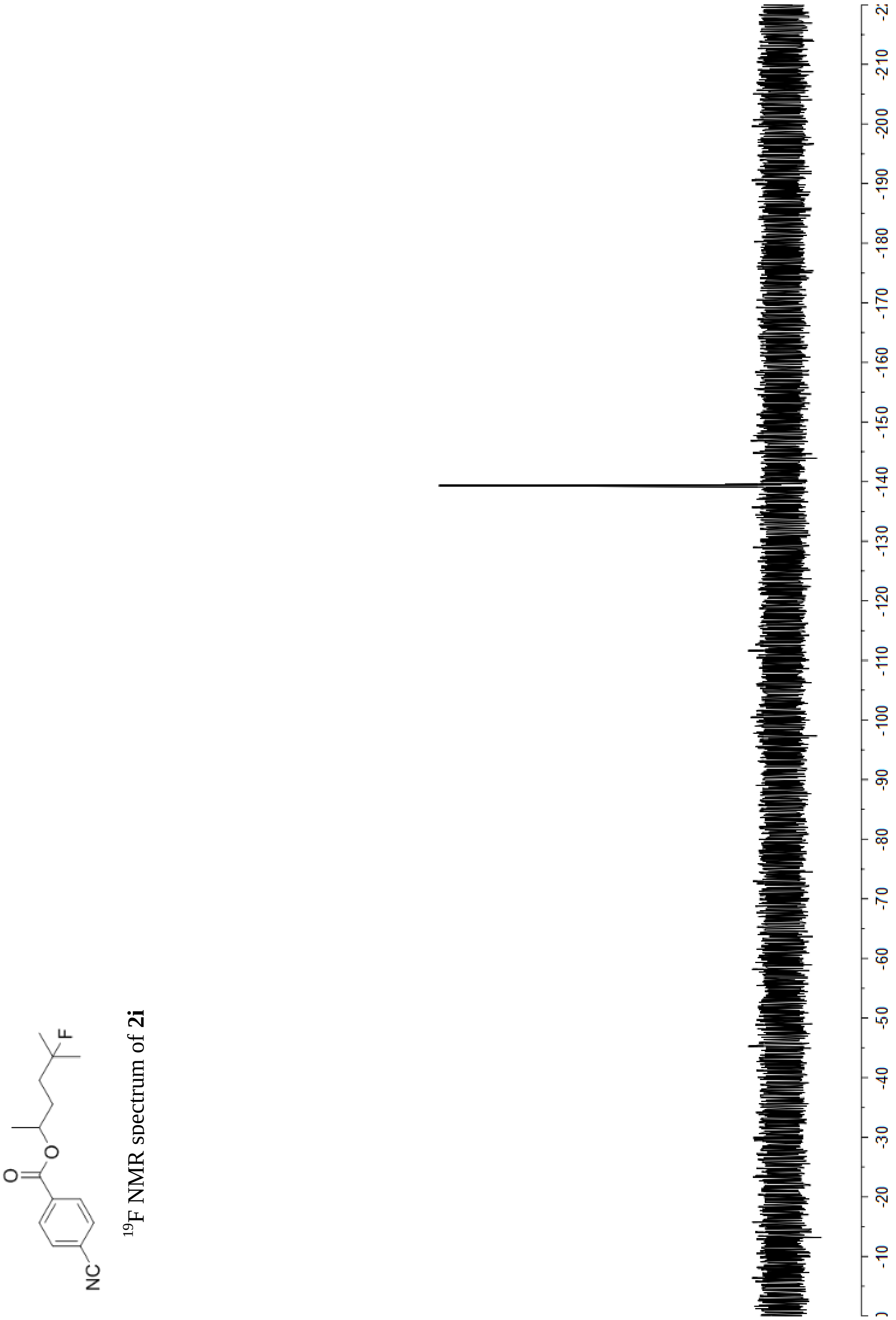
^{19}FNMR spectrum (375 MHz, CDCl$_3$, 23 ℃) of **2h**



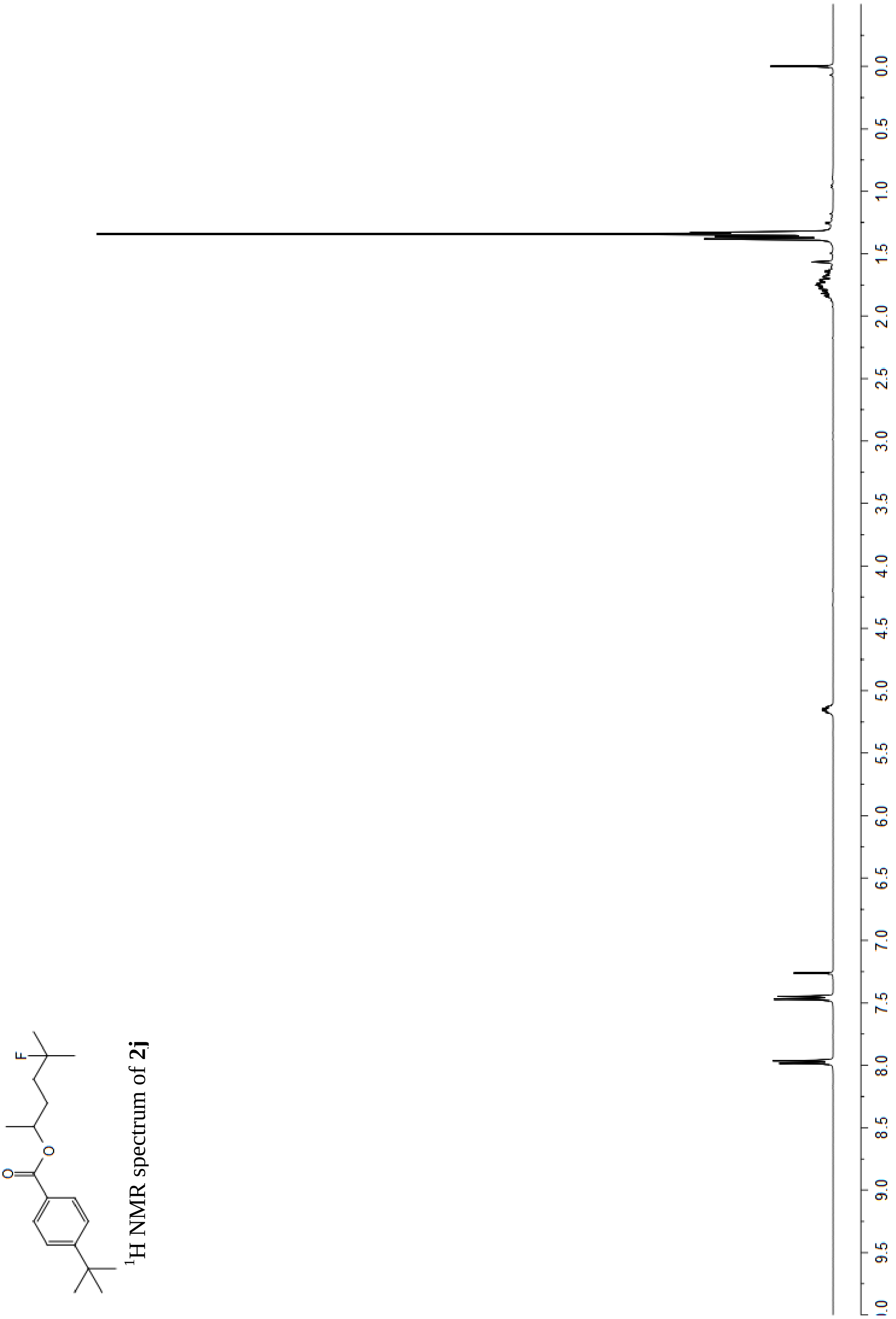
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2i**



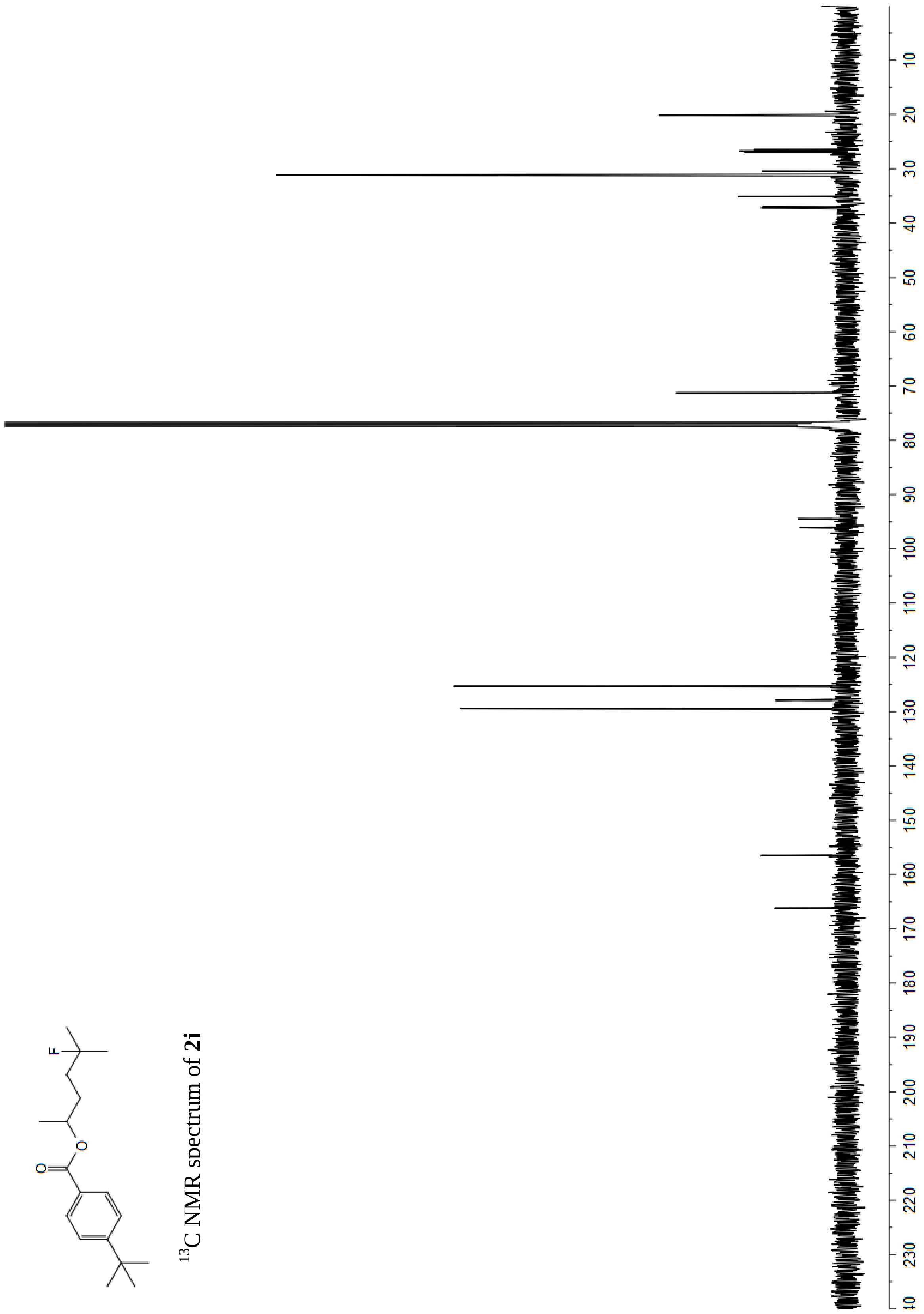
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 °C) of **2i**



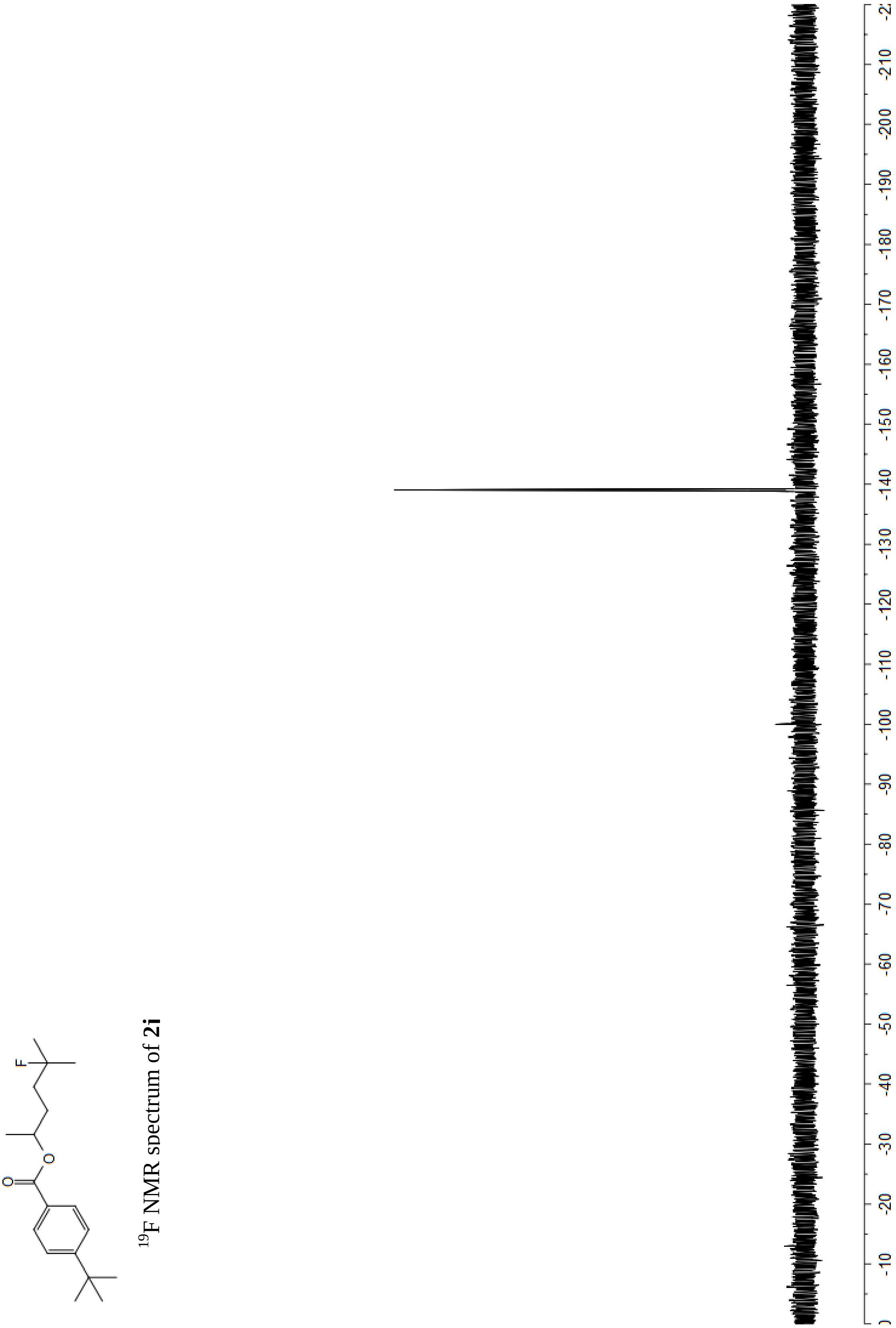
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2i**



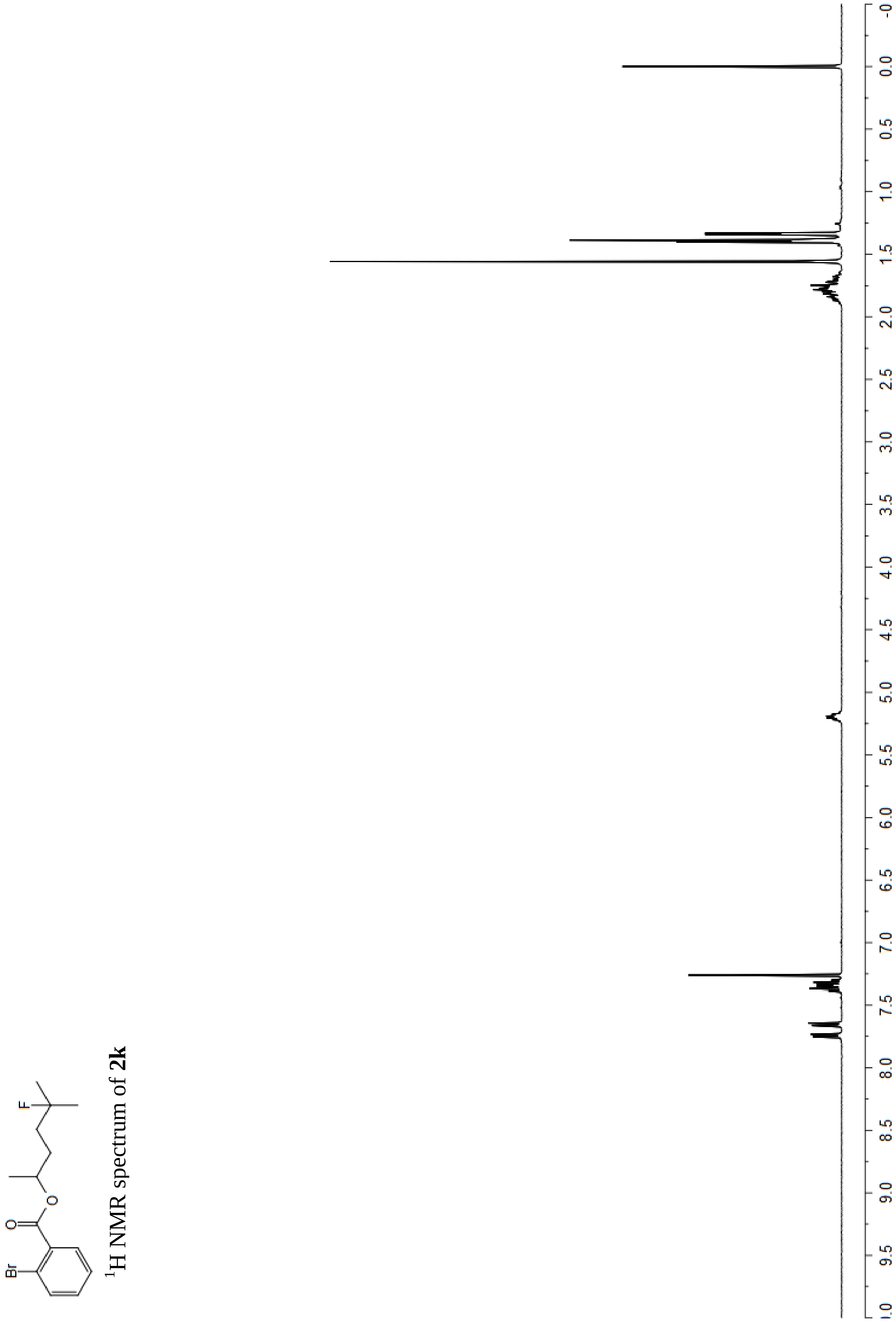
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2j**



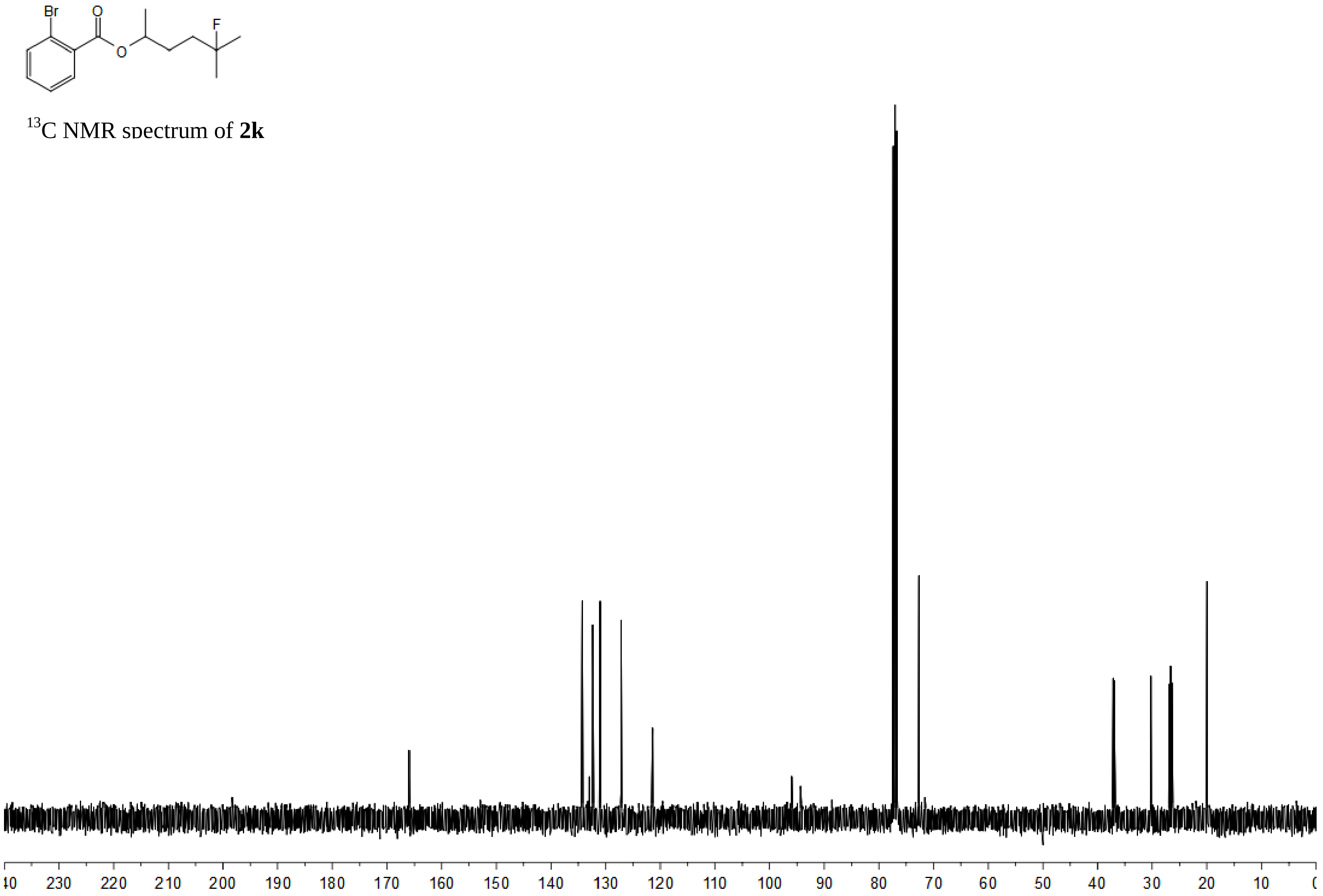
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2j**



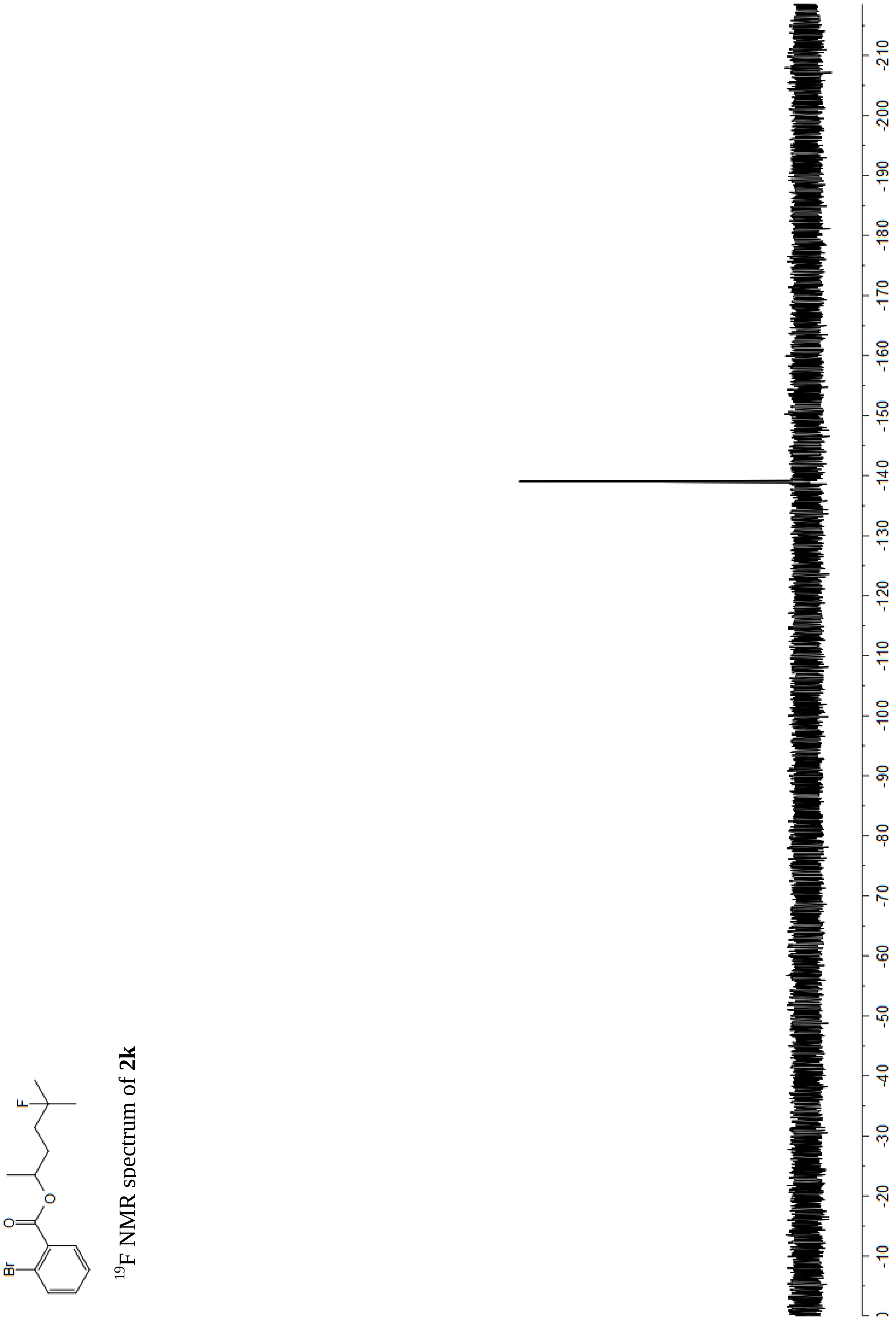
^{19}FNMR spectrum (375 MHz, CDCl$_3$, 23 ℃) of **2j**



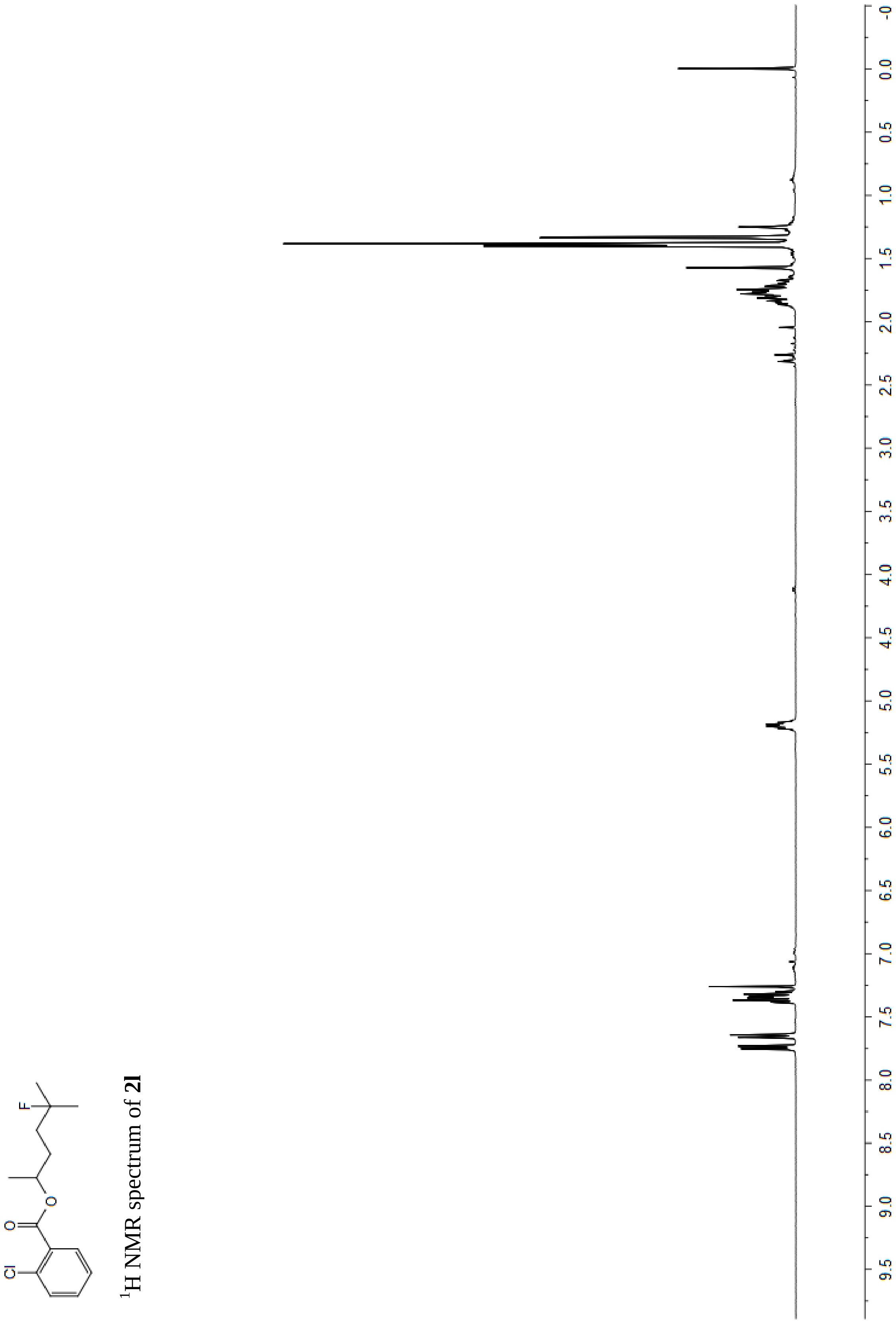
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of **2k**



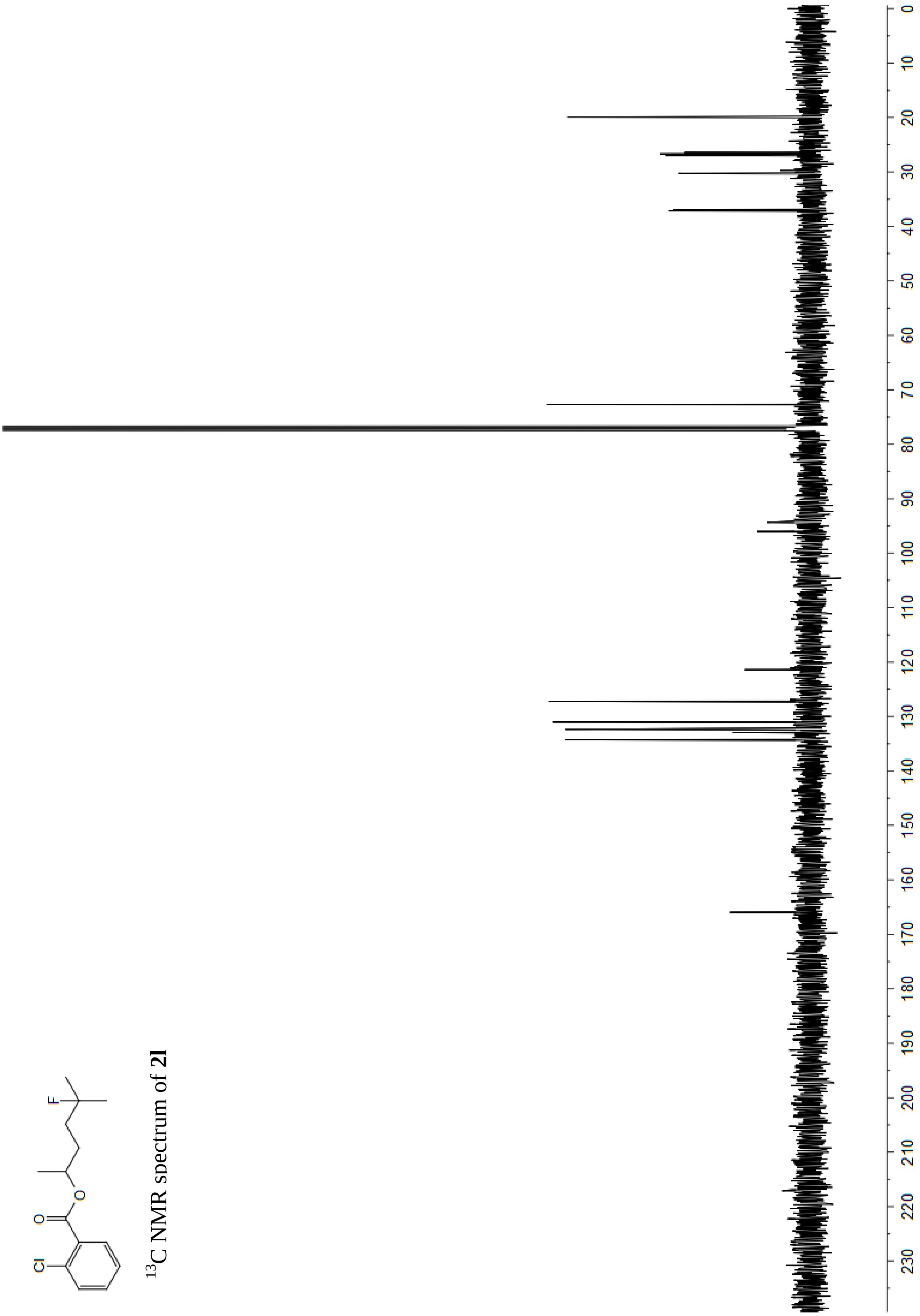
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2k**



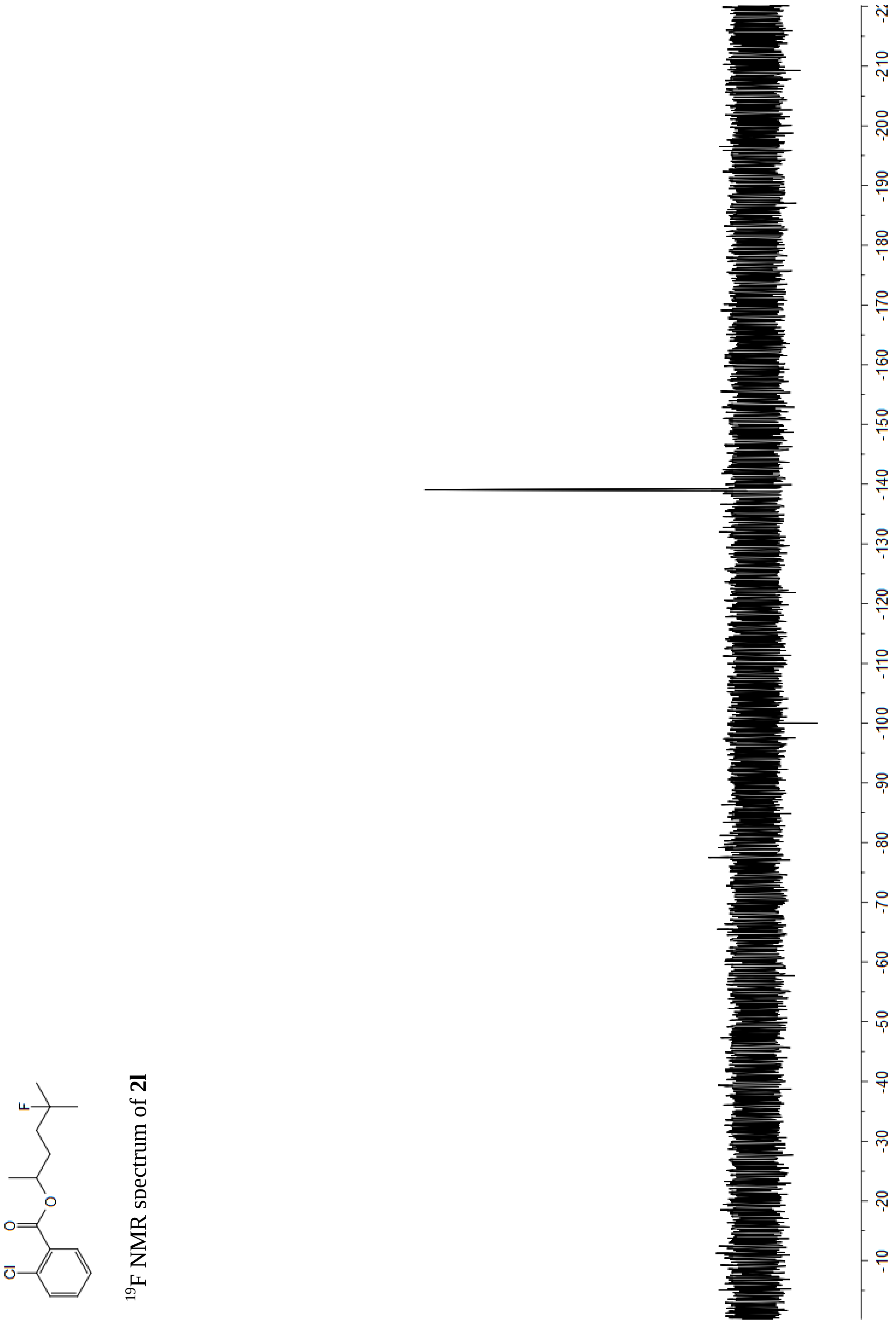
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2k**



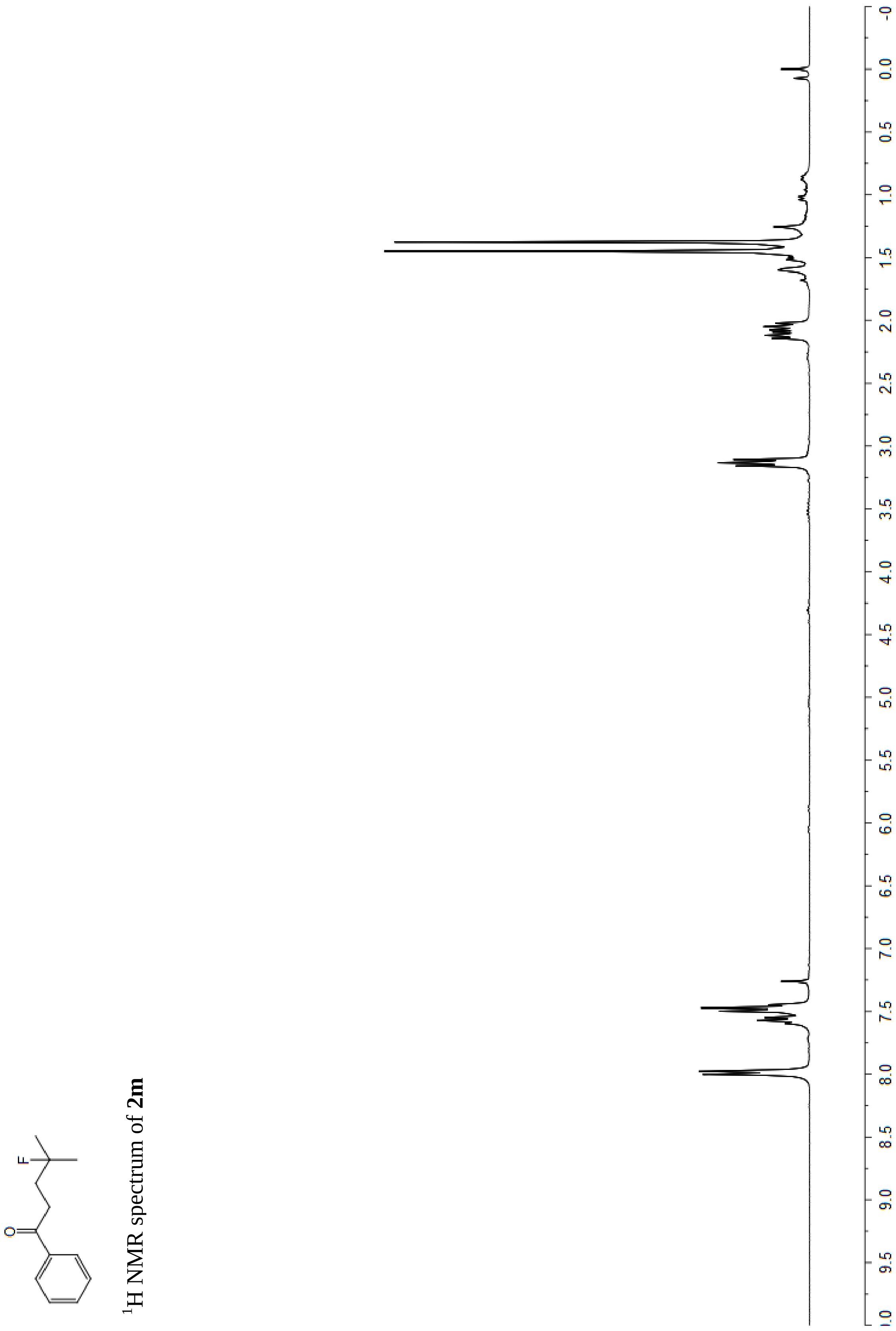
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2l**



^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 °C) of **2l**

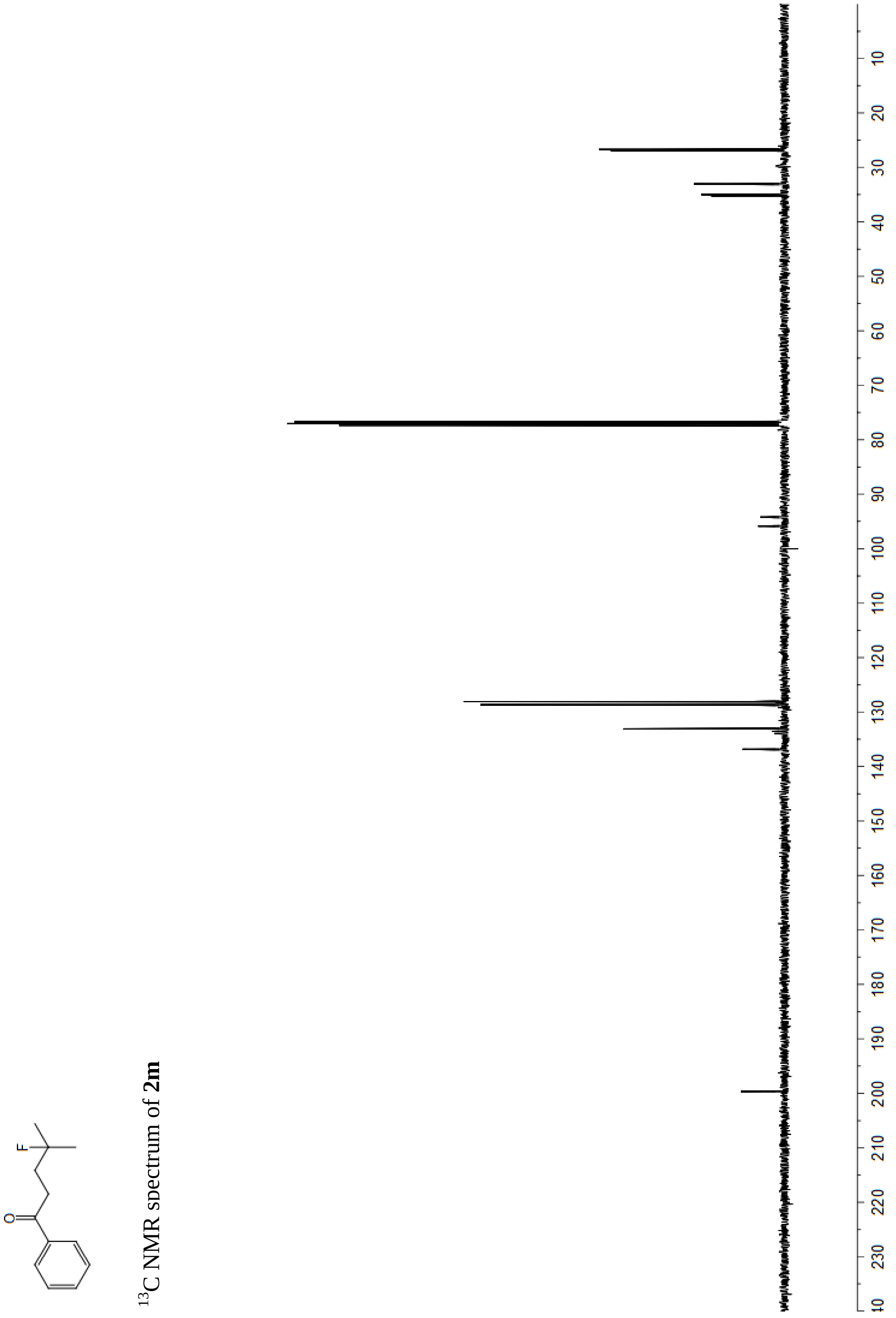


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2l**

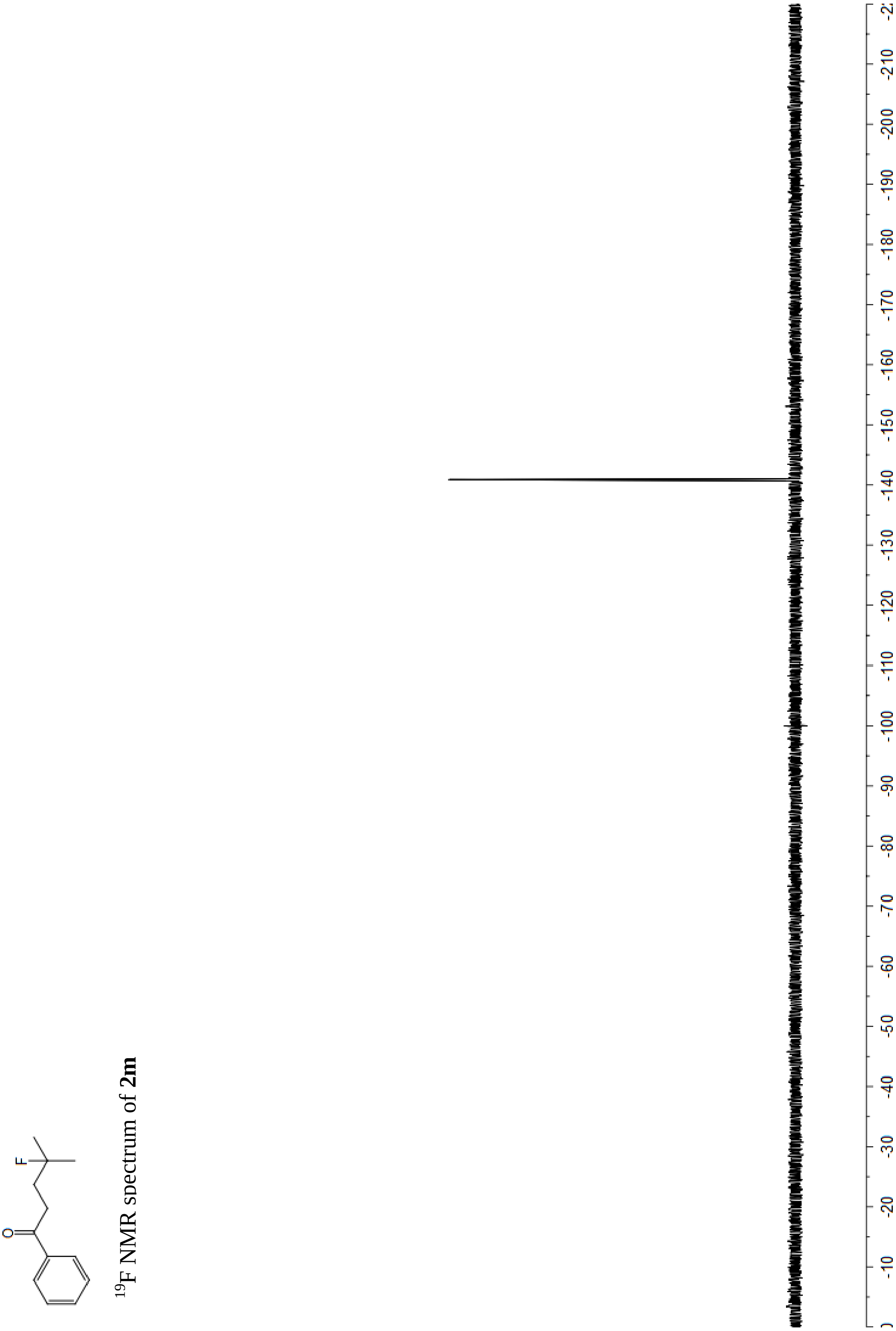


^{1}H NMR spectrum of **2m**

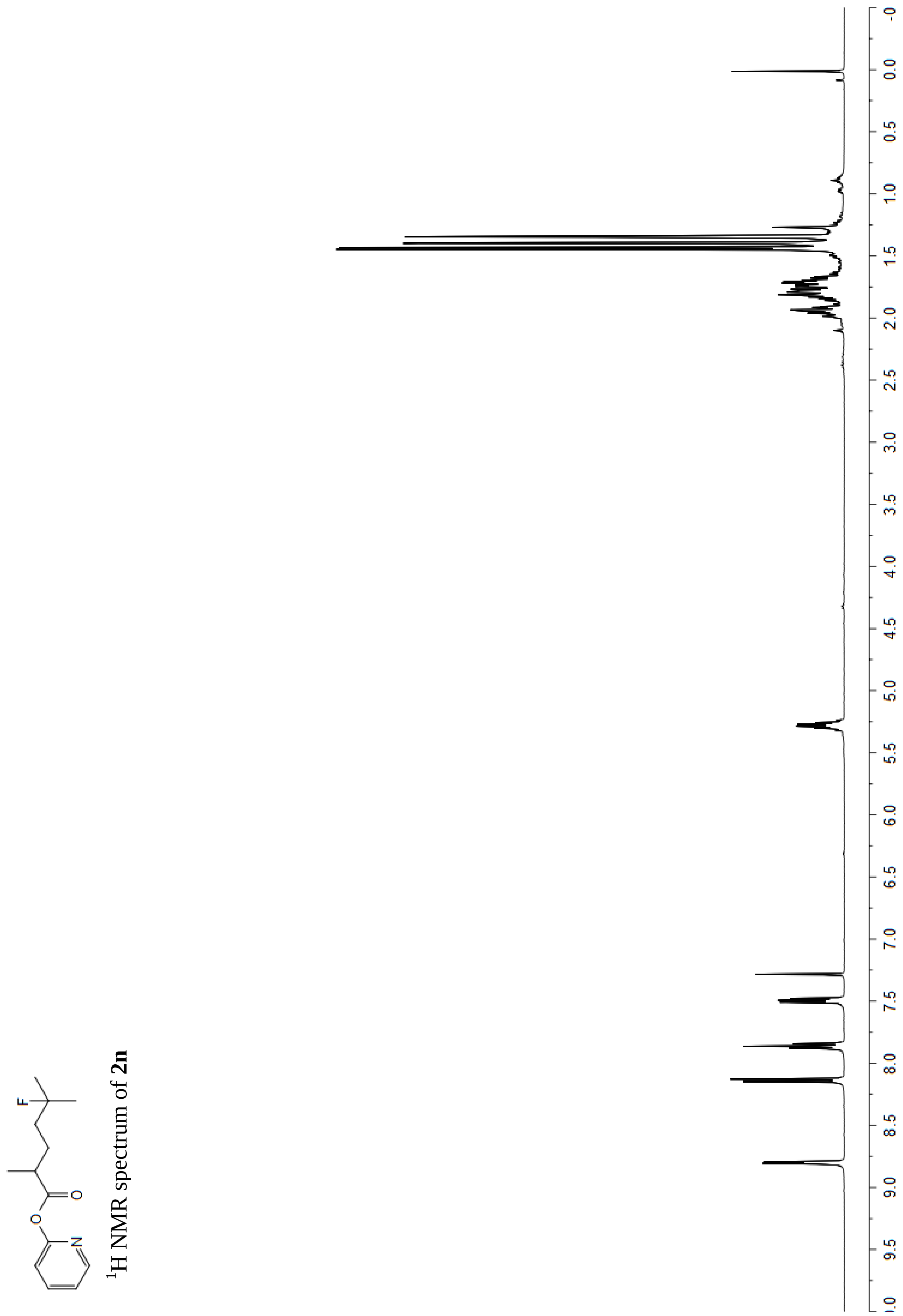
^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23 ℃) of **2m**



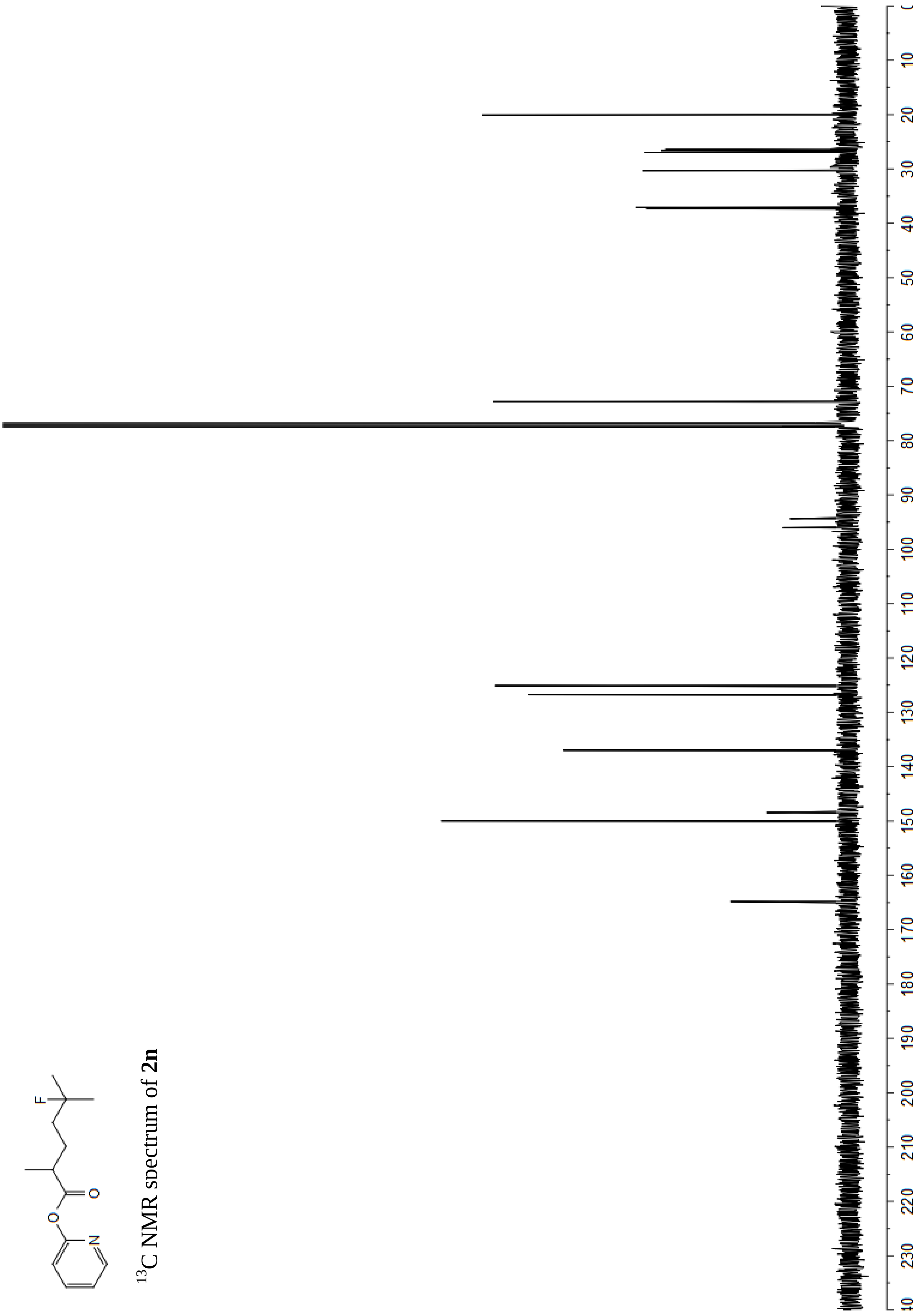
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 °C) of **2m**



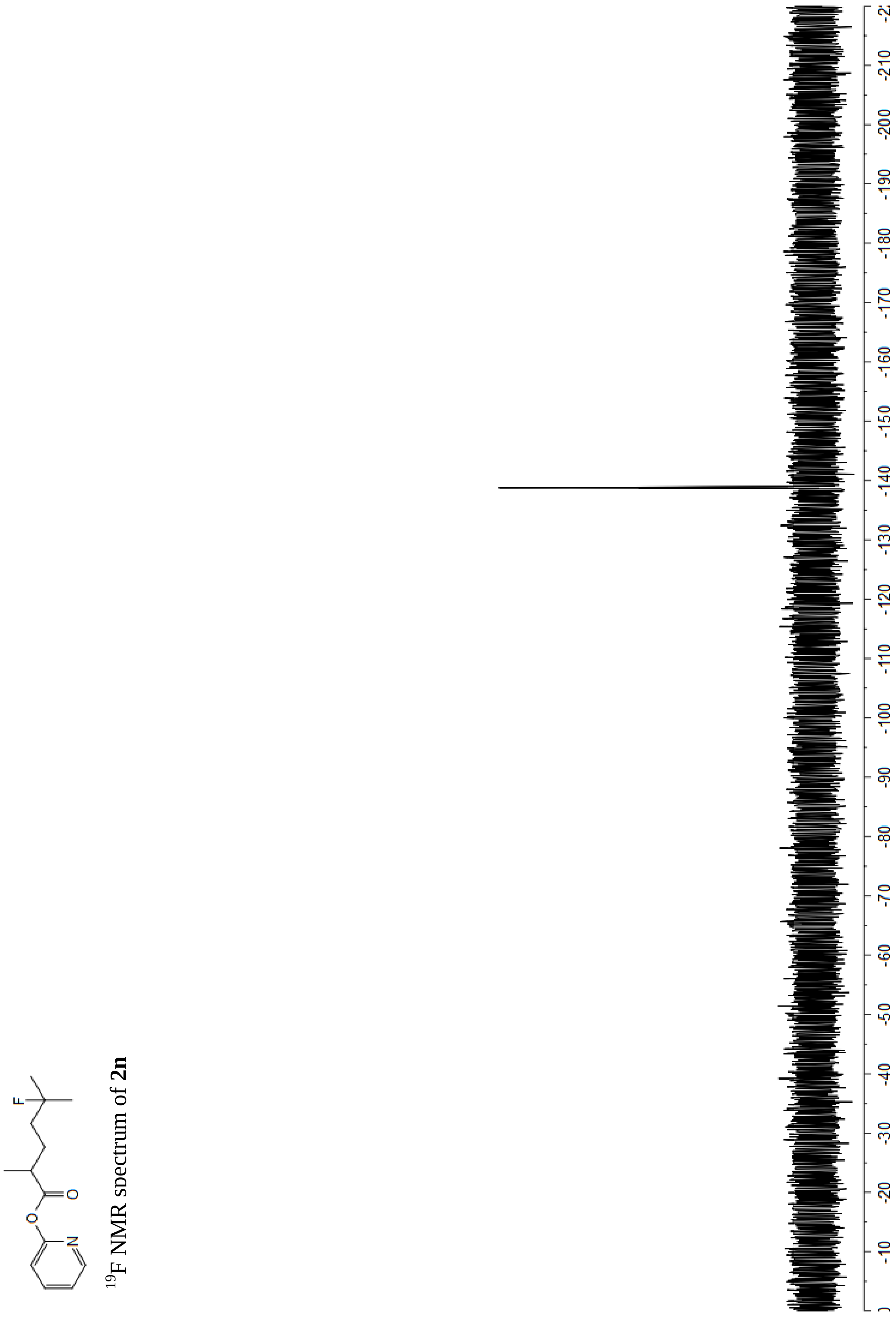
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2m**



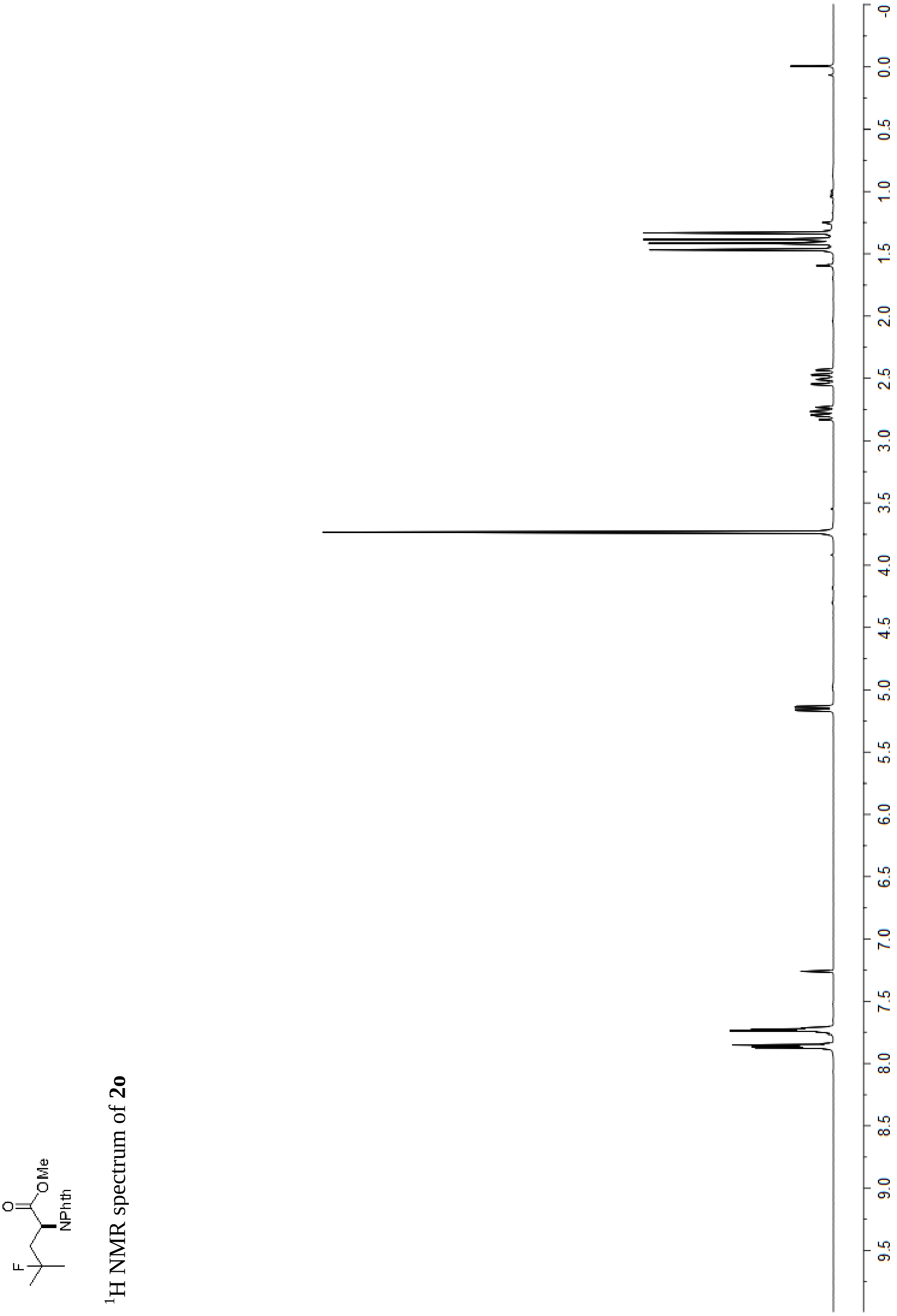
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2n**



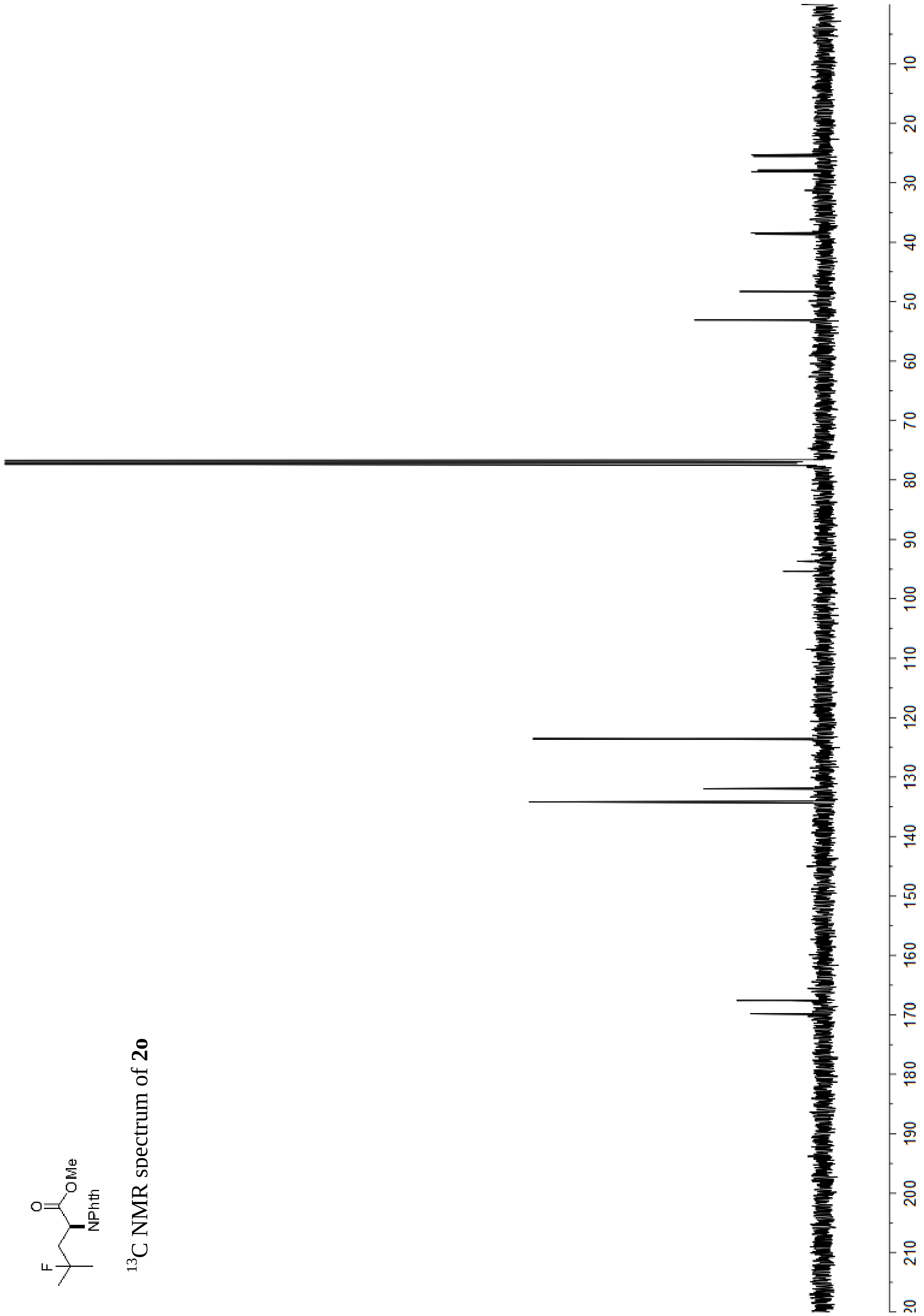
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2n**



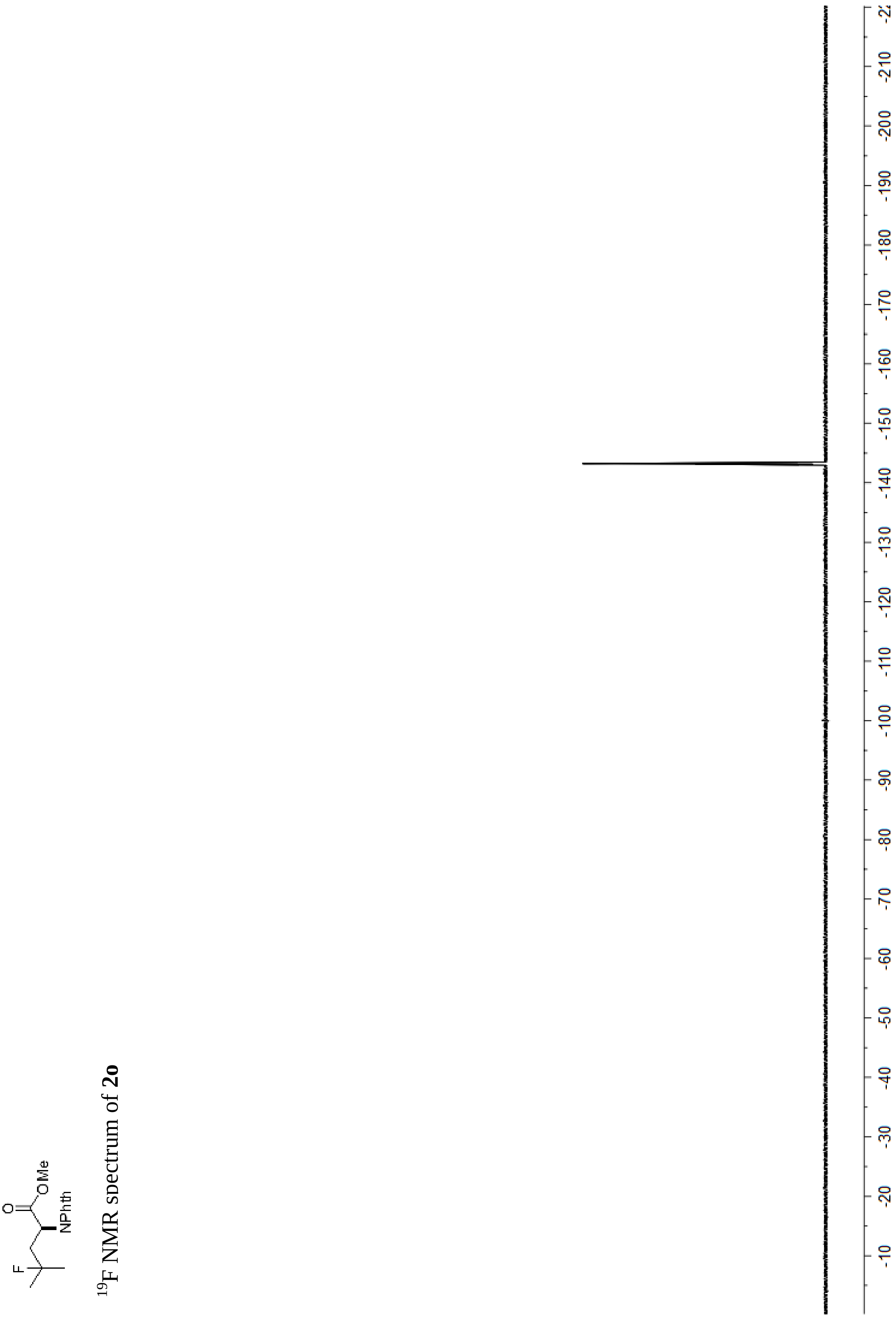
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2n**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2o**

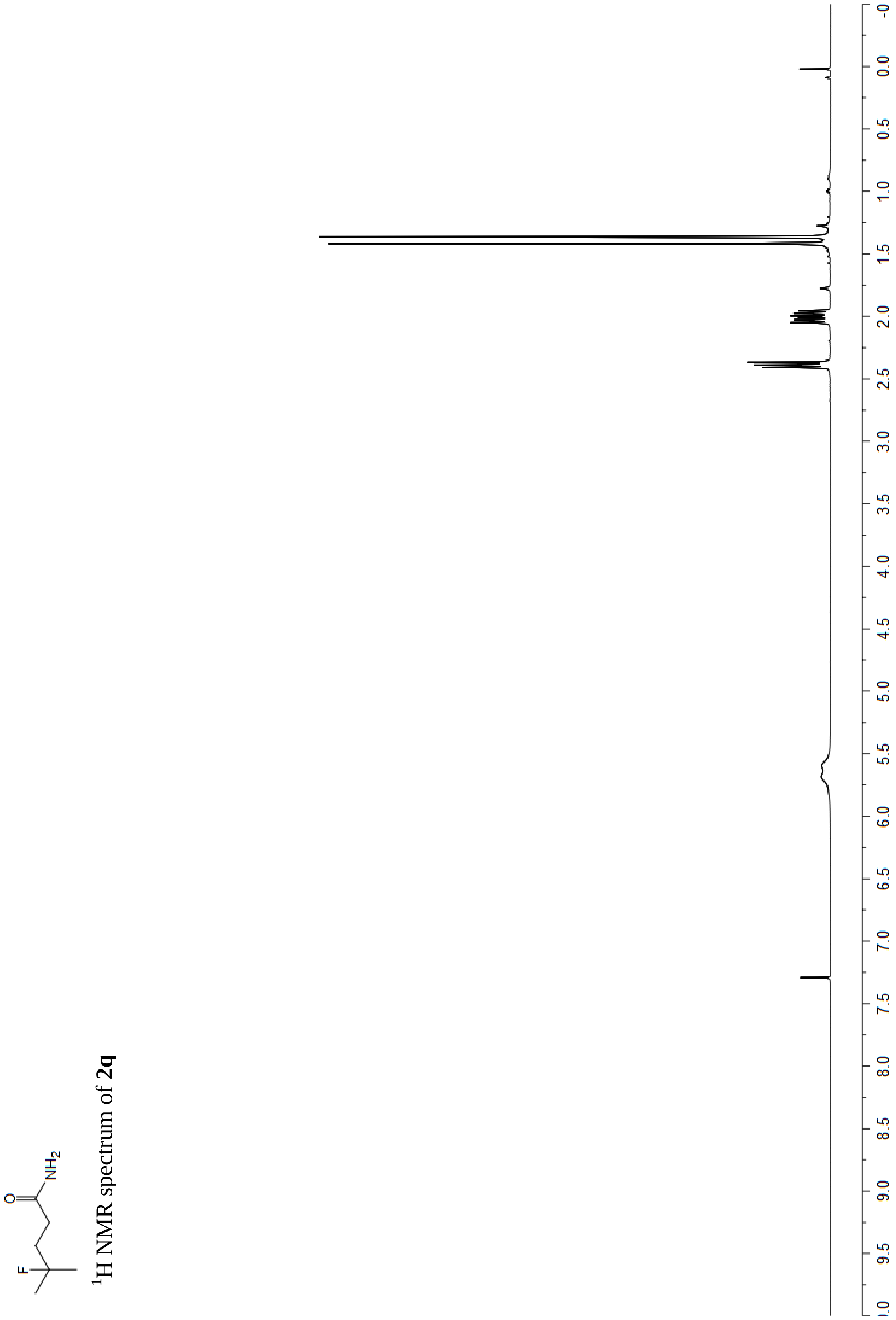


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2o**

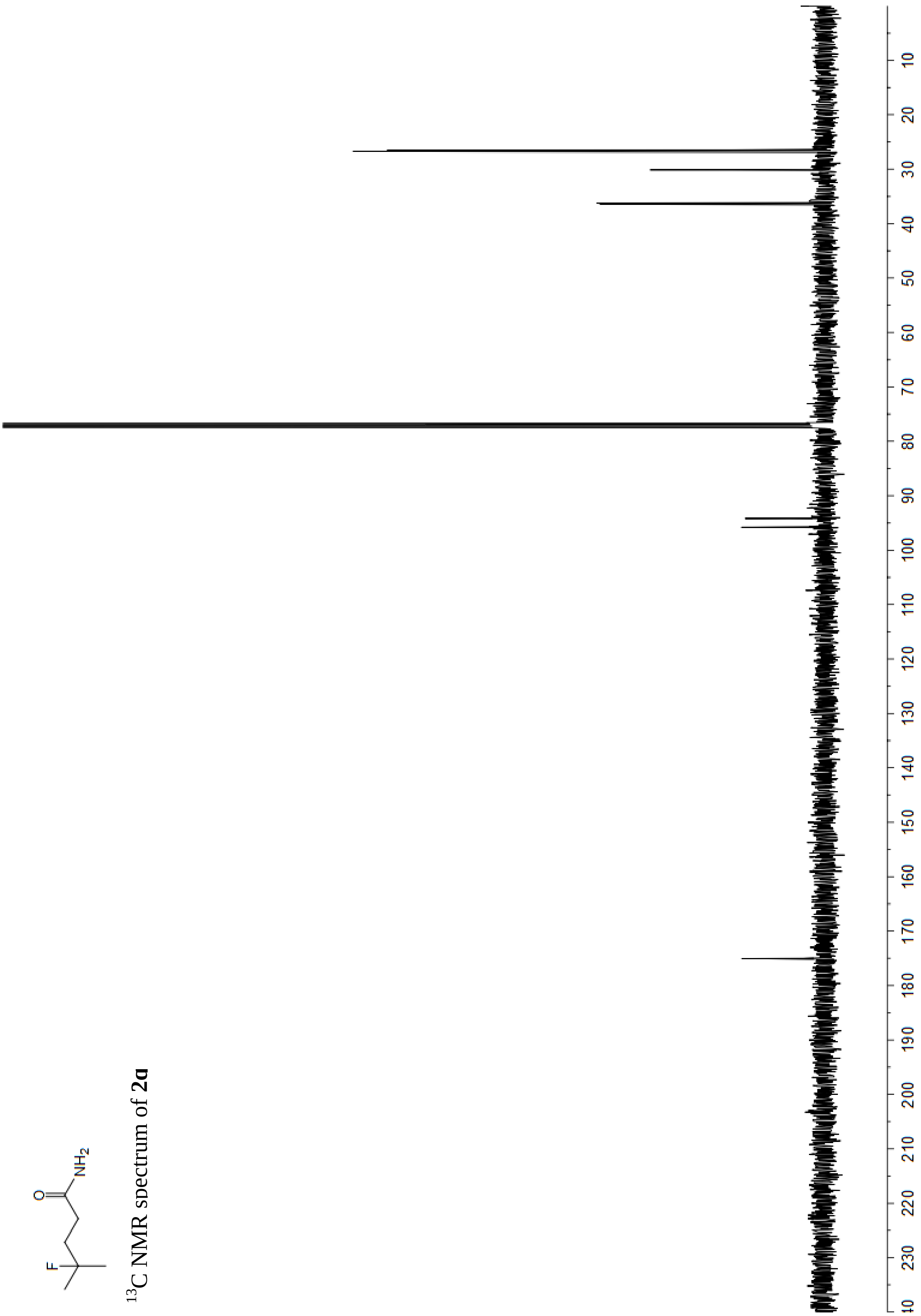


^{19}F NMR spectrum of **2o**

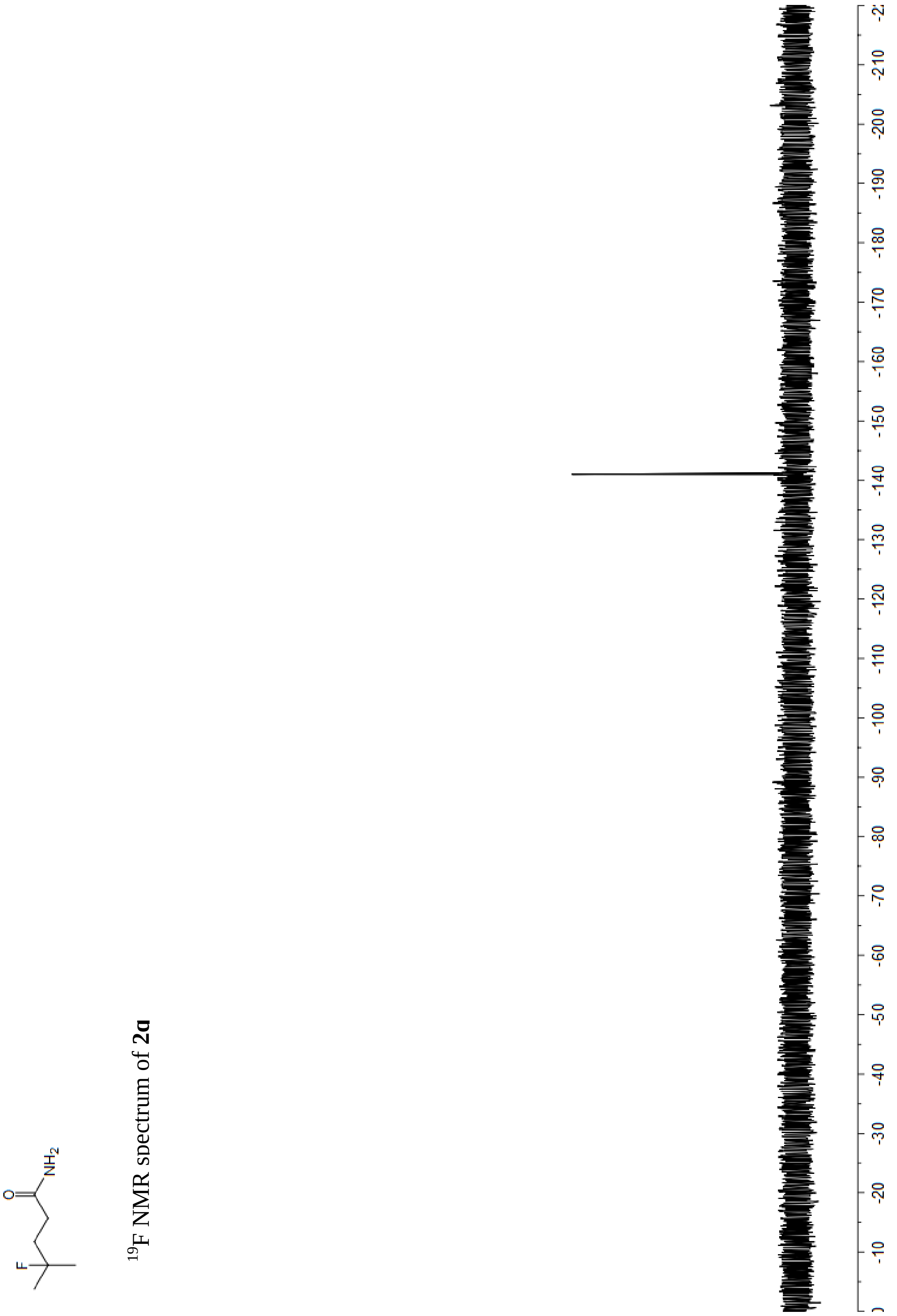
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2o**



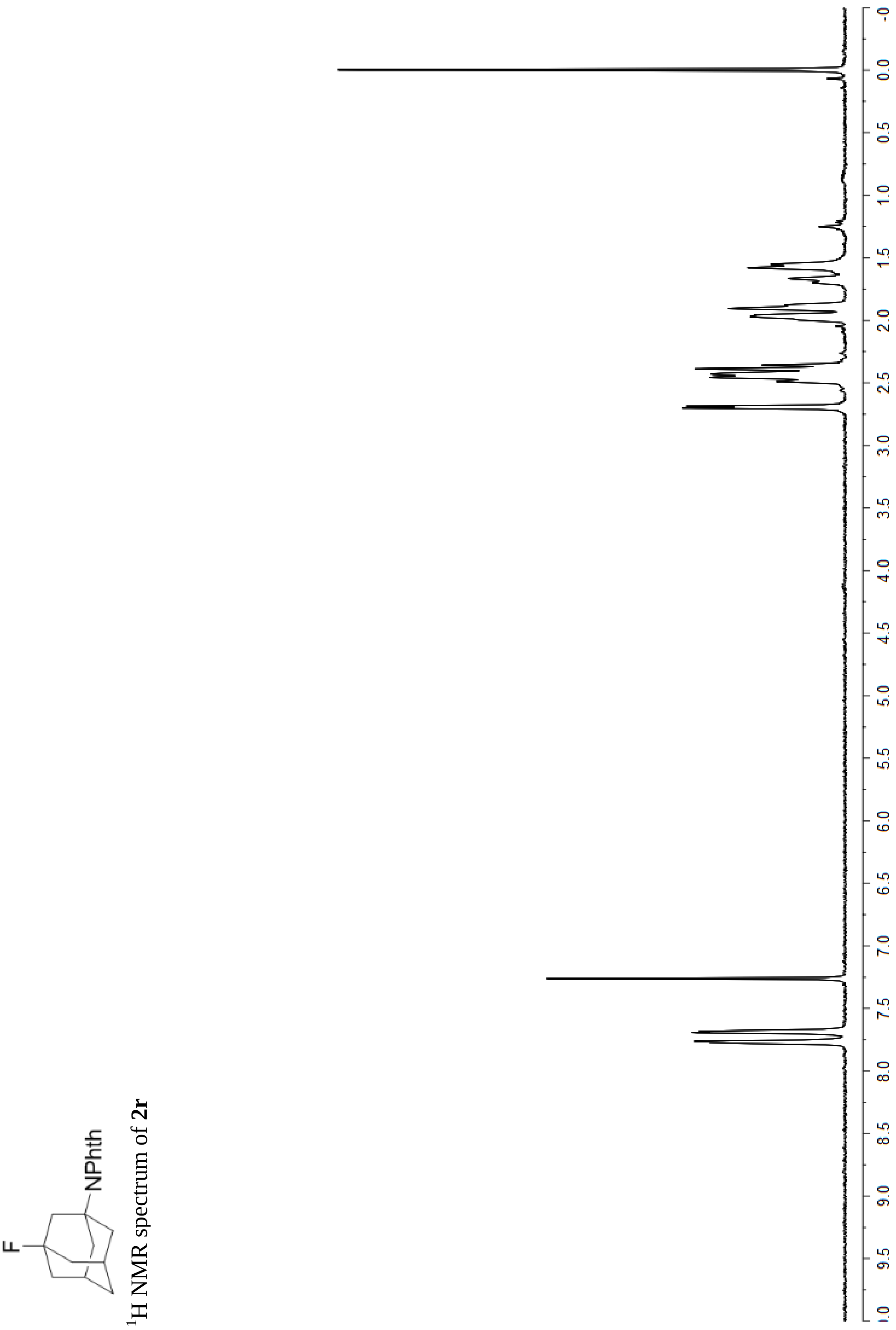
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2q**



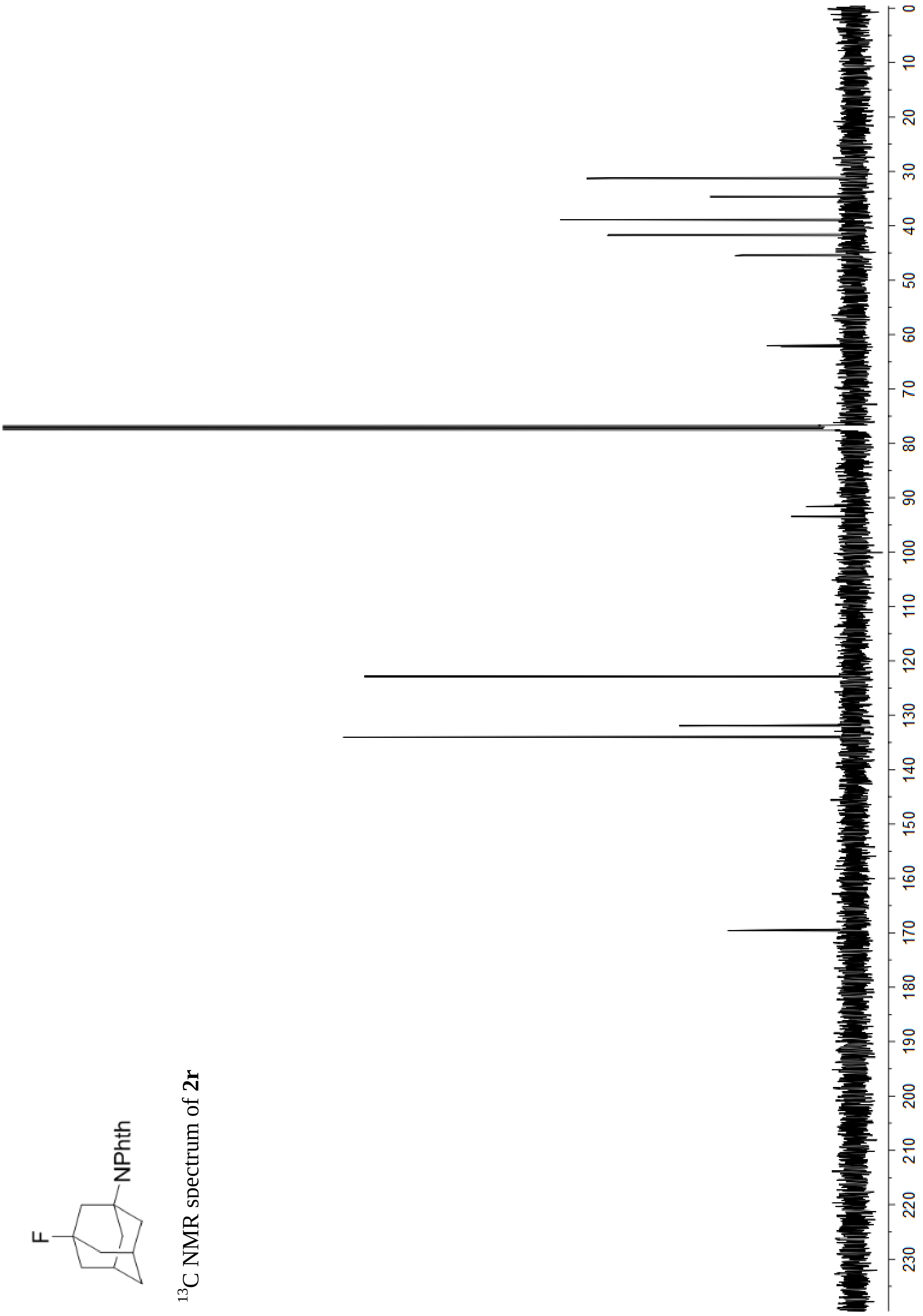
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2q**



^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2q**

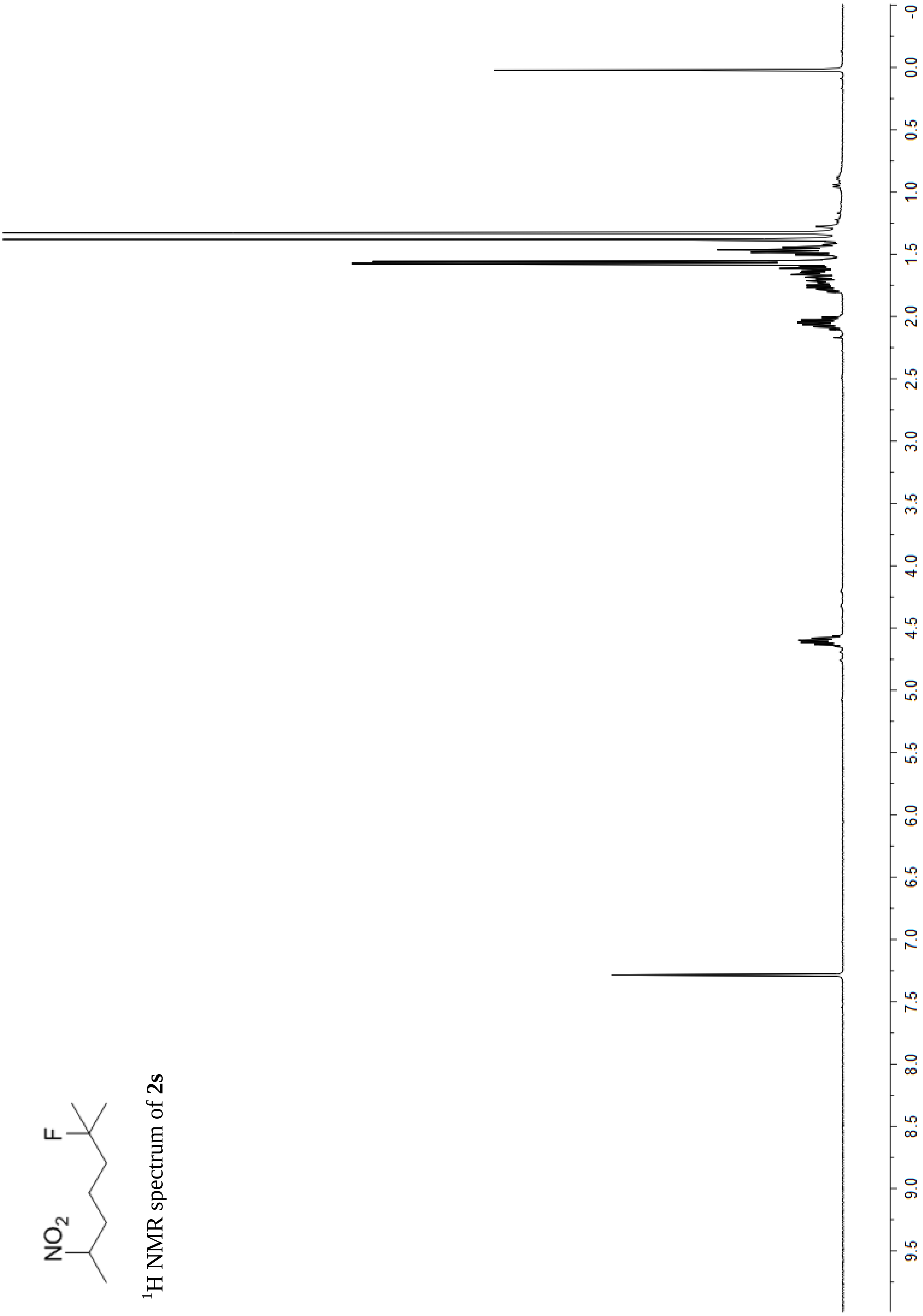


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2r**

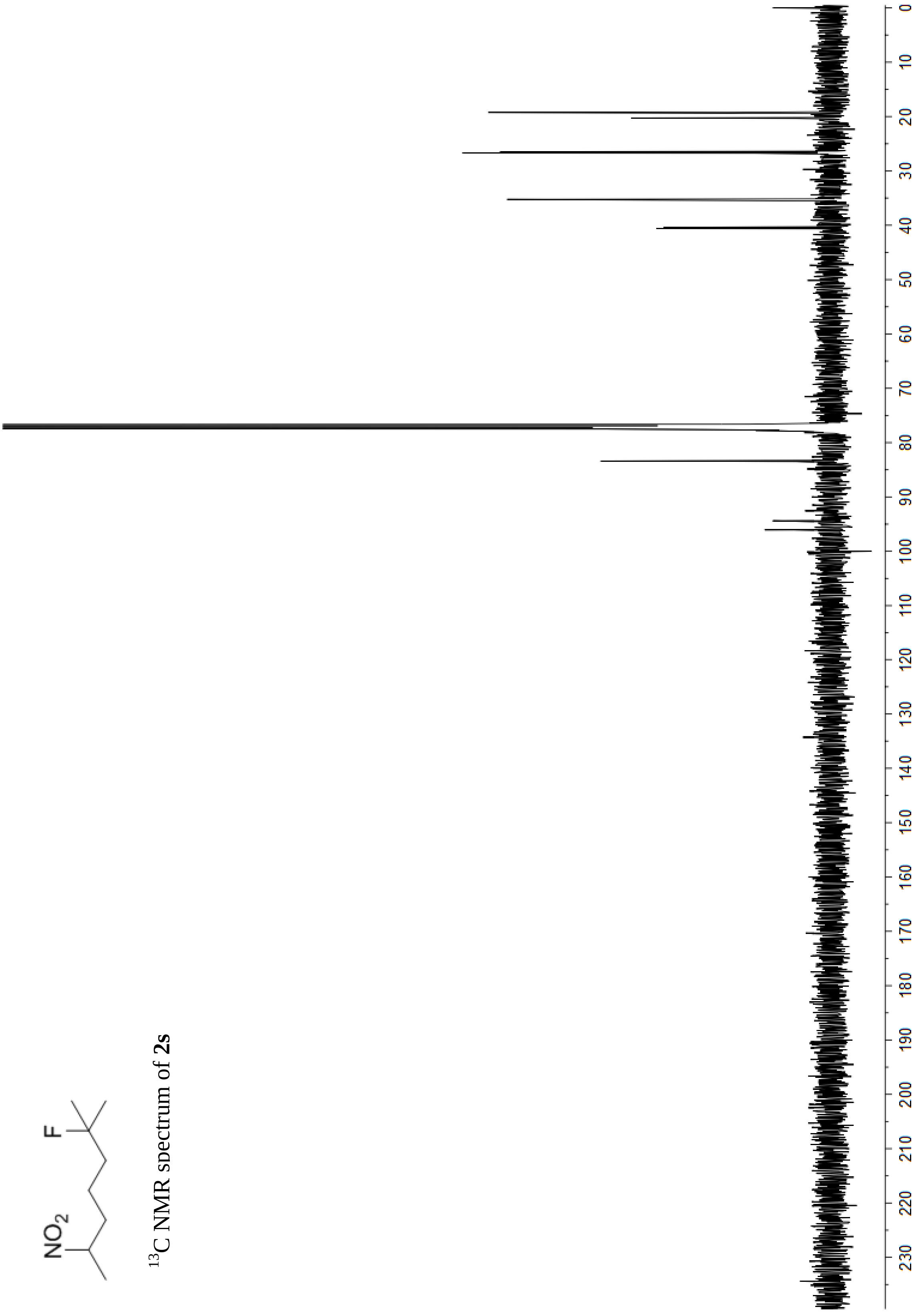


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **2r**

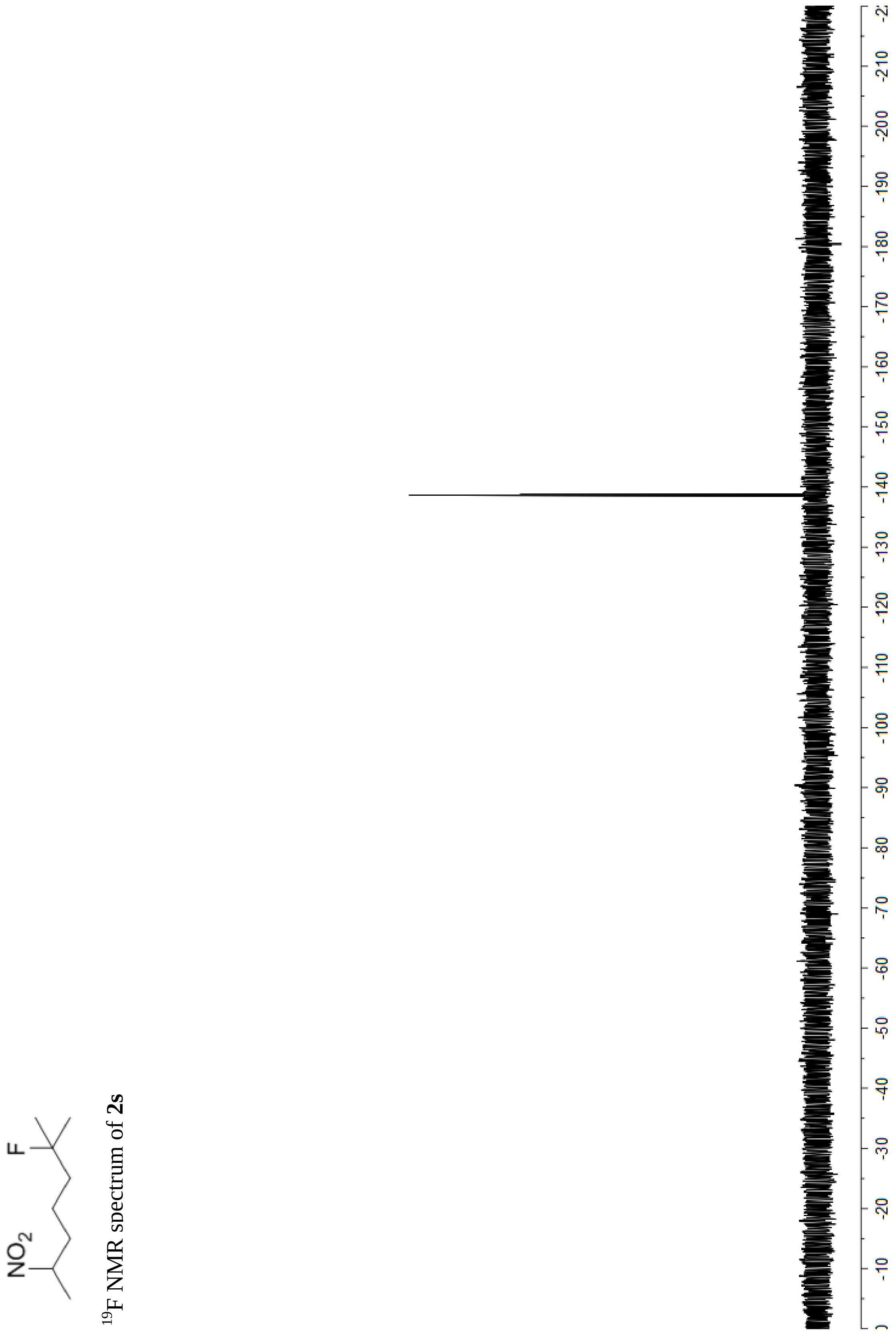
^{19}FNMR spectrum (375 MHz, CDCl$_3$, 23 ℃) of **2r**



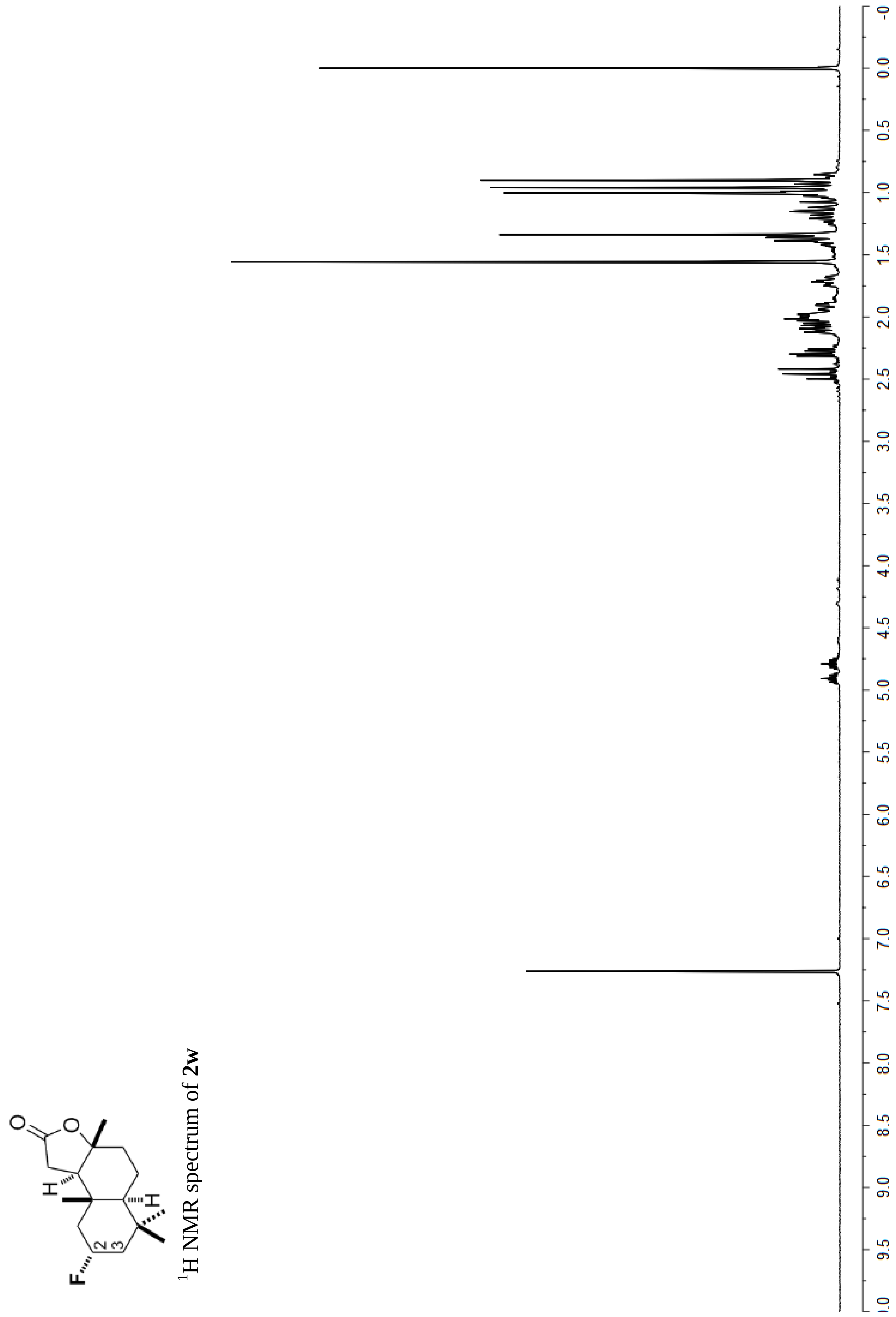
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **2s**



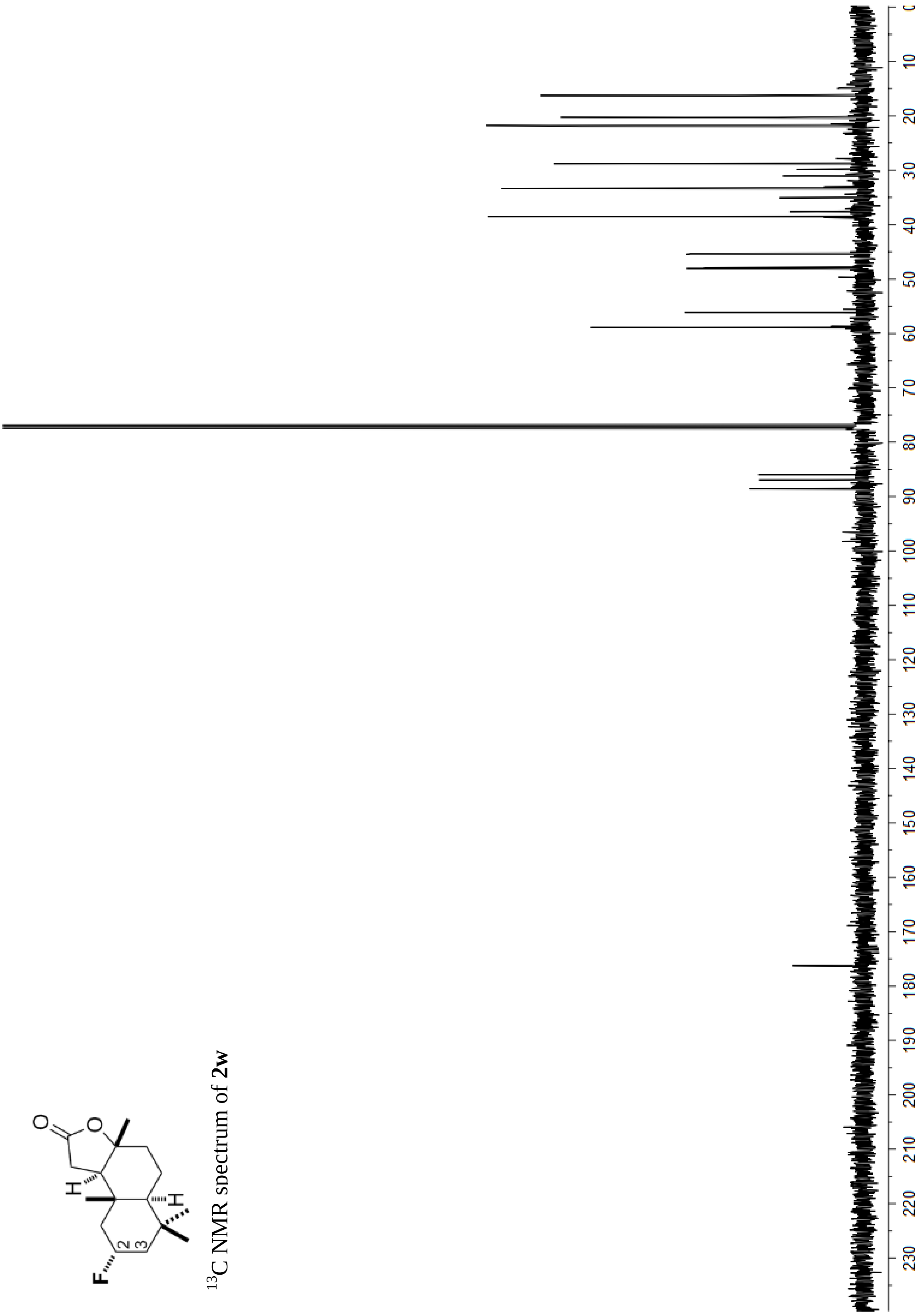
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2s**



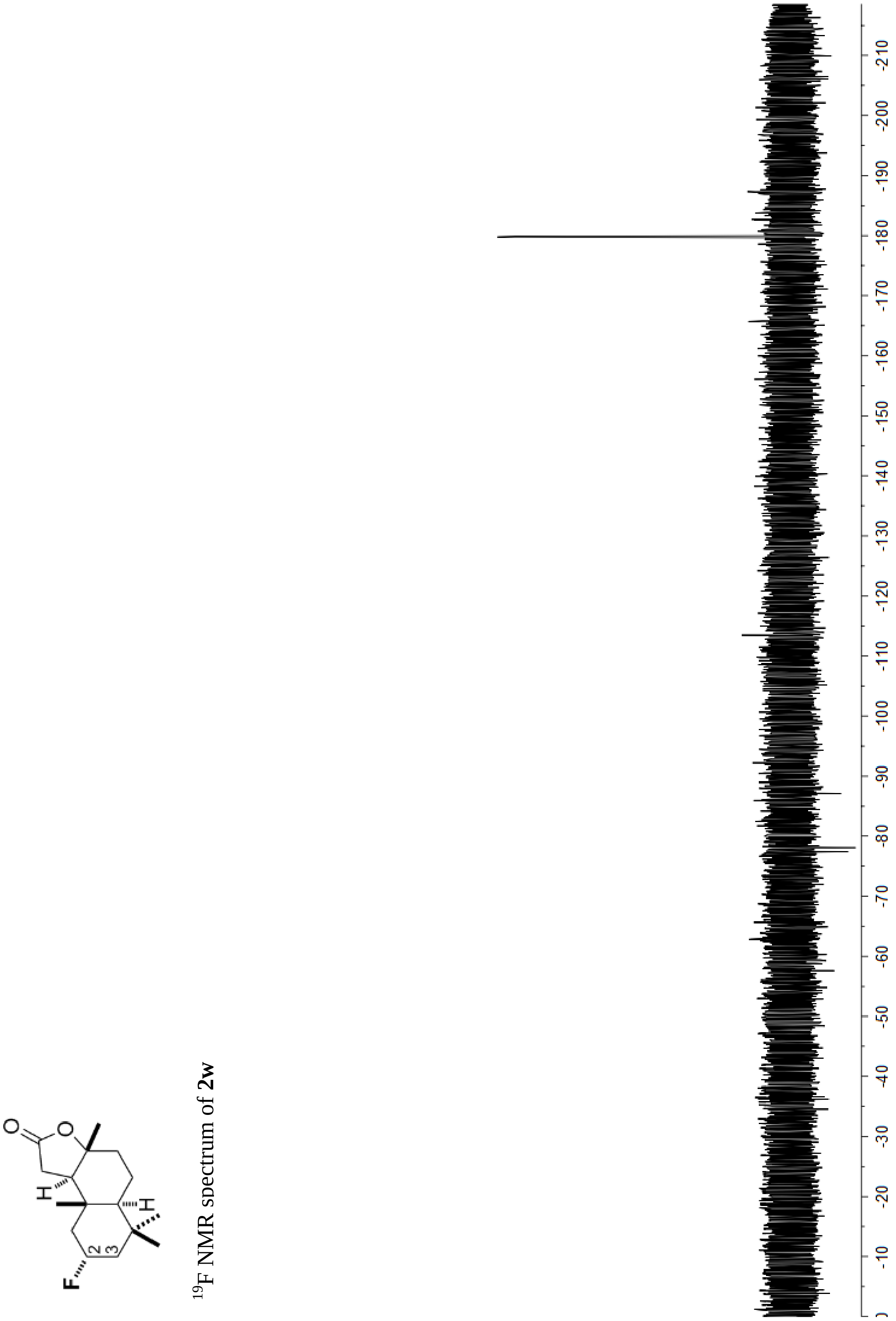
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2s**



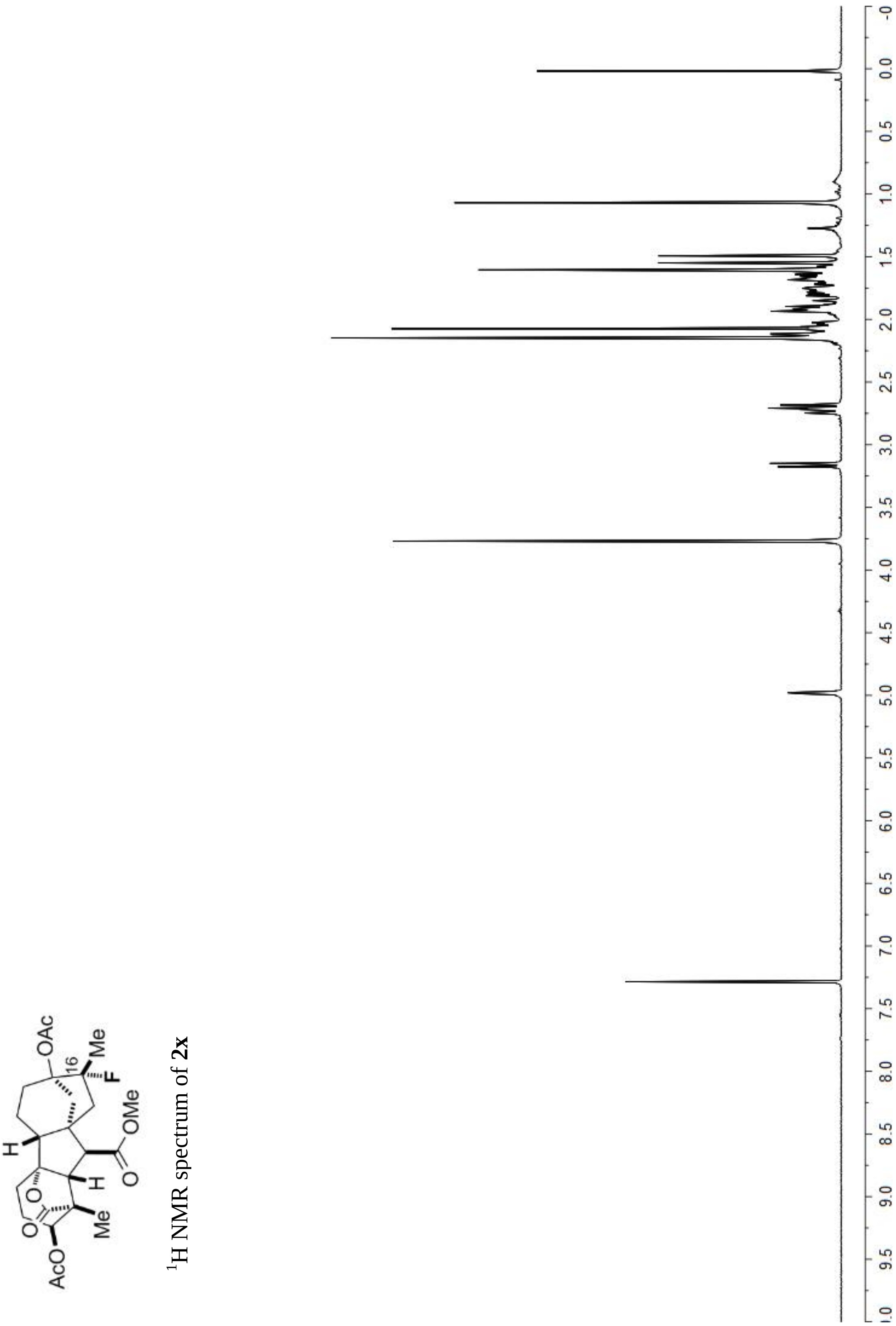
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of **2w**



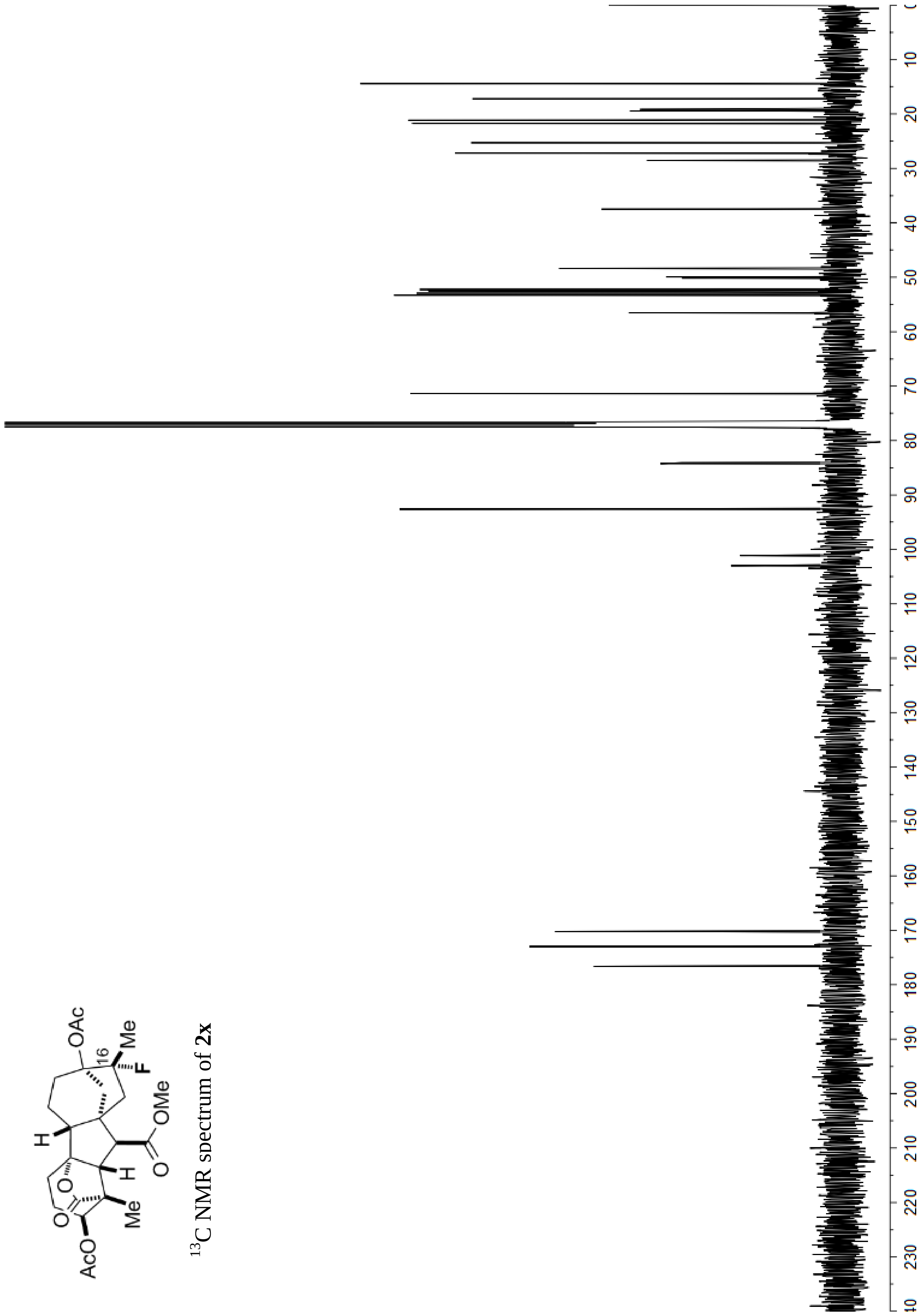
^{13}C NMR spectrum (101 MHz, CDCl$_3$, 23 ℃) of **2w**



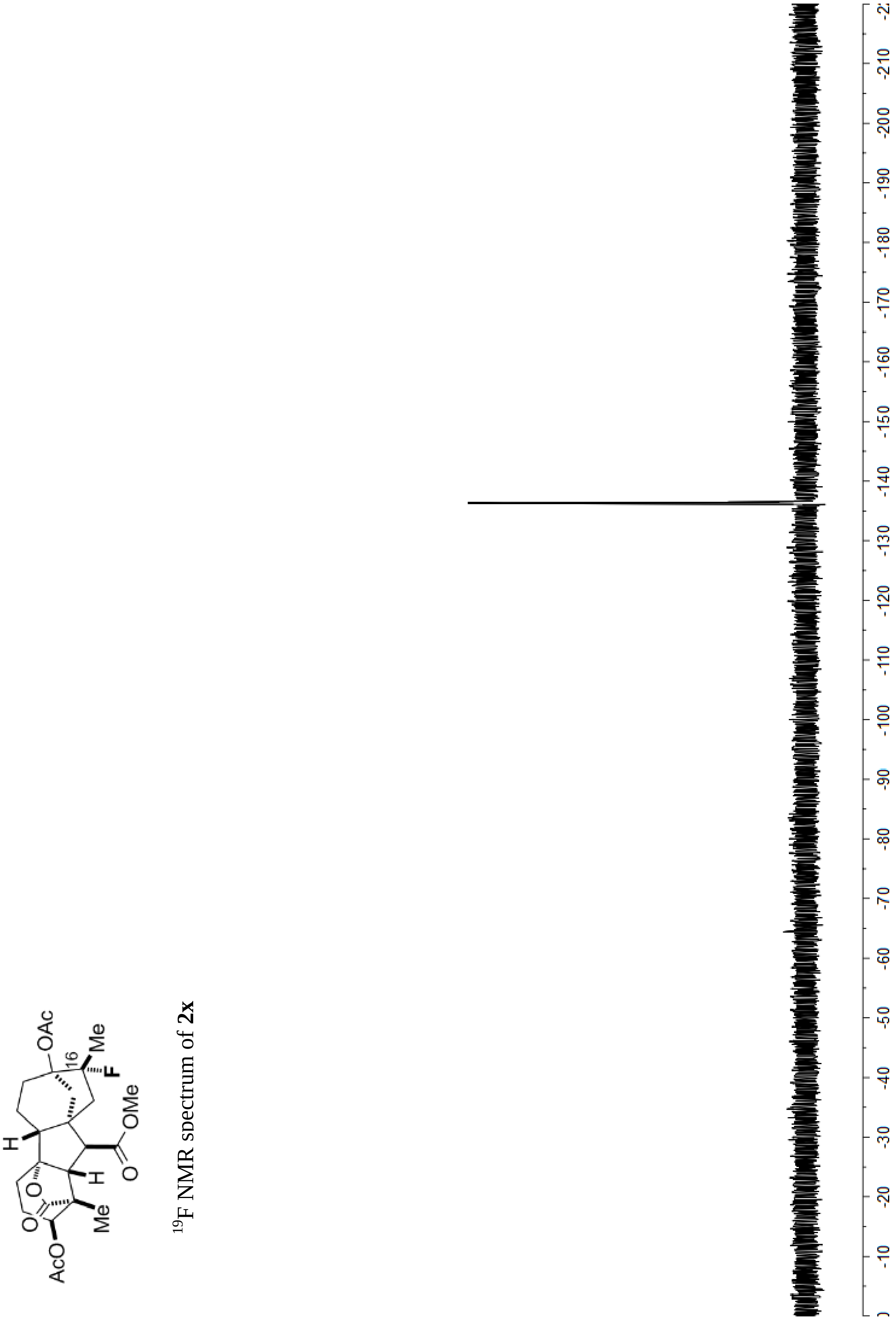
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2w**



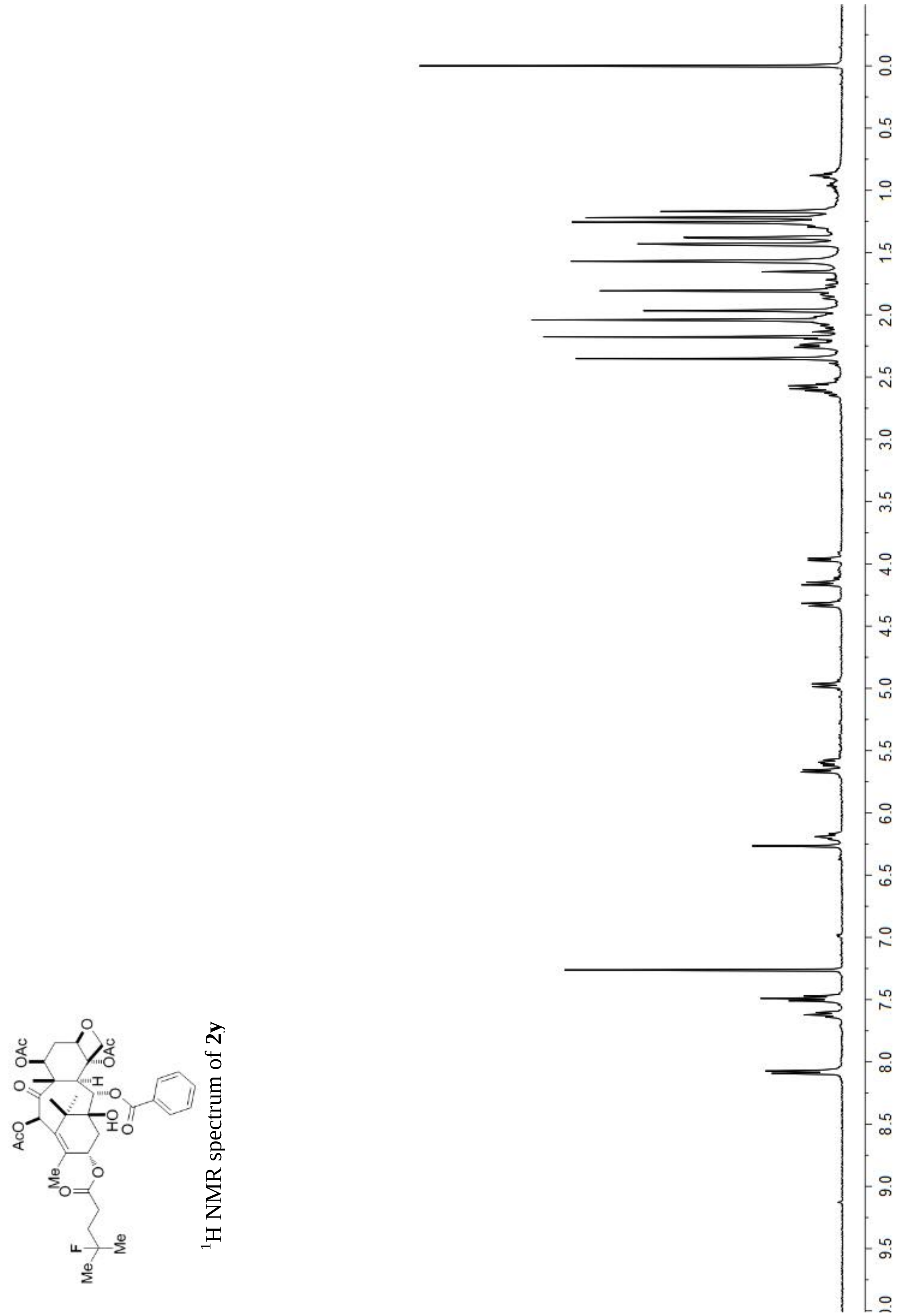
^{1}H NMR spectrum (400 MHz, CDCl$_3$, 23 ℃) of **2x**



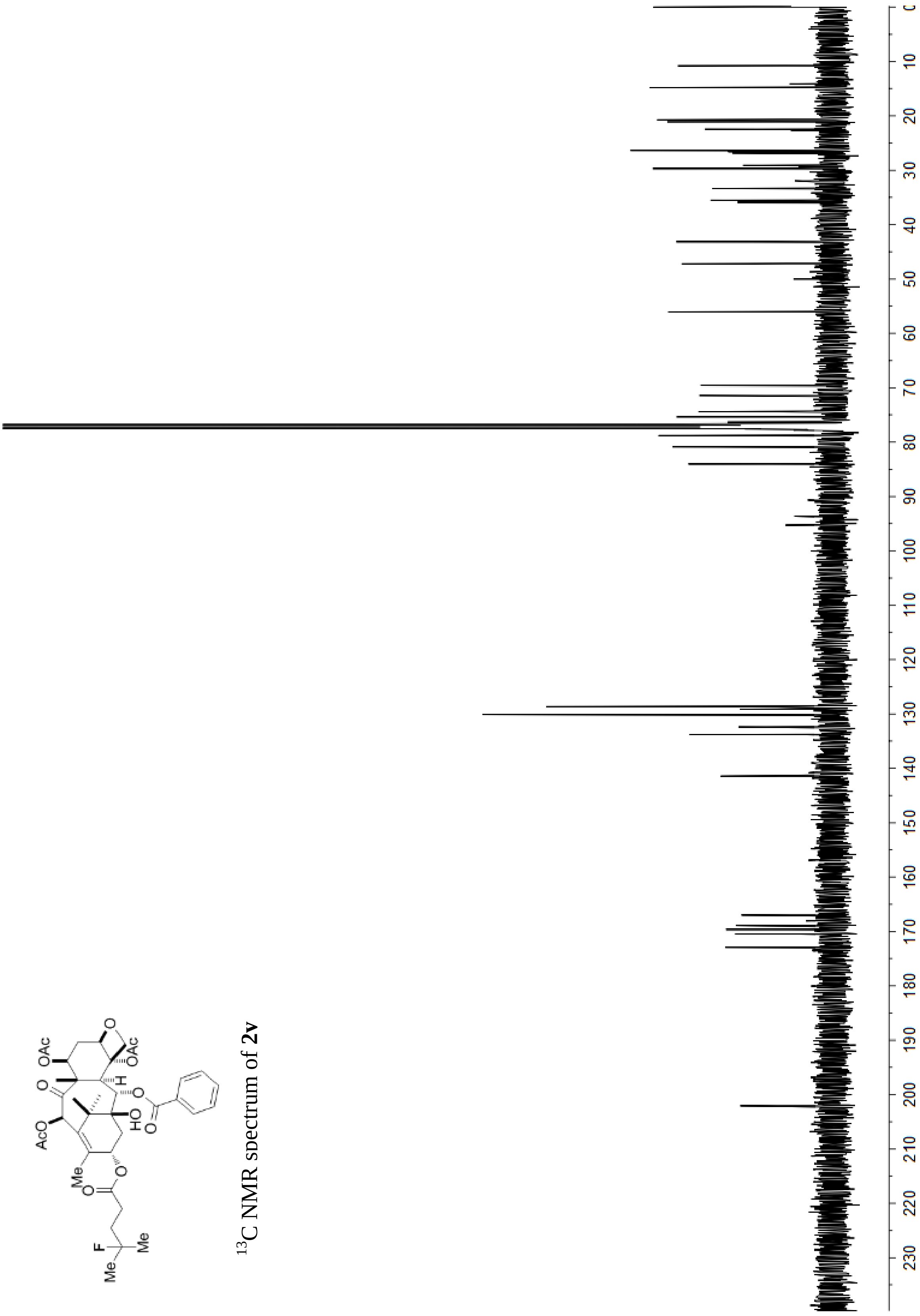
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 °C) of **2x**



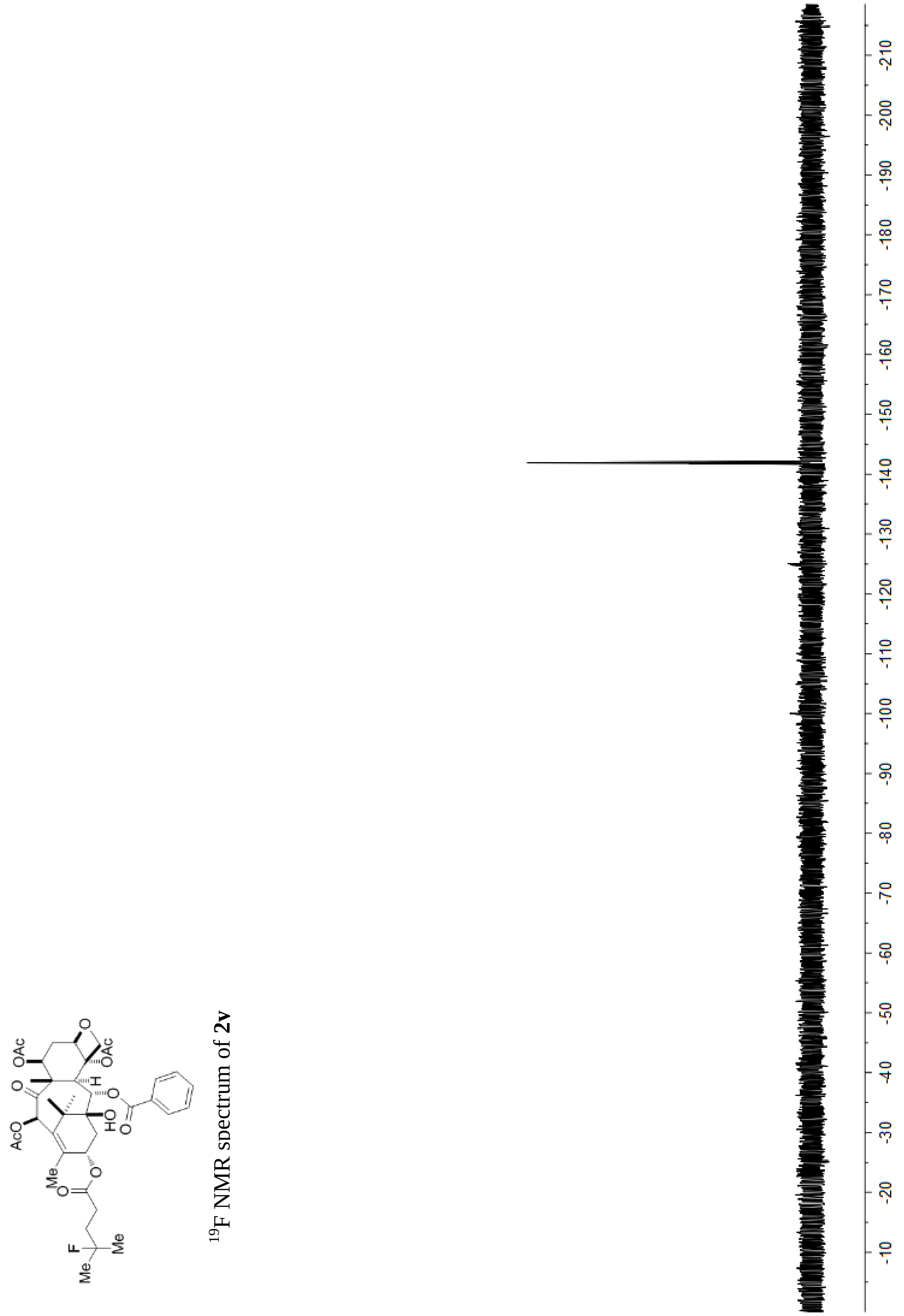
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2x**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of **2y**



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 °C) of **2y**



^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **2y**

X-ray Crystal Structure Data

X-ray Crystal Structure Data for 2α-Fluorosclareolide (2w)

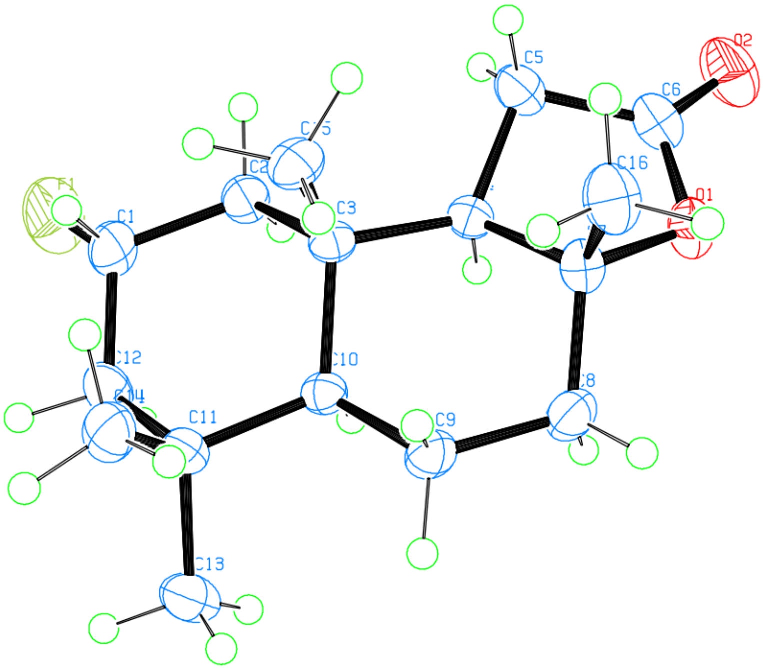


Table S11. Crystal data and structure refinement for R131219D1.

Identification code	r131219d1
Empirical formula	C16 H25 F O2
Formula weight	268.36
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.9958(12) A alpha = 90 deg.
	b = 13.644(3) A beta = 90 deg.
	c = 17.789(4) A gamma = 90 deg.
Volume	1455.2(5) A^3
Z, Calculated density	4, 1.225 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	584
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	1.88 to 27.98 deg.
Limiting indices	-7<=h<=7, -17<=k<=17, -23<=l<=23
Reflections collected / unique	17044 / 3480 [R(int) = 0.0470]

Completeness to theta =	27.98 99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9896 and 0.9828
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3480 / 0 / 177
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.1577
R indices (all data)	R1 = 0.0574, wR2 = 0.1600
Absolute structure parameter	-1.0(12)
Extinction coefficient	0.063(11)
Largest diff. peak and hole	1.024 and -0.251 e.A^-3

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for R131219D1. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	9019(4)	1691(1)	5863(1)	60(1)
O(1)	6716(3)	1267(1)	1960(1)	35(1)
O(2)	5472(3)	2801(1)	1833(1)	50(1)
C(1)	9864(4)	1155(1)	5251(1)	33(1)
C(2)	8948(4)	1601(1)	4530(1)	29(1)
C(3)	9616(3)	1005(1)	3829(1)	22(1)
C(4)	8138(3)	1335(1)	3166(1)	23(1)
C(5)	7969(4)	2388(2)	2883(1)	33(1)
C(6)	6591(4)	2226(2)	2174(1)	34(1)
C(7)	8402(3)	761(1)	2430(1)	27(1)
C(8)	7782(4)	-300(2)	2573(1)	32(1)
C(9)	9178(4)	-703(1)	3235(1)	29(1)
C(10)	8919(3)	-92(1)	3956(1)	22(1)
C(11)	9830(3)	-573(1)	4689(1)	28(1)
C(12)	9170(4)	97(2)	5354(1)	33(1)
C(13)	8677(4)	-1567(2)	4810(1)	41(1)
C(14)	12367(4)	-760(2)	4692(1)	34(1)
C(15)	12121(3)	1172(2)	3664(1)	30(1)
C(16)	10589(4)	847(2)	1992(1)	38(1)

Table S13. Bond lengths [A] and angles [deg] for R131219D1.

F(1)-C(1)	1.406(2)
O(1)-C(6)	1.364(3)
O(1)-C(7)	1.483(2)
O(2)-C(6)	1.198(3)
C(1)-C(12)	1.512(3)
C(1)-C(2)	1.522(3)
C(1)-H(1)	1.0000
C(2)-C(3)	1.542(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.541(2)
C(3)-C(15)	1.547(2)
C(3)-C(10)	1.570(2)
C(4)-C(5)	1.526(3)
C(4)-C(7)	1.534(2)
C(4)-H(4)	1.0000
C(5)-C(6)	1.525(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(7)-C(8)	1.516(3)
C(7)-C(16)	1.531(3)
C(8)-C(9)	1.546(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.538(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.558(2)
C(10)-H(10)	1.0000
C(11)-C(13)	1.538(3)
C(11)-C(14)	1.542(3)
C(11)-C(12)	1.546(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9800

C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(6)-O(1)-C(7)	109.02(15)
F(1)-C(1)-C(12)	107.69(18)
F(1)-C(1)-C(2)	108.31(16)
C(12)-C(1)-C(2)	112.61(17)
F(1)-C(1)-H(1)	109.4
C(12)-C(1)-H(1)	109.4
C(2)-C(1)-H(1)	109.4
C(1)-C(2)-C(3)	112.16(15)
C(1)-C(2)-H(2A)	109.2
C(3)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2B)	109.2
C(3)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
C(4)-C(3)-C(2)	108.38(14)
C(4)-C(3)-C(15)	111.70(14)
C(2)-C(3)-C(15)	109.13(16)
C(4)-C(3)-C(10)	103.67(13)
C(2)-C(3)-C(10)	108.44(14)
C(15)-C(3)-C(10)	115.22(15)
C(5)-C(4)-C(7)	101.86(14)
C(5)-C(4)-C(3)	124.45(15)
C(7)-C(4)-C(3)	116.36(15)
C(5)-C(4)-H(4)	104.0
C(7)-C(4)-H(4)	104.0
C(3)-C(4)-H(4)	104.0
C(6)-C(5)-C(4)	99.92(16)

C(6)-C(5)-H(5A)	111.8
C(4)-C(5)-H(5A)	111.8
C(6)-C(5)-H(5B)	111.8
C(4)-C(5)-H(5B)	111.8
H(5A)-C(5)-H(5B)	109.5
O(2)-C(6)-O(1)	121.2(2)
O(2)-C(6)-C(5)	128.9(2)
O(1)-C(6)-C(5)	109.92(16)
O(1)-C(7)-C(8)	111.83(16)
O(1)-C(7)-C(16)	105.11(15)
C(8)-C(7)-C(16)	111.61(17)
O(1)-C(7)-C(4)	100.04(14)
C(8)-C(7)-C(4)	108.61(15)
C(16)-C(7)-C(4)	118.98(17)
C(7)-C(8)-C(9)	109.55(16)
C(7)-C(8)-H(8A)	109.8
C(9)-C(8)-H(8A)	109.8
C(7)-C(8)-H(8B)	109.8
C(9)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.2
C(10)-C(9)-C(8)	112.86(15)
C(10)-C(9)-H(9A)	109.0
C(8)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9B)	109.0
C(8)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(9)-C(10)-C(11)	115.73(14)
C(9)-C(10)-C(3)	111.66(14)
C(11)-C(10)-C(3)	115.43(14)
C(9)-C(10)-H(10)	104.1
C(11)-C(10)-H(10)	104.1
C(3)-C(10)-H(10)	104.1
C(13)-C(11)-C(14)	107.28(17)
C(13)-C(11)-C(12)	107.46(17)
C(14)-C(11)-C(12)	110.32(17)
C(13)-C(11)-C(10)	109.32(16)
C(14)-C(11)-C(10)	114.74(17)

C(12)-C(11)-C(10)	107.50(14)
C(1)-C(12)-C(11)	113.65(16)
C(1)-C(12)-H(12A)	108.8
C(11)-C(12)-H(12A)	108.8
C(1)-C(12)-H(12B)	108.8
C(11)-C(12)-H(12B)	108.8
H(12A)-C(12)-H(12B)	107.7
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(3)-C(15)-H(15A)	109.5
C(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(7)-C(16)-H(16A)	109.5
C(7)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(7)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters (A^2 x 10^3) for R131219D1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	93(1)	55(1)	33(1)	-12(1)	1(1)	20(1)
O(1)	37(1)	40(1)	27(1)	1(1)	-6(1)	6(1)
O(2)	57(1)	49(1)	44(1)	14(1)	-5(1)	17(1)
C(1)	44(1)	31(1)	24(1)	-8(1)	-1(1)	5(1)
C(2)	35(1)	24(1)	26(1)	-3(1)	0(1)	3(1)
C(3)	20(1)	22(1)	24(1)	-1(1)	3(1)	-2(1)
C(4)	21(1)	23(1)	24(1)	1(1)	2(1)	0(1)
C(5)	38(1)	29(1)	30(1)	6(1)	1(1)	3(1)
C(6)	37(1)	37(1)	29(1)	7(1)	2(1)	5(1)
C(7)	28(1)	31(1)	23(1)	0(1)	-2(1)	3(1)
C(8)	36(1)	28(1)	31(1)	-6(1)	-6(1)	0(1)
C(9)	33(1)	22(1)	32(1)	-5(1)	-5(1)	2(1)
C(10)	20(1)	21(1)	26(1)	0(1)	0(1)	-1(1)
C(11)	29(1)	24(1)	31(1)	4(1)	-3(1)	1(1)
C(12)	40(1)	35(1)	24(1)	4(1)	2(1)	6(1)
C(13)	45(1)	29(1)	47(1)	10(1)	-5(1)	-4(1)
C(14)	31(1)	32(1)	38(1)	-1(1)	-9(1)	7(1)
C(15)	22(1)	33(1)	35(1)	-1(1)	1(1)	-6(1)
C(16)	40(1)	49(1)	27(1)	-3(1)	8(1)	5(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for R131219D1.

	x	y	z	U(eq)
H(1)	11528	1198	5248	40
H(2A)	9516	2279	4478	34
H(2B)	7302	1633	4562	34
H(4)	6588	1177	3335	27
H(5A)	7189	2817	3247	39
H(5B)	9454	2667	2767	39
H(8A)	8071	-694	2116	38
H(8B)	6174	-348	2694	38
H(9A)	8715	-1386	3340	35
H(9B)	10770	-714	3088	35
H(10)	7270	-61	4038	26
H(12A)	7531	70	5420	40

H(12B)	9863	-159	5819	40
H(13A)	9333	-2055	4471	61
H(13B)	7080	-1503	4703	61
H(13C)	8884	-1777	5332	61
H(14A)	12757	-1172	5124	50
H(14B)	13158	-133	4729	50
H(14C)	12798	-1093	4226	50
H(15A)	12733	596	3407	45
H(15B)	12921	1277	4137	45
H(15C)	12296	1750	3341	45
H(16A)	10369	604	1478	58
H(16B)	11745	457	2241	58
H(16C)	11055	1535	1975	58

Table S16. Torsion angles [deg] for R131219D1.

F(1)-C(1)-C(2)-C(3)	-174.93(17)
C(12)-C(1)-C(2)-C(3)	-55.9(2)
C(1)-C(2)-C(3)-C(4)	165.07(17)
C(1)-C(2)-C(3)-C(15)	-73.1(2)
C(1)-C(2)-C(3)-C(10)	53.1(2)
C(2)-C(3)-C(4)-C(5)	57.1(2)
C(15)-C(3)-C(4)-C(5)	-63.1(2)
C(10)-C(3)-C(4)-C(5)	172.21(16)
C(2)-C(3)-C(4)-C(7)	-174.69(15)
C(15)-C(3)-C(4)-C(7)	65.0(2)
C(10)-C(3)-C(4)-C(7)	-59.61(19)
C(7)-C(4)-C(5)-C(6)	37.94(18)
C(3)-C(4)-C(5)-C(6)	171.91(17)
C(7)-O(1)-C(6)-O(2)	173.8(2)
C(7)-O(1)-C(6)-C(5)	-8.0(2)
C(4)-C(5)-C(6)-O(2)	158.5(2)
C(4)-C(5)-C(6)-O(1)	-19.5(2)
C(6)-O(1)-C(7)-C(8)	146.77(17)
C(6)-O(1)-C(7)-C(16)	-91.96(18)
C(6)-O(1)-C(7)-C(4)	31.92(19)
C(5)-C(4)-C(7)-O(1)	-42.94(18)

C(3)-C(4)-C(7)-O(1)	178.54(14)
C(5)-C(4)-C(7)-C(8)	-160.21(16)
C(3)-C(4)-C(7)-C(8)	61.3(2)
C(5)-C(4)-C(7)-C(16)	70.7(2)
C(3)-C(4)-C(7)-C(16)	-67.8(2)
O(1)-C(7)-C(8)-C(9)	-163.84(15)
C(16)-C(7)-C(8)-C(9)	78.7(2)
C(4)-C(7)-C(8)-C(9)	-54.4(2)
C(7)-C(8)-C(9)-C(10)	56.2(2)
C(8)-C(9)-C(10)-C(11)	166.83(16)
C(8)-C(9)-C(10)-C(3)	-58.4(2)
C(4)-C(3)-C(10)-C(9)	55.73(18)
C(2)-C(3)-C(10)-C(9)	170.77(15)
C(15)-C(3)-C(10)-C(9)	-66.6(2)
C(4)-C(3)-C(10)-C(11)	-169.36(14)
C(2)-C(3)-C(10)-C(11)	-54.3(2)
C(15)-C(3)-C(10)-C(11)	68.3(2)
C(9)-C(10)-C(11)-C(13)	-57.2(2)
C(3)-C(10)-C(11)-C(13)	169.72(17)
C(9)-C(10)-C(11)-C(14)	63.3(2)
C(3)-C(10)-C(11)-C(14)	-69.7(2)
C(9)-C(10)-C(11)-C(12)	-173.58(16)
C(3)-C(10)-C(11)-C(12)	53.4(2)
F(1)-C(1)-C(12)-C(11)	175.62(17)
C(2)-C(1)-C(12)-C(11)	56.3(2)
C(13)-C(11)-C(12)-C(1)	-170.46(18)
C(14)-C(11)-C(12)-C(1)	72.9(2)
C(10)-C(11)-C(12)-C(1)	-52.9(2)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure Data for 16*β*-Fluorotetrahydrogibberellate diacetate methyl ester (2x)

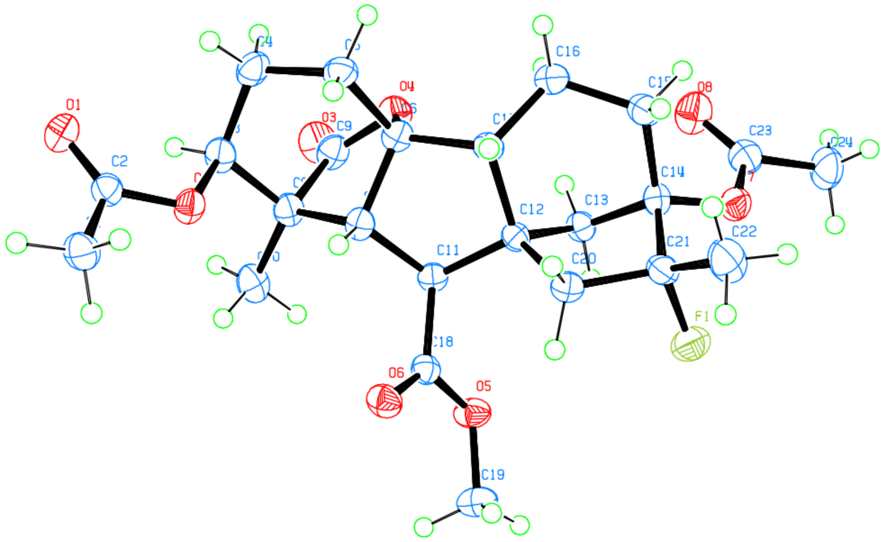


Table S17. Crystal data and structure refinement for shelxl.

Identification code	shelxl
Empirical formula	C24 H31 F O8
Formula weight	466.49
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.7359(17) A alpha = 90 deg.
	b = 12.804(3) A beta = 90 deg.
	c = 20.625(4) A gamma = 90 deg.
Volume	2307.0(8) A^3
Z, Calculated density	4, 1.343 Mg/m^3
Absorption coefficient	0.105 mm^-1
F(000)	992
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	1.87 to 28.02 deg.
Limiting indices	-11<=h<=9, -16<=k<=16, -27<=l<=27
Reflections collected / unique	22246 / 5526 [R(int) = 0.1118]
Completeness to theta = 28.02	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9875 and 0.9793

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5526 / 0 / 304
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0615, wR2 = 0.1225
R indices (all data)	R1 = 0.0843, wR2 = 0.1344
Absolute structure parameter	0.7(10)
Extinction coefficient	0.0128(14)
Largest diff. peak and hole	0.330 and -0.268 e.A^-3

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for shelxl. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	1920(2)	4204(1)	10226(1)	39(1)
O(1)	-492(2)	5961(2)	5431(1)	33(1)
O(2)	455(2)	5426(1)	6394(1)	28(1)
O(3)	1516(3)	8350(2)	7571(1)	40(1)
O(4)	-119(2)	7249(1)	8064(1)	29(1)
O(5)	4251(2)	4864(2)	8709(1)	30(1)
O(6)	3104(2)	3998(2)	7896(1)	29(1)
O(7)	268(2)	5713(2)	10674(1)	31(1)
O(8)	-239(3)	7419(2)	10531(1)	43(1)
C(1)	305(4)	4177(2)	5583(1)	32(1)
C(2)	40(3)	5276(2)	5771(1)	27(1)
C(3)	275(4)	6466(2)	6657(1)	29(1)
C(4)	-1373(4)	6667(2)	6862(1)	33(1)
C(5)	-1837(3)	6077(2)	7480(1)	29(1)
C(6)	-559(3)	6124(2)	7977(1)	23(1)
C(7)	923(3)	5662(2)	7722(1)	23(1)
C(8)	1412(3)	6493(2)	7232(1)	27(1)
C(9)	985(4)	7484(2)	7622(1)	31(1)
C(10)	3060(4)	6488(2)	7007(1)	33(1)
C(11)	1921(3)	5549(2)	8332(1)	22(1)
C(12)	789(3)	5330(2)	8906(1)	22(1)
C(13)	1121(3)	5991(2)	9515(1)	24(1)
C(14)	16(3)	5472(2)	9991(1)	25(1)

C(15)	-1658(3)	5686(2)	9798(1)	29(1)
C(16)	-1803(3)	6199(2)	9125(1)	28(1)
C(17)	-829(3)	5615(2)	8628(1)	23(1)
C(18)	3140(3)	4724(2)	8272(1)	23(1)
C(19)	5380(3)	4035(2)	8736(2)	35(1)
C(20)	766(3)	4200(2)	9188(1)	24(1)
C(21)	451(3)	4311(2)	9914(1)	26(1)
C(22)	-544(4)	3489(2)	10223(2)	42(1)
C(23)	81(4)	6695(3)	10888(1)	33(1)
C(24)	314(4)	6757(3)	11601(1)	45(1)

Table S19. Bond lengths [A] and angles [deg] for shelxl.

F(1)-C(21)	1.442(3)
O(1)-C(2)	1.216(3)
O(2)-C(2)	1.349(3)
O(2)-C(3)	1.447(3)
O(3)-C(9)	1.206(3)
O(4)-C(9)	1.361(4)
O(4)-C(6)	1.501(3)
O(5)-C(18)	1.336(3)
O(5)-C(19)	1.449(3)
O(6)-C(18)	1.212(3)
O(7)-C(23)	1.342(4)
O(7)-C(14)	1.459(3)
O(8)-C(23)	1.216(4)
C(1)-C(2)	1.478(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(3)-C(4)	1.522(4)
C(3)-C(8)	1.547(4)
C(3)-H(3)	1.0000
C(4)-C(5)	1.536(4)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.517(4)

C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(17)	1.512(4)
C(6)-C(7)	1.518(4)
C(7)-C(8)	1.527(4)
C(7)-C(11)	1.539(3)
C(7)-H(7)	1.0000
C(8)-C(10)	1.513(4)
C(8)-C(9)	1.549(4)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(18)	1.504(4)
C(11)-C(12)	1.568(4)
C(11)-H(11)	1.0000
C(12)-C(13)	1.543(4)
C(12)-C(20)	1.560(4)
C(12)-C(17)	1.568(4)
C(13)-C(14)	1.529(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.540(4)
C(14)-C(21)	1.543(4)
C(15)-C(16)	1.542(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.528(4)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.530(4)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.506(4)

C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.488(4)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(2)-O(2)-C(3)	117.3(2)
C(9)-O(4)-C(6)	108.3(2)
C(18)-O(5)-C(19)	115.0(2)
C(23)-O(7)-C(14)	119.8(2)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-O(2)	123.3(3)
O(1)-C(2)-C(1)	126.5(3)
O(2)-C(2)-C(1)	110.1(2)
O(2)-C(3)-C(4)	111.2(2)
O(2)-C(3)-C(8)	103.7(2)
C(4)-C(3)-C(8)	113.0(2)
O(2)-C(3)-H(3)	109.6
C(4)-C(3)-H(3)	109.6
C(8)-C(3)-H(3)	109.6
C(3)-C(4)-C(5)	113.4(2)
C(3)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4B)	108.9
C(5)-C(4)-H(4B)	108.9
H(4A)-C(4)-H(4B)	107.7
C(6)-C(5)-C(4)	110.3(2)
C(6)-C(5)-H(5A)	109.6
C(4)-C(5)-H(5A)	109.6
C(6)-C(5)-H(5B)	109.6
C(4)-C(5)-H(5B)	109.6

H(5A)-C(5)-H(5B)	108.1
O(4)-C(6)-C(17)	110.3(2)
O(4)-C(6)-C(5)	107.9(2)
C(17)-C(6)-C(5)	117.9(2)
O(4)-C(6)-C(7)	101.3(2)
C(17)-C(6)-C(7)	105.8(2)
C(5)-C(6)-C(7)	112.2(2)
C(6)-C(7)-C(8)	101.3(2)
C(6)-C(7)-C(11)	103.7(2)
C(8)-C(7)-C(11)	116.6(2)
C(6)-C(7)-H(7)	111.5
C(8)-C(7)-H(7)	111.5
C(11)-C(7)-H(7)	111.5
C(10)-C(8)-C(7)	117.8(2)
C(10)-C(8)-C(3)	112.0(2)
C(7)-C(8)-C(3)	108.2(2)
C(10)-C(8)-C(9)	113.0(3)
C(7)-C(8)-C(9)	99.2(2)
C(3)-C(8)-C(9)	105.2(2)
O(3)-C(9)-O(4)	122.4(3)
O(3)-C(9)-C(8)	128.0(3)
O(4)-C(9)-C(8)	109.7(2)
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(18)-C(11)-C(7)	113.6(2)
C(18)-C(11)-C(12)	112.5(2)
C(7)-C(11)-C(12)	106.1(2)
C(18)-C(11)-H(11)	108.2
C(7)-C(11)-H(11)	108.2
C(12)-C(11)-H(11)	108.2
C(13)-C(12)-C(20)	102.0(2)
C(13)-C(12)-C(11)	113.4(2)
C(20)-C(12)-C(11)	117.1(2)

C(13)-C(12)-C(17)	109.9(2)
C(20)-C(12)-C(17)	109.9(2)
C(11)-C(12)-C(17)	104.6(2)
C(14)-C(13)-C(12)	99.5(2)
C(14)-C(13)-H(13A)	111.9
C(12)-C(13)-H(13A)	111.9
C(14)-C(13)-H(13B)	111.9
C(12)-C(13)-H(13B)	111.9
H(13A)-C(13)-H(13B)	109.6
O(7)-C(14)-C(13)	115.6(2)
O(7)-C(14)-C(15)	110.8(2)
C(13)-C(14)-C(15)	110.9(2)
O(7)-C(14)-C(21)	105.3(2)
C(13)-C(14)-C(21)	101.4(2)
C(15)-C(14)-C(21)	112.3(2)
C(14)-C(15)-C(16)	112.7(2)
C(14)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15A)	109.1
C(14)-C(15)-H(15B)	109.1
C(16)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.8
C(17)-C(16)-C(15)	110.5(2)
C(17)-C(16)-H(16A)	109.6
C(15)-C(16)-H(16A)	109.6
C(17)-C(16)-H(16B)	109.6
C(15)-C(16)-H(16B)	109.6
H(16A)-C(16)-H(16B)	108.1
C(6)-C(17)-C(16)	118.1(2)
C(6)-C(17)-C(12)	106.5(2)
C(16)-C(17)-C(12)	111.8(2)
C(6)-C(17)-H(17)	106.6
C(16)-C(17)-H(17)	106.6
C(12)-C(17)-H(17)	106.6
O(6)-C(18)-O(5)	123.6(3)
O(6)-C(18)-C(11)	124.9(2)
O(5)-C(18)-C(11)	111.4(2)
O(5)-C(19)-H(19A)	109.5

O(5)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(5)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(12)	106.4(2)
C(21)-C(20)-H(20A)	110.5
C(12)-C(20)-H(20A)	110.5
C(21)-C(20)-H(20B)	110.5
C(12)-C(20)-H(20B)	110.5
H(20A)-C(20)-H(20B)	108.6
F(1)-C(21)-C(22)	105.0(2)
F(1)-C(21)-C(20)	105.6(2)
C(22)-C(21)-C(20)	116.9(2)
F(1)-C(21)-C(14)	105.4(2)
C(22)-C(21)-C(14)	119.2(2)
C(20)-C(21)-C(14)	103.5(2)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(8)-C(23)-O(7)	123.0(3)
O(8)-C(23)-C(24)	126.0(3)
O(7)-C(23)-C(24)	111.0(3)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S20. Anisotropic displacement parameters (A^2 x 10^3) for shelxl. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	42(1)	38(1)	38(1)	1(1)	-6(1)	10(1)
O(1)	37(1)	35(1)	28(1)	3(1)	-6(1)	0(1)
O(2)	41(1)	19(1)	23(1)	1(1)	-2(1)	4(1)
O(3)	56(2)	19(1)	46(1)	-1(1)	7(1)	-7(1)
O(4)	37(1)	18(1)	31(1)	-3(1)	3(1)	1(1)
O(5)	26(1)	29(1)	35(1)	-7(1)	-7(1)	3(1)
O(6)	31(1)	27(1)	30(1)	-7(1)	0(1)	1(1)
O(7)	39(1)	31(1)	23(1)	-4(1)	-2(1)	6(1)
O(8)	60(2)	29(1)	39(1)	-1(1)	-1(1)	-1(1)
C(1)	35(2)	30(2)	31(2)	-7(1)	-1(1)	1(1)
C(2)	24(2)	32(2)	24(1)	1(1)	1(1)	0(1)
C(3)	45(2)	16(1)	25(1)	-2(1)	1(1)	5(1)
C(4)	44(2)	26(2)	28(2)	1(1)	-5(1)	9(1)
C(5)	30(2)	29(2)	29(2)	-4(1)	-4(1)	5(1)
C(6)	30(2)	15(1)	25(1)	-1(1)	-2(1)	-1(1)
C(7)	29(2)	18(1)	22(1)	-4(1)	-2(1)	-3(1)
C(8)	35(2)	19(1)	26(1)	2(1)	3(1)	0(1)
C(9)	39(2)	24(2)	29(2)	1(1)	-3(1)	0(1)
C(10)	40(2)	26(2)	32(2)	3(1)	8(1)	-7(1)
C(11)	27(1)	14(1)	24(1)	-1(1)	1(1)	1(1)
C(12)	21(1)	22(1)	22(1)	-1(1)	1(1)	-1(1)
C(13)	26(2)	23(2)	24(1)	-2(1)	0(1)	0(1)
C(14)	28(2)	27(2)	20(1)	-1(1)	1(1)	-2(1)
C(15)	25(2)	33(2)	29(2)	-4(1)	2(1)	2(1)
C(16)	26(2)	27(2)	31(2)	-2(1)	-2(1)	2(1)
C(17)	22(1)	22(1)	24(1)	-3(1)	0(1)	2(1)
C(18)	20(1)	25(1)	23(1)	1(1)	2(1)	-2(1)
C(19)	29(2)	34(2)	44(2)	-1(1)	-6(1)	7(1)
C(20)	25(1)	20(1)	28(1)	-1(1)	0(1)	0(1)
C(21)	25(2)	26(2)	29(1)	1(1)	5(1)	2(1)
C(22)	55(2)	28(2)	44(2)	6(1)	16(2)	1(2)
C(23)	32(2)	36(2)	32(2)	-2(1)	1(1)	-1(1)
C(24)	62(2)	47(2)	26(2)	-5(1)	-1(2)	5(2)

Table S21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for shelxl.

	x	y	z	U(eq)
H(1A)	95	4092	5119	48
H(1B)	-377	3722	5832	48
H(1C)	1372	3989	5671	48
H(3)	588	6993	6325	35
H(4A)	-2064	6457	6504	39
H(4B)	-1512	7425	6935	39
H(5A)	-2776	6393	7663	35
H(5B)	-2062	5339	7372	35
H(7)	746	4972	7507	27
H(10A)	3741	6496	7384	49
H(10B)	3254	7108	6740	49
H(10C)	3254	5859	6750	49
H(11)	2436	6234	8415	26
H(13A)	2199	5923	9657	29
H(13B)	874	6737	9447	29
H(15A)	-2131	6149	10126	35
H(15B)	-2231	5019	9798	35
H(16A)	-2888	6192	8986	33
H(16B)	-1464	6936	9149	33
H(17)	-1363	4938	8540	27
H(19A)	4859	3358	8758	53
H(19B)	6022	4126	9121	53
H(19C)	6021	4061	8346	53
H(20A)	-47	3780	8978	29
H(20B)	1762	3851	9114	29
H(22A)	-104	2797	10142	63
H(22B)	-1575	3522	10036	63
H(22C)	-602	3612	10691	63
H(24A)	255	7487	11740	67
H(24B)	1322	6473	11712	67
H(24C)	-482	6351	11821	67

Table S22. Torsion angles [deg] for shelxl.

C(3)-O(2)-C(2)-O(1)	-1.2(4)
C(3)-O(2)-C(2)-C(1)	179.8(2)

C(2)-O(2)-C(3)-C(4)	80.9(3)
C(2)-O(2)-C(3)-C(8)	-157.4(2)
O(2)-C(3)-C(4)-C(5)	72.5(3)
C(8)-C(3)-C(4)-C(5)	-43.7(3)
C(3)-C(4)-C(5)-C(6)	42.0(3)
C(9)-O(4)-C(6)-C(17)	141.0(2)
C(9)-O(4)-C(6)-C(5)	-88.8(3)
C(9)-O(4)-C(6)-C(7)	29.2(3)
C(4)-C(5)-C(6)-O(4)	52.2(3)
C(4)-C(5)-C(6)-C(17)	178.0(2)
C(4)-C(5)-C(6)-C(7)	-58.6(3)
O(4)-C(6)-C(7)-C(8)	-43.4(2)
C(17)-C(6)-C(7)-C(8)	-158.5(2)
C(5)-C(6)-C(7)-C(8)	71.5(3)
O(4)-C(6)-C(7)-C(11)	77.9(2)
C(17)-C(6)-C(7)-C(11)	-37.3(3)
C(5)-C(6)-C(7)-C(11)	-167.2(2)
C(6)-C(7)-C(8)-C(10)	162.7(2)
C(11)-C(7)-C(8)-C(10)	51.0(3)
C(6)-C(7)-C(8)-C(3)	-69.0(2)
C(11)-C(7)-C(8)-C(3)	179.3(2)
C(6)-C(7)-C(8)-C(9)	40.5(2)
C(11)-C(7)-C(8)-C(9)	-71.3(3)
O(2)-C(3)-C(8)-C(10)	69.8(3)
C(4)-C(3)-C(8)-C(10)	-169.6(2)
O(2)-C(3)-C(8)-C(7)	-61.7(3)
C(4)-C(3)-C(8)-C(7)	58.9(3)
O(2)-C(3)-C(8)-C(9)	-167.0(2)
C(4)-C(3)-C(8)-C(9)	-46.4(3)
C(6)-O(4)-C(9)-O(3)	177.6(3)
C(6)-O(4)-C(9)-C(8)	-3.0(3)
C(10)-C(8)-C(9)-O(3)	29.7(4)
C(7)-C(8)-C(9)-O(3)	155.3(3)
C(3)-C(8)-C(9)-O(3)	-92.8(4)
C(10)-C(8)-C(9)-O(4)	-149.6(2)
C(7)-C(8)-C(9)-O(4)	-24.0(3)
C(3)-C(8)-C(9)-O(4)	87.8(3)

C(6)-C(7)-C(11)-C(18)	155.6(2)
C(8)-C(7)-C(11)-C(18)	-94.0(3)
C(6)-C(7)-C(11)-C(12)	31.5(3)
C(8)-C(7)-C(11)-C(12)	141.9(2)
C(18)-C(11)-C(12)-C(13)	101.3(3)
C(7)-C(11)-C(12)-C(13)	-133.9(2)
C(18)-C(11)-C(12)-C(20)	-17.1(3)
C(7)-C(11)-C(12)-C(20)	107.7(2)
C(18)-C(11)-C(12)-C(17)	-139.0(2)
C(7)-C(11)-C(12)-C(17)	-14.2(3)
C(20)-C(12)-C(13)-C(14)	-44.8(2)
C(11)-C(12)-C(13)-C(14)	-171.6(2)
C(17)-C(12)-C(13)-C(14)	71.7(2)
C(23)-O(7)-C(14)-C(13)	64.8(3)
C(23)-O(7)-C(14)-C(15)	-62.6(3)
C(23)-O(7)-C(14)-C(21)	175.8(2)
C(12)-C(13)-C(14)-O(7)	165.1(2)
C(12)-C(13)-C(14)-C(15)	-67.6(3)
C(12)-C(13)-C(14)-C(21)	51.8(2)
O(7)-C(14)-C(15)-C(16)	139.5(2)
C(13)-C(14)-C(15)-C(16)	9.6(3)
C(21)-C(14)-C(15)-C(16)	-103.0(3)
C(14)-C(15)-C(16)-C(17)	48.0(3)
O(4)-C(6)-C(17)-C(16)	46.3(3)
C(5)-C(6)-C(17)-C(16)	-78.3(3)
C(7)-C(6)-C(17)-C(16)	155.2(2)
O(4)-C(6)-C(17)-C(12)	-80.4(3)
C(5)-C(6)-C(17)-C(12)	155.0(2)
C(7)-C(6)-C(17)-C(12)	28.5(3)
C(15)-C(16)-C(17)-C(6)	-167.5(2)
C(15)-C(16)-C(17)-C(12)	-43.4(3)
C(13)-C(12)-C(17)-C(6)	113.6(2)
C(20)-C(12)-C(17)-C(6)	-135.0(2)
C(11)-C(12)-C(17)-C(6)	-8.5(3)
C(13)-C(12)-C(17)-C(16)	-16.8(3)
C(20)-C(12)-C(17)-C(16)	94.6(3)
C(11)-C(12)-C(17)-C(16)	-138.8(2)

C(19)-O(5)-C(18)-O(6)	-4.2(4)
C(19)-O(5)-C(18)-C(11)	173.1(2)
C(7)-C(11)-C(18)-O(6)	-22.1(4)
C(12)-C(11)-C(18)-O(6)	98.4(3)
C(7)-C(11)-C(18)-O(5)	160.6(2)
C(12)-C(11)-C(18)-O(5)	-78.9(3)
C(13)-C(12)-C(20)-C(21)	21.5(3)
C(11)-C(12)-C(20)-C(21)	145.9(2)
C(17)-C(12)-C(20)-C(21)	-95.0(2)
C(12)-C(20)-C(21)-F(1)	-100.4(2)
C(12)-C(20)-C(21)-C(22)	143.3(3)
C(12)-C(20)-C(21)-C(14)	10.1(3)
O(7)-C(14)-C(21)-F(1)	-48.5(2)
C(13)-C(14)-C(21)-F(1)	72.3(2)
C(15)-C(14)-C(21)-F(1)	-169.2(2)
O(7)-C(14)-C(21)-C(22)	69.0(3)
C(13)-C(14)-C(21)-C(22)	-170.2(3)
C(15)-C(14)-C(21)-C(22)	-51.7(3)
O(7)-C(14)-C(21)-C(20)	-159.2(2)
C(13)-C(14)-C(21)-C(20)	-38.3(3)
C(15)-C(14)-C(21)-C(20)	80.1(3)
C(14)-O(7)-C(23)-O(8)	-2.9(5)
C(14)-O(7)-C(23)-C(24)	177.0(3)

Symmetry transformations used to generate equivalent atoms:

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